

## 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, CH<sub>2</sub>Cl<sub>2</sub>, hexane) or by drying over calcium hydride (CHCl<sub>3</sub>). Deuterated solvents (Aldrich) were vacuum transferred from potassium (C<sub>6</sub>D<sub>6</sub>, THF-*d*<sub>8</sub>) or calcium hydride (CDCl<sub>3</sub>).

Ru(PPh<sub>3</sub>)<sub>3</sub>(CO)HCl, *i*Pr<sub>2</sub>Me<sub>2</sub> and IEt<sub>2</sub>Me<sub>2</sub> were prepared according to the literature.<sup>1,2</sup> NMR spectra were recorded on Bruker Avance 300 and 400 MHz NMR spectrometers, and referenced for <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} spectra as follows: C<sub>6</sub>D<sub>6</sub> (δ 7.15, δ 128.0), THF (δ 3.58), CDCl<sub>3</sub> (δ 7.24; δ 77.7). <sup>31</sup>P{<sup>1</sup>H} NMR chemical shifts were referenced externally to 85% H<sub>3</sub>PO<sub>4</sub> (δ 0.0). 2D experiments (<sup>1</sup>H COSY, <sup>1</sup>H-X (X = <sup>13</sup>C, <sup>31</sup>P) HMQC/HMBC) were performed using standard Bruker pulse sequences. IR spectra were recorded as nujol mulls or in C<sub>6</sub>D<sub>6</sub> on a Nicolet Protégé 460 FTIR spectrometer. Elemental analyses were performed by Elemental Microanalysis Ltd, Okehampton, Devon, UK.

**Ru(*i*Pr<sub>2</sub>Me<sub>2</sub>)'(PPh<sub>3</sub>)<sub>2</sub>(CO)H (3).** Anal. Found (calcd) for C<sub>48</sub>H<sub>50</sub>N<sub>2</sub>OP<sub>2</sub>Ru: C, 68.57 (69.13); H, 6.40 (6.04); N, 3.25 (3.36). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 298 K): δ 7.70-7.66 (m, 6H, PPh<sub>3</sub>), 7.37-7.32 (m, 6H, PPh<sub>3</sub>), 7.02-6.96 (m, 18H, PPh<sub>3</sub>), 5.50 (sept, *J*<sub>HH</sub> = 7.1 Hz, 1H, CH), 4.28 (m, 1H,

CH), 1.99 (m, 1H, CH), 1.76 (s, 3H, CH<sub>3</sub>), 1.66 (s, 3H, CH<sub>3</sub>), 1.37 (d,  $J_{\text{HH}} = 7.1$  Hz, 3H, CH<sub>3</sub>), 1.28 (d, 6.0 Hz, 3H, CH<sub>3</sub>), 0.54 (d,  $J_{\text{HH}} = 7.1$  Hz, 3H, CH<sub>3</sub>), 0.49 (m, 1H, CH), -7.72 (dd,  $J_{\text{HP}} = 104.8$  Hz,  $J_{\text{HP}} = 28.0$  Hz, 1H, Ru-H). <sup>31</sup>P{<sup>1</sup>H} (C<sub>6</sub>D<sub>6</sub>, 298 K): δ 56.5 (d,  $J_{\text{PP}} = 16.7$  Hz, PPh<sub>3</sub>), 35.8 (d,  $J_{\text{PP}} = 16.7$  Hz, PPh<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} (C<sub>6</sub>D<sub>6</sub>, 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<sub>iPr<sub>2</sub>Me<sub>2</sub></sub>), 140.3 (dd,  $J_{\text{CP}} = 34.9$  Hz,  $J_{\text{CP}} = 1.8$  Hz, PPh<sub>3</sub>), 140.0 (dd,  $J_{\text{CP}} = 23.0$  Hz,  $J_{\text{CP}} = 1.8$  Hz, PPh<sub>3</sub>), 135.5 (d,  $J_{\text{CP}} = 11.0$  Hz, PPh<sub>3</sub>), 134.8 (d,  $J_{\text{CP}} = 11.0$  Hz, PPh<sub>3</sub>), 129.4-129.0 (m, PPh<sub>3</sub>), 128.4-128.1 (m, PPh<sub>3</sub>), 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, CH<sub>2</sub>), 23.9 (s, CH<sub>3</sub>), 22.4 (s, CH<sub>3</sub>), 21.4 (s, CH<sub>3</sub>), 11.3 (s, CH<sub>3</sub>), 10.0 (s, CH<sub>3</sub>). IR (C<sub>6</sub>D<sub>6</sub>, cm<sup>-1</sup>): 1884 (ν<sub>CO</sub>).

**Ru(C-<sup>i</sup>PrHMe<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>(CO)HCl (4).** THF (20 mL) was added to <sup>i</sup>Pr<sub>2</sub>Me<sub>2</sub> (125 mg, 0.69 mmol) and Ru(PPh<sub>3</sub>)<sub>3</sub>(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 <sup>i</sup>Pr<sub>2</sub>Me<sub>2</sub>H<sup>+</sup>Cl<sup>-</sup>) 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-<sup>i</sup>PrHMe<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>(CO)HCl (**4**) as colorless prisms. Yield: 162 mg (31%). Anal. Found (calcd) for C<sub>45</sub>H<sub>45</sub>ClN<sub>2</sub>OP<sub>2</sub>Ru(CHCl<sub>3</sub>): C, 58.34 (58.30); H, 5.06 (4.89); N, 2.93 (2.96). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 298 K): δ 9.73 (s, 1H, NH), 7.48-7.43 (m, 12H, PPh<sub>3</sub>), 7.26-7.18 (m, 18H, PPh<sub>3</sub>), 5.43 (sept,  $J_{\text{HH}} = 7.1$  Hz, 1H, CH), 1.98 (s, 3H, NCCCH<sub>3</sub>), 1.51 (s, 3H, NCCCH<sub>3</sub>), 0.51 (d,  $J_{\text{HH}} = 7.1$  Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), -14.78 (t, 1H,  $J_{\text{HP}} = 18.1$  Hz, Ru-H). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 298 K): δ 48.1. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 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<sub>iPrHMe<sub>2</sub></sub>), 136.7 ('vt',  $|J_{\text{CP}} + J_{\text{CP}}| = 20.2$  Hz, PPh<sub>3</sub>), 134.7 ('vt',  $|J_{\text{CP}} + J_{\text{CP}}| = 5.5$  Hz, PPh<sub>3</sub>), 129.3 (s, PPh<sub>3</sub>), 127.7 ('vt',  $|J_{\text{CP}} + J_{\text{CP}}| = 4.6$  Hz, PPh<sub>3</sub>), 126.1 (s, im C), 123.8 (s, im C), 52.2 (s, CH), 21.5 (s, CH<sub>3</sub>), 11.1 (s, CH<sub>3</sub>), 9.9 (s, CH<sub>3</sub>). IR (C<sub>6</sub>D<sub>6</sub>, cm<sup>-1</sup>): 1925 (ν<sub>CO</sub>).

**Ru(*N*-<sup>i</sup>PrHMe<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>(CO)HCl (5).** THF (10 mL) was added to <sup>i</sup>Pr<sub>2</sub>Me<sub>2</sub> (57 mg, 0.32 mmol) and Ru(PPh<sub>3</sub>)<sub>3</sub>(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 CHCl<sub>3</sub>/hexane afforded Ru(*N*-<sup>i</sup>PrHMe<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>(CO)HCl (**5**) as a cream crystalline solid. Yield: 63.1 mg (49%). Anal. Found (calcd) for C<sub>45</sub>H<sub>45</sub>ClN<sub>2</sub>OP<sub>2</sub>Ru(CHCl<sub>3</sub>): C, 58.13 (58.30); H, 4.87 (4.89); N, 2.98 (2.96). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 298 K): δ 7.98 (s, 1H, CH), 7.57-7.53 (m, 12H, PPh<sub>3</sub>), 7.25-7.19 (m, 18H, PPh<sub>3</sub>), 3.64 (sept, *J*<sub>HH</sub> = 6.8 Hz, 1H, CH), 1.65 (s, 3H, NCCH<sub>3</sub>), 1.40 (s, 3H, NCCH<sub>3</sub>), 1.06 (d, *J*<sub>HH</sub> = 6.8 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), -13.41 (t, 1H, *J*<sub>HP</sub> = 20.0 Hz, Ru-*H*). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 298 K): δ 47.1. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 298 K): δ 205.4 (t, *J*<sub>CP</sub> = 16.1 Hz, Ru-CO), 136.5 (s, im C-H), 135.8 ('vt', |*J*<sub>CP</sub> + *J*<sub>CP</sub>| = 20.1 Hz, PPh<sub>3</sub>), 135.0 ('vt', |*J*<sub>CP</sub> + *J*<sub>CP</sub>| = 6.0 Hz, PPh<sub>3</sub>), 133.9 (s, im C), 129.6 (s, PPh<sub>3</sub>), 128.1 ('vt', |*J*<sub>CP</sub> + *J*<sub>CP</sub>| = 4.0 Hz, PPh<sub>3</sub>), 122.3 (s, im C), 50.0 (s, CH), 23.6 (s, CH<sub>3</sub>), 14.4 (s, im CH<sub>3</sub>), 9.6 (s, im CH<sub>3</sub>). IR (C<sub>6</sub>D<sub>6</sub>, cm<sup>-1</sup>): 1912 (ν<sub>CO</sub>).

**Ru(IEt<sub>2</sub>Me<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>(CO)HCl (6).** Ru(PPh<sub>3</sub>)<sub>3</sub>(CO)HCl (200 mg, 0.21 mmol) and IEt<sub>2</sub>Me<sub>2</sub> (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 C<sub>46</sub>H<sub>47</sub>N<sub>2</sub>OP<sub>2</sub>ClRu(CHCl<sub>3</sub>): C, 58.56 (58.70); H, 5.18 (5.03); N, 3.00 (2.91). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 298 K): δ 7.95-7.91 (m, 12H, PPh<sub>3</sub>), 7.04-6.96 (m, 18H, PPh<sub>3</sub>), 3.56 (m, 4H, CH<sub>2</sub>), 1.42 (s, 3H, NCCH<sub>3</sub>), 1.38 (s, 3H, NCCH<sub>3</sub>), 0.77 (t, *J*<sub>HH</sub> = 7.1 Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>), 0.53 (t, *J*<sub>HH</sub> = 7.1 Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>), -14.31 (t, *J*<sub>HP</sub> = 19.8 Hz, 1H, RuH). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 298 K): δ 45.3. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 298 K): δ 204.7 (t, 16.1 Hz, Ru-CO), 181.0 (t, 14.6 Hz, C<sub>IEt<sub>2</sub>Me<sub>2</sub></sub>), 137.3 ('vt', |*J*<sub>CP</sub> + *J*<sub>CP</sub>| = 19.8 Hz, PPh<sub>3</sub>), 134.7 ('vt', |*J*<sub>CP</sub> + *J*<sub>CP</sub>|

= 5.9 Hz, PPh<sub>3</sub>), 128.6 (s, PPh<sub>3</sub>), 127.8 ('vt',  $|J_{CP} + J_{CP}| = 4.4$  Hz, PPh<sub>3</sub>), 126.3 (s, im C), 124.7 (s, im C), 43.8 (s, CH<sub>2</sub>), 42.4 (s, CH<sub>2</sub>), 16.3 (s, CH<sub>3</sub>), 14.6 (s, CH<sub>3</sub>), 9.8 (s, CH<sub>3</sub>), 9.6 (s, CH<sub>3</sub>). IR (C<sub>6</sub>D<sub>6</sub>, cm<sup>-1</sup>): 1919 (ν<sub>CO</sub>).

## References

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