Unprecedented Comonomer Dependence of the Stereochemistry Control in Pd-Catalyzed CO/Vinyl Arene Polyketone Synthesis

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Two pyrene-tagged iminopyridines (N–N') were used to synthesize neutral and monocationic, palladium(II) complexes, [Pd(Me)Cl(N–N')] and [Pd(Me)(MeCN)(N–N')][PF$_6$]. The monocationic complexes generated active catalysts in the CO/vinyl arene copolymerization, leading to polyketones with yields and molecular weight strongly dependent on N-N', with the ketimine catalysts one order of magnitude more productive than the aldimine counterpart. The stereochemistry of polyketones synthesized with the aldimine catalyst was found to be dependent on the vinyl comonomer: prevailingly syndiotactic copolymers were obtained for styrene, prevailingly isotactic copolymers were produced for 4-methyl styrene, and atactic macromolecules were formed for 4-tert-butyl styrene. The statistical analysis demonstrated that the control of the stereochemistry switched from enantioselective site control for 4-methyl styrene to a combination of chain-end and enantioselective site control for styrene.

Introduction

Homogeneous catalysis represents a powerful tool for polymerization reactions.[1–3] Indeed, by tailoring the coordination environment on the metal center, it should be possible to develop single-site catalysts that are able to control the key features of the synthesized macromolecules, such as the mode of main chain linkages, the molecular weight and molecular weight distribution, the nature of the end-groups, the comonomer incorporation and sequence along the chain, the linear or branching structure, and the polymer stereochemistry.[4–6] The latter is one of the most fascinating properties of a macromolecule, since it greatly affects the potential applications of a polymeric material and its control is the result of the unique characteristics of single-site catalysts.

Polypropylene is the macromolecule of excellence if the control of the stereochemistry in polymerization reactions is under debate, and a huge number of homogeneous catalysts has been studied with the aim to unravel the nature of the stereochemical control during its synthesis.[7, 8]

During the last few decades, another macromolecule that has received considerable attention in terms of the control of its stereochemistry is represented by the CO/terminal alkene polyketones.[9–11] Unlike polypropylene, polyketones are one of the few examples of polymers with main chain chirality, thus the isotactic polyketones, if synthesized by catalysts with enantiomerically pure ancillary ligands, are optically active macromolecules.

Polyketones are obtained through the direct, alternating copolymerization of carbon monoxide with terminal alkenes, homogeneously catalyzed by palladium(II) complexes (Scheme 1). The nature of the alkene comonomer dictates the choice of the ancillary ligand present in the palladium coordination sphere: the P-donor molecules are the ligands of choice for ali-

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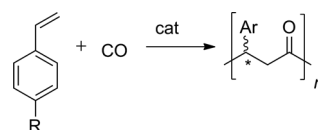
Scheme 1. The CO/vinyl arene copolymerization (R=H, Me, tBu).

phatic alkenes and N-donor molecules more suited for vinyl arenes.[12] The phosphino-phosphite BINAPHOS ligand was found to be able to promote the copolymerization of carbon monoxide with both propene and styrene.[13,14]

Focusing the discussion on aromatic alkenes, the researches published up to now allowed establishing a relationship between the symmetry of the bidentate N-donor ligand in the palladium catalyst and the copolymer stereochemistry. Pd complexes with C_{2v} symmetric ligands, such as 2,2′-bipyridine[15] and 1,10-phenanthroline,[16] afforded syndiotactic polyketones, whereas Pd derivatives with enantiomerically pure C_2 symmetric ligands, such as bi- or bis-oxazolines,[17–19] aza bis-oxazolines,[20] and diketimines[21] led to the formation of isotatic copolymers. C_s ligands have been reported to yield both syndio- and atactic polyketones,[22] whereas all the possible microstructures can be obtained by using C_1 ligands.[23–26] CO/vinyl arene polyketones with isotactic stereoblocks have been synthesized by Pd catalysts with α-diimine ligands.[27–29]

Up to now, the tacticity of the produced polyketones was always dictated by the ligand bonded to the catalytic center and it was not affected by the variation of the substituent in para position on the vinyl arene comonomer. In other words, no effect on polymer stereochemistry was observed on changing the vinyl arene from styrene (S) to its 4-substituted derivatives such as 4-methyl styrene (MS) and 4-tert-butyl styrene (TBS). Only if the 2-substituted styrene was used as a comonomer, the [Pd(phen)(MeCN)$_2$][BF$_4$]$_2$ catalyst yielded an atactic polyketone instead of the expected syndiotactic macromolecule.[30]

Iminopyridines are versatile bidentate ligands that can be easily prepared by condensation of the appropriate pyridine carbonyl compound with the desired amine.[31–33] Post-functionalization can also be performed by using, for example, Stille[34] or Kumada[35] coupling at the pyridine ring. In catalysis, the relevant late transition metal complexes have been used, amongst others, in alkene oligo- and polymerization,[36] and in a few examples for polyketone synthesis. In particular, in situ generated Pd catalysts containing pyridylimines derived by the condensation of 2-pyridinecarboxaldehyde with aliphatic amines led to syndiotactic or isotactic CO/styrene copolymers depending on the aliphatic group on the imino nitrogen atom.[30] The same in situ system was applied to the copolymerization of CO with 4-vinylcyclohexene.[37] The iminopyridyl functionality was also exploited to obtain both dinuclear[38] and dendritic[39] palladium catalysts applied in the CO/vinyl arene copolymerization to yield the corresponding polyketones with different stereochemistry depending on the ligand itself. Moreover, palladium complexes with pyridilimines that have a 2,6-disubstituted aryl ring on the imino nitrogen atom were found to catalyze the bis-alkoxycarbonylation of styrene, leading only to traces of the expected copolymer.[40]

Despite the wide variety of studied iminopyridines, only two reports have described a pyrene group attached to the imino nitrogen atom: one about the one-pot generation of an iridium complex,[41] the other about the generation of a nickel catalyst for ethylene polymerization.[42] In the latter study it was found that the presence of the pyrene arm led to higher mo-
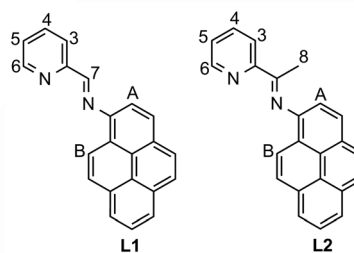

Figure 1. Structure and numbering Scheme of the ligands studied in this work.

lecular weight waxes than other pyridilimines. We report here the synthesis and the coordination chemistry to palladium(II) of two pyrene-tagged iminopyridines (Figure 1), together with their catalytic behavior in the CO/vinyl arene copolymerization, resulting, for the first time, in a comonomer-dependent stereochemistry of the produced polyketones.

Results and Discussion

Synthesis and characterization of ligands and Pd complexes

Pyrene-tagged iminopyridine ligands **L1** and **L2** (N−N′, Figure 1) were prepared by condensation of 1-aminopyrene with either 2-pyridinecarboxaldehyde or 2-acetylpyridine, respectively, according to the modification of a procedure previously reported for ligand **L2**.[42] The NMR characterization was in agreement with literature (see the Supporting Information).

Comparison of the NMR spectroscopic data of **L1** and **L2** highlighted very similar proton and carbon chemical shift values for the signals of the atoms of the pyridine ring, which were unambiguously assigned, and for most of the signals belonging to the pyrene fragment, which overlapped each other ■■ok?■■, with only the resonances of H^A and H^B clearly separated from the rest. The latter protons resonate at lower frequencies moving from **L1** to **L2**, in agreement with the presence of the electron-releasing group on the imino carbon atom, which resulted in an increase in the electron density on the corresponding nitrogen, and, therefore, ligand **L2** should be a stronger Lewis base than ligand **L1**.

Ligands **L1** and **L2** were used to synthesize the corresponding organometallic, neutral complexes [Pd(Me)Cl(N−N′)] (**1a**, **2a**; N−N′ = **L1**, **L2**), following the well-known synthetic procedure based on the substitution reaction of 1,5-cis,cis-cyclooctadiene (cod) on the palladium precursor [Pd(Me)Cl(cod)] by the N−N′ ligand.[16,43] Complexes **1a** and **2a**, obtained as yellow or orange solids in yields ranging from 40 to 90%, were fully characterized both in solid state, by elemental analysis, and in solution, by NMR spectroscopy (see the Supporting Information). In the ^{1}H NMR spectra recorded at room temperature in CD$_2$Cl$_2$ solution, the number of signals and their integration revealed that only one of the two possible isomers was present (Figure 2).

The value of the chemical shift of the Pd-Me group, at 0.36 and 0.08 ppm for **1a** and **2a**, respectively, remarkably lower
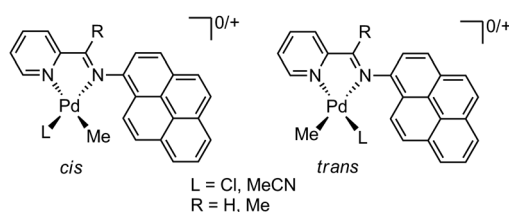
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Figure 2. Possible *cis* and *trans* isomers for the neutral and cationic complexes.

than 1.00 ppm, clearly indicated that in the observed species the Pd-Me group was *cis* to the pyrene fragment.[16,22,29,44–46] For sake of clarity, we identified this species as the *cis* isomer. This assignment was confirmed by the value of the chemical shift of H^6, at higher frequency with respect to the same signal in the free ligand, due to the deshielding effect of the chlorido *cis* to it.[43,47] The geometry was unambiguously defined by the correlation peaks between the singlet of Pd-Me and the peaks of the pyrene protons in the NOESY spectrum (see the Supporting Information).

Moreover, upon coordination, the peaks of H^7 in **1a**, of the methyl on the imino carbon (CH_3^8) in **2a**, and of H^3 for both complexes were shifted at low frequency with respect to the same signals in the free ligand, thus confirming that the free ligands are in *E,trans* conformation.[47]

The neutral complexes were converted into the cationic precatalysts [Pd(Me)(MeCN)(N–N')][PF$_6$] (**1b**, **2b**; N-N'=**L1**, **L2**) through the reaction of halogen abstraction with AgPF$_6$ in the presence of MeCN, according to the published protocol.[16,43] Complexes **1b** and **2b**, obtained as yellow or red solids in yields ranging from 60 to 93%, were fully characterized both in solid state, by elemental analysis, and in solution, by NMR spectroscopy (see the Supporting Information). Unlike what was observed for the neutral derivatives, **1b** and **2b** were a mixture of the two isomers, as evidenced by NMR spectroscopy. The *cis/trans* ratio as well as the prevailing isomer are depending on the nature of N-N': the *trans* isomer is the major species for **1b** (*cis/trans* ratio 1/2), whereas almost an equimolar ratio, with a slight prevalence of the *cis* isomer, was found for **2b** (*cis/trans* ratio 1/0.8). For *trans* isomers, the MeCN bonded to palladium resonated at low frequency (1.21 and 1.07 ppm for **1b** and **2b**, respectively) compared to the frequencies typically observed for this group (2.20–2.60 ppm), confirming that it fell in the shielding cone of the pyrene fragment. In the NOESY spectra of both cationic complexes, in addition to the NOE cross peaks, correlation peaks originated by ■■from?■■ an exchange process were observed, indicating that, at room temperature, the two isomers were in equilibrium at a slow rate on the NMR time scale.

A survey of the literature of analogous palladium complexes with iminopyridine ligands different from **L1** and **L2** pointed out that for all the neutral derivatives (i.e., [Pd(Me)Cl(N–N')]), the prevailing or the only species present was the *cis* isomer,[39,47,48] where-

as for the corresponding cationic complexes (i.e., [Pd(Me)(MeCN)(N–N')][PF$_6$]), a mixture of the two isomers was always formed, in a ratio that depended on N-N'. Reasoning that the prevailing species formed is the result of steric and electronic effects, for the neutral complexes the preference towards the *cis* isomer indicates that the coordination is dictated by electronic parameters: the ligand with the stronger *trans* influence—the methyl group—is coordinated *trans* to the nitrogen atom with the lowest Lewis basicity; whereas the methyl group and the chlorido have a similar steric hindrance. In agreement with this consideration, the loss of stereoselectivity observed going from the neutral to the monocationic complexes may be related to the fact that the chlorido is substituted by acetonitrile, a less hindered molecule, and that, therefore, the steric requirements start to play a role in determining the major species formed, hampering the prediction about its nature. This phenomenon appears to be a more general behavior, which is also valid for analogous palladium complexes with other nonsymmetric nitrogen ligands, such as pyridiylimidazolines,[46] and the nonsymmetric bis(aryl-imino)acenaphthenes.[22,44,49]

Notably, in the NMR spectra of the neutral derivatives and of both isomers of the cationic complexes, the singlet of the Pd-Me fragment moves at low frequency going from complexes with ligand **L1** to those with ligand **L2**, confirming that the presence of the electron-releasing group on the imino carbon atom is reflected in a higher electron density on palladium.

CO/vinyl arene copolymerization reactions

Cationic complexes **1b** and **2b** were tested as precatalysts for the copolymerization of carbon monoxide with styrene (S), 4-methyl styrene (MS), and 4-*tert*-butyl styrene (TBS). The copolymerization reactions were performed in 2,2,2-trifluoroethanol (TFE), under 1 bar of CO, at $T=303$ K, with a slight excess of 1,4-benzoquinone (BQ) with respect to palladium (Table 1). The produced polyketones precipitated during the copolymerization reaction as solids, either white or grey, depending on the catalyst.

Both complexes generated active catalysts for the copolymerization of CO with all three different vinyl arenes. The pro-

Table 1. CO/vinyl arene copolymerization: effect of ancillary ligand, and of vinyl arene.[a] Precatalyst: [Pd(Me)(MeCN)(N–N')][PF$_6$].

Run	N-N'	Vinyl arene	Yield [g]	kg$_{CP}$ g$_{Pd}^{-1}$[b]	Mw [g mol^{-1}]	Mw/Mn	RU[c]	TON[d]
1	**L1**	S	0.86	0.64	31000	2.0	235	2.18
2	**L1**	MS	0.57	0.42	8000	1.5	55	5.61
3	**L1**	TBS	0.39	0.29	8000	1.7	42	3.84
4	**L2**	S	5.10	3.78	256000	2.2	1937	1.57
5	**L2**	MS	7.27	5.38	302000	2.6	2066	1.89
6	**L2**	TBS	6.26	4.64	471000	2.1	2502	1.05

[a] Reaction conditions: $n_{Pd}=1.27\times10^{-5}$ mol, TFE $V=20$ mL, $T=303$ K, $P_{CO}=1$ bar, [BQ]/[Pd]=5, $t=24$ h, vinyl arene $V=10$ mL, [S]/[Pd]=6800, [MS]/[Pd]=6000, [TBS]/[Pd]=4300. [b] kg$_{CP}$ g$_{Pd}^{-1}$=kilograms of copolymer per gram of palladium. [c] RU=number of repetitive units inserted into the polymer chain. [d] TON=moles of copolymer per mole of Pd.

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ductivity was significantly influenced by the ancillary ligand. The catalyst with ligand **L2** was more than one order of magnitude more productive than catalyst with ligand **L1**. This result is in agreement with the data previously reported for the ethylene homopolymerization catalyzed by iron complexes with bis(imino)pyridine ligands, in which ketimine catalysts were found to be more productive than their aldimine analogues.[50] In the copolymerization under investigation, the ligand effect on catalyst productivity appeared to be related to catalyst stability: with precatalyst **1 b**, the formation of inactive palladium black was already observed after 3 h of reaction, whereas for precatalyst **2 b**, no palladium metal was observed for at least 72 h. Because the deactivation pathways imply the dissociation of the N-N' ligand from the palladium coordination sphere,[49] the ligand effect on catalyst stability is in agreement with the NMR data about the ligand coordination capability.

Concerning the effect of the vinyl comonomer, if using precatalyst **1 b**, the productivity decreased going from S to MS to TBS (Table 1, entries 1–3), whereas with precatalyst **2 b**, the lowest productivity was obtained in the CO/styrene copolymerization (Table 1, entry 4 vs. 5, 6). The latter trend is in agreement with most of the catalytic systems described in the literature, for which the introduction of an alkyl group in para position on the vinyl arene comonomer resulted in an enhanced reactivity.[16,51] The opposite trend, analogous to that observed here for **1 b**, was, however, reported for palladium catalysts containing bis(aryl-imino)acenaphthenes, for which productivities in the CO/MS copolymerization were similar or lower compared to those obtained in the CO/S counterpart.[22,49]

The literature catalytic systems with iminopyridines showed remarkably lower productivities than those reported here, that is, from 0.097 to 0.541 $kg_{CP} g_{Pd}^{-1}$ for CO/TBS, even considering that the reactions were performed with [TBS]/[Pd] = 620, that is almost one order of magnitude lower than the ratio applied here.[39]

The effects of both the ligands and the vinyl arenes on the productivity were reflected on the molecular weight (Mw) values of the synthesized polyketones. For all the three vinyl arenes, moving from the aldimine to the ketimine catalyst, a steep improvement of the Mw values was achieved, yielding polyketones with Mw data ranging from 250 000 to almost 500 000 $g mol^{-1}$, which are among the highest reported so far.[16,51] The increase in the molecular weight indicated that the increase in the productivity obtained with **2 b** was due to an increase in the length of the polymer chains rather than in their number, as also revealed by the differences in the turnover numbers (TON, Table 1). This suggests that, in the case of the ketimine catalyst, the increase in the ratio between the propagation and the termination rate might be due to both an increase in the propagation rate and a decrease in the termination rate.

With precatalyst **2 b**, that originated the most stable catalyst, the effect of reaction time was analyzed in CO/S and CO/MS copolymerizations. Prolonging the reaction time resulted in an increase in the productivity, reaching the values of 6.86 $kg_{CP} g_{Pd}^{-1}$ in the CO/S copolymerization after 72 h and of 6.43 $kg_{CP} g_{Pd}^{-1}$ in CO/MS copolymerization after 48 h, with no evident catalyst decomposition in both cases (see the Supporting Information). These data are among the highest values ever reported for monocationic, monochelated precatalysts.[16] The large amount of solid precipitated during the copolymerization for longer reaction time suggested that the rate of the reaction might be affected by the diffusion-limited comonomers concentration at the catalytic center and that the catalytic system might switch from homogeneous to heterogeneous with the catalyst anchored to the solid polyketone. A similar phenomenon was already reported in the Pd-diphosphine catalyzed CO/ethylene copolymerization[52] and in CO/MS reaction catalyzed by dicationic palladium complexes with 3-substituted 1,10-phenanthrolines.[51]

With precatalyst **1 b**, the effect of CO pressure was investigated in the range 1–20 bar (Table 2). Slightly different reaction

Table 2. CO/vinyl arene copolymerization: effect of CO/pressure.[a] Precatalyst: **1 b**.

Run	Vinyl arene	P_{CO} [bar]	Yield [g]	$kg_{CP} g_{Pd}^{-1}$[b]	Mw [g mol^{-1}]	Mw/ Mn	RU[c]
1	S	1	0.86	0.64	31 000	2.0	235
2	S	10	0.59	0.29	21 000	1.6	159
3	S	20	0.32	0.16	14 000	1.3	106
4	MS	1	0.57	0.42	8000	1.4	55
5	MS	10	0.30	0.15	8000	1.3	55
6	MS	20	0.20	0.10	n.d.[d]	n.d.[d]	n.d.[d]
7	TBS	1	0.39	0.29	8000	2.1	42
8	TBS	10	0.04	0.02	n.d.[d]	n.d.[d]	n.d.[d]

[a] Reaction conditions: for $n_{Pd} = 1.89 \times 10^{-5}$ mol, TFE $V = 30$ mL, $T = 303$ K, [BQ]/[Pd] = 5, $t = 24$ h, vinyl arene $V = 15$ mL, [S]/[Pd] = 7000, [MS]/[Pd] = 6000, [TBS]/[Pd] = 4300 except for entries 1, 4 and 7 see Table 1. [b] $kg_{CP} g_{Pd}^{-1}$ = kilograms of copolymer per gram of palladium. [c] RU = number of repetitive units inserted into the polymer chain. [d] n.d. = not determined.

conditions were required to be applied due to the different experimental set up of the reaction. Regardless of the nature of the vinyl comonomer, an increase in the CO pressure resulted in a remarkable decrease in the productivity owing to the contemporary decrease in catalyst stability, rather than to the inhibiting effect of carbon monoxide. This effect was not unexpected, since it is known that, to have high productivity at CO pressures higher than 1 bar, an ancillary ligand to palladium ratio of 2 was required.[53]

The decrease in the Mw values on increasing CO pressure was in line with the detrimental effect of CO on catalyst stability. This was particularly evident in the CO/MS copolymerization, in which the same Mw value was obtained at 1 and 10 bar of CO, thus indicating that the reduced productivity was a result of a decrease in the number of the polymer chains and, therefore, in the number of the completed catalytic cycles.

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Stereochemistry of the synthesized polyketones

The stereochemistry of the obtained polyketones was determined by ^{13}C NMR spectroscopy, recording the spectra in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP), at room temperature (Table 3).

Table 3. Triads distribution in the CO/vinyl arene polyketones.[a] Precatalyst: [Pd(Me)(MeCN)(N−N′)][PF$_6$]

Run	N-N′	Vinyl arene	ll [%]	lu [%]	ul [%]	uu [%]
1	**L1**	S	16	16	16	52
1′[b]	**L1**	S	16	16	16	52
2	**L1**	MS	47	17	18	18
2′[b]	**L1**	MS	51	20	20	9
3	**L1**	TBS	30	37		33
4	**L2**	S	–	13	16	71
4′[b]	**L2**	S	3	13	13	71
5	**L2**	MS	–	21	19	60
5′[b]	**L2**	MS	5	17	17	61
6	**L2**	TBS	–	15	10	75

[a] Determined by ^{13}C NMR spectra recorded in HFIP/CDCl$_3$, $T = 298$ K, integration of C$_{ipso}$ signals. [b] Calculated on the basis of probability values of Table 5.

The nature of the ligand present in the catalyst remarkably influenced the stereochemistry of the produced macromolecules. With precatalyst **2b**, all the copolymers had a prevailingly syndiotactic microstructure, with a content of the *uu* triad around 70%, which is in line with the values reported in the literature for copolymers produced with other iminopyridine based catalysts (Table 3; entries 4–6).[39] However, for the polyketones obtained with precatalyst **1b**, the stereochemistry was strongly dependent on the vinyl arene comonomer. Indeed, whereas the CO/styrene copolymer was prevailingly syndiotactic (Table 3; entry 1), the CO/MS polyketone was prevailingly isotactic (Table 3; entry 2), and the CO/TBS macromolecule was atactic (Table 3; entry 3). To the best of our knowledge, this is the first report concerning the influence of a substituent in para position of the vinyl arene on the stereochemistry of the produced polyketones.

To gain insights into the parameters that affect the stereochemistry of the polyketones synthesized with precatalyst **1b**, the effect of the CO pressure was investigated (see above). In the C$_{ipso}$ region of the ^{13}C NMR spectra of the copolymers produced at higher CO pressure, the signals of all the four triads were present with a different distribution depending on both the vinyl arene and the CO pressure (Table 4).

From a general point of view, regardless to the vinyl arene comonomer, on increasing the CO pressure the content of the *uu* triad increased at expenses of that of the *ll* triad. For instance, in the case of the CO/MS copolymer a prevailingly isotactic macromolecule was obtained at 1 bar of CO, whereas a prevailingly syndiotactic copolymer was produced at 20 bar of CO. In all cases, at 20 bar of CO, copolymers with a higher stereoregularity were obtained.

Table 4. Triads distribution in the CO/vinyl arene polyketones.[a] Precatalyst: **1b**.

Run	Vinyl arene	P_{CO} [bar]	ll [%]	lu [%]	ul [%]	uu [%]
1	S	1	16	16	16	52
2	S	10	11	15	17	57
3	S	20	4	16	16	64
4	MS	1	47	17	18	18
5	MS	10	37	19	13	31
6	MS	20	11	19	13	57
7	TBS	1	30	37		33
8	TBS	10	31	21		48

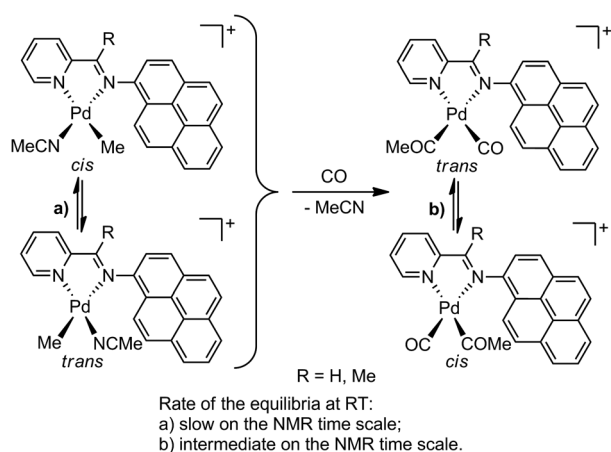[a] Determined by ^{13}C NMR spectra recorded in HFIP/CDCl$_3$, $T = 298$ K, integration of C$_{ipso}$ signals.

Although the effect of comonomer pressure on the stereochemistry of the synthesized polymer is well documented for polypropylene synthesis,[8] for polyketones the effect of CO pressure on the stereochemistry was reported only in the CO/styrene copolymerization catalyzed by a palladium pyridine-dihydrooxazole complex.[54] It was found that the stereoregularity of the copolymer decreased at higher CO pressure, an effect opposite to that found here, and, even though the content of the triads was not specified, it was much less pronounced than in the present case. Therefore, to the best of our knowledge, this paper is the first report concerning a remarkable effect of CO pressure on the polyketones stereochemistry.

To tentatively explain the effect of ligand, vinyl comonomer and CO pressure on the stereochemistry, a mechanistic study by in situ NMR spectroscopy and a statistical analysis were performed.

The reactivity of complexes **1b** and **2b** with carbon monoxide was investigated by bubbling CO for 5 min into a 10 mM dichloromethane solution of the two complexes, at room temperature, leading to a clear red solution with no formation of palladium black in both cases. The two precatalysts showed the same reactivity. In the ^{1}H NMR spectra recorded after adding CO, no signal of the precatalyst was observed, indicating that, for each complex, either both isomers reacted with CO or only one isomer reacted with CO, but since they were in equilibrium, the other one was transformed into the reactive species, and so no precatalyst remained in solution. In both cases the signals were very broad at room temperature and became sharper at 253 K, showing the singlet of free acetonitrile and a broad signal at 2.76 and 2.80 ppm for the Pd-acetyl species with ligand **L1** and **L2**, respectively. Therefore, both precatalysts were transformed into the Pd-acetyl-carbonyl intermediate; the broad signals indicated that a dynamic process was taking place in solution, suggesting that *cis* and *trans* isomers were formed and were in exchange on a rate intermediate on the NMR time scale, at room temperature (Scheme 2).

Because no difference in the reactivity with CO between **1b** and **2b** was evident, the different stereochemistry of the polyketones should be originated at the step of vinyl comonomer coordination and insertion.

The statistical analysis was performed by taking into account two main mechanisms of stereocontrol, according to a simple

Scheme 2. The CO migratory insertion reaction on precatalysts **1b** and **2b**.

Rate of the equilibria at RT:
a) slow on the NMR time scale;
b) intermediate on the NMR time scale.

R = H, Me

N-N′	Vinyl arene	p(Re)lk	p(Re)ul	p(Si)lk	p(Si)ul
L1	S	0.16	0.84	0.16	0.84
L1	MS	0.22	0.78	0.22	0.78
L2	S	0.3	0.7	0.27	0.73
L2	MS	0.8	0.2	0.2	0.8

Table 5. Values of probability sets applied. Precatalyst: [Pd(Me)(-MeCN)(N–N′)][PF$_6$]

Markov process:[55–58] one-parameter chain end and one-parameter enantiomorphic site control. This kind of statistical approach was already applied to investigate the stereocontrol observed in the CO/propene copolymerization by using stereoselective Pd catalysts.[59] The innate asymmetry of the catalytic sites for **1b** and **2b** catalysts allows to assume also both types of control acting in the same process in a two-parameters statistic control, whereas the influence of the penultimate and preceding units can be considered negligible.

In the ^{13}C NMR spectra of polyketones synthesized with **2b**, the signals of only three triads were present in the region of the C$_{ipso}$, with the signal of the *ll* triad missing or negligible, thus indicating that the Bernoullian statistical model is suited for this analysis and that the enantioface selection is under chain-end control. However in the ^{13}C NMR spectra of polyketones synthesized with **1b**, the signals of all the four triads were observed, thus indicating a larger influence by the enantiomorphic catalytic site. The relative area of each peak was calculated with respect to the total area of the signals, and the values are summarized in Table 3.

According to the definition of Bovey tacticity,[60,61] for catalysts with a preference for the (*Re*)-enantioface, *p(Re)lk* and *p(Si)ul* represent the probabilities, as independent parameters, for maintain the (*Re*)-enantioface selection to give an isotactic sequence and to return to the preferred enantioface selection after a non-regular (*Si*)-insertion, respectively. Similarly, *p(Si)lk* and *p(Re)ul* are the probabilities for maintaining the (*Si*)-enantioface selection.

The value for the triad with the largest relative area in the spectra was calculated by arbitrarily changing the two independent probabilities and by testing the different models (see the Supporting Information). Among the various possibilities, the conclusive sets of probabilities were selected to mimic also the values for the other peaks as close as possible to the experimental distribution. In Table 5 the list of the sets of probabilities is summarized. In Table 3 a comparison between the values relative to the experimental triad distribution and the values calculated by this statistical analysis is reported.

Following the described approach, the statistical analysis confirms that the syndiotactic copolymer obtained with the ke-

timine catalyst was the result of the chain-end control, regardless to the nature of the vinyl arene. On the other hand, in the case of the aldimine catalyst, the control of the stereochemistry was related to the vinyl comonomer: both the chain-end and the enantiomorphic site control are active for styrene, and only the enantiomorphic site control operative for 4-methyl styrene.

A reasonable hypothesis about the relationship between the ligand present in the catalyst and the polyketone stereochemistry might be based on the precatalyst isomer population observed by NMR spectroscopy: for **1b**, the *trans* isomer was the major species, indicating the preference for the Pd–C bond to be *trans* to the Pd–N$_{imino}$ bond. For **2b**, almost an equimolar ratio of the two isomers was found, indicating no preference for the position of the Pd–C bond with respect to the two halves of the ligand. Translating this information on the polymerization mechanism, it suggests that in the case of the ketimine catalyst, both sites on palladium can accommodate either the growing polymer chain or the incoming monomer, leading to the syndiotactic copolymer under chain-end control.

However, in the case of the aldimine catalyst, the growing polymer chain might be preferentially (not site-selectively) located *trans* to the Pd–N$_{imino}$ bond, with the incoming vinyl arene preferentially coordinated *cis* to the pyrene fragment. Because for an efficient enantiomorphic site control the site-selective coordination of the vinyl arene is required,[45,54] the obtained stereochemistry and the statistical analysis suggest that the degree of site-selective coordination depends on the vinyl comonomer. With styrene, the preference for the growing polymer chain to be coordinated *trans* to the Pd–N$_{imino}$ bond is not as strong as it is in the case of 4-methyl styrene, thus the chain-end control is the main mechanism and the stereoerrors are originated by the contribution of the enantiomorphic site control. On the other hand, with 4-methyl styrene, in addition to the electronic effect also the steric hindrance might be in favor to the coordination of the growing polymer chain *trans* to the Pd–N$_{imino}$ bond, leaving only the coordination site *cis* to the pyrene fragment available for the coordination of the incoming alkene. The pyrene moiety should be able to discriminate between the two enantiofaces of the incoming 4-methyl styrene, leading to two diastereoisomers of different encumbered situations (Figure 3).

According to this hypothesis, the effect of CO pressure on the stereochemistry might be explained, as well. A preferential site coordination of the polymer chain *trans* to the Pd–N$_{imino}$ bond implies that, after each migratory insertion of the comonomer into the growing polymer chain, a back skip of the
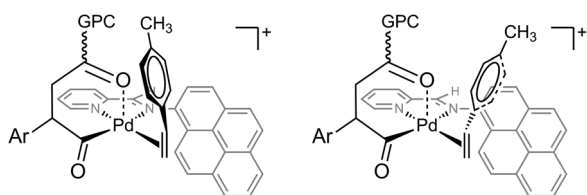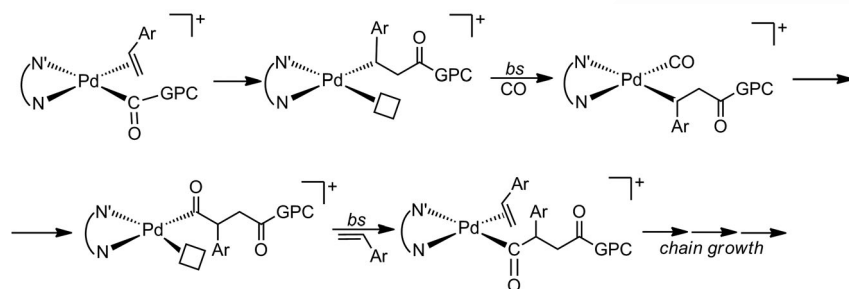
Figure 3. The two possible diastereoisomers as models for 4-methyl styrene enantioface discrimination (GPC = growing polymer chain).

Scheme 3. Proposed mechanism for the growth of the polymer chain, including back skip (bs).

chain takes place (Scheme 3).[8, 45] This mechanism requires the availability of a coordination site *cis* to the growing polymer chain. Owing to the high affinity of palladium to carbon monoxide, the CO favorably competes for the fourth coordination site on the metal center, thus hampering the mobility of the polymer chain, allowing the chain-end control to prevail over the enantiomorphic site control and leading to an increasingly syndiotactic macromolecule.

Conclusions

In this paper we have used two iminopyridines (N−N′), derived from 2-pyridinecarboxaldehyde or 2-acetylpyridine and characterized by a pyrene pendant arm, as ancillary ligands for palladium, synthesizing both neutral, [Pd(Me)Cl(N−N′)], and monocationic, [Pd(Me)(MeCN)(N−N′)][PF₆], derivatives. The NMR characterization provided evidence ■■ok?■■ that for the neutral species only the *cis* isomer, featured by the Pd-Me bond *cis* to the pyrene fragment, was formed, whereas for the monocationic complexes both *cis* and *trans* isomers were present in a different ratio depending on the N−N′ ligand.

The monocationic complexes generated very efficient catalysts for the copolymerization of carbon monoxide with vinyl arenes, such as styrene, 4-methyl styrene and 4-*tert*-butyl styrene leading to the corresponding alternating polyketones. It was found that the catalyst performances were strongly affected by the ancillary ligand. In particular, the catalyst with the ketimine ligand led to productivities up to 6.86 kg$_{CP}$ g$_{Pd}^{-1}$ and to polyketones with Mw values up to 471 000 g mol^{-1}, with no evident formation of inactive palladium metal. On the other hand, the catalyst with the aldimine ligand was found to be much less productive, yielding copolymers of low molecular weight.

Of high interest is the effect of the ligand on the polyketone stereochemistry: all the polyketones produced with the ketimine catalyst were syndiotactic, whereas for the macromolecules produced with the aldimine catalyst the stereochemistry was found to be dependent on both the nature of the vinyl comonomer and the CO pressure. If the copolymerization reactions were performed at 1 bar of CO, the CO/styrene polyketones were prevailingly syndiotactic, the CO/MS prevailingly isotactic, and the CO/TBS atactic. On increasing the CO pressure, the degree of stereoregularity increased and all the polyketones showed a prevailingly syndiotactic microstructure at 20 bar of CO, regardless to the vinyl arene comonomer.

The statistical analysis of the microtacticity of the polyketones confirmed that the syndiotactic copolymers produced with the ketimine catalyst were originated by the chain-end control, whereas the vinyl arene dependent stereochemistry for the macromolecules synthesized with the aldimine catalyst was a result of the switch from the enantiomorphic site control for 4-methyl styrene to a combination of enantiomorphic and chain-end control for styrene.

Overall, the reported catalytic data indicate that the simple substitution of the hydrogen atom by the methyl group on the imino carbon atom of the ligand was reflected in remarkable effects on catalysis: very high values of both productivity and molecular weight were achieved, together with unprecedented outcomes on the polymer stereochemistry. For the first time, in the homogeneously catalyzed polyketone synthesis it was found that the tacticity of the produced macromolecule was determined by the comonomers.

To get deeper insights into the nature of the peculiar stereocontrol, Pd catalysts with iminopyridines having different polyaromatic groups on the imino nitrogen are currently under investigation.

Experimental Section

General considerations

All complex manipulations were performed by using standard Schlenk techniques under argon. Anhydrous dichloromethane was obtained by distillation over CaH₂ and under argon. Deuterated solvents (Cambridge Isotope Laboratories, Inc. (CIL)) were stored as recommended by CIL. Carbon monoxide (SIAD, CP grade 99.9%), 1-aminopyrene, 2-pyridinecarboxaldehyde, 2-acetylpyridine, [PdCl₂(cod)], the three vinyl arenes, TFE, and all the other reagents and solvents were purchased from Sigma–Aldrich and used without further purification for synthetic, spectroscopic, and catalytic purposes. [Pd(Me)(Cl)(cod)] was obtained from [PdCl₂(cod)] according to a reported procedure.[43]

NMR spectra of ligands were recorded on a Brucker AV 300 MHz spectrometer. The NMR spectra of complexes, polyketones, and

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the in situ reactivity investigations were recorded on a Varian 500 spectrometer at the following frequencies: 500 MHz (^{1}H) and 125.68 MHz (^{13}C); the resonances are reported in ppm (δ) and referenced to the residual solvent peak versus Si(CH$_3$)$_4$: CDCl$_3$ at $\delta = 7.26$ (^{1}H) and 77.0 ppm (^{13}C), CD$_2$Cl$_2$ at $\delta = 5.32$ (^{1}H) and 54.0 ppm (^{13}C). NMR experiments were performed employing the automatic software parameters; for NOESY experiments, a mixing time of 500 ms was used. ^{13}C NMR spectra of polyketones were recorded in 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) with addition of CDCl$_3$ for locking purposes. **Caution: HFIP is a very volatile and highly toxic solvent, so proper protection should be used when it is handled.**

IR spectra were recorded in Nujol on a PerkinElmer System 2000 FT-IR. Elemental analyses were performed at the Laboratoire de Chimie de Coordination in Toulouse on an Analyzer PERKIN ELMER 2400 série II. The average molecular weight (Mw) and polydispersity (Mw/Mn) values of CO/vinyl arene copolymers were measured in the laboratories of Prof. Carla Carfagna through gel permeation chromatography by using polystyrene standards. Analyses were determined by a Knauer HPLC (K-501 pump, K-2501 UV detector) with a PL gel 5 μm 10^4 Å column. Chloroform was used as eluent, with a flow rate of 0.6 mL min^{-1}. Samples were prepared by dissolving the copolymer (2 mg) in chloroform (10 mL). Calculations were performed with the Bruker Chromstar software.

Synthesis of ligands L1 and L2

Ligands **L1** and **L2** were prepared according to a modification of the procedure we reported for the synthesis of ligand **L2**.[42]

Ligand **L1**: p-Toluenesulfonic acid (27 mg) and 2-pyridinecarboxaldehyde (2.42 mmol) were added to a stirred solution of 1-aminopyrene (2.30 mmol) in toluene at 343 K over 30 min. The reaction mixture was then heated to reflux for 2.5 h, using a Dean–Stark apparatus to remove water. After filtration, the solvent was removed under reduced pressure and addition of pentane caused the precipitation of a brown solid that was filtrated and washed with pentane. Yield: 51%.

^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 298 K): $\delta = 8.89$ (s, 1H, H^7), 8.78–8.71 (m, 2H, H^{6,B}), 8.53 (dt, 1H, H^3), 8.29–7.98 (m, 7H, H^{pyrene}), 7.98–7.90 (m, 1H, H^4), 7.88 (d, 1H, H^A), 7.45 ppm (ddd, 1H, H^5); ^{13}C NMR (77.21 MHz, CD$_2$Cl$_2$, 298 K): $\delta = 161.93$ (C^2), 155.67 (C^7), 150.31 (C^6), 137.24 (C^4), 125.72 (C^5), 123.69 (C^B), 122.19 (C^3), 115.86 ppm (C^A); elemental analysis ■■ok?■■ calcd (%) for C$_{22}$H$_{14}$N$_2$ (■■Mw?■■): C 86.25, H 4.61, N 9.14; found: C 86.28, H 4.54, N 9.13.

Ligand **L2**: was prepared in a similar manner from 1-aminopyrene (2.41 mmol), p-toluenesulfonic acid (60 mg), and 2-acetylpyridine (2.67 mmol) in toluene heated to reflux for 7 h. Yield: 59%.

^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 298 K): $\delta = 8.72$ (ddd, 1H, H^6), 8.55 (dt, 1H, H^3), 8.25–7.87 (m, 9H, H^4, H^{pyrene}), 7.56–7.42 (m, 2H, H^{5A}), 2.35 ppm (s, 3H, Me^8); ^{13}C NMR (77.21 MHz, CD$_2$Cl$_2$, 298 K): $\delta = 169.44$ (C^2), 157.06 (C^7), 149.22 (C^6), 137.02 (C^4), 125.24 (C^5), 121.50 (C^3), 117.15 (C^A), 17.36 (C^8) ppm; elemental analysis ■■ok?■■ calcd (%) for C$_{23}$H$_{16}$N$_2$ (■■Mw?■■): C 86.22, H 5.03, N 8.84; found: C 85.92, H 5.01, N 9.07.

Synthesis of palladium complexes [Pd(Me)Cl(N—N′)] (1a, 2a)

The corresponding ligand (1.1 equiv) was added to a stirred solution of [Pd(Me)Cl(cod)] (1 mmol) in CH$_2$Cl$_2$. After 1 h, the formed precipitate was filtered and washed with cold diethyl ether, afford-

ing **1a** as an orange solid (86% yield) and **2a** as a yellow solid (64% yield).

[Pd(Me)Cl**L1**] (**1a**): ^{1}H NMR (500 MHz, CD$_2$Cl$_2$, 298 K): $\delta = 9.20$ (d, 1H, H^6), 8.72 (s, 1H, H^7), 8.42 (d, 1H, H^B), 8.35–8.03 (m, 8H, H^{4,pyrene}), 7.90 (dt, 1H, H^3), 7.84 (ddd, 1H, H^5), 7.77 (d, 1H, H^A), 0.36 ppm (s, 3H, Pd-Me); ^{13}C NMR (125.68 MHz, CD$_2$Cl$_2$, 298 K): $\delta = 169.46$ (C^7), 150.05 (C^6), 129.43 (C^5), 127.71 (C^3), 127.30 (C^4), 122.10 (C^B), 119.90 (C^A), −0.63 ppm (Pd-Me); elemental analysis ■■ok?■■ calcd (%) for C$_{23}$H$_{17}$N$_2$PdCl (■■Mw■■): C 59.63, H 3.70, N 6.05; found: C 59.59, H 3.52, N 5.97.

[Pd(Me)Cl**L2**] (**2a**): ^{1}H NMR (500 MHz, CD$_2$Cl$_2$, 298 K): $\delta = 9.28$ (ddd, 1H, H^6), 8.36–8.02 (m, 8H, H^{4,B,pyrene}), 8.00 (dt, 1H, H^3), 7.83 (ddd, 1H, H^5), 7.64 (d, 1H, H^A), 2.19 (s, 3H, Me), 0.08 ppm (s, 3H, Pd-Me). ^{13}C NMR (125.68 MHz, CD$_2$Cl$_2$, 298 K): $\delta = 149.83$ (C^6), 139.46 (C^4), 129.28 (C^5), 125.56 (C^3), 120.02 (C^A), 19.37 (C^B), −0.77 ppm (Pd-Me); elemental analysis ■■ok?■■ calcd (%) for C$_{24}$H$_{19}$N$_2$PdCl (■■Mw?■■): C 60.39, H 4.01, N 5.87; found: C 60.22, H 3.93, N 5.98.

Synthesis of palladium complexes [Pd(Me)(MeCN)(N—N′)] (1b, 2b)

The synthesis of the cationic complexes was performed by adding a suspension of AgPF$_6$ (1.2 equiv) in acetonitrile to a stirred solution of the corresponding neutral complex in CH$_2$Cl$_2$. The solution was stirred for 45 min and was then filtered, concentrated, and the final product precipitated upon addition of diethyl ether. Filtration and drying under reduced pressure afforded **1b** as a red solid and **2b** as a yellow solid (average yield: 75%).

[Pd(Me)(MeCN)**L1**] (**1b**): ^{1}H NMR (500 MHz, CD$_2$Cl$_2$, 298 K): $\delta = 8.87$ (d, 1H, H^6), 8.77 (s, 1H, H^7), 8.71 (s, 1H, H^7), 8.68 (d, 1H, H^6), 8.65 (d, 1H, H^B), 8.37–8.09 (m, 18H, H$^{3′,4,4′,B,pyrene,pyrene′}$), 8.07–8.00 (m, 2H, H^{3,5}), 7.88–7.81 (m, 2H, H$^{5′,A′}$), 7.76 (d, 1H, H^A), 2.51 (s, 3H, Pd-NCMe), 1.28 (s, 3H, Pd-Me′), 1.21 (s, 3H, Pd-NCMe′), 0.51 ppm (s, 3H, Pd-Me). ^{13}C NMR (125.68 MHz, CD$_2$Cl$_2$, 298 K): $\delta = 173.06$ (C^7), 165.12 (C^7), 150.03 (C^6), 129.48 (C^5), 122.79 (C^B), 119.84 (C^A), 119.21 (C^A), 4.59 (Pd-Me), 4.21 (Pd-Me′), 3.73 (Pd-NCMe), 2.58 ppm (Pd-NCMe′); elemental analysis ■■ok?■■ calcd (%) for C$_{25}$H$_{20}$N$_3$PdPF$_6$ (■■Mw?■■): C 48.92, H 3.28, N 6.85; found: C 48.77, H 3.18, N 6.92.

[Pd(Me)(MeCN)**L2**] (**2b**): ^{1}H NMR (500 MHz, CD$_2$Cl$_2$, 298 K): $\delta = 8.87$ (d, 1H, H^6), 8.70 (d, 1H, H^6), 8.40–8.09 (m, 19H, H$^{3,3′ 4,4′,pyrene,pyrene′}$), 8.02 (dd, 1H, H^5), 7.97 (d, 1H, H^B), 7.91–7.85 (m, 1H, H^5), 7.69 (d, 1H, H$^{A′}$), 7.61 (d, 1H, H^A), 2.48 (s, 3H, Pd-NCMe), 2.43 (s, 3H, Me′), 2.30 (s, 3H, Me), 1.09 (s, 3H, Pd-Me′), 1.07 (s, 3H, Pd-NCMe′), 0.21 ppm (s, 3H, Pd-Me); elemental analysis ■■ok?■■ calcd (%) for C$_{26}$H$_{22}$N$_3$PdPF$_6$ (■■Mw?■■): C 49.74, H 3.53, N 6.69; found: C 49.63, H 3.40, N 6.63.

CO/vinyl arene copolymerization reactions

At 1 bar of CO: All experiments were performed at atmospheric CO pressure in a three-necked, thermostated, 75 mL glass reactor equipped with a magnetic stirrer. After establishment of the reaction temperature, the precatalyst (1.27×10^{-5} mol), 1,4-benzoquinone ([BQ]/[Pd] = 5), vinyl arene (10 mL), and TFE (20 mL) were added. CO was bubbled through the solution for 10 min. Afterwards, two 4 L balloons, previously filled with CO, were connected to the reactor. After the desired time, the reaction mixture was poured into methanol (100 mL) and stirred for 1.5 h at RT. The

solid was filtered and washed thoroughly with methanol, then dried under vacuum to constant weight.

At high CO pressure: All experiments were performed in a stainless steel autoclave (150 mL), equipped with a Teflon liner, magnetic stirrer, heating mantle, and temperature controller. The complex, the vinyl arene, 1,4-benzoquinone, and the solvent were placed in the reactor. CO was bubbled through the solution for 10 min. Afterwards, the reactor was pressurized at the desired pressure and heated. After 24 h, the reactor was vented, and methanol (200 mL) was added. The solid was filtered and washed thoroughly with methanol, then dried under vacuum to constant weight.

CO/styrene copolymers purification

Polyketones (100 mg) were dissolved in CHCl₃ (50 mL) and stirred at room temperature for 10 min. The solution was then filtered over SiO₂ ■■ok?■■ and the solvent was removed from the mother liquor under vacuum. The solid was suspended in ethanol, filtered, washed with ethanol, and dried under vacuum. For CO/MS copolymers, the mother liquor was concentrated and added dropwise to ethanol (20 mL) to precipitate the solid, which was then filtered, washed with ethanol, and dried under vacuum.

In situ NMR investigations

To a solution of the complex (10 mм) in CD₂Cl₂ in an NMR tube (5 mm), CO was bubbled for 5 min through a needle inserted into the rubber cap of the NMR tube. The NMR spectra were recorded after a total time of 10 min.

Modellization

The evaluation of the triads was made according to the equations reported in the Supporting Information, applying a set of probabilities arbitrarily changed to match the calculated values with the experimental ones. Some conditions between the various probabilities were considered for each statistic model to be applied, as reported below. In particular:

For Two Parameters Statistic model [Eq. (1)]

$$p(Re)ul + p(Re)lk = 1$$
$$p(Si)ul + p(Re)lk = 1 \tag{1}$$
$$p(Si)ul + p(Re)ul > 1 > p(Re)lk + p(si)lk$$

for One Parameter *Enantiomorphic site* control [Eq. (2)]

$$p(Si)ul = p(Re)lk$$
$$p(Re)ul = p(Si)lk \tag{2}$$
$$p(Si)ul + p(Re)ul = 1$$

for One Parameter *Chain-end* control [Eq. (3)]

$$p(Re)lk = p(Si)lk = plk$$
$$p(Si)ul = p(Re)ul = pul$$
$$p(Si)ul \neq p(Re)lk$$
$$p(Re)ul \neq p(Si)lk$$
$$p(Re)lk + p(Re)ul = 1$$
$$p(Si)lk + p(Si)ul = 1 \tag{3}$$

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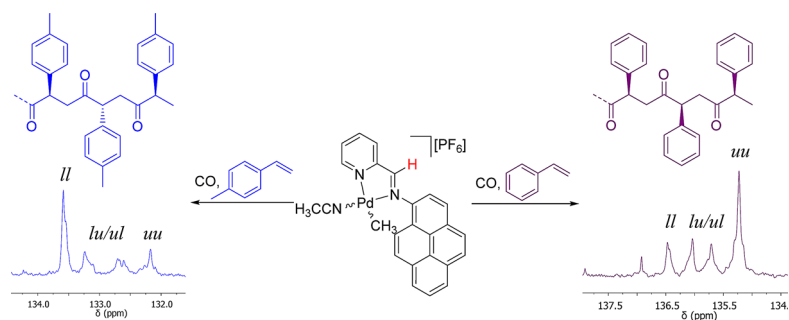
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■■ – ■■

Unprecedented Comonomer Dependence of the Stereochemistry Control in Pd-Catalyzed CO/Vinyl Arene Polyketone Synthesis

For the (very) first time: it was found that in the palladium catalyzed CO/vinyl arene copolymerization reaction the stereochemistry of the synthesized polyketones was dictated by the vinyl arene comonomer: an isotactic copolymer was obtained for 4-methyl styrene. A syndiotactic macromolecule was produced for styrene.

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