Supplementary Information

Utilisation of water soluble iridium catalysts for Signal Amplification by Reversible Exchange (SABRE)

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**PASADENA and ALTADENA**

Para\textsubscript{h}ydrogen incorporation into a sample at high field has been given the name Para\textsubscript{h}ydrogen And Synthesis Allow Dramatically Enhanced Nuclear Alignment (PASADENA). Under these conditions in the corresponding \textsuperscript{1}H NMR spectrum we obtain characteristic out of phase signals. The incorporation of para\textsubscript{h}ydrogen can also occur at low magnetic field. This variation was named Adiabatic Longitudinal Transport After Dissociation Engenders Net Alignment (ALTADENA) due to the adiabatic transfer into a magnetic field after the addition of para\textsubscript{h}ydrogen. The result of this change is that only the lower energy \(\alpha\beta\) or \(\beta\alpha\) spin state is populated (Figure S1). Under PASADENA conditions, the resulting NMR signals appear as two equal intense pairs. An individual resonance therefore features one line in absorption, pointing upwards and a second in emission, pointing downwards (antiphase doublets). Under ALTADENA conditions only two components are observed for each resonance, with different phase.

![Figure S1](image)

**Figure S1:** Schematic representation of the NMR characteristics of reaction products that form from natural abundant hydrogen addition (left) and para\textsubscript{h}ydrogen addition under PASADENA (middle) and ALTADENA (right). The pictures reflect spin configurations while the lower traces correspond to the predicted NMR spectra.

**Instrumentation and procedures**

All NMR measurements were recorded on Bruker Avance III series 400 MHz or 500 MHz systems. NMR samples were prepared in 5 mm NMR tubes that were fitted with a Young’s valve. In order to complete the field dependent polarisation transfer studies a flow system was designed to enable a solution containing the catalyst (in our case complexes 1 and 3) and the ligand (pyridine or acetonitrile) to be polarised using para\textsubscript{h}ydrogen within a reaction chamber outside of the main NMR magnet. This solution was then transferred into the Bruker Avance III series 400 MHz spectrometer for interrogation in a NMR flow probe. Once interrogated, the solution could be returned to a polarising chamber and this process repeated as required. A coil surrounded the reaction chamber such that a magnetic field could be generated in the \(z\) direction. This coil was designed to produce static DC fields in the range of 0 to 150 G.

**General experimental conditions**

All experimental procedures were carried out under dinitrogen by using standard Schlenk techniques or in a MBraun Unilab glovebox. General solvents for synthetic chemistry were dried using an Innovative Technology anhydrous solvent engineering system or were distilled from an appropriate drying agent under \(N_2\) as necessary.

**Sample preparation**

Samples for substrate polarization were prepared in a glove box. The complex was dissolved in a solvent (deuterated or protic or in mixture of them) to get around 9 mM solution. Pyridine (5-10 fold) was then added by eppendorf. For the SABRE – shake method experiments, the resulting solutions were then taken up by syringe and transferred into a Young’s tap capped NMR tube. The sample was then degassed on a high-vacuum line via three ‘cool’-pump-thaw cycles (the sample was cooled to -78 ºC using of acetone-dry ice bath). This NMR tube was filled with 3 bar para\textsubscript{h}ydrogen. For the SABRE – flow method experiments the complexes were dissolved in 3 mL of methanol-\(d_4\) (5 mM) and pyridine (20 or 5 fold) was added by Eppendorf. This solution was then transferred in to a sample vial in a flow probe.

**Polarization step**

The sample was shaken (to replenish the $\textit{p}$-H$_2$ in solution) for approximately 10 seconds in a magnetic field of about 65 G, and then rapidly (within 5 seconds) inserted into the NMR spectrometer, after which NMR spectra were immediately acquired.

**Calculations of enhancement factors**

For calculation of the signal enhancement of the $^1$H NMR signals the following formula was used:

$$E = \frac{S_{pol}}{S_{unpol}}$$

$E =$ enhancement
$S_{pol} =$ signal of polarized sample
$S_{unpol} =$ signal of unpolarized (reference) sample

Experimentally the reference spectra were acquired on the same sample that was used for the hyperpolarized measurements after it had fully relaxed (typical 5-10 minutes at high magnetic field). Reference and polarized spectra were collected using identical acquisition parameters, particularly the receiver gain. The raw integrals of the relevant resonances in the polarized and unpolarized spectra were then used to determine the enhancement level.

**Kinetics of hydride and ligand exchange**

The ligand exchange studies were completed using the EXSY protocol. A selected resonance was probed and the magnetisation flow was followed as a function of the reaction time between zero and 1 second, in steps typically of 0.1 seconds. The intensity data was then simulated using a differential model, bases on a least-mean squares fit to experiment, in order to extract the associated experimental site-exchange rate constants.

**Table S1.** Experimentally determined observed ligand exchange rate constants for 2 in methanol-d$_4$ solution in the 290 - 310 K temperature range.

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>complex</th>
<th>H$_2$ loss (s$^{-1}$)</th>
<th>Hydride exchange (s$^{-1}$)</th>
<th>Pyridine exchange (s$^{-1}$)</th>
<th>MeCN exchange (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>290</td>
<td>2c</td>
<td>0.0138</td>
<td>-</td>
<td>0.025</td>
<td>0.214</td>
</tr>
<tr>
<td>295</td>
<td>2c</td>
<td>0.0286</td>
<td>-</td>
<td>0.050</td>
<td>0.353</td>
</tr>
<tr>
<td></td>
<td>2d</td>
<td></td>
<td>-</td>
<td>0.018</td>
<td>0.150</td>
</tr>
<tr>
<td></td>
<td>2a</td>
<td></td>
<td>-</td>
<td>0.009</td>
<td>0.106</td>
</tr>
<tr>
<td>298</td>
<td>2b</td>
<td>0.0449</td>
<td>0.240</td>
<td>0.022</td>
<td>0.711</td>
</tr>
<tr>
<td></td>
<td>2e</td>
<td></td>
<td>0.057</td>
<td>0.073</td>
<td>0.466</td>
</tr>
<tr>
<td>300</td>
<td>2c</td>
<td>0.0565</td>
<td>0.116</td>
<td>0.097</td>
<td>0.559</td>
</tr>
<tr>
<td></td>
<td>2d</td>
<td></td>
<td>0.225</td>
<td>0.040</td>
<td>0.218</td>
</tr>
<tr>
<td></td>
<td>2a</td>
<td></td>
<td>0.034</td>
<td>0.014</td>
<td>0.195</td>
</tr>
<tr>
<td>305</td>
<td>2c</td>
<td>0.1038</td>
<td>0.235</td>
<td>0.182</td>
<td>0.921</td>
</tr>
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<td>2d</td>
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<td>0.580</td>
<td>0.103</td>
<td>0.342</td>
</tr>
<tr>
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<td>0.101</td>
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<td>0.388</td>
</tr>
<tr>
<td>310</td>
<td>2b</td>
<td>1.380</td>
<td>0.111</td>
<td>2.52</td>
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</tr>
<tr>
<td></td>
<td>2d</td>
<td>1.011</td>
<td>0.118</td>
<td>0.606</td>
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<td></td>
<td>2a</td>
<td>0.230</td>
<td>0.059</td>
<td>0.717</td>
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</tbody>
</table>

Figure S1. Plot of hydride signal enhancement versus time for 2

Table S2. Experimentally determined observed ligand exchange rate constants at 300 K for 2 and 4 in methanol-d$_4$

<table>
<thead>
<tr>
<th>Complex</th>
<th>Hydride exchange (s$^{-1}$)</th>
<th>Pyridine exchange (s$^{-1}$)</th>
<th>MeCN exchange (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>0.507 ± 0.008</td>
<td>0.039 ± 0.004</td>
<td>0.966 ± 0.009</td>
</tr>
<tr>
<td>2b</td>
<td>0.034 ± 0.001</td>
<td>0.0143 ± 0.0004</td>
<td>0.195 ± 0.003</td>
</tr>
<tr>
<td>2c</td>
<td>0.064 ± 0.001</td>
<td>0.097 ± 0.001</td>
<td>0.559 ± 0.006</td>
</tr>
<tr>
<td>2d</td>
<td>0.360 ± 0.005</td>
<td>0.040 ± 0.005</td>
<td>0.218 ± 0.001</td>
</tr>
<tr>
<td>4a</td>
<td></td>
<td>1.23 ± 0.08</td>
<td></td>
</tr>
<tr>
<td>4b</td>
<td></td>
<td>0.171 ± 0.004</td>
<td></td>
</tr>
</tbody>
</table>

Experiments with $^{15}$N labelled pyridine

When using $^{15}$N labelled pyridine instead of normal pyridine we could observe an additional splitting of 19.0 Hz on the hydride NMR signal for the ligand which lies trans to the pyridine molecule, as shown in Figure S2.

Figure S2. Hydride signals of complex 2c in the corresponding $^1$H NMR spectra using normal (lower) and $^{15}$N labelled pyridine (upper).
Field dependent polarisation transfer studies

The reaction chamber contained a solution comprising the Ir-complex (5 mM), the ligand for polarization (5 – 20 fold excess) and 3 mL of the specified deuterated solution. Parahydrogen, prepared by cooling hydrogen gas over charcoal in a copper block at 30 K, was then bubbled through the solution at the pressure of 3 bar for the range of times which was present. The solution was then allowed to settle for 1 s before a single scan 1H NMR spectrum was collected.

The polarization transfer field profile of the absolute values of the total signal enhancement for pyridine in methanol-\textit{d}_{4} solution, catalyzed by the highlighted complex, is shown in Figure S3.

Figure S3. Absolute values of the total signal enhancement of pyridine in methanol-\textit{d}_{4} solution using 2c (upper left), 4a (upper right), 4b (lower left), 4c (lower right) complex with 2 (blue) and 34 (red) fold excesses of pyridine respectively as a function of polarization transfer field.

Figure S4: Polarisation transfer field profiles for the pyridine 1H NMR signal enhancement in the methanol-\textit{d}_{4} solution using 2c (left) and 4a (right), when a 2-fold excess of acetonitrile is present.
**Figure S5**: (left) Polarisation transfer field profiles for the pyridine total $^1$H NMR signal enhancement (fold) in the methanol-$d_4$ and ethanol-$d_6$ solution. (right) PTF profile of the meta proton signal enhancement in the methanol-$d_4$ and ethanol-$d_6$ solution using $[2a] = 5.5$ mM, 20 fold pyridine, 2 fold NCMe, 3 mL solvent.

**Figure S6**: Structure of oxazole and 3-hydroxypyridine.

**Figure S7**: Left: Polarisation transfer field profile under SABRE of oxazole $^1$H NMR signal enhancement in methanol-$d_4$ solution using 2c as the catalyst with a 5 fold excess of oxazole and 2 fold excess of NCMe. red: $H_A$, green: $H_B$ and blue: $H_C$. Right: Absolute value plot of the total proton signal enhancement of oxazole versus polarization transfer field under SABRE.
**Figure S8:** Left: Polarisation transfer field profile under SABRE of oxazole $^1$H NMR signal enhancement in ethanol-$d_6$ solution using 2c as the catalyst with a 5 fold excess of oxazole and 2 fold excess of NCMe. red: $H_A$, green: $H_B$ and blue: $H_C$. Right: Absolute value plot of the total proton signal enhancement of oxazole versus polarization transfer field under SABRE.

**Figure S9:** Left: Polarisation transfer field profile under SABRE of the oxazole $^1$H NMR signal enhancement in methanol-$d_4$ solution using 4a as the catalyst with a 5 fold excess of oxazole and 2 fold excess of NCMe. blue: $H_A$, red: $H_B$ and green: $H_C$. Right: Absolute value plot of the total proton signal enhancement of oxazole versus polarization transfer field under SABRE.

**Figure S10:** Left: Polarisation transfer field profile under SABRE of 3-hydroxypyridine $^1$H NMR signal enhancement in methanol-$d_4$ solution using 2c as the catalyst with a 5 fold excess of 3-hydroxypyridine. blue: $H_A$ and $H_B$ and red: $H_C$. Right: Absolute value plot of the total proton signal enhancement of 3-hydroxypyridine versus polarization transfer field under SABRE.
Figure S11: Polarisation transfer field profile of 3-hydroxypyridine proton signal enhancement in the methanol-$d_4$ solution using 4a as the catalyst with a 5 fold excess of 3-hydroxypyridine.

Figure S12: Absolute values of the total $^1$H NMR signal enhancement of pyridine in methanol-$d_4$ solution using 4a (black) and 5a (white), when a 19-fold excess of pyridine is present.
Synthesis and characterisation

Preparation of the diimine precursor:

\[
\begin{align*}
\text{NH}_2 & \quad \text{NaN}_3, \text{Cul, N,N'-Me}_2\text{en} \\
\text{Cul, N,N'-Me}_2\text{en} \quad \text{DMSO-H}_2\text{O} \quad \text{glyoxal, MeOH} \\
\text{N}_3 & \quad \text{NH}_2
\end{align*}
\]

4-azidoaniline: 4-ido-2,6-dimethylaniline\(^3\) (24.4 g, 98.9 mmol, 1.0 eq.), NaN\(_3\) (12.9 g, 197.9 mmol, 2.0 eq.) and N,N\(^\text{'}\)-dimethylthelyenediamine (1.60 mL, 14.9 mmol, 15 mol%) were dissolved in dmso/water (180 mL/45 mL). Ascorbic acid (1.70 g, 9.9 mmol, 10 mol%) and NaOH (400 mg, 9.9 mmol, 10 mol%) were added and the mixture degassed by argon bubbling for 20 min at 50 °C. Cul (1.90 g, 9.9 mmol, 10 mol%) was then added and the resulting mixture stirred at 50 °C for 4 h. Brine (200 mL) was added and the aqueous layer extracted with 3 × 100 mL of diethyl ether, then dried over MgSO\(_4\) and evaporated under reduced pressure to afford 12.6 g of a brownish oil (77.7 mmol, 79%). \(^1\)H NMR (400 MHz, dmso-d\(_6\), 298 K): \(? 2.07\) (s, 6H, Me), \(4.59\) (s, 2H, NH\(_2\)), \(6.59\) (s, 2H, HAr). \(^1^3\)C\(^{1}\)H NMR (101 MHz, dmso-d\(_6\), 298 K): \(? 17.8\) (CH\(_3\)), \(118.2\) (Carom), \(122.3\) (Carom-N\(_2\)), \(125.8\) (Carom-CH\(_3\)), \(142.2\) (Carom-NH\(_2\)).

N,N\(^\text{'}\)-bis(4-azido-2,6-dimethylphenyl)1,4-diazabuta-1,3-diene: 4-azido-2,6-dimethylaniline (12.6 g, 77.9 mmol, 1.0 eq.) was dissolved in 44 mL of methanol at 50 °C. Glyoxal (30% w/w in water, 5.7 mL, 55 mmol, 0.45 eq.) and acetic acid (0.4 mL, 6.2 mmol, 0.21 eq.) added. The resulting mixture was stirred at room temperature for 4 h. A yellow solid separated. It was filtered and washed with cold methanol to afford, after drying under vacuum, 10.69 g of a yellow powder (30.9 mmol, 80%). \(^1\)H NMR (400 MHz, CDCl\(_3\), 298 K): \(\delta 2.11\) (s, 12H, Me), \(7.19\) (s, 4H, HAr), \(8.02\) (s, 2H, HImine). \(^1^3\)C\(^{1}\)H NMR (101 MHz, CDCl\(_3\), 298 K): \(\delta 18.5\) (CH\(_3\)), \(118.8\) (CHaram), \(128.7\) (Carom-N\(_2\)), \(136.3\) (Carom-CH\(_3\)), \(146.8\) (Carom-N), \(163.7\) (Cimine).

N,N\(^\text{'}\)-bis[2,6-dimethyl-1-[N,N,N-trimethylammonium methyl]-1,2,3,1H-triazol-1-yl]phenylenethane-1,2-diamine dichloride hydrochloride: N,N\(^\text{'}\)-bis[4-azido-2,6-dimethylphenyl]-ethane-1,2-diamine (5.78 g, 16.50 mmol, 1 eq.), N,N,N-trimethylprop-2-yn-1-aminium chloride\(^4\) (5.50 g, 41.2 mmol, 2.5 eq.) and [CuCl(SIMes)(4,7-

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cold ethyl acetate, and cold diethyl ether/aceton v/v 1:1. 3.160 g of a yellow powder (6.89 mmol, 92%)
was obtained. 1H NMR (400 MHz, dmso-d_{6}, 298 K): δ 2.23 (s, 12H, Me), 4.61 (d, 4H, J = 5.3 Hz, CH_{2}), 5.53 (t, 2H, J = 5.3 Hz, OH), 7.70 (s, 4H, H_{para}), 8.28 (s, 2H, H_{meta}), 8.63 (s, 2H, H_{ortho}). 13C NMR (100 MHz, dmso-d_{6}, 298 K): 17.7 (CH_{3}), 54.6 (CH_{2}), 119.8 (CH=arom). 127.5 (CH= triazole). Very poor solubility in common NMR solvents prevented the recording of a standard 13C NMR spectrum. HRMS (EI): calcd. for \text{C}_{32}\text{H}_{32}\text{N}_{12}\text{O}_{12}: [M+H]^{+}: 459.2252. Found: 459.2233.

\text{N,N′-bis(4-(4-hydroxymethyl)-1,2,3-1H-triazolyl)-2,6-dimethylphenyl} imidazolium chloride (IMesOH.HCI, s3c) and \text{N,N′-bis(4-(4-hydroxymethyl)-1,2,3-triazolyl)-2,6-dimethylphenyl} imidazolium chloride (IMesH chloride, 459.2233.

Characterization of iridium complexes

NMR data for \text{[Ir(H)](NCMe)(py)(IMes)(tpptps)} BF_{4} (2b): 1H NMR (400 MHz, methanol-d_{4}, 298 K): δ -21.97 (dd, 1H, J_{HP} = 18.4 Hz, J_{HH} = 7.3 Hz), δ -21.07 (dd, 1H, J_{HP} = 16.6 Hz, J_{HH} = 6.7 Hz) 1.73 (s, 3H, CHCH_{3}), 1.94 (s, 6H, -CH_{2} of IMes), 2.09 (s, 6H, -CH_{2} of IMes), 2.37 (s, 6H, -CH_{2} of IMes), (s, 4H, -CH=), 6.76 (t, 2H, meta proton of pyridine), 7.01 (s, 2H, -CH=), 7.08 (s, 2H, -CH=), 7.13 (t, 4H, tpptps), 7.25 (t, 4H, tpptps), 7.34 (t, 2H, meta proton of pyridine), 7.51 (s, 2H, -CH=), 7.62 (s, 2H, -CH=), 7.66 (t, 1H, para proton of pyridine), 7.75 (t, 4H, tpptps), 7.97 (d, 2H, ortho proton of pyridine). 1H NMR (162 MHz, MeOD, 298 K): δ 24.3 ppm.

NMR data for \text{[Ir(H)](NCCH_{3})(py)(IMes)(tpptps)} BF_{4} (2c): 1H NMR (400 MHz, methanol-d_{4}, 298 K): δ -22.17 (dd, 1H, J_{HP} = 18.5 Hz), δ -21.05 (dd, 1H, J_{HP} = 16.3 Hz), 1.61 (s, 3H, NCHCH_{3}), 1.89 (s, 6H, -CH_{2} of IMes), 2.11 (s, 6H, -CH_{2} of IMes), 2.39 (s, 6H, -CH_{2} of IMes), (s, 4H, -CH=), 6.76 (t, 2H, meta proton of pyridine), 6.95 (s, 2H, -C=), 1.73 (s, 3H, NCCCH_{3}), 7.07 (t, 4H, tpptps), 7.10 (s, 2H, -CH=), 7.16 (t, 4H, tpptps), 7.25 (s, 2H, IMes), 7.30 (m, 6H, tpptps), 7.51 (t, 1H, para proton of pyridine), 7.67 (t, 2H, tpptps), 7.77 (d, 2H, ortho proton of pyridine). 1H NMR (162 MHz, methanol-d_{4}, 298 K): δ 18.27 ppm.

NMR data for \text{[Ir(H)(NCCH_{3})(py)(IMes)(tpptps)]} BF_{4} (2d): 1H NMR (400 MHz, methanol-d_{4}, 298 K): δ -22.23 (dd, 1H, J_{HP} = 19.1 Hz), δ -21.08 (dd, 1H, J_{HP} = 16.2 Hz), 1.61 (s, 3H, NCHCH_{3}), 1.89 (s, 6H, -CH_{2} of IMes), 2.11 (s, 6H, -CH_{2} of IMes), 2.39 (s, 6H, -CH_{2} of IMes), (s, 4H, -CH=), 6.78 (t, 2H, meta proton of pyridine), 6.83 (t, 1H, tpptps), 6.95 (s, 2H, -C=), 1.73 (s, 3H, NCCCH_{3}), 7.19 (t, 4H, tpptps), 7.26 (s, 2H, IMes), 7.30 (m, 6H, tpptps), 7.51 (t, 1H, para proton of pyridine), 7.55 (d, 1H, tpptps), 7.62 (d, 1H, tpptps), 7.71 (d, 2H, ortho proton of pyridine). 1H NMR (162 MHz, methanol-d_{4}, 298 K): δ 19.82 ppm.

NMR data for \text{[Ir(H)(pyridine)_{3}(SIMesCh)]}^{+} (4a): 1H NMR (400 MHz, methanol-d_{4}, 298 K): δ -22.54 (2H, hydrides), 2.57-2.53 (br, 2H, CH(CH_{3})_{2}), 2.70 (m, 4H, CH(CH_{3})_{2}), 4.89 (d, J_{HH} = 5.95 Hz), 5.29 (br, 2H, OH), 7.14 (t, 1H, para proton, py_{pa}), 7.65 (t, 2H, meta proton py_{ma}), 7.74 (t, 1H, para py_{pa}), 7.77 (s, 2H, H_{ortho}), 7.83 (s, 2H, H_{ortho}), 7.95 (s, 2H, NCH-
NMR data for [Ir(H)(pyridine)$_2$(SIMesTrimet)]$^+$ (4b) : $^1$H NMR (400 MHz, methanol-d$_4$, 298 K): δ -22.72 (2H, hydrides), 2.65 (s, 12H, CH(CH$_3$)$_2$), 3.29 (12H, (CH$_3$)$_2$-N$^+$), 4.16 (4H, -CH$_2$-imid), 4.74 (s, 4H, N'-CH$_2$-C$_{triazol}$), 6.71 (t, 2H, meta proton py$_{eq}$), 7.71 (t, 1H, para proton py$_{eq}$), 7.96 (s, 2H, -CH=, H$_{Ar}$), 8.20 (d, 2H, ortho proton py$_{eq}$), 8.751 (d, 2H, ortho proton py$_{ax}$), 8.80 (s, 2H, H$_{triazole}$), 9.06 (s, 1H, H$_{triazole}$).

NMR data for [Ir(H)$_2$(pyridine)$_3$(IMesOH)]$^+$ (4c) : $^1$H NMR (400 MHz, methanol-d$_4$, 298 K): δ -22.66 (2H, hydrides), 8.78 (d, 2H, ortho proton py$_{ax}$), 8.35 (d, 2H, ortho proton py$_{eq}$), 8.49 (s, 2H, -CH=, imid), 8.31 (t, 1H, para proton py$_{ax}$), 8.09 (t, 2H, meta proton py$_{ax}$ and 2H, -CH=, triazol), 7.80 (s, 2H, -CH=, H$_{trim}$), 7.67 (t, 1H, para proton py$_{eq}$), 7.25 (t, 2H, meta proton py$_{eq}$), 4.85 (s, 4H, -CH$_2$-C$_{triazol}$), 2.84 (4H, -CH$_2$-imid), 2.30 (s, 12H, CH(CH$_3$)$_2$).

NMR data for [Ir(H)$_2$(NCMe)(pyridine)$_2$(SIMesCh)]$^+$ (5a) : $^1$H NMR (400 MHz, methanol-d$_4$, 298 K) δ -21.15 (d, $J_{HH}$ = 5 Hz, trans to NCMe) and -22.26 (d, $J_{HH}$ = 5 Hz, trans to pyridine).

NMR data for [Ir(H)$_2$(NCMe)(pyridine)$_2$(SIMesTrimet)]$^+$ (5b) : $^1$H NMR (400 MHz, methanol-d$_4$, 298 K) δ -21.24 (d, $J_{HH}$ = 5 Hz, trans to NCMe) and -22.38 (d, $J_{HH}$ = 5 Hz, trans to pyridine).

NMR data for [Ir(H)$_2$(NCMe)(pyridine)$_2$(IMesOH)]$^+$ (5c) : $^1$H NMR (400 MHz, methanol-d$_4$, 298 K) δ -21.06 (d, $J_{HH}$ = 5 Hz, trans to NCMe) and -22.17 (d, $J_{HH}$ = 5 Hz, trans to pyridine).