Steric and Electronic Effects on Arylphosphonate Elimination from Organopalladium Complexes

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To study the effects of electronic and steric manipulation of metal-bound aryl fragments on arylphosphonate formation, model organopalladium complexes have been prepared and investigated. While no phosphorus−carbon bond formation was observed at 25 °C, all of the arylpalladium phosphonates underwent clean reductive elimination in C_6D_6 solutions at elevated temperatures. The incorporation of electron-donating groups into the metal-bound aryl fragments accelerated the elimination process, while palladium complexes containing aryl groups with electron-withdrawing or ortho substituents exhibited slower elimination rates. While the rate of arylphosphonate formation was dependent upon the nature of the metal-bound aryl fragment, it was rather insensitive to the identity of the phosphonate moiety. These results demonstrate the results of subtle changes in the electronic and steric composition of the eliminating species in P(O)−C bond-forming reactions.

Introduction

The transition-metal-promoted coupling of aryl halides with $HP(O)(OR)_2$ is one of the most effective ways to prepare arylphosphonates.[1,2] Typically, $NiCl_2$ or $PdCl_2$ promotes these transformations; however, high temperatures (100−200 °C) are often needed to obtain high yields of the $ArP(O)(OR)_2$ targets.[1,2] As a result of the harsh conditions needed for an efficient coupling reaction, difficulties have been encountered in extending this chemistry to sensitive substrates. One of the challenges for the design of new protocols that proceed under mild conditions is a limited understanding of the factors that accelerate specific steps of the reaction.

A plausible mechanism for the coupling reaction is shown in Figure 1. The first step in the process is oxidative addition of an aryl halide to a low-valent metal species. This step and the factors that accelerate or retard reactions of this type are well-known in organometallic chemistry and have been the subject of a number of investigations.[3] The second step is base-assisted phosphonylation of the intermediate generated from the oxidative addition reaction. The final step is reductive elimination from the $L_nM(aryl)(P(O)(OR)_2)$ intermediate to generate the desired C−P(O) bond and regenerate the low-valent metal catalyst. Although the metal-promoted formation of C−C, C−O, C−S, and C−N bonds has been studied in detail,[4] analogous investigations focused on understanding the factors that will accelerate the generation of C−P(O) bonds are rare.[5] To increase the understanding of this important reaction, a detailed investigation of the phosphorus−carbon bond-forming step has been carried out using model systems in order to probe the influence of electronic and steric manipulation on the rate of the elimination reaction.

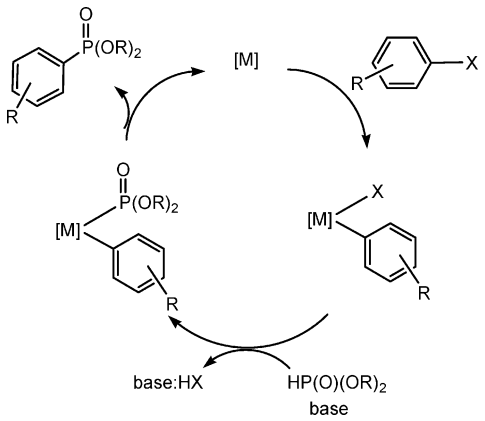

Figure 1. Metal-catalyzed synthesis of arylphosphonates.

Results

Palladium precursors of the type (bu_2bipy)Pd(aryl)I (bu_2bipy = 4,4′-di-*tert*-butyl-2,2′-bipyridine) were prepared by treatment

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(1) (a) Defacqz, N.; de Bueger, B.; Touillaux, R.; Cordi, A.; Marchand-Brynaert, J. *Synthesis* **1999**, 1368. (b) Beletskaya, I. P.; Kazankova, M. A. *Russ. J. Org. Chem.* **2002**, *38*, 1391. (c) Huang, C.; Tang, X.; Fu, H.; Jiang, Y.; Zhao, Y. *J. Org. Chem.* **2006**, *71*, 5020. (d) Hirao, T.; Masunaga, T.; Ohshiro, Y.; Agawa, T. *Synthesis* **1981**, 56. (e) Gelman, D.; Jiang, L.; Buchwald, S. L. *Org. Lett.* **2003**, *5*, 2315. (f) Rao, H. H.; Jin, Y.; Fu, H.; Jiang, Y. Y.; Zhao, Y. F. *Chem. Eur. J.* **2006**, *12*, 3636. (g) Bravo-Altamirano, K.; Huang, Z. H.; Montchamp, J. L. *Tetrahedron* **2005**, *61*, 6315. (h) Beletskaya, I. P. *Pure. Appl. Chem.* **1997**, *69*, 471. (i) Kim, Y. C.; Brown, S. G.; Harden, T. K.; Boyer, J. L.; Dubyak, G.; King, B. F.; Burnstock, G.; Jacobson, K. A. *J. Med. Chem.* **2001**, *44*, 340.

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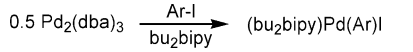
Table 1. Arylpalladium Precursors

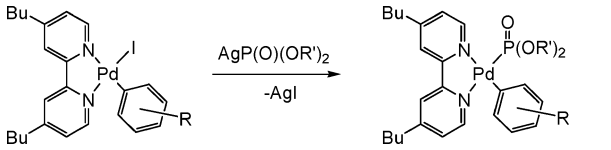


	Ar		Ar
1	C_6H_5	**6**	2-C_6H_4OMe
2	4-$C_6H_4NH_2$	**7**	2,6-$C_6H_3Me_2$
3	4-C_6H_4Me	**8**	4-C_6H_4CN
4	2-C_6H_4Me	**9**	4-$C_6H_4NO_2$
5	4-C_6H_4OMe	**10**	4-C_6H_4Cl

of $Pd_2(dba)_3$ with aryl iodides and bu_2bipy (Table 1).[6] For example, stirring a benzene solution of $Pd_2(dba)_3$ with 2 equiv of 4-iodotoluene and bu_2bipy for 24 h at 25 °C followed by filtration, concentration of the effluent, and trituration with a 1:1 mixture of hexane/diethyl ether afforded (bu_2bipy)-Pd(4-C_6H_4Me)I as a yellow powder. Aryl iodides with bulky substituents as well as electron-donating and -withdrawing groups were well tolerated by this reaction, and moderate to high yields of the desired complexes were obtained with minimal purification. Compounds **1**−**10** were quite stable in the solid state for extended periods of time. No decomposition or elimination was observed from **1**−**10** in C_6D_6 or $CDCl_3$ solvents. The ^1H and $^{13}C\{^1H\}$ NMR spectra of **1**−**10** displayed the expected resonances for a C_s-symmetric species. No rotamers were detected for species containing ortho-substituted aryl groups (**4**, **6**, **7**).

Arylpalladium phosphonates of the type (bu_2bipy)Pd(aryl)-(P(O)(OR)$_2$) (R = phenyl, ethyl) were prepared by treatment of the (bu_2bipy)Pd(aryl)I precursors with Ag[P(O)(OR)$_2$] (R = Et, Ph) (Table 2). Diphenyl and diethyl phosphite were chosen as prototypical alkyl and aryl phosphites, due to their widespread use in synthetic applications. As a representative example, treatment of **4** with Ag[P(O)(OEt)$_2$] in CH_2Cl_2 for 2 h followed by filtration, concentration, trituration with ether/hexane, and drying afforded **17** as a light gray solid. Compounds **1**−**10** were all successfully phosphonylated using variations of this general procedure to afford **11**−**30** as white to pale yellow solids. Even compounds containing two ortho substituents were readily isolated in high yield (**23** and **24**). Compounds **11**−**30** exhibited a single resonance in the $^{31}P\{^1H\}$ NMR spectrum, with the chemical shift following the donor ability of the aryl group (Table 2). The arylpalladium phosphonates containing electron-donating substituents were found to higher frequency than those containing electron-withdrawing groups. The ^1H and $^{13}C\{^1H\}$ NMR spectra of the arylpalladium phosphonate compounds without ortho substituents exhibited the expected resonances for a C_s-symmetric compound. For **17**, **18**, **21**, and **22** the presence of the ortho substituent resulted in inequivalence of the alkoxy groups of the phosphonate fragment. Despite having the phosphonate group cis to the aryl moiety, **11**−**30** were remarkably robust. No decomposition was observed in the solid state for extended periods of time. Additionally, no elimination or decomposition was observed from solutions of **11**−**30** ($CDCl_3$, acetone-d_6, CD_3CN, C_6D_6, dmso-d_6) at 25 °C.

Table 2. Arylpalladium Phosphonate Compounds[a]



	Ar	R′	yield, %[b]	^{31}P NMR, ppm[c]
11	C_6H_5	Et	90	69.6
12	C_6H_5	Ph	98	67.8
13	4-$C_6H_4NH_2$	Et	79	69.7
14	4-$C_6H_4NH_2$	Ph	70	68.4
15	4-C_6H_4Me	Et	90	70.1
16	4-C_6H_4Me	Ph	71	68.3
17	2-C_6H_4Me	Et	79	70.2
18	2-C_6H_4Me	Ph	73	68.6
19	4-C_6H_4OMe	Et	91	69.4
20	4-C_6H_4OMe	Ph	84	67.8
21	2-C_6H_4OMe	Et	67	69.1
22	2-C_6H_4OMe	Ph	93	67.0
23	2,6-$C_6H_3Me_2$	Et	93	71.3
24	2,6-$C_6H_3Me_2$	Ph	78	69.4
25	4-C_6H_4CN	Et	95	65.5
26	4-C_6H_4CN	Ph	94	63.6
27	4-$C_6H_4NO_2$	Et	74	64.4
28	4-$C_6H_4NO_2$	Ph	93	63.0
29	4-C_6H_4Cl	Et	86	68.9
30	4-C_6H_4Cl	Ph	73	65.9

[a] Reactions employing Ag[P(O)(OPh)$_2$] were carried out in THF; reactions using Ag[P(O)(OEt)$_2$] were carried out in dichloromethane. [b] Yields were based upon isolated material. [c] In $CDCl_3$ solution.

While the arylpalladium phosphonates were quite stable in solution at 25 °C, heating solutions of **11**−**30** (95−120 °C) induced arylphosphonate formation. The (bu_2bipy)Pd^0 species decomposed and released free bu_2bipy.[7] ^1H NMR spectroscopy was a convenient way to monitor these phosphorus−carbon bond-forming reactions, and the concentrations of the arylpalladium phosphonates and other products were quantified using hexamethylbenzene as an internal standard. Heating solutions of **11**−**30** to 95 °C induced significant amounts of elimination from substrates containing electron-donating groups in the para position (**13**, **14**, **19**, and **20**) of the aryl substituent, while complexes containing electron-withdrawing groups or ortho substituents only generated small amounts of arylphosphonate (Figure 2, Tables 3 and 4) at this temperature. It was noteworthy that the rates of reductive elimination showed little differences

(4) (a) Zuidema, E.; van Leeuwen, P. W. N. M.; Bo, C. *Organometallics* **2005**, *24*, 3703. (b) Culkin, D. A.; Hartwig, J. F. *Organometallics* **2004**, *23*, 3398. (c) Hartwig, J. F. *Acc. Chem. Res.* **1998**, *31*, 852. (d) Hartwig, J. F.; Richards, S.; Baranano, D.; Paul, F. *J. Am. Chem. Soc.* **1996**, *118*, 3626. (e) Ozawa, F.; Ito, T.; Yamamoto, A. *J. Am. Chem. Soc.* **1980**, *102*, 6457. (f) Komiya, S.; Shibue, A. *Organometallics* **1985**, *4*, 684. (g) Shekhar, S.; Ryberg, P.; Hartwig, J. F.; Mathew, J. S.; Blackmond, D. G.; Strieter, E. R.; Buchwald, S. L. *J. Am. Chem. Soc.* **2006**, *128*, 3584. (h) Muci, A. R.; Buchwald, S. L. *Top. Curr. Chem.* **2002**, *219*, 131. (i) Sawyer, J. S. *Tetrahedron* **2000**, *56*, 5045. (j) Lira, R.; Wolfe, J. P. *J. Am. Chem. Soc.* **2004**, *126*, 13906. (k) Widenhoefer, R. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1998**, *120*, 6504. (l) Singh, U. K.; Strieter, E. R.; Blackmond, D. G.; Buchwald, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 14104. (m) Canty, A. J.; Denney, M. C.; Skelton, B. W.; White, A. H. *Organometallics* **2004**, *23*, 1122. (n) Canty, A. J.; Denney, M. C.; van Koten, G.; Skelton, B. W.; White, A. H. *Organometallics* **2004**, *23*, 5432. (o) Widenhoefer, R. A.; Zhong, H. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1997**, *119*, 6787. (p) Mann, G.; Hartwig, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 13109. (q) Driver, M. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **1997**, *119*, 8232. (r) Mann, G.; Baranano, D.; Hartwig, J. F.; Rheingold, A. L.; Guzei, I. A. *J. Chem. Soc.* **1998**, *120*, 9205. (s) Kuniyasu, H.; Ohtaka, A.; Nakazano, T.; Kinomoto, M.; Kurosawa, H. *J. Am. Chem. Soc.* **2000**, *122*, 2375. (t) Mann, G.; Shelby, Q.; Roy, A. H.; Hartwig, J. F. *Organometallics* **2003**, *22*, 2775.

(5) (a) Levine, A. M.; Stockland, R. A., Jr.; Clark, R.; Guzei, I. *Organometallics* **2002**, *21*, 3278. (b) Stockland, R. A., Jr.; Levine, A. M.; Giovine, M. T.; Guzei, I. A.; Cannistra, J. C. *Organometallics* **2004**, *23*, 647. (c) Han, L.-B.; Choi, N.; Tanaka, M. *Organometallics* **1996**, *15*, 3259. (d) Han, L.-B.; Zhao, C.-Q.; Onozawa, S.-Y.; Goto, M.; Tanaka, M. *J. Am. Chem. Soc.* **2002**, *124*, 3842. For related studies of reductive elimination of phosphines from metal phosphides see: (e) Moncarz, J. R.; Brunker, T. J.; Jewett, J. C.; Orchowski, M.; Glueck, D. S.; Sommer, R. D.; Lam, K. C.; Incarvito, C. D.; Concolino, T. E.; Ceccarelli, C.; Zakharov, L. N.; Rheingold, A. L. *Organometallics* **2003**, *22*, 3205. (f) Blank, N. F.; McBroom, K. C.; Glueck, D. S.; Kassel, W. S.; Rheingold, A. L. *Organometallics* **2006**, *25*, 1742.

(6) Markies, B. A.; Canty, A. J.; de Graaf, W.; Boersma, J.; Janssen, M. D.; Hogerheide, M. P.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *J. Organomet. Chem.* **1994**, *482*, 191.

(7) The decomposition of a similar species has been reported: de Graaf, W.; Boersma, J.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics* **1989**, *8*, 2907.

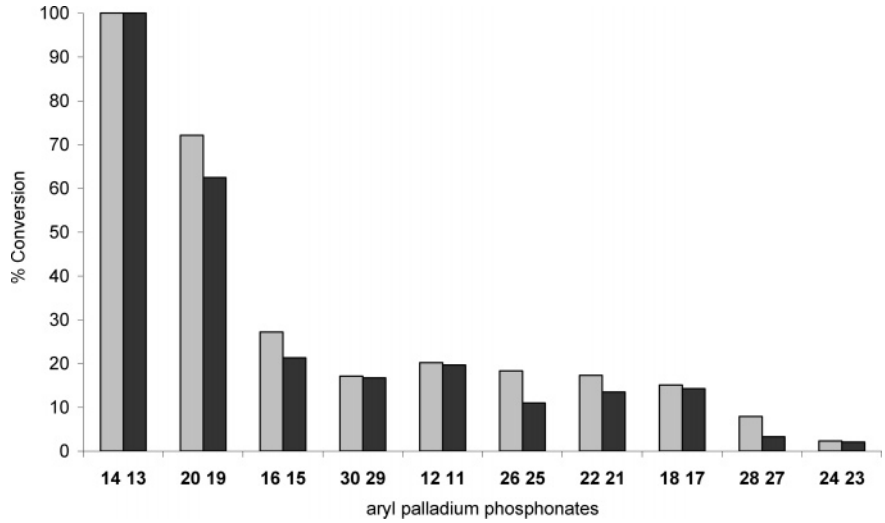
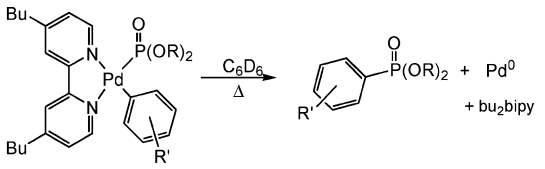
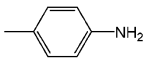
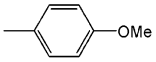
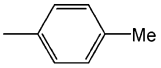
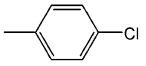
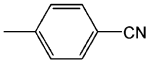
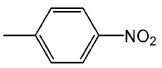


Figure 2. Arylphosphonate elimination from **11**−**30** in C_6D_6 at 95 °C after 3 h.

Table 3. Arylphosphonate Elimination from (bu_2bipy)Pd(Ar)(P(O)(OR)$_2$) Species[a]

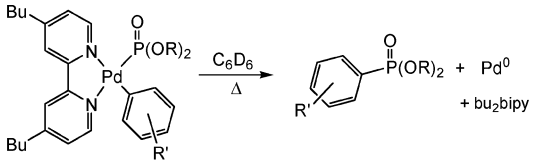


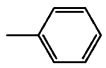
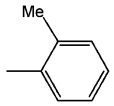
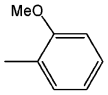
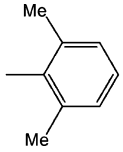
	Arene	R	T(°C)	$k_{obs\ (s^{-1})}$
1		Et	95	4.9(5) x 10 -4
		Ph	95	7.4(7) x 10 -4
2		Et	95	9.7(9) x 10 -5
		Ph	95	9.3(9) x 10 -5
3		Et	95	3.3(3) x 10 -5
		Ph	95	3.3(3) x 10- 5
4		Et	120	8.8(9) x 10-5
		Ph	120	1.2(1) 10 -4
5		Et	120	5.2(5) x 10 -5
		Ph	120	4.6(5) x 10 -5
6		Et	120	1.0(1) x 10 -5
		Ph	120	6.5(7) x 10 -6
7		Et	120	1.0(1) x 10 -5
		Ph	120	3.0(3) x 10-6

[a] Elimination reactions were carried out in C_6D_6 (0.5 mL) at 120 °C using hexamethylbenzene as an internal standard.

between [Pd]−P(O)(OPh)$_2$ and [Pd]−P(O)(OEt)$_2$ species (Figure 3). The relative ease of elimination correlated with the donor ability of the para substituent (e.g. NH_2 > OMe > Me).

Table 4. Arylphosphonate Elimination from (bu_2bipy)Pd(Ar)(P(O)(OR)$_2$) Species Incorporating Ortho Substituents[a]



	Arene	R	T(°C)	$k_{obs\ (s^{-1})}$
1		Et	120	8.8(9) x 10 -5
		Ph	120	1.2(1) x 10 -4
2		Et	120	2.9(3) x 10 -5
		Ph	120	3.7(4) x 10 -5
3		Et	120	1.3(1) x 10 -5
		Ph	120	1.7(2) x 10 -5
4		Et	120	2.3(2) x 10 -6
		Ph	120	1.8(2) x 10 -6

[a] Elimination reactions were carried out in C_6D_6 (0.5 mL) at 120 °C using hexamethylbenzene as an internal standard.

Additionally, there was no indication in the $^{31}P\{^1H\}$ NMR spectrum of phosphoryl oxygen coordination to palladium.

While sluggish elimination occurred from substrates containing electron-withdrawing groups at 95 °C, increasing the temperature to 120 °C resulted in elimination from all model compounds (Tables 3 and 4). Even substrates containing bulky aryl groups such as 2-C_6H_4R (R = Me, OMe) and 2,6-$C_6H_3Me_2$ cleanly eliminated the arylphosphonate. The elimination reactions were quite clean, as evidenced by the ^1H and $^{31}P\{^1H\}$ NMR spectra routinely showing only the resonances for the starting palladium complex, bu_2bipy, and the arylphosphonate (Figure 4 and the Supporting Information). The only exceptions were **29** and **30**. Analysis of the $^{31}P\{^1H\}$ NMR spectrum revealed the presence of small amounts of secondary

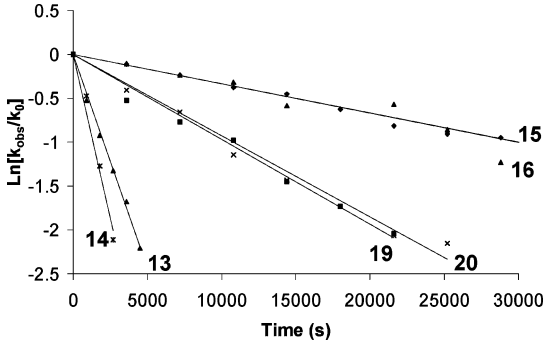


Figure 3. Elimination from arylpalladium phosphonates at 95 °C.

products (totaling less than 5%). These products could be generated from small amounts of aryl chloride oxidative addition to the generated Pd(0). Similar to the reactions carried out at 95 °C, there were no significant differences in the rates of elimination of [Pd]−P(O)(OPh)$_2$ and [Pd]−P(O)(OEt)$_2$ species. Arylphosphonate formation from model compounds containing electron-withdrawing groups was sluggish and required extended periods of time for complete elimination. For example, while elimination from **13**−**16** was too fast at 120 °C for accurate rate determination, the incorporation of a cyano group (**25** and **26**) required 18.1 and 18.3 h, respectively, at 120 °C to reach 50% conversion. The effect of different solvents on the rate of elimination was probed using **12** as the model arylpalladium phosphonate complex (Figure 5). While acetone-d_6 and CD_3-CN solutions of **12** afforded similar conversions (37−47%; 120 °C, 1.5 h), thermolysis reactions carried out in dmso-d_6 resulted in increased consumption of **12** (69%). The effect of excess free ligand on the elimination reaction was probed using **12** and 5 equiv of bu$_2$bipy. Heating a C_6D_6 solution of pure **12** (120 °C; 5 h) resulted in the generation of PhP(O)(OPh)$_2$ (80 ± 5%). The analogous reaction carried out in the presence of 5 equiv of bu$_2$bipy afforded a similar conversion (84 ± 5%), showing that the free ligand neither accelerated nor retarded the formation of the arylphosphonate.

The molecular structures of **1** and **29** were determined by X-ray diffraction. The crystallographic data are presented in Table 5, with the structure diagrams shown in Figure 6. Complex **1** crystallizes in the monoclinic space group $P2_1/c$, with four molecules per unit cell, while **29** crystallizes in $P2_1/n$ with four

Table 5. Crystallographic Data for 1 and 29

	1	**29**
formula	$C_{24}H_{29}IN_2Pd$	$C_{28}H_{38}ClN_2O_3PPd$
formula wt	578.78	623.42
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$
a (Å)	9.9177(3)	13.4268(4)
b (Å)	12.0637(4)	11.1315(3)
c (Å)	19.3038(7)	19.8695(6)
β (deg)	101.295(2)	105.323(2)
temp (K)	100(2)	100(2)
V (Å^3)	2264.85(13)	2864.13(14)
Z	4	4
θ_{max} (deg)	32.5	30.55
D(calcd) (Mg m^{-3})	1.697	1.446
no. of rflns collected	101081	85376
no. of indep rflns	8165 (R(int) = 0.043)	8767 (R(int) = 0.053)
R ($I > 2\sigma(I)$)	0.0247	0.0340
GOF	1.012	1.035

molecules per unit cell. The palladium−carbon bond length in **1** (1.983(2) Å) is similar to that found in **29** (2.006(2) Å) and similar to the Pd−C(Ar) bond lengths in bipyPd(C_6F_5)(CH_2-COMe) (2.009(2) Å),[8] bipyPd(3,5-$C_6H_3(CF_3)_2$)I (1.990(5) Å),[9] and bipyPd(C_6H_5)I (1.996(10) Å).[6] Both of the Pd−C bond lengths are shorter than the Pd−C bond length in the alkyl derivative bipyPdMe(P(O)(OPh)$_2$) (2.044(3) Å).[5a] The Pd−P bond length in **29** (2.2316(5) Å) is similar to the metal−phosphorus bond lengths found in bipyPdMe(P(O)(OPh)$_2$) (2.2203(8) Å)[5a] and bipyPd(P(O)(OPh)$_2$)$_2$ (2.2369(6) Å).[5b] The N−Pd−N angles (**1**, 78.39(5)°; **29**, 76.69(6)°) are smaller than the C−Pd−X (X = I, P) angles (**1**, 89.34(5)°; **29**, 87.43(6)°) due to the constraint of the chelate rings.

Discussion

The formation of carbon−carbon and carbon−heteroelement bonds by reductive elimination from transition-metal centers is one of the key steps in cross-coupling reactions, since this process typically results in the formation of new bonds.[4,5] Even for well-known reactions, predicting the effect of electronic manipulation of the metal-bound alkyl or aryl species on the rate and outcome of the elimination process is often challenging. In several experimental investigations of C−X (X = N, O) bond-forming reactions, metal-bound aryl groups containing electron-withdrawing groups increased the rate of the elimination

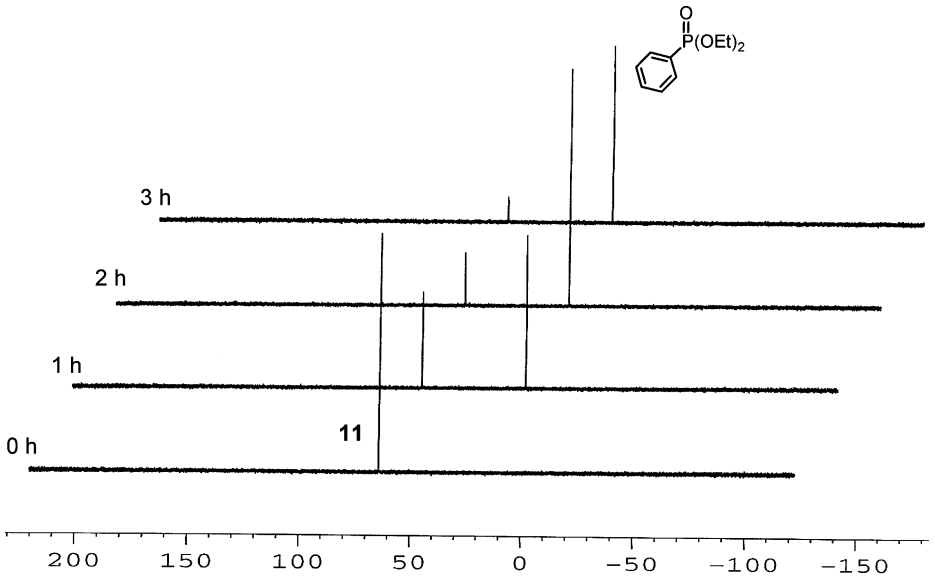


Figure 4. Elimination from (bu$_2$bipy)Pd(C_6H_5)(P(O)(OEt)$_2$) in C_6D_6 for 3 h at 120 °C.

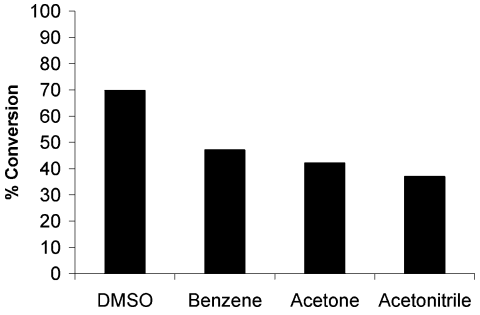


Figure 5. Arylphosphonate elimination from **12** in different solvents at 120 °C after 1.5 h.

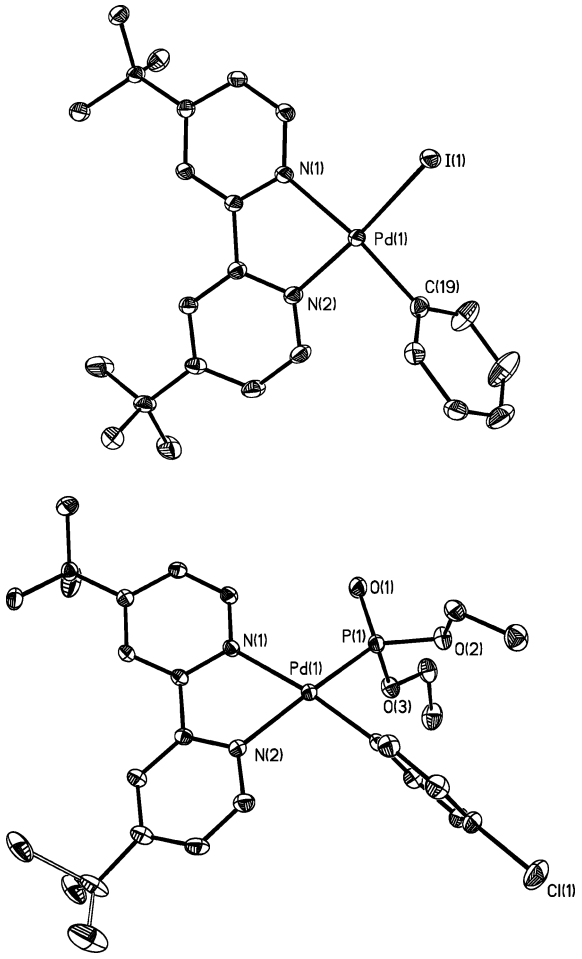


Figure 6. Molecular structures of **1** and **29**. Thermal ellipsoids are shown at 50% probability for both **1** and **29**. Selected bond distances (Å) and angles (deg) for **1**: Pd(1)−C(19) = 1.983(2), Pd(1)−N(1) = 2.1325(14), Pd(1)−N(2) = 2.0730(15); C(19)−Pd(1)−N(2) = 93.84(7), C(19)−Pd(1)−N(1) = 172.18(7), N(2)−Pd(1)−N(1) = 78.39(5). Selected bond distances (Å) and angles (deg) for **29**: Pd(1)−C(19) = 2.006(2), Pd(1)−N(2) = 2.1341(17), Pd(1)−N(1) = 2.1353(17), Pd(1)−P(1) = 2.2316(5); C(19)−Pd(1)−N(2) = 95.34(7), C(19)−Pd(1)−N(1) = 171.85(7), N(2)−Pd(1)−N(1) = 76.69(6), C(19)−Pd(1)−P(1) = 87.43(6), N(2)−Pd(1)−P(1) = 169.88(5), N(1)−Pd(1)−P(1) = 100.71(5).

process, while the metal-bound $-NR_2$ and $-OR$ fragments containing electron-donating substituents accelerated the reaction.[4c,r] Along these lines, heteroarylpalladium systems in which the metal was attached to the more electron rich position of the heteroaryl groups had slower rates of reductive elimination.[10] In contrast, computational studies have predicted that reductive eliminations should be faster from metal-bound aryl groups bearing electron-donating groups.[11] In a recent report, Hartwig found that L_2PtAr_2 complexes incorporating electron-donating substituents exhibited faster rates of reductive elimination.[12] Thus, the overall effect of electronic manipulation on the elimination rate is quite sensitive to subtle changes in the electronic composition of the transition-metal complex.

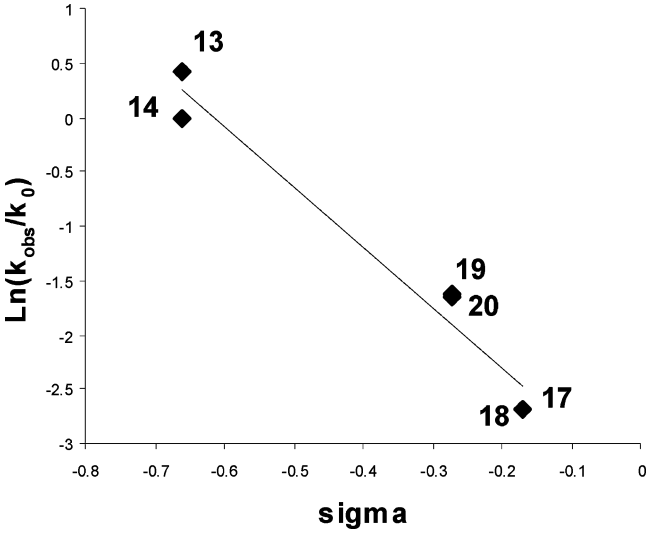


Figure 7. Representative Hammett plot of elimination from (bu_2-bipy)Pd(Ar)(P(O)$(OR)_2$) at 95 °C.

The presence of electron-donating groups in the para position of the metal-bound aryl fragment accelerated arylphosphonate formation from our model compounds (**13**−**16**, **19**, and **20**), while the incorporation of electron-withdrawing groups (**25**−**30**) resulted in a slower elimination rate. The correlation of Hammett parameters with reaction rates has been used in related studies to explain the electronic effects of various functional groups in the para or meta positions.[13] Plotting the reaction rates for the arylpalladium phosphonates that underwent elimination at 95 °C (**13**−**16**, **19**, and **20**) against the σ parameters resulted in a fair correlation (Figure 7, $R^2 = 0.96$). For the model systems incorporating electron-withdrawing groups, the temperature was increased to 120 °C in order to induce significant amounts of elimination, and a representative Hammett plot is shown in Figure 8 for the diphenyl phosphonate containing compounds. The correlation between σ^- and the observed reaction rates has a slightly better fit (σ, $R = 0.97$; σ^-, $R = 0.99$), suggesting that resonance effects may be important in the elimination process.[16]

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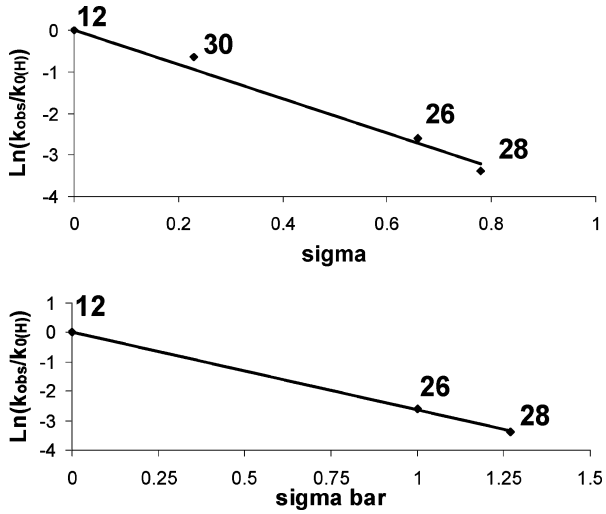

Figure 8. Representative Hammett plot for elimination from (bu_2bipy)Pd(Ar)(P(O)($OPh)_2$) species at 120 °C.

The incorporation of ortho substituents into the metal-bound aryl group resulted in a significant reduction in the reaction rate. For example, the relative rate of elimination from **11** was 3.0 times faster than when one *o*-methyl group was added (**17**) and 18.0 times faster than when two *o*-methyl groups were incorporated into the model system (**23**). While heating **11** (120 °C) for 3 h resulted in 68% consumption, **23** required over 83 h for 50% conversion (120 °C). This reduction in the rate when bulky groups were present is similar to other reductive elimination reactions and could be due to the relative stability of Pd(0) arene species generated from the reaction.

The coordination number and geometry of the metal species have a significant impact on the rate of reductive elimination. The reaction is typically proposed to occur from three- or four-coordinate Pd(II) T-shaped or square-planar species, with the rate of elimination from the three-coordinate species being faster.[4q] For the arylpalladium phosphonates studied, the zero-order dependence upon added ligand, the insensitivity to moderate changes in the solvent polarity, and the presence of the strong chelating bipyridine ligand suggest that the elimination occurred from a four-coordinate Pd(II) species. However, our kinetic studies cannot rule out dissociation of one end of the chelate followed by rapid reductive elimination and either trapping by the free end of the chelating ligand or direct decomposition to Pd(0) and free bu_2bipy. This dissociation process is predicted to be unfavorable, due to the strongly chelating bipyridine ligand and the noncoordinating solvent (benzene). The accelerated rate of reductive elimination in dmso-d_6 could be due to the formation of three-coordinate species that would be favored by the polar solvent. It is also noteworthy to point out that these elimination reactions proceeded in high yield (as determined by NMR: Figure 4 and the Supporting Information) in the absence of a trapping agent for the generated Pd(0). This is in contrast to other carbon−heteroelement bond-forming reactions where additional equivalents of ligand were needed for a high-yielding process.[12a] It is possible that the phosphoryl oxygen could act as a ligand and stabilize the metal center prior to formation of free Pd(0); however, no coordination was observed in the $^{31}P\{^1H\}$ NMR spectrum of the thermolysis reactions, although the coordination/release could be rapid.

Conclusion

The effect of electronic and steric manipulation on arylphosphonate formation from model palladium complexes has been studied. For these compounds, the incorporation of electron-donating groups into the metal-bound aryl fragments accelerated the elimination reaction. Electron-withdrawing groups as well as aryl groups containing ortho substituents induced slower rates of elimination. Little differences were observed in the elimination rates of diethyl and diphenyl phosphonate species.

Experimental Section

General Considerations. Diethyl ether, dichloromethane, and hexane were dried using a Grubbs-style solvent purification system. THF was dried by distillation from Na/benzophenone. The aryl iodides, bu_2bipy, and phosphites were obtained from Aldrich and used as received. $Pd_2(dba)_3$, Ag[P(O)($OEt)_2$], and Ag[P(O)($OPh)_2$] were prepared by following literature procedures.[14] All yields are based upon isolated material unless specified. Elemental analyses were performed by Midwest Microlabs. ^1H and ^{13}C chemical shifts were determined by reference to residual protonated solvent resonances or Me_4Si. All coupling constants are given in hertz. $^{31}P\{^1H\}$ NMR spectra were referenced to external H_3PO_4 (0 ppm). Arylphosphonates were identified by comparison of the spectroscopic data to authentic samples or literature values.[15] Previously uncharacterized arylphosphonates were isolated from the thermolysis reactions as described below. The reaction mixtures were analyzed using ^1H NMR spectroscopy as well as GC and GC-MS for products resulting from secondary reactions. In all cases, less than 1% unidentified material was found.

General Procedure for the Preparation of Arylpalladium Iodides. A reactor vial was charged with $Pd_2(dba)_3$, aryl iodide (1 equiv per Pd), bu_2bipy (1 equiv per Pd), a magnetic stirring bar, and benzene. The reaction mixture was stirred at 23 °C for 48 h. The mixture was filtered, concentrated under vacuum, and triturated with hexane/ether to afford the arylpalladium iodide as a fine powder.

Preparation of (bu_2bipy)Pd(C_6H_5)I (1). The general procedure was followed with iodobenzene (244 μL, 2.18 mmol), bu_2bipy (0.586 g, 2.18 mmol), and $Pd_2(dba)_3$ (1.00 g, 1.09 mmol) to afford 0.415 g (33%) of the title compound as a yellow powder. Anal. Calcd for $C_{24}H_{29}IN_2Pd$: C, 49.80; H, 5.05. Found: C, 49.97; H, 5.04. ^1H NMR ($CDCl_3$, 25 °C): δ 9.50 (d, 1H, J = 5.7, Ar-H), 7.96 (s, 2H, Ar-H), 7.56 (d, 1H, J = 5.9, Ar-H), 7.50 (dd, 1H, J = 5.8, 1.8, Ar-H), 7.40 (d, 2H, J = 6.9, Ar-H), 7.32 (dd, 1H, J = 5.9, 1.9, Ar-H), 7.04 (t, 2H, J = 7.4, Ar-H), 6.91 (t, 1H, J = 7.3, Ar-H), 1.42 (s, 9H, −C*Me*$_3$), 1.38 (s, 9H, −C*Me*$_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 163.11 (s, quat), 163.08 (s, quat), 155.8 (s, quat), 153.8 (s, quat), 152.4 (s, Ar-CH), 149.7 (s, Ar-CH), 146.6 (s, quat), 136.5 (s, Ar-CH), 127.2 (s, Ar-CH), 123.8 (s, Ar-CH), 123.5 (s, Ar-CH), 123.0 (s, Ar-CH), 118.3 (s, Ar-CH), 117.9 (s, Ar-CH), 35.5 (s, −*C*Me$_3$), 35.4 (s, −*C*Me$_3$), 30.4 (s, −C*Me*$_3$), 30.2 (s, −C*Me*$_3$).

Preparation of (bu_2bipy)Pd(4-$C_6H_4NH_2$)I (2). The general procedure was followed with 4-iodoaniline (0.478 g, 2.18 mmol), bu_2bipy (0.586 g, 2.18 mmol), and $Pd_2(dba)_3$ (1.00 g, 1.09 mmol) to afford 0.455 g (35%) of the title compound as a yellow powder. Anal. Calcd for $C_{24}H_{30}IN_3Pd$: C, 48.54; H, 5.09. Found: C, 48.39; H, 4.95. ^1H NMR ($CDCl_3$, 25 °C): δ 9.51 (d, 1H, J = 5.7, Ar-H), 7.95 (s, 2H, Ar-H), 7.74 (d, 1H, J = 5.9, Ar-H), 7.50 (dd, 1H, J = 5.8, 1.8, Ar-H), 7.36 (dd, 1H, 5.9, 1.9, Ar-H), 7.14 (m, 2H, $C_6H_4NH_2$), 6.58 (m, 2H, $C_6H_4NH_2$), 3.39 (s, 2H, $-NH_2$), 1.43 (s, 9H, $-CMe_3$), 1.40 (s, 9H, $-CMe_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 163.0 (s, quat), 162.9 (s, quat), 155.8 (s, quat), 153.8 (s, quat), 152.4 (s, Ar-CH), 149.9 (s, Ar-CH), 142.1 (s, quat), 136.3 (s, Ar-CH), 131.8 (s, quat), 123.7 (s, Ar-CH), 123.4 (s, Ar-CH),

118.2 (s, Ar-CH), 117.8 (s, Ar-CH), 115.8 (s, Ar-CH), 35.4 (s, −*C*Me$_3$), 35.4 (s, −*C*Me$_3$), 30.4 (s, −C*Me*$_3$), 30.2 (s, −C*Me*$_3$).

Preparation of (bu$_2$bipy)Pd(4-C$_6$H$_4$Me)I (3). The general procedure was followed with 4-iodotoluene (0.476 g, 2.18 mmol), bu$_2$bipy (0.586 g, 2.18 mmol), and Pd$_2$(dba)$_3$ (1.00 g, 1.09 mmol) to afford 0.357 g (28%) of the title compound as a yellow powder. Anal. Calcd for $C_{25}H_{31}IN_2Pd$: C, 50.65; H, 5.27. Found: C, 50.56; H, 4.87. ^{1}H NMR (CDCl$_3$, 25 °C): δ 9.52 (d, 1H, J = 5.7, Ar-H), 7.96 (s, 2H, Ar-H), 7.66 (AA′BB′, 1H, J = 5.9, Ar-H), 7.50 (dd, 1H, J = 5.7, 1.7, Ar-H), 7.34 (dd, 1H, J = 5.9, 1.8, Ar-H), 7.28 (d, 2H, J = 7.8, Ar-H), 6.90 (d, 2H, J = 7.8, Ar-H), 2.30 (s, 3H, -Me), 1.43 (s, 9H, CMe$_3$), 1.39 (s, 9H, CMe$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C): δ 163.04 (s, quat), 162.98 (s, quat), 155.8 (s, quat), 153.8 (s, quat), 152.5 (s, Ar-CH), 149.9 (s, Ar-CH), 141.7 (s, quat), 136.2 (s, Ar-CH), 132.1 (s, quat), 128.4 (s, Ar-CH), 123.8 (s, Ar-CH), 123.5 (s, Ar-CH), 118.2 (s, Ar-CH), 117.8 (s, Ar-CH), 35.5 (s, −*C*Me$_3$), 35.4 (s, −*C*Me$_3$), 30.4 (s, −C*Me*$_3$), 30.3 (s, −C*Me*$_3$), 20.7 (s, −Me).

Preparation of (bu$_2$bipy)Pd(2-C$_6$H$_4$Me)I (4). The general procedure was followed with 2-iodotoluene (278 μL, 2.18 mmol), bu$_2$bipy (0.586 g, 2.18 mmol), and Pd$_2$(dba)$_3$ (1.00 g, 1.09 mmol) to afford 0.401 g (31%) of the title compound as a yellow powder. Anal. Calcd for $C_{25}H_{31}IN_2Pd$: C, 50.65; H, 5.27. Found: C, 51.00; H, 5.38. ^{1}H NMR (CDCl$_3$, 25 °C): δ 9.51 (d, 1H, J = 5.7, Ar-H), 7.97 (s, 2H, Ar-H), 7.52 (dd, 1H, J = 5.7, 1.8, Ar-H), 7.42 (m, 1H, Ar-H), 7.40 (d, 1H, J = 5.9, Ar-H), 7.30 (dd, 1H, J = 5.9, 1.9, Ar-H), 6.99 (m, 1H, Ar-H), 6.87 (m, 2H, Ar-H), 2.61 (s, 3H, -Me), 1.44 (s, 9H, −CMe$_3$), 1.40 (s, 9H, −CMe$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C): δ 163.1 (s, quat), 163.0 (s, quat), 155.9 (s, quat), 153.7 (s, quat), 152.4 (s, Ar-CH), 149.3 (s, Ar-CH), 147.3 (s, quat), 141.3 (s, quat), 136.2 (s, Ar-CH), 128.7 (s, Ar-CH), 124.0 (s, Ar-CH), 123.9 (s, Ar-CH), 123.7 (s, Ar-CH), 123.2 (s, Ar-CH), 118.3 (s, Ar-CH), 117.8 (s, Ar-CH), 35.5 (s, −*C*Me$_3$), 35.4 (s, −*C*Me$_3$), 30.4 (s, −C*Me*$_3$), 30.3 (s, −C*Me*$_3$), 26.9 (s, −Me).

Preparation of (bu$_2$bipy)Pd(4-C$_6$H$_4$OMe)I (5). The general procedure was followed with 4-iodoanisole (0.511 g, 2.18 mmol), bu$_2$bipy (0.586 g, 2.18 mmol), and Pd$_2$(dba)$_3$ (1.00 g, 1.09 mmol) to afford 0.310 g (23%) of the title compound as a yellow powder. Anal. Calcd for $C_{25}H_{31}IN_2OPd$: C, 49.32; H, 5.13. Found: C, 49.23; H, 5.73. ^{1}H NMR (CDCl$_3$, 25 °C): δ 9.52 (d, 1H, J = 5.7, Ar-H), 7.96 (s, 2H, Ar-H), 7.64 (d, 1H, J = 5.9, Ar-H), 7.51 (dd, 1H, J = 5.7, 1.7, Ar-H), 7.34 (dd, 1H, J = 5.9, 1.9, Ar-H), 7.27 (d, 2H, J = 7.1, Ar-H), 6.76 (d, 2H, J = 7.0, Ar-H), 3.79 (s, 3H, −OMe), 1.43 (s, 9H, −CMe$_3$), 1.40 (s, 9H, −CMe$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C): δ 163.09 (s, quat), 163.05 (s, quat), 156.6 (s, quat), 155.9 (s, quat), 153.8 (s, quat), 152.5 (s, Ar-CH), 149.8 (s, Ar-CH), 136.3 (s, Ar-CH), 134.1 (s, quat), 123.8 (s, Ar-CH), 123.5 (s, Ar-CH), 118.2 (s, Ar-CH), 117.9 (s, Ar-CH), 113.6 (s, Ar-CH), 55.1 (s, −OMe), 35.5 (s, −*C*Me$_3$), 35.4 (s, −*C*Me$_3$), 30.4 (s, −C*Me*$_3$), 30.2 (s, −C*Me*$_3$).

Preparation of (bu$_2$bipy)Pd(2-C$_6$H$_4$OMe)I (6). The general procedure was followed with 2-iodoanisole (284 μL, 2.18 mmol), bu$_2$bipy (0.586 g, 2.18 mmol), and Pd$_2$(dba)$_3$ (1.00 g, 1.09 mmol) to afford 0.489 g (37%) of the title compound as a yellow powder. Anal. Calcd for $C_{25}H_{31}IN_2OPd$: C, 49.32; H, 5.13. Found: C, 48.93; H, 5.01. ^{1}H NMR (CDCl$_3$, 25 °C): δ 9.55 (d, 1H, J = 5.7, Ar-H), 7.95 (s, 2H, Ar-H), 7.57 (d, 1H, J = 5.9, Ar-H), 7.49 (dd, 1H, J = 5.7, 1.6, Ar-H), 7.42 (dd, 1H, J = 7.2, 1.4, Ar-H), 7.29 (dd, 1H, J = 6.0, 1.9, Ar-H), 6.97 (dt, 1H, J = 8.0, 1.4, Ar-H), 6.73 (dt, 1H, J = 7.1, 1.0, Ar-H), 6.68 (dt, 1H, J = 8.0, 1.0, Ar-H), 3.81 (s, 3H, −OMe), 1.42 (s, 9H, −CMe$_3$), 1.38 (s, 9H, −CMe$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C): δ 163.05 (s, quat), 162.94 (s, quat), 156.0 (s, quat), 154.1 (s, quat), 152.7 (s, Ar-CH), 149.8 (s, Ar-CH), 138.1 (s, Ar-CH), 132.5 (s, quat), 128.9 (s, quat), 124.3 (s, Ar-CH), 123.7 (s, Ar-CH), 123.4 (s, Ar-CH), 120.3 (s, Ar-CH), 118.3 (s, Ar-CH), 117.8 (s, Ar-CH), 111.6 (s, Ar-CH), 56.3 (s, −OMe), 35.42 (s, −*C*Me$_3$), 35.39 (s, −*C*Me$_3$), 30.3 (s, −C*Me*$_3$), 30.2 (s, −C*Me*$_3$).

Preparation of (bu$_2$bipy)Pd(2,6-C$_6$H$_3$Me$_2$)I (7). The general procedure was followed with 2-iodo-*m*-xylene (315 μL, 2.18 mmol), bu$_2$bipy (0.586 g, 2.18 mmol), and Pd$_2$(dba)$_3$ (1.00 g, 1.09 mmol) to afford 0.659 g (50%) of the title compound as a yellow powder. Anal. Calcd for $C_{26}H_{33}IN_2Pd$: C, 51.46; H, 5.48. Found: C, 51.42; H, 5.49. ^{1}H NMR (CDCl$_3$, 25 °C): δ 9.50 (d, 1H, J = 5.7, Ar-H), 7.97 (s, 2H, Ar-H), 7.53 (dd, 1H, J = 5.8, 1.7, Ar-H), 7.33−7.26 (m, 2H, Ar-H), 6.80 (m, 3H, Ar-H), 2.65 (s, 6H, −Me), 1.43 (s, 9H, −C*Me*$_3$), 1.39 (s, 9H, −C*Me*$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C): δ 162.98 (s, quat), 162.95 (s, quat), 156.0 (s, quat), 153.6 (s, quat), 152.2 (s, Ar-CH), 148.8 (s, Ar-CH), 148.0 (s, quat), 141.1 (s, quat), 125.5 (s, Ar-CH), 123.9 (s, Ar-CH), 123.8 (s, Ar-CH), 123.7 (s, Ar-CH), 118.4 (s, Ar-CH), 117.8 (s, Ar-CH), 35.5 (s, −*C*Me$_3$), 35.4 (s, −*C*Me$_3$), 30.4 (s, −C*Me*$_3$), 30.2 (s, −C*Me*$_3$), 27.4 (s, −Me).

Preparation of (bu$_2$bipy)Pd(4-C$_6$H$_4$CN)I (8). The general procedure was followed with 4-iodobenzonitrile (0.500 g, 2.18 mmol), bu$_2$bipy (0.586 g, 2.18 mmol), and Pd$_2$(dba)$_3$ (1.00 g, 1.09 mmol) to afford 0.653 g (49%) of the title compound as a yellow powder. Anal. Calcd for $C_{25}H_{28}IN_3Pd$: C, 49.73; H, 4.67. Found: C, 49.68; H, 4.58. ^{1}H NMR (CDCl$_3$, 25 °C): δ 9.50 (d, 1H, J = 5.7, Ar-H), 7.98 (d, 1H, J = 1.8, Ar-H), 7.97 (d, 1H, J = 1.8, Ar-H), 7.61 (AA′BB′, 2H, Ar-H), 7.53 (dd, 1H, J = 5.7, 1.8, Ar-H), 7.45 (d, 1H, J = 5.9, Ar-H), 7.37 (dd, 1H, J = 6.0, 1.9, Ar-H), 7.28 (AA′BB′, 2H, Ar-H), 1.43 (s, 9H, −C*Me*$_3$), 1.41 (s, 9H, −C*Me*$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C): δ 163.8 (s, quat), 163.6 (s, quat), 158.1 (s, quat), 156.0 (s, quat), 153.8 (s, quat), 152.6 (s, Ar-CH), 149.3 (s, Ar-CH), 137.7 (s, Ar-CH), 128.9 (s, Ar-CH), 124.1 (s, Ar-CH), 123.7 (s, Ar-CH), 120.2 (s, quat), 118.7 (s, Ar-CH), 118.2 (s, Ar-CH), 106.4 (s, quat), 35.6 (s, −*C*Me$_3$), 35.5 (s, −*C*Me$_3$), 30.3 (s, −C*Me*$_3$), 30.2 (s, −C*Me*$_3$).

Preparation of (bu$_2$bipy)Pd(4-C$_6$H$_4$NO$_2$)I (9). The general procedure was followed with 4-iodonitrobenzene (0.543 g, 2.18 mmol), bu$_2$bipy (0.586 g, 2.18 mmol), and Pd$_2$(dba)$_3$ (1.00 g, 1.09 mmol) to afford 0.541 g (40%) of the title compound as a yellow powder. Anal. Calcd for $C_{24}H_{28}IN_3O_2Pd$: C, 46.21; H, 4.52. Found: C, 46.46; H, 4.41. ^{1}H NMR (CDCl$_3$, 25 °C): δ 9.50 (d, 1H, J = 5.8, Ar-H), 8.00 (d, 1H, J = 1.8, Ar-H), 7.98 (d, 1H, J = 1.7, Ar-H), 7.89 (AA′BB′, 2H, Ar-H), 7.69 (AA′BB′, 2H, Ar-H), 7.54 (dd, 1H, J = 5.8, 1.7, Ar-H), 7.44 (d, 1H, J = 5.9, Ar-H), 7.36 (dd, 1H, J = 5.9, 1.8, Ar-H), 1.44 (s, 9H, −C*Me*$_3$), 1.40 (s, 9H, −C*Me*$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C): δ 163.9 (s, quat), 163.7 (s, quat), 162.7 (s, quat), 156.0 (s, quat), 153.8 (s, quat), 152.8 (s, Ar-CH), 149.3 (s, Ar-CH), 145.3 (s, quat), 137.2 (s, Ar-CH), 124.1 (s, Ar-CH), 123.8 (s, Ar-CH), 120.6 (s, Ar-CH), 118.7 (s, Ar-CH), 118.2 (s, Ar-CH), 35.6 (s, −*C*Me$_3$), 35.5 (s, −*C*Me$_3$), 30.4 (s, −C*Me*$_3$), 30.2 (s, −C*Me*$_3$).

Preparation of (bu$_2$bipy)Pd(4-C$_6$H$_4$Cl)I (10). The general procedure was followed with 4-iodochlorobenzene (0.521 g, 2.18 mmol), bu$_2$bipy (0.586 g, 2.18 mmol), and Pd$_2$(dba)$_3$ (1.00 g, 1.09 mmol) to afford 0.526 g (39%) of the title compound as a yellow powder. Anal. Calcd for $C_{24}H_{28}ClIN_2Pd$: C, 47.00; H, 4.60. Found: C, 47.33; H, 4.72. ^{1}H NMR (CDCl$_3$, 25 °C): δ 9.48 (d, 1H, J = 5.7, Ar-H), 7.97 (s, 2H, Ar-H), 7.58 (d, 1H, J = 5.9, Ar-H), 7.51 (dd, 1H, J = 5.6, 1.3, Ar-H), 7.35 (m, 3H, Ar-H), 7.04 (d, 2H, J = 8.15, Ar-H), 1.43 (s, 9H, Ar-H), 1.40 (s, 9H, Ar-H). ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C): δ 163.4 (s, quat), 163.3 (s, quat), 155.9 (s, quat), 153.8 (s, quat), 152.6 (s, Ar-CH), 149.6 (s, Ar-CH), 144.1 (s, quat), 137.5 (s, Ar-CH), 129.4 (s, quat), 126.9 (s, Ar-CH), 123.9 (s, Ar-CH), 123.6 (s, Ar-CH), 118.4 (s, Ar-CH), 118.0 (s, Ar-CH), 35.5 (s, −*C*Me$_3$), 35.4 (s, −*C*Me$_3$), 30.4 (s, −C*Me*$_3$), 30.2 (s, −C*Me*$_3$).

General Procedure for the Preparation of the Arylpalladium Phosphonates. A 10 mL reactor vial was charged with the arylpalladium iodide, Ag[P(O)(OR)$_2$], solvent, and a magnetic stirring bar. The reaction mixture was stirred for 2 h in the dark and filtered to remove the silver salts. After purification by column

chromatography (Et_2O/CH_2Cl_2), the residue was triturated with ether/hexane to afford the aryl palladium phosphonates as fine powders.

Synthesis of (bu$_2$bipy)PdPh(P(O)(OEt)$_2$) (11). The general procedure was followed using (bu$_2$bipy)PdPhI (0.215 g, 0.371 mmol), Ag[P(O)(OEt)$_2$] (0.0910 g, 0.371 mmol), and CH_2Cl_2 (5 mL). After purification by column chromatography, the title compound was isolated as a tan solid (0.196 g, 90%). Anal. Calcd for $C_{28}H_{39}N_2O_3PPd$: C, 57.10; H, 6.67. Found: C, 56.84; H, 6.45. ^{1}H NMR ($CDCl_3$, 25 °C): δ 10.01 (d, 1H, J = 5.7, Ar-H), 7.96 (s, 2H, Ar-H), 7.60−7.53 (m, 3H, Ar-H), 7.48 (dd, 1H, Ar-H), 7.31−7.24 (m, 1H, Ar-H), 7.08 (t, 2H, J = 7.3, Ar-H), 7.00 (t, 1H, Ar-CH), 3.91 (m, 4H, −OCH_2CH$_3$), 1.42 (s, 9H, −CMe_3), 1.37 (s, 9H, −CMe_3), 1.13 (t, 6H, −OCH$_2$CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ 163.5 (s, quat), 163.0 (s, quat), 155.3 (s, quat), 155.2 (d, J = 1.8, quat), 154.4 (d, J = 1.7, quat), 153.8 (s, Ar-CH), 149.8 (d, J = 1.9, Ar-CH), 136.5 (d, J = 5.3, Ar-CH), 127.0 (d, J = 3.2, Ar-CH), 123.5 (s, Ar-CH), 123.1 (d, J = 3.1, Ar-CH), 123.0 (s, Ar-CH), 117.7 (s, Ar-CH), 117.6 (d, J = 2.9, Ar-CH), 57.8 (d, J = 4.8, −OCH_2CH$_3$), 35.4 (s, −CMe$_3$), 35.3 (s, −CMe$_3$), 30.37 (s, −CMe_3), 30.32 (s, −CMe_3), 16.6 (d, J = 4.8, −OCH$_2$$CH_3$). ^{31}P{^{1}H} NMR ($CDCl_3$, 25 °C): δ 69.6 (s).

Synthesis of (bu$_2$bipy)PdPh(P(O)(OPh)$_2$) (12). The general procedure was followed using (bu$_2$bipy)PdPhI (0.246 g, 0.425 mmol), Ag[P(O)(OPh)$_2$] (0.145 g, 0.425 mmol), and THF (5 mL). After purification by column chromatography, the title compound was isolated as a white solid (0.285 g, 98%). Anal. Calcd for $C_{36}H_{39}N_2O_3PPd$: C, 63.11; H, 5.74. Found: C, 63.46; H, 5.32. ^{1}H NMR ($CDCl_3$, 25 °C): δ 10.01 (d, 1H, J = 5.73, Ar-H), 7.98 (s, 2H, Ar-H), 7.55 (dd, 1H, J = 5.8, 1.8, Ar-H), 7.40 (m, 3H, Ar-H), 7.23 (m, 8H, Ar-H), 7.02 (m, 6H, Ar-H), 1.44 (s, 9H, −CMe$_3$), 1.37 (s, 9H, −CMe$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ 163.8 (s, quat), 163.2 (s, quat), 155.2 (d, J = 1.8, quat), 154.4 (d, J = 1.0, quat), 154.2 (d, J = 1.8, quat), 153.7 (s, Ar C), 152.9 (d, J = 8.5, quat), 149.9 (d, J = 2.0, Ar C), 136.1 (d, J = 5.3, Ar C), 128.8 (s, Ar C), 127.0 (d, J = 3.55, Ar C), 123.7 (s, Ar C), 123.3 (s, Ar C), 123.2 (s, J = 3.1, Ar C), 122.3 (s, Ar C), 121.2 (d, J = 5.5, Ar C), 117.8 (s, Ar C), 117.7 (d, J = 3.0, Ar C), 35.4 (s, −CMe$_3$), 35.3 (s, −CMe$_3$), 30.4 (s, −CMe_3), 30.3 (s, −CMe_3). ^{31}P{^{1}H} NMR ($CDCl_3$, 25 °C): δ 67.8 (s).

Synthesis of (bu$_2$bipy)Pd(4-C$_6$H$_4$NH$_2$)(P(O)(OEt)$_2$) (13). The general procedure was followed using (bu$_2$bipy)Pd(4-C$_6$H$_4$NH$_2$)I (0.232 g, 0.391 mmol), Ag[P(O)(OEt)$_2$] (0.0958 g, 0.391 mmol), and CH_2Cl_2 (5 mL). After purification by column chromatography, the title compound was isolated as an orange solid (0.187 g, 79%). Anal. Calcd for $C_{28}H_{40}N_3O_3PPd$: C, 55.68; H, 6.67. Found: C, 55.60; H, 6.51. ^{1}H NMR ($CDCl_3$, 25 °C): δ 10.25 (d, 1H, J = 5.7, Ar-H), 8.19 (s, 2H, Ar-H), 7.85 (dd, 1H, J = 5.6, 3.1, Ar-H), 7.76 (dd, 1H, J = 4.0, 5.8, Ar-H), 7.67−7.50 (m, 3H, Ar-H), 6.87 (m, 2H, Ar-H), 4.20 (m, 4H, −OCH_2CH$_3$), 3.67 (s, 2H, −NH$_2$), 1.66 (s, 9H, −CMe$_3$), 1.61 (s, 9H, −CMe$_3$), 1.40 (t, 6H, −OCH$_2$CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ 163.3 (s, quat), 162.8 (s, quat), 155.0 (d, J = 1.7, quat), 154.4 (d, J = 1.3, quat), 153.7 (s, Ar-CH), 149.9 (d, J = 1.9, Ar-CH), 136.4 (d, J = 5.4, Ar-CH), 130.5 (s, quat), 123.4 (s, Ar-CH), 123.0 (d, J = 2.9, Ar-CH), 117.6 (s, Ar-CH), 117.5 (d, J = 3.0, Ar-CH), 115.5 (s, Ar-CH), 57.7 (d, J = 4.5, −OCH$_2$CH$_3$), 35.32 (s, −CMe$_3$), 35.26 (s, −CMe$_3$), 30.32 (s, −CMe_3), 30.28 (s, −CMe_3), 16.6 (d, J = 7.3, −OCH$_2$CH$_3$). ^{31}P{^{1}H} NMR ($CDCl_3$, 25 °C): δ 69.7 (s).

Synthesis of (bu$_2$bipy)Pd(4-C$_6$H$_4$NH$_2$)(P(O)(OPh)$_2$) (14). The general procedure was followed using (bu$_2$bipy)Pd(4-C$_6$H$_4$NH$_2$)I (0.254 g, 0.428 mmol), Ag[P(O)(OPh)$_2$] (0.146 g, 0.428 mmol), and THF (5 mL). After purification by column chromatography, the title compound was isolated as an orange solid (0.209 g, 70%). Anal. Calcd for $C_{36}H_{40}N_3O_3PPd$: C, 61.76; H, 5.76. Found: C, 61.50; H, 5.51. ^{1}H NMR ($CDCl_3$, 25 °C): δ 10.16 (d, 1H, J = 5.6, Ar-H), 8.04 (s, 2H, Ar-H), 7.62−7.00 (m, 15H, Ar-H), 6.60 (AA′BB′, 2H, Ar-H), 3.49 (s, 2H, −NH$_2$), 1.51 (s, 9H, −CMe$_3$), 1.44 (s, 9H, −CMe$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ 163.7 (s, quat), 163.1 (s, quat), 155.1 (s, quat), 154.3 (s, quat), 153.6 (d, J = 153.6, Ar-CH), 152.9 (d, J = 8.08, quat), 150.1 (s, quat), 136.1 (d, J = 5.5, Ar-CH), 129.6 (s, quat), 128.8 (s, Ar-CH), 123.7 (s, Ar-CH), 123.2 (s, Ar-CH), 122.3 (s, Ar-CH), 121.2 (d, J = 5.6, Ar-CH), 117.8 (s, Ar-CH), 117.6 (d, J = 2.1, Ar-CH), 115.5 (s, Ar-CH), 35.39 (s, −CMe$_3$), 35.35 (s, −CMe$_3$), 30.34 (s, −CMe_3), 30.29 (s, −CMe_3). ^{31}P{^{1}H} NMR ($CDCl_3$, 25 °C): δ 69.4 (s).

Synthesis of (bu$_2$bipy)Pd(4-C$_6$H$_4$Me)(P(O)(OEt)$_2$) (15). The general procedure was followed using (bu$_2$bipy)Pd(4-C$_6$H$_4$Me)I (0.257 g, 0.433 mmol), Ag[P(O)(OEt)$_2$] (0.106, 0.433 mmol), and CH_2Cl_2 (5 mL). After purification by column chromatography, the title compound was isolated as a white solid (0.234 g, 90%). Anal. Calcd for $C_{29}H_{41}N_2O_3PPd$: C, 57.76; H, 6.85. Found: C, 57.83; H, 6.89. ^{1}H NMR ($CDCl_3$, 25 °C): δ 9.96 (d, 1H, J = 5.7, Ar-H), 7.87 (s, 2H, Ar-H), 7.45 (m, 2H, Ar-H), 7.36 (m, 2H, Ar-H), 7.18 (m, 1H, Ar-H), 6.83 (AA′BB′, 2H, Ar-H), 3.85 (m, 4H, −OCH_2-CH$_3$), 2.20 (s, 3H, ArMe), 1.33 (s, 9H, −CMe_3), 1.28 (s, 9H, −CMe_3), 1.06 (t, 6H, J = 7.0, −OCH$_2$CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ 163.4 (s, quat), 162.8 (s, quat), 155.1 (d, J = 1.7, quat), 154.4 (d, J = 1.7, quat), 153.8 (s, Ar-CH), 150.5 (s, quat), 149.9 (d, J = 1.9, Ar-CH), 136.1 (d, J = 5.3, Ar-CH), 131.9 (s, quat), 127.9 (d, J = 3.5, Ar-CH), 123.5 (s, Ar-CH), 123.1 (d, J = 3.0, Ar-CH), 117.7 (s, Ar-CH), 117.5 (d, J = 3.0, Ar-CH), 57.7 (d, J = 4.5, −OCH$_2$CH$_3$), 35.35 (s, −CMe$_3$), 35.29 (s, −CMe$_3$), 30.33 (s, −CMe_3), 30.29 (s, −CMe_3), 21.0 (s, −ArMe), 16.6 (d, J = 7.3, −OCH$_2$$CH_3$). ^{31}P{^{1}H} NMR ($CDCl_3$, 25 °C): δ 70.1 (s).

Synthesis of (bu$_2$bipy)Pd(4-C$_6$H$_4$Me)(P(O)(OPh)$_2$) (16). The general procedure was followed using (bu$_2$bipy)Pd(4-C$_6$H$_4$Me)I (0.250, 0.422 mmol), Ag[P(O)(OPh)$_2$] (0.144 g, 0.422 mmol), and THF (5 mL). After purification by column chromatography, the title compound was isolated as a white solid (0.210 g, 71%). Anal. Calcd for $C_{37}H_{41}N_2O_3PPd$: C, 63.56; H, 5.91. Found: C, 63.41; H, 5.92. ^{1}H NMR ($CDCl_3$, 25 °C): δ 10.08 (d, 1H, J = 5.7, Ar-H), 7.95 (s, 2H, Ar-H), 7.53 (dd, 1H, J = 5.8, 1.8, Ar-H), 7.42 (dd, 1H, J = 5.8, 3.5, Ar-H), 7.30−7.13 (m, 11H, Ar-H), 6.94 (t, 2H, J = 7.05, Ar-H), 6.86 (d, 2H, J = 7.7, Ar-H), 2.28 (s, 3H, −Me), 1.42 (s, 9H, −CMe$_3$), 1.35 (s, 9H, −CMe$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ 163.7 (s, quat), 163.1 (s, quat), 155.2 (d, J = 1.7, quat), 154.2 (d, J = 2.0, quat), 153.6 (s, Ar-CH), 152.9 (d, J = 8.3, quat), 149.9 (d, J = 1.9, Ar-CH), 149.6 (s, quat), 135.7 (d, J = 5.4, Ar-CH), 132.2 (s, quat), 128.7 (s, Ar-CH), 127.9 (d, J = 3.6, Ar-CH), 123.6 (s, Ar-CH), 123.2 (d, J = 3.2, Ar-CH), 122.3 (s, Ar-CH), 121.2 (d, J = 5.5, Ar-CH), 117.8 (s, Ar-CH), 117.7 (d, J = 3.0, Ar-CH), 35.4 (s, −CCH$_3$), 35.3 (s, −CCH$_3$), 30.33 (s, −CMe_3), 30.25 (s, −CMe_3), 21.0 (s, −CH$_3$). ^{31}P{^{1}H} NMR ($CDCl_3$, 25 °C): δ 68.3 (s).

Synthesis of (bu$_2$bipy)Pd(2-C$_6$H$_4$Me)(P(O)(OEt)$_2$) (17). The general procedure was followed using (bu$_2$bipy)Pd(2-C$_6$H$_4$Me)I (0.383 g, 0.646 mmol), Ag[P(O)(OEt)$_2$] (0.158 g, 0.646 mmol), and CH_2Cl_2 (5 mL). After purification by column chromatography, the title compound was isolated as a gray solid (0.306 g, 79%). Anal. Calcd for $C_{29}H_{41}N_2O_3PPd$: C, 57.76; H, 6.85. Found: C, 57.52; H, 6.92. ^{1}H NMR ($CDCl_3$, 25 °C): δ 9.99 (d, 1H, J = 5.7, Ar-H), 7.96 (s, 2H, Ar-H), 7.59−7.54 (m, 2H, Ar-H), 7.32 (m, 1H, Ar-H), 7.24 (m, 1H, Ar-H), 7.03−6.87 (m, 3H, Ar-H), 3.86 (m, 4H, −OCH_2CH$_3$), 2.60 (s, 3H, Ar Me), 1.43 (s, 9H, −CMe_3), 1.37 (s, 9H, −CMe_3), 1.17 (t, 3H, J = 7.0, −OCH_2CH$_3$), 1.09 (t, 3H, J = 7.0, −OCH_2CH$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ 163.3 (s, quat), 162.8 (s, quat), 156.4 (d, J = 2.3, quat), 155.1 (d, J = 1.7, quat), 154.2 (d, J = 1.6, quat), 153.5 (s, Ar-CH), 149.1 (d, J = 2.0, Ar-CH), 142.04 (s, quat), 142.00 (s, quat), 136.3 (d, J = 6.5, Ar-CH), 127.9 (s, Ar-CH), 123.5 (d, J = 5.2, Ar-CH), 123.4 (s, Ar-CH), 123.2 (d, J = 3.0, Ar-CH), 122.9 (s, Ar-CH), 117.6 (s, Ar-CH), 117.5 (d, J = 3.2, Ar-CH), 57.6 (d, J = 5.1, −OCH_2-CH$_3$), 57.4 (d, J = 6.3, −OCH$_2$CH$_3$), 35.3 (s, −CMe$_3$), 35.2 (s,

−*C*Me$_3$), 30.24 (s, −C*Me*$_3$), 30.19 (s, −C*Me*$_3$), 26.7 (s, −Me), 26.6 (s, −Me), 16.6 (d, J = 7.3, −OCH$_2$*C*H$_3$), 16.5 (d, J = 6.9, −OCH$_2$*C*H$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$, 25 °C): δ 70.2 (s).

Synthesis of (bu$_2$bipy)Pd(2-C$_6$H$_4$Me)(P(O)(OPh)$_2$) (18). The general procedure was followed using (bu$_2$bipy)Pd(2-C$_6$H$_4$Me)I (0.456, 0.769 mmol), Ag[P(O)(OPh)$_2$] (0.262 g, 0.769 mmol), and THF (5 mL). After purification by column chromatography, the title compound was isolated as a white solid (0.395 g, 73%). Anal. Calcd for $C_{37}H_{41}N_2O_3PPd$: C, 63.56; H, 5.91. Found: C, 63.83; H, 5.99. ^{1}H NMR (CDCl$_3$, 25 °C): δ 10.04 (d, 1H, J = 5.7, Ar-H), 7.98 (s, 2H, Ar-CH), 7.52 (dd, 1H, J = 5.8, 1.9, Ar-H), 7.43 (m, 1H, Ar-H), 7.32 (m, 1H, Ar-H), 7.26−6.87 (m, 14H, Ar-H), 2.47 (s, 3H, Ar Me), 1.43 (s, 9H, −CMe$_3$), 1.36 (s, 9H, −CMe$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C): δ 163.8 (s, quat), 163.1 (s, quat), 155.7 (d, J = 3.0, quat), 155.4 (d, J = 1.7, quat), 154.2 (d, J = 2.1, quat), 153.5 (s, Ar-CH), 152.9 (d, J = 8.5, quat), 152.7 (d, J = 11.1, quat), 149.4 (d, J = 2.0, Ar-CH), 142.00 (d, J = 2.8, quat), 136.0 (d, J = 7.02, Ar-CH), 128.8 (s, Ar-CH), 128.6 (s, Ar-CH), 128.4 (s, Ar-CH), 123.8 (d, J = 4.0, Ar-CH), 123.7 (s, Ar-CH), 123.37 (d, J = 3.2, Ar-CH), 123.35 (s, Ar-CH), 122.4 (s, Ar-CH), 122.3 (s, Ar-CH), 121.3 (d, J = 5.6, Ar-CH), 121.2 (d, J = 5.1, Ar-CH), 117.9 (d, J = 3.2, Ar-CH), 117.8 (s, Ar-CH), 35.42 (s, −*C*Me$_3$), 35.36 (s, −*C*Me$_3$), 30.34 (s, −C*Me*$_3$), 30.28 (s, −C*Me*$_3$), 26.44 (s, −Me), 26.37 (s, −Me). ^{31}P{^{1}H} NMR (CDCl$_3$, 25 °C): δ 68.6 (s).

Synthesis of (bu$_2$bipy)Pd(4-C$_6$H$_4$OMe)(P(O)(OEt)$_2$) (19). The general procedure was followed using (bu$_2$bipy)Pd(4-C$_6$H$_4$OMe)I (0.218 g, 0.358 mmol), Ag[P(O)(OEt)$_2$] (0.0877 g, 0.358 mmol), and CH$_2$Cl$_2$ (5 mL). After purification by column chromatography, the title compound was isolated as a off-white solid (0.201 g, 91%). Anal. Calcd for $C_{29}H_{41}N_2O_4PPd$: C, 56.27; H, 6.68. Found: C, 56.20; H, 6.56. ^{1}H NMR (CDCl$_3$, 25 °C): δ 10.04 (d, 1H, J = 5.7, Ar-H), 7.96 (s, 1H, Ar-H), 7.95 (s, 1H, Ar-H), 7.53 (m, 2H, Ar-H), 7.45 (m, 2H, Ar-H), 7.26 (m, 1H, Ar-H), 6.75 (AA′BB′, 2H, Ar-H), 3.94 (m, 4H, −OC*H*$_2$CH$_3$), 3.80 (s, 3H, −OMe), 1.42 (s, 9H, −C*Me*$_3$), 1.37 (s, 9H, −C*Me*$_3$), 1.15 (t, 6H, −OCH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C): δ 163.4 (s, quat), 162.9 (s, quat), 156.4 (d, J = 1.8, quat), 155.1 (d, J = 1.7, quat), 154.4 (s, quat), 153.8 (s, Ar-CH), 149.9 (d, J = 1.5, Ar-CH), 143.7 (s, quat), 136.4 (d, J = 5.5, Ar-CH), 123.5 (s, Ar-CH), 123.1 (d, J = 3.0, Ar-CH), 117.7 (s, Ar-CH), 117.5 (d, J = 3.0, Ar-CH), 113.1 (d, J = 3.6, Ar-CH), 57.7 (d, J = 4.5, −OCH$_2$CH$_3$), 55.0 (s, −OMe), 35.4 (s, −*C*Me$_3$), 35.3 (s, −*C*Me$_3$), 30.33 (s, −C*Me*$_3$), 30.30 (s, −C*Me*$_3$), 16.6 (d, J = 7.3, −OCH$_2$*C*H$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$, 25 °C): δ 69.4 (s).

Synthesis of (bu$_2$bipy)Pd(4-C$_6$H$_4$OMe)(P(O)(OPh)$_2$) (20). The general procedure was followed using (bu$_2$bipy)Pd(4-C$_6$H$_4$OMe)I (0.304 g, 0.499 mmol), Ag[P(O)(OPh)$_2$] (0.170 g, 0.499 mmol), and THF (5 mL). After purification by column chromatography, the title compound was isolated as a white solid (0.301 g, 84%). Anal. Calcd for $C_{37}H_{41}N_2O_4PPd$: C, 62.14; H, 5.78. Found: C, 62.11; H, 5.73. ^{1}H NMR (CDCl$_3$, 25 °C): δ 10.08 (d, 1H, J = 5.7, Ar-H), 7.96 (s, 2H, Ar-H), 7.54 (dd, 1H, J = 5.9, 1.9, Ar-H), 7.41 (dd, 1H, J = 5.8, 3.4, Ar-H), 7.26−7.14 (m, 11H, Ar-H), 6.95 (t, 2H, J = 7.15, Ar-H), 6.69 (AA′BB′, 2H, Ar-H), 3.79 (s, 3H, −OMe), 1.42 (s, 9H, −CMe$_3$), 1.36 (s, 9H, −CMe$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C): δ 163.8 (s, quat), 163.2 (s, quat), 156.6 (s, quat), 155.2 (d, J = 1.7, quat), 154.3 (d, J = 1.8, quat), 153.6 (s, Ar-CH), 152.9 (d, J = 8.4, quat), 149.9 (d, J = 1.8, Ar-CH), 142.7 (s, quat), 136.1 (d, J = 5.8, Ar-CH), 128.8 (s, Ar-CH), 123.7 (s, Ar-CH), 123.2 (d, J = 3.2, Ar-CH), 122.3 (s, Ar-CH), 121.2 (d, J = 5.6, Ar-CH), 117.8 (s, Ar-CH), 117.7 (d, J = 3.2, Ar-CH), 113.1 (d, J = 3.8, Ar-CH), 55.1 (s, −OMe), 35.4 (s, −*C*Me$_3$), 35.3 (s, −*C*Me$_3$), 30.33 (s, −C*Me*$_3$), 30.27 (s, −C*Me*$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$, 25 °C): δ 67.8 (s).

Synthesis of (bu$_2$bipy)Pd(2-C$_6$H$_4$OMe)(P(O)(OEt)$_2$) (21). The general procedure was followed using (bu$_2$bipy)Pd(2-C$_6$H$_4$OMe)I (0.257 g, 0.422 mmol), Ag[P(O)(OEt)$_2$] (0.103 g, 0.422 mmol), and CH$_2$Cl$_2$ (5 mL). After purification by column chromatography, the title compound was isolated as a pale yellow solid (0.175 g, 67%). Anal. Calcd for $C_{29}H_{41}N_2O_4PPd$: C, 56.27; H, 6.68. Found: C, 56.65; H, 6.69. ^{1}H NMR (CDCl$_3$, 25 °C): δ 10.02 (d, 1H, J = 5.0, Ar-H), 7.94 (s, 2H, Ar-H), 7.59−7.49 (m, 3H, Ar-H), 7.23 (m, 1H, Ar-H), 7.06 (dt, 1H, J = 8.6, 1.5, Ar-H), 6.78 (t, 1H, J = 7.3, Ar-H), 6.69 (m, 1H, Ar-H), 3.90 (m, 4H, −OC*H*$_2$CH$_3$), 3.76 (s, 3H, −OMe), 1.42 (s, 9H, −CMe$_3$), 1.36 (s, 9H, −CMe$_3$), 1.13 (t, 3H, J = 7.0, −OCH$_2$C*H*$_3$), 1.06 (t, 3H, J = 7.0, −OCH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C): δ 163.3 (s, quat), 162.9 (s, quat), 162.0 (s, quat), 155.3 (d, J = 2.0, quat), 154.6 (d, J = 2.0, quat), 153.8 (s, Ar-CH), 149.7 (d, J = 2.0, Ar-CH), 142.2 (s, quat), 137.8 (d, J = 5.1, Ar-CH), 124.1 (s, Ar-CH), 123.5 (s, Ar-CH), 123.0 (d, J = 3.2, Ar-CH), 120.1 (d, J = 3.5, Ar-CH), 117.65 (s, Ar-CH), 117.62 (d, J = 3.4, Ar-CH), 109.7 (s, Ar-CH), 57.8 (d, J = 5.2, −OCH$_2$CH$_3$), 57.7 (d, J = 3.7, −OCH$_2$CH$_3$), 55.4 (s, −OMe), 35.33 (s, −*C*Me$_3$), 35.29 (s, −*C*Me$_3$), 30.33 (s, −C*Me*$_3$), 30.29 (s, −C*Me*$_3$), 16.6 (d, J = 5.2, −OCH$_2$*C*H$_3$), 16.5 (d, J = 5.2, −OCH$_2$*C*H$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$, 25 °C): δ 69.1 (s).

Synthesis of (bu$_2$bipy)Pd(2-C$_6$H$_4$OMe)(P(O)(OPh)$_2$) (22). The general procedure was followed using (bu$_2$bipy)Pd(2-C$_6$H$_4$OMe)I (0.316 g, 0.519 mmol), Ag[P(O)(OPh)$_2$] (0.177 g, 0.519 mmol), and THF (5 mL). After purification by column chromatography, the title compound was isolated as a white solid (0.346 g, 93%). Anal. Calcd for $C_{37}H_{41}N_2O_4PPd$: C, 62.14; H, 5.78. Found: C, 62.11; H, 5.73. ^{1}H NMR (CDCl$_3$, 25 °C): δ 10.02 (d, 1H, J = 5.4, Ar-H), 7.95 (s, 1H, Ar-H), 7.94 (s, 1H, Ar-H), 7.51−7.43 (m, 3H, Ar-H), 7.26−7.03 (m, 10H, Ar-H), 6.94−6.87 (m, 2H, Ar-H), 6.77 (t, 1H, J = 7.2, Ar-H), 6.59 (d, 1H, J = 8.1, Ar-H), 3.50 (s, 3H, −OMe), 4.41 (s, 9H, −CMe$_3$), 1.34 (s, 9H, −CMe$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C): δ 163.6 (s, quat), 163.0 (s, quat), 161.8 (s, quat), 155.3 (d, J = 2.3, quat), 154.4 (d, J = 2.3, quat), 153.5 (s, Ar-CH), 152.9 (d, J = 8.6, quat), 152.7 (d, J = 9.2, quat), 149.8 (d, J = 2.0, Ar-CH), 141.1 (s, quat), 137.3 (d, J = 5.1, Ar-CH), 128.7 (s, Ar-CH), 128.5 (s, Ar-CH), 124.4 (s, Ar-CH), 123.5 (s, Ar-CH), 123.1 (d, J = 3.3, Ar-CH), 122.3 (s, Ar-CH), 121.9 (s, Ar-CH), 121.3 (d, J = 5.1, Ar-CH), 120.9 (d, J = 5.5, Ar-CH), 120.1 (d, J = 3.8, Ar-CH), 117.8 (d, J = 3.1, Ar-CH), 117.7 (s, Ar-CH), 109.7 (s, Ar-CH), 55.1 (s, −OMe), 35.31 (s, −*C*Me$_3$), 35.26 (s, −*C*Me$_3$), 30.3 (s, −C*Me*$_3$), 30.2 (s, −C*Me*$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$, 25 °C): δ 67.0 (s).

Synthesis of (bu$_2$bipy)Pd(2,6-C$_6$H$_3$Me$_2$)(P(O)(OEt)$_2$) (23). The general procedure was followed using (bu$_2$bipy)Pd(2,6-C$_6$H$_3$Me$_2$)I (0.531 g, 0.875 mmol), Ag[P(O)(OEt)$_2$] (0.214, 0.875 mmol), and CH$_2$Cl$_2$ (5 mL). After purification by column chromatography, the title compound was isolated as a pale yellow solid (0.501 g, 93%). Anal. Calcd for $C_{30}H_{43}N_2O_3PPd$: C, 58.39; H, 7.02. Found: C, 58.65; H, 6.63. ^{1}H NMR (CDCl$_3$, 25 °C): δ 9.86 (d, 1H, J = 5.8, Ar-H), 7.97 (s, 2H, Ar-H), 7.56 (dd, 1H, J = 5.7, 1.9, Ar-H), 7.31−7.21 (m, 2H, Ar-H), 6.92−6.82 (m, 3H, Ar-H), 3.78 (m, 4H, −OC*H*$_2$CH$_3$), 2.64 (s, 6H, Ar Me), 1.43 (s, 9H, −C*Me*$_3$), 1.37 (s, 9H, −C*Me*$_3$), 1.10 (t, 6H, J = 7.0, −OCH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C): δ 163.4 (s, quat), 162.9 (s, quat), 157.5 (d, J = 3.7, quat), 155.4 (d, J = 1.7, quat), 154.3 (d, J = 1.7, quat), 153.4 (s, Ar-CH), 148.9 (d, J = 2.0, Ar-CH), 142.3 (s, quat), 142.2 (s, quat), 124.9 (d, J = 1.1, Ar-CH), 123.7 (s, Ar-CH), 123.5 (s, Ar-CH), 123.3 (d, J = 3.0, Ar-CH), 117.8 (d, J = 2.9, Ar-CH), 117.7 (s, Ar-CH), 57.6 (d, J = 6.8, −OCH$_2$CH$_3$), 35.4 (s, −*C*Me$_3$), 35.3 (s, −*C*Me$_3$), 30.33 (s, −C*Me*$_3$), 30.28 (s, −C*Me*$_3$), 26.94 (s, −Me$_3$), 26.87 (s, −Me), 16.6 (d, J = 6.4, −OCH$_2$*C*H$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$, 25 °C): δ 71.3 (s).

Synthesis of (bu$_2$bipy)Pd(2,6-C$_6$H$_3$Me$_2$)(P(O)(OPh)$_2$) (24). The general procedure was followed using (bu$_2$bipy)Pd(2,6-C$_6$H$_3$Me$_2$)I (0.412 g, 0.679 mmol), Ag[P(O)(OPh)$_2$] (0.232 g, 0.679 mmol), and THF (5 mL). After purification by column chromatography, the title compound was isolated as a white solid (0.377 g, 78%).

Anal. Calcd for $C_{38}H_{43}N_2O_3PPd$: C, 64.00; H, 6.08. Found: C, 64.14; H, 6.13. ^{1}H NMR ($CDCl_3$, 25 °C): δ 9.92 (d, 1H, J = 5.7, Ar-H), 8.00 (s, 2H, Ar-H), 7.51 (dd, 1H, J = 5.8, 1.8, Ar-H), 7.33 (dd, 1H, J = 5.7, 3.5, Ar-H), 7.23 (m, 1H, Ar-H), 7.09 (m, 4H, Ar-H), 7.00 (m, 4H, Ar-H), 6.91 (m, 3H, Ar-H), 6.81 (d, 2H, J = 7.2, Ar-H), 2.58 (s, 6H, Ar Me), 1.43 (s, 9H, $-CMe_3$), 1.38 (s, 9H, $-CMe_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ 163.8 (s, quat), 163.1 (s, quat), 157.0 (d, J = 5.4, quat), 155.5 (d, J = 1.7, quat), 154.2 (d, J = 1.9, quat), 153.4 (s, Ar-CH), 152.8 (d, J = 11.7, quat), 149.1 (d, J = 2.3, Ar-CH), 141.9 (s, quat), 141.8 (s, quat), 128.7 (s, Ar-CH), 125.4 (d, J = 1.2, Ar-CH), 123.8 (d, J = 3.7, Ar-CH), 123.5 (d, J = 3.2, Ar-CH), 122.3 (s, Ar-CH), 121.4 (d, J = 4.7, Ar-CH), 118.0 (d, J = 3.2, Ar-CH), 117.9 (s, Ar-CH), 35.4 (s, $-CMe_3$), 35.3 (s, $-CMe_3$), 30.33 (s, $-CMe_3$), 30.27 (s, $-CMe_3$), 26.7 (s, $-$Me), 26.6 (s, $-$Me). ^{31}P{^{1}H} NMR ($CDCl_3$, 25 °C): δ 69.4 (s).

Synthesis of (bu_2bipy)Pd(4-C_6H_4CN)(P(O)(OEt)$_2$) (25). The general procedure was followed using (bu_2bipy)Pd(4-C_6H_4CN)I (0.418, 0.692 mmol), Ag[P(O)(OEt)$_2$] (0.170, 0.692 mmol), and CH_2Cl_2 (5 mL). After purification by column chromatography, the title compound was isolated as a white solid (0.402 g, 95%). Anal. Calcd for $C_{29}H_{38}N_3O_3PPd$: C, 56.73; H, 6.24. Found: C, 56.72; H, 5.96. ^{1}H NMR ($CDCl_3$, 25 °C): δ 10.03 (d, 1H, J = 5.4, Ar-H), 7.98 (s, 1H, Ar-H), 7.97 (s, 1H, Ar-H), 7.76 (m, 2H, Ar-H), 7.57 (dd, 1H, J = 5.9, 1.9, Ar-H), 7.38−7.29 (m, 4H, Ar-H), 3.94 (m, 4H, $-OCH_2CH_3$), 1.43 (s, 9H, $-CMe_3$), 1.39 (s, 9H, $-CMe_3$), 1.14 (t, 6H, J = 7.0, $-OCH_2CH_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ 167.1 (s, quat), 164.1 (s, quat), 163.4 (s, quat), 155.1 (d, J = 2.0, quat), 154.4 (d, J = 1.6, quat), 153.8 (s, Ar-CH), 149.4 (d, J = 1.7, Ar-CH), 137.4 (d, J = 4.9, Ar-CH), 129.3 (d, J = 3.2, Ar-CH), 123.7 (s, Ar-CH), 123.3 (d, J = 3.3, Ar-CH), 120.6 (s, quat), 117.9 (s, Ar-CH), 117.9 (d, J = 3.6, Ar-CH), 106.2 (s, quat), 58.0 (d, J = 5.3, $-OCH_2CH_3$), 35.5 (s, $-CMe_3$), 35.4 (s, $-CMe_3$), 30.31 (s, $-CMe_3$), 30.28 (s, $-CMe_3$), 16.5 (d, J = 7.2, $-OCH_2CH_3$). ^{31}P{^{1}H} NMR ($CDCl_3$, 25 °C): δ 65.5 (s).

Synthesis of (bu_2bipy)Pd(4-C_6H_4CN)(P(O)(OPh)$_2$) (26). The general procedure was followed using (bu_2bipy)Pd(4-C_6H_4CN)I (0.274 g, 0.454 mmol), Ag[P(O)(OPh)$_2$] (0.155 g, 0.454 mmol), and THF (5 mL). After purification by column chromatography, the title compound was isolated as a white solid (0.303 g, 94%). Anal. Calcd for $C_{37}H_{38}N_3O_3PPd$: C, 62.58; H, 5.39. Found: C, 62.71; H, 5.42. ^{1}H NMR ($CDCl_3$, 25 °C): δ 10.09 (d, 1H, J = 5.7, Ar-H), 8.00 (s, 2H, Ar-H), 7.55 (m, 3H, Ar-H), 7.30−7.14 (m, 12H, Ar-H), 6.97 (m, 2H, Ar-H), 1.44 (s, 9H, $-CMe_3$), 1.38 (s, 9H, $-CMe_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ 165.3 (s, quat), 164.4 (s, quat), 163.7 (s, quat), 155.3 (d, J = 1.8, quat), 154.3 (d, J = 1.8, quat), 153.7 (s, Ar-CH), 152.5 (d, J = 8.6, quat), 149.5 (d, J = 1.7, Ar-CH), 137.1 (d, J = 5.2, Ar-CH), 129.3 (d, J = 3.3, Ar-CH), 129.0 (s, Ar-CH), 123.9 (s, Ar-CH), 123.5 (d, J = 3.2, Ar-CH), 22.7 (s, Ar-CH), 120.9 (d, J = 5.5, Ar-CH), 120.4 (s, quat), 118.1 (s, Ar-CH), 118.1 (d, J = 2.0, Ar-CH), 106.6 (s, quat), 35.5 (s, $-CMe_3$), 35.4 (s, $-CMe_3$), 30.31 (s, $-CMe_3$), 30.25 (s, $-CMe_3$). ^{31}P{^{1}H} NMR ($CDCl_3$, 25 °C): δ 63.6 (s).

Synthesis of (bu_2bipy)Pd(4-$C_6H_4NO_2$)(P(O)(OEt)$_2$) (27). The general procedure was followed using (bu_2bipy)Pd(4-$C_6H_4NO_2$)I (0.161 g, 0.258 mmol), Ag[P(O)(OEt)$_2$] (0.063 g, 0.258 mmol), and CH_2Cl_2 (5 mL). After purification by column chromatography, the title compound was isolated as a white solid (0.121 g, 74%). Anal. Calcd for $C_{28}H_{38}N_3O_5PPd$: C, 53.04; H, 6.04. Found: C, 53.20; H, 5.96. ^{1}H NMR ($CDCl_3$, 25 °C): δ 10.06 (d, 1H, J = 6.0, Ar-H), 7.99 (s, 2H, Ar-H), 7.94−7.92 (m, 2H, Ar-H), 7.86−7.81 (m, 2H, Ar-CH), 7.58 (dd, 1H, J = 5.2, 1.8, Ar-H), 7.37−7.33 (m, 1H, Ar-H), 7.30−7.26 (m, 1H, Ar-H), 3.95 (m, 4H, $-OCH_2CH_3$), 1.43 (s, 9H, $-CMe_3$), 1.38 (s, 9H, $-CMe_3$), 1.15 (t, 6H, J = 7.0, $-OCH_2CH_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ 172.0 (s, quat), 164.2 (s, quat), 163.5 (s, quat), 155.2 (d, J = 1.8, quat), 154.4 (d, J = 1.2, quat), 153.8 (s, Ar-CH), 149.4 (d, J = 1.8, Ar-CH), 145.0 (s, quat), 136.9 (d, J = 5.0, Ar-CH), 123.8 (s, Ar-CH), 123.4 (d, J = 3.2, Ar-CH), 120.6 (d, J = 3.5, Ar-CH), 118.00 (s, Ar-CH), 117.98 (d, J = 2.0, Ar-CH), 58.1 (d, J = 5.2, $-OCH_2CH_3$), 35.5 (s, $-CMe_3$), 35.4 (s, $-CMe_3$), 30.35 (s, $-CMe_3$), 30.30 (s, $-CMe_3$), 16.6 (d, J = 5.2, $-OCH_2CH_3$). ^{31}P{^{1}H} NMR ($CDCl_3$, 25 °C): δ 64.4 (s).

Synthesis of (bu_2bipy)Pd(4-$C_6H_4NO_2$)(P(O)(OPh)$_2$) (28). The general procedure was followed using (bu_2bipy)Pd(4-$C_6H_4NO_2$)I (0.447 g, 0.717 mmol), Ag[P(O)(OPh)$_2$] (0.244 g, 0.717 mmol), and THF (5 mL). After purification by column chromatography, the title compound was isolated as a white solid (0.485 g, 93%). Anal. Calcd for $C_{36}H_{38}N_3O_5PPd$: C, 59.22; H, 5.25. Found: C, 58.82; H, 5.18. ^{1}H NMR ($CDCl_3$, 25 °C): δ 10.10 (d, 1H, Ar-H), 8.01 (s, 2H, Ar-CH), 7.85 (AA′BB′, 2H, Ar-H), 7.59 (m, 3H, Ar-H), 7.28−7.15 (m, 10H, Ar-H), 6.98 (m, 2H, Ar-CH), 1.44 (s, 9H, $-CMe_3$), 1.37 (s, 9H, $-CMe_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ 169.8 (s, quat), 164.5 (s, quat), 163.8 (s, quat), 155.3 (d, J = 2.1, quat), 154.3 (d, J = 1.8, quat), 153.6 (s, Ar-CH), 152.4 (d, J = 8.6, quat), 149.4 (d, J = 1.7, Ar-CH), 145.1 (s, quat), 136.7 (d, J = 5.4, Ar-CH), 129.0 (s, Ar-CH), 124.0 (s, Ar-CH), 123.5 (d, J = 3.4, Ar-CH), 122.8 (s, Ar-CH), 120.9 (d, J = 5.5, Ar-CH), 120.5 (d, J = 3.4, Ar-CH), 118.1 (s, Ar-CH), 35.5 (s, $-CMe_3$), 35.4 (s, $-CMe_3$), 30.3 (s, $-CMe_3$), 30.2 (s, $-CMe_3$). ^{31}P{^{1}H} NMR ($CDCl_3$, 25 °C): δ 63.0 (s).

Synthesis of (bu_2bipy)Pd(4-C_6H_4Cl)(P(O)(OEt)$_2$) (29). The general procedure was followed using (bu_2bipy)Pd(4-C_6H_4Cl)I (0.251 g, 0.409 mmol), Ag[P(O)(OEt)$_2$] (0.100 g, 0.409 mmol), and CH_2Cl_2 (5 mL). After purification by column chromatography, the title compound was isolated as an off-white solid (0.219 g, 86%). Anal. Calcd for $C_{28}H_{38}ClN_2O_3PPd$: C, 53.94; H, 6.14. Found: C, 54.18; H, 6.08. ^{1}H NMR ($CDCl_3$, 25 °C): δ 9.94 (d, 1H, J = 5.3, Ar-H), 7.98 (s, 2H, Ar-H), 7.57−7.44 (m, 4H, Ar-H), 7.28 (m, 1H, Ar-H), 7.08 (AA′BB′, 2H, Ar-H), 3.93 (m, 4H, $-OCH_2CH_3$), 1.42 (s, 9H, $-CMe_3$), 1.38 (s, 9H, $-CMe_3$), 1.13 (d, 6H, J = 7.0, $-OCH_2CH_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ 163.8 (s, quat), 163.3 (s, quat), 155.2 (d, J = 1.7, quat), 154.4 (d, J = 1.7, quat), 153.6 (s, Ar-CH), 153.0 (s, quat), 149.6 (d, J = 1.7, Ar-CH), 137.3 (d, J = 5.4, Ar-CH), 129.2 (s, quat), 126.9 (d, J = 3.3, Ar-CH), 123.7 (s, Ar-CH), 123.2 (d, J = 3.1, Ar-CH), 117.9 (s, Ar-CH), 117.8 (d, J = 2.9, Ar-CH), 58.0 (d, J = 7.3, $-OCH_2CH_3$), 35.4 (s, $-CMe_3$), 35.3 (s, $-CMe_3$), 30.31 (s, $-CMe_3$), 30.28 (s, $-CMe_3$), 16.52 (d, J = 7.3, $-OCH_2CH_3$). ^{31}P{^{1}H} NMR ($CDCl_3$, 25 °C): δ 68.9 (s).

Synthesis of (bu_2bipy)Pd(4-C_6H_4Cl)(P(O)(OPh)$_2$) (30). The general procedure was followed using (bu_2bipy)Pd(4-C_6H_4Cl)I (0.152 g, 0.248 mmol), Ag[P(O)(OPh)$_2$] (0.085, 0.248 mmol), and THF (5 mL). After purification by column chromatography, the title compound was isolated as a white solid (0.130 g, 73%). Anal. Calcd for $C_{36}H_{38}N_3O_5PPd$: C, 60.08; H, 5.32. Found: C, 59.98; H, 5.25. ^{1}H NMR ($CDCl_3$, 25 °C): δ 10.09 (d, 1H, J = 5.5, Ar-H), 7.98 (s, 2H, Ar-H), 7.55 (dd, 1H, J = 5.7, 1.9, Ar-H), 7.38 (dd, 1H, J = 5.8, 3.5, Ar-H), 7.31−7.14 (m, 11H, Ar-H), 7.01−6.93 (m, 4H, Ar-H), 1.43 (s, 9H, $-CMe_3$), 1.36 (s, 9H, $-CMe_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ 164.1 (s, quat), 163.4 (s, quat), 155.2 (d, J = 1.8, quat), 154.3 (d, J = 1.7, quat), 153.6 (s, Ar-CH), 152.7 (d, J = 8.3, quat), 152.0 (s, quat), 149.7 (d, J = 2.0, Ar-CH), 137.1 (d, J = 5.5, Ar-CH), 129.4 (s, quat), 128.8 (s, Ar-CH), 126.7 (d, J = 3.6, Ar-CH), 123.8 (s, Ar-CH), 123.3 (d, J = 3.2, Ar-CH), 122.5 (s, Ar-CH), 121.0 (d, J = 5.7, Ar-CH), 117.9 (s, Ar-CH), 117.8 (d, J = 3.1, Ar-CH), 35.44 (s, $-CMe_3$), 35.36 (s, $-CMe_3$), 30.3 (s, $-CMe_3$), 30.2 (s, $-CMe_3$). ^{31}P{^{1}H} NMR ($CDCl_3$, 25 °C): δ 65.9 (s).

Thermolysis Reactions. A 5 mm NMR tube was charged with the arylpalladium phosphonate (7.1 μmol), hexamethylbenzene (7.1 μmol), and C_6D_5 (0.5 mL). After an initial ^{1}H NMR spectrum was collected for standardization, the tube was sealed and placed in an oil bath at the desired temperature (95 or 120 °C). At regular

intervals, the NMR tube was removed and immediately immersed into ice water. After collection of a ^{1}H NMR spectrum, the tube was placed back into the oil bath for further heating. No elimination was observed from **1**−**30** at 25 °C. The arylpalladium phosphonates, arylphosphonates (where discernible from **11**−**30** and bu_2bipy), and bu_2bipy concentrations were readily obtained by comparison of the integral values for the individual species relative to the internal standard. Errors in the rate constants were calculated at 10%. For almost all thermolysis reactions, the only signals in the $^{31}P\{^1H\}$ NMR spectrum after heating were small amounts of remaining **11**−**30** and the desired arylphosphonate (Supporting Information).

General Procedure for the Isolation of Arylphosphonates. A 10 mL reaction vial was charged with the arylpalladium phosphonate and toluene (3.0 mL). After it was heated in an oil bath for 20 h at 150 °C, the reaction mixture was cooled to 25 °C, filtered, and evaporated to dryness. The free bu_2bipy was trapped with 1.0 equiv of $Pd(cod)Cl_2$ in CH_2Cl_2. After removal of the volatiles, the residue was extracted with hexane and the extract filtered and dried to afford the desired arylphosphonate.

Preparation of (2-C_6H_4Me)P(O)(OPh)$_2$. The general procedure was followed using **18** (0.05 g, 0.071 mmol) to afford the title compound as a waxy solid (0.020 g, 87%). Anal. Calcd for $C_{19}H_{17}O_3P$: C, 70.37; H, 5.28. Found: C, 70.32; H, 5.41. ^{1}H NMR ($CDCl_3$, 25 °C): δ 8.01 (m, 1H, Ar-H), 7.43 (t, 1H, J = 7.6, Ar-H), 7.28−7.04 (m, 12H, Ar-H), 2.70 (s, 3H, Ar Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 150.4 (d, J = 7.9, quat), 142.1 (d, J = 10.9, quat), 134.5 (d, J = 11.0, Ar-CH), 133.3 (d, J = 3.0, Ar-CH), 131.5 (d, J = 15.8, Ar-CH), 129.7 (s, Ar-CH), 125.7 (d, J = 188.6, quat), 125.7 (d, J = 15.9, Ar-CH), 125.0 (d, J = 1.1, Ar-CH), 120.4 (d, J = 4.8, Ar-CH), 21.5 (d, J = 3.6, Ar Me). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 11.7 (s).

Preparation of (2-C_6H_4OMe)P(O)(OPh)$_2$. The general procedure was followed using **22** (0.05 g, 0.070 mmol) to afford the title compound as a waxy solid (0.018 g, 75%). Anal. Calcd for $C_{19}H_{17}O_4P$: C, 67.06; H, 5.04. Found: C, 67.43; H, 5.37. ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.96 (m, 1H, Ar-H), 7.55 (t, 1H, J = 9.0, Ar-H), 7.32−6.93 (m, 12H, Ar-H), 3.88 (s, 3H, −OMe). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 161.4 (d, J = 2.5, quat), 150.7 (d, J = 7.5, quat), 135.8 (d, J = 7.9, Ar-CH), 135.3 (d, J = 2.3, Ar-CH), 129.5 (s, Ar-CH), 124.8 (d, J = 1.1, Ar-CH), 120.7 (d, J = 4.8, Ar-CH), 114.9 (d, J = 192.1, quat), 111.2 (d, J = 9.9, Ar-CH), 55.8 (s, −OMe). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 9.7 (s).

Preparation of (4-$C_6H_4NO_2$)P(O)(OPh)$_2$. The general procedure was followed using **28** (0.05 g, 0.068 mmol) to afford the title compound as a waxy solid (0.014 g, 58%). Anal. Calcd for $C_{18}H_{14}NO_5P$: C, 60.85; H, 3.97. Found: C, 61.00; H, 4.54. ^{1}H NMR ($CDCl_3$, 25 °C): δ 8.37−8.32 (m, 2H, Ar-CH), 8.20−8.13 (m, 2H, Ar-CH), 7.35−7.27 (m, 4H, Ar-CH), 7.21−7.16 (m, 6H, Ar-CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 149.9 (d, J = 7.9, quat), 133.9 (d, J = 191.8, quat), 133.6 (d, J = 11.2, Ar-CH), 130.0 (s, Ar-CH), 125.6 (d, J = 1.1, Ar-CH), 123.5 (d, J = 16.0, Ar-CH), 120.5 (d, J = 4.7, Ar-CH). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 6.8 (s).

Preparation of (4-C_6H_4CN)P(O)(OPh)$_2$. The general procedure was followed using **26** (0.05 g, 0.070 mmol) to afford the title compound as a waxy solid (0.012 g, 51%). Anal. Calcd for $C_{19}H_{14}NO_3P$: C, 68.06; H, 4.21. Found: C, 67.73; H, 4.10. ^{1}H NMR ($CDCl_3$, 25 °C): δ 8.11−8.04 (m, 2H, Ar-H), 7.81−7.72 (m, 2H, Ar-H), 7.43−7.29 (m, 4H, Ar-H), 7.15 (m, 6H, Ar-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 149.9 (d, J = 7.9, quat), 132.8 (d, J = 10.3, Ar-CH), 132.2 (d, J = 15.8, Ar-CH), 132.1 (d, J = 192.1, quat), 129.9 (s, Ar-H), 125.5 (d, J = 1.1, Ar-CH), 120.5 (d, J = 4.8, Ar-CH), 117.6 (d, J = 1.0, quat), 116.9 (d, J = 3.6, quat). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 7.20 (s).

Preparation of (4-C_6H_4Cl)P(O)(OPh)$_2$. The general procedure was followed using **30** (0.05 g, 0.069 mmol) to afford the title compound as a waxy solid (0.019 g, 79%). Anal. Calcd for $C_{18}H_{14}O_3PCl$: C, 62.71; H, 4.09. Found: C, 62.38; H, 4.25. ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.93−7.85 (m, 2H, Ar-H), 7.51−7.46 (m, 2H, Ar-H), 7.32−7.25 (m, 4H, Ar-H), 7.20−7.12 (m, 6H, Ar-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 150.2 (d, J = 7.5, quat), 139.9 (d, J = 4.2, quat), 133.7 (d, J = 11.1, Ar-CH), 129.8 (s, Ar-CH), 129.1 (d, J = 16.5, Ar-CH), 125.3 (d, J = 1.1, Ar-CH), 125.3 (d, J = 195.9, quat), 120.5 (d, J = 4.8, Ar-CH). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 9.7 (s).

Preparation of (4-$C_6H_4NH_2$)P(O)(OPh)$_2$. The general procedure was followed using **14** (0.05 g, 0.071 mmol) to afford the title compound as a waxy solid (0.010 g, 43%). Anal. Calcd for $C_{18}H_{16}NO_3P$: C, 66.46; H, 4.96. Found: C, 66.10; H, 4.68. ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.65−7.60 (m, 2H, Ar-H), 7.36−6.99 (m, 10H, Ar-H), 6.64−6.60 (m, Ar-H), 4.00 (s, 2H, $-NH_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 151.2 (d, J = 5.5, quat), 150.6 (d, J = 7.3, quat), 134.3 (d, J = 12.1, Ar-CH), 129.6 (s, Ar-CH), 124.8 (d, J = 1.1, Ar-CH), 120.7 (d, J = 4.6, Ar-CH), 114.2 (d, J = 16.9, Ar-CH), 113.8 (d, J = 203.2, quat). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 13.1 (s).

Preparation of (2,6-$C_6H_3Me_2$)P(O)(OPh)$_2$. The general procedure was followed using **24** (0.10 g, 0.14 mmol) to afford the title compound as a waxy solid (0.030 g, 64%). Anal. Calcd for $C_{20}H_{19}O_3P$: C, 71.00; H, 5.66. Found: C, 70.85; H, 5.69. ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.31 (m, 13H, Ar-H), 2.77 (d, 6H, J = 1.7, Ar Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 150.4 (d, J = 7.7, quat), 144.2 (d, J = 12.2, quat), 132.5 (d, J = 3.2, Ar-CH), 129.9 (d, J = 16.4, Ar-CH), 129.7 (d, J = 0.8, Ar-CH), 124.9 (d, J = 0.9, Ar-CH), 124.2 (d, J = 182.9, quat), 120.4 (d, J = 4.8, Ar-CH), 23.5 (d, J = 2.9, Ar Me). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 11.4 (s).

Molecular Structures of 1 and 29. Crystals of **1** and **29** were grown by slow diffusion of pentane into saturated $CDCl_3$ solutions. Suitable crystals were selected and mounted on glass fibers. Preliminary examination and data collection were performed using a Bruker SMART 1K charge coupled device (CCD) detector system single-crystal X-ray diffractometer using graphite-monochromated Mo Kα radiation. SMART and SAINT software packages were used for data collection and data integration.[16] Structure solution and refinement were carried out using the SHELXTL-PLUS software package.[17]

In the molecular structure of **29**, there is a positional disorder in one of the *tert*-butyl groups that was refined using partial occupancy. In the structure of **1**, there is a minor cocrystallized component (~2%) that is refined well as $bu_2bipyPdI_2$, which could be formed by small amounts of aryl−aryl exchange between two molecules of **1**.

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Supporting Information Available: Figures giving selected $^{31}P\{^1H\}$ NMR spectra from the thermolysis reactions and CIF files giving crystallographic data for **1** and **29**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Sheldrick, G. M. SHELXTL-PLUS; Bruker Analytical X-ray Division, Madison, WI, 2002.