Palladium Catalyzed Synthesis of Aqueous, Fluorous, and Supercritical CO_2-Soluble Phosphines

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Supporting Information

Experimental section for selected compounds

2c: A mixture of tris(4-bromophenyl)phosphane oxide (1.030 g, 2.0 mmol), 1H, 1H, 2H-perfluoro-1-octene (2.284 g, 6.6 mmol), palladacycle (56 mg, 0.06 mmol), NaOAc (656 mg, 8.0 mmol), and DMF (20 ml) was stirred at 125 °C for 24 h. After cooling to room temperature, the solvent was removed under reduced pressure. The residue was dissolved in $CHCl_3$ (100 ml), washed with water (2 × 100 ml) and brine (100 ml), dried ($MgSO_4$), and evaporated under reduced pressure. The residue was purified by flash chromatography (SiO_2, EtOAc:$CHCl_3$ = 1:8) to give tris[4-(1H,2H-perfluoro-1-octenyl)phenyl]phosphane oxide **2c** as a pale-yellow oil (2.384 g, 91%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 6.32 (dt, ^3J (H,H) = 16.2, ^3J (H,F) = 12.0 Hz, 3H), 7.22 (d, ^3J(H,H) = 16.2 Hz, 3H), 7.60 (d, ^3J(H,H) = 8.2 Hz, 6H), 7.73 (dd, ^3J(H,P) = 11.6, ^3J(H,H) = 8.2 Hz, 6H); ^{13}C{^{1}H } NMR (75 MHz, $CDCl_3$): δ = 117.6 (t, ^2J(C,F) = 23.5 Hz), 127.4 (d, ^3J(C,P) = 12.5 Hz), 132.8 (d, ^2J(C,P) = 10.4 Hz), 133.9 (d, ^1J(C,P) = 103.7 Hz), 137.5, 138.5 (t, ^3J(C,F) = 9.2 Hz); ^{31}P{^{1}H } NMR ($CDCl_3$): δ = 26.8 (s); MS (CI): *m*/*z* (%): 1311 (100) [M^+ + H]; elemental analysis calcd for $C_{42}H_{18}F_{39}PO$: C 38.49, H 1.38; Found: C 38.24, H 1.00.

3c: A mixture of **2c** (2.611 g, 2.0 mmol), 10% Pd/C (50 mg), and EtOAc (40 ml) was stirred for 5 h at room temperature under 10 bar of hydrogen, and filtered through a pad of Celite after releasing the hydrogen. The filtrate was evaporated under reduced pressure to give tris[4-(1H,1H,2H,2H-perfluorooctyl)phenyl]phosphane oxide **3c** as a pale-yellow oil which solidified on stand (2.660 g, 100%), and was used directly in next step without further purification. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 2.39 (m, 6H), 2.98 (t, ^{3}J (H,H) = 7.8 Hz, 6H), 7.33 (dd, ^{3}J (H,H) = 8.1, ^{4}J(H,P) = 2.4 Hz, 6H), 7.63 (dd, ^{3}J (H,P) = 11.7, ^{3}J(H,H) = 8.1 Hz, 6H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 26.5, 32.5 (t, ^{2}J(C,F) = 29.9 Hz), 128.6 (d, ^{3}J(C,P) = 12.0 Hz), 131.2 (d, ^{1}J(C,P) = 104.8 Hz), 132.6 (d, ^{2}J(C,P) = 9.8 Hz), 143.6; ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 28.1 (s).

4c: A mixture of **3c** (666 mg, 0.5 mmol), trichlorosilane (339 mg, 2.5 mmol), triethylamine (380 mg, 2.75 mmol) and toluene (10 ml) was stirred at 120 °C for 5 h. After cooling to room temperature, saturated $NaHCO_3$ aqueous solution (0.5 ml) was added. The mixture was stirred for 5 min at room temperature, filtered through a pad of alumina, and washed with toluene (3 × 15 ml). The filtrate was then evaporated under reduced pressure to give tris[4-(1H,1H,2H,2H-perfluorooctyl)phenyl]phosphane **4c** as white solids (630 mg, 96%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 2.40 (m, 6H), 2.92 (m, 6H), 7.17 ~ 7.29 (m, 12H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 26.2, 32.7 (t, ^{2}J(C,F) = 22.4 Hz), 128.5, 134.2 (d, ^{1}J(C,P) = 19.7 Hz), 135.6, 140.0; ^{31}P{^{1}H} NMR ($CDCl_3$): δ = -7.6 (s).

2g: The procedure was similar to that for **2c**. Starting from tris(4-bromophenyl)phosphane oxide (2.060 g, 4.0 mmol), *n*-butyl acrylate (2.307 g, 18 mmol), palladacycle (56 mg, 0.06 mmol), and NaOAc (1.312mg, 16.0 mmol) in DMF (50 ml) and after reacting at 125 °C for 15 h, tris[4-(2-butoxycarbonylvinyl)phenyl]phosphane oxide **2g** was obtained as white crystals

(2.602 g, 98%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 0.97 (t, ^{3}J (H,H) = 7.2 Hz, 9H), 1.43 (m, 6H), 1.69 (m, 6H), 4.25 (t, ^{3}J (H,H) = 6.6 Hz, 6H), 6.52 (d, ^{3}J (H,H) = 16.1 Hz, 3H), 7.61 ~ 7.73 (m, 15H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ = 13.7, 19.2, 30.7, 64.7, 121.2, 128.1 (d, ^{3}J(C,P) = 12.5 Hz), 132.6 (d, ^{2}J(C,P) = 9.8 Hz), 133.7 (d, ^{1}J(C,P) = 103.7 Hz), 138.4, 142.9, 166.6; $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ = 27.3 (s); MS (EI): *m*/*z* (%): 656 (23) [M^{+}]; elemental analysis calcd for $C_{39}H_{45}O_7P$: C 71.32, H 6.91; Found: C 71.27, H 6.88.

3g: The procedure was similar to that for **3c**. Starting from **2g** (4.150 g, 6.3 mmol), tris[4-(2-butoxycarbonylethyl)phenyl]phosphane oxide **3g** was obtained as a colorless oil (4.18 g, 100%), which was used directly in the next step without further purification. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 0.91 (t, ^{3}J (H,H) = 7.7 Hz, 9H), 1.33 (m, 6H), 1.58 (m, 6H), 2.61 (t, ^{3}J (H,H) = 7.7Hz, 6H), 2.99 (t, ^{3}J (H,H) = 7.7Hz, 6H), 4.07 (t, ^{3}J (H,H) = 6.6Hz, 6H), 7.29 (dd, ^{4}J (H,P) = 2.4, ^{3}J (H,H) = 8.2 Hz, 6H), 7.57 (dd, ^{3}J (H,H) = 8.2, ^{3}J (H,P) = 11.2 Hz, 6H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ = 13.6, 19.1, 30.6, 30.9, 35.3, 64.5, 128.5 (d, ^{3}J(C,P) = 12.0 Hz), 130.7 (d, ^{1}J(C,P) = 105.4 Hz), 132.4 (d, ^{2}J(C,P) = 10.4 Hz), 144.9, 172.7; $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ = 28.7 (s).

4g: The procedure was similar to that for **4c**. Starting from **3g** (3.983 g. 6.0 mmol), tris[4-(2-butoxycarbonylethyl)phenyl]phosphane **4g** was obtained as a colorless oil (3.610 g, 93%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 0.91 (t, ^{3}J (H,H) = 7.5 Hz, 9H), 1.34 (m, 6H), 1.58 (m, 6H), 2.62 (t, ^{3}J (H,H) = 7.8 Hz, 6H), 2.95 (t, ^{3}J (H,H) = 7.8 Hz, 6H), 4.07 (t, ^{3}J (H,H) = 6.9 Hz, 6H), 7.18 ~ 7.30 (m, 12H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ = 13.6, 19.0, 30.6, 30.7, 35.5, 64.4, 128.8 (d, ^{1}J (C,P) = 8.0 Hz), 133.9, 134.1, 142.2, 172.9; $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ = -7.2 (s).

5: A mixture of **4g** (3.557 g, 5.5 mmol), NaOH (800 mg, 20 mmol), water (5 ml), MeOH (10 ml) and THF (10 ml) was stirred for 5h at room temperature. The solvents were removed under reduced pressure. EtOH (20 ml) was added to the solid residue. The suspension was stirred for 2 h at room temperature and then left for standing in an ice bath for 1 h. The resultant precipitate was collected by filtration, washed with cold EtOH, and dried under reduced pressure to give the sodium salt of tris[4-(2-carboxylethyl)phenyl]phosphane **5** as white powder (2.660 g, 89%). ^{1}H NMR (300 MHz, D_2O, TMS): δ = 2.38 (t, ^{3}J (H,H) = 7.8 Hz, 6H), 2.79 (t, ^{3}J (H,H) = 7.8 Hz, 6H), 7.19 ~ 7.20 (m, 12); ^{13}C NMR (75 MHz, D_2O): δ = 31.4, 38.6, 128.4, 133.2, 133.4, 143.1, 182.1; ^{31}P{^{1}H} NMR (D_2O): δ = -9.1 (s); MS (FAB): *m*/*z* (%): 521 (8) [M^+ – Na].