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Phosphaalkenes Palladium(II) Complexes in the Suzuki and Sonogashira Cross-Coupling Reactions

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ABSTRACT: *The 1-methoxy-2-(supermesitylphosphanylidenemethyl)-benzene ligand (**1**) was prepared by reacting the phospha-Wittig reagent [Mes*P=PMe$_3$] with o-methoxybenzaldehyde. Reaction of 1 with one equivalent of the [Pd(allyl)Cl]$_2$ dimer in the presence of Ag(OTf) affords a neutral complex (**4**) in which the triflate ligand is coordinated to the palladium atom. DFT calculations show that the formation of complex **4** is favored by 22.4 kcal/mol with respect to that of a chelate species involving coordination of the ligand through the phosphorus atom of one lone pair at the oxygen of the pendant methoxy group. Reaction of two equivalents of ligand 1 with the [Pd(allyl)Cl]$_2$ dimer affords complex **5**, in which the two ligands are coordinated through their phosphorus atom. The catalytic activity of complex **5** was compared to that of the 1,3-bis[2-(supermesityl)phosphanediylmethyl]benzene palladium chloride complex (6). Performances of the two catalysts were found to be similar in the Suzuki cross-coupling reaction between phenylboronic acid and some arylbromides (TON between 55.10^5 and 99.10^5) as well as in the Sonogashira coupling between phenylacetylene and arylbromides (TON between 400 and 950).* © 2007 Wiley Periodicals, Inc. Heteroatom Chem 18:363–371, 2007; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20307

INTRODUCTION

Low-coordinated phosphorus compounds display unusual electronic properties that make them very attractive ligands in coordination chemistry [1]. Thus, their good π-accepting capacity has been exploited for the stabilization of highly electron-rich or electron-excessive transition metal fragments [2]. However, these molecules have not been widely used as ligands in catalysis so far. This situation mainly results from their limited stability. Thus, without appropriate kinetic (use of bulky groups at phosphorus) or thermodynamic (conjugation, aromaticity) stabilization, most low coordinated phosphorus compounds are too reactive to be engaged in the elaboration of viable catalysts. This explains why studies were only limited to derivatives such as phosphaferrocenes (stabilization through π-coordination), sterically protected phosphaalkenes (kinetic stabilization), and phosphinines (stabilized by aromaticity) in some cases. With phosphaalkenes, most of the developments have been reported by the groups of Yoshifuji and Ozawa, who published a series of articles on the use of DCPB ligands (1,2-diaryl-3,4-diphosphinidenecyclobutene

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For further details on the theoretical structure of complexes **I** and **II** and the X-ray structural data for complexes **4** and **5**, contact Pascal Le Floch.

ligands) [3]. Group 10 and 11 complexes of these ligands proved to be very efficient catalysts in processes such as the polymerization of ethylene [4], the dehydrogenative silylation of ketones [5], the allylation of amines [6], the hydroamination of 1,3-dienes [7], the cyanation of arylbromides [8], the cyclodehydration of diols [9], and the amination of bromoarenes [10]. As part of a program aimed at exploring the use of mono-, bi-, and tridentate ligands featuring phosphaalkenes as ancillary ligands in catalysis, we have recently investigated their use in two very popular palladium-mediated cross-coupling processes, the Suzuki [11] and the Sonogashira reactions [12]. The use of low-coordinated phosphorus compounds in these two processes is not totally unprecedented. In 1995, Yoshifuji reported on the use of a [(DCPB)$PdCl_2$] complex in the Sonogashira coupling between trimethylsilylacetylene and *p*-bromonitrobenzene (TON about 75) [13]. In 2000, we reported on the very good activity (TON about 1.10^6) of an octaethyldiphosphaferrocene Pd(0) complex in the Suzuki coupling of aryliodides [14] with phenylboronic acid. Later the group of Yoshifuji reported on the coupling of iodobenzene with phenylboronic acid or phenylacetylene catalyzed by DCPB and 1,3-diphosphapropene (and their P=S derivatives) palladium complexes in a series of consecutive papers [15]. All these couplings afforded the expected biaryl derivatives and functional alkynes in fair to good yields and were carried out with 1 to 4 mol% of catalyst. Note that a report also mentions that polymers featuring DCPB-based ligands were also employed in the coupling of trimethylsilylacetylene with *p*-bromonitrobenzene [16]. Herein we wish to report on our most recent results.

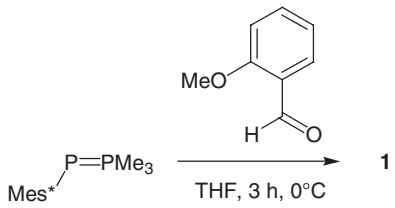
RESULTS AND DISCUSSION

Three types of phosphaalkene ligands were selected for this study. We selected ligand **1**, which features one methoxy group at the α-position on the aryl group in order to test the ability of this methoxy group to act as an hemilabile ligand. Compound **2**, whose synthesis we recently reported, is a bidentate ligand that features two phosphaalkene units grafted on a dibenzofurane skeleton [17]. Finally, in view of the importance of palladacycles in catalysis [18] we have also explored the reactivity of ligand **3**, whose synthesis was reported by the group of Stephan and Geoffroy some years ago. As will be seen further a new synthetic approach toward this interesting ligand has been developed.

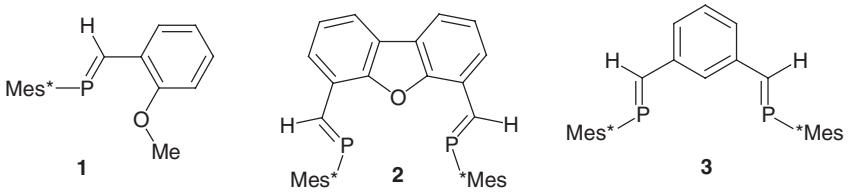
Synthesis of phosphaalkene **1** was conventionally achieved through the phospha-Wittig approach by reacting the Mes*P=PMe_3 reagent with *o*-methoxybenzaldehyde in THF at 0°C for 3 hours [19]. After usual workup, **1** (only the *E* isomer) was isolated as an air-stable white powder whose NMR data compared with other related species (Scheme 2) [20].

Ligand **3** was synthesized by the group of Geoffroy in 1992 using the Yoshifuji procedure [21] (phospha-Petersen reaction) using Mes*PH($SiMe_2$-*t*-Bu) as starting precursor [22]. The group of Stephan later proposed an alternative pathway that relied on the reaction of the metalla-Wittig reagent [Cp_2Zr(=PMes*)(PMe_3)] complex with isophtalaldehyde [23]. We found here the classical phospha-Wittig reaction to be the most straightforward approach, and bidentate ligand **3** was readily obtained by reacting 2.5 equivalents of Mes*P=PMe_3 with isophtalaldehyde at 0°C for 3 hours. Following this procedure, compound **3** was obtained with a 70% yield as a very stable yellow solid (Scheme 3). Note that, in this case again, only the *E,E*-isomer was formed.

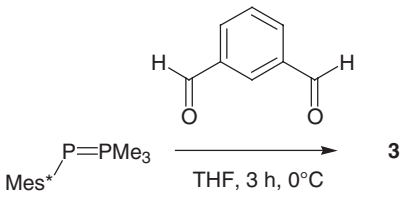
Ligand **1** was reacted with half an equivalent of [Pd(COD)Cl_2] in dichloromethane at room



SCHEME 2 Synthesis of ligand **1**.



SCHEME 1 Ligands studied.

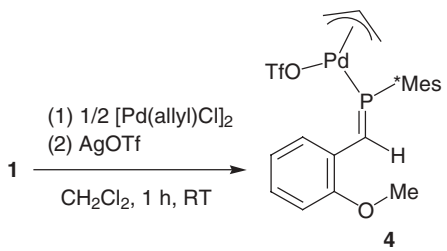


SCHEME 3 Synthesis of ligand **3**.

temperature to afford a highly insoluble complex within minutes for which only a weak signal ($\delta(CH_2Cl_2) = 189.0$ ppm) could be observed in ^{31}P NMR. Although elemental analyses confirm the presence of two phosphaalkene ligands for one $PdCl_2$ fragment, the lack of other NMR data precluded the determination of the stereochemistry of the complex (*cis* or *trans*) or the monomeric nature of the complex. An interesting result was obtained by reacting half an equivalent of $[Pd(allyl)Cl]_2$ with one equivalent of **1** in the presence of AgOTf as chloride abstractor in dichloromethane at room temperature. After filtration of AgCl salts, complex **4** was isolated in excellent yield as a white powder. However, the structure of **4** was difficult to establish on the sole basis of NMR data, which indicate that only one phosphaalkene ligand is present in the molecule. Single crystals were thus grown by diffusing a solution of hexanes (mixture of isomers) into a dichloromethane solution of the complex at room temperature (Scheme 4).

A view of one molecule of **4** is presented in Fig. 1. Crystal data and structure refinement parameters are listed in Table 1. As can be seen, in this complex, ligand **1** does not behave as a chelate. Only the phosphorus atom is coordinated to the palladium center and the triflate couteranion completes the coordination sphere. Apart from this, the structure of **4** does not deserve further remarks, metric parameters being comparable with other palladium(II) phosphaalkene complexes reported in the literature.

Calculations were carried out to estimate the energetic difference between a complex featuring ligand **1** as chelate species and the isolated complex



SCHEME 4 Synthesis of complex **4**.

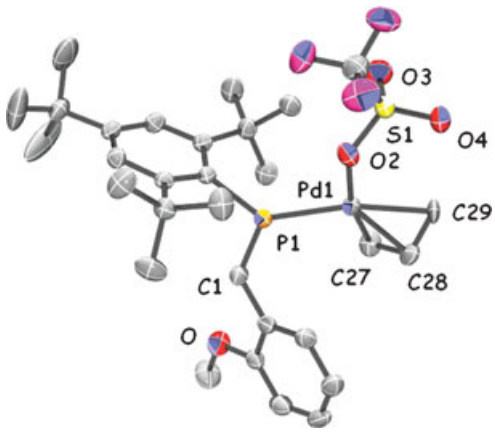


FIGURE 1 One molecule of complex **4**.

4 that features the triflate as ligand. Optimizations were carried out using the ONIOM method and the Gaussian set of programs. The B3PW91 functional was used in combination with the 6-31G* basis set for all nonmetallic atoms and the LANL2DZ basis set for palladium. Two tertiobutyl groups of the Mes* group were computed at the molecular mechanics level of theory using the UFF force field to save computation time. The third tertiobutyl group located at the para position was replaced by a H atom. Energies of the complexes were given by single-point calculations (quantum level for all atoms) of the ONIOM optimized structures. The two optimized structures **I** (coordinated triflate) and **II** (uncoordinated triflate) are presented in Fig. 2. Note that metric parameters in complex **I** are very close to those of the experimental structure (complex **4**). The structure of **II** proved to be very difficult to optimize and we found that the issue of optimization depends on the initial location of the triflate anion. Thus, preliminary calculations in which the triflate anion was initially positioned in close proximity to the cationic palladium atom (above the plane of the anisole ligand) invariably yielded structure **I** as minimum, a ligand displacement reaction taking place along the optimization process. Finally, a structure of **II** could be computed by initially locating the triflate in an area where no interaction with the cationic palladium can occur. In line with experimental observations, we found that the energetic difference between the two complexes is indeed very important (**I–II** = −22.4 kcal/mol) and thus explains why the formation of the chelate species is never observed.

Reaction of two equivalents of ligand **1** with $[Pd(allyl)Cl]_2$ afforded complex **5**, which was isolated as a very stable white solid (Scheme 5). All NMR data and elemental analyses confirm the proposed structure. Additional evidence was provided

TABLE 1 Crystal Data and Structure Refinement Parameters for complexes **4** and **5**

Compound	**4**	**5**
Empirical formula	$C_{30}H_{42}O_4F_3SPPd$	$C_{55}H_{79}O_2P_2Pd.CF_3O_2S$
M	693.07	1073.59
T (K)	150(1)	150(1)
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	*P*–1
a (Å)	10.027(1)	10.245(1)
b (Å)	30.878(1)	19.195(1)
c (Å)	11.001(1)	19.405(1)
α (°)	90.00	116.51(1)
β (°)	110.35(1)	100.96(1)
γ (°)	90.00	94.40(1)
V (Å^3)	3193.5(4)	3295.0(4)
Z	4	2
μ (cm^{-1})	0.746	0.406
F(000)	1432	1132
D_{calc} (g cm^{-1})	1.442	1.082
Index range	$-14 < h < 14$ $-40 < k < 43$ $-15 < l < 15$	$-12 < h < 12$ $-23 < k < 23$ $-24 < l < 24$
Scan type	Phi and omega scans	Phi and omega scans
$2\theta_{max}$ (°)	30.03	26.37
Reflectance measured	16503	22036
Independent reflectance	9295	13349
R_{int}	0.0207	0.0248
Completeness to θ_{max} (%)	99.5	99.1
Parameters	381	555
$R_1(F_{hkl})$	0.0379	0.0481
ωR_2	0.1124	0.1454
GOF	1.096	1.043
ρ_{max}/ρ_{min} (eÅ^{-3})	0.861/–0.838	0.734/–0.543

by an X-ray crystallographic study. A view of one molecule of **5** is presented in Fig. 2. Crystal data and structure refinement parameters are listed in Table 1. As can be seen, despite their bulkiness the two phosphaalkene ligands adopt a spatial arrangement that minimizes steric repulsion between the tertiobutyl groups without dramatically expanding the P—Pd—P angle, which is comparable to those recorded in other structures of Pd(allyl) complexes (110.9°) [24] (Fig. 2).

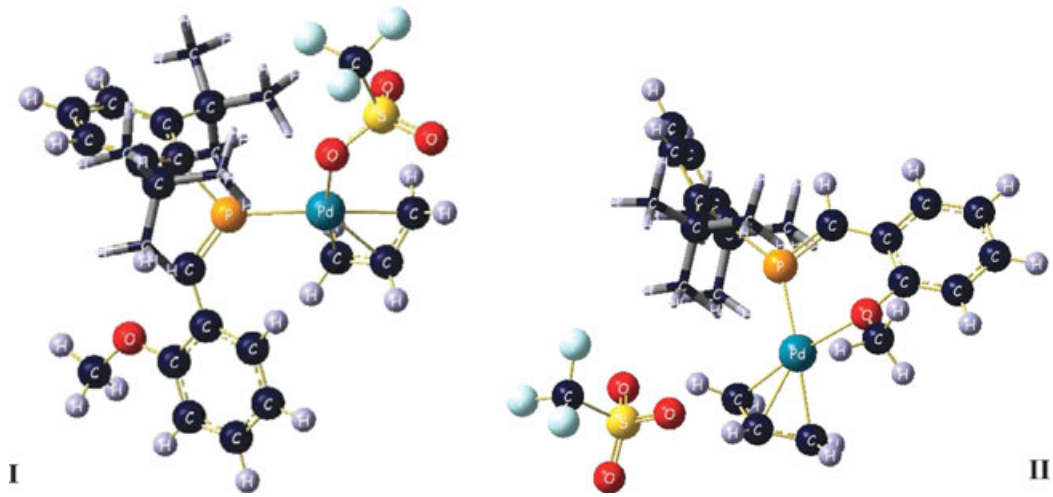
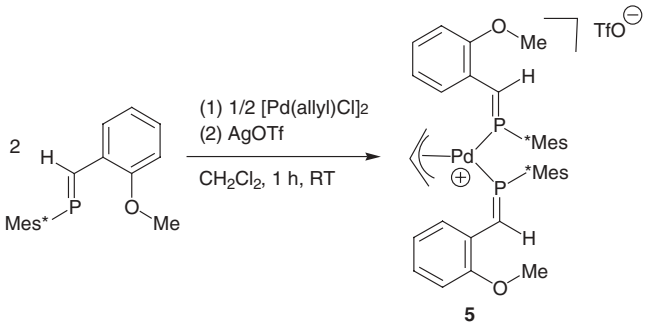


FIGURE 2 Optimized geometries of model complexes **I** and **II** as given by ONIOM calculations.



SCHEME 5 Synthesis of complex **5**.

Less satisfying results were obtained when one equivalent of ligand **2** was reacted with both metallic precursors. Thus, reaction with $[Pd(COD)Cl_2]$ afforded an insoluble material that could neither be crystallized nor characterized by NMR techniques. On the other hand, reaction of **2** with the $[Pd(allyl)Cl]_2$ yielded a complicated mixture of complexes whose formulation could not be established, as attested by the ^{31}P NMR spectrum of the crude mixture.

Complex **6**, which had previously been characterized by the group of Geoffroy, was conventionally prepared by heating one equivalent of the ligand **3** with $[(PhCN)_2PdCl_2]$ in dichloromethane. Contrary to the initially reported procedure, we found that a longer heating period was needed to complete the reaction (40°C for 10 h) (Scheme 6).

The catalytic activity of complexes **4, 5**, and **6** was evaluated in two well-known transformations that allow the formation of C–C bonds: the Suzuki and the Sonogashira cross-coupling reactions (Scheme 7). Complexes **5** and **6** exhibited the

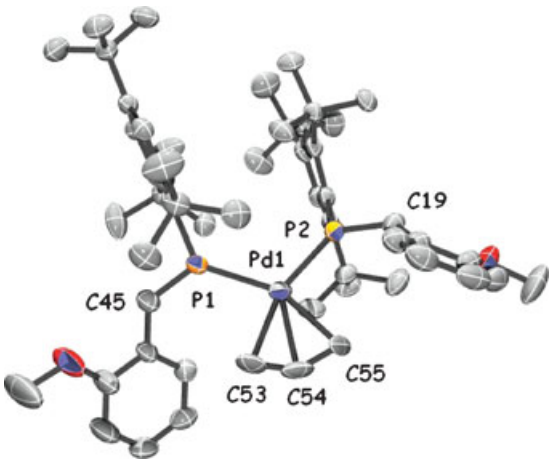
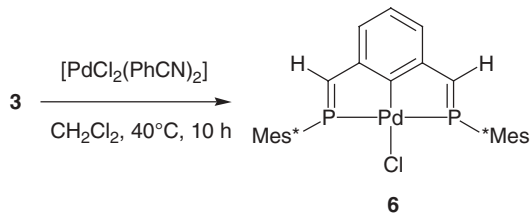
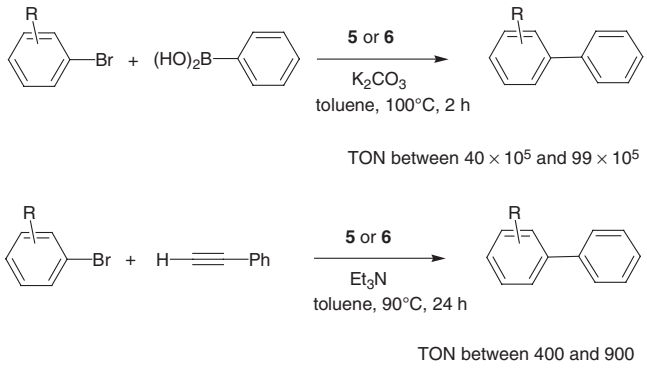


FIGURE 3 One molecule of complex **5**.



SCHEME 6 Synthesis of complex **6** from **3**.



SCHEME 7 Suzuki and Sonogashira cross-coupling reactions using complexes **5** or **6** as catalysts.

most important activity in both processes. Thus, in the Suzuki coupling, TON fall in the range from 40×10^5 to 99×10^5. To the best of our knowledge, these yields are the most important recorded so far for low-coordinated phosphorus ligands and the performance of these two catalysts compare with those of the most efficient systems. Interestingly, we found that the Sonogashira coupling could be carried out without the presence of copper(I) salts. Unfortunately, as previously observed with phosphaferocene ligands, this coupling process could not be transposed to the conversion of chloroaromatics, most experiments resulting in the recovery of starting materials and/or reduced compounds (see Table 2). Both complexes also exhibited an interesting activity in the Sonogashira coupling, which is known to be much more difficult to catalyze than the Suzuki coupling, and TONs ranging from 400 to 950 were obtained (see Table 3).

In conclusion, we have shown that phosphaalkene-based palladium complexes such as **5** and **6** can lead to important conversions in the Suzuki and the Sonogashira cross-coupling processes. Further studies will now focus on the use of ligands **1** and **3** in other catalytic transformations with different metals.

TABLE 2 Results Obtained in the Coupling of Phenylboronic Acid with Some Bromoarenes

Entry	*Arylbromide*	*Catalyst*	*Yield*	*TON*
1	Bromobenzene	**5**	99	99×10^5
2		**6**	88	88×10^5
3	*p*-Bromoacetophenone	**5**	40	40×10^5
4		**6**	54	54×10^5
5	*p*-Bromoanisole	**5**	99	99×10^5
6		**6**	68	68×10^5
7	*p*-Bromotoluene	**5**	99	99×10^5
8		**6**	87	87×10^5
9	1-Bromo-3,5-dimethylbenzene	**5**	99	99×10^5
10		**6**	55	55×10^5

TABLE 3 Results Obtained in the Coupling of Phenylacetylene with Some Bromoarenes

Entry	*Arylbromide*	*Catalyst*	*Yield*	*TON*
1	Bromobenzene	**5**	85	850
2		**6**	78	780
3	*p*-Bromoacetophenone	**5**	95	950
4		**6**	95	950
5	*p*-Bromoanisole	**6**	40	400
6	*p*-Bromotoluene	**6**	76	760
7	1-Bromo-3,5-dimethylbenzene	**5**	78	780
8		**6**	68	680

EXPERIMENTAL

General

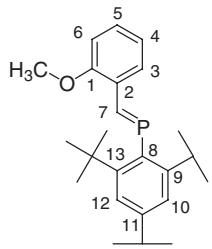
All reactions were routinely performed under an inert atmosphere of argon or nitrogen by using Schlenk and glove-box techniques and dry deoxygenated solvents. Dry THF and hexanes were obtained by distillation from Na/benzophenone. Dry dichloromethane was distilled from P_2O_5, dry toluene and THF from Na. NMR spectra were recorded on a Bruker Avance 300 spectrometer operating at 300 MHz for ^{1}H, 75.5 MHz for ^{13}C, and 121.5 MHz for ^{31}P. Solvent peaks are used as internal reference relative to Me_4Si for ^{1}H and ^{13}C chemical shifts (ppm); ^{31}P chemical shifts are relative to an 85% H_3PO_4 external reference and coupling constants are expressed in Hertz. The following abbreviations are used: b, broad; s, singlet; d, doublet; t, triplet; m, multiplet; p, pentuplet; sext, sextuplet; sept, septuplet; v, virtual. Elemental analyses were performed by the "Service d'analyse du CNRS," at Gif sur Yvette, France. [Pd(COD)Cl_2], [Pd(allyl)Cl]$_2$, and [$(PhCN)_2PdCl_2$] were prepared according to literature procedures. All other reagents and chemicals were obtained commercially and used as received.

*Synthesis of the Phospha-Wittig Reagent Mes*P=PPh$_3$*

To a mixture of Mes*PCl_2 (1.0 g, 2.9 mmol) and Zn (1.0 g, 15.0 mmol) in THF (10 mL) at 0°C, was syringed PMe_3(1 M, 7.5 mmol, 7.5 mL). The crude mixture was allowed to warm to room temperature and was stirred for 3 h. The ^{31}P NMR spectrum showed the formation of the desired reagent, which was used without further purification.

^{31}P NMR (121.5 MHz, THF, 298K): δ 6.6 ppm (^1J(P—P) = 577.9, Mes*P), −132.5 ppm (^1J(P—P) = 577.9, PMe_3).

*Synthesis of 1-Methoxy-2-(supermesitylphosphanylidenemethyl)-benzene (**1**)*



The phospha-Wittig reagent [Mes*P=PMe_3] was cooled to 0°C and cannulated onto a suspension of *o*-methoxybenzaldehyde (0.165 g, 1.2 mmol, 0.4 equiv) at 0°C in THF (10 mL). The crude mixture was stirred for 3 h. CH_2Cl_2(10 mL), water (10 mL), and ice were then added. The organic phase was separated, dried over $MgSO_4$, and filtered. The solvent was then evaporated and MeOH (10 mL) was added, resulting in the formation of a precipitate, which was filtered off and dried under vacuum. The title compound was obtained as a white solid (between 0.60 and 0.72 g, yield: 50–60%).

^{1}H NMR (300 MHz, CD_2Cl_2, 298 K : δ 1.28 (s, 9H, para C(CH_3)$_3$), 1.45 (s, 18H, ortho C(CH_3)$_3$), 3.72 (s, 3H, OCH_3), 6.77 (d, 1H, ^3J(H—H) = 8.2 Hz, H_6), 6.83 (t, 1H, ^3J(H—H) = 7.5 Hz, H_4), 7.13 (tt, 1H, ΣJ(H—H) = 17.4, H_5), 7.36 (s, 2H, H_{10}, H_{12}), 7.65, 1H, ΣJ = 11.9 Hz, H_3), 8.28 (d, 1H, ^2J(H—P) = 25.6 Hz, H_7) ; ^{31}P NMR (121.5 MHz, CD_2Cl_2, 298 K): δ 259.0; ^{13}C NMR (75.5 MHz, CD_2Cl_2, 298 K) : δ 0.3 (s, para C(CH_3)$_3$), 32.9 (d, ^3J(C—P) = 7.4 Hz, ortho C(CH_3)$_3$), 34.1 (s, para C(CH_3)$_3$), 37.4 (s, ortho C(CH_3)$_3$), 54.5 (s, OCH_3), 110.2 (d, ^4J(C—P) = 2.8 Hz, C_6), 119.8 (d, ^4J(C—P) = 3.0 Hz, C_4), 121.0 (s, C_{10}, C_{12}), 125.5 (d, ^3J(C—P) = 24.6 Hz, C_3), 128.3 (d, ^5J(C—P) = 7.0 Hz, C_5), 128.5 (d, ^2J(C—P) = 10.6 Hz, C_2), 140.1 (d, ^1J(C—P) = 55.2 Hz, C_8), 148.7 (s, C_9, C_{13}), 153.3 (d, ^4J(C—P) = 1.1 Hz, C_{11}), 154.8 (d, ^3J(C—P) = 12.2 Hz,

C_1), 169.8 (d, ^1J(C—P) = 37.1 Hz, C_7). Mass spectrum *m/z* (%) 396 (M^+, 100%). Anal. $C_{26}H_{37}OP$ (396.55): C 78.75, H 9.40; found C 78.50, H 9.55.

*Synthesis of 1,3-Bis[2-(supermesityl)phosphanediylmethyl]benzene (**3**)*

The phospha-Wittig reagent [Mes*P=PMe_3] was cooled to 0°C and cannulated on a suspension of isophtalaldehyde (0.160 g, 1.2 mmol, 0.4 equiv) at 0°C in THF (10 mL). The crude mixture was stirred for 3 h. CH_2Cl_2 (10 mL), water (10 mL), and ice were then added. The organic phase was separated, dried over $MgSO_4$, and filtered. The solvent was then evaporated and MeOH (10 mL) was added, resulting in the formation of a precipitate, which was filtered off and dried under vacuum. The title compound was obtained as a white solid (0.33–0.46 g, yield: 50–70%). For complete characterization, see reference 20.

Synthesis of Complex **4**

To ligand **1** (79.8 mg, 0.2 mmol, 1 equiv) in dichloromethane (3 mL) was added, at room temperature, $[Pd(Allyl)Cl]_2$ (36.7 mg, 0.1 mmol, 0.5 equiv.). The reaction was followed by ^{31}P NMR. After checking the formation of the corresponding cationic complex (with a chloride as counteranion), AgOTf (51.4 mg, 0.2 mmol, 1 equiv) was added and the mixture was stirred for 1 hour. The precipitate (AgCl) was filtered under vacuum and the solvent was evaporated. A white solid was obtained (0.125 g, yield: 90%).

^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ 1.29 (s, 9H, para $C(CH_3)_3$), 1.54 (s, 9H, ortho $C(CH_3)_3$), 3.69 (s, 3H, OCH_3), 5.48 (m, 1H, CH allyle), 6.81 (d, ^3J(H—H) = 7.7 Hz, H_6), 6.91 (t, ΣJ(H—H) = 7.4 Hz, H_4), 7.31 (m, ΣJ(H—H) = 9.4 Hz, H_5), 7.46 (s, H_{10}, H_{12}), 7.75 (m, ΣJ(H—H) = 10.3 Hz, H_3), 8.20 (d, ^2J(H—P) = 27.3 Hz, H_7); ^{31}P NMR (121.5 MHz, CD_2Cl_2, 298 K) δ 206.0 ppm; ^{13}C NMR (75.5 MHz, CD_2Cl_2, 298 K) δ 30.1 (s, para $C(CH_3)_3$), 33.6 (d, ^3J(C—P) = 1.5 Hz, ortho $C(CH_3)_3$), 34.3 (para $C(CH_3)_3$), 37.3 (s, ortho $C(CH_3)_3$), 54.8 (s, OCH_3), 110.03 (d, ^4J(C—P) = 3.9 Hz, C_6), 116.2 (d, ^5J(C—P) = 6.0 Hz C_5), 119.6 (s, C_{10}, C_{12}), 125.9 (d, ^4J(C—P) = 1.7 Hz, C_4), 127.5 (d, ^3J(C—P) = 22.5 Hz, C_3), 128.4 (s, C_2), 130.7 (d, ^5J(C—P) = 6.3 Hz, C_5), 151.8 (d, ^2J(C—P) = 2.1 Hz, C_9, C_{13}), 155.1 (d, ^3J(C—P) = 17.3 Hz, C_1), 163.4 (d, ^2J(C—P) = 46.0 Hz, C_7). Anal. $C_{30}H_{42}F_3O_4PPdS$ (693.11): C 51.99, H 6.11; found C 51.60, H 6.24.

Synthesis of Complex **5**

To ligand **1** (158.6 mg, 0.4 mmol, 2 equiv) in dichloromethane (3 mL) was added, at room temperature, $[Pd(Allyl)Cl]_2$ (36.7 mg, 0.1 mmol, 0.5 equiv). The reaction was followed by ^{31}P NMR. After checking the formation of the corresponding cationic complex (with a chloride as counteranion), AgOTf (51.4 mg, 0.2 mmol, 1 equiv) was added and the mixture was stirred for 1 hour. The precipitate (AgCl) was filtered under vacuum and the solvent was evaporated. A white solid was obtained (0.185 g, yield: 85%).

^{1}H NMR (300 MHz, CD_2Cl_2, 298 K) 1.29 (s, *t*-Bu), 1.34 (s, *t*-Bu), 1.45 (s, *t*-Bu), 3.11 (s, 2H, CH_2allyl), 3.71 (s, 3H, OCH_3), 5.24 (broad s, 2H, CH_2 allyl), 5.40 (m, 1H, CH allyl), 6.85 (m, 2H, H_6, H_4), 7.13 (m, 1H,H_5), 7.33 (m, 1H, H_3), 7.52 (s, 2H, H_{10}, H_{12}), 8.71 (pseudo t, 1H, ΣJ(H—P) = 29.3 Hz, H_7); ^{31}P NMR (121.5 MHz, CD_2Cl_2, 298 K) δ 188.0 ppm. ; ^{13}C NMR (75.5 MHz, CD_2Cl_2, 298 K) δ 30.1 (s, para $C(CH_3)_3$), 33.5 (s, ortho $C(CH_3)_3$), 34.5 (s, para $C(CH_3)_3$), 38.1 (ortho $C(CH_3)_3$), 55.0 (s, OCH_3), 76.0 (broad s, CH_2 allyl), 110.5 (s, C_6), 119.3 (s, CH allyl), 123.1 (s, C_{10}, C_{12}), 125.7 (s,) 126.2 (s, C_2), 127.6 (d, J = 13.3 Hz, C_3), 131.9 (s, C_5), 153.0 (s, C_9, C_{13}), 154.4 (broad s, C_{11}), 155.2 (pseudo t, ΣJ = 18.8 Hz, C_1), 169.9 (pseudo t, ΣJ = 43.6 Hz, C_7). Anal. $C_{56}H_{79}F_3O_5P_2PdS$ (1089.65): C 61.73, H 7.31; found C 61.49, H 7.28.

Synthesis of Complex **6**

A solution of ligand **3** (100 mg, 0.15 mmol) in dichloromethane (5 mL) was added to [$PdCl_2$ $(PhCN)_2$] (58 mg, 0.15 mmol). The orange mixture obtained was stirred for 10 hours at 40°C. Then, EtOH (3 mL) was added to precipitate the complex. Orange crystals of **6** were grown after slow evaporation of the solution under nitrogen atmosphere: yield 75–85 mg (62–70%).

General Procedures for the Coupling Reactions

Suzuki Reaction. The catalysts were prepared by dilution of the precursor in dichloromethane at room temperature under an inert atmosphere. For example, 2.6 mg (0.0024 mmol) of complex **5** were diluted in CH_2Cl_2 (10 mL), and 85 μL (0.00002 mmol, 0.00001%) of the solution was poured into a Schlenck tube with a syringe and the solvent was evaporated. To the Schlenck tube, phenylboronic acid (3 mmol, 0.366 mg), K_2CO_3 (4 mmol, 0.55 g), and the halogenoarene (2 mmol) in toluene (20 mL) were added. The mixture was heated at 110°C for 2 h. The reaction was monitored by GC. The products were isolated by column chromatography on silica

gel (petroleum ether 40–65°C) and characterized by comparison with literature data.

Sonogashira Reaction. A solution of the catalyst (0.1%) was added to a mixture of the aryl halide (1.0 mmol), phenylacetylene (220 μL, 2 mmol), and triethylamine (3 mL). The resultant mixture was heated at 90°C for 24 h. The progress of the reaction was monitored by GC. At the end of the reaction, the flask was cooled to room temperature. The workup consists of quenching with water (5 mL), extraction with dichloromethane (10 mL) and drying of the resulting solution over $MgSO_4$. The solution was then filtered and the solvent was removed under reduced pressure. NMR data of the isolated compounds were compared with those reported in literature.

X-Ray Crystallography. All data were collected on a Nonius Kappa CCD diffractometer at 150(1) K using Mo K_α ($\lambda = 0.71073$ Å) X-ray source and a graphite monochromator. Experimental details are described in Table 1. The crystal structures were solved in SIR 97 [25] and refined in SHELXL-97 [26] by full-matrix least squares using anisotropic thermal displacement parameters for all non-hydrogen atoms. All the hydrogen atoms were placed in geometrically calculated positions. ORTEP drawings were made using ORTEP-3 for Windows [27].

Theoretical Methods. Calculations were performed with the GAUSSIAN 03 series of programs [28]. The geometries of the model compounds **I** and **II** were optimized using the ONIOM method [29] with the B3PW91 functional [30] and the UFF force field. The standard 6-31G* basis set was used for all atoms (H, C, P, O, S, and F). The Hay and Wadt [31] small core quasirelativistic effective core potential with the double-ζ valence basis set (441s/2111p/311d) was used for Pd. Single-point calculations were carried out at the quantum level for all toms using the 6-31G* basis set (H, C, P, O, S, and F) and the double-ζ LANL2DZ for the Pd atom.

SUPPLEMENTARY DATA

Views of the optimized structures with the complete numbering; atomic coordinates (x,y,z parameters) and energies of computed structures **I** and **II** (as given by single point calculations); atomic coordinates, thermal parameters, bond lengths, and bond angles for complexes **4** and **5** have been deposited to the Cambridge Crystallographic Data Center, CCDC nos. 606 332 and 606 333. Copies of the information may be obtained free of charge from the Director, CCDC, 2 Union Road, Cambridge CB2 1EZ, UK, on request (fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk or URL: http://www.ccdc.cam.ac.uk), quoting the deposition numbers for **4** and **5**.

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