Carbon−Carbon Bond-Forming Reductive Elimination from Arylpalladium Complexes Containing Functionalized Alkyl Groups. Influence of Ligand Steric and Electronic Properties on Structure, Stability, and Reactivity

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A series of arylpalladium alkyl complexes of the formula [(DPPBz)Pd(Ar)(R)] (DPPBz = 1,2-bis(diphenylphosphino)benzene; R = methyl, benzyl, enolate, cyanoalkyl, trifluoroalkyl, or malonate) has been prepared to reveal the influence of steric and electronic parameters on structure, stability, and reactivity. Arylpalladium enolate and cyanoalkyl complexes ligated by $EtPh_2P$, 1,1′-bis(diisopropylphosphino)ferrocene (D^iPrPF), and BINAP were prepared to evaluate the effect of the ancillary ligand. The coordination modes of the enolate and cyanoalkyl complexes were determined by spectroscopic methods, in combination with X-ray crystallography. In the absence of steric effects, the C-bound isomer was favored electronically if the enolate or cyanoalkyl group was located trans to a phosphine, and the O-bound isomer was favored if the enolate was located trans to an aryl group. The thermodynamic stability of the enolate and cyanoalkyl complexes was controlled by the steric properties of the enolate or cyanoalkyl group, and complexes with more substitution at the α-carbon were less stable. Arylpalladium methyl, benzyl, enolate, cyanoalkyl, and trifluoroethyl complexes underwent carbon−carbon bond-forming reductive elimination upon heating. Reductive elimination was faster from complexes with electron-withdrawing substituents on the palladium-bound aryl group and with sterically hindered alkyl groups. The electronic properties of the alkyl group had the largest impact on the rate of reductive elimination: electron-withdrawing groups on the α-carbon retarded the rate of reductive elimination. The rates of reductive elimination correlated with the Taft polar substituent constants of the groups on the carbon alpha to the metal.

Introduction

Studies of the reactivities of transition metal alkyl complexes have provided fundamental information about elementary organometallic reactions.[1,2] Most of these studies focus on complexes of methyl, higher alkyl, or aryl groups. However, synthetic applications usually involve alkyl groups containing functional groups.[3] The functional group can affect the rate of classic organometallic reactions that comprise catalytic cycles, such as oxidative addition, transmetalation, and reductive elimination.

For many transition metal-catalyzed reactions, reductive elimination is the step that forms the product. For example, carbon−carbon bond-forming reductive elimination forms the products of palladium-catalyzed couplings of aryl halides with a range of nucleophiles.[1−3] The electronic properties of the ligands such as alkyl, aryl, and enolate groups that undergo the reductive elimination process can be diverse.

The palladium-catalyzed coupling of aryl bromides with a variety of ketone enolates was first reported by several groups in 1997.[4−6] This method displays a high degree of regioselectivity and functional group tolerance. After the development of improved catalysts, the process now encompasses reactions of a variety of carbonyl compounds, nitriles, and nitroalkanes.[7−9]

These coupling processes have generated questions about the relationship between the functional group on the α-carbon and both the structure and stability of the complexes and the rates and mechanism by which they undergo carbon−carbon bond-forming reductive elimination. For example, the structures of transition metal

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enolates of monocarbonyl compounds include C-bound,[10−18] O-bound,[19−23] and η^3-oxaallyl[24−27] forms, and the structures of transition metal complexes of the anions of β-dicarbonyl compounds include κ^1-C- and κ^2-O,O-bound forms.[28] In addition, anions of nitriles can coordinate to a single metal center through the α-carbon[29−31] or the cyano-nitrogen,[32−36] or they can bridge two metals in a μ^2-C,N fashion.[37,38] These structures may interconvert and allow access to the one that undergoes reductive elimination, but some structures could be too stable (or unstable) to undergo the desired reaction.

Furthermore, the electronic effects of the coupling partners on the rate of reductive elimination are difficult to predict. Carbon−carbon bond-forming reductive eliminations from arylpalladium enolates and cyanoalkyls resemble C−C reductive eliminations from palladium dimethyl or arylpalladium methyl complexes, which occur with nonpolar transition states.[39−42] However, the pK_b values of enolates and cyanoalkyls[43−46] are more similar to those of amides than of alkyls. Thus, the electronic effects on C−C reductive eliminations from enolate and cyanoalkyl complexes may resemble those of C−N bond-forming reductive eliminations of amines.[47] The reductive elimination of amines from arylpalladium amido complexes is faster for complexes with more electron-rich amido groups and electron-poor aryl groups. If C−C elimination does depend on the electronic properties of the alkyl and aryl groups, it is unclear whether pairing of an electron-poor aryl group and an electron-rich enolate, cyanoalkyl, or haloalkyl would lead to faster reactions or if pairing of an electron-rich aryl group and an electron-poor alkyl group would lead to faster reactions. Few reductive eliminations from complexes with varied electronic properties of the carbon-bound ligand are known,[48] and theoretical predictions of electronic effects[49] on carbon−carbon bond-forming reductive elimination were never systematically evaluated experimentally.

A better knowledge of how the alkyl group's binding modes and steric and electronic properties influence reductive elimination should help to design improved catalysts for the palladium-catalyzed coupling of aryl halides with various nucleophiles and provide fundamental information about the mechanism of reductive elimination to form sp^2-sp^3 carbon−carbon bonds. In communication form, we reported preliminary mechanistic results on C−C bond-forming reductive elimination of α-aryl carbonyl compounds and α-aryl nitriles from isolated palladium(II) enolate and cyanoalkyl complexes.[50,51] The differences in reactivity between arylpalladium enolate and cyanoalkyl complexes suggested that the inductive effect of the alkyl group dictates the rates of reductive elimination.

We have thus considered whether Taft polar substituent constants[52] would predict the influence of the electronic properties of the α-functional group on the rate of reductive elimination. We report here the results of an extensive synthetic and mechanistic study of a series of arylpalladium complexes including those of methyl, benzyl, enolate, cyanoalkyl, trifluoroalkyl, and malonate groups. This study enabled us to generate some guiding principles to predict the effect of ligand steric and electronic properties on the structure, stability, and reactivity of complexes containing functionalized alkyl groups.

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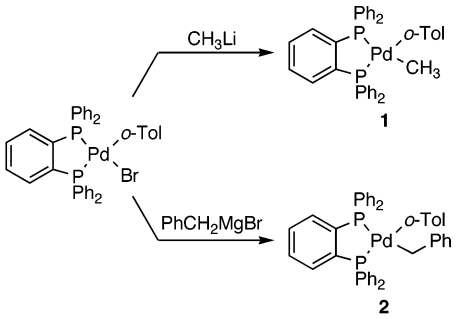
Scheme 1



Results

1. Synthesis and Characterization of Arylpalladium Complexes Containing Functionalized Alkyl Groups. A diverse spectrum of arylpalladium complexes of functionalized alkyl groups ligated by 1,2-bis(diphenylphosphino)benzene (DPPBz) was prepared. In addition, several arylpalladium enolate and cyanoalkyl complexes ligated by $EtPh_2P$, 1,1′-bis(di-isopropylphosphino)ferrocene (D^{i}PrPF), and racemic-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP) were prepared to evaluate the influence of the ancillary ligand on structure, stability, and reductive elimination rates. The syntheses of these complexes are organized by alkyl group.

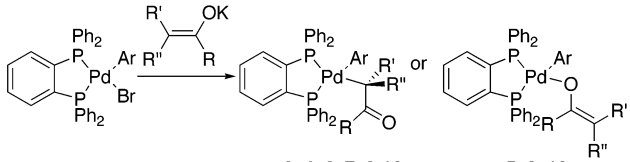
a. Arylpalladium(II) Methyl and Benzyl Complexes. The syntheses of arylpalladium methyl and benzyl complexes of 1,2-bis(diphenylphosphino)benzene (DPPBz) are shown in Scheme 1. Complexes **1** and **2** were prepared in 66% and 43% yield by addition of methyllithium or benzylmagnesium bromide to (DPPBz)-Pd(C_6H_4-2-Me)(Br) and were characterized by standard spectroscopic and analytical techniques. Complex **1** displayed a single ^{1}H NMR signal at δ 1.19 for the palladium-bound methyl group, which was split by the two inequivalent phosphine ligands (J_{H-P} = 2.1, 1.6 Hz). The ^{1}H NMR signals of the methylene protons in complex **2** also displayed ^{31}P−^{1}H coupling and were diastereotopic because of hindered rotation about the palladium−aryl bond.

b. Arylpalladium(II) Enolate Complexes. Arylpalladium enolate complexes ligated by DPPBz were prepared as summarized in Scheme 2. C- and O-bound arylpalladium enolates **3**−**23** were synthesized by addition of the potassium enolate to a toluene solution of the corresponding arylpalladium halide complex and isolated as analytically pure solids in 44−81% yield.

Arylpalladium enolate complexes bearing monophosphine ligands that were sufficiently stable to isolate in pure form, but sufficiently reactive to undergo reductive elimination of α-aryl ketones in high yield, were challenging to prepare. PPh_3-ligated arylpalladium complexes of ketones were generated at 0 °C but underwent reductive elimination of α-aryl ketone below room temperature. Enolate complexes ligated by $MePh_2P$ were too stable to undergo reductive elimination. However, enolate complexes ligated by ethyldiphenylphosphine ($EtPh_2P$) exhibited the required stability and reactivity. $EtPh_2P$-ligated arylpalladium enolate complexes **24** and **25** were prepared in 76 and 74% yield, respectively, as illustrated in Scheme 3.

Enolate connectivity was determined by NMR spectroscopic methods. For example, DPPBz-ligated C-bound

Scheme 2

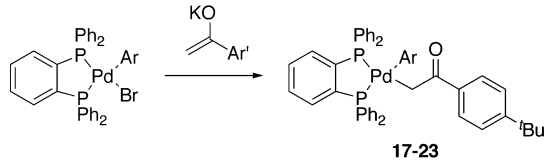


Ar = C_6H_4-4-*t*-Bu
3, R = C_6H_4-4-Me; R', R'' = H
4, R = C_6H_5; R' = H, R'' = Me
5, R = C_6H_5; R', R'' = Me

Ar = C_6H_4-2-Me
6, R = C_6H_4-4-Me; R', R'' = H
7, R = C_6H_5; R' = H, R'' = Me
8, R = C_6H_5; R', R'' = Me

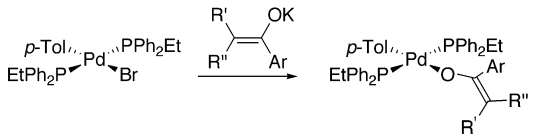
9, R = CH_2CH_3; R', R'' = H
10, R = $C(CH_3)_3$; R', R'' = H
11, R = C_6H_4-4-OMe; R', R'' = H
12, R = C_6H_4-4-CF_3; R', R'' = H

13, R = O-*t*-Bu; R', R'' = H
14, R = NMe_2; R', R'' = H
15, R = NEt_2; R', R'' = H
16, R, R'' = Ph; R' = H



17, Ar = C_6H_5
18, Ar = C_6H_4-4-Me
19, Ar = C_6H_4-4-CN
20, Ar = C_6H_4-4-Cl
21, Ar = C_6H_4-3-Cl
22, Ar = C_6H_4-4-OMe
23, Ar = C_6H_4-4-CF_3

Scheme 3



24, Ar = C_6H_4-4-Me; R', R'' = H
25, Ar = C_6H_5; R' = H, R'' = Me

3 displayed a single ^{1}H NMR signal for the methylene resonance at δ 3.88, which was split by the two inequivalent phosphines (J_{H-P} = 10.3, 6.9 Hz). In addition, the ^{13}C NMR spectrum displayed a doublet of doublets for the palladium-bound methylene carbon and a triplet at δ 202.7 (J_{C-P} = 4.1 Hz) for the carbonyl carbon. The carbonyl band in the IR spectrum was at 1601 cm^{-1}.

In contrast, the ^{1}H NMR spectrum for $EtPh_2P$-ligated O-bound **24** displayed two singlets at δ 4.90 and 4.99 for the two different enolate hydrogens. The ^{13}C NMR spectrum contained a singlet vinyl C−O resonance at δ 168.9 and a second vinyl resonance at δ 77.9. The ν(CO) band in the IR spectrum of **24** (1580 cm^{-1}) was slightly lower than that observed for C-bound **3**. The ^{31}P NMR spectrum of **24** displayed a single resonance at δ 18.5, which established the trans arrangement of the $EtPh_2P$ ligands.

The connectivities of DPPBz-ligated C-bound **6** and $EtPh_2P$-ligated O-bound **25** were confirmed by X-ray diffraction. The ORTEP diagram of **6** is shown in Figure 1; selected bond distances and bond angles are provided in Tables 1 and 2. The sum of the angles around the palladium center is 361.1°, demonstrating planarity at the metal with only minor distortions. The bond angles around the C(2) atom (118.4°, 122.9°, 118.8°) are consistent with sp^2 hybridization. The O(1)−C(2) bond distance of 1.23 Å concurs with that expected for a C−O double bond (1.20 Å).[53] The Pd(1)−C(1) distance of 2.15 Å is similar to the corresponding bond distance reported

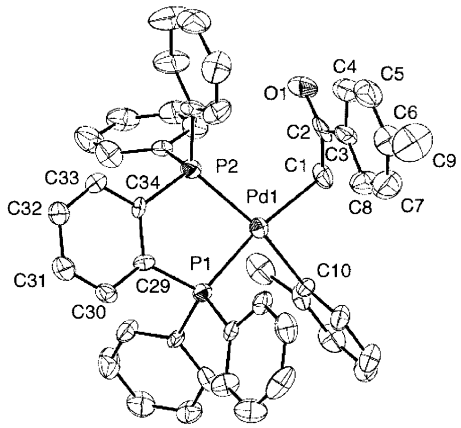


Figure 1. ORTEP diagram of (DPPBz)Pd($CH_2C(O)C_6H_4$-4-Me)(C_6H_4-2-Me)·1/2C_5H_{12} (**6**). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at 30% probability.

Table 1. Selected Intramolecular Bond Distances Involving the Non-Hydrogen Atoms of (DPPBz)Pd($CH_2C(O)C_6H_4$-4-Me)(C_6H_4-2-Me)·1/2C_5H_{12} (6)

atom	atom	distance (Å)	atom	atom	distance (Å)
Pd(1)	P(1)	2.258(2)	C(1)	C(2)	1.454(10)
Pd(1)	P(2)	2.323(2)	O(1)	C(2)	1.225(8)
Pd(1)	C(1)	2.145(7)	C(2)	C(3)	1.52(1)
Pd(1)	C(10)	2.054(7)	C(29)	C(34)	1.389(8)

Table 2. Selected Intramolecular Bond Angles Involving the Non-Hydrogen Atoms of (DPPBz)Pd($CH_2C(O)C_6H_4$-4-Me)(C_6H_4-2-Me)·1/2C_5H_{12} (6)

atom	atom	atom	angle (deg)	atom	atom	atom	angle (deg)
P(1)	Pd(1)	P(2)	85.81(7)	Pd(1)	P(1)	C(29)	109.7(2)
P(1)	Pd(1)	C(10)	87.3(2)	Pd(1)	P(2)	C(34)	107.0(2)
P(1)	Pd(1)	C(1)	170.2(2)	Pd(1)	C(1)	C(2)	109.4(5)
P(2)	Pd(1)	C(1)	102.7(2)	C(1)	C(2)	C(3)	118.4(8)
P(2)	Pd(1)	C(10)	166.5(2)	O(1)	C(2)	C(1)	122.9(8)
C(1)	Pd(1)	C(10)	85.3(3)	O(1)	C(2)	C(3)	118.8(8)

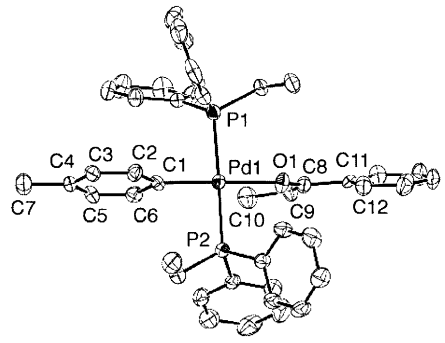


Figure 2. ORTEP diagram of $(PPh_2Et)_2Pd[OC(CHCH_3)C_6H_5](C_6H_4$-4-Me) (**25**). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at 30% probability.

for a C-bound palladium enolate of acetophenone,[13] and the C(1)−C(2) distance of 1.45 Å is consistent with a C−C single bond.[53]

An ORTEP diagram of **25** is shown in Figure 2. Selected bond distances and angles are included in Tables 3 and 4. The geometry about the palladium atom

Table 3. Selected Intramolecular Bond Distances Involving the Non-Hydrogen Atoms of $(PPh_2Et)_2Pd[OC(CHCH_3)C_6H_5](C_6H_4$-4-Me) (25)

atom	atom	distance (Å)	atom	atom	distance (Å)
Pd(1)	P(1)	2.328(2)	O(1)	C(8)	1.316(7)
Pd(1)	P(2)	2.311(2)	C(8)	C(9)	1.346(8)
Pd(1)	C(1)	2.008(6)	C(8)	C(11)	1.508(1)
Pd(1)	O(1)	2.089(4)	C(9)	C(10)	1.480(8)

Table 4. Selected Intramolecular Bond Angles Involving the Non-Hydrogen Atoms of $(PPh_2Et)_2Pd[OC(CHCH_3)C_6H_5](C_6H_4$-4-Me) (25)

atom	atom	atom	angle (deg)	atom	atom	atom	angle (deg)
P(1)	Pd(1)	P(2)	177.28(6)	Pd(1)	O(1)	C(8)	129.5(3)
P(1)	Pd(1)	O(1)	93.5(1)	O(1)	C(8)	C(9)	127.6(5)
P(1)	Pd(1)	C(1)	87.8(2)	O(1)	C(8)	C(11)	111.7(5)
P(2)	Pd(1)	O(1)	88.1(1)	C(9)	C(8)	C(11)	120.6(5)
P(2)	Pd(1)	C(1)	90.7(2)	C(8)	C(9)	C(10)	128.6(6)
O(1)	Pd(1)	C(1)	177.3(2)	C(8)	C(11)	C(12)	119.5(5)

is square planar, and the sum of the angles around the palladium atom is 360.1°. The bond angles around the C(8) atom (127.6°, 111.7°, 120.6°) and the C(8)−C(9)−C(10) angle of 119.5° are consistent with sp^2-hybridization of C(8) and C(9). The C(8)−C(9) bond distance of 1.35 Å corresponds to that expected for a C−C double bond.[53] The O(1)−C(8) bond distance of 1.32 Å for the predominantly single bond of the O-bound enolate is longer than the 1.23 Å O−C bond distance for the C-bound enolate **6**. The O−C bond distance in **25** is similar to the average O−C bond distance of 1.34 Å reported for the hexameric lithium enolate of pinacolone.[54] X-ray analysis also confirmed the connectivity of DPPBz-ligated O-bound **8**, but the structure refined poorly due to weak diffraction.

c. Arylpalladium(II) Cyanoalkyl Complexes. Arylpalladium cyanoalkyl complexes of DPPBz, 1,1′-bis(di-isopropylphosphino)ferrocene (D^{i}PrPF), racemic-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP), and $EtPh_2P$ were prepared as summarized in Scheme 4. Addition of the potassium salt of the nitrile anion to toluene solutions of arylpalladium halide complexes formed **26**−**34**, which were isolated as analytically pure solids. Some of these complexes were isolated as C-bound cyanoalkyl complexes, and others were isolated as *N*-bound keteniminate isomers.

The coordination mode of the cyanoalkyl and keteniminyl complexes was revealed by NMR and IR spectroscopic techniques. For example, DPPBz-ligated complex **29** was determined to be C-bound by the typical nitrile ^{13}C NMR resonance at δ 125.8 and nitrile IR band at 2170 cm^{-1}. In contrast, the ^{13}C NMR spectrum of D^{i}PrPF-ligated N-bound **31** displayed a doublet for the N=C resonance at δ 175.5 (J_{C-P} = 8.2 Hz), which is far downfield of that observed for **29** and closer to the N=C resonance of ketenimines.[55,56] The two strong bands at 1997 and 2186 cm^{-1} in the IR spectrum of **31** also resemble those of ketenimines.

The observation of a single phosphine per palladium-bound cyanoalkyl in the ^1H NMR spectrum of $EtPh_2P$-ligated **34** implied a dimeric structure, most likely with the nitrile bridging the metals by a μ^2-*C,N* coordination

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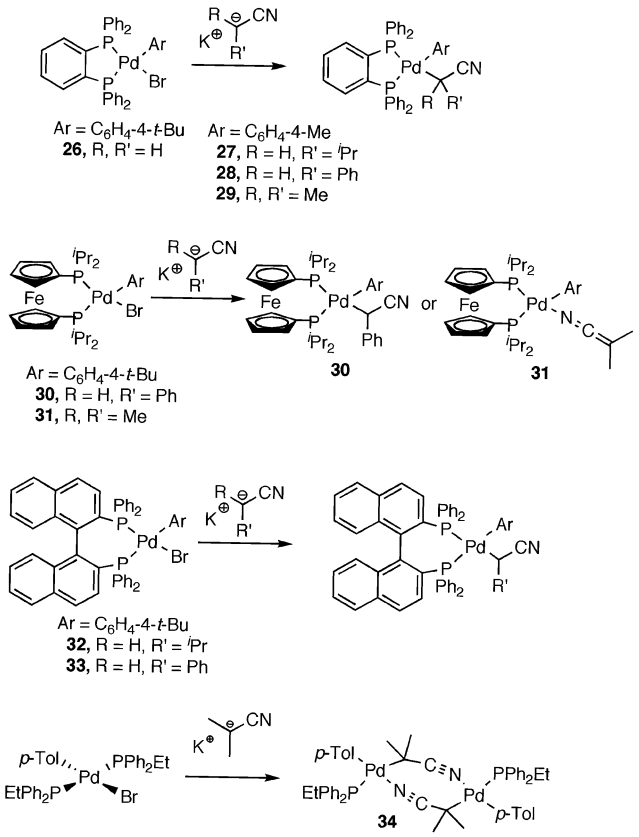
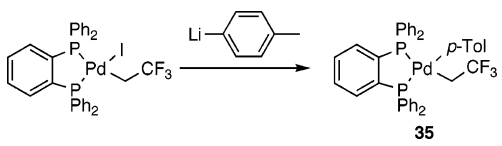
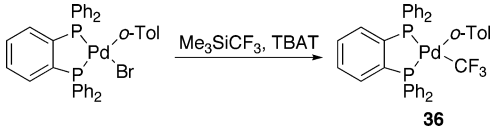
Scheme 4



Scheme 5



Scheme 6



mode. The ^{13}C NMR resonance of this bridging nitrile was located at δ 138.8, which is only slightly downfield from the ^{13}C NMR resonance of the nitrile in **29**, and the nitrile IR bands of **34** and **29** were at similar frequencies. The coordination modes of the isobutyronitrile anion in monomers **29** and **31** and dimer **34** were confirmed by X-ray crystallographic studies in previously communicated work.[51]

d. Arylpalladium(II) Trifluoroalkyl Complexes. Arylpalladium trifluoroethyl complex **35** was prepared in 46% yield by reaction of (DPPBz)Pd(CH_2CF_3)(I) with *p*-tolyllithium (Scheme 5). The trifluoroalkyl group was identified by $^{31}P-^{1}H$ and $^{19}F-^{1}H$ NMR coupling within the methylene resonance at δ 1.60 in the ^{1}H NMR spectrum and a doublet of doublets resonance at δ −48.6 ppm (J_{F-P} = 36.1, 18.8 Hz) in the ^{19}F NMR spectrum.

Arylpalladium trifluoromethyl complex **36** was prepared in 52% yield as illustrated in Scheme 6 by addition of an equimolar amount of tetrabutylammonium triphenyldifluorosilicate (TBAT) and excess (trifluoromethyl)trimethylsilane (Me_3SiCF_3) to a THF solution of (DPPBz)Pd(C_6H_4-2-Me)(Br). Similar procedures have been used for the nucleophilic addition of a trifluoromethyl group to ketones and aldehydes.[57−59] A doublet of doublets resonance at δ −18.3 in the ^{19}F NMR spectrum (J_{F-P} = 53.1, 17.7 Hz) and two doublets of quartets at δ 45.7 and 44.9 in the ^{31}P NMR spectrum demonstrated the presence of the trifluoromethyl group, and the structure was confirmed by X-ray diffraction. An ORTEP diagram of **36** is shown in Figure 3, and selected bond distances and angles are included in Tables 5 and 6. The Pd−CF_3 distances for the three independent molecules in the unit cell were 2.14−2.17 Å, which are comparable to the Pd−C distances of C-bound enolate **6** and cyanoalkyl complexes **29** and **34**.[51]

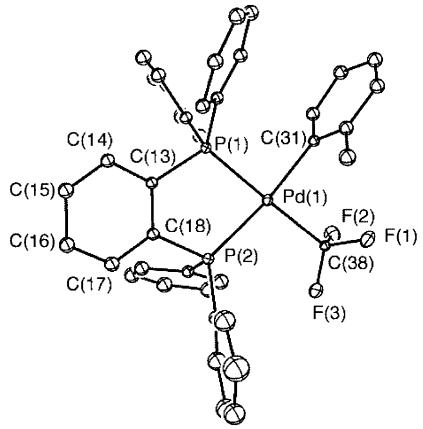


Figure 3. ORTEP diagram of (DPPBz)Pd(CF_3)(C_6H_4-2-Me)·2/3CD_2Cl_2 (**36**). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at 30% probability.

Table 5. Selected Intramolecular Bond Distances Involving the Non-Hydrogen Atoms of (DPPBz)Pd(CF_3)(C_6H_4-2-Me)·2/3CD_2Cl_2 (36)

atom	atom	distance (Å)	atom	atom	distance (Å)
Pd(1)	P(1)	2.2750(17)	C(13)	C(18)	1.390(5)
Pd(1)	P(2)	2.3141(12)	F(1)	C(38)	1.335(4)
Pd(1)	C(31)	2.085(4)	F(2)	C(38)	1.346(4)
Pd(1)	C(38)	2.166(4)	F(3)	C(38)	1.306(4)

Table 6. Selected Intramolecular Bond Angles Involving the Non-Hydrogen Atoms of (DPPBz)Pd(CF_3)(C_6H_4-2-Me)·2/3CD_2Cl_2 (36)

atom	atom	atom	angle (deg)	atom	atom	atom	angle (deg)
P(1)	Pd(1)	P(2)	85.01(6)	C(31)	Pd(1)	C(38)	89.90(14)
P(1)	Pd(1)	C(31)	87.79(11)	Pd(1)	P(2)	C(18)	107.35(13)
P(1)	Pd(1)	C(38)	176.77(10)	F(3)	C(38)	F(1)	107.7(3)
P(2)	Pd(1)	C(38)	97.25(10)	F(3)	C(38)	F(2)	107.1(3)
P(2)	Pd(1)	C(31)	172.71(10)	F(1)	C(38)	F(2)	106.2(3)

e. Arylpalladium(II) Malonate Complex. The arylpalladium complex of a C-bound dimethylmalonate anion **37** was prepared as shown in Scheme 7 by addition of the potassium enolate of isobutyrophenone to a toluene solution of (DPPBz)Pd(C_6H_4-2-Me)(Br), followed by addition of excess dimethyl malonate to the resulting enolate complex. The C-bound geometry of the

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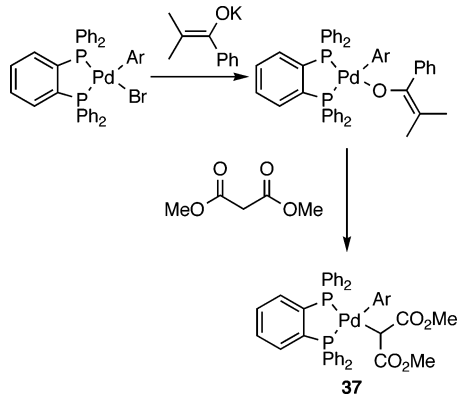
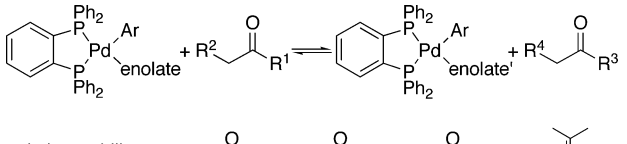
(58) Prakash, G. K. S.; Mandal, M.; Olah, G. A. *Org. Lett.* **2001**, *3*, 2847−2850.
(59) Prakash, G. K. S.; Krishnamurti, R.; Olah, G. A. *J. Am. Chem. Soc.* **1989**, *111*, 393−395.

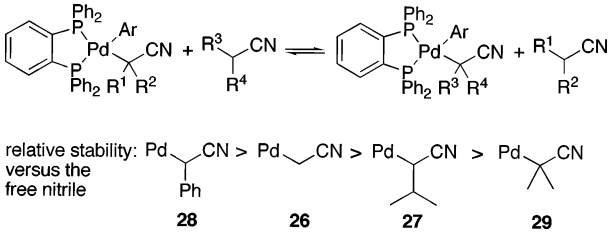
Scheme 7



Scheme 8



Scheme 9

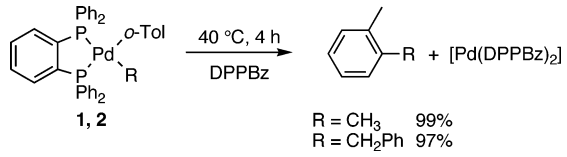


malonate complex was demonstrated by the doublet of doublets resonance at δ 3.78 (J_{H-P} = 9.6, 7.2 Hz) for the methine hydrogen of the C-bound malonate ligand.

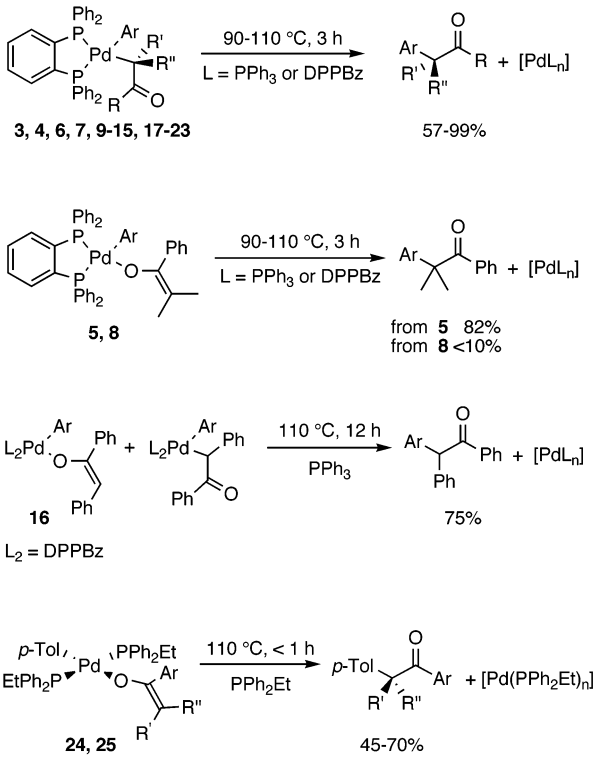
2. Relative Thermodynamic Stabilities of Enolate and Cyanoalkyl Complexes. We investigated the thermodynamic stability of DPPBz-ligated arylpalladium enolate and cyanoalkyl complexes (Schemes 8 and 9). The stability of the enolate complexes, relative to the corresponding carbonyl compounds, was determined by adding one carbonyl compound to the palladium enolate complex of another (Scheme 8). In some cases, catalytic amounts of potassium enolates were added to promote the rate of equilibration. Similar procedures were used to evaluate the stability of the cyanoalkyl complexes (Scheme 9). We were unable to establish conditions to compare the stability of palladium enolate complexes to the stability of cyanoalkyl complexes.

DPPBz-ligated arylpalladium enolates **6**, **9**, **13**, and **15** derived from acetophenone, 2-butanone, *tert*-butyl acetate, and diethylacetamide were similar in stability. The α-substituted palladium enolate **7** of propiophenone was less stable, and O-bound enolate **8** of isobutyrophenone was the least stable of the series. Thus, stability was controlled by the number of substituents at the α-carbon and not by the pK_a of the carbonyl compound. The stability of complex **16**, derived from the enolate of benzyl phenyl ketone, was similar to that of complexes **6**, **9**, **13**, and **15**, however. Apparently, the electronic effect of the α-phenyl group balances its unfavorable steric effect.

Scheme 10



Scheme 11

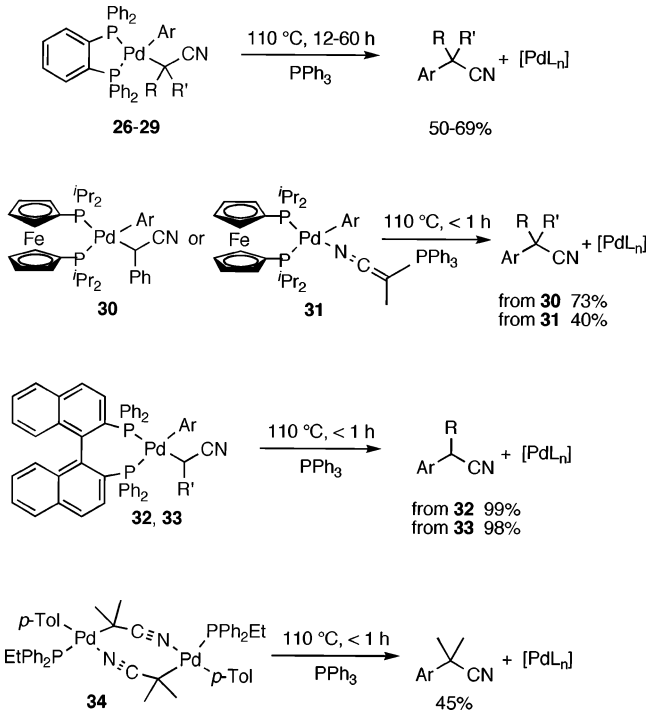


Experiments evaluating the thermodynamic stability of the cyanoalkyl complexes revealed a similar trend (Scheme 9). The stability of the arylpalladium complex of the anion of acetonitrile (**26**), relative to that of the free nitrile, was greater than the stability of the complex of the anion of isovaleronitrile (**27**), relative to free isovaleronitrile. The complex of the anion of isobutyronitrile (**29**) was the least stable. The cyanoalkyl complex derived from the stabilized anion of phenylacetonitrile (**28**) was the most stable of the series.

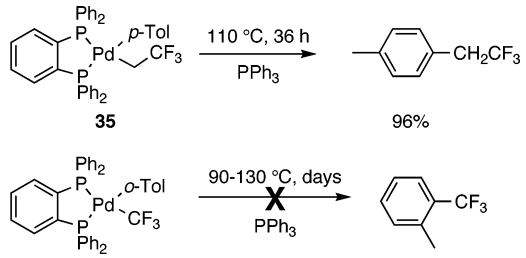
3. Carbon−Carbon Bond-Forming Reductive Elimination. a. Scope. The reductive eliminations of arylpalladium alkyl complexes containing varied functional groups α to the metal are displayed in Schemes 10−14. Reactions were conducted in C_6D_6 solutions at elevated temperatures in the presence of added DPPBz or PPh_3 to bind the released Pd(0) fragment that results from the reductive elimination process. Yields of coupled product were determined by ^{1}H NMR spectroscopy with an internal standard. $Pd(DPPBz)_2$ was the only phosphorus-containing product observed at the end of the reductive elimination reactions of the DPPBz-ligated complexes conducted in the presence of DPPBz. $(DPPBz)_2$-Pd(0) and the equilibrating combination of $Pd(PPh_3)_3$ and PPh_3 were the phosphorus-containing products at the end of reductive eliminations conducted with added PPh_3.[60] Reactions of $EtPh_2P$-ligated complexes con-

(60) Amatore, C.; Pflüger, F. *Organometallics* **1990**, *9*, 2276−2282.

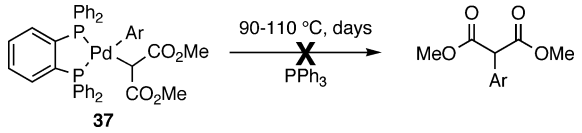
Scheme 12



Scheme 13



Scheme 14



ducted in the presence of $EtPh_2P$ formed $Pd(PPh_2Et)_4$ as the only phosphorus-containing product.

Arylpalladium methyl and arylpalladium benzyl complexes **1** and **2** underwent reductive elimination to form *o*-xylene and 2-methyldiphenylmethane in 99% and 97% yield in 2 and 4 h, respectively, upon heating at 40 °C in the presence of DPPBz (Scheme 10). Reactions conducted at 90 °C were complete in less than 10 min. These results provide an unusual example of reductive elimination from isolated arylpalladium alkyl or benzyl complexes. Eliminations from complexes of this type containing other phosphines are typically facile.[40]

Higher temperatures were required to induce reductive elimination from complexes possessing an enolate group in the α-position. C- and O-bound DPPBz-ligated arylpalladium enolates underwent reductive elimination upon thermolysis at 90−110 °C (Scheme 11). C-bound enolates **3**, **4**, **6**, **7**, **9**−**15**, and **17**−**23** underwent reductive elimination to form the α-aryl ketone, ester, or amide product in 57−99% yield in less than 3 h. O-bound palladium enolate **5**, containing a sterically unhindered palladium-bound aryl group, underwent reductive elimination to form α-aryl ketone in 82% yield within 3 h. However, O-bound palladium enolate **8**, containing a sterically hindered palladium-bound aryl group, generated less than 10% of aryl ketone upon thermolysis. The mixture of C- and O-bound isomers of complex **16**, derived from the enolate of benzyl phenyl ketone, underwent reductive elimination of aryl ketone in 75% yield in 12 h. Thermolysis of $EtPh_2P$-ligated O-bound arylpalladium enolates **24** and **25** in the presence of $EtPh_2P$ generated α-aryl ketones in 70 and 45% yield at 110 °C in less than 1 h.

Complexes of both C- and N-bound cyanoalkyls also underwent reductive elimination at elevated temperatures to form α-aryl nitriles (Scheme 12). However, the yields of coupled product for reductive elimination from DPPBz-ligated, C-bound arylpalladium cyanoalkyls **26**−**29** were lower and reaction times were longer than those of reductive elimination from similar arylpalladium methyl, benzyl, and enolate complexes. Reductive elimination of α-aryl nitrile from complexes **26**−**29** occurred in only 50−69% yield and required 12−60 h. In contrast, elimination from the more sterically crowded D^{i}PrPF- and BINAP-ligated, C-bound arylpalladium cyanoalkyls **30**, **32**, and **33** generated α-aryl nitriles in higher yields (73−99%) and shorter reaction times (<1 h). Elimination of α-aryl nitrile from D^{i}PrPF-ligated N-bound cyanoalkyl **31** and from PPh_2Et-ligated C,N-bridged dimer **34** was complete in less than 1 h, but coupled product was observed in only 40 and 45% yield, respectively.

DPPBz-ligated arylpalladium trifluoroethyl complex **35** underwent reductive elimination to form 1-methyl-4-(2,2,2-trifluoroethyl)benzene in 96% yield in 36 h upon heating at 110 °C (Scheme 13). However, DPPBz-ligated arylpalladium trifluoromethyl complex **36** did not undergo reductive elimination at any temperature or time. Complex **36** was stable for days at temperatures up to 130 °C.

In addition, arylpalladium malonate complex **37** did not undergo reductive elimination upon thermolysis (Scheme 14). This complex generated PPh_3- and DPPBz-ligated Pd(0) after 4 days at 110 °C, but no arylmalonate was formed. Biphenyl and toluene were the major organic products.

b. Mechanism. The reaction orders in metal and ligand were determined from kinetic experiments conducted with DPPBz-ligated arylpalladium enolate **6**. The rate constants derived from first-order plots of reactions conducted with different initial concentrations of **6** were independent of the initial concentrations of **6**, confirming a first-order dependence on the metal complex. Observed rate constants for reactions conducted with a 0.01 mM concentration of **6** and concentrations of DPPBz ranging from 0.02 to 0.2 mM were independent of the concentration of DPPBz.

To assess whether a portion of the chelating phosphine dissociated from the metal during the reductive elimination process, we evaluated reductive elimination from [(DPPE)Pd(*o*-Tol)($CH_2C(O)C_6H_4$-4-Me)] (**38**), which is analogous to **6** except that it contains the more flexible bis(diphenylphosphino)ethane ligand. If reductive elimination occurs by dissociation of one arm of the phos-

Table 7. Rates of Reductive Elimination from Arylpalladium Methyl, Benzyl, Enolate, Cyanoalkyl, and Trifluoroethyl Complexes [Pd(DPPBz)(Ar)(R)]

complex	Ar	R	$t_{1/2}$[a] (min)
1	C_6H_4-2-Me	CH_3	<5[b] (90 °C); 23 (40 °C)
2	C_6H_4-2-Me	CH_2Ph	<5[b] (90 °C); 57 (40 °C)
3	C_6H_4-4-*t*-Bu	$CH_2C(O)C_6H_4$-4-Me	39
4	C_6H_4-4-*t*-Bu	$CHCH_3C(O)C_6H_5$	18
5	C_6H_4-4-*t*-Bu	$OC(=CMe_2)C_6H_5$	~30[b]
6	C_6H_4-2-Me	$CH_2C(O)C_6H_4$-4-Me	31
7	C_6H_4-2-Me	$CHCH_3C(O)C_6H_5$	20
9	C_6H_4-2-Me	$CH_2C(O)CH_2CH_3$	43
10	C_6H_4-2-Me	$CH_2C(O)CMe_3$	26
11	C_6H_4-2-Me	$CH_2C(O)C_6H_4$-4-OMe	39
12	C_6H_4-2-Me	$CH_2C(O)C_6H_4$-4-CF_3	32
13	C_6H_4-2-Me	$CH_2C(O)O$-*t*-Bu	44
14	C_6H_4-2-Me	$CH_2C(O)NMe_2$	31
15	C_6H_4-2-Me	$CH_2C(O)NEt_2$	18
17	C_6H_5	$CH_2C(O)C_6H_4$-4-*t*-Bu	48
18	C_6H_4-4-Me	$CH_2C(O)C_6H_4$-4-*t*-Bu	53
19	C_6H_4-4-CN	$CH_2C(O)C_6H_4$-4-*t*-Bu	12
20	C_6H_4-4-Cl	$CH_2C(O)C_6H_4$-4-*t*-Bu	82
21	C_6H_4-3-Cl	$CH_2C(O)C_6H_4$-4-*t*-Bu	77
22	C_6H_4-4-OMe	$CH_2C(O)C_6H_4$-4-*t*-Bu	89
23	C_6H_4-4-CF_3	$CH_2C(O)C_6H_4$-4-*t*-Bu	32
26	C_6H_4-4-*t*-Bu	CH_2CN	~1200[c] (110 °C)
27	C_6H_4-4-Me	$CH(CHMe_2)CN$	~800[c] (110 °C)
28	C_6H_4-4-Me	CHPhCN	~1800[c] (110 °C)
29	C_6H_4-4-Me	CMe_2CN	~300[c] (110 °C)
35	C_6H_4-4-Me	CH_2CF_3	~720[c] (110 °C)

[a] Unless otherwise noted, half-lives were calculated from k_{obs} values, which were determined from kinetic measurements over 3 half-lives at 90 °C. [b] In these cases, the half-life was estimated from the time of reaction required to consume half of the starting complex at 90 °C. [c] In these cases, the half-life was estimated from the time of reaction required to consume half of the starting complex at 110 °C.

phine, then DPPBz-ligated **6** should undergo elimination at a slower rate than its DPPE analogue **38**. Complex **6** reacted roughly 2-fold faster ($t_{1/2}$ = 31 min) than **38** ($t_{1/2}$ = 72 min). Thus, reductive elimination occurs directly from the four-coordinate complex.

Preliminary mechanistic experiments on reductive elimination from $EtPh_2P$-ligated complexes suggested that elimination proceeds from a monophosphine complex that is formed by phosphine dissociation. However, the concentration of ligand added to the reactions of **24** and **25** affected both reaction rate and yield. The added ligand inhibited the reaction, but the rate was not simply inverse first-order in added ligand. This rate behavior complicated the interpretation of kinetic data. Thus, only qualitative studies were conducted on reductive elimination reactions of $EtPh_2P$-ligated complexes.

c. Relative Rates. To evaluate the effect of structural and electronic perturbations on C−C bond-forming reductive elimination in the absence of any competing processes, such as phosphine dissociation, enolate rearrangement, or cis/trans isomerization, we focused on reductive elimination from DPPBz-ligated arylpalladium complexes containing functionalized alkyl groups, which appear to eliminate the coupled product directly from the four-coordinate complex. The half-lives for reductive elimination from DPPBz-ligated arylpalladium methyl, benzyl, enolate, cyanoalkyl, and trifluoroethyl complexes are given in Table 7.

Kinetic data for reductive elimination from DPPBz-ligated arylpalladium methyl and benzyl complexes **1** and **2** and from C-bound DPPBz-ligated aryl palladium enolate complexes **3**, **4**, **6**, **7**, **9**−**15**, and **17**−**23** were obtained at 40 or 90 °C in toluene in the presence of excess DPPBz by monitoring the appearance of Pd(DPPBz)$_2$ by UV−vis spectroscopy. The half-lives in Table 7 for reactions of these complexes were derived from first-order rate constants measured over 3-half-lives. Kinetic data for reductive elimination from O-bound arylpalladium enolate **5**, C-bound arylpalladium cyanoalkyl complexes **26**−**29**, and arylpalladium trifluoroethyl complex **35** were obtained at 90−110 °C in benzene-d_6 in the presence of PPh_3 and an internal standard by monitoring the decay of the aromatic *t*-Bu or tolyl methyl resonances by ^{1}H NMR spectroscopy until the reaction was complete. In some cases, half-lives were estimated by integration of the resonances of the reactant relative to those of the internal standard at several time points during the reaction. Data from reaction of these complexes are presented as approximate values.

Discussion

1. Bonding Modes of Functionalized Alkyl Groups. Transition metal complexes of enolate, cyanoalkyl, and malonate anions can display several coordination modes, and both the anion and phosphine influenced the connectivity. With the exception of the complex of the enolate of benzyl phenyl ketone, enolate complexes derived from carbonyl compounds with α-methyl or methylene protons and DPPBz as phosphine were C-bound. Anions of aceto, primary, and benzylic nitriles bound to palladium ligated by the chelating ligands DPPBz, D^{i}PrPF, and BINAP were connected to the metal through the α-carbon and trans to a phosphine. $EtPh_2P$-ligated palladium enolate complexes displayed a geometry with the enolate located trans to the palladium-bound aryl group and favored the O-bound form. These data suggest that the C-bound isomer is favored electronically in these systems if the enolate or cyanoalkyl group is located trans to a phosphine, but the O-bound form of the enolate is favored if the enolate is located trans to an aryl group.

However, connectivity is more strongly controlled by steric effects than electronic influences. A C-bound enolate complex that would be analogous to a tertiary alkyl complex was less stable than its O-bound tautomer, regardless of the ancillary phosphine. DPPBz-ligated enolate complexes from ketones with α-methine protons were O-bound, and the enolate of benzyl phenyl ketone was a mixture of O- and C-bound isomers.

Steric properties also affected the connectivity of the cyanoalkyl complexes. For example, the anion of isobutyronitrile coordinated to palladium through the carbon atom when the metal was bound by DPPBz but coordinated through nitrogen when the metal was ligated by the more sterically demanding D^{i}PrPF. When a more labile phosphine, such as $EtPh_2P$, bound the metal, the nitrogen of the isobutyronitrile anion displaced a phosphine donor to create a bridging cyanoalkyl complex that contained the α-carbon trans to the phosphine.

The coordination mode of arylpalladium complexes of malonate anions was dictated by the structure of the phosphine. Arylpalladium fragments containing monophosphines bound the malonate anion in the κ^2-O,O-

bound form, even in the presence of additional phosphine.[61] Arylpalladium fragments bound by chelating ligands and an κ^2-O,O-bound malonate anion would be five-coordinate. Thus, the malonate anion was coordinated to palladium through the central carbon in an κ^1-binding mode when the metal was bound by the chelating DPPBz.

2. Relative Thermodynamic Stabilities of Enolate and Cyanoalkyl Complexes. The stability of DPPBz-ligated arylpalladium enolate and cyanoalkyl complexes with hydrogens or alkyl groups at the α-carbon was controlled by the number of substituents and not by the pK_a of the parent carbonyl or nitrile compound. Arylpalladium enolate complexes of ketones, esters, and amides with similar substitution at the α-carbon were similar in stability despite the different pK_a values of the carbonyl compounds. However, enolate and cyanoalkyl complexes containing an aryl group bound directly to the α position displayed enhanced stability relative to analogous complexes substituted with alkyl groups at the α position. The stabilizing effect of the electron-withdrawing aryl group overrode the unfavorable steric effect of the substitution at the α-carbon.

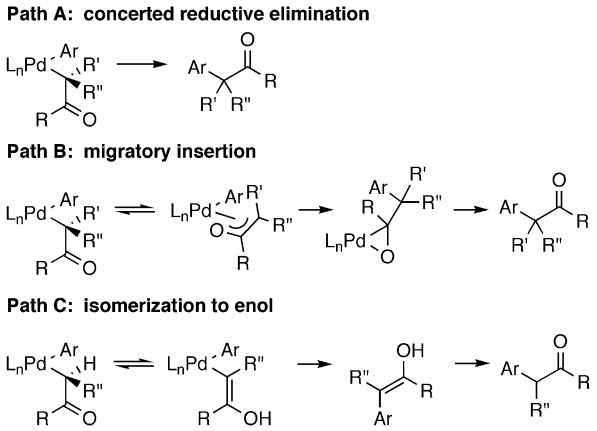
The relative ground state stabilities of arylpalladium cyanoalkyl complexes correlated closely with the relative rates of reductive elimination. Reductive elimination from the cyanoalkyl complex of the anion of phenylacetonitrile (**28**) required days at 110 °C, while that from the less stable complex of the anion of isobutyronitrile (**29**) was complete within 12 h. Thus, the ground state energetics of the arylpalladium complexes with functionalized alkyl groups contributes to the relative rates of reductive elimination.

However, ground state effects alone cannot explain the reactivity within groups of compounds, such as closely related enolates. The stabilities of arylpalladium enolates of ketones, esters, and amides, relative to the free carbonyl compounds, did not correlate with the reactivities of these complexes. The arylpalladium enolates of acetophenone (**6**) and diethylacetamide (**15**) were similar in stability and were more stable than the arylpalladium enolate of propiophenone (**7**). However, the enolate of propiophenone **7** underwent reductive elimination with a rate constant between that of the enolates **6** and **15**. In addition, complex **16**, derived from the enolate of benzyl phenyl ketone, underwent reductive elimination much more slowly than the palladium enolates of acetophenone **6** or propiophenone **7**, although the relative stability of this complex to the carbonyl compound was similar to that of **6**.

3. Mechanism. Carbon−carbon bond-forming reductive elimination was observed from arylpalladium methyl, benzyl, C- and O-bound enolate, C- and N-bound cyanoalkyl, and trifluoroethyl complexes ligated by various ancillary ligands. Discussion of the mechanism of reductive elimination from arylpalladium complexes of functionalized alkyl groups will focus on the results from studies of complexes ligated by DPPBz because the kinetic data for these reactions are the most complete.

Detailed kinetic studies of reductive elimination reactions of arylpalladium enolate **6** revealed a first-order dependence on [**6**] and a zero-order dependence on [DPPBz]. These data rule out association of the phosphine followed by reductive elimination from a five-coordinate complex.[62,63] A mechanism involving reductive elimination from a four-coordinate intermediate or three-coordinate intermediate formed by dissociation[41,42] of one arm of the chelate cannot be distinguished by kinetic data. However, complex **6**, which contains the more rigid chelating ligand, did not react slower than its DPPE analogue **38**, as would be expected if partial dissociation of the ligand occurred before reductive elimination. Thus, reductive elimination from DPPBz-ligated C-bound complexes containing functionalized alkyl groups most likely proceeds from the four-coordinate palladium complex.

Scheme 15



Several pathways can be envisioned for reductive elimination from four-coordinate Pd(II) enolate complexes (Scheme 15). In addition to concerted C−C reductive elimination (path A), coupling could occur by migratory insertion of the C=C unit of an O-bound enolate into the Pd−Ar bond (path B) or isomerization of a C-bound enolate to its enol tautomer, followed by favorable C(sp^2)−C(sp^2) reductive elimination (path C). If path B operated, O-bound enolates should react faster. If path C operated, enolates derived from isobutyrophenone should not undergo coupling.

The low yield of reductive elimination product from DPPBz-ligated O-bound **8**, containing a sterically hindered palladium-bound aryl group, and the high yields observed from the analogous C-bound arylpalladium enolates **6** and **7** disfavor path B. The high yield of reductive elimination product from O-bound **5**, containing a sterically unhindered palladium-bound aryl group, argues against the palladaenol intermediate in path C. Thus, products appear to form by the simple reductive elimination in path A.

4. Effect of Ancillary Ligand on Reductive Elimination. Reductive elimination is typically accelerated by the presence of ancillary ligands with increased steric and electron-withdrawing properties[1,2,64] and for complexes of chelating ligands with large bite angles (P−M−P angles).[65−69] The steric and electronic properties

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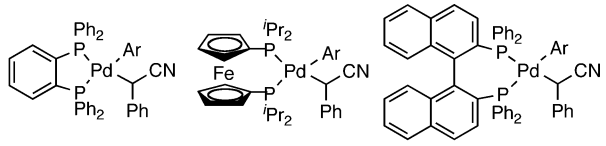
Chart 1. Effect of Bite Angle on Reaction Rates



	28	**30**	**33**
bite angle	86°	104°	92.7°
k_{rel}	1	60	60

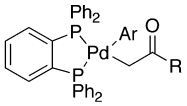
of the phosphine, along with its bite angle, affected the propensity of arylpalladium enolates and cyanoalkyls to undergo reductive elimination. These effects followed the expected trends, but the rates of the reactions were highly sensitive to these properties of the ancillary ligands. For example, arylpalladium enolate complexes ligated by PPh_3 underwent reductive elimination of α-aryl ketone at room temperature, while complexes of the more electron-donating $EtPh_2P$ were stable at room temperature and underwent reductive elimination upon thermolysis at 110 °C. Analogous enolate complexes ligated by $MePh_2P$ were too stable to undergo reductive elimination, even at elevated temperatures.

Complexes containing ligands with larger bite angles underwent faster reductive elimination. As illustrated in Chart 1 for arylpalladium complexes of cyanoalkyls, reductive elimination from D^{i}PrPF-ligated **30** was approximately 60 times faster than from DPPBz-ligated **28** despite the more electron-donating properties of D^{i}PrPF, and elimination from BINAP-ligated **33** was 60 times faster than from **28**. Similarly, reductive elimination from arylpalladium enolates ligated by DPPF (bite angle = 99.1°[70]) occurred at room temperature,[4] while enolates ligated by DPPBz were stable at room temperature and underwent reductive elimination only at elevated temperatures. An increase in the rate of reductive elimination with an increase in bite angle has also been observed during studies of C−C bond-forming reductive elimination of toluene[66] and C−S bond-forming reductive elimination of dialkyl sulfide from palladium(II) complexes.[71]

The complexes with larger bite angles contained smaller C−Pd−C angles. The bite angle of D^{i}PrPF-ligated arylpalladium cyanoalkyl **31** is larger than that of its DPPBz analogue **29** by 17.9°, while the angle between the coupling partners in **31** is smaller than that in **29** by 5°.[51] This smaller C−Pd−C angle, along with formation of a more stable Pd(0) product when the P−Pd−P angle is closer to that of the preferred linear geometry, likely accounts for the faster rates of reductive elimination.

5. Effects of the Alkyl Group on Reductive Elimination. a. Electronic Effects. At the outset of this work, it was difficult to predict how the electronic properties of the functionalized alkyl group and palladium-bound aryl group would affect the rate of reductive elimination. Often, the rate of reductive elimination is faster for complexes with less electron density at the metal center.[1,2] Thus, both electron-withdrawing functionalized alkyl groups and aryl groups could accelerate reductive elimination. However, theoretical studies on reductive elimination from dialkyl complexes predicted that complexes with more σ-donating covalent ligands would undergo reductive elimination from Pd(II) faster than those with less σ-donating covalent ligands.[49] Moreover, recent mechanistic studies on reductive elimination of arylamines from arylpalladium amido complexes have indicated that a complementary pairing of a nucleophilic amido group and an electrophilic aryl group dominates any variations in electron density at the metal due to the electronic properties of these two groups.[47]

Chart 2. Relative Rate Constants for Reductive Elimination and pK_a Values (DMSO) of the Conjugate Acids of the Enolate Groups



R =	pK_a	k_{rel}
C_6H_4-4-Me (**6**)	25.2	1.4
Et (**9**)	24.1	1
t-Bu (**10**)	27.7	1.7
C_6H_4-4-OMe (**11**)	25.7	1.1
C_6H_4-4-CF_3 (**12**)	22.7	1.4
O-*t*-Bu (**13**)	30	1
NMe_2 (**14**)	34-35	1.4

The rates of reductive elimination could correlate with the basicity of the functionalized alkyl ligand. This parameter effectively predicted the rates for reductive elimination of arylamines from arylpalladium complexes of amido ligands[47] that possess a range of proton basicities that overlap with those of many of the functionalized alkyl groups.[44] However, as illustrated in Chart 2, reductive elimination from arylpalladium enolate complexes occurred with rates that were independent of the type of enolate ligand, despite the differences in pK_a values between ketones, esters, and amides.[43,44,46] Instead, complexes of C-bound enolates most likely undergo reductive elimination at similar rates because the M−C bond is predominantly covalent, and the different carbonyl groups impart similar electronic effects on the α-carbon in this covalent bond.

Instead, we propose that the Taft polar substituent constants[52] effectively predict the influence of the electronic properties of the α-functional group on the rate of reductive elimination. The electronic properties of the functionalized alkyl group significantly influenced the rate of reductive elimination when electronic differences were larger than those between enolates. Arylpalladium methyl and benzyl complexes underwent reductive elimination much faster than the enolate complexes, while arylpalladium cyanoalkyl complexes underwent reductive elimination much slower than the enolate complexes.

Our quantitative kinetic data for reductive elimination from arylpalladium complexes of functionalized alkyl groups further support this correlation (Chart 3). Reductive elimination from arylpalladium benzyl complex **2** was measurably slower than from the analogous

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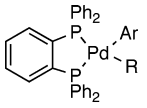
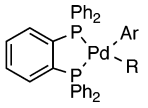
Chart 3. Correlation between Taft Substituent Constants and the Relative Rate Constants for Reductive Elimination

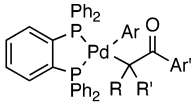


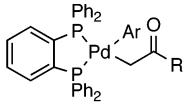


	σ*	k_{rel}(40 °C)
R = CH_3 (**1**)	0.00	2.5
R = CH_2Ph (**2**)	0.22	1

	σ*	k_{rel}(110 °C)
R = CH_3 (**1**)	0.00	>600
R = CH_2Ph (**2**)	0.22	>250
R = $CH_2C(O)Ar$ (**3**)	0.60	31
R = CH_2CF_3 (**35**)	0.92	1.7
R = CH_2CN (**26**)	1.30	1
R = CF_3 (**36**)	2.60	no rxn

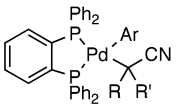
Chart 4. Steric Effects on the Reductive Eliminations





	k_{rel}(90 °)
R, R' = H (**3**)	1
R = H, R' = Me (**4**)	2.2

	k_{rel}(90 °C)
R = Et (**9**)	1
R = *t*-Bu (**10**)	1.7
R = NMe_2 (**14**)	1.4
R = NEt_2 (**15**)	2.4



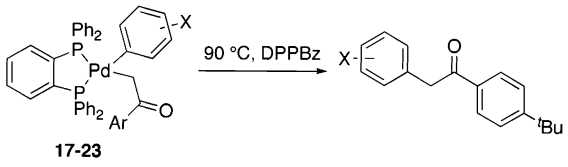
	k_{rel}(110 °C)
R, R' = H (**26**)	1
R = H, R' = *i*-Pr (**27**)	1.5
R, R' = Me (**29**)	4

methyl complex **1** when reactions were conducted at 40 °C. A benzyl group has a more positive Taft polar substituent constant (+0.22) than a methyl group (0.00). The benzyl complex reacted much faster than all the enolate complexes, and the substituent constant for a benzyl group is less positive than that for an acetophenone enolate (0.60). The arylpalladium enolates reacted faster than the arylpalladium trifluoroethyl complex **35**, which reacted faster than arylpalladium cyanoalkyl complex **26**. The value of the Taft polar substituent constant for a trifluoroethyl group (+0.92) lies between those for enolate and cyanoalkyl groups (1.30). The trifluoromethyl complex was the most stable, and a trifluoromethyl group has the highest Taft polar substituent constant (+2.60) of any of the groups in the complexes studied.

The effects of the electron-withdrawing groups were cumulative. For example, arylpalladium malonate complex **37**, which possesses two electron-withdrawing groups on the α-carbon, did not undergo C−C bond-forming reductive elimination at any temperature or time from DPPBz-ligated palladium. Reductive elimination of arylmalonates has been observed from complexes of malonate anions ligated by more sterically hindered phosphines.[61]

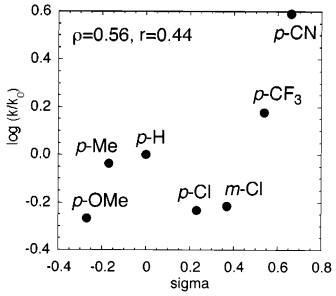
b. Steric Effects. Reductive elimination is typically faster from complexes with greater steric crowding around the metal center, presumably due to steric relief upon reductive elimination of the coupled product.[1,2] The rates for reductive elimination from DPPBz-ligated arylpalladium complexes with sterically distinct enolate and cyanoalkyl groups followed this trend (Chart 4), but the magnitude of the steric effect was surprisingly

Scheme 16



17-23

Free energy relationship for reductive elimination from **17-23**.



small. Reductive elimination from the arylpalladium propiophenone enolate **4** was faster than that from the less crowded acetophenone enolate **3** by a factor of only 2. Likewise, pinacolone enolate **10** reacted faster than 2-butanone enolate **9** by less than a factor of 2. Further unexpected, diethylacetamide enolate **15** reacted faster than dimethylacetamide enolate **14** by a similar factor of roughly 2, despite the more remote position of the substituents to the metal center. Reductive elimination from arylpalladium cyanoalkyl complexes was faster from complexes with more substituted cyanoalkyl groups, but the effect was again small. Reductive elimination from the complex of the anion of isobutyronitrile (**29**), which contains the most substituted cyanoalkyl group, was faster than elimination from the less hindered complex of the anion of isovaleronitrile (**27**) by a factor of 2−3, and elimination from the least sterically hindered arylpalladium complex of the anion of acetonitrile (**26**) was slower than elimination from **27** by less than a factor of 2. Steric effects can be important when the type of functional group is constant, but changes in the type of functional group dominated steric effects. For this reason, the Taft parameters predicted the trends in rate constants for reductive elimination from methyl, benzyl, enolate, cyanoalkyl, trifluoroalkyl, and malonate complexes.

6. Effect of Palladium-Bound Aryl Group. The results from kinetic studies on reductive elimination from DPPBz-ligated complexes **17**−**23**, which contain para- and meta-substituted aryl groups, are summarized by the Hammett plot in Scheme 16. Though scattered, the plot in Scheme 16 shows the general effect that reductive elimination occurred faster from arylpalladium enolate complexes containing palladium-bound aryl groups with electron-withdrawing substituents than from those with electron-donating substituents. For instance, the order of reaction rates for five of the para-substituted complexes was *p*-CN > *p*-CF_3 > *p*-H > *p*-Me > *p*-OMe. However, *p*- and *m*-Cl complexes **20** and **21** underwent reductive elimination more slowly than the parent phenyl complex, despite the chloride substituent's positive σ-value. In either case, the magnitude of this effect is much smaller than that for the reductive elimination of amines,[47] ethers,[72] and sulfides[71] and indicates a relatively small change in the charge on the aryl group between the ground and

transition state. The small magnitude of the electronic effect leads to the greater scatter in the free energy relationship.

Conclusions

The effect of ligand steric and electronic properties on the structure, stability, and reactivity of arylpalladium alkyl complexes containing varied functional groups alpha to the metal was evaluated. To reveal this effect, reactions of DPPBz-ligated complexes of methyl, benzyl, enolate, cyanoalkyl, trifluoroalkyl, and malonate groups were studied. Reactions of arylpalladium enolate and cyanoalkyl complexes of different ancillary ligands were also studied. These experiments led to the following conclusions.

(1) The identity of both the anion and phosphine influenced the connectivity of enolate, cyanoalkyl, and malonate complexes. Coordination to palladium through the α-carbon was favored electronically when the enolate, cyanoalkyl, or malonate anion was located trans to the phosphine, but increased steric properties of the ancillary ligand or anion induced other coordination modes.

(2) The thermodynamic stability of DPPBz-ligated arylpalladium enolates and cyanoalkyls was controlled by the steric properties of the alkyl group. However, complexes containing an aryl group directly bound to the α position displayed enhanced stability.

(3) Reductive elimination from DPPBz-ligated complexes occurred directly from the four-coordinate palladium complex by an intramolecular, concerted mechanism.

(4) Reductive elimination was faster from DPPBz-ligated arylpalladium complexes containing electron-poor palladium-bound aryl groups than from analogous complexes containing more electron-rich palladium-bound aryl groups, but the magnitude of this electronic effect was small.

(5) Reductive elimination was faster from DPPBz-ligated arylpalladium complexes with more sterically hindered enolate and cyanoalkyl groups than from analogous complexes containing less hindered enolate and cyanoalkyl groups, though the magnitude of this steric effect was small.

(6) Reductive elimination from arylpalladium enolate and cyanoalkyl complexes was accelerated by the presence of ancillary ligands with increased steric and electron-withdrawing properties and larger bite angles.

(7) The electronic properties of the alkyl group had the largest impact on reaction rates. Reductive elimination was markedly slower from complexes containing groups on the α-carbon of the functionalized alkyl group that have a stronger electron-withdrawing influence.

(8) The order of the relative rates of reductive elimination correlated with the magnitudes of the Taft polar substituent constants of the substituted alkyl groups. This parameter effectively predicted the influence of ligand electronic properties on the rate of reductive elimination because changes in the type of functional group α to the metal imparted a greater effect on the rate of reductive elimination than changes in the steric properties of the alkyl group.

Experimental Section

General Methods. All reactions were performed in a drybox or with Schlenk techniques under N_2. All solvents, except dichloromethane, were dried over Na/benzophenone. Dichloromethane was dried over calcium hydride. Unless otherwise stated, all reagents were used as received from commercial suppliers. Potassium hydride (KH) was freed from oil before use by washing three times with pentane and drying under vacuum. $Pd[P(o\text{-tol})_3]_2$ was prepared by a literature procedure.[73] Dimeric arylpalladium halide complexes that were ligated by $P(o\text{-tol})_3$ and used as synthetic intermediates were prepared by a procedure based on literature methods.[73] *trans*-$[Pd(PPh_3)_2(CH_2CF_3)(I)]$ was prepared by a procedure based on literature methods.[74] ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on 400 or 500 MHz spectrometers, with shifts reported in parts per million downfield from tetramethylsilane and referenced to residual protiated (^1H) or deuterated solvent (^{13}C). The aromatic regions of the $^{13}C\{^1H\}$ NMR spectra of 2-methylphenyl palladium complexes contained multiple overlapping signals and were not fully assigned. In these cases, $^{13}C\{^1H\}$ NMR data for the carbonyl or vinyl and alkyl resonances are provided as selected $^{13}C\{^1H\}$ NMR data. $^{31}P\{^1H\}$ NMR spectra were obtained at 121 or 162 MHz with shifts reported relative to an external 85% H_3PO_4 standard. UV−visible spectra were collected with a thermostated multicell block.

General Procedure for the Synthesis of [Pd(DPPBz)(Ar)(Br)]. Reaction of $Pd[P(o\text{-tol})_3]_2$ with 2.5 equiv of ArBr in benzene formed $\{Pd[P(o\text{-tol})_3](Ar)(\mu\text{-Br})\}_2$. The solution was filtered through Celite, and the product was isolated by precipitation after addition of pentane and used without further purification. Reaction of 2 equiv of 1,2-bis(diphenylphosphino)benzene (DPPBz) with $\{Pd[P(o\text{-tol})_3](Ar)(\mu\text{-Br})\}_2$ in benzene formed [Pd(DPPBz)(Ar)(Br)], which was isolated by precipitation after addition of pentane and used without further purification. The ^1H and $^{31}P\{^1H\}$ spectra for [Pd(DPPBz)(Ar)(Br)] complexes are as follows. [Pd(DPPBz)(C_6H_4-2-Me)(Br)]: ^1H NMR (CD_2Cl_2) δ 1.76 (s, 3H), 6.56 (t, 1.8 Hz, 1H), 6.70 (m, 4H), 6.94 (m, 1H), 7.17 (td, 2.0 Hz, <1 Hz, 2H), 7.39 (m, 3H), 7.46−7.61 (m, 10 H), 7.67 (m, 5H), 7.79 (m, 2H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 52.9 (d, 26.9 Hz), 42.2 (d, 26.9 Hz). [Pd(DPPBz)(C_6H_4-4-*t*-Bu)(Br)]: ^1H NMR (CD_2Cl_2) δ 1.52 (s, 9H), 6.82 (m, 4H), 7.27 (m, 8H), 7.41−7.53 (m, 9H), 7.57 (m, 1H), 7.62 (m, 1H), 7.72 (m, 5H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 52.8 (d, 27.0 Hz), 41.3 (d, 27.0 Hz). [Pd(DPPBz)(C_6H_5)(Br)]: ^1H NMR (CD_2Cl_2) δ 6.76 (m, 3H), 6.97 (m, 2H), 7.29−7.33 (m, 8H), 7.41−7.51 (m, 6H), 7.54 (m, 3H), 7.60 (m, 2H), 7.73 (m, 5H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 53.9 (d, 27.8 Hz), 43.4 (d, 27.8 Hz). [Pd(DPPBz)(C_6H_4-4-Me)(Br)]: ^1H NMR (CD_2Cl_2) δ 2.15 (s, 3H), 6.62 (dd, 7.6 Hz, 2.0 Hz, 2H), 6.83 (td, 8.1 Hz, 2.4 Hz, 2H), 7.32 (m, 8H), 7.42−7.54 (m, 9H), 7.57 (m, 2H), 7.73 (m, 5H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 53.4 (d, 27.5 Hz), 43.0 (d, 27.5 Hz). [Pd(DPPBz)(C_6H_4-4-CN)(Br)]: ^1H NMR (CD_2Cl_2) δ 6.91 (m, 2H), 7.09 (m, 2H), 7.17−7.26 (m, 8H), 7.37−7.56 (m, 11H), 7.63 (m, 5H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 54.2 (d, 26.9 Hz), 44.8 (d, 26.9 Hz). [Pd(DPPBz)(C_6H_4-4-Cl)(Br)]: ^1H NMR (CD_2Cl_2) δ 6.77 (dd, 7.5 Hz, 2.0 Hz, 2H), 6.93 (td, 8.5 Hz, 1.5 Hz, 2H), 7.30−7.37 (m, 8H), 7.45−7.49 (m, 6H), 7.52 (m, 3H), 7.59 (m, 2H), 7.72 (m, 5H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 54.1 (d, 26.9 Hz), 44.4 (d, 26.9 Hz). [Pd(DPPBz)(C_6H_4-3-Cl)(Br)]: ^1H NMR (CD_2Cl_2) δ 6.74 (m, 2H), 6.85 (d, 8.8 Hz, 1H), 6.96 (m, 1H) 7.29−7.34 (m, 7H), 7.45−7.75 (m, 12H), 7.72 (m, 5H); $^{31}P\{^1H\}$ NMR

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(CD_2Cl_2) δ 54.4 (d, 26.9 Hz), 44.6 (d, 26.9 Hz). [Pd(DPPBz)(C_6H_4-4-OMe)(Br)]: ^{1}H NMR (CD_2Cl_2) δ 3.65 (s, 3H), 6.43 (dd, 8.5 Hz, 2.0 Hz, 2H), 6.82 (td, 8.5 Hz, 2.0 Hz, 2H), 7.29−7.33 (m, 8H), 7.44−7.53 (m, 9H), 7.58 (m, 2H), 7.73 (m, 5H); ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 53.8 (d, 26.9 Hz), 43.5 (d, 26.9 Hz). [Pd(DPPBz)(C_6H_4-4-CF_3)(Br)]: ^{1}H NMR (CD_2Cl_2) δ 6.98 (m, 2H), 7.15 (t, 7.0 Hz, 2H), 7.28−7.33 (m, 8H), 7.44−7.49 (m, 6H), 7.51−7.65 (m, 5H), 7.72 (m, 5H); ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 54.7 (d, 26.4 Hz), 44.7 (d, 26.4 Hz).

Synthesis of *trans*-[Pd(PPh_2Et)$_2$(C_6H_4-4-Me)(Br)]. A solution of 1.543 g (9.021 mmol) of 4-bromotoluene in 20 mL of benzene was added to a stirred solution of 2.580 g (3.607 mmol) of Pd[P(*o*-tol)$_3$]$_2$ in 200 mL of benzene. After stirring for 1.5 h, the cloudy orange solution was filtered through Celite to remove insoluble material originally present in Pd[P(*o*-tol)$_3$]$_2$. The resulting clear orange solution was returned to the reaction vessel and allowed to stir for another 8 h. When the reaction was complete, as indicated by ^{31}P{^{1}H} NMR spectroscopy, the solution was concentrated, and pentane was added to precipitate {Pd[P(*o*-tol)$_3$](C_6H_4-4-Me)(μ-Br)}$_2$ as a yellow solid in 74.7% yield (1.569 g). Ethyldiphenylphosphine (0.46 mL, 2.2 mmol) was added dropwise by syringe to a stirred solution of 645 mg (0.554 mmol) of {Pd[P(*o*-tol)$_3$](C_6H_4-4-Me)(μ-Br)}$_2$ in 50 mL of benzene. The solution changed from cloudy to clear yellow immediately. The solution was stirred at room temperature for 2 h. When the reaction was complete, as indicated by ^{31}P{^{1}H} NMR spectroscopy, the clear yellow solution was concentrated, and pentane was added to precipitate the product as a pale yellow solid in 90.0% yield (705 mg). The product was filtered, washed with pentane, and used without further purification. ^{1}H NMR (C_6D_6) δ 0.82 (m, 6H), 2.03 (s, 3H), 2.08 (m, 4H), 6.48 (d, 2.0 Hz, 2H), 6.82 (dt, 2.0 Hz, <1 Hz, 2H), 7.01 (m, 12 H), 7.64 (m, 8H); ^{31}P{^{1}H} NMR (toluene) δ 18.9 (s).

Synthesis of [Pd(D^{i}PrPF)(C_6H_4-4-*t*-Bu)(Br)]. A solution of 436 mg (1.04 mmol) of 1,1′-bis(di-isopropylphenylphosphino)-ferrocene in 5 mL of benzene was added dropwise by pipet to a stirred solution of 650 mg (0.521 mmol) of {Pd[P(*o*-tol)$_3$](C_6H_4-4-*t*-Bu)(μ-Br)}$_2$ in 50 mL of benzene. The solution changed from cloudy yellow to cloudy orange immediately. The solution was stirred at room temperature for 2 h. When the reaction was complete, as indicated by ^{31}P{^{1}H} NMR spectroscopy, the solution was concentrated. After the addition of pentane, the product precipitated and the orange solid was isolated in 82.7% yield (636 mg). The product was filtered, washed with pentane, and used without further purification. ^{1}H NMR (C_6D_6) δ 0.85 (dd, 15.0 Hz, 7.0 Hz, 6 Hz), 1.09 (m, 12H), 1.34 (s, 9H), 1.72 (dd, 15.8 Hz, 7.3 Hz, 6H), 2.13 (m, 2H), 2.91 (m, 2H), 3.95 (m, 4H), 4.08 (m, 4H), 7.28 (dd, 8.0 Hz, 2.5 Hz, 2H), 7.72 (virtual t, 8.0 Hz, 2H); ^{31}P{^{1}H} NMR (toluene) δ 27.6 (d, 21.9 Hz), 38.1 (d, 21.9 Hz).

Synthesis of [Pd(*rac*-BINAP)(C_6H_4-4-*t*-Bu)(Br)].[75] A suspension of 649 mg (1.04 mmol) of racemic-2,2′-bis(diphenylphosphino)-1−1′-binaphthyl in 50 mL of benzene was added by pipet to a stirred solution of 650 mg (0.521 mmol) of {Pd[P(*o*-tol)$_3$](C_6H_4-4-*t*-Bu)(μ-Br)}$_2$ in 200 mL of benzene. The solution changed from cloudy yellow to cloudy green immediately. The solution was stirred at room temperature for 2 h. When the reaction was complete, as indicated by ^{31}P{^{1}H} NMR spectroscopy, the solvent was removed in vacuo. The remaining solid was dissolved in toluene, and the yellow product was obtained in 84.0% yield (825 mg) by layering the toluene solution with ether and cooling at −35 °C. ^{1}H NMR (CD_2Cl_2) δ 1.25 (s, 9H), 6.69 (m, 4H), 6.91−6.99 (m, 8H), 7.18 (m, 2H), 7.30−7.41 (m, 10 H), 7.50−7.61 (m, 8H), 7.78 (m, 4H); ^{31}P{^{1}H} NMR (toluene) δ 11.6 (d, 39.0 Hz), 28.1 (d, 39.0 Hz).

Synthesis of [Pd($Ph_2P(C_6H_4)PPh_2$)(CH_2CF_3)(I)]. A suspension of 1.595 g (3.572 mmol) of 1,2-bis(diphenylphosphino)-benzene (DPPBz) in 30 mL of benzene was added by pipet to a stirred solution of 1.502 g (1.786 mmol) of *trans*-[Pd(PPh_3)$_2$(CH_2CF_3)(I)] in 35 mL of benzene. The solution was stirred at room temperature for 72 h. When the reaction was complete, as indicated by ^{31}P{^{1}H} NMR spectroscopy, the solution was concentrated, and ether was added to precipitate the product as a pale yellow solid in 69.7% yield (925 mg). The product was filtered, washed with pentane, and used without further purification. ^{1}H NMR (CD_2Cl_2) δ 2.15 (m, 2H), 7.18 (m, 4H) 7.24−7.32 (m, 4H), 7.37−7.43 (m, 5H), 7.45−7.55 (m, 6H), 7.60 (m, 5H); ^{31}P{^{1}H} NMR (CD_2Cl_2) δ (d, 20.6 Hz), (dq, 20.6 Hz, 19.6 Hz).

Synthesis of [Pd($Ph_2PCH_2CH_2PPh_2$)(C_6H_4-2-Me)(Br)]. A solution of 928 mg (5.43 mmol) of 2-bromotoluene in 20 mL of benzene was added to a stirred solution of 1.553 g (2.171 mmol) of Pd[P(*o*-tol)$_3$]$_2$ in 200 mL of benzene. After stirring for 1.5 h, the cloudy orange solution was filtered through Celite to remove insoluble material originally present in Pd[P(*o*-tol)$_3$]$_2$. The resulting clear orange solution was returned to the reaction vessel and allowed to stir for another 8 h. When the reaction was complete, as indicated by ^{31}P{^{1}H} NMR spectroscopy, the solution was concentrated, and pentane was added to precipitate {Pd[P(*o*-tol)$_3$](C_6H_4-2-Me)(μ-Br)}$_2$ as a yellow solid in 81.6% yield (1.031 g). A solution of 1,2-bis(diphenylphosphino)ethane (308 mg, 0.773 mmol) in 15 mL of benzene was added dropwise to a stirred solution of 450 mg (0.387 mmol) of {Pd[P(*o*-tol)$_3$](C_6H_4-2-Me)(μ-Br)}$_2$ in 35 mL of benzene. The solution changed from cloudy yellow to cloudy white immediately. The solution was stirred at room temperature for 3 h. When the reaction was complete, as indicated by ^{31}P{^{1}H} NMR spectroscopy, the solution was concentrated, and pentane was added to precipitate the product as a white solid in 84.6% yield (442 mg). The product was filtered, washed with pentane, and used without further purification. ^{1}H NMR (CD_2Cl_2) δ 1.80 (m, 1H), 1.93 (s, 3H), 2.34−2.48 (m, 2H), 2.62 (m, 1H), 6.65 (m, 2H), 6.71 (d, 7.5 Hz, 1H), 6.80 (m, 2H), 7.12 (td, 8.0 Hz, 2.5 Hz, 2H), 7.17 (m, 1H), 7.35 (m, 1H), 7.43−7.50 (m, 9H), 7.77 (m, 2H), 7.86 (m, 2H), 8.06 (m, 2H); ^{31}P{^{1}H} NMR (toluene) δ 27.2 (d, 25.0 Hz), 48.2 (d, 25.0 Hz).

General Procedure for the Preparation of Potassium Enolates. Unless otherwise noted, potassium enolates were formed by the addition of 1 equiv of the corresponding ketone, amide, or ester to a suspension of 1 equiv of KH in pentane. After 30 min of reaction time, pentane was evaporated under vacuum, and the resulting solid potassium enolates were used without further purification and stored in the drybox at −40 °C.

Synthesis of the Potassium Enolate of Deoxybenzoin. A pentane suspension of 500 mg (2.55 mmol) of deoxybenzoin was added to a stirred homogeneous solution of 508 mg (2.55 mmol) of KN($SiMe_3$)$_2$ in toluene/pentane, 1:100. The resulting cloudy solution was stirred at room temperature for 3 h, during which time a fine yellow powder precipitated. The precipitated enolate was filtered, washed with pentane, and isolated in 69.7% yield (416 mg).

General Procedure for the Preparation of Deprotonated Nitriles. The potassium salts of acetonitrile, isovaleronitrile, benzyl cyanide, and isobutyronitrile were formed by the addition of 1 equiv of the corresponding nitrile to a solution of KN($SiMe_3$)$_2$ in a 1:50 mixture of toluene and pentane. After 1 h of reaction time, the mixture was concentrated, and the solid potassium salt was filtered, washed with pentane, and used without further purification. The salts were stored in the drybox at −35 °C.

[Pd($Ph_2P(C_6H_4)PPh_2$)(CH_3)(C_6H_4-2-Me)] (1). To a 20 mL vial was added 190 mg (0.262 mmol) of [Pd(DPPBz)(C_6H_4-2-Me)(Br)]. This solid was suspended in 5 mL of toluene, and 0.19 mL (0.26 mmol, 1.4 M Et_2O) of MeLi was added dropwise via syringe to the stirred solution. The mixture immediately changed from cloudy to clear yellow. The solution was stirred for 5 min at room temperature, after which time it was filtered

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through Celite. The product was obtained as a brown powder in 66.2% (115 mg) yield by layering the toluene solution with pentane at −35 °C. The compound was recrystallized as brown crystals from a THF solution of the product layered with pentane at −35 °C. ^{1}H NMR (C_6D_6) δ 1.19 (dd, 2.1 Hz, 1.6 Hz, 3H), 2.36 (s, 3H), 6.85−6.91 (m, 5H), 6.94 (m, 4H), 6.99−7.06 (m, 10H), 7.46−7.54 (m, 4H), 7.59 (m, 2H), 7.69 (t, 1.8 Hz, 1H), 7.78 (m, 2H); ^{31}P{^{1}H} NMR (C_6D_6) δ 42.0 (d, 9.8 Hz), 46.3 (d, 9.8 Hz). Anal. Calcd for $C_{38}H_{34}P_2Pd\cdot C_4H_8O$: C, 68.99; H, 5.79. Found: C, 68.85; H, 5.75.

[Pd(Ph$_2$P(C$_6$H$_4$)PPh$_2$)(CH$_2$C$_6$H$_5$)(C$_6$H$_4$-2-Me)] (2). Following the procedure for the preparation of **1**, reaction of 241 mg (0.332 mmol) of [Pd(DPPBz)(C$_6$H$_4$-2-Me)(Br)] and 0.35 mL (0.35 mmol, 1.0 M Et$_2$O) of benzylmagnesium bromide in 5 mL of toluene gave 104 mg (42.7%) of the product as a light brown powder after layering a toluene solution with pentane and cooling at −35 °C. ^{1}H NMR (C_6D_6) δ 2.08 (s, 3H), 3.47 (m, 1H), 3.57 (m, 1H), 6.79−6.88 (m, 12H), 6.93 (m, 1H), 6.97−7.08 (m, 11H), 7.29−7.39 (m, 4H), 7.52 (m, 2H), 7.63 (m, 1H), 7.72 (m, 2H); ^{31}P{^{1}H} NMR (C_6D_6) δ 42.7 (d, 6.7 Hz), 41.9 (d, 6.7 Hz). Anal. Calcd for $C_{44}H_{38}P_2Pd$: C, 71.89; H, 5.21. Found: C, 71.69; H, 5.40.

[Pd(Ph$_2$P(C$_6$H$_4$)PPh$_2$)(CH$_2$C(O)C$_6$H$_4$-4-Me)(C$_6$H$_4$-4-*t*-Bu)] (3). To a 20 mL vial was added 300 mg (0.392 mmol) of [Pd(DPPBz)(C$_6$H$_4$-4-*t*-Bu)(Br)] and 81 mg (0.47 mmol) of KOC(CH$_2$)C$_6$H$_4$-4-Me as solids. The mixture was suspended in 5 mL of toluene and stirred at room temperature for 30 min. When the reaction was complete, as indicated by ^{31}P{^{1}H} NMR spectroscopy, the yellow solution was filtered through Celite to remove residual salts. The resulting solution was then concentrated, and the white product was obtained in 61.9% (199 mg) yield by layering the concentrated toluene solution with pentane and cooling at −35 °C. ^{1}H NMR (C_6D_6) δ 1.28 (s, 9H), 2.07 (s, 3H), 3.88 (dd, 10.3 Hz, 6.9 Hz, 2H), 6.76 (m, 2H), 6.86−6.93 (m, 8H), 7.01 (dd, 8.2 Hz, 2.0 Hz, 2H), 7.08 (m, 6H), 7.23 (dd, 10.7 Hz, 1.3 Hz, 2H), 7.24 (dd, 10.7 Hz, 1.3 Hz, 2H), 7.31 (m, 3H), 7.35 (m, 1H), 7.89 (m, 4H), 7.99 (d, 8 Hz, 2H); ^{31}P{^{1}H} NMR (C_6D_6) δ 47.3 (d, 14.7 Hz), 47.7 (d, 14.7 Hz); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 21.66 (s), 31.96 (s), 34.25 (s), 35.00 (dd, 69.3 Hz, 3.6 Hz), 124.19 (d, 8.3 Hz), 128.25 (s), 128.59 (s), 128.82 (d, 10.2 Hz), 128.99 (d, 8.85 Hz), 130.62 (d, 2.4 Hz), 130.67 (d, 2.7 Hz), 131.69 (d, 4.1 Hz), 131.83 (d, 44.1 Hz), 131.89 (d, 3.9 Hz), 132.08 (d, 33.9 Hz), 133.84 (d, 11.4 Hz), 134.14 (d, 13.2 Hz), 134.20 (d, 15.0 Hz), 134.80 (d, 15.2 Hz), 136.54 (dd, 4.2 Hz, 2.2 Hz), 138.89 (s), 140.22 (s), 143.98 (virtual t, 43.0 Hz), 144.81 (virtual t, 44.0 Hz), 144.81 (s), 161.28 (dd, 123.5 Hz, 7.2 Hz), 202.65 (virtual t, 4.1 Hz); IR (KBr, cm^{-1}) ν(C=O) 1601. Anal. Calcd for $C_{49}H_{46}P_2OPd$: C, 71.84; H, 5.66. Found: C, 71.65; H, 5.69.

[Pd(Ph$_2$P(C$_6$H$_4$)PPh$_2$)(CHCH$_3$C(O)C$_6$H$_5$)(C$_6$H$_4$-4-*t*-Bu)] (4). Following the procedure for the preparation of **3**, reaction of 250 mg (0.326 mmol) of [Pd(DPPBz)(C$_6$H$_4$-4-*t*-Bu)(Br)] and 68 mg (0.39 mmol) of KOC(CHCH$_3$)C$_6$H$_5$ in 8 mL of toluene gave 217 mg (81.2%) of the product as a white solid after crystallization from toluene layered with pentane cooled at −35 °C. ^{1}H NMR (C_6D_6) δ 1.28 (s, 9H), 1.91 (dd, 7.0 Hz, 6.0 Hz, 3H), 4.59 (ddq,13.0 Hz, 6.5 Hz, 6.5 Hz, 1H), 6.97 (m, 2H), 6.88−7.01 (m, 10H), 7.06 (dd, 8.3 Hz, 1.8 Hz, 2H), 7.10 (dd, 7.3 Hz, 1.5 Hz, 2H), 7.16−7.28 (m, 9H), 7.48 (m, 4H), 8.00 (m, 2H), 8.22 (dd, 7.5 Hz, 2.0 Hz, 2H); ^{31}P{^{1}H} NMR (C_6D_6) δ 45.0 (d, 14.7 Hz), 48.7 (d, 14.7 Hz); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 14.50 (d, 5.5 Hz), 32.05 (s), 34.32 (s), 40.12 (dd, 68.0 Hz, 4.3 Hz), 124.54 (d, 7.4 Hz), 127.68 (s), 128.13 (s), 128.82 (d, 9.1 Hz), 128.85 (d, 11.0 Hz), 128.91 (d, 9.4 Hz), 129.17 (d, 9.8 Hz), 129.82 (s), 130.59 (d, 1.6 Hz), 130.64 (d, 2.1 Hz), 130.72 (br. s), 131.87 (dd, 4.8 Hz, 1.9 Hz), 132.24 (dd, 4.7 Hz, 1.8 Hz), 131.40−132.49 (four overlapping doublets), 133.70 (d, 11.6 Hz), 133.79 (d, 10.2 Hz), 133.92 (d, 11.6 Hz), 134.23 (d, 14.3 Hz), 133.96 (d, 14.6 Hz), 134.55 (d, 15.5 Hz), 135.53 (dd, 4.8 Hz, 2.8 Hz), 142.29 (s), 143.78 (dd, 41.2 Hz, 38.9 Hz), 144.93 (s), 145.87 (dd, 42.3 Hz, 40.3 Hz), 162.60 (dd, 120.0 Hz, 9.8 Hz), 201.14 (virtual t, 4.0 Hz); IR (KBr, cm^{-1}) ν(C=O) 1605. Anal. Calcd for $C_{49}H_{46}P_2OPd$: C, 71.84; H, 5.66. Found: C, 71.80; H, 5.77.

[Pd(Ph$_2$P(C$_6$H$_4$)PPh$_2$)(OC(CMe$_2$)C$_6$H$_5$)(C$_6$H$_4$-4-*t*-Bu)] (5). Following the procedure for the preparation of **3**, reaction of 200 mg (0.261 mmol) of [Pd(DPPBz)(C$_6$H$_4$-4-*t*-Bu)(Br)] and 53 mg (0.29 mmol) of KOC(CMe$_2$)C$_6$H$_5$ in 8 mL of toluene gave 96.7 mg (44.4%) of the product as a rust-colored solid after crystallization from toluene layered with pentane cooled at −35 °C. ^{1}H NMR (C_6D_6) δ 1.28 (s, 9H), 1.95 (d, 2.2 Hz, 3H), 2.33 (d, 1.4 Hz, 3H), 6.72−6.93 (m, 12H), 7.07−7.13 (m, 9H), 7.20−7.25 (m, 8H), 7.97 (m, 4H); ^{31}P{^{1}H} NMR (C_6D_6) δ 37.3 (d, 25.0 Hz), 50.5 (d, 25.0 Hz); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 20.04 (s), 21.76 (s), 31.98 (s), 34.40 (s), 100.09 (d, 3.3 Hz), 123.72 (d, 8.9 Hz), 124.85 (s), 126.72 (s), 128.88 (d, 11.4 Hz), 129.19 (d, 9.4 Hz), 129.86 (s), 130.97 (d, 2.0 Hz), 131.02 (d, 2.4 Hz), 131.29 (d, 54.7 Hz), 131.32 (d, 1.9 Hz), 131.51 (d, 3.3 Hz), 132.37 (d, 32.6 Hz), 133.99 (d, 11.9 Hz), 134.06 (d, 11.9 Hz), 134.42 (d, 14.0 Hz), 134.68 (d, 14.7 Hz), 136.23 (virtual t, 3.5 Hz), 141.58 (dd, 40.4 Hz, 32.6 Hz), 145.54 (virtual t, 46.7 Hz), 145.90 (s), 146.51 (s), 158.01 (virtual t, 3.1 Hz), 159.34 (dd, 127.1 Hz, 6.3 Hz); IR (KBr, cm^{-1}) ν(C−O) 1592. Anal. Calcd for $C_{50}H_{48}P_2OPd$: C, 72.07; H, 5.81. Found: C, 71.86; H, 5.91.

[Pd(Ph$_2$P(C$_6$H$_4$)PPh$_2$)(CH$_2$C(O)C$_6$H$_4$-4-Me)(C$_6$H$_4$-2-Me)] (6). Following the procedure for the preparation of **3**, reaction of 200 mg (0.276 mmol) of [Pd(DPPBz)(C$_6$H$_4$-2-Me)(Br)] and 55 mg (0.32 mmol) of KOC(CH$_2$)C$_6$H$_4$-4-Me in 5 mL of toluene gave 151 mg (70.4%) of the product as pale yellow crystals after layering a toluene solution with pentane at −35 °C. Recrystallization by vapor diffusion of pentane into a THF solution at −35 °C gave crystals that were suitable for X-ray structural analysis. ^{1}H NMR (C_6D_6) δ 1.84 (s, 3H), 2.07 (s, 3H), 3.77 (m, 1H), 3.86 (m, 1H), 6.74−6.78 (m, 4H), 6.83 (m, 2H), 6.88 (m, 3H), 6.92−6.95 (m, 5H), 7.00 (t, 7.5 Hz, 2H), 7.09−7.13 (m, 5H), 7.29 (m, 1H), 7.38 (m, 1H), 7.49 (t, 7.3 Hz, 1H), 7.61 (m, 2H), 7.82 (m, 2H), 7.98 (d, 7.9 Hz, 2H), 8.03 (m, 2H); ^{31}P{^{1}H} NMR (C_6D_6) δ 47.1 (d, 16.7 Hz), 47.7 (d, 16.7 Hz); selected ^{13}C{^{1}H} NMR data (CD_2Cl_2) δ 21.65 (s), 25.56 (d, 2.3 Hz), 32.16 (dd, 4.7 Hz, 68.2 Hz), 202.58 (virtual t, 4.1 Hz); IR (KBr, cm^{-1}) ν(C=O) 1612. Anal. Calcd for $C_{46}H_{40}P_2OPd$: C, 71.09; H, 5.19. Found: C, 71.42; H, 5.58.

[Pd(Ph$_2$P(C$_6$H$_4$)PPh$_2$)(CHCH$_3$C(O)C$_6$H$_5$)(C$_6$H$_4$-2-Me)] (7). Following the procedure for the preparation of **3**, reaction of 230 mg (0.318 mmol) of [Pd(DPPBz)(C$_6$H$_4$-2-Me)(Br)] and 60 mg (0.35 mmol) of KOC(CHCH$_3$)C$_6$H$_5$ in 5 mL of toluene gave 196 mg (79.0%) of the product as a white solid after crystallization from toluene layered with pentane cooled at −35 °C. ^{1}H NMR (two diastereomers in a 1:1 ratio) (C_6D_6) δ1.83 (virtual t, 7 Hz, 1.5H), 1.85 (s, 1.5H), 1.97 (s, 1.5H), 2.00 (virtual t, 6.5 Hz, 1.5H), 4.69 (m, 1H), 6.63 (m, 1H), 6.69 (m, 1H), 6.72 (m, 2H), 6.82 (m, 2H), 6.92−7.06 (m, 11H), 7.11 (m, 2H), 7.17−7.31 (m, 5H), 7.43 (m, 1H), 7.48 (td, 7.5 Hz, 1.0 Hz, 0.5H), 7.58 (m, 0.5H), 7.63 (m, 1H), 7.71 (m, 1H), 7.81 (m, 1H), 7.85 (dd, 8.3 Hz, 1.3 Hz, 1H), 7.95 (m, 1H), 8.07 (m, 1H), 8.14 (m, 1H); ^{31}P{^{1}H} NMR (C_6D_6) δ 44.7 (d, 16.6 Hz), 45.6 (d, 16.6 Hz), 47.7 (d, 6.3 Hz), 47.9 (d, 6.3 Hz) (relative intensities 1:1); selected ^{13}C{^{1}H} NMR data (two diastereomers in a 1:1 ratio) (CD_2Cl_2) δ 16.16 (d, 5.0 Hz), 16.53 (d, 6.0 Hz), 25.07 (2 overlapping doublets), 38.6 (dd, 67.8 Hz, 3.2 Hz), 41.4 (dd, 68.2 Hz, 3.7 Hz), 200.59 (virtual t, 5.0 Hz), 201.61 (virtual t, 4.7 Hz); IR (KBr, cm^{-1}) ν(C=O) 1606. Anal. Calcd for $C_{46}H_{40}P_2OPd$: C, 71.09; H, 5.19. Found: C, 71.29; H, 5.35.

[Pd(Ph$_2$P(C$_6$H$_4$)PPh$_2$)(OC(CMe$_2$)C$_6$H$_5$)(C$_6$H$_4$-2-Me)] (8). Following the procedure for the preparation of **3**, reaction of 220 mg (0.304 mmol) of [Pd(DPPBz)(C$_6$H$_4$-2-Me)(Br)] and 65 mg (0.35 mmol) of KOC(CMe$_2$)C$_6$H$_5$ in 7 mL of toluene gave 174 mg (72.2%) of the product as an orange solid after crystallization from toluene layered with pentane cooled at −35 °C. ^{1}H NMR (C_6D_6) δ 1.97 (d, 2.1 Hz, 3H), 2.05 (s, 3H), 2.35 (d, 1.6 Hz, 3H), 6.58 (m, 2H), 6.68−6.85 (m, 8H), 6.93 (m, 4H), 7.06 (m, 4H), 7.11 (m, 2H), 7.17−7.26 (m, 4H), 7.32 (dd,

2.0 Hz, <1 Hz, 2H), 7.45 (m, 1H), 7.60 (m, 2H), 7.69 (m, 2H), 8.40 (m, 2H); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 36.6 (d, 24.4 Hz), 50.0 (d, 24.4 Hz); selected $^{13}C\{^1H\}$ NMR data (CD_2Cl_2) δ 19.79 (s), 21.20 (s), 24.37 (virtual t, 2.8 Hz), 99.96 (d, 4.7 Hz, OCPh=*C*Me$_2$), 158.45 (virtual t, 2.9 Hz, O*C*Ph=CMe$_2$); IR (KBr, cm^{-1}) ν(C−O) 1593. Anal. Calcd for $C_{47}H_{42}P_2OPd\cdot C_5H_{12}$: C, 72.34; H, 6.30. Found: C, 72.41; H, 6.11.

[Pd(Ph$_2$P(C$_6$H$_4$)PPh$_2$)(CH$_2$C(O)CH$_2$CH$_3$)(C$_6$H$_4$-2-Me)] (9). Following the procedure for the preparation of **3**, reaction of 200 mg (0.276 mmol) of [Pd(DPPBz)(C$_6$H$_4$-2-Me)(Br)] and 32 mg (0.29 mmol) of KOC(CH$_2$)CH$_2$CH$_3$ in 5 mL of toluene gave 151 mg (76.4%) of the product as pale yellow crystals after cooling a toluene solution layered with pentane at −35 °C. ^1H NMR (C_6D_6) δ 1.05 (t, 7.4 Hz, 3H), 2.07 (s, 3H), 2.11−2.28 (m, 2H), 3.20 (m, 1H), 3.31 (m, 1H), 6.78−7.13 (m, 19H), 7.35−7.38 (m, 2H), 7.55−7.62 (m, 3H), 7.87 (m, 4H); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 46.20 (d, 16 Hz), 46.38 (d, 16 Hz); selected $^{13}C\{^1H\}$ NMR data (CD_2Cl_2) δ 9.76 (s), 25.62 (d, 3.6 Hz), 33.93 (dd, 69.1 Hz, 4.4 Hz), 35.85 (s), 213.76 (dd, 3.0 Hz, 2.0 Hz); IR (KBr, cm^{-1}) ν(C=O) 1625. Anal. Calcd for $C_{41}H_{38}P_2OPd$: C, 68.86; H, 5.36. Found: C, 68.95; H, 5.26.

[Pd(Ph$_2$P(C$_6$H$_4$)PPh$_2$)(CH$_2$C(O)C(CH$_3$)$_3$)(C$_6$H$_4$-2-Me)] (10). Following the procedure for the preparation of **3**, reaction of 200 mg (0.276 mmol) of [Pd(DPPBz)(C$_6$H$_4$-2-Me)(Br)] and 38 mg (0.28 mmol) of KOC(CH$_2$)C(CH$_3$)$_3$ in 5 mL of toluene gave 153 mg (74.7%) of the product as a white powder after cooling a toluene solution layered with pentane at −35 °C. ^1H NMR (C_6D_6) δ 1.22 (s, 9H), 1.95 (s, 3H), 3.23 (m, 1H), 3.40 (m, 1H), 6.72−6.77 (m, 4H), 6.84 (m, 2H), 6.90 (m, 1H), 7.00 (m, 6H), 7.06 (m, 2H), 7.10−7.19 (m, 4H), 7.33 (m, 2H), 7.63 (t, 7.2 Hz, 1H), 7.78 (m, 4H), 8.18 (t, 8.7 Hz, 2H); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 46.5 (d, 16 Hz), 46.7 (d, 16 Hz); selected $^{13}C\{^1H\}$ NMR data (CD_2Cl_2) δ 25.76 (d, 1.9 Hz), 28.52 (s), 30.02 (dd, 71.1 Hz, 4.0 Hz), 42.44 (s), 220.48 (virtual t, 3.3 Hz); IR (KBr, cm^{-1}) ν(C=O) 1621. Anal. Calcd for $C_{43}H_{42}P_2OPd$: C, 69.50; H, 5.70. Found: C, 69.62; H, 5.74.

[Pd(Ph$_2$P(C$_6$H$_4$)PPh$_2$)(CH$_2$C(O)C$_6$H$_4$-4-OMe)(C$_6$H$_4$-2-Me)] (11). Following the procedure for the preparation of **3**, reaction of 250 mg (0.345 mmol) of [Pd(DPPBz)(C$_6$H$_4$-2-Me)-(Br)] and 72 mg (0.38 mmol) of KOC(CH$_2$)C$_6$H$_4$-4-OMe in 4 mL of toluene gave 214 mg (78.1%) of the product as yellow crystals after cooling a toluene solution layered with pentane at −35 °C. ^1H NMR (C_6D_6) δ 1.88 (s, 3H), 3.24 (s, 3H), 3.75 (m, 1H), 3.84 (m, 1H), 6.69−7.01 (m, 18H), 7.11 (m, 3H), 7.31 (m, 1H), 7.38 (m, 1H), 7.51 (t, 1.9 Hz, 1H), 7.61 (m, 2H), 7.82 (m, 2H), 8.04 (m, 4H); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 47.1 (d, 17.0 Hz), 47.9 (d, 17.0 Hz); selected $^{13}C\{^1H\}$ NMR data (CD_2Cl_2) δ 25.57 (d, 2.3 Hz), 31.97 (dd, 68.3 Hz, 3.6 Hz), 55.71 (s), 201.88 (virtual t, 3.9 Hz); IR (KBr, cm^{-1}) ν(C=O) 1606. Anal. Calcd for $C_{46}H_{40}P_2O_2Pd$: C, 69.66; H, 5.08. Found: C, 69.90; H, 5.30.

[Pd(Ph$_2$P(C$_6$H$_4$)PPh$_2$)(CH$_2$C(O)C$_6$H$_4$-4-CF$_3$)(C$_6$H$_4$-2-Me)] (12). Following the procedure for the preparation of **3**, reaction of 250 mg (0.345 mmol) of [Pd(DPPBz)(C$_6$H$_4$-2-Me)-(Br)] and 86 mg (0.38 mmol) of KOC(CH$_2$)C$_6$H$_4$-4-CF$_3$ in 4 mL of toluene gave 225 mg (78.5%) of the product as dark yellow crystals after cooling a toluene solution layered with pentane at −35 °C. ^1H NMR (C_6D_6) δ 1.78 (s, 3H), 3.74 (m, 2H), 6.70−6.83 (m, 8H), 6.88 (m, 3H), 6.91 (m, 2H), 7.06 (m, 4H), 7.12 (d, 6 Hz, 2H), 7.27−7.32 (m, 5H), 7.54 (m, 2H), 7.70 (m, 2H), 7.86 (d, 8.2 Hz, 2H), 7.93 (m, 2H); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 47.2 (d, 17.1 Hz), 47.8 (d, 17.1 Hz); selected $^{13}C\{^1H\}$ NMR data (CD_2Cl_2) δ 25.38 (d, 2.2 Hz), 32.61 (dd, 5.1 Hz, 65.0 Hz), 200.99 (virtual t, 4.4 Hz); IR (KBr, cm^{-1}) ν(C=O) 1614. This compound appeared to be more thermally sensitive or light sensitive than the other enolate compounds and discolored as a solid, precluding satisfactory elemental analysis.

[Pd(Ph$_2$P(C$_6$H$_4$)PPh$_2$)(CH$_2$C(O)O-*t*-Bu)(C$_6$H$_4$-2-Me)] (13). Following the procedure for the preparation of **3**, reaction of 250 mg (0.345 mmol) of [Pd(DPPBz)(C$_6$H$_4$-2-Me)(Br)] and 54 mg (0.35 mmol) of KOC(CH$_2$)O-*t*-Bu in 5 mL of toluene gave 128 mg (48.9%) of the product as a pale yellow solid after crystallization from toluene layered with pentane cooled at −35 °C. ^1H NMR (C_6D_6) δ 1.39 (s, 9H), 2.24 (s, 3H), 2.76 (m, 1H), 2.90 (m, 1H), 6.77−6.81 (m, 4H), 6.85−6.92 (m, 6H), 6.96−7.03 (m, 4H), 7.05−7.12 (m, 5H), 7.38 (m, 2H), 7.56 (t, 7.5 Hz, 1H), 7.62 (m, 2H), 7.77−7.85 (m, 4H); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 47.1 (d, 17.0 Hz), 47.9 (d, 17.0 Hz); selected $^{13}C\{^1H\}$ NMR data (CD_2Cl_2) δ 20.95 (dd, 78.9 Hz, 4.8 Hz), 25.90 (d, 3.0 Hz), 28.78 (s), 76.35 (s), 180.21 (dd, 4.5 Hz, 2.0 Hz); IR (KBr, cm^{-1}) ν(C=O) 1661. Anal. Calcd for $C_{46}H_{40}P_2O_2Pd$: C, 68.03; H, 5.58. Found: C, 68.25; H, 5.80.

[Pd(Ph$_2$P(C$_6$H$_4$)PPh$_2$)(CH$_2$C(O)NMe$_2$)(C$_6$H$_4$-2-Me)] (14). Following the procedure for the preparation of **3**, reaction of 220 mg (0.304 mmol) of [Pd(DPPBz)(C$_6$H$_4$-2-Me)(Br)] and 42 mg (0.33 mmol) of KOC(CH$_2$)NMe$_2$ in 5 mL of toluene gave 140 mg (63.0%) of the product as a dark red solid after crystallization from toluene layered with pentane cooled at −35 °C. ^1H NMR (C_6D_6) δ 2.05 (s, 3H), 2.55 (br s, 3H), 2.65 (br s, 3H), 2.83 (m, 1H), 2.92 (m, 1H), 6.81 (m, 2H), 6.86 (m, 5H), 6.94 (m, 8H), 7.01−7.09 (m, 4H), 7.36 (m, 2H), 7.55 (t, 7.0 Hz, 1H), 7.65 (m, 2H), 7.96−8.05 (m, 4H); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 45.8 (d, 12.2 Hz), 46.8 (d, 12.2 Hz); selected $^{13}C\{^1H\}$ NMR data (CD_2Cl_2) δ 22.14 (dd, 85.1 Hz, 9.2 Hz), 25.89 (d, 2.2 Hz), 34.75 (br s), 38.38 (br s), 181.82 (dd, 4.4 Hz, 2.4 Hz); IR (KBr, cm^{-1}) ν(C=O) 1590. Anal. Calcd for $C_{41}H_{39}P_2NOPd$: C, 67.45; H, 5.38; N, 1.92. Found: C, 67.47; H, 5.38; N, 1.67.

[Pd(Ph$_2$P(C$_6$H$_4$)PPh$_2$)(CH$_2$C(O)NEt$_2$)(C$_6$H$_4$-2-Me)] (15). Following the procedure for the preparation of **3**, reaction of 220 mg (0.304 mmol) of [Pd(DPPBz)(C$_6$H$_4$-2-Me)(Br)] and 51 mg (0.33 mmol) of KOC(CH$_2$)NEt$_2$ in 5 mL of toluene gave 136 mg (58.9%) of the product as a dark red solid after crystallization from toluene layered with pentane cooled at −35 °C. ^1H NMR (C_6D_6) δ 0.93 (t, 6.9 Hz, 3H), 1.02 (t, 6.9 Hz, 3H), 2.07 (s, 3H), 2.78−2.92 (m, 3H), 3.14 (m, 2H), 3.30 (m, 1H), 6.79 (m, 2H), 6.86 (m, 5H), 6.95 (m, 8H), 7.04−7.12 (m, 4H), 7.37 (m, 2H), 7.54 (t, 7.2 Hz, 1H), 7.66 (m, 2H), 7.97 (m, 2H), 8.06 (m, 2H); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 45.8 (d, 12.2 Hz), 46.8 (d, 12.2 Hz); ^{1}IR (KBr, cm^{-1}) ν(C=O) 1585. Anal. Calcd for $C_{43}H_{43}P_2NOPd$: C, 68.12; H, 5.72; N, 1.85. Found: C, 68.38; H, 5.70; N, 1.70.

[Pd(Ph$_2$P(C$_6$H$_4$)PPh$_2$)(CHPhC(O)C$_6$H$_5$)(C$_6$H$_4$-2-Me)] (16). Following the procedure for the preparation of **3**, reaction of 189 mg (0.261 mmol) of [Pd(DPPBz)(C$_6$H$_4$-2-Me)(Br)] and 64 mg (0.27 mmol) of KOC(CHPh)C$_6$H$_5$ in 5 mL of toluene gave 123 mg (56.2%) of the product as a bright yellow powder after crystallization from toluene layered with pentane cooled at −35 °C. ^1H NMR (C_6D_6) (three diastereomers in a 2:2:1 ratio) δ 1.58 (s, 0.6H), 1.80 (s, 1.2H), 1.97 (s, 1.2H), 5.93 (m, 0.8H), 5.95 (s, 0.2H), 6.43−6.57 (m, 2.4H), 6.67 (m, 3.4H), 6.80−7.08 (m, 13.6H), 7.09−7.19 (m, 5H), 7.25 (m, 2.2H), 7.30 (m, 0.8H), 7.43 (m, 1.6H), 7.50 (m, 0.8H), 7.66 (m, 1.8H), 7.76 (m, 2.8H), 7.98 (m, 2H), 8.36 (m, 1.6H); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 51.3 (d, 24.3 Hz), 39.5 (d, 24.3 Hz), 49.9 (d, 18.7 Hz), 43.7 (d, 18.7 Hz), 48.4 (d, 18.0 Hz), 42.7 (d, 18.0 Hz) (relative intensities 2:2:1). Anal. Calcd for $C_{51}H_{42}P_2OPd$: C, 72.99; H, 5.04. Found: C, 73.13; H, 5.25.

[Pd(Ph$_2$P(C$_6$H$_4$)PPh$_2$)(CH$_2$C(O)C$_6$H$_4$-4-*t*-Bu)(C$_6$H$_5$)] (17). Following the procedure for the preparation of **3**, reaction of 220 mg (0.309 mmol) of [Pd(DPPBz)(C$_6$H$_5$)(Br)] and 79 mg (0.37 mmol) of KOC(CH$_2$)C$_6$H$_4$-4-*t*-Bu in 5 mL of toluene gave 123 mg (49.5%) of the product as a white solid after crystallization from toluene layered with pentane cooled at −35 °C. ^1H NMR (C_6D_6) δ 1.16 (s, 9H), 3.86 (dd, 11.0 Hz, 7.0 Hz, 2H), 6.76 (m, 2H), 6.87 (m, 4H), 6.91−7.01 (m, 6H), 7.07−7.12 (m, 7H), 7.23 (m, 4H), 7.27 (m, 1H), 7.34 (m, 1H), 7.38 (m, 2H), 7.88 (m, 4H), 8.01 (d, 9.0 Hz, 2H); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 47.9 (d, 16.7 Hz), 47.2 (d, 16.7 Hz). Anal. Calcd for $C_{48}H_{44}P_2OPd$: C, 71.60; H, 5.51. Found: C, 71.35; H, 5.57.

[Pd(Ph$_2$P(C$_6$H$_4$)PPh$_2$)(CH$_2$C(O)C$_6$H$_4$-4-*t*-Bu)(C$_6$H$_4$-4-Me)] (18). Following the procedure for the preparation of **3**, reaction of 191 mg (0.264 mmol) of [Pd(DPPBz)(C$_6$H$_4$-4-Me)-(Br)] and 73 mg (0.34 mmol) of KOC(CH$_2$)C$_6$H$_4$-4-*t*-Bu in 6 mL

of toluene gave 169 mg (78.2%) of the product as a white solid after crystallization from toluene layered with pentane cooled at −35 °C. ^{1}H NMR (C_6D_6) δ 1.16 (s, 9H), 2.21 (s, 3H), 3.87 (dd, 11.0 Hz, 7.0 Hz, 2H), 6.76 (m, 2H), 6.84−6.89 (m, 6H), 6.92 (m, 2H), 7.09−7.11 (m, 8H), 7.23−7.30 (m, 7H), 7.35 (m, 1H), 7.89 (m, 4H), 8.03 (d, 9.0 Hz, 2H); ^{31}P{^{1}H} NMR (C_6D_6) δ 48.0 (d, 17.1 Hz), 46.9 (d, 17.1 Hz). Anal. Calcd for $C_{49}H_{46}P_2$-OPd: C, 71.84; H, 5.66. Found: C, 72.01; H, 5.79.

[Pd(Ph$_2$P(C$_6$H$_4$)PPh$_2$)(CH$_2$C(O)C$_6$H$_4$-4-*t*-Bu)(C$_6$H$_4$-4-CN)] (19). Following the procedure for the preparation of **3**, reaction of 180 mg (0.245 mmol) of [Pd(DPPBz)(C_6H_4-4-CN)-(Br)] and 68 mg (0.32 mmol) of KOC(CH_2)C_6H_4-4-*t*-Bu in 6 mL of toluene gave 127 mg (62.7%) of the product as a pale yellow solid after crystallization from toluene layered with pentane cooled at −35 °C. ^{1}H NMR (C_6D_6) δ 1.91 (s, 9H), 3.61 (dd, 11.0 Hz, 7.0 Hz, 2H), 6.74−6.81 (m, 8H), 6.89 (m, 2H), 7.04−7.13 (m, 14H), 7.23 (m, 1H), 7.30 (m, 1H), 7.77−7.82 (m, 6H); ^{31}P-{^{1}H} NMR (C_6D_6) δ 48.5 (d, 16.7 Hz), 47.8 (d, 16.7 Hz). Anal. Calcd for $C_{49}H_{43}NP_2OPd\cdot C_7H_8$: C, 72.92; H, 5.57; N, 1.52. Found: C, 72.94; H, 5.93; N, 1.50.

[Pd(Ph$_2$P(C$_6$H$_4$)PPh$_2$)(CH$_2$C(O)C$_6$H$_4$-4-*t*-Bu)(C$_6$H$_4$-4-Cl)] (20). Following the procedure for the preparation of **3**, reaction of 200 mg (0.269 mmol) of [Pd(DPPBz)(C_6H_4-4-Cl)-(Br)] and 69 mg (0.32 mmol) of KOC(CH_2)C_6H_4-4-*t*-Bu in 5 mL of toluene gave 104 mg (46.1%) of the product as a white solid after crystallization from toluene layered with pentane cooled at −35 °C. ^{1}H NMR (C_6D_6) δ 1.18 (s, 9H), 3.74 (dd, 11.0 Hz, 7.0 Hz, 2H), 6.76 (m, 2H), 6.83 (m, 4H), 6.90 (m, 2H), 6.95 (m, 2H), 7.09−7.14 (m, 12H), 7.16 (m, 2H), 7.22 (m, 1H), 7.33 (m, 1H), 7.85 (m, 4H), 7.90 (d, 9.0 Hz, 2H); ^{31}P{^{1}H} NMR (C_6D_6) δ 48.6 (d, 17.3 Hz), 47.4 (d, 17.3 Hz). Anal. Calcd for $C_{48}H_{43}$-ClP_2OPd: C, 68.66; H, 5.16. Found: C, 68.36; H, 4.85.

[Pd(Ph$_2$P(C$_6$H$_4$)PPh$_2$)(CH$_2$C(O)C$_6$H$_4$-4-*t*-Bu)(C$_6$H$_4$-3-Cl)] (21). Following the procedure for the preparation of **3**, reaction of 200 mg (0.269 mmol) of [Pd(DPPBz)(C_6H_4-3-Cl)-(Br)] and 75 mg (0.35 mmol) of KOC(CH_2)C_6H_4-4-*t*-Bu in 5 mL of toluene gave 102 mg (45.1%) of the product as a white solid after crystallization from toluene layered with pentane cooled at −35 °C. ^{1}H NMR (C_6D_6) δ 1.18 (s, 9H), 3.77 (dd, 11.0 Hz, 7.5 Hz, 2H), 6.76 (m, 3H), 6.85 (m, 4H), 6.92 (m, 2H), 6.94 (m, 1H), 7.07−7.13 (m, 7H), 7.18 (m, 5H), 7.21 (m, 1H), 7.25 (m, 2H), 7.34 (m, 1H), 7.86 (m, 4H), 7.91 (d, 8.5 Hz, 2H); ^{31}P{^{1}H} NMR (C_6D_6) δ 49.3 (d, 16.7 Hz), 48.0 (d, 16.7 Hz). Anal. Calcd for $C_{48}H_{43}ClP_2OPd$: C, 68.66; H, 5.16. Found: C, 68.98; H, 5.45.

[Pd(Ph$_2$P(C$_6$H$_4$)PPh$_2$)(CH$_2$C(O)C$_6$H$_4$-4-*t*-Bu)(C$_6$H$_4$-4-OMe)] (22). Following the procedure for the preparation of **3**, reaction of 200 mg (0.271 mmol) of [Pd(DPPBz)(C_6H_4-4-OMe)-(Br)] and 69 mg (0.32 mmol) of KOC(CH_2)C_6H_4-4-*t*-Bu in 5 mL of toluene gave 175 mg (77.4%) of the product as a white solid after crystallization from toluene layered with pentane cooled at −35 °C. ^{1}H NMR (C_6D_6) δ 1.16 (s, 9H), 3.41 (s, 3H), 3.88 (dd, 11.0 Hz, 7.0 Hz, 2H), 6.72 (dd, 9.0 Hz, 2.0 Hz, 2H), 6.76 (m, 2H), 6.88 (m, 4H), 6.92 (m, 2H), 7.09−7.11 (m, 6H), 7.16 (m, 2H), 7.22−7.27 (m, 7H), 7.36 (m, 1H), 7.90 (m, 4H), 8.03 (d, 9.0 Hz, 2H); ^{31}P{^{1}H} NMR (C_6D_6) δ 48.5 (d, 15.3 Hz), 47.2 (d, 15.3 Hz). Anal. Calcd for $C_{49}H_{46}P_2O_2Pd$: C, 70.46; H, 5.55. Found: C, 70.71; H, 5.80.

[Pd(Ph$_2$P(C$_6$H$_4$)PPh$_2$)(CH$_2$C(O)C$_6$H$_4$-4-*t*-Bu)(C$_6$H$_4$-4-CF$_3$)] (23). Following the procedure for the preparation of **3**, reaction of 175 mg (0.225 mmol) of [Pd(DPPBz)(C_6H_4-4-CF_3)-(Br)] and 58 mg (0.27 mmol) of KOC(CH_2)C_6H_4-4-*t*-Bu in 5 mL of toluene gave 154 mg (78.3%) of the product as a white solid after crystallization from toluene layered with pentane cooled at −35 °C. ^{1}H NMR (C_6D_6) δ 1.17 (s, 9H), 3.72 (dd, 10.5 Hz, 7.0 Hz, 2H), 6.76 (m, 2H), 6.82 (m, 4H), 6.89 (m, 2H), 7.08−7.14 (m, 14H), 7.25 (m, 1H), 7.29 (m, 3H), 7.81−7.85 (m, 6H); ^{31}P{^{1}H} NMR (C_6D_6) δ 47.9 (d, 16.6 Hz), 47.5 (d, 16.6 Hz). Anal. Calcd for $C_{49}H_{43}F_3P_2OPd\cdot C_7H_8$: C, 69.67; H, 5.33. Found: C, 69.86; H, 5.31.

[Pd(PPh$_2$Et)$_2$(OC(CH$_2$)C$_6$H$_4$-4-Me)(C$_6$H$_4$-4-Me)] (24). Following the procedure for the preparation of **3**, reaction of 200 mg (0.283 mmol) of *trans*-[Pd(PPh_2Et)$_2$(C_6H_4-4-Me)(Br)] and 54 mg (0.31 mmol) of KOC(CH_2)C_6H_4-4-Me in 5 mL of toluene gave 162 mg (75.5%) of the product as a pale yellow powder after crystallization from toluene layered with pentane cooled at −35 °C. ^{1}H NMR (C_6D_6) of the major isomer δ 0.86 (m, 6H), 2.03 (s, 3H), 2.18 (m, 4H), 2.21 (s, 3H), 4.90 (s, 1H), 4.99 (s, 1H), 6.45 (d, 7.6 Hz, 2H), 6.76 (d, 8.0 Hz, 2H), 7.01 (m, 14H), 7.57 (m, 8H), 8.10 (d, 8.4 Hz, 2H); ^{31}P{^{1}H} NMR of the three isomers (C_6D_6) δ 18.5 (s), 21.1 (s), 22.9 (s) (relative intensities 26:2.5:1). The resonance at 21.1 was not observed in the presence of added PPh_2Et. ^{13}C{^{1}H} NMR of the major isomer (CD_2Cl_2) δ 8.69 (s), 18.80 (virtual t, 13.3 Hz), 20.86 (s), 21.64 (s), 77.86 (s), 126.37 (s), 128.00 (s), 128.33 (s), 128.38 (virtual t, 4.3 Hz), 130.07 (s), 131.51 (s), 131.74 (virtual t, 20.8 Hz), 134.20 (virtual t, 6.5 Hz), 135.90 (s), 137.37 (virtual t, 3.8 Hz), 141.95 (s), 143.24 (virtual t, 8.1 Hz), 168.92 (s); IR (KBr, cm^{-1}) ν(C−O) 1580. Anal. Calcd for $C_{44}H_{46}P_2OPd$: C, 69.61; H, 6.11. Found: C, 69.45; H, 6.05.

[Pd(PPh$_2$Et)$_2$(OC(CHCH$_3$)C$_6$H$_5$)(C$_6$H$_4$-4-Me)] (25). Following the procedure for the preparation of **3**, reaction of 250 mg (0.354 mmol) of *trans*-[Pd(PPh_2Et)$_2$(C_6H_4-4-Me)(Br)] and 73 mg (0.43 mmol) of KOC($CHCH_3$)C_6H_5 in 5 mL of toluene gave 198 mg (73.5%) of the product as bright orange crystals after cooling a toluene solution layered with pentane at −35 °C. Recrystallization by vapor diffusion of pentane into a toluene solution at −35 °C afforded yellow prism crystals that were suitable for an X-ray structural analysis. ^{1}H NMR (C_6D_6) of the major isomer δ 0.78 (m, 6H), 2.04 (s, 3H), 2.07 (m, 4H), 2.76 (d, 6.4 Hz, 3H), 5.13 (q, 6.4 Hz, 1H), 6.47 (d, 7.2 Hz, 2H), 6.79 (d, 7.6 Hz, 2H), 7.02 (m, 14H), 7.28 (t, 10.2 Hz, 1H), 7.48 (br m, 8H), 8.05 (dd, 8.4 Hz, 1.2 Hz, 2H); ^{31}P{^{1}H} NMR of two isomers (C_6D_6) δ 17.1 (s), 17.6 (s) (relative intensities 10:1); ^{13}C{^{1}H} NMR of the major isomer (CD_2Cl_2) δ 8.34 (s), 13.80 (s), 18.40 (virtual t, 12.7 Hz), 20.83 (s), 85.57 (s), 125.55 (s), 126.06 (s), 127.52 (s), 128.34 (s), 128.34 (virtual t, 4.7 Hz), 129.99 (s), 131.50 (virtual t, 20.1 Hz), 131.59 (s), 134.12 (virtual t, 4.7 Hz), 137.30 (virtual t, 4.9 Hz), 142.91 (virtual t, 7.8 Hz), 147.45 (s), 162.14 (s); IR (KBr, cm^{-1}) ν(C−O) 1592. Anal. Calcd for $C_{44}H_{46}P_2OPd$: C, 69.61; H, 6.11. Found: C, 69.48; H, 6.10.

[Pd(Ph$_2$P(C$_6$H$_4$)PPh$_2$)(CH$_2$CN)(C$_6$H$_4$-4-*t*-Bu)] (26). To a 20 mL vial was added 200 mg (0.261 mmol) of [Pd(DPPBz)-(C_6H_4-4-*t*-Bu)(Br)] and 165 mg (2.09 mmol) of KN(C)CH_2 as solids. The mixture was suspended in 5 mL of toluene and stirred at room temperature for 1 h. When the reaction was complete, as indicated by ^{31}P{^{1}H} NMR spectroscopy, the mixture was filtered through Celite to remove residual salts. The resulting clear yellow solution was then concentrated, and the white product was obtained in 61.2% (116 mg) yield by layering the concentrated toluene solution with pentane and cooling at −35 °C. The compound was recrystallized as colorless needles from a THF solution of the product layered with pentane at −35 °C. ^{1}H NMR (C_6D_6) δ 1.23 (s, 9H), 1.93 (virtual t, 8.8 Hz, 2H), 6.81 (m, 2H), 6.88−6.94 (m, 6H), 7.00−7.05 (m, 6H), 7.07 (dd, 8.3 Hz, 1.8 Hz, 2H), 7.25 (m, 4H), 7.34 (m, 2H), 7.51 (dd, 8.3 Hz, 7.3 Hz, 2H), 7.63 (m, 4H); ^{31}P{^{1}H} NMR (C_6D_6) δ 44.6 (d, 17.1 Hz), 47.2 (d, 17.1 Hz); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ −7.76 (dd, 92.8 Hz, 7.4 Hz), 31.93 (s), 34.31 (s), 124.33 (d, 7.0 Hz), 128.82 (dd, 7.1 Hz, 2.5 Hz), 128.98 (d, 10.8 Hz), 129.54 (d, 10.2 Hz), 130.87 (d, 1.6 Hz), 131.27 (d, 2.3 Hz), 131.47 (d, 43.9 Hz), 132.01 (d, 36.5 Hz), 132.29−132.37 (overlapping doublets), 133.90 (d, 12.6 Hz), 134.00 (d, 12.6 Hz), 134.44 (d, 15.3 Hz), 134.61 (d, 16.4 Hz), 136.07 (virtual t, 3.6 Hz), 143.43 (virtual t, 40.7 Hz), 144.26 (dd, 41.4 Hz, 43.0 Hz), 145.25 (s), 160.47 (dd, 124.8 Hz, 7.5 Hz); IR (KBr, cm^{-1}) ν(CN) 2184. Anal. Calcd for $C_{42}H_{39}NP_2Pd$: C, 69.47; H, 5.41; N, 1.93. Found: C, 69.28; H, 5.37; N, 1.95.

[Pd(Ph$_2$P(C$_6$H$_4$)PPh$_2$)(CH(CHMe$_2$)CN)C$_6$H$_5$)(C$_6$H$_4$-4-Me)] (27). Following the procedure for the preparation of **26**, reaction of 200 mg (0.276 mmol) of [Pd(DPPBz)(C_6H_4-4-Me)-(Br)] and 37 mg (0.31 mmol) of KN(C)$CH(CHMe_2)$ in 5 mL of

toluene gave 138 mg (68.7%) of the product as a slightly yellow solid after crystallization from toluene layered with pentane cooled at −35 °C. The compound was recrystallized as colorless needles from a THF solution of the product layered with pentane at −35 °C. ^{1}H NMR (C_6D_6) δ 0.90 (d, 6.5 Hz, 3H), 1.06 (d, 6.5 Hz, 3H), 1.99 (m, 1H), 2.17 (s, 3H), 2.52 (ddd, 8.8 Hz, 3.8 Hz, 1.5 Hz, 1H), 6.81 (m, 2H), 6.89−6.94 (m, 8H), 7.00−7.03 (m, 4H), 7.12 (m, 2H), 7.23 (m, 2H), 7.29 (virtual t, 7.0 Hz, 1H), 7.33−7.41 (m, 3H), 7.47 (m, 2H), 7.70 (br s, 2H), 7.87 (dd, 8.3 Hz, 1 Hz, 2H); ^{31}P{^{1}H} NMR (C_6D_6) δ 45.8 (d, 14.6 Hz), 47.3 (d, 14.6 Hz); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 19.32 (dd, 90.4 Hz, 6.1 Hz), 21.13 (s), 24.93 (d, 10.3 Hz), 25.71 (s), 31.75 (dd, 4.7 Hz, 1.9 Hz), 125.81 (s), 127.77 (d, 8.2 Hz), 128.96 (d, 10.4 Hz), 128.98 (d, 9.9 Hz), 129.35 (d, 9.1 Hz), 129.61 (d, 9.7 Hz), 130.80 (d, 3.1 Hz), 130.89 (d, 2.9 Hz), 130.95 (d, 2.3 Hz), 131.08−132.66 (4 overlapping doublets), 131.64 (d, 2.0 Hz), 132.22 (dd, 5.5 Hz, 2.0 Hz), 132.36 (dd, 4.7 Hz, 1.8 Hz), 133.63 (d, 13.1 Hz), 133.81 (d, 12.6 Hz), 134.07 (d, 12.6 Hz), 134.20 (d, 14.3 Hz), 134.60 (d, 15.3 Hz), 134.74 (d, 15.1 Hz), 136.34 (virtual t, 3.3 Hz), 138.54 (s), 144.14 (dd, 69.2 Hz, 40.2 Hz), 144.61 (virtual t, 36.7 Hz), 161.48 (dd, 120.8 Hz, 9.2 Hz); IR (KBr, cm^{-1}) ν(CN) 2171. Anal. Calcd for $C_{42}H_{39}NP_2Pd\cdot C_4H_8O$: C, 69.21; H, 5.93; N, 1.75. Found: C, 69.52; H, 5.93; N, 1.49.

[Pd(Ph$_2$P(C$_6$H$_4$)PPh$_2$)(CHPhCN)(C$_6$H$_4$-4-Me)] (28). Following the procedure for the preparation of **26**, reaction of 200 mg (0.276 mmol) of [Pd(DPPBz)(C$_6$H$_4$-4-Me)(Br)] and 49 mg (0.32 mmol) of KN(C)CHPh in 10 mL of toluene gave 171 mg (81.3%) of the product as a yellow solid after crystallization from toluene layered with pentane cooled at −35 °C. ^{1}H NMR (C_6D_6) δ 2.16 (s, 3H), 4.40 (dd, 11.3 Hz, 9.8 Hz, 1H), 6.75−6.85 (m, 9H), 6.88−6.91 (m, 6H), 6.98 (m, 4H), 7.08−7.13 (m, 4H), 7.17−7.27 (m, 6H), 7.34 (br s, 2H), 7.66 (ddd, 11.0 Hz, 8.5 Hz, 1.5 Hz, 2H); ^{31}P{^{1}H} NMR (C_6D_6) δ 42.3 (d, 17.1 Hz), 47.3 (d, 17.1 Hz); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 17.25 (dd, 81.4 Hz, 5.2 Hz), 21.08 (s), 122.35 (d, 2.1 Hz), 125.87 (d, 3.5 Hz), 127.38 (dd, 7.2 Hz, 2 Hz), 127.96 (s), 128.07 (d, 6.8 Hz), 128.86 (d, 10.6 Hz), 128.97 (d, 10.4 Hz), 129.42 (d, 4.2 Hz), 129.49 (d, 4.3 Hz), 130.82 (d, 2.3 Hz), 131.02 (d, 1.8 Hz), 131.18 (d, 1 Hz), 131.28 (d, 2.4 Hz), 130.86−131.75 (4 overlapping doublets), 132.24 (dd, 4.2 Hz, 2.0 Hz), 132.38 (dd, 4.5 Hz, 2.1 Hz), 133.84 (d, 12.6 Hz,), 134.10 (d, 12.8 Hz), 134.30 (d, 12.3 Hz), 134.38 (d, 14.1 Hz), 134.05−134.44 (2 obscured doublets), 136.40 (virtual t, 3.6 Hz), 138.53 (s), 143.86 (virtual t, 42.3 Hz), 144.26 (dd, 39.7 Hz, 39.2 Hz), 144.70 (dd, 5.7 Hz, 3.1 Hz), 161.29 (dd, 118.4 Hz, 9.4 Hz); IR (KBr, cm^{-1}) ν(CN) 2180. Anal. Calcd for $C_{45}H_{37}NP_2Pd$: C, 71.10; H, 4.91; N, 1.84. Found: C, 71.07; H, 4.94; N, 1.77.

[Pd(Ph$_2$P(C$_6$H$_4$)PPh$_2$)(CMe$_2$CN)(C$_6$H$_4$-4-Me)] (29). Following the procedure for the preparation of **26**, reaction of 190 mg (0.262 mmol) of [Pd(DPPBz)(C$_6$H$_4$-4-Me)(Br)] and 56 mg (0.53 mmol) of KN(C)CMe$_2$ in 5 mL of toluene gave 104 mg (55.6%) of the product as pale yellow crystals after layering a toluene solution with pentane at −35 °C. Recrystallization by vapor diffusion of pentane into a toluene solution at −35 °C gave colorless prism crystals of the toluene solvate that were suitable for X-ray structural analysis. ^{1}H NMR (C_6D_6) δ 1.51 (d, 7.0 Hz, 6H), 2.14 (s, 3H), 6.76 (m, 4H), 6.88−6.96 (m, 6H), 7.00−7.11 (m, 7H), 7.25 (ddd, 10.6 Hz, 8.3 Hz, 1.0 Hz, 4H), 7.33 (m, 1H), 7.38 (dd, 7.3 Hz, 6.5 Hz, 2H), 7.91 (ddd, 11.0 Hz, 8.0 Hz, 1.5 Hz, 4H); ^{31}P{^{1}H} NMR (C_6D_6) δ 43.7 (d, 12.2 Hz), 45.5 (d, 12.2 Hz); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 12.45 (dd, 100.8 Hz, 4.1 Hz), 21.06 (s), 30.27 (virtual t, 4.0 Hz), 125.81 (s), 127.95 (d, 7.8 Hz), 128.79 (d, 10.1 Hz), 129.27 (d, 9.8 Hz), 131.07 (d, 2.9 Hz), 131.24 (d, 2.1 Hz), 131.43 (d, 46.7 Hz), 131.92 (dd, 3.0 Hz, 1.8 Hz), 132.16 (d, 49.4 Hz), 132.19 (dd, 3.5 Hz, 1 Hz), 134.03 (d, 11.2 Hz), 134.07 (d, 14.3 Hz), 134.31 (d, 15.6 Hz), 134.71 (d, 13.6 Hz), 136.67 (virtual t, 3.3 Hz), 138.52 (s), 143.67 (virtual t, 39.9 Hz), 146.25 (virtual t, 40.9 Hz), 163.55 (dd, 114.5, 12.5 Hz); IR (KBr, cm^{-1}) ν(CN) 2170. Anal. Calcd for $C_{41}H_{37}NP_2Pd\cdot C_7H_8$: C, 71.68; H, 5.64; N, 1.74. Found: C, 71.45; H, 5.83; N, 1.63.

[Pd(D^{i}PrPF)(CHPhCN)(C$_6$H$_4$-4-*t*-Bu)] (30). Following the procedure for the preparation of **26**, reaction of 215 mg (0.291 mmol) of [Pd(D^{i}PrPF)(C$_6$H$_4$-4-*t*-Bu)(Br)] and 59 mg (0.38 mmol) of KN(C)CHPh in 6 mL of toluene gave 124 mg (55.0%) of the product as a bright yellow solid after crystallization from toluene layered with pentane cooled at −35 °C. ^{1}H NMR (C_6D_6) δ 0.73 (dd, 12.8 Hz, 6.8 Hz, 3H), 0.83 (dd, 14.8 Hz, 7.3 Hz, 6H), 0.94 (dd, 11.8 Hz, 6.3 Hz, 3H), 1.17 (dd, 13.8 Hz, 6.8 Hz, 3H), 1.28 (dd, 16.0 Hz, 7.0 Hz, 3H), 1.35 (s, 9H), 1.43 (dd, 14.5 Hz, 7.5 Hz, 3H), 1.56 (dd, 14.3 Hz, 7.3 Hz, 3H), 1.99 (m, 1H), 2.10 (m, 1H), 2.23 (m, 2H), 3.92 (m, 1H), 3.95 (m, 2H), 3.97 (m, 1H), 3.99 (m, 1H), 4.05 (m, 2H), 4.10 (m, 1H), 4.35 (dd, 14.5 Hz, 9.5 Hz, 1H), 6.69 (m, 1H), 6.75 (dt, 7.5 Hz, 2.3 Hz, 1H), 6.90 (td, 7.0 Hz, 1.0 Hz, 1H), 7.03 (m, 4H), 7.30 (dt, 7.5 Hz, 2.0 Hz, 1H), 8.09 (m, 1H); ^{31}P{^{1}H} NMR (C_6D_6) δ 25.5 (d, 22.0 Hz), 32.7 (d, 22.0 Hz); ^{13}C NMR (C_4D_8O) δ 15.25 (dd, 82.9 Hz, 7.5 Hz), 18.57 (s), 19.23 (s), 19.33 (s), 19.45 (br s), 19.96 (s), 20.45 (d, 6.0 Hz), 21.01 (d, 5.3 Hz), 21.54 (d, 6.8 Hz), 25.44 (d, 23.1 Hz), 25.70 (d, 22.3 Hz), 25.80 (d, 15.5 Hz), 26.07 (d, 15.8 Hz), 32.13 (s), 34.39 (s), 71.38 (d, 3.5 Hz), 71.87 (d, 4.0 Hz), 71.97 (d, 3.6 Hz), 72.41 (d, 5.0 Hz), 73.73 (d, 4.8 Hz), 74.04 (d, 5.3 Hz), 74.12 (d, 7.3 Hz), 74.20 (d, 8.4 Hz), 76.07 (dd, 27.4 Hz, 4.8 Hz), 79.98 (dd, 23.7 Hz, 8.4 Hz), 121.84 (s), 123.82 (d, 7.8 Hz), 124.57 (d, 7.7 Hz), 125.15 (d, 8.4 Hz), 126.09 (s), 127.62 (s), 135.36 (virtual t, 3.2 Hz), 137.68 (virtual t, 3.6 Hz), 145.19 (s), 145.74 (dd, 4.0 Hz, 4.0 Hz), 158.25 (dd, 110.9 Hz, 16.5 Hz); IR (KBr, cm^{-1}) ν(CN) 2176. Anal. Calcd for $C_{37}H_{57}FeNP_2Pd$: C, 62.06; H, 7.16; N, 1.81. Found: C, 62.01; H, 7.21; N, 1.78.

[Pd(D^{i}PrPF)(N(C)CMe$_2$)(C$_6$H$_4$-4-*t*-Bu)] (31). Following the procedure for the preparation of **26**, reaction of 152 mg (0.206 mmol) of [Pd(D^{i}PrPF)(C$_6$H$_4$-4-*t*-Bu)(Br)] and 42 mg (0.39 mmol) of KN(C)CMe$_2$ in 7 mL of toluene gave 62 mg (41%) of the product as red crystals after crystallization from toluene layered with pentane cooled at −35 °C. These crystals were suitable for X-ray structural analysis. ^{1}H NMR (C_6D_6) δ 0.88 (dd, 14.0 Hz, 7.0 Hz, 6H), 1.12 (m, 12H), 1.41 (s, 9H), 1.62 (dd, 15.8 Hz, 7.3 Hz, 6H), 1.71 (d, 6.5 Hz, 6H), 2.05 (m, 2H), 2.46 (m, 2H), 3.94 (m, 2H), 3.98 (m, 2H), 4.07 (m, 2H), 4.10 (m, 2H), 7.32 (dd, 8.3 Hz, 1.8 Hz, 2H), 7.76 (dd, 8.0 Hz, 7.0 Hz, 2H); ^{31}P{^{1}H} NMR (C_6D_6) δ 28.2 (d, 31.7 Hz), 36.7 (d, 31.7 Hz); ^{13}C{^{1}H} NMR (C_4D_8O, −10 °C) δ 18.39 (d, 4.8 Hz), 19.37 (br s), 19.89 (d, 4.15 Hz), 20.02 (br s), 20.81 (d, 7.0 Hz), 25.13 (d, 17.0 Hz), 26.14 (d, 26.7 Hz), 32.31 (s), 33.52 (d, 12.6 Hz), 34.71 (s), 71.53 (d, 5.4 Hz), 72.23 (d, 4.8 Hz), 74.01 (d, 7.8 Hz), 74.16 (d, 6.4 Hz), 75.46 (dd, 24.5 Hz, 3.2 Hz), 81.99 (dd, 29.5 Hz, 9.9 Hz), 123.68 (d, 8.6 Hz), 137.48 (s), 145.32 (s), 159.99 (dd, 116.5 Hz, 16.7 Hz) 175.45 (d, 8.2 Hz); IR (KBr, cm^{-1}) ν(N═C═C) 2186, 1997. Anal. Calcd for $C_{36}H_{55}FeNP_2Pd$: C, 59.55; H, 7.64; N, 1.93. Found: C, 59.09; H, 7.61; N, 1.73.

[Pd(BINAP)(CH(CHMe$_2$)CN)(C$_6$H$_4$-4-*t*-Bu)] (32). Following the procedure for the preparation of **26**, reaction of 190 mg (0.202 mmol) of [Pd(BINAP)(C$_6$H$_4$-4-*t*-Bu)(Br)] and 28 mg (0.23 mmol) of KN(C)CH(CHMe$_2$) in 5 mL of toluene gave 119 mg (62.4%) of the product as a pink solid or a mixture of white and red crystals after cooling a toluene solution layered with pentane at −35 °C. The bulk material obtained from this crystallization consistently contained about 10% Pd(BINAP)$_2$, which was the red crystals. ^{1}H NMR (C_6D_6) (ratio = 1:1) δ 0.87 (d, 6.5 Hz, 3H), 1.21 (d, 7.0 Hz, 3H), 1.27 (s, 4.5H), 1.31 (s, 4.5H), 1.80 (m, 0.5H), 1.90 (m, 1.5H), 6.23 (br, 1H), 6.31 (m, 2H), 6.40 (m, 1.5H), 6.46 (m, 2H), 6.54 (m, 1.5H), 6.67 (m, 0.5H), 6.76 (m, 1H), 6.81−6.89 (m, 3H), 6.91 (m, 0.5H), 6.99 (m, 2.5H), 7.01 (m, 1.5H), 7.07−7.15 (m, 3H), 7.17−7.26 (m, 6H), 7.38−7.50 (m, 4H), 7.60 (br, 2H), 7.67 (m, 1H), 7.76 (m, 1H), 7.98−8.07 (m, 2H); ^{31}P{^{1}H} NMR (C_6D_6) (ratio = 1:1) δ 18.3 (d, 24.2 Hz), 19.3 (d, 24.2 Hz), 20.3 (d, 22.2 Hz), 22.5 (d, 24.2 Hz); IR (KBr, cm^{-1}) ν(CN) 2176.

[Pd(BINAP)(CHPhCN)(C$_6$H$_4$-4-*t*-Bu)] (33). Following the procedure for the preparation of **26**, reaction of 190 mg (0.202 mmol) of [Pd(BINAP)(C$_6$H$_4$-4-*t*-Bu)(Br)] and 63 mg (0.40 mmol) of KN(C)CHPh in 7 mL of toluene gave 111 mg (56.1%) of the

product as a yellow solid after cooling a toluene solution layered with pentane at −35 °C. The compound was recrystallized as a pale yellow powder from a THF solution of the product layered with ether at −35 °C. ^{1}H NMR (C_6D_6) (ratio = 2:1) δ 1.31 (s, 3H), 1.32 (s, 6H), 3.71 (dd, 15.3 Hz, 9.3 Hz, 0.67H), 3.85 (dd, 15.3 Hz, 9.8 Hz, 0.33H), 6.22 (m, 2H), 6.31−6.38 (m, 2.33H), 6.45−6.60 (m, 5H), 6.72−6.82 (m, 5H), 6.87−7.12 (m, 11.67H), 7.20−7.31 (m, 4H), 7.36−7.52 (m, 5H), 7.61 (br, 2H), 7.83 (m, 2H), 8.04−8.12 (m, 2H); ^{31}P{^{1}H} NMR (C_6D_6) (ratio = 2:1) δ 19.9 (d, 29.3 Hz), 23.2 (d, 29.3 Hz); 16.2 (d, 29.3 Hz), 23.0 (d, 29.3 Hz); IR (KBr, cm^{-1}) ν(CN) 2183. Anal. Calcd for $C_{62}H_{51}NP_2Pd\cdot C_4H_{10}O$: C, 75.31; H, 5.84; N, 1.33. Found: C, 75.01; H, 5.85; N, 1.20.

{Pd(PPh$_2$Et)(C$_6$H$_4$-4-Me)(μ-CMe$_2$CN)}$_2$ (34). Following the procedure for the preparation of **26**, reaction of 160 mg (0.227 mmol) of *trans*-[Pd(PPh$_2$Et)$_2$(C$_6$H$_4$-4-Me)(Br)] and 49 mg (0.45 mmol) of KN(C)CMe$_2$ in 5 mL of toluene gave 77 mg (70%) of the product as pale yellow crystals after crystallization from toluene layered with pentane cooled at −35 °C. Recrystallization by vapor diffusion of pentane into a toluene solution at −35 °C gave crystals that were suitable for X-ray structural analysis. ^{1}H NMR (C_6D_6) δ 0.74 (m, 6H), 1.38 (d, 5.5 Hz, 12H), 1.55 (m, 4H), 2.19 (s, 6H), 6.85 (d, 7.5 Hz, 4H), 7.01 (m, 12H), 7.32 (d, 8.0 Hz, 4H), 7.47 (m, 8H); ^{31}P{^{1}H} NMR (C_6D_6) δ 19.4 (s), 21.1; ^{13}C{^{1}H} NMR (C_4D_8O, −10 °C) δ 8.42 (s), 15.38 (d, 97.7 Hz), 19.97 (br d, 26.0 Hz), 21.04 (s), 25.66 (br virtual t, 20.2 Hz), 128.11 (s), 128.82 (m), 130.41 (s), 130.93 (s), 134.05 (dd, 36.3 Hz, 1.8 Hz), 135.35 (m), 135.62 (br s), 138.78 (br s), 156.7 (m); IR (KBr, cm^{-1}) ν(CN) 2195 (br). Anal. Calcd for $C_{50}H_{56}N_2P_2Pd_2$: C, 62.57; H, 5.88; N, 2.92. Found: C, 62.51; H, 5.96; N, 2.86.

[Pd(Ph$_2$P(C$_6$H$_4$)PPh$_2$)(CH$_2$CF$_3$)(C$_6$H$_4$-4-Me)] (35). A solution of *p*-tolyllithium (26 mg, 0.26 mmol) in 5 mL of THF was added dropwise to a stirred solution of 200 mg (0.262 mmol) of [Pd(DPPBz)(CH$_2$CF$_3$)(I)] in 10 mL of THF. The solution was stirred for 30 min at room temperature. When the reaction was complete, as indicated by ^{31}P{^{1}H} NMR spectroscopy, the solution was washed with degassed H_2O (3 × 5 mL), dried over $MgSO_4$, filtered, and concentrated. The product was obtained as a yellow solid in 46% (87 mg) yield by layering the THF solution with ether at −35 °C. ^{1}H NMR (CD_2Cl_2) δ 1.60 (m, 2H), 2.14 (s, 3H), 6.64 (d, 6.5 Hz, 2H), 6.94 (t, 7.5 Hz, 2H), 7.21 (m, 4H), 7.28 (m, 4H), 7.38−7.47 (m, 11H), 7.59 (m, 4H), 7.65 (m, 1H); ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 46.3 (m); ^{19}F NMR (CD_2Cl_2) δ −48.6 (dd, 36.1 Hz, 18.8 Hz). This compound was determined to be >95% pure as judged by NMR spectroscopy. The ^{1}H, ^{31}P, and ^{19}F NMR spectra are included as Supporting Information.

[Pd(Ph$_2$P(C$_6$H$_4$)PPh$_2$)(CF$_3$)(C$_6$H$_4$-2-Me)] (36). To a 20 mL vial was added 200 mg (0.276 mmol) of [Pd(DPPBz)(C$_6$H$_4$-2-Me)(Br)] and 157 mg of TBAT (0.291 mmol). The solid materials were dissolved in 5 mL of THF, and 82 μL (0.55 mmol) of TMSCF$_3$ was added via syringe to the stirred solution. The mixture immediately changed from cloudy to clear yellow. The solution was stirred for 5 min at room temperature, after which time an additional 41 μL (0.28 mmol) of TMSCF$_3$ was added to the solution. The solution was concentrated under vacuum, and a yellow solid was isolated by precipitation after addition of pentane. This solid was dissolved in CH_2Cl_2 and washed with degassed H_2O (3 × 5 mL). The solution was dried over $MgSO_4$, filtered, and concentrated. The product was obtained as a colorless crystalline solid in 52.2% (111 mg) yield by layering the CH_2Cl_2 solution with ether at −35 °C. Crystals suitable for X-ray structural analysis were obtained by layering a deuterated methylene chloride solution of **36** with ether and cooling to −35 °C. ^{1}H NMR (C_6D_6) δ 2.27 (s, 3H), 6.71 (m, 2H), 6.78−6.89 (m, 7H), 6.93−7.09 (m, 10H), 7.33 (m, 2H), 7.59 (m, 5H), 7.90 (m, 2H); ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 45.7 (dq, 17.7 Hz, 51.5 Hz), 44.9 (dq, 17.7 Hz, 18.0 Hz); ^{19}F NMR (CD_2Cl_2) δ −18.3 (dd, 53.1 Hz, 17.7 Hz). Anal. Calcd for $C_{38}H_{31}F_3P_2Pd\cdot 2/3CH_2Cl_2$: C, 60.34; H, 4.23. Found: C, 60.40; H, 3.94.

[Pd(Ph$_2$P(C$_6$H$_4$)PPh$_2$)(CH(CO$_2$CH$_3$)$_2$)(C$_6$H$_4$-2-Me)] (37). To a 20 mL vial was added 220 mg (0.304 mmol) of [Pd(DPPBz)(C$_6$H$_4$-2-Me)(Br)] and 62 mg (0.33 mmol) of KOC(CMe$_2$)C$_6$H$_5$ as solids. The mixture was suspended in 7 mL of toluene and stirred at room temperature for 15 min. After the formation of **8**, as indicated by ^{31}P{^{1}H} NMR spectroscopy, the red solution was filtered through Celite to remove residual salts. Dimethyl malonate (69 μL, 0.61 mmol) was added to the stirred solution of **8**, and the solution immediately changed from clear red to clear yellow. When the reaction was complete, as indicated by ^{31}P{^{1}H} NMR spectroscopy, the solution was concentrated, and the white product was obtained in 51.6% (122 mg) yield by layering the concentrated toluene solution with pentane and cooling at −35 °C. ^{1}H NMR (CD_2Cl_2) δ 1.69 (s, 3H), 2.90 (s, 3H), 2.95 (s, 3H), 3.78 (dd, 9.6 Hz, 7.2 Hz, 1H), 6.55 (m, 4H), 6.71 (t, 7.2 Hz, 1H), 6.86 (t, 8.0 Hz, 1H), 7.11 (m, 2H), 7.37 (m, 3H), 7.42−7.53 (m, 10H), 7.57 (m, 1H), 7.62−7.78 (m, 6H); ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 51.7 (d, 20.8 Hz), 44.8 (d, 20.8 Hz); IR (KBr, cm^{-1}) ν(C=O) 1724. Anal. Calcd for $C_{42}H_{38}O_4P_2Pd$: C, 65.08; H, 4.94. Found: C, 65.09; H, 5.12.

[Pd(Ph$_2$PCH$_2$CH$_2$PPh$_2$)(CH$_2$C(O)C$_6$H$_4$-4-Me)(C$_6$H$_4$-2-Me)] (38). Following the procedure for the preparation of **3**, reaction of 200 mg (0.296 mmol) of [Pd(DPPE)(C$_6$H$_4$-2-Me)(Br)] and 61 mg (0.35 mmol) of KOC(CH$_2$)C$_6$H$_4$-4-Me in 7 mL of toluene gave 114 mg (53.0%) of the product as a white powder after layering a toluene solution with pentane at −35 °C. ^{1}H NMR (C_6D_6) δ 1.54−1.67 (m, 2H), 1.73 (m, 1H), 1.85 (s, 3H), 1.96 (m, 1H), 2.06 (s, 3H), 3.88 (m, 2H), 6.64 (m, 2H), 6.79 (td, 7.8 Hz, 2.5 Hz, 2H), 6.87−7.00 (m, 10H), 7.09−7.17 (m, 3H), 7.19 (m, 2H), 7.56 (m, 2H), 7.67 (m, 1H), 7.87 (m, 2H), 7.92 (m, 4H); ^{31}P{^{1}H} NMR (C_6D_6) δ 38.1 (d, 15.9 Hz), 39.5 (d, 15.9 Hz); selected ^{13}C{^{1}H} NMR data (CD_2Cl_2) δ21.65 (s), 25.87 (virtual t, 2.5 Hz), 26.96 (dd, 19.9 Hz, 17.7 Hz), 27.15 (dd, 20.8 Hz, 17.3 Hz), 32.31 (dd, 66.7 Hz, 4.2 Hz), 202.14 (virtual t, 3.8 Hz); IR (KBr, cm^{-1}) ν(C=O) 1608. Anal. Calcd for $C_{42}H_{40}P_2OPd$: C, 69.19; H, 5.53. Found: C, 68.88; H, 5.58.

Determination of Half-Lives for Reductive Elimination from 5, 26−29, and 35: Representative Procedure. Into an NMR tube with a Teflon-lined screw-cap was placed 0.6 mL of a C_6D_6 solution containing 8.0 mg (0.011 mmol) of complex **26**, 11.6 mg (0.0441 mmol) of PPh_3, and 1.9 mg (0.011 mmol) of 1,3,5-trimethoxybenzene as an internal standard. A ^{1}H NMR spectrum was obtained of this initial mixture. The tube was then placed in an oil bath at 110 °C, and the reaction was monitored at timed intervals by ^{1}H NMR spectroscopy. Concentration of the starting material was determined by integrating the *tert*-butyl resonance of the palladium complex with respect to the internal standard. The half-life was estimated from the time of reaction to consume half of the starting complex relative to the internal standard.

Phosphine Dependence on the Reductive Elimination of 4. A 1.0 × 10^{-3} M stock solution of **4** was prepared by dissolving 3.9 mg (0.0050 mmol) of **4** in 5 mL of toluene. A 1.0 × 10^{-3} M stock solution of DPPBz was prepared by dissolving 4.5 mg (0.0100 mmol) of DPPBz in 10 mL of toluene. Similar solutions of DPPBz with concentrations between 2.0 × 10^{-5} and 2.0 × 10^{-4} M were also prepared. Reaction mixtures were assembled by mixing 0.1 mL of the stock solution of **4** with a stock solution of DPPBz in a 10 mL volumetric flask and adding toluene to bring the total volume to 10 mL. Solutions were then transferred to quartz cuvettes that were sealed with screw caps, and reaction rates were measured by UV−visible spectroscopy at 90 °C as described above. The following rate constants were obtained for [**4**] = 1.0 × 10^{-5} M at different concentrations of DPPBz (k, [DPPBz]): (3.6 ± 0.1) × 10^{-4} s^{-1}, 2.0 × 10^{-5} M; (3.7 ± 0.2) × 10^{-4} s^{-1}, 5.0 × 10^{-5} M; (3.7 ± 0.3) × 10^{-4} s^{-1}; 1.0 × 10^{-4} M; (3.5 ± 0.1) × 10^{-4} s^{-1}, 2.0 × 10^{-4} M.

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Supporting Information Available: X-ray diffraction data for complexes **6**, **25**, and **36** in the form of CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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