Electronic Supplementary Information for Dalton Transactions

Rh(I) and Ir(I) Catalysed Intermolecular Hydroamination with Substituted Hydrazines

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Supporting Information

General Procedures

All manipulations of metal complexes and air sensitive reagents were carried out using standard Schlenk or vacuum techniques, or in a nitrogen or argon-filled glove box.[1] Solvents were dried and distilled under an atmosphere of nitrogen or argon using standard procedures[2] and stored under an inert atmosphere in glass ampoules, each fitted with a Youngs© Teflon valve. Except where specified, chemicals were purchased from either Aldrich Chemical Company Inc. or Lancaster Inc. and used as received. Liquid organic reagents were dried over molecular sieves (4 Å) and distilled *in vacuo* or under $Ar_{(g)}$ prior to use. The metal halide salts $RhCl_3.xH_2O$ and $IrCl_3.xH_2O$ were purchased from Precious Metals Online PMO P/L or Strem Inc. and were used without further purification. $[Ir(\mu\text{-}Cl)(COD)]_2$,[3] $[Rh(\mu\text{-}Cl)(CO)_2]_2$,[4] $[Ir(\mu\text{-}Cl)(COE)_2]_2$,[3] *bis*(*N*-methylimidazol-2-yl)methane,[5] $[Ir(bpm)(CO)_2]BArF$[6] and $[Rh(bim)(CO)_2]BPh_4$[5] were synthesised using the reported methods. $[Ir(\mu\text{-}Cl)(CO)_2]_n$[7] was kindly provided by Dr Sarah Rumble and were prepared using the reported method. *Bis*(1-pyrazolyl)methane was kindly provided by Dr Danielle Kennedy and synthesised by the reported method.[8] NaBArF[9] and $[Ir(Ph_2PyP)(COD)]BArF$[6] were kindly provided by Dr Richard Hodgson using the literature methods reported. $[Rh(bpm)(CO)_2]BArF$[6] was kindly provided by Joanne Hui Hui Ho and synthesised by the reported method.

Air sensitive NMR spectroscopy samples were prepared either in a nitrogen or argon filled glove box or on a high vacuum line by vacuum transfer of solvent into an NMR tube fitted with a concentric Teflon Valve (Youngs©). Deuterated solvents for NMR purposes were obtained from Cambridge Isotopes Laboratories (CIL), except $CDCl_3$ which was purchased from either CIL or Aldrich Chemical Company Inc. Deuterated solvents for use with air sensitive compounds were either degassed *via* three freeze-pump-thaw cycles and vacuum distilled from suitable drying reagents immediately prior to use, or handled exclusively under a nitrogen or argon atmosphere.

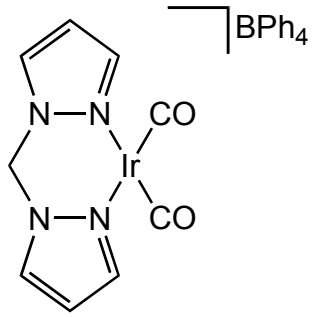
The ^1H, and ^{13}C NMR spectra were recorded on Bruker DPX300, DMX500 and DMX600 spectrometers operating at 300.13, 300.17, 500.13 and 600.13 MHz (^1H); 75.49, 75.48, 125.79 and 150.92 MHz (^{13}C); respectively. The spectra were recorded at 298 K unless otherwise specified. Chemical shifts (δ) are quoted in ppm. ^1H NMR and ^{13}C NMR chemical shifts were referenced internally to residual solvent resonances. ^{19}F NMR chemical shifts were referenced externally using

α,α,α-trifluorotoluene in $CDCl_3$. Uncertainties in chemical shifts are typically ±0.01 ppm for ^{1}H and ±0.05 ppm for ^{13}C and ^{31}P and ^{15}N. Coupling constants (*J*) are given in Hz and have an uncertainty of ±0.05 Hz for ^{1}H-^{1}H. The following abbreviations are used in reporting the multiplicity of NMR resonances: s, singlet; d, doublet; t, triplet; q, quartet; p, pentet; m, multiplet; br, broad. The following two-dimensional NMR techniques were routinely used for the assignment of organic and organometallic compounds: COSY (**CO**rrelation **S**pectroscos**Y**), NOESY (**N**uclear **O**verhauser **E**ffect **S**pectroscop**Y**), HMQC (**H**eternuclear correlation through **M**ultiple **Q**uantum **C**oherence) and HMBC (**H**eteronuclear **M**ultiple **B**ond **C**orrelation). NMR data were processed using standard Bruker software (xwin-nmr and Topspin).

IR spectra were recorded using an ATI Mattson *Genesis Series* F.T.I.R. spectrometer or an Avatar 370 FTIR spectrometer as KBr discs or nujol mulls. Elemental analyses were carried out at the Campbell Microanalytical Laboratory, University of Otago, New Zealand.

ESI-MS were performed by Dr Russel Pickford using a Finnigan or Micromass QToF mass spectrometer. In reporting mass spectral data, M is defined as the molecular weight of the compound of interest. In the case of the ESI-MS of cationic compounds M is defined as the molecular weight of the cationic fragments.

Synthesis of $[Ir(bpm)(CO)_2]BPh_4$ (2)



$[Ir(bpm)(CO)_2]BPh_4$ was synthesised from the reported methods.[10,11] *Bis*pyrazolylmethane (0.109 g, 0.738 mmol), $[Ir(\mu\text{-}Cl)(COD)]_2$ (0.225 g. 0.336 mmol) and $NaBPh_4$ (0.238 g, 0.695 mmol) were suspended in MeOH and stirred for 18 h. After this time half the solvent was removed to precipitate a bright yellow solid which was collected by filtration and washed with MeOH (3 x 2 mL). The solid was dried *in vacuo* to produce $[Ir(bpm)(COD)]BPh_4$ which was used without further purification for the next step.

$[Ir(bpm)(COD)]BPh_4$ was suspended in MeOH and *n*-hexane (1:1) and the flask was evaporated and re-filled with $CO_{(g)}$ (x 3). The suspension was stirred for ~2 min during which time it had changed to a pale yellow colour. The $CO_{(g)}$ atmosphere was replaced with $Ar_{(g)}$ and the solid was collected by filtration, washed with MeOH (2 x 1 mL) and *n*-hexane (3 x 5 mL), with 10 min of stirring for each washing. The solid was dried *in vacuo* to give $[Ir(bpm)(CO)_2]BPh_4$ (**2**) as a yellow solid. Yield: 0.323 g, 67 %.

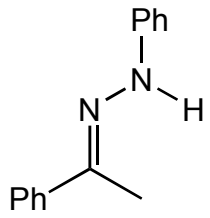
^{1}H NMR (300 MHz, THF-d_8) δ 8.17 (d, 2H, $^{3}J_{H5\text{-}H4}$ = 2.3 Hz, **H**5), 7.40-7.35 (m, 10H, **H**3 and *o*-C**H** of BPh_4), 6.88 (apparent t, 8H, *J* = 7.2 Hz, *m*-C**H** of BPh_4), 6.74 (apparent t, 4H, *J* = 7.3 Hz, *p*-C**H** of BPh_4), 6.52 (aparent t, 2H, *J* = 2.6 Hz, **H**4), 5.37 (s, 2H, C$\mathbf{H}_2$) ppm.

IR (KBr disc) υ 2081.27, 2063.92, 2016.42, 1981.99 cm^{-1}.

Synthesis of products of the catalysed hydroamination of alkynes with hydrazines

^{1}H and $^{13}C\{^{1}H\}$ NMR spectral data was consistent with available reported data. For compounds with no reported ^{1}H and ^{13}C NMR spectral data 2D NMR spectroscopy and mass spectroscopy were performed to confirm identification of the compound.

Synthesis of acetophenone phenylhydrazone (1)

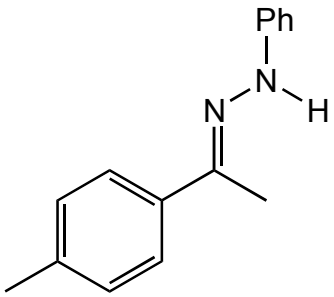


Phenylhydrazine (0.2 mL, 2.031 mmol), acetophenone (0.2 mL, 1.704 mmol), glacial acetic acid (5 drops) and EtOH (30 mL) were refluxed over mol. sieves (4 Å) under Ar for 5 h. The mixture was filtered through Celite™ and the filtrate concentrated *in vacuo*. *n*-Hexane was layered over the EtOH solution and the flask placed in a -30°C freezer O/N. The precipitated was collected by filtration, washed with *n*-hexane and dried *in vacuo* to give the product as a crystalline white solid. Yield: 0.191 g, 53 %. MP 102-106°C (lit.[12,13] 104°C).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83-7.80 (m, 2H, *o*-C**H** of -NHPh), 7.43-6.92 (m, 8H, 7 x Ar**H** and N**H**), 6.90 (t, J = 7.2 Hz, 1H, *p*-C**H** of Ph), 2.25 (s, 3H, C$\mathbf{H}_3$) ppm.

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 145.0, 140.9, 138.9, 129.0, 128.1, 127.7, 125.29, 120.0, 113.0, 11.6 ppm.

Synthesis of 4-methylacetophenone phenylhydrazone



4-Methylacetophenone (1 mL, 7.490 mmol), phenylhydrazine (0.8 mL, 8.123 mmol) and EtOH (30 mL) were refluxed over molecular sieves (4 Å) for 5 h. The mixture was cooled to room temperature and filtered through Celite™. The filtrate was evaporated to dryness to give the solid as a yellow waxy solid. Yield: 1.211 g, 72 %. MP 88-93°C (lit.[14] 79-80°C).

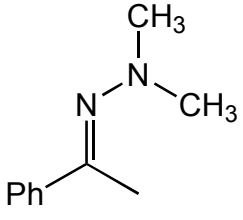
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (d, J = 8.1 Hz, 2H, -$C_5\mathbf{H}_4CH_3$), 7.33-7.28 (m, 3H, *m*-C**H** of Ph and N**H**), 7.22-7.19, (m, 4H, *o*-C**H** of Ph and -$C_5\mathbf{H}_4CH_3$), 6.92-6.87 (m, 1H, *p*-C**H** of Ph), 2.39 (s, 3H, C$\mathbf{H}_3$), 2.23 (s, 3H, C$\mathbf{H}_3$) ppm.

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 145.3 (s, $\mathbf{C}_q$), 141.4 (s, $\mathbf{C}_q$), 137.8 (s, $\mathbf{C}_q$), 136.3 (s, $\mathbf{C}_q$), 129.2, 129.0, 125.4, 120.0, 113.1, 21.1 (s, $\mathbf{C}H_3$), 11.8 (s, $\mathbf{C}H_3$) ppm.

ESI-MS (DCM), *m/z* (%): 224.46 (100) $[M+H]^+$.

Synthesis of acetophenone 1,1-dimethylhydrazone

Acetophenone 1,1-dimethylhydrazone was synthesised from a method adapted from the literature.[15]

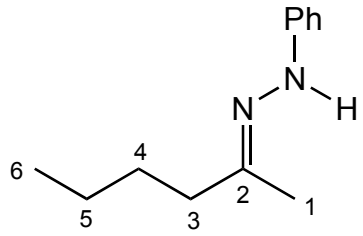


Acetophenone (1.992 g, 16.58 mmol) and 1,1-dimethylhydrazine (1.266 g, 21.07 mmol) were dissolved in benzene. Triflic acid (5 drops) was added and the solution was refluxed for 24 h with removal of water by means of a Dean-Stark trap. The solution was cooled to RT and diluted with LP. The organic layer was washed with water (2 x 30 mL) and brine solution (1 x 30 mL), dried over $MgSO_4$ and filtered. The volatiles were removed by rotary evaporation and the crude oil was distilled to give the product as a yellow oil. Yield: 0.73 g, 27 %. BP 42-44°C/1.5 Torr (lit.[15] 40-42°C/0.08 Torr).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74-7.72 (m, 2H, Ar**H**), 7.36-7.34 (m, 3H, Ar**H**), 2.60 (s, 6H, N(C**H**$_3$)$_2$), 2.34 (s, 3H, C**H**$_3$) ppm.

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 161.9, 139.0, 129.1, 128.2, 126.3, 47.1, 15.4 ppm.

Synthesis of 2-hexanone phenylhydrazone



2-Hexanone phenylhydrazone was synthesised from a method adapted from the literature.[16]

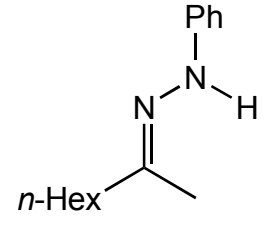
2-Hexanone (0.582 g, 5.810 mmol) was added dropwise to freshly distilled phenylhydrazine (0.630 g, 5.816 mmol). After completion of the exothermic reaction (~5 min) glacial acetic acid (5 drops) was added. The mixture was heated on a boiling water bath for 1 h under a flow of $Ar_{(g)}$. After cooling of the mixture to RT EtOH/H_2O (1:1) was added and the organic layer separated. The aqueous layer was washed with EtOAc (3 x 10 mL). The combined organic layers were evaporated to dryness and the residue distilled *in vacuo* to give the product as a yellow oil. Yield: 0.476 g, 43 %. BP 108-112 °C/1.5 Torr (lit.[16] 141-144°C/3 mm Hg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28-7.25 (m, 2H, *m*-C**H** of Ph), 7.09-7.06 (m, 2H, *o*-C**H** of Ph), 6.88 (br s, -N**H**), 6.86-6.83 (m, 1H, *p*-C**H** of Ph), 2.44 (t, 2H, C^3**H**$_2$, *J*= 7.5 Hz), 1.86 (s, 3H, C^1**H**$_3$), 1.63-1.54 (m, 2H, C^4**H**$_2$), 1.46-1.39 (m, 2H, C^5**H**$_2$), 1.01-0.95 (m, 3H, C^6**H**$_3$) ppm.

^{13}C{^{1}H} NMR (121 MHz, $CDCl_3$) δ 147.1 (**C**$_q$), 146.0 (**C**$_q$), 129.1 (*m*-**C** of Ph), 119.4 (*p*-**C** of Ph), 112.9 (*o*-**C** of Ph), 38.5 (**C**3), 28.8 (**C**4), 22.3 (**C**5), 14.2 (**C**1), 13.9 (**C**6) ppm.

ESI-MS (DCM), *m/z* (%): 191.1 (100) $[M+H]^+$.

Synthesis of 2-octanone phenylhydrazone (7)



2-Octanone (0.826 g, 6.435 mmol) was added dropwise to freshly distilled phenylhydrazine (0.7236 g, 6.691 mmol). After completion of the exothermic reaction (~ 5 min) glacial acetic acid (8 drops) was added. The mixture was heated at 110°C for 1.5 h under a flow of $Ar_{(g)}$. The reaction mixture was dried *in vacuo* at 200°C to give the product as a brown oil. Yield: 0.613 g, 44 %.

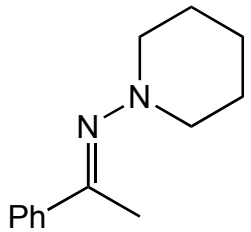
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32-7.24 (m, 2H, *m*-C**H** of Ph), 7.09-7.06 (m, 2H, *o*-C**H** of Ph), 6.93-6.82 (m, 2H, *p*-C**H** of Ph, -N**H**), 2.35-2.30 (m, 2H, $C^3\mathbf{H}_2$), 1.85 (s, 3H, $C^1C\mathbf{H}_3$), 1.65-1.55 (m, 2H, $C\mathbf{H}_2$), 1.40-1.31 (m, 6H, $C\mathbf{H}_2$), 0.97-0.91 (m, 3H, $-CH_2C\mathbf{H}_3$) ppm.

^{13}C{^{1}H} NMR (121 MHz, $CDCl_3$) δ 147.1 ($\mathbf{C}_q$), 146.0 ($\mathbf{C}_q$), 129.1 (*m*-**C** of Ph), 119.4 (*p*-**C** of Ph), 112.9 (*o*-**C** of Ph), 38.9 ($-\mathbf{C}^3H_2-$), 31.5, ($-\mathbf{C}H_2-$), 28.9 ($-\mathbf{C}H_2-$), 26.6 ($-\mathbf{C}H_2-$), 25.1 ($-\mathbf{C}H_2-$), 22.6($-\mathbf{C}H_2-$), 14.2 ($-C\mathbf{C}H_3$), 14.0 ($-CH_2\mathbf{C}H_3$) ppm.

ESI-MS (DCM), *m/z* (%): 218.2 (100) $[M+H]^+$.

Synthesis of N-(1-phenylethylidene)-1-piperidinamine

Dried and degassed *N*-aminopiperidine (0.322 g, 3.210 mmol), acetophenone (0.376 g, 3.129 mmol), glacial acetic acid (8-10 drops) and benzene (dried and degassed) (20-30 mL) were refluxed over molecular sieves (4 Å), under an atmosphere of $Ar_{(g)}$ for 3 h. The mixture was cooled to RT, filtered and the molecular sieves washed with DCM. The filtrate and washings were combined, concentrated *in vacuo* and *n*-hexane added to precipitate out a white solid. The mixture was filtered and the filtrate evaporated to dryness to give the product as a yellow oil. Yield: 0.405 g, 64 %. BP 79-81°C/1.5 Torr.

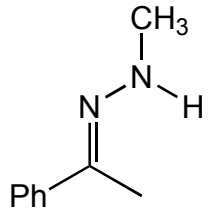


^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73-7.71 (m, 2H, Ar**H**), 7.37-7.26 (m, 3H, Ar**H**), 2.79 (apparent t, 4H, J = 5.3 Hz, *o*-$C\mathbf{H}_2$ of NC_5H_5), 2.35 (s, 3H, $C\mathbf{H}_3$), 1.77-1.70 (m, 4H, *m*-$C\mathbf{H}_2$ of NC_5H_5), 1.53-1.48 (m, 2H, *p*-$C\mathbf{H}_2$ of NC_5H_5) ppm.

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 162.2 ($\mathbf{C}_q$), 139.3 ($\mathbf{C}_q$), 129.1 (Ar**C**H), 128.2 (Ar**C**H), 126.4 (Ar**C**H), 56.2 (*o*-**C** of NC_5H_5), 25.4 (*m*-**C** of NC_5H_5), 24.0 (*p*-**C** of NC_5H_5), 15.7 ($\mathbf{C}H_3$) ppm.

Synthesis of acetophenone methylhydrazone

Dried and degassed methylhydrazine (0.5 mL, 9.496 mmol), acetophenone (0.4 mL, 3.408 mmol), glacial acetic acid (8-10 drops) and benzene (dried and degassed) (20-30 mL) were refluxed over molecular sieves (4 Å), under an atmosphere of argon, for 5 h. The mixture was cooled to RT, filtered and the molecular sieves washed with benzene. The filtrate and washings were combine and evaporated to dryness to give a viscous oil which was distilled *in vacuo* to give the product as a pale yellow oil. Yield: 0.358 g, 77 %. BP 64-68°C/1.5 Torr.



^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69-7.66 (m, 2H, Ar**H**), 7.38-7.25 (m, 3H, Ar**H**), 4.86 (br s, 1H, N**H**), 3.11 (s, 3H, N(H)$C\mathbf{H}_3$), 2.10 (s, 3H, -$CC\mathbf{H}_3$ ppm.

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 143.5 ($\mathbf{C}_q$), 139.5 ($\mathbf{C}_q$), 128.2 (Ar**C**H), 127.6 (Ar**C**H), 125.3 (Ar**C**H), 38.3 ($N\mathbf{C}H_3$), 12.2 ($C\mathbf{C}H_3$) ppm.

General procedures for catalysis reactions monitored by NMR spectroscopy

Catalysed hydroamination reactions were conducted on a small scale in NMR tubes fitted with concentrated Teflon valves (from Young's). The complex used as catalyst was either dissolved or suspended in deuterated solvent in the NMR tube, prior to injection of the internal standard and substrates. The deuterated solvents were either dried and degassed and transferred on a high vac line ($CDCl_3$, C_6D_6, THF-d_8, toluene-d_8) or opened and used, as received from the manufacturer, in the glove box ($(CDCl_2)_2$, toluene-d_8). All catalytic reactions were performed under argon or nitrogen at elevated temperatures in a variable temperature NMR probe or in an oil bath. The temperature of the NMR probe was calibrated using neat ethylene glycol.[17] The identity of the catalysis products was confirmed by comparison to literature NMR data and/or by comparison with the ^{1}H NMR spectra of authentic samples.

All catalytic reactions contained a dry and degassed liquid internal standard, which was injected into the reaction mixture prior to the substrates. Yield of the product was determined by integration of the product resonances versus that of the resonances of the internal standard (of which there is a constant and known amount) in the ^{1}H NMR spectra which were acquired at pre-determined time intervals. Conversion was then determined from the yield of the product compared to the original amount of alkyne substrate, as the hydrazine was always used in slight excess.

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