

# Electronic Supporting Information (ESI)

## Ligand effects of NHC-iridium catalysts for Signal Amplification By Reversible Exchange (SABRE)

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### S1 General procedures

Unless stated otherwise, all experimental procedures were performed under an atmosphere of either nitrogen or argon using standard Schlenk line techniques or an MBraun Unilab glovebox. General solvents for synthetic chemistry were dried using an mBraun SPS 800 solvent purification system and were degassed prior to use. The iridium dimer was purchased from Strem Chemicals or Sigma-Aldrich. All ligands were obtained from Sigma-Aldrich, only 1,3-diiisopropylimidazolium tetrafluoroborate was ordered from TCI. Deuterated solvents ( $d_4$ -methanol,  $CDCl_3$ ) were obtained from Cambridge Isotopes. All purchased chemicals were used as supplied.

A Bruker Avance 500 MHz NMR and a Varian Inova 500 MHz NMR spectrometer were used for NMR measurements. NMR samples were prepared in 5 mm Wilmad quick pressure valve NMR tubes.

### S2 Synthetic procedures and determination of electronic and steric properties

All  $[Ir(NHC)(COD)Cl]$  and  $[Ir(NHC)(CO)_2Cl]$  metal complexes were prepared according to published methods.<sup>1,2</sup> The buried volume, %  $V_{bur}$ , was calculated with SambVca, using the crystal structure of the  $[Ir(NHC)(CO)_2Cl]$  complexes.<sup>3</sup> The following settings were used: sphere radius 3.5 Å, Mesh spacing 0.05, omit H atoms, Bondi radii scaled by 1.17, and the distance from the center of the sphere (M-(NHC)) was derived from the X-ray structure.<sup>1</sup> The infrared carbonyl stretching frequencies ( $\nu_{CO}$ ) of  $[Ir(NHC)(CO)_2Cl]$  complexes were measured on a Tensor 27 Bruker FT-IR spectrometer and were used to quantify the modified Tolman Electronic Parameter analogue of complexes **3** and **4**.<sup>1</sup>

### S3 Performing SABRE experiments

A typical NMR experiment was performed by adding 33  $\mu$ l pyridine (100 mM) and 10% catalyst (10 mM) to a total volume of 4 ml deuterated methanol in a vial. Hydrogen was cooled to 36 K in the presence of a conversion catalyst ( $Fe_2O_3$ ) in a *para*-hydrogen generator from Bruker (BPHG90), resulting in approximately 92.5 % *p*- $H_2$ . Sample polarization and transport was controlled by means of a prototype Bruker polarizer (BPHP) in the following steps: The sample (3.1 mL) was pneumatically transferred to a mixing chamber in the polariser which was positioned in a polarizing magnet underneath the NMR magnet. The formed parahydrogen was delivered to the mixing chamber and bubbled through the sample at a pressure of 3 bar. The stray field underneath the NMR magnet was determined to be -120 Gauss (-12 mT) relative to the polarization magnet (resulting in polarization fields ranging from +10 to -230 Gauss). The sample was then transferred by a stopped-flow system to a 200 MHz Bruker Avance spectrometer, and the spectrum was recorded in a single scan. The sample was then transferred back and forth between the polarization magnet and the NMR to record a series of 25 measurements at different polarization fields. After a series of measurements, an automatic washing process cleaned the polarizer. However, we observed that approximately 0.5-1.0 mL of cleaning solvent (protonated methanol) was left in the tubing. This amount of solvent is not released before sample charging and is therefore mixed with the sample, thus lowering the actual measured concentrations of pyridine (~ 88.7 mM) and catalyst (~8.7 mM).

### S4 Calculation of enhancement factors

We calculated the enhancement of  $^1H$ -NMR signals using the following equation:

$$Eq. 1: \text{Enhancement factor} = \frac{SNR_{hyp}}{SNR_{ref}} = \frac{Signal_{hyp}}{Signal_{ref}} \times \frac{Noise_{ref}}{Noise_{hyp}}$$










Experimentally, the reference spectra were acquired using the same sample as for the hyperpolarized measurement after thermal equilibrium was reached. Reference and polarized spectra were collected using identical acquisition parameters, in particular the receiver gain, and with a single excitation in both cases. The noise was determined by calculating the root mean square of the last 500 points of the spectra, where no signal was present. The noise of all hyperpolarized spectra was comparable ( $0.0108 \pm 0.0003$ ). The raw integrals of the relevant resonances in the polarized and unpolarized spectra were used to determine the enhancement level. From duplicate experiments 20 times after each other with the same mixing field and *p*- $H_2$  pressure the estimated error in the determination of the enhancement levels is 5%.

### S5 Determination of pyridine and dihydrogen exchange rates for $[Ir(NHC)(H)_2(Py)_3]$ complexes

NMR tubes containing 1 mM catalyst and 10 mM pyridine in deuterated methanol were prepared in a glovebox. Air was removed from the NMR tube, and hydrogen gas was added to a pressure of 3 bar. The NMR tubes were vigorously shaken before inserting them into the NMR spectrometer. The *ortho* peak of free pyridine (8.53 ppm) was inverted by using a selective inversion recovery experiment on a 500 MHz Varian spectrometer. A series of 20 of such experiments was performed, varying the waiting time between the selective  $180^\circ$  pulse and the strong  $90^\circ$  pulse from  $1 \times 10^{-6}$  to 20 seconds. After recording the free induction decay (FID) and processing the spectra, the integrals of the free and bound *ortho* peaks of pyridine were extracted from the data, resulting in 40 data points per catalyst. The recorded data were fitted to the exchange equation using Origin version 8.5.1. By using the previously measured  $T_1$  time of free pyridine (25.7 s), pyridine exchange rates could be determined for the iridium complexes. During these experiments we observed the formation of H-D gas<sup>4</sup> and also the deuteration of pyridine especially on the *ortho* position.

## S6 Overview experimental data









Table S1: Overview experimental data

No	Abbreviation	Ligand	%V <sub>Bur</sub>	ν <sub>CO(avg)</sub> (cm <sup>-1</sup> )	Max S.E. *	Polari- zation (%)	Pol. Field (G) *	Exchange rate (s <sup>-1</sup> ) Py <sup>a</sup>	
								Rate	Error <sup>c</sup>
3	SImNPr <sub>2</sub>		28.5	2024.5	43	0.07	70	4.5	0.18
4	ImNPr <sub>2</sub>		26.4	2024.1	72	0.12	110	1.6	0.07
5	ItBu		35.5	2022.3	11	0.02	120	3.2	0.4
6	SIPr		35.7	2024.9	103	0.17	80	116	9
7	IPr		33.6	2023.9	125	0.20	70	34	2.3
8	Icy		27.1	2023.0	18	0.03	90	4.3	0.6
9	SIMes		32.7	2024.6	369	0.60	90	49	5.6
10	IMes		31.6	2023.1	680	1.11 1.16 <sup>d</sup>	70	9.0 10.2 <sup>b</sup>	0.31 0.63
11	Iad		36.1	2021.6	n.d.	n.d.	n.d.	n.d.	

\* Max. S.E. = Maximal Signal Enhancement, Pol. Field = Prepolarization Field (Gauss); <sup>a</sup> Measurement at 298 K; <sup>b</sup> Measurement at 300 K; <sup>c</sup> Fitting error in Origin; <sup>d</sup> at 400 MHz and 300 K, reported by Duckett *et al.*<sup>5</sup>

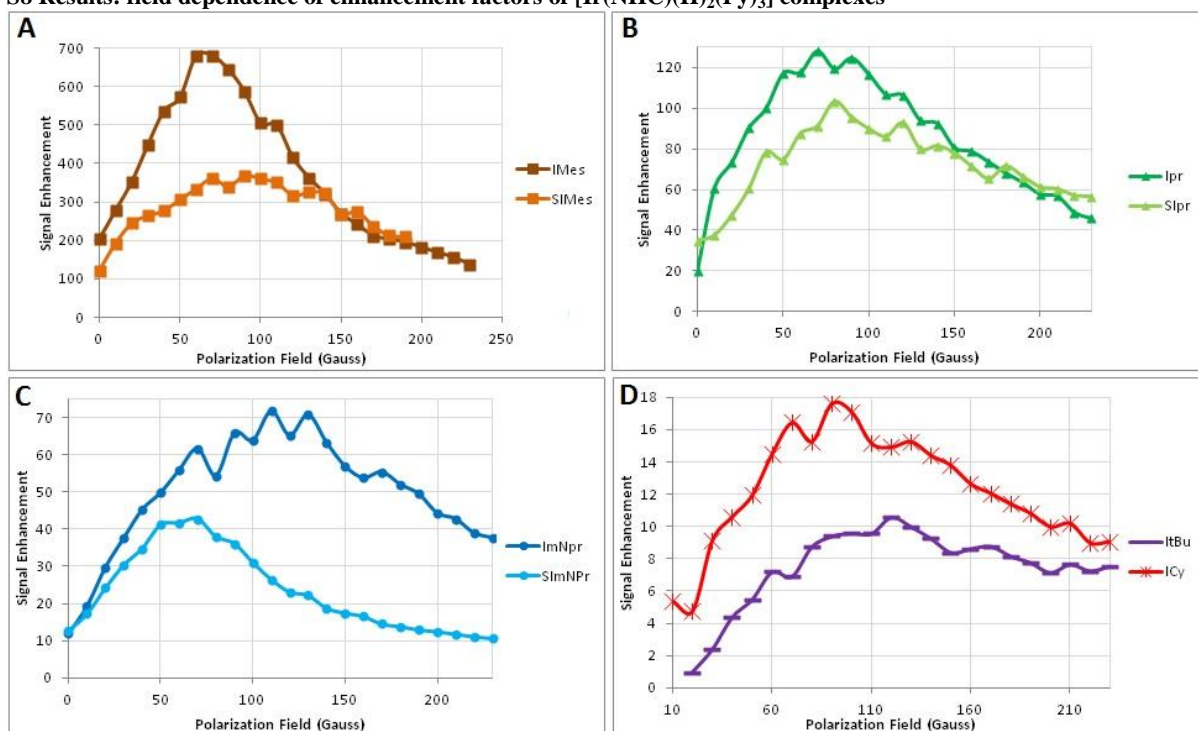
## S7 NMR Data for [Ir(NHC)(H)<sub>2</sub>(Py)<sub>3</sub>] complexes in CD<sub>3</sub>OD at 298 K

Table S2: Chemical shifts of pyridine and hydrides for [Ir(NHC)(H)<sub>2</sub>(Py)<sub>3</sub>] complexes in CD<sub>3</sub>OD at 298 K

No	Abbreviation	Ligand	Chemical Shift <sup>a</sup>						
			Ir-H	<i>trans</i> -Py <sup>b</sup>			<i>cis</i> -Py <sup>b</sup>		
				ortho	para	meta	ortho	para	meta
3	SImNPr		-22.57	8.73	7.92	7.26 <sup>c</sup>	8.23	7.98	7.25 <sup>c</sup>
4	ImNPr		-22.57	8.72	7.90	7.24 <sup>c</sup>	8.30	7.98	<sup>d</sup>
5	ItBu		-22.60	8.17	<sup>d</sup>	<sup>d</sup>	<sup>d</sup>	<sup>d</sup>	<sup>d</sup>
6	SIPr		-22.49	8.16	7.77	<sup>d</sup>	<sup>d</sup>	7.69	<sup>d</sup>
7	IPr		-22.59	8.20	7.73	7.12 <sup>c</sup>	7.89	7.68	6.98 <sup>c</sup>
8	Icy		-22.53	8.73	7.93	7.26 <sup>c</sup>	8.30	7.99	7.19 <sup>c</sup>
9	SIMes		-22.74	8.29	7.75	7.09	7.95	7.64	6.94
10	IMes		-22.82	8.32	7.75	7.09	8.03	7.65	6.95

<sup>a</sup> in ppm <sup>b</sup> *trans*-Py = py *trans* to H, *cis*-Py = py *cis* to H. <sup>c</sup> Uncertain assignment due to overlapping signals. <sup>d</sup> Assignment not possible due to overlapping signals <sup>e</sup> Free pyridine σ 8.53, 7.85, 7.44

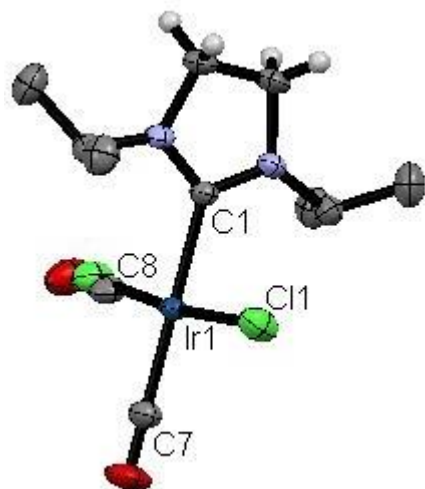
### S8 Results: field dependence of enhancement factors of $[\text{Ir}(\text{NHC})(\text{H})_2(\text{Py})_3]$ complexes



**Fig. S1:** Signal enhancement of pyridine with different polarization catalysts at various polarization fields. A Catalysts **9** SIMes and **10** IMes. B Catalysts **6** SIpr and **7** Ipr. C Catalysts **3** SImNPr and **4** ImNPr. D Catalysts **5** ItBu and **8** ICy. The plot depicts clearly the difference between the saturated and unsaturated carbene ligands.

### S9 X-ray structure of **3** $[\text{Ir}(\text{SImNPr})(\text{CO})_2\text{Cl}]$

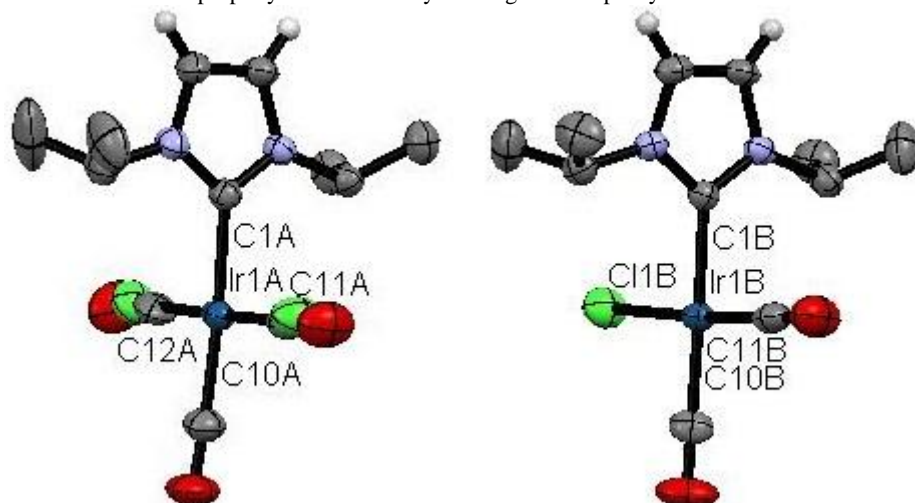
Crystals of **3** were obtained by preparing a saturated solution of  $[\text{Ir}(\text{SImNPr})(\text{CO})_2\text{Cl}]$  in dichloroethane. Next, vapour diffusion of pentane into the solution yielded the crystals after a week at room temperature. A single crystal was mounted in air on a glass fibre. Intensity data were collected at  $-65^\circ\text{C}$ . A Nonius KappaCCD single-crystal diffractometer was used ( $\varphi$  and  $\omega$  scan mode) using graphite monochromated Mo-K $\alpha$  radiation. Unit cell dimensions were determined from the angular setting of 348 reflections. Intensity data were corrected for Lorentz and polarization effects. SADABS multiscan correction<sup>6</sup> was applied. The structure was solved by the program DIRDIF<sup>7</sup> and was refined with standard methods using SHELXL97<sup>8</sup> with anisotropic parameters for the nonhydrogen atoms. All hydrogens were placed at calculated positions and were refined riding on the parent atoms. The molecule shows static disorder: the chlorine and one of the CO ligands partly occupy the same positions. This disorder could properly be described by refining the occupancy factors for the atoms involved.



**Fig. S2:** ORTEP plot of the complex **3**. Ellipsoids are set at 50 % probability; most hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles ( $^\circ$ ): C1–Ir1 2.076, Ir1–Cl1 2.331, Ir1–C7 1.901, Ir1–C8 1.826, C1–Ir1–Cl1 86.54, C1–Ir1–C8 89.9

### S10 X-ray structure of **4** [Ir(ImNPr)(CO)<sub>2</sub>Cl]

X-ray quality crystals were obtained by slow evaporation of a saturated pentane solution. A single crystal was mounted in air on a glass fibre. Intensity data were collected at -65 °C. A Nonius KappaCCD single-crystal diffractometer was used ( $\phi$  and  $\omega$  scan mode) using graphite monochromated Mo-K $\alpha$  radiation. Unit cell dimensions were determined from the angular setting of 462 reflections. Intensity data were corrected for Lorentz and polarization effects. SADABS multiscan correction<sup>6</sup> was applied. The structure was solved by the program DIRDIF<sup>7</sup> and was refined with standard methods using SHELXL97<sup>8</sup> with anisotropic parameters for the nonhydrogen atoms. All hydrogens were placed at calculated positions and were refined riding on the parent atoms. There are two independent molecules in the asymmetric unit. One of these molecules shows static disorder: the chlorine and one of the CO ligands partly occupy the same positions. This disorder could properly be described by refining the occupancy factors for the atoms involved.



**Fig. S3:** ORTEP plot of the complex **3**. Ellipsoids are set at 50 % probability; most hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): C1B–Ir1B 2.069, Ir1B–C11B 2.345, IRB1–C10B 1.881, IR1B–C11B 1.840, C1B–Ir1B–C11B 87.53, C1B–IRB–C11B 89.37.

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