Supporting information for

Resting State and Elementary Steps of the Coupling of Aryl Halides with Thiols Catalyzed by Alkylbisphosphine Complexes of Palladium

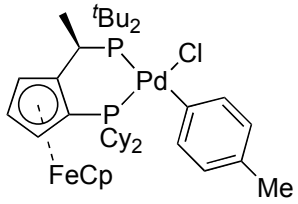
*Elsa Alvaro and John F. Hartwig**

Department of Chemistry, University of Illinois, 600 S Mathews Avenue, Urbana, Illinois, 61801

General methods. All reactions were performed in a drybox or with Schlenk techniques under N_2. ^1H and ^{31}P NMR spectra were recorded on 400 or 500 MHz Varian Unity or Innova instruments. For ^1H NMR, chemical shifts are reported in ppm, relative to residual protiated solvent (C_6HD_5 = 7.15 ppm, $C_6D_5CHD_2$ = 2.09 ppm). For $^{31}P\{^1H\}$ NMR, shifts are reported relative to an external 85% H_3PO_4 standard (shifts downfield of the standard are reported as positive). Elemental Analyses were performed by Robertson Microlit Laboratories, Inc. (Madison, NJ). GC analyses were obtained on an Agilent 6890 GC equipped with an HP-5 column (25 m x 0.20 mm ID x 0.33 μmfilm) and a FID detector. Commercial solvents and reagents were used as received with the following exceptions. Toluene, pentane, tetrahydrofuran, benzene and diethyl ether were purified by passing the degassed solvent (Ar) through a column of activated alumina (Solvent purification system purchased from Innovative Technologies, Newburyport, MA). Toluene-d_8, tetrahydrofuran-d_8 and benzene-d_6 were vacuum transferred from sodium benzophenone ketyl and degassed by three freeze-pump-thaw cycles. NEt_3 was distilled from CaH_2. $\{Pd[P(o\text{-tolyl})_3](p\text{-}C_6H_4\text{-}Me)(\mu\text{-}Br)\}_2$,[1,2] $Pd[P(o\text{-tolyl})_3]_2$,[2] $Pd(CyPF\text{-}^tBu)Cl_2$,[3]

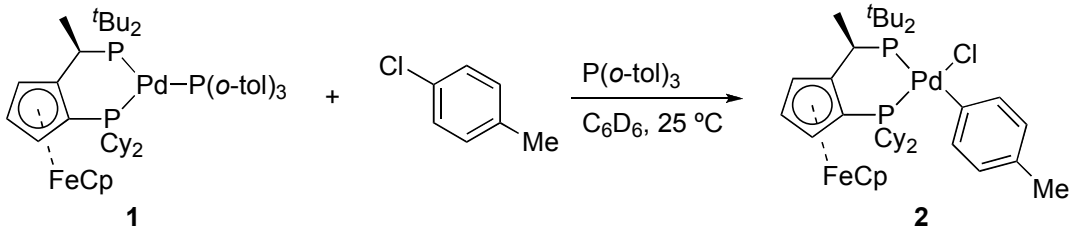
$Pd(CH_3CN)_2Br_2$,[4] $\{Pd(PPh_3)(C_6H_4\text{-}4\text{-}Me)(\mu\text{-}OH)\}_2$[5] and Pd(CyPF-^{t}Bu)(Br)(C_6H_4-4-OMe)[6] were prepared following literature procedures.

Independent synthesis of Pd(CyPF-^{t}Bu)(Cl)(C_6H_4-4-Me) (2).



A solution of CyPF-^{t}Bu (115 mg, 0.207 mmol) in benzene (2 mL) was added to a mixture of Pd[P(*o*-tolyl)$_3$]$_2$ (138 mg, 0.193 mmol) and 4-chlorotoluene (212 mg, 1.67 mmol) in 6 mL of benzene. The mixture was stirred for 3 h at room temperature. Then, it was filtered through Celite and concentrated. The product was obtained as an orange solid (99 mg, 78%) by layering a benzene solution with pentane at -35 ºC. ^{1}H NMR (C_6D_6): 7.70 (br s, 2H), 7.15 (br s, 1H), 7.00 (br s, 1H), 4.59 (br s, 1H), 4.02 (s, 1H), 3.97 (s, 6H), 3.07 (m, 1H), 2.66 (br s, 1H), 2.27 (s, 3H), 1.96-1.02 (m, 24H), 1.65 (d, J = 11.4 Hz, 9H), 1.32 (d, J = 13.1 Hz, 9H). ^{31}P{^{1}H} NMR (C_6D_6): δ 71.0 (br s), 17.0 (br s). Anal. Calcd for $C_{39}H_{59}ClFeP_2Pd$: C, 59.48; H, 7.55. Found: C, 59.70; H, 7.45.

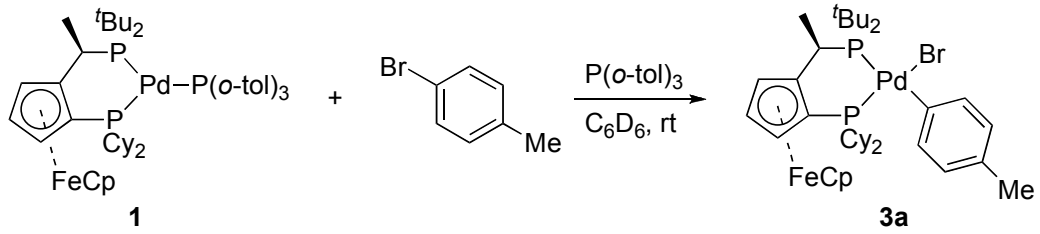
Measurement of the half-life for the oxidative addition of 4-chlorotoluene to (CyPF-^{t}Bu)Pd[P(*o*-tolyl)$_3$] (1).



1 **2**

Into a small vial was placed 14 mg of Pd[P(*o*-tolyl)$_3$]$_2$ (0.020 mmol), 11 mg of CyPF-^{t}Bu (0.021 mmol) and PMes$_3$ (2.4 mg, internal standard). The solids were dissolved in 0.5 mL of C_6D_6, and the solution was transferred to an NMR tube with a septum-lined screw cap. A $^{31}P\{^1H\}$ NMR spectrum was obtained at 25 °C. 20 μL (0.17 mmol) of 4-chlorotoluene were injected into the tube and $^{31}P\{^1H\}$ NMR spectra were recorded at 25 °C every 2 min for at least 5 half-lives by an automated program.

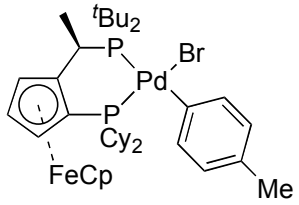
Oxidative addition of 4-bromotoluene to (CyPF-^{t}Bu)Pd[P(*o*-tolyl)$_3$] (1).



Preparation of the stock solution of (CyPF-^{t}Bu)Pd[P(o-tolyl)$_3$]. Into a small vial was placed Pd[P(*o*-tolyl)$_3$]$_2$ (29 mg, 0.040 mmol), 22 mg of CyPF-^{t}Bu (0.040 mmol) and PMes$_3$ (3.1 mg, internal standard). The solids were dissolved in 1 mL of C_6D_6, and the solution was stirred for 5 min at room temperature. A $^{31}P\{^1H\}$ NMR spectrum was recorded.

Into an NMR tube with a septum-lined screw cap was placed 35 mg of 4-bromotoluene (0.20 mmol). 0.5 mL of the stock solution of (CyPF-^{t}Bu)Pd[P(*o*-tolyl)$_3$] were injected into the tube and a $^{31}P\{^1H\}$ NMR spectrum was obtained, showing 96% yield of the arylpalladium bromide complex **3a**.

Independent synthesis of Pd(CyPF-^{t}Bu)(Br)(C$_6$H$_4$-4-Me) (3a).

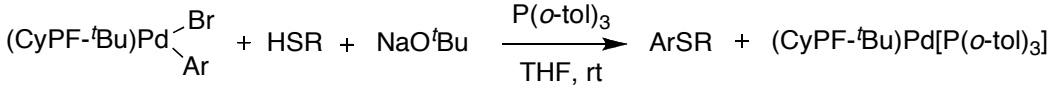


A solution of 232 mg (0.418 mmol) of CyPF-*t*Bu in THF (3 mL) was added to a suspension of 250 mg (0.215 mmol) of {Pd[P(*o*-tolyl)$_3$](4-C$_6$H$_4$-Me)(μ-Br)}$_2$ in THF (5 mL). The reaction mixture was stirred at room temperature for 1 h during which time all the solids dissolved. After that time, the reaction was complete, as determined by ^{31}P{^{1}H} NMR spectroscopy. The orange solution was filtered through Celite and concentrated. The product was obtained as an orange solid (258 mg, 74%) by layering a THF solution with pentane at -35 ºC. ^{1}H NMR (C$_6$D$_6$): 7.72 (br s, 2H), 7.15 (br s, 1H), 6.95 (br s, 1H), 4.64 (br s, 1H), 4.02 (s, 1H), 3.99 (s, 1H), 3.98 (s, 5H), 3.10 (m, 1H), 2.79 (br s, 1H), 2.29 (m, 1H), 2.26 (s, 3H), 1.92 (m, 1H), 1.78-1.02 (m, 19H), 1.67 (d, *J* = 11.6 Hz, 9H), 1.61 (t, *J* = 7.3 Hz, 3H), 1.32 (d, *J* = 12.9 Hz, 9H). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 73.2 (d, *J* = 32.1 Hz), 17.1 (br). Anal. Calcd for C$_{39}$H$_{59}$BrFeP$_2$Pd: C, 56.30; H, 7.15. Found: C, 56.50; H, 7.38.

Preparation of the stock solution A. Into a small vial equipped with a magnetic stir bar was placed the corresponding arylpalladium halide complex (**2**, **3a** or **3b**, c = 0.024 M), tri(*o*-tolyl)phosphine (c = 0.24 M) and PMes$_3$ (22.2 mg) and dodecane (40 μL, 0.17 mmol) as internal standards. THF was added, and the mixture was stirred at room temperature for 5 min. A ^{31}P{^{1}H} NMR spectrum was recorded.

General procedure for the stoichiometric reaction of arylpalladium halide complexes (2 and 3a-b) with thiols in the presence of NaO^{t}Bu.

Into an NMR tube with a septum-lined screw cap was placed NaO^{t}Bu (0.036 mmol) and 0.5 mL of the stock solution A. The corresponding thiol (0.024 mmol) was injected into the NMR tube and $^{31}P\{^1H\}$ NMR spectra were obtained. The starting material was consumed in less than 5 min in all the cases. The yield of the sulfide was determined by GC analysis.

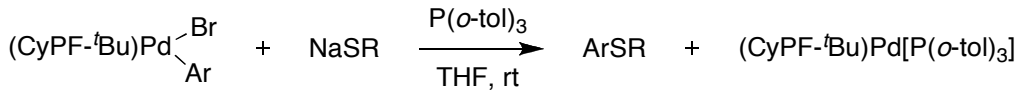


Entry	X	Ar	R	Yield (%) ArSR	Yield (%) Pd(0)
1	Br	C_6H_4-4-Me	^{t}Bu	92	99
2	Br	C_6H_4-4-Me	C_6H_4-4-OMe	94	84
3	Br	C_6H_4-4-OMe	^{t}Bu	99	93
4	Cl	C_6H_4-4-Me	C_6H_4-4-OMe	95	80
5	Cl	C_6H_4-4-Me	^{t}Bu	85	99

General procedure for the stoichiometric reactions of arylpalladium halide complexes (2 and 3a) with sodium thiolates.

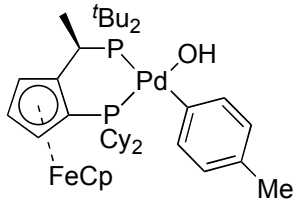
Into an NMR tube with a septum-lined screw cap was placed the thiolate salt (0.024 mmol). 0.5 mL of the stock solution A were injected into the tube and $^{31}P\{^1H\}$ NMR spectra were recorded until the starting material was consumed. In all the cases, the

starting material was consumed in less than 5 min. The yield of the sulfide was determined by GC analysis using dodecane as internal standard.



Entry	X	Ar	R	Yield (%) ArSR	Yield (%) Pd(0)
1	Br	C_6H_4-4-Me	Ph	99	93
2	Br	C_6H_4-4-Me	C_6H_4-4-OMe	99	92
3	Cl	C_6H_4-4-Me	C_6H_4-4-OMe	99	85

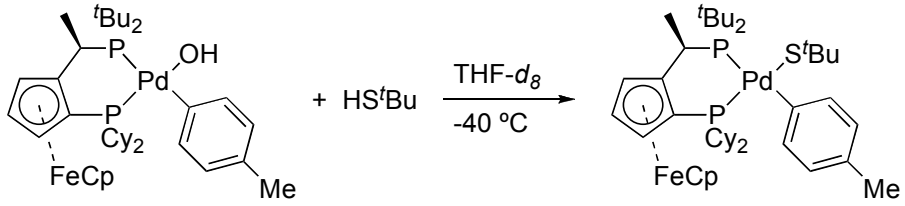
Synthesis of Pd(CyPF-^{t}Bu)(OH)(C_6H_4-4-Me) (5).



A solution of 116 mg (0.209 mmol) of CyPF-^{t}Bu in THF (3 mL) was added to a solution of 99 mg (0.10 mmol) of $\{Pd(PPh_3)(p\text{-}C_6H_4\text{-}Me)(\mu\text{-}OH)\}_2$ in THF (6 mL). The reaction mixture was stirred at room temperature for 5 h. After that time, the reaction was complete, as determined by $^{31}P\{^1H\}$ NMR spectroscopy. The reaction mixture was filtered through Celite and concentrated. The product was obtained as an orange solid (97 mg, 61%) by layering a THF solution with pentane at -35 ºC. ^1H NMR (C_6D_6): 7.92 (br s, 1H), 7.64 (br s, 1H), 7.08 (br s, 1H), 7.03 (br s, 1H), 4.64 (br s, 1H), 4.49 (br s, 1H), 4.07 (s, 1H), 3.98 (s, 6H), 3.09 (m, 1H), 2.24 (s, 3H), 2.24-1.13 (m, 21H), 1.78 (d, J = 11.4 Hz, 9H), 1.66 (t, J = 7.1 Hz, 3H), 1.42 (d, J = 13.3 Hz, 9H), 0.65 (dd, J = 7.1, 4.9 Hz,

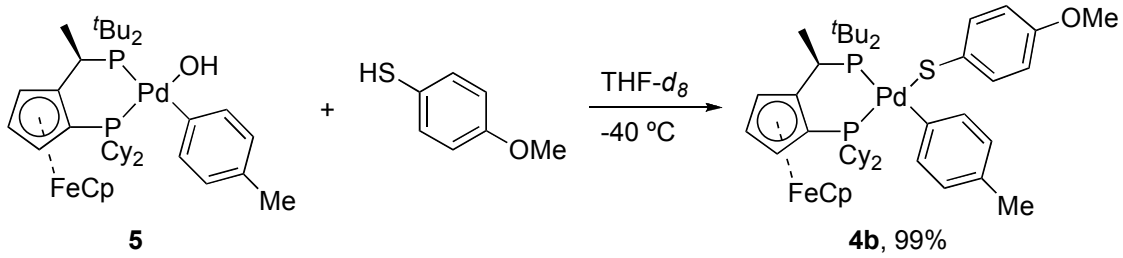
1H). $^{31}P\{^{1}H\}$ NMR (Tol-d_8, -78 ºC): δ 66.0 (d, J = 31.9 Hz, major), 64.4 (d, J = 30.5 Hz, minor), 25.0 (d, J = 30.5 Hz, minor), 19.5 (d, J = 33.5 Hz, major), 1:4 mixture of isomers. Anal. Calcd for $C_{39}H_{60}FeOP_2Pd$: C, 60.90; H, 7.86. Found: C, 60.75; H, 7.77.

Synthesis and characterization of Pd(CyPF-^{t}Bu)(S^{t}Bu)(C_6H_4-4-Me) (4a).



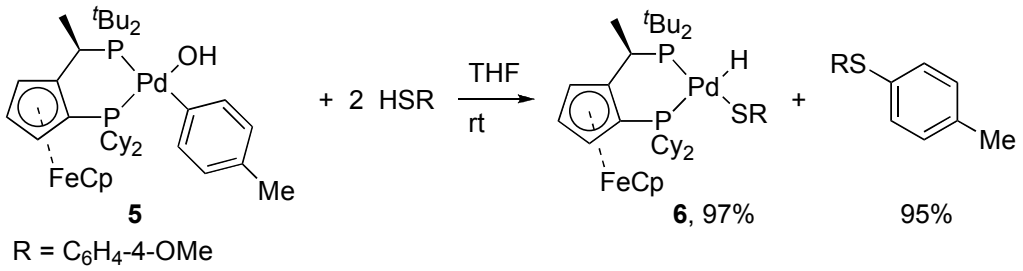
A solution of 8.6 mg (0.011 mmol) of Pd(CyPF-^{t}Bu)(OH)(C_6H_4-4-Me) (**5**) and 1,3,5-trioxane (internal standard) in 0.45 mL of THF-d_8 was placed into an NMR tube with a septum-lined screw-cap. A ^{1}H NMR spectrum was recorded. The sample was cooled to -40 °C, and 1.4 μL (0.012 mmol) of 2-methyl-2-propanethiol were added. The sample was quickly placed into a precooled NMR spectrometer probe at -40 °C. The arylpalladium thiolate complex **4a** was formed in 94% yield. This complex was characterized by NMR spectroscopy at -40 °C. ^{1}H NMR (THF-d_8): 7.63 (virtual t, J = 6.9 Hz, 1H), 7.20 (virtual t, J = 6.7 Hz, 1H), 6.81 (d, J = 7.4 Hz, 1H), 6.68 (d, J = 7.6 Hz, 1H), 4.98 (br s, 1H), 4.65 (br s, 1H), 4.48 (br s, 1H), 3.98 (s, 5H), 3.11 (m, 1H), 3.01 (m, 1H), 2.68 (m 1H), 2.19 (s, 3H), 2.25-0.98 (m, 23H), 1.62 (d, J = 11.0 Hz, 18 H), 0.89 (s, 9H). $^{31}P\{^{1}H\}$ NMR (THF-d_8): δ 68.5 (d, J = 38.2 Hz), 12.5 (d, J = 33.3 Hz).

Synthesis of Pd(CyPF-^{t}Bu)[S(C_6H_4-4-OMe)](C_6H_4-4-Me) (4b).



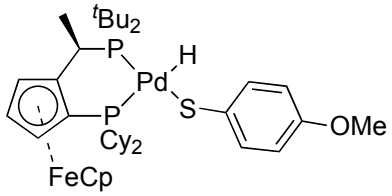
A solution of 9.8 mg (0.013 mmol) of Pd(CyPF-^{t}Bu)(OH)(C_6H_4-4-Me) (**5**) and 1,3,5-trioxane (internal standard) in 0.45 mL of THF-d_8 was placed into an NMR tube with a septum-lined screw-cap. A ^{1}H NMR spectrum was recorded. The sample was cooled to -40 °C, and 1.8 μL (0.014 mmol) of 4-methoxybenzenethiol were added. The sample was quickly placed into a precooled NMR spectrometer probe at -40 °C. The palladium thiolate complex **4b** was formed in 99% yield. Complex **4b** was characterized by NMR spectroscopy at -40 °C. ^{1}H NMR (THF-d_8): 7.55 (t app, J = 6.4 Hz, 1H), 6.68 (d, J = 8.1 Hz, 2H), 6.53 (d, J = 7.5 Hz, 1H), 6.33 (d, J = 7.5 Hz, 1H), 6.28 (d, J = 8.6 Hz, 3H), 5.78 (t app, J = 7.3 Hz, 1H), 4.96 (br s, 1H), 4.69 (br s, 1H), 4.50 (br s, 1H), 4.28 (s, 5H), 3.62 (s, 3H), 3.17 (m, 1H), 2.57 (m, 2H), 3.31-0.80 (m, 19H), 2.1 (s 3H), 2.03 (t, J = 7.3 Hz, 3H), 1.65 (d, J = 11.4 Hz, 18 H). ^{31}P{^{1}H} NMR (THF-d_8): 73.2 (d, J = 34.7 Hz), 16.7 (d, J = 33.7 Hz).

Stoichiometric reaction of the terminal hydroxo complex Pd(CyPF-^{t}Bu)(OH)(C_6H_4-4-Me) (5) with 2 equiv of 4-methoxybenzenethiol at room temperature.



A solution of 6.0 mg (7.8 x 10^{-3} mmol) of Pd(CyPF-^{t}Bu)(OH)(C_6H_4-4-Me) (**5**), 10 μL (0.044 mmol) of dodecane (internal standard) and $PMes_3$ (5 mg, internal standard) in 0.5 mL of THF was placed into an NMR tube with a septum-lined screw-cap. A $^{31}P\{^1H\}$ NMR spectrum was recorded. 4-methoxybenzenethiol (3.0 μL, 0.024 mmol) was added. 97% of the hydrido complex **6** was observed after 5 min of reaction, together with 95% of the thioether.

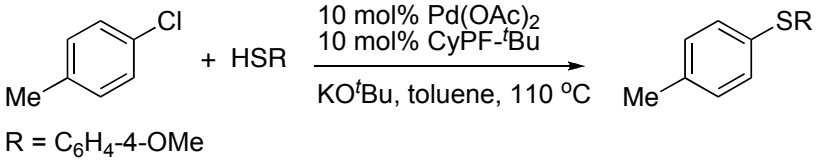
Independent synthesis of (CyPF-^{t}Bu)Pd(H)[S(C_6H_4-4-OMe)] (6).



A solution of 60 mg (0.11 mmol) of CyPF-^{t}Bu in THF (2 mL) was added to a suspension of 70 mg (0.10 mmol) of Pd[P(*o*-tolyl)$_3$]$_2$ in THF (4 mL). The suspension was stirred at room time for 15 min, during which time all the solids dissolved. Then, 25 μL (0.020 mmol) of 4-methoxybenzenethiol were added. The orange mixture was stirred at room temperature for 5 min, filtered through Celite and concentrated. The product was obtained as orange needles (40 mg, 60%. 7.6:1 mixture of isomers) by layering a benzene solution with pentane at -35 ºC. ^{1}H NMR (C_6D_6): 8.22 (d, *J* = 8.8 Hz, 2H, major isomer), 8.17 (d, *J* = 8.7 Hz, 2H, minor isomer), 6.82 (d, *J* = 8.8 Hz, 2H, minor isomer), 6.80 (d, *J*

= 8.7 Hz, 2H, major isomer), 4.57 (s, 1H, major + minor isomers), 4.00 (s, 1H, major + minor isomers), 3.98 (s, 6H, major + minor isomers), 3.36 (s, 3H, minor isomer), 3.31 (s, 3H, major isomer), 3.13 (m, 1H, major + minor isomers), 3.02 (m, 1H, major + minor isomers), 2.65 (m, 1H, major + minor isomers), 2.40-2.02 (m, 5H, major + minor isomers), 1.78-1.01 (m, 18H, major + minor isomers), 1.35 (d, J = 13.1 Hz, 9H, major + minor isomers), 0.94 (d, J = 13.6 Hz, 9H, major + minor isomers), -6.74 (d, J = 206.6 Hz, 1H, major isomer), -7.78 (dd, J = 195.5, 9.0 Hz, 1H, minor isomer). $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ 101.2 (d, J = 26.1 Hz, major isomer), 74.5 (d, J = 30.5 Hz, minor isomer), 35.3 (br s, minor isomer), 11.8 (d, J = 26.3 Hz, major isomer). Anal. Calcd for $C_{39}H_{60}FeOP_2PdS$: C, 58.47; H, 7.55. Found: C, 58.93; H, 7.64.

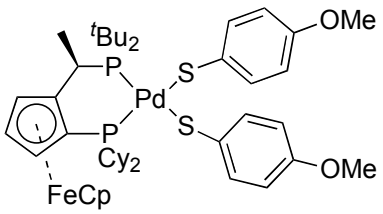
Identification of the resting state of the catalyst in the reaction of 4-chlorotoluene with 4-methoxybenzenethiol catalyzed by a combination of $Pd(OAc)_2$ and CyPF-^{t}Bu.



R = C_6H_4-4-OMe

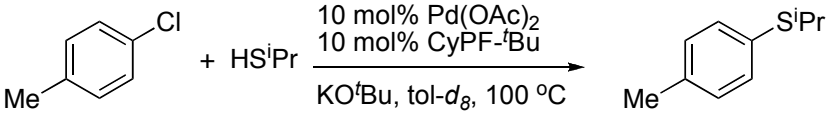
4-chlorotoluene (13 mg, 0.10 mmol), KO^{t}Bu (13 mg, 0.11 mmol) and $PMes_3$ (2.9 mg, internal standard) were weighed into a vial. Dodecane (10 μL, 0.044 mmol internal standard), 0.5 mL of toluene and a solution of $Pd(OAc)_2$ (2.2 mg, 0.010 mmol) and CyPF-^{t}Bu (5.5 mg, 0.010 mmol) in 0.5 mL of toluene were added. The mixture was stirred at room temperature for 1 min prior to the addition of 4-methoxybenzenethiol (13 μL, 0.10 mmol). The mixture was transferred to an NMR tube with a septum-lined screw-cap and heated at 110 °C. $^{31}P\{^{1}H\}$ NMR were obtained during the course of the reaction until the conversion of the starting material was complete.

Independent synthesis of Pd(CyPF-^{t}Bu)[S(C_6H_4-4-OMe)]$_2$ (7).



A solution of 167 mg (0.228 mmol) of Pd(CyPF-^{t}Bu)(Cl)$_2$ in 4 mL of THF was treated with 4-methoxybenzenethiol (62 μL, 0.51 mmol) and NEt_3 (71 μL, 0.51 mmol). After 5 min of stirring at room temperature, the dark red solution was evaporated. The crude was dissolved in toluene, filtered through Celite and concentrated. The product was obtained as a dark red solid (122 mg, 56%) by layering a benzene solution with diethyl ether at -35 ºC. ^{1}H NMR (C_6D_6): 8.07 (d, *J* = 8.3 Hz, 2H), 8.01 (d, *J* = 8.1 Hz, 2H), 6.88 (d, *J* = 8.5 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 4.44 (s, 1H), 3.99 (s and m, 7H), 3.38 (s, 3H), 3.37 (s, 3H), 3.19 (br s, 1H), 2.96 (m, 1H), 2.80 (br s, 1H), 2.41 (m, 2H), 2.16 (m, 2H), 1.78-1.09 (m, 16H), 1.60 (t, *J* = 7.6 Hz, 3H), 1.52 (d, *J* = 12.2 Hz, 9H), 1.37 (d, *J* = 13.4 Hz, 9H). ^{31}P{^{1}H} NMR (C_6D_6): δ 86.6 (d, *J* = 29.1 Hz), 19.0 (br s). Anal. Calcd for $C_{46}H_{66}FeO_2P_2PdS_2$: C, 58.82; H, 7.08. Found: C, 58.61; H, 7.24.

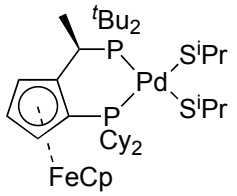
Identification of the resting state of the catalyst in the reaction of 4-chlorotoluene with 2-propanethiol catalyzed by a combination of Pd(OAc)$_2$ and CyPF-^{t}Bu.



4-chlorotoluene (13 mg, 0.10 mmol), 1,3,5-trioxane (internal standard), KO^{t}Bu (13 mg, 0.11 mmol) and 1,3,5-trioxane (2.4 mg, internal standard) were weighed into a vial. A solution of Pd(OAc)$_2$ (2.2 mg, 0.010 mmol) and CyPF-^{t}Bu (7.0 mg, 0.013 mmol) in 0.5

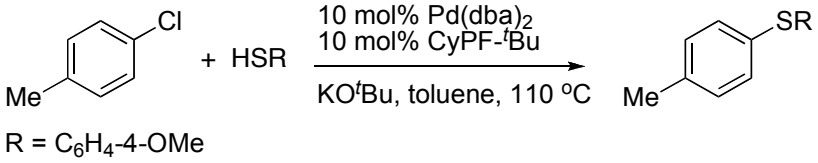
mL of toluene-d_8 were added. The mixture was stirred at room temperature for 1 min and 2-propanethiol was added (9.8 μL, 0.10 mmol). The mixture was transferred to an NMR tube with a septum-lined screw-cap. A ^{1}H NMR spectrum was recorded. The mixture was heated at 100 °C. ^{31}P{^{1}H} NMR spectra were obtained during the course of until full conversion of the starting material was determined by ^{1}H NMR spectroscopy. The yield of the thioether was 88%.

Independent synthesis of Pd(CyPF-^{t}Bu)[S(^{i}Pr)]$_2$ (8).



A solution of 90 mg (0.13 mmol) of Pd(CyPF-^{t}Bu)(Cl)$_2$ in 6 mL of toluene was treated with a 2-propanethiol (27 μL, 0.29 mmol) and NaO^{t}Bu (37 mg, 0.39 mmol). After 1 h of stirring at room temperature, the mixture was filtered through Celite and concentrated. The product was obtained as a red solid (65 mg, 62%) by layering a benzene solution with pentane at -35 ºC. ^{1}H NMR (C_6D_6): 4.77 (m, 2H), 4.53 (s, 1H), 4.02 (s, 1H), 4.00 (s, 6H), 3.95 (s, 1H), 3.34 (br s, 1H), 3.08 (br s, 1H), 2.98 (m, 1H), 2.60 (m, 2H), 2.26 (m, 2H), 1.99 (d, J = 6.3 Hz, 3H), 1.97-1.14 (m, 15H), 1.88 (d, J = 6.8 Hz, 3H), 1.80 (d, J = 6.3 Hz, 3H), 1.75 (d, J = 6.8 Hz, 3H), 1.61 (t, J = 7.3 Hz, 3H), 1.54 (d, J = 12.0 Hz, 9H), 1.41 (d, J = 13.2 Hz, 9H). ^{31}P{^{1}H} NMR (C_6D_6): 82.3 (d, J = 26.1 Hz), 14.3 (br s). MS (FD+): 810.2 (M^+). Anal. Calcd for $C_{38}H_{66}FeP_2PdS_2$: C, 56.26; H, 8.20. Found: C, 56.31; H, 8.45.

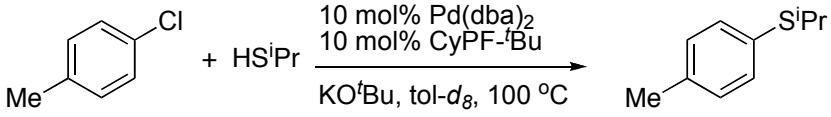
Identification of the resting state of the catalyst in the reaction of 4-chlorotoluene with 4-methoxybenzenethiol catalyzed by a combination of $Pd(dba)_2$ and CyPF-^{t}Bu.



R = C_6H_4-4-OMe

4-chlorotoluene (13 mg, 0.10 mmol), KO^{t}Bu (13 mg, 0.11 mmol) and $PMes_3$ (1.4 mg, internal standard) were weighed into a vial. Dodecane (10 μL, 0.044 mmol, internal standard), 0.5 mL of toluene and a solution of $Pd(dba)_2$ (5.8 mg, 0.010 mmol) and CyPF-^{t}Bu (5.5 mg, 0.010 mmol) in 0.5 mL of toluene were added. The mixture was stirred at room temperature for 1 min prior to the addition of 4-methoxybenzenethiol. The mixture was transferred to an NMR tube with a septum-lined screw-cap and heated at 110 °C. $^{31}P\{^1H\}$ NMR spectra were obtained during the course of the reaction until the conversion of the starting material was complete, as determined by GC analysis.

Representative procedure for the identification of the resting state of the catalyst in the reaction of 4-chlorotoluene with 2-propanethiol catalyzed by a combination of $Pd(dba)_2$ and CyPF-^{t}Bu.



4-chlorotoluene (13 mg, 0.10 mmol), 1,3,5-trioxane (internal standard), KO^{t}Bu (13 mg, 0.11 mmol) and 1,3,5-trioxane (2.1 mg, internal standard) were weighed into a vial. A solution of $Pd(dba)_2$ (5.8 mg, 0.010 mmol) and CyPF-^{t}Bu (5.6 mg, 0.010 mmol) in 0.5 mL of toluene-d_8 was added. The mixture was stirred at room temperature for 1 min prior

to the addition of 2-propanethiol (9.8 μL, 0.10 mmol). The mixture was transferred to an NMR tube with a septum-lined screw-cap. A ^{1}H NMR spectrum was recorded. The mixture was heated at 100 °C. ^{31}P{^{1}H} and ^{1}H NMR spectra were obtained during the course of the reaction until the yield of the thioether was 50%, as determined by ^{1}H NMR spectroscopy.

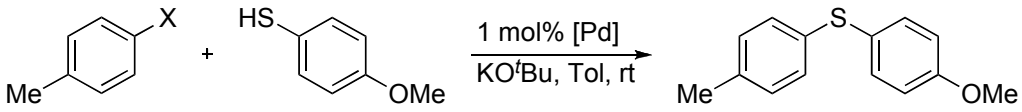
Independent synthesis of [(CyPF-^{t}Bu)Pd]$_2$(dba) (9). Into a 20 mL scintillation vial equipped with a magnetic stir bar was placed (CyPF-^{t}Bu)Pd(dba) (89 mg, 0.099 mmol), NaO^{t}Bu (24 mg, 0.25 mmol) and dioxane (4 mL). Isopropylamine (80 μL, 0.92 mmol) was added and the mixture was heated at 100 °C for 3 h. The reaction was allowed to cool, filtered through Celite and concentrated. The crude product was dissolved in toluene, filtered again through Celite and concentrated. Pentane was added to the resulting solid, affording an orange solution with a precipitate. The precipitate was filtered off and the solvent was evaporated, to yield the product as an orange solid (60 mg, 39%). ^{1}H NMR (C_6D_6): 7.57-6.85 (m), 5.10-5.02 (m), 4.26-4.18 (m), 4.06-3.86 (m), 4.04 (s), 4.03 (s), 4.01 (s), 4.00 (s), 2.98 (m), 2.42-0.82 (m), 1.59 (d, J = 11.7 Hz), 1.52 (d, J = 11.7 Hz), 0.98 (d, J = 12.4 Hz), 0.97 (d, J = 12.7 Hz), 0.63 (d, J = 11.0 Hz) 0.58 (d, J = 12.2 Hz. ^{31}P{^{1}H} NMR (C_6D_6): 82.7 (m), 77.4 (m), 22.9 (m), 20.3 (br s). MS (FD+): 1554.9 (M^+), 894.3 (M^+ - [(CyPF-^{t}Bu)Pd]), 660.2 (M^+ - [(CyPF-^{t}Bu)Pd(dba)]).

Preparation of stock solution B (0.02 M). Toluene (1 mL) was added to a mixture of $Pd(OAc)_2$ (4.4 mg, 0.020 mmol) and CyPF-^{t}Bu (11 mg, 0.020 mmol). The resulting mixture was stirred for 1 min at room temperature prior to use.

Preparation of stock solution C (0.02 M). Toluene (1 mL) was added to a mixture of $Pd(dba)_2$ (11 mg, 0.019 mmol) and CyPF-^{t}Bu (11 mg, 0.020 mmol). The resulting mixture was stirred for 1 min at room temperature prior to use.

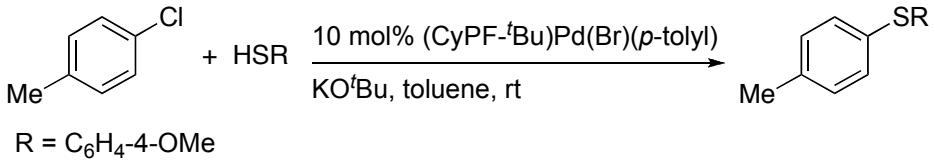
Preparation of stock solution D (0.02 M). Pd(CyPF-^{t}Bu)(*p*-tolyl)(Br) (**3a**) (17 mg, 0.020 mmol) was weighed into a vial. Toluene (1 mL) was added and the resulting solution was stirred for 1 min at room temperature prior to use.

Representative procedure for the catalytic reaction of 4-bromo or chlorotoluene with 4-methoxybenzenethiol.



Into a small vial equipped with a magnetic stir bar was placed 4-bromo or chlorotoluene (1 mmol), KO^{t}Bu (1.4 mmol) and 25 μL (0.11 mmol) of dodecane (internal standard). Toluene (1 mL) and 0.5 mL of the appropriate stock solution of the palladium catalyst (B, C or D) were added. After stirring the mixture for 1 min, 4-methoxybenzenethiol (1 mmol) was added. The reaction was stirred at room temperature for 24 h. The yield was determined by GC analysis.

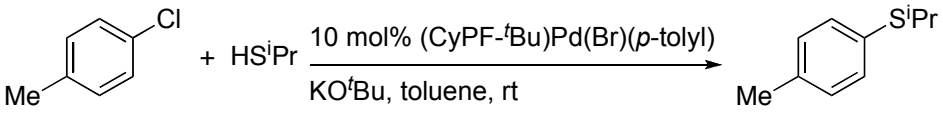
Determination of the resting state of the catalyst in the reaction of 4-chlorotoluene and 4-methoxybenzenethiol catalyzed by Pd(CyPF-^{t}Bu)(C_6H_4-4-Me)(Br) (3a).



R = C_6H_4-4-OMe

4-chlorotoluene (13 mg, 0.10 mmol), KO^{t}Bu (13 mg, 0.11 mmol) and $PMes_3$ (1.6 mg, internal standard) were weighed into a vial. Dodecane (10 μL, 0.044 mmol, internal standard for GC), 0.5 mL of toluene and a solution of Pd(CyPF-^{t}Bu)(*p*-tolyl)(Br) (**3a**) (8.4 mg, 0.010 mmol) in 0.5 mL of toluene were added. The mixture was stirred at room temperature for 1 min prior to treatment with 4-methoxybenzenethiol (13 μL, 0.10 mmol). The mixture was transferred to an NMR tube with a septum-lined screw-cap. $^{31}P\{^1H\}$ NMR spectra were obtained during the course of the reaction until the conversion of the starting material was complete, as determined by GC analysis. The yield of the thioether was 99%.

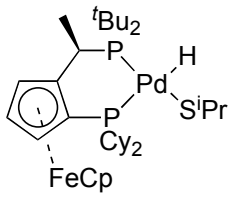
Identification of the resting state of the catalyst in the reaction of 4-chlorotoluene with 2-propanethiol catalyzed by Pd(CyPF-^{t}Bu)(*p*-tolyl)(Br).



4-chlorotoluene (13 mg, 0.10 mmol), 1,3,5-trioxane (internal standard), KO^{t}Bu (13 mg, 0.11 mmol) and Pd(CyPF-^{t}Bu)(*p*-tolyl)(Br) (4.6 mg, 5.5 x 10^{-3} mmol) were weighed into a vial. 0.5 mL of toluene-d_8 were added and the mixture was transferred to an NMR tube with a septum-lined screw-cap. A ^1H NMR spectrum was recorded. 2-propanethiol (9.8 μL, 0.10 mmol) was added to the reation mixture. $^{31}P\{^1H\}$ and ^1H NMR spectra were obtained during the course of the reaction until the conversion 42% conversion of the

starting material, as determined by ^{1}H NMR spectroscopy. The yield of the thioether at this time was 40%.

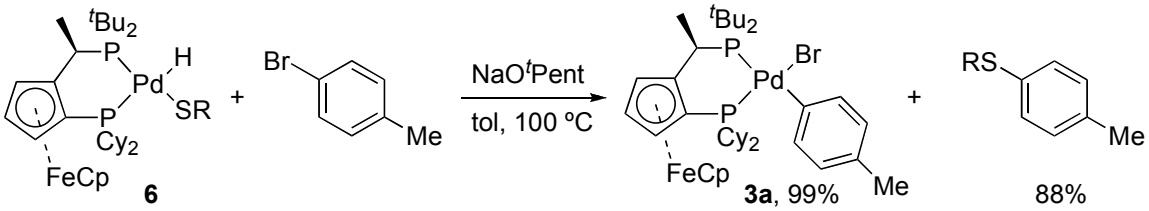
Independent synthesis of (CyPF-^{t}Bu)Pd(H)(S^{i}Pr) (10).



A solution of 266 mg (0.480 mmol) of CyPF-^{t}Bu in THF (3 mL) was added to a suspension of 344 mg (0.481 mmol) of Pd[P(*o*-tolyl)$_3$]$_2$ in THF (6 mL). The suspension was stirred at room time for 15 min, during which time all the solids dissolved. Then, 100 μL (1.08 mmol) of 2-propanethiol were added. The orange mixture was stirred at room temperature for 5 min. After evaporation of the solvent, the crude product was dissolved in toluene, filtered through Celite and concentrated. The product was obtained as an orange solid (50 mg, 15%. 15:1 mixture of isomers) by layering a benzene solution with pentane at -35 ºC. ^{1}H NMR (C_6D_6): 4.59 (s, 1H, major + minor isomers), 4.02 (s, 1H, major + minor isomers), 3.98 (s, 6H, major + minor isomers), 3.97 (s, 1H, major + minor isomers), 3.84 (m, 1H, major + minor isomers), 3.16 (m, 1H, major + minor isomers), 3.02 (m, 1H, major + minor isomers), 2.70 (m, 1H, major + minor isomers), 2.41-2.03 (m, 5H), 1.84 (t, *J* = 6.2 Hz, 6H, major + minor isomers), 1.77-1.23 (m, 17H), 1.42 (d, *J* = 12.7 Hz, 9H, major + minor isomers), 1.00 (d, *J* = 13.2 Hz, 9H, major + minor isomers), -6.79 (d, *J* = 206.9 Hz, 1H, major isomer), -7.83 (dd, *J* = 193.0 Hz, 1H, minor isomer). ^{31}P{^{1}H} NMR (C_6D_6): 99.8 (d, *J* = 27.5 Hz, major isomer), 76.3 (br s, minor isomer), 32.8

(br s, minor isomer), 13.1 (d, J = 27.5 Hz, major isomer). MS (ES+): 737.1 (M^+ + H). Anal. Calcd for $C_{35}H_{60}FeP_2PdS \cdot C_6H_6$: C, 60.40; H, 8.16. Found: C, 60.01; H, 8.31.

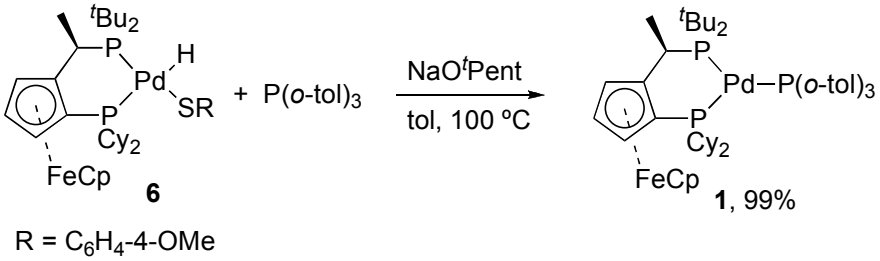
Stoichiometric reaction of Pd(CyPF-^{t}Bu)(H)[S(C_6H_4-4-OMe)] (6) with 4-bromotoluene and NaO^{t}Pent.



R = C_6H_4-4-OMe

Into a small vial equipped with a magnetic stir bar was placed complex **6** (4.5 mg, 5.6 x 10^{-3} mmol), NaO^{t}Pent (3.8 mg, 3.2 x 10^{-2} mmol), 4-bromotoluene (28.1 mg, 0.164 mmol), and $PMes_3$ (1.6 mg) and dodecane (10 μL, 0.044 mmol) as internal standards. Toluene (0.4 mL) was added and the mixture was transferred to an NMR tube with a septum-lined screw-cap. The reaction was heated for 1 h at 100 °C. After that time, 99% conversion to the arylpalladium bromide complex Pd(CyPF-^{t}Bu)(*p*-tolyl)(Br) (**3a**) was observed by $^{31}P\{^1H\}$ NMR spectroscopy, and 88% yield of the thioether was determined by GC analysis.

Stoichiometric reaction of Pd(CyPF-^{t}Bu)(H)[S(C_6H_4-4-OMe)] (6) with NaO^{t}Pent and P(*o*-tol)$_3$.

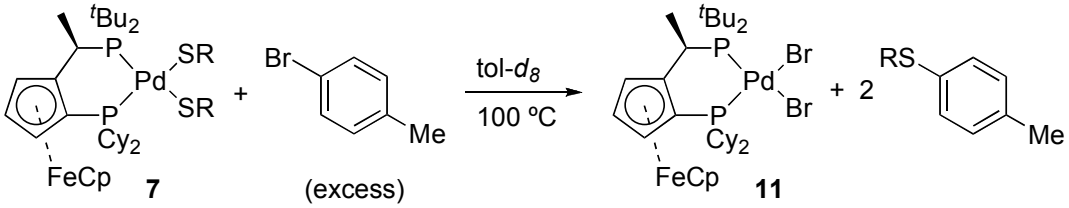


6

R = C_6H_4-4-OMe

Into a small vial equipped with a magnetic stir bar was placed complex **6** (6.9 mg, 8.6 x 10^{-3} mmol), NaO^{t}Pent (4.9 mg, 0.040 mmol), P(*o*-tol)$_3$ (13 mg, 0.042 mmol), and PMes$_3$ (1.5 mg) as internal standard. Toluene (0.4 mL) was added and the mixture was transferred to an NMR tube with a septum-lined screw-cap. A $^{31}P\{^1H\}$ NMR spectrum was recorded. The reaction was heated for 1 h at 100 °C. After that time, full conversion to the Pd(0) complex Pd(CyPF-^{t}Bu)[P(*o*-tol)$_3$] (**1**) was observed by $^{31}P\{^1H\}$ NMR spectroscopy.

Representative procedure for the reaction of Pd(CyPF-^{t}Bu)[S(C_6H_4-4-OMe)]$_2$ (7) with aryl halides.



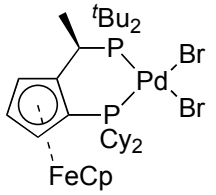
7 (excess) **11**

R = C_6H_4-4-OMe

Into a small vial was placed Pd(CyPF-^{t}Bu)[S(C_6H_4-4-OMe)]$_2$ (**7**) (0.009 mmol), 4-halotoluene, and PMes$_3$ (internal standard). Toluene-d_8 was added to a total volume of 360 μL. The solution was transferred to an NMR tube equipped with a screw cap and a Teflon seal. A $^{31}P\{^1H\}$ NMR spectrum was obtained. The sample was heated at 100 °C and $^{31}P\{^1H\}$ NMR spectra were recorded at different times.

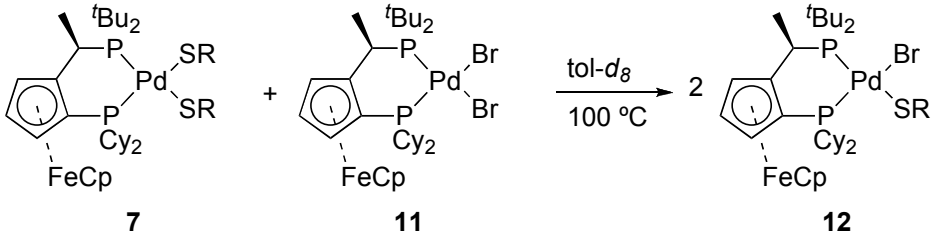
Representative procedure for the reaction of Pd(CyPF-^{t}Bu)[S(C_6H_4-4-OMe)]$_2$ (7) with aryl halides and bis(4-methoxyphenyl) disulfide. Into a small vial was placed Pd(CyPF-^{t}Bu)[S(C_6H_4-4-OMe)]$_2$ (**7**) (0.009 mmol), 4-halotoluene, bis(4-methoxyphenyl) disulfide and $PMes_3$ (internal standard). Toluene-d_8 was added to a total volume of 360 μL. The solution was transferred to an NMR tube equipped with a screw cap and a Teflon seal. A $^{31}P\{^1H\}$ NMR spectrum was obtained. The sample was heated at 100 °C and $^{31}P\{^1H\}$ NMR spectra were recorded at different times.

Independent synthesis of Pd(CyPF-^{t}Bu)(Br)$_2$ (11).



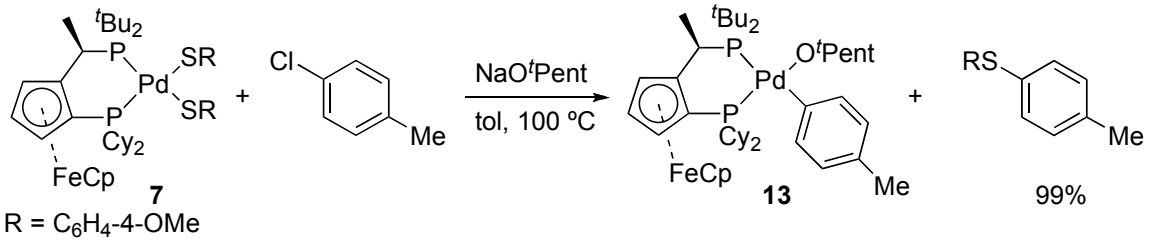
A solution of 138 mg CyPF-^{t}Bu (0.249 mmol) in 4 mL of THF was added to a suspension of 87 mg of $Pd(CH_3CN)_2Br_2$ (0.25 mmol) in THF (8 mL) at room temperature. The mixture was stirred for 24 h. Then, it was evaporated, dissolved in toluene, filtered through Celite and concentrated. The product was obtained as an orange solid (195 mg, 95%) by layering a THF solution with pentane at -35 ºC. ^1H NMR (C_6D_6): 4.45 (s, 1H), 4.02 (s, 1H), 3.98 (s, 6H), 3.60 (br s, 1H), 2.88-2.80 (m, 3H), 2.52 (m, 1H), 2.35 (m, 1H), 2.03-1.11 (m, 20H), 1.52 (d, J = 13.2 Hz, 9H), 1.31 (d, J = 14.2 Hz, 9H). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 112.5 (d, J = 18.4 Hz), 31.6 (br). Anal. Calcd for $C_{32}H_{52}Br_2FeP_2Pd$: C, 46.83; H, 6.39. Found: C, 47.18; H, 6.57.

Reaction of Pd(CyPF-^{t}Bu)[S(C_6H_4-4-OMe)]$_2$ (7) with Pd(CyPF-^{t}Bu)(Br)$_2$ (11) to form Pd(CyPF-^{t}Bu)[S(C_6H_4-4-OMe)](Br) (12).



Into a small vial equipped with a magnetic stir bar was placed Pd(CyPF-^{t}Bu)[S(C_6H_4-4-OMe)]$_2$ (**7**) (5.0 mg, 5.3 x 10^{-3} mmol), Pd(CyPF-^{t}Bu)(Br)$_2$ (**11**) (4.6 mg, 5.6 x 10^{-3} mmol) and $PMes_3$ (2.9 mg, internal standard). Toluene-d_8 (0.4 mL) was added and the mixture was transferred to an NMR tube equipped with a screw cap and a Teflon seal. The sample was heated at 100 °C. After 4 h, $^{31}P\{^1H\}$ NMR spectroscopy data showed a 1: 1: 3.8 ratio of **7**, **11** and a new complex (**12**), respectively. The new complex was assigned as Pd(CyPF-^{t}Bu)[S(C_6H_4-4-OMe)](Br) (2.8:1 mixture of isomers). $^{31}P\{^1H\}$ NMR (C_6D_6): 100.4 (br s, M), 99.2 (br s, m), 26.2 (br s, M), 24.3 (br s, m).

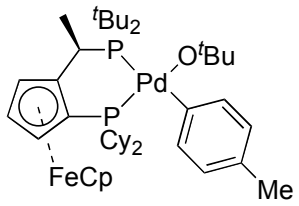
Reaction of Pd(CyPF-^{t}Bu)[S(C_6H_4-4-OMe)]$_2$ (7) with 4-chlorotoluene in the presence of NaO^{t}Pent.



Into a small vial equipped with a magnetic stir bar was placed Pd(CyPF-^{t}Bu)[S(C_6H_4-4-OMe)]$_2$ (8.2 mg, 8.7 x 10^{-3} mmol), NaO^{t}Pent (5.8 mg, 0.050 mmol), 4-chlorotoluene (63 mg, 0.50 mmol) and $PMes_3$ (2.1 mg, internal standard). Toluene (0.3 mL) and dodecane

(10 μL, 0.044 mmol, internal standard) were added and the mixture was transferred to an NMR tube equipped with a screw cap and a Teflon seal. The sample was heated at 100 °C. After 20 min, $^{31}P\{^{1}H\}$ NMR spectroscopy data showed complete consumption of the starting complex. GC analysis showed 99% yield after 40 min of heating.

Independent synthesis of Pd(CyPF-^{t}Bu)(O^{t}Bu)(C_6H_4-4-Me) (14).

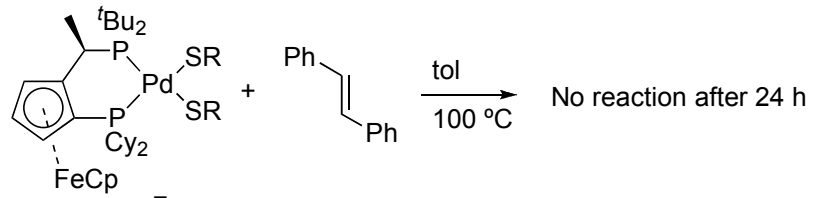


Into a 20 mL scintillation vial equipped with a magnetic stir bar was placed Pd(CyPF-^{t}Bu)(*p*-tolyl)(Cl) (**2**) (98 mg 0.12 mmol) and NaO^{t}Bu (60 mg, 0.61 mmol). Toluene (6 mL) was added and the mixture was stirred at room temperature for 12 h. The reaction mixture was filtered through Celite and concentrated. 60 mg (70%) of an orange solid, which was identified as Pd(CyPF-^{t}Bu)(O^{t}Bu)(C_6H_4-4-Me) was obtained (11:1 mixture of isomers). ^{1}H NMR (C_6D_6): 8.25 (virtual t, J = 7.3 Hz, 1H), 7.60 (virtual t, J = 7.6 Hz, 1H), 7.15 (overlapped m, 1H), 7.02 (d, J = 7.3 Hz, 1H), 4.72 (s, 1H), 4.02-3.97 (m + s, 7H), 3.29 (m, 1H), 3.10 (m, 2H), 2.27 (s, 3H), 2.10-1.08 (m, 20H), 1.83 (d, J = 11.0 Hz, 9H), 1.60 (t, J = 7.1 Hz, 3H), 1.37 (s, 9H) 1.31 (d, J = 12.7 Hz, 9H). $^{31}P\{^{1}H\}$ NMR (C_6D_6): 91.9 (br s, m), 64.3 (d, J = 36.6 Hz, M), 32.6 (br s, m), 15.6 (d, J = 36.6 Hz, M).

Preparation of stock solution E. Into a small vial equipped with a magnetic stir bar was placed Pd(CyPF-^{t}Bu)[S(C_6H_4-4-OMe)]$_2$ (**7**) (10 mg, 0.011 mmol), *trans*-stilbene (30

mg, 0.22 mmol) and $PMes_3$ (1.7 mg, internal standard). Toluene (0.8 mL) was added and the resulting mixture was stirred for 1 min at room temperature prior to use.

Stoichiometric reaction of Pd(CyPF-^{t}Bu)[S(C_6H_4-4-OMe)]$_2$ (7) with *trans*-stilbene.

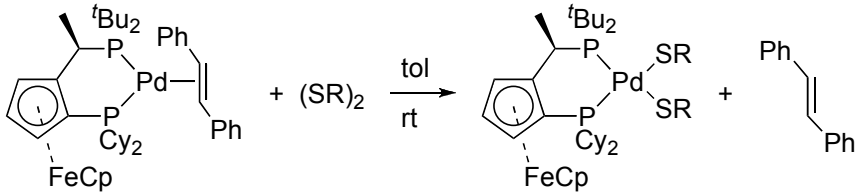


7

R = C_6H_4-4-OMe

0.4 mL of the stock solution E were transferred to an NMR tube with a septum-lined screw-cap. The mixture was heated at 100 °C for 24 h. Several $^{31}P\{^1H\}$ spectra were recorded at different times, showing just starting material unreacted.

Stoichiometric reaction of Pd(CyPF-^{t}Bu)(*trans*-stilbene) (15) with bis(4-methoxyphenyl) disulfide.



15

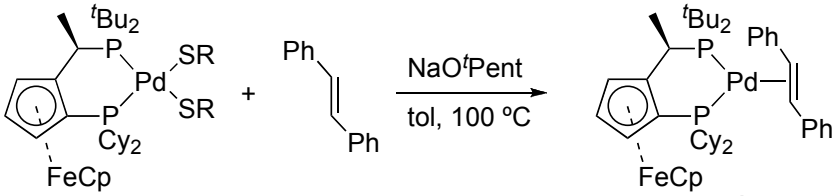
R = C_6H_4-4-OMe

7, 99%

Into a small vial equipped with a magnetic stir bar was placed Pd(CyPF-^{t}Bu)(*trans*-stilbene) (**15**) (6 mg, 7 x 10^{-3} mmol), bis(4-methoxyphenyl) disulfide (22 mg, 0.077 mmol) and $PMes_3$ (2.8 mg, internal standard). The mixture was stirred and transferred to an NMR tube with a septum-lined screw-cap. A color change from orange to dark red

was observed. After 50 min, full conversion to the bis-thiolate complex **7** was determined by $^{31}P\{^{1}H\}$ NMR spectroscopy.

Stoichiometric reaction of Pd(CyPF-^{t}Bu)[S(C_6H_4-4-OMe)]$_2$ (7) with *trans*-stilbene and NaO^{t}Pent.

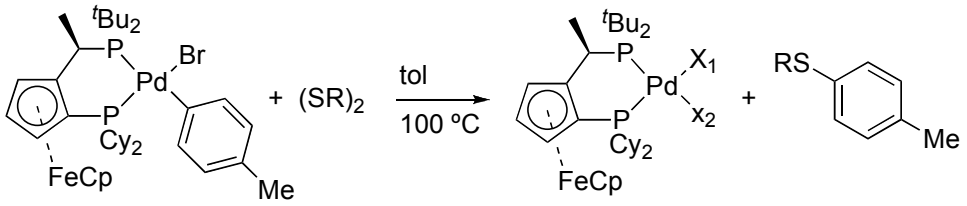


7
R = C_6H_4-4-OMe

15

Into a small vial equipped with a magnetic stir bar was placed NaO^{t}Pent (7.5 mg, 0.065 mmol) and 0.4 mL of the stock solution D. The mixture was transferred to an NMR tube with a septum-lined screw-cap and heated at 100 °C. After 6 h, a 2.8:1 mixture of Pd(CyPF-^{t}Bu)[S(C_6H_4-4-OMe)]$_2$ (**7**) and the *trans*-stilbene complex **15** were observed.

Stoichiometric reaction of Pd(CyPF-^{t}Bu)(*p*-tolyl)(Br) (3a) with bis(4-methoxyphenyl) disulfide.



3a
R = C_6H_4-4-OMe

12, X_1 = SR, X_2 = Br
11, X_1 = X_2 = Br
7, X_1 = X_2 = SR
12:11:7, 3.7:1:1

88%

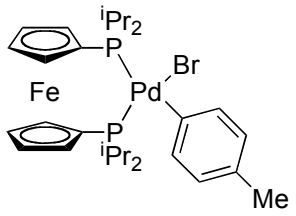
Into a small vial equipped with a magnetic stir bar was placed Pd(CyPF-^{t}Bu)(*p*-tolyl)(Br) (**3a**) (12 mg, 0.015 mmol), bis(4-methoxyphenyl) disulfide (4.2 mg, 0.015

mmol), dodecane (25 μL, 0.11 mmol) and $PMes_3$ (2.4 mg, internal standards). Toluene (0.5 mL) was added and the mixture was transferred to an NMR tube with a septum-lined screw-cap. The reaction mixture was heated at 100 °C for 24 h. Several $^{31}P\{^1H\}$ NMR spectra were recorded, showing a mixture (1: 3.5: 1) of Pd(CyPF-^{t}Bu)[S(C_6H_4-4-OMe)]$_2$ (**7**), Pd(CyPF-^{t}Bu)(Br)[S(C_6H_4-4-OMe)] (**12**), and Pd(CyPF-^{t}Bu)$(Br)_2$ (**11**). The yield of thiother was 88%, as determined by GC analysis.

Oxidative addition of 4-chlorotoluene to [(CyPF-^{t}Bu)Pd]$_2$(dba) (9).

Into a small vial equipped with a magnetic stir bar was placed [(CyPF-^{t}Bu)Pd]$_2$(dba) (**9**) (5 mg, 0.003 mmol), 4-chlorotoluene (16 mg, 0.12 mmol) and $PMes_3$ (2.4 mg, internal standard). Toluene (0.4 mL) was added and the mixture was transferred to an NMR tube with a septum-lined screw-cap. A $^{31}P\{^1H\}$ NMR spectrum was recorded. The reaction mixture was heated at 100 °C for 20 h. Several $^{31}P\{^1H\}$ NMR spectra were recorded.

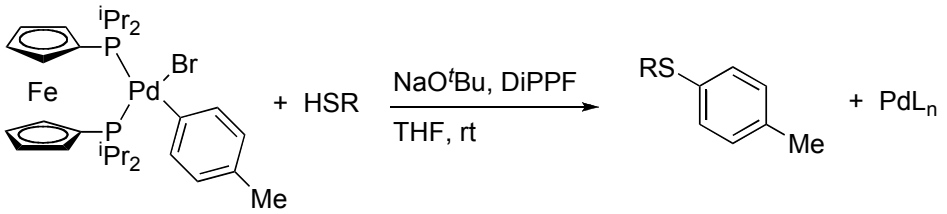
Synthesis of Pd(DiPPF)(Br)(C_6H_4-4-Me) (16).



A solution of 84 mg (0.20 mmol) of DiPPF in THF was added to a suspension of 116 mg (0.100 mmol) of {Pd[P(*o*-tolyl)$_3$](*p*-C_6H_4-Me)(μ-Br)}$_2$ in THF. The reaction mixture was stirred at room temperature for 2 h during which time all the solids dissolved. After that time, the reaction was complete, as determined by $^{31}P\{^1H\}$ NMR spectroscopy. The yellow solution was filtered through Celite and concentrated. The product was obtained

as a yellow solid (105 mg, 85%) by layering a THF solution with pentane at -35 ºC. ^{1}H NMR (C_6D_6): 7.68 (virtual t, *J* = 7.6 Hz, 2H), 7.06 (d, *J* = 6.8 Hz, 2H), 4.08 (s, 2H), 4.06 (s, 2H), 3.96 (s, 2H), 3.94 (s, 2H), 2.92 (m, 2H), 2.25 (s, 3H), 2.11 (m, 2H), 1.71 (dd, *J* = 15.6, 7.1 Hz, 6H), 1.08 (m, 12H), 0.86 (dd, *J* = 14.9, 6.8Hz, 6H). ^{31}P{^{1}H} NMR (C_6D_6): δ 38.2 (d, *J* = 24.4 Hz), 27.7 (d, *J* = 24.2 Hz). Anal. Calcd for $C_{29}H_{43}BrFeP_2Pd$: C, 50.06; H, 6.23. Found: C, 50.11; H, 6.28.

Reaction of Pd(DiPPF)(Br)(C_6H_4-4-Me) (16) with 4-methoxybenzenethiol in the presence of NaO^{t}Bu and DiPPF.



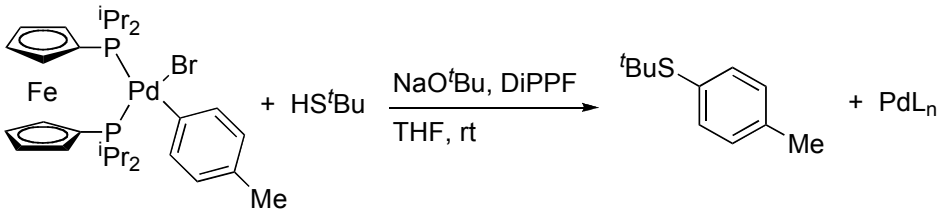
16

R = C_6H_4-4-OMe

89%

Into a small vial equipped with a magnetic stir bar was placed Pd(DiPPF)(Br)(C_6H_4-4-Me) (**16**) (4.4 mg, 6.3 x 10^{-3} mmol), NaO^{t}Bu (2.9 mg, 0.029 mmol), DiPPF (2.5 mg, 6.0 x 10^{-3} mmol), and $PMes_3$ (2.1 mg) and dodecane (10 μL, 0.044 mmol) as internal standards. THF (0.4 mL) was added, and the mixture was transferred to an NMR tube that was sealed with a septum-lined screw-cap. A ^{31}P{^{1}H} NMR spectrum was recorded. 4-methoxybenzenethiol (1.5 μL, 0.012 mmol) was added. Several ^{31}P{^{1}H} NMR spectra were recorded during the course of the reaction. The yield of the thioether was determined by GC analysis after 2 h.

Reaction of Pd(DiPPF)(Br)(C_6H_4-4-Me) (16) with 2-methyl-2-propanethiol in the presence of NaO^{t}Bu.



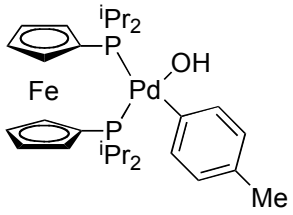
16 78%

Into a small vial equipped with a magnetic stir bar was placed Pd(DiPPF)(Br)(C_6H_4-4-Me) (**16**) (3.9 mg, 5.6 x 10^{-3} mmol), NaO^{t}Bu (2.6 mg, 0.026 mmol), DiPPF (2.8 mg, 6.7 x 10^{-3} mmol), and $PMes_3$ (2.3 mg) and dodecane (10 μL, 0.044 mmol) as internal standards. THF (0.4 mL) was added, and the mixture was transferred to an NMR tube that was sealed with a septum-lined screw-cap. A $^{31}P\{^1H\}$ NMR spectrum was recorded. 2-methyl-2-propanethiol (1.3 μL, 0.012 mmol) was added. Several $^{31}P\{^1H\}$ NMR spectra were recorded during the course of the reaction. The yield of the thioether was determined by GC analysis after 2 h.

Independent synthesis of Pd(DiPPF)$_2$ (17) and Pd$_2$(DiPPF)$_3$ (18).

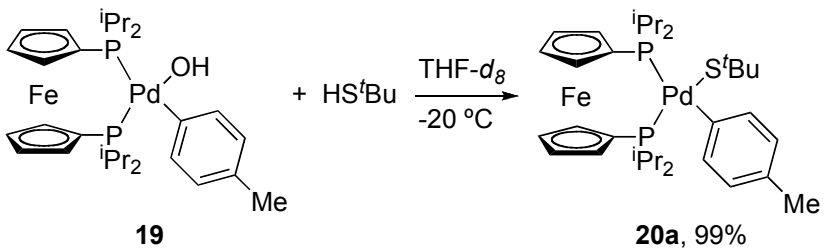
A solution of DiPPF (18 mg, 0.044 mmol) and Pd[P(*o*-tol)$_3$]$_2$ (7 mg, 0.01 mmol) in 1.0 mL of THF was stirred at room temperature for 10 min. The reaction mixture was then transferred to an NMR tube and analyzed by $^{31}P\{^1H\}$ NMR spectroscopy. $^{31}P\{^1H\}$ NMR (THF): 33.9 (t, J = 98.8 Hz), 21.0 (d, J = 98.8 Hz), 21.0 (br s).

Synthesis of (DiPPF)Pd(OH)(C_6H_4-4-Me) (19).



A solution of 83 mg (0.20 mmol) of DiPPF in THF was added to a solution of 88 mg (0.092 mmol) of $\{Pd(PPh_3)(p\text{-}C_6H_4\text{-}Me)(\mu\text{-}OH)\}_2$ in THF. The reaction mixture was stirred at room temperature for 12 h. After that time, the reaction was complete, as determined by $^{31}P\{^1H\}$ NMR spectroscopy. The reaction mixture was filtered through Celite and concentrated. The crude product was dissolved in toluene, and the solution was filtered through Celite and evaporated. The product was obtained as a yellow solid (52 mg, 49%) by layering a toluene solution with pentane at -35 ºC. ^1H NMR (C_6D_6): 7.94 (virtual t, J = 7.3 Hz, 2H), 7.20 (d, J = 6.3 Hz, 2H), 4.29 (s, 2H), 4.24 (s, 2H), 4.10 (s, 2H), 4.07 (s, 2H), 2.93 (m, 2H), 2.36 (s, 3H), 2.15 (m, 2H), 1.90 (dd, J = 15.4, 7.1 Hz, 6H), 1.34 (dd, J = 13.4, 7.1 Hz, 6H), 1.21 (dd, J = 15.4, 7.3 Hz, 6H), 1.07 (dd, J = 14.4, 6.8 Hz, 6H), 0.89 (t, J = 7.3 Hz, 1H). $^{31}P\{^1H\}$ NMR (C_6D_6): 39.40 (d, J = 22.8 Hz), 32.5 (d, J = 22.8 Hz). Anal. Calcd for $C_{29}H_{44}FeOP_2Pd$: C, 55.04; H, 7.01. Found: C, 54.68; H, 6.75.

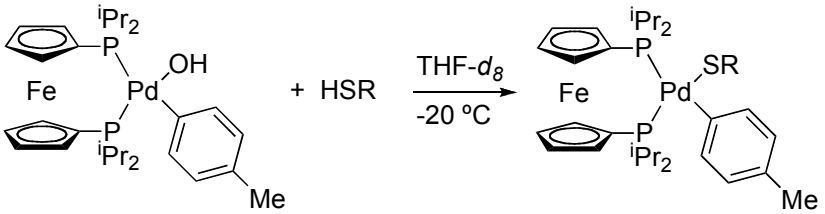
Synthesis and characterization of Pd(DiPPF)(S^{t}Bu)(C_6H_4-4-Me) (20a).



19 **20a**, 99%

A solution of 9.2 mg (0.015 mmol) of Pd(DiPPF)(OH)(C_6H_4-4-Me) (**19**) and 1,3,5-trioxane (internal standard) in 0.5 mL of THF-d_8 was placed into an NMR tube with a septum-lined screw-cap. A ^{1}H NMR spectrum was recorded. The sample was cooled to -20 °C, and 1.8 μL (0.016 mmol) of 2-methyl-2-propanethiol were added. The sample was quickly placed into a precooled NMR spectrometer probe at -20 °C. The palladium thiolate complex **20a** was formed in 99% yield and characterized by NMR spectroscopy at this temperature. ^{1}H NMR (THF-d_8): 7.49 (virtual t, J = 7.1 Hz, 2H), 6.76 (d, J = 7.1 Hz, 2H), 4.43 (s, 6H), 4.40 (s, 2H), 3.00 (m, 2H), 2.39 (m, 2H), 2.19 (s, 3H), 1.56 (dd, J = 15.2, 7.3 Hz, 8H), 1.17 (dd, J = 12.2, 6.6 Hz, 8H), 1.03 (dd, J = 13.9, 6.4 Hz, 8H), 0.95 (s, 9H). ^{31}P{^{1}H} NMR (THF-d_8): δ 27.7 (d, J = 28.9 Hz), 24.6 (d, J = 29.1 Hz).

Synthesis and characterization of Pd(DiPPF)[S(C_6H_4-4-OMe)](C_6H_4-4-Me) (20b).



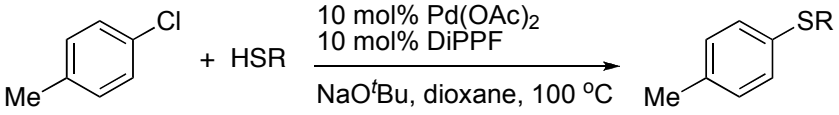
19
R = C_6H_4-4-OMe

20b, 96%

A solution of 10 mg (0.016 mmol) of Pd(DiPPF)(OH)(C_6H_4-4-Me) (**19**) and 1,3,5-trioxane (internal standard) in 0.5 mL of THF-d_8 was placed into an NMR tube with a septum-lined screw-cap. A ^{1}H NMR spectrum was recorded. The sample was cooled to -20 °C, and 2.0 μL (0.016 mmol) of 4-methoxybenzenethiol were added. The sample was quickly placed into a precooled NMR spectrometer probe at -20 °C. The palladium thiolate complex **20b** was formed in 96% yield and characterized by NMR spectroscopy at this temperature. ^{1}H NMR (THF-d_8): 6.99 (virtual t, J = 7.3 Hz, 2H), 6.77 (d, J = 8.4

Hz, 2H), 6.40 (d, J = 6.7 Hz, 2H), 6.24 (d, J = 8.6 Hz, 2H), 4.47 (s+m overlaped, 8H), 3.61 (s, 3H), 2.79 (m, 2H), 2.23 (m, 2H), 2.04 (s, 3H), 1.60 (dd, J = 15.2, 7.1 Hz, 6H), 1.25 (dd, J = 12.9, 6.9 Hz, 6H), 1.05 (m, 12H). $^{31}P\{^{1}H\}$ NMR (THF-d_8): δ 32.2 (d, J = 27.5 Hz), 26.2 (d, J = 25.6 Hz).

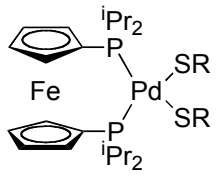
Representative procedure for the determination of the resting state of the catalyst in the reaction of 4-chlorotoluene and 4-methoxybenzenethiol catalyzed by a combination of $Pd(OAc)_2$ and DiPPF.



R = C_6H_4-4-OMe

4-chlorotoluene (13 mg, 0.10 mmol), NaO^{t}Bu (11 mg, 0.11 mmol), $Pd(OAc)_2$ (2.2 mg, 0.010 mmol) and DiPPF (4.3 mg, 0.010 mmol) were weighed into a vial. Dodecane (25 μL, 0.11 mmol, internal standard) and 1 mL of dioxane were added. The mixture was stirred at room for 1 min and 4-methoxybenzenethiol (12 μL, 0.10 mmol) was added. The mixture was transferred to an NMR tube with a septum-lined screw-cap and heated at 100 °C. $^{31}P\{^{1}H\}$ NMR spectra were obtained during the course of the reaction until the conversion of the starting material was complete.

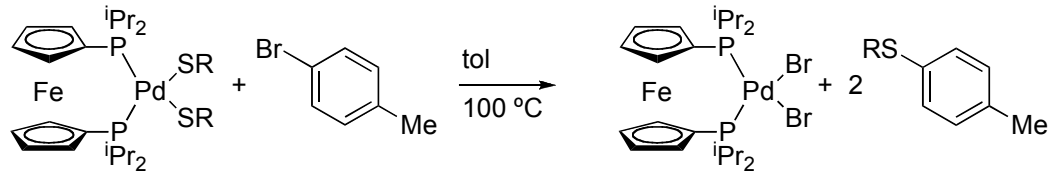
Independent synthesis of Pd(DiPPF)[S(C_6H_4-4-OMe)]$_2$ (21).



R = C_6H_4-4-OMe

A solution of DiPPF (100 mg, 0.239 mmol) in THF (2 mL) was added to a suspension of 165 mg of Pd[P(*o*-tolyl)$_3$]$_2$ (0.231 mmol) in THF (3 mL). The reaction mixture was stirred at room temperature for 30 min during which time all the solids dissolved. Then, the mixture was treated with a solution of bis(4-methoxyphenyl) disulfide (80 mg, 0.28 mmol) in THF (2 mL). After 30 min of additional stirring at room temperature, the red solution was filtered through Celite and concentrated. The product was obtained as a red solid (97 mg, 52%) by layering a THF solution with pentane at -35 ºC. ^{1}H NMR (C_6D_6): 7.82 (d, *J* = 8.5 Hz, 4H), 6.79 (d, *J* = 8.8 Hz, 4H), 4.06 (s, 4H), 3.94 (s, 4H), 3.36 (s, 6H), 2.95 (m, 4H), 1.51 (dd, *J* = 16.4, 7.3 Hz, 12H), 1.01 (dd, *J* = 13.7, 7.1 Hz, 12H). ^{31}P{^{1}H} NMR (C_6D_6): δ 42.5 (s). Anal. Calcd for $C_{36}H_{50}FeO_2P_2PdS_2$: C, 53.84; H, 6.28. Found: C, 53.89; H, 6.50.

Stoichiometric reaction of Pd(DiPPF)[S(C$_6$H$_4$-4-OMe)]$_2$ (21) with 4-bromotoluene.

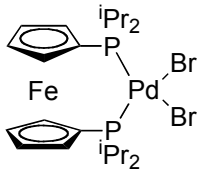


Into a small vial was placed Pd(DiPPF)[S(C$_6$H$_4$-4-OMe)]$_2$ (**21**) (5.8 mg, 7.2 x 10^{-3} mmol), 4-bromotoluene (84 mg, 0.49 mmol), dodecane (20 μL, 0.087 mmol, internal standard) and PMes$_3$ (2.9 mg, internal standard). Toluene was added (0.4 mL), and the mixture was transferred to an NMR tube equipped with a screw-cap and a Teflon seal. A ^{31}P{^{1}H} NMR spectrum was obtained. The sample was heated at 100 °C and ^{31}P{^{1}H}

NMR spectra were recorded at different times. After 20 h, the yield of the thioether (86%) was determined by GC analysis.

Stoichiometric reaction of Pd(DiPPF)[S(C_6H_4-4-OMe)]$_2$ (21) with 4-bromotoluene and bis(4-methoxyphenyl) disulfide. Into a small vial was placed Pd(DiPPF)[S(C_6H_4-4-OMe)]$_2$ (**21**) (5.8 mg, 7.2 x 10^{-3} mmol), 4-bromotoluene (84 mg, 0.49 mmol), bis(4-methoxyphenyl) disulfide (4.2 mg, 0.015 mmol), dodecane (20 μL, 0.11 mmol, internal standard) and $PMes_3$ (1.5mg, internal standard). Toluene was added (0.4 mL) and the mixture was transferred to an NMR tube equipped with a screw cap and a Teflon seal. A $^{31}P\{^1H\}$ NMR spectrum was obtained. The sample was heated at 100 °C and $^{31}P\{^1H\}$ NMR spectra were recorded at different times. $^{31}P\{^1H\}$ NMR spectroscopy showed no progress of the reaction. After 20 h of heating, no thioether was observed by GC analysis.

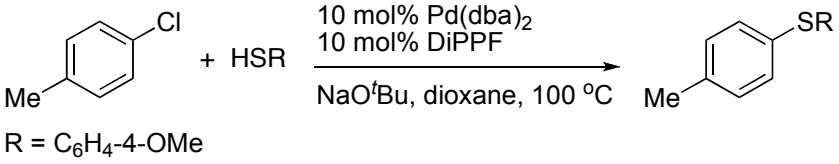
Independent synthesis Pd(DiPPF)(Br)$_2$ (23).



A solution of 102 mg DiPPF (0.244 mmol) in 3 mL of DCM was added to a suspension of 83 mg of Pd(CH_3CN)$_2$Br$_2$ (0.24 mmol) in 5 mL of DCM at room temperature. The mixture was stirred for 24 h. Then, it was filtered through Celite and concentrated. The product was obtained as a red solid (143 mg, 95%) by layering a DCM solution with Et_2O at -35 ºC. ^1H NMR (CD_2Cl_2): 4.61 (s, 4H), 4.53 (s, 4H), 3.13 (m, 4H), 1.61 (dd, *J* = 17.3, 7.1 Hz, 12H), 1.21 (dd, *J* = 15.6, 6.8 Hz, 12H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 63.4 (s). MS

(FD+): 683.9 (M^+). Anal. Calcd for $C_{22}H_{36}Br_2FeP_2Pd \cdot 0.5\ CH_2Cl_2$: C, 37.17; H, 5.13. Found: C, 37.46; H, 5.12.

Determination of the resting state of the catalyst in the reaction of 4-chlorotoluene and 4-methoxybenzenethiol catalyzed by a combination of $Pd(dba)_2$ and DiPPF.



R = C_6H_4-4-OMe

4-chlorotoluene (26 mg, 0.20 mmol), NaO^{t}Bu (23 mg, 0.24 mmol), $Pd(dba)_2$ (11 mg, 0.019 mmol) and DiPPF (8.7 mg, 0.020 mmol) were weighed into a vial. Dodecane (17 μL, 0.074 mmol, internal standard) and 1 mL of dioxane were added. The mixture was stirred at room for 1 min and 4-methoxybenzenethiol (13 μL, 0.10 mmol) was added. The mixture was heated at 100 °C with stirring. $^{31}P\{^1H\}$ NMR spectra were obtained during the course of the reaction until the conversion of the starting material was 72%. The yield of the thioether was 66%.

Independent synthesis of $[(DiPPF)Pd]_2(dba)$ (22).

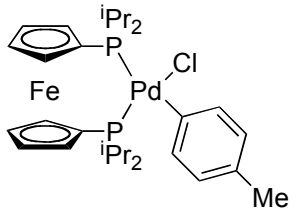
Into a 20 mL scintillation vial equipped with a magnetic stir bar was placed $Pd(dba)_2$ (214 mg, 0.372 mmol), DiPPF (158 mg, 0.378 mmol), NaO^{t}Bu (94 mg, 0.98 mmol) and dioxane (4 mL). Isopropylamine (0.26 mL, 3.0 mmol) was added and the mixture was heated at 100 °C for 2 h. The reaction was allowed to cool, at which point it was filtered through Celite and concentrated. The crude product was dissolved in toluene, and the resulting solution was filtered through Celite and concentrated. The product was obtained as a yellow solid (86 mg, 36%) by layering a THF solution with pentane at -35 °C. ^1H

NMR (C_6D_6): 7.49 (d, J = 7.3 Hz), 7.23-7.11 (m), 7.00 (m), 6.90 (m), 5.52 (m), 5.43 (m), 5.31 (m), 5.06 (m), 4.82 (m), 4.29 (s), 4.25 (s), 4.12 (s, overlapped), 4.07 (s), 4.00-3.89 (m, overlapped s), 2.75 (m), 2.64 (m), 2.04 (m), 1.94 (m), 1.82 (m), 1.67 (dd, J = 14.4, 6.8 Hz), 1.59 (m), 1.36 (m), 0.48 (m). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 34.9 (s), 34.0 (s), 31.8 (d, J = 4.6 Hz), 31.0 (s), 29.6 (s), 29.3 (s). MS (FD+): 1282.9 (M^+). Anal. Calcd for $C_{61}H_{86}Fe_2P_4Pd_2$: C, 57.07; H, 6.75. Found: C, 57.36; H, 7.04.

Oxidative addition of 4-chlorotoluene to [(DiPPF)Pd]$_2$(dba) (22).

Into a small vial equipped with a magnetic stir bar was placed [(DiPPF)Pd]$_2$(dba) (**22**) (4 mg, 0.003 mmol), 4-chlorotoluene (16 mg, 0.12 mmol) and $PMes_3$ (1.9 mg, internal standard). Toluene (0.4 mL) was added and the mixture was stirred for 1 min. Then, it was transferred to an NMR tube with a septum-lined screw-cap and heated at 100 ºC. Several $^{31}P\{^1H\}$ NMR spectra were recorded during the course of the reaction.

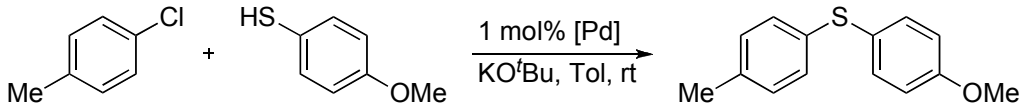
Independent synthesis of (DiPPF)Pd(C_6H_4-4-Me)(Cl) (24).



Into a 20 mL scintillation vial was placed DiPPF (92 mg, 0.22 mmol), Pd[P(*o*-tolyl)$_3$]$_2$ (157 mg, 0.219 mmol) and toluene (6 mL). The mixture was stirred for 15 min at room temperature. Then, it was treated with 4-chlorotoluene (213 mg, 1.68 mmol) and heated at 60 ºC for 3 h. The orange solution was filtered through Celite and concentrated. The product was obtained as a yellow solid (45 mg, 31%) by layering a benzene solution with

pentane at -35 ºC. ^{1}H NMR (C_6D_6): 7.68 (virtual t, *J* = 7.6 Hz, 2H), 7.06 (d, *J* = 6.3 Hz, 2H), 4.08 (s, 2H), 4.07 (s, 2H), 3.95 (s, 2H), 3.93 (s, 2H), 2.83 (m, 2H), 2.26 (s, 3H), 2.10 (m, 2H), 1.71 (dd, *J* = 15.6, 7.3 Hz, 6H), 1.09 (m, 12H), 0.87 (dd, *J* = 14.9, 6.8 Hz, 6H). ^{31}P{^{1}H} NMR (C_6D_6): δ 40.13 (d, *J* = 24.4 Hz), 29.1 (d, *J* = 24.2 Hz).

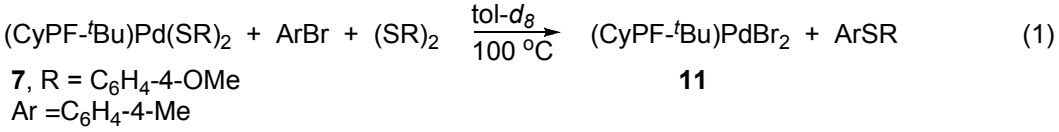
Representative procedure for the catalytic reaction of 4-chlorotoluene with 4-methoxybenzenethiol in the presence of KO^{t}Bu catalyzed by (DiPPF)Pd(C_6H_4-4-Me)(Br) at room temperature.



[Pd] = (DiPPF)Pd(Br)(*p*-tolyl)

Into a small vial equipped with a magnetic stir bar was placed 4-chlorotoluene (1 mmol), KO^{t}Bu (1.4 mmol), (DiPPF)Pd(C_6H_4-4-Me)(Br) (0.01 mmol) and dodecane (30 μL, 0.13 mmol, internal standard). Toluene (1.5 mL) was added. After stirring the mixture for 1 min, 4-methoxybenzenethiol (1 mmol) was added. The reaction was stirred at room temperature for 24 h. The yield was determined by GC analysis.

Kinetic measurements



Preparation of the stock solution of bis(4-methoxyphenyl) disulfide. In a 1.00 mL volumetric flask was added bis(4-methoxyphenyl) disulfide (10 mg, 0.035 mmol). Toluene-d_8 was added to the 1.00 mL mark.

Representative procedure for the determination of the order in 4-bromotoluene. Into a small vial was placed Pd(CyPF-^{t}Bu)[S(C_6H_4-4-OMe)]$_2$ (8.6 mg, 9.2 x 10^{-3} mmol), 4-bromotoluene (84 mg, 0.49 mmol), 5.7 μL of stock solution of bis(4-methoxyphenyl) disulfide, and $PMes_3$ (internal standard). Toluene-d_8 was added to a total volume of 360 μL. The solution was transferred to an NMR tube equipped with a screw cap and a Teflon seal. A $^{31}P\{^1H\}$ NMR spectrum was obtained. The sample was heated at 100 °C and $^{31}P\{^1H\}$ NMR spectra were recorded at fixed intervals for at least three half-lives. This procedure was repeated using different initial concentrations of 4-bromotoluene. The final concentrations were [Pd(CyPF-^{t}Bu)[S(C_6H_4-4-OMe)]$_2$] = 2.6 x 10^{-2} M, [4-bromotoluene] = 1.4 M and [{S(C_6H_4-4-OMe)}$_2$] = 5.6 x 10^{-4} M.

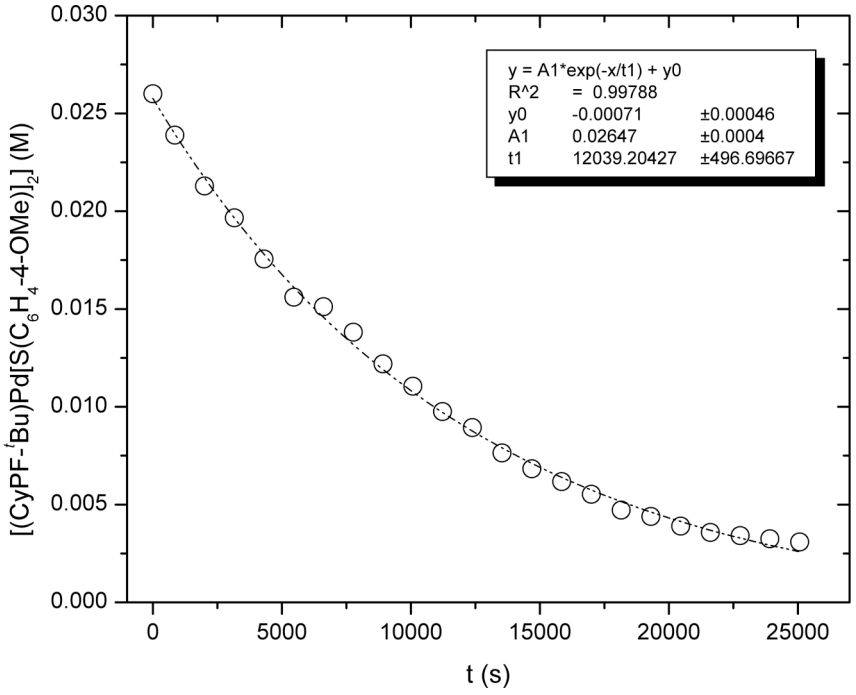


Figure S.1. Representative curve for the decay of Pd(CyPF-^{t}Bu)[S(C_6H_4-4-OMe)]$_2$ during the reaction of [Pd(CyPF-^{t}Bu)[S(C_6H_4-4-OMe)]$_2$] = 2.6 x 10^{-2} M, [4-bromotoluene] = 1.4 M and [{S(C_6H_4-4-OMe)}$_2$] = 5.6 x 10^{-4} M.

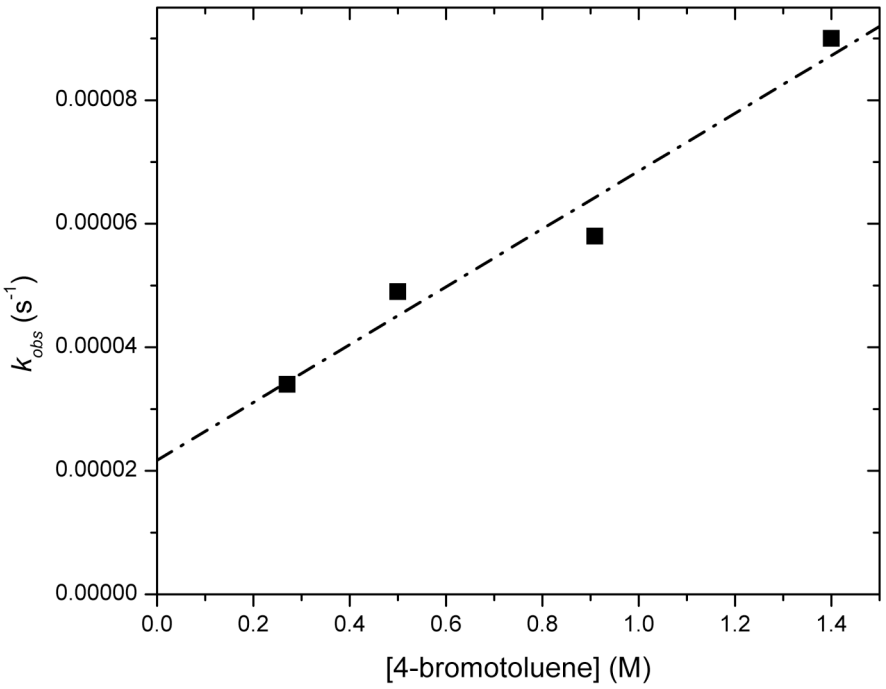


Figure S.2. Kinetic data plotted as k_{obs} (s^{-1}) vs [4-bromotoluene] (M) collected for the reaction in eq 1 conducted with [Pd(CyPF-^{t}Bu)[S(C_6H_4-4-OMe)]$_2$] = 2.6 x 10^{-2} M, [4-bromotoluene] = 0.27 – 1.4 M and [{S(C_6H_4-4-OMe)}$_2$] = 5.6 x 10^{-4} M.

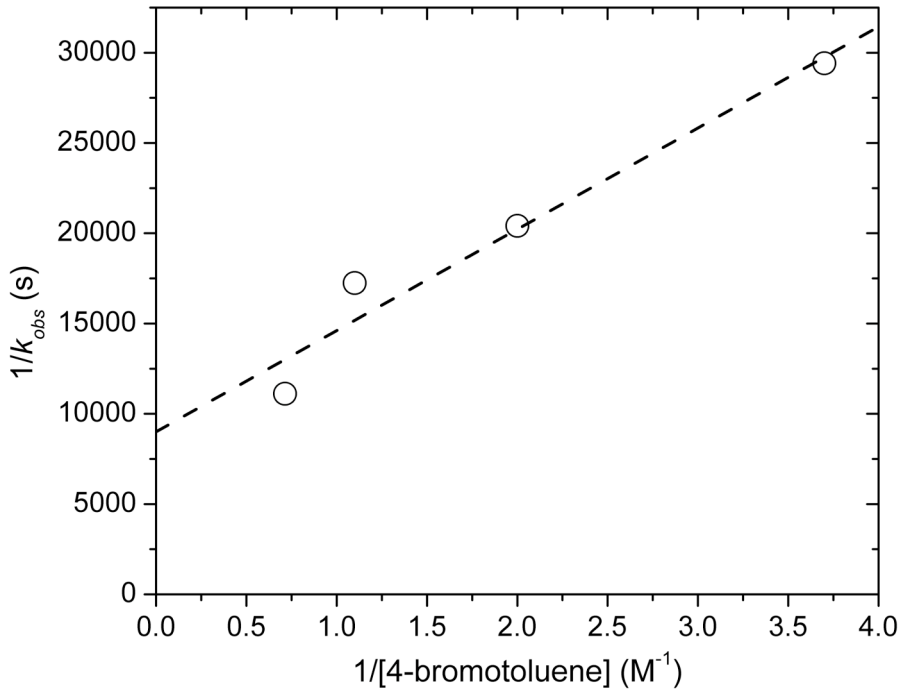


Figure S.3. Kinetic data plotted as $1/k_{obs}$ (s) vs 1/[4-bromotoluene] (M^{-1}) collected for the reaction in eq 1 conducted with [Pd(CyPF-^{t}Bu)[S(C_6H_4-4-OMe)]$_2$] = 2.6 x 10^{-2} M, [4-bromotoluene] = 0.27 – 1.4 M and [{S(C_6H_4-4-OMe)}$_2$] = 5.6 x 10^{-4} M.

Table S.1. Data for Figure S.2.

[4-bromotoluene] (M)	k_{obs} (s^{-1})
0.27	(3.4 ± 0.1) x10^{-5}
0.50	(4.9 ± 0.4) x10^{-5}
0.89	(5.8 ± 0.3) x10^{-5}
1.4	(9.0 ± 0.1) x10^{-5}

Determination of the order in bis(4-methoxyphenyl) disulfide. Into a small vial was placed Pd(CyPF-^{t}Bu)[S(C_6H_4-4-OMe)]$_2$ (8.9 mg, 9.5 x 10^{-3} mmol), 4-bromotoluene (84 mg, 0.49 mmol), and $PMes_3$ (internal standard). Tol-d_8 was added to a total volume of 360 μL. The solution was transferred to an NMR tube equipped with a screw cap and a Teflon seal. A $^{31}P\{^1H\}$ NMR spectrum was obtained. The sample was heated at 100 °C and $^{31}P\{^1H\}$ NMR spectra were recorded at fixed intervals for at least three half-lives. The final concentrations were [Pd(CyPF-^{t}Bu)[S(C_6H_4-4-OMe)]$_2$] = 2.6 x 10^{-2} M and [4-bromotoluene] = 1.4 M. This procedure was repeated using different initial concentrations of bis(4-methoxyphenyl) disulfide.

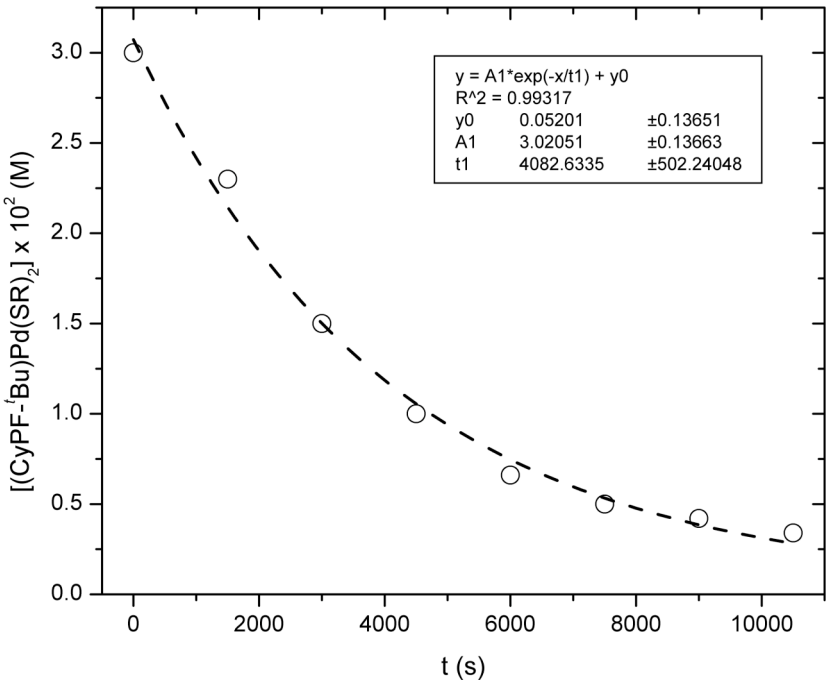


Figure S.4. Representative curve for the decay of Pd(CyPF-^{t}Bu)[S(C_6H_4-4-OMe)]$_2$ during the reaction of [Pd(CyPF-^{t}Bu)[S(C_6H_4-4-OMe)]$_2$] = 2.6 x 10^{-2} M and [4-bromotoluene] = 1.4 M.

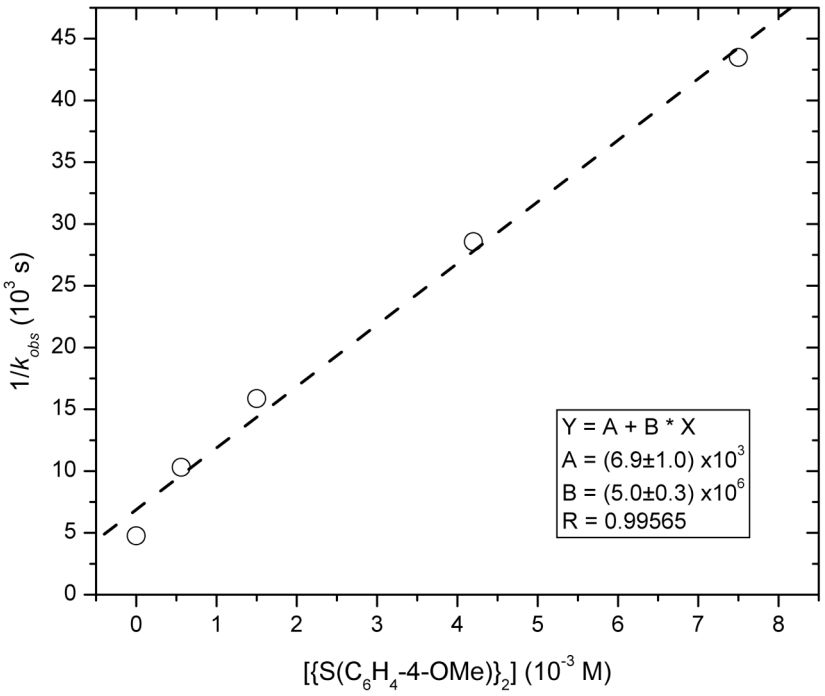


Figure S.5. Kinetic data plotted as 1/kobs (10^3 s) vs [{S(C_6H_4-4-OMe)}$_2$] (10^{-3} M) collected for the reaction in eq 1 conducted with [Pd(CyPF-^{t}Bu)[S(C_6H_4-4-OMe)]$_2$] = 2.6 x 10^{-2} M, [4-bromotoluene] = 1.4 M, [{S(C_6H_4-4-OMe)}$_2$] = 0 – 7.5 x 10^{-3} M.

Table S.2. Table of data for Figure S.5.

[{S(C_6H_4-4-OMe)}$_2$] x10^3 (M)	k_{obs} (s^{-1})
0	(2.1 ± 0.1) x10^{-4}
0.56	(9.0 ± 0.1) x10^{-5}
1.5	(6.3 ± 0.5) x10^{-5}
4.2	(3.5 ± 0.1) x10^{-5}
7.5	(2.3 ± 0.1) x10^{-5}

References

(1) Widenhoefer, R. A.; Zhong, H. A.; Buchwald, S. L. *Organometallics* **1996**, *15*, 2745.

(2) Paul, F.; Patt, J.; Hartwig, J. F. *Organometallics* **1995**, *14*, 3030.

(3) Fernandez-Rodriguez, M. A.; Shen, Q. L.; Hartwig, J. F. *Chem.-Eur. J.* **2006**, *12*, 7782.

(4) Ademi, L.; Constable, E. C.; Housecroft, C. E.; Neuburger, M.; Schaffner, S. *Acta Crystallographica Section E-Structure Reports Online* **2006**, *62*, M1059.

(5) Grushin, V. V.; Alper, H. *Organometallics* **1993**, *12*, 1890.

(6) Shen, Q. L.; Hartwig, J. F. *J. Am. Chem. Soc.* **2006**, *128*, 10028.