Electronic and Steric Effects on the Reductive Elimination of Diaryl Ethers from Palladium(II)

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Arylpalladium aryloxide complexes containing sterically and electronically varied phosphine ligands were prepared, and the rates for reductive elimination of diaryl ethers from these complexes were studied to determine the ligand properties that most strongly accelerate this unusual reaction. Electronic and steric effects were probed by preparing monomeric palladium complexes of the type (L)Pd(Ar)(OAr′), in which L = DPPF (1,1′-bis-diphenylphosphinoferrocene), CF_3-DPPF (1,1′-bis[di(4-(trifluoromethyl)phenyl)phosphino]ferrocene), and D-*t*-BPF (1,1′-bis(di-*tert*-butylphosphino)ferrocene) and Ar = electron-deficient and electron-neutral aryl groups. Direct C−O bond-forming reductive elimination to form diaryl ethers in high yield was observed after warming the complexes that contained an electron-deficient aryl group bound to palladium. The rate constant for C−O bond-forming reductive elimination from the CF_3-DPPF-ligated palladium complex was twice that obtained for the analogous DPPF-ligated complex. Reductive elimination of diaryl ether from the more bulky D-*t*-BPF complex occurred roughly 100 times faster than from the DPPF complex. Thermolysis of DPPF and CF_3-DPPF complexes containing an electron-neutral aryl group did not form diaryl ether. Thermolysis of (D-*t*-BPF)Pd(Ph)(OC_6H_4-4-OMe) also did not form diaryl ether and generated the two monophosphines PhP(*t*-Bu)$_2$ and FcP(*t*-Bu)$_2$ (di-*tert*-butylphosphinoferrocene). However, heating of a FcP(*t*-Bu)$_2$-ligated aryloxide complex containing an electron-neutral, palladium-bound aryl group generated diaryl ether in 10−25% yield. Moreover, heating of this complex in the presence of an excess of P(*t*-Bu)$_3$ or Ph_5FcP(*t*-Bu)$_2$ or 1 equiv of 2-di-*tert*-butylphosphino-1,1′-binaphthyl generated diaryl ether in higher, 58−95%, yields. The effect of ligand concentrations on reaction yields implied that exchange of the bulkier ligands with FcP(*t*-Bu)$_2$ induced the reductive elimination of diaryl ether.

Introduction

Palladium-mediated cross-coupling that forms an aromatic carbon−heteroatom bond in amines,[1−8] ethers,[9−21] and sulfides[22−30] has become a powerful synthetic method. The reductive elimination of aryl sulfides,[31−33] arylamines,[33−40] and aryl ethers[9,33,41−43] is the product-forming step of these catalytic processes, as

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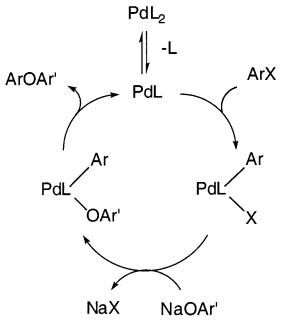
Scheme 1



shown for formation of ethers in Scheme 1. As a result, fundamental studies have been conducted on these unusual elementary reactions. These investigations have shown that increasing electron density on the heteroatom and decreasing electron density on the palladium-bound aryl group leads to increasing reaction rates.[32,34,41] Because alkoxide ligands are less electron-donating than amide or thiolate ligands, the formation of aryl ethers by reductive elimination is especially challenging.

Thus, the palladium-catalyzed formation of ethers[10,11,13−15,17−21] occurs in a less general fashion than the formation of arylamines, and the palladium-catalyzed formation of diaryl ethers has been particularly challenging.[10,11,15,21] Diaryl ethers are substructures found in many natural products with potential biological activity. The formation of the diaryl ether unit is often one of the most difficult steps in the synthesis of these materials. Thus, new methods for the construction of diaryl ethers have been actively pursued.[16,44−59] On a more fundamental level, the reductive elimination to form the C−O bond in ethers is an elementary reaction that has been limited to special cases or to examples that form ether in low yields.[1,9,41−43,60] Thus, we sought to define the steric and electronic properties of a phosphine ligand that would create large enough rate accelerations to observe reductive elimination of diaryl ethers in a general fashion.

Both electronic and steric properties of ancillary ligands could significantly influence the rate of reductive elimination of diaryl ethers. For two complexes with similar steric properties, the complex with the more weakly donating ancillary ligands tends to undergo reductive elimination faster than the complex with the more donating ligands.[61] This effect has been predicted by theory;[62] it has also been observed by experiment, but the observed effect has been difficult to interpret and the magnitude of the effect difficult to measure when equilibria precede reductive elimination.[63] For two complexes with similar steric properties, the opposite reaction, oxidative addition, is clearly faster to the complex with the more electron-donating ancillary ligands.[64]

Because reductive elimination relieves steric hindrance, one might expect that a complex with similarly electron-donating, but sterically more demanding, ancillary ligands would undergo reductive elimination faster than a complex with less sterically demanding ligands. Indeed, studies on the rate of reductive elimination of arene from arylrhodium hydrides[65] showed that complexes ligated by *tert*-butyldimethylphosphine eliminated arene faster than those containing *n*-butyldimethylphosphine. However, the magnitude of this steric effect on rate was small. Other pertinent studies have involved simultaneous variation of steric and electronic properties.[66] The effect of sterically hindered ligands on the rate of stoichiometric carbon−heteroatom bond-forming reductive eliminations is not well documented, but recent catalytic formation of diaryl ethers suggests that steric hindrance may promote reductive elimination.[10,15,21]

The number of donor atoms in a ligand or the number of coordinated monodentate ligands can also influence the rate of reductive elimination. Yamamoto[62] and Stille[67] showed that reductive elimination to form C−C bonds occurs from complexes containing bisphosphines and monophosphines, but that reductive elimination from three-coordinate monophosphine complexes occurs

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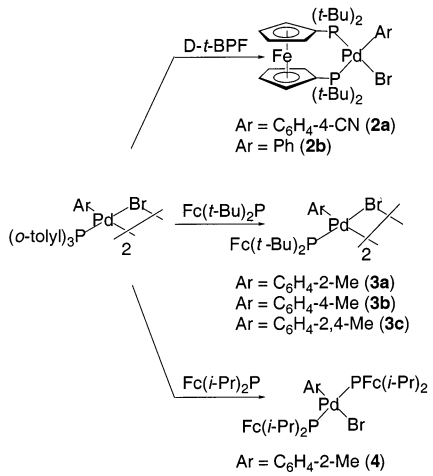
Scheme 2



faster than it does from four-coordinate bisphosphine complexes. The authors' laboratory has shown that reductive elimination of amines from arylpalladium amido complexes occurs from both three-coordinate monophosphine and four-coordinate bisphosphine complexes and that the elementary step of reductive elimination is faster from the three-coordinate species.[34] Thus, sterically hindered ligands may also promote the formation of monophosphine three-coordinate complexes that undergo reductive elimination of diaryl ether faster than four-coordinate, bisphosphine complexes.

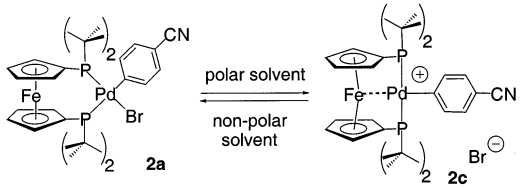
Because catalytic processes are multistep and often involve changes in catalyst composition and reaction medium, it is difficult to assess how a single step of a catalytic process is affected by perturbations of the catalyst structure. In particular, studies on the overall catalytic process do not reveal the effect of a structural perturbation on the portion of a catalytic cycle that occurs after the turnover-limiting step. To define quantitatively the relative effects of ligand steric and electronic properties on the rates of reductive elimination of diaryl ethers, we report the thermal chemistry of isolated arylpalladium aryloxide complexes. Our results demonstrate that alterations in ligand steric hindrance and number of donor atoms have a more pronounced effect on reaction rate than do readily accessible changes in phosphine electronic properties.

Results

A. Synthesis of Arylpalladium Halide and Arylpalladium Aryloxide Complexes. 1. Arylpalladium Bromide Complexes. The synthesis of arylpalladium bromide complexes used in this study is shown in Scheme 2. Complexes of the structure (D-*t*-BPF)Pd(Ar)(Br) (**2a**, Ar = C_6H_4-4-CN; **2b**, Ar = Ph) were obtained from the addition of D-*t*-BPF to a solution of the appropriate $\{Pd[P(o\text{-tolyl})_3](Ar)(Br)\}_2$[68−70] compound. The dimeric palladium bromide complex $\{Pd[FcP(t\text{-Bu})_2](C_6H_4\text{-2-Me})(\mu\text{-Br})\}_2$ (**3**) was isolated in pure form in 31% yield after reaction of $FcP(t\text{-Bu})_2$ (**1a**) with $\{Pd[P(o\text{-tolyl})_3](C_6H_4\text{-2-Me})(\mu\text{-Br})\}_2$. Addition of $FcP(i\text{-Pr})_2$ to the dimeric $\{Pd[P(o\text{-tolyl})_3](C_6H_4\text{-2-Me})(\mu\text{-Br})\}_2$ formed the monomeric Pd bromide complex $Pd[FcP(i\text{-Pr})_2]_2(C_6H_4\text{-2-Me})(Br)$, **4**.

The ^{31}P NMR spectra of **2a** deserve comment. The ^{31}P NMR spectrum of **2a** in benzene-d_6 contained two doublets at δ 37.5 and 46.8, which are consistent with a simple square-planar, cis geometry. The ^{31}P NMR spectrum of **2a** in THF-d_8, however, consisted of two doublets (δ 38.5 and 48.4) and a singlet (δ 22.3). No signal near that of free D-*t*-BPF was observed, and the singlet was not that of the potential decomposition product $Pd(D\text{-}t\text{-BPF})_n$ (δ 55.9). Furthermore, the ^{31}P NMR spectrum of a solution of **2a** in $CDCl_3$ displayed one singlet at δ 21.6. The species that displayed two doublet resonances was regenerated from this complex by evaporation of $CDCl_3$ under vacuum and dissolution of the solid in benzene-d_6. Thus, complex **2** displays a solvent-dependent equilibrium between two arylpalladium complexes.[71]

The second isomer clearly resulted from dissociation of halide in the more polar solvent. Conductivity measurements on 1.0 mM solutions of **2a**, NBu_4Br, and $(PPh_3)_2Pd[C_6H_3\text{-2-Me-5-}(t\text{-Bu})](Br)$ in dry, degassed nitromethane gave molar conductances of 70.3, 74.5, and 6.8 Ω^{-1} cm^2 mol^{-1}, respectively. These values are consistent with literature values for 1 mM solutions of 1:1 electrolytes in nitromethane.[71] Moreover, the same ^{31}P NMR resonance was obtained after addition of $AgBF_4$ to **2a** in THF. Three-coordinate d^8 complexes are commonly T-shaped;[62,72−76] however, this complex adopts a square-planar structure with a Pd−Fe interaction. The structures of the two species in equilibrium are depicted in eq 1. A related cationic D-*t*-BPF complex containing



(1)

a palladium-bound methyl group and a related cationic bis-diphenylphosphino omoscene complex have been reported recently.[77,78] The BF_4 analogue of **2c** was isolated in pure form after addition of $AgBF_4$ to **2a** and recrystallization from THF.

2. Monomeric Palladium Aryloxide Complexes Containing Ferrocenyl Bisphosphines. The synthe-

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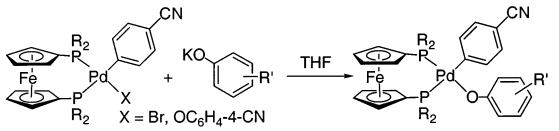
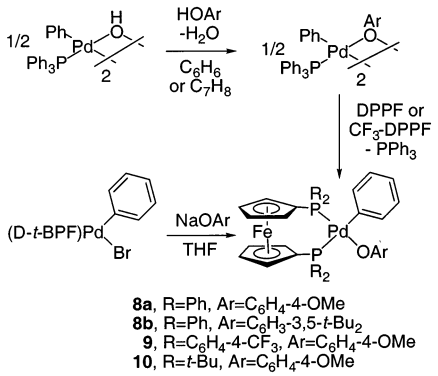
Scheme 3



Scheme 4

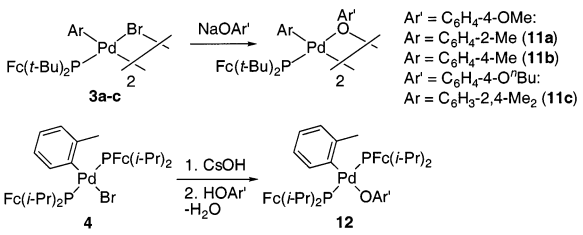


8a, R=Ph, Ar=C_6H_4-4-OMe
8b, R=Ph, Ar=C_6H_3-3,5-*t*-Bu_2
9, R=C_6H_4-4-CF_3, Ar=C_6H_4-4-OMe
10, R=*t*-Bu, Ar=C_6H_4-4-OMe

sis of palladium aryloxide complexes (L)Pd(C_6H_4-4-CN)(OAr), in which L = DPPF (Ar = OC_6H_4-4-OMe, **5a**; Ar = OC_6H_4-4-O-*n*-Bu, **5b**; Ar = OC_6H_3-3,5-(*t*-$Bu)_2$, **5c**), CF_3-DPPF (Ar = OC_6H_4-4-OMe, **6a**; Ar = OC_6H_3-3,5-(*t*-$Bu)_2$, **6b**) or D-*t*-BPF (Ar = OC_6H_6-4-OMe, **7a**; Ar = OC_6H_3-3,5-(*t*-$Bu)_2$, **7b**) is summarized in Scheme 3. Addition of KOAr to a THF solution of (L)Pd(C_6H_4-4-CN)(Br) or addition of NaOAr to a THF solution of (L)-Pd(C_6H_4-4-CN)(OC_6H_4-4-CN) formed complexes **5a**−**6b**. Analytically pure yellow solids were isolated in 56−83% yields. D-*t*-BPF-ligated palladium bromide **2a** reacted with $NaOC_6H_4$-4-OMe or KOC_6H_3-3,5-*t*-Bu_2 to give palladium aryloxide complexes (D-*t*-BPF)Pd(C_6H_4-4-CN)(OC_6H_4-4-OMe), **7a**, and (D-*t*-BPF)Pd(C_6H_4-4-CN)-(OC_6H_3-3,5-*t*-Bu_2), **7b**. The ^{31}P NMR spectra of both **7a** and **7b** were, again, unusual. The spectrum in benzene-d_6 contained the expected two doublets (δ 42.1 and 55.4 for **7a**; δ 42.1 and 55.6 for **7b**) but the ^{31}P NMR spectrum of each compound in THF-d_8 contained one singlet near δ 21.8, in addition to the expected two doublets. Thus, the arylpalladium phenoxide complex generates the same cationic palladium species, this time by dissociation of a phenoxide counterion. Consistent with this assertion, the ^{31}P NMR signal assigned to the cations generated from **2a**, **7a**, and **7b** are nearly identical in THF solvent. Nevertheless, the reductive elimination chemistry of this complex presented below occurred in the highest yields in nonpolar solvents such as toluene and THF, in which the compound adopts predominantly a monomeric square-planar structure, although a distorted one (vide infra).

Palladium aryloxide complexes with an electron-neutral palladium-bound aryl group were synthesized as shown in Scheme 4. Addition of DPPF or CF_3-DPPF to a toluene or benzene solution of [(PPh_3)Pd(Ph)(μ-OAr)]$_2$ (Ar = C_6H_4OMe, C_6H_3-3,5-*t*-Bu), which was formed in situ by protonation of [(PPh_3)Pd(Ph)(μ-OH)]$_2$[79] with 4-methoxyphenol or 3,5-di-*tert*-butylphenol, produced the DPPF and CF_3-DPPF arylpalladium aryloxides **8a**,**b** and **9** in 67%, 66%, and 55% isolated yield.

Scheme 5



The arylpalladium aryloxide complex (D-*t*-BPF)Pd(Ph)-(OC_6H_4-4-OMe) (**10**) was isolated in analytically pure form in 32% yield after reaction of (D-*t*-BPF)Pd(Ph)(Br) with the sodium aryloxide in THF solvent.

3. Arylpalladium Aryloxide Complexes Containing Ferrocenyl Monophosphines. Dimeric arylpalladium aryloxide complexes {Pd[FcP(*t*-$Bu)_2$](Ar)(μ-OC_6H_4-4-R)}$_2$ (**11a**, Ar = C_6H_4-2-Me, R = OMe; **11b**, Ar = C_6H_4-4-Me, R = OMe; **11c**, Ar = C_6H_3-2,4-Me_2, R = O-*n*-Bu) were synthesized as shown in Scheme 5. Addition of sodium aryloxide to the arylpalladium bromide complexes (**3a**−**c**) containing ligand **1a**, which were formed in situ by phosphine exchange in THF solvent, formed the desired aryloxide complexes. Monomeric Pd[FcP(*i*-$Pr)_2]_2$(C_6H_4-2-Me)(OC_6H_4-4-OMe) (**12**) was isolated in 43% yield by reaction of [FcP(*i*-$Pr)_2]_2$Pd(Ar)(Br) (**4**) with $CsOH\cdot H_2O$, which gave Pd[FcP(*i*-$Pr)_2]_2$(C_6H_4-2-Me)(OH) as a mixture of cis and trans isomers, followed by addition of *p*-methoxyphenol.

4. Synthesis of Nickel Carbonyl Complexes of the Ferrocenyl Ligands. Nickel carbonyl complexes containing the ferrocenyl ligands were prepared to allow comparison of the electronic properties of these ligands to those of ligands on Tolman's classic scale.[80] These complexes were prepared by addition of ligand to $Ni(CO)_4$ at room temperature. (Caution: Nickel carbonyl is highly toxic. It was handled under vacuum on a Schlenk line in a well-ventilated hood.) The ν_{CO} values for $L_2Ni(CO)_2$ complexes in which L_2 = DPPF were 1999 and 1940 cm^{-1}, and the ν_{CO} values for $L_2Ni(CO)_2$ in which L_2 = 4-CF_3-DPPF were 2010 and 1950 cm^{-1}.[81] The difference between these ν_{CO} values is similar to the difference in ν_{CO} values between complexes of triaryl and trialkylphosphines, but one should realize this difference in ν_{CO} results from the effect of two phosphine donor atoms.[80] The $L_2Ni(CO)_2$ complex with L_2 = D^{t}BPF did not form, but the binuclear complex {[$(CO)_3Ni]_2$-(D-*t*-BPF)} with one $Ni(CO)_3$ unit bound to each of the two phosphorus was isolated. This complex showed an A_1 ν_{CO} value of 2055 cm^{-1}, which is nearly identical to the value of 2056 cm^{-1} for {$(CO)_3$Ni[P(*t*-$Bu)_3$]}.[80] {Ni$(CO)_3$[FcP(*t*-$Bu)_2$]} was also prepared, and the A_1 ν_{CO} value was an identical 2055 cm^{-1}. Clearly, D-*t*-BPF and **1a** are strongly electron-donating ligands. One might imagine that the large phosphine substituents of D-*t*-BPF and **1a** would lengthen the Pd−P bond distance, but Tolman showed long ago that the A_1 ν_{CO} value for L$Ni(CO)_3$ is lower when L = P(*t*-$Bu)_3$ than when L = PMe_3.[82]

(79) Grushin, V. V.; Kuznetsov, V. F.; Bensimon, C.; Alper, H. *Organometallics* **1995**, *14*, 3927−3932.
(80) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313−348.
(81) Hamann, B.; Hartwig, J. F. *J. Am. Chem. Soc.* **1998**, *120*, 3694−3703.

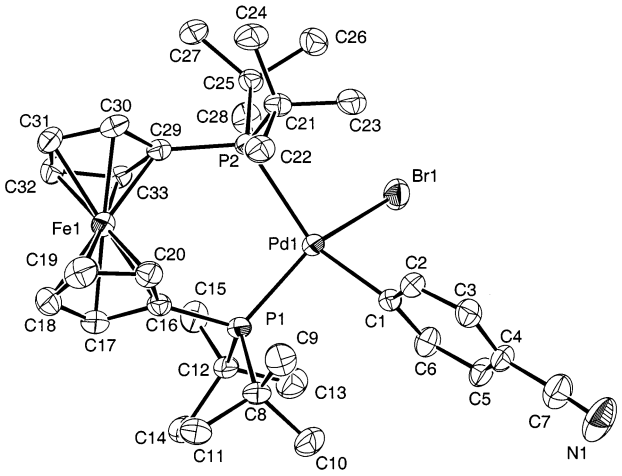


Figure 1. ORTEP drawing of (D-*t*-BPF)Pd(Br)(C_6H_4-4-CN) (**2a**). Hydrogen atoms and solvent molecule are omitted for clarity. Thermal ellipsoids are drawn at 30% probability.

Table 1. Selected Intramolecular Bond Distances and Angles Involving the Non-Hydrogen Atoms of (D-*t*-BPF)Pd(Br)(C_6H_4-4-CN) (2a)

Bond Distances (Å)			
Pd(1)−Br(1)	2.4934(7)	Pd(1)−P(1)	2.345(1)
Pd(1)−P(2)	2.492(1)	Pd(1)−C(1)	2.033(5)
Bond Angles (deg)			
Br(1)−Pd(1)−P(1)	151.59(4)	Br(1)−Pd(1)−P(2)	92.30(4)
Br(1)−Pd(1)−C(1)	82.2(1)	P(1)−Pd(1)−P(2)	104.28(5)
P(1)−Pd(1)−C(1)	92.1(1)	P(2)−Pd(1)−C(1)	153.3(1)
angle between the planes: [P(1)−Pd(1)−P(2)] and [Br(1)−Pd(1)−C(1)]			35.2

5. X-ray Structures of D-*t*-BPF and FcP(*t*-Bu)$_2$ Palladium Complexes. X-ray structures were obtained of D-*t*-BPF-ligated bromide **2a**, **2c**, and **7a** and FcP(*t*-Bu)$_2$-ligated phenoxide **11b.** The structure of palladium bromide complex **2a** is shown in Figure 1. Crystal data for each structure are included in the Supporting Information, and selected bond distances and angles for **2a** are provided in Table 1. The geometry about the metal center is a highly distorted square plane in which the P1−Pd1−P2 bond angle is a large 104.28(5)° and the Br1−Pd1−C1 bond angle a small 82.2(1)°. The dihedral angle between P1−Pd1−P2 and Br1−Pd1−C1 planes is 35.20°; this angle shows a large distortion toward a tetrahedron from an ideal square-planar geometry in which this angle would be 0°. This distortion was also shown by the large sum of the four angles about the Pd center, 370.9°. The Pd1−P1 and Pd1−P2 bond distances were 2.345(1) and 2.492(1) Å. The Pd1−P2 bond is one of the longest Pd−P bond lengths reported.[83]

The structure of complex **2c**, which resulted from halide dissociation from **2a**, is shown in Figure 2. Selected bond distances and angles for **2c** are provided in Table 2. The formation of a dative Pd−Fe bond creates a distorted square-planar geometry around Pd with a P1−Pd1−P2 bond angle of 159.75(4)°. This angle is slightly larger than the 158.21(2)° P−Pd−P angle in the analogous cationic palladium methyl complex[77] or the 155.9(1)° angle in a similar dicationic palladium

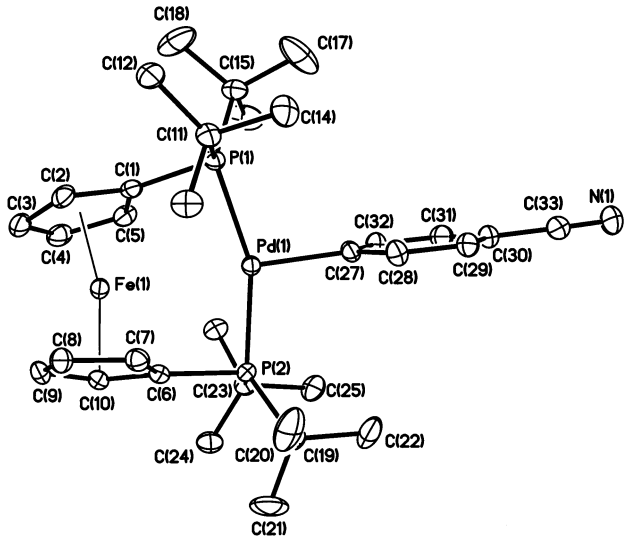


Figure 2. ORTEP drawing of the cationic portion of [(D-*t*-BPF)Pd(C_6H_4-4-CN)](BF_4) (**2c**). Hydrogen atoms and solvent molecule are omitted for clarity. Thermal ellipsoids are drawn at 30% probability.

Table 2. Selected Intramolecular Bond Distances and Angles Involving the Non-Hydrogen Atoms of [(D-*t*-BPF)Pd(C_6H_4-4-CN)](BF_4) (2c)

Bond Distances (Å)			
Pd(1)−P(1)	2.3103(12)	Pd(1)−P(2)	2.3065(12)
Pd(1)−Fe(1)	2.9988(8)	Pd(1)−C(27)	2.001(4)
Bond Angles (deg)			
Fe(1)−Pd(1)−P(1)	80.31(4)	Fe(1)−Pd(1)−P(2)	79.44(4)
Fe(1)−Pd(1)−C(27)	177.67(12)	P(1)−Pd(1)−P(2)	159.75(4)
P(1)−Pd(1)−C(27)	100.87(12)	P(2)−Pd(1)−C(27)	99.37(12)

containing PPh_3 instead of the phenyl at palladium.[84] The Pd−Fe distance of 2.999(8) Å is significantly shorter than the 4.4 Å Pd−Fe distance in complex **2a**, which contains no interaction between Fe and the Pd center. It is also slightly shorter than the 3.0683 Å Pd−Fe distance in the analogous cationic methyl[77] and slightly longer than the 2.877(2) Å distance in the PPh_3-ligated dication. To accommodate this short distance, the Cp(centroid)−Fe−Cp(centroid) angle is only 166.2°. These P1−Pd−P2 angles, Fe−Pd bond lengths, and Cp ring distortions are similar to those in related complexes of metallocenyl phosphine and thiolate ligands with M−Pd interactions.[78,85]

The structure of phenoxide **7a** is shown in Figure 3. Selected bond distances and angles are collected in Table 3. This complex displays distortions similar to those found in the bromide complex **2a**. The P1−Pd1−P2 and O1−Pd1−C1 bond angles were 104.93(3)° and 85.99(10)°. The dihedral angle between the P1−Pd1−P2 and O1−Pd1−C1 planes was a large 23.92°, and the sum of angles at the Pd center was 365.3°. Again, the Pd−P bond trans to the aryl group (Pd1−P1, 2.4819(7) Å) was significantly longer than the other Pd−P bond (Pd1−P2, 2.3051(8) Å).

An ORTEP diagram of **11b** is shown in Figure 4. Selected bond distances and angles are provided in Table 4. The sum of the four angles about the palladium

(82) Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2953−2956.
(83) Woo, T. K.; Pioda, G.; Rothlisberger, U.; Togni, A. *Organometallics* **2000**, *19*, 2144−2152.
(84) Sato, M.; Shigeta, H.; Sekino, M. *J. Organomet. Chem.* **1993**, *458*, 199−204.
(85) Seyferth, D.; Hames, B. W.; Rucker, T. G.; Cowie, M.; Dickson, R. S. *Organometallics* **1983**, *2*, 472−474.

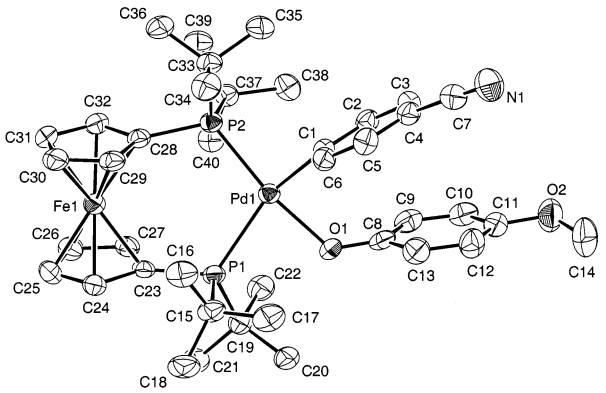


Figure 3. ORTEP drawing of (D-*t*-BPF)Pd(OC_6H_4-4-OMe)-(C_6H_4-4-CN) (**7a**). Hydrogen atoms and solvent molecule are omitted for clarity. Thermal ellipsoids are drawn at 30% probability.

Table 3. Selected Intramolecular Bond Distances and Angles Involving the Non-Hydrogen Atoms of (D-*t*-BPF)Pd(OC_6H_4-4-OMe)(C_6H_4-4-CN) (7a)

Bond Distances (Å)			
Pd(1)−P(1)	2.4819(7)	Pd(1)−P(2)	2.3051(8)
Pd(1)−O(1)	2.077(2)	Pd(1)−C(1)	2.028(3)
Bond Angles (deg)			
P(1)−Pd(1)−P(2)	104.93(3)	P(2)−Pd(1)−O(1)	163.78(6)
P(1)−Pd(1)−O(1)	81.00(6)	P(2)−Pd(1)−C(1)	93.36(8)
P(1)−Pd(1)−C(1)	155.24(8)	O(1)−Pd(1)−C(1)	85.99(10)
angle between the planes [P(1)−Pd(1)−P(2)] and [C(1)−Pd(1)−O(1)]			23.92

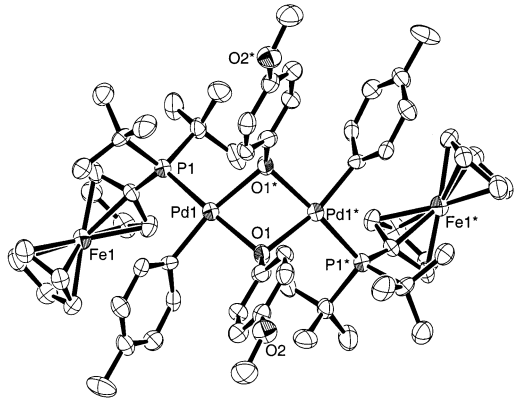


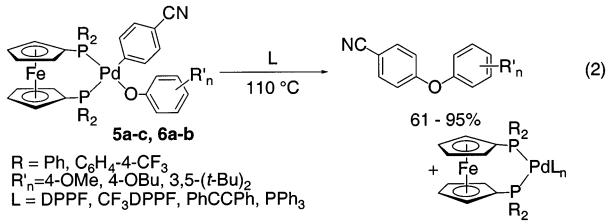
Figure 4. ORTEP drawing of {Pd[$P(C_5H_4FeC_5H_5)(t\text{-}Bu)_2$]-($C_6H_4$-4-Me)($OC_6H_4$-4-OMe)}$_2$ (**11b**). Hydrogen atoms and solvent molecule are omitted for clarity. Thermal ellipsoids are drawn at 50% probability.

Table 4. Selected Intramolecular Bond Distances and Angles of {Pd[$P(C_5H_4FeC_5H_5)(t\text{-}Bu)_2$]-($C_6H_4$-2-Me)($OC_6H_4$-4-OMe)}$_2$ (11b)

Bond Distances (Å)			
Pd(1)−P(1)	2.279(3)	Pd(1)−O(1*)	2.121(6)
Pd(1)−O(1)	2.189(6)	Pd(1)−C(1)	1.966(9)
Bond Angles (deg)			
P(1)−Pd(1)−O(1)	167.6(2)	P(1)−Pd(1)−O(1*)	102.9(2)
P(1)−Pd(1)−C(1)	93.4(3)	O(1)−Pd(1)−O(1*)	76.6(3)
O(1)−Pd(1)−C(1)	88.8(3)	O(1*)−Pd(1)−C(1)	162.8(3)

center was 361.7°, demonstrating the near planarity at the metal. The Pd−O−Pd−O torsion angle was 33.2°, and this angle indicates that the central Pd and bridging oxygen atoms adopt the puckered geometry that is common for dimeric complexes with bridging heteroatoms.[86] The C(ipso)−Pd−O angle was 88.8°, but the P−Pd−O bond angle was a much larger 102.9°. The Pd−P distance in **11b** was 2.279(3) Å, which is similar to the 2.288(3) Å distance in analogous dimeric P(*o*-tolyl)$_3$-ligated aryl halide complexes[68] and to the 2.30−2.32 Å Pd−P distances in typical four-coordinate, PPh_3-ligated Pd(II) complexes.[87]

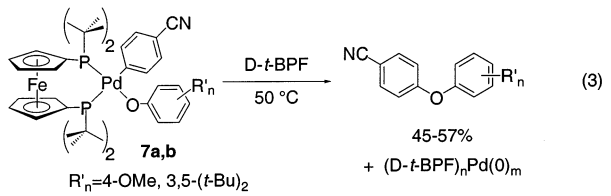
B. Carbon−Oxygen Bond-Forming Reductive Elimination of Diaryl Ethers. 1. Reactions of Monomeric Arylpalladium Aryloxide Complexes Containing Bisphosphines. Thermolysis of complexes **5a**−**7b**, which contain bidentate phosphines and an electron-poor aryl group bound to the palladium, and thermolysis of **8**−**10**, which contain a phenyl group bound to palladium, were conducted in the presence of dative ligands, such as PPh_3, PhCCPh, D-*t*-BPF, or DPPF, to bind the Pd(0) product. The only metal products observed at the end of all of the thermal reactions were homoleptic Pd(0) phosphine complexes or Pd(0) complexes ligated by phosphine and alkyne. In all cases, reactions of **5a**,**c** and **6a**,**b** led to the reductive elimination of diaryl ethers and the formation of Pd(0) complexes in good yield (eq 2). Reactions of DPPF-



(2)

ligated palladium complex **5a** conducted at 110 °C for 5 h in the presence of 2 equiv of added PPh_3 formed diaryl ether in greater than 90% yield, and the same reaction conducted in the presence of 1−2 equiv of DPPF formed diaryl ether in 83% yield. CF_3-DPPF complexes **6a** and **6b** reductively eliminated diaryl ether at 110 °C after 5 h in 95% and 62% yield, respectively, in the presence of 2−3 equiv of PPh_3. Reactions in the presence of PhCCPh and CF_3-DPPF formed diaryl ether in similar yields. Reductive elimination from DPPF-ligated **5a** at the lower temperature of 50 °C occurred with a half-life greater than 60 h.

Reductive elimination of diaryl ether from D-*t*-BPF-ligated **7a**,**b** containing an electron-poor aryl group bound to the metal (eq 3) occurred at rates that were



(3)

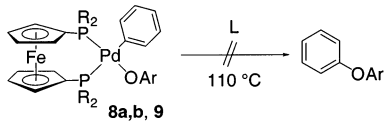
faster than those for reductive elimination from its DPPF analogues. Palladium complexes **7a** and **7b** were consumed after 1 h at 50 °C and gave ether in 45% and 57% yield in the presence of 4 equiv of D-*t*-BPF to coordinate the Pd(0) product. Thermolysis of **5a**−**7b** in

(86) Aullon, G.; Ujaque, G.; Lledos, A. *Inorg. Chem.* **1998**, *37*, 804−813.

(87) Pierpont, C. G.; Downs, H. H. *Inorg. Chem.* **1975**, *14*, 343−347.

the presence or absence of excess sodium aryloxide occurred in a similar fashion. Sodium alkoxides had been suggested to accelerate the formation of alkyl ethers in previous studies.[42]

In contrast to these reactions, heating of DPPF and CF_3-DPPF complexes **8a**,**b** and **9**, containing an electron-neutral Pd-bound aryl group, did not produce detectable amounts of diaryl ether in the presence or absence of a trap or sodium aryloxide (eq 4). Though quantitative



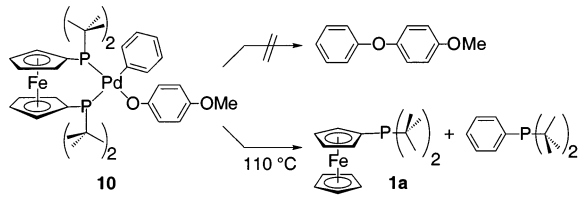
(4)

8a,b, 9

R = Ph, C_6H_4-4-CF_3
Ar=3,5-di-*tert*-butylphenyl, 4-$MeOC_6H_4$

rate data on the reactions of **8a**,**b** and **9** were not obtained because of the absence of ether product, the rate of decomposition of these species was similar to the rate of elimination from **5a**−**7b**. Half-lives for decay of **8b** at 100 °C in the presence of 2 equiv of PPh_3 or DPPF were within a factor of 2 of the half-lives for decay of **5c**, which contained an electron-poor palladium-bound aryl group. Complex **8b** reacted slightly slower in most experiments. Thus, the absence of product formed from complexes with unactivated aryl groups is due partly to slower reductive elimination and partly to a faster mode for decomposition other than reductive elimination. We considered that the similar rate was due to rate-limiting dissociation of phenoxide as occurs from **10** in polar solvents. Consistent with this hypothesis, complexes **8b** and **5c** reacted faster in polar solvents such as DMF and NMP. However, thermolyses in this medium formed arene, biaryl compounds, and phenol, but no ether. Thus, competing decomposition could occur by dissociation of phenoxide, but diaryl ether does not appear to form by this path.

Even though complexes generated from palladium precursors of D-*t*-BPF catalyzed the formation of diaryl ethers from electron-neutral aryl halides in 40−50% yield, thermolysis at 110 °C of D-*t*-BPF complex **10**, which contains an electron-neutral aryl group, produced no detectable diaryl ether (eq 5). These conditions

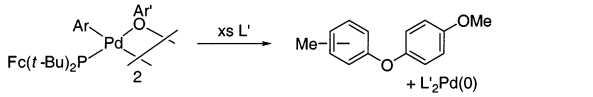


(5)

10 **1a**

consumed **10** completely. Addition of various species that would be present in the catalytic system (D-*t*-BPF, sodium aryloxide, NaBr, aryl halide, DBA), as well as the addition of PhCCPh or PPh_3 to coordinate the Pd(0) product, had no effect on this reaction. Careful analysis of all reaction products by GC/MS showed the formation of aryl alcohol, biaryls, and the monophosphines PhP(*t*-Bu)$_2$ and FcP(*t*-Bu)$_2$ (**1a**) (eq 5). These two phosphines did not form in detectable amounts during the high-yield reductive elimination of diaryl ether from complexes **7a**,**b**, which contain electron-poor, palladium-bound aryl groups. However, formation of the ferrocenylphosphine from D-*t*-BPF was the first step toward the generation of the pentaphenylferrocenylphosphine, which generates catalysts that are active for the formation of biaryl ethers.[21]

2. Reductive Elimination of Diaryl Ethers from Palladium Aryloxide Complexes Containing Monophosphines. Thermolysis of FcP(*t*-Bu)$_2$-ligated arylpalladium aryloxide **11a**, which contains an electron-neutral aryl group, at 70 °C in the presence or absence of sodium aryloxide, aryl bromide, or ligand **1a** gave diaryl ether in 5−25% yields (eq 6) and Pd[FcP-



(6)

Ar' = C_6H_4-4-OMe
Ar = C_6H_4-2-Me **(11a)**
Ar = C_6H_4-4-Me **(11b)**

yield from **11a**, L' = FcP(*t*-Bu)$_2$ 5-25%
L' = P(*t*-Bu)$_3$ 95%
L' = Ph_5FcP(*t*-Bu)$_2$ 66%
L' = 2-P(*t*-Bu)-1,1'-binaphthyl 10-58%
yield from **11b**, L' = P(*t*-Bu)$_3$ 25%

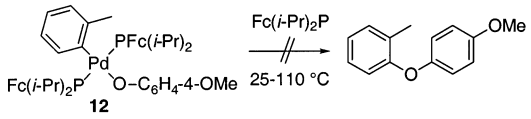
(*t*-Bu)$_2$]$_2$.[10] Addition of sodium aryloxide to dimeric bromide complex **3**, followed by heating at 80 °C for 1 h, gave diaryl ether in a similar 22% yield. Thus, dimeric **11a** does generate some diaryl ether by reductive elimination, but this complex is not a true intermediate in the catalytic process. FcP(*t*-Bu)$_2$ undergoes arylation of the unsubstituted cyclopentadienyl ligand to generate Ph_5FcP(*t*-Bu)$_2$ (**1b**), which is present in the true catalyst.[21]

Thus, heating of FcP(*t*-Bu)$_2$-ligated **11a** in the presence of 40 equiv of pentaphenylferrocenyl **1b** gave diaryl ether in a higher 66% yield. This result demonstrates the high reactivity of a complex containing ferrocene ligand **1b**, relative to that containing only **1a**, and further substantiates the intermediacy of arylpalladium phenoxides ligated by **1b** as intermediates in the recently reported catalytic process. The two homoleptic and one mixed-ligand palladium(0) complexes were the metal products. These complexes were prepared independently by addition of the two ligands together to CpPd(allyl) or Pd[P(*o*-tolyl)$_3$]$_2$, or by mixing of the two homoleptic Pd(0) complexes containing these ligands.

Reaction of **11b** at 40 °C in the presence of 1 equiv of 2-(di-*tert*-butylphosphino)-1,1′-binaphthyl (**1c**), which is a ligand present on catalysts for the formation of diaryl ethers,[15] formed the diaryl ether in 58% yield. Reaction in the presence of a large excess of **1c** (20 equiv), however, formed the diaryl ether in only 10% yield. These reactions formed {Pd[FcP(*t*-Bu)$_2$]$_2$} as the exclusive phosphine-ligated Pd(0) product, along with palladium black. Thus, ligand **1c** is not consumed during this reaction and acts as a catalyst to induce the reductive elimination from **11a**. The highest yield of diaryl ether occurred upon warming of *o*-tolyl complex **11a** at 70 °C in the presence of 10 equiv of P(*t*-Bu)$_3$. This reaction gave diaryl ether and Pd[P(*t*-Bu)$_3$]$_2$ in 95% yield (eq 6). Clearly, the equilibrium for ligand exchange and the rate of reductive elimination from the resulting species both influence the yields of reductive elimination from **11a** in the presence of the added ligand.

In contrast to the high yields of ether formed from heating of *o*-tolyl complex **11a** in the presence of P(*t*-Bu)$_3$, heating of *p*-tolyl complex **11b** formed diaryl ether in only 25% yield in the presence of P(*t*-Bu)$_3$. Moreover heating of **11b** in the presence of excess **1a**

or **1b** did not form ether. Thermolysis of monomeric, FcP(*i*-Pr)$_2$-ligated **12** formed Pd[FcP(*i*-Pr)$_2$]$_2$, but generated free 4-methoxyphenol as only the product from the aryloxo group (eq 7). The Pd(0) product was prepared independently by the reaction of FcP(*i*-Pr)$_2$ with Cp(allyl)Pd.



(7)

C. Mechanistic Studies of the Formation of Diaryl Ethers. 1. Reductive Elimination from Monomeric, Bis-phosphine-Ligated Palladium Aryloxides. The rates of reductive elimination of the high-yield formation of diaryl ethers from **5c** and **6b** were measured by ^{1}H NMR spectroscopy in toluene-d_8. Kinetic data were obtained by monitoring the disappearance of the arylpalladium aryloxo complex in sealed NMR tubes completely immersed in an oil bath maintained at 105 °C. ^{1}H NMR spectra were obtained periodically at room temperature.

Reductive elimination from the more electron-poor CF_3-DPPF complex **6b** was roughly 2 times faster than it was from the DPPF complex **5c**. Plots of ln[**5c**] or ln[**6b**] versus time were linear over three half-lives for reaction in the presence of 4 equiv of diphenylacetylene and either no added sodium aryloxide or 5 equiv of added sodium aryloxide. The reductive elimination at 105 °C occurred with a half-life of 7000 s, and the reaction at 50 °C occurred with a half-life of about 3 days (2.4×10^5 s). In contrast to a previous system,[42] the rate constants for reductive elimination from **5c** and **6b** at 105 °C in the presence or absence of 5 equiv of sodium aryloxide were indistinguishable ($k_{obs} = (1.0 \pm 0.3) \times 10^{-4}$ s^{-1} and $(1.0 \pm 0.3) \times 10^{-4}$ s^{-1} for **5c**, and $k_{obs} = (1.7 \pm 0.3) \times 10^{-4}$ s^{-1} versus $(2.0 \pm 0.3) \times 10^{-4}$ s^{-1} for **6b**). The rate constant for reductive elimination did not depend on the identity or quantity of added dative ligand and is, therefore, zero order in the reagent that traps the Pd(0). The rate constants for thermolysis of DPPF-ligated complex **5c** in the presence of 1.6×10^{-2} to 6.7×10^{-2} M DPPF, instead of PhCCPh, were $(1.5 \pm 0.4) \times 10^{-4}$ s^{-1}.

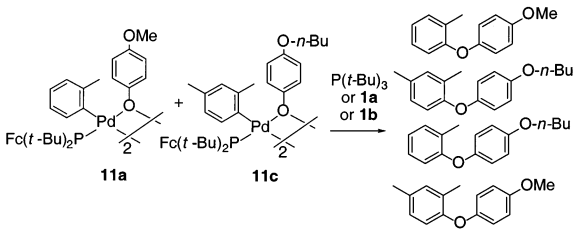
D-*t*-BPF-ligated **7b** reacted roughly 2 orders of magnitude faster than the analogous phenylphosphine complex. Reactions of **7b** were first-order in palladium complex, and the rate constant at 50 °C was $(2.8 \pm 0.3) \times 10^{-4}$ s^{-1}. This rate constant corresponds to a half-life of 2400 s. Even after considering that the ether is formed from **7b** in only 56% yield, the rate constant for reaction of **7b** indicates that reductive elimination from this hindered complex occurs at a time scale that is much shorter than the 2.4×10^5 s half-life for reaction of the analogous DPPF-ligated complex **5c** at the same temperature.

2. Mechanism of Reductive Elimination from Dimeric, Monophosphine-Ligated Palladium Aryloxides. Mechanistic studies were also conducted on the high-yield elimination of diaryl ether from **11a** in the presence of added P(*t*-Bu)$_3$. Crossover experiments were conducted to probe for reversible cleavage of dimeric **11a** to form monomeric intermediates prior to reductive elimination. First, a 1:1 mixture of 2-methylphenylpalladium *p*-methoxyaryloxo complex **11a** and 2,4-dimethylphenylpalladium *p*-butoxyaryloxo complex **11c** was heated at 75 °C in the presence of 5−7 equiv of added P(*t*-Bu)$_3$, **1a**, or **1b** (eq 8). Each reaction gave all four possible diaryl ethers in nearly equal amounts. The exchange could occur by an associative mechanism or by a process involving a catalytic amount of phenol, but these data are at least consistent with reversible generation of monomeric arylpalladium phenoxide complexes from **11a**−**c**.

Table 5. Effect of Ligand Concentration on Yield of Reductive Elimination of Diaryl Ether from 11a[a]

[**1a**][b]	[P(*t*Bu)$_3$][b]	[**1b**][b]	[**1c**][b]	yield (%)
	15.0			95
0.15	15.0			71
15.	15.0			22
		6.7		74
0.070		6.8		64
3.6		7.1		33
			0.65	58
0.070			0.65	27
			29.0	0

[a] [**11a**] = 7.0×10^{-3} M. [b] M $\times 10^2$.



(8)

Addition of P(*t*-Bu)$_3$ to **11a** appeared to partially displace ligand **1a**, and this equilibrium precluded simple kinetic studies. Small amounts of free **1a** were observed after addition of P(*t*-Bu)$_3$. Addition of excess pentaphenylferrocenyl ligand **1b** to **11a** did not generate free ligand **1a**. However, reaction of phenoxide **11a** in the presence and absence of excess phosphine **1b** at 60 °C occurred at similar rates, even though the yields of diaryl ether were substantially different.

Thus, we evaluated the yields, instead of rates, for the formation of diaryl ether in the presence of varying concentrations of added phosphine, as summarized in Table 5. The yield of diaryl ether produced from the reaction between **11a** and P(*t*-Bu)$_3$, **1b**, or **1c** was significantly lower in the presence of added FcP(*t*-Bu)$_2$. For example, reactions containing a 1:1 ratio of **1a** and P(*t*-Bu)$_3$ formed diaryl ether in only 22% yield, while reactions containing a 1:100 ratio of **1a** and P(*t*-Bu)$_3$ formed the ether in 71% yield. Reactions performed with a 1:1 ratio of **1a** and **1b** formed diaryl ether in only 30% yield, while reactions containing a 1:100 ratio formed diaryl ether in 64% yield.

Discussion

A. Evaluation of Factors That Control Reductive Elimination of Diaryl Ether. The Pd(II) compounds described here are the first isolated aryloxide complexes that undergo reductive elimination of ethers. Organopalladium aryloxide complexes have been generated

previously,[88−90] but they have not formed ethers. For example, thermolysis of (Tol-BINAP)Pd(C_6H_4-4-CN)(OC_6H_4-4-Me) at 60 °C resulted in <5% yield of diaryl ether,[42] and (DMPE)PdMe(OPh) generated products from phenoxyl radicals, but no ether, after one-electron oxidation.[91] In contrast, thermolysis of arylpalladium complexes containing the dative ligand DPPF, an electron-poor palladium-bound aryl group, and the phenoxide OC_6H_4-4-OMe resulted in formation of diaryl ether in high yield. Thermolysis of the analogous DPPF complexes containing an electron-neutral aryl group bound to Pd generated biaryl compounds and phenol, but no ether. These results show that reductive elimination of diaryl ethers from monomeric arylpalladium aryloxide complexes with unactivated, Pd-bound aryl groups is a particularly difficult transformation to observe.

Several possible relationships between ligand properties and reductive elimination rates and the relative importance of each perturbation on the rates and yields for the formation of diaryl ethers were evaluated in the present study. This work showed that steric hindrance can dramatically increase the rate of reductive elimination and that monodentate ligands are so far required to observe reductive elimination of diaryl ethers from arylpalladium complexes that lack activating substituents on the palladium-bound aryl ring.

1. Evaluation of Phosphine Ligand Electronic Effects. Studies to evaluate the importance of phosphine electronics on reductive elimination showed that the CF_3-DPPF complex **6a** underwent reductive elimination only 2 times faster than the analogous DPPF complex **5a**. Neither the DPPF- nor CF_3-DPPF complex with a neutral phenyl group bound to the palladium formed diaryl ether. Thus, conventional electronic effects on the rate of reductive elimination were observed, but the magnitude of the rate difference was small. The difference in electron-donating ability of the two arylphosphine ligands in this study certainly does not span the full range of possible ligand electronic properties, but modification of aromatic substituents at phosphorus is unlikely to allow reductive elimination to form diaryl ether from complexes with unactivated, Pd-bound aryl groups. Importantly, electron-donating properties of alkylphosphines should not dramatically retard the rate for reductive elimination because the difference between the ν_{CO} values in $Ni(CO)_2$ complexes of DPPF and CF_3-DPPF is similar to the difference between the value for $Ni(CO)_3L$ in which L is an arylphosphine and for $Ni(CO)_3L$ in which L is an alkylphosphine.

2. Evaluation of Steric Effects. In contrast to these small differences in rate resulting from changes in electronic properties, large differences in rate were observed from changes in ligand steric properties. In particular, thermolysis of D-*t*-BPF-ligated cyanophenyl aryloxide **7b** formed diaryl ether with a rate that was two or more orders of magnitude faster than that for reductive elimination from analogous Pd complexes containing a closely related arylphosphine. The A_1 ν_{CO} value of 2055 cm^{-1} for {$[(CO)_3Ni]_2$(D-*t*-BPF)} showed that the D^{t}BPF ligand is strongly electron-donating. Thus, the acceleration of reductive elimination from **7b** due to steric effects clearly exceeds any decelerating effect due to the strong electron-donating ability of the ligand.

The importance of steric effects on reductive elimination of diaryl ether from complexes of monophosphines was clearly demonstrated by observing reductive elimination of diaryl ether from FcP(*t*-Bu)$_2$-ligated complexes, but no reductive elimination from FcP(*i*-Pr)$_2$-ligated complexes. FcP(*t*-Bu)$_2$ and FcP(*i*-Pr)$_2$ have similar electronic properties, but the latter ligand is, of course, less sterically demanding. The effect of steric hindrance was also shown by the increased yields of diaryl ether formed from reaction of FcP(*t*-Bu)$_2$-ligated **11a** after addition of the more hindered P(*t*-Bu)$_3$, (Ph_5Fc)P(*t*-Bu)$_2$, or 2-di-*tert*-butylphosphino-1,1′-binaphthyl.

3. Effect of Coordination Number: Reductive Elimination from Phenoxo Complexes Containing Sterically Hindered Monophosphines. Previous kinetic studies on C−N and C−C bond-forming reductive elimination have shown that reductive elimination occurs faster from three-coordinate palladium species than from four-coordinate species.[34,62,67] However, reductive elimination of aryl ethers did not occur from complexes containing standard monophosphines. During unpublished exploratory studies we found that thermolysis of the products from addition of alkali aryloxides to P(*o*-tolyl)$_3$-ligated arylpalladium halides[92] and heating of known triphenylphosphine-ligated palladium aryloxides produced no ether.[89,91] In contrast, complexes in this study containing particularly hindered alkylmonophosphines underwent reductive elimination of diaryl ethers, even when the complex contained electron-neutral, palladium-bound aryl groups. Thus, the combination of phosphine steric hindrance and the generation of three-coordinate complexes allows the formation of diaryl ethers by C−O bond-forming reductive elimination.

B. Mechanism of the Reductive Elimination of Diaryl Ether. 1. Reductive Elimination from D-*t*-BPF-Ligated Complexes. Kinetic data ruled out a reductive elimination that is induced by the added dative ligand and implied that a simple intramolecular reductive elimination occurs directly from the starting arylpalladium phenoxide. Reductive elimination of diaryl ether from the D-*t*-BPF-ligated arylpalladium phenoxides **5**−**7** was first-order in the palladium complex and zero-order in added ligands. The demanding steric properties of **7** could lead to partial dissociation of the chelating ligand. Our kinetic data cannot distinguish between direct elimination and elimination after dissociation of one phosphorus donor in the coordinated D-*t*-BPF. However, dissociation of one phosphorus of D-*t*-BPF from D-*t*-BPF-ligated **10** bearing an electron-neutral palladium-bound aryl group would generate nearly the same intermediate that is, presumably, generated during reaction of dimeric **11a** containing the ferrocenylmonophosphine **1a**. Because **11a** forms some diaryl ether but thermolysis of **10** does not, we disfavor reaction of D-*t*-BPF-ligated **7** after opening of the

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chelating ligand. Generation of a monophosphine complex from **7** by P−C bond cleavage prior to reductive elimination does not occur. Although cleavage of the phosphine during thermolysis of **10** was observed, none of the monophosphines formed by P−C cleavage were observed during the thermolysis of **7**. Thus, the increased steric properties of D-*t*-BPF appear to promote elimination by accelerating C−O bond formation directly from the starting complex **7**.

2. Reductive Elimination from FcP(*t*-Bu)$_2$ Complexes. Quantitative rate data that uncovered a detailed mechanistic pathway for reductive elimination from **11a**−**c** were difficult to obtain. Yet, reductive elimination of diaryl ether from **11b** is clearly induced by substitution of **1a** by the larger phosphine ligand **1b**, P(*t*-Bu)$_3$, or binaphthyl **1c**. Reactions conducted in the presence of high concentrations of **1b** or P(*t*-Bu)$_3$ formed diaryl ether in high yields, while reactions conducted with low concentrations of added ligand formed diaryl ether in low yields. Moreover, reactions conducted with **1b**, **1c**, or P(*t*-Bu)$_3$ along with FcP(*t*-Bu)$_2$ generated lower yields of diaryl ether. The presence of FcP(*t*-Bu)$_2$ in the latter reactions will decrease the concentration of the ligand substitution product.

Reductive elimination from dimeric **11b** most likely occurs after formation of a monomeric species. Products from thermolysis of a mixture of **11a** and **11c** in the presence or absence of added P(*t*-Bu)$_3$ suggested that three-coordinate monomeric arylpalladium phenoxides were generated reversibly. Moreover, previous studies on dimeric amides and thiolates[32,34,37,93] have shown clearly that reductive elimination occurs from monomeric complexes. Rate constants for reaction of **11a** in the presence and absence of ligand **1b** were nearly identical, even though the yields were significantly different. These data suggest that the added ligand intercepts the chemistry of a reactive intermediate formed from **11a**. Although not shown unambiguously, this intermediate that reacts with the incoming ligand is likely to be the three-coordinate arylpalladium phenoxide or a species that gives rise to this three-coordinate phenoxide.

C. Relationship between Catalytic and Stoichiometric Reactions. There is a strong parallel between complexes that undergo reductive elimination and the types of palladium complex that catalyze the formation of diaryl ethers. First, palladium complexes of arylphosphines catalyze the formation of diaryl ethers from aryl halides bearing electron-withdrawing groups, and a combination of CF$_3$-DPPF and palladium precursors leads to formation of diaryl ethers with faster rates and higher yields than a combination of DPPF and palladium precursors.[11] Moreover, complexes of sterically hindered monodentate ligands are the most efficient at formation of diaryl ethers.[10,15,21] The only bidentate ligand that has generated a catalyst for the formation of diaryl ethers from electron-neutral aryl halides has generated this catalyst by cleavage and reaction with the aryl halide substrate to form a new hindered monophosphine.[10]

The contrast between the low yields of diaryl ether generated by reductive elimination from FcP(*t*-Bu)$_2$-ligated arylpalladium phenoxide **11a** and the excellent yields of diaryl ether generated from coupling of aryl halides with phenoxides in the presence of catalytic amounts of **1a** and Pd(DBA)$_2$ was initially perplexing. These results clearly ruled out arylpalladium bromide and phenoxide complexes **3** and **11a**, which contain FcP(*t*-Bu)$_2$ ligand **1a**, as intermediates in the catalytic process. However, we have shown that transformation of the parent ferrocenyl ligand **1a** to the perarylated ferrocenyl ligand **1b** under the conditions of the catalytic reaction generated the true catalyst.[21] Reactions catalyzed by complexes of this more hindered ligand **1b** proceeded in higher yields and with faster rates than those catalyzed by complexes of FcP(*t*-Bu)$_2$.[21] Consistent with these faster rates and higher yields for the catalytic system bearing ligand **1b** or the di-*tert*-butylphosphinobinaphthyl ligand of Buchwald, the rate of reductive elimination from **11a** in the current work was faster and occurred in high yield when heated in the presence of excess Ph$_5$FcP(*t*-Bu)$_2$ or the binaphthyl ligand.

D. Conclusions. Variation of electronic properties of palladium complexes with bidentate phosphines showed only small effects on the rate of C−O bond-forming reductive elimination, but changes in steric properties of the ligand had a dramatic effect. The presence of a single donor atom on the sterically hindered ligand is important for generating a three-coordinate arylpalladium phenoxide intermediate that forms diaryl ether product from complexes with electron-neutral, palladium-bound aryl groups. The relative size of P(*t*-Bu)$_3$, FcP(*t*-Bu)$_2$, Ph$_5$FcP(*t*-Bu)$_2$, and 2-(di-*tert*-butylphosphino)-1,1′-binaphthyl in the transition state structure is unclear; simple modeling of Pd(0) complexes showed that the steric demands of the FcP(*t*-Bu)$_2$ ligand on the metal center dramatically change with conformation. Nevertheless, the results presented here demonstrate clearly that increased steric hindrance in palladium complexes with monodentate phosphines increases the rate of reductive elimination enough to allow new reaction chemistry.

Previous reactions of aryl halides with phenoxides were catalyzed by palladium complexes of arylphosphines and led to C−C bond formation at the *o*- or *p*-position of the phenoxide.[94−96] The reductive elimination reactions of the isolated phenoxides studied in the present work form C−O instead of C−C bonds. Presumably the C−C couplings with phenoxides observed during previous work occur by reductive elimination after rearrangement of an O-bound phenoxide to a less stable C-bound form that resembles an enolate. The steric and electronic properties of the ligands presented in the current work, therefore, accelerate C−O bond-forming reductive elimination enough to allow reaction from the thermodynamically preferred, but less reactive, O-bound arylpalladium phenoxide complex.

Experimental Section

General Methods. All reactions were performed in a drybox under N$_2$ using solvents that were distilled from

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sodium/benzophenone ketyl (toluene, benzene, ether, and THF) or from calcium hydride (methylene chloride) unless otherwise stated. ^{1}H NMR spectra were obtained on a 300 MHz spectrometer and were referenced to residual protiated solvents. ^{13}C NMR spectra were obtained on an AM 500 MHz spectrometer. ^{31}P{^{1}H} NMR spectra were obtained on an Omega 300 MHz spectrometer with shifts reported relative to an external 85% H_3PO_4 standard, and ^{19}F{^{1}H} NMR spectra were obtained on an Omega 500 MHz spectrometer with shifts reported relative to an external $CFCl_3$ standard. GC data were obtained on an HP 5890 gas chromatograph. GC/MS data were obtained on a HP 5890 gas chromatograph equipped with an HP5971A mass spectral analyzer. IR spectra were obtained on a MIDAC M Series spectrometer. Ligands **1a** and **1b** were prepared according to published methods.[10,21]

(D-*t*-BPF)Pd(Br)(C_6H_4-4-CN) (2a). D-*t*-BPF (0.386 g, 0.506 mmol) in 4 mL of THF was added to a solution of {Pd[P(*o*-tolyl)$_3$](C_6H_4-4-CN)(Br)}$_2$[18] in 6 mL of THF. The mixture was stirred for 1.5 h. The solvent was removed under vacuum. The yellow solid was dissolved in 4 mL of benzene and 15 mL of pentane was added to precipitate the product. The yellow solid was washed with pentane (3 × 5 mL). The solid was redissolved in THF, concentrated, layered with pentane, and cooled to −35 °C. Yellow crystals of product were obtained (0.2288 g, 59%). ^{1}H (C_6D_6): δ 1.08 (v br d, 10.2 Hz, 18H, P*t*-Bu), 1.63 (v br d, 11.9 Hz, 18H, P*t*-Bu), 3.92 (br, s, 4H, C_5H_4P), 4.13 (br s, 4H, C_5H_4P), 7.01 (d, 8.2 Hz, 2H, *m*-C_6H_4CH), 7.81 (t, 7.5 Hz, 2H, *o*-C_6H_4CN). ^{1}H ($CDCl_3$): δ 1.38 (t, 7.6 Hz, 36H, P*t*-Bu), 4.33 (t, 1.9 Hz, 4H, C_5H_4P), 5.68 (t, 1.8 Hz, 4H, C_5H_4P), 7.41 (d, 8.1 Hz, 2H, C_6H_4CN), 7.83 (d, 8.3 Hz, 2H, C_6H_4CN). ^{1}H (CD_3NO_2): δ 1.44 (t, 7.5 Hz, 36H, P*t*-Bu), 4.46 (t, 2.0 Hz, 4H, C_5H_4P), 5.32 (t, 2.0 Hz, 4H, C_5H_4P), 7.50 (d, 8.0 Hz, 2H, C_6H_4CN), 8.08 (d, 8.0 Hz, 2H, C_6H_4CN). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 30.71 (s, C*Me*$_3$), 36.81 (t, 6.8 Hz, *C*Me$_3$), 53.93 (t, 8.9 Hz, *i*-C_5H_4P), 70.91 (t, 3.4 Hz, α-C_5H_4P), 79.18 (s, *β*-C_5H_4P), 107.09 (s, C_6H_4CN), 118.92 (s, C_6H_4CN), 130.24 (s, *m*-C_6H_4CN), 138.648 (t, 3.2 Hz, *o*-C_6H_4CN), 154.12 (d, 2.3 Hz, *i*-C_6H_4CN). ^{31}P{^{1}H} NMR (C_6D_6): δ 37.46 (d, 22.2 Hz, 1P), 46.85 (d, 22.2 Hz, 1P). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 21.56 (s). ^{31}P{^{1}H} NMR (CD_3NO_2): δ 23.36 (s). Anal. Calcd for $C_{33}H_{48}BrFeNP_2Pd$: C, 51.96; H, 6.34; N, 1.84. Found: C, 52.06; H, 6.36; N, 1.60.

Pd(D-*t*-BPF)(C_6H_5)(O-C_6H_4-4-OMe) (2b). To a solution of 104 mg (0.0921 mmol) of {Pd[P(*o*-tol)$_3$](C_6H_5)(Br)}$_2$ in 2 mL of THF was added 89.6 mg (0.189 mmol) of D-*t*-BPF in 2 mL of THF. The solution was stirred for 30 min, over whch time a clear yellow solution resulted. The solvent was removed under vacuum, and the resulting yellow solid was redissolved in ca. 1 mL of benzene. This benzene mixture was then precipitated from ca. 20 mL of pentane, which yielded a yellow solid. This yellow solid was filtered through a medium-fritted funnel and washed twice with pentane. The yellow solid, presumed to be Pd(D-*t*-BPF)(C_6H_5)(O-C_6H_4-4-OMe), which displayed a chemical shift at 45.11 (d, 25.7 Hz), 36.4 (d, 25.7 Hz) ppm in the ^{31}P NMR spectrum, was isolated in 74.7% yield (101.3 mg).

[(D-*t*-BPF)Pd(C_6H_4-4-CN)](BF_4) (2c). $AgBF_4$ (22 mg, 0.11 mmol) was added to a solution of (D-*t*-BPF)Pd(Br)(C_6H_4-4-CN) (65 mg, 0.085 mmol) in 5 mL of THF. The suspension was stirred at room temperature for 5 min. The solid was then filtered from solution, and the solvent was removed under vacuum. The crude material was recrystallized from THF at −35 °C. Dark orange crystals were obtained (52.1 mg, 80% yield). ^{1}H NMR (CD_2Cl_2): δ 1.38 (t, 8.0 Hz, 36H), 1.81 (m, 4H, THF), 3.67 (m, 4H, THF), 4.29 (m, 4H), 5.31 (m, 4H), 7.44 (d, 4.0 Hz, 2H), 7.85 (d, 4.0 Hz, 2H). ^{13}C NMR (CD_2Cl_2): δ 25.95 (THF), 31.06 (t, 3.0 Hz), 37.46 (t, 8.3 Hz), 55.15 (t, 8.2 Hz), 68.12 (THF), 71.54 (t, 3.4 Hz), 78.80, 107.88, 119.53, 131.04, 139.29 (t, 4.2 Hz), 154.01. ^{31}P NMR (CD_2Cl_2): δ 21.71(s); Anal. Calcd for $C_{33}H_{48}NP_2F_4BFePd$·THF: C, 52.78; H, 6.72; N, 1.66. Found: C, 52.66, H, 6.67; N, 1.60.

{Pd[P($C_5H_4FeC_5H_5$)(*t*-Bu)$_2$](C_6H_4-2-Me)(Br)}$_2$ (3). To a solution of {Pd[P(*o*-tolyl)$_3$](*o*-MeC_6H_4)(Br)}[97] (246 mg, 0.211 mmol) in 3 mL of THF was added 199 mg (0.503 mmol) of P($C_5H_4FeC_5H_5$)(*t*-Bu)$_2$ in 2 mL of THF. The solution was stirred at room temperature for 2 h. The solvent was removed under vacuum, and the solids were redissolved in pentane. The resulting suspension was filtered through Celite to give an orange solution. The pentane was removed under vacuum, and the resulting orange solid was redissolved in toluene, layered with pentane, and cooled at −35 °C for 2 days. Orange crystals (78.7 mg, 31% yield) were obtained. ^{1}H NMR (C_6D_6, 25 °C): δ 1.36 (d, 13.9 Hz, 18H), 1.44 (d, 13.9 Hz, 18H), 2.10 (s, 6H), 3.72 (s, 2H), 3.77 (s, 2H), 3.82 (s, 2H), 3.86 (s, 2H), 3.97 (s, 10H), 6.75−6.84 (m, 6H), 7.49 (dd, 7.3 Hz, 3.1 Hz, 2H). ^{31}P-{^{1}H} NMR (C_6D_6): δ 54.04 (s). Anal. Calcd for $C_{50}H_{68}Br_2Fe_2P_2Pd_2$·$C_7H_8$: C, 52.36; H, 5.86. Found: C, 52.11; H, 5.96.

[FcP(*i*-Pr)$_2$]$_2$Pd(C_6H_4-2-Me)(Br) (4). ($C_5H_4FeC_5H_5$)P(*i*-Pr)$_2$ (0.130 g, 0.430 mmol) and {Pd[P(*o*-tolyl)$_3$](C_6H_4-2-CH_3)(Br)}$_2$ (0.100 g, 0.086 mmol) were dissolved in 20 mL of toluene and stirred for 3 h. Solvent was removed under vacuum. Benzene (1 mL) and pentane (10 mL) was added to the orange solid to dissolve free phosphines. The remaining solid was washed with pentane (3 × 5 mL) and dried under vacuum (0.1048 g, 69%). ^{1}H NMR (C_6D_6): δ 1.28 (q, 7.1 Hz, 6H, CH*Me*$_2$), 1.45 (q, 7.9 Hz, 6H, CH*Me*$_2$), 1.53 (q, 7.5 Hz, 6H, CH*Me*$_2$), 1.54 (q, 7.1 Hz, 6H, CH*Me*$_2$), 2.15 (s, 3H, C_6H_4*Me*), 2.81 (m, 2H, C*H*Me$_2$), 3.39 (m, 2H, C*H*Me$_2$), 3.65 (br s, 2H, C_5H_4P), 3.81 (br s, 2H, C_5H_4P), 3.90 (br s, 2H, C_5H_4P), 4.00 (s, 10H, C_5H_5), 4.17 (br s, 2H, C_5H_4P), 6.57 (d, 7.2 Hz, 1H, C_6H_4Me), 6.67 (t, 7.10 Hz, 1H, C_6H_4Me), 6.75 (t, 7.12 Hz, C_6H_4Me), 7.40 (d, 7.3 Hz, 1H, C_6H_4Me). ^{13}C{^{1}H} NMR (C_6D_6): δ 19.73 (s, CH*Me*$_2$), 20.03 (s, CH*Me*$_2$), 20.54 (s, CH*Me*$_2$), 21.38 (s, CH*Me*$_2$), 27.04 (t, 12.2 Hz, *C*HMe$_2$), 27.75 (s, C_6H_4*Me*), 30.46 (t, 11.6 Hz, *C*HMe$_2$), 68.60 (t, 3.4 Hz, C_5H_4P), 69.41 (t, 3.2 Hz, C_5H_4P), 69.73 (s, C_5H_5), 73.09 (t, 5.6 Hz, C_5H_4P), 73.67 (br s, C_5H_4P), 76.35 (t, 16.1 Hz, *i*-C_5H_4P), 122.51 (s, C_6H_4Me), 123.09 (s, C_6H_4Me), 129.45 (s, C_6H_4Me), 138.16 (t, 4.9 Hz, C_6H_4Me), 143.13 (t, 3.8 Hz, C_6H_4Me). ^{31}P{^{1}H} NMR (C_6D_6): δ 23.94 (s). Anal. Calcd for $C_{39}H_{53}BrFe_2P_2Pd$: C, 53.12; H, 6.06. Found: C, 52.91; H, 5.95.

[Pd(DPPF)(C_6H_4-4-CN)(OC_6H_4-4-OMe)] (5a). A 100 mL flask was charged with 484 mg (0.676 mmol) of Pd[P(*o*-tolyl)$_3$]$_2$,[68] 456 mg (0.823 mmol) of DPPF, 197 mg (2.05 mmol) of Na-O-^{t}Bu, and 382 mg (1.52 mmol) of 4-cyanophenyl trifluoromethylsulfonate in 20 mL of THF. The solution was stirred overnight in the drybox, and a brownish-yellow solid precipitated from solution. The precipitate was isolated by filtration and redissolved in 2 mL of a 1:1 mixture of THF and benzene. A 1:1 mixture of Et_2O and pentane was added to the resulting brown solution to bring the total volume to 10 mL. [Pd(DPPF)(C_6H_4-4-CN)(OC_6H_4-4-CN)] was precipitated from this solution and isolated in 80% yield (665 mg). This compound was used without further purification. ^{1}H NMR (CD_2Cl_2): δ 3.86 (d, 1.6 Hz, 2H), 4.28 (s, 2H), 4.59 (s, 2H), 4.73 (d, 1.8 Hz, 2H), 6.29 (d, 8.6 Hz, 2H), 6.74 (dd, 8.1 Hz, 1.9 Hz, 2H), 6.90 (d, 8.7 Hz, 2H), 7.13−7.19 (m, 6H), 7.22−7.46 (m, 12H), 7.84 (dd, 9.5 Hz, 7.0 Hz, 4H). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 32.40 (d, 30.0 Hz), 13.65 (d, 30.0 Hz).

To a solution containing 0.205 mg (0.232 mmol) of [Pd(DPPF)(C_6H_4-4-CN)(OC_6H_4-4-CN)] in 5 mL of THF was added 35.9 mg (0.246 mmol) of Na(OC_6H_4-4-OMe). The solution was stirred at room temperature for 20 min, after which time a light brown solution remained. The solution was filtered through Celite, concentrated under vacuum, and crystallized by layering the THF solution with pentane at −35 °C. The product (149 mg, 82%) was obtained as yellow blocks. ^{1}H NMR (C_6D_6): δ 3.40 (s, 3H), 3.68 (d, 1.2 Hz, 2H), 3.72 (d, 1.5 Hz, 2H), 3.95 (br s, 2H), 4.48 (d, 1.7 Hz, 2H), 6.54 (d, 1.9 Hz, 1H), 6.57 (d, 2.6 Hz, 1H), 6.66 (s, 4H), 6.71−6.76 (m, 4H), 6.82−6.89 (m, 2H), 7.06−7.19 (m, 6H), 7.21−7.33 (m, 6H), 8.25 (td, 7.1 Hz, 1.1 Hz, 4H). ^{31}P{^{1}H} NMR (C_6D_6): δ 31.40 (d, 31 Hz),

10.64 (d, 31 Hz). IR (KBr, cm^{-1}): ν_{CN} 2216.0. Anal. Calcd for $C_{48}H_{39}FeNO_2P_2Pd$: C, 65.07; H, 4.44. Found: C, 64.76; H, 4.31.

[Pd(DPPF)(C_6H_4-4-CN)(OC_6H_4-4-O-*n*-C_4H_9)] (5b). Following a similar procedure for the synthesis of **5a**, 232 mg (0.264 mmol) of [Pd(DPPF)(C_6H_4-4-CN)(OC_6H_4-4-CN)] and 76.7 mg (0.408 mmol) of Na(OC_6H_4-4-O-*n*-C_4H_9) were stirred at room temperature for 1.5 h in 5 mL of THF. The THF was removed under vacuum, and the resulting solids were redissolved in 25 mL of toluene. After filtering through a medium-fritted funnel, the solution was concentrated, layered with pentane, and allowed to crystallize at −35 °C. The product was isolated in 56% yield (137 mg). ^{1}H NMR (C_6D_6): δ 0.80 (t, 7.3 Hz, 3H), 1.34 (sextet, 7.3 Hz, 2H), 1.58 (quintet, 8.0 Hz, 2H), 3.68 (m, 4H), 3.72 (d, 2.0 Hz, 2H), 3.96 (br s, 2H), 4.48 (d, 1.4 Hz, 2H), 6.55 (d, 1.9 Hz, 1H), 6.65 (d, 1.9 Hz, 1H), 6.65−6.76 (m, 8H), 6.83−6.88 (m, 2H), 7.09−7.20 (m, 5H), 7.22−7.31 (m, 7H), 8.26(dd, 9.7 Hz, 7 Hz, 4H). ^{31}P{^{1}H} NMR (C_6D_6): δ 31.39 (d, 30.5 Hz), 10.64 (d, 30.5 Hz). IR (KBr, cm^{-1}): ν_{CN} 2219.0. Anal. Calcd for $C_{51}H_{45}FeNO_2P_2Pd$: C, 66.00; H, 4.89. Found: C, 65.93; H, 4.97.

[Pd(DPPF)(C_6H_4-4-CN)(OC_6H_4-3,5-(*t*-C_4H_9)$_2$)] (5c). Into a vial was placed 233 mg (0.276 mmol) of (DPPF)Pd(C_6H_4-4-CN)(Br)[42] and 86.8 mg (0.356 mmol) of K(OC_6H_4-3,5-(*t*-C_4H_9)$_2$). To this was added 10 mL of THF. The solution was stirred at room temperature for 1.5 h, after which time the solvent was removed under vacuum. The resulting solids were dissolved in 100 mL of toluene and filtered through Celite. The toluene was removed under vacuum, and the remaining solids were dissolved in THF and crystallized by layering the THF solution with Et_2O at −35 °C. The product was obtained as yellow flakes in 181.9 mg (68%). ^{1}H NMR (C_6D_6): δ 1.35 (s, 18H), 3.70 (d, 1.1 Hz, 2H), 3.78 (d, 1.7 Hz, 2H), 3.94 (br s, 2H), 4.52 (d, 1.4 Hz, 2H), 6.55 (dd, 7.8 Hz, 1.7 Hz, 2H), 6.63−6.64 (m, 3H), 6.78 (t, 7 Hz, 4H), 6.85−6.90 (m, 2H), 6.99−7.15 (m, 5H), 8.17−8.23 (m, 4H). ^{31}P{^{1}H} NMR (C_6D_6): δ 31.12 (d, 30.2 Hz), 11.01 (d, 30.2 Hz). IR (THF, cm^{-1}): ν_{CN} 2219.5. Anal. Calcd for $C_{55}H_{53}FeNOP_2Pd\cdot 0.5C_7H_8$: C, 69.27; H, 5.66. Found: C, 69.51; H, 5.85.

{**Pd[(C_6H_4-4-CF_3)$_2$P((C_5H_4)$_2$Fe)P(C_6H_4-4-CF_3)$_2$](C_6H_4-4-CN)(OC_6H_4-4-OMe)**} **(6a).** A vial was charged with 0.1658 g (0.1398 mmol) of {Pd[P(*o*-tolyl)$_3$](C_6H_4-4-CN)(Br)}$_2$,[42] 0.2483 g (0.3006 mmol) of CF_3-DPPF,[98] and 10 mL of THF. This mixture was stirred at room temperature for 1 h, after which time the solvent was removed under vacuum. Unreacted CF_3-DPPF was removed by suspending the resulting yellow solid in 20 mL of pentane and filtering the solution through a medium-fritted funnel. The yellow precipitate collected was then dissolved in 2 mL of toluene. Pentane (20 mL) was added to the toluene solution to precipitate the product (CF_3-DPPF)Pd(C_6H_4-4-CN)(Br). The yellow powder (0.1956 g, 63%) was washed three times with pentane and used without further purification. ^{31}P{^{1}H} NMR (C_7D_8): δ 29.1 (d, 34 Hz), 10.2 (d, 33 Hz).

A vial was charged with 46.0 mg (0.0413 mmol) of (CF_3-DPPF)Pd(C_6H_4-4-CN)(Br) and 80.0 mg (0.049 mmol) of K(OC_6H_4-4-OMe) in 3 mL of THF. The solution was stirred at room temperature for 10 min, after which time the solvent was removed under vacuum. The resulting solids were dissolved in Et_2O and filtered through Celite. The product was isolated in 66% yield (31.4 mg) after crystallization by layering the Et_2O solution with pentane at −35 °C. ^{1}H NMR (C_6D_6): δ 3.93 (s, 3H), 3.57−3.58 (m, 2H), 3.68−3.58 (m, 2H), 3.98 (br s, 2H), 4.28−4.30 (m, 2H), 6.44−6.52 (m, 4H), 6.60 (d, 8.8 Hz, 2H), 6.93−7.10 (m, 10H), 7.36 (d, 8.1 Hz, 4H), 8.04 (virtual t, 9 Hz, 4H). ^{31}P{^{1}H} NMR (C_7D_8): δ 31.14 (d, 33 Hz), 9.85 (d, 33 Hz). ^{19}F{^{1}H} NMR (C_7D_8): δ −62.75 (s), −63.04 (s). IR (THF, cm^{-1}): ν_{CN} 2222.0. Anal. Calcd for $C_{52}H_{35}FeNO_2P_2Pd$: C, 53.93; H, 3.05. Found: C, 53.59; H, 3.11.

Pd[(C_6H_4-4-CF_3)$_2$P((C_5H_4)$_2$Fe)P(C_6H_4-4-CF_3)$_2$](C_6H_4-4-CN)(OC_6H_4-3,5-(*t*-C_4H_9)$_2$ (6b). Following a similar procedure for the synthesis of **5c**, reaction of 90.0 mg (0.0807 mmol) of (CF_3-DPPF)Pd(C_6H_4-4-CN)(Br) and 30.4 mg (0.125 mmol) of K(OC_6H_4-3,5-(*t*-C_4H_9)$_2$) provided the product in 53% yield (52.8 mg) after crystallization by layering a toluene solution with pentane and cooling to −35 °C. ^{1}H NMR (C_6D_6): δ 1.26 (s, 18H), 3.65−3.67 (m, 2H), 3.70−3.71 (m, 2H), 3.96 (br s, 2H), 4.29−4.31 (m, 2H), 6.45−6.49 (m, 2H), 6.62 (d, 1.2 Hz, 1H), 6.99−7.06 (m, 7H), 7.10−7.15 (m, 5H), 7.27 (d, 7.3 Hz, 4H), 8.02 (dd, 9.4 Hz, 8.1 Hz, 4H). ^{31}P{^{1}H} NMR (C_6D_6): δ 30.61 (d, 30.9 Hz), 10.43 (d, 30.9 Hz). ^{19}F{^{1}H} NMR (C_6D_6): δ −63.96 (s), −64.20 (s). IR (THF, cm^{-1}): ν_{CN} 2221.9. Anal. Calcd for $C_{59}H_{49}F_{12}FeNOP_2Pd$: C, 57.14; H, 3.98. Found: C, 57.37; H, 4.24.

(D-*t*-BPF)Pd(OC_6H_4-4-OMe)(C_6H_4-4-CN) (7a). (D-*t*-BPF)-Pd(C_6H_4-4-CN)(Br), **2** (0.200 g, 0.262 mmol), and NaOC_6H_4-4-OMe (0.048 g, 0.330 mmol) were dissolved in THF (5 mL) and stirred for 1 h. The solution was filtered through Celite and dried in vacuo. The orange solid was dissolved in toluene, concentrated, layered with pentane, and cooled to −35 °C. Orange crystals were obtained (0.0431 g, 20%). ^{1}H NMR (C_6D_6): δ 1.11 (d, 13.8 Hz, 18H, CMe_3), 1.60 (d, 12.2 Hz, 18H, CMe_3), 3.49 (s, 3H, OMe), 3.94 (br s, 4H, C_5H_4P), 4.18 (br s, 4H, C_5H_4P), 6.65 (d, 8.3 Hz, 2H, Ph), 6.80 (d, 8.8 Hz, 2H, Ph) 6.90 (d, 8.0 Hz, 2H, Ph), 7.63 (t, 7.3 Hz, 2H, *o*-C_6H_4CN). ^{31}P-{^{1}H} NMR (C_6D_6): δ 42.07 (d, 25.9 Hz, 1P), 55.36 (d, 25.9 Hz, 1P). Anal. Calcd for $C_{40}H_{55}FeNO_2P_2Pd\cdot 0.61C_7H_8$: C, 61.67; H, 7.00; N, 1.62. Found: C, 61.40; H, 6.84; N, 1.43.

(D-*t*-BPF)Pd(OC_6H_4-3,5-(*t*-C_4H_9)$_2$(C_6H_4-4-CN) (7b). A sample of **2** (0.100 g, 0.131 mmol) and KOC_6H_3-3,5-(*t*-Bu)$_2$ (0.040 g, 0.164 mmol) were dissolved in THF (15 mL) and stirred for 15 min. The solution was filtered through Celite and dried in vacuo. The yellow solid was dissolved in toluene, concentrated, layered with pentane, and cooled to −35 °C. Yellow feathers were obtained (0.084 g, 72%). ^{1}H NMR (C_6D_6): δ 1.15 (d, 14.0 Hz, 18H, P*t*-Bu), 1.47 (s, 18H, C_6H_3*t-Bu*), 1.59 (d, 12.2 Hz, 18H, P*t*-Bu), 3.95 (br s, 4H, C_5H_4P), 4.19 (br s, 4H, C_5H_4P), 6.60 (s, 2H, *o*-C_6H_3*t*-Bu$_2$), 6.82 (s, 1H, *p*-C_6H_3*t*-Bu$_2$), 6.88 (d, 8.4 Hz, 2H, *m*-C_6H_4CN), 7.60 (t, 7.2 Hz, 2H, *o*-C_6H_4CN). ^{31}P{^{1}H} NMR (C_6D_6): δ 42.06 (d, 22.2 Hz, 1P), 55.59 (d, 22.2 Hz, 1P). Anal. Calcd for $C_{47}H_{69}FeNOP_2Pd$: C, 63.55; H, 7.83; N, 1.58. Found: C, 63.80; H, 7.72; N, 1.38.

Pd(DPPF)(C_6H_5)(OC_6H_4-4-OMe) (8a). Into a vial was added 74.7 mg (0.0808 mmol) of {Pd(Ph)(PPh_3)(μ-OH)}$_2$,[99] 21.8 mg (0.176 mmol) of *p*-methoxyphenol, and 3 mL of benzene. The solution was stirred at room temperature for 5 min, after which time 102 mg of DPPF (0.183 mmol) dissolved in 5 mL of benzene was added to the clear solution. This mixture was stirred for 10 min to give a yellow solution. This solution was filtered through Celite, and the solution volume was reduced to 1 mL under vacuum. The product was precipitated from this solution by addition of pentane. The product was recrystallized by layering an Et_2O solution with pentane at −35 °C (95.6 mg, 69%). ^{1}H NMR (C_6D_6): δ 3.39 (s, 3H), 3.71 (d, 1.5 Hz, 2H), 3.81 (d, 1.4 Hz, 2H), 3.96 (br s, 2H), 4.54 (d, 1.5 Hz, 2H), 6.62−6.70 (m, 5H), 6.80 (virtual t, 8 Hz, 5H), 6.86−6.90 (m, 3H), 6.91−7.15 (m, 5H), 7.35−7.48 (m, 7H), 8.33 (td, 8 Hz, 1.2 Hz, 4H). ^{31}P{^{1}H} NMR (THF): δ 31.53 (d, 30.5 Hz), 10.31 (d, 30.5 Hz).

Pd(DPPF)(C_6H_5)[OC_6H_4-3,5-(*tert*-butyl)] (8b). Into a vial was added 200 mg (0.218 mmol) of {Pd(Ph)(PPh_3)(μ-OH)}$_2$,[99] 111 mg (0.538 mmol) of 3,5-di-*tert*-butylphenol, and 5 mL of toluene. The solution was stirred at room temperature for 5 min, after which time 250 mg (0.450 mmol) of DPPF dissolved in 10 mL of toluene was added to the clear solution. This mixture was stirred for 10 min to give a yellow solution. This

(97) This ortho-methyl isomer was synthesized by a procedure similar to the synthesis of the para-methyl isomer, whose preparation is found in: Paul, F.; Patt, J.; Hartwig, J. F. *Organometallics* **1995**, *14*, 3030−3039.

(98) Unruh, J. D.; Christenson, J. R. *J. Mol. Catal.* **1995**, *177*, 5373−5374.

(99) Grushin, V. V.; Alper, H. *Organometallics* **1993**, *12*, 1890−1901.

solution was filtered through Celite, and the solution volume was reduced to 1 mL under vacuum. The product was precipitated from this solution by addition of pentane. The solid was filtered, washed with pentane, and dried under vacuum to give 272 mg (66%) of product. ^{1}H NMR (C_6D_6): δ 1.39 (s, 18H), 3.72 (m, 2H), 3.83 (m, 2H), 3.97 (br s, 2H), 4.60 (m, 2H), 6.60−6.62 (m, 4H), 6.77 (d, 1.6 Hz, 2H), 6.83−6.90 (m, 6H), 7.08−7.16 (m, 6H), 7.46−7.53 (m, 6H), 8.29 (td, 8 Hz, 1.2 Hz, 4H). ^{31}P{^{1}H} NMR (C_6D_6): δ 31.1 (d, 30.9 Hz), 9.56 (d, 31.4 Hz). Anal. Calcd for $C_{54}H_{54}FeOP_2Pd$: C, 68.75; H, 5.78. Found: C, 68.51; H, 5.86.

Pd[(C$_6$H$_4$-4-CF$_3$)$_2$P((C$_5$H$_4$)$_2$Fe)P(C$_6$H$_4$-4-CF$_3$)$_2$](C$_6$H$_5$)(OC$_6$H$_4$-4-OMe) (9). Following a similar procedure for the synthesis of **8**, reaction of 101 mg (0.109 mmol) of {Pd(Ph)(PPh$_3$)(μ-OH)}$_2$ and 28.8 mg (0.232 mmol) of *p*-methoxyphenol provided the product in 23% yield (55.2 mg) after crystallization from a solution of toluene layered with pentane at −35 °C. ^{1}H NMR (C_6D_6): δ 3.39 (s, 3H), 3.62−3.63 (m, 2H), 3.69 (d, 1.7 Hz, 2H), 3.99 (br s, 2H), 4.32−4.34 (m, 2H), 6.55−6.59 (m, 5H), 6.62−6.65 (m, 3H), 6.93−7.37 (m, 8H), 7.41 (d, 3.1 Hz, 4H), 7.66−7.68 (m, 1H), 8.13 (virtual t, 9 Hz, 4H). ^{31}P{^{1}H} NMR (C_6D_6): δ 31.13 (d, 30.5 Hz), 8.59 (d, 30.5 Hz).

Pd[(*t*-C$_4$H$_9$)$_2$P((C$_5$H$_4$)$_2$Fe))P(*t*-C$_4$H$_9$)$_2$](C$_6$H$_5$)(OC$_6$H$_4$-4-OMe) (10). To a solution of 104 mg (0.0921 mmol) of {Pd[P(*o*-tolyl)$_3$](C$_6$H$_5$)(Br)}$_2$[34] in 2 mL of THF was added 89.6 mg (0.189 mmol) of D-*t*-BPF[100] in 2 mL of THF. The reaction was stirred for 30 min, over which time a clear yellow solution resulted. The solvent was removed under vacuum, and the resulting yellow solid was redissolved in ca. 1 mL of benzene. (D-*t*-BPF)Pd(Ph)(Br) was then precipitated from this solution by addition of ca. 20 mL of pentane. This yellow solid was isolated by filtration through a medium fritted funnel and was washed twice with pentane to give 101 mg (75%) of a compound presumed to be Pd[(*t*-C$_4$H$_9$)$_2$P((C$_5$H$_4$)$_2$Fe))P(*t*-C$_4$H$_9$)$_2$](C$_6$H$_5$)(Br). ^{31}P{^{1}H} NMR: δ 45.11 (d, 25.7 Hz), 36.39 (d, 25.7 Hz). To a solution of 101.3 mg of Pd[(*t*-C$_4$H$_9$)$_2$P((C$_5$H$_4$)$_2$Fe))P(*t*-C$_4$H$_9$)$_2$](C$_6$H$_5$)(Br) in 2 mL of THF was added 35.3 mg (0.218 mmol) of KOC$_6$H$_4$-4-OMe. This mixture was stirred for 1 h. The ^{31}P NMR spectrum indicated complete conversion of the material to {Pd[P(C$_5$H$_4$FeC$_5$H$_5$)(*t*-Bu)$_2$](*p*-MeC$_6$H$_4$)(Br)}$_2$. The solvent was then removed under vacuum, and the resulting orange solid was dissolved in 250 mL of pentane. The pentane solution was filtered through Celite, and the solvent was removed under vacuum. Orange crystals (32.4 mg, 30%) were isolated from a solution of toluene layered with pentane cooled at −35 °C. ^{1}H NMR (C_6D_6): δ 1.25 (d, 13.3 Hz, 18H), 1.67 (d, 12.0 Hz, 18H), 3.49 (s, 3H), 3.96 (s, 4H), 4.24 (d, 5.4 Hz, 4H), 6.82−6.96 (m, 7H), 7.75 (virtual t, 7.3 Hz, 2H). ^{31}P{^{1}H} NMR (C_6D_6): δ 40.74 (d, 24.4 Hz), 53.07 (d, 24.4 Hz). Anal. Calcd for $C_{39}H_{56}FeO_2P_2Pd_2$: C, 59.97; H, 7.23. Found: C, 60.00; H, 7.61.

{Pd[P(C$_5$H$_4$FeC$_5$H$_5$)(*t*-Bu)$_2$](C$_6$H$_4$-2-Me)(OC$_6$H$_4$-4-OMe)}$_2$ (11a). To a solution of {Pd[P(*o*-tolyl)$_3$](*o*-MeC$_6$H$_4$)(Br)}$_2$[97] (100 mg, 0.171 mmol) in 10 mL of toluene was added 170 mg (0.513 mmol) of P(C$_5$H$_4$FeC$_5$H$_5$)(*t*-Bu)$_2$. The solution was stirred for 30 min, over which time the starting palladium complex dissolved, and ^{31}P NMR spectrometry showed conversion of roughly 80% of the material to {Pd[P(C$_5$H$_4$FeC$_5$H$_5$)(*t*-Bu)$_2$](*o*-MeC$_6$H$_4$)(Br)}$_2$, **3a**. At this time, 50 mg (0.342 mmol) of NaOC$_6$H$_4$-*p*-OMe was added, and the resulting suspension was stirred for 30 min. ^{31}P NMR spectrometry showed complete conversion to {Pd[P(C$_5$H$_4$FeC$_5$H$_5$)(*t*-Bu)$_2$](*o*-MeC$_6$H$_4$)(O-*p*-C$_6$H$_4$OMe)}$_2$. The solids were removed by filtration through Celite. The filtrate was concentrated to 0.5 mL, layered with pentane, and cooled at −35 °C overnight. Orange-brown material (86 mg) was obtained and was isolated by removing the solvent with a pipet and washing with pentane. This material was redissolved in toluene, and the toluene solution was layered with pentane and cooled to −35 °C. This recrystallization provided 45 mg (40% yield) of orange disks that contained 0.5 equiv of toluene per dimer by ^{1}H NMR spectrometry and were analytically pure. ^{1}H NMR (C_7D_8, −50 °C): δ 1.05 (br d, 13.7 Hz, 18H), 1.99 (d, 14.2 Hz, 18H), 2.61 (s, 6H), 3.43 (s, 6H), 3.56 (br s, 2H), 3.61 (br s, 2H), 3.69 (br s, 2H), 3.74 (br s, 2H), 3.82 (s, 10H), 4.93 (br d, 7 Hz, 2H), 6.55 (br d, 7 Hz, 2H), 6.7−7.0 (m 8H), 7.60 (br d, 7 Hz, 2H), 7.94 (br d, 7 Hz, 2H). ^{31}P{^{1}H} NMR (C_7D_8): δ 54.1 (s). Anal. Calcd for $C_{64}H_{82}Fe_2O_4P_2Pd_2\cdot 0.5\ C_7H_8$: C, 60.15; H, 6.43. Found: C, 60.27; H, 6.77.

{Pd[P(C$_5$H$_4$FeC$_5$H$_5$)(*t*-Bu)$_2$](C$_6$H$_4$-4-Me)(OC$_6$H$_4$-4-OMe)}$_2$ (11b). To a solution of {Pd[P(*o*-tolyl)$_3$](C$_6$H$_4$-4-Me)(Br)}$_2$[68] (80.0 mg, 0.137 mmol) in 2−3 mL of toluene was added 136 mg (0.413 mmol) of P(C$_5$H$_4$FeC$_5$H$_5$)(*t*-Bu)$_2$. The solution was stirred for 10 min, over which time the starting palladium complex dissolved, and ^{31}P NMR spectrometry showed conversion of roughly 80% of the material to {Pd[P(C$_5$H$_4$FeC$_5$H$_5$)(*t*-Bu)$_2$](C$_6$H$_4$-4-Me)(Br)}$_2$, **3b**. At this time, 40 mg (0.274 mmol) of NaOC$_6$H$_4$-4-OMe was added, and the resulting suspension was stirred for 30 min. ^{31}P NMR spectrometry showed complete conversion to {Pd[P(C$_5$H$_4$FeC$_5$H$_5$)(*t*-Bu)$_2$](C$_6$H$_4$-4-Me)(OC$_6$H$_4$-4-OMe)}$_2$. The solids were removed by filtration through Celite. The filtrate was concentrated to 0.5 mL, layered with pentane, and cooled at −35 °C overnight. Orange-red crystals (34 mg, 38% yield) suitable for X-ray diffraction were obtained and were isolated by removing the solvent using a pipet and washing with pentane. ^{1}H NMR (C_7D_8, 25 °C): δ 1.47 (br d, 12.5 Hz, 36H), 2.28 (s, 6H), 3.44 (s, 6H), 3.70 (s, 10H), 3.98 (br s, 4H), 4.10 (br s, 4H), 6.40 (br d, 8.5 Hz, 4H), 6.62 (d, 8.6 Hz, 4H), 6.85 (d, 6.6 Hz, 4H), 7.48 (br d, 7 Hz, 4H). ^{31}P{^{1}H} NMR (C_7D_8): δ 54.2 (s).

{Pd[P(C$_5$H$_4$FeC$_5$H$_5$)(*t*-Bu)$_2$](C$_6$H$_3$-2,4-(CH$_3$)$_2$)(OC$_6$H$_4$-4-O-*n*-Bu)}$_2$ (11c). Into a vial was added 103 mg (0.0864 mmol) of {Pd[P(*o*-tolyl)$_3$](C$_6$H$_4$-2,4-Me$_2$)(Br)}$_2$ and 97.7 mg (0.296 mmol) of FcP(*t*-Bu)$_2$ in 5 mL of THF. This solution was stirred for 45 min, after which time the solvent was removed under vacuum. The remaining solids were dissolved in pentane, filtered through a medium fritted funnel, and washed with Et$_2$O. This isolated yellow solid {Pd[P(C$_5$H$_4$FeC$_5$H$_5$)(*t*-Bu)$_2$](C$_6$H$_3$-2,4-(CH$_3$)$_2$)(Br)}$_2$, **3c**, was dissolved in 5 mL of THF, and 81.2 mg (0.432 mmol) of NaO−C$_6$H$_4$-*n*-Bu was added to the solution. This mixture was stirred at room temperature for 10 min, and the solvent was removed under vacuum. The resulting brown solid was dissolved in pentane, and the solution was filtered through Celite and concentrated. The product was isolated by crystallization from pentane solution at −35 °C to give 29% yield (35.2 mg) of product. ^{1}H NMR (C_6D_6, 25 °C): δ 0.81 (t, 7.3 Hz, 6H), 1.13 (d, 14.0 Hz, 18H), 1.33−1.37 (m, 4H), 1.49−1.55 (m, 4H), 1.98 (d, 13.7 Hz, 18H), 2.32 (s, 6H), 2.56 (s, 6H), 3.73−3.81 (m, 12H), 3.83 (s, 10H), 6.77−6.84 (m, 12H), 7.55 (br d, 6.6 Hz, 2H). ^{31}P{^{1}H} NMR (C_6D_6): δ 53.71 (s).

[FcP(*i*-Pr)$_2$]$_2$Pd(C$_6$H$_4$-2-Me)(OC$_6$H$_4$-4-OMe) (12). Compound **4** (0.050 g, 0.055 mmol) and CsOH·H$_2$O (0.033 g, 0.200 mmol) were dissolved in THF (5 mL) and stirred 18 h. HOC$_6$H$_4$-4-OMe in 1 mL of THF was added to the reaction mixture and stirred for 3 h. Solvent was removed in vacuo. Product was extracted with toluene (2 × 2 mL), and the solution was filtered through Celite. The solution was concentrated, layered with pentane, and cooled to −35 °C to yield 0.022 g (43%) of product. ^{1}H NMR (C_6D_6): δ 1.28 (q, 7.2 Hz, 6H, CH*Me*$_2$), 1.35 (q, 7.2 Hz, 6H, CH*Me*$_2$), 1.35 (q, 7.3 Hz, 6H, CH*Me*$_2$), 1.49 (q, 7.7 Hz, 6H, CH*Me*$_2$), 2.39 (m, 2H, C*H*Me$_2$), 2.42 (s, 3H, C$_6$H$_4$*Me*), 2.56 (m, 2H, C*H*Me$_2$), 3.58 (s, 3H, OMe), 3.61 (br s, 2H, C$_5$H$_4$P), 3.89 (br s, 12H, C$_5$H$_5$ and C$_5$H$_4$P), 3.956 (br s, 2H, C$_5$H$_4$P), 4.05 (br s, 2H, C$_5$H$_4$P), 6.75 (d, 7.2 Hz, 1H, C$_6$*H*$_4$Me), 6.80 (t, 6.7 Hz, 1H, C$_6$*H*$_4$Me), 6.88 (t, 6.9 Hz, 1H, C$_6$*H*$_4$Me), 6.96 (d, 8.7 Hz, 2H, C$_6$*H*$_4$OMe), 7.03 (d, 8.9 Hz, 2H, C$_6$*H*$_4$OMe), 7.45 (d, 7.2 Hz, 1H, C$_6$*H*$_4$Me). ^{13}C{^{1}H} NMR (C_6D_6): δ 19.24 (s, CH*Me*$_2$), 19.70 (s, CH*Me*$_2$), 20.16 (s, CH*Me*$_2$),

(100) Hamann, B. C.; Hartwig, J. F. *J. Am. Chem. Soc.* **1998**, *120*, 7369−7370.

21.07 (s, CH*Me*$_2$), 25.00 (t, 10.8 Hz, *C*HMe$_2$), 27.78 (t, 10.4 Hz, *C*HMe$_2$), 27.83 (s, C$_6$H$_4$*Me*), 55.90 (s, OMe), 69.06 (t, 3.1 Hz, C$_5$H$_4$P), 69.48 (t, 4.0 Hz, C$_5$H$_4$P), 69.59 (s, C$_5$H$_5$), 72.91 (t, 4.5 Hz, C$_5$H$_4$P), 73.31 (t, 5.4 Hz, C$_5$H$_4$P), 75.46 (t, 15.0 Hz, *i*-C$_5$H$_4$P), 115.17 (s, *C*$_6$H$_4$OMe), 120.39 (s, *C*$_6$H$_4$OMe), 122.52 (s, *C*$_6$H$_4$Me), 123.05 (s, *C*$_6$H$_4$Me), 128.72 (s, *C*$_6$H$_4$Me), 138.86 (s, *C*$_6$H$_4$Me), 143.83 (s, *C*$_6$H$_4$Me), 148.61 (s, *C*$_6$H$_4$OMe), 164.82 (s, *C*$_6$H$_4$OMe)). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 20.62 (s).

Ni[(C$_6$H$_4$-4-CF$_3$)$_2$P((C$_5$H$_4$)$_2$Fe)P(C$_6$H$_4$-4-CF$_3$)$_2$](CO)$_2$ (13). Ni(CO)$_2$(PPh$_3$)$_2$ (0.064 g, 0.100 mmol) and (C$_6$H$_4$-4-CF$_3$)$_2$P-((C$_5$H$_4$)$_2$Fe)P(C$_6$H$_4$-4-CF$_3$)$_2$ (0.083 g, 0.100 mmol) were dissolved in THF (9 mL). After 48 h the reaction mixture was concentrated, pentane (4 mL) was added, and a precipitate formed. The yellow solids were washed with ether and dried under vacuum to give 45.3 mg of product in 48% yield. ^{1}H NMR (THF-d_8): δ 4.18 (virtual quartet, 1.74 Hz, 4H, α-C$_5$H$_4$P), 4.45 (virtual triplet, 1.62 Hz, 4H, β-C$_5$H$_4$P), 7.76 (m, 16H, C$_6$H$_4$CF$_3$). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 26.85 (s). IR (KBr, cm^{-1}): 2010 (s), 1950 (s). Anal. Calcd for C$_{40}$H$_{24}$F$_{12}$FeNiO$_2$P$_2$: C, 51.05; H, 2.57. Found: C, 50.75; H, 2.76.

(CO)$_3$Ni[(*t*-Bu)$_2$P((C$_5$H$_4$)$_2$Fe)P(*t*-Bu)$_2$]Ni(CO)$_3$. *Caution: Ni(CO)$_4$ is highly toxic. This material was used in a well-ventilated hood by vacuum transfer and syringe techniques.* Ni(CO)$_4$ (20 μL, 0.15 mmol) was added by syringe to a screw-capped NMR tube containing a Teflon-lined septum and 0.7 mL of a C$_6$D$_6$ solution of D^{t}BPF (18 mg, 0.038 mmol). ^{31}P NMR spectrometry showed immediate conversion to product. The solvent was then removed under vacuum from the sample tube. The tube containing the resulting orange crystalline residue was brought into the drybox, and the solid was crystallized from pentane at −35 °C to give 15 mg (52%) of light orange crystals. ^{1}H NMR (C$_6$D$_6$): δ 4.48 (s, 4H), 4.30 (s, 4H), 1.08 (d, 13.2 Hz, 36 H). ^{31}P NMR δ 65.5 (s); IR (KBr, cm^{-1}) ν_{CO} 2055 (sharp), 1971 (br). Anal. Calcd for C$_{32}$H$_{44}$FeNi$_2$O$_6$P$_2$: C, 50.58; H, 5.84. Found: C, 50.44; H, 5.73.

(CO)$_3$Ni[(*t*-Bu)$_2$P(C$_5$H$_4$)FeCp]. *Caution: Ni(CO)$_4$ is highly toxic. This material was used in a well-ventilated hood by vacuum transfer and syringe techniques.* Ni(CO)$_4$ (20 μL, 0.15 mmol) was added by syringe to a screw-capped NMR tube containing a Teflon-lined septum and 0.7 mL of a C$_6$D$_6$ solution of FcP(*t*-Bu)$_2$ (18 mg, 0.038 mmol). ^{31}P NMR spectrometry showed immediate conversion to product. The solvent was then removed under vacuum from the sample tube. The tube containing the resulting orange crystalline residue was brought into the drybox, and the solid was crystallized from pentane at −35 °C to give 12 mg (47%) of light orange crystals. ^{1}H NMR (C$_6$D$_6$): δ 4.19 (virtual q, 1.5 Hz, 2H), 4.07 (s, 5H), 4.02 (m, 2H), 1.10 (d, 13.2 Hz, 36 H). ^{31}P NMR: δ 65.8 (s). IR (KBr, cm^{-1}): ν_{CO} 2055 (sharp), 1966 (br). Anal. Calcd for C$_{32}$H$_{44}$-FeNi$_2$O$_6$P$_2$: C, 53.33; H, 5.75. Found: C, 53.50; H, 5.91.

(FcP-*i*-Pr$_2$)$_2$Pd. (Cp)Pd(allyl) (0.100 g, 0.470 mmol) and FcP(*i*-Pr)$_2$ (0.426 g, 1.41 mmol) were dissolved in 15 mL of benzene. After 3 h, the solvent was evaporated under vacuum and the orange solids were redissolved in pentane (10 mL). The solution was filtered through Celite, concentrated, and cooled to −35 °C to give 108.5 mg of product in 33% yield. ^{1}H NMR (C$_6$D$_6$): δ 1.29 (q, 6.9 Hz, 12H, CH*Me*$_2$), 1.39 (q, 7.5 Hz, 12H, CH*Me*$_2$), 1.98 (sept of d, 7.0 Hz and 1.8 Hz, 4H, C*H*Me$_2$), 4.12 (br s, 4H, C$_5$H$_4$P), 4.35 (br s, 4H, C$_5$H$_4$P), 4.44 (s, 10H, C$_5$H$_5$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 20.33 (t, 3.2 Hz, CH*Me*$_2$), 21.11 (t, 5.4 Hz, CH*Me*$_2$), 26.02 (t, 9.1 Hz, *C*HMe$_2$), 69.58 (t, 2.2 Hz, β-C$_5$H$_4$P), 70.56 (s, C$_5$H$_5$), 72.11 (t, 5.3 Hz, α-C$_5$H$_4$P), 77.13 (t, 11.6 Hz, *i*-C$_5$H$_4$P). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 32.77(s). Anal. Calcd for C$_{32}$H$_{46}$Fe$_2$P$_2$Pd: C, 54.07; H, 6.52. Found: C, 53.85; H, 6.40.

{Pd[P(C$_5$H$_4$FeC$_5$H$_5$)(*t*-Bu)$_2$]}$_2$. To a solution of 392.1 mg (0.5480 mmol) of Pd[P(*o*-tolyl)$_3$]$_2$[68] in 5 mL of THF was added 365.9 mg (1.108 mmol) of P(C$_5$H$_4$FeC$_5$H$_5$)(*t*-Bu)$_2$. The solution was heated in a sealed vial under N$_2$ at 65 °C for 1 h. The solvent was then removed under vacuum in the drybox. The resulting orange solid was redissolved in pentane, filtered through Celite, and concentrated under vacuum. Orange crystals (163.2 mg, 77% yield) suitable for X-ray diffraction were obtained at −35 °C. ^{1}H NMR (C$_6$D$_6$): δ 1.52 (t, 6.3 Hz, 36H), 4.14 (br d, 1.3 Hz, 4H), 4.37 (s, 10H), 4.53 (br s, 4H). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 31.78 (t, 5.4 Hz), 35.66 (t, 4.2 Hz), 69.22, 70.56, 73.89 (t, 5.9 Hz), 79.51 (t, 6.4 Hz). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 56.35 (s). Anal. Calcd for C$_{36}$H$_{54}$Fe$_2$P$_2$Pd: C, 56.38; H, 7.10. Found: C, 56.46; H, 7.22.

{Pd[P(C$_5$H$_4$FeC$_5$Ph$_5$)(*t*-Bu)$_2$]}$_2$. To a solution of 104.6 mg (0.4968 mmol) of [Pd(Cp)(allyl)] in 5 mL of toluene was added a solution of 741.5 mg (1.043 mmol) of **1b** in 2 mL of toluene. The solution was stirred at room temperature overnight, and the formation of a pink solid was observed. The solvent was evaporated under reduced pressure, and pentane was added to fully precipitate the product. The pink solid was separated from the red solution by filtration, washed with pentane and ether, and then dried under vacuum to obtain 60% yield of the highly insoluble product. ^{1}H NMR (C$_6$D$_6$): δ 1.16 (t, 6.0 Hz, 36H), 4.42 (br s, 4H), 5.06 (br s, 4H), 6.97−7.30 (m, 50H). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 61.1. Anal. Calcd for C$_{96}$H$_{94}$Fe$_2$P$_2$Pd: C, 75.46; H, 6.21. Found: C, 75.20; H, 6.10.

{Pd[P(C$_5$H$_4$FeC$_5$H$_5$)(*t*-Bu)$_2$][P(C$_5$H$_4$FeC$_5$Ph$_5$)(*t*-Bu)$_2$]. To a solution of 214.4 mg (0.2796 mmol) of {Pd[P(C$_5$H$_4$FeC$_5$H$_5$)-(*t*-Bu)$_2$]}$_2$ in 20 mL of THF was added 426.8 mg of {Pd[P(C$_5$H$_4$-FeC$_5$Ph$_5$)(*t*-Bu)$_2$]}$_2$. The suspension was stirred under N$_2$ at 70 °C for 2 h. The resulting red solution was determined to be a mixture of three compounds, the two starting materials and the mixed ligand Pd(0) complex in equilibrium ratios. No further reaction was observed after heating the solution overnight. The solvent was then evaporated, and ether was added to precipitate and remove {Pd[P(C$_5$H$_4$FeC$_5$Ph$_5$)(*t*-Bu)$_2$]}$_2$. Again, the solvent was evaporated from the ether solution, and pentane was added to precipitate the desired product as a pink/red solid. Red crystals were obtained in 4% yield from toluene/pentane upon standing two weeks at −35 °C. ^{1}H NMR (C$_6$D$_6$): δ 1.40 (d, 12.4 Hz, 18H), 1.44 (d, 12.4 Hz, 18H), 4.15 (t, 1.6 Hz, 2H), 4.29 (s, 5H), 4.34 (br t, 1.6 Hz, 2H), 4.53 (m, 2H), 5.13 (br s, 2H), 7.01−7.02 (m, 15H), 7.43−7.45 (m, 10H). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 55.93 (d, 615.9 Hz), 61.97 (d, 615.9 Hz).

Kinetic Analysis of the Reductive Elimination of 5c and 6b. Into two separate vials were placed 6.2 mg (0.0050 mmol) of **5c**, and into two other vials was placed 5.1 mg (0.0053 mmol) of **6b**. Into each vial was added 3.5 mg (0.020 mmol) of diphenylacetylene, 0.7 mg (0.004 mmol) of phenanthrene as internal standard, and 0.6 mL of toluene-d_8. Into one vial containing **5c** and one vial containing **6b** was added 5.5 mg (0.024 mmol) of NaO-3,5-C$_6$H$_3$(^{t}Bu)$_2$. The solutions were transferred to NMR tubes, frozen under N$_2$(l), and flame-sealed. The entire tubes were simultaneously submerged in an oil bath maintained at a constant 105 °C. Prior to obtaining periodic ^{1}H NMR spectra for kinetic analysis, the tubes were removed from the bath and submerged in ice for at least 5 min.

Phosphine Dependence on the Reductive Elimination from 5c. Into four separate vials were weighed **5c** (5.0 mg, 0.0052 mmol) and the appropriate amount of DPPF (5.3 mg, 0.0096 mmol; 12 mg, 0.022 mmol; 19 mg, 0.033 mmol; or 22 mg, 0.040 mmol). Phenanthrene (0.8 mg, 0.005 mmol) was added as internal standard. Into each vial was syringed 0.6 mL of toluene-d_8. The solutions were transferred to NMR tubes, frozen in N$_2$(l), and flame-sealed. The samples were heated at 105 °C and were monitored periodically by ^{1}H NMR.

Reductive Elimination from 3, 5a, 5b, 6a, 7b, and 11a. For reactions of compound **3**, 3−5 mg of **3**, ca. 1.5 mg of sodium aryloxide, and ca. 2 mg of 1,3,5-trimethoxybenzene as internal standard were placed into a vial. For experiments with **5a**, **5b**, **6a**, and **7b**, ca. 3 mg of the complex and ca. 1 mg of 1,3,5-trimethoxybenzene as internal standard were placed into vials. For experiments with **11a**, a vial was charged with 3.3 mg of **11a** and ca. 1.7 mg of 1,3,5-trimethoxybenzene as internal

standard. A ^{1}H NMR spectrum was obtained of each mixture in toluene-d_8. Into a separate vial was placed the appropriate amount of either PPh_3-d_{15}, PhCCPh, DPPF, D-*t*-BPF, CF_3-DPPF, FcP(*t*-Bu)$_3$, or P(*t*-Bu)$_3$. The NMR sample was poured into the vial of ligand and was returned to the NMR sample tube. The mixture was heated at the appropriate temperature until complete reaction had occurred, as judged by ^{1}H and ^{31}P NMR spectroscopy. Integration of the final ^{1}H NMR spectrum and integration of the product and internal standard signals in the final gas chromatogram (corrected for response factors) provided the yields of Pd(0) complex and the yields of diaryl ether.

Reductive Elimination of Diaryl Ether from 11a: Representative Procedure. A vial was charged with 6.0 mg (0.0046 mmol) of complex **11a**. 1,3,5-Trimethoxybenzene (1.8 mg, 0.011 mmol) was added as internal standard, and the solids were dissolved in 0.6 mL of C_6D_6. A ^{1}H NMR spectrum was obtained. Into a separate vial was weighed either ligand **1a**, pentaphenyl ligand **1b**, or binaphthyl ligand **1c**. The NMR sample was poured into the vial of ligand, and the mixture was returned to the NMR tube. The resulting solution was heated at 60 °C until complete reaction had occurred, as determined by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. Integration of the final ^{1}H NMR spectrum and comparison with the initial spectrum provided the yield of diaryl ether.

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Supporting Information Available: Procedures and full tables of crystallographic data for **2a**, **2c**, **7a**, and **11b**.

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