Neutral and Cationic Dendritic Palladium(II) Complexes Containing *N,N′*-Iminopyridine Chelating Ligands. Synthesis and Their Use for the Syndiospecific Copolymerization of CO/4-*tert*-Butylstyrene†

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Series of neutral and cationic palladium carbosilane dendritic compounds of the general formula G*n*-ONNMe$_m$[Pd(X)Y] (X, Y = Cl; X = Me, Y = Cl; X = Me, Y = MeCN), containing 4 (*n* = 1), 8 (*n* = 2) or 16 (*n* = 3) terminal pyridylimine complexes, substituted with *m* methyl groups (*m* = 0, 2, 3), along with the corresponding monometallic counterparts (*n* = 0), have been synthesized. Monometallic or dendritic chloro methyl or cationic methyl palladium compounds consist of a cis/trans mixture of diastereoisomers, with compositions according to their electronic and steric features. The cationic compounds G*n*-ONNMe$_m$[PdMe(MeCN)]$^+$ are found to be active catalysts for the alternating copolymerization of CO and 4-*tert*-butylstyrene, producing mainly syndiotactic polyketones due to a chain-end stereocontrolled mechanism. Modification of the pyridylimine ligand framework by methyl substituents has a decisive influence on the activities of the palladium compounds. Some of them are found to retain some activity after several days of catalytic reaction. Also, the size (i.e., generation *n*) of the dendritic precursor affects the catalyst performance and the microstructure of the copolymerization products. Thus, higher generation catalysts show superior activities and produce shorter and less stereoregular copolymer chains.

Introduction

Sen[1] established in 1982 that the use of cationic complexes with weakly coordinating anions and phosphine ligands improved the stability and activity of palladium catalysts in ethene/CO copolymerization. Afterward, the studies carried out by Drent[2] on cationic palladium complexes containing chelating bidentate diphosphine ligands made the commercial production of aliphatic polyketones economically attractive. The work of Drent, together with the contributions of Brookhart and others,[3] highlighted the role of late-transition-metal catalysts based on cationic complexes with multidentate ligands in olefin homo- and copolymerization. For example, such catalysts can be highly active in novel copolymerization reactions, such as those of olefins with functionalized polar comonomers (e.g., acrylates),[4] or in perfect alternating copolymerization of carbon monoxide and olefins to give high-molecular-weight polyketones.[5,6] Whereas palladium(II) catalysts with bidentate phosphorus-donor chelating ligands are efficient in CO/aliphatic olefin copolymerization, those with bidentate nitrogen-donor chelates show the best performance in CO/aromatic olefin copolymerization.[5−9] The polyketones obtained are characterized by chemoregularity, in the sense that their propagation occurs by perfect alternation of olefin and CO comonomers. The process is also regioregular in copolymerization reactions involving styrenes, because the secondary migratory insertion of Pd−acyl into the aromatic olefin produces electronically stabilized benzylic intermediates. Besides, the polymer stereoregularity can be tuned by the choice of the ligand. Planar achiral precursors (C_{2v} or C_s

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† Dedicated to Prof. José Antonio Abad on the occasion of his retirement.

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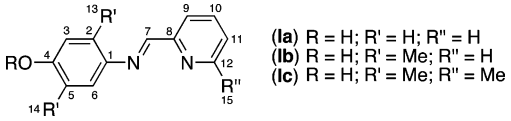
symmetry) give highly syndiotactic polyketones due to chain-end control produced by the interaction of the growing chain with the incoming styrene comonomer,[7,8] while C_2-symmetric chiral catalysts provide an enantiomorphic site-controlled propagation and give isotactic microstructures.[9] Additionally, chiral C_1-symmetric active compounds, containing *N*,*N*′-unsymmetrical ligands, yield syndiotactic or isotactic copolymers, since the influences of chain-end and site controls are in a sensitive equilibrium.[8] Even though P,N[8b] or P,O[10] chelates have been applied successfully to copolymerize styrenes, most of the reported catalysts contain *N*,*N*-symmetrical or *N*,*N*′-unsymmetrical related donor ligands, such as bipyridine, phenanthroline, pyridine−pyrazole, pyridine−oxazoline, and pyridine−imidazoline.

Unsymmetrical *N*,*N*′-pyridylimine-type compounds have been used as catalysts in ethylene polymerization reactions with group 10 metals[11] or applied in solid-phase organometallic synthesis and radical polymerization with molybdenum and copper complexes,[12] respectively. On the other hand, there are in the literature a few reports describing CO/styrene copolymerization reactions using *N*,*N*′-alkylpyridylimine palladium(II) compounds.[13]

Metallodendrimer research has been steadily gaining ground during the past few years, and a considerable number of dendritic macromolecules containing transition metals at their core, branches, or periphery[14] have been prepared for use in metal-based catalysis,[15] including oligomerization and polymerization.[16,17] We have contributed to the chemistry of carbosilane dendrimers containing early-transition-metal complexes bonded to the dendritic periphery or focal point, usually through O- or N-donor anchoring ligands.[17,18] In our study of the catalytic performance in ethylene polymerization of nickel(II) complexes coordinated to carbosilane dendrimers through the pyridylimine ligands **Ia**−**c** (Chart 1), we found that the microstructure and oligomer/polymer product distribution are significantly affected by the size of the dendritic precursor.[19] Since dendritic moieties bring about distinctive catalytic environments, and the CO/styrene copolymerization reaction is sensitive to the active site surroundings, we decided to extend and explore the capacity of metallodendrimer chemistry into this type of process. This paper describes the synthesis, characterization, and performance, as catalyst precursors for CO/4-*tert*-butylstyrene copolymerization, of different neutral and cationic palladium−pyridylimine-ended carbosilane dendrimers, as well as monometallic model complexes. The influence of the dendrimer generation on the catalytic results has been analyzed. Dendrimers containing $PdCl_2$ or PdClMe substituents anchored at their periphery by bidentate chelate ligands have been previously reported.[20]

Chart 1



Results and Discussion

Synthesis of Mononuclear Palladium Compounds. Dichloro- (**1**) and chloro methyl (**2**) palladium complexes were synthesized in dichloromethane or diethyl ether by displacement of the labile ligand in [$PdCl_2$(COD)] or [PdClMe(COD)] (COD = η^4-1,4-cyclooctadiene) by the corresponding pyridylimine ligand **I** (Scheme 1).[12a,19] They were isolated in good yield as yellow to orange (**1**) or ochre (**2**) air-stable solids. Their solubility increases with the number of methyl groups on the pyridylimine ligand (**c** > **b** > **a**) or the metal center (**2** > **1**). Thus, compound **1c** is soluble in chlorinated solvents, partially

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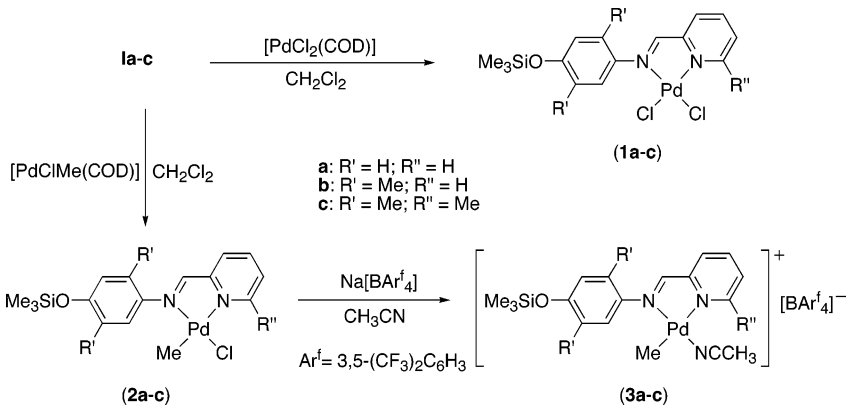
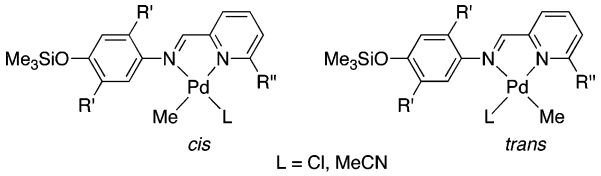
Scheme 1



soluble in toluene and ethers, and insoluble in alkanes, whereas **1a** is only partially soluble in dichloromethane. Compounds **2** are fairly soluble in ethers and aromatic or chlorinated solvents, although slow conversion to compounds **1** together with decomposition to black Pd(0) was observed in the last class of solvents.[21] Attempts to prepare complexes **2** by methylation of **1** with 1 equiv of LiMe or $SnMe_4$ led to impure chloro methyl compounds **2** with the formation of much metallic palladium. The cationic methyl acetonitrile complexes **3** were readily obtained in acetonitrile by the abstraction of the chloro ligand in **2** with Na[BAr^f_4] (BAr^f_4 = 3,5-$(CF_3)_2C_6H_3$) (Scheme 1). These cationic compounds are air-stable, hygroscopic orange-yellow solids, soluble in common organic solvents but not in alkanes.

The new compounds have been characterized by NMR, IR, MS, and elemental analysis (see Experimental Section). Complexes **2a** and **3a**,**b** consisted of a mixture of diastereoisomers, designated cis or trans with regard to the relative positions of the methyl and imine groups on the square-planar palladium environment (Figure 1). The assignment of NMR resonances



%	2a	2b	2c	3a	3b	3c
cis	76	100	100	20	44	100
trans	24	0	0	80	56	0

Figure 1. Diatereoisomeric composition for compounds **2** and **3**.

to each isomer is based on the nuclear Overhauser effect measured between the ^{1}H resonances of the Pd−Me group and the pyridylimine protons. The integration of those methyl resonances, at ca. 1 ppm, also was used for the determination of the cis/trans composition shown in Figure 1. The different diastereoisomer ratios observed in solution can be rationalized by a combination of steric and electronic arguments. Thus, cis isomers are favored for chloro complexes **2**, following Pearson's maximum hardness principle,[22] according to which the hardest part of the pyridylimine ligand, i.e., the imine group, is placed preferably trans to the softest ligand, i.e., the methyl group in **3** and the chloro group in **2**.[23] On the other hand, the cis isomer is favored for **2c** and **3c** because of the steric hindrance caused by the methyl substituent in the ortho position of the pyridine ring.[24]

The proton and carbon atom signals of the pyridylimine groups undergo large shifts in the NMR spectra of compounds **1**−**3** in comparison with the NMR data observed for ligands **I** (see Supporting Information).[19] The general remark is that proton and carbon resonances shift to lower field on complexation, as might be expected for a lowering in electron density of the N,N ligands.[25] The most affected chemical shifts are those due to the imine group and the pyridine ring, in a phenomenon termed the CIS effect (CIS = coordination-induced shift).[24] The remarkable negative CIS effect observed for H^9 ($\Delta\delta \cong -0.4$) and H^7 ($\Delta\delta \cong -0.3$) (the numbering scheme for the pyridylimine fragment is given in Chart 1) is explained by the fact that the transoid conformation of the free ligands **I** in solution[12a] changes to cisoid by coordination to the metal center (Scheme 1).[11b,24] Conversely, in compounds **1** and *cis*-**2** (Figure 1), H^{12} (or CH_3^{15}) shows the largest coordination shifts ($\Delta\delta \cong +0.6$), owing to the strong deshielding effect of the chloro ligand cis to the pyridyl ring. On the other hand, the chemical shifts of the Pd−Me, H^{12}, and the imine proton (H^7) are at δ 1.2, 8.63, and 8.31, respectively, for *trans*-**2a**, whereas they are at δ 0.77, 9.10, and 8.35, respectively, for *cis*-**2a** with the Pd−Me group closer to the shielding aromatic ring and with the electron-withdrawing and deshielding chloro ligand trans to the imine group. The ^{1}H, ^{13}C, and ^{19}F NMR data of the [BAr^f_4]$^-$ counterion are invariable for compounds **3**, in correspondence with a noncoordinating anion. The proton NMR spectra of these cationic complexes in CD_3CN show free acetonitrile resonances, indicating exchange between the free and coordinated solvent.

Mass spectra (EI/MS) for compounds **1**−**3** show the corresponding bidentate ligand ion peak **I**. The positive ion electrospray mass spectra (ESI+/MS) of compounds **1** and **2**, carried out in acetonitrile solutions, exhibit the fragments after the loss of a chloride anion and coordination of an acetonitrile molecule $[M - Cl + MeCN]^+$ and peaks due to dimetallic species formed by chloro bridges $[M_2 - Cl]^+$ (i.e., $[\{PdX(\mathbf{I})\}_2(\mu\text{-Cl})]$, X = Cl, Me). The formation of both types of species has been reported

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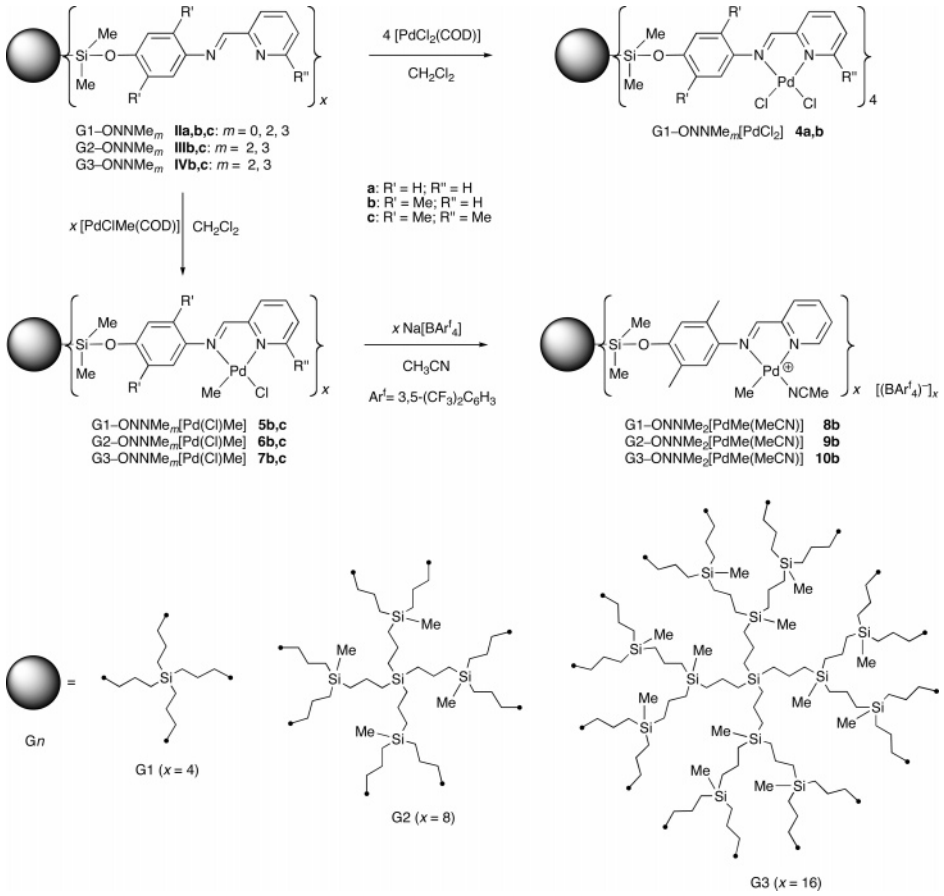
Scheme 2



to occur in related nickel and palladium complexes.[26] The cation parent ion peak $[M - BR_4]^+$ is observed for compounds **3** by ESI+/MS.

The IR spectra of compounds **1** and **2** show a single medium to strong absorption at ca. 1589−1596 cm^{-1}, together with a much weaker band, instead of the group of three intense absorptions observed in the range 1565−1627 cm^{-1} for the imine and pyridine groups in the free ligands **I**.[19] The disappearance or shift of C═N vibrations in the IR spectra of related complexes is explained as a result of the bonding of the pyridylimine ligand to the metal center, reducing the electron density in the C═N bond and, consequently, leading to a lower $\nu_{C=N}$ value.[11b] A single absorption appears at 1610 cm^{-1} in the cationic compounds **3**, probably due to the presence of the harder donor character of acetonitrile compared to that of the chloro ligand.

Synthesis and Characterization of Dendrimers. The pyridylimine ligands described above have been used to link carbosilane dendrimers and metal complexes by procedures similar to those applied in the preparation of complexes **1**−**3**. Thus, neutral and cationic polymetallic dendrimers of first to third generations containing 4, 8, or 16 dichloro, chloro methyl, or methyl acetonitrile palladium complexes at their periphery were prepared from the dendritic pyridylimine ligands G1-ONNMe$_m$ (**II**), G2-ONNMe$_m$ (**III**), and G3-ONNMe$_m$ (**IV**) (Scheme 2 and Figure 2). The neutral dendrimers G1-ONNMe$_m$-[$PdCl_2$] (**4a**,**b**) and Gn−ONNMe$_m$[PdClMe] (n = 1, **5b**,**c**; n = 2, **6b**,**c**; n = 3, **7b**,**c**) were obtained by reaction of **II**−**IV** and [$PdCl_2$(COD)] or [PdClMe(COD)] in CH_2Cl_2, and isolated as yellow to orange diamagnetic air-stable solids. Subsequent addition of Na[BAr^f_4] to the chloro(methyl)palladium dendrimers **5b**−**7b** in acetonitrile gave Gn−ONNMe$_2$[PdMe(MeCN)] (n = 1, **8b**; n = 2, **9b**; n = 3, **10b**), obtained as air-stable orange solids that become sticky oily solids in the presence of moisture or vapors of organic solvents.

An important issue related with metallodendrimers is their solubility. Peripheral polymetallic dendrimers are often less soluble as the number of metal centers increases, and this feature habitually renders impracticable the preparation of high-generation derivatives wholly metalated at their terminal functional groups. Compounds **4**−**10** are more soluble when the dendrimer generation is lower, the pyridylimine group bears more methyl substituents, the palladium metal is methylated, or the complex is cationic. Accordingly, the dichloro derivatives **4a**,**b** precipitate out from the CH_2Cl_2 solution during their preparation and are found to be only moderately soluble in very polar organic solvents such as DMSO. A similar behavior has been described for an alkylpyridylimine palladium derivative based on a first-generation poly(propyleneimine) dendrimer (DAB).[27] This lack of solubility explains why the dichloropalladium dendrimers were prepared only in the first generation. Surprisingly, attempts to synthesize compound **4c** failed, giving a mixture of inseparable products.

The solubility of these systems is significantly enhanced when methyl groups are present on the pyridylimine ligands and on each palladium center and when an acetonitrile molecule is coordinated to cationic metal centers. Thus, neutral chloro(methyl)- and cationic methyl(acetonitrile)palladium dendrimers, which are soluble in dichloromethane, THF, or acetonitrile and

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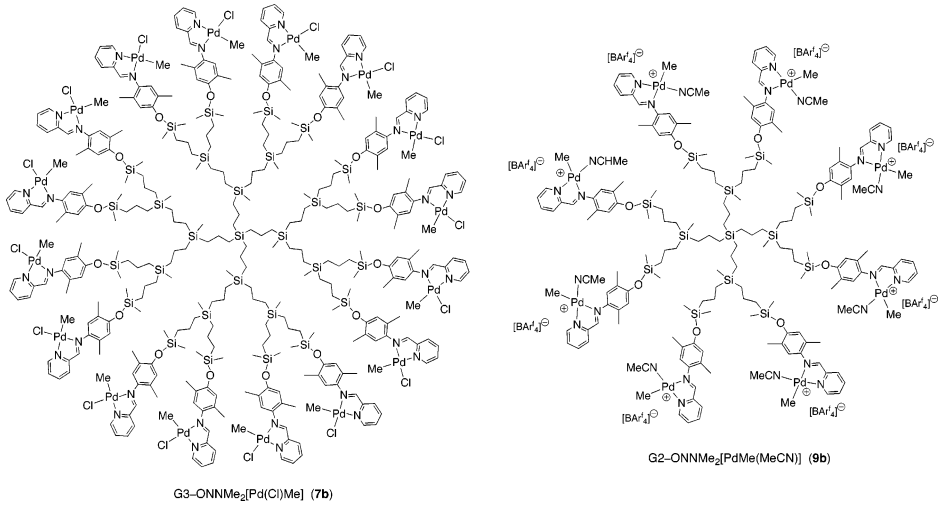

Figure 2. Metallodendrimers **7b** and **9b**.

slightly soluble in diethyl ether or toluene were readily synthesized not only in the first generation (**5** and **8**) but also in the second (**6** and **9**) and third generations (**7** and **10**). As pointed out for the monometallic complexes, solutions of these compounds in chlorinated solvents slowly decompose by Pd-Me/Pd−Cl exchange, and black Pd(0) becomes visible after about 24 h.

Palladium dendrimers have been characterized by NMR and IR spectroscopy. However, mass spectrometric techniques, including MALDI-TOF, were not informative. Elemental analyses were satisfactory for the metallic dendrimers, with the exception of those for the third-generation neutral complexes **7b**,**c** and polycationic compounds **9b** and **10b**, which are slightly low in the percent of C, most likely due to persistent trapping of some impurities in the dendritic matrix. The broad characteristics of the ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of the carbosilane framework in dendrimers **4**−**10** are almost identical with those described for the metal-free dendrimers,[19] whereas chemical shifts of the terminal pyridylimine groups are comparable with those found for the model complexes **1**−**3** and, therefore, CIS effects are parallel to those described above for mononuclear complexes. Accordingly, in general the most affected protons are H^{12} ($\Delta\delta \cong +0.3$ for dichloropalladium dendrimers **4a**,**b** and chloro(methyl)palladium dendrimers **5b**−**7b**) and CH_3[15] ($\Delta\delta \cong +0.4$ for dendrimers **5c**−**7c**), due to the presence of a chloro ligand cis to the pyridyl ring, and the H^{12} CIS effect becomes negative for the cationic dendrimers **8b**−**10b**, with acetonitrile instead of chloro ligands ($\Delta\delta \cong -0.4$). Again, H^9 and H^7 shift to higher field ($\Delta\delta$ ranging from −0.1 to −0.5 ppm) in all metallodendrimers because the free ligands rotate to a cisoid conformation to coordinate to a metal center.

The isomer composition (cis:trans ratio) in dendrimers **5**−**10** also follows a behavior parallel to that observed for the related mononuclear complexes. Thus, only the cis isomer is observed by NMR for the chloro(methyl)palladium dendrimers **5b**,**c**, **6b**,**c**, and **7b**,**c**, as was observed for the monometallic complexes **2b**,**c**. Diastereoisomer ratios for cationic dendrimers **8b**−**10b** are difficult to discern, because their spectra show broad and overlapped resonances of the isomers. Nevertheless, we estimate a cis:trans ratio of about 40:60, as judged by the result described for the reference cationic complex **3b** and by the relative integral of H^{12}, which appears clearly defined for each isomer in the NMR spectra of polycationic dendrimers. The typical broadened and unstructured NMR resonances observed for dendrimers on increasing the generation[28] is favored in the cationic dendrimers by the positive charge that repels the metal centers from each other in a radial-spherical mode, contributing to restrict the mobility of the dendrimer arms. In fact, very complex and inscrutable ^{13}C NMR spectra were registered for the second- and third-generation derivatives **9** and **10**.

The IR spectra of all metallodendrimers **4**−**10** are also consistent with coordination of the pyridylimine groups, showing a strong absorption at ca. 1589−1596 cm^{-1} for neutral compounds **4**−**7** and at ca. 1610 cm^{-1} for the cationic dendrimers **8**−**10**, instead of the group of three intense absorptions observed in the range 1565−1627 cm^{-1} for the corresponding free dendritic ligands **II**−**IV**.[19]

CO/4-*tert*-Butylstyrene Catalyses using (Pyridylimine)-palladium Compounds. Compounds **3** and polycationic dendrimers **8b**−**10b** were used as single-component catalysts for the copolymerization of carbon monoxide and 4-*tert*-butylstyrene (TBS), under the same mild conditions using the same concentration of palladium centers; the results are summarized in Table 1. Alternatively, cationic active species were generated in situ from the chloro(methyl)palladium compounds **2** and **5c** using $Na[BAr^f_4]$ in the presence of acetonitrile.

As shown in Table 1, all the catalysts produced polyketone, with the exception of precursors with a methyl group on the 12-position of the pyridine ring (**2c** and **5c** activated with $Na[BAr^f_4]$/MeCN and **3c**). According to earlier findings with related complexes, the presence of a methyl substituent ortho to the coordinating N atom of the pyridine causes enough hindrance to encumber either the CO insertion or the coordination−insertion of the substrate.[7c,8] Also, an interference effect attributable to an excess of competing acetonitrile must be responsible for lower activities when the cationic species are prepared in situ, in comparison to the observed behavior for the isolated cationic compounds (entries 1 and 2 vs entries 4 and 5). The productivities of the active catalysts ($(0.3-2.6) \times 10^3$ g of copolymer (mol of Pd)$^{-1}$ h^{-1}) are comparable to those found for other precursors containing different N,N ligands.[8,9] Additionally, the productivity increases in reactions carried out in neat TBS, in the absence of CH_2Cl_2 (compare entries 5 vs 7 or 9−11 vs 12−14), in agreement with the generally accepted copolymerization mechanism with styrene insertion as the rate-determining step.[6,7e] Degradation of the catalysts is evident in

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Table 1. CO/TBS Copolymerization Catalyzed by Complexes 2 and 3 and Pd Dendrimers 5c and 8b−10b[a]

entry	precursor	CP yield (g)[d]	activity[e]	% conversn[f]	% s-CP[g]	g of CP/mol of Pd	M_w[h]	PDI[h]
1	**2a**[b]	0.095	0.31	6.6	64	7 600	n.d.[i]	n.d.[i]
2	**2b**[b]	0.130	0.43	8.9	70	10 400	n.d.[i]	n.d.[i]
3	**2c**[b]							
4	**3a**	0.130	0.43	8.9	66	10 400	4633	1.70
5	**3b**	0.243	0.81	16.7	71	19 440	18 293	2.12
6	**3c**							
7	**3b**[c]	0.543	1.81	20.9	60	43 440	79 733	2.87
8	**5c**[b] (G1-ONNMe$_3$[Pd(Cl)Me])							
9	**8b** (G1-ONNMe$_2$[Pd(L)Me]$^+$)	0.100	0.33	6.8	70	8 000	22 282	1.80
10	**9b** (G2-ONNMe$_2$[Pd(L)Me]$^+$)	0.099	0.33	6.8	67	7 920	11 320	1.56
11	**10b** (G3-ONNMe$_2$[Pd(L)Me]$^+$)	0.164	0.54	11.2	66	51 200	20 741	2.70
12	**8b**[c] (G1-ONNMe$_2$[Pd(L)Me]$^+$)	0.729	2.43	28.1	66	58 320	53 937	2.79
13	**9b**[c] (G2-ONNMe$_2$[Pd(L)Me]$^+$)	0.750	2.50	28.9	64	60 000	43 583	3.00
14	**10b**[c] (G3-ONNMe$_2$[Pd(L)Me]$^+$)	0.792	2.64	30.6	63	63 360	38 775	3.64
15	**3b**[c,j]	0.720	0.60	28.5	60	57 600	82 951	2.77
16	**9b**[c,j] (G1-ONNMe$_2$[Pd(L)Me]$^+$)	1.005	0.84	39.1	60	80 400	42 702	3.45

[a] Copolymerization conditions: 5 mL of dichloromethane; n(Pd) = 12.5 μmol; V(TBS) = 1.4 mL; n(TBS)/n(Pd) = 620; t_p = 24 h; T_p = 20 °C; P_{CO} = 1 atm. [b] Activated in situ by addition of 1 equiv of Na[BAr$^f_4$] in a CH_2Cl_2/MeCN mixture. [c] Same conditions but in neat TBS: V(TBS) = 2.5 mL; n(TBS)/n(Pd) = 1100. [d] CP = copolymer. [e] In untis of kg of CP (mol of Pd)$^{-1}$ h^{-1}. [f] TBS conversion calculated from the CP weight. [g] Percent of syndiotactic triads (*uu*) determined from ^{13}C NMR intensities of ipso carbon atom resonances. [h] Determined by GPC in THF at 40 °C. [i] Not determined. [j] t_p = 96 h.

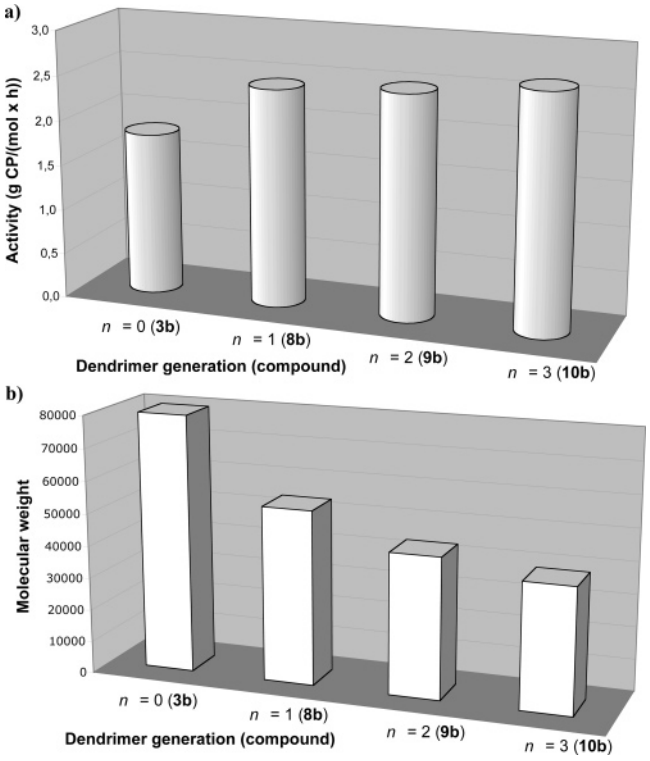

Figure 3. (a) Activities for Gn-ONNMe$_2$[Pd(MeCN)Me$^+$] and (b) copolymer M_w values obtained using neat TBS as a solvent.

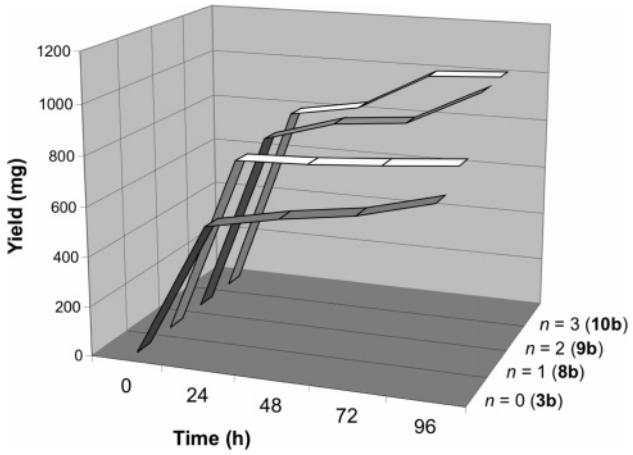

Figure 4. Effect of time on yield of copolymer produced by compounds Gn-ONNMe$_2$[Pd(L)Me]$^+$ in neat TBS.

all of the polymerizations, by the appearance of some metallic palladium over the course of the reaction, and solutions become very viscous in neat aromatic monomer as a solvent.

Among the mononuclear compounds, the most active precursors are those containing methyl substituents on the aryl ring (compounds "**b**", entry 1 vs 2 or entry 4 vs 5). A parallel result was found in ethylene polymerization reactions with analogous nickel compounds activated with MAO.[19b] In CH_2Cl_2, the cationic dendrimers are less active than the corresponding monometallic derivative (entries 5 and 9−11), but the opposite trend is observed in neat TBS, where a slight increase of the productivity is additionally observed with the generation of the dendrimer, giving the third-generation dendrimer **10b** the highest conversion (Table 1, Figure 3a).

An important aspect of these types of catalysts is their stability or durability under catalytic conditions, because the chain transfer process is accompanied, in most cases, by decomposition of the active centers (e.g., reduction of unstable Pd(II) hydride species formed by β-H elimination).[6] Some workers overcame this problem by including quinones, combined with a protic solvent, in the catalytic system.[8] Metallic palladium(0) appeared in suspension after 24 h of reaction time with compounds **2**−**10**, although for compounds "**b**" the initial color of their solutions (yellow-orange) remains very intense, as a sign of catalyst endurance. More copious precipitation of black particles was observed in the reactions carried out in CH_2Cl_2 as compared to those in neat TBS. Faster deactivation of the catalysts induced by the solvent, through Pd−C/Pd−Cl bond exchange and Pd(0) formation, might help in the above-noted decrease of productivity in CH_2Cl_2.[21] Analyses of the evolution of yields over a 96 h period in neat TBS (Figure 4) or CH_2Cl_2 using monometallic complex **3b** and dendrimers **8b**−**10b** show apparently that the dendritic supports have no noticeable effect on the lifetime of the active species. Therefore, the reverse activity shown by monometallic versus dendritic catalysts in neat TBS and CH_2Cl_2 is more likely to be caused by the different rates of the insertion steps than by catalyst degradation. It is well-known that adaptation of the dendritic conformation to the polarity of the solvent can lead to changes in the catalytic behavior.[29] On the other hand, it is remarkable that activities seem to stabilize after 24 h, and their values are, 4 days later,

about 10% of those registered during the first day. In a longer run with compound **3b** the CP yield (815 mg) still rises after 8 days.

The observed molecular weights of the polyketones produced (up to $M_w = 80\,000$) are within the upper range reported for other bis-nitrogen systems, while showing wider molecular weight distributions (PDI $= M_w/M_n = 1.5-3.5$), in particular those obtained from neat TBS.[7−9,13] The ratio of mass of polymer produced per mole of palladium to M_w, which indicates the number of chains produced by the Pd center, is in most cases close to 1 (Table 1). All these data point to a mechanism in which the polymer chain grows until the active complex decomposes. Catalysts with a greater stability in relation to the rate of chain growth should give higher molecular weights and polydispersities, as observed for cationic monometallic compound "**b**", whose improved stability was mentioned above (entry 4 vs 5), or in the absence of solvent (entries 5, 9, 10, and 11 vs 7, 12, 13, and 14). On the other hand, no linear correlation is observed between M_w and the monomer conversion, while molecular weights, and polydispersities, are insignificantly affected by the polymerization time (entry 7 vs 15, or 13 vs 16). Moreover, the ratio of mass of polymer produced per mole of palladium to M_w is in several cases close to but appreciably greater than 1 (entries 4, 11, 14, and 16). This clearly means that chain transfer processes must be accompanied by decomposition of the active centers in most instances, but some of them should be able to restart the polymerization cycle.

Among the reactions carried out in CH_2Cl_2, the trend observed with the dendrimer generation is unclear. In neat TBS, however, the increase in generation results in a decrease in M_w (Figure 3b) and in broader molecular weight distributions (Table 1, entries 7 and 12−14). These results might be related to our previous work with nickel complexes for ethylene polymerization in which the changes in the oligomer/polymer distribution by the generation of the dendritic precursor were interpreted as a consequence of the steric pressure that bulkier dendrimers caused on the growing chains, enhancing chain transfer processes and favoring the formation of an assortment of shorter polymers.[19]

As far as the microstructure of the produced polyketone is concerned, quantitative examination of the $^{13}C\{^1H\}$ NMR spectra shows that all active catalytic systems afford a regioregular copolymer with a degree of syndiotacticity above 60% (*uu* triad proportion, Table 1), indicating that the processes proceed mainly by a chain-end stereocontrolled mechanism.[7,8,30,31] The syndiotactic component is slightly higher in copolymer produced by compounds "**b**" (e.g., compare entries 1 and 2) and in the presence of CH_2Cl_2 (e.g., entry 5 vs 7) and slightly decreases at higher metallodendrimer generation (e.g., compare entries 5 and 9−11). At this point, it is worth recalling that the catalytic mixture becomes very viscous in reactions carried out without solvent and, therefore, the lower syndiotacticity in neat TBS might be ascribed to a stalled motion of the reactants and the growing chain, in combination with an easier displacement of the coordinated carbonyl group of the polymer chain by an augmented concentration of comonomer.[8b] The lowering in *uu* triad portions with increasing dendrimer generation could be the result of the increased size of the dendritic precursor, which diminishes the effectiveness of the chain-end control, in a way similar to that in which the stereoregularity of styrene/CO copolymers produced by alkylpyridylimine derivatives is affected by the bulkiness of the alkyl group of the ligand.[13] Finally, syndiotacticities are insignificantly affected by the polymerization time (compare entry 7 vs 15 or 13 vs 16).

Conclusion

In summary, a series of neutral and cationic palladium coordination compounds with a set of versatile monochelating or carbosilane-dendritic pyridylimine ligands has been synthesized and characterized. The cationic compounds are found to be active catalysts for alternating syndiospecific copolymerization of carbon monoxide and 4-*tert*-butylstyrene, and their catalytic performance is definitely sensitive to the dendrimer generation. Several dendritic effects on activity or selectivity have been reported to date.[16d,19,32] In this paper, we have shown an example in which the presence of the dendrimer is almost irrelevant in terms of stability of the active species, but the dendritic support affects the activity of the active center, and the molecular weight and weight distribution, as well as the stereoregularity of the polyketones produced from CO/4-*tert*-butylstytrene.

Experimental Section

Reagents and General Techniques. All operations were performed under an argon atmosphere using Schlenk or drybox techniques. Unless otherwise stated, reagents were obtained from commercial sources and used as received. $[PdCl_2(COD)]$,[33] $[PdClMe(COD)]$,[24b] $Na[BAr^f_4]$ ($Ar^f = 3,5\text{-}(CF_3)_2C_6H_3$),[34] pyridylimine ligands **I**,[12a,19] and carbosilane−pyridylimine dendritic ligands G*n*ONNMe$_m$ **II** ($n = 1$), **III** ($n = 2$), and **IV** ($n = 3$)[19] were prepared according to literature procedures. Solvents were dried prior to use and distilled under argon as described elsewhere.[35] NMR spectra were recorded on Varian Unity 500+, Varian Unity VR-300, and Varian Unity 200 NMR spectrometers. Chemical shifts δ are reported in ppm referenced to $SiMe_4$ for ^1H, ^{13}C, and ^{29}Si, and assignments for the pyridylimine ligands are according to the numbering of the positions depicted in Chart 1. IR spectra were recorded on a Perkin-Elmer FT-IR Spectrum-2000 spectrophotometer. Elemental analyses and mass spectra were performed by the Microanalytical Laboratories of the University of Alcalá (MLUAH) on a Heraeus CHN-O-Rapid microanalyzer and on Hewlett-Packard 5988A Quadruplo (EI) and Thermo Quest Finningan Automass Multi (ESI) mass spectrometers. Polyketone molecular weight determinations were made by the MLUAH on Waters GPCV 2000 equipment operating at 40 °C with THF solvent and polystyrene calibration standards.

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Preparation of Dichloropalladium Complexes 1. The synthesis of the dichloropalladium compounds **1a**−**c** is exemplified by the preparation of **1a**.

PdCl$_2$(Me$_3$SiO-4-Ph-N=CH-2-Py) (1a). [PdCl$_2$(COD)] (266 mg, 0.94 mmol) was added to ligand **Ia** (254 mg, 0.94 mmol) in dichloromethane (50 mL), and the resulting solution was stirred at room temperature overnight. Removal of the solvent, followed by washings of the residue with pentane (4 × 15 mL), gave compound **1a** as a yellow solid. Yield: 370 mg (88%). Anal. Calcd for $C_{15}H_{18}N_2OSiCl_2Pd$ (447.73): C, 40.24; H, 4.05; N, 6.26. Found: C, 39.86; H, 3.71; N, 6.31. ^{1}H NMR ($CDCl_3$): δ 0.28 (s, 9H, $SiMe_3$), 6.77 (AA′ part of an AA′BB′ spin system, 2H, H^{3,5}), 7.37 (BB′ part of an AA′BB′ spin system, 2H, H^{2,6}), 7.61 (pt, 1H, H^{11}), 7.88 (d, 1H, $J_{H,H}$ = 7.2 Hz, H^9), 8.10 (pt, 1H, H^{10}), 8.17 (s, 1H, H^7), 9.27 (d, 1H, $J_{H,H}$ = 5.6 Hz, H^{12}). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 0.4 ($SiMe_3$), 119.5 (C^{3,5}), 125.6 (C^{2,6}), 128.0 (C^9), 128.2 (C^{11}), 140.3 (C^{10}), 140.5 (C^1), 151.0 (C^{12}), 155.4 (C^4), 156.5 (C^8), 166.8 (C^7). IR (KBr): ν 1617 (w), 1596 cm^{-1} (s, C=N). MS (70 eV, EI): *m*/*z* 270 [**Ia**]$^+$. MS (ESI+ in CH_3CN): *m*/*z* 861 [M_2 − Cl]$^+$, 489 [M + CH_3CN]$^+$, 454 [M − Cl + CH_3CN]$^+$.

PdCl$_2$[Me$_3$SiO-4-(2,5-Me$_2$Ph)-N=CH-2-Py] (1b). Yellow solid. Yield: 64%. Anal. Calcd for $C_{17}H_{22}N_2OSiCl_2Pd$ (475.79): C, 42.92; H, 4.66; N, 5.89. Found: C, 43.31; H, 4.69; N, 6.07. ^{1}H NMR ($CDCl_3$): δ 0.26 (s, 9H, $SiMe_3$), 2.10 (s, 3H, Me^{14}), 2.45 (s, 3H, Me^{13}), 6.56 (s, 1H, H^3), 6.88 (s, 1H, H^6), 7.71 (pt, 1H, H^{11}), 7.87 (d, 1H, $J_{H,H}$ = 7.3 Hz, H^9), 8.15 (pt and s overlapping, 2H, H^{10} and H^7), 9.36 (d, 1H, $J_{H,H}$ = 5.9 Hz, H^{12}). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 0.6 ($SiMe_3$), 16.1 and 19.1 (Me^{13,14}), 120.5 (C^3), 124.7 (C^6), 127.0 (C^5), 127.6 (C^9), 128.5 (C^{11}), 130.1 (C^2), 140.1 (C^{10}), 140.4 (C^1), 151.5 (C^{12}), 154.1 (C^4), 154.8 (C^8), 167.9 (C^7). IR (KBr): ν 1615 (w), 1594 cm^{-1} (m, C=N). MS (70 eV, EI): *m*/*z* 298 [**Ib**]$^+$. MS (ESI+ in CH_3CN): *m*/*z* 917 [M_2 − Cl]$^+$, 482 [M − Cl + CH_3-CN]$^+$.

PdCl$_2$[Me$_3$SiO-4-(2,5-Me$_2$Ph)-N=CH-2-(6-MePy)] (1c). Yellow solid. Yield: 72%. Anal. Calcd for $C_{18}H_{24}N_2OSiCl_2Pd$ (489.81): C, 44.14; H, 4.94; N, 5.72. Found: C, 43.89; H, 4.86; N, 5.90. ^{1}H NMR ($CDCl_3$): δ 0.26 (s, 9H, $SiMe_3$), 2.12 (s, 3H, Me^{14}), 2.44 (s, 3H, Me^{13}), 3.16 (s, 3H, Me^{15}), 6.56 (s, 1H, H^3), 6.86 (s, 1H, H^6), 7.47 (d, 1H, $J_{H,H}$ = 7.8 Hz, H^{11}), 7.66 (d, 1H, $J_{H,H}$ = 7.0 Hz, H^9), 7.94 (pt, 1H, H^{10}), 8.10 (s, 1H, H^7). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 0.8 ($SiMe_3$), 16.3 and 19.2 (Me^{13,14}), 27.8 (Me^{15}), 120.3 (C^3), 124.2 (C^6), 125.4 (C^9), 126.8 (C^5), 130.8 (C^{11}), (C^2 not observed), 138.8 (C^{10}), 140.4 (C^1), 154.0 (C^4), 154.7 (C^8), 167.3 (C^{12}), 167.6 (C^7). IR (KBr): ν 1622 (w), 1594 cm^{-1} (m, C=N). MS (ESI+ and APCI in CH_3CN): *m*/*z* 945 [M_2 − Cl]$^+$, 496 [M − Cl + CH_3CN]$^+$, 312 [**Ic**]$^+$.

Preparation of Chloro(methyl)palladium Complexes 2. The synthesis of the chloro(methyl)palladium compounds **2a**−**c** is exemplified by the preparation of **2a**.

PdClMe(Me$_3$SiO-4-Ph-N=CH-2-Py) (2a). [PdClMe(COD)] (145 mg, 0.55 mmol) was added to **Ia** (148 mg, 0.55 mmol) in diethyl ether or dichloromethane (10 mL), and the resulting orange solution was stirred at room temperature for 2 h. The solvent was removed under vacuum, and the residue was washed with pentane (2 × 20 mL) and cold diethyl ether (2 × 10 mL) to give compound **2a** as a yellow solid, consisting of a mixture of 76% cis and 24% trans isomers, according to the relative position of the methyl ligand with regard to the position of the imine nitrogen. When needed, purer samples were obtained by repetition of the operations: redissolution in CH_2Cl_2, followed by filtration and precipitation by adding pentane. Yield: 170 mg (73%). Anal. Calcd for $C_{16}H_{21}N_2$-$OSiClPd$ (427.31): C, 44.97; H, 4.95; N, 6.56. Found: C, 45.09; H, 4.96; N, 6.66. NMR data for the major isomer are as follows. ^{1}H NMR ($CDCl_3$): δ 0.24 (s, 9H, $SiMe_3$), 0.77 (s, 3H, PdMe), 6.83 (AA′ part of an AA′BB′ spin system, 2H, H^{3,5}), 7.03 (BB′ part of an AA′BB′ spin system, 2H, H^{2,6}), 7.64 (pt, 1H, H^{11}), 7.70 (d, 1H, $J_{H,H}$ = 7.5 Hz, H^9), 7.96 (pt, 1H, H^{10}), 8.35 (s, 1H, H^7), 9.10 (d, 1H, $J_{H,H}$ = 4.6 Hz, H^{12}). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 0.3 ($SiMe_3$), 1.7 (PdMe), 120.2 (C^{3,5}), 123.7 (C^{2,6}), 126.3 (C^9), 128.3 (C^{11}), 138.5 (C^{10}), 142.2 (C^1), 149.6 (C^{12}), 151.6 (C^8), 155.3 (C^4), 165.9 (C^7). NMR data for the minor isomer are as follows. ^{1}H NMR ($CDCl_3$): δ 0.23 (s, 9H, $SiMe_3$), 1.20 (s, 3H, PdMe), 6.81 (AA′ part of an AA′BB′ spin system, 2H, H^{3,5}), 7.47 (BB′ part of an AA′BB′ spin system, 2H, H^{2,6}), 7.57 (pt, 1H, H^{11}), 7.74 (d partially obscured by the major isomer, 1H, H^9), 8.02 (pt, 1H, H^{10}), 8.31 (s, 1H, H^7), 8.63 (d, 1H, $J_{H,H}$ = 5.3 Hz, H^{12}). IR (KBr): ν 1614 (w), 1598 cm^{-1} (m, C=N). MS (70 eV, EI): *m*/*z* 270 [**Ia**]$^+$. MS (ESI+ in CH_3CN): *m*/*z* 819 [M_2 − Cl]$^+$, 432 [M − Cl + CH_3CN]$^+$.

PdClMe[Me$_3$SiO-4-(2,5-Me$_2$Ph)-N=CH-2-Py] (2b). Yellow solid. Yield: 66%. Anal. Calcd for $C_{18}H_{25}N_2OSiClPd$ (455.37): C, 47.48; H, 5.53; N, 6.15. Found: C, 47.14; H, 5.47; N, 6.14. ^{1}H NMR ($CDCl_3$): δ 0.27 (s, 9H, $SiMe_3$), 0.68 (s, 3H, PdMe), 2.14 (s, 3H, Me^{14}), 2.24 (s, 3H, Me^{13}), 6.62 (s, 1H, H^3), 6.72 (s, 1H, H^6), 7.71 (m, 2H, H^9 and H^{11}), 8.00 (pt, 1H, H^{10}), 8.35 (s, 1H, H^7), 9.14 (d, 1H, $J_{H,H}$ = 4.4 Hz, H^{12}). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 0.5 ($SiMe_3$), 0.7 (PdMe), 16.2 and 17.9 (Me^{13,14}), 120.6 (C^3), 123.8 (C^6), 126.1 (C^9), 127.2 (C^5), 128.3 (C^2), 128.4 (C^{11}), 138.5 (C^{10}), 141.0 (C^1), 149.7 (C^{12}), 151.3 (C^8), 152.9 (C^4), 166.6 (C^7). IR (KBr): ν 1616 (w), 1586 cm^{-1} (s, C=N). MS (70 eV, EI): *m*/*z* 298 [**Ib**]$^+$. MS (ESI+ in CH_3CN): *m*/*z* 875 [M_2 − Cl]$^+$, 460 [M − Cl + CH_3CN]$^+$.

PdClMe[Me$_3$SiO-4-(2,5-Me$_2$Ph)-N=CH-2-(6-MePy)] (2c). Yellow solid. Yield: 81%. Anal. Calcd for $C_{19}H_{27}N_2OSiClPd$ (469.39): C, 48.62; H, 5.80; N, 5.97. Found: C, 48.29; H, 5.62; N, 6.11. ^{1}H NMR ($CDCl_3$): δ 0.26 (s, 9H, $SiMe_3$), 0.83 (s, 3H, PdMe), 2.14 (s, 3H, Me^{14}), 2.24 (s, 3H, Me^{13}), 3.08 (s, 3H, Me^{15}), 6.60 (s, 1H, H^3), 6.71 (s, 1H, H^6), 7.47 (d, 1H, $J_{H,H}$ = 8.0 Hz, H^{11}), 7.49 (d, 1H, $J_{H,H}$ = 7.5 Hz, H^9), 7.82 (pt, 1H, H^{10}), 8.33 (s, 1H, H^7). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 0.6 ($SiMe_3$), 4.6 (PdMe), 16.2 and 17.9 (Me^{13,14}), 25.8 (Me^{15}), 120.6 (C^3), 124.1 (C^6), 124.6 (C^9), 127.2 (C^5), 128.5 (C^2), 130.2 (C^{11}), 137.9 (C^{10}), 141.1 (C^1), 151.1 (C^8), 152.7 (C^4), 164.5 (C^{12}), 167.7 (C^7). IR (KBr): ν 1625 cm^{-1} (w), 1591 cm^{-1} (s, C=N). MS (70 eV, EI): *m*/*z* 312 [**Ic**]$^+$. MS (ESI+ in CH_3CN): *m*/*z* 903 [M_2 − Cl]$^+$, 474 [M − Cl + CH_3-CN]$^+$.

Preparation of Cationic Methylpalladium Complexes 3. The synthesis of the cationic compounds **3a**−**c** is exemplified by the preparation of **3a**.

[PdMe(MeCN)(Ia)]$^+$[BAr$^f_4$]$^-$ (3a). Compound **2a** (75 mg, 0,-175 mmol) and Na[BAr$^f_4$] (Ar^f = 3,5-$(CF_3)_2C_6H_3$; 155.5 mg, 0.175 mmol) were combined in a Schlenk tube and stirred in acetonitrile (10 mL) at room temperature overnight. The greenish yellow suspension was evaporated to dryness, the residue was dissolved in dichloromethane (2 × 10 mL), and the resulting yellow solution was filtered. Removal of the solvent under reduced pressure gave **3a** as an orange-yellow oily solid, consisting of a mixture of 20% cis and 80% trans isomers, according to the relative position of the methyl ligand with regard to the position of the imine nitrogen. The compound can be purified by redissolution in CH_2Cl_2, followed by filtration and precipitation by addition of pentane, isolating **3a** as a yellow solid. Yield: 130 mg (57%). Anal. Calcd for $C_{50}H_{36}N_3$-$OSiPdBF_{24}$ (1296.14): C, 46.33; H, 2.80; N, 3.24. Found: C, 46.20; H, 2.74; N, 3.31. NMR data for the major isomer are as follows. ^{1}H NMR ($CDCl_3$): δ 0.27 (s, 9H, $SiMe_3$), 1.12 (s, 3H, PdMe), 2.17 (s, 3H, CH_3CN), 6.91 (AA′ part of an AA′BB′ spin system, 2H, H^{3,5}), 7.15 (BB′ part of an AA′BB′ spin system, 2H, H^{2,6}), 7.49 (broad s, 4H, Ar^f H$_p$), 7.57 (pt, 1H, H^{11}), 7.68 (broad s, 9H, H^9 and Ar^f H$_o$ overlapping), 7.96 (pt, 1H, H^{10}), 8.25 (s, 1H, H^7), 8.43 (d, 1H, $J_{H,H}$ = 5.3 Hz, H^{12}). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 0.1 ($SiMe_3$), 3.0 (PdMe), 4.9 (CH_3CN), 117.4 (Ar^f C$_p$), 120.9 (C^{3,5}), 123.0 (C^{2,6}), 124.4 (q, $J_{C,F}$ = 272.1 Hz, CF_3), 128.4 (C^9 and C^{11}), 128.8 (q, $J_{C,F}$ = 29.0 Hz, Ar^f C$_m$), 134.7 (Ar^f C$_o$), 140.3 (C^1), 140.6 (C^{10}), 149.2 (C^{12}), 155.7 (C^8), 157.2 (C^4), 159.5 (C^7), 161.6 (q, $J_{C,B}$ = 49.5 Hz, Ar^f C$_{ipso}$). NMR data for the minor isomer are as

follows. ^{1}H NMR ($CDCl_3$): δ 0.28 (s, 9H, $SiMe_3$), 0.84 (s, 3H, PdMe), 2.30 (s, 3H, CH_3CN), 6.84 (AA′ part of an AA′BB′ spin system, 2H, $H^{3,5}$), 7.13 (BB′ part of an AA′BB′ spin system, 2H, $H^{2,6}$), 7.42 (pt, 1H, H^{11}), 7.49 (broad s, 4H, Ar^f H_p), 7.68 (broad s, 9H, H^9 and Ar^f H_o overlapping), 7.88 (pt, 1H, H^{10}), 8.22 (s, 1H, H^7), 8.31 (d, 1H, $J_{H,H}$ = 5.1 Hz, H^{12}). ^{19}F{^{1}H} NMR ($CDCl_3$): δ −106.3 (s, CF_3). IR (KBr): ν 1610 cm^{-1} (m, C═N). MS (ESI+ in CH_3CN): *m*/*z* 432 [M − BAr^f_4]$^+$, 270 [**Ia**]$^+$. MS (ESI− in CH_3CN): *m*/*z* 863 [BAr^f_4]$^-$.

[PdMe(MeCN)(Ib)]$^+$[BAr$^f_4$]$^-$ (3b). Orange-yellow solid. Mixture of 44% cis and 56% trans isomers. Yield: 69%. Anal. Calcd for $C_{52}H_{40}N_3OSiPdBF_{24}$ (1324.19): C, 47.17; H, 3.04; N, 3.17. Found: C, 46.80; H, 2.94; N, 3.17. NMR data for the major isomer are as follows. ^{1}H NMR ($CDCl_3$): δ 0.27 (s, 9H, $SiMe_3$), 1.08 (s, 3H, PdMe), 2.04 (s, 3H, Me^{14}), 2.15 (s, 3H, CH_3CN), 2.31 (s, 3H, Me^{13}), 6.66 (s, 1H, H^3), 6.74 (s, 1H, H^6), 7.49 (broad s, 4H, Ar^f H_p), 7.58 (pt, 1H, H^{11}), 7.68 (broad s, 9H, H^9 and Ar^f H_o overlapping), 8.00 (pt, 1H, H^{10}), 8.20 (s, 1H, H^7), 8.42 (d, 1H, $J_{H,H}$ = 5.0 Hz, H^{12}). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 0.6 ($SiMe_3$), 2.9 (PdMe), 4.6 (CH_3CN), 16.3 and 18.2 ($Me^{13,14}$), 117.3 (Ar^f C_p), 120.9 (C^3), 123.0 (C^6), 124.3 (q, $J_{C,F}$ = 271.7 Hz, CF_3), (C^2 and C^5 not assigned), 128.3 (C^9), 128.5 (C^{11}), 128.7 (q, $J_{C,F}$ = 28.1 Hz, Ar^f C_m), 134.5 (Ar^f C_o), 139.7 (C^1), 140.4 (C^{10}), 149.2 (C^{12}), 154.1 (C^8), 155.3 (C^4), 161.3 (q, $J_{C,B}$ = 49.6 Hz, Ar^f C_{ipso}), 161.4 (C^7). NMR data for the minor isomer are as follows. ^{1}H NMR ($CDCl_3$): δ 0.28 (s, 9H, $SiMe_3$), 0.72 (s, 3H, PdMe), 2.14 (s, 3H, Me^{14}), 2.17 (s, 3H, Me^{13}), 2.30 (s, 3H, CH_3CN), 6.64 (s, 1H, H^3), 6.69 (s, 1H, H^6), 7.40 (pt, 1H, H^{11}), 7.49 (broad s, 4H, Ar^f H_p), 7.68 (broad s, 9H, H^9 and Ar^f H_p overlapping), 7.85 (pt, 1H, H^{10}), 8.27 (s, 1H, H^7), 8.31 (d, 1H, $J_{H,H}$ = 5.0 Hz, H^{12}). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 0.7 ($SiMe_3$), 3.3 (PdMe), 6.4 (CH_3CN), 16.4 and 17.8 ($Me^{13,14}$), 117.3 (Ar^f C_p), 120.8 (C^3), 123.5 (C^6), 124.3 (q, $J_{C,F}$ = 271.7 Hz, CF_3), (C^1, C^2, and C^5 not assigned), 127.7 (C^9), 129.4 (C^{11}), 128.7 (q, $J_{C,F}$ = 28.1 Hz, Ar^f C_m), 134.5 (Ar^f C_o), 140.0 (C^{10}), 148.6 (C^{12}), 150.2 (C^8), 153.6 (C^4), 161.3 (q, $J_{C,B}$ = 49.6 Hz, Ar^f C_{ipso}), 169.9 (C^7). ^{19}F{^{1}H} NMR ($CDCl_3$): δ −106.3 (s, CF_3). IR (KBr): ν 1611 cm^{-1} (m, C═N). MS (ESI+ in CH_3CN): *m*/*z* 460 [M − BAr^f_4]$^+$, 298 [**Ib**]$^+$. MS (ESI− in CH_3CN): *m*/*z* 863 [BAr^f_4]$^-$.

[PdMe(MeCN)(Ic)]$^+$[BAr$^f_4$]$^-$ (3c). Orange-yellow solid. Yield: 93%. Anal. Calcd for $C_{53}H_{42}N_3OSiPdBF_{24}$ (1338.21): C, 47.57; H, 3.16; N, 3.14. Found: C, 47.12; H, 3.08; N, 2.88. ^{1}H NMR ($CDCl_3$): δ 0.27 (s, 9H, $SiMe_3$), 0.79 (s, 3H, PdMe), 2.14 (s, 3H, Me^{14}), 2.16 (s, 3H, Me^{13}), 2.25 (s, 3H, CH_3CN), 2.53 (s, 3H, Me^{15}), 6.63 (s, 1H, H^3), 6.67 (s, 1H, H^6), 7.35 (d, 1H, $J_{H,H}$ = 7.8 Hz, H^{11}), 7.49 (broad s, 5H, H^9 and Ar^f H_p overlapping), 7.67 (broad s, 8H, Ar^f H_o), 7.76 (pt, 1H, H^{10}), 8.25 (s, 1H, H^7). ^{1}H NMR (CD_2Cl_2): δ 0.28 (s, 9H, $SiMe_3$), 0.81 (s, 3H, PdMe), 2.17 (s, 3H, Me^{14}), 2.20 (s, 3H, Me^{13}), 2.37 (s, 3H, CH_3CN), 2.70 (s, 3H, Me^{15}), 6.68 (s, 1H, H^3), 6.70 (s, 1H, H^6), 7.55 (broad s, 4H, Ar^f H_p), 7.60 (d, 1H, $J_{H,H}$ = 8.0 Hz, H^{11}), 7.66 (d, 1H, $J_{H,H}$ = 7.7 Hz, H^9), 7.71 (broad s, 8H, Ar^f H_o), 7.98 (pt, 1H, H^{10}), 8.33 (s, 1H, H^7). DEPT experiments were useful for the assignation of ^{13}C{^{1}H} NMR ($CDCl_3$): δ 0.5 ($SiMe_3$), 3.2 (PdMe), 8.7 (CH_3CN), 16.3 and 17.7 ($Me^{13,14}$), 25.1 (Me^{15}), 117.4 (Ar^f C_p), 120.8 (C^3), 123.7 (C^6), 124.4 (q, $J_{C,F}$ = 270.0 Hz, CF_3), 126.0 (C^9), 128.0 (C^5), 128.1 (C^2), 128.8 (q, $J_{C,F}$ = 31.1 Hz, Ar^f C_m), 130.5 (C^{11}), 134.6 (Ar^f C_o), 139.4 (C^1),- 139.6 (C^{10}), 150.6 (C^8), 153.6 (C^4), 161.4 (C^{12}), 161.5 (q, $J_{C,B}$ = 49.7 Hz, Ar^f C_{ipso}), 171.0 (C^7). ^{19}F{^{1}H} NMR ($CDCl_3$): δ −106.3 (s, CF_3). IR (KBr): ν 1611 cm^{-1} (m, C═N). MS (ESI+ in CH_3CN): *m*/*z* 474 [M − BAr^f_4]$^+$, 312 [**Ic**]$^+$. MS (ESI− in CH_3CN): *m*/*z* 863 [BAr^f_4]$^-$.

Preparation of G1-pyridylimine−PdCl$_2$ Dendritic Complexes 4. Compounds **4a**,**b** were synthesized as described above for **1** by starting from the corresponding pyridylimine dendritic ligands G1-ONNMe$_m$ (**IIa**,**b**). The preparation of **4a** is reported as an example.

G1-ONN[PdCl$_2$] (4a). [$PdCl_2$(COD)] (200 mg, 0.70 mmol) was added to G1-ONN (**IIa**; 213 mg, 0.175 mmol) in dichloromethane (40 mL), and the resulting yellow suspension was stirred at room temperature for 48 h. Removal of the solvent, followed by washings of the residue with pentane (4 × 5 mL), gave compound **4a** as a yellow solid, soluble in DMSO and insoluble in alkanes and aromatic and chlorinated solvents. Yield: 300 mg (89%). Anal. Calcd for $C_{68}H_{84}N_8O_4Si_5Cl_8Pd_4$ (1927.20): C, 42.38; H, 4.39; N, 5.81. Found: C, 42.05; H, 4.57; N, 5.25. ^{1}H NMR (DMSO-d_6): δ 0.22 (s, 6H, $SiMe_2$), 0.60 (m, 2H, $SiCH_2$), 0.81 (m, 2H, CH_2SiMe_2), 1.39 (m, 2H, $CH_2CH_2CH_2$), 6.81 (AA′ part of an AA′BB′ spin system, 2H, $H^{3,5}$), 7.34 (BB′ part of an AA′BB′ spin system, 2H, $H^{2,6}$), 7.88 (m, 1H, H^{11}), 8.16 (m, 1H, H^9), 8.35 (m, 1H, H^{10}), 8.66 (s, 1H, H^7), 8.98 (m 1H, H^{12}). ^{13}C{^{1}H} NMR (DMSO-d_6): δ −1.8 ($SiMe_2$), 15.9 (CH_2), 16.9 (CH_2), 20.2 (CH_2), 118.4 ($C^{3,5}$), 125.2 ($C^{2,6}$), 128.1 (C^9), 128.8 (C^{11}), 140.4 (C^1), 140.7 (C^{10}), 149.4 (C^{12}), 154.7 (C^4), 155.3 (C^8), 170.9 (C^7). IR (KBr): ν 1615 (vw), 1595^{-1} (s, C═N).

G1-ONNMe$_2$[PdCl$_2$] (4b). Orange solid slightly soluble in polar solvents and insoluble in alkanes and halogenated solvents. Yield: 80%. Anal. Calcd for $C_{76}H_{100}N_8O_4Si_5Cl_8Pd_4$ (2039.41): C, 44.76; H, 4.94; N, 5.49. Found: C, 45.57; H, 5.44; N, 5.19. ^{1}H NMR (DMSO-d_6): δ 0.21 (s, 6H, $SiMe_2$), 0.63 (m, 2H, $SiCH_2$), 0.81 (m, 2H, CH_2SiMe_2), 1.47 (m, 2H, $CH_2CH_2CH_2$), 2.28 (s, 3H, Me^{14}), 2.31 (s, 3H, Me^{13}), 6.61 (AA′ part of an AA′BB′ spin system, 2H, $H^{3,5}$), 7.03 (BB′ part of an AA′BB′ spin system, 2H, $H^{2,6}$), 7.89 (m, 1H, H^{11}), 8.13 (m, 1H, H^9), 8.36 (m, 1H, H^{10}), 8.61 (s, 1H, H^7), 8.92 (m 1H, H^{12}). IR (KBr): ν 1615 (vw), 1594 cm^{-1} (m, C═N).

Preparation of G1-pyridylimine−Pd(Cl)Me Dendritic Complexes 5. Compounds **5b**,**c** were synthesized as described above for **2** by starting from the corresponding G1-pyridylimine dendritic ligands G1-ONNMe$_m$ (**IIb**,**c**). The preparation of **5c** is reported as an example.

G1-ONNMe$_2$[Pd(Cl)Me] (5b). Yellow solid. Yield: 86%. Anal. Calcd for $C_{80}H_{112}N_8O_4Si_5Cl_4Pd_4$ (1957.74): C, 49.08; H, 5.77; N, 5.72. Found: C, 49.13; H, 5.95; N, 5.38. ^{1}H NMR ($CDCl_3$): δ 0.22 (s, 6H, $SiMe_2$), 0.64 (m, 2H, $SiCH_2$), 0.60 (s, 3H, PdMe), 0.81 (m, 2H, CH_2SiMe_2), 1.50 (m, 2H, $CH_2CH_2CH_2$), 2.06 (s, 3H, Me^{14}), 2.21 (s, 3H, Me^{13}), 6.58 (s, 1H, H^3), 6.71 (s, 1H, H^6), 7.62 (m, 1H, H^{11}), 7.88 (m, 1H, H^9), 7.99 (pt, 1H, H^{10}), 8.42 (s, 1H, H^7), 8.97 (m, 1H, H^{12}). ^{13}C{^{1}H} NMR ($CDCl_3$): δ −0.9 ($SiMe_2$), 0.5 (PdMe), 16.1 and 17.8 ($Me^{13,14}$), 17.1 (CH_2), 17.9 (CH_2), 21.7 (CH_2), 120.4 (C^3), 124.0 (C^6), 126.8 (C^9), 127.1 (C^5), 128.3 (C^2), 128.4 (C^{11}), 138.6 (C^{10}), 141.0 (C^1), 149.3 (C^{12}), 151.6 (C^8), 152.9.3 (C^4), 167.3 (C^7). IR (KBr): ν 1615 cm^{-1} (w), 1586 cm^{-1} (m, C═N), 1565 cm^{-1} (w).

G1-ONNMe$_3$[Pd(Cl)Me] (5c). [PdClMe(COD)] (59 mg, 0.22 mmol) was added to **IIc** (77 mg, 0.055 mmol) in dichloromethane (15 mL), and the resulting yellow solution was stirred at room temperature for 24 h. The solvent was removed under vacuum, and the residue was washed with pentane (2 × 25 mL) and diethyl ether (4 × 25 mL) to give compound **5c** as an orange solid. Analytically pure samples were obtained by operations of dissolution in CH_2Cl_2, filtration, and precipitation by adding pentane. Yield: 50 mg (45%). Anal. Calcd for $C_{84}H_{120}N_8O_4Si_5Cl_4Pd_4$ (2013.85): C, 50.10; H, 6.01; N, 5.56. Found: C, 49.74; H, 5.87; N, 5.49. ^{1}H NMR ($CDCl_3$): δ 0.22 (s, 6H, $SiMe_2$), 0.66 (m, 2H, $SiCH_2$), 0.78 (s, 3H, PdMe), 0.80 (m, 2H, CH_2SiMe_2), 1.50 (m, 2H, $CH_2CH_2CH_2$), 2.09 (s, 3H, Me^{14}), 2.23 (s, 3H, Me^{13}), 3.03 (s, 3H, Me^{15}), 6.58 (s, 1H, H^3), 6.70 (s, 1H, H^6), 7.42 (m, 1H, H^{11}), 7.63 (m, 1H, H^9), 7.82 (pt, 1H, H^{10}), 8.40 (s, 1H, H^7). ^{13}C{^{1}H} NMR ($CDCl_3$): δ −1.0 ($SiMe_2$), 4.4 (PdMe), 16.2 and 17.9 ($Me^{13,14}$), 17.2 (CH_2), 17.9 (CH_2 overlapping), 21.9 (CH_2), 25.7 (Me^{15}), 120.4 (C^3), 124.2 (C^6), 125.3 (C^9), 127.1 (C^5), 128.7 (C^2), 130.1 (C^{11}), 138.1 (C^{10}), 141.2 (C^1), 151.3 (C^8), 152.8 (C^4), 164.3 (C^{12}), 168.2 (C^7). IR (KBr): ν 1621 (m), 1590 cm^{-1} (s, C═N).

Preparation of G2-pyridylimine−Pd(Cl)Me Dendritic Complexes 6. Compounds **6b**,**c** were synthesized as described above

for **2**, starting from the corresponding G2-pyridylimine dendritic ligands G2-ONNMe$_m$ (**IIIb**,**c**).

G2-ONNMe$_2$[Pd(Cl)Me] (6b). Yellow solid. Yield: 79%. Anal. Calcd for $C_{176}H_{260}N_{16}O_8Si_{13}Cl_8Pd_8$ (4228.20): C, 50.00; H, 6.20; N, 5.30. Found: C, 49.66; H, 6.34; N, 4.98. ^{1}H NMR ($CDCl_3$): δ −0.06 (s, 3H, SiMe), 0.21 (s, 12H, $SiMe_2$), 0.57 (m, 8H, SiCH_2), 0.60 (s, 6H, PdMe), 0.81 (m, 4H, CH_2SiMe_2), 1.31 (m, 2H, $CH_2CH_2CH_2$), 1.45 (m, 4H, $CH_2CH_2CH_2$), 2.07 (s, 6H, Me^{14}), 2.19 (s, 6H, Me^{13}), 6.56 (s, 2H, H^3), 6.71 (s, 2H, H^6), 7.64 (m, 2H, H^{11}), 7.91 (m, 2H, H^9), 8.00 (pt, 2H, H^{10}), 8.44 (s, 2H, H^7), 8.98 (s, 2H, H^{12}). ^{13}C{^{1}H} NMR ($CDCl_3$): δ −4.9 (SiMe), −0.9 ($SiMe_2$), 0.4 (PdMe), 16.2 and 17.8 (Me^{13,14}), 17.9, 18.5, 18.7, 19.1, and 21.8 (CH_2), 120.4 (C^3), 123.9 (C^6), 126.9 (C^{5,9}), 128.5 (C^{2,11}), 138.7 (C^{10}), 140.9 (C^1), 149.0 (C^{12}), 151.4 (C^8), 152.7 (C^4), 167.5 (C^7). IR (KBr): ν 1615 (w), 1586 (s, C═N), 1566 cm^{-1} (w).

G2-ONNMe$_3$[Pd(Cl)Me] (6c). Yellow solid. Yield: 53%. Anal. Calcd for $C_{184}H_{276}N_{16}O_8Si_{13}Cl_8Pd_8$ (4340.41): C, 50.92; H, 6.41; N, 5.16. Found: C, 50.45; H, 6.48; N, 4.97. ^{1}H NMR ($CDCl_3$): δ −0.06 (s, 3H, SiMe), 0.22 (s, 12H, $SiMe_2$), 0.60 (m, 8H, SiCH_2), 0.75 (s, 6H, PdMe), 0.85 (m, 4H, CH_2SiMe_2), 1.23 (m, 2H, $CH_2CH_2CH_2$), 1.50 (m, 4H, $CH_2CH_2CH_2$), 2.09 (s, 6H, Me^{14}), 2.21 (s, 6H, Me^{13}), 3.03 (s, 6H, Me^{15}), 6.56 (s, 2H, H^3), 6.69 (s, 2H, H^6), 7.43 (m, 2H, H^{11}), 7.64 (m, 2H, H^9), 7.82 (pt, 2H, H^{10}), 8.41 (s, 2H, H^7). ^{13}C{^{1}H} NMR ($CDCl_3$): δ −4.9 (SiMe), −0.8 ($SiMe_2$), 4.5 (PdMe), 16.3 and 18.0 (Me^{13,14}), 17.8, 18.5, 18.7, 19.1 and 21.8 (CH_2), 25.7 (Me^{15}), 120.4 (C^3), 124.2 (C^6), 125.3 (C^9), 127.0 (C^5), 128.6 (C^2), 130.1 (C^{11}), 138.0 (C^{10}), 141.0 (C^1), 151.2 (C^8), 152.7 (C^4), 164.0 (C^{12}), 168.2 (C^7). IR (KBr): ν 1621 (m), 1590 cm^{-1} (s, C═N).

Preparation of G3-pyridylimine−Pd(Cl)Me Dendritic Complexes 7. Compounds **7b**,**c** were synthesized as described above for **2** by starting from the corresponding G3-pyridylimine dendritic ligands G3-ONNMe$_m$ (**IVb**,**c**).

G3-ONNMe$_2$[Pd(Cl)Me] (7b). Yellow-orange solid. Yield: 71%. Anal. Calcd for $C_{368}H_{556}N_{32}O_{16}Si_{29}Cl_{16}Pd_{16}$ (8769.11): C, 50.40; H, 6.39; N, 5.11. Found: C, 49.18; H, 6.34; N, 4.50. ^{1}H NMR ($CDCl_3$): δ −0.07 (s, 9H, SiMe), 0.21 (s, 24H, $SiMe_2$), 0.57 (m, 20H, SiCH_2), 0.65 (s, 12H, PdMe), 0.81 (m, 8H, CH_2SiMe_2), 1.31 (m, 6H, $CH_2CH_2CH_2$), 1.44 (m, 8H, $CH_2CH_2CH_2$), 2.07 (s, 12H, Me^{14}), 2.18 (s, 12H, Me^{13}), 6.55 (s, 4H, H^3), 6.71 (s, 4H, H^6), 7.63 (m, 4H, H^{11}), 7.90 (m, 4H, H^9), 7.99 (pt, 4H, H^{10}), 8.44 (s, 4H, H^7), 8.97 (s, 4H, H^{12}). ^{13}C{^{1}H} NMR ($CDCl_3$): δ −4.8 (SiMe, only one peak can be distinguished), −0.8 ($SiMe_2$), 0.5 (PdMe), 16.3 and 17.9 (Me^{13,14}), 17.8, 18.5, 18.6, and 21.8 (CH_2), 120.4 (C^3), 123.9 (C^6), 127.0 (C^{5,9}), 128.3 (C^{2,11}), 138.7 (C^{10}), 140.9 (C^1), 149.2 (C^{12}), 151.5 (C^8), 152.6 (C^4), 167.4 (C^7). IR (KBr): ν 1615 (m), 1585 (s, C═N), 1565 cm^{-1} (w).

G3-ONNMe$_3$[Pd(Cl)Me] (7c). Dark orange solid. Yield: 70%. Anal. Calcd for $C_{384}H_{588}N_{32}O_{16}Si_{29}Cl_{16}Pd_{16}$(8993.54): C, 51.28; H, 6.59; N, 4.98. Found: C, 50.32; H, 6.76; N, 4.56. ^{1}H NMR ($CDCl_3$): δ −0.07 (s, 9H, SiMe), 0.20 (s, 24H, $SiMe_2$), 0.57 (m, 20H, SiCH_2), 0.73 (s, 12H, PdMe), 0.80 (m, 8H, CH_2SiMe_2), 1.31 and 1.45 (2 × m, 14H, $CH_2CH_2CH_2$), 2.08 (s, 12H, Me^{14}), 2.20 (s, 12H, Me^{13}), 3.01 (s, 12H, Me^{15}), 6.55 (s, 4H, H^3), 6.68 (s, 4H, H^6), 7.42 (m, 4H, H^{11}), 7.67 (m, 4H, H^9), 7.82 (pt, 4H, H^{10}), 8.42 (s, 4H, H^7). ^{13}C{^{1}H} NMR ($CDCl_3$): δ −4.8 (SiMe, only one peak can be distinguished), −0.8 ($SiMe_2$), 4.5 (PdMe), 16.3 and 17.9 (Me^{13,14}), 17.8, 18.5, 18.6, 19.1, and 21.8 (CH_2), 25.7 (Me^{15}), 120.4 (C^3), 124.2 (C^6), 125.4 (C^9), 127.0 (C^5), 128.6 (C^2), 130.1 (C^{11}), 138.1 (C^{10}), 141.0 (C^1), 151.2 (C^8), 152.6 (C^4), 163.9 (C^{12}), 168.6 (C^7). IR (KBr): ν 1621 (m), 1590 cm^{-1} (s, C═N).

Preparation of Cationic G*n*-pyridylimine−[Pd(MeCN)Me]$^+$ Dendritic Complexes (8b−10b). Compounds **8b**−**10b** were synthesized as described above for **3**, starting from the corresponding chloro(methyl)palladium dendritic complex G*n*-ONNMe$_2$Pd(Cl)Me(**5b**, n = 1; **6b**, n = 3; **7b**, n = 3). In each case, most parts of the ^{1}H NMR resonances for the minor isomer (*cis*-Me−Pd−N$_{imine}$) are obscured by the signals corresponding to the major isomer.

G1-ONNMe2[PdMe(MeCN)] (8b). Orange-yellow solid. Yield: 69%. Anal. Calcd for $C_{216}H_{172}N_{12}O_4Si_5Pd_4B_4F_{96}$ (5433.02): C, 47.75; H, 3.19; N, 3.09. Found: C, 47.29; H, 2.97; N, 2.66. NMR data for the major isomer (60% *trans*-Me−Pd−N$_{imine}$) are as follows. ^{1}H NMR ($CDCl_3$): δ 0.20 (s, 6H, $SiMe_2$), 0.65 (m, 2H, SiCH_2), 0.83 (m, 2H, CH_2SiMe_2), 0.86 (s, 3H, PdMe), 1.50 (m, 2H, $CH_2CH_2CH_2$), 2.10 (bs, 3H, Me^{14}), 2.20 (bs, 6H, CH_3CN and Me^{13} overlapping), 6.63 (bs, 1H, H^3), 6.74 (bs, 1H, H^6), 7.45 (bs, 4H, Ar^f H$_p$), 7.55 (m, 1H, H^{11}), 7.65 (m, 1H, H^9), 7.66 (bs, 8H, Ar^f H$_o$), 7.92 (m, 1H, H^{10}), 8.18 (s, 1H, H^7), 8.25 (m, 1H, H^{12}). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ −1.4 ($SiMe_2$), 2.6 (PdMe), 4.4 (CH_3CN), 15.2 and 17.8 (Me^{13,14} and CH_2), 17.5 (CH_2), 21.8 (CH_2), 117.4 (Ar^f C$_p$), 120.7 (C^3), 123.2 (C^6), 124.3 (q, $J_{C,F}$ = 272 Hz, CF_3), (C^2 and C^5 not assigned), 128.4 (C^9), 128.5 (C^{11}), 128.8 (q, $J_{C,F}$ = 28 Hz, Ar^f C$_m$), 134.6 (Ar^f C$_o$), 139.5 (C^1), 140.6 (C^{10}), 149.2 (C^{12}), 154.4 (C^8), 155.5 (C^4), 161.6 (q, $J_{C,B}$ = 50 Hz, Ar^f C$_{ipso}$), 161.6 (C^7). IR (KBr): ν 1610 cm^{-1} (m, C═N).

G2-ONNMe$_2$[PdMe(MeCN)] (9b). Orange-yellow solid. Yield: 74%. Anal. Calcd for $C_{448}H_{380}N_{24}O_8Si_{13}Pd_8B_8F_{192}$ (11 178.76): C, 48.14; H, 3.42; N, 3.01. Found: C, 47.48; H, 3.25, N, 2.80. NMR data for the major isomer (60% *trans*-Me−P−N$_{imine}$) are as follows. ^{1}H NMR ($CDCl_3$): δ −0.07 (s, 3H, SiMe), 0.16 (s, 12H, $SiMe_2$), 0.62 (m, 8H, SiCH_2), 0.83 (m, 4H, CH_2SiMe_2), 0.84 (s, 6H, PdMe), 1.40 (bm, 6H, $CH_2CH_2CH_2$), 2.07 (bs, 6H, Me^{14}), 2.20 (bs, 12H, CH_3CN and Me^{13} overlapping), 6.60 (bs, 4H, H^{3,6}), 7.42 (bs, 8H, Ar^f H$_p$), 7.50−7.78 (m, 20H, H^{9,11} and Ar^f H$_o$), 7.97 (m, 2H, H^{10}), 8.16 (s, 2H, H^7), 8.27 (m, 2H, H^{12}). IR (KBr): ν 1611 cm^{-1} (m, C═N).

G3-ONNMe$_2$[PdMe(MeCN)] (10b). Orange-yellow solid. Yield: 87%. Anal. Calcd for $C_{928}H_{828}N_{48}O_{16}Si_{29}Pd_{16}B_{16}F_{384}$ (22894.66): C, 48.68; H, 3.65; N, 2.94. Found: C, 47.50; H, 3.68; N, 2.55. NMR data for the major isomer (55% *trans*-Me−P−N$_{imine}$) are as follows. ^{1}H NMR ($CDCl_3$): δ −0.08 (s, 9H, SiMe), 0.16 (s, 24H, $SiMe_2$), 0.62 (m, 20H, SiCH_2), 0.83 (m, 8H, CH_2SiMe_2), 0.84 (s, 12H, PdMe), 1.40 (bm, 14H, $CH_2CH_2CH_2$), 2.07 (s, 12H, Me^{14}), 2.20 (bs, 24H, CH_3CN and Me^{13} overlapping), 6.50−6.80 (bs, 8H, H^{3,6}), 7.42 (bs, 16H, Ar^f H$_p$), 7.66 (bm, 40H, H^{9,11} and Ar^f H$_o$), 8.00 (m, 4H, H^{10}), 8.16 (s, 4H, H^7), 8.27 (m, 4H, H^{12}). IR (KBr): ν 1611 cm^{-1} (m, C═N).

General Procedure for CO/4-*tert*-Butylstyrene Copolymerization Reactions. Prior to use, 4-*tert*-butylstyrene (TBS) was passed through neutral alumina (70−230 mesh) to remove the stabilizer. All runs were made under the same catalytic conditions, at room temperature, P_{CO} = 1 atm, in CH_2Cl_2 (TBS/Pd = 620) or neat TBS (TBS/Pd = 1100). The corresponding catalyst precursor was weighed (8−16 mg, 12.5 μmol of Pd), and when necessary, the cocatalyst Na[BAr$^f_4$] (10−15 mg) was also introduced into 30 mL screw-capped glass pressure reactors (Schlenk) equipped with a magnetic stirrer. The reactor was capped and sealed with a septum, purged by repeated argon/vacuum operations, and, if used, purified CH_2Cl_2 (5 mL) was charged, and flushed with CO gas. Copolymerization was initiated by the addition of 1.4 mL (reaction in CH_2Cl_2) or 2.5 mL (neat styrene) of TBS with vigorous stirring, under 1 atm of CO. After a desired time interval the CO feeding was stopped, and CH_2Cl_2 (25 mL) was added in the case of viscous mixtures. Palladium metal particles were removed by filtration through a Celite column, and the solvent was removed under reduced pressure. The polyketones were coagulated by vigorous stirring in methanol and purified by reprecipitation with methanol from a CH_2Cl_2 solution (5 mL). Finally the product was dried in an oven at 80 °C to constant weight. The characterization of these

materials was carried out by ^{1}H and $^{13}C\{^{1}H\}$ NMR (room temperature, $CDCl_3$), IR, and GPC.

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Supporting Information Available: Table S1, summarizing coordination-induced shift values observed by NMR for compounds **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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