Subtle Balance of Steric and Electronic Effects for the Synthesis of Atactic Polyketones Catalyzed by Pd Complexes with Meta-Substituted Aryl-BIAN Ligands

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Both symmetric and nonsymmetric bis(aryl)acenaphthenequinonediimine ligands, featured by substituents in meta-positions of the aryl rings, have been applied for the first time as ancillary ligands for the palladium-catalyzed CO/vinyl arene copolymerization. The nature and the number of substituents affect both the productivity and the molecular weight of the synthesized copolymers. Palladium complexes containing the nonsymmetric ligands are the most efficient catalysts reported so far for the synthesis of atactic polyketones.

Introduction

The discovery by Brookhart that late transition metal complexes modified with α-diimine ligands, having a 1,4-diaza-1,3-butadiene or an acenaphthene (Ar-BIAN) skeleton, are extremely efficient catalysts for homopolymerization of alkenes had a galvanizing effect for the research in this field, resulting in the development of a huge number of bis(nitrogen) ligands of this nature.[1,2] All the Ar-BIAN ligands applied to the polymerization reactions share the following common features: (i) the two nitrogen atoms bear identical aryl rings; (ii) these aryl rings are almost invariably substituted in the ortho and/or para positions; and (iii) the nature and the number of substituents affect the yield[3] in the polymer, the selectivity[1,4] in the product, the microstructure of the polymer,[4] and the relative amount[5] of the comonomers inserted into the polymer chain in α-olefins copolymerization.

During the last two decades considerable interest has been given to the CO/alkene copolymerization reaction yielding perfectly alternating polyketones.[6–10] In particular, when prochiral alkenes are the comonomers the control of the stereochemistry of the synthesized macromolecules is a main target[11] and in the case of vinyl arene comonomers a considerable number of nitrogen-donor ligands have been applied to this reaction with this aim.[12] This collection of data allowed a relationship between the symmetry of the ligand and the tacticity of the obtained polyketones to be defined: generally, C_{2v} symmetric ligands lead to syndiotactic copolymers, while polyketones with isotactic microstructure are obtained with ligands of C_2 symmetry. Atactic CO/styrene polyketones were obtained for the first time with P−N ligands of C_1 symmetry, under drastic reaction conditions like a CO pressure of 320 bar, and reaching a productivity of 3.42 g CP/g Pd·h (g CP/g Pd·h = grams of copolymer per gram of palladium per hour).[13,14] Also, Pd complexes containing pyridine-imidazoline ligands led to atactic CO/4- *tert*-butylstyrene copolymers under mild reaction conditions. For this system, both the productivity and the stereoregularity of the obtained polyketones were affected by the electronic properties and the stereochemistry of the ligand: (*R*,*S*)-pyridine-imidazolines yielded the atactic polyketones with moderate productivities, while the corresponding (*R*,*R*)-diastereoisomer generated very efficient catalysts for the synthesis of the syndiotactic copolymer.[15,16]

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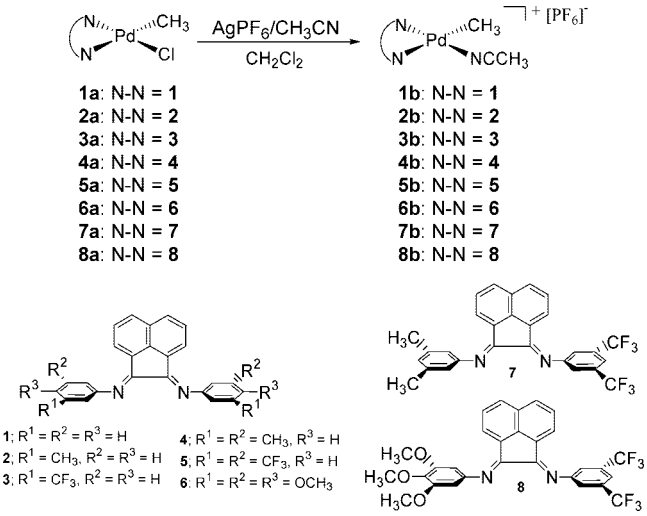
Scheme 1. Synthetic Pathway for the Monocationic Palladium Complexes 1b–8b and the Studied Ar-BIAN Ligands



Palladium complexes of ortho-substituted Ar-BIAN were introduced[17] and used as model compounds for unraveling the mechanism of the polymer chain growth during the CO/alkene copolymerization.[17–20] When monocationic Pd(II) complexes with ortho-disubstituted Ar-BIAN ligands were tested as pre-catalysts in the CO/4-Me-styrene copolymerization, low productivity (15 g CP/g Pd corresponding to 0.3 g CP/g Pd·h) or complete inactivity were observed depending on the nature of the substituents.[21–23] Moreover, these copolymers have a prevailingly isotactic microstructure despite the C_{2v} symmetry of the Ar-BIAN ligand present in the catalyst.

So far, Ar-BIAN ligands with substituents in the meta position have not been applied to CO/alkene copolymerizations, nor have any nonsymmetric Ar′,Ar-BIAN ligands (Ar′ ≠ Ar) been tested in catalysis, in general. We envisaged that attenuation of steric effects—compared to the presence of ortho substituents—and/or the creation of subtle electronic unbalance on the N-atoms could be advantageous for the copolymerization reaction; hence, we have now focused our attention on Ar-BIAN ligands substituted in the meta position by methyl (**2** and **4**) or trifluoromethyl (**3** and **5**) or methoxy (**6**) groups (Scheme 1).[24–26] Moreover, the nonsymmetric Ar′,Ar-BIAN ligands (**7** and **8**) are studied for the first time.[27] Ligands **6** and **8** have not been reported before and they have been synthesized for this purpose. Here, we discuss the catalytic behavior of a series of Pd(II) complexes, $[Pd(CH_3)(CH_3CN)(N{-}N)][PF_6]$ **1b–8b** (N−N = **1–8**), in the CO/vinyl arene copolymerization.

Results and Discussion

The new mixed ligand **8** was prepared by a transimination reaction, in a way analogous to that already reported for **7** and other mixed Ar′,Ar-BIAN ligands (Scheme 2),[27] but an improved chromatographic separation was employed. Quite surprisingly, the symmetrical 3,4,5-$(CH_3O)_3C_6H_3$-BIAN (**6**) could not be obtained by the direct reaction of the corresponding amine with acenaphthenequinone in refluxing acetic acid. Apparently the quinone is acting as an oxidant for trimethoxyaniline under these conditions, highlighting the very electron-rich nature of the latter. To the best of our knowledge, this is the first time this synthetic strategy fails with an electron-rich aniline.[24] Ligand **6** could be obtained without problems by transimination from ligand **5** by the same procedure employed for ligand **8**, but employing a 3-fold molar excess of amine (Scheme 2). Transimination proceeds under much milder conditions and no oxidant is present.

The new monocationic complexes **1b–8b** were prepared starting from the corresponding neutral derivatives **1a–8a**, following the well-established procedure reported in the literature (Scheme 1).[28]

Both neutral and monocationic complexes were characterized by elemental analysis and ^{1}H NMR spectroscopy recording the spectra in CD_2Cl_2 solution, at room temperature. The ^{1}H assignments are based on the number of signals, on their integration, on NOE, and on homonuclear COSY experiments. From a general point of view, the spectra can be divided into three regions, respectively those of the aromatic protons, of the protons of the substituents of the aryl rings, and of the Pd-CH_3 fragment. The signals that are more diagnostic for the coordination of ligand to palladium are those of H^3 and H^{10} for the acenaphthene skeleton and that due to the Pd-CH_3 moiety (Chart 1, Table 1).

For complexes **1a–6a** and **1b–6b**, having the symmetric Ar-BIAN ligands, the number of signals and their integration confirm the coordination of the α-diimine to palladium in a nonsymmetric environment. No signal due to the free ligand is present (Table 1). The protons of the two halves of the ligand were distinguished thanks to NOE experiments based on the irradiation of the signal of $H^{14',18'}$ and resulting in the increase in the intensity of the singlet due to the Pd-CH_3 fragment and of the doublet assigned to H^{10}. In analogy, when the signal of $H^{14,18}$ was irradiated, an increase in the intensity of the doublet assigned to H^3 was observed, while no interaction with the Pd-CH_3 fragment was evidenced. In addition, both NOE experiments highlighted the presence of an exchange equilibrium between the two halves of the ligand. This equilibrium is slow on the NMR time scale.

H^3 and H^{10} protons were the most affected by the coordination to palladium: they generated two well-separated doublets that were at low frequency with respect to the signals of H^5 and H^8, both in the free ligand and in the Pd complexes, due to the fact that they fall in the shielding cone of the aryl rings. The coordination to palladium shifted the signal of H^3 to high frequency, whereas that of H^{10} was shifted to low frequency with respect to the same signals in the free ligand, confirming

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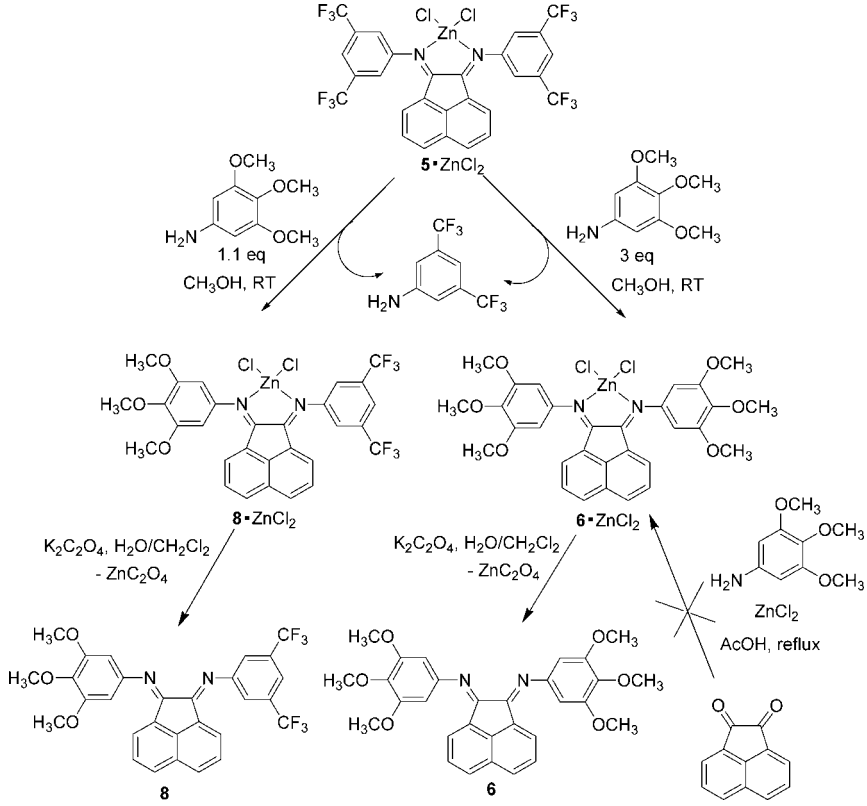
Scheme 2. Synthetic Pathway for Ligands 6 and 8



the assignment that H^3 is cis to the chloride.[29] The Pd-CH_3 fragment gave one singlet centered at 0.90 ppm in the neutral derivatives, while it was shifted to low frequency by about 0.10 ppm in the cationic complexes. No effect of the nature of the ligand on the chemical shift of this signal was observed (Table 1).

As far as ^{1}H NMR spectra of Pd complexes with the nonsymmetric Ar′,Ar-BIAN ligands are concerned (**7a**, **8a**, **7b**, **8b**) the number of signals and their integration indicated the presence in solution of two species, in different amounts, which are due to the cis and trans isomers, that differ in the relative position of the Pd-CH_3 fragment with respect to the two halves of the ligand. For the sake of convenience, the isomer with the Pd-CH_3 moiety trans to the Pd−N bond with the iminic N-atom having the aryl ring bearing the CF_3 groups was conventionally called trans (Chart 1). For all four complexes, NOE experiments, performed upon irradiation of the Pd-CH_3 signal, proved that the major species was the trans isomer. For the neutral complexes the ratio between the trans and cis isomers was 10:1 and 6:1 for **7a** and **8a**, respectively. In the case of the monocationic derivatives, the trans-to-cis ratio was decreased

Chart 1. Numbering Scheme for Free and Coordinated Ligands

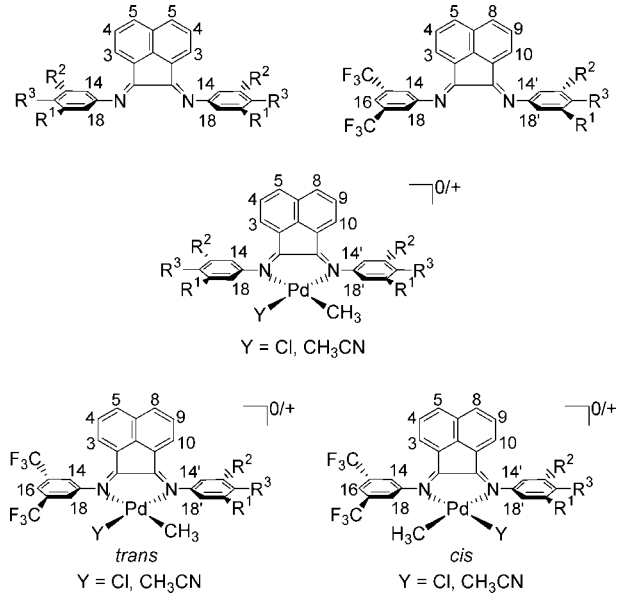


Table 1. Selected ^{1}H NMR Data for Complexes 1a–8a and 1b–8b[a]

N−N/complex	H^3	H^{10}	Pd−CH_3
1	6.84 (d)	6.84 (d)	
1a	7.16 (d)	6.54 (d)	0.91(s)
1b	7.30 (d)	6.54 (d)	0.81(s)
2	6.86 (d)	6.86 (d)	
2a	7.01 (m)	6.58 (d)	0.91(s)
2b	7.03 (m)	6.57 (d)	0.83(s)
3	6.86 (d)	6.86 (d)	
3a	7.16 (d)	6.56 (d)	0.90(s)
3b	7.25 (br)	6.51 (d)	0.80(s)
4	6.92 (d)	6.92 (d)	
4a	7.16 (d)	6.62 (d)	0.91(s)
4b	7.32 (d)	6.61 (d)	0.84(s)
5	6.89 (d)	6.89 (d)	
5a	7.21 (d)	6.63 (d)	0.77(s)
5b	7.26 (d)	6.57 (d)	0.86(s)
6	7.12 (d)	7.12 (d)	
6a	7.47 (d)	6.81 (d)	0.87(s)
6b	7.44 (d)	6.82 (d)	0.93(s)
7	6.81 (d)	7.01 (d)	
7a	7.11 (m)	6.67 (d)	1.01(s,trans),0.79(s,cis)
7b	7.22 (d)	6.60 (d)	0.96(s,trans),0.71(s,cis)
8	6.82 (d)	7.20 (d)	
8a	7.15 (d)	6.88 (d)	0.95(s,trans),0.69(s,cis)
8b	7.24 (d)	6.85 (d)	1.05(s,trans),0.74(s,cis)

[a] Recorded in CD_2Cl_2, at room temperature; s = singlet, d = doublet, m = multiplet, br = broad; δ values are in ppm.

Table 2. CO/Styrene Copolymerization: Effect of the Ligand and of BQ (Catalyst Precursor: [Pd(CH$_3$)(CH$_3$CN)(N−N)][PF$_6$] 1b–8b)[a]

run	N−N	[BQ]/[Pd]	kg CP/g Pd	MW (M_w/M_n)
1	**1**	0	1.23	43000 (2.2)
2	**2**	0	0.42	37500 (2.2)
3	**3**	0	1.34	41000 (2.1)
4	**4**	0	0.93	33000 (2.1)
5	**5**	0	0.46	14000 (2.0)
6	**6**	0	1.45	20000 (2.9)
7	**7**	0	1.45	47000 (2.0)
8	**8**	0	1.16	20000 (3.3)
9	**1**	5	2.18	29000 (1.9)
10	**2**	5	0.74	20000 (1.9)
11	**3**	5	2.50	20500 (1.8)
12	**4**	5	1.82	22000 (1.9)
13	**5**	5	1.26	7000 (1.6)
14	**6**	5	3.45	7500 (1.7)
15	**7**	5	2.54	20500 (1.7)
16	**8**	5	3.70	22000 (1.7)

[a] Reaction conditions: $n_{Pd} = 1.27 \times 10^{-5}$ mol; TFE $V = 20$ mL; styrene $V = 10$ mL; [styrene]/[Pd] = 6800; $T = 303$ K; $P_{CO} = 1$ atm; $t = 24$ h.

Table 3. CO/4-Me-Styrene Copolymerization: Effect of the Ligand and of BQ (Catalyst Precursor: [Pd(CH$_3$)(CH$_3$CN)(N−N)][PF$_6$]1b–8b)[a]

run	N−N	[BQ]/[Pd]	kg CP/g Pd	MW (M_w/M_n)
1	**1**	0	1.05	33000 (1.9)
2	**2**	0	1.33	30000 (1.9)
3	**3**	0	0.21[b]	16000 (2.6)
4	**4**	0	1.32	38500 (2.0)
5	**5**	0	0.78[b]	n.d.
6	**6**	0	1.79	23000 (1.7)
7	**7**	0	1.59	16000 (1.5)
8	**8**	0	1.33	11000 (1.7)
9	**1**	5	1.19	20500 (1.6)
10	**2**	5	1.48	26000 (1.8)
11	**3**	5	0.69[b]	7000 (1.6)
12	**4**	5	1.58	29000 (1.7)
13	**5**	5	1.35[b]	9000 (1.4)
14	**6**	5	1.95	7000 (1.5)
15	**7**	5	2.36	22000 (1.6)
16	**8**	5	1.64	6500 (1.5)

[a] Reaction conditions: $n_{Pd} = 1.27 \times 10^{-5}$ mol; TFE $V = 20$ mL; 4-Me-styrene $V = 10$ mL; [4-Me-styrene]/[Pd] = 5900; $T = 303$ K; $P_{CO} = 1$ atm; $t = 24$ h. [b] Productivity based on the amount of copolymer; n.d. = not determined.

to 3:1 for both **7b** and **8b**. These observations are in agreement with the literature data, which indicate a preferential tendency to coordinate the methyl group trans to less basic N atom for Pd−methyl complexes with electronically nonequivalent N-donor atoms.[16,28,30,31]

As observed for complexes **1a**–**6a** and **1b**–**6b**, even for **7a**,**b** and **8a**,**b** in solution an exchange equilibrium was present, in this case the equilibrium involves the two isomers. The rate of this equilibrium was slow on the NMR time scale. The mechanism of this equilibrium might occur via the cleavage of one Pd−N bond, the rotation around the other Pd−N bond, and the closure of the chemical bond, resulting in the exchange of the two halves of the ligand with respect to the Pd-methyl fragment. The lability of the Pd−N bond for the Ar-BIAN ligands and their fluxional behavior in solution was already reported.[32]

Copolymerization Reactions. Complexes **1b**–**8b** were tested as precatalysts in the CO/vinyl arene copolymerization in 2,2,2-trifluoroethanol (TFE), at $T = 30$ °C, under 1 atm of CO, in the presence or absence of 1,4-benzoquinone (BQ) as oxidant. All the complexes generated active species for the studied reaction and the solids isolated at the end of the runs were perfectly alternating polyketones.

In the case of CO/styrene copolymerization, regardless of the presence of the oxidant in the reaction mixture, the substitution of one of the two meta positions on the aryl rings with a methyl group resulted in a remarkable decrease in the productivity with respect to the data obtained with the nonsubstituted ligand **1** (Table 2, run 1 vs 2; run 9 vs 10). On the other hand, when a CF_3 group is introduced on one *meta* position a slight increase in the productivity was observed (Table 2, run 1 vs 3; run 9 vs 11). This trend of productivity is in agreement with that showed by analogous complexes with 4,7-disubstituted-1,10-phenanthrolines, which evidenced an increase in the productivity on decreasing the Lewis basicity of the N−N ligand.[28] In that case the complex with the 5,5,6,6-tetrafluoro-5,6-dihydro-1,10-phenanthroline was found to be the best catalyst ever reported, in terms of catalytic activity, productivity, molecular weight, and stereoregularity, for the synthesis of CO/vinyl arene polyketones with a syndiotactic microstructure.

When the aryl rings both have meta positions substituted by CH_3 or CF_3 groups in a symmetrical way, a decrease in the productivity was found with respect to data obtained with **1b** regardless of the substituents (Table 2, run 1 vs 4 and 5; run 9 vs 12 and 13), thus suggesting that steric hindrance is the prevailing effect when all the *meta* positions bear substituents.

When 4-Me-styrene was the comonomer, the effect of the ligand on the productivity was less pronounced and different than that in the case of styrene (Table 3). The introduction of one methyl group on one of the two meta positions resulted in an increase in the productivity with respect to the values obtained both with the reference ligand **1** and ligand **3** with one CF_3 on one meta position, regardless of the presence of benzoquinone (Table 3, run 2 vs 1 and 3; run 10 vs 9 and 11). Even catalyst **4b**, containing the ligand with both meta positions substituted with methyl groups, was found to be more productive than **1b** and **5b** (Table 3, run 4 vs 1 and 5; run 12 vs 9 and 13). These trends of productivity are the opposite of those observed for styrene. In addition, with styrene no formation of inactive palladium metal was observed, while with 4-Me-styrene catalysts **3b** and **5b** decomposed to palladium metal and decomposition was more pronounced when benzoquinone was not present in the reaction mixture. These results suggest that in the case of 4-Me-styrene the trend of productivity is mainly affected by the stability of the catalyst, which is higher for ligands having a higher Lewis basicity, such as **2** and **4**, which generate more productive catalysts. The effect that the stability of the catalyst conceals the effect of the ligand was also found by us in the catalytic system based on the 4,7-disubstituted-1,10-phenanthrolines.[28]

It should be noted that, whereas in the CO/styrene copolymerization the selectivity of the reaction was always 100% in the polyketone, in the CO/4-Me-styrene reaction when complexes containing the symmetric Ar-BIAN ligands with CF_3 substituents, **3b** and **5b**, were applied, the concomitant formation of homopolymer was observed. The amount of poly-4-Me-styrene was very low (4% and 7% for **3b** and **5b**, respectively)

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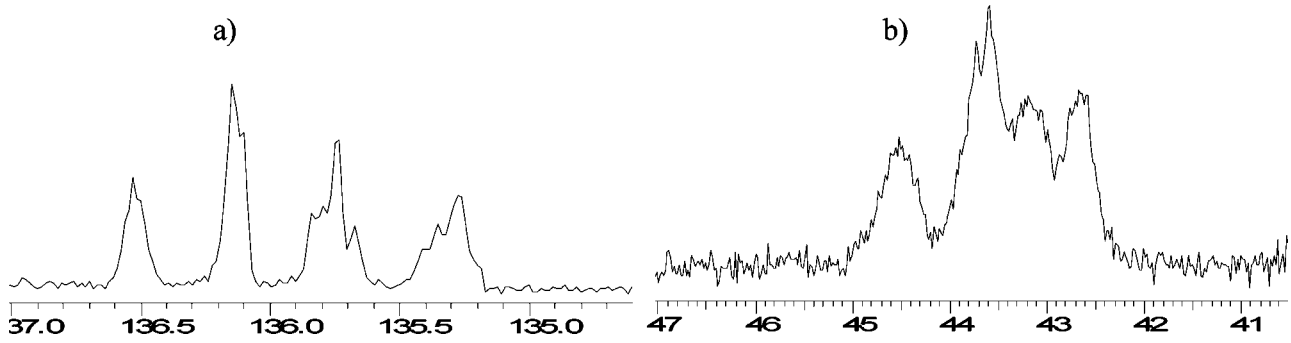

Figure 1. ^{13}C NMR spectra of polyketones synthesized with complex **6b**: (a) the *ipso* carbon atom region of the CO/styrene copolymer and (b) the methylenic carbon atom region of the CO/4-Me-styrene copolymer.

when benzoquinone was present in the reaction mixture, while when the reaction was carried out in the absence of the oxidant the amount of coproduced homopolymer was considerably higher: 27% for **3b** and 80% for **5b**. With the aim to shed light on the mechanism of the homopolymerization, three experiments were performed at $T = 303$ K and for 24 h as in the copolymerization tests, but varying the components of the system: (1) when 4-Me-styrene was treated in TFE with BQ, without addition of CO, no polymerization was observed; (2) the same happened when 4-Me-styrene was treated in TFE with BQ, without addition of CO, in the presence of complex **5b**; (3) only traces of homopolymer were formed when 4-Me-styrene was treated in TFE in the presence of **5b**, but neither with BQ nor with CO. These results are not an absolute proof that the homopolymerization occurs via a radical rather than an insertion mechanism. However, they suggest that the palladium complex and CO are required to start the homopolymerization of 4-Me-styrene, which might occur through the Pd-alkyl bond homolysis. The propensity of neutral Pd-alkyl species to undergo Pd−C bond homolysis has been recently reported.[33] The nature of the mechanism of the homopolymerization of alkenes catalyzed by palladium complexes has been recently debated.[34]

For both alkenes, the active species containing ligand **6** showed a productivity higher than that of **1** (Table 2, run 6 vs 1; run 14 vs 9; Table 3, run 6 vs 1; run 14 vs 9), regardless of the presence of benzoquinone in the reaction mixture.

The highest values of productivity were reached with complexes **7b** or **8b**, having the nonsymmetric Ar′,Ar-BIAN (Tables 2 and 3). In particular, ligand **8b** led to the most productive catalyst among those tested, achieving the value of 3.70 kg CP/g Pd (corresponding to 154 g CP/g Pd·h) in the CO/styrene copolymerization, while in the case of 4-Me-styrene the highest value of productivity was reached with **7b**. The comparison of the productivity data of the Ar′,Ar-BIAN-containing catalysts with those of the complexes having the related symmetric ligands evidenced that, for both alkenes, **7b** showed a productivity remarkably higher than that of **4b** and **5b**. The same was observed for **8b** in the CO/styrene copolymerization carried out in the presence of BQ, while in both CO/4-Me-styrene and CO/styrene with no addition of BQ, **8b** was found less productive than **6b** together with a slight formation of palladium metal. In all cases, with catalysts containing the nonsymmetric ligands the selectivity was 100% in the polyketone.

These data suggest that the unbalance of electron density on the nitrogen-donor atoms of the ligand has a positive effect on the catalyst performances. Moreover, in this case the favorable electronic effect might be partially attenuated by the negative effect of the steric hindrance created by substituents on all meta positions. The effect of two electronically nonequivalent ligand fragments was previously reported for the CO/propene and the CO/1-hexene copolymerizations catalyzed by Pd-diphosphine systems based on ligands belonging to the Josiphos[35,36] and to the dppp families,[37] respectively.

In contrast with the literature,[38–41] where 4-Me-styrene was claimed to be a more reactive alkene than styrene, we observed that, in the present system, productivities in the CO/4-Me-styrene copolymerization were similar or slightly lower compared to those obtained in the CO/styrene reaction (Tables 2 and 3).

The effect of the nature of the ligand on the molecular weight values was not very pronounced: the introduction of a group on one or both meta positions generally led to polyketones with lower molecular weight values than those prepared with complex **1b** (Tables 2 and 3). The highest M_w value ($M_w = 47000$) was reached for the CO/styrene copolymer synthesized with **7b**. In agreement with the literature,[42–44] the introduction of BQ into the reaction mixture, even if it increased the productivity, resulted in the synthesis of shorter polyketone chains, for both alkenes (Tables 2 and 3).

The stereochemistry of these polyketones was studied by ^{13}C NMR spectroscopy and the microtacticity was determined by integration of the signal of the *ipso* carbon atom in the case of styrene-containing copolymers, and of that of the methylenic carbon in the case of CO/4-Me-styrene copolymers (Figure 1). The ^{13}C NMR spectra showed that atactic copolymers were obtained in all cases, suggesting that all these ligands create an active site with the same steric environment around palladium regardless of the symmetry of the ligand itself, namely C_{2v} for **1**, **4**, **5**, and **6**, C_s or C_2 for **2** and **3**, and C_s for **7** and **8**.

A detailed mechanistic investigation on the CO/4-Me-styrene copolymerization catalyzed by palladium complexes with aryl-

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α-diimmine ligands, having the 1,4-diaza-1,3-butadiene skeleton and aryl rings substituted in the ortho or in the para position has been reported. The latter leads to copolymers with an atactic microstructure.[45] The intermediates involved in the insertion of the first molecules of comonomers on the palladium complexes were detected and characterized by multinuclear NMR. These species are open-chain intermediates and the formation of the six-membered metallacycle, up to now considered responsible for the stereochemical control in the catalytic systems based on N-donor complexes, was not observed. In the case of the more flexible para-substituted diimmine ligands the oscillation of the aryl rings around the $N-C_{ipso}$ bond[23] was proposed as responsible for a statistical insertion of the styrene enantiotopic faces leading to the formation of atactic copolymers. It is reasonable to speculate that analogous intermediates and an analogous mechanism might be present in the catalytic system under investigation based on aryl-α-diimmine ligands substituted in the meta position.

The productivity value of 1.23 kg CP/g Pd obtained with complex **1b**, having the nonsubstituted Ar-BIAN ligand, in the CO/styrene copolymerization with no addition of BQ, can be compared with the value of 0.68 kg CP/g Pd obtained with complex $[Pd(CH_3)(CH_3CN)(phen)][PF_6]$, highlighting the higher activity of the present complex with respect to the catalyst with the simple phen. However, it should be evidenced that the phen catalyst led to the syndiotactic copolymer.

To confirm the positive effect of the substituents in the meta position, the Ar-BIAN ligand with all the ortho positions substituted by methyl groups, namely (2,6-$(CH_3)_2C_6H_3)_2$-BIAN (**9**), was prepared and used to synthesize the corresponding palladium−monocationic complex **9b**, which was tested as a precatalyst in the studied copolymerizations under the same reaction conditions of complexes **1b**–**8b**. **9b** yielded, working with [BQ]/[Pd] = 5, the CO/styrene and CO/4-Me-styrene polyketones with productivity values of 0.31 and 0.13 kg CP/g Pd, respectively. These values are remarkably lower than those obtained with **4b** (Tables 2 and 3, run 12). Even the molecular weight values (16000 (1.3) for the CO/styrene and 10000 (1.3) for the CO/4-Me-styrene polyketones) are lower than those of the polymers synthesized with **4b**. In agreement with the literature,[22] the stereochemistry of the polyketones synthesized with **9b** differs from that of the copolymers obtained with ligands substituted in the meta position, being mainly isotactic with a content of 70% of the *ll* triad and 30% of the heterotactic triads.

Conclusions

In this paper we have applied, for the first time, palladium complexes with both symmetric and nonsymmetric Ar-BIAN ligands substituted in the meta position to the CO/vinyl arene copolymerization reaction. These palladium complexes generate very efficient catalysts, under atmospheric CO pressure, for the synthesis of regioregular, atactic polyketones. Both productivity and molecular weight are affected by the nature and the number of meta substitutents, which is equally unprecedented.

As we envisaged at the beginning, moving the substituents on the aryl rings from ortho to meta positions resulted in a remarkable increase in the productivity (from 0.3 g CP/g Pd·h to 5 g CP/g Pd·h). This trend together with the molecular weight values point out an important difference between this catalytic system and the Brookhart's system. In that case the introduction of substituents on the ortho positions of the aryl rings of α-diimines was a crucial requirements for directing the selectivity of the homopolymerization of alkenes from oligomers to polymers. In the present system, the introduction of substituents on ortho positions had a negative effect on the productivity and on the molecular weight; thus to obtain very efficient catalysts, aryl-α-diimines substituted in the meta position were required.

In addition, among the ligands tested, the nonsymmetric Ar′,Ar-BIAN generated the most active catalysts providing the atactic CO/vinyl arene copolymers in very high yield, thus pointing out the importance of the electronic unbalance on the two donor atoms of the ligand and, at the same time, opening the possibility to study their chemical, physical, and mechanical properties for evaluating their potential applications.

Experimental Section

General Considerations. $[Pd(OAc)_2]$ was a loan from Engelhard Italia and was used as received. The Ar-BIAN ligands **1**–**5** and **7** were prepared according to the procedures reported in the literature.[24–27,46] For ligands **2** and **4** a simplified procedure with respect to that published was applied. 2,2,2-Trifluoroethanol (TFE) (Aldrich) and the analytical grade solvents (Fluka) were used without further purification for synthetic, spectroscopic, and catalytic purposes. Dichloromethane used for the synthesis of complexes was purified through distillation over CaH_2 under inert atmosphere and was used freshly distilled. THF used for the synthesis of **2** and **4** was distilled over sodium, under inert atmosphere. Carbon monoxide (CP grade 99.9%) was supplied by SIAD. ^{1}H NMR spectra were recorded at 400 MHz on a JEOL EX 400; the resonances were referenced to the solvent peak versus TMS ($CDCl_3$ at δ 7.26 and CD_2Cl_2 at δ 5.32) ^{13}C NMR 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 δ 77.0. **Caution:** HFIP is a very volatile and highly toxic solvent, so proper protection should be used when it is handled.

Synthesis of Ligands 2 and 4. Acenaphthenequinone (2 mmol) was dissolved in distilled THF (40 mL). To this solution was added anhydrous Na_2SO_4, followed by the addition of the proper aniline (9 mmol), which was 3-methylaniline for ligand **2** or 3,5-dimethylaniline for ligand **4**. The suspension was kept at 50 °C for 1 h or until the complete dissolution of the solid. Then the solution was kept under reflux. The reaction was monitored by TLC. The reaction went to completion in 1 week. The solution was concentrated almost to dryness and then was used, as it was, to charge a chromatography column. The product was separated from the excess of aniline and from the monoketoimine by chromatography on silica gel (230–400 mesh) with a mixture of CH_2Cl_2 (50%), *n*-hexane (44%), diethyl ether (5%), and triethylamine (1%) as eluent. Average yield: 70%. Elemental analysis: **2** calcd for $C_{26}H_{20}N_2$: C, 86.64; H, 5.59, N, 7.77. Found: C, 86.90; H, 5.42; N, 7.40. **4** calcd for $C_{28}H_{24}N_2$: C, 86.56; H, 6.23, N, 7.21. Found: C, 86.40; H, 6.40; N, 7.10.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): **2**, δ 7.88 (d, 2H, $H^{5,8}$), 7.38 (t, 2H, $H^{4,9}$), 7.35 (t, 2H, $H^{15,15'}$), 7.07 (d, 2H, $H^{14,14'}$), 6.95 (s, 2H, $H^{18,18'}$), 6.92 (d, 2H, $H^{16,16'}$), 6.86 (d, 2H, $H^{3,10}$), 2.39 (s, 6H, CH_3); **4**, δ 7.90 (d, 2H, $H^{5,8}$), 7.40 (t, 2H, $H^{4,9}$), 6.92 (d, 2H, $H^{3,10}$), 6.90 (d, 2H, $H^{16,16'}$), 6.75 (d, 4H, $H^{14,14',18,18'}$), 2.38 (s, 12H, CH_3).

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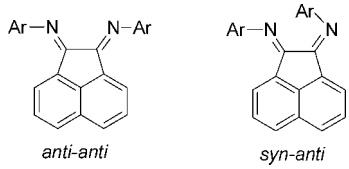
Synthesis of Ligands 6 and 8. (3,4,5-$(CH_3O)_3C_6H_2$)(3,5-$(CF_3)_2C_6H_3$)-BIAN (8). To a 100 mL Schlenk flask under N_2 and with magnetic stirring were added at room temperature (3,5-$(CF_3)_2C_6H_3$-BIAN)$ZnCl_2$ (460 mg, 0.63 mmol),[24] 3,4,5-$(CH_3O)_3C_6H_2NH_2$ (120 mg, 0.66 mmol), and methanol (20 mL). The complex completely dissolved. The reaction was monitored by TLC (alumina, CH_2Cl_2). To do so, a 0.5 mL aliquot of the solution was withdrawn and coordinated $ZnCl_2$ was eliminated by the method detailed below for the final product. The reaction terminated after 2 h, during which time the solution turned from orange to red. At this stage, a precipitate had formed, but the solution still contained appreciable amounts of the product, so the suspension was evaporated in vacuo and the solid washed with a 1:1 hexane/toluene mixture (10 mL) to remove the free anilines. To eliminate the coordinated $ZnCl_2$, the solid was dissolved in CH_2Cl_2 (25 mL) in a separating funnel and shaken with a saturated $K_2C_2O_4$ aqueous solution (10 mL) for 10 min. The organic phase was separated, washed with water (3 × 10 mL), dried with Na_2SO_4, and evaporated in vacuo. The obtained solid was purified by column chromatography on silica, using 10:0.5 hexane/triethylamine as eluent. Ligand **8** was eluted first (85 mg, 24% yield), followed by a small amount of **6**. However, the latter compound is better prepared as described in the next paragraph. Anal. Calcd for $C_{29}H_{20}F_6N_2O_3$: C, 62.37, H, 3.61, N, 5.02. Found: C, 61.99, H, 3.50, N, 5.10.

As for all other known asymmetric Ar′,Ar-BIAN compounds, the free ligand is present in solution as a mixture of the *anti*−*anti* and *syn*−*anti* isomers, with the former prevailing.[27]



anti-anti *syn-anti*

The ratio between the two isomers calculated from both the ^1H and the ^{19}F NMR is 8:1, which is comparable to that found for other ligands of the same class.[27] For the minor isomer, only some signals could be clearly assigned in the ^1H NMR spectrum and are reported below.

Major isomer (*anti*−*anti*). ^1H NMR ($CDCl_3$, 298 K) δ 8.00 (d, J = 7.6 Hz, 1H, H^5), 7.96 (d, J = 7.63 Hz, 1H, H^8), 7.80 (s, 1H, H^{16}), 7.62 (s, 2H, H^{14}, H^{18}), 7.52 (pst, H^9), 7.47 (pst, H^4), 7.20 (d, J = 7.2 Hz, 1H, H^{10}), 6.82 (d, J = 7.2 Hz, 1H, H^3), 6.40 (s, 2H, $H^{14'}$, $H^{18'}$), 3.96 (s, 3H, *p*-OCH_3), 3.86 (s, 6H, *m*-OCH_3). ^{19}F NMR ($CDCl_3$, 298 K) δ −63.2 (s, CF_3).

Minor isomer (*syn*−*anti*. ^1H NMR ($CDCl_3$, 298 K) δ 6.00 (s, 2H, $H^{14'}$, $H^{18'}$), 3.86 (s, 3H, *p*-OCH_3), 3.74 (s, 6H, *m*-OCH_3). ^{19}F NMR ($CDCl_3$, 298 K) δ −63.07 (s, CF_3).

(3,4,5-$(CH_3O)_3C_6H_2)_2$-BIAN (6). To a 100 mL Schlenk flask under N_2 and with magnetic stirring were added at room temperature (3,5-$(CF_3)_2C_6H_3$-BIAN)$ZnCl_2$ (305.5 mg, 0.412 mmol), 3,4,5-$(CH_3O)_3C_6H_2NH_2$ (227.3 mg, 1.241 mmol), and methanol (20 mL). The complex completely dissolved. The reaction was stirred at room temperature overnight, during which time the solution turned from orange to red and a red precipitate formed. The solid was collected by filtration and washed with hexane (3 × 10 mL) to remove any free amine. The free ligand was obtained by the same procedure described for **8**, but in this case no chromatographic purification was necessary and the ligand is obtained analytically pure (126.7 mg, 60.0% yield). Anal. Calcd for $C_{30}H_{28}N_2O_6$: C, 70.30, H, 5.51, N, 5.47. Found: C, 70.01, H, 5.80, N, 5.12.

^1H NMR ($CDCl_3$, 298 K) δ 7.97 (d, J = 8.3 Hz, 2H, H^5), 7.47 (pst, J = 7.9 Hz, 2H, H^4), 7.12 (d, J = 7.2 Hz, 2H, H^3), 6.40 (s, 4H, $H^{14,18}$), 3.96, (s, 2H, *p*-OCH_3), 3.85 (s, 4H, *m*-OCH_3).

Synthesis of Complexes. All manipulations were carried out under argon atmosphere with Schlenk technique and at room temperature.

Synthesis of Neutral Complexes [Pd(CH_3)(Cl)(N−N)] (1a–8a). All the complexes were prepared starting from $[Pd(Cl)_2(cod)]$, following the procedure reported in the literature.[29,47] In particular, 1.1 equiv of N−N ligand was added to 0.40 mmol of [Pd(CH_3)(Cl)(cod)], dissolved in dichloromethane, at room temperature. After 1 h, diethyl ether was added and the product precipitated as a red-orange solid. Average yield: 94%.

[Pd(CH_3)(Cl)(1)] (1a). Elemental Anal. Calcd for $C_{25}H_{19}ClN_2Pd$: C, 61.37; H, 3.91, N, 5.73. Found: C, 61.11; H, 3.78; N, 5.67. ^1H NMR (400 MHz, CD_2Cl_2, 298 K): δ 8.04 (dd, 2H, $H^{5,8}$), 7.61 (t, 2H, $H^{15',17'}$), 7.55 (t, 2H, $H^{15,17}$), 7.51–7.40 (m, 4H, $H^{4,9}$ and $H^{16,16'}$), 7.38 (d, 2H, $H^{14,18}$), 7.23 (d, 2H, $H^{14',18'}$), 7.16 (d, 1H, H^3), 6.54 (d, 1H, H^{10}), 0.91 (s, 3H, *CH*$_3$-Pd).

[Pd(CH_3)(Cl)(2)] (2a). Elemental Anal. Calcd for $C_{27}H_{23}ClN_2Pd$: C, 62.68; H, 4.48, N, 5.41. Found: C, 62.40; H, 4.30; N, 4.97. ^1H NMR (400 MHz, CD_2Cl_2, 298 K): δ 8.04 (dd, 2H, $H^{5,8}$), 7.50–7.41 (m, 4H, $H^{4,9}$ and $H^{17,17'}$), 7.29–7.14 (m, 5H, $H^{16,18,16',18'}$ e H^{14}), 7.01 (m, 2H, $H^{14'}$ and H^3), 6.58 (d, 1H, H^{10}), 2.47 (s, 3H, *CH*$_3$-Ph), 2.44 (s, 3H, *CH*$_3$-Ph), 0.91 (s, 3H, *CH*$_3$-Pd).

[Pd(CH_3)(Cl)(3)] (3a). Elemental Anal. Calcd for $C_{27}H_{17}ClF_6N_2Pd$: C, 51.86; H, 2.74, N, 4.48. Found: C, 52.06; H, 2.65; N, 4.60. ^1H NMR (400 MHz, CD_2Cl_2, 298 K): δ 8.16 (dd, 2H, $H^{5,8}$), 7.80–7.46 (m, 6H, $H^{16,17,18,16',17',18'}$), 7.64 (s, 2H, $H^{14,14'}$), 7.53–7.46 (m, $H^{4,9}$), 7.16 (d, 1H, H^3), 6.56 (d, 1H, H^{10}), 0.90 (s, 3H, *CH*$_3$-Pd).

[Pd(CH_3)(Cl)(4)] (4a). Elemental Anal. Calcd for $C_{29}H_{27}ClN_2Pd$: C, 63.86; H, 4.99, N, 5.14. Found: C, 63.70; H, 4.66; N, 5.12. ^1H NMR (400 MHz, CD_2Cl_2, 298 K): δ 8.03 (dd, 2H, $H^{5,8}$), 7.45 (dt, 2H, $H^{4,9}$), 7.16 (d, 1H, H^3), 7.08 (s, 1H, $H^{16'}$), 7.02 (s, 1H, H^{16}), 6.95 (s, 2H, $H^{14,18}$), 6.81 (s, 2H, $H^{14',18'}$), 6.62 (d, 1H, H^{10}), 2.41 (s, 6H, 15′,17′-(*CH*$_3$)$_2$-Ph), 2.39 (s, 6H, 15,17-(C*H*$_3$)$_2$-Ph), 0.91 (s, 3H, C*H*$_3$-Pd).

[Pd(CH_3)(Cl)(5)] (5a). Elemental Anal. Calcd for $C_{29}H_{15}ClF_{12}N_2Pd$: C, 45.75; H, 1.99, N, 3.68. Found: C, 45.50; H, 1.96; N, 3.92. ^1H NMR (400 MHz, CD_2Cl_2, 298 K): δ 8.22 (dd, 2H, $H^{5,8}$), 8.09 (s, 1H, $H^{16'}$), 8.01 (s, 1H, H^{16}), 7.92 (s, 2H, $H^{14,18}$), 7.83 (s, 2H, $H^{14',18'}$), 7.58 (dt, 2H, $H^{4,9}$), 7.21 (d, 1H, H^3), 6.63 (d, 1H, H^{10}), 0.77 (s, 3H, C*H*$_3$−Pd).

[Pd(CH_3)(Cl)(6)] (6a). Elemental Anal. Calcd for $C_{31}H_{31}ClO_6N_2Pd$: C, 55.62; H, 4.67; N, 4.18. Found: C, 55.35; H, 4.55; N, 4.00. ^1H NMR (400 MHz, CD_2Cl_2, 298 K): δ 8.11 (dd, 2H, $H^{5,8}$), 7.55 (dd, 2H, $H^{4,9}$), 7.44 (d, 1H, H^3), 6.81 (d, 1H, H^{10}), 6.66 (s, 2H, H^{ortho} cis to Pd−Cl), 6.48 (s, 2H, H^{ortho} cis to Pd-CH_3), 3.90 (s, 6H, OCH_3 para), 3.86 (s, 6H, OCH_3 meta), 3.84 (s, 6H, OCH_3 meta), 0.87 (s, 3H, C*H*$_3$-Pd).

[Pd(CH_3)(Cl)(7)] (7a). Elemental Anal. Calcd for $C_{29}H_{15}ClF_6N_2Pd$: C, 53.31; H, 3.24, N, 4.29. Found: C, 53.50; H, 2.96; N, 3.92. ^1H NMR (400 MHz, CD_2Cl_2, 298 K): δ 8.12 (dd, 2H, $H^{5,8}$), 7.93 (s, 1H, H^{16}), 7.89 (s, 2H, $H^{14,18}$), 7.52 (dt, 2H, $H^{4,9}$), 7.11 (m, 2H, $H^{16'}$ and H^3), 6.81 (s, 2H, $H^{14',18'}$), 6.67 (d, 1H, H^{10}), 2.43 (s, 6H, 15′,17′-(*CH*$_3$)$_2$-Ph), 1.01 (s, 3H, C*H*$_3$-Pd major isomer, it is trans to the aryl ring substituted with CF_3), 0.79 (s, 3H, C*H*$_3$-Pd minor isomer, it is trans to the aryl ring substituted with CH_3), in the aromatic region also the signals due to the minor isomer are visible, with the ratio between the two isomers 10/1.

[Pd(CH_3)(Cl)(8)] (8a). Elemental Anal. Calcd for $C_{30}H_{23}ClF_6N_2O_3Pd$: C, 50.37; H, 3.24, N, 3.91. Found: C, 40.95; H, 3.06; N, 3.92. ^1H NMR (400 MHz, CD_2Cl_2, 298 K): δ 8.16 (d, 2H, $H^{5,8}$), 7.80 (s, 1H, H^{16}), 7.90 (s, 2H, $H^{14,18}$), 7.55 (m, 2H, $H^{4,9}$), 7.15 (d, 1H, H^3), 6.88 (d, 1H, H^{10}), 6.49 (s, 2H, $H^{14',18'}$), 3.90 (s, 3H, OCH_3 para), 3.88 (s, OCH_3 meta, minor isomer), 3.85 (s, 6H, OCH_3 meta, major isomer), 0.95 (s, 3H, C*H*$_3$-Pd major

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isomer, it is trans to the aryl ring substituted with CF_3), 0.69 (s, 3H, CH_3-Pd minor isomer, it is trans to the aryl ring substituted with CH_3), in the aromatic region also the signals due to the minor isomer are visible, with the ratio between the two isomers 6/1.

Synthesis of Cationic Complexes [Pd(CH_3)(CH_3CN)(N−N)][PF_6] (1b–8b). All the complexes were obtained starting from the corresponding neutral derivatives upon addition of $AgPF_6$ in a mixture of CH_2Cl_2 and CH_3CN. [Pd(CH_3)(Cl)(N−N)] (**1a–8a**) (0.40 mmol) was dissolved in the minimal amount of CH_2Cl_2 under Ar. To the obtained solution was added a solution of $AgPF_6$ in CH_3CN (1.1 equiv in 6 mL), leading to the precipitation of AgCl. After 30 min, the solution was filtered over Celite and concentrated to half-volume under vacuum. Upon addition of diethyl ether the product precipitated as a yellow solid. Average yield: 90%.

[Pd(CH_3)(CH_3CN)(1)][PF_6] (1b). Elemental Anal. Calcd for $C_{27}H_{22}F_6N_3PPd$: C, 50.68; H, 3.46, N, 6.57. Found: C, 50.90; H, 3.78; N, 6.59. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 8.12 (pst, 2H, $H^{5,8}$), 7.68 (t, 2H, $H^{15',17'}$), 7.65 (t, 2H, $H^{15,17}$), 7.57–7.45 (m, 4H, $H^{4,9}$ and $H^{16,16'}$), 7.43 (d, 2H, $H^{14,18}$), 7.30 (d, 1H, H^3), 7.25 (d, 2H, $H^{14',18'}$), 6.54 (d, 1H, H^{10}), 2.14 (s, 3H, CH_3CN), 0.81 (s, 3H, CH_3-Pd).

[Pd(CH_3)(CH_3CN)(2)][PF_6] (2b). Elemental Anal. Calcd for $C_{29}H_{26}F_6N_3PPd$: C, 52.15; H, 3.92, N, 6.29. Found: C, 52.50; H, 3.72; N, 6.30. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 8.12 (pst, 2H, $H^{5,8}$), 7.58–7.47 (m, 4H, $H^{4,9}$ and $H^{17,17'}$), 7.34–7.21 (m, 5H, $H^{16,18,16',18'}$ and H^{14}), 7.03 (m, 2H, $H^{14'}$ and H^3), 6.57 (d, 1H, H^{10}), 2.49 (s, 6H, 15,15′-(CH_3)$_2$-Ph), 2.16 (s, 3H, CH_3CN), 0.83 (s, 3H, CH_3-Pd).

[Pd(CH_3)(CH_3CN)(3)][PF_6] (3b). Elemental Anal. Calcd for $C_{29}H_{20}F_{12}N_3PPd$: C, 44.89; H, 2.60, N, 5.42. Found: C, 44.70; H, 2.70; N, 5.62. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 8.15 (pst, 2H, $H^{5,8}$), 7.91–7.48 (m, 8H, $H^{16,17,18,16',17',18'}$ and $H^{14,14'}$), 7.63–7.48 (m, 2H, $H^{4,9}$), 7.25 (br, 1H, H^3), 6.51 (d, 1H, H^{10}), 2.14 (s, 3H, CH_3CN), 0.80 (s, 3H, CH_3-Pd).

[Pd(CH_3)(CH_3CN)(4)][PF_6] (4b). Elemental Anal. Calcd for $C_{31}H_{30}F_6N_3PPd$: C, 53.50; H, 4.34, N, 6.04. Found: C, 53.20; H, 4.28; N, 6.10. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 8.12 (pst, 2H, $H^{5,8}$), 7.57 (pst, 1H, H^4), 7.50 (pst, 1H, H^9), 7.32 (d, 1H, H^3), 7.14 (s, 1H, $H^{16'}$), 7.13 (s, 2H, H^{16}), 6.98 (s, 2H, $H^{14,18}$), 6.81 (s, 2H, $H^{14',18'}$), 6.61 (d, 1H, H^{10}), 2.45 (s, 6H, 15′,17′-(CH_3)$_2$-Ph), 2.44 (s, 6H, 15,17-(CH_3)$_2$-Ph), 2.17 (s, 3H, CH_3CN), 0.84 (s, 3H, CH_3-Pd).

[Pd(CH_3)(CH_3CN)(5)][PF_6] (5b). Elemental Anal. Calcd for $C_{31}H_{18}F_{18}N_3PPd$: C, 40.83; H, 1.99, N, 4.61. Found: C, 40.70; H, 1.68; N, 4.65. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 8.27 (dd, 2H, $H^{5,8}$), 8.13 (s, 1H, $H^{16'}$), 8.09 (s, 1H, H^{16}), 8.02 (s, 2H, $H^{14,18}$), 7.88 (s, 2H, $H^{14',18'}$), 7.63 (dt, 2H, $H^{4,9}$), 7.26 (d, 1H, H^3), 6.57 (d, 1H, H^{10}), 2.17 (s, 3H, CH_3CN), 0.86 (s, 3H, CH_3-Pd).

[Pd(CH_3)(CH_3CN)(6)][PF_6] (6b). Elemental Anal. Calcd for $C_{33}H_{34}F_6N_3O_6PPd$: C, 48.33; H, 4.18, N, 5.12. Found: C, 48.07; H, 4.28; N, 5.28. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 8.18 (t, 2H, $H^{5,8}$), 7.67–7.55 (dt, 2H, $H^{4,9}$), 7.44 (d, 1H, H^3), 6.82 (d, 1H, H^{10}), 6.62 (s, 2H, $H^{14,18}$), 6.45 (s, 2H, $H^{14',18'}$), 3.90, 3.88, 3.85 (3s, 18H, OCH_3 para and meta), 2.17 (s, 3H, CH_3CN), 0.93 (s, 3H, CH_3-Pd).

[Pd(CH_3)(CH_3CN)(7)][PF_6] (7b). Elemental Anal. Calcd for $C_{31}H_{24}F_{12}N_3PPd$: C, 46.31; H, 3.01, N, 5.23. Found: C, 46.47; H, 3.28; N, 5.28. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 8.14 (dd, 2H, $H^{5,8}$), 8.04 (s, 2H, $H^{14,18}$), 8.00 (s, 1H, H^{16}), 7.54 (dt, 2H, $H^{4,9}$), 7.22 (d, 1H, H^3), 7.14 (br, 1H, $H^{16'}$), 6.87 (s, 2H, $H^{14',18'}$), 6.60 (d, 1H, H^{10}), 2.45 (s, 6H, 15′,17′-(CH_3)$_2$-Ph minor isomer), 2.43 (s, 6H, 15′,17′-(CH_3)$_2$-Ph major isomer), 2.17 (s, 3H, CH_3CN major isomer), 2.14 (s, 3H, CH_3CN, minor isomer), 0.96 (s, 3H, CH_3-Pd, major isomer, it is trans to the aryl ring substituted with CF_3), 0.71 (s, 3H, CH_3-Pd, minor isomer, it is trans to the aryl ring substituted with CH_3), in the aromatic region also the signals due to the minor isomer are visible, with the ratio between the two isomers 3/1.

[Pd(CH_3)(CH_3CN)(8)][PF_6] (8b). Elemental Anal. Calcd for $C_{32}H_{26}F_{12}N_3O_3PPd$: C, 44.39; H, 3.03, N, 4.85. Found: C, 44.47; H, 3.28; N, 4.82. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 8.23 (t, 2H, $H^{5,8}$), 8.07 (s, 1H, H^{16}), 7.98 (s, 2H, $H^{14,18}$), 7.61 (m, 2H, $H^{4,9}$), 7.24 (d, 1H, H^3), 6.85 (d, 1H, H^{10}), 6.50 (s, 2H, $H^{14',18'}$), 3.90 (s, 6H, OCH_3 meta), 3.86 (s, 3H, OCH_3 para), 2.16 (s, 3H, CH_3CN major isomer), 2.12 (s, 3H, CH_3CN, minor isomer),1.05 (s, 3H, CH_3-Pd major isomer, it is trans to the aryl ring substituted with CF_3), 0.74 (s, 3H, CH_3-Pd minor isomer, it is trans to the aryl ring substituted with CH_3), in the aromatic region also the signals due to the minor isomer are visible, with the ratio between the two isomers 3/1.

General Procedure for Copolymerization Reactions. All copolymerization experiments were carried out in a three-necked, thermostated, 75 mL glass reactor equipped with a magnetic stirrer and connected to a temperature controller. After establishment of the reaction temperature (30 °C), the precatalyst, 1,4-benzoquinone (when required), the vinyl arene, and TFE were placed inside. CO was bubbled through the solution for 10 min; afterward a 4 L balloon filled with CO was connected to the reactor. The system was stirred at the same temperature for 24 h to give a cloudy white suspension. The reaction mixture was then poured into methanol (100 mL) and stirred for 1 h at room temperature, causing the precipitation of the polymer, which was filtered, washed with methanol, and dried under vacuum until constant weight was reached.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): CO/styrene: δ 6.69–7.41 (aromatic protons), 3.90–4.04 (broad, CH), 3.14 (broad, CH_2), 2.59 (broad, CH_2). ^{13}C NMR (100.5 MHz, HFIP + $CDCl_3$, 298 K) δ_C 209.5–210.4 (broad, CO), 136.5, 136.1, 135.8, 135.3 (C_{ipso}), 129.4, 128.3, 128.0 (C_{arom}), 53.5 (CH), 42.3–44.5 (broad, CH_2).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): CO/4-Me-styrene: δ 6.55–7.33 (aromatic protons), 3.84–3.95 (broad, CH), 3.10 (broad, CH_2), 2.54 (broad, CH_2), 2.24 (broad, CH_3). ^{13}C NMR (100.5 MHz, HFIP + $CDCl_3$, 298 K) δ_C 210.1–210.9 (broad, CO), 133.4, 133.0, 132.5, 131.9 (C_{ipso}), 129.9–130.1, 128.0 (C_{arom}), 52.6–53.4 (broad, CH), 42.6–44.8 (broad, CH_2), 20.4 (s, CH_3).

Polyketone Recrystallization. The copolymers (100 mg) were dissolved in chloroform (100 mL). The solution was filtered over Celite, which was then washed with chloroform. The solution was concentrated under vacuum to initiate precipitation of the polymer that was completed upon addition of ethanol. The white polymer was filtered, washed with methanol, and dried under vacuum.

Homopolymer/Copolymer Separation. The solids that are a mixture of homopolymer and copolymer are treated according to the following procedures to separate the two polymers. (a) If the amount of homopolymer is higher than 50%, the solid is dissolved in the minimum volume of CH_2Cl_2. The solution is added dropwise to diethyl ether (the volume of diethyl ether is three times the volume of CH_2Cl_2). The copolymer immediately precipitates. The suspension is stirred overnight at room temperature, filtrated under vacuum, washed with diethyl ether and vaccuum dried. (b) If the solid contains less than 50% of homopolymer, the procedure is the same, but after the precipitation with diethyl ether the suspension is stirred at room temperature for 2 h only before filtering the copolymer.

Molecular Weight Measurements. The molecular weights (MW) of copolymers and molecular weight distributions (M_w/M_n) were determined by gel permeation chromatography versus polystyrene standards. The analyses were recorded on a Kanuer 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/4-Me-styrene copolymers were directly soluble in chloroform. The statistical calculations were performed with the Bruker Chromstar software program.

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Supporting Information Available: ^{13}C NMR of the two polyketones. This material is available free of charge via the Internet at http://pubs.acs.org.

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