Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

for

Pd-Complexation Driven Formation of Single-Chain Nanoparticles

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Methods

Characterization

Size Exclusion Chromatography (SEC)

THF-SEC measurements were performed on a Polymer Laboratories PL-GPC 50 Plus Integrated System, comprising an autosampler, a PLgel 5 µm bead-size guard column (50 × 7.5 mm) followed by three PLgel 5 µm Mixed-C and one PLgel 3 µm Mixed-E columns (300 × 7.5 mm) and a differential refractive index detector using THF as the eluent at 35 °C with a flow rate of 1 mL min^{-1}. The SEC system was calibrated using linear poly(styrene) (PS) standards ranging from 474 to 2.5×10^6 g mol^{-1}. Calculation of the molecular weight proceeded *via* the Mark-Houwink parameters for polystyrene, i.e. $K = 14.1 \cdot 10^{-5}$ dL·g^{-1}, $\alpha = 0.70$.[1]

DMAc-SEC measurements were performed on a Polymer Laboratories PL-GPC 50 Plus Integrated System, comprising an autosampler, a PLgel 5 µm bead-size guard column (50 × 7.5 mm) followed by three PLgel 5 µm Mixed-C (300 × 7.5 mm) and a differential refractive index detector using DMAc as the eluent at 50 °C with a flow rate of 1 mL min^{-1}. The SEC system was calibrated using linear poly(styrene) (PS) standards ranging from 474 to 2.5×10^6 g mol^{-1}.

Nuclear Magnetic Resonance (NMR) Spectroscopy

The synthesized compounds were analyzed *via* ^{1}H- and ^{31}P{^{1}H }-NMR spectroscopy using a Bruker Avance 400 spectrometer (^{1}H, 400 MHz; ^{31}P, 162 MHz). Samples were dissolved in $CDCl_3$. The δ-scale was referenced with the solvent residual peak of $CHCl_3$ ($\delta = 7.26$). Abbreviations used in the description of the materials' syntheses include singlet (s), broad singlet (bs), doublet (d), triplet (t), quartet (q), broad multiplet (bm), and unresolved multiplet (m).

The copolymer composition was calculated by utilizing the integral values for the proton resonances at 6.22 - 7.28 ppm (aromatic protons) and the resonance close to 4.51 ppm (CH_2Cl) (see Figure S1). The content of CMS in the copolymer was determined to be 12 %.

The molar number of triphenylphosphine ligands n(L) in a given amount m of the functionalized linear precursor polymer was calculated from the following formula,

$$n(L) = \%L \times \frac{m}{\%L\, M(L) + (1 - \%L)\, M(St)}$$

where M(L) = 422,5 g mol^{-1} and M(St) = 104,2 g mol^{-1} are the molecular weights of the triphenylphosphin repeating unit and the styrene repeating unit, respectively.

The transversal relaxation time T_2 was measured by applying the Car-Purcel-Meiboom-Gill (CPMG) echo train acquisition. The 90 ° pulses were 9.14 µs, the relaxation delay 3 s, and the fixed echo time 0.001 s. Processing was achieved using Topspin 3.1 with the Dynamics Center 2.0.4 software. The resulting decay curves were fitted with a mono exponential decay function to calculate T_2:

$$I(t) = I(0)e^{-(\frac{t}{T_2})}$$

Dynamic Light Scattering (DLS)

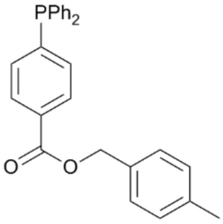
Dynamic light scattering (DLS) was performed on a NICOMP 380 DLS spectrometer (Particle Sizing Systems, Santa Barbara, USA) with a 90 mW laser diode operating at 658 nm equipped with an avalanche photodiode detector. The polymer solutions were prepared by dissolving the polymer in THF at a concentration of 4 mg mL^{-1} and subsequent filtering over a 0.2 µL filter before being analyzed by DLS. The measurements were performed in automatic mode and evaluated with a standard Gaussian and an advanced evaluation method, the latter using an inverse Laplace algorithm to analyze for multimodal distributions. Numbers given in text are the number weighted average values as calculated by the NICOMP evaluation. All measurements were determined at 90° to the incident beam.

X-Ray Photoelectron Spectroscopy (XPS)

XPS measurements were performed using a K-Alpha XPS spectrometer (ThermoFisher Scientific, East Grinstead, UK). Data acquisition and processing using the Thermo Avantage software is described elsewhere.[2] All samples were analyzed using a microfocused, monochromated Al Kα X-ray source (400 µm spot size). The K-Alpha charge compensation system was employed during analysis, using electrons of 8 eV energy, and low-energy argon ions to prevent any localized charge build-up. The spectra were fitted with one or more Voigt profiles (BE uncertainty: ±0.2eV) and Scofield sensitivity factors were applied for quantification.[3] All spectra were referenced to the C1s peak (C-C, C-H) at 285.0 eV binding energy controlled by means of the well-known photoelectron peaks of metallic Cu, Ag, and Au, respectively.

Additional Experimental Section

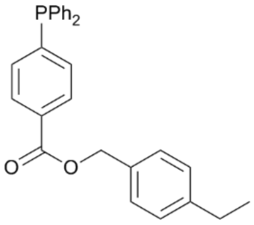
*Synthesis of 4-Methylbenzyl 4-(diphenylphosphino)benzoate (**L1**)*



To a solution of 4-(diphenylphosphino)benzoic acid (204 mg, 0.67 mmol, 1.00 equiv.) in dichloromethane (10 mL), 4-methylbenzyl alcohol (81.4 mg, 0.67 mmol, 1.00 equiv.) and *N*,*N*-dimethylaminopyridine (18.7 mg, 0.15 mmol, 0.23 equiv.) was added. Then a solution of diisopropylcarbodiimide (0.11 mL, 88.3 mg, 0.70 mmol, 1.05 equiv.) in dichloromethane was slowly added over the course of 5 min. The resulting yellow suspension was stirred under inert atmosphere at room temperature for 24 h. The reaction mixture was filtered and the solvent was removed under reduced pressure. The filtrate was diluted with ethyl acetate (20 mL) and washed consecutively with aqueous 10 % HCl (10 mL), aqueous saturated $NaHCO_3$ (10 mL) and brine (10 mL). The organic phase was separated and dried over $MgSO_4$, filtered and dried under reduced pressure. 4-Methylbenzyl 4-(diphenylphosphino)benzoate was obtained after flash chromatography (5% ethyl acetate/n-pentane) as a slightly yellow oil (215 mg, 0.52 mmol, 79 %).

^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.03-7.96 (m, 2H, Ph), 7.42-7.14 (m, 16H, Ph), 5.31 (s, 2H, C*H*$_2$OC=O), 2.36 (s, 3H, C*H*$_3$Ph). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, δ): 166.4 (s, 1C, *C*OOR), 144.1 (d, $^1J_{\text{C-P}}$ = 13.6 Hz, 1C, P*Ph*COO$_{\text{(ipso)}}$), 138.3 (s, 1C, *Ph*), 136.2 (d, $^1J_{\text{C-P}}$ = 10.0 Hz, 2C, P*Ph*$_{2\text{(ipso)}}$), 134.1 (d, $^2J_{\text{C-P}}$ = 19.9 Hz, 4C, P*Ph*$_{2\text{(ortho)}}$), 133.3 (d, $^2J_{\text{C-P}}$ = 18.7 Hz, 2C, P*Ph*COO$_{\text{(ortho)}}$), 133.1 (s, 1C, *Ph*), 130.3 (s, 1C, P*Ph*COO$_{\text{(para)}}$), 129.6 (d, $^3J_{\text{C-P}}$ = 6.4 Hz, 2C, P*Ph*COO$_{\text{(meta)}}$), 129.4 (s, 2C, *Ph*), 129.3 (s, 2C, P*Ph*$_{2\text{(para)}}$), 128.8 (d, $^3J_{\text{C-P}}$ = 7.2 Hz, 4C, P*Ph*$_{2\text{(meta)}}$), 128.5 (s, 2C, *Ph*), 66.9 (s, 1C, *C*H$_2$OC=O), 21.4 (s, 1C, *C*H$_3$Ph). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, δ): -5.0 (s, 1P, *P*Ph$_2$Ar).

*Synthesis of 4-Ethylbenzyl 4-(diphenylphosphino)benzoate (**L2**)*



The desired product was prepared from 4-(diphenylphosphino)benzoic acid (254 mg, 0.83 mmol, 1.00 equiv.) and ethylbenzyl alcohol (113 mg, 0.83 mmol, 1.00 equiv.) according to the procedure described above for the synthesis of 4-methylbenzyl 4-(diphenylphosphino)benzoate. 4-Ethylbenzyl 4-(diphenylphosphino)benzoate was obtained after flash chromatography (5% ethyl acetate/n-pentane) as a colourless oil (209 mg, 0.49 mmol, 59 %).

^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.04-7.97 (m, 2H, Ph), 7.40-7.16 (m, 16H, Ph), 5.32 (s, 2H, CH_2OC=O), 2.66 (q, $^3J_{H\text{-}H}$ = 7.6 Hz, 2H, CH_2Ph), 1.24 (t, $^3J_{H\text{-}H}$ = 7.6 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, δ): 166.4 (s, 1C, *C*OOR), 144.6 (s, 1C, *Ph*), 144.2 (d, $^1J_{C\text{-}P}$ = 13.6 Hz, 1C, P*Ph*$COO_{(ipso)}$), 136.2 (d, $^1J_{C\text{-}P}$ = 10.0 Hz, 2C, P$Ph_{2(ipso)}$), 134.1 (d, $^2J_{C\text{-}P}$ = 19.9 Hz, 4C, P$Ph_{2(ortho)}$), 133.3 (s, 1C, *Ph*), 133.3 (d, $^2J_{C\text{-}P}$ = 18.7 Hz, 2C, P*Ph*$COO_{(ortho)}$), 130.3 (s, 1C, P*Ph*$COO_{(para)}$), 129.6 (d, $^3J_{C\text{-}P}$ = 6.5 Hz, 2C, P*Ph*$COO_{(meta)}$), 129.3 (s, 2C, P$Ph_{2(para)}$), 128.8 (d, $^3J_{C\text{-}P}$ = 7.2 Hz, 4C, P$Ph_{2(meta)}$), 128.6 (s, 2C, *Ph*), 128.2 (s, 2C, *Ph*), 66.9 (s, 1C, CH_2OC=O), 28.8 (s, 1C, CH_2Ph), 15.7 (s, 1C, CH_3). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, δ): -5.1 (s, 1P, *P*Ph_2Ar).

*Synthesis of the complex [Pd(**L1**)$_2$Cl$_2$]*

To a solution of dichloro(1,5-cyclooctadiene)palladium(II) (16.2 mg, 0.06 mmol, 1.00 equiv.) in dichloromethane (5 mL), a solution of 4-methylbenzyl 4-(diphenylphosphino)benzoate (**L1**) (46.5 mg, 0.11 mmol, 2.00 equiv.) in dichloromethane

(5 mL) was added. The resulting reaction mixture was stirred under inert atmosphere at room temperature for 16 h. Subsequently, the solution was concentrated in vacuo and after the addition of n-pentane (10 mL) a yellow solid precipitated. The solid was washed with n-pentane (10 mL) and dried under high vacuum to afford the product [Pd(**L1**)$_2$Cl$_2$] as a yellow solid. Yellow crystals (49 mg, 0.05 mmol, 86 %) were obtained by diffusion of n-pentane into a solution of dichloromethane of the yellow powder.

^{1}H NMR (300 MHz, CDCl$_3$, δ): 8.09-7.99 (m, 4H, Ph), 7.80-7.14 (m, 32H, Ph), 5.31 (s, 4H, CH_2OC=O), 2.35 (s, 6H, CH_3Ph). ^{31}P{^{1}H} NMR (121 MHz, CDCl$_3$, δ): 23.5 (s, 2P, *P*Ph$_2$Ar-PdCl$_2$-*P*Ph$_2$Ar).

*Synthesis of the complex [Pd(**L2**)$_2$Cl$_2$]*

The desired complex was prepared from dichloro(1,5-cyclooctadiene)palladium(II) (19.8 mg, 0.07 mmol, 1.00 equiv.) and 4-ethylbenzyl 4-(diphenylphosphino)benzoate (**L2**) (58.9 mg, 0.14 mmol, 2.00 equiv.) according to the procedure described above for the synthesis of [Pd(**L1**)$_2$Cl$_2$]. The complex [Pd(**L2**)$_2$Cl$_2$] was obtained as yellow crystals (62 mg, 0.06 mmol, 87 %) by diffusion of n-pentane into a solution of dichloromethane of the yellow powder.

^{1}H NMR (300 MHz, CDCl$_3$, δ): 8.10-8.00 (m, 4H, Ph), 7.79-7.16 (m, 32H, Ph), 5.32 (s, 4H, CH_2OC=O), 2.66 (q, $^3J_{\text{H-H}}$ = 7.6 Hz, 4H, CH_2Ph), 1.24 (t, $^3J_{\text{H-H}}$ = 7.6 Hz, 6H, CH_3). ^{31}P{^{1}H} NMR (121 MHz, CDCl$_3$, δ): 23.5 (s, 2P, *P*Ph$_2$Ar-PdCl$_2$-*P*Ph$_2$Ar).

Mixing Experiment

In addition, a statistical mixture (1:2:1) of the complexes [Pd(**L1**)$_2$Cl$_2$], [Pd(**L1**)(**L2**)Cl$_2$] and [Pd(**L2**)$_2$Cl$_2$] was synthesized in order to examine the effects on the resulting ^{31}P{^{1}H} NMR spectrum. Therefore a solution of the synthesized ligands 4-methylbenzyl 4-

(diphenylphosphino)benzoate (**L1**) (72.5 mg, 0.18 mmol, 1.00 equiv.) and 4-ethylbenzyl 4-(diphenylphosphino)benzoate (**L2**) (75.0 mg, 0.18 mmol, 1.00 equiv.) in dichloromethane (5 mL) was added simultaneously over the course of 5 min to a solution of dichloro(1,5-cyclooctadiene)palladium(II) (50.4 mg, 0.18 mmol, 1.00 equiv.) in dichloromethane (10 mL). The remaining preparation followed the procedure described above for the synthesis of [Pd(**L1**)$_2$Cl$_2$]. The corresponding ^{1}H NMR spectrum shows the expected signals of both ligands **L1** and **L2** in almost the same ratio, which implies that they coordinate to the Pd-center to the same extent. In the ^{31}P{^{1}H} NMR spectrum a singulett signal at $\delta = 23.5$ ppm is observed, analogously to the complexes [Pd(**L1**)$_2$Cl$_2$] and [Pd(**L2**)$_2$Cl$_2$]. The signal is slightly broadened, but no coupling is observed in the ^{31}P{^{1}H} NMR spectrum.

Additional Characterization Data

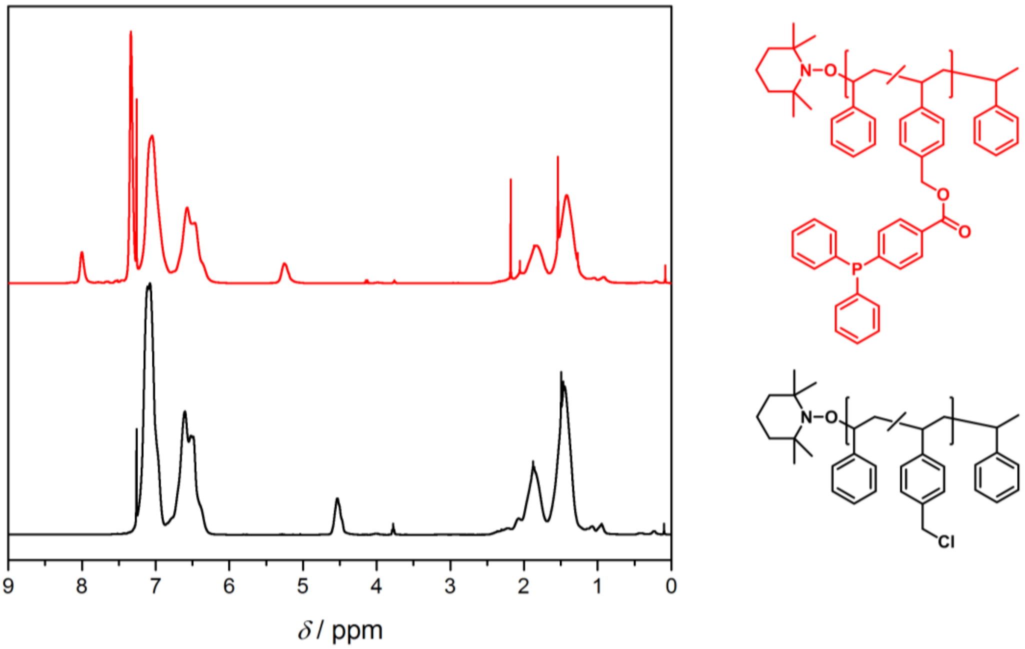


Figure S1. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of the poly(styrene-*co*-chloromethylstyrene) copolymer **P1** (bottom) and the functional linear precursor **P2** (top).

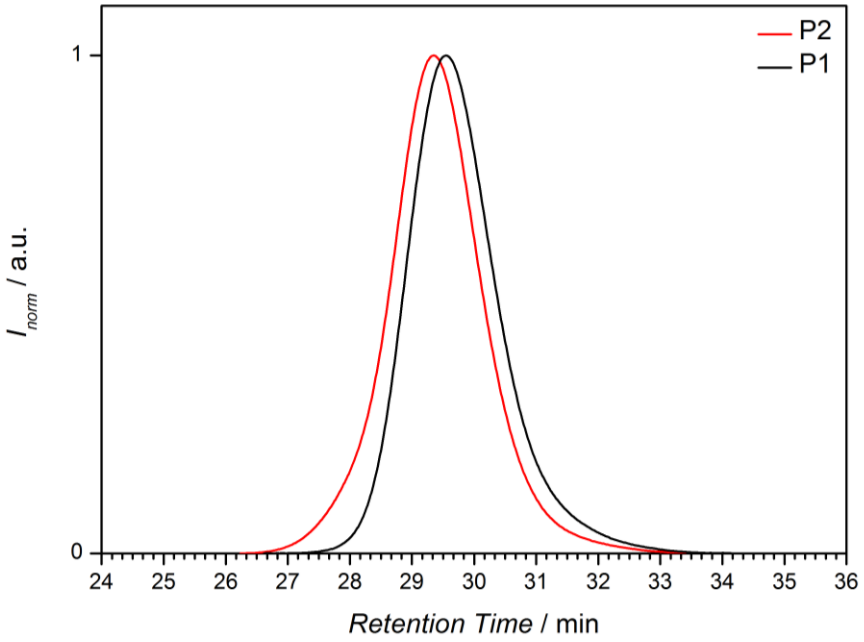


Figure S2. Normalized SEC traces (THF, RI) of the poly(styrene-*co*-chloromethylstyrene) copolymer **P1** (black) and the functional linear precursor **P2** (red).

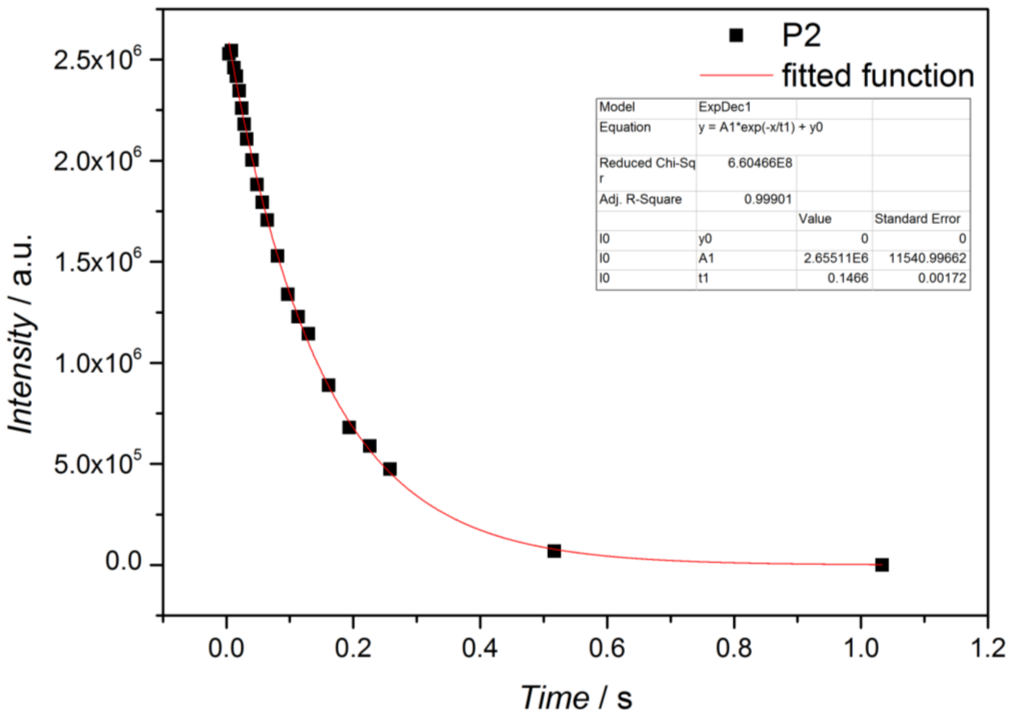


Figure S3. T_2 decay curve for the protons of the methylene bridge in the linear precursor **P2**.

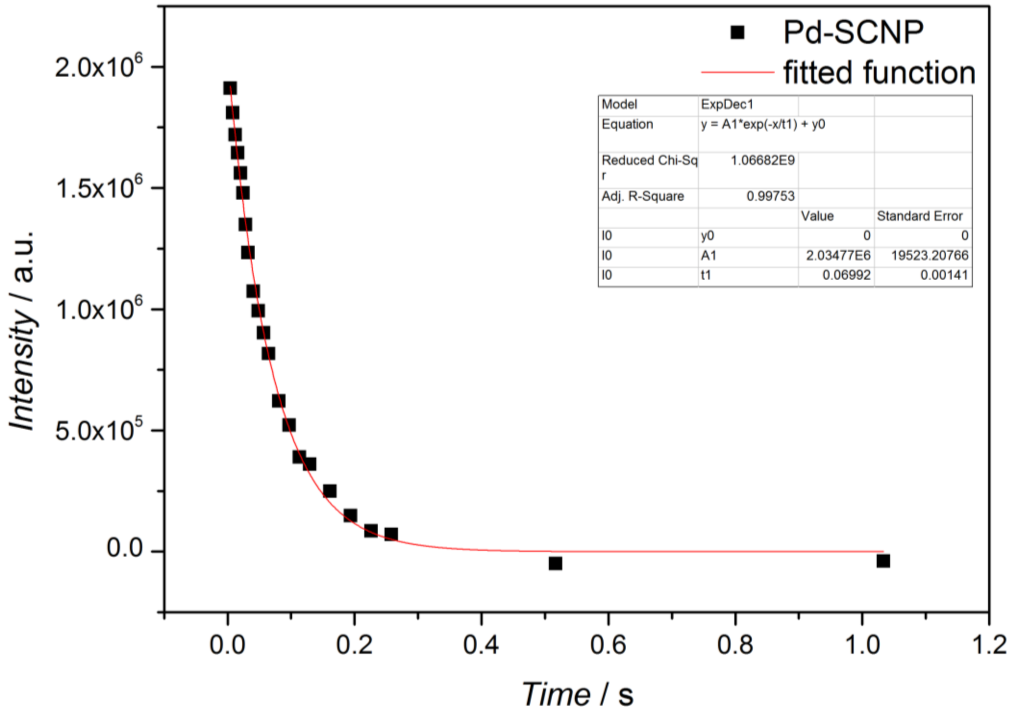


Figure S4. T_2 decay curve for the protons of the methylene bridge in the palladium(II) crosslinked single-chain nanoparticle.

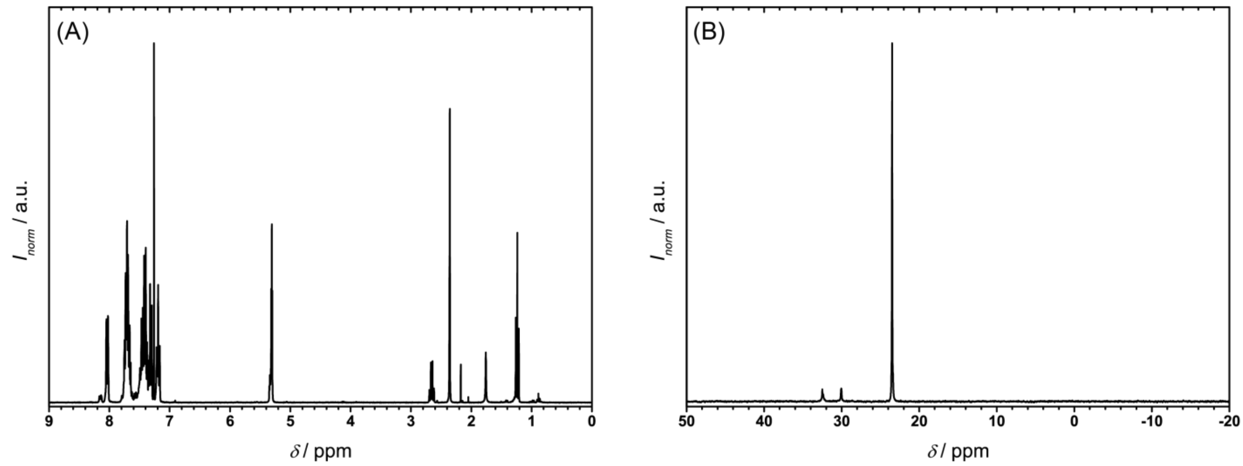


Figure S5. ^{1}H NMR (300 MHz) (A) and ^{31}P{^{1}H} NMR (121 MHz) (B) spectra of a statistical mixture of [Pd(**L1**)$_2$Cl$_2$], [Pd(**L1**)(**L2**)Cl$_2$], and [Pd(**L2**)$_2$Cl$_2$] in $CDCl_3$ at 25 °C.

Crystallographic Appendix

X-ray crystallographic studies: A suitable crystal was covered in mineral oil (Aldrich) and mounted on a glass fiber. The crystal was transferred directly to the cold stream of a STOE IPDS 2 diffractometer. All structures were solved by direct methods or by the Patterson method (SHELXS-2013).[4] The remaining non-hydrogen atoms were located from difference in Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on *F*, minimizing the function $(F_0 - F_c)^2$, where the weight is defined as $4F_0^2/2(F_0^2)$ and F_0 and F_c are the observed and and calculated structure factor amplitudes using the program SHELXL-2013.[4] Carbon-bound hydrogen atom positions were calculated. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication no. CCDC 1060115-1060116. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+(44)1223-336-033; email: deposit@ccdc.cam.ac.uk)

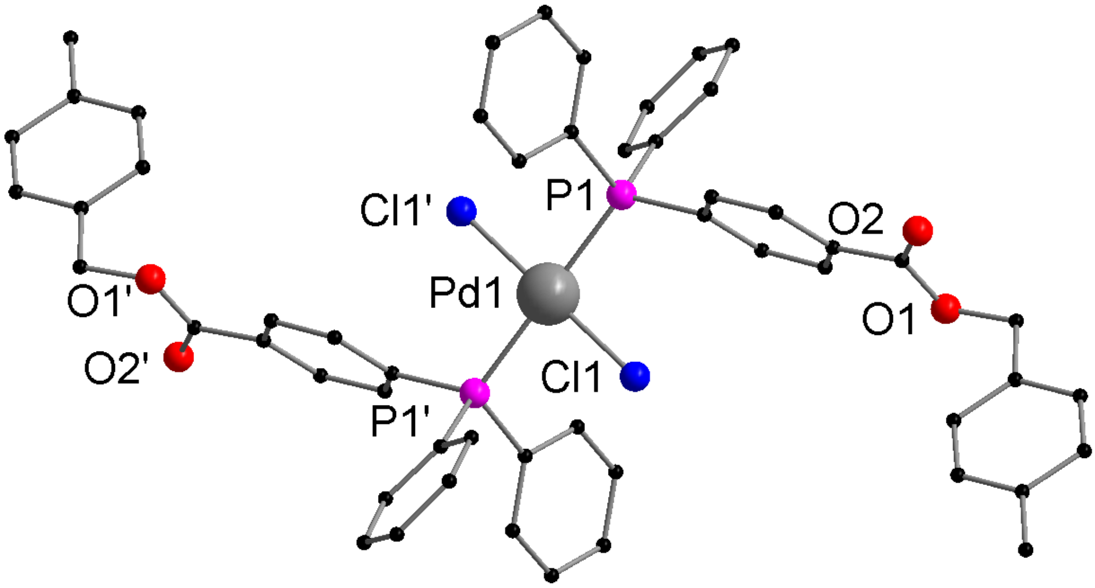


Figure S6. Solid-state structure of $[Pd(\mathbf{L1})_2Cl_2]$. Hydrogen atoms are omitted for clarity.

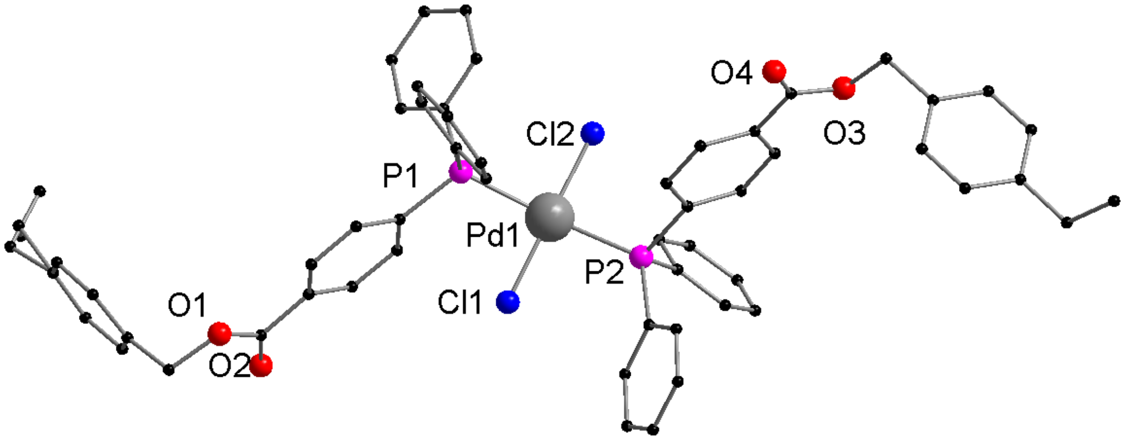


Figure S7. Solid-state structure of [Pd(**L2**)$_2$Cl$_2$]. Hydrogen atoms are omitted for clarity.

Table S1. Crystal data and structure refinement for [Pd(L1)$_2$Cl$_2$].

Empirical formula	$C_{54}H_{46}Cl_2O_4P_2Pd$
Formula weight	998.15
Temperature/K	200.15
Crystal system	triclinic
Space group	P-1
a/Å	9.5159(19)
b/Å	9.961(2)
c/Å	14.355(3)
α/°	72.77(3)
β/°	70.85(3)
γ/°	66.35(3)
Volume/Å^3	1155.9(5)
Z	1
ρ_{calc}g/cm^3	1.434
μ/mm^{-1}	0.633
F(000)	512.0
Crystal size/mm^3	0.336 × 0.217 × 0.071
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.06 to 51.998
Index ranges	$-11 \leq h \leq 11$, $-12 \leq k \leq 12$, $-17 \leq l \leq 17$
Reflections collected	8439
Independent reflections	4449 [R_{int} = 0.0455, R_{sigma} = 0.0529]
Data/restraints/parameters	4449/0/287
Goodness-of-fit on F^2	0.955
Final R indexes [I>=2σ (I)]	R_1 = 0.0315, wR_2 = 0.0735
Final R indexes [all data]	R_1 = 0.0421, wR_2 = 0.0756
Largest diff. peak/hole / e Å^{-3}	0.85/-0.47

Table S2. Crystal data and structure refinement for $[Pd(L2)_2Cl_2]$.

Empirical formula	$C_{56}H_{50}Cl_2O_4P_2Pd$
Formula weight	1026.20
Temperature/K	150.15
Crystal system	triclinic
Space group	P-1
a/Å	10.118(2)
b/Å	14.622(3)
c/Å	17.316(4)
α/°	89.46(3)
β/°	87.53(3)
γ/°	73.09(3)
Volume/Å^3	2448.8(9)
Z	2
ρ_{calc}g/cm^3	1.392
μ/mm^{-1}	0.600
F(000)	1056.0
Crystal size/mm^3	0.35 × 0.194 × 0.068
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.738 to 52
Index ranges	$-11 \leq h \leq 12$, $-18 \leq k \leq 18$, $-21 \leq l \leq 21$
Reflections collected	18856
Independent reflections	9493 [R_{int} = 0.0607, R_{sigma} = 0.0804]
Data/restraints/parameters	9493/0/607
Goodness-of-fit on F^2	0.866
Final R indexes [I>=2σ (I)]	R_1 = 0.0322, wR_2 = 0.0654
Final R indexes [all data]	R_1 = 0.0556, wR_2 = 0.0745
Largest diff. peak/hole / e Å^{-3}	1.09/-0.54

References

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4. G. Sheldrick, *Acta Cryst. Sect. A*, 2008, **64**, 112-122.