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Cyclodimers versus Cyclotrimers via Solvent or Temperature Effects on Metallacyclization

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The reaction of (COD)$PdCl_2$ (COD = 1,5-cyclooctadiene) with bis(3-pyridyl)methylphenylsilane (L) in acetone affords single crystals consisting of cyclodimers, $[PdCl_2(L)]_2$, whereas the reaction in a mixture of dichloromethane and ethanol yields amorphous spheres consisting of cyclotrimers, $[PdCl_2(L)]_3$. The interconversion and morphology control between the crystals and the microspheres can be explained by the difference in flexibility between the cyclodimer and cyclotrimer.

The rapid expansion in supramolecular chemistry dealing with the chemistry of molecular assembly and of the intermolecular bonds has resulted in an enormous diversity of chemical systems.[1] Recent research works have focused on the development of “molecular construction via crystal engineering”, “morphological control via intermolecular interaction”, and macrocyclic chemistry.[2–10] The facile manipulation of morphology remains an important issue for the development of advanced materials. Thus, a variety of well-defined microshapes of metal chalcogenides have been produced by various driving forces such as steric effects, surface tension, capillary effects, electric and magnetic forces, van der Waals interaction, and the surfactant/precursor ratio.[11–15] Even though intermolecular affinity is the discerning factor in the formation of a particle-based amorphous morphology versus single crystals,[16] a comparative investigation of single crystals versus amorphous metal complex morphology still remains a keen challenge. The ability to control macrocyclic rings by means of chemical triggers is of importance in the construction of task-specific molecular materials such as molecular machines, switches, recognition, selective transformation, drug-delivery systems, catalysts, storage, and biomimics.[17–26] Thus, it is worthy considering a new, facile method of the morphogenesis via labile metal−ligand coordination or thermodynamic control without any organic additive. In particular, diaminepalladium(II) complexes have contributed to the synthesis of a “magic ring” with dual-character Pd−N bonds.[27,28] In this context, we report the formation and interconversion process of single crystals versus amorphous spheres via solvent or temperature

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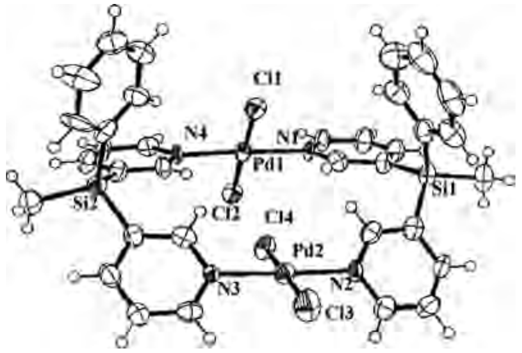
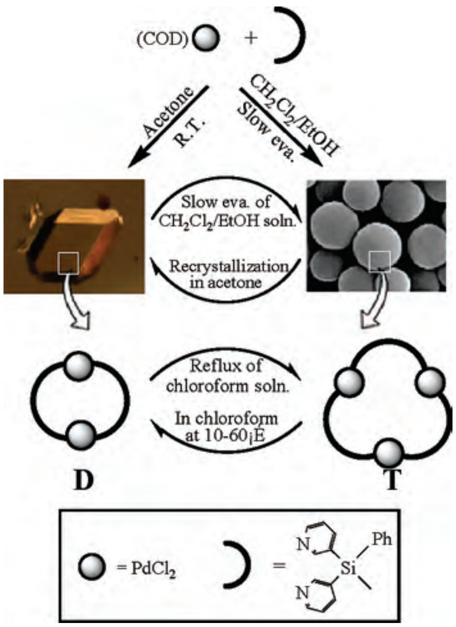


Figure 1. X-ray structure of **D**. The solvate acetone molecules are omitted for clarity.

Scheme 1



effects on the metallacyclization. Our first goal was to fully investigate the solvent effects on the Pd−N bonds, but additionally this is the first direct control of single crystal versus spherical morphology via the molecular ring size.

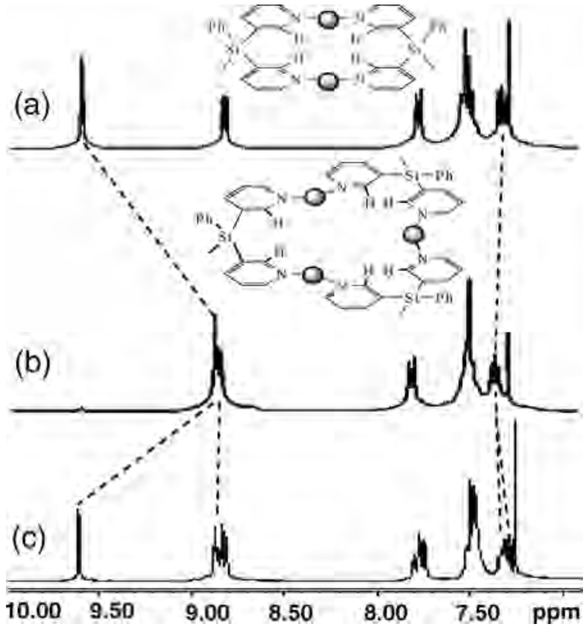


Figure 2. ^{1}H NMR spectra of **D** (a), **T** (b), and a mixture of **D** and **T** after **D** was refluxed in chloroform for 12 h (c).

The reaction of $(COD)PdCl_2$ with bis(3-pyridyl)methylphenylsilane (L)[29] in acetone at room temperature yields single crystals in high yield, whereas the same reaction in a mixture of dichloromethane and ethanol produces monomodal microspheres, as shown in Scheme 1. In the present study, the single crystals were treated in a mixture of dichloromethane and ethanol to produce microspheres. The spherical morphology was more smoothly formed by the addition of hexane to the solution. Furthermore, recrystallization of the microspheres in acetone yielded single crystals, the spheres of which are more soluble than those of single crystals in an organic solvent. The crystal structure indicates that the single crystal consists of $[PdCl_2(L)]_2 \cdot Me_2CO$ (Figure 1). The local geometry around palladium(II) approximates to a typical square-planar arrangement with two chlorides in the trans position [Cl−Pd−Cl = 176.9(1)°, 178.29(9)°; Pd−Cl = 2.302(2) Å, 2.307(2) Å; Pd−N = 2.047(6) Å, 2.050(6) Å]. L connects two palladium(II) ions to form a 16-membered cyclodimer (**D**), and the two phenyl groups are positioned in the same direction. The ^{1}H NMR spectra of both the crystalline **D** and the microspherical product were measured in chloroform at room temperature (Figure 2). The two sets of spectra show a similar pattern except for the chemical shifts of 2H-Py. 2H-Py of the sphere relative to **D** was significantly shifted upfield, from 9.61 to 8.88 ppm. **D** is unusually rigid in solution, as shown in its crystal structure, and thus 2H-Py is strongly affected by the anisotropy effect. The weak interaction (C−H···Cl = 2.59 Å) of **D** can partly be ascribed to the downfield shift. In contrast, for microspheres, the upfield shift of 2H-Py can be explained by the more fluxional motion of the Py group. The slight shift of 5H-Py (para position to 2H-Py) supports the free rotation of the Py group. That is, microspheres are an aggregate of fluxional cyclotrimers (**T**). The mass data were obtained in order to characterize the chemical structure of the spherical morphology. The mass peaks (*m*/*e* = 1327 [**T**−Cl]$^+$, 1051 [**T**−Cl−L]$^+$, and 1192 [**T**−$PdCl_2$]$^+$) indicate that the microsphere consists of **T** molecules. The mass data of the crystalline **D** show the dimer (*m*/*e* = 837 [**D**-Cl]$^+$; Supporting Information). When solvate acetone molecules for single crystals were thoroughly evaporated, the analytical values (C, H, and N) of both materials were the same. Furthermore, the reflux of **D** in chloroform for 24 h exclusively transformed to **T**. Reflux for 12 h yielded a 1:1 ratio of **D** and **T**. The more interesting feature is that **T** partly returns to **D** in solution in the range of 10−60 °C. Only two species of **D** and **T** exist under the reflux condition, but another species besides **D** and **T** exists in the 10−60 °C range (Supporting Information). The new species might be a chain intermediate between **D** and **T**. The equilibria are dependent on the temperature and concentration. High concentration favors **T**.

Slow evaporation of $(COD)PdCl_2$ (0.01 mmol in 5 mL of CH_2Cl_2) with L (0.01 mmol in 6 mL of EtOH) yields

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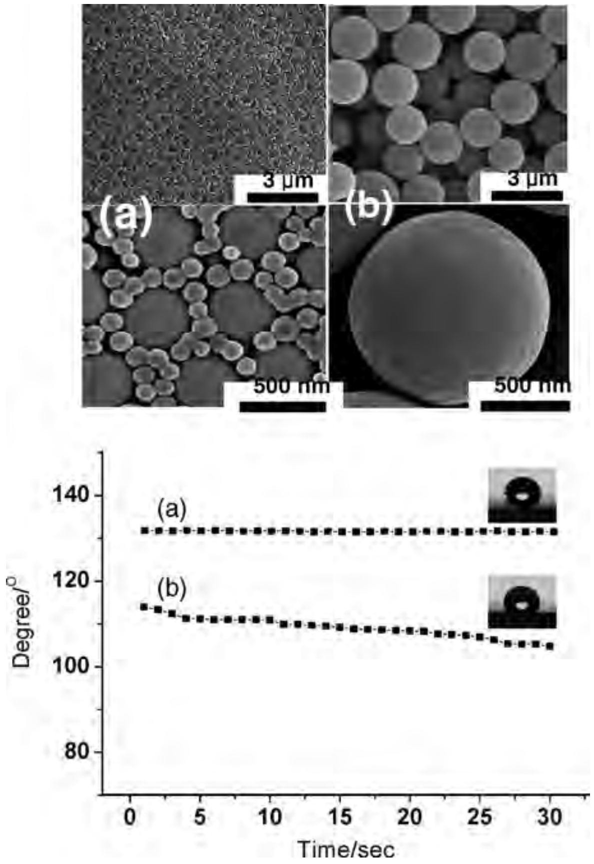

Figure 3. Scanning electron microscopy (SEM) images of self-arrayed bimodal submicrospheres [top (a)] and microspheres [top (b)] and the contact angles of water droplets on the self-arrayed bimodal submicrospheres [bottom (a)] and microspheres [bottom (b)].

microspheres of $\sim$2 μm diameter, as shown in Figure 3. The reaction of (COD)PdCl_2 (0.05 mmol) with L (0.05 mmol) was refluxed in 12 mL of chloroform (6 mL) or dichloromethane (6 mL) for 48 h, and the final solution was reduced to 1 mL. The reaction solution was cooled to room temperature, after which 2 mL of ethanol was added into the solution to obtain bimodal submicrospheres of $\sim$400 and $\sim$90 nm diameter.[30] This process reproducibly results in self-arrayed bimodal submicrospheres. The formation of one-pot bimodal submicrospheres seems to be induced by the two-step nucleation via a two-step process (cooling and solvent addition). This method represents a conceptually advanced method for producing the bimodal morphology. Generally, organic additives and/or templates have been used to control the nucleation, growth, and alignment of inorganic morphology,[31,32] but the formation of self-arrayed bimodal spheres via such a two-step process is an unprecedented process. Preliminary experiments showed that the spherical size can be controlled by the concentration and evaporation rates. In order to investigate surface properties such as wettability, adhesion, and biocompatibility, the contact angles of water droplets on both the layer of the microspheres ($\sim$2 μm) and the layer of the bimodal submicrospheres ($\sim$400 and $\sim$90 nm) were measured, as shown in Figure 3 (bottom). The contact angles of the water droplets on the layer of the submicrospheres (132°) proved to be higher than those on the layer of the bimodal microspheres (120°). This slight difference arises from the difference in compactness between the microspheres and bimodal submicrospheres, indicating that the smaller bimodal submicrospheres are well-arrayed. The contact angles of the present spheres were comparable to those of the analogues.[33]

This system is an effective means of clearly showing the difference in flexibility between **D** and **T**. Indeed, the most significant difference between **D** and **T**, as established by the ^{1}H NMR spectra, is this molecular flexibility. The rigid **D** produces single crystals, but the fluxional **T** affords amorphous spheres via intermolecular interactions. The formation of the spheres seems to be determined by a combination of surface tension, macrocyclic flexibility, and solvent effects. The formation of bimodal submicrospheres seems to be induced by two-step nucleation via growth kinetics in addition to those factors combined. The growth kinetics are determined by the interplay between the internal lattice structure and the external environment. The formation of spheres without water or any additive is a rare case.

In conclusion, the present palladium complexes containing bidentate bis(3-pyridyl)methylphenylsilane are an effective system for explaining the relationship between the molecular structure and physicochemical properties such as NMR behavior, morphology, temperature, and solvent. Such morphology control via the entropy effects of the molecular ring size is unprecedented. The formation of arrayed bimodal spheres via a "two-step process" is another important contribution. The structural pliability of metal complexes will contribute to the development of molecular materials.

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Supporting Information Available: Synthesis of **D** and **T**, mass data of **D** and **T**, SEM and energy-dispersive X-ray spectra of **T**, IR spectra of L (a), **T** (b), and **D** (c) along with a solvate acetone peak, and ^{13}C NMR spectra of **D** and **T**. This material is available free of charge via the Internet at http://pubs.acs.org.

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