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Review

The role of nitrogen-donor ligands in the palladium-catalyzed polyketones synthesis

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Dedicated to Professor Giovanni Mestroni on the occasion of his 65th birthday.

Contents

Abstract

During the last decade there has been increased interest in the development of homogeneous catalytic systems to promote homo- or copolymerization reactions of unsaturated hydrocarbons. This review is focused on systems based on palladium complexes with nitrogen-donor ligands and on their application as catalysts (or precatalysts) for co- and terpolymerization of carbon monoxide and olefins. Detailed catalytic performance is reported (productivity, molecular weight values and stereoregularity of the copolymers) allowing comparison between different systems. Particular attention will be addressed to the relationship between catalyst structure and structural features of the polymers synthesized. A comment on the mechanism involved in the various reactions is also given.

Keywords: Nitrogen-donor ligand; Palladium; Polymerization; Polyketone; Olefin; Homogeneous catalysis

1. Introduction

Over the past years, there has been much development of the application in homogeneous catalysis of transition metal complexes containing heterocyclic sp^2 nitrogen-donor chelating ligands [1]. Among them, 2,2′-bipyridine, 1,10-phenanthroline [2] and oxazoline-based [3] ligands have attracted particular attention.

The controlled synthesis of new and known polymeric materials represents a key issue for modern society and single-site metal promoted polymerization is a powerful tool to achieve the synthesis of macromolecules suited for well-defined applications. Indeed, this allows the fine tuning of microscopic features of the macromolecules, such as molecular weight and molecular weight distribution, the insertion of co-monomers, the

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Abbreviations: BArF, $B(3,5\text{-}(CF_3)_2C_6H_3)_4$; bpy, 2,2′-bipyridine; BQ, 1,4-benzoquinone; DMP, 2,2-dimethoxypropane; dppp, 1,3-bis(diphenylphosphino)propane; NQ, naphthoquinone; phen, 1,10-phenanthroline; TFE, 2,2,2-trifluoroethanol

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stereochemistry and so on, which determine the macroscopic properties of the synthesized polymers and, in the end, their potential applications [4].

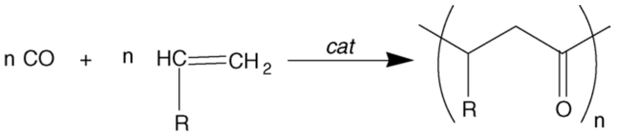
On the basis of the transition metal involved, homogeneous polymerization catalysts can be divided into two categories: catalysts based on early transition metals [5–8] and catalysts based on late transition metals [6–10]. However, homogeneous polymerization catalysts based on metals of Groups 6 and 7 have also been developed [6]. The catalytic behavior of coordination compounds is determined by the ancillary ligands bound to the metal center and a huge number of molecules have been tailored with the aim to synthesize macromolecules having desired macroscopic properties. From the literature, a correlation between the transition metal and the nature of the ancillary ligand spontaneously arises, i.e. ligands with a cyclopentadienyl moiety are generally associated with early transition metals, while non-carbon donor ligands are preferentially related to late transition metals.

Within this wide variety of molecules, *sp*^{2} nitrogen-donor ligands find applications in several polymerization reactions; some examples are homopolymerization of olefins [10,11], copolymerization of olefins with CO [12], atom transfer radical polymerization [13], free-radical polymerization involving catalytic chain transfer processes [14].

This review is focused on the CO/olefin co- and terpolymerization reactions promoted exclusively by palladium complexes containing *sp*^{2} nitrogen-donor ligands and covers the literature published until the end of 2004.

2. CO/olefin copolymerization reactions

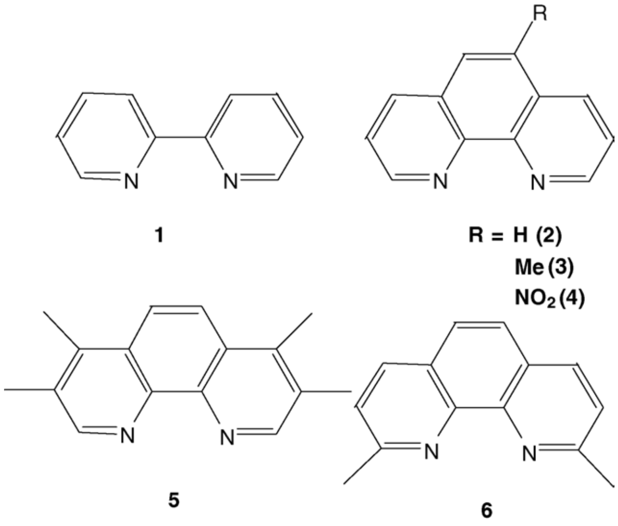
The copolymerization reaction of carbon monoxide with terminal alkenes (Eq. (1)) or strained cyclic olefins leads to the synthesis of perfectly alternated polyketones:



(1)

Most of the catalyst precursors contain a palladium center, though the use of some other transition metals have been reported [15,16]. Very active systems based on diphosphine-modified palladium catalysts have been developed for the co- and terpolymerization of aliphatic α-olefins allowing their commercial production [17]. On the other hand, aromatic olefins, such as styrene and its derivatives, are efficiently copolymerized, with a few exceptions [18], by bidentate nitrogen (N–N) or hybrid P–N ligands [19].

During the last few years, an increasing number of publications concerning the synthesis of polyketones have appeared in the literature as well as several detailed reviews [12]. We wish to focus here on the comparison among catalytic systems based on nitrogen-donor ligands, on the basis of their catalytic properties: productivity of the corresponding palladium catalysts, molecular weight and stereoregularity of the polymers obtained. All data reported in the literature were converted in order to make comparisons easier. Thus, pressure values are expressed in bar; productivity and productivity per hour, when data available, are expressed in grams of copolymer per gram of palladium (g CP/g Pd) and grams of copolymer per gram of palladium per hour (g CP/g Pd h), respectively. As far as the molecular weight is concerned, when available, M_w values are given together with the molecular weight distribution (M_w/M_n). In some cases, only the M_n values are reported.



Scheme 1.

2.1. N–N ligands with a bipyridine or a phenanthroline backbone

The use of 2,2′-bipyridine (bpy) (**1**) and 1,10-phenanthroline (phen) (**2**) (Scheme 1) in Pd-based catalytic systems for CO/styrene copolymerization was reported for the first time in the Shell's patent literature [20]. In a following more detailed study, Consiglio demonstrated that nitrogen-donor ligands were necessary to promote the synthesis of polyketones from aromatic olefins; while, when diphosphines were used, only *E*-1,5-diphenylpent-1-en-3-one, resulting from the monocarbonylation of styrene, was the product [21]. The catalytic system based on phen ligand yielded the CO/styrene copolymer ($M_n \approx 2000$) with a syndiotactic microstructure under a chain end control. The tacticity of this copolymer is determined by integration of signals due to the *ipso* carbon atom in the ^{13}C NMR spectrum [22]. With phen ligands the content of *uu* triad is 80%, the remaining 20% being related to the heterotactic triads, *ul* and *lu*.

In 1993, Sen et al. compared the catalytic activity of Pd complexes containing a phenanthroline or one of its substituted derivatives in the CO/olefin co- and terpolymerization reactions [23]. The catalytic systems consisted in the in situ formed catalyst, by co-dissolving a 1:1 molar ratio of the dicationic $[Pd(MeCN)_4][BF_4]_2$ and the phenanthroline ligand in a nitromethane/methanol mixture, in the presence of 1,4-benzoquinone (BQ). The comparison between ligands **2–6** (Scheme 1) in the CO/styrene copolymerization demonstrated that **4**, containing a nitro substituent in position 5, was the most efficient ligand, both in terms of productivity and

Table 1
CO/styrene copolymerization: effect of the phenanthroline derivative ligand

Catalyst precursor	g CP/g Pd	g CP/g Pd h	M_w (M_w/M_n)
$[Pd(MeCN)_4][BF_4]_2$ + **2**	4.9	0.10	170000 (4.1)
$[Pd(MeCN)_4][BF_4]_2$ + **3**	6.6	0.14	n.r.
$[Pd(MeCN)_4][BF_4]_2$ + **4**	10.2	0.21	n.r.
$[Pd(MeCN)_4][BF_4]_2$ + **5**	3.2	0.07	n.r.
$[Pd(MeCN)_4][BF_4]_2$ + **6**	0	–	–

Reaction conditions: $n_{Pd} = 68$ mmol; styrene $V = 2$ mL; solvent: nitromethane/methanol $V = 4/2$ mL; $T = 60$ °C; $P_{CO} = 69$ bar, reaction time: 48 h; [BQ]/[Pd] = 1.4; n.r. = not reported; catalyst precursor: $[Pd(MeCN)_4][BF_4]_2$ + N–N.

stereoregularity (90% of the *uu* triad content), whereas **6** led to the formation of an inactive complex due to the steric hindrance generated by the presence of the two methyl substituents in 2,9 positions (Table 1).

However, the higher activity of the catalyst containing ligand **4**, when compared to the unsubstituted phenanthroline **2**, depends on the olefin co-monomer. Actually, it was reported that, at least under the conditions used, the catalytic system containing **4** displayed a lower catalytic activity than the one containing **2** for the CO/norbornadiene reaction (Table 2) [24]. The same trend was observed in the CO/4-vinylcyclohexene copolymerization (see below, Table 25).

Starting from these initial studies on copolymerization carried out by in situ catalytic systems, most research has been focused on the use of presynthesized Pd(II) complexes as catalyst precursors, ranging from neutral to monocationic and dicationic systems.

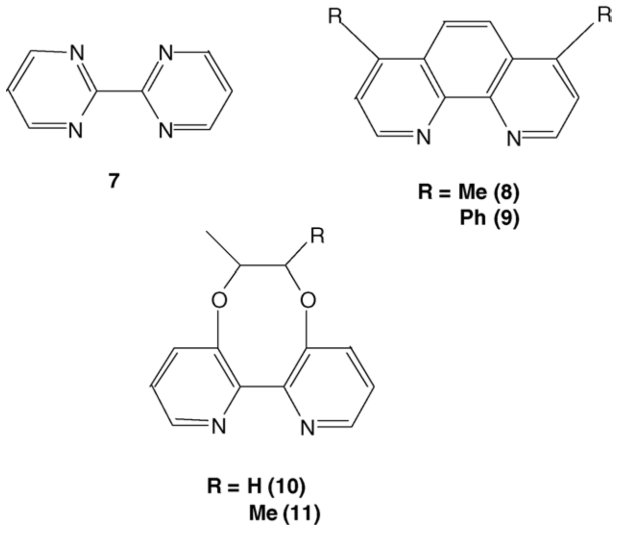
The first well-defined precatalyst was reported by Brookhart et al. in 1992. He found that the monocationic, organometallic complex [Pd(Me)(MeCN)(N–N)][BArF] (BArF = B(3,5-$(CF_3)_2C_6H_3)_4$), with N–N = **1** or **2**, promoted the CO/*p*-^{t}Bu-styrene copolymerization in chlorobenzene, at room temperature, leading to the formation of syndiotactic polyketones [25a]. The degree of stereoregularity was increased up to 90%, when N–N was the 2,2′-bipyrimidine **7** (Scheme 2) [25b]. This catalytic system was also used for the synthesis of CO/norbornene copolymer and for the CO/ethylene/styrene and CO/propylene/styrene terpolymerization [25]. This reaction represents a rare example of *living* alternating copolymerization.

In 1994, we reported active catalytic systems for the CO/styrene copolymerization based on neutral Pd complexes of general formula $[Pd(RCO_2)_2(N–N)]$ (R = Me, CF_3) [26]. The copolymerization reactions were carried out in methanol, in the presence of benzoquinone (Table 3). A remarkable influence of the nature of the carboxylato anion was observed, the acetate derivative being almost inactive. This effect could be related both to the relative ability of acetate and trifluoroacetate to undergo esterification and to their σ-donor power. The analysis of the effect of the N–N ligand showed that the bpy complex is more active than the phenanthroline derivatives. The 3,4,7,8-tetramethyl-1,10-phenanthroline **5** is less active and the catalyst containing the 2,9-dimethyl-1,10-phenanthroline **6** is totally inactive. In the former case the low activity was attributed to the electron donor properties of the ligand, whereas in the latter, steric hindrance was claimed to be responsible for the loss of activity. The copolymers obtained have the usual syndiotactic microstructure and molecular weights are in the range 5000–7000, as evaluated by ^{13}C NMR.

Table 2
CO/norbornadiene copolymerization: effect of the phenanthroline derivative ligand

Catalyst precursor	g CP/g Pd	g CP/g Pd h	M_w
$[Pd(MeCN)_4][BF_4]_2$ + **1**	245	49	6360
$[Pd(MeCN)_4][BF_4]_2$ + **2**	300	60	8680
$[Pd(MeCN)_4][BF_4]_2$ + **4**	255	51	7690

Reaction conditions: $n_{Pd} = 0.1$ mmol; $n_{norbornadiene} = 5 \times 10^{-2}$ mol; solvent: methanol $V = 10$ mL; *p*-toluenesulfonic acid 2 mmol; $T = 50$ °C; $P_{CO} = 33$ bar; reaction time: 5 h; [BQ]/[Pd] = 100; catalyst precursor: $[Pd(MeCN)_4][BF_4]_2$ + N–N.



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R = Me (8)
Ph (9)

R = H (10)
Me (11)

Scheme 2.

An analogous trend was observed in a study on catalytic systems containing $[Pd(MeCO_2)_2(N–N)]$ (N–N being a phenanthroline or one of its substituted derivatives), naphthoquinone and 1 equiv. of $[(N–N)H][PF_6]$ as co-catalyst (Table 4) [27]. The addition of 1 equivalent of $[(phen)H][PF_6]$ to the catalytic system based on $[Pd(MeCO_2)_2(phen)]$ resulted in an increase in the productivity of one order of magnitude. The authors attributed this effect both to the acidic function of $[(phen)H][PF_6]$, acting as a co-catalyst, and its capability to provide an additional stability to the active species. For the ligands tested, the activity in the

Table 3
CO/styrene copolymerization: effect of the catalyst precursor

Catalyst precursor	g CP/g Pd	g CP/g Pd h
$[Pd(MeCO_2)_2(\mathbf{2})]$	4	0.4
$[Pd(CF_3CO_2)_2(\mathbf{2})]$	300	30
$[Pd(CF_3CO_2)_2(\mathbf{1})]$	376	37.6
$[Pd(CF_3CO_2)_2(\mathbf{5})]$	141	14.1
$[Pd(CF_3CO_2)_2(\mathbf{6})]$	0	0

Reaction conditions: $n_{Pd} = 0.5$ mmol; solvent: methanol $V = 500$ mL; $T = 40$ °C; $P_{CO} = 40$ bar; reaction time: 10 h; [BQ]/[Pd] = 80; catalyst precursor: $[Pd(RCO_2)_2(N–N)]$.

Table 4
CO/styrene copolymerization: effect of the addition of 1 equiv. of $[(N–N)H][PF_6]$

Catalyst precursor	pK_a[a]	g CP/g Pd	g CP/g Pd h
$[Pd(MeCO_2)_2(\mathbf{2})]$		109	18.1
$[Pd(MeCO_2)_2(\mathbf{2})] + [(\mathbf{2})H][PF_6]$	4.86	1165	194
$[Pd(MeCO_2)_2(\mathbf{9})] + [(\mathbf{9})H][PF_6]$	4.84	586	97.7
$[Pd(MeCO_2)_2(\mathbf{8})] + [(\mathbf{8})H][PF_6]$	5.94	357	59.5
$[Pd(MeCO_2)_2(\mathbf{5})] + [(\mathbf{5})H][PF_6]$	6.31	266	44.3
$[Pd(MeCO_2)_2(\mathbf{6})] + [(\mathbf{6})H][PF_6]$	6.17	0	0
$[Pd(MeCO_2)_2(\mathbf{6})] + [(\mathbf{2})H][PF_6]$		533	88.8
$[Pd(MeCO_2)_2(\mathbf{8})] + [(\mathbf{2})H][PF_6]$		620	103.3
$[Pd(MeCO_2)_2(\mathbf{5})] + [(\mathbf{2})H][PF_6]$		617	102.8
$[Pd(MeCO_2)_2(\mathbf{9})] + [(\mathbf{2})H][PF_6]$		567	94.5
$[Pd(MeCO_2)_2(\mathbf{1})] + [(\mathbf{1})H][PF_6]$		597	99.5
$[Pd(MeCO_2)_2(\mathbf{1})] + [(\mathbf{2})H][PF_6]$		1054	175.7

Reaction conditions: $n_{Pd} = 3.6 \times 10^{-2}$ mmol; styrene $V = 10$ mL; solvent: methanol $V = 20$ mL; $T = 65\,°C$; $P_{CO} = 40$ bar; reaction time: 6 h; [NQ]/[Pd] = 20; catalyst precursor: $[Pd(MeCO_2)_2(N–N)]$.

[a] pK_a values of the N–N ligands **2**, **5**, **6**, **8** and **9** [28].

CO/styrene copolymerization was found to be linearly dependent on the pK_a of the substituted nitrogen ligand: in particular, it decreases on increasing the Lewis basicity of N–N. The influence of addition of $[(phen)H][PF_6]$ as co-catalyst to systems containing ligands **1**, **5**, **6**, **8** or **9** was studied and the results obtained attributed to ligand exchange reactions (Table 4).

The catalytic system based on $[Pd(MeCO_2)_2(\mathbf{2})]$ efficiently copolymerizes CO with *para*-substituted styrene derivatives such as acetoxystyrene, hydroxystyrene or formyloxystyrene, but no data concerning the productivity are available [29]. $[Pd(MeCO_2)_2(\mathbf{1})]$ generated in situ was reported to catalyze the copolymerization of CO with various styrene derivatives such as *p*-methoxystyrene, *p*-ethylstyrene, *m*- and *o*-bromostyrene, 3,4-dimethoxystyrene, 3,4-dimethylstyrene, 2-methyl-5-^{t}Bu-styrene [30]. As previously, no productivity data are provided. These copolymers have been characterized by spectroscopy and elemental analysis, but no information is given concerning their molecular weight. In both cases polymerization reactions were carried out in methanol at high CO pressure, in the presence of a large excess of free ligand and of benzoquinone with respect to palladium. Moreover, an acid co-catalyst (*p*-toluenesulfonic acid) was also added, as typical for the in situ catalytic systems.

Due to the chain-end control, copolymers prepared using phen or bpy containing catalysts have a prevailingly syndiotactic structure. Based on the fact that bpy **1** is the most active ligand for CO/styrene copolymerization and that a twist around its C(2)–C(2′) axis is a potential source of conformational isomerism, atropisomeric ligands *R*-**10** and *S,S*-**11** (Scheme 2) were prepared and their corresponding $[Pd(CF_3CO_2)_2(N–N)]$ complexes tested in the CO/styrene copolymerization reaction, where they showed a catalytic activity similar to that of $[Pd(CF_3CO_2)_2(\mathbf{1})]$. Moreover, short isotactic sequences were observed in the copolymer chains (Table 5) [31].

In the beginning of our investigation in this field we found that dicationic bischelated complexes of general formula $[Pd(N–N)_2][PF_6]_2$ act as efficient precatalysts for the CO/olefin copolymerization reaction in general, and for the CO/aromatic olefin in particular, by carrying out the polymerization in methanol, with no addition of any acid co-catalyst and in the presence of benzoquinone [32]. One of the main problems encountered with the catalytic systems based on palladium complexes with N–N ligands is related to the stability of the active species that, under the reducing reaction conditions, easily decomposes to palladium metal, thus preventing the synthesis of this polyketone in yields and with molecular weight values that make feasible the investigation of potential industrial applications [33].

Table 5
CO/styrene copolymerization: effect of the bpy-derived ligand

Catalyst precursor	g CP/g Pd	g CP/g Pd h	α (589 nm, 25°)
$[Pd(CF_3CO_2)_2(\mathbf{1})]$	282	141	0°
$[Pd(CF_3CO_2)_2(R\text{-}\mathbf{10})]$	235	117.5	4°
$[Pd(CF_3CO_2)_2(S,S\text{-}\mathbf{11})]$	260	130	−36°

Reaction conditions: $n_{Pd} = 1.7$ mmol; styrene $V = 10$ mL; solvent: methanol $V = 20$ mL; $T = 30\,°C$; $P_{CO} = 1$ bar; reaction time: 2 h; $n_{BQ} = 0.66$ mmol; catalyst precursor: $[Pd(CF_3CO_2)_2(N–N)]$.

Starting from these observations, a systematic study was conducted on the system based on $[Pd(\mathbf{1})_2][PF_6]_2$, in order to understand the factors that affect the catalyst stability. The first important breakthrough with respect to the literature data was achieved by changing the reaction medium from methanol to 2,2,2-trifluoroethanol (TFE). Actually, when the reaction is carried out in methanol the catalyst is deactivated after 14 h due to its complete decomposition to inactive palladium metal (Fig. 1). On the other hand, when the reaction medium is trifluoroethanol, the catalyst is still active after 24 h and negligible formation of palladium metal is observed [34], thus suggesting that the main difference between the two solvents is related to the catalyst lifetime, which is much longer in the fluorinated alcohol than in methanol. The ability of TFE to stabilize the active species allows the synthesis of polymers in high yields, even in the absence of BQ. It was thus possible to obtain polyketones of higher molecular weight, since the presence of the oxidant is known to reduce the length of the polymeric chains [21a].

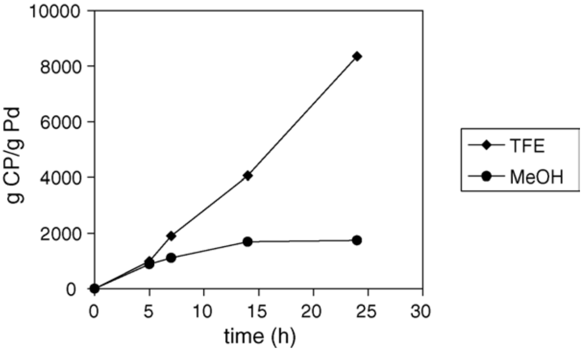


Fig. 1. CO/styrene copolymerization: effect of solvent. Catalyst precursor: $[Pd(\mathbf{1})_2][PF_6]_2$. Reaction conditions: $n_{Pd} = 5.4 \times 10^{-3}$ mmol; styrene $V = 30$ mL; solvent $V = 20$ mL; $T = 60\,°C$; $P_{CO} = 40$ bar; [BQ]/[Pd] = 64; DMP $V = 0.5$ mL.

Table 6
CO/styrene copolymerization: effect of solvent and of benzoquinone

N–N	Solvent	[BQ]/[Pd]	g CP/g Pd	g CP/g Pd h	M_w (M_w/M_n)
bpy	MeOH	64	1700	121.4	10000 (1.4)
bpy	MeOH	0	200	14.3	16000 (1.6)
bpy	TFE	64	4100	292.9	58500 (2.3)
bpy	TFE	0	1800	128.6	85000 (1.8)
phen	TFE	64	2200	157.1	66000 (1.9)
phen	TFE	0	1800	128.6	72000 (1.8)

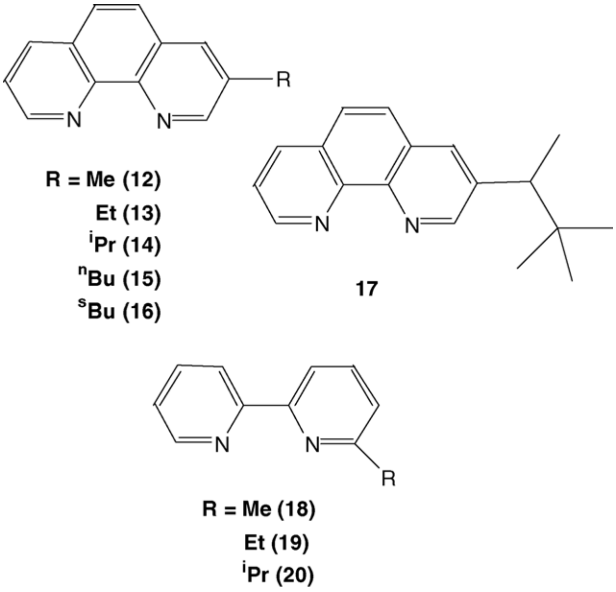
Reaction conditions: $n_{Pd} = 5.4 \times 10^{-3}$ mmol; styrene $V = 30$ mL; solvent $V = 20$ mL; $T = 60$ °C; $P_{CO} = 40$ bar; reaction time: 14 h; DMP $V = 0.5$ mL; catalyst precursor: $[Pd(N–N)_2][PF_6]_2$.

Moreover, in trifluoroethanol the higher activity of bpy-containing catalyst with respect to that of phen catalyst was confirmed when the reaction was carried out in the presence of the oxidant. However, in the absence of BQ the two catalysts showed comparable productivities due to the different stability of the corresponding active species. Actually, the bpy-containing catalyst suffered from lower stability when compared to its phen counterpart. The latter, less active but more stable, displayed a longer lifetime allowing thus comparable overall productivity to be reached (Table 6) [35].

Another important parameter affecting both the catalyst stability and the molecular weight of the polyketones obtained, is the carbon monoxide pressure (Table 7). In the presence of benzoquinone, the carbon monoxide has a clear inhibiting effect: the productivity increases of almost three times when the CO pressure is decreased from 40 to 10 bar. Whereas, when no oxidant is present, CO is important both to ensure the catalyst stability and to obtain polyketones of higher molecular weight values. In this case the inhibiting role becomes evident only at a pressure of 50 bar [35].

A further improvement of the productivity (up to 190 g CP/g Pd h at 40 bar) was realized upon addition of a mixture of free phenanthroline and $[(phen)H][PF_6]$ (in the proper ratio) to the system based on the $[Pd(\mathbf{2})_2][PF_6]_2$ complex, while no variation in the molecular weight was observed [35].

A clear decrease in productivity was evident when the bischelated complexes containing ligand **5** or **8** were tested, and, in particular, the activity of complex $[Pd(\mathbf{5})_2][PF_6]_2$ was negligible, without showing any decomposition to palladium metal, thus indicating that the loss of activity is related to the inertness of the precatalyst and not to the instability of the catalyst [36]. In this case the influence of the ligand was more pronounced than when the monochelated complexes were used [26].



Scheme 3.

A remarkable, further improvement of the catalyst performance was very recently realized by using phenanthrolines substituted in position 3 by an alkyl group (3-*R*-phen, Scheme 3, ligands: **12–17**) [36,37]. Productivity and molecular weight values appear to be related to the steric hindrance of the alkyl group in position 3, both of them increase on increasing the bulkiness of the substituent (Table 8). Catalysis were carried out in trifluoroethanol, with no addition of any co-catalyst.

No catalyst decomposition was observed, thus allowing one to prolong the reaction time up to 96 h and to improve the olefin to palladium ratio up to 96 000. Under these reaction conditions, both the productivity and the molecular weight values achieved with the 3-tmp-phen-catalyst **17** are the highest numbers ever reported for the synthesis of both CO/styrene and CO/*p*-methylstyrene polyketones.

These catalytic results should be related to the high stability shown by the active species containing the phenanthroline substituted in position 3 with a bulky alkyl group, in combination with the use of trifluoroethanol as reaction medium.

Table 7
CO/styrene copolymerization: effect of CO pressure

P_{CO} (bar)	[BQ]/[Pd]	g CP/g Pd	g CP/g Pd h	M_w (M_w/M_n)
40	64	3900	162.5	n.r.
20	64	7100	295.8	n.r.
10	64	9900	412.5	n.r.
50	0	2300	95.8	80000 (1.9)
40	0	2800	116.7	70000 (2.2)
20	0	2600	108.3	53500 (2.3)
10	0	2000	83.3	36000 (2.0)

Reaction conditions: $n_{Pd} = 5.4 \times 10^{-3}$ mmol; styrene $V = 30$ mL; solvent: TFE $V = 20$ mL; $T = 60$ °C; reaction time: 24 h; DMP $V = 0.5$ mL; catalyst precursor: $[Pd(\mathbf{2})_2][PF_6]_2$.

Table 8
CO/styrene copolymerization: effect of the 3-*R*-phen ligand

Catalyst precursor	g CP/g Pd	g CP/g Pd h	M_w (M_w/M_n)
$[Pd(\mathbf{2})_2][PF_6]_2$	1500	62.5	108000 (1.86)
$[Pd(\mathbf{12})_2][PF_6]_2$	1100	45.8	104000 (1.85)
$[Pd(\mathbf{13})_2][PF_6]_2$	1570	65.4	124000 (1.81)
$[Pd(\mathbf{14})_2][PF_6]_2$	2000	83.3	151000 (1.62)
$[Pd(\mathbf{15})_2][PF_6]_2$	2120	88.3	149000 (1.86)
$[Pd(\mathbf{16})_2][PF_6]_2$	2160	90.0	147000 (1.56)
$[Pd(\mathbf{17})_2][PF_6]_2$	2660	110.8	206000 (1.54)

Reaction conditions: $n_{Pd} = 5.4 \times 10^{-3}$ mmol; styrene $V = 30$ mL; solvent: TFE $V = 20$ mL; $T = 50$ °C; $P_{CO} = 40$ bar; reaction time: 24 h; catalyst precursor: $[Pd(3\text{-}R\text{-phen})_2][PF_6]_2$.

Table 9
CO/p-^{t}Bu-styrene copolymerization: effect of the N–N ligand

Catalyst precursor	g CP/g Pd	g CP/g Pd h	M_w (M_w/M_n)
[Pd(**1**)$_2$][BArF]$_2$	11452	818	33400 (1.50)
[Pd(**1**)(**18**)][BArF]$_2$	6888	492	n.r.
[Pd(**1**)(**19**)][BArF]$_2$	6594	471	44800 (1.45)
[Pd(**1**)(**20**)][BArF]$_2$	4522	323	44400 (1.48)

Reaction conditions: n_{Pd} = 0.926 mmol; p-^{t}Bu-styrene V = 10 mL; solvent: TFE V = 6.7 mL; T = 60 °C; P_{CO} = 10 bar; reaction time: 14 h; [BQ]/[Pd] = 5; catalyst precursor: [Pd(**1**)(N–N)][BArF]$_2$.

Moreover, it has been questioned whether the presence of two molecules of chelating ligand is strictly necessary. The replacement in the complex [Pd(phen)$_2$][PF$_6$]$_2$ of one of the chelating ligands by two monodentate ligands (pyridine or picolines), yielding as precatalysts the complexes [Pd(phen)(L)$_2$][PF$_6$]$_2$, had no effect either on the productivity or on the molecular weight of the polyketones produced, for short reaction times [38]. The main difference is the stability of the complex, since decomposition to palladium metal was observed when complexes containing the two monodentate ligands are used. The second molecule of chelating ligand is thus of importance to ensure the stability of the catalyst.

Recently, a study of the use of substituted bipyridine ligands for the copolymerization of p-^{t}Bu-styrene with CO carried out in TFE was reported. [Pd(N–N)$_2$][BArF]$_2$ complexes containing 6-alkyl-2,2′-bipyridines **18**–**20** (Scheme 3) were inactive due to the presence of a sterically demanding group in the *ortho* position. However, copolymers could be obtained using [Pd(**1**)(N–N)][BArF]$_2$ catalyst precursors containing one molecule of 2,2′-bipyridine and one of 6-alkyl-2,2′-bipyridine. Catalytic results (Table 9) showed that in all cases the activity of these complexes, containing two different nitrogen-donor ligands, is around half of that shown by [Pd(**1**)$_2$][BArF]$_2$. This observation, together with NMR investigations, indicated that the active species contains the moiety [Pd(bpy)]$^{2+}$ and that the 6-alkyl substituted bpy acts as a poison of the catalyst [39]. The influence of the anion on the catalytic activity of [Pd(**1**)$_2$][X]$_2$ in the CO/styrene copolymerization was also reported, showing a positive effect on the productivity of the use of BArF as a counterion (Table 10). Moreover, an increase of CO pressure seems to lead to a decrease in productivity, even though direct comparison cannot be performed since data were obtained using different amounts of catalyst (Table 10). A similar effect was observed in the CO/styrene copolymerization catalyzed by [Pd(**1**)(H$_2$O)$_2$][OTf]$_2$, where the influence of high pressure was reported to be negative since it resulted in a decrease of productivity (from 7.1 to 1.7 g CP/g Pd h when the pressure is raised from 100 to 320 bar) and in an increase in the amount of polystyrene formed [19].

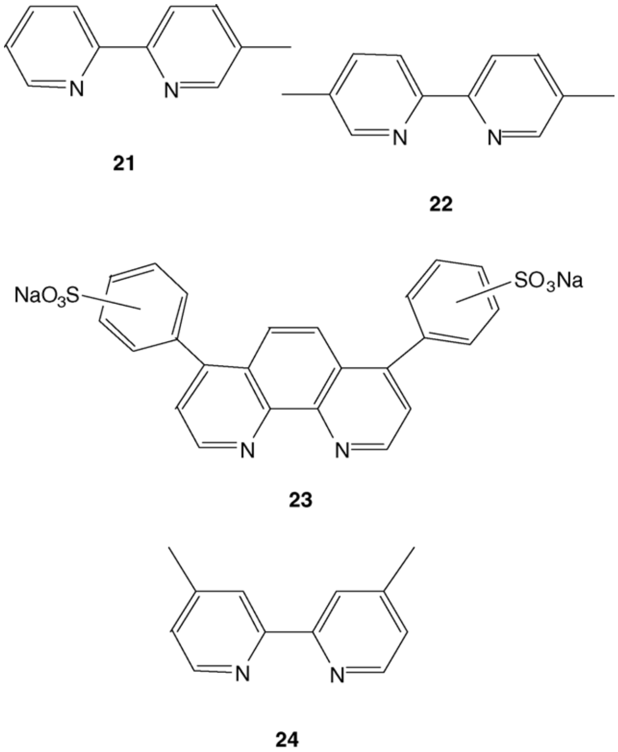
Table 10
CO/styrene copolymerization: effect of the anion and of CO pressure

Catalyst precursor	P_{CO} (bar)	g CP/g Pd	g CP/g Pd h
[Pd(**1**)$_2$][PF$_6$]$_2$[a]	10	15 162	1 083
[Pd(**1**)$_2$][BArF]$_2$[a]	10	17 010	1 215
[Pd(**1**)$_2$][PF$_6$]$_2$[b]	35	5 180	370
[Pd(**1**)$_2$][BArF]$_2$[b]	35	5 866	419

Reaction conditions: styrene V = 30 mL; solvent: TFE V = 20 mL; T = 60 °C; reaction time: 14 h; n_{BQ} = 0.35 mmol; catalyst precursor: [Pd(**1**)$_2$][X]$_2$.

[a] $n_{Pd} = 2.7 \times 10^{-3}$ mmol.

[b] $n_{Pd} = 5.4 \times 10^{-3}$ mmol.



Scheme 4.

Unlike that which was observed for the 6-substituted ligands, the presence of one or two methyl groups in position 5 of 2,2′-bipyridine (**21**, **22**, Scheme 4) led to a moderate increase of productivity of both mono- and bischelated catalysts (Table 11) [40].

The use of non coordinating ionic liquids as solvent was also reported to improve the activity of [Pd(MeCO$_2$)$_2$(**1**)]

Table 11
CO/p-^{t}Bu-styrene copolymerization: effect of the N–N ligand

Catalyst precursor	g CP/g Pd	g CP/g Pd h	M_w (M_w/M_n)
[Pd(Me)(MeCN)(**21**)][BArF][a]	360	15.0	32500 (1.6)
[Pd(Me)(MeCN)(**22**)][BArF][a]	386	16.1	18500 (1.5)
[Pd(Me)(MeCN)(**1**)][BArF][a]	334	13.9	16800 (1.5)
[Pd(**21**)$_2$][BArF]$_2$[b]	11289	806	120300 (2.5)
[Pd(**22**)$_2$][BArF]$_2$[b]	11521	823	166652 (3.2)
[Pd(**1**)$_2$][BArF]$_2$[b]	10608	758	128903 (2.5)
[Pd(**1**)(**22**)][BArF]$_2$[b]	11429	816	n.r.

Catalyst precursor: [Pd(Me)(MeCN)(N–N)][BArF] or [Pd(N–N)$_2$][BArF]$_2$.

[a] Reaction conditions: n_{Pd} = 0.0374 mmol; p-^{t}Bu-styrene V = 1.7 mL; solvent: dichloromethane V = 15 mL; T = 0 °C for 30 min and then room temperature; P_{CO} = 1 bar; reaction time: 24 h.

[b] Reaction conditions: n_{Pd} = 0.0027 mmol; p-^{t}Bu-styrene V = 24 mL; solvent: TFE V = 10 mL; T = 60 °C; P_{CO} = 40 bar; reaction time: 14 h; [BQ]/[Pd] = 64.

Table 12
CO/styrene copolymerization in ionic liquids

Catalyst precursor	g CP/g Pd	M_w (M_w/M_n)
$[Pd(MeCO_2)_2(\mathbf{1})]$	2700	34000 (1.3)
$[Pd(MeCO_2)_2(\mathbf{2})]$	2900	23000 (1.6)

Reaction conditions: $n_{Pd} = 0.028$ mmol; styrene $V = 10$ mL; solvent: 1-hexylpyridinium bis(trifluoromethanesulfonyl)imide/methanol (4/0.4 mL); $T = 70\,°C$; $P_{CO} = 40$ bar; reaction time: not available; [BQ]/[Pd] = 80; *p*-toluenesulfonic acid = 0.5 mmol; free ligand = 0.475 mmol; catalyst precursor: $[Pd(MeCO_2)_2(N–N)]$.

Table 13
CO/ethylene copolymerization: effect of the N–N ligand

Catalytic precursor	g CP/g Pd	g CP/g Pd h	η (dL g^{-1})
$[Pd(dppp)(\mathbf{1})][PF_6]_2$	42300	8460	1.52
$[Pd(dppp)(\mathbf{24})][PF_6]_2$	18200	3640	2.88
$[Pd(dppp)(\mathbf{2})][PF_6]_2$	11200	2240	2.13
$[Pd(dppp)(\mathbf{5})][PF_6]_2$	3900	780	1.2
$[Pd(dppp)_2][PF_6]_2$	3500	700	n.r.

Reaction conditions: $n_{Pd} = 0.1$ mmol; $P_{ethylene} = 28$ bar; $P_{CO} = 28$ bar; solvent: methanol $V = 1200$ mL; $T = 80\,°C$; reaction time: 5 h; [BQ]/[Pd] = 8; catalyst precursor: $[Pd(dppp)(N–N)][PF_6]_2$.

and $[Pd(MeCO_2)_2(\mathbf{2})]$ in the CO/styrene copolymerization when compared to the productivity obtained in methanol. Some results obtained using 1-hexylpyridinium bis(trifluoromethanesulfonyl)imide are shown in Table 12 [41]. The authors claimed a productivity approaching that obtained in TFE, however the lack of information concerning the reaction time for the catalysis makes any comparison difficult, since no data concerning the productivity per hour is available. Moreover, an excess of BQ and of free ligand (more than 15 equiv. with respect to palladium) are necessary to obtain copolymers, thus indicating that this solvent, unlike TFE, has a poor capability to stabilize the active species. Molecular weight values of the polymeric materials, if higher than those obtained in methanol, still remain lower than those measured for the polyketones prepared in TFE. Attempts were made to recycle the ionic liquid catalyst. The recovered solution was washed with hexane, dried and reused for a second run after addition of 0.475 mmol of **1**. A lower yield (1 900 g of CP/g Pd) was obtained and a third run gave a significantly lower productivity, attributed to palladium precipitation during the copolymerization and/or the work up.

A resin supported catalytic system containing ligand **1** was studied in order to investigate the possibility of recycling the catalyst. Activity is lower than that obtained using an homogeneous system but some reusability of the supported Pd complex was observed [42].

Even though N–N-containing palladium complexes are considered as the catalysts of choice for CO/aromatic olefin copolymerization, they were also applied for the copolymerization of carbon monoxide with aliphatic olefins, mainly ethylene.

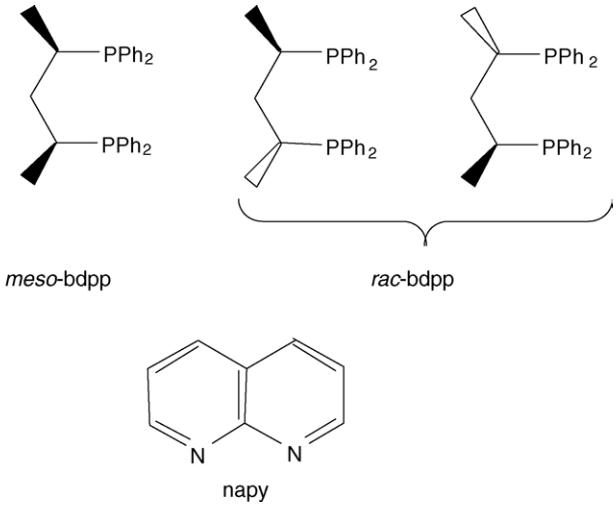
Based on the observation that palladium catalysts containing a phenanthroline ligand are tolerant to oxygen and water, the disodium salt of 4,7-diphenyl-1,10-phenanthrolinedisulfonic acid (ligand **23**, Scheme 4) was used to prepare water soluble catalysts. Under the reaction conditions used, the in situ generated complex $[Pd(\mathbf{23})(MeCN)_2][BF_4]_2$ displayed for the CO/ethylene copolymerization a productivity of 80 g CP/g Pd, that corresponds to 3.6 g CP/g Pd h [43].

Catalysts containing ligand **2** were reported to be more active in the CO/ethylene copolymerization carried out in methanol when supported on Nafion. The activity of $[Pd(CF_3CO_2)_2(\mathbf{2})]$ was calculated to be of 14 g CP/g Pd, whereas it was of 70 g CP/g Pd for the supported $[Pd(\mathbf{2})_2]^{2+}$ under the same conditions [44].

Dicationic bischelated Pd(II) complexes $[Pd(dppp)(N–N)][PF_6]_2$, containing the 1,3-bis(diphenyl-phosphino)propane (dppp) and a nitrogen-donor ligand (N–N = **1**, **24**, **2**, **5**, Schemes 1 and 4), were found to be excellent precatalysts for the CO/ethylene copolymerization, under reaction conditions similar to those reported in Shell's patents, but with no addition of the acid co-catalyst (Table 13) [45]. The nature of the nitrogen ligand has a strong influence on the catalytic performances of these complexes: ligands **5** and **24**, having a stronger coordinating ability if compared to **2** and **1** respectively, led to a remarkable decrease of the catalytic activity. The N–N ligand affects the length of the polymeric chains as attested by the value of the limiting viscosity number η (Table 13).

These complexes were also found to be much more active than the symmetrical bischelated $[Pd(dppp)_2][PF_6]_2$ (Table 13). The latter result, combined with the observation that no copolymer was formed, when complex $[Pd(dppp)(\mathbf{1})][PF_6]_2$ was used in the CO/styrene copolymerization, indicates that the active species should be a monochelated complex containing the diphosphine ligand, generated by dissociation of the nitrogen ligand from the precursor $[Pd(dppp)(N–N)][PF_6]_2$. The free nitrogen ligand can bind the protons obtained through the activation step yielding the weak acid $[(N–N)H][PF_6]$, buffering the protons concentration and affecting the molecular weight of the copolymers synthesized [45].

A further development of the latter work consisted in the evaluation of the catalytic behavior of mixed-ligand complexes $[Pd(P–P)(N–N)_x][PF_6]_2$, where the P–P ligands were dppp derivatives with methyl substituents in 1,3-positions, and the N–N ligand was bpy or napy (Scheme 5) [46]. The complexes



Scheme 5.

Table 14
CO/ethylene copolymerization: effect of both the P–P and the N–N ligands

Catalytic precursor	*p*-Toluenesulfonic acid/Pd	g CP/g Pd	g CP/g Pd h
[Pd(dppp)(**1**)][PF_6]$_2$	0	11700	3900
[Pd(*meso*-bdpp)(**1**)][PF_6]$_2$	0	25600	8533
[Pd(*rac*-bdpp)(**1**)][PF_6]$_2$	0	9700	3233
[Pd(dppp)(napy)$_2$][PF_6]$_2$	0	13600	4533
[Pd(*meso*-bdpp)(napy)$_2$][PF_6]$_2$	0	15400	5133
[Pd(*rac*-bdpp)(napy)$_2$][PF_6]$_2$	0	9500	3167
[Pd(dppp)(**1**)][PF_6]$_2$	2	24300	8100
[Pd(*meso*-bdpp)(**1**)][PF_6]$_2$	2	25700	8567
[Pd(*rac*-bdpp)(**1**)][PF_6]$_2$	2	16100	5367
[Pd(dppp)(napy)$_2$][PF_6]$_2$	2	21000	7000
[Pd(*meso*-bdpp)(napy)$_2$][PF_6]$_2$	2	20500	6833
[Pd(*rac*-bdpp)(napy)$_2$][PF_6]$_2$	2	14200	4733

Reaction conditions: $n_{Pd} = 0.1$ mmol; $P_{ethylene} = 21$ bar; $P_{CO} = 21$ bar; solvent: methanol $V = 100$ mL; $T = 85\,^\circ$C; reaction time: 3 h; [BQ]/[Pd] = 8; catalyst precursor: [Pd(P–P)(N–N)$_x$][PF_6]$_2$.

Table 15
CO/ethylene copolymerization: influence of the ligand and of the anion

Catalyst precursor	g CP/g Pd	g CP/g Pd h	η (dL g^{-1})
[Pd(**2**)$_2$][PF_6]$_2$[a]	2010	402	1.13
[Pd(**2**)$_2$][CF_3COO]$_2$[a]	880	176	0.10
[Pd(**2**)$_2$][MeCOO]$_2$[a]	20	4	n.r.
[Pd(**1**)$_2$][PF_6]$_2$[b]	2292	458	1.42
[Pd(**1**)$_2$][BF_4]$_2$[b]	226	45	n.r.

Catalyst precursor: [Pd(N–N)$_2$][X]$_2$.

[a] Reaction conditions: $n_{Pd} = 0.5$ mmol; $P_{ethylene} = 28$ bar; $P_{CO} = 28$ bar; solvent: methanol $V = 500$ mL; $T = 90\,^\circ$C; reaction time: 5 h; $n_{BQ} = 40$ mmol.

[b] $n_{Pd} = 0.25$ mmol; $P_{ethylene} = 28$ bar; $P_{CO} = 28$ bar; solvent: methanol $V = 200$ mL; $T = 70\,^\circ$C; reaction time: 5 h; $n_{BQ} = 20$ mmol.

were tested in the CO/ethylene copolymerization, by carrying out the reaction in methanol in the presence of both benzoquinone and *p*-toluenesulfonic acid (selected data are reported in Table 14).

The ligand combination *meso*-bdpp/bpy was apparently optimal among those investigated. Unlike that which was reported in the previous paper [45], under the reaction conditions used in the former case, the addition of some equivalents of the non-esterifiable protic acid had a beneficial effect on the catalytic system, and also demonstrated the positive role played by the two nitrogen ligands on the productivity. Between the two nitrogen ligands, the bpy complexes are generally more efficient than the napy ones (Table 14). Finally, the higher activity shown by the *meso*-bdpp with respect to the corresponding *rac* stereoisomer suggested that steric factors should be important to control the ethylene coordination/insertion. Indeed, NMR investigation showed that the solution structures of [Pd(*meso*-bdpp)(bpy)]$^{2+}$ and of [Pd(*rac*-bdpp)(bpy)]$^{2+}$ differ from the conformation of the six-membered metallaring and from the spatial distribution of the phenyl rings around the palladium center [46].

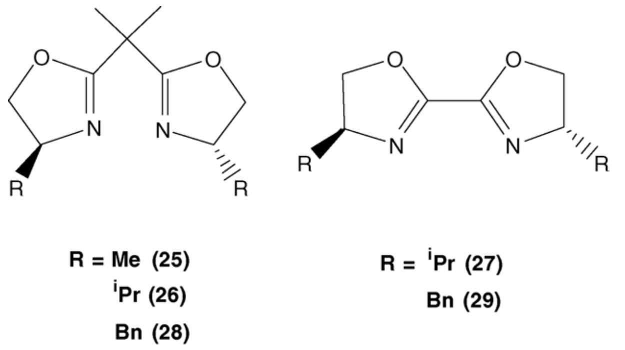
The dicationic, bischelated complexes [Pd(N–N)$_2$][X]$_2$, presenting only N–N ligands in the palladium coordination sphere, were also found to be active in the CO/ethylene copolymerization, in methanol, with addition of benzoquinone [32]. As reported for the [Pd($MeCO_2$)$_2$(N–N)] complexes in the CO/styrene copolymerization, a strong effect of the counterion on the productivity was clearly evident even in the CO/ethylene copolymerization (Table 15) [34]. A remarkable decrease in productivity and in molecular weight was found on going from hexafluorophosphate to trifluoroacetate to acetate, and also from hexafluorophosphate to tetrafluoroborate. For both bpy- and phen-catalyst the highest productivity was achieved with the PF_6^- derivative.

The bischelated complexes containing the 3-*R*-phen ligands **2**, **12–17** (Schemes 1 and 3) appeared to be active also in the CO/ethylene copolymerization in TFE, but, unlike in the case of the copolymerization of aromatic olefins, addition of benzoquinone was necessary to avoid fast decomposition of the catalyst [36]. Productivity values around 6 kg CP/g Pd and M_w values of 50 000 were achieved after 24 h, the catalytic activity not, in this case, being significantly influenced by the presence of the substituent on the ligand. Note that this productivity though quite high, is still lower than that typically obtained with diphosphine-modified palladium catalysts.

2.2. *N**–*N** *ligands with a bisoxazoline skeleton*

Bisoxazoline ligands have been widely used in asymmetric catalysis. This interest could be related to their facile synthesis in enantiomerically pure form starting from commercially available products and to the possibility to introduce different chiral substituents in the *ortho* position. Thus the chiral information of the ligand is close to the metal where the transformations take place. Indeed, these ligands have already shown very good results in term of enantioselectivity for several metal-catalyzed asymmetric reactions [3].

The use of catalysts containing the C_2-symmetric bisoxazolines **25–26** (Scheme 6) in the polyketone synthesis was reported for the first time by Brookhart in 1994, yielding the alternating CO/*p*-^{t}Bu-styrene copolymer with a highly isotatic microstructure [25b], and achieving a rare example of *living*, enantioselective, alternating copolymerization. Performing the copolymerization reactions at 1 bar of CO pressure and using the olefin as reaction medium, both complexes [Pd(Me)(MeCN)(N*–N*)][BArF] containing the methyl- (**25**) or the *iso*-propyl-disubstituted (**26**) ligands yielded 1.9 g of copolymer (2.48 g CP/g Pd h; $M_w = 26\,000$; $M_w/M_n = 1.4$).



Scheme 6.

Table 16
CO/styrene and CO/*p*-methylstyrene copolymerization: effect of the olefin

Olefin	g CP/g Pd	g CP/g Pd h
Styrene	3.5	0.29
p-Methylstyrene	31	2.58

Reaction conditions: $n_{Pd} = 0.032$ mmol (CO/styrene) or 0.086 mmol (CO/*p*-methylstyrene); olefin $V = 11$ mL (styrene) or 10 mL (*p*-methylstyrene); solvent: methanol $V = 50$ mL; T = room temperature; $P_{CO} = 1$ bar for CO/styrene or 4 bar for CO/*p*-methylstyrene; reaction time: 12 h; catalyst precursor: [Pd(Me)(MeCN)(*S*,*S*-**27**)][BArF].

Thanks to the *living* nature of this copolymerization, the synthesis of stereo block CO/*p*-^{t}Bu-styrene copolymers was also achieved using ligands **25** and **1** [47]. Initially, an isotactic segment is grown with the catalyst [Pd(Me)(MeCN)(**25**)][BArF]. Subsequently, the addition of **1**, which is able to displace the bisoxazoline ligand from palladium, allowed a switch to the growth of a syndiotactic fragment. On the other hand, when the catalysis is carried out with [Pd(Me)(MeCN)(**25**)][BArF] in the presence of 1 equiv. of the alternative enantiomer of **25**, the polymer has a prevailingly syndiotactic structure [47]. The formation of this microstructure was assigned to the ligand exchange process during the polymerization, taking place with a rate higher than that of olefin insertion in the growing chain.

Isotactic CO/styrene and CO/*p*-methylstyrene copolymers were also obtained with a bioxazoline-containing complex [Pd(Me)(MeCN)(*S*,*S*-**27**)] [BArF] (Scheme 6; Table 16) [48].

A more complete study together with a detailed mechanistic investigation has recently been published concerning the copolymerization of CO with styrene or *p*-methylstyrene catalyzed by complexes containing *S*,*S*-**27** and *S*,*S*-**28** (Scheme 6; Table 17) [49]. The polymerizations were carried out in dichloromethane, at room temperature, under atmospheric CO pressure. Comparison of the productivity of the two complexes demonstrated that the bioxazoline derivative is more reactive than the corresponding bisoxazoline complex. However, from the data reported, it cannot be concluded whether the different catalytic behavior is due to the variation of the size of the metallacycle (five members versus six members), to the different substituents (^{i}Pr versus Bn) in *ortho* position or to both of them.

The copolymers obtained, are, in both cases, regio- and stereoregular, alternating, isotactic, optically active polyketones. The in situ NMR investigation of the first and second *p*-methylstyrene and CO insertions showed that only one diastereoisomer is formed, thus indicating that the stereocontrol is already very efficient at this level of the growing of the chain.

Table 17
CO/styrene and CO/*p*-methylstyrene copolymerization: effect of the olefin and of the ligand

Catalyst precursor	g CP/g Pd	g CP/g Pd h	M_w (M_w/M_n)
[Pd(Me)(MeCN)(*S*,*S*-**27**)][BArF]	46[a]	6.6	4600 (1.4)
[Pd(Me)(MeCN)(*S*,*S*-**28**)][BArF]	38[a]	1.8	7300 (1.4)
[Pd(Me)(MeCN)(*S*,*S*-**27**)][BArF]	82[b]	11.7	7000 (1.3)
[Pd(Me)(MeCN)(*S*,*S*-**28**)][BArF]	28[b]	1.3	6700 (1.2)

Reaction conditions: $n_{Pd} = 0.1$ mmol; [olefin]/[Pd] = 400; solvent: dichloromethane $V = 4$ mL; $T = 25$ °C; $P_{CO} = 1$ bar; reaction time: 7 h for **27** and 21 h for **28**; catalyst precursor: [Pd(Me)(MeCN)(*S*,*S*-N*–N*)][BArF] (N*–N* = **27** or **28**).

[a] CO/styrene.

[b] CO/*p*-methylstyrene.

Table 18
CO/styrene copolymerization: effect of the ligand chirality

Catalyst precursor	Time (h)	g CP/g Pd	g CP/g Pd h	M_w	Tacticity
[Pd(*S*,*S*-**29**)(H_2O)$_2$][OTf]$_2$	2.75	38.8	20	2200	Isotactic
[Pd(*S*,*S*-**29**)(H_2O)$_2$][OTf]$_2$ + 1 equiv. *R*,*R*-**29**	16.5	6.3	0.4	5500	Atactic
[Pd(*R*,*S*-**29**)(H_2O)$_2$][OTf]$_2$	6.25	23.8	4	12000	Isotactic
[Pd(*R*,*S*-**29**)(H_2O)$_2$][OTf]$_2$ + 1equiv. *R*,*S*-**29**	0.26	16.3	1	7900	Syndiotactic

Reaction conditions: $n_{Pd} = 0.15$ mmol; styrene $V = 50$ mL; solvent: dichloromethane/methanol $V = 9/1$ mL; $T = 25$ °C; $P_{CO} = 1.5$ bar; catalyst precursor: [Pd(**29**)(H_2O)$_2$][OTf]$_2$.

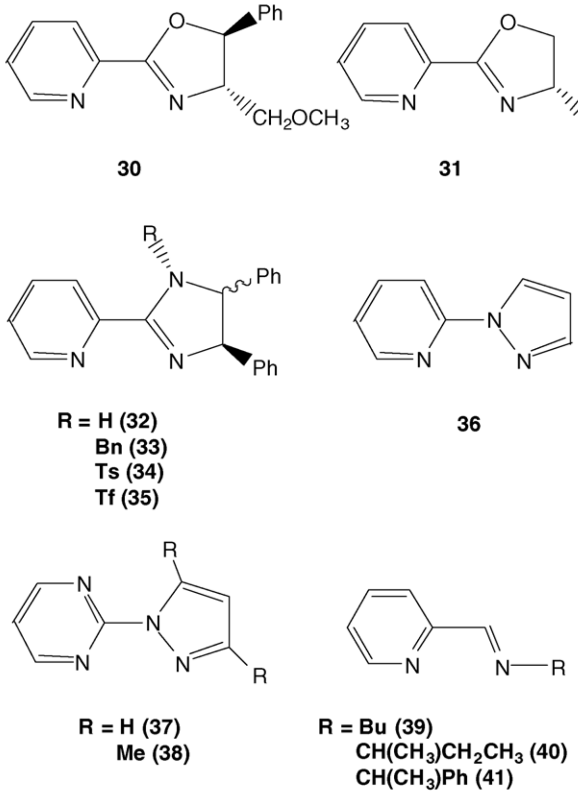
The bioxazoline bearing benzyl groups on the stereogenic carbon atoms (**29**; Scheme 6) was applied to CO/styrene copolymerization. The most interesting result is related to the influence of the ligand chirality and of the ligand-to-palladium ratio on the microstructure of the polyketone synthesized (Table 18). Catalysis carried out using the palladium complex containing the *S*,*S* ligand gave the expected isotactic copolymer. However, addition of 1 equiv. of the *R*,*R* ligand to the catalytic system slowed down the reaction (in contrast to the previously mentioned case of **25**) and led to the formation of an atactic polymer. Surprisingly, even the catalyst containing the *meso* ligand afforded an isotactic copolymer, whereas upon addition of 1 equiv. of free *meso* ligand to the catalytic system, the polyketone with syndiotactic structure was the product [50].

The alternating, isotactic CO/aromatic olefin polyketones are optically active copolymers and, therefore, they might constitute materials of potential industrial interest. However all the catalytic systems studied, based on either the bis- or bioxazoline ligands, showed rather poor catalytic activity due to the quite fast decomposition of the catalyst to inactive palladium black, thus preventing the synthesis of the isotactic polyketones in yields and with molecular weight values suitable for industrial studies.

2.3. *N–N′ ligands with a pyridine-oxazoline or pyridine-imidazoline skeleton*

As far as control of the stereochemistry in the CO/aromatic olefin copolymerization is concerned, ligands of C_{2v}-symmetry lead to syndiotactic polyketones, while copolymers with an isotactic microstructure are obtained with ligands of C_2-symmetry. When C_s- or C_1-symmetry ligands are used, the stereochemistry of the resulting copolymers is hard to predict.

Some of the various C_1-symmetry ligands applied to the synthesis of CO/aromatic olefin polyketones are characterized by the common presence of a pyridine ring, while the other half of the molecule can be either an oxazoline moiety (**30**, **31** in Scheme 7) or an imidazoline ring (**32**–**35** in Scheme 7) or a pyrazole fragment (**36** in Scheme 7). In general, these heterocyclic rings bear one or more substituents in different positions.



Scheme 7.

The enantiomerically pure pyridine-dihydrooxazole ligand **30** was used to prepare both monocationic, [Pd(Me)(MeCN)(**30**)][BArF] [25b], and dicationic [Pd(**30**)(H_2O)$_2$][OTf]$_2$ [19] Pd(II) complexes, tested as precatalysts in CO/*p*-^{t}Bu-styrene and CO/styrene copolymerization, respectively, performing the reactions under quite different conditions (Table 19). Nevertheless, at low CO pressure they showed similar productivities, while the inhibiting effect of carbon monoxide at a pressure as low as 20 bar was clearly demonstrated on the dicationic derivative (Table 19).

When the pyridine-dihydrooxazole ligand substituted with a benzyl group (**31** in Scheme 7) was used, a six times increase of productivity was observed with respect to the value obtained with the ether-substituted ligand **30**, thus indicating that the nature of the group in position 5 plays a crucial role in this reaction (runs 2 in Tables 19 and 20).

Table 19
CO/styrene and CO/*p*-methylstyrene copolymerization: effect of the precatalyst and of the CO pressure

Catalyst precursor	P_{CO} (bar)	g CP/g Pd h	M_n
[Pd(Me)(MeCN)(**30**)][BArF][a]	1	34.9	14000 (1.8)
[Pd(**30**)(H_2O)$_2$][OTf]$_2$[b]	5	30.8	3800
[Pd(**30**)(H_2O)$_2$][OTf]$_2$[b]	20	1.31	3000
[Pd(**30**)(H_2O)$_2$][OTf]$_2$[b]	50	0.81	2900

[a] Reaction conditions: $n_{Pd} = 0.05$ mmol; *p*-^{t}Bu-styrene $V = 5$ mL; solvent: dichloromethane $V = 20$ mL; $T = 25$ °C; reaction time: 22 h.

[b] $n_{Pd} = 0.11$ mmol; styrene $V = 50$ mL; solvent: methanol $V = 10$ mL; $T = 50$ °C; [BQ]/[Pd] = 18.

Table 20
CO/styrene copolymerization: influence of [BQ]/[Pd]

Catalyst precursor	[BQ]/[Pd]	Reaction time (h)	Yield (g)	g CP/g Pd h	M_n
[Pd(**31**)(H_2O)$_2$][OTf]$_2$	40	7.6	14.39	182	5000
[Pd(**31**)(H_2O)$_2$][OTf]$_2$	20	5.4	10.36	181	5800
[Pd(**31**)(H_2O)$_2$][OTf]$_2$	10	3.7	7.27	185	6400

Reaction conditions: $n_{Pd} = 0.1$ mmol; styrene $V = 50$ mL; solvent: methanol $V = 10$ mL; $T = 50$ °C; $P_{CO} = 5$ bar; catalyst precursor: [Pd(**31**)(H_2O)$_2$][OTf]$_2$.

Analysis of the effect of the amount of benzoquinone demonstrated that the oxidant has no influence on the productivity per hour, while it strongly affects the polymer yield (Table 20). This is related to a sudden cessation of the reaction, as shown by the profile of the gas uptake, due to catalyst decomposition [51]. In agreement with the previous results on the bpy or phen-containing catalysts [27,35], the catalyst stability was enhanced upon addition of free ligand (Table 21).

Despite the chiral nature of the pyridine-dihydrooxazole ligands **30** and **31**, all the copolymers synthesized show a prevailingly syndiotactic microstructure. On the other hand, when the dicationic complex with the enantiomerically pure 2-diphenylphosphinophenyl-dihydrooxazole ligand (P–N′) having the same dihydrooxazole ring as in **30** was used, the optically active isotactic polyketone was the product [19]. These data in association with model studies for CO and olefin insertion indicate that the different enantioface discrimination is the result of a site-selective coordination of the olefin before the migratory insertion of the growing chain. On the basis of this interpretation, olefin coordination should occur *cis* to the chiral dihydrooxazole ring on the P–N′ catalyst leading to the isotactic polyketone, while it should take place *cis* to the achiral pyridine ring on the pyridine-dihydrooxazole catalyst yielding the syndiotactic copolymer [19,51].

Strong electronic effects both on productivity and on stereoregularity were observed with [Pd(Me)(MeCN)(N–N′)][BArF] complexes containing the pyridine-imidazoline ligands *R*,*S*- or *R*,*R*-**32**–**35** (Scheme 7). These ligands are characterized by the presence of different groups on the sp^3-nitrogen atom that were found to affect the stereochemistry of the complexes synthesized as well as their catalytic behavior (Table 22) [52,53].

As far as the productivity of these systems is concerned, catalysts containing the ligand with the 4,5-*trans*-substituted-imidazoline ring (*R*,*R* ligands) are more active than the corresponding complexes with the *cis*-substituted ligand (*R*,*S* ligands), with the exception of ligand **33** (Table 22). The higher

Table 21
CO/styrene copolymerization: influence of the addition of free ligand

Catalyst precursor	g CP/g Pd	g CP/g Pd h	M_n
[Pd(**31**)(H_2O)$_2$][OTf]$_2$	1870	170	5600
[Pd(**31**)(H_2O)$_2$][OTf]$_2$ + 1 equiv. **31**	3078	228	6000
[Pd(**31**)(H_2O)$_2$][OTf]$_2$ + 2 equiv. **31**	3108	210	5900

Reaction conditions: $n_{Pd} = 0.05$ mmol; styrene $V = 50$ mL; solvent: methanol $V = 10$ mL; $T = 50$ °C; $P_{CO} = 5$ bar; [BQ]/[Pd] = 40; catalyst precursor: [Pd(**31**)(H_2O)$_2$][OTf]$_2$.

Table 22
CO/p-^{t}Bu-styrene copolymerization: effect of the ligand nature and ligand chirality

Catalytic system	g CP/g Pd	g CP/g Pd h	% of *l* diads	M_w (M_w/M_n)
[Pd(Me)(MeCN)(*R*,*S*-**32**)][BArF]	48	2	65	46400 (1.1)
[Pd(Me)(MeCN)(*R*,*S*-**33**)][BArF]	213.6	8.9	52	74600 (1.5)
[Pd(Me)(MeCN)(*R*,*S*-**34**)][BArF]	168	7	15	71100 (1.2)
[Pd(Me)(MeCN)(*R*,*S*-**35**)][BArF]	307.2	12.8	18.4	59600 (1.5)
[Pd(Me)(MeCN)(*R*,*R*-**32**)][BArF]	81.6	3.4	37.3	20600 (1.2)
[Pd(Me)(MeCN)(*R*,*R*-**33**)][BArF]	96	4	26.4	n.r.
[Pd(Me)(MeCN)(*R*,*R*-**34**)][BArF]	652.8	27.2	30.2	76600 (1.4)
[Pd(Me)(MeCN)(*R*,*R*-**35**)][BArF]	350.4	14.6	23	52400 (2.0)

Reaction conditions: n_{Pd} = 0.0125 mmol; [p-^{t}Bu-styrene]/[cat] = 620; solvent: chlorobenzene V = 5 mL; T = room temperature; P_{CO} = 1 bar; reaction time: 24 h; catalyst precursor: [Pd(Me)(MeCN)(N–N′)][BArF].

productivities were obtained with the less basic ligands (*R*,*R*-**34** and *R*,*R*-**35**), the best value being reached with ligand bearing the tosyl group, *R*,*R*-**34**. In the case of catalysts containing the *R*,*S* ligands, the differences in productivity appear to be less affected by the nature of the substituent on the sp^3-nitrogen atom. This different catalytic behavior might be related to the higher stability of active species with *R*,*R* ligands with respect to that of the catalyst containing *R*,*S* ligands [53]. An analogous trend is observed for the molecular weight values of the copolymers synthesized: no clear relationship is found between the structural features of the ligand and the size of the polymer for the *R*,*S*-ligands, while in the case of the *R*,*R*-ligands, the less basic ligands led to polyketones of higher M_w values (Table 22).

The effect of the ligand on the stereochemistry of the copolymer was the opposite with respect to the trends reported above: all catalysts with *R*,*R* ligands led to syndiotactic polyketones with similar percentages of the diads, whereas a higher differentiation in the polymer microstructure was observed with catalysts containing the *R*,*S* ligands (Table 22). Syndiotactic polymers were obtained with the less basic ligands *R*,*S*-**34** and *R*,*S*-**35**, while atactic polyketones, with a slightly higher content of *l* diads, were produced when ligands *R*,*S*-**32** and *R*,*S*-**33** were used.

From a general point of view, even these pyridine-oxazoline or pyridine-imidazoline ligands generate an active species of low stability, as reported for the bis- and bioxazoline Pd-complexes. Nevertheless, the effect of the ligands on the polymer microstructure is clearly demonstrated.

2.4. Other N–N ligands

[Pd(Me)(MeCN)(N–N)][BArF] complexes with N–N = **36–38** containing a pyrazole moiety were also reported to copolymerize CO with p-^{t}Bu-styrene under mild conditions (Scheme 7, Table 23) [54]. The best data, both in term of productivity and molecular weight, were obtained with ligand **37**. Moreover, the comparison of the results obtained with **37** and **38** shows, once again, the important influence of the presence of substituents in the proximity of the nitrogen-donor atom. The study of the effect of CO pressure demonstrated a decrease of both the productivity and the molecular weights on going from 1 to 5 bar. Copolymers with a syndiotactic microstructure are obtained with these C_s-symmetry ligands [54].

Table 23
CO/p-^{t}Bu-styrene copolymerization: effect of the ligand

Catalyst precursor	g CP/g Pd	g CP/g Pd h	M_w (M_w/M_n)
[Pd(Me)(MeCN)(**36**)][BArF]	211	8.83	21440 (1.1)
[Pd(Me)(MeCN)(**37**)][BArF]	282	11.75	36353 (1.3)
[Pd(Me)(MeCN)(**38**)][BArF]	141	5.88	15720 (1.5)

Reaction conditions: n_{Pd} = 0.0125 mmol; [p-^{t}Bu-styrene]/[Pd] = 310; solvent: chlorobenzene V = 5 mL; T = room temperature; P_{CO} = 1 bar; reaction time: 24 h; catalyst precursor: [Pd(Me)(MeCN)(N–N′)][BArF].

Pyridine-imine ligands **39–41** (Scheme 7) were studied in order to evaluate the influence of the substituents present on the imine moiety of the compound on the tacticity of CO/styrene copolymers obtained with in situ palladium systems (Table 24) [55]. A decrease in the syndiotacticity was found on increasing the size of the substituent. However, further increase in the bulkiness (i.e. R = *tert*-butyl group) led to inactive catalysts. From a general point of view, the system based on ligands **39–41** shows a very low activity, if compared to that usually reported for a good catalytic system based, for instance, on ligand **24** (Table 24).

The pyridine-imine ligand **39** was also used for the palladium-catalyzed copolymerization of CO with 4-vinylcyclohexene [56]. Comparison with results obtained under the same

Table 24
CO/styrene and CO/p-methylstyrene copolymerization: effect of the ligand

Catalyst precursor	g CP/g Pd	g CP/g Pd h	% of *uu* triads	M_w (M_w/M_n)
CO/styrene				
[Pd(MeCN)$_4$][BF$_4$]$_2$ + **39**[a]	69	1.7	80	n.r.
[Pd(MeCN)$_4$][BF$_4$]$_2$ + **40**[a]	n.r.	n.r.	70	n.r.
[Pd(MeCN)$_4$][BF$_4$]$_2$ + **41**[a]	n.r.	n.r.	56	5600 (1.3)
CO/p-methylstyrene				
[Pd(MeCN)$_4$][BF$_4$]$_2$ + **24**[b]	290	14.5	n.r.	n.r.
[Pd(MeCN)$_4$][BF$_4$]$_2$ + **39**[c]	83	1.7	n.r.	22000 (1.4)
[Pd(MeCN)$_4$][BF$_4$]$_2$ + **40**[c]	41	0.9	n.r.	9000 (1.2)
[Pd(MeCN)$_4$][BF$_4$]$_2$ + **41**[c]	41	0.9	n.r.	14000 (1.2)

Reaction conditions: n_{Pd} = 0.068 mmol; olefin V = 4 mL; solvent: nitromethane/methanol V = 4/2 mL; T = 60 °C; P_{CO} = 69 bar; n_{BQ} = 0.093 mmol; catalyst precursor: [Pd(MeCN)$_4$][BF$_4$]$_2$ + N–N.

[a] Reaction time: 40 h.

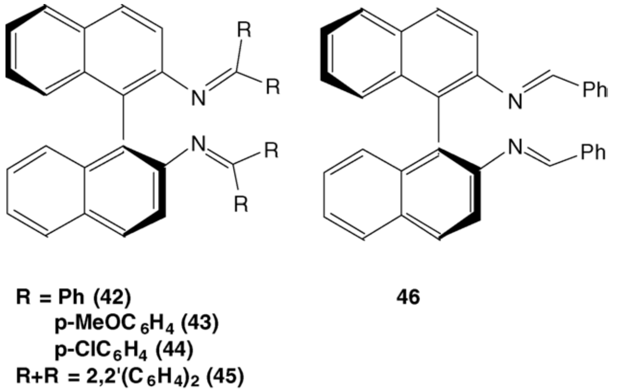
[b] Reaction time: 20 h.

[c] Reaction time: 48 h.

Table 25
CO/4-vinylcyclohexene copolymerization: effect of the ligand

Catalyst precursor	g CP/g Pd h	M_n
$[Pd(MeCN)_4][BF_4]_2$ + **1**	0.73	4430
$[Pd(MeCN)_4][BF_4]_2$ + **2**	0.87	3790
$[Pd(MeCN)_4][BF_4]_2$ + **4**	0.57	2360
$[Pd(MeCN)_4][BF_4]_2$ + **39**	0.61	2520

Reaction conditions: n_{Pd} = 0.5 mmol; $n_{vinylcyclohexene}$ = 0.05 mol; solvent: tetrahydrofurane/methanol V = 30/6 mL; T = 60 °C; P_{CO} = 55 bar; n_{BQ} = 0.093 mmol; catalyst precursor: $[Pd(MeCN)_4][BF_4]_2$ + N–N.



Scheme 8.

conditions using ligands **1**, **2**, or **4** indicates that, in this case, the values of productivity per hour and of molecular weight are very similar (Table 25).

In an elegant study, the trend of the catalytic activity of a series of chiral diketimines ligands (**42–44**, Scheme 8) in the in situ palladium-promoted CO/*p*-^{t}Bu-styrene copolymerization was nicely predicted by applying the AMS model, even though electronic effects are not considered in this simple method (Table 26) [57]. Under the same reaction conditions, ligands **45** and **46** led to the formation of inactive complexes.

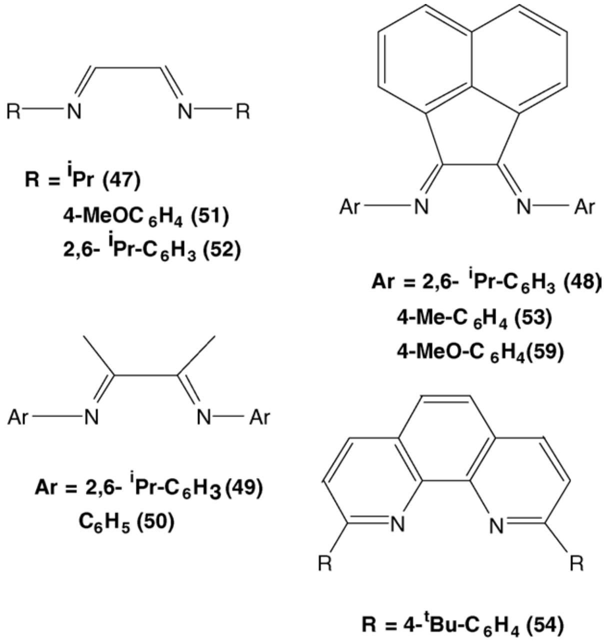
These diketimine ligands afforded highly isotactic copolymers, with productivities similar to those typical of the other ligands [25b,48], but with values of molecular weight higher than those previously reported.

α-Diimine ligands derived from the condensation reaction of diacetyl or of the more rigid acenaphthenquinone with a proper amine (ligands **47–50** in Scheme 9) have been tested in the copolymerization of CO with aromatic olefins in order to evaluate whether the introduction of steric hindrance above and below the square planar coordination plane might affect the catalytic system. The palladium monocationic derivative [Pd(Me)(MeCN)(**47**)][BArF], containing the 1,4-diisopropyl-1,4-diaza-buta-1,3-diene (**47**), copolymerizes CO with styrene or *p*-methylstyrene, under mild conditions, to afford highly syndiotatic copolymers (92% of the *uu* triad in the ^{13}C NMR spectra; Table 27) [58]. Under the reported reaction conditions, no remarkable difference either in the productivity or in the molecular weight was observed by changing the olefin from styrene to *p*-methylstyrene, as was the case when 3-*R*-phen ligands were used [36,37].

Table 26
CO/*p*-^{t}Bu-styrene copolymerization: effect of the diketimine ligand

Catalyst precursor	g CP/g Pd	g CP/g Pd h	M_w (M_w/M_n)
[Pd(Me)(MeCN)(**42**)][BArF]	188	4	37500 (1.8)
[Pd(Me)(MeCN)(**43**)][BArF]	378	8	46200 (1.4)
[Pd(Me)(MeCN)(**44**)][BArF]	152	3	13200 (1.7)

Reaction conditions: n_{Pd} = 0.011 mmol; *p*-^{t}Bu-styrene V = 2 mL; solvent: dichloromethane V = 2 mL; T = room temperature; P_{CO} = 1 bar; reaction time: 48 h; catalyst precursor: [Pd(Me)(MeCN)(N–N)][BArF].



Scheme 9.

Palladium complexes $[Pd(\eta^1,\eta^2\text{-}C_8H_{12}OMe)(N–N)][PF_6]$ containing ligands **48–50** were tested in the CO/*p*-methylstyrene copolymerization. When ligands **48** and **49** bearing isopropyl groups in *ortho* positions of the aryl rings were used, no copolymer was formed and the product of the reaction was only a small amount of the homopolymers. On the other hand, an atactic polyketone was obtained (154 g CP/g Pd; M_w = 17 680; M_w/M_n = 1.68), when ligand **50** was used [59]. These data support the hypothesized mechanism, according to which the polymerization process requires a free apical position on palladium [60].

Ligands of this family, but bearing different substituents on different positions of the aryl rings (ligands **51–53** in Scheme 9),

Table 27
CO/styrene and CO/*p*-methylstyrene copolymerization: influence of the olefin

Catalyst precursor	g CP/g Pd	g CP/g Pd h	M_w (M_w/M_n)
[Pd(Me)(MeCN)(**47**)][BArF]	98	4.1[a]	8400 (1.2)
[Pd(Me)(MeCN)(**47**)][BArF]	116	4.8[b]	9200 (1.3)

Reaction conditions: [olefin]/[Pd] = 250; solvent: dichloromethane; T = 0 °C; P_{CO} = 1 bar; reaction time: 24 h; catalyst precursor: [Pd(Me)(MeCN)(**47**)][BArF].

[a] CO/styrene.

[b] CO/*p*-methylstyrene.

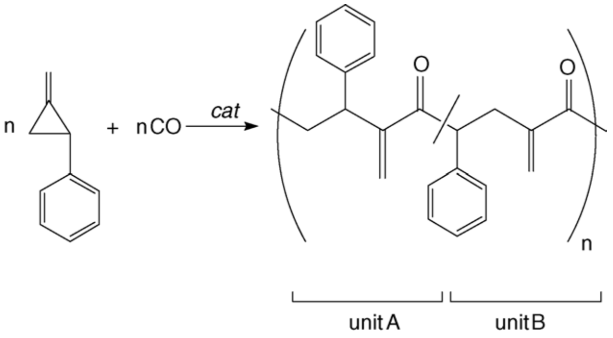
Table 28
CO/methylene-2-phenyl-cyclopropane copolymerization

Catalytic system	Conversion (%)	M_n (M_w/M_n)	A:B
[Pd(Cl)(Me)(**1**)] + AgBArF	88	23800 (1.74)	64:36
[Pd(Cl)(Me)(**1**)] + $AgBF_4$	94	19700 (3.26)	64:36
[Pd(Cl)(Me)(**2**)] + $AgBF_4$	64	51500 (2.58)	64:36
[Pd(Cl)(Me)(**1**)] + AgOTf	92	23200 (3.19)	58:42
[Pd(Cl)(Me)(**51**)][a]	63	12500 (1.82)	n.r.

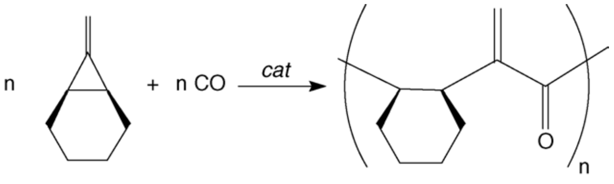
Reaction conditions: n_{Pd} = 0.025 mmol; n_{olefin} = 2.50 mmol; solvent: acetonitrile V = 1 mL; T = room temperature; P_{CO} = 1 bar; reaction time: 3 h unless otherwise stated; catalyst precursor: [Pd(Me)(Cl)(N–N)] + AgX.

[a] Reaction time: 4 h.

were used for the ring-opening copolymerization of CO with strained alkenes, such as methylene-2-phenyl-cyclopropane (Eq. (2)) [61] or 7-methylenebicyclo[4,1,0]heptane (Eq. (3)) [62]. In both cases, the catalyst was generated in situ by abstraction of the halide from the corresponding neutral complex [Pd(Cl)(Me)(N–N)].



(2)



(3)

The Pd complex containing the diimine ligand **51** was used for the copolymerization of CO with methylene-2-phenyl-cyclopropane (Eq. (2)). Comparison with catalytic systems containing ligands **1**, **2** is reported in Table 28. During the copolymerization, opening of the cycle can occur in two different ways. In all cases, cleavage of the C–CH_2 bond is favored, but cleavage of the C–CH(Ph) bond also occurs leading to the existence of two different units, A and B respectively, in the polymeric chain [61].

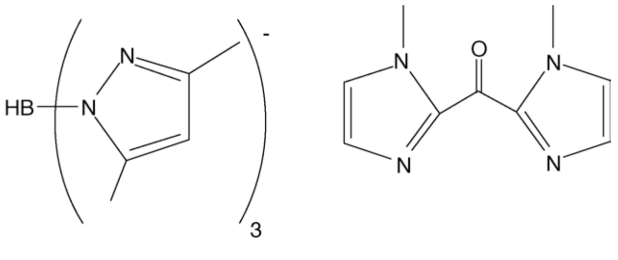
An analogous copolymerization reaction of CO with 7-methylenebicyclo[4,1,0]heptane (Eq. (3)) was studied using in situ generated [Pd(Me)(MeCN)(N–N)][BArF] complexes with N–N = **1**, **2**, **48**, **52–54**, as catalysts. Different solvents were used, but no remarkable influence on the catalytic activity was found [62]. A selection of results obtained is presented in Table 29. Note that, surprisingly, [Pd(Cl)(Me)(**52**)] is reported to promote the copolymerization also in the absence of NaBArF with a catalytic activity similar to that of the reaction carried out in the presence of the salt. The stereochemistry of the polyketones obtained depends on the catalytic system; not only the ligand used but also the solvent has an influence on the structure of the polymer as demonstrated by NMR spectroscopy.

Table 29
CO/7-methylenebicyclo[4,1,0]heptane copolymerization

Catalytic system	Yield (%)	g CP/g Pd	g CP/g Pd h	M_n (M_w/M_n)
[Pd(Cl)(Me)(**1**)] + NaBArF	88	112	37.5	6500 (1.34)
[Pd(Cl)(Me)(**2**)] + NaBArF[a]	72	92	30.7	7100 (1.23)
[Pd(Cl)(Me)(**52**)]	44	56	19	16900 (1.22)
[Pd(Cl)(Me)(**52**)] + NaBArF	48	61	20.5	13900 (1.11)
[Pd(Cl)(Me)(**48**)] + NaBArF	58	74	24.7	13600 (1.20)
[Pd(Cl)(Me)(**53**)] + NaBArF	55	70	23.4	9800 (1.10)
[Pd(Cl)(Me)(**54**)] + NaBArF	35	45	14.9	22300 (1.43)

Reaction conditions: n_{Pd} = 0.025 mmol; n_{olefin} = 2.5 mmol; solvent: tetrahydrofurane V = 2 mL unless otherwise stated; T = room temperature; P_{CO} = 1 bar; reaction time: 3 h; catalyst precursor: [Pd(Me)(Cl)(N–N)] + NaBArF.

[a] Solvent: acetonitrile.



55 **56**

Scheme 10.

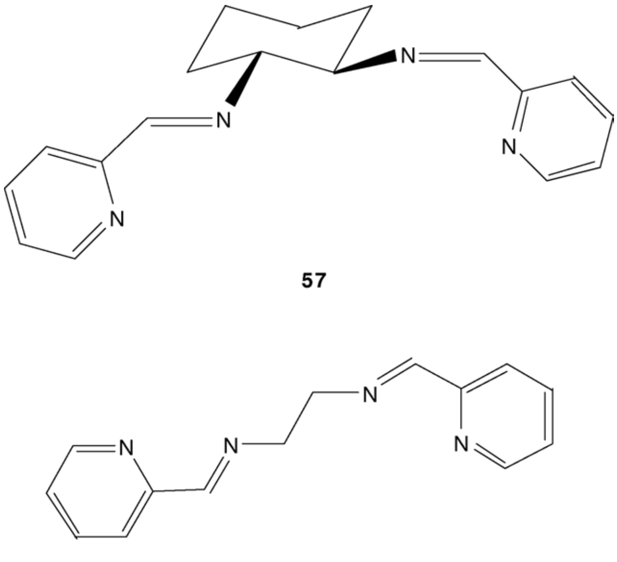
[Pd(**55**)(*p*-tol)(PPh_3)] (Scheme 10) was reported to catalyze the formation of polyketone from CO and norbornadiene. However, no catalytic data are reported, the polymer formation being only monitored by infra-red spectroscopy [63].

[Pd(Me)(MeCN)(**56**)][X] with different anions promotes the copolymerization of CO with ethylene (Scheme 10). However, activities are low compared to those obtained with catalysts containing diphosphine ligands. Low stability of the palladium complex is claimed to be one of the reason for this behavior. The results (Table 30) allow a comparison among the different anions studied, confirming that the catalyst with BArF as counterion is the most active among the three tested, while no activity was found with BPh_4^-, probably due to the transfer of one phenyl ring to palladium [64]. The absence of data in terms of productivity expressed in grams of copolymer per gram of palladium and of molecular weight values does not afford the possibility of a comparison with other systems [65].

Table 30
CO/ethylene copolymerization: influence of the anion

Catalytic system	*n* Pd (mmol)	mol CP/mol catalyst (TON)
[Pd(Me)(MeCN)(**56**)][BF_4]	0.126	213
[Pd(Me)(MeCN)(**56**)][BPh_4]	0.079	0
[Pd(Me)(MeCN)(**56**)][BArF]	0.074	222

Reaction conditions: $P_{ethylene}$ = 20 bar; P_{CO} = 20 bar; solvent: dichloromethane V = 40 mL; T = 50 °C; reaction time: 1 h; catalyst precursor: [Pd(Me)(MeCN)(**56**)][X].



57

58

Scheme 11.

One paper appeared on the use of binuclear Pd-complexes containing tetradentate ligands **57** and **58** (Scheme 11) as precatalysts for CO/styrene and CO/*p*-methylstyrene copolymerization to evaluate if cooperativity effects might occur. The latter is more active than the former, even if yields in copolymer are limited by the low stability of the corresponding catalyst (Table 31) [66]. As far as the stereochemistry of the polyketones obtained is concerned, in the ^{13}C NMR spectrum of the CO/styrene copolymer prepared with [{Pd(Me)(MeCN)}$_2$**57**][BArF]$_2$ the signals of all the four triads are present: the *uu* triad has a relative intensity of ca. 50%, while the *ll* triad is present for 10%, indicating a small amount of isotacticity. In the case of CO/styrene polyketones synthesized with complex [{Pd(Me)(MeCN)}$_2$**58**][BArF]$_2$, containing an achiral ligand, the usual syndiotactic stereochemistry is observed. Analogous results are obtained for the CO/*p*-methylstyrene copolymers.

The overall data indicate that in the dinuclear species the two palladium centers act essentially independently.

3. CO/olefin terpolymerization reactions

Even though the polyketones exploited at a commercial level by Shell, under the name of Carilon®, and by BP, under the name of Ketonex®, belong to the family of CO/ethylene/propylene terpolymers, little attention has been addressed to the terpolymerization reaction, if compared to the corresponding copolymerization. Most of the studies are related to the use of P–P, P–N, phosphino–phosphite ligands, mainly due to the fact that at least one of the two olefin co-monomers is an aliphatic olefin.

Table 31
CO/styrene and CO/*p*-methylstyrene copolymerization

Catalytic system	g CP/g Pd h	M_w (M_w/M_n)
[{Pd(Me)(MeCN)}$_2$**57**][BArF]$_2$	16.0[a]	5120 (1.62)
[{Pd(Me)(MeCN)}$_2$**58**][BArF]$_2$	36.6[a]	22500 (1.49)
[{Pd(Me)(MeCN)}$_2$**57**][BArF]$_2$	36.6[b]	4780 (1.58)
[{Pd(Me)(MeCN)}$_2$**58**][BArF]$_2$	291.4[b]	n.r.

Reaction conditions: no solvent; T = room temperature; P_{CO} = 1 bar; reaction time 15 h; catalyst precursor: [{Pd(Me)(MeCN)}$_2$(N–N)][BArF]$_2$.

[a] CO/styrene.

[b] CO/*p*-methylstyrene.

Both in situ generated systems and preformed complexes ([Pd(Me)(MeCN)(N–N)][BArF], N–N = **1** or **2**) were claimed to catalyze the formation of CO/ethylene/styrene and CO/propylene/styrene terpolymers [23,25]. In particular, for the polyketones prepared with the in situ system, the relative amount of the aliphatic olefin present in the polymeric chain, determined by ^{13}C NMR, indicates that, under the reaction conditions used, styrene is preferentially inserted (Table 32).

CO/ethylene/α-olefin terpolymers were obtained using the bischelated complex [Pd(dppp)(**1**)][PF$_6$]$_2$ as catalyst (Table 33) achieving very high productivities. The amount of propylene in the polymeric chain is around 10–5% and the CO/propylene units are randomly distributed along the chain [45].

CO/ethylene/styrene terpolymers can also be prepared in methanol using a catalytic system containing palladium acetate, *p*-toluenesulfonic acid and ligand **1**, yielding terpolymers with a wide range of composition by varying the relative amount of the two olefins present in the initial reaction mixture. Molecular weights for these terpolymers are in the range 3000–7000, increasing with the percentage of styrene inserted in the chain, but no data concerning the productivity were reported [67].

Recently, we have reported the synthesis of CO/styrene/*p*-methylstyrene terpolymers catalyzed by [Pd(**2**)$_2$][PF$_6$]$_2$, in trifluoroethanol. These polymers represent the first example of polyketones obtained from CO and two different aromatic olefins. In agreement with the different reactivity shown by the two olefins in the copolymerization reactions, a decrease in productivity and molecular weight was found on increasing the amount of styrene with respect to *p*-methylstyrene in the reaction mixture (Table 34) [68].

The variation of the initial relative amount of the two olefins affects also the composition of the synthesized terpolymers yielding polymeric materials having different styrene content, as determined by ^{13}C NMR spectroscopy (Table 34). Moreover, the polymers were analyzed by MALDI-TOF mass spectrometry thus allowing the unambiguous determination of chemical composition of the synthesized macromolecules [68].

4. Mechanism

The mechanistic aspects of the CO/olefin copolymerization reaction have been extensively studied and discussed [12,69]. In this section, we highlight the steps that can be considered as milestones for the comprehension of the mechanism.

From a general point of view, the catalytic cycle for a metal-promoted polymerization reaction is comprised of three parts: the initiation, propagation and termination steps. In the case of CO/olefin copolymerization, palladium complexes containing nitrogen-donor ligands are well suited to be model compounds for understanding the intimate mechanism of this reaction,

Table 32
CO/styrene/aliphatic olefin terpolymerization

Catalytic system	Aliphatic-olefin	g TP/g Pd	g TP/g Pd h	M_w (M_w/M_n)	% of aliphatic-olefin
$[Pd(MeCN)_4][BF_4]_2$ + **3**	Ethylene[a]	234	10.7	130000 (1.6)	11
$[Pd(MeCN)_4][BF_4]_2$ + **2**	Propylene	n.r.	n.r.	110000 (2.4)	12
$[Pd(MeCN)_4][BF_4]_2$ + **2**	ω-Undecylenyl alcohol[b]	165	2.5	59000 (1.8)	14
$[Pd(MeCN)_4][BF_4]_2$ + **2**	ω-Undecylenyl acid[c]	83	4.6	50000 (2.1)	14

Reaction conditions: n_{Pd} = 0.068 mmol; styrene V = 6 mL unless otherwise stated; solvent: nitromethane/methanol (4/2 mL); T = 60 °C; P_{CO} = 69 bar unless otherwise stated; reaction time: 22 h unless otherwise stated; n_{BQ} = 0.093 mmol; catalyst precursor: $[Pd(MeCN)_4][BF_4]_2$ + N–N.

[a] 0.10 g ethylene.

[b] Styrene V = 2 mL; ω-undecylenyl alcohol V = 1 mL; P_{CO} = 62 bar, reaction time: 67 h.

[c] Styrene V = 2.1 mL; ω-undecylenyl acid 1.1 g; P_{CO} = 62 bar, reaction time: 18 h.

Table 33
CO/ethylene/α-olefin terpolymerization

Catalyst precursor	α-Olefin	g TP/g Pd	g TP/g Pd h
$[Pd(dppp)(\mathbf{1})][PF_6]_2$	Hex-1-ene	31800	6360
$[Pd(dppp)(\mathbf{1})][PF_6]_2$	Propylene	36700	7340

Reaction conditions: n_{Pd} = 0.1 mmol; $P_{ethylene}$ = 28 bar; α-olefin: 50 g; solvent: methanol V = 1200 mL; T = 70 °C; P_{CO} = 28 bar; reaction time: 5 h; [BQ]/[Pd] = 80; catalyst precursor: $[Pd(dppp)(\mathbf{1})][PF_6]_2$.

thanks to their low activity if compared to that typical of the corresponding derivatives with diphosphines.

The pioneering work was performed by Elsevier et al. [70] on the monochelated neutral complex [Pd(Me)(Cl)(**59**)] (Scheme 9). Palladium-intermediates, resulting from the sequential insertion of CO and norbornadiene, were isolated and completely characterized, for the first time. This study provided direct evidence that the propagation step of the CO/olefin copolymerization proceeds via successive alternating migratory insertion of CO into the Pd–alkyl bond and of olefin into the Pd–acyl bond. A schematic representation for the propagation steps of CO/styrene copolymerization is reported in Scheme 12.

Since then, many other studies on the elementary steps of the copolymerization reaction were carried out on monocationic palladium complexes with different families of nitrogen-donor ligands, such as rigid bidentate ligands such as the acenaphthene derivatives [71a,b] and other α-diimines [71c], or flexible compounds like bpy [72a–d] and other pyridyl derivatives [72c,e–h]. Some studies have been also performed on complexes containing terdentate ligands [73] or two molecules of bidentate ligands $[Pd(CH_3)(L–L)(N–N)][OTf]$ [74].

Table 34
CO/styrene/*p*-methylstyrene terpolymerization: effect of the relative amount of the two olefins

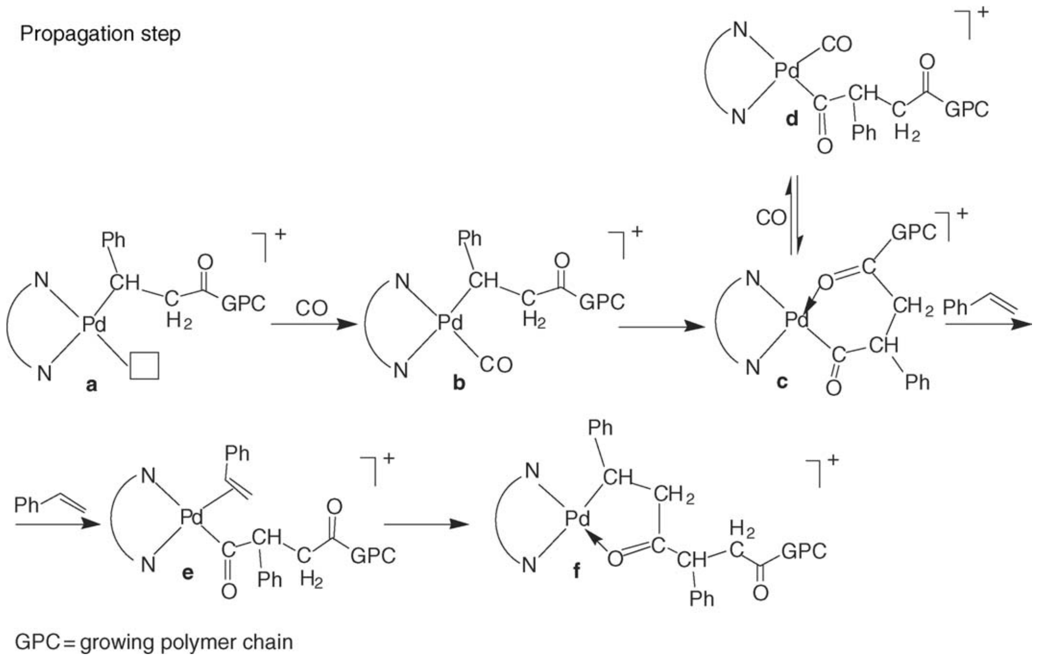
Styrene/*p*-methylstyrene (v/v)	g TP/g Pd	g TP/g Pd h	M_w (M_w/M_n)	% of styrene
1/0	1500	62.5	108000 (1.9)	100
0/1	4000	166.7	130000 (1.9)	0
1/1	2500	104	125000 (2.6)	42
2/1	2070	86.3	130000 (2.5)	58
5/1	1710	71.3	101000 (2.3)	70
10/1	1580	65.8	110000 (3.0)	80

Reaction conditions: n_{Pd} = 0.0054 mmol; olefin V = 30 mL; solvent: TFE V = 20 mL; T = 50 °C; P_{CO} = 40 bar; reaction time: 24 h; catalyst precursor: $[Pd(\mathbf{2})_2][PF_6]_2$.

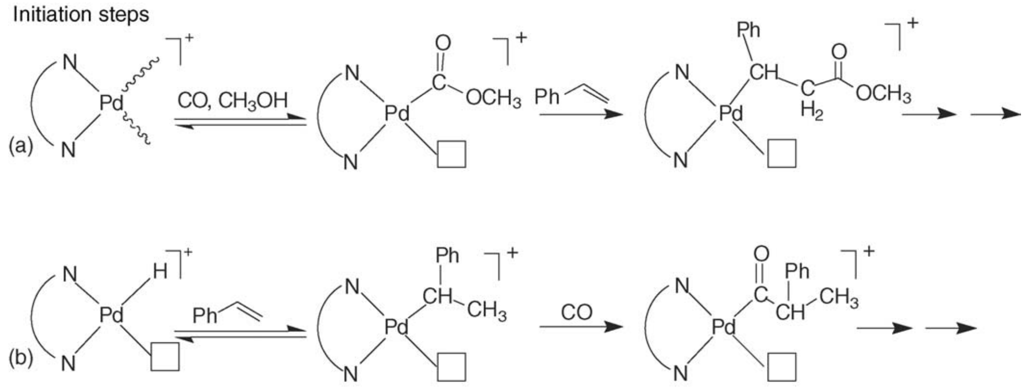
Kinetic and thermodynamic data of CO/ethylene and CO/styrene copolymerizations were determined through elegant mechanistic studies performed on $[Pd(CH_3)(L)(phen)][BArF]$ (where L is a monodentate ligand of varying coordinating capability, like CO, CH_3CN, C_2H_4, etc.) [75]. This study also demonstrated that the catalyst resting state is the palladium-acyl-carbonyl species, $[Pd(COCH_3)(CO)(phen)]^+$ (i.e. species d in Scheme 12).

The palladium intermediate present after the insertion of the olefin into the Pd–acyl bond is a five-membered metallacycle originating through the interaction with palladium of the growing chain through the last inserted carbonyl group (species f in Scheme 12). This metallacycle is considered to be responsible for the perfect alternation of the growing chain [12a]. The palladium intermediate formed after the insertion of carbon monoxide into the Pd–alkyl bond is a six-membered metallacycle deriving from the interaction with palladium of the second last inserted carbonyl group of the growing chain (species c in Scheme 12). This metallacycle is considered to be responsible for the efficient stereochemical control in the CO/aromatic olefin copolymerization leading to the syndiotactic polyketone [76].

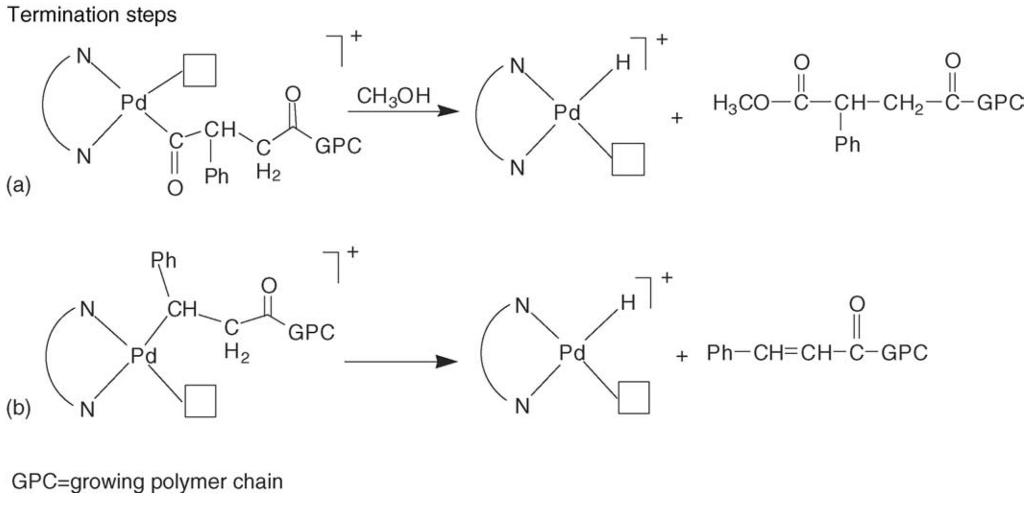
Another important discovery concerning the propagation step is related to the difference in the regioselectivity of the chain propagation mode in the CO/vinyl arene copolymerization catalyzed by complexes containing nitrogen ligands when compared to that occurring in the CO/propene polymerization promoted by diphosphine derivatives. Indeed, while in the case of the aliphatic olefin, regioregular and regioirregular polyketones can be obtained depending on the nature of the P–P ligand [76], in the case of styrene, the olefin insertion takes place with a 2,1 mechanism with all the N–N ligands studied. Moreover, with aromatic olefins the copolymerization implies the formation of an η^3–π-benzyl derivative, characterized even by X-ray analysis [25a,75b]. This intermediate might be responsible for the fact that the copolymerization does not proceed when complexes with diphosphine ligands are used [77]. As further support for this hypothesis, in the case of the Pd-(phosphino–phosphite) complex, which also promotes the CO/vinyl arene copolymerization, the olefin insertion occurs with a 1,2 mechanism, thus preventing the formation of the η^3–π-benzyl intermediate [78].



Scheme 12.



Scheme 13.



Scheme 14.

While it is generally accepted that the propagation step is the same for all the catalytic systems studied, reactions involved in the initiation and termination steps are strongly dependent on the olefin co-monomer, on the bidentate ligand present in the palladium coordination sphere and on the reaction medium. Most of the studies in this field have been carried out on palladium complexes with diphosphine ligands and ethylene as co-monomer [79]. The results can be summarized by noting that with (P–P)–Pd-complexes and aliphatic olefins, in alcoholic medium such as methanol, several initiation steps are operative yielding the Pd-hydride or the Pd-carbomethoxy initiators. As far as the termination step (chain transfer) is concerned, three different reactions can occur: solvolysis and hydrogenolysis (both implying the alcohol as chain transfer agent), and the β-hydrogen elimination [79].

When an aromatic olefin is the co-monomer, the end groups of the polyketones synthesized in methanol indicate the preferential initiation through the Pd-carbomethoxy pathway and the termination through alcoholysis or β-hydrogen elimination (Schemes 13a and 14) [12a,35]. No saturated end groups were observed. On the contrary, when the copolymers were obtained in a fluorinated alcohol, such as 2,2,2-trifluoroethanol, complete suppression of alcoholysis was achieved, the β-hydrogen elimination being the only effective termination process. Saturated end groups were found at one head of the polymeric chains, deriving from the insertion of styrene into the Pd–H bond (Scheme 13b) [35].

Finally, no chain transfer reaction occurs when the copolymerization is carried out in aprotic solvents, such as dichloromethane or chlorobenzene, thus allowing a *living* polymerization to be achieved [25,47].

5. Summary

The present review underlines the importance of the role of nitrogen-donor ligands in palladium-catalyzed polyketones synthesis. It confirms the relationship, established by Consiglio et al. [21] in the early stage of the studies on this reaction, between the nature of the olefin and the nature of the ancillary ligand bound to palladium: phosphorus-donor ligands are the ligands of choice for the synthesis of CO/aliphatic olefin copolymers, while nitrogen-donor ligands should be chosen when CO/vinyl arene polyketones are the desired products.

Analysis of the literature data indicates that CO/vinyl arene copolymers with a syndiotactic microstructure are easily accessible in high yield (close to 200 g CP/g Pd h) and with high molecular weight values (up to 300 000). As far as the synthesis of the corresponding polyketones with an isotactic microstructure is concerned, enantiomerically pure, nitrogen-donor ligands possessing C_2-symmetry have to be applied. However, all the ligands tested generate an active species of limited stability and the isotactic polyketones are obtained only with rather poor yields and with molecular weight values not higher than 46 000. Therefore, a proper catalytic system able to promote the synthesis of the CO/vinyl arene copolymer with an isotactic microstructure in reasonable yield has still to be discovered.

Finally, the discovery by Brookhart and coworkers [10] and Gibson and Spitzmesser [6b] that iron, cobalt and palladium complexes with tridentate or bidentate nitrogen-donor ligands are very efficient catalysts for olefin homopolymerization had a galvanizing effect in this field by stimulating new research, most associated with the development of new N–N ligands.

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