# **Supporting Information**

# Relayed hyperpolarization from *para*-hydrogen improves the NMR detectability of alcohols

Peter J. Rayner,<sup>[a]</sup> Ben. J. Tickner,<sup>[a]</sup> Wissam Iali,<sup>[a]</sup> Marianna Fekete,<sup>[a]</sup> Alastair D. Robinson, <sup>[a]</sup> and Simon B. Duckett,<sup>[a]</sup>

<sup>[a]</sup> Centre for Hyperpolarisation in Magnetic Resonance, Department of Chemistry, University of York, Heslington, YO10 5DD

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### 1. Synthetic procedures and characterisation data

# 1.1 General experimental

All compounds were purchased from Sigma-Aldrich, Fluorochem or Alfa-Aesar and used as supplied unless otherwise stated. The following compounds were synthesised according to literature procedures; [IrCl(COD)(IMes)] (1),<sup>1</sup> [IrCl(COD)(1,3-bis(4-*tert*-butyl-2,6-dimethylphenyl)imidazole-2-ylidine)] (2),<sup>2</sup> [IrCl(COD)(1,3-bis(2,4,6-trimethylphenyl)-4,5-dimethylimidazol-2-ylidine)] (3)<sup>2</sup> and 1,3-bis-(2,4,6-trimethylphenyl)-4-(dimethylamino)imidazolium triflate.<sup>3</sup>

Water is distilled water. Brine refers to a saturated aqueous solution of NaCl. THF was freshly distilled from sodium and benzophenone ketyl or dried using a Grubbs solvent purification system. Petrol refers to the fraction of petroleum ether boiling in the range 40-60 °C. All reactions were carried out under O<sub>2</sub>-free Ar or N<sub>2</sub> using oven-dried and/or flame-dried glassware.

Flash column chromatography was carried out using Fluka Chemie GmbH silica (220-440 mesh). Thin layer chromatography was carried out using Merck  $F_{254}$  aluminium-backed silica plates. <sup>1</sup>H (400 MHz) and <sup>13</sup>C (100.6 MHz) NMR spectra were recorded on a Bruker-400 instrument with an internal deuterium lock. Chemical shifts are quoted as parts per million and referenced to  $CHCl_3$  ( $\delta_H$  7.27), ( $CH_3$ )<sub>2</sub>SO ( $\delta_H$  2.54),  $CDCl_3$  ( $\delta_C$  77.0) or ( $CD_3$ )<sub>2</sub>SO ( $\delta_C$  40.45). <sup>13</sup>C NMR spectra were recorded with broadband proton decoupling. <sup>13</sup>C NMR spectra were assigned using DEPT experiments where necessary. Coupling constants (J) are quoted in Hertz. Electrospray high and low resolution mass spectra were recorded on a Bruker Daltronics microOTOF spectrometer.

# 1.2 Synthesised compounds

# [IrCl(COD)(1,3-bis(2,4,6-trimethylphenyl)-4-(dimethylamino)imidazol-2-ylidine)] (4)

KO<sup>t</sup>Bu (14 mg, 0.12 mmol, 2.4 eq.) was added to a stirred solution of 1,3-bis-(2,4,6trimethylphenyl)-4-(dimethylamino)imidazolium triflate (50 mg, 0.10 mmol, 2.0 eq.) in THF at rt under N<sub>2</sub>. The resulting suspension was stirred at rt for 30 min. Then, a solution of [Ir(COD)Cl]<sub>2</sub> (34 mg, 0.05 mmol, 1.0 eq.) in THF (5 mL) was added and the resulting solution was stirred at rt for 2 h. The solvent was removed under reduced pressure to give the crude product. Purification by flash column chromatography on silica with CH<sub>2</sub>Cl<sub>2</sub> gave the title complex **4** (61 mg, 89%) as a yellow crystalline solid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.03 (s,1H), 7.01 (s, 1H) 6.97 (s, 2H), 6.33 (s, 1H), 4.17 (td, *J* = 7.8 Hz, 3.9 Hz, 1H), 4.10-4.05 (m, 1H), 3.083.04 (m, 1H), 2.78 (td, J = 7.5 Hz, 3.2 Hz, 1H), 2.46 (s, 6H), 2.42 (s, 3H), 2.41 (s, 3H), 2.38 (s, 3H), 2.37 (s, 3H), 2.19 (s, 3H), 2.14 (s, 3H), 1.78-1.63 (m, 4H), 1.40-1.14 (m, 4H); <sup>13</sup>**C** NMR (100.6 MHz, CDCl<sub>3</sub>)  $\delta$  178.1 (s), 146.7 (s), 138.4 (s), 138.3 (s), 137.7 (s), 137.4 (s), 136.6 (s), 135.5 (s), 134.4 (s), 134.0 (s), 129.53 (s), 129.45 (s), 128.2 (s), 128.0 (s), 108.0 (s), 82.1 (s), 81.5 (s), 51.5 (s), 51.1 (s), 43.2 (s), 33.8 (s), 33.2 (s), 29.2 (s), 28.6 (s), 21.2 (s), 21.1 (s), 20.3 (s), 17.7 (s), 18.7 (s), 18.2 (s); HRMS m/z calculated for C<sub>33</sub>H<sub>47</sub><sup>193</sup>IrN<sub>3</sub> (M – Cl)<sup>+</sup> 678.3399, found 678.3394.

#### 1.3 <sup>1</sup>H and <sup>13</sup>C NMR spectra of 4



Figure S1: <sup>1</sup>H (top) and <sup>13</sup>C (bottom) NMR spectra of 4

#### 2 NMR polarization transfer experiment data

#### 2.1 SABRE-Relay polarization transfer method

The polarization transfer experiments that are reported were conducted in 5 mm NMR tubes that were equipped with a J. Young's tap. Samples for these polarization transfer experiments were based on a 5 mM solution of [IrCl(COD)(NHC)], amine, and the indicated additional substrate at the specified loading in dichloromethane- $d_2$  (0.6 mL). The samples were degassed by two freeze-pump-thaw cycles prior to the introduction of *para*hydrogen

at a pressure of 3 bar. *Para*-hydrogen (p-H<sub>2</sub>) was produced by passing hydrogen gas over a spin-exchange catalyst (Fe<sub>2</sub>O<sub>3</sub>) at 28 K and used for all hyperpolarization experiments. This method produces constant p-H<sub>2</sub> with ca. 93% purity.

The shake & drop method was employed for recording hyperpolarized SABRE NMR spectra.<sup>4</sup> Once filled with p-H<sub>2</sub>, samples were then shaken vigorously for 10 s in the specified fringe field of an NMR spectrometer before being rapidly transported into the magnet for subsequent interrogation by NMR spectroscopy.

# 2.2 Polarization factors

<sup>1</sup>H, <sup>31</sup>P, and <sup>19</sup>F signal enhancements were calculated according to equation 1 where, E = enhancement level, SI(pol) = signal of polarized sample, SI(unpol) = signal of unpolarized (reference) sample.

$$E = \frac{SI(pol)}{SI(unpol)} \tag{1}$$

Experimentally, both spectra were recorded on the same sample using identical acquisition parameters, including the receiver gain. The raw integrals of the relevant resonances in the polarized and unpolarized spectra were then used to determine the enhancement levels. The quoted values reflect the signal strength gain (fold) per proton/phosphorus/fluorine nucleus in the specified group.

<sup>13</sup>C enhancements ( $^{E}_{13C}$ ) were calculated relative to the raw integral of the <sup>13</sup>CD<sub>2</sub>Cl<sub>2</sub> peak observed from the solvent in the sample after equilibration inside the magnet for >1 minute. CD<sub>2</sub>Cl<sub>2</sub> was present in each sample at a concentration of 15.67 M and the resulting SABRE-Relay hyperpolarized signal was then scaled according to the concentration of substrate in solution to give the final enhancement value for <sup>13</sup>C. This is shown in Equation 2 where  $^{S}_{Hy}$  is the total hyperpolarized substrate signal,  $^{Mr}_{Sub}$ ,  $^{D}_{Sub}$  and  $^{V}_{Sub}$  are the molecular weight, density and volume of substrate respectively,  $^{V}_{sol}$ ,  $^{D}_{sol}$  and  $^{Mr}_{sol}$  is the volume, density and molecular weight of the DCM solvent used and  $^{S}_{sol}$  is the DCM <sup>13</sup>C signal from a 1 scan thermal. These values were corroborated by further measurements on samples containing CHCl<sub>3</sub> as an internal standard and by comparison to spectra recorded using signal averaging.

$$E_{13C} = \frac{S_{Hy} M r_{Sub} V_{sol} D_{sol}}{D_{Sub} V_{Sub} S_{sol} M r_{sol}}$$
(2)

# 2.3 NMR Spectrometer

Spectra were typically acquired on a 400 MHz Bruker, Avance III console using a 5 mm BBI probe which was tuned to <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P or <sup>19</sup>F as specified. Resonances are referenced relative to the residual proton signal of the indicated deuterated solvent.

#### **3** Representative NMR spectra of Hyperpolarised Alcohols



Fig. S2: Thermal (top) and hyperpolarised (bottom) <sup>1</sup>H spectra of **3**, 5 eq. 1-propanol and 5 eq. NH<sub>3</sub> in dichloromethane- $d_2$  shaken for 10 seconds with 3 bar p-H<sub>2</sub> at 70 G.



Figure S3: Thermal (top) and hyperpolarised (bottom) <sup>1</sup>H spectra of [IrCl(COD)(IMes)], 5 eq. 3-methyl-1-butanol and 7 eq. NH<sub>3</sub> in dichloromethane- $d_2$  shaken for 10 seconds with 3 bar p-H<sub>2</sub> at 65 G.



Figure S4: Thermal (top) and hyperpolarised (bottom) <sup>13</sup>C spectra of [IrCl(COD)(IMes)], 5 eq. 3-methyl-1-butanol and 7 eq. NH<sub>3</sub> in dichloromethane- $d_2$  shaken for 10 seconds with 3 bar p-H<sub>2</sub> at 65 G.



Figure S5: Thermal (top) and hyperpolarised (bottom) <sup>1</sup>H spectra of [IrCl(COD)(IMes)], 5 eq. 3-pentanol and 6 eq. NH<sub>3</sub> in dichloromethane- $d_2$  shaken for 10 seconds with 3 bar p-H<sub>2</sub> at 65 G.



Figure S6: Thermal (top) and hyperpolarised (bottom) <sup>13</sup>C spectra of [IrCl(COD)(IMes)], 5 eq. 3-pentanol and 6 eq.  $NH_3$  in dichloromethane- $d_2$  shaken for 10 seconds with 3 bar p- $H_2$  at 65 G.



Figure S7: Thermal (top) and hyperpolarised (bottom) <sup>1</sup>H spectra of [IrCl(COD)(IMes)], 5 eq. 2-methyl-2-butanol and 8 eq. NH<sub>3</sub> in dichloromethane- $d_2$  shaken for 10 seconds with 3 bar p-H<sub>2</sub> at 65 G.



Fig. S8: Thermal polarised <sup>13</sup>C NMR spectrum (top) and hyperpolarised <sup>1</sup>H-<sup>13</sup>C INEPT NMR spectrum (bottom) of **3**, 5 eq. methyl glycolate and 5 eq. NH<sub>3</sub> in dichloromethane- $d_2$  shaken for 10 seconds with 3 bar p-H<sub>2</sub> at 70 G.



Fig. S9: Thermal polarised <sup>19</sup>F NMR spectrum (top) and hyperpolarised <sup>1</sup>H-<sup>19</sup>F NMR spectrum (bottom) of **3**, 5 eq. methyl glycolate and 5 eq. NH<sub>3</sub> in dichloromethane- $d_2$  shaken for 10 seconds with 3 bar p-H<sub>2</sub> at 70 G.



Fig. S10: Thermal polarised <sup>31</sup>P NMR spectrum (top) and hyperpolarised <sup>1</sup>H-<sup>31</sup>P NMR spectrum (bottom) of **3**, 5 eq. diethyl (hydroxymethyl)phosphate and 5 eq. NH<sub>3</sub> in dichloromethane- $d_2$  shaken for 10 seconds with 3 bar p-H<sub>2</sub> at 70 G.



Fig. S11: Thermal polarised <sup>1</sup>H NMR spectrum (top) and hyperpolarised <sup>1</sup>H NMR spectrum (bottom) of **1**, 5 eq. (–)-menthol and 5 eq. NH<sub>3</sub> in dichloromethane- $d_2$  shaken for 10 seconds with 3 bar p-H<sub>2</sub> at 65 G.



Fig. S12: Hyperpolarised <sup>13</sup>C NMR spectrum of **1**, 5 eq. (–)-menthol and 5 eq. NH<sub>3</sub> in dichloromethane- $d_2$  shaken for 10 seconds with 3 bar p-H<sub>2</sub> at 65 G.

# 4 Effect of Contaminant H<sub>2</sub>O on the SABRE-Relay effect

A sample containing [IrCl(COD)(IMes)],  $d_7$ -BnNH<sub>2</sub> (10 eq.) and 1-propanol (1 µL) in dichloromethane- $d_2$  was activated under 3 bar H<sub>2</sub>. The resulting solution was doped with the volumes of H<sub>2</sub>O indicated in Table 1 and exposed to 3 bar p-H<sub>2</sub> and shaken for 10 seconds at 70 G. The resulting signal gains are given below.

Table S1: Signal gains for 1-propanol after SABRE-Relay transfer whilst doping with varying volumes of H<sub>2</sub>O.

Volume of water	Signal Gain		
added (µL)	OCH₂	CH <sub>2</sub>	CH <sub>3</sub>
0	537	690	489
1	48	59	31
5	11	22	8

Similar effects were observed when  $H_2O$  or  $D_2O$  was added to a sample containing [IrCl(COD)(IMes)], NH<sub>3</sub> (4-5 eq.), 3-methyl-1-butanol (1.8  $\mu$ L) and 3-bar H<sub>2</sub> in 0.6 mL dichloromethane- $d_2$  as shown in Figure S13.



Figure S13: Total <sup>1</sup>H enhancements of 3-methyl-1-butanol shaken with [IrCl(COD)(IMes)] and 4-5 eq NH<sub>3</sub> in DCM- $d_2$  for 10 seconds with 3 bar p-H<sub>2</sub> after the addition of H<sub>2</sub>O or D<sub>2</sub>O.

# **5** Effect of Amine and Alcohol concentrations

The effect of alcohol and amine concentrations on the <sup>1</sup>H signal enhancements of 1propanol are shown in Figure S14.



Figure S14: (left) Effect of varying the concentration of  $d_7$ -BnNH<sub>2</sub> on the signal gain for the OCH<sub>2</sub> position in 1-propanol (1 µL) when using [IrCl(COD)(IMes)] in dichlormethane- $d_2$  when shaken for 10 seconds with 3 bar p-H<sub>2</sub> at 65 G. (right) Effect of varying the equivalents of 1-propanol on the signal gain for its OCH<sub>2</sub> position when using [IrCl(COD)(IMes)] and  $d_7$ -BnNH<sub>2</sub> (5 eq.) in dichlormethane- $d_2$  when shaken for 10 seconds with 3 bar p-H<sub>2</sub> at 65 G.

The effect of alcohol and amine concentrations on the <sup>1</sup>H and <sup>13</sup>C signal enhancements of 3methyl-1-butanol (Figure S15a and c) and <sup>1</sup>H signal enhancement of the NH<sub>3</sub> carrier (Figure S15b) are shown.



Figure S15: a) Total <sup>1</sup>H enhancements of 3-methyl-1-butanol b) total free NH<sub>3</sub> enhancement and c) total <sup>13</sup>C enhancements of 3-methyl-1-butanol as a function of alcohol and carrier NH<sub>3</sub> amounts when shaken for 10 seconds with 3 bar p-H<sub>2</sub> at 65 G.

#### 6 Ligand exchange dynamics of [Ir(H)<sub>2</sub>(NHC)(amine)<sub>3</sub>]Cl

The kinetic behaviour of the active catalysts **1-4** under 3 bar  $H_2$  was examined using well established exchange spectroscopy methods.<sup>5</sup> A series of exchange spectroscopy (EXSY) measurements were performed to probe the dynamic behaviour of these systems. This process involved the selective excitation of a single resonance and the subsequent

measurement of a <sup>1</sup>H NMR spectrum at time, *t*, after the initial pulse. The resulting measurements consisted of a series of data arrays such that t is varied typically between 0.1 to 1.0 s, to encode the reaction profile. Integrals for the interchanging peaks in the associated <sup>1</sup>H EXSY spectra were obtained and converted into a percentage of the total detected signal. These data were then analysed as a function of the mixing time according to a differential kinetic model.

Table S2: Observed dissociation rate of equatorially bound  $NH_3$  from  $[Ir(H)_2(NHC)(NH_3)_3]Cl$  at 298 K.

Catalyst	Rate of Dissociation / s <sup>-1</sup>
1	1.65 ± 0.02
2	3.20 ± 0.02
3	2.99 ± 0.02
4	6.29 ± 0.05

Table S3: Observed rate of hydride ligand loss from  $[Ir(H)_2(NHC)(NH_3)_3]Cl$  at 298 K.

Catalyst	Rate of Dissociation / s <sup>-1</sup>
1	0.32 ± 0.01
2	0.17 ± 0.01
3	0.74 ± 0.02
4	0.86 ± 0.03

# 7 References

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