Electronic Supplementary Information

1. General experimental methods

All organic reagents unless specified were purchased from Aldrich, Alfa Aesar, BDH and Lancaster, and were used as received. $[Rh(COD)Cl]_2$ was prepared using a literature method.[1] Preparations were performed using dried and degassed solvents only when specified. All reported compounds were dried over phosphorus pentoxide *in vacuo*. ^1H and $^{13}C\{^1H\}$ spectra were recorded on Bruker 300 MHz DXP and 600 MHz Avance spectrometers. Melting point measurements were performed on a Reichert apparatus and are uncorrected. Mass spectra were run on a Finnigan LCQ DecaXP Quadrupole Ion Trap Mass Spectrometer in the Bioanalytical Mass Spectrometry Facility (BMSF), University of New South Wales. Elemental analyses were performed by the Microanalytical Unit of the Research School of Chemistry, Australian National University. Cyclic voltammetry measurements were performed in a conventional three electrode cell using a computer-controlled Pine Instrument Co. AFCBP1 bipotentiostat as described in detail elsewhere.[2] The UV-vis spectroelectrochemical experiments were performed using a modified UV-vis-NIR cuvette with a Pt gauze working electrode, a Pt wire counter electrode, and an Ag/AgCl reference electrode.[2] UV-vis-NIR spectra were recorded using a Cary 5 spectrometer.

2. Syntheses

2.1 (HL-nic)

5-Bromo-N,N-diisopropylnicotinamide[3] (255 mg, 0.89 mmol), imidazole (90 mg, 1.44 mmol), cesium carbonate (585 mg, 1.80 mmol) and copper(I) iodide (34 mg, 0.18 mmol) in deoxygenated dimethylformamide were heated under dinitrogen at 110-120 °C for 24 hours. The solvent was then purged from the reaction mixture using a flow of dinitrogen. The crude solid was purified using flash column chromatography on silica gel using chloroform-methanol (9:1) as eluent. The second fraction was collected and the solvent removed to afford a pale yellow oil. Addition of hexane caused the product to crystallize. The cream-white crystals were collected by filtration and washed once with hexane to afford the title compound (130 mg, 70%). M.p.: 155-156 °C. ESI(+)-MS *m/z* 273 ($[M\text{-}H^+]^+$, 100%). ^1H NMR (300 MHz, $(CD_3)_2CO$): δ 8.96 (d, J = 2.6 Hz, 1H, pyridyl-**H**), 8.55 (d, J = 1.7 Hz, 1H, pyridyl-**H**), 8.26 (s, br, 1H, imidazolyl-**H**), 8.03 (dd, J = 2.0, 0.6 Hz, 1H, pyridyl-**H**), 7.77 (s,

br, 1H, imidazolyl-**H**), 7.21 (s, br, 1H, imidazolyl-**H**), 3.80 (m, br, 2H $(Me)_2C$-**H**), 1.38 (m, br, 12H, C**H**$_3$).

2.2 (HL^+-nic^+-Me).2X^- (X^- = I^-, PF_6^-)

5-(1H-Imidazol-1-yl)-N,N-diisopropylnicotinamide (HL-nic) (163 mg, 0.60 mmol) and methyl iodide (350 mg, 2.47 mmol) in acetone (10 ml) were refluxed overnight to give a yellow precipitate. The reaction mixture was thoroughly cooled to -15 ° C and the precipitate collected by filtration and washed once with hexane to afford the diiodide salt of the title compound (285 mg, 86%). M.p.: >190 ° dec. ESI(+)-MS *m/z* 429 ($[M^{2+}+I^-]^+$, 100%). ^{1}H NMR (300 MHz, $(CD_3)_2SO$): δ 10.00 (s, 1H, Ar-**H**), 9.77 (s, 1H, Ar-**H**), 9.36 (s, 1H, Ar-**H**), 9.00 (s, 1H, Ar-**H**), 8.38 (t, J = 2.0 Hz, 1H, Ar-**H**), 8.09 (t, J = 2.0 Hz, 1H, Ar-**H**), 4.47 (s, 3H, C**H**$_3$-N), 4.05 (s, 3H, C**H**$_3$-N), 3.74 (m, br, 2H $(Me)_2C$-**H**), 1.50 (d, br, J = 5.7 Hz, 6H, C**H**$_3$-C), 1.20 (d, br, J = 3.0 Hz, 6H, C**H**$_3$-C). $^{13}C\{^1H\}$ NMR (75.5 MHz, (D_2O)): δ 215.40 (**C**=O), 162.93, 143.60, 138.58, 138.47, 136.08, 135.27, 125.65, 121.83 (Ar-**C**), 53.03, 49.66, 47.23 ($(Me)_2$**C**-H), 36.88 (**C**H_3N), 30.29 (**C**H_3-N), 19.64 (**C**H_3-C), 19.41 (**C**H_3-C). Anal. Calcd. for $C_{17}H_{26}I_2N_4O$: C, 36.71; H, 4.71; N, 10.07. Found: C, 36.83; H, 4.76; N 9.96 %. The hexafluorophosphate salt was made by dissolving the diiodide salt in water and adding a saturated aqueous solution of ammonium hexafluorophosphate, then collecting the white precipitate by filtration. ^{1}H NMR data were identical to those given above for the diiodide salt. Anal. Calcd. for $C_{17}H_{26}F_{12}N_4OP_2$: C, 34.47; H, 4.42; N, 9.46. Found: C, 34.40; H, 4.38; N 9.30 %. ^{31}P (121 MHz, $(CD_3)_2CO$): δ -143.03 (sept, J = 705 Hz, PF_6^-). ^{19}F (282 Hz, $(CD_3)_2CO$): δ -73.06 (d, J = 705 Hz, PF_6^-).

2.3 [Rh(COD)X(L-nic^+-Me)][PF_6] (<u>1</u>: X = I; <u>2</u>: X = Cl)

The preparation of the iodo species **<u>1</u>**. (HL-nic)$[I]_2$ (135.6 mg, 0.24 mmol) and $[Rh(COD)Cl]_2$ (60.1 mg, 0.12 mmol) were dissolved in acetonitrile. Triethylamine (30 mg, 0.30 mmol) was added, at which point the solution immediately turned bright orange-red. The solution was stirred for 30 min., and the solvent purged from the reaction mixture using a stream of dinitrogen. The red residue was redissolved in the minimum amount of methanol, and added dropwise to a saturated aqueous solution of ammonium hexafluorophosphate. The resulting bright orange-red precipitate was filtered, washed once with cold water, with copious diethyl ether, then once with hexane. The orange powder was recrystallized from acetone/hexane at ambient temperature to give compound **<u>1</u>** as a bright red powder (164.4 mg, 86%). Data for **<u>1</u>**: ESI(+)-MS *m/z* 639.0 ($[M]^+$, 70%), 276.47 ($[Rh(COD)(L\text{-}nic^+\text{-}Me)(MeCN)]^{2+}$. ^{1}H NMR

(600 MHz, $(CD_3)_2CO$): δ 10.89 (s, 1H, Ar-**H**), 10.13 (s, 1H, Ar-**H**), 9.29 (s, 1H, Ar-**H**), 7.97 (s, 1H, Ar-**H**), 7.63 (s, 1H, Ar-**H**), 5.25 (m, br, 2H, C**H** of COD), 4.76 (s, 3H, C**H**$_3$-N), 4.20 (s, 3H, C**H**$_3$-N), 3.90 (m, br, 1H, $(Me)_2$C-**H**), 3.78 (m, br, 1H, $(Me)_2$C-**H**), 3.64 (m, br, 1H, C**H** of COD), 2.90 (m, br, 1H, C**H** of COD), 2.20-2.50 (m, 4H, C**H**$_2$ of COD), 1.75-2.00 (m, 4H, C**H**$_2$ of COD), 1.58 (m, br, 6H, C**H**$_3$-C), 1.26 (m, br, 6H, C**H**$_3$-C). $^{13}C\{^1H\}$ NMR (100.6 MHz, $(CD_3)_2CO$): δ 185.99 (d, $J_{C\text{-}Rh}$ = 49.6 Hz, **C**$_{carbene}$), 162.63 (**C**=O), 141.87, 139.93, 139.42, 137.71, 133.12, 125.76, 120.96 (Ar-**C**), 97.84 (d, $J_{C\text{-}Rh}$ = 6.4 Hz, allyl-**C**), 97.2 (d, $J_{C\text{-}Rh}$ = 7.0 Hz, allyl-**C**), 73.60 (d, $J_{C\text{-}Rh}$ = 3.5 Hz, allyl-**C**), 73.46 (d, $J_{C\text{-}Rh}$ = 3.3 Hz, allyl-**C**), 51.72 (br, $(Me)_2$**C**-H), 49.02 (**C**H$_3$-N), 46.32 (br, $(Me)_2$**C**-H), 38.81 (**C**H$_3$-N), 31.78 (**C**H$_3$-C), 31.36 (**C**H$_3$-C), 19.48-20.15 (m, **C**H$_2$ of COD). ^{31}P (121 MHz, $(CD_3)_2CO$): δ -143.51 (sept, J = 705 Hz, PF_6^-). ^{19}F (282 Hz, $(CD_3)_2CO$): δ -73.24 (d, J = 705 Hz, PF_6^-). Anal. Calcd. for $C_{25}H_{37}F_6IN_4OPRh$: C, 38.28; H, 4.75; N, 7.14. Found: C, 38.18; H, 4.65; N 7.00 %.

The chloro species **2** was prepared analogously from (HL-nic)$[PF_6]_2$ and $[Rh(COD)Cl]_2$ in > 80% yield. Data for **2**: ESI(+)-MS *m/z* 547.1 ($[M]^+$, 25%), 276.47 ($[Rh(COD)(L\text{-}nic^+\text{-}Me)(MeCN)]^{2+}$. ^1H NMR (300 MHz, $(CD_3)_2CO$): δ 10.62 (s, 1H, Ar-**H**), 10.13 (s, 1H, Ar-**H**), 9.30 (s, 1H, Ar-**H**), 7.88 (s, 1H, Ar-**H**), 7.60 (s, 1H, Ar-**H**), 5.52 (s, 1H, C**H** of COD), 5.04 (m, br, 2H, C**H** of COD), 4.76 (s, 3H, C**H**$_3$-N), 4.26 (s, 3H, C**H**$_3$-N), 3.93 (m, br, 1H, $(Me)_2$C-**H**), 3.80 (m, br, 1H, $(Me)_2$C-**H**), 3.42 (m, br, 2H, C**H** of COD), 2.25-2.50 (m, 4H, C**H**$_2$ of COD), 1.80-1.95 (m, 4H, C**H**$_2$ of COD), 1.56 (m, br, 6H, C**H**$_3$-C), 1.32 (m, br, 6H, C**H**$_3$-C). ^{31}P (121 MHz, $(CD_3)_2CO$): δ -144.28 (sept, J = 705 Hz, PF_6^-). ^{19}F (282 Hz, $(CD_3)_2CO$): δ -72.61 (d, J = 705 Hz, PF_6^-). Anal. Calcd. for $C_{25}H_{37}F_6ClN_4OPRh.2H_2O$: C, 41.19; H, 5.67; N, 7.69. Found: C, 40.61; H, 5.56; N 7.51 %.

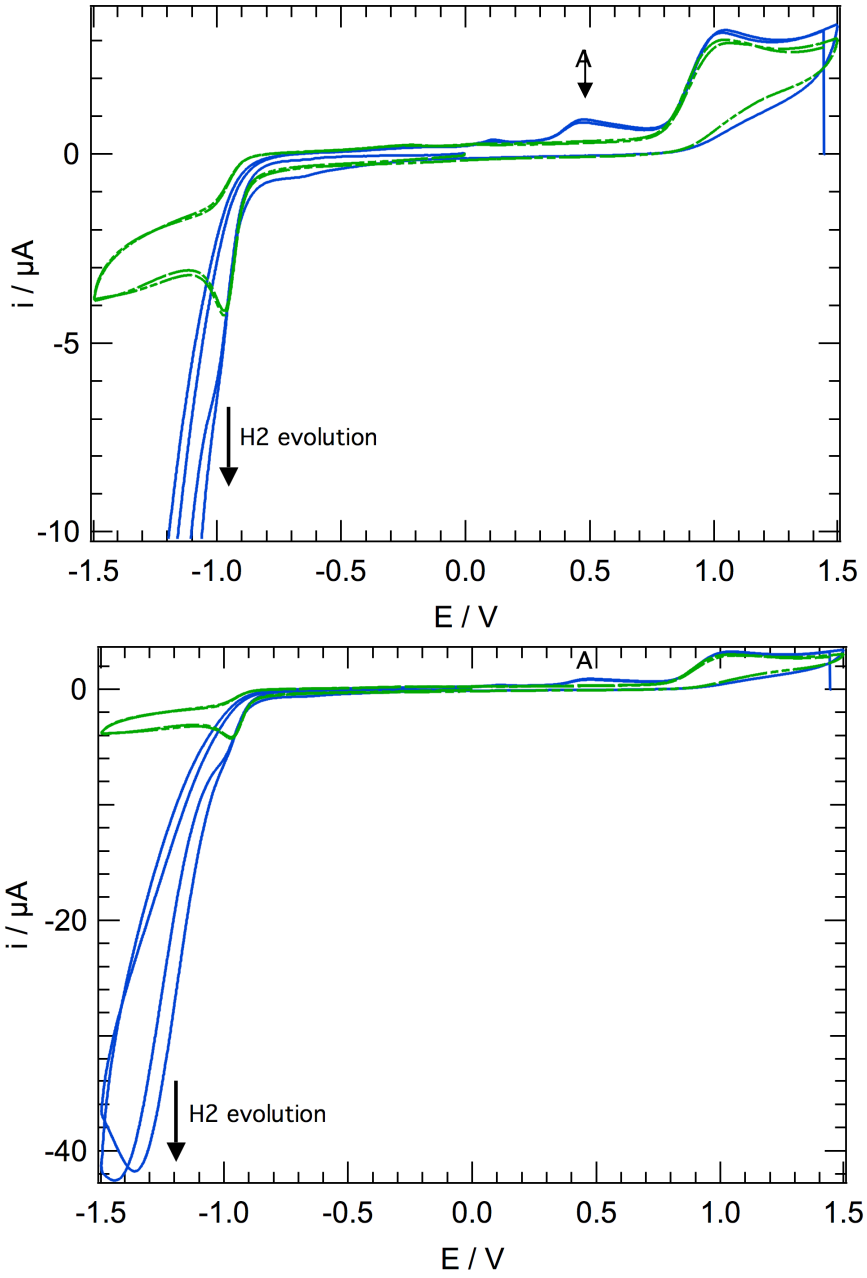
2.4 Chemical Reduction of $(HL^+\text{-}nic^+\text{-}Me)[PF_6]_2$

$(HL^+\text{-}nic^+\text{-}Me)[PF_6]_2$ (0.1 mmol) was dissolved in dichloromethane (5 mL) and to this solution was added a saturated 1:1 aqueous solution of sodium dithionite and sodium bicarbonate (10 mL). The biphasic mixture was shaken for 30 minutes, the organic phase separated and the solvent removed to afford a yellow residue which was analysed by NMR spectroscopy without further purification. ^1H NMR (300 MHz, $(CD_3)_2CO$): δ 9.10 (s, 1H, imidazolium-**H**), 7.99 (s, 1H, imidazolium-**H**), 7.80 (s, 1H, imidazolium-**H**), 6.93 (s, 1H, dihydronicotinamide-C**H**), 6.15 (s, 1H, dihydronicotinamide-C**H**), 4.09 (s, 3H, C**H**$_3$-

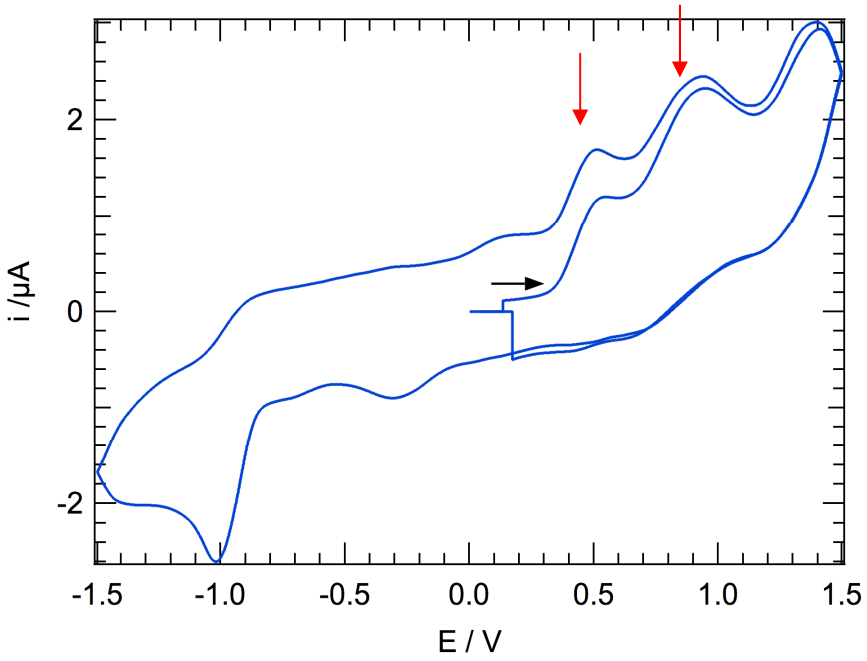
$N_{imidazolium}$), 3.56 (s, 2H, dihydronicotinamide-C**H$_2$**), 3.09 (s, 3H, C**H**$_3$- $N_{dihydronicotinamide}$), 3.92 (m, br, 2H $(Me)_2$C-**H**), 1.29 (d, br, J = 9 Hz, 12H, C**H**$_3$-C).

In the ^{1}H-^{1}H NOESY spectrum, the dihydronicotinamide-C**H$_2$** protons at δ 3.56 show a strong cross-peak to the 2-imidazolium C-**H** proton at δ 9.10 and <u>not</u> to the methyl protons of the dihydronicotinamide group at δ 3.09. Also, the dihydronicotinamide methyl group peak at δ 3.09 shows cross peaks to <u>both</u> the dihydronicotinamide C-H proton peaks at δ 6.93 and 6.15. The 1,4-regiospecific addition of hydride ion in the product is thus confirmed.

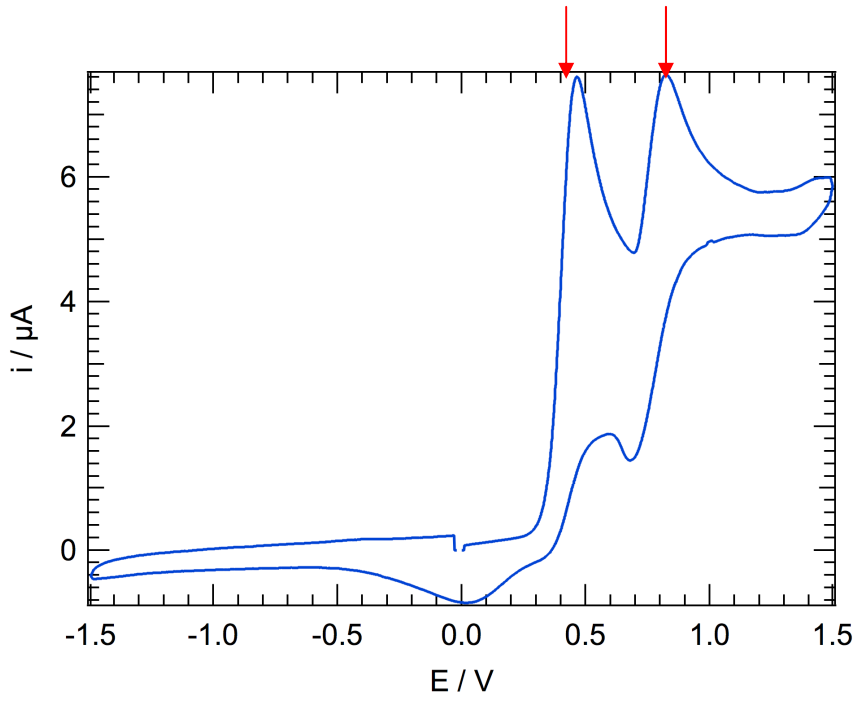
3. Additional Cyclic Voltammograms



3.1 Cyclic voltammograms of the complex [RhCl(COD)(L-nic^{+}-Me)][PF_6] (**2**) (~1 mM) in acetonitrile – 0.1M [(*n*-Bu)$_4$N][PF_6] at scan rate = 100 mV s^{-1} before (green traces) and after (blue traces) buffering the solution with excess 1:1 2,4,6-collidinium {pK_a (MeCN) = 7.3) triflate/ collidene. The upper figure is an expansion of the complete cyclic voltammogram (lower figure) with peak A at +0.48 V, attributed to re-oxidation of the dihydronicotinamide substituent (see text), marked.



3.2 Cyclic voltammogram of the complex [Rh(COD)I(L-nic^{+}-Me)][PF_6] (**1**) in acetonitrile – 0.1M [(*n*-Bu)$_4$N][PF_6] at scan rate = 100 mV s^{-1}.



3.3 Cyclic voltammogram of [(*n*-Bu)$_4$N]I (iodide ion) in acetonitrile – 0.1M [(*n*-Bu)$_4$N][PF_6] at scan rate = 100 mV s^{-1} showing the anticipated I^-/I_3^- and I_3^-/I_2 couples,[4] the potentials of which vary slightly with the concentration of iodide ion.

(The red arrows are drawn only to give an approximate guide to the eye.)

4. References

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