Highly Active, Air-Stable Versatile Palladium Catalysts for the C−C, C−N, and C−S Bond Formations via Cross-Coupling Reactions of Aryl Chlorides

George Y. Li,* Gang Zheng, and Andrew F. Noonan

The DuPont Company, Central Research and Development Department, Experimental Station, P.O. Box 80328, Wilmington, Delaware 19880-0328

george.y.li@usa.dupont.com

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The transition-metal-catalyzed carbon−carbon and carbon−heteroatom bond-forming reactions are important fundamental transformations in synthetic chemistry.[1,2] These reactions have been widely used for a variety of cross-coupling reactions of aryl halides in the processes of C−C (Suzuki,[3] Kumada,[4] Stille,[5] Heck cross-coupling[6]), C−N,[7,8] and C−S[9] bond-forming reactions. Moreover, promising catalytic systems for the unactivated aryl chlorides have been developed.[3−7,10,11] However, to the best of our knowledge, no separable air-stable homogeneous catalysts[12] have ever been reported involving unactivated aryl chlorides and olefins, amines, and thiols. This is partly due to the unstabilized active catalytic species, and a mechanism that active catalytic species are derived from the in situ reduction of Pd(II) by free phosphine ligands to Pd^0,[13] leading to difficulties in separating and purifying these complexes.

Herein, we report the first example of simple, readily accessible, and air-stable palladium(II) complexes (POPd, POPd1, and POPd2) that serve as catalyst precursors for the efficient cross-coupling reactions of aryl chlorides in the processes of C−C, C−N, and C−S bond-forming reactions to access a variety of such architec-

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(12) (a) $Pd(P(t\text{-}Bu)_3)_2$ does not appear to be the active catalyst for the cross-coupling reactions; see ref 3a. (b) For an example of using isolated catalysts for Heck couplings of aryl chlorides, see: Herrmann, W. A.; Brossmer, C.; Reisinger, C.-P.; Riermeier, T. H.; Ofele, K.; Beller, M. *Chem. Eur. J.* **1997**, *3*(8), 1357−1364.

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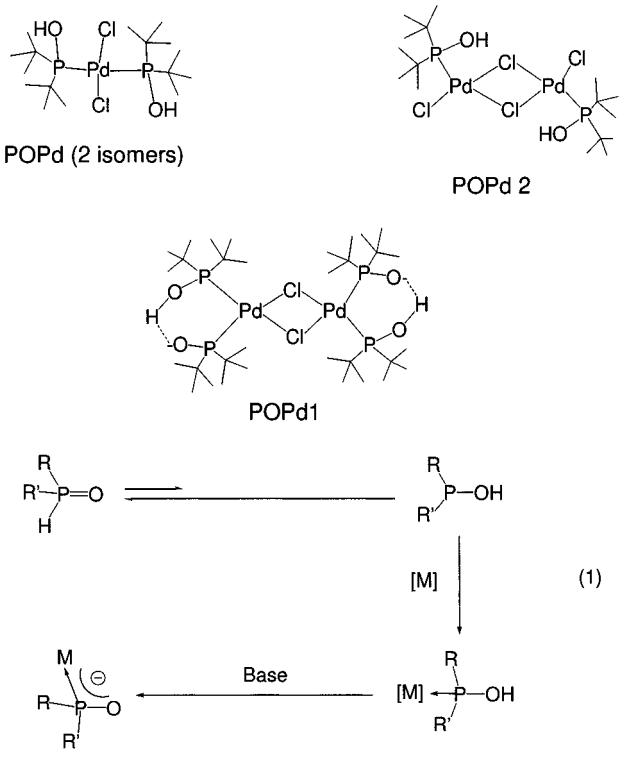
Chart 1. Structures of Palladium(II) Complexes Employed in the Examples of Table 1



tures, as well as initial observations regarding scope and mechanism.

The air-stable complexes (POPd, POPd1, and POPd2) were straightforwardly synthesized, separated and purified in the air by our published procedures (Chart 1).[10,11,14] The cross-coupling reactions of a variety of aryl chlorides and olefins, amines, and thiols (typically [catalyst] = 10−20 mM, 0.5−3 mol %) proceed to completion in a variety of bases and solvents as shown in Table 1. All the catalytic reactions were carried out under nitrogen or open-to-air conditions using $[(t\text{-Bu})_2P(OH)]_2PdCl_2$ (POPd), $\{[(t\text{-Bu})_2P(OH)][(t\text{-Bu})_2P(O^-)]PdCl\}_2$ (POPd1), and $[(t\text{-Bu})_2P(OH)PdCl_2]_2$ (POPd2) as precatalysts, and isolated yields in Table 1 refer to products isolated by column chromatography or distillation.[15] Known products were identified by comparison with literature data and/or with those of authentic samples.

It can be seen that the present process, employing the air-stable POPd, POPd1, and POPd2 as precatalysts, effects efficient cross-couplings of aryl chlorides with olefins, amines, and thiols in the presence of bases. These air-stable palladium(II) complexes are all capable of catalyzing a variety of coupling reactions of aryl halides including aryl chlorides to yield the desired olefin products (Table 1, entries 1 and 2), arylamines (Table 1, entries 3−6), and thioethers (Table 1, entries 7−11) in high isolated yields. Entries 1−2 of Table 1 illustrate that aryl chlorides could be coupled with *tert*-butyl acrylate generating Heck arylation products. Entries 3−6 of Table 1 demonstrate that both alkylamines and arylamines were coupled with aryl chlorides. It also shown that POPd and POPd1 can be employed to mediate C−S bond-forming reactions of aryl chlorides (Table 1, entries 8−11) and aryl bromides (Table 1, entry 7). The alkylthiols (Table 1, entries 8−11) and arylthiols (Table 1, entry 7) are tolerated by the present system as demonstrated by 2-methylpropylphenylthiol ether, pyridylalkylthiol ether, and phenyl sulfide. Also noteworthy are the successful catalytic activities on C−S bond-forming processes of electron-rich 4-chloroanisole (Table 1, entry 10).

Several features of these air-stable complexes are noteworthy and provide both informative parallels and contrasts to the corresponding Pd/phosphine oxide[10,11] and Pd/phosphine[6,7,9] catalysts that are generated in-situ for the cross-coupling reactions of aryl chlorides. These palladium chloride complexes (POPd, POPd1, POPd2) possessing novel phosphinous acid ligands[16] can be easily isolated in air as Pd(II) complexes and directly employed as efficient catalyst precursors for a variety of C−C, C−N, and C−S bond-forming reactions. The present processes are effective for the coupling reactions of both aryl bromides (Table 1, entries 7) and aryl chlorides. In regard to effects of molar ratio of ligand/metal in these palladium complexes on the catalytic activities, it can be seen that both a 1:1 ratio of ligand/palladium (POPd2) and a 2:1 ratio of ligand/palladium (POPd) are effective for C−N bond-forming processes of aryl chlorides (Table 1, entries 3−6). In regard to comparisons of catalytic effects of these air-stable POPd, POPd1, and POPd2, Table 1 offers data comparing these catalysts to those that are generated in situ in the processes of C−N, C−S bond formations.[11] It can be seen that the transformations are equally effective under comparable conditions of catalyst, concentration, and temperature. More importantly, from a purely practical point of view, the direct use of air-stable complexes POPd, POPd1, and POPd2 as precatalysts for cross-couplings of aryl chlorides would be more convenient and practical owing to the difficulties in handling air-sensitive phosphine ligands. Furthermore, the present phosphinous acid ligands can be synthesized by using polymer-supported combinatorial methods,[11,17] therefore easily offering ligand libraries for further catalyst optimizations.

With regard to a plausible mechanism, ^1H and ^{31}P NMR studies of the reaction of POPd2 with CsF in CD_3OD or D_2O solution argue that the palladium(II) chloride dimer (POPd2) is subject to cleavage and deprotonolysis giving mononuclear species at room temperature in the presence of bases,[18,19] yielding an electron-rich phosphine-containing anionic complex, which would be anticipated to accelerate the rate-determining oxidative addition of aryl chlorides in the catalytic cycle.[20] In regard to POPd1 $\{[(t\text{-Bu})_2P(OH)][(t\text{-Bu})_2P(O^-)]PdCl\}_2$, the active catalytic

(14) POPd, POPd1, and POPd2 are available exclusively from CombiPhos Catalysts, Inc. Web site: http://www.combiphos.com.

(15) See the Supporting Information for full synthetic details and characterization of new compounds.

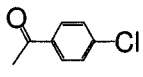
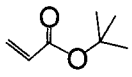
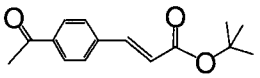
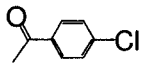
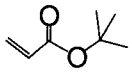
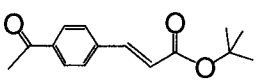
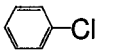
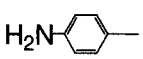
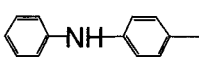
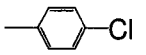
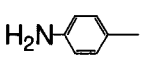
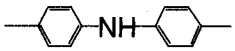
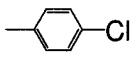
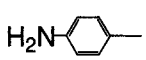
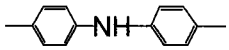
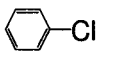
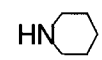
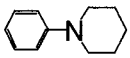
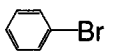
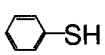
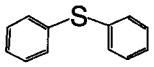
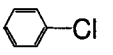
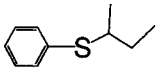
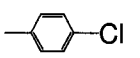
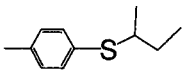
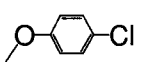
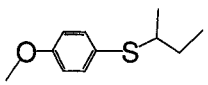
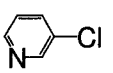
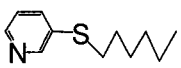
(16) For examples of metal−phosphinous acid complexes, see: (a) Cobley, C. J.; Heuvel, M. van den; Abbadi, A.; de Vries, J. G. *Tetrahedron Lett.* **2000**, *41*, 2467, 2467−2470. (b) Ghaffar, T.; Parkins, A. W. *Tetrahedron Lett.* **1995**, *36*, 8657−8660; UK Patent Application 9506389.7. (c) Goerlich, J. R.; Fischer, A.; Jones, P. G.; Schmutzler, R. *Z. Naturforsch., B: Chem. Sci.* **1994**, *49*, 801−811. (d) Heuer, L.; Jones, P. G.; Schmutzler, R. *New J. Chem.* **1990**, *14*, 891−900. (e) Arif, A. M.; Bright, T. A.; Jones, R. A. *J. Coord. Chem.* **1987**, *16*, 45−50.

(17) For combinatorial approaches to the synthesis of phosphorous-containing ligands, see: (a) Li, G. Y.; Fagan, P. J.; Watson, P. L. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 1106−1109. (b) Li, G. Y. US Patent Application (DuPont), 60/197,031, Case Number: BC 1048 US PRV (2000). (c) Fagan, P. J.; Li, G. Y. PCT Int. Appl WO 2000021663 A2 20000420, 169 pp. Application: WO 1999-US23509 19991013.

(18) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; John Wiley & Sons: New York, 1988; pp 921−922.

(19) For an excellent paper on tricoordinated anionic complexes $Pd^0L_2Cl^-$ as the real active catalysts, see: Amatore, C.; Jutand, A. *Acc. Chem. Res.* **2000**, *33*, 314−321.

Table 1. Air-Stable Palladium Complex-Catalyzed Cross-Coupling Results of Aryl Chlorides

Entry	Halide	Coupling Partner	Catalyst	Base (Solvent)	Product	Yield (%) (Isolated)
1			POPd (3 % mol)	NaOAc (DMF)		66[a]
2			POPd1 (1.5 % mol)	K_2CO_3 (DMF)		77[a]
3			POPd (5.0 % mol)	NaO(*t*-Bu) (Toluene)		97[b]
4			POPd (5.0 % mol)	NaO(*t*-Bu) (dioxane)		97[b]
5			POPd2 (2.5 % mol)	NaO(*t*-Bu) (dioxane)		76[b]
6			POPd2 (3 % mol)	NaO(*t*-Bu) (Toluene)		43[b]
7			POPd (2.8 % mol)	NaO(*t*-Bu) (Toluene)		66[c]
8			POPd (5 % mol)	NaO(*t*-Bu) (DMSO)		60[c]
9			POPd (5 % mol)	NaO(*t*-Bu) (DMSO)		70[c]
10			POPd (10 % mol)	NaO(*t*-Bu) (DMSO)		30[c]
11			POPd1 (2.5 % mol)	NaO(*t*-Bu) (Toluene)		97[c]

Reaction conditions (not optimized): [a] 1.0 equiv of aryl chloride, 1.4 equiv of olefin, 1.1 equiv of base, 135 °C/5−24 h. [b] 1.0 equiv of aryl chloride, 1.2 equiv of amine, 1.4 equiv of Base, 110 °C/4 h. [c] 1.0 equiv of aryl halide, 1.0 equiv of thiol, 2 equiv of base, 110 °C/16−24 h.

species are possibly derived from the cleavage of POPd1 in the presence of nucleophiles followed by the reduction to yield an anionic mononuclear complex Pd(0) for the catalytic cycle (Scheme 1).[21]

In summary, we have discovered practical new catalysts for a variety of cross-coupling reactions of aryl chlorides with olefins, amines, and thiols. Our results demonstrate that palladium complexes possessing phosphinous acid ligands are competents for the generating catalytically active electron-rich anionic species in the presence of bases and that such anionic complexes can be incorporated into catalytic oxidative addition and reductive elimination processes for cross-coupling reactions of aryl halides by facilitating the rate-limiting oxidative addition of unactivated aryl chlorides to palladium complexes. Noteworthy are the efficiency for unactivated aryl chlorides and simplicity of use, low cost, air-stability, and ready accessibility of these separable complexes. Future work regarding these air-stable palladium complexes will be directed on additional cross-coupling reactions and catalytic transformations.

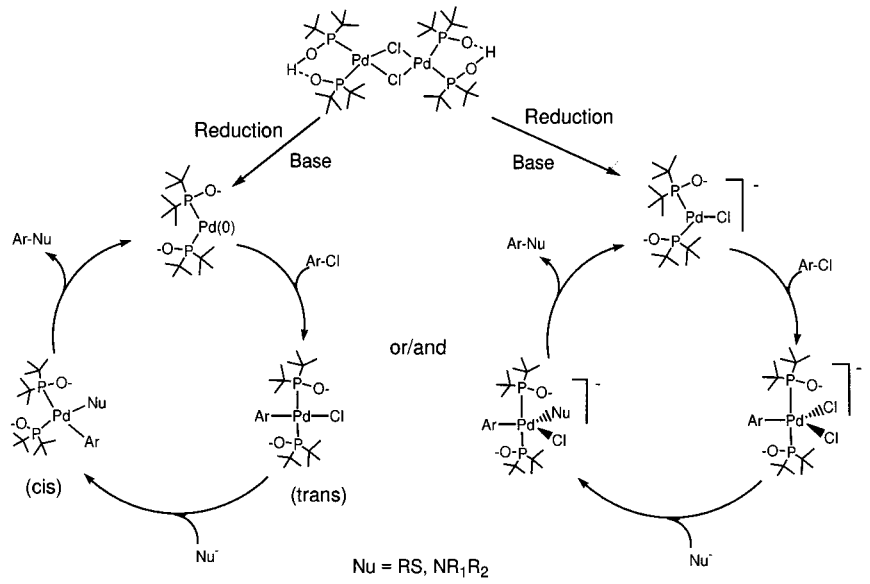
Experimental Section

All reagents were used as supplied commercially without further purification. Dihydrogen dichlorobis(di-*tert*-butylphosphinito-*κP*)palladate(2−) [$(t\text{-Bu})_2POH)_2PdCl_2$ referred as POPd], dihydrogen di-*μ*-chlorotetrakis(di-*tert*-butylphosphinito-*κ*-*P*)dipalladate(2−) ($\{[(t\text{-Bu})_2PO\cdots H\cdots OP(t\text{-Bu})_2]PdCl\}_2$ referred as POPd1), and dihydrogen di-*μ*-chlorodichlorobis(di-*tert*-butylphosphinito-*κP*)dipalladate(2−) $\{[(t\text{-Bu})_2P(OH)PdCl_2]_2$ referred as POPd2} were purchased from CombiPhos Catalysts, Inc., or prepared according to our reported procedures.[10,11,14] NMR

(20) The low catalytic reactivity of aryl chlorides in cross-coupling reactions is usually attributed to their reluctance towards oxidative addition to Pd(0). For a discussion, see: (a) Grushin, V. V.; Alper, H. *Chem. Rev.* **1994**, *94*, 1047−1062 and references therein. (b) Grushin, V. V. *Organometallics* **2000**, *19*, 1888−1900.

(21) A reaction of POPd2 (100 mg, 0.147 mmol, ^{31}P NMR (CD_3OD) δ 148.0 (singlet) ppm) and CsF (50.0 mg, 0.329 mmol) in 1.0 mL of CD_3OD at room temperature for 5 min generates an insoluble mixture.

Scheme 1. Plausible Catalytic Cycle for the Cross-Coupling Reactions of Aryl Chlorides with Amines and Thiols



spectra were recorded on either a Nicolet NMC-300 wide-bore (FT, 300 MHz, ^{1}H; 75 MHz, ^{13}C, 121 MHz, ^{31}P) or a GE QM-300 narrow-bore (FT, 500 MHz, ^{1}H) instrument. Chemical shifts (δ) for ^{1}H, ^{13}C are referenced to internal solvent resonances and reported relative to $SiMe_4$. ^{31}P NMR shifts are reported relative to external phosphoric acid.

2-Propenoic Acid, 3-[4-Acetylphenyl]-*tert*-butyl Ester.[22] **Method A.** $[(t\text{-Bu})_2POH]_2PdCl_2$ (POPd, 468.0 mg, 0.933 mmol, 5.6 mol %), 4-chloroacetophenone (2.58 g, 16.7 mmol), anhydrous tetrabutylammonium bromide (1.07 g, 3.33 mmol), anhydrous sodium acetate (1.51 g, 18.4 mmol), and *tert*-butylacrylate (2.99 g, 23.3 mmol) were weighed in air and transferred to a 50 mL reactor equipped with a magnetic stir bar and 10 mL of DMF. The reaction mixture was vigorously stirred and heated to 135−140 °C for 24 h before the mixture was cooled to room temperature and quenched with 25 mL of H_2O. The mixture was transferred to a separatory funnel and diluted with 300 mL of diethyl ether. The layers were separated, the organic layer was washed with H_2O (2 × 100 mL) and brine (100 mL), dried over $MgSO_4$, and filtered, and the solvents were removed from the filtrate by rotary evaporation. The product was isolated by bulb-to-bulb distillation. The final product was obtained as a colorless solid (2.73 g, 66% yield). It was >95% pure by ^{1}H NMR and GC/MS: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, J = 8.28 Hz, 2H), 7.53 (m, 3H), 6.39 (d, J = 16.01 Hz, 1H), 2.54 (s, 3H), 1.47 (s, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.2, 165.7, 141.9, 139.0, 137.8, 128.8, 128.0, 122.8, 80.9, 28.1, 26.6 ppm.

Method B. $\{[(t\text{-Bu})_2PO\cdots H\cdots OP(t\text{-Bu})_2]PdCl\}_2$ (POPd1, 233.0 mg, 0.25 mmol, 1.5 mol %), 4-chloroacetophenone (2.58 g, 16.7 mmol), anhydrous tetrabutylammonium bromide (1.07 g, 3.33 mmol), and K_2CO_3 (2.53 g, 18.3 mmol), *tert*-butylacrylate (2.99 g, 23.3 mmol) were weighed in air and transferred to a 50 mL of reactor equipped with magnetic stir bar and 10 mL of DMF. The reaction mixture was vigorously stirred and heated to 135−140 °C for 5 h before the mixture was cooled to room temperature and quenched with H_2O. The reaction was transferred to a separatory funnel and diluted with 300 mL of hexane and 100 mL of H_2O. The layers were separated; the organic layer was washed with H_2O (100 mL) and brine (100 mL), dried over $MgSO_4$, and filtered; and the solvents were removed from the filtrate by rotary evaporation. The crude product was concentrated and purified by flash chromatography on silica gel to afford 3.2 g (77% yield) of the final product.

General Procedure for the Reaction of Amines with Aryl Chlorides. A 50 mL reactor equipped with magnetic stir bar was charged with 250 mg (0.50 mmol) of $[(t\text{-Bu})_2POH]_2PdCl_2$, 1.27 g (10.0 mmol) of 4-chlorotoluene, 1.29 g (12.0 mmol) of 4-methylaniline, and 1.35 g (14.0 mmol) of NaO(*t*-Bu) in 15.0 mL of dioxane. The resulting mixture was refluxed for 4 h before the reaction was cooled to room temperature and quenched with 50 mL of H_2O. The mixture was transferred to a separatory funnel, and diluted with 300 mL of diethyl ether. The layers were separated, and the organic layer was washed with H_2O (2 × 30 mL) and brine (30 mL) and dried over $MgSO_4$. The crude product was concentrated and purified by flash chromatography on silica gel.

***N*-Phenyl-*p*-toluidine.**[23] The general procedure gave 1.78 g (97% yield) of a white solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13 (t, J = 7.91 Hz, 2H), 6.98 (m, 2H), 6.89 (m, 4H), 6.78 (t, J = 7.32 Hz, 1H), 5.46 (s, br. 1H), 2.20 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.9, 140.3, 130.8, 129.8, 129.2, 120.2, 118.9, 116.8, 20.6 ppm.

4-Methyl-*N*-(4-methylphenyl)benzenamine.[23] The general procedure using 2.5 mol % of $[(t\text{-Bu})_2P(OH)PdCl_2]_2$ (POPd2) gave 1.50 g (76% yield) of a white solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.88 (d, J = 8.35 Hz, 4H), 6.78 (d, J = 8.35 Hz, 4H), 5.31 (s, br. 1H), 2.12 (s, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.2, 130.2, 129.8, 117.9, 20.6 ppm.

1-Phenylpiperidine.[24] The general procedure using 3.0 mol % of $[(t\text{-Bu})_2P(OH)PdCl_2]_2$ (POPd2), 1.12 g (10.0 mmol) of chlorobenzene, 1.02 g (12.0 mmol) of piperidine, and 1.35 g (14.0 mmol) of NaO(*t*-Bu) in 20.0 mL of toluene afforded 700 mg (43% yield) of *N*-phenylpiperidine: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (m, 2H), 6.84 (m, 2H), 6.72 (m, 1H), 3.06 (t, J = 5.48 Hz, 4H), 1.61 (m, 4H), 1.48 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.3, 129.0, 119.2, 116.5, 50.7, 25.9, 24.4 ppm.

General Procedure for the Reaction of Aryl Halides with Thiols. A 50 mL of reactor equipped with magnetic stir bar was charged with 450 mg (0.897 mmol, 5.0 mol %) of $[(t\text{-Bu})_2P(OH)]_2PdCl_2$, 2.03 g (18.0 mmol) of chlorobenzene, 1.63 g (18.0 mmol) of 1-methyl-1-propanethiol, and 3.46 g (36.0 mmol) of NaO-*t*-Bu in 20.0 mL of DMSO. The resulting mixture was heated to 100 °C for 20 h before the mixture was cooled to room temperature and quenched with 100 mL of H_2O. The mixture was transferred to a separatory funnel and extracted with EtOAc (2 × 200 mL). The layers were separated, the organic layer was washed with H_2O (100 mL) and brine (150 mL), dried over $MgSO_4$, and filtered, and the solvents were removed from the filtrate by rotary evaporation. The final product was chromatographed on silica gel using *tert*-butylmethyl ether/hexane (1% volume ratio) as eluant.

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1-Methyl-1-propylphenyl Sulfide.[25] The general procedure gave 1.78 g (60% yield) of the titled compound: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 (m, 2H), 7.14−7.03 (m, 3H), 3.00 (m, 1H), 1.55−1.37 (m, 2H), 1.13 (d, J = 6.74 Hz, 3H), 0.87 (t, J = 7.38 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.5, 131.7, 128.9, 126.6, 44.8, 29.4, 20.6, 11.3 ppm.

Phenyl Sulfide.[26] The general procedure using 252 mg (0.50 mmol, 2.8 mol %) of $[(t\text{-Bu})_2P(OH)]_2PdCl_2$ (POPd), 2.90 g (18.47 mmol) of bromobenzene, 1.98 g (18.0 mmol) of PhSH, and 3.46 g (36.0 mmol) of NaO-*t*-Bu in 20.0 mL of toluene gave 2.24 g (66% yield) of the title product: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, J = 7.45 Hz, 4H), 7.44 (m, 4H), 7.38 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.7, 130.9, 129.1, 126.9 ppm; HRMS calcd for $C_{12}H_{11}S$ 187.0581, found 187.0582.

1-Methyl-1-propyl-4-methylphenyl Sulfide.[27] The general procedure using 5 mol % $[(t\text{-Bu})_2P(OH)]_2PdCl_2$ (POPd) gave 2.27 g (70% yield) of the titled compound: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (d, J = 8.09 Hz, 2H), 7.14 (d, J = 7.93 Hz, 2H), 3.15 (m, 1H), 2.38 (s, 3H), 1.63 (m, 2H), 1.31 (d, J = 6.6 Hz, 3H), 1.07 (t, J = 7.4 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.7, 132.7, 131.5, 129.4, 45.3, 29.4, 21.0, 20.5, 11.4 ppm; HRMS calcd for $C_{11}H_{16}S$ 180.0973, found 180.0976.

1-Methyl-1-propyl-4-methoxylphenyl Sulfide.[28] The general procedure using 895 mg (1.78 mmol, 10 mol %) of $[(t\text{-Bu})_2P(OH)]_2PdCl_2$ (POPd), 2.57 g (18.0 mmol) of 4-chloroanisole, 1.62 g (18.0 mmol) of 1-methyl-1-propenethiol, and 3.46 g (36 mmol) of Na-O(*t*-Bu) in 20 mL of DMSO gave 1.05 g (30% yield) of the titled compound: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.3 (d, J = 6.9 Hz, 2H), 6.8 (d, J = 8.8 Hz, 2H), 3.7 (s, 3H), 2.9 (m, 1H), 1.5 (m, 2H), 1.1 (d, J = 6.8 Hz, 3H), 0.92 (t, J = 7.4 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.3, 135.6, 125.3, 114.3, 55.3, 46.2, 29.4, 20.5, 11.5 ppm; HRMS calcd for $C_{11}H_{16}OS$ 196.0922, found 96.0921.

3-Hexylthiopyridine. The general procedure using 232.5 mg (0.25 mmol, 2.5 mol %) of $\{[(t\text{-Bu})_2PO\cdots H\cdots OP(t\text{-Bu})_2]PdCl\}_2$ (POPd1), 1.36 g (12.0 mmol) of 3-chloropyridine, 1.18 g (10.0 mmol) of 1-hexanethiol, and 1.92 g (20 mmol) of Na−O(t-Bu) in 15 mL of toluene gave 1.9 g (97% yield) of the titled compound: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.48 (d, J = 1.95 Hz, 1H), 8.31 (m, 1H), 7.56−7.53 (m, 1H), 7.13−7.09 (m, 1H), 2.84 (t, J = 7.34 Hz, 2H), 1.54 (m, 2H), 1.37−1.68 (m, 6H), 0.81 (t, J = 6.83 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.7, 146.5, 136.3, 133.9, 123.2, 33.4, 31.0, 28.8, 28.1, 22.2, 13.7 ppm; HRMS calcd for $C_{11}H_{17}NS$ 196.1158, found 196.1160.

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