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Effect of 5-Me substituent(s) on the catalytic activity of palladium(II) 2,2′-bipyridine complexes in CO/4-*tert*-butylstyrene copolymerization

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Abstract

The coordination of two 5-substituted-2,2′-bipyridines L (L^1 = 5-methyl-2,2′-bipyridine, L^2 = 5,5′-dimethyl-2,2′-bipyridine) to palladium was studied. The neutral complexes $[Pd(L)Cl_2]$ and [Pd(L)(Me)Cl], and the cationic complexes obtained after chlorine abstraction $[Pd(L)_2][BAr'_4]_2$ and $[Pd(L)(Me)(NCMe)][BAr'_4]$ ($Ar' = 3,5\text{-}(CF_3)_2\text{-}C_6H_3$), respectively, were isolated and characterized by NMR and FAB mass spectroscopy. The complex $[Pd(L^2)(L^3)][BAr'_4]_2$ (L^3 = 2,2′-bipyridine) bearing different ligands, was prepared for comparison purposes. The activity of the monocationic and dicationic complexes as catalytic precursors in the CO/4-*tert*-butylstyrene copolymerization was compared with that of related well-known catalysts containing the unsubstituted 2,2′-bipyridine as nitrogen ligand, to evaluate the influence of the substituents in 5- and 5,5′-position. The presence of one or two substituents on the nitrogen ligand has a positive effect on productivity using both types of precursors. No influence was observed on the polymer properties in terms of molecular weight and tacticity. Analysis of the reactivity of the methyl–palladium complexes towards carbon monoxide shows further differences depending on the nitrogen ligand.

Keywords: Catalysis; Copolymerization; 4-*tert*-Butylstyrene; Palladium complexes; Nitrogen ligands

1. Introduction

In the copolymerization of CO with aromatic olefins using palladium catalysts [1], it has been shown that while chelating diphosphines lead only to monocarbonylated products [2], bidentate N-donor ligands afford polyketones with high selectivity [1e,1f]. This intriguing effect exerted by the chelating ligands in the reactivity of the palladium catalysts makes the synthesis of new precatalysts and, in particular, the study of the influence of different N–N ligands, very attractive.

Most of the reported precursors in the CO/styrene copolymerization are monocationic or dicationic palladium species which contain the unsubstituted 2-2′-bipyridine or 1,10-phenanthroline as N–N ligand as well as other heterocyclic related N–N ligands as for instance pyridine–pyrazole, pyridine–oxazoline and pyridine–imidazoline [3]. Although recently the enhanced activity shown by a substituted phenanthroline has been reported [4], the effect of substituents on these heterocyclic ligands has not been thoroughly investigated. In the case of the bis-chelated derivatives $[Pd(L)_2]^{2+}$, little attention has been given to species having both unsubstituted and substituted ligands [3d,3e,3p,4,5]. We have reported a series of $[Pd(bipy^R)_2]^{2+}$ and $[Pd(bipy)(bipy^R)]^{2+}$ complexes, where $bipy^R$ is a 6-substituted-2-2′-bipyridine (R = Me, Et, i-Pr): we studied their activity as catalytic precursors in the CO/styrene and 4-*tert*-butylstyrene copolymerization and observed that rather than an electronic effect, the presence of the substituent in *alpha*

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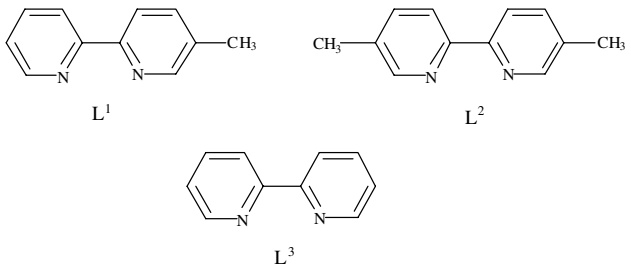
position to the coordinating nitrogen accounted for a steric effect [5d]. We decided it was worthwhile investigating the behaviour of 2-2′-bipyridines with substituents in 5- and 5,5′- i.e., in positions not sterically significant. Different palladium(II) complexes of formula $[Pd(L)_2][BAr'_4]_2$, $[Pd(L)(2,2'\text{-bipy})][BAr'_4]_2$ and $[Pd(Me)(L)(MeCN)][BAr'_4]$ (L = 5-Me or 5,5′-Me_2-2,2′-bipyridine; Ar′ = 3,5-$(CF_3)_2C_6H_3$) were prepared and tested as catalysts in the CO/4-*tert*-butylstyrene copolymerization. All catalysts showed activity comparable to that of some of the most efficient systems reported up to now [3k,3m]. The effect of the substitution of the $[BAr'_4]^-$ anion for other poorly co-ordinating counterions is commented on. In all cases prevailing syndiotactic copolymers were obtained.

The reactivity of the monocationic complexes $[Pd(Me)(L)(MeCN)][BAr'_4]$ with carbon monoxide was analysed by NMR.

2. Results and discussion

To analyze systematically the effect of a given substituent on the N–N ligand, we chose a monosubstituted bipyridine (5-Me-2,2′-bipyridine, L^1), the disubstituted (5,5′-Me_2-2,2′-bipyridine, L^2) and the unsubstituted 2,2′-bipyridine, L^3 (Scheme 1).

The monosubstituted ligand L^1, was obtained according to a published method [6], whereas the disubstituted L^2 and the nonsubstituted L^3 are commercially available. The cationic bis-chelated complexes $[Pd(L)_2][BAr'_4]_2$, (**1**: L = L^1; **2**, L = L^2; **3**, L = L^3) were synthesized by the following two-step reaction:



Scheme 1.

The second step of reaction (1) allowed us to synthesize species with two different chelating L ligands, such as complex **4**, $[Pd(L^2)(L^3)][BAr'_4]_2$, obtained from $[Pd(L^2)Cl_2]$ (**2a**), L^3 and $Na[BAr'_4]$. Yields are fairly good owing to the insolubility of NaCl in dichloromethane which drives the reaction to completeness. As expected for $[BAr'_4]$ salts, complexes **1**–**4** are highly soluble in most organic solvents. After filtration of NaCl, evaporation of the solvent allows isolation of the cationic complexes, which are then washed with pentane or hexane. The new complexes were completely characterized by elemental analyses, conductivity measurements, ^1H NMR and FAB-MASS spectroscopy.

In particular, the ^1H NMR spectra of complexes **1** and **4** deserve a few comments. For complex **1**, owing to the unsymmetrical nature of the ligand, two isomers are possible. However the ^1H NMR spectrum shows only one species in solution. A NOE difference experiment confirmed the presence of the *transoid* isomer as a single isomer (Scheme 2). A ^1H–^1H COSY spectrum allowed the complete assignment of the resonances. In particular, the assignment of the signals of H6 (at δ 8.63) and H6′ (at δ 8.73) is required for the right interpretation of the NOE experiment (see Scheme 3 for numbering). Comparison with the spectra of the symmetric complexes **2** and **3** was used as confirmation.

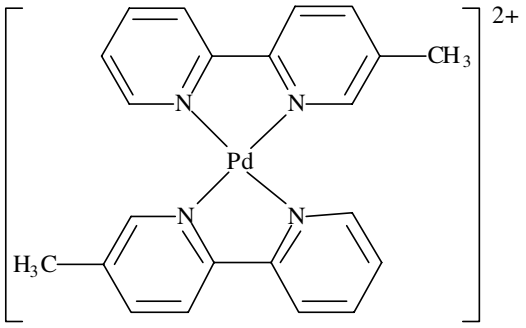
$$Na_2[PdCl_4] + L \xrightarrow{MeOH} [Pd(L)Cl_2] + 2\,NaCl \qquad (1)$$

	L^1	**1a**
	L^2	**2a**
	L^3	**3a**

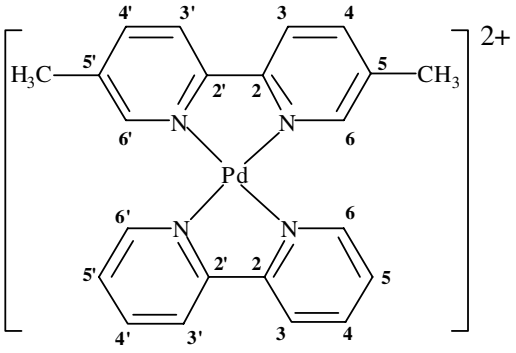
$$[Pd(L)Cl_2] + L + 2\,Na[BAr'_4] \xrightarrow{CH_2Cl_2} [Pd(L)_2][BAr'_4]_2 + 2\,NaCl$$

1a	L^1	**1**
2a	L^2	**2**
3a	L^3	**3**
2a	L^3	**4**

The neutral complexes $[Pd(L)Cl_2]$ (L = L^1: **1a**; L = L^2: **2a**; L = L^3: **3a**), slightly soluble in several organic solvents, were prepared according to methods described in the literature [7] and fully characterized by ^1H NMR and FAB mass spectroscopy (see Section 5).



Scheme 2. Cation of complex **1**.



Scheme 3. Cation of complex **4**.

Irradiation of the H6, H6′ (L^2) resonance gives enhancement of both the signals of the methyl groups in 5,5′- and of H6, H6′ (L^3) protons, whereas by irradiating the resonance of the latter protons, enhancement of the signals of H6, H6′ (L^2) and H5, H5′ (L^3) is observed (Scheme 3). It is worth noting that mixtures of species have been previously observed in solution for bis-chelated complexes having different N–N ligands such as $[Pd(bipy^R)(bipy)]^{2+}$ ($bipy^R$ = 6-substituted-2,2′-bipyridine) [5d], $[Pd(bipy)(phen)]^{2+}$ [5d], and $[Pd(bipy)(tmphen)]^{2+}$ (tmphen = 3,4,7,8-tetramethyl-1,10-phenanthroline) [8].

In the FAB mass spectra (positive ions) the molecular ions $[M]^+$ at m/z 446, 474, 418 for **1**, **2**, **3**, respectively, provide evidence for the stability of these species even in gas phase. In the case of complex **4**, the FAB mass spectrum shows the expected peak for $[M]^+$ at m/z 446 (ca. 20%), flanked by less abundant peaks at m/z 474 (15%) and m/z 418 (10%) corresponding to the symmetric species $[Pd(L^2)_2]^+$ and $[Pd(L^3)_2]^+$. In the fragmentation pattern, peaks due to $[M–L]^+$ are observed in all cases.

Additionally, a second series of complexes, [Pd(L)(Me)(MeCN)][BAr'_4], (**8**, L = L^1; **9**, L = L^2; **10**, L = L^3 = 2,2′-bipyridine) was obtained by a two-step reaction scheme:

$$[Pd(COD)(Me)Cl] + L \longrightarrow [Pd(L)(Me)Cl] + COD \quad (2a)$$

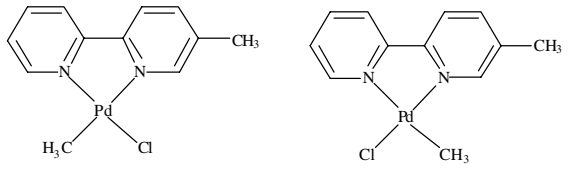
L: L^1, L^2, L^3 — **5**, **6**, **7**

$$[Pd(L)(Me)Cl] + Na[BAr'_4] \xrightarrow[-\ NaCl]{CH_2Cl_2/MeCN} [Pd(L)(Me)(MeCN)][BAr'_4] \quad (2b)$$

5, **6**, **7** — **8**, **9**, **10**

In the case of complex **4**, the ^{1}H NMR spectrum shows only one set of signals, consistent with one species having both ligands L^2 and L^3 co-ordinated to the palladium atom. The hypothesis of a mixture of two symmetric species $[Pd(L^2)_2]^{2+}$ and $[Pd(L^3)_2]^{2+}$ was also ruled out by a NOE difference experiment.

The chloride intermediates, **5**–**7**, (**5**, L = L^1; **6**, L = L^2; **7**, L = L^3 = 2,2′-bipyridine) could be isolated in good yields. The ^{1}H NMR spectrum of complex **5**, [Pd(L^1)(Me)Cl], indicates the presence of the two stereoisomers, **5a** and **5b**, in a ca. 1:1 ratio (Scheme 4).



5a **5b**

Scheme 4.

Very small differences, if any, are observed in the two isomers as regards the methyl resonances, Pd–Me and 5-Me. Nevertheless, assignment of the resonances to each of the two isomers is possible by comparison with the spectra of the symmetric species **2a** and **3a** and by taking into account the strong deshielding effect exerted by the chlorine atom, indicating proximity to H6 or H6′ [9]. Assignment of the signals was confirmed by a NOE difference experiment. Two isomers also are observed in the case of the ionic complex **8**, [Pd(L^1)(Me) (MeCN)]-[BAr'_4], (ca. 1:1 ratio) obtained through reaction (2b). The assignment of the ^{1}H resonances was possible with the help of a ^{1}H NOESY spectrum.

3. CO insertion studies

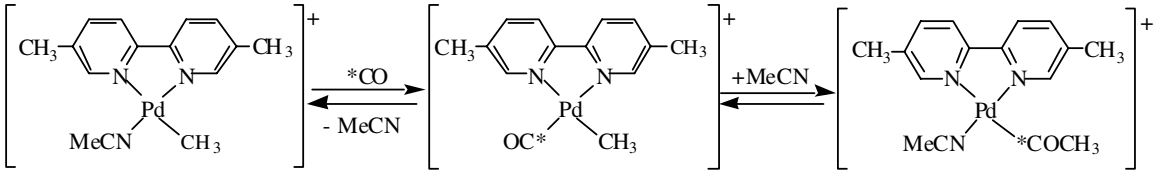
For the complexes [Pd(L)(Me)(MeCN)][BAr'_4] (**8** L = L^1; **9** L = L^2) the reactivity with labelled CO, was studied by in situ ^{1}H and ^{13}C NMR experiments at low temperature.

3.1. Complex *9*

The spectrum recorded after reacting complex **9** with ^{13}CO at 0 °C for 5 min showed, besides the signals corresponding to the starting complex, the appearance of two new species, molar ratio ca. 1:2. The minor of the new species, which decreased with time, exhibited three rather sharp resonances in the aliphatic region of the ^{1}H spectrum, δ 1.36 (Pd–Me), δ 2.30 and 2.42 (non-equivalent methyl groups of the ligand); in the ^{13}C spectrum a resonance was observed at δ 175.8, i.e. in the range previously assigned to coordinated CO in analogous species [3c,3q]. These data provided clear evidence for the presence of complex [Pd(L^2)(Me)(^{13}CO)][BAr'_4] (Scheme 5, **9a**). The ^{1}H spectrum of the major species showed, in addition to the resonances at δ 2.30 and 2.40 (corresponding to the methyl substituents) a doublet at δ 2.54 [$^2J(^1H–^{13}C) = 6.7$ Hz] assignable to a Pd–C(O)Me group. The presence in the ^{13}C spectrum of a resonance at δ 224.9 confirmed the presence of the insertion product [Pd(L^2)(^{13}COMe)(MeCN)][BAr'_4] (**9b**). The resonance of the coordinated MeCN, partially hidden in the ^{1}H spectrum at 0 °C, was well resolved at low temperature (at −80 °C, δ 2.41). It is worth noting that the three complexes were observed on lowering the temperature from 0 to −80 °C throughout the experiment (ca. 1.5 h) indicating that the reactivity with carbon monoxide was not very high.

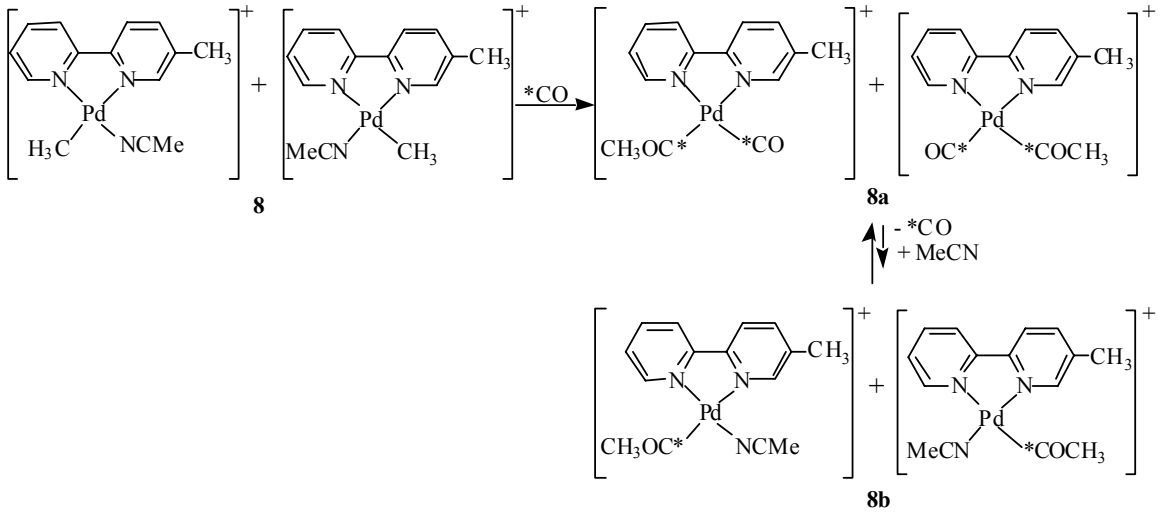
3.2. Complex *8*

As previously discussed, complex **8** is a mixture of two geometric isomers arising from the non-symmetric nature of the ligand, therefore a more complex situation may be expected after reaction with carbon monoxide. In fact the NMR spectra gave evidence of a different behaviour from that of complex **9** (Scheme 6). After reacting **8** with ^{13}CO at 0 °C for 5 min the ^{1}H spectrum, recorded at this temperature, showed only one set of rather broad signals, suggesting a dynamic process. The presence of a broad signal in the region typical for Pd–C(O)Me complexes (δ 2.77) and the lack of resonances in the Pd–Me region indicated that the ^{13}CO insertion into the Pd–Me bond was quite fast. On lowering the temperature at −40 °C the presence of two species became evident in a ratio of 8.6:1. The major species characterized in the ^{1}H spectrum by a resonance at δ 2.77 (d, $^2J(^1H–^{13}C) = 6.0$ Hz) and in the ^{13}C spectrum by resonances at δ 215.5 and δ 172.5 was identified as the carbonyl-acetyl species [Pd(L^1)(^{13}COMe)(^{13}CO)][BAr'_4] (**8a**). The minor species was characterized by a resonance at δ 2.56 in the ^{1}H NMR spectrum and at δ 226.2 in the ^{13}C spectrum. The absence of other ^{13}CO resonances in the range δ 170–180 and the chemical shift of the new ^{13}C(O)Me resonance, at low field, suggested an acetonitrile solvato of the acetyl complex, [Pd(L^1)(^{13}COMe)(MeCN)][BAr'_4] (**8b**). On further lowering the temperature down to −60 °C, in the ^{13}C NMR spectrum, both resonances corresponding to Pd–^{13}C(O)Me groups were split (δ 216.6 and 216.4; δ 227.5 and 227.8), possibly owing to a complicated set of



9 **9a** **9b**

Scheme 5.



Scheme 6.

equilibria involving also geometrical isomers frozen on the NMR time scale only at low temperature (Scheme 6).

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

Our previous investigations [5d] on the catalytic activity of a series of $[Pd(L)_2]^{2+}$ and $[Pd(L)(bipy)]^{2+}$ complexes with L = 6-substituded-2,2′-bipyridine showed that: (i) the 6-substituted ligands inhibit the activity and (ii) increase of the CO pressure (from 10 to 40 bar) leads to a decrease in productivity. Accordingly, at low pressure (10 bar), the $[Pd(bipy)_2][BAr'_4]_2$ salt is one of the best precatalysts. The same negative effect on the catalytic activity of substituents close to the nitrogen donors has been previously reported for the $[Pd(2,9\text{-}R_2\text{-phen})(MeCN)_2]^{2+}$ species (phen = 1,10-phenanthroline) [3d]. In the case of the latter derivatives, substituents in other positions have been shown to have modest positive (5-methyl or 5-nitro) or negative (3,4,7,8-methyl) effects [3d]. In contrast, quite recently, the dicationic bis-chelated Pd(II) compound $[Pd(3\text{-R-phen})_2][PF_6]_2$ (R = 1,2,2-trimethylpropyl) was shown to provide very high productivity in CO/styrene copolymerization, giving a polymer with molecular weight values higher than 300,000 [4].

Here, we report the effects of 5-alkyl substituents in the bis-chelated compounds $[Pd(bipy)_2]^{2+}$ on the CO/4-*tert*-butylstyrene copolymerization. The tests were run in 2,2,2-trifluroethanol, at 60 °C, under 40 bar of CO, in presence of 1,4-benzoquinone. The results are shown in Table 1.

Under these experimental conditions, the productivity of complexes **1**, **2** and **4**, containing at least one substituted bipyridine, showed a ca. 10% increase compared with that of $[Pd(bipy)_2][BAr'_4]_2$, **3**. The M_w values were in the range 120,000 (compound **1**)–166,000 (compound **2**). The absence of palladium black after 14 h of reaction accounts for the high stability of catalysts **1**, **2** and **4**.

Table 1
CO/4-*tert*-butylstyrene (TBS) copolymerization using dicationic **1**–**4** catalyst precursors

Precursor	g (CP)	g (CP)/g (Pd)	Productivity g (CP)/g (Pd) h	M_w (M_w/M_n)
1	3.24	11289	806	120300 (2.5)
2	3.31	11521	823	166652 (3.2)
3	3.10	10608	758	128903 (2.5)
4	3.28	11429	816	n.d.

Reaction conditions: $n(Pd) = 2{,}7 \times 10^{-3}$ mmol; $n(BQ)/n(Pd) = 64$; $V(TBS) = 24$ mL (0.131 mmol); $V(TFE) = 10$ mL; $P(CO) = 40$ bar; $T = 60$ °C; $t = 14$ h.

A comparison of the activity of the $[BAr'_4]$ salts with the corresponding $[PF_6]$ compounds, under strictly comparable conditions, confirms, even in this case, the positive effect of the $[BAr'_4]$ anion, as previously observed in the CO/styrene copolymerization [5d]. Productivities of 758 and 543 g(CP)/g(Pd) h were obtained with **3** and with $[Pd(bipy)_2][PF_6]_2$ [10], respectively.

The catalytic activity of the complexes $[Pd(L^1)(Me)(MeCN)][BAr'_4]$, **8**, and $[Pd(L^2)(Me)(MeCN)]$ $[BAr'_4]$, **9**, was compared with that of the corresponding salt of the unsubstituted 2,2′-bipyridine (L^3), **10**. The results of our tests and the details of the experimental conditions are shown in Fig. 1 and 2.

Both increasing of productivity and molecular weight are observed. After 48 h of reaction time the productivity of the catalysts **8** and **9** remains constant probably due to the combined effects of partial decomposition of the catalysts and increase of the concentration of the

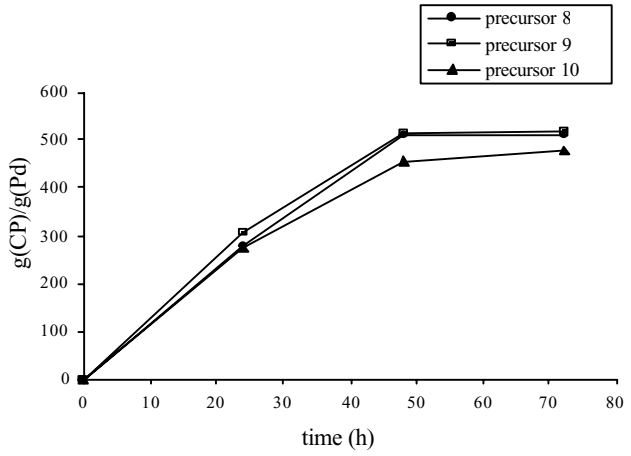


Fig. 1. CO/TBS copolymerization using catalyst precursors **8**, **9** and **10**: effect of time on productivity. Reaction conditions: $n(\mathrm{Pd}) = 5 \times 10^{-2}$ mmol; TBS/Pd = 310; $V(\mathrm{TBS}) = 2.8$ ml (15.5 mmol); $V(\mathrm{C_6H_5Cl}) = 20$ ml; $P(\mathrm{CO}) = 1$ bar; $T = 25$ °C.

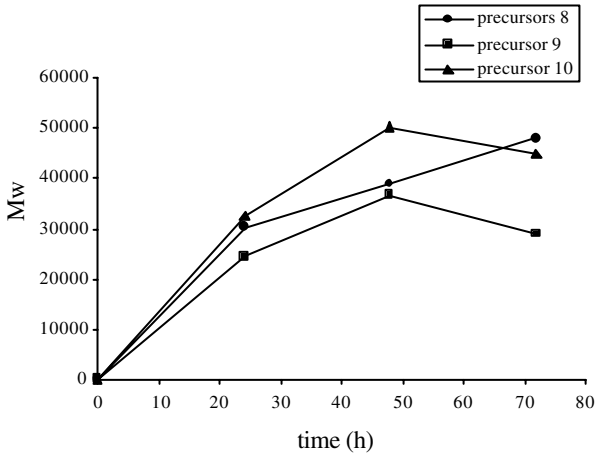


Fig. 2. CO/TBS copolymerization using catalyst precursors **8**, **9** and **10**: effect of time on molecular weight. For the reaction conditions, see Fig. 1.

copolymer in solution hindering the access of the monomer to the catalyst. In our study, working under [3c] conditions (Fig.1), a moderate but significant increase in the activity was observed when the ligand was a modified bypiridine, particularly in the case of the 5,5′-substituted-2,2′-bipyridine (L^2). A comparable effect was observed also under the same conditions of [3o] (Table 2).

Table 2

Precursor	g (CP)	g (CP)/g (Pd)	g (CP)/g (Pd) h	M_w (M_w/M_n)
8	1.43	360.5	15.02	32500 (1.6)
9	1.53	386.1	16.10	18500 (1.5)
10	1.33	334.5	13.94	16800 (1.5)

Reactions condition: $n(\mathrm{Pd}) = 3.74 \times 10^{-2}$ mmol; TBS/Pd = 250; $V(\mathrm{TBS}) = 1.7$ ml (9.34 mmol); $V(\mathrm{CH_2Cl_2}) = 15$ ml; $P(\mathrm{CO}) = 1$ bar; $t = 24$ h; $T = 0$ °C for 30 min and room temperature for 24 h.

The syndiotacticity of the polyketones obtained with the complexes bearing substituted bipyridine ligands was basically the same as that of the copolymer obtained using bipy as ligand. In conclusion, it seems that the productivity of both types of precursors is somewhat favoured by an alkyl substituent(s) in **5**.

5. Experimental

All reactions were carried out in a nitrogen atmosphere at room temperature (r.t.) using standard Schlenk techniques. Solvents for synthetic purposes were distilled and purified prior to use unless otherwise stated. Solvents for spectroscopy were used without further purification. Carbon monoxide labelled (CP grade 99%) was supplied by Aldrich. The bidentate nitrogen-donor chelating ligands L (5,5′-Me_2-2,2′-bipyridine, L^2, and 2,2′-bipyridine, L^3) were purchased from Aldrich and used as received, whereas the ligand L^1 (5-Me-2,2′-bipyridine) was prepared according to methods described in the literature. $Na_2[PdCl_4]$ (29.15% Pd) was obtained from Enghelard. The salt $Na[BAr'_4]$ {sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate} and the compound [Pd(COD)(Me)Cl] were prepared by reported methods [11,12].

^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian Gemini VXR 300 spectrometer with a ^1H resonance frequency of 300 MHz and a ^{13}C frequency of 75.4 MHz; on a Varian Mercury VX spectrometer with a ^1H resonance frequency of 400 MHz and a ^{13}C frequency of 100.5 MHz. Chemical shifts are given in ppm relative to internal TMS (^1H, ^{13}C). The NOE difference experiments and two-dimensional ^1H NOESY were obtained by means of standard pulse sequences. The mass spectrometric measurements were performed on a VG7070EQ instrument, equipped with a PDP 11-250J data system and operating under positive ion fast atom bombardment (FAB) conditions with 3-nitrobenzyl alcohol as supporting matrix.

Elemental analyses (C, H, N) were performed with a Perkin–Elmer elemental analyzer 240B, by Mr. A. Canu (Dipartimento di Chimica, Università degli Studi di Sassari). Conductivities were measured with a Philips PW 9505 conductimeter. The molecular weight of the copolymers and molecular weight distributions were determined by gel permeation chromatography measurements made in THF on a Waters 515-GPC device using a linear Waters Untrastyragel column with a Waters 2410 refractive index detector using polystyrene standards.

5.1. *[Pd(L)Cl_2] [$L = L^1$ **1a**, $L = L^2$ **2a**, $L = L^3$ **3a**]*

To a solution of $Na_2[PdCl_4]$ (308.8 mg, 1.00 mmol) in CH_3OH (10 mL) were added 1.09 mmol of L (185.6,

200.8, and 170.2 mg for L^1, L^2 and L^3, respectively). In a few minutes the product began to precipitate. The mixture was stirred at room temperature for 1 h. The precipitate formed was filtered off and washed with water, ethanol and diethyl ether to obtain the analytical sample as a yellow solid.

1a. Yield: 98%, mp: stable up to 290 °C. Found: C, 37.52; H, 2.61; N 7.79 (Calcd for $C_{11}H_{10}N_2Cl_2Pd$: C, 37.98; H, 2.88; N, 8.05). ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.45 s [3H], 5-Me; 8.90 s [1H], H6; 9.08 d [1H], H6′; 7.70–8.53 [5H] other aromatics. FAB mass spectrum, m/z: 311 $[M–Cl]^+$; 276 $[M–2Cl]^+$.

2a. Yield: 92%, mp: stable up to 290 °C. Found: C, 39.58; H, 2.91; N 7.45 (Calcd for $C_{12}H_{12}N_2Cl_2Pd$: C, 39.83; H, 3.32; N, 7.74). ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.44 s [6H], 5,5′-Me_2; 8.89 s [2H], H6, H6′; 8.17–8.42 [4H] other aromatics. FAB mass spectrum, m/z: 325 $[M–Cl]^+$; 290 $[M–2Cl]^+$.

3a. Yield: 98%, mp: stable up to 290 °C. Found: C, 36.11; H, 2.53; N 8.18 (Calcd for $C_{10}H_8N_2Cl_2Pd$: C, 35.98; H, 2.40; N, 8.39). ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.13 d [2H], H6, H6′; 7.81–8.58 [6H] other aromatics.

5.2. $[Pd(L)_2][BAr'_4]_2$ [$L = L^1$ **1**, $L = L^2$ **2**, $L = L^3$ **3**]

To a solution of $Na[BAr'_4]$ (291.0 mg, 0.33 mmol) and L (0.17 mmol, 29.1, 31.3 and 26.5 mg for L^1, L^2 and L^3, respectively) in 20 mL of CH_2Cl_2, was added slowly, under stirring at room temperature, a solution of $[Pd(L)Cl_2]$ (0.16 mmol, 56.4, 57.8 and 53.4 mg, for L^1, L^2 and L^3, respectively) in 40 mL of CH_2Cl_2. The solution was left to react for 1 h. After filtration of NaCl, the solution was evaporated to dryness in vacuo. The crude product, as pale-yellow foam, was converted to a solid by triturating with pentane or hexane. The analytical sample was obtained by repeated washings of the solid with the same solvents and drying for 24 h in vacuo.

1. Yield: 94%, mp: 125–127 °C. Found: C, 47.98; H, 2.23; N 2.83 (Calcd for $C_{86}H_{44}B_2F_{48}N_4Pd$: C, 47.53; H, 2.04; N, 2.58). ^{1}H NMR (300 MHz, CD_3OD): δ 2.54 s [6H], 5-Me; 7.59 s [24H] $[BAr'_4]^-$ ($Ar' = 3,5\text{-}(CF_3)_2\text{-}C_6H_3$); 7.76 m [2H], H5′; 8.20 d [2H], H4; 8.33 t [2H], H4′; 8.41 d [2H], H3; 8.48 d [2H], H3′; 8.63 s [2H], H6; 8.73 d [2H], H6′. Λ_M (5×10^{-4} M, acetone): 126 Ω^{-1} cm^2 mol^{-1}. FAB mass spectrum, m/z: 446 $[M]^+$; 276 $[M–L^1]^+$.

2. Yield: 90%, mp: 215–217 °C. Found: C, 47.91; H, 2.01; N 2.68 (Calcd for $C_{88}H_{48}B_2F_{48}N_4Pd$: C, 48.01; H, 2.20; N, 2.55). ^{1}H NMR (300 MHz, CD_3OD): δ 2.61 s [12H], 5,5′-Me_2; 7.59 s [24H] $[BAr'_4]^-$ ($Ar' = 3,5\text{-}(CF_3)_2\text{-}C_6H_3$); 8.31 d [4H] H4,H4′; 8.46 d [4H] H3,H3′; 8.62 s [4H], H6, H6′. Λ_M (5×10^{-4} M, acetone): 148 Ω^{-1} cm^2 mol^{-1}. FAB mass spectrum, m/z: 474 $[M^+]$, 290 $[M–L^2]^+$.

3. Yield: 74%, mp: 138–140 °C. Found: C, 46.90; H, 2.13; N 2.34 (Calcd for $C_{84}H_{40}B_2F_{48}N_4Pd$: C, 47.03; H, 1.88; N, 2.61). ^{1}H NMR (300 MHz, CD_3OD): δ 7.59 s [24H] $[BAr'_4]^-$ ($Ar' = 3,5\text{-}(CF_3)_2\text{-}C_6H_3$); 7.97 t [4H], H5, H5′; 8.52 t [4H], H4, H4′; 8.66 d [4H] H3,H3′; 8.84 d [4H], H6, H6′. FAB mass spectrum, m/z: 418 $[M]^+$; 262 $[M–L^3]^+$.

5.3. $[Pd(L^2)(L^3)][BAr'_4]_2$, **4**

To a solution of $Na[BAr'_4]$ (483.8 mg, 0.55 mmol) and L^3 (42.8 mg, 0.27 mmol) in 20 mL of CH_2Cl_2, was added slowly, under stirring at room temperature, a solution of $[Pd(L^2)Cl_2]$ (98.7 mg, 0.27 mmol, in 40 mL of CH_2Cl_2). The solution was left to react for 1 h. After filtration of NaCl, the solution was evaporated to dryness in vacuo. The crude product, as pale-yellow foam, was converted to a solid by triturating with pentane or hexane. The analytical sample was obtained by repeated washings of the solid with the same solvents and drying for 24 h in vacuo.

Yield: 93%, mp: 191–193 °C. Found: C, 47.70; H, 1.75; N 2.61 (Calcd for $C_{86}H_{44}B_2F_{48}N_4Pd$: C, 47.53; H, 2.04; N, 2.58). ^{1}H NMR (300 MHz, CD_3OD): δ 2.61 s [6H], 5,5′-Me_2; 7.59 s [24H] $[BAr'_4]^-$ ($Ar' = 3,5\text{-}(CF_3)_2\text{-}C_6H_3$); 7.99 t [2H] H5, H5′ ($L^3$); 8,31 d [2H] H4, H4′ ($L^2$); 8,46 d [2H] H3, H3′ ($L^2$); 8,52 t [2H] H4, H4′ ($L^3$); 8.61 s [2H], H6, H6′ (L^2); 8,66 d [2H] H3, H3′ (L^3); 8.86 d [2H], H6, H6′ (L^3). Λ_M (5×10^{-4} M, acetone): 151 Ω^{-1} cm^2 mol^{-1}. FAB mass spectrum, m/z: 446 $[M]^+$ of $[Pd(L^2)(L^3)]^{2+}$; 474 $[M]^+$of $[Pd(L^2)_2]^{2+}$; 418 $[M]^+$ of $[Pd(L^3)_2]^{2+}$.

5.4. $[Pd(L)(Me)Cl]$ [$L = L^1$ **5**, $L = L^2$ **6**, $L = L^3$ **7**]

To a solution of [Pd(COD)(Me)Cl] (235.9 mg, 0.89 mmol) in benzene (20 mL) was added under stirring at room temperature 1.14 mmol of L(194.7, 210.0, 178.1 mg for L^1, L^2 and L^3, respectively) in 20 mL of diethyl ether. In a few minutes the product began to precipitate as a yellow solid that after 1 h was filtered off, washed with Et_2O to obtain, after drying in vacuo, the analytical sample as a yellow solid. In the case of L^1, the product was obtained as a mixture of two geometrical isomers (**5a/5b** ca. 1:1; NMR criterion).

5. Yield: 91%, mp: 225 °C (dec). Found: C, 44.19; H, 4.28; N 8.34 (Calcd for $C_{12}H_{13}ClN_2Pd$: C, 44.02; H, 3.97; N, 8.56). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.00 s [3H+3H], Pd–Me (**5a**, **5b**, overlapping signals); 2.44 s [3H], 5-Me (**5a**); 2.49 s [3H], 5-Me(**5b**); 8.43 s [1H], H6 (**5b**); 8.63 d [1H], H6′, (**5a**); 8.97 s [1H], H6 (**5a**); 9.15 d [1H], H6′ (**5b**); 7.27–8.09 [5H+5H] other aromatics. FAB mass spectrum, m/z: 311 $[M–Me]^+$; 291 $[M–Cl]^+$; 276 $[M–Me–Cl]^+$.

6. Yield: 95%, mp 235 °C. Found: C, 45.18; H, 4.01; N 8.44 (Calcd for $C_{13}H_{15}ClN_2Pd$: C, 45.77; H, 4.43; N,

8.21). ^{1}H NMR (300 MHz, $CDCl_3$; in the structure formula N1 *trans* Me and N1′ *trans* Cl): δ 0.98 s [3H], Pd–Me; 2.42 s [3H], 5-Me; 2.47 s [3H], 5′-Me; 8.40 s [1H], H6′; 8.95 s [1H], H6; 7.74-7.95 [4H] other aromatics. FAB mass spectrum, m/z: 325 $[M–Me]^+$; 305 $[M–Cl]^+$; 290 $[M–Me–Cl]^+$.

7. Yield: 98%, mp: 216 °C (dec). Found: C, 42.62; H, 3.40; N 8.81 (Calcd for $C_{11}H_{11}ClN_2Pd$: C, 42.16; H, 3.51; N, 8.94). ^{1}H NMR (300 MHz, $CDCl_3$, in the structure formula N1 *trans* Me and N1′ *trans* Cl): δ 1.05 s [3H], Pd–Me; 8.68 s [1H], H6′; 9.21 s [1H], H6; 7.51-8.14 [6H] other aromatics. FAB mass spectrum, m/z: 297 $[M–Me]^+$; 277 $[M–Cl]^+$; 262 $[M–Me–Cl]^+$.

5.5. *[Pd(L)(Me)(MeCN)][BAr′$_4$] [L = L^1 **8**, L = L^2 **9**, L = L^3 **10**]*

To a solution of Na[BAr′$_4$] (338.1 mg, 0.38 mmol) in 1.20 mL of MeCN, were added under stirring at room temperature 0.38 mmol of [Pd(L)(Me)Cl] (118.7, 124.3, 118.9 mg for L^1, L^2 and L^3, respectively) in 20 mL of CH_2Cl_2. The yellow solution immediately faded and a NaCl precipitate was formed. The mixture was stirred for 1 h. The NaCl precipitate was filtered through fine paper and the yellow solution obtained was evaporated to dryness. The crude product was crystallized from CH_2Cl_2/pentane to give **8**, **9** and **10**. In the case of L^1, the product was obtained as a mixture of two geometrical isomers as compound **5** (**8a**/**8b**, ca. 1:1, NMR criterion).

8. Yield: 87%, mp: 53–55 °C. Found: C, 46.66; H, 2.65; N 3.39 (Calcd for $C_{46}H_{28}BF_{24}N_3Pd$: C, 46.16; H, 2.34; N, 3.51). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.02 s [3H], Pd–Me (**8a**); 1.04 s [3H], Pd–Me (**8b**); 2.35 s [3H], 5-Me (**8a**); 2.38 s [3H], Pd-NCMe; 2.39 s [3H], Pd-NCMe; 2.44 s [3H], 5-Me (**8b**); 7.50 s [4H] H*p* $[BAr'_4]^-$ (Ar′ = 3,5-$(CF_3)_2$-C_6H_3); 7.70 s [8H] H*o* $[BAr'_4]^-$ (Ar′ = 3,5-$(CF_3)_2$-C_6H_3); 8.17 s [1H], H6, (**8a**); 8.30 s [1H], H6, (**8b**); 8.32 d [1H], H6′ (**8b**); 8.44 d [1H], H6′ (**8a**); 7.32–7.99 [5H+5H] other aromatics. Λ_M (5×10^{-4} M, acetone): 56 $\Omega^{-1}\,cm^2\,mol^{-1}$. FAB mass spectrum, m/z: 332 $[M^+]$, 291 $[M–MeCN]^+$, 276 $[M–MeCN–Me]^+$.

9. Yield: 83%, mp: 56–58 °C. Found: C, 46.84; H, 2.37; N 3.36 (Calcd for $C_{47}H_{30}BF_{24}N_3Pd$: C, 46.61; H, 2.48; N, 3.47). ^{1}H NMR (300 MHz, $CDCl_3$, in the structure formula N1 *trans* Me and N1′ *trans* MeCN): δ 1.03 s [3H], Pd–Me; 2.33 s [3H], 5-Me; 2.40 s [3H], Pd-NCMe; 2.44 s [3H], 5′-Me; 7.50 s [4H] H*p*$[BAr'_4]^-$ (Ar′ = 3,5-$(CF_3)_2$-C_6H_3); 7.70 s [8H] H*o*$[BAr'_4]^-$ (Ar′ = 3,5-$(CF_3)_2$-C_6H_3); 8.13 s [1H], H6; 8.28 s [1H], H6′; 7.72-7.80 [4H] other aromatics. Λ_M (5×10^{-4} M, acetone): 56 $\Omega^{-1}\,cm^2\,mol^{-1}$. FAB mass spectrum, m/z: 346 $[M^+]$, 305 $[M–MeCN]^+$, 290 $[M–MeCN–Me]^+$.

10. Yield: 92%, mp: 85–87 °C. Found: C, 45.82; H, 2.02; N 3.54 (Calcd for $C_{45}H_{26}BF_{24}N_3Pd$: C, 45.72; H, 2.20; N, 3.55). ^{1}H NMR (300 MHz, $CDCl_3$, in the structure formula N1 *trans* Me and N1′ *trans* MeCN): δ 1.04 s [3H], Pd–Me; 2.38 s [3H], Pd-NCMe; 7.50 s [4H] H*p*$[BAr'_4]^-$ (Ar′ = 3,5-$(CF_3)_2$-C_6H_3); 7.70 s [8H] H*o* $[BAr'_4]^-$ (Ar′ = 3,5-$(CF_3)_2$-C_6H_3); 8.35 d [1H], H6; 8.50 d [1H], H6′; 7.37–8.02 [8H] other aromatics. Λ_M (5×10^{-4} M, acetone): 99 $\Omega^{-1}\,cm^2\,mol^{-1}$. FAB mass spectrum, m/z: 318 $[M]^+$; 277 $[M–MeCN]^+$; 262 $[M–MeCN–Me]^+$.

5.5.1. Copolymerization reactions – general procedure

4-*tert*-Butylstyrene, TBS (passed through a small column of basic Al_2O_3 prior to use), 2,2,2-trifluorethanol, TFE (dried on anhydrous $CaSO_4$ prior to use), 1,4-benzoquinone (BQ used as received) and chlorobenzene (used as received) were purchased from Aldrich.

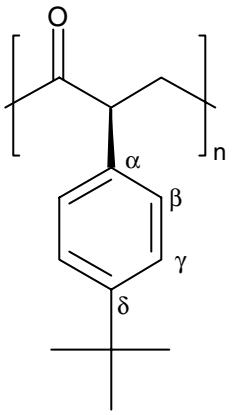
The reactions (with precursors **1**, **2**, **3**, **4**) were carried out in a stainless steel autoclave (150 mL), equipped with a magnetic stirrer and a temperature regulator. The precursor, 4-*tert*-butyl-styrene, 1,4-benzoquinone, and the alcohol were placed in the autoclave, which was purged then pressurized with CO and heated. After cooling and releasing the residual gas, the solution was poured dropwise into 200 mL of methanol under stirring. The white precipitate was collected by filtration, washed with methanol and dried in a vacuum oven at 70 °C overnight.

In a typical procedure the cationic precursor **8**, **9** or **10** was dissolved in chlorobenzene (or dichloromethane) in a previously flushed Schlenk flask and the N_2 atmosphere replaced with CO. 4-*tert*-Butylstyrene was then introduced and the reaction was allowed to take place at r.t. (or initially at 0 °C in dichloromethane) and 1bar of CO. Reaction time varied from 24 to 72 h. Work-up included filtration of the reaction mixture through Kieselghur and precipitation of the polymeric material by pouring the reaction solution dropwise into 200 ml of methanol under stirring. The off-white precipitate was collected by filtration, washed with methanol and dried in a vacuum oven at 70 °C overnight. Percentage conversions were calculated from the weight of the isolated polymeric material. The polymer was purified by reprecipitation and then polymer weights were measured. The copolymers were dissolved in the minimum amount of THF, the solution was filtered through a 0.22 μm filter and added dropwise to methanol under stirring. The solid was then filtered and dried as previously stated.

5.5.2. Copolymer CO/4-tert-butylstyrene characterization

^{1}H NMR (300 MHz, $CDCl_3$, r.t.): δ 7.0 (d $^3J = 8.1$ Hz), 2H H_β or H_γ; 6.6 (d $^3J = 8.1$ Hz), 2H H_γ or H_β; 4.11 (t $^3J = 7.1$ Hz), 1H CH; 3.0 (dd $^2J = 18.1$ Hz, $^3J = 6.8$ Hz), 1H CH_2; 2.6 (dd $^2J = 18.1$ Hz, $^3J = 6.8$ Hz), 1H CH_2; 1.23 (s, 9H, $C(CH_3)_3$).

^{13}C NMR (75.4 MHz, $CDCl_3$, r.t.): δ 206.7 (-C(O)-); 149.6 (C_δ); 134.0 (C_α); 128.0 (C_γ); 125.4 (C_β); 52.6 (CH); 43.0(CH_2); 34.3 ($C(CH_3)_3$); 31.3 ($C(CH_3)_3$).



5.5.3. ^{13}CO NMR study

The reactivity of the complexes **8** and **9** with carbon monoxide was studied in situ by ^1H and ^{13}C NMR spectroscopy. CD_2Cl_2 (0.7 mL) was added to a 5 mm NMR tube charged with the complex (7×10^{-3} mmol). After cooling the solution to 0 °C, ^{13}CO was bubbled for 5 min via a needle into the NMR tube. The sample was placed in a precooled NMR probe and ^1H and ^{13}C NMR spectra were recorded after 15 min. The spectra were recorded at 0; −20; −60 and −80 °C.

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