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Supporting Information

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Heterogeneous Solution NMR Signal Amplification by Reversible Exchange**

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Supporting Information

Experimental Methods: Synthesis

Homogeneous SABRE catalyst synthesis

0.38 g IMS (1,3-Bis(2,4,6-trimethylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene; Aldrich) and 0.403 g [{Ir(µ-Cl)(cod)}2] (Aldrich) were added in a small Schlenk tube (Kontes). Then 10 ml dried and deoxygenated benzene was transferred into the vial with a syringe. After 2 hours of stirring, the Schlenk tube was evacuated in order to concentrate the compound via solvent removal until only ~20% of the solution volume remained. 5 ml dried and deoxygenated pentane was added into the Schlenk tube. The supernatant from the Schlenk tube was transferred into a small beaker. This process was repeated twice. Yellow flake crystals were left on the bottom of the Schlenk tube. The Schlenk tube was left to evacuate for 12 hours. To make it purer, the synthesized chemical was recrystallized.

Heterogeneous SABRE catalyst synthesis

The homogeneous SABRE catalyst (synthesized as described above) was used as a starting material for the preparation of the HET-SABRE catalyst material. 0.1 g of the homogeneous SABRE catalyst, 41.7 mg of $AgPF_6$ (Aldrich), and ~5.6 g of polymer-bound 4-dimethylamino-pyridine (200-400 mesh, extent of labeling: ~6.0 mmol/g loading, 2 % cross-linked) were transferred into a glove box with N_2 atmosphere. The yellow SABRE catalyst was dissolved in THF (about 4 ml). $AgPF_6$ was dissolved in the SABRE catalyst solution. It was observed that the solution became opaque. Aluminum foil paper was wrapped around the reaction vial to reduce light exposure. After stirring for 2 hours, the AgCl precipitate was filtered out to give a red solution. Next, 5.6 g of polymer was transferred into the 40 ml vial with ~15 ml THF. The previously prepared red solution, containing PF_6-replaced SABRE catalyst, was added into the 40 mL vial. It was stirred in the dark for 12 hours. The color of supernatant turned to be much lighter. This whole cycle was repeated 3 times to maximize the amount of SABRE catalyst attached onto the surface of the polymer base. The polymer was evacuated for 24 hours.

Characterization

Characterization of Homogeneous SABRE catalyst

Once synthesized, successful creation of the homogeneous SABRE catalyst was confirmed via ^1H and ^{13}C NMR. Deuterated solvents were purchased from Cambridge Isotope Laboratories. The chemical shifts are (referenced to TMS):

- ^1H NMR (400 MHz, C_6D_6, 294 K) δ (ppm) = 6.78 (s, 2H, Mes); 6.81 (s, 2H, Mes); 6.15 (s, 2H, =CHN); 4.70 (m, 2H, cod); 3.19 (m, 2H, cod); 2.59 (s, 6H, CH_3); 2.15 (s, 6H, CH_3); 2.05 (s, 6H, CH_3); 1.80 (m, 4H, cod); 1.35 (m, 4H, cod).
- ^{13}C NMR (100.56 MHz, C_6D_6, 294 K) δ (ppm) = 182.11 (CN_2); 138.65; 137.96; 136.77; 134.40; 130.13 (Mes); 123.12 (=CHN–); 83.38; 50.77 (—CH–, cod); 34.07; 29.3 (–CH_2–, cod); 21.0; 20.13; 18.24 (–CH_3, Mes).

These chemical shifts are in good agreement with those provided previously in Ref. S1 for this Ir catalyst; assignments were taken from this reference.

Characterization of Heterogeneous SABRE Catalyst

Successful preparation of the desired heterogeneous SABRE catalyst is supported by a combination of qualitative observation, NMR, AAS, and MS experiments (IR was also attempted). The first indication of a change consistent with successful immobilization of the catalyst on the polymer supports is a slight color change in the material (Figure S1): Once the pyridine groups at the terminal positions of the polymer supports become tethered to the catalyst moieties (via binding to the Ir centers), the color of the polymer support material took on a slightly brownish hue.

Figure S1. Photos showing slight color change of the polymer support before (left) and after (right) the Ir catalyst moieties were linked to the polymer particles.

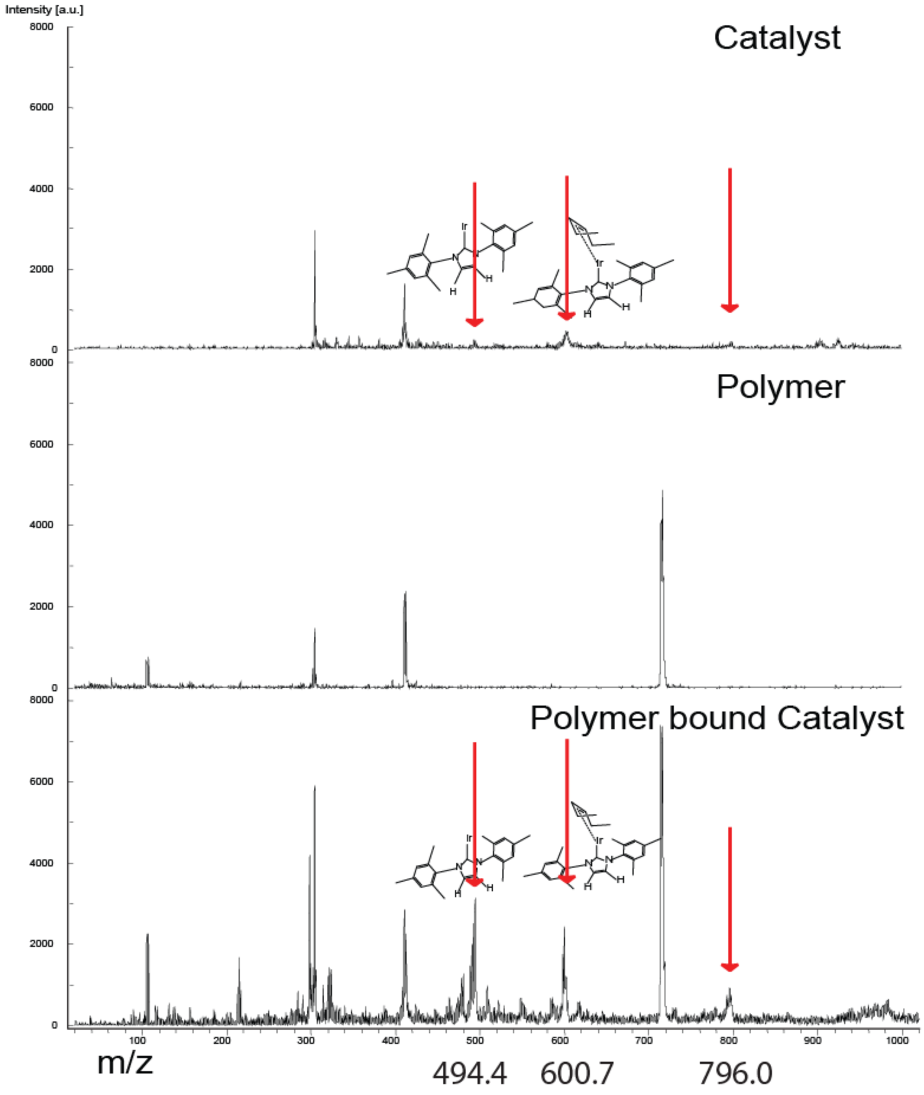

Figure S2. Mass spectra comparison (~10 mg of each sample was ground and tested by LDI-TOF mass spectrometry in SIUC Mass Spectrometry Facility). The top spectrum is from homogeneous catalyst; the middle spectrum is from the bare polymer support material, and the bottom spectrum is from the completed heterogeneous catalyst. Some characteristic peaks shown in the spectrum of homogeneous SABRE catalyst (top) are also shown in the heterogeneous SABRE catalyst (bottom) but are missing from that of the polymer support (middle). Additional peaks (not marked) above 900 units may also be indicative of catalyst presence.

More specific information is provided by mass spectrometry (e.g. **Fehler! Verweisquelle konnte nicht gefunden werden.**). For each sample (homogeneous catalyst, bare polymer, and the combined HET-SABRE catalyst), particles were attached to a stainless steel sample plate using an adhesive and the plate was loaded into a Bruker Daltonics MicroFlexLR Time-of-Flight mass spectrometer for Laser Desorption Ionization (LDI) mass spectrometry (SIUC Mass Spectrometry Facility). Each sample was irradiated with a pulsed nitrogen laser (337 nm, 20 kHz repetition rate). The positive ions were observed and recorded to generate mass spectra (e.g. Fig. S2).

Upon comparison of MS data from the homogenous SABRE catalyst (Fig. S2, top), the bare polymer support (Fig. S2, middle), and the completed heterogeneous SABRE catalyst (Fig. S2, bottom), several characteristic fragments are detected (e.g., those with m/z ratios of 494.4, 600.7, and 796.0). Such peaks, which manifest for both the original homogeneous SABRE catalyst and the supported catalyst (but not the bare polymer), support the conclusion that the catalyst was successfully tethered to the polymer particles.

Prior to performing MS, IR spectroscopy was attempted to see if it could be used to confirm the presence of the SABRE catalyst on the polymer particles. A sample from each of the three substances was crushed and suspended in mineral oil and placed between two KBr plates prior to IR acquisition. Spectra (not shown) did appear to exhibit a unique peak at ~3000 cm^{-1} (in the crowded C-H stretch region) that seemed specific to the presence of the SABRE catalyst moiety (i.e., not present in the spectrum of the bare polymer); however, while suggestive, these results were not considered to be definitive.

Atomic absorption spectroscopy (AAS) was also performed to support various aspects of this work. During the synthetic process (after creation of the homogeneous SABRE catalyst, but prior to tethering it to the polymer supports), the Cl atom is stripped from the SABRE catalyst using $AgPF_6$ to result in AgCl precipitate. To validate this process, a small amount of the precipitate in the reaction vial (a few percent) was extracted and placed into a Schlenk tube and washed by THF for three times. The remaining solvent was the removed via vacuum drying, and then ~20 mL Milli-Q water was added to the Schlenk tube. The Schlenk tube was shaken until an even suspension was formed. Finally, the suspension was transferred to an empty vial and used as the AAS sample (Varian, the AAS was calibrated with standard samples of $AgNO_3$); Table S1.

Trial	Concentration (PPM)
1	18.26
2	17.92
3	18.58
	Average
	18.25

Table S1. Results from AAS on precipitate, showing detection of Ag.

The average Ag concentration value was in good agreement with that expected based on calculation, supporting the successful creation of AgCl precipitate, and by extension, the successful stripping of Cl from the Ir atom in the SABRE catalyst (as required for the next step of the synthesis).

The completed HET-SABRE catalyst was also characterized via AAS. Following washing of the completed HET-SABRE catalyst and acid digestion, AAS was used to confirm the presence of Ir metal atoms on the particle surfaces (using an Ir-specific bulb with the AA spectrometer). Three different experiments were performed, with each value reported in Table S2 representing an average of three measurements). Significant (and similar) values of Ir were found in all samples tested, supporting the successful immobilization of the organometallic catalyst moieties on the polymer particles.

Trial	Concentration (ppm)
1	57.33
2	58.89
3	58.64

Table S2. Results from three separate AAS runs, which found significant quantities of Ir metal on the HET-SABRE catalyst particles—indicating successful coordination of the Ir metal atoms to the polymer surface.

Separately, AAS was also performed on the supernatant liquid of the HET-SABRE catalyst after soaking in a methanol solution containing the substrate (1.25% pyridine by volume) and pH_2 (32 psi, ~220 kPa above atmospheric pressure) in order to test to see if exposure to SABRE conditions might result in leaching of the catalyst moiety into the solution (Table S3).

Trial	Ir Concentration (ppm)
Before PH2	0*
After PH2	0*

Table S3. Results from AAS on a supernatant liquid taken from a sample containing the HET-SABRE catalyst, before (top) and after (bottom) exposure to pH_2 gas (32 psi, ~220 kPa above atmospheric pressure). Asterisk (*) indicates that a small negative value was reported by the instrument, similar to what is reported from testing simple MilliQ water samples (negative control). Thus, no Ir was observed within the detection limits of the instrument.

AAS did not detect the presence of Ir in the supernatant liquid after residing in the methanol solution containing the substrate—either before or after administration of pH_2.

Similarly, a long-time ^{1}H NMR acquisition (1000 scans) also did not show signals that could be assigned to freely floating catalyst molecules. Taken together, these results are consistent with the conclusion that the supported catalyst is stable and does not appear to significantly leach into the solvent under typical experimental conditions.

SABRE NMR Experiments and Related Information

Para-hydrogen

Quantities of para-hydrogen were generated using a custom-built generator at Vanderbilt University, and stored in small low-pressure (<250 psi, <1720 kPa) gas cylinders; decay of the parahydrogen was sufficiently slow to allow useful experiments to be performed for up to a few weeks after loading. At SIUC, parahydrogen was administered to samples using a dedicated gas manifold. The fraction of pH_2 (versus oH_2) was determined by loading a known amount of pH_2 gas from its tank into a stopcock-sealed NMR tube, and comparing the integral to a calibration curve obtained using variable pressures of “normal” (thermal) H_2 gas. Such measurements were performed throughout the decay “lifetime” of a given pH_2 tank (typically lasting a few weeks); values for specific days of SABRE experiments reported in the Main Document were obtained by fitting the decay data to an exponential model and interpolating.

Experiments with the ‘Standard’ homogeneous SABRE catalyst

SABRE experiments were performed with the homogeneous SABRE catalyst to ensure its function and to test protocols. Enhancements were generally much less than those reported by the York group (and thus it is more instructive to compare the HET-SABRE results in the Main Document with those reported below). Typical results from our efforts are shown in Figure S3.

These results are taken from an example where, instead of using a single 90º pulse, a series of acquisitions with low tipping-angle pulses was obtained to observe the decay of the SABRE enhancements. The first such scan exhibited a >70-fold enhancement of the ^{1}H pyridine substrate resonances.

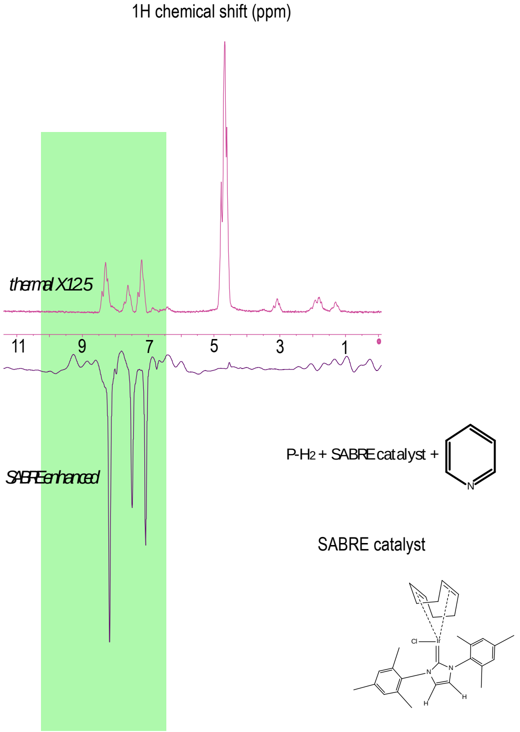

Figure S3. Observation of ^{1}H NMR signal enhancement obtained with the homogeneous SABRE catalyst under our typical conditions (bottom spectrum), compared to the corresponding spectrum obtained when the sample was thermally polarized.

The polarized spectrum (lower spectrum) shows obvious SABRE enhancement, validating the homogeneous SABRE catalyst and providing a benchmark for the HET-SABRE experiments.

Experiments with the HET-SABRE catalyst—additional details

Samples of pyridine-h5 and pyridine-d5 used as the substrate were obtained from Acros and Cambridge Isotope Laboratories, respectively. Spectra shown in the Main Document and below were performed without ^{2}H lock, and chemical shifts were referenced to the methyl peak of solvent at 21 ºC (set to 3.33 ppm); spectral acquisition time: 3.25 s. Upon administration of pH_2, the sample tube was typically shaken for a few seconds (~4-5 times) in a ~100 G fringe field and then placed at the top of the NMR magnet for pneumatic lowering into the probe region; the fringe field—manually mapped using a digital gaussmeter—was provided by the Oxford AS400 actively-shielded wide-bore NMR magnet. The spectrum was acquired (using an Agilent DD2 NMR console; nominal ^{1}H frequency of 399.466 MHz) as soon as possible after it settled into the magnet (typically several seconds after the first moment that pH_2 was shaken into the sample solution). Each spectrum shown is from a single scan (90º pulse, 16 μs); all spectra shown used the same acquisition parameters (including gain). For the thermally polarized spectra, samples were allowed to reside in the magnet for at least 60 s prior to acquisition.

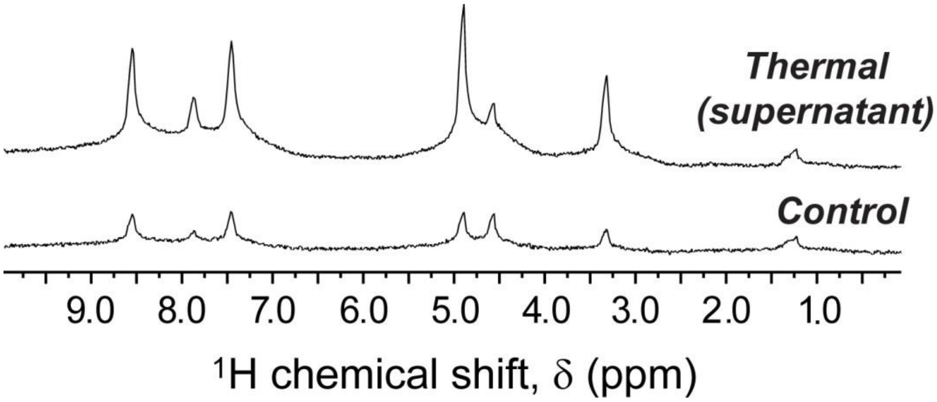

Figure S4. (Top) Thermally polarized proton NMR spectrum from a supernatant solution; the corresponding control experiment using the same supernatant solution is shown in the Bottom spectrum—no SABRE enhancement is observed upon addition of ~2400 Torr (~220 kPa above atmospheric pressure) pH_2 gas and subsequent immediate transfer to high field for NMR acquisition. All spectra shown were acquired with a single scan (90º pulse); assignments are provided in the main text. Note: (1) the absence of negative enhancements in the Bottom spectrum (similar to Fig. 2d of the main document); and (2) the relative weakness in the appearance of most of the peaks in the Bottom spectrum. In this run, acquisition was successfully obtained in just ~1-2 s after administration of pH_2 and lowering into the magnet, a time much shorter than the pyridine ^{1}H T_1s (and thus more time is required for the spins to fully magnetize in the external field).

References for Supporting Information:

S1. Kownacki, I.; Kubicki, M.; Szubert, K.; Marciniec, B. *J. Organomet. Chem.* **2008**, *693*, 321-328.