Supplementary material

Synthesis and spectroscopic data for $Ru(BO_2C_6H_4)Cl(CO)(PCy_3)_2$:

The complex was prepared according to a procedure analogous to that described for $Ru(BO_2C_6H_4)Cl(CO)(PPh_3)_2$ see ref. 12. $RuHCl(CO)(PCy_3)_2$ (0.125 g, 0.165 mmol) was partially dissolved in benzene (10 mL) and then catecholborane (0.053 mL, 0.50 mmol) was added. The mixture was heated under reflux for 30 min., during which time all suspended materials dissolved and a yellow solution resulted. Concentration of the solution in vacuum followed by slow addition of hexane afforded $Ru(BO_2C_6H_4)Cl(CO)PCy_3)_2$. Recrystallization from benzene/hexane afforded pale yellow microcrystals of pure $Ru(BO_2C_6H_4)Cl(CO)(PCy_3)_2$ (0.112g).

^{1}H NMR (300.1 MHz, C_6D_6, ppm, coupling constants in Hz), 0.90-2.60 (m, 66H, PCy_3), 6.87-6.87 (m, 2H, Ph), 7.22-7.27 (m, 2H, Ph); ^{13}C NMR (75.5 MHz, C_6D_6): 26.9, 28.0-28.2, 30.1, 30.8, 35.2-35.5 (PCy_3), 111.1, 121.5, 150.2 (Ph); ^{31}P NMR (121.5 MHz, C_6D_6) 127.4MHz: 38.2 (PCy_3)

MS *m/z* (rel. int.): 246 (M^+, 3%), 232 (19), 231 (100), 230 (9), 203 (9), 169 (21), 161 (11), 151 (6), 143 (11), 135 (7); 121(7), 105(7), 53(6).

Synthesis and spectroscopic data for E-$PhCH=CHBO_2C_2H_4$

An oven dried Schlenk flask equipped with a condenser and a magnetic stirring bar was charged under argon with benzene (10 mL), vinyldioxaborinane (1 mL, 10.22 mmol) and styrene (5.3 mL, 46.2 mmol). The reaction mixture was heated to 80°C, ruthenium hydride complex $RuHCl(CO)(PCy_3)_2$ (0.074 g, 0.10 mmol) was added and the reaction was carried out for 3 h. The solvent was removed under atmospheric pressure. The product was isolated by vacuum distillation with the use of an efficient column. The fraction boiling at 79-82°C/1mmHg was collected (1.62g, 91%).

^{1}H NMR (300.1 MHz, C_6D_6, ppm, coupling constants in Hz), 3.70 (s, 4H, OCH_2), 6.42 (d, J=18.4, 1H, =CH), 7.0-7.10 (m, 3H, Ph), 7.30-7.35 (m 2H, Ph), 7.71 (d, J=18.4, =CH);

^{13}C NMR (75.5 MHz, C_6D_6): 65.6 (OCH_2), 115.9 (broad, =CHB), 127.2, 128.5, 128.8, 137.5 (Ph), 149.4 (=CHPh);

MS *m/z* (rel. int.): 174.0 (M^+, 100), 173.0 (22), 129.1 (45), 115.1 (31), 102.1 (25), 91.1 (13), 77.1 (33)

HRMS: calcd for $C_{10}H_{11}BO_2$: 174.08488; observed: 174.08488

Synthesis and spectroscopic data for E-PhCH=CHBO$_2$C$_3$H$_6$

An oven dried Schlenk flask equipped with a condenser and a magnetic stirring bar was charged under argon with benzene (10 mL), vinyldioxaborinane (1 mL, 8.93 mmol) and styrene (5.3 mL, 46.2 mmol). The reaction mixture was heated to 80°C, ruthenium hydride complex RuHCl(CO)(PCy$_3$)$_2$ (0.074 g, 0.10 mmol) was added and the reaction was carried out for 3 h. The solvent was removed under atmospheric pressure. The product was isolated by vacuum distillation with the use of an efficient column. Fraction boiling at 83-86°C/1mmHg was collected (1.35g, 80%).

^{1}H NMR (300.1 MHz, C$_6$D$_6$, ppm, coupling constants in Hz), 1.29-1.37 (m, 2H, CH$_2$); 3.63 (t, J=5.8, 4H, OCH$_2$); 6.38 (d, J=18.4, 1H, =CH); 7-7.12 (m, 3H, Ph); 7.38-7.7.41 (m, 2H, Ph); 7.61 (d, J=18.4, =CH);

^{13}C NMR (75.5 MHz, C$_6$D$_6$): 27.7 (CH$_2$), 61.7 (OCH$_2$), 122.4 (broad, =CHB), 127.1, 128.5, 128.8, 138.4, 150.4 (Ph), 147 (=CHPh);

MS *m/z* (rel. int.): 189 (M$^+$, 100), 188 (21), 187 (14), 156 (26), 145 (41), 131 (46), 117 (18), 102 (14).