

## Pd-Catalyzed CO/Vinyl Arene Copolymerization: when the Stereochemistry is Controlled by the Comonomer

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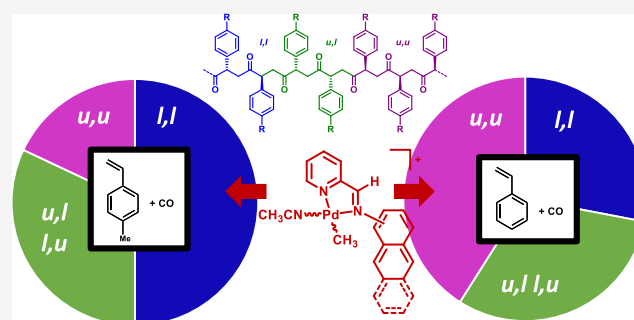


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**ABSTRACT:** The control of the stereochemistry of macromolecules is a very important goal, and coordination-insertion polymerization is superior with respect to the other polymerization methods for its achievement. In this contribution, we focus on Pd(II) homogeneous catalysts for the stereocontrolled synthesis of CO/vinyl arene polyketones. We developed a library of aldo- and keto-iminopyridine ligands N-N' that feature an  $\alpha$ - or  $\beta$ -naphthyl or anthracenyl moiety on the imino nitrogen atom ( $N_{imm}$ ). With such ligands, the Pd(II) monocationic complexes  $[Pd(CH_3)(CH_3CN)(N-N')][PF_6]$  were synthesized. NMR spectroscopy shows that in solution, each complex exists as an equilibrium mixture of cis and trans stereoisomers, the latter having the  $CH_3$  ligand opposite to the Pd– $N_{imm}$  bond. The isomeric population depends on the N-N' ligand: an almost 1:1 ratio is found for the ketimine complexes, whereas those with the aldimines show a preference for the trans geometry. These complexes generate very efficient catalysts for the CO/vinyl arene copolymerization. Catalyst performances depend both on the nature of N-N' and of the vinyl arene comonomer. The ketimine-based catalysts are more stable and more productive than the aldimine counterpart, leading to prevalently syndiotactic macromolecules of high  $M_w$  (up to 280 kDa). The aldimine derivatives produce copolymers with isotactic and syndiotactic stereoblocks of different lengths depending on the vinyl arene. The effect of the prochiral monomer on the copolymer tacticity is steric in nature as demonstrated by the stereochemistry of the obtained CO/4-fluorostyrene polyketone, whose synthesis is reported here for the first time. As a conclusion, we have now demonstrated that when catalysts with nonsymmetric ancillary ligands are used, and stereoisomers are present, the stereochemistry of the copolymerization is driven by both the catalyst isomeric distribution and the prochiral comonomer.



### INTRODUCTION

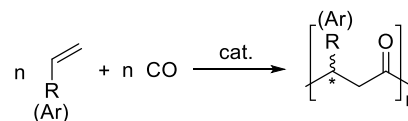
The potential applications of a polymeric material are strictly dependent on its physicochemical properties and its architecture, that in turn are determined by parameters such as molecular weight and molecular weight distribution, the presence of functional groups, linear and branching structure, and stereochemistry.<sup>1,2</sup> Coordination-insertion polymerization is thus far superior with respect to the other polymerization methods in controlling the stereochemistry of the synthesized macromolecules.<sup>3–6</sup> The huge industrial production of stereoregular polypropylene is an outstanding example of the powerful role played by catalysis for precision polymerization, and the design of new homogeneous catalysts for this reaction receives continuous attention.

In the last two decades, the CO/terminal alkene polyketones have attracted much academic and industrial interest. After the withdrawal from the market of the CO/ethylene/propylene terpolymer, commercialized by Shell Company under the trademark of Carilon,<sup>7</sup> in 2015 its industrial renaissance was

announced by Hyosung Company that produces it under the name of Poketone.<sup>8</sup>

Polyketones are the product of the direct, homogeneously catalyzed copolymerization of carbon monoxide with terminal alkenes (Scheme 1),<sup>7,9,10</sup> very cheap and abundant comonomers. They feature a perfectly alternating microstructure

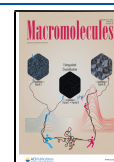
### Scheme 1. CO/Terminal Alkene Copolymerization



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and present unique properties. In addition, the reactivity of the carbonyl groups can be further exploited by post-polymerization functionalization, leading to different macromolecules.<sup>11–15</sup>

The control of regio- and stereochemistry of the macromolecules obtained with terminal alkenes is of high importance, in particular in consideration that polyketones possess main chain chirality. Therefore, when the isotactic copolymers are synthesized by using enantiomerically pure catalysts, optically active materials are obtained.<sup>16–19</sup>

The current catalysts for this reaction are palladium(II) complexes with different ancillary ligands, whose choice depends on the comonomer: bidentate phosphines are used for aliphatic alkenes,<sup>20</sup> whereas bidentate N-donors (N-N) for vinyl arenes.<sup>21</sup>

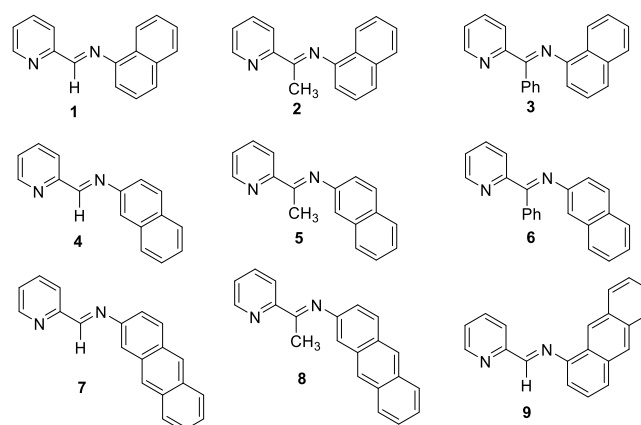
For this latter class of comonomers, a relationship between the symmetry of the N-N ligand and the tacticity of the synthesized macromolecule was established. In particular, C<sub>2</sub> symmetric ligands, such as bi- or bisoxazolines,<sup>18,19</sup> azabisoxazolines,<sup>22</sup> and diketimines,<sup>23</sup> produce isotactic polyketones; whereas C<sub>2v</sub> symmetric ligands [*i.e.* 2,2'-bipyridine or 1,10-phenanthroline (**phen**)] yield syndiotactic copolymers.<sup>24,25</sup> When ligands of lower symmetry (C<sub>s</sub> or C<sub>1</sub>) are used, the stereochemistry is hardly predictable, and polyketones with all the possible microstructures can be obtained.<sup>26–29</sup> In particular, Pd catalysts with bis(aryl)iminoacene  $\alpha$ -diimines (BIAN) afforded atactic copolymers,<sup>30,31</sup> whereas  $\alpha$ -diimines featuring the dibenzobarrelene backbone yielded prevalently syndiotactic polyketones.<sup>32</sup> Finally,  $\alpha$ -diimines with the 1,4-diaza-1,3-butadiene skeleton (DAB) and ortho-substituted aryl rings lead to isotactic stereoblocks CO/vinyl arene copolymers.<sup>33–36</sup> This analysis points out that, as for coordination-insertion polypropylene synthesis, the stereochemistry of the CO/vinyl arene polyketones is dictated by the ancillary ligand bound to palladium: depending on its nature, the enantioface discrimination of the incoming vinyl arene is under the control of either the *enantiomeric site* or the *chain-end*.

Recently, we have studied the catalytic behaviour of Pd(II) complexes with pyrene-tagged iminopyridines (**L1** and **L2** in Chart 1) in the CO/vinyl arene copolymerization.<sup>37</sup> We discovered that the catalyst with the ketimine ligand **L2** led to syndiotactic polyketones, regardless of the nature of the vinyl

arene. Conversely with the aldimine ligand **L1** we found, for the first time, that the tacticity of the macromolecule was determined by the comonomer, being prevalently syndiotactic for the CO/styrene polyketone, prevalently isotactic in the case of CO/4-methyl styrene and atactic for CO/4-*tert*-butyl styrene. However, we later found that homologous Pd(II) catalysts with simpler iminopyridines, that is ligands **L3–L6** in Chart 1 that bear a phenyl or a 2,6-dimethyl phenyl ring on the imino nitrogen atom, led to prevalently syndiotactic copolymers, regardless of the vinyl arene comonomer.<sup>38</sup> Therefore, a rather unclear situation emerged.

With the aim to elucidate this picture, we have now expanded the library of aldo- and keto-iminopyridines to ligands that bear an  $\alpha$ - or  $\beta$ -naphthyl or -anthracenyl moiety on the imino nitrogen atom (N-N', ligands **1–9** in Chart 2). We

Chart 2. Iminopyridines under Investigation.



have synthesized and characterized both neutral and monocationic Pd(II) complexes of the general formula [Pd(CH<sub>3</sub>)Cl(N-N')] and [Pd(CH<sub>3</sub>)(CH<sub>3</sub>CN)(N-N')][PF<sub>6</sub>], respectively, and investigated their catalytic behaviour in the CO/vinyl arene copolymerization with a particular focus on the control of the stereochemistry of the obtained macromolecules.

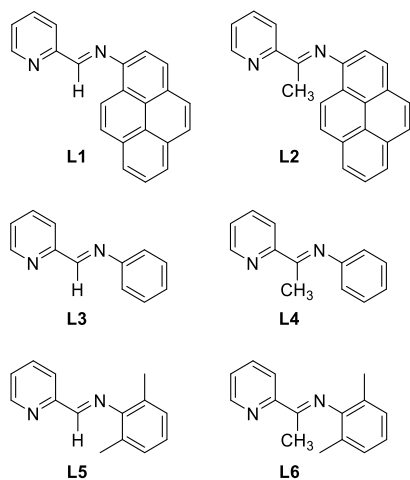
In addition, for the first time, we have also successfully performed the copolymerization of carbon monoxide with the polar styrene monomer 4-fluorostyrene (FS), gaining clear indications on how the nature of the comonomer affects the stereochemistry of the synthesized macromolecule.

In this study, we conclusively demonstrate that for catalysts based on ancillary ligands with condensed aromatic rings, the stereochemistry of the polymer is controlled by the comonomer. This finding led us to introduce the concept of *comonomer-driven stereochemical control*.

## RESULTS AND DISCUSSION

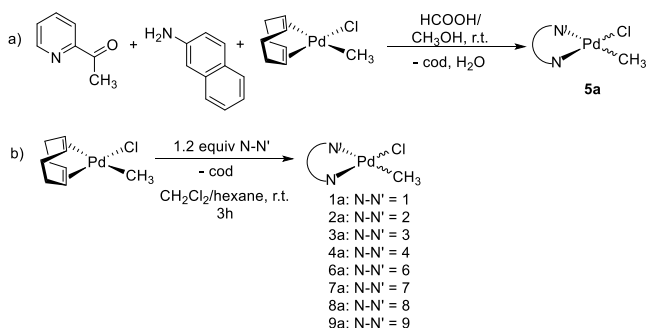
**Synthesis and Characterization of Ligands 1–9 and Relevant Pd(II) Complexes.** Whereas ligands **1**, **2**, **4**, **7**, and **8** are already known from the literature,<sup>39–42</sup> to the best of our knowledge, ligands **3**, **5**, **6**, and **9** are reported here for the first time. Ligand **9** was synthesized through a simple condensation reaction between pyridine-2-aldehyde and 1-aminoanthracene in the presence of an acid catalyst. Ligands **3** and **6** were obtained through a template synthesis by reacting benzoylpyridine with the appropriate amine using ZnCl<sub>2</sub> as the templating agent. The desired products, isolated as yellow solids (**7–9**) or brown oils (**3**, **6**) in acceptable to good yields (41–65%), were

Chart 1. Previously Studied Iminopyridines



characterized by NMR spectroscopy (Figures S1–S24). These synthetic procedures were unsuccessful for the preparation of **5**. Instead, the corresponding Pd(II) neutral complex [Pd(CH<sub>3</sub>)Cl(**5**)], **5a**, was directly synthesized using [Pd(cod)(CH<sub>3</sub>)Cl] (cod = 1,5-*cis,cis*-cyclooctadiene) as the templating agent (Scheme 2a). For all the other ligands, **1–4** and **6–9**, the

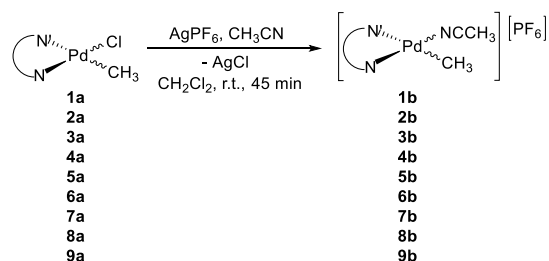
**Scheme 2. Synthesis of the Neutral Complexes: (a) 5a; (b) 1a–4a, 6a–9a**



neutral Pd(II) complexes [Pd(CH<sub>3</sub>)Cl(N-N')] **1a–4a** and **6a–9a** were obtained through the consolidated procedure based on the substitution of the diolefin in [Pd(cod)(CH<sub>3</sub>)Cl] with N-N' (Scheme 2b).<sup>43,44</sup> Complexes **1a–9a** were isolated as yellow or orange solids in good to excellent yields (49–94%).

Complexes **1a–9a** were transformed into the corresponding monocationic derivatives [Pd(CH<sub>3</sub>)(CH<sub>3</sub>CN)(N-N')][PF<sub>6</sub>], **1b–9b**, through a silver-induced dehalogenation in the presence of acetonitrile (Scheme 3). The desired compounds were obtained as yellow or orange solids in yields ranging from 55 to 95%.<sup>37,38</sup>

**Scheme 3. Synthesis of the Cationic Complexes 1b–9b**

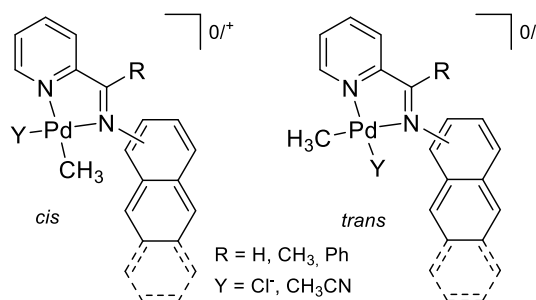


Both series of complexes were characterized in solution by NMR spectroscopy. In addition, the molecular structures of the neutral derivatives **1a–4a**, **8a**, and **9a**, were determined by X-ray diffraction.

Due to the nonsymmetrical nature of the ligands and palladium chemical environment, two stereoisomers are possible. Consistent with our previous work on similar complexes,<sup>37,38</sup> the *cis* geometry was assigned to the isomer having the CH<sub>3</sub> ligand adjacent to the Pd–N<sub>imino</sub> bond (N<sub>imino</sub> = imino nitrogen) (Chart 3).

In the <sup>1</sup>H NMR spectra of all complexes, two sets of signals are observed, indicating the presence in the solution of an equilibrium mixture of both *cis* and *trans* isomers and their ratio depending on the nature of the ligand and on the charge of the complex (Table 1). In particular, the neutral derivatives have a clear preference for the *cis* geometry: with the exception of **4a** and **7a**, the equilibrium content of the *trans* isomer is

**Chart 3. *cis* and *trans* Isomers for the Neutral and Monocationic Complexes.**



**Table 1. Isomeric Distribution at the Equilibrium for the Neutral and Cationic Complexes<sup>a</sup>**

N-N'	[Pd(CH <sub>3</sub> )Cl(N-N')]		[Pd(CH <sub>3</sub> )(CH <sub>3</sub> CN)(N-N')][PF <sub>6</sub> ]	
	<i>cis</i> (%)	<i>trans</i> (%)	<i>cis</i> (%)	<i>trans</i> (%)
1	93	7	31	69
2	96	4	65	35
3	96 <sup>b</sup>	4 <sup>b</sup>	44 <sup>c</sup>	56 <sup>c</sup>
4	78	22	25	75
5	95	5	50	50
6	92	8	42	58
7	72	28	21 <sup>d</sup>	79 <sup>d</sup>
8	94	6	48 <sup>d</sup>	52 <sup>d</sup>
9	95	5	35	65

<sup>a</sup>Data obtained from <sup>1</sup>H NMR spectra in CD<sub>2</sub>Cl<sub>2</sub> at 298 K. <sup>b</sup>Data obtained from <sup>1</sup>H NMR spectra in CD<sub>2</sub>Cl<sub>2</sub> at 273 K. <sup>c</sup>Data obtained from <sup>1</sup>H NMR spectra in CD<sub>2</sub>Cl<sub>2</sub> at 253 K. <sup>d</sup>Data obtained from <sup>1</sup>H NMR spectra recorded in CD<sub>3</sub>NO<sub>2</sub> at 298 K. The two isomers are in equilibrium at slow rate on the NMR timescale, as demonstrated by NOESY spectra.

lower than 10% (Table 1). The cationic derivatives show different and more varied isomeric distributions: the *cis* isomer remains prevailing only for **2b**, the complexes **1b**, **4b**, **7b**, and **9b** with aldimine ligands have a preference for the *trans* geometry and those with ketimine ligands **3**, **5**, **6**, and **8** show no preference (Table 1).

The observed isomeric distribution is in line with previous findings for similar palladium(II) complexes with iminopyridines<sup>37,38,45</sup> and other unsymmetric bidentate N ligands, such as  $\alpha$ -diimines<sup>46–48</sup> or pyridylidene amides,<sup>49</sup> and further substantiates our hypothesis on its origin. More precisely, in the neutral complexes, the preferential isomer is mainly determined by electronic factors: the methyl group prefers to bind *trans* to the N atom with the lowest Lewis basicity, that is the N<sub>pyr</sub> (N<sub>pyr</sub> = pyridino nitrogen) for iminopyridine ligands. Instead, in the monocationic derivatives, both electronic and steric effects play a role in directing the methyl coordination, thus making any predictions on the prevailing isomer difficult.

As already observed for the corresponding *cis*- and *trans*-Pd(II) complexes with **L1–L6**,<sup>37,38</sup> the Pd–CH<sub>3</sub> singlet shifts to low frequency on going from an aldimine to the corresponding ketimine ligand (Table 2). This finding is in agreement with the expected increase in the electron density on the metal center because of the higher Lewis basicity of the ketimine ligands. This trend further supports our hypothesis that the Pd–CH<sub>3</sub> signal is a good probe for assessing the electron density donated by the ligand to the metal.<sup>37,38,46</sup> In addition, for both series of complexes, in the *cis* isomer, the

**Table 2.** Chemical Shift Values for the Pd–CH<sub>3</sub> Singlet in the Neutral and Cationic Complexes<sup>a</sup>

N–N'	[Pd(CH <sub>3</sub> )Cl(N–N')]		[Pd(CH <sub>3</sub> )(CH <sub>3</sub> CN)(N–N')][PF <sub>6</sub> ]	
	cis	trans	cis	trans
1	0.35	1.12	0.50	1.23
3	0.20 <sup>b</sup>	1.11 <sup>b</sup>	0.35 <sup>c</sup>	1.19 <sup>c</sup>
2	0.11	0.98	0.26	1.05
4	0.60	1.17	0.81	1.27
6	0.43	1.12	0.57	1.21
5	0.34	1.00	0.49	1.08
7	0.71	1.18	0.75 <sup>d</sup>	1.21 <sup>d</sup>
8	0.40	1.02	0.43 <sup>d</sup>	1.02 <sup>d</sup>
9	0.35	1.14	0.48	1.25

<sup>a</sup>Data obtained from <sup>1</sup>H NMR spectra in CD<sub>2</sub>Cl<sub>2</sub> at 298 K. <sup>b</sup>Data obtained from <sup>1</sup>H NMR spectra in CD<sub>2</sub>Cl<sub>2</sub> at 273 K. <sup>c</sup>Data obtained from <sup>1</sup>H NMR spectra in CD<sub>2</sub>Cl<sub>2</sub> at 253 K. <sup>d</sup>Data obtained from <sup>1</sup>H NMR spectra recorded in CD<sub>3</sub>NO<sub>2</sub> at 298 K.

Pd–CH<sub>3</sub> singlet shifts to lower frequency upon going from the β- to the α-connected ligand, indicating an increase in the shielding effect of the aromatic fragment. This finding suggests that, as observed in the solid state (*vide infra*), also in solution, the orientation of the α-naphthyl and α-anthracenyl rings with respect to the coordination plane is closer to orthogonal than

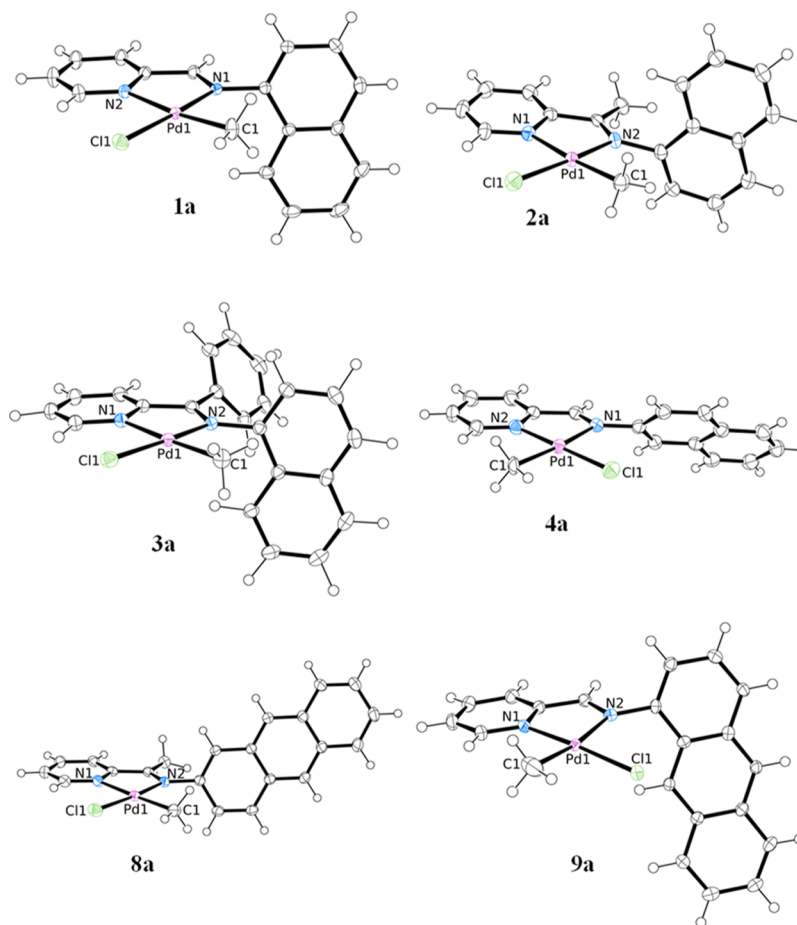
for the corresponding β-ones (Table 2, 4 vs 1, 5 vs 2, 6 vs 3, 7 vs 9).

Single crystals suitable for X-ray diffraction were obtained for 1a–4a, 8a, and 9a, upon slow diffusion of either diethyl ether or *n*-hexane in the dichloromethane solution of the complexes at 4 °C.

The X-ray analysis reveals that the unit cell of 1a–3a, and 8a contains the cis isomer (*i.e.* the most abundant in solution) exclusively, whereas that of 4a contains the trans species. For 9a, both isomers are found with a preferred population (71%) for the trans species (Figure 1).

All the complexes have the expected square planar geometry with no significant distortions, with the exception of the bite angle of the N–N' ligand that is narrower than 90°, as usually observed for five-membered palladacycles formed by N–N ligands.<sup>22,38</sup> In each complex, the two Pd–N bond distances are significantly different because of the higher trans-influence of the methyl group compared to the chlorido (Table S1). The dihedral angle between the average coordination plane and the naphthyl plane is closer to 90° for the α- than the β-naphthyl group (*e.g.* crfr. 1a and 4a).

**CO/Vinyl Arene Copolymerization.** Cationic complexes 1b–9b were tested as precatalysts for the copolymerization of carbon monoxide with styrene (S), 4-methyl styrene (MS), and 4-*tert*-butyl styrene (TBS). The catalytic tests were performed under the same reaction conditions previously applied by us for [Pd(CH<sub>3</sub>)(CH<sub>3</sub>CN)(L1–L6)][PF<sub>6</sub>],<sup>37,38</sup>



**Figure 1.** ORTEP representation (thermal ellipsoids at the 50% probability level) of complexes: (a) *cis*-1a; (b) *cis*-2a; (c) *cis*-3a; (d) *trans*-4a; (e) *cis*-8a; and (f) *trans*-9a.

Table 3. CO/Vinyl Arene Copolymerization: Effect of the N-N' Ligand and of the Vinyl Arene<sup>a</sup>

entry	precat.	vinyl arene	yield (g)	kg CP/g Pd <sup>b</sup>	mol R.U. <sub>t</sub> /g Pd <sup>c</sup>	M <sub>w</sub> kDa (M <sub>w</sub> /M <sub>n</sub> )	R.U. <sub>c</sub> <sup>d</sup>	TON <sup>e</sup>
1	1b	S	0.51	0.37	2.80	16 (1.8)	121	2.51
2	1b	MS	0.42	0.31	2.12	9 (1.6)	62	3.67
3	1b	TBS	0.11	0.08	0.42	n.d. <sup>f</sup>	n.d. <sup>f</sup>	n.d. <sup>f</sup>
4	2b	S	5.63	4.17	31.55	141 (1.9)	1067	3.14
5	2b	MS	6.05	4.48	30.65	174 (2.7)	1190	2.74
6	2b	TBS	5.74	4.25	22.58	151 (2.4)	802	2.99
7	3b	S	5.01	3.71	28.07	134 (2.0)	1014	2.94
8	3b	MS	5.21	3.86	26.40	191 (2.4)	1306	2.15
9	3b	TBS	6.26	4.63	24.59	245 (2.8)	1301	2.01
10	4b	S	0.97	0.72	5.45	19 (2.1)	144	4.02
11	4b	MS	0.56	0.41	2.80	13 (1.8)	89	3.39
12	4b	TBS	0.34	0.25	1.33	21 (2.0)	112	1.27
13	5b	S	7.56	5.60	42.37	209 (2.5)	1581	2.85
14	5b	MS	6.02	4.46	30.51	138 (2.5)	944	3.43
15	5b	TBS	7.77	5.75	30.54	236 (2.4)	1254	2.59
16	6b	S	5.62	4.16	31.48	117 (2.0)	885	3.78
17	6b	MS	5.83	4.31	29.48	147 (2.9)	1006	3.12
18	6b	TBS	7.00	5.18	27.52	162 (3.0)	860	3.40
19	7b	S	0.60	0.44	4.54	19 (2.0)	144	2.49
20	7b	MS	0.43	0.32	2.19	11 (1.5)	75	3.08
21	7b	TBS	0.35	0.26	1.38	15 (1.7)	80	1.84
22	8b	S	5.77	4.27	32.31	104 (2.7)	787	4.37
23	8b	MS	6.20	4.58	31.33	209 (2.7)	1430	2.34
24	8b	TBS	6.93	5.13	27.25	284 (3.0)	1508	1.92
25	9b	S	0.63	0.47	4.77	26 (2.9)	197	1.91
26	9b	MS	0.40	0.30	2.05	17 (2.8)	116	1.85
27	9b	TBS	0.23	0.17	0.90	31 (2.8)	165	0.58

<sup>a</sup>Reaction conditions:  $n_{\text{Pd}} = 1.27 \times 10^{-5}$  mol;  $V_{\text{TFE}} = 20$  mL;  $V_{\text{vinyl arene}} = 10$  mL;  $[\text{BQ}]/[\text{Pd}] = 5$ ;  $[\text{S}]/[\text{Pd}] = 6800$ ;  $[\text{MS}]/[\text{Pd}] = 6000$ ;  $[\text{TBS}]/[\text{Pd}] = 4300$ ;  $T = 303$  K;  $P_{\text{CO}} = 1$  bar;  $t = 24$  h. <sup>b</sup>Productivity in kg CP/g Pd = kilograms of copolymer per gram of palladium, where  $\text{g Pd} = n_{\text{Pd}} \times$  molar mass of palladium. <sup>c</sup>Productivity in mol R.U.<sub>t</sub>/g Pd = number of moles of total inserted repetitive units per gram of palladium. <sup>d</sup>R.U.<sub>c</sub> = number of inserted repetitive units per polymer chain, calculated as  $M_{\text{W,polymer}}/M_{\text{R.U.}}$ . <sup>e</sup>TON calculated as moles of copolymer per mole of palladium. <sup>f</sup>n.d. = not determined.

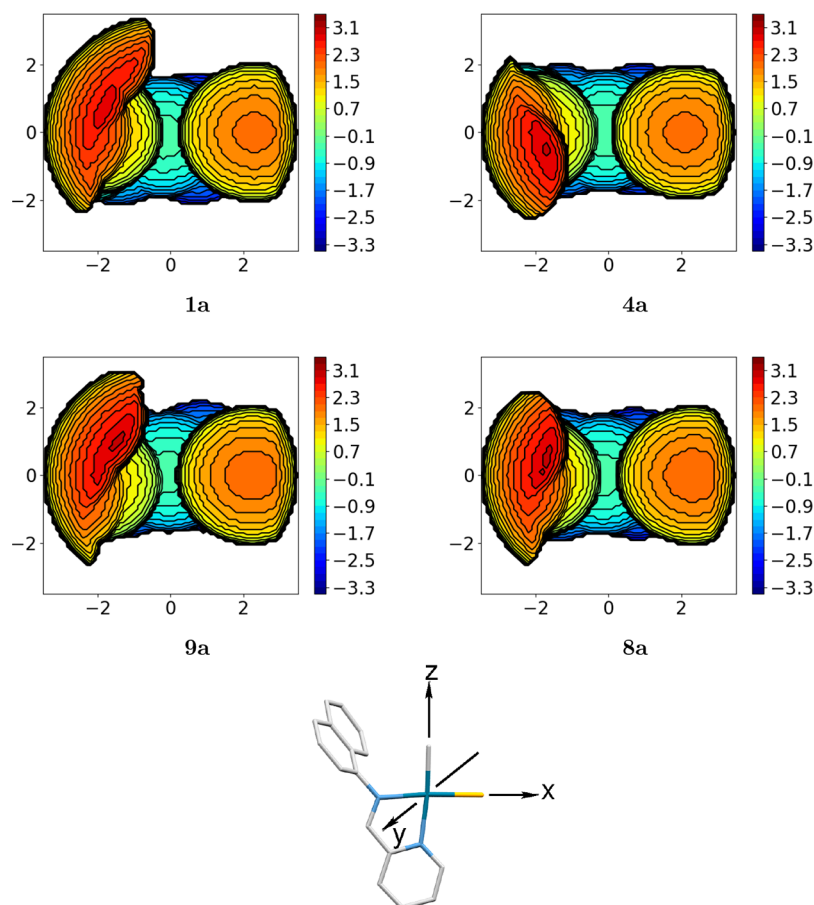
that is 2,2,2-trifluoroethanol (TFE) as the solvent, 1 bar of CO,  $T = 303$  K, and in the presence of a slight excess of 1,4-benzoquinone (BQ) with respect to palladium (Table 3). The produced CO/S, CO/MS, and most of the CO/TBS polyketones precipitated in the reactor during the catalytic process and, at the end of the reaction, were separated by filtration as white or grey solids. A different procedure was followed for the CO/TBS copolymers synthesized with the precatalysts 1b, 7b, and 9b (see Experimental Section in Supporting Information).

In all cases, both the nature of the N-N' ligand and of the vinyl arene remarkably affected the catalyst productivity, as well as the copolymer molecular weight and stereochemistry. Because of the different molecular weight of the vinyl arene comonomers, productivity data are discussed in terms of number of moles of total inserted repetitive units per gram of palladium (mol R.U.<sub>t</sub>/g Pd; R.U.<sub>t</sub> = number of moles of total inserted repetitive units). The precatalyst 5b generated the most productive species for styrene and 4-*tert*-butyl styrene, whereas for 4-methyl styrene, the highest productivity was obtained with the precatalyst 8b (Table 3, entries 13, 15, and 23). Productivities higher than 5.5 kg of CP/g Pd, among the highest ever reported for this reaction, were achieved. The lowest productivities were found with aldimine precatalysts, in particular with 1b and 9b (Table 3, entries 1, 3, and 26).

Regardless of the vinyl arene used, ketimine catalysts are much more productive than the corresponding aldimine ones,

most often by more than one order of magnitude (Table 3, entries 4–6 and 7–9 vs 1–3; 13–15 and 16–18 vs 10–12; 22–24 vs 19–21). This trend, similar to that reported by us for catalysts  $[\text{Pd}(\text{CH}_3)(\text{CH}_3\text{CN})(\text{L1–L6})][\text{PF}_6]$ ,<sup>37,38</sup> is mainly dictated by the higher stability of the ketimine catalysts with respect to the aldimine counterparts. Indeed, in the copolymerization reactions carried out with the aldimine catalysts formation of inactive palladium black was observed already after 1 h for 1b and 4b, 1.5 h for 7b, and 4 h for 9b. On the contrary, the formation of palladium metal was not evident for the catalysts based on ketimines, at least within the first 24 h of the reaction. The observed trend correlates well with the NMR data about the coordination capability of the N-N' ligands.

Concerning the effect of the vinyl arene, for all the investigated catalysts, the productivity decreases in the order styrene, 4-methyl styrene, 4-*tert*-butyl styrene (Table 3). This trend, consistent with what found by us with catalysts  $[\text{Pd}(\text{CH}_3)(\text{CH}_3\text{CN})(\text{L1–L5})][\text{PF}_6]$ , is in contrast to what is reported for active species with ligands such as 1,10-phenanthroline and its substituted derivatives,<sup>44</sup> bisoxazoline,<sup>18</sup> bioxazoline,<sup>19</sup> and  $\alpha$ -diimines.<sup>50</sup> The observed effect of the vinyl arene seems to be steric rather than electronic in nature: in fact, MS and TBS are more nucleophilic than S and—on this ground—they would be expected to be copolymerized more efficiently.



**Figure 2.** Steric maps for complexes **1a**, **4a**, **9a**, and **8a**. The complexes are oriented as shown in the diagram (using **1a** as a prototype). To better evidence the topographic contours of the naphthyl/anthracenyl group, both the Pd atom at the origin and the ligand along the positive  $z$  axis were not included in the generation of the maps.

The catalyst productivity was found to depend also on the nature of the condensed aromatic rings on  $N_{imm}$ : all the catalysts with the  $\beta$ -connected ligands are more productive than those with the corresponding  $\alpha$ -derivatives (Table 3, entries 10–12 vs 1–3; 13, 15 vs 4, 6; 16–18 vs 7–9; 20, 21 vs 26, 27). In addition, for the ketimine complexes, very similar increments were found on going from  $\alpha$ - to  $\beta$ -ligands, regardless of the vinyl arene (*i.e.* 1.35 for **2b** vs **5b**, and 1.12 for **3b** vs **6b**). This effect might be related to the different orientation of the polycyclic aromatic fragment with respect to the coordination plane, observed both in the solid state and in solution: the  $\beta$ -naphthyl (or  $\beta$ -anthracenyl) moiety is more distant from the catalytic center than the corresponding  $\alpha$ -counterpart, creating a lower steric congestion in the coordination plane with positive effects on both the growing polymeric chain and the incoming comonomer. This point is illustrated in Figure 2, where the steric maps<sup>51</sup> for the comparable couples **1a** ( $\alpha$ -naphthyl)/**4a** ( $\beta$ -naphthyl) and **9a** ( $\alpha$ -anthracenyl)/**8a** ( $\beta$ -anthracenyl) are shown. The larger steric hindrance of the  $\alpha$ -bonded naphthyl and anthracenyl group (complexes **1a** and **9a**) is quantified by the calculated free volume fractions: 47.2/50.1% for **1a/4a** and 47.3/49.3% for **9a/8a**.

For the catalysts with the aldimine ligands, the increment achieved on going from  $\alpha$ - to  $\beta$ -ligands depends on the nature of the vinyl arene, reasonably because it is also affected by the catalyst stability.

The molecular weight values of the produced polyketones cover a broad range from 9 to 284 kDa. For comparative purposes, the number of inserted repetitive units per polymer chain ( $R.U._c$  = number of inserted repetitive units per polymer chain) is usually considered; in our case, the highest value is obtained for the CO/S copolymer synthesized with the precatalyst **5b** (1581 repetitive units corresponding to  $M_w$  = 209 kDa; Table 3 entry 13), whereas the lowest value is obtained for the CO/MS macromolecule produced with **1b** (62 repetitive units corresponding to  $M_w$  = 9 kDa; Table 3 entry 2). In agreement with the productivity data, a remarkable increase in the molecular weight is achieved going from the aldimine- to the ketimine-based catalysts. In addition, the molecular weight of the polyketones produced with the aldimine derivatives increases in the order **1b** < **7b** < **4b** < **9b**, regardless of the nature of the vinyl arene. However, clear trends of molecular weight values with respect to catalytic parameters, such as the nature of the vinyl arene or  $\alpha$ - versus  $\beta$ -ligands, are hardly evident, even by inspection of the TON values (Table 3), and in particular when the ketimine-based catalysts are considered. This might be due to the fact that the copolymerization runs are stopped after 24 h, when the ketimine-based catalysts are still very active, and this might be also the reason for having polydispersity values slightly higher than 2.

The stereochemistry of the synthesized copolymers was determined by <sup>13</sup>C NMR spectroscopy (Tables 4 and 5).

**Table 4. Triads Distribution in the CO/Vinyl Arene Polyketones Synthesized with Ketimine-Based Cationic Catalysts<sup>a</sup>**

entry	precat	vinyl arene	ll (%)	lu (%)	ul (%)	uu (%)
1	2b	S	2	15	13	70
2	2b	MS	2	17	15	66
3	2b	TBS			28	72
4	3b	S	3	15	9	73
5	3b	MS		13	11	76
6	3b	TBS			23	77
7	5b	S		11	10	79
8	5b	MS		12	11	77
9	5b	TBS			18	82
10	6b	S		8	7	85
11	6b	MS		9	7	84
12	6b	TBS			15	85
13	8b	S		10	9	81
14	8b	MS		12	10	78
15	8b	TBS			19	81

<sup>a</sup>Determined by <sup>13</sup>C NMR spectra recorded in HFIP/CDCl<sub>3</sub>, T = 298 K; integration of C<sub>ipso</sub> signals.

**Table 5. Triads Distribution in the CO/Vinyl Arene Polyketones Synthesized with Aldimine-Based Cationic Catalysts<sup>a</sup>**

entry	precat	vinyl arene	ll (%)	lu (%)	ul (%)	uu (%)	n <sub>i</sub> <sup>b</sup>	n <sub>u</sub> <sup>b</sup>
1	1b	S	28	15	16	41	2.8	3.6
2	1b	MS	50	17	15	18	4.1	2.1
3	1b	TBS	31		26	43	3.4	4.3
4	4b	S	7	10	12	71	1.6	7.5
5	4b	MS	24	15	13	48	2.7	4.4
6	4b	TBS	18		22	60	2.6	6.5
7	7b	S	17	15	16	52	2.1	4.4
8	7b	MS	30	19	16	35	2.7	3.0
9	7b	TBS	24		35	41	2.4	3.3
10	9b	S	38	16	13	33	3.6	3.3
11	9b	MS	56	8	9	27	7.6	4.2
12	9b	TBS	33		27	40	3.4	4.0

<sup>a</sup>Determined by <sup>13</sup>C NMR spectra recorded in HFIP/CDCl<sub>3</sub>, T = 298 K; integration of C<sub>ipso</sub> signals. <sup>b</sup>n<sub>i</sub> = length of the isotactic stereoblock, and n<sub>u</sub> = length of the syndiotactic stereoblock, determined according to ref 52.

The nature of the N-N' ligand remarkably affects the stereochemistry of the polyketones. In particular, macromolecules obtained with the ketimine-based catalysts have a prevalently syndiotactic microstructure (Table 4, Figures S113, S114, S116, S117, S119). For each vinyl arene comonomer, the content of the *uu* triad slightly increases going from the methyl- to phenyl-substituted ketimine catalyst (Table 4, entries 1, 2, 3 vs 4, 5, 6 and 7, 8, 9 vs 10, 11, 12), thus suggesting that the enantioface discrimination is more efficient when a phenyl ring—rather than a methyl group—is present on the imino carbon atom. Remarkably, the <sup>13</sup>C NMR spectra of copolymers synthesized by cationic catalysts with ligands **5**, **6**, and **8** show no signal for the *ll* triad, indicating that enantioface discrimination of the incoming vinyl arene comonomer is under *chain end* control.

The polyketones obtained with the aldimine-based catalysts showed a completely different microtacticity. In the <sup>13</sup>C NMR spectra of these macromolecules, the signals of all the four

triads are present, their relative abundance depending on both the catalyst and the vinyl arene comonomer (Table 5, Figures S112, S115, S118, S120). For each catalyst, an increase in the content of the *ll* triad was observed going from CO/S to CO/MS copolymers, with a concomitant decrease in the amount of the *uu* triad together with a similar distribution of the heterotactic triads. The observed microtacticity indicates that the produced macromolecules contain isotactic and syndiotactic stereoblocks with the heterotactic triads representing the junction points. This is further supported by the monomodal distribution of the GPC curves recorded for the molecular weight measurements (Figures S127–S129). Moreover, for each catalyst, the length of each stereoblock (n<sub>i</sub> and n<sub>u</sub>, Table 5) depends on the nature of the vinyl arene comonomer, indicating that the group in para position of the vinyl arene affects the stereochemistry of the obtained polyketones. As an example, with the catalyst [Pd(CH<sub>3</sub>)(CH<sub>3</sub>CN)(**1**)] [PF<sub>6</sub>], the CO/S and CO/TBS copolymers are mainly made by syndiotactic stereoblocks, whereas the isotactic stereoblocks prevail in the CO/MS polyketone (Table 5, entries 1, 3, 2). In addition, the isotactic blocks are longer for the copolymers obtained with catalysts having the α- rather than β-naphthyl or -anthracenyl moieties (Table 5, entry 1–3 vs 4–6, and 10–12 vs 7–9). This trend might be related to the different orientations of the α- and the β-bonded polycyclic aromatic fragments (see above).

These results are fully consistent with the hypothesis first advanced by us for catalysts based on pyrene-tagged iminopyridines,<sup>37</sup> that is that with aldimines bearing condensed aromatic rings on the N<sub>imm</sub>, the vinyl arene comonomer plays a fundamental role in controlling the stereochemistry of the synthesized macromolecules.

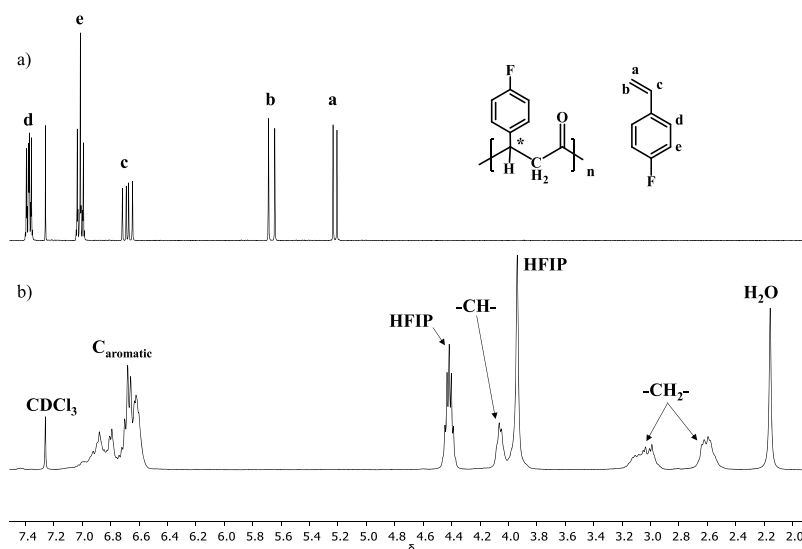
To shed light on the nature of the vinyl arene effect on the polyketone stereochemistry, the unprecedented copolymerization of carbon monoxide with 4-fluorostyrene (FS) was performed by using three different [Pd(CH<sub>3</sub>)(CH<sub>3</sub>CN)(N-N')][PF<sub>6</sub>] precatalysts, with N-N' = **phen** (**phenb**), **L4** (**L4b**), **4** (**4b**). In general, polar styrenes such as 4-fluorostyrene are challenging comonomers for coordination-insertion polymerization, and they are investigated for obtaining polar-functionalized ethylene/styrene copolymers.<sup>53</sup>

The phenanthroline-based complex is considered as a reference catalyst because it is known to generate a very efficient active species for the CO/vinyl arene copolymerization leading, under *chain end* control, to syndiotactic polyketones with 80% content of the *uu* triad.<sup>44,54,55</sup> All the three complexes, **phenb**, **L4b**, and **4b**, generate active catalysts for the CO/FS copolymerization, yielding the corresponding alternating polyketone that precipitated as a white or a grey solid (Table 6).

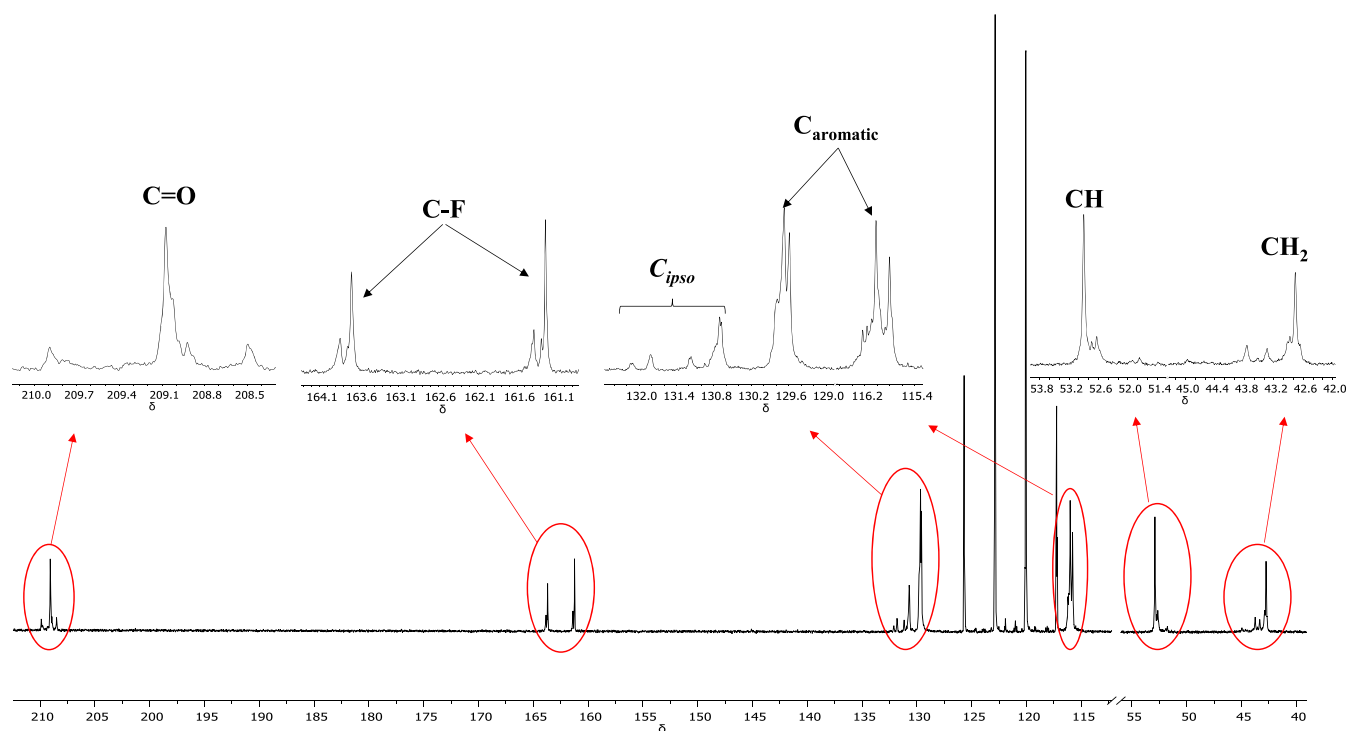
**Table 6. CO/FS Copolymerization: Effect of the N-N' Ligand<sup>a</sup>**

entry	precat.	yield (g)	kg CP/g Pd <sup>b</sup>
1	<b>phenb</b>	0.51	1.53
2	<b>L4b</b>	1.33	3.93
3	<b>4b</b>	0.12	0.36

<sup>a</sup>Reaction conditions: n<sub>Pd</sub> = 3.17 × 10<sup>-5</sup> mol; V<sub>TPE</sub> = 5 mL; V<sub>vinyl arene</sub> = 2.5 mL; [BQ]/[Pd] = 5; [FS]/[Pd] = 6600; T = 303 K; P<sub>CO</sub> = 1 bar; t = 24 h. <sup>b</sup>Productivity in kg CP/g Pd = kilograms of copolymer per gram of palladium.



**Figure 3.**  $^1\text{H}$  NMR spectra (HFIP/ $\text{CDCl}_3$ ,  $T = 298\text{ K}$ ) of: (a) 4-fluorostyrene, (b) CO/FS copolymer obtained with **4b**.



**Figure 4.**  $^{13}\text{C}$  NMR spectrum (HFIP/ $\text{CDCl}_3$ ,  $T = 298\text{ K}$ ) of the CO/FS copolymer obtained with **4b** with enlargements of the regions included in the red circles.

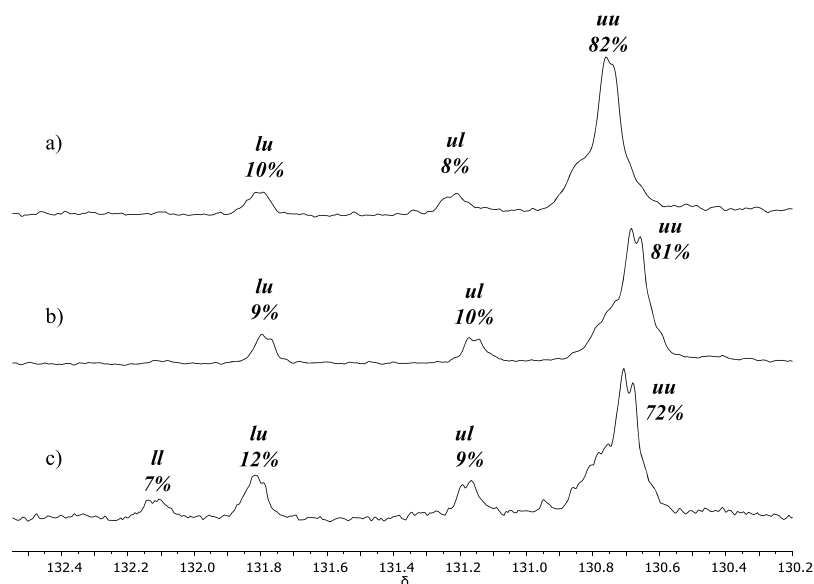
The N-N' ligand had a remarkable effect on the productivity, with **L4b** being more than twice as active as **phenb**. The low productivity of the catalyst **4b** is consistent with what observed above (Table 3) and is mainly because of the low stability of the active species; in fact, decomposition to palladium metal was observed within the first hour of the reaction. On the other hand, no evident formation of palladium black was observed with **phenb**, while slight decomposition took place for the catalyst **L4b**, thus suggesting that its higher productivity is because of its higher intrinsic activity compared to **phenb**.

The obtained CO/FS polyketones were characterized by mono- and bi-dimensional NMR spectroscopy recording  $^1\text{H}$ -,  $^{13}\text{C}$ -, and  $^{19}\text{F}$  NMR spectra in a HFIP/ $\text{CDCl}_3$  mixture, at room

temperature. In the  $^1\text{H}$  NMR spectrum, the presence of signals for the methinic and two diastereotopic methylenic protons, in addition to those of the aromatic rings, confirms the formation of the expected alternating copolymer (Figure 3). In the  $^{13}\text{C}$  NMR spectrum (Figure 4), the signal at 209 ppm indicates the presence of the carbonyl group ( $\nu_{\text{CO}} = 1696\text{ cm}^{-1}$  in IR spectrum). The carbon atom bonded to fluorine resonates as a doublet centered at 162.4 ppm, and the corresponding fluorine gives a broad peak at  $-115.5\text{ ppm}$  in the  $^{19}\text{F}$  NMR spectrum (Figure S125). The  $\text{C}_{\text{ipso}}$  resonance falls in the range 130.0–132.5 ppm (Figure 4).

As for the already known CO/vinyl arene polyketones, also for the newly synthesized CO/FS copolymer, the signal of the

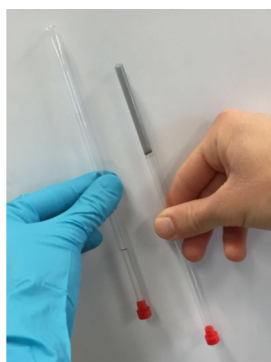




**Figure 5.**  $C_{\text{ipso}}$  region of the  $^{13}\text{C}$  NMR spectra (HFIP/ $\text{CDCl}_3$ ,  $T = 298\text{ K}$ ) of the CO/FS copolymers obtained with: (a) **phenb**; (b) **L4b**; and (c) **4b**.

$C_{\text{ipso}}$  atom is the most diagnostic feature for the stereochemistry characterization. The CO/FS polyketone synthesized with **phenb** shows in this region of the  $^{13}\text{C}$  NMR spectrum the signals of *uu* (82%), *ul* (8%) and *lu* (10%) triads (Figure 5a), thus indicating that the macromolecule—as expected for a **phen**-based catalyst—has a prevailing syndiotactic microstructure obtained under *chain end* control. A very similar microstructure is observed for the CO/FS copolymer produced with the ketimine-based catalyst **L4b** (Figure 5b), consistent with what previously found in the CO/vinyl arene copolymerization carried out with this ligand.<sup>38</sup> The  $^{13}\text{C}$  NMR spectrum of the CO/FS polyketone synthesized with **4b** has the signals of all the four triads (Figure 5c), in a distribution similar to that of the CO/S copolymer obtained with the same precatalyst, but different from that found for the CO/MS macromolecule (Table 5, entries 4 and 5). This result suggests that the effect of the vinyl arene on the stereochemistry of the copolymers is more steric than electronic in nature.

Finally, unlike the other CO/vinyl arene copolymers, the CO/FS polyketone makes a gel in the HFIP/ $\text{CDCl}_3$  solution (Figure 6).

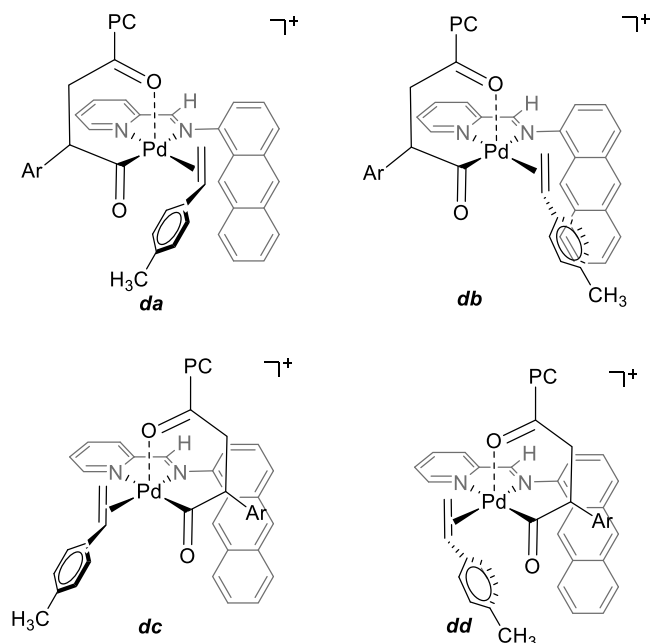


**Figure 6.** Picture of a HFIP/ $\text{CDCl}_3$  solution of: CO/S (left) and CO/FS (right) polyketones.

To tentatively explain the effects of the N-N' ligand and of the vinyl arene comonomer on the stereochemistry of the produced macromolecules, the intermediate responsible for the enantioface selection needs to be considered. According to the literature,<sup>7,56</sup> this species is the six-membered palladacycle resulting from the interaction with palladium of the oxygen atom of the second last inserted carbonyl group of the growing polymer chain; as a consequence, the palladium ion becomes a stereogenic center. In addition, because of the nonsymmetric nature of iminopyridine ligands, *cis* and *trans* isomers are possible depending on the relative position of the Pd-C bond of the growing polymer chain with respect to the two inequivalent halves of the ligand. Therefore, when the vinyl arene coordinates, four diastereoisomers can be obtained (Chart 4), depending on which prochiral face binds to palladium. It should be noted that the insertion of the vinyl arene into the growing polymer chain occurs regioselectively with a secondary regiochemistry; therefore, the diastereoisomers leading to the insertion with the primary regiochemistry are not considered. Assuming that for each diastereoisomer the ratio between *cis* and *trans* isomers is similar to that found for the precatalyst by NMR spectroscopy, a relationship between the ancillary ligand and the stereochemistry of the produced polyketone is unravelled. In particular, for precatalysts **3b**, **5b**, **6b**, and **8b**, that lead to syndiotactic copolymers, a 1:1 ratio between *cis* and *trans* isomers is observed. When this information is translated to the polymerization mechanism, it suggests that both sites on palladium can accommodate either the growing polymer chain or the incoming monomer, with no site-selective coordination. Therefore, all the four diastereoisomers are possible, leading to the obtained syndiotactic macromolecule under *chain end* control.

On the contrary, for precatalysts **1b**, **4b**, **7b**, and **9b**, the *trans* isomer is the prevailing species in solution, thus suggesting that during the polymerization process, the growing polymer chain might be preferentially (not site-selectively) located *cis* to the Pd-N<sub>pyr</sub> bond; therefore, the coordination of the vinyl arene occurs *cis* to the condensed aromatic rings on the imino nitrogen. As a consequence, diastereoisomers *da* and

**Chart 4. Four Possible Diastereoisomers Involved in the 4-Methyl styrene Enantioface Discrimination with Precatalyst 9b**



PC = growing polymeric chain

*db* are those preferred, and the aromatic fragment is capable to discriminate between the two enantiotopic faces of the incoming vinyl arene. This eventually leads to a preferential diastereoisomer, either *da* or *db*, and to a prevalingly isotactic stereoblock. In this scenario, the enantioface recognition is affected by the vinyl arene, being the result of  $\pi$ - $\pi$  stacking interactions between the arene comonomer and the polycyclic aromatic rings. This interaction becomes more efficient upon going from styrene to 4-methyl styrene, leading to the increased content of the *ll* triad. This hypothesis is also in agreement with the finding that catalysts with  $\alpha$ -naphthyl or  $\alpha$ -anthracenyl ligands led to copolymers with a higher content of the *ll* triad than the corresponding  $\beta$ -ones. Indeed, as observed above, the orientation of the  $\alpha$ -connected aromatic rings leads to more efficient interactions with the vinyl arene comonomer (compared to the  $\beta$ -ones) and, in turn, to a better enantioface discrimination. It is worth noting that  $\pi$ - $\pi$  stacking interactions between the ancillary ligand and styrene have been recently considered to be responsible for the production of syndiotactic CO/styrene polyketones by dibenzobarrelene- $\alpha$ -diimine-Pd catalysts.<sup>32</sup>

## CONCLUSIONS

In summary, we have investigated a library of aldo- and keto-iminopyridines (N-N') that feature an  $\alpha$ - or  $\beta$ -naphthyl or -anthracenyl group on the imino nitrogen atom. These molecules were used as ancillary ligands to obtain the neutral and cationic Pd(II)-complexes,  $[\text{Pd}(\text{CH}_3)\text{Cl}(\text{N-N}')]^+$  and  $[\text{Pd}(\text{CH}_3)(\text{CH}_3\text{CN})(\text{N-N}')][\text{PF}_6]^-$ , respectively. According to NMR spectroscopy, in solution, each complex is present as an equilibrium mixture of the *trans* and *cis* stereoisomers. In particular, the isomeric distribution of the cationic complexes depends on the nature of N-N': the ketimine-based complexes show a *ca.* equimolar *cis/trans* ratio, whereas the aldimine derivatives prefer the *trans* species.

The cationic complexes generate active catalysts for the copolymerization of carbon monoxide with styrene, 4-methyl styrene, 4-*tert*-butyl styrene, and 4-fluorostyrene, whose polyketone was synthesized for the first time with the catalysts under investigation. The catalytic results point out that catalyst productivity as well as copolymer molecular weight and stereochemistry depend both on the nature of N-N' and of the vinyl arene comonomer. In particular:

- Ketimine-based catalysts are more stable and more productive than the aldimine counterparts, reaching productivities higher than 5 kg CP/g Pd;
- They produce prevalingly syndiotactic polyketones with molecular weight values up to 280 kDa;
- Catalysts with the  $\beta$ -connected polycyclic fragment show higher productivities than the corresponding  $\alpha$ -derivatives;
- Among the tested vinyl arene comonomers, the highest productivity is achieved with styrene;
- The highest productivity (5.60 kg CP/Pd) is achieved in the CO/S copolymerization performed with the catalyst having the  $\beta$ -naphthyl-ketimine ligand **5**;
- The highest stereocontrol is obtained with precatalyst **6b** that produces both CO/S and CO/TBS syndiotactic copolymers with 85% content of the *uu* triad;
- The aldimine-based catalysts lead to copolymers with isotactic and syndiotactic stereoblocks;
- The length of each stereoblock depends on the nature of the vinyl arene: CO/4-methyl styrene polyketones are mainly made by isotactic stereoblocks, whereas syndiotactic blocks prevail in both CO/styrene and CO/4-*tert*-butyl styrene copolymers, thus indicating that the stereochemistry of the polyketones is affected by a slight variation of the vinyl arene comonomer on a position remote from the vinylic double bond.

As a general point, the results presented in this paper conclusively demonstrate that when the catalyst is based on a nonsymmetric ancillary ligand that leads to an equilibrium mixture of two stereoisomers, the stereochemistry of the obtained copolymers is driven by both the catalyst isomeric distribution and the prochiral comonomer.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.macromol.0c01461>.

Crystallographic data for **1a** (CIF)

Crystallographic data for **2a** (CIF)

Crystallographic data for **3a** (CIF)

Crystallographic data for **4a** (CIF)

Crystallographic data for **8a** (CIF)

Crystallographic data for **9a** (CIF)

Experimental Section including synthesis and characterization of ligands and complexes, procedure of catalytic reactions, NMR spectra, X-ray data, NMR spectra, and GPC traces of the polyketones (PDF)

### Accession Codes

CCDC 2009573 for **1a**, 2010094 for **2a**, 2009574 for **3a**, 2009575 for **4a**, 2009576 for **8a**, and 2009577 for **9a**, contain the supplementary crystallographic data for this paper.

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### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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### Notes

The authors declare no competing financial interest.

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