Supporting Information

The feasibility of formation and kinetics of NMR Signal Amplification by Reversible Exchange (SABRE) at high magnetic field (9.4 T)

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Extra figures

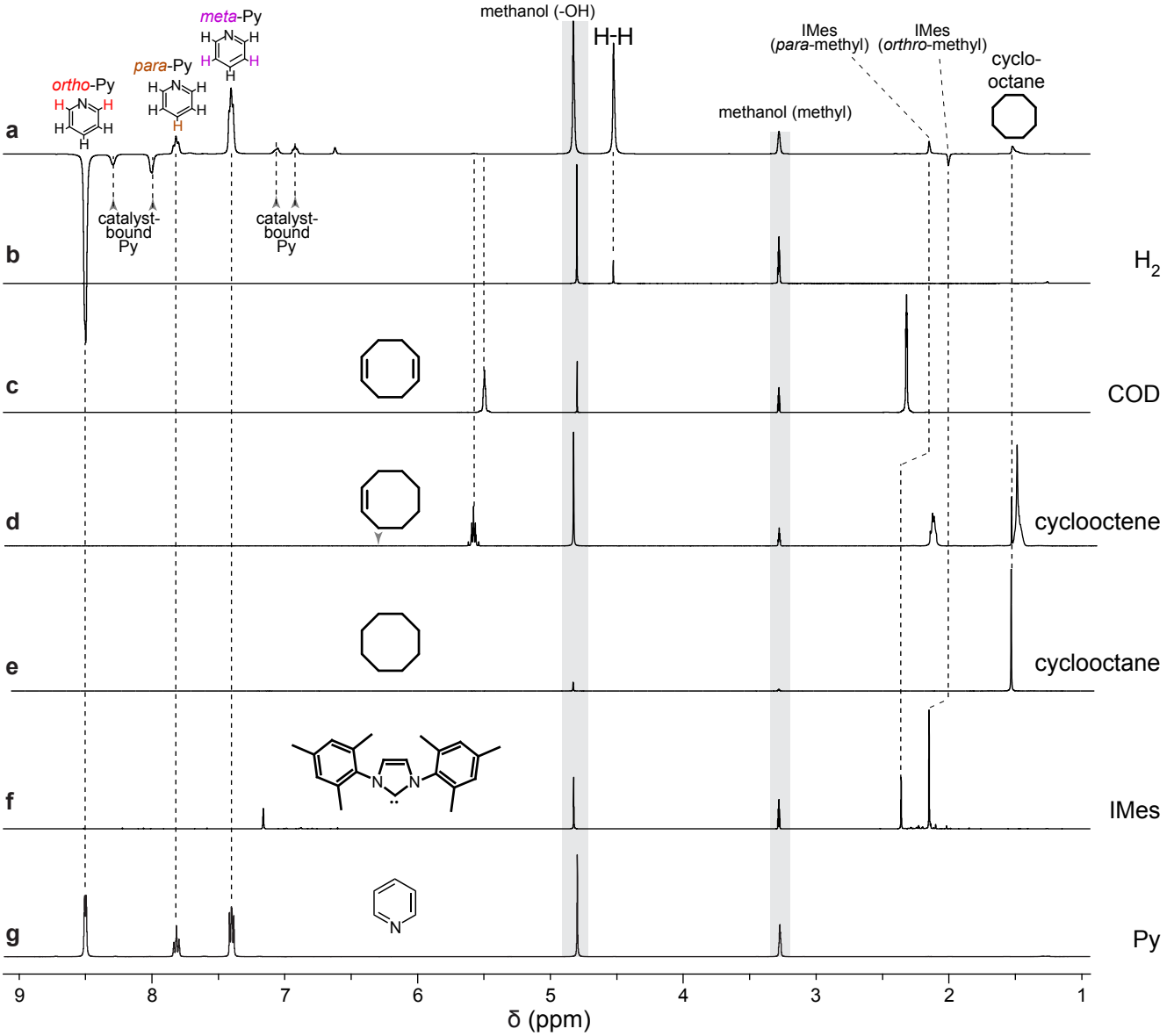

Figure S1. [1]H NMR spectra of a) SABRE polarized Py-h_5 by Ir catalyst *in situ* at 9.4 T, b) "normal" (thermally equilibrated) H_2 in CD_3OD, c) COD in CD_3OD, d) cyclooctene in CD_3OD, e) cyclooctane in CD_3OD, f) 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes) in CD_3OD, g) Pyridine (Py) in CD_3OD.

Figure S1.a. Peak assignments (from left to right). The proton peaks of Py-h_5 were assigned based on the reference spectrum of Py-h_5 in methanol-d_4 (ca. 8.5 ppm, Fig. S1g). Catalyst-bound Py was assigned using Ref. # [1] as follows: trans (8.32 ppm) and cis (8.03 ppm) of ortho-protons of Py-h_5, trans (7.75 ppm) and cis (7.65 ppm) of para-protons of Py-h_5, trans (7.09 ppm) and cis (6.95 ppm) of meta-protons of Py-h_5. This assignment was supported by a simple one-dimensional exchange experiment that showed that the 'bound' peak at ~8.3 ppm exchanged readily with the peak assigned to ortho protons of 'free' pyridine at ~8.5 ppm; moreover, the peaks at ~8.5 and ~8.3 ppm exhibited similar SABRE enhancements (data not shown). The peak of orthohydrogen was assigned using a reference sample of normal hydrogen dissolved in methanol-d_4 (Fig. S1b). The peaks of para- and ortho-methyls of IMes were assigned using the 1:2 integral ratio of the two peaks in reference spectrum of IMes in methanol-d_4 (Fig. S1f) and in the 'cold' spectrum (Fig. 1d). We note that the methyl proton resonances of IMes chemical shifts in the free and catalyst-integrated form are different. Measuring 1:2 peak integral ratio allows for additional confirmation that these two peaks indeed belong to IMes methyls. More importantly, SABRE polarized resonance in Fig. S1a belongs to IMes ortho-methyl protons. The peak of cyclooctane was assigned based on the reference spectrum of cyclooctane (resonance at ca. 1.5 ppm, Fig. S1e) and the absence of characteristic resonances of protons adjacent to C=C bond of COD and cyclooctene shown in Figs. S1c and S1d respectively (*ca.* 5.5 ppm).

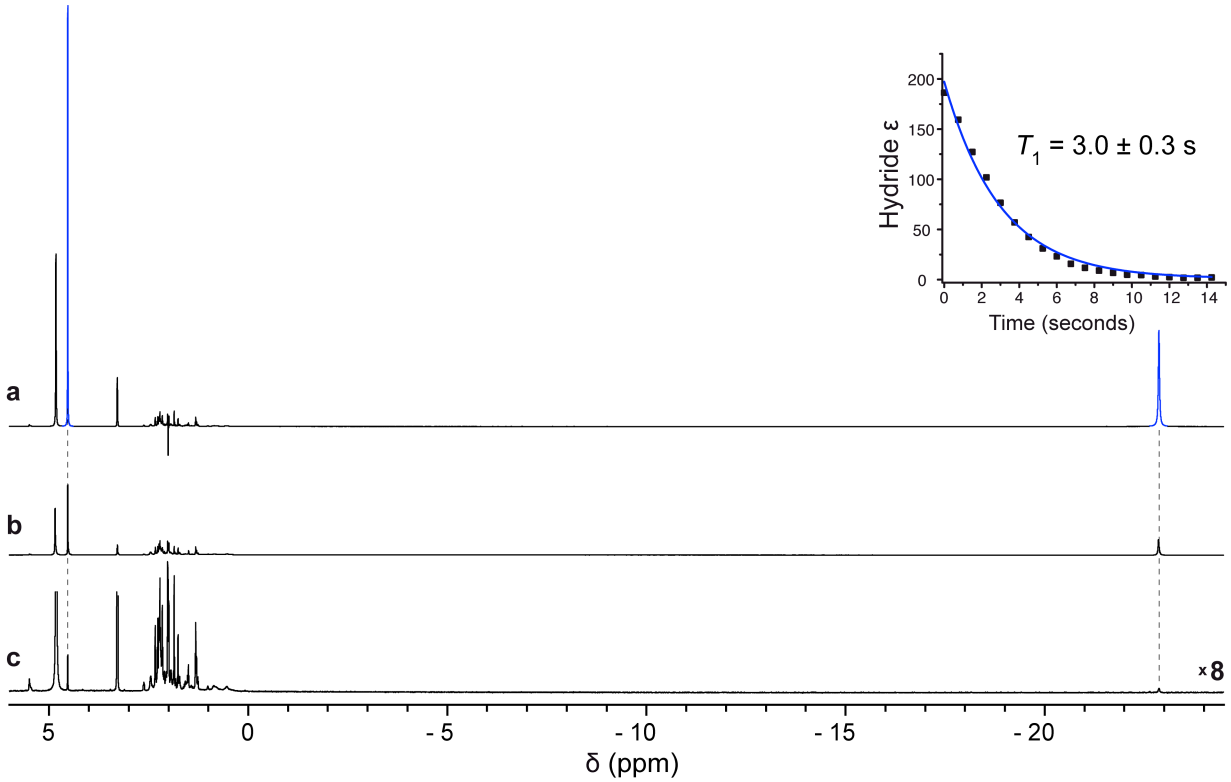

Figure S2. [1]H NMR spectra of a) solution containing SABRE-polarized Py-h_5 and Ir catalyst with the measurement performed *in situ* at 9.4 T, b) same solution as in (a), but with SABRE occurring *ex situ* in the fringe field of 9.4 T magnet, c) same solution as in (a) but thermally polarized at 9.4 T. The inset shows the T_1 decay of the hyperpolarized hydride resonance at *ca.* -23 ppm.[1]

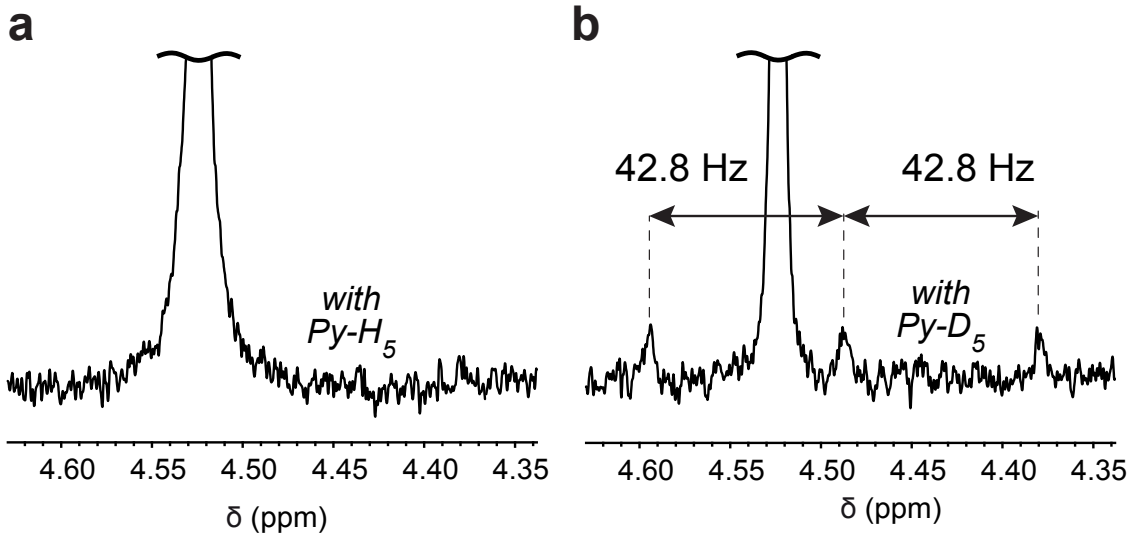

Figure S3. Deuterium exchange studies using Py-h_5 and Py-d_5 (99.96 %D) at ~1 atm of H_2. a) H_2 region of NMR spectrum of the Ir catalyst mixed with Py-h_5 after parahydrogen bubbling through catalyst solution, b) H_2 region of NMR spectrum of the Ir catalyst mixed with Py-d_5 after parahydrogen bubbling through catalyst solution.

Experimental details

Synthesis of [IrCl(COD)(IMes)] catalyst

The synthesis of the catalyst of interest [IrCl(COD)(IMes)] (where IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) was first reported by Vazquez.[2,3] Two similar approaches have been utilized to synthesize the Ir catalyst at Southern Illinois University in Carbondale (SIU). Following the synthetic work of Vazquez and co-workers, the synthetic scheme is shown in Fig. S4. In a glove box, a solution of 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes) dissolved in THF was added to $[Ir(COD)Cl]_2$ solution in THF over a 5 minute period, Fig. S5a. Upon evaporating the solvent, a yellow solid was isolated, Fig. S5b. The product was purified by recrystallization from a mixture of THF and isopropanol, yielding the final yellow-orange crystals formed after storing in a refrigerator over 24-48 hours, Fig. S5c. The final product was not found to be significantly sensitive to either air or water, and it is effectively insoluble in water. High-resolution NMR (data not shown) was used to confirm the successful synthesis. A second synthetic approach that has been used for the same Ir SABRE catalyst followed the previously described procedure.[4] Portions of 0.380 g (1.25 mmol) of IMes and 0.403 g (0.6 mmol) of $[Ir(COD)Cl]_2$ were placed in a Schlenk flask equipped with magnetic bar in argon atmosphere. Then 10 mL of dried and deoxygenated benzene was added and the mixture was stirred with a magnetic stirrer. The reaction was continued for 2 h, and then benzene was evaporated to 1/5 of the initial volume, and 5 mL of dried and deoxygenated pentane was added. The precipitate was three times washed with pentane by decantation. The complex was dried under vacuum for about 4 h.

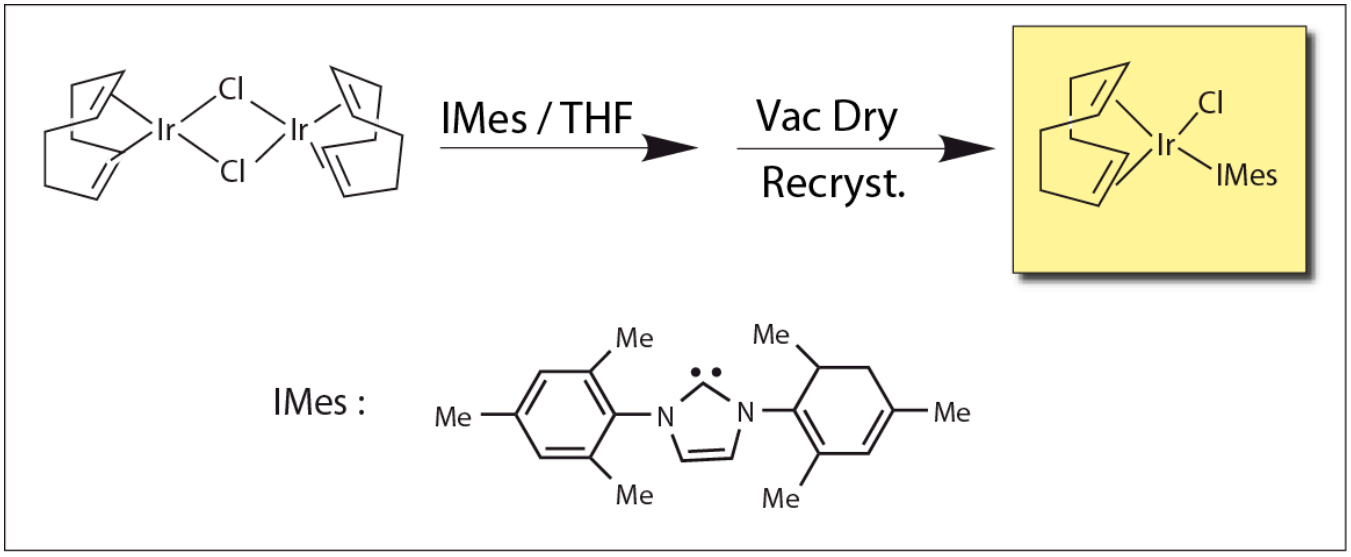

Figure S4. Synthetic scheme of [IrCl(COD)(IMes)] catalyst.

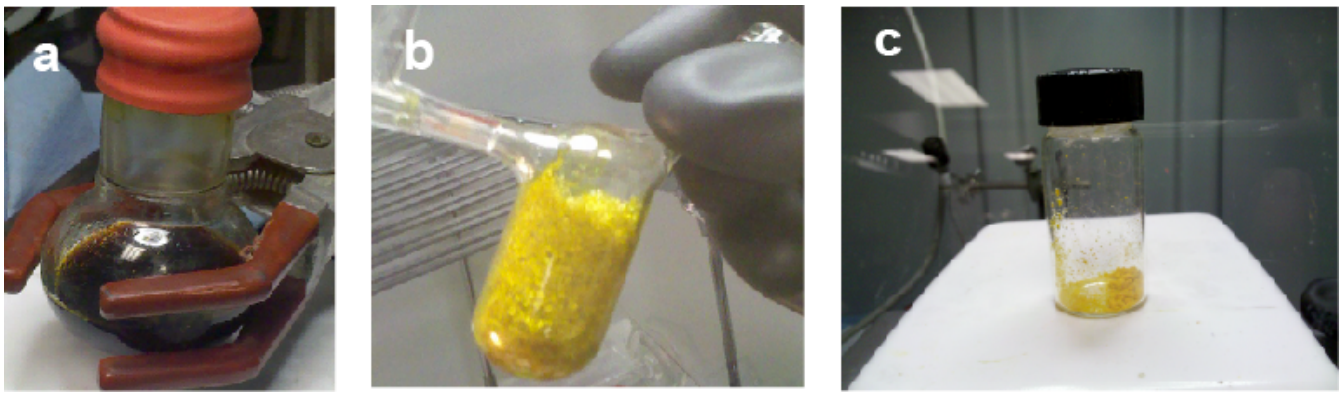

Figure S5. Different stages during the synthesis of [IrCl(COD)(IMes)] catalyst.

NMR samples preparation

Pyridine-h_5 (Py-h_5) samples were prepared as follows. 1 mL of CD_3OD was added to 22.4 mg of previously prepared catalyst to dissolve [IrCl(COD)(IMes)] (MW = 640) in CD_3OD. 5 μL of pyridine was dissolved in 400 μL of CD_3OD and placed into a 5 mm NMR tube. Then 200 μL of catalyst solution was added to the NMR tube and thoroughly mixed with pyridine solution. The resulting pyridine concentration was ~100 mM, while the catalyst concentration was ~7 mM. For samples with deuterated substrate, pyridine-d_5 (Py-d_5, 99.96 atom % of D) was used instead of Py-h_5 yielding the same substrate concentration and using the same stock solution of [IrCl(COD)(IMes)] in CD_3OD (solution (**1**)) as for Py-h_5 samples.

NMR external signal reference samples preparation

"Normal" hydrogen (i.e., with thermally populated spin states from a standard cylinder of compressed H_2) was bubbled for a few seconds through the ~600 μL of CD_3OD placed in the NMR tube. Then, an NMR spectrum of the sample was recorded (Fig. S1b) to yield a reference sample of H_2 in deuterated methanol. 10 μL of COD was dissolved in ~600 μL of CD_3OD (Fig. S1c) to yield a reference sample of COD in deuterated methanol. Similar quantities of cyclooctene (Fig. S1d) and cyclooctane (Fig. S1e) were used for preparation of their reference NMR samples in ~600 μL of CD_3OD. 3.9 mg of IMes was dissolved in ~600 μL of CD_3OD (Fig. S1f) to yield a reference sample of IMes in deuterated methanol. 5 μL of pyridine was dissolved in 600 μL of CD_3OD (Fig. S1g) to yield a reference sample of pyridine in deuterated methanol.

References

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(2) Vazquez, L., Purdue University, Ph.D dissertation, 2004.
(3) Vazquez-Serrano, L. D.; Owens, B. T.; Buriak, J. M. *Inorg. Chim. Acta* **2006**, *359*, 2786-2797.
(4) Kownacki, I.; Kubicki, M.; Szubert, K.; Marciniec, B. *J. Organomet. Chem.* **2008**, *693*, 321-328.