First Hydrogelation of Discrete Metal Complexes. Structures and Fluxional Behavior of Cyclopalladium(II) Complexes

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Received October 31, 2008, Accepted December 15, 2008

The reaction of $(en)Pd(NO_3)_2$ (en = ethylenediamine) with 1,4-bis(dimethyl-4-pyridylsilyl)benzene (L) affords cyclodimer, $[(en)Pd(L)]_2(NO_3)_4$, whereas the reaction of $(tmeda)Pd(NO_3)_2$ (tmeda = *N,N,N',N'*-tetramethylethylenediamine) with L gives cyclotrimer, $[(tmeda)Pd(L)]_3(NO_3)_6$. Both complexes exist as catenane in water. The catenated cyclodimer is rigid whereas the catenated cyclotrimer is dynamic in water. The catenated cyclotrimers afford hydrogel containing 98.5% water below 2 °C. The hydrogel changes to its sol around 38 °C, and to its clear solution at 78 °C. Such a notable difference between $[(en)Pd(L)]_2(NO_3)_4$ and $[(tmeda)Pd(L)]_3(NO_3)_6$ might be explained by their different dynamic behavior *via* ring size effects.

Key Words: Catenane, Hydrogelation, Metallacycles, Palladium, Si ligands

Introduction

Research on the prediction and control of bulk properties on the basis of molecular structure and motion is a current important issue.[1-3] One aspect of particular interest is the formation of stimuli-responsive hydrogels that have potential applications such as foods, cosmetics, textile fibers, drug delivery agents, superabsorbents, and tissue engineering scaffolds.[4-7] In particular, supramolecular self-assembly through weak intermolecular interactions has been employed as a general method for the formation of task-specific hydrogels.[8,9] These weak intermolecular interactions, *via* intermediary water molecules, are a significant factor in hydrogelation of polymeric compounds. Whereas numerous organic/polymeric hydrogels have been developed,[10-13] reversible hydrogelation of discrete metal complexes is, to our best knowledge, unprecedented. Discrete organic molecules such as steroids, carbohydrates, anthryl derivatives, and urea have been known to form useful hydrogels.[14-17]

On the other hand, the ability to control metallacyclic rings by means of chemical triggers is of importance in the construction of molecular machines, recognition, selective transformation, catalysts, storage, and biomimics materials.[18-20] Simple, readily applicable controllable methods of rings are ring-expansion and the "magic ring" phenomenon by means of labile Pd−N dual character.[21-23] Hydrogelation *via* the fluxional motion of such discrete cyclopalladium(II) complexes remains a tough challenge.

In this context, we report the first hydrogelation and sructural properties of a fluxional cyclopalladium(II) system along with coligand effects. Our first goal was to achieve the coligand effects of the Pd−N bonding properties, but this was also an unprecedented reversible hydrogelation of discrete palladium(II) complex in water. These materials undergo a well characterized sol↔gel transition (sol→gel below 2 °C; gel→sol above 38 °C).

Experimental Section

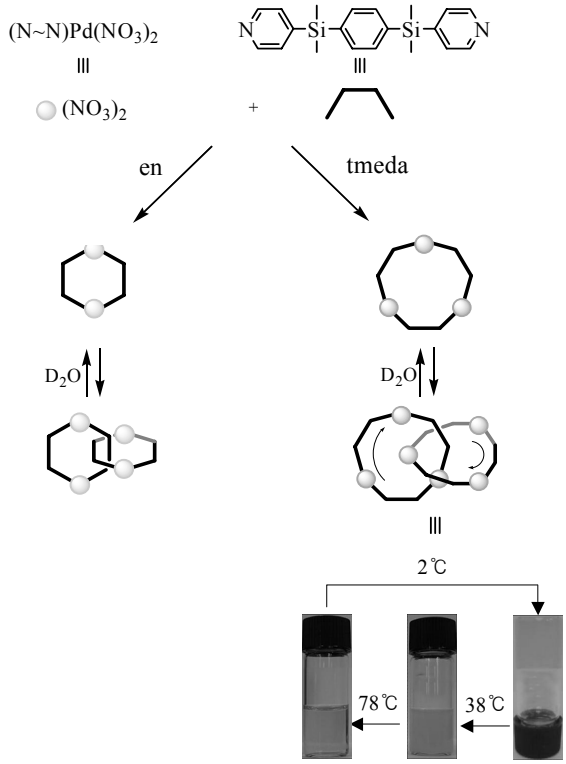
Materials and Measurements. Potassium tetrachloropalladate (K_2PdCl_4), *N,N,N',N'*-tetramethylethylenediamine (tmeda), ethylenediamine (en), 1,4-bis(chlorodimethylsiyl)benzene, and $AgNO_3$ were purchased from Aldrich, and used without further purification. $(en)PdCl_2$ and $(tmeda)PdCl_2$ were prepared by the literature procedure.[24] 1,4-Bis(dimethyl-4-pyridylsilyl)benzene (L) was prepared by a method outlined in two of our previous literatures.[25,26] ^{1}H NMR spectra were recorded on a Varian Mercury Plus 300 operating at 300.00 MHz, and the chemical shifts were relative to the internal Me_4Si. Infrared spectra were obtained on a Perkin Elmer 16F PC FTIR spectrophotometer with samples prepared as KBr pellet. Elemental microanalyses (C, H, N) were performed on solid samples by the Advanced Analytical Division at Pusan Center, KBSI using a Perkin Elmer 2400 CHNS analyzer. Mass spectrometric analysis was performed in chloroform by KMS-700 Mstation Mass Spectrometer (Jeol, Japan) using a MS-MP9020D data system. High resolution transmission electron microscope images were obtained by a Phillips model CM 200 HR-TEM, and scanning electron microscope images were obtained on a JEM 2011.

Preparation of $[(tmeda)Pd(L)]_3(NO_3)_6$. $(tmeda)PdCl_2$ (45 mg, 0.15 mmol) was suspended in water (15 mL) and stirred for 2 h at 50 °C with $AgNO_3$ (51 mg, 0.3 mmol). After the mixture was cooled and AgCl removed by filtration, a methanol (10 mL) solution of L (53 mg, 0.15 mmol) was added to the filtrate, and the mixture stirred for 3 h at room temperature. The solution was then filtered and evaporated to dryness to yield the yellow solid under vacuum. ^{1}H NMR (300 MHz, D_2O, δ) of **T** (cyclotrimer): 0.38 (s, CH_3), 2.51 (s, CH_3), 2.92 (s, $-NCH_2CH_2N-$), 7.06 (s, C_6H_4), 7.38 (d, J = 5.7 Hz, PyH_β), 8.60 (d, J = 5.7 Hz, PyH_α), **CT** (catenated cyclotrimer): 0.25 (s, CH_3), 2.51 (s, CH_3), 2.92 (s, $-NCH_2CH_2N-$), 6.20 (s, C_6H_4), 7.45 (d, J = 5.7 Hz, PyH_β), 8.77 (d, J = 5.7 Hz, PyH_α).

IR (KBr, cm^{-1}): ν = 3435(m), 1604(w), 1383(s), 1130(w), 809(m), 506(w). Anal. Calcd for $C_{78}H_{120}N_{18}O_{18}Pd_3Si_6$: C, 44.92; H, 5.80; N, 12.09. Found: C, 44.96; H, 5.87; N, 12.03.

Preparation of [(en)Pd(L)]$_2$(NO$_3$)$_4$. (en)$PdCl_2$ (36 mg, 0.15 mmol) was suspended in water (15 mL) and stirred for 2 h at 50 °C with $AgNO_3$ (51 mg, 0.3 mmol). After the mixture was cooled and AgCl removed by filtration, a methanol (10 mL) solution of L (53 mg, 0.15 mmol) was added to the filtrate, and the mixture stirred for 3 h at room temperature. The solution was then filtered and evaporated to dryness to yield the yellow solid under vacuum. ^{1}H NMR (300 MHz, D_2O, δ) of **D** (cyclodimer): 0.38 (s, CH_3), 2.75 (s, -NCH_2CH_2N-), 7.18 (s, C_6H_4), 7.34 (d, J = 6.6 Hz, PyH_β), 8.38 (d, J = 6.6 Hz, PyH_α), **CD** (catenated cyclodimer): 0.38 (s, 24 H, CH_3), 2.75 (s, 8 H, -NCH_2CH_2N-), 5.78 (s, C_6H_4–inside), 6.88 (d, J = 6.6 Hz, PyH_β – inside), 7.02 (s, C_6H_4–outside), 7.54 (d, J = 6.6 Hz, PyH_β – outside), 8.45 (d, J = 6.6 Hz, PyH_α–inside), 8.60 (d, J = 6.6 Hz, PyH_α–outside). IR (KBr, cm^{-1}): ν = 3050(w), 2954(w), 1604(w), 1384 (s), 1252(m), 1133(m), 1059(w), 803(m), 775(m), 670(w), 491(m). Anal. Calcd for $C_{44}H_{64}N_{12}O_{12}Pd_2Si_4$: C, 41.34; H, 5.05; N, 13.15. Found: C, 41.37; H, 5.15; N, 13.11.

Hydrogelation of [(tmeda)Pd(L)]$_3$(NO$_3$)$_6$. The reaction of an aqueous solution (15 mL) of (tmeda)$Pd(NO_3)_2$ (45 mg, 0.15 mmol) with a methanol (10 mL) solution of L (53 mg, 0.15 mmol) was carried out for 3 h at room temperature. The reaction solution was filtered and reduced to an aqueous solution of 5 mL. The safe-keeping of the aqueous solution below 2 °C affords hydrogel containing 98.5% water.



Scheme 1

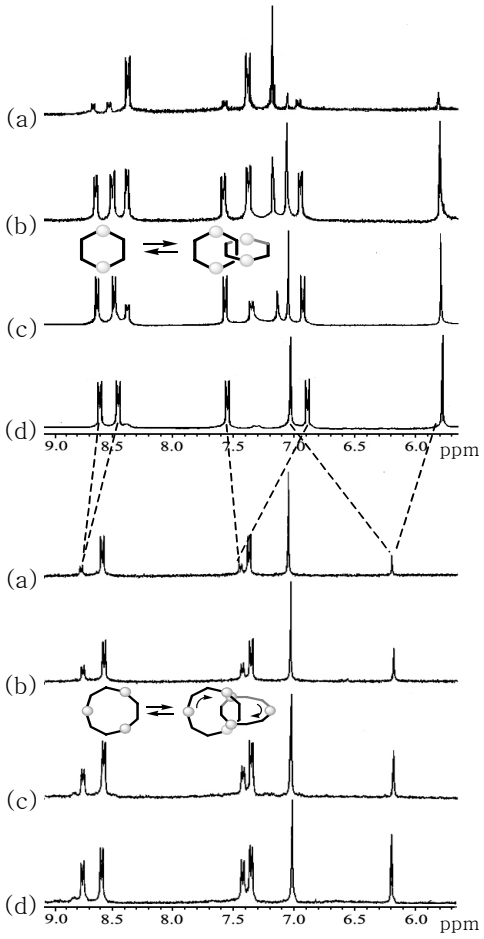


Figure 1. Concentration-dependent ^{1}H NMR of [(en)Pd(L)]$_2$(NO$_3$)$_4$ (top: 2 mM (a), 10 mM (b), 25 mM (c), 50 mM (d)) and [(tmeda)-Pd(L)]$_3$(NO$_3$)$_6$ (bottom: 2 mM (a), 5 mM (b), 10 mM (c), 15 mM (d)).

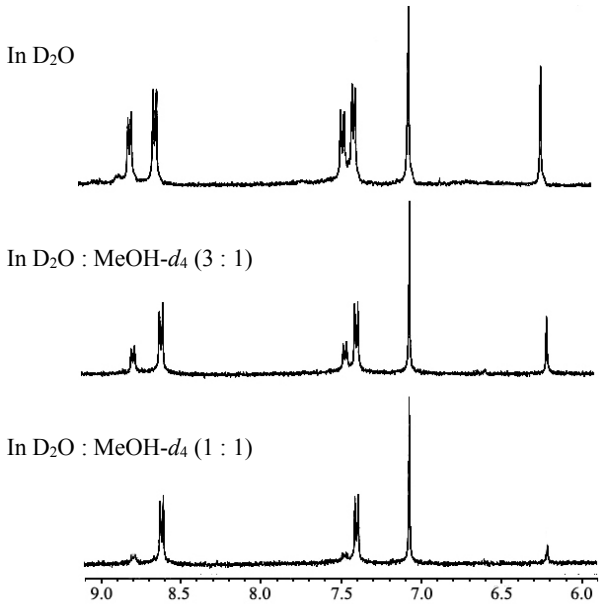


Figure 2. ^{1}H NMR spectra of [(tmeda)Pd(L)]$_3$(NO$_3$)$_6$ in a mixture of D_2O and MeOH-d_4 (15 mM).

Results and Discussion

Synthesis. The reaction of (en)$Pd(NO_3)_2$ (en = ethylene-diamine) with 1,4-bis(dimethyl-4-pyridysilyl)benzene (L) in

a mixture of water and methanol at room temperature yields the cyclodimer (**D**), $[(en)Pd(L)]_2(NO_3)_4$, whereas the reaction of (tmeda)$Pd(NO_3)_2$ (tmeda = *N*,*N*,*N*',*N*,'-tetramethylethylenediamine) with L produces the cyclotrimer (**T**) $[(tmeda)Pd(L)]_3(NO_3)_6$ (Scheme 1). The water-solubility of $[(en)Pd(L)]_2(NO_3)_4$ is better than that of $[(tmeda)Pd(L)]_3(NO_3)_6$, and both complexes are stable in solid state. Thus, the metallacyclization is significantly affected by coligands. The formation of products seems to be induced from the steric difference between tmeda and en rather than from electronic difference. The bulky tmeda prefers **T** to **D** in order to decrease the ring constraint.

Formation of Catenane. The ^{1}H NMR spectra in water at room temperature indicate the equilibrium between the metallacycles and its corresponding catenanes. Figure 1 shows the concentration-dependent ^{1}H NMR, indicating that the high concentration favors catenation. The signals of the pyridyl and phenyl groups exhibited two sets of ^{1}H resonances, confirming the coexistence of two species in the solution. $[(en)Pd(L)]_2(NO_3)_4$ in low concentrations predominantly exists as **D**, and the increase of the concentration resulted in the growth of the catenated cyclodimer (**CD**) peaks, and finally **D** was completely converted to **CD**. The two signals (8.60, 8.45; 7.54, 6.88; 7.02, 5.78 ppm) of each peak reflected the catenane. The signal at 7.18 ppm of **D** separated into two signals at 7.02 ppm (outside -C_6H_4-) and 5.78 ppm (inside -C_6H_4-). $[(tmeda)Pd(L)]_3(NO_3)_6$ similarly coexists as **T** and **CT** in the aqueous solution. The NMR spectra indicate that linear and higher oligomers do not exist except for **T** and **CT** in the solution in the temperature range. In striking contrast to **CD**, for **CT**, one set of signals appeared instead of two sets of signals, indicating that the catenated cyclotrimer (**CT**) is fluxional owing to the large ring size of **T** in water even at room temperature. The chemical shift of the phenyl group (-C_6H_4-) at 6.20 ppm is a median value between 7.02 ppm (outside -C_6H_4-) and 5.78 ppm (inside -C_6H_4-) of **CD**. The **CT** increased with the concentration, but complete conversion did not occur in contrast to **D** species owing to the low water-solubility of **T** species. That is, **T** is less water-soluble than **D**. The low concentrated aqueous solution is an obstacle to measure the low temperature NMR spectrum for the separated signals of **CT**. Of course, ^{1}H NMR spectra of $[(tmeda)Pd(L)]_3(NO_3)_6$ in a mixture of D_2O and MeOH-d_4 (15 mM) indicate that the **CT** species drastically decreases (Figure 2). Furthermore, salt effects on the aqueous media were observed in aqueous solution (Supporting Information: Fig. S5). That is, the catenated species increases with the addition of salts in aqueous solution. In order to more clearly characterize the species in aqueous solution, their mass data were obtained. The mass data of $[(tmeda)Pd(L)]_3(NO_3)_6$ were obtained for the aqueous solution containing a 5 : 6 mixture of **T** and **CT** (as confirmed by ^{1}H NMR spectrum). The FAB mass data (matrix: nitrobenzylalcohol) of $[(tmeda)Pd(L)]_3(NO_3)_6$ (*m/e* = 570.2 $[\mathbf{CT}\text{-}6NO_3\text{-}HNO_3]^{6+}$ or $[\mathbf{T}\text{-}3NO_3\text{-}HNO_3]^{3+}$; 632.1 $[\mathbf{CT}\text{-}6NO_3]^{6+}$ or $[\mathbf{T}\text{-}3NO_3]^{3+}$; 916.1 $[\mathbf{CT}\text{-}4NO_3\text{-}HNO_3]^{4+}$ or $[\mathbf{T}\text{-}2NO_3\text{-}HNO_3]^{2+}$; 980.0 $[\mathbf{CT}\text{-}4NO_3]^{4+}$ or $[\mathbf{T}\text{-}2NO_3]^{2+}$; 1082.0 $[\mathbf{CT}\text{-}3NO_3\text{-}4HNO_3]^{3+}$; 1144.2 $[\mathbf{CT}\text{-}3NO_3\text{-}3HNO_3]^{3+}$; 1266.0 $[\mathbf{CT}\text{-}3NO_3\text{-}HNO_3]^{3+}$; 1327.9 $[\mathbf{CT}\text{-}3NO_3]^{3+}$) indicated that $[(tmeda)Pd(L)]_3(NO_3)_6$ coexists as a mixture of **T** and **CT** in water (Supporting Information: mass of $[(tmeda)Pd(L)]_3(NO_3)_6$ and $[(en)Pd(L)]_2(NO_3)_4$). The anion exchange of $[(tmeda)Pd(L)]_3(NO_3)_6$ with PF_6^- was attempted to identify the product, but unfortunately afforded only a cyclodimer, $[(tmeda)Pd(L)]_2(PF_6)_4$ (Supporting Information: CCDC No.: 684329; Fig. S3). That is, the counteranions play important role in the formation of the present labile metallacyclization. Of course, the aromatic ^{1}H NMR of $[(tmeda)Pd(L)]_3(NO_3)_6$ is significantly different form that of $[(tmeda)Pd(L)]_2(PF_6)_4$ in acetone (Supporting Information), indicating that $[(tmeda)Pd(L)]_3(NO_3)_6$ is cyclotrimer rather than cyclodimer in the solution.

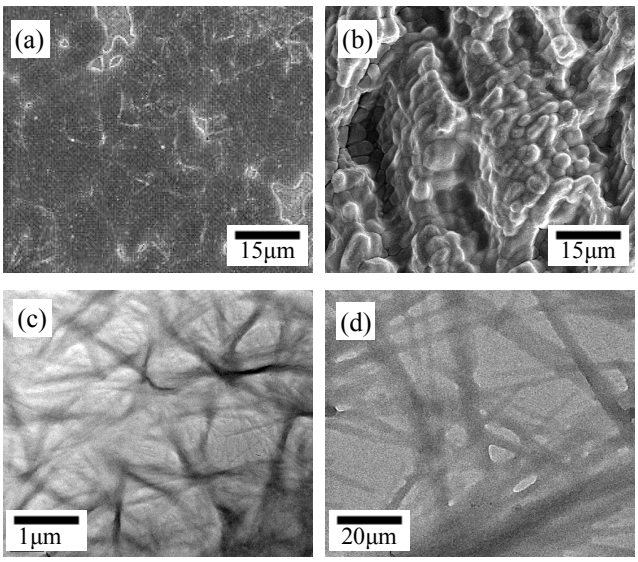


Figure 3. SEM images of hydrogel-surface after quick-freezing at 1 °C (a) and at 38 °C (b). TEM images of dried hydrogel in pure water (1% solute (c) and 0.5% solute (d)).

Hydrogelation. Surprisingly the hydrogelation of a mixture of **T** and **CT** in water below 2 °C was observed, as shown in Scheme 1. The reaction of an aqueous solution (15 mL) of (tmeda)$Pd(NO_3)_2$ (44 mg, 0.15 mmol) with a methanol (10 mL) solution of L (53 mg, 0.15 mmol) was carried out for 3 h at room temperature. The reaction solution was filtered and reduced to an aqueous solution of 5 mL. The safe-keeping of the aqueous solution below 2 °C affords hydrogel containing 98.5% water. The hydrogel changed to sol at 38 °C, and to clear solution at 78 °C. This is a reproducible process with sol/gel. The hydrogels at both 1 °C and 38 °C were quick-freezed by a Jet Freezer JFD-030. SEM images of the frozen surfaces were obtained (Figure 3(a) and 3(b)). The two SEM images reveal differences in the microstructures. The surface at 1 °C was smooth whereas at 38 °C it consisted of winding ripples, indicating that the hydrogel at 38 °C was fluidic. Differences in the surface between 1 °C and 38 °C seem to be the dominant contributor to the fluidic behavior. TEM photographs (Figure 3(c) and 3(d)) show the morphology of the dried hydrogel prepared in pure water. The morphology shows a network structure composed of fibers with nano dimension which is similar to the Maitra's results for the discrete hydrophobic pocket molecule.[5] Even though the

mechanism of hydrogelation is not clear at this stage, electrostatic interaction through NO_3^- as a mediator and hydrophobic interaction via a mixture of fluxional **CT** and **T** may be responsible for the formation of network fibers.

Organic additives and/or polymers have been used to control the formation of hydrogel,[11-13] the present hydrogelation of discrete metal complexes described in this paper is unprecedented. This system is an effective means of clearly showing the difference in motion between **D** and **T**. The **D** species is similar to the Fujita's results,[22] but the **T** species is unprecedented in the catenation. Indeed, the most significant difference between **D** and **T**, as established by the ^{1}H NMR spectra, may be ascribed to the molecular motion. That is, **CD** is rigid whereas **CT** is fluxional in aqueous solution. The rigid **D** produces a simple solid product, but the fluxional large-cyclic **T** affords hydrogel in water. Formation of the hydrogel can be ascribed to a suitable combination of the hydrophobic Si properties, the charged hydrophilic NO_3^-, electrostatic interaction, and the fluxional motion. Another important factor in both catenation and hydrogelation is solvent effects. **T** in a mixture of D_2O and MeOH-d_4 was not hydrogelated, and **CT** was drastically decreased with addition of methanol. Thus, the compound in organic solvents did not form the gel. The intermolecular interactions of fluxional metallacyclic molecules via intermediary water molecules seem to be a driving force of the formation of hydrogels. **T** is more prone to self-assembly due to amphiphilicity and van der Waals interaction, but how this hydrogel is formed from the individual molecules is not clear at this stage. This system is a genuine hydrogelation of discrete metal complexes in water without any organic solvent. These hydrogels have the ability to sense the changes of pH, temperature, or the concentration.

Conclusions

The present system shows the subtle coligand effects on metallacyclization and catenation. This fluxional catenated cyclotrimer (**CT**) is an unprecedented system. The first reversible hydrogelation of discrete metal complexes in pure water without any additives or organic solvent seems to have been induced from equilibrium between fluxional cyclotrimers (**T** + **CT**) in water. This process is a conceptually advanced method of producing hydrogels. The 38 ^oC transition temperature and pH changes of the present hydrogels can contribute to the desirable cyclic materials applicable to sensor technology, transport, and drug delivery system in the human body.

Acknowledgments. This research was supported by a grant from the Fundamental R&D Program for Core Technology of Materials funded by the Ministry of Knowledge Economy, Republic of Korea.

Supporting Information. FAB mass data of $[(en)Pd(L)]_2(NO_3)_4$ (Fig. S1) and $[(tmeda)Pd(L)]_3(NO_3)_6$ (Fig. S2); X-ray crystal structure of $[(tmeda)Pd(L)]_2(PF_6)_4$ (Fig. S3); ^{1}H NMR of $[(tmeda)Pd(L)]_3(NO_3)_6$ (a) and $[(tmeda)Pd(L)]_2(PF_6)_4$ (b) in acetone-d_6 (Fig. S4); ^{1}H NMR spectra of $[(tmeda)Pd(L)]_3(NO_3)_6$ along with addition of $NaNO_3$ (Fig. S5). Crystallographic data for $[(tmeda)Pd(L)]_2(PF_6)_4$ is deposited at the Cambridge Crystallographic Data Centre under supplementary publication numbers CCDC-684329. Copies of available material may be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44 1223 336 033, or e-mail: deposit@ccdc.cam.ac.uk.

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