

**Selectivity of Mechanochemical Chain Scission in Mixed Palladium(II) and
Platinum(II) Coordination Polymers**

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Electronic Supplementary Information

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General procedures. ^1H NMR (400 MHz), ^{13}C NMR (100 MHz) and ^{31}P NMR (162 MHz) spectra were recorded on a Bruker 400 spectrometer in deuterated chloroform unless stated otherwise. Chemical shifts are reported in ppm and referenced to tetramethylsilane and chloroform (proton and carbon) and external 85% phosphoric acid (phosphorus). Size exclusion chromatography was performed on a Shimadzu LC10-AT, using Polymer Laboratories PL Gel 5 μm mixed-D column (linear range of MW: 200 – 400000 g/mol), a Shimadzu SPD-10AV UV-vis detector at 254 nm and chloroform as eluent at a flow rate of 1 mL/min (20 °C). Polytetrahydrofuran samples were used for calibration. Sonication experiments were carried out with a Sonics VCX 500 Watt Ultrasonic Processor purchased from Sonics & Materials Inc. A 13 mm probe was used at a frequency of 20 kHz, at 30% of the maximum amplitude of 125 μm . Syntheses of the ligands and complexes were carried out under dry Argon atmosphere using standard Schlenk techniques. Tetrahydrofuran was distilled from sodium-potassium; dichloromethane and deuterated chloroform were distilled from P_2O_5 . Diethyl ether, and methanol were degassed before use. *n*-Butyl lithium was titrated before use. Basic aluminum oxide 90 (0.063-0.200 mm) and silica gel 60 (0.040-0.063 mm) were purchased from Merck; palladium dichloride (99.9%), platinum dichloride (99.9%), dichloro(1,5-cyclooctadiene) platinum (99%), dichloro(1,5-cyclooctadiene) palladium (99%) and dicyclohexylphosphine (98%) were purchased from STREM. *n*-Butyl lithium in hexanes (1.6 M, 2.5 M), trifluoromethanesulfonic anhydride (99%) and methyl trifluoromethanesulfonate (96%) were purchased from ACROS. Potassium diphenylphosphide (0.5 M in THF) and 1-bromododecane (97%) were purchased from Aldrich. Syntheses of polymeric ligand **1**, coordination polymer **2**¹ and ligands **A** and **B**² have been reported earlier.

Syntheses

α,ω -Bis(dicyclohexylphosphino)polytetrahydrofuran (1). Dicyclohexylphosphine (1.04 g, 5.24 mmol, 2.2 equivalents) was dissolved in tetrahydrofuran (30 mL) and the stirred solution was cooled to -90 °C. *n*-Butyl lithium (1.6 M, 3.27 mL, 5.2 mmol, 2.2 equivalents) was slowly added to the mixture. After complete addition the yellow mixture was stirred and left to warm to room temperature.

A mixture of di-*tert*-butyl-pyridine (42.6 mg, 0.22 mmol, 0.09 equivalents) and dry tetrahydrofuran (100 mL) was cooled to 0 °C with ice. Trifluoromethane sulfonic anhydride (0.67 g, 2.4 mmol) was added to the mixture. After stirring for 50 minutes at 0 °C, the solution of lithium dicyclohexylphosphine in tetrahydrofuran was added to the reaction mixture. This mixture was stirred for 30 minutes and left to warm to room temperature. Solvent was removed in vacuo resulting in a yellow oil. In order to remove residual impurities, the oil was dissolved in 150 mL diethyl ether and this mixture was filtered over silica that was dried from water and air. At -18 °C the polytetrahydrofuran crystallizes out and precipitates. This was repeated once, in order to remove all impurities. Finally the solvent was removed in vacuo, yielding a white solid (10.9 g, 68%). δ_{H} (400 MHz): 3.55-3.20 (m, $n \times 4\text{H}$, CH_2O), 1.74-1.17 (m, $n \times 4\text{H}$, $\text{CH}_2\text{CH}_2\text{O}$ and 44H, alkyl). δ_{C} (100 MHz) 70.70 (s, $n \times 2\text{C}$, CH_2O), 33.40 (d, 4C, alkyl), 30.45 (d, 8C, alkyl), 29.09 (d, 8C, alkyl) 27.44-25.34 (m, $n \times 2\text{C}$, $\text{CH}_2\text{CH}_2\text{O}$ and 4C, alkyl), 21.27 (d, 2C, PCH_2). δ_{P} (162 MHz): -3.25 (s, 2P). Molecular weight via end-group determination (^1H NMR): $M_n = 1.2 \times 10^4$ g/mol. Polydispersity index (SEC): $M_w/M_n = 1.14$, based on polystyrene standards.

Palladium dichloride (α,ω -bis(dicyclohexylphosphino)polytetrahydrofuran) (2). Palladium(II) dichloride (1,5-cyclooctadiene) (91 mg, 0.32 mmol, 0.75 equivalents), palladium(II) dichloride (27 mg, 0.15 mmol, 0.35 equivalents) and α,ω -bis(dicyclohexylphosphino)polytetrahydrofuran **1** (2.69 g, ~ 0.27 mmol) were dissolved in 270 mL dry toluene and this mixture was stirred for 7 days. The mixture was filtered in order to remove the excess palladium(II) dichloride yielding a clear yellow solution. Solvent was not evaporated; the 10 g/L solution was immediately used in sonication experiments. Only a small sample was dried for analysis purposes. δ_{H} (400 MHz): 3.58-3.22 (m, $n \times 4\text{H}$, CH_2O), 1.90-1.19 (m, $m \times n \times 4\text{H}$, $\text{CH}_2\text{CH}_2\text{O}$ and $m \times 44\text{H}$, alkyl). δ_{C} (100 MHz): 70.74 (s, $m \times n \times 2\text{C}$, CH_2O), 33.03 (s, $m \times 4\text{C}$, alkyl), 29.43 (s, $m \times 8\text{C}$, alkyl), 28.96 (d, $m \times 8\text{C}$, alkyl), 27.52-26.3 (m, $m \times n \times 2\text{C}$, $\text{CH}_2\text{CH}_2\text{O}$ and 4C, alkyl), 22.09 (s, 2C, PCH_2). δ_{P} (162 MHz): 23.24 (s, $m \times 2\text{P}$). (n is the degree of

polymerization of polymer **1**, m is the degree of supramolecular polymerization of coordination polymer **2**)

Platinum dichloride (α,ω -bis(dicyclohexylphosphino)polytetrahydrofuran) (3**).** Platinum(II) dichloride (14 mg, 0.053 mmol) and α,ω -bis(dicyclohexylphosphino) polytetrahydrofuran **1** (635 mg, 0.053 mmol) were dissolved in dry toluene (63.5 mL) and the mixture was stirred overnight. The mixture was filtered yielding a faint yellow solution. Solvent was not evaporated; the 10 g/L solution was immediately used in sonication experiments. δ_{H} (400 MHz, CD_2Cl_2): 3.56-3.28 (m, $n \times 4\text{H}$, CH_2O), 2.10-1.05 (m, $m \times n \times 4\text{H}$, $\text{CH}_2\text{CH}_2\text{O}$ and $m \times 44\text{H}$, alkyl). δ_{C} (100 MHz, CD_2Cl_2): 70.85 (s, $m \times n \times 2\text{C}$, CH_2O), 33.16 (s, $m \times 4\text{C}$, alkyl), 29.55 (s, $m \times 8\text{C}$, alkyl), 29.05 (d, $m \times 8\text{C}$, alkyl), 27.70-26.40 (b, $m \times n \times 2\text{C}$, $\text{CH}_2\text{CH}_2\text{O}$ and 4C, alkyl), 22.25 (s, 2C, PCH_2). δ_{P} (162 MHz, CD_2Cl_2): 14.62 (s, $m \times 2\text{P}$, $J_{\text{Pt-P}} = 2414$ Hz.). (n is the degree of polymerization of polymer **1**, m is the degree of supramolecular polymerization of coordination polymer **3**)

Platinum dichloride, palladium dichloride (α,ω -bis(dicyclohexylphosphino) polytetrahydrofuran) (4**).** Platinum(II) dichloride (8.0 mg, 0.029 mmol) and palladium(II) dichloride (5 mg, 0.029 mmol) were mixed with α,ω -bis(dicyclohexylphosphino) polytetrahydrofuran **1** (692 mg, 0.058 mmol) in dry toluene (69 mL). The mixture was stirred for 6 days. The mixture was filtered to remove any residual palladium(II) dichloride and yielded a yellow solution. Solvent was not evaporated; the 10 g/L solution was immediately used in sonication experiments. δ_{H} (400 MHz): 3.65-3.20 (m, $n \times 4\text{H}$, CH_2O), 1.89-1.10 (m, $m \times n \times 4\text{H}$, $\text{CH}_2\text{CH}_2\text{O}$ and $m \times 44\text{H}$, alkyl). δ_{C} (100 MHz): 70.10 (s, $m \times n \times 2\text{C}$, CH_2O), 32.58 (s, $m \times 4\text{C}$, alkyl), 28.75 (s, $m \times 8\text{C}$, alkyl), 28.30 (d, $m \times 8\text{C}$, alkyl), 26.80-25.60 (m, $m \times n \times 2\text{C}$, $\text{CH}_2\text{CH}_2\text{O}$ and 4C, alkyl), 21.45 (s, 2C, PCH_2). δ_{P} (162 MHz): 22.30 (s, palladium(II) centers 53%, $m \times 2\text{P}$), 15.48 (s, platinum(II) centers 47%, $m \times 2\text{P}$, $J_{\text{Pt-P}} = 2414$ Hz.). (n is the degree of polymerization of polymer **1**, m is the degree of supramolecular polymerization of coordination polymer **4**)

1-(Diphenylphosphino)dodecane (A). 1-Bromododecane (1.87 g, 7.50 mmol) was dissolved in dry THF (50 mL) and the stirred solution was cooled to -78 °C with acetone/dry ice. A solution of potassium diphenylphosphide in THF (0.5 M, 15.0 mL, 7.50 mmol) was slowly added to the mixture. After complete addition, the mixture was stirred for an hour at -78 °C and left to warm to room temperature. The mixture was stirred overnight. Solvent was removed in vacuo and the solids were suspended in dry dichloromethane (40 mL) and filtered over a glass filter. To remove residual impurities the mixture was filtered over silica, which was dried from water and air before use. Solvent was removed in vacuo. The product, a clear liquid was obtained in 78% yield. The liquid crystallizes when cooled to 5 °C. δ_{H} (400 MHz): 7.35-7.49 (m, 10H, Ph), 2.08 (t, 4H, CH_2P), 1.13-1.53 (m, 20H, CH_2), 0.92 (t, 3H, CH_3). δ_{C} (121 MHz): 139.44 (d, 2C, Ph) 132.73 (d, 4C, Ph), 128.42 (s, 4C, Ph), 128.33 (d, 2C, Ph), 31.94 (s, 1C, alkyl), 31.24 (d, 1C, alkyl), 29.68 (s, 1C, alkyl), 29.64 (s, 1C, alkyl), 29.37 (m, 3C, alkyl) 29.28 (s, 1C, alkyl), 28.06 (d, 1C, alkyl), 26.05 (d, 1C, alkyl), 22.72 (s, 1C, alkyl), 14.15 (s, 1C, alkyl). δ_{P} (162 MHz): -16.0 (s, 1P).

Palladium dichloride bis(1-(diphenylphosphino)dodecane) (5**).** A mixture of palladium(II) dichloride (37 mg, 0.21 mmol, 0.55 equivalents) and 1-(diphenylphosphino) dodecane **A** (133 mg, 0.38 mmol) in dry dichloromethane (7 mL) was stirred for 24 hours. The mixture was filtered in order to remove the excess palladium(II) dichloride and solvent was removed in vacuo, yielding a bright yellow solid in 92% yield. δ_{H} (400 MHz): 7.70-7.22 (m, 20H, Ph), 2.41-2.27 (m, 4H CH_2P), 1.28-0.98 (m, 40H, CH_2), 0.91 (t, 6H, CH_3). δ_{C} (121 MHz): 133.83 (s, 2C, Ph), 130.61 (d, 4C, Ph), 128.34 (s, 4C, Ph), 128.28 (s, 2C, Ph), 32.08 (s, 1C, alkyl), 31.38 (d, 1C, alkyl), 29.79-29.42 (m, 6C, alkyl), 28.21 (d, 1C, alkyl), 26.12 (d, 1C, alkyl), 22.85 (s, 1C, alkyl), 14.28 (s, 1C, alkyl). δ_{P} (162 MHz): 16.5 (s, 2P). Elemental analysis calcd (%) for $\text{C}_{48}\text{H}_{70}\text{Cl}_2\text{P}_2\text{Pd}$: C 65.04, H 7.96. Found: C 64.84, H 7.91. MALDI-TOF MS: 851.5 ($\text{M}^+ - \text{Cl}$).

1-(Dicyclohexylphosphino)dodecane (B). Dicyclohexylphosphine (2.00 g, 10.1 mmol) was dissolved in dry THF (50 mL) and cooled to -78 °C and n -butyl lithium (1.6 M, 6.3 mL, 10 mmol) was added.

This mixture was left to warm to room temperature and then added to, an ice-cooled, 0 °C mixture of 1-bromododecane (2.51 g, 10.1 mmol) in 50 mL of dry THF. This mixture was stirred for 30 minutes and left to warm to room temperature. Solvent was removed in vacuo and the solids were suspended in dry diethyl ether (50 mL). To remove residual impurities the mixture was filtered over silica that was dried from water and air. Solvent was removed in vacuo. The product, a clear liquid was obtained in 63% yield. δ_{H} (400 MHz, toluene- d_8): 2.07-1.43 (m, 44H, CH_2+CH), 1.15 (t, 3H, CH_3). δ_{C} (75 MHz, toluene- d_8): 34.50 (d, 2C, alkyl), 32.86 (s, 1C, alkyl), 32.55 (d, 1C, alkyl), 31.31 (d, 2C, alkyl), 30.67 (d, 4C, alkyl), 30.42 (d, 2C, alkyl), 29.92 (d, 2C, alkyl), 29.67 (d, 1C, alkyl), 28.30-28.14 (m, 4C, alkyl), 27.47 (s, 2C, alkyl), 23.62 (s, 1C, alkyl), 22.55 (d, 1C, alkyl), 14.80 (s, 1C, CH_3). δ_{P} (162 MHz, toluene- d_8): -4.8 (s, 1P).

Computational details. Geometry optimizations and frequency calculations were performed using density functional theory (DFT). The Gaussian03 program³ was used with Becke's three-parameter functional (B3)⁴ and Lee, Yang and Parr's (LYP)⁵ correlation (B3LYP) with LANL2DZ basis sets. Total energies were calculated for a set of model complexes based on the palladium(II) and platinum(II) halides in combination with pentyldicyclohexylphosphine. The geometries of bis-ligated and mono-ligated complexes were optimized and the energy differences were determined, giving an indication of the bond dissociation energy. The data is depicted in Table S1.

Table S1. Total energies of optimized geometries and bond dissociation energies of palladium(II) and platinum(II) bis(pentyldicyclohexylphosphine) complexes.

	Palladium (kJ/mol)	Platinum (kJ/mol)	Energy difference (kJ/mol)
Chloride	141.3	168.6	27.3
Bromide	129.1	150.2	21.1
Iodide	112.4	131.5	19.1

Sonication experiments. A water-cooled glass vessel was filled with 30.0 mL of a solution of coordination polymer **2**, **3** or **4** (~1.45 mM with respect to the monomeric unit, 4.36×10^{-5} mol). To this solution were added 10 equivalents of complex **5** (4.36×10^{-4} mol, 386 mg). The solution was sonicated while slowly bubbling Argon through and samples for SEC-analysis were taken at regular intervals. These samples were immediately frozen in liquid nitrogen and left to warm to room temperature only just before SEC-measurements and ^{31}P NMR experiments.

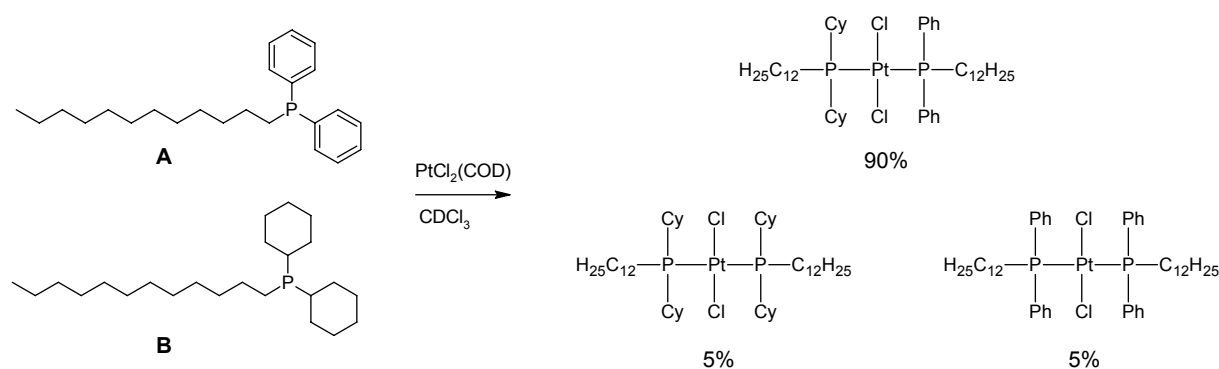
Control experiments. Similarly to the sonication experiments, the water-cooled glass vessel was filled with 30.0 mL of a solution of either palladium(II) or platinum(II) based coordination polymer **2** or **3** (~1.45 mM with respect to monomeric unit, 4.36×10^{-5} mol). To these solutions were added 10 equivalents of complex **5** (4.36×10^{-4} mol, 386 mg). These solutions were stirred, while bubbling through Argon. Samples for SEC-analysis were taken at regular intervals. Samples were immersed in liquid nitrogen and brought back to room temperature only just before SEC-measurements. As observed in earlier studies¹, ligand exchange is very slow under these conditions. For the palladium(II) based coordination polymer **2**, approximately 1.4% exchange was observed after 1 hour and 1.6% after 2 hours. For the platinum(II) based coordination polymer **3**, an even lower exchange rate was observed, with approximately 0.3% exchange after 1 hour and 0.4% after 2 hours.

Quantification of ultrasonic scission

Using SEC. During sonication, **5** is consumed by ligand exchange with polymer chain ends created by scission. The extent of ultrasonic scission was determined by monitoring the decrease in intensity of the signal of **5** in SEC.

Using ^{31}P NMR

Assignment For assignment of the signals observed with ^{31}P NMR, equimolar amounts of 1-dodecyldiphenylphosphine (**A**) and 1-dodecyldicyclohexylphosphine (**B**) were complexed with platinum(II) dichloride 1,5-cyclooctadiene in CDCl_3 , which led to 90% heterocomplex formation and 5% of the corresponding homocomplexes. The heterocomplex results in two doublets at $\delta = 17.7$ ppm (dicyclohexylphosphine part, $J_{\text{Pt-P}} = 2555$ Hz) and $\delta = 12.1$ ppm (diphenylphosphine part, $J_{\text{Pt-P}} = 2435$ Hz) with $J_{\text{P-P}} = 460$ Hz. The relatively small platinum-phosphorus coupling constant indicate *trans*-coordination,⁶ which is confirmed by the large phosphorus-phosphorus coupling constant.⁷ Resonances of the platinum(II) dichloride bis(1-(dicyclohexylphosphino)dodecane) complex correspond to those of coordination polymer **3**.



Scheme S1. Preparation of platinum(II) dichloride (1-dodecyldicyclohexylphosphine) (1-dodecyldiphenylphosphine) mixed complex.

Quantification All resonances were integrated via peak deconvolution. The extent of ultrasonic scission in homonuclear coordination polymers **2** and **3** was calculated as reported earlier,¹ by determining the ratio of heterocomplex vs. the initial amount. In the case of the palladium(II) dichloride based coordination polymer, (Figure S1, top) resonances of both the diphenylphosphine and dicyclohexylphosphine moieties give the same results.

In the case of platinum(II) dichloride based coordination polymer, (Figure S1, center) two sets of heterocomplexes form, either containing a palladium or platinum metal center. Because of overlapping signals of the dicyclohexylphosphine moiety of the platinum heterocomplex with scavenger complex **5**, the resonances of the palladium heterocomplexes were used for quantification. Dicyclohexylphosphine and diphenylphosphine moieties give comparable results.

Quantification of ultrasonic scission of heteronuclear coordination polymer **4** is slightly more complicated, because the intensity of the platinum heterocomplexes formed is too low to observe. Quantification was therefore performed using the decrease in intensity of the palladium and platinum homocomplexes. (Figure S1, bottom) In this calculation, the relative abundance of ^{195}Pt (33.8%) has to be taken into account, since the satellite-signals cannot be observed, and therefore not integrated.

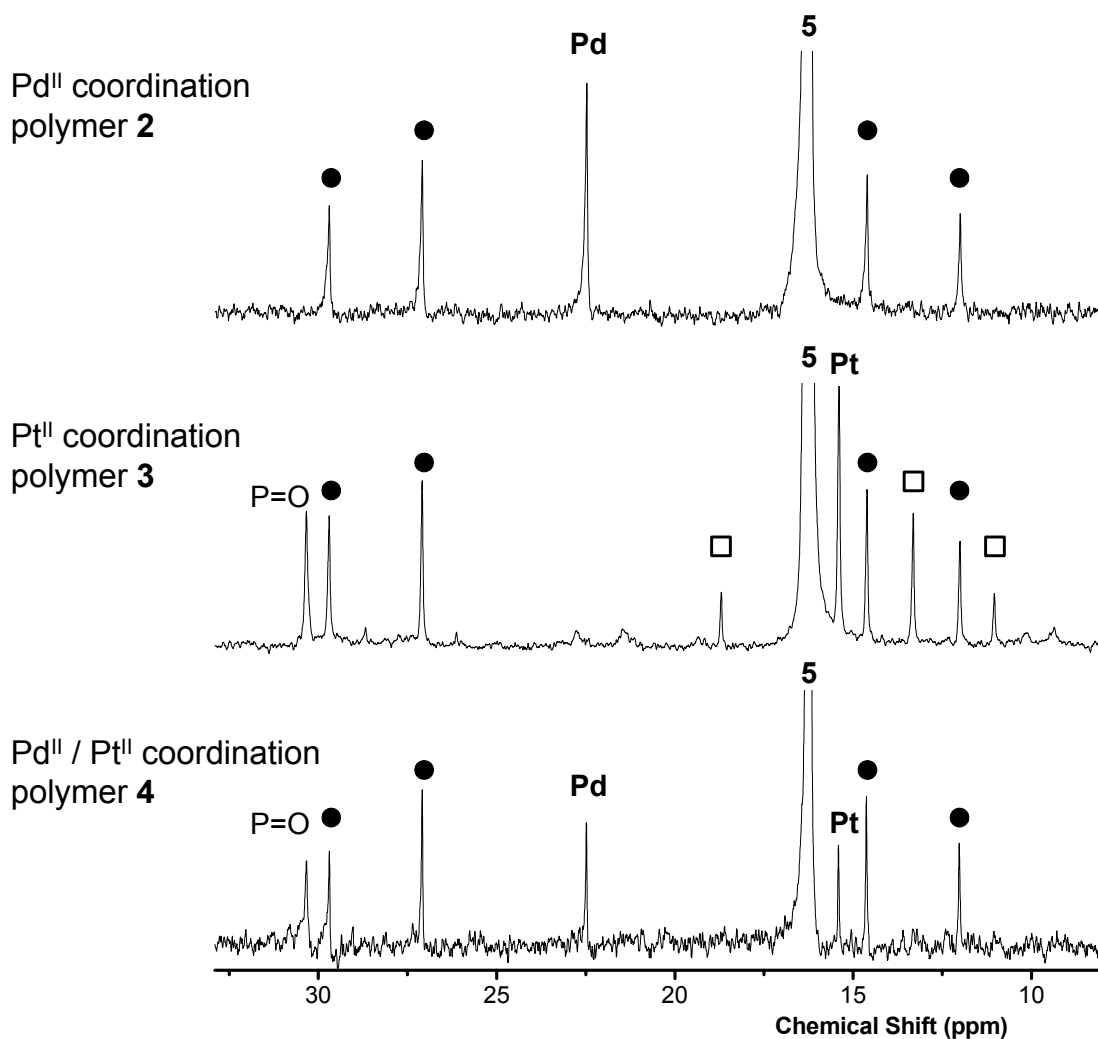


Figure S1. ³¹P NMR spectra of homo- and heteronuclear coordination polymers **2**, **3** and **4** after respectively 6, 6 and 5 hours of sonication in the presence of scavenger complex **5**. (black dot: palladium(II) heterocomplex; open square: platinum(II) heterocomplex; Pd, Pt: corresponding homocomplex; P=O: phosphine-oxide stemming from complex **5**).

Table S2. Normalized integrals of observed resonances in ³¹P NMR spectra, measured during sonication of coordination polymer **4**.

Time	PPh ₂ Pd Complex 5	PPh ₂ Pd, homocomplex	PPh ₂ Pt homocomplex	PCy ₂ Pd heterocomplex	PPh ₂ Pd heterocomplex
0	93.12	4.46	2.41	0.00	0.00
60	91.33	3.08	2.19	1.65	1.75
120	91.09	2.65	1.71	2.37	2.17
180	90.37	2.05	1.59	3.02	2.98
300	90.17	1.66	1.14	3.71	3.32

Table S3. Percentages of palladium(II) and platinum(II) metal complexes broken in heteronuclear coordination polymer **4**.

Time	Pd converted (%)	Pt converted (%)
0	0.00	0.00
60	31.0	9.3
120	40.5	29.1
180	54.2	34.3
300	62.7	52.8

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