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Trans Influence on the Rate of Reductive Elimination. Reductive Elimination of Amines from Isomeric Arylpalladium Amides with Unsymmetrical Coordination Spheres

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Abstract: To determine the trans effect on the rates of reductive eliminations from arylpalladium(II) amido complexes, the reactions of arylpalladium amido complexes bearing symmetrical and unsymmetrical DPPF (DPPF = bis(diphenylphosphino)ferrocene) derivatives were studied. THF solutions of LPd(Ar)(NMeAr′) (L = DPPF, DPPF−OMe, DPPF−CF_3, DPPF−OMe,Ph, DPPF−Ph,CF_3, and DPPF−OMe,CF_3; Ar = C_6H_4-4-CF_3; Ar′ = C_6H_4-4-CH_3, Ph, and C_6H_4-4-OMe) underwent C−N bond forming reductive elimination at −15 °C to form the corresponding *N*-methyldiarylamine in high yield. Complexes ligated by symmetrical DPPF derivatives with electron-withdrawing substituents on the DPPF aryl groups underwent reductive elimination faster than complexes ligated by symmetrical DPPF derivatives with electron-donating substituents on the ligand aryl groups. Studies of arylpalladium amido complexes containing unsymmetrical DPPF ligands revealed several trends. First, the complex with the weaker donor trans to nitrogen and the stronger donor trans to the palladium-bound aryl group underwent reductive elimination faster than the regioisomeric complex with the stronger donor trans to nitrogen and the weaker donor trans to the palladium-bound aryl group. Second, the effect of varying the substituents on the phosphorus donor trans to the nitrogen was larger than the effect of varying the substituents on the phosphorus donor trans to the palladium-bound aryl group. Third, the difference in rate between the isomeric arylpalladium amido complexes was similar in magnitude to the differences in rates resulting from conventional variation of substituents on the symmetric phosphine ligands. This result suggests that the geometry of the complex is equal in importance to the donating ability of the dative ligands. The ratio of the differences in rates of reaction of the isomeric complexes was similar to the relative populations of the two geometric isomers. This result and consideration of transition state geometries suggest that the reaction rates are controlled more by substituent effects on ground state stability than on transition state energies. In addition, variation of the aryl group at the amido nitrogen showed systematically that complexes with more electron-donating groups at nitrogen undergo faster reductive elimination than those with less electron-donating groups at nitrogen.

Introduction

The trans effect[1−5]—the effect of one ligand on the rate of substitution of the ligand trans to it—is a classic phenomenon in coordination chemistry. The origin of this effect is complex, but phosphines that are stronger σ-donors tend to impart a stronger trans effect than those that are weaker donors.[1−5] Ligands located trans to the point of reaction are also known to influence the rates and regiochemistry of classic organometallic reactions. For example, attack of a nucleophile at the terminus of an allyl ligand located trans to a π-acceptor or weak σ-donor is known to be faster than attack at the terminus trans to the weaker π-acceptor or stronger σ-donor.[6,7] The electronic properties of two dative ligands within a chelating phosphine have also been shown to affect the linear-to-branched ratio in hydroformylation[8,9] and to affect the rate of olefin insertion and C−C bond-forming reductive elimination during asymmetric hydrocyanations.[10,11]

The influence of one ligand on the ground-state bonding properties of the ligand located trans to it has also been studied extensively.[2,3,12−15] A trans ligand has been shown to influence

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bond lengths and metal−ligand coupling constants. This phenomenon has been named the "trans influence."[12,15]

Electronic effects of the dative ligand have been typically interpreted in terms of the overall electron density at the metal center.[2,16,17] The isomeric complexes would possess the same donor set at the metal but would differ by the orientation of the donors relative to the two groups undergoing reductive elimination. Considering the large effects of a trans ligand on reaction rates, regioselectivity, and ground state properties, one might expect that the relative orientation of strong and weak dative ligands located trans to two electronically distinct covalent ligands might affect the rate of reductive elimination. This effect could be observed in two types of complexes. It could be observed with complexes containing chelating ligands that are unsymmetrical or, in a more extreme case, with a T-shaped, three-coordinate complex containing a dative ligand trans to one of the covalent ligands and an empty coordination site trans to the other.

Many examples of reductive elimination occur between groups with distinct electronic properties. In some cases, one ligand is a hydride and one an alkyl, aryl, enolate or other carbon-bound ligand with varying degrees of electron-donating ability.[18−35] In reaction intermediates that are common in palladium-catalyzed cross-coupling, one ligand is often an electron-poor aryl group and one an electron-rich aryl or alkyl group.[36−39] Finally, complexes with one alkyl or aryl group and one more weakly donating alkoxide,[40−47] carboxylate,[48,49] amide,[50−57] or thiolate[58−61] undergo reductive elimination. In these cases, strong effects of the electronic properties of the covalent ligands on the rate of reductive elimination have been observed. Thus, the dative ligand located trans to these groups could influence the electronic properties of the covalent ligands undergoing reductive elimination and, thereby, the overall rate of reductive elimination.

Because palladium-catalyzed carbon-heteroatom coupling processes[62−66] have become powerful tools for organic synthesis and because carbon-heteroatom bond-forming reductive elimination is the final step of these cycles, information on the geometry of the species that undergoes reductive elimination would be valuable. In many cases, reductive elimination occurs from a three-coordinate T-shaped complex with the two reacting groups located cis to each other and an open coordination site located trans to one of the groups undergoing reductive elimination.[2,3,16,52−54,62,64,67−78] In other cases, chelating ligands are employed, and reductive elimination occurs from a four-coordinate complex. Many of these chelating ligands are unsymmetrical, with one of the two ligands of the chelate more electron-donating than the other.[9−11,79−89] To determine the

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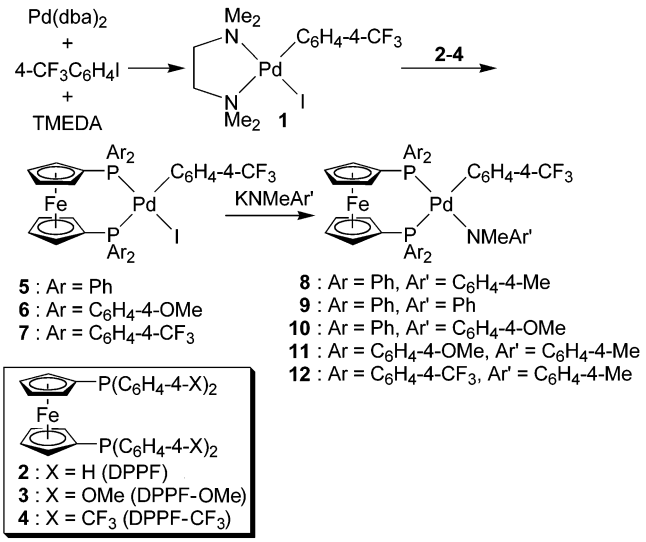
effect of geometry on this type of reductive elimination, we prepared complexes with unsymmetrical chelating phosphines and have measured the rate constants for reductive elimination from the two isomeric species. Our data suggest that ground-state effects, or the "trans influence", dominates the control of the rate of reductive elimination and that the effect of the orientation of two ligands of unequal electron-donating ability is similar in magnitude to the effect of conventional variation of the overall donating property of the ligands.

Results

Design of the System for Study. Several conditions must be met ensure that the differences in rates result from electronic effects and to observe directly the rates for reductive elimination from isomeric complexes. First, the ligand must possess two sterically equivalent but electronically distinct donor sets. For this reason, we have studied complexes with a chelating ligand containing two diarylphosphino groups bearing different para-substituents. Second, a system must be devised in which the rate of reductive elimination is faster than the rate of interconversion of isomers. If the rate of elimination were slower than the rate of interconversion, then the decay of both isomers would occur with the same apparent rate constant, and the thermodynamic ratio of the two isomers would be observed throughout the reaction. For this reason, we have studied reactions of palladium complexes bound by an electron-poor aryl group and by *N*-methyl para-anisidine. Finally, the geometry of the two isomers must be determined. Identification of the geometry was difficult because of the large number of aryl groups in the complexes. Therefore, we prepared complexes with perdeuterioaryl groups at phosphorus and with ^{15}N labeled *N*-methyl arylamides to determine the identity of the phosphino group located trans to the amide.

Synthesis of Arylpalladium Amido Complexes Ligated by Symmetric DPPF Derivatives. The synthesis of arylpalladium amido species ligated by symmetric DPPF derivatives (DPPF = 1,1′-bis(diphenylphosphino)ferrocene) is shown in Scheme 1. Reaction of symmetric 1,1′-bis(diarylphosphino)ferrocenes and TMEDA-ligated arylpalladium(II) iodide **1** (TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) formed the arylpalladium iodide complexes **5**−**7**.[90−93] Addition of a solution of **5**−**7** in THF to 1.1 equiv of the potassium *N*-methyl arylamides KNMe(C$_6$H$_4$-4-Me), KNMePh, or KNMe(C$_6$H$_4$-4-OMe) in THF at −78 °C generated arylpalladium(II) amido complexes **8**−**12**.

Scheme 1



Palladium amido complexes **8**−**12** were unstable and underwent reductive elimination (vide infra) upon warming to room temperature.

Thus, the amido complexes were characterized at −45 °C by NMR spectroscopy. The ^{31}P NMR spectrum of **8**−**12** contained two doublet resonances ($^2J_{PP}$ = 33−34 Hz). The lower field resonance of **9** was split into a doublet of doublets when the *N*-methyl anilide was labeled with ^{15}N ($^2J_{PN}$ = 49 Hz). The ^{1}H NMR spectrum of **12** showed 10 well-separated, singlet resonances for the tolyl-methyl, *N*-methyl, and eight inequivalent Cp protons. Although the ^{1}H NMR spectra of **8**−**11** were not well resolved at a temperature that they did not decompose, the resonances of the *N*-methyl groups of the palladium complexes were observed clearly between 2.07 and 2.30 ppm. The *N*-methyl resonances of potassium *N*-methylanilide derivatives are distinct (2.73−2.75 ppm) from the resonances of the palladium *N*-methylanilides. The ^{19}F NMR spectrum of **8**−**11** showed one singlet resonance for the CF_3 substituent on the palladium-bound aryl group. The ^{19}F NMR spectrum of DPPF−CF_3 complex **12** consisted of five singlets. One resonance corresponded to the palladium-bound aryl group, and four resonances were observed for the CF_3 groups of the ligand, as a result of hindered rotation about the Pd−N bond.

Synthesis of Arylpalladium Amido Complexes Ligated by Unsymmetrical DPPF Derivatives. The unsymmetrical diarylphosphinoferrocenes **16**−**18** were prepared by iterative lithiation of a bromoferrocene and quenching with the appropriate chlorodiarylphosphine, as shown in Scheme 2. Monolithiation of 1,1′-dibromoferrocene[94] **13** and quenching with chlorodiphenylphosphine or chlorodianisylphosphine generated the 1-diphenylphosphino-1′-bromoferrocene **14** and 1-dianisylphosphino-1′-bromoferrocene **15**. Lithiation of these bromophosphinoferrocenes and quenching with the appropriate chlorodiarylphosphine produced the unsymmetrical bis(diarylphosphino)ferrocene derivatives **16**−**18** (abbreviated as DPPF−OMe,Ph (**16**), DPPF−Ph,CF_3 (**17**), DPPF−OMe,CF_3 (**18**), unless otherwise noted). The ^{31}P NMR spectrum of each unsymmetrical DPPF derivative consisted of two singlets.

Synthesis of Arylpalladium Amido Complexes Ligated by Unsymmetrical Bis-diarylphosphinoferrocenes. TMEDA-

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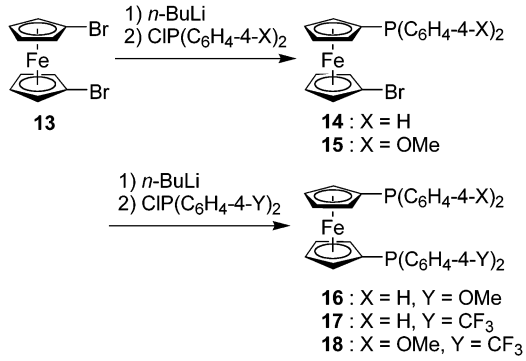
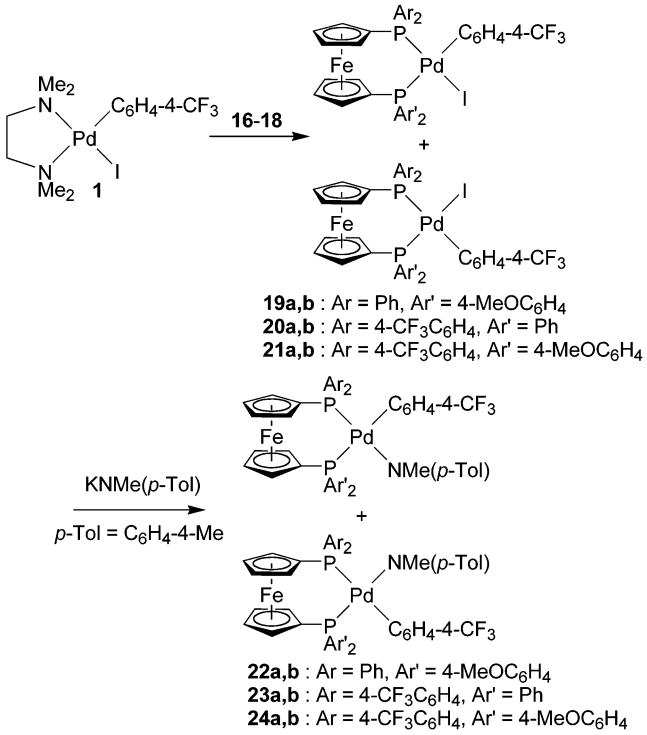
Scheme 2



Scheme 3



ligated Pd(II) complex **1** was converted to three sets of two regioisomeric arylpalladium iodide complexes (LPd(C_6H_4-*p*-CF_3)I) (**19a,b**−**21a,b**) by ligand substitution of **16**−**18** for TMEDA (Scheme 3). The ^{31}P NMR spectra of **19a,b**−**21a,b** contained two sets of doublets corresponding to the two regioisomers. The ratio of **19a** to **19b** was 1:1.2. The ratio of **20a** to **20b** was 1:2.7, and the ratio of **21a** to **21b** was 1:7.2, as determined from integration of the ^{1}H and ^{19}F NMR spectra.

Important for interpretation of the electronic effects in the discussion section, the ratios of isomeric arylpalladium iodide complexes observed in solution were equilibrium ratios. The ratios of isomers were measured by ^{19}F NMR spectroscopy at different temperatures to determine if the complexes were undergoing interconversion. The ratio of isomeric complexes **21a,b** should show the greatest temperature dependence because the ratio of isomers was the largest. Thus, we evaluated the temperature dependence of the ratio of isomers of this set of complexes. The ratio of **21a** to **21b** at −10 °C was 5.5:1. This ratio decreased to 4.7:1 at 30 °C and to 4.0:1 at 90 °C. These changes were fully reversible, and the equilibrium ratio at −10 °C was observed after several minutes.

Reaction of potassium *N*-methylarylamides with the arylpalladium iodide complexes, as described above for the formation of the arylpalladium amides with symmetrical phosphines, formed three sets of two regioisomeric arylpalladium amido complexes **22a,b**−**24a,b**. All of these palladium amido complexes **22a,b**−**24a,b** underwent reductive elimination upon warming to room temperature (vide infra) and were, therefore, characterized by NMR spectroscopic methods at −45 °C. The ^{31}P NMR spectrum of each regioisomeric mixture of **22a,b**−**24a,b** at −45 °C consisted of two large and two small doublet resonances with $^2J_{PP}$ of 33−34 Hz. Although one of the higher field ^{31}P NMR resonances of **22a**,**b** and **24a**,**b** and both higher field resonances of **23a**,**b** were broad, the two lower field signals of each set of regioisomers were well-resolved and indicated that no equilibration between the two regioisomers occurred on the NMR time scale at −45 °C. The ^{19}F NMR spectrum of the regioisomeric mixture of DPPF−OMe,Ph complexes **22a** and **22b** consisted of one large and one small singlet. The ^{19}F NMR spectrum of DPPF−Ph,CF_3 and DPPF−OMe,CF_3 complexes **23a,b** and **24a,b** contained three large and three small singlets. These three singlets resulted from the palladium-bound aryl group and the two phosphorus-bound aryl groups that are inequivalent because of hindered rotation about the Pd−N bond. The two regioisomers of **22a** and **22b** were generated in a ratio of 1:1.3 The regioisomers of **23a** and **23b** were generated in a ratio of 1:3.0, and the regioisomers of **24a** and **24b** were generated in a ratio of 1:5.8, as determined from the integral ratios of the ^{19}F NMR spectrum. Two clear resonances due to the *N*-methyl group of the palladium-bound *N*-methyl toluidides of **22a,b**−**24a,b** were observed between 2.12 and 2.27 ppm.

Use of Isotopic Labeling to Assign the Regiochemistry of Arylpalladium Complexes with Unsymmetrical Phosphine Ligands. To assign the geometry of each regioisomer of **22a,b**−**24a,b**, two types of isotopically labeled compounds were prepared. First, the amide was labeled with ^{15}N to reveal the location of the two phosphorus atoms by the difference in $^2J_{N-P}$ coupling constants for the trans and cis phosphines. Second, the aryl rings on one of the two diarylphopshino groups were perdeuterated to identify which substituents were bound to the diarylphosphino group that was located trans to the amide ligand. Perdeuteration of the substituents on a phosphine leads to a large change in ^{31}P NMR chemical shift.[95,96] Thus, the ^{31}P NMR resonance that is different between the deuterated and undeuterated complexes corresponds to the resonance of the group that had been labeled.

The reaction of **19a,b**−**21a,b** with ^{15}N-labeled potassium *N*-methylanilide at −45 °C generated the corresponding palladium amido species **25a,b**−**27a,b**. The ^{31}P NMR spectrum of these regioisomers contained four resonances. The two peaks at lower field were observed as doublet of doublet resonances resulting from cis ^{31}P−^{31}P and trans ^{31}P−^{15}N coupling. The two higher field resonances were doublets resulting from cis ^{31}P−^{31}P coupling and no additional ^{31}P−^{15}N coupling. These data indicate that the two lower field resonances of **22a,b**−**27a,b** correspond to the phosphorus atoms located trans to the amido group.

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Scheme 4

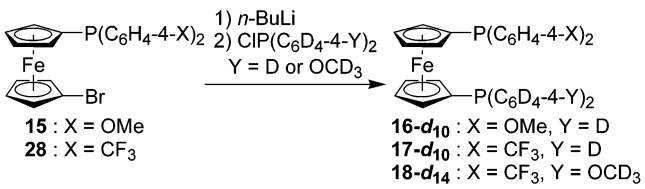

Table 1. ^{31}P NMR Spectroscopic Data of Labeled and Unlabeled Complexes **19a,b**−**24a,b**

complex (labeled Ar)	^{31}P δ	$\Delta\delta$	ratio from ^{19}F	trans ligand	PAr_2 group
19a,b (C_6D_5)	6.3	0.0	1.0	C_6H_4-4-CF_3	C_6H_4-4-OMe
	9.1	−0.4	1.2	C_6H_4-4-CF_3	C_6D_5
	23.6	0.1	1.2	iodide	C_6H_4-4-OMe
	26.2	−0.4	1.0	iodide	C_6D_5
20a,b (C_6D_5)	8.9	−0.3	1.0	C_6H_4-4-CF_3	C_6D_5
	9.1	0.0	2.7	C_6H_4-4-CF_3	C_6H_4-4-CF_3
	25.0	0.0	1.0	iodide	C_6H_4-4-CF_3
	25.7	−0.3	2.7	iodide	C_6D_5
21a,b (C_6D_4-4-OCD_3)	6.2	−0.4	1.0	C_6H_4-4-CF_3	C_6D_4-4-OCD_3
	9.2	0.0	7.2	C_6H_4-4-CF_3	C_6H_4-4-CF_3
	23.4	−0.4	7.2	iodide	C_6D_4-4-OCD_3
	25.0	0.0	1.0	iodide	C_6H_4-4-CF_3
22a,b (C_6D_5)	6.7	0.1	1.0	C_6H_4-4-CF_3	C_6H_4-4-OMe
	8.9	−0.2	1.3	C_6H_4-4-CF_3	C_6D_5
	21.4[a]	0.1	1.3	amide	C_6H_4-4-OMe
	24.3[a]	−0.4	1.0	amide	C_6D_5
23a,b (C_6D_5)	7.6	−0.4	1.0	C_6H_4-4-CF_3	C_6H_4-4-CF_3
	8.2	0.1	3.0	C_6H_4-4-CF_3	C_6D_5
	23.3[a]	−0.4	3.0	amide	C_6H_4-4-CF_3
	25.3[a]	0.0	1.0	amide	C_6D_5
24a,b (C_6D_4-4-OCD_3)	5.1	−0.5	1.0	C_6H_4-4-CF_3	C_6D_4-4-OCD_3
	8.0	0.0	5.8	C_6H_4-4-CF_3	C_6H_4-4-CF_3
	20.5[a]	−0.4	5.8	amide	C_6D_4-4-OCD_3
	25.4[a]	0.0	1.0	amide	C_6H_4-4-CF_3

[a] Coupled to ^{15}NMePh in ^{15}N labeled **25**−**27**.

The synthesis of deuterium-labeled, unsymmetrical DPPF ligands for the second labeling experiment was conducted in a manner similar to the syntheses of unlabeled **16**−**18** (Scheme 4). Deuterium-labeled chlorodiarylphosphines were derived from commercially available bromobenzene-d_5 and anisole-d_8. The ^{31}P NMR chemical shifts of the phosphorus bearing deuterated aromatic rings in **16-*d*$_{10}$**, **17-*d*$_{10}$**, and **18-*d*$_{14}$** were located upfield of those of the unlabeled ligands **16**−**18** by 0.5−0.6 ppm. Exchange of these ligands for the TMEDA in arylpalladium halide complex **1** generated the deuterated arylpalladium iodide complexes **19a,b-*d*$_{10}$**, **20a,b-*d*$_{10}$**, and **21a,b-*d*$_{14}$**. Mixing of **19a,b-*d*$_{10}$**, **20a,b-*d*$_{10}$**, and **21a,b-*d*$_{14}$** with KNMe(C_6H_4-4-Me) afforded the corresponding arylpalladium amido products **22a,b-*d*$_{10}$**, **23a,b-*d*$_{10}$**, and **24a,b-*d*$_{14}$**.

The difference ($\Delta\delta$) in ^{31}P NMR chemical shift between protiated compounds **19a,b**−**24a,b** and deuterated compounds **19a,b-*d*$_{10}$**, **20a,b-*d*$_{10}$**, **21a,b-*d*$_{14}$**, **22a,b-*d*$_{10}$**, **23a,b-*d*$_{10}$**, and **24a,b-*d*$_{14}$** are summarized in Table 1. The ^{31}P NMR chemical shifts of two of the four resonances corresponding to the deuterated ligand in each set of regioisomers were significantly different from ^{31}P NMR chemical shifts corresponding to the protiated ligand in each set of regioisomers. The phosphorus nuclei corresponding to these altered resonances, therefore, contain the deuterated aryl groups. With this information and the ^{31}P NMR spectra of the complexes labeled with ^{15}N, the ^{31}P NMR spectra of all three sets of arylpalladium amido complexes were assigned.

The assignment of the ^{31}P NMR spectrum of the regioisomeric mixture of **22a** and **22b** is presented as an example. The ^{15}N labeling experiment showed that the two ^{31}P NMR resonances at lower field (δ 21.4 and 24.3 in a ratio of 1.3 to 1) correspond to the phosphorus atoms located trans to the amido group. Deuterium labeling of the diphenylphosphino group altered the chemical shift of the resonance of the unlabeled complex at δ 24.3. Thus, the resonance at δ 24.3 corresponds to the diphenylphosphino group, and the resonance at δ 21.4 corresponds to the dianisylphosphino group. Thus, the minor regioisomer contains the amide trans to the diphenylphosphino group, and the major regioisomer contains the amide trans to the dianisylphosphino group. Similar analysis of the other complexes showed that the major regioisomer of each set of complexes **22a,b**−**24a,b** contains the aryl ligand trans to the phosphine donor that bears the less electron-rich aryl ring. The greater stability of this isomer is consistent with our expectation that the phenyl group has a larger trans influence than the amido ligand.[97] We expect the amido group to be a weaker donor than the aryl group for several reasons. First, the amido group is simply bound to the metal through a more electronegative atom. Second, the amido group of these studies contains an aryl substituent. Third, the geometry is inappropriate for π-donation. The geometry of a related diarylamido complex was shown to place the electron pair in the square plane, rather than along the axial direction with a pi-acceptor orbital,[52] and the ^{1}H and ^{19}F NMR spectra of the amido complexes show that **22a,b**−**24a,b** adopt the same conformation.

Considering the chemical shifts of the phosphines in the arylpalladium amido complexes, the resonances of the phosphorus atoms located trans to the iodide of **19a,b**−**21a,b** would be expected to lie downfield of the resonances of the phosphorus atoms located trans to the aryl group. The resonances of the phosphorus atoms of **22a,b**−**24a,b** trans to the amido groups resonated downfield of those trans to the aryl group and the bonding of the amido group is related to that of an iodide. In this case, the major isomer of the arylpalladium iodide complexes **19a,b**−**21a,b** would also contain the stronger phosphorus donor trans to the iodide ligand, which has a weaker trans influence than the aryl group. The similarity of the regioisomeric ratio of the arylpalladium iodide complexes **19a,b**−**21a,b** and the arylpalladium amido complexes **22a,b**−**24a,b** (1:1.2 for **19a,b**, 1:2.7 for **20a,b**, and 1:7.2 for **21a,b**, 1:1.3 for **22a,b**, 1:3.0 for **23a,b**, and 1:5.8 for **24a,b**) indicates that the substitution of iodide by amide proceeded with almost complete retention of configuration or that the thermodynamic ratio of the two regioisomers is similar for the iodide and amide complexes.

Reductive Elimination of Diarylmethylamine from Arylpalladium *N*-Methyl Anilido Complexes Containing Symmetrical DPPF Derivatives. Arylpalladium amido complexes **8**−**12** containing symmetrical DPPF derivatives underwent reductive elimination of diarylmethylamine upon warming to −15 °C (Scheme 5). These reactions were conducted in THF solution with 4.4 equiv of added PPh_3 to trap the Pd(0) species that results from the reductive elimination process. The reactions of **8**−**12** occurred in high yields. The yields determined by gas chromatography with an internal standard for the combination

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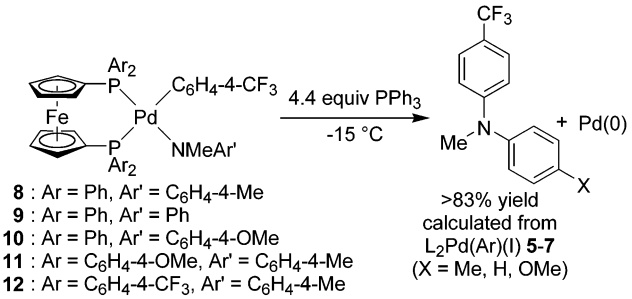
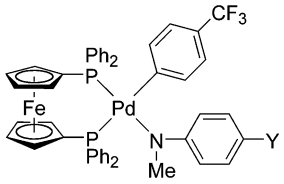
Scheme 5



8 : Ar = Ph, Ar' = C_6H_4-4-Me
9 : Ar = Ph, Ar' = Ph
10 : Ar = Ph, Ar' = C_6H_4-4-OMe
11 : Ar = C_6H_4-4-OMe, Ar' = C_6H_4-4-Me
12 : Ar = C_6H_4-4-CF_3, Ar' = C_6H_4-4-Me

Table 2. Rate Constants for Reductive Elimination from Complexes **8**−**10** with Varied Aryl Groups on the Amido Nitrogen Atom



complex	k_{obs} (10^4 s^{-1})[a]	standard deviation[a]
8 (Y = Me)	12.8	0.5
9 (Y = H)	2.94	0.04
10 (Y = OMe)	37.7	0.5

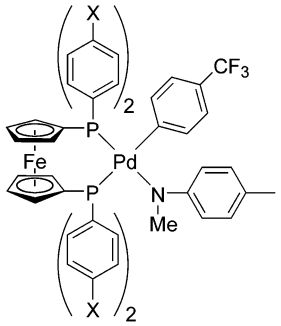
[a] estimated from 3 independent experiments

of the generation and reductive elimination of the arylpalladium amido complexes exceeded 83% in all cases.

Kinetic data for the reductive elimination of *N*,*N*-diarylmethylamine from complexes **8**−**12** in THF solution were obtained by monitoring the disappearance of **8**−**12** by ^{19}F NMR spectroscopy. The intensity of the resonance of the CF_3 group on the aromatic ring bound to palladium relative to that of PhOTf in a glass capillary was monitored for greater than three half-lives at −15 °C. All of the rate constants were determined by fits of the ratio of integrations of the ^{19}F NMR signals vs time to the equation for an exponential decay. The R^2 values of these plots were greater than 0.999, and the standard deviations from three measurements were less than 4% of the value of the rate constant. The first-order rate constants are presented in Tables 2 and 3.

Reductive Elimination of Diarylmethylamine from Regioisomeric Arylpalladium Amido Complexes 22a,b−24a,b Containing Unsymmetrical DPPF Derivatives. The three sets of two regioisomeric complexes **22a,b**−**24a,b** ligated by unsymmetrical DPPF derivatives also underwent reductive elimination (Scheme 6) at −15 °C to form the corresponding *N*,*N*-diarylmethylamine in high yield in the presence of 4.4 equiv of PPh_3. The yields for the two steps of generation and reductive elimination of the amido complexes exceeded 95%. Kinetic studies on the reductive elimination of diarylmethylamine from palladium amido complexes **22a,b**−**24a,b** were conducted by ^{19}F NMR spectroscopy, as described for studies of complexes **8**−**12** ligated by symmetric DPPF derivatives. The first-order rate constants from an average of three experiments recorded over three half-lives are presented in Chart 1. The exponential fits and relative magnitudes of the standard deviations were similar to those from experiments with complexes **8**−**12**, even for decay of the minor regioisomer.

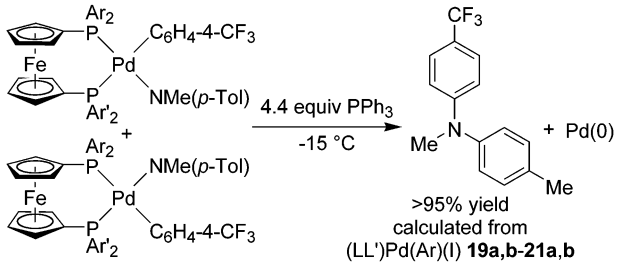
Table 3. Rate Constants for Reductive Elimination from the Complexes **8**, **11**, and **12** with Varied Aryl Groups on the Symmetrical DPPF Ligands



complex	k_{obs} (10^4 s^{-1})[a]	standard deviation[a]
8 (X = H)	12.8	0.5
11 (X = OMe)	4.16	0.08
12 (X = CF_3)	27.0	0.2

[a] Estimated from 3 independent experiments

Scheme 6



22a,**b** : Ar = Ph, Ar' = 4-$MeOC_6H_4$
23a,**b** : Ar = 4-$CF_3C_6H_4$, Ar' = Ph
24a,**b** : Ar = 4-$CF_3C_6H_4$, Ar' = 4-$MeOC_6H_4$

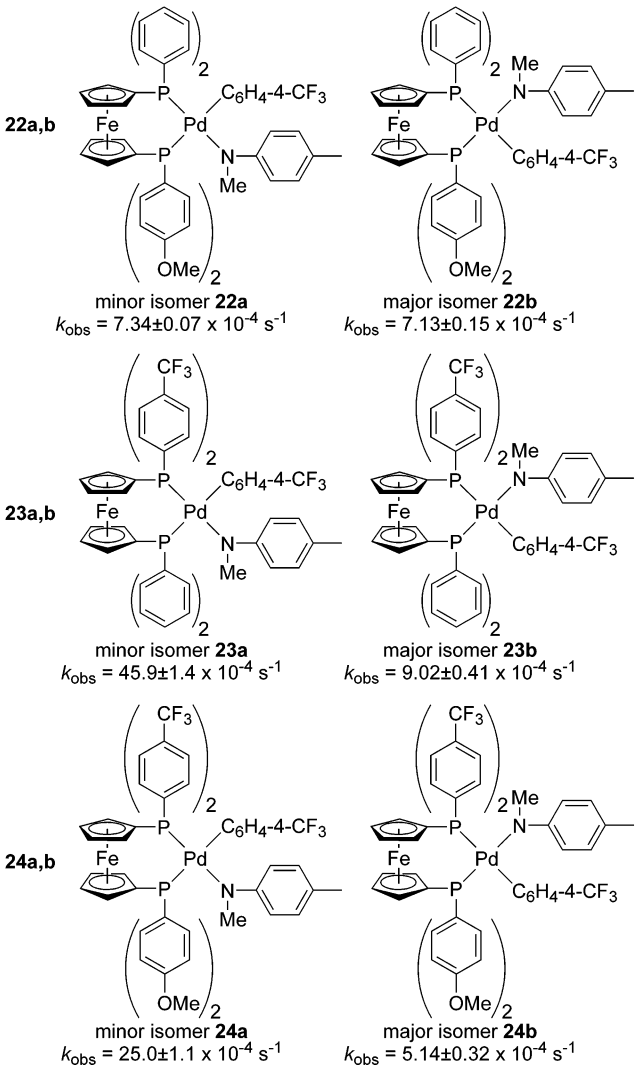
Reductive elimination of the minor regioisomers **22b**, **23b**, and **24b** occurred faster than reductive elimination of the major regioisomers **22a**, **23a**, and **24a**. The different rate constants for reaction of the two regioisomers of each pair indicate that reductive elimination is faster than isomerization. Thus, the rate of reductive elimination is affected by the orientation of the unsymmetrical ligand.

Discussion

1. Electronic Effect of Symmetric DPPF Derivatives on the Reductive Elimination from Arylpalladium Amido Complexes. The relative magnitude of electron density at two transition metal centers is often used to explain their relative rates for reductive elimination.[2] The rate constants for reductive elimination from the DPPF complex **8**, DPPF−OMe complex **11**, and DPPF−CF_3 complex **12** in Table 3 followed the expected trend. The complex with the most electron-rich metal center, DPPF−OMe complex **11**, reacted the slowest, and the complex with the least electron-rich metal center, DPPF−CF_3 complex **12**, reacted the fastest. Moreover, the ratio of rate constants for reductive elimination of amine from DPPF−CF_3-complex **12** and DPPF-complex **8** was almost the same as the ratio of rate constants for reductive elimination of diaryl ether from arylpalladium phenoxides ligated by the same two DPPF derivatives.[44]

2. Effect of Regiochemistry on Reductive Elimination from Arylpalladium Amido Complexes with Unsymmetrical DPPF Derivatives. Previous studies on DPPF-ligated arylpalladium

Chart 1



amido complexes showed that the reactions occurred directly from the isolated 4-coordinate complex, not from a 3- or 5-coordinate intermediate.[52] The close structural relationship between the parent DPPF complexes of the previous work and the electronically varied DPPF complexes of the current study imply that the rates for reactions of the electronically perturbed systems also occur from the isolated 4-coordinate complex. Thus, differences in the reaction rates reflect electronic effects on the elementary reductive elimination step, not on ligand dissociation or association to form 3- or 5-coordinate intermediates[2,3,16,52−54,62,64,67−78,98−100] prior to reductive elimination.

2a. Origin of the Effect of the Trans Ligand on the Rate of Reductive Elimination. The minor regioisomer underwent reductive elimination faster than the major regioisomer in all reactions of regioisomeric arylpalladium amido complexes of this work. This faster reductive elimination of the minor regioisomer can be explained by ground-state energies. Although we could not determine the precise thermodynamic ratio of

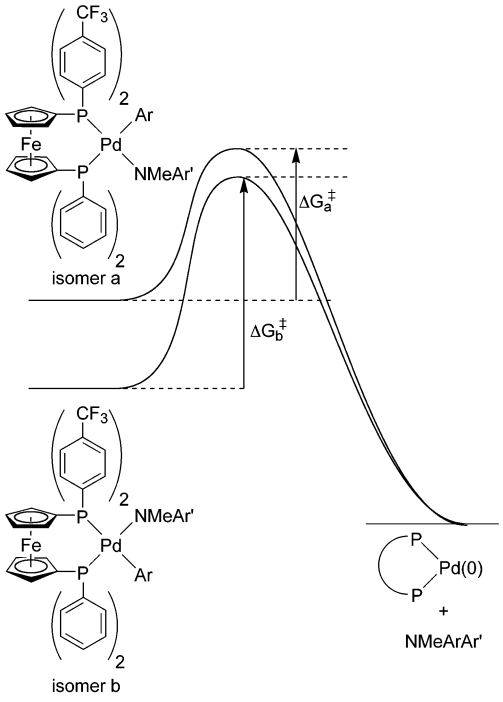


Figure 1. Qualitative energy diagram for the reductive elimination from isomeric arylpalladium amido complexes.

regioisomeric amido complexes, our data suggest that the observed ratio is close to the thermodynamic ratio. The arylpalladium iodide complexes were obtained as thermodynamic mixtures of the two regioisomers, and the trans influences of an arylamide and an iodide should be more similar to each other than trans influences of an amide and an aryl group. As mentioned in the Results section, the amido group of this study bears an aryl group, and the geometry of these complexes prevents substantial π-donation. Thus, the greater electronegativity of nitrogen, the electron-accepting property of the aryl group, and the absence of strong π-donation will make it a poorer electron-donor than the aryl group. Subsequent arguments on the origin of the effect of the trans ligand on the rate of reductive elimination are based on the assumption that the equilibrium ratio of regioisomeric anilide complexes is similar to the equilibrium ratio of regioisomeric iodide complexes determined experimentally.

A qualitative energy diagram for the reductive elimination from regioisomeric arylpalladium amido complexes with unsymmetrical DPPF derivatives is shown in Figure 1. Our data suggest that the difference in ground-state energies is larger than the difference in transition state energies. The relative rates of reductive elimination of amine from the two isomeric arylpalladium amido complexes are similar to the inverse of the relative ratios of regioisomers. For example, the relative rates for reaction of the major and minor regioisomers in the mixture of DPPF−CF_3,OMe_3-ligated **24a,b** was 1:4.9, and the ratio of regioisomers was 5.8:1. If the ratio of regioisomers is close to the true thermodynamic value, then the difference in transition state energies for reaction of the two regioisomers will be smaller than the difference in energies of the two ground states, as shown in Figure 1. Thus, ground-state effects appear to dominate the relative rates of reductive elimination from the two regioisomers. In other words, the reaction rates appear to depend on the identity of the ligands trans to the two groups

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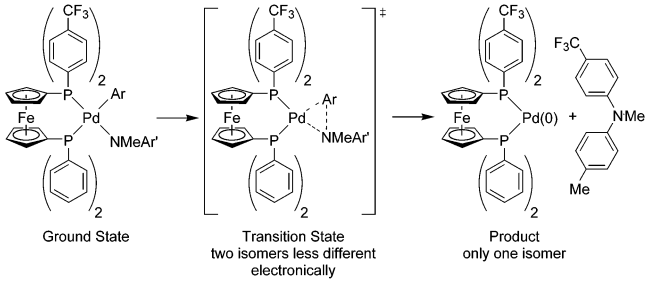


Figure 2. Changes in the geometry during the reductive elimination of arylamine from a complex with an unsymmetrical chelating ligand.

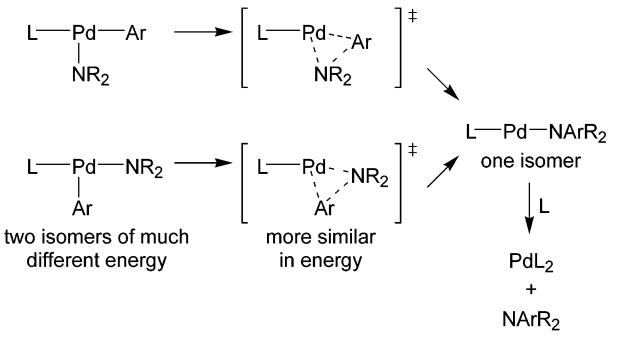


Figure 3. Changes in the geometry during the reductive elimination of arylamine from a T-shaped complex with a single dative ligand.

that undergo reductive elimination more because of a ground-state effect analogous to the "trans influence" than a transition state effect analogous to the "trans effect" in ligand substitution.

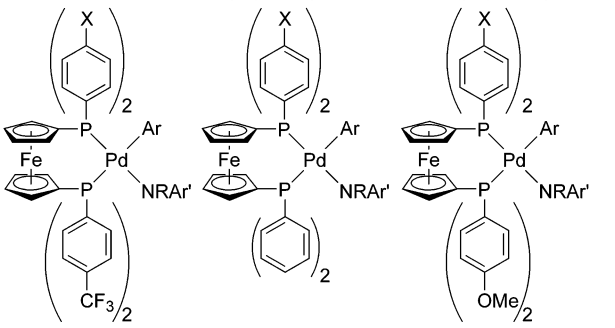
Figure 2 depicts a rationalization for the greater impact of ground state effects. The reactants are square planar complexes, and this geometry maximizes the trans influence. As the reaction proceeds, the unsymmetrical nature of the complex is reduced until the initial product, which probably contains coordinated amine, is formed. Both regioisomers will form identical or nearly identical amine complexes and identical Pd(0) products after release of the amine. Thus, the magnitude of the electronic asymmetry decreases from ground state to transition state, and the difference in energy between the two regioisomeric forms of the complexes decreases as the reaction progresses.

2b. Comparisons of the Magnitude of the Effects of the Ligand Substituents on the Relative Rates of Reaction of the Two Regioisomers. The relative magnitudes of the ratio of rate constants for reaction of **22a,b**−**24a,b** (Chart 2) depended on the substituents on the ligand. The relative magnitude can be rationalized by the differences in the values of σ^{Ph} determined from the pK_a values of phosphorus acid derivatives containing substituted aryl groups.[101] The σ^{Ph} values of C_6H_4-4-OMe, Ph, and C_6H_4-4-CF_3 are −0.12, 0, and 0.70. Thus, the smaller ratio of rate constants for reaction of regioisomeric complexes with one P(C_6H_4-4-OMe)$_2$ and one PPh_2 group in the ligand (1.03:1), relative to that for regioisomeric complexes with one PPh_2 and one P(C_6H_4-4-CF_3)$_2$ group in the ligand (5.1:1), is consistent with the relative magnitudes of the σ^{Ph} values.

2c. Comparison of the Magnitudes of the Effect of Perturbing the Electronic Properties of the Ligand Trans to the Amido Group and Trans to the Aryl Group. The compounds in this work allow an estimate of the relative importance of the electronic effects of the ligand trans to the amido group and the ligand trans to the palladium-bound aryl group. As shown in the series of compounds at the top of Chart 2 that contain the same donor ligand trans to the palladium-bound aryl group, variation of the group trans to the amido nitrogen led to a significant electronic effect. The relative rates of reaction of the complexes followed the trend X = OMe < H < CF_3. In contrast, the effect of the group Y on the aryl substituent of the phosphine donor located trans to the phenyl group summarized at the bottom of Chart 2 was smaller. The P−Pd bond trans to the amido group in the solid-state structure of (DPPF)Pd(C_6H_4-*p*-NMe_2)N(*p*-Tol)$_2$[52] was shorter than the P−Pd bond trans to the aryl group. *Thus, the smaller effect of substituents on the dative ligand trans to the covalent ligand with the stronger trans influence could result from a longer bond between the metal and the dative ligand and a corresponding weaker electronic communication.*

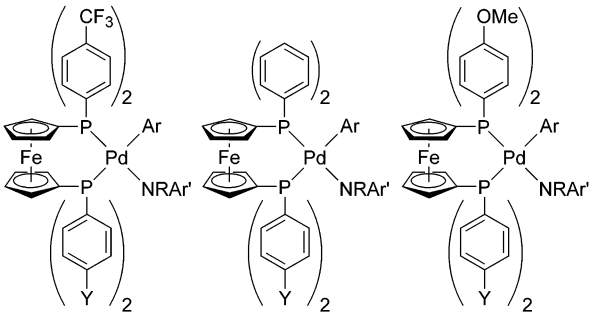
Chart 2

Electronic effect of aryl groups on the phosphorus atom located trans to the amido nitrogen (Ar = C_6H_4-4-CF_3, R = Me, Ar' = C_6H_4-4-CH_3)



	k_{rel}		k_{rel}		k_{rel}
X = OMe (**24b**)	1	X = OMe (**22b**)	1	X = OMe (**11**)	1
X = H (**23b**)	1.8	X = H (**8**)	1.8	X = H (**22a**)	1.8
X = CF_3 (**12**)	5.3	X = CF_3 (**23a**)	6.4	X = CF_3 (**24a**)	6.0

Electronic effect of aryl groups on the phosphorus atom located trans to the Pd-bounded Ar group (Ar = C_6H_4-4-CF_3, R = Me, Ar' = C_6H_4-4-CH_3)



	k_{rel}		k_{rel}		k_{rel}
Y = OMe (**24a**)	1	Y = OMe (**22a**)	1	Y = OMe (**11**)	1
Y = CF_3 (**12**)	1.1	Y = CF_3 (**23b**)	1.2	Y = CF_3 (**24b**)	1.2
Y = H (**23a**)	1.8	Y = H (**8**)	1.7	Y = H (**22b**)	1.7

2d. Comparison of the Effect of Geometry to Typical Ligand Electronic Effects. One can also compare the changes in rate constants from perturbation of the overall electron density on the metal to that from changing the orientation of the unsymmetrical ligands, relative to the aryl and amido groups. This comparison leads to the conclusion that the influence of changing the geometry of an unsymmetrical ligand can be similar in magnitude to the influence of changing the overall donating ability of the ligand.

Changing the four aryl groups of the symmetric DPPF ligands from C_6H_4-*p*-CF_3 in **12** to C_6H_4-*p*-OMe in **11** led to a change in rate constant of 6.5-fold. This difference in rate constant

(101) Mastryukova, T. A.; Kabachnik, M. I. *Russ. Chem. Rev. (Engl. Transl.)* **1969**, *38(10)*, 795−811.

corresponds to a difference in free energy of activation of 0.9 kcal/mol. By comparison, interconversion of the geometry of the two regioisomers of **24a**,**b**, which contain one P(C_6H_4-*p*-CF_3)$_2$ group and one P(C_6H_4-*p*-OMe)$_2$ group, led to a change in rate constant of a factor of 5. If the free energy contributions of varying the two diarylphosphino groups in the symmetric DPPF derivatives are additive, then changing two aryl substituents on one diarylphosphino group from *p*-CF_3 to *p*-OMe, in the absence of an effect of the orientation of the stronger and weaker donor, would lead to a difference in energy of 0.45 kcal/mol. This difference in energy leads to a 2.5-fold difference in rate constant, or the square root of the ratio of rate constants (6.5) from changing all of the substituents on the aryl groups of the DPPF derivative from *p*-CF_3 to *p*-OMe. This value of 2.5 is half of the ratio of rate constants that results from changing the orientation of the diarylphosphino groups, relative to the aryl and amido groups.

A similar comparison between complexes **8** and **12** containing DPPF and CF_3-DPPF shows that the overall change in electron density that results from varying the two aryl substituents on one diarylphosphino group changes the rate constant by a factor of 2.1, whereas the difference in reaction rates of the two regioisomers is again a factor of 5. Regardless of whether the energetic contributions of the substituents on the symmetric DPPF derivatives to the differences in rates are truly additive, the effect of geometry is similar in magnitude to the effect of varying substituents on the arylphosphine ligands. Thus, changes in rate constants for reductive elimination resulting from changing the orientation of two ancillary ligands can equal the more commonly considered effect of altering the overall electron-donating ability of the ancillary ligands.

3. Implications for Reactions of Complexes with More Common Chelating Ligands and for Complexes with Monodentate Ligands. The conclusions obtained from this well-defined system can be extrapolated to complexes with unsymmetrical ligands, such as those containing one dialkyl- and one diarylphosphino group, one phosphine and one phosphite donor, one phosphorus and one sulfur donor, or one phosphorus and one nitrogen donor, in the species undergoing reductive elimination.[9−11,79−89] These electronically unsymmetrical coordination spheres are commonly found in catalytic intermediates that undergo reductive elimination.[11] Moreover, the conclusions from this work can be extrapolated to complexes with a three-coordinate T-shaped geometry containing one phosphine ligand and two covalent ligands. Such T-shaped complexes typically undergo reductive elimination in a reaction that is initiated with four-coordinate complexes containing monodentate ligands.[2,3,16,52−54,62,64,67−78]

In the absence of large steric effects, the stronger trans influence of the aryl group, relative to the amido group, would dictate the stability of regioisomeric complexes. The more stable of the isomeric arylpalladium amido complexes with an unsymmetrical bidentate ligand would contain the phenyl group trans to the more weakly donating dative ligand. In the absence of steric effects, the more stable T-shaped arylpalladium amido complex would contain the phenyl group trans to the open coordination site. Indeed, only one isomer with an aryl group trans to the open site was detected for 3-coordinate T-shaped arylpalladium halide complexes containing an additional, but weakly donating C−H agostic interaction.[102]

Both complexes with unsymmetrical bidentate ligands and complexes with monodentate ligands will undergo reductive elimination faster from the less thermodynamically stable complex because of the reduction in asymmetry that occurs along the reaction coordinate. For example, a T-shaped arylpalladium amido complex with a single phosphine donor would undergo reductive elimination faster when the amido group is trans to the open site than when the aryl group is trans to the open site (Figure 3). Thus, the origin of the electronic effect of geometry on reductive elimination from 3-coordinate Pd(II) complexes or from 4-coordinate Pd(II) complexes with one strong and one weak donor should be analogous to that shown by the studies with the 4-coordinate Pd(II) complexes containing unsymmetrical DPPF derivatives.

4. Electronic Effects of the Amido Group on the Rate of Reductive Elimination. The effect of the electron-donating ability of the amido group on the rate of reductive elimination was revealed by reactions with complexes **8**−**10** of the general formula (DPPF)Pd(C_6H_4-4-CF_3)(NMeC_6H_4-4-X) (Table 2). The magnitude of the sensitivity of the reaction to electronic effects of the aryl group on nitrogen was larger than it was to electronic effects of the aryl group on sulfur during reductive eliminations of sulfides from the arylpalladium thiolate complexes (DPPE)-Pd(C_6H_4-4-*n*-Bu)(S−C_6H_4-4-Y) (DPPE = 1,2-bis-diphenylphosphinoethane). The relative magnitudes of the reductive elimination of diarylsulfides were k_{rel} = 1 (H): 1.5 (Me): 1.7 (OMe),[59] whereas the magnitudes of the reductive elimination of diaryl methylamines were k_{rel} = 1 (H): 4.4 (Me): 12.8 (OMe)]. This larger substituent effect on the reductive elimination of amines likely reflects a greater polarity in the transition state for C−N reductive elimination than in the transition state for C−S bond-forming reductive elimination. Moreover, the effect of the substituents on the aryl group attached to nitrogen was larger than the effect of the substituents on the aryl groups attached to phosphorus. Thus, the effect of substituents on the groups undergoing reductive elimination was larger than the effect of substituents on the ancillary ligands.

Conclusion

The effect of the orientation of two dative ligands with distinct electronic properties on the reductive elimination from square planar Pd(II) complexes was evaluated. To reveal this effect, reactions of arylpalladium amido complexes with symmetrical DPPF derivatives and of regioisomeric pairs of arylpalladium amido complexes with unsymmetrical DPPF derivatives were studied. These experiments led to the following conclusions: (1) The orientation of the unsymmetrical ligand affected the rate of reductive elimination. (2) The minor regioisomer reductively eliminated faster than the major regioisomer. (3) The rate of C−N bond-forming reductive elimination of regioisomeric arylpalladium halide complexes was controlled by ground-state effects more than transition state effects because the asymmetry of the complex decreases during the reductive elimination process. (4) The electronic effect of the phosphine trans to the amido nitrogen atom was larger than the electronic effect of the phosphine trans to the Pd-bound aryl group, most likely because the Pd−P bond trans to the amido group is shorter than the Pd−P bond trans to the aryl group. (5) The magnitude

(102) Stambuli, J. P.; Buhl, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 9346−9347.

of the difference in rates of the two regioisomeric arylpalladium amide complexes with unsymmetrical DPPF derivatives was similar to the magnitude of the difference in rate between complexes of symmetric DPPF derivatives with electron-donating or electron-withdrawing substituents on all four aryl groups of the dative ligand. (6) The magnitude of the electronic effect of the aryl group on the amido nitrogen was larger than the electronic effect of the aryl group on the phosphorus atom.

These results show that the relative geometry of square planar and T-shaped intermediates should be considered when rationalizing or predicting the rates of reductive elimination. These results also imply that related effects could be observed during reductive elimination from octahedral and five-coordinate square-based pyramidal complexes. Finally, these results suggest that a steric preference for the regioisomer that contains the covalent ligands in an electronically less favored orientation can lead to significant acceleration of the rate of reductive elimination.

Experimental Section

General Methods. ^{1}H, ^{2}H, ^{13}C{^{1}H}, ^{19}F{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded on 300, 400, or 500 MHz Spectrometers with residual protiated solvent, deuterated solvent, $CFCl_3$, or 85% H_3PO_4 used as a reference. Elemental analyses were performed by Robertson Microlabs, Inc., Madison, NJ. GC analyses were performed with an HP-1 methyl silicone column. Ether, toluene, tetrahydrofuran, benzene, and pentane were distilled from sodium/benzophenone. $Pd(dba)_2$,[103] Dibromoferrocene,[94] 1-bromo-1′-diphenylphosphinoferrocene,[104] $ClP(C_6H_4$-*p*-$OMe)_2$,[10] $ClP(C_6H_4$-*p*-$CF_3)_2$,[105] OMe-DPPF,[106] and CF_3-DPPF[105] were synthesized according to literature procedures.

Synthesis of (TMEDA)Pd(C_6H_4-*p*-CF_3)I (1).[90−93] In a glovebox, tetramethylethylenediamine (0.720 mL, 4.80 mmol) and 4-iodobenzotrifluoride (0.730 mL, 5.00 mmol) were added at room temperature to a mixture of $Pd(dba)_2$ (2.00 g, 3.48 mmol) and benzene (15 mL) contained in a screw capped vial. The vial was covered with a Teflon-lined cap and removed from the glovebox. The reaction was stirred at 50 °C for 2 h. The vial was returned to the glovebox, and the reaction mixture was filtered through a pad of diatomaceous earth. After most of the solvents (>95%) were removed under reduced pressure, ether (15 mL) was added. After stirring for 3 min, the supernatant was removed by pipet. This washing process was repeated 3 times, and ether was added. The orange suspension was filtered through a glass fritted funnel and the solid product was washed again with ether (1.13 g, 65%). ^{1}H NMR (C_6D_6, 400 MHz) δ 1.48 (t, J = 5.2 Hz, 2H), 1.56 (s, 8H), 2.29 (s, 6H), 7.35 (d, J = 8 Hz, 2H), 7.58 (d, J = 8 Hz, 2H); ^{13}C{^{1}H} NMR (CD_2Cl_2, 125 MHz) δ 50.2, 50.4, 58.9, 62.7, 122.4 (q, $^3J_{CF}$ = 3.2 Hz), 125.2 (q, $^2J_{CF}$ = 30.9 Hz), 125.7 (q, $^1J_{CF}$ = 270 Hz), 137.4, 154.0; ^{19}F{^{1}H} NMR (C_6D_6, 376 MHz) δ -61.3; Anal. Calcd. for $C_{13}H_{20}F_3IN_2Pd$: C, 31.57; H, 4.08; N, 5.66. Found: C, 31.44; H, 3.89; N, 5.53.

Synthesis of (DPPF)Pd(C_6H_4-*p*-CF_3)I (5). In a glovebox, a solution of 1,1′-bis(diphenylphoshino)ferrocene (204 mg, 0.413 mmol) in THF (5 mL) was added to a solution of (TMEDA)Pd(C_6H_4-*p*-CF_3)I (280 mg, 0.424 mmol) in THF (5 mL) at room temperature. After stirring for 5 min, the solvents were removed under reduced pressure until approximately 3 mL remained. The reaction mixture was then added at room temperature to a vial containing vigorously stirred pentane (18 mL) to give a yellow precipitate. The resulting yellow powder was isolated by filtration through a glass fritted funnel (380 mg, 99%). ^{1}H NMR (THF-d_8, 500 MHz) δ 3.68 (q, J = 1.7 Hz, 2H), 4.19 (t, J = 1.7 Hz, 2H), 4.55 (s, 2H) 4.79 (q, J = 1.7 Hz, 2H), 6.65 (d, J = 7.0 Hz, 2H), 7.08 (t, J = 7.5 Hz, 2H), 7.14 (dt, J = 1.8, 8.0 Hz, 4H), 7.29−7.49 (m, 12H), 8.04−8.11 (m, 4H); ^{31}P{^{1}H} NMR (THF-d_8, 162 MHz) δ 10.5 (d, J = 33 Hz), 27.6 (d, J = 33 Hz); ^{19}F{^{1}H} NMR (THF-d_8, 376 MHz) δ -61.5; Anal. Calcd. for $C_{41}H_{32}F_3FeIP_2Pd$: C, 52.72; H, 3.46. Found: C, 52.74; H, 3.35.

Synthesis of (DPPF-OMe)Pd(C_6H_4-*p*-CF_3)I (6). In a glovebox, a solution of 1,1′-bis(di(4-methoxyphenyl)phosphino)ferrocene (283 mg, 0.420 mmol) in THF (5 mL) was added to a solution of (TMEDA)Pd(C_6H_4-*p*-CF_3)I (200 mg, 0.404 mmol) in THF (5 mL) at room temperature. After stirring for 5 min at room temperature, the solvents were removed under reduced pressure until about 5 mL. The reaction mixture was then added dropwise to vigorously stirred pentane (40 mL) at room temperature to give yellow precipitate. The resulting yellow powder was isolated by filtration through a glass fritted funnel (320 mg, 75%). ^{1}H NMR (THF-d_8, 500 MHz) δ 3.72 (d, J = 1.5 Hz, 2H), 3.75 (s, 6H), 3.85 (s, 6H), 4.17 (s, 2H), 4.45 (s, 2H) 4.69 (d, J = 1.5 Hz, 2H), 6.67−6.72 (m, 6H), 7.00 (d, J = 8.0 Hz, 4H), 7.07 (t, J = 8.0 Hz, 2H), 7.27 (d, J = 9.0 Hz, 2H), 7.29 (d, J = 9.0 Hz, 2H), 7.96 (t, J = 9.0 Hz, 4H); ^{31}P{^{1}H} NMR (THF-d_8, 162 MHz) δ 7.8 (d, J = 33 Hz), 25.1 (d, J = 33 Hz); ^{19}F{^{1}H} NMR (THF-d_8, 376 MHz) δ -61.3; Anal. Calcd. for $C_{45}H_{40}F_3FeIO_4P_2Pd$: C, 51.33; H, 3.83. Found: C, 51.17; H, 3.61.

Synthesis of (DPPF-CF_3)Pd(C_6H_4-*p*-CF_3)I (7). In a glovebox, THF (4 mL) was added to a mixture of 1,1′-bis(di(4-trifluoromethylphenyl)-phoshino)ferrocene (130 mg, 0.262 mmol) and (TMEDA)Pd(C_6H_4-*p*-CF_3)I (217 mg, 0.262 mmol) at room temperature. After stirring for 5 min at room temperature, the solvents were removed under reduced pressure until the solvents was about 2 mL. The reaction mixture was then added dropwise at room temperature to vigorously stirred pentane (20 mL) to give yellow precipitate. The resulting yellow powder was isolated by filtration through a glass fritted funnel (290 mg, 92%). ^{1}H NMR (THF-d_8, 500 MHz) δ 3.85 (q, J = 1.5 Hz, 2H), 4.36 (t, J = 1.5 Hz, 2H), 4.67 (s, 2H), 4.86 (q, J = 1.5 Hz, 2H), 6.72 (d, J = 7.0 Hz, 2H), 7.06 (t, J = 7.5 Hz, 2H), 7.56 (d, J = 7.0 Hz, 4H), 7.58−7.64 (m, 4H), 7.84 (d, J = 7.5 Hz, 4H), 8.27 (t, J = 7.5 Hz, 4H); ^{31}P{^{1}H} NMR (THF-d_8, 162 MHz) δ 10.4 (d, J = 34 Hz), 25.9 (d, J = 34 Hz); ^{19}F{^{1}H} NMR (THF-d_8, 376 MHz) δ −63.1 (s, 6F), −62.8 (s, 6F), −61.8 (s, 3F); Anal. Calcd. for $C_{45}H_{28}F_{15}FeIP_2Pd$: C, 44.86; H, 2.34. Found: C, 44.94; H, 2.28.

Synthesis of Potassium *N*-Methylanilide Derivatives (KNMe(C_6H_4-*p*-Me), KNMePh, KNMe(C_6H_4-*p*-OMe)). In a drybox, a solution of *N*-methylaniline derivatives (417 μL, 3.30 mmol of HNMe(C_6H_4-*p*-Me) in 6 mL of toluene, 119 μL, 1.10 mmol of HNMePh in 0.5 mL of toluene, 453 mg, 3.30 mmol of HNMe(C_6H_4-*p*-OMe) in 6 mL of toluene) was added to a solution of potassium bis(trimethylsilyl)-amide (599 mg, 3.0 mmol in 15 mL of toluene for HNMe(C_6H_4-*p*-Me, 200 mg, 1.0 mmol in 5 mL of toluene and 5 mL of pentane for HNMePh, 599 mg, 3.0 mmol in 15 mL of toluene for HNMe(C_6H_4-*p*-OMe)) at room temperature. The resulting suspension was stirred at room temperature for 1 to 1.5 h, and the solid product was isolated by filtration through a glass fritted funnel (437 mg, 92% for KNMe(C_6H_4-*p*-Me), 137 mg, 94% for KNMePh, 512 mg, 97% for KNMe(C_6H_4-*p*-OMe)). KNMePh and KNMe(C_6H_4-*p*-OMe) were reprecipitated from THF by addition of pentane to remove small amounts of remaining potassium bis(trimethylsilyl)amide. **KNMe(C_6H_4-*p*-Me)**: ^{1}H NMR (THF-d_8, 400 MHz) δ 2.01 (s, 3H), 2.75 (s, 3H), 5.94 (d, J = 8.4 Hz, 2H), 6.56 (d, J = 8.4 Hz, 2H); ^{13}C{^{1}H} NMR (THF-d_8, 100 MHz) δ 20.8, 38.3, 110.8, 111.63, 130.9, 162.1; **KNMePh**: ^{1}H NMR (THF-d_8, 400 MHz) δ 2.76 (s, 3H), 5.66 (t, J = 6.4 Hz, 1H), 6.00 (d, J = 8.4 Hz, 2H), 6.70 (dd, J = 6.4, 8.4 Hz, 2H); **KNMe(C_6H_4-*p*-OMe)**: ^{1}H NMR (THF-d_8, 400 MHz) δ 2.75 (s, 3H), 3.52 (s, 3H), 5.91 (d, J = 8.4 Hz, 2H), 6.47 (d, J = 8.4 Hz, 2H).

Generation of (L)Pd(C_6H_4-4-CF_3)NMe(C_6H_4-4-Me) (8, 11, 12; L = DPPF, DPPF-OMe, DPPF-CF_3). In drybox, (L)Pd(C_6H_4-4-CF_3)I

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(9.3 mg, 10 μmol of **5** for **8**, 10.5 mg, 10.0 μmol of **6** for **11**, 12.0 mg, 10.0 μmol of **7** for **12**) was placed into a 4 mL vial and was dissolved in THF-d_8 (300 μL). The solution was transferred to screw-capped NMR tube and the NMR tube was removed from drybox. A solution of potassium *N*-methyltoluidide (0.150 M in THF-d_8, 100 μL, 15.0 μmol) was added at −78 °C with a gastight syringe sealed with Teflon tape to the solution of the palladium complex. After shaking the mixture, the NMR tube was quickly placed into the pre-cooled NMR spectrometer probe at −45 °C. The palladium amido complexes were characterized by NMR spectroscopy at −45 °C. **8**: ^{1}H NMR data of tolyl methyl and *N*-methyl groups (THF-d_8, 500 MHz, −45 °C) δ 1.95 (s, 3H, Tol-Me), 2.16 (s, 3H, NMe); ^{31}P{^{1}H} NMR (THF, 162 MHz, −45 °C) δ 9.3 (br), 24.3 (d, J = 38 Hz); ^{19}F{^{1}H} NMR (THF, 376 MHz, −45 °C) δ −60.4 (s); **11**: ^{1}H NMR data of tolyl methyl and *N*-methyl groups (THF-d_8, 500 MHz, −45 °C) δ 1.92 (s, 3H, Tol-Me), 2.14 (s, 3H, NMe); ^{31}P{^{1}H} NMR (THF, 162 MHz, −45 °C) δ 6.5 (br), 21.4 (d, J = 37 Hz); ^{19}F{^{1}H} NMR (THF, 376 MHz, −45 °C) δ −60.3 (s); **12**: ^{1}H NMR data of tolyl methyl and *N*-methyl groups (THF-d_8, 500 MHz, −45 °C) δ 1.95 (s, 3H, Tol-Me), 2.30 (s, 3H, NMe), 3.91 (s, 1H), 4.34 (s, 1H), 4.47 (s, 1H), 4.52 (s, 1H), 4.56 (s, 1H), 4.60 (s, 1H), 4.71 (s, 1H), 5.13 (s, 1H), 5.62 (brs, 1H), 6.38 (br, 2H), 6.56 (br, 2H), 6.76 (br, 1H), 7.06 (br, 4H), 7.32 (br, 4H), 7.60 (br, 2H), 8.05 (br, 4H), 8.41 (br, 4H); ^{31}P{^{1}H} NMR (THF, 162 MHz, −45 °C) δ 6.3 (d, J = 39 Hz), 24.3 (d, J = 39 Hz); ^{19}F{^{1}H} NMR (THF, 376 MHz, −15 °C) δ −60.9 (s, 3F), −61.9 (s, 3F), −62.0 (s, 3F), −62.1 (s, 3F), −62.3 (s, 3F).

Generation of (DPPF)Pd(C_6H_4-4-CF_3)NMeAr (Ar = Ph (9), C_6H_4-4-OMe (10)). In a drybox, the potassium amide (2.2 mg, 15 μmol of KNMePh for **9**, 2.6 mg, 15 μmol of KNMe(C_6H_4-4-OMe) for **10**) was placed into a 4 mL vial and was dissolved in 300 μL of THF-d_8. The solution was transferred to a screw-capped NMR tube, and the NMR tube was removed from the drybox. A solution of (DPPF)Pd(C_6H_4-4-CF_3)I (**5**; 50.0 μM in THF-d_8, 200 μL, 10.0 μmol) was added at −78 °C with a gastight syringe sealed with Teflon tape to the solution of potassium amide. After shaking the mixture, the NMR tube was quickly placed into the pre-cooled NMR spectrometer probe at −45 °C. The palladium amido complexes were characterized by NMR spectroscopy at −45 °C. **9**: ^{1}H NMR data of *N*-methyl group (THF-d_8, 500 MHz, −45 °C) δ 2.12 (s, 3H, NMe); ^{31}P{^{1}H} NMR (THF, 162 MHz, −45 °C) δ 9.8 (br), 24.1 (d, J = 37 Hz); ^{19}F{^{1}H} NMR (THF, 376 MHz, −15 °C) δ −60.6 (s); **10**: ^{1}H NMR data of *N*-methyl group (THF-d_8, 500 MHz, −45 °C) δ 2.07 (s, 3H, NMe); ^{31}P{^{1}H} NMR (THF, 162 MHz, −45 °C) δ 8.3 (br), 24.3 (d, J = 41 Hz); ^{19}F{^{1}H} NMR (THF, 376 MHz, −45 °C) δ −60.4 (s).

Synthesis of the Reductive Elimination Product (*p*-$CF_3C_6H_4$)NMe(C_6H_4-*p*-Me).[107] In a drybox, di-*tert*-butyl-(1′,2′,3′,4′,5′-pentaphenyl-1-ferrocenyl)phosphine (142 mg, 0.200 mmol), Pd(dba)$_2$ (57.5 mg, 0.100 mmol), and *t*-BuONa (577 mg, 6.00 mmol) were placed into a 20 mL vial. To the mixture were added at room temperature, toluene (5 mL), 4-bromobenzotrifluoride (0.700 mL, 5.00 mmol), and *N*-methyl-*p*-toluidine (0.759 mL, 6.00 mmol). The vial was sealed with a cap and removed from the drybox. The reaction mixture was stirred at 110 °C for 42 h. After cooling to room temperature, the reaction mixture was filtered through diatomaceous earth and washed with ether. Silica gel was added to the resulting solution, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography, eluting with 2.5% ether in hexane to give the product as a colorless liquid (1.19 g, 90%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.31 (s, 3H), 3.23 (s, 3H), 6.72 (d, J = 8.1 Hz, 2H), 7.02 (d, J = 8.6 Hz, 2H), 7.14 (d, J = 8.1 Hz, 2H), 7.35 (d, J = 8.6 Hz, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 20.7, 40.0, 113.8, 119.1 (q, $^2J_{CF}$ = 32.6 Hz), 123.0 (q, $^1J_{CF}$ = 270 Hz), 126.1 (q, $^3J_{CF}$ = 3.6 Hz), 130.5, 135.2, 145.1, 151.7; ^{19}F{^{1}H} NMR (THF, 376 MHz) δ -60.8; Anal. Calcd. for $C_{15}H_{14}F_3N$: C, 67.91; H, 5.32; N, 5.28. Found: C, 67.87; H, 5.33; N, 5.27.

Synthesis of the Reductive Elimination Products (*p*-$CF_3C_6H_4$)NMePh and (*p*-$CF_3C_6H_4$)NMe(C_6H_4-*p*-OMe).[108] In a drybox, *rac*-BINAP (156 mg, 0.250 mmol), Pd(dba)$_2$ (144 mg, 0.25 mmol), and *t*-BuONa (577 mg, 6.00 mmol) were placed into a 20 mL vial. To the mixture was added at room temperature, toluene (5 mL), 4-bromobenzotrifluoride (0.700 mL, 5.00 mmol), and *N*-methylaniline (0.759 mL, 7.00 mmol) or *N*-methyl-*p*-anisidine (823 mg, 6.00 mmol). The vial was sealed with a cap and removed from the glovebox. The reaction mixture was stirred at 110 °C for 24 h. After cooling to room temperature, the reaction mixture was filtered through diatomaceous earth, and the diatomaceous earth was washed with ether. Silica gel was added to the resulting solution, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography, eluting with 5% ether in hexane to give the product as a colorless liquid (983 mg, 78% for (*p*-$CF_3C_6H_4$)NMePh, 1.23 g, 87% for (*p*-$CF_3C_6H_4$)NMe(C_6H_4-*p*-OMe)). **(*p*-$CF_3C_6H_4$)NMePh**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.36 (s, 3H), 6.86 (d, J = 9.2 Hz, 2H), 7.18−7.23 (m, 3H), 7.39 (d, J = 8.0 Hz, 2H), 7.44 (d, J = 9.2 Hz, 2H); ^{19}F{^{1}H} NMR (THF-d_8, 376 MHz) δ -60.9; **(*p*-$CF_3C_6H_4$)NMe(C_6H_4-*p*-OMe)**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.29 (s, 3H), 3.84 (s, 3H), 6.71 (d, J = 9.0 Hz, 2H), 6.93−6.98 (m, 2H), 7.12−7.17 (m, 2H), 7.39 (d, J = 9.0 Hz, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 40.1, 55.2, 112.9, 115.1, 118.5 (q, $^2J_{CF}$ = 40.4 Hz), 125.1 (q, $^1J_{CF}$ = 336 Hz), 126.0 (q, $^3J_{CF}$ = 4.6 Hz), 127.9, 140.4, 152.0, 157.6; ^{19}F{^{1}H} NMR (THF, 376 MHz) δ -60.6; Anal. Calcd. for $C_{15}H_{14}F_3NO$: C, 64.05; H, 5.02; N, 4.98. Found: C, 64.20; H, 4.99; N, 4.92.

Synthesis of 1-Bromo-1′-bis(4-methoxyphenyl)phosphinoferrocene (15). A solution of *n*-butyllithium in hexane (2.5 M; 4.65 mL, 11.6 mmol) was added to a solution of 1,1′-dibromoferrocene (4.00 g, 11.6 mmol) in THF (120 mL) at −78 °C under nitrogen in a Schlenk flask. The resulting solution was stirred for 75 min at −78 °C. A solution of ClP(C_6H_4-*p*-OMe)$_2$ (3.26 g, 11.6 mmol) in THF (14 mL) was then added to the reaction mixture at −78 °C, and the solution was allowed to warm to room temperature and was stirred at room temperature for 2.5 h. The reaction mixture was poured into water (200 mL) and extracted with CH_2Cl_2. The combined organic layer was dried over Na_2SO_4, and evaporated under reduced pressure. The residue was purified by silica gel chromatography (CH_2Cl_2/hexane = 0−100%) to give the orange product in roughly 95% purity. This material was purified by recrystallization from hot *i*-PrOH to afford orange crystals (2.14 g, 36%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.82 (s, 6H), 4.01 (t, J = 2.0 Hz, 2H), 4.13 (t, J = 2.0 Hz, 2H), 4.32 (dd, J = 4.0, 2.0 Hz, 2H), 4.40 (dd, J = 4.0, 2.0 Hz, 2H), 6.88 (m, 4H), 7.29 (m, 4H); ^{31}P-{^{1}H} NMR ($CDCl_3$, 202 MHz) δ −19.9 (s); Anal. Calcd. For $C_{24}H_{22}O_2$-PBrFe: C, 56.62; H, 4.36. Found: C, 56.83; H, 4.15.

Synthesis of 1-Diphenylphosphino-1′-bis(4-methoxyphenyl)phosphinoferrocene (16, DPPF-OMe,Ph). A solution of *n*-butyllithium in hexane (2.5 M; 1.68 mL, 4.20 mmol) was added to a solution of 1-bromo-1′-diphenylphosphinoferrocene (1.80 g, 4.00 mmol) in THF (50 mL) at −78 °C under nitrogen in a Schlenk flask. The resulting solution was stirred for 1 h at −78 °C. A solution of ClP(C_6H_4-*p*-OMe)$_2$ (1.18 g, 4.2 mmol) in THF (10 mL) was then added to the reaction mixture at −78 °C, and the solution was stirred at room temperature for 2 h. The reaction mixture was poured into water (50 mL) and extracted with CH_2Cl_2. The combined organic layer was dried over Na_2SO_4 and evaporated under reduced pressure. The residue was purified by silica gel chromatography (CH_2Cl_2/hexane = 40−100%) to give an orange solid (1.65 g, 67%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.81 (s, 6H), 3.96−4.06 (br, 4H), 4.23−4.32 (br, 2H), 4.32−4.41 (br, 2H), 6.79−6.89 (br, 4H), 7.20−7.36 (br, 14 H); ^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz) −20.5 (s), −16.6 (s); Anal. Calcd for $C_{36}H_{32}O_2P_2Fe$: C, 70.37; H, 5.25. Found: C, 70.09; H, 5.51.

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Synthesis of 1-Diphenylphosphino-1′-bis(4-trifluoromethylphenyl)phosphino-ferrocene (17, DPPF-Ph,CF_3). A solution of *n*-butyllithium in hexane (2.5 M; 0.88 mL, 2.2 mmol) was added to a solution of 1-bromo-1′-diphenylphosphinoferrocene (898 mg, 2.00 mmol) in THF (50 mL) at −78 °C under nitrogen in Schlenk flask. The resulting solution was stirred for 1 h at −78 °C. $ClP(C_6H_4$-*p*-$CF_3)_2$ (824 mg, 2.31 mmol) was then added at −78 °C, and the solution was stirred at room temperature for 4 h. The reaction mixture was poured into water (50 mL) and extracted with CH_2Cl_2. The combined organic layer was dried over Na_2SO_4 and evaporated under reduced pressure. The residue was purified twice by silica gel chromatography (CH_2Cl_2/hexane = first 10%; second 0−10%) to give an orange solid (746 mg, 54%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.98 (m, 4H); 4.28 (m, 2H); 4.37 (m, 2H); 7.24−7.30 (m, 10H); 7.33−7.39 (m, 4H), 7.55 (d, J = 8.0 Hz, 4H); ^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz) δ −17.1 (s), −15.8 (s); ^{19}F{^{1}H} NMR ($CDCl_3$, 376 MHz) δ −62.1 (s); Anal. Calcd. For $C_{36}H_{26}F_6P_2Fe$: C, 62.63; H, 3.80. Found: C, 62.74; H, 3.84.

Synthesis of 1-Bis(4-methoxyphenyl)phosphino-1′-bis(4-trifluoromethylphenyl)-ferrocene (18, DPPF-OMe,CF_3). A solution of *n*-butyllithium in hexane (2.5 M; 0.85 mL, 2.1 mmol) was added to a solution of 1-bromo-1′-bis(4-methoxyphenyl)phosphinoferrocene (1.08 g, 2.12 mmol) in THF (40 mL) at −78 °C under nitrogen in Schlenk flask. The resulting solution was stirred for 1.5 h at −78 °C. A solution of $ClP(C_6H_4$-*p*-$CF_3)_2$ (820 mg, 2.3 mmol) in THF (5 mL) was then added to the reaction mixture at −78 °C, and the solution was stirred at room temperature for 1 h. The solvents were removed under reduced pressure, and the crude product was purified by silica gel chromatography (CH_2Cl_2/hexane = 50−100%) to give an orange solid (1.28 g, 83%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.81 (s, 6H), 3.98 (m, 2H), 4.02 (m, 2H), 4.22 (m, 2H), 4.36 (m, 2H), 6.85 (d, J = 8.5 Hz, 4H), 7.23 (m, 4H), 7.41 (t, J = 7.6 Hz, 4H), 7.56 (d, J = 7.8 Hz, 4H); ^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz) δ −20.7 (s), −15.5 (s); ^{19}F{^{1}H} NMR ($CDCl_3$, 376 MHz) δ −62.1 (s); Anal. Calcd. For $C_{38}H_{30}F_6O_2P_2Fe$: C, 60.79; H, 4.03. Found: C, 61.01; H, 4.17.

General Synthetic Procedure for (LL′)Pd(C_6H_4-*p*-CF_3)I (LL′ = DPPF-OMe,Ph (19a,b), DPPF-Ph,CF_3 (20a,b), and DPPF-OMe,CF_3 (21a,b)). In a glovebox, a solution of unsymmetrical ligand LL′ (Ph,-OMe-DPPF (**16**, 399 mg, 0.650 mmol), Ph,CF_3-DPPF (**17**, 171 mg, 0.248 mmol), or OMe,CF_3-DPPF (**18**, 810 mg, 1.11 mmol)) in THF (4 mL for **16**, 2 mL for **17**, 5 mL for **18**) was added at room temperature to a solution of (TMEDA)Pd(C_6H_4-*p*-CF_3)I (300 mg, 0.607 mmol for **19a**,**b**, 109 mg, 0.220 mmol for **20a**,**b**, or 495 mg, 1.00 mmol for **21a**,**b**) in THF (4 mL for **19a**,**b**, 2 mL for **20a**,**b**, or 5 mL for **21a**,**b**). After stirring for 5 min at room temperature, solvents were removed under reduced pressure until the volume was about 2 mL or 4 mL for **19a**,**b** or **21a**,**b**, or until the solvents were completely removed for **20a**,**b**. The resulting solution of **19a**,**b** and **21a**,**b** in THF or solution of **20a**,**b** in 2 mL of ether was added dropwise at room temperature to vigorously stirred pentane (18 mL) to give yellow precipitate. The resulting yellow powder was isolated by filtration through a glass fritted funnel to afford the product (561 mg, 93% for **19a**,**b**, 187 mg, 79% for **20a**,**b**, 928 mg, 82% for **21a**,**b**) as a mixture of 2 regioisomers (major: minor = 1.2:1 for **19a**,**b**; 2.7:1 for **20a**,**b**; 7.2:1 for **21a**,**b**; calculated from ^{1}H and ^{19}F{^{1}H} NMR spectra). **19a**,**b**: ^{1}H NMR data for Cp and OMe groups (THF-d_8, 400 MHz) major isomer, δ 3.72 (br, 2H), 3.74 (s, 3H), 4.20 (brs, 2H), 4.51 (brs, 2H), 4.73 (m, 2H); minor isomer, 3.67 (br, 2H), 3.85 (s, 3H), 4.16 (brs, 2H), 4.53 (brs, 2H), 4.75 (m, 2H); ^{31}P{^{1}H} NMR (THF-d_8, 162 MHz); major isomer, δ 9.1 (d, J = 33 Hz), 23.7 (d, J = 33 Hz); minor isomer, δ 6.3 (d, J = 34 Hz), 26.2 (d, J = 34 Hz); ^{19}F{^{1}H} NMR (THF-d_8, 376 MHz); major isomer, δ −62.7 (s, 6F), −61.6 (s, 3F); minor isomer, δ −63.0 (s, 6F), −61.7 (s, 3F); Anal. Calcd. for $C_{43}H_{36}F_3FeIO_2P_2Pd$: C, 52.02; H, 3.65. Found: C, 51.78; H, 3.53; **20a**,**b**: ^{1}H NMR data of the Cp groups (THF-d_8, 400 MHz); major isomer, δ 3.76 (q, J = 1.6 Hz, 2H), 4.28 (t, J = 1.6 Hz, 2H), 4.63 (brs, 2H), 4.85 (q, J = 1.6 Hz, 2H); minor isomer, 3.73 (q, J = 1.6 Hz, 2H), 4.26 (t, J = 1.6 Hz, 2H), 4.60 (brs, 2H), 4.82 (q, J = 1.6 Hz, 2H); ^{31}P{^{1}H} NMR (THF-d_8, 162 MHz); major isomer, δ 9.1 (d, J = 33 Hz), 25.7 (d, J = 33 Hz); minor isomer, δ 8.9 (d, J = 34 Hz), 25.0 (d, J = 34 Hz); ^{19}F{^{1}H} NMR (THF-d_8, 376 MHz); major isomer, δ −62.7 (s, 6F), −61.6 (s, 3F); minor isomer, δ −63.0 (s, 6F), −61.7 (s, 3F); Anal. Calcd. for $C_{43}H_{30}F_9FeIP_2Pd$: C, 48.32; H, 2.83. Found: C, 48.54; H, 2.75; **21a**,**b**: ^{1}H NMR data of the Cp and OMe groups (THF-d_8, 400 MHz); major isomer, δ 3.76 (s, 3H), 3.80 (q, J = 1.6 Hz, 2H), 4.29 (t, J = 1.6 Hz, 2H), 4.60 (brs, 2H), 4.76 (q, J = 1.6 Hz, 2H); minor isomer, 3.73 (q, J = 1.6 Hz, 2H), 3.86 (s, 3H), 4.23 (t, J = 1.6 Hz, 2H), 4.61 (brs, 2H), 4.80 (q, J = 1.6 Hz, 2H); ^{31}P{^{1}H} NMR (THF-d_8, 162 MHz); major isomer, δ 9.2 (d, J = 33 Hz), 23.9 (d, J = 33 Hz); minor isomer, δ 6.2 (d, J = 35 Hz), 25.0 (d, J = 35 Hz); ^{19}F{^{1}H} NMR (THF-d_8, 376 MHz); major isomer, δ −62.7 (s, 6F), −61.4 (s, 3F); minor isomer, δ −63.0 (s, 6F), −61.7 (s, 3F); major: minor = 7.2:1; Anal. Calcd. for $C_{45}H_{34}F_9FeIO_2P_2Pd$: C, 47.88; H, 3.04. Found: C, 47.79; H, 3.00.

General Procedure for Generation of (LL′)Pd(C_6H_4-4-CF_3)NMe-(C_6H_4-4-Me) (LL′ = DPPF-OMe,Ph (22a,b), DPPF-Ph,CF_3 (23a,b), and DPPF-OMe,CF_3 (24a,b)). In drybox, (LL′)Pd(C_6H_4-4-CF_3)I (LL′ = Ph,OMe-DPPF (**19a**,**b**, 9.3 mg, 10 μmol), Ph,CF_3-DPPF (**20a**,**b**, 10.7 mg, 10.0 μmol), or OMe-CF_3-DPPF (**21a**,**b**, 10.7 mg, 10.0 μmol) was placed into a 4-mL vial and was dissolved in THF-d_8 (300 μL). The solution was transferred to screw-capped NMR tube and the NMR tube was removed from the drybox. A potassium *N*-methyltoluidide solution (0.150 M in THF-d_8, 100 μL, 15.0 μmol) was added at −78 °C to the solution of palladium complex (with a gastight syringe sealed with Teflon tape). After shaking the mixture, the NMR tube was quickly placed into a pre-cooled NMR spectrometer probe (−45 °C). The palladium amido complexes were confirmed by NMR spectroscopy at −45 °C. **22a**,**b**: ^{1}H NMR data of tolyl methyl and *N*-methyl groups (THF-d_8, 500 MHz, −45 °C); major isomer, δ 1.95 (s, 3H, Tol-Me), 2.11 (s, 3H, NMe); minor isomer, δ 1.97 (s, 3H, Tol-Me), 2.14 (s, 3H, NMe); ^{31}P{^{1}H} NMR (THF, 162 MHz, −45 °C); major isomer, δ 8.9 (br), 21.4 (d, J = 38 Hz); minor isomer, δ 6.7 (br), 24.3 (d, J = 39 Hz); ^{19}F{^{1}H} NMR (THF, 376 MHz, −15 °C); major isomer, δ −60.5 (s); minor isomer, δ −60.6 (s); major: minor = 1.3:1; **23a**,**b**: ^{1}H NMR data of tolyl methyl and *N*-methyl groups (THF-d_8, 500 MHz, −45 °C); major isomer, δ 1.94 (s, 3H, Tol-Me), 2.24 (s, 3H, NMe); minor isomer, δ 1.96 (s, 3H, Tol-Me), 2.12 (s, 3H, NMe); ^{31}P{^{1}H} NMR (THF, 162 MHz, −45 °C); major isomer, δ 8.2 (br), 23.3 (d, J = 37 Hz); minor isomer, δ 7.6 (br), 25.3 (d, J = 40 Hz); ^{19}F{^{1}H} NMR (THF, 376 MHz, −15 °C); major isomer, δ −60.7 (s, 3F), −61.8 (s, 3F), −62.1 (s, 3F); minor isomer, δ −60.8 (s, 3F), −62.0 (s, 3F), −62.3 (s, 3F); major: minor = 3.0:1; **24a**,**b**: ^{1}H NMR data of tolyl methyl and *N*-methyl groups (THF-d_8, 500 MHz, −45 °C); major isomer, δ 1.95 (s, 3H, Tol-Me), 2.27 (s, 3H, NMe); minor isomer, δ 1.99 (s, 3H, Tol-Me), 2.16 (s, 3H, NMe); ^{31}P{^{1}H} NMR (THF, 162 MHz, −45 °C); major isomer, δ 8.0 (br), 20.5 (d, J = 37 Hz); minor isomer, δ 5.1 (br), 25.4 (d, J = 40 Hz); ^{19}F{^{1}H} NMR (THF, 376 MHz, −15 °C); major isomer, δ −60.6 (s, 3F), −61.8 (s, 3F), −62.1 (s, 3F); minor isomer, δ −60.8 (s, 3F), −62.0 (s, 3F), −62.3 (s, 3F); major: minor = 5.8:1.

Synthesis of H^{15}NMePh.[109,110] In a drybox, ^{15}N-aniline (410 mg, 4.40 mmol) and K_2CO_3 (1.20 g, 8.65 mmol) were placed into a 20 mL vial. After addition of THF (5 mL), the vial was sealed with a rubber septum and was removed from the drybox. Water (5 mL) and Boc_2O (Di-*tert*-butyl dicarbonate, 1.15 mL, 5.00 mmol) were added to the vial at room temperature. The resulting solution was stirred for 19 h at room temperature, and the reaction was quenched by addition of water. After extraction of the reaction mixture with CH_2Cl_2, and the combined organic phase was dried with Na_2SO_4. Removal of solvents afforded a white solid (1.02 g) of the BOC-protected 15N-labeled aniline. This solid was brought into a drybox and dissolved in DMF (4 mL). MeI

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(859 mg, 6.05 mmol) and NaH (148 mg, 6.17 mol) were sequentially added to the vial at room temperature. After stirring for 5 h at room temperature, the reaction mixture was poured into water. The reaction mixture was extracted with CH_2Cl_2, and the combined organic phase was dried with Na_2SO_4. The solvents were removed under reduced pressure. The crude product was purified by silica gel column chromatography (CH_2Cl_2/*n*-hexane = 20−50%) to give the *N*-BOC-*N*-methylaniline as a colorless liquid (812 mg). The colorless liquid was dissolved in CH_2Cl_2 (5 mL) under nitrogen. CF_3SO_3H (0.5 mL, 5.65 mmol) was added to the solution at room temperature. After stirring for 1.5 h at room temperature, the reaction mixture was poured into 1.0 M aqueous NaOH. The mixture was extracted with CH_2Cl_2, and the combined organic phase was dried with K_2CO_3. Evaporation of the solvents gave the desired ^{15}N-labeled *N*-methylaniline (245 mg, 52% overall) as a brown liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.84 (s, 3H), 3.52−3.88 (brd, J = 58 Hz, 1H), 6.63 (m, 2H), 6.72 (tt, J = 7.6, 1.2 Hz, 1H), 7.20 (m, 2H).

Synthesis of K^{15}NMePh. Same procedure for unlabeled potassium *N*-methylanilide was applied for the preparation. 65.0 mg, 44%, brown solid.

Generation of ^{15}N-Labeled Palladium Amido Species Bearing Unsymmetrical DPPF Derivatives (25a,b−27a,b). In a manner similar to the generation of symmetrical DPPF ligated palladium aryl amido derivatives with opposite direction of addition, **25a,b**−**27a,b** were generated by addition of a THF solution (50.0 μM, 0.200 mL, 10.0 μmol) of arylpalladium iodide complexes **19a,b**−**21a,b** to a THF solution of K^{15}NMePh (0.150 M, 15.0 μmol) in screw-capped NMR tubes at −78 °C. The ^{31}P NMR spectra were obtained at −45 °C or −35 °C for **27a,b**. **25a**,**b**: ^{31}P{^{1}H} NMR (THF, 162 MHz, −45 °C); major isomer, δ 9.5 (br), 21.2 (dd, $^2J_{PP}$ = 36 Hz, $^2J_{PN}$ = 49 Hz); minor isomer, δ 7.3 (br), 24.2 (dd, $^2J_{PP}$ = 37 Hz, $^2J_{PN}$ = 49 Hz); **26a**,**b**: ^{31}P{^{1}H} NMR (THF, 162 MHz, −45 °C); major isomer, δ 9.0 (brd), 23.3 (dd, $^2J_{PP}$ = 36 Hz, $^2J_{PN}$ = 47 Hz); minor isomer, δ 7.9 (br), 25.1 (dd, $^2J_{PP}$ = 39 Hz, $^2J_{PN}$ = 46 Hz); **27a**,**b**: ^{31}P{^{1}H} NMR (THF, 162 MHz, −35 °C); major isomer, δ 9.2 (brd), 20.3 (dd, $^2J_{PP}$ = 36 Hz, $^2J_{PN}$ = 48 Hz); minor isomer, δ 5.7 (br), 25.3 (dd, $^2J_{PP}$ = 39 Hz, $^2J_{PN}$ = 48 Hz).

Synthesis of 1-Bromo-1′-bis(4-trifluoromethylphenyl)phosphinoferrocene (28). A solution of *n*-butyllithium in hexane (1.6 M; 5.00 mL, 8.00 mmol) was added at −78 °C to a solution of 1,1′-dibromoferrocene (2.75 g, 8.00 mmol) in THF (30 mL) under nitrogen in a Schlenk flask. The resulting solution was stirred for 1 h at −78 °C. A solution of ClP(C_6H_4-*p*-CF_3)$_2$ (3.01 g, 8.43 mmol) in ether (10 mL) was then added to the reaction mixture at −78 °C and the solution was further stirred to room-temperature for 1 h. After this time, the reaction mixture was filtered through diatomaceous earth, and the diatomaceous earth was washed with ether. After addition of silica gel to the resulting solution, the solvents were removed under reduced pressure. The crude product was purified by silica gel chromatography (ether/hexane = 0−5%) to give the product as an orange-brown solid (3.83 g, 82%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.00 (t, J = 1.8 Hz, 2H), 4.13 (q, J = 1.7 Hz, 2H), 4.35 (t, J = 1.8 Hz, 2H), 4.49 (t, J = 1.7 Hz, 2H), 7.45 (t, J = 7.7 Hz, 4H), 7.59 (d, J = 7.7 Hz, 4H); ^{31}P{^{1}H} NMR ($CDCl_3$, 122 MHz) δ −17.3 (s); ^{19}F{^{1}H} NMR ($CDCl_3$, 376 MHz) δ −62.1 (s); Anal. Calcd. For $C_{24}H_{16}BrF_6FeP$: C, 49.27; H, 2.76. Found: C, 49.49; H, 2.52.

Synthesis of ClP(C_6D_5)$_2$.[10,105] A solution of *n*-butyllithium in hexane (9.50 mL, 15.2 mmol) was added at −78 °C to a solution of 4-bromobenzene-d_5 (2.45 g, 15.1 mmol) in THF (10 mL) under nitrogen in a two-necked flask. The resulting solution was stirred for 1 h at −78 °C to give white suspension of PhLi-d_5. A solution of Cl_2PNEt_2 (1.33 g, 7.60 mmol) in THF (10 mL) was then added to the reaction mixture at −78 °C, and the solution was stirred at room temperature for 16.5 h. A solution of HCl in 1,4-dioxane (4.0 M; 15.0 mL, 60.0 mmol) was added to the reaction mixture at room temperature, and the reaction mixture was stirred for 15 min at room temperature. After evaporation of solvents, 50 mL of ether was added. The resulting suspension was filtered through a glass filter under nitrogen, and the solvents were removed under reduced pressure. After the flask was brought into drybox, the crude product was dissolved in ether and filtered through diatomaceous earth. The resulting solution was evaporated under reduced pressure to give a yellow liquid (1.17 g, 33%) that contained a small amount of white solid. This material was used without further purification. ^{2}H NMR (C_6H_6, 46 MHz) δ 7.24 (s, 6D), 7.75 (s, 4D); ^{31}P{^{1}H} NMR ($CDCl_3$, 122 MHz) δ 82.1 (s).

Synthesis of Bromoanisole-d_7.[111] A solution of $(NH_4)_2Ce(NO_3)_6$ (11.0 g, 20.0 mmol) in CH_3CN (50 mL) was added at room temperature to a mixture of anisole-d_8 (2.02 g, 17.4 mmol), LiBr (1.74 g, 20.0 mmol), and CH_3CN (50 mL) under nitrogen in a two-necked flask. After stirring 1 h at room temperature, the reaction was quenched with water (100 mL). The reaction mixture was extracted with ether, and the combined organic phase was washed with saturated aqueous $NaHCO_3$, water, and brine. After drying with Na_2SO_4 and addition of silica gel, the solvents were removed under reduced pressure. The crude material was purified by silica gel chromatography (ether/hexane = 0−5%) to give the product as a colorless oil (2.65 g, 79%). ^{2}H NMR (CH_2Cl_2, 77 MHz) δ 3.74 (s, 3D), 6.84 (s, 2D), 7.43 (s, 2D).

Synthesis of ClP($C_6D_4OCD_3$)$_2$.[10,105] A solution of *n*-butyllithium in hexane (5.71 mL, 9.14 mmol) was added at −78 °C to a solution of 4-bromoanisole-d_7 (1.77 g, 9.14 mmol) in THF (10 mL) under nitrogen in a two-necked flask. The resulting solution was stirred for 1 h at −78 °C to give white suspension of 4-$D_3COC_6D_4Li$. A solution of Cl_2PNEt_2 (760 mg, 4.57 mmol) in THF (5 mL) was then added to the reaction mixture at −78 °C and the solution was stirred at room temperature for 3 h. A solution of HCl in 1,4-dioxane (4.0 M; 10.0 mL, 40.0 mmol) was added to the reaction mixture at room temperature, and the resulting mixture was stirred at room temperature for 15 min. After addition of pentane (30 mL), the resulting suspension was filtered through a glass filter under nitrogen, and the solvents were removed under reduced pressure. After the flask was brought into a drybox, the crude product was dissolved in ether and filtered through diatomaceous earth. The resulting solution was evaporated under reduced pressure to give a white solid (830 mg, 62%). This white solid was used without further purification. ^{2}H NMR (C_6H_6, 46 MHz) δ 3.10 (s, 6D), 6.65 (s, 4D), 7.53 (s, 4D); ^{31}P{^{1}H} NMR ($CDCl_3$, 122 MHz) δ 84.6 (s).

Synthesis of Deuterated Unsymmetrical DPPF Derivatives (16,-17-d_{10} and 18-d_{14}). From monophosphine **15** or **28**, the labeled DPPF derivatives were synthesized in a manner similar to **16**−**18** with *n*-BuLi and deuterated chlorodiphenylphosphine or chlorobis(4-methoxyphenyl)phosphine (**16**-d_{10}: 524 mg, 65%; **17**-d_{10}: 594 mg, 65%; **18**-d_{14}: 717 mg, 51%). **16**-d_{10}, ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.80 (s, 6H), 3.97 (q, J = 1.6 Hz, 2H), 4.00 (q, J = 1.6 Hz, 2H), 4.25 (t, J = 1.6 Hz, 2H), 4.36 (br, 2H), 6.83 (d, J = 8.0 Hz, 4H), 7.24 (t, J = 8.0 Hz, 4H); ^{2}H NMR (CH_2Cl_2, 77 MHz) δ 7.10−7.54 (m); ^{31}P{^{1}H} NMR (CH_2Cl_2, 202 MHz) δ −20.4 (s), −17.1 (s); **17**-d_{10}, ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.97 (s, 2H), 3.99 (s, 2H), 4.28 (s, 2H), 4.37 (s, 2H), 7.39 (t, J = 6.4 Hz, 4H), 7.55 (d, J = 8.0 Hz, 4H); ^{2}H NMR (CH_2Cl_2, 77 MHz) δ 7.10−7.70 (m); ^{31}P{^{1}H} NMR (CH_2Cl_2, 202 MHz) δ −17.6 (s), −15.8 (s); ^{19}F{^{1}H} NMR ($CDCl_3$, 376 MHz) δ −61.8 (s); **18**-d_{14}, ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.00 (s, 2H), 4.02 (s, 2H), 4.24 (s, 2H), 4.42 (s, 2H), 7.38 (d, J = 7.8 Hz, 4H), 7.54 (d, J = 7.8 Hz, 4H); ^{2}H NMR (CH_2Cl_2, 77 MHz) δ 3.76 (s, 3D), 6.90 (s, 2D), 7.31 (s, 2D); ^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz) δ −21.3 (s), −15.7 (s); ^{19}F{^{1}H} NMR ($CDCl_3$, 376 MHz) δ −63.6 (s).

Synthesis of Deuterated Arylpalladium Iodide Complexes 19a,b-d_{10}, 20a,b-d_{10}, and 21a,b-d_{14}. From TMEDA complex **1**, the arylpalladium iodide complexes **19a,b**-d_{10}, **20a,b**-d_{10}, and **21a,b**-d_{14} were synthesized by ligand exchange reactions similar to those need to synthesize **19a,b**−**21a,b** (**19**-d_{10}: 152 mg, 93%; **20**-d_{10}: 121 mg, 69%; **21**-d_{14}: 161 mg, 87%). **19**-d_{10}: ^{31}P{^{1}H} NMR (THF, 162 MHz); major

(111) Roy, S. C.; Guin, C.; Ranaa, K. K.; Maitib, G. *Tetrahedron Lett.* **2001**, *42*, 6941−6942.

isomer, δ 8.7 (d, J = 33 Hz), 23.7 (d, J = 33 Hz); minor isomer, δ 6.3 (d, J = 34 Hz), 26.6 (d, J = 34 Hz); $^{19}F\{^1H\}$ NMR (THF, 376 MHz); major isomer, δ −59.4 (s, 3F); minor isomer, δ −59.6 (s, 3F); major: minor = 1.4:1; **20-*d*$_{10}$**: $^{31}P\{^1H\}$ NMR (THF, 162 MHz); major isomer, δ 9.1 (d, J = 33 Hz), 25.4 (d, J = 33 Hz); minor isomer, δ 8.6 (d, J = 34 Hz), 25.0 (d, J = 34 Hz); $^{19}F\{^1H\}$ NMR (THF, 376 MHz); major isomer, δ −59.7 (s, 3F), −60.8 (s, 6F); minor isomer, δ −59.9 (s, 3F), −61.2 (s, 6F); major: minor = 3.1:1; **21-*d*$_{14}$**: $^{31}P\{^1H\}$ NMR (THF, 162 MHz); major isomer, δ 9.2 (d, J = 33 Hz), 23.0 (d, J = 33 Hz); minor isomer, δ 5.4 (d, J = 34 Hz), 25.0 (d, J = 34 Hz); $^{19}F\{^1H\}$ NMR (THF, 376 MHz); major isomer, δ −59.5 (s, 3F), −60.8 (s, 6F); minor isomer, δ −59.8 (s, 3F), −61.1 (s, 6F); major: minor = 4.0:1.

Generation of Deuterated Arylpalladium Amido Complexes 22a,b-*d*$_{10}$, 23a,b-*d*$_{10}$, and 24a,b-*d*$_{14}$. From **19a,b-*d*$_{10}$**, **20a,b-*d*$_{10}$**, and **21a,b-*d*$_{14}$**, the arylpalladium amido complexes **22a,b-*d*$_{10}$**, **23a,b-*d*$_{10}$**, and **24a,b-*d*$_{14}$** were generated by procedures similar to those used to generate unlabeled **22a,b**−**24a,b**. **22a,b-*d*$_{10}$**: $^{31}P\{^1H\}$ NMR (THF, 162 MHz, −45 °C); major isomer, δ 8.7 (br), 21.5 (d, J = 33 Hz); minor isomer, δ 6.8 (br), 23.9 (d, J = 34 Hz); **23a,b-*d*$_{10}$**: $^{31}P\{^1H\}$ NMR (THF, 162 MHz, −45 °C); major isomer, δ 8.2 (d, J = 33 Hz), 22.9 (d, J = 33 Hz); minor isomer, δ 7.2 (br), 25.3 (d, J = 34 Hz); **24a,b-*d*$_{14}$**: $^{31}P\{^1H\}$ NMR (THF, 162 MHz, −45 °C); major isomer, δ 8.0 (d, J = 33 Hz), 20.1 (d, J = 33 Hz); minor isomer, δ 4.6 (br), 25.4 (d, J = 34 Hz).

Kinetic Measurement of Reductive Elimination from Arylpalladium Amido Species 8−**12 Ligated by Symmetrical DPPF Derivatives.** A solution of PhOTf (ca. 0.1 mM) and $(PhO)_3P{=}O$ (ca. 0.1 mM) in THF-d_8 (ca. 50 μL) was placed into a glass capillary and the capillary was sealed with a flame under atmospheric pressure. This sample was used for deuterium lock and as an integration standard for $^{19}F\{^1H\}$ or $^{31}P\{^1H\}$ NMR measurements at low temperature. In the drybox, the potassium amides salt (79.6 mg (0.500 mmol) for KNMe(C_6H_4-4-Me), 14.5 mg (0.100 mmol) for KNMePh, 17.5 mg (0.100 mmol) for KNMe(C_6H_4-4-OMe)) and PPh_3 (525 mg (2.00 mmol) with KNMe(C_6H_4-4-Me), 105 mg (0.400 mmol) with KNMePh, KNMe(C_6H_4-4-OMe)) were placed into a 5 mL (for KNMe(C_6H_4-4-Me)) or a 1 mL (for KNMePh, KNMe(C_6H_4-4-OMe)) screw-capped volumetric flask and dissolved in THF. The solution was diluted to 5 mL or 1 mL to afford a solution that is 100 μM potassium amide and 400 μM PPh_3. A portion of this solution (110 μL) was transferred to screw-capped NMR tube containing the internal standard glass capillary described above. THF (300 μL for **8**−**10** and **12**, 100 μL for **11**) was then added to the NMR tube. After removing NMR tube from the drybox, the NMR tube was cooled in dry ice/acetone bath. In a drybox, LPd(C_6H_4-*p*-CF_3)I (L = ligand; 46.6 mg (50.0 μmol) for **5**, 26.3 mg (25.0 μmol) for **6**, 60.2 mg (50.0 μmol) for **7**) was weighed into a 1 mL screw-capped volumetric flask and dissolved in THF. The solution was diluted to 1 mL to afford a 50.0 μM (for **5** and **7**) or 25.0 μM (for **6**) THF solution of LPd(C_6H_4-*p*-CF_3)I (**5**−**7**). A portion of the palladium complex (200 μL (for **8**−**10** and **12**) or 400 μL (for **11**), 10.0 μmol) was removed from the volumetric flask with a 500 μL gastight syringe equipped with a stainless steel needle and PTFE tape. The needle was sealed with a rubber septum. After removing syringes from the drybox, the solution of LPd(C_6H_4-*p*-CF_3)I (**5**-**7**) was slowly added at −78 °C to the screw-capped NMR tube containing the solution of potassium amido and PPh_3. The NMR tube was left at −78 °C for 5 min, and then shaken several times. The NMR tube was quickly placed into precooled (−45 °C) NMR spectrometer probe. $^{19}F\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were measured at −45 °C to check for complete generation of the palladium amide prior to acquiring kinetic data. The decay of the palladium amido complexes **8**−**12** were monitored at −15 °C by the intensity of the $^{19}F\{^1H\}$ NMR resonance of the CF_3 group on the aromatic ring bound vs the PhOTf standard contained in the glass capillary. All measurements were performed with the multizg program of the Brucker DPX 400 spectrometer. The temperature of probe was elevated from −45 °C to −15 °C when the automated measurement started. The first 3 to 5 measurements collected while the temperature was stabilizing were deleted. $^{19}F\{^1H\}$ NMR spectra were obtained every 40 (for **8**, **11**), 71 (for **9**, **12**), or 134 (for **10**) seconds at −15 °C. All data sets were fit to a first-order exponential decay and contained data from more than 3 half-lives. After the kinetic measurement was complete, a solution of *n*-dodecane in toluene (ca. 0.05 M, 0.2 mL, ca. 10 μmol) was added to NMR tube, and the solution was well mixed. The resulting solution was analyzed by GC to determine the yield of amine from reductive elimination. Yields were determined with response factors measured with amine prepared independently and *n*-dodecane. All the reaction yields were greater than 85%. The following first-order rate constants were obtained. **8**: 13.5×10^{-4} s^{-1}, 12.6×10^{-4} s^{-1}, 12.3×10^{-4} s^{-1}; **9**: 2.97×10^{-4} s^{-1}, 2.96×10^{-4} s^{-1}, 2.89×10^{-4} s^{-1}; **10**: 37.6×10^{-4} s^{-1}, 37.2×10^{-4} s^{-1}, 38.4×10^{-4} s^{-1}; **11**: 4.08×10^{-4} s^{-1}, 4.26×10^{-4} s^{-1}, 4.13×10^{-4} s^{-1}; **12**: 27.2×10^{-4} s^{-1}, 27.1×10^{-4} s^{-1}, 26.8×10^{-4} s^{-1}. The average rate constants and standard deviations from the three kinetic measurements are summarized in Tables 1 and 2.

Kinetic Measurement of Reductive Elimination from Palladium Amido Species 22a,b−**24a,b Ligated by Unsymmetrical DPPF Derivatives as Ligand.** Reductive elimination from each set of two regioisomers **22a,b**−**24a,b** were monitored by $^{19}F\{^1H\}$ NMR spectroscopy at −15 °C as described for kinetic measurements of the reactions of compounds **8**−**12**. $^{19}F\{^1H\}$ NMR spectra were measured every 40 (for **22**) or 24 (for **23**,**24**) seconds at −15 °C. Yields of amine were determined as described for the reactions of compounds **8**−**12**. All reaction yields were greater than 95%. The following first-order rate constants were obtained. **22a** (minor isomer): 7.39×10^{-4} s^{-1}, 7.24×10^{-4} s^{-1}, 7.38×10^{-4} s^{-1}; **22b** (major isomer): 7.09×10^{-4} s^{-1}, 6.97×10^{-4} s^{-1}, 7.34×10^{-4} s^{-1}; **23a** (minor isomer): 47.8×10^{-4} s^{-1}, 44.8×10^{-4} s^{-1}, 45.0×10^{-4} s^{-1}; **23b** (major isomer): 9.50×10^{-4} s^{-1}, 8.50×10^{-4} s^{-1}, 9.05×10^{-4} s^{-1}; **24a** (minor isomer): 23.7×10^{-4} s^{-1}, 25.0×10^{-4} s^{-1}, 26.4×10^{-4} s^{-1}; **24b** (major isomer): 5.53×10^{-4} s^{-1}, 4.74×10^{-4} s^{-1}, 5.15×10^{-4} s^{-1}. The average rate constants and standard deviations from the three kinetic measurements are summarized in Chart 1.

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