Supporting Information

for

Backbone tuning in indenylidene–ruthenium complexes bearing an unsaturated *N*-heterocyclic carbene

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General considerations: All reagents were used as received. Dichloromethane and toluene were dispensed from a solvent purification system from Innovative Technology. Catalyst syntheses were performed in a MBraun glovebox containing dry argon and less than 1 ppm oxygen. ¹H, ³¹P, and ¹³C NMR spectra were recorded on a Bruker Avance 300 or a Bruker Avance II 400 Ultrashield NMR spectrometers. Elemental analyses were performed by the University of St Andrews Analytical Service. IR measurements were performed in a Perkin Elmer Spectrum GX IR spectrometer. Complex **6b** [1] and substrates and products **7-9** [2], **10** [3], **11** [4], **12** [5], **13** [2], **14** [6] **15–16** [2] have been previously described in the literature.

Synthesis of [RhCl(CO)₂(IMesMe)] (5a)

In the glovebox, in a vial with a solution of $[Rh(CO)_2CI]_2$ (50 mg, 0.127 mmol) in 5 mL of THF, a solution of free IMesMe (85 mg, 0.255 mmol) was added dropwise, the reaction mixture was stirred for 4 h, taken out of the glovebox and the solvents removed under vacuum. The remaining solid was washed with pentane (3 x 10 mL) and dried under vacuum to afford **4a** as a pale yellow solid (96.3 mg, 0.183 mmol, 72%). Suitable crystals for single X-ray diffraction were grown by vapour diffusion of pentane into a concentrated solution of **4a** in DCM.

¹H NMR (CD₂Cl₂, 300 MHz): δ = 7.05 (s, 4H, H^{Ar}), 2.39 (s, 6H, *p*-CH₃^{Mes}), 2.10–2.18 (m, 12H, *o*-CH₃^{Mes}), 1.86 ppm (s, 6H). ¹³C NMR (CD₂Cl₂, 75 MHz) δ ppm 185.83 (d, *J* = 53.99 Hz, 1C) 183.53 (d, *J* = 74.34 Hz, 1C) 173.33 (d, *J* = 44.60 Hz, 1C) 139.58 (s, 2C) 136.17 (s, 4C) 134.01 (s, 2C) 129.55 (s, 4CH) 127.55 (s, 2C) 21.31 (s, 2CH₃) 18.50 (s, 4CH₃) 9.22 (s, 5CH₃). IR (v_{CO}) in CH₂Cl₂: 2076.98, 1992.54 cm⁻¹. Anal. calcd for C₂₅H₃₀ClN₂O₂Rh (MW 528.88): C, 56.77; H, 5.72; N, 5.30. Found: C, 56.35; H, 5.27; N, 5.15.





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Synthesis of [RhCl(CO)₂(IMes)] (5b)

In the glovebox, in a vial with a solution of $[Rh(CO)_2CI]_2$ (50 mg, 0.127 mmol) in 5mL of THF, a solution of free IMes (78.0 mg, 0.255 mmol) was added dropwise, the reaction mixture was stirred for 4h, take out of the glovebox and the solvents removed under vacuum. The remaining solid was washed with pentane (3 x 10mL) and dried under vacuum to afford **4b** as a pale yellow solid. Suitable crystals for single X-ray diffraction were grown by vapour diffusion of pentane into a concentrated solution of **4b** in THF (101.8 mg, 0.203 mmol, 80%). ¹H NMR (CD₂Cl₂, 400 MHz): δ = 7.17 (s, 2H, H^{Ar}), 7.07 (s, 4H), 2.41 (s, 6H, *p*-CH₃^{Mes}), 2.22 ppm (s, 12H, *o*-CH₃^{Mes}). ¹³C NMR (101 MHz, CD₂Cl₂-*d*₂): δ ppm 185.61 (d, *J* = 57.22 Hz, 1 C) 183.12 (d, *J* = 80.70 Hz, 1C) 177.17 (d, *J* = 46.95 Hz, 1C) 139.77 (s, 2C) 135.38–136.06 (m, 6C) 129.49 (s, 4CH) 124.34 (s, 2CH) 21.29 (s, 2CH₃) 18.59 (s, 4CH₃) IR (v_{CO}) in CH₂Cl₂: 2079.13, 1996.02 cm⁻¹. Anal. calcd for C₂₃H₂₄ClN₂O₂Rh (MW 498.81): C, 55.38; H, 4.85; N, 5.62. Found: C, 55.65; H, 4.65; N, 5.63.





Synthesis of [RhCl(CO)₂(IMesBr)] (5c)

In the glovebox, in a vial with free IMes (78.0 mg, 0.255 mmol) and 2 mL of THF, a solution of carbontetrabromide (169.0 mg, 0.510 mmol) in 2 mL of THF was added dropwise and stirred for 2 h. This mixture was then added to a solution of [Rh(CO)₂Cl]₂ (50 mg, 0.127 mmol) in 5 mL of THF, and stirred for 4 h, take out of the glovebox and the solvents removed under vacuum. The remaining solid was washed with pentane (3 x 10 mL) and dried under vacuum to afford **4c** as a yellow solid. Suitable crystals for single X-ray diffraction were grown by vapour diffusion of pentane into a concentrated solution of **4c** in DCM (118.4 mg, 0.18 mmol, 71%). ¹H NMR (400 MHz, CD₂Cl₂): δ ppm 7.00 (s, 4H, H^{Ar}) 2.32 (s, 6H, *p*-CH₃^{Mes}) 2.09 (s, 12H, *o*-CH₃^{Mes}). ¹³C NMR (101 MHz, CD₂Cl₂): δ ppm 185.14 (d, *J* = 58.69 Hz, 1C) 183.01 (d, *J* = 79.23 Hz, 1C) 180.77 (d, *J* = 46.22 Hz, 1C) 141.04 (s, 2C) 136.48 (s, 4C) 134.13 (s, 2C) 129. 87 (m, 4CH) 110.59 (s, 2C) 21.55 (s, 2CH₃) 18.75 (m, 4CH₃). IR (v_{CO}) in CH₂Cl₂: 2082.88, 1999.83 cm⁻¹. Anal. calcd for C₂₃H₂₂Br₂ClN₂O₂Rh (MW 656.60): C, 42.07; H, 3.38; N, 4.27. Found: C, 41.62; H, 3.42; N, 4.06.





Synthesis of [RhCl(CO)₂(IMesCl)] (5d)

In the glovebox, in a vial with free IMes (78.0 mg, 0.255 mmol) and 2 mL of THF, a solution of carbontetrachloride (78.0 mg, 0.510 mmol) in 2 mL of THF was added dropwise and stirred for 2 h. This mixture was then added to a solution of $[Rh(CO)_2CI]_2$ (50 mg, 0.127 mmol) in 5 mL of THF, and stirred for 4 h, take out of the glovebox and the solvents removed under vacuum. The remaining solid was washed with pentane (3 x 10 mL) and dried under vacuum to afford **4c** as a yellow solid (108.6 mg, 0.19 mmol, 75%). Suitable crystals for single X-ray diffraction were grown by vapour diffusion of pentane into a concentrated solution of **4d** in DCM. ¹H NMR (400 MHz, CD₂Cl₂): δ ppm 7.08 (br s, 4H, H^{Ar}) 2.40 (br s., 6H, *p*-CH₃^{Mes}) 2.19 (br s, 12H, *o*-CH₃^{Mes}) ¹³C NMR (101 MHz, CD₂Cl₂): δ ppm 185.08 (d, *J* = 55.75 Hz, 1C) 182.78 (d, *J* = 73.36 Hz, 1C) 178.75 (d, *J* = 46.22 Hz, 1C) 141.01 (s, 4C) 136.42 (br s, 4C) 132.58 (s, 2C) 129.77 (s, 4CH) 119.55 (br s, 2C) 21.39 (s, 2CH₃) 18.54 (s, 4CH₃) IR (v_{CO}) in CH₂Cl₂: 2084.73, 2000.23 cm⁻¹. Anal. calcd for C₂₃H₂₂Cl₃N₂O₂Rh (MW 567.70): C, 48.66; H, 3.91; N, 4.93. Found: C, 48.32; H, 3.86; N, 4.28





Synthesis of [RuCl₂(IMesMe)(PCy₃)(Ind)] (6a)

In the glovebox, $[RuCl_2(PCy_3)_2(Ind)]$ (461.5 mg, 0.5 mmol) and free IMesMe (166.3 mg, 0.5 mmol) were weighted, then hexane (30 mL) was added, the reaction mixture was heated at 60 °C for 3 h outside the glovebox. After solvent evaporation, the remaining solid was purified by column chromatography on silica gel (Hexane:Et₂O, 9:1), affording **5a** as a red solid (253.1 mg, 0.26 mmol, 52%).

¹H NMR (CD₂Cl₂, 400 MHz): δ ppm 8.48 (d, *J* = 7.34 Hz, 1H) 7.62–7.68 (m, 2 H) 7.43 (d, *J* = 7.52 Hz, 1 H) 7.29–7.37 (m, 2H) 7.14–7.21 (m, 2H) 7.10 (d, *J* = 7.52 Hz, 1H) 7.01 (s, 2H) 6.39 (s, 1H) 5.94 (s, 1H) 2.30 (d, *J* = 2.56 Hz, 9H) 1.85 (s, 3H) 1.78 (s, 3H) 1.68 (s, 3H) 1.64 (s, 3H) 1.51 (s, 5H) 1.31–1.48 (m, 13H) 1.15–1.24 (m, 3H) 0.84–1.08 (m, 17H) 0.74–0.83 (m, 5H). ³¹P NMR (CD₂Cl₂, 121 MHz) δ ppm 27.07 (s). ¹³C NMR (CD₂Cl₂, 101 MHz): δ = 291.4 (d, *J* = 8.3), 181.5 (d, *J* = 79.0), 145.3, 141.3, 139.4, 139.1, 138.9, 138.3, 137.8, 137.6, 136.7, 136.5, 136.2, 135.3, 134.2, 129.9, 129.3, 129.1, 128.9, 128.6, 128.3, 128.2, 127.9, 127.7, 127.1, 126.5, 116.2, 33.4, 33.2, 29.8, 29.7, 28.3, 28.2, 28.2, 28.1, 27.0, 26.6, 21.4, 21.2, 20.2, 20.1, 18.8, 18.7, 9.6, 9.0 ppm. Anal. calcd for C₅₆H₇₁Cl₂N₂PRu (MW 975.13): C, 68.98; H, 7.34; N, 2. 87. Found: C, 69.47; H, 7.47; N, 2.68





Synthesis of [RuCl₂(IMesBr)(PCy₃)(Ind)] (6c)

To a solution of IMesBF₄ (800 mg, 2 mmol) in THF (25 mL), sodium hydride (100 mg, 4 mmol) and potassium *tert*-butoxide (1 spatula) were added, the suspension was stirred overnight, and filtered under argon to remove the excess of NaH. To the filtrate, CBr₄ (1.34 g, 4 mmol) was added, after stirring for 1 h and removal of the solvents to afford a black solid. [RuCl₂(PCy₃)₂(Ind)] (1.23 g, 1.5 mmol) and hexane (25 mL) were added, the reaction mixture was heated at 70 °C for 3 h, filtration through silica gel with DCM as a solvent and recrystallization with Et₂O afforded the **5c** as a dark red solid (900 mg, 0. 81 mmol, 54%). ¹H NMR (CD₂Cl₂, 300 MHz): δ = 8.53 (d, *J* = 7.3 Hz, 1H), 7.65–7.87 (m, 2H), 7.50–7.65 (m, 2H), 7.38–7.50 (m, 3H), 6.93–7.38 (m, 10H), 6.51 (s, 1H), 6.07 (s, 1H), 2.33–2.55 (m, 11H), 2.09–2.26 (m, 4H), 2.00 (s, 3H), 1.88 (s, 3H), 1.82 (s, 3H), 1.36–1.73 (m, 19H), 1.26 (s, 2H), 0.89–1.21 ppm (m, 18H). ³¹P NMR (CD₂Cl₂, 121 MHz): δ ppm 27.28 (s). ¹³C NMR (75 MHz, CD₂Cl₂): δ = 279.1, 188.8, 145.1, 140.1, 139.6, 138.4, 138.2, 138.0, 136.0, 135.7, 128.9, 128.3, 127.9, 127.6, 126.9, 126.5, 125.4, 115.3, 109.2, 32.4, 32.2, 28.9, 28.6, 28.6, 27.1, 27.0, 26.9, 25.5, 20.3, 20.2, 19.2, 19.1, 17.7, 17.6 ppm. Anal. calcd for C₅₄H₆₅Br₂Cl₂N₂PRu (MW 1104. 87): C, 58.70; H, 5.93; N, 2. 54. Found: C, 58.50; H, 5.83. 10; N, 2.38.





Synthesis of [RuCl₂(IMesCl)(PCy₃)(Ind)] (6d)

To a solution of IMesBF₄ (3.26 g, 8.3 mmol) in THF (50 mL), sodium hydride (3.984 g, 16.6 mmol), and potassium tert-butoxide (1 spatula) were added, the suspension was stirred overnight, and filtered under argon to remove the excess of NaH. To the filtrate, CCl₄ (1.6 mL g, 16.6 mmol) was added, after stirring for 1 h and removal of the solvents to afford a black solid. [RuCl₂(PCy₃)₂(Ind)] (1.23 g, 1.5 mmol) and toluene (50 mL) were added, the reaction mixture was heated at 70 °C for 3 h, filtration through silica gel with DCM as a solvent and recrystallization with hexane afforded the **5c** as a dark red solid (4.99 g, 4.9 mmol, 79%). ¹H NMR (CD₂Cl₂, 300MHz): δ = 8.52 (dd, J = 7.4, 0.9 Hz, 1H), 7.68–7.79 (m, 3H), 7.49–7.58 (m, 2H), 7.38–7.46 (m, 3H), 7.23–7.30 (m, 3H), 7.16–7.23 (m, 1H), 7.13 (s, 2H), 7.05–7.11 (m, 2H), 6.51 (s, 1H), 6.08 (s, 1H), 2.34–2.48 (m, 12H), 2.08–2.29 (m, 4H), 2.01 (s, 4H), 1.88 (s, 4H), 1.84 (s, 4H), 1.38–1.71 (m, 20H), 0.92–1.21 (m, 20H), 0.76–0.90 ppm (m, 4 H). ³¹P NMR (CD₂Cl₂, 121 MHz): δ = 26.55 ppm (s). ¹³C NMR (CD₂Cl₂, 75 MHz): δ = 296.1 (d, J = 9.36 Hz) 188.6 (d, J = 82.19 Hz), 145.3, 141.4, 141.0, 139.8, 139.6, 139.4, 138.7, 137.8, 137.4, 137.3, 137.1, 134.0, 132.8, 130.2, 129.6, 129.5, 129.3, 128.9, 128.3, 127.9, 126.8, 120.3, 119.7, 116.7, 33.7, 33.5, 30.0, 28.4, 28.3, 28.2, 26.8, 21.7, 21.5, 20.3, 18.9, 18.8 ppm. Anal. calcd for C₅₆H₆₅Cl₄N₂PRu (MW 975.13): C, 63.84; H, 6.45; N, 2. 76. Found: C, 63.62; H, 6.45; N, 2.76.





General procedure for RCM reactions: A Schlenk flask under nitrogen was charged with the substrate (0.5 mmol) and dry dichloromethane (5 mL, c = 0.1 M), then the catalyst (5 x 10^{-3} mmol) was added. The reaction mixture was magnetically stirred at the desired temperature and the progress of the reaction was monitored by TLC. After completion of the reaction, the volatiles were removed under vacuum and the crude reaction mixture was analyzed by ¹H NMR spectroscopy. The crude residue was purified by flash column chromatography (pentane:ether 9:1) to yield the pure product.

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