Asymmetric Synthesis of Monodentate Phosphine Ligands Based on Chiral η^6-Cr[arene] Templates

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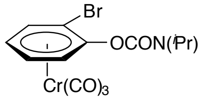
Supporting Information

General Information: Optical rotations were measured on a Perkin-Elmer 241 digital polarimeter with a sodium lamp at ambient temperature and are reported as follows: $[\alpha]_\lambda$ (*c* g/100mL). Infrared spectra were recorded on a Nicolet Avatar 360 FT-IR spectrometer. ^{1}H NMR spectra were recorded on Bruker Avance-300 (300 MHz) or DMX-500 (500 MHz) spectrometers. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (deuterochloroform: δ 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), integration, coupling constants (Hz), and assignment. ^{13}C NMR spectra were recorded on a Bruker Avance-300 (75 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent as the internal standard (deuterochloroform: δ 77.0 ppm). Mass spectra were obtained on a VG-7070 or Fisons Autospec high resolution magnetic sector mass spectrometer.

Analytical thin layer chromatography was performed on EM Reagent 0.25 mm silica gel 60-F plates. Flash chromatography was performed as previously described on EM silica gel 60 (230-240 mesh).[1] Analytical high performance liquid chromatograph (HPLC) was performed on a Hewlett Packard 1100 liquid chromatograph equipped with a variable wavelength UV detector (deuterium lamp, 190-600 nm), using a Daicel Chiralcel™ OD-H column (250 × 4.6 mm) (Daicel Inc.). HPLC grade isopropanol and hexanes were used as the eluting solvents.

All experiments were carried out under a nitrogen atmosphere in oven or flame-dried glassware using standard inert atmosphere techniques for introducing reagents and solvents. Dichloromethane (CH_2Cl_2) was distilled from CaH_2 under N_2. Tetrahydrofuran was distilled from potassium/benzophenone ketyl. Diethylether was distilled from sodium/benzophenone ketyl. All other commercially obtained reagents were used as received.



Diisopropyl carbamic acid 2-bromophenyl ester chromium tricarbonyl (6). To a 0 °C solution of 0.22 g of chiral amine 5 (0.86 mmols) in 1.0 mL of THF was added 0.60 mL of *n*-BuLi (0.88 mmols, 1.47 M in hexanes). This yellow solution was stirred for five minutes at 0 °C and then transferred via cannula to a -78 °C solution of 0.30 g of arene chromium tricarbonyl 3 (0.84 mmols) in 1.8 mL of THF. The resulting reaction mixture was stirred at -78 °C for 2 h. A solution of 0.30 g of dibromotetrachloroethane (0.92 mmols) in 7.2 mL of Et_2O was added to the reaction mixture via cannula. The reaction was then allowed to warm slowly to ambient temperature over 12 h. The reaction mixture was filtered through a plug of silica gel and concentrated *in vacuo*. The chiral amine base (5) was separated from the product via silica gel chromatography using hexanes as the eluent. The title compound was quickly washed off the silica gel using EtOAc and concentrated *in vacuo* as a yellow film. This was brought into a drybox and recrystallized at -23 °C using Et_2O/pentane mixtures. The resulting yellow crystals were stored in the drybox at -23 °C indefinitely: $[\alpha]^{20}_{589}$ = +2.86° (95 %ee, *c* 0.7, CH_2Cl_2); ^{1}H NMR (d_6-acetone) δ 6.18 (d, J = 6.4 Hz, 1 H), 5.90 (d, J = 6.6 Hz, 1 H), 5.75 (dd, J = 6.0, 6.0 Hz, 1 H), 5.47 (dd, J = 6.2, 6.2 Hz, 1 H), 4.16-3.98 (m, 2 H), 1.37 (d, J = 5.8 Hz, 6 H), 1.29 (d, J = 6.6 Hz, 6 H); ^{13}C NMR (d_6-acetone) δ 233.1, 152.4, 131.5, 98.2, 94.0, 92.4, 91.3, 89.8, 47.9, 21.6, 20.6, 20.4; EI-MS *m/e* 436 (M^+), 421, 408 (M^+-CO), 380 (M^+-2CO), 350, 300 (M^+-$Cr(CO)_3$), 272, 223, 194, 173, 144, 128; HPLC (90/10 hexanes/^{i}PrOH, 1 mL/min) R_t = 19.65, 24.31.

General Procedure A: Suzuki coupling of bromide (6) with arylboronic acids. A 25 mL Schlenk flask was charged with 0.44 g of bromide **6** (1.0 mmol), 2.0 mmols of the boronic acid, and 0.058 g of $Pd(PPh_3)_4$ (0.05

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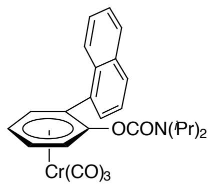
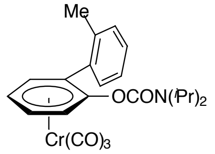
[1] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923-2925.

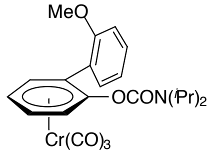
mmols) and then fitted with a reflux condenser and septum in a glovebox. To this flask was added 13 mL of methanol and 1.3 mL of aqueous Na_2CO_3 solution (2.6 mmols). The reaction mixture was subjected to three freeze/pump/thaw cycles in order to degas the solvents. The reaction mixture was heated to reflux for 0.5 h and then quenched with 2.0 mL of saturated aqueous NH_4Cl solution. The organics were extracted into EtOAc (3 X 20 mL). The combined organics were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The product was purified by silica gel chromatography using EtOAc/hexane mixtures as the eluent.



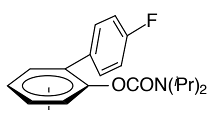
Diisopropylcarbamic acid, 2-naphthalen-1-yl-phenyl ester chromium tricarbonyl (7a): General Procedure A was followed using 344 mg of 2-naphthylboronic acid (2.0 mmols). Purification by flash chromatography (20% EtOAc in hexanes) gave 362 mg (75 %) of the title compound: ^{1}H NMR (d_6-acetone) δ 7.98 (dd, J = 8.2, 8.2 Hz, 2 H), 7.78 (d, J = 7.3 Hz, 1 H), 7.73 (d, J = 7.7 Hz, 1 H), 7.62 (dd, J = 8.2, 8.2 Hz, 1 H), 7.56 - 7.44 (m, 2 H), 6.15 (dd, J = 6.6, 6.6 Hz, 1 H), 6.09 (d, J = 7.6 Hz, 1 H), 5.88 (d, J = 6.5 Hz, 1 H), 5.44 (dd, J = 6.7, 6.7 Hz, 1 H), 3.58 - 3.40 (m, 2 H), 0.96 (d, J = 6.5 Hz, 3 H), 0.75 (d, J = 6.4 Hz, 3 H), 0.70 - 0.50 (m, 6 H); ^{13}C NMR (d_6-acetone) δ 234.3, 151.7, 132.0, 130.2, 129.4, 129.1, 128.7, 128.3, 127.4, 126.9, 126.6, 126.2, 124.5, 108.2, 101.0, 97.7, 88.0, 87.8, 47.5, 46.9, 20.6, 20.3, 20.0; EI-MS *m/e* 483 (M^+), 451, 423, 399 (M^+-3CO), 356, 347 (M^+-$Cr(CO)_3$), 338, 324, 271, 256, 220, 202, 189, 165, 151, 128; HPLC (90/10 hexanes/^{i}PrOH, 1 mL/min) R_f = 6.06, 7.28.



Diisopropylcarbamic acid, 2'-methylbiphenyl-2-yl ester chromium tricarbonyl (7b): General Procedure A was followed employing 272 mg of 2-methylphenylboronic acid (2.0 mmols). Purification by flash chromatography (10% EtOAc in hexanes) gave 282 mg (63 %) of the title compound: ^{1}H NMR (d_6-benzene) δ 7.73 (d, J = 6.7 Hz, 1 H), 7.10-6.94 (m, 3 H), 4.87-4.83 (m, 2 H), 4.63 (dd, J = 6.4, 6.4 Hz, 1 H), 3.96 (dd, J = 6.0, 6.0 Hz, 1 H), 3.71 (m, 1 H), 3.24 (m, 1 H), 2.20 (s, 0.3 H), 2.13 (s, 2.7 H), 0.93-0.73 (m, 12 H); ^{13}C NMR (d_6-acetone) δ 234.4, 138.0, 134.4, 133.0, 130.8, 129.6, 126.5, 110.0, 100.4, 97.5, 88.2, 87.3, 47.9, 46.8, 29.4, 21.0, 20.2; EI-MS *m/e* 447 (M^+), 419 (M^+-CO), 391 (M^+-2CO), 363 (M^+-3CO), 311 (M^+-$Cr(CO_3)$), 235, 184, 165, 152, 128, 115; HPLC (90/10 hexanes/^{i}PrOH, 1 mL/min) R_t = 5.26, 7.75.

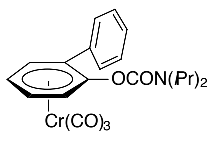


Diisopropylcarbamic acid, 2'-methoxybiphenyl-2-yl ester chromium tricarbonyl (7c): General Procedure A was followed using 304 mg of 2-methoxyphenylboronic acid (2.0 mmols). This compound was prepared as stated in General Procedure A with the following additional purification steps. The combined EtOAc layers were washed with 1N NaOH (3 X 10 mL), saturated aqueous $NaHCO_3$ (1 X 10 mL), and brine (1 X 10 mL). The organic layers were then dried over $MgSO_4$, filtered, and concentrated *in vacuo* as in the general procedure. Purification by flash chromatography (20% EtOAc in hexanes) gave 306 mg (66 %) of the title compound: 1H NMR (d_6-acetone) δ 7.81 (d, J = 7.2 Hz, 1 H), 7.49 - 7.39 (m, 3 H), 6.00 - 5.90 (m, 2 H), 5.80 (d, J = 6.6 Hz, 1 H), 5.33 (dd, J = 6.0, 6.0 Hz, 1 H), 3.78 (s, 3 H), 3.95 - 3.65 (m, 2 H), 1.19 (d, J = 6.4 Hz, 3 H), 1.11 (d, J = 6.4 Hz, 3 H), 1.02 (d, J = 6.8 Hz, 3 H), 0.96 (d, J = 6.7 Hz, 3 H); ^{13}C NMR (d_6-acetone) δ 234.6, 177.5, 168.0, 158.5, 151.8, 134.3, 132.0, 131.2, 121.1, 111.8, 105.3, 100.5, 96.7, 88.5, 56.0, 47.7, 47.0, 21.1, 20.5; EI-MS *m/e* 407 (M^+-2CO), 379 (M^+-3CO), 364, 327 (M^+-$Cr(CO_3)$), 200, 184, 169, 157, 139, 128; HPLC (90/10 hexanes/^{i}PrOH, 1 mL/min) R_t = 7.91, 8.78.



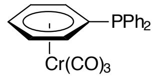
Diisopropylcarbamic acid, 4'-fluorobiphenyl-2-yl ester chromium tricarbonyl (7d): General Procedure A was followed employing 280 mg of 4-fluorophenylboronic acid (2.0 mmols). Purification by flash chromatography (20% EtOAc in hexanes) gave 329 mg (73 %)

of the title compound: ^{1}H NMR (d$_6$-acetone) δ 7.57 (dd, J = 1.2, 5.4 Hz, 2 H), 7.24 (t, J = 8.7 Hz, 2 H), 6.04 (d, J = 6.4 Hz, 1 H), 5.94 (dd, J = 1.2, 6.5 Hz, 1 H), 5.73 (d, J = 6.6 Hz, 1 H), 5.46 (dd, J = 1.1, 6.5 Hz, 1 H), 4.00 (m, 1 H), 3.75 (m, 1 H), 1.19-0.84 (m, 12 H); ^{13}C NMR (d$_6$-acetone) δ 234.1, 163.7 (d, J = 245.6 Hz), 152.6, 142.8, 133.2 (d, J = 7.7 Hz), 131.2, 115.9 (d, J = 21.6 Hz), 107.3, 98.6, 96.7, 89.7, 88.6, 47.8, 47.3, 21.2, 20.5, 20.2; EI-MS *m/e* 451 (M$^+$), 423 (M$^+$-CO), 395 (M$^+$-2CO), 367 (M$^+$-3CO), 239, 188, 159, 151, 128; HPLC (90/10 hexanes/^{i}PrOH, 1 mL/min)R$_t$ = 9.06, 9.86.

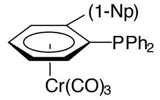


Diisopropyl carbamic acid, biphenyl-3-yl ester chromium tricarbonyl (7e): General Procedure A was followed employing 244 mg of phenylboronic acid (2.0 mmols). Purification by flash chromatography (20% EtOAc in hexanes) gave 277 mg (64 %) of the title compound: ^{1}H NMR (d$_6$-acetone) δ 7.55-7.51 (m, 2 H), 7.46-7.40 (m, 2 H), 6.04 (dd, J = 1.2, 6.6 Hz, 1 H), 5.94 (dd, J = 1.1, 6.3 Hz, 1 H), 5.72 (dd, J = 1.0, 6.7 Hz, 1 H), 5.45 (dd, J = 6.0, 5.7 Hz, 1 H), 3.99 (m, 1 H), 3.79 (m, 1 H), 1.17 (d, J = 6.5 Hz, 3 H), 1.15-1.10 (m, 9 H); ^{13}C NMR (d$_6$-acetone) δ 234.3, 135.0, 131.1, 129.5, 129.1, 98.7, 96.7, 89.6, 88.7, 47.8, 47.7, 21.2, 20.5; EI-MS *m/e* 433 (M$^+$), 377 (M$^+$-2CO), 349 (M$^+$-3CO), 306, 273, 221, 205, 170, 151, 128, 115; HPLC (90/10 hexanes/^{i}PrOH, 1 mL/min) R$_t$ = 7.94, 12.64.

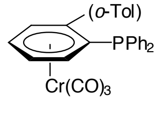
General Procedure B: Synthesis of triphenylphosphine chromium tricarbonyl and its derivatives. To a -78 °C solution of 0.38 g diphenylphosphine (2.05 mmols) in 2 mL of THF was added 1.39 mL of *n*BuLi (2.04 mmols). To this orange Ph$_2$PLi solution was added 1.0 mmol of the carbamate in 3 mL of THF via cannula. The reaction was stirred at -78 °C for 20 min. and then allowed to warm slowly to room temperature. The reaction was stirred at ambient temperature until complete consumption of the starting material was evidenced by TLC. The reaction mixture was passed through a plug of silica gel and concentrated *in vacuo*. The product was then purified by silica gel chromatography using EtOAc/hexane mixtures as the eluent.



Triphenylphosphine chromium tricarbonyl (8): General Procedure B was followed employing 357 mg of compound **3** (1.0 mmol). Purification by flash chromatography (10% EtOAc in hexane) gave 382 mg (96 %) of the title compound: ^{1}H NMR (d$_6$-acetone) δ 7.51–7.39 (m, 10 H), 5.80 (t, J = 6.1 Hz, 1 H), 5.56 (dd, J = 6.3, 6.3 Hz, 1 H), 5.41 (d, J = 6.2 Hz, 1 H); ^{13}C NMR (d$_6$-acetone) δ 233.8, 136.0 (d, J = 12.0 Hz), 134.8 (d, J = 20.0 Hz), 130.5, 129.8 (d, J = 6.9 Hz), 104 (d, J = 12.0 Hz), 100.0 (d, J = 16.8 Hz), 96.3, 93.4 (d, J = 6.9 Hz); EI-MS *m/e* 398 (M$^+$), 370 (M$^+$-CO), 342 (M$^+$-2CO), 314 (M$^+$-3CO), 262, 183, 152, 128, 108.

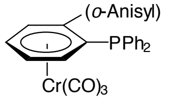


(2-Naphthalen-1-yl-phenyl)diphenylphosphine chromium tricarbonyl (9a): General Procedure B was followed using 483 mg of compound **7a** (1.0 mmol). Purification by flash chromatography (5% EtOAc in hexanes) gave 456 mg (87 %) of the title compound: $[\alpha]^{20}_{580}$ = -266° (97 %ee, *c* 0.41, acetone); ^{1}H NMR (CDCl$_3$) δ 8.12 (d, J = 7.1 Hz, 1 H), 7.77 (d, J = 7.1 Hz, 1 H), 7.63 (d, J = 7.1 Hz, 1 H), 7.56 (dd, J = 7.1, 7.1 Hz, 1 H), 7.47 - 7.27 (m, 3 H), 7.22 (d, J = 7.1 Hz, 2 H), 7.10 (d, J = 6.6 Hz, 2 H), 6.99 - 6.91 (m, 4 H), 6.87 (dd, J = 6.6, 6.6 Hz, 2 H), 5.56 (dd, J = 6.4, 6.4 Hz, 1 H), 5.52 (d, J = 6.2 Hz, 1 H), 5.38 (dd, J = 6.2 Hz, 1 H), 4.87 (d, J = 6.4 Hz, 1 H); ^{13}C NMR (CDCl$_3$) δ 232.9, 134.7, 134.4 (d, J = 4.8 Hz), 134.0, 133.8, 131.1, 132.4, 132.3, 131.5 (d, J = 4.8 Hz), 129.5 (d, J = 4.8 Hz), 129.3, 129.0 (d, J = 4.8 Hz), 128.2, 128.1 (d, J = 4.8 Hz), 126.6, 125.7, 125.4, 125.1, 124.8, 117.3, 111.3, 98.9, 94.2, 92.1, 89.4; EI-MS *m/e* 513, 492, 440 (M$^+$-3CO), 404, 387 (M$^+$-Cr(CO)$_3$), 362, 347, 327, 310, 255, 233, 220, 202, 183, 155, 128, 108.

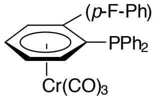


(2'-Methylbiphenyl-2-yl)diphenylphosphine chromium tricarbonyl (9b): General Procedure B was followed employing 447 mg of compound **7c** (1.0 mmol). Purification by flash chromatography (10% EtOAc in hexanes) gave 366 mg (75 %) of the title compound: $[\alpha]^{20}_{580}$ = -279.9° (97 %ee, *c* 3.8, CH$_2$Cl$_2$); ^{1}H NMR (d$_6$-acetone) δ 7.87 (d, J = 6.5 Hz, 1 H), 7.46-7.18 (m, 12 H), 6.80 (d, J = 6.5 Hz, 1 H), 5.86 (dd, J = 6.2, 6.2 Hz, 1 H), 5.77 (d, J = 6.5 Hz, 1 H), 5.68 (dd, J = 1.2, 7.4 Hz, 1 H), 4.94 (d, J

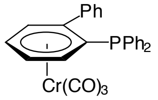
= 6.5 Hz, 1 H), 1.58 (s, 2.5 H), 1.41 (s, 0.5 H); ^{13}C NMR (d_6-acetone) δ 234.3, 138.4 (d, J = 12.0 Hz), 135.8, 135.3 (d, J = 20 Hz), 134.5 (d, J = 21.5 Hz), 132.2, 131.3, 130.7, 130.4, 129.6 (d, J = 8.6 Hz), 129.4 (d, J = 8.9 Hz), 127.1, 125.9, 111.6, 100.6, 98.8, 96.6, 95.9, 93.4, 92.7, 91.8, 20.1; EI-MS *m/e* 488 (M^+), 460 (M^+-CO), 404 (M^+-3CO), 351 (M^+-Cr(CO_3)), 337, 326, 277, 259, 202, 165, 152.



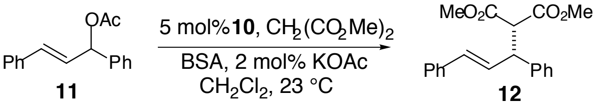
(2'-Methoxybiphenyl-2-yl)diphenylphosphine chromium tricarbonyl (9c): General Procedure B was followed using 463 mg of compound **7b** (1.0 mmol). Purification by flash chromatography (10% EtOAc in hexanes) gave 318 mg (63 %) of the title compound: $[\alpha]^{20}_{580}$ = -167° (95 %ee, *c* 0.7, CH_2Cl_2); ^{1}H NMR (d_6-acetone) δ 7.74 (m, 1 H), 7.42-7.23 (m, 10 H), 7.05-6.92 (m, 2 H), 6.65 (d, J = 7.8 Hz, 1 H), 5.75-5.63 (m, 3 H), 4.96 (d, J = 6.1 Hz, 1 H), 3.20 (s, 3 H); ^{13}C NMR (d_6-acetone) δ 234.3, 158.3, 136.4 (d, J = 7.5 Hz), 136.2, 135.9 (d, J = 19.5 Hz), 135.5, 134.8 (d, J = 20.3 Hz), 131.3, 130.5, 129.9, 129.6 (d, J = 5.6 Hz), 129.1 (d, J = 6.0 Hz), 128.8, 125.2, 120.4, 117.3, 110.8, 100.4, 95.3, 92.7, 83.1, 54.9; EI-MS *m/e* 504 (M^+), 476 (M^+-CO), 436, 420 (M^+-3CO), 353, 337, 277, 257, 228, 202, 183, 170, 152, 139, 107.



(4'-Fluorobiphenyl-2-yl)diphenylphosphine chromium tricarbonyl (9d): General Procedure B was followed employing 451 mg of compound **7d** (1.0 mmol). Purification by flash chromatography (10% EtOAc in hexanes) gave 374 mg (76 %) of the title compound: $[\alpha]^{20}_{580}$ = -115.3° (95 %ee, *c* 0.6, CH_2Cl_2); ^{1}H NMR (d_6-acetone) δ 7.44 - 7.32 (m, 12 H), 7.00 (t, J = 8.8 Hz, 2 H), 5.83 (dd, J = 6.4, 6.4 Hz, 1 H), 5.72 - 5.68 (m, 2 H), 4.97 (d, J = 6.6 Hz, 1 H); ^{13}C NMR (d_6-acetone) δ 233.8, 163.7 (d, J = 245.6 Hz), 135.7 (d, J = 20.9 Hz), 134.7 (d, J = 21.1 Hz), 133.8 (m, 4 C), 130.6, 130.4, 129.7 (d, J = 7.1 Hz), 115.4 (d, J = 21.8 Hz), 107.5, 106.4, 98.1, 96.8, 94.7, 94.2; EI-MS *m/e* 408 (M^+-3CO), 372, 355 (M^+-Cr(CO_3)), 295, 277, 246, 217, 201, 183, 170, 149, 128, 105.



Biphenyl-2-yl-diphenylphosphine chromium tricarbonyl (9e): General Procedure B was followed employing 433 mg of compound **7e** (1.0 mmol). Purification by flash chromatography (10% EtOAc in hexanes) gave 270 mg (57 %) of the title compound: $[\alpha]^{20}_{589}$ = -116.25° (95 %ee, *c* 0.8, CH_2Cl_2); ^{1}H NMR (d_6-acetone) δ 7.44-7.20 (m, 15 H), 5.83 (dd, J = 6.3, 6.3 Hz, 1 H), 5.70-5.66 (m, 2 H), 4.99 (d, J = 6.3 Hz, 1 H); ^{13}C NMR (d_6-acetone) δ 233.1, 134.8 (d, J = 20.0 Hz), 133.8 (d, J = 20.6 Hz), 130.9, 129.7, 129.4, 129.0, 128.8 (d, J = 6.8 Hz), 128.6, 127.7, 97.2, 96.4, 93.7, 93.5; EI-MS *m/e* 474 (M^+), 446 (M^+-CO), 406, 390 (M^+-3CO), 353, 337 (M^+-Cr(CO)$_3$), 277, 259, 228, 199, 183, 170, 152, 128, 115.



Allylic alkylation of 1,3-diphenyl-2-propenyl acetate (11): A flame-dried 10 mL round-bottom flask was charged with 0.013 g of compound **9a** (0.025 mmols) and 0.005 g of (allylPdBr)$_2$ (0.0095 mmols) and purged with nitrogen. The solid mixture was dissolved in 0.5 mL of CH_2Cl_2. The resulting yellow solution was allowed to stir for twenty minutes at room temperature. To this solution was added 0.076 mL of dimethyl malonate (0.66 mmols) and 0.163 mL of *bis*-trimethylsilylacetamide (0.66 mmols). A solution of 0.111 g 1,3-diphenyl-2-propenyl acetate **11** (0.44 mmols) in 1.0 mL CH_2Cl_2 was transferred via cannula to the reaction solution. To the reaction solution was added 0.004 g KOAc (0.04 mmols) under a stream of nitrogen. After 15 h the reaction was quenched with 5 mL of H_2O. The product was extracted into EtOAc. The organics were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Silica gel chromatography using 90:10 hexanes:EtOAc as the eluent yielded product **12** as a clear, colorless oil (97%, 90%ee).

X-Ray data for Pd(II) complex 10.

Table 1. Crystal data and structure refinement for hilf199.

Identification code	hilf199
Empirical formula	C34 H26 Br Cr O3 P Pd
Formula weight	751.83
Temperature	298(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 291)/n
Unit cell dimensions	a = 9.5660(19) A alpha = 90 deg. b = 21.622(4) A beta = 106.97(3) deg. c = 15.309(3) A gamma = 90 deg.
Volume	3028.6(10) A^3
Z, Calculated density	4, 1.649 Mg/m^3
Absorption coefficient	2.358 mm^-1
F(000)	1496
Crystal size	0.15 x 0.08 x 0.08 mm
Theta range for data collection	1.88 to 24.10 deg.
Limiting indices	-10<=h<=0, 0<=k<=24, -16<=l<=17
Reflections collected / unique	5077 / 4767 [R(int) = 0.0938]
Completeness to theta = 24.10	99.2 %
Max. and min. transmission	0.8338 and 0.7187
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4767 / 0 / 370
Goodness-of-fit on F^2	0.949
Final R indices [I>2sigma(I)]	R1 = 0.0801, wR2 = 0.1644
R indices (all data)	R1 = 0.1967, wR2 = 0.2239
Extinction coefficient	0.0005(3)
Largest diff. peak and hole	0.634 and -0.863 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for hilf199.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Pd	-3128(1)	-2375(1)	1831(1)	37(1)
Br	-4793(2)	-2944(1)	2556(1)	54(1)
Cr	-2661(3)	-959(1)	4927(2)	54(1)
P	-3641(4)	-1401(2)	2313(3)	35(1)
C(1)	-780(20)	-681(10)	5285(14)	81(7)
O(1)	462(18)	-538(8)	5515(12)	122(6)
O(2)	-3770(20)	318(7)	4297(14)	125(7)
C(2)	-3370(20)	-169(11)	4509(14)	69(6)
O(3)	-2780(20)	-540(9)	6760(12)	146(8)
C(3)	-2720(30)	-699(12)	6041(16)	98(8)
C(4)	-2020(15)	-1734(7)	4129(9)	31(3)
C(5)	-3339(15)	-1461(6)	3568(9)	31(3)
C(6)	-4537(16)	-1407(7)	3939(10)	36(4)
C(7)	-4490(19)	-1601(8)	4798(11)	50(4)
C(8)	-3185(18)	-1852(8)	5346(11)	51(5)
C(9)	-1999(19)	-1908(8)	5016(11)	50(5)
C(10)	-680(16)	-1852(7)	3808(10)	40(4)
C(11)	123(16)	-1367(7)	3597(10)	41(4)
C(12)	1382(16)	-1479(9)	3307(12)	58(5)
C(13)	1869(19)	-2068(9)	3271(11)	53(5)
C(14)	1093(17)	-2565(9)	3477(10)	46(4)
C(15)	1620(20)	-3192(12)	3444(13)	78(7)
C(16)	880(20)	-3672(9)	3627(14)	64(5)
C(17)	-370(20)	-3598(9)	3922(13)	70(6)
C(18)	-900(18)	-3020(8)	3961(10)	43(4)
C(19)	-196(15)	-2481(7)	3760(9)	37(4)
C(20)	-6531(16)	-1579(8)	1268(10)	43(4)
C(21)	-7978(17)	-1416(9)	871(12)	56(5)
C(22)	-8486(18)	-857(9)	1042(11)	51(5)
C(23)	-7541(18)	-446(9)	1629(12)	54(5)
C(24)	-6106(17)	-596(7)	1981(10)	44(4)
C(25)	-5591(16)	-1196(7)	1845(9)	35(4)
C(26)	-2864(19)	-658(8)	1098(10)	52(5)
C(27)	-2310(20)	-144(10)	781(13)	69(6)
C(28)	-1600(20)	301(9)	1330(15)	68(6)
C(29)	-1536(18)	264(7)	2228(13)	55(5)
C(30)	-2142(17)	-226(8)	2581(12)	51(5)
C(31)	-2779(16)	-706(7)	2013(10)	37(4)
C(32)	-2320(20)	-3207(9)	1277(16)	82(7)
C(34)	-1595(19)	-2138(9)	1095(12)	58(5)
C(33A)	-2090(40)	-2722(19)	840(30)	57(10)
C(33B)	-1330(40)	-2775(19)	1370(30)	64(11)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for hilf199.

	x	y	z	U(eq)
H(6A)	-5356	-1143	3614	43
H(7A)	-5281	-1496	5058	60
H(8A)	-3069	-1932	5994	62
H(9A)	-1055	-2016	5449	60
H(11A)	-170	-962	3647	50
H(12A)	1875	-1150	3141	70
H(13A)	2720	-2139	3109	63
H(15A)	2487	-3259	3294	94
H(16A)	1198	-4070	3557	77
H(17A)	-821	-3940	4088	84
H(18A)	-1757	-2975	4125	52
H(20A)	-6202	-1962	1132	52
H(21A)	-8608	-1692	483	67
H(22A)	-9456	-749	770	62
H(23A)	-7890	-71	1780	64
H(24A)	-5452	-303	2314	53
H(26A)	-3295	-973	696	63
H(27A)	-2443	-108	157	83
H(28A)	-1169	626	1109	82
H(29A)	-1068	579	2620	66
H(30A)	-2117	-230	3193	61

X-Ray data for phosphine 9c.

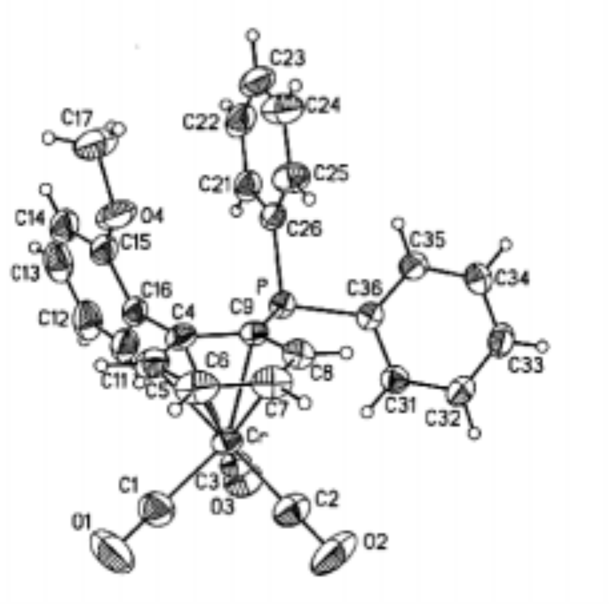
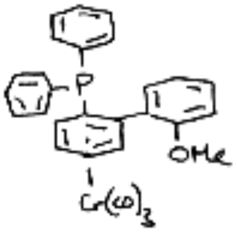


Table 1. Crystal data and structure refinement for hilf799.



Identification code	hilf799
Empirical formula	$C_{28}H_{21}CrO_4P$
Formula weight	504.42
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C 2/c
Unit cell dimensions	a = 31.8398(17) Å alpha = 90° b = 10.5258(5) Å beta = 105.5570(10)° c = 15.0995(7) Å gamma = 90°
Volume, Z	4875.0(4) $Å^3$, 8
Density (calculated)	1.375 Mg/m^3
Absorption coefficient	0.567 mm^{-1}
F(000)	2080
Crystal size	0.14 x 0.33 x 0.38 mm
θ range for data collection	2.05 to 23.26°
Limiting indices	$-34 \le h \le 35$, $-11 \le k \le 10$, $-16 \le l \le 9$
Reflections collected	8189
Independent reflections	3343 (R_{int} = 0.0164)
Completeness to θ = 23.26°	95.2 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3343 / 0 / 392
Goodness-of-fit on F^2	1.328
Final R indices [$I>2\sigma(I)$]	R1 = 0.0294, wR2 = 0.0866
R indices (all data)	R1 = 0.0348, wR2 = 0.0906
Extinction coefficient	0.00003(12)
Largest diff. peak and hole	0.213 and -0.256 $eÅ^{-3}$

Table 2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for hilf799. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Cr	3854(1)	10179(1)	6817(1)	42(1)
P	3610(1)	8361(1)	4678(1)	41(1)
O(1)	4591(1)	11510(2)	8148(2)	115(1)
C(1)	4306(1)	10995(3)	7643(2)	69(1)
O(2)	3284(1)	12420(2)	6810(2)	114(1)
C(2)	3507(1)	11553(2)	6826(2)	66(1)
O(3)	4118(1)	11564(2)	5324(1)	73(1)
C(3)	4023(1)	11004(2)	5904(2)	50(1)
C(4)	4053(1)	8206(2)	6549(1)	44(1)
O(4)	4255(1)	5727(2)	6761(1)	80(1)
C(5)	4101(1)	8357(2)	7495(2)	57(1)
C(6)	3753(1)	8779(2)	7830(2)	63(1)
C(7)	3354(1)	9039(2)	7221(2)	57(1)
C(8)	3296(1)	8886(2)	6268(2)	48(1)
C(9)	3642(1)	8496(2)	5916(1)	39(1)
C(11)	4674(1)	8423(3)	5810(2)	63(1)
C(12)	5005(1)	7915(4)	5492(2)	79(1)
C(13)	5093(1)	6657(4)	5611(2)	89(1)
C(14)	4857(1)	5892(4)	6037(2)	86(1)
C(15)	4515(1)	6392(2)	6347(2)	63(1)
C(16)	4425(1)	7688(2)	6228(2)	49(1)
C(17)	4276(2)	4377(3)	6759(5)	112(2)
C(21)	3778(1)	6033(3)	4001(2)	59(1)
C(22)	3737(1)	4738(3)	3846(2)	77(1)
C(23)	3473(1)	4040(3)	4238(2)	82(1)
C(24)	3246(1)	4617(3)	4767(2)	81(1)
C(25)	3278(1)	5907(2)	4919(2)	64(1)
C(26)	3544(1)	6633(2)	4536(1)	45(1)
C(31)	2975(1)	10246(2)	4222(2)	48(1)
C(32)	2588(1)	10788(2)	3735(2)	56(1)
C(33)	2283(1)	10067(2)	3128(2)	64(1)
C(34)	2362(1)	8813(3)	3014(2)	68(1)
C(35)	2748(1)	8252(2)	3509(2)	56(1)
C(36)	3062(1)	8967(2)	4124(1)	42(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for hilf799.

	x	y	z	U(eq)
H(5)	4377(7)	8160(20)	7898(16)	54(6)
H(6)	3800(7)	8910(20)	8444(17)	62(7)
H(7)	3127(8)	9390(20)	7432(15)	58(7)
H(8)	3030(7)	9107(19)	5828(14)	45(6)
H(11)	4641(8)	9240(30)	5771(17)	62(8)
H(12)	5158(10)	8390(30)	5169(19)	85(10)
H(13)	5310(11)	6320(30)	5430(20)	101(11)
H(14)	4896(9)	5120(30)	6170(20)	73(9)
H(17A)	4255(12)	4180(40)	6190(30)	110(15)
H(17B)	4037(18)	4190(50)	6940(40)	170(30)
H(17C)	4524(12)	4110(30)	7130(20)	108(13)
H(21)	3957(8)	6530(20)	3767(17)	65(8)
H(22)	3883(8)	4410(30)	3494(19)	73(8)
H(23)	3451(10)	3160(30)	4080(20)	106(10)
H(24)	3084(11)	4230(30)	4980(20)	97(13)
H(25)	3124(8)	6300(20)	5293(17)	67(7)
H(31)	3177(6)	10704(19)	4595(14)	38(5)
H(32)	2547(7)	11620(20)	3824(16)	59(7)
H(33)	2034(8)	10400(20)	2787(17)	61(7)
H(34)	2158(8)	8320(20)	2560(17)	69(7)
H(35)	2800(7)	7390(20)	3427(16)	61(7)