Experimental procedure: **1** was prepared by the method of Fox *et al*.[10] and 1,7-Ph_2-1,7-*closo*-$C_2B_{10}H_{10}$ by the method of Coult *et al*.[a]

Reduction of **1** (same procedure for reduction of 1,7-Ph_2-1,7-*closo*-$C_2B_{10}H_{10}$): (a) in liquid NH_3; the carborane (0.444 g, 1.5 mmol) was treated with Na metal (0.242 g, 10.5 mmol) in liquid ammonia at −78°C for 2 hours. The reaction mixture was warmed to RT and the residual solid extracted into oxygen-free THF (30 mL) giving a deep red solution. (b) in THF; the carborane (0.444 g, 1.5 mmol) and Na metal (0.460 g, 20 mmol) were stirred overnight in oxygen-free THF (30 mL), giving a deep-red solution.

Synthesis of **2**: The deep-red solution above was filtered under nitrogen into a Schlenk tube containing [Ru(*p*-cymene)Cl_2]$_2$ (0.459 g, 0.75 mmol) and oxygen-free THF (20 mL), frozen in liquid nitrogen. After refreezing the contents were allowed to warm to RT overnight with stirring. The resulting suspension was filtered through Celite and, following initial column chromatography on silica, applied to a preparative TLC plate. Elution with DCM:petroleum ether (40:60) 1:1 gave several bands, of which the major canary-yellow band (R_f = 0.40) was collected and identified[12] as 1,6-Ph_2-4-*p*-cymene-4,1,6-*closo*-$RuC_2B_{10}H_{10}$ (*ca*. 8% not optimised).

Synthesis of **3**: Similarly, reaction of the reduced carborane (from 0.888 g, 3.0 mmol of **1**) with NaCp (9 mmol) and $CoCl_2$ (1.443 g, 11.1 mmol) in THF at 0°C afforded **3** (R_f = 0.47) and a trace of **4** (R_f = 0.56) in *ca*. 3% yield, not optimised, following work-up involving TLC. For **3**: IR (DCM throughout): ν_{max} 2548 cm^{-1} (B-H). ^1H NMR (200 or 400 MHz, $CDCl_3$, 298 K throughout): δ 7.88-7.78 (m, 4H, Ph), 7.32-7.22 (m, 6H, Ph), 5.01 (s, 5H, Cp). $^{11}B\{^1H\}$ NMR (128 MHz throughout): δ 15.1 (1B), 2.8 (2B), -2.9 (3B), -5.5 (3B), -12.9 (1B). MS: *m/z* envelope centred on 418 (M^+). For **4**: IR: ν_{max} 2540 cm^{-1} (B-H). ^1H NMR: δ 7.70-7.60 (m, 2H, Ph), 7.53-7.47 (m, 2H, Ph), 7.30-7.26 (m, 3H, Ph), 7.23-7.15 (m, 3H, Ph), 5.20 (s, 5H, Cp). $^{11}B\{^1H\}$ NMR: δ 21.6 (1B), 7.9 (1B), 3.9 (2B), -1.3 (3B), -4.1 (2B), -13.0 (2B). MS: *m/z* envelope centred on 418 (M^+).

Isomerisation of **3**: (a) at 65°C; **3** (0.055 g) was dissolved in 20 mL THF and heated to reflux for 1 hour. Following removal of solvent analysis by TLC as above revealed the product to be **4** in effectively quantitative yield. (b) at 110°C; **3** (or **4**) (0.050 g) was dissolved in 30 mL toluene and heated to reflux overnight. Following removal of solvent analysis by TLC as above revealed **5** in effectively quantitative yield. For **5**: IR: ν_{max} 2542 cm^{-1} (B-H). ^1H NMR: δ 7.63-7.57 (m, 2H, Ph), 7.46-7.36 (m, 2H, Ph), 7.30-7.23 (m, 3H, Ph), 7.16-7.10 (m, 3H, Ph), 5.25 (s, 5H, Cp). $^{11}B\{^1H\}$ NMR: δ 7.7 (2B), 5.4 (1B), -1.6 (1B), -5.0 (2B), -7.4 (2B), -13.8 (2B). MS: *m/z* envelope centred on 420 (M^+), 196 (M – CoCp).

Isomerisation of **2**: **2** (0.368 g, 0.69 mmol) was dissolved in 50 mL of oxygen-free tetra(ethylene glycol) dimethyl ether (dried by vacuum distillation over Na metal) and heated to 180°C for 6 hours. After removal of solvent the yellow oily residue was washed with 10 mL petroleum ether and separated into yellow **6** (4,1,8 isomer, 0.180 g, 0.338 mmol) and yellow **7** (4,1,12 isomer, 0.080 g, 0.151 mmol) by a combination of solubility (**6** much less soluble) and TLC (DCM:petroleum ether 1:1; R_f = 0.44, **6**; R_f = 0.51, **7**). For **6**: IR: ν_{max} 2531 cm^{-1} (B-H). ^1H NMR: δ 7.65-7.57 (m, 4H, Ph), 7.32-7.17 (m, 6H, Ph), 5.56-5.35 (m, 4H, cym), 2.94 (app. sept., 1H, C*H*Me_2), 2.31 (s, 3H, Me), 1.28-1.21 (2×overlapping d, 6H, CH*Me*$_2$). $^{11}B\{^1H\}$ NMR: δ 16.3 (1B), 5.3 (1B), -4.3 (4B), -7.0 (1B), -9.8 (1B), -20.4 (2B). MS: *m/z* envelope centred on 531 (M^+). For **7**: IR: ν_{max} 2532 cm^{-1} (B-H). ^1H NMR: δ 7.59-7.42 (m, 4H, Ph), 7.27-7.08 (m, 6H, Ph), 5.50-5.22 (m, 4H, cym), 2.85 (app. sept., 1H, C*H*Me_2), 2.25 (s, 3H, Me), 1.23-1.15 (2×overlapping d, 6H, CH*Me*$_2$). $^{11}B\{^1H\}$ NMR: δ 3.7 (2B), 2.7 (1B), -8.3 (2B), -9.5 (1B), -19.8 (2B), -21.2 (2B). MS: *m/z* envelope centred on 531 (M^+).

[a]R. Coult, M. A. Fox, W. R. Gill, P. L Herbertson, J. A. H. MacBride and K. Wade, *J. Organomet. Chem.*, 1993, **462**, 19.