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Hiyama Cross-Coupling of Arenediazonium Salts under Mild Reaction Conditions

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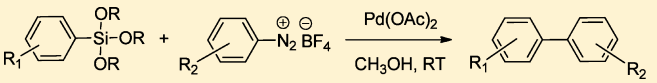
Supporting Information

ABSTRACT: Palladium acetate [$Pd(OAc)_2$]-catalyzed Hiyama cross-coupling of arenediazonium salts with organosilanes was found to generate biaryl products in high yields in alcoholic solutions. The simple and efficient protocol does not require any bases, ligands, or air/moisture. The transformation can tolerate either electron-donating or electron-withdrawing functional groups. Theoretical studies show that the transmetalation is the rate-limiting step for the cross-coupling reaction and both acetate and tetrafluoroborate anions may be involved in the direct reaction with the silicon atom.



INTRODUCTION

The importance of palladium catalyzed cross-coupling reactions for the carbon−carbon chemical bond formation can hardly be overestimated in synthetic organic chemistry.[1] Indeed in the past several decades, palladium-catalyzed reactions have been developed into a routine method for the preparation of fine chemicals, polymers, agrochemicals, and pharmaceutical intermediates in the academic laboratory as well as the large-scale industrial applications.[2] The key step for the cross-coupling is the transmetalation of the organometallic reagents with electrophiles such as in Kumada,[3] Negishi,[4] Stille,[5] and Suzuki coupling reactions.[6] However, these catalyzed couplings suffer many drawbacks for the practical applications. For example, a large excess of toxic tin reagents are needed for the Stille cross-coupling, resulting in a large amount of the organotin waste. For the Suzuki cross-coupling, the highly functionalized organoboron reagents are difficult to prepare and are also not easy to purify and handle. Moreover, they frequently lose the boron functional groups to form the undesirable homocoupling products.

Recently, the use of silicon-derived compounds as alternative reagents for the cross-coupling transformations (Hiyama coupling reaction)[7] has attracted much attention due to their low cost, easy availability, environmentally benign nature, as well as the tolerance to the different functional groups.[8] Although organosilicon reagents have been employed for the synthesis for a wide variety of applications such as natural products and biologically active compounds, the highly complex phosphine ligand and catalyst are expensive and difficult to prepare and handle together with the difficulty for the postprocessing. Moreover, activation by base such as fluoride and hydroxide are essential for the formation of biaryls.[9] Thus, it is still desirable to develop inexpensive and efficient catalytic methods for the Hiyama cross-coupling reaction under mild reaction conditions.

Arenediazonium salts are both attractive and useful electrophiles for the palladium-catalyzed chemistry.[10] Compared to other coupling partners such as aryl halides and triflates, arenediazonium salts have much higher reactivity as well as the wider availability from inexpensive anilines. Although arenediazonium salts have been used in some palladium-catalyzed coupling reactions including Mizoroki−Heck,[11] Suzuki−Miyaura,[12] and Stille reactions,[13] the studies are scarce in the literature for the palladium catalyzed Hiyama cross-coupling of arenediazonium salts. As far as we know, the only attempt was the $PdCl_2$-catalyzed reaction of phenyltrimethoxysilane with arenediazonium salts, which gave only at 20−48% of the desired biaryl products.[14] In this paper, we report a practical and efficient protocol for the $Pd(OAc)_2$-catalyzed Hiyama-type cross-coupling without the need for additional bases and ligands under mild reaction conditions. The reaction mechanism has also been examined by theoretical calculations.

RESULTS AND DISCUSSION

Pd(II)-Catalyzed Hiyama Cross-Coupling of Arenediazonium Salts. The initial reaction conditions were optimized using phenyltriethoxysilane and 4-methylbenzenediazonium tetrafluoroborate salt as the model substrates in methanol with 5 mol % of $PdCl_2$ at 25 °C for 6 h under air. Only 45% yield of the desired cross-coupling product was isolated from the $PdCl_2$-catalyzed reaction (Table 1, entry 1). A slight improvement was observed for the PdI_2-catalyzed reaction (Table 1, entry 2). No significant improvement of the cross-coupling yields was achieved for the palladium catalysts containing phosphine ligands (Table 1, entries 3−5). Interestingly, the desired cross-coupling product was obtained in 81% yield from the $Pd(OAc)_2$-catalyzed reaction (Table 1,

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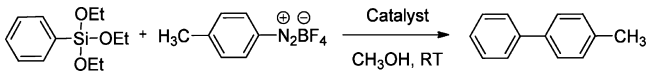
Table 1. Effects of Catalysts on the Cross-Coupling Reaction[a]



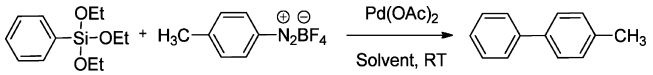
entry	catalyst	yield[b] (%)
1	$PdCl_2$	45
2	PdI_2	54
3	$PdCl_2$(dppf)	63
4	$PdCl_2$ $(PPh_3)_3$	42
5	$Pd(PCy_3)_2Cl_2$	40
6	$Pd(OAc)_2$	81
7	$RhCl(PPh_3)_3$	–
8	[RuCl2(*p*-cymene)]2	–
9	$Pd(PPh_3)_4$	29
10	$Pd_2(dba)_3$	23
11	$Pd(OAc)_2$	75[c]

[a]Reaction conditions: phenyltriethoxysilane (0.6 mmol), 4-methylbenzenediazonium tetrafluoroborate salt (0.5 mmol), catalyst (5.0 mol %), CH_3OH (2 mL), 25 °C, 6 h. [b]Isolated yields. [c]Using 1.0 mol % of $Pd(OAc)_2$ as catalyst.

entry 6). Also, the transition-metal sources were critical for the cross-coupling reaction (Table 1, entries 7 and 8). Relatively lower cross-coupling yields were obtained for the zerovalent palladium catalysts such as $Pd(PPh_3)_4$ and $Pd_2(dba)_3$ (Table 1, entries 9 and 10). It is worth noting that a decent yield was still obtained at 1.0 mol % of the $Pd(OAc)_2$ catalyst loading (Table 1, entry 11).

Among the solvents tested, the cross-coupling product was found to be negligible in both nonpolar solvents (such as ethers, aromatics, and chloromethanes) and polar aprotic solvents (such as DMF and DMSO) (Table 2, entries 1–9).

Table 2. Solvent Effects on the Cross-Coupling Reaction[a]



entry	solvent	yield[b] (%)	entry	solvent	yield[b] (%)
1	THF	–	10	methanol	81
2	1,4-dioxane	–	11	ethanol	66
3	DME	–	12	propan-1-ol	58
4	hexane	–	13	butan-1-ol	53
5	toluene	–	14	pentan-1-ol	44
6	CH_2Cl_2	–	15	propan-2-ol	–
7	CCl_4	–	16	cyclohexanol	–
8	DMF	–	17	pentan-3-ol	–
9	DMSO	–	18	*tert*-butyl alcohol	–

[a]Reaction conditions: phenyltriethoxysilane (0.6 mmol), 4-methylbenzenediazonium tetrafluoroborate salt (0.5 mmol), $Pd(OAc)_2$ (5 mol %), solvent (2 mL), 25 °C, 6 h. [b]Isolated yields.

Similarly, no cross-coupling products were obtained in secondary or tertiary alcohols (Table 2, entries 15–18). However, decent cross-coupling yields were obtained when carried out in the primary alcoholic solvents (Table 2, entries 10–14). Interestingly, the cross-coupling yield decreases with increase of the alkyl moiety size of the primary alcohol solvent.

Various arylsiloxanes were also tested for the cross-coupling with 4-methylbenzenediazonium tetrafluoroborate salt, and the results are summarized in Table 3. Excellent yields were obtained for phenyltriethoxysilane, phenyltrimethoxysilane, and dimethoxydiphenylsilane (Table 3, entries 1–3). The methyl, fluoro, and trifluoromethyl groups seem to have negligible effects on the cross-coupling (Table 3, entries 4–6). Also, the heterocyclic derivative (benzofuran-2-yltrimethoxysilane) could be employed as the electrophile to give 2-(*p*-tolyl)benzofuran in a yield of 80% (Table 3, entry 7).

Table 4 summarizes the cross-coupling reactions for a series of arenediazonium tetrafluoroborate salts with dimethoxydiphenylsilane in moderate to good yields. The catalytic system not only tolerates various functional groups such as NO_2, Cl, Br, and OMe, but the substituents have similar effects on the cross-coupling yields regardless of their polarity (Table 4, entries 1–6). In addition, the steric effects of arenediazonium salts seem to be negligible on the coupling yields (Table 4, entries 7–10). Most interestingly, the cross-coupling of 4-bromobenzenediazonium tetrafluoroborate salt with diphenyldimethoxysilane gave exclusively 4-bromobiphenyl in 89% yield (Table 4, entry 4). The high chemoselectivity is in contrast to the traditional Hiyama cross-coupling.[7]

Primary alcohols are essential for this catalytic transformation, suggesting that they were involved with the reduction of the oxidative Pd(II) into the reductive Pd(0) species.[1g] This conclusion is consistent with no cross-coupling product in non- or weakly reductive alcohols such as *t*-BuOH and *i*-PrOH. In order to study the effects of alcohol further, we chose THF which is a completely inert solvent for the cross-coupling of the model reaction. Addition of the reductive PVA 8000 [poly(vinyl alcohol)] (0.05 mmol) resulted in 24% of the cross-coupling product (4-methylbiphenyl) after reaction for 0.5 h. Interestingly, the cross-coupling reaction did not stop even when the PVA was removed from the reaction system by filtration since the final cross-coupling yield was reached to 65% after reaction for another 5.5 h.

Mechanism Investigation. The catalytic cycle of the Hiyama reaction is generally believed to proceed via three steps (Scheme 1): (1) oxidative insertion of the aryl complex to the Pd(0) complex to form the aryl-Pd(II) complex; (2) transmetalation between the aryl-Pd(II) complex and the arylsilane to generate the (aryl)(aryl)palladium(II) species; (3) reductive elimination of the (aryl)(aryl)palladium(II) species to produce the biaryl product with the regeneration of Pd(0) complex. Hiyama et al. have found that the acceleration of the transmetalation was caused by fluoride anion for the Pd-catalyzed cross-coupling reaction between vinyl iodide and vinylsilane.[15] The Hammett correlation slope was found to be positive for the Pd-catalyzed cross-coupling reaction of allyl carbonate with arylsiloxane, suggesting that the rate-determining step should be involved with a negatively charged transition state, which could be either the transmetalation or reductive elimination.[16] Although fluoride anion (e.g., TBAF) was required to facilitate these reactions, there are no additional bases (e.g., fluoride anion) and phosphine ligands in our catalytic system. Thus, we propose that the tetrafluoroborate anion may react as the nucleophilic reagent to attack the Si atom. In order to test this hypothesis, we have carried out a systematic study of this reaction system using the density functional theory (DFT) calculation.[17]

Oxidative Addition. The active Pd(0) species from the reduction of the divalent Pd(II) species by alcoholic solvent have different configurations as shown in Scheme 2. Our calculations indicate that the most stable Pd(0) species is **1a** in which the Pd(0) coordinates with an acetate anion and the

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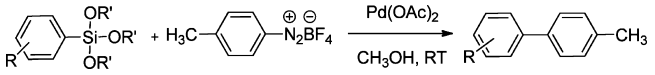
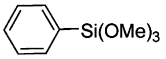
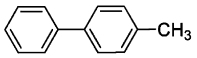
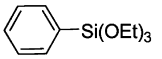
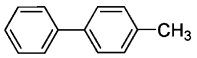
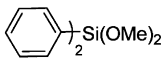
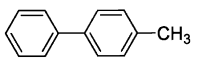
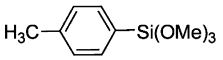
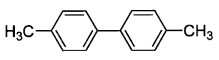
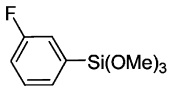
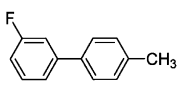
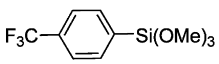
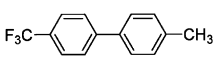
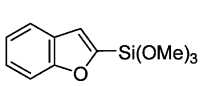
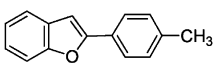
Table 3. Cross-Coupling Reactions of Arenediazonium Tetrafluoroborate Salt with Various Organosilanes[a]



Entry	Organosilanes	Products	Yield (%) [b]
1			80
2			81
3			86[c]
4			87
5			83
6			78
7			80

[a]Reaction conditions: organosilane (0.6 mmol), 4-methylbenzenediazonium tetrafluoroborate salt (0.5 mmol), $Pd(OAc)_2$ (5 mol %), CH_3OH (2 mL), 25 °C, 6 h. [b]Isolated yields. [c]The amount of dimethoxydiphenylsilane was 0.3 mmol.

N═N double bond of the benzenediazonium cation. The oxidative addition step is feasible since the activation energy is only 10.7 kcal/mol for the oxidative addition from the **1c** configuration. The optimized structures of **1a**, **1c**, and the oxidative addition transition state **TS1-2** are shown in Figure 1. The oxidative addition leads to the formation of the phenyl-Pd(II) complex, which will release 20.5 kcal/mol. Similarly, the oxidative addition may also lead to other benzenediazonium-Pd(0) complexes (e.g., benzenediazonium-Pd(0) tetrafluoroborate) to form the corresponding phenyl-Pd(II) complexes.

Transmetalation. For the Hiyama reaction, the much more reactive pentacoordinated arylsilicate anion can be in situ formed from the tetracoordinated arylsilicate anion through the nucleophilic attack of fluoride ion at the arylsiloxane.[18] Thus, we speculated that the BF_4 anion may play a similar role to form the pentacoordinated silicate to facilitate the cross-coupling reaction. First, we tried to optimize the geometry of the pentacoordinated silicate anion from the reaction of phenyltrimethoxysilane and BF_4 anion, but we failed to optimize the geometric structures regardless of the initial distance of the Si–F bond, suggesting that the pentacoordinated silicate anion may not be stable for the reaction of BF_4 anion with phenyltrimethoxysilane. These results led us to search for other possible mechanisms for the transmetalation between the phenyl-Pd(II) complex and phenyltrimethoxysilane. The possible transition states with their relative energies are summarized in Scheme 3, and their optimized structures are illustrated in Figure S1 of the Supporting Information.

Our calculations clearly show that the most favored route is the attack of the Si atom by one of the oxygen atoms of the acetate anion, followed by the phenyl transfer from the Si to the Pd via the six-membered transition state **TS2-3b** and the related activation energy barrier is 21.4 kcal/mol. But this will not be the primary pathway due to the limited source of the acetate anion only from the precatalyst $Pd(OAc)_2$. The calculations also indicate that the other favored route is the attack of tetrafluoroborate anion on the Si atom from the back side of phenyltrimethoxysilane. The transition state is shown in **TS2-3d** with an activation energy of 17.4 kcal/mol (relative to phenyl-Pd(II) tetrafluoroborate and phenyltrimethoxysilane). The relatively low energy barrier could be attributed to the stabilization by the coordination of Pd with one of the methoxyl group of the phenyltrimethoxysilane.

Reductive Elimination. The resulting (phenyl)(phenyl)-Pd(II) species undergoes reductive elimination to give the cross-coupling product. The reductive elimination step is very fast since the activation energy is less than 6 kcal/mol. The optimized structures of relevant transition states are summarized in Figure S2 of the Supporting Information.

Overall Mechanism. The calculated reactive intermediates and free-energy contour diagram for the cross-coupling reaction are summarized in Figure 2. The Pd(II) precatalyst is first reduced into the active Pd(0) species which initiates the catalytic cycle by reaction with arenediazonium salt to form the aryl-Pd(II) intermediate and nitrogen gas. The resulting aryl-Pd(II) intermediate will couple with phenyltrimethoxysilane to afford the (aryl)(aryl)-Pd(II) species with the release of SiR_3OAc or $FSiR_3$ and BF_3. Reductive elimination of the biaryl product will concomitantly regenerate the active Pd(0) species to complete the catalytic cycle. Although there are two possible pathways for the cross-coupling reaction, the reaction will proceed via pathway 1 instead of pathway 2 provided that acetate anion is present. Thus, we believe that the cross-coupling reaction will predominantly proceed via pathway 1 in the presence of acetate anion and the transmetalation step is

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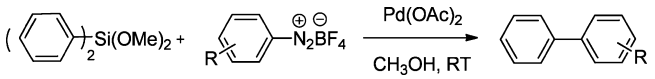
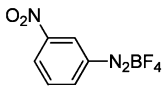
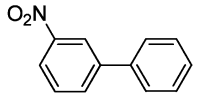
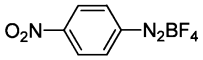
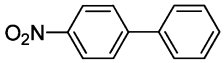
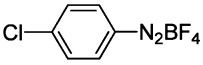
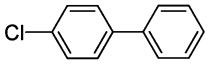
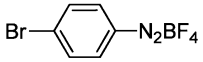
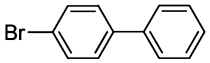
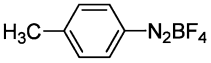
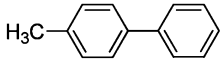
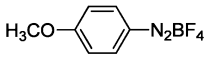
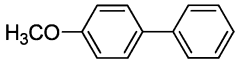
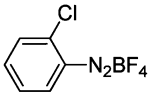
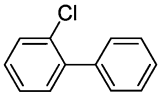
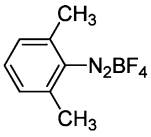
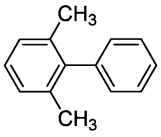
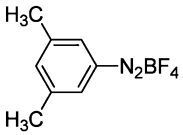
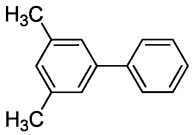
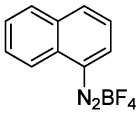
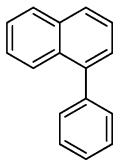
Table 4. Cross-Coupling Reactions of Various Arenediazonium Tetrafluoroborate Salts with Dimethoxydiphenylsilane[a]



Entry	Arenediazonium salts	Products	Yield (%)[b]
1			73
2			72
3			67
4			89
5			86
6			65
7			78
8			75
9			85
10			77

[a]Reaction conditions: diphenyldimethoxysilane (0.3 mmol), 4-methylbenzenediazonium tetrafluoroborate salt (0.5 mmol), $Pd(OAc)_2$ (5 mol %), solvent (2 mL), 25 °C, 6 h. [b]Isolated yields.

the rate-limiting step regardless of the presence of the acetate anion.

CONCLUSIONS

In summary, we have demonstrated that the palladium-catalyzed Hiyama cross-coupling reactions of arenediazonium salts with organosilanes could afford the corresponding biaryls in good yields under mild reaction conditions. The transformation can tolerate either electron-donating or electron-withdrawing functional groups. As part of our continuing exploration for new chemistry of the arenediazonium salts, this reaction has great prospects of applications in organic syntheses. Theoretical analysis shows that both acetate and tetrafluoroborate anions may be involved in the attack on the Si atom for the rate-limiting transmetalation step of the catalytic cycle.

EXPERIMENTAL SECTION

General Remarks. All solvents are analytical grade and used without further purification. ^1H NMR spectra were recorded on a 400 MHz spectrometer using TMS as an internal standard. The multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), multiplet (m), and broad resonance (br). Mass

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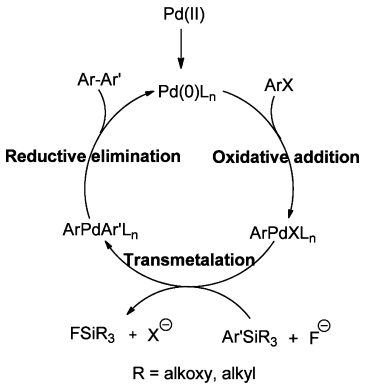
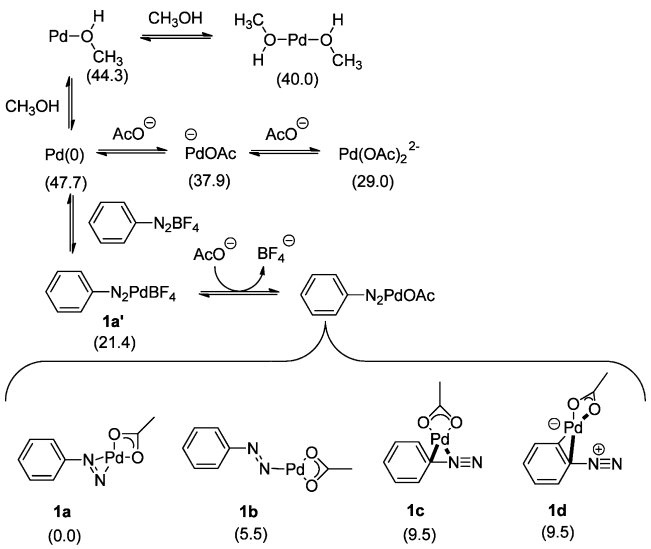
spectra were obtained on an HRMS-EI instrument. Arenediazonium salts were synthesized according to the literature procedures if they were not commercially available.

Scheme 1. General Catalytic Cycle of Hiyama Reaction



Scheme 2. Possible Structures for the Active Pd(0) Species



Preparation of Arenediazonium Salts. To a 500 mL flask containing 63 mL of HCl and 63 mL of water was added 0.25 mol of aniline. Aniline hydrochloride crystals were formed at 0−5 °C, and then 18 g of sodium nitrite in 40 mL water was added dropwise, followed by addition of 40 g of sodium tetrafluoroborate in 80 mL of water. The reaction mixture was allowed to stir for another 10 min at temperature below 5 °C. The arenediazonium salt solids were filtered out and then washed with 10 mL of 5% sodium tetrafluoroborate three times, followed by 15 mL of methanol two times.

General Procedure. A solution of silyl ether (0.6 mmol) in anhydrous methanol (2 mL) was slowly added to an oven-dried Schlenk tube containing arenediazonium salts (0.5 mmol) and $Pd(OAc)_2$ (5 mol %). The resulting mixture was allowed to stir at room temperature for 6 h, and the solid catalyst was then removed by filtration. The reaction mixture was quenched with 10 mL of water and then extracted three times with ethyl acetate (3 × 20 mL). The combined organic layer was washed with water and saturated brine and then dried over anhydrous Na_2SO_4. Solvent was removed under a reduced pressure, and the cross-coupling products were purified by silica gel chromatography with petroleum ether and ethyl acetate.

4-Methyl-1,1′-biphenyl (T3-1, CAS no. 644-08-6): ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.55 (t, J = 6.8 Hz, 2 H), 7.38−7.48 (m, 4 H), 7.32 (t, J = 7.2 Hz, 1 H), 7.21 (d, J = 7.6 Hz, 2 H), 2.33 (s, 3 H); HRMS (EI) calcd for $C_{13}H_{12}$ (M^+) 168.0939, found 168.0936.

4,4′-Dimethyl-1,1′-biphenyl (T3-4, CAS no. 613-33-2): ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.47 (d, J = 8.0 Hz, 4 H), 7.45 (d, J = 7.6 Hz, 4 H), 2.37 (s, 6 H); HRMS (EI) calcd for $C_{14}H_{14}$ (M^+) 182.1096, found 182.1099.

3-Fluoro-4′-methyl-1,1′-biphenyl (T3-5, CAS no. 72093-42-6): ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.44 (t, J = 8.0 Hz, 2 H), 7.28−7.35 (m, 2 H), 7.19−7.23 (m, 3 H), 7.02 (t, J = 8.0 Hz, 1 H), 2.35 (s, 3 H); HRMS (EI) calcd for $C_{13}H_{11}F$ (M^+) 186.0841, found 186.0841.

4-Methyl-4′-(trifluoromethyl)-1,1′-biphenyl (T3-6, CAS no. 97067-18-0): ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.65−7.72 (m, 4 H), 7.46 (d, J = 7.2 Hz, 2 H), 7.21 (d, J = 7.6 Hz, 2 H), 2.37 (s, 3 H); HRMS (EI) calcd for $C_{14}H_{11}F_3$ (M^+) 236.0813, found 236.0815.

2-(p-Tolyl)benzofuran (T3-7, CAS no. 25664-48-6): ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.73 (d, J = 8.4 Hz, 2 H), 7.48−7.54 (m, 2 H), 7.17−7.26 (m, 4 H), 6.92 (s, 1 H), 2.36 (s, 3 H); HRMS (EI) calcd for $C_{15}H_{12}O$ (M^+) 208.0888, found 208.0889.

3-Nitro-1,1′-biphenyl (T4-1, CAS no. 2113-58-8): ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.45 (s, 1 H), 8.19 (d, J = 8.4 Hz, 1 H), 7.91 (t, J = 8.0 Hz, 1 H), 7.58−7.63 (m, 3 H), 7.50 (t, J = 7.2 Hz, 2 H), 7.43 (t, J = 7.6 Hz, 1 H); HRMS (EI) calcd for $C_{12}H_9NO_2$ (M^+) 199.0633, found 199.0631.

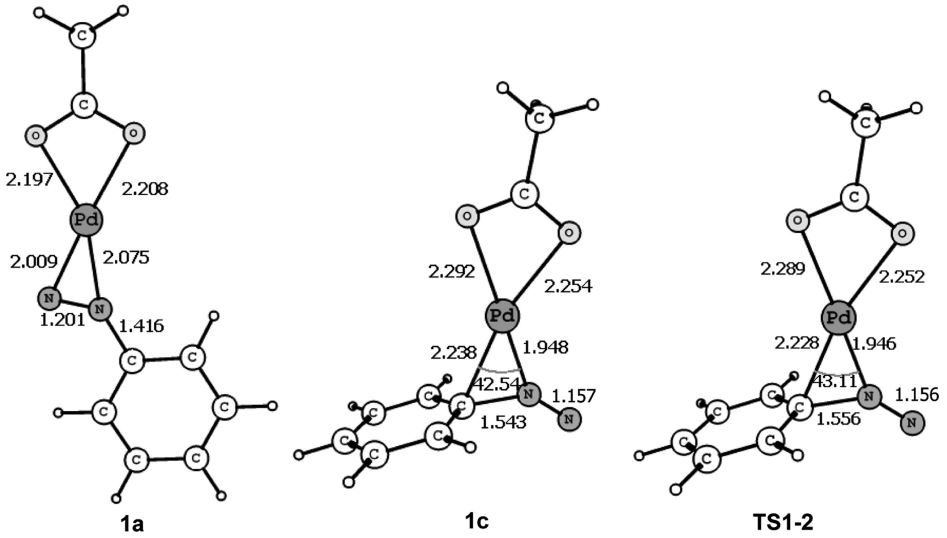


Figure 1. Optimized structures for the Pd(0) complexes **1a** and **1c** and the oxidative addition transition state **TS1-2**.

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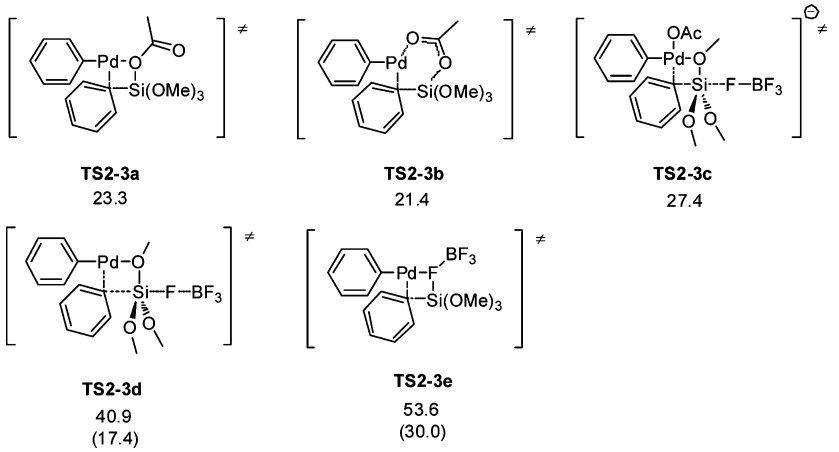
Scheme 3. Possible Transition States for Transmetalation and Their Energies Relative to Phenyl-Pd(II) acetate and Phenyltrimethoxysilane[a]



[a]The values in parentheses are relative to phenyl-Pd(II) tetrafluoroborate and phenyltrimethoxysilane.

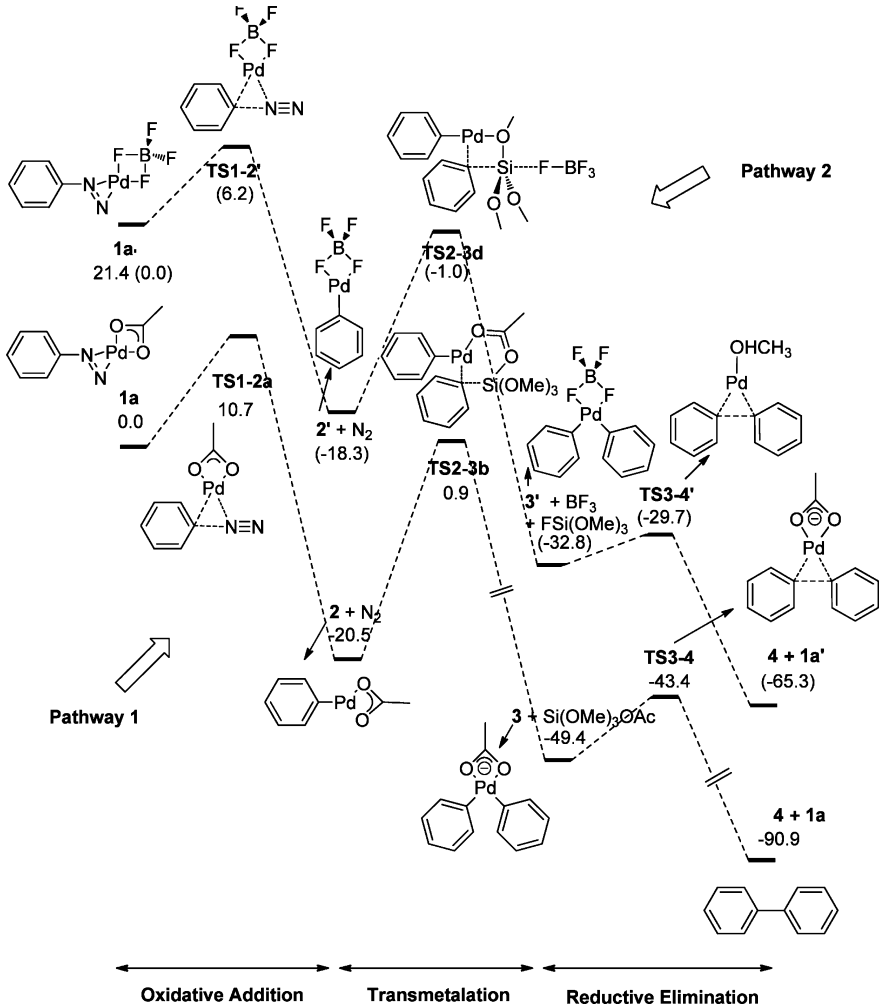


Figure 2. Calculated free energy contour diagram for the Pd-catalyzed cross-coupling reaction of phenyldiazonium tetrafluoroborate salt with phenyltrimethoxysilane. Energies are in kcal/mol. The values in parentheses are relative to phenyldiazonium-Pd tetrafluoroborate **1a**.

4-Nitro-1,1′-biphenyl (T4-2, CAS no. 92-93-3): ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.28 (d, J = 8.4 Hz, 2 H), 7.72 (d, J = 9.2 Hz, 2 H), 7.62 (d, J = 6.8 Hz, 2 H), 7.42−7.51 (m, 3 H); HRMS (EI) calcd for $C_{12}H_9NO_2$ (M^+) 199.0633, found 199.0634.

4-Chloro-1,1′-biphenyl (T4-3, CAS no. 644-08-6): ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.56 (t, J = 6.8 Hz, 2 H), 7.40−7.48 (m, 4 H), 7.32 (t, J = 7.2 Hz, 1 H), 7.22 (d, J = 7.6 Hz, 2 H); HRMS (EI) calcd for $C_{12}H_9Cl$ (M^+) 188.0393, found 188.0396.

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4-Bromo-1,1′-biphenyl (T4-4, CAS no. 92-66-0): ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.58 (d, J = 7.2 Hz, 1 H), 7.51−7.54 (m, 3 H), 7.39−7.43 (m, 3 H), 7.30−7.37 (m, 2 H); HRMS (EI) Calcd for $C_{12}H_9Br$ (M^+) 231.9888, Found 231.9887.

4-Methoxy-1,1′-biphenyl (T4-6, CAS no. 613-37-6): ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.54 (d, J = 8.4 Hz, 4 H), 7.41 (t, J = 7.6 Hz, 2 H), 7.30 (t, J = 7.2 Hz, 1 H), 6.98 (d, J = 8.4 Hz, 2 H), 3.85 (s, 3 H); HRMS (EI) calcd for $C_{13}H_{12}O$ (M^+) 184.0888, found 184.0884.

2-Chloro-1,1′-biphenyl (T4-7, CAS no. 2051-60-7): ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.59 (d, J = 8.4 Hz, 2 H), 7.40−7.49 (m, 4 H), 7.25−7.36 (m, 3 H); HRMS (EI) calcd for $C_{12}H_9Cl$ (M^+) 188.0393, found 188.0391.

2,6-Dimethyl-1,1′-biphenyl (T4-8, CAS no. 3976-34-9): ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.60 (d, J = 7.2 Hz, 3 H), 7.44 (t, J = 7.6 Hz, 3 H), 7.34 (t, J = 7.2 Hz, 1 H), 6.92 (t, J = 7.2 Hz, 1 H), 2.29 (s, 6 H); HRMS (EI) Calcd for $C_{14}H_{14}$ (M^+) 182.1096, Found 182.1097.

3,5-Dimethyl-1,1′-biphenyl (T4-9, CAS no. 17057-88-4): ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.56−7.60 (m, 3 H), 7.39−7.45 (m, 3 H), 7.34 (t, J = 7.2 Hz, 1 H), 7.20 (t, J = 8.0 Hz, 1 H), 2.38 (s, 3 H), 2.29 (s, 3 H); HRMS (EI) calcd for $C_{14}H_{14}$ (M^+) 182.1096, found 182.1098.

1-Phenylnaphthalene (T4-10, CAS no. 605-02-7): ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.90 (t, J = 8.0 Hz, 1 H), 7.59 (d, J = 8.4 Hz, 2 H), 7.48−7.53 (m, 3 H), 7.41−7.47 (m, 5 H), 7.33 (t, J = 7.2 Hz, 1 H); HRMS (EI) calcd for $C_{16}H_{12}$ (M^+) 204.0939, found 204.0937.

COMPUTATIONAL METHODS

All calculations were carried out with the Gaussian 09 programs[19] in the Supercomputing Center of the University of Science and Technology of China. The geometrical optimizations in methanol were performed using Becke's three-parameter exchange functional and the nonlocal correlation functional of Lee, Yang, and Parr (B3LYP)[20] with the 6-31G(d) basis set for all atoms except Pd, which was described by the LANL2DZ basis set, in collaboration with the polarized continuum model (PCM)[21] with Bondi radii. The optimized structures of the reactants, intermediates, and products were confirmed to be real minima on the potential energy surface by the frequency calculations. Transition states were identified as having one imaginary frequency in the Hessian matrix. Single-point energy calculations were performed on the stationary points by using the M06 method with a larger basis set, i.e., LANL2DZ with an added f-polarization shell for Pd and 6-311++G(2df,2p) for the other elements, in collaboration with the same solvation model as optimization. All solution-phase free energies reported in the paper correspond to the reference state of 1 mol/L, 298.15 K.

ASSOCIATED CONTENT

Supporting Information

^{1}H NMR spectra for the cross-coupling products, optimized structures of the transitional states, and computational details including energy properties and Cartesian coordinates of reactants, intermediates, and their transition states. This material is available free of charge via the Internet at http://pubs.acs.org.

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REFERENCES

(1) For selected reviews, see: (a) Farina, V. *Adv. Synth. Catal.* **2004**, *346*, 1553. (b) Blaser, H.-U.; Indolese, A.; Naud, F.; Nettekoven, U.; Schnyder, A. *Adv. Synth. Catal.* **2004**, *346*, 1583. (c) Zapf, A.; Beller, M. *Chem. Commun.* **2005**, 431. (d) Nicolaou, K. C.; Bulger, P. G.; Sarlah, D. *Angew. Chem., Int. Ed.* **2005**, *44*, 4442. (e) Zeni, G.; Larock, R. C. *Chem. Rev.* **2006**, *106*, 4644. (f) Yin, L.; Liebscher, J. *Chem. Rev.* **2007**, *107*, 133. (g) Zeng, M.; Du, Y.; Shao, L.; Qi, C.; Zhang, X. M. *J. Org. Chem.* **2010**, *75*, 2556.

(2) (a) *Transition Metals for Organic Synthesis: Building Blocks and Fine Chemicals*, 2nd ed.; Beller, M., Bolm, C., Eds.; Wiley-VCH: Weinheim, 2004. (b) *Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E., de Meijere, A., Eds.; Wiley: New York, 2002. (c) Hassan, J.; Sévignon, M.; Gozzi, C.; Schulz, E.; Lemaire, M. *Chem. Rev.* **2002**, *102*, 1359. (d) Cepanec, I. *Synthesis of Biaryls*; Elsevier: Amsterdam, 2004.

(3) (a) Martin, R.; Buchwald, S. L. *J. Am. Chem. Soc.* **2007**, *129*, 3844. (b) Huang, J.; Nolan, S. P. *J. Am. Chem. Soc.* **1999**, *121*, 9889. (c) Tamao, K.; Sumitani, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 4374. (d) Phan, N. T. S.; Brown, D. H.; Styring, P. *Green Chem.* **2004**, *6*, 526.

(4) (a) Kienle, M.; Knochel, P. *Org. Lett.* **2010**, *12*, 2702. (b) Liu, J.; Deng, Y.; Wang, H.; Zhang, H.; Yu, G.; Wu, B.; Zhang, H.; Li, Q.; Marder, T. B.; Yang, Z.; Lei, A. W. *Org. Lett.* **2008**, *10*, 2661. (c) Milne, J. E.; Buchwald, S. L. *J. Am. Chem. Soc.* **2004**, *126*, 13028. (d) Luzung, M. R.; Patel, J. S.; Yin, J. *J. Org. Chem.* **2010**, *75*, 8330. (e) Negishi, E. *Acc. Chem. Res.* **1982**, *15*, 340. (f) Negishi, E.; Anastasia, L. *Chem. Rev.* **2003**, *103*, 1979.

(5) (a) Milstein, D.; Stille, J. K. *J. Am. Chem. Soc.* **1978**, *100*, 3636. (b) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508. (c) Littke, A. F.; Fu, G. C. *Angew. Chem., Int. Ed.* **1999**, *38*, 2411. (d) Garcia-Martinez, J. C.; Lezutekong, R.; Crooks, R. M. *J. Am. Chem. Soc.* **2005**, *127*, 5097. (e) Su, W. P.; Urgaonkar, S.; McLaughlin, P. A.; Verkade, J. G. *J. Am. Chem. Soc.* **2004**, *126*, 16433. (f) Li, J. H.; Liang, Y.; Wang, D. P.; Liu, W. J.; Xie, Y. X.; Yin, D. L. *J. Org. Chem.* **2005**, *70*, 2832. (g) Zhou, W. J.; Wang, K. H.; Wang, J. X. *J. Org. Chem.* **2009**, *74*, 5599.

(6) (a) Miyaura, N.; A. Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457. (b) Suzuki, A. *J. Organomet. Chem.* **1999**, *576*, 147. (c) Wolfe, J. P.; Singer, R. A.; Yang, B. H.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 9550. (d) Littke, A. F.; Dai, C.; Fu, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 4020. (e) Navarro, O.; Oonishi, Y.; Kelly, R. A.; Stevens, E. E.; Briel, O.; Nolan, S. P. *J. Organomet. Chem.* **2004**, *689*, 3722.

(7) (a) Hiyama, T. In *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F., Stang, P. J., Eds.; Wiley-VCH: Weinheim, 1998; Chapter 10. (b) Hiyama, T. *J. Organomet. Chem.* **2002**, *653*, 58. (c) Denmark, S. E.; Sweis, R. F. In *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed.; de Meijere, A., Diederich, F., Eds.; Wiley-VCH: Weinheim, 2004; Chapter 4. (d) Handy, C. J.; Manoso, A. S.; McElroy, W. T.; Seganish, W. M.; DeShong, P. *Tetrahedron* **2005**, *61*, 12201. (e) Denmark, S. E.; Sweis, R. F. *Acc. Chem. Res.* **2002**, *35*, 835. (f) Denmark, S. E.; Ober, M. H. *Aldrichim. Acta* **2003**, *36*, 75.

(8) (a) Hatanaka, Y.; Hiyama, T. *J. Org. Chem.* **1988**, *53*, 918. (b) Pierrat, P.; Gros, P.; Fort, Y. *Org. Lett.* **2005**, *7*, 697. (c) Jayanth, E. T.; Jeganmohan, M.; Ching, C. H. *Org. Lett.* **2005**, *7*, 2921. (d) Hatanaka, Y.; Fukushima, S.; Hiyama, T. *Chem. Lett.* **1989**, 1711. (e) Gouda, K.; Hagiwara, E.; Hatanaka, Y.; Hiyama, T. *J. Org. Chem.* **1996**, *61*, 7232. (f) Mowery, M. E.; DeShong, P. *J. Org. Chem.* **1999**, *64*, 3266. (g) Denmark, S. E.; Sweis, R. F. *Org. Lett.* **2002**, *4*, 3771. (h) Hirabayashi, K.; Mori, A.; Kawashima, J.; Suguro, M.; Nishihara, Y.; Hiyama, T. *J. Org. Chem.* **2000**, *65*, 5342. (i) Denmark, S. E.; Baird, J. D. *Org. Lett.* **2004**, *6*, 3649. (j) Denmark, S. E.; Ober, M. H. *Org. Lett.* **2003**, *5*, 1357. (k) Riggleman, S.; DeShong, P. *J. Org. Chem.* **2003**, *68*, 8106. (l) Sahoo, A. K.; Oda, T.; Nakao, Y.; Hiyama, T. *Adv. Synth. Catal.* **2004**, *346*, 1715. (m) Nokami, T.; Tomida, Y.; Kamei, T.; Itami, K.; Yoshida, J.-i. *Org. Lett.* **2006**, *8*, 729. (n) Seganish, W. M.; DeShong, P. *J. Org. Chem.* **2004**, *69*, 1137. (o) Astruc, D. *Inorg. Chem.* **2007**, *46*, 1884. (p) Astruc, D.; Lu, F.; Aranzaes, J. R. *Angew. Chem., Int. Ed.* **2005**, *44*, 7852.

(9) (a) Gordillo, A.; de Jesus, E.; Lopez-Mardomingo, C. *Org. Lett.* **2006**, *8*, 3517. (b) Shi, S.; Zhang, Y. *J. Org. Chem.* **2007**, *72*, 5927. (c) Alacid, E.; Najera, C. *Adv. Synth. Catal.* **2006**, *348*, 2085. (d) Ju, J.; Nam, H.; Jung, H. M.; Lee, S. *Tetrahedron Lett.* **2006**, *47*, 8673. (e) Pierrat, P.; Gros, P.; Fort, Y. *Org. Lett.* **2005**, *7*, 697. (f) Lerebours, R.; Wolf, C. *Synthesis* **2005**, 2287. (g) Li, J. H.; Deng, C. L.; Liu, W. J.; Xie, Y. X. *Synthesis* **2005**, 3039. (h) Seganish, W. M.; DeShong, P. *Org. Lett.* **2004**, *6*, 4379. (i) Manoso, A. S.; Ahn, C.; Soheili, A.; Handy, C. J.; Correia, R.; Seganish, W. M.; DeShong, P. *J. Org. Chem.* **2004**, *69*, 8305. (j) Wolf, C.; Lerebours, R. *Org. Lett.* **2004**, *6*, 1147. (k) Lee, J. Y.; Fu, G. C. *J. Am. Chem. Soc.* **2003**, *125*, 5616. (l) Murata, M.; Shimazaki, R.; Watanabe, S.; Masuda, Y. *Synthesis* **2001**, 2231. (m) Lee, H. M.; Nolan, S. P. *Org. Lett.* **2000**, *2*, 2053. (n) Srimani, D.; Sawoo, S.; Sarkar, A. *Org. Lett.* **2007**, *9*, 3639. (o) Mino, T.; Shirae, Y.; Saito, T.; Sakamoto, M.; Fujita, T. *J. Org. Chem.* **2006**, *71*, 9499–9502. (p) Pan, C.; Liu, M.; Zhao, L.; Wu, H.; Ding, J.; Cheng, J. *Catal. Commun.* **2008**, *9*, 1685. (q) Ranu, B. C.; Dey, R.; Chattopadhyay, K. *Tetrahedron Lett.* **2008**, *49*, 3430. (r) Zhang, X. M.; Xia, Q. Q.; Chen, W. Z. *Dalton Trans.* **2009**, 7045.

(10) (a) Roglans, A.; Pla-Quintana, A.; Moreno-Mañas., M. *Chem. Rev.* **2006**, *106*, 4622. (b) Fabrizi, G.; Goggiamani, A.; Sferrazza, A.; Cacchi, S. *Angew. Chem., Int. Ed.* **2010**, *49*, 4067. (c) Cacchi, S.; Fabrizi, G.; Goggiamani, A.; Persiani, D. *Org. Lett.* **2008**, *10*, 1597. (d) Robinson, M. K.; Kochurina, V. S.; Hanna, J. M. Jr. *Tetrahedron Lett.* **2007**, *48*, 7687. (e) Panda, B.; Sarkar, T. K. *Chem. Commun.* **2010**, *46*, 3131. (f) Cacchi, S.; Fabrizi, G.; Goggiamani, A.; Perboni, A.; Sferrazza, A.; Stabile, P. *Org. Lett.* **2010**, *12*, 3279.

(11) (a) Sabino, A. A.; Machado, A. H. L.; Correia, C. R. D.; Eberlin, M. N. *Angew. Chem., Int. Ed.* **2004**, *43*, 2514. (b) Sabino, A. A.; Machado, A. H. L.; Correia, C. R. D.; Eberlin, M. N. *Angew. Chem., Int. Ed.* **2004**, *43*, 4389. (c) Masllorens, J.; Bouquillon, S.; Roglans, A.; Henin, F.; Muzart, J. *J. Organomet. Chem.* **2005**, *690*, 3822. (d) Garcia, A. L. L.; Carpes, M. J. S.; Montes de Oca, A. C. B.; dos Santos, M. A. G.; Santana, C. C.; Correia, C. R. D. *J. Org. Chem.* **2005**, *70*, 1050. (e) Artuso, E.; Barbero, M.; Degani, I.; Dughera, S.; Fochi, R. *Tetrahedron* **2006**, *62*, 3146. (f) Pastre, J. C.; Correia, C. R. D. *Org. Lett.* **2006**, *8*, 1657. (g) Perez, R.; Veronese, D.; Coelho, F.; Antunes, O. A. C. *Tetrahedron Lett.* **2006**, *47*, 1325. (h) Peixoto da Silva, K.; Godoi, M. N.; Correia, C. R. D. *Org. Lett.* **2007**, *9*, 2815. (i) Moro, A. V.; Cardoso, F. S. P.; Correia, C. R. D. *Tetrahedron Lett.* **2008**, *49*, 5668. (j) Felpin, F.-X.; Fouquet, E.; Zakri, C. *Adv. Synth. Catal.* **2008**, *350*, 2559. (k) Felpin, F.-X.; Ibarguren, O.; Nassar-Hardy, L.; Fouquet, E. *J. Org. Chem.* **2009**, *74*, 1349. (l) Machado, A. H. L.; de Sousa, M. A.; Patto, D. C. S.; Azevedo, L. F. S.; Bombonato, F. I.; Correia, C. R. D. *Tetrahedron Lett.* **2009**, *50*, 1222. (m) Ahmed-Omer, B.; Barrow, D. A.; Wirth, T. *Tetrahedron Lett.* **2009**, *50*, 3352. (n) Felpin, F. -X.; Coste, J.; Zakri, C.; Fouquet, E. *Chem.—Eur. J.* **2009**, *15*, 7238. (o) Moro, A. V.; Cardoso, F. S. P.; Correia, C. R. D. *Org. Lett.* **2009**, *11*, 3642. (p) Schmidt, B.; Hoelter, F. *Chem.—Eur. J.* **2009**, *15*, 11948. (q) Cacchi, S.; Fabrizi, G.; Goggiamani, A.; Sferrazza, A. *Synlett* **2009**, 973. (r) Cacchi, S.; Fabrizi, G.; Goggiamani, A.; Sferrazza, A. *Synlett.* **2009**, 1277. (s) Pastre, J. C.; Correia, C. R. D. *Adv. Synth. Catal.* **2009**, *351*, 1217. (t) Taylor, J. G.; Moro, A. V.; Correia, C. R. *Eur. J. Org. Chem.* **2011**, 1403. (u) Felpin, F.-X.; Nassar-Hardy, L.; Callonnec, F. L.; Fouquet, E. *Tetrahedron* **2011**, *67*, 2815.

(12) (a) Selvakumar, K.; Zapf, A.; Spannenberg, A.; Beller, M. *Chem.—Eur. J.* **2002**, *8*, 3901. (b) Willis, D. M.; Strongin, R. M. *Tetrahedron Lett.* **2000**, *41*, 6271. (c) Babudri, F.; Farinola, G. M.; Naso, F.; Panessa, D. *J. Org. Chem.* **2000**, *65*, 1554. (d) Andrus, M. B.; Song, C. *Org. Lett.* **2001**, *3*, 3761. (e) Frohn, H. J.; Adonin, N. Y.; Bardin, V. V.; Starichenko, V. F. *J. Fluorine Chem.* **2002**, *117*, 115. (f) Peyroux, E.; Berthiol, F.; Doucet, H.; Santelli, M. *Eur. J. Org. Chem.* **2004**, 1075. (g) Jo, J.; Chi, C.; Höger, S.; Wegner, G.; Yoon, D. Y. *Chem.—Eur. J.* **2004**, *10*, 2681. (h) Gallo, V.; Mastrorilli, P.; Nobile, C. F.; Paolillo, R.; Taccardi, N. *Eur. J. Inorg. Chem.* **2005**, 582. (i) Darses, S.; Genet, J. P. *Eur. J. Org. Chem.* **2003**, 4313. (j) Liu, C. Y.; Gavryushin, A.; Knochel, P. *Chem. Asian J.* **2007**, *2*, 1020. (k) Kuethe, J. T.; Childers, K. G. *Adv. Synth. Catal.* **2008**, *350*, 1577. (l) Felpin, F.-X.; Fouquet, E.; Zakri, C. *Adv. Synth. Catal.* **2009**, *351*, 649.

(13) (a) Kikukawa, K.; Kono, K.; Wada, F.; Matsuda, T. *Chem. Lett.* **1982**, 35. (b) Kikukawa, K.; Kono, K.; Wada, F.; Matsuda, T. *J. Org. Chem.* **1983**, *48*, 1333. (c) Kikukawa, K.; Idemoto, T.; Katayama, A.; Kono, K.; Wada, F.; Matsuda, T. *J. Chem. Soc., Perkin Trans. 1* **1987**, 1511. (d) Dughera, S. *Synthesis* **2006**, 1117. (e) Koza, D. J.; Nsiah, Y. A. *Bioorg. Med. Chem. Lett.* **2002**, *12*, 2163. (f) Andrus, M. B.; Ma, Y.; Zang, Y.; Song, C. *Tetrahedron Lett.* **2002**, *43*, 9137. (g) Siegrist, U.; Rapold, T.; Blaser, H. U. *Org. Process Res. Dev.* **2003**, *7*, 429.

(14) Spivak, D. A. US Patent 6838585, 2005.

(15) Sugiyama, A.; Ohnishi, Y. Y.; Nakaoka, M.; Nakao, Y.; Sato, H.; Sakaki, S.; Nakao, Y.; Hiyama, T. *J. Am. Chem. Soc.* **2008**, *130*, 12975.

(16) Shukla, K. H.; DeShong, P. *J. Org. Chem.* **2008**, *73*, 6283.

(17) For recent theoretical analysis on Pd-catalyzed cross-coupling reactions, see: (a) Liu, Q.; Lan, Y.; Liu, J.; Li, G.; Wu, Y. D.; Lei, A. W. *J. Am. Chem. Soc.* **2009**, *131*, 10201. (b) Lam, K. C.; Marder, T. B.; Lin, Z. Y. *Organometallics* **2010**, *29*, 1849. (c) Shang, R.; Fu, Y.; Li, J. B.; Zhang, S. L.; Guo, Q. X.; Liu, L. *J. Am. Chem. Soc.* **2009**, *131*, 5738. (d) Xue, L. Q.; Lin, Z. Y. *J. Am. Chem. Soc.* **2010**, *39*, 1692. (e) Xue, L. Q.; Lin, Z. Y. *Chem. Soc. Rev.* **2010**, *39*, 1692. (f) Shang, R.; Xu, Q.; Jiang, Y. Y.; Wang, Y.; Liu, L. *Org. Lett.* **2010**, *12*, 1000. (g) Shen, X. Q.; Jones, G. O.; Watson, D. A.; Bhayana, B.; Buchwald, S. L. *J. Am. Chem. Soc.* **2010**, *132*, 11278. (h) Shang, R.; Yang, Z. W.; Wang, Y.; Zhang, S. L.; Liu, L. *J. Am. Chem. Soc.* **2010**, *132*, 14391. (i) Zhang, S. L.; Fu, Y.; Shang, R.; Guo, Q. X.; Liu, L. *J. Am. Chem. Soc.* **2010**, *132*, 638. (j) Ball, N. D.; Gary, J. B.; Ye, Y. D.; Sanford, M. S. *J. Am. Chem. Soc.* **2011**, *133*, 7577.

(18) (a) Hatanaka, Y.; Goda, K.; Hiyama, T. *J. Organomet. Chem.* **1994**, *465*, 97. (b) Chuit, C.; Corriu, R. J. P.; Reye, C. In *Chemistry of Hyper Valent Compounds*; Akiba, K.-Y., Ed.; Wiley-VCH: New York, 1999; pp 81–146.

(19) Gaussian 09, R. A.:Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.;Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.;Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.;Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

(20) (a) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(21) Miertus, S.; Scrocco, E.; Tomasi. *J. Chem. Phys.* **1981**, *55*, 117.