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Reversible, High Molecular Weight Palladium and Platinum Coordination Polymers Based on Phosphorus Ligands

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ABSTRACT: A general strategy for the preparation and characterization of high molecular weight coordination polymers based on bifunctional phosphorus ligands and palladium or platinum dichloride is described. Metal-to-ligand stoichiometry is of key importance for the formation of linear coordination polymers with high degrees of polymerization and was studied in detail. Heating of precursor complexes in the melt led to the highest degrees of polymerization. Peak molecular weights of 71 000 g/mol were reached, corresponding to a degree of polymerization of 100 units. The coordination polymers based on palladium dichloride were demonstrated to be linear by performing a stopper experiment. Complexation with platinum resulted in the formation of a network polymer due to platinum's ability to coordinate three phosphorus atoms. The palladium coordination polymers form reversibly and are in equilibrium with rings. The concentration dependence of the ring–chain equilibria was studied for the palladium complexes with ^{31}P NMR and size exclusion chromatography, and critical concentrations of 70–180 mM were determined, below which no polymers are present.

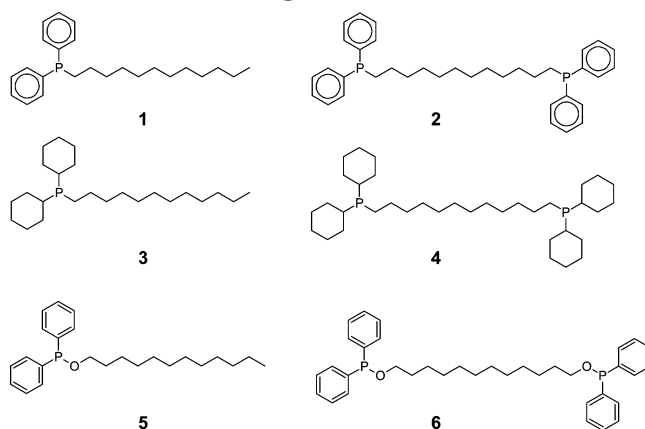
Introduction

Reversible coordination polymers are a subset of supramolecular polymers,¹ whose monomeric units are linked by kinetically labile coordinative bonds to metal atoms or ions. Dynamic ligand exchange allows the material to establish equilibrium in response to changes in its environment, which should lead to novel mechanical properties. Although a large diversity of kinetically inert coordination polymers has been studied, particularly in the solid state, mounting interest in supramolecular polymers has only recently resulted in intensive exploration of the potential of reversible coordination polymers.^{2–10} Those investigations treat how individual aspects of the coordination chemistry, such as the nature of ligand and metal, solvent,⁷ and stoichiometry, influence structure and dynamics⁸ of the reversible polymers.

Just like for covalent condensation polymers, the degree of polymerization (DP) of coordination polymers is highly dependent on factors such as monomer purity, complex stoichiometry, and the presence of rings.^{11,12} To date, these factors have not been addressed comprehensively with reversible coordination polymers. Here, we report our synthetic efforts to address these factors in phosphine-based coordination polymers with the aim to obtain high degrees of polymerization.

Our interest in phosphine-based coordination polymers stems from the desire to incorporate catalytically active transition metal complexes in the main chain of a polymer.^{13,14} Many of the transition metal coordination complexes used in catalysis contain phosphorus ligands. Phosphorus coordination chemistry is highly suitable for the construction of reversible polymers because the electronic and steric properties of the ligands can be tuned to control binding strength and exchange kinetics. The latter is highly advantageous because analytical techniques such as size exclusion chromatography (SEC)

Scheme 1. Mono- and Bifunctional Phosphorus Ligands 1–6



and NMR can be used for polymer characterization when equilibration is decreased to a rate slower than the experimental time scale.

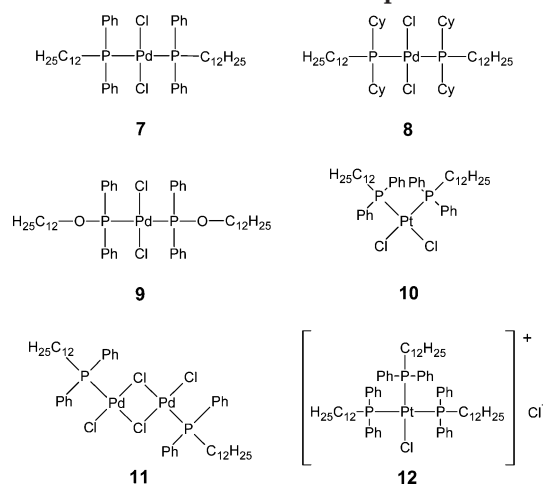
The present paper outlines a general strategy for the synthesis of high molecular weight reversible coordination polymers based on bifunctional phosphorus ligands with palladium(II) and platinum(II) metal salts, extending the scope of our initial communication in this area.¹³

Results and Discussion

Ligands. To study suitable ligands for palladium(II)- and platinum(II)-based coordination polymers, three different classes of monofunctional phosphorus ligands (compounds **1**, **3**, and **5**) and bifunctional phosphorus ligands (compounds **2**, **4**, and **6**) with widely differing coordination properties were synthesized (Scheme 1). Alkyldiphenylphosphines and alkyldicyclohexylphosphines are widely applied in coordination chemistry¹⁵ because of their good σ -donor properties, while the less known alkyldiphenylphosphinites were prepared as a complement to the σ -donating phosphines.

Monofunctional phosphine ligand **1** and bifunctional 1,12-bis(diphenylphosphino)dodecane (**2**) were synthe-

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Scheme 2. Structures of Complexes 7–12

sized in 78% and 88% yield via nucleophilic substitution on 1-bromododecane and 1,12 dibromododecane, respectively, with commercially available potassium diphenylphosphide. Ligand **1** is a liquid at room temperature that crystallizes upon cooling to 4 °C. Hence, purification by recrystallization or precipitation was not practical. Diphosphine **2**, alternatively, is a solid and was recrystallized from boiling acetonitrile.

Alkyldicyclohexylphosphine ligands were synthesized by lithiation of dicyclohexylphosphine and subsequent nucleophilic attack on the bromo precursors to give ligands **3** and **4**. The products were obtained as clear liquids in yields of 63% and 50%, respectively. Both compounds are rather sensitive to oxidation and hydrolysis.

Phosphinite ligands **5** and **6** were synthesized by reacting chlorodiphenylphosphine with 1-dodecanol and 1,12-dodecanediol, respectively, in THF in the presence of triethylamine. Removal of hydrochloric acid salts by filtration yielded pure **5** and **6** in 90% and 48% yield. Both ligands crystallized upon cooling to 4 °C.

Complexation Stoichiometry. One of the main considerations in the preparation of coordination polymers with a high degree of polymerization is to obtain a perfect stoichiometry between ligand and metal. The slightest deviation will result in a low molecular weight material.⁷ Moreover, stoichiometry control is critical in phosphine-based coordination polymers as the effect of excess ligand on dynamics of exchange can be pronounced. Ligand exchange in palladium and platinum complexes is known to follow an associative mechanism, and small quantities of free ligand can dramatically affect this process.¹⁶ The exclusive formation of complexes with the stoichiometry required for polymerization (2:1 ligand to metal) was first investigated with monofunctional ligands.

Complexes **7–9** (Scheme 2) were prepared by stirring the ligands with a 10% excess of palladium dichloride in dichloromethane at room temperature. The complexation was monitored by ³¹P NMR and required ~3 days for the alkyldiphenylphosphine and alkyldiphenylphosphinite ligands (**1** and **5**) and at least 7 days for alkyldicyclohexylphosphine (**3**). After this time, the excess palladium salt was filtered away, and the solvent was evaporated. All three complexes were dried in vacuo, resulting in yellow powders in high yields. ³¹P NMR analysis showed complete formation of the new complexes (Table 1). The high yield and purity of the complexes may be explained by the use of a small excess of metal, which drives formation of 2:1 complexes to completion. Weaker 2:2 complexes are not formed due to an unfavorable equilibrium when a very low concentration of uncomplexed palladium dichloride is present in solution. This is supported by the observation that, in the presence of an equimolar amount of a soluble palladium source (palladium dichloride 1,5-cyclooctadiene), chloro-bridged complex **11** was identified by a single peak at $\delta = 30.8$ ppm in ³¹P NMR,¹⁷ and its identity was further confirmed by MALDI-TOF mass spectroscopic analysis. Formation of complexes with a ligand-to-metal stoichiometry higher than 2:1 giving rise to networks with bifunctional ligands was not observed, even when an excess of ligand **1** was used in combination with palladium dichloride. ³¹P NMR showed the presence of complex **7** and free ligand **1**, but no additional peaks or changes in chemical shift were observed.

Platinum(II) forms kinetically very stable complexes with phosphorus ligands, exhibiting exchange rates which are ~10⁵ times slower than the corresponding palladium(II) complexes.¹⁸ This difference is of importance for the study of coordination polymers, as it may allow for direct investigation of the effect of kinetics on polymer properties.⁸ Ligand **1** was complexed with platinum dichloride, leading to complex **10**. In contrast to palladium dichloride, platinum dichloride is indeed soluble in dichloromethane and therefore cannot be used in excess. Complexation was completed within 24 h, and removal of the solvent afforded a yellow solid. ³¹P NMR analysis shows a singlet at $\delta = 7.0$ ppm; the platinum-phosphorus coupling of 3656 Hz is indicative of a cis-coordinated complex.¹⁹

In contrast to palladium dichloride, platinum dichloride can coordinate more than two phosphine ligands.¹⁹ When 3 equiv of the phosphine was mixed with the metal, 35% of tris-phosphine complex **12** was formed. Addition of 5 equiv of ligand **1** led to 71% formation of **12**, and the complex was isolated by crystallization from acetonitrile. ³¹P NMR analysis of these crystals indicated that complex **12** was obtained in high purity. A characteristic doublet at $\delta = 16.4$ ppm ($J_{\text{Pt-P}} = 3605$

Table 1. ³¹P NMR Chemical Shifts (ppm) of Free Ligands and Their Complexes in Deuterated Chloroform

free ligand	shift (ppm)	ligand:metal stoichiometry	complexes			
			PdCl ₂	shift (ppm)	PtCl ₂	shift (ppm) $J_{\text{Pt-P}}$ (Hz), $J_{\text{P-P}}$ (Hz)
1	-16.0	2:1	7	16.5	10	7.0 (3656)
		1:1	11	30.8		
		3:1				
2	-16.0	1:1	13	16.5	16	7.0 (3656)
3	-4.8 ^a	2:1	8	21.8 ^a		
4	-4.8 ^a	1:1	14	21.8 ^a		
5	112.4	2:1	9	110.0		
6	112.4	1:1	15	110.0		

^a In deuterated toluene.



Figure 1. Flexible fiber drawn from melt polymer **13**.

Hz, $J_{P-P} = 18$ Hz) and a triplet at $\delta = 6.4$ ppm ($J_{Pt-P} = 2379$ Hz, $J_{P-P} = 18$ Hz) were observed originating from the two phosphorus atoms cis to the chloride atom and the single phosphorus atom trans to the chloride.

High Molecular Weight Coordination Polymers.

Having established the conditions to obtain 2:1 ligand-to-metal coordination complexes in monofunctional systems, we decided to prepare coordination polymers from bifunctional ligands **2**, **4**, and **6** and palladium(II) or platinum(II) dichloride in two sequential steps. In the first step, relatively concentrated (80 mM) solutions of bifunctional phosphorus ligands were stirred with a 10% excess of palladium dichloride, until ^{31}P NMR showed complete disappearance of uncomplexed ligand. Similar complexation times as for the monofunctional ligands (3–7 days) were required. When the reaction had reached completion, the complexes were filtered in order to remove remaining palladium dichloride. After evaporation of solvent, the samples were dried in vacuo to give yellow powders in quantitative yields. The platinum dichloride complex of bifunctional alkyldi-phenylphosphine ligand **2** was prepared in a similar way, except that a stoichiometric amount of metal (PtCl_2) was used. In the second step, the powders were heated as melts at a temperature of 185 °C for 10 min in vacuo. All complexes changed color from yellow to red/brown.

After cooling to room temperature, palladium polymers **13**–**15** were obtained as brittle brown solids whereas platinum polymer **16** was a completely insoluble black material. Thermal behavior of polymer **13** was studied with differential scanning calorimetry (DSC), which showed a glass transition at 68 °C, above which temperature flexible fibers could be drawn (see Figures 1 and 2). Both the presence of a T_g and the fiber-forming properties of the melt are indicative of the polymeric nature of **13**. Palladium complexes **13**–**15** dissolved in chloroform without residue and were characterized using ^1H NMR, ^{13}C NMR, ^{31}P NMR, and size exclusion chromatography (SEC). ^1H and ^{13}C NMR spectra of the products provided no indication of ligand decomposition, while ^{31}P NMR analysis (Table 1) showed simple spectra with single peaks at positions corresponding to those of the monofunctional model compounds. In melt polymer **13** all palladium was trans-coordinated. Cis–trans equilibration took place very rapidly after dissolution in deuterated chloroform and equilibrium was reached within 15 min, with a final 1:4 cis-to-trans ratio.

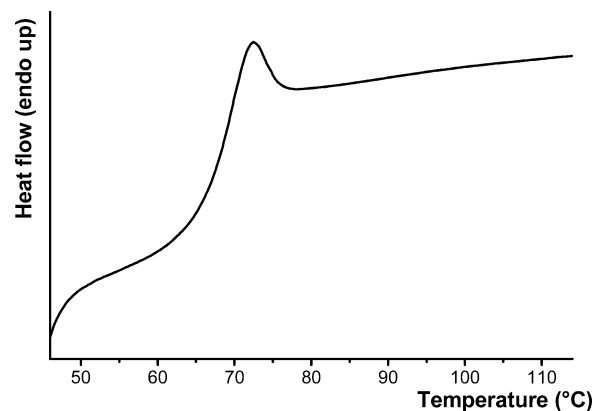


Figure 2. DSC trace of polymer **13**.

Table 2. Size Exclusion Chromatography (SEC) Data of Pd Coordination Polymers **13**–**15** after Polymerization in the Melt and Pt Coordination Polymer **16** before Polymerization in the Melt^a

complex	M_{top} (g/mol)	DP_{top}^c
13	71000	100
14	5000	7
15	3200	4
16	32000	40

^a Values are based on polystyrene standards. ^b M_{top} is defined as the molecular weight at the top of the elution peak. ^c DP_{top} is the corresponding degree of polymerization.

SEC analysis (Table 2) of the melt polymers in CHCl_3 gave evidence of high molecular weight polymers for all three PdCl_2 complexes as well as peaks corresponding in molecular weight to monomer, dimer, and oligomers. The traces in Figure 3a show that especially **13** has a very high molecular weight, the top of the band eluting with a molecular weight of 7.1×10^4 g/mol, based on polystyrene standards.²⁰ This corresponds to a DP of 100. Dicyclohexylphosphine complex **14** and phosphinite complex **15** also showed the presence of polymeric material, although M_{top} was significantly lower than for **13**. The higher molecular weight of complex **13** is in line with the high purity with which ligand **2** was obtained via recrystallization. Ligands **4** and **6** were unfortunately liquid at room temperature and could not be recrystallized. The elution of the coordination complexes at high hydrodynamic volumes on SEC demonstrates the polymeric nature of the materials. It also indicates that the kinetics of ligand exchange is slow under chromatographic conditions because equilibration during chromatography is expected to lead to dissociation and low molecular weight and/or cyclic material. In fact, any exchange on the column will lead to lower molecular weight material. Therefore, the actual molecular weight distribution before chromatography is only correctly reflected by the SEC trace in the limit of kinetically inert coordination complexes.

The insolubility of platinum dichloride complex **16** prompted us to investigate SEC of the precursor material that had not been melted. Figure 3b shows the presence of remarkably high molecular weight material. Presence of polymer with a molecular weight that exceeds the exclusion limit of the SEC column (4×10^5 g/mol) results in an erroneous peak at a mass of 10^6 g/mol. The main peak elutes at a molecular weight of 32×10^3 g/mol, corresponding to a DP of ~ 40 . The solubility of PtCl_2 may have led to a slight deviation from 2 of the ligand/metal ratio in **16**, although the imbalance must be small since a signal of a platinum

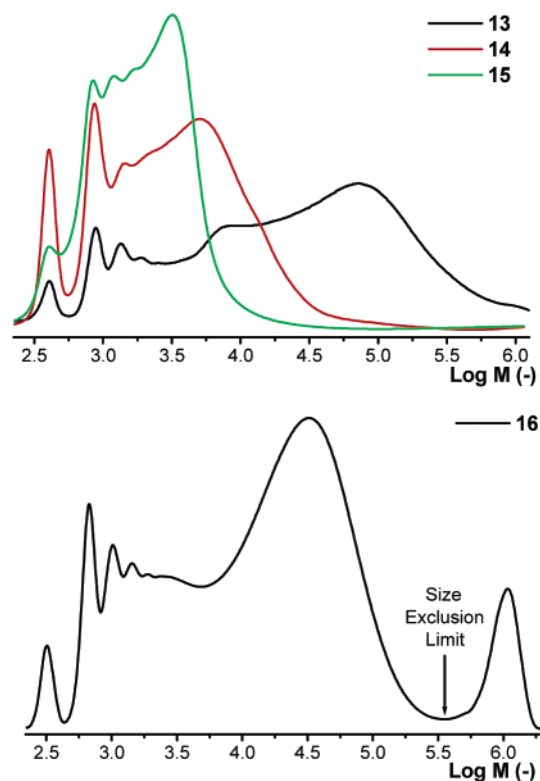


Figure 3. Size exclusion chromatography (SEC) traces of (a, top) Pd coordination polymers **13**–**15** after polymerization in the melt and (b, bottom) Pt coordination polymer **16** before polymerization in the melt.

complex with three phosphine ligands was not observed in ^{31}P NMR of **16**. In complexes with a fixed 2:1 ligand-to-metal stoichiometry, deviations from a 2:1 ligand/metal ratio will lead to a lowering of the DP. However, from the studies on complex **12**, we have learned that it is possible for a platinum center to coordinate three phosphines. Exceeding a 2:1 ligand/metal ratio will therefore lead eventually to network formation, depending on the exact value of the ligand/metal ratio and the amount of rings present in the mixture. We ascribe the high molecular weight of **16** before melting to the presence of branch points in the form of tris-coordinated Pt, coexisting with an approximately equal number of rings. Opening of rings upon melting of **16** would result in network formation. The complete insolubility of **16** after melting supports this explanation.

To further investigate the exchange kinetics and the effect of dilution, freshly prepared CDCl_3 solutions of the three palladium polymers were diluted to a concentration of 1 mM in monomer, and SEC was performed on samples taken after 0 and 24 h (Figure 4). For polymers **13** and **15**, dilution results in the formation of new species at significantly lower molecular masses and equilibrium was approached after 24 h, whereas the SEC trace of the solution of **14** did not change at all over the course of the experiment. Quantitative information on the rates of these processes was obtained by monitoring the appearance of new signals (of low molecular weight cyclic material, see below) in the ^{31}P NMR spectrum. For polymer **13**, equilibration, as judged by the time-dependent increase of the new signals, follows first-order kinetics with a half-life of ~ 13 h. Monitoring equilibration of complex **15** under similar conditions yielded a half-life of 11 h, while the equilibration process of complex **14** at 1 mM in CDCl_3 was so

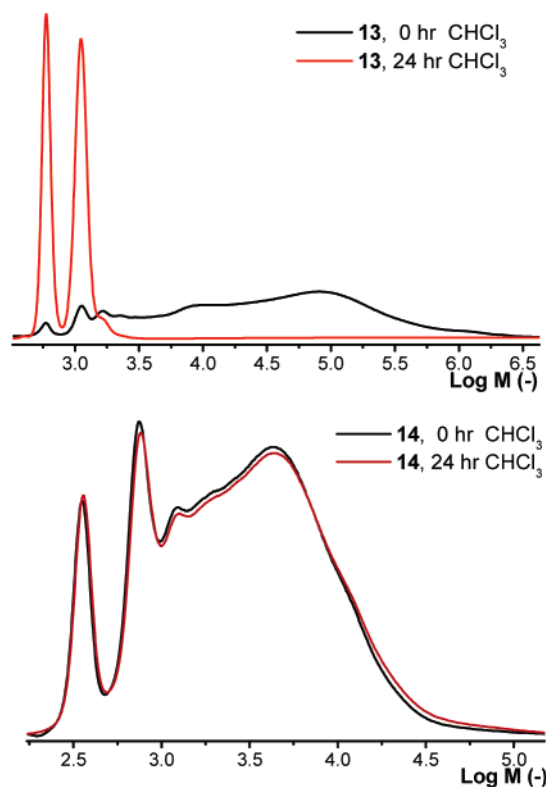


Figure 4. Normalized size exclusion chromatography (SEC) traces of Pd-alkyldiphenylphosphine coordination polymer **13** (a, top) and Pd-alkyldicyclohexylphosphine coordination polymer **14** (b, bottom) immediately after dissolution and after equilibration at 1 mM for 24 h.

slow that after 11 days only minute formation of monomeric cyclic material was observed.

Linearity of the Coordination Polymers. Linear polymers can be distinguished from branched or other less well-defined polymers by the effect of monofunctional material. As derived by Flory for condensation polymers, the degree of polymerization of a polymer remains high as long as the average functionality is higher than 2.²¹ However, in systems with a functionality of close to 2 (linear polymers), reduction of the functionality by mixing in monofunctional material immediately leads to a drastic reduction in DP. This so-called “stopper experiment” has been used to demonstrate the linearity of hydrogen-bonded supramolecular polymers.²² A stopper experiment on polymer **13** was performed by mixing the solid polymer precursor complex with specific amounts of solid complex **7**. Complex **7** was used instead of free ligand **2** in order to maintain the correct stoichiometry. Upon heating to 185 °C, the molten mixture starts equilibrating to a degree of polymerization which is limited by the monofunctional phosphine ligands. Melt polymers from mixtures containing 0%, 1%, 5%, 10%, and 50% of **7** were prepared, and their molecular weights were determined by SEC (Figure 5).

The values of M_{top} , shown in Table 3, strongly decrease when increasing amounts of **7** are added. This confirms the linearity of the polymers. M_{top} of polymer prepared in the absence of stopper complex **7** is $\sim 71\,000$ g/mol, corresponding to a degree of polymerization of 100 units. This DP is expected for a material containing 2% of monofunctional impurity. The identity of the monofunctional impurity is at present not known, but most probably these are monofunctionalized or partially

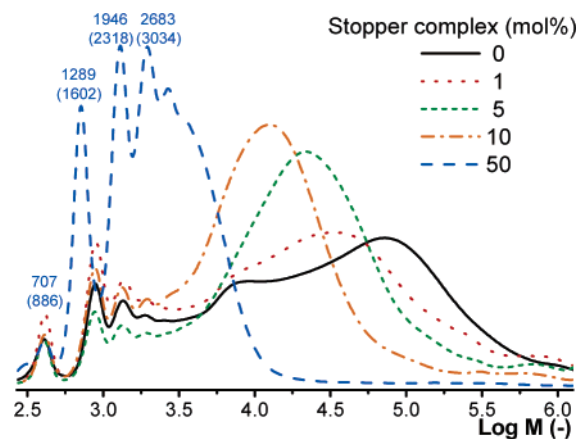


Figure 5. Size exclusion chromatography (SEC) traces of coordination polymer **13** prepared in the presence of monofunctional complex **7** acting as a chain stopper and subsequent polymerization in the melt. Measured molecular weights (based on PS standards) of oligomers are indicated at the top, with actual molecular weights in brackets.

Table 3. Molecular Weights of Melt Polymer 13 Prepared in the Presence of complex 7

percentage chain stopper 7	M_{top} (g/mol) ^a	M_{top} (calc)	M_{top} (calc) for 2% monofunctional impurity
0	71×10^3	∞	71.6×10^3
1	35×10^3	143×10^3	47.7×10^3
5	23×10^3	28.6×10^3	20.5×10^3
10	13×10^3	14.3×10^3	11.9×10^3
50	$2.0 \times 10^3; 1.3 \times 10^3$	2.86×10^3	2.75×10^3

^a Values are based on polystyrene standards

oxidized ligands that can coordinate to palladium dichloride only once. Taking this 2% impurity into account, good agreement is found between calculated and experimental values for M_{top} (Table 3).

Ring-Chain Equilibria. The identity of the low molecular weight species formed upon equilibration of dilute solutions of polymers **13–15** was studied in detail using SEC on chloroform solutions at a concentration of ~ 1 mM in monomers. These solutions were prepared from the precursor polymers without going through the melting step. In control experiments, identical results were obtained with equilibrated solutions of the melt polymers. SEC analysis on precursor polymers of **13**, **14**, and **15**, obtained immediately after dissolution, indicates the presence of oligomeric species in addition to polymeric material. Since the ^{31}P NMR spectrum of the material does not show signals of uncomplexed phosphine or oxidized phosphine, it must be concluded that these oligomers are cyclic. SEC analysis reveals that mononuclear cyclic palladium complex **13** (MW = 716 g/mol) has a longer retention time (corresponding to a smaller hydrodynamic volume) than ligand **2** (MW = 538 g/mol). This observation is entirely in line with the smaller hydrodynamic volume of cycles compared to corresponding linear species.^{14,23} Similar observations

were made for the oligomers in the SEC traces of **14** and **15**.

^{31}P NMR spectra of precursor polymers obtained immediately after dissolution showed for all three complexes **13–15** the presence of several signals close to that of the peak in the corresponding melt polymer. Precursor polymer **13** shows two sets of signals: one set around $\delta = 17$ ppm (80%), which originates from *trans*-palladium dichloride complexes, and the second set at $\delta = 26$ ppm (20%) corresponds to *cis*-palladium dichloride complexes. Complex **14** showed a single set at $\delta = 22$ ppm, which belongs to *trans*-palladium dichloride complexes. Complex **15** showed one set of signals at $\delta = 110$ ppm, which corresponds to *trans*-palladium dichloride complexes.

Diffusion-ordered spectroscopy (DOSY) was used to identify the relative sizes of the different species in complexes **13–15**. The ^{31}P -DOSY data are summarized in Table 4. Relative diffusion coefficients are normalized to the highest value. All three complexes show the presence of small and large species. This can be seen most pronouncedly in the DOSY spectra of phosphine complexes **13** and **14** (Figure 6) where species with very low diffusion coefficients were identified, corresponding to high molecular weight material.

^{31}P NMR peak integrals are in good agreement with SEC results. The SEC trace of complex **13** shows similar amounts of monomeric and dimeric cycles, a smaller amount of trimers, and a large amount of polymeric material, whereas ^{31}P NMR shows four distinct signals: 9% of the smallest species, 14% of a larger species, 5% of the third species, and by far the largest intensity comes from the last signal, 72%. We assign these signals respectively to the monomeric, dimeric, and trimeric cycles and polymeric material. ^{31}P chemical shifts are very sensitive to changes in the environment, and the fact that all these species can be identified separately is most probably caused by decreasing ring strain in the cyclic complexes.

Determination of the Critical Concentration. In reversible systems, cyclic structures are in equilibrium with linear polymeric species (Scheme 4). This equilibrium is characterized by a critical polymerization concentration, below which only cyclic material is present and above which the concentration of cyclic material is constant and only linear polymer is formed.^{11,12} This critical concentration can be determined by assessing the partial concentration of one or more cycles, while changing the total concentration. Knowing which ^{31}P NMR resonance arises from which cycle makes it possible to study the concentration behavior of the three complexes. Concentration series of complexes **13–15**, ranging from 0.5 mM to 0.2 M, in deuterated chloroform were prepared. The solutions of complexes **13** and **15**, with fast exchange, were left standing for 1 week to ensure that equilibrium was fully reached. In Figure 7a, the partial concentration of the *trans* monomeric cycle of complex **13** is plotted against total concentra-

Table 4. ^{31}P NMR Chemical Shifts and Relative Diffusion Coefficients of Pd Complexes 13–15^a

complex	chemical shift (ppm)	relative diffusion coefficient (-)	complex	chemical shift (ppm)	relative diffusion coefficient (-)	complex	chemical shift (ppm)	relative diffusion coefficient (-)
13	17.1	1.00	14	23.8	1.00	15	107.4	1.00
	16.6	0.78		22.4	0.68		107.9	0.83
	16.5	0.42		22.0	0.56		108.5	0.68
			21.7	0.24		108.9	0.47	

^a Complexes in chloroform-*d*, 100 mM; complexes **13–15**: see Scheme 3.

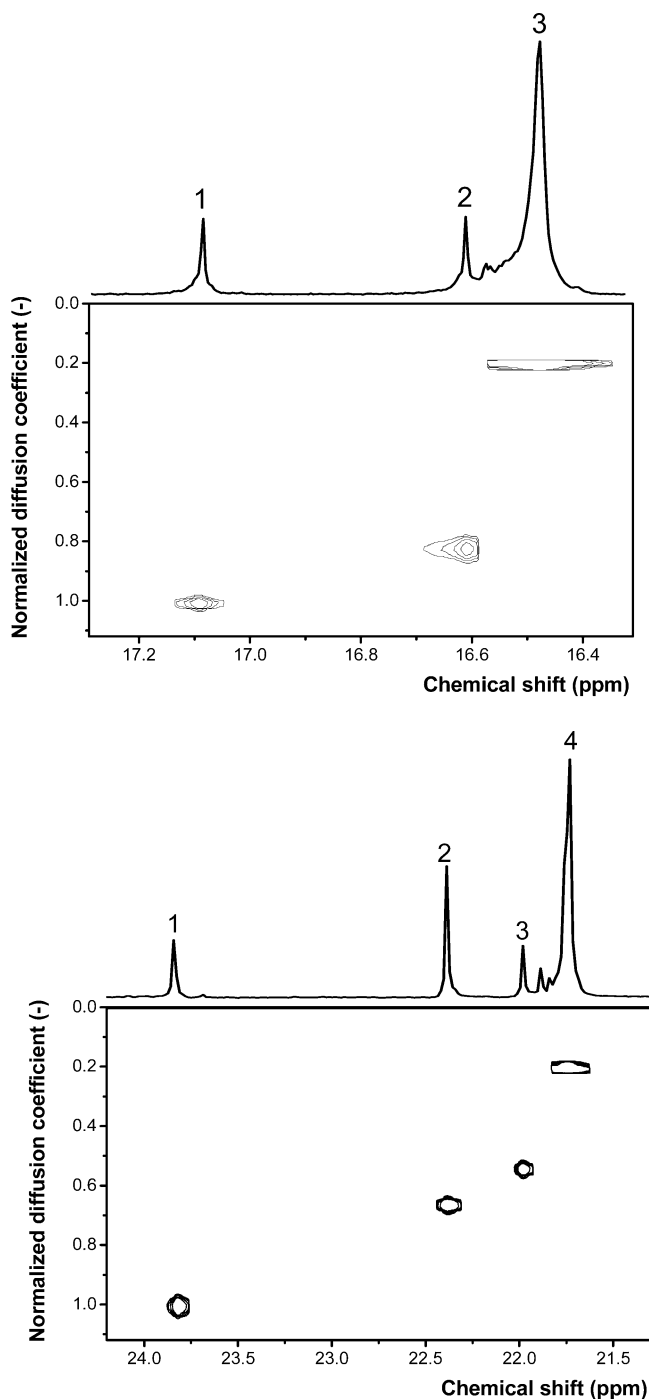


Figure 6. Diffusion-ordered spectroscopy (^{31}P -DOSY-NMR) of (a, top) Pd-alkyldiphenylphosphine complex **13** and (b, bottom) Pd-alkyldicyclohexylphosphine complex **14**.

tion. In Figure 7c this is done for the partial concentrations of monomeric, dimeric, and trimeric cycles of complex **15**. Up to a certain concentration, the partial concentration of the monomeric cycle increases approximately linearly, but above this concentration it is constant. The critical polymerization concentration of complex **13** is ~ 70 mM in deuterated chloroform. Similar behavior was observed for complex **15**; the critical concentration was determined to be ~ 180 mM. A concentration series was also prepared for complex **14**, but because of the extremely slow exchange, it took ~ 60 days for the complex to reach equilibrium. In Figure 7b, the partial concentrations of the monomeric,

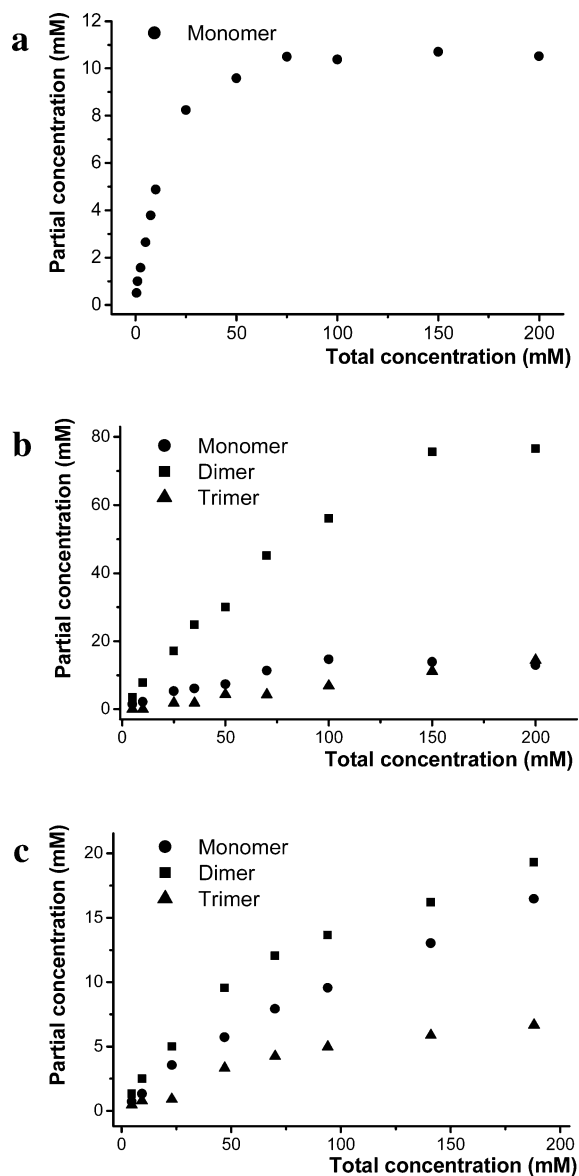
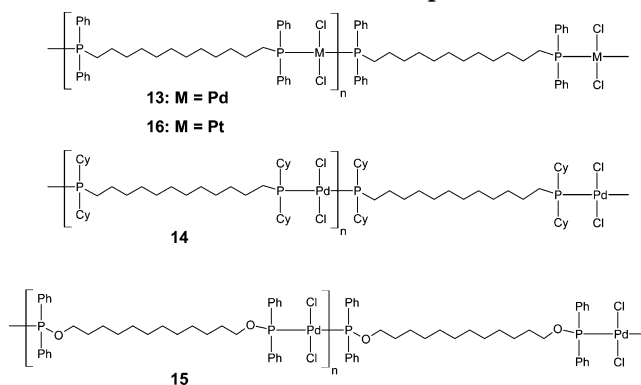


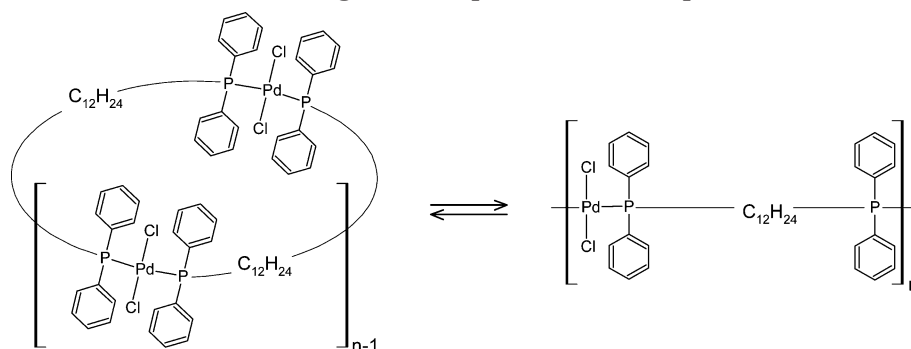
Figure 7. Concentration dependence of the partial concentration of oligomers in equilibrated CDCl_3 solutions of Pd-alkyldiphenylphosphine complex **13** (a), Pd-alkyldicyclohexylphosphine complex **14** (b), and Pd-alkyldiphenylphosphinite complex **15** (c).

Scheme 3. Structures of Complexes 13–16



dimeric, and trimeric cycles are plotted, resulting in a critical concentration of ~ 150 mM.

Theory predicts that the equilibrium concentrations of strainless cycles is a monotonically decreasing function of ring size.^{11,12} The fact that the dimeric cycle of

Scheme 4. Ring–Chain Equilibrium of Complex **13**

complex **14** is more abundant than the monomeric cycle indicates that the latter is not strainless. The same holds for complex **15**, for which the monomeric and dimeric cycle are present in similar concentrations. The pronounced differences in shifts of ^{31}P NMR signals of monomeric, dimeric, and trimeric cycles of **13** suggest that also in these complexes some ring strain is present.

Conclusions

High molecular weight coordination polymers with DP's up to several hundreds have been prepared by complexation of bifunctional phosphorus ligands with palladium dichloride and subsequent polymerization in the melt. The complexes were shown to have exchange kinetics which are fast enough to obtain equilibrium materials, while still slow enough to allow analysis with SEC. Platinum(II) dichloride complexes of alkylidiphosphine ligands also gave high molecular weight coordination polymers, but here exchange is slow. Moreover, the possibility of forming complexes with 3:1 ligand-to-metal stoichiometry made it difficult to suppress the formation of networks. Control over stoichiometry by carefully choosing a solvent in which PdCl_2 was poorly soluble proved to be the key to successful preparation of polymers with high DP's. Ligand purifiability was also shown to have a strong effect on DP; solid ligand **2**, which could be purified by recrystallization, gave significantly higher DP's than the ligands that were obtained as oils. Ligand exchange in the complexes establishes a ring–chain equilibrium which was studied using SEC and ^{31}P NMR. The concentration dependence of the equilibria was shown to conform to theory, which predicts a critical concentration below which only rings are present. The value of this critical concentration is relatively high for the monomer lengths studied and shows that, for the study and application of reversible coordination polymers at low concentrations, diphosphines with longer spacer lengths will be useful since these will decrease the critical concentration further.¹⁴

By identifying key factors for the preparation of high molecular weight phosphine metal coordination polymers, we have outlined a general method for obtaining reversible coordination polymers, and the behavior and potential of these materials can now be studied in full detail.

Experimental Section

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. Chemical shifts are reported in ppm and referenced to tetramethylsilane and chloroform (proton and carbon) and external 85% phosphoric acid (phosphorus). Diffusion-ordered ^{31}P NMR (202 MHz) spectra were recorded

on a Varian Inova 500 spectrometer, with 85% phosphoric acid as an external reference. Diffusion measurements were evaluated with the Varian DOSY software incorporated in VNMR. Elemental analyses were carried out using a Perkin-Elmer 240. MALDI–TOF spectra were obtained on a Perceptive Biosystems Voyager DE-Pro MALDI–TOF mass spectrometer (accelerating voltage 20 kV; grid voltage 74.0%; guide wire voltage 0.030%; delay 200 ms; low mass gate, 900 amu). Samples for MALDI–TOF were prepared by adding a solution of the corresponding complex in THF (20 μL , $c = 1$ mg/mL) to a solution of α -cyano-4-hydroxycinnamic acid in THF (10 μL , $c = 20$ mg/mL) and subsequent thorough mixing. This mixture (0.3 μL) was brought on a sample plate, and solvent was evaporated. Differential scanning calorimetry (DSC) measurements were obtained with a Perkin-Elmer Pyris-1, calibrated to cyclohexane and indium. Glass transition temperatures were determined at a heating rate of 20 $^\circ\text{C}/\text{min}$ (half C_p extrapolated). Syntheses of the ligands and the complexes were carried out under a 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, acetonitrile, and *n*-hexane were degassed before use. *n*-Butyllithium (1.6 M) was titrated before use. Potassium diphenylphosphide (0.5 M in THF), chlorodiphenylphosphine (98%), *n*-butyllithium (1.6 M), 1,12-dihydroxydodecane (99%), 1-dodecanol (98%), 1-bromododecane (97%), and 1,12-dibromododecane (98%) were purchased from Aldrich; palladium dichloride (99.9%), platinum dichloride (99.9%), and dicyclohexylphosphine (98%) were purchased from STREM; palladium dichloride bis(benzonitrile) (99%) was purchased from ACROS.

SEC Analysis. Size exclusion chromatography (SEC) was performed on a Shimadzu LC10-AT, using Polymer Laboratories PL Gel 5 μm mixed-D column (linear range of MW: 200–400 000 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 $^\circ\text{C}$). Polystyrene standards were used for calibration. Alternatively, molecular weights of the lower oligomers of complex **13** (observed as separate peaks in Figure 5) were used for calibration. Comparison with polystyrene standards revealed that the actual molecular weight is underestimated by 25% or less when polystyrene standards are used.

1-(Diphenylphosphino)dodecane (1). 1-Bromododecane (1.87 g, 7.50 mmol) was dissolved in dry THF (50 mL), and the stirred solution was cooled to -78 $^\circ\text{C}$ 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 $^\circ\text{C}$ 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 $^\circ\text{C}$. 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).

1,12-Bis(diphenylphosphino)dodecane (2). 1,12-Dibromododecane (3.28 g, 10.0 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, 40.0 mL, 20.0 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. Solvent was removed in vacuo. White crystals were obtained in 88% yield by recrystallization from boiling acetonitrile. δ_H (400 MHz): 7.47–7.28 (m, 20H, Ph), 2.01 (t, 4H, CH_2P), 1.47–1.18 (m, 20H, CH_2). δ_C (121 MHz): 139.44 (d, 4C, Ph) 133.05 (d, 8C, Ph), 128.76 (s, 8C, Ph), 128.70 (d, 4C, Ph), 31.57 (d, 2C, CH_2P), 29.88 (d, 2C, alkyl), 29.60 (s, 4C, alkyl), 28.40 (d, 2C, alkyl), 26.32 (d, 2C, alkyl). δ_P (162 MHz): -16.0 (s, 2P). Elemental analysis calcd (%) for $C_{36}H_{44}P_2$: C 80.27, H 8.23. Found: C 79.83, H 7.97.

1-(Dicyclohexylphosphino)dodecane (3). Dicyclohexylphosphine (2.00 g, 10.1 mmol) was dissolved in 50 mL of dry THF and cooled to -78 °C, and *n*-butyllithium (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 min 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).

1,12-Bis(dicyclohexylphosphino)dodecane (4). Dicyclohexylphosphine (3.0 g, 15 mmol, 2 equiv) was dissolved in 50 mL of dry THF. This solution was cooled to -78 °C, and *n*-butyllithium (1.6 M, 9.5 mL, 15 mmol) was added. This mixture was left to warm to room temperature and then added to an ice-cooled mixture of 1,12-dibromododecane (2.5 g, 7.6 mmol) in 50 mL of dry THF. This mixture was stirred for 30 min 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 50% yield. The liquid crystallized when cooled to 4 °C. δ_H (200 MHz): 2.25–1.31 (m, 68H, $CH_2 + CH$). δ_C (100 MHz): 33.44 (d, 4C, PCH), 31.73 (d, 2C, alkyl), 30.49 (d, 4C, alkyl), 29.73 (d, 4C, alkyl), 29.49 (s, 2C, alkyl), 29.12 (d, 4C, alkyl), 28.63 (d, 2C, alkyl), 27.58–27.42 (m, 8C, alkyl), 26.70 (s, 4C, alkyl), 21.40 (d, 2C, PCH₂). δ_P (162 MHz, toluene- d_8): -4.8 (s, 2P).

1-(Diphenylphosphinito)dodecane (5). 1-Dodecanol (2.5 g, 13 mmol), which was dried from water with dry toluene, and 1.9 mL of triethylamine (1.4 g, 13 mmol) were dissolved in dry THF (50 mL), and the stirred solution was cooled to 0 °C with ice. Chlorodiphenylphosphine (3.0 g, 13.4 mmol) was slowly added to the mixture. After complete addition, the solution was stirred for an hour at 0 °C and left to warm to room temperature. Solvent was removed in vacuo, and the solids were suspended in dry dichloromethane (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 was obtained as a clear liquid in 90% yield. The liquid crystallizes when cooled to 5 °C. δ_H (400 MHz): 7.54–7.34 (m, 10H, Ph), 3.87 (q, 2H, CH_2O), 1.71 (t, 2H, C

H_2CH_2O), 1.38–1.28 (m, 18H, CH_2), 0.91 (t, 3H, CH_3). δ_C (75 MHz): 142.32 (d, 2C, Ph), 130.43 (d, 4C, Ph), 129.29 (s, 2C, Ph), 128.40 (d, 4C, Ph), 70.43 (d, 1C, CH_2O), 32.08 (s, 1C, alkyl), 31.59 (d, 1C, alkyl), 29.80–29.46 (m, 6C, alkyl), 25.99 (s, 1C, alkyl), 22.84 (s, 1C, alkyl), 14.28 (s, 1C, alkyl). δ_P (162 MHz): 112.4 (s, 1P).

1,12-Bis(diphenylphosphinito)dodecane (6). 1,12-Dodecanediol (2.50 g, 12.4 mmol) was dried from water by coevaporation with dry toluene and subsequently dissolved in 100 mL of dry THF. Triethylamine (2.49 g, 24.7 mmol, 2 equiv) was added, and the stirred solution was cooled to 0 °C with ice. Chlorodiphenylphosphine (5.45 g, 24.7 mmol, 2 equiv) was slowly added to the mixture. After complete addition, the solution was stirred for an hour at 0 °C and left to warm to room temperature. Solvent was removed in vacuo, and the solids were suspended in dry dichloromethane (50 mL). To remove the triethylamine salt, 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 48% yield. The liquid crystallized when cooled to 5 °C. δ_H (400 MHz): 7.57–7.35 (m, 20H, Ph), 3.93–3.87 (m, 4H, CH_2O), 1.77–1.70 (m, 4H, CH_2CH_2O), 1.41–1.29 (m, 16H, CH_2). δ_C (75 MHz): 142.41 (d, 2C, Ph), 130.40 (d, 4C, Ph), 129.26 (s, 2C, Ph), 128.37 (d, 4C, Ph), 70.38 (d, 2C, CH_2O), 31.55 (d, 2C, alkyl), 29.65–29.41 (m, 6C, alkyl), 25.96 (s, 2C, alkyl). δ_P (162 MHz): 112.4 (s, 2P).

Palladium Dichloride Bis(1-(diphenylphosphino)dodecane) (7). A mixture of palladium(II) dichloride (37 mg, 0.21 mmol, 0.55 equiv) and 1-(diphenylphosphino)dodecane (133 mg, 0.375 mmol) in dry dichloromethane (7 mL) was stirred for 24 h. 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 $C_{48}H_{70}Cl_2P_2Pd$: C 65.04, H 7.96. Found: C 64.84, H 7.91. MALDI-TOF MS: 851.5 ($M^+ - Cl$).

Palladium Dichloride Bis(1-(dicyclohexylphosphino)dodecane) (8). A mixture of palladium(II) dichloride (56 mg, 0.32 mmol, 0.55 equiv) and 1-(dicyclohexylphosphino)dodecane (210 mg, 0.571 mmol) in dry dichloromethane (10 mL) was stirred for 48 h. The mixture was filtered in order to remove the excess palladium(II) dichloride, and solvent was removed in vacuo, yielding an orange oil in 99% yield. δ_H (400 MHz): 2.30–1.25 (m, 88H, $CH_2 + CH$), 0.94 (t, 6H, CH_3). δ_C (75 MHz): 33.25–32.94 (m, 4C, alkyl), 32.08 (s, 4C, alkyl), 29.83–29.44 (m, 18C, alkyl), 29.07 (s, 4C, alkyl), 27.57–27.41 (m, 8C, alkyl), 26.62 (s, 4C, alkyl), 25.52 (s, 2C, alkyl), 22.85 (s, 2C, alkyl), 14.27 (s, 2C, CH_3). δ_P (162 MHz): 21.8 (s, 2P). Elemental analysis calcd (%) for $C_{48}H_{94}Cl_2P_2Pd$: C 63.32, H 10.41. Found: C 63.10, H 10.67.

Palladium Dichloride Bis(1-(diphenylphosphinito)dodecane) (9). A mixture of palladium(II) dichloride (74 mg, 0.41 mmol, 0.53 equiv) and 1-(diphenylphosphinito)dodecane (0.28 g, 0.79 mmol) in dry dichloromethane (20 mL) was stirred for 48 h. 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 99% yield. δ_P (300 MHz): 7.87–7.42 (m, 40H, Ph), 3.68 (q, 2H, CH_2O), 1.37–1.13 (m, 40H, CH_2), 0.92 (t, 3H, CH_3). δ_C (75 MHz): 133.16–128.12 (m, 20C, Ph), 69.40 (s, 1C, CH_2O), 31.86 (s, 1C, alkyl), 30.01–29.07 (m, 8C, alkyl), 25.37 (s, 1C, alkyl), 22.63 (s, 1C, alkyl), 14.08 (s, 1C, alkyl). δ_P (162 MHz): 110.0 (s, 2P).

Platinum Dichloride Bis(1-(diphenylphosphino)dodecane) (10). A mixture of platinum(II) dichloride (30.5 mg, 0.114 mmol, 0.50 equiv) and 1-(diphenylphosphino)dodecane (81.0 mg, 0.228 mmol) in dry dichloromethane (5 mL) was stirred for 24 h. The mixture was filtered in order to remove the residual platinum(II) dichloride, and solvent was removed in vacuo, yielding a light brown solid in 84% yield. δ_H (400

MHz): 7.76–7.20 (m, 20H, Ph), 2.27–2.14 (m, 4H CH_2P), 1.60–1.05 (m, 40H, CH_2), 0.88 (t, 6H, CH_3). δ_C (121 MHz): 133.79 (s, 4C, Ph), 131.16 (d, 8C, Ph), 128.50 (s, 8C, Ph), 128.45 (s, 4C, Ph), 32.25 (s, 2C, alkyl), 31.02 (s, 2C, alkyl), 29.94–29.31 (m, 14C, alkyl), 25.47 (d, 2C, alkyl), 23.03 (s, 2C, alkyl), 14.46 (s, 2C, alkyl). δ_P (162 MHz): 7.0 (s, 2P, $J_{Pt-P} = 3656$ Hz). ESI MS: 849.3 ($M^+ - Cl$).

μ -Chloropalladium Chloride (1-(Diphenylphosphino)dodecane) Dimer (11). A mixture of palladium(II) dichloride bis(benzonitrile) (138.5 mg, 0.361 mmol) and 1-(diphenylphosphino)dodecane (128.1 mg, 0.361 mmol) in dry dichloromethane (10 mL) was stirred for 24 h. The mixture was filtered and dried in vacuo in order to remove all solvent and benzonitrile, yielding a red solid in 90% yield. δ_H (400 MHz): 7.81–7.20 (m, 20H, Ph), 2.40–2.30 (m, 4H CH_2P), 1.50–1.08 (m, 40H, CH_2), 0.87 (t, 6H, CH_3). δ_C (121 MHz): 133.57 (s, 4C, Ph), 132.01 (d, 8C, Ph), 129.08 (s, 8C, Ph), 128.95 (s, 4C, Ph), 32.20 (s, 2C, alkyl), 31.14 (d, 2C, alkyl), 29.94–29.31 (m, 12C, alkyl), 27.82 (d, 2C, alkyl), 24.21 (d, 2C, alkyl), 23.03 (s, 2C, alkyl), 14.37 (s, 2C, alkyl). δ_P (162 MHz): 30.8 (s, 2P). Elemental analysis calcd (%) for $C_{48}H_{70}Cl_4P_2$: C 54.20, H 6.63. Found: C 55.38, H 6.91. MALDI–TOF MS: 1061.2 ($M^+ - 2H$).

Platinum Dichloride Tris(1-(diphenylphosphino)dodecane) (12). A mixture of platinum(II) dichloride (72.0 mg, 0.271 mmol, 0.20 equiv) and 1-(diphenylphosphino)dodecane (480.0 mg, 1.354 mmol) in dry dichloromethane (20 mL) was stirred for 24 h. The mixture was filtered in order to remove the excess platinum (II) dichloride, and solvent was removed in vacuo. Subsequently, the white solid was dissolved in acetonitrile (30 mL); heating the mixture was necessary to dissolve the entire solid. The mixture was left standing at 4 °C. After 2 days spherulites started crystallizing out and yielded pure platinum dichloride tris-phosphine compound (56%). δ_H (400 MHz): 7.50–6.84 (m, 30H, Ph), 2.38–2.22 (m, 6H CH_2P), 1.70–1.10 (m, 60H, CH_2), 0.89 (t, 9H, CH_3). δ_C (121 MHz): 136.64 (s, Ph), 133.67 (s, Ph), 129.68 (s, Ph), 129.57 (s, Ph), 129.14 (s, Ph), 125.74 (s, Ph), 121.82 (s, Ph), 32.21 (s, 3C, alkyl), 30.65 (s, 3C, alkyl), 29.93–29.36 (m, 21C, alkyl), 26.19 (s, 3C, alkyl), 22.99 (s, 3C, alkyl), 14.43 (s, 3C, alkyl). δ_P (162 MHz): 16.4 (d, 2P, $J_{Pt-P} = 3605$ Hz, $J_{P-P} = 18$ Hz), 6.4 (t, 1P, $J_{Pt-P} = 2379$ Hz, $J_{P-P} = 18$ Hz).

Palladium Dichloride (1,12-Bis(diphenylphosphino)dodecane) (13). A mixture of palladium(II) dichloride (72.4 mg, 0.408 mmol, 1.1 equiv) and 1,12-bis(diphenylphosphino)dodecane (200.0 mg, 0.371 mmol) in dry dichloromethane (10 mL) was stirred for 24 h. 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 97% yield. δ_H (400 MHz): 7.73–7.33 (m, 20H, Ph), 2.46–2.37 (m, 4H, CH_2P), 1.54–1.04 (m, 20H, CH_2). δ_C (121 MHz): 134.04 (t, 8C, Ph) 130.64 (s, 4C, Ph), 128.50 (t, 8C, Ph), 31.57 (d, 2C, CH_2P), 29.88 (d, 2C, alkyl), 29.60 (s, 4C, alkyl), 28.40 (d, 2C, alkyl), 26.32 (d, 2C, alkyl). δ_P (162 MHz): 16.5 (s, $n \times 2P$, polymer). Elemental analysis calcd (%) for $C_{36}H_{44}Cl_2P_2$: C 60.39, H 6.19. Found: C 58.26, H 5.92.

Palladium Dichloride Bis(1,12-bis(dicyclohexylphosphino)dodecane) (14). A mixture of palladium(II) dichloride (400 mg, 2.26 mmol, 1.05 equiv) and 1,12-bis(dicyclohexylphosphino)dodecane (1.2 g, 2.2 mmol) in dry dichloromethane (40 mL) was stirred for 48 h. The mixture was filtered in order to remove the excess palladium(II) dichloride, and solvent was removed in vacuo, yielding a yellow-orange solid in 98% yield. δ_H (200 MHz): 2.19–1.26 (m, 68H, $CH_2 + CH$). δ_C (100 MHz): 33.17–32.95 (m, 4C, alkyl), 32.11 (s, 2C, alkyl), 29.85–29.05 (m, 14C, alkyl), 27.56–27.40 (m, 8C, alkyl), 26.60 (s, 4C, alkyl), 25.51 (s, 2C, alkyl), 18.76 (s, 2C, PCH_2). δ_P (162 MHz, toluene- d_6): 21.8 (s, $n \times 2P$, polymer) (s, $n \times 2P$). Elemental analysis calcd (%) for $C_{36}H_{68}Cl_2P_2$: C 58.41, H 9.26. Found: C 58.02, H 9.22.

Palladium Dichloride Bis(1,12-bis(diphenylphosphino)dodecane) (15). A mixture of palladium(II) dichloride

(0.32 g, 1.8 mmol, 1.1 equiv) and 1,12-bis(diphenylphosphino)dodecane (0.93 g, 1.6 mmol) in dry dichloromethane (20 mL) was stirred for 48 h. The mixture was filtered in order to remove the excess palladium(II) dichloride, and solvent was removed in vacuo, yielding a yellow-orange solid in 99% yield. δ_H (400 MHz): 7.80–7.37 (m, 20H, Ph), 3.74–3.51 (m, 4H, CH_2O), 1.35–1.04 (m, 20H, CH_2). δ_C (75 MHz): 132.53–131.78 (m, 16C, Ph), 128.28 (s, 8C, Ph), 69.67 (s, 2C, CH_2O), 30.31–29.54 (m, 8C, alkyl), 25.82 (s, 2C, alkyl). δ_P (162 MHz): 110.0 (s, $n \times 2P$, polymer). Elemental analysis calcd (%) for $C_{36}H_{44}O_2Cl_2P_2$: C 57.81, H 5.93. Found: C 56.83, H 5.92.

Platinum Dichloride (1,12-Bis(diphenylphosphino)dodecane) (16). A mixture of platinum(II) dichloride (276.3 mg, 1.035 mmol, 1.1 equiv) and 1,12-bis(diphenylphosphino)dodecane (557.8 mg, 1.035 mmol) in dry dichloromethane (50 mL) was stirred for 24 h. The mixture was filtered in order to remove the excess platinum(II) dichloride, and solvent was removed in vacuo, yielding a yellow solid in 93% yield. δ_H (400 MHz): 7.58–7.15 (m, 20H, Ph), 2.30–2.14 (m, 4H, CH_2P), 1.90–1.00 (m, 20H, CH_2). δ_C (121 MHz): 133.74 (s, 4C, Ph), 131.26 (s, 8C, Ph), 129.55 (s, 8C, Ph), 128.54 (s, 4C, Ph), 30.97 (s, 2C, alkyl), 29.70–29.20 (m, 8C, alkyl), 25.41 (d, 2C, alkyl). δ_P (162 MHz): 7.0 (s, $n \times 2P$, polymer, $J_{Pt-P} = 3656$ Hz). Elemental analysis calcd (%) for $C_{36}H_{44}Cl_2P_2Pt$: C 53.73, H 5.51. Found: C 53.45, H 5.42.

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