

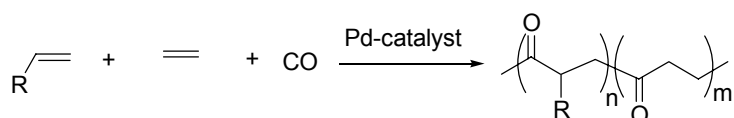
## Terpolymerization of 4-*tert*-butylstyrene and ethene with carbon monoxide using N-ligands

### Abstract

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

## 6.1. Introduction

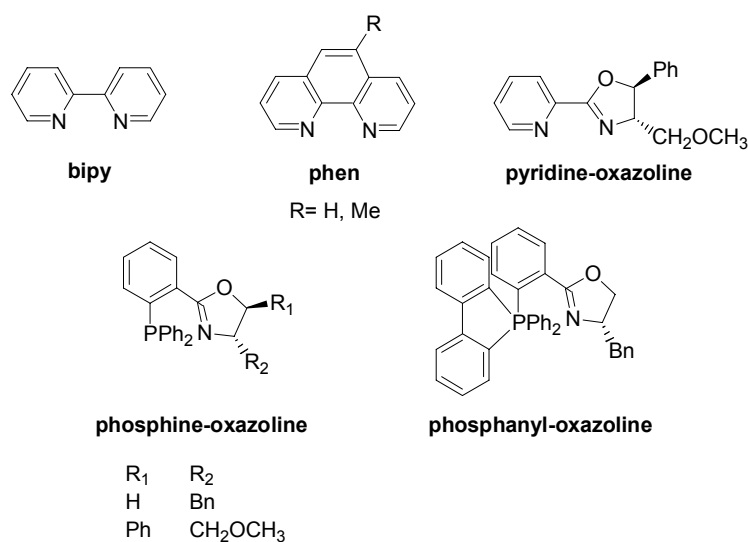
Since the discovery that palladium(II) complexes of diphosphines efficiently catalyze the perfectly alternating terpolymerization of CO, ethene and propene, polyketones have become a commercial reality in the form of *Carilon* for Shell<sup>1</sup> and *Ketonex* for BP<sup>2</sup>, with other companies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



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

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

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

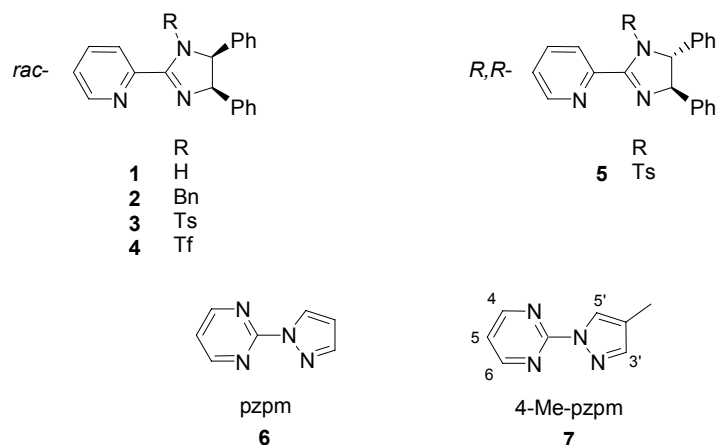


Scheme 2. Ligands used in the terpolymerization of ethene and styrene with CO

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

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

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



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

## 6.2. Results and discussion

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

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

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

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

Comparing planar ligands **6** and **7** with the bulkier chiral ones **1-5**, it seems easier to accept that the latter interfere more with the coordination/insertion of the alkene, which is the rate-determining step of the reaction. This would explain the higher activity of systems containing ligands **6** and **7**, but not that of **5**. Although all the pyridine-imidazoline ligands may create a similar environment, the X-ray diffraction of the molecule [PdCl<sub>2</sub>(**5**)] showed that ligand **5** has a unique distortion in the imidazoline plane to favour the intramolecular  $\pi$ -stacking of the tosyl ring with the most distant phenyl ring of the imidazoline.<sup>14</sup> This feature may account for the high reactivity observed with this ligand, which is also observed in the copolymerization of CO/TBS.<sup>14</sup>

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

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

Reaction conditions: catalyst: 0.0125 mmol; [TBS]/[catalyst] = 620; p(CO/E) = 10 atm; 5 mL of dichloromethane as solvent; room temperature; 24 hours.

<sup>a</sup>Calculated by relative integration of the <sup>1</sup>H NMR signals of the terpolymers. <sup>b</sup>Productivity calculated from the isolated terpolymers.

The ethene/TBS molar ratio in the terpolymers was calculated by integrating, in the <sup>1</sup>H NMR spectra, the signals corresponding to the methylene groups (Figure 1). The two CH<sub>2</sub> protons of the TBS/CO blocks, which are diastereotopic, appear at 3.1 and 2.5 ppm, respectively. On the other hand, the four methylenic protons of the CO/E units, which are equivalent, also appear at 2.5 ppm. We found that the terpolymers obtained with ligands 1-7 have a surprisingly different composition. While pyridine-imidazolines 1-4 lead to terpolymers with high ethene contents (entries 1-4), ligands 5-7 lead to polymers with similar concentration of both alkenes (entries 5-7).

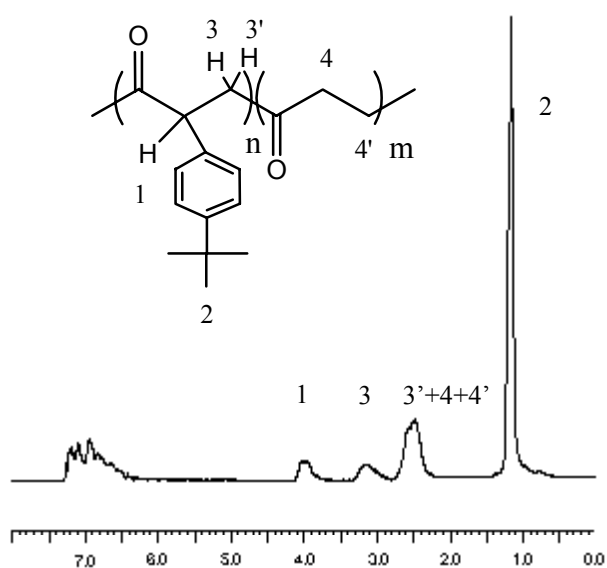


Figure 1.  $^1\text{H}$  NMR spectrum of an ethene/4-*tert*-butylstyrene/CO terpolymer

#### 6.2.1.1. Dependence of pressure

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

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



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

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

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

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

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

Reaction conditions: catalyst 0.0125 mmol; [TBS]/[catalyst]: 620; 5 mL of CH<sub>2</sub>Cl<sub>2</sub> as solvent; room temperature; 24 hours. <sup>a</sup> Calculated from the volume of the autoclave. <sup>b</sup> Calculated from the isolated terpolymer.

<sup>c</sup>Determined by GPC measurements in CHCl<sub>3</sub> vs. polystyrene standards. <sup>d</sup>

Determined by GPC in THF. n.d.: not determined.

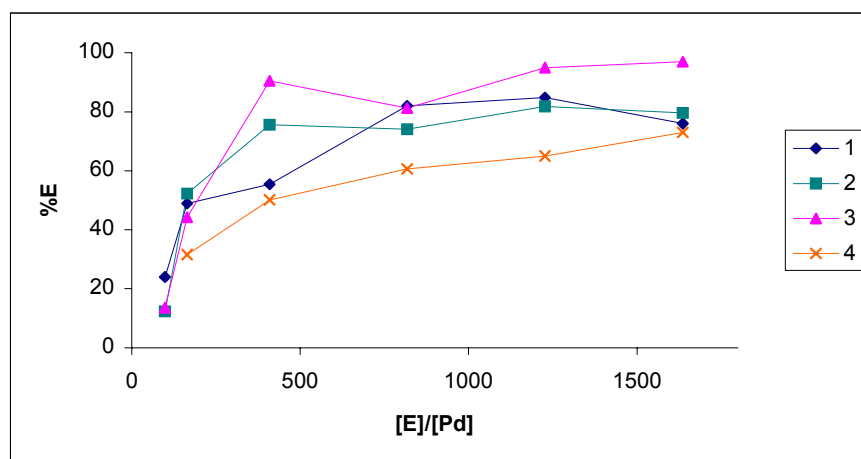


Figure 2. Ethene content in the terpolymer chain as a function of the ethene/catalyst ratio

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

Table 3. Co- and terpolymerization experiments using [PdMe(NCMe)(N-N')][BAR'<sub>4</sub>] (N-N' = 5-7)

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

Reaction conditions: [catalyst]= 0.0125 mmol; 5 mL of CH<sub>2</sub>Cl<sub>2</sub> as solvent; 24 hours; room temperature. <sup>a</sup> Calculated from the volume of the autoclave. <sup>b</sup> pCO = 1 atm; 5 mL of chlorobenzene as solvent. <sup>c</sup> [catalyst]= 0.00625 mmol. n.d. : not determined.

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

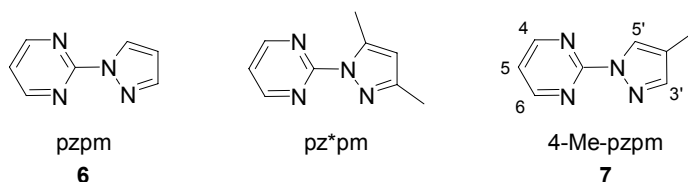
was involved in the reaction (entries 1 *vs.* 2 or 4 *vs.* 6). The presence of ethene is also reflected in the molecular weight, which clearly decreases. The molecular weights of the terpolymers obtained with catalyst precursors [PdMe(NCMe)(N-N')][BAR'<sub>4</sub>] (N-N' = 5-7) are higher than those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

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

### 6.2.2. Synthesis and characterization of [PdMe(NCMe)(7)][BAR'<sub>4</sub>]

The activity of [PdMe(NCMe)(6)][BAR'<sub>4</sub>] in the copolymerization of CO/TBS was high. When the pyrazol ring was modified with two methyl groups to create a bulkier ligand (pz\*pm) (Scheme 4), a clear decrease both in productivity and molecular weight was observed.<sup>18</sup> The reason for this could be steric although the higher basicity of the ligand may also have an effect. To analyze just an electronic effect, ligand 6 was modified by placing a methyl group in position 4' of the pyrazol, resulting in ligand 7 (Scheme 4).<sup>19</sup> The catalyst [PdMe(NCMe)(7)][BAR'<sub>4</sub>] was synthesized by reacting the precursor [PdClMe(7)] with NaBAR'<sub>4</sub> (Ar' = 3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) to abstract the

chlorine ligand, as previously reported.<sup>18</sup> Analysis of the stereochemistry of the complex was done by NOE experiments and it shows an interaction between the Pd-Me group and the pyrazol ring (H<sub>3</sub>). Again for pyrazol-containing palladium cationic complexes of formula [PdMe(NCMe)(N-N')][BAR'<sub>4</sub>], the methyl group is *trans* to the less basic ring.<sup>18</sup>



Scheme 4. Pyrazol-pyrimidine ligands

### 6.2.3. Analysis of tacticity of the terpolymers

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

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

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

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

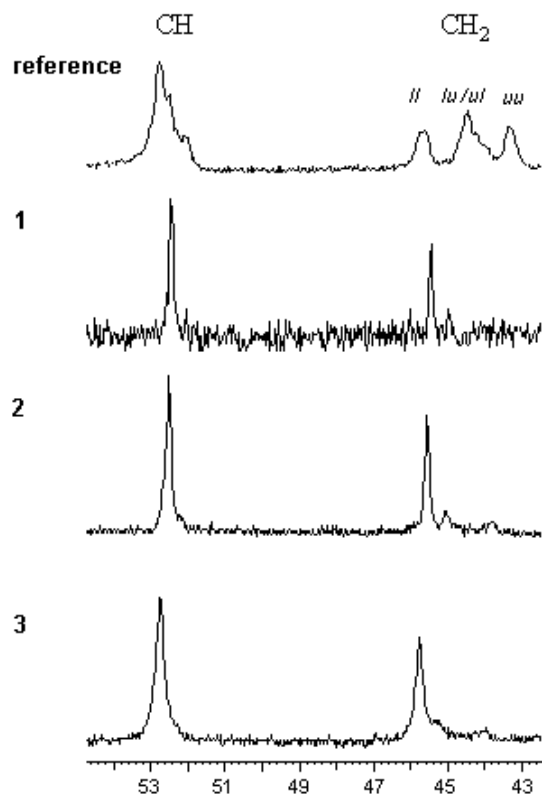


Figure 3. Comparative  $^{13}\text{C}$  NMR spectra of terpolymer with ca. 90% ethene content obtained using different pyridine-imidazoline ligands **1-3**

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



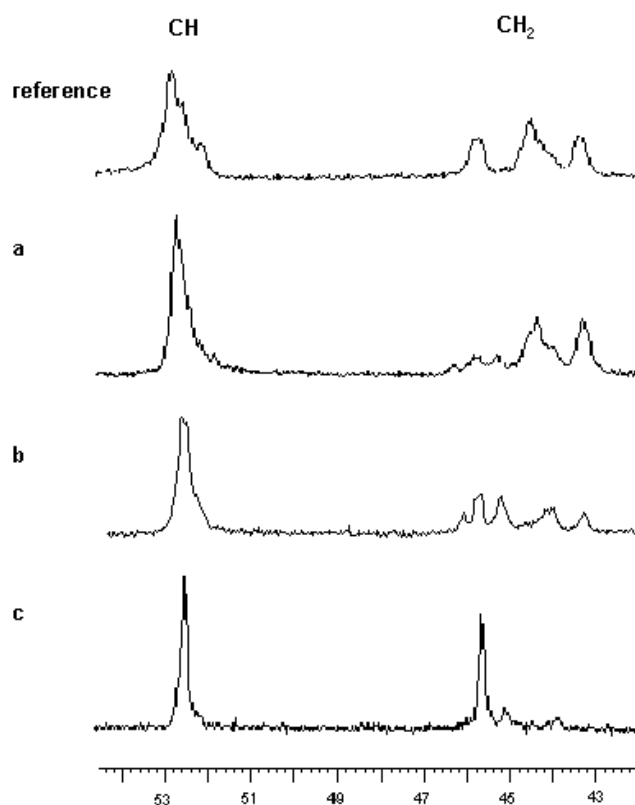


Figure 4. Comparative <sup>13</sup>C NMR spectra of an atactic TBS/CO copolymer as reference and E/TBS/CO terpolymers with increasing ethene content (**a**: 12.3%; **b**: 52.3%; **c**: 81.8%, respectively), obtained with catalyst [PdMe(NCMe)(2)][BAR'<sub>4</sub>].

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

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

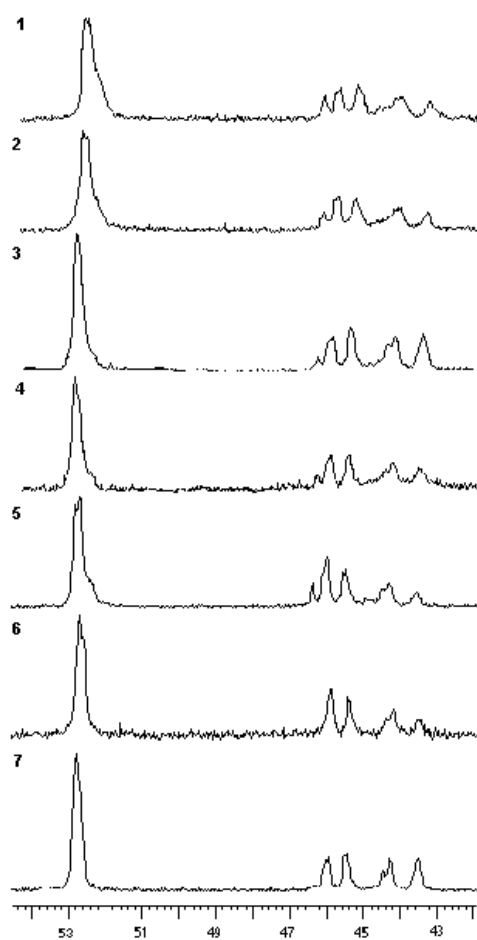


Figure 5.  $^{13}\text{C}$  NMR of terpolymers with ca. 50% ethene content obtained with ligands **1-7**

### 6.3. Conclusions

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

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

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

## 6.4. Experimental

### 6.4.1. General procedure

All reactions were carried out using standard Schlenk techniques under nitrogen atmosphere at room temperature. Solvents were distilled and deoxygenated prior to use unless otherwise stated. The salt  $\text{NaBAr}'_4$  ( $\text{Ar}' = 3, 5\text{-}(\text{CF}_3)_2\text{-C}_6\text{H}_3$ ) was prepared according to reported methods.<sup>20</sup> The ligands **1-6** and the palladium precursors  $[\text{PdMe}(\text{NCMe})(\mathbf{1-6})][\text{BAr}'_4]$  were prepared as previously described.<sup>13,14,18,21</sup> Compound  $[\text{PdMeCl}(\mathbf{7})]$  was used as received.<sup>19</sup>

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Varian Mercury VX spectrometer with a  $^1\text{H}$  resonance frequency of 400 MHz. Chemical shifts were reported relative to  $\text{CDCl}_3$  (7.26 ppm for  $^1\text{H}$  and 77.23 for  $^{13}\text{C}$ ). Some assignments in NMR spectra were determined by DEPT and NOE experiments. Elemental analyses were carried out on a Carlo Erba Microanalyser EA 1108. The molecular weight of the terpolymers and molecular weight distributions were determined by gel permeation chromatography (GPC) in  $\text{CHCl}_3$  on a Waters 515-GPC device using a lineal Waters Ultrastaygel column with a Waters 2410 refractive index detector and polystyrene standards.

### 6.4.2. Synthesis of $[\text{PdMe}(\text{NCMe})(\mathbf{7})][\text{BAr}'_4]$

The cationic complex  $[\text{PdMe}(\text{NCMe})(\mathbf{7})][\text{BAr}'_4]$  was obtained by adding a previously prepared solution of the neutral complex  $[\text{PdCl}(\text{Me})(\mathbf{7})]$ <sup>19</sup> in  $\text{CH}_2\text{Cl}_2$ , to an equimolar solution of  $\text{NaBAr}'_4$  in MeCN, as previously reported with ligand **6**.<sup>18</sup>  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ , RT):  $\delta$  8.70

(dd,  $^3J = 5.2$  Hz,  $^4J = 2.5$  Hz, 1H, H<sub>4</sub> or H<sub>6</sub>), 8.33 (s, 1H, H<sub>5</sub>), 8.29 (dd,  $^3J = 5.2$  Hz,  $^4J = 2.5$  Hz, 1H, H<sub>6</sub> or H<sub>4</sub>), 7.69 (s, 8H, H<sub>b</sub>), 7.67 (s, 1H, H<sub>3</sub>), 7.51 (s, 4H, H<sub>d</sub>), 7.09 (t,  $^3J = 5.2$  Hz, 1H, H<sub>5</sub>), 2.31 (s, 3H, CH<sub>3</sub>CN), 2.24 (s, 3H, (CH<sub>3</sub>)<sub>4</sub>), 1.27 (s, 3H, Pd-CH<sub>3</sub>).

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

The 4-*tert*-butylstyrene was passed through a small column of Al<sub>2</sub>O<sub>3</sub> prior to use. Dichloromethane was distilled over P<sub>2</sub>O<sub>5</sub> and under N<sub>2</sub> atmosphere and stored over molecular sieves. Ethene / carbon monoxide (1/1 mixture) was purchased from Air Liquid with a purity grade of 98%.

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

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

The cationic precursor [PdMe(NCMe)(7)][BAR'<sub>4</sub>] (0.0125 mmol) was dissolved in 5 mL of chlorobenzene in a previously flushed Schlenk and the N<sub>2</sub> atmosphere replaced with CO. 4-*tert*-butylstyrene (0.7 mL, 3.875 mmol) was then introduced and the reaction was allowed to take place at room temperature and 1 atm. of CO. After 24 hours the reaction was stopped and a similar workup to that of the terpolymerization experiments was done.

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## 6.5. References

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