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Palladium complexes with simple iminopyridines as catalysts for polyketone synthesis

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# Dalton Transactions

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## Palladium complexes with simple iminopyridines as catalysts for polyketone synthesis

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Four iminopyridines (N–N') differing for the nature of the substituents on the iminic carbon and on the *ortho* positions of the aryl ring (H or CH<sub>3</sub>) on the iminic nitrogen were used for the synthesis of neutral and monocationic palladium(II) complexes of general formula [Pd(CH<sub>3</sub>)Cl(N–N')] and [Pd(CH<sub>3</sub>)(NCCH<sub>3</sub>)(N–N')][PF<sub>6</sub>]. The detailed NMR characterization in solution highlighted that: *i.* for both series of complexes, the Pd–CH<sub>3</sub> signal is progressively shifted at lower frequency on increasing the number of methyl groups on the ligand skeleton; *ii.* for the neutral derivatives, the chemical shift of the <sup>15</sup>N NMR signals, determined through {<sup>1</sup>H,<sup>15</sup>N}-HMBC spectra, is significantly affected by the coordination to palladium; *iii.* the coordination induced shift (CIS) of the nitrogen atom *trans* to the CH<sub>3</sub> ligand is smaller than the other. The structure in solid state for the neutral derivatives with all the four ligands was solved, pointing out that: *iv.* the Pd–C bond distance increases with the basicity of the nitrogen-donor ligand; *v.* the Pd–N bond distance correlates well with the CIS value. The combining of the solution and solid state structural features allows to state that: *vi.* the Pd–CH<sub>3</sub> singlet is a good probe for the electron donor capability of the ligand; *vii.* the CIS value might be used as a probe for the strength of the Pd–N bond. All monocationic complexes generated active catalysts for the CO/vinyl arene copolymerization, leading to prevalently syndiotactic polyketones. The catalyst performances, both in terms of catalyst productivity and polymer molecular weight, correlate well with the precatalyst structural features.

### Introduction

The discovery, independently made by Brookhart and Gibson, that iron and cobalt complexes with bis(imino)pyridine ligands are excellent catalysts for ethylene polymerization had a galvanizing effect on this field, leading to the development of a huge number of nitrogen-donor ligands belonging to this class and to the related family of the bidentate iminopyridines (N–N').<sup>1–4</sup>

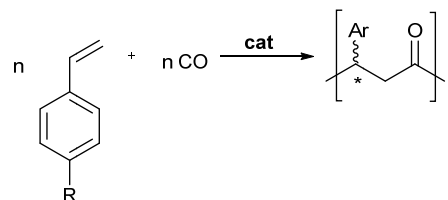
By virtue of their inexpensive, relatively easy and modular synthesis, iminopyridines are widely used as ancillary ligands in coordination chemistry. Their relevant iron, cobalt, nickel and palladium complexes have been extensively applied as homogeneous catalysts for alkene oligomerization and homopolymerization.<sup>5–7</sup>

In the catalytic polymerization of terminal alkenes, the control

on the polymer stereochemistry is a very important goal. Many efforts have been, and are currently, addressed to the development of homogeneous catalysts capable of controlling the stereochemistry in propylene polymerization. Similarly, the control of the stereochemistry is also highly relevant in the polyketones, obtained through the direct, alternating copolymerization of carbon monoxide with terminal alkenes.<sup>8–</sup>

<sup>10</sup> Unlike polypropylene, polyketones are one of the few examples of polymers with main chain chirality. Thus, when synthesized by catalysts having enantiomerically pure ancillary ligands, the isotactic polyketones are optically active macromolecules.

The synthesis of polyketones is typically catalyzed by palladium(II) complexes. In the case of vinyl arene comonomers, nitrogen-donor ancillary ligands were found to give the best results (Scheme 1).<sup>11,12</sup>



**Scheme 1.** The CO/vinyl arene copolymerization (R = H, Me, <sup>t</sup>Bu).

In analogy to Ewen's symmetry rules that rationalize the stereochemistry control in the polypropylene synthesis,<sup>13</sup> a

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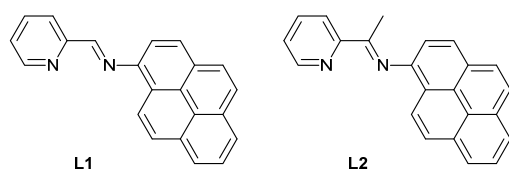
† Footnotes relating to the title and/or authors should appear here.

Electronic Supplementary Information (ESI) available: Essential crystal and refinement data (Table 1S); <sup>1</sup>H NMR spectra of compounds 1-4; <sup>1</sup>H, NOE, COSY, {<sup>1</sup>H,<sup>13</sup>C}-HSQC NMR spectra of compounds 1a,b-4a,b; {<sup>1</sup>H,<sup>15</sup>N}-HMBC NMR spectra of compounds 1,2,4 and 2a-4a; <sup>1</sup>H NMR spectra of the reactivity of 1b with CO; CCDC 1496465 (1a), 1496466 (2a), 1496468 (3a), 1496469 (4a). See DOI: 10.1039/x0xx00000x

relationship between the symmetry of the support ligand on the Pd catalyst and the tacticity of the macromolecule was established also for CO/vinyl arene copolymerization. In fact, whereas Pd complexes with  $C_{2v}$  symmetric ligands like 2,2'-bipyridine<sup>14</sup> and 1,10-phenanthroline<sup>15</sup> afforded syndiotactic polyketones, enantiomerically pure  $C_2$  symmetric ligands such as bi- or bis-oxazolines,<sup>16-18</sup> aza bis-oxazolines,<sup>19</sup> and diketimines<sup>20</sup> led to the formation of isotactic copolymers.  $C_s$  ligands have been reported to yield both syndio- and atactic polyketones,<sup>21</sup> whereas all the possible microstructures are obtained using  $C_1$  ligands.<sup>22-25</sup> CO/vinyl arene polyketones with isotactic stereoblocks have been synthesized using Pd catalysts with  $\alpha$ -diimine ligands.<sup>26-28</sup>

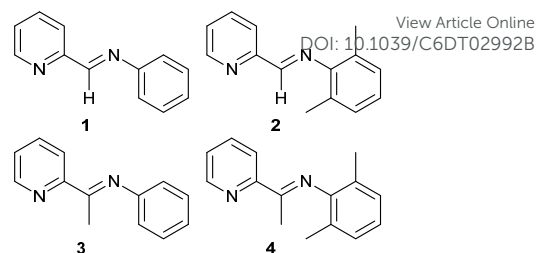
In contrast to the polyethylene synthesis, the application of catalysts based on iminopyridines for the CO/vinyl arene polyketone synthesis is much less developed. The reported examples include Pd-catalysts with iminopyridines having aliphatic groups on the imino nitrogen atom,<sup>29</sup> dinuclear complexes<sup>30</sup> and dendritic species.<sup>31</sup> In addition, palladium complexes with pyridylimines having 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.<sup>32</sup>

We have recently reported the unprecedented finding that, in the Pd-catalyzed CO/vinyl arene copolymerization, the stereochemistry of the polyketone depends on the nature of the comonomer.<sup>33</sup> In particular, we found that – using a palladium catalyst based on a pyrene-tagged iminopyridine (Figure 1) – the tacticity of the polyketone changed from syndiotactic to isotactic and to atactic when styrene, 4-methyl styrene and 4-butyl styrene were used as comonomer, respectively. The statistical analysis of the microtacticity of the obtained macromolecules showed that the vinyl arene dependent stereochemistry was due to a switch from the *enantiomorphic site* control for 4-methyl styrene to a combination of *enantiomorphic* and *chain-end* control for styrene.



**Figure 1.** The reported pyrene-tagged iminopyridines **L1**, **L2**.

With the aim to get a deeper understanding on the nature of this peculiar stereocontrol mechanism, we investigated the catalytic behavior of Pd complexes with four different iminopyridines: the imino nitrogen bears either a phenyl or a 2,6-dimethylphenyl and the imino carbon atom has either a hydrogen atom or a methyl group (Figure 2).

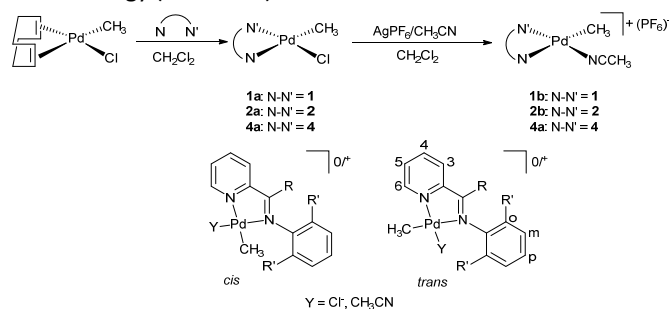


**Figure 2.** The currently investigated iminopyridines **1-4**.

## Results and discussion

**Synthesis and characterization of ligands 1-4 and of their Pd(II) complexes.** Ligands **1**, **2** and **4** were synthesized by slightly modified literature procedures,<sup>34</sup> based on the condensation reaction between the carbonyl derivative of pyridine and the desired aniline, optimizing the reaction time and the reagents ratio. Ligands **1**, **2** and **4** were obtained as brown oils, with yields in the range 40 – 80 %, and their NMR characterization in solution is in agreement with the literature.<sup>34, 35</sup> The NMR spectra highlighted that upon going from **1** to **2**, the singlet of the iminic proton moves to lower frequency (8.59 vs 8.31 ppm, respectively), and the singlet of the methyl groups on the phenyl ring shifts in the same direction from **2** to **4** (2.14 vs 2.01 ppm, respectively). This indicates that these groups are mutually affected, thus suggesting that these positions might be crucial in determining the electron density on the imino nitrogen and therefore they might have a key role in the catalytic behavior of the complexes.

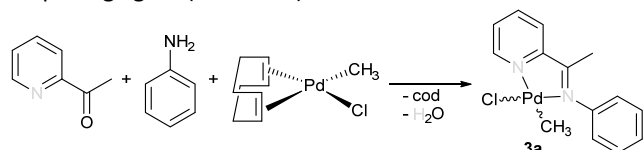
The ligands were reacted with [Pd(cod)(CH<sub>3</sub>)Cl] (cod = 1,5-*cis,cis*-cyclooctadiene) to obtain the corresponding neutral derivatives [Pd(CH<sub>3</sub>)Cl(N–N')] (**1a**, **2a**, **4a**; N–N' = **1**, **2**, **4**) as yellow solids in high yields (87 – 94 %) following the literature methodology (Scheme 2).<sup>15, 36</sup>



**Scheme 2.** Synthesis of palladium neutral **1a**, **2a**, **4a** and monocationic **1b**, **2b**, **4b** complexes. *cis* and *trans* isomers for the neutral and monocationic complexes and related numbering scheme.

When the synthetic procedure used for ligands **1**, **2** and **4** was applied to **3**, a modest yield of 15 % was achieved after 72 h of reaction. Longer reaction times afforded lower yields and increasing amounts of unidentified byproducts. An improved yield of **3** (30%) was obtained by following the literature procedure, that uses a Dean-Stark apparatus.<sup>35</sup> However, its purification from the several byproducts was unsuccessful, and

it was not possible to obtain **3** as a pure compound by this route. Therefore, the neutral complex  $[\text{Pd}(\text{CH}_3)\text{Cl}(\mathbf{3})]$ , **3a**, was obtained in pure form in 85 % yield through a template synthetic procedure, by reacting 2-acetyl pyridine with a slight excess of aniline in the presence of  $[\text{Pd}(\text{cod})(\text{CH}_3)\text{Cl}]$  as templating agent (Scheme 3).



**Scheme 3.** Template synthesis of complex **3a**.

The neutral complexes are fully characterized both in solid state, through elemental analysis and X-ray diffraction, and in solution by NMR spectroscopy, recording the spectra in  $\text{CD}_2\text{Cl}_2$ , at room temperature (ESI). The assignments are accomplished on the basis of homo- and heteronuclear bidimensional NMR spectroscopy. According to NMR spectroscopy, each neutral complex exists in solution as a mixture of two isomers. NOE experiments established that the major species is always that with the  $\text{CH}_3$  ligand *cis* to the imino nitrogen; for the sake of clarity, this species is defined as the *cis* isomer (Scheme 2).<sup>33</sup> Moreover, at room temperature, the two isomers are in slow exchange on the NMR timescale.

These findings are in agreement with what found by us and others with similar, neutral Pd–methyl complexes bearing pyridylimine ligands<sup>31, 33</sup> or other bidentate nitrogen-donor ligands with inequivalent N-donor atoms,<sup>15, 24, 37-40</sup> in each case the most abundant isomer is that with the methyl group to be coordinated *trans* to the N-atom with the lowest Lewis basicity.

The *cis* : *trans* ratio depends on the nature of the ligand coordinated and increases in the order **1a** (75 : 25) < **3a** (94 : 6) < **2a** (97 : 3) < **4a** (98 : 2). This trend seems to be mainly electronic in nature, since it goes along with the number of methyl groups on the ligand, which increases the basicity of the imino nitrogen atom. It also confirms our previous hypothesis that the distribution of the two isomers in the neutral complexes of this type is mainly driven by the electronic properties of the chelating ligand, assuming that the methyl and the chlorido ligands have similar steric bulk.<sup>33</sup>

The coordination of the iminopyridine to palladium involves also a conformational change from *E,trans* (in the free ligand) to *E,cis*. The most affected protons are  $\text{H}^6$  and  $\text{H}^3$ , whose signals move in opposite directions upon coordination (proton  $\text{H}^6$  to higher frequency,  $\text{H}^3$  to lower frequency, Table 1).

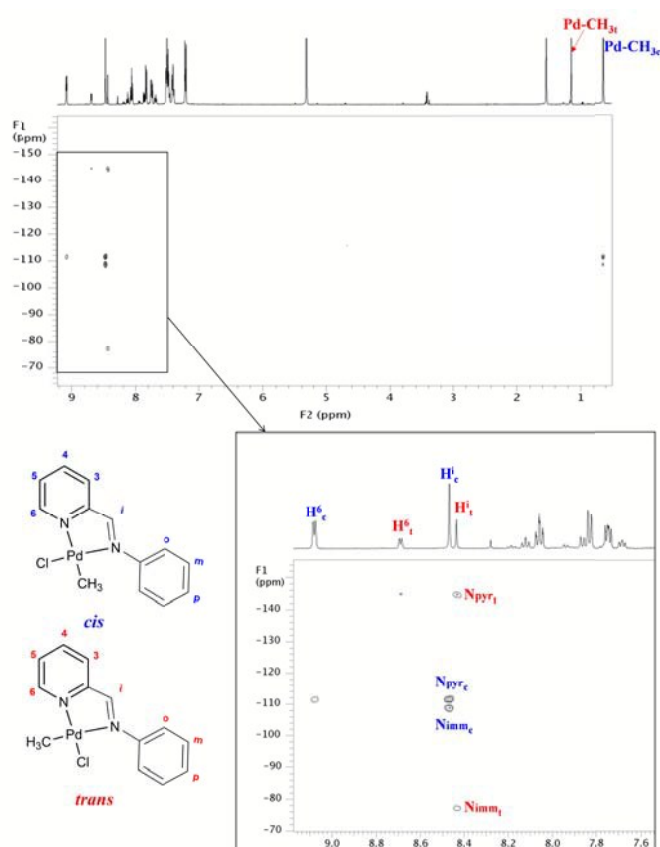
**Table 1.** Selected chemical shift values for free ligands and palladium complexes (*cis* isomer). DOI: 10.1039/C6DT02992P

Ligand/ complex	$\text{H}^6$	$\text{H}^1/\text{CH}_3^i$	$\text{H}^3$	Ar- $\text{CH}_3$	Pd- $\text{CH}_3$ ( <i>cis</i> )	Pd- $\text{CH}_3$ ( <i>trans</i> )
<b>1</b>	8.69	8.59	8.21	-	-	-
<b>2</b>	8.69	8.31	8.28	2.14	-	-
<b>4</b>	8.65	2.15	8.36	2.01	-	-
<b>1a</b>	9.09	8.46	7.83	-	0.63	1.15
<b>2a</b>	9.10	8.35	7.84	2.26	0.38	1.06
<b>3a</b>	9.16	2.24	7.91	-	0.35	0.98
<b>4a</b>	9.19	2.14	7.90	2.18	0.18	0.94
<b>1b</b>	8.74	8.46	7.98	-	0.78	1.24
<b>2b</b>	8.79	8.35	7.97	2.23	0.53	1.17
<b>3b</b>	8.74	2.34	8.04	-	0.49	1.05
<b>4b</b>	8.76	2.25	8.04	2.15	0.33	1.06

<sup>1</sup>H NMR spectra recorded in  $\text{CD}_2\text{Cl}_2$  at 298 K; chemical shifts are reported in ppm.

For both isomers, moving from **1a** to **4a**, the Pd- $\text{CH}_3$  singlet progressively shifts at low frequency (Table 1), in agreement with the expected increase in the electron density on the metal center due to the higher Lewis basicity of the ligand. This trend supports our hypothesis that this signal might be considered as a good probe for assessing the electron density donated by the ligand to the metal center.<sup>37</sup>

For ligands **1**, **2** and **4** and complexes **1a-4a**, the <sup>15</sup>N NMR spectra were recorded by  $\{^1\text{H}, ^{15}\text{N}\}$ -HMBC experiments at natural abundance of the <sup>15</sup>N isotope. In the spectrum of each ligand, the cross peak of the imino nitrogen (*Nimm*) with the singlet of the substituent on the imino carbon atom ( $\text{H}$  or  $\text{CH}_3$ ) is observed. In addition, for ligand **1** the cross peak between the pyridine nitrogen (*Npyr*) and  $\text{H}^5$  is also present (Table 2).



**Figure 3.**  $\{^1\text{H}, ^{15}\text{N}\}$ -HMBC spectrum of **1a** in  $\text{CD}_2\text{Cl}_2$  at 298 K. Enlargement of the aromatic region in the box.

The  $^{15}\text{N}$  chemical shifts in the neutral complexes (both isomers) were assigned mainly through the cross peaks with the resonances of the ligand protons (Figure 3, ESI). In addition, for all the *cis* isomers (as well as for *trans* **1a** and **3a**) the cross peaks of both nitrogen atoms with the Pd-CH<sub>3</sub> singlet are observed (Table 2, ESI). In agreement with the literature,<sup>36, 41, 42</sup> the cross peak between the Pd-CH<sub>3</sub> singlet and the N-atom *trans* to it is more intense than the other.

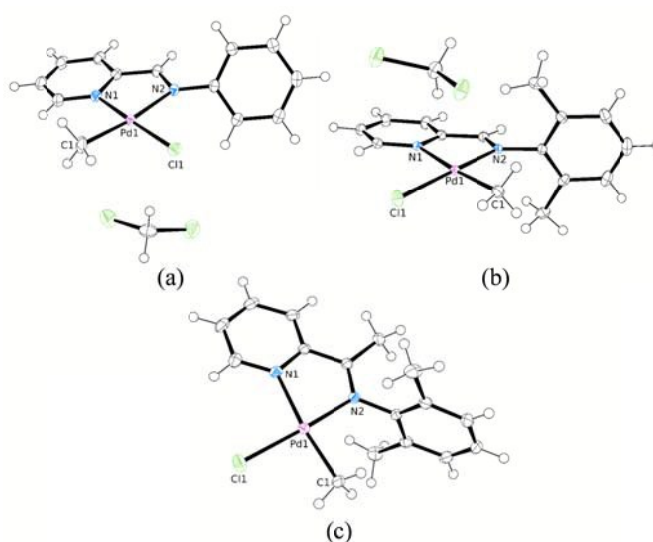
**Table 2.** Chemical shift values of  $^{15}\text{N}$  for ligands **1**, **2**, **4** and complexes **1a-4a**.<sup>[a]</sup>

Ligand/complex	Npyr (CIS)	Nimm (CIS)
<b>1</b>	-63.0	-43.9
<b>1a</b>	-111.4 (-48.4) <sub>cis</sub>	-109.0 (-65.1) <sub>cis</sub>
	-144.8 (-81.8) <sub>trans</sub>	-77.2 (-33.3) <sub>trans</sub>
<b>2</b>	n.o.	-34.3
<b>2a</b>	-111.7 <sub>cis</sub>	-107.9 (-73.6) <sub>cis</sub>
		-91.7 (-57.4) <sub>trans</sub>
<b>3a</b>	-112.5 <sub>cis</sub>	-116.9 <sub>cis</sub> , -80.8 <sub>trans</sub>
<b>4</b>	n.o.	-44.2
<b>4a</b>	-112.3 <sub>cis</sub>	-118.6 (-74.4) <sub>cis</sub>

<sup>[a]</sup> Measured at 50.64 MHz in  $\text{CD}_2\text{Cl}_2$  at 298 K; chemical shifts are reported in ppm; CIS = Coordination Induced Shift, obtained as difference between the chemical shift of the complex and that of the related ligand.

Coordination to palladium resulted in Coordination Induced Shifts (CIS) of 30 – 90 ppm of the  $^{15}\text{N}$  resonances (Table 2). In

each complex the resonance of the nitrogen atom (either *Npyr* or *Nimm*) *trans* to the CH<sub>3</sub> ligand has a CIS value smaller than when it is *trans* to the Cl (Table 2, i.e. for **1a** 48.4 vs 81.8 ppm and 33.3 vs 65.1 ppm). This trend is in agreement with the literature,<sup>36, 41-43</sup> and suggests that the CIS value might be directly related to the strength of the Pd-N bond, i.e. inversely related to the *trans*-influence of the ligand in *trans* (CH<sub>3</sub> > Cl). Slow diffusion of n-hexane into a  $\text{CH}_2\text{Cl}_2$  solution of each complex at 277 K resulted in single crystals suitable for X-ray analysis (Figures 4, 5).



**Figure 4.** ORTEP representation (thermal ellipsoids at 50% probability level) of complexes: (a) *trans*-**1a**; (b) *cis*-**2a**; (c) *cis*-**4a**.

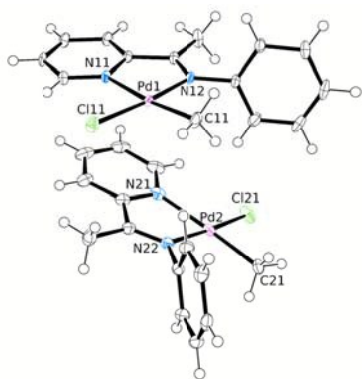
**Table 3.** Selected bond lengths (Å) and angles (°) for **1a**, **2a** and **4a**.

	<b>1a</b>	<b>2a</b>	<b>4a</b>
Pd(1)-N(1)	2.0545(16)	2.1495(13)	2.1319(15)
Pd(1)-N(2)	2.1707(15)	2.0343(14)	2.0352(14)
Pd(1)-C(1)	2.0417(19)	2.0284(15)	2.0414(17)
Pd(1)-Cl(1)	2.3027(5)	2.2954(8)	2.3049(5)
N(1)-Pd(1)-N(2)	79.02(6)	79.05(5)	78.40(6)
C(1)-Pd(1)-Cl(1)	88.56(6)	91.09(5)	89.25(5)
C(1)-Pd(1)-N(1)	93.96(8)	173.15(6)	173.01(6)
C(1)-Pd(1)-N(2)	172.31(7)	94.11(6)	94.70(6)
N(2)-Pd(1)-Cl(1)	98.50(4)	173.07(4)	174.52(4)
N(1)-Pd(1)-Cl(1)	177.43(4)	95.76(4)	97.71(4)
Dihedral angle	52.65(4)	81.70(6)	86.05(3)

In all complexes the palladium ion, coordinated by the N-donor bidentate ligand, the chlorido and the methyl group, displays the expected square planar coordination geometry (Figures 4, 5; Tables 3, 4). In each complex the iminopyridine ligand has a very similar and relatively small bite angle (ca 78–79°). The dihedral angle between the aryl ring and the coordination plane is close to 90° for the complexes having the methyl groups on either the aryl ring or the imino carbon atom, whereas it is 52° for **1a** (Tables 3, 4).

For complexes **1a**, **2a**, **4a** the unit cell contains four molecular entities, one of which is crystallographically independent. The unit cell of complex **3a** is substantially larger and contains eight molecules, the asymmetric unit consisting of two molecular entities (Figures 4, 5 and Table S1).

The crystals of complexes **2a**, **3a** and **4a** contain the *cis* isomer, which is also the species present in higher concentration in solution, as indicated by the NMR analysis. On the other hand, the crystals of **1a** contain the *trans* isomer, which is the minority species in solution.



**Figure 5.** ORTEP representation (thermal ellipsoids at 50% probability level) of the asymmetric unit of the crystal structure of complex *cis*-**3a**.

Table 4. Selected bond lengths (Å) and angles (°) for <b>3a</b> .		
Pd(1)–N(11)	2.125(2)	2.121(2)
Pd(1)–N(12)	2.039(2)	2.051(2)
Pd(1)–C(11)	2.021(2)	2.040(2)
Pd(1)–Cl(11)	2.2909(6)	2.2996(7)
N(11)–Pd(1)–N(12)	78.59(6)	78.09(7)
C(11)–Pd(1)–Cl(11)	90.36(6)	88.07(6)
C(11)–Pd(1)–N(11)	172.66(7)	175.72(8)
C(11)–Pd(1)–N(12)	94.68(7)	97.63(7)
N(12)–Pd(1)–Cl(11)	174.64(4)	173.58(5)
N(11)–Pd(1)–Cl(11)	96.28(4)	96.20(5)
Dihedral angle	80.63(5)	76.25(5)
Correspondent atom labels for the second molecule are Pd(2), N(21), N(22), C(21), and Cl(21) (see Figure 4).		

In all complexes the Pd–N bond distance *trans* to CH<sub>3</sub> is remarkably longer than the other one, in agreement with the stronger *trans* influence of the methyl group with respect to the chlorido. For the nitrogen atom *trans* to CH<sub>3</sub>, the Pd–N bond length correlates well with the CIS value, that is the longest is the Pd–N bond and the lowest is the CIS value, thus supporting the hypothesis that, in the absence of an X-ray structure, the CIS value might be used as a probe for the strength of the Pd–N bond.

In the *cis* isomers, the Pd–C bond distance increases in the order **2a** = **3a** < **4a** (2.0284(15) vs 2.030(2) (average value) vs 2.0414(17)), i.e. with the basicity of the iminopyridine ligand, indicating that the  $\sigma$ -donation from the methyl group to palladium decreases in the same order. This trend is consistent

with the progressive shift to lower frequency of the <sup>1</sup>H NMR Pd–CH<sub>3</sub> singlet moving from **1a** to **4a** and, therefore, it strongly supports our hypothesis that this signal is a good probe for the electron donor capability of the ligand.

The neutral complexes were converted into the cationic precatalysts [Pd(CH<sub>3</sub>)(NCCH<sub>3</sub>)(N–N')][PF<sub>6</sub>] (**1b–4b**; N–N' = **1–4**) through the chloride abstraction with AgPF<sub>6</sub> at room temperature in the presence of CH<sub>3</sub>CN, according to the published protocol.<sup>15, 36</sup> Complexes **1b–4b** were obtained as white solids in yields ranging from 70 to 90 %, and fully characterized both in solid state, by elemental analysis, and in solution by NMR spectroscopy (see ESI). As for the neutral complexes, also **1b–4b** were obtained as mixtures of *cis* and *trans* isomers, identified by NOE experiments, in slow exchange on the NMR timescale at room temperature. While for the neutral complexes the *cis* isomer always prevails in solution, for the cationic derivatives the major isomer depends on the nature of the ligand: the *cis* isomer prevails for **2b** (*cis* : *trans* = 87 : 13) and **4b** (97 : 3), while it is the minor species for **1b** (26 : 74) and a nearly 1 to 1 ratio between the two isomers is found for **3b** (46 : 54). This might be related to the fact that when the chlorido ion is replaced by the linear acetonitrile, the difference in steric hindrance of the two groups coordinated on palladium (methyl vs acetonitrile) is increased with respect to the difference between methyl and chloride, thus suggesting that steric effects start to play a role in determining the prevailing isomer. In fact, whereas the prevalence of the *cis* isomer for **2b** and **4b**, both featured by methyl groups on the aryl ring of the ligand, indicates that the electronic effects are still dominating, for complexes **1b** and **3b** the higher relative amount of the *trans* isomer suggests that the isomer distribution in solution is the result of both electronic and steric factors.

In the cationic complexes, the CH<sub>3</sub> ligand resonates at higher frequency than in the parent neutral compounds, in agreement with the net charge. Moreover, as for the neutral complexes, this singlet progressively shifts towards lower frequency moving from **1b** to **4b**, in both *cis* and *trans* isomers, thus further confirming that its resonance is a sensitive probe for the donating capability of the ligand. In addition, for both series of complexes this shift is more pronounced for the *cis* than for the *trans* isomer ( $\Delta\delta$  = 0.45 ppm vs  $\Delta\delta$  = 0.21 – 0.18 ppm, respectively), thus suggesting that it might be originated by the combination of the increase in the electronic density on the metal center and the shielding effect of the aryl ring *cis* to the Pd–CH<sub>3</sub> moiety.

**CO/vinyl arene copolymerization reactions.** Cationic complexes **1b–4b** were tested as precatalysts for the copolymerization of carbon monoxide with styrene (S) or 4-methyl styrene (MS). The copolymerization reactions were performed in 2,2,2-trifluoroethanol (TFE) at 303 K and under 1 bar of CO, and with a slight excess of 1,4-benzoquinone (BQ) with respect to palladium (Table 5), i.e. the same reaction conditions previously applied by us with the catalysts having the pyrine-tagged pyridylimines.<sup>33</sup> The produced polyketones



precipitated during the copolymerization reaction as white or grey solids.

**Table 5.** CO/vinyl arene copolymerization: effect of ancillary ligand, and of vinyl arene.<sup>[a]</sup> Precatalyst: [Pd(CH<sub>3</sub>)(NCCH<sub>3</sub>)(N–N')][PF<sub>6</sub>], **1b–4b**.

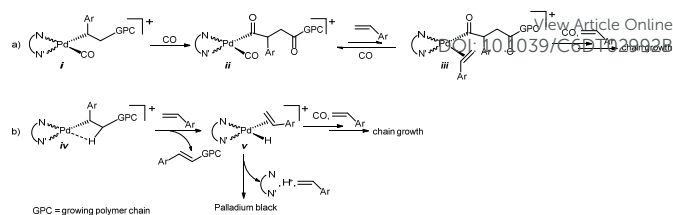
RUN	N–N'	Vinyl arene	Yield (g)	kg CP/g Pd <sup>[b]</sup>	Mw (Mw/Mn)
1	<b>1</b>	S	1.54	1.14	8 000 (2.6)
2	<b>2</b>	S	4.82	3.57	84 000 (1.7)
3	<b>3</b>	S	5.86	4.34	138 000 (2.4)
4	<b>4</b>	S	3.56	2.64	278 000 (1.4)
5	<b>1</b>	MS	0.80	0.59	11 000 (1.6)
6	<b>2</b>	MS	3.61	2.67	46 000 (1.7)
7	<b>3</b>	MS	5.23	3.87	85 000 (2.8)
8	<b>4</b>	MS	4.24	3.14	244 000 (2.00)

<sup>[a]</sup> Reaction conditions:  $n_{\text{Pd}} = 1.27 \cdot 10^{-5}$  mol,  $V_{\text{TFE}} = 20$  mL,  $V_{\text{arene}} = 10$  mL,  $[S]/[\text{Pd}] = 6800$ ,  $[\text{MS}]/[\text{Pd}] = 6000$ ,  $[\text{BQ}]/[\text{Pd}] = 5$ ,  $T = 303$  K,  $P_{\text{CO}} = 1$  bar,  $t = 24$  h. <sup>[b]</sup> kg CP/g Pd = kilograms of copolymer per gram of palladium.

All complexes generated active catalysts for the target copolymerization, showing a remarkable effect of the N–N' ligand on the productivity. Regardless of the vinyl arene used, compound **1b** was the least productive, while the highest value of productivity (4.34 kg CP/g Pd) was obtained with **3b** (Table 5). In the CO/S copolymerization, negligible decomposition to inactive palladium black was observed after 24 h, with the exception of **1b**, for which traces of palladium black were detected already after 4 h of reaction. In the case of CO/MS copolymerization, traces of palladium black were detected within the first hour of reaction for **1b**, and after 6 h for **2b** and **3b**, whereas no decomposition was detectable for **4b**.

A meaningful comparison with the catalysts reported in the literature, that use other iminopyridines, is made difficult by the very different reaction conditions employed. Nevertheless, remarkably lower productivities in the synthesis of polyketones, with lower molecular weights, compared to those found here were reported.<sup>29–31</sup> Also catalysts having ligands **L1** and **L2**, that were tested under the same reaction conditions as here, afforded a slightly lower productivity.<sup>33</sup> In addition, as found for **L1** and **L2**,<sup>33</sup> the ketimine derivatives **3b** and **4b** have, in general, a higher productivity compared to the corresponding aldimine compounds **1b** and **2b**, respectively. The only exception was found with styrene, where **2b** was more productive than **4b** (Table 5).

To explain the effect of the ligand nature on the productivity, the propagation and termination steps of the catalytic cycle will be considered. It is well accepted that the propagation step consists of two alternating migratory insertions (Scheme 4a): 1) that of CO into the Pd–alkyl bond, leading to the formation of the Pd–acyl carbonyl species, the *catalyst resting state* (ii), and 2) that of the vinyl arene into the Pd–acyl bond, the rate determining step of the catalytic cycle. The termination reaction is the  $\beta$ -hydrogen elimination leading to the formation of the Pd–H intermediate ( $\nu$ ), on which either catalyst decomposition, through the dissociation of the N-donor ligand, or the growth of a new polymeric chain can occur (Scheme 4b).<sup>26, 44, 45</sup>



**Scheme 4.** a) The propagation and b) the termination steps of the copolymerization catalytic cycle.

Therefore, the growth in productivity from **1b** to **3b** is reasonably ascribed to the higher catalyst stability that - in agreement with the NMR data about the ligand coordination capability - increases in the same order. The same consideration is valid for the CO/MS copolymerization catalyzed by **2b** and **4b**. Instead, the lower productivity of **4b** compared to **2b** in the CO/S copolymerization is not related to the catalyst stability, since negligible decomposition to palladium black is observed in both cases, and might be due to the different intrinsic activity of the two catalysts. Indeed, the higher electron density on the metal center for **4b**, suggested by the NMR data, might both increase the strength of the CO coordination in the *catalyst resting state* (ii) and disfavor the nucleophilic attack of styrene, resulting in a less active catalyst. In the case of 4-methyl styrene, the effect of ligand **4** on the palladium electron density is counterbalanced by the higher nucleophilicity of the more electron rich comonomer.

The effect of the ligand nature on the productivity is reflected on the molecular weight values of the polyketones, that increase in the order **1b** < **2b** < **3b** < **4b** regardless of the vinyl arene, thus indicating that the ratio between the propagation and the termination rates increases in the same order. The highest values of Mw obtained with catalyst having ligand **4** are in agreement with the fact that the termination step occurs with an associative mechanism assisted by an incoming vinyl arene molecule (Scheme 4b),<sup>45</sup> that is disfavored by the steric hindrance created by the methyl groups on ligand **4**.

The reactivity with carbon monoxide was investigated by *in situ* NMR spectroscopy bubbling CO into a 10 mM, CD<sub>2</sub>Cl<sub>2</sub> solution of complex **1b**, at room temperature. In the <sup>1</sup>H NMR spectrum recorded after 10 min from the treatment with the gaseous comonomer no signal of **1b** was present, whereas the singlet of free acetonitrile, a broad signal at 2.78 ppm and broad signals for the aromatic protons of the ligands were observed, thus indicating that both isomers immediately react with CO leading to the palladium-acetyl carbonyl intermediate. The stereochemistry of the obtained polyketones is determined by <sup>13</sup>C NMR spectroscopy, recording the spectra in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) at room temperature (Table 6).

**Table 6.** Triads distribution in the CO/vinyl arene polyketones.<sup>[a]</sup>  
Precatalyst: [Pd(CH<sub>3</sub>)(NCCH<sub>3</sub>)(N–N')][PF<sub>6</sub>].

RUN	N–N'	Vinyl arene	Stereochemistry			
			ll (%)	lu (%)	ul (%)	uu (%)
1	<b>1</b>	S	1	12	11	76
2	<b>2</b>	S	3	17	16	64
3	<b>3</b>	S	-	7	8	85
4	<b>4</b>	S	5	16	17	62
5	<b>1</b>	MS	7	17	14	62
6	<b>2</b>	MS	3	15	16	66
7	<b>3</b>	MS	-	12	9	79
8	<b>4</b>	MS	5	17	17	61

<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.

All the isolated macromolecules have a prevailing syndiotactic microstructure, with a content of *uu* triad ranging from 61 to 85 %, depending on the nature of the ligand. These values are in line with those reported in the literature for copolymers produced with other pyridylimino ligands.<sup>31</sup> In contrast to our previous results obtained with catalysts based on ligands **L1** and **L2**,<sup>33</sup> no effect of the vinyl arene comonomer on the stereochemistry of the corresponding polyketones was observed.

However, for the polyketones obtained with precatalysts **1b**, **2b** and **4b** the signals of all the four triads are present, thus suggesting that the stereochemistry is originated by a combination of the *chain-end* and the *enantiomorphic* site control. On the other hand, the CO/S and CO/MS copolymers synthesized with precatalyst **3b** are the most stereoregular of the series having the highest content of *uu* triad, and no signal for the *ll* triad, thus indicating that in this case the stereochemistry of the copolymer is the result of a pure *chain-end* control.<sup>46</sup>

## Conclusions

We investigated two series of neutral and cationic Pd(II) complexes of the general formula [Pd(CH<sub>3</sub>)Cl(N–N')] (**1a–4a**) and [Pd(CH<sub>3</sub>)(NCCH<sub>3</sub>)(N–N')][PF<sub>6</sub>] (**1b–4b**) with four pyridylimino ligands (N–N', **1–4**), that differ for the nature of the substituents on the iminic carbon atom and on the *ortho* positions of the phenyl ring (in both cases H or CH<sub>3</sub>). NMR spectroscopy demonstrated that the complexes are present in CD<sub>2</sub>Cl<sub>2</sub> solution as equilibrium mixtures of *cis* and *trans* isomers, where the geometrical descriptor concerns the relative positions of the CH<sub>3</sub> ligand and the iminic nitrogen. The X-ray structures of *trans-1a*, *cis-2a*, *cis-3a*, and *cis-4a* were also determined. For the neutral complexes **1a–4a** the *cis* isomer was the major species in solution, with a percentage that grows with the electron donor capacity of the ligand from 75 % (**1a**) to 98 % (**4a**). The combined e NMR data in solution and X-ray data in the solid state indicate that:

- in the <sup>1</sup>H NMR spectra the change in the frequency of the Pd–CH<sub>3</sub> singlet is in good agreement with the variation of the Pd–C bond length. Therefore this chemical shift is a good probe for assessing the donor strength of the pyridylimino ligand;

- in the <sup>15</sup>N NMR spectra the *CIS* value of the nitrogen atom *trans* to CH<sub>3</sub> correlates well with the Pd–N bond distance, thus it might be used as a probe for the strength of the Pd–N bond.

The monocationic complexes generated very efficient catalysts for the copolymerization of carbon monoxide with vinyl arenes such as styrene and 4-methyl-styrene, leading to the corresponding alternating polyketones with a prevailing syndiotactic microstructure.

In contrast with the data previously obtained by us with other Pd(II) catalysts, no effect of the vinyl arene nature on the stereochemistry of the polymers was observed. In order to get a deeper insight into the parameters that affect the stereocontrol, new Pd(II) catalysts with iminopyridines having different polyaromatic groups on the imino nitrogen atom are currently under investigation.

## Experimental Section

**General considerations.** All complex manipulations were performed using standard Schlenk techniques under argon. Anhydrous dichloromethane was obtained by freshly distilling it over CaH<sub>2</sub> and under argon. Deuterated solvents (Cambridge Isotope Laboratories, Inc. (CIL)) were stored as recommended by CIL. Carbon monoxide (SIAD, CP grade 99.9%), 2-pyridinecarboxaldehyde, 2-acetylpyridine, aniline and 2,6-dimethylaniline, the 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. Ligands **1**, **2** and **4** were synthesized according to literature procedures.<sup>34</sup> Palladium(II) neutral complexes were synthesized from [Pd(cod)(CH<sub>3</sub>)Cl], obtained from [Pd(OAc)<sub>2</sub>], HCl 37 % Fluka and [*cis,cis*-cyclooctadiene] Fluka without further purification. [Pd(OAc)<sub>2</sub>] was a donation from BASF Italia and used as received.

NMR spectra of ligands, complexes and catalytic products were recorded on a Varian 500 spectrometer at the following frequencies: 500 MHz (<sup>1</sup>H), 125.68 MHz (<sup>13</sup>C) and 50.65 MHz (<sup>15</sup>N). The resonances are reported in ppm (δ) and referenced to the residual solvent peak versus Si(CH<sub>3</sub>)<sub>4</sub>: CDCl<sub>3</sub> at δ 7.26 (<sup>1</sup>H) and δ 77.0 (<sup>13</sup>C), CD<sub>2</sub>Cl<sub>2</sub> at δ 5.32 (<sup>1</sup>H) and δ 54.0 (<sup>13</sup>C). NMR experiments were performed employing the automatic software parameters. <sup>13</sup>C NMR spectra of polyketones were recorded in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) with addition of CDCl<sub>3</sub> for locking purposes. **Caution: HFIP is a very volatile and highly toxic solvent, so proper protection should be used when it is handled.**

The <sup>15</sup>N NMR spectra were recorded using the standard {<sup>1</sup>H,<sup>15</sup>N} gHMBC sequence of the 500 MHz Varian spectrometer. Multiple bond-correlation experiments were optimized with the coupling constants in the range 2 – 5 Hz. A relaxation delay of 1 s was used in all cases. The number of transients per increment was 16 for the ligands and 64 for the neutral complexes, with a total acquisition time ranging from 2.5 to 5.5 h.

IR spectra were recorded in Nujol on a Perkin Elmer System 2000 FT-IR. Elemental analyses were performed in the analytic

laboratories of University of Bologna. Average molecular weight (Mw) and polydispersity (Mw/Mn) values of CO/vinyl arene copolymers were measured through gel permeation chromatography using polystyrene standards. Analyses were determined by a Knauer HPLC (K-501 pump, K-2501 UV detector) with a PLgel 5  $\mu\text{m}$   $10^4$  Å column. Chloroform was used as the eluent, with a flow rate of 0.6 mL  $\text{min}^{-1}$ . Samples were prepared by dissolving the copolymer (2 mg) in chloroform (10 mL). Calculations were performed with the Bruker Chromstar software.

**Synthesis of Pd complexes [Pd(CH<sub>3</sub>)Cl(N–N')] (1a, 2a, 4a).** To a stirred solution of [Pd(cod)(CH<sub>3</sub>)Cl] (0.35 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1.5 mL) a solution of the ligand (1.1 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (1.5 mL) was added. After 1.5 h at room temperature the reaction mixture was concentrated and the product precipitated upon addition of diethyl ether at 277 K. Average yield: 90 %.

**1a.** Found: C, 45.97; H, 3.77; N, 7.96. Calc. for C<sub>13</sub>H<sub>13</sub>N<sub>2</sub>ClPd: C, 46.04; H, 3.86; N, 8.16%.  $\delta\text{H}$  (500 MHz; CD<sub>2</sub>Cl<sub>2</sub>; 298 K) *cis* : *trans* = 3 : 1. *cis* isomer: 9.09 (1H, d, H<sup>6</sup>), 8.46 (1H, s, H<sup>1</sup>), 8.06 (1H, t, H<sup>4</sup>), 7.83 (1H, d, H<sup>3</sup>), 7.75 (1H, t, H<sup>5</sup>), 7.54 – 7.36 (3H, m, H<sup>m,p</sup>), 7.20 (2H, d, H<sup>o</sup>), 0.63 (3H, s, Pd–CH<sub>3</sub>); *trans* isomer: 8.70 (1H, d, H<sup>6</sup>), 8.43 (1H, s, H<sup>1</sup>), 8.12 (1H, t, H<sup>4</sup>), 7.86 (1H, d, H<sup>3</sup>), 7.68 (1H, t, H<sup>5</sup>), 7.54 – 7.36 (5H, m, H<sup>m,p,o</sup>), 1.15 (3H, s, Pd–CH<sub>3</sub>).  $\delta\text{C}$  *cis* isomer: 167.30 (C<sup>i</sup>), 149.37 (C<sup>6</sup>), 138.81 (C<sup>4</sup>), 128.98 (C<sup>m</sup>), 128.78 (C<sup>3</sup>), 128.06 (C<sup>p</sup>), 126.77 (C<sup>5</sup>), 122.38 (C<sup>o</sup>), –0.02 (Pd–CH<sub>3</sub>).

**2a.** Found: C, 48.96; H, 4.49; N, 7.58. Calc. for C<sub>15</sub>H<sub>17</sub>N<sub>2</sub>ClPd: C, 49.09; H, 4.67; N, 7.63%.  $\delta\text{H}$  (500 MHz; CD<sub>2</sub>Cl<sub>2</sub>; 298 K) *cis* : *trans* = 97 : 3. *cis* isomer: 9.10 (1H, d, H<sup>6</sup>), 8.35 (1H, s, H<sup>1</sup>), 8.08 (1H, t, H<sup>4</sup>), 7.84 – 7.74 (2H, m, H<sup>3,5</sup>), 7.19 – 7.14 (3H, m, H<sup>m,p</sup>), 2.26 (6H, s, Ar–CH<sub>3</sub>), 0.38 (3H, s, Pd–CH<sub>3</sub>); *trans* isomer: 1.06 (3H, s, Pd–CH<sub>3</sub>).  $\delta\text{C}$  *cis* isomer: 168.33 (C<sup>i</sup>), 149.47 (C<sup>6</sup>), 138.71 (C<sup>4</sup>), 128.91 (C<sup>3</sup>), 127.84 (C<sup>m,p</sup>), 126.67 (C<sup>5</sup>), 17.91 (Ar–CH<sub>3</sub>), –1.88 (Pd–CH<sub>3</sub>).

**4a.** Found: C, 50.60; H, 5.02; N, 7.28. Calc. for C<sub>16</sub>H<sub>19</sub>N<sub>2</sub>ClPd: C, 50.41; H, 5.02; N, 7.35%.  $\delta\text{H}$  (500 MHz; CD<sub>2</sub>Cl<sub>2</sub>; 298 K) *cis* : *trans* = 98 : 2. *cis* isomer: 9.19 (1H, d, H<sup>6</sup>), 8.08 (1H, t, H<sup>4</sup>), 7.90 (1H, d, H<sup>3</sup>), 7.75 (1H, t, H<sup>5</sup>), 7.21 – 7.10 (3H, m, H<sup>m,p</sup>), 2.18 (6H, s, Ar–CH<sub>3</sub>), 2.14 (3H, s, CH<sub>3</sub><sup>i</sup>), 0.18 (3H, s, Pd–CH<sub>3</sub>); *trans* isomer: 0.94 (3H, s, Pd–CH<sub>3</sub>).  $\delta\text{C}$  *cis* isomer: 149.04 (C<sup>6</sup>), 138.82 (C<sup>4</sup>), 128.62 (C<sup>3</sup>), 128.21 – 126.53 (C<sup>m,p</sup>), 17.76 (Ar–CH<sub>3</sub>), 17.32 (CH<sub>3</sub><sup>i</sup>), –1.92 (Pd–CH<sub>3</sub>).

**Synthesis of Pd complex [Pd(CH<sub>3</sub>)Cl(3)] (3a).** To a solution of 0.566 mmol (0.063 mL) of 2-acetylpyridine in 3 mL of methanol, 1.2 equiv of aniline (0.679 mmol, 0.062 mL) were added, and the reaction mixture was stirred with 2 drops of formic acid for 2.5 h at 298 K. 1 equiv of [Pd(cod)(CH<sub>3</sub>)Cl] (0.566 mmol, 150.0 mg) was suspended in 1 mL of methanol and added quantitatively to the reaction mixture using a total of 1.5 mL of methanol to wash. The solution was stirred at 298 K for 1.5 h, then it was concentrated to half the volume, cooled in an ice bath and the precipitation of the product was completed upon addition of cold diethyl ether. The solid was filtered and washed thoroughly with cold diethyl ether, and it was isolated in a 85 % yield.

**3a.** Found: C, 47.49; H, 4.16; N, 7.76. Calc. for C<sub>14</sub>H<sub>15</sub>N<sub>2</sub>ClPd: C, 47.61; H, 4.28; N, 7.93%.  $\delta\text{H}$  (500 MHz; CD<sub>2</sub>Cl<sub>2</sub>; 298 K) *cis* : *trans* = 94 : 6. *cis* isomer: 9.16 (1H, d, H<sup>6</sup>), 8.07 (1H, t, H<sup>4</sup>), 7.91 (1H, d, H<sup>3</sup>), 7.74 (1H, t, H<sup>5</sup>), 7.50 (2H, t, H<sup>m</sup>), 7.31 (1H, t, H<sup>p</sup>), 6.96 (2H, d, H<sup>o</sup>), 2.24 (3H, s, CH<sub>3</sub><sup>i</sup>), 0.35 (3H, s, Pd–CH<sub>3</sub>); *trans* isomer: 8.72 (1H, d, H<sup>6</sup>), 8.12 (1H, t, H<sup>4</sup>), 7.94 (1H, m, H<sup>3</sup>), 7.69 (1H, t, H<sup>5</sup>), 7.45 (2H, m, H<sup>m</sup>), 7.27 (1H, m, H<sup>p</sup>), 7.10 (2H, m, H<sup>o</sup>), 2.29 (3H, s, CH<sub>3</sub><sup>i</sup>), 0.98 (3H, s, Pd–CH<sub>3</sub>).  $\delta\text{C}$  *cis* isomer: 149.04 (C<sup>6</sup>), 138.71 (C<sup>4</sup>), 129.13 (C<sup>m</sup>), 128.50 (C<sup>5</sup>), 126.50 (C<sup>p</sup>), 125.00 (C<sup>3</sup>), 121.68 (C<sup>o</sup>), 18.46 (CH<sub>3</sub><sup>i</sup>), –0.47 (Pd–CH<sub>3</sub>).

**Synthesis of Pd complexes [Pd(CH<sub>3</sub>)(NCCH<sub>3</sub>)(N–N')][PF<sub>6</sub>] (1b–4b).** To a solution of neutral precursor (0.205 mmol) in 10 mL of CH<sub>2</sub>Cl<sub>2</sub> a solution of 1.3 equivalents of AgPF<sub>6</sub> (0.267 mmol) in 1.5 mL of anhydrous acetonitrile was added. The reaction mixture was protected from light and stirred at room temperature for 2.5 h, then it was filtered over Celite<sup>®</sup>, concentrated and the product was precipitated upon addition of cold diethyl ether. Average yield 70 – 90 %.

**1b.** Found: C, 36.27; H, 3.36; N, 8.33. Calc. for C<sub>15</sub>H<sub>16</sub>N<sub>3</sub>PdPF<sub>6</sub>: C, 36.79; H, 3.29; N, 8.58%. IR:  $\nu_{\text{max}}$  = 842.18  $\text{cm}^{-1}$  (PF<sub>6</sub><sup>–</sup>).  $\delta\text{H}$  (500 MHz; CD<sub>2</sub>Cl<sub>2</sub>; 298 K) *cis* : *trans* = 1 : 3. *cis* isomer: 8.74 (1H, d, H<sup>6</sup>), 8.46 (1H, s, H<sup>1</sup>), 8.20 (1H, t, H<sup>4</sup>), 7.98 (1H, d, H<sup>3</sup>), 7.92 (1H, t, H<sup>5</sup>), 7.60 – 7.41 (3H, m, H<sup>m,p</sup>), 7.17 (2H, d, H<sup>o</sup>), 2.51 (3H, s, Pd–NCCH<sub>3</sub>), 0.78 (3H, s, Pd–CH<sub>3</sub>); *trans* isomer: 8.58 (1H, d, H<sup>6</sup>), 8.55 (1H, s, H<sup>1</sup>), 8.25 (1H, t, H<sup>4</sup>), 8.08 (1H, d, H<sup>3</sup>), 7.78 (1H, t, H<sup>5</sup>), 7.60 – 7.41 (3H, m, H<sup>m,p</sup>), 7.37 (2H, d, H<sup>o</sup>), 2.23 (3H, s, Pd–NCCH<sub>3</sub>), 1.24 (3H, s, Pd–CH<sub>3</sub>).  $\delta\text{C}$  *cis* isomer: 171.20 (C<sup>i</sup>), 150.15 (C<sup>6</sup>), 140.29 (C<sup>4</sup>), 130.76 (C<sup>5</sup>), 129.62 (C<sup>m</sup>), 128.86 (C<sup>p</sup>), 128.38 (C<sup>3</sup>), 122.20 (C<sup>o</sup>), 4.76 (Pd–CH<sub>3</sub>), 3.38 (Pd–NCCH<sub>3</sub>); *trans* isomer: 162.79 (C<sup>i</sup>), 149.40 (C<sup>6</sup>), 141.09 (C<sup>4</sup>), 129.76 (C<sup>3</sup>), 129.58 (C<sup>m</sup>), 129.46 (C<sup>p</sup>), 128.95 (C<sup>5</sup>), 121.80 (C<sup>o</sup>), 3.78 (Pd–CH<sub>3</sub>), 3.28 (Pd–NCCH<sub>3</sub>).

**2b.** Found: C, 39.77; H, 4.02; N, 8.28. Calc. for C<sub>17</sub>H<sub>20</sub>N<sub>3</sub>PdPF<sub>6</sub>: C, 39.44; H, 3.89; N, 8.12%. IR:  $\nu_{\text{max}}$  = 847.91  $\text{cm}^{-1}$  (PF<sub>6</sub><sup>–</sup>).  $\delta\text{H}$  (500 MHz; CD<sub>2</sub>Cl<sub>2</sub>; 298 K) *cis* : *trans* = 7 : 1. *cis* isomer: 8.79 (1H, d, H<sup>6</sup>), 8.35 (1H, s, H<sup>1</sup>), 8.22 (1H, t, H<sup>4</sup>), 7.97 (2H, m, H<sup>3,5</sup>), 7.25 – 7.15 (3H, m, H<sup>m,p</sup>), 2.50 (3H, s, Pd–NCCH<sub>3</sub>), 2.23 (3H, s, Ar–CH<sub>3</sub>), 0.53 (3H, s, Pd–CH<sub>3</sub>); *trans* isomer: 8.61 (1H, d, H<sup>6</sup>), 8.44 (1H, s, H<sup>1</sup>), 8.30 (1H, t, H<sup>4</sup>), 8.09 (1H, d, H<sup>3</sup>), 7.84 (1H, t, H<sup>5</sup>), 7.25 – 7.15 (3H, m, H<sup>m,p</sup>), 2.32 (3H, s, Ar–CH<sub>3</sub>), 1.92 (3H, s, Pd–NCCH<sub>3</sub>), 1.17 (3H, s, Pd–CH<sub>3</sub>).  $\delta\text{C}$  *cis* isomer: 172.41 (C<sup>i</sup>), 150.77 (C<sup>6</sup>), 140.54 (C<sup>4</sup>), 128.51 (C<sup>3,5</sup>), 128.73 (C<sup>m,p</sup>), 17.95 (Ar–CH<sub>3</sub>), 3.32 (Pd–NCCH<sub>3</sub>), 3.21 (Pd–CH<sub>3</sub>); *trans* isomer: 165.77 (C<sup>i</sup>), 150.08 (C<sup>6</sup>), 141.01 (C<sup>4</sup>), 129.88 (C<sup>3</sup>), 128.37 (C<sup>m,p</sup>), 18.31 (Ar–CH<sub>3</sub>), 3.39 (Pd–CH<sub>3</sub>), 2.32 (Pd–NCCH<sub>3</sub>).

**3b.** Found: C, 38.10; H, 3.28; N, 8.29. Calc. for CHNPdPF<sub>6</sub>: C, 38.15; H, 3.60; N, 8.34%. IR:  $\nu_{\text{max}}$  = 842.80  $\text{cm}^{-1}$  (PF<sub>6</sub><sup>–</sup>).  $\delta\text{H}$  (500 MHz; CD<sub>2</sub>Cl<sub>2</sub>; 298 K) *cis* : *trans* = 5 : 6. *cis* isomer: 8.74 (1H, d, H<sup>6</sup>), 8.22 (1H, t, H<sup>4</sup>), 8.04 (1H, d, H<sup>3</sup>), 7.93 (1H, t, H<sup>5</sup>), 7.59 – 7.47 (2H, m, H<sup>m</sup>), 7.43 – 7.32 (1H, m, H<sup>p</sup>), 6.94 (2H, d, H<sup>o</sup>), 2.49 (3H, s, Pd–NCCH<sub>3</sub>), 2.34 (3H, s, CH<sub>3</sub><sup>i</sup>), 0.49 (3H, s, Pd–CH<sub>3</sub>); *trans* isomer: 8.60 (1H, d, H<sup>6</sup>), 8.28 (1H, t, H<sup>4</sup>), 8.10 (1H, d, H<sup>3</sup>), 7.79 (1H, t, H<sup>5</sup>), 7.59 – 7.47 (2H, m, H<sup>m</sup>), 7.43 – 7.32 (1H, m, H<sup>p</sup>), 7.05 (d, 2H, H<sup>o</sup>), 2.41 (s, 3H, CH<sub>3</sub><sup>i</sup>), 1.94 (s, 3H, Pd–NCCH<sub>3</sub>), 1.05 (3H, s, Pd–CH<sub>3</sub>).  $\delta\text{C}$  *cis* isomer: 149.87 (C<sup>6</sup>), 141.15 (C<sup>4</sup>), 129.69 (C<sup>m</sup>), 129.00 (C<sup>5</sup>), 127.78 (C<sup>3</sup>), 127.41 (C<sup>p</sup>), 121.70 (C<sup>o</sup>), 17.65 (CH<sub>3</sub><sup>i</sup>),

2.74 (Pd-CH<sub>3</sub>), 2.63 (Pd-NCCH<sub>3</sub>); *trans* isomer: 149.74 (C<sup>6</sup>), 140.56 (C<sup>4</sup>), 130.53 (C<sup>5</sup>), 129.69 (C<sup>m</sup>), 127.41 (C<sup>p</sup>), 121.09 (C<sup>o</sup>), 19.06 (CH<sub>3</sub><sup>i</sup>), 4.49 (Pd-CH<sub>3</sub>), 3.48 (Pd-NCCH<sub>3</sub>).

**4b.** Found: C, 40.50; H, 4.28; N, 7.92. Calc. for C<sub>18</sub>H<sub>22</sub>N<sub>3</sub>PdPF<sub>6</sub>: C, 40.66; H, 4.17; N, 7.90%. IR:  $\nu_{\max}$  = 841.16 cm<sup>-1</sup> (PF<sub>6</sub><sup>-</sup>).  $\delta$ H (500 MHz; CD<sub>2</sub>Cl<sub>2</sub>; 298 K) *cis* : *trans* = 97 : 3. *cis* isomer: 8.76 (1H, d, H<sup>6</sup>), 8.23 (1H, t, H<sup>4</sup>), 8.04 (1H, d, H<sup>3</sup>), 7.95 (1H, t, H<sup>5</sup>), 7.20 (3H, s, H<sup>m,p</sup>), 2.49 (3H, s, Pd-NCCH<sub>3</sub>), 2.25 (3H, s, CH<sub>3</sub><sup>i</sup>), 2.15 (6H, s, Ar-CH<sub>3</sub>), 0.33 (3H, s, Pd-CH<sub>3</sub>); *trans* isomer: 2.30 (3H, s, CH<sub>3</sub><sup>i</sup>), 2.23 (6H, s, Ar-CH<sub>3</sub>), 1.83 (3H, s, Pd-NCCH<sub>3</sub>), 1.06 (3H, s, Pd-CH<sub>3</sub>).  $\delta$ C *cis* isomer: 149.80 (C<sup>6</sup>), 140.36 (C<sup>4</sup>), 130.52 (C<sup>5</sup>), 128.42 (C<sup>m,p</sup>), 126.35 (C<sup>3</sup>), 17.72 (CH<sub>3</sub><sup>i</sup>), 17.64 (Ar-CH<sub>3</sub>), 3.27 (Pd-NCCH<sub>3</sub>), 2.72 (Pd-CH<sub>3</sub>).

### X Ray diffraction

Data collections were performed at the X-ray diffraction beamline (XRD1) of the Elettra Synchrotron of Trieste (Italy), with a Pilatus 2M image plate detector. Complete datasets were collected at 100 K (nitrogen stream supplied through an Oxford Cryostream 700) with a monochromatic wavelength of 0.700 ang with the rotating crystal method. The crystals were dipped in N-paratone and mounted on the goniometer head with a nylon loop. The diffraction data were indexed, integrated and scaled using XDS.<sup>47</sup> When needed, multiple collections of different crystals from the same batch were merged together in order to increase completeness. The structures were solved by direct methods using SIR2014.<sup>48</sup> Fourier analysis and refinement were performed by the full-matrix least-squares methods based on F<sup>2</sup> implemented in SHELXL-2014.<sup>49</sup> The Coot program was used for modeling.<sup>50</sup> Anisotropic thermal motion was allowed for all non-hydrogen atoms. Hydrogen atoms were included at calculated positions with isotropic factors U = 1.2 U<sub>eq</sub>, U<sub>eq</sub> being the equivalent isotropic thermal factor of the bonded non hydrogen atom. Essential crystal and refinement data, together with selected bond distances and angles, are reported in the SI.

**CO/vinyl arene copolymerization reactions.** All experiments were performed at atmospheric CO pressure in a three-necked, thermostatted, 75 mL glass reactor equipped with a magnetic stirrer. After establishment of the reaction temperature, the precatalyst (1.27·10<sup>-5</sup> 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.

**CO/vinyl arene copolymers purification.** Polyketones (100 mg) were dissolved in CHCl<sub>3</sub> (50 mL) and stirred at room temperature for 10 min. The solution was then filtered over Celite®. For CO/S copolymers, 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 investigation

To a solution of **1b** (10 mM) in CD<sub>2</sub>Cl<sub>2</sub> 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.

### Acknowledgements

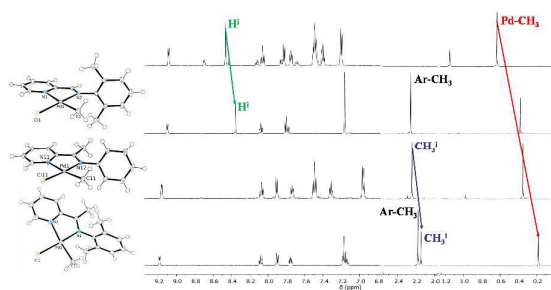
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## Table of Content



The systematic study on iminopyridine palladium complexes demonstrates the relationship among NMR chemical shifts, ligand donor capability and catalytic performances.