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

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Palladium complexes of a variety of $\beta$- and $\gamma$-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 $\gamma$-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, $\beta$-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 *acyclic*-imino phosphines has been investigated.

Very recently[11] we reported the synthesis of new bi- and tricyclic $\beta$-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 $\gamma$-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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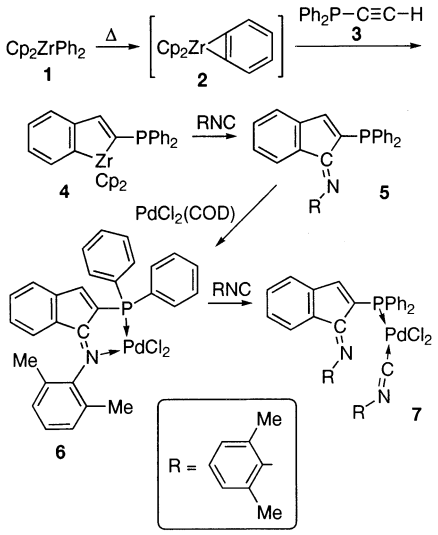
**Scheme 1**




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 olefins[19] 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 $\gamma$-iminophosphine Pd complexes on the surface and that of some related monomers in three different classical Stille coupling reactions.

## Results and Discussion

The $\beta$-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 $\gamma$-iminophosphine **13**[21] and the dendrimer **15**[22] were

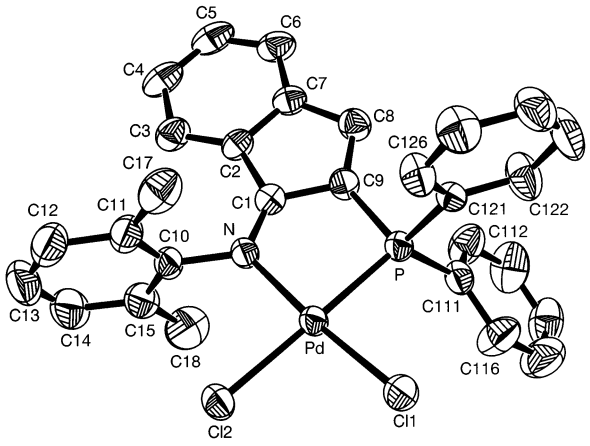
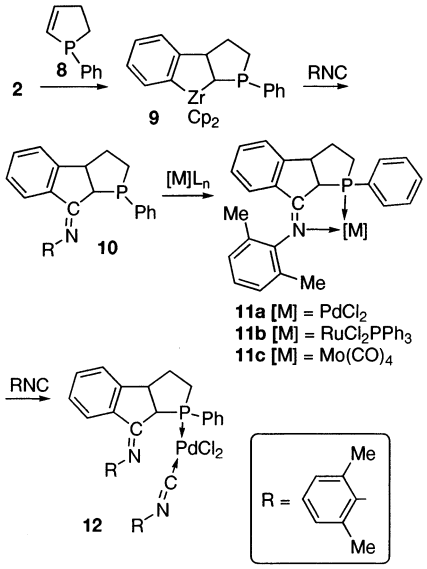



**Figure 1.** ORTEP drawing of **6** (50% probability of the thermal ellipsoids). Selected bond distances (Å) and angles (deg): P−Pd 2.2322 (11), P−C(9) 1.801(4), N−Pd 2.056(3), C(1)−N 1.292(5), C(1)−C(9) 1.459(5), N−Pd−P 86.02(9), C(1)−N−Pd 119.0(3), C(9)−P−Pd 99.18(13), N−C(1)−C(9) 120.8(3), C(1)−C(9)−P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

**Scheme 2**




prepared according to previously reported procedures. The $\gamma$-iminophosphine chain end dendrimer **17** was prepared via a substitution reaction between **15**, bearing six terminal $P(S)Cl_2$ 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 $\beta$-iminophosphine **5** ($\delta^{31}P = -23.8$ ppm) in solution in dichloromethane was first reacted with $PdCl_2$(COD). The resulting complex **6**, obtained in 84% yield, was characterized by means of $^{31}P$ ($\delta = +19$ ppm), $^1H$ NMR, and elemental analysis. An X-ray diffraction study corroborated the postulated structure in which the $PdCl_2$ unit is linked both to the imino nitrogen atom and to the phosphino group (Figure 1, Table 1).

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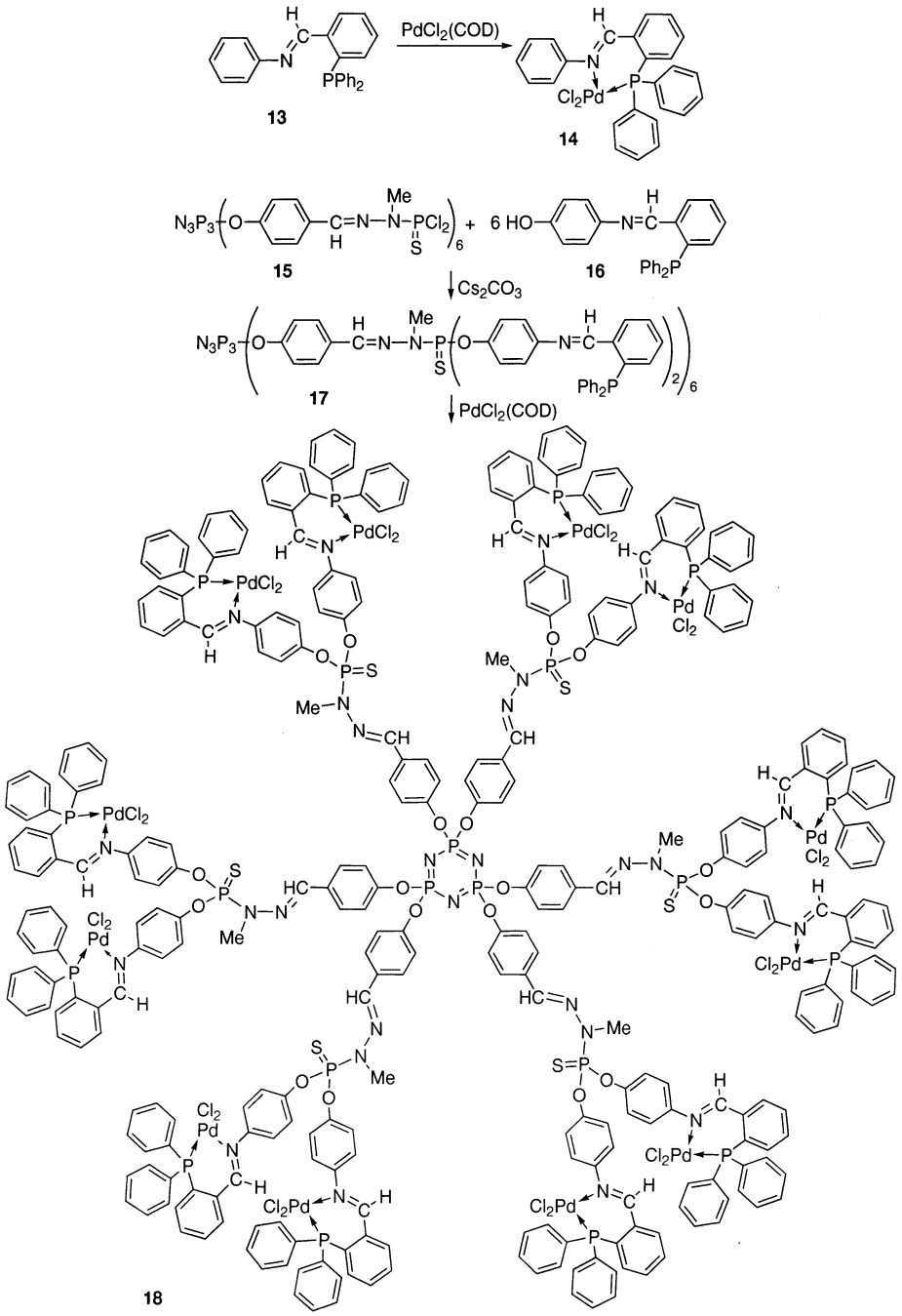
**Scheme 3**






Addition of the isocyanide 2,6-$Me_2C_6H_3$-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 $PdCl_2$ 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 $\beta$-iminophosphine **10**. Complexes with $PdCl_2$ (**11a**), $RuCl_2(PPh_3)$ (**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 $PdCl_2$ unit to the imino nitrogen atom and to phosphorus. A ligand exchange readily occurred when **11a** was reacted with 2,6-$Me_2C_6H_3$-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** → **11a** → **12** transformations, was monitored by $^{31}P$ NMR ($\delta = +9$, $+34.8$, and $+52.2$ ppm, respectively, for **10**, **11a**, and **12**). The palladium complex **14** of the $\gamma$-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)$_2$** ($\delta^{31}P$ (DMF) = 28.2 ppm), **10-Pd(OAc)$_2$** ($\delta^{31}P$ (DMF) = 30.4 ppm), **13-Pd(OAc)$_2$** ($\delta^{31}P$ (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 | $C_{29}H_{24}Cl_2NPPd$ | $C_{38}H_{33}Cl_2N_2PPd$, $CH_2Cl_2$ | $C_{25}H_{24}Cl_2NPPd$ | $C_{34}H_{33}Cl_2N_2PPd$, $CHCl_3$ | $C_{25}H_{20}Cl_2NPPd$, $CH_2Cl_2$ |
| 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 | $P2_1/n$ | $P\bar{1}$ | $P2_12_12_1$ | $P2_1/c$ | $P\bar{1}$ |
| $a$ (Å) | 11.381(2) | 10.161(2) | 12.631(2) | 10.459(2) | 9.002(5) |
| $b$ (Å) | 17.129(2) | 10.305(2) | 8.6180(8) | 14.405(3) | 10.159(5) |
| $c$ (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) |
| $\beta$ (deg) | 96.930(17) | 75.58(2) | 90.0 | 102.04(3) | 80.303(5) |
| $\gamma$ (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) |
| $Z$ | 4 | 2 | 4 | 4 | 2 |
| $D_c$ (g/cm$^3$), $\mu$ (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 |

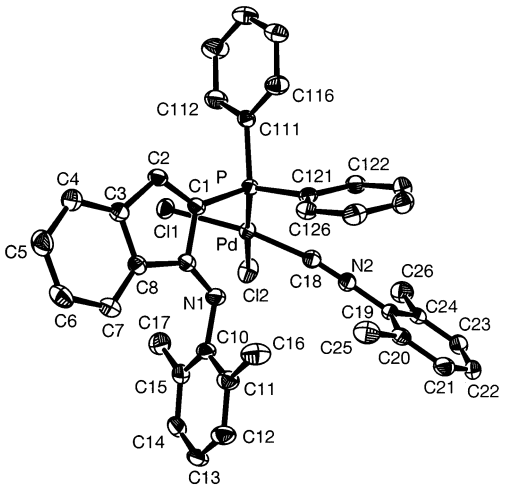



**Figure 2.** ORTEP drawing of **7** (50% probability of the thermal ellipsoids). Selected bond distances (Å) and angles (deg): P−Pd 2.2631(9), P−C(1) 1.792(3), C(9)−N(1) 1.271-(4), C(18)−Pd 1.921(3), C(18)−N(2) 1.146(4), C(18)−Pd−P 93.92(9), C(1)−P−Pd, 109.41(9).

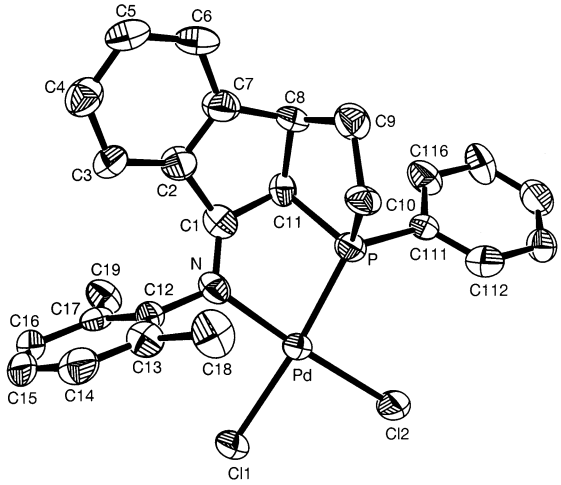



**Figure 3.** ORTEP drawing of **11a** (50% probability of the thermal ellipsoids). Selected bond distances (Å) and angles (deg): P−Pd 2.225(2), N−Pd 2.044(7), C(1)−N 1.311(12), P−C(11) 1.820(9), C(1)−C(11) 1.534(4), N−Pd−P 81.9(2), C(1)−N−Pd 118.7(6), Pd−P−C(11) 101.7(3).

($\delta^{31}$P = 30.4 ppm for terminal P−Pd 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 $PdCl_2$ 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 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 $PdCl_2$ 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.

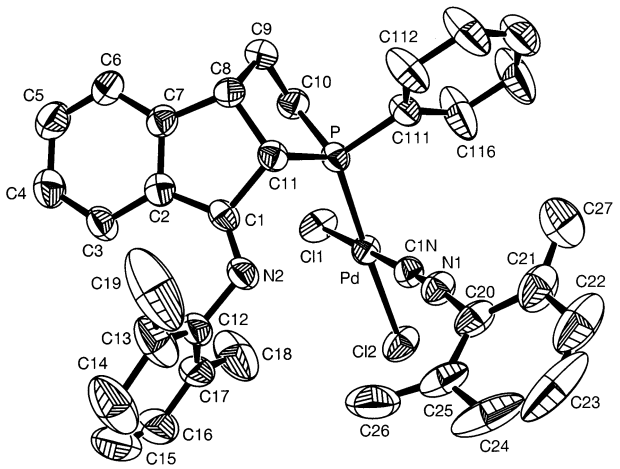



**Figure 4.** ORTEP drawing of **12** (50% probability of the thermal ellipsoids). Selected bond distances (Å) and angles (deg): P−Pd 2.2358(16), C(1)−N(2) 1.265(8), C(1N)−N(1) 1.169(8), P−Pd−C(1N) 88.64(18), Pd−C(1N)−N(1) 177.9-(5).

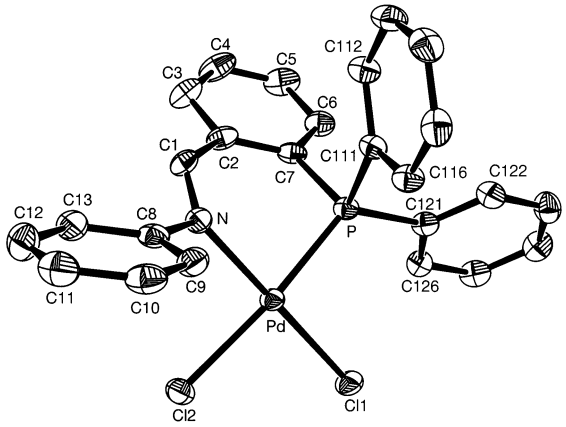



**Figure 5.** ORTEP drawing of **14** (50% probability of the thermal ellipsoids). Selected bond distances (Å) and angles (deg): P−Pd 2.2205(10), N−Pd 2.053(2), N−C(1) 1.275(4), C(1)−C(2) 1.470(4), C(2)−C(7) 1.399(4), C(7)−P 1.819(3), N−Pd−P 86.34(8), C(1)−N−Pd 125.39(18), Pd−P−C(7) 103.84(10).

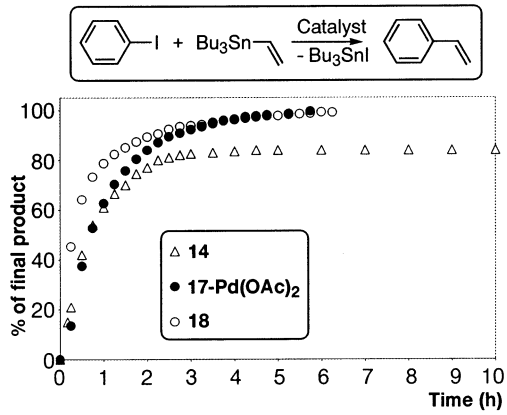



**Figure 6.** Stille coupling of iodobenzene with tributylvinyltin at 50 °C in DMF in the presence of 2 mol % Pd of catalyst **14**, **17-Pd(OAc)$_2$**, or **18**.

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) | *T* (°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) | *T* (°C) | 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.

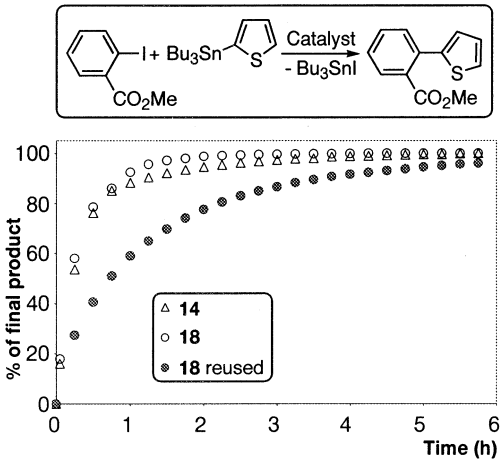



**Figure 7.** Stille coupling of methyl-2-iodobenzoate with 2-(tributylstannyl)thiophene at 50 °C in DMF in the presence of 5 mol % Pd of catalyst **14**, **18**, or recycled **18**.

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 $\beta$-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 $PdCl_2$ complexes coordinated with $\beta$- or $\gamma$-iminophosphines **5**, **10**, and **13** and dendrimer **17** was also demonstrated in the cross-

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

| entry | catalyst | mol % Pd | time (h) | *T* (°C) | solvent | conversion (%) |
|---|---|---|---|---|---|---|
| 1 | **6** | 1 | 20 | 20 | DMF | 65 |
| 2 | **6** | 2.5 | 4 | 20 | DMF | 90 |
| 3 | **11a** | 1 | 20 | 20 | DMF | 70 |
| 4 | **11a** | 2.5 | 20 | 20 | DMF | 90 |
| 5 | **14** | 1 | 10 | 20 | DMF | 90 |
| 6 | **18** | 1 | 15 | 20 | DMF | 75 |

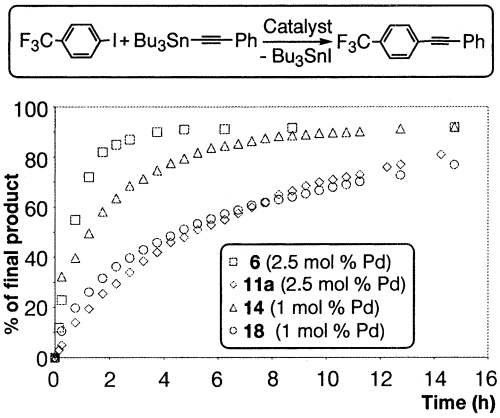



**Figure 8.** Stille coupling of 4-(trifluoromethyl)iodobenzene with phenylethynyltributyltin at 20 °C in DMF in the presence either of 1 mol % Pd of catalyst **14** or **18** or of 2.5 mol % Pd of catalyst **6** or **11a**.

coupling reaction of 4-(trifluoromethyl)iodobenzene with phenylethynyltributyltin (Table 4, Figure 8). The conversion was readily monitored by $^{19}F$ 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 $\beta$-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)$_2$**, **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.

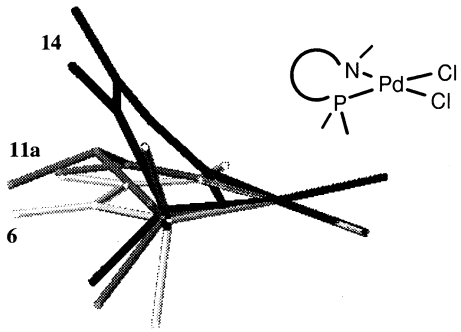



**Figure 9.** Conformation of the palladium five- and six-membered ring in complexes **6**, **11a**, and **14**. For clarity only the location of the substituents (and not the substituents themselves) on phosphorus, nitrogen, and carbon are represented. The largest deviation of the carbon atoms of the palladium ring from the mean $PPdCl_2$ 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 $\gamma$-iminophosphine **13** and the corresponding metalladendrimer **18** are better catalysts than the complexes formed from bi- or tricyclic $\beta$-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 $\gamma$-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. $^1H$, $^{13}C$, and $^{31}P$ NMR and $^{19}F$ spectra were recorded with Bruker AC200, AC250, DPX300, or AMX 400 spectrometers. References for NMR chemical shifts are 85% $H_3PO_4$ for $^{31}P$ NMR, $SiMe_4$ for $^1H$ and $^{13}C$ NMR, and $CF_3CO_2H$ for $^{19}F$. The attribution of $^{13}C$ NMR signals has been done using Jmod, two-dimensional HBMC and HMQC, broad band, or CW $^{31}P$ 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 $\beta$-iminophosphine **5** (0.417 g, 1 mmol) in 10 mL of $CH_2Cl_2$ was added $(COD)PdCl_2$ (0.291 g, 1 mmol) in solution in 20 mL of $CH_2Cl_2$. The resulting solution was stirred for 2 h at room temperature,

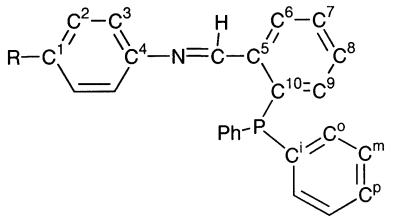


**Figure 10.** Numbering used for NMR.

then the solvent was evaporated to give a yellow solid, which was washed two times with a 1:10 $CH_2Cl_2$/pentane solution. Yellow crystals suitable for X-ray diffraction studies were obtained from a $CH_2Cl_2$/pentane/ether solution of **6**. $^{31}P\{^1H\}$ NMR ($CH_2Cl_2$) $\delta$: 19.0. $^1H$ NMR ($CD_2Cl_2$) $\delta$: 2.28 (s, 6H, $CH_3$), 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 $^{13}C$ NMR. Anal. Calcd for $C_{29}H_{24}Cl_2NPPd$ (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-$Me_2C_6H_3$-NC (0.013 g, 0.1 mmol) in 5 mL of $CH_2Cl_2$. 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. $^{31}P\{^1H\}$ NMR ($CDCl_3$) $\delta$: 15.5. $^1H$ NMR ($CDCl_3$) $\delta$: 1.92 (s, 6H, $CH_3$), 2.06 (s, 6H, $CH_3$), 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 $^{13}C$ NMR. Anal. Calcd for $C_{38}H_{33}Cl_2N_2PPd$ (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 $CH_2Cl_2$ (5 mL) was added (COD)$PdCl_2$ (0.060 g, 0.21 mmol) in $CH_2Cl_2$ (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 × 10 mL) and pentane (2 × 10 mL), to give **11a** in 82% yield (0.094 g). Crystals were obtained from a 1:1 $CH_2Cl_2$/pentane solution. $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$) $\delta$: 34.8. $^1H$ NMR ($CD_2Cl_2$) $\delta$: 2.12−2.40 (m, 1H), 2.31 (s, 6H, $CH_3$), 2.43−2.63 (m, 2H), 2.75−2.93 (m, 1H), 3.90−3.98 (m, 1H), 5.11 (ddd, $^3J_{HH}$ = 1.1 Hz, $^4J_{HH}$ = 5.4 Hz, $^2J_{PH}$ = 6.9 Hz, 1H, CH−C=N), 5.95 (d, $^3J_{HH}$ = 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-$C_6H_5P$). The compound was not soluble enough to be characterized by $^{13}C$ NMR. Anal. Calcd for $C_{25}H_{24}Cl_2NPPd$ (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 $CH_2Cl_2$ was added $(Ph_3P)_3RuCl_2$ (0.138 g, 0.14 mmol) in 5 mL of $CH_2Cl_2$. The resulting deep brown solution was stirred for 1 h at room temperature, then evaporated to dryness. The resulting brown powder was dissolved in $CH_2Cl_2$ (1 mL) then precipitated with 10 mL of pentane. **11b** was obtained as a brown powder in 78% yield (0.088 g). $^{31}P\{^1H\}$ NMR ($CDCl_3$) $\delta$: 55.1 (d, $^2J_{PP}$ = 43.9 Hz, CH−P−$CH_2$), 79.5 (d, $^2J_{PP}$ = 43.9 Hz, $PPh_3$). $^1H$ NMR ($CDCl_3$) $\delta$: 2.02 (s, 3H, $CH_3$), 2.05−2.52 (m, 3H, $CH_2$), 2.52 (s, 3H, $CH_3$), 2.61−2.89 (m, 1H, $CH_2$−P), 3.58−3.72 (m, 1H, CH), 5.37 (dd, $^3J_{HH}$ = 6.0 Hz, $^2J_{HP}$ = 7.1 Hz, 1H, CHP), 6.23 (d, $^3J_{HH}$ = 7.7 Hz, 1H, $H_{arom}$), 6.93−7.73 (m, 26H, $H_{arom}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) $\delta$: 19.9 (s, $CH_3$), 21.2 (s, $CH_3$), 25.6 (d, $^2J_{CP}$ = 24.6 Hz, $CH_2P$), 32.4 (s, $CH_2CH_2P$), 41.9 (s, CH), 65.3 (d, $^1J_{CP}$ = 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, $^2J_{CP}$ = 9.7 Hz, CH), 145.5 (s, CCC=N), 155.9 (d, $^3J_{CP}$ = 4.3 Hz, CC=N), 184.1 (d, $^2J_{CP}$ = 5.0 Hz, C=N), $C_{ipso}$−P not detected. Anal. Calcd for $C_{43}H_{39}Cl_2NP_2Ru$ (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 $CH_2Cl_2$ (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 × 5 mL of pentane, then with 1 mL of $Et_2O$, to give **11c** as a yellow powder in 58% yield (0.040 g). $^{31}P\{^1H\}$ NMR ($CDCl_3$) $\delta$: 51.4. $^1H$ NMR ($CDCl_3$) $\delta$: 1.85 (s, 3H, $CH_3$), 1.96−2.68 (m, 4H, $CH_2$), 2.35 (s, 3H, $CH_3$), 4.04 (m, 1H, CH), 4.52 (dd, $^2J_{HP}$ = 7.3 Hz, $^3J_{HH}$ = 7.0 Hz, 1H, CHP), 5.99 (d, $^3J_{HH}$ = 8.1 Hz, 1H, $H_{arom}$), 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, $H_{arom}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) $\delta$: 17.9 (s, $CH_3$), 18.2 (s, $CH_3$), 31.4 (d, $^2J_{CP}$ = 13.1 Hz, $CH_2$), 33.7 (d, $^1J_{CP}$ = 5.3 Hz, $CH_2$), 45.4 (s, CH), 63.8 (d, $^1J_{CP}$ = 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, $^4J_{CP}$ = 4.1 Hz, CH), 129.1 (d, $^3J_{CP}$ = 18.2 Hz, CH), 130.3 (s, CH), 131.1 (d, $^2J_{CP}$ = 12.4 Hz, CH, o−$C_6H_5P$), 132.1 (s, $C_{ipso}$−N), 132.9 (s, CH), 149.1 (s, CCC=N), 154.8 (d, $^3J_{CP}$ = 3.0 Hz, CC=N), 183.4 (d, $^2J_{CP}$ = 10.3 Hz, C=N), 208.0 (d, $^2J_{CP}$ = 10.0 Hz, C=O), 209.7 (d, $^2J_{CP}$ = 10.1 Hz, C=O), 215.0 (d, $^2J_{CP}$ = 36.2 Hz, C=O), 224.1 (d, $^2J_{CP}$ = 7.8 Hz, C=O), $C_{ipso}$−P not detected. Anal. Calcd for $C_{29}H_{24}NO_4MoP$ (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-$Me_2C_6H_3$-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 $Et_2O$ (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 $CH_2Cl_2$/pentane solution. $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$) $\delta$: 52.2. $^1H$ NMR ($CD_2Cl_2$) $\delta$: 1.67 (s, 3H, $CH_3$), 2.03 (s, 6H, $CH_3$), 2.07−2.65 (m, 4H, $CH_2$), 2.66 (s, 3H, $CH_3$), 4.25 (dd, $^2J_{HP}$ = 7.8 Hz, $^2J_{HH}$ = 8.0 Hz, 1H, CHP), 4.29 (dd, $^2J_{HH}$ = 8.0 Hz, $^2J_{HP}$ = 9.8 Hz, 1H, CHP), 6.60 (d, $^3J_{HH}$ = 8.0 Hz, 1H, $H_{arom}$), 6.93−7.58 (m, 12H, $H_{arom}$), 7.94−8.04 (m, 2H, $H_{arom}$). The compound was not soluble enough to be characterized by $^{13}C$ NMR. Anal. Calcd for $C_{34}H_{33}Cl_2N_2PPd$ (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)-$PdCl_2$ (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. $^{31}P\{^1H\}$ NMR (DMSO-$d_6$) $\delta$: 36.3. $^1H$ NMR (DMSO-$d_6$) $\delta$: 7.15 (dd, $^3J_{HH}$ = 7.7 Hz, $^3J_{HP}$ = 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 $^{13}C$ NMR. Anal. Calcd for $C_{25}H_{20}Cl_2NPPd$ (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). $^{31}P\{^1H\}$ NMR ($CDCl_3$) $\delta$: −13.3. $^1H$ NMR ($CDCl_3$) $\delta$: 5.40 (s, 1H, OH), 6.70−7.45 (m, 12H, $H_{arom}$), 6.72 (d, $^3J_{HH}$ = 8.8 Hz, 2H, $HC^2$), 6.88 (d, $^3J_{HH}$ = 8.8 Hz, 2H, $HC^3$), 6.91 (m, 1H, $HC^9$), 8.16 (ddd, $^3J_{HH}$ = 7.6 Hz, $^4J_{HP}$ = 3.8 Hz, $^4J_{HH}$ = 1.25 Hz, 1H, $HC^6$), 9.07 (d, $^4J_{HP}$ = 5.2 Hz, 1H, CH=N). $^{13}C\{^1H\}$ NMR ($CDCl_3$) $\delta$: 115.7 (s, $C^2$), 122.5

(s, $C^3$), 127.9 (d, $^4J_{CP}$ = 4 Hz, $C^p$), 128.6 (s, $C^7$ or $C^6$), 128.7 (s, $C^6$ or $C^7$), 128.8 (d, $^3J_{CP}$ = 15 Hz, $C^m$), 130.6 (s, $C^8$), 133.6 (s, $C^9$), 134.0 (d, $^2J_{CP}$ = 19.6 Hz, $C^o$), 136.4 (d, $^1J_{CP}$ = 10 Hz, $C^i$), 138.3 (d, $^1J_{CP}$ = 17 Hz, $C^{10}$), 139.5 (s, $C^5$), 144.5 (s, $C^4$), 154.8 (s, $C^1$), 156.9 (d, $^3J_{CP}$ = 21.6 Hz, CH=N). Anal. Calcd for $C_{25}H_{20}NOP$ (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 **15**[22] (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). $^{31}P\{^1H\}$ NMR ($CDCl_3$) $\delta$: −13.1 (s, $PPh_2$), 8.5 (s, $N_3P_3$), 63.2 (s, P=S). $^1H$ NMR ($CDCl_3$) $\delta$: 3.18 (d, $^3J_{HP}$ = 10.3 Hz, 18H, $CH_3$), 6.79 (d, $^3J_{HH}$ = 8.8 Hz, 24H, $H_{arom}$), 6.88 (m, 12H, $H_{arom}$), 7.01 (d, $^3J_{HH}$ = 8.7 Hz, 12H, $H_{arom}$), 7.08 (dd, $^3J_{HH}$ = 8.8 Hz, $^4J_{HP}$ = 1.2 Hz, 24H, $H_{arom}$), 7.22−7.42 (m, 144H, $H_{arom}$), 7.50 (d, $^3J_{HP}$ = 2.0 Hz, 6H, CH=NN), 7.58 (d, $^3J_{HH}$ = 8.7 Hz, 12H, $C_0^3$), 8.09 (ddd, $^4J_{HH}$ = 1.2 Hz, $^4J_{HP}$ = 3.9 Hz, $^3J_{H-H}$ = 7.7 Hz, 12H, $HC^6$), 8.95 (d, $^4J_{HP}$ = 5.2 Hz, 12H, CH=NC). Anal. Calcd for $C_{348}H_{276}N_{27}O_{18}P_{21}S_6$ (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 $(COD)PdCl_2$ (0.114 g, 0.4 mmol) in solution in $CH_2Cl_2$ (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). $^{31}P\{^1H\}$ (DMF-$d_7$) $\delta$: 12.8 (s, $N_3P_3$), 35.5 (s, $PPh_2$), 66.9 (s, P=S). $^1H$ NMR (DMF-$d_7$) $\delta$: 3.41 (d, $^3J_{HP}$ = 10.4 Hz, 18H, $CH_3$), 6.80−8.02 (m, 234 H, $H_{arom}$ and CH=NN), 8.29 (m, 12H, $HC^6$), 8.70 (s, 12H, CH=NC). Anal. Calcd for $C_{348}H_{276}Cl_{24}N_{27}O_{18}P_{21}Pd_{12}S_6$ (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$\alpha$ 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 SIR92[24] and refined by least-squares procedures on $F^2$ with the aid of SHELXL97[25] 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 $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$. 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 refinement 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 ORTEP32[28] 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 $^{19}F$ 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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