SUPPLEMENTARY MATERIAL FOR THE ARTICLE

Spin Polarization Transfer Mechanisms of SABRE: a magnetic field dependent study

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This Supplementary Material file contains: NMR spectra of SABRE complexes; TOCSY spectra; EXSY spectra; high-field SABRE spectra; NMR parameters of SABRE complexes used in simulations.

Before starting with the SABRE experiments we performed a systematic NMR study of the complexes, which are involved in the formation of the SABRE effect.

Figure 1S shows the NMR spectra of complexes with the Imes catalyst. First, we have taken the spectrum of the ImesCOD pre-catalyst (complex **1**); addition of Py results in the formation of complex **3** as indicated by the single bound Py (see Scheme 2 in the main text). Then, addition of H_2 results in formation of complex **2** (*cf.* Ref. [1] and Scheme 2). In the spectrum obtained before bubbling one can see two forms of pyridine, bound Py (less intense signals) and free Py in solution, hereafter denoted as fPy (more intense signals). In the spectrum obtained after bubbling there are signals from three Py species, and each of them has NMR lines corresponding to the *ortho*-, *para*- and *meta*-protons. The most intense signals correspond to fPy; the other two species are the Py molecules bound to the complex corresponding to the equatorial and axial Py, denoted as ePy, and aPy, respectively. When p-H_2 is used instead of thermally polarized H_2 it is possible to observe NMR signals from intermediate **4** (see Figure 5S). The NMR linewidths of aPy are narrower than those of ePy indicating that fPy mainly exchanges with ePy rather than with aPy; this is also supported by our TOCSY data, see Figures 2S-4S. Other lines are coming from H_2 dissolved in methanol (at approximately 4.6 ppm) and Ir-HH (at –22.7 ppm), see Figure 1S, bottom trace.

Likewise, NMR spectra a sample prepared by mixing of Crabtree’s catalyst **5** with pyridine in CD_3OD were obtained before (top, complex **5**) and after bubbling (bottom, complex **6**) normal H_2 gas through the solution, see Figure 6S. In the NMR spectrum there are now signals present from three different forms of Py: fPy, ePy and aPy. As in the case of the Imes catalyst one can see the signal of dissolved H_2; there is a signal of Ir-HH.

The two hydrogen positions undergo exchange, which is demonstrated by EXSY experiments, see Figure 7S.

Finally, we show SABRE spectra obtained at a high polarization field of 16.4 T, see Figure 8S.

References

[1] M.J. Cowley, R.W. Adams, K.D. Atkinson, M.C.R. Cockett, S.B. Duckett, G.G.R. Green, J.A.B. Lohman, R. Kerssebaum, D. Kilgour, R.E. Mewis, Iridium N-Heterocyclic Carbene Complexes as Efficient Catalysts for Magnetization Transfer from para-Hydrogen, J. Am. Chem. Soc., 133 (2011) 6134-6137.

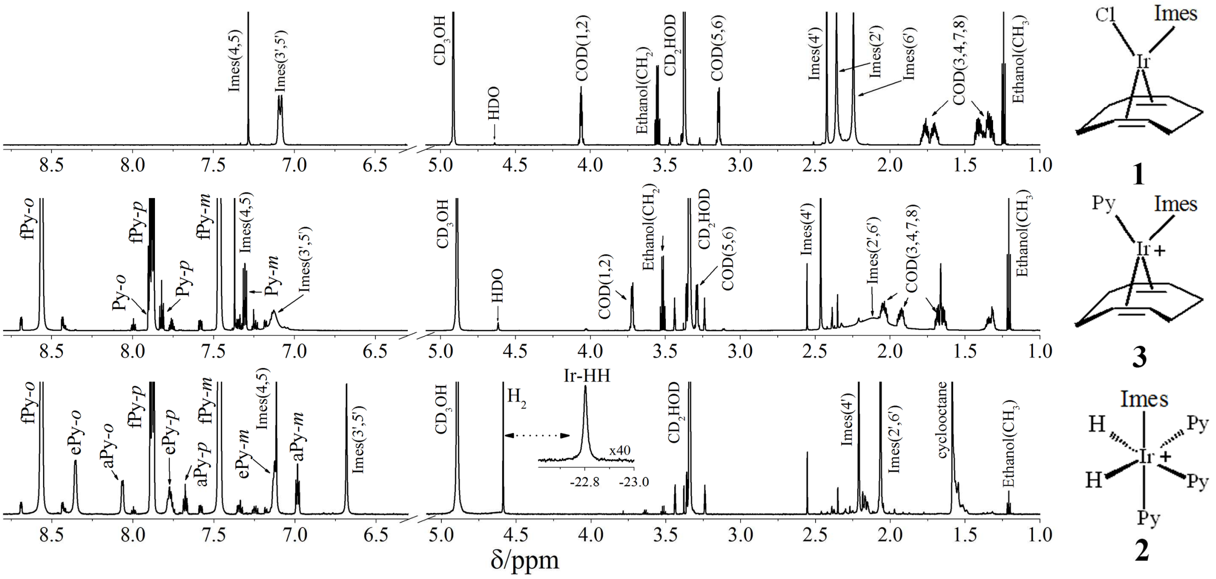

Figure 1S. 700 MHz NMR spectra of complex **1** (top), complex **3** (middle) and complex **2** (bottom), see Scheme 2. Complex **3** is formed after adding Py (60 mM) to complex **1** (4 mM); bubbling with H_2 (for about 5 minutes) results in formation of complex **2**. Here ePy refers to the two equatorial Py coordinated by Ir, aPy is the axial Py, Py stands for bound Py in complex **3**, fPy is free Py in the solvent bulk; Ir-HH are the hydride protons of complex **2** and H_2 is hydrogen in the bulk. Spectral assignment has been done by using the TOCSY technique. The peak of Ir-HH at −22.8 ppm is shown in the insert.

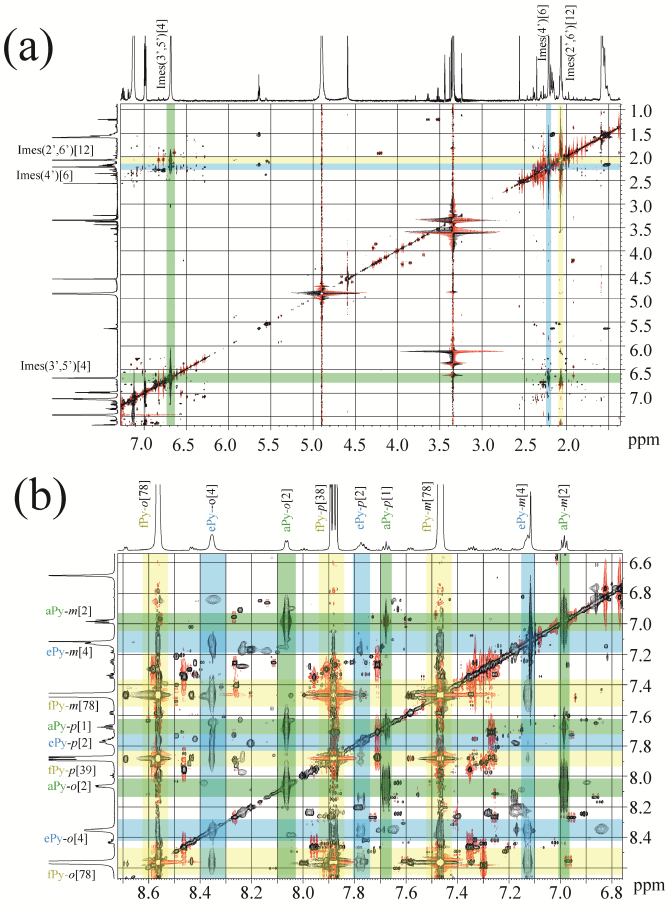

Figure 2S. Two-dimensional TOCSY spectrum of complex **2** taken at 700 MHz. Here (a) shows the 7.5-1 ppm spectral region and (b) shows the 8.7-6.8 ppm region. Cross-peaks belonging to different Py species are marked with different color: yellow for fPy, light blue for ePy and green for aPy. Peak assignments are given in the 1D spectra. The presence of the TOCSY cross-peak between fPy-*o* and ePy-*o* and its absence between fPy-*o* and aPy-*o* is an indication that fPy mainly exchanges with ePy.

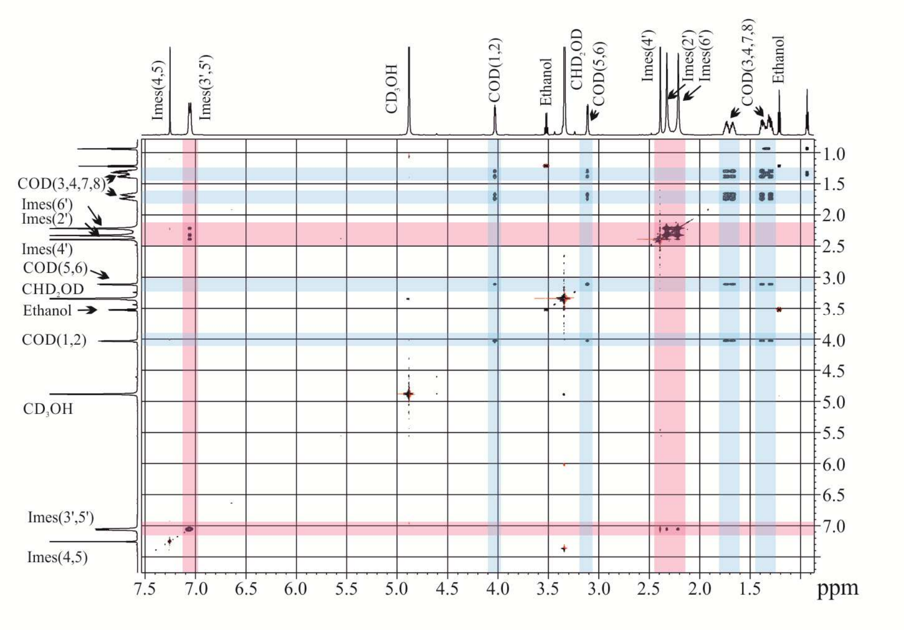

Figure 3S. Two-dimensional TOCSY spectrum of complex **1** taken at 700 MHz before bubbling the H_2 gas and adding pyridine. Peak assignments are given in the 1D spectra. Ethanol signals are due to impurities from the synthesis of Imes.

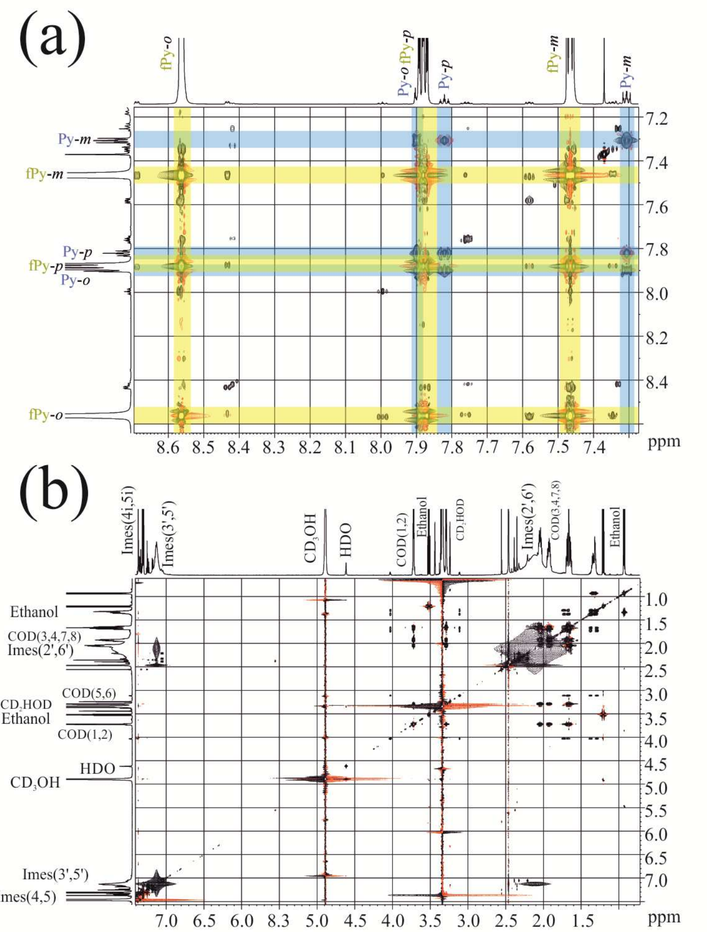

Figure 4S. Two-dimensional TOCSY spectrum of complex **3** taken at 700 MHz. The sample contains Py (60 mM) and complex **1** (4 mM) in CD_3OD. The spectrum was taken for complex **3** before bubbling by H_2. Here (a) shows the 8.7-7.3 ppm region and (b) shows the 7.5-0.5 ppm region. Peak assignments are given in the 1D spectra. Cross-peaks belonging to different Py species are marked with different color: yellow for fPy, light blue for bound Py. Peak assignments are given in the 1D spectra.

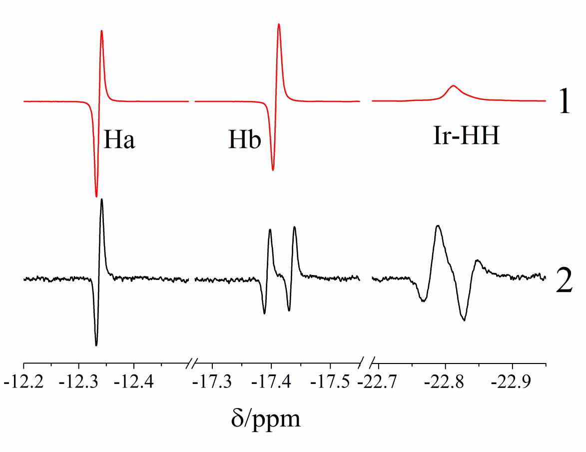

Figure 5S. NMR spectrum recorded at 9.6 T after 30 seconds of bubbling by p-H_2 the sample containing Py (60 mM) and complex **1** (4 mM) in CD_3OD. Two anti-phase doublets are seen in the hydride spectral region corresponding to the two hydride protons of the intermediate complex **4**; the singlet line at − 22.8 ppm corresponds to complex **2**. Trace 1 (red) shows the spectrum obtained for Py with nitrogen in natural abundance; Trace 2 (black) shows the spectrum for ^{15}N-labelled Py (resulting in additional splitting of NMR lines of the Hb proton). The different J_{NH}-couplings in **4** indicate that in this complex the two protons originating from p-H_2 occupy non-equivalent positions. This symmetry breaking is a pre-requisite for observing PHIP spectra.

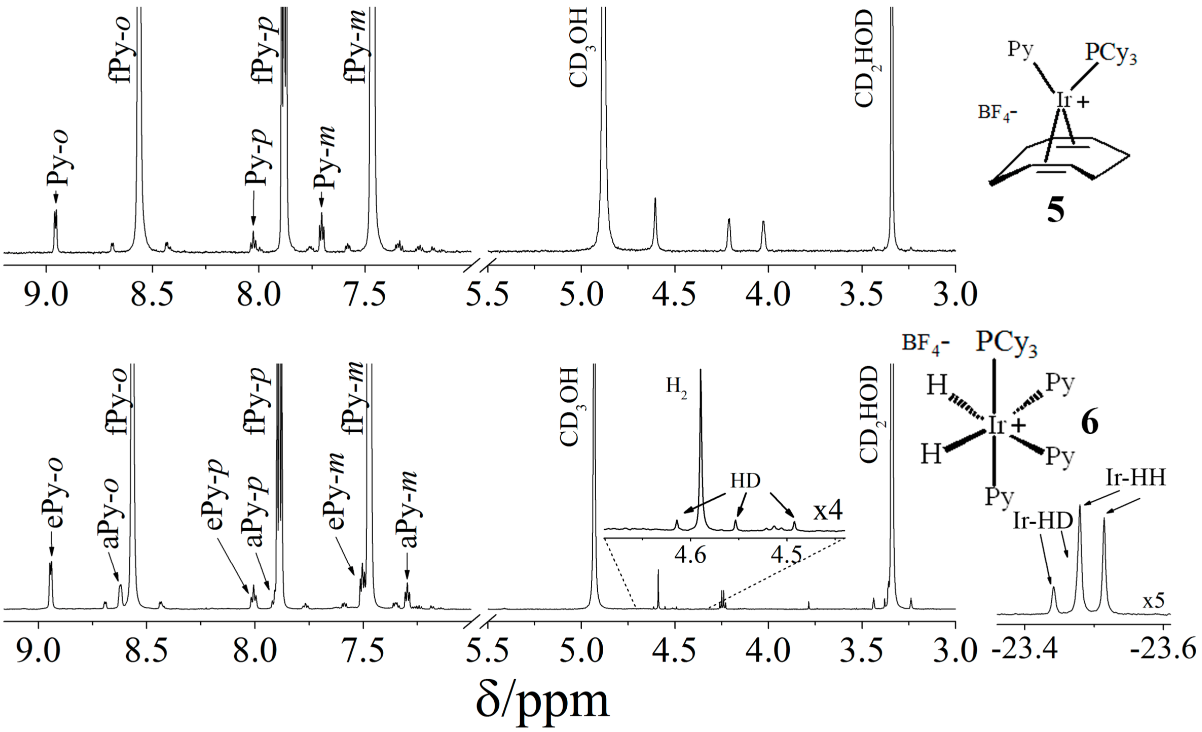

Figure 6S. (Top) 700 MHz ^{1}H NMR spectrum of Crabtree's catalyst **5** (4 mM) and Py (60 mM) in CD_3OD before bubbling by H_2. Here, Py refers to Py molecules bound to Iridium and fPy refers to Py in the bulk; -*o*, -*m*, -*p* stand for *ortho*, *meta* and *para* positions. (Bottom) 700 MHz NMR spectrum of complex **6** (see Scheme 2), which is formed by bubbling thermally polarized H_2 gas through the solution. Here ePy refers to two equatorial Py's coordinated by Ir, aPy is the axial Py, Ir-HH (Ir-HD) are the hydride protons of complex **6** and H_2 (HD) is hydrogen in the bulk. Spectral assignment has been done by using the TOCSY technique in the same way as for the Imes complexes.

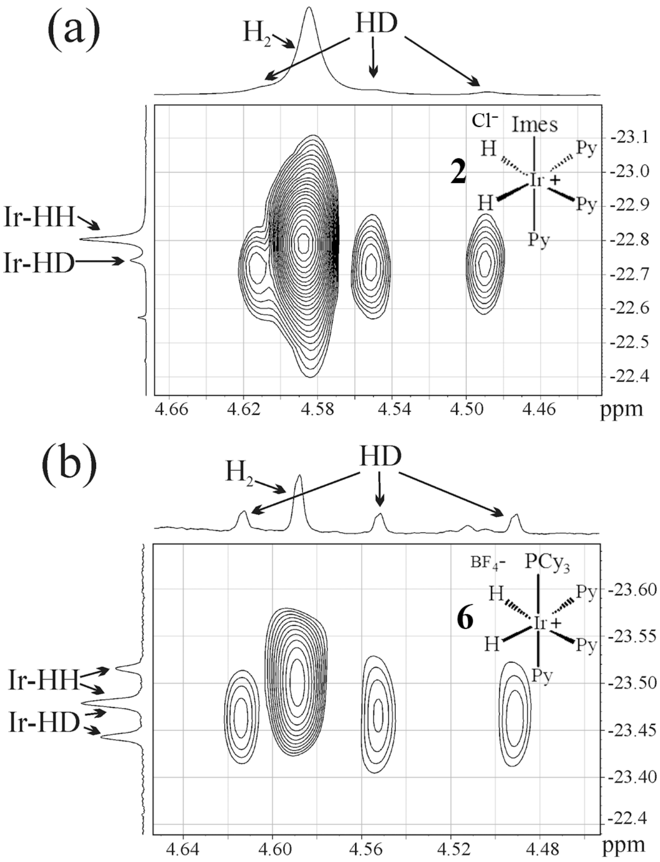

Figure 7S. Cross-peaks in two-dimensional EXSY spectra of complex **2** (a) and complex **6** (b). Spectra are taken at 700 MHz; peak assignments are given in the 1D spectra. The strongest peak corresponds to exchange between Ir-HH and free H_2; three small cross-peaks are coming from exchange between free HD and Ir-HD. The J-coupling between the proton and deuterium in HD is about 43 Hz resulting in the splitting of the HD peak. Here Ir-HH and Ir-HD denote the protonated and deuterated form of H_2 in the SABRE complexes, respectively.

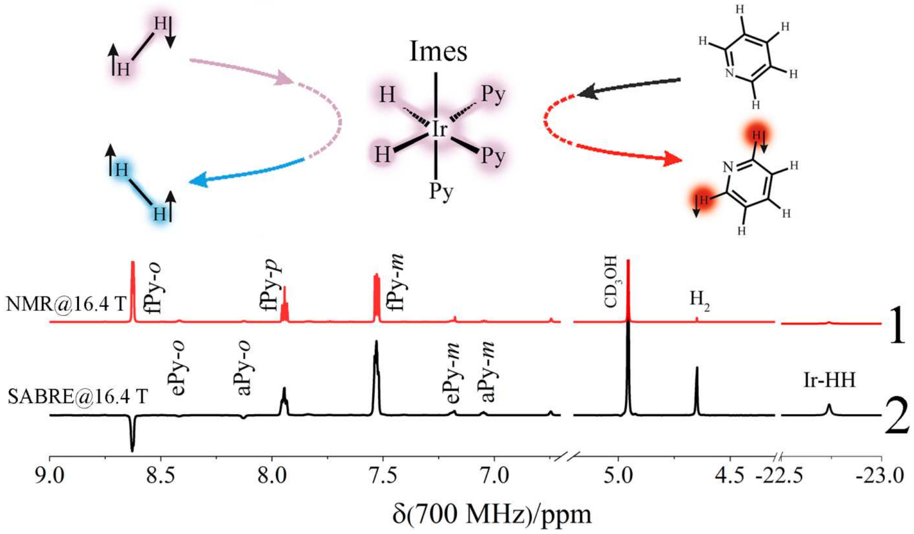

Figure 8S. Thermal spectrum of complex **2** obtained at 16.4 Tesla (spectrum 1) and high-field SABRE spectrum measured at 16.4 Tesla (spectrum 2); the spectra were taken with a $\pi/2$ RF-pulse Signal assignment is given in the spectra.

Table 1S. Chemical shifts and J-coupling in the active form of the Crabtree's catalyst with pyridine.

J/Hz	Ir-H^1	Ir-H^2	Ortho1	Ortho2	Meta1	Meta2	Para
Ir-H^2	-7		-	-	-	-	-
Ortho1	3	0.3		-	-	-	-
Ortho2	1	1	-0.11		-	-	-
Meta1	-0.3	-	4.98	0.97		-	-
Meta2	0.9	0.6	0.97	4.98	1.41		-
Para	-		1.79	1.79	7.66	7.66	
^{31}P	23.4		1	2	0.4	0.6	-
δ/ppm	Ir-H$_2$		Ortho		Meta		Para
Crabtree [H$_2$**P**Ir–aPy]	-23.4		8.682		7.357		7.969
Crabtree [H$_2$**P**Ir–ePy]			9.00		7.565		8.067
Crabtree [fPy]	-		8.626		7.532		7.947

Table 2S. Chemical shifts and J-coupling in the active form of the Imes catalyst with pyridine.

J/Hz	Ir-H^1	Ir-H^2	Ortho1	Ortho2	Meta1	Meta2	Para
Ir-H^2	-7		-	-	-	-	-
Ortho1	3	0.3		-	-	-	-
Ortho2	1	1	-0.11		-	-	-
Meta1	-0.3	-	4.98	0.97		-	-
Meta2	0.9	0.6	0.97	4.98	1.41		-
Para	-	-	1.79	1.79	7.66	7.66	
δ/ppm	Ir-H$_2$		Ortho		Meta		Para
IrImes [H$_2$Ir–aPy]	-22.8		8.355		7.126		7.775
IrImes [H$_2$Ir–ePy]			8.064		6.984		7.677
IrImes [fPy]	-		8.56		7.466		7.881