## SUPPLEMENTARY INFORMATION

# Ni(I) and Ni(II) ring-expanded N-heterocyclic carbene complexes: C-H activation, indole formation and catalytic hydrodehalogenation

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#### Synthesis and Characterisation of 1-3.

All manipulations were carried out using standard Schlenk, high vacuum and glovebox techniques using dried and degassed solvents. Ni(cod)<sub>2</sub>, Ni(PPh<sub>3</sub>)<sub>2</sub>Br<sub>2</sub> and KN(SiMe<sub>3</sub>)<sub>2</sub> were purchased from Sigma Aldrich and used as received. 1,3-Bis(2,4,6-trimethylphenyl)-3,4,5,6-tetrahydropyrimidinium tetrafluoroborate, [6-MesH]BF<sub>4</sub>, was prepared according to the literature.<sup>1</sup> C<sub>6</sub>D<sub>6</sub> was vacuum transferred from potassium. NMR spectra were recorded on a Bruker Avance 500 MHz NMR spectrometer at 298 K and referenced to  $\delta$  7.16 (<sup>1</sup>H) and  $\delta$  128.0 (<sup>13</sup>C). Elemental analyses were performed by Elemental Microanalysis Ltd, Okehampton, Devon, UK and the Elemental Analysis Service, London Metropolitan University, London, UK.

**Ni(6-Mes)** ( $\eta^3$ -C<sub>8</sub>H<sub>13</sub>) (1). The free N-heterocyclic carbene 6-Mes was prepared *in-situ* by reaction of the pyrimidinium salt [6-MesH]BF<sub>4</sub> (222 mg, 0.54 mmol) with KN(SiMe<sub>3</sub>)<sub>2</sub> (108 mg, 0.54 mmol) in toluene (15 mL) for 20 min. This solution was then added to Ni(cod)<sub>2</sub> (150 mg, 0.54 mmol) and the mixture stirred at room temperature for 1 h. The resulting orange solution was reduced to dryness and the resulting residue extracted into hexane (3 x 15 mL) and filtered. The eluent was concentrated to 10 mL to afford an orange precipitate of the product. This was filtered, washed with cold hexane (2 mL), and dried *in vacuo*. Analytically pure compound was obtained by recrystallization of the product from hexane at 243 K. Yield: 105 mg (40 %). Analysis found (calculated) for C<sub>30</sub>H<sub>40</sub>N<sub>2</sub>Ni: C, 73.98 (73.94); H, 8.21 (8.27); N, 5.79 (5.75). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz):  $\delta$  7.05 (s, 1H, ArH), 6.68 (s, 1H, ArH), 6.67 (s, 1H, ArH), 6.58 (s, 1H, ArH), 3.69 (t, 1H, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz, CH), 3.42 (q, 1H, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz, CH), 3.24 (m, 1H, CH<sub>2</sub>), 2.97 (q, 1H, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz, CH), 2.83 (d, 1H, <sup>2</sup>J<sub>HH</sub> = 7.1 Hz, NiCH<sub>2</sub>), 2.82 (m, 1H, CH<sub>2</sub>), 2.74 (m, 1H, CH<sub>2</sub>), 2.67 (m, 1H, CH<sub>2</sub>), 2.39 (s, 3H, CH<sub>3</sub>), 2.29 (d, 1H,  ${}^{2}J_{HH}$  = 7.1 Hz, Ni-CH<sub>2</sub>), 2.24 (s, 3H, CH<sub>3</sub>), 2.14 (s, 3H, CH<sub>3</sub>), 2.10 (s, 3H, CH<sub>3</sub>), 2.10 (m, 1H, CH<sub>2</sub>), 2.07 (s, 3H, CH<sub>3</sub>), 1.85 (m, 2H, CH<sub>2</sub>), 1.67-1.37 (m, 6H, CH<sub>2</sub>), 1.31-1.06 (m, 3H, CH<sub>2</sub>).  ${}^{13}C{}^{1}H{}$  NMR (C<sub>6</sub>D<sub>6</sub>, 125 MHz):  $\delta$  226.8 (s, NCN), 146.3 (s, ArC), 146.0 (s, ArC), 143.5 (s, ArC), 137.1 (s, ArC), 136.4 (s, ArC), 135.7 (s, ArC), 135.3 (s, ArC), 129.7 (s, ArCH), 129.1 (s, ArCH), 128.5 (ArC underneath C<sub>6</sub>D<sub>6</sub>), 125.1 (s, ArCH), 124.2 (s, ArCH), 106.4 (s, CH), 71.4 (s, CH), 61.8 (s, CH), 46.4 (s, CH<sub>2</sub>), 46.1 (s, CH<sub>2</sub>), 32.3 (s, CH<sub>2</sub>), 31.1 (s, CH<sub>2</sub>), 30.2 (s, CH<sub>2</sub>), 30.1 (s, CH<sub>2</sub>), 24.7 (s, CH<sub>2</sub>), 22.6 (s, CH<sub>2</sub>), 21.7 (s, CH<sub>3</sub>), 21.3 (s, CH<sub>3</sub>), 19.6 (s, CH<sub>3</sub>), 19.2 (s, CH<sub>3</sub>), 18.2 (s, CH<sub>3</sub>), 15.6 (s, Ni-CH<sub>2</sub>).

**Degradation of 1 to 2.** A solution of 1 (53 mg, 10.9 mmol) in toluene (10 mL) was heated at 343 K for 16 h to form a grey precipitate and dark yellow solution. The solution was filtered and reduced to dryness *in vacuo*. The residue was extracted with hexane (2 x 5 mL), filtered and the volume reduced to 1 mL to afford white crystals of **2**. Yield: 19 mg (62 %). Analysis found (calculated) for C<sub>22</sub>H<sub>26</sub>N<sub>2</sub>: C, 82.95 (82.98); H, 8.30 (8.23); N, 8.93 (8.79). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz):  $\delta$  7.09 (s, 1H, ArH), 6.84 (s, 2H, ArH), 6.65 (s, 1H, ArH), 5.05 (s, 1H, C=CH), 3.87 (t, 2H, <sup>3</sup>*J*<sub>HH</sub> = 5.5 Hz, NCH<sub>2</sub>), 2.97 (t, 2H, <sup>3</sup>*J*<sub>HH</sub> = 5.5 Hz, NCH<sub>2</sub>), 2.51 (s, 3H, CH<sub>3</sub>), 2.43 (s, 3H, CH<sub>3</sub>), 2.18 (s, 3H, CH<sub>3</sub>), 2.16 (s, 6H, CH<sub>3</sub>), 1.54 (apparent quin, 2H, <sup>3</sup>*J*<sub>HH</sub> = 5.5 Hz, CH<sub>2</sub>). <sup>13</sup>C {<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 125 MHz):  $\delta$  144.0 (s, NCN), 140.6 (s, ArC), 137.9 (s, ArC), 137.3 (s, ArC), 132.1 (s, ArC), 131.7 (s, ArC), 130.4 (s, ArCH), 129.1 (s, ArC), 122.7 (s, ArCH), 118.6 (s, ArC), 116.5 (s, ArCH), 78.2 (s, C=CH), 46.0 (s, NCH<sub>2</sub>), 43.3 (s, NCH<sub>2</sub>), 23.8 (s, CH<sub>2</sub>), 22.0 (s, CH<sub>3</sub>), 21.4 (s, CH<sub>3</sub>), 20.3 (s, CH<sub>3</sub>), 18.5 (s, CH<sub>3</sub>).

Ni(6-Mes)(PPh<sub>3</sub>)Br (3). A solution of 6-Mes (prepared as for 1 from pyrimidinium salt (515 mg, 1.26 mmol) and KN(SiMe<sub>3</sub>)<sub>2</sub> (251 mg, 1.26 mmol)) in toluene (20 mL) was added to a mixture of Ni(cod)<sub>2</sub> (173 mg, 0.63 mmol) and

Ni(PPh<sub>3</sub>)<sub>2</sub>Br<sub>2</sub> (468 mg, 0.63 mmol) and the mixture stirred at room temperature for 1 h to yield a yellow precipitate and dark yellow solution. The solution was filtered and the yellow precipitate extracted into THF (3 x 15 mL), filtered, and the THF and toluene fractions combined. The volume of the resulting solution was reduced to 30 mL and hexane (30 mL) added to form a bright yellow precipitate. This was filtered, washed with hexane (10 mL) and MeOH (2 x 10 mL), and dried *in vacuo*. Analytically pure compound was obtained by recrystallization from THF/hexane. Yield: 390 mg (43 %). Analysis found (calculated) for  $C_{40}H_{43}N_2PNiBr$ : C, 66.45 (66.60); H, 6.16 (6.01); N, 3.95 (3.88). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz):  $\delta$  30.4 (2H), 16.2 (1H), 10.8 (7H), 9.6, 8.8, 7.8 (10H for overlapping resonances 9.6-7.8), 4.0 (7H), 1.9 (3H), 0.7 (10H), -1.2 (1H), -16.9 (2H).

#### Catalytic hydrodehalogenation.

The following describes a typical catalytic run. 1-Chloro-4-fluorobenzene (35 mg, 0.268 mmol) in THF (1 mL) was added to a mixture of **3** (8.7 mg, 0.012 mmol) and NaO<sup>i</sup>Pr (66 mg, 0.804 mmol) in a resealable J. Youngs NMR tube. A capillary containing a reference standard,  $\alpha, \alpha, \alpha$ -trifluorotoluene in C<sub>6</sub>D<sub>6</sub>, was inserted into the tube. The <sup>19</sup>F NMR spectrum of the sample (500 MHz, locked to C<sub>6</sub>D<sub>6</sub>) was acquired at regular intervals and the resonance frequencies (1-chloro-4-fluorobenzene;  $\delta$  -116.4; 1-bromo-4-fluorobenzene,  $\delta$  -115.9; fluorobenzene,  $\delta$  -113.6) referenced to  $\alpha, \alpha, \alpha$ -trifluorotoluene at  $\delta$  -62.4. Normalization of the substrate and product integrals relative to  $\alpha, \alpha, \alpha$ -trifluorotoluene afforded the percentage conversions.

### Molecular structure of 2.



**Figure S1**. Molecular structure of **2**. Ellipsoids are shown at 50 % probability with all hydrogen atoms removed for clarity. Selected bond lengths (Å) and angles (°): N(1)-C(1) 1.3755(16), N(2)-C(1) 1.3858(16), C(1)-C(7) 1.3724(18), C(6)-C(7) 1.4291(18), C(7)-C(1)-N(1) 129.76(11), C(7)-C(1)-N(2) 110.19(11).

## References

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