Borrowing Hydrogen: A Catalytic Route To C-C bond Formation From Alcohols

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General Experimental Information: Unless stated all experiments were carried out under an atmosphere of argon using standard Schlenk line techniques and anhydrous freeze/thaw degassed solvents. Toluene and d^6-benzene were distilled from sodium and potassium respectively and stored in sealed ampoules. Phosphorane ylides ($Ph_3P{=}CHCO_2R$) were freshly prepared prior to use and used immediately. Although several of these are commercially available, superior results were obtained with freshly prepared ylides. Methyl (triphenylphosphoranylidene)acetate was prepared according to Lugtenburg,[1] benzyl and *tert*-butyl (triphenylphosphoranylidene)acetate were prepared by the method of Aitken.[2] In all cases the ylide was recrystallised from toluene to remove the triphenylphosphine oxide by-product present. All other reagents were purchased from commercial suppliers and used as received. Thin layer chromatography (TLC) was performed using Macherey-Nagel precoated Alugram Sil G/UV_{254nm} plates and the developed plates visualised by staining with *p*-anisaldehyde dip and heating. Column chromatography was performed on Davisil LC 60A silica gel (35-70 micron).

$Ru(IMes)(PPh_3)_2(CO)H_2$ 1. To a solution of $Ru(PPh_3)_3(CO)H_2$ (1.00 g, 1.09 mmol, 1.0 equiv.) in toluene (30 mL) was added IMes (1.00 g, 3.29 mmol, 3.02 equiv.) and the mixture heated to 80 ºC for 2 weeks. $^{31}P\{^1H\}$ NMR spectroscopy at this stage showed signals for **1** and residual $Ru(PPh_3)_3(CO)H_2$. Thermolysis for a further week afforded just **1**. Removal of solvent gave a dark oily residue; addition of ethanol (30 mL) and stirring at room temperature gave a white solid. This was washed with ethanol (3 × 10 mL) and hexane (1 × 10 mL) to afford **1** (0.69 g, 65%). **1:** ^{1}H-NMR (300 MHz, C_6D_6, 25 °C): δ = -8.08 (ddd, J_{HPb} = 81.2, J_{HPa} = 33.6, J_{HHb} = 6.0 Hz, 1H, H_a); -6.36 (ddd, J_{HPb} = 26.8 Hz, J_{HPa} = 23.6 Hz, J_{HHb} = 6.0 Hz, 1H, H_b), 1.82 (s, 6H, *H-8*), 2.20 (s, 6H, *H-1*), 2.26 (s, 6H, *H-5*), 6.25 (br s, 2H, *H-10*), 6.82 (br s, 2H, *H-6*), 6.86 (br s, 2H, *H-3*), 6.93 (m, 18H, PC_6H_5), 7.30-7.42 (m, 12H, PC_6H_5); $^{13}C\{^1H\}$-NMR (75 MHz, C_6D_6, 25 °C): δ = 21.4 (s, CH_3-*1*, *5* and *8*), 122.4 (br s, C-*10*), 127.0 (d, J_{CP} = 8.9 Hz, PC_6H_5), 127.4 (d, J_{CP} = 8.4 Hz, PC_6H_5), 127.9 (s, PC_6H_5), 129.4 (br s, C-*3* or *6*), 134.4 (d, J_{CP} = 6.7 Hz, PC_6H_5), 134.6 (d, J_{CP} = 5.4 Hz, PC_6H_5), 137.7 (br s, C-*2* or *7*), 140.1 (br s, C-*9*), 142.1 (br d, PC_6H_5), 142.2 (br d, PC_6H_5), 205.2 (t, J_{CP} = 8.8 Hz, Ru-*C*O), 197.7 (dd, J_{CPa} = 75.5, J_{CPb} = 6.7 Hz, *C-11*); $^{31}P\{^1H\}$-NMR (121 MHz, C_6D_6, 25 °C): δ = 47.8 (d, P_b, J_{PP} = 14.8 Hz), 59.0 (d, P_a, J_{PP} = 14.8 Hz);

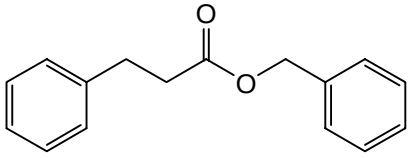
IR (C_6D_6): ν_{max} (cm^{-1}) = 1937 (CO), 1987 (Ru-H), 1872 (Ru-H); CHN analysis: $RuC_{57}H_{49}P_3O$ requires C 72.4 %, H 5.88 %, N 2.93 %, found C 72.56 %, H 5.88 %, N 2.92 %.

General procedure for crossover transfer hydrogenation experiments: A Young's NMR tube was charged with $Ru(IMes)(PPh_3)_2(CO)H_2$ **1** (10 mg, 0.0105 mmol) followed by the alcohol donor and alkene acceptor (see below). The solvent, d^6-benzene (0.75 mL) was added *via* cannula and the tube sealed under argon. The tube was then heated at the required temperature and the reaction progress monitored by ^1H and $^{31}P\{^1H\}$-NMR. **Reagents**: (a) 2 mol% **1**, isopropanol (63 mg, 1.04 mmol, ρ = 0.785 gmL^{-1}, 80 μL, 2.0 equiv.), vinyltrimethylsilane **3** (52 mg, 0.52 mmol, ρ = 0.684 gmL^{-1}, 58 μL, 1.0 equiv.) (b) 5 mol% **1**, (±)-phenethyl alcohol **6** (25 mg, 0.210 mmol, ρ = 1.013 gmL^{-1}, 24.6 μL, 1.0 equiv.), *tert*-butyl cinnamate **5** (42.5 mg, 0.210 mmol, 1.0 equiv.).

Carbene experiments with ruthenium precursors: An oven-dried (150 °C) Radley Carousel tube was charged in a glove box with the required ruthenium precursor (0.025 mmol, 5 mol%), benzyl (triphenylphosphoranylidene)acetate (227 mg, 0.55 mmol, 1.1 equiv.) and IMes [as required] (7.6 mg, 0.025 mmol, 5 mol%). The tube was sealed and then benzyl alcohol **9** (54 mg, 0.5 mmol, ρ = 1.045 gmL^{-1}, 52 mL, 1.0 equiv.), toluene (1.5 mL) and vinyltrimethylsilane **3** (2.5 mg, 0.025 mmol, ρ = 0.684 gmL^{-1}, 5 mol%) added *via* syringe. The tubes were placed in a Carousel synthesiser and heated at 80 °C for 24 hours before cooling to room temperature. Following quenching with wet diethyl ether (5 mL) the reaction mixture was concentrated *in vacuo* and then analysed by NMR.

General procedure for the indirect Wittig reaction: A flame dried Schlenk flask was charged with $Ru(IMes)(PPh_3)_2(CO)H_2$ **1** (10 mg, 0.0105 mmol, 0.01 equiv.), the required phosphorane ylide (1.16 mmol, 1.1 equiv.) and the alcohol substrate (1.05 mmol, 1.0 equiv.). Toluene (1.05 mL) and vinyltrimethylsilane **3** (1.1 mg, 0.0021 mmol, ρ = 0.684 gmL^{-1}, 3 μL, 0.02 equiv) were then added *via* syringe and the Schlenk tube sealed. The reaction was then stirred gently and heated at 80 °C for the required time. Upon completion the reaction was cooled to room temperature and the reaction quenched by the addition of wet diethyl ether (5 mL). The mixture was concentrated *in vacuo* and the crude reaction mixture pre-adsorbed upon silica. Purification *via* column chromatography on silica using a petroleum ether (b.p 40-60 °C)/diethyl ether eluent afforded the desired indirect Wittig adduct.

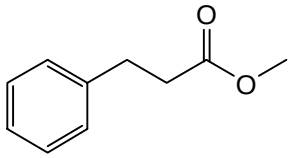
Benzyl dihydrocinnamate 11.[3]



According to the general procedure using benzyl alcohol **9** (114 mg, 1.05 mmol, ρ = 1.045 gmL^{-1}, 109 μL, 1.0 equiv.), benzyl (triphenylphosphoranylidene)acetate **10** (475 mg, 1.16 mmol, 1.1 equiv.), 24 hours reaction time and 40:1 petroleum ether (b.p 40-60 °C)/diethyl ether as the eluent, the title compound was obtained as a colourless liquid (200 mg, 80%). **11**: R_f = 0.64 (7:3 petroleum ether (b.p.

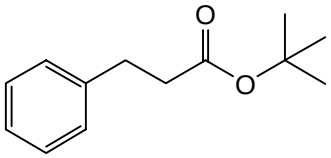
40-60 °C/diethyl ether); ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.67 (2H, t, *J* = 7.4 Hz), 2.96 (2H, t, *J* = 7.4 Hz), 5.10 (2H, s), 7.16-7.21 (3H, m), 7.24-7.37 (7H, m); ^{13}C-NMR (100 MHz, $CDCl_3$, 25 °C): δ = 31.4, 36.3, 66.7, 126.5, 128.5, 128.5 , 128.7, 128.8, 136.1, 140.6, 172.8; IR (liquid film): ν_{max} (cm^{-1}) = 3061, 3026, 2948, 1735, 1603, 1495, 1453, 1159, 1077, 1027, 1001, 985, 748, 695; MS (FAB+): *m/z* 240 [$M^{\cdot+}$]; HRMS (FAB+): $C_{16}H_{16}O_2$ requires 240.1150 found 240.1149.

Methyl dihydrocinnamate 12.[4]



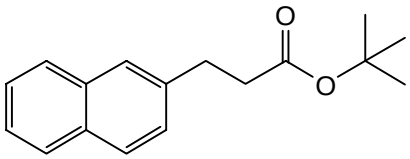
According to the general procedure using benzyl alcohol **9** (114 mg, 1.05 mmol, ρ = 1.045 gmL^{-1}, 109 μL, 1.0 equiv.), methyl (triphenylphosphoranylidene)acetate (388 mg, 1.16 mmol, 1.1 equiv.), 24 hours reaction time and 40:1 petroleum ether (b.p 40-60 °C)/diethyl ether as the eluent, the title compound was obtained as a colourless liquid (134 mg , 78%). **12**: R_f = 0.67 (7:3 petroleum ether (b.p. 40-60 °C)/diethyl ether; ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.63 (2H, t, *J* = 8.2 Hz), 2.95 (2H, t, *J* = 8.2 Hz), 3.66 (3H, s), 7.18-7.22 (3H, m), 7.26-7.30 (2H, m); ^{13}C-NMR (100 MHz, $CDCl_3$, 25 °C): δ = 31.4, 36.1, 52.0, 126.5, 128.4, 128.7, 140.7, 173.5; IR (liquid film): ν_{max} (cm^{-1}) = 3061, 3025, 2951, 1734, 1603, 1496, 1452, 1437, 1161, 1078, 1028, 985, 749, 694; MS (EI+, 70 eV): *m/z* (%) 164 (39) [$M^{\cdot+}$], 133 (12), 105 (36), 104 (100), 91 (62), 77 (13); HRMS (EI+, 70 eV): $C_{10}H_{12}O_2$ requires 164.0837 found 164.0838.

***tert*-Butyl dihydrocinnamate 13**.[4]



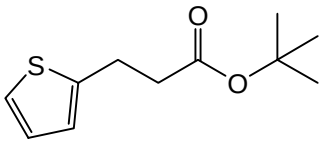
According to the general procedure using benzyl alcohol **9** (114 mg, 1.05 mmol, ρ = 1.045 gmL^{-1}, 109 μL, 1.0 equiv.), *tert*-butyl (triphenylphosphoranylidene)acetate (437 mg, 1.16 mmol, 1.1 equiv.), 24 hours reaction time and 50:1 petroleum ether (b.p 40-60 °C)/diethyl ether as the eluent, the title compound was obtained as a colourless liquid (151 mg, 70%). **13**: R_f = 0.70 (7:3 petroleum ether (b.p. 40-60 °C)/diethyl ether); ^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.34 (9H, s), 2.46 (2H, t, *J* = 7.1 Hz), 2.83 (2H, t, *J* = 7.1 Hz), 7.08-7.12 (3H, m), 7.19-7.23 (2H, m); ^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C): δ = 27.0, 30.1, 36.1, 79.3, 125.1, 127.3, 127.4, 139.8, 171.2; IR (liquid film): ν_{max} (cm^{-1}) = 3086, 3063, 2976, 2930, 1729, 1604, 1496, 1453, 1146, 1078, 846, 743, 698; MS (EI+, 70 eV): *m/z* (%) 206 (1.5) [$M^{\cdot+}$], 150 (82), 133 (37), 105 (49), 104 (52), 91 (60), 57 (100); HRMS (EI+, 70 eV): $C_{13}H_{18}O_2$ requires 206.1305 found 206.1306.

***tert*-Butyl 3-(2-naphthyl)propanoate 15**.



According to the general procedure using naphthalene-2-methanol **14** (166 mg, 1.05 mmol, 1.0 equiv.), *tert*-butyl (triphenylphosphoranylidene)acetate (437 mg, 1.16 mmol, 1.1 equiv.), 24 hours reaction time and 40:1 petroleum ether (b.p 40-60 °C)/diethyl ether as the eluent, the title compound was obtained as a white powder (191 mg, 71%). **15**: m.p. 39-41 °C; R_f = 0.54 (7:3 petroleum ether (b.p. 40-60 °C)/diethyl ether); ^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.35 (9H, s), 2.56 (2H, t, *J* = 7.4 Hz), 3.01 (2H, t, *J* = 7.4 Hz), 7.28 (1H, d, *J* = 8.5 Hz), 7.35-7.41 (2H, m), 7.57 (1H, s), 7.71 (3H, m); ^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C): δ = 28.2, 31.4, 37.2, 80.6, 125.4, 126.1, 127.4, 126.6, 127.2, 127.6, 127.7, 128.1, 132.2, 138.5, 172.4; IR (KBr): ν_{max} (cm^{-1}) = 3051, 2971, 2976, 2931, 2872, 1720, 1506, 1597, 1506, 1370, 1299, 1260, 1154, 1098, 1018, 863, 849, 819, 747; MS (EI+, 70 eV): *m/z* (%) 256 (11) [$M^{\cdot+}$], 220 (23), 205 (100), 200 (47), 183 (12), 141 (61), 57 (87); HRMS (EI+, 70 eV): $C_{17}H_{20}O_2$ requires 256.1463 found 256.1456.

***tert*-Butyl 3-(2-thienyl)propanoate 17**.[5]



According to the general procedure using thiophene-2-methanol **16** (120 mg, 1.05 mmol, ρ = 1.205 gmL^{-1}, 99 μL, 1.0 equiv.), *tert*-butyl (triphenylphosphoranylidene)acetate (437 mg, 1.16 mmol, 1.1 equiv.), 48 hours reaction time and 40:1 petroleum ether (b.p 40-60 °C)/diethyl ether as the eluent, the title compound was obtained as a colourless liquid (187 mg, 84%). **17**: R_f = 0.66 (7:3 petroleum ether (b.p. 40-60 °C)/diethyl ether); ^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.45 (9H, s), 2.69 (2H, t, *J* = 7.3 Hz), 3.13 (2H, t, *J* = 7.3 Hz), 6.83 (1H, dd, *J* = 1.1, 3.4 Hz), 6.92 (1H, dd, *J* = 3.4, 5.1 Hz), 7.13 (dd, *J* =1.1, 5.0 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C): δ = 24.3, 27.0, 36.3, 79.6, 122.3, 123.5, 125.7, 142.4, 170.7; IR (liquid film): ν_{max} (cm^{-1}) = 3071, 2977, 2930, 1731, 1478, 1456, 1440, 1392, 1367, 1257, 1153, 1040, 848, 694; MS (EI+, 70 eV): *m/z* (%) 212 (7) [$M^{\cdot+}$], 156 (30), 139 (17), 110 (18), 97 (87), 57 (100); HRMS (EI+, 70 eV): $C_{11}H_{16}O_2S$ requires 212.0871 found 212.0870.

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