Use of $InCl_3$ as a Cocatalyst and a $Cl_2Pd(DPEphos)$–$P(2\text{-Furyl})_3$ Catalyst System for One-Pot Hydrometalation–Cross-Coupling and Carbometalation–Cross-Coupling Tandem Processes

Mingxing Qian, Zhihong Huang, Ei-ichi Negishi*

Herbert C. Brown Laboratories of Chemistry, Purdue University, 560 Oval Drive, West Lafayette, Indiana 47907-2084

Supplementary Data

General. All experiments were conducted under argon atmosphere. THF and diethyl ether were dried and distilled by the standard methods. $ZnBr_2$ was flame-dried under vacuum prior to use. $Pd(PPh_3)_4$,[a] Pd(DPEPhos)Cl_2,[b] and $Pd(TFP)_2Cl_2$[c] were prepared according to the literature procedures. $PdCl_2$, PPh_3, DPEPhos, tri(2-furyl)phosphine (TFP), dppf, P(*t*-Bu)$_3$, $Pd_2(dba)_3$, Pd(dppf)Cl_2 were purchased from Strem and used as received. $InCl_3$ was purchased from Johnson Matthey.

Flash chromatographic separations were carried out on 230 – 400 mesh silica gel 60. Gas chromatography was performed on an HP 6890 Gas Chromatograph using a HP-5 capillary column (30 m × 0.32 mm, 0.5 μm film) with appropriate hydrocarbons as internal standards. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Varian Inova-300 spectrometer. IR spectra were recorded on a Perkin-Elmer Spectrum 2000 FT-IR spectrometer. LRMS and HRMS were obtained on Hewlett Packed 5995 GC-MS and Finnigan MATL95 mass spectrometers, respectively. Microanalyses were performed on a Perkin-Elmer 2400 Series II CHNS/O Analyzer.

Use of $InCl_3$ as a Cocatalyst and a Cl_2Pd(DPEphos)−P(2-Furyl)$_3$ Catalyst System for One-Pot Hydroalumination−Cross-Coupling. Representative Procedure A. (a) (1*E*,3*E*)-1-Bromo-1,3-decadiene. To 0.30 mL (2.0 mmol) 1-octyne in 1 mL of heptane was added 0.37 mL (2.1 mmol, 98%) of DIBAH at 23 °C. This mixture was stirred at 50 °C for 4 h, then cooled to 0 °C, followed by addition of a suspension of dry $InCl_3$ (150 mg, 0.68 mmol, 0.34 molar equiv) in THF (5 mL) at 0 °C. After 30 min., to this solution was added via cannula a mixture of (*E*)-1-iodo-2-bromoethylene (559 mg, 2.4 mmol), Pd(DPEPhos)Cl_2 (14 mg, 20 μmol), TFP (9.3 mg, 40 μmol) and DIBAH (40 μL, 1.0 M in hexane, 40 μmol) in THF (2 mL) at 0 °C. The reluctant mixture was stirred at 0 °C and monitored by GLC analysis. After 4 h, the reaction was quenched with water, extracted with ether, dried over $MgSO_4$, filtered and concentrated. Flash chromatography (silica gel, hexane) afforded the title compound (354 mg, 82%, stereoisomeric purity ≥98%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.91 (t, *J* = 6.7 Hz, 3 H), 1.1-1.35 (m, 8 H), 1.8-1.9 (m, 2 H), 5.47 (dt, *J* = 6.9 and 15.1 Hz, 1 H), 5.72 (dd, *J* = 10.8 and 15.1 Hz, 1 H), 5.92 (d, *J* = 13.5 Hz, 1 H), 6.62 (dd, *J* = 10.8 and 13.5 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.05, 22.58, 28.81, 28.89, 31.66, 32.59, 105.99, 127.49, 136.55, 137.71; IR (neat) 3066, 3019, 1645, 1583, 977, 734, 649 cm^{-1}; HRMS calculated for $C_{10}H_{17}Br$ [M]$^+$: 216.0514; found: 216.0517.

In two other runs of the same reaction, 0.10 and 0.068 molar equiv of $InCl_3$ were used, and the title compound was formed in 82 and 76% yields, respectively, in 8-10 h.

(b) (1*E*,3*E*)-1-Chloro-1,3-decadiene.[d] The title compound was prepared according to Representative Procedure A except that (*E*)-1-iodo-2-chloroethylene (452 mg, 2.4 mmol) was used. Flash chromotograph (silica gel, hexane) afforded the title compound (293 mg, 85%, stereoisomeric purity >98%): ^{1}H NMR (300 MHz, CDCl3) 0.88 (t, *J* = 7.2 Hz, 3 H), 1.2-1.45 (m, 8 H), 2.0-2.15 (m, 2 H), 5.74 (dt, *J* = 6.9 and 15.1 Hz, 1 H), 6.00 (dd, *J* = 11.0 and 15.1 Hz, 1 H), 6.09 (d, *J* = 13.2 Hz, 1 H), 6.45 (dd, *J* = 11.0 and 13.2 Hz, 1 H); ^{13}C NMR (75 MHz, CDCl3) 14.05, 22.59, 28.83, 29.01, 31.68, 32.63, 118.18, 126.02, 133.87, 136.28; IR (neat) 3066, 2958, 1693, 1583, 1467, 1379, 1284, 908 cm^{-1}.

In another run, 0.1 molar equiv of $InCl_3$ was used, and the desired product was formed in 80% yield over 8 h.

Use of $InCl_3$ as a Cocatalyst and a Cl_2Pd(DPEphos)–P(2-Furyl)$_3$ Catalyst System for One-Pot Hydrozirconation–Cross-Coupling. Representative Procedure B. (a) (1*E*,3*E*)-1-Bromo-1,3-decadiene. To 0.15 mL (1.0 mmol) 1-octyne in 3 mL of THF was added 284 mg (1.1 mmol) of Cp_2ZrHCl at 23 °C. This mixture was stirred at 23 °C for 4 h, then cooled to 0 °C, followed by addition of a suspension of dry $InCl_3$ (75 mg, 0.34 mmol, 0.34 molar equiv) in THF (2 mL) at 0 °C. After 30 min., to this solution was added via cannula a mixture of (*E*)-1-iodo-2-bromoethylene (280 mg, 1.2 mmol), Pd(DPEPhos)Cl_2 (7.0 mg, 10 μmol), TFP (4.7 mg, 20 μmol), and DIBAH (20 mL, 1.0 M in hexane, 20 μmol) in THF (1 mL) at 0 °C. The resultant mixture was stirred at 0 °C and monitored by GLC analysis. After 4 h, an aliquot was analyzed by GLC with decane

as an internal standard. Analysis indicated the formation of the title compound in 77% yield.

In two other runs, the same reaction was run in the presence of 0.10 and 0.068 molar equiv of $InCl_3$. These reactions produced the title product in 76 and 70% yields, respectively, in 8-10 h.

(b) (1*E*,3*E*)-1-Bromo-4-phenyl-1,3-butadiene.[e] The title compound was prepared according to Representative Procedure B except that phenylacetylene (204 mg, 2.0 mmol) was used. Yield: 351 mg (84%); Stereoisomeric purity: >99%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.36 (d, *J* = 13.5 Hz, 1 H), 6.45-6.6 (m, 2 H), 6.84 (dd, J = 10.3 and 13.5 Hz, 1 H), 7.2-7.35 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 108.89, 125.89, 126.43 (2C), 127.96, 128.62 (2C), 133.24, 136.43, 137.55; IR (neat) 3152, 3066, 1949, 1627, 1570, 1183, 975, 912 cm^{-1}; Anal. Calcd. for $C_{10}H_9Br$: C, 57.44; H, 4.34; Found: C, 57.82; H, 4.46.

(c) (1*E*,3*E*)-1-Bromo-3-ethyl-1,3-hexadiene: The title compound was prepared according to Representative Procedure B except that 3-hexyne (164 mg, 2.0 mmol) was used. Yield: 308 mg (82%); Stereoisomeric purity: >98%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.97 (t, *J* = 7.4 Hz, 6 H), 2.0-2.2 (m, 4 H), 5.38 (t, *J* = 7.3 Hz, 1H), 6.14 (d, *J* = 13.9 Hz, 1H), 6.58 (d, *J* = 13.9 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.26, 14.72, 20.44, 21.84, 102.82, 135.08, 137.72, 140.03; IR (neat) 2969, 2876, 1676, 1585, 1471, 1377, 945, 861, 734, 651 cm^{-1}.

Use of $InCl_3$ as a Cocatalyst and a Cl_2Pd(DPEphos)–P(2-Furyl)$_3$ Catalyst System for One-Pot Carboalumination–Cross-Coupling. Representative Procedure C. (a) (1*E*,3*E*)-1-Bromo-4-methyl-1,3-decadiene. To 117 mg (0.40 mmol) of Cp_2ZrCl_2 in 1 mL of CH_2Cl_2 was added 0.20 mL (2.1 mmol) of Me_3Al at 23 °C. After this mixture was added to 0.30 mL (2.0 mmol) of 1-octyne, the resultant mixture was stirred at 23 °C for 6 h. To this was sequentially added a suspension of dry $InCl_3$ (150 mg, 0.68 mmol, 0.34 molar equiv) in THF (5 mL) at 0 °C. After 30 min., to this solution was added via cannula a mixture of (*E*)-1-iodo-2-bromoethylene (559 mg, 2.4 mmol), Pd(DPEPhos)Cl_2 (14 mg, 20 μmol), TFP (9.3 mg, 40 μmol) and DIBAH (40 μL, 1.0 M in hexane, 40 μmol) in THF (2 mL) at 0 °C, this mixture was prepared in this order at 0 °C for 5 min.. The reluctant mixture was stirred at 0 °C and monitored by GLC analysis. After 4 h, the reaction was quenched with water, extracted with ether, dried over $MgSO_4$, filtered and concentrated. Flash chromatograph (silica gel, hexane) afforded the title compound (402 mg, 87%, stereoisomeric purity >98%): ^{1}H NMR (300 MHz, $CDCl_3$) 0.88 (t, *J* = 6.5 Hz, 3 H), 1.1-1.45 (m, 8 H), 1.70 (s, 3 H), 2.01 (t, *J* = 7.1 Hz, 2 H), 5.76 (d, *J* = 11.3 Hz, 1 H), 6.16 (d, *J* = 13.2 Hz, 1 H), 6.95 (dd, *J* = 11.3 and 13.2 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) 14.03, 16.67, 22.58, 27.57, 28.93, 31.71, 39.76, 106.04, 121.93, 134.21, 140.86; IR (neat) 3065, 2923, 1697, 1643, 975, 869 cm^{-1}; Anal. Calcd. for $C_{11}H_{19}Br$: C, 57.15; H, 8.29; Found: C, 56.78; H, 8.18.

In two other runs, the same reaction was run in the presence of 0.10 and 0.068 molar equiv of $InCl_3$. These reactions produced the title product in 85 and 77% yield, respectively, in 8-10 h.

(b) (1*E*,3*E*)-1-Chloro-4-methyl-1,3-decadiene. The title compound was prepared according to Representative Procedure C except that (*E*)-1-iodo-2-chloroethylene (452 mg, 2.4 mmol) was used. Yield: 347 mg (93%); Stereoisomeric purity: >99%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, *J* = 6.4 Hz, 3 H), 1.2-1.35 (m, 8 H), 1.71 (s, 3 H), 2.03 (t, *J* = 7.0 Hz, 2 H), 5.77 (d, *J* = 11.1 Hz, 1 H), 6.06 (d, *J* = 12.9 Hz, 1 H), 6.64 (dd, *J* = 11.1 and 12.9 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) 14.03, 16.45, 22.62, 27.68, 28.97, 31.75, 39.80, 118.15, 120.41, 130.35, 140.61; IR (neat) 3064, 2927, 1699, 1647, 977, 858 cm^{-1}; Anal. Calcd. for $C_{11}H_{19}Cl$: C, 72.96; H, 5.51; Found: C, 73.09; H, 5.65.

(c) (3*E*,5*E*)-3-Methyl-6-bromo-3,5-hexadien-1-ol. The title compound was prepared according to Representative Procedure C except that 3-butyn-1-ol (0.15 mL, 140 mg, 2.0 mmol) and Me_3Al (0.58 mL, 6 mmol) were used. Yield: 267 mg (70%); Stereoisomeric purity: >98%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.76 (s, 3 H), 2.15 (s, 1H), 2.28 (t, J = 6.3 Hz, 2 H), 3.69 (t, J = 6.3 Hz, 2 H), 5.85 (d, J = 11.3 Hz, 1 H), 6.25 (d, J = 13.3 Hz, 1 H), 6.93 (dd, J = 11.3 and 13.3 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) 16.63, 42.56, 60.07, 107.37, 124.22, 133.63, 136.55; IR (neat) 3067, 2252, 1644, 1046, 907, 733 cm^{-1}; Anal. Calcd. for $C_7H_{11}BrO$: C, 44.00; H, 5.80; Found: C, 43.96; H, 5.85.

Use of Preformed Organozincs and a Cl_2Pd(DPEphos)–P(2-Furyl)$_3$ Catalyst System for Cross-Coupling. Representative Procedure D. (a) (1*E*,3*E*)-1-Bromo-1,3-decadiene. To (*E*)-1-iodo-1-octene (476 mg, 2.0 mmol) in ether (5 mL) cooled to -78 ^{o}C was added *t*-BuLi (2.4 mL, 1.7 M in pentane, 4.1 mmol). The resultant solution was

stirred at -78 °C for 30 min., followed by addition of dry $ZnBr_2$ (450 mg, 2.0 mmol) in THF (3 mL). The mixture thus obtained was stirred at -78 °C for 5 min. and then warmed to 0 °C over 25 min. To this was added *via* cannula a mixture of (*E*)-1-iodo-2-bromoethylene (559 mg, 2.4 mmol), Pd(DPEPhos)Cl_2 (14 mg, 20 μmol), TFP (9.3 mg, 40 μmol) and DIBAH (40 μL, 1.0 M in hexane, 40 μmol) in THF (2 mL) at 0 °C. The resultant mixture was stirred at 0 °C and monitored by GLC analysis. After 4 h, an aliquot was analyzed by GLC with decane as an internal standard. Analysis indicated the formation of the title compound in75% yield.

(b) (1*E*,3*E*)-1-Chloro-4-phenyl-1,3-butadiene. The title compound was prepared according to Representative Procedure D except that (*E*)-1-iodo-2-phenylethylene (460 mg, 2.0 mmol) and (*E*)-1-iodo-2-chloroethylene (452 mg, 2.4 mmol) were used. Yield: 280 mg (85%); Stereoisomeric purity: >99%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.24 (d, *J* = 13.5 Hz, 1 H), 6.4-6.7 (m, 3 H), 7.15-7.3 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 120.88, 124.56, 126.39 (2C), 127.88, 128.60 (2C), 133.13, 133.80, 136.53; IR (neat) 3154, 3066, 1949, 1638, 1584, 1196, 974, 908 cm^{-1}.

(c) (1*E*,3*Z*)-1-Bromo-1,3-octadiene. The title compound was prepared according to Representative Procedure D except that (*Z*)-1-iodo-1-hexene (420 mg, 2.0 mmol) was used. Yield: 308 mg (82%); Stereoisomeric purity: >98%; ^{1}H NMR (300 MHz, C_6D_6) δ 0.93 (t, *J* = 6.5 Hz, 3 H), 1.2-1.3 (m, 4 H), 1.9-2.0 (m, 2 H), 5.42 (dt, *J* = 7.8 Hz, 10.6 Hz, 1 H), 5.80 (dd, *J* = 10.6 and 11.1 Hz, 1 H), 6.08 (d, *J* = 13.3 Hz, 1 H), 7.13 (dd, *J* = 11.1 and 13.3 Hz, 1 H); ^{13}C NMR (75 MHz, C_6D_6) δ 14.03, 22.44, 27.70, 31.73, 109.21,

126.14, 133.42, 133.51; IR (neat) 2958, 1696, 1466, 732 cm^{-1}; HRMS calculated for $C_8H_{13}Br$ $[M]^+$: 188.0201; found: 188.0205.

(d) (*E*)-1-Bromo-2-phenylethylene.[f] The title compound was prepared according to Representative Procedure D except that iodobenzene (408 mg, 2.0 mmol) was used. Yield: 329 mg (90%); Stereoisomeric purity: >99%; ^1H NMR (300 MHz, $CDCl_3$) δ 6.71 (d, *J* = 14.0 Hz, 1 H), 7.07 (d, *J* = 14.0 Hz, 1 H), 7.2-7.35 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 106.47, 126.00 (2C), 128.15, 128.67 (2C), 135.78, 137.03; IR (neat) 3105, 3060, 1874, 1802, 1675, 1608, 1574, 940, 732 cm^{-1} .

(e) (*E*)-1-Bromo-2-(4'-cyanophenyl)ethylene.[g] The title compound was prepared according to Representative Procedure D except that 4-bromobenzonitrile (364 mg, 2.0 mmol) was used. Yield: 295 mg (70%); Stereoisomeric purity: >99%; ^1H NMR (300 MHz, $CDCl_3$) δ 6.95 (d, *J* = 14.1 Hz, 1 H), 7.11 (d, *J* = 14.1 Hz, 1 H), 7.38 (d, *J* = 8.3 Hz, 2 H), 7.61 (d, *J* = 8.3 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 110.75, 111.46, 118.48, 126.44 (2C), 132.50 (2C), 135.51, 139.90; IR (neat) 2255, 2230, 1923, 1795, 1601, 958, 846, 783 cm^{-1}.

(f) (*E*)-1-Bromo-2-(4'-methyloxy-phenyl)ethylene.[h] The title compound was prepared according to Representative Procedure D except that 4-iodoanisole (468 mg, 2.0 mmol) was used. Yield: 349 mg (82%); Stereoisomeric purity: >99%; ^1H NMR (300 MHz, $CDCl_3$) δ 3.80 (s, 3 H), 6.60 (d, *J* = 14.1 Hz, 1 H), 6.84 (d, *J* = 8.6 Hz, 2 H), 7.03 (d, *J* = 14.1 Hz, 1 H), 7.22 (d, *J* = 8.6 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 56.30,

104.54, 114.62 (2C), 127.69 (2C), 129.05, 136.78, 159.66. IR (neat) 3000, 2958, 2838, 1952, 1880, 1724, 1607, 1441, 1370, 945, 905, 732 cm^{-1}.

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