ORGANOMETALLICS

New Aryl α -Diimine Palladium(II) Catalysts in Stereocontrolled CO/Vinyl Arene Copolymerization

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Supporting Information

ABSTRACT: The effect of the catalyst structure on the stereoselectivity of CO/vinyl arene copolymerization has been studied with the aim of developing catalytic systems able to improve the yields while maintaining the high degree of copolymer isotacticity previously obtained using achiral nitrogen ligands. Aryl α -diimine ligands having extended aromatic rings (Ar)₂DABMe₂, with Ar = 1-C₁₀H₇ (e), 1-C₁₄H₉ (f), 9-C₁₄H₉ (g), have been synthesized, and α -diimine coordination to cationic methylpalladium complexes has been investigated in solution, by means of NMR spectroscopy, and in the solid state for [Pd(Me)(NCMe)((9-C₁₄H₉)₂DABMe₂)][PF₆] (2g). The performance of these catalysts in CO/vinyl arene



copolymerization, under mild conditions, was analyzed in terms of productivity and degree of stereoregularity of the resulting polyketones. In comparison with previous results, a remarkable enhancement in the yield of isotactic copolymer was observed using the new achiral 9-anthryl α -diimine ligand **g**, confirming that the ortho disubstitution and the extended aromatic rings play key roles in obtaining good stereoselectivity and good productivity. To perform a structural analysis of the first steps of the CO/*p*-methylstyrene copolymerization, complex [Pd(Me)(CO)((9-C₁₄H₉)₂DABMe₂)][BAr'₄] (**3g**) was used as a starting point: NMR investigation reveals the stereoselective formation of the olefin/CO/olefin insertion product (**6g**), which prevalently exists in solution in only one diastereoisomeric form, thus justifying the observed high polymer isotacticity.

1. INTRODUCTION

Late-transition-metal catalysts bearing nitrogen ligands have found applications in several polymerization reactions. Within these numerous kinds of complexes, palladium(II) catalysts containing ortho-substituted aryl diimines appear to be rather peculiar. Depending on the steric hindrance of the ortho substituents, they are excellent catalysts for homopolymerization of olefins¹ or quite good catalysts for the alternating copolymerization of aromatic olefins with carbon monoxide.² The latter is one of the best ways to efficiently synthesize polar functionalized polymers through a coordination-insertion mechanism.³ The resulting polyketone possesses valuable properties: mechanical and surface characteristics can be easily tuned, and the polymer chain can be postfunctionalized, due to the presence of the carbonyl group.⁴ These characteristics, together with the promising biocompatibility of produced materials,⁵ make the CO/olefin copolymerization still an attractive research field.⁶ Nevertheless, few examples of this process, using α -diimine catalysts, have been reported.² The key role played by the aryl-substituted α -diimine structure on the reactivity of the metal complex is well-known. In olefin polymerization, the presence of bulky nitrogen ligands is crucial for blocking the axial coordination sites on the metal toward incoming monomer, retarding the chain transfer.¹ Conversely, in CO/olefin copolymerization the presence of large ortho substituents on the aryl rings⁷ is critical in determining the stereoselectivity of the Pd(II) catalysts,^{2b-d} as observed by some of us during recent investigations on CO/vinyl arene copolymerization catalyzed by the complexes $[Pd(\eta^1, \eta^2 - C_8H_{12}OMe)((Ar)_2DABR_2)]X$ and $[Pd(Me)(NCMe)((Ar)_2DABR_2)]X$ bearing achiral α -diimine ligands $((Ar)_2 DABR_2 \equiv ArN = C(R)C(R) = NAr)$.^{2a-c,8} These catalysts are able to produce atactic or stereoblock isotactic CO/ *p*-methylstyrene copolymers, depending on the aryl substituents, through a "ligand assisted" chain-end control mechanism: both the ligand and the growing chain cooperate in selecting the enantioface and the direction of the incoming olefin during the copolymerization process.^{2d,8} This behavior is different from that observed with other achiral ligands ($C_{2\nu}$ or C_s symmetry), which generally produce highly syndiotactic polyketones due to

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chain-end control,⁹ while isotactic microstructures are commonly obtained with optically active C_2 -symmetric ligands that provide an enantiomorphic site-control propagation.¹⁰ The isotacticity strongly increases using bulky groups in the phenyl ortho positions and in the ligand backbone. From a DFT study it appears that the strong steric interactions between the substituents of the backbone and those in the phenyl ortho positions constrain the phenyl rings to arrange almost perpendicularly with respect to the palladium mean coordination plane and parallel to each other.⁸ Reasonably, this affects the coordination of the aromatic olefin and the stereochemistry of the resulting intermediate, inducing high enantioface discrimination and the consequent synthesis of isotactic copolymer. Unfortunately, moderate productivities are generally observed, due to the crowded coordination sites of the catalysts as well as to the low catalyst stability in the copolymerization medium. For example, the complex with the methyl substituents in phenyl ortho positions and in the ligand backbone (i.e., bearing the (2,6-Me₂Ph)₂DABMe₂ ligand) gives a copolymer characterized by a high degree of isotacticity (ll = 74%) but with a modest productivity (about 0.7 (g of CP)) $(g \text{ of } Pd)^{-1} h^{-1})$ in comparison with that of the atactic copolymer obtained using the $(4\text{-MeOPh})_2\text{DABMe}_2$ ligand (about 4 (g of CP) (g of Pd)⁻¹ h⁻¹).^{2d} With the main intention of improving the performance of stereoselective CO/vinyl arene copolymerization, our approach was to synthesize complexes in which the structure of the nitrogen ligand, especially its ability to shield the axial positions, allows the production of a stereoregular isotactic polymer without suppressing the catalyst activity. Ligands e-g, having two or three fused aromatic rings, were synthesized and the catalytic properties of the corresponding novel catalysts 2e-g were tested and compared with those of complexes 2a-d (Scheme 1). Structural analysis was performed

Scheme 1. Synthesis of Complexes 2a-g from 1a-g



for all compounds, as well as for the first intermediates of the stereoselective CO/p-methylstyrene copolymerization catalyzed by complex 2g.

2. RESULTS AND DISCUSSION

2.1. Synthesis and Characterization of Ligands f and g and Complexes 1e–g and 2a–g. Ligands $(1-C_{14}H_9)_2$ -DABMe₂ (f) and $(9-C_{14}H_9)_2$ DABMe₂ (g) were synthesized by condensation of 2,3-butanedione with $(1-C_{14}H_9)NH_2$ and $(9-C_{14}H_9)NH_2$, respectively; meanwhile ligand e was synthesized according to literature methods.¹¹ Recently the synthesis of a series of α -diimine ligands with substituted naphthyl groups has been reported.¹² Palladium(II) complexes 1e-g were obtained from the reaction of [Pd(Me)(Cl)(COD)] (COD = 1.5-cyclooctadiene) with the α -dimine ligands e-g, in dichloromethane at 25 °C (Scheme 1); the diene was substituted quantitatively by the nitrogen ligand within a few hours. Complexes 1a-g react with AgPF₆ at 0 °C in a CH₂Cl₂/MeCN (5/1, v/v) mixture, leading to the cationic acetonitrile compounds 2a-g with satisfactory to excellent yield (60-98%) (Scheme 1). Structures of all compounds were investigated in CD₂Cl₂ or CDCl₂ by ¹H and ¹³C NMR spectroscopy. The assignments of the ¹H and ¹³C resonances were performed by following the scalar and dipolar nuclear interactions in the ¹H-COSY, ¹H, ¹³C-HSQC, ¹H, ¹³C-HMBC, and ¹H-NOESY spectra (data are reported in the Experimental Section).

The comparative analysis of the chemical shifts of the Pd–Me protons in complexes 1a-g and 2a-g suggests that the shielding effect exerted by the π electrons of the 9-anthracenediimine ligand in 1g and 2g is more important than that of the other ligands (Table 1).

Table 1. Chemical Shift Values (CDCl₃, 19 °C) of the Pd-Me Resonance in Complexes $Pd(Me)Cl((Ar)_2DABMe_2)$ (1a-g) and $[Pd(Me)(NCMe)((Ar)_2DABMe_2)]^+[PF_6]^-$ (2a-g)

Ar	complex 1a–g	δ (ppm)	complex 2a-g	δ (ppm)
Ph	1a	0.63	2a	0.41
4-MeOPh	1b	0.65	2b	0.47
2,6-Me ₂ Ph	1c	0.44	2c	0.29
2,6- <i>i</i> Pr ₂ Ph	1d	0.36	2d	0.42
$1 - C_{10}H_7$	1e	0.46	2e	0.18, 0.19 ^a
$1 - C_{14}H_9$	1f	0.31	2f	0.07, 0.12 ^a
$9-C_{14}H_9$	1g	0.05	2g	-0.03

^{*a*}Two resonances are detected due to the presence in solution of two conformational isomers (vide infra).

A plausible explanation could be found in the larger size of the aromatic portion of ligand g, in comparison to a-e, and in the symmetric placement of the aromatic rings above and below the coordination plane in complexes 1g and 2g, differently from what occurs in 1e,f and 2e,f. The almost perpendicular orientation of the aromatic rings with respect to the coordination plane (see the X-ray structure of 2g; Figure 2) favors the observed upfield shift. For complexes 1e,f and 2e,f, the NMR investigations indicated that the two possible conformational diastereoisomers in which the nitrogen ligand adopts a C_2 - or a C_s -symmetric coordination geometry (Scheme 2: *a* and *b*, C_2 -conformational enantiomers; c and d, C_s -conformational enantiomers), are simultaneously present in CD₂Cl₂ (and CDCl₃) solution at 19 °C, with an approximate equimolar ratio. This finding agrees well with previously reported theoretical results for the $[PdCl_2(Ar-BIAN)]$ complex¹³ (Ar-BIAN = bis(1-naphthylimino)acenaphthene), where the syn and anti isomers are almost isoenergetic. Besides ab initio calculations performed on the e and f nitrogen ligands (Scheme 1) show that the syn and anti conformers differ by a maximum of ca. 1 kcal mol⁻¹, the anti isomer being more stable than the corresponding syn isomer, as expected.^{12,13}

The presence (in solution) of both C_2 and C_s conformational isomers generates split signals in both the ¹H and ¹³C NMR

Scheme 2. C₂ and C_s Conformational Isomers of Complex 2e



spectra of complexes **1e**,**f** and **2e**,**f**. For instance, two defined doublets for the H5 resonance are present in the ¹H spectrum of **2e**, centered at 8.25 and 8.17 ppm (CDCl₃, 19 °C, ²J_{HH} = 8.2 Hz), corresponding to two carbon signals at 123.8 and 123.4 ppm. Analogously, two singlets are observed at 0.18 and 0.19 ppm attributable to the Pd–Me protons of the two isomers, which correspond to two ¹³C resonances at 4.43 and 4.37 ppm. Unfortunately, the overlapping of many resonances precludes the unambiguous assignment of all signals.

2.2. CO/Vinyl Arene Copolymerization. Complexes 2a-g were tested as catalysts in the copolymerization of CO with *p*-methylstyrene (Table 2) or styrene (Table 4); reactions were carried out for 27 h at room temperature (26 °C), under 1 atm pressure of CO, in dichloromethane or TFE (TFE = 2,2,2-trifluoroethanol) (Scheme 3, Tables 2 and 4).



Table 2. CO/p-Methylstyrene Copolymerization Results^a

From Table 2 it appears that in CH₂Cl₂ the productivity in CO/p-methylstyrene copolymer tends to diminish with an increase in the size of the substituents in the ortho positions of the aromatic rings of the ligand, in fact passing from catalysts 2a,b, in which the productivity is around 100 (g of CP) (g of Pd)⁻¹ (Table 2, entries 1 and 2), to the hemihindered 2e,f (83 and 58 (g of CP) (g of Pd)⁻¹; Table 2, entries 7 and 9) and the hindered 2c,d (52 and 0 (g of CP) (g of Pd)⁻¹; Table 2, entries 3 and 6), a reduction in yields was observed. The only catalyst that does not follow this trend is 2g, which, although it has encumbered apical positions, is the most active, producing 130 (g of CP) (g of Pd)⁻¹ (Table 2, entry 10). An increase in CO pressure up to 5 bar results in a decrease of productivity together with a significant increase of M_w (weight-average molecular weight) (Table 2, entry 10 vs entry 12). Formation of inactive palladium metal was generally observed at the end of the reaction (2a-c,f); meanwhile, with catalyst 2e it was possible to prolong the reaction time up to 51 h, obtaining a yield of 296 (g of CP) (g of Pd)⁻¹ (Table 2, entry 8). With styrene as comonomer instead of *p*-methylstyrene an increase in yield and M_w was achieved (see Table 4, entry 1, vs Table 2, entry 10). In addition, considering that the capacity of the TFE as solvent and BQ (1,4-benzoquinone) as oxidant was previously observed to increase the yield of the CO/styrene copolymerization catalyzed by analogous Pd complexes,^{2t} reactions with catalysts 2c,e-g were also carried out in TFE plus BQ. A beneficial effect was observed in all cases, and mainly isotactic copolymer (vide infra) was produced. In particular with catalysts 2g,c the yield in p-methylstyrene/CO copolymer was more than doubled in TFE and BQ in comparison to that in methylene chloride (Table 2, entry 10 vs entry 11 and entry 3 vs entry 5). Combining the use of styrene as comonomer and TFE as solvent plus BQ, a sharp increase in productivity was recorded with catalysts 2e-g, giving up to 564 (g of CP) (g of Pd)⁻¹ (Table 4, entry 3). In agreement with the literature, the productivity is affected by four main factors: the structure of the nitrogen ligand and therefore of the catalyst, the kind of olefin comonomer, the nature of the reaction solvent, and the presence of the oxidant.

The influence of the catalyst structure on the productivity $((g \text{ of } CP) (g \text{ of } Pd)^{-1})$ is evident from the trend found in

						triad $(\%)^c$			
entry	cat.	yield $(g)^b$	CP (%)	productivity ((g of CP) (g of Pd) ^{-1})	11	ul/lu	ии	n_l	$10^{-3}M_{\rm w} \ ({\rm PDI})^d$
1	2a	0.480	78	101	30	49	21	2.2	7.5 (1.9)
2	2b	0.450	94	114	25	53	22	2.0	10.5 (1.8)
3	2c	0.200	96	52	71	26	3	6.5	9.2 (1.3)
4^e	2c	0.355	96	91	69	29	2	5.8	15.4 (1.2)
5^{f}	2c	0.535	87	125	71	26	3	6.5	6.6 (1.6)
6	2d	0.096	<1						
7	2e	0.448	69	83	53	37	10	3.9	4.4 (1.6)
8^g	2e	1.160	95	296	51	41	8	3.5	18.0 (3.2)
9	2f	0.221	97	58	45	44	11	3.1	10.5 (1.4)
10	2g	0.495	>99	130	71	25	4	6.7	16.7 (1.2)
11^{f}	2g	1.080	>99	290	72	25	3	6.8	8.5 (1.6)
12^{h}	2g	0.608	60	98	73	23	4	7.4	27.6 (1.8)

^{*a*}Reaction conditions: $n_{Pd} = 0.035$ mmol; volume of *p*-methylstyrene 2.8 mL (21 mmol, Pd/olefin = 1/600); solvent CH₂Cl₂ (2.8 mL); T = 26 °C; $P_{CO} = 1$ atm; t = 27 h. ^{*b*}Total yield of homopolymer (HP) and copolymer (CP). ^{*c*}Evaluated from the intensities of the ¹³C NMR ipso carbon atom resonances. ^{*d*}PDI = M_w/M_n . ^{*c*}Solvent 2,2,2-trifluoroethanol. ^{*f*}Solvent 2,2,2-trifluoroethanol (2.8 mL); Pd/1,4-benzoquinone = 1/5. ^{*g*}t = 51 h. ^{*h*} $P_{CO} = 5$ atm.

CH₂Cl₂: **2g** (130) > **2b** (114) > **2a** (101) > **2e** (83) > **2f** (58) > **2c** (52) > **2d** (0) (Table 2, entries 10, 2, 1, 7, 9, 3, and 6, respectively), which seems related to the pK_a values of the anilines employed in the synthesis of the corresponding ligands (except for **2d**) (Table 3).¹⁴

Table 3. Relationship between the pK_a Values of the Anilines and the Productivities of the Corresponding Complexes 2a-g

entry	aniline	pK _a	cat.	productivity ((g of CP) (g of Pd) ⁻¹)
1	$9-C_{14}H_9NH_2$	6.34 ^{15a}	2g	130
2	4-MeOC ₆ H ₄ NH ₂	5.29 ^{14a,15b}	2b	114
3	$C_6H_5NH_2$	4.58 ^{14a,15b}	2a	101
4	$1-C_{10}H_7$	4.11 ^{15c}	2e	83
5	$1-C_{14}H_9NH_2$	3.85 ^{15a}	2f	58
6	2,6-Me ₂ C ₆ H ₃ NH ₂	3.89 ^{15b}	2c	52
7	$2,6\text{-}i\mathrm{Pr}_{2}\mathrm{C}_{6}\mathrm{H}_{3}\mathrm{NH}_{2}$	4.41 ^{14a}	2d	0

In fact, on analyzing the pK_a value of anilines (Table 3),^{14b,15} it appears that when the basicity of the anilines, and accordingly the coordination ability of the ligands is decreased,¹⁴ the productivity of the corresponding catalysts diminishes (Table 3), possibly due to a higher decomposition rate. Thus, the productivity seems to be governed mainly by the catalyst stability, which correlates with the binding strength of the ligand.

Therefore, catalyst **2g** is the most active probably because of the high basicity of the anthryl ligand, which tends to stabilize the complex, dramatically reducing the deactivation rate. However, a stabilizing effect deriving from a π stacking interaction between the three condensed aromatic rings of **2g** and the styrene in the olefin insertion transition state cannot be ruled out (vide infra). Conversely, the steric hindrance at the ortho position, together with a lower basicity, causes a decrease of the productivity of the process involving **2e**,**f**,**c** (see Table 2, entries 7, 9 and 3). The steric effect is remarkable especially in the reaction with complex **2d**, which, despite a basicity almost comparable to that of **2a** for the corresponding anilines (4.41 vs 4.58), is not productive. In this case probably the isopropyl groups block the copolymerization due to a difficult access of monomers to the catalytic center (Table 2, entry 6).¹⁴

Concerning the effect of the solvent on the productivity, while in dichloromethane catalysts 2a-g show a different performance, depending on the electronic and steric features, in TFE catalysts 2e-g, with fused aromatic rings, have similar rather high activities, reaching a plateau of productivity at about 500 (g of CP) (g of Pd)⁻¹ (Table 4). We attribute this behavior to a stabilizing effect of the TFE solvent that prolongs the life of the catalysts 2e-g in the reaction medium. This extra stabilization was previously ascribed to the higher acidity of the

fluorinated alcohol;¹⁶ however, a coordination of the CF₃ moiety of the alcohol to the metal center might play a role in the stabilization process of the catalyst, as highlighted by the X-ray structures of **4g**,**c** (vide infra). Regarding the effect of the monomer, a greater productivity of styrene in comparison to that of *p*-methylstyrene either in CH₂Cl₂ (130 and 142 (g of CP) (g of Pd)⁻¹; Table 2, entry 10, vs Table 4, entry 1) and in TFE (290 and 495 (g of CP) (g of Pd)⁻¹; Table 2, entry 10, vs Table 4, entry 11, vs Table 4, entry 2) was found, similarly to what was observed with palladium catalysts bearing meta-substituted aryl-BIAN ligands.^{2f} This might be linked to an easier complexation of styrene versus *p*-methylstyrene due to a higher π^* acidity of the former compound.

In general, moderate to good results in terms of M_w (weightaverage molecular weight) and polydispersity were achieved; M_w ranges from 4400 with catalyst **2e** (Table 2, entry 7) to 35000 for catalyst **2f** in TFE (Table 4, entry 4). We can identify different responses of M_w with the variation of the reaction conditions: for example, with TFE as the reaction medium an increase of M_w was detected (Table 2, compare entries 3 and 4), meanwhile the presence of benzoquinone gives a decrease of M_w and an increase of polydispersity (Table 2, entry 4 vs entry 5).^{16a,e} Although an increase of CO pressure has a beneficial effect on the M_w of the polymer, we could record a detrimental effect regarding the polydispersity (Table 2, compare entries 12 and 10).

2.3. Copolymer Stereochemistry. The polyketones were characterized by means of ¹H NMR (CDCl₃) and ¹³C NMR spectroscopy (1,1,1,3,3,3-hexafluoro-2-propanol/CDCl₃ 1/1 (v/v), 298 K), and their tacticity was evaluated by integrating the ¹³C NMR resonances corresponding to the ipso carbon atoms of the aryl groups. The microstructures of copolymers range from atactic to isotactic even if achiral $C_{2\nu}$ or C_s nitrogen ligands generally produce syndiotactic polyketones. Catalysts 2a (Ar = Ph) and 2b (Ar = 4-MeOPh) afforded regioregular p-methylstyrene/CO polyketones with an atactic microstructure^{2a-c} (Table 2, entries 1 and 2), while a slight prevalence of the *ll* triad is observed for the copolymers produced by the hemihindered complexes 2e (Ar = $1-C_{10}H_7$) and 2f $(Ar = 1-C_{14}H_9)$ (53% and 45% *ll*, Table 2, entries 7 and 9). A remarkable increment of the isotactic component was instead observed using complexes 2c (Ar = 2,6-MePh)^{2a,c,d} and 2g $(Ar = 9-C_{14}H_9)$, which produced a copolymer with a value for the *ll* triad of 71% (Table 2, entries 3 and 10), in line with the highest value found in previous work.^{2c} Similarly, with styrene as comonomer, prevailingly isotactic copolymer was obtained with 2e (43% *ll*, Table 4, entry 3) and 2f (46% *ll*, Table 4, entry 3), while **2g** (Ar = $9 - C_{14}H_9$) gave an isotactic polyketone with an *ll* value of 73% (Table 4, entry 2). As a result, stereoregularity is mainly dictated by the catalyst regardless of the nature of comonomer, solvent, and reaction conditions. As triad distribution points out¹⁷ (ll = 73%, ul/lu = 25%, uu = 2%)

Table 4.	CO/Styrene	Copolymerization	Results "

					triad (%) ^c				
entry	cat.	yield $(g)^b$	CP (%)	productivity ((g of CP) (g of Pd) ^{-1})	11	ul/lu	ии	n_l	$10^{-3}M_{\rm w}~({\rm PDI})^d$
1^e	2g	0.530	>99	142	71	26	3	7.2	25.7 (1.2)
2	2g	1.846	>99	495	73	25	2	6.8	10.0 (1.5)
3	2e	2.100	>99	564	43	47	10	2.8	12.0 (2.0)
4	2f	1.757	>99	472	46	46	8	3.0	35.9 (1.4)

^{*a*}Reaction conditions: $n_{Pd} = 0.035$ mmol; volume of styrene 2.6 mL (21 mmol, Pd/olefin = 1/600); solvent 2,2,2-trifluoroethanol (2.8 mL); Pd/1,4-benzoquinone = 1/5; T = 26 °C; $P_{CO} = 1$ atm; t = 27 h. ^{*b*}Total yield of homopolymer (HP) and copolymer (CP). ^{*c*}Evaluated from the intensities of the ¹³C NMR ipso carbon atom resonances. ^{*d*}PDI = M_w/M_n . ^{*e*}Solvent CH₂Cl₂, without 1,4-benzoquinone.

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(Table 4 entry 2) and due to the achiral nature of the catalyst, junctions of the type ...RRRSSS... (...SSSRRR...) must be present along the polymer chains. As previously reported for 2c, a ligand-assisted chain-end control mechanism should be responsible for the production of isotactic copolymer with 2g.8 Using the relationship $n_l = 1 + 2(ll)/(lu)$,¹⁸ which takes into account the intensities of the isotactic (ll) and heterotactic (ul)triads, it was possible to calculate the average length of the isotactic sequences n_{l_1} assuming a Bernoulli propagation model, commonly observed for copolymers obtained with these kinds of Pd-complexes. The stereoblock length with catalysts 2c,g was around 7 (n_1) , while with the hemihindered complexes this value was about 3.5 (Tables 2 and 4). The strong steric interactions between the methyl groups of the DAB backbone and the groups in the phenyl ortho positions constrain the phenyl rings to arrange almost perpendicularly with respect to the palladium mean coordination plane (vide infra).8 This catalyst geometry, together with the conformation of the growing polymer chain, is able to select the same olefin enantioface within each stereoblock, producing isotactic copolymer. Since catalyst 2g gives, in term of stereoregularity, results similar to those for 2c, we attribute this behavior to an analogous disposition of the N-aryl rings. In this regard, the two model complexes 5g',c',¹⁹ intermediates of the copolymerization process,^{2d,8} appear similarly hindered in the region close to the metal reaction center, as shown by their van der Waals surfaces, depicted in Figure 1.



Figure 1. van der Waals surfaces of the carbonylated species 5g' (left, red) and 5c' (right, blue).

Finally, the next intermediate, having a structure similar to that of 5g' but with the styrene in place of CO,^{2d,8} was analyzed by rigid potential energy surface scans performed along both the N–Ar bonds (for details, see Computational Methods in the Experimental Section). A comparative analysis, performed for all analogous complexes with ligands **a**, **c**, **f**, and **g**, shows that the 9-anthryl derivative is by far the most rigid.

In conclusion, introducing a new set of achiral diaryl diazabutadiene ligands with extended fused aromatic rings, we have optimized the copolymerization reaction under different conditions, achieving good results in terms of copolymer productivity, stereoregularity, and M_w . In particular, in chlorinated solvent we obtained good productivity, up to 130 (g of CP) (g of Pd)⁻¹ of stereoblock isotactic CO/*p*-methylstyrene polyketone, with a tacticity of 71%, $M_w = 16700$, and good polydispersity (1.2); meanwhile, by using fluorinated ethanol we attained excellent productivity, up to 500 (g of CP) (g of Pd)⁻¹ of CO/styrene copolymer with a tacticity of 73% ($n_l = 7$), $M_w = 10000$, and good polydispersity (1.5).

2.4. Mechanistic Studies: Synthesis and Characterization of Complexes 3g-6g. Initial steps of the copolymerization reaction were investigated to understand how the steric arrangement of the catalyst, bearing the achiral α -diimine g, is able to determine the stereoselective insertion of the olefin (Scheme 4). For this purpose, complex 3g was used,

Scheme 4. First Intermediates of Copolymerization Reaction $\!\!\!\!\!\!^a$



^{*a*}For clarity 1,1′-methyls are not depicted in complexes **4g**–**6g**.

since it was previously observed that methyl acetonitrile Pd complexes with α -diimine ligands led, under a CO atmosphere,

to the corresponding methyl carbonyl derivatives that are the real catalytic initiators (Scheme 4).²⁰ In addition, the less coordinating tetraarylborate counterion was chosen to favor alkene insertion in the stoichiometric reactions.

The insertion of *p*-methylstyrene in the Pd–acetyl bond, derived from the methyl migration in **3g**, leads to complex **4g**, having the *p*-methylstyrene unit coordinated in an η^3 -allyl fashion. Complex **4g** shows chemical shift values typical of allyl systems (C22–C22', 107.2 ppm; C20, 54.8 ppm; H20, 2.73 ppm (CDCl₃, 4 °C)) and a considerable shielding of the H19a and H19b resonances (0.29 and 1.58 ppm, respectively) due to the anisotropy effects of the aryl rings of the nitrogen ligand. The NMR characterization in CDCl₃ allowed the determination of the intramolecular structure of **4g** (Scheme 4). The assignment of the ¹H resonances of the allyl fragment of **4g** was made on the basis of the dipolar and scalar interactions detected in the ¹H-NOESY and ¹H-COSY spectra, respectively, and confirmed with previous reported studies^{2d} (see section 4.5.2 in the Experimental Section).

A comparative analysis between the ¹H NMR spectra of 4g and 4c was made. Interestingly the upfield shift of several ¹H resonances of the allyl fragment in 4g was more pronounced than that observed for the analogous α -diimine complex $[Pd(\eta^3-C_{11}H_{13}O)((2,6-MePh)_2DABMe_2)]^+[BAr'_4]^-$ (4c) bearing the 2,6-dimethyl-substituted phenyl ring^{2d} (Table 5).

Table 5. Chemical Shifts (¹H NMR, δ ppm) of the Growing Chain in the Intermediate Complexes 4g,c^{2d} and 5g,c^{2d}

	complex 4g ^a	$\operatorname{complex}_{4\mathbf{c}^a}$	$\Delta\delta$	complex 5g ^b	complex 5c ^c	$\Delta\delta$
H25	0.92	1.79	0.87	2.06	2.22	0.16
H23/H23'	5.80	6.54	0.74	6.91	7.14	0.23
H22/H22'	6.11	6.33	0.22	6.77	7.01	0.24
H20	2.8	3.17	0.37	3.92	4.20	0.28
H19a	0.30	1.12	0.82	0.62	1.67	1.05
H19b	1.63	2.31	0.68	2.23	2.72	0.49
H17	1.33	1.89	0.56	1.61	1.92	0.31
^{<i>a</i>} Conditions ^{<i>c</i>} Conditions:	: CDCl ₃ , CDCl ₃ , 20	4 °C.) °C.	^b Condi	tions: CI	$D_2Cl_2, -17$	′ °C.

This could be reasonably ascribed to the larger size of the magnetic anisotropy shielding cone on top of the anthryl moiety in 4g in comparison to the phenyl ring in 4c. As a consequence, for example, the H23/H23' resonances are observed at 6.54 ppm in 4c and at 5.80 ppm in 4g, and protons H22/H22' are found at 6.33 ppm in 4c and 6.11 ppm in 4g. As expected, the value $\Delta\delta$ decreases on going from H25 to H23/H23' and then to H22/H22' (Scheme 4): i.e., from the external side of the nitrogen ligand toward the palladium center, moving away from the shielding cone of the anthracene ring. The same occurs on going from H19a, H19b to H20. These ¹H NMR upfield shifts of 4g relative to the signals for 4c could point toward a greater π stacking interaction in the former between the η^3 -allylc moiety and the N-aryl counterpart.²¹ A π stacking interaction, between the rings of the ligand and the styrene unit, could be present also in the olefin insertion transition states relative to intermediates 4g and 6g, producing the stabilization needed for the productivity of 2g being greater than that of 2c.

The next step of the copolymerization process was investigated by bubbling carbon monoxide into a CD_2Cl_2 solution of 4g for 10 min at -70 °C. The NMR analysis

reveals the formation of an equilibrium mixture between the starting species 4g and the corresponding carbonylated product 5g (Scheme 4). The equilibrium ratio appears to be affected by the temperature, and the maximum conversion in 5g (60%) was observed at -17 °C after 3 days under an atmospheric pressure of CO. From the NMR analysis of 5g (for details, see section 4.5.3 in the Experimental Section) some similarities with 4g can be recognized. ¹H signals of protons H19a, H19b and H20 (0.62, 2.23, and 3.92 ppm, respectively) appear strongly shielded in comparison with those of the analogous complex bearing the (iPr)₂DABMe₂ ligand (2.67, 3.50, and 4.54 ppm, respectively).^{20a} This suggests that they are located in the shielding cone of the aromatic rings of the N-anthryl ligand. Furthermore, since the ¹³C resonance of C18 in 5g (202.7 ppm) is notably different from the typical value reported for a palladium O-coordinated acetyl moiety (around 230 ppm),^{10b,20,22} a sixmembered chelate structure (with the acetyl linked to palladium²³) was ruled out. In addition, both the NOE interactions involving the growing chain and the nitrogen ligand and the strong shielding effect observed for H19a, H19b and H20 give evidence in favor of the open-chain structure of complex 5g (Scheme 4). The structure of 5g in solution, depicted according to the NMR evidence, is in agreement with the fully optimized $5g'^{19}$ model (Figure 1) with the DFT method (see Computational Methods in the Experimental Section). Finally, the upfield shift of the ¹H resonances of the acetyl fragment in 5g is more pronounced than that observed for the analogous α -diimine complex $[Pd{C(O)CH(p-Me-C_6H_4)CH_2C(O)Me}((2,6-Me_2Ph)_2DABMe_2)]^+[BAr'_4]^-$ (**5**c) bearing the 2,6-dimethyl-substituted phenyl ring^{2d} (Table 5).

The addition of *p*-methylstyrene to the equilibrium mixture of 4g and 5g (40/60) in CD_2Cl_2 under 1 atm of carbon monoxide leads to the formation of the allyl intermediate 6g as the major product (NMR yield 74%) (Scheme 4). NMR investigation reveals that 6g exists prevalently as a single diastereoisomeric form that should correspond to a RR (or SS) configuration, considering the isotacticity of the copolymer obtained with the precatalyst 2g (Scheme 1). Similarly to 4g, in **6g** the growing chain is coordinated in an η^3 -allyl fashion involving one double bond of the aryl ring of the second inserted olefin (Scheme 4). For analogous complexes bearing the $(2,6-Me_2Ph)_2DABMe_2$ ligand c, a 25/75 mixture of the two η^3 -allyl complexes 4c and 6c was obtained instead.^{2d} This different behavior outlines that the reaction performed with catalyst 2g is much more efficient than that performed with 2c and the process is efficiently driven toward the insertion of the new styrene unit. The analysis of the ¹H-NOESY spectrum of 6g (see section 4.5.4 in the Experimental Section) depicts the molecular structure illustrated in Scheme 4; moreover, due to the presence of an aromatic ring in the growing chain H10, H8, and H12 resonances were quite shielded in 6g (Table S3 in the Supporting Information).

As a result of the magnetic anisotropy shielding cone in **6g**, we suppose the presence of π stacking interactions that stabilize the **6g**-like intermediates, increasing their population.²¹ In addition, a π stacking interaction could be responsible for lowering the energy transition of the olefin insertion reaction, driving the copolymerization process toward higher productivity.²¹

2.5. Solid-State Molecular Structures of Complexes 2g and 4g. The solid-state structure was obtained, by means of X-ray single-crystal studies, for catalyst **2g** and remarkably for intermediate **4g**, which proved to be stable enough to obtain crystals. The molecular structure of the catalyst **2g** is shown in



Figure 2. ORTEP 3 views of the complex cation of 2g (top left), the relative cation-anion positions in 2g (top right), and the complex cation of 4g (bottom center). Hydrogen atoms have been omitted for sake of clarity. All atoms are drawn at 30% probability.

Figure 2 (selected bond lengths and angles are given in Table S2 in the Supporting Information).

The metal center adopts the usual square-planar coordination. Bond lengths and angles featuring the metal environment are in line with those of structural related complexes retrieved in the Cambridge Structural Database (CSD version 5.34, November 2012).²⁴

Because of their size and due to the presence of the methyl groups on the back, both anthracene units are almost perpendicular with respect to the metal coordination mean plane (dihedral angles of 75.7(1) and 86.5(1)°). As a consequence of this arrangement, the four anthryl hydrogen atoms in 1- and 8- positions are facing each other, thus preventing the counterion from locating near the metal center. In fact, the closest counterion,²⁵ as already found in the crystal lattice of similar catalysts,^{2c,26} is located in the back, above the diimine carbons of the nitrogen ligand (Figure 2), and weakly interacts with the aromatic hydrogen atoms of the ligand. Interestingly the interionic structure of 2g closely resembles that found in a similar dimethyl ortho-substituted aryl α -diimine complex.^{2c} The horizontal distance between the Pd atom and the intercept of the vertical distance which separates the P atom from the metal coordination mean plane²⁷ are roughly the same: 4.639(2) vs 4.723 Å (compare 2g with 7a in ref 2c), while in 2g the PF_6^- ion is slightly higher with respect to the metal coordination mean plane (4.226(2) vs 3.994 Å). Finally, the next closest PF_6^- ion (related by the symmetry operation -x + 1, $y - \frac{1}{2} - z + \frac{1}{2}$) is also shown in Figure 2, together with selected distances involving the phosphorus atoms in order to determine the position of both the anions with respect to the metal complex.²

The similarity between the interionic structures discussed above (**2g** vs **7a** in ref 2c) suggests that the anthracene units and the *o*-dimethylphenyl moieties cause comparable steric hindrance in the metal apical positions. As a consequence, for **2g,c** a similar accessibility of the carbonyl moiety and then of the monomers to the metal apical position should be expected. Thus, the steric features of **2g** must be balanced by the already mentioned high basicity of the corresponding diimine ligand and/or by a possible π stacking interaction between the aromatic ring of the growing chain and the anthracene ligand;²¹ both effects could significantly trigger and enhance the productivity.

In the complex cation of intermediate 4g, the palladium ion is coordinated to the *p*-methylstyrene unit in a η^3 -allyl fashion, involving the C(1a) (C(1b)), C(2a) (C(2b)), and C(8a) (C(8b)) atoms (Figure 2). For the *p*-methylstyrene unit, which appears disordered except for the acetyl group, the two models **a** and **b** were found. The least-squares planes defined by the atoms of **a** and **b** are nearly coplanar. The three Pd-C bond distances are significantly different in model **a**, while in **b** they are comparable (Table S2 in the Supporting Information). The resulting coordination geometry about the metal ion can be conveniently described as distorted square planar (Table S2).

The four donor atoms (N(1), N(2), C(2a) (C(2b)) and C(8a) (C(8b))) define a mean plane which is almost perpendicular both to the anthracene units (about 65 and 75° for models **a** and **b**, respectively) and to the *p*-methylstyrene unit (79.4(2) and 76.8(2)° for **a** and **b**, respectively) (Figure 2). A comparison with structurally related complexes deposited in the CSD does not reveal any peculiar geometrical feature for

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Figure 3. (left) Shape match between the cation and anion in the crystal lattice of 4g. (right) Closest cation-anion interaction in the crystal lattice of 4c.

the palladium complex. As shown in Figure 3, a good shape match between the two ions occurs in the crystal lattice: the closest BArF anion places a fluorine atom in the metal apical position 3.646(3) Å from the palladium cation. A longer Pd–F distance (ca. 4.0 Å) was found in the crystal structure of the analogous complex having the *o*-dimethyl substituted ligand **4c** (Figure 3, right).^{2d} The unexpectedly short Pd–F distance in **4g** could indicate the presence of an interaction between the palladium and the fluoro atom that stabilizes the crystal lattice (Figure 3). A similar contact might occur between palladium complexes and the fluorinated alcohol in the copolymerization reaction carried out in TFE. In particular, we suppose that a Pd–F interaction might contribute to the catalyst stability, in combination with the acidity of the alcohol,¹⁶ increasing the productivity in polyketones.¹⁶

To validate this hypothesis, a copolymerization reaction with catalyst **2g** was performed using α, α, α -trifluorotoluene as solvent, giving a copolymer yield of 423 (g of CP) (g of Pd)⁻¹, $M_w = 24000$ and a value for the *ll* triad of 75%; these data are comparable to those achieved carrying out the reaction in TFE (Table 4, entry 2).

3. CONCLUSION

In this paper we have shown the synthesis and coordination chemistry of a series of cationic Pd(II) complexes, bearing new α -diimine ligands with fused aromatic rings, and their application in CO/vinyl arene copolymerization. Among all species, the catalyst with the $C_{2\nu}$ -symmetric 9-anthracenyl diimine ligand $(9-C_{14}H_9)_2$ DABMe₂ (g) provides stereoblock isotactic CO/p-methylstyrene and CO/styrene polyketones in yields that are the highest reported for the stereoselective copolymerization of aromatic olefins with carbon monoxide using achiral nitrogen ligands. The structural analysis of the first steps of the CO/p-methylstyrene copolymerization revealed the stereoselective formation of the olefin/CO/olefin insertion product (6g), which prevalently exists in solution in only one diastereoisomeric form, thus justifying the observed high polymer isotacticity provided by complex 2g. Moreover, both analyzing the copolymerization results and the structure of the first intermediates, we postulated that the donor capacity of the ligand, a possible π stacking interaction in the olefin insertion

transition states, and fluoro—palladium interactions between catalyst and fluorinated alcohol, in combination with the alcohol acidity, could reasonably be the origin for the high productivity found with the new 9-anthryl catalyst.

4. EXPERIMENTAL SECTION

4.1. Materials and Methods. All manipulations were carried out under a nitrogen atmosphere by using Schlenk techniques. Solvents were dried by standard methods and freshly distilled under nitrogen. p-Methylstyrene (Aldrich) was dried over calcium hydride and distilled before use. Carbon monoxide (Cp grade 99.99%) was supplied by Air Liquide. CP grade chemicals were used as received unless otherwise stated. Chloroform-d and methylene chloride- d_2 were degassed and stored over 4 Å molecular sieves. Ligands $a-d^{28}$ and complexes 1a-c,^{1,2d,29} 1d,³⁰ and 2b, c^{2d} were synthesized according to literature methods. NaBAr'₄ (Ar' = $3,5-(CF_3)_2C_6H_3$) was synthesized as previously reported. 31 Elemental analyses (C, H, N) were carried out with a Fisons Instruments 1108 CHNS-O Elemental Analyzer. Infrared spectra were measured in the range 4000-600 cm⁻¹ on a Nicolet FT-IR Avatar 360 spectrometer. NMR spectra were measured on a Bruker Advance 200 spectrometer with a multinuclear 5 mm probe head. ¹H and ¹³C NMR chemical shifts are relative to TMS and were measured using the residual proton or carbon resonance of the deuterated solvents.

4.2. Synthesis of Ligands e-g. 4.2.1. Synthesis of (N,N'E,N,N'E)-N,N'-(Butane-2,3-diylidene)dinaphthalen-1-amine (e).



Ligand e was synthesized according to literature methods.¹² ¹H NMR (200.13 MHz, CDCl₃, 19 °C): δ 7.86 (m, 4H; H8 and H5), 7.68 (d, ³J_{H,H} = 8.28 Hz, 2H; H10), 7.52 (m, 6H; H6, H7 and H11), 6.87 (d, 2H; H12), 2.33 ppm (s, 6H; H1). ¹³C NMR (50.32 MHz, CDCl₃, 19 °C): δ 169.1 (s; C2), 147.0 (s; C3), 134.1 (s; C9), 128.1 (s; C8), 126.3 (s; C7), 125.8 (s; C11), 125.7 (s; C6), 125.5 (s; C4), 124.1 (s; C10), 123.4 (s; C5), 113.0 (s, C12), 16.0 ppm (s; C1). Anal. Calcd for C₂₄H₂₀N₂ (336.43): C, 85.68; H, 5.99; N, 8.33. Found: C, 85.73; H, 5.92; N, 8.37.

4.2.2. Synthesis of (N,N'E,N,N'E)-N,N'-(Butane-2,3-diylidene)dianthracen-1-amine (f).



2,3-Butanedione (114 μ L, 1.30 mmol) and 1 drop of formic acid were added to a solution of $(1\text{-}C_{14}H_9)NH_2$ (510 mg, 2.64 mmol) in methanol (6 mL), and the mixture was stirred for 48 h at 25 °C. The formed precipitate was collected by filtration, washed with methanol (2 \times 10 mL), and dried under vacuum. The product was than solubilized in hot toluene (10 mL), precipitated with cold methanol, collected by filtration, washed with methanol $(2 \times 10 \text{ mL})$, and dried under vacuum. Ligand f was obtained as a brown powder (320 mg, 0.73 mmol; yield 56%). ¹H NMR (200.13 MHz, CD₂Cl₂, 19 °C): δ 8.53 (s, 2H; H12), 8.47 (s, 2H; H5), 8.08 (m, 4H; H10 and H7), 7.89 (d, ${}^{3}J_{H,H}$ = 7.2 Hz, 2H; H14), 7.55 (m, 6H; H15, H8 and H9), 6.89 (br d, 2H; H16), 2.45 ppm (s, 6H; H1). ¹³C NMR (50.32 MHz, CD₂Cl₂, 19 °C): δ 169.4 (s; C2), 147.1 (s; C3), 132.3 (s; C6 or C11 or C13), 131.9 (s; C6 or C11 or C13), 131.4 (s; C6 or C11 or C13), 128.4 (s; C7 or C10), 128.0 (s; C7 or C10), 126.3 (s; C12), 125.7 (s; C8 or C9), 125.5 (s; C8 or C9), 125.3 (s; C15), 125.0 (s; C4), 124.3 (s; C14), 122.2 (s, C5), 111.4 (s; C16), 15.8 ppm (s; C1). Anal. Calcd for C32H24N2 (436.55): C, 88.04; H, 5.54; N, 6.42. Found: C, 88.09; H, 5.50; N, 6.47.

4.2.3. Synthesis of (N,N'E,N,N'E)-N,N'-(Butane-2,3-diylidene)dianthracen-9-amine (g).



9-Aminoanthracene $(9-C_{14}H_9)NH_2$ was synthesized as follows: palladium on charcoal (10%, 30 mg) was added to a solution of 9-nitroanthracene (300 mg, 1.34 mmol) in ethyl acetate (15 mL). The reaction mixture was transferred into a steel autoclave which was charged with H₂ (3 atm) and stirred for 5.5 h at 20 °C. The mixture was then filtered under a nitrogen atmosphere, and the solvent was evaporated under vacuum. 9-Aminoanthracene was obtained as a yellow powder (242 mg, 1.25 mmol; yield 94%). ¹H NMR (200.13 MHz, CDCl₃, 19 °C): δ 7.98–7.90, 7.47–7.40 (m, 9H; aromatic protons), 4.87 ppm (br s, 2H; NH₂). Ligand g was synthesized as follows: 2,3-butanedione (85 μ L, 0.97 mmol) and 1 drop of formic acid were added to a solution of (9-C₁₄H₉)NH₂ (374 mg, 1.94 mmol) in methanol (1 mL), and the mixture was stirred overnight at 25 °C. The formed precipitate was collected by filtration, washed with cold methanol, and dried under vacuum. Ligand g was obtained as an orange powder (245 mg, 0.56 mmol; yield 58%). ¹H NMR (200.13 MHz, CD₂Cl₂, 19 °C): δ 8.32 (s, 2H; H10), 8.10 (d, ${}^{3}J_{H,H}$ = 5.1 Hz, 4H; H8), 7.91 (d, ${}^{3}J_{H,H}$ = 4.3 Hz, 4H; H5), 7.56 (m, 8H; H6 and H7), 2.26 ppm (s, 6H; H1). ¹³C NMR (50.32 MHz, CD₂Cl₂, 18 °C): δ 170.8 (s; C2), 143.1 (s; C3), 131.84 (s; C4), 128.4 (s; C8), 125.6 (s; C6 or C7), 125.2 (s; C7 or C6), 123.5 (s; C5), 121.8 (s; C10), 119.7 (s; C9), 16.9 ppm (s; C1). Anal. Calcd for C₃₂H₂₄N₂ (436.55): C, 88.04; H, 5.54; N, 6.42. Found: C, 88.00; H, 5.56; N, 6.45.

4.3. Synthesis of Complexes 1e–g. *4.3.1. General Procedure for the Synthesis of Complexes* 1e-g. A solution of the appropriate ligand in 5 mL of dichloromethane was added to a solution of [Pd(Me)(Cl)(COD)] in 5 mL of the same solvent. The reaction mixture was stirred overnight at 25 °C. The solvent was reduced up to 2 mL by evaporation under vacuum, and diethyl ether (30 mL) was added to precipitate the desired compound. After filtration, the

resulting solid was washed with diethyl ether (5 mL) and dried under vacuum.





Reagents: (1-C₁₀H₇)₂DABMe₂ ligand, 200 mg (0.59 mmol); [Pd-(Me)(Cl)(COD)], 158 mg (0.59 mmol). Yield: 148 mg (0.30 mmol, 50%) of 1e as a red-orange powder. The NMR analysis indicated that the two possible conformational isomers, in which the nitrogen ligand adopts a C_2 - or a C_s -symmetric coordination geometry, are simultaneously present in CD₂Cl₂ solution at 19 °C with an approximate equimolar ratio. ¹H NMR (200.13 MHz, CDCl₃, 19 °C): δ 7.96 (br d, 2H; H8(C₂ and C_s) and H8'(C_2 and C_s)), 7.93 (br d, 1H; H5'(C_2 and C_s)), 7.90 (br d, 1H; H5(C₂ and C_s)), 7.87 (br d, 1H; H10') (C₂ and C_s), 7.82 (br d, 1H; H10(C₂ and C_s)), 7.59 (m, 6H; H6, (C₂ and C_s) H6'(C₂ and C_s), H7(C_2 and C_s), H7'(C_2 and C_s), H11(C_2 and C_s) and H11'(C_2 and *C*_s)), 7.18 (br dd, 1H; H12(*C*₂ and *C*_s)), 7.14 (br dd, 1H; H12'(*C*₂ and (C_s) , 2.12 (s, 3H; H1(C_2 and C_s)), 2.06 (br s, 3H; H1'(C_2 and C_s)), 0.46 ppm (s, 3H; H13(C_2 and C_s)). ¹³C NMR (50.32 MHz, CDCl₃, 19 °C) δ 175.7 (s; C2'(C_2 and C_s)), 170.3 (s; C2(C_2 and C_s)), 143.1, 143.0 (s; C3(C_2 and C_s)), 142.7 (s; C3'(C_2 and C_s)), 133.8 (s; C9(C_2 and C_s) and C9'(C₂ and C_s)), 128.66, 128.63, 128.56, 128.50 (s; C8(C₂ and C_s) and $C8'(C_2$ and C_s)), 127.5 (br s; C10'(C_2 and C_s) and C11(C₂ and C_s)), 127.2, 127.1, 126.8, 126.7 125.2 (s; C6(C₂ and C_s), $C6'(C_2 \text{ and } C_s)$, $C7(C_2 \text{ and } C_s)$, and $C7'(C_2 \text{ and } C_s)$), 127.1 (s; $C10(C_2$ and C_s)), 126.5 (s; C11'(C_2 and C_s)), 125.5 (s; C4(C_2 and C_s) and $C4'(C_2 \text{ and } C_s))$, 122.9, 122.8 (s; $C5(C_2 \text{ and } C_s)$), 122.3, 122.2 (s; $C5'(C_2 \text{ and } C_s))$, 117.6 (s; $C12'(C_2 \text{ and } C_s)$), 117.1 (s, $C12(C_2 \text{ and } C_s)$) C_s)), 20.8 (s; C1'(C_2 and C_s)), 19.8 (s; C1(C_2 and C_s)), 2.8, 2.6 ppm (s; C13(C₂ and C_s)). Anal. Calcd for C₂₅H₂₃ClN₂Pd (493.33): C, 60.86; H, 4.70; N, 5.68. Found: C, 60.80; H, 4.66; N, 5.63. 4.3.3. Synthesis of $Pd(Me)Cl((1-C_{14}H_9)_2DABMe_2)$ (1f).



Reagents: (1-C₁₄H₉)₂DABMe₂ ligand, 100 mg (0.23 mmol); [Pd-(Me)(Cl)(COD)], 56 mg (0.21 mmol). Yield: 83 mg (0.14 mmol, 67%) of 1f as a brown powder. The NMR analysis indicated that the two possible conformational isomers, in which the nitrogen ligand adopts a C_2 - or a C_s -symmetric coordination geometry, are simultaneously present in CD₂Cl₂ solution at 19 °C with an approximate equimolar ratio. ¹H NMR (200.13 MHz, CD₂Cl₂, 4 °C): δ 8.78-8.52 (m; 4H; H12(C_2 and C_s), H12'(C_2 and C_s), H5(C_2 and C_s), H5'(C_2 and C_s)), 8.32 (t, 1H; H7(C_2 and C_s)), 8.20 (brt, 1H; H7'(C_2 and C_s)), 8.08 (m, 4H; H10(C_2 and C_s), H10'(C_2 and C_s), H14(C_2 and C_s) and H14'(C_2) and C_s)), 7.63 (m, 6H; H8(C_2 and C_s), H8'(C_2 and C_s), H9(C_2 and C_s), $H9'(C_2 \text{ and } C_s), H15(C_2 \text{ and } C_s) \text{ and } H15'(C_2 \text{ and } C_s)), 7.23 (m, 2H;$ $H16(C_2 \text{ and } C_s)$ and $H16'(C_2 \text{ and } C_s)$, 2.23, 2.15 (s, 6H; $H1(C_2 \text{ and } C_s)$) C_s) and H1'(C_2 and C_s)), 0.28, 0.27 ppm (s, 3H; H17(C_2 and C_s)). ¹³C NMR (50.32 MHz, CD₂Cl₂, 19 °C) δ 176.84 (s; C2'(C₂ and C_s) or $C2(C_2 \text{ and } C_s))$, 171.59 (s; $C2(C_2 \text{ and } C_s)$ or $C2'(C_2 \text{ and } C_s))$, 143.6 (br s; C3'(C₂ and C_s) and C3(C₂ and C_s)), 132.21, 132.09, 131.99, 131.67 (s; C11(C₂ and C_s), C11'(C₂ and C_s), C13(C₂ and C_s), C13'(C₂ and C_s), C6(C_2 and C_s), C6'(C_2 and C_s), C4(C_2 and C_s) and C4'(C_2 and C_s)), 128.43 (s; C7(C_2 and C_s)), 128.11 (br s; C7'(C_2 and C_s)), 127.42 (s; C12(C_2 and C_s) or C12'(C_2 and C_s)), 127.07 (br s; C12'(C_2

and C_s) or C12(C_2 and C_s)), 128.11, 127.7, 127.07 (br s; C10(C_2 and C_s), C10'(C_2 and C_s), C14(C_2 and C_s) and C14'(C_2 and C_s)), 126.36, 126.00 (br s; C9(C_2 and C_s), C9'(C_2 and C_s), C15(C_2 and C_s) and C15'(C_2 and C_s)), 124.31, 124.14 (s; C8(C_2 and C_s) and C8'(C_2 and C_s)), 121.71, 121.00 (C5(C_2 and C_s) and C5'(C_2 and C_s)), 117.06, 115.86 (s; C16(C_2 and C_s) and C16'(C_2 and C_s)), 20.83, 19.75 (s; C1(C_2 and C_s) and C1'(C_2 and C_s)), 1.23 ppm (s; C17(C_2 and C_s)). Anal. Calcd for C₃₃H₂₇ClN₂Pd (593.45): C, 66.79; H, 4.59; N, 4.72. Found: C, 66.82; H, 4.60; N, 4.72.

4.3.4. Synthesis of $Pd(Me)Cl((9-C_{14}H_9)_2DABMe_2)$ (1g).



Reagents: (9-C₁₄H₉)₂DABMe₂ ligand, 167 mg (0.38 mmol); [Pd-(Me)(Cl)(COD)], 87 mg (0.32 mmol). Yield: 145 mg (0.24 mmol, 75%) of 1g as a brown powder. ¹H NMR (200.13 MHz, CD₂Cl₂, 19 °C): δ 8.59 (s, 1H; H10 or H10'), 8.51 (s, 1H; H10' or H10), 8.23-8.12 (m, 8H; H8, H8', H12, H12', H5, H5', H15 and H15'), 7.81-7.60 (m, 8H; H7, H7', H6, H6', H13, H13', H14 and H14'), 2.05 (s, 3H; H1), 1.98 (s, 3H; H1'), 0.05 ppm (s, 3H; H17); ¹³C NMR (50.32 MHz, CD₂Cl₂, 19 °C) δ 177.6 (s; C2'), 172.8 (s; C2), 144.8 (s; C3 and C3'), 131.1 (s; C4, C4', C16 and C16'), 129.0 (s; C8' or C12' or C8 or C12), 128.9 (s; C8' or C12' or C8 or C12), 128.8 (s; C8 or C12 or C8' or C12'), 128.7 (s; C8 or C12 or C8' or C12'), 127.5 (s; (C7 and C13) or (C7' and C13')), 126.6 (s; C10 or C10'), 126.4 (s; (C7' and C13') or (C7 and C13)), 126.1 (s; (C6 and C14) or (C6' and C14')), 125.8 (s; (C6' and C14') or (C6 and C14), 125.5 (s; C10' or C10), 122.9 (s; (C5 and C15) or (C5' and C15')), 122.0 (s; (C5' and C15') or (C5 and C15)), 115.9 (s; C9 and C9' and C11 and C11'), 20.8 (s, C1'), 19.9 (s; C1), 0.81 (s; C17). Anal. Calcd for C33H27ClN2Pd (593.45): C, 66.79; H, 4.59; N, 4.72. Found: C, 66.84; H, 4.63; N, 4.74.

4.4. Synthesis of Complexes 2a,d–g. 4.4.1. General Procedure for the Synthesis of Complexes 2a,d-2g. AgPF₆ was added to a dichloromethane/acetonitrile (5/1) solution (6 mL) of 1a,d-gcooled at 0 °C. The mixture was allowed to react for 2 h, during which time AgCl precipitated. The mixture was filtered through Celite, and a solid was obtained after evaporation of the solvent under vacuum. The solid gave the desired complex on treatment with hexane (2 × 5 mL).

4.4.2. Synthesis of $[Pd(Me)(MeCN)(Ph_2DABMe_2)]^+[PF_6]^-$ (2a).



Reagents: AgPF₆, 55 mg (0.22 mmol); **1a**, 80 mg (0.20 mmol). Yield: 65 mg (0.12 mmol, 60%) of **2a** as a yellow powder. ¹H NMR (200.13 MHz, CDCl₃, 19 °C): δ 7.47, 7.33, 7.13, 6.99 (10H; aromatic protons), 2.32, 2.26 (3H each; ligand backbone protons), 1.92 (s, 3H; Pd-NCCH₃), 0.41 (s, 3H; Pd-CH₃). ¹³C NMR (50.32 MHz, CDCl₃, 19 °C) 180.7, 171.6, 132.9, 132.7, 130.6, 130.4, 128.8, 128.5, 122.1, 21.5, 19.7, 6.2, 3.0. Anal. Calcd for $C_{19}H_{22}F_6N_3PPd$ (543.78): C, 41.97; H, 4.08; N, 7.73. Found: C, 41.92; H, 4.03; N, 7.77. 4.4.3. Synthesis of $[Pd(Me)(MeCN)((2,6-i-Pr_2Ph)_2DABMe_2)]^+[PF_6]^-$ (2d).

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Reagents: AgPF₆, 30.5 mg (0.11 mmol); **1d**, 70 mg (0.11 mmol). Yield: 61 mg (0.086 mmol, 78%) of **2d** as a yellow powder. ¹H NMR (200.13 MHz, CD₂Cl₂, 19 °C): δ 7.32 (m, 6H; aromatic protons), 2.99 (sept, 4H; $-CH(CH_3)_2$), 2.35 (s, 6H; ligand backbone protons), 1.83 (s, 3H; Pd-NCCH₃), 1.38 (d, ²J_{HH} = 6.8 Hz, 3H; $-CH(CH_3)_2$), 1.33 (d, ²J_{HH} = 6.8 Hz, 3H; $-CH(CH_3)_2$), 1.24 (d, ²J_{HH} = 6.9 Hz, 3H; $-CH(CH_3)_2$), 0.42 (s, 3H; Pd-CH₃). ¹³C NMR (50.32 MHz, CDCl₃, 19 °C) 179.8, 174.6, 141.8, 141.2, 137.6, 137.2, 128.8, 128.2, 126.3, 125.6, 122.8, 30.5, 29.6, 24.2, 23.8, 23.5, 23.2, 21.8, 20.5, 7.2, 2.8. Anal. Calcd for C₃₁H₄₆F₆N₃PPd (712.01): C, 52.29; H, 6.51; N, 5.90. Found: C, 52.22; H, 6.47; N, 5.86.

4.4.4. Synthesis of $[Pd(Me)(MeCN)((1-C_{10}H_7)_2DABMe_2)]^+[PF_6]^-$ (**2e**).



Reagents: AgPF₆, 50 mg (0.2 mmol); 1e, 90 mg (0.182 mmol). Yield: 114 mg (0.18 mmol, 98%) of 2e as a yellow-orange crystalline powder. The NMR analysis indicated that the two possible conformational isomers, in which the nitrogen ligand adopts a C_2 - or a C_s -symmetric coordination geometry, are simultaneously present in CD₂Cl₂ solution at 19 °C with an approximate equimolar ratio. ¹H NMR (200.13 MHz, CDCl₃, 19 °C): δ 8.25 (d, ² $J_{\rm HH}$ = 8.2 Hz; H5(C_2) or H5(C_s)), 8.17 (d, ${}^{2}J_{\text{HH}} = 8.2 \text{ Hz}; \text{H5}(C_{s}) \text{ or } \text{H5}(C_{2})), 7.96 \text{ (m, 3H; } \text{H5}'(C_{s} \text{ and } C_{2})),$ $H8(C_s \text{ and } C_2)$ and $H8'(C_s \text{ and } C_2)$, 7.85 (d, 2H; H10($C_s \text{ and } C_2$) and H10'(C_s and C_2)), 7.66 (m, 6H; H6(C_s and C_2), H6'(C_s and C_2), $H7(C_s \text{ and } C_2)$, $H7'(C_s \text{ and } C_2)$, $H11(C_s \text{ and } C_2)$ and $H11'(C_s \text{ and } C_2)$ C_2)), 7.45 (d, ${}^2J_{HH}$ = 4.7 Hz; H12(C_s or C_2)), 7.41 (d, ${}^2J_{HH}$ = 4.7 Hz; H12(C_2 or C_s)), 7.37 (d, ${}^2J_{HH}$ = 7.5 Hz; H12'(C_s or C_2)), 7.30 (d, ${}^{2}J_{\text{HH}} = 7.5 \text{ Hz}; \text{H12'}(C_2 \text{ or } C_s)), 2.42 \text{ (s, 3H; H1}(C_s \text{ and } C_2)), 2.28,$ 2.29 (s, 3H; H1'(C_s and C₂)), 1.338, 1.331 (s, 3H; NCCH₃(C_s and (C_2) , 0.18, 0.19 ppm (s, 3H; H13(C_2 and C_2)). ¹³C NMR (50.32 MHz, CDCl₃, 19 °C) & 182.78, 182.68 (s; C2'(C_s and C₂)), 173.94, 173.81 (s; C2(C_s and C₂)), 142.02, 141.88, 141.83 (s; C3(C_s and C₂) and $C3'(C_s \text{ and } C_2)$, 133.63, 133.57 (s; $C9(C_s \text{ and } C_2)$ and $C9'(C_s \text{ and } C_2)$ (C_2) , 128.62, 128.30, 128.07, 127.76 (s; C8(C_s and C_2) and C8'(C_s and C₂)), 127.76, 127.19 (s; C10(C_s and C₂) and C10'(C_s and C₂)), 127.19 (br s; $C7(C_s \text{ and } C_2)$, $C7'(C_s \text{ and } C_2)$, $C6(C_s \text{ and } C_2)$ and C6'(C_s and C₂)), 125.94, 125.79, 125.48, 125.20, 125.20, 125.11 (s; C4(C_s and C_2), C4'(C_s and C_2), C11(C_s and C_2) and C11'(C_s and (C_2)), 123.75, 123.39 (s; C5(C_s and C_2)), 122.54, 122.03 (s; C5'(C_s and C_2), 120.82 (br s; CH₃CN(C_c and C_2)), 118.49, 118.17 (s; C12'(C_s and C₂)), 117.43, 117.23 (s; C12(C_s and C₂)), 21.08 (s; $C1'(C_s \text{ and } C_2)$), 19.57 (s; $C1(C_s \text{ and } C_2)$), 4.43, 4.37 (s; $C13(C_s \text{ and } C_2)$) (C_2)), 1.33 ppm (br s; CH₃CN(C_s and C_2)). Anal. Calcd for C₂₇H₂₆F₆N₃PPd (643.91): C, 50.36; H, 4.07; N, 6.53. Found: C, 50.40; H, 4.10; N, 6.55.





Reagents: AgPF₆, 33 mg (0.13 mmol); 1f, 70 mg (0.118 mmol). Yield: 58 mg (0.078 mmol, 66%) of 2f as a brown powder. The NMR analysis indicated that the two possible conformational isomers, in which the nitrogen ligand adopts a C_2 - or a C_s -symmetric coordination geometry, are simultaneously present in CD_2Cl_2 solution at 19 $^\circ C$ with an approximate equimolar ratio. ¹H NMR (200.13 MHz, CD₂Cl₂, 19 °C): δ 8.78, 8.59, 8.53 (s, 2H; H5(C_2 and C_s) and H5'(C_2 and C_s)), 8.50 (m, 2H; H12(C₂ and C_s) and H12'(C₂ and C_s)), 8.38 (br d, 2H; H7(C_2 and C_s) and H7'(C_2 and C_s)), 7.99–7.92 (mbr, 4H; H10(C_2 and C_s), H10'(C_2 and C_s), H14(C_2 and C_s) and H14'(C_2 and C_s)), 7.65-7.21 (m, 8H; H8(C_2 and C_s), H8'(C_2 and C_s), H9(C_2 and C_s), H9', H16(C_2 and C_2), H16'(C_2 and C_2), H15(C_2 and C_3) and H15'(C_2) and C_s)), 2.41, 2.40, 2.28 (s, 6H; H1(C_2 and C_s) and H1'(C_2 and C_s)), 1.02 (br s, 3H; NCCH₃(C_2 and C_s)), 0.12, 0.07 ppm (s, 3H; H17(C_2 and C_c)). ¹³C NMR (50.32 MHz, CDCl₃, 19 °C) δ 183.06, 182.94 (s; C2(C₂ and C_s) or C2'(C₂ and C_s)), 174.17, 173.94 (s; C2'(C₂ and C_s) or C2(C2 and Cs)), 142.16, 142.01, 141.8 (s; C3(C2 and Cs) and $C3'(C_2 \text{ and } C_2)$, 132.48–131.78 (br; $C11(C_2 \text{ and } C_2)$, $C11'(C_2 \text{ and } C_2)$ C_s), C13(C_2 and C_s), C13'(C_2 and C_s), C6(C_2 and C_s) and C6'(C_2 and (C_s) , 130.93 (br s; C4(C_2 and C_s) and C4'(C_2 and C_s)), 129.30, 129.03 (s; C7(C₂ and C_s) and C7'(C₂ and C_s)), 128.22, 128.15, 128.04, 127.96, 127.72, 127.49, 127.29, 126.86, 126.70, 126.60, 126.43, 126.23 (s; $C8(C_2 \text{ and } C_s)$, $C8'(C_2 \text{ and } C_s)$, $C10(C_2 \text{ and } C_s)$, $C10'(C_2 \text{ and } C_s)$, $C14(C_2 \text{ and } C_s)$, $C14'(C_2 \text{ and } C_s)$, $C12(C_2 \text{ and } C_s)$, $C12'(C_2 \text{ and } C_s)$ and $[(C15'(C_2 \text{ and } C_s) \text{ and } C15(C_2 \text{ and } C_s)) \text{ or } (C9'(C_2 \text{ and } C_s) \text{ and } C15(C_2 \text{ and } C_s))$ C9(C₂ and C_s))], 124.95, 124.84, 124.36, 124.16 (s; (C9(C₂ and C_s) and $C9'(C_2$ and $C_3)$ or $(C15(C_2 \text{ and } C_3) \text{ and } C15'(C_2 \text{ and } C_3))$ 122.78, 122.51, 121.41, 121.14 (s; $C5(C_2 \text{ and } C_s)$ and $C5'(C_2 \text{ and } C_s)$ C_s)), 120.19 (br s; CH₃CN(C₂ and C_s)), 117.82, 117.68, 116.36 (s; $C16(C_2 \text{ and } C_s) \text{ and } C16'(C_2 \text{ and } C_s))$, 21.10, 19.59, 19.48 (s; $C1(C_2$ and C_s) and $C1'(C_2$ and C_s)), 4.53, 4.33 (s; $C17(C_2$ and C_s)), 1.17 ppm (br s; CH₃CN). Anal. Calcd for C₃₅H₃₀F₆N₃PPd (744.00): C, 56.50; H, 4.06; N, 5.65. Found: C, 56.55; H, 4.08; N, 5.65.

4.4.6. Synthesis of $[Pd(Me)(MeCN)((9-C_{14}H_9)_2DABMe_2)]^+[PF_6]^-$ (2g).



Reagents: AgPF₆, 37.4 mg (0.148 mmol); **1g**, 80 mg (0.135 mmol). Yield: 97 mg (0.13 mmol, 96%) of **2g** as a brown-violet powder. ¹H NMR (200.13 MHz, CD₂Cl₂, 4 °C): δ 8.64 (s, 1H; H10'), 8.62 (s, 1H; H10), 8.22 (br d, 6H; H8, H12, H8', H12',H5 and H15), 8.11 (br d, 2H; H5' and H15'), 7.83 (m, 4H; H6, H14, H6' and H14'), 7.71 (m, 4H; H7, H13, H7' and H13'), 2.32 (s, 3H; H1), 2.23 (s, 3H; H1'), 1.16 (s, 3H; NCCH₃), 0.03 ppm (s, 3H; H17). ¹³C NMR (50.32 MHz, CD₂Cl₂, 4 °C): δ 183.98 (s; C2'), 175.51 (s; C2), 136.19 (s; C3), 135.89 (s; C3'), 131.20 (s; (C4 and C16) or (C4' and C16')), 130.97 (s; (C4' and C16') or (C4 and C16)), 129.12 (s; (C8 and C12) or (C8' and C12')), 128.96 (s; (C8' and C12') or (C8 and C12)), 128.11 (s; (C6 and C14) or (C6' and C14')), 127.79 (s; (C6' and



C14') or (C6 and C12)), 127.45 (s; C10'), 126.77 (s; C10), 126.36 (s; (C7 and C13) or (C7' and C13')), 126.30 (s; (C7' and C13') or (C7 and C13)), 122.56 (s; C5 and C15), 122.19 (s; (C9 and C11) or (C9' and C11')), 121.67 (s; C5' and C15'), 121.56 (s; (C9' and C11') or (C9 and C11)), 120.98 (s; NCCH₃), 21.30 (s; C1'), 20.37 (s; C1), 4.15 (s; C17), 1.49 ppm (s; NCCH₃). Anal. Calcd for $C_{35}H_{30}F_6N_3PPd$ (744.00): C, 56.50; H, 4.06; N, 5.65. Found: C, 56.56; H, 4.10; N, 5.65.

Intramolecular Structures of Complexes 1e-g and 2e-g, Determined by NMR Experiments. The Pd–Me resonance (H17, in 1e-g and 2e-g) was used as the starting point for the assignment of the protons of complexes 1g and 2g, because its chemical shift is known from previous studies and it is well separated from other resonances (H17 in 1g is at 0.05 ppm (CD₂Cl₂, 19 °C) and in 2g at -0.03 ppm (CDCl₃, 19 °C)).

Signals of the nitrogen ligand were essentially assigned on the basis of intramolecular dipolar interactions detected in the ¹H-NOESY spectrum. The H17 protons strongly interact with the aromatic H5' and H15' protons, which give interactions with $CH_3(1')$, allowing assignment of the ligand backbone resonances $CH_3(1')$ and $CH_3(1)$. The other protons were then assigned from either the ¹H-COSY or ¹H-NOESY spectra, while their carbons were identified by ¹H, ¹³C-HSQC and ¹H,¹³C-HMBC spectra. Also in the case of complexes 1e,f and 2e,f the Pd-Me resonance was helpful to assign aromatic protons. In compounds 1e and 2e H13 showed a strong NOE contact with H12' and H5'. The interactions of the latter with $CH_3(1')$ allow discrimination between $CH_3(1')$ and $CH_3(1)$. At the same time, $CH_3(1)$ interacts both with H12 and H5 of the other half of the ligand. H5-H5' and H12-H12' are well separated in the ¹H NMR spectrum (for example, in 1e: H5', 7.93; H5, 7.90; H12, 7.18; H12', 7.14 ppm (CDCl₃, 19 °C)). Similarly, in 1f and 2f NOE interactions of Pd–Me protons with H5' and H16' and those of $CH_3(1)$ with H5 and H16 define the structures of complexes, and the remaining ¹H and ¹³C resonances were then assigned following scalar and dipolar interactions.

4.5. Synthesis and Characterization of the First Intermediates **3g–6g in the CO**/*p*-Methylstyrene Copolymerization Reaction. *4.5.1.* Synthesis of $[Pd(Me)(CO)((9-C_{14}H_9)_2DABMe_3)]^+[BAr'_4]^-$ (**3g**).



A 60 mg (0.101 mmol) sample of 1g and a 93.4 mg (0.105 mmol) sample of NaBAr'₄ were dissolved at 0 °C in dichloromethane (4 mL) previously saturated with CO. The reaction mixture was filtered through Celite to remove NaCl. The solvent was evaporated under vacuum, and the resulting oil was washed with hexane $(3 \times 5 \text{ mL})$. A 119.5 mg (0.08 mmol, yield 81%) sample of 3g was collected as a violet powder. ¹H NMR (200.13 MHz, CDCl₃, -20 °C): δ 8.67 (s, 1H; H10'), 8.65 (s, 1H, H10), 8.23 (m, 4H; H8, H8', H12 and H12'), H87 (br d, 2H; H5 and H15), 7.71 (s, 10H; H5', H15' and Ar'-H_a), 7.64 (m, 8H; H7, H7', H13, H13', H6, H6', H14 and H14'), 7.49 (s, 4H; Ar'-H_v), 2.30 (s, 3H; H1'), 2.27 (s, 3H; H1), 0.40 ppm (s, 3H; H17). ¹³C NMR (50.32 MHz, CDCl₃, -20 °C): δ 186.5 (s; C2), 177.3 (s; C2'), 173.7 (s; CO), 161.5 (q, ${}^{1}J$ (C,B) = 49.5 Hz; Ar'-C_i), 136.7 (s; C3), 134.8 (s; Ar'-C_o), 132.7 (s; C3'), 131.1 (s; (C4 and C16) or (C4' and C16')), 130.9 (s; (C4' and C16') or (C4 and C16)), 130.1 (s; (C8 and C12) or (C8' and C12')), 129.9 (s; C8' and C12') or (C8 and C12)), 129.0 (s; (C6, C14, C6' and C14') or (C7, C13, C7' and C13') C10 and C10'), 128.6 (q, ${}^{2}J_{C,F}$ = 27.0 Hz; Ar'-C_m), 126.6 (s; (C7, C13, C7' and C13') or (C6, C14, C6' and C14')), 124.2 (q, ${}^{1}J_{C,F}$ = 267.7 Hz; CF₃), 121.9 (s; C9' and C11'), 120.6 (s; C9, C11, C5 and C15), 120.1 (s; C5' and C15'), 117.6 (s; Ar'-C_n), 21.9 (s; C1'), 20.6 (s; C1), 8.3 ppm (s; C17). Anal. Calcd for C₆₆H₃₉F₂₄N₂OBPd (1449.22): C, 54.70; H, 2.71; N, 1.93. Found: C, 54.77; H, 2.80; N. 1.94

4.5.2. Synthesis of $[Pd(\eta^3-C_{11}H_{13}O)((9-C_{14}H_9)_2DABMe_2)]^+[BAr'_4]^-$ (**4g**).

BAr'₄





A 82.3 mg (0.056 mmol) sample of 3g was dissolved in dichloromethane (5 mL) at 0 °C; then p-methylstyrene (7.5 μ L, 0.056 mmol) was added. After 1 h the solution was filtered trough Celite and the solvent was evaporated under vacuum. The resulting oil was washed with hexane $(2 \times 3 \text{ mL})$ to yield complex 4g (83 mg, 0.053 mmol, yield 95%) as a red-brown powder. ¹H NMR (200.13 MHz, CDCl₃, 4 °C): δ 8.70 (s, 1H; H10), 8.68 (s, 1H; H10'), 8.33 (br d, 1H; H15), 8.29 (br d, 2H; H8 and H12), 8.28 (br d, 1H; H12'), 8.19 (d, ${}^{3}J_{H,H} = 8.4$ Hz, 1H; H8'), 8.07 (d, ${}^{3}J_{H,H} = 8.6$ Hz, 1H; H15'), 7.89-7.58 (m, 18H; Ar'-H_o, Ar'-H_v, H6, H14, H14', H7, H13, H13'), 7.70 (brt, 1H; H7'), 7.66 (br d, 1H; H5), 7.50 (brt, 1H; H6'), 7.18 (d, ³*J*_{H,H} = 8.6 Hz, 1H; H5′), 6.11 (br d, 2H; H22 and H22′), 5.80 (d, 2H; H23 and H23'), 2.80 (dd, ${}^{3}J_{H,H}$ = 4.2 Hz and ${}^{3}J_{H,H}$ = 9.5 Hz, 1H; H20), 2.24 (s, 3H; H1'), 2.14 (s, 3H; H1), 1.63 (dd, ${}^{3}J_{H,H} = 9.4$ Hz and ${}^{2}J_{H,H} = 18.5$ Hz, 1H; H19b), 1.33 (s, 3H; H17), 0.92 (s, 3H; H25), 0.30 (dd, ${}^{3}J_{H,H}$ = 4.3 Hz and ${}^{2}J_{H,H}$ = 18.8 Hz, 1H; H19a). ${}^{13}C$ NMR (50.32 MHz, CDCl₃, 4 °C) δ 202.7 (s; C18), 178.8 (s; C2), 176.5 (s; C2'), 161.5 (q, ${}^{1}J_{C,B}$ = 49.7 Hz; Ar'-C_i), 142.0 (s; C24), 137.2 (s; C3), 136.5 (s; C3'), 134.8 (s; Ar'-C_o), 133.6 (s; C23 and C23'), 131.4, 131.2, 130.9 (s; 4C; C4, C4', C16 and C16'), 129.7 (s; C12 or

C8), 129.6 (s, 2C; (C12' or C8') and (C12 or C8)), 129.2 (s; C8' or C12'), 128.8 (q, ${}^{2}J_{C,F}$ = 27.0 Hz; Ar'-C_m), 128.7, 128.5, 128.3, 127.6 (s; 4C; C6, C6', C14 and C14'), 127.2 (s; C10), 127.0 (s; C7 or C13), 126.5 (s, 4C; C10', C7', C14' and (C13 or C7)), 124.2 (q, ${}^{1}J_{C,F}$ = 272.7 Hz; CF₃), 121.18 (s; C9 or C9' or C11 or C11'), 120.94 (s; C15), 120.88 (s; C15' or C5'), 120.7, 120.6, 120.3 (s, 3C; C9 and/or C9' and/or C11 and/or C11'), 120.0 (s; C5), 119.7 (s; C5' or C15'), 117.6 (s; Ar'-C_p), 115.7 (s; C21), 107.2 (br; C22 and C22'), 54.8 (s; C20), 41.0 (s; C19), 29.0 (s; C17), 20.9 (s; C25), 20.3 (s; C1), 20.0 (s; C1'). Anal. Calcd for C₇₅H₄₉F₂₄N₂OBPd (1567.40): C, 57.47; H, 3.15; N, 1.79. Found: C, 57.60; H, 3.22; N, 1.91.

Intramolecular Structure of Complex 4g Determined by NMR Experiments. The assignment of the ¹H resonances of the allyl fragment of 4g was made on the basis of the dipolar and scalar interactions detected in the ¹H-NOESY and ¹H-COSY spectra, respectively, and confirmed by previously reported studies.^{2d} The starting point was H17, the aliphatic signals integrating for three protons at 1.33 ppm ,which shows long-range correlation with the C=O singlets at 202.7 (C18) ppm in the ¹H-¹³C HMBC spectrum. The remaining resonances were individuated following the interactions H17-H19a/ H19b, H19a-H19b, H19a/H19b-H20, H20-H22/H22', H22/ H22'-H23/H23' ,and H23/H23'-H25. In the aromatic region of the ¹H NMR spectrum, the only two singlets were ascribable to H10 and H10' protons. Due to the NOE interactions of H17 with H10 and of H25 with H10', it was possible to discriminate between the two signals, and so, the halves of the nitrogen ligand (*n* and n') were differentiated. The overlap of most aromatic resonances makes difficult the assignment of other signals starting from H10, H10' and following the scalar or dipolar interactions. Despite this, the following assignments were made: (i) H8' was identified thanks to its NOE contacts with both H10' and H25; (ii) H12' was assigned due to its interactions with H10', H22/H22', and H23/ H23'; (iii) H15' was defined from its NOE contact with H22/ H22'; (iv) H8 and H12 were assigned on the base of their interactions with H10 and H17; (v) H15 was assigned from the interaction with H20.

The similar intensities of the NOE interactions H1-H5, H1-H15 and of H1'-H5', H1'-H15' suggest the nearly perpendicular placement of the halves of the N-anthryl ligand with respect to the square-planar coordination plane of the complex, as observed in the solid state (Figure 2). Following the NOE connectivity, from H15' and H15 it was possible to assign H1' and H1 signals, of methyl groups of the DAB backbone, and consequently H5' and H5. Both H15'-H22/H22' and H5'-H22/H22' contacts were detected in the ¹H-NOESY spectrum; however, the stronger intensity of the former confirms the rather inclined orientation of the *p*-methylstyrene ring with respect to the n' half of the 9-anthryl ligand, delineating a solution structure essentially similar to that determined in the solid state by means of X-ray analysis (Figure 2). Other main observations that allow us to define the intramolecular structure of 4g were the following: (i) a stronger intensity of the H5'-H23/H23' contact is detected relative to the H5'-H22/H22' contact; (ii) H25 interacts with H10' and H8' with approximately the same intensity; (iii) H23/H23' preferentially interacts with H10', H12', and H5'; (iv) H22/H22' preferentially interacts with H15', H12', and H15; (v) H20 interacts almost exclusively with H15; (vi) H19a weakly interacts with H10 and H5; (vii) H19b weakly interacts with H5; (viii) H17 interacts with H10 and, weakly, with H8 and/or H12.

4.5.3. Synthesis of $[Pd{C(0)CH(4-Me-C_6H_4)CH_2C(0)CH_3}((9-C_{14}H_9)_2DABMe_2)]^+[BAr'_4]^- ($ **5g**).



Complex 4g (42 mg, 0.027 mmol) was dissolved in CD₂Cl₂ (0.5 mL) in an NMR tube. Carbon monoxide was bubbled through the solution for 10 min at -70 °C, resulting in the formation of an equilibrium mixture of compounds 4g and 5g. The equilibrium ratios appear to be strongly affected by temperature, and the highest conversion in compound 5g (60%) was observed at -17 °C in 3 days under 1 atm of CO.¹H NMR (200.13 MHz, CD₂Cl₃, -17 °C): δ 8.69 (br s, 2H; H10, H10'), 8.31-8.19 (m, 3H; H8', H12, H12'), 8.21 (m, 1H; H8), 8.02-7.78 (m, 3H; H13, H14, H15), 8.02-7.58 (m, 21H; H5, H5', H6, H6', H7, H7', H13', H14', H15', Ar'-Ho, Ar'-Hn), 6.91 (d, 2H; H23 and H23'), 6.77 (d, 2H; H22 and H22'), 3.92 (dd, 1H; H20), 2.39 (s, 3H; H1 or H1'), 2.23 (m, 1H; H19b), 2.20 (s, 3H; H1' or H1), 2.06 (s, 3H; H25), 1.61 (s, 3H; H17), 0.62 (dd, 1H; H19a). ¹³C NMR (50.32 MHz, CD₂Cl₃, -17 °C): δ 210.1 (s; C26), 202.7 (s; C18), 169.6 (s; C27), 179.5, 173.9 (s; C2 and C2'), 161.7 (q, ${}^{1}J_{CB} = 49.8$ Hz; Ar'-C_i), 134.8 (s; Ar'-C₀), 131.4–120.8 (aromatic carbons and Ar'-C_m), 130.2 (br s; C23 and C23'), 129.7 (br; C22 and C22'), 124.0 (q, ${}^{1}J_{C,F}$ = 272.5 Hz; CF₃), 117.5 (s; Ar'-C_p), 60.0 (br s; C20), 44.2 (s; C19), 29.2 (s; C17), 21.4 (s; C1 or C1'), 20.7 (s; C25), 20.4 (s; C1' or C1).

Intramolecular Structure of Complex 5g Determined by NMR Experiments. The assignment of the ¹H resonances of the growing polymer chain of 5g was made starting from the H20 resonance, since it is well identified at around 4 ppm, in analogy with previous results,^{2d} and it is the only -CH- aliphatic signal in the ¹H NMR spectrum. The other proton resonances H19a and H19b were easily recognized, due to their direct correlation with the only $-CH_2$ – carbon of the ¹³C NMR spectrum. As observed in 4g, the H22/H22' protons (as well as H23/H23') give a single broad doublet because of the free rotation of the *p*-methylstyrene aryl around the C20-C21 single bond. Following the dipolar interactions in the ¹H-NOESY spectrum and the scalar interactions in the ¹H-¹³C HSQC and ¹H-¹³C HMBC spectra, most of the proton and carbon resonances of the acetyl moiety were defined. Due to the presence in solution of both 4g and 5g and to the overlap of most aromatic signals, NOE interactions cannot be addressed to describe the intramolecular structure of 5g. However, similarly to previous findings^{2c} the preferred conformation of the growing chain was assumed to be that reported for 5g, as confirmed from the following NMR evidence: (i) the absence of dipolar interactions involving H25 and the anthracenyl protons of the nitrogen ligand; (ii) the weak NOE contacts between H22/H22', H23/H23', H20 and the N-anthryl protons H15, H14, and H13; (iii) the interactions of H19a and H17 with H8.

4.5.4. Synthesis of $[Pd(\eta^3-C_{21}H_{22}O_2)((9-C_{14}H_9)_2DABMe_2)]^+[BAr'_4]^-$ (6g).



p-Methylstyrene (3.5 μ L, 0.027 mmol) was added to the CD₂Cl₂ equilibrium mixture of 4g and 5g (40/60) in an NMR tube. Then carbon monoxide was bubbled through the solution for 5 min at -20 °C. The mixture was allowed to react for 9 days at -18 °C under 1 atm of CO. The solvent was evaporated under vacuum, and the resulting oil was washed with hexane $(2 \times 3 \text{ mL})$. The NMR analysis indicates the formation of complex 6g as the major product (74%), together with other unidentified species. ¹H NMR (200.13 MHz, CD_2Cl_2 , 4 °C): δ 8.68 (s, 1H; H10'), 8.32 (s, 1H; H10), 8.30 (d, ${}^{3}J_{\rm H,H} = 8.8$ Hz, 1H; H12′), 8.23 (d, ${}^{3}J_{\rm H,H} = 8.4$ Hz, 1H; H15), 8.18 (d, ${}^{3}J_{\rm H,H} = 8.4$ Hz, 1H; H15), 8.18 (d, ${}^{3}J_{\rm H,H} = 8.4$ Hz, 1H; H15′), 7.98 (d, ${}^{3}J_{\text{H,H}} = 8.4 \text{ Hz}, 1\text{H}; \text{H8}), 7.80 \text{ (br d, 1H; H12)}, 7.78-7.62 \text{ (m, 17H; }$ H6, H13, H13', H14, Ar'-H_a and Ar'-H_n), 7.66 (br d, 1H; H5), 7.63 (brt, 1H; H7'), 7.61 (br t, 1H; H7'), 7.56 (br t, 1H; H6'), 7.14 (d, ${}^{3}J_{H,H} = 8.5 \text{ Hz}, 1\text{H}; \text{H5}') 7.12 \text{ (br d, 2H; H23, H23'), 6.52 (br d, 2H; }$ H22 and H22'), 6.19 (br, 2H; H30 and H30'), 5.83 (br, 2H; H31 and H31'), 3.16 (dd, 1H; H20), 3.08 (m, 1H; H19a), 2.50 (br s, 3H; H25), 2.45 (dd, 1H; H28), 2.41 (m, 1H; H19b), 2.21 (s, 3H; H1), 2.13 (s, 3H; H1'), 1.95 (m, 1H; H27b), 1.93 (s, 3H; H17), 0.93 (s, 3H; H33), 0.21 (dd, 1H; H27a). ¹³C NMR (50.32 MHz, CD₂Cl₂, 4 °C) δ 207.2 (s; C18), 204.6 (s; C26), 178.7 (s; C2), 176.5 (s; C2'), 161.7 (q, ${}^{1}J_{C,B}$ = 49.8 Hz; Ar'-C_i), 141.9 (s; C32), 137.4 (s; C3), 137.3 (s; C21), 136.6 (s; C3'), 134.8 (s; Ar'-C₀), 133.5 (s; C31 and C31'), 132.7 (s; C24), 131.3, 130.9, 130.6 (s; C4, C4', C16 and C16'), 129.6 (s; C23 and C23'), 129.5 (s; C8'), 129.4 (s; C8), 129.3 (C12'), 128.8 $(q, {}^{2}J_{C,F} = 27.0 \text{ Hz}; \text{Ar'-C}_{m})$, 128.7, 126.5 (s; C7, C13, C7', C13', C6, C14, C14' and C10'), 128.2 (s; C12), 127.4 (s; C22, C22', C10 and C6'), 124.2 (q, ${}^{1}J_{C,F}$ = 272.7 Hz; CF₃), 121.8 (s, C9 or C9' or C11 or C11'), 121.1 (s; C15'), 121.0 (s; C15), 120.8 (s, C9 or C9' or C11 or C11'), 120.4 (s, C9 or C9' or C11 or C11'), 120.3 (s; C5), 119.9 (s; C5'), 117.5 (s; Ar'- C_p), 116.9 (s, C9 or C9' or C11 or C11'), 55.5 (s; C28), 51.5 (s; C20), 47.6 (s; C19), 40.1 (s; C27), 29.1 (s; C17), 21.0 (s; C25), 20.7 (s; C33), 20.4 (s; C1), 20.2 (s; C1').

Intramolecular Structure of Complex 6g Determined by NMR *Experiments.* The analysis of the ¹H-NOESY spectrum of **6g** depicts the molecular structure illustrated above. Starting from H27a (a doublet of doublets at 0.21 ppm, separated from other signals in the 1 H NMR spectrum), the 1 H and 13 C resonances of the allyl systems were assigned on the basis of the ${}^{1}H{-}^{1}H$ and ${}^{1}H{-}^{13}C$ NMR correlations. In the aromatic region of the ¹H spectrum, the only singlets were ascribable to the H10 and H10' protons. The NOE interactions of H33 with H10' and that of H25 with H10 allow discrimination between the two signals and, then, between the halves of the 9-anthryl ligand. H10' interacts with H8' and H12' and a selective NOE interaction is observed between H33 and H8'. Similarly, H10 shows dipolar interactions with H8 and H12, and the H8-H25 contact leads to assignment of the two aromatic doublets. H15' shows a NOE interaction with the H30/H30' resonance, while H5' interacts preferentially with the H31/H31' resonance, and H1' and H1 were assigned through the interactions with H15' and H5' (Scheme 4). Following the NOE connectivity, from H1 it was possible to individuate H15 and H5, which were discriminated thanks to the selective H15-H28 interaction. The dipolar interactions in 6g, involving the second *p*-methylstyrene unit and the *N*-anthryl moiety, are the same as those observed for 4g, although with lower intensity. The position of the aryl ring of the first inserted olefin was deduced from the following observations: (i) H25 interacts with H10 and H8; (ii) H23/ H23' interact with H10 and H8 and, weakly, with H12 and H5; (iii) H22/H22' interact with H10, H15, and H12.

4.6. General Procedures for Copolymerization Processes. *4.6.1. CO/Vinyl Arene Copolymerization in CH*₂*Cl*₂ *under 1 atm of CO.* In a typical copolymerization reaction, the Pd(II) complex (0.035 mmol) was dissolved in dichloromethane (2.8 mL) at 17 °C under a nitrogen atmosphere. The solution was transferred into a thermostated Schlenk flask equipped with a carbon monoxide gas line and a tank for the CO. Then 21 mmol of the vinyl arene (*p*-methylstyrene, 2.8 mL; styrene, 2.6 mL) was added (olefin/ palladium molar ratio 600/1). The solution was allowed to react for 27 h (or 51 h) at 26 °C. The resulting gray polymer was precipitated with methanol and washed with methanol. To remove metallic palladium, the polymer was dissolved in chloroform, filtered through

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Celite, precipitated with methanol, washed with methanol, and dried under vacuum. When mixtures of copolymer and poly(*p*-methylstyrene) were obtained from the reaction, diethyl ether was added to the mixture in order to extract the homopolymer. The resulting suspension was stirred vigorously for several hours and the ether solution was decanted off of the powder. ¹H and ¹³C NMR spectroscopic data are consistent with the isolation of atactic copolymer when catalysts **2a,b,e,f** were used^{2c,f} or predominantly isotactic polyketone when catalysts **2c,g** were employed.^{2c}

4.6.2. CO/Vinyl Arene Copolymerization in 2,2,2-Trifluoroethanol. In a typical copolymerization reaction, the Pd(II) complex (0.035 mmol) was dissolved in 2,2,2-trifluoroethanol (2.8 mL) at 17 °C under a nitrogen atmosphere. The solution was transferred into a thermostated Schlenk flask containing 1,4-benzoquinone (19 mg, 0.175 mmol), equipped with a carbon monoxide gas line and a tank for the CO. Then 21 mmol of the vinyl arene (*p*-methylstyrene, 2.8 mL; styrene, 2.6 mL) was added (olefin/palladium molar ratio 600/1). The solution was allowed to react for 27 h at 26 °C. The resulting gray polymer was precipitated with methanol and washed with methanol. To remove metallic palladium, the polymer was dissolved in chloroform, filtered through Celite, precipitated with methanol, washed with methanol, and dried under vacuum.

4.6.3. CO/p-Methylstyrene Copolymerization in CH_2Cl_2 under 5 atm of CO. The Pd(II) complex (0.035 mmol) was dissolved in methylene chloride (2.8 mL) at 17 °C under a nitrogen atmosphere. The solution was transferred into a thermostated steel autoclave equipped with a magnetic stirring bar and a carbon monoxide gas line. Then *p*-methylstyrene (2.8 mL, 21 mmol) was introduced into the autoclave (olefin/palladium molar ratio 600/1). The nitrogen atmosphere was replaced by carbon monoxide, and the autoclave was charged with CO at 5 atm. The polymerization was allowed to run for 27 h at 26 °C. The run was terminated by venting the reactor vessel and pouring the polymerization mixture into methanol. The resulting gray polymer was washed with methanol. To remove metallic palladium, the polymer was dissolved in chloroform, filtered through Celite, precipitated with methanol, washed with methanol, and dried under vacuum.

4.7. Molecular Weight Measurements. The weight-average molecular weights (M_w) of copolymers and molecular weight distributions (PDI = M_w/M_n) were determined by gel permeation chromatography versus polystyrene standards. The analyses were recorded on a Knauer HPLC (K-501 Pump, K-2501 UV detector) with a Plgel 5 μ m 10⁴ 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 in 120 μ L of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) and chloroform was added up to 10 mL; however, CO/*p*-methylstyrene copolymers were directly soluble in chloroform. The statistical calculations were performed with the Bruker Chromstar software program.

4.8. X-ray Crystallographic Structure Determinations for 2g and 4g. Single crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into a solution of the complex in dichloromethane with several drops of methanol at -30 °C. Diffraction data for compound 2g and 4g were collected on an Oxford Diffraction Xcalibur3 diffractometer equipped with a CCD area detector and Mo K α radiation (λ = 0.71073 Å). Data collections were carried out at 150 K by means of the program Crysalis CCD,⁸ and data were reduced with the program Crysalis RED.³² The absorption correction was applied through the routine ABSPACK in the Crysalis RED program. The structures were solved with the direct methods of the SIR2004³³ package and refined by full-matrix least squares against F^2 with the program SHELX97.³⁴ In the crystal lattice of 2g, additional electron density peaks were modeled as disordered acetonitrile and methanol crystallization molecules, with site occupation factor 0.5 and isotropic temperature factor (the hydrogen atoms were not introduced). In 4g, the η^3 fragment appears disordered, except for the acetyl group. Two models for the $CH_2CH(p-Me-C_6H_4)$ moiety were found, each (a and b) with occupancy factor 0.5. In the η^3 fragment all of the atoms were refined isotropically and the hydrogen atoms were not introduced. Also for a $-CF_3$ grouping two models were found in the difference

Fourier map. In this case the fluorine atoms were refined isotropically with the occupancy factor set to 0.5. In both the crystal structures all of the other non-hydrogen atoms were given anisotropic displacement parameters, and all of the other hydrogen atoms were input at calculated positions and refined by using a riding model, with isotropic thermal parameters varying in accord with those of the bound atoms. Geometrical calculations were performed by PARST97,³⁵ and molecular plots were produced by the program ORTEP3.³⁶ Crystallographic data and refinement parameters for **2g** and **4g** are reported in Table S1 in the Supporting Information.

4.9. Computational Methods. The Gaussian 09 (revision C.01)³⁷ package was used. Metal complexes **5c'** and **5g'**¹⁹ were fully optimized by using the density functional theory (DFT) method by means of Becke's three-parameter hybrid method using the LYP correlation functional.³⁸ The effective core potential of Hay and Wadt³⁹ was used for the palladium atom, and the 6-31G*⁴⁰ basis set was used for the remaining atomic species. The same model chemistry was used for the rigid potential energy surface scans performed on the postulated intermediates, resulting from the coordination of a second styrene unit to the carbonylated products **5a'**, *c'*, *f'*, *g'*. For the starting geometries of all the species modeled above, see ref 8. For the nitrogen ligands **e** and **f** the full optimization was performed at the HF-SCF level of theory, with the basis set 6-311G**.⁴¹ The starting geometries of all cases the reliability of all the found stationary points (minima on the potential energy surface) was assessed by evaluating the vibrational frequencies.

ASSOCIATED CONTENT

Supporting Information

A CIF file giving crystallographic data for 2g and tables giving crystal data and bond distances and angles for 2g and 4g and Cartesian coordinates of the calculated structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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