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A high molecular weight reversible coordination polymer of $PdCl_2$ and 1,12-bis(diphenylphosphino)dodecane†

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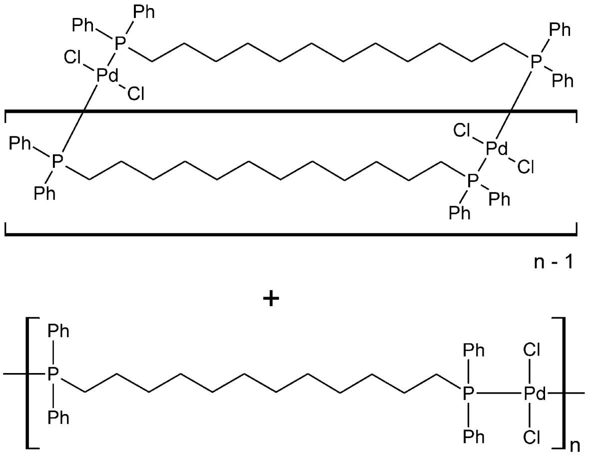
1,12-Bis(diphenylphosphino)dodecane and $PdCl_2$ are shown to form linear supramolecular polymers in equilibrium with cyclic structures; high molecular weight material was obtained by melt polymerisation.

In supramolecular polymers the monomers are connected by reversible, non-covalent bonds, leading to unique properties.[1] Coordinative interactions have been used to obtain self-assembled structures with many different architectures ranging from discrete structures such as nanotubes,[2a] cages,[2b] grids[2c] and honeycombs[2d] to polymeric structures such as linear polymers[3a,b] and coordination-block copolymers.[3c] Reversible linear coordination polymers, however, have been studied in much less detail.[4]

In a project aimed at exploring the use of coordination polymers as catalysts, we have focused our attention on the complexation of 1,12-bis(diphenylphosphino)dodecane (dppdd) with palladium dichloride, which has been studied before by Hill *et al.*[5a] and by Gray *et al.*[5b] The latter authors described solutions of [$PdCl_2$(dppdd)] as an equilibrium system consisting of cyclic monomers and oligomers. In reversible systems, cyclic structures are generally in equilibrium with linear polymeric species.[6] This equilibrium is characterized by a critical concentration, below which no polymer is present, and above which the concentration of cycles is constant and only linear polymer is formed. In view of the fundamental interest in supramolecular coordination polymers, we have studied the possibility of obtaining linear chains of [$PdCl_2$(dppdd)]$_n$ with a high molecular weight.

An equilibrium mixture of [$PdCl_2$(dppdd)] (Scheme 1) was obtained by stirring a solution of dppdd in chloroform-d with palladium(II) dichloride.

The complex was characterized with ^{31}P-NMR spectroscopy. *cis*- and *trans*-coordinated monomeric, dimeric and oligomeric species gave separate resonances in agreement with the reported spectra.[5b] In addition, assignment of individual *trans*-peaks was confirmed by diffusion ordered ^{31}P-NMR[7] (Fig. 1 and Table 1).



Scheme 1 Cycles and polymers of [$PdCl_2$(dppdd)], *trans*-species shown.

Diffusion coefficients of all peaks were normalized to the diffusion coefficient of the *trans*-monomeric species. The dimeric species have a slightly lower relative diffusion coefficient (0.78) at a concentration of 0.2 M, whereas the oligomeric species have a significantly lower diffusion coefficient than the monomeric cycle (0.19).

Relative diffusion coefficients of the monomeric and dimeric cycles are independent of concentration (Table 1). The relative diffusion coefficients of the *trans*-oligomers, however, decrease from 0.58 at 0.025 M to 0.19 at 0.2 M. The average size of the oligomeric species thus becomes larger as the concentration is raised. This observation confirms the concentration dependent size and the equilibrium nature of [$PdCl_2$(dppdd)]$_n$ in chloroform-d.

A key feature of ring–chain equilibria is the existence of a critical concentration, above which the partial concentration of each individual cyclic species (and as a consequence the total concentration of cycles) does not increase and linear polymers are formed. Integration of the signals in the ^{31}P-NMR spectra of [$PdCl_2$(dppdd)] in chloroform-d at a range of concentrations shows that the partial concentration of monomeric *trans*-cycles remains constant at 10.5 mM, above a critical concentration of approximately 70 mM (Fig. 2). This result indicates that linear polymeric [$PdCl_2$(dppdd)] is formed at concentrations higher than 70 mM. It also implies that under equilibrium conditions, significant amounts of linear polymer can only be obtained at

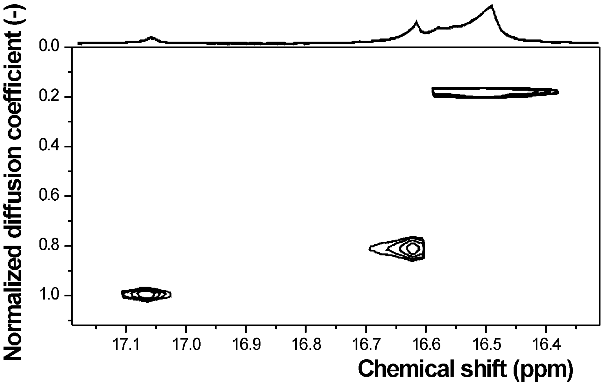


Fig. 1 ^{31}P-NMR DOSY of a 0.2 M solution of [$PdCl_2$(dppdd)] in chloroform-d.

Table 1 Normalized diffusion coefficients of *trans* centers

Conc./M	Monomer	Dimer	Oligomer
0.025	1.0	0.74	0.58
0.050	1.0	0.77	0.54
0.075	1.0	0.85	0.52
0.100	1.0	0.86	0.42
0.200	1.0	0.78	0.19

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† Electronic supplementary information (ESI) available: experimental details, SEC results and NMR spectra. See http://www.rsc.org/suppdata/cc/b3/b301874a/

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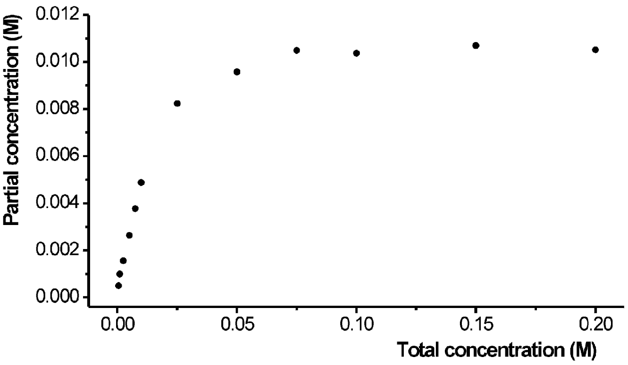

Fig. 2 Partial concentration of *trans* monomeric cycle. $[PdCl_2(dppdd)]_1$.

high concentrations, because at any concentration above the critical concentration, 70 mM of the product remains in a cyclic form, of which approximately one seventh is cyclic monomer.

Therefore, the isolation of polymeric $[PdCl_2(dppdd)]_n$ was attempted by slow evaporation of a dichloromethane solution. After several days, a highly viscous orange oil separated from solution, which was isolated by removal of residual solvent. ^{31}P-NMR of this product showed that it contained approximately 5% cyclic *trans* monomer, to give a calculated content of 34% cyclic and 61% linear polymeric material.

For characterization and for applications in dilute solution, it is necessary that the linear polymer has a sufficient lifetime before equilibration results in the formation of cycles. The kinetics of cyclization of a freshly prepared solution of polymeric $[PdCl_2(dppdd)]_n$ were determined at 298 K in chloroform-d at a concentration of 15 mM by monitoring signal intensities in the ^{31}P-NMR spectrum as a function of time. An excellent fit ($R^2 = 0.998$) to the data was obtained assuming first-order kinetics with a τ of 774 min for the formation of the monomeric cycle. A small imbalance in stoichiometry was found to have a strong effect on the lifetime of the polymer. Addition of 0.5 mol% dppdd to the coordination polymer resulted in a decrease of τ to 47 min. Addition of other phosphines such as triphenylphosphine or 1-(diphenylphosphino)dodecane resulted in a similar reduction of polymer lifetime, in line with the known effect of excess ligand on exchange processes in Pd–phosphine complexes.[8]

The relatively slow depolymerization of pure $[PdCl_2(dppdd)]_n$ in dilute solution suggests the use of size exclusion chromatography (SEC) for the analysis of molecular weight of the material obtained by slow solvent evaporation (Fig. 3). In samples that were measured immediately after redissolution, polymers consisting of up to 80 units ($M \approx 5.8 \times 10^4$ g mol^{-1}) were observed, in addition to peaks that could be assigned to oligomeric cycles by comparison to chromatograms of completely equilibrated solutions.

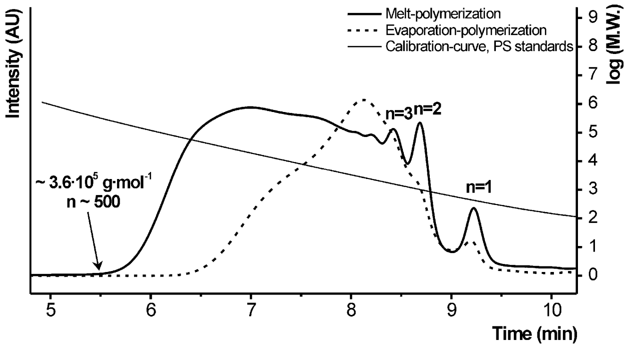

Fig. 3 SEC-trace of $[PdCl_2(dppdd)]_n$ obtained by evaporation and melt polymerisation.

Much higher molecular weights were observed in SEC traces of polymer obtained by melt polymerization. This material was prepared by heating $[PdCl_2(dppdd)]_n$ under argon at 185 °C for 15 min. The yellow solid melted and became a bright orange viscous oil. Upon cooling, the oil became a brown brittle solid. ^1H-NMR and ^{31}P-NMR did not show any evidence of decomposition. Remarkably, the ^{31}P-NMR spectrum of freshly prepared solutions of this material indicated that all phosphines in the melt polymer are *trans*-coordinated, and no monomeric cycles are detected. The SEC-trace of this polymer (Fig. 3) shows a broad distribution and proves the presence of polymers of up to 500 units ($M \approx 3.6 \times 10^5$ g mol^{-1}).

Due to the dynamic nature of the system and the low concentration at which the SEC analysis was performed, this number represents a lower limit of the DP's (degrees of polymerisation) that are actually present in the melt polymer. SEC analysis of melt polymer prepared with 1%, 5%, 10% and 50% of a monofunctional phosphine, 1-(diphenylphosphino)dodecane, as endcapper shows molecular weights in good agreement with calculated DP's (see Supplementary Information†).

In summary, we have given experimental evidence for the formation of high molecular weight coordination polymer in a dynamic system. Established theories[6] of ring–chain equilibria predict that this high molecular weight material is linear, and not cyclic, as was assumed in previous studies[5] of this system. Although the present system is sufficiently stable to be analyzed in dilute solution, exact stoichiometry is crucial for the observation of high DP's for two reasons: excess ligand or excess metal will reduce the degree of polymerization in the same way as an imbalance in stoichiometry reduces the DP in condensation polymerization,[9] while an excess of ligand will also drastically reduce the lifetime of the polymer.

For future work directed towards the use of polymeric Pd–phosphine complexes at low concentration, a reduction of the critical concentration will be sought by using longer bifunctional phosphorus ligands.

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