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During my first year I spent ten weeks in Amsterdam and although we never succeeded in doing kinetics (!) I learnt a lot in the group of Piet van Leeuwen. Thanks Piet for accepting me in your nice group, for solving the thousand of questions I was always asking you and for discussing chemistry every time you came to Tarragona. Also thanks to Karina and Mary who made me feel home with their hospitality in Amsterdam. Special thanks to Barbara Milani for the nice time spent in Trieste, for her company during the weekends and for her enthusiasm and ideas. Also thanks to Elisabetta for offering me good alternatives to chemistry. Also I am very much indebted to Prof. Consiglio and Prof. Bianchini for accepting to review this memory.

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Prof. Dra. CARMEN CLAVER CABRERO, Catedrática del Departament de Química Física i Inorgànica de la Facultat de Química de la Universitat Rovira i Virgili y la Dra. AURORA RUIZ MANRIQUE, Profesora Titular del Departament de Química Física i Inorgánica de la Facultad de Química de la misma Universidad,

CERTIFICAN:

Que la memoria que lleva por título "PALLADIUM COMPLEXES FOR CO/STYRENE COPOLYMERIZATION. STUDY OF THE INFLUENCE OF THE LIGAND", que presenta Amaia Bastero Rezola para obtener el grado de Doctora en Química, ha sido realizada bajo nuestra dirección en el Departament de Química Física i Inorgànica de la Universitat Rovira i Virgili.

Tarragona, Octubre de 2002

Prof. Dra. Carmen Claver Cabrero Dra. Aurora Ruiz Manrique

1. General introduction

1.1 Organometallic chemistry and homogeneous catalysis

Organometallic compounds are defined as materials which possess direct, more or less polar bonds between metal and carbon atoms.[1] Since Zeise synthesized in 1827 the first organometallic compound, $K[PtCl_3(CH_2=CH_2)]$, the organometallic chemistry has grown enormously although most of its applications have only been developed in recent decades. Some of the key points in the fast expansion of organometallic chemistry are the selectivity of organometallic complexes in organic synthesis (discovered with Grignard reagents at the end of the 19th century),[2,3] and the interesting role that metals play in biological systems (e.g. enzymes, hemoglobin, etc.).[4]

One of the most interesting things about organometallic compounds is that they can be used as homogeneous catalysts in processes where all the reacting partners are present in one phase, usually the liquid one.[5] Transition metal complexes act in different ways within the catalytic reaction: they bring the substrates together, activate the substrates by coordinating to the metal and lower the activation energy of the reaction between substrates. In general the use of a homogeneous catalyst in a reaction provides a new pathway, because the reactants interact with the metallic complex. These interactions make it possible for thermodynamically favored reactions, which need long times to reach equilibrium, to be accomplished within hours. Therefore, homogeneous

catalysts can be used to synthesize compounds which can hardly be obtained by conventional methods.

Although heterogeneous catalysts are widely used, particularly in oil processes, homogeneous transition metal catalysts are increasingly being applied in industrial processes[6] to obtain fine chemicals and polymers. Some of these processes are: toluene and xylene oxidation to acids, oxidation of ethene to aldehyde, ester condensation to polyesters, carbonylation of methanol and of methyl acetate, polymerization of dienes to unsaturated polymers, hydroformylation of alkenes, oligomerization of ethene and propene, hydrocyanation of 1,3-butadiene, cyclodi(tri)-merization of 1,3-butadiene, asymmetric hydrogenation, asymmetric isomerization, asymmetric epoxidation, codimerization of 1,3-butadiene and ethene, hydrosilylation of alkenes, ring opening metathesis polymerization of dicyclopentadiene and norbornene, alternating copolymerization of ethene and carbon monoxide, etc.[5-7]

One interesting application of homogeneous catalysis is enantioselective (asymmetric) catalysis. It deals with the synthesis of enantiopure compounds, which are active ingredients of pharmatheuticals, agricultural products, flavors, fragrances and some advanced materials.[8-10] Life itself depends on chiral recognition because living systems identify the enantiomers as different substances and interact with them in different ways. For example, for many drugs only one of these enantiomers has a beneficial effect, being the other enantiomer either inactive or even toxic. Although the resolution of racemates is a way of obtaining enantiopure compounds, enantioselective synthesis enables just a single enantiomer to

be obtained. The advantage that enantioselective catalysis has over stoichiometric synthesis is that one organometallic catalyst molecule can generate millions of chiral product molecules. Catalytic synthesis also generates smaller amounts of chemical waste than stoichiometric organic synthesis. Therefore the search for homogeneous enantioselective catalysts that selectively react to give the desired product is one of the most interesting trends in organometallic chemistry.[11]

The success of organometallic catalysts lies in the easy modification of their environment by ligand exchange. A very large number of different types of ligands can coordinate to transition metal ions. Once the ligands are coordinated, the reactivity of the metals may change dramatically. In fact the rate and selectivity of a given process can be optimized to the desired level by controlling the ligand environment. Understanding the role played by the different ligands coordinated to a metal is one of the main themes in homogeneous catalysis.[12] Because organometallic complexes are highly soluble in organic solvents their behavior throughout the catalytic reaction can be studied using different techniques to do *in-situ* measurements. Fundamental knowledge about the catalytic systems and studies about the steps of the catalytic processes can help to improve the efficiency of the catalysts. In this respect kinetic studies and stoichiometric model reactions with well-defined transition metal complexes are used to elucidate the steps of the catalytic cycle. The use of labeled compounds allows the spectroscopic identification of intermediates.

Palladium is one of the most extensively studied metals in organometallic chemistry because it is versatile and catalyzes a considerable

number of organic reactions. The most important palladium-catalyzed reactions are those leading to C-C bond formation such as oligomerization and polymerization of alkenes, carbonylation of alkenes and organic halides, Wacker oxidation of alkenes, Heck reaction, allylic alkylation, Suzuki reaction, cross coupling reactions, polyamide synthesis, etc.[13] The main steps in the mechanism of reactions catalyzed by palladium complexes are oxidative addition, reductive elimination, ligand substitution, transmetallation and migratory insertion. Migratory insertion is the fundamental step in coordination polymerization reactions such as the copolymerization of alkenes and carbon monoxide which is described in greater detail in the paragraphs below.

1.2. Alkene polymerization reactions

The catalytic conversion of accessible alkenes into high molecular weight polymers is a very important industrial process. The profit generated by this business has made polyolefins the fastest growing part of the polymer industry.[14] In particular, the different types of polyethylene make up more than 50% of the polyolefin production nowadays. Polyethylene, polypropylene and polystyrene are produced commercially using coordination polymerization technology with early transition metals (Ziegler-Natta and metallocene catalysts) or in high-temperature and high-pressure free-radical processes. Copolymers of ethene with polar monomers or functionalized alkenes (methyl(meth)acrylate, vinyl acetate, etc.) are also important commercial polymers. Most functionalized alkenes, particularly the commercially available polar monomers, poison metal catalysts based on early transition metals (titanium, zirconium or chromium), that are

highly oxophilic. For this reason copolymers containing functionalized alkenes with ethene are still produced industrially by free radical polymerization.

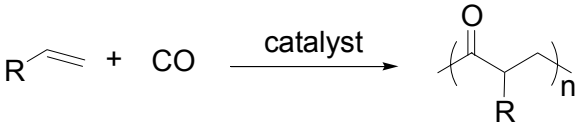
Late transition metal catalysts have both low oxophilicity and greater tolerance towards functional groups than early metals. Considering that coordination polymerization provides better selectivity than radical polymerization, the development of polymerization catalysts based on late transition metals is of great interest. The disadvantages of using late-metal polymerization catalysts rather than early-metal catalysts are the lower activity for alkene insertion and the more favoured β-H elimination, which competes with chain growth.[15] For the insertion polymerization of olefins some catalysts have been reported based on iron,[16] cobalt,[16a,17] rhodium,[18] nickel,[19] palladium[20] and platinum. Late-metal catalysts are also used for the polymerization of dienes[21] and for the alternating copolymerization of alkenes with carbon monoxide.

1.3. Alternating copolymerization of alkenes with carbon monoxide

The alternating copolymerization of carbon monoxide with alkenes to yield polyketones is an attractive reaction for various reasons. One of these is that carbon monoxide is an accessible and inexpensive monomer and so the final products are low cost polymers. Moreover, polyketones have interesting properties; they are thermal plastics, they are photo- and biodegradable and they can be starting material for a variety of functionalized polymers due to the chemical transformation of the carbonyl

groups.[22-25] Thermoplastics with high-performance properties are in increasing demand because of their strength, toughness, wear resistance, chemical resistance, UV stability, etc.[26] The applications of these materials include automotive components such as gears, fittings, containers, fibres, packaging, etc.[27] Shell[28] and more recently BP[29] have commercialized polyketones as aliphatic terpolymers (CO/ alkene$_1$/ alkene$_2$) (*Carilon* and *Ketonex*, respectively).

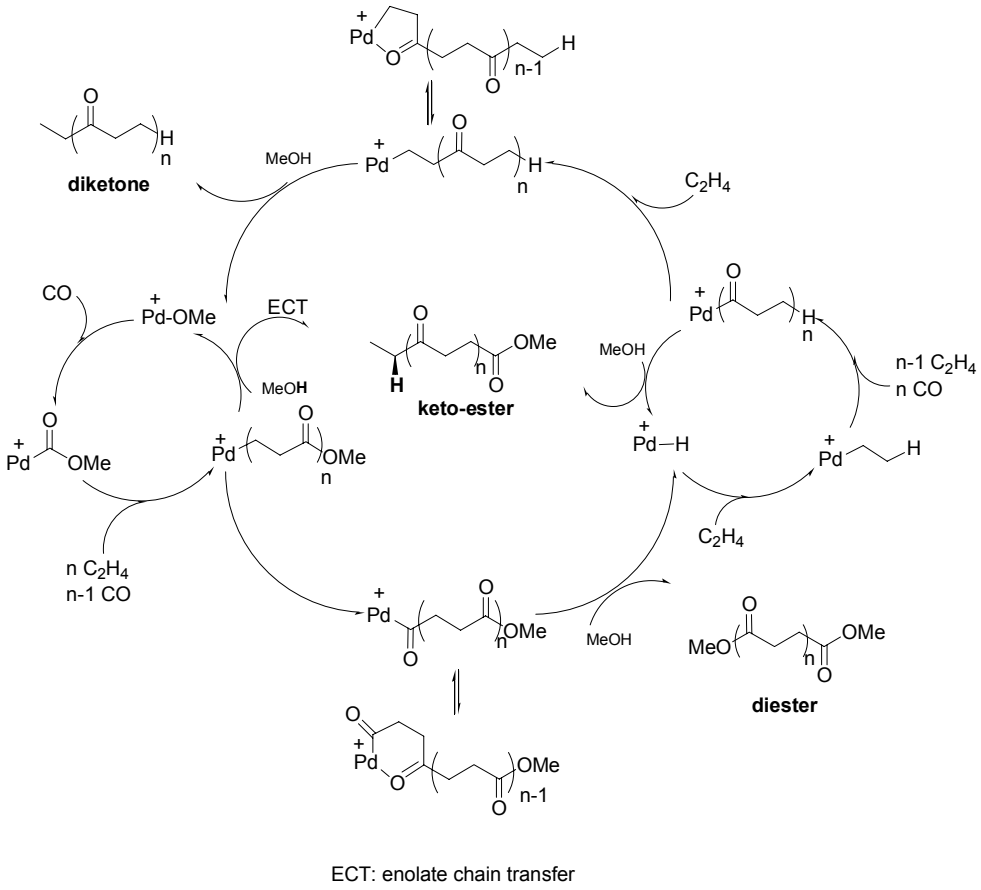
The metal-catalyzed copolymerization reaction started when it was discovered that $K_2[Ni(CN)_4]$ catalyzed the alternating copolymerization of carbon monoxide and ethene.[30] Homogeneous copolymerization catalysts provided greater control of the polymer properties than polymerization initiated via free radicals or γ–rays, and gave a perfect alternation of the alkene and carbon monoxide (Scheme 1). After nickel (II)[31,32] other metal complexes containing rhodium (I)[33,34] and palladium (II)[35] were used as catalysts, always in severe conditions of pressure and temperature. The first catalyst that was active in the copolymerization of carbon monoxide and ethene, in mild conditions, was a palladium complex of formula $[Pd(PR_3)_n(NCMe)_{4-n}][BF_4]_2$ with at least one molecule of phosphine ligand.[36] However, the essential improvement to the efficient synthesis of polyketones at industrial level came with the discovery of the combined importance of using bidentate ligands and weakly coordinating anions in catalytic systems of the type PdX_2(L-L) where (L-L) is a bidentate phosphine and X a weakly or non-coordinating anion.[37]



Scheme 1. Alternating CO/alkene copolymerization

1.3.1. Copolymerization of ethene with carbon monoxide

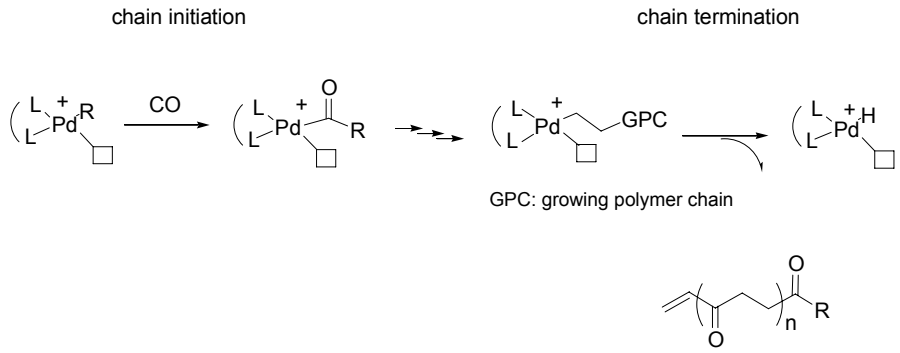
In 1996 the copolymerization of ethene and carbon monoxide was extensively reviewed and the complete mechanism, which is applicable to other alkenes, proposed.[23] The alternating copolymerization of alkenes with carbon monoxide consists of the following steps: i) the initiation of the chain growth; ii) the propagation mechanism, with the perfect alternation of monomers; iii) the termination of the chain together with the chain transfer, because of the importance for a polymerization catalyst of making more than one chain per metal center (Scheme 2).[38]



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

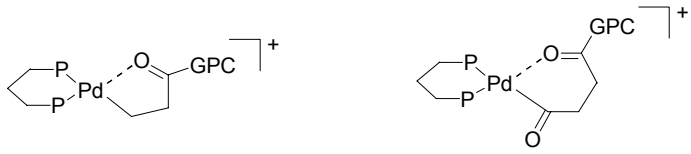
The analysis of the end groups of the polyketones enabled the initiation and termination steps of the mechanism to be understood. Depending on the reaction conditions and on the nature of the alkene, the chain initiation process has different possibilities. It is generally accepted that for catalysts of the type PdX_2(L-L), made *in-situ*, or for the preformed ones $[Pd(L\text{-}L)(S)_2][X_2]$ (S = solvent molecule), in alcoholic medium and

under CO pressure, the mechanism starts with CO being inserted into a Pd-OMe bond or the alkene being inserted into a Pd-H species.[23] Reaction of the palladium precatalyst in methanol with carbon monoxide generates the Pd-carbometoxy species (Pd-COOMe).[22,23] The starting palladium hydride species might be formed by β-hydride elimination from a palladium methoxy species[36] although the traces of water present in the reaction medium also lead to the formation of Pd-H species by β-H elimination of the Pd-COOH species formed (shift reaction).[39] β-H elimination reaction from a Pd-methoxyethyl complex (formed by a Wacker type reaction) also generates the Pd-H species.[38] When the precatalyst is an alkyl complex, the insertion of CO into the Pd-alkyl bond is the initiation step. This alkyl complex is only the initiator species, and is not regenerated after the first copolymer molecule is made. Generally, precatalysts of the type [PdR(L-L)(S)][X] (where R is a methyl group) have been used,[40] although recently it has been shown that an *in-situ* system formed by PdX_2(L-L) and a borane BR_3 (where R is the aryl group C_6F_5) is a good catalyst precursor due to the formation of the Pd-C_6F_5 species which inserts CO.[41] When the copolymerization reaction is performed in non-protic solvents an alkylpalladium species is necessary so that the first monomer can be inserted (Scheme 3).



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

The propagation mechanism consists of the successive migratory insertion of carbonyl into an alkylpalladium complex and of alkene into an acylpalladium complex, in an alternating way (Scheme 2).[42] Cationic complexes with non-coordinating anions ensure the presence of accessible coordination sites and chelate ligands cause *cis*-coordination of the monomers and, thus, enable migratory insertion reactions.[43] Errors in the alternation of the insertions have never been observed and it has been stated that they are not possible. The CO insertion into a Pd-acyl bond is thermodynamically not favored and the insertion of an alkene into an alkylpalladium bond, although thermodynamically possible, is avoided because CO is more strongly coordinated and inserts faster in a Pd-alkyl bond than the alkene.[22,44] It has been shown that the growing polymer chain, σ-bonded to palladium, also coordinates internally to the metal by the last inserted carbonyl to form 5- or 6-membered ring metallacycles (Scheme 4).[23,45,46] This seems to help to the perfect alternation.

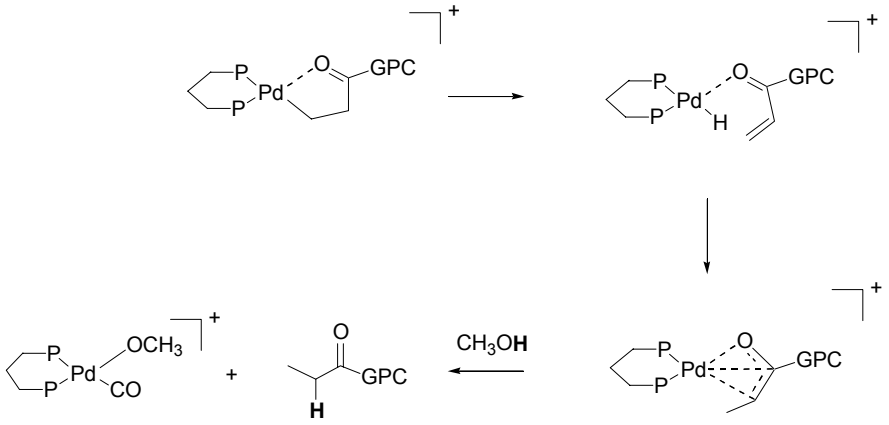


Scheme 4. β- and γ- chelates formed during CO/ethene copolymerization

Several studies have been made about the detection and isolation of carbon monoxide and alkene insertion intermediates in the copolymerization reaction.[42,47-50] Theoretical calculations have shown that there is a correlation with the experimental data in the perfect alternation of comonomers.[51,52]

The termination step, like the initiation one, depends on the reaction conditions and on the alkene. When the reaction solvent is an alcohol, it acts as a chain transfer agent leading to two termination ways. The alcoholysis of an acylpalladium species regenerates the Pd-H and gives an ester end-group; while the protonolysis of an alkylpalladium bond regenerates Pd-COMe and forms a ketone end-group (Scheme 2).[23] Recently it has been shown that protonolysis does not imply the expected protonation of the alkylpalladium species. In fact, deuterium experiments have shown that previously hydrogen is β- eliminated from the alkylpalladium species, to form an enolate, and is then reinserted (Scheme 5).[53] The hydrolysis of an alkylpalladium bond, due to the water present in the reaction, has also been observed, giving carboxylic end-groups and regenerating the Pd-H species.[54] Another possible termination pathway is the β-H elimination from an alkylpalladium species forming Pd-H bonds and unsaturated-end groups. This is the termination step in the reactions performed in non-protic

solvents (Scheme 3) and in the case of other alkenes, like propene and styrene, is the main termination reaction.

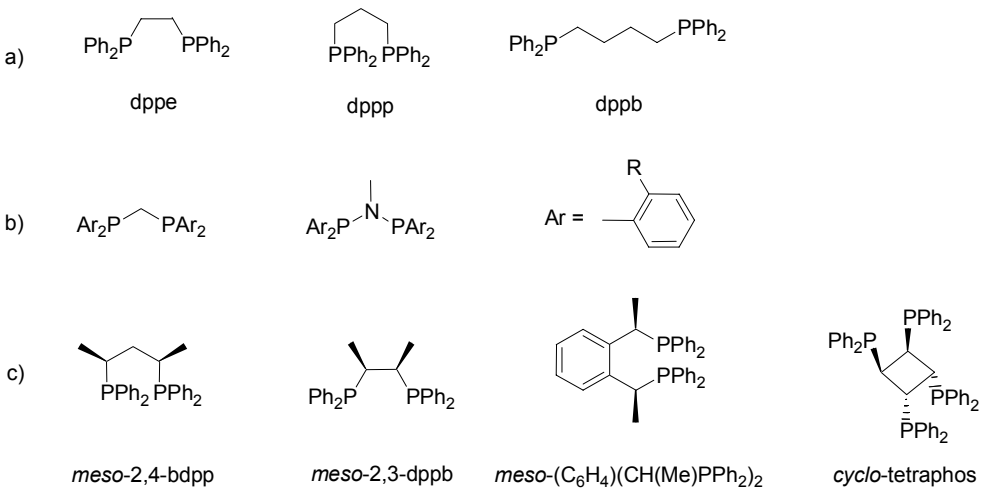


Scheme 5. Enolate chain transfer mechanism

Since the discovery of the efficiency of dppp (1,3-bis(diphenylphosphino)propane) as chelating ligand for the CO/ethene copolymerization reaction,[23] many studies have been made of various diphosphine ligands as well as of modifications to the dppp backbone. An interesting observation concerning diphosphines is that the size of the chelate ring dramatically affects productivity.[55,56] Although it was stated that the most productive catalysts were those with a diphosphine containing a three-carbon backbone (Scheme 6a),[23,39] it has been shown that four-membered diphosphine chelates may indeed lead to efficient catalysts if the ligands are sterically demanding enough (Scheme 6b).[57]

Additionally modifications on the (1,3-bis-(diphenylphosphino)-propane) backbone creating chirality in the 1- and 3-centers by introduction of a methyl group (2,4-bis(diphenylphosphino)pentane) have led to a

considerable increase of productivity.[58] It has also been found that *meso*-diphosphines lead to higher activities than catalysts with similar ligands but without the *meso* structure (Scheme 6c).[59-61] The explanation seems to be that catalysts containing *meso*-diphosphines are more active since the metallacycles formed during the catalytic reaction are less stable. In agreement with this, calculations on the CO migratory insertion barriers for catalysts containing diphosphines with different chelate ring sizes showed that the larger the chelate ring size is, the faster the migratory insertion. Likewise, when the steric bulk of the ligand is increased the migratory insertion is accelerated.[62]



Scheme 6. Diphosphines used in CO/ethene copolymerization

It has been said that Pd(II) complexes are the best choice for the copolymerization of carbon monoxide not only with ethene, but also with propene and with styrene. These alkenes may be considered as models for more complicated substrates like strained alkenes,[63] α-alkenes substituted

with polar groups,[64-66] carbamates,[67] alkynes,[68,69] imines[70], amines,[71] etc. However, other late-metal catalysts such as nickel[72,73] and rhodium[74] have been used to a lesser extent in the copolymerization of alkenes with carbon monoxide. Monodentate ligands and bidentate ligands with relatively large bite angles are not used to avoid coordination in *trans* position in mono or bimetallic complexes, respectively.[75] Therefore, depending on the alkene involved in the catalysis, different types of chelating ligands are used, containing P-, N-, S-, O- or C- donor atoms.[25]

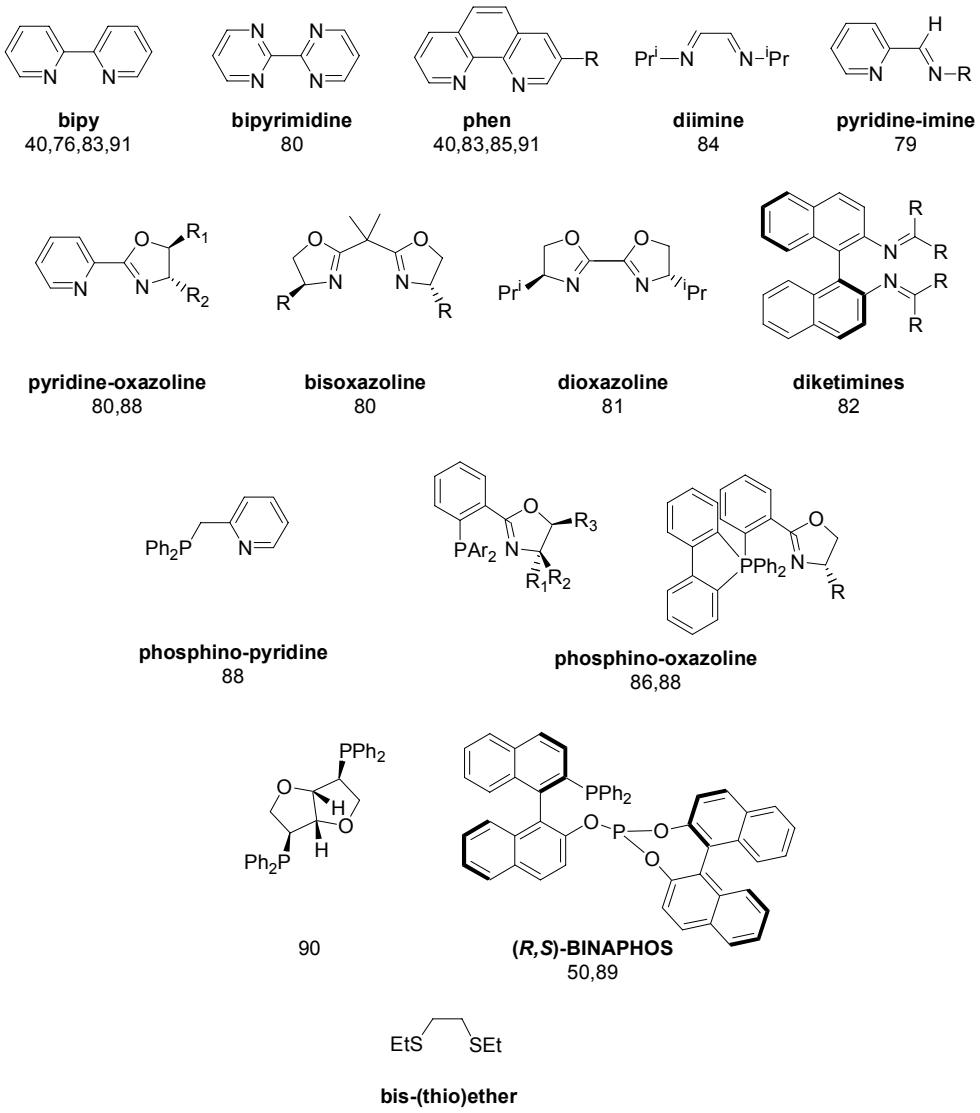
1.3.2. Copolymerization of styrene with carbon monoxide

As already stated for the copolymerization of ethene with carbon monoxide, palladium (II) complexes that contain both a non-coordinating anion and a chelating ligand are necessary if catalysts are to be active. Of the different anions tested, the BAr'_4 anion (Ar' = 3,5-$(CF_3)_2C_6H_3$) has been claimed to be the most appropriate because of its combination of bulkiness and low coordinating ability.[40,76] For this anion, multinuclear NMR studies showed the weakest contacts with the cationic part of the catalysts.[76]

Preformed catalysts containing one[40] or two molecules of chelating ligand[77] have generally been used for CO/styrene copolymerization. Bisnitrogen-donating ligands have been mostly used for effective CO/styrene copolymerization (Scheme 7).[40,78-85] The combination of a phosphorous and a nitrogen-donating atom was also found to be active, although severer conditions of pressure and temperature are needed to obtain polyketones.[86] Unlike the co- and terpolymerization of ethene and propene with CO, catalysts containing diphosphine ligands are not active in

the copolymerization of styrene (and its derivatives) with CO since only low molecular weight oligomers are obtained.[23,87] It has been stated that when a phosphine is coordinated to palladium, β-H elimination is more favoured than polymer growth because of the higher electron density existing on the metal.[23] Moreover, the strongly stabilized π-benzylic intermediate formed after styrene insertion prevents subsequent carbon monoxide coordination and insertion.[88]

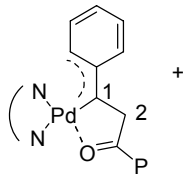
Surprisingly a palladium complex containing a phosphine-phosphite ligand (BINAPHOS) has also shown activity.[89] This was explained in terms of the reverse regiochemistry observed in the styrene insertion (1,2-insertion) (see below).[50] Very recently a palladium catalyst containing a diphosphine derived from *L*-iditol was reported to be active in the CO/styrene copolymerization, giving polymers with a highly regular microstructure. It seems that the iditol-derived diphosphine coordinates almost in a monodentate fashion (a strong coordination with one phosphorous and a weak one with the other, which can be exchanged during the catalysis) although the system has not been explained clearly (Scheme 7).[90] As well as nitrogen and phosphorous donating ligands, there is an example in the literature with sulfur-donating ligands, yielding polyketones with an irregular microstructure (Scheme 7).[23]



Scheme 7. Ligands reported for the CO/styrene copolymerization

As well as having an effect on the activity of catalysts, ligands may influence the selectivity in which the copolymerization proceeds. When 1-alkenes are used as monomers, one important goal is the control of the

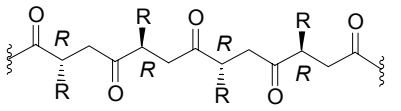
regio- and stereochemistry of the alkene insertion in the growing chain. It has been reported that in complexes containing bisnitrogen ligands, styrene insertion always takes place in a secondary fashion (2,1 insertion),[40,91] because of the stabilization of the π-benzylic intermediates (Scheme 8).[40] However, this situation changes when the ligand is varied: steric modifications in P-N ligands yield regioirregular polyketones containing some 1,2-inserted styrene units,[86b] while only 1,2- insertions were found in the regioregular copolymer obtained with the BINAPHOS ligand. The reverse insertion of styrene, observed with the phosphine-phosphite ligand, prevents the β-H elimination and might explain the activity of this ligand in CO/ styrene copolymerization.[50]



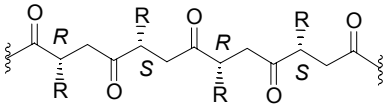
Scheme 8. π-benzylic intermediate formed after 2,1 insertion of styrene in a Pd-acyl bond

The stereochemistry of the alkene insertion along the chain determines the copolymer tacticity: isotactic, syndiotactic or atactic (Scheme 9). Two facts may be responsible for the control of the stereochemistry to give stereoregular (isotactic or syndiotactic) copolymers. On the one hand the enantioselective environment created by the chiral ligand may govern the stereoregularity of the alkene insertion, which is known as *enantiosite control*, and this leads to isotactic polymers. On the other hand the growing polymer chain, which is also chiral because of its successive stereogenic

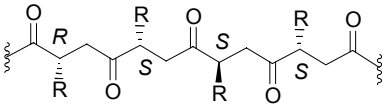
carbon centers, may lead to a controlled stereoregular insertion of styrene. This control is known as *chain-end control*, and it gives syndiotactic polymers.



isotactic



syndiotactic



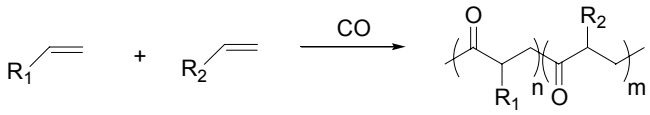
atactic

Scheme 9. Tacticity of CO / alkene copolymers

C_2- and C_{2v}- achiral ligands give completely stereoregular syndiotactic copolymers due to the *chain-end control*.[40,80,83,84,91] For C_2-symmetrical chiral ligands, *enantiosite control* overrides the effect of the growing chain to give isotactic polymers.[80-82] However, for C_1-symmetrical ligands the relative influence of both effects cannot be inferred *a priori*. There are examples reported where the use of C_1-symmetrical ligands led to isotactic,[86,89] syndiotactic[79,80,85,88] or even atactic copolymers.[88]

1.4. Terpolymerization of styrene and ethene with carbon monoxide

The CO/alkene copolymer chains are packed together in an orderly fashion giving highly crystalline materials. This makes polyketones to be very strong but also very brittle. To avoid this problem, another alkene, e.g. propene, can be introduced in the chain to disturb somehow the crystal packing. Inserting a second alkene into the palladium-catalyzed CO/alkene copolymerization reaction gives strictly alternating CO/alkene polyketones in which two different units are obtained (CO/alkene$_1$) and (CO/alkene$_2$) (Scheme 10). The relative amount of both units inside the polymer chain depends on the conditions of the reaction as well as on the different reactivity of each alkene.



Scheme 10. Terpolymerization reaction of alkenes with CO

Different alkenes have been terpolymerized with CO using cationic palladium catalysts although combinations of ethene and 1-alkenes have been more studied.[59,79,92-94] Recently some reports have appeared on terpolymerization of 1-alkenes and vinylarenes with CO.[95,96]

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2. Scope and objectives of the thesis

Although in recent years several reports have appeared about the copolymerization of styrene and carbon monoxide catalyzed by palladium(II) complexes, in comparison to the CO/ethene copolymerization or other catalytic processes, relatively few ligands have been discussed. In fact most of the reports deal with the optimization of reaction conditions or the mechanistic investigations of well-known catalytic systems. Therefore, the search for new ligands for this reaction, which would enlarge the scope of effective catalysts, seemed an attractive proposition.

The electronic and steric properties that ligands require for making active palladium catalysts for CO/styrene copolymerization have not been disclosed. In fact we found that there is a gap between the structure of the different ligands, which have been successfully reported, and the behavior of the palladium catalysts formed with those ligands. Therefore we decided to perform systematic studies on the effects of chelating ligands in the CO/styrene copolymerization reaction. Some of the ligands used in this work have been previously reported, while others have been designed and synthesized with this purpose. The modular design of the latter allowed systematic variations. The study of the coordination of these ligands to palladium, in solution and when possible in the solid state, enabled us to analyze how these modifications affect both the structure of the organometallic complexes and the activity of the copolymerization catalysts.

In *Chapter 3* sulfur donating ligands, bis-(thio)ethers, are used to synthesize new palladium(II) complexes. Bis-(alkylthio)ethers have been briefly reported previously for CO/styrene copolymerization. The ligands presented in this chapter were chosen from various sulfur ligands known for other catalytic processes and have different chelating ring sizes, and steric and electronic properties. The different behavior of the catalysts under copolymerization conditions as well as the influence of the sulfur ligand on the copolymer microstructure is analyzed.

In *Chapter 4* several nitrogen-donating bidentate ligands, containing the pyrazol fragment, are studied as chelating ligands for palladium(II) complexes. The effects of the various electronic and steric properties of the ligands are analyzed both in the coordination to palladium as well as in the activity of the catalysts in the copolymerization reaction. The stability of the complexes enabled their behavior to be studied over time.

Chapter 5 discusses the design and synthesis of a new group of bisnitrogen chiral ligands derived from imidazolines. The electronic properties of the series of synthesized ligands vary systematically. The structure of the palladium complexes that contain the various ligands is investigated in solution and, in some cases, in the solid state. The effect that the ligands have on the copolymerization reaction of *tert*-butylstyrene with CO is studied. The polyketones obtained with these catalysts are analyzed and their properties rationalized with the ligands used. The reactivity of the palladium catalysts with carbon monoxide is monitored by *in-situ* ^{1}H and ^{13}C NMR spectroscopy and the intermediates are determined.

Chapter 6 deals with the application of some of the new palladium catalysts, presented in the previous chapters, to the terpolymerization of *tert*-butylstyrene and ethene with carbon monoxide. A detailed investigation of the parameters that affect both productivity and the amount of the two olefins incorporated in the terpolymer chain is presented.

Bis-(thio)ethers as chelating ligands for the Pd-catalyzed alternating CO/4-*tert*-butylstyrene copolymerization

Abstract

We synthesized and characterized new neutral and cationic palladium (II) complexes containing bis-(thio)ether ligands. Depending on the rigidity of the ligand backbone and on the chelating ring size, single diastereoisomers or mixtures were obtained. The cationic compounds catalyzed the alternating CO/4-*tert*-butylstyrene copolymerization leading to polyketones with different degree of stereoregularity depending on the nature of the S-S ligand.

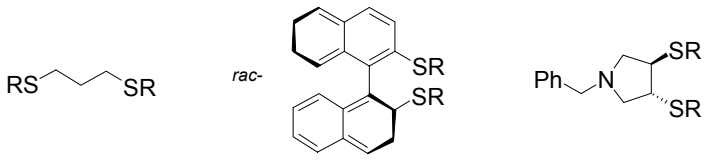
3.1. Introduction

In the last few years there has been much interest in the copolymerization of alkenes with carbon monoxide for yielding perfectly alternating polyketones.[1,2,3] The main topics of interest today are the search for new catalytic systems and the study of the steps of the catalytic cycle.[4] Several types of cationic palladium (II) precatalysts (isolated or "in situ") containing chelating ligands have been reported. Bisnitrogen ligands have been successful in CO/styrene copolymerization[5] as well as P-N ligands.[6] There are only a few examples of phosphorous ligands that have proved to be active in this reaction.[3,7]

Sulfur-containing ligands have been rarely used in this process. It was reported that bis-(alkylthio)ethers are active ligands for the CO/styrene copolymerization process,[2,8] but they have received less attention than N-N or P-P ligands because they involve a loss of stereochemical control. An example with a hemilabile bis-phosphine monosulfide P-P(S) has recently been reported for the CO/ethylene copolymerization.[9] Our experience with thioether ligands in different catalytic processes[10] prompted us to test several bis-(thio)ethers as modifying ligands for palladium copolymerization precatalysts.

Although P-P ligands with relatively large bite angles and flexible backbones, such as dppp, enhance the rate of CO and alkene-insertion reactions, the best N-N ligands are those with small bite angles and rigid backbones, such as bipy or phen.[11,12] We therefore proposed a comparative

study with bis-(thio)ethers that have different rigidities and coordinate to palladium to form five-, six-, and seven-membered ring chelates (Scheme 1).

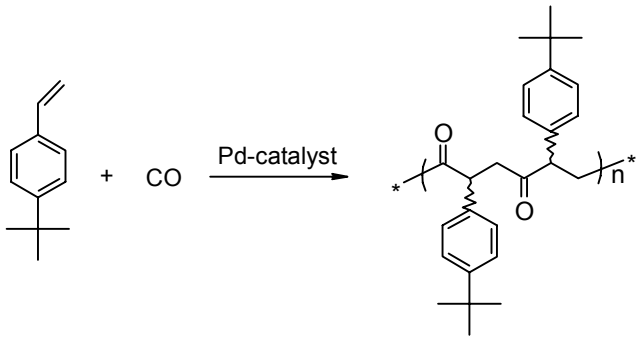


1 2 3

Ligand	R
1	Pr^i
2	Me
3	Pr^i

Scheme 1. Bis-(thio)ethers used in this study

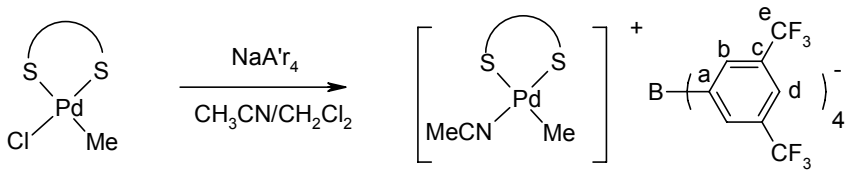
Here we report on the synthesis and characterization of the neutral [PdClMe(S-S)] (**1a-3a**) and cationic [PdMe(NCMe)(S-S)][BAr'$_4$] (**1b-3b**) (Ar' = 3,5-$(CF_3)_2C_6H_3$) palladium(II) complexes. The activity and stereocontrol provided by the cationic ones as catalysts in the CO/4-*tert*-butylstyrene copolymerization is also described (Scheme 2).



Scheme 2. Copolymerization reaction of *tert*-butylstyrene with CO

3.2. Results and discussion

In this work three bis-(thio)ethers -1,3-bis-(isopropylthio)propane (**1**), *rac*-1,1′ binaphtalene-2,2′-dimethylthiol (binasMe_2) (**2**) and (-)-1-benzyl-3,4-bis (isopropylsulfanyl)pirrolidine ((-)-deguspr^i) (**3**)- were coordinated to palladium to obtain the neutral and cationic complexes (**1a**-**3a**, **1b**-**3b**). The neutral complexes [PdClMe(S-S)] (**1a-3a**) were obtained by reaction of [PdClMe(cod)] (cod = 1,5-cyclooctadiene) with an equimolar amount of the corresponding bis-(thio)ether ligands in dichloromethane. Displacement of the chloro ligand using NaBAr′$_4$ in the presence of acetonitrile gave the cationic derivatives (**1b- 3b**) (Scheme 3). The ligand with the more flexible backbone (**1**) led to broad signals in the NMR spectra of **1a** and **1b.** This was probably because there were several diastereomeric species in equilibrium in solution, since the sulfur atoms became stereogenic centers upon coordination to palladium.[16] There was no evidence of similar behavior with the complexes containing ligands **2** and **3**, whose ^{1}H NMR signals at room temperature remained sharp. However it was reported the fluxional behaviour of complex [Pd$(Cl)_2$(**2**)] in solution, due to the different spatial arrangements of the S-methyl substituents and the different conformations of a seven-membered chelate ring.[17] It the case of hindered ligand **3** the more rigid backbone together with the five-membered chelate ring may account for the presence of a give single diastereomeric species in solution, which agrees with the behavior observed in the related complex [Pd$(Cl)_2$(**3**)], which gives a single diastereomer in solution.[18]



S-S	Neutral	Cationic
1	**1a**	**1b**
2	**2a**	**2b**
3	**3a**	**3b**

Scheme 3. Synthesis of the cationic complexes **1b-3b**

Complexes **1b-3b** were tested as catalysts for the alternating CO/4-tert-butylstyrene (TBS) copolymerization and turned out to be active (Table 1). In general an increase of CO pressure led to a faster decomposition of the catalyst to palladium metal together with increasing amounts of poly-(4-*tert*-butyl)styrene. All the experiments were performed at room temperature and reaction times were varied between 24–64 hours. To avoid decomposition of the catalyst also one experiment at low temperature (273 K) was done, but in this case inhibition of activity was observed. Although **1b** had the lowest activity at atmospheric pressure (entry 1), it was active at higher pressures (entries 4 and 6). It is remarkable that **1b** is more active at 5 atm. than at 1 atm. unlike what happens with N-N donor ligands.[6] Precursor **3b** decomposed so readily under CO atmosphere that no experiments at higher pressures were performed.

Table 1. Comparative activity of precursors [PdMe(NCMe)(S-S)][BAr'$_4$] (**1b-3b**) as copolymerization catalysts.

Entry	Precursor	PCO (atm)	TBS/cat	M_n (M_W/M_n)	Prod (g CP/g Pd.h)
1	**1b**	1	300	3300 (1.1)[a]	0.8
2	**2b**	1	250	10080 (1.4)[b]	2.4
3	**3b**	1	400	7950 (1.8)[b]	3.4
4	**1b**	5	300	15700 (1.3)[a]	6.9
5	**2b**	5	250	7700 (1.5)[b]	1.4
6	**1b**	10	300	10100 (1.5)[b]	1.8

Reaction conditions: 0.025 mmol catalyst, 5 mL chlorobenzene, room temperature, 24 hours. [a] Determined by SEC-MALLS measurements. [b] Determined by GPC measurements relative to polystyrene standards.

We were able to study the behavior of **1b** and **2b** over time because of their greater stability under CO atmosphere (Table 2). When we increased the ratio of substrate to catalyst we observed higher productivity (entries 1-2, 4-5). This could be attributed to the higher stability of the catalysts when we increased the amount of styrene.[4i] For both precursors longer reaction times led to a decrease in productivity. This was probably

due to the increasing difficulty of the monomers to access the catalytic site and the decomposition of the catalysts.

Table 2. Influence of time and amount of alkene in catalytic experiments.

Entry	Precursor	t (h)	TBS/cat	M_n (M_W/M_n)	Prod (gCP/gPd.h)
1	**1b**	24	300	3300 (1.1)[a]	0.8
2	**1b**	24	600	11000 (1.4)[a]	2.9
3	**1b**	64	600	8600 (1.4)[a]	1.6
4	**2b**	24	250	10080 (1.4)[b]	2.4
5	**2b**	24	1600	5900 (1.8)[b]	5.3
6	**2b**	64	1600	9600 (1.6)[b]	4.3

Reaction conditions: 0.025 mmol catalyst, 5 mL chlorobenzene, room temperature, 1 atm CO. [a] Determined by SEC-MALLS measurements. [b] Determined by GPC measurements, relative to polystyrene standards.

Although the activities and molecular weights with bis-(thio)ethers as chelating ligands were not as high as with planar N-N ligands (bipy, phen, etc.), they were similar to those with chiral P-OP, N-N or P-N ligands.[3,5a,7] However with these S-S ligands molecular weights up to 15700 g/mol have been obtained in milder conditions. The rather high

polydispersity values together with a non linear relationship between time and molecular weight of the copolymers show that these system do not behave as living ones.[19]

It has been suggested that the bis-(thio)ethers produce atactic copolymers probably because their structure in the donor atom is flexible.[2] Comparison of the ^{13}C NMR spectra of the copolymers obtained with **1b**-**3b** and an epimerized copolymer suggested us that the tacticity of the materials strongly depended on the structure of the S-S ligand (Figure 1).

The reference spectrum shows in the region of the methylenic carbon the broad signals attributed to the four triads *ll*, *ul*, *lu* and *uu* in a ratio 1:2:1 due to the overlapping of the two heterotactic triads. The palladium precursor substituted with the achiral bis-(thio)ether **1** showed a major signal in the region of the *uu*-triad relative to a tendency to syndiotacticity, as observed for achiral N-N ligands.[5a] However the copolymer produced with the catalyst **2b** modified with a chiral racemic ligand was atactic, as previously reported for S-S ligands. Finally the copolymer obtained with **3b** showed a main signal relative to the *ll*-triad which is an evidence for the prevailing isotactic structure.[5c]

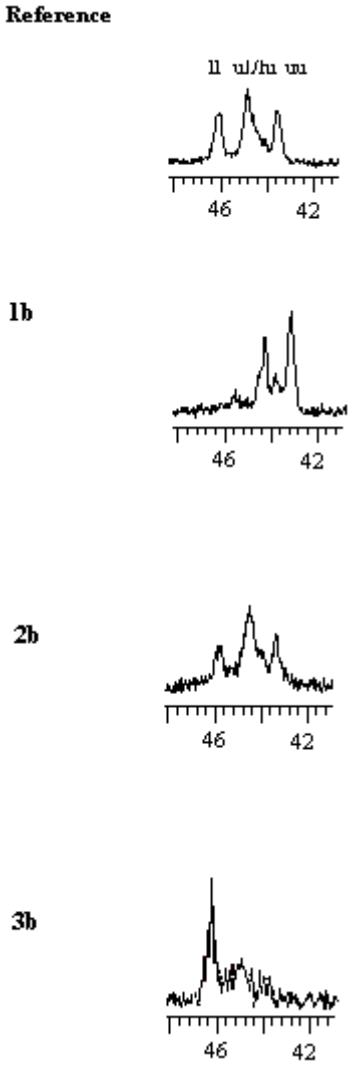


Figure 1. Methylene carbon atom-region of the copolymers obtained with precursors **1b**, **2b** and **3b**. The reference spectrum is epimerized poly (4-tert- butylstyrene- alt- CO)

3.3. Conclusions

We have shown that palladium (II) complexes with bis-(thio)ether ligands (**1-3**) are active in the alternating CO/4-*tert*-butylstyrene copolymerization under mild conditions of pressure and temperature. Additionally we have proved that, in contrast with what has been proposed for bis-(thio)ethers, choosing the right S-S ligand a control on stereoregularity can be achieved.

3.4. Experimental

3.4.1. General procedures

All syntheses were carried out in a nitrogen atmosphere at room temperature using standard Schlenk techniques. Solvents were distilled and deoxygenated prior to use unless otherwise stated. The salt $NaBAr'_4$ (Ar'= 3,5-$(CF_3)_2$-C_6H_3) and the palladium precursor [PdClMe(cod)] (cod= 1,5-cyclooctadiene) were prepared according to reported method.[13,14] Ligands **1**, **2** and **3** were prepared according to literature.[10b,15] Elemental analyses were carried out on a Carlo Erba Microanalyser EA 1108.^{1}H NMR spectra were recorded on a Varian Gemini spectrometer with a ^{1}H resonance frequency of 300 MHz. Chemical shifts were reported relative to tetramethylsilane as internal standard. IR spectra were recorded on a Brucker Equinox 55 FT-IR spectrophotometer. Molecular weight of the copolymers and molecular weight distributions were determined by size exclusion chromatography (SEC - MALLS) measurements made in THF on a Waters 510-GPC device using a SHODEX K-800P precolumn and a three-serial column system (SHODEX K80M and PLGEL MIXED-D and MIXED-E linear columns) with

a Wyatt mini-DAWN Light Scattering and a SHIMADZU RID-6A refractive index detector or on a Waters 515-GPC device using a lineal Waters Ultrastyragel column with a Waters 2410 refractive index detector using polystyrene standards.

3.4.2. Synthesis of the neutral complexes

[PdClMe(1)] (1a) (**1** = 1,4-bis(isopropylthio)propane)

A solution of [PdClMe(cod)] in CH_2Cl_2 was added to a solution of **1** (in 10% excess) in CH_2Cl_2 and the mixture was stirred for an hour. After the solvent evaporated to 1 ml, the addition of Et_2O gave a yellow compound. Yield: 67%. Anal. Found for $C_{10}H_{23}ClPdS_2$: C, 34.45; H, 6.55; S, 18.57; Calc.: C, 34.41; H, 6.59; S, 18.37. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.64 (sp, ^3J = 6.6 Hz, 1H, CH), 3.36 (sp, ^3J = 6.6 Hz, 1H, CH), 2.8 (m, 2H, CH_2S), 2.61 (m, 2H, CH_2S), 2.22 (m, 2H, CH_2), 1.43 (d, ^3J = 6.6Hz, 6H, CH_3), 1.37 (d, ^3J = 6.6Hz, 6H, CH_3), 0.77 (s, 3H, Pd-CH_3).

[PdClMe(2)] (2a) (**2** = binasMe_2)

A similar synthesis as for **1a** was performed using hexane to precipitate an orange compound. Yield: 80%. Anal. Found for $C_{23}H_{21}ClPdS_2$: C, 54.16; H, 4.33; S, 11.14; Calc.: C, 54.89; H, 4.17; S, 12.74. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.14- 6.97 (12H, Harom.), 2.66 (s, 3H, CH_3S), 2.43 (m, 3H, CH_3S), 1.04 (Pd-CH_3).

[PdClMe(3)] (3a) (**3** = degusPr^i_2)

A similar synthesis as for **2a** was performed. This yielded a white-brownish oily compound. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.7- 7.32 (m, 5H,

Harom.), 4.75 (d, ^{2}J= 12.8 Hz, 1H, CH_2), 4.21 (m, 1H, CH_2N), 3.53 (d, ^{2}J= 12.8 Hz, 1H, CH_2), 3.45 (m, 1H, CH_2N), 3.2 (m, 1H, CH_2N), 3.0 (sp, ^{3}J= 6.7 Hz, 1H, CH), 2.86 (sp, ^{3}J= 6.7 Hz, 1H, CH), 2.6 (d, ^{3}J= 10.1 Hz, 1H, CHS), 2.43 (d, ^{3}J= 10.1 Hz, 1H, CHS), 2.15 (m, 1H, CH_2N), 1.3 (d, ^{3}J= 6.7 Hz, 12H, CH_3), 1.25 (s, 3H, Pd-CH_3).

3.4.3. Synthesis of the cationic complexes

[PdMe(NCMe)(1)][BAr′$_4$] (1b)

A solution of **1a** in 2 ml of CH_2Cl_2 was added to a solution of NaBAr′$_4$ in the minimum volume of CH_3CN and allowed to react for one hour. The suspension was filtered over Kieselghur, the solvent reduced to 1 ml and pentane added to give a white-brownish compound. Yield: 74%. Anal. Found for $C_{44}H_{38}BF_{24}NPdS_2$: C, 43.57; H, 3.30; N, 1.05; S, 5.61; Calc.: C, 43.39; H, 3.12; N, 1.15; S, 5.27. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.69 (s, 8H, H_b), 7.54 (s, 4, H_d), 3.25 (sp, ^{3}J = 6.8Hz, 1H, CH), 3.06 (sp, ^{3}J = 6.8Hz, 1H, CH), 2.79 (m, 4H, CH_2S), 2.24 (s, 3H, Pd-$NCCH_3$), 2.16 (m, 2H, CH_2), 1.42 (d, ^{3}J = 6.8Hz, 6H, CH_3), 1.32 (d, ^{3}J= 6.8 Hz, 6H, CH_3), 1.01 (s, 3H, Pd-CH_3).

[PdMe(NCMe)(2)][BAr′$_4$] (2b)

Complex **2b** was synthesized in a similar way. A dark red compound was obtained. Yield: 64%. Anal. Found for $C_{57}H_{36}BF_{24}NPdS_2$: C, 48.60; H, 2.39; N, 1.02; S, 4; Calc.: C, 49.88; H, 2.63; N, 1.02; S, 4.7. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.18- 6.99 (m, 24H, Harom.), 2.5 (s, 3H, Pd-$NCCH_3$), 2.4 (s, 3H, CH_3S), 2.06 (s, 3H, CH_3S), 1.25 (s, 3H, Pd-CH_3).

[PdMe(NCMe)(3)][BAr'$_4$] (3b)

Complex **2b** was synthesized in a similar way. An orange oil was obtained. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.71 (s, 8H, H_b), 7.54 (s, 8H, H_d), 7.39 (m, 5H, Harom.), 4.26 (d, ^2J= 13.4 Hz, 1H, CH_2), 3.99 (m, 1H, CH_2N), 3.65 (d, ^2J= 13.4 Hz, 1H, CH_2), 3.28 (m, 2H, CH_2N), 2.98 (sp, ^3J= 6.8 Hz, 2H, CH), 2.7 (d, ^3J= 10.7 Hz, 1H, CHS), 2.55 (d, ^3J= 10.7 Hz, 1H, CHS), 2.36 (m, 1H, CH_2N), 2.2 (s, 3H, Pd-$NCCH_3$), 1.32 (d, ^3J= 6.8 Hz, 6H, CH_3), 1.26 (s, 1H, Pd-CH_3), 1.25 (d, ^3J= 6.8 Hz, 6H, CH_3).

3.4.4. CO/ 4-*tert*-butylstyrene copolymerization experiments

The 4-tert-butylstyrene was passed through a small column of Al_2O_3 prior to use. Chlorobenzene was used as purchased from Aldrich. In a typical procedure, the cationic precursor **1b**, **2b** or **3b** (0.025 mmol) was dissolved in 5 ml of chlorobenzene in a previously purged Schlenk and placed under CO atmosphere. 4-*tert*-butylstyrene was then introduced and the reaction was allowed to take place at room temperature and 1 atm of CO. The experiments under higher CO pressure were carried out in a 100 mL stainless steel Berghoff autoclave. The reaction mixture was introduced into the autoclave by suction and the pressure level was kept constant by continuous feeding from a gas reservoir. Reaction times varied from 24 to 64 hours. Workup included filtration of the reaction mixture through Kieselghur and precipitation of the polymeric material by adding the reaction solution dropwise into 100 ml of rapidly stirring methanol. The off-white powder was collected by filtration and then purified by column chromatography through silica. The homopolymer impurity was eluted first with CH_2Cl_2, and pure copolymer was then obtained by elution with ethyl

acetate. The product was then washed with methanol and dried in a vacuum oven at 70º C overnight.

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Pyrazol-containing catalysts for the alternating copolymerization of CO/4-*tert*-butylstyrene

Abstract

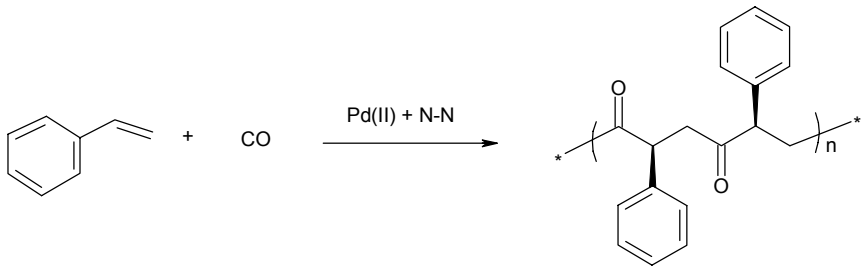
The activity of new cationic palladium (II) complexes, containing bisnitrogen ligands with a pyrazol moiety, in the copolymerization of 4-*tert*-butylstyrene with CO, is studied. The C_S-symmetry of the ligands leads to the synthesis of copolymers with syndiotactic microstructure. The molecular weight and the polydispersity of the obtained polymers are among the best reported for bisnitrogen planar ligands when mild reaction conditions are used.

4.1. Introduction

The copolymerization of carbon monoxide and alkenes using palladium catalyst is providing much interest.[1-3] Ethylene/carbon monoxide copolymerization has been widely studied and results have been best with diphosphine ligands. The high activity of these systems has raised industrial interest in the process.[4-9] Several groups are reporting on the exploration of new systems.[10-15]

Chiral ligands have been successfully used for the copolymerization of carbon monoxide with propene[16,17] and styrene.[18-21] With styrene, however, only oligomers with low molecular weight are obtained with phosphine ligands. This has been attributed to a favoured β-hydride elimination.[1]

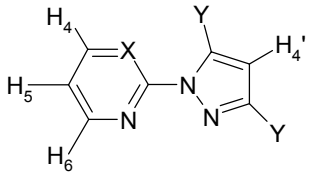
The first systems studied with styrene were Pd (II) catalyst based on planar 2,2'- bypiridine or 1,10 - phenantroline to give syndiotactic poly (styrene-alt- CO) (Scheme 1).[22-24] This high stereochemical control (>90%) has been attributed to a chain-end control due to the interaction of the growing chain with the incoming styrene unit, which inserts exclusively in the 2,1- fashion. [3,25]



Scheme 1. Syndiotactic polyketones are obtained using bipy or phen as N-N ligands

Chiral N-N ligands have also been successfully explored to yield isotactic copolymers,[18,19,25,26] although in some cases the chain-end control is more efficient than the enantiosite control caused by the ligand and this results in the formation of syndiotactic polymers.[25] C_1-symmetric chiral P-N ligands have been used to yield isotactic polymers due to the site-selective coordination of the alkene in the chiral environment generated by the ligand.[21,25] For these systems, using P-N ligands, high CO pressures and moderate temperatures are required.

Since planar N-N ligands are efficient and since there is an interest in exploring new types of ligands, we report on the synthesis of new well-defined cationic Pd(II) catalyst using the unsymmetrical chelate ligands 2-(1-pyrazolyl)pyridine (pzpy, **1**), 2-(1-pyrazolyl)pyrimidine (pzpm, **2**) and 2-(1-(3,5-dimethyl)pyrazolyl)pyrimidine (pz*pm, **3**), which yield syndiotactic alternating copolymers of *tert*- butylstyrene and CO at mild pressure and temperature.



X = CH Y = H pzpy (**1**)
X = N Y = H pzpm (**2**)
X = N Y = Me pz*pm (**3**)

Scheme 2. (N-N′) - ligand systems

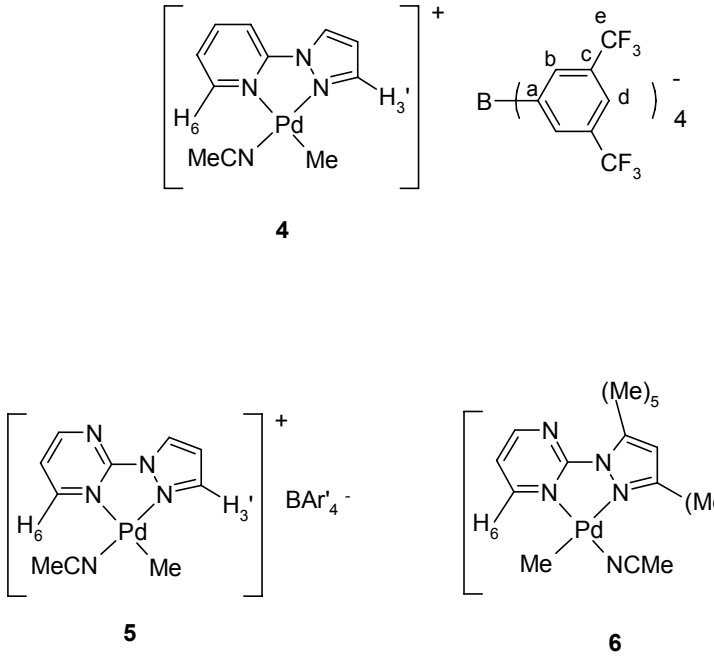
4.2. Results and discussion

4.2.1. Synthesis and characterization of the palladium catalyst precursors [PdMe(NCMe)(N-N′)][BAr$_4$′] (4-6)

The cationic complexes [PdMe(NCMe)(N-N′)][BAr$_4$′] were obtained by adding a previously prepared solution of the neutral complexes [PdClMe(N-N′)][27] to an equimolar solution of NaBAr′$_4$ in MeCN.

NOE difference NMR experiments showed that cationic precursors **4** and **5** had the methyl group *trans* to pyridine and pyrimidine ring, respectively, while **6** had the methyl group *trans* to the pyrazole moiety (Scheme 3). Because of the large *trans* influence of the methyl group, we should expect it to be coordinated *trans* to the less basic ring (pyrazole in compound **4** and pyrimidine in compounds **5** and **6**). We therefore believe that this stereochemistry cannot be explained in terms of electronic effects. The sterical hindrance caused by the hydrogen H_6 in compounds **4** and **5** may be larger than the one caused by the $H_{3'}$ of the pyrazole fragment, which could force the methyl to be *cis* to the pyrazole in both molecules. This agrees with the stereochemistry observed in **6**, where the steric

demand of the methyl group $(Me)_3$ of the pyrazole ring is greater than the bulkiness of H_6, thus placing the methyl group trans to the pyrazole moiety.



4 **5** **6**

Scheme 3. Stereochemistry around palladium of compounds **4**, **5** and **6**

Spectroscopic data suggest that these configurations are in agreement with the stereochemistry of the related [PdClMe(N-N)], although in the case of [PdClMe(pz*pm)] there is also a minor isomer with the methyl ligand *trans* to the pyrimidine ring.[27] In the case of **6**, it is also noteworthy the fluxional behaviour found for the pz*pm ligand (**3**). An NOE experiment carried out at low temperature (243 K) reflects the expected NOE interaction between the methyl group and H_6. However, at room temperature an NOE effect has been found not only with this proton

but also with H_4 being the observed percent of 2.4 % for H_6 and 0.6 % for H_4. This implies a process of Pd-N bond rupture, internal rotation of the ligand around the pz*-pm bond and reformation of the Pd-N bond. The two separated resonances for H_4 and H_6 at room temperature indicate that the process is in a slow exchange regime at this temperature. This Pd-N bond rupture is also observed in related Pd (II) complexes with this type of ligands.[28]

4.2.2. Copolymerization experiments

Whereas C_{2v} -symmetric bipyridyl- or phenantroline- type ligands are a well-known class of planar ligands for the styrene/CO copolymerization reaction, few systems have been reported in which a non symmetrical N-N' planar ligand leads to similar activities and molecular weights.[29] The new complexes **4**, **5** and **6** were explored as catalysts in this reaction at mild conditions (room temperature and 1 atmosphere of CO) (Table 1).

The catalyst precursor **5** seemed the most active after 24 h, with a productivity of 11.75 g/(g Pd. h), although the cationic system **4** behaved in a similar way (entries 1 and 2). Increasing the reaction time from 24 hours to 48 hours led, as expected, to higher conversions and molecular weights although the difference in activity between the two catalysts (**4** and **5**) narrowed, probably due to the combined effects of the increasing difficulty of the monomers to access the catalytic site and decomposition of catalyst **5** to palladium metal (entries 4 and 5). The molecular weights (20000 - 70000)

and the polydispersities (1.1 - 1.3) are in the order of the best ones reported for bisnitrogen systems using styrene derivatives.[24,26] The activity and molecular weight obtained with catalyst precursor **6** were lower than those obtained with precursors **4** and **5** (entries 1-3). This lower productivity may be attributed to the sterically more demanding ligand pz*pm (**3**), as previously reported for other systems.[25] When the substrate / catalyst ratio is 620 for precursor **4,** productivity and molecular weight increased (entries 1 and 6).

We also studied the effect of CO pressure. When the CO pressure was increased to 5 atm., conversion and molecular weight decreased, although polydispersities remained stable (entries 7 and 8).

Table 1. Copolymerization of 4- tert- butylstyrene and CO with **4**, **5** and **6** at 1 atm. CO and RT

Entry	Catalyst precursor	pCO (atm.)	t (h)	% Conv.[a]	M_n (M_W/M_n) (g CP/g Pd.h)
1	**4**	1	24	38.45	21440 (1.1)
2	**5**	1	24	55	36353 (1.3)
3	**6**	1	24	25.78	15720 (1.5)
4	**4**	1	48	67.49	72360 (1.1)
5	**5**	1	48	68.88	70680 (1.2)
6[b]	**4**	1	24	43.15	30380 (1.4)
7	**4**	5	24	14.59	15570 (1.1)
8	**5**	5	24	10.73	7155 (1.2)

Reaction conditions: Solvent: 5 mL chlorobenzene, alkene/catalyst = 310. [a]Styrene conversion calculated from the isolated polymer weight. [b]alkene/catalyst = 620.

To compare the activity of the most active catalyst precursors **4** and **5**, we varied reaction times from 7 h to 72 h and plotted styrene conversion against reaction time (Fig. 1). With catalyst **5** the initial reaction rate was

higher but prolonged reaction time with **4**, however, resulted in similar conversions, as mention above.

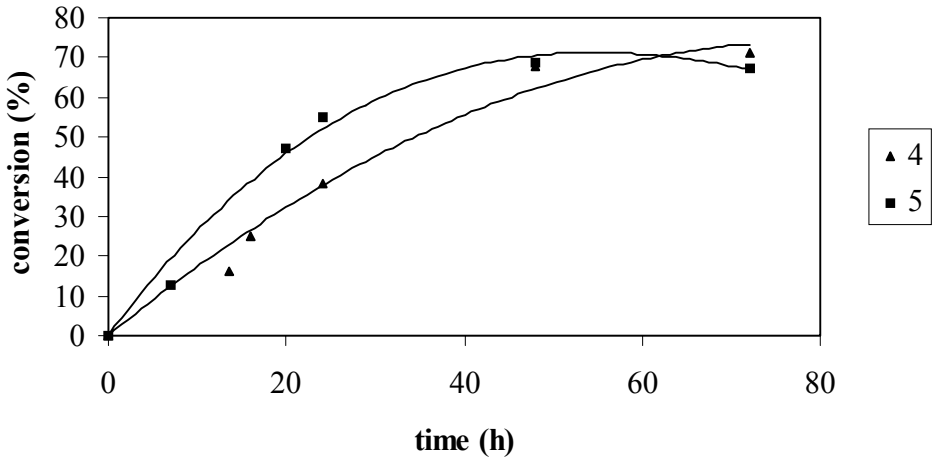


Fig.1. Compared activity of catalysts **4** and **5**, containing ligands pzpy and pzpm, respectively

All the systems we studied yield prevailing syndiotactic copolymers, which is indicative of a stereocontrol from the growing polymer chain (chain-control). Analysis of the decoupled ^{13}C spectra indicated a substantial degree of stereoregularity (ca. 92% of syndiotactic diads) by integration of the signals of the methylene carbon atoms. The greater resonance at 43.2 ppm was assigned to the syndiotactic *uu*- triad by comparison with the spectrum of the epimerized polymer and with literature values (Fig. 2).[18,21]

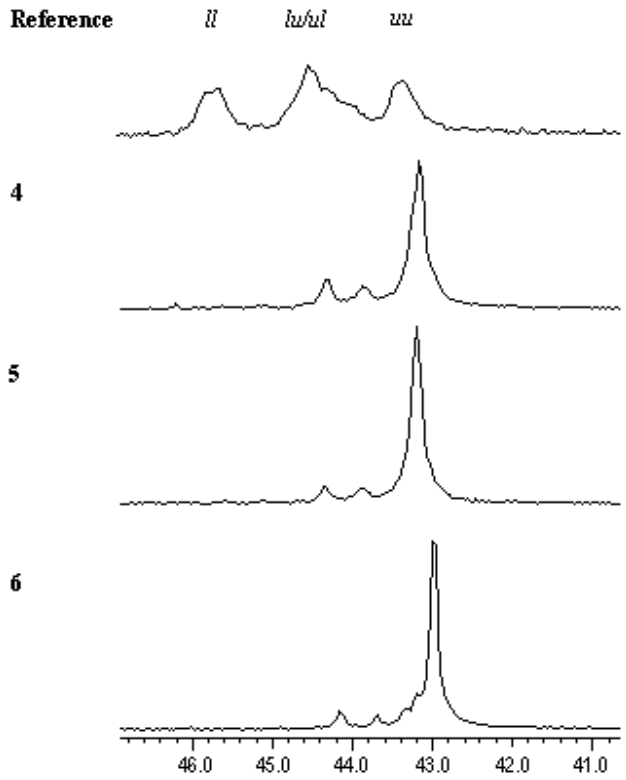


Fig.2. Methylene carbon atom-region of the copolymers obtained with precursors **4**, **5** and **6**. The reference spectrum is epimerized poly (4-*tert*-butylstyrene- alt- CO)

4.3. Conclusions

This study shows that new cationic palladium(II) compounds containing the bisnitrogen ligands pzpy (**1**), pzpm (**2**) and pz*pm (**3**) are active as catalyst precursors in the alternating CO/4-*tert*-butylstyrene

copolymerization. The C_S-symmetry of the ligands did not seem to affect stereocontrol, which was determined by the chain end. These systems behave similar to the previously studied C_{2v}-symmetric bipyridyl and phenantroline ligands that yield readily syndiotactic copolymers.

4.4. Experimental

4.4.1. General procedure

All reactions were carried out in a nitrogen atmosphere at room temperature using standard Schlenk techniques. Solvents were distilled and deoxygenated prior to use unless otherwise stated. The salt $NaBAr'_4$ (Ar'= 3, 5- $(CF_3)_2$-C_6H_3) was prepared according to reported methods.[30] Ligands **1** and **2** were prepared according to published methods.[28] **3** was prepared in a similar way.

^1H and ^{13}C NMR spectra were recorded on a Varian Gemini spectrometer with a ^1H resonance frequency of 300 MHz and on a Varian Mercury VX spectrometer with a ^1H resonance frequency of 400 MHz. Chemical shifts were reported relative to tetramethylsilane for ^1H and ^{13}C. Some assignments in NMR spectra were determined by ^1H - ^{13}C COSY, DEPT and NOE experiments. IR spectra (range 4000-400 cm^{-1}) were recorded on a Midac Grams/386 spectrophotometer in KBr pellets. Elemental analyses were carried out on a Carlo Erba Microanalyser EA 1108. The molecular weight of the copolymers and molecular weight distributions were determined by gel permeation chromatography (GPC - MALLS) measurements made in THF on a Waters 510 gel-permeation

chromatography device using a three-serial column system (SHODEX K80M and PLGEL MIXED-D and MIXED-E linear columns) with a Wyatt mini-DAWN Light Scattering and a SHIMADZU RID-6A refractive index detector.

4.4.2. Synthesis of catalyst precursors

[PdMe(NCMe)(pzpy)][BAr'$_4$] (4)

A previously prepared solution of [PdClMe(pzpy)][27] (0.05 g, 0.17 mmol) in 3 mL of CH_2Cl_2 was added to a solution of NaBAr'$_4$ (Ar'= 3,5-$(CF_3)_2C_6H_3$) (0.147 g, 0.17 mmol) in the minimum amount of MeCN. The light orange solution formed was stirred for about an hour, filtrated through Kieselghur and evaporated to dryness. The white-brownish compound was crystallised from CH_2Cl_2 / hexane. Yield: 75%. Anal. Found: C, 44.71; H, 2.11; N, 4.75%. Calc. for $C_{43}H_{25}BF_{24}N_4Pd$: C, 44.10; H, 2.14; N, 4.78%. ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 8.15 (ddd, ^3J = 5.2 Hz, ^4J = 1.6 Hz, ^5J = 0.8 Hz, 1H, H_6), 8.08 (d, ^3J = 3.2 Hz, 1H, $H_{5'}$), 7.9 (ddd, ^3J = 8.4 Hz, ^3J = 7.6 Hz, ^4J = 1.6 Hz, 1H, H_4), 7.8 (d, ^3J = 2.0 Hz, 1H, $H_{3'}$), 7.71 (s, 8H, H_b), 7.52 (s, 4H, H_d), 7.45 (td, ^3J = 8.4 Hz, ^4J = 0.8 Hz, ^5J = 0.8 Hz, 1H, H_3), 7.23 (ddd, ^3J = 7.6 Hz, ^3J = 5.2 Hz, ^4J = 0.8 Hz, 1H, H_5), 6.7 (dd, ^3J = 3.2 Hz, ^3J = 2 Hz, 1H, $H_{4'}$), 2.38 (s, 3H,Pd-CH_3CN), 1.21 (s, 3H, Pd-CH_3). ^{13}C NMR (100.5 MHz, $CDCl_3$, RT): δ 161.9 (q, J_{C-B} = 198.3 Hz, C_a), 147.5 (s, C_6), 142.4 (s, $C_{3'}$or C_4), 142.3 (s, C_4 or $C_{3'}$), 135 (s, C_b), 129.5 (s, $C_{5'}$), 129.1 (m, C_e), 126 (s, C_c), 124.4 (s, C_5), 123.3 (s, Pd-CH_3CN), 117.7 (s, C_d), 111.2 (s, $C_{4'}$or C_3), 111.1 (s, C_3 or $C_{4'}$), 3.3 (s, Pd-CH_3CN), -0.8 (s, Pd-CH_3).

[PdMe(NCMe)(pzpm)][BAr′$_4$] (5)

Compound **5** was obtained from [PdClMe(pzpm)][27] as a white-brownish solid in a similar way to compound **4**, although it does not analyse as a pure solid. Yield: 72%. Anal. Found: C, 43.29; H, 2.22; N, 6.07%. Calc. for $C_{43}H_{24}BF_{24}N_5Pd$: C, 43.03; H, 3.59; N, 5.98%. ^{1}H NMR (300 MHz, $CDCl_3$, RT): δ 8.74 (dd, ^3J = 4.8 Hz, ^4J = 2.4 Hz, 1H, H_4), 8.57 (dd, ^3J = 3.2 Hz, ^4J = 0.8 Hz, 1H, $H_{5'}$), 8.33 (dd, ^3J = 5.2 Hz, ^4J = 2.4 Hz, 1H, H_6), 7.84 (dd, ^3J = 2.4 Hz, ^4J = 0.8 Hz, 1H, $H_{3'}$), 7.71 (s, 1H, H_b), 7.52 (s, 1H, H_d), 7.14 (dd, ^3J = 5.2 Hz, ^3J = 4.8 Hz, 1H, H_5), 6.76 (dd, ^3J = 3.2 Hz, ^3J = 2.4 Hz, 1H, $H_{4'}$), 2.32 (s, 3H, Pd-CH_3CN), 1.3 (s, 3H, Pd-CH_3). ^{13}C NMR (100.5 MHz, $CDCl_3$, RT): δ 161.9 (q, $J_{C\text{-}B}$ = 198.3 Hz, C_a), 161.6 (s, C_6), 156.3 (s, C_4), 143.8 (s, $C_{3'}$), 135 (s, C_b), 132.3 (s, $C_{5'}$), 129.2 (m, C_e), 126 (s, C_c), 123.3 (s, Pd-CH_3CN), 120.8 (s, C_5), 117.7 (s, C_d), 111.2 (s, $C_{4'}$), 3.2 (s, Pd-CH_3CN), -0.1 (s, Pd-CH_3).

[PdMe(NCMe)(pz*pm)][BAr′$_4$] (6)

Compound **6** was synthesised from [PdClMe(pz*pm)][27] following a similar procedure to compound **4** and isolated as a light grey solid. Yield: 82.1%. Anal. Found: C, 44.6; H, 2.3; N, 5.6%. Calc. for $C_{44}H_{28}BF_{24}N_5Pd$: C, 44.1; H, 2.3; N, 5.8%. ^{1}H NMR (400MHz, $CDCl_3$, RT): δ 8.80 (dd, ^3J = 4.8 Hz, ^4J = 2.2 Hz, 1H, H_4), 8.48 (dd, ^3J = 6 Hz, ^4J= 2.2 Hz, 1H, H_6), 7.71 (s, 8H, H_b), 7.53 (s, 4H, H_d), 7.29 (dd, ^3J = 6 Hz, ^3J = 4.8 Hz, 1H, H_5), 6.19 (s, 1H, $H_{4'}$), 2.7 (s, 3H, $(Me)_3$ or $(Me)_5$), 2.35 (s, 3H, Pd-CH_3CN), 2.23 (s, 3H, $(Me)_5$ or $(Me)_3$), 1 (s, 3H, Pd-CH_3). ^{13}C NMR (75.4 MHz, $CDCl_3$, RT): δ 161.9 (q, $J_{C\text{-}B}$ = 198.2 Hz, C_a), 160.6 (s, C_6), 156 (s, C_4), 135 (s, C_b), 129.1 (m, C_e) 126.5 (s, C_c), 122.9 (s, Pd-CH_3CN), 119.3 (s, C_5), 117.7 (s, C_d), 113.5 (s, $C_{4'}$), 15.4 (s, $(Me)_3$ or $(Me)_5$), 13.3 (s, $(Me)_5$ or $(Me)_3$), 5.5 (s, Pd-CH_3CN), 3.4 (s, Pd-CH_3).

4.4.3. Copolymerization reactions- General Procedure

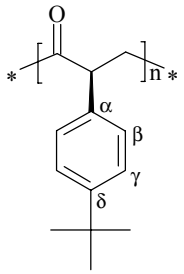
The 4-*tert*-butylstyrene was passed through a small column of Al_2O_3 prior to use. Chlorobenzene was used as purchased from Aldrich.

In a typical procedure the cationic precursor **4**, **5** or **6** (0.0125 mmol) was dissolved in 5 mL of chlorobenzene in a previously flushed Schlenk and the N_2 atmosphere replaced with CO. 4-*tert*-butylstyrene (0.7 mL, 3.875 mmol) was then introduced and the reaction was allowed to take place at room temperature and 1 atm. of CO. The experiments under 5 atm. of CO pressure were carried out in a 100 mL stainless steel Berghoff autoclave. The reaction mixture was introduced into the autoclave by suction and the pressure level was kept constant by continuous feeding from a gas reservoir. Reaction times varied from 7 hours to 96 hours. Workup included filtration of the reaction mixture through Kieselghur and precipitation of the polymeric material by adding the reaction solution dropwise into 100 mL of rapidly stirring methanol. The off-white powder was collected by filtration, washed with methanol and dried in a vacuum oven at 70^o C overnight. Percentage conversions were calculated from the weight of the isolated polymeric material.

The polymers were purified by reprecipitation and then polymer weights were measured. The copolymers were dissolved in the minimum amount of THF, the solutions were filtered over a 0.22 μm filter and added dropwise to stirring methanol. The solid was then filtered and dried as previously stated.

4.4.4. Copolymer characterization

^{1}H NMR (300 MHz, $CDCl_3$, RT): δ 7.0 (d, ^{3}J = 8.1 Hz, 2H, H_β or H_γ), 6.59 (d, ^{3}J = 8.1 Hz, 2H, H_γ or H_β), 4.11 (t, ^{3}J = 6.9 Hz, 1H, CH), 3 (dd, ^{2}J = 18.1 Hz, ^{3}J = 6.9 Hz, 1H, CH_2), 2.64 (dd, ^{2}J = 18.1 Hz, ^{3}J = 6.9 Hz, 1H, CH_2), 1.23 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (75.4 MHz, $CDCl_3$, RT): δ 206.9 (-C(O)-), 149.8 (C_δ), 134.3 (C_α), 128.2 (C_γ), 125.6 (C_β), 52.9 (CH), 43.2 (CH_2), 34.5 ($\underline{C}(CH_3)_3$), 31.5 ($C(\underline{C}H_3)_3$). IR (KBr, cm^{-1}): ν 1709 (C = O).



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Influence of pyridine-imidazoline ligands on the reactivity of palladium-methyl complexes with carbon monoxide

Abstract

New C_1-symmetrical pyridine-imidazoline ligands were synthesized and used in the preparation of neutral complexes [PdClMe(N-N')] and two series of monocationic complexes [PdMe(NCMe)(N-N')][X] (X = PF_6^-, BAr'_4^-). The pyridine-imidazoline ligands are modified with various R substituents at the aminic N atom of the imidazoline ring. These substituents make it possible to vary the electronic properties of the nitrogen-donor atoms. The crystal structures of two neutral palladium precursors [$PdCl_n(Me)_{2-n}$ (N-N')] (n = 1, 2) with different R substituents show different Pd-N coordination distances and geometrical distortions in the imidazoline ring. The characterization in solution of the neutral derivatives evidences the presence of the complex with the Pd-Me group cis to the imidazoline ring (*cis* isomer). For the cationic complexes, the number and the kind of stereoisomers present in solution depend on the nature of

both the ligand and the anion. The reactivity of the cationic complexes with carbon monoxide was studied in solution by multinuclear NMR spectroscopy, and it was shown that the Pd-acyl-carbonyl species was formed as the final product. The cationic complexes with BAr'_4^- behave as catalysts in the CO/4-*tert*-butylstyrene copolymerization and yield polyketones whose stereoregularity depends on the nature of the ligand. The stereocontrol in the copolymerization process is tentatively explained on the basis of the results of this mechanistic investigation.

5.1.1. Introduction

The insertion of unsaturated molecules into metal-carbon bonds is a fundamental step for C-C bond formation reactions catalyzed by organometallic compounds.[1] In the last fifteen years, the carbon monoxide/alkene copolymerization reaction has attracted much interest from both the academic and industrial scientific community. This reaction is homogeneously catalyzed by palladium(II) salts modified with P- or N-donor ligands and its products are perfectly alternating polyketones.[2] The study of the intimate mechanism of the copolymerization reaction started with the demonstration that the propagation step consists of two successive alternate migratory insertion reactions of Pd-alkyl to CO and of Pd-acyl to alkene.[3] While the reactions responsible for the growth of the polymeric chain are common to all catalytic systems, the initiation and termination steps depend on the nature of both the alkene and the palladium catalyst precursor. Most mechanistic investigations have been carried out in solution. Recently, however, there has been a study in the solid state.[4]

The various reactions involved in the initiation step are: (i) insertion of CO into the Pd-Me bond; (ii) insertion of CO into the Pd-OMe group; (iii) insertion of alkene into the Pd-H bond. Several groups have focused on the study of these insertion reactions and used Pd(II) systems containing bidentate nitrogen ligands. For the phenanthroline-based system $[PdMe(L)(phen)][BAr'_4]$ (L = solvent molecule; Ar' = 3,5-$(CF_3)_2C_6H_3$), a complete catalytic cycle has been constructed from kinetic and thermodynamic studies for the copolymerization of ethylene and CO.[5]

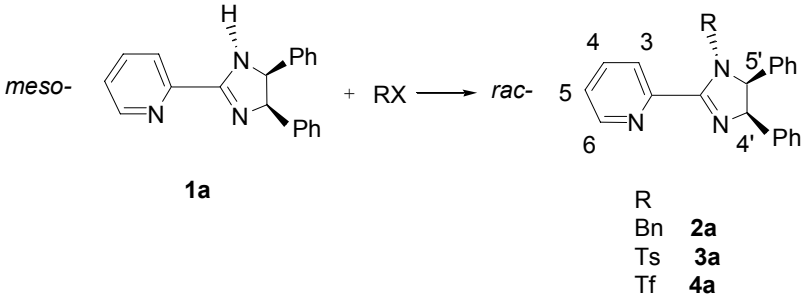
For unsymmetrical ligands, the insertion reactions may afford two different stereoisomers. The formation of one or both stereoisomers could influence the products of the copolymerization reaction. An intermediate resulting from the insertion of ethylene into a Pd-acyl bond has recently been isolated and characterized by X-ray for the first time for a complex containing the unsymmetrical 6-methyl-2,2'-bipyridine. A single stereoisomer was observed throughout the reaction sequence.[6]

When the copolymerization reaction involves styrene, the ligand can also play a role in controlling the stereoregularity of the synthesized polyketone. In the case of bisnitrogen planar ligands of C_{2v} or C_s symmetry (e.g. 2,2'-bipyridine, 1,10-phenanthroline, 5-NO_2-1,10-phenanthroline, 2,2'-bipyrimidine, diazabutadiene derivatives, pyridine-pyrazole) the syndiotactic polyketone is obtained.[7-12] C_2-symmetry chiral bidentate ligands (e.g. bisoxazoline, dioxazoline, diketiimines) provide good enantioface control and give isotactic copolymers.[10,13,14] Interestingly the C_1-symmetrical chiral ligands (e.g. N-N', P-N, P-OP) led to syndiotactic[15] or isotactic microstructures,[16] depending on the relative influence of the chain-end or the enantiomorphic control.

It has been reported that the site selective coordination of the alkene on the palladium complex determines its enantioface discrimination. In the case of palladium complexes modified with unsymmetrical N-N' ligands, the different *trans* effect of nitrogen atoms and the steric properties of the ligand seem to be responsible for the site-selective coordination.[15] Moreover, for P-N ligands, the isolation and characterization of some

insertion intermediates have always shown that a single stereoisomer is formed.[17-19]

We report on the synthesis of C_1-symmetrical pyridine-imidazoline ligands (N-N' = **1a-1d**) (Scheme 1) and their coordination to palladium. The modification of the R substituent on the imidazoline moiety leads to variation of the electronic properties of the nitrogen donors. The Pd(II) complexes of general formula [PdMe(NCMe)(N-N')][BAr'$_4$] (**4a-4d**) behave as catalyst precursors for the copolymerization of carbon monoxide and 4-*tert*-butylstyrene (TBS). By changing the electronic properties in the pyridine-imidazoline ligands the stereochemistry of these complexes, and therefore of the polyketones obtained, can be modified.



Scheme 1. Racemic (*R*,*S*) pyridine-imidazolines **1a-4a**

In order to learn more about the influence of our electronic tunable ligands, we studied the stereochemistry and the reactivity of intermediates involved in the mechanism. The X-ray structures of two neutral complexes [PdCl$_n$(Me)$_{2-n}$ (N-N')] (n = 1, 2; N-N' = **1d**, **1b**) were determined. The reactivity of the palladium-methyl precursors [PdMe(NCMe)(N-N')][PF$_6$]

(**3a-3d**) towards CO was investigated in depth by *in situ* ^{1}H and ^{13}C NMR experiments. The complete sequence of intermediates was established for complexes with ligands **1a** and **1b**. The [Pd(COMe)(CO)(**1a**)][PF_6] was isolated and characterized. Some correlations between NMR results and the catalytic activity of the precursors are also discussed.

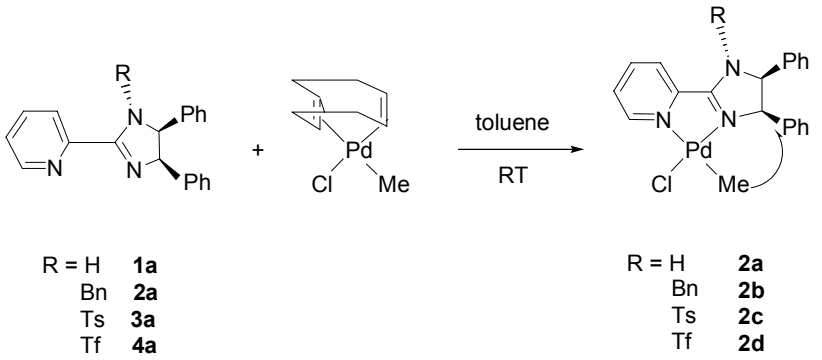
5.1.2. Results and discussion

5.1.2.1. Synthesis of ligands 1a-1d

Pyridine-imidazoline ligand **1a** was prepared similarly to the reported synthesis of oxazolines by reaction of 2-cyanopyridine with *meso*-1,2-diphenylethylenediamine but using $Yb(OTf)_3$ as catalyst.[20] Further reaction of **1a** with BnBr, TsCl or Tf_2O, provided the racemic *R*,*S*-(*S*,*R*)-1-substituted-4,5-dihydro-4,5-diphenyl-2-(2-pyridyl)-imidazoles **1b-1d**, respectively, in a racemic way (Scheme 1).

5.1.2.2. Synthesis and characterization of [PdClMe(N-N')] 2a-2d

Neutral [PdClMe(N-N')] **2a-2d** were isolated from the stoichiometric reaction of [PdClMe(cod)] (cod= 1,5-cyclooctadiene) and the ligands **1a-1d** in anhydrous toluene (Scheme 2).



R = H **1a**
Bn **2a**
Ts **3a**
Tf **4a**

R = H **2a**
Bn **2b**
Ts **2c**
Tf **2d**

Scheme 2. Synthesis of the neutral complexes **2a**-**2d**

Single crystals suitable for X-ray analysis were obtained for the neutral derivative **2d** with the ligand bearing the triflate substituent (Figure 1). Efforts to obtain single crystals of the neutral complex **2b**, with the ligand bearing an electron donating group, resulted in the dichloride species [$PdCl_2$(**1b**)], **2b'** being isolated, because the methyl group exchanged with the chloride in the chlorinated solvent (Figure 2). Figures 1 and 2 show the molecular structures of **2b'** and **2d** complexes together with the atom numbering scheme and Table 1 shows a selection of bond lengths and angles.

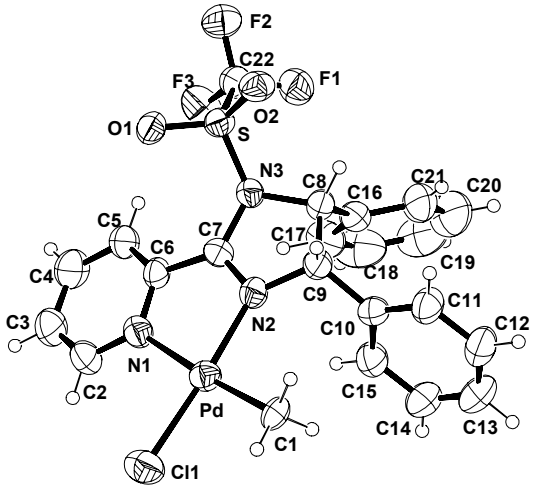


Figure 1. Molecular structure (ORTEP drawing, 50% thermal ellipsoids) with atom numbering scheme of **2d**

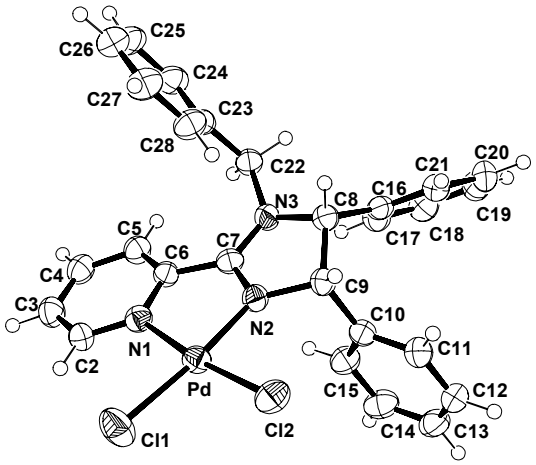


Figure 2. Molecular structure (ORTEP drawing, 40% thermal ellipsoids) with atom numbering scheme of **2b'**

Table 1. Selected bond lengths (Å) and angles (°) for complexes **2b'** and **2d**.

	2b'·$CDCl_3$	**2d**
	X = Cl(2) [a]	X = C(1)
Pd-N(1)	2.088(3)	2.149(5)
Pd-N(2)	2.000(3)	2.065(4)
Pd-Cl(1)	2.304(1)	2.282(2)
Pd-X	2.194(2)	2.071(4)
N(1)-C(2)	1.336(5)	1.325(7)
N(1)-C(6)	1.364(5)	1.352(7)
N(2)-C(7)	1.303(5)	1.279(6)
N(2)-C(9)	1.481(4)	1.480(7)
N(3)-C(7)	1.358(5)	1.423(6)
N(3)-C(8)	1.486(5)	1.503(6)
N(3)-C(22)	1.461(5)	-
N(3)-S	-	1.631(4)
N(1)-Pd-N(2)	78.6(1)	77.5(2)
N(1)-Pd-Cl(1)	96.62(9)	97.3(1)
N(1)-Pd-X	172.6(1)	175.7(2)
N(2)-Pd-Cl(1)	174.51(9)	174.7(1)
N(2)-Pd-X	94.0(1)	98.3(2)
Cl(1)-Pd-X	90.77(6)	86.9(1)

[a] The chloride is partially disordered with a methyl ligand (see Experimental)

The structural determination of complex **2b'** shows a significant difference in the Pd-Cl bond lengths (Pd-Cl(1) = 2.304(1), Pd-Cl(2) =

2.194(2) Å). This, together with the short Pd-N(py) bond distance *trans* to Cl(2) (2.088(3) Å), is further evidence for the previously mentioned exchange reaction at the methyl, and suggests that the Pd-Cl(2) bond length actually appears as an artifact arising from a mixed chloride/methyl ligand (see Experimental). The square planar geometry of palladium is slightly tetrahedrally distorted and the donor atoms deviate by ± 0.023 Å from the coordination mean plane. Both the Pd-N bond distances with pyridine and imidazoline, 2.088(3) and 2.000(3) Å, respectively, are significantly shorter than those measured in **2d** (see below). For purposes of comparison, the Pd-N(py) and Pd-N(imidazoline) bond lengths in the crystal structure of the bischelated head-tail $[Pd(\mathbf{1b})_2]^{2+}$ complex are similar (mean value 2.017(7) and 2.021(7) Å, respectively).[21]

In complex **2d** the square planar geometry around Pd involves the nitrogen atoms of the chelating ligand and, as expected, a chloride and a methyl group with donor atoms that are coplanar within ± 0.017 Å. The data in Table 1 indicates that the coordination distances for the chelating ligand are considerably different, Pd-N(1) = 2.149(5), Pd-N(2) = 2.065(4) Å, and longer than those found in **2b'**. In fact, the former is induced by the *trans* influence of the methyl, while the latter is affected by the strong electron withdrawing properties of the CF_3SO_2 group which provides a less basic iminic N donor. The Pd-Cl(1) and Pd-C(1) bond distances, 2.282(2) and 2.071(4) Å, respectively, fall in the range usually observed for Pd(II) complexes and follow the trend of those detected, for example, in the [PdClMe(2,9-dm-phen)] derivative (2,9-dm-phen = 2,9-dimethyl-1,10-

phenanthroline; Pd-Me = 2.015(6), Pd-Cl = 2.312(1), Pd-N(1) = 2.229(4), Pd-N(2) = 2.066(4) Å).[22]

In both complexes, the rings of the chelating ligand are not coplanar, but slightly tilted, as indicated by the N(1)-C(6)-C(7)-N(2) torsion angle of 9.0(4) (in **2b'**) and 11.2(7)° (in **2d**). On the other hand, the dihedral angles formed by the planes through the pyridine and imidazoline atoms are 13.0(2) and 18.1(1)°, respectively. The phenyl rings at C(8) and C(9) are oriented, as expected, on the same side of the imidazoline plane and avoid an eclipsed conformation through a torsion angle C(16)-C(8)-C(9)-C(10) of 20.3(5) (**2b'**) and 27.9(7)° (**2d**). This causes considerable distortions inside the five-membered ring of both complexes, and induces a certain degree of strain. The ring atoms (principally N(3), C(8), and C(9)) deviate by up ±0.15 Å from the mean plane. Moreover, in **2b'** the N(2)-C(7) and N(3)-C(7) bond distances, 1.303(5) and 1.358(5) Å, are consistent with a delocalization inside the N(2)-C(7)-N(3) fragment, as already observed in the molecular structure of two ruthenium derivatives where the pyridine-imidazoline ligand has a hydrogen or a methyl bound to the aminic nitrogen N(3).[23] In addition, in **2b'** the sum of the bond angles around N(3) is 353.9° (in **2d** 349.1°) which supports the degree of delocalization across the amidine.

On the other hand, the corresponding figures in **2d** agree with a double (N(2)-C(7) = 1.279(6) Å) and a single bond character (N(3)-C(7) = 1.423(6) Å), a feature that seems to be induced by the electronic properties of CF_3SO_2. Therefore, the Pd-N(2) and the N-C distances in the N(2)-C(7)-

N(3) fragment can be regarded as a proof of the electronic properties of the R substituent.

The analysis of the crystal packing in **2d** shows pairs of complexes arranged head-to-tail about a symmetry center with a short intermetallic Pd---Pd' distance of 3.440 Å (Figure 3), a feature often encountered in square planar Pd and Pt complexes.[24,25] Similar packing is also observed in the crystal structure of **2b'**, but the pair of complexes are related in such a way that Cl(2) lies almost at the metal apical position of the symmetry related molecule (Cl(2)---Pd' = 3.966 Å, Pd---Pd' = 4.980 Å). This arrangement prevents steric clashes between Cl(2) and the benzyl ring of the second molecule. The stacking of this latter ring with that of a nearby complex (shortest C---C distance 3.88 Å) accounts for the narrow torsion angle of 19.1 (5)° detected in the N(3)-C(22)-C(23)-C(28) fragment.

Finally in **2d**, it is worthwhile to point out the short intramolecular distance (3.81 Å) between the methyl carbon atom and the centroid of phenyl C(10-15) (see Figure 1).

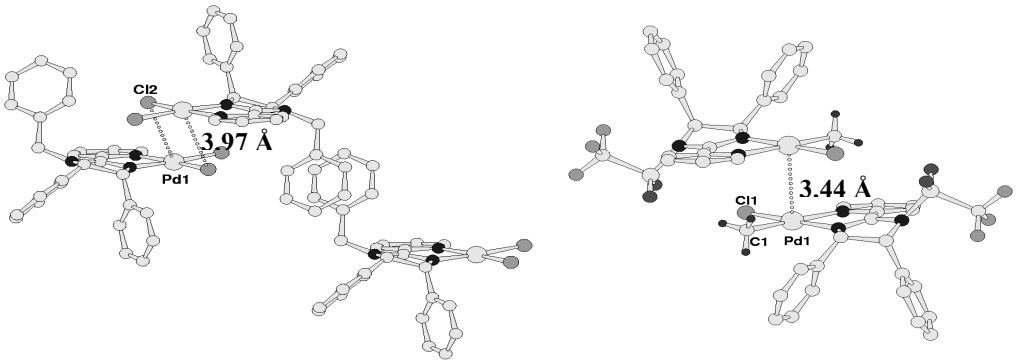
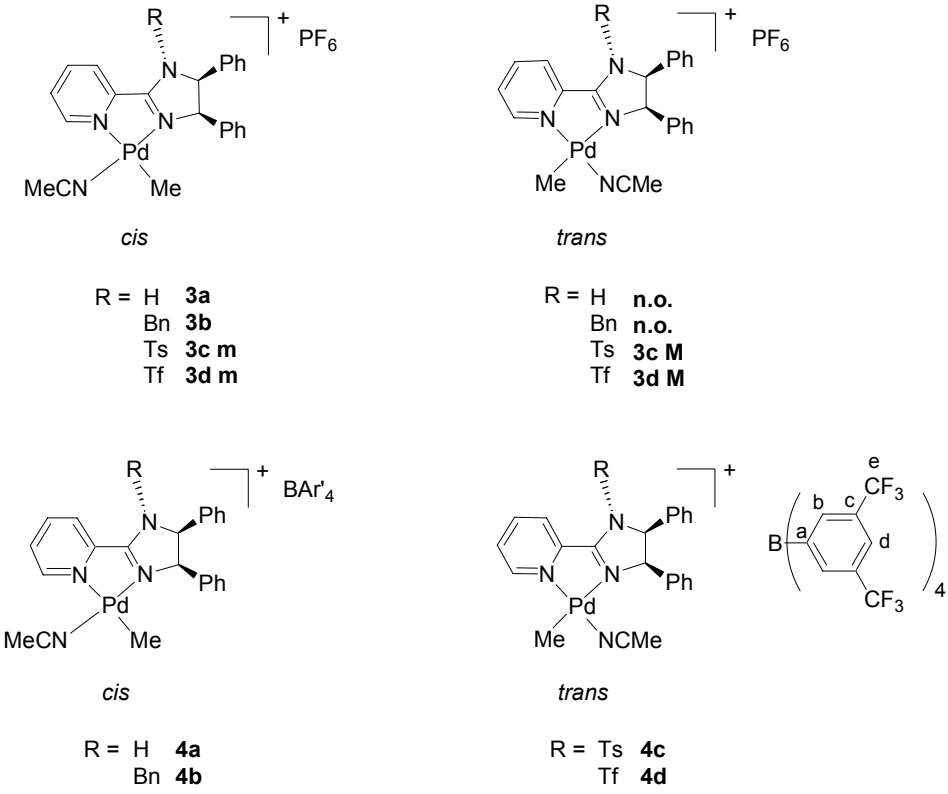


Figure 3. Crystal packing: head-to-tail arrangement of molecules related by a center of symmetry in compound **2b'** and in **2d**

The neutral derivatives **2a-2d** were characterized in solution by ^{1}H NMR spectroscopy. For all the complexes **2a-2d** in the aromatic region of the spectra, the H_6 signal (Scheme 1) is considerably downfield shifted with respect to the one in the free ligand ($\Delta\delta$ = 0.55 ppm), indicating that the chloride is *cis* coordinated to the pyridine moiety.[26] This coordination is confirmed by NOE experiments: irradiation of the Pd-Me protons show an NOE effect with the $H_{4'}$ of the imidazoline. The Pd-Me singlets are in the 0.50 - 0.25 ppm range, upfield shifted with respect to the same resonance in similar complexes [PdClMe(pzpy)] (pzpy = 2-(pyrazol-1-yl)pyridine).[27] This shift is related to the proximity of the shielding cone of the phenyl ring in position 4' on the imidazoline ring, as indicated by the X-ray analysis (Figure 1). For all the neutral derivatives, only the isomer that corresponds to the one found in the solid state is observed in solution, as found in the related pyridine-oxazoline (pyox) complexes [PdClMe(pyox)].[28]

5.1.2.3. Synthesis and characterization of [PdMe(NCMe)(N-N')][X] 3a-3d, 4a-4d

The cationic palladium complexes **3a-3d** [PdMe(NCMe)(N-N')][PF_6] and **4a-4d** [PdMe(NCMe)(N-N')][BAr_4'] were prepared starting from the corresponding neutral derivatives [PdClMe(N-N')], **2a-2d**, and reacting them with $AgPF_6$ or $NaBAr'_4$ to abstract the chloride ligand. No crystal suitable for structural determination was obtained for the cationic complexes **3a-3d** or **4a-4d** (Scheme 3). They were completely characterized in solution by recording the NMR spectra. The most significant signals are those related to H_6 (for the ligand), to the Pd-Me and to the Pd-NCMe fragments (Table 2). The signals were assigned to the protons on the basis of selective decoupling experiments and on the multiplicity of the signals.



Scheme 3. The cationic palladium complexes **3a**-**3d** and **4a**-**4d** (M = major isomer, m = minor isomer; n.o. = not observed). The numbering scheme of BAr'_4 is included

Table 2. Selected ^{1}H NMR data for complexes **3a**-**3d**, **4a**-**4d** and free ligands **1a**-**1d**[a]

	H_6	Pd-Me	Pd-NCMe
1a	8.63 (d, ^3J = 5.0)	-	-
3a	8.59 (d, ^3J = 5.1)	0.54 (s)	2.41 (s)
4a	9.37 (d, ^3J = 5.8)	0.31 (s)	2.16 (s)
1b	8.69 (d, ^3J = 4.8)	-	-
3b	8.99 (d, ^3J = 4.4)	0.47 (s)	2.47 (s)
4b	8.44 (d, ^3J = 5.2)	0.56 (s)	2.27 (s)
1c	8.64 (d, ^3J = 5.0)	-	-
3c[b]	M 8.64[c]	M 1.10 (s)	M 1.59 (s)
	m 8.79 (d, ^3J = 4.4)	m 0.32 (s)	m 2.45 (s)
4c	8.52 (d, ^3J = 5.6)	0.99 (s)	1.40 (s)
1d	8.78 (d, ^3J = 4.8)	-	-
3d[b]	M 8.69 (d, ^3J = 5.7)	M 1.22 (s)	M 1.64 (s)
	m 8.88 (d, ^3J = 5.1)	m 0.46 (s)	m 2.47 (s)
4d	8.51 (d, ^3J =5.6)	1.06 (s)	1.50 (s)

[a] ^{1}H NMR spectra recorded in $CDCl_3$ at room temperature; (s)= singlet, (d)= doublet; δ values are in ppm, J in Hz; M = major isomer, m = minor isomer. [b] ^{1}H NMR spectra recorded in CD_2Cl_2 at room temperature. [c] Overlapped with signals of H_3, no multiplicity could be assigned.

For both complexes **3a** and **3b** one set of signals related to the N-N' ligand is evident at room temperature. All the signals are shifted with respect to the free ligand. By irradiating the signal of the methyl group bound to palladium, an NOE effect with $H_{4'}$ was evident. This indicates

that only one species was present in solution, whose Pd-Me bond was *cis* to the imidazoline ring (Scheme 3). This stereochemistry is analogous to that observed in the neutral derivatives and in the cationic species **4a**-**4b** with BAr'_4^- as anion.[f]

In the spectra of complexes with the electron-withdrawing substituents a different situation is found depending on the anion. For **3c** and **3d**, two sets of signals of different intensity are clearly evident (Table 2). In the aromatic region of the spectra the signals of each pyridine ring can be recognized through homonuclear COSY experiments. No signal belongs to the free N-N' ligand. In particular, for **3d** two H_6 signals are clearly evident. For **3c**, however, one of them overlaps the H_3 signals. In the aliphatic region of the spectra, there are also two sets of resonances for the Pd-Me group (minor species: 0.32 ppm for **3c** and 0.46 ppm for **3d**; major species: 1.10 ppm for **3c** and 1.22 ppm for **3d**) and the Pd-NCMe fragment (minor species: 2.45 ppm for **3c** and 2.47 ppm for **3d**; major species: 1.59 ppm for **3c** and 1.64 ppm for **3d**). For both complexes, in each species the ratio between Pd-Me and Pd-NCMe is 1. When NOE experiments were performed on **3c** or **3d** by irradiating the Pd-Me singlet of the minor species, the spectrum also shows a negative signal for the Pd-Me singlet of the major species, thus indicating that they are in equilibrium. This is confirmed because the signals broaden when the temperature is increased to 313 K. Moreover, an NOE effect is observed between the Pd-Me and $H_{4'}$

[f] Isomers are *cis* or *trans* depending on the position of the methyl group with respect to the imidazoline ring.

for the minor species in both the **3c** and **3d** complexes. On the basis of these NMR data, it is clear that the two species present in solution are the two stereoisomers [PdMe(NCMe)(N-N')][PF_6] (N-N' = **1c**, **1d**), which are differentiated by the *trans* or *cis* coordination of the methyl group to the imidazoline ring (Scheme 3). In particular, the Pd-Me fragment of the major species is *trans* to the imidazoline ring. The ratio between the *trans* and *cis* isomers is 2:1 for **3c** and 3:1 for **3d**. The chemical shifts for the Pd-Me protons in the *trans* isomer are very close to those observed for complexes [PdMe(NCMe)(N-N')][BAr'_4], **4c-4d**, which show only the *trans* isomer in solution even at low temperatures (Table 2).

In summary, for complexes **4a-4d** only one stereoisomer is observed in solution, regardless of the nature of the ligand. The stereoisomer formed depends on the R substituent on the imidazoline ring: it is the *cis*, when R is H or Bn (**4a** and **4b**) and the opposite for R = Ts, Tf (**4c** and **4d**) (Scheme 2). When the anion changes from BAr'_4^- to PF_6^-, there is no difference for complexes with the ligands **1a** or **1b**. With **1c** or **1d,** however, stereochemical control is partially lost, even though the preferential isomer has the same stereochemistry found in **4c** and **4d**. These results suggest that, in all cases, the methyl group of the stereoisomer that is preferentially formed is *trans* to the less basic nitrogen atom.

The effect of the anion on the stereochemistry of the complexes might be related to its position in solution with respect to the cation. Studies in solution on complexes [Pd(OMe-COD)(bipy)][Y] (OMe-COD = η^1,η^2-$C_8H_{12}OMe$; Y = BPh_4^-, $CF_3SO_3^-$, BF_4^-, PF_6^-, SbF_6^-, BAr'_4^-) showed

that the anion is preferentially located above or below the coordination plane and shifted towards the bipy ring *trans* to the Pd-C σ-bond. When BAr'_4^- changes to PF_6^- the strength of the interionic interactions increases and favours the dissociation of one N-arm of the bipy molecule.[29] Therefore, in the case of complexes **3c** and **3d**, this may be responsible for the *trans* to *cis* isomerization process.

The presence of stereochemical isomers in Pd(II) complexes of general formula [PdMe(NCMe)(L-L')][X], involved in the copolymerization process, has been observed in two other examples, where L-L' is 2-(1-(3,5-dimethyl)pyrazolyl)pyrimidine[12] or diphosphinoferrocene ligands derived from Josiphos.[30] In the first case, the presence of the less favored isomer, on the basis of electronic consideration, has been explained in terms of the steric hindrance of the ligand. In the diphosphine derivatives, a strict relationship was not found between the electronic effect of the ligand and the ratio of the stereoisomers mixture.

5.1.2.4. Copolymerization of carbon monoxide with 4-*tert*-butylstyrene using complexes 4a-4d

The new cationic Pd(II) complexes **4a-4d**, which have different stereochemistry depending on the R substituent of the imidazoline ring (Scheme 3), were tested as catalysts for the alternating CO/4-*tert*-butylstyrene (TBS) copolymerization. In a typical experiment **4a-4d** were placed in chlorobenzene under atmospheric pressure of CO and TBS was added. Table 3 shows the results of the catalytic experiments. There is a

clear effect of the R substituent on the productivity of the system. An improvement is observed when the catalyst contains a ligand with an electron-withdrawing substituent (entry 1 *vs.* entry 4). Regarding the molecular weights of the polyketones, they were high and similar in all the cases.

Table 3. Alternating CO/ TBS copolymerization catalyzed by **4a-4d**[a]

Entry	Precursor	Productivity[b] (gCP/gPd.h)	Stereoregularity (% *l* diads)	M_n (M_W/M_n)
1	**4a**	2	65	42200 (1.1)
2	**4b**	8.9	52	49750 (1.5)
3	**4c**	7	15	59250 (1.2)
4	**4d**	12.8	18	39700 (1.5)

[a] Reaction conditions: 0.0125 mmol catalyst, [TBS]/[cat] = 620, 5 mL chlorobenzene, p(CO) = 1 atm., 24h at room temperature. [b] Productivity calculated from the isolated copolymer.

Under copolymerization conditions the successive coordination of carbon monoxide to the palladium precursor and the migratory insertion of the methyl group take place to form an acyl species. This generates a vacant position which is filled by the coordination of styrene. As previously stated the site selective coordination of the alkene on the palladium complex may determine its enantioface discrimination, if unsymmetrical chiral ligands are used. The electronic determination caused by the pyridine-imidazoline ligands could therefore affect the stereoregularity of the copolymer obtained with the catalytic precursors **4a**-**4d**.

The degree of stereoregularity was evaluated from the ^{13}C NMR spectrum of the copolymers by integrating the signals in the region of the methylene carbon atom using an epimerized copolymer as reference (Figure 4). As Table 3 shows, introducing electron-withdrawing groups (entries 3 and 4) leads to a greater proportion of *u* diads giving highly syndiotactic copolymers. With the substituents H and Bn (entries 1 and 2 respectively) such a clear effect is not observed probably due to the smaller electronic differentiation of the two rings (pyridine and imidazoline) but there is a bigger proportion of *l* diads.

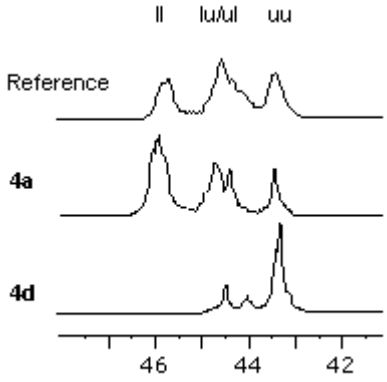


Figure 4. Comparative ^{13}C NMR spectrum of the copolymers, obtained with precatalysts **4a** and **4d,** in the region of the methylene carbon atom. An epimerized copolymer is used as reference

5.1.2.5. Reactivity of [PdMe(NCMe)(N-N')][X] complexes, 3a-3d and 4b, 4d with carbon monoxide

In order to simplify the ^{1}H and ^{13}C NMR spectra, the cationic palladium complexes with PF_6^- as counterion **3a-3d** were reacted with carbon monoxide and the reaction was studied by *in situ* NMR spectroscopy.

When carbon monoxide is bubbled for 5 minutes through a solution of [PdMe(NCMe)(**1a**)][PF_6], **3a**, or of [PdMe(NCMe)(**1b**)][PF_6], **3b**, in CD_2Cl_2, at 273 K, five new singlets (e.g., for **3a**+CO: 0.88 ppm, 1.52 ppm, 1.69 ppm, 2.10 ppm, 2.37 ppm) are present in the aliphatic region of the ^{1}H NMR spectra, recorded after 15 min, together with the resonance due to the methyl group of the precursor (Figure 5a-b) (Table 4). When labeled ^{13}CO is used, in the ^{1}H NMR spectrum two singlets (e.g., for **3a**+CO: 1.52 ppm and 1.69 ppm) become doublets, indicating that they belong to two acyl groups (Figure 5c). In the corresponding ^{13}C NMR spectra there are four signals (e.g., for **3a**+CO: 174.3 ppm, 176.6 ppm, 210.8 ppm, 220.9 ppm), the two at lower frequency are typical for Pd-CO fragments, while the other two are related to Pd-COMe species.[5b] When the concentration of CO in the same solution is increased, only two signals are still present in the ^{1}H NMR spectra: a doublet and a singlet (e.g., for **3a**+CO: 1.69 ppm, 2.10 ppm) (Figure 5d). The same is true of the ^{13}C NMR spectra (e.g., for **3a**+CO: 174.3 ppm, 210.8 ppm). The signal at 2.10 ppm in the ^{1}H NMR spectra is due to free acetonitrile.

Table 4. Selected NMR data for reactivity of complexes **3a** and **3b** with CO[a]

^{1}H NMR				
Compound	Me Pd NCMe	Me Pd CO	COMe Pd NCMe	COMe Pd CO
3a + CO	0.48	0.88	1.52	1.69
3b + CO	0.47	0.87	1.51	1.67
^{13}C NMR				
3a + CO	n.d.	176.6	220.9	174.3, 210.8
3b + CO	n.d.	176.7	222.3	174.3, 212.6

[a] NMR spectra recorded in CD_2Cl_2 at 273 K; δ values are in ppm; n.d.: not determined.

These NMR data indicate that the final product corresponds to the palladium-acyl-carbonyl species [Pd(COMe)(CO)(N-N')][PF_6] (N-N' = **1a**, **1b**), **7a** or **7b**, which is the result of inserting CO into the Pd-Me bond (Scheme 4). The other signals observed at lower CO concentrations are attributed to the intermediates of the insertion reaction. In particular, for the complex with ligand **1a**, the signal at 0.88 ppm, which is still a singlet in the presence of ^{13}CO, is due to the palladium-methyl-carbonyl derivative [PdMe(CO)(**1a**)][PF_6], **5a**, whose corresponding signal in the ^{13}C NMR spectrum is at 176.6 ppm. Finally, the resonance at 1.52 ppm, which becomes a doublet after bubbling ^{13}CO, and the singlet at 2.37 ppm belong to the acyl-acetonitrile intermediate [Pd(COMe)(NCMe)(**1a**)][PF_6], **6a**. The corresponding signal in the ^{13}C NMR spectrum is at 220.9 ppm.

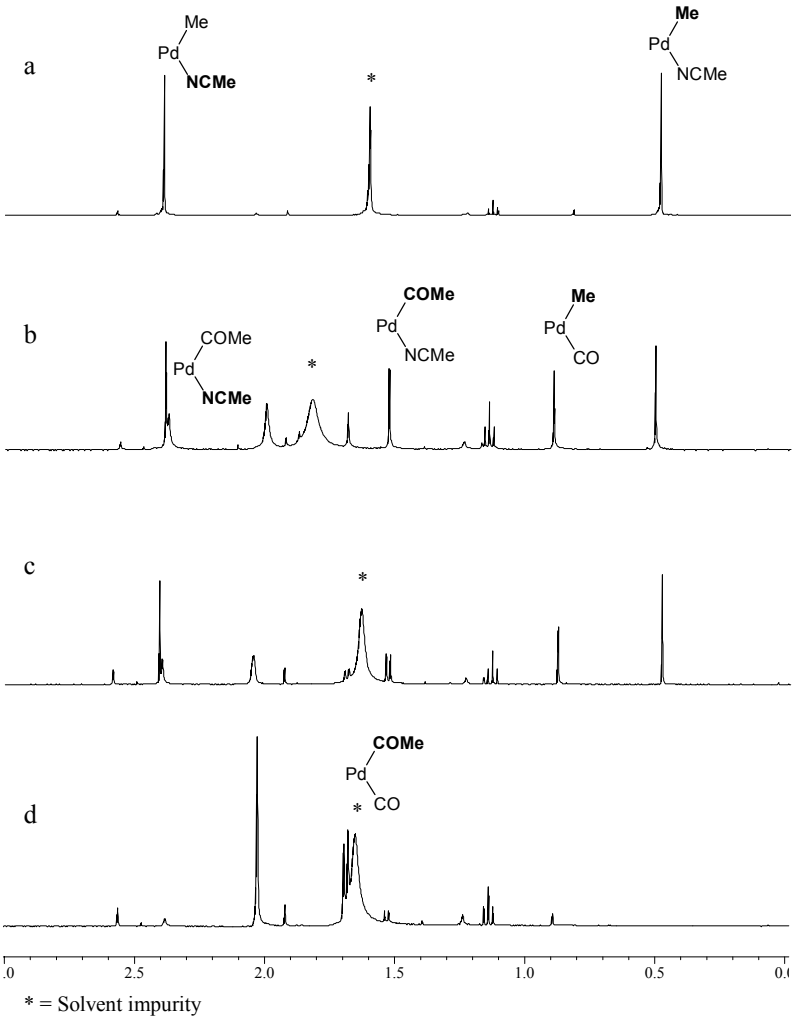
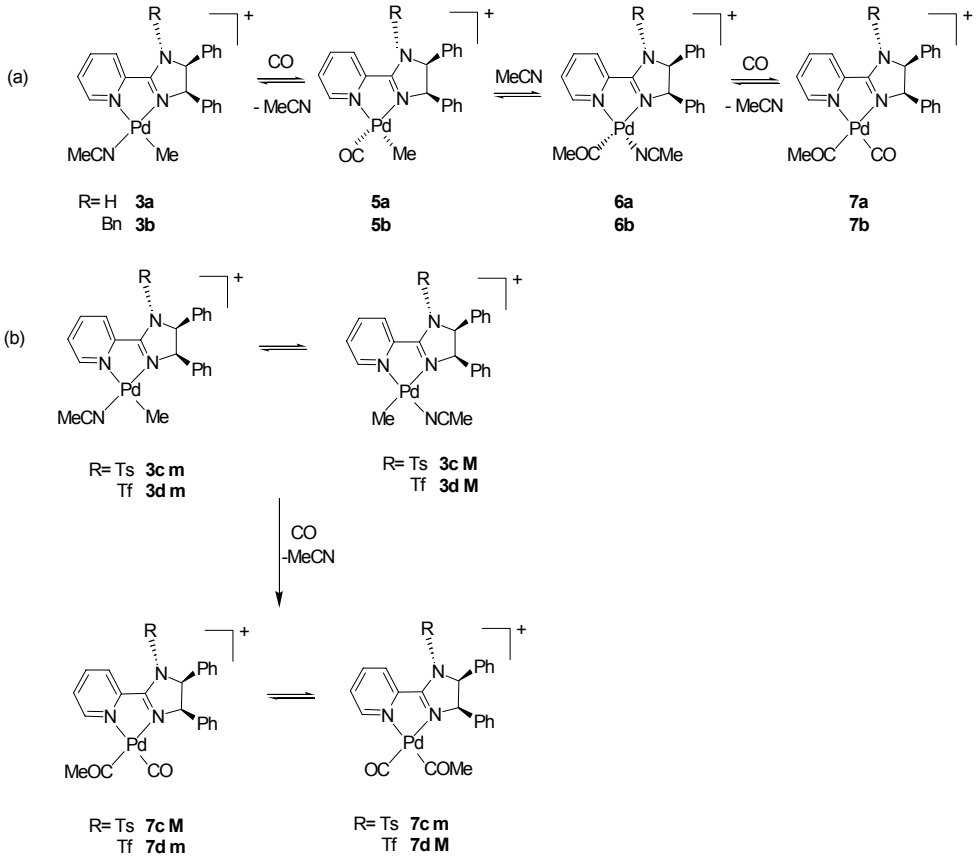


Figure 5. Reactivity of **3a** with carbon monoxide: ^{1}H NMR spectra recorded in CD_2Cl_2 at 273 K, region of aliphatic protons: a) spectrum of **3a**; b) spectrum of **3a** + CO; c) spectrum of **3a** + ^{13}CO; d) spectrum of **3a** + exc. of ^{13}CO



Scheme 4. Reactivity of complexes with carbon monoxide: a) **3a** and **3b**; b) **3c** and **3d**

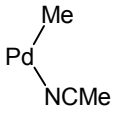
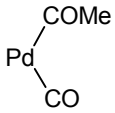
The most significant signal in the aromatic region of the spectra is the one related to the H_6 in the pyridine ring. For the intermediates, three signals are attributed to H_6, but they could not be clearly assigned to the corresponding species. In the final palladium-acyl-carbonyl species **7a**, H_6 gives a doublet at 8.48 ppm, upfield shifted with respect to the precursor. Thanks to the NOE effect between H_6 and the protons in the acyl group of

7a, it was possible to recognize this species as the *trans* isomer. The same situation is observed for **7b**. The ^{1}H NMR spectra of both **7a** and **7b** did not vary when the temperature was decreased by as much as 213 K, which confirmed the presence of a single stereoisomer. No direct experiment was performed on the stereochemistry of the intermediates.

The palladium-acyl-carbonyl derivative **7a** was also isolated by bubbling CO in a dichloromethane solution of [PdMe(NCMe)(**1a**)][PF_6] at 273 K. It was stored at 278 K without decomposition. Its ^{1}H NMR spectrum shows the same signals observed in the *in-situ* NMR experiments.

When carbon monoxide is bubbled for 5 min through a solution of [PdMe(NCMe)(**1c**)][PF_6], **3c**, or of [PdMe(NCMe)(**1d**)][PF_6], **3d**, in CD_2Cl_2, at 273 K, the ^{1}H NMR spectra, recorded after 15 min at 263 K, showed only two broad signals in the aliphatic region (e.g., for **3c**+CO: 1.65 ppm, 1.98 ppm) and the complete disappearance of the precursor's resonance (Table 5).

Table 5. Selected ^{1}H and ^{13}C NMR data for reactivity of complexes **3c** and **3d** with CO[a]

^{1}H NMR			
Compound	T		
3c + CO	263 K	M 1.10	1.65 (b)
		m 0.31	
	183 K	M 1.0	M 1.41
		m 0.16	m 2.74
3d + CO	263 K	M 1.18	2.33 (b)
		m 0.41	
	183 K	M 1.11	M 2.76
		m 0.23	m 1.52
^{13}C NMR			
3c + CO	263 K	n.d.	172.8, 211.5
	183 K	n.d.	M 172.4, 211
			m 170.7, 217.1
3d + CO	263 K	n.d.	171.9, 212.1
	183 K	n.d.	M 170.3, 216.4
			m 171.7, 210.2

[a] NMR spectra recorded in CD_2Cl_2; δ values are in ppm; b = broad.

When the labeled ^{13}CO was used, no variation was observed in the ^{1}H NMR spectrum. In the corresponding ^{13}C NMR spectrum two broad signals appeared (e.g. for **3c**+CO: 172.8 ppm, 211.5 ppm) (Figure 6a and Table 5) due to a Pd-CO and a Pd-COMe moiety, respectively. Low temperature NMR studies were performed by decreasing the temperature from 263 K to 183 K. In the case of **3c**, the signal at 1.65 ppm disappeared at 233 K. Two peaks became evident at 183 K (1.41 ppm and 2.74 ppm), and a sharp singlet appeared at 1.99 ppm. The two peaks were of different intensity, being the resonance at 1.41 ppm higher than that at 2.74 ppm in a ratio of 4.2:1. Moreover, the weighted sum of the two resonances corresponds to the chemical shift (1.66 ppm) of the signal observed at 263 K. At the same temperature in the ^{13}C NMR spectrum four signals appeared that can be grouped into two pairs on the basis of their intensities (170.7 and 217.1 ppm, 172.4 and 211 ppm) (Figure 5b). The reaction of **3d** with carbon monoxide was similar: the peak at 2.33 ppm at 263 K, which disappears at 233 K, splits into two peaks (2.76 ppm and 1.52 ppm) at 183 K. For this complex, the intensity of the signals was just the reverse of what was found for **3c**: in the ^{1}H NMR spectrum, the most intense peak was at the highest frequency (2.76 ppm), with a ratio of 1.7:1 (Table 4). The same inversion of intensity is observed in the corresponding ^{13}C NMR spectrum.

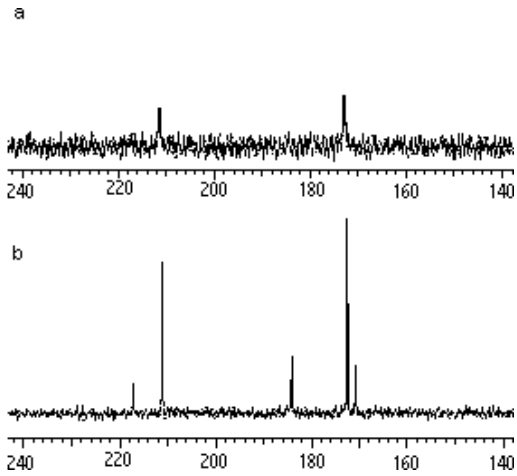


Figure 5. Reactivity of **3c** with ^{13}CO: ^{13}C NMR spectra recorded in CD_2Cl_2: a) at T = 273 K; b) at T = 183 K

The signal at 1.99 ppm in the ^1H NMR spectra is due to free acetonitrile. At the lowest temperature reached, the two resonances at 1.41 ppm and at 2.74 ppm, for the reactivity of **3c** with CO (or 1.52 ppm and 2.76 ppm for **3d** + CO), are attributed to two Pd-COMe groups. The resonances found in the ^{13}C NMR spectrum at the same temperature confirm that two Pd-COMe groups and two Pd-CO moieties are present. Therefore, these NMR data indicate that the final product is the palladium-acyl-carbonyl species [Pd(COMe)(CO)(N-N')][PF_6] (N-N' = **1c**, **1d**), **7c** or **7d**, which is present as a mixture of two isomers in equilibrium (Scheme 4). The rate of this equilibrium is intermediate on the NMR time scale at 263 K.

In the temperature range we investigated, the analysis of the H_6 signal for both complexes always reveals broad signals and, even at the

lowest temperature reached, no assignment was possible, since decoalescence was not complete. Therefore, the stereochemistry of the two isomers could not be determined. Finally, no signals from the intermediates were observed for either of the complexes, and the resonances of the precursors disappeared, indicating a higher reactivity with carbon monoxide than with **3a** and **3b**.

In view of the differences between complexes **3c**-**3d** and **4c**-**4d**, the reactivity with carbon monoxide was also investigated for two exponents of the series with BAr'_4^-, namely **4b** and **4d**. They behaved similarly to the corresponding PF_6^- derivatives: one isomer for the complex with ligand **1b** and two isomers for the species containing **1d**. Indeed, in the spectrum at 273 K, recorded after bubbling CO in a solution of **4b**, only the signal at 1.65 ppm is present in the aliphatic region. This indicates that *trans*-[Pd(COMe)(CO)(**1b**)][BAr'_4] (**8b**) has been formed. This signal is shifted at 1.50 ppm when the spectrum is recorded at 193 K. In the reaction of **4d** with CO, only one broad signal is present at 2.11 ppm at 273 K. It is split into two signals (2.72 ppm and 1.50 ppm) when the temperature was decreased down to 193 K. Therefore, both *cis* and *trans* [Pd(COMe)(CO)(**1d**)][BAr'_4] (**8d**) isomers are present in a ratio of 1:1.

No successful direct experiment was done to unambiguously assign the stereochemistry of the two isomers for complexes **7c**, **7d** and **8d**. However, comparing the chemical shifts at the lowest temperature reached, in particular for **8b** and **8d**, suggests that the resonance at 1.5 ppm is due to the Pd-acyl-carbonyl species with the acyl group *trans* to the imidazoline

ring. Finally, it should be noted that the stereocontrol observed in the BAr'_4 precursors **4a**-**4d** is partially lost after reaction of **4c** and **4d** with carbon monoxide.

Our study of the insertion of 4-*tert*-butylstyrene in the Pd-acyl-carbonyl species formed *in situ* (**7a-7d**) was unsuccessful, maybe due to the combined effect of decomposition and slow insertion of the alkene.

Complexes **4a-4d** have shown activity as catalyst precursors for the CO/4-*tert*-butyl-styrene copolymerization reaction. The nature of the ligand has an effect both on the productivity of the system and on the tacticity of the polyketones obtained. Complexes **4a-4b** show little activity and gave atactic polyketones with a slight prevalence of the isotactic triad. On the other hand, the syndiotactic polyketone is obtained with **4c** and **4d**. Moreover, the last precursor shows the highest catalytic activity. This catalytic behavior might be correlated with the different reactivity of these complexes with carbon monoxide. Only one stereoisomer is obtained for Pd-Me complexes with ligands **1a-1b**. It slowly reacts with carbon monoxide and yields only one Pd-acyl stereoisomer (Pd-acyl fragment *trans* to imidazoline). Both stereoisomers were found for Pd-Me complexes with ligands **1c-1d**. They react with CO faster than the complexes with **1a** and **1b**, to yield the corresponding Pd-acyl stereoisomers. The ratio between the stereoisomers depended on the ligand. The higher catalytic activity found for the precursor with **1d**, together with the prevailing presence of the opposite stereoisomer with respect to **1a** (or **1b**), might indicate that the Pd-acyl fragment *cis* to imidazoline is more reactive than the *trans* one.

It is well known that the insertion of the alkene is the rate determining step of the copolymerization reaction and that the enantioface selection during the alkene insertion is due to the chain end or to the enantiomorphic site control. The fact that the polyketone obtained with ligands **1a** and **1b** tends to isotacticity, together with the presence of a single stereoisomer (Pd-COMe *trans* to imidazoline), might indicate that there is site selective coordination of the alkene *cis* to the chiral moiety of the ligand. The enantioface selection of the ligand is nevertheless not efficient enough to completely overcome the chain end control, and the result is, therefore, the synthesis of an atactic copolymer. On the other hand, the synthesis of the syndiotactic copolymer, together with the presence of the two isomers in the case of **1c** and **1d** ligands, might indicate that isomerization takes place very easily by exchanging the coordination site of the polymer growing chain and the alkene. The greater reactivity of the stereoisomer with the Pd-COMe fragment *cis* to imidazoline might favour the insertion of the alkene preferentially under chain-end control and lead to a prevailing syndiotactic copolymer. However, due to the similarity of species **3a**-**3d**, two regioisomeric olefin intermediates might be present for all the complexes. As a consequence, the variation in the microstructure of the produced copolymers should arise from the different contribution of these regioisomers.

5.1.3. Conclusions

Pyridine-imidazoline ligands of C_1 symmetry, electronically modified with different R substituents, were prepared. Their coordination to palladium leads to efficient catalysts for the CO/4-*tert*-butylstyrene copolymerization. Depending on the electronic modification of the pyridine-imidazolines, polyketones with different degree of stereoregularity are obtained. Moreover these ligands provide information about the stereochemistry of the intermediates in the copolymerization reaction.

The neutral complexes [PdClMe(N-N')] have the same stereochemistry irrespectively of the N-N' ligand, with the methyl group *cis* to imidazoline. The behavior of the cationic complexes in solution depends on the ligand (**1a-1b** or **1c-1d**) as well as on the counterion (PF_6^- or BAr'_4^-). It is straightforward to note that the Pd-Me and the Pd-NCMe chemical shifts in the two isomers are very different and they can be considered as a probe for the stereochemistry of the resulting complexes.

All the intermediates of the reaction of the Pd-Me precursors with carbon monoxide, which yields the Pd-acyl-carbonyl final species, were detected in solution using ^1H and ^{13}C NMR spectroscopy. Depending on the R substituent of the ligand, one or both [Pd(COMe)(CO)(N-N')][X] stereoisomers were detected and characterized. Finally, the reactivity of the cationic Pd-Me complexes towards CO was seen to be related to the copolymerization results.

5.1.4. Experimental

5.1.4.1. General procedure

Commercial $Na_2[PdCl_4]$ and $[Sn(CH_3)_4]$ were purchased from Johnson Matthey and Aldrich, respectively, and used as received. Solvents for synthetic purposes were distilled and deoxygenated prior to use unless otherwise stated. Solvents for spectroscopy were used without further purification. Carbon monoxide (labeled and unlabeled, CP grade, 99 %) was supplied by Aldrich. The salt $NaBAr'_4$ (Ar' = 3,5-$(CF_3)_2$-C_6H_3) was prepared according to the reported method.[31] All reactions were carried out under nitrogen atmosphere, at room temperature, using standard Schlenk techniques.

^1H and ^{13}C NMR spectra were recorded on a Varian Gemini spectrometer with a ^1H resonance frequency of 300 MHz and a ^{13}C frequency of 75.4 MHz, on a Varian Mercury VX spectrometer with a ^1H resonance frequency of 400 MHz and a ^{13}C frequency of 100.5 MHz, and on a Jeol EX 400 spectrometer with a ^1H frequency at 400 MHz and a ^{13}C frequency of 100.5 MHz. The resonances were referenced to the solvent peak versus tetramethylsilane (TMS) ($CDCl_3$ at 7.26 δ for ^1H and 77.23 δ for ^{13}C, CD_2Cl_2 at 5.32 δ for ^1H and 54.0 δ for ^{13}C). The NOE experiments were run with a ^1H pulse of 12 μs (300 MHz) and of 13.3 μs (400 MHz). Two-dimensional correlation spectra (gCOSY) were obtained with the automatic program of the instrument. MS (FAB positive) were obtained on a Fisons V6-Quattro instrument. The molecular weight of the copolymers and molecular weight distributions were determined by gel permeation

chromatography (GPC - MALLS) measurements made in THF on a Waters 510 gel-permeation chromatography device using a three-serial column system (SHODEX K80M and PLGEL MIXED-D and MIXED-E linear columns) with a Wyatt mini-DAWN Light Scattering and a SHIMADZU RID-6A refractive index detector.

5.1.4.2. Synthesis of pyridine-imidazoline ligands 1a-1d

1a: 2-cyanopyridine (9 mmol) and *meso*-1,2-diphenylethylenediamine (9.5 mmol) were refluxed in chlorobenzene during 72 h using $Yb(OTf)_3$ (0.31 mmol) as catalyst. Recrystallisation from CH_2Cl_2/hexane afforded a white crystalline solid. Yield: 83%. Anal. Found: C, 79.25; H, 4.96; N, 13.78%. Calc. for $C_{20}H_{17}N_3$: C, 80.24; H, 5.39; N, 14.04%. ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 8.63 (ddd, ^3J = 5 Hz, ^4J = 1.8 Hz, ^5J = 1.1 Hz, 1H, H_6), 8.36 (dt, ^3J = 7.7 Hz, ^4J = 1.1 Hz, ^5J = 1.1 Hz, 1H, H_3), 7.81 (td, ^3J = 7.7 Hz, ^4J = 1.8 Hz, 1H, H_4), 7.40 (ddd, ^3J = 7.7 Hz, ^3J = 5 Hz, ^4J = 1.1 Hz, 1H, H_5), 7.02- 6.94 (m, 10H, Ph), 5.51 (s, 2H, $H_{4'}$ + $H_{5'}$). ^{13}C NMR (100.5 MHz, $CDCl_3$, RT): 164.3 (s, $C_{2'}$ or C_2), 149 (s, C_6), 148.4 (s, C_2 or $C_{2'}$), 138.8 (s, Ph), 136.9 (s, C_4), 127.7 (s, Ph), 127.6 (s, Ph), 126.9 (s, Ph), 125.6 (s, C_5), 122.8 (s, C_3), 71.0 (br, $C_{4'}$ + $C_{5'}$).

1b: Compound **1a** (0.33 mmol) was dissolved in THF (3 mL) and reacted with NaH (0.50 mmol) for about an hour. To the reaction mixture, benzyl bromide (0.35 mmol) was added dropwise at room temperature. After reacting for 5 hours evaporation gave a brown paste which was purified by column chromatography using a hexane/ethyl acetate mixture

(1:1) as eluent. Rf = 0.10. Yield: 67%. Anal. Found: C, 82.65; H, 6.17; N, 9.42%. Calc. for $C_{27}H_{23}N_3$: C, 83.26; H, 5.95; N, 10.78%. ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 8.69 (ddd, ^3J = 4.8 Hz, ^4J = 2 Hz, ^5J = 1 Hz, 1H, H_6), 8.08 (dt, ^3J = 7.9 Hz, ^4J = 1.1 Hz, ^5J = 1.1 Hz, 1H, H_3), 7.78 (td, ^3J = 7.7 Hz, ^4J = 1.9 Hz, 1H, H_4), 7.35 (ddd, ^3J = 7.7 Hz, ^3J = 4.8 Hz, ^4J = 1.1 Hz, 1H, H_5), 7.15- 6.9 (m, 15H, Ph), 5.58 (d, ^2J = 15.6 Hz, 1H, CH_2), 5.44 (d, ^3J = 11.6 Hz, 1H, $H_{4'}$), 4.92 (d, ^3J = 11.6 Hz, 1H, $H_{5'}$), 3.82 (d, ^2J = 15.6 Hz, 1H, CH_2). ^{13}C NMR (100.5 MHz, $CDCl_3$, RT): 164.7 (C_2), 149.1 (C_6), 137.5 (C_4), 132.2 (C_5), 128.8–126.8 (Ph), 125.7 (C_3), 71.5 ($C_{4'}$), 69.3 ($C_{5'}$), 48.6 (CH_2).

1c: To a solution of ligand **6** (0.33 mmol) and 4-(dimethylamino) pyridine (73.1 mg, 0.6 mmol) in dichloromethane (3 mL) at 273 K, a solution of *p*-toluenesulphonylchloride (0.4 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 5 hours. Evaporation of the mixture gave a yellow solid that was purified by column chromatography using a hexane/ethyl acetate mixture (1:1) as eluent to obtain a white solid. Rf = 0.52. Yield: 42%. Anal. Found: C, 71.36; H, 5.37; N, 8.93; S, 6.90%. Calc. for $C_{27}H_{23}N_3O_2S$: C, 71.50; H, 5.11; N, 9.26; S, 7.06%. ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 8.67 (ddd, ^3J = 5 Hz, ^4J = 1.6 Hz, ^5J = 0.8 Hz, 1H, H_6), 7.97(dt, ^3J = 7.5 Hz, ^4J = 0.8 Hz, ^5J = 0.8 Hz, 1H, H_3), 7.86 (td, ^3J = 7.5 Hz, ^4J = 1.6 Hz, 1H, H_4), 7.5 (d, ^3J = 8.2 Hz, 2H, Harom.-Ts-), 7.47 (ddd, ^3J = 7.5 Hz, ^3J = 5 Hz, ^4J = 0.8 Hz, 1H, H_5), 7.11 (d, ^3J = 8.2 Hz, 2H, Harom.-Ts-), 7.12- 6.86 (m, 10H, Ph), 5.93 (d, ^3J = 10Hz, 1H, $H_{4'}$ or $H_{5'}$), 5.8 (d, ^3J = 10Hz, 1H, $H_{5'}$ or $H_{4'}$), 2.37 (s, 3H, CH_3). ^{13}C NMR (100.5 MHz, $CDCl_3$, RT): 148.8 (s, C_6), 136.9 (s, C_4), 129.1 – 127.2 (Ph) 125.6 (s, C_5), 124.9 (s, C_3), 75.3 ($C_{4'}$ or $C_{5'}$), 69.2 ($C_{5'}$ or $C_{4'}$), 21.8 (CH_3).

1d: Similar to the synthesis of **1d** but using trifluoromethanesulfonic anhydride as the electrofile. The purification was done by column chromatography using ethyl acetate as eluent. Rf = 0.89. Anal. Found: C, 58.85; H, 3.82; N, 9.42; S, 7.28%. Calc. for $C_{21}H_{16}N_3O_2SF_3$: C, 58.44; H, 3.71; N, 9.73; S, 7.42%. ^{1}H NMR (300 MHz, $CDCl_3$, RT): δ 8.78 (ddd, ^3J = 4.8 Hz, ^4J = 1.8 Hz, ^5J = 1 Hz, 1H, H_6), 7.96 (dt, ^3J = 7.7 Hz, ^4J = 1 Hz, ^5J = 1 Hz, 1H, H_3), 7.87 (td, ^3J = 7.7 Hz, ^4J = 1.8 Hz, 1H, H_4), 7.49 (ddd, ^3J = 7.7 Hz, ^3J = 4.8 Hz, ^4J = 1 Hz, 1H, H_5), 7.11- 6.99 (m, 10H, Ph), 5.98 (d, ^3J = 8.7 Hz, 1H, $H_{4'}$ or $H_{5'}$), 5.92 (d, ^3J = 8.7 Hz, 1H, $H_{5'}$ or $H_{4'}$). ^{13}C NMR (75.4 MHz, $CDCl_3$, RT): δ 149.3 (s, C_6), 136.9 (s, C_4), 128.2 - 127. 2 (Ph), 126.1 (s, C_5), 124.7 (s, C_3), 76.1 (s, $C_{4'}$ or $C_{5'}$), 70.5 (s, $C_{5'}$ or $C_{4'}$).

5.1.4.3. Synthesis of [PdClMe(N-N')] (2a-2d)

$Na_2[PdCl_4]$, used as starting material, was transformed into $[PdCl_2(cod)]$ (cod = 1,5-cyclooctadiene) according to the literature.[32] [PdClMe(cod)] was obtained from $[PdCl_2(cod)]$.[26] The neutral complexes **2a-2d** were synthesized by adding the ligand (**1a-1d**) to a solution of [PdClMe(cod)] in toluene, [ligand]/[Pd] = 1. The solution was stirred at room temperature for 1 hour yielding a yellow precipitate. After evaporation of the solvent, the compounds were washed with diethylether and filtered off.

[PdClMe(1a)] (2a)

Yield: 90%. ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 8.91 (ddd, ^3J = 5.1 Hz, ^4J = 1.7 Hz, ^5J = 0.6 Hz, 1H, H_6), 8.05 (ddd, ^3J = 7.8 Hz, ^4J = 1.2 Hz, ^5J = 0.6 Hz, 1H, H_3), 7.90 (td, ^3J = 7.8 Hz, ^4J = 1.7 Hz, 1H, H_4), 7.52 (ddd, ^3J = 7.8 Hz,

^{3}J = 5.1 Hz, ^{4}J = 1.2 Hz, 1H, H_5), 6.89-6.75 (m, 10H, Ph), 5.60 (d, ^{3}J = 11.4 Hz, 1H, $H_{5'}$), 5.4 (d, ^{3}J = 11.4 Hz, 1H, $H_{4'}$), 0.36 (s, 3H, Pd-CH_3). ^{13}C NMR (100.5 MHz, $CDCl_3$, RT): δ 149.2 (s, C_6), 138.4 (s, C_4), 128 (s, C_5), 127.7- 126.2 (Ph), 123.2 (s, C_3), 71.3 (s, $C_{4'}$), 66.8 (s, $C_{5'}$), -8.5 (s, Pd-CH_3). MS (FAB positive) *m/z*: 404 $[M\text{-}Cl]^+$.

[PdClMe(1b)] (2b)

Yield: 75%. Anal. Found: C, 60.50; H, 4.73; N, 7.48%. Calc. for $C_{28}H_{26}N_3ClPd$: C, 61.55; H, 4.80; N, 7.69%. ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 9.22 (d, ^{3}J = 4.8 Hz, 1H, H_6), 7.86 (m, 2H, H_3 + H_4), 7.59 (q, ^{3}J = 5.2 Hz, ^{4}J = 5.2 Hz, 1H, H_5), 7.25-6.76 (m, 15H, Ph), 5.46 (d, ^{3}J = 11.6 Hz, 1H, $H_{5'}$), 5.37 (d, ^{3}J = 11.6 Hz, 1H, $H_{4'}$), 5.03 (d, ^{2}J = 17.2 Hz, 1H, CH_2), 4.33 (d, ^{2}J = 17.2 Hz, 1H, CH_2), 0.49 (s, 3H, Pd- CH_3). ^{13}C NMR (75.4 MHz, $CDCl_3$, RT): δ 168 (s, C_2 or $C_{2'}$), 150.7 (s, C_6), 145. 3 (s, $C_{2'}$ or C_2), 138.4 (s, C_4), 136.3 (s, Ph), 134.8 (s, Ph), 133.4 (s, Ph), 129.5 (s, Ph), 128.8 (s, Ph), 128.5 (s, Ph), 128.34 (s, Ph), 128.3 (s, C_5), 128 (s, Ph), 127.7(s, Ph), 127.5 (s, Ph), 127 (s, Ph), 124 (s, C_3), 72.9 (s, $C_{4'}$), 69.6 (s, $C_{5'}$), 50.3 (s, CH_2), -6.6 (s, Pd-CH_3).

[PdClMe(1c)] (2c)

Yield: 69%. Anal. Found: C, 52.82; H, 4.29; N, 6.40; S, 5.35%. Calc. for $C_{28}H_{26}N_3ClO_2PdS$: C, 55.04; H, 4.26; N, 6.88; S, 5.24%. ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 9.20 (ddd, ^{3}J = 5.1 Hz, ^{4}J = 2.7 Hz, ^{5}J = 1.2 Hz, 1H, H_6), 8.64 (dt, ^{3}J = 7.9 Hz, ^{4}J = 1.3 Hz, ^{5}J = 1.3 Hz, 1H, H_3), 8.16 (td, ^{3}J = 7.9 Hz, ^{4}J = 2.7 Hz, 1H, H_4), 7.82 (ddd, ^{3}J = 7.9 Hz, ^{3}J = 5.1 Hz, ^{4}J = 1.3 Hz, 1H, H_5), 7.75 (d, ^{3}J = 7.5 Hz, 2H, Harom.-Ts-), 7.51 (d, ^{3}J = 7.5 Hz, 2H, Harom.-Ts-), 7.07- 6.71 (m,

10H, Ph), 5.67 (d, ^3J = 9Hz, 1H, $H_{5'}$), 5.05 (d, ^3J = 9Hz, 1H, $H_{4'}$), 2.55 (s, 3H, CH_3 -Ts-), 0.28 (s, 3H, Pd-CH_3).

[PdClMe(1d)] (2d)

Yield: 84%. Anal. Found: C, 45.42; H, 3.84; N, 6.45%. Calc. for $C_{22}H_{19}ClF_3N_3O_2PdS$: C, 44.95; H, 3.26; N, 7.15%. ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 9.27 (ddd, ^3J = 5.1 Hz, ^4J = 1.7 Hz, ^5J = 0.8 Hz, 1H, H_6), 8.32 (ddd, ^3J = 7.9 Hz, ^4J = 1.2 Hz, ^5J = 0.8 Hz, 1H, H_3), 8.15 (dt, ^3J = 7.9 Hz, ^4J = 1.7 Hz, 1H, H_4), 7.83 (ddd, ^3J = 7.9 Hz, ^3J = 5.1 Hz, ^4J = 1.2 Hz, 1H, H_5), 7.24 - 6.69 (m, 10H, Ph), 6.11 (s, 2H, $H_{4'}$ + $H_{5'}$), 0.45 (s, 3H, Pd-CH_3). ^{13}C NMR (100.5 MHz, $CDCl_3$, RT): δ 150.5 (s, C_6), 138.9 (s, C_4), 129.7 (s, C_5), 129.1-127 (Ph), 126.7 (s, C_3), 74.8 (s, $C_{4'}$or $C_{5'}$), 72.5 (s, $C_{5'}$ or $C_{4'}$), - 4.5 (s, Pd-CH_3).

5.1.4.4. Synthesis of [PdMe(NCMe)(N-N')][PF_6] (3a-3d)

To a solution of [PdClMe(N-N')] (0.18 mmol) in dichloromethane (3 mL), 1.2 equivalents of $AgPF_6$ (0.22 mmol) dissolved in acetonitrile (1 mL) were added. After stirring for 1 h in the absence of light, the AgCl formed was filtrated and, when diethyl ether was added, the solution concentrated under vacuum to yield a pale yellow solid. Average yield: 75 %.

[PdMe(NCMe)(1a)][PF_6] (3a)

^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 8.59 (dd, ^3J = 5.1 Hz, ^4J = 0.6 Hz, 1H, H_6), 8.21 (td, ^3J = 8 Hz, ^4J = 0.7 Hz, 1H, H_4), 8.06 (dd, ^3J = 8 Hz, ^4J = 0.7 Hz, 1H, H_3), 7.83 (dd, ^3J = 8 Hz, ^3J = 5.1 Hz, 1H, H_5), 5.81 (d, ^3J = 11.2 Hz, 1H, $H_{5'}$), 5.48 (d, ^3J = 11.2 Hz, 1H, $H_{4'}$), 2.41 (s, 3H, Pd-$NCCH_3$), 0.54 (s, 3H, Pd-CH_3). MS (FAB positive) *m/z*: 461.2 $[M]^+$, 404 $[M - NCMe]^+$.

[PdMe(NCMe)(1b)][PF_6] (3b)

^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 8.99 (d, ^3J = 4.4 Hz, 1H, H_6), 8.02 (m, 3H, H^3, H_4 + H_5), 7.35-6.80 (m, 10H, Ph), 5.50 (d, ^3J = 11.7 Hz, 1H, $H_{5'}$), 5.40 (d, ^3J = 11.7 Hz, 1H, $H_{4'}$), 5.19 (d, ^3J = 17.6 Hz, 1H, CH_2), 4.42 (d, ^3J = 17.6 Hz, 1H, CH_2), 2.47 (s, 3H, Pd-NCCH_3), 0.47 (s, 3H, Pd-CH_3).

[PdMe(NCMe)(1c)][PF_6] (3c)

Ratio of isomers in CD_2Cl_2 M:m = 2:1. Major: ^{1}H NMR (400 MHz, CD_2Cl_2, RT): δ 8.67 (m, ^3J = 7.9 Hz, 1H, H_3), 8.64 (m, 1H, H_6), 8.35 (td, ^3J = 7.9 Hz, ^4J = 1.1 Hz, 1H, H_4), 7.92 (dd, ^3J = 7.9 Hz, ^3J = 6Hz, 1H, H_5), 7.76-6.71 (m, 14H, Ph), 5.86 (d, ^3J = 8.8 Hz, 1H, $H_{5'}$), 5.44 (d, ^3J = 8.8 Hz, 1H, $H_{4'}$), 2.5 (s, 3H, CH_3 -Ts-), 1.59 (s, 3H, Pd-NCCH_3), 1.10 (s, 3H, Pd-CH_3); minor: 8.79 (d, ^3J = 4.6 Hz, 1H, H_6), 8.64 (m, 1H, H_3), 8.28 (td, ^3J = 7.7 Hz, ^4J = 1.2 Hz, 1H, H_4), 8.03 (dd, ^3J = 7.7 Hz, ^3J = 4.6 Hz, 1H, H_5), 7.76-6.71 (m, 14H, Ph), 5.85 (d, ^3J = 9.6 Hz, 1H, $H_{5'}$), 5.29 (d, ^3J = 9.6 Hz, 1H, $H_{4'}$), 2.50 (s, 3H, CH_3-Ts-), 2.45 (s, 3H, Pd-NCCH_3), 0.32 (s, 3H, Pd-NCCH_3). MS (FAB positive) *m/z*: 615.1 $[M]^+$, 558 $[M - Me, NCMe]^+$, 403 $[M – Me, NCMe, Ts]^{2+}$.

[PdMe(NCMe)(1d)][PF_6] (3d)

Ratio of isomers in CD_2Cl_2 M:m = 3:1. Major: ^{1}H NMR (400 MHz, CD_2Cl_2, RT): 8.69 (d, ^3J = 5.7 Hz, 3H, H_6), 8.44 (m, 1H, H_3), 8.38 (td, ^3J = 7.8 Hz, ^4J = 1.5 Hz, 1H, H_4), 7.97 (ddd, ^3J = 7.8 Hz, ^3J = 5.7 Hz, ^4J = 1.5 Hz, 1H, H_5), 6.17 (m, 2H, $H_{4'}$ + $H_{5'}$), 1.64 (s, 3H, Pd-NCCH_3), 1.22 (s, 3H, Pd-CH_3); minor: 8.88 (d, ^3J = 5.1 Hz, 1H, H_6), 8.44 (m, 1H, H_3), 8.30 (t, 1H, ^3J = 7.8 Hz, H_4), 8.10 (dd, ^3J = 7.8 Hz, ^3J = 5.1 Hz, 1H, H_5), 6.17 (m, 1H, $H_{4'}$ or $H_{5'}$), 6.03 (d, ^3J = 8.8 Hz, 1H, $H_{4'}$ or $H_{5'}$), 2.47 (s, 3H, Pd-NCCH_3), 0.46 (s, 3H, Pd-CH_3). MS

(FAB positive) *m/z*: 593.1 $[M]^+$, 536.0 [M - Me, NCMe]$^+$, 403.1 [M- Me, NCMe, Tf]$^{2+}$.

5.1.4.5. Synthesis of [PdMe(NCMe)(N-N')][BAr'$_4$] (4a-4d)

To a solution of [PdClMe(N-N')] (0.22 mmol) in dichloromethane (3 mL), 1 equivalent of NaBAr'$_4$ (0.22 mmol) dissolved in the minim volume of acetonitrile was added. After stirring for 1 hour, the NaCl formed was filtrated. The solution was concentrated under vacuum and hexane was added to yield pale yellow solids.

[PdMe(NCMe)(1a)][BAr'$_4$] (4a)

Yield: 80%. Anal. Found: C, 50.70; H, 2.99; N, 4.45%. Calc. for $C_{55}H_{35}N_4BF_{24}Pd$: C, 49.85; H, 2.66; N, 4.23%. ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 9.37 (d, ^3J = 5.8 Hz, 1H, H_6), 9.06 (m, 1H, H_4), 8. 12 (d, ^3J = 7.2 Hz, 1H, H_3), 8.04 (t, ^3J = 5.8 Hz, 1H, H_5), 7.71 (s, 8H, H_b), 7.52 (s, 4H, H_d), 7.11- 6.84 (m, 10 H, Ph), 5.72 (d, ^3J = 11.4 Hz, 1H, $H_{5'}$), 5.49 (d, ^3J = 11.4 Hz, 1H, $H_{4'}$), 2.16 (s, 3H, Pd-NCCH_3), 0.31 (s, 3H, Pd-CH_3). ^{13}C NMR (100.5 MHz, $CDCl_3$, RT): 161.9 (q, $J_{C\text{-}B}$= 198.1 Hz, C_a), 152.3 (s, C_6), 140.4 (s, C_5), 135 (s, C_b), 129.5 – 123.4 (Ph), 117.7 (C_d), 70.7 (s, $C_{4'}$), 67.3 (s, $C_{5'}$), 31.3 (s, Pd-NCCH_3), 1.3 (s, Pd-CH_3).

[PdMe(NCMe)(1b)][BAr'$_4$] (4b)

Yield: 85%. Anal. Found: C, 50.76; H, 2.88; N, 3.44%. Calc. for $C_{62}H_{41}BF_{24}N_4Pd$: C, 52.62; H, 2.92; N, 3.96%. ^{1}H NMR (300 MHz, $CDCl_3$, RT): δ 8.44 (dd, ^3J = 5.2 Hz, ^4J = 1.8 Hz, 1H, H_6), 7.98 (dd, ^3J = 8.1 Hz, ^4J = 1 Hz, 1H, H_3), 7.86 (td, ^3J = 8.1 Hz, ^4J = 1.8 Hz, 1H, H_4), 7.72 (s, 8H, H_b), 7.53 (s, 4H,

H_d), 7.43 (ddd, ^3J = 8.1 Hz, ^4J = 5.2 Hz, ^5J = 1Hz, 1H, H_5), 7.36- 6.77 (m, 15H, Ph), 5.54 (d, ^3J = 11.7 Hz, 1H, $H_{5'}$), 5.43 (d, ^3J = 11.7 Hz, 1H, $H_{4'}$), 5.11 (d, ^2J = 17.6 Hz, 1H, CH_2), 4.45 (d, ^2J = 17.6 Hz, 1H, CH_2), 2.27 (s, 3H, CH_3CN), 0.56 (s, 3H, Pd-CH_3). ^{13}C NMR (75.4 MHz, $CDCl_3$, RT): δ 161.9 (q, ^2J= 49.8 Hz, 4C, Ca), 149.9 (s, C_6), 140.0 (s, C_4), 135.0 (s, 8C, C_b), 133.7-125.3 (Ph + C_5), 122.9 (s, C_3), 117.7 (s, 4C, C_d), 73.0 (s, $C_{5'}$), 69.1 (s, $C_{4'}$), 49.9 (s, CH_2), 3.2 (s, Pd-$NCCH_3$), -1.9 (s, Pd-CH_3).

[PdMe(NCMe)(1c)][BAr'$_4$] (4c)

Yield: 79%. Anal. Found: C, 50.29; H, 2.81; N, 3.33; S, 1.73%. Calc. for $C_{62}H_{41}N_4BClF_{24}O_2PdS$: C, 50.34; H, 2.79; N, 3.79; S, 2.17%. ^{1}H NMR (300 MHz, $CDCl_3$, RT): δ 8.58 (d, ^3J = 7.7 Hz, H_3), 8.52 (dd, ^3J = 5.6 Hz, ^4J = 1.4 Hz, H_6), 8.24 (dt, ^3J = 7.7 Hz, ^4J = 1.4 Hz, H_4), 7.75 (dd, ^3J = 7.7 Hz, ^3J = 5.6 Hz, H_5), 7.72 (s, 8H, H_b), 7.53 (s, 4H, H_d), 7.4 - 6.6 (m, 14 H, Harom.), 5.82 (d, ^3J = 11.6 Hz, 1H, $H_{5'}$), 5.39 (d, ^3J = 11.6 Hz, 1H, $H_{4'}$), 2.41 (s, 3H, CH_3-Ts-), 1.4 (s, 3H, Pd-$NCCH_3$), 0.99 (s, 3H, Pd-CH_3). ^{13}C NMR (100.5 MHz, $CDCl_3$, RT): 161.9 (J_{C-B}= 198.3 Hz, C_a), 150.1 (C_6), 140.3 (C_4), 135 (C_b), 130.4 (s, C_3), 129.9 (s, C_5), 129-120.4 (Ph), 117.7 (C_d), 74.1 ($C_{4'}$), 71.6 ($C_{5'}$), 21.8 (CH_3-Ts-), 5.32 (s, Pd-CH_3), 1.8 (s, Pd-NCCH_3).

[PdMe(NCMe)(1d)][BAr'$_4$] (4d)

Yield: 75%. Anal. Found: C, 48.34; H, 2.35; N, 3.71, S, 2.34%. Calc. for $C_{44}H_{34}BF_9N_4O_2PdS$: C, 46.16; H, 2.35; N, 3.84, S, 2.20%. ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 8.51 (dt, ^3J = 5.6 Hz, ^4J = 0.8 Hz, 1H, H_6), 8.41 (ddd, ^3J = 7.8 Hz, ^4J = 1.4 Hz, ^5J = 0.8 Hz, 1H, H_3), 8.24 (td, ^3J = 7.8 Hz, ^4J = 1.5 Hz, 1H, H_4), 7.76 (ddd, ^3J = 7.8 Hz, ^3J = 5.6 Hz, ^4J = 1.4 Hz, 1H, H_5), 7.72 (s, 8H, H_b), 7.53 (s,

4H, H_d), 7.2- 6.64 (m, 10H, Ph), 6.09 (d, ^3J = 8 Hz, 1H, $H_{4'}$ + $H_{5'}$), 6.01 (d, ^3J = 8 Hz, 1H, $H_{5'}$ + $H_{4'}$), 1.5 (s, 3H, Pd-NCCH_3), 1.06 (s, 3H, Pd-CH_3). ^{13}C NMR (100.5 MHz, $CDCl_3$, RT): δ 150.6 (s, C_6), 140.7 (s, C_4), 135 (s, C_b), 130.5 (s, C_5), 129.4 (s, C_3), 129.3- 123.4 (Ph), 117.7 (s, C_d), 74.9 (s, $C_{4'}$or $C_{5'}$), 73.2 (s, $C_{5'}$ or $C_{4'}$), 6.5 (s, Pd-CH_3), 2.0 (s, Pd-NCCH_3).

5.1.4.6. X-ray structure determination for complexes 2b' and 2d. For both complexes crystals suitable for X-ray analysis were obtained. Efforts to crystallize **2b** from $CDCl_3/Et_2O$ gave suitable crystals of **2b'**. Complex **2d** was crystallized from a CH_2Cl_2 /Et_2O mixture.

Crystal and experimental data are summarized in Table 5. All the data were collected on a Nonius DIP-1030H system with Mo-Kα radiation. A total of 30 frames were collected, each with an exposure time of 15 min, over half of the reciprocal space with a rotation of 6° about φ. The detector was at a distance of 90 mm from the crystal. Cell refinement, indexing and scaling of the data sets were carried out using Mosflm[33] and Scala.[33] The structures were solved by Patterson and Fourier analyses[34] and refined by the full-matrix least-squares method based on F^2 with all observed reflections.[35] Anisotropic temperature factors for all non-H atoms of the two complexes were used. In **2b'** the methyl ligand was partially exchanged by a chlorine atom and the site was refined with a mixed Cl/C species (any attempt to refine two separate peaks was unsatisfactory). Since the relative occupancies indicate a slight excess of the chlorine, 0.53/0.47, the compound is reported as a dichloro species. Moreover, a $CDCl_3$ solvent molecule was located in the difference Fourier map. The contribution of the

hydrogen atoms (excluding those of the disordered methyl) was included at calculated positions in the final cycles of refinements. All the calculations were performed using the WinGX System, Ver 1.64.03.[36]

Table 5. Crystal data and details of structure refinements for compounds **2b'** and **2d**.

	2b'. $CDCl_3$	**2d**
formula	$C_{28}H_{23}DCl_5N_3Pd$	$C_{22}H_{19}ClF_3N_3O_2PdS$
fw	686.15	588.31
temperature, K	150(2)	298(2)
crystal system	monoclinic	monoclinic
space group	P $2_1/c$ (No. 14)	P $2_1/c$ (No. 14)
a, Å	13.186(3)	10.698(3)
b, Å	12.405(3)	10.368(4)
c, Å	17.813(5)	21.206(5)
β, deg	105.01(2)	99.84(2)
V, Å^3	2814.3(12)	2317.5(12)
Z	4	4
density (calcd), g cm^{-3}	1.619	1.686
μ (Mo-Kα), mm^{-1}	1.158	1.055
F(000)	1376	1176
ϑ range for data collection	2.38 – 28.62	2.19 – 29.06
no. reflns collected/unique	13441/ 6978	11040/ 5719
R(int)	0.0565	0.0547
refinement method	Full-matrix least-squares on F^2	

no. reflections $I > 2\sigma(I)$	4790	3296
no. of parameters	335	299
goodness-of-fit	1.034	1.0
$R1$ (Fo)	0.0424	0.05
$wR2$ (Fo^2)	0.1035	0.1319
residuals, e Å^{-3}	0.531, –0.639	0.713, –0.803

5.1.4.7. CO/TBS copolymerization experiments

The 4-*tert*-butylstyrene was passed through a small column of Al_2O_3 prior to use. Chlorobenzene was used as purchased from Aldrich. In a typical procedure, the cationic precursor **4a-4d** (0.0125 mmol) was dissolved in 5 mL of chlorobenzene in a previously purged Schlenk and placed under CO at atmospheric pressure. 4-*tert*-butylstyrene was then introduced and the reaction was allowed to take place at room temperature. Workup included filtration of the reaction mixture through Kieselghur and precipitation of the polymeric material by adding the reaction solution dropwise into 100 mL of rapidly stirring methanol. The off-white powder was collected by filtration, washed with methanol and dried under vacuum.

5.1.4.8. Reactivity of the complexes [PdMe(NCMe)(N-N')][PF_6] (3a-3d) and [PdMe(NCMe)(N-N')][BAr'_4] (4b, 4d) with carbon monoxide

The reactivity of all the complexes [PdMe(NCMe)(N-N')][PF_6] (**3a-3d**) and [PdMe(NCMe)(N-N')][BAr'_4] (**4b, 4d**) with carbon monoxide was

studied *in situ* by ^{1}H and ^{13}C NMR spectroscopy. CD_2Cl_2 (0.7 mL) was placed in a NMR tube charged with the complex (7 x 10^{-3} mmol). The solution was cooled at 273 K and CO was bubbled for 5 min. The NMR sample was placed in a precooled NMR probe and spectra were obtained after 15 min.

[Pd(COMe)(CO)(1a)][PF_6] (7a). ^{1}H NMR (400 MHz, 273 K, CD_2Cl_2): see synthesis of the complex. ^{13}C NMR (100.5 MHz, CD_2Cl_2): δ 174.3 (s, Pd-CO), 210.8 (s, Pd-COMe).

[Pd(COMe)(CO)(1b)][PF_6] (7b). ^{1}H NMR (400 MHz, 273 K, CD_2Cl_2): δ 8.63 (d, ^{3}J = 4.9 Hz, 1H, H_6), 8.23 (m, 2H, H_3 + H_4), 7.89 (dd, ^{3}J= 6.4 Hz, ^{3}J= 4.9 Hz, 1H, H_5), 7.37-6.86 (m, 15H, Ph), 5.54 (d, ^{3}J = 12.7 Hz, 1H, $H_{5'}$ or $H_{4'}$), 5.47 (d, ^{3}J = 12.7 Hz, 1H, $H_{4'}$ or $H_{5'}$), 5.29 (d, ^{3}J = 17.1 Hz, 1H, CH_2), 4.50 (d, ^{3}J = 17.1 Hz, 1H, CH_2), 1.67 (s, 3H, Pd-COMe). ^{13}C NMR (100.5 MHz, 273 K, CD_2Cl_2): δ 174.3 (s, Pd-CO), 212.5 (s, Pd-COMe).

[Pd(COMe)(CO)(1c)][PF_6] (7c). Ratio of isomers in CD_2Cl_2 M:m = 4.2:1. ^{1}H NMR (400 MHz, 183 K, CD_2Cl_2): δ 8.64 (broad), 8.36 (broad), 8.00 (broad), 7.65-6.31 (broad), 5.76 (d, ^{3}J = 9.6 Hz, $H_{5'}$ or $H_{4'}$), 5.08 (d, ^{3}J = 9.6 Hz, $H_{4'}$ or $H_{5'}$), 2.74 (s, Pd-$COMe_m$), 2.48 (s, Me), 1.41 (s, Pd-$COMe_M$). ^{13}C NMR (100.5 MHz, 183 K, CD_2Cl_2): δ 170.7 (s, Pd-CO_m), 172.4 (s, Pd-CO_M), 211 (s, Pd-$COMe_M$), 217.1 (s, Pd-$COMe_m$).

[Pd(COMe)(CO)(1d)][PF_6] (7d). Ratio of isomers in CD_2Cl_2 M:m = 1.7:1. ^{1}H NMR (400 MHz, 183 K, CD_2Cl_2): δ 8.67–6.21 (broad), 2.76 (s, Pd-

$COMe_M$), 1.53 (s, Pd-$COMe_m$). ^{13}C NMR (100.5 MHz, 183 K, CD_2Cl_2): δ 170.3 (s, Pd-CO_M), 171.7 (s, Pd-CO_m), 210.2 (s, Pd-C(O)Me_m), 216.4 (s, Pd-$COMe_M$).

[Pd(COMe)(CO)(1b)][BAr'$_4$] (**8b**)**.** ^1H NMR (400 MHz, 193 K, CD_2Cl_2): δ 8.49 (d, ^3J = 5.2 Hz, 1H, H_6), 8.07 (t, ^3J = 7.7 Hz, 1H, H_4), 7.98 (d, ^3J = 7.7 Hz, 1H, H_3), 7.72 (s, 8H, H_b), 7.35 (s, 4H, H_d), 7.33-6.64 (m, 16H, H_5 + Ph), 5.59 (d, ^3J = 13 Hz, 1H, $H_{5'}$ or $H_{4'}$), 5.45 (d, ^3J = 13 Hz, 1H, $H_{5'}$ or $H_{4'}$), 5.23 (d, ^3J = 17.6 Hz, 1H, CH_2), 4.47 (d, ^3J = 17.6 Hz, 1H, CH_2), 1.50 (s, 3H, Pd-COMe).

[Pd(COMe)(CO)(1d)][BAr'$_4$] (8d). Ratio of isomers in CD_2Cl_2 M:m = 1.2:1. ^1H NMR (400 MHz, 193 K, CD_2Cl_2): δ 8.50-7.90 (broad), 7.71 (s, H_b), 7.52 (s, H_d), 7.44-5.96 (broad), 2.72 (s, 3H, Pd-$COMe_m$), 1.50 (s, 3H, Pd-$COMe_M$).

Synthesis of [Pd(COMe)(CO)(1a)][PF$_6$] (7a). 3a was dissolved in the minimum amount of dichloromethane and the solution was cooled to 273 K. CO was bubbled through the solution for 20 minutes and the color changed from light to bright yellow. Addition of diethyl ether at room temperature resulted in the precipitation of the desired complex as a light yellow solid. Yield: 70 %. Anal. Calc. for $C_{23}H_{20}F_6N_3O_2PPd$: C, 44.43; H, 3.24; N, 6.75. Found: C, 43.56; H, 3.62; N, 6.50. ^1H NMR (400 MHz, CD_2Cl_2, RT): δ 8.50 (d, ^3J = 5.2 Hz, 1H, H_6), 8.33 (m, 2H, H_3 and H_4), 7.85 (m, 1H, H_5), 7.52 (s, 1H, Ph), 7.13-6.89 (m, 9H, Ph), 5.84 (d, 1H, ^3J = 12.2 Hz, $H_{5'}$ or $H_{4'}$), 5.49 (d, 1H, ^3J = 12.2 Hz, $H_{4'}$ or $H_{5'}$), 1.74 (s, 3H, Pd-COMe).

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Modular pyridine-imidazolines as ligands for the CO/4-*tert*-butylstyrene copolymerization

Abstract

The modular nature of pyridine-imidazoline ligands allows to synthesize a series of C_1-symmetrical (*R*,*R*) pyridine-imidazolines to be compared with the previously reported racemic (*R*,*S*) ones. The different stereochemistry and substituents of the ligands, allow studying steric and electronic effects in the coordination to Pd(II) and Rh(I). Series of neutral complexes [PdMeCl(N-N')] and cationic ones [PdMe(NCMe)(N-N')][BAr'$_4$], [Rh(cod)(N-N')][BF_4] and [Rh(CO)$_2$(N-N')][BF_4] are prepared. The characterization in solution using ^{1}H NMR and IR techniques evidences the different basicity of the ligands. The crystal structures of two neutral palladium precursors [PdCl$_n$(Me)$_{2-n}$(N-N')] (n = 1, 2) and of two cationic rhodium complexes [Rh(cod)(N-N')][BF_4], with different R substituents in the imidazoline, show that larger distortions are induced in the imidazoline ring by the (*R*,*S*) and (*S*,*R*) configuration. Moreover depending on the R substituent in the imidazoline, the ligands show different coordination

distances and different degree of electronic delocalization across the imidazoline ring. The cationic complexes [PdMe(NCMe)(N-N')][BAr'$_4$] behave as precatalysts for the copolymerization of carbon monoxide and 4-*tert*-butylstyrene. The activity of the catalytic systems is shown to be largely dependent on the basicity and on the stereochemistry of the ligands. Moreover while using the racemic (*R*,*S*) pyridine-imidazolines, polyketones with different degree of stereoregularity may be obtained, using the (*R*,*R*) ligands the polyketones are always syndiotactic. The reactivity of the palladium precursors with carbon monoxide in solution is used to tentatively explain the catalytic results.

5.2.1. Introduction

The alternating copolymerization of carbon monoxide with alkenes is an attractive reaction because the polyketones it provides are low cost plastics with an environmentally friendly nature.[1-3] The use of homogeneous catalysts in the copolymerization reaction offers more control over the polymer properties than radical polymerization. Since the structures of the single-site catalysts are well defined, many research groups study the organometallic reactions involved in the mechanism.[4-9]

Nowadays Pd(II) complexes are the best choice for producing alternating copolymers of carbon monoxide with ethene, propene or styrene,[1] and they may be used for other unsaturated substrates like alkenes substituted with polar groups,[10] strained alkenes,[11] alkynes,[12] carbamates[13] and amines[14]. However, the commercialization of polyketones still raises many questions, the most important of which is the instability of the palladium precatalysts, which decompose to palladium metal during both the catalytic process and the copolymer workup. Therefore, the search for active catalysts in this process is of current interest.

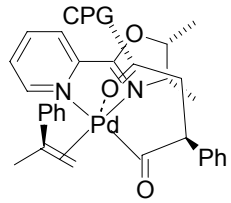
Palladium-bisnitrogen ligand (N-N) catalysts have been shown to be effective for CO/styrene copolymerization,[1,15] unlike palladium-diphosphine catalysts which, in general, form oligomers.[16] Therefore, bidentate nitrogen ligands have mainly been used,[7,16-23] although hemilabile P-N ligands have also shown activity.[6,24] The common feature, in all these nitrogen-containing ligands, is the sp^2 character of the coordinating nitrogen.

Oxazolines behave as effective ligands in several metal-catalyzed homogeneous reactions,[25] one of which is the CO/styrene copolymerization.[18,24] Imidazolines may be good alternatives since they are structurally analogous to oxazolines with different electronic properties. It has been shown that chelating ligands with a combination of a 6- and 5-membered N-containing heterocycles are good ligands for this process.[18,23] Therefore, we developed the racemic (*R,S*)-1-substituted-4,5-dihydro-4,5-diphenyl-2-(2-pyridyl)-imidazoles which have the advantage that the substituent in the aminic nitrogen N_1 can be easily modified and lead to a series of chiral ligands.[26] This substitution allows the electronic properties of the imidazoline ring to be tuned over a wide range without changing the chiral environment around the donor nitrogen (Scheme 1).[27,28] Recently some groups have also reported that 1-substitued-imidazolines can be used, as a possible alternative to oxazolines, for various catalytic processes.[29-31]

Scheme 1. General structure of pyridine-oxazoline and pyridine-imidazoline ligands

Modifying the electronic properties of the palladium center with different ligands may lead to variations not only in the activity of the catalysts but also in the selectivity of the copolymerization reaction, as has been shown for phosphorous-containing ligands.[32] The use of palladium(II) catalysts containing chiral C_1-symmetrical pyridine-oxazoline ligands in the

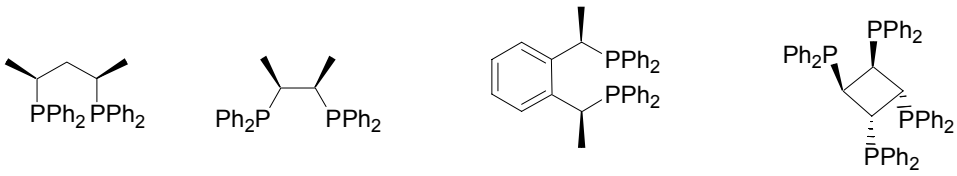
copolymerization of CO/styrene leads to syndiotactic polyketones, like the achiral ligands do.[18,24] The explanation is that because of the site-selective coordination of the styrene *cis* to the pyridine moiety the stereocontrol of the reaction is provided by the chain-end control and not by the chiral ligand (enantiosite control) (Scheme 2).[24] To increase the copolymer content on *l*-diads, using the similar pyridine-imidazolines, it seems that the styrene must be selectively coordinated *cis* to the chiral imidazoline. Therefore we decided to have take into account both steric and electronic factors in the ligand design.



GPC: growing polymer chain

Scheme 2. Model proposed by Consiglio et al. for styrene insertion to give prevailing syndiotactic copolymer

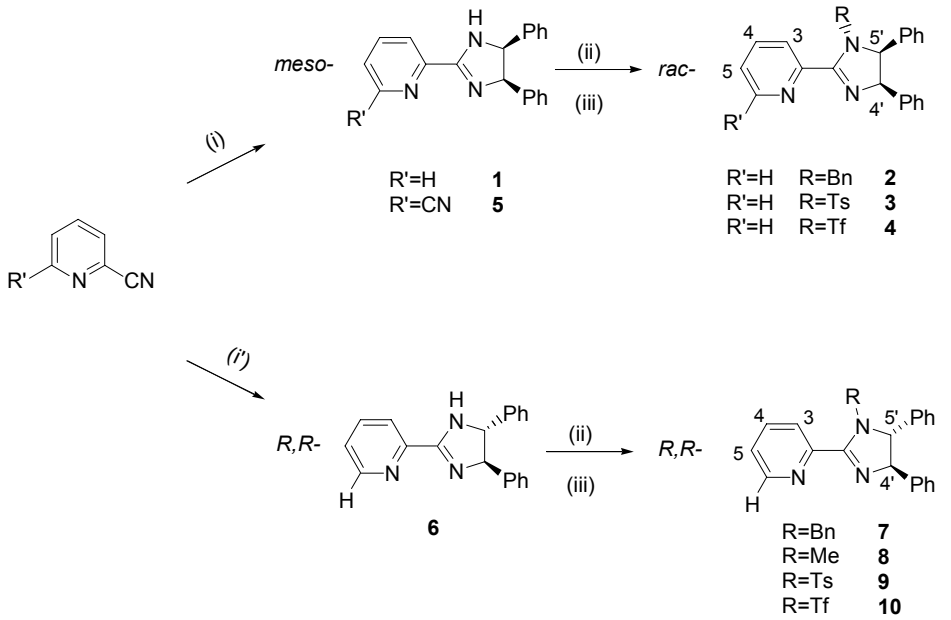
Recently some groups have reported that the activity in the alternating CO/ethene copolymerization of palladium catalysts containing (*R,S*) or (*S,R*) *meso*-diphosphines is higher than the activity of catalysts bearing the same ligands with (*R,R*) or (*S,S*) configuration (Scheme 3).[33,34]



meso-2,4-bdpp *meso*-2,3-dppb *meso*-$(C_6H_4)(CH(Me)PPh_2)_2$ *cyclo*-tetraphos

Scheme 3. *Meso*-diphosphines used as ligands in the CO/ethene copolymerization

Continuing our study of the pyridine-imidazoline ligands, we synthesized the (*R,R*)-1-substituted-4,5-dihydro-4,5-diphenyl-2-(2-pyridyl)-imidazoles with both phenyl rings of the imidazoline moiety in mutual *trans* position (Scheme 4). The "trans" pyridine-imidazoline ligands were coordinated to palladium neutral and cationic complexes. The palladium(II) cationic complexes were tested, as catalytic precursors, in the alternating copolymerization of CO/4-*tert*-butylstyrene and the results were compared with our previously reported data. The reactivity of the new palladium precursors towards carbon monoxide is also analyzed, trying to understand the stereocontrol obtained in copolymerization using these ligands.



(i) *meso*-(1*R*,2*S*)-1,2-diphenylethylenediamine; (i') (1*R*,2*R*)- 1,2-diphenylethylenediamine; (ii) 4-dimethylamino-pyridine for **3**, **4**, **9**, **10**; NaH for **2**, **7**, **8**; (iii) BnBr for **2**, **7**; TsCl for **3**, **9**; $(Tf)_2O$ for **4**, **10**; MeI for **8**.

Scheme 4. Synthesis of ligands **1-10** with their numbering scheme

5.2.2.Results and discussion

5.2.2.1. Synthesis and characterization of ligands

Pyridine-imidazoline ligands **1-4,** whose phenyl rings in the imidazoline moiety are in *cis* position (Scheme 4), were prepared and they enabled us to obtain a series of palladium(II) neutral [PdClMe(**1-4**)] (**1a-4a**) and cationic [PdMe(NCMe)(**1-4**)][BAr'$_4$] (BAr'$_4$= 3,5-$(CF_3)_2C_6H_3$) complexes (**1b-4b**). Modifying the R substituent in the imidazoline ring influenced the properties of the binding nitrogen and, therefore, the metal environment. This, in turn, led to palladium complexes with different stereochemistries. When the complexes **1b-4b** were used as precatalysts in the CO/4-*tert*-butylstyrene copolymerization, the degree of stereoregularity of the polyketones obtained depended on the R substituent.[26]

To get a better control of the stereoregularity, we tried to promote the coordination of styrene *cis* to the imidazoline through steric and electronic modifications. We first increased the steric hindrance near the pyridine nitrogen and simultaneously decreased the basicity of the pyridine ring. With this aim we synthesized the racemic *R,S-(S,R)*-4,5-dihydro-4,5-diphenyl-2-[2-(6-cyano)-pyridil]imidazol (**5**) (Scheme 4). The product was obtained in a low yield (20%) because the bis-anellation compound also formed.[35] Characterization by ^{1}H NMR shows the characteristic three aromatic signals related to the pyridinic protons $H_{3\text{-}5}$, the signal of the aminic proton at 6.5 ppm and a broad singlet at 5.6 ppm corresponding to protons $H_{4'}$ and $H_{5'}$ (Table 1). The relative integration of the pyridine to imidazoline proton signals together with the appearance in

the ^{13}C NMR spectrum of the signal at 117.0 ppm (CN) indicates the presence of the desired mono-imidazoline product.

Table 1. Selected ^{1}H NMR data for ligands **1-10**[a]

Ligand	R	$H_{4'}$, $H_{5'}$	$^{3}J_{4'-5'}$
1	H	5.51	-
2	Bn	5.44, 4.92	11.6
3	Ts	5.93, 5.80	10
4	Tf	5.98, 5.92	8.7
5	H	5.58	-
6	H	5.0	-
7	Bn	5.0, 4.42	9.2
8	Me	4.86, 4.25	10.5
9	Ts	5.36, 5.17	4.8
10	Tf	5.45, 5.37	3.8

[a] Spectra performed in $CDCl_3$ at room temperature. Coupling constants are given in Hz.

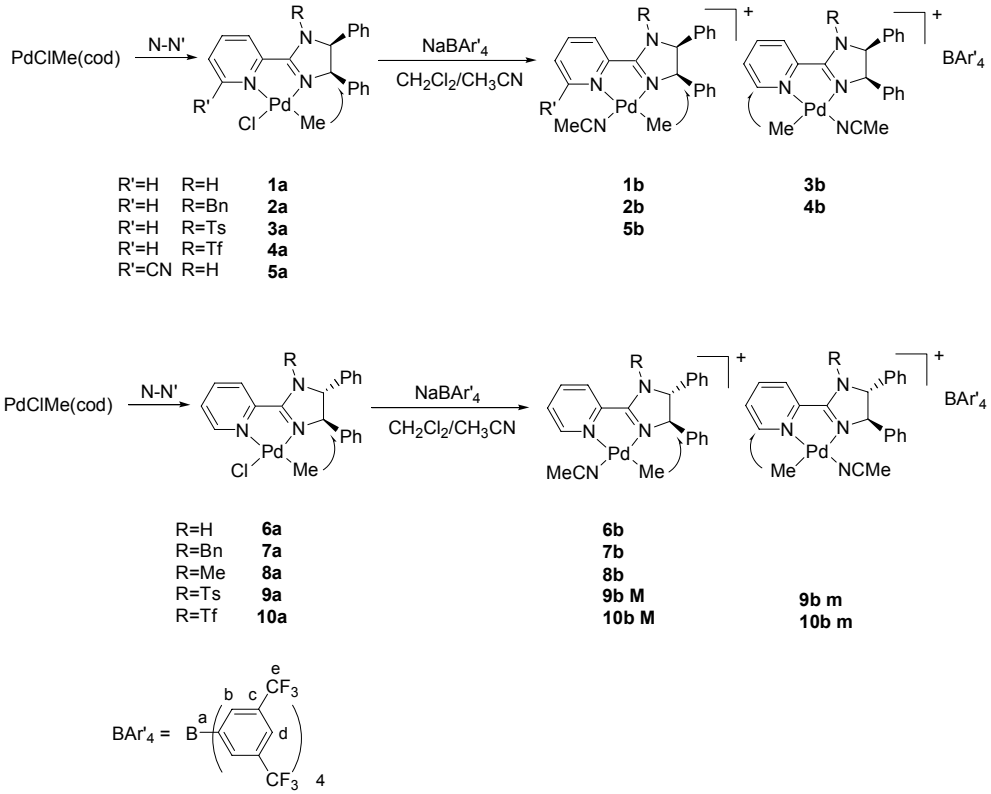
Trying to modify further the properties of the ligands, the stereochemistry of the imidazolines was changed. We prepared the enantiomeric pure (*R*,*R*) pyridine-imidazoline **6** quantitatively by reacting the corresponding diamine and 2-cyanopyridine, similarly to **1** (Scheme 4).

Reaction of **6** with different electrophiles (benzyl bromide, methyl iodide, *p*-toluenesulphonyl chloride and trifluoromethylsulphonyl anhydride), in the presence of a base, gave the (*R*,*R*) pyridine-imidazolines **7-10** (Scheme 4). The ^{1}H NMR spectra of the ligands show the signals of the pyridine ring and the two doublets (AB system) corresponding to $H_{4'}$ and $H_{5'}$ of the imidazoline (Table 1). In the case of **6**, the two doublets become a singlet at 5 ppm due to the tautomeric equilibrium. A comparison of the coupling constants within the compounds **1-10** shows that the nature of the R substituent has an effect on the coupling constant $^{3}J_{4'\text{-}5'}$, which decreases for the electron-withdrawing, bulkiest *p*-toluenesulphonyl (Ts) and trifluoromethylsulphonyl (Tf) groups (Table 1).[36] It is worth noting that in the case of the "trans" ligands **7-10** these variations are more noticeably than in the case of the "cis" ligands **2-4**.[26]

5.2.2.2. Synthesis, solution and solid state structures of neutral methylpalladium (II) complexes

When the ligands **5-10** were treated with [PdClMe(cod)] (cod = 1,5-cyclooctadiene) in toluene at room temperature the complexes [PdClMe(N-N′)] (**5a-10a**) precipitated (Scheme 5). The ^{1}H NMR spectrum of complex **5a** shows the signals corresponding to the ligand and the Pd-Me signal as a singlet at 0.72 ppm. In the spectra of complexes **6a-8a** the methyl group bonded to palladium appears as a singlet upfield shifted (average shift: 0.45 ppm) (Table 2). Since the methyl group σ-bonded to palladium normally appears at around 1 ppm,[37] the presence of the Pd-Me signals at lower frequencies may account for the unusual proximity between the

methyl group and the phenyl ring in 4' position. This proximity is observed in the solid state for complexes **4a**[38] and **8a** (see below).



Scheme 5. Synthesis of compounds **1a-10a** and **1b-10b**. The numbering scheme of BAr'_4 is included

Table 2. Selected ^{1}H NMR data for complexes **5a-10a** and **5b-10b** in $CDCl_3$ at room temperature

Compound	H_6	Pd-Me	Pd-NCMe
5a[a]	-	0.72	-
6a	8.82 (d)	0.34	-
7a	9.26 (d)	0.52	-
8a	9.28 (d)	0.48	-
9a	9.24 (d)	0.55	-
10a	9.29 (d)	0.75	-
5b	-	0.90	2.33
6b	8.34 (d)	0.56	2.30
7b	8.38 (d)	0.54	2.28
8b	8.38 (d)	0.48	2.30
9b[b]	M: 8.35 (dd) m: 8.50 (d)	0.57 0.97	2.20 1.61
10b[b]	M: 8.38 (d) m: 8.52 (d)	0.74 1.07	2.26 1.73

The signals are singlets unless another multiplicity is stated; (d): doublet; (t): triplet; (q): quadruplet; (m): multiplet. Coupling constants are omitted for clarity. [a] Spectrum made in $(CD_3)_2(CO)$. [b] M: major isomer; m: minor isomer.

As far as the pyridine-imidazoline signals are concerned, H_6 is sensitive to coordination being 0.5 ppm downfield shifted with respect to the free ligand. This indicates that H_6 feels the anisotropic effect of the neighboring chlorine.[39] Therefore the methyl group is *cis* to the imidazoline ring in all the neutral complexes. The chemical shift of both the methyl group and H_6 are useful for establishing the *cis* stereochemistry of complexes **6a**-**10a**. NOE experiments showed the interaction between the Pd-Me group and the $H_{4'}$ of the imidazoline ring which confirmed that all the neutral complexes **5a**- **10a** are the *cis* isomers. [To avoid confusion, *cis* and *trans* isomers indicate the stereochemical relationship between the methyl group and the imidazoline ring].

The *cis* stereochemistry was also observed in the solid state for complex **8a**, which contains the pyridine-imidazoline ligand **8** (R=Me) (Scheme 5). Suitable single crystals were obtained and analyzed by X-ray diffraction (Figure 1). Efforts to obtain single crystals of a neutral complex with the pyridine-imidazoline ligand bearing an electron-withdrawing group, resulted in the dichloro species **9a'**, [$PdCl_2$(**9**)] being isolated (Figure 2). Table 3 shows a selection of bond lengths and angles of the molecular structures for the neutral complexes **8a** and **9a'**.

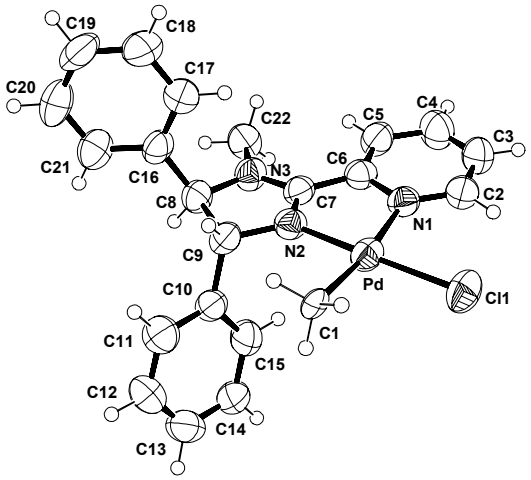


Figure 1. ORTEP drawing (thermal ellipsoids 50% probability) and atom numbering scheme of the molecular structure of **8a**

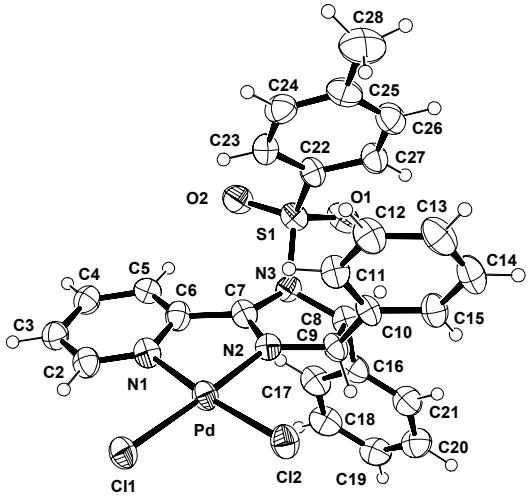


Figure 2. ORTEP drawing (thermal ellipsoids 40% probability) of the molecular structure of **9b'**

The Pd-N(py) distances are longer than those involving the iminic nitrogen of the imidazoline N2 (Table 3). The distance Pd-N(1) observed in **8a** is particularly long (2.121(6) Å) because the methyl group exerts *trans* influence. On the other hand, the Pd-N(2) bond length, 2.021(5) in **8a**, and 2.013(5) Å in **9a'**, seem to be slightly influenced by the different electron properties of the R group in the imidazoline ring.

Table 3. Selected bond distances (Å) and angles (°) and geometrical parameters (°) for **8a** and **9a'**

	8a X = C(1)	**9a'** X = Cl(2)
Pd-N(1)	2.121(6)	2.049(5)
Pd-N(2)	2.021(5)	2.013(5)
Pd-Cl(1)	2.303(2)	2.289(2)
Pd-X	2.181(4)	2.277(2)
N(2)-C(7)	1.293(9)	1.281(8)
N(2)-C(9)	1.462(8)	1.444(8)
N(3)-C(7)	1.330(8)	1.427(8)
N(3)-C(8)	1.467(9)	1.480(8)
N(3)-C(22)	1.477(9)	-
N(3)-S(1)	-	1.693(5)
N(1)-Pd-N(2)	78.4(2)	79.9(2)
N(1)-Pd-Cl(1)	96.00(16)	95.41(16)
N(1)-Pd-X	171.9(2)	172.57(15)
N(2)-Pd-Cl(1)	173.22(16)	175.15(14)
N(2)-Pd-X	94.5(2)	92.79(15)
Cl(1)-Pd-X	91.30(12)	91.81(6)
N(3)-S(1)-C(22)	-	108.2(3)
N(1)-C(6)-C(7)-N(2)	5.2(8)	2.1(9)
C(16)-C(8)-C(9)-C(10)	125.8(6)	139.7(6)
dihedral angle py/im	2.6(4)	17.9(3)

The Pd-Cl and Pd-C coordination distances fall in a range usually observed in other Pd(II) complexes.[38] In the chelating ligand the small N(1)-C(6)-C(7)-N(2) torsion angle of 5.2(8)° in **8a** and 2.1(9)° in **9a'** indicates a negligible tilt between the rings. However, the dihedral angle formed by the best fit planes through the rings are significantly distinct, being 2.6(4) and 17.9(3)°, respectively. The large angle in **9a'** might be ascribed to a distortion in the imidazoline plane to favour the intramolecular π stacking of the tosyl ring with the adjacent phenyl (distance between centroids 3.747 Å).

The electron withdrawing tosyl group in **9a'** causes the N(2)-C(7) and N(3)-C(7) distances to be different (1.281(8) and 1.427(8) Å, respectively), while in **8a** (R = Me) these bond lengths are comparable to 2σ. Correspondingly, the sum of the bond angles about the imidazoline N(3) is 360.0° in **8a** and 348.1° in **9a'**.

Analyzing the distance between the chloride ligand and the H_6 (2.80 Å for **8a** and 2.68 Å for **9a'**), a Cl-H interaction cannot be excluded. This may be the reason for the *cis* stereochemistry observed for all the neutral complexes **1a**-**10a**, since in view of the large *trans* influence of the methyl group it should be expected to be *trans* to the less basic ring (pyridine in **5a**-**8a** and imidazoline in **9a** and **10a**).

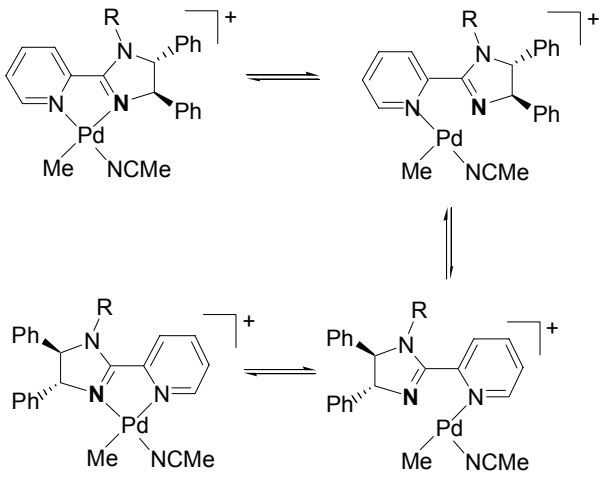
5.2.2.3. Synthesis and characterization of cationic palladium (II) complexes

The neutral complexes were treated with $NaBAr'_4$ in the presence of acetonitrile to obtain the cationic complexes $[PdMe(NCMe)(N\text{-}N')][BAr'_4]$ (**5b-10b**) (Scheme 5). ^1H and ^{13}C NMR analysis of the complexes at room temperature showed that both the Pd-Me and the Pd-NCMe signals were present, which confirmed the abstraction of the Cl ligand. For complexes **6b-8b** the signals of the methyl and the acetonitrile ligands, coordinated to palladium, appeared as singlets between 0.48-0.56 ppm and 2.28-2.30 ppm, respectively (Table 2). These shifts are indicative of *cis* stereoisomers.[26] For complex **5b**, however, the Pd-Me signal is downfield shifted because of the withdrawing effect of the substituted pyridine in *trans*. Irradiation of the protons of the Pd-Me group showed NOE interaction with $H_{4'}$ of the imidazoline ring, which confirmed the presence of *cis* stereoisomers as single products.

On the other hand, the characterization in solution of **9b** and **10b** showed two sets of resonances at room temperature, both in the aromatic and in the aliphatic part of the spectra (Table 2). COSY experiments together with selective irradiation of the aromatic signals confirmed the presence of *cis/trans* stereoisomers in a ratio of 3:1 for **9b** and 2:1 for **10b**. ^1H NMR spectra at higher temperatures (323 K in $CDCl_3$) showed broadening of the signals, which confirmed that both species are in equilibrium even though the process is in slow exchange regime at this temperature. Irradiation of the Pd-Me signal of the major isomer at room temperature

gave a NOE interaction with $H_{4'}$ but the Pd-Me signal of the minor species also appeared irradiated, thus confirming the *cis*/*trans* isomerization.

The equilibrium probably involves a process of Pd-N bond rupture, rotation of the ligand around the remaining Pd-N bond and reformation of the former Pd-N bond, as observed for similar compounds.[40] This behaviour may be attributed to the weaker donating ability of ligands **9** and **10**. The electron-withdrawing character of tosyl and trifil groups in the imidazoline ring lead to a weaker Pd-N (imidazoline) bond than the Pd-N (pyridine) one. Likewise, the methyl group *trans* to the less basic ring exerts a high *trans* influence and consequently facilitates the Pd-N(imidazoline) bond rupture (Scheme 6).



Scheme 6. Proposed isomer interconversion for complexes **9b** and **10b**

To sum up, for complexes **1b**-**5b**, bearing the pyridine-imidazoline ligands with the phenyl rings on the same side of the coordination plane, the coordination of the Me group to palladium is determined by the electronic properties of R substituents in the imidazoline. The methyl group is always *trans* to the less basic ring (pyridine for complexes **1b**, **2b**, **5b** and imidazoline for **3b** and **4b**). The behaviour of the complexes **6b**-**10b**, which have ligands with the phenyl rings up and down the coordination plane, depends also on the electron-donating or withdrawing character of the R substituent. However in the case of ligands **9** and **10** the electron-withdrawing substituent exerts a larger effect in the imidazoline (as seen also in the coupling constants in Table 1) and leads to a weaker coordination and therefore the mixture of stereoisomers is obtained (Schemes 5 and 6).

5.2.2.4. Synthesis of cationic rhodium complexes 1c-4c, 1d-4d

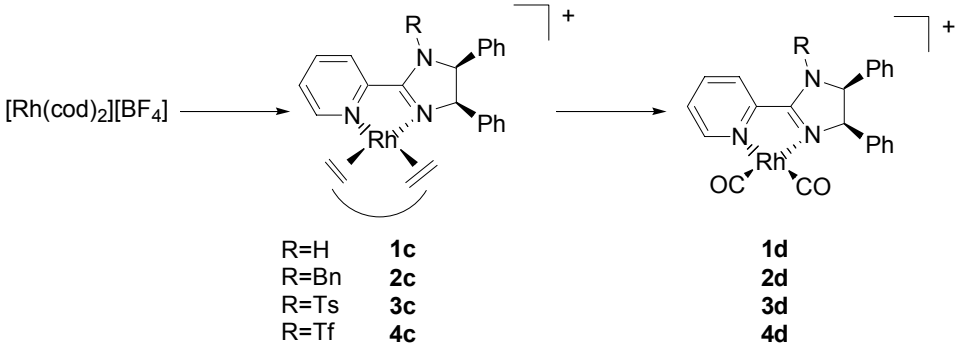
In order to get more information about the different basicities of the substituted pyridine-imidazoline ligands **1**-**4** (Scheme 4), which provide better electronic differentiation when coordinated to palladium cationic complexes, we synthesized a series of bis-carbonyl rhodium complexes and comparatively measured their CO frequencies by infrared spectroscopy.

The corresponding [Rh(cod)(N-N´)][BF_4] (**1c**-**4c**) were obtained by reacting [$Rh(cod)_2$][BF_4] with the pyridine-imidazoline ligands **1**-**4**. The ^1H NMR spectra show the expected signals for the nitrogen ligand and those corresponding to the diene (see Experimental). Considering that the symmetry of the rhodium(I) cation is C_1, four signals are expected although

fewer signals may be observed because the diene rotates easily around the coordination plane. In fact the number of signals observed at room temperature for the CH protons depends on the nitrogen ligand. For complexes **1c** and **2c** the four signals are observed (for **1c** two of them are partially overlapped), while for **3c** and for **4c** only one and two broad signals are present, respectively. Lower temperature experiments gave the four expected signals also for complexes **3c** and **4c**. These NMR data indicate that the rhodium complexes differentiate the ligands, which gives further proof of the influence of the R substituent in the pyrimidine-imidazoline properties.

Bubbling CO through the reddish solutions of the diolefinic derivatives displaces the coordinated cyclooctadiene and forms yellow solutions of the corresponding bis-carbonyl complexes **1d**-**4d** (Scheme 8).[41] As a reference the analogous complex containing 2,2'-bipyridine (bipy) as the nitrogen ligand has also been synthesized. This would let us compare with one of the best ligands for the CO/styrene copolymerization reaction.[42] The ^{1}H NMR spectra of the isolated complexes show the disappearance of the diene signals together with the shift of the pyridine-imidazoline signals, as expected for the change of the electronic properties of the ligands in *trans*.

Table 4 shows the data of the stretching frequencies, ν(CO), of the carbonyl complexes. All the complexes show two frequencies ($\Delta\delta$= 59 cm^{-1}) which we have assigned to *cis* bis-carbonyl complexes.[41] The frequencies vary and increase in the order **1** < **2** < bipy < **3** < **4**, indicating the decreasing order of basicity of the nitrogen ligands coordinated *trans* to the carbonyls.



Scheme 8. Synthesis of the Rh(I) complexes **1c**-**4c**, **1d**-**4d**

Table 4. Selected IR data for $[Rh(CO)_2(N\text{-}N')][BF_4]$ complexes[a]

Ligand	ν(CO) (cm^{-1})	Δδ
1	2093, 2030	63
2	2093, 2033	60
bipy	2099, 2042	57
3	2104, 2045	59
4	2106, 2050	56

[a] Measured in dichloromethane

5.2.2.5. X-ray crystal structures of 2c and 3c

The X-ray structural determination of **2c** and **3c** shows the rhodium atom in the expected square planar coordination through the N donors of the chelating pyridine-imidazoline ligand and the two double bonds of 1,5-cyclooctadiene. Figures 3 and 4 show perspective views of the complexes.

The Rh-C bonds (Table 5), which fall in a wide range (2.124(8) -

2.169(7) Å) and the alkene C-C bonds (1.38 Å mean value) agree with those detected in other Rh(cod) complexes.[43] Assuming C(1m) and C(5m) as the midpoint of the C-C alkene bonds, the calculated distances, *trans* to N(2) and to N(1), are Rh-C(1m) 2.008 and 2.009 Å, and Rh-C(5m) 2.033 and 2.047 Å, for **2c** and **3c**, respectively. These distances indicate a stronger *trans* influence of the ligand **3**. The coordination N(1)/N(2)/C(1m)/C(5m) mean plane forms an angle close to 88° with the plane calculated through the alkene C atoms.

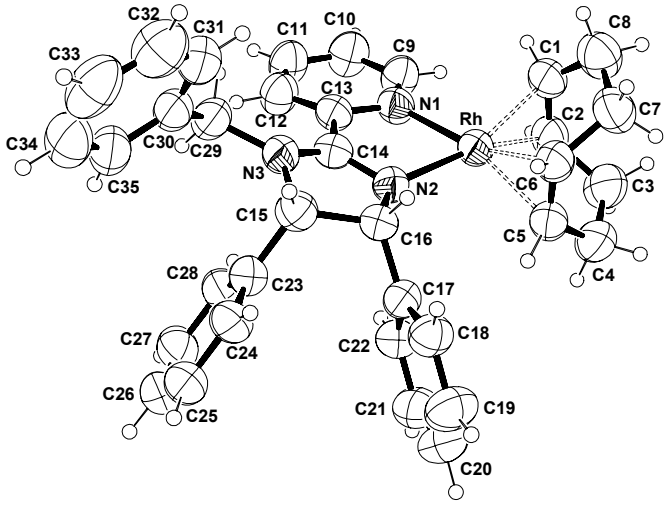


Figure 3. Molecular structure of **2c** cation. (ORTEP drawing, thermal ellipsoids at 40% probability level)

In both complexes the Rh-N1(pyridine) bond length is slightly longer than the Rh-N2(imidazoline) one. Moreover, the electronic effects exerted by the R group at N(3) are mainly evident in the imidazoline ring,

rather than in the metal coordination environment. In fact, in **2c** the N(2)-C(14) and N(3)-C(14) bond distances, 1.324(7) and 1.336(8) Å, are consistent with a delocalization inside the N(2)-C(14)-N(3) fragment, while the corresponding values in **3c** (1.283(8), 1.387(9) Å), induced by the tosyl group, indicate a double bond quite short. The degree of delocalization across the amidine is confirmed by the sum of the bond angles about N(3) of 359.5° in **2c** *vs*. 349.1° in **3c**.

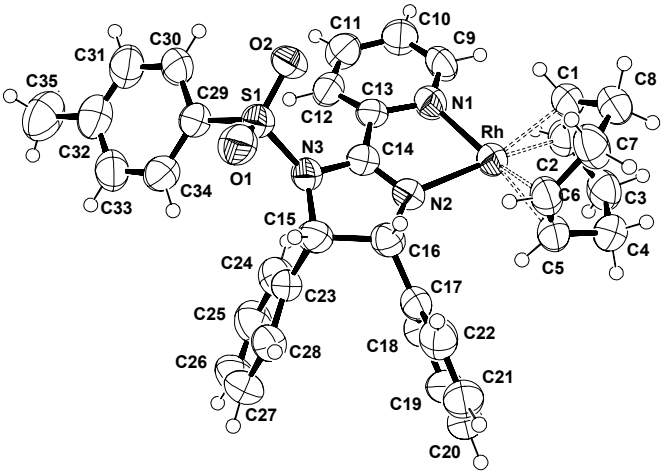


Figure 4. Molecular structure of **3c** cation. (ORTEP drawing, thermal ellipsoids at 50% probability level)

The chelating ligands are not coplanar, and the distortions are very similar to those found in the Pd derivatives with *cis* disposed phenyls.[38] The torsion angle N(1)-C(13)-C(14)-N(2) is -13.5(8) and -16.5(9)° in **2c** and **3c**, respectively, and the phenyls on the imidazoline ring avoid an eclipsed

conformation through a torsion angle C(16)-C(8)-C(9)-C(10) of 20.3(5) (**2c**) and 27.9(7)° (**3c**).

Table 5. Selected bond distances (Å) and angles (°) and geometrical parameters for **2c** and **3c**[a]

	2c	**3c**
Rh-N(1)	2.099(5)	2.112(6)
Rh-N(2)	2.078(5)	2.090(6)
Rh-C(1)	2.124(8)	2.125(7)
Rh-C(2)	2.139(7)	2.131(7)
Rh-C(5)	2.139(6)	2.169(7)
Rh-C(6)	2.147(6)	2.152(7)
Rh-C(1m)	2.008	2.009
Rh-C(5m)	2.033	2.047
N(2)-C(14)	1.324(7)	1.283(8)
N(2)-C(16)	1.484(7)	1.502(8)
N(3)-C(14)	1.336(8)	1.387(9)
N(3)-C(15)	1.483(8)	1.496(8)
N(3)-C(29)	1.480(8)	-
N(3)-S(1)	-	1.692(5)
C(1)-C(2)	1.393(10)	1.375(10)
C(5)-C(6)	1.378(10)	1.363(11)
N(1)-Rh-N(2)	78.2(2)	77.9(2)
C(1m)-Rh-C(5m)	87.41	87.32
N(3)-C(29)-C(30)	112.0(5)	-
N(3)-S(1)-C(29)	-	105.7(3)
N(1)-C(13)-C(14)-N(2)	–13.5(8)	–16.5(9)

C(23)-C(15)-C(16)-C(17)	–16.9(7)	–26.9(9)
C(29)-N(3)-C(15)-C(23)	62.8(7)	-
S(1)-N(3)-C(15)-C(23)	-	110.4(6)
dihedral angle py/im	16.2(3)	14.9(4)

[a] C(1m) and C(5m) are the midpoints of the C(1)-C(2) and C(5)-C(6) bond, respectively.

The X-ray structural results show that: i) significant distortions in the imidazoline ring are induced by *cis* disposed phenyl rings; ii) the nitrogen in the imidazoline substituted with a benzyl group is planar and shows a delocalization inside the amidine fragment, as was found with the methyl substituent (see **8a**, Figure 1); iii) the R substituent influences the coordination of the cyclooctadiene *trans* to the pyridine-imidazoline and not the direct coordination of the imidazoline to the rhodium. This is in agreement with the different behaviour found in solution for **2c** and **3c**.

5.2.2.6. Copolymerization of carbon monoxide and 4-*tert*-butylstyrene

Compounds **5b-10b** (Scheme 5) have been tested as catalyst precursors in the copolymerization of CO and 4-*tert*-butylstyrene and in the same experimental conditions as those used for precatalysts **1b-4b**.[26] Table 6 shows that **6b-10b** give rise to efficient catalysts while **5b** is inactive. In ligand **5**, the cyano substituent (Scheme 4) is *ortho* to the coordinating nitrogen, and this probably causes enough steric hindrance as to interfere the chain growth sequence. In the copolymerization reaction, 2,9-substituted phenantrolines and 6-substituted bipyridines have been

reported to behave in a similar fashion,[44] although in ligand **5** some activity was expected due to the presence of a five membered ring in the backbone.

Interestingly complexes **6b-10b** are more stable in solution, during copolymerization, than the corresponding **1b-5b**. This may be because of the relative disposition of both phenyl rings, which seems to stabilize the cationic intermediates. The most surprising feature of these catalysts is their disparate productivity. The catalysts containing the less basic ligands **4b**, **9b** and **10b**, are more productive than the more basic catalysts **1b**, **2b**, **6b-8b**. It is worth noting that the productivity observed for complex **9b** is high, ten times higher than the productivity obtained with other pyridine-imidazoline derived catalysts (entry 9 versus 1). The amount of copolymer produced by this system falls in the range of the productivities obtained with the most active systems reported for CO/styrene copolymerization at mild conditions.

For those precatalysts containing the more basic ligands (R = H, Bn, Me) the arrangement of both phenyl rings in the imidazoline moiety also affects the copolymer production. The racemic (*R*,*S*)-pyridine-imidazoline ligands (**1**, **2**), which show more significant distortions and create a larger steric hindrance than the related (*R*,*R*)-ligands (**6-8**), lead to more active catalysts (entries 1, 2 *versus* entries 6-8). This behaviour seems related to the *meso* effect reported for basic diphosphine-containing catalysts in the polymerization of ethene and/or propene with CO (Scheme 3).[33,34]

Table 6. CO/4-*tert*-butylstyrene copolymerization using complexes **1b-10b** at room temperature and 1 atm of CO pressure

Entry	Complex	Prod (gr CP/grPd.h)	M_n (M_w/M_n)	%*l* diads
1[a,b]	**1b**	2	42200 (1.1)[c]	65
2[b]	**2b**	8.9	49750 (1.5)[c]	52
3[b]	**3b**	7	59250 (1.2)[c]	15
4[b]	**4b**	12.8	39700 (1.5)[c]	18.4
5[b]	**5b**	-	-	-
6	**6b**	3.4	17200 (1.2)[d]	37.3
7	**7b**	4	n.d.	26.4
8	**8b**	5	13500 (1.3)[d]	34.5
9	**9b**	27.2	54700 (1.4)[d]	30.2
10	**10b**	14.6	26200 (2.0)[d]	23

Reaction conditions: sust/cat= 620; 1atm CO; 5 mL of chlorobenzene; t = 24h. [a] nPd= 0.083 mmol; [b] See Chapter 5.1; [c] Determined by SEC-MALLS in THF; [d] Determined by GPC in THF, relative to polystyrene standards.

The productivity of the different systems can be rationalized in terms of the basicity of the pyridine-imidazoline ligands. The catalysts containing the less basic ligands show higher productivity than the more basic ones. This seems to be consistent with the need to use π acidic imine donors instead of phosphines for the CO/styrene copolymerization.

The size of the polyketones obtained using the precursors with the new ligands **6-10** are related to the productivity of the catalytic systems

(Table 6). The molecular weights (M_n) of the polyketones obtained using the precursors **9b** and **10b** are high (up to 54700), while those obtained with the more basic catalysts **6b** and **8b** are lower. Comparing the two series of ligands (phenyl rings in *cis* and *trans* arrangement) (Scheme 4) structural factors and electronic effects again seem to be involved. On the one hand, there is no clear relationship between size of the polyketones obtained with the precursors containing the ligands **1-4** and the R substituent. On the other, the polyketones obtained with the precursors **6b-10b** had molecular weights that varied considerably according to the nature of the R substituent of the ligand used.

The tacticity of the polyketones was analyzed by integrating the ^{13}C NMR spectra in the $CH(Ph)CH_2$ region (Figure 5). It is interesting to note that the structure of the pyridine-imidazoline ligand used has a considerable effect on the stereoregularity of the polymer. While using the ligands **1-4**, the different substitutions of the imidazoline influenced the stereoregularity (see **1b** *vs.* **4b** in Figure 5), using the ligands **6-10** this effect was overridden. In fact, when precatalysts **6b-10b** were used, a prevailing syndiotactic microstructure was observed in all the cases as previously reported for the similar pyridine-oxazoline ligand.[18,24] The polyketone content of *l*-diads ranges between 23-37% (Table 6).

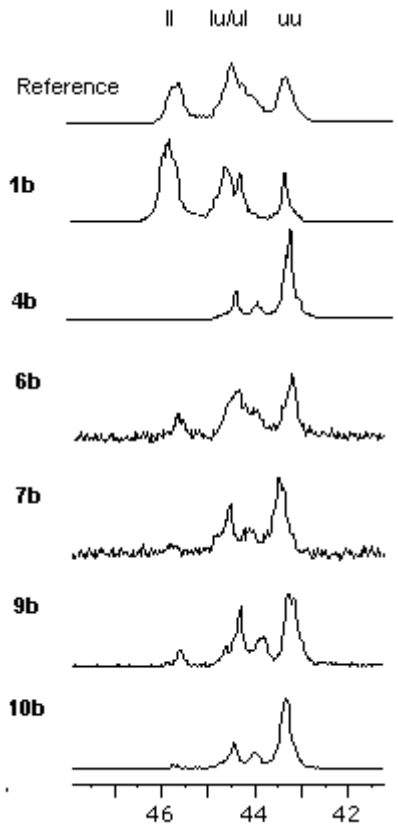


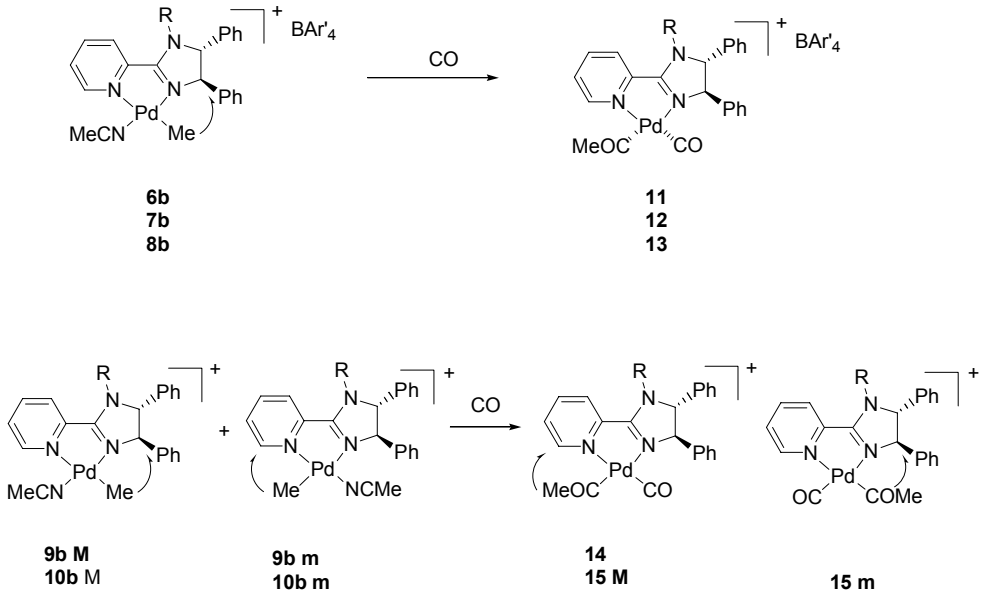
Figure 5. Comparative ^{13}C NMR spectrum of the copolymers, obtained using the complexes indicated, in the region of the methylene carbon atom. The reference is an epimerized copolymer

According to the results previously reported,[24] the syndiotacticity observed should be produced by the chain-end control, which overcomes the enantiosite control created by the chiral ligand. The reason for this may be that: 1) the styrene coordinates selectively *cis* to pyridine and prevents the alkene from being influenced by the chiral part of the ligand; 2) the chiral environment created by the pyridine-imidazoline ligand is not

enantioselective enough to force stereoregular styrene insertions. In an attempt to have more information of the role played by the pyridine-imidazoline ligands **6-10**, we monitored by NMR spectroscopy the reactivity of the palladium precursors with carbon monoxide.

5.2.2.7. Insertion of carbon monoxide in the palladium cationic complexes

The cationic complexes **6b-10b** were carbonylated in CD_2Cl_2 solution by bubbling CO for five minutes at 273 K. Selected ^{1}H and ^{13}C NMR data are given in Table 7 and indicate the formation of acyl-carbonyl complexes [Pd(COMe)(CO)(N-N')][BAr'$_4$], which result from inserting CO into the Pd-Me bond (**11-15**) (Scheme 8). The ^{1}H NMR spectra at 273 K show only two new singlets (e.g. for **7b** + CO: 1.72 ppm and 1.97 ppm) in the aliphatic part. When labeled ^{13}CO is used, in the ^{1}H NMR spectra one of these singlets become a doublet indicating that it corresponds to an acyl group. In the case of complex **15**, however, the acyl appears as a broad signal. The other singlet is due to free acetonitrile. The ^{13}C NMR spectra at 273 K, after the CO bubbling show two signals (e.g. for **7b** + CO: 174 ppm and 210.5 ppm), the one at lower frequency is typical for a Pd-CO fragment, while the other belongs to a Pd-COMe species.[17]



Scheme 8. Carbonylation of the cationic palladium compounds **6b-10b**. M: major isomer; m: minor isomer

Table 7. Selected ^{1}H and ^{13}C NMR resonances for the reaction of complexes **6b-10b** with ^{13}CO[a]

^{1}H NMR					
Compound	T	Me / Pd / NCMe	Me / Pd / CO	COMe / Pd / NCMe	COMe / Pd / CO
6b+CO	273	0.51	n.o.	n.o.	1.72
	183				1.53
7b+CO	273	0.49	n.o.	n.o.	1.72
	183				1.54
8b+CO	273	0.44	0.86	1.52 (d)	1.70 (d)
	183				1.52 (d)

9b+CO	273	M: 0.52 m: 1.04	0.90	1.46 (d)	1.62
	183				1.36 (d)
10b+CO	273	M: 0.72 m: 1.15	n.o.	n.o.	2.05
	183				M: 1.56 (d) m: 2.69 (br)
^{13}C NMR					
6b+CO	183		n.o.	n.o.	173.2, 211.6
7b+CO	273				174.0, 210.5
	183				173.1, 213.3
8b+CO	273		176.3	219.9	174.1, 210.3
	183				173.4, 212.7
9b+CO	273		175.0	215.4	173.2, 206.6
	183				172.5, 208.2
10b+CO	273		n.o.	n.o.	173.2, 207.2
	183				M:172.3, 208.2 m: 170.3, 212.9

[a] NMR spectra recorded in CD_2Cl_2; δ values are in ppm; d= doublet; br = broad; n.d.: not determined; n.o.: not observed. M: major isomer; m: minor isomer.

Low temperature NMR experiments were performed, by decreasing the temperature from 263 K to 183 K, with all the acyl-carbonyl complexes. Complexes **11-14** showed sharp singlets in all the temperature range, probing to be single isomers. In the case of **15**, the signal at 2.05 ppm

disappeared at 233 K. Two doublets became evident at 183 K (1.56 and 2.69 ppm; **15** major and minor isomer, respectively). In ^{13}C NMR the initial two signals at 273 K (at 173.2 and 207.2 ppm) became four at 183 K (172.3 and 208.2 for **15** major, 170.3 and 212.9 for **15** minor) as expected for the presence of two acyl-carbonyl species. This indicates the presence of *cis*/*trans* equilibrium in the case of complex **15** (Scheme 8).

The intermediates of the carbon monoxide migratory insertion reaction were detected in two additional experiments with complexes **8b** and **9b** (Table 7). After CO bubbling at 273 K the tube was carefully placed in the probe without shaking, so that the carbon monoxide could slowly diffuse into the solution. Three more signals in ^{1}H NMR and two more in ^{13}C NMR were observed. For example, complex **8b** showed two singlets at 0.86 and 2.35 ppm, and a doublet at 1.52 ppm in ^{1}H NMR together with two new signals at 176.3 and at 219.9 in ^{13}C NMR. These two new species were unequivocally assigned to the methyl-carbonyl (0.86 and 176.3 ppm) and acyl-acetonitrile species (1.52, 2.35 and 219.9 ppm).[17]

The stereochemistry of the acyl-carbonyl complexes **13**, **14** and **15** (major isomer) was assigned by NOE experiments. Irradiation of H_6 gave interaction with the Pd-COMe signal indicating that they are *trans* isomers (Scheme 8). In the case of complexes **11** and **12** the stereochemistry could not be unequivocally assigned by NOE experiments. Nevertheless as the signals of the Pd-COMe group for complexes **11**-**14** and **15** major appear, in ^{1}H NMR, at similar shifts (ca. 1.5 ppm) and the signal of **15** minor appears at 2.96 ppm, it could be state that also **11** and **12** are the *trans* isomers.

5.2.3. Conclusions

Modular pyridine-imidazoline ligands (**1-10**) allow studying structural influences of the ligands in the palladium-catalyzed copolymerization reaction. The modification of the ligand stereochemistry, racemic (*R*,*S*) or enantiomerically pure (*R*,*R*), leads to imidazolines with different degree of distortion. Variation of the R substituents on the imidazoline allows tuning their basicity. A larger effect of the R substituent is observed in the (*R*,*R*) imidazolines. Both structural changes are reflected in the coordination to Pd(II) and Rh(I) complexes.

All the neutral [PdClMe(N-N')] complexes have the methyl group *cis* with respect to the imidazoline ring, while the cationic complexes [PdMe(NCMe)(N-N')][BAr'$_4$] present different situations depending on the R substituent in the imidazoline ring, as we observed for ligands **1-4**. Ligands **5-8** with electron-donating substituents lead to the *cis* isomers **5b-8b**. Ligands **9** and **10** feel stronger the effect due to the electron-withdrawing R and therefore have less coordinating ability. This leads to a *cis*/*trans* equilibrium due to ligand fluxionality.

Differences are observed when the cationic palladium complexes are used as catalyst in copolymerization of CO/4-*tert*-butylstyrene: complexes **6b-10b** show higher stability in solution during the copolymerization reaction than the corresponding **1b-4b** and, in most of the cases, lower activity. For the first time a ligand effect that is similar to the *meso*-effect is observed using nitrogen ligands. Concerning the productivity of the systems there is a clear influence of the substituent R, being it more

evident for the precatalysts **6b-10b**. Higher productivities are observed using less basic ligands, probably because the insertion reactions are more favored. The special structural disposition of ligand **9**, when it is coordinated to palladium, may account for its outstanding performance.

While the polyketones obtained with the complexes **1b-4b** have different degree of stereoregularity depending on the R substituent, using complexes **6b-10b** always syndiotactic polyketones are obtained. The study of the insertion reaction of CO to form the species [Pd(COMe)(CO)(N-N')][BAr'$_4$] shows the selective formation of the *trans* stereoisomer using ligands **6-9**. This seems to indicate that using complexes **6b-9b** we are able to induce a site-selective coordination of the styrene *cis* to the chiral part of the ligand. Both low enantiomorphic control of the (*R*,*R*) ligands or isomerization processes during chain growth, may be responsible for the synthesis of syndiotactic polyketones.

5.2.4. Experimental

5.2.4.1. General procedure

All reactions were carried out under nitrogen atmosphere, at room temperature, using standard Schlenk techniques. Solvents for synthetic purposes were distilled and deoxygenated prior to use unless otherwise stated. Solvents for spectroscopy were used without further purification. Carbon monoxide (labeled and unlabeled, CP grade, 99 %) was supplied by Aldrich. The palladium precursor [PdClMe(cod)][39] and the salt NaBAr'$_4$ (Ar' = 3,5-(CF$_3$)$_2$-C$_6$H$_3$)[45] were prepared according to the reported methods. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini spectrometer with

a ^{1}H resonance frequency of 300 MHz and a ^{13}C frequency of 75.4 MHz and on a Varian Mercury VX spectrometer with a ^{1}H resonance frequency of 400 MHz and a ^{13}C frequency of 100.5 MHz. The resonances were referenced to the solvent peak versus TMS ($CDCl_3$ at 7.26 δ for ^{1}H and 77.23 δ for ^{13}C, CD_2Cl_2 at 5.32 δ for ^{1}H and 54.0 δ for ^{13}C). The NOE experiments were run with a ^{1}H pulse of 12 μs (300 MHz) and 13.3 μs (400 MHz). Two-dimensional correlation spectra (gCOSY) were obtained with the automatic program of the instrument. Elemental analyses were carried out on a Carlo Erba Microanalyser EA 1108. MS (FAB positive) were obtained on a Fisons V6-Quattro instrument. The molecular weights of the copolymers and the molecular weight distributions were determined by size exclusion chromatography on a Waters 515-GPC device using a lineal Waters Ultrastyragel column with a Waters 2410 refractive index detector *versus* polystyrene standards.

5.2.4.2. Synthesis of ligands

5: The 2,6-dicyanopyridine (100 mg, 0.77 mmol) was reacted with the *meso*-1,2-diphenylethylenediamine (164 mg, 0.77 mmol) in chlorobenzene (5 mL) in the presence of $Yb(OTf)_3$ (46 mg, 0.14 mmol). The mixture was stirred for 24 hours under reflux. The desired product was separated from the bis-imidazoline product by column chromatography with hexane/ ethyl acetate (1:2) as eluent.[35] Rf = 0.41. Yield = 20%. Anal. Found: C, 77.52; H, 4.73; N, 17.21%. Calc. for $C_{21}H_{16}N_4$: C, 77.76; H, 4.97; N, 17.27%. ^{1}H NMR (300 MHz, $CDCl_3$, RT): δ 8.58 (d, ^{3}J = 7.8 Hz, 1H, H_5), 7.99 (t, ^{3}J = 7.8 Hz, 1H, H_4), 7.83 (d, ^{3}J = 7.8 Hz, 1H, H_3). 7.04- 6.95 (m, 10H, Ph), 6.49 (s, 1H, NH), 5.58 (br, 2H, $H_{4'}$ + $H_{5'}$). ^{13}C NMR (75.4 MHz, $CDCl_3$, RT): δ

162.5 (s, C_2), 150.0 (s, $C_{2'}$), 138.4 (s, C_6), 130.2 (s, $C_{3\text{-}5}$), 130.0 (s, $C_{3\text{-}5}$), 127.9 (s, Ph), 127.1 (s, Ph), 126.2 (s, $C_{3\text{-}5}$), 117.0 (s, C≡N), 67 (br, $C_{4'}$+$C_{5'}$).

6: 2-cyanopyridine (500 mg, 2.36 mmol) was reacted with (1*R*,2*R*)-1,2-diphenylethylenediamine (228 mg, 2.21 mmol) in chlorobenzene (10 mL) in the presence of $Yb(OTf)_3$ (50 mg, 0.16 mmol). The mixture was stirred for 72 h under reflux. The resulting mixture was evaporated to dryness, dissolved in CH_2Cl_2 and washed with three portions of H_2O (15 mL). The organic layers were extracted, dried over $MgSO_4$ and evaporated to give a light-coloured solid. Recrystallisation from CH_2Cl_2/ hexane afforded white crystals. Yield: 84%. Anal. Found: C, 80.09; H, 5.30; N, 13.77%. Calc. for $C_{20}H_{17}N_3$: C, 80.2; H, 5.4; N, 14%. ^{1}H NMR (300 MHz, $CDCl_3$, RT): δ 8.64 (d, ^3J = 5.4 Hz, 1H, H_6), 8.35 (d, ^3J = 8 Hz, 1H, H_3), 7.85 (t, ^3J = 8 Hz, 1H, H_4), 7.44 (dd, ^3J = 8, ^3J = 5.4 Hz, 1H, H_5), 7.36 - 7.31 (m, 10H, Ph), 5 (s, 2H, $H_{4'}$ + $H_{5'}$). ^{13}C NMR (75.4 MHz, $CDCl_3$, RT): δ 162.7 (s, C_2), 149 (s, C_6), 148.5 (s, $C_{2'}$), 143.3 (s, Ph), 136.9 (s, C_4), 128.9 (s, Ph), 127.7 (s, Ph), 126.8 (s, Ph), 125.6 (s, C_5), 123 (s, C_3), 75.6 (s, $C_{4'}$+$C_{5'}$).

7: Compound **6** (100 mg, 0.33 mmol) was dissolved in THF (3 mL) and reacted with NaH in excess for about an hour. To the reaction mixture, benzyl bromide (42.5 µL) was added dropwise at room temperature. After reacting for 5 hours, evaporation gave a brown paste which was purified by column chromatography using a hexane/ethyl acetate mixture (1:1) as eluent. Rf = 0.10. Yield: 71%. Anal. Found: C, 83.02; H, 5.82; N, 10.74%. Calc. for $C_{27}H_{23}N_3$: C, 83.26; H, 5.95; N, 10.79%. ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ δ 8.72 (ddd, ^3J = 5.5 Hz, ^4J = 1.6 Hz, ^5J = 1 Hz, 1H, H_6), 8.17 (dt, ^3J = 8 Hz, ^4J = 1.4 Hz, 1H, H_3), 7.83 (td, ^3J = 5.5 Hz, ^4J = 1.4 Hz, 1H, H_4), 7.4 (m, 1H, H_5),

7.35- 6.97 (m, 15H, Ph), 5.63 (d, ^3J = 15.6 Hz, 1H, CH_2), 5.0 (d, ^3J = 9.6 Hz, 1H, $H_{4'}$ or $H_{5'}$), 4.42 (d, ^3J = 9.6 Hz, 1H, $H_{5'}$ + $H_{4'}$), 3.95 (d, ^3J = 15.6 Hz, 1H, CH_2). ^{13}C NMR (100.5 MHz, $CDCl_3$, RT): 148.9 (s, C_6), 137.1 (s, C_4), 129.1 (s, Ph), 128.6 (s, Ph), 128.3 (s, Ph), 128.0 (s, Ph), 127.7 (s, Ph), 127.5 (s, Ph), 127.3 (s, Ph), 127.2 (s, Ph), 125.4 (s, C_3 or C_5), 124.9 (s, C_5 or C_3), 77.9 (s, $C_{4'}$ or $C_{5'}$), 73.6 (s, $C_{5'}$ or $C_{4'}$), 49.1 (s, CH_2).

8: This compound was prepared in a similar way to **7** but with methyl iodide as the electrophile.[29] ^{1}H NMR (300 MHz, $CDCl_3$, RT): δ 8.59 (d, ^3J = 3.6 Hz, 1H, H_6), 7.99 (d, ^3J = 7.9 Hz, 1H, H_3), 7.70 (td, ^3J = 7.9 Hz, ^4J = 1.5 Hz, 1H, H_4), 7.28- 7.15 (m, 11H, H_5 + 10Ph), 4.86 (d, ^3J = 10.5 Hz, 1H, $H_{4'}$ or $H_{5'}$), 4.25 (d, ^3J = 10.5 Hz, 1H, $H_{4'}$ or $H_{5'}$), 2.88 (s, 3H, CH_3-N).

9: To a solution of ligand **6** (100mg, 0.33 mmol) and 4-(dimethylamino)pyridine (73.1 mg, 0.6 mmol) in dichloromethane (3 mL) at 273 K, a solution of *p*-toluenesulphonylchloride (75.7 m, 0.4 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 5 hours. Evaporation of the mixture gave a yellow solid that was purified by column chromatography using a hexane/ethyl acetate mixture (1:1) as eluent to obtain a white solid. Rf = 0.54. Yield: 77%. Anal. Found: C, 9.24; H, 70.88; N, 5.64%. Calc. for $C_{27}H_{23}N_3O_2S$: C, 9.26; H, 71.50; N, 5.11%. ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 8.62 (d, ^3J = 5 Hz, 1H, H_6), 7.96 (d, ^3J = 7.4 Hz, 1H, H_3), 7.84 (t, ^3J = 7.4 Hz, 1H, H_4), 7.43 (dd, ^3J = 7.4 Hz, ^3J = 5 Hz, 1H, H_5), 7.39- 7.09 (m, 14H, 10Ph + 4 Harom.-Ts-), 5.36 (d, ^3J = 4.8 Hz, 1H, $H_{4'}$ + $H_{5'}$), 5.17 (d, ^3J = 4.8 Hz, 1H, $H_{5'}$ + $H_{4'}$), 2.39 (s, 3H, CH_3). ^{13}C NMR (100.5 MHz, $CDCl_3$, RT): δ 158.5 (s, C_2), 148.6 (s, C_6), 136.5 (s, C_4), 129.1 (s, Ph), 128.9 (s, Ph), 128.3 (s, Ph), 128.1 (s,

Ph), 127.9 (s, Ph), 126.7 (s, Ph), 126.4 (s, Ph), 125.3 (s, C_5), 124.9 (s, C_3), 78.6 (s, $C_{4'}$ or $C_{5'}$), 72.1 (s, $C_{5'}$ or $C_{4'}$), 21.9 (s, CH_3).

10: Similar to the synthesis of **9** but using trifluoromethanesulfonic anhydride as the electrophile. Purification was done by column chromatography using ethyl acetate as eluent. Rf = 0.89. Anal. Found: C, 58.52; H, 3.39; N, 9.49%. Calc. for $C_{21}H_{16}N_3F_3O_2S$: C, 58.44; H, 3.71; N, 9.73%. ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 8.71 (ddd, ^3J = 4.8 Hz, ^4J = 1.7 Hz, ^5J = 0.8 Hz, 1H, H_6), 8.01 (d, ^3J = 7.7 Hz, 1H, H_3), 7.85 (td, ^3J = 7.7 Hz, ^4J = 1.7 Hz, 1H, H_4), 7.48- 7.31 (m, 11H, H_5+ 10Ph), 5.45 (d, ^3J = 3.8 Hz, 1H, $H_{4'}$ or $H_{5'}$), 5.37 (d, ^3J = 3.8 Hz, 1H, $H_{5'}$ or $H_{4'}$). ^{13}C NMR (100.5 MHz, $CDCl_3$, RT): 156.0 (s, C_2), 148.8 (s, C_6), 147.9 (s, $C_{2'}$), 139.9 (s, Ph), 139.4 (s, Ph), 136.7 (s, C_4), 129.3 (s, Ph), 129.3 (s, Ph), 128.9 (s, Ph), 128.6 (s, Ph), 126.2 (s, Ph), 126.2 (s, Ph), 125.8 (s, C_5), 124.5 (s, C_3), 78.9 (s, $C_{5'}$ or $C_{4'}$), 72.8 (s, $C_{4'}$ or $C_{5'}$).

5.2.4.3. Synthesis of [PdClMe(N-N')] (5a-10a)

The ligands (**5-10**) were added to a solution of [PdClMe(cod)] in toluene. The solution was stirred at room temperature for 1 hour yielding a yellow precipitate. After the solvent had evaporated, the compounds were washed with diethylether and filtered off.

[PdClMe(5)] (5a)

Yield: 61%. ^{1}H NMR (400 MHz, $(CD_3)_2CO$, RT): 8.55 (d, ^3J = 7.7 Hz, 1H, H_5), 8.46 (s, 1H, NH), 8.32 (t, ^3J = 7.7 Hz, 1H, H_4), 8.12 (d, ^3J = 7.7 Hz, 1H, H_3), 7.26-6.85 (m, 10H, Ph), 5.72 (d, ^3J = 11.2 Hz, 1H, $H_{5'}$), 5.53 (d, ^3J = 11.2 Hz, 1H, $H_{4'}$), 0.72 (s, 3H, Pd-CH_3).

[PdClMe(6)] (6a)

Yield: 81%. Anal. Found: C, 55.59; H, 4.67; N, 9.50%. Calc. for $C_{21}H_{20}N_3ClPd$: C, 55.28; H, 4.42; N, 9.21%. ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 8.82 (d, ^3J = 4.7 Hz, 1H, H_6), 8.60 (s, 1H, NH), 8.41 (d, ^3J = 7.8 Hz, 1H, H_3), 7.75 (td, ^3J = 7.8 Hz, ^4J = 1.9Hz, 1H, H_4), 7.41 (dd, ^3J = 7.8, ^3J = 4.7 Hz, 1H, H_5), 7.28-7.16 (m, 10H, Ph), 4.90 (d, ^3J = 6.8 Hz, 1H, $H_{4'}$), 4.83 (d, ^3J = 6.8 Hz, 1H, $H_{5'}$), 0.34 (s, 1H, Pd-CH_3). ^{13}C NMR (100.5 MHz, $CDCl_3$, RT): δ 149 (s, C_6), 138.6 (s, C_4), 129.2 (s, Ph), 129 (s, Ph), 128.1 (s, Ph), 127.9 (s, Ph), 126.6 (s, Ph), 126.2 (s, Ph), 128.4 (s, C_5), 124.3 (s, C_3), 76.6 (s, $C_{4'}$), 70.3 (s, $C_{5'}$), -8.6 (s, Pd-CH_3).

[PdClMe(7)] (7a)

Yield: 60%. Anal. Found: C, 60.50; H, 4.73; N, 7.48%. Calc. for $C_{28}H_{26}N_3ClPd$: C, 61.50; H, 4.80; N, 7.70%. ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 9.26 (d, ^3J = 5 Hz, 1H, H_6), 7.87 (t, ^3J = 7.8 Hz, 1H, H_4), 7.76 (d, ^3J = 7.8 Hz, 1H, H_3), 7.63 (dd, ^3J = 7.8 Hz, ^3J = 5 Hz, 1H, H_5), 5.15 (d, ^3J = 6.4 Hz, 1H, $H_{4'}$), 5.02 (d, ^2J = 17.2 Hz, 1H, CH_2), 4.64 (d, ^3J = 6.4 Hz, 1H, $H_{5'}$), 4.42 (d, ^2J = 17.2 Hz, 1H, CH_2), 0.52 (s, 3H, Pd-CH_3). ^{13}C NMR (100.5 MHz, $CDCl_3$, RT): 150.8 (s, C_6), 138.3 (s, C_4), 129.7, 129.4, 129.1, 128.4 (s, C_5), 127.2, 126.3, 126, 123.5 (s, C_3), 76.8 (s, $C_{5'}$), 74.3 (s, $C_{4'}$), 50.4 (s, CH_2), -3.4 (s, Pd-CH_3).

[PdClMe(8)] (8a)

Yield: 62%. Anal. Found: C, 56.30; H, 5.11; N, 8.67%. Calc. for $C_{22}H_{22}N_3ClPd$: C, 56.18; H, 4.71; N, 8.93%. ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 9.28 (d, ^3J = 4.8 Hz, 1H, H_6), 8.03 (m, 2H, H_3 + H_4), 7.67 (q, ^3J = 4.8 Hz, 1H, H_5), 7.46- 7.25 (m, 10H, Harom.), 5.04 (d, ^3J = 7 Hz, 1H, $H_{4'}$), 4.58 (d, ^3J = 7 Hz, 1H, $H_{5'}$), 3.26 (s, 3H, NCH_3), 0.48 (s, 3H, Pd-CH_3). ^{13}C NMR (100.5 MHz,

$CDCl_3$, RT): δ 150.8 (s, C_6), 138.1 (s, C_4), 129.7 (s, Ph), 129.3 (s, C_5), 129.0 (s, Ph), 128.1 (s, Ph), 126.8 (s, Ph), 126.2 (s, Ph), 123.5 (s, C_3), 79.5 (s, $C_{4'}$ or $C_{5'}$), 73.9 (s, $C_{5'}$ or $C_{4'}$), 35.5 (s, CH_3), -7.1 (s, Pd-CH_3).

[PdClMe(9)] (9a)

Yield: 75%. Anal. Found: C, 55.17; H, 4.32; N, 6.64%. Calc. for $C_{28}H_{26}N_3ClO_2PdS$: C, 55.04; H, 4.26; N, 6.88%. ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 9.24 (d, ^3J = 4 Hz, 1H, H_6), 8.72 (d, ^3J = 8 Hz, 1H, H_3), 8.09 (d, ^3J = 8 Hz, ^4J = 1.6 Hz 1H, H_4), 7.80 (m, 1H, H_5), 7.49- 6.91 (m, 14H, Harom.), 5.31 (d, ^3J = 5.6 Hz, 1H, $H_{4'}$), 5.19 (d, ^3J = 5.6 Hz, 1H, $H_{5'}$), 2.44 (s, 3H, CH_3-Ts-), 0.55 (s, 3H, Pd-CH_3). ^{13}C NMR (100.5 MHz, $CDCl_3$, RT): δ 150.4 (s, C_6), 138.3 (s, C_4), 130.6 - 125.5 (C_3 + C_5+ 8 Ph), 74.7 (s, $C_{4'}$ or $C_{5'}$), 73.7 (s, $C_{5'}$or $C_{4'}$), 22.1 (s, CH_3-Ts-), -4.9 (s, Pd-CH_3).

[PdClMe(10)] (10a)

Yield: 61%. Anal. Found: C, 44.80; H, 3.72; N, 7.50. Calc. for $C_{22}H_{19}N_3ClF_3O_2PdS$: C, 44.95; H, 3.26; N, 7.15. ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 9.29 (d, ^3J = 4.7 Hz, 1H, H_6), 8.22 (d, ^3J = 7.7 Hz, 1H, H_3), 8.10 (td, ^3J = 7.7 Hz, ^4J = 1.7 Hz, 1H, H_4), 7.84 (dd, ^3J = 7.7 Hz, ^3J = 4.7 Hz, 1H, H_5), 7.47 - 7.35 (m, 10H, Ph), 5.55 (d, ^3J = 1.8 Hz, 1H, $H_{4'}$), 5.43 (d, ^3J = 1.8 Hz, 1H, $H_{5'}$), 0.75 (s, 3H, Pd-CH_3). ^{13}C NMR (100.5 MHz, $CDCl_3$, RT): δ 150.5 (s, C_6), 138.4 (s, C_4), 130.1 (s, C_5), 130.0 (s, Ph), 129.6 (s, Ph), 129.5 (s, C_3), 125.8 (s, Ph), 125.4 (s, Ph), 75.8 (s, $C_{4'}$ or $C_{5'}$), 75.5 (s, $C_{5'}$ or $C_{4'}$), -3.7 (s, Pd-CH_3).

5.2.4.4. Synthesis of [PdMe(NCMe)(N-N′)][BAr′$_4$] (5b-10b)

To a solution of [PdClMe(N-N′)] in CH_2Cl_2, the stoichiometric amount of NaBAr′$_4$ (Ar′= 3,5-$(CF_3)_2C_6H_3$) was added together with 0.5 mL

of MeCN. The light yellow solution formed was stirred for about an hour, filtrated through Kieselghur and evaporated to dryness. The light-yellow compounds were crystallised from CH_2Cl_2/hexane.

[PdMe(NCMe)(5)][BAr'$_4$] (5b)

Yield: 61%. ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 9.05 (s, 1H, NH), 7.91 (m, 2H, H_4 + H_5), 7.79 (s, ^3J = 7.6 Hz, 1H, H_3), 7.69 (s, 8H, H_b), 7.51 (s, 4H, H_d), 7.13- 6.79 (m, 10H, Ph), 5.70 (d, ^3J = 11.2 Hz, 1H, $H_{5'}$), 5.50 (d, ^3J = 11.2 Hz, 1H, $H_{4'}$), 2.33 (s, 3H, Pd-NCCH_3), 0.90 (s, 3H, Pd-CH_3).

[PdMe(NCMe)(6)][BAr'$_4$] (6b)

Yield: 78%. Anal. Found: C, 50.02; H, 2.60; N, 4.04%. Calc. for $C_{55}H_{35}N_4BF_{24}Pd$: C, 49.85; H, 2.66; N, 4.23%. ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 8.34 (d, ^3J = 4.8 Hz, 1H, H_6), 7.84 (t, ^3J =8 Hz, 1H, H_4), 7.7 (s, 8H, C_b), 7.64 (d, ^3J = 8 Hz, 1H, H_3), 7.45 (s, 4H, C_d), 7.43-7.2 (m, 11H, H_5 + 10Ph), 6.31 (s, 1H, NH), 5.05 (d, ^3J = 7 Hz, 1H, $H_{4'}$), 4.96 (d, ^3J = 7 Hz, 1H, $H_{5'}$), 2.30 (s, 3H, Pd-NCCH_3), 0.56 (s, 3H, Pd-CH_3). ^{13}C NMR (100.5 MHz, $CDCl_3$, RT): δ 161.6 (q, $^1J_{C\text{-}B}$ = 197.2 Hz, 4C, C_a), 149.2 (s, C_6), 139.9 (s, C_4), 134.8 (s, C_b), 129.8 (s, Ph), 129.7 (s, Ph), 129.5 (s, Ph), 129.4 (s, Ph), 129.2 (m, C_e), 128.9 (s, C_5), 126.1 (s, Ph), 123.3 (s, C_3), 117.6 (s, C_d), 76.6 (s, $C_{4'}$), 70.7 (s, $C_{5'}$), 3.4 (s, Pd-NCCH_3), -3.1 (s, Pd-CH_3). MS FAB(*m/z*): 703.2 [M – Me, -NCMe, + **6**]$^{2+}$, 404.1 [M – Me, -NCMe]$^+$, 298.1 [**6**]$^+$.

[PdMe(NCMe)(7)][BAr'$_4$] (7b)

Yield: 81%. Anal. Found: C, 51.95; H, 3.20; N, 3.83%. Calc. for $C_{62}H_{41}N_4BF_{24}Pd$: C, 52.62; H, 2.92; N, 3.96%. ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 8.38 (d, ^3J = 4Hz, 1H, H_6), 7.84 (m, 2H, H_4 + H_5), 7.70 (s, 8H, H_b), 7.51

(s, 4H, H_d), 7.45-7.02 (m, 16H, H_3 + 15Ph), 5.05 (d, ^3J = 5.6 Hz, 1H, $H_{4'}$), 5.02 (d, ^3J = 17.2 Hz, 1H, CH_2), 4.72 (d, ^3J = 5.6 Hz, 1H, $H_{5'}$), 4.46 (d, ^3J = 17.2 Hz, 1H, CH_2), 2.28 (s, 3H, Pd-NCCH_3), 0.54 (s, 3H, Pd-CH_3). ^{13}C NMR (100.5 MHz, $CDCl_3$, RT): δ 161.7 (q, $^1J_{C\text{-}B}$ = 197.2 Hz, C_a), 149.6 (s, C_6), 139.9 (s, C_4), 134.8 (s, C_b), 130.0 (s, Ph), 129.6 (s, Ph), 129.5 (s, Ph), 129.0 (s, C_5), 128.8 (m, C_e), 127.0 (s, Ph), 126.1 (s, Ph), 125.6 (Ph) 124.9 (s, C_3), 117.6 (s, C_d), 76.8 (s, $C_{4'}$ or $C_{5'}$), 73.6 (s, $C_{5'}$ or $C_{4'}$), 50.1 (s, CH_2), 3.4 (s, Pd-NCCH_3), -2.2 (s, Pd-CH_3). MS FAB(*m/z*): 883.3 [M – Me, -NCMe, + **7**]$^{2+}$, 494.1 [M – Me, -NCMe]$^+$, 390.2 [**7**]$^+$.

[PdMe(NCMe)(8)][BAr′$_4$] (8b)

Yield: 82%. Anal. Found: C, 49.35; H, 3.03; N, 3.99%. Calc. for $C_{56}H_{37}N_4BF_{24}Pd$: C, 50.23; H, 2.78; N, 4.18%. ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 8.38 (d, ^3J = 4 Hz, 1H, H_6), 8.03 (d, ^3J = 8 Hz, 1H, H_3), 7.86 (t, ^3J = 8 Hz, 1H, H_4), 7.69 (s, 8H, H_b), 7.5 (s, 4H, H_d), 7.46- 7.19 (m, 11H, H_5 + 10Ph), 4.92 (d, ^3J = 7.2 Hz, 1H, $H_{5'}$), 4.64 (d, ^3J = 7.2 Hz, 1H, $H_{4'}$), 3.25 (s, 3H, NCH_3), 2.30 (s, 3H, Pd-NCCH_3), 0.48 (s, 3H, Pd-CH_3). ^{13}C NMR (100.5 MHz, $CDCl_3$, RT): δ 161.6 (q, $^1J_{C\text{-}B}$ = 197.2 Hz, C_a), 149.6 (s, C_6), 139.7 (s, C_4), 134.8 (s, C_b), 130.0 (s, Ph), 129.8 (s, Ph), 129.4 (s, Ph), 129.2 (m, C_e), 128.9 (s, Ph), 128.7 (s, C_5), 126.6 (s, Ph), 125.9 (s, Ph), 124.7 (s, C_3), 117.6 (s, C_d), 79.3 (s, $C_{4'}$), 73.5 (s, $C_{5'}$), 35.1 (s, CH_3-N), 3.5 (s, 1C, Pd-NCCH_3), -2.5 (s, 1C, Pd-CH_3). MS FAB(*m/z*): 731.2 [M – Me, -NCMe, + **8**]$^{2+}$, 418.1 [M – Me, -NCMe]$^+$, 314.2 [**8**]$^+$.

[PdMe(NCMe)(9)][BAr′$_4$] (9b)

Yield: 83%. Anal. Found: C, 50.21; H, 2.68; N, 3.66. Calc. for $C_{62}H_{41}N_4BClF_{24}O_2PdS$: C, 50.34; H, 2.79; N, 3.79. Ratio M:m = 3:1. ^{1}H NMR (400 MHz, $CDCl_3$, RT): Major: δ 8.62 (d, ^3J = 8 Hz, 1H, H_3), 8.35 (dd, ^3J = 5

Hz, ^4J = 1.3 Hz, 1H, H_6), 8.05 (td, ^3J = 8 Hz, ^4J = 1.3 Hz, 1H, H_4), 7.71 (s, 8H, H_b), 7.52 (s, 5H, H_5 + 4H_d), 7.50-6.80 (m, 14H, Ph), 5.36 (d, ^3J =3.2 Hz, 1H, $H_{5'}$), 5.06 (d, ^3J =3.2 Hz, 1H, $H_{4'}$), 2.41 (s, 3H, CH_3-Ts-), 2.20 (s, 3H, Pd-NCCH_3), 0.57 (s, 3H, Pd-CH_3). ^{13}C NMR (100.5 MHz, $CDCl_3$, RT): δ 161.7 (q, $^1J_{C-B}$= 198.1 Hz, C_a), 149.3 (s, C_6), 140.1 (s, C_4), 134.8 (s, C_b), 130.8- 123.2 (C_3 + C_4 + Ph), 117.6 (s, C_d), 74.3 (s, $C_{5'}$), 74.1 (s, $C_{4'}$), 22.0 (s, CH_3), 3.2 (s, Pd-NCCH_3), -0.03 (s, Pd-CH_3). Minor: δ 8.63 (d, ^3J = 8.2 Hz, 1H, H_3), 8.50 (d, ^3J = 4.4 Hz, 1H, H_3), 8.17 (td, ^3J = 8.2 Hz, ^4J = 1.6 Hz, 1H, H_4), 7.71 (s, 9H, H_5 + 8H_b), 7.52 (s, 4H, H_d), 7.50-6.80 (m, 14H, Ph), 5.24 (d, ^3J =4.8 Hz, 1H, $H_{5'}$), 5.08 (d, ^3J =4.8 Hz, 1H, $H_{4'}$), 2.45 (s, 3H, CH_3-Ts-), 1.61 (s, 3H, Pd-NCCH_3), 0.97 (s, 3H, Pd-CH_3). ^{13}C NMR (100.5 MHz, $CDCl_3$, RT): δ 161.7 (q, $^1J_{C-B}$= 198.1 Hz, C_a), 147.2 (s, C_6), 137.8 (s, C_4), 134.8 (s, 8C, C_b), 130.8- 123.2 (C_3 + C_4 + Ph), 117.6 (s, 4C, C_d), 76.4 (s, $C_{4'}$), 74.1 (s, $C_{5'}$), 22.0 (s, CH_3), 5.67 (s, Pd-CH_3), 2.44 (s, Pd-NCCH_3).

[PdMe(NCMe)(10)][BAr'$_4$] (10b)

Yield: 68%.Anal. Found: C, 46.36, H, 2.60, N, 3.10%. Calc. for $C_{56}H_{34}N_4BF_{27}O_2PdS$: C, 46.16; H, 2.35; N, 3.84%. ^{1}H NMR (400 MHz, $CDCl_3$, RT): Ratio M:m = 2:1. Major: δ 8.38 (d, ^3J = 5.2 Hz, 1H, H_6), 8.28 (d, ^3J = 7.9 Hz, 1H, H_3), 8.04 (td, ^3J = 7.9 Hz, ^4J = 1.6 Hz, 1H, H_4), 7.70 (s, 8H, H_b), 7.51 (s, 4H, H_d), 7.48-7.14 (m, 11H, H_5 + 10Ph), 5.55 (d, ^3J = 2.2 Hz, 1H, $H_{5'}$), 5.28 (d, ^3J = 2.2 Hz, 1H, $H_{4'}$), 2.26 (s, 3H, Pd-NCCH_3), 0.74 (s, 3H, Pd-CH_3). ^{13}C NMR (100.5 MHz, $CDCl_3$, RT): δ 161.7 (q, $^1J_{C-B}$= 198.1 Hz, C_a), 149.6 (s, C_6), 140.1 (s, C_4), 134.8 (s, C_b), 130.7 – 123.2 (C_5 + C_3 + C_e + Ph), 117.6 (s, C_d), 77.4 (s, $C_{4'}$ or $C_{5'}$), 75.5 (s, $C_{5'}$ or $C_{4'}$), 3.3 (s, Pd-CH_3), 0.9 (s, Pd-NCCH_3). Minor: δ 8.52 (d, ^3J = 5.8 Hz, 1H, H_6), 8.29 (m, 1H, H_3), 8.18 (td, ^3J = 7.9 Hz, ^4J = 1.3 Hz, 1H, H_4), 7.74 (dd, ^3J = 7.9 Hz, ^3J = 5.8 Hz, 1H, H_5), 7.70 (s, 8H, H_b), 7.51 (s, 4H, H_d),

7.48-7.14 (m, 10H, Ph), 5.53 (d, ^3J = 3.4 Hz, 1H, $H_{5'}$), 5.32 (d, ^3J = 3.4 Hz, 1H, $H_{4'}$), 1.73 (s, 3H, Pd-NCCH$_3$), 1.07 (s, 3H, Pd-CH$_3$). ^{13}C NMR (100.5 MHz, $CDCl_3$, RT): 161.7 (q, $^1J_{C\text{-}B}$= 198.1 Hz, C_a), 150.4 (s, C_6), 140.4 (s, C_4), 134.8 (s, C_b), 130.7 – 123.2 (C_5 + C_3 + C_e + Ph), 117.6 (s, C_d), 75.7 (s, $C_{4'}$ or $C_{5'}$), 75.2 (s, $C_{4'}$ or $C_{5'}$), 6.8 (s, Pd-CH$_3$), 2.6 (s, Pd-NCCH$_3$).

5.2.4.5. Synthesis of [Rh(cod)(N-N')][BF$_4$]

When the pyridine-imidazoline ligands **1**-**4** (0.12 mmol) were added to a solution of [Rh(cod)$_2$][BF$_4$] (0.12 mmol) in CH_2Cl_2 (2 mL) there was an instantaneous color change. After reacting for 5 minutes, diethylether was added to precipitate the complexes **1c**-**4c**.

[Rh(cod)(1)][BF$_4$] (1c)

Yield: 69%. Anal. Found: C, 56.14; H, 4.96; N, 6.70%. Calc. for $C_{28}H_{29}N_3BF_4Rh$: C, 56.29; H, 4.89; N, 7.03%. ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 8.57 (d, ^{3}J = 7.8 Hz, 1H, H_3), 8.39 (s, 1H, NH), 8.22 (dd, ^{3}J = 7.8 Hz, ^{3}J = 6.9 Hz, 1H, H_4), 7.78 (d, ^{3}J = 5.6 Hz, 1H, H_6), 7.67 (dd, ^{3}J = 6.9 Hz, ^{3}J = 5.6 1H, H_5), 7.08-6.83 (m, 10H, Ph), 5.74 (d, ^{3}J = 11.7 Hz, 1H, $H_{4'}$ or $H_{5'}$), 5.25 (d, ^{3}J = 11.7 Hz, 1H, $H_{5'}$ or $H_{4'}$), 4.44 (m, 1H, CH= cod), 4.17 (m, 2H, CH= cod), 3.51 (m, 1H, CH= cod), 2.51 – 2.37 (m, 4H, CH_2-cod), 1.90 – 1.68 (m, 4H, CH_2-cod).

[Rh(cod)(2)][BF$_4$] (2c)

Yield: 69%. Anal. Found: C, 61.03; H, 5.24; N, 5.56%. Calc. for $C_{35}H_{35}N_3BF_4Rh$: C, 61.15; H, 5.13; N, 6.11%. ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 8.37 (d, ^3J = 8 Hz, 1H, H_3), 8.27(t, ^3J = 8 Hz, 1H, H_4), 7.91 (d, ^3J = 5.5 Hz, 1H, H_6), 7.79 (dd, ^3J = 8 Hz, ^3J = 5.5 Hz, 1H, H_5), 5.47 (d, ^3J = 12 Hz, 1H, $H_{4'}$ or

$H_{5'}$), 5.32 (d, ^3J = 17.2 Hz, 1H, CH_2), 5.2 (d, ^3J = 12 Hz, 1H, $H_{5'}$ or $H_{4'}$), 4.55 (d, ^3J = 17.2 Hz, 1H, CH_2), 4.41 (m, 1H, CH= cod), 4.31 (m, 1H, CH= cod), 4.22 (m, 1H, CH= cod), 3.56 (m, 1H, CH= cod), 2.5 (m, 2H, CH_2-cod), 2.3 (m, 2H, CH_2-cod), 1.97 (m, 2H, CH_2-cod), 1.8 (m, 2H, CH_2-cod).

[Rh(cod)(3)][BF_4] (3c)

Yield: 83%. Anal. Found: C, 55.75; H, 3.78; N, 5.58%. Calc. for $C_{35}H_{35}N_3BF_4SO_2$: C, 55.9; H, 3.19; N, 5.59%. ^{1}H NMR (300 MHz, $CDCl_3$, RT): δ 8.56 (d, ^3J = 8.1 Hz, 1H, H_3), 8.34 (m, 1H, H_4), 8.04 (m, 2H, H_5 + H_6), 7.76 (d, ^2J = 8.3 Hz, 2H, Harom.-Ts), 7.45 (d, ^2J = 8.3 Hz, 2H, Harom.-Ts), 7.06-6.67 (m, 10H, Ph), 5.96 (d, ^3J = 9.5 Hz, 1H, $H_{4'}$ or $H_{5'}$), 5.37 (d, ^3J = 9.5 Hz, 1H, $H_{5'}$ or $H_{4'}$), 4.34 (m, 4H, CH= cod), 2.3 (m, 4H, CH_2-cod), 1.81 (m, 4H, CH_2-cod).

[Rh(cod)(4)][BF_4] (4c)

Yield: 73%. Calc. for $C_{29}H_{28}N_3BF_7SO_2$: C, 47.77; H, 3.87; N, 5.76 %. ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 8.30 (m, 2H, H_6+H_3), 8.14 (m, 1H, H_4 or H_5), 8.10 (m, 1H, H_5 or H_4), 7.15 (m, 6H, Ph), 7.00 (br, 1H, Ph), 6.72 (m, 2H, Ph), 6.52 (br, 1H, Ph), 6.12 (d, ^3J = 8.8 Hz, 1H, $H_{4'}$ or $H_{5'}$), 5.95 (d, ^3J = 8.8 Hz, 1H, $H_{5'}$ or $H_{4'}$), 4.56 (m, 2H, CH= cod), 3.96 (m, 2H, CH= cod), 2.43 (m, 2H, CH_2-cod), 2.31 (m, 2H, CH_2-cod), 1.85 (m, 4H, CH_2-cod).

5.2.4.6. Synthesis of [$Rh(CO)_2$(N-N')][BF_4] (1d-4d)

Bubbling carbon monoxide through solutions of **1c-4c** in CH_2Cl_2 leads to the formation of yellow solutions of the dicarbonyl complexes, which are precipitated by adding Et_2O.

$[Rh(CO)_2(1)][BF_4]$ (1d)

Yield: 98%. ^{1}H NMR (300 MHz, $CDCl_3$, RT): δ 9.08 (s, 1H, NH), 8.84 (d, ^3J = 8.4 Hz, 1H, H_3), 8.65 (d, ^3J = 5.3 Hz, 1H, H_6), 8.43 (dd, ^3J = 8.4 Hz, ^3J = 7.1 Hz, 1H, H_4), 7.82 (dd, ^3J = 7.1 Hz, ^3J = 5.3 Hz, 1H, H_5), 7.13- 6.92 (m, 10H, Ph), 5.83 (d, ^3J = 12.2 Hz, 1H, $H_{4'}$ or $H_{5'}$), 5.67 (d, ^3J = 12.2 Hz, 1H, $H_{5'}$ or $H_{4'}$).

$[Rh(CO)_2(2)][BF_4]$ (2d)

^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 8.72 (d, ^3J = 4.8 Hz, 1H, H_6), 8.44 (d, ^3J = 8 Hz, 1H, H_3), 8.38 (t, ^3J = 8 Hz, 1H, H_4), 7.82 (dd, ^3J = 8 Hz, ^3J = 4.8 Hz, 1H, H_5), 7.37- 6.89 (m, 15 H, Ph), 5.72 (d, ^3J = 12.4 Hz, 1H, $H_{4'}$ or $H_{5'}$), 5.58 (m, 2H, $H_{5'}$ or $H_{4'}$ + CH_2), 4.64 (d, ^3J = 17.2 Hz, 1H, CH_2).

$[Rh(CO)_2(3)][BF_4]$ (3d)

Yield: 87%. ^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 8.86 (m, 2H, H_6 + H_3), 8.49 (t, ^3J = 8 Hz, 1H, H_4), 8.04 (t, ^3J = 6.6 Hz, 1H, H_5), 7.78 (d, ^2J = 8.2 Hz, 2H, Harom.-Ts-), 7.41 (d, ^2J = 8.2 Hz, 2H, Harom.-Ts-), 7.16 – 6.74 (m, 10H, Ph), 5.98 (d, ^3J = 9.6 Hz, 1H, $H_{4'}$ or $H_{5'}$), 5.71 (d, ^3J = 9.6 Hz, 1H, $H_{5'}$ or $H_{4'}$).

$[Rh(CO)_2(4)][BF_4]$ (4d)

^{1}H NMR (400 MHz, $CDCl_3$, RT): δ 8.92 (d, ^3J = 5.3 Hz, 1H, H_6), 8.50 (d, ^3J = 7.8 Hz, 1H, H_3), 8.42 (td, ^3J = 7.8 Hz, ^4J = 1.2 Hz, 1H, H_4), 8.09 (ddd, ^3J = 7.8 Hz, ^3J = 5.3 Hz, ^4J = 1.2 Hz, 1H, H_5), 7.18 (m, 8H, Ph), 6.84 (m, 2H, Ph), 5.58 (m, 2H, $H_{4'}$ and $H_{5'}$).

5.2.4.7. X-Ray Crystallography

Crystal data, data collections and refinement parameters for the structures reported are summarized in Table 8. All the data sets were carried out on a Nonius DIP-1030H system with Mo-Kα radiation (λ = 0.71073 Å) graphite monochromatized. For each crystal a total of 30 frames were collected with an exposure time of 12 min, a rotation of 6° about φ and the detector at a distance of 90 mm from the crystal. Cell refinement, indexing and scaling of the data sets were carried out using Mosflm and Scala.[46]

Table 8. Crystal data and details of structure refinements for compounds **2c**, **3c**, **8a,** and **9a'**

	2c	**3c**	**8a**	**9a'**·CH_2Cl_2
Empirical formula	$C_{35}H_{35}BF_4N_3Rh$	$C_{35}H_{35}BF_4N_3O_2RhS$	$C_{22}H_{22}ClN_3Pd$	$C_{28}H_{25}Cl_4N_3O_2PdS$
Formula weight	687.38	751.44	470.28	715.77
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Triclinic
Space group	$P\,2_1/n$	$P\,2_1/c$	$P\,2_12_12_1$	$P\,\bar{1}$
a/Å	11.068(3)	15.071(3)	11.335(3)	9.481(3)
b/Å	25.636(5)	10.445(5)	13.280(4)	10.207(3)
c/Å	11.581(4)	20.830(4)	13.327(4)	16.059(4)
α/°				101.71(2)
β/°	105.25(2)	99.86(2)		95.82(2)
γ/°				108.38(2)
U/Å^3	3170.3(15)	3230.5(18)	2006.1(10)	1421.0(7)
*D*calcd/g cm^{-3}	1.440	1.545	1.557	1.673
Z	4	4	4	2

Temperature	293(2)	293(2)	150(2)	150(2)
μ (Mo-Kα) mm^{-1}	0.591	0.654	1.069	1.135
F(000)	1408	1536	952	720
θ range, deg	2.27 - 26.02	1.98 - 25.02	2.36 - 27.10	2.24 - 27.10
Reflections collected	9764	10603	4678	9780
Independent reflections	5285	5604	4252	5805
*R*int	0.0498	0.0709	0.0363	0.0707
Reflections $I > 2\sigma(I)$	3202	3483	3681	4239
Parameters	397	453	246	353
Flack parameter	-	-	-0.04(6)	-
Goodness-of-fit (F^2)	1.007	1.038	1.076	1.048
$R1$ ($I > 2\ \sigma\ (I)$) [a]	0.0594	0.0554	0.0539	0.0635
$wR2$ ($I > 2\ \sigma\ (I)$) [a]	0.1579	0.1402	0.1478	0.1914
residuals, e/Å3	0.942, –0.449	0.614, –0.540	1.137,[b] –1.011	1.407,[b] –1.043

[a] $R1 = \Sigma\ ||Fo| - |Fc||\ /\ \Sigma|Fo|$, $wR2 = [\Sigma\ w\ (Fo^2 - Fc^2)^2\ /\ \Sigma w\ (Fo^2)^2]^{1/2}$. [b] residual close to Pd ion.

All the structures were solved by Patterson and Fourier analyses[47] and refined by the full-matrix least-squares method based on F2 with all observed reflections.[47] The final cycles include the contribution of hydrogen atoms at calculated positions. In **3c** the BF_4^- anion was found to be disordered over two positions consequent to a rotation about a B-F bond with refined occupancies to 0.59(2)/0.41(2). A molecule of CH_2Cl_2 was detected in the ΔF map of **9a'**. All the calculations were performed using the WinGX System, Ver 1.64.02.[48]

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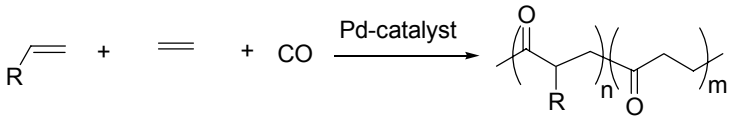
Terpolymerization of 4-*tert*-butylstyrene and ethene with carbon monoxide using N-ligands

Abstract

The activity of palladium(II) precursors [PdMe(NCMe)(N-N')][BAr'$_4$], containing chiral and achiral N-N' ligands, towards the terpolymerization of 4-*tert*-butylstyrene and ethene with carbon monoxide is tested. A clear influence of the bisnitrogen ligand is found both on the activity of the catalytic systems and on the properties of the obtained terpolymers.

6.1. Introduction

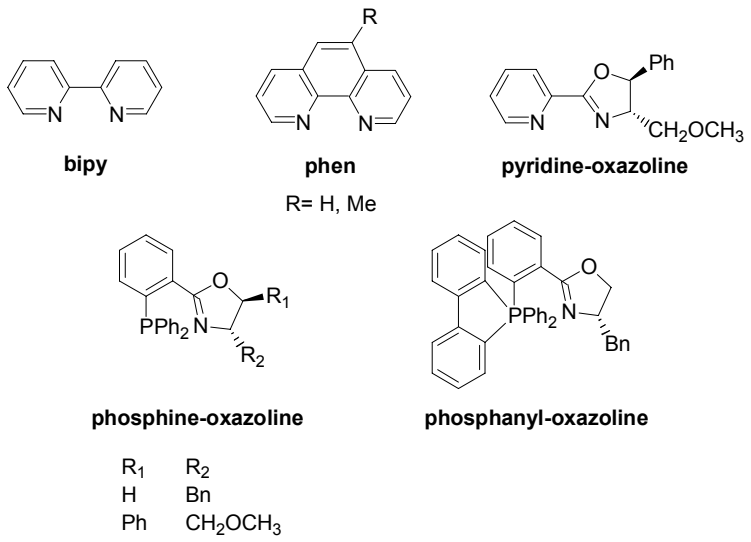
Since the discovery that palladium(II) complexes of diphosphines efficiently catalyze the perfectly alternating terpolymerization of CO, ethene and propene, polyketones have become a commercial reality in the form of *Carilon* for Shell[1] and *Ketonex* for BP[2], with other companies showing a keen interest, as evidenced by the escalating number of patents in this area. These terpolymers are thermoplastics with perfectly alternating microstructure (Scheme 1). Although the alternating copolymerization of various alkenes with CO has been widely studied,[3] the synthesis of terpolymers has received less attention.[4-11] Most reports deal with the terpolymerization of ethene and 1-alkenes with carbon monoxide and, depending on the type of precatalyst, use protic or non-protic organic solvents.[4-6,7b] It has been claimed that catalysts containing diphosphines modified with polar groups can provide clean and effective systems using water as the reaction solvent.[7a,9,11]



Scheme 1. Terpolymerization of ethene and 1-alkenes with carbon monoxide

The chain-propagation of the coordination terpolymerization reaction is based on the alternating insertion of CO into a Pd-alkyl bond and of an alkene, from the different alkenes present in the reaction mixture, into a Pd-acyl bond. Therefore, depending on the relative characteristics of

both the alkenes and the catalysts, the terpolymers obtained may have different properties. It is well known that the ligands coordinated to the metal have a considerable effect on the performance of a homogeneous catalyst. For example, palladium catalysts bearing chelating nitrogen ligands effectively copolymerize styrene and carbon monoxide. For the alternating copolymerization of ethene and CO, diphosphines have been said to be the best option, although nitrogen ligands have also shown to be active.[3] Both N-N and P-N ligands have been successfully used in the terpolymerization of ethene and styrene with carbon monoxide catalyzed by palladium catalysts (Scheme 2).[5,6,12]



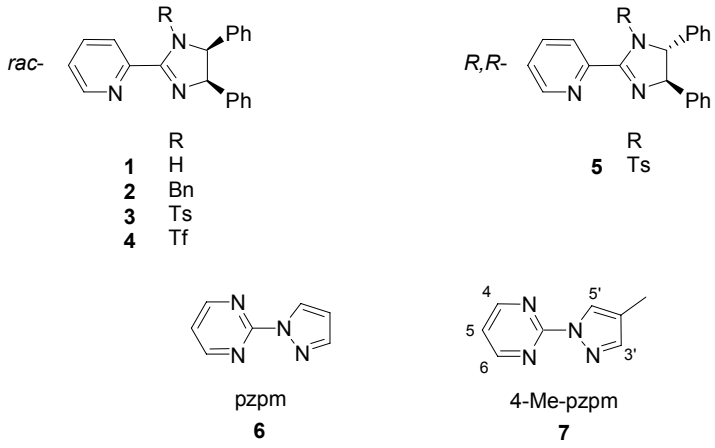
R_1	R_2
H	Bn
Ph	CH_2OCH_3

Scheme 2. Ligands used in the terpolymerization of ethene and styrene with CO

There have been very few investigations into how the ligands affect the terpolymerization reaction. Based on our experience on nitrogen

ligands, we found of interest to make a comparative study of the effects of relatively similar N-N' ligands on the terpolymerization reaction. Therefore, we tested catalysts containing a bisnitrogen ligand that were active in the CO/4-*tert*-butylstyrene (TBS) copolymerization (Scheme 3). We analyzed the activity of methylpalladium precatalysts of the type [PdMe(NCMe)(N-N')][BAr'$_4$] containing chiral pyridine-imidazolines ligands, racemic (*R,S)*-1-substituted-imidazoles (**1**-**4**).[13] A stereochemical modification of ligand **3** leads to ligand **5**, (*R,R*)-1-(trifluoromethanesulfonyl)-4,5-dihydro-4*R*,5*R*-diphenyl-2-(2-pyridyl)-imidazol,[14] which is also tested as ligand. We also studied the effect of substituting the chiral imidazoline by a pyrazol ring. For this we used ligand **6** (2-(1-pyrazolyl)pyrimidine) and ligand **7** (2-(1-(4-methyl)pyrazolyl) pyrimidine), which is electronically different from ligand **6** (Scheme 3).

The unprecedented different behavior against ethylene and styrene, which is observed for palladium precursors containing similar bisnitrogen ligands, is here presented.



Scheme 3. Nitrogen-donating ligands used in this work. Numbering scheme of ligand **7** is included

6.2. Results and discussion

6.2.1. CO/ethene/4-*tert*-butylstyrene terpolymerization using ligands 1-7

All the precatalysts were first tested in standard conditions, 10 atmospheres of pressure (CO/ethene = 1:1) and 24 hours of reaction time. The performance of the palladium precatalyst [PdMe(NCMe)(N-N')][BAr'$_4$] (N-N' = **1-7**) is shown in Table 1.

The bisnitrogen ligand coordinated to palladium clearly affects the productivity of the catalytic systems (Scheme 3). In fact, systems containing ligands **5-7** produce higher amounts of terpolymer by one order of magnitude. The yellowish solution found at the end of the reaction, which is indicative of the palladium(II) species, shows that the catalysts with

ligands **5-7** are more stable.[15] The colorless solution and the greater amounts of palladium metal at the end of the reaction found with precatalysts containing ligands **1-4** show that these precursors are less stable.

Comparing planar ligands **6** and **7** with the bulkier chiral ones **1-5**, it seems easier to accept that the latter interfere more with the coordination/insertion of the alkene, which is the rate-determing step of the reaction. This would explain the higher activity of systems containing ligands **6** and **7**, but not that of **5**. Although all the pyridine-imidazoline ligands may create a similar environment, the X-ray diffraction of the molecule [$PdCl_2$(**5**)] showed that ligand **5** has a unique distortion in the imidazoline plane to favour the intramolecular π-stacking of the tosyl ring with the most distante phenyl ring of the imidazoline.[14] This feature may account for the high reactivity observed with this ligand, which is also observed in the copolymerization of CO/TBS.[14]

Table 1. Terpolymerization of 4-*tert*-butylstyrene (TBS) and ethene (E) with carbon monoxide using [PdMe(NCMe)(N-N')][BAr'$_4$] (N-N' = **1**-**7**)

Entry	Ligand	%E[a]	Productivity (gTP/gPd.h)[b]
1	**1**	76	0.3
2	**2**	80	1.0
3	**3**	97	1.6
4	**4**	82	1.4
5	**5**	60	10.6
6	**6**	45	6.9
7	**7**	50	9.6

Reaction conditions: catalyst: 0.0125 mmol; [TBS]/[catalyst] = 620; p(CO/E) = 10 atm; 5 mL of dichloromethane as solvent; room temperature; 24 hours. [a]Calculated by relative integration of the ^{1}H NMR signals of the terpolymers. [b]Productivity calculated from the isolated terpolymers.

The ethene/TBS molar ratio in the terpolymers was calculated by integrating, in the ^{1}H NMR spectra, the signals corresponding to the methylene groups (Figure 1). The two CH_2 protons of the TBS/CO blocks, which are diastereotopic, appear at 3.1 and 2.5 ppm, respectively. On the other hand, the four methylenic protons of the CO/E units, which are equivalent, also appear at 2.5 ppm. We found that the terpolymers obtained with ligands **1**-**7** have a surprisingly different composition. While pyridine-imidazolines **1**-**4** lead to terpolymers with high ethene contents (entries 1-4), ligands **5**-**7** lead to polymers with similar concentration of both alkenes (entries 5-7).

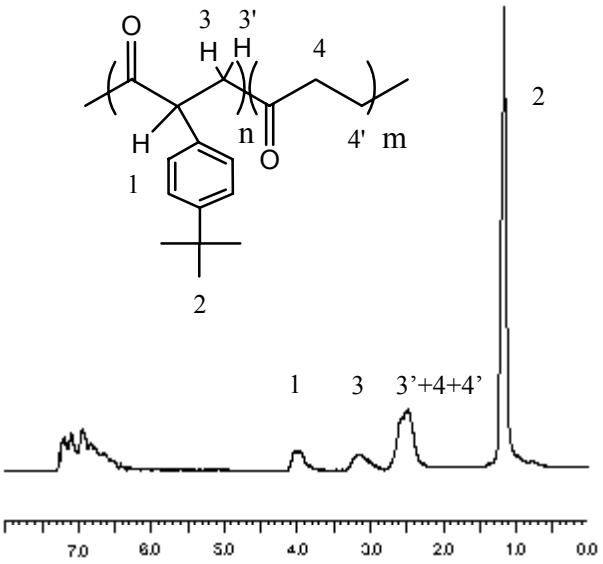


Figure 1. ^{1}H NMR spectrum of an ethene/4-*tert*-butylstyrene/CO terpolymer

6.2.1.1. Dependence of pressure

In order to analyze the different behaviour of precatalysts [PdMe(NCMe)(**1-7**)][BAr'$_4$] towards pressure, we carried out various terpolymerization experiments using a constant amount of 4-*tert*-butylstyrene and palladium precatalyst but varying the amount of carbon monoxide/ethene mixture (CO/ethene = 1:1).

The productivities of catalysts containing ligands **1-4** show, in general, an inverse dependency on the pressure of the catalytic experiment (Table 2). Therefore, an increase in CO/ethene pressure leads to a decrease

in productivity. This matches with the negative order in carbon monoxide reported for the CO/ethene copolymerization catalyzed by an analogous palladium precatalyst bearing phen (1,10-phenanthroline) as chelating ligand.[16] No clear influence of the electronic variations of the pyridine-imidazolines **1**-**4**, in the amount of terpolymer produced, is observed. Ligand **3** shows a disparate activity at 1 atm. of total pressure (entry 9).

Sequential experiments carried out at increasing CO/E pressures show a clear increase in the terpolymer's ethene content. Figure 2 shows the variation in the ethene content towards the ethene/catalyst ratio introduced in the autoclave. The content of ethene in the terpolymer chain is already high (80-90%) when the experiment is performed at 5 atm. of ethene partial pressure ([E]/[TBS] = 1.3) (Table 1). This content is lower (< 25%) when the [E]/[catalyst] ratio is decreased. Therefore precatalysts containing ligands **1**-**4** can provide terpolymers of a desired composition. This preferential enchainment of ethene versus 4-*tert*-butylstyrene during terpolymerization, at similar concentrations of the two alkenes has been reported previously for precatalysts containing N-N and P-N ligands.[5a,b,17]

The molecular weight of the terpolymers was determined by GPC, relative to polystyrene standards, and gave values in a wide range (3500-35000) (Table 2). Although a clear relationship between the basicity of the ligand (depending on the R substituent) and the size of the polymers cannot be ruled out, the most basic ligand (**1**) lead to the largest terpolymers.

Table 2. Terpolymerization of 4-*tert*-butylstyrene (TBS) and ethene (E) with carbon monoxide using [PdMe(NCMe)(N-N')][BAr'$_4$] (N-N' = **1**-**4**)

Entry	Ligand	p(CO/E) (atm)	E/cat.[a]	Prod[b] (gTP/gPd.h)	M_n (M_w/M_n)[c]
1	**1**	1	163.6	2.4	23600 (1.7)
2		2.5	409	3.5	35250 (1.6)
3		5	818.1	1.3	23090 (1.4)
4		7.5	1227.1	0.8	25550 (1.3)
5	**2**	1	163.6	3.1	7990 (1.5)
6		2.5	409	2.9	20350 (1.4)
7		5	818.1	1.8	9680 (1.4)
8		7.5	1227.1	1.5	10580 (1.3)
9	**3**	1	163.6	13.7	12220 (2.2)
10		2.5	409	1.5	8620 (1.3)
11		5	818.1	1.7	8200 (1.4)
12		7.5	1227.1	3.2	12610 (1.7)
13	**4**	1	163.6	2.2	3460 (1.8)
14		2.5	409	2.8	5690 (1.8)
15		5	818.1	1.7	9960 (1.4)[d]
16		7.5	1227.1	1.6	n.d.

Reaction conditions: catalyst 0.0125 mmol; [TBS]/[catalyst]: 620; 5 mL of CH_2Cl_2 as solvent; room temperature; 24 hours. [a] Calculated from the volume of the autoclave. [b] Calculated from the isolated terpolymer.

[c]Determined by GPC measurements in $CHCl_3$ *vs.* polystyrene standards. [d] Determined by GPC in THF. n.d.: not determined.

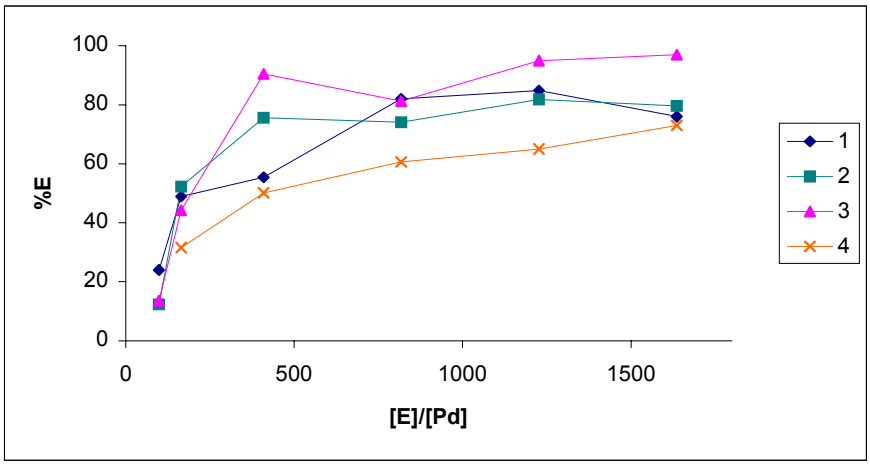


Figure 2. Ethene content in the terpolymer chain as a function of the ethene/catalyst ratio

Table 3 shows selected results of experiments performed with the more active systems [PdMe(NCMe)(N-N')][BAr'$_4$] (N-N' = **5**-**7**). In the case of pyridine-imidazoline **5**, the increase in the ratio of the two alkenes ([E]/[TBS] = 2 and 2.6 in entries 2 and 3, respectively) has no marked effect on the ethene content in the terpolymer, contrary to what is observed using ligands **1**-**4** (Tables 1 and 2). When precursor [PdMe(NCMe)(**6**)][BAr'$_4$] is reacted at 1 atm. of CO/E, ethene is not inserted. Higher pressure of the gas mixture is needed if the content of ethene is to be just slightly higher than 4-*tert*-butylstyrene in the terpolymer chain (entry 6). The situation is similar when the precursor [PdMe(NCMe)(**7**)][BAr'$_4$] is used in the terpolymerization reaction.

Table 3. Co- and terpolymerization experiments using [PdMe(NCMe)(N-N')][BAr'$_4$] (N-N' = **5**-**7**)

Entry	Ligand	p(CO/E) (atm)	E/cat.[a]	TBS/cat.	Prod.	%E	M_n (M_w/M_n)
1	**5**	-[b]	-	620	27.2	-	54700 (1.4)
2		7.5	1227.1	620	6.7	57.5	29090 (1.3)
3		10	1636.1	620	10.6	60.5	n.d.
4	**6**	-[b]	-	310	11.8	-	36350 (1.3)
5		1	98.2	620	21.6	0	n.d.
6		10	1636.1	620	6.9	45.4	20620 (1.8)
7		18	2945	620	5.6	64.3	24110 (1.6)
8	**7**	-[b]	-	310	7.5	-	15400 (1.7)
9		10	1631	620	9.6	50	29800 (1.8)
10		10[c]	3272.2	620	5.9	59.2	25610 (1.8)

Reaction conditions: [catalyst]= 0.0125 mmol; 5 mL of CH_2Cl_2 as solvent; 24 hours; room temperature. [a] Calculated from the volume of the autoclave. [b] pCO = 1 atm; 5 mL of chlorobenzene as solvent. [c] [catalyst]= 0.00625 mmol. n.d. : not determined.

To analyze the reactivity of precursors with ligands **5**-**7** towards both alkenes, we carried out some experiments without ethene pressure (Table 3, entries 1, 4 and 8). The productivity of the catalytic systems depends strongly on the presence of ethene in the reaction mixture. When ligands **5** and **6** were used, productivity decreased considerably if ethene

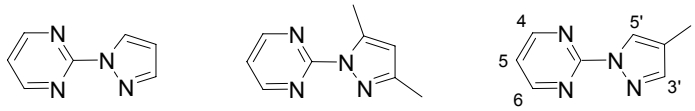
was involved in the reaction (entries 1 *vs*. 2 or 4 *vs*. 6). The presence of ethene is also reflected in the molecular weight, which clearly decreases. The molecular weights of the terpolymers obtained with catalyst precursors [PdMe(NCMe)(N-N')][BAr'$_4$] (N-N' = **5**-**7**) are higher than those obtained with ligands **1**-**4**.

For the reference experiments performed at 10 atm. of total pressure (see Table 1), 2.6 times more ethene than 4-*tert*-butylstyrene was placed in the autoclave (close to 70% ethene), so the reactivity of the Pd-acyl intermediates with 4-*tert*-butylstyrene is higher for complexes with ligands **5-7** than for complexes with ligands **1**-**4**. Although there is an example of similar reactivity in the terpolymerization of 1-hexene/TBS/CO,[10] to the best of our knowledge, this is the first time that such low ethene insertion, a nearly 50:50 ratio, is reported in these conditions with palladium precatalysts containing bisnitrogen ligands.

6.2.2. Synthesis and characterization of [PdMe(NCMe)(7)][BAr'$_4$]

The activity of [PdMe(NCMe)(**6**)][BAr'$_4$] in the copolymerization of CO/TBS was high. When the pyrazol ring was modified with two methyl groups to create a bulkier ligand (pz*pm) (Scheme 4), a clear decrease both in productivity and molecular weight was observed.[18] The reason for this could be steric although the higher basicity of the ligand may also have an effect. To analyze just an electronic effect, ligand **6** was modified by placing a methyl group in position 4' of the pyrazol, resulting in ligand **7** (Scheme 4).[19] The catalyst [PdMe(NCMe)(**7**)][BAr'$_4$] was synthesized by reacting the precursor [PdClMe(**7**)] with NaBAr'$_4$ (Ar' = 3,5-(CF$_3$)$_2$C$_6$H$_3$) to abstract the

chlorine ligand, as previously reported.[18] Analysis of the stereochemistry of the complex was done by NOE experiments and it shows an interaction between the Pd-Me group and the pyrazol ring ($H_{3'}$). Again for pyrazol-containing palladium cationic complexes of formula [PdMe(NCMe)(N-N')][BAr'$_4$], the methyl group is *trans* to the less basic ring.[18]



6 **7**

Scheme 4. Pyrazol-pyrimidine ligands

6.2.3. Analysis of tacticity of the terpolymers

The tacticity of the terpolymers obtained with the catalytic systems containing ligands **1-7** was analyzed by means of ^{13}C NMR. The spectra of the ethene/4-*tert*-butylstyrene/carbon monoxide terpolymers are similar to those of the TBS/CO copolymers, with two additional signals at 36.3 and 35.5 ppm corresponding to the E/CO units. The first signal corresponds to the methylenic carbons of an ethene unit in a E/CO copolymer environment; the second corresponds to an ethene unit followed by a TBS/CO unit. These signals were assigned by comparing spectra of terpolymers with different contents of ethene.

When ligands **1-4** were used in the CO/TBS copolymerization, the polyketones showed different degree of stereoregularity depending on the ligand used.[13] To see whether there is also an effect of the pyridine-

imidazolines on the tacticity of the terpolymers, we analyzed the ^{13}C NMR spectra of the terpolymers in the 46.5 - 43.0 ppm range, the region of the methylenic carbon of 4-*tert*-butylstyrene. Apart from the effect of the tacticity, the different environments in which the TBS/CO unit may appear within the chain, due to the various alkene content, may lead to a greater number of signals in this region.

The terpolymers with a high content on ethene (ca. 90%) show only a major signal at 45.9 ppm, irrespectively of the ligand used (Figure 3). This indicates the high stereoregularity of the polymers and the presence of isolated CO/4-*tert*-butylstyrenic units. The coincidence of this signal with that of the isotactic triad (*ll*) of a CO/TBS copolymer (Figure 3, reference) may indicate the high isotacticity of the terpolymers, as reported previously by other authors.[8,10] However the CO/E environment which surrounds the styrenic unit could make the shift of the signals change with respect to the CO/4-*tert*-butylstyrene copolymers. Therefore analysis of the optical properties of the terpolymers seems necessary to state the tacticity of the terpolymers.

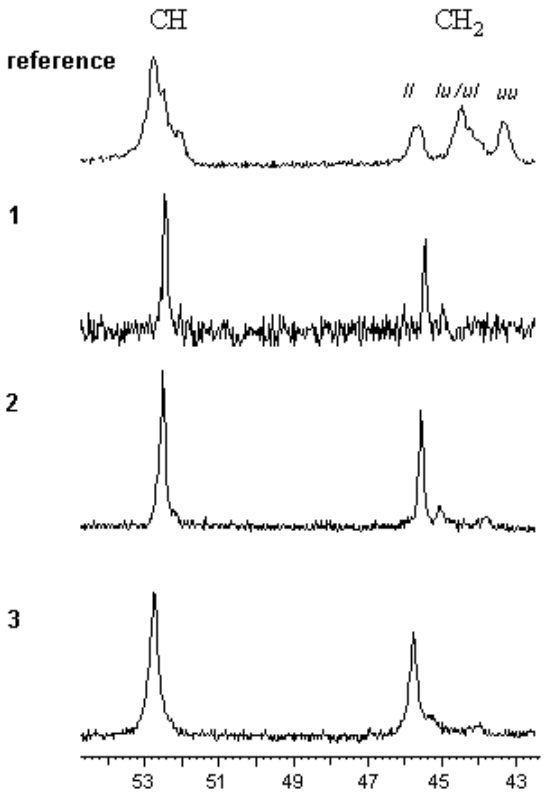


Figure 3. Comparative ^{13}C NMR spectra of terpolymer with ca. 90% ethene content obtained using different pyridine-imidazoline ligands **1-3**

We also analyzed the ^{13}C NMR spectra of terpolymers with different ethene contents obtained with ligands **1-4** (e.g. for ligand **2** in Figure 4). Terpolymers with an ethene content lower than 25% show spectra similar to that of TBS/CO copolymers although in place of the isotactic triad signal (*ll*), three small signals appear (Figure 4a). These three new signals enlarge with increasing the ethene content in the terpolymers (Figure 4b). At higher contents, as stated above, only one of these signals remain (Figure 4c).

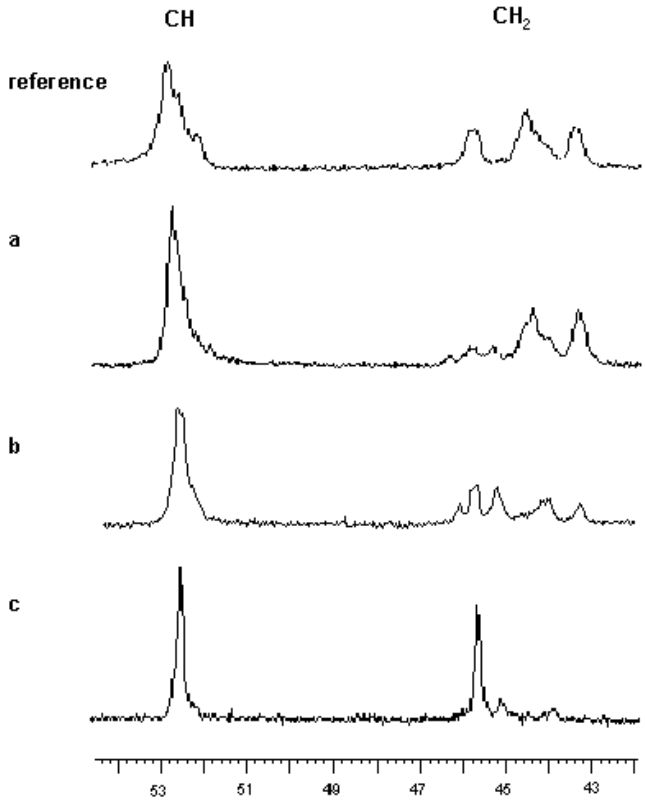


Figure 4. Comparative ^{13}C NMR spectra of an atactic TBS/CO copolymer as reference and E/TBS/CO terpolymers with increasing ethene content (**a**: 12.3%; **b**: 52.3%; **c**: 81.8%, respectively), obtained with catalyst [PdMe(NCMe)(**2**)][BAr'$_4$].

Trying to understand the origin of these new signals, we compare terpolymers, with ca. 50% ethene content, obtained with all the ligands studied in this work (**1**-**7**) (Figure 5). It is worth noting that the appearance of the lowerfield shifted signal clearly varies depending on the ligand used. So, for ligands **1**-**5** this signal shows different intensities, while for ligands **6**

and **7** it is not present. Since the composition of these terpolymers is similar, this signal may be related to the tacticity. If we consider that planar nitrogen ligands lead to syndiotactic terpolymers (as previously stated for CO/styrene copolymers),[3] it is clear that the use of the chiral pyridine-imidazoline ligands **1-5** lead to variations in the degree of stereoregularity of the terpolymers.

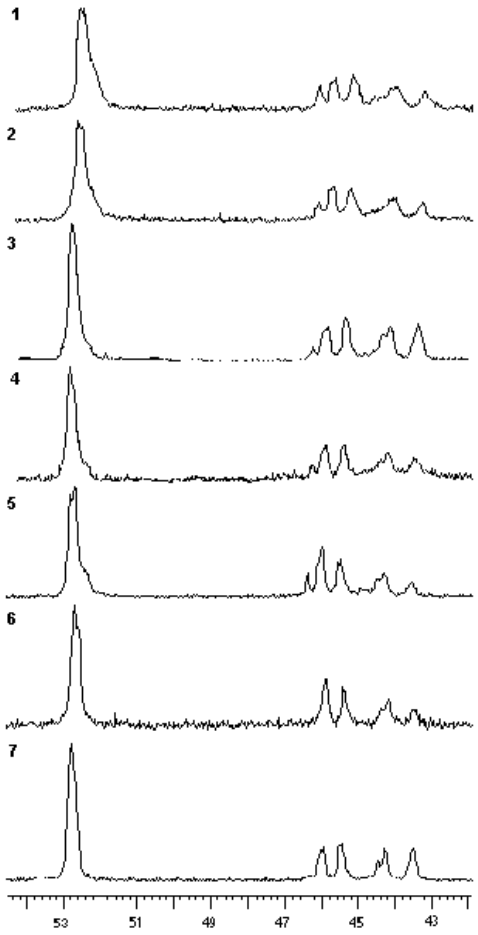


Figure 5. ^{13}C NMR of terpolymers with ca. 50% ethene content obtained with ligands **1-7**

6.3. Conclusions

When palladium catalysts with bisnitrogen ligands are used, the terpolymerization of ethene, 4-*tert*-butylstyrene and CO depends strongly on the ligand used. So, pyridine-imidazolines **1-4** lead to a perfectly controlled composition of the obtained terpolymers, while ligands **5-7** are less versatile. It seems that the steric properties of these ligands, more than the electronic ones, are responsible for the different activity of these systems. The bulkier ligands (**1-4**) may slow the coordination and insertion of styrene in the Pd-acyl bond, leading to lower productivities and to terpolymers with a higher ethene content.

The size of the polymer chain is related to the presence of ethene in the chain, since molecular weights obtained with the same catalysts in CO/TBS copolymerization were higher. This seems to be explained by the more favored β-H elimination when ethene is inserted.

The use of the chiral ligands **1-4** in the terpolymerization reaction leads to the synthesis of very stereoregular materials, when the ethene content is high. This seems to indicate that all the ligands behave equally under these conditions and as there is not *chain-control*, the ligand controls the styrene insertion.

6.4. Experimental

6.4.1. General procedure

All reactions were carried out using standard Schlenk techniques under nitrogen atmosphere at room temperature. Solvents were distilled and deoxygenated prior to use unless otherwise stated. The salt $NaBAr'_4$ (Ar'= 3, 5- $(CF_3)_2$-C_6H_3) was prepared according to reported methods.[20] The ligands **1-6** and the palladium precursors [PdMe(NCMe)(**1-6**)][BAr'_4] were prepared as previously described.[13,14,18,21] Compound [PdMeCl(**7**)] was used as received.[19]

^1H and ^{13}C NMR spectra were recorded on a Varian Mercury VX spectrometer with a ^1H resonance frequency of 400 MHz. Chemical shifts were reported relative to $CDCl_3$ (7.26 ppm for ^1H and 77.23 for ^{13}C). Some assignments in NMR spectra were determined by DEPT and NOE experiments. Elemental analyses were carried out on a Carlo Erba Microanalyser EA 1108. The molecular weight of the terpolymers and molecular weight distributions were determined by gel permeation chromatography (GPC) in $CHCl_3$ on a Waters 515-GPC device using a lineal Waters Ultrastyragel column with a Waters 2410 refractive index detector and polystyrene standards.

6.4.2. Synthesis of [PdMe(NCMe)(7)][BAr'_4]

The cationic complex [PdMe(NCMe)(**7**)][BAr_4'] was obtained by adding a previously prepared solution of the neutral complex [PdCl(Me)(**7**)][19] in CH_2Cl_2, to an equimolar solution of $NaBAr'_4$ in MeCN, as previously reported with ligand **6**.[18] ^1H NMR (400MHz, $CDCl_3$, RT): δ 8.70

(dd, ^3J = 5.2 Hz, ^4J = 2.5 Hz, 1H, H_4 or H_6), 8.33 (s, 1H, $H_{5'}$), 8.29 (dd, ^3J = 5.2 Hz, ^4J= 2.5 Hz, 1H, H_6 or H_4), 7.69 (s, 8H, H_b), 7.67 (s, 1H, $H_{3'}$), 7.51 (s, 4H, H_d), 7.09 (t, ^3J = 5.2 Hz, 1H, H_5), 2.31 (s, 3H, CH_3CN), 2.24 (s, 3H, $(CH_3)_{4'}$), 1.27 (s, 3H, Pd-CH_3).

6.4.3.Terpolymerization of 4-*tert*-butylstyrene/ethene/carbon monoxide

The 4-*tert*-butylstyrene was passed through a small column of Al_2O_3 prior to use. Dichloromethane was distilled over P_2O_5 and under N_2 atmosphere and stored over molecular sieves. Ethene / carbon monoxide (1/1 mixture) was purchased from Air Liquid with a purity grade of 98%.

In a typical procedure the cationic precursor [PdMe(NCMe)(N-N')][BAr'$_4$] (N-N' = **1-7**) (0.0125 mmol) was dissolved in 5 mL of dichloromethane in a previously purged Schlenk. 4-*tert*-butylstyrene (1.4 ml, 7.75 mmol) was then introduced and the reaction mixture was introduced into the 100 mL stainless steel Berghoff autoclave by suction. The autoclave had been previously purged with the CO/E mixture. The reaction mixture was then pressurized at the desired level and left to react at room temperature for 24 hours. At the end of the reaction time the unreacted gases were released. Workup included filtration of the reaction mixture through Kieselghur and precipitation of the polymeric material by adding the reaction solution dropwise into 100 ml of rapidly stirred methanol. The terpolymers were collected by filtration, washed with methanol and dried under vacuum.

6.4.4. Copolymerization of 4-*tert*-butylstyrene/carbon monoxide

The cationic precursor [PdMe(NCMe)(**7**)][BAr′$_4$] (0.0125 mmol) was dissolved in 5 mL of chlorobenzene in a previously flushed Schlenk and the N_2 atmosphere replaced with CO. 4-*tert*-butylstyrene (0.7 mL, 3.875 mmol) was then introduced and the reaction was allowed to take place at room temperature and 1 atm. of CO. After 24 hours the reaction was stopped and a similar workup to that of the terpolymerization experiments was done.

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PALLADIUM COMPLEXES FOR CO/STYRENE COPOLYMERIZATION. STUDY OF THE INFLUENCE OF THE LIGAND

Memoria presentada por

Amaia Bastero Rezola

Tarragona, Octubre 2002

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