Synthesis of 1-Phosphabarrelene Phosphine Sulfide Substituted Palladium(II) Complexes: Application in the Catalyzed Suzuki Cross-Coupling Process and in the Allylation of Secondary Amines

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The reactivity of 2-phosphine sulfide substituted phosphinines toward alkynes was examined. 2,6-bis(diphenylphosphine sulfide)-3,5-diphenylphosphinine **2** reacts with diphenylacetylene to yield the corresponding 1-phosphabarrelene derivative **3**, resulting from the [4 + 2] cycloaddition. Compound **2** and 2-(diphenylphosphine sulfide)-3-methyl-5,6-diphenylphosphinine **1** react with dimethyl acetylenedicarboxylate in a similar fashion to yield the expected 1-phosphabarrelenes **4** and **5**, respectively. Ligand **3** acts as a tridentate ligand in its reaction with $[Pd(COD)Cl_2]$ to afford the expected cationic Pd−Cl complex **6**. The reaction of $[Pd(COD)Cl_2]$ and $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ with ligand **5** yielded the corresponding complexes **7** and **8**, in which the ligand behaves as a bidentate ligand. Complex **8** was isolated as a cationic derivative after chloride abstraction with AgOTf. DFT calculations, carried out at the B3LYP/6-311+G(d,p) level of theory, have shown that formation of 1-phosphabarrelenes is thermodynamically favored when dimethyl acetylenedicarboxylate is used as the alkyne. Complexes **6** and **8** proved to be very active catalysts in the Suzuki−Miyaura reaction, which allows the synthesis of functionalized biphenyl derivatives from the coupling of bromoarenes with phenylboronic acid (TON up to 7×10^6 using complex **8** as catalyst). The cationic complex **8** also catalyzes the coupling between allyl alcohol and secondary amines to afford the corresponding *N*-allylamines in toluene at 70 °C using 2% of the catalyst.

Introduction

Low-coordinated phosphorus ligands exhibit unique electronic properties that make them very attractive for catalytic purposes. Though the intrinsic high reactivity of the P=C double-bonded systems means that only kinetically or thermodynamically protected ligands can be employed, very promising results have recently been obtained with molecules such as phosphaferrocenes[1] and 1,4-diphosphabutadienes.[2] Though many synthetic routes have been devised to produce polyfunctional phosphinines, another important class of low-coordinated phosphorus ligands, these heterocycles have not found numerous applications so far as ligands in catalysis. This mainly results from the high electrophilicity of the phosphorus atom as well as from the reactivity of the aromatic π-system. So far, λ^3-phosphinines have only found application in two catalytic processes: Rh(I) complexes in the hydroformylation of olefins[3] and the η^6 ligand at an Fe(0) center in the catalyzed cyclotrimerization of alkynes with nitriles to form functional pyridines.[4]

Two years ago, we launched an important synthetic program aimed at exploiting the phosphinines as ligands in catalysis. Indeed, though the ligand itself proves to be too reactive to be employed in standard catalytic transformations, its reactivity offers interesting structural possibilities. Thus, reactions with nucleophiles yield λ^4-phosphinine anions,[5] which bind transition-metal centers in an η^1 (type A),[6,7] η^2 (type B),[8] or η^5 fashion (type C),[9] depending on the substitution scheme of the ring (Scheme 1). The first class of complex (type A), incorporating a phosphino sulfide as ancillary ligand and a λ^4-phosphinine as the central subunit, exhibits an interesting activity for the activation of several metal

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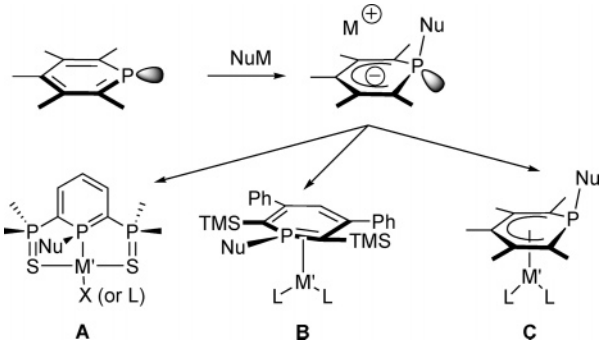
Scheme 1



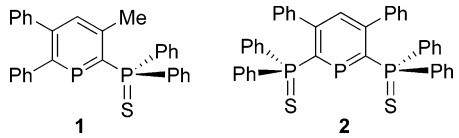
centers and was employed, for example, with Rh(I) complex to activate small molecules such as O_2, CO_2, and CS_2.[10] On the other hand, palladium(II) complexes showed a high catalytic activity in the Miyaura cross-coupling reaction between bromoarenes and pinacolborane.[11] Much more recently, we showed that η^5 Rh(I) complexes (type C) of these anions could be successfully employed in the hydroformylation of olefins under mild conditions.[12]

As explained above, a second interesting possibility consists of taking advantage of the reactivity of the π-system. It is well-known that phosphinines can behave as masked 1-cyclophosphabutadienes, and many studies have focused on their use as dienes in [4 + 2] cycloadditions with alkynes to form 1-phosphabarrelenes. However, except in very rare cases when activated alkynes are employed, these cycloadditions occur when the ring has been activated by coordination[13] or sulfurization[14] of the lone pair at phosphorus. Only a few examples of free barrelenes, obtained by the direct [4 + 2] cycloaddition of phosphinines with alkynes, have been reported so far.[15] Thus, the use of 1-phosphabarrelenes as ligands in homogeneous catalysis has hardly been explored. Only Breit reported on the use of such ligands in the Rh-catalyzed hydroformylation of olefins.[16] In this article, we report on the synthesis of mixed bidentate P−S and tridentate S−P−S ligands featuring a 1-phosphabarrelene moiety as ligand. As will be seen, we also show that palladium(II) complexes of these new ligands exhibit a significant catalytic activity in two processes of synthetic importance, the Suzuki−Miyaura cross-coupling reaction and the allylation of secondary amines.

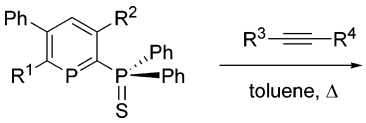
Results and Discussion

In the course of our previous studies we have noticed that the presence of diphenylphosphine sulfide ligands at the α-position of phosphorus enhanced the electrophilicity of the phosphorus atom.[7] When we initiated this study, our initial aim was to evaluate the reactivity of these mixed ligands as dienes toward alkynes in [4 + 2] cycloaddition processes. All our experiments were carried out with the 2-diphenylphosphine sulfide phosphinine **1** and the 2,6-bis(diphenylphosphine sulfide) phosphinine **2** (Chart 1), which were prepared according to reported procedures (see Experimental Section).

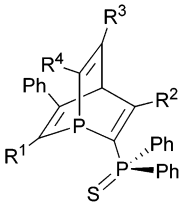
Chart 1



Scheme 2



1: R^1 = Ph; R^2 = Me
2: R^1 = PPh_2(=S); R^2 = Ph



3: R^1 = PPh_2(=S); R^2 = Ph; R^3 = R^4 = Ph
4: R^1 = PPh_2(=S); R^2 = Ph; R^3 = R^4 = CO_2Me
5: R^1 = Ph; R^2 = Me; R^3 = R^4 = CO_2Me

Reaction of **2** with diphenylacetylene proved to be quite difficult to achieve, and heating for 10 days at 120 °C was necessary for complete conversion. Phosphabarrelene **3**, which was obtained in good yield after purification, was isolated as a very stable beige powder and fully characterized by means of NMR and mass spectroscopy and elemental analyses. In ^{31}P NMR, whereas the chemical shift of the phosphine sulfide group remains roughly unchanged (43.4 ppm in **2** vs 40.5 ppm in **3**), the formation of the bicyclic structure results in a very important upfield shift of the ring phosphorus atom (from 253.1 ppm in **2** vs −39.1 ppm in **3**) (see Scheme 2). The same reaction was attempted with the P−S phosphinine **1**, but no reaction occurred, despite a prolonged reaction time (several weeks of heating at 120 °C).

More satisfactory results were obtained when dimethyl acetylenedicarboxylate was used as the dienophile. With the phosphinine **2**, the Diels−Alder reaction takes place at 80 °C and the phosphabarrelene **4** was isolated in good yield after only 8 h of heating. Like its diphenyl analogue **3**, phosphabarrelene **4** is a very stable molecule which can be handled in air without oxidation of the phosphorus atom, even after several days (see Scheme 2).

Similarly, phosphinine **1** proved to be sufficiently reactive to undergo the same reaction, but a longer heating period was needed. Thus, heating for 18 h at 90 °C was necessary to convert **1** into phosphabarrelene **5**, which was recovered as a very stable beige powder

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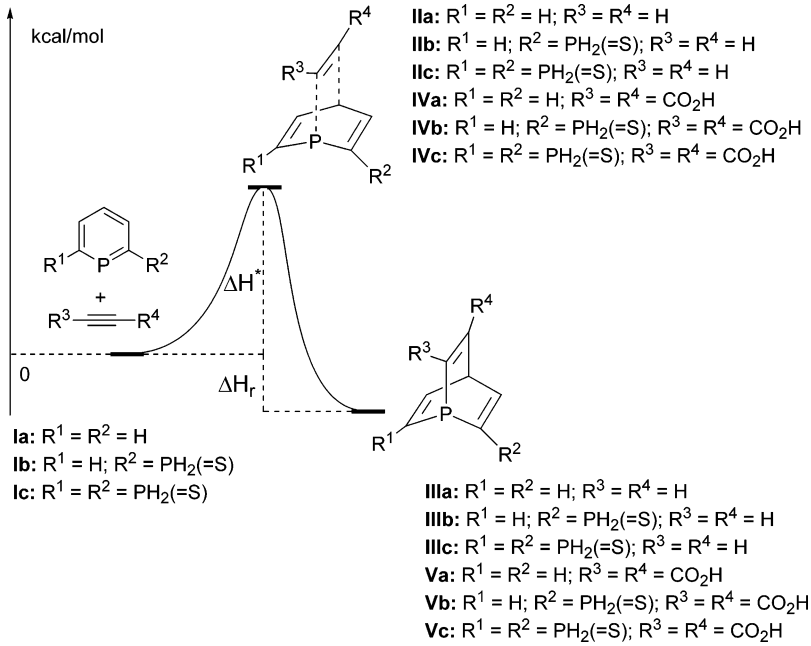
Scheme 3



and fully characterized by conventional techniques and elemental analyses (Scheme 2).

The higher reactivity of phosphinine **2** can be rationalized on the basis of both kinetic and thermodynamic arguments. Theoretical calculations were carried out within the framework of DFT using the Gaussian 03 suite of programs. Computational details (functional and basis sets used) are given in the Experimental Section. Three reaction profiles were computed, those corresponding to the reaction of the parent phosphinine C_5H_5P **Ia** and the model compounds **Ib** and **Ic** with acetylene. In **Ib** and **Ic**, the phenyl groups of the diphenylphosphine sulfide groups and those grafted on the phosphinine ring in **2** as well as the methyl group in **1** were replaced by H atoms. The first interesting piece of information is given by the examination of the HOMO−LUMO gaps of the reactants. All these transformations involve an inverse electron demand process, the most important interaction occurring between the LUMO of the phosphinine and the HOMO of acetylene. Most importantly, these calculations show that formation of barrelene **IIIa** is only weakly exothermic ($\Delta H_r = -2.8$ kcal mol^{-1}), thus explaining why phosphinines usually do not react with classical alkynes, even under forced conditions. Model compounds **Ib** and **Ic** are calculated to be much more reactive, and the formation of barrelenes **IIIb** and **IIIc** is thermodynamically favored, in good agreement with experimental observations. Note, however, that they are not significantly kinetically favored (enthalpies of transition states **IIb** and **IIc** compare with that required to form **IIIa**) (see Scheme 3). All of these values are reported in Table 1.

Nevertheless, no definitive conclusion can be drawn from these results, since dimethyl acetyledicarboxylate is a strongly activated alkyne for which acetylene is not an optimal model. Therefore, the same calculations were carried out using acetylenedicarboxylic acid as the model. Whereas the formation of barrelenes **Va** and **Vb** follows a normal electron demand process, the phosphinine playing the role of the diene and the alkyne the role of the dienophile, it is much more risky to conclude on the process involved in the case of **Vc**, since the HOMO−LUMO gaps in the two processes (classical or inverse electron demand) are quite similar (5.60 eV for the classical process and 5.66 eV for the inverse electron demand process). Nevertheless, here again, formation of barrelenes **Vb** and **Vc** is more thermodynamically favored than that of **Va** (see Table 1 for theoretical data). This second set of data suggests that the reaction of phosphinines with DMADC would probably be favored thermodynamically. So far, no systematic studies on the reactivity of functionalized phosphinines toward this activated alkyne have been reported. This point is currently under investigation in our laboratories, and results will be reported in due course. To conclude, one could add that Diels−Alder reactions between alkynes and phosphinines have been mostly studied with C4-substituted (para position) compounds and it would be of interest to assess the importance of the substitution scheme in these transformations.

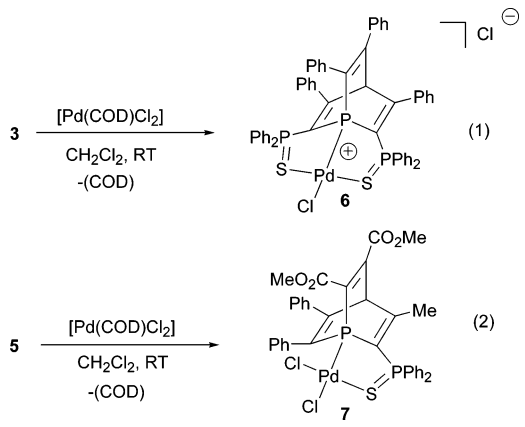
Table 1. Calculated Enthalpies (ZPE corrected) of Diels−Alder Reactions of Model Compounds Ia, IIa, and IIIa with Acetylene and Acetylenedicarboxylic Acid[a]

transformation	II (TS)	III	IV(TS)	V
Ia to **IIIa** or **Va**	+31.7	−2.8	+26.3	−7.9
Ib to **IIIb** or **Vb**	+28.7	−6.7	+25.2	−10.4
Ic to **IIIc** or **Vc**	+25.7	−10.5	+23.9	−13.0

[a] Single point calculations were carried out at the B3LYP/6-311+G(d,p) level of theory. TS denotes the transition state. All energies are expressed in kcal/mol.

Having these new barrelenes at hand, we then focused our study on their coordinating behavior toward palladium(II) centers. The cationic monochloride complex **6** (see eq 1) and neutral complex **7** (see eq 2) were conventionally prepared by a displacement of the COD (1,5-cyclooctadiene) ligand from $[Pd(COD)Cl_2]$ in dichloromethane at room temperature. In the synthesis of **6** one chloride ligand is also displaced and acts as a counteranion. In both cases the substitution of the ligand was quantitative, yielding **6** as an orange powder

Scheme 4



and **7** as a brown powder after the usual workup (Scheme 4). Both complexes were fully characterized by NMR techniques and elemental analyses. The symmetrical structure of complex **6** was ascertained by NMR spectroscopy. Thus, in ^{31}P NMR, **6** exhibits as a classical AX_2 spin system pattern: δ_A ($CDCl_3$) 39.6 ppm with $^2J(AX)$ = 83.6 Hz and δ_X ($CDCl_3$) 50.2 ppm. Definite proof of the structure of **7** was given by an X-ray crystallographic study.

Suitable crystals of **7** were obtained by diffusing hexanes into a dichloromethane solution of the complex at room temperature. A view of one molecule of **7** is presented in Figure 1, and the most significant bond distances and bond angles are listed below. As can be seen, the overall geometry around the palladium center is square planar, as expected for a d^8 complex. An interesting comparison can be established between other

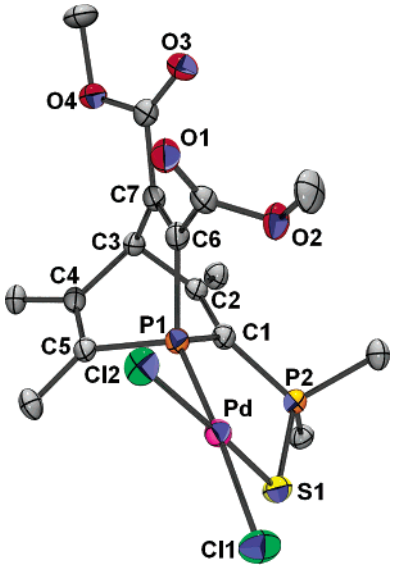
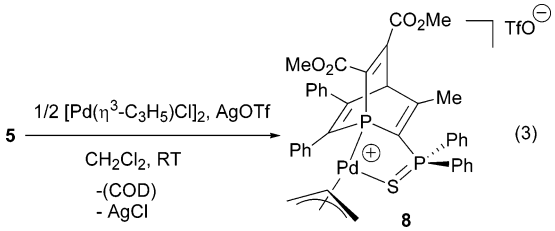


Figure 1. ORTEP view of one molecule of complex **7**. Ellipsoids are scaled to enclose 50% of the electron density. The phenyl groups at phosphorus atom P2 and at carbons atoms C4 and C5 have been omitted for clarity. Relevant distances (Å) and bond angles (deg): Pd−P1 = 2.1753(8), Pd−S1 = 2.3070(8), Pd−Cl2 = 2.3158(8), Pd−Cl1 = 2.3570(8), S1−P2 = 2.026(1), P1−C1 = 1.823(3), P1−C6 = 1.825(3), P1−C5 = 1.831(3), P2−C1 = 1.790(3), C2−C3 = 1.533(4), C3−C7 = 1.522(4), C3−C4 = 1.547(4) C4−C5 = 1.355(4) C6−C7 = 1.328(4); P1−Pd−S1 = 90.67(3), P1−Pd−Cl2 = 83.33(3), S1−Pd−Cl1 = 88.47(3), Cl2−Pd−Cl1 = 97.26(3).

analogous systems featuring a similar PS chelate backbone. In complex **7**, the two Pd−Cl bonds are different, reflecting the difference between the σ-donor strengths of the phosphorus and sulfur ligands (trans influence). Thus, the Pd−Cl(1) distance (trans to P) is longer (2.3570(8) Å) than the Pd−Cl(2) distance (trans to P=S) which falls at 2.3158(8) Å. This structural feature is not unusual and appears to be relatively common in similar complexes featuring an sp^3-hybridized phosphorus atom. For example, in the $[Cp_2Fe(PPh_2)(PPh_2{=}S)PdCl_2]$ complex the Pd−Cl bond length trans to the P atom is longer (2.3696(7) Å) than that which is located trans to the P=S ligand (2.3160(7) Å).[17] From these data one may conclude that the phosphabarrelene ligand in **7** exhibits electronic properties that are equivalent to those of classical triarylphosphines. Interestingly, Ito and Yoshifuji reported on the synthesis of a mixed P−S ligand containing both a phosphaalkene and a P=S ligand.[18−20] Phosphaalkenes are known to act as poor σ-donor ligands but generally exhibit a strong π-accepting capacity, as low-coordinated phosphorus ligands in general. Therefore, it is not surprising to note that the Pd−Cl bond length which is located trans to the phosphaalkene ligand is short (2.319(3) Å) compared to the above-mentioned complexes. Interestingly, we note that in **7** the P−Pd bond distance is relatively short (2.1753(8) Å) compared to classical complexes (2.23 Å on average) and is similar to that reported by Itoh and Yoshifuji in their complex (2.186(3) Å).[19] This would suggest that the 1-phosphabarrelene ligand also displays a significant π-accepting capacity. Note that this is expected from the substitution scheme of the phosphorus atom (three vinylic susbtituents, among which one is substituted by two strong π-acceptor substituents). However, no direct comparison can be drawn between **7** and this complex because of the difference of hybridization of the two phosphorus atoms.

In pursuing our investigations on the coordination chemistry of ligand **5**, we found that the cationic derivative $[Pd(\eta^3\text{-}C_3H_5)(\mathbf{5})][TfO]$ **8** could also be conventionally prepared by reacting the ligand with $^1/_2$ equiv of the $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ precursor in the presence of AgOTf as chloride abstractor. The presence of AgOTf proved to be crucial, and no stable complex could be isolated when the chloride ligand was left as the counteranion. The presence of two diastereomeric complexes, resulting from the orientation of the η^3-allyl ligand, was evidenced in ^{31}P NMR, where **8** appears as two different AB systems in a 45/55 ratio. No detailed NMR studies have been undertaken to ascribe the stereochemistry of these complexes. This complex was isolated as a brown powder in 95% yield (eq 3) (only one diastereomer is represented in eq 3).



An X-ray crystallographic study was carried out on suitable microcrystals obtained by diffusing hexanes

Table 2. Crystal Data and Structural Refinement Details for 7, 8, and 10

	7	8	10
formula	$C_{36}H_{30}Cl_2O_4P_2PdS{\cdot}CH_2Cl_2$	$C_{39}H_{35}O_4P_2PdS(CF_3O_3S)$	$C_{28}H_{27}P_2PdS(CF_3O_3S)$
M_r	882.83	917.14	2851.86
cryst syst	orthorhombic	triclinic	orthorhombic
space group	$P2_12_12_1$	$P\bar{1}$	$Pca2_1$
a (Å)	11.0880(10)	9.8490(10)	15.5700(10)
b (Å)	17.2800(10)	11.2220(10)	9.2190(10)
c (Å)	19.3660(10)	19.0690(10)	20.3650(10)
α (deg)		92.4700(10)	
β (deg)		101.4400(10)	
γ (deg)		109.4600(10)	
V (Å^3)	3710.5(4)	1934.1(3)	2923.2(4)
Z	4	2	1
ρ (g cm^{-3})	1.580	1.575	1.620
μ (cm^{-1})	0.970	0.735	0.937
cryst size (mm)	0.22 × 0.14 × 0.08	0.20 × 0.16 × 0.14	0.20 × 0.20 × 0.05
F(000)	1784	932	1440
index ranges	−9 to + 15; −24 to +24; −27 to +25	−13 to +13; −15 to +15; −26 to +25	−18 to +21; −12 to +12; −28 to +23
$2\theta_{max}$ (deg)/criterion	30.00/$I > 2\sigma(I)$	30.03/$I > 2\sigma(I)$	30.03/$I > 2\sigma(I)$
no. of params refined; data/param	446; 19	529; 17	362; 18
no. of rflns collected	24 611	16 812	18 989
no. of indep rflns	10 818	11 233	7658
no. of rflns used	8689	9303	6565
wR2[a]	0.0903	0.0959	0.0850
R1[b]	0.0347	0.0342	0.0332
goodness of fit	1.008	1.030	1.012
largest diff peak/hole (e Å^{-3})	0.610(0.093)/−0.525(0.093)	0.914(0.078)/−0.940(0.078)	1.065(0.076)/−0.776(0.076)

[a] wR2 = $(\sum w||F_o| - |F_c||^2/\sum w|F_o|^2)^{1/2}$. [b] R1 = $\sum||F_o| - |F_c||/\sum|F_o|$.

into a solution of the complex in $CDCl_3$. The two diastereomeric complexes cocrystallize in the unit cell in ratios of 2/3 to 1/3. A view of one molecule of one diastereomer is presented in Figure 2, and the most significant metric parameters are presented in the corresponding caption. This structure does not display a particular feature, and metric parameters within the barrelene ligand are comparable with those of complex **7**. As in **7**, the Pd1−C8 bond length (trans to the P ligand) is longer (2.229(7) Å) than the Pd1−C10 one (2.13(1) Å), thus reflecting the stronger trans influence of the phosphine ligand. These data compare with those already reported for similar allylic complexes incorporating a five-membered palladacycle with P=S and P ligands.[19]

To the best of our knowledge, if one excepts their recent use in the hydroformylation of olefins,[16] 1-phosphabarrelenes have never been employed as ligands in homogeneous catalysis. Therefore, to complete this study, we launched a preliminary screening program aimed at evaluating the catalytic activity of complexes **6** and **8**. Our first attempt was to use these three palladium(II) complexes in the well-known Suzuki−Miyaura process,[21] because it is now well established that this type of coupling process requires bulky phosphines that combine both a good σ-donor strength and π-accepting capacity.

Complexes **6** and **8** proved to be very active, and excellent conversion and TON were obtained (see Table 3). For example, biphenyl can be produced in 2 h in 90% yield using 10^{-5} equiv of complex **8** (TON = 90 000) as catalyst in toluene under reflux. A conversion of 70% was obtained using 10^{-7} equiv of **8**, although a longer heating period was required (24 h; TON = 7 × 10^6). Finally, a conversion of 95% was obtained using 10^{-5}

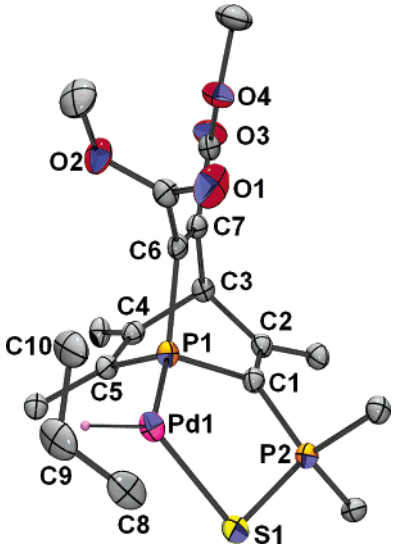
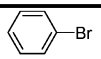
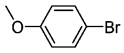
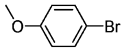
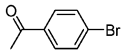
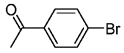
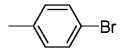
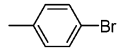


Figure 2. ORTEP view of one molecule of complex **8** (cationic part). Ellipsoids are scaled to enclose 50% of the electron density. The numbering is arbitrary and different from that used in the assignment of NMR spectra. The phenyl groups at phosphorus atom P2 and at carbons atoms C4 and C5 have been omitted for clarity. Relevant distances (Å) and bond angles (deg): Pd1−C8 = 2.229(7), Pd1−C9 = 2.128(3), Pd1−C10 = 2.13(1), Pd1−P1 = 2.2541(5), Pd1−S1 = 2.3877(5), S1−P2 = 2.0090(6), P1−C1 = 1.826(2), P1−C6 = 1.828(2), P1−C5 = 1.842(2), P2−C1 = 1.793(2), C1−C2 = 1.338(2), C2−C3 = 1.541(2), C3−C7 = 1.523(3), C3−C4 = 1.545(2), C4−C5 = 1.346(2), C6−C7 = 1.336(2), C8−C9 = 1.441(7), C9−C10 = 1.45(1); P1−Pd1−S1 = 89.70(2), C10−Pd1−C8 = 69.9(3), C10−Pd1−P1 = 102.5(3).

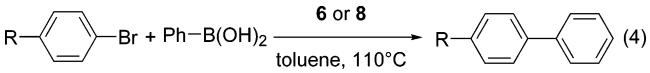
(17) Broussier, R.; Bentabet, E.; Laly, M.; Richard, P.; Kuz'mina, L. G.; Serp, P.; Wheatley, N.; Kalck, P.; Gautheron, B. *J. Organomet. Chem.* **2000**, *613*, 77−85.
(18) Ito, S.; Liang, H.; Yoshifuji, M. *Chem. Commun.* **2003**, 398−399.
(19) Liang, H. Z.; Ito, S.; Yoshifuji, M. *Org. Lett.* **2004**, *6*, 425−427.
(20) Liang, H.; Ito, S.; Yoshifuji, M. *Org. Biomol. Chem.* **2003**, *1*, 3054−3058.

Table 3. Cross-Coupling Reactions between Bromoarenes and Phenylboronic Acid using Complex 8 or 6 as Catalyst[a]

Substrate	complex	% of **N**	T (°C)	Time (h)	Yield (%)	TON
	**8**	10^{-3}	110	2	90	9×10^4
	**8**	10^{-5}	110	24	70	7×10^6
	**6**	10^{-3}	110	24	95	9.5×10^4
	**8**	10^{-3}	110	24	84	8.4×10^4
	**8**	10^{-4}	110	24	24	2.4×10^5
	**8**	10^{-3}	110	24	97	9.7×10^4
	**8**	10^{-4}	110	24	62	6.2×10^5
	**8**	10^{-3}	110	24	63	6.3×10^4
	**8**	10^{-4}	110	24	28	2.8×10^5

[a] All experiments were carried out in toluene using K_2CO_3 as a base.

equiv of complex **6** in 24 h (TON = 95 000). Though these results do not compare with those obtained by the group of Buchwald using the di-*tert*-butylbiphenylphosphine, these catalysts do prove to be very efficient.[22] These results, and the experimental conditions used, also confirm that no metal poisoning results from the presence of a sulfide group in the catalyst (eq 4).



(4)

More interestingly, we found that complex **8** could also be employed in the allylation of amines. This coupling process, reported by Yoshifuji and Ozawa using cationic allylpalladium complexes of a 1,4-diphosphabutadiene (phosphorus analogues of 1,4-diazadienes), was used to produce several allylic amines from the reaction of allylic alcohols with primary amines.[23,24] Importantly, in comparison to the classical Tsuji−Trost process,[25] this method does not require as a prerequisite the activation of the OH function through conversion into a carboxylate, a carbonate, a phosphate, or other related derivatives. Recently, the cationic Pd(allyl) complex of a mixed 3-thioxo-1,3-diphosphapropene featuring both a phosphaalkene and P=S group as ligands was also successfully employed in this transformation.[19] In the first series of experiments using Yoshifuji's conditions (toluene, room temperature in the presence of $MgSO_4$), we found that complex **8** proved to be less reactive, but interestingly, we noted that the formation of the desired monoallylation compound was always accompanied by a non-negligible amount of the bis(allyl)amine. More satisfactory results in terms of conversion were obtained using THF as solvent. Thus, using 2% of catalyst **8**, aniline was quantitatively converted into allylaniline (60%) and bis(allyl)aniline (40%) in 24 h at 70 °C. Whatever the experimental conditions used, the formation of bis(allyl)aniline could not be avoided. Importantly, we noted that the presence of $MgSO_4$ could be avoided, the presence of water not being detrimental to the course of the reaction.

This observation prompted us to investigate the allylation of secondary amines, a transformation which has not been studied in depth so far and apparently remains difficult to catalyze. The monoallylation of diethylamine was reported by Mortreux et al., using the $Ni(COD)_2$/dppb system (dppb = 1,2-bis(diphenylphosphino)butane) as catalyst, in very good yields.[26] In 2001, Yang and co-workers reported on the use of $[Pt(acac)_2]$/PPh_3 as a catalyst for the transformation of anilines (1 mol %), but the presence of a Lewis acid ($[Ti(OiPr)_4]$ (25 mol %) proved to be necessary to accelerate the transformation.[27] More recently, Kimura et al. also showed that the allylation of secondary amines and the bisallylation of primary amines could be achieved using

(21) (a) an der Heiden, M.; Plenio, H. *Chem. Eur. J.* **2004**, *10*, 1789−1797. (b) Bedford, R. B.; Cazin, C. S. J.; Coles, S. J.; Gelbrich, T.; Hursthouse, M. B.; Scordia, V. J. M. *Dalton* **2003**, 3350−3356. (c) Kondolff, I.; Doucet, H.; Santelli, M. *Tetrahedron* **2004**, *60*, 3813−3818. (d) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457−2483. (e) Miyaura, N. *Top. Curr. Chem.* **2002**, *219*, 11−59. (f) Miyaura, N. *Angew. Chem., Int. Ed.* **2004**, *43*, 2201−2203. (g) Navarro, O.; Kelly, R. A.; Nolan, S. P. *J. Am. Chem. Soc.* **2003**, *125*, 16194−16195. (h) Suzuki, A. *J. Organomet. Chem.* **1999**, *576*, 147−168. (i) Walker, S. D.; Barder, T. E.; Martinelli, J. R.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2004**, *43*, 1871−1876.

(22) Wolfe, J. P.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **1999**, *38*, 2413−2416.

(23) Ozawa, F.; Okamoto, H.; Kawagishi, S.; Yamamoto, S.; Minami, T.; Yoshifuji, M. *J. Am. Chem. Soc.* **2002**, *124*, 10968−10969.

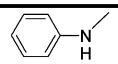
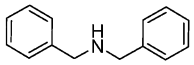
(24) Ozawa, F.; Ishiyama, T.; Yamamoto, S.; Kawagishi, S.; Murakami, H.; Yoshifuji, M. *Organometallics* **2004**, *23*, 1698−1707.

(25) (a) Tsuji, J. *Transition Metal Reagents and Catalysts*; Wiley: New York, 2000. (b) Davis, J. A. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 9, p 291. (c) Godleski, S. A. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1991; Vol. 3, p 535. (d) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 259. (d) Trost, B. M. *Science* **1991**, *254*, 1471.

(26) Bricout, H.; Carpentier, J.-F.; Mortreux, A. *J. Mol. Catal. A* **1998**, *136*, 243−251.

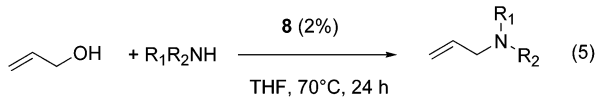
(27) Yang, S.-C.; Tsai, Y.-C.; Shue, Y.-J. *Organometallics* **2001**, *20*, 5326−5330.

Table 4. Amination of Allylic Alcohol by Secondary Amines Using Complex 8 as Catalyst[a]

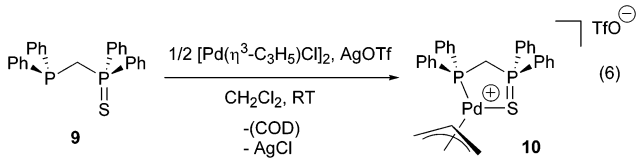
Substrate	% of N	T (°C)	Yield (%)
	2	70	85
	2	70	57
	2	70	96

[a] All reactions were performed in THF as solvent with 2 equiv of allyl alcohol.

$[PdL_4]$ complexes as catalyst (5 mol %) in the presence of BEt_3 as additive.[28] As can be seen in Table 4, complex **8** is a very efficient catalyst for this transformation and good conversion yields were obtained by heating allylic alcohol with secondary amines in the presence of 2% of catalyst without additive in THF at 70 °C for 24 h (see eq 5).



On the basis of these different results, we logically wondered about both the role played by the sulfur atom in our catalyst and about the importance of the electronic nature of the phosphorus atom of the barrelene ligand. To establish a comparison, the cationic palladium allyl complex of the dppm monosulfide ligand **9** was prepared. The procedure employed is in all points identical with that used for the synthesis of complex **8**. Ligand **9** was reacted with $[Pd(allyl)Cl]_2$ in dichloromethane in the presence of AgOTf as chloride abstractor. Formation of complex **10** immediately occurred at room temperature, and a combination of NMR studies and elemental analyses confirmed the proposed structure (eq 6).



Additional evidence was given by an X-ray crystallographic study, which was carried out on single crystals obtained by diffusing hexanes into a solution of the complex in THF. A view of one molecule of **10** is presented in Figure 3, and the most significant metric parameters are listed in the corresponding caption. This structure deserves no particular comment and, as previously discussed, the trans influence of the phosphine ligand is clearly visible upon examining Pd−C bond distances: e.g., the Pd−C(4) distance (trans to P) is longer (2.192(3) Å) than the Pd−C(2) distance (trans to P=S) at 2.115(3) Å.

Complex **10** was tested in the allylation of secondary and primary amines, using the same experimental conditions as those used above, but no conversion was

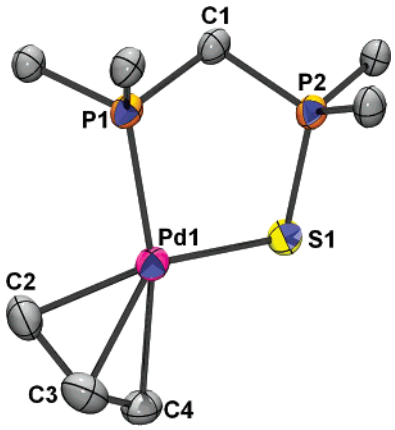


Figure 3. ORTEP view of one molecule of complex **10** (cationic part). Ellipsoids are scaled to enclose 50% of the electron density. The numbering is arbitrary and different from that used in the assignment of NMR spectra. Relevant distances (Å) and bond angles (deg): Pd1−C2 = 2.115(3), Pd1−C3 = 2.155(4), Pd1−C4 = 2.192(3), Pd1−P1 = 2.2828(8), Pd1−S1 = 2.364(1), S1−P2 = 2.005(1), P1−C1 = 1.854(3), P2−C1 = 1.805(1); P1−Pd1−S1 = 95.74(3), C2−Pd1−C4 = 67.9(2), C2−Pd1−P1 = 98.3(1), C4−Pd1−S1 = 97.1(1).

obtained. This last result clearly suggests that the issue of this allylation process is highly dependent on the electronic nature of the phosphine ligand. The rigidity of the ligand's backbone very likely plays an important role, as shown by the comparison between catalyst **8**, Yoshifuji's systems, and complex **10**. Suzuki cross-coupling reactions were also carried out with bromobenzene and chlorobenzene under the same conditions, using phenylboronic acid as reagent. The reaction with chlorobenzene yielded no conversion like complex **8**. More interestingly, the reaction with bromobenzene yielded a large amount of benzene (70% with 0.5 mol % of **10**) and no coupling product, showing that the reactivities of **10** and **8** are very different.

Conclusion

In conclusion, we have shown that mono- and disubstituted diphenylphosphine sulfide phosphinines can be used as convenient precursors for the synthesis of bidentate P−S and tridentate S−P−S ligands featuring a 1-phosphabarrelene unit as the central ligand. Interestingly, the palladium allyl complex of the bidentate P−S ligand presents a promising catalytic activity in the Suzuki−Miyaura cross-coupling process and, more importantly, in the allylation of secondary amines. Investigation of the electronic properties of these barrelene ligands are currently underway in our laboratories, as well as a systematic program aimed at generalizing their use as ligands in catalysis. We will report on these results in due course.

Experimental Section

All reactions were routinely performed under an inert atmosphere of argon or nitrogen by using Schlenk and glovebox techniques and dry deoxygenated solvents. Dry THF and hexanes were obtained by distillation from Na/benzophenoe; dry ether was obtained by distillation from $CaCl_2$ and then NaH and dry CH_2Cl_2 from P_2O_5 and dry toluene on metallic Na. $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ was purchased from Strem Chemical and

(28) Kimura, M.; Futamata, M.; Shibata, K.; Tamaru, Y. *Chem. Commun.* **2003**, 234−235.

stored under nitrogen in the refrigerator. Nuclear magnetic resonance spectra were recorded on a Bruker 300 Advance spectrometer operating at 300.0 MHz for ^{1}H, 75.5 MHz for ^{13}C, and 121.5 MHz for ^{31}P. Solvent peaks were used as internal references relative to Me_4Si for ^{1}H and ^{13}C chemical shifts (ppm); ^{31}P chemical shifts are relative to a 85% H_3PO_4 external reference. Coupling constants are given in hertz. The following abbreviations are used: s, singlet; d, doublet; t, triplet; m, multiplet. Phosphinines **1**[11] and **2**,[29] $Ph_2PCH_2PPh_2$(=S),[30] and $[Pd(COD)Cl_2]$[31] were prepared by following procedures described in the literature. Amines were filtrated over alumina before use. Elemental analyzes were performed by the "Service d'analyses du CNRS" at Gif sur Yvette.

Synthesis of Phosphabarrelene 3. A solution of **2** (200 mg, 0.29 mmol) and diphenylacetylene (209.5 mg, 1.18 mmol) in toluene (5 mL) was heated at 120 °C for 10 days. The initially white and nonhomogeneous solution slowly turned homogeneous and beige. After removal of the solvent under vacuum, the solid was washed three times with Et_2O (3 × 2 mL). Phosphabarrelene **3** was isolated as a brown-green solid. Yield: 65% (156 mg, 0.19 mmol).

^{31}P NMR ($CDCl_3$): δ −38.1 (t, $^2J(P_A-P_B)$ =106.9, P_A bridgehead), 41.5 (d, $^2J(P_A-P_B)$ = 106.9, P_BPh_2). ^{1}H NMR ($CDCl_3$): δ 5.69 (t, 1H, $^4J(H-P_B)$ = 3.4, H_4), 6.87−7.85 (m, 40H, H of Ph). ^{13}C NMR ($CDCl_3$): δ 80.1 (AB_2X, dt, $^3J(C-P_B)$ = 8.8, $^3J(C-P_A)$ = 3.4, C_4H), 125.64−131.15 (m, CH of Ph), 132.45 (ABX, dd, $^1J(C-P_B)$ = 86.1, $^3J(C-P_A)$ = 3.0, C of Ph), 132.4−132.5 (m, CH of Ph), 132.8 (ABX, dd, $^1J(C-P_B)$ = 86.8, $^3J(C-P_A)$ = 3.0, C of Ph), 138.8 (d, $J(C-P)$ = 27.9, C), 138.8 (dd, $J(C-P)$ = 27.9, $J(C-P)$ = 3.0, C), 139.4 (d, $J(C-P)$ = 5.3, C), 139.9 (d, $J(C-P)$ = 1.5, C), 147.1 (dd, $J(C-P)$ = 30.2, $J(C-P)$ = 3.0, C_2), 153.3 (q, $J(C-P)$ = 2.3, C), 172.6 (dd, $J(C-P)$ = 6.4, $J(C-P)$ = 2.0, C). m/z^+ = 859 (M). Anal. Calcd for $C_{55}H_{41}P_3S_2$ (858.2): C, 76.90; H, 4.81. Found: C, 76.45; H, 4.51.

Synthesis of Phosphabarrelene 4. A solution of **2** (300 mg, 0.44 mmol) and dimethyl acetylenedicarboxylate (54 μL, 0.44 mmol) in toluene (10 mL) was heated at 80 °C for 12 h. The solution, initially white and nonhomogeneous, slowly turned brown and became homogeneous. After evaporation of the solvent under vacuum, the solid obtained was washed with Et_2O (3 × 2 mL). Compound **4** was recovered as a yellow-brown solid. Yield: 71% (257 mg, 0.31 mmol).

^{31}P NMR ($CDCl_3$): δ −47.4 (t, $^2J(P_A-P_B)$ = 110.2, P_A bridgehead), 41.7 (d, $^2J(P_A-P_B)$ = 110.2, P_BPh_2). ^{1}H NMR ($CDCl_3$): δ 3.78 (s, 3H, Me), 3.92 (s, 3H, Me), 6.00 (t, $^4J(H-P_B)$ = 3.0, 1H, H_4), 6.87−7.78 (m, 30H, CH of Ph). ^{13}C NMR ($CDCl_3$): δ 51.7 (d, $J(C-P_A)$ = 3.8, Me), 52.2 (d, $J(C-P_A)$ = 3.8, Me), 71.1 (m, C_4H), 126.8−131.0 (m, CH of Ph), 136.4 (m, C of Ph), 137.0 (d, $J(C-P)$ = 5.3, C of Ph), 149.1 (m, C), 150.8 (m, C), 164.3 (s, C), 166.2 (d, $J(C-P)$ = 27.9, C), 170.6 (d, $J(C-P)$ = 4.5, C). MS: m/z^+ 822 (M). Anal. Calcd for $C_{47}H_{37}O_4P_3S_2$ (822.1): C, 68.60; H, 4.53. Found: C, 68.53; H, 4.25.

Synthesis of Phosphabarrelene 5. To a solution of **1** (2 g, 4.2 mmol) in toluene (100 mL) was added dimethyl acetylenedicarboxylate (0.52 mL, 4.2 mmol). After 18 h of heating at 90 °C, the solvent was removed under vacuum and the residue obtained was washed with diethyl ether (3 × 4 mL). **5** was recovered as a beige solid. Yield: 50% (1.3 g, 2.1 mmol).

^{31}P NMR ($CDCl_3$): δ −43.5 (d, $^2J(P_A-P_B)$ = 106.3, P_A bridgehead), 40.3 (d, $^2J(P_A-P_B)$ = 106.3, P_BPh_2). ^{1}H NMR ($CDCl_3$): δ 2.09 (s, 3H, Me), 3.76 (s, 3H, Me of CO_2Me), 3.88 (s, 3H, Me of CO_2Me), 5.68 (d, $^4J(H-P_B)$ = 2.9, 1H, H_4), 6.97−7.85 (m, 20H, CH of Ph). ^{13}C NMR ($CDCl_3$): δ 23.9 (d, $^2J(C-P)$ = 6.3, Me), 52.9 (s, Me of CO_2Me), 53.4 (s, Me of CO_2Me), 69.4 (dd, $^3J(C-P)$ = 9.7, $^3J(C-P)$ = 3.0, C_4H), 127.4−132.3 (m, CH of Ph), 133.4 (m, C), 133.5 (m, C), 133.8 (m, C), 138.1 (d, $^2J(C-P)$ = 27.6, C), 138.8 (d, $J(C-P)$ = 1.2, C), 144.1 (d, $J(C-P)$ = 28.5, C), 151.3 (s, C), 151.8 (dd, $J(C-P)$ = 40.7, $J(C-P)$ = 3.8, C), 154.6 (d, $J(C-P)$ = 2.2, C), 164.8 (s, C), 168.0 (d, $J(C-P)$ = 26.3, C=O), 173.3 (dd, $J(C-P)$ = 8.2, $J(C-P)$ = 2.3, C=O). MS: m/z^+ 620 (M), 480 (M − dimethyl acetylenedicarboxylate). Anal. Calcd for $C_{36}H_{30}O_4P_2S$ (620.1): C, 69.67; H, 4.87. Found: C, 69.3; H, 4.42.

Synthesis of Complex 6. To a mixture of **3** (100 mg, 0.12 mmol) and $[Pd(COD)Cl_2]$ (33.2 mg, 0.12 mmol) was added 3 mL of CH_2Cl_2. The formation of the complex was followed by ^{31}P MNR. After 5 min, the solvent was removed under vacuum and the solid obtained was washed with hexanes (3 × 2 mL) and with ether (1 mL). Complex **6** was recovered as an orange solid. Yield: 40% (48 mg, 0.05 mmol).

^{31}P NMR ($CDCl_3$): δ 39.6 (t, $^2J(P_A-P_B)$ = 84.0, P_A bridgehead), 50.2 (d, $^2J(P_A-P_B)$ = 84.0, P_BPh_2). ^{1}H NMR ($CDCl_3$): δ 6.07 (td, 1H, $^4J(H-P_B)$ = 4.4, $^4J(H-P_A)$ = 3.7, H_4), 6.88−7.77 (m, 40H, H of Ph). ^{13}C NMR ($CDCl_3$): δ 75.3 (d, $^4J(C-P_B)$ = 23.4, C_4H), 123.4 (s, C), 123.5 (d, $J(C-P)$ = 89.6, C), 124.4 (dd, $J(C-P)$ = 84.4, $J(C-P)$ = 9.8, C), 126.6−131.8 (m, CH of Ph), 131.9 (s, C), 132.6 (m, CH of Ph), 133.4 (m, C), 134.8 (m, C), 134.9−135.3 (m, CH of Ph), 138.5 (d, $J(C-P)$ = 34.6, C), 154.7 (s, C), 178.7 (d, $J(C-P)$ = 5.4, C). Anal. Calcd for $C_{55}H_{41}Cl_2P_3PdS_2$ (1034.0): C, 63.75; H, 3.99. Found: C, 63.28; H, 3.67.

Synthesis of Complex 7. To a solution of **5** (100 mg, 0.16 mmol) in dichloromethane (5 mL) was added $[Pd(COD)(Cl)_2]$ (46 mg, 0.16 mmol). The formation of complex **7** was followed by ^{31}P NMR. After 5 min, the solvent was removed under vacuum and the residue obtained was washed with hexanes (3 × 2 mL) and Et_2O (1 mL). **7** was obtained as a yellow solid. Suitable crystals for X-ray diffraction were obtained by slow diffusion of hexanes into a dichloromethane solution of the complex at room temperature. Yield: 89% (113 mg, 0.14 mmol).

^{31}P NMR ($CDCl_3$): δ 19.7 (d, $^2J(P_A-P_B)$ = 90.9, P_A bridgehead), 48.0 (d, $^2J(P_A-P_B)$ = 90.9, P_BPh_2). ^{1}H NMR ($CDCl_3$): δ 1.95 (s, 3H, Me), 3.77 (s, 3H, Me of CO_2Me), 3.91 (s, 3H, Me of CO_2Me), 5.94 (d, $^4J(H-P)$ = 2.9, 1H, H_4), 7.12−7.15 (m, 20H, CH of Ph). ^{13}C NMR ($CDCl_3$): δ 23.1 (vt, $^3J(C-P_A)$ = $^3J(C-P_B)$ = 4.6, Me), 53.5 (s, Me of CO_2Me), 53.8 (s, Me of CO_2Me), 64.5 (dd, $^3J(C-P)$ = 20.2, $^3J(C-P)$ = 9.3, C_4H), 124.1 (dd, $J(C-P)$ = 86.8, $J(C-P)$ = 4.3, C),124.6 (dd, $J(C-P)$ = 84.4, $J(C-P)$ = 7.0, C), 128.2−132.6 (m, CH of Ph), 133.5 (d, $J(C-P)$ = 13.8, C), 134.5 (d, $J(C-P)$ = 3.1, CH of Ph), 134.6 (d, $J(C-P)$ = 3.0, CH of Ph), 134.8 (dd, $J(C-P)$ = 85.2, $^3J(C-P)$ = 22.7, C), 136.3 (d, $J(C-P)$ = 8.9, C), 137.4 (dd, $J(C-P)$ = 35.1, $J(C-P)$ = 1.1, C), 144.8 (dd, $J(C-P)$ = 27.1, $J(C-P)$ = 2.5, C), 147.0 (dd, $J(C-P)$ = 4.9, $J(C-P)$ = 1.8, C), 155.0 (vt, $J(C-P_A)$ = $J(C-P_B)$ = 1.7, C), 162.7 (d, $J(C-P)$ = 9.7, C), 163.5 (d, $J(C-P)$ = 14.6, C), 178.3 (vt, $J(C-P)$ = 4.2, C). Anal. Calcd for $C_{36}H_{30}Cl_2O_4P_2PdS$ (796.0): C, 54.19; H, 3.79. Found: C, 53.80; H, 3.42.

Synthesis of Complex 8. Dichloromethane (5 mL) was added to a mixture of **5** (150 mg, 0.24 mmol), $[Pd(\eta^3-C_3H_5)(Cl)]_2$ (44.3 mg, 0.12 mmol), and silver trifluoroacetate (61.6 mg, 0.24 mmol) at room temperature. Formation of complex **8** was followed by ^{31}P NMR and was almost instantaneous. ^{31}P NMR spectroscopy revealed the presence of the two diastereomers **8a** and **8b** (in a 55:45 ratio). The solution was filtrated through Celite, and then the solvent was removed under vacuum, affording a brown powder. Yield: 95% (210 mg, 0.23 mmol). Crystals suitable for X-ray diffraction were obtained by slow diffusion of hexanes into a solution of this complex in $CDCl_3$ at room temperature. Both diastereomers were present in the unit cell. Anal. Calcd for $C_{40}H_{35}F_3O_7P_2PdS_2$ (916.0): C, 52.38; H, 3.85. Found: C, 51.89; H, 3.46.

Data for diastereomer **8a** are as follows. ^{31}P NMR (CD_2Cl_2): δ 12.7 (d, $^2J(P_A-P_B)$ = 116.7, P_A bridgehead), 49.8 (d, $^2J(P_A-P_B)$ = 116.7, P_BPh_2). ^{1}H NMR (CD_2Cl_2): δ 1.92 (s, 3H, Me), 2.01 (d, 1H, $^3J(H-H)$ = 12.6, H of CH_{2a} allyl), 3.39−3.54 (m, 1H, H of CH_{2b} allyl), 3.62−3.89 (m, 6H, Me of CO_2Me),

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4.14 (m, 1H, H of CH_{2a} allyl), 4.92 (m, 1H, H of CH_{2b} allyl), 5.34 (m, 1H, CH allyl), 5.98 (s, H, H_4), 6.52 (m, 2H, H of Ph), 7.07−7.23 (m, 10H, H of Ph), 7.47−7.69 (m, 8H, H of Ph). ^{13}C NMR (CD_2Cl_2): δ 24.0 (m, Me), 53.6 (m, Me of CO_2Me), 54.1 (m, Me of CO_2Me), 65.5 (s, CH_{2a} of allyl), 67.6 (vt, $^3J(C-P_A) = {}^3J(C-P_B) = 21.3$, C_4H), 78.1 (d, $^2J(C-P) = 32.2$, CH_{2b} of allyl), 119.1 (s, C), 119.9 (d, $^2J(C-P) = 6.6$, CH of allyl), 126.0 (dd, $J(C-P) = 87.0$, $J(C-P) = 3.0$, C), 128.4−134.8 (s, CH of Ph), 135.6 (d, $J(C-P) = 18.3$, C), 136.0 (d, $J(C-P) = 7.0$, C), 138.4 (d, $J(C-P) = 21.7$, C), 144.4 (d, $J(C-P) = 11.4$, C), 151.8 (m, C), 156.7 (m, C), 163.6 (d, $J(C-P) = 6.8$, C), 164.7 (d, $J(C-P) = 19.1$, C), 178.8−179.1 (m, C). CF_3 not seen.

Data for diastereomer **8b** are as follows. ^{31}P NMR (CD_2Cl_2): δ 12.1 (d, $^2J(P_A-P_B) = 115.6$, P_A bridgehead), 49.6 (d, $^2J(P_A-P_B) = 115.6$, P_BPh_2). ^{1}H NMR (CD_2Cl_2): δ 1.92 (s, 3H, Me), 2.75 (d, 1H, $^3J(H-H) = 12.6$, H of CH_{2a} allyl), 3.39−3.54 (m, 2H, 1H of CH_{2a} and 1H of CH_{2b} allyl), 3.62−3.89 (m, 6H, Me of CO_2Me), 4.92 (m, 1H, H of CH_{2b} allyl), 5.04 (m, 1H, CH allyl), 5.98 (s, H, H_4), 6.67 (m, 2H, H of Ph), 7.07−7.23 (m, 10H, H of Ph), 7.47−7.69 (m, 8H, H of Ph). ^{13}C NMR (CD_2Cl_2): δ 24.0 (m, Me), 53.6 (m, Me of CO_2Me), 54.1 (m, Me of CO_2Me), 65.5 (s, CH_{2a} of allyl), 67.6 (vt, $^3J(C-P_A) = {}^3J(C-P_B) = 20.9$, C_4H), 78.3 (d, $^2J(C-P) = 31.2$, CH_{2b} of allyl), 120.3 (d, $^2J(C-P) = 7.5$, CH of allyl), 123.4 (s, C), 126.0 (dd, $J(C-P) = 87.0$, $J(C-P) = 3.0$, C), 128.4−134.8 (s, CH of Ph), 135.3 (d, $J(C-P) = 17.9$, C), 136.0 (d, $J(C-P) = 7.0$, C), 138.4 (d, $J(C-P) = 21.7$, C), 144.1 (d, $J(C-P) = 12.1$, C), 151.3 (m, C), 156.5 (m, C), 163.3 (d, $J(C-P) = 7.6$, C), 164.7 (d, $J(C-P) = 19.1$, C), 178.8−179.1 (m, C). CF_3 not observed.

Synthesis of Complex 10. Dichloromethane (5 mL) was added to a mixture of **9** (150 mg, 0.36 mmol), $[Pd(\eta^3-C_3H_5)(Cl)]_2$ (65 mg, 0.18 mmol), and silver trifluoromethanesulfonate (93 mg, 0.36 mmol) at room temperature. The formation of complex **10** was followed by ^{31}P NMR and was almost instantaneous. The solution was then filtrated through Celite. After evaporation of the solvent under vacuum, the powder obtained was washed with hexanes (3 × 2 mL) and Et_2O (2 mL). **10** was then recovered as a pale yellow powder. Yield: 82% (210 mg, 0.29 mmol). Crystals suitable for X-ray diffraction were obtained by slow diffusion of hexanes into a solution of the complex in THF at room temperature.

^{31}P NMR ($CDCl_3$): δ 27.3 (d, $^2J(P_A-P_B) = 59.9$, P_A), 62.4 (d, $^2J(P_A-P_B) = 59.9$, P_B=S). ^{1}H NMR ($CDCl_3$): δ 3.14 (d, 1H, $^3J(H-H) = 12.4$, H of CH_{2a} allyl), 3.68 (dd, $^3J(H-H) = 13.8$, $^3J(H-P) = 10.2$, 1H, H of CH_{2b} allyl), 4.21−4.48 (m, 3H, 2H of PCH_2P and 1H of CH_{2a} allyl), 5.01 (vtd, $^3J(P-H) = {}^3J(H-H) = 7.5$, $^4J(H-H) = 2.0$, 1H, H of CH_{2b} allyl), 5.79 (vtt, 1H, $^3J(H-H) = 13.8$, $^3J(H-H) = 7.5$, CH allyl), 7.20−7.58 (m, 16H, H of Ph), 7.76−7.93 (m, 4H, H of Ph). ^{13}C NMR ($CDCl_3$): δ 37.1 (dd, $^1J(C-P) = 55.0$, $^1J(C-P) = 20.8$, PCH_2P), 64.9 (d, $^2J(C-P) = 3.0$, CH_{2a} allyl), 75.4 (dd, $^2J(C-P) = 29.6$, $^3J(C-P) = 3.6$, CH_{2b} allyl), 119.4 (d, $^2J(C-P) = 6.0$, CH allyl), 126.0 (d, $^1J(C-P) = 81.9$, C of Ph), 126.1 (d, $^1J(C-P) = 82.0$, C of Ph), 126.3 (d, $^1J(C-P) = 82.3$, C of Ph), 126.4 (d, $^1J(C-P) = 82.2$, C of Ph), 129.1−133.4 (m, CH of Ph). CF_3 not observed. Anal. Calcd for $C_{29}H_{27}F_3O_3P_2PdS_2$ (712.0): C, 48.85; H, 3.82. Found: C, 48.47; H, 3.34.

Typical Procedure for Suzuki−Miyaura Cross-Coupling Reactions (Described in the Preparation of Biphenyl). A solution of **8** in toluene (10^{-5} mmol) was prepared by multiple volumetric dilutions of a stock solution. Bromobenzene (102 μL, 1 mmol), phenylboronic acid (183 mg, 1.5 mmol), and potassium carbonate (276 mg, 2 mmol) were successively added at room temperature. The solution was then heated to 110 °C, stirred for 24 h, cooled, and quenched with HCl(aq) (2 M, 40 mL). The organic layer was removed, the aqueous layer was extracted with toluene (3 × 50 mL), the combined organic layers were washed with water, dried ($MgSO_4$), and filtered, and the solvent was removed under vacuum. The residue was dissolved in toluene (6 mL), hexadecane (0.068 M in CH_2Cl_2, 1.00 mL, internal standard) was added, and the conversion yields were determined by GC. After purification on silica gel using hexanes as solvent, NMR spectra of all the functional biphenyl derivatives prepared were compared with those of the commercial compounds (Aldrich) 4-methylbiphenyl,[32] 4-methoxybiphenyl,[32] and 4-acetylbiphenyl.[33]

General Procedure for Allylic Substitution of Secondary Amines. Methylaniline (129 μL, 1 mmol) and allyl alcohol (136 μL, 2 mmol) were successively added to a solution of **8** (18.3 mg, 0.01 mmol) in dichloromethane (2 mL) at room temperature. The solution was then stirred at 70 °C for 24 h. The product yields were based on GC analysis of the resulting solution. All allylamine derivatives prepared were then purified by chromatography on alumina using hexane as eluent. NMR data of *N*-allylaniline and *N*,*N*-diallylaniline were compared with those reported in the literature.[23]

***N*-Allylmorpholine.** ^{1}H NMR ($CDCl_3$): δ 2.45 (t, $^3J(H-H) = 4.4$, 4H, H of CH_2−N), 3.01 (dt, $^3J(H-H) = 6.6$, $^4J(H-H) = 1.2$, 2H, H of $NCH_2CH=CH_2$), 3.72 (t, $^3J(H-H) = 4.4$, 4H, H of CH_2O), 5.14−5.23 (m, 2H, H of CH_2=CH−), 5.85 (ddt, $^3J(H-H) = 10.1$, $^3J(H-H) = 6.8$, H of CH allyl). ^{13}C NMR ($CDCl_3$): δ 53.6 (s, C of CH_2N), 62.3 (s, C of $NCH_2CH=CH_2$), 67.1 (s, C of CH_2O), 118.5 (s, C of CH_2=CH−), 134.6 (s, CH of allyl). MS: m/z^+ 128 (M + 1).

Theoretical Methods. All calculations were carried out within the framework of density functional theory (DFT)[34] using the Gaussian 03 suite of programs.[35] Geometry optimizations, single-point energy calculations, and populations were carried out by means of a pure gradient-corrected exchange functional and the Lee−Yang−Parr nonlocal correlation functional B3LYP,[36] as implemented in the Gaussian suite of programs. The 6-311+G(d,p) basis set was systematically used for all atoms (H, C, P, O). The stationary points (minima, transition states) located at the DFT-B3LYP level were characterized by frequency calculations (see the Supporting Information). Transition states were located using the STQN method, and reaction path calculations were carried out using the IRC procedure to verify that a transition structure connects the starting and ending structures proposed.

X-ray Structural Determination. Pale orange plates of complex **7** were obtained by slow diffusion of hexanes into a solution of this complex in dichloromethane at room temperature. Pale yellow blocks of complex **8** were similarly obtained from a $CDCl_3$ solution and colorless plates of **10** from THF solution. Data were collected at 150 K by ψ and ω scans on a Nonius Kappa CCD diffractometer using a Mo Kα (λ = 0.710 70 Å) X-ray source and a graphite monochromator. Experimental details are described in Table 2. The crystal structures were solved using SIR-97[37] and Shelxl-97.[38] ORTEP

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drawings were made using ORTEP III for Windows.[39] The files CCDC-262187 to CCDC-262189 give additional crystallographic information. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, U.K.; fax (internat.) +44-1223/336-033).

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Supporting Information Available: Tables of crystal data, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and bond angles, anisotropic displacement parameters and hydrogen coordinates for **7**, **8**, and **10** and figures and tables giving optimized geometries of **Ia**−**c, IIa**−**c, IIIa**−**c, IVa**−**c, Va**−**c,** acetylene, and acetylenedicarboxylic acid; crystallographic data for **7**, **8**, and **10** are also given as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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