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Long-Lived Palladium Catalysts for CO/Vinyl Arene Polyketones Synthesis: A Solution to Deactivation Problems

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Abstract: A series of cationic palladium complexes of general formula $[Pd(Me)(MeCN)(N\text{–}N)][PF_6]$ (N–N = (phen) **1a**, 4,7-dichloro-1,10-phenanthroline (4,7-Cl_2-phen) **2a**, 4,7-diphenyl-1,10-phenanthroline (4,7-Ph_2-phen) **3a**, 4-methyl-1,10-phenanthroline (4-Me-phen) **4a**, 4,7-dimethyl-1,10-phenanthroline (4,7-Me_2-phen) **5a**, 5,5,6,6-tetrafluoro-5,6-dihydro-1,10-phenanthroline (F_4-phen) **6a**, containing different substituted phenanthroline ligands, have been prepared from the corresponding neutral chloro derivatives [Pd(Me)(Cl)(N–N)], (**1b**–**6b**). The X-ray crystal structure of $[Pd(Cl)_2(4,7\text{-}Cl_2\text{-phen})]$ (**2b′**) was determined. DFT calculations show that the electron density on the metal is tuned by the substituents on the ligands. The catalytic behavior of complexes **1a**–**6a** in the CO/styrene and CO/*p*-Me-styrene copolymerizations was studied in detail, showing that the generated catalysts are active for at least 90 h, yielding copolymers of high molecular weight. A firm correlation between the electron density on palladium on the one hand and the catalytic activity of the complexes and the molecular weight and the stereochemistry of the polyketones synthesized on the other hand has been established: the catalyst containing the F_4-phen is thus far the most active among those tested, yielding the syndiotactic CO/styrene copolymer with a stereoregularity of 96 % (*uu* triad) and with an M_w value of 1 000 000.

Keywords: N ligands · palladium · polyketones · polymerization · stereochemistry

Introduction

The performance of a catalyst in a general sense and of a catalyst for polymerization in particular, results from a combination of several factors such as activity, selectivity, lifetime, deactivation processes and the properties of the products. These factors are related to the components of the catalytic system only, such as the ancillary ligands, the comonomers, the reaction medium, the cocatalysts, the temperature. Catalyst deactivation is a very common phenomenon in homogeneous catalysis and represents a problem that cannot be easily overcome.[1]

In particular, the perfectly alternating palladium-catalyzed CO/vinyl arene copolymerization represents a well-known example of a reaction suffering from this problem.[2] In this case, the deactivation is mainly due to the decomposition of the active species to inactive palladium metal thus resulting in the catalyst death and limiting also the possibility of obtaining high molecular weight polymers.

During the last few years, we have studied in detail the factors affecting the catalyst stability and we found that the catalyst lifetime can be greatly enhanced when the copolymerization reaction is carried out in 2,2,2-trifluoroethanol (TFE) instead of methanol and when the complexes $[Pd(N\text{–}N)_2][PF_6]_2$ (N–N = 1,10-phenanthroline (phen), 2,2′-bipyridine (bpy), their symmetrically and unsymmetrically substituted derivatives), with an N–N to Pd ratio of 2, are used.[3]

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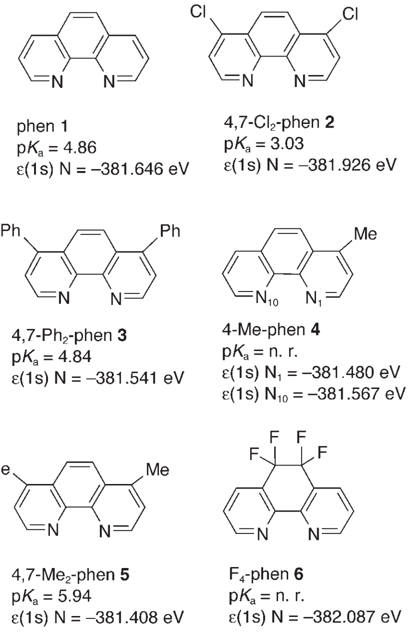


Scheme 1. The phenanthrolines studied with indication of the pK_a values (from ref. [7]) and of the DFT calculated core eigenvalues (n.r. = not reported).

Not only high catalytic activities could be reached, but also the synthesis of macromolecules with high molecular weight was achieved.

We have recently demonstrated that the fluorinated solvent, CF_3CH_2OH, gives better results than dichloromethane and the positive effect is retained when monochelated complexes $[Pd(Me)(MeCN)(N{-}N)][X]$ (X = OTf, PF_6^-) are used instead of the corresponding bischelated derivatives.[4]

As part of our studies on the factors affecting the catalyst stability, we decided to perform a systematic investigation of ligand electronic effects on catalyst performance. Up to date, phenanthroline based Pd catalysts are the most efficient systems for the synthesis of CO/aromatic alkene polyketones.[3d] Few reports have appeared on the use of substituted phenanthroline ligands and they mainly concern the commercially available, methyl-containing phenanthrolines. For instance, we[5] and others[6] reported that a remarkable decrease in the activity is found with the monochelated carboxylato Pd derivatives, $[Pd(RCOO)_2(N{-}N)]$ (R = Me, CF_3), on going from phen to 4,7-dimethyl-1,10-phenanthroline (4,7-Me_2-phen), to 3,4,7,8-tetramethyl-1,10-phenanthroline (Me_4-phen), to 2,9-dimethyl-1,10-phenanthroline (2,9-Me_2-phen), the latter being completely inactive. The influence of the ligand is even more pronounced when the bischelated complexes, $[Pd(N{-}N)_2][PF_6]_2$, are used (N–N = phen, 4,7-Me_2-phen, Me_4-phen).[3d] Only traces of polyketones were obtained with the $[Pd(Me_4\text{-phen})_2][PF_6]_2$ precatalyst, without showing any decomposition to palladium metal. These trends correlate well with the pK_a values of the tested ligands[7] and with the electron density present on the N atoms of the ligands and on palladium, as shown by theoretical analysis,[3d] both of them increasing on going from phen to Me_4-phen. The inactivity of the 2,9-Me_2-phen catalyst was attributed to the steric hindrance caused by the two methyl groups in close proximity to the palladium center.

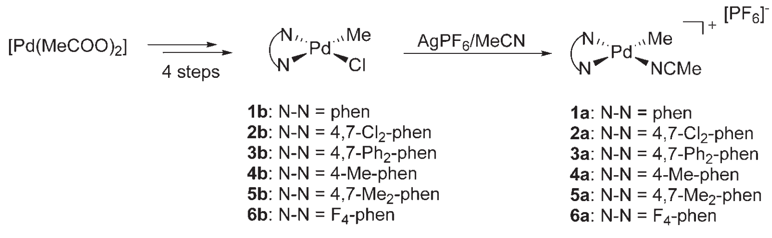
The use of a phenanthroline bearing an electron-withdrawing substituent, the 5-nitro-1,10-phenanthroline (5-NO_2-phen, pK_a 3.57),[8] was reported at the very beginning of the studies on this reaction, in the in situ catalytic system based on $[Pd(MeCN)_4][BF_4]_2$.[9] Although it showed better results than unsubstituted phenanthroline, both in terms of productivity and stereoregularity, it was not studied further.

We have now performed a detailed investigation of the ligand electronic effects on the CO/vinyl arene copolymerization promoted by the monocationic, organometallic palladium(II) complexes $[Pd(Me)(MeCN)(N{-}N)][PF_6]$ mainly focusing our attention on 4,7-disubstituted-1,10-phenanthrolines (Scheme 1), including 4,7-dichloro-1,10-phenanthroline (4,7-Cl_2-phen), but also 5,5,6,6-tetrafluoro-5,6-dihydro-1,10-phenanthroline (F_4-phen). While the 4,7-Cl_2-phen was previously studied in catalysis[10] and in kinetic investigations,[11] the only application of the F_4-phen has been reported last year in the copper-catalyzed N-arylation of azaheterocycles with aryl halides.[10d]

Results and Discussion

Synthesis and characterization of $[Pd(Me)(MeCN)(N{-}N)][PF_6]$ (1a–6a): The palladium complexes $[Pd(Me)(MeCN)(N{-}N)][PF_6]$, **1a–6a**, (N–N = phen **1a**, 4,7-Cl_2-phen **2a**, 4,7-diphenyl-1,10-phenanthroline (4,7-Ph_2-phen) **3a**, 4-methyl-1,10-phenanthroline (4-Me-phen) **4a**, 4,7-Me_2-phen **5a**, F_4-phen **6a**; Scheme 2) are easily synthesized starting from $[Pd(MeCOO)_2]$ and following the five-steps procedure reported in the literature.[12] The last step is the dehalogenation reaction of the neutral derivatives $[Pd(Me)(Cl)(N{-}N)]$, **1b–6b**, by $AgPF_6$ in the presence of acetonitrile.

Single crystals of the neutral derivative $[Pd(Cl)_2(4,7\text{-}Cl_2\text{-phen})]$ (**2b′**) were obtained upon addition of diethyl ether to a chloroform solution of **2b**. The X-ray analysis revealed that, during the crystallization process, an exchange reaction of the methyl group bound to palladium with chloride had



Scheme 2. Synthetic pathway of the monocationic palladium complexes **1a–6a**.

occurred on [Pd(Me)(Cl)(4,7-Cl_2-phen)] (**2b**), leading to complex **2b′** (Figure 1). An analogous behavior during the crystallization process was exhibited by compound **3b**, and the structure of [Pd(Cl)$_2$(4,7-Ph$_2$-phen)], published two decades ago,[13] was resolved. Similar methyl/chloride exchange has been recently reported also for other Pd–Me complexes with nitrogen-donor ligands.[4,14]

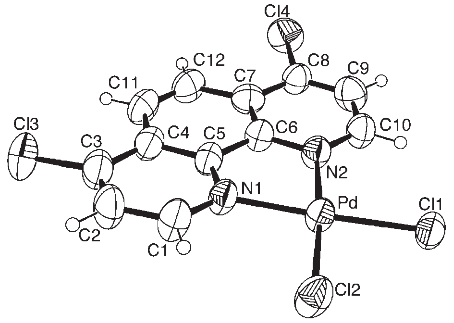


Figure 1. ORTEP drawing (thermal ellipsoids 40% probability level) of the complex [Pd(Cl)$_2$(4,7-Cl$_2$-phen)] **2b′**. Coordination bond lengths [Å] and angles [°]: Pd–N1 2.039(5), Pd–N2 2.045(4), Pd–Cl1 2.290(2), Pd–Cl2 2.289(2), N1-Pd-N2 81.27(18), N1-Pd-Cl1 175.66(12), N1-Pd-Cl2 93.56(13), N2-Pd-Cl1 94.41(14), N2-Pd-Cl2 174.37(13), Cl1-Pd-Cl2 90.74(6).

In complex **2b′** the metal attains the usual square planar geometry with coordination bond lengths and angles (Figure 1) close comparable within their e.s.d. values (e.s.d. = estimated standard deviation) to those detected in the two independent molecules of the crystal structure of [Pd(Cl)$_2$(4,7-Ph$_2$-phen)],[13] thus suggesting that the different electronic effect of chlorine and phenyl substituents at 4,7 positions does not have a remarkable influence on the Pd–N bond lengths measured in the solid state. Complex **2b′** is perfectly planar and the crystal packing shows pairs of complexes arranged head-to-tail related by a center of symmetry with the metals separated by 3.654 Å.

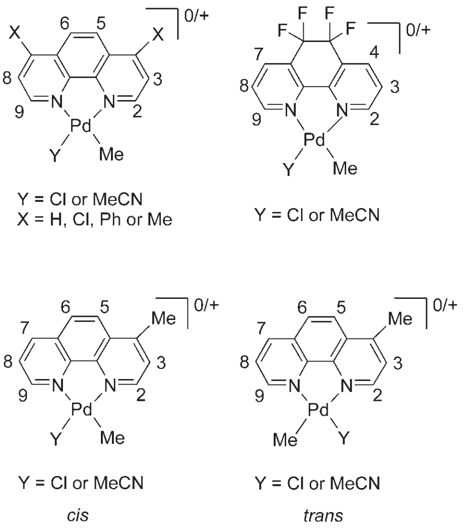
Table 1. Selected ^{1}H NMR data for complexes **1a**–**6a** and **1b**–**6b**.[a]

N–N/complex	Pd-Me	H^2	H^9	CIS (δ_c–δ_l)[b]
phen		9.20(dd)	9.20(dd)	
[Pd(Me)(Cl)(phen)] (**1b**)	1.22(s)	9.02(dd)	9.49(dd)	−0.18; 0.29
[Pd(Me)(MeCN)(phen)][PF$_6$] (**1a**)	1.26(s)	8.90(dd)	9.00(dd)	−0.30; −0.20
4,7-Cl$_2$-phen		9.09(d)	9.09(d)	
[Pd(Me)(Cl)(4,7-Cl$_2$-phen)] (**2b**)	1.23(s)	8.95(d)	9.44(d)	−0.14; 0.35
[Pd(Me)(MeCN)(4,7-Cl$_2$-phen)][PF$_6$] (**2a**)	1.24(s)	8.78(d)	8.99(d)	−0.31; −0.10
4,7-Ph$_2$-phen		9.25(d)	9.25(d)	
[Pd(Me)(Cl)(4,7-Ph$_2$-phen)] (**3b**)	1.23(s)	9.04(d)	9.54(d)	−0.21; 0.29
[Pd(Me)(MeCN)(4,7-Ph$_2$-phen)][PF$_6$] (**3a**)	1.29(s)	8.95(d)	9.07(d)	−0.30; −0.18
4-Me-phen		9.06(d)	9.20(dd)	
[Pd(Me)(Cl)(4-Me-phen)] (**4b**)				
cis	1.15(s)	8.80(d)	9.46(dd)	−0.26; 0.26
trans	1.16(s)	9.29(d)	8.98(dd)	0.23; −0.22
[Pd(Me)(MeCN)(4-Me-phen)][PF$_6$] (**4a**)				
cis	1.22(s)	8.71(d)	8.96(dd)	−0.35; −0.24
trans	1.23(s)	8.80(d)	8.87(dd)	−0.26; −0.33
4,7-Me$_2$-phen		9.05(d)	9.05(d)	
[Pd(Me)(Cl)(4,7-Me$_2$-phen)] (**5b**)	1.15(s)	8.85(d)	9.34(d)	−0.20; 0.29
[Pd(Me)(MeCN)(4,7-Me$_2$-phen)][PF$_6$]**5a**	1.19(s)	8.74(d)	8.81(d)	−0.31; −0.24
F$_4$-phen		9.01(dd)	9.01(dd)	
[Pd(Me)(Cl)(F$_4$-phen)] (**6b**)	1.19(s)	8.85(d)	9.32(d)	−0.16; 0.31
[Pd(Me)(MeCN)(F$_4$-phen)][PF$_6$] (**6a**)	1.27(s)	8.73(d)	8.96(d)	−0.28; −0.05

[a] Spectra recorded in CDCl$_3$ for **1b**–**6b** and in CD$_2$Cl$_2$ for **1a**–**6a**, at room temperature, δ in ppm, d = doublet, dd = doublet of doublets, s = singlet. [b] CIS = Coordination Induced Shift for H^2 and H^9 in the complexes (δ_c) and in the free ligand (δ_l).

The characterization in solution of both neutral and cationic series of complexes was performed by ^{1}H NMR spectroscopy recording the spectra in CDCl$_3$ and CD$_2$Cl$_2$, respectively, at room temperature. For the sake of clarity we numbered the protons of phenanthrolines starting from the heterocyclic ring in *cis* position to the Pd–Me fragment and, for complexes **4a** and **4b** containing the nonsymmetrical ligand 4-Me-phen, the isomer with the substituent on the ligand on the same side of the Pd–Me group has been conventionally called *cis* (Scheme 3). In all cases, signal assignments of the protons were based on NOE experiments, by irradiating the frequency corresponding to the signal of the Pd–Me, and on 2D homonuclear COSY experiments. Selected ^{1}H NMR data for **1a**–**6a** and **1b**–**6b** are given in Table 1.

For both series of complexes the singlet of the methyl bound to palladium falls in a range of frequency between δ 1.10 and 1.30 ppm. Contrary to the results previously reported by us for the monocationic complexes [Pd(Me)(N–N)$_2$][OTf],[12c] no clear correlation between the chemical shift of the Pd–Me group and the nature of the N–N ligand appears to be evident for both series of complexes. In each case, the number of peaks for the phenanthroline and their integration are in agreement with its coordination in a non symmetric chemical environment. In the neutral derivatives the coordination induced shift (CIS) for the protons in *ortho* position to the nitrogen donors is opposite in sign due to the fact that the frequency of H^2 is upfield shifted, while that of H^9 is shifted downfield with respect to the same signals in the free ligand, in agreement with the presence of the Pd–Cl group.[12a] For the monocationic complexes the signals of H^2 and H^9 are shifted to lower frequency with respect to the free ligand, as already found for the [Pd(Me)(N–N)$_2$][OTf] complexes.[12c] The CIS value does not significantly change on going from one ligand to the other inside both series of complexes, thus suggesting that the coordination to palladium affects in the same way the chemical shift of H^2 and H^9, regardless of the nature of the substituents on the ligand. Finally, the number of peaks in the spectra of complexes **4a**



Scheme 3. Numbering scheme of ligands in the corresponding neutral and monocationic palladium complexes.

and **4b**, containing 4-Me-phen, the only N–N ligand of the series not possessing a C_{2v} symmetry, indicates the presence of *cis* and *trans* isomers in different ratio in solution, depending on the nature of the complex (*cis*/*trans* 1.6 for **4b**, 1.2 for **4a**). The *cis* isomer is the most abundant in both cases, confirming the tendency of the methyl group to coordinate *trans* to the less basic nitrogen donor.[14a]

Theoretical analysis: A set of density functional theory (DFT) calculations has been performed in order to evaluate the electronic structure of the complexes. The geometries of complexes **1a**–**6a** have been optimized, and for complex **4a** both *cis* and *trans* isomers have been considered. Once the optimized geometries have been obtained, a further analysis on the eigenvalues of core electrons has been performed, in order to monitor the differences on the electron density on the metal atom and on N1 and N10 nitrogen atoms of the phenanthroline ligands. The same analysis has also been performed on the free ligands.

In order to assess quantitatively the relative stability between *cis* and *trans* isomers of **4a**, their relative total energy has been calculated at the GGA level. The calculations result in almost equal energies for *cis* and *trans*, the experimentally observed *cis* being only 0.2 kcal mol^{-1} more stable.

To discuss the effect of the ligand nature on the electron charge distribution of the complexes, we have chosen to monitor the core electron eigenvalues of the 1s orbital of Pd and of N1 and N10 atoms. This approach has been employed with success to discuss electron structures of metal clusters,[15] and has been shown to be more meaningful than conventional Mulliken population analysis in analoguous transition metal complexes.[3d] The core eigenvalues for complexes **1a**–**6a** are reported in Table 2, in the order of increasing negative eigenvalue relative to the Pd 1s orbital. Since the Pd 1s orbital is localized on the Pd atom, such eigenvalue feels the electron density on the metal, and the less electron density is present on the metal the more negative will be the eigenvalue; the electron density destabilizes the 1s orbital and therefore increases its energy. From Table 2 it appears that, following the values of the Pd 1s eigenvalues, complex **3a** displays the higher electron density on the metal, which then decreases in the order: **3a**, **5a**, **4a** *cis*, **4a** *trans*, **1a**, **2a** and **6a**. This trend is in agreement with the expected variations of electron-donor properties of the ligand caused by changing the substituents from phenyl to methyl, to hydrogen, up to halogens.

It is worth noting that the same analysis on the N1 and N10 1s orbital gives the same trend as on the metal, with only one minor exception in the ordering of the **4a** *cis* and *trans* isomers. Moreover, for all complexes of the series the eigenvalues of the two nitrogen atoms, N1 and N10, are significantly different, being those related to N10 more positive than those of N1, in agreement with the fact that N10 is *trans* to the Pd–Me moiety (Table 2).

The comparison of the calculated eigenvalues for the coordinated (Table 2) and the free ligand (Scheme 1) along the series reveals the same trend, with the exception that, for the free ligand, the 4,7-Me$_2$-phen would have been a more effective electron donor than 4,7-Ph$_2$-phen.

On the basis of these results, we concluded that the electron density on the metal is tuned by the substituents on the ligands: it decreases on going from the 4,7-Ph$_2$-phen to the F$_4$-phen, reflecting the trend of the Lewis basicity of the ligand.

The lower Lewis basicity of the 4,7-Cl$_2$-phen and of the F$_4$-phen ligands compared with phen is also confirmed by simple competitive ^{1}H NMR experiments. Addition of one equivalent of phen to a solution of **2b** or **6b** resulted in ligand exchange, yielding the complex **1b** and the corresponding free ligand. The time required for this exchange reaction to be completed depends on the substituted phen bound to palladium: in the case of F$_4$-phen the exchange takes place immediately, while for the 4,7-Cl$_2$-phen it is slower and after 30 min 55 % of the starting complex has reacted.

CO/styrene and CO/p-Me-styrene copolymerization reactions: A first series of preliminary CO/styrene and CO/*p*-Me-styrene copolymerization experiments was performed

Table 2. DFT calculated core eigenvalues (ε, in eV) for the Pd complexes **1a**–**6a**.

	3a	**5a**	**4a** *cis*	**4a** *trans*	**1a**	**2a**	**6a**
ε(1s)N1	−386.440	−386.470	−386.567	−386.169	−386.783	−386.861	−387.156
ε(1s)N10	−386.040	−386.078	−386.281	−386.675	−386.387	−386.482	−386.766
ε(1s)Pd	−23 442.911	−23 442.941	−23 443.044	−23 443.047	−23 443.153	−23 443.241	−23 443.432

with the monocationic complexes **1a**, **2a**, **4a**, **5a**, at $T = 30\,^{\circ}\mathrm{C}$, under 1 atm CO, in the presence or absence of 1,4-benzoquinone as oxidant, using 2,2,2-trifluoroethanol as solvent and at $[\mathrm{alkene}]/[\mathrm{Pd}] = 6\,800$ (Figure 2 and Table 3). The solids isolated at the end of the runs are perfectly alternating polyketones.

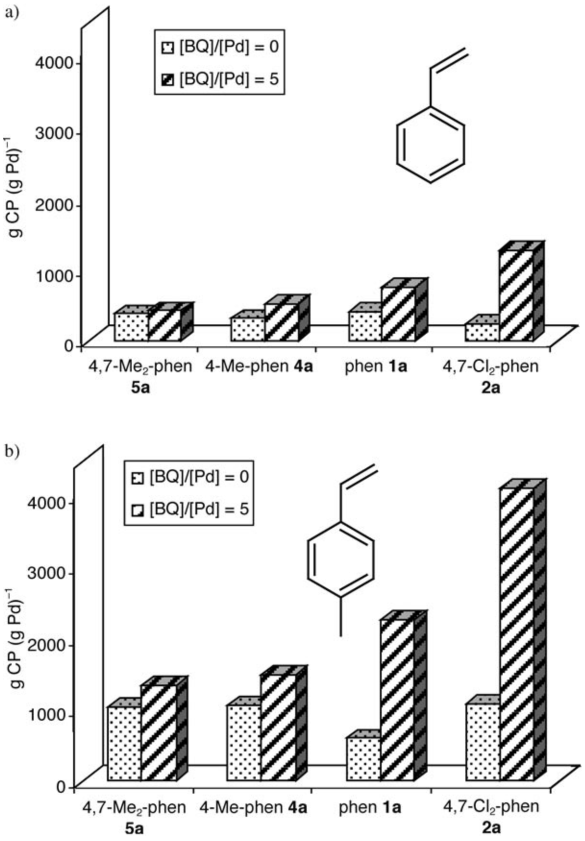


Figure 2. a) CO/styrene and b) CO/*p*-Me-styrene copolymerization: effect on productivity of the N–N ligand and of addition of 1,4-benzoquinone. Catalyst precursor: $[\mathrm{Pd(Me)(MeCN)(N{-}N)}][\mathrm{PF_6}]$ (**1a**, **2a**, **4a**, **5a**). Reaction conditions: $n_{\mathrm{Pd}} = 1.27\times10^{-5}$ mol; $p_{\mathrm{CO}} = 1$ atm; $T = 30\,^{\circ}\mathrm{C}$; alkene $V = 10$ mL; solvent: TFE $V = 20$ mL; $t = 8$ h.

When no benzoquinone is present, small differences in the productivities of the different precursors are observed for both the tested alkenes and no correlation with the nature of the N–N ligands is established (Figure 2). Since in all cases formation of black palladium metal is found, these results appear to be mainly affected by the low stability of the active species. Under these conditions, the molecular weights of the polyketones obtained are slightly influenced by the variation of the substituents on the N–N ligands and no clear relationship between the ligand and the length of the polymeric chains is observed (Table 3).

The addition of an excess of 1,4-benzoquinone with respect to palladium ($[\mathrm{BQ}]/[\mathrm{Pd}] = 5$) results in the stabilization of the active species and no formation of palladium metal is observed over the investigated range of time ($t = 8$ h). Such a positive effect of BQ is well known and was previously reported by us[3a] and others.[16] Moreover, kinetic measurements performed during the CO/styrene copolymerization proved that the oxidant does not affect the reaction rate and that the increase of productivity is due to the increased catalyst lifetime.[16] Once the problem of stability was solved, the influence of the ligand on the productivity of the system became clear: the productivity of the $[\mathrm{Pd(Me)(NCMe)(N{-}N)}][\mathrm{PF_6}]$ catalysts increases in the order:

4,7-Me$_2$-phen < 4-Me-phen < phen < 4,7-Cl$_2$-phen

regardless of the alkene comonomer (Figure 2). In particular, the value of 4.12 kg CP $(\mathrm{g\,Pd})^{-1}$ (corresponding to 515 g CP $(\mathrm{g\,Pd})^{-1}\mathrm{h}^{-1}$; CP = copolymer) is reached in the CO/*p*-Me-styrene copolymerization, when complex **2a**, containing the 4,7-Cl$_2$-phen, is used.

The analysis of the catalytic data proves that the effect of the substituents on the phenanthroline backbone is of the same magnitude for both the alkenes used. For instance, replacing the 4,7-Me$_2$-phen with the 4,7-Cl$_2$-phen results in a threefold increase of the productivity, both in the CO/styrene and in the CO/*p*-Me-styrene copolymerizations. Moreover, as previously observed by us with the bischelated complexes $[\mathrm{Pd(3\text{-}R\text{-}phen)_2}][\mathrm{PF_6}]_2$ (3-R-phen = 3-alkyl substituted-1,10-phenanthroline),[3c,d] when *p*-Me-styrene is the comonomer, the productivity is three times higher than that typical for styrene, with all the ligands tested.

As far as the molecular weight values are concerned, a ligand depending variation is found. Nevertheless, even in the presence of benzoquinone, no clear relationship between the nature of the N–N ligand and the M_{w} values is evident (Table 3). In agreement with previous results,[2b,17,18] the addition of benzoquinone to the reaction mixture of the CO/styrene copolymerization resulted in a decrease of the M_{w} values with respect to those obtained when no oxidant is present. On the other hand, rather surprisingly, the CO/*p*-Me-styrene pol-

Table 3. CO/styrene and CO/*p*-Me-styrene Copolymerization: effect of the N–N ligand and of addition of 1,4-benzoquinone. Catalyst precursor: $[\mathrm{Pd(Me)(MeCN)(N{-}N)}][\mathrm{PF_6}]$.[a]

Catalyst precursor	[BQ]/[Pd]	CO/styrene M_{w} ($M_{\mathrm{w}}/M_{\mathrm{n}}$)	CO/styrene R.U.[b] (TON)[c]	CO/*p*-Me-styrene M_{w} ($M_{\mathrm{w}}/M_{\mathrm{n}}$)	CO/p-Me-styrene R.U.[b] (TON)[c]
5a	0	19 000 (2.3)	144 (2.1)	28 500 (2.3)	195 (3.9)
4a	0	14000 (3.1)	106 (2.3)	23500 (3.0)	161 (4.8)
1a	0	17000 (2.1)	129 (2.5)	8400 (2.1)	58 (7.6)
2a	0	18000 (2.1)	136 (1.4)	31500 (2.2)	216 (3.6)
5a	5	5000 (1.5)	38 (8.9)	61000 (2.6)	418 (2.3)
4a	5	7000 (2.0)	53 (7.7)	53000 (3.4)	360 (3.0)
1a	5	3500 (1.4)	27 (23)	21500 (2.2)	147 (11.2)
2a	5	13500 (2.0)	102 (10)	44300 (3.1)	303 (9.9)

[a] Reaction conditions: see Figure 2. [b] R.U. = number of repetitive units inserted in the polymeric chain. [c] TON calculated as mole of CP per mole of Pd.

yketones synthesized in the presence of benzoquinone are characterized by M_w values significantly higher than those obtained with no oxidant (Table 3). This effect, opposite to that found for styrene, was neither reported nor investigated before.

The number of repetitive units inserted in the CO/*p*-Me-styrene polymeric chains, obtained with these monochelated complexes, is significantly higher than that found for the CO/styrene copolymers (Table 3), in particular when benzoquinone is used, suggesting that the molecular weight values are related both to the nature of the ligand and to the nature of the alkene. This result represents a difference with the catalytic system based on the bischelated complexes, where the length of the polymeric chains was found to be dictated basically by the catalyst (better by the ligand present in the catalyst) rather than by the nature of the substrate.[3d]

Kinetic investigations on this catalytic system have been performed by taking advantage of a multivessel reactor (AMTEC), allowing to monitor the CO uptake during the copolymerization reactions. All the catalytic tests were performed in the presence of BQ ([BQ]/[Pd]$=$5), at $T=30\,°C$, under a CO pressure of 5 or 10 bar, in trifluoroethanol, and with a ratio [alkene]/[Pd] of 24800 for all runs but one ([alkene]/[Pd]$=$6200) with styrene and of 22000 for those involving *p*-Me-styrene. In all experiments, the amount of copolymer obtained at the end of the runs was in good agreement with the value of the CO consumption measured by the instrument.

As a general comment, for all the tested catalysts a linear dependence of CO uptake with time was found and no catalyst deactivation was observed over the investigated range of time (up to 90 h). The large excess of the aromatic alkene used ensures to be in conditions of pseudo-zero order with respect to the alkene even at prolonged reaction times.

The catalytic behavior of complexes **1a** and **5a** in the CO/styrene copolymerization was evaluated both at 5 and 10 bar of CO working at [styrene]/[Pd]$=$6200. The higher activity of the complex containing phen, **1a**, with respect to that of the complex with 4,7-Me_2-phen, **5a**, is clearly shown at both CO pressures (Figure 3). The effect of doubling the CO pressure from 5 to 10 bar is almost negligible for complex **1a**, while for **5a** the inhibiting role of carbon monoxide is evident. A reasonable explanation might be based on the fact that, according to the DFT calculations (Table 2), on going from phen to 4,7-Me_2-phen the electron density on palladium increases, thus resulting in a better π back donation from Pd to CO, which competes more favorably with styrene for the fourth coordination site (Scheme 4).

Analogous experiments were conducted using **1a**, **4a** and **5a** as catalysts in the CO/*p*-Me-styrene copolymerization both at 5 and 10 bar of CO, working with a substrate to catalyst ratio of [*p*-Me-styrene]/[Pd]$=$22000 (Figure 4), which was obtained by decreasing the amount of palladium to one fourth with respect to the experiments reported in Figure 3. This modification was necessary to avoid the clogging of the reactors by the copolymer formed in large quantity due to

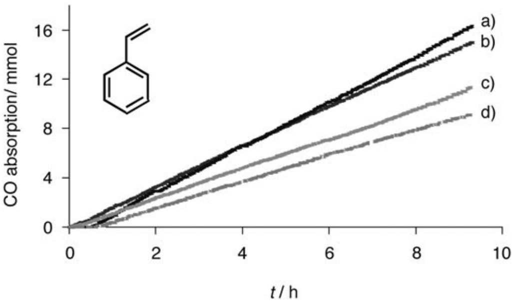
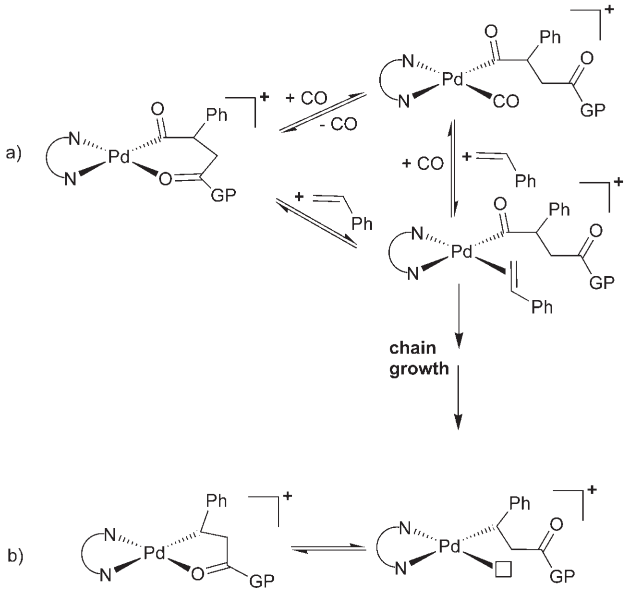


Figure 3. CO/styrene copolymerization: effect of N–N ligand and of CO pressure on CO uptake. Catalyst precursor: [Pd(Me)(MeCN)(N–N)][PF_6] (**1a**, **5a**). Reaction conditions: $n_{Pd}=0.425\times10^{-5}$ mol; $T=30\,°C$; styrene $V=3$ mL; solvent: 2,2,2-trifluoroethanol, $V=5$ mL; [BQ]/[Pd]$=$5; $t=9$ h. a) N–N = phen, $p_{CO}=10$ bar; b) N–N = phen, $p_{CO}=5$ bar; c) N–N = 4,7-Me_2-phen, $p_{CO}=5$ bar; d) N–N$=$4,7-Me_2-phen, $p_{CO}=10$ bar.



Scheme 4. Two key steps for the copolymerization reaction (GP$=$growing polymer).

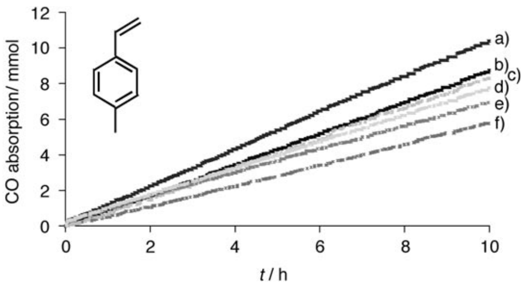


Figure 4. CO/*p*-Me-styrene copolymerization: effect of N–N ligand and of CO pressure on CO uptake. Catalyst precursor: [Pd(Me)(MeCN)(N–N)][PF_6] (**1a**, **4a**, **5a**). $n_{Pd}=0.106\times10^{-5}$ mol; $T=30\,°C$; *p*-Me-styrene $V=3$ mL; solvent: 2,2,2-trifluoroethanol, $V=5$ mL; [BQ]/[Pd]$=$5. a) N–N = phen, $p_{CO}=5$ bar; b) N–N = phen, $p_{CO}=10$ bar; c) N–N = 4-Me-phen, $p_{CO}=10$ bar; d) N–N = 4-Me-phen, $p_{CO}=5$ bar; e) N–N = 4,7-Me_2-phen, $p_{CO}=5$ bar; f) N–N = 4,7-Me_2-phen, $p_{CO}=10$ bar.

the high activity of the catalysts. As observed for the copolymerization of styrene, even for *p*-Me-styrene the introduction of electron-donor substituents on the ligand backbone causes a decrease of the catalytic activity in the order:

phen (**1a**) > 4-Me-phen (**4a**) > 4,7-Me_2-phen (**5a**)

The inhibiting effect of the CO pressure was observed once again for catalyst **5a**, while the activity of complex **4a** is almost unaffected by the variation of CO pressure.

A direct comparison of the activity of the two alkenes with different precatalysts, **1a**, **3a**, **4a** and **5a**, was performed by running the copolymerization at 10 bar of CO (Figure 5). The trends reported in Figure 5 show that in the CO/styrene copolymerization, 60 h of reaction time are necessary to reach values of CO uptake similar to those obtained in the CO/*p*-Me-styrene copolymerization after 20 h, confirming the higher activity of *p*-Me-styrene with respect to styrene. This trend is in agreement with the calculated 1s eigenvalues for Cα and Cβ of the two alkenes (ε(1s)Cα = −270.073 and −269.979 eV for styrene and *p*-Me-styrene, respectively; ε(1s)Cβ = −269.789 and −269.670 eV for styrene and *p*-Me-styrene, respectively). For both alkenes, the activity of catalyst **3a** containing the 4,7-Ph_2-phen lies between that of complex **4a** with the 4-Me-phen and that of **5a** with the 4,7-Me_2-phen. It should be noted that, according to the trend of the electron density on palladium by varying the substituents on the ligands, the activity of **3a** should be expected lower than that of **5a** (Table 2). The lack of correlation for the 4,7-Ph_2-phen ligand inside the series of substituted 1,10-phenanthrolines has been already reported in other studies,[7] but up to now no rationalization was possible.

The complexes containing the N–N ligands modified with the electron-withdrawing substituents, 4,7-Cl_2-phen or F_4-phen, **2a** and **6a**, respectively, have been tested in the CO/*p*-Me-styrene copolymerization at 5 bar of CO, in comparison with all the other ligands (Figure 6). Complex **6a** with the F_4-phen turned out to be the most active thus far, while complex **5a** with the 4,7-Me_2-phen is the least active among those tested. The complete trend of activity is:

F_4-phen (**6a**) ≫ 4,7-Cl_2-phen (**2a**) > phen (**1a**) > 4-Me-phen (**4a**) > 4,7-Me_2-phen (**5a**)

The significantly higher activity of catalyst **6a** is also confirmed in the CO/styrene copolymerization. It should be noted that the activity of **6a** in the CO/styrene polyketone synthesis is even higher than the activities of the catalysts with all the other ligands in the CO/*p*-Me-styrene copolymerization (Figure 6).

The effect of CO pressure was also investigated for the catalyst based on complex **6a**. For both the CO/vinyl arene copolymerizations, the increase of CO pressure from 5 to 10 bar resulted in a remarkable increase of the rate of CO uptake, particularly for the *p*-Me-styrene. Thus, no inhibiting role of carbon monoxide is evident, under these reaction conditions, with complex **6a** (Figure 7).

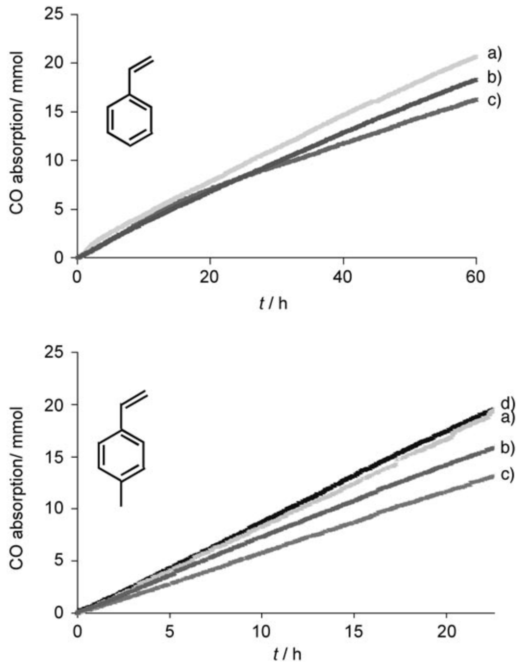


Figure 5. CO/vinyl arene copolymerization: effect of N–N ligand on CO uptake. Catalyst precursor: [Pd(Me)(MeCN)(N–N)][PF_6] (**1a**, **3a**, **4a**, **5a**). Reaction conditions: $n_{Pd} = 0.106 \times 10^{-5}$ mol; $T = 30$ °C; $p_{CO} = 10$ bar; alkene $V = 3$ mL; solvent: 2,2,2-trifluoroethanol, $V = 5$ mL; [BQ]/[Pd] = 5. Top: CO/styrene; bottom: CO/*p*-Me-styrene; a) N–N = 4-Me-phen; b) N–N = 4,7-Ph_2-phen; c) N–N = 4,7-Me_2-phen; d) N–N = phen.

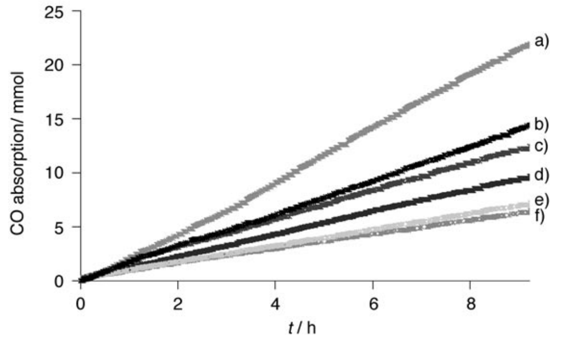


Figure 6. CO/*p*-Me-styrene copolymerization: effect of N–N ligand on CO uptake. Catalyst precursor: [Pd(Me)(MeCN)(N–N)][PF_6] (**1a**, **2a**, **4a**, **5a**, **6a**). Reaction conditions: $n_{Pd} = 0.106 \times 10^{-5}$ mol; $T = 30$ °C; $p_{CO} = 5$ bar; alkene $V = 3$ mL; solvent: 2,2,2-trifluoroethanol, $V = 5$ mL; [BQ]/[Pd] = 5. a) N–N = F_4-phen; b) N–N = F_4-phen, CO/styrene; c) N–N = 4,7-Cl_2-phen; d) N–N = phen; e) N–N = 4-Me-phen; f) N–N = 4,7-Me_2-phen.

The trend of CO uptake with time for complexes **2a** and **5a** proves that these catalysts are still active after 90 h of reaction without showing any decomposition to palladium metal (Figure 8).

On the basis of these catalytic results we conclude that a clear correlation between the catalytic activity of the complexes and the electron density on palladium (Table 2) exists. In particular, the activity decreases on increasing the electron density on the metal center, which, in turn, is tuned

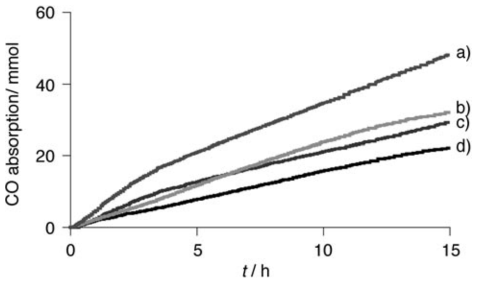


Figure 7. CO/vinyl arene copolymerization: effect of CO pressure on CO uptake. Catalyst precursor: [Pd(Me)(MeCN)(F_4-phen)][PF_6] (**6a**). Reaction conditions: $n_{Pd}=0.106\times10^{-5}$ mol; $T=30$ °C; alkene $V=3$ mL; solvent: 2,2,2-trifluoroethanol, $V=5$ mL; [BQ]/[Pd] = 5. Alkene = p-Me-styrene: a) p_{CO} = 10 bar; b) $p_{CO}=5$ bar; alkene = styrene: c) $p_{CO}=$ 10 bar; d) $p_{CO}=5$ bar.

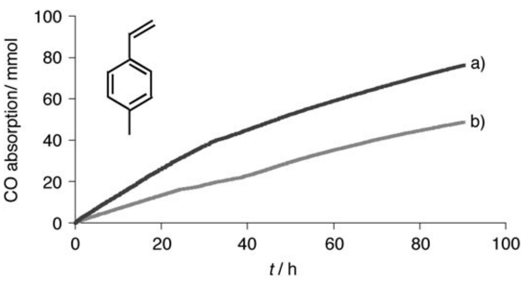


Figure 8. CO/p-Me-styrene copolymerization: effect of N–N ligand on CO uptake. Catalyst precursor: [Pd(Me)(MeCN)(N–N)][PF_6] (**2a**, **5a**). Reaction conditions: $n_{Pd}=0.106\times10^{-5}$ mol; $T=30$ °C; $p_{CO}=5$ bar; alkene $V=3$ mL; solvent: 2,2,2-trifluoroethanol, $V=5$ mL; [BQ]/[Pd] = 5; $t=$ 96 h. a) N–N = 4,7-Cl_2-phen; b) N–N = 4,7-Me_2-phen.

by substituents on the ligands. Taking into account that different steps are involved in the copolymerization process (i.e., CO coordination and insertion, alkene coordination and insertion), it is quite hard to speculate, which step is mainly affected by the variation on the ligand substituents. Nevertheless, the overall data on the effect of CO pressure on the rate of CO uptake suggests that the step mainly affected by the CO pressure is the equilibrium between the Pd–acyl–carbonyl species, which represents the resting state of the catalytic cycle, and the Pd–acyl–alkene intermediate (Scheme 4a). When a phenanthroline with electron-donor substituents, such as 4,7-Me_2-phen, is present on palladium, the Pd–acyl–carbonyl (the resting state) is stabilized due to a better π back donation from Pd to CO and the inhibiting role of carbon monoxide becomes evident; on the other hand, with a phenanthroline bearing electron-withdrawing substituents, such as F_4-phen, the dissociation of carbon monoxide from the resting state should be more facile favoring the alkene coordination and carbon monoxide does not play any inhibiting effect at the tested pressures. Finally, for catalysts containing phenanthrolines with a Lewis basicity intermediate between that of **5** and **6**, such as ligands **1** or **4**, the role of carbon monoxide is not so clearly established.

In addition, the ligand might also affect the stability of the six- and the five-membered palladacycles reported in Scheme 4. With less basic ligands, such as **6**, the interaction between palladium and the oxygen atom of the second last inserted carbonyl group is strengthened, which stabilizes both metallacycles.

The molecular weight values of selected polyketones have been measured (Table 4). For instance, the CO/styrene copolymers synthesized with **1a** or **5a** have similar M_w values, that are only slightly affected by the increase of CO pressure from 5 to 10 bar. Nevertheless, these values are one order of magnitude higher than those of the polyketones obtained at 1 atm of CO.

Table 4. M_w values of CO/styrene copolymers; catalyst precursor: [Pd(Me)(MeCN)(N–N)][PF_6].

N–N	p_{CO} [bar]	M_w (M_w/M_n)
phen (**1a**)	5	51000 (4.1)
4,7-Me_2-phen (**5a**)	5	51000 (1.5)
phen (**1a**)	10	44000 (1.9)
4,7-Me_2-phen (**5a**)	10	43000 (2.8)

Reaction conditions: see Figure 3.

The CO/p-Me-styrene copolymers obtained after 90 h of reaction are characterized by high molecular weight values: 371000 ($M_w/M_n=1.9$) for the polyketones prepared with **2a** and 307000 ($M_w/M_n=3.5$) for those prepared with **5a**. Finally, the polyketones synthesized with complex **6a** are characterized by very high molecular weight values ranging from 200000 to 1000000 depending on both the nature of the olefin and the CO pressure (Table 5). As observed for the polyketones obtained in the batch experiments, an increase of molecular weight is realized, when p-Me-styrene is used as comonomer in place of styrene, at both CO pressures. Moreover, in the case of CO/p-Me-styrene copolymers, the M_w value of 1000000 is reached for the first time. This represents the highest value ever reported for this kind of polymers. The enhancement of molecular weight obtained with the F_4-phen-containing catalyst might be attributed either to an increase of the propagation rate or to a decrease of the termination rate, or to both factors. Since the termination reaction is a β-hydrogen elimination of the open-chain intermediate reported in Scheme 4b, and since ligand **6** stabilizes the five-membered metallacycle, it seems likely that the chain transfer reaction will be slowed down when ligand **6** is used (Scheme 4b).

Table 5. CO/styrene and CO/p-Me-styrene Copolymerization: effect of the vinyl arene and of CO pressure. Catalyst precursor: [Pd(Me)(MeCN)(F_4-phen)][PF_6].[a]

p_{CO} [bar]	CO/styrene M_w (M_w/M_n)	CO/styrene R.U.[b]	CO/p-Me-styrene M_w (M_w/M_n)	CO/p-Me-styrene R.U.[b]
5	197000 (3.4)	1490	336500 (3.0)	2301
10	336000 (3.3)	2540	1030000 (2.3)	7051

[a] Reaction conditions: see Figure 8. [b] R.U. = number of repetitive units inserted in the polymeric chain.

Polyketones characterization: The stereochemistry of the CO/styrene copolymers was characterized by ^{13}C NMR spectroscopy recording the spectra in a mixture of 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) and $CDCl_3$. The microtacticity was determined by integration of the signals assigned to the *ipso*-carbon atom. The copolymers obtained with catalysts **1a**, **3a**, **4a** and **5a** show the expected syndiotactic microstructure with the usual triads distribution (80 % of *uu* triad and 20 % of the *ul* + *lu* triads) (Figure 9a).[19] In the ^{13}C NMR spectrum of the CO/styrene copolymers synthesized with catalyst **6a** the content of the *uu* triad is raised to 96 %, the remaining 4 % being related to the *ul* and *lu* triads (Figure 9b). This data represents the first time that the syndiotactic CO/styrene copolymer is obtained with such a high degree of stereoregularity. Higher values than the common 80 % have been previously reported: 90 % was reached with the 5-NO_2-phen,[9] or with the 2,2′-bipyrimidine,[20] while the value of 92 % was obtained with 1,4-diisopropyl-1,4-diazabuta-1,3-diene.[21] The stereochemical control of enantioface selection leading to the polyketones with a syndiotactic microstructure is attributed to the six-membered metallacycle (Scheme 4a).[22] The highest stereoregularity of the polyketones obtained with catalyst **6a** might be associated, again, to the higher stability of this metallacycle, when a poor basic ligand is bound to palladium.

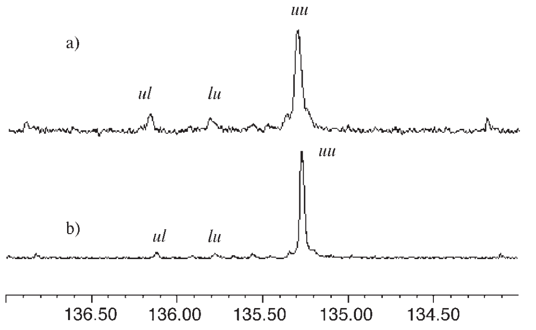
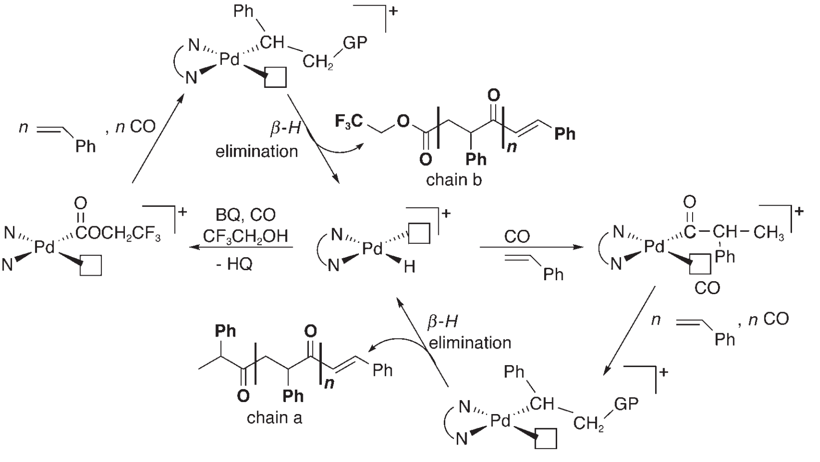


Figure 9. ^{13}C NMR spectra in HFIP + $CDCl_3$, at room temperature, region of *ipso* carbon atom, of: CO/styrene polyketone synthesized with a) **4a**; b) **6a**.

The CO/styrene copolymers end-groups were characterized by MALDI-TOF mass spectrometry (Figure 10). The repetitive unit (132 Da) is that expected for this kind of copolymerization. The solids synthesized are formed mainly by one kind of chain, cationized with K^+, which is the same regardless of the presence of benzoquinone in the catalytic mixture and it is featured by the saturated and the unsaturated termination fragments (chain a in Scheme 5). The clusters of minor intensity present in the spectrum of the polyketones obtained without addition of BQ to the reaction mixture are also associated to this kind of chain, which is cationized with Li^+ (Figure 10a). An additional polymeric chain is evident in the spectrum of the polyketones synthesized in the presence of benzoquinone (Figure 10b). This chain initiates with a trifluorocarbalkoxy fragment and it terminates with an unsaturated end group (chain b in Scheme 5).



Scheme 5. Polymeric chains present in the CO/styrene polyketones and the proposed mechanism for their formation (GP = growing polymer).

On the basis of this MALDI-TOF analysis it is deduced that the initiation step consists in the migratory insertion of the vinyl arene into the Pd−H bond yielding the saturated moiety. Moreover, in agreement with the literature data,[3a,18,23] in the presence of BQ, the Pd–H species is transformed into the trifluorocarbalkoxy species with the concomitant reduction of benzoquinone to 1,4-hydroquinone and starting a new polymeric chain. Finally, the β-hydrogen elimination is the unique chain transfer reaction taking place in this catalytic system, leading to polymer chains with an unsaturated fragment and to the Pd–H intermediate. These initiation and termination pathways are the only ones occurring also in the CO/styrene copolymerization promoted by the bischelated complexes $[Pd(N{-}N)_2][PF_6]_2$.[3b] Very recently, we have reported that also other termination reactions implying 1,4-hydroquinone or water are involved when the same copolymerization is promoted by the cationic complexes $[Pd(Me)(MeCN)(N^*\text{-}N^*)][PF_6]$, where the N*-N* ligand is the bioxazoline (4*S*,4′*S*)-2,2′-bis(4-isopropyl-4,5-dihydrooxazole), under analogous reaction conditions.[18]

The comparison of the present data with the previous ones suggests that, in trifluorethanol, the kind of termination reaction is determined by the nature of the N–N ligand present in the catalyst: when phen-catalysts are used, the chain transfer occurs selectively through the β-hydrogen

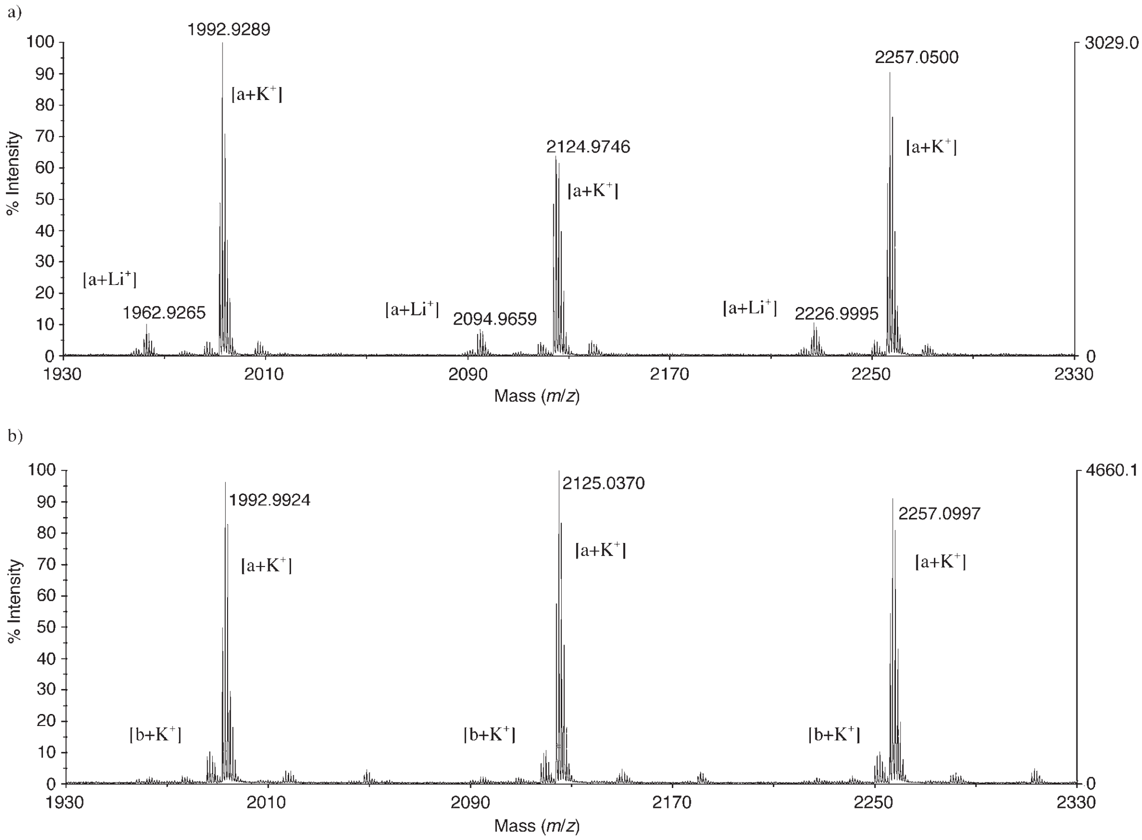


Figure 10. MALDI-TOF mass spectra of CO/styrene polyketones synthesized with precatalyst **2a**: a) with no addition of BQ to the reaction mixture; b) in the presence of BQ.

elimination, while with the bioxazoline ligands several pathways take place.

Conclusion

We have investigated the catalytic behavior of a series of monocationic, monochelated palladium(II) complexes containing substituted-1,10-phenanthrolines by varying the nature of the substituents, in the CO/vinyl arene copolymerization. We have demonstrated that, under proper reaction conditions, these complexes afford very stable active species and no decomposition to inactive palladium metal is observed for at least 90 h of reaction, thus allowing us to define these complexes as long-lived catalysts.

Most likely, the catalytic performance of these complexes is related to the electron density on palladium that is modulated by the substituents on the N–N ligand. In particular, it has been proved that the least basic ligand, F_4-phen, generates the most active and productive catalyst. This trend is opposite to that found for the CO/aliphatic alkene copolymerization promoted by diphosphine catalysts, where the replacement of the phenyl groups of the dppp ligand by *ortho*-anisyl groups afforded a more productive albeit slower catalyst.[24]

As far as the effect of these substituted 1,10-phenathrolines in other catalytic reactions is concerned, it should be noted that the catalytic behavior of palladium complexes with the F_4-phen has never been reported before, while the bischelated Pd^{II} complex with the 4,7-Cl_2-phen was tested in the reductive carbonylation of nitrobenzene into the corresponding carbamate, in methanol.[10a] In this reaction the $[Pd(4,7\text{-}Cl_2\text{-phen})_2][X]_2$ (X = triflate, BF_4^-) was found to be completely inactive together with the formation of a significant amount of palladium metal.

The comparison of the catalytic results in the CO/aromatic alkene copolymerization reported in this paper, related to the monochelated complexes, with those previously obtained with the bischelated derivatives,[3b–d] allows us to recognize some important milestones:

a) The stability of the active species is not only strongly dictated by the reaction medium, but it is also related to the chelating ligand to palladium ratio: a ligand to palladium ratio of 2 is necessary to avoid catalyst decomposition, even in trifluoroethanol. In fact, with a ligand to palladium ratio of 1, a small excess of benzoquinone with respect to palladium is required to prevent catalyst decomposition.
b) The molecular weight values of the synthesized polyketones are related to the carbon monoxide pressure: a

CO pressure of at least 5 atm is necessary to obtain copolymers with M_w values around 50000.

c) In trifluoroethanol, the preferential chain transfer reaction appears to be determined by the N–N ligand present in the catalyst: with phenanthroline-type ligands the β-hydrogen elimination occurs, while with bioxazoline ligands different pathways are possible.

Finally, up to now the lack of activity of the Pd complexes containing the 2,9-Me_2-phen has been attributed to the steric hindrance by the two methyl groups, which disfavors styrene coordination. On the basis of the electronic effects reported in this paper and taking into consideration the pK_a value of 2,9-Me_2-phen (6.17), the alkene coordination/insertion is negatively affected by this ligand also from an electronic point of view. Therefore, the inactivity of the Pd complexes containing 2,9-Me_2-phen might be better considered as a result of the combination of electronic and steric effects, both of them having a detrimental effect on the productivity of the system.

In conclusion, this study allows us to recognize the (F_4-phen)-Pd complex, [Pd(Me)(MeCN)(F_4-phen)][PF_6] **6a**, as the best catalyst ever reported for the CO/vinyl arene copolymerization reaction: it shows very high catalytic activity and productivity, yielding the corresponding polyketones with an M_w value of 1000000 and with a degree of stereoregularity of 96% in the *uu* triad.

Experimental Section

General: 4,7-Cl_2-phen and the F_4-phen were synthesized following the procedure reported in the literature.[25] All the other phenanthrolines (Aldrich) together with the analytical grade solvents (Carlo Erba), 2,2,2-trifluoroethanol, styrene and *p*-Me-styrene are commercial and used as received without further purification for synthetic and spectroscopic purposes.

Dichloromethane used for the synthesis of complexes was purified through distillation over $CaCl_2$ and stored under inert atmosphere. [Pd(MeCOO)$_2$] was a loan from Engelhard Italiana. Carbon monoxide (CP grade, 99.9%) was supplied by SIAD.

^{1}H NMR spectra were recorded at 400 MHz, on a JEOL EX 400 spectrometer; the resonances were referenced to the solvent peak versus TMS ($CDCl_3$ at 7.26 δ, CD_2Cl_2 at 5.33 δ). Two-dimensional correlation spectra (COSY) were obtained with the automatic program of the instrument. The NOE experiments were run with ^{1}H pulse of 90° of 12.3 µs. ^{13}C NMR spectra of polyketones were recorded in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) with a small amount of $CDCl_3$ for locking purposes at 100.5 MHz and referenced at 77.0.

CAUTION: HFIP is a very volatile and highly toxic solvent, so proper protection should be used when it is handled.

Elemental analyses (C, H, N), performed at Dipartimento di Scienze Chimiche (Università di Trieste), were in perfect agreement with the proposed stoichiometry (Table 6).

Table 6. Elemental analyses of complexes **2a**–**6a** and **2b**–**6b**.[a]

Compound	C [%]	H [%]	N [%]
[Pd(Me)(NCMe)(4,7-Cl_2-phen)][PF_6] (**2a**)	31.8 (32.37)	1.92 (2.17)	7.11 (7.55)
[Pd(Me)(Cl)(4,7-Cl_2-phen)] (**2b**)	37.9 (38.46)	2.01 (2.23)	6.8 (6.90)
[Pd(Me)(NCMe)(4,7-Ph_2-phen)][PF_6] (**3a**)	50.3 (50.68)	3.1 (3.47)	6.8 (6.57)
[Pd(Me)(Cl)(4,7-Ph_2-phen)] (**3b**)	61.1 (61.37)	3.70 (3.91)	5.50 (5.73)
[Pd(Me)(NCMe)(4-Me-phen)][PF_6] (**4a**)	37.8 (38.30)	2.9 (3.21)	7.9 (8.38)
[Pd(Me)(Cl)(4-Me-phen)] (**4b**)	47.1 (47.89)	3.28 (3.73)	7.75 (7.98)
[Pd(Me)(NCMe)(4,7-Me_2-phen)][PF_6] (**5a**)	39.5 (39.59)	3.18 (3.52)	7.97 (8.15)
[Pd(Me)(Cl)(4,7-Me_2-phen)] (**5b**)	49.4 (49.34)	4.99 (4.14)	7.64 (7.67)
[Pd(Me)(NCMe)(F_4-phen)][PF_6] (**6a**)	31.8 (32.08)	1.90 (2.15)	7.17 (7.48)
[Pd(Me)(Cl)(F_4-phen)] (**6b**)	37.2 (37.98)	1.8 (2.21)	6.16 (6.81)

[a] Calculated values are reported in parenthesis.

Synthesis of complexes: All manipulations were carried out under argon atmosphere by using Schlenk techniques and at room temperature. [Pd(MeCOO)$_2$], used as starting material, was transformed in *trans*-[Pd(Cl)$_2$(PhCN)$_2$] following the procedure reported in the literature.[12c] [Pd(Cl)$_2$(cod)] was obtained from *trans*-[Pd(Cl)$_2$(PhCN)$_2$].[26]

[Pd(Me)(Cl)(N–N)] 1b–6b

The synthesis of [Pd(Me)(Cl)(N–N)] **1b**–**6b** from [Pd(Cl)$_2$(cod)] was made following the literature method.[12a] Average yield: 90%.

[Pd(Me)(Cl)(4,7-Cl_2-phen)] (2b): ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.23 (s, 3H, Pd-Me), 7.97 (d, 1H, J=5.7 Hz, H^3), 7.98 (d, 1H, J=5.3 Hz, H^8), 8.44 (m, 2H, $H^{5,6}$), 8.95 (d, 1H, H^2), 9.44 ppm (d, 1H, H^9).

[Pd(Me)(Cl)(4,7-Ph_2-phen)] (3b): ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.23 (s, 3H, Pd-Me), 7.57 (m, 10H, aromatics), 7.78 (d, 1H, J=5.4 Hz, H^3), 7.80 (d, 1H, J=5.0 Hz, H^8), 8.00 (m, 2H, $H^{5,6}$), 9.04 (d, 1H, H^2), 9.54 ppm (d, 1H, H^9).

[Pd(Me)(Cl)(4-Me-phen)] (4b): ^{1}H NMR ($CDCl_3$, 400 MHz): *cis* isomer δ = 1.15 (s, 3H, Pd-Me), 2.89 (s, 3H, Me), 7.65 (m, 1H, H^3), 7.83 (m, 1H, H^8), 7.96 or 8.11 (m, 2H, $H^{5,6}$), 8.43 (d, 1H, J=8.4 Hz, H^7), 8.80 (d, 1H, J=5.2 Hz, H^2), 9.46 ppm (dd, 1H, H^9); *trans* isomer δ = 1.16 (s, 3H, Pd-Me), 2.86 (s, 3H, Me), 7.65 (m, 1H, H^3), 7.83 (m, 1H, H^8), 7.96 or 8.11 (m, 2H, $H^{5,6}$), 8.51 (d, 1H, J=7.8 Hz, H^7), 8.98 (dd, 1H, H^9), 9.29 ppm (d, 1H, J=4.8 Hz, H^2).

[Pd(Me)(Cl)(4,7-Me_2-phen)] (5b): ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.15 (s, 3H, Pd-Me), 2.86 (s, 3H, Me), 2.88 (s, 3H, Me), 7.64 (d, 1H, J=5.4 Hz, H^3), 7.67 (d, 1H, J=4.9 Hz, H^8), 8.12 (m, 2H, $H^{5,6}$), 8.85 (d, 1H, H^2), 9.34 ppm (d, 1H, H^9).

[Pd(Me)(Cl)(F_4-phen)] (6b): ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.19 (s, 3H, Pd-Me), 7.80 (m, 2H, $H^{3,8}$), 8.33 (d, 1H, J=7.9 Hz, H^7), 8.41 (d, 1H, J=7.8 Hz, H^4), 8.85 (d, 1H, J=5.4 Hz, H^2), 9.32 ppm (d, 1H, J=5.2 Hz, H^9).

[Pd(Me)(MeCN)(N–N)][PF_6] 1a–6a

The monocationic complexes **1a**–**6a** were obtained according to the method reported below.

1.2 equivalents of $AgPF_6$ dissolved in anhydrous acetonitrile were added to a stirred solution, or suspension, of the corresponding neutral complex **1b**–**6b** in dichloromethane. After 30 minutes, the solution was filtered over paper and concentrated under vacuum. Addition of diethyl ether causes the precipitation of the desired product, which was filtered off, washed with diethyl ether and dried under vacuum. Average yield: 75%.

[Pd(Me)(MeCN)(4,7-Cl_2-phen)][PF_6] (2a): ^{1}H NMR (CD_2Cl_2, 400 MHz): δ = 1.24 (s, 3H, Pd-Me), 2.58 (s, 3H, MeCN), 8.02 (d, 1H, J=5.9 Hz, H^3), 8.17 (d, 1H, J=5.4 Hz, H^8), 8.47 (m, 2H, $H^{5,6}$), 8.78 (d, 1H, H^2), 8.99 ppm (d, 1H, H^9).

[Pd(Me)MeCN)(4,7-Ph_2-phen)][PF_6] (3a): ^{1}H NMR (CD_2Cl_2, 400 MHz): δ = 1.29 (s, 3H, Pd-Me), 2.62 (s, 3H, MeCN), 7.58–7.65 (m, 10H, aromatics), 7.88 (d, 1H, $J=5.6$ Hz, H^3), 8.01 (d, 1H, $J=5.2$ Hz, H^8), 8.09 (m, 2H, $H^{5,6}$), 8.95 (d, 1H, H^2), 9.07 ppm (d, 1H, H^9).

[Pd(Me)(MeCN)(4-Me-phen)][PF$_6$] (4a): ^{1}H NMR (CD_2Cl_2, 400 MHz): *cis* isomer δ = 1.22 (s, 3H, Pd-Me), 2.59 (s, 3H, MeCN), 2.93 (s, 3H, Me), 7.75 (d, 1H, $J=5.3$ Hz, H^3), 8.05 (dd, 1H, $J=8.3$, 4.8 Hz, H^8), 8.1–8.3 (m, 2H, $H^{5,6}$), 8.62 (m, 1H, H^7), 8.71 (d, 1H, H^2), 8.96 ppm (dd, 1H, H^9); *trans* isomer δ = 1.23 (s, 3H, Pd-Me), 2.59 (s, 3H, MeCN), 2.93 (s, 3H, Me), 7.84 (d, 1H, $J=5.1$ Hz, H^3), 7.89 (dd, 1H, $J=8.1$, 5.2 Hz, H^8), 8.1–8.3 (m, 2H, $H^{5,6}$), 8.62 (m, 1H, H^7), 8.80 (d, 1H, $J=4.9$ Hz, H^2), 8.87 ppm (dd, 1H, H^9).

[Pd(Me)(MeCN)(4,7-Me$_2$-phen)][PF$_6$] (5a): ^{1}H NMR (CD_2Cl_2, 400 MHz): δ = 1.19 (s, 3H, Pd-Me), 2.58 (s, 3H, MeCN), 2.90 (s, 3H, Me), 2.91 (s, 3H, Me), 7.74 (d, 1H, $J=5.4$ Hz, H^3), 7.85 (d, 1H, $J=5.3$ Hz, H^8), 8.23 (m, 2H, $H^{5,6}$), 8.74 (d, 1H, H^2), 8.81 ppm (d, 1H, H^9).

[Pd(Me)(MeCN)(F$_4$-phen)][PF$_6$] (6a): ^{1}H NMR (CD_2Cl_2, 400 MHz): δ = 1.27 (s, 3H, Pd-Me), 2.57 (s, 3H, MeCN), 7.88 (dd, 1H, $J=5.6$, 8.3 Hz, H^3), 8.05 (dd, 1H, $J=4.8$, 8.2 Hz, H^8), 8.47 (d, 1H, H^7), 8.51 (d, 1H, H^4), 8.73 (d, 1H, H^2), 8.96 ppm (d, 1H, H^9).

X-ray crystallography: Diffraction data of compound **2b′** were collected at room temperature on a Bruker-Nonius FR591 rotating anode ($Cu_{K\alpha}$) equipped with a KappaCCD detector. Cell refinement, indexing and scaling of the data set were performed using program Denzo and Scalepack.[27] The structure was solved by Patterson and Fourier analyses and refined by the full-matrix least-squares method based on F^2 with all observed reflections.[28] The ΔF map revealed the presence of a molecule of chloroform in the lattice. The hydrogen atoms were located at geometrically calculated positions. All the calculations were performed using the WinGX System, Ver 1.70.00.[29] Crystal data and details of structure refinement are reported in Table 7.

Table 7. Crystallographic data for **2b′**·$CHCl_3$.

empirical formula	$C_{13}H_7Cl_7N_2Pd$
Z	2
M [g mol^{-1}]	545.76
μ [mm^{-1}]	18.012
λ [Å]	1.54178
F[000]	528
crystal system	triclinic
θ range [°]	6.15–64.70
space group	$P\bar{1}$
reflns collcd	11354
a [Å]	8.070(3)
b [Å]	10.683(4)
c [Å]	10.957(4)
unique reflns	2566
R_{int}	0.0520
observed reflns [$I>2\sigma(I)$]	2375
α [°]	80.00(3)
β [°]	88.41(2)
γ [°]	73.72(3)
refined params	209
GOF on F^2	1.077
$R1$ [$I > 2\sigma(I)$][a]	0.0529
V [Å^3]	892.7(6)
$wR2$ [a]	0.1387
ρ_{calcd} [g cm^{-3}]	2.030
residuals [e Å^{-3}]	0.571, −0.779

[a] $R1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR2=[\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

CCDC-282003 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Theoretical analysis: The electronic structure of the systems considered in this work has been calculated solving the Kohn-Sham (KS) equations, according to the Density Functional Theory (DFT) formalism.[30] The ADF program[31] based on the LCAO molecular orbital expansion has been employed to solve the KS equations. The basis sets belonging to the ADF database have been adopted, of the following types: Pd TZP frozen core 3d, N and C DZP frozen core 1s, H DZP. Such choice has proven accurate and computationally economic in previous works on transition metal complexes.[32,3d] For the geometry optimizations the Local Density Approximation for the exchange-correlation functional has been employed, with the VWN parametrization,[33] while for a more accurate calculation of the relative energy differences between isomers a single point calculation with GGA BP functional[34,35] has been employed.

CO/styrene and CO/*p*-Me-styrene copolymerization reactions at 1 bar: The copolymerization reactions were carried out in a glass reactor (75 mL), equipped with a magnetic stirrer and a temperature controller. The catalyst, 1,4-benzoquinone (when used), the aromatic alkene and the solvent were placed in the reactor, CO was bubbled through the solution for 10 minutes, then a balloon filled with CO was connected to the reactor and the system heated at 30 °C. At the end of the reaction, after cooling and releasing of the residual gas, the reaction mixture was poured into methanol (100 mL) causing the precipitation of the polymer which was then filtered, washed with methanol and dried under vacuum.

CO/styrene and CO/*p*-Me-styrene copolymerization reactions at 5 or 10 bar: Catalytic experiments were performed simultaneously in the parallel autoclave system AMTEC SPR16,[36] equipped with pressure sensors and a mass-flow controller and suitable for monitoring and recording gas uptakes throughout the reactions.

General procedure for the catalytic experiments: Four stainless steel autoclaves (12 mL) of the AMTEC SPR16 were flushed with argon one time. A solution of the Pd catalyst and 1,4-benzoquinone in trifluoroethanol (20 mL) was prepared and the reactors were charged each with 5 mL of the catalyst-solution as well as 3 mL of the alkene comonomer. The atmosphere was exchanged with carbon monoxide (gas exchange cycle 1) and the reactors were pressurized to 5 bar or 10 bar. After heating to the desired temperature (30 °C), the final pressures were adjusted and kept constant throughout the experiment. The carbon monoxide uptake was monitored and recorded automatically.

Molecular weight measurements of polyketones: The molecular weights (M_w) of copolymers and the molecular weight distributions (M_w/M_n) were determined by gel permeation chromatography versus polystyrene standards. The analyses were recorded on a Knauer HPLC (K-501 Pump, K-2501 UV detector) with a PLgel 5 μm 10^4 Å GPC column and chloroform as solvent (flow rate 0.6 mL min^{-1}). CO/styrene samples were prepared as follows: 2 mg of the copolymer was solubilized with 120 μL of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) and chloroform was added up to 10 mL; instead, CO/*p*-methylstyrene copolymers were directly soluble in chloroform. The statistical calculations were performed using the Bruker Chromstar software program.

MALDI-TOF measurements of polyketones: The characterization of the CO/styrene copolymer was performed on a Voyager-DE-STR (Applied Biosystems, Franingham, MA) instrument equipped with a 337 nm nitrogen laser. All spectra were acquired in the positive ion reflector mode. *trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) was used as matrix. Potassium trifluoracetate (Aldrich, 98 %) was added as the cationic ionization agent. The matrix was dissolved in THF at a concentration of 40 mg mL^{-1}. The polymer was dissolved in HFIP (1 mg mL^{-1}) and was deposited (0.5 μL) prior to the matrix on the target. For each spectrum 1000 laser shots were accumulated. In a typical MALDI experiment, the matrix and the salt solutions were premixed in the ratio: 5 μL matrix: 0.5 μL salt. Approximately 0.5 μL of the obtained mixture was hand spotted on the target plate.

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