Understanding the Coupling of Heteroaromatic Substrates: Synthesis, Structures, and Reductive Eliminations of Heteroarylpalladium Amido Complexes

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Palladium furyl- and thiophenyl complexes have been studied to uncover the origin of the difference in reactivity between coupling of five-membered heterocyclic halides and coupling of aryl halides and six-membered heteroaryl halides. A range of DPPF-ligated furanylpalladium and thiophenylpalladium halide and amido complexes were synthesized, and several examples were structurally characterized. The heteroatom in the 2-heteroaryl groups did not coordinate palladium to generate η^2-heteroaryl complexes. The furyl- and thiophenylpalladium complexes underwent reductive elimination of heteroarylamines in yields that were much different for related 2- and 3-isomers. The yields of reductive elimination from these isomeric complexes paralleled the yields from catalytic aminations of 2- and 3-halofurans and 2- and 3-halothiophenes. This correlation suggests that the scope of the amination of five-membered heteroaryl halides is controlled by the reductive elimination step. The yields of reductive elimination correlated with the distribution of electron density at different positions of furans and thiophenes, and this correlation between electron density at different positions of the heteroarenes explains why yields are higher for reductive elimination from 2-furyl and 3-thiophenyl complexes than they are from 3-furyl and 2-thiophenyl complexes.

Introduction

Many, if not most, palladium-catalyzed cross-coupling reactions conducted in the context of pharmaceutical synthesis contain heteroaromatic groups.[1−3] Yet, mechanistic data on the palladium-catalyzed coupling of heteroaryl reactants are limited.[4] Therefore, mechanistic studies with heteroaryl substrates would provide useful information to understand and predict the scope of coupling reactions that are conducted in common synthetic applications. The absence of this mechanistic data applies to recently developed carbon−heteroatom coupling processes, as well as more classic C−C coupling chemistry.

Five-membered heteroarylamines are substructures of biologically active compounds and novel electronic materials.[5−7] Many of the classical routes to five-membered heteroarylamines are limited in scope or occur at high temperatures. Direct, nucleophilic amination of the more electron-rich five-membered heteroaryl halides containing a single heteroatom is restricted to substrates containing strongly electron-withdrawing substituents, such as nitro or acyl groups.[8] To address this limitation in scope of uncatalyzed reactions, palladium-catalyzed amination[9−13] of heterocyclic halides has been reported.[14−28] Yet, yields of the

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(1) Bradley, D. A.; Godfrey, A. G.; Schmid, C. R. *Tetrahedron Lett.* **1999**, *40*, 5155−5159.
(2) Lopez-Rodriguez, M. L.; Viso, A.; Benhamu, B.; Rominguera, J. L.; Murcia, M. *Bioorg. Med. Chem. Lett.* **1999**, *9*, 2339−2342.
(3) Yin, J.; Zhao, M. M.; Huffman, M. A.; McNamara, J. M. *Org. Lett.* **2002**, *4*, 3481−3484.
(4) Paul, F.; Patt, J.; Hartwig, J. F. *Organometallics* **1995**, *14*, 3030.
(5) Cui, Y.; Zhang, X.; Jenekhe, S. A. *Macromolecules* **1999**, *32*, 3824.
(6) Thayumanavan, S.; Mendez, J.; Marder, S. R. *J. Org. Chem.* **1999**, *64*, 4289.
(7) Noda, T.; Ogawa, H.; Noma, N.; Shirota, Y. *Appl. Phys. Lett.* **1997**, *70*, 699.
(8) Prim, D.; Kirsch, G. *Tetrahedron* **1999**, *55*, 6511.
(9) Hartwig, J. F. *Angew. Chem., Int. Ed.* **1998**, *37*, 2046.
(10) Hartwig, J. F. In *Modern Amination Methods;* Ricci, A., Ed.; Wiley-VCH: Weinheim, 2000.
(11) Hartwig, J. F. In *Handbook of Organopalladium Chemistry for Organic Synthesis;* Negishi, E. I., Ed.; John Wiley and Sons: New York, 2002; p 1051.
(12) Yang, B. H.; Buchwald, S. L. *J. Organomet. Chem.* **1999**, *576*, 125−146.
(13) Muci, A. R.; Buchwald, S. L. *Top. Curr. Chem.* **2002**, *219*, 131−209.
(14) Hooper, M. W.; Utsunomiya, M.; Hartwig, J. F. *J. Org. Chem.* **2003**, *68*, 2861−2873.
(15) Wagaw, S.; Buchwald, S. L. *J. Org. Chem.* **1996**, *61*, 7240.
(16) Lopez-Rodriguez, M. L.; Benhamu, B.; Ayala, D.; Rominguera, J. L.; Murcia, M.; Ramos, J. A.; Viso, A. *Tetrahedron* **2000**, *56*, 3245−3253.
(17) Hong, Y. P.; Tanoury, G. J.; Wilkinson, H. S.; Bakale, R. P.; Wald, S. A.; Senanayake, C. H. *Tetrahedron Lett.* **1997**, *38*, 5607−5610.
(18) Tanoury, G. J.; Senanayake, C. H.; Hett, R.; Kuhn, A. M.; Kessler, D. W.; Wald, S. A. *Tetrahedron Lett.* **1998**, *39*, 6845−6848.
(19) Arterburn, J. B.; Pannala, M.; Gonzalez, A. M. *Tetrahedron Lett.* **2001**, *42*, 1475−1477.
(20) Arterburn, J. B.; Rao, K. V.; Ramdas, R.; Dible, B. R. *Org. Lett.* **2001**, *3*, 1351−1354.
(21) Grasa, G. A.; Viciu, M. S.; Huang, J. K.; Nolan, S. P. *J. Org. Chem.* **2001**, *66*, 7729−7737.
(22) Kosmrlj, J.; Maes, B. U. W.; Lemiere, G. L. F.; Haemers, A. *Synlett* **2000**, 1581−1584.
(23) Wang, Z.; Rizzo, C. J. *Org. Lett.* **2001**, *3*, 565−568.
(24) Stauffer, S. R.; Lee, S.; Stambuli, J. P.; Hauck, S. I.; Hartwig, J. F. *Org. Lett.* **2000**, *2*, 1423.
(25) Harwood, E. A.; Sigurdsson, S. T.; Edfeldt, N. B. F.; Reid, B. R.; Hopkins, P. B. *J. Am. Chem. Soc.* **1999**, *121*, 5081−5082.

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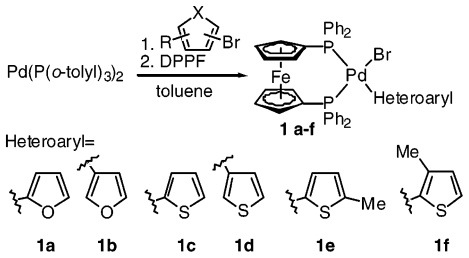
Scheme 1



heteroaryl halide amination process vary with the substitution pattern and the position of the halogen. In particular, yields from reactions of 2-halofurans were higher than those from reactions of 2-halothiophenes, but yields from reactions of 3-halothiophenes were higher than those from reactions of 3-halofurans.[14]

These trends in reactivity were difficult to rationalize with existing data. A few bisphosphine-ligated furanyl- and thiophenylpalladium(II) halide complexes have been reported, but these complexes encompass only 2-substituted derivatives.[29−33] No 3-furanyl- or 3-thiophenylpalladium complexes that would begin to reveal how the different electronic properties of the 2- and 3-positions of these heterocycles[1,34] influence reactivity are known. The 2-furanyl- and 2-thiophenylpalladium halides have generated products from homocoupling,[30] but reductive elimination of heteroaryl products from an isolated furanyl- or thiophenylpalladium complex has not been observed directly.

To address this absence of mechanistic data on heterocyclic systems, we have begun to evaluate how to extrapolate mechanistic information on coupling of aryl halides to coupling of heteroaryl halides. As a first case study, we have focused on the factors that control the amination of deactivated five-membered heteroaryl halides. We report the synthesis, structures, and reactions of furyl and thiophenylpalladium halide and amido complexes ligated by bis-diphenylphosphinoferrocene (DPPF). The yields of heteroarylamine product correlated with electronic properties of the heteroaromatic systems in a manner that explain the reversal in reactivity of 2- and 3-halo thiophenes versus 2- and 3-halofurans. The data generated from this study should aid in the understanding of other palladium-catalyzed reactions of heteroaryl substrates.

Results

Synthesis of DPPF-Ligated Heteroarylpalladium Bromide and Amide Complexes. Scheme 1 shows the synthesis of DPPF-ligated heteroarylpalladium bromide complexes. Both DPPF- and P^{t}Bu$_3$-ligated arylpalladium halide complexes are likely intermediates in the reactions of heteroaryl bromides with amines catalyzed by complexes generated from Pd(dba)$_2$ and these phosphines.[14] Arylpalladium complexes ligated by P^{t}Bu$_3$ are unstable,[35,36] and we have been unable to generate thiophenyl or furanylpalladium complexes ligated by P^{t}Bu$_3$. However, heteroarylpalladium halide and amido complexes ligated by DPPF were stable enough to isolate. These DPPF complexes possess the same two reactive ligands as the more reactive tri-*tert*-butyl phosphine-ligated heteroarylpalladium amido compounds, and they possess the same dative ligand as the DPPF-ligated arylpalladium amido complexes we investigated previously.[37]

DPPF-ligated arylpalladium halide complexes were previously prepared from the reaction of DPPF with isolated tris(*ortho*-tolyl)phosphine-ligated arylpalladium halide dimers.[37] However, (P(*o*-tol)$_3$)$_2$PdBr$_2$ was the major isolated product from reactions of Pd(P(*o*-tol)$_3$)$_2$ with 2- or 3-bromofuran or -thiophene. This product was obtained previously from oxidative addition of electron-rich aryl bromides to Pd[P(*o*-tol)$_3$]$_2$.[38]

Thus, one method to prepare the desired DPPF-ligated arylpalladium halide complexes **1a**−**f** involved reaction of the heteroaryl bromides with Pd[P(*o*-tol)$_3$]$_2$ and subsequent reaction of the unstable heteroarylpalladium halide in situ with DPPF. Alternatively, the thiophenyl complexes were prepared from Pd(dba)$_2$, DPPF, and the heteroaryl bromide. Complexes **1c** and **1d** were generated cleanly by this reaction at 100 °C for 4−12 h, as determined by ^{31}P NMR spectroscopy, and complex **1c** was isolated in 70% yield by this procedure. Reactions of the less stable bromofurans were conducted by the milder route starting with Pd[P(*o*-tol)$_3$]$_2$. Complexes **1a**−**f** were nearly insoluble in benzene and toluene after isolation, but were soluble enough in dichloromethane to obtain spectroscopic data.

To confirm that the heteroarylpalladium halide complexes were kinetically and chemically competent to be intermediates in the catalytic process, we compared the rates and yields for reactions catalyzed by a 1:1 combination of Pd(dba)$_2$ and DPPF to those for reactions catalyzed by isolated 2-thiophenylpalladium bromide **1c**. Consistent with the intermediacy of the heteroarylpalladium bromides in the catalytic process, the two reactions occurred with yields that were indistinguishable. The amounts of amidine formed as side product (vide infra) were also similar. In addition, the rate of reaction catalyzed by isolated **1c** was slightly faster than the rate of reaction catalyzed by Pd(dba)$_2$ and DPPF.

The heteroarylpalladium halide complexes **1a**−**f** were converted to the corresponding deep purple, crystalline amido complexes **2a**−**f** by reaction with KN(*p*-tolyl)$_2$ (Scheme 2). Complexes **2a**−**f** were stable at room temperature. Complexes **1a**−**f** were also converted to the red heteroarylpalladium *N*-methylanilides **3a**−**f** by

(26) De Riccardis, F.; Bonala, R. R.; Johnson, F. *J. Am. Chem. Soc.* **1999**, *121*, 10453−10460.
(27) De Riccardis, F.; Johnson, F. *Org. Lett.* **2000**, *2*, 293−295.
(28) Lakshman, M. K.; Keeler, J. C.; Hilmer, J. H.; Martin, J. Q. *J. Am. Chem. Soc.* **1999**, *121*, 6090−6091.
(29) Xie, Y.; Wu, B.-M.; Xue, F.; Ng, S.-C.; Mak, T. C. W.; Hor, T. S. A. *Organometallics* **1998**, *17*, 3988.
(30) Xie, Y.; Tan, G. K.; Yan, Y. K.; Vittal, J. J.; Ng, S.-C.; Hor, T. S. A. *J. Chem. Soc., Dalton Trans.* **1999**, *5*, 773.
(31) Amatore, C.; Carre, E.; Jutand, A.; Tanaka, H.; Ren, Q.; Torii, S. *Chem. Eur. J.* **1996**, *2*, 957.
(32) Morita, D. K.; Stille, J. K.; Norton, J. R. *J. Am. Chem. Soc.* **1995**, *117*, 8576.
(33) Chia, L.-Y.; McWhinnie, W. R. *J. Organomet. Chem.* **1980**, *188*, 121.
(34) Jones, G. B.; Chapman, B. J. In *Comprehensive Heterocyclic Chemistry II;* Katritzky, R., Rees, C. W., Scriven, E. F. V., Ed.; Pergamon: New York, 1996; Vol. 2, p 3.
(35) Roy, A. H.; Hartwig, J. F. *J. Am. Chem. Soc.* **2001**, *123*, 1232.
(36) Stambuli, J. P.; Bühl, M.; Hartwig, J. F. *J. Am Chem. Soc.* **2002**, *124*, 9346−9347.
(37) Driver, M. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **1997**, *119*, 8232.
(38) Widenhoefer, R. A.; Zhong, H. A.; Buchwald, S. L. *Organometallics* **1995**, *15*, 2745.

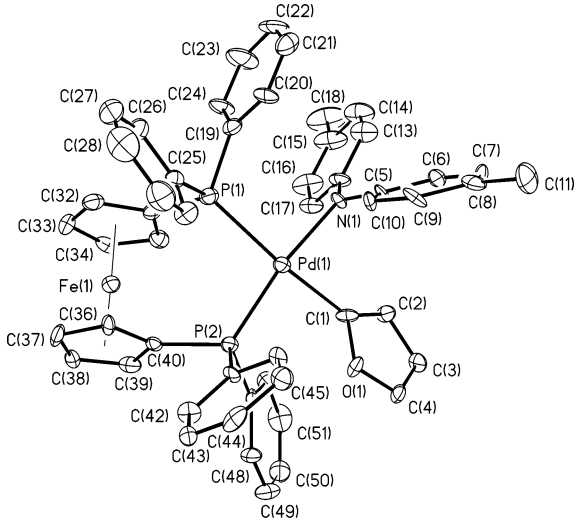


Figure 1. ORTEP drawing of (DPPF)Pd(2-furyl)[N(C_6H_4-4-Me)$_2$] (**2a**) with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

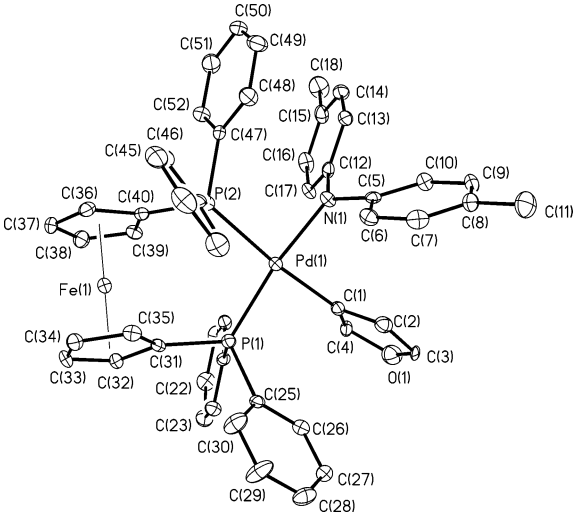
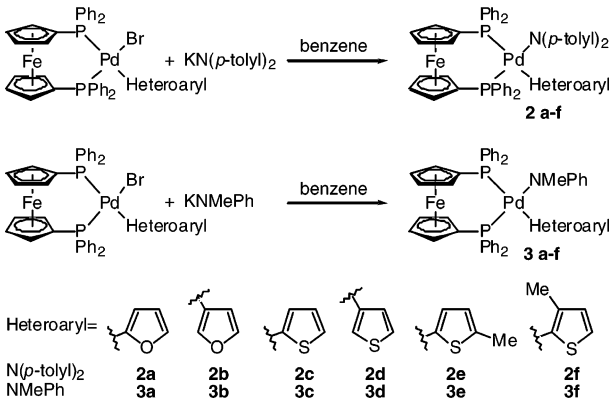


Figure 2. ORTEP drawing of (DPPF)Pd(3-furyl)[N(C_6H_4-4-Me)$_2$] (**2b**) with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

Scheme 2



reaction with KNMePh. These complexes were less stable than **2a**−**f**. All the heteroarylpalladium amido complexes were soluble in benzene and toluene. The heteroarylpalladium halides were also cleanly converted to the corresponding DPPF-ligated heteroarylpalladium anilides, but the high reactivity of these derivatives prevented isolation. For example, reaction of (DPPF)Pd[2-(5-CH_3)C_4H_3S](Br) (**1e**) with a combination of H_2NPh and NaO^{t}Bu formed a product, **4**, which displayed two new doublets in the ^{31}P NMR spectrum and a new methyl and four new ferrocenyl signals in the ^{1}H NMR spectrum. These data indicate that the desired heteroarylpalladium anilide is formed. However, this complex decomposed at room temperature and was not isolated in pure form. Reaction of **1e** with hexylamine or piperidine in the presence of NaO^{t}Bu did not form an amido complex that could be detected by ^{1}H NMR spectroscopy.

Structural Analysis of (DPPF)Pd(heteroaryl)[N(*p*-tolyl)$_2$] Complexes 2a−d. Structures of 2- and 3-furanyl diarylamido complexes and 2- and 3-thiophenyl diarylamido complexes were obtained by X-ray diffraction. ORTEP diagrams are provided in Figures 1−4. Crystal data are provided in Table 1, and selected bond distances and angles are provided in Tables 2 and 3. The thiophenyl group in the 2-thiophenyl complex **2c** was disordered between two conformers related by a 180° rotation about the Pd−C bond. The two conformers

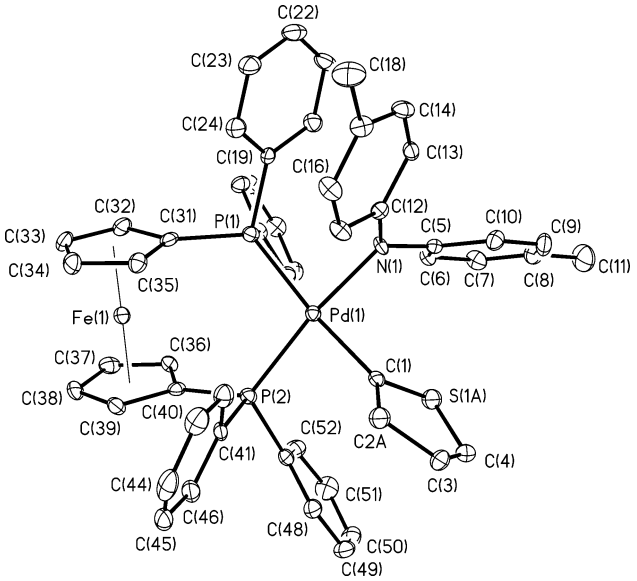


Figure 3. ORTEP drawing of (DPPF)Pd(2-thiophenyl)[N(C_6H_4-4-Me)$_2$] (**2c**) with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

were present in 75% and 25% occupancies. 3-Thiophenyl complex **2d** was disordered between two analogous conformers that were present in 55% and 45% occupancies.

No evidence for a secondary interaction between the heteroatom of the heteroaryl group and the palladium was observed for the 2-furanyl or the 2-thiophenyl complexes; the Pd−X (X = O, S) distances were greater than 2.99 Å. The identity of the heteroatom did, however, affect the Pd−C bond distances. The Pd−C bond in the 2-furanyl complex is shorter than that in the 2-thiophenyl complex by 0.04 Å, and the Pd−C bond in the 3-furanyl complex is shorter than that in the 3-thiophenyl complex by 0.01 Å. The Pd−C bonds of the heteroaryl complexes are shorter than the Pd−C bond in the arylpalladium ditolylamido complex reported previously (2.000−2.047 vs 2.048 Å).[37] The Pd−N bonds of the heteroarylpalladium diarylamido complexes are also shorter than that of the arylpalladium ditolylamido complex (2.084−2.090 vs 2.097 Å).[37]

Table 1. Data Collection and Refinement Parameters for X-ray Structures of (DPPF)Pd(X-furanyl)[N(*p*-$CH_3C_6H_4$)$_2$] (2a, X = 2; 2b, X = 3) and (DPPF)Pd(X-thiophenyl)[N(*p*-$CH_3C_6H_4$)$_2$] (2c, X = 2; 2d, X = 3)

	2a	2b	2c	2d
empirical formula	$C_{52}H_{45}NOP_2FePd\cdot1.75C_6H_6$	$C_{63}H_{63}NOP_2FePd$	$C_{59}H_{53}NP_2SFePd$	$C_{59}H_{53}NP_2SFePd$
fw	1060.83	1074.39	1032.33	1032.33
cryst color, habit	red, needle	red, plate	dark red, column	dark red, plate
cryst syst	monoclinic	triclinic	monoclinic	monoclinic
lattice params	a = 11.5842(4) Å	a = 11.2535(10) Å	a = 11.1159(4)Å	a = 11.1442(2) Å
	b = 39.513(1) Å	b = 15.0540(10) Å	b = 21.836(1) Å	b = 21.8246(5) Å
	c = 12.3266(4) Å	c = 16.5496(10) Å	c = 20.646(1) Å	c = 20.7322(4) Å
	α = 111.763(2) o	α = 109.615(3) o	α = 104.485(2) o	α = 104.870(1) o
		β = 97.804(3)°		
		γ = 92.340(3)°		
volume	5240.1(3) Å^3	2605.3(3) Å^3	4852.1(3) Å3	4873.6(2) Å3
space group	*P*21/*a* (#14)	*P*$\bar{1}$ (#2)	*P*21/*c* (#14)	*P*21/*c* (#14)
Z value	4	2	4	4
diffractometer	Nonius KappaCCD			
radiation	Mo Kα (λ = 0.71069 Å) graphite monochromated			
temperature	−90.0 °C	−90.0 °C	−90.0 °C	−90.0 °C
residuals: R; R_w	0.052; 0.048	0.033; 0.037	0.043; 0.039	0.037; 0.040
goodness of fit indicator	1.79	1.43	1.42	2.04

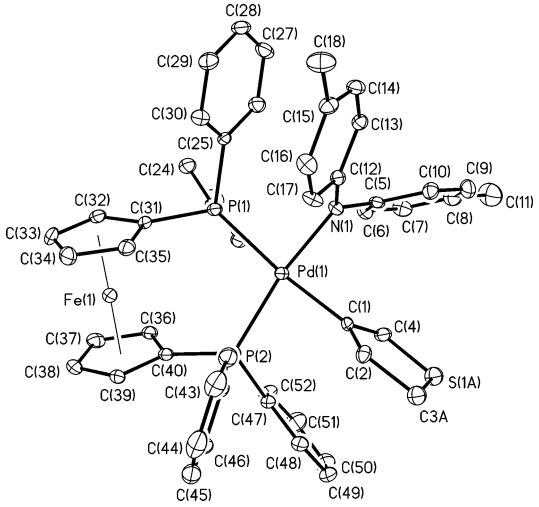


Figure 4. ORTEP drawing of (DPPF)Pd(3-thiophenyl)-[N(C_6H_4-4-Me)$_2$] (**2d**) with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

Table 2. Selected Intramolecular Bond Distances (Å) of DPPF-Ligated Furyl and Thiophenyl Ditolylamides 2a−d

atom	atom	distance	atom	atom	distance
	2a			**2c**	
Pd(1)	P(1)	2.379(3)	Pd(1)	P(1)	2.365(1)
Pd(1)	N(1)	2.090(7)	Pd(1)	N(1)	2.085(4)
Pd(1)	P(2)	2.278(3)	Pd(1)	P(2)	2.291(1)
Pd(1)	C(1)	2.00(1)	Pd(1)	C(1)	2.037(4)
	2b			**2d**	
Pd(1)	P(1)	2.289(1)	Pd(1)	P(1)	2.3742(9)
Pd(1)	N(1)	2.090(4)	Pd(1)	N(1)	2.084(3)
Pd(1)	P(2)	2.3796(13)	Pd(1)	P(2)	2.2853(9)
Pd(1)	C(1)	2.035(5)	Pd(1)	C(1)	2.046(3)

Reductive Elimination from (DPPF)Pd(heteroaryl)(amido) Complexes 2a−f and 3a−f. The isolated (DPPF)Pd(heteroaryl)(amido) complexes **2** and **3** were heated in benzene-d_6 to evaluate the yields for reductive elimination of heteroarylamines (Scheme 3). Reactions were conducted in the presence of PPh_3 to generate stable Pd(0) products. A ligand to trap the unstable, initially formed Pd(0) complex was required to observe high yields of arylamine by reductive elimination from arylpalladium amido complexes.[37]

Table 3. Selected Intramolecular Bond Angles (deg) of DPPF-Ligated Furyl and Thiophenyl Ditolylamides 2a−d

atom	atom	atom	angle	atom	atom	atom	angle
	2a				**2c**		
P(1)	Pd(1)	P(2)	99.50(10)	P(1)	Pd(1)	P(2)	101.26(5)
P(1)	Pd(1)	C(1)	172.5(3)	P(1)	Pd(1)	C(1)	173.7(1)
P(2)	Pd(1)	C(1)	86.6(3)	P(2)	Pd(1)	C(1)	84.0(1)
C(5)	N(1)	C(12)	124.1(9)	C(5)	N(1)	C(12)	119.8(4)
P(1)	Pd(1)	N(1)	88.7(2)	P(1)	Pd(1)	N(1)	87.0(1)
P(2)	Pd(1)	N(1)	171.9(2)	P(2)	Pd(1)	N(1)	171.6(1)
N(1)	Pd(1)	C(1)	85.3(4)	N(1)	Pd(1)	C(1)	87.9(2)
	2b				**2d**		
P(1)	Pd(1)	P(2)	101.30(5)	P(1)	Pd(1)	P(2)	101.53(3)
P(1)	Pd(1)	C(1)	84.5(1)	P(1)	Pd(1)	C(1)	172.92(9)
P(2)	Pd(1)	C(1)	174.1(1)	P(2)	Pd(1)	C(1)	84.09(9)
P(1)	Pd(1)	N(1)	171.44(11)	C(5)	N(1)	C(12)	120.1(3)
P(2)	Pd(1)	N(1)	87.13(11)	P(1)	Pd(1)	N(1)	87.75(8)
N(1)	Pd(1)	C(1)	87.2(2)	P(2)	Pd(1)	N(1)	170.55(8)
C(5)	N(1)	C(12)	119.9(4)	N(1)	Pd(1)	C(1)	86.8(1)

Scheme 3

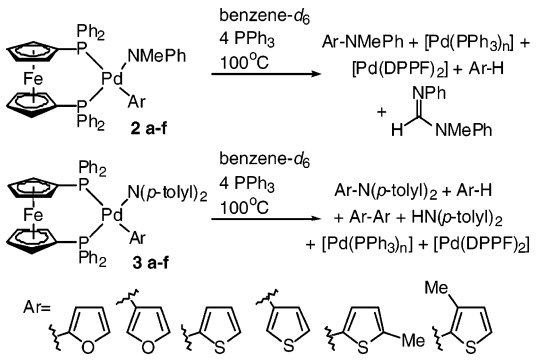
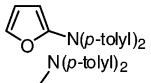
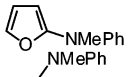
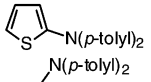
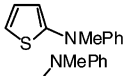
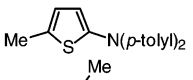
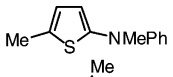
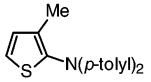
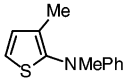


Table 4 summarizes the yields of heteroarylamines formed by reductive elimination from complexes **2a−f** and **3a−f** and from catalytic amination of the heteroaryl bromides in the presence of Pd(dba)$_2$ and DPPF as catalyst and NaO-^{t}Bu as base (see Experimental Section for procedures). The 2-furyl complexes formed the two heteroarylamines in higher yields than did the corresponding 3-furyl complexes (54% and 71% yield vs 3% and 0% yield). This trend was reversed for reaction of the thiophenyl complexes. The 3-thiophenylpalladium amides consistently formed the two heteroarylamines in higher yields than did the two 2-thiophenylpalladium complexes (39% and 59% yield vs 26% and 32% yield).

Table 4. Comparison of Yields from Reductive Elimination and Yields from Catalytic Reactions Involving DPPF-Ligated Palladium Complexes

Complex	Product	Reductive Elimination[a]	Catalytic Amination[b]	Complex	Product	Reductive Elimination[a]	Catalytic Amination[b]
2a		54%	34%	**3a**		71%	72%
2b		3%	0%	**3b**		0%	5%
2c		26%	15%	**3c**		32%	39%
2d		39%	28%	**3d**		59%	40%
2e		13%	2%	**3e**		40%	2%
2f		11%	8%	**3f**		4%	18%

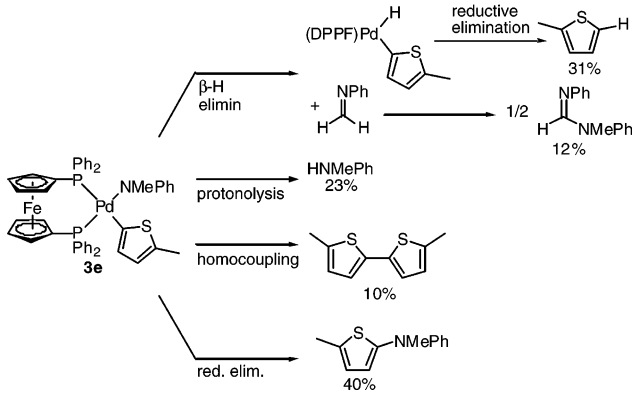
[a] Yields determined by NMR. [b] Yields determined by GC for reactions catalyzed by 2% $Pd(dba)_2$ and 2% DPPF in toluene at 100 °C for 12 h.

The data in Table 4 reveal the parallel trends in yields resulting from stoichiometric reductive elimination from isomeric heteroarylpalladium amides and resulting from catalytic amination of the different heteroaryl halides. The yields were higher for formation of 2-furylamines than for formation of 3-furylamines, but the yields were higher for formation of 3-thiophenylamines than for formation of 2-thiophenylamines.

We also evaluated whether the anilide complex (DPPF)Pd(2-(5-CH_3)C_4H_3S)(NHPh), **4**, which was unstable at room temperature, formed heteroaryl arylamine from reductive elimination. Studies on reductive elimination from arylpalladium amido complexes showed that the anilides underwent reductive elimination of diarylamine in high yields at room temperature.[37] Warming of the heteroarylpalladium anilido complex at 60 °C for 30 min in the presence of PPh_3 formed $(DPPF)_2Pd(0)$ and $(PPh_3)_4Pd(0)$. However, no heteroaryl arylamine product was formed. The absence of coupled product from this stoichiometric reaction is consistent with the low yield of coupled product from the reaction of aniline with the five-membered heteroaryl halides in the presence of palladium catalysts containing either DPPF or P^tBu_3 as ligand.

The yields of products from reductive elimination depend not only on the rate of reductive elimination but on the rate of competing reactions. To identify reactions that compete with reductive elimination, we determined the yields of all major organic products formed from heating the heteroarylpalladium amido complexes. These experiments were conducted with the 5-methyl-2-thiophenylpalladium *N*-methylanilide **3e** because the substituted thiophenyl products could be identified more readily by NMR spectroscopy and GC than the parent thiophenyl side products. The products were identified by a combination of ^{1}H NMR spectroscopy, GC/mass spectroscopy, and independent synthesis. Scheme 4 summarizes the yields of the various organic products formed from heating of **3e** in benzene-d_6 with added PPh_3. The major side products were amine from protonolysis, amidine from β-hydrogen elimination and imine disproportionation, and bithiophene from a homocoupling process. These products, along with the heteroarylamine from reductive elimination, accounted for

Scheme 4



91% of the heteroaryl groups and 86% of the amido groups of the starting complex.

Discussion

Connections between Heteroaryl Halide Substitution Pattern and Reductive Elimination. The isomeric furyl and thiophenyl complexes have significantly different electronic properties, and the yields of the catalytic reactions can be understood, in part, by the relationship between electronics and reductive elimination rates. Carbon−nitrogen bond-forming reductive elimination of arylamines is faster from complexes with more electron-donating amido groups and less electron-donating aryl groups.[37] Thus, the complexes with more electron-donating heteroaryl groups on palladium should undergo slower reductive elimination. We did not measure the rates for reaction of each heteroaryl compound. However, slower reductive elimination would allow side reactions to occur and could reduce the yields of the desired heteroarylamine products.

Figure 5 shows the Mulliken charge distributions on furans and thiophenes, as determined by RHF calculations with a 6-31G* basis set. Similar calculations have been performed previously at various levels,[34,39] but not in an identical manner for the two systems. These calculations show that the 3-position of furan is much

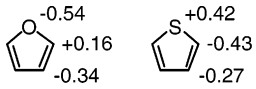


Figure 5. Natural charges of furan and thiophene obtained by a 6-31G* RHF calculation.

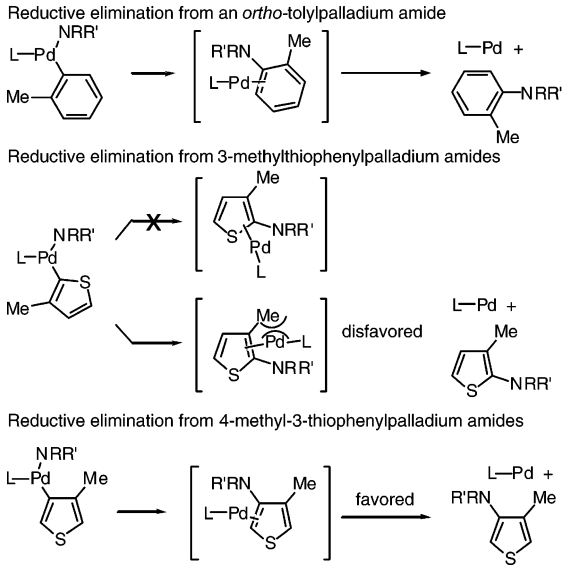
more electron rich than the 2-position. In contrast, the calculations showed that the 2-position of thiophene is more electron-rich. Thus, reductive elimination from complexes containing 3-furanyl and 2-thiophenyl groups should be less favorable than reductive elimination from complexes containing 2-furanyl and 3-thiophenyl groups. This prediction is consistent with the yields of reductive elimination product from heating of complexes **2a**−**d** and **3a**−**d**.

Structural Effects on the Reaction Rates and Yields. The position of the donor atom and the pattern of substitution of the heterocycles could be envisioned to influence the reductive elimination from isolated thiophenyl- and furanylpalladium amido complexes by mechanisms other than electronic effects. First, the heteroatom could coordinate to palladium in the ground or transition state structures. However, structures of the amido complexes determined by X-ray diffraction showed M−S and M−O bond lengths that are beyond bonding distance.

The combination of the heteroatom position and the presence of substituents contiguous to the metal on the heteroaryl group did influence the yields of reductive elimination, however. This effect on reductive elimination was distinct from that of *ortho* substituents located on an aromatic ring. A detailed study of structural effects on the reductive elimination of sulfides has suggested that arylpalladium thiolate complexes first generate an arylsulfide complex that is coordinated through the arene π-system.[40] Similar arene π-complexes have been suggested by computational studies to be intermediates in the oxidative addition of aryl halides to Pd(0).[41] Thus, the stability of such π-arene intermediates should influence the rates for reductive elimination.

Stable η^2, π-complexes of thiophenes are coordinated through C=C bonds between the 2- and 3-carbons.[42,43] As shown in Scheme 5, the 3-methyl-2-amidopalladium thiophenyl π-complex and the 4-methyl-3-amidopalladium thiophenyl π-complex have different structures and, therefore, different stabilities. The intermediate thiophenyl π-complex in the top reaction of Scheme 5 will be the least stable of the three π-complexes because it is coordinated through a C−S bond. The middle intermediate will be more stable, but will experience large steric effects because the palladium is coordinated to a fully substituted thiophene C=C bond. The bottom intermediate, which would be formed from reductive elimination of a 4-methyl-3-amidopalladium thiophenyl complex, is the most stable and should, therefore, have the lowest energy transition state to form it by reductive elimination. In accord with this argument, the amidopalladium complexes formed from 2-bromo-3-methylthiophene underwent reductive elimination in lower yields, and 2-bromo-3-methylthiophene coupled with amines in lower yields than the equivalent unsubsituted thiophene.

Scheme 5. π-Complexes in the Reductive Elimination from Aryl- and Heteroarylpalladium Amides



Conclusions

To begin to understand the factors that control reductive eliminations and the scope of coupling reactions with electron-rich heteroaryl halides, we prepared a range of DPPF-ligated furanylpalladium and thiophenylpalladium amido complexes. The observed trends in reductive elimination can be explained by the distribution of electron density within the heteroaryl systems. Heteroarylpalladium amido complexes in which the palladium was attached to the less electron-rich position of the heteroaryl groups underwent reductive elimination faster and in higher yields than did complexes in which the palladium was attached to the more electron-rich position. Because the position that is more electron-rich and less electron-rich is reversed in thiophenes and furans, the yields of reductive elimination for isomeric thiophenes and furans are different. Coordination of the heteroatom in 2-thiophenyl and 2-furanyl complexes does not appear to influence the yields and scope of the reductive elimination. However, the presence of the heteroatom does alter the effect of substituents proximal to the metal center. In contrast to the general accelerating effect of an *ortho* substituent on the rate and yields of reductive elimination of arylamines, -sulfides, and -ethers, a pseudo-*ortho* substituent decreases the yields of reductive elimination from 2-thiophenyl complexes.

Experimental Section

General Methods. Unless otherwise noted, all reactions and manipulations were performed in an inert atmosphere glovebox. All $^{31}P\{^1H\}$ NMR chemical shifts are reported in parts per million relative to an 85% H_3PO_4 external standard. Shifts downfield of the standard are reported as positive. Benzene, toluene, and pentane solvents were distilled from

(39) Lazzaroni, R.; Boutique, J. P.; Riga, J.; Verbist, J. J.; Fripiat, J. G.; Delhalle, J. *J. Chem. Soc., Perkin Trans. 2* **1985**, 97−102.
(40) Mann, G.; Barañano, D.; Hartwig, J. F.; Rheingold, A. L.; Guzei, I. A. *J. Am. Chem. Soc.* **1998**, *120*, 9205.
(41) Sundermann, A.; Uzan, O.; Martin, J. M. L. *Chem. Eur. J.* **2001**, *7*, 1703.
(42) Spera, M. L.; Harman, W. D. *Organometallics* **1995**, *14*, 1559−1561.
(43) Rauchfuss, T. B. *Prog. Inorg. Chem.* **1991**, *39*, 259.

sodium/ benzophenone prior to use. 3-Bromofuran was distilled prior to use. 2-Bromofuran,[44] 2-bromo-5-methylfuran, [44] 2-bromo-5-methylthiophene,[44] and 3-bromo-*N*-methylindole[45] were all prepared according to literature procedures. All other chemicals were used as received from commercial suppliers.

General Procedure for the Preparation of (DPPF)Pd-(Heteroaryl)Br Complexes, 1a−f. In a drybox, Pd(P(*o*-tolyl)$_3$)$_2$ (0.71 mmol) was weighed directly into a screw-capped vial. A stir bar was added, followed by 10 mL of benzene. The heteroaryl bromide (2.84 mmol, 4 equiv) was added and stirred for 10 min. DPPF (391 mg, 0.71 mmol) was dissolved in 10 mL of benzene and added dropwise over 2 min. The reaction was monitored by removing an aliquot, adding 0.5 mL of CH_2Cl_2 to ensure homogeneity, and obtaining a ^{31}P NMR spectrum. Upon completion of the reaction, the yellow precipitate was filtered, washed with 5 mL of benzene, then 2 × 5 mL of pentane, and dried in vacuo.

(DPPF)Pd(2-C$_4$H$_3$O)(Br), 1a. The above general procedure was followed using Pd(P(*o*-tolyl)$_3$)$_2$ (500 mg, 0.71 mmol), 2-bromofuran (418 mg, 251 μL, 2.8 mmol), and DPPF (391 mg, 0.71 mmol) in 20 mL of benzene to give 476 mg (83%) of (DPPF)Pd(2-C$_4$H$_3$O)(Br) as a yellow solid: ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.99 (m, 4H), 7.51 (m, 10H), 7.40 (m, 2H), 7.26 (m, 4H), 7.10 (bs, 1H), 5.94 (bs, 1H), 5.65 (bs, 1H), 4.61 (bs, 2H), 4.46 (bs, 2H), 4.21 (m, 2H), 3.83 (bs, 2H); ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 154.73 (dd, J_{CP} = 164.3, 9.8 Hz), 146.56 (d, J_{CP} = 5.6 Hz), 136.14 (d, J_{CP} = 11.9 Hz), 134.76 (d, J_{CP} = 12.2 Hz), 133.62(d, J_{CP} = 51.7 Hz), 133.53 (d, J_{CP} = 45.8 Hz), 131.24, 131.23, 128.85 (d, J_{CP} = 9.9 Hz), 128.79 (d, J_{CP} = 11.1 Hz), 115.13 (dd, J_{CP} = 5.5 Hz, 13.4 Hz), 111.78 (d, J_{CP} = 6.1 Hz), 77.40 (dd, J_{CP} = 58.3, 7.9 Hz), 76.77 (d, J_{CP} = 11.1 Hz), 75.32 (d, J_{CP} = 8.7 Hz), 75.05 (dd, J_{CP} = 45.0, 3.3 Hz), 74.32 (d, J_{CP} = 7.3 Hz), 73.49 (d, J_{CP} = 5.3 Hz); ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2) δ 28.36 (d, J_{PP} = 21.3 Hz), 13.17 (d, J_{PP} = 21.7 Hz). Anal. Calcd for $C_{38}H_{31}BrFeOP_2Pd$: C, 56.58; H, 3.88. Found: C, 56.82; H, 3.60.

(DPPF)Pd(3-C$_4$H$_3$O)(Br), 1b. The above general procedure was followed using Pd(P(*o*-tolyl)$_3$)$_2$ (500 mg, 0.71 mmol), 3-bromofuran (418 mg, 256 μL, 2.8 mmol), and DPPF (391 mg, 0.71 mmol) in 20 mL of benzene to give 482 mg (84%) of (DPPF)Pd(3-C$_4$H$_3$O)(Br) as a yellow solid: ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.99 (m, 4H), 7.51 (m, 10H), 7.40 (m, 2H), 7.26 (m, 4H), 6.90 (bs, 1H), 6.20 (m, 1H), 5.72 (m, 1H), 4.58 (q, J = 1.9 Hz, 2H), 4.44 (m, 2H), 4.19 (m, 2H), 3.83 (q, J = 1.8 Hz, 2H); ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 140.64 (d, J_{CP} = 8.1 Hz), 139.66 (m), 136.18 (d, J_{CP} = 11.9 Hz), 134.86 (d, J_{CP} = 11.9 Hz), 134.04 (d, J_{CP} = 25.2 Hz), 134.56 (d, J_{CP} = 43.3 Hz), 131.29 (d, J_{CP} = 2.5 Hz), 131.15 (d, J_{CP} = 2.4 Hz), 128.83 (d, J_{CP} = 5.2 Hz), 128.73 (d, J_{CP} = 6.4 Hz), 124.21 (dd, J_{CP} = 138.2, 10.3 Hz), 116.83 (m), 77.83 (dd, J_{CP} = 49.9, 8.0 Hz), 76.65 (d, J_{CP} = 11.0 Hz), 75.26 (dd, J_{CP} = 40.6, 3.4 Hz), 75.20 (d, J_{CP} = 8.7 Hz), 74.26 (d, J_{CP} = 7.1 Hz), 73.46 (d, J_{CP} = 4.8 Hz); ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ 30.18 (d, J_{CP} = 21.8 Hz), 11.98 (d, J_{CP} = 21.7 Hz).

(DPPF)Pd(2-C$_4$H$_3$S)(Br), 1c. The above general procedure was followed using Pd(P(*o*-tolyl)$_3$)$_2$ (500 mg, 0.71 mmol), 2-bromothiophene (457 mg, 273 μL, 2.8 mmol), and DPPF (391 mg, 0.71 mmol) in 20 mL of benzene to give 509 mg (87%) of (DPPF)Pd(2-C$_4$H$_3$S)(Br) as a yellow solid: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.02 (m, 4H), 7.52 (m, 6H), 7.46 (dd, J_{HH} = 7.2 Hz, J_{HP} = 12.1 Hz, 4H), 7.37 (m, 2H), 7.20 (t of d, J_{HH} = 7.9 Hz, J_{HP} = 2.4 Hz, 4H), 7.06 (m, 1H), 6.56 (m, 1H), 6.17 (dd, J_{HH} = J_{HP} = 3.9 Hz, 1H), 4.66 (q, J = 1.9 Hz, 2H), 4.49 (m, 2H), 4.19 (m, 2H), 3.74 (q, J = 1.7 Hz, 2H); ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 146.79 (dd, J_{CP} = 150.3, 10.5 Hz), 135.92 (d, J_{CP} = 11.8 Hz), 134.50 (d, J_{CP} = 11.8 Hz), 133.39 (d, J_{CP} = 40.1 Hz), 133.13 (d, J_{CP} = 57.4 Hz), 130.99, 130.97, 129.46 (m), 129.17 (m), 128.60 (d, J_{CP} = 10.0 Hz), 128.44 (d, J_{CP} = 11.1 Hz), 127.04 (d, J_{CP} = 11.3 Hz), 77.22 (dd, J_{CP} = 51.3, 8.3 Hz), 76.70 (d, J_{CP} = 11.3 Hz), 74.92 (d, J_{CP} = 8.5 Hz), 74.85 (dd, J_{CP} = 33.0, 2.3 Hz), 74.21 (d, J_{CP} = 7.5 Hz), 73.18 (d, J_{CP} = 5.3 Hz); ^{31}P{^{1}H} (202 MHz, CD_2Cl_2) NMR δ 30.77 (d, J_{PP} = 21.0 Hz), 12.68 (d, J_{PP} = 20.8 Hz). Anal. Calcd for $C_{38}H_{31}BrFeSP_2Pd$: C, 55.48; H, 3.77; S, 3.89. Found: C, 55.50; H, 3.98; S, 3.62.

(DPPF)Pd(3-C$_4$H$_3$S)(Br), 1d. The above general procedure was followed using Pd(P(*o*-tolyl)$_3$)$_2$ (500 mg, 0.71 mmol), 3-bromothiophene (457 mg, 262 μL, 2.8 mmol), and DPPF (391 mg, 0.71 mmol) in 20 mL of benzene to give 374 mg (64%) of (DPPF)Pd(3-C$_4$H$_3$S)(Br) as a yellow solid: ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.02 (m, 4H), 7.51 (m, 6H), 7.44 (dd, J_{HH} = 7.9 Hz, J_{HP} = 12.1 Hz, 4H), 7.36 (m, 2H), 7.20 (t of d, J_{HH} = 7.8 Hz, J_{HP} = 2.2 Hz, 4H), 6.76 (quin, J = 2.3 Hz, 1H), 6.48 (m, 1H), 6.24 (m, 1H), 4.63 (m, 2H), 4.47 (m, 2H), 4.18 (m, 2H), 3.77 (q, J = 1.8 Hz, 2H); ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) 144.88 (dd, J_{CP} = 130.8, 7.2 Hz), 135.91 (d, J_{CP} = 12.0 Hz), 134.41 (d, J_{CP} = 11.9 Hz), 133.72 (d, J_{CP} = 37.0 Hz), 133.49 (d, J_{CP} = 56.4 Hz), 133.31 (m), 130.85, 130.84, 128.57 (d, J_{CP} = 9.8 Hz), 128.51 (d, J_{CP} = 11.1 Hz), 122.20 (d, J_{CP} = 11.8 Hz), 119.35 (m), 77.48 (dd, J_{CP} = 51.3, 7.9 Hz), 76.46 (d, J_{CP} = 11.3 Hz), 75.15 (dd, J_{CP} = 39.5, 3.0 Hz), 74.84 (d, J_{CP} = 8.6 Hz), 74.01 (d, J_{CP} = 7.4 Hz), 73.04 (d, J_{CP} = 5.0 Hz); ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ 30.07 (d, J_{PP} = 26.0 Hz), 11.33 (d, J_{PP} = 25.9 Hz).

(DPPF)Pd(2-(5-CH$_3$)C$_4$H$_3$S)(Br), 1e. The above general procedure was followed using Pd(P(*o*-tolyl)$_3$)$_2$ (500 mg, 0.71 mmol), 2-bromo-5-methylthiophene (496 mg, 315 μL, 2.8 mmol), and DPPF (391 mg, 0.71 mmol) in 20 mL of benzene to give 297 mg (50%) of (DPPF)Pd(2-(5-CH$_3$)C$_4$H$_3$S)(Br) as a yellow solid: ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.00 (m, 4H), 7.53−7.46 (m, 10H), 7.39 (m, 2H), 7.21 (t of d, J_{HH} = 8.0 Hz, J_{HP} = 2.4 Hz, 4H), 6.19 (bs, 1H), 5.89 (m, 1H), 4.64 (m, 2H), 4.47 (bs, 2H), 4.18 (m, 2H), 3.75 (m, 2H), 2.18 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2) δ 144.23 (m), 142.70 (dd, J_{CP} = 150.9, 10.6 Hz) 135.96 (d, J_{CP} = 11.7 Hz), 134.65 (d, J_{CP} = 12.0 Hz), 133.53 (d, J_{CP} = 38.8 Hz), 132.14 (d, J_{CP} = 57.1 Hz), 130.94 (m), 130.89 (m), 129.45 (m), 128.60 (d, J_{CP} = 9.7 Hz), 128.39 (d, J_{CP} = 10.9 Hz), 126.21 (d, J_{CP} = 10.2 Hz), 77.42 (dd, J_{CP} = 50.2, 8.0 Hz), 76.66 (d, J_{CP} = 11.1 Hz), 74.95 (dd, J_{CP} = 43.2, 3.8 Hz), 74.92 (d, J_{CP} = 8.5 Hz), 74.13 (d, J_{CP} = 7.4 Hz), 73.14 (d, J_{CP} = 5.1 Hz), 15.68; ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ 30.18 (d, J_{PP} = 22.2 Hz), 12.32 (d, J_{PP} = 22.2 Hz). Anal. Calcd for $C_{39}H_{33}BrFeSP_2Pd$: C, 55.99; H, 3.98. Found: C, 55.83; H, 4.05.

(DPPF)Pd(2-(3-CH$_3$)C$_4$H$_3$S)(Br), 1f. The above general procedure was followed using Pd(P(*o*-tolyl)$_3$)$_2$ (500 mg, 0.71 mmol), 2-bromo-3-methylthiophene (496 mg, 311 μL, 2.8 mmol), and DPPF (391 mg, 0.71 mmol) in 20 mL of benzene to give 315 mg (53%) of (DPPF)Pd(2-(3-CH$_3$)C$_4$H$_3$S)(Br) as a yellow solid: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.06 (m, 2H), 7.98 (m, 2H), 7.81 (m, 2H), 7.56 (m, 2H), 7.49 (m, 4H), 7.31 (t of d, J_{HH} = 7.8 Hz, J_{HP} = 2.4 Hz, 2H), 7.22 (m, 2H), 7.01 (m, 5H), 6.32 (dd, J_{HH} = 4.8 Hz, J_{HP} = 2.2 Hz, 1H), 4.88 (m, 1H), 4.58 (m, 1H), 4.47 (bs, 1H), 4.44 (m, 1H), 4.17 (m, 2H), 3.75 (m, 1H), 3.58 (m, 1H), 1.91 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2) 140.97 (dd, J_{CP} = 146.8, 8.6 Hz), 137.25 (m), 136.63 (d, J_{CP} = 12.3 Hz), 136.36 (d, J_{CP} = 13.3 Hz), 135.67 (d, J_{CP} = 10.9 Hz), 134.86 (d, J_{CP} = 62.6 Hz), 134.48 (d, J_{CP} = 41.6 Hz), 133.33 (d, J_{CP} = 104.8 Hz), 133.17 (d, J_{CP} = 10.8 Hz), 132.51 (d, J_{CP} = 55.2 Hz), 132.22 (m), 131.47 (m), 130.91 (m), 130.59 (d, J_{CP} = 11.2 Hz), 130.24 (m), 129.38 (m), 128.97 (d, J_{CP} = 9.8 Hz), 128.94 (d, J_{CP} = 11.2 Hz), 128.72 (d, J_{CP} = 9.6 Hz), 127.89 (d, J_{CP} = 10.7 Hz), 78.00 (d, J_{CP} = 16.9 Hz), 77.36 (dd, J_{CP} = 51.0, 7.4 Hz), 76.08 (d, J_{CP} = 6.3 Hz), 75.34 (dd, J_{CP} = 42.1, 3.6 Hz), 75.27, 75.22 (m), 75.21 (d, J_{CP} = 6.7 Hz), 74.21 (d, J_{CP} = 5.9 Hz), 73.74 (d, J_{CP} = 6.0 Hz), 72.39 (d, J_{CP} = 4.4 Hz), 18.96; ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ 30.50 (d, J_{CP} = 22.5 Hz), 11.79 (d, J_{CP} = 22.3 Hz). Anal. Calcd for $C_{39}H_{33}BrFeSP_2Pd\cdot CD_2Cl_2$: C, 51.95; H, 3.57. Found: C, 51.58; H, 3.69.

(44) Keegstra, M. A.; Klomp, A. J. A.; Brandsma, L. *Synth. Commun.* **1990**, *20*, 3371.
(45) Bocchi, V.; Palla, G. *Synlett* **1982**, 1096.

Preparation of 1d from $Pd(dba)_2$, DPPF, and 2-Bromothiophene. Into a vial were placed 55.4 mg (0.100 mmol) of DPPF and 52.4 mg (0.100 mmol) of $Pd(dba)_2$. Into a second vial were placed 82 mg (0.50 mmol) of 2-bromothiophene and 1 mL of toluene. The toluene solution was added to the mixture of metal and ligand, and the vial was sealed with a screw cap. The resulting solution was heated at 100 °C for 1 h, after which time a yellow solid had crystallized. The toluene was removed by pipet, and the resulting solid was washed with pentane. The mother liquor and pentane washes were combined, and after 2 h additional solid had formed. The solvent was removed from this solid, and the solid was washed with pentane. The two crops were combined to total 58 mg (70%) of yellow product, which was identical by ^{1}H and ^{31}P NMR spectroscopy to samples prepared by the above procedure.

General Procedure for the Preparation of (DPPF)Pd(Heteroaryl)[N(*p*-$CH_3C_6H_4)_2$] Complexes, 2a−f. In a drybox, (DPPF)Pd(HetAr)Br (0.12 mmol) and KN(*p*-$CH_3C_6H_4)_2$ (0.18 mmol) were weighed directly into a screw-capped vial. A stir bar was added followed by 5 mL of toluene, and the mixture was stirred. The reaction was monitored by removing an aliquot and obtaining a ^{31}P NMR spectrum. Upon completion of the reaction, the mixture was filtered through Celite, concentrated in vacuo to approximately 2 mL, layered with 10 mL of pentane, and placed at −40 °C for 24 h. The supernatant was removed, and the resulting purple crystals were washed with 3 × 5 mL of pentane and dried in vacuo.

(DPPF)Pd(2-C_4H_3O)[N(*p*-$CH_3C_6H_4)_2$], 2a. The above general procedure was followed using (DPPF)Pd(2-C_4H_3O)Br (100 mg, 0.12 mmol) and KN(*p*-$CH_3C_6H_4)_2$ (42.3 mg, 0.18 mmol) in 5 mL of toluene to give 78 mg (70%) of (DPPF)Pd(2-C_4H_3O)-[N(*p*-$CH_3C_6H_4)_2$] as purple crystals: ^{1}H NMR (400 MHz, C_6D_6) δ 8.08 (m, 4H), 7.60 (d, J = 8.2 Hz, 4H), 7.57 (m, 4H), 7.13−6.81 (m, 13H), 6.94 (d, J = 8.1 Hz, 4H), 6.37 (d, J = 3.1 Hz, 1H), 5.97 (m, 1H), 4.70 (m, 2H), 4.01 (m, 2H), 3.68 (m, 2H), 3.61 (bs, 2H), 2.26 (s, 6H); ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2) δ 164.38 (dd, J_{CP} = 161.5, 9.7 Hz), 152.95, 143.19 (d, J_{CP} = 6.8 Hz), 135.20 (d, J_{CP} = 14.4 Hz), 135.13 (d, J_{CP} = 12.5 Hz), 135.01 (d, J_{CP} = 33.4 Hz), 133.88 (d, J_{CP} = 50.7 Hz), 130.98, 130.72, 128.96, 128.76 (d, J_{CP} = 10.7 Hz), 128.16 (d, J_{CP} = 9.9 Hz), 123.82, 121.27, 116.30 (d, J_{CP} = 12.9 Hz), 110.20 (d, J_{CP} = 5.2 Hz), 79.36 (dd, J_{CP} = 49.1, 6.7 Hz), 77.08 (d, J_{CP} = 11.8 Hz), 75.73 (d, J_{CP} = 8.6 Hz), 74.64 (dd, J_{CP} = 40.2, 1.9 Hz), 74.58 (d, J_{CP} = 6.4 Hz), 72.64 (d, J_{CP} = 5.7 Hz), 20.97; ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ 27.10 (d, J_{PP} = 32.1 Hz), 22.83 (d, J_{PP} = 32.2 Hz). Anal. Calcd for $C_{52}H_{45}FeNOP_2Pd$: C, 67.60; H, 4.91; N, 1.51. Found: C, 67.26; H, 4.71; N, 1.46. See below for X-ray structural determination.

(DPPF)Pd(3-C_4H_3O)[N(*p*-$CH_3C_6H_4)_2$], 2b. The above general procedure was followed using (DPPF)Pd(3-C_4H_3O)Br (100 mg, 0.12 mmol) and KN(*p*-$CH_3C_6H_4)_2$ (42.3 mg, 0.18 mmol) in 5 mL of toluene to give 84 mg (76%) of (DPPF)Pd(3-C_4H_3O)-[N(*p*-$CH_3C_6H_4)_2$] as purple crystals: ^{1}H NMR (400 MHz, C_6D_6) δ 7.90 (m, 4H), 7.69 (m, 4H), 7.46 (d, J = 8.3 Hz, 4H), 7.09−6.87 (m, 13H), 6.92 (d, J = 8.2 Hz, 4H), 6.36 (m, 1H), 6.14 (m, 1H), 4.64 (m, 2H), 4.04 (m, 2H), 3.87 (m, 2H), 3.62 (m, 2H), 2.26 (s, 6H); ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 152.57, 141.90 (m), 138.25 (d, J_{CP} = 7.7 Hz), 135.17 (d, J_{CP} = 12.9 Hz), 134.93 (d, J_{CP} = 11.8 Hz), 134.91 (d, J_{CP} = 39.5 Hz), 132.99 (d, J_{CP} = 51.0 Hz), 130.97 (m), 130.49 (m), 128.70, 128.64 (d, J_{CP} = 8.6 Hz), 127.93 (d, J_{CP} = 9.5 Hz), 125.17 (dd, J_{CP} = 134.8, 13.6 Hz), 123.58, 120.98 (d, J_{CP} = 2.0 Hz), 117.77 (d, J_{CP} = 3.3 Hz), 79.57 (dd, J_{CP} = 46.2, 7.4 Hz), 76.63 (d, J_{CP} = 11.8 Hz), 75.26 (d, J_{CP} = 8.8 Hz), 74.44 (dd, J_{CP} = 38.6, 3.1 Hz), 74.23 (d, J_{CP} = 6.2 Hz), 72.51 (d, J_{CP} = 5.6 Hz), 20.76; ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ 25.79 (d, J_{PP} = 31.6 Hz), 21.32 (d, J_{PP} = 31.7 Hz). Anal. Calcd for $C_{52}H_{45}FeNOP_2Pd$: C, 67.60; H, 4.91; N, 1.51. Found: C, 67.55; H, 4.81; N, 1.43. See below for X-ray structural determination.

(DPPF)Pd(2-C_4H_3S)[N(*p*-$CH_3C_6H_4)_2$], 2c. The above general procedure was followed using (DPPF)Pd(2-C_4H_3S)Br (100 mg, 0.12 mmol) and KN(*p*-$CH_3C_6H_4)_2$ (42.3 mg, 0.18 mmol) in 5 mL of toluene to give 81 mg (72%) of (DPPF)Pd(2-C_4H_3S)-[N(*p*-$CH_3C_6H_4)_2$] as purple crystals: ^{1}H NMR (400 MHz, C_6D_6) δ 7.84 (m, 4H), 7.72 (m, 4H), 7.43 (d, J = 8.3 Hz, 4H), 7.09−7.02 (m, 6H), 6.92 (m, 7H), 6.91 (d, J = 8.3 Hz, 4H), 6.62 (m, 1H), 6.37 (m, 1H), 4.63 (m, 2H), 4.00 (m, 2H), 3.95 (m, 2H), 3.65 (m, 2H), 2.25 (s, 6H); ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2) δ 152.69, 149.85 (dd, J_{CP} = 145.15, 14.4 Hz), 135.47 (d, J_{CP} = 12.5 Hz), 135.20 (d, J_{CP} = 11.6 Hz), 135.02 (d, J_{CP} = 40.32 Hz), 132.90 (d, J_{CP} = 50.9 Hz), 131.69 (m), 131.09 (m), 130.81 (m), 128.84, 128.79 (d, J_{CP} = 11.5 Hz), 128.17 (d, J_{CP} = 9.6 Hz), 127.34 (d, J_{CP} = 4.7 Hz), 125.40 (d, J_{CP} = 10.6 Hz), 124.09, 121.60 (d, J_{CP} = 2.1 Hz), 78.86 (dd, J_{CP} = 49.9, 6.7 Hz), 76.78 (d, J_{CP} = 11.7 Hz), 75.63 (d, J_{CP} = 8.7 Hz), 74.59 (d, J_{CP} = 6.5 Hz), 74.27 (dd, J_{CP} = 39.4, 2.9 Hz), 72.97 (d, J_{CP} = 5.8 Hz), 20.98; ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ 23.86 (d, J_{PP} = 33.8 Hz), 20.37 (d, J_{PP} = 34.0 Hz). Anal. Calcd for $C_{52}H_{45}FeNP_2PdS\cdot C_7H_8$: C, 68.66; H, 5.18; N, 1.36. Found: C, 68.79; H, 5.20; N, 1.25. See below for X-ray structural determination.

(DPPF)Pd(3-C_4H_3S)[N(*p*-$CH_3C_6H_4)_2$], 2d. The above general procedure was followed using (DPPF)Pd(3-C_4H_3S)Br (100 mg, 0.12 mmol) and KN(p-$CH_3C_6H_4)_2$ (42.3 mg, 0.18 mmol) in 5 mL of toluene to give 53 mg (47%) of (DPPF)Pd(3-C_4H_3S)-[N(p-$CH_3C_6H_4)_2$] as purple crystals: ^{1}H NMR (400 MHz, C_6D_6) δ 7.80−7.70 (m, 8H), 7.37 (d, J = 8.3 Hz, 4H), 7.03 (m, 6H), 6.97 (m, 6H), 6.90 (d, J = 8.2 Hz, 4H), 6.78 (m, 1H), 6.65 (m, 1H), 6.25 (m, 1H), 4.57 (m, 2H), 4.05 (m, 2H), 3.99 (m, 2H), 3.68 (m, 2H), 2.25 (s, 6H); ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2) δ 153.08, 147.93 (dd, J_{CP} = 125.8, 11.6 Hz), 135.59 (d, J_{CP} = 12.7 Hz), 135.33 (d, J_{CP} = 37.3 Hz), 134.96 (d, J_{CP} = 11.6 Hz), 134.59 (m), 133.08 (d, J_{CP} = 51.4 Hz), 130.89 (m), 130.71 (m), 128.89, 128.70 (d, J_{CP} = 10.2 Hz), 128.20 (d, J_{CP} = 9.5 Hz), 123.92, 121.65 (m), 121.55 (m), 119.68 (d, J_{CP} = 11.0 Hz), 78.96 (dd, J_{CP} = 43.9, 7.2 Hz), 76.39 (d, J_{CP} = 11.3 Hz), 75.45 (d, J_{CP} = 9.2 Hz), 74.39 (d, J_{CP} = 6.4 Hz), 73.95 (dd, J_{CP} = 37.4, 2.9 Hz), 74.02 (d, J_{CP} = 5.9 Hz), 20.99; ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ 23.45 (d, J_{PP} = 33.7 Hz), 17.39 (d, J_{PP} = 33.7 Hz). Anal. Calcd for $C_{52}H_{45}FeNP_2PdS$: C, 66.45; H, 4.83; N, 1.49. Found: C, 66.57; H, 4.62; N, 1.36. See below for X-ray structural determination.

(DPPF)Pd(2-(5-CH_3)C_4H_3S)[N(*p*-$CH_3C_6H_4)_2$], 2e. The above general procedure was followed using (DPPF)Pd(2-(5-CH_3)C_4H_3S)Br (100 mg, 0.12 mmol) and KN(*p*-$CH_3C_6H_4)_2$ (42.3 mg, 0.18 mmol) in 5 mL of toluene to give 90 mg (79%) of (DPPF)Pd(2-(5-CH_3)C_4H_3S)[N(*p*-$CH_3C_6H_4)_2$] as purple crystals: ^{1}H NMR (400 MHz, C_6D_6) δ 7.90 (ddd, J_{HH} = 6.6 Hz, J_{HP} = 11.1, 1.6 Hz, 4H), 7.72 (m, 4H), 7.46 (d, J = 8.3 Hz, 4H), 7.14−6.90 (m, 12H), 6.91 (d, J = 8.2 Hz, 4H), 6.27 (m, 1H), 6.09 (m, 1H), 4.62 (q, J = 1.8 Hz, 2H), 4.01 (m, 2H), 3.96 (q, J = 1.8 Hz, 2H), 3.67 (m, 2H), 2.25 (s, 6H), 2.07 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2) 156.78, 146.45 (dd, J_{CP} = 145.0, 13.9 Hz), 141.93 (d, J_{CP} = 4.5 Hz), 135.48 (d, J_{CP} = 12.5 Hz), 135.29 (d, J_{CP} = 11.6 Hz), 135.16 (d, J_{CP} = 39.7 Hz), 132.99 (d, J_{CP} = 51.2 Hz), 131.81 (dd, J_{CP} = 5.7, 5.7 Hz), 130.97 (d, J_{CP} = 2.0 Hz), 130.76 (d, J_{CP} = 1.8 Hz), 128.83, 128.74 (d, J_{CP} = 10.6 Hz), 128.16 (d, J_{CP} = 9.7 Hz), 124.51 (d, J_{CP} = 9.7 Hz), 123.98, 121.66 (d, J_{CP} = 2.3 Hz), 78.88 (dd, J_{CP} = 46.0, 6.7 Hz), 76.69 (d, J_{CP} = 11.5 Hz), 75.64 (d, J_{CP} = 8.7 Hz), 74.54 (d, J_{CP} = 6.3 Hz), 74.27 (dd, J_{CP} = 38.6, 2.9 Hz), 72.96 (d, J_{CP} = 5.8 Hz), 21.00, 15.65; ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ 24.03 (d, J_{PP} = 33.7 Hz), 20.09 (d, J_{PP} = 33.7 Hz). Anal. Calcd for $C_{53}H_{47}FeNP_2PdS$: C, 66.71; H, 4.96; N, 1.47. Found: C, 66.48; H, 5.01; N, 1.30.

(DPPF)Pd(2-(3-CH_3)C_4H_3S)[N(p-$CH_3C_6H_4)_2$], 2f. The above general procedure was followed using (DPPF)Pd(2-(3-CH_3)-C_4H_3S)Br (100 mg, 0.12 mmol) and KN(p-$CH_3C_6H_4)_2$ (42.3 mg, 0.18 mmol) in 5 mL of toluene to give 61 mg (54%) of (DPPF)-Pd(2-(3-CH_3)C_4H_3S)[N(p-$CH_3C_6H_4)_2$] as purple crystals: ^{1}H NMR (400 MHz, C_6D_6) 8.43 (m, 4H), 7.46 (dd, J_{HH} = 8.2 Hz, J_{HP} = 8.8 Hz, 2H), 7.38 (d, J = 8.2 Hz, 2H), 7.29−7.13 (m, 4H), 7.06−7.01 (m, 4H), 6.97−6.83 (m, 13H), 6.49 (dd, J_{HH} =

4.8 Hz, J_{HP} = 1.7 Hz, 1H), 5.14 (s, 1H), 4.78 (s, 1H), 3.95 (s, 1H), 3.85 (s, 1H), 3.83 (s, 1H), 3.81 (s, 1H), 3.70 (s, 1H), 3.53 (s, 1H), 2.32 (s, 3H), 2.18 (s, 3H), 1.49 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2) δ 151.64, 151.42, 143.77 (dd, J_{CP} = 140.1, 16.0 Hz), 137.35 (m), 135.92 (d, J_{CP} = 14.4 Hz), 135.56 (d, J_{CP} = 13.1 Hz), 132.84 (d, J_{CP} = 39.7 Hz), 132.67 (d, J_{CP} = 49.9 Hz), 132.40 (d, J_{CP} = 38.5 Hz), 131.57 (d, J_{CP} = 10.0 Hz), 131.19 (d, J_{CP} = 9.6 Hz), 130.15, 129.92, 129.70 (d, J_{CP} = 53.9 Hz), 128.24, 127.60, 127.17, 126.79 (d, J_{CP} = 10.2 Hz), 126.69, 126.54 (d, J_{CP} = 12.1 Hz), 125.25 (d, J_{CP} = 9.7 Hz), 125.08 (d, J_{CP} = 9.9 Hz), 125.09 (m), 123.77, 123.08, 120.67, 118.62, 116.12 (d, J_{CP} = 5.5 Hz), 75.44 (dd, J_{CP} = 41.8, 6.4 Hz), 75.22 (d, J_{CP} = 22.4 Hz), 74.12 (d, J_{CP} = 16.2 Hz), 73.38 (d, J_{CP} = 8.7 Hz), 72.82, 72.78 (d, J_{CP} = 7.7 Hz), 71.99, 71.10 (dd, J_{CP} = 37.0, 2.6 Hz), 71.04 (m), 69.74 (d, J_{CP} = 3.9 Hz), 18.74, 18.65, 15.44 (m); $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6) δ 18.66 (d, J_{PP} = 34.1 Hz), 14.20 (d, J_{PP} = 34.0 Hz).

General Procedure for the Preparation of (DPPF)Pd(Hetoroaryl)(NMePh) Complexes, 3a−f. In a drybox, (DPPF)Pd(HetAr)Br (0.12 mmol) and KNMePh (0.14 mmol) were weighed directly into a screw-capped vial. A stir bar was added followed by 5 mL of toluene. The mixture was stirred for 10 min. The reaction was monitored by removing an aliquot and obtaining a ^{31}P NMR spectrum. Upon completion of the reaction, the mixture was filtered through Celite, concentrated in vacuo to approximately 2 mL, layered with 10 mL of pentane, and placed at −40 °C for 24 h. The supernatant was removed, and the resulting red precipitate was washed with 3 × 5 mL of pentane and dried in vacuo. The complexes were obtained in approximately 90−95% purity by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy.

(DPPF)Pd(2-C_4H_3O)(NMePh), 3a. The above general procedure was followed using (DPPF)Pd(2-C_4H_3O)Br (100 mg, 0.12 mmol) and KNMePh (19.4 mg, 0.14 mmol) in 5 mL of toluene to give 42 mg (42%) of (DPPF)Pd(2-C_4H_3O)(NMePh) as a red solid: ^1H NMR (500 MHz, C_6D_6) δ 7.99 (dd, J_{HP} = 11.3 Hz, J_{HH} = 7.1 Hz, 2H), 7.84−7.77 (m, 6H), 7.68 (m, 2H), 7.25 (t, J = 7.9 Hz, 2H), 7.14−6.90 (m, 13H), 6.55 (t, J = 7.2 Hz, 1H), 6.25 (d, J = 3.1 Hz, 1H), 6.04 (m, 1H), 4.56 (s, 1H), 4.45 (s, 1H), 3.96 (m, 2H), 3.90 (m, 2H), 3.71 (s, 1H), 3.69 (s, 1H), 2.78 (d, J_{HP} = 4.6 Hz, 3H); $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6) δ 25.47 (d, J_{PP} = 36.7 Hz), 18.97 (d, J_{PP} = 36.2 Hz).

(DPPF)Pd(3-C_4H_3O)(NMePh), 3b. The above general procedure was followed using (DPPF)Pd(3-C_4H_3O)Br (100 mg, 0.12 mmol) and KNMePh (19.4 mg, 0.14 mmol) in 5 mL of toluene to give 55 mg (55%) of (DPPF)Pd(3-C_4H_3O)(NMePh) as a red solid: ^1H NMR (400 MHz, C_6D_6) δ 7.90 (m, 4H), 7.69 (m, 4H), 7.27 (t, J = 7.7 Hz, 2H), 7.07−6.95 (m, 15H), 6.57 (t, J = 7.0 Hz, 1H), 6.47 (s, 1H), 6.29 (m, 1H), 4.58 (s, 1H), 4.22 (s, 1H), 4.16 (s, 1H), 4.01 (s, 1H), 3.96 (s, 1H), 3.88 (s, 1H), 3.73 (s, 1H), 3.70 (s, 1H), 2.54 (d, J_{HP} = 4.6 Hz, 3H); $^{31}P\{^1H\}$ NMR (C_6D_6, 162 MHz) δ 24.69 (d, J_{PP} = 35.4 Hz), 16.26 (d, J_{PP} = 35.6 Hz).

(DPPF)Pd(2-C_4H_3S)(NMePh), 3c. The above general procedure was followed using (DPPF)Pd(2-C_4H_3S)Br (100 mg, 0.12 mmol) and KNMePh (19.4 mg, 0.14 mmol) in 5 mL of toluene to give 63 mg (61%) of (DPPF)Pd(2-C_4H_3S)(NMePh) as a red solid: ^1H NMR (400 MHz, C_6D_6) δ 7.87−7.80 (m, 6H), 7.60 (m, 2H), 7.22 (t, J = 7.5 Hz, 2H), 7.09−6.95 (m, 15H), 6.84 (m, 1H), 6.66 (dd, J_{HP} = 3.8 Hz, J_{HH} = 3.1 Hz, 1H), 6.55 (t, J = 7.0 Hz, 1H), 4.38 (s, 1H), 4.33 (s, 1H), 4.21 (s, 1H), 4.17 (m, 1H), 3.90 (m, 1H), 3.85 (s, 1H), 3.76 (m, 2H), 2.65 (d, J_{HP} = 4.9 Hz, 3H); $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6) δ 22.74 (d, J_{PP} = 38.1 Hz), 14.29 (d, J_{PP} = 38.1 Hz).

(DPPF)Pd(3-C_4H_3S)(NMePh), 3d. The above general procedure was followed using (DPPF)Pd(3-C_4H_3S)Br (100 mg, 0.12 mmol) and KNMePh (19.4 mg, 0.14 mmol) in 5 mL of toluene to give 52 mg (51%) of (DPPF)Pd(3-C_4H_3S)(NMePh) as a red solid: ^1H NMR (400 MHz, C_6D_6) δ 7.92−7.81 (m, 6H), 7.44 (m, 2H), 7.23 (t, J = 7.5 Hz, 2H), 7.08−6.91 (m, 15H), 6.75 (m, 1H), 6.55 (t, J = 7.2 Hz, 1H), 6.45 (dd, J_{HP} = 3.4 Hz, J_{HH} = 2.1 Hz, 1H), 4.33 (m, 2H), 4.27 (s, 1H), 4.22 (s, 1H), 3.92 (m, 1H), 3.86 (m, 1H), 3.80 (s, 1H), 3.77 (s, 1H), 2.56 (d, J_{HP} = 4.5 Hz, 3H); $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6) δ 23.99 (d, J_{PP} = 36.5 Hz), 12.70 (d, J_{PP} = 36.8 Hz).

(DPPF)Pd(2-(5-CH_3)C_4H_3S)(NMePh), 3e. The above general procedure was followed using (DPPF)Pd(2-(5-CH_3)C_4H_3S)-Br (100 mg, 0.12 mmol) and KNMePh (19.4 mg, 0.14 mmol) in 5 mL of toluene to give 62 mg (60%) of (DPPF)Pd(2-(5-CH3)-C4H3S)(NMePh) as a red solid: ^1H NMR (C_6D_6, 400 MHz) δ 7.91 (m, 2H), 7.84 (m, 4H), 7.61 (m, 2H), 7.20 (t, J = 7.8 Hz, 2H), 7.13−6.94 (m, 14H), 6.52 (t, J = 7.1 Hz, 1H), 6.37 (m, 2H), 4.35 (q, J = 1.8 Hz, 2H), 4.17 (q, J = 1.8 Hz, 2H), 3.90 (m, 1H), 3.86 (m, 1H), 3.77 (m, 1H), 3.75 (m, 1H), 2.72 (d, J_{HP} = 4.8 Hz, 3H), 2.10 (s, 3H); $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6) δ 22.57 (d, J_{PP} = 37.5 Hz), 14.28 (d, J_{PP} = 37.3 Hz).

(DPPF)Pd(2-(3-CH_3)C_4H_3S)(NMePh), 3f. The above general procedure was followed using (DPPF)Pd(2-(3-CH_3)C_4H_3S)-Br (100 mg, 0.12 mmol) and KNMePh (19.4 mg, 0.14 mmol) in 5 mL of toluene to give 50 mg (49%) of (DPPF)Pd(2-(3-CH_3)-C_4H_3S)(NMePh) as a red solid: 2 conformers; selected ^1H NMR (C_6D_6, 400 MHz) δ 2.85 (d, J_{HP} = 4.8 Hz, 3H, NMe^aPh), 2.68 (d, J_{HP} = 5.0 Hz, 3H, NMe^bPh), 2.15 (s, 3H, 3-Me^a-thiophene), 2.03 (s, 3H, 3-Me^b-thiophene); $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6) δ 22.11 (d, J_{PP} = 37.3 Hz, P1^b), 21.40 (d, J_{PP} = 37.1 Hz, P1^a), 12.14 (d, J_{PP} = 36.7 Hz, P2^b), 8.84 (d, J_{PP} = 36.9 Hz, P2^a).

Procedure for in-Situ Generation of (DPPF)Pd(2-(5-CH_3)C_4H_3S)(NHPh), 4. In a drybox, (DPPF)Pd(2-(5-CH_3)-C_4H_3S)Br (25 mg, 0.03 mmol), NaO^{t}Bu (3.4 mg, 0.035 mmol), and H_2NPh (4.2 μL, 0.035 mmol) were weighed directly into a small vial. Then 0.5 mL of benzene-d_6 was added, and the resulting suspension was transferred to a screw-capped NMR tube. The reaction was monitored by obtaining ^1H and ^{31}P NMR spectrum. The yellow suspension was converted to a bright orange solution with clean formation of the amido complex. This complex decomposed at room temperature over 1 h. (DPPF)Pd(2-(5-CH_3)C_4H_3S)(NHPh): ^1H NMR (C_6D_6, 500 MHz) δ 7.87 (m, 2H), 7.46 (m, 4H), 7.15−6.74 (m, 17H), 6.50 (m, 2H), 6.12 (m, 14H), 4.22 (m, 2H), 3.78 (m, 2H), 3.70 (m, 2H), 3.55 (m, 2H), 1.90 (s, 3H). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6) δ 24.86 (d, J_{PP} = 37.1 Hz), 9.90 (d, J_{PP} = 37.1 Hz).

Procedure for Amination of Heteroaromatic Halides Catalyzed by Pd(dba)$_2$ and DPPF or Isolated 1d (Data for Table 4). In a drybox, aryl bromide (0.5−2.5 mmol), amine (0.5−2.5 mmol), and NaOtBu (0.55−2.75 mmol) were placed directly into a screw-capped vial. A stir bar and 0.5−2.5 mL of toluene or 1 mL of C_6D_6 for comparisons of reactivity of Pd(dba)$_2$ and DPPF to **1d** were added. In a separate vial was placed 2 mol % Pd(dba)$_2$ (0.01−0.05 mmol) and 2 mol % DPPF (0.01−0.05 mmol) or 2 mol % of **1d**. These solids were suspended or dissolved (for **1d**) in 0.5−2.5 mL of toluene. The catalyst suspension or solution was then added to the reactants. The vial was sealed with a screw cap containing a Teflon-lined septum, and the mixture was stirred for 4−16 h at 100 °C outside the drybox. After this time, the mixture was poured into pentane (15 mL), filtered, and concentrated in vacuo. The crude product was adsorbed onto neutral alumina and purified by flash chromatography eluting with 5% diethyl ether in hexanes. Naphthalene and trimethoxybenzene were used as internal standards when obtaining yields by GC. The yields from reactions in the presence of **1d** and in the presence of Pd(dba)$_2$ and DPPF were determined by integration of the product resonances to those of trimethoxybenzene internal standard.

2-(Di-*p*-tolylamino)furan (Independent Synthesis for Data in Table 4). The above general procedure with 2-bromofuran (184 mg, 110 μL, 1.3 mmol), 1.0 equiv of di-*p*-tolylamine (246 mg, 1.3 mmol), 1.1 equiv of NaOtBu (132 mg, 1.4 mmol), 2 mol % Pd(dba)$_2$, and 2 mol % tri-*tert*-butylphosphine in 2.5 mL of toluene gave 160 mg (49%) of 2-(di-*p*-tolylamino)furan as a white solid: ^1H NMR (400 MHz, C_6D_6) δ 7.14 (bs, 1H), 7.05 (d, J = 8.5 Hz, 4H), 6.87 (d, J = 8.5 Hz,

4H), 6.06 (m, 1H), 5.76 (m, 1H), 2.04 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2) δ 154.50, 144.89, 138.18, 132.82, 130.48, 122.84, 111.83, 100.26, 21.08; MS (EI) 263 (M+), 234, 220, 91, 65. Anal. Calcd for $C_{18}H_{17}NO$: C, 82.13; H, 6.46; N, 5.32. Found: C, 81.92; H, 6.47; N, 5.24.

3-(Di-*p*-tolylamino)furan (Independent Synthesis for Data in Table 4). The above general procedure with 3-bromofuran (184 mg, 113 μL, 1.3 mmol), 1.0 equiv of di-*p*-tolylamine (246 mg, 1.3 mmol), 1.1 equiv of NaO^{t}Bu (132 mg, 1.4 mmol), 2 mol % $Pd(dba)_2$, and 2 mol % tri-*tert*-butylphosphine in 2.5 mL of toluene gave 231 mg (70%) of 3-(di-*p*-tolylamino)furan as a white solid: ^1H NMR (400 MHz, C_6D_6) δ 7.21 (d, J = 8.5 Hz, 4H), 7.07 (dd, J_1 = 1.8, 1.8 Hz, 1H), 7.01 (m, 1H), 7.00 (d, J = 8.3 Hz, 4H), 6.30 (m, 1H), 2.20 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2) δ 143.98, 140.79, 133.91, 132.76, 130.07, 128.19, 121.18, 106.87, 18.80; MS (EI) 263 (M+), 234, 218, 204, 91, 65. Anal. Calcd for $C_{18}H_{17}NO$: C, 82.13; H, 6.46; N, 5.32. Found: C, 81.97; H, 6.48; N, 5.32.

2-(Di-*p*-tolylamino)thiophene (Independent Synthesis for Data in Table 4). Method A of the above general procedure with 2-bromothiophene (204 mg, 122 μL, 1.3 mmol), 1.0 equiv of di-*p*-tolylamine (246 mg, 1.3 mmol), 1.1 equiv of NaO^{t}Bu (132 mg, 1.4 mmol), 2 mol % $Pd(dba)_2$, and 2 mol % tri-*tert*-butylphosphine in 2.5 mL of toluene gave 188 mg (54%) of 2-(di-*p*-tolylamino)thiophene as a white solid: ^1H NMR (400 MHz, C_6D_6) δ 7.24 (d, J = 8.5 Hz, 4H), 6.98 (d, J = 8.2 Hz, 4H), 6.71 (bs, 1H), 6.70 (m, 1H), 6.65 (m, 1H), 2.17 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2) δ 153.43, 146.94, 132.77, 130.49, 126.46, 123.41, 120.72, 120.30, 21.10; MS (EI) 279 (M+), 173, 147, 91, 65. Anal. Calcd for $C_{18}H_{17}NS$: C, 77.38; H, 6.13; N, 5.01; S, 11.47. Found: C, 77.46; H, 6.28; N, 4.97; S, 11.61.

3-(Di-*p*-tolylamino)thiophene (Independent Synthesis for Data in Table 4). The above general procedure with 3-bromothiophene (204 mg, 117 μL, 1.3 mmol), 1.0 equiv of di-*p*-tolylamine (246 mg, 1.3 mmol), 1.1 equiv of NaO^{t}Bu (132 mg, 1.4 mmol), 2 mol % $Pd(dba)_2$, and 2 mol % tri-*tert*-butylphosphine in 2.5 mL of toluene gave 307 mg (88%) of 3-(di-*p*-tolylamino)thiophene as a white solid: ^1H NMR (400 MHz, C_6D_6) δ 7.18 (d, J = 8.4 Hz, 4H), 6.99 (d, J = 8.5 Hz, 4H), 6.92 (m, 1H), 6.88 (m, 1H), 6.54 (m, 1H), 2.20 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2) δ 148.11, 146.66, 132.60, 130.52, 125.37, 125.15, 124.21, 111.71, 21.14; MS (EI) 279 (M+), 231, 91, 65. Anal. Calcd for $C_{18}H_{17}NS$: C, 77.38; H, 6.13; N, 5.01; S, 11.47. Found: C, 77.26; H, 6.19; N, 5.08; S, 11.43.

2-(Di-*p*-tolylamino)-5-methylthiophene (Independent Synthesis for Data in Table 4). The above general procedure with 2-bromo-5-methylthiophene (177 mg, 111 μL, 1.0 mmol), 1.0 equiv of di-*p*-tolylamine (197 mg, 1.0 mmol), 1.1 equiv of NaO^{t}Bu (106 mg, 1.1 mmol), 2 mol % $Pd(dba)_2$, and 2 mol % tri-*tert*-butylphosphine in 2 mL of toluene gave give 221 mg (75%) of 2-(di-*p*-tolylamino)-5-methylthiophene as a white solid: ^1H NMR (400 MHz, C_6D_6) δ 7.30 (d, J = 8.5 Hz, 4H), 7.01 (d, J = 8.2 Hz, 4H), 6.61 (d, J = 3.6 Hz, 1H), 6.42 (m, 1H), 2.18 (s, 9H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 149.61, 146.25, 135.32, 132.32, 130.04, 123.79, 122.43, 121.70, 21.16, 16.32; MS (EI) 293 (M+), 187, 170, 91, 65. Anal. Calcd for $C_{19}H_{19}NS$: C, 77.77; H, 6.53; N, 4.77; S, 10.93. Found: C, 77.51; H, 6.47; N, 4.81; S, 10.78.

2-(Di-*p*-tolylamino)-3-methylthiophene (Independent Synthesis for Data in Table 4). The above general procedure with 2-bromo-3-methylthiophene (177 mg, 108 μL, 1.0 mmol), 1.0 equiv of di-*p*-tolylamine (197 mg, 1.0 mmol), 1.1 equiv of NaO^{t}Bu (106 mg, 1.1 mmol), 2 mol % $Pd(dba)_2$, and 2 mol % tri-*tert*-butylphosphine in 2 mL of toluene gave 215 mg (73%) of 2-(di-*p*-tolylamino)-3-methylthiophene as a white solid: ^1H NMR (400 MHz, C_6D_6) δ 7.19 (d, J = 8.5 Hz, 4H), 6.99 (d, J = 8.1 Hz, 4H), 6.78 (d, J = 5.6 Hz, 1H), 6.65 (d, J = 5.6 Hz, 1H), 2.18 (s, 6H), 2.00 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 145.53, 132.53, 131.85, 130.08, 129.51, 129.16, 128.70, 121.67, 21.17, 16.35; MS (EI) 293 (M+), 187, 91, 65. Anal. Calcd for $C_{19}H_{19}NS$: C, 77.77; H, 6.53; N, 4.77. Found: C, 77.50; H, 6.40; N, 4.61.

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Supporting Information Available: Experimental procedures and full tabular data for the determinations of the structures of **2a**−**d** by X-ray diffraction. This material is available free of charge via the Internet at http://pubs.acs.org.

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