A Formulation Protocol with Pyridine to Enable Dynamic Nuclear Polarization Surface-Enhanced NMR Spectroscopy on Reactive Surface Sites: Case Study with Olefin Polymerization and Metathesis Catalysts

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Synthesis

Preparation of molecular precursors, supports and grafted materials, as well as further manipulations (including characterization) were carried out under dry and oxygen free nitrogen atmosphere using an MBraun glove-box and high-vacuum lines (10^{-5} mbar). Et_2O solvent was purified using double MBraun SPS alumina columns. Benzene and C_6D_6 were distilled from Na/benzophenone and degassed by three consecutive freeze-pump-thaw cycles.

Ziegler-Natta propylene polymerization precatalysts containing ethyl benzoate as internal donor (ZN-EB)

Industrial ZN-EB precatalyst with the composition $TiCl_4$/$MgCl_2$/PhCOOEt (2.0 wt. % Ti) was obtained from SABIC and treated as described above.

Dry and ball-milled $MgCl_2$ support for ZN-EB

Industrial $MgCl_2$ (dry and ball-milled) support for ZN-EB precatalyst was obtained from SABIC and treated as described above.

Sulfated zirconia supported dimethyl zirconocene olefin polymerization catalysts (ZrMe$^+$@SZO$_{300}$)

Sulfated zirconia was received from M. Conley prepared by precipitation of zirconium nitrate with NH_4OH followed by treatment with H_2SO_4 and thermal treatment [1]. SZO_{300} was dehydroxylated at 300°C under high vacuum and titration with $(PhCH_2)_2Mg(THF)_2$ showed 0.13 mmol(OH)/g. $Cp_2Zr(^{13}CH_3)_2$ was prepared in 3 stages:

1. Preparation of $^{13}CH_3MgI$:

On a Schlenk line CH_3I (852 mg, 6.00 mmol, 1.00 equiv.) was dissolved in 5 mL Et_2O and added to suspension of Mg (258 mg, 10.75 mmol, 1.79 equiv.) in 5 mL Et_2O. The mixture was refluxed

at 40°C for 30 min and then liquid part was cannula transferred to empty Schlenk flask and used for the next step.

2. Preparation of ($^{13}CH_3$)$_2$Mg:

Liquid part from the step 1 was mixed with dioxane (0.6 mL, 7.00 mmol, 1.17 equiv.) overnight followed by filtering over celite and drying. The product was recrystallized in THF overnight, separated and dried again. ^{1}H NMR (300 MHz, C$_6$D$_6$(+1 drop of THF)): δ = -0.855 ppm (d, J$_{C-H}$ = 106 Hz, Mg($^{13}C\underline{H}_3$)$_2$), 1.41 ppm (m, (C$\underline{H}_2$CH$_2$)$_2$O), 3.56 ppm (m, (CH$_2$C$\underline{H}_2$)$_2$O); ^{13}C NMR (300 MHz, C$_6$D$_6$(+1 drop of THF)): δ = -15.56 ppm (s, Mg($^{13}\underline{C}$H$_3$)$_2$), 25.81 ppm (s, ($\underline{C}$H$_2$CH$_2$)$_2$O), 67.84 ppm (s, (CH$_2$$\underline{C}H_2$)$_2$O).

3. Preparation of Cp$_2$Zr($^{13}CH_3$)$_2$:

Cp$_2$ZrCl$_2$ (13 mg, 0.045 mmol, 1 equiv.) was mixed with and ($^{13}CH_3$)$_2$Mg (3 mg, 0.054 mmol, 1.2 equiv.) in 10 mL Et$_2$O overnight followed by filtering over celite and drying. ^{13}C NMR (300 MHz, C$_6$D$_6$): δ = 30.27 ppm (s, (C$_5$H$_5$)$_2$Zr($^{13}\underline{C}$H$_3$)$_2$), 110.38 ppm (s, ($\underline{C}_5$H$_5$)$_2$Zr(^{13}CH$_3$)$_2$).

Grafting of Cp$_2$Zr($^{13}CH_3$)$_2$ (8 mg, 0.032 mmol, 1.33 equiv.) onto SZO$_{300}$ (180 mg, 0.024 mmol, 1.00 equiv.) was performed in 10 mL benzene overnight. Afterwards, washing 3 times with benzene and drying under high vacuum were performed. The structure of product was confirmed by transmission IR spectroscopy.

Mo-containing silica-supported olefin metathesis catalysts (Mo=CHR$^+$@SiO$_{2-700}$)

Mo@SiO$_{2-700}$ was received from M. Pucino prepared by grafting in benzene of Mo-containing molecular precursor onto SiO$_{2-700}$ (dehydroxylated at 700°C under 10^{-5} mbar for 48 h) [2]. The molecular precursor used for grafting was Mo$^+$(=N-Ar)(=^{13}CH-C(CH$_3$)$_2$Ph)(NHC)(OCH(CF$_3$)$_2$) B$^-$(Ar^F)$_4$, where Ar was 2-(t-Bu)C$_6$H$_3$, NHC – ^{13}C-1,3-(2,4,6-(CH$_3$)$_3$C$_6$H$_2$)imidazol-2-ylidene and Ar^F –3,5-(CF$_3$)$_2$C$_6$H$_3$; NHC and alkylidene carbon were enriched by 30 % of ^{13}C isotope.

Modification of catalysts surfaces by Py adsorption

For all pyridine adsorption studies ^{15}N-Py (99% [15]N isotopic enrichment) purchased from CortecNet Corp. was used. It was dried at $60^{\circ}C$ (72 hours) over CaH_2 under Ar and degassed using 3 consecutive freeze-pump-thaw cycles before every adsorption experiment.

Typically, 100-150 mg of each material was evacuated for 30 min at ambient temperature under high vacuum prior adsorption. Py was adsorbed at the samples via direct saturation during 10 min, followed by evacuation of physisorbed Py for at least 30 min under high vacuum. Reaction of Py with molecular $Mo^+(=N-Ar)(=CH-C(CH_3)_2Ph)(NHC)(OCH(CF_3)_2)B^-(Ar^F)_4$ was performed in J-young NMR tube filled with saturated C_6D_6 solution of complex .

The same procedures were used for deuterated Py (C_5D_5N) adsorption studies.

Characterization

Solution NMR

^1H and ^{13}C solution NMR spectra were measured on Bruker DRX 300 spectrometer in C_6D_6 at room temperature. The ^1H and ^{13}C chemical shifts were referenced relative to the residual solvent peak. 5 mm J-young NMR tubes were used for all the measurements. In case of measurements of molecular compounds with and without modification by Py recycle delays of 2 s were used.

For the determination of OH density 50 mg of support, 20 mg of $(PhCH_2)_2Mg(THF)_2$ and 10 mg of ferrocene $(FeCp_2)$ internal standard were mixed in C_6D_6 in the NMR tube. ^1H NMR spectra with relaxation delay of 10 s were recorded. Then the ratios between toluene released and ferrocene standard were evaluated in the resulting spectra, allowing to derive mmol(OH) per 1 g of support. For the evaluation of grafting process, 10 mg of $FeCp_2$ as internal standard was added to residual washings solution and the mixture was additionally mixed with C_6D_6 (1:1) in J-young NMR tube. Subsequently, the ^1H NMR spectra with relaxation delays of 10 s were recorded. Then the ratios between compound formed by leaving group released upon grafting and ferrocene standard were evaluated in the resulting spectra, allowing to derive the amount of molecular precursor reacted with the surface.

FTIR

Transmission Fourier-transform infrared (FTIR) spectra were recorded using a Bruker Alpha FT-IR spectrometer inside Ar-filled glovebox. For all the measurements typically 10 mg of sample was pressed into a pellet, the measurement was done in the range 4000-400 cm^{-1}.

EPR

All CW-EPR measurements were conducted at the X band (9.5 GHz EPR frequency) on a Bruker EMX spectrometer in a range of 300-400 mT at a sample temperatures of 300 and 110 K. The samples were formulated in exactly the same way as for DNP studies: all the sample in pristine

state as well as with preadsorbed Py were impregnated with TEKPol/TCE solution. Prior to EPR measurements the sample was placed inside the tube under Ar, then evacuated at 10^{-5} mbar and flame sealed in 4 mm quartz EPR tubes.

Solid-State NMR

^{1}H DQ-SQ (BABA [3]) measurements were done at Bruker Avance III 700 MHz in 1.3 mm rotor spinning at 60 kHz by applying 32 scans. ^{13}C{^{1}H} CP/MAS NMR measurements were carried out at Bruker Avance III 400 MHz in 3.2 mm rotor spinning at 8 kHz by applying 8404 scans with contact time 2 ms and recycle delay 2 s.

DNP-SENS

All the samples (with and without preadsorbed Py) were prepared in an argon-filled glove box by incipient wetness impregnation with 16 mM TEKPol solution in 1,1,2,2-tetrachloroethane (TCE). The mixture was then packed into a 3.2 mm sapphire rotor and closed with zirconia cap. Afterwards, the rotor was inserted in the cryogenic probe within a short period of time (ca. 5 min). ^{1}H, ^{13}C and ^{15}N DNP-SENS studies were carried out on a Bruker 600 MHz (14.1 T) spectrometer using a 3.2 mm HX probe at 100 K with 8 kHz MAS. The spectra were referenced with respect to adamantane by setting the most downfield signal to 38.5 ppm.

DNP build-up times (T_{DNP}) were measured by ^{1}H saturation–recovery experiment with microwaves turned on. ^{1}H direct excitation and ^{15}N{^{1}H} and ^{13}C{^{1}H} cross-polarization magic-angle spinning (CP-MAS) experiments were measured. Recycle delays for CP-MAS experiments were set as 2 s for ^{1}H, 5 s for ^{15}N and 2 s for ^{13}C spectra.

DNP enhancements were determined for every sample by comparing NMR spectra measured with gyrotron on and off (MW ON and MW OFF correspondingly). For ^{1}H nuclei only enhancement of signal from TCE (^{1}H$_{solv}$) was determined, for ^{13}C – from solvent (^{13}C$_{solv}$) and surface (^{13}C$_{surf}$) and

for ^{15}N – only from surface (^{15}N$_{surf}$). Difference in integral intensity of the corresponding peaks was considered as enhancements.

All the processing of NMR spectroscopic data was performed using Bruker Topspin 4.0.7 software package.
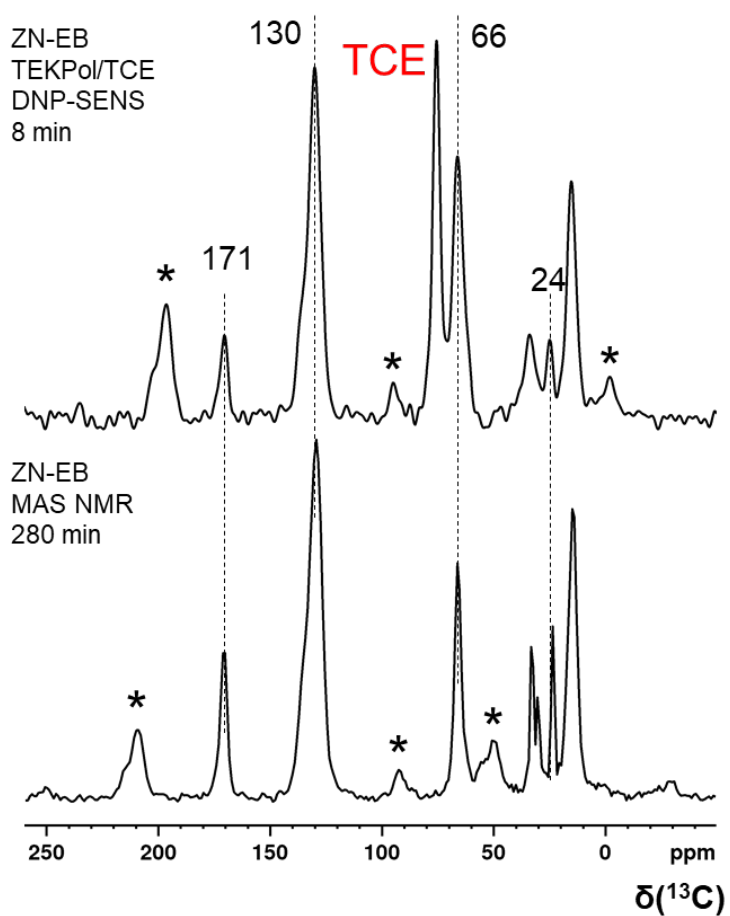
Results

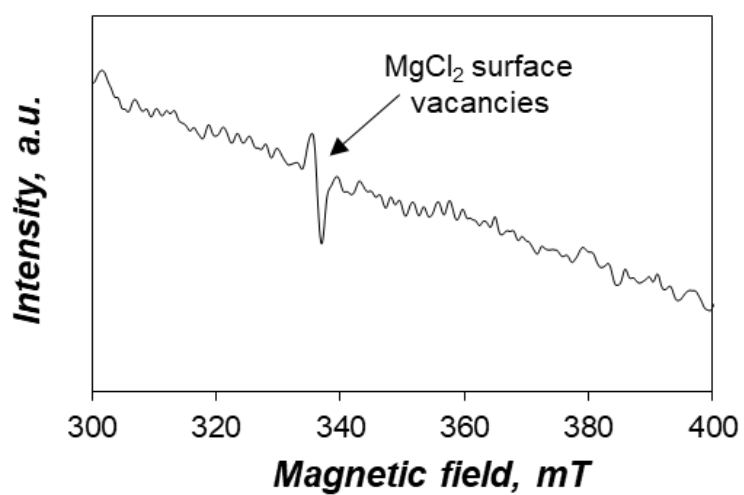Fig. S1. Comparison of ^{13}C DNP-SENS (top) and MAS NMR (bottom) spectra of ZN-EB.

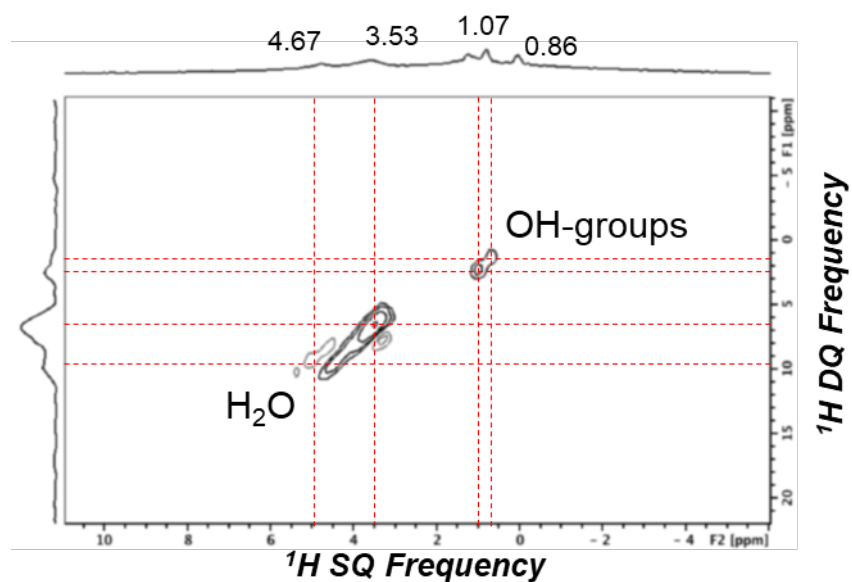Fig. S2. EPR spectrum of pristine dry and ball-milled $MgCl_2$ support.

Fig. S3. ¹H 2D DQ-SQ correlation NMR spectrum of dry and ball-milled MgCl₂ support.

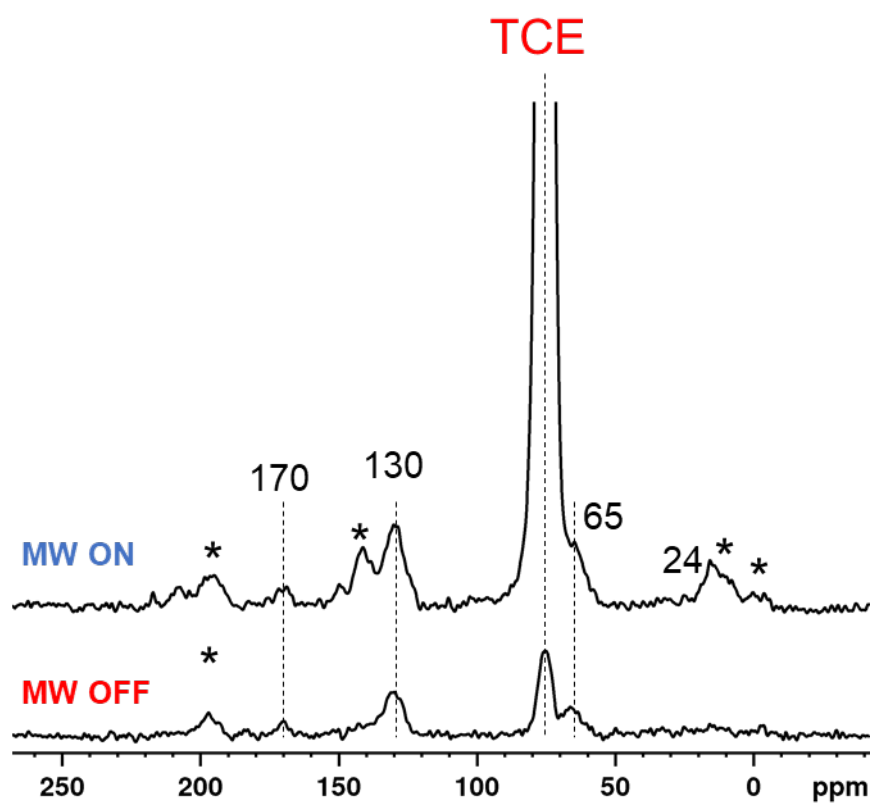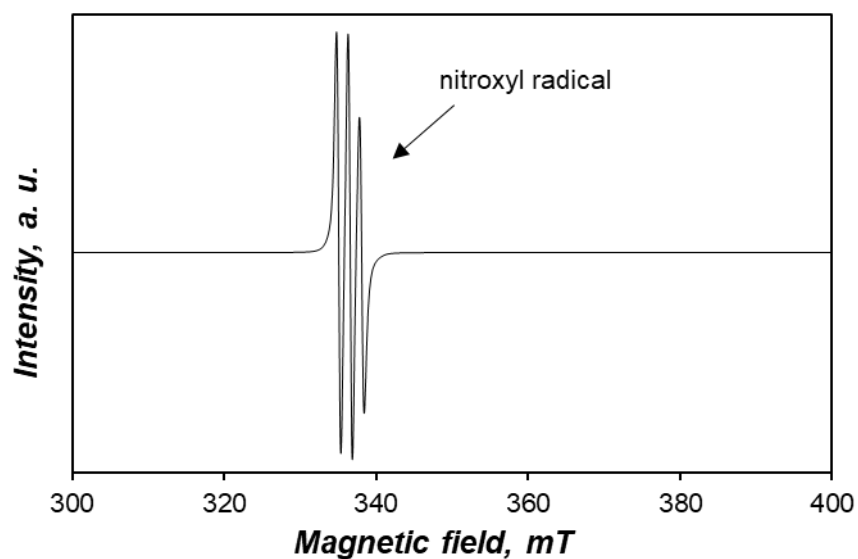Fig. S4. ¹³C DNP-SENS spectra of ZN-EB with Py-d₅ preadsorbed.

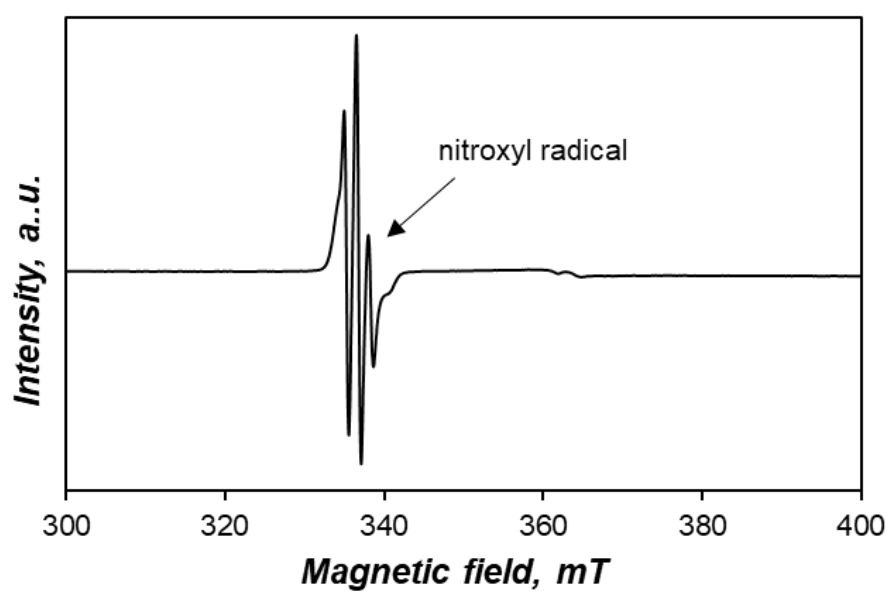Fig. S5. EPR spectrum of ZrMe$^+$@SZO$_{300}$ with preadsorbed Py and impregnated with TEKPol/TCE solution (300 K).

Fig. S6. EPR spectrum of Mo=CHR$^+$@SiO$_{2\text{-}700}$ with preadsorbed Py and impregnated with TEKPol/TCE solution (300 K).
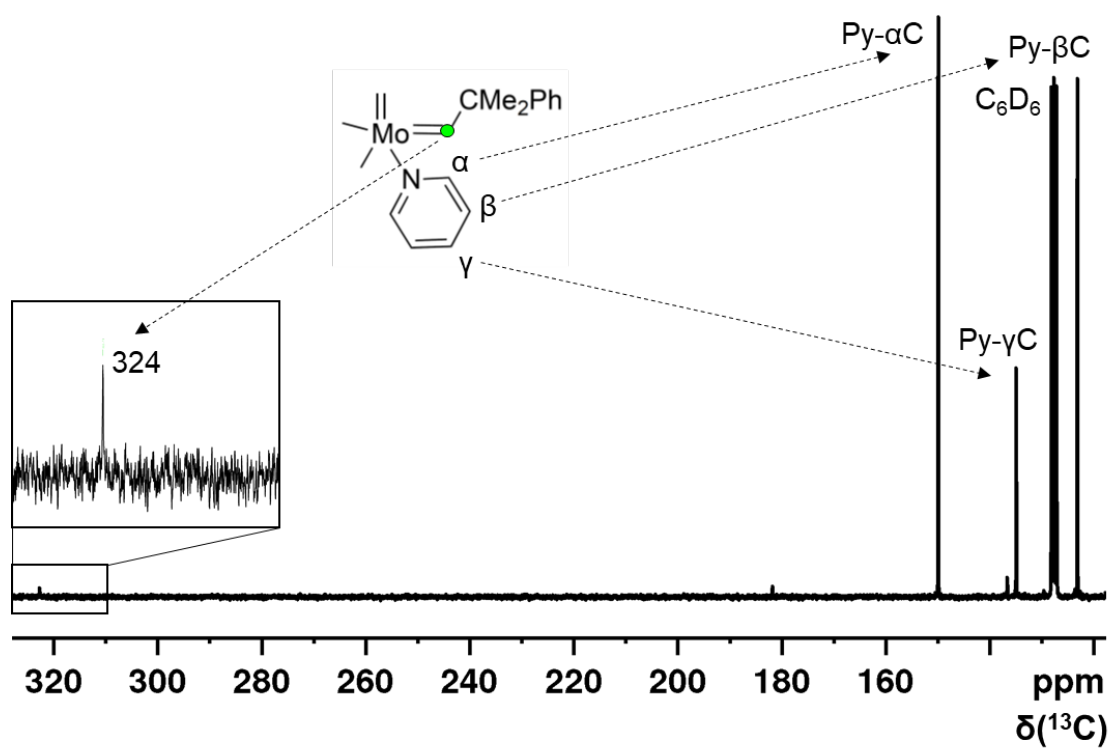
Fig. S7. ^{13}C NMR spectrum of Mo$^+$(=N-Ar)(=CH-C(CH$_3$)$_2$Ph)(NHC)(OCH(CF$_3$)$_2$)B$^-$(Ar^F)$_4$ with preadsorbed Py in C$_6$D$_6$.

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