

SUPPLEMENTARY INFORMATION

Ruthenium Induced C-N Bond Activation of an N-Heterocyclic Carbene: Isolation of C- and N-Bound Tautomers

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General Comments. All manipulations were carried out using standard Schlenk, high vacuum and glovebox techniques. Solvents were purified using an MBraun SPS solvent system (THF, CH₂Cl₂, hexane) or by drying over calcium hydride (CHCl₃). Deuterated solvents (Aldrich) were vacuum transferred from potassium (C₆D₆, THF-*d*₈) or calcium hydride (CDCl₃).

Ru(PPh₃)₃(CO)HCl, IⁱPr₂Me₂ and IEt₂Me₂ were prepared according to the literature.^{1,2} NMR spectra were recorded on Bruker Avance 300 and 400 MHz NMR spectrometers, and referenced for ¹H and ¹³C{¹H} spectra as follows: C₆D₆ (δ 7.15, δ 128.0), THF (δ 3.58), CDCl₃ (δ 7.24; δ 77.7). ³¹P{¹H} NMR chemical shifts were referenced externally to 85% H₃PO₄ (δ 0.0). 2D experiments (¹H COSY, ¹H-X (X = ¹³C, ³¹P) HMQC/HMBC) were performed using standard Bruker pulse sequences. IR spectra were recorded as nujol mulls or in C₆D₆ on a Nicolet Protégé 460 FTIR spectrometer. Elemental analyses were performed by Elemental Microanalysis Ltd, Okehampton, Devon, UK.

Ru(IⁱPr₂Me₂)'(PPh₃)₂(CO)H (3). Anal. Found (calcd) for C₄₈H₅₀N₂OP₂Ru: C, 68.57 (69.13); H, 6.40 (6.04); N, 3.25 (3.36). ¹H NMR (C₆D₆, 298 K): δ 7.70-7.66 (m, 6H, PPh₃), 7.37-7.32 (m, 6H, PPh₃), 7.02-6.96 (m, 18H, PPh₃), 5.50 (sept, *J*_{HH} = 7.1 Hz, 1H, CH), 4.28 (m, 1H,

CH), 1.99 (m, 1H, CH), 1.76 (s, 3H, CH₃), 1.66 (s, 3H, CH₃), 1.37 (d, $J_{\text{HH}} = 7.1$ Hz, 3H, CH₃), 1.28 (d, 6.0 Hz, 3H, CH₃), 0.54 (d, $J_{\text{HH}} = 7.1$ Hz, 3H, CH₃), 0.49 (m, 1H, CH), -7.72 (dd, $J_{\text{HP}} = 104.8$ Hz, $J_{\text{HP}} = 28.0$ Hz, 1H, Ru-H). $^{31}\text{P}\{^1\text{H}\}$ (C₆D₆, 298 K): δ 56.5 (d, $J_{\text{PP}} = 16.7$ Hz, PPh₃), 35.8 (d, $J_{\text{PP}} = 16.7$ Hz, PPh₃). $^{13}\text{C}\{^1\text{H}\}$ (C₆D₆, 298 K): δ 207.4 (dd, $J_{\text{CP}} = 5.5$ Hz, $J_{\text{CP}} = 13.8$ Hz, Ru-CO), 187.8 (dd, $J_{\text{CP}} = 10.1$ Hz, $J_{\text{CP}} = 82.7$ Hz, Ru-C_{LiPr₂Me₂}), 140.3 (dd, $J_{\text{CP}} = 34.9$ Hz, $J_{\text{CP}} = 1.8$ Hz, PPh₃), 140.0 (dd, $J_{\text{CP}} = 23.0$ Hz, $J_{\text{CP}} = 1.8$ Hz, PPh₃), 135.5 (d, $J_{\text{CP}} = 11.0$ Hz, PPh₃), 134.8 (d, $J_{\text{CP}} = 11.0$ Hz, PPh₃), 129.4-129.0 (m, PPh₃), 128.4-128.1 (m, PPh₃), 124.0 (s, im C), 123.2 (s, im C), 59.1-58.8 (m, CH), 54.0 (s, CH), 24.5 (t, $J_{\text{CP}} = 7.4$ Hz, CH₂), 23.9 (s, CH₃), 22.4 (s, CH₃), 21.4 (s, CH₃), 11.3 (s, CH₃), 10.0 (s, CH₃). IR (C₆D₆, cm⁻¹): 1884 (ν_{CO}).

Ru(C-ⁱPrHMe₂)(PPh₃)₂(CO)HCl (4). THF (20 mL) was added to ⁱPr₂Me₂ (125 mg, 0.69 mmol) and Ru(PPh₃)₃(CO)HCl (600 mg, 0.63 mmol) in an ampoule under argon. The mixture was heated at 50 °C with stirring for 6 days. The resulting precipitate was removed by filtration (found to be ⁱPr₂Me₂H⁺Cl⁻) and the filtrate was reduced *in vacuo*. The residue was washed with hexane (2 x 10 mL) and the resulting solid dissolved in chloroform and layered with hexane, affording Ru(C-ⁱPrHMe₂)(PPh₃)₂(CO)HCl (**4**) as colorless prisms. Yield: 162 mg (31%). Anal. Found (calcd) for C₄₅H₄₅ClN₂OP₂Ru(CHCl₃): C, 58.34 (58.30); H, 5.06 (4.89); N, 2.93 (2.96). ^1H NMR (CDCl₃, 298 K): δ 9.73 (s, 1H, NH), 7.48-7.43 (m, 12H, PPh₃), 7.26-7.18 (m, 18H, PPh₃), 5.43 (sept, $J_{\text{HH}} = 7.1$ Hz, 1H, CH), 1.98 (s, 3H, NCCH₃), 1.51 (s, 3H, NCCH₃), 0.51 (d, $J_{\text{HH}} = 7.1$ Hz, 6H, CH(CH₃)₂), -14.78 (t, 1H, $J_{\text{HP}} = 18.1$ Hz, Ru-H). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl₃, 298 K): δ 48.1. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl₃, 298 K): δ 205.5 (t, $J_{\text{CP}} = 14.7$ Hz, Ru-CO), 180.6 (t, $J_{\text{CP}} = 15.6$ Hz, Ru-C_{LiPrHMe₂}), 136.7 ('vt', $|J_{\text{CP}} + J_{\text{CP}}| = 20.2$ Hz, PPh₃), 134.7 ('vt', $|J_{\text{CP}} + J_{\text{CP}}| = 5.5$ Hz, PPh₃), 129.3 (s, PPh₃), 127.7 ('vt', $|J_{\text{CP}} + J_{\text{CP}}| = 4.6$ Hz, PPh₃), 126.1 (s, im C), 123.8 (s, im C), 52.2 (s, CH), 21.5 (s, CH₃), 11.1 (s, CH₃), 9.9 (s, CH₃). IR (C₆D₆, cm⁻¹): 1925 (ν_{CO}).

Ru(*N*-ⁱPrHMe₂)(PPh₃)₂(CO)HCl (5). THF (10 mL) was added to ⁱPr₂Me₂ (57 mg, 0.32 mmol) and Ru(PPh₃)₃(CO)HCl (150 mg, 0.16 mmol) in an ampoule under argon. The mixture was heated at 70 °C with stirring for 5 days. During this time a precipitate appeared. The mixture was filtered and the solid washed with hexane (2 x 5 mL). Recrystallisation from CHCl₃/hexane afforded Ru(*N*-ⁱPrHMe₂)(PPh₃)₂(CO)HCl (**5**) as a cream crystalline solid. Yield: 63.1 mg (49%). Anal. Found (calcd) for C₄₅H₄₅ClN₂OP₂Ru(CHCl₃): C, 58.13 (58.30); H, 4.87 (4.89); N, 2.98 (2.96). ¹H NMR (CDCl₃, 298 K): δ 7.98 (s, 1H, CH), 7.57-7.53 (m, 12H, PPh₃), 7.25-7.19 (m, 18H, PPh₃), 3.64 (sept, *J*_{HH} = 6.8 Hz, 1H, CH), 1.65 (s, 3H, NCCCH₃), 1.40 (s, 3H, NCCCH₃), 1.06 (d, *J*_{HH} = 6.8 Hz, 6H, CH(CH₃)₂), -13.41 (t, 1H, *J*_{HP} = 20.0 Hz, Ru-*H*). ³¹P{¹H} NMR (CDCl₃, 298 K): δ 47.1. ¹³C{¹H} NMR (CDCl₃, 298 K): δ 205.4 (t, *J*_{CP} = 16.1 Hz, Ru-CO), 136.5 (s, im C-H), 135.8 ('vt', |*J*_{CP} + *J*_{CP}| = 20.1 Hz, PPh₃), 135.0 ('vt', |*J*_{CP} + *J*_{CP}| = 6.0 Hz, PPh₃), 133.9 (s, im C), 129.6 (s, PPh₃), 128.1 ('vt', |*J*_{CP} + *J*_{CP}| = 4.0 Hz, PPh₃), 122.3 (s, im C), 50.0 (s, CH), 23.6 (s, CH₃), 14.4 (s, im CH₃), 9.6 (s, im CH₃). IR (C₆D₆, cm⁻¹): 1912 (ν_{CO}).

Ru(IEt₂Me₂)(PPh₃)₂(CO)HCl (6). Ru(PPh₃)₃(CO)HCl (200 mg, 0.21 mmol) and IEt₂Me₂ (39.5 mg, 0.26 mmol) were charged to an ampoule and suspended in THF (10 mL). The reaction was heated at reflux with stirring overnight. During this time an off-white solid precipitated. The solid was filtered, washed with ethanol (2 x 5 mL) and hexane (1 x 5 mL) and the residue dissolved in chloroform and layered with hexane, affording **6** as colorless crystals. Yield: 119.0 mg (67%). Anal. Found (calcd) for C₄₆H₄₇N₂OP₂ClRu(CHCl₃): C, 58.56 (58.70); H, 5.18 (5.03); N, 3.00 (2.91). ¹H NMR (C₆D₆, 298 K): δ 7.95-7.91 (m, 12H, PPh₃), 7.04-6.96 (m, 18H, PPh₃), 3.56 (m, 4H, CH₂), 1.42 (s, 3H, NCCCH₃), 1.38 (s, 3H, NCCCH₃), 0.77 (t, *J*_{HH} = 7.1 Hz, 3H, CH₂CH₃), 0.53 (t, *J*_{HH} = 7.1 Hz, 3H, CH₂CH₃), -14.31 (t, *J*_{HP} = 19.8 Hz, 1H, RuH). ³¹P{¹H} NMR (C₆D₆, 298 K): δ 45.3. ¹³C{¹H} NMR (CDCl₃, 298 K): δ 204.7 (t, 16.1 Hz, Ru-CO), 181.0 (t, 14.6 Hz, C_{IEt₂Me₂}), 137.3 ('vt', |*J*_{CP} + *J*_{CP}| = 19.8 Hz, PPh₃), 134.7 ('vt', |*J*_{CP} + *J*_{CP}|

= 5.9 Hz, PPh₃), 128.6 (s, PPh₃), 127.8 ('vt', $|J_{\text{CP}} + J_{\text{CP}}| = 4.4$ Hz, PPh₃), 126.3 (s, im C), 124.7 (s, im C), 43.8 (s, CH₂), 42.4 (s, CH₂), 16.3 (s, CH₃), 14.6 (s, CH₃), 9.8 (s, CH₃), 9.6 (s, CH₃). IR (C₆D₆, cm⁻¹): 1919 (ν_{CO}).

References

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