Oxidative Addition of Aryl Sulfonates to Palladium(0) Complexes of Mono- and Bidentate Phosphines. Mild Addition of Aryl Tosylates and the Effects of Anions on Rate and Mechanism

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Oxidative additions of aryl halides to palladium complexes have been studied extensively in recent years, but studies on the oxidative addition of aryl sulfonates to palladium complexes are less common. Here, oxidative additions of aryl triflates to palladium(0) complexes of hindered mono- and bis(phosphines) and the rare oxidative addition of aryl tosylates to palladium(0) complexes of hindered bis(phosphines) are reported. Pd[P(*o*-tolyl)$_3$]$_2$ reacted with PhOTf in the presence of added halide salts to produce the corresponding {Pd[P(*o*-tolyl)$_3$](Ar)(μ-X)}$_2$ complexes (X = halide). The rate of oxidative addition was accelerated by the addition of coordinating anions but was not affected by the addition of weakly coordinating anions. This result suggests that the oxidative addition of aryl triflates occurs to an anionic palladium complex ligated by halide. The addition of phenyl triflate to Pd(PPF-*t*-Bu)[P(*o*-tolyl)$_3$] in the presence of added bromide produced [(PPF-*t*-Bu)Pd(Ph)(Br)]. The rate of this oxidative addition was accelerated by added bromide but was more greatly accelerated by the addition of PF_6^-, a typically noncoordinating anion. This result indicates that a medium effect, not coordination of bromide prior to oxidative addition, accounts for the acceleration of the rate of addition of aryl triflates to Pd(PPF-*t*-Bu)[P(*o*-tolyl)$_3$]. The oxidative addition of phenyl tosylate to Pd(PPF-*t*-Bu)[P(*o*-tolyl)$_3$] and to Pd(CyPF-*t*-Bu)[P(*o*-tolyl)$_3$] also occurred at room temperature to produce the corresponding phenylpalladium tosylate complexes. In the presence of added bromide, arylpalladium bromide complexes were formed. Like the addition of phenyl triflate to Pd(PPF-*t*-Bu)[P(*o*-tolyl)$_3$], the rate of oxidative addition was accelerated by addition of either strongly or weakly coordinating anions. The additions of aryl tosylates were also faster in more polar solvents. Thus, the effect of halide on the rate of addition of aryl tosylates to Pd(PPF-*t*-Bu)[P(*o*-tolyl)$_3$] is also more likely to result from a medium effect, rather than from coordination of anion to palladium prior to oxidative addition.

Introduction

The oxidative addition of aryl halides and sulfonates to palladium(0) is a fundamental organometallic transformation.[1] Many studies have been conducted on the oxidative addition of aryl halides to palladium(0) complexes,[2−11] but fewer studies have been conducted on the oxidative addition of aryl sulfonates.[9,11,12] The products from the oxidative addition of aryl triflates tend to be unstable, and few have been isolated.[12−14] This product instability has restricted studies on the oxidative addition of aryl triflates to palladium(0). Jutand and Mosleh reported the oxidative addition of aryl triflates to Pd(PPh$_3$)$_4$ in the absence of added halide ions to form σ-ArPd(PPh$_3$)$_2^+$.[12] Addition of chloride either before or after the oxidative addition resulted in the formation of σ-ArPdCl(PPh$_3$)$_2$. Jutand and Brown reported the mechanism of oxidative addition of aryl triflates to the zerovalent (DPPF)Pd(η^2-methylacrylate) in DMF.[9] Alcazar-Roman and Hartwig studied the mechanism of the oxidative addition of aryl triflates to Pd(BINAP)$_2$ in the presence of amine. They found the oxidative addition to be rate-determining, and trapping

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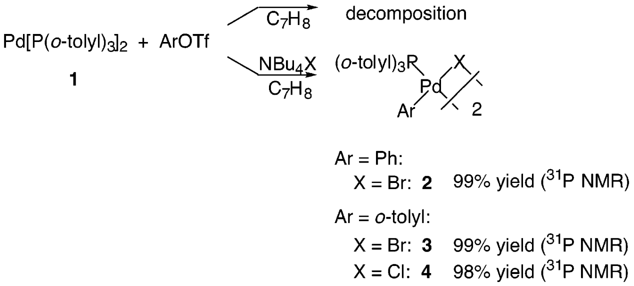
of the arylpalladium triflate complex with amine rapidly formed [Pd(BINAP)(Ph)(NH_2octyl)](OTf).[11]

Added anions have been shown to influence the mechanisms of oxidative addition of aryl halides and triflates to palladium(0).[5,15−18] This effect has been mainly attributed to coordination of the halide to palladium prior to oxidative addition. Several reports by Amatore, Jutand, and co-workers suggest that oxidative addition of aryl triflates and iodides to $Pd(PPh_3)_4$ is accelerated by the addition of chloride ions due to the formation of $Pd(PPh_3)_2Cl^-$ prior to oxidative addition.[5,12,19] Scott and Stille studied the oxidative addition of vinyl triflates to $Pd(PPh_3)_4$ in the presence of LiCl and reported a mechanism that involves initial coordination of chloride to palladium and subsequent oxidative addition to the resulting anionic palladium complex.[18] The role of added halide ions in the Stille reaction with aryl triflates was examined by Espinet and coworkers.[20] Their studies revealed that added chloride ions accelerated the rate of the overall reaction when $AsPh_3$ was used as ligand and oxidative addition was the rate-determining step. In this case, oxidative addition appeared to be accelerated by coordination of halide to the palladium(0) species. In contrast, added chloride *retarded* the rate of the overall reaction when catalyzed by PPh_3 complexes of palladium and transmetalation was the rate-determining step. Transmetalation of $ArPdClL_2$ is slower than that of $[ArPd(PPh_3)_2]^+$, which was proposed to form by oxidative addition in the absence of chloride.

The oxidative addition of aryl tosylates is particularly rare because of the low reactivity of these substrates. The reactivity of aryl halide and sulfonate electrophiles toward palladium(0) typically follows the trend ArI > ArBr ≈ ArOTf ≫ ArOTs > ArCl.[21,22] To our knowledge, there are no previous examples of oxidative addition of aryl tosylates to produce isolated arylmetal tosylate complexes. Cross couplings of aryl tosylates with nickel,[22−24] iron,[25,26] and copper[27] catalysts have required high temperatures, activated aryl tosylates, or high catalyst loadings. Previous palladium-catalyzed couplings of aryl tosylates are rare and have required activated substrates or elevated temperatures.[24,28−32] Although catalytic reactions of aryl chlorides with complexes of hindered alkylphosphines have recently been observed,[33] most complexes with this type of ligand do not add aryl tosylates that lack activating groups.[34]

Scheme 1



Here the oxidative addition of aryl triflates and aryl tosylates to palladium(0) at room temperature, followed by trapping with halide to form arylpalladium(II) halide complexes, is reported.[35] The oxidative addition of aryl tosylates to palladium(0) in the absence of added halide formed arylpalladium tosylate complexes. The mechanisms of these processes were studied in the presence of added halide ions because of the ambiguous role of halides in these reactions and the instability of the product of addition of aryl triflate in the absence of trapping agents.

Results

Oxidative Addition of ArOTf to Palladium(0) Complexes. The oxidative addition of aryl triflates to Pd[P(*o*-tolyl)$_3$]$_2$ (**1**) was examined and is summarized in Scheme 1. Reaction between Pd[P(*o*-tolyl)$_3$]$_2$ and aryl triflates in toluene without additives produced free P(*o*-tolyl)$_3$ and palladium black. In contrast, reaction between phenyl triflate and palladium(0) in the presence of N(octyl)$_4$Br at room temperature produced {Pd[P(*o*-tolyl)$_3$](Ph)(μ-Br)}$_2$ (**2**) in 99% yield, as determined by NMR spectroscopy with an internal standard (Scheme 1). Reaction of the more hindered *o*-tolyl triflate at room temperature also produced {Pd[P(*o*-tolyl)$_3$](*o*-tolyl)(μ-Br)}$_2$ (**3**) in 99% yield by NMR spectroscopy. At 70 °C the oxidative addition of *o*-tolyl triflate was faster than at room temperature, but the yield of aryl bromide complex **3** was only 83%. Reaction of *o*-tolyl triflate and Pd[P(*o*-tolyl)$_3$]$_2$ in the presence of N(octyl)$_4$Cl at room temperature produced {Pd[P(*o*-tolyl)$_3$](*o*-tolyl)(μ-Cl)}$_2$ (**4**) in 98% yield.

The reactivities of palladium(0) complexes of bulky, electron-rich phosphines toward the oxidative addition of aryl tosylates were also examined, but these reactions occurred in lower yields than the reactions with Pd[P(*o*-tolyl)$_3$]$_2$. For example, treatment of palladium(0) complexes of ligands such as PCy$_2$(*t*-Bu) and PCy(*t*-Bu)$_2$[36] with phenyl or *o*-tolyl triflate in the absence of added halide did not yield products from oxidative addition. However, oxidative addition of aryl triflate to these complexes did occur in the presence of added halide. The steric properties of the ligand and of the aryl triflate

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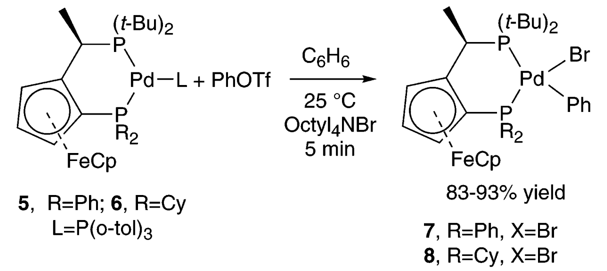
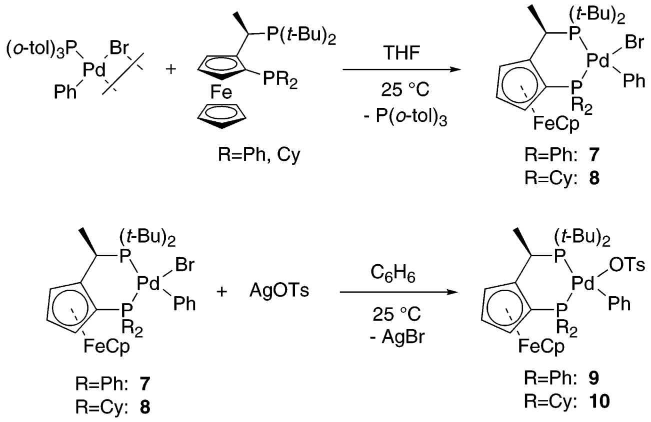
Scheme 2



Scheme 3

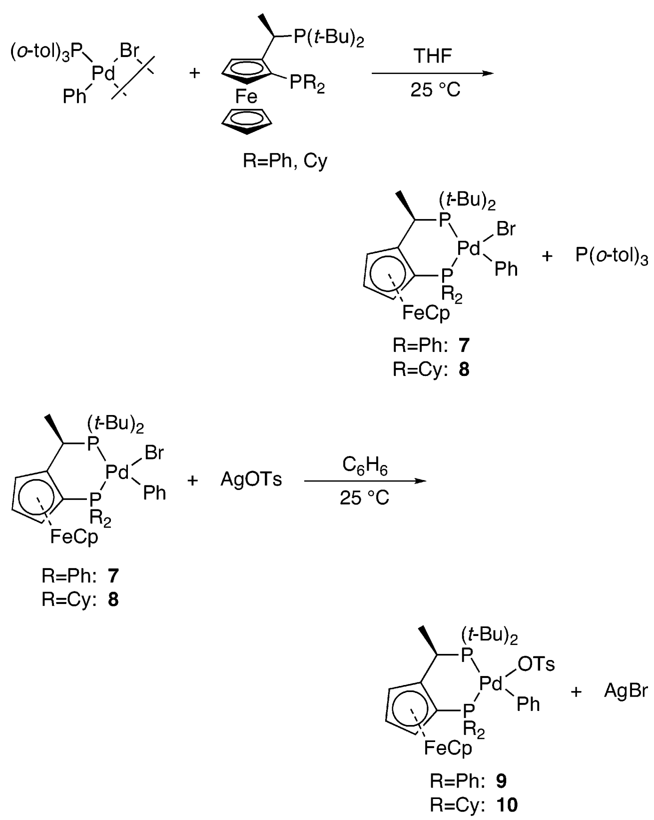


dictated the rate of reaction and the yield of oxidative addition product. Reaction between $Pd[PCy_2(t\text{-}Bu)]_2$[36] and PhOTf in the presence of NBu_4Br at 70 °C produced $Pd[PCy_2(t\text{-}Bu)]_2(Ph)(Br)$ in 98% yield, but reaction of the larger *o*-tolyl triflate occurred in lower yield due to the slower reaction rate and the presence of byproducts. Reaction between the bulkier $Pd[PCy(t\text{-}Bu)_2]_2$[36] and PhOTf was very slow at 70 °C in the presence of added bromide and occurred in low yield. Significant amounts of side products formed.

Palladium(0) complexes of sterically hindered versions of the Josiphos ligands underwent addition of phenyl triflate in the presence of added halide ions under mild conditions, as illustrated in Scheme 2.[37] Reaction between $Pd[P(o\text{-tolyl})_3]_2$ and PPF-*t*-Bu and CyPF-*t*-Bu at room temperature formed Pd(PPF-*t*-Bu)[P(*o*-tolyl)$_3$] (**5**) or Pd(CyPF-*t*-Bu)[P(*o*-tolyl)$_3$] (**6**; Scheme 2). Subsequent treatment of **5** or **6** with PhOTf in the presence of N(octyl)$_4$Br produced the corresponding phenylpalladium bromide complexes **7** and **8** in 93% and 83% yields in less than 5 min at room temperature.

Oxidative Addition of ArOTs to Palladium(0) Complexes. Reaction between $Pd[P(o\text{-tolyl})_3]_2$ and PhOTs in the presence or absence of halide did not occur. However, palladium(0) complexes generated from sterically hindered versions of the Josiphos ligands underwent oxidative addition of phenyl tosylate under mild conditions.[37] Treatment of the PPF-*t*-Bu complex **5** with PhOTs produced the phenylpalladium tosylate complex **9** in 85% yield (Scheme 3) after 16 h at room temperature. Reaction in the presence of NBu_4Br formed the phenylpalladium bromide complex **7** in 95% yield after only 9 h. Reactions of phenyl tosylate with CyPF-*t*-Bu complex **6** were even faster. Phenylpalladium tosylate **10** was formed from **6** in 92% yield in less than 5 min. The same reaction in the presence of bromide formed the bromide complex **8** in 94% yield in less than 5 min. However, reactions of the analogues of **5** containing Josiphos ligands that lack a *tert*-butyl group formed the addition product in lower yields and with slower rates. The reactions of phenyl tosylate with **5** and **6** constitute the first oxidative additions of aryl tosylates to form isolated aryl complexes.

Scheme 4



Complexes **7**−**10** were independently synthesized, as summarized in Scheme 4. Bromide complexes **7** and **8** were formed by the reaction between {Pd[P(*o*-tolyl)$_3$](Ph)(Br)}$_2$ and the appropriate RPF-*t*-Bu ligand (R = Ph, Cy) in THF at room temperature. The reactions were complete within 20 min; the rates were limited by the solubility of the palladium(II) dimer. Reaction of **7** and **8** with AgOTs in C_6H_6 produced arylpalladium tosylate complexes **9** and **10** within minutes at room temperature.

Crystals of both **7** and **8** were obtained from a concentrated toluene solution layered with pentane at −35 °C. The structure of **7** is shown in Figure 1. Selected bond distances and angles for **7** are provided in Table 1; other structural data are given in Table 4. The geometry around palladium can be described as distorted square planar. The Pd−P(2) bond is significantly longer than the Pd−P(1) bond. This difference in Pd−P distances can be attributed to the greater steric properties of the *t*-Bu groups on P(2) and to the stronger trans influence[38] of the phenyl group located trans to P(2), relative to the halide located trans to P(1). Two isomeric versions of complexes **7**−**10** could form, but only the

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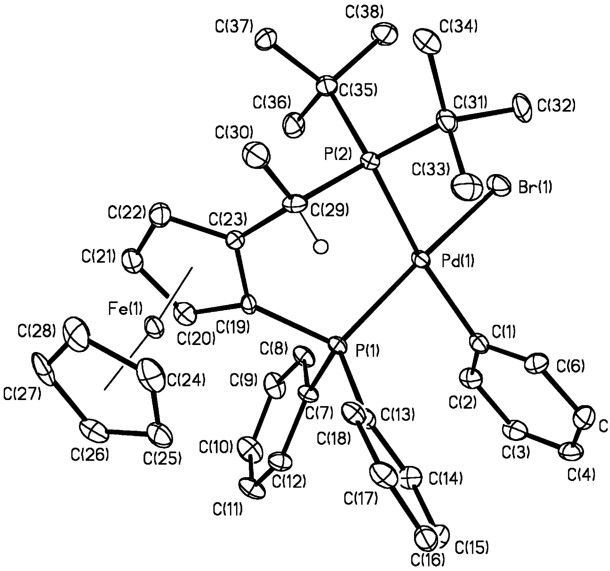


Figure 1. ORTEP diagram of [Pd(PPF-*t*-Bu)(Ph)(Br)] (**7**) with 30% ellipsoids.

Table 1. Selected Intramolecular Bond Distances and Angles Involving the Non-Hydrogen Atoms of (PPF-*t*-Bu)Pd(Ph)(Br) (7)

	Bond Distances (Å)		
Pd(1)−P(1)	2.240(1)	Pd(1)−P(2)	2.436(2)
Pd(1)−Br(1)	2.5301(6)	Pd(1)−C(1)	2.045(6)
	Bond Angles (deg)		
Br(1)−Pd(1)−P(2)	98.97(4)	P(1)−Pd(1)−C(1)	83.8(2)
Br(1)−Pd(1)−C(1)	86.1(2)	P(1)−Pd(1)−P(2)	96.73(5)

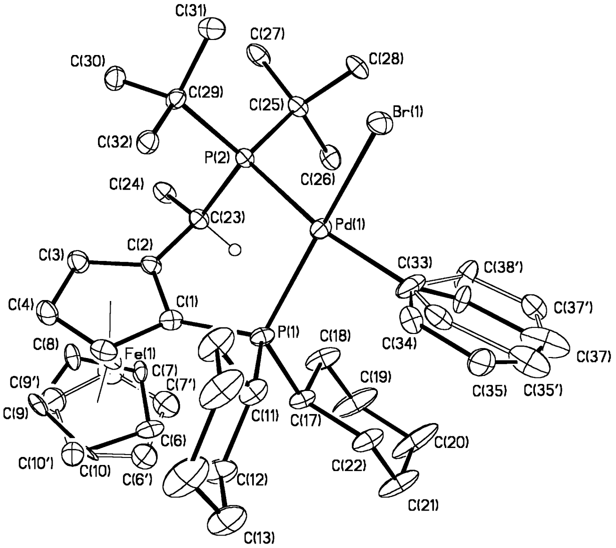


Figure 2. ORTEP diagram of [Pd(CyPF-*t*-Bu)(Ph)(Br)] (**8**) with 30% ellipsoids.

product containing the palladium-bound phenyl group cis to the smaller phosphine was observed by NMR spectroscopy or X-ray diffraction.

Table 2. Selected Intramolecular Bond Distances and Angles Involving the Non-Hydrogen Atoms of (CyPF-*t*-Bu)Pd(Ph)(Br) (8)

	Bond Distances (Å)		
Pd(1)−P(1)	2.2847(5)	Pd(1)−P(2)	2.4157(5)
Pd(1)−Br(1)	2.5031(4)	Pd(1)−C(33)	2.0291(19)
	Bond Angles (deg)		
Br(1)−Pd(1)−P(2)	97.833(16)	P(1)−Pd(1)−C(33)	88.27(5)
Br(1)−Pd(1)−C(33)	82.61(5)	P(1)−Pd(1)−P(2)	98.045(19)

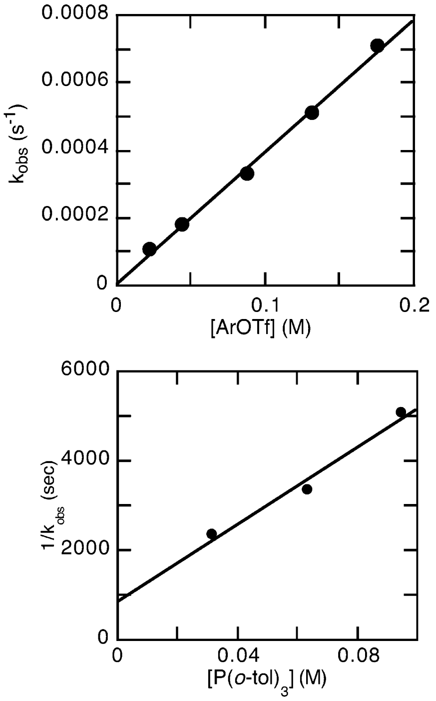
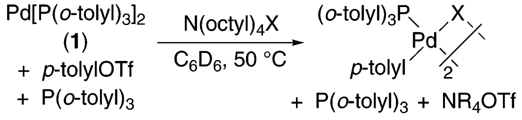


Figure 3. Plots of k_{obs} vs [ArOTf] and 1/k_{obs} vs [P(*o*-tolyl)$_3$] for the oxidative addition of ArOTf to Pd[P(*o*-tolyl)$_3$]$_2$ in benzene-d_6 in the presence of NR_4Br.

The structure of **8** determined by X-ray diffraction is shown in Figure 2. A high degree of positional disorder in both the palladium complex and the cocrystallized solvent was observed. Two alternative positions for the unsubstituted Cp ring, C(6−10), and the phenyl ring, C(33−38), were modeled and refined with anisotropic displacement parameters. Selected bond distances and angles for **8** are provided in Table 2; other structural data are given in Table 4. Again, the geometry around Pd can be described as distorted square planar. The Pd−P(1) bond in **8** is slightly longer than the same bond in complex **7**, presumably because the steric demand of the PCy_2 group in **8** is larger than that of the PPh_2 group in **7**.

Mechanism of the Oxidative Addition of Aryl Triflates to Palladium(0). Added anions have been shown to influence the mechanisms of oxidative addition of aryl halides and sulfonates to palladium(0). This effect has been typically attributed to coordination of the anion to palladium(0) prior to oxidative addition.[3,5,12,18] Thus, we measured the kinetic order of the various reaction components in eq 1 by ^1H NMR spectroscopy at 50 °C in C_6D_6 solvent in the presence of added halide. The concentration of *p*-tolyl triflate was varied from 0.022 to 0.18 M, the concentration of $N(octyl)_4Br$ was varied from 0 to 0.12 M, and the concentration of P(*o*-tolyl)$_3$ was varied from 0.032 to 0.095 M. Excellent fits to a first-order decay of Pd[P(*o*-tolyl)$_3$]$_2$ were obtained. Figure 3 shows the dependence of k_{obs} on the concentration of ArOTf and P(*o*-tolyl)$_3$. The



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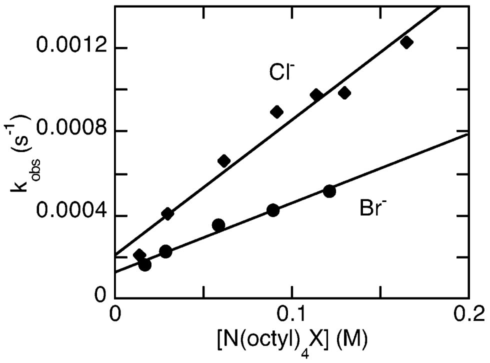


Figure 4. Plots of k_{obs} vs [N(octyl)$_4$Br] (circles) and k_{obs} vs [N(octyl)$_4$Cl] (diamonds) for the oxidative addition of ArOTf to Pd[P(*o*-tolyl)$_3$]$_2$ in benzene-d_6 solvent in the presence of added halide.

Table 3. Dependence of $t_{1/2}$ on [anion] for the Oxidative Addition of PhOTf to 5

[**5**] (M)	[N(octyl)$_4$Br] (M)	[NBu$_4$PF$_6$] (M)	$t_{1/2}$ (min)
0.023	0.024	0	23
0.023	0.093	0	11
0.023	0.026	0.075	10

linear plot of k_{obs} vs [ArOTf] in the presence of added bromide indicated a first-order dependence of the rate on [ArOTf]. The linear plot of 1/k_{obs} vs [P(*o*-tolyl)$_3$] for reactions in the presence of added N(octyl)$_4$Br indicated that the reaction was inverse first order in P(*o*-tolyl)$_3$.

Linear plots of k_{obs} vs [N(octyl)$_4$X] with a positive slope and clear, nonzero *y* intercept were obtained from reactions conducted in benzene-d_6 with added bromide and chloride, as shown in Figure 4. Reaction in the absence of added bromide was slow; the value of $t_{1/2}$ was greater than 24 h. Thus, the observed nonzero *y* intercept was not due to decomposition of the starting material. Reactions in the presence of chloride ions were 2 times faster than those conducted in the presence of added bromide ions. Reactions in the presence of the combination of N(octyl)$_4$Br and NBu$_4$PF$_6$ proceeded at the same rate as those conducted with the same concentration of added bromide and no added NBu$_4$PF$_6$. These data indicate that the effect of added halogen on the rate of oxidative addition of aryl triflates to Pd[P(*o*-tolyl)$_3$]$_2$ does not simply result from a change in polarity of the medium.

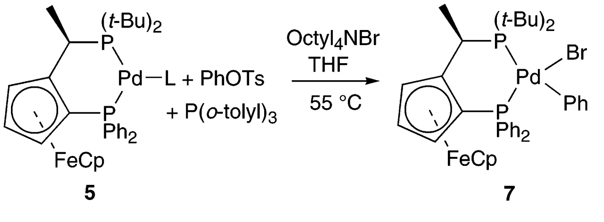
The oxidative addition of phenyl triflate to Pd(PPF-*t*-Bu)[P(*o*-tolyl)$_3$] was performed in benzene-d_6 solvent in the presence of bromide ions and in the presence and absence of NBu$_4$PF$_6$ ions to probe for a medium effect. The rate of reaction between phenyl triflate and Pd(PPF-*t*-Bu)[P(*o*-tolyl)$_3$] at −30 °C in the presence of 4 equiv of added bromide was faster than the rate of reaction in the presence of only 1 equiv of added bromide, as seen in Table 3. However, the reaction in the presence of 4 equiv of added ions, consisting of a mixture of 1 equiv of bromide and 3 equiv of PF$_6^-$, occurred at the same rate as the reaction with 4 equiv of bromide. These data indicate that the rate of reaction is influenced by the polarity of the medium, not by coordination of anion to palladium prior to oxidative addition. The low solubility of **5** in DMF and NMP at −30 °C limited our ability to obtain quantitative data on the rate of oxidative addition of phenyl triflate to **5** in polar solvents.

Table 4. Structural Data for Compounds 7 and 8[a]

	7	**8**
empirical formula	$C_{42}H_{53}OP_2BrFePd$	$C_{47}H_{77}BrFeOP_2Pd$
formula wt	877.98	962.19
cryst dimens (mm^3)	0.10 × 0.15 × 0.29	0.35 × 0.20 × 0.20
cryst syst	monoclinic	orthorhombic
lattice params		
a (Å)	9.4928(2)Å	22.412(5)
b (Å)	15.1888(5) Å	24.106(5)
c (Å)	13.5344(4) Å	16.388(3)
β (deg)	91.7135	
V (Å^3)	1950.57(8)	8854(3)
space group	$P2_1$ (No. 4)	$C222_1$
Z	2	8
D_{calc} (g/cm^3)	1.495	1.444
F_{000}	900.00	4032
μ(Mo Kα) (cm^{-1})	19.74	17.43
diffractometer	Nonius KappaCCD	
radiation	Mo Kα (λ = 0.710 69 Å), graphite monochromated	
temp	−90.0 °C	183(2) K
2θ_{max} (deg)	61.2	56.56
no. of rflns measd		
total	13 797	10 177
unique	5823 (R_{int} = 0.061)	10 177
structure soln	direct methods	
refinement	full-matrix least squares	
anomalous dispersion	all non-hydrogen atoms	
no. of observns ($I > 3.00\sigma(I)$)	4363	10 177
no. of variables	432	4811
rfln/param ratio	10.10	21.16
residuals: *R*; R_w	0.042; 0.041	0.0696, 0.1361
goodness of fit indicator	1.37	0.931
max peak in final diff map (e/Å^3)	0.70	0.599
min peak in final diff map (e/Å^3)	−1.34	−0.732

[a] Full experimental details on the structure solution of compounds **7** and **8** have been published previously.[35]

Mechanism of the Oxidative Addition of Aryl Tosylates to Pd(PPF-*t*-Bu)[P(*o*-tolyl)$_3$]. To determine the kinetic order of the various components of the oxidative addition of aryl tosylates to PPF-*t*-Bu complexes of palladium(0) shown in eq 2, we measured the rate behavior of the reaction by ^{31}P NMR spectroscopy at 55 °C in THF solvent in the presence and absence of added bromide. The concentration of PhOTs was varied from 0.062 to 0.45 M, the concentration of N(octyl)$_4$Br was varied from 0 to 0.34 M, and the concentration of P(*o*-tolyl)$_3$ was varied from 0.088 to 0.26 M. Compound **5** was formed in situ from Pd[P(*o*-tolyl)$_3$]$_2$ and PPF-*t*-Bu. Excellent fits to a first-order decay of **5** were obtained. The plot of k_{obs} vs [PhOTs] in Figure 5 in the presence and absence of added bromide showed a first-order dependence on this reagent. Linear plots of 1/k_{obs} vs [P(*o*-tolyl)$_3$] from reactions in the presence and absence of added N(octyl)$_4$Br indicated that the reaction is inverse first order in P(*o*-tolyl)$_3$.



(2)

Linear plots of k_{obs} vs [NR$_4$X] with a positive slope and clear, nonzero *y* intercept were obtained from

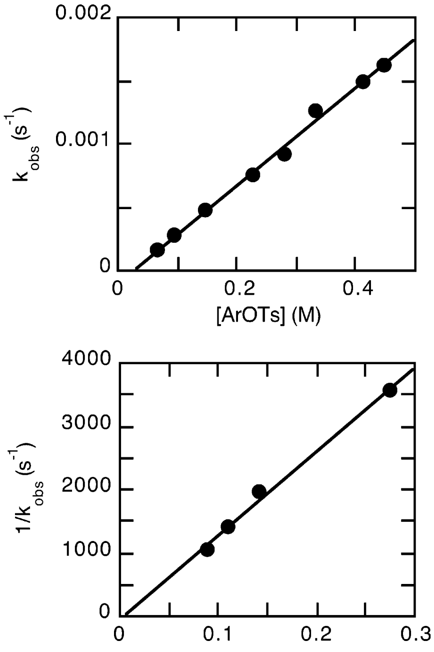


Figure 5. Plots of k_{obs} vs [PhOTs] and $1/k_{obs}$ vs [P(*o*-tol)$_3$] for the oxidative addition of phenyl tosylate to complex **5**.

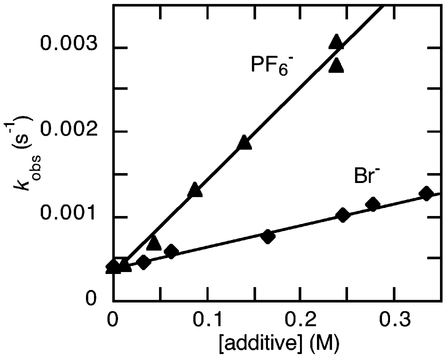


Figure 6. Plots of k_{obs} vs [additive] for the oxidative addition of phenyl tosylate to **5**. Additives: NBu_4PF_6 (triangles) and NBu_4Br (diamonds).

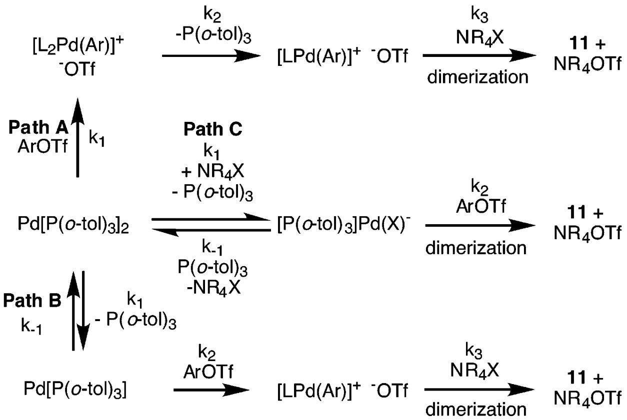
reactions conducted with added bromide and PF_6^-, as shown in Figure 6. The value of k_{obs} for the reaction in the absence of bromide ((4.1 ± 0.6) × 10^{-4} s^{-1}) matched the *y* intercept of the plot of k_{obs} vs [N(octyl)$_4$Br] ((3.9 ± 0.6) × 10^{-4} s^{-1}) and of the plot of k_{obs} vs [NBu_4PF_6] ((3.3 ± 0.7) × 10^{-4}). The slope of the plot of k_{obs} vs [NBu_4PF_6] was roughly 4 times greater than that of the plot of k_{obs} vs [N(octyl)$_4$Br]. Thus, reactions in the presence of [NBu_4PF_6] were *faster* than those conducted with added bromide.

Low solubility of the palladium(0) complex **5** in polar solvents such as DMF and NMP limited our ability to obtain quantitative data on solvent effects, but reactions in these polar solvents were significantly faster than reactions in less polar solvents. With 5 equiv of P(*o*-tolyl)$_3$ at 55 °C, reactions in DMF and NMP appeared complete in 0.5 h instead of 3.5 h in C_6H_6 and THF. Oxidative addition of PhOTs to **6** was complete within 5 min at 25 °C in THF, C_6H_6, or DMF.

Discussion

Mechanism of the Oxidative Addition of Aryl Triflates to Pd[P(*o*-tolyl)$_3$]$_2$. Potential mechanisms for the addition of *p*-tolyl triflate to Pd[P(*o*-tolyl)$_3$]$_2$ are shown in Scheme 5. Path A begins with direct oxidative addition of aryl triflate to complex **1**, followed by dissociation of P(*o*-tolyl)$_3$. In this mechanism, the added halide would replace the coordinated triflate after oxidative addition, and dimerization of this three-coordinate monomer would form the final product. This pathway predicts first-order behavior in aryl triflate and zero-order behavior in both halide and P(*o*-tolyl)$_3$. This pathway is inconsistent with the observed positive order in halide and the inverse order in P(*o*-tolyl)$_3$.

Scheme 5

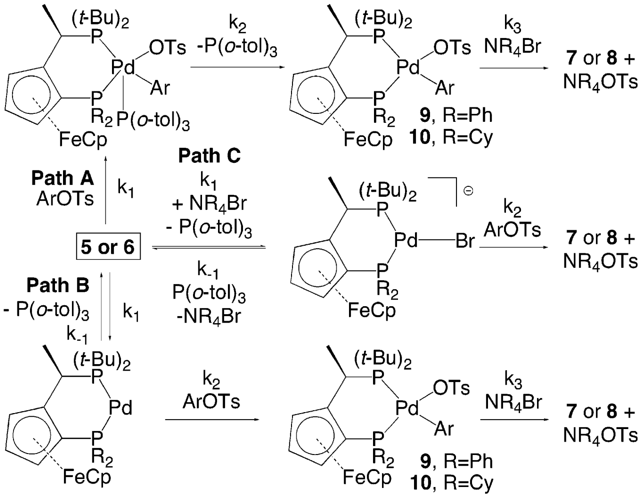


Path B is initiated by dissociation of P(*o*-tolyl)$_3$ from **1**. Irreversible oxidative addition of aryl triflate and subsequent rapid exchange of halide for triflate and dimerization forms the final product. This pathway predicts first-order behavior in aryl triflate, inverse-order behavior in P(*o*-tolyl)$_3$, and zero-order behavior in added halide. These predictions are inconsistent with the observed effects of anions. A positive order in added halide was observed, and less coordinating anions such as PF_6^- did not influence the rate of reaction.

Our data is more consistent with path C, which involves initial associative or dissociative exchange of halide for P(*o*-tolyl)$_3$ and subsequent irreversible oxidative addition of aryl triflate to the halide-ligated palladium species. This pathway predicts a reaction that is first order in aryl triflate, inverse order in added P(*o*-tolyl)$_3$, and first order in added halide. Our kinetic data are consistent with these predictions. In particular, this pathway is consistent with the positive reaction order in added halide and the absence of an effect of added weakly coordinating anions, such as that in NBu_4PF_6. The plot of k_{obs} vs [X] (X = Br, Cl) did contain a small nonzero *y* intercept. This *y* intercept most likely corresponds to the k_{obs} value for reaction by path B.

Mechanism of the Oxidative Addition of Aryl Tosylates to Pd(PPF-*t*-Bu)[P(*o*-tolyl)$_3$]. Potential mechanisms for the oxidative addition of PhOTs to Pd(PPF-*t*-Bu)[P(*o*-tolyl)$_3$] are shown in Scheme 6. Path A begins with direct oxidative addition of aryl tosylate to the 16-electron complex **5**, followed by dissociation of P(*o*-tolyl)$_3$. In this mechanism the halogen would replace the coordinated tosylate after oxidative addition. This pathway predicts a first-order dependence on the concentration of aryl tosylate and zero-order dependence on the concentration of both bromide and P(*o*-tolyl)$_3$. This pathway is inconsistent with the observed inverse order dependence on P(*o*-tolyl)$_3$ and the positive order in bromide.

Scheme 6



Path B is initiated by dissociation of P(*o*-tolyl)$_3$ from **5**, irreversible oxidative addition of aryl tosylate to the unsaturated intermediate, and subsequent more rapid exchange of bromide for tosylate to form **7** if bromide is present. This pathway predicts a first-order dependence on the concentration of aryl tosylate, inverse-order dependence on the concentration of P(*o*-tolyl)$_3$, and zero-order dependence on the concentration of added bromide. The kinetic orders in PhOTs and added P(*o*-tol)$_3$ are consistent with reaction by path B in the absence of added bromide or PF_6^-.

Path C involves initial associative or dissociative exchange of bromide for P(*o*-tolyl)$_3$ and subsequent irreversible oxidative addition of aryl tosylate to the anionic palladium(0). This pathway predicts a reaction that is first order in aryl tosylate and inverse order in P(*o*-tolyl)$_3$. This pathway predicts that the reaction rate will also be first order in bromide and that added NBu_4PF_6 would not strongly influence the rate of oxidative addition because the PF_6^- would bind more weakly to palladium. The strong effect of added NBu_4PF_6 argues against reaction by path C.

Faster rates in the presence of more weakly coordinating anions implies that the more polar medium created by the added bromide and not direct coordination of this ion to palladium accounts for the faster rates. The difference in observed rate constants for reactions conducted with the different added anions presumably results from differences in the degree or type of ion pairing of ammonium PF_6^- and Br^- salts in the nonpolar arene solvents. Consistent with the proposed acceleration of the reactions from increasing the polarity of the medium, reactions in more polar solvents in the absence of added halogen occurred faster than those in the arene solvents. This large acceleration of oxidative addition of an aryl electrophile to palladium(0) in more polar solvents[39] is unusual.[2,10,11,40]

Comparison of the Effect of Anions on the Reactions of Aryl Sulfonates with Palladium(0) Complexes Containing Hindered Monodentate and Bidentate Ligands. The role of anions in the oxidative addition of aryl sulfonates to complexes of PPF-*t*-Bu was distinct from the role of anions in the oxidative addition to complexes of P(*o*-tolyl)$_3$. The effect of anions on the oxidative addition of phenyl triflate to the two palladium(0) complexes could result from a medium effect or from direct coordination of anion prior to oxidative addition. Our data indicate that the acceleration of the oxidative addition to Pd[P(*o*-tolyl)$_3$]$_2$ by added halide results from coordination of halide, while the acceleration of the oxidative addition to Pd(PPF-*t*-Bu)[P(*o*-tolyl)$_3$] by added halide results from a medium effect.

The different effect of halide on the reactions of the two types of palladium(0) complexes in this study likely results from a different effect of coordination on the ability of the two palladium(0) species to undergo oxidative addition. Coordination of an anion to a palladium(0) complex containing a hindered monophosphine, such as P(*o*-tolyl)$_3$, would form a two-coordinate anionic palladium complex after dissociation of phosphine, as shown in Path C of Scheme 5. In contrast, coordination of halide to Pd(PPF-*t*-Bu)[P(*o*-tolyl)$_3$] would likely form the three-coordinate anionic [Pd(PPF-*t*-Bu)X]$^-$ after dissociation of P(*o*-tolyl)$_3$. Oxidative addition to two-coordinate palladium complexes is fast, but oxidative addition to three-coordinate palladium complexes is slow.[2,40−42] Thus, the oxidative addition of aryl triflates to Pd[P(*o*-tolyl)$_3$]$_2$ in the presence of added halide can proceed through a mechanism involving exchange of halide for one P(*o*-tolyl)$_3$ to generate a two-coordinate palladium(0) anion. Addition to this anionic complex could be faster than addition to the neutral complex because it may be more electron-rich. However, oxidative addition of aryl triflates and tosylates to the neutral two-coordinate Pd(PPF-*t*-Bu) is likely to occur faster without coordination of bromide to generate a three-coordinate complex, because addition to Y-shaped, three-coordinate complexes is slow.[2,41] The medium effect observed in this case would then result from increased polarization of the aryl sulfonate linkage during the reaction or a reflection of the ionic character of the palladium sulfonate product in the transition state.

Conclusions

The studies on the oxidative addition of aryl triflates and tosylates reported here have several important consequences. The oxidative addition of aryl triflates in the presence of halide, combined with the reported reductive elimination of aryl halide from arylpalladium halide complexes,[43] could lead to the development of a stoichiometric or catalytic exchange of halide for triflates or tosylates. In addition, the mild activation of aryl tosylates may allow for cross-coupling reactions of aryl tosylates under mild conditions. The rapid oxidative addition step shows that the scope of the couplings of aryl tosylates may be limited by transmetalation and reductive elimination[22] instead of oxidative addition. As a result, aryl tosylates could replace the more expensive

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and less convenient aryl triflates in many coupling applications.

Experimental Section

General Methods. ^{1}H, ^{13}C, and ^{31}P{^{1}H} NMR spectra were recorded on a Bruker DPX 400 or 500 MHz spectrometer, a General Electric QE 300 MHz spectrometer, or a General Electric Omega 500 spectrometer with tetramethylsilane or residual protiated solvent as a reference. Elemental analyses were performed by Robertson Microlabs, Inc., Madison, NJ. All ^{31}P and ^{13}C NMR spectra were proton decoupled. GC and GC/MS analyses were conducted with an HP-1 methyl silicone column. Ether, toluene, tetrahydrofuran, benzene, and pentane were distilled from sodium/benzophenone. PPF-*t*-Bu (PPF-*t*-Bu = 1-diphenylphosphino-2-di-*tert*-butylphosphinoethylferrocene) was purchased from Strem Chemicals and used without further purification. CyPF-*t*-Bu (CyPF-*t*-Bu = 1-dicyclohexylphosphino-2-di-*tert*-butylphosphinoethylferrocene) was obtained from Solvias AG and Strem Chemicals and used without further purification. {Pd[P(*o*-tolyl)$_3$](Ar)(μ-X)}$_2$,[44,45] Pd(dba)$_2$,[46] and Pd[P(*o*-tolyl)$_3$]$_2$[45] were prepared by literature procedures. Structural data for complexes **7** and **8** have been published previously.[35]

Synthesis of Pd(PPF-*t*-Bu)[P(*o*-tolyl)$_3$] (5). A solution of 9.1 mg (0.017 mmol) of PPF-*t*-Bu in C_6D_6 was added dropwise to a suspension of 12.0 mg (0.0168 mmol) of Pd[P(*o*-tolyl)$_3$]$_2$ in C_6D_6. The suspension was stirred at room temperature for 10 min, during which time the solids dissolved. The solution was transferred to an NMR sample tube and was characterized by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. ^{1}H NMR (C_6D_6): δ 0.98 (d, J = 12.0 Hz, 9H), 1.24 (d, J = 11.2 Hz, 9H), 1.86 (t, J = 6.4 Hz, 3H), 2.35 (s, 9H, coordinated P(*o*-tolyl)$_3$), 3.32 (m, 1H), 3.72 (br s, 1H), 3.86 (s, 5H), 3.91 (t, J = 2.8 Hz, 1H), 4.18 (br s, 1H), 6.87−7.18 (m, 16H), 7.32 (t, J = 10.0 Hz, 2H), 7.90 (br s, 2H), 7.99 (br t, J = 8.0 Hz, 2H). ^{31}P{^{1}H} NMR (C_6D_6): δ 1.28 (dd, J = 88 Hz, 88 Hz), 19.78 (br dd, J = 88 Hz, 82 Hz), 71.69 (dd, J = 88 Hz, 82 Hz).

Synthesis of Pd(CyPF-*t*-Bu)[P(*o*-tolyl)$_3$] (6). A solution of 9.4 mg (0.017 mmol) of CyPF-*t*-Bu in C_6D_6 was added dropwise to a suspension of 12.1 mg (0.0169 mmol) of Pd[P(*o*-tolyl)$_3$]$_2$ in C_6D_6. The suspension was stirred at room temperature for 10 min, during which time the solids dissolved. The solution was transferred to an NMR sample tube and was characterized by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. ^{1}H NMR (C_6D_6): δ 0.90−2.0 (m, 22 Cy H), 1.05 (br d, J = 8.8 Hz, 9H), 1.26 (d, J = 11.6 Hz, 9H), 1.88 (t, J = 6.8 Hz, 3H), 2.2−2.6 (br, 9H), 3.15 (m, 1H), 4.05 (t, J = 2.0 Hz, 1H), 4.13 (s, 5H), 4.25 (br s, 1H), 4.36 (br s, 1H), 6.99−7.10 (m, 12H). ^{31}P{^{1}H} NMR (C_6D_6): δ 11.72 (br), 21.42 (br), 69.59 (t, J = 88 Hz).

Independent Synthesis of Pd(PPF-*t*-Bu)(Ph)(Br) (7). A solution of 218 mg (0.400 mmol) of PPF-*t*-Bu in THF was added dropwise to a suspension of 200 mg (0.180 mmol) of {Pd[P(*o*-tolyl)$_3$](Ph)(μ-Br)}$_2$ in THF. The reaction mixture was stirred at room temperature for 20 min, during which time all the solids dissolved. After 20 min the reaction was complete, as determined by ^{31}P{^{1}H} NMR spectroscopy. The orange solution was filtered through Celite and concentrated. Addition of pentane led to precipitation of 226 mg (78% yield) of the product as an orange solid. The product was filtered, washed with pentane, and dried under vacuum. ^{1}H NMR (CD_2Cl_2): δ 1.39 (d, J = 12.8 Hz, 9H), 1.72 (d, J = 12.0 Hz, 9H), 2.07 (t, J = 8.0 Hz, 3H), 3.43 (m, 1H), 3.67 (s, 5H), 4.22 (m, 1H), 4.33 (m, 1H), 4.59 (m, 1H), 6.36−7.28 (m, 10H), 7.60−7.66 (m, 3H), 8.18−8.24 (m, 2H). ^{13}C NMR (CD_2Cl_2, −15 °C): δ 18.18 (d, J = 3.0 Hz), 31.05 (d, J = 4.3 Hz), 32.00 (br), 32.66 (dd, J = 5.7, 3.1 Hz), 38.17 (s at 25 °C, d with J = 1.8 Hz at −80 °C) 38.86, 67.92 (d, J = 7.0 Hz), 70.20 (d, J = 7.8 Hz), 70.42, 75.28 (d, J = 4.7 Hz), 78.00 (dd, J = 41.1, 8.7 Hz), 95.61 (dd, J = 18.2, 6.3 Hz), 121.07, 124.51 (d, J = 7.5 Hz), 127.38 (d, J = 12.1 Hz), 127.65 (d, J = 7.0 Hz), 128.57 (d, J = 11.6 Hz), 128.74 (d, J = 1.3 Hz), 131.33 (d, J = 2.0 Hz), 131.80 (d, J = 51.9 Hz), 132.49 (d, J = 64.1 Hz), 132.61 (d, J = 7.8 Hz), 133.33 (d, J = 6.0 Hz), 136.23 (d, J = 14.0 Hz), 139.56, 160.44 (d, J = 113.1 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 21.2 (d, J = 38 Hz), 67.6 (d, J = 38 Hz). Anal. Calcd for $C_{38}H_{45}P_2BrFePd$: C, 56.63; H, 5.64. Found: C, 56.59; H, 5.49.

Independent Synthesis of Pd(CyPF-*t*-Bu)(Ph)(Br) (8). A solution of 157 mg (0.28 mmol) of CyPF-*t*-Bu in THF was added dropwise to a suspension of 150 mg (0.13 mmol) of {Pd[P(*o*-tolyl)$_3$](Ph)(μ-Br)}$_2$ in THF. The reaction mixture was stirred at room temperature for 20 min, during which time all the solids dissolved. After 20 min the reaction was complete, as determined by ^{31}P{^{1}H} NMR spectroscopy. The orange solution was filtered through Celite and concentrated. Addition of pentane led to precipitation of the product as an orange solid. The solid was filtered, washed with cold pentane, and dried under vacuum. The solid was then recrystallized from a toluene solution layered with pentane and cooled to −35 °C to give 126 mg (58% yield) of the product. ^{1}H NMR (C_6D_6): δ 0.80−2.80 (m, 22 Cy H), 1.32 (d, J = 12.8 Hz, 9H), 1.61 (t, J = 7.2 Hz, 3H), 1.67 (d, J = 11.6 Hz, 9H), 2.19 (s, 1H, $^{1}/_{3}$ molecule of toluene), 3.10 (m, 1H), 3.98 (s, 5H), 4.01 (m, 1H), 4.04 (br s, 1H), 4.64 (br s, 1H), 7.01−7.06 (m, 2H), 7.10−7.15 (m, C_6D_6 and $^{1}/_{3}$ molecule of toluene), 7.35 (br, 1H), 7.84 (br, 2H). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 19.0 (d, J = 29 Hz), 74.8 (d, J = 34 Hz). Anal. Calcd for $C_{38}H_{57}P_2BrFePd\cdot{}^{1}/_{3}C_7H_8$: C, 57.1; H, 7.05. Found: C, 57.32; H, 7.19.

Independent Synthesis of Pd(PPF-*t*-Bu)(Ph)(OTs) (9). A solution of 200 mg (0.240 mmol) of Pd(PPF-*t*-Bu)(Ph)(Br) (**7**) in C_6H_6 was added to a suspension of 68 mg (0.24 mmol) of AgOTs in C_6H_6. The reaction was complete after stirring for 20 min, as determined by ^{31}P{^{1}H} NMR spectroscopy. The suspension was filtered through Celite, and the orange solution was concentrated under vacuum. Addition of pentane and stirring of the resulting mixture led to precipitation of the product as an orange solid. The product was filtered, washed with pentane, and dried under vacuum to give 162 mg (75% yield) of product. ^{1}H NMR (CD_2Cl_2): δ 1.36 (d, J = 13.2 Hz, 9H), 1.63 (d, J = 12.0 Hz, 9H), 2.01 (t, J = 7.2 Hz, 3H), 2.21 (s, 3H), 3.28 (m, 1H), 3.69 (s, 5H), 4.10 (br s, 1H), 4.34 (br s, 1H), 4.61 (br s, 1H), 6.45 (br, 2H), 6.45 (t, J = 7.2 Hz, 1H), 6.58 (br, 2H), 6.80 (d, J = 8.4 Hz, 2H), 6.90 (d, J = 7.6 Hz, 2H), 7.09−7.19 (m, 4H), 7.26−7.31 (m, 1H), 7.59−7.64 (m, 3H), 8.17−8.22 (m, 2H). ^{13}C NMR (CD_2Cl_2, 40 °C): δ 17.71 (d, J = 5.0 Hz), 21.30, 31.64 (d, J = 5.9 Hz), 31.70 (d, J = 6.8 Hz), 32.43 (m), 37.47, 38.52, 68.62 (d, J = 7.0 Hz), 70.88 (d, J = 8.3 Hz), 70.95, 75.73 (d, J = 5.2 Hz), 78.26 (dd, J = 47.63, 10.80 Hz), 95.96 (dd, J = 16.8, 6.5 Hz), 123.22, 126.40, 126.77, 128.04 (d, J = 11.3 Hz), 128.31, 128.77 (d, J = 11.4 Hz), 129.92 (J = 2.8 Hz), 131.77 (br), 132.12 (d, J = 58.1 Hz), 132.24 (d, J = 58.1 Hz), 133.73 (d, J = 9.6 Hz), 136.02 (d, J = 12.6 Hz), 136.67 (br), 139.05, 140.95, 157.83 (d, J = 103.3 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 25.4 (d, J = 37 Hz), 67.5 (d, J = 37 Hz). Anal. Calcd for $C_{45}H_{52}P_2O_3SFePd$: C, 60.24; H, 5.85. Found: C, 59.94; H, 5.78.

Independent Synthesis of Pd(CyPF-*t*-Bu)(Ph)(OTs) (10). A solution of 113 mg (0.140 mmol) of Pd(CyPF-*t*-Bu)(Ph)(Br) (**8**) in C_6H_6 was added to a suspension of 48 mg (0.17 mmol) of AgOTs in C_6H_6. The reaction was complete after stirring for 20 min, as determined by ^{31}P{^{1}H} NMR spectroscopy. The suspension was filtered through Celite, and the orange solution was concentrated under vacuum. Addition of pentane and stirring of the resulting mixture led to precipitation of the product as an orange solid. The product was filtered, washed with pentane, and dried under vacuum to give 90 mg (71% yield) of product. ^{1}H NMR (CD_2Cl_2): δ 0.76−2.95 (m, 22

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Cy H), 1.11 (d, $J = 13.5$ Hz, 9H), 1.62 (d, $J = 12.0$ Hz, 9H), 1.92 (t, $J = 8.0$ Hz, 3H), 2.26 (s, 3H), 3.02 (m, 1H), 4.26 (s, 5H), 4.52 (t, $J = 2.0$ Hz, 1H), 4.56 (br s, 1H), 4.95 (br s, 1H), 6.79−6.84 (m, 4H), 6.89 (d, $J = 7.0$ Hz, 2H), 7.05−7.12 (m, 3H). $^{31}P\{^1H\}$ NMR (C_7H_8, −40 °C): δ 25.2 (d, $J = 31.9$ Hz), 71.6 (d, $J = 30.5$ Hz). Anal. Calcd for $C_{45}H_{64}P_2O_3SFePd$: C, 59.44; H, 7.11. Found: C, 59.71; H, 7.34.

General Procedure for the Oxidative Addition of ArOTf to 1. Into a small vial was placed 15 mg (0.021 mmol) of Pd[P(*o*-tolyl)$_3$]$_2$, 56 mg (0.24 mmol) of PhOTs, 115 mg (0.21 mmol) of N(octyl)$_4$Br, and PMes$_3$ as internal standard. The reactants were dissolved in 1 mL of C_6H_6, and the resulting solution was stirred at room temperature. A $^{31}P\{^1H\}$ NMR spectrum was obtained periodically until all starting material had been consumed. The yield of compound **3** was calculated to be 99% yield.

General Procedure for the Oxidative Addition of PhOTf to 5 and 6. Into a small vial was placed 10 mg (0.014 mmol) of Pd[P(*o*-tolyl)$_3$]$_2$, 7.7 mg (0.014 mmol) of PPF-*t*-Bu, and 11.6 mg of PMes$_3$ as internal standard. The solid materials were dissolved in 1 mL of C_6H_6 and stirred at room temperature for 10 min. The solution was transferred to an NMR tube. A $^{31}P\{^1H\}$ NMR spectrum was obtained. The solution was poured into a vial containing 12 μL (0.074 mmol) of PhOTf and 79 mg (0.14 mmol) of N(octyl)$_4$Br, and the resulting solution was stirred at room temperature. After 10 min, a second $^{31}P\{^1H\}$ NMR spectrum was obtained, and this spectrum showed that all starting material had been consumed and that compound **7** was produced in 93% yield.

General Procedure for the Oxidative Addition of PhOTs to 5 and 6. Into a small vial was placed 10.0 mg (0.0140 mmol) of Pd[P(*o*-tol)$_3$]$_2$, 7.8 mg (0.0140 mol) of CyPF-*t*-Bu, and 5.4 mg of PMes$_3$ as internal standard. The solid materials were dissolved in 0.60 mL of C_6H_6, and the solution was transferred to an NMR tube. A $^{31}P\{^1H\}$ NMR spectrum was obtained. The solution was poured into a vial containing 17.3 mg (0.0697 mmol) of PhOTs, and the resulting solution was stirred at room temperature. After 30 min, a second $^{31}P\{^1H\}$ NMR spectrum was obtained, and this spectrum showed that all starting material had been consumed and that compound **10** was produced in 92% yield.

Measurement of Rate Constant for Oxidative Addition of Aryl Triflate to Palladium(0): Representative Procedure. Into a small vial was placed 2.5 mg (0.0035 mmol) of Pd[P(o-tolyl)$_3$]$_2$, 10 μL (0.056 mmol) of *p*-tolylOTf, 31.0 mg (0.0567 mmol) of N(octyl)$_4$Br, 0.20 mL (0.020 mmol) of a 0.1 M solution of P(*o*-tolyl)$_3$ in C_6D_6, and PMes$_3$ as internal standard. Exactly 0.40 mL of C_6H_6 was added to the vial, and the solution was transferred to an NMR tube with a septum-lined screw cap. The sample was heated to 50 °C, and $^{31}P\{^1H\}$ NMR spectra were obtained every 3 min for at least 5 half-lives by an automated data acquisition program.

Measurement of Rate Constant for Oxidative Addition of Aryl Tosylate to Palladium(0): Representative Procedure. Into a small vial was placed 12.0 mg (0.0170 mmol) of Pd[P(o-tolyl)$_3$]$_2$, 9.2 mg (0.017 mmol) of PPF-*t*-Bu, 34.0 mg (0.140 mmol) of PhOTs, 92.0 mg (0.170 mmol) of N(octyl)$_4$Br, 26.0 mg (0.0850 mmol) of P(*o*-tolyl)$_3$, and PMes$_3$ (as internal standard). The solids were dissolved in 0.60 mL of THF, and the solution was transferred to an NMR tube with a septum-lined screw cap. The sample was heated to 55 °C, and $^{31}P\{^1H\}$ NMR spectra were obtained every 3 min for at least 5 half-lives by an automated data acquisition program.

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