An Exploratory Study of Regiocontrol in the Heck Type Reaction. Influence of Solvent Polarity and Bisphosphine Ligands

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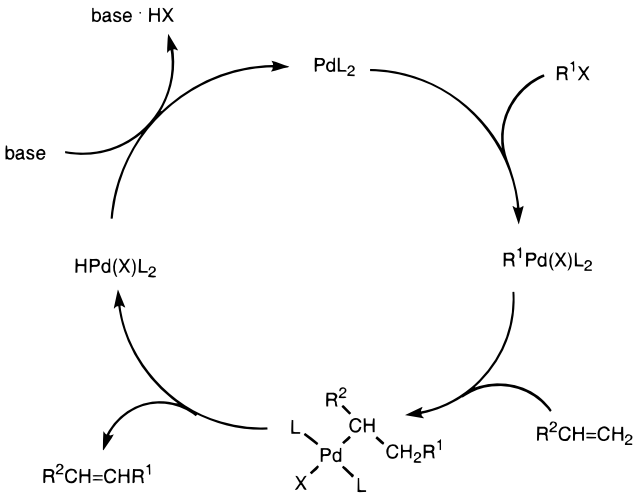
The regiochemistry of the addition of arylpalladium species to styrene and propene has been studied. It was found that for the reaction of $P_2Pd(Ph)X$ the counterion X, the polarity of the solvent, and the structure of the bisphosphine ligand P_2 all have an influence. Using bis(diphenylphosphino)ethane as ligand, triflate as counterion, and a moderately polar solvent mixture, 98% selectivity for addition of the phenyl group to the β-carbon of styrene could be obtained. Finally, using low-temperature NMR, some of the palladium intermediates in the addition could be observed, specifically those where the palladium species is stabilized by η^3-allylic interaction with a phenyl group.

Introduction

The Heck reaction is one of the most important methods for the preparation of aryl-functionalized alkenes, and it is used both in synthetic chemistry and in the pharmaceutical industry. The scope and the limitations of the reaction have been reviewed in a number of recent publications.[1] The reaction is often referred to as a selective reaction, and a large number of synthetically optimized Heck reactions are found in the literature. However, general and good rationales for the observed selectivity are rare. For example, it has been observed that regioselectivity is strongly affected by the substitution pattern of the alkene and by the use of mono vs bidentate ligands.[1b] The selectivity is rationalized mainly on the basis of empirical results. It therefore seems likely that the development of the Heck reaction into a more general procedure which tolerates different starting materials and is highly regioselective requires a deeper understanding of the mechanism, including probable intermediates and transition states.

As a first attempt toward fine-tuning the catalyst for higher stereo- and regioselectivity, we set out to identify intermediates in the reaction between arylpalladium species and the alkenes styrene and propene using diphosphines as ligands for the catalyst. Styrene seemed particularly interesting as substrate because it is known to react in a nonregioselective fashion in the presence of a $Pd(OAc)_2$/dppp catalyst (dppp = bis(diphenylphosphino)propane).[2] To improve the understanding of the factors which determine regioselectivty in Heck type reactions, we have varied the steric and electronic factors by varing solvent, the counterions, and the bisphosphine ligands.

Scheme 1. General Mechanism of the Heck Reaction



Results and Discussion

In the now-classic Heck cycle (Scheme 1),[3] the regiochemistry in the reaction of a monosubstituted alkene with an arylpalladium species is determined by the balance between addition of the aryl group at the terminal or internal position of the alkene. The cycle is completed by β-elimination, generating a palladium hydride species.

The classic Heck cycle has been modified by Cabri et al.[1b] and Hayashi et al.,[3d] who have shown that the counterion (X in Scheme 1)[4] plays an important role.

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(1) Recent reviews: (a) de Meijere, A.; Meyer, F. E. *Angew. Chem.* **1994**, *106*, 2473; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2379. (b) Cabri, W.; Candiani, I. *Acc. Chem. Res.* **1995**, *28*, 2.

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(4) While this work was in progress, a related and complementary study on the addition of arylpalladium triflates to methyl acrylate was published: Brown, J. M.; Hii, K. K. *Angew. Chem.* **1996**, *108*, 679; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 657.

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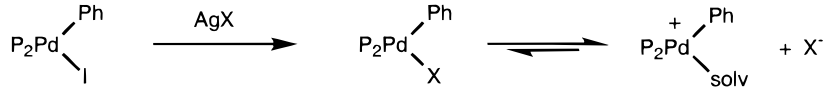
Scheme 2. Preparation of the Complexes $P_2Pd(Ph)X$



(**1a**) P_2 = Ph_2P–PPh_2 = dppp

(**2a**) P_2 = Ph_2P–PPh_2 = dppe

(**3a**) P_2 = Cy_2P–PCy_2 = dcpe

(**4a**) P_2 = Ph_2P–PPh_2 = dppet

(**1b**) P_2 = dppp, X = OTf, (**1c**)X = PF_6,(**1d**)X = BF_4 ,(**1e**)X =OAc

(**2b**) P_2 = dppe, X = OTf

(**3b**) P_2 = dcpe, X = OTf

(**4b**) P_2 = dppet, X = OTf

When X = halide, it probably remains coordinated during the cycle and one of the ligands L has to dissociate prior to coordination of the alkene. In contrast, when X is less strongly coordinating, e.g. X = triflate (OTf), it dissociates to give a cationic palladium species. The alkene then coordinates and the ligands L remain coordinated throughout the catalytic cycle.[1b,3d]

The intermediate palladium hydride species are known to isomerize alkenes, presumably by readdition and renewed β-elimination. This may preclude detection of the primary intermediates in a catalytic reaction. We have therefore chosen to perform the reactions under stoichiometric conditions, using well-defined arylpalladium complexes as reactants.

The complexes $P_2Pd(Ph)I$[5] (**1a**−**4a**) were prepared and then converted into the corresponding complexes $P_2Pd(Ph)X$ (Scheme 2). The conversions were monitored by ^{31}P NMR: the two doublets of the compounds **1a**−**4a** were progressively replaced by two doublets at lower field. In all compounds, the high-field shifts were assigned to the phosphorus atom P_b in a position *trans* to the organo group on the palladium by using P−H COSY experiments on selected compounds (**1a**,**b**, **2a**,**b**, **3a**). In the compounds $P_2Pd(Ph)X$ (**1**−**3**) a strong influence of the counterion X on the ^{31}P chemical shift $\delta(^{31}P)$ was observed. Among the compounds (dppp)Pd(Ph)X (**1**) the $\delta(^{31}P)$ increased in the following order: I < OAc < OTf ≈ PF_6, BF_4. As might be expected, the influence of X on $\delta(^{31}P)$ is larger for the phosphorus atom situated in a *trans* position relative to the exchanged counterion (P_a, Table 1). The shifts at P_a on going from the strongly coordinating I^- to the noncoordinating OTf^- were 12.9 ppm for complex **1**, 5.7 ppm for **2**, 8.1 ppm for **3**, and 2.0 ppm for **4** (Table 1). It is not clear if this means that the dppp ligand is the most polarizable, but it is evident from Table 2 that the regiochemistry of the reaction of the dppp complexes **1** with styrene is strongly affected by the counterion. Using DMF as the solvent, the selectivity for **8** was reduced by weakly coordinating anions, probably because of the increased cationic character of the phenylpalladium complex. Thus, with the complex **1** and styrene the selectivity for **8** was decreased from ca. 80% using iodide or acetate as the counterion X to ca. 55% (X = PF_6, BF_4) (Table 2).

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Table 1. ^{31}P NMR Data of the Phenylpalladium Compounds $P_2Pd(Ph)X$ (1−4) at 0 °C in DMF unless Otherwise Stated

	X (compd no.)	$\delta(P_a)$ (ppm)	$\delta(P_b)$ (ppm)	$J(P_a,P_b)$ (Hz)	$\delta(P)^a$ (ppm)
(dppp)Pd(Ph)X	I (**1a**)[b]	13.1	−8.0	52.8	−17.3
	I (**1a**)	12.9	−8.4	53.2	
	OTf (**1b**)	25.8	−1.7	48.9	
	PF_6 (**1c**)[c]	26.2	−1.3	50.4	
	BF_4 (**1d**)	26.2	−1.3	50.4	
	OAc (**1e**)	19.4	−3.7	48.5	
(dppe)Pd(Ph)X	I (**2a**)[b]	50.7	35.3	27.7	−12.5
	OTf (**2b**)	56.4	39.0	25.0	
(dcpe)Pd(Ph)X	I (**3a**)[b]	67.0	61.7	18.8	0.5
	OTf (**3b**)	75.1	66.8	15.8	
(dppet)Pd(Ph)X	I (**4a**)[b]	56.8	49.3	14.9	−22.7
	OTf (**4b**)	58.8	52.8	*d*	

[a] Free ligand. [b] In $CDCl_3$. [c] $\delta(PF_6)$ −142.9 ppm, $^1J(P-F) = 709.5$ Hz. [d] Broad signals.

Table 2. Influence of the Counterion X on the Regioselectivity of the Phenylation of Styrene with $[(dppp)Pd(Ph)]^+X^-$ (1a−e) in DMF.

	X	**7**/**8**	cis/trans for **8**
1a	I	20/80	2/98
1b	OTf	35/65	<1/99
1c	PF_6	43/57	<1/99
1d	BF_4	42/58	<1/99
1e	OAc	18/82	<1/99

The importance of cationic character is also illustrated by the solvent dependence of the regiochemistry of the reaction between $[(dppp)Pd(Ph)]^+OTf^-$ (**1b**) and styrene. Using the complex (dppp)Pd(Ph)OTf (**1b**) in DMF or acetonitrile solution, there is a balance between addition of the aryl group at the terminal position (65% or 67% of **8**) and at the internal position (35% or 33% of **7**). This is approximately the same result as in catalytic reactions reported earlier by Cabri et al.[2] The selectivity of 65% for **8** that was observed in DMF solution was lowered to 58% when the polarity was increased by addition of water (DMF/water 9:1). Likewise, decreasing the solvent polarity increased the selectivity for **8** to 78% with DMF/CH_2Cl_2 (1:1) and further to 92% and 95% with THF and DMF/CH_2Cl_2 (1:9), respectively, as solvent (Table 3). This is clearly in accordance with a decreased cationic character in the complex **1b** as the polarity of the solvent is decreased.

Also, the bisphosphine ligand P_2 had a strong influence on the regioselectivity of the phenylation of styrene (Table 4). In a comparison of the reactions of the triflate complexes in DMF solution, it was found that the dppp complex **1b** gave by far the lowest selectivity for the product **8** from addition of the phenyl group to the 2-position of styrene, 65%. With the complexes **3b** and

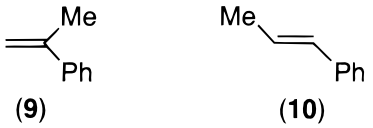

Figure 1. Reaction products of the phenylation of propene.

Table 3. Influence of the Solvent on the Regioselectivity of the Phenylation of Styrene with [(dppp)Pd(Ph)]$^+$OTf$^-$

solvent	**7**/**8**	cis/trans for **8**
DMF/H_2O (9/1)	42/58	<1/99
DMF	35/65	<1/99
acetonitrile	33/67	<1/99
DMF/CH_2Cl_2 (1/1)	22/78	<1/99
DMF/CH_2Cl_2 (1/9)	5/95	<1/99
THF	8/92	4/96

Table 4. Influence of the Bisphosphine Ligand P_2 on the Regioselectivity of the Phenylation of Styrene with [P_2Pd(Ph)]$^+$OTf$^-$ in DMF

	[P_2Pd(Ph)]$^+$OTf$^-$	**7**/**8**	cis/trans for **8**
1b	(dppp)Pd(Ph)]$^+$OTf$^-$	35/65	<1/99
2b	(dppe)Pd(Ph)]$^+$OTf$^-$	5/95	<1/99
3b	(dcpe)Pd(Ph)]$^+$OTf$^-$	16/84	2/98
4b	(dppet)Pd(Ph)]$^+$OTf$^-$	14/86	<1/99

4b ca. 85% selectivity was obtained and the dppe complex **2b** gave very high selectivity for **8**, 95%. The reasons for this great difference in the effects of fairly closely related ligands are not clear at present. However, it is interesting to note that these differences correspond roughly to the changes in the ^{31}P shifts as the P_2 ligands are bound to palladium. Thus, the shift for P_a of the dppp ligand is ca. 40 ppm to lower field on going to the triflate complex, while it is 70−80 ppm for the other three ligands (Table 1). Also, the phosphorus couplings are very different, ca. 50 Hz for **1b** and 25−15 Hz for **2b**−**4b**. These effects might be related to the "bite angle", which should be greater for the dppp ligand than for dppe and the related ligands, as demonstrated by the values 90.6° for (dppp)$PdCl_2$ and 85.8° for (dppe)-$PdCl_2$.[6] Irrespective of the exact nature of the observed effects, it is evident that they can be used for controlling the regiochemistry of the addition of arylpalladium complexes to styrenes. In fact, by using the dppe complex **1b** and DMF/CH_2Cl_2 (1:9) as solvent, the selectivity for the product **8** over the isomer **7** can be increased to 98%.

The strong influence of alkene structure on the regiochemistry has been demonstrated in a large number of earlier studies.[1b,2,3a,10] It is also nicely demonstrated by the reaction between **1b** and the fairly electron rich propene, which in DMF solution gave 1-methylstyrene (**9**) from addition at the internal position as the main product (>85%; Figure 1). In analogy with observations with styrene as reactant, the amount of terminally substituted product *trans*-*β*-methylstyrene (**10**) was increased slightly, from 12 to 19%, when the

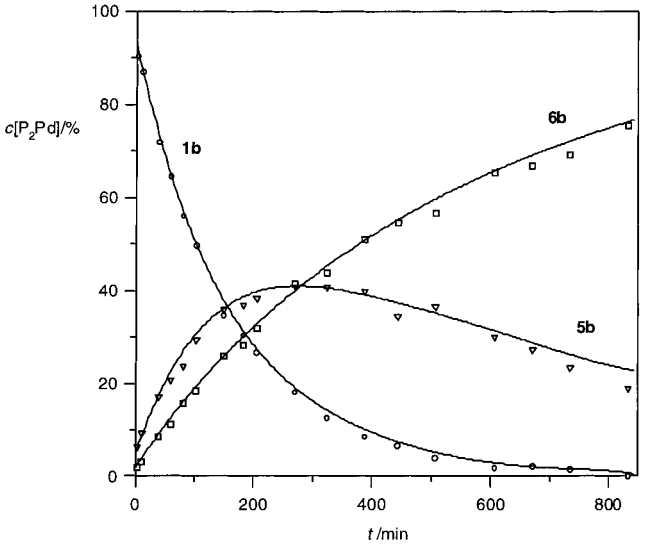

Figure 2. Reaction of (dppp)Pd(Ph)OTf (**1b**) with 10 equiv of styrene at −20 °C.

Table 5. Regioselectivity of the Phenylation of Propene with P_2Pd(Ph)X

P_2Pd(Ph)	X	solvent	**9**/**10**	cis/trans for **10**
(dppp)Pd(Ph)	OTf	DMF/H_2O (9/1)	87/13	1/99
	OTf	DMF	88/12	3/97
	OTf	acetonitrile	88/12	1/99
	OTf	THF	85/15	12/88
	OAc	DMF	88/12	6/94
(dppe)Pd(Ph)	OTf	DMF	81/19	6/94

complex **2b** (P_2 = dppe) was used in place of **1b** (P_2 = dppp). The influence of the solvent polarity on the regioselectivity was even smaller (Table 5).

To get more information on the mechanism, we have finally tried to detect intermediates in the phenylation of styrene. To ensure fast reaction at low temperature, we have worked with the triflate complex[3,4] [(dppp)-Pd(Ph)]$^+$OTf$^-$ (**1b**). The progress of the reaction and the appearance of intermediates were monitored by ^{31}P NMR, and the intermediates were identified by 1D and 2D NMR techniques.

On addition of 2−10 equiv of styrene to a solution of the complex **1b**, in DMF at −20 °C, four new doublets appeared in the ^{31}P NMR spectrum. These signals correspond to two new palladium species, one minor (**5b**) and one major (**6b**) (Scheme 3). The kinetic results (Figure 2) indicate that **5b** is the primary product which is converted to **6b** as the reaction proceeds. The structures of the compounds could be determined by NMR: for the compound **6b**, the ^{13}C DEPT NMR showed three high-field peaks from the CH_2 groups of the dppp ligand and a double doublet (C_1) at 67.4 ppm corresponding to a CH group directly bounded to palladium. Furthermore, there was a doublet at 13.3 ppm (C_2), corresponding to a CH_3 group bounded to the carbon C_1. The assignments were confirmed by ^{1}H NMR and H−H and C−H COSY experiments.

When the reaction between styrene and **1b** was performed in a 9:1 mixture of CD_2Cl_2 and DMF-d_7 at −20 °C, the conversion of **5b** to **6b** could be slowed and **5b** was formed exclusively in ca. 90% yield. Its ^{13}C NMR DEPT spectrum showed the three high-field peaks of the methylene chain of the dppp ligand. In addition, there was a double doublet at 72.3 ppm corresponding

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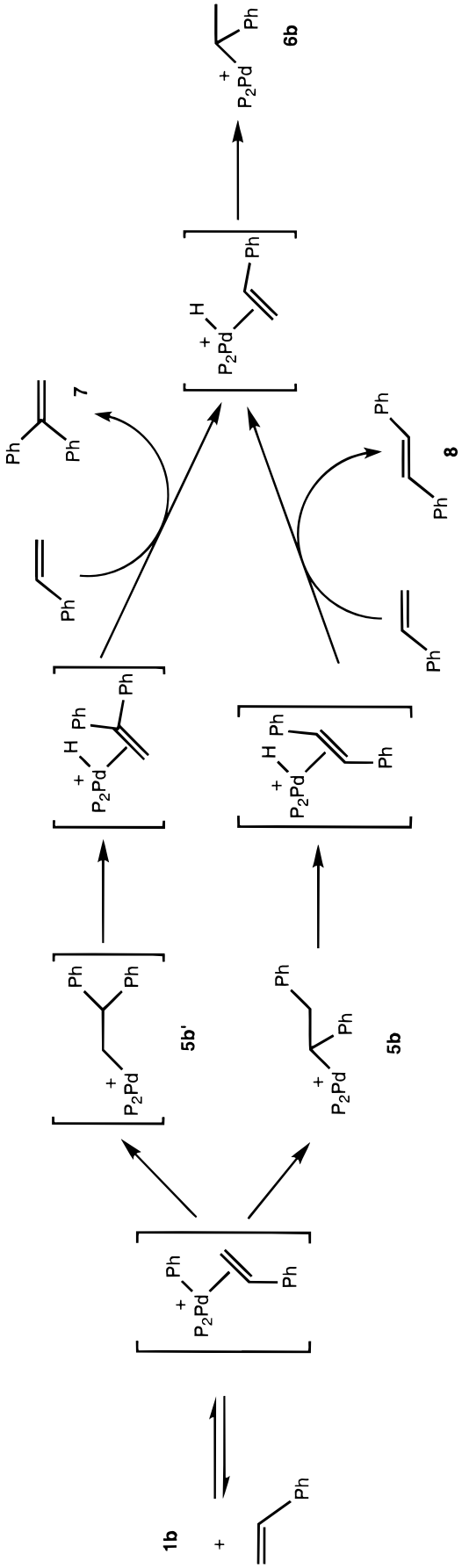
Scheme 3. Mechanism of the Phenylation of Styrene



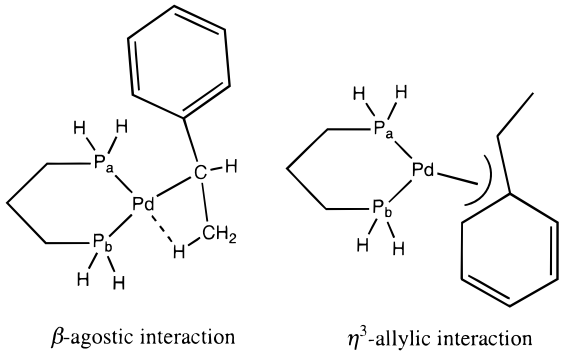


Figure 3. Conformers with a β-agostic or η^3-allylic interaction.

to a CH group bonded to palladium (C_1) and a doublet at 34.3 ppm corresponding to a benzylic CH_2 group (C_2). The connection between C_1 and C_2 was again established by H−H and C−H COSY NMR.

When the reaction between styrene and **1b** was performed in DMF and allowed to go to complete conversion to **6b**, the organic products 1,1-diphenylethylene (**7**) and *trans*-stilbene (**8**) were formed in a ratio of ca. 2:3. The product **8** is clearly derived from the intermediate **5b**, in which the phenyl group has been added to the terminal position of styrene. Similarly, the product **7** must stem from addition of the phenyl group to the internal position of styrene via the intermediate **5b′**, which was not observed. Thus, although the two pathways via **5b** and **5b′** are of comparable efficiency at −20 °C, only **5b** could be detected. Perhaps the reason is a relative stabilization of the intermediate **5b** by coordination of the phenyl group to give a system with η^3-allyl character, which is indicated by theoretical calculations.[7] The difference in the energies of the two low-energy conformers, the β-agostic[8] and the η^3-allylic,[9] was calculated to be 8 kcal mol^{-1} in favor of the latter form (Figure 3). This stabilization is probably also responsible for the detection of **6b** as the final product in the stoichiometric reaction described in Figure 2. The regiochemistry of the Heck reaction is determined by the insertion step, and it is therefore possible that the energy of the transition state leading to **8** is also affected by the η^3-allylic stabilization.

Conclusion

A number of factors clearly affect the regiochemistry of of Heck type reactions. As shown by addition of cationic phenylpalladium species, the reaction with propene, an electron-rich alkene, gave mainly phenylation at the more substituted position of the double bond. In contrast, an electron-poor alkene such as methyl acrylate gave predominant addition of the phenyl group to the less substituted position.[4] Styrene appears to occupy a position intermediate between propene and acrylate and gave initially approximately equal addition to both termini of the alkene. The decrease of the cationic character of the phenylpalladium species, either by an increase in the coordinating power of the counterion or by a decrease in the polarity of the solvent, led to an increase in the relative phenylation at the less substituted position of styrene, and in CH_2Cl_2/DMF (9:1) stilbene (**8**) was the major product (Table 2). With propene, however, no such effect was

observed (Table 3). A reasonable explanation for the result with styrene is to assume that η^3-allylic stabilization of the transition state will increase in a less polar solvent. Since such stabilization is only possible in the transition state leading to **5b**, this product would become favored over **5b′** as the solvent polarity goes down and as less coordinating counterions are added.

Thus, decreasing the cationic character of the intermediate arylpalladium species is an excellent way of controlling regiochemistry in the Heck type of addition to aryl-substituted alkenes. The effect on the addition to simple alkenes such as propene appears to be small. This is also true for changes in the structure of the bisphosphine ligands, which strongly affect the addtion to styrene. In summary, changes of solvent polarity and ligand structure have a moderate effect on the addition of arylpalladium species to unactivated alkenes but seem to offer a general way of controlling the regiochemistry of the addition to arylalkenes. The exact nature of the ligand effects is not clear, but we are presently trying to understand them, using quantum chemical and molecular mechanics calculations in combination with experiments.

Experimental Section

The compound (tmeda)Pd(Ph)I was prepared by a literature procedure.[5c,d] DMF was dried over molecular sieves (4 Å). All other chemicals were used as received. 1,2-Bis(dicyclohexylphosphino)ethane (dcpe) and *cis*-1,2-bis(diphenylphosphino)-ethylene (dppet) were purchased from Strem and Aldrich, respectively. The compounds **1a**−**4a** were handled in air but stored under nitrogen.

GC measurements were recorded on a Varian 3700 or on a Varian 3400 GC. GC-MS measurements were recorded on a Finnigan SSQ 7000 GC-MS system, including a Varian 3400 GC.

^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded at 400, 100, and 162 MHz on a Bruker AMX400 spectrometer or at 500, 126, and 202 MHz on a Bruker DMX500 spectrometer, respectively. The NMR measurements were run in $CDCl_3$ at 0 °C unless otherwise stated. The assignments of the peaks in the 1D NMR spectra were clarified using 2D NMR spectra (H−H COSY, H−C COSY, and H−P COSY) which were recorded on a Bruker DMX500 spectrometer using gradient pulse techniques. ^{1}H and ^{13}C chemical shifts are reported in ppm downfield from $SiMe_4$ and are referenced to the solvent peaks (δ(C*H*Cl$_3$) 7.25 ppm, δ(CD*H*Cl$_2$) 5.31 ppm, δ(Me$_2$CON*H*) 8.02 ppm, δ(*C*DCl$_3$) 77.0 ppm, δ(*C*D$_2$Cl$_2$) 53.8 ppm, δ(Me$_2$*C*OND) 162.7 ppm). ^{31}P chemical shifts are in ppm downfield from 85% H_3PO_4 (external).

The phenylated products **7**−**10** were identified using ^{1}H NMR and GC-MS.

(dppp)Pd(Ph)I (1a) and (dppe)Pd(Ph)I (2a). To a solution of (tmeda)Pd(Ph)I (417 mg, 1.17 mmol) in chloroform (5 mL) was added 1 equiv of the chelating phosphine (dppp, 483 mg, dppe, 467 mg). After the mixture was stirred for 5−10 min at room temperature, the solvent was evaporated and the resulting yellow solid was powdered and dried in vacuo (at least 4 h). Recrystallization (CH_2Cl_2/*n*-pentane) afforded yellow microcrystals (882 mg of **1a** (96%), 723 mg of **2a** (87%).

(dppp)Pd(Ph)I (1a). ^{1}H NMR: Pd−Ph, δ 6.90 (2H, m, H$_o$), 6.55 (2H, m, H$_m$), 6.45 (1H, t, ^1J(H$_p$,H$_m$) = 7.5 Hz, H$_p$); dppp, δ 2.54 (2H, m, P$_a$−C*H*$_2$), 2.42 (2H, m, P$_b$−C*H*$_2$), 1.89 (2H, m, C*H*$_2$), 7.81 (4H, m, H$_{o,a}$), 7.44 (6H, m, H$_{m,a}$ + H$_{p,a}$), 7.29 (6H, m, H$_{o,b}$ + H$_{p,b}$), 7.14 (4H, m, H$_{m,b}$). ^{31}P{^{1}H} NMR: δ 13.1 (d, J(P$_a$,P$_b$) = 52.8 Hz, P$_a$), −8.0 (d, P$_b$). ^{13}C{^{1}H} NMR: Pd−Ph, δ 158.6 (dd, ^2J(P$_b$,C) = 126.6 Hz, ^2J(P$_a$,C) = 3.8 Hz, C$_i$), 137.0 (dd, ^3J(P$_b$,C) = 4.6 Hz, ^3J(P$_a$,C) = 2.3 Hz, C$_o$), 127.0 (dd, ^4J(P$_b$,C) = 9.1 Hz, ^3J(P$_a$,C) = 1.5 Hz, C$_m$), 121.6 (C$_p$); dppp, δ 28.5 (dd, ^1J(P$_a$,C) = 25.0 Hz, ^3J(P$_b$,C) = 7.6 Hz, P$_a$−*C*H$_2$), 27.0 (dd, ^1J(P$_b$,C) = 19.0 Hz, ^3J(P$_a$,C) = 3.8 Hz, P$_b$−*C*H$_2$), 19.0 (d, ^2J(P$_a$,C) = 3.8 Hz, *C*H$_2$), 131.0 (d, ^1J(P$_a$,C) = 50.8 Hz, C$_{i,a}$), 132.9 (d, ^1J(P$_b$,C) = 35.6 Hz, C$_{i,b}$), 133.7 (d, ^2J(P$_a$,C) = 10.6 Hz, C$_{o,a}$), 133.1 (d, ^2J(P$_b$,C) = 10.6 Hz, C$_{o,b}$), 128.3 (d, ^3J(P$_a$,C) = 7.6 Hz, C$_{m,a}$), 128.1 (d, ^3J(P$_b$,C) = 10.6 Hz, C$_{m,b}$), 131.1 (d, ^4J(P$_a$,C) = 2.3 Hz, C$_{p,a}$), 131.1 (d, ^4J(P$_b$,C) = 2.3 Hz, C$_{p,b}$).

(dppe)Pd(Ph)I (**2a**). ^{1}H NMR: Pd−Ph, δ 7.05 (2H, t, ^1J(H$_o$,H$_m$) = 7.7 Hz, H$_o$), 6.72 (2H, m, H$_m$), 6.63 (1H, dt, ^1J(H$_p$,H$_m$) = 7.2 Hz, H$_p$; dppe, δ 2.36 (2H, m, P$_a$−C*H*$_2$), 2.20 (2H, m, P$_b$−C*H*$_2$), 7.33 (8H, m, H$_{o,a}$ + H$_{m,a}$), 7.88 (4H, m, H$_{o,b}$), 7.45 (8H, m, H$_{m,a}$ + H$_{p,a}$ + H$_{p,a}$). ^{31}P{^{1}H} NMR: δ 50.7 (d, J(P$_a$,P$_b$) = 27.7 Hz, P$_a$), 35.3 (d, P$_b$). ^{13}C{^{1}H} NMR: Pd−Ph, δ 154.6 (d, ^2J(P$_b$,C) = 130.5 Hz, C$_i$), 137.4 (C$_o$), 127.1 (d, ^4J(P$_b$,C) = 9.2 Hz, C$_m$), 122.2 (C$_p$); dppe, δ 29.4 (dd, ^1J(P$_a$,C) = 29.8 Hz, ^3J(P$_b$,C) = 22.1 Hz, P$_a$−*C*H$_2$), 24.5 (dd, ^1J(P$_b$,C) = 25.2 Hz, ^3J(P$_a$,C) = 13.0 Hz, P$_b$−*C*H$_2$), 129.2 (d, ^1J(P$_a$,C) = 49.6 Hz, C$_{i,a}$), 131.1 (d, ^1J(P$_b$,C) = 33.6 Hz, C$_{i,a}$), 133.1 (d, ^2J(P$_a$,C) = 11.4 Hz, C$_{o,a}$), 133.6 (d, ^2J(P$_b$,C) = 11.4 Hz, C$_{o,a}$), 128.6 (d, ^3J(P$_a$,C) = 10.7 Hz, C$_{m,a}$), 128.7 (d, ^3J(P$_b$,C) = 9.2 Hz, C$_{m,a}$), 130.8 (C$_{p,a}$), 131.1 (C$_{p,a}$).

(dcpe)Pd(Ph)I (3a). A degassed solution of (tmeda)Pd(Ph)I (324 mg, 0.759 mmol) in chloroform (10 mL) was cooled to 0 °C, and a cold solution (0 °C) of 1,2-bis(dicyclohexylphosphino)-ethane (dcpe; 324 mg, 0.776 mmol) in degassed chloroform (10 mL) was added under nitrogen. The resulting clear solution was stirred for 10 min at 0 °C, evaporated to dryness, and dried for 6 h in vacuo to give a white solid. Column chromatography (silica gel, chloroform) yielded 289 mg (52%) of **3a**.

^{1}H NMR: Pd−Ph, δ 7.39 (2H, t, ^1J(H$_o$,H$_m$) = 7.3 Hz, H$_o$), 7.01 (2H, m, H$_m$), 6.83 (1H, t, ^1J(H$_p$,H$_m$) = 7.3 Hz, H$_p$); dppe, δ 1.88 (m, P$_a$−C*H*$_2$), 1.67 (m, P$_b$−C*H*$_2$), 1.9 (m, H$_{i,a}$), 2.2 (m, H$_{i,a}$), 1.75 (m), 1.65 (m), 1.45 (m), 1.1−1.4 (m), 0.7−0.8 (m). ^{31}P{^{1}H} NMR: δ 67.0 (d, J(P$_a$,P$_b$) = 18.8 Hz, P$_a$), 61.7 (d, P$_b$). ^{13}C{^{1}H} NMR: Pd−Ph, δ 155.6 (d, ^2J(P$_b$,C) = 129.5 Hz, C$_i$), 138.3 (C$_o$), 126.7 (d, ^4J(P$_b$,C) = 8.5 Hz, C$_m$), 122.5 (C$_p$); dppe, δ 25.3 (dd, ^1J(P$_a$,C) = 23.1 Hz, ^3J(P$_b$,C) = 23.1 Hz, P$_a$−*C*H$_2$), 20.8 (dd, ^1J(P$_b$,C) = 18.8 Hz, ^3J(P$_a$,C) = 12.0 Hz, P$_b$−*C*H$_2$), 34.2 (d, ^1J(P$_a$,C) = 25.4 Hz, C$_{i,a}$), 34.7 (d, ^1J(P$_b$,C) = 17.8 Hz, C$_{i,a}$), 29.5 (d, ^2J = 3.9 Hz, C$_o$), 28.7 (C$_o$), 28.2 (C$_o$), 27.7 (C$_o$), 27.1 (d, ^3J = 13.1 Hz, C$_m$), 27.0 (d, ^3J = 12.3 Hz, C$_m$), 26.8 (d, ^3J = 9.2 Hz, C$_m$), 26.6 (d, ^3J = 10.0 Hz, C$_m$), 25.9 (C$_p$), 25.7 (C$_p$).

(dppet)Pd(Ph)I (4a). To a solution of (tmeda)Pd(Ph)I (500 mg, 0.977 mmol) in chloroform (5 mL) was added *cis*-1,2-bis-(diphenylphosphino)ethylene (dppet; 400 mg, 1.01 mmol), and the solution was stirred for 5 min at room temperature. After fast evaporation of the solvent, the resulting solid was dried overnight in vacuo. Due to the formation of unspecified dppet oligomers, an additional portion of dppet (110 mg) was added to a chloroform solution of the product mixture. The solvent was evaporated, and the resulting solid was dried in vacuo for 4 h and purified by column chromatography (silica gel, methylene chloride) to give 94 mg (14%) of pure **4a** and 69 mg of a mixture of (tmeda)Pd(Ph)I and **4a**.

^{1}H NMR: Pd−Ph: δ 7.01 (2H, t, ^1J(H$_o$,H$_m$) = 8.0 Hz, H$_o$), 6.76 (2H, m, H$_m$), 6.70 (1H, m, H$_p$); dppet, δ 7.02 (1H, ddd, ^3J(P$_b$,H$_a$) = 54.1 Hz, ^2J(P$_a$,H$_a$) = 9.9 Hz, ^2J(H$_a$,H$_b$) = 9.9 Hz, P$_a$−C*H*), 7.39 (ü, P$_b$−C*H*), 7.25 (4H, m, H$_{o,a}$), 7.77 (4H, m, H$_{o,a}$), 7.30 (4H, m, H$_{m,a}$), 7.42 (8H, m, H$_{m,a}$ + H$_{p,a}$ + H$_{p,a}$). ^{31}P{^{1}H} NMR: δ 56.8 (d, J(P$_a$,P$_b$) = 14.9 Hz, P$_a$), 49.3 (d, P$_b$). ^{13}C{^{1}H} NMR: Pd−Ph, δ 153.4 (d, ^2J(P$_b$,C) = 133.3 Hz, C$_i$), 138.0 (C$_o$), 126.9 (d, ^4J(P$_b$,C) = 9.3 Hz, C$_m$), 122.7 (C$_p$); dppet, δ 146.7 (dd, ^1J(P$_a$,C) = 40.8 Hz, ^3J(P$_b$,C) = 40.8 Hz, P$_a$−*C*H), 146.0 (dd, ^1J(P$_b$,C) = 34.7 Hz, ^3J(P$_a$,C) = 33.1 Hz, P$_b$−*C*H), 128.2 (d, ^1J(P$_a$,C) = 53.2 Hz, C$_{i,a}$), 130.9 (d, ^1J(P$_b$,C) = 37.8 Hz, C$_{i,a}$), 132.9 (d, ^2J(P$_a$,C) = 11.6 Hz, C$_{o,a}$), 133.5 (d, ^2J(P$_b$,C) = 12.3 Hz, C$_{o,a}$), 128.7 (d, ^3J(P$_a$,C) = 10.8 Hz, C$_{m,a}$), 128.8 (d, ^3J(P$_b$,C) = 10.8 Hz, C$_{m,a}$), 130.9 (d, ^4J(P$_a$,C) = 1.5 Hz, C$_{p,a}$), 131.2 (d, ^4J(P$_b$,C) = 2.3 Hz, C$_{p,a}$).

[P_2Pd(Ph)]$^+$OTf$^-$ (1b−4b). In a typical procedure AgOTf (28.6 mg, 0.111 mmol) was added to a precooled (−20 °C) solution of (P_2)Pd(Ph)I (**1a**−**4a**; 0.117 mmol) in 0.87 mL of DMF-d_7. After 2−4 min the precipitate was removed (centrifugation followed by filtration through 0.45 μm PTFE), resulting in a clear, colorless, or slightly reddish solution (135 mmol of Pd/mL of solvent), which was immediately used for NMR experiments or stored at −196 °C.

[(dppp)Pd(Ph)]$^+$OTf$^-$ (1b; 1/9 DMF-d_7/CD_2Cl_2, −80 °C). ^{1}H NMR: Pd−Ph, δ 6.90 (2H, m, H_o), 6.57 (3H, m, H_m + H_p); dppp, δ 2.67 (2H, br, P_a−CH_2), 2.52 (2H, br, P_b−CH_2), 1.69 (2H, m, CH_2), 7.58 (4H, m, $H_{o,a}$), 7.45 (6H, m, $H_{p,a}$ + $H_{m,a}$), 7.27 (6H, m, $H_{o,a}$ + $H_{p,a}$), 7.10 (4H, m, $H_{m,a}$). ^{31}P{^{1}H} NMR: δ 25.5 (d, J(P_a,P_b) = 49.6 Hz, P_a), −3.3 (d, P_b). ^{13}C{^{1}H} NMR: Pd−Ph, δ 162 (d, one satellite overlapped with the solvent peak, C_i), 133.5 (C_o), 127.4 (d, ^4J(P_b,C) = 6.9 Hz, C_m), 123.3 (C_p); dppp, δ 27.2 (dd, ^1J(P_a,C) = 33.6 Hz, ^3J(P_b,C) = 7.6 Hz, P_a−CH_2), 23.8 (d, ^1J(P_b,C) = 22.1 Hz, P_b−CH_2), 17.6 (CH_2), 129.1 (d, ^1J(P_a,C) = 59.5 Hz, $C_{i,a}$), 129.0 (d, ^1J(P_b,C) = 35.9 Hz, $C_{i,a}$), 132.7 (d, ^2J(P_a,C) = 10.7 Hz, $C_{o,a}$), 132.5 (d, ^2J(P_b,C) = 11.4 Hz, $C_{o,a}$), 127.4 (d, ^3J(P_a,C) = 10.7 Hz, $C_{m,a}$), 128.7 (d, ^3J(P_b,C) = 9.2 Hz, $C_{m,a}$), 130.4 ($C_{p,a}$), 130.4 ($C_{p,a}$), CF_3: 120.2 (q, ^1J(C,F) = 320.4 Hz).

[(dppe)Pd(Ph)]$^+$OTf$^-$ (2b; DMF-d_7, −60 °C). ^{1}H NMR: Pd−Ph, δ 7.12 (2H, br, H_o), 6.77 (3H, br, H_m + H_p); dppe, δ 3.05 (2H, d, ^2J(P_a,H) = 29.3 Hz, P_a−CH_2), 2.53 (2H, d, ^2J(P_b,H) = 26.4 Hz, P_b−CH_2), 7.70 (4H, br, $H_{o,a}$), 7.96 (4H, br, $H_{o,a}$), 7.47 (4H, br, $H_{m,a}$), 7.62 (8H, br, $H_{m,a}$ + $H_{p,a}$ + $H_{p,a}$). ^{31}P{^{1}H} NMR: δ 57.2 (d, J(P_a,P_b) = 24.8 Hz, P_a), 38.3 (d, P_b). ^{13}C{^{1}H} NMR: Pd−Ph, δ 162 (d, one satellite overlapped with the solvent peak, C_i), 135.9 (C_o), 128.1 (d, ^4J(P_b,C) = 7.7 Hz, C_m), 124.6 (C_p), dppe: δ 30.6 (dd, ^1J(P_a,C) = 33.9 Hz, ^3J(P_b,C) = 20.2 Hz, P_a−CH_2), 20.9 (d, ^1J(P_b,C) = 29.3 Hz, P_b−CH_2), 129.9 (d, ^1J(P_a,C) = 57.8 Hz, $C_{i,a}$), 131.4 (d, ^1J(P_b,C) = 33.9 Hz, $C_{i,a}$), 134.2 (d, ^2J(P_a,C) = 11.6 Hz, $C_{o,a}$), 133.6 (d, ^2J(P_b,C) = 13.1 Hz, $C_{o,a}$), 129.5 (d, ^3J(P_a,C) = 10.8 Hz, $C_{m,a}$), 130.0 (d, ^3J(P_b,C) = 10.0 Hz, $C_{m,a}$), 132.4 ($C_{p,a}$), 132.0 ($C_{p,a}$), CF_3: 121.6 (q, ^1J(C,F) = 322.1 Hz).

[(dcpe)Pd(Ph)]$^+$OTf$^-$ (3b; DMF-d_7, −60 °C). ^{1}H NMR: Pd−Ph, δ 7.38 (2H, m, H_o), 7.13 (2H, m, H_m), 7.02 (1H, t, ^1J(H_p,H_m) = 7.3 Hz, H_p); dcpe, δ 2.3 (m, P−CH_2), 2.04 (m), 1.85−2.15 (m), 1.75 (br), 1.55 (br), 1.05−1.50, 0.95 (br). ^{31}P-{^{1}H} NMR: δ 75.1 (d, J(P_a,P_b) = 15.8 Hz, P_a), 66.8 (d, P_b), ^{13}C-{^{1}H} NMR: Pd−Ph, δ 160.7 (d, ^2J(P_b,C) = 116.4 Hz, C_i), 136.1 (C_o), 127.5 (C_m), 124.3 (C_p); dcpe, δ 16.8 (d, ^1J(P_b,C) = 22.4 Hz, P_b−CH_2), 32.6 (d, ^1J(P_b,C) = 17.0 Hz, $C_{i,a}$), 28.1 (C_o), 27.7 (C_o), 24.4 (C_o), 26.1−26.5 (C_m), 25.5 (C_p), 25.3 (C_p), CF_3: 121.0 (q, ^1J(C,F) = 322.1 Hz).

[(dppet)Pd(Ph)]$^+$OTf$^-$ (4b; DMF-d_7, −60 °C). ^{1}H NMR: Pd−Ph, δ 7.09 (2H, br, H_o), 6.84 (2H, br, H_m), 6.87 (1H, br, H_p), dppet, δ 7.0 (1H, d, one satellite is overlapped, P_a−CH), 8.33 (1H, d, ^3J(P_a,H_b) = 54.5 Hz, P_b−CH), 7.55 (8H, br, $H_{o,a}$ + $H_{m,a}$), 7.90 (4H, br, $H_{o,a}$), 7.65 (8H, br, $H_{m,a}$ + $H_{p,a}$ + $H_{p,a}$). ^{31}P-{^{1}H} NMR: δ 58.8 (br, P_a), 52.8 (br, P_b). ^{13}C{^{1}H} NMR: Pd−Ph, δ 160.8 (d, ^2J(P_b,C) = 120.2 Hz, C_i), 136.3 (C_o), 128.2 (C_m), 125.2 (C_p), dppet, δ 149.9 (dd, ^1J(P_a,C) = 43.2 Hz, ^3J(P_b,C) = 40.8 Hz, P_a−CH_2), 143.4 (dd, ^1J(P_b,C) = 38.5 Hz, ^3J(P_a,C) = 16.6 Hz, P_b−CH_2), 128.0 (d, ^1J(P_a,C) = 53.1 Hz, $C_{i,a}$), 131.0 (d, ^1J(P_b,C) = 37.8 Hz, $C_{i,a}$), 134.1 (d, ^2J(P_a,C) = 10.8 Hz, $C_{o,a}$), 133.5 (d, ^2J(P_b,C) = 12.2 Hz, $C_{o,a}$), 129.8 (d, ^3J(P_a,C) = 10.8 Hz, $C_{m,a}$), 130.2 (d, ^3J(P_b,C) = 7.8 Hz, $C_{m,a}$), 132.8 ($C_{p,a}$), 132.3 ($C_{p,a}$); CF_3, δ 121.7 (q, ^1J(C,F) = 322.1 Hz).

[(dppp)Pd(Ph)]$^+$X$^-$ (X = PF_6 (1c), BF_4 (1d), OAc (1e)). These complexes were prepared similarly to the triflate complexes **1b**−**4b** using a DMF/DMF-d_7 mixture (9/1) and the silver salts $AgPF_6$, $AgBF_4$, and AgOAc instead of triflate.

[(dppp)Pd(Ph)]$^+$$PF_6^-$ (1c). ^{31}P{^{1}H} NMR: δ 26.2 (d, J(P_a,P_b) = 50.4 Hz, P_a), −1.3 (d, P_b), −142.9 (sept, ^1J(P−F) = 709.5 Hz, PF_6).

[(dppp)Pd(Ph)]$^+$$BF_4^-$ (1d). ^{31}P{^{1}H} NMR: δ 26.2 (d, J(P_a,P_b) = 50.4 Hz, P_a), −1.3 (d, P_b).

[(dppp)Pd(Ph)]$^+$OAc$^-$ (1e). ^{31}P{^{1}H} NMR: δ 19.4 (d, J(P_a,P_b) = 48.5 Hz, P_a), −3.7 (d, P_b).

[(dppp)Pd(CHPhCH_2Ph)]$^+$OTf$^-$ (5b). A solution of [(dppp)-Pd(Ph)]$^+$OTf$^-$ (**1b**) (135 mmol of Pd/L) in 9/1 CD_2Cl_2/DMF-d_7 was prepared in a way similar to that described above and cooled to −80 °C. After addition of 1.2 equiv of styrene the sample was inserted into the NMR (−20 °C) and the reaction was followed via ^{31}P NMR spectroscopy. After ca. 20 min **1b** was converted mainly to **5b**, whose composition (80−90% **5b**) did not change during the ^{1}H, ^{13}C, DEPT-135, H−C COSY, and H−H COSY experiments (10 h). The signals of the performed NMR experiments (−20 °C) could be partially assigned as follows.

^{1}H NMR: Pd−R, δ 3.64 (1H, m, H_1), 2.09 (1H, m, H_2), 2.93 (1H, m, H′$_2$); dppp, δ 2.80 (1H, m, P_a−CH_2), 2.95 (1H, m, P_a−CH'_2), 2.57 (2H, m, P_b−CH_2), 1.8 (2H, br, CH_2). ^{31}P{^{1}H} NMR: δ 18.9 (d, J(P_a,P_b) = 74.6 Hz, P_a), 6.2 (d, P_b). ^{13}C{^{1}H} NMR: Pd−R, δ 72.3 (dd, ^2J(P_b,C) = 43.2 Hz, ^2J(P_a,C) = 10.6 Hz, C_1), 34.3 (d, ^3J(P_b,C) = 4.5 Hz, C_2), dppp, δ 26.7 (dd, ^1J(P_a,C) = 27.5 Hz, ^1J(P_b,C) = 3.8 Hz, P_a−CH_2), 25.3 (d, ^1J(P_b,C) = 23.7 Hz, P_b−CH_2), 18.3 (CH_2); CF_3, δ 120.2 (q, ^1J(C,F) = 320.4 Hz).

[(dppp)Pd(CHMePh)]$^+$OTf$^-$ (6b). To a solution of [(dppp)-Pd(Ph)]$^+$OTf$^-$ (**1b**) (135 mmol of Pd/L) in DMF-d_7 was added 10 equiv of styrene at −20 °C. After 12 h at −20 °C the conversion of **1b** via the intermediate **5b** into **6b** was completed by warming to room temperature (5 min) to give a mixture containing **6b** and the Heck products *trans*-stilbene and 1,1-diphenylethylene. The NMR signals at −20 °C could partially be assigned as follows.

^{1}H NMR: Pd−R, δ 3.28 (1H, m, H_1), 0.86 (3H, m, H_2); dppp, δ 2.74 (2H, m, P_a−CH_2), 2.55 (2H, m, P_b−CH_2), 1.40 (1H, m, CH_2), 1.88 (1H, m, CH'_2). ^{31}P{^{1}H} NMR: δ 18.3 ppm (d, J(P_a,P_b) = 76.0 Hz, P_a), 6.3 (d, P_b). ^{13}C{^{1}H} NMR: Pd−R, δ 67.4 (dd, ^2J(P_b,C) = 42.7 Hz, ^2J(P_a,C) = 11.9 Hz, C_1), 13.3 (d, ^3J(P_b,C) = 5.4 Hz, C_2); dppp, δ 26.6 (d, ^1J(P_a,C) = 28.5 Hz, P_a−CH_2), 24.7 (d, ^1J(P_b,C) = 24.7 Hz, P_b−CH_2), 17.9 (CH_2); CF_3, δ 120.2 (q, ^1J(C,F) = 320.4 Hz).

General Procedure for the Reaction with Styrene and Propene. To a solution of [P_2Pd(Ph)]$^+$OTf$^-$ (0.5 mL of **1a**−**1d**, **2b**, **3b**, and **4b**) containing 45 mmol of Pd/L, prepared as described above, was added styrene (2−10 equiv) or propylene (excess) were added at 0 °C, and the solutions were stirred at room temperature overnight. The resulting dark mixture was partitioned between diethyl ether (2 × 2 mL) and water (2 × 2 mL). The ethereal layers were dried over sodium sulfate and concentrated to 1 mL by rotary evaporation before analyses by GC.

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