Iminophosphine Palladium Complexes in Catalytic Stille Coupling Reactions: From Monomers to Dendrimers

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Palladium complexes of a variety of β - and γ -iminophosphines have been prepared and characterized by X-ray diffraction studies. Their properties as catalyst for three different Stille coupling reactions have been investigated and compared to catalytic performances of a phosphorus-containing dendrimer incorporating analogous γ -iminophosphine palladium complexes on the surface.

Introduction

Phosphorus and nitrogen donor ligands are among the most attractive and useful ligands used in catalysis because of the presence of both soft and hard donor atoms, which allows tailoring their complexation properties.¹ Generally, the phosphorus part of these derivatives is constituted by phosphines or phosphites, while the nitrogen coordinating site involves amines, pyridines, quinolines, pyrazoles, and oxazolines to name a few. Among these mixed donor ligands, β -iminophosphines were found useful ligands and their complexes very efficient in a number of catalytic reactions as for example in the Heck reaction,² the cross-coupling reaction of alkylstannanes with aryl iodides,³ the hydrogenation of unsaturated carbon-carbon bonds,⁴ the enantioselective allylic substitutions using ketene silyl acetals and others,⁵⁻⁹ and the copolymerization of CO-ethylene.¹⁰ In most of these reactions the behavior of acyclicimino phosphines has been investigated.

Very recently¹¹ we reported the synthesis of new bi-

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and tricyclic β -iminophosphines via a reductive elimination reaction of α -phosphino zirconocene-iminoacyl complexes. We envisaged that the corresponding complexes and mainly the palladium complexes should be active as catalysts. For this purpose, we prepared a variety of these complexes, most of them being characterized by X-ray diffraction analysis, and compared their catalytic activity, in typical reactions such as Stille coupling reactions, with that of metalladendrimers incorporating γ -iminophosphines. Indeed, transition metal catalysis based on functionalized dendrimers is an attractive area of research, not only because metalladendrimers are generally easily recyclable homogeneous catalysts but also because they can be more active, more selective, or more stable than the corresponding monomers. The wide scope of applications of metalladendrimers has been recently reviewed.^{12,13} Recently also we demonstrated that phosphorus-containing metalladendrimers of generation 3, with either 24 terminal palladium or ruthenium diphosphine complexes, are efficient, recoverable catalysts in some classical reactions.¹⁴ However this finding does not reflect the very contrasted results found for the comparison between dendritic catalysts and the corresponding monomers in terms of reaction rate or selectivity. For instance considering only Pd catalysts, some Pd complexes of dendrimers were found much less active than models for the hydrovinylation of styrene^{15,16} or for hydroformylation.¹⁷ An equal activity between mod-

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els and Pd metalladendrimers was found for allylic amination.¹⁸ In contrast a higher activity for the dendrimer compared to the monomer model was found for the hydrogenation of olefins¹⁹ and for Heck reactions.²⁰ Different explanations were given for these findings. The decreased activity of Pd complexes of some dendrimers was ascribed to decomposition due to the close proximity of the metallic centers, which could facilitate the formation of elemental Pd.¹⁵ On the other hand, the significantly higher activity compared to monomeric parent compounds obtained with some other dendrimers which are also Pd complexes was attributed to a higher thermal stability, inducing the absence of formation of elemental Pd.20

A deeper insight into dendritic effects observed in catalysis is also required. Therefore, it is necessary to investigate the catalytic properties of more metalladendrimers and to compare their activity with that of related monomers in the hope of offering additional information which might help to understand the role of dendrimer complexes and their scope and limitations. Hereafter we present some preliminary results concerning the use of dendrimers incorporating γ -iminophosphine Pd complexes on the surface and that of some related monomers in three different classical Stille coupling reactions.

Results and Discussion

The β -iminophosphines **5** and **10** (Schemes 1 and 2) were readily prepared by thermolysis of diphenylzirconocene 1, which leads to the benzyne zirconocene 2, in the presence of either the acetylenic phosphine 3 or the phospholene 8, followed by treatment of the resulting phosphinozircona fused bi- or tricyclic phosphines 4 and 9 with the isocyanide $2,6-Me_2C_6H_3-NC.^{11}$ The γ -iminophosphine **13**²¹ and the dendrimer **15**²² were



Figure 1. ORTEP drawing of 6 (50% probability of the thermal ellipsoids). Selected bond distances (Å) and angles (deg): P-Pd 2.2322 (11), P-C(9) 1.801(4), N-Pd 2.056(3), C(1)-N 1.292(5), C(1)-C(9) 1.459(5), N-Pd-P 86.02(9), C(1)-N-Pd 119.0(3), C(9)-P-Pd 99.18(13), N-C(1)-C(9) 120.8(3), C(1)-C(9)-P 115.0(3).



prepared according to previously reported procedures. The γ -iminophosphine chain end dendrimer **17** was prepared via a substitution reaction between 15, bearing six terminal P(S)Cl₂ units, and the phenol 16 in the presence of cesium carbonate: the reaction proceeded cleanly at room temperature for 12 h, leading to 17, isolated in 93% yield (Scheme 3).

Palladium Complexes. The β -iminophosphine **5** $(\delta^{31}P = -23.8 \text{ ppm})$ in solution in dichloromethane was first reacted with PdCl₂(COD). The resulting complex 6, obtained in 84% yield, was characterized by means of ³¹P (δ = +19 ppm), ¹H NMR, and elemental analysis. An X-ray diffraction study corroborated the postulated structure in which the PdCl₂ unit is linked both to the imino nitrogen atom and to the phosphino group (Figure 1, Table 1).

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Scheme 3



Addition of the isocyanide 2,6-Me₂C₆H₃-NC to the complex **6** afforded the new complex **7** ($\delta^{31}P = +15.5$ ppm), also characterized by single-crystal X-ray diffraction studies (Figure 2, Table 1). As expected, the isocyanide group is a better ligand than the imino nitrogen atom, and the PdCl₂ unit in **7** is now linked to the carbon atom of the isocyanide as well as to the phosphino group.

The same type of complex could be obtained from the fused tricyclic β -iminophosphine **10**. Complexes with PdCl₂ (**11a**), RuCl₂(PPh₃) (**11b**), and Mo(CO)₄ (**11c**) were isolated in high yield. Single crystals of **11a** suitable for X-ray structure determination were obtained from a dichloromethane pentane solution. The structure (Figure 3, Table 1) undoubtedly proved the coordination of the PdCl₂ unit to the imino nitrogen atom and to

phosphorus. A ligand exchange readily occurred when **11a** was reacted with 2,6-Me₂C₆H₃-NC, affording the new complex **12**, which was also subjected to an X-ray structure analysis (Figure 4, Table 1). The course of the reaction, i.e., the **10** \rightarrow **11a** \rightarrow **12** transformations, was monitored by ³¹P NMR ($\delta = +9$, +34.8, and +52.2 ppm, respectively, for **10**, **11a**, and **12**). The palladium complex **14** of the γ -iminophosphine **13** was prepared in quantitative yield using a classical procedure. **14** was also characterized by X-ray diffraction studies (Figure 5, Table 1).

Catalytic Tests. The catalytic activity of complexes **6**, **11a**, **14**, and **18** was examined for three Stille coupling reactions. Complexes **5-Pd(OAc)**₂ (δ^{31} P (DMF) = 28.2 ppm), **10-Pd(OAc)**₂ (δ^{31} P (DMF) = 30.4 ppm), **13-Pd(OAc)**₂ (δ^{31} P (DMF) = 31.5 ppm), and **17-Pd(OAc)**₂

Table 1. Crystallographic Data for Compounds 6, 7, 11a, 12, and 14

	6	7	11a	12	14
formula	C ₂₉ H ₂₄ Cl ₂ NPPd	$C_{38}H_{33}Cl_2N_2PPd$,	C25H24Cl2NPPd	$C_{34}H_{33}Cl_2N_2PPd$,	C ₂₅ H ₂₀ Cl ₂ NPPd,
		CH_2Cl_2		CHCl ₃	CH_2Cl_2
fw	594.76	810.86	546.72	797.26	627.62
temp (K)	293	160	150	160	180
cryst syst	monoclinic	triclinic	orthorhombic	monoclinic	triclinic
space group	$P2_1/n$	<i>P</i> 1	$P2_12_12_1$	$P2_{1}/c$	P1
a (Å)	11.381(2)	10.161(2)	12.631(2)	10.459(2)	9.002(5)
$b(\mathbf{A})$	17.129(2)	10.305(2)	8.6180(8)	14.405(3)	10.159(5)
<i>c</i> (Å)	13.558(2)	17.860(4)	20.653(2)	24.422(5)	14.252(5)
α (deg)	90.0	84.88(2)	90.0	90.0	78.586(5)
β (deg)	96.930(17)	75.58(2)	90.0	102.04(3)	80.303(5)
γ (deg)	90.0	84.43(2)	90.0	90.0	89.794(5)
V (Å)	2623.9(6)	1798.5(6)	2248.0(4)	3598.5(13)	1258.7(10)
Ζ	4	2	4	4	2
$D_{\rm c}$ (g/cm ³), μ (mm ⁻¹)	1.506, 0.990	1.497, 0.889	1.615, 1.147	1.472, 0.958	1.656, 1.242
no. of reflns collcd	20 251	14 049	13 048	20 845	12 354
no. of reflns unique	4459	5668	3198	5161	4566
no. of variables	309	428	274	428	298
GOF	0.901	1.096	0.988	0.914	1.011
R1 (all data)	0.0671	0.0379	0.0707	0.0795	0.0377
wR2 (all data)	0.0724	0.0905	0.1103	0.1335	0.0839
R1 ($I > 2\sigma(I)$)	0.0328	0.0348	0.0504	0.0485	0.0319
wR2 $(I > 2\sigma(I))$	0.0637	0.0886	0.1023	0.1177	0.0805



Figure 2. ORTEP drawing of **7** (50% probability of the thermal ellipsoids). Selected bond distances (Å) and angles (deg): P-Pd 2.2631(9), P-C(1) 1.792(3), C(9)–N(1) 1.271-(4), C(18)–Pd 1.921(3), C(18)–N(2) 1.146(4), C(18)–Pd–P 93.92(9), C(1)–P–Pd, 109.41(9).

 $(\delta^{31}P = 30.4 \text{ ppm for terminal } P-Pd \text{ units})$ were prepared "in situ" by mixing **5**, **10**, **13**, or **17** with Pd-(OAc)₂ in a P/Pd ratio = 1.

The first reaction investigated was the Stille coupling of iodobenzene with tributylvinyltin (Figure 6, Table 2). The catalytic properties of the PdCl₂ monomers were first analyzed under the same conditions, i.e., 5 mol % Pd, for 20 h at 50 °C with THF as solvent (Table 2, entries 2, 5, 7). It clearly appeared that the reaction is faster with the monomer 14 (90% conversion) than with the fused "tricyclic" system 11a (30% conversion), which in turn is more effective than the fused bicyclic ligand complex 6 (20% conversion). Precipitation of Pd was frequently observed. To try to avoid this, DMF was used as solvent instead of THF, and the activity of the best catalyst, i.e., 14, was compared with that of dendrimer 18, bearing on the surface the same complexed units. Reactions were performed with only 2 mol % Pd during 5 h at 50 °C in DMF. Under these conditions, it can be noticed that the rate of conversion is very high in all



Figure 3. ORTEP drawing of **11a** (50% probability of the thermal ellipsoids). Selected bond distances (Å) and angles (deg): P–Pd 2.225(2), N–Pd 2.044(7), C(1)–N 1.311(12), P–C(11) 1.820(9), C(1)–C(11) 1.534(4), N–Pd–P 81.9(2), C(1)–N–Pd 118.7(6), Pd–P–C(11) 101.7(3).

cases and that the metalladendrimer appeared to be more efficient than the corresponding monomer (Table 2, entries 9, 11, and Figure 6). Moreover the metalladendrimer can be reused several times.²³ Indeed **18** can be recovered via precipitation with dry ether, while no precipitation of monomers **6**, **11a**, and **14** occurred under the same experimental conditions. Furthermore no undesired formation of elemental Pd was observed.

Complexes **5-Pd(OAc)**₂, **10-Pd(OAc)**₂, **13-Pd(OAc)**₂, and **17-Pd(OAc)**₂ were also used, but they have shown lower activity (except for **17-Pd(OAc)**₂) (Table 2, entries 1, 4, 6, 10) than the corresponding PdCl₂ complexes. Moreover they were found unstable (abundant forma-

⁽²³⁾ All the amount of dendritic catalyst was precipitated during the recycling procedure. No detectable traces of the catalyst were found in the solution. However it was always difficult during the workup (filtration) not to lose a small amount of catalyst, as we were working with a very small quantity of it. We do believe that this fact explains why we observed the slight decrease of activity of the dendritic catalyst **18** when reused. Obviously several other options (membrane reactors, etc.) can be envisaged.



Figure 4. ORTEP drawing of **12** (50% probability of the thermal ellipsoids). Selected bond distances (Å) and angles (deg): P-Pd 2.2358(16), C(1)-N(2) 1.265(8), C(1N)-N(1) 1.169(8), P-Pd-C(1N) 88.64(18), Pd-C(1N)-N(1) 177.9-(5).



Figure 5. ORTEP drawing of **14** (50% probability of the thermal ellipsoids). Selected bond distances (Å) and angles (deg): P-Pd 2.2205(10), N-Pd 2.053(2), N-C(1) 1.275(4), C(1)-C(2) 1.470(4), C(2)-C(7) 1.399(4), C(7)-P 1.819(3), N-Pd-P 86.34(8), C(1)-N-Pd 125.39(18), Pd-P-C(7) 103.84(10).



Figure 6. Stille coupling of iodobenzene with tributylvinyltin at 50 °C in DMF in the presence of 2 mol % Pd of catalyst **14**, **17-Pd(OAc)**₂, or **18**.

tion of elemental Pd), and recycling of **5-Pd(OAc)**₂, **10-Pd(OAc)**₂, and **13-Pd(OAc)**₂ failed. The recycling of **17-Pd(OAc)**₂ was possible (precipitation with dry ether) but was accompanied by formation of elemental Pd and by a dramatic decrease of the catalytic activity.

Table 2. Stille Coupling of Iodobenzene with
Tributylvinyltin

entry	catalyst	mol % Pd	time (h)	<i>T</i> (°C)	solvent	conversion %
1	5-Pd(OAc) ₂	5	20	50	THF	10 ^a
2	6	5	20	50	THF	20
3	6	5	37	50	THF	48
4	10-Pd(OAc) ₂	5	20	50	THF	20 ^a
5	11a	5	20	50	THF	30 ^a
6	13-Pd(OAc) ₂	5	20	50	THF	65 ^a
7	14	5	20	50	THF	90 ^a
8	14	5	5	50	DMF	91
9	14	2	5	50	DMF	83
10	17-Pd(OAc) ₂	2	5	50	DMF	98 ^a
11	18 first run	2	5	50	DMF	98
12	18 second run	2	5	50	DMF	92
13	18 third run	2	5	50	DMF	86

^a Pd precipitate observed.

 Table 3. Stille Coupling of Methyl-2-iodobenzoate

 with 2-(Tributylstannyl)thiophene

entry	catalyst	mol % Pd	time (h)	Т (°С)	solvent	conversion (%)
1	6	5	4	50	DMF	65
2	6	5	30	67	THF	91
3	11a	5	4	50	DMF	73 ^a
4	14	5	4	50	DMF	99
5	18	5	3	50	DMF	100

^a Pd precipitate observed.



Figure 7. Stille coupling of methyl-2-iodobenzoate with 2-(tributylstannyl)thiophene at 50 °C in DMF in the presence of 5 mol % Pd of catalyst **14**, **18**, or recycled **18**.

The Stille coupling of methyl-2-iodobenzoate with 2-(tributylstannyl)thiophene was then investigated (Table 3). Reactions were performed in DMF at 50 °C with 5 mol % Pd. The metalladendrimer **18** and the monomer **14** exhibited close catalytic activities: 100% conversion was reached after 3-4 h depending on the complex (Figure 7), while a lower activity was observed for **11a** (Table 3, entries 3, 4, 5). The metalladendrimer **18** was also found to be efficient with a slightly decreased activity when recycled (Figure 7). In contrast here again, the β -iminophosphine complex **6** is poorly efficient when used in the same experimental conditions (Table 3, entry 1). However 91% conversion was observed using **6** as catalyst (5 mol % Pd) in THF but at 67 °C and for 30 h (Table 3, entry 2).

The catalytic activity of the PdCl₂ complexes coordinated with β - or γ -iminophosphines **5**, **10**, and **13** and dendrimer **17** was also demonstrated in the cross-

Table 4. Stille Coupling of 4-(Trifluoromethyl)iodobenzene with Phenylethynyltributyltin



Figure 8. Stille coupling of 4-(trifluoromethyl)iodobenzene with phenylethynyltributyltin at 20 °C in DMF in the presence either of 1 mol % Pd of catalyst **14** or **18** or of 2.5 mol % Pd of catalyst **6** or **11a**.

coupling reaction of 4-(trifluoromethyl)iodobenzene with phenylethynyltributyltin (Table 4, Figure 8). The conversion was readily monitored by ¹⁹F NMR spectroscopy of the reaction mixture. Reactions were performed in DMF at 20 °C using 1 mol % Pd. The monomer 14 is more efficient than the corresponding metalladendrimer 18 (Figure 8). Conversion was 75% with 18 for 15 h of reaction (Table 4, entry 6), whereas it reached 90% for 10 h with 14, respectively, with 1 mol % Pd in all cases. The complexes formed with the cyclic β -iminophosphines 5 and 10, i.e., 6 and 11a, are again less active: it is necessary to use a larger amount of catalyst (2.5 mol % Pd) and generally longer reaction times to observe a comparable conversion (Table 4, entries 1-4). The more efficient catalyst was 6 (2.5 mol % Pd), which allowed 90% conversion for 4 h at room temperature.

At this stage of this preliminary study, it is difficult to rationalize the catalytic activity of the monomer ligands. One might evoke that the difference of activity of the corresponding Pd complexes can be due to the difference of geometry of the palladium five-membered rings (compounds 5-Pd(OAc)₂, 6, 10-Pd(OAc)₂, 11a) or six-membered rings (compounds 13-Pd(OAc)₂, 14, 17-Pd(OAc), 18), and therefore to the more or less easy access of the reagents to the palladium center. Palladium cycles for compounds 6, 11a, and 14 are represented in Figure 9. Complex 6 appears practically planar, while an envelope form can be detected for 11a and a quite distorted chair form for **14**. Anyway these differences in geometry do not preclude other effects responsible for the activities for the different complexes, as for example electronic properties of the ligands. Therefore at the present state of the art, discussion appears only speculative.



Figure 9. Conformation of the palladium five- and sixmembered ring in complexes **6**, **11a**, and **14**. For clarity only the location of the substituents (and not the substituents themselves) on phosphorus, nitrogen, and carbon are represented. The largest deviation of the carbon atoms of the palladium ring from the mean PPdCl₂ plane is 0.05 Å for **6**, 1.46 Å for **11a**, and 1.69 Å for **14**.

Conclusion

It clearly appears from these preliminary experiments concerning cross-coupling reactions that palladium complexes of the γ -iminophosphine **13** and the corresponding metalladendrimer 18 are better catalysts than the complexes formed from bi- or tricyclic β -iminophosphines. The catalytic performances of the metalladendrimer depend on the reagents involved in the investigated Stille coupling reactions: besides the fact that it can be easily recycled, it also allowed improvement of the catalytic activity of γ -iminophosphine palladium complexes in the case of the reaction of iodobenzene with tributylvinyltin. Such an unpredictable and versatile behavior of metalladendrimers in catalysis brings new examples reflecting the very contrasted results already reported in the literature. It is clear that numerous investigations have to be performed in order to clarify the role of metalladendrimers and their usefulness in addition to recycling. In the continuation of the present work further investigations in understanding the role of steric effects and electronic influence of ligands, the effect of the size of dendrimers (number of generations), and the role of the complex inside the dendrimer or on the surface are presently underway.

Experimental Section

General Procedures. All manipulations were carried out with standard high-vacuum and dry-argon techniques. ¹H, ¹³C, and ³¹P NMR and ¹⁹F spectra were recorded with Bruker AC200, AC250, DPX300, or AMX 400 spectrometers. References for NMR chemical shifts are 85% H₃PO₄ for ³¹P NMR, SiMe₄ for ¹H and ¹³C NMR, and CF₃CO₂H for ¹⁹F. The attribution of ¹³C NMR signals has been done using Jmod, twodimensional HBMC and HMQC, broad band, or CW ³¹P decoupling experiments when necessary. The numbering used for NMR of compounds 14, 16, 17, and 18 is depicted in Figure 10. Iminophosphines **5** and **10**¹¹ as well as **13**²¹ were prepared according to literature procedures. Dendrimer 15 was prepared in our lab, according to the procedure that we developed.²² Complexes 5-Pd(OAc)₂, 10-Pd(OAc)₂, 13-Pd(OAc)₂, and 17-Pd(OAc)₂ were prepared "in situ" by mixing 5, 10, 13, or 17 with $Pd(OAc)_2$ (P/Pd = 1).

Synthesis of Complex 6. To a solution of the β -iminophosphine **5** (0.417 g, 1 mmol) in 10 mL of CH₂Cl₂ was added (COD)PdCl₂ (0.291 g, 1 mmol) in solution in 20 mL of CH₂Cl₂. The resulting solution was stirred for 2 h at room temperature,



Figure 10. Numbering used for NMR.

then the solvent was evaporated to give a yellow solid, which was washed two times with a 1:10 CH₂Cl₂/pentane solution. Yellow crystals suitable for X-ray diffraction studies were obtained from a CH₂Cl₂/pentane/ether solution of **6**. ³¹P{¹H} NMR (CH₂Cl₂) δ : 19.0. ¹H NMR (CD₂Cl₂) δ : 2.28 (s, 6H, CH₃), 6.85–7.70 (m, 13H, H_{arom}), 7.8–8.3 (m, 5H, H_{arom}). The compound was not soluble enough to be characterized by ¹³C NMR. Anal. Calcd for C₂₉H₂₄Cl₂NPPd (594.8): C, 58.56; H, 4.06; N, 2.35. Found: C, 58.27; H, 3.89; N, 2.25.

Synthesis of Complex 7. To a solution of complex **6** (0.059 g, 0.1 mmol) dissolved in 20 mL of CH_2Cl_2 was added the isocyanide 2,6-Me₂C₆H₃-NC (0.013 g, 0.1 mmol) in 5 mL of CH_2 -Cl₂. The solution was stirred for 2 h at room temperature, then evaporated, and the residue was washed with EtOH (2 × 10 mL) and then pentane (2 × 10 mL) and dried in a vacuum. Yield: 94% (0.068 g). Yellow crystals suitable for X-ray diffraction studies were obtained from a 2:1 CH_2Cl_2 /pentane solution. ³¹P{¹H} NMR (CDCl₃) δ : 15.5. ¹H NMR (CDCl₃) δ : 1.92 (s, 6H, CH₃), 2.06 (s, 6H, CH₃), 6.43 (d, ³J_{HP} = 7.4 Hz, 1H, =CH), 6.85–7.95 (m, 20H, H_{arom}). The compound was not soluble enough to be characterized by ¹³C NMR. Anal. Calcd for C₃₈H₃₃Cl₂N₂PPd (726): C, 62.87; H, 4.58; N, 3.86. Found: C, 62.71; H, 4.51; N, 3.79.

Synthesis of Complex 11a. To a solution of 10 (0.077 g, 0.21 mmol) in CH₂Cl₂ (5 mL) was added (COD)PdCl₂ (0.060 g, 0.21 mmol) in CH₂Cl₂ (5 mL). The resulting orange solution was stirred for 1 h at room temperature, then evaporated, and the residue was washed with Et_2O (2 \times 10 mL) and pentane $(2 \times 10 \text{ mL})$, to give **11a** in 82% yield (0.094 g). Crystals were obtained from a 1:1 CH₂Cl₂/pentane solution. ³¹P{¹H} NMR (CD₂Cl₂) δ: 34.8. ¹H NMR (CD₂Cl₂) δ: 2.12-2.40 (m, 1H), 2.31 (s, 6H, CH₃), 2.43-2.63 (m, 2H), 2.75-2.93 (m, 1H), 3.90-3.98 (m, 1H), 5.11 (ddd, ${}^{3}J_{HH} = 1.1$ Hz, ${}^{4}J_{HH} = 5.4$ Hz, ${}^{2}J_{PH} = 6.9$ Hz, 1H, CH-C=N), 5.95 (d, ${}^{3}J_{HH} = 8.1$ Hz, 1H, H_{arom}), 7.01-7.37 (m, 6H, H_{arom}), 7.38-7.68 (m, 3H, H_{arom}), 7.90-8.00 (m, 2H, o-C₆H₅P). The compound was not soluble enough to be characterized by ^{13}C NMR. Anal. Calcd for $C_{25}H_{24}\text{Cl}_2\text{NPPd}$ (546.7): C, 54.90; H, 4.42; N, 2.56. Found: C,54.71; H,4.40; N. 2.47.

Synthesis of Complex 11b. To a solution of 10 (0.053 g, 0.14 mmol) in 5 mL of CH₂Cl₂ was added (Ph₃P)₃RuCl₂ (0.138 g, 0.14 mmol) in 5 mL of CH₂Cl₂. The resulting deep brown solution was stirred for 1 h at room temperature, then evaporated to dryness. The resulting brown powder was dissolved in CH₂Cl₂ (1 mL) then precipitated with 10 mL of pentane. 11b was obtained as a brown powder in 78% yield (0.088 g). ${}^{31}P{}^{1}H$ NMR (CDCl₃) δ : 55.1 (d, ${}^{2}J_{PP} = 43.9$ Hz, CH-P-CH₂), 79.5 (d, ${}^{2}J_{PP}$ = 43.9 Hz, PPh₃). ¹H NMR (CDCl₃) δ: 2.02 (s, 3H, CH₃), 2.05-2.52 (m, 3H, CH₂), 2.52 (s, 3H, CH₃), 2.61-2.89 (m, 1H, CH₂-P), 3.58-3.72 (m, 1H, CH), 5.37 (dd, ${}^{3}J_{\rm HH} = 6.0$ Hz, ${}^{2}J_{\rm HP} = 7.1$ Hz, 1H, CHP), 6.23 (d, ${}^{3}J_{\rm HH} = 7.7$ Hz, 1H, H_{arom}), 6.93–7.73 (m, 26H, H_{arom}). $^{13}C\{^{1}H\}$ NMR (CDCl₃) δ : 19.9 (s, CH₃), 21.2 (s, CH₃), 25.6 (d, ²J_{CP} = 24.6 Hz, CH₂P), 32.4 (s, CH₂CH₂P), 41.9 (s, CH), 65.3 (d, ${}^{1}J_{CP} =$ 31.9 Hz, =CCHP), 124.5 (s, CH), 125.9 (s, CH), 126.3 (s, CH), 127.1 (d, $J_{CP} = 8.9$ Hz, CH), 127.4 (s, CH), 128.0 (d, $J_{CP} = 9.3$ Hz, CH), 128.3 (d, $J_{CP} = 7.5$ Hz, CH), 128.6 (d, $J_{CP} = 11.4$ Hz, CH), 128.7 (s, CH), 129.1 (s, CH), 130.0 (s, CH), 131.0 (s, C_{quat}), 131.1 (d, $J_{CP} = 7.6$ Hz, CH), 131.4 (s, C_{ipso} -N), 131.8 (s, CH), 131.9 (d, $J_{CP} = 9.4$ Hz, CH), 133.4 (s, C_{quat}), 134.3 (d, ${}^{2}J_{CP} =$ 9.7 Hz, CH), 145.5 (s, CCC=N), 155.9 (d, ${}^{3}J_{CP} = 4.3$ Hz, CC=N), 184.1 (d, ${}^{2}J_{CP} = 5.0$ Hz, C=N), C_{ipso}-P not detected. Anal. Calcd for C₄₃H₃₉Cl₂NP₂Ru (803.7): C, 64.26; H, 4.89; N, 1.74. Found: C, 64.09; H, 4.78; N, 1.70.

Synthesis of Complex 11c. To a solution of 10 (0.044 g, 0.12 mmol) in CH₂Cl₂ (5 mL) was added bicyclo[2.2.1]hepta-2,5-diene molybdenum tetracarbonyl in solution in CH_2Cl_2 (2 mL). The resulting solution was stirred for 1 h at room temperature and then evaporated to dryness. The resulting brown powder was washed with 2 \times 5 mL of pentane, then with 1 mL of Et₂O, to give **11c** as a yellow powder in 58% yield (0.040 g). ${}^{31}P{}^{1}H$ NMR (CDCl₃) δ : 51.4. ${}^{1}H$ NMR (CDCl₃) δ : 1.85 (s, 3H, CH₃), 1.96-2.68 (m, 4H, CH₂), 2.35 (s, 3H, CH₃), 4.04 (m, 1H, CH), 4.52 (dd, ${}^{2}J_{HP} = 7.3$ Hz, ${}^{3}J_{HH} = 7.0$ Hz, 1H, CHP), 5.99 (d, ${}^{3}J_{HH} = 8.1$ Hz, 1H, H_{aron}), 6.95–7.20 (m, 5H, $H_{arom}), \ 7.35{-}7.38 \ (m, \ 2H, \ H_{arom}), \ 7.45{-}7.55 \ (m, \ 2H, \ H_{arom}),$ 7.60–7.82 (m, 2H, H_{arom}). ${}^{13}C{}^{1}H$ NMR (CDCl₃) δ : 17.9 (s, CH₃), 18.2 (s, CH₃), 31.4 (d, ${}^{2}J_{CP} = 13.1$ Hz, CH₂), 33.7 (d, ${}^{1}J_{CP} = 5.3$ Hz, CH₂), 45.4 (s, CH), 63.8 (d, ${}^{1}J_{CP} = 20.9$ Hz, CH), 124.6 (s, CH), 124.9 (s, C_{quat}), 125.6 (s, CH), 126.0 (s, CH), 127.8 (s, CH), 128.4 (s, C_{quat}), 128.8 (d, ${}^{4}J_{CP} = 4.1$ Hz, CH), 129.1 (d, ${}^{3}J_{CP} = 18.2$ Hz, CH), 130.3 (s, CH), 131.1 (d, ${}^{2}J_{CP} = 12.4$ Hz, CH, o–C₆H₅P), 132.1 (s, C_{ipso}–N), 132.9 (s, CH), 149.1 (s, CCC=N), 154.8 (d, ${}^{3}J_{CP}$ = 3.0 Hz, CC=N), 183.4 (d, ${}^{2}J_{CP}$ = 10.3 Hz, C=N), 208.0 (d, ${}^{2}J_{CP} = 10.0$ Hz, C=O), 209.7 (d, ${}^{2}J_{CP} = 10.1$ Hz, C=O), 215.0 (d, ${}^{2}J_{CP} = 36.2$ Hz, C=O), 224.1 (d, ${}^{2}J_{CP} = 7.8$ Hz, C=O), C_{ipso}-P not detected. Anal. Calcd for C₂₉H₂₄NO₄MoP (577.4): C, 60.32; H, 4.19; N, 2.43. Found: C, 60.06; H, 4.11; N, 2.30.

Synthesis of Complex 12. To a solution of **11a** (0.203 g, 0.37 mmol) in 20 mL of CH_2Cl_2 was added the isocyanide 2,6-Me₂C₆H₃-NC (0.049 g, 0.37 mmol) in 5 mL of CH_2Cl_2 . The resulting solution was stirred for 1 h at room temperature, then evaporated, and the residue was washed with Et₂O (2 × 10 mL) and pentane (2 × 10 mL) and dried in a vacuum to give **12** in 88% yield (0.220 g). Crystals were obtained from a 1:1 CH₂Cl₂/pentane solution. ³¹P{¹H} NMR (CD₂Cl₂) δ : 52.2. ¹H NMR (CD₂Cl₂) δ : 1.67 (s, 3H, CH₃), 2.03 (s, 6H, CH₃), 2.07–2.65 (m, 4H, CH₂), 2.66 (s, 3H, CH₃), 4.25 (dd, ²*J*_{HP} = 7.8 Hz, ²*J*_{HH} = 8.0 Hz, 1H, CHP), 4.29 (dd, ²*J*_{HH} = 8.0 Hz, ²*J*_{HP} = 9.8 Hz, 1H, CHP), 6.60 (d, ³*J*_{HH} = 8.0 Hz, 1H, H_{arom}). The compound was not soluble enough to be characterized by ¹³C NMR. Anal. Calcd for C₃₄H₃₃Cl₂N₂PPd (677.9): C, 60.24; H, 4.90; N 4.13. Found: C, 60.01; H, 4.81; N, 4.07.

Synthesis of Complex 14. To a solution of the phosphine **13** (0.372 g, 1 mmol) in 10 mL of CH_2Cl_2 was added (COD)-PdCl₂ (0.291 g, 1 mmol) in solution in 25 mL of CH_2Cl_2 . The resulting solution was stirred for 3 h at room temperature, then the solvent was evaporated to give a yellow solid, which was washed three times with a 1:10 CH_2Cl_2 /pentane solution. Slow evaporation of a CH_2Cl_2 /pentane/ether solution of **14** gave yellow crystals. ³¹P{¹H} NMR (DMSO-*d*₆) δ : 36.3. ¹H NMR (DMSO-*d*₆) δ : 7.15 (dd, ³*J*_{HH} = 7.7 Hz, ³*J*_{HP} = 17.9 Hz, 1H, H_{arom}), 7.40–8.10 (m, 17H, H_{arom}), 8.30 (m, 1H, H_{arom}), 8.80 (s, 1H, CH=N). The compound was not soluble enough to be characterized by ¹³C NMR. Anal. Calcd for C₂₅H₂₀Cl₂NPPd (542.7): C, 55.33; H, 3.71; N, 2.58. Found: C, 55.08; H, 3.62; N, 2.49.

Synthesis of Compound 16. To a solution of 2-(diphenylphosphino)benzaldehyde (0.29 g, 1 mmol) in hot ethanol (2 mL) was added a hot solution of 4-aminophenol (0.11 g, 1 mmol) in ethanol (2 mL). The resulting solution was refluxed in a sealed Schlenk for 2 h. Then the solution was concentrated and cooled at 5 °C for 3 h. Compound **16** precipitated as a yellow solid in 83% yield (0.31 g). ³¹P{¹H} NMR (CDCl₃) δ : -13.3. ¹H NMR (CDCl₃) δ : 5.40 (s, 1H, OH), 6.70–7.45 (m, 12H, H_{arom}), 6.72 (d, ³J_{HH} = 8.8 Hz, 2H, HC²), 6.88 (d, ³J_{HH} = 8.8 Hz, 2H, HC³), 6.91 (m, 1H, HC⁹), 8.16 (ddd, ³J_{HH} = 7.6 Hz, ⁴J_{HP} = 3.8 Hz, ⁴J_{HH} = 1.25 Hz, 1H, HC⁶), 9.07 (d, ⁴J_{HP} = 5.2 Hz, 1H, CH=N). ¹³C{¹H} NMR (CDCl₃) δ : 115.7 (s, C²), 122.5 (s, C³), 127.9 (d, ${}^{4}J_{CP} = 4$ Hz, C^p), 128.6 (s, C⁷ or C⁶), 128.7 (s, C⁶ or C⁷), 128.8 (d, ${}^{3}J_{CP} = 15$ Hz, C^m), 130.6 (s, C⁸), 133.6 (s, C⁹), 134.0 (d, ${}^{2}J_{CP} = 19.6$ Hz, C⁰), 136.4 (d, ${}^{1}J_{CP} = 10$ Hz, Cⁱ), 138.3 (d, ${}^{1}J_{CP} = 17$ Hz, C¹⁰), 139.5 (s, C⁵), 144.5 (s, C⁴), 154.8 (s, C¹), 156.9 (d, ${}^{3}J_{CP} = 21.6$ Hz, CH=N). Anal. Calcd for C₂₅H₂₀-NOP (381.4): C, 78.72; H, 5.28; N, 3.67. Found: C, 78.59; H, 5.17; N, 3.59.

Synthesis of Dendrimer 17. To a solution of the dendrimer 15²² (0.110 g, 0.06 mmol) in THF (5 mL) was added the phosphine 16 (0.300 g, 0.78 mmol) dissolved in THF (5 mL). After stirring overnight at room temperature, the solvent was evaporated under reduced pressure. The residue was washed with a 1:10 THF/pentane solution, giving rise to a white powder. Yield: 93% (0.326 g). ${}^{31}P{}^{1}H{}$ NMR (CDCl₃) δ : -13.1 (s, PPh₂), 8.5 (s, N₃P₃), 63.2 (s, P=S). ¹H NMR (CDCl₃) δ: 3.18 (d, ${}^{3}J_{HP} = 10.3$ Hz, 18H, CH₃), 6.79 (d, ${}^{3}J_{HH} = 8.8$ Hz, 24H, H_{arom}), 6.88 (m, 12H, H_{arom}), 7.01 (d, ${}^{3}J_{HH} = 8.7$ Hz, 12H, H_{arom}), 7.08 (dd, ${}^{3}J_{HH} = 8.8$ Hz, ${}^{4}J_{HP} = 1.2$ Hz, 24H, H_{arom}), 7.22–7.42 (m, 144H, H_{arom}), 7.50 (d, ${}^{3}J_{HP} = 2.0$ Hz, 6H, CH= NN), 7.58 (d, ${}^{3}J_{\text{HH}} = 8.7$ Hz, 12H, C₀³), 8.09 (ddd, ${}^{4}J_{\text{HH}} = 1.2$ Hz, ${}^{4}J_{HP} = 3.9$ Hz, ${}^{3}J_{H-H} = 7.7$ Hz, 12H, HC⁶), 8.95 (d, ${}^{4}J_{HP} =$ 5.2 Hz, 12H, CH=NC). Anal. Calcd for C₃₄₈H₂₇₆N₂₇O₁₈P₂₁S₆ (5967): C, 70.05; H, 4.66, N, 6.34. Found: C, 69.69; H, 4.59; N, 6.23.

Synthesis of Metalladendrimer 18. To a solution of the dendrimer 17 (0.198 g, 0.03 mmol) in CH_2Cl_2 (30 mL) was added (COD)PdCl₂ (0.114 g, 0.4 mmol) in solution in CH₂Cl₂ (20 mL). The resulting mixture was stirred for 3 h at room temperature, then the solvent was evaporated, and the residue was washed with a 1:1 THF/pentane solution (20 mL). 18 was obtained as a yellow solid in 99% yield (0.268 g). ${}^{31}P{}^{1}H{}$ (DMF-d7) d: 12.8 (s, N3P3), 35.5 (s, PPh2), 66.9 (s, P=S). ¹H NMR (DMF- d_7) δ : 3.41 (d, ${}^{3}J_{\text{HP}} = 10.4$ Hz, 18H, CH₃), 6.80– 8.02 (m, 234 H, H_{arom} and CH=NN), 8.29 (m, 12H, HC⁶), 8.70 (s, 12H, CH=NC). Anal. Calcd for C348H276Cl24N27O18P21Pd12S6 (8094.9): C, 51.63; H, 3.44; N, 4.67. Found: C, 51.40; H, 3.36; N, 4.49.

X-ray Analysis. Data were collected at low temperature for 7, 11a, 12, and 14 and at room temperature for 6 on a IPDS STOE diffractometer equipped with an Oxford Cryosystems Cryostream cooler device and using a graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Final unit cell parameters were obtained by means of a least-squares refinement of a set of well-measured reflections, and crystal decay was monitored during the data collection. No significant fluctuations of intensities have been observed. Structures have been solved by direct methods using SIR92²⁴ and refined by least-squares procedures on F^2 with the aid of SHELXL97²⁵ included in the program package WinGX version 1.64,²⁶ and atomic scattering factors were taken from International Tables for X-Ray Crystallography.²⁷ All hydrogen atoms were located on a difference Fourier map refined by using a riding model. For all structures non-hydrogen atoms were anisotropically refined, and in the last cycles of refinement a weighting scheme was used, where weights are calculated from the following formula $w = 1/[\sigma^2(F_0^2) + (aP)^2 + bP]$, where $P = (F_0^2 + 2F_c^2)/(aP)^2 + bP$ 3. Compound 11a crystallizes in the non-centrosymmetric space group $P2_12_12_1$; however it was not possible to properly define the absolute configuration for this structure, as refine-

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ment of the Flack parameters led to a value close to 0.5, which denotes the presence of the racemic twin. The refinement has been carried out using the following twin matrix: $-1 \ 0 \ 0 \ 0 - 1$ $0 \ 0 \ 0 \ -1$

Drawings of molecules were performed with the program ORTEP32²⁸ with 50% probability displacement ellipsoids for non-hydrogens.

General Conditions for Catalytic Experiments. Stille Coupling with Complexes 6, 11a, 14, and 18. Complexes 6 (5% molar, 32 mg, 0.054 mmol), 11a (1% molar, 6 mg, 0.011 mmol; 2.5% molar, 15 mg, 0.027 mmol; 5% molar, 29 mg, 0.054 mmol), 14 (1% molar, 6 mg, 0.011 mmol; 2% molar, 12 mg, 0.021 mmol; 5% molar, 29 mg, 0.054 mmol), and 18 (1% molar [Pd], 7 mg, 0.0008 mmol; 2% molar [Pd], 13 mg, 0.0016 mmol; 5% molar [Pd], 34 mg, 0.0042 mmol) were dissolved in 5 mL of distilled THF or DMF. The iodo derivative (1.07 mmol) was added, and the mixture was stirred 15 min at room temperature. Then the tin derivative (1.07 mmol for tributylvinyltin or 1.18 mmol for tributylstannyl thiophene and phenylethynyltributyltin) was added and the mixture was stirred at 20, 50, or 67 °C. Reactions were monitored either by ¹H NMR (integration of the signals due to the vinyl protons in the case of the coupling of iodobenzene with tributylvinyltin, integration of the signals due to methyl groups in the case of coupling of methyl-2-iodobenzoate with 2-(tributylstannyl)thiophene) or by ¹⁹F NMR (coupling of 4-(trifluoromethyl)iodobenzene with phenylethynyltributyltin).

Stille Coupling with Complexes 5-Pd(OAc)₂, 10-Pd- $(OAc)_2$, 13-Pd $(OAc)_2$, and 17-Pd $(OAc)_2$ (P/Pd = 1). Five percent molar ligand 5 (22 mg, 0.053 mmol), or 5% molar ligand 10 (20 mg, 0.054 mmol), or 5% molar of ligand 13 (20 mg, 0.054 mmol), or 2% molar phosphine of dendrimer 17 (10 mg, 0.0017 mmol) and Pd(OAc)₂ (2%: 4.7 mg; 5%: 12 mg) were dissolved in 5 mL of distilled THF or DMF. The mixture was stirred 15 min at 50 °C. After cooling to room temperature, iodobenzene (1.07 mmol) was added and the mixture was stirred 15 min at room temperature. Then tributylvinyltin (1.07 mmol) was added, and the mixture was stirred at 50 °C. Reactions were monitored by ¹H NMR.

Catalyst Recycling. Degassed and distilled ether (100 mL) was added to the DMF solution to precipitate the catalyst when the reaction was performed in the presence of 17-Pd(OAc)₂ or 18. After filtration, the dendrimer complex was washed with ether (15 mL) and dried under vacuum. For reuse, the resulting powder was solubilized in DMF and the starting reagents were added to the resulting solution. It can be noted that the recycling of monomer 5-Pd(OAc)₂, 6, 10-Pd(OAc)₂, 11a, 13-Pd(OAc)₂, or 14 cannot be done using this procedure since no precipitation of these complexes occurred by adding degassed and distilled ether to the DMF or the THF solution containing reagents and final products involved in the different Stille coupling reactions.

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Supporting Information Available: Tables of crystal data, data collection, structure refinement, atomic coordinates, full list of bond lengths and angles, and anisotropic displacement parameters for complexes 6, 7, 11a, 12, and 14. This material is available free of charge via the Internet at http://pubs.acs.org.

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