Supporting Information

A Phosphorous-Rich Polymer as a Homogeneous Catalyst Scavenger

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I General Procedures, Materials and Instrumentation.

All reactions were manipulated under N_2 using standard Schlenk or glovebox techniques. All glassware was oven dried prior to use. $RhCl(PPh_3)_3$ and PEt_3 (90%) were used as received. Styrene (≥99%) and diethyldiallylmalonate (98%) were degassed by purging with N_2 and stored over 4 Å sieves. TMEDA was dried over CaH and distilled prior to use. $RuCl_2(PCy_3)_2(=CHPh)$ (**GI**) was gifted and purified by successive washings with acetone and pentane. **SPN1** was prepared according to literature procedures.[1] Dry and degassed solvents were obtained from an Innovative Technology 400-5 Solvent Purification System and stored over 4 Å molecular sieves (Fluka and activated at 150 ˚C for 12 h) under N_2 unless otherwise noted. Chloroform-*d* (99.8%) was obtained from Cambridge Isotope Laboratories, was dried with 4 Å molecular sieves and degassed by bubbling with N_2.

All solution-state NMR spectra were recorded on either an Inova 600 MHz or Mercury 400 MHz instrument. ^{1}H spectra acquired were referenced internally against the residual solvent signal to TMS at 0 ppm. ^{31}P spectra were referenced externally to 85% phosphoric acid at 0.00 ppm. Solid-state ^{31}P NMR experiments were performed using a Varian Infinity Plus 400 NMR spectrometer (ν_L (^{31}P = 161.71 MHz) equipped with a Varian 4 mm triple-resonance HXY magic-angle spinning NMR probe. Chemical shifts were referenced with respect to the ^{31}P NMR peak of H_3PO_4 ($\delta(^{31}P)$ = 0.0 ppm) by setting the ^{31}P NMR peak of solid ammonium dihydrogen phosphate to +0.81 ppm. The powder samples were stored inside a glove box filled with nitrogen gas and packed tightly into 4 mm o.d. ZrO_2 rotors, then sealed. For the samples having low glass-transition temperature samples, the NMR spectra were acquired using a standard one pulse sequence with high-power ^{1}H TTPM decoupling, 12.0 kHz spinning rate, 50 kHz spectral width, between 140-160 scans, a 1.8 μs π/4-pulse width, 30 s recycle delay and 20.4 ms acquisition time, and a 6.25 μs TPPM ^{1}H decoupling pulse with 83 kHz decoupling field. For samples having high glass-transition temperature samples, the NMR spectra were acquired using cross-polarization (CP) with high-power ^{1}H TTPM decoupling, 12.0 kHz spinning rate, 50 kHz

spectral width, between 164-380 scans, 4.6 μs ^{1}H π/2-pulse width, 1 ms contact time, 15 s recycle delay, between 8.5-20.4 ms acquisition time, and a 6.25 μs TPPM ^{1}H decoupling pulse with 83 kHz decoupling field. In hydrogenation reactions, styrene and ethylbenzene were quantified relative to an internal standard (cyclodecane) and analyzed with an Agilent 7890A GC-FID with an HP-5 column. Authentic samples of each were used to construct calibration curves. ICP-MS samples were first digested in aqua-regia for 2 hours then data was collected on an Agilent 7700 Series ICP-MS. SEM and EDX analysis were performed using a LEO (Zeiss) 1540XB SEM at Western's Nanofab facility, equipped with an Oxford X-Max 50 x-ray detector. The backscattering detector is a four-quadrant backscattered electron detector, Type 815/U. SEM images were collected at an acceleration voltage of 1kV, and EDX spectra were collected at 10kV. Backscattering detection was used to identify potential Pd nanoparticles in the sample.

Preparation of Rh-SPN1

$RhCl(PPh_3)_3$ (**WI**) (42 mg, 0.0449 mmol) and **SPN1** (45 mg) were stirred in CH_2Cl_2 (20 mL) at room temperature for 24 hours. A colour change of the solution from deep red to orange was observed. The resulting functionalized polymer (orange) **Rh-SPN1** was washed with CH_2Cl_2 (3 × 30 mL) and pentane (1 × 30 mL). After the final wash **Rh-SPN1** was suspended in pentane and dried *in vacuo*. Elemental Analysis by ICP-MS (μg g^{-1}): Rh, 71 200; P, 56 600; S, 61 200.

General Procedure for the Catalytic Hydrogenation of Styrene

In a glovebox, the following stock solutions were prepared: styrene (104 mg, 1 mmol, 500 mM) in toluene (2.00 mL); tetradecane (70 mg, 0.25 mmol, 250 mM) in toluene (2.00 mL); **WI** (9.3 mg, 0.01 mmol, 10 mM) in CH_2Cl_2 (1.00 mL). To a 100 mL Schlenk flask containing a stir bar, the catalyst stock solution was added (200 μL), and CH_2Cl_2 was removed *in vacuo*. Added to the same flask was a portion of the styrene (400 μL) and cyclodecane (400 μL) stock solutions. Toluene was added (5.20 mL) to give a final volume of 6.00 mL and the flask was sealed with a rubber septum. The final concentrations of the reaction mixture were 33.0 mM styrene, 8.3 mM cyclodecane, and 0.33 mM **WI** (1 mol%). The flask was removed from the glovebox and H_2 gas was bubbled into solution for 2 minutes using a needle pierced through the rubber septum of the Schlenk flask. The contents were allowed to stir at room temperature and every 10 minutes for 90 minutes, 200 μL aliquots were removed and exposed to air to quench. From each aliquot, 150 μL was removed and diluted with acetone (850 μL) giving final concentrations of 5 mM for styrene and tetradecane and the diluted samples were analyzed by calibrated GC-FID.

General Procedure for the Quenching of the Hydrogenation of Styrene

The procedure for the catalytic hydrogenation of styrene was followed as outlined above. Added to the reaction set-up, prior to addition of **WI**, was an excess of **SPN1** (32 mg, 0.04 mmol, ca. 1.5 mol P equiv.). **SPN1** was present from the outset and 200 μL aliquots taken at 10 minutes intervals, up to 50 minutes. From each aliquot 150 μL was removed and diluted with acetone (850 μL) giving final concentrations of 5 mM for styrene and tetradecane and the diluted samples were analyzed by calibrated GC-FID. After the final aliquot for GC-FID analysis was taken from the quenched reaction, the mixture was allowed to stir for 24 hours. The mixture was then taken up in a syringe and filtered through a syringe filter (Promax Syringe Filter, 13 mm, 0.22 μm PTFE) into a preweighed vial. Solvent was removed *in vacuo* leaving a residue. The residue was submitted for ICP-MS analysis. Additionally, a control reaction to which no polymer was added was submitted for ICP-MS analysis, for a comparison of the trace metal amounts in each sample.

Scavenging of GI following RCM of Diethyl diallylmalonate

Diethyl diallylmalonate (488 mg, 2.12 mmol), **GI** (16.4 mg, 0.02 mmol), and CH_2Cl_2 (20 mL) were combined in a Schlenk round bottom in a glovebox with a stir bar. The flask was removed from the glovebox and heated to 30 °C in an oil bath for 1 hour under an N_2 atmosphere. The resulting solution was brought back into the glovebox, and divided into 1 mL portions in small glass vials with a specific amount of **SPN1** (1, 5, or 10 mg) with a stir bar. An additional portion was added to a vial that did not contain **SPN1** to act as the control. The vials were capped, sealed with Teflon tape and stirred for a specific amount of time (20 minutes, 12, 24, 48, and 72 hours) at room temperature. The mixtures were filtered through a 0.2 μm syringe filter into a tared vial. The reaction vial was washed with 1 mL of CH_2Cl_2 and filtered through the same filter and combined with the initial filtrate. The filtrate solvent was removed *in vacuo* and the mass recorded. These resulting solids were digested with aqua regia (1 mL) and analyzed by ICP-MS for Ru content. The Ru content was compared to the control sample that was also filtered, the volatiles were removed in vacuo and a mass was measured prior to digestion (aqua regia) and ICP-MS analysis.

Preparation of Ru-SPN1 and regeneration to remove Ru

SPN1 (400 mg), **GI** (32.8 mg, 0.04 mmol), and CH_2Cl_2 (40 mL) were combined with a stir bar in a Schlenk round bottom and stirred for 24 hours under an N_2 atmosphere. The yellow solid was isolated using a Pall Microsep™ Advanced Centrifugal Device with a 10 kg/mol molecular weight cut off. The resulting solid was washed with CH_2Cl_2 and isolated, and this was repeated two additional times. The solid was dried *in vacuo* and divided into 100 mg samples into four glass vials (A-D) with stir bars. Samples A-C were subjected to 3 mL of neat regeneration conditions: PEt_3 at room temperature, PEt_3 at 80 °C, and tetramethyl ethylene diamine (TMEDA) at room temperature. The solutions were then stirred for 24 hours at the desired temperature under N_2. The solid was allowed to settle, and was isolated by filtration with a Microsep™ Centrifugal Device and washed with three portions of CH_2Cl_2. The solid was then dried *in vacuo*, and analyzed by ICP-MS and solid-state ^{31}P NMR spectrscopy. The final sample D underwent the same procedure except it was not subjected to the regeneration step. This sample was also analyzed by ICP-MS and solid-state ^{31}P NMR spectrscopy.

Scavenging of Pd following Suzuki Coupling

In a glovebox, the following stock solutions were prepared: bromobenzene (77 mg, 0.49 mmol, 830 mM) and dimethyl terephthalate (31 mg, 0.16 mmol, 270 mM) in DMF (590 μL); 4-methylbenzeneboronic acid (75 mg, 0.55 mmol, 870 mM) in DMF (630 μL); $Pd(OAc)_2$ (10 mg, 0.045 mmol, 15 mM) in DMF (3000 μL); PCy_3 (18 mg, 0.064 mmol, 63 mM) in DMF (1.000 μL). To 3 vials (A-C) containing stir bars and K_2CO_3 (22.9 mg, 0.166 mmol) the following was added: 100.0 μL of bromobenzene/dimethyl terephthalate, 100 μL of 4-methylboronic acid, 166 μL of $Pd(OAc)_2$, and 100.0 μL of PCy_3. This gives a final catalyst loading of 3 mol% (10483 ppm). An additional 34 μL of DMF was added to all of vials to give a final volume of 500 μL. All vials were sealed, removed from the glovebox and placed on a hotplate at 110 ˚C with stirring. At time points of 24 hours all five vials were removed from the heat, cooled, and taken back into the glovebox. One vial (A) was checked by ^1H NMR showing complete conversion of bromobenzene to 4-tolylbenzene. SPN polymer (25 mg) was added to a vial (B) and left to stir. After 24 h, vial B and C were both filtered using a 0.2 μm syringe filter. The precipitate removed

on these syringe filters was used for SEM analysis. The solvent for each vial was removed at 75 ˚C under vacuum in tared vials to find the mass of the remaining residue. The residue was digested using 2 mL of aqua regia at 50 ˚C for 4 h for ICP analysis. The proportion of Pd in the resulting residues were: B, 622 ppm (94% Pd removal); C, 3494 ppm (67% Pd removal).

II Solid-State $^{31}P\{^{1}H\}$ NMR Spectra

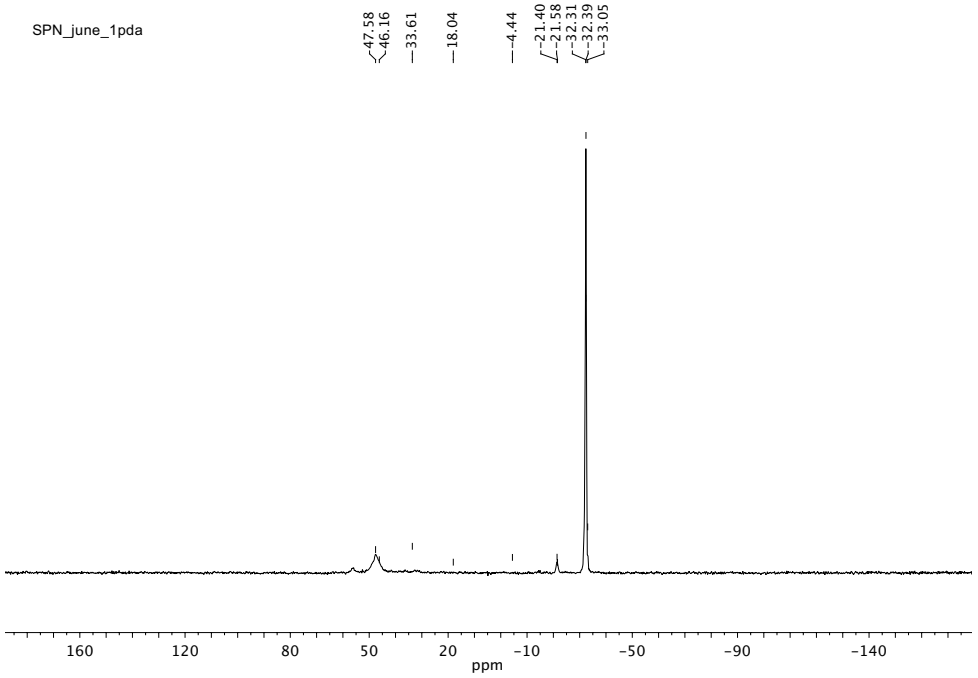


Figure S1. SS-$^{31}P\{^{1}H\}$ NMR spectrum (161.71 MHz) of **SPN1** acquired with a standard one pulse sequence. The signal a δ = –32 corresponds to tertiary phosphine sites, the broad signals at δ = ca. 50 are consistent with phosphine oxide sites.

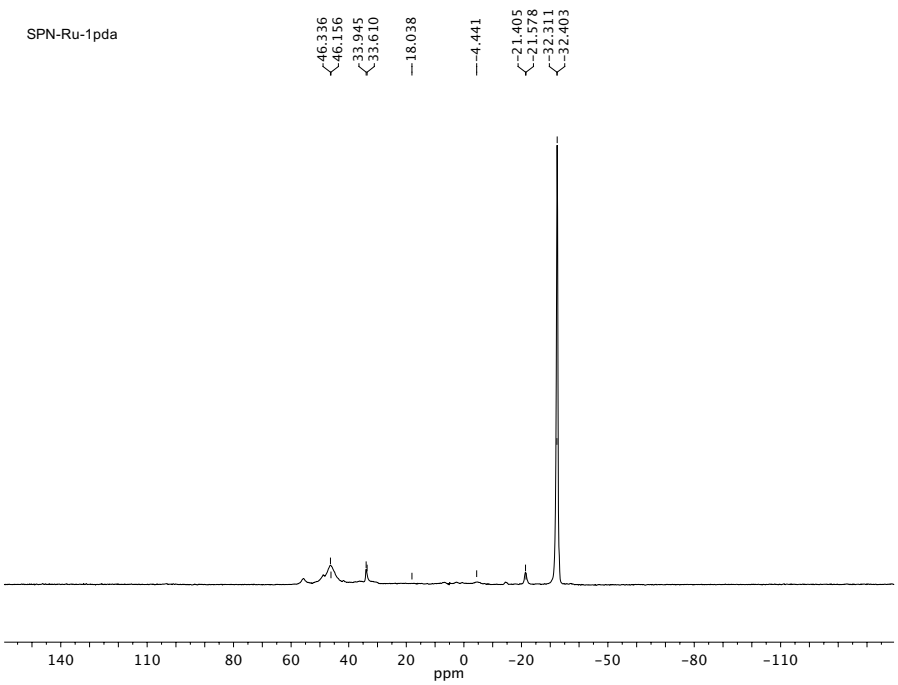


Figure S2. SS-$^{31}P\{^{1}H\}$ NMR spectrum (161.71 MHz) of **Ru-SPN1** acquired with a standard one pulse sequence. The signal a δ = –32 corresponds to tertiary phosphine sites, the broad signals at δ = ca. 50 are consistent with phosphine oxide sites.

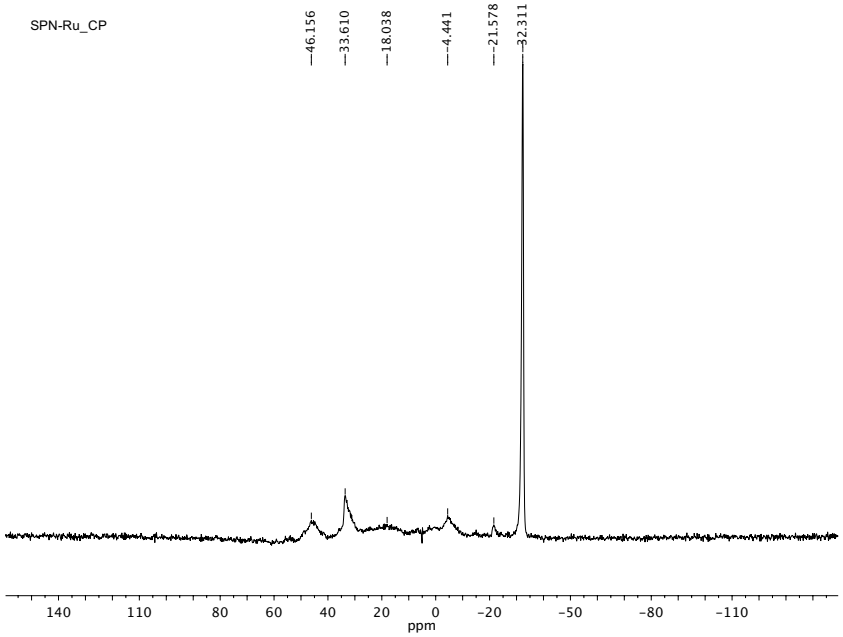
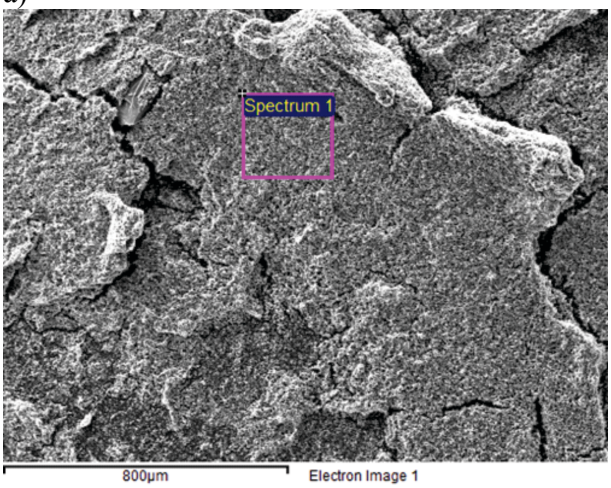


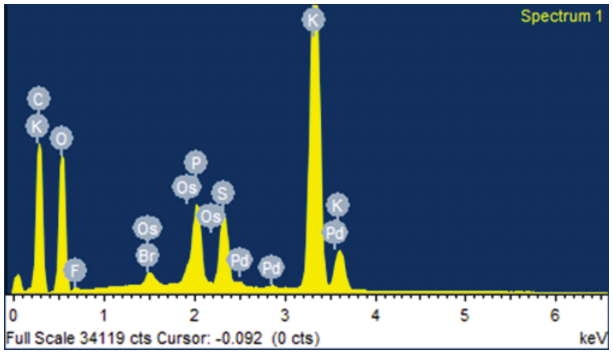
Figure S3. SS-$^{31}P\{^{1}H\}$ NMR spectrum (161.71 MHz) of **Ru-SPN1** acquired with a cross polarization pulse sequence. The signal a δ = –32 corresponds to tertiary phosphine sites, the broad signals at δ = ca. 50 are consistent with phosphine oxide sites. The broad signals in the range of 0–40 ppm are consistent with Ru-phosphine adduct formation.

III SEM/EDX Data

a)



b)

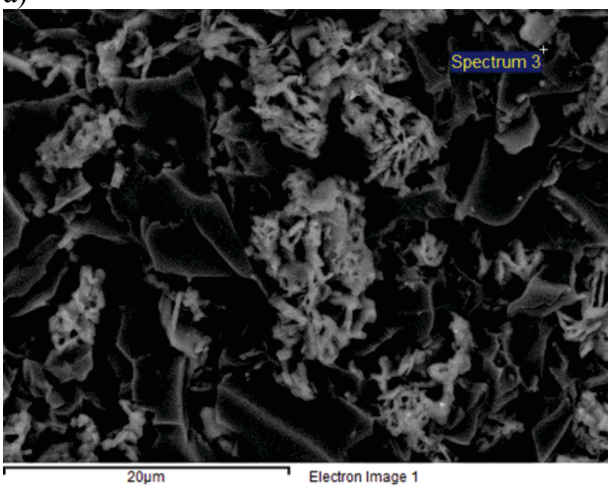


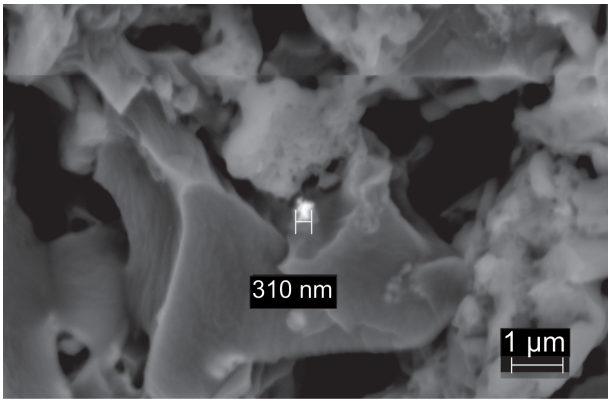
c)

Element	Weight%	Atomic%
C K	32.09	45.92
O K	37.92	40.74
F K	1.23	1.12
P K	2.93	1.63
S K	2.95	1.58
K K	19.52	8.58
Br L	0.80	0.17
Pd L	0.33	0.05
Os M	2.22	0.20
Totals	100.00	

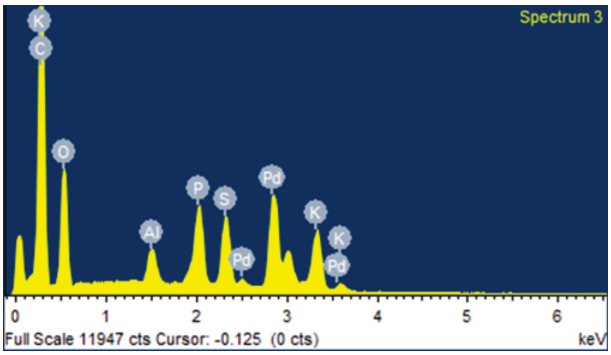
Figure S4. Analysis of the SPN polymer after Pd sequestration from a Suzuki coupling reaction. a) SEM image; b) EDX spectra collected at 15 kV; and c) Element compositions as determined by EDX analysis. The data is consistent with the composition for the **SPN** polymer containing low levels of Pd throughout.

a)





b)



c)

Element	Weight%	Atomic%
C K	34.56	59.57
O K	17.43	22.56
Al K	1.52	1.16
P K	4.88	3.26
S K	5.43	3.51
K K	8.61	4.56
Pd L	27.57	5.37
Totals	100.00	

Figure S5. Analysis of the **SPN** polymer after Pd sequestration from a Suzuki coupling reaction. a) SEM images showing the only observed evidence of a nanoparticle associated with the polymer (see bright spot on the bottom image visualized using a backscatter detector); b) EDX spectra; and c) Element compositions of the potential Pd nanoparticle.

IV Reference

1. R. Guterman, A. Rabiee Kenaree, J. B. Gilroy, E. R. Gillies and P. J. Ragogna, *Chem. Mater.*, 2015, **27**, 1412-1419.