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

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The reaction of (en)Pd(NO3)2 (en = ethylenediamine) with 1,4-bis(dimethyl-4-pyridylsilyl)benzene (L) affords cyclodimer, [(en)Pd(L)]2(NO3)4, whereas the reaction of (tmeda)Pd(NO3)2 (tmeda = N,N',N'-tetramethyl-ethylenediamine) with L gives cyclotrimer, [(tmeda)Pd(L)]3(NO3)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(NO3)4 and [(tmeda)Pd(L)]3(NO3)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.13 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.24 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,10,11 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 metallaclycic 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.21,22 Hydrogelation via the fluxional motion of such discrete cyclopalladium(II) complexes remains a tough challenge.

In this context, we report the first hydrogelation and structural 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 (K2PdCl4), N,N,N',N'-tetramethyl-ethylenediamine (tmeda), ethylenediamine (en), 1,4-bis(chlorodimethylsilyl)benzene, and AgNO3 were purchased from Aldrich, and used without further purification. (en)PdCl2 and (tmeda)PdCl2 were prepared by the literature procedure.24 The reaction of (en)Pd(NO3)2 (en = ethylenediamine) with 1,4-bis(dimethyl-4-pyridylsilyl)benzene (L) was prepared by a method outlined in two of our previous literatures.25,26 1H NMR spectra were recorded on a Varian Mercury Plus 300 operating at 300.00 MHz, and the chemical shifts were relative to the internal Me4Si. Infrared spectra were obtained on a Perkin Elmer 16F 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(NO3)6. (tmeda)PdCl2 (45 mg, 0.15 mmol) was suspended in water (15 mL) and stirred for 2 h at 50 °C with AgNO3 (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.1H NMR (300 MHz, D2O, δ) of T (cyclotrimer): 0.38 (s, CH3), 2.51 (s, CH3), 2.92 (s, -NCH2CH2N-), 7.06 (s, C6H4), 7.38 (d, J = 5.7 Hz, PyH0), 8.60 (d, J = 5.7 Hz, PyH0), CT (catenated cyclotrimer): 0.25 (s, CH3), 2.51 (s, CH3), 2.92 (s, -NCH2CH2N-), 6.20 (s, C6H4), 7.45 (d, J = 5.7 Hz, PyH0), 8.77 (d, J = 5.7 Hz, PyH0),
IR (KBr, cm⁻¹): v = 3435(m), 1604(w), 1383(s), 1130(w), 809(m), 506(w). Anal. Calcd for C₇₈H₁₂₀N₁₈O₁₈Pd₃Si₆: 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(NO₃)₄. (en)PdCl₂ (36 mg, 0.15 mmol) was suspended in water (15 mL) and stirred for 2 h at 50 °C with AgNO₃ (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. ¹H NMR (300 MHz, D₂O, δ) of D (cyclodimer): 0.38 (s, CH₃), 2.75 (s, -NCH₂CH₂N-), 7.18 (s, C₆H₄), 7.34 (d, J = 6.6 Hz, PyHβ), 8.38 (d, J = 6.6 Hz, PyHα), CD (catenated cyclodimer): 0.38 (s, 24 H, CH₃), 2.75 (s, 8 H, -NCH₂CH₂N-), 5.78 (s, C₆H₄-inside), 6.88 (d, J = 6.6 Hz, PyHβ-inside), 7.02 (s, C₆H₄-outside), 7.54 (d, J = 6.6 Hz, PyHβ-outside), 8.45 (d, J = 6.6 Hz, PyHα-inside), 8.60 (d, J = 6.6 Hz, PyHα-outside). IR (KBr, cm⁻¹): v = 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 C₄₄H₆₄N₁₂O₁₂Pd₂Si₄: 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(NO₃)₆. The reaction of an aqueous solution (15 mL) of (tmeda)Pd(NO₃)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.

Results and Discussion

**Synthesis.** The reaction of (en)Pd(NO₃)₂ (en = ethylenediamine) 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(NO3)4, whereas the reaction of (tmeda)Pd(NO3)2 (tmeda = N,N',N',N'-tetramethyl-ethylenediamine) with L produces the cyclotrimer (T) [(tmeda)Pd(L)]3(NO3)6 (Scheme 1). The water-solubility of [(en)Pd-L]2(NO3)4 is better than that of [(tmeda)Pd(L)]3(NO3)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 1H NMR spectra in water at room temperature indicate the equilibrium between the metallacycles and its corresponding catenanes. Figure 1 shows the concentration-dependent 1H NMR, indicating that the high concentration favors catenation. The signals of the pyridyl and phenyl groups exhibited two sets of 1H resonances, confirming the coexistence of two species in the solution. [(en)Pd(L)]3(NO3)6 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 -C6H4-) and 5.78 ppm (inside -C6H4-) 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 watersoluble 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, H NMR spectra of [(tmeda)Pd(L)]3(NO3)6 in a mixture of D2O and MeOH-d4 (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(NO3)6 were obtained for the aqueous solution containing a 5:6 mixture of T and CT (as confirmed by 1H NMR spectrum). The FAB mass data (matrix: nitrobenzylalcohol) of [(tmeda)Pd(L)]3(NO3)6 (m/e = 570.2 [CT-6NO3-HNO3]+ or [T-3NO3-HNO3]+; 632.1 [CT-6NO3]+ or [T-3NO3]+; 916.1 [CT-4NO3-HNO3]+ or [T-2NO3-HNO3]+; 980.0 [CT-4NO3]+ or [T-2NO3]+; 1082.0 [CT-3NO3-4HNO3]+; 1144.2 [CT-3NO3-3HNO3]+; 1266.0 [CT-3NO3-2HNO3]+; 1327.9 [CT-3NO3]+) indicated that [(tmeda)Pd(L)]3(NO3)6 coexists as a mixture of T and CT in water (Supporting Information: mass of [(tmeda)Pd(L)]3(NO3)6 and [en(Pd(L)]3(NO3)6). The anion exchange of [(tmeda)Pd(L)]3(NO3)6 with PF6 was attempted to identify the product, but unfortunately afforded only a cyclodimer, [(tmeda)Pd(L)]2(PF6)4 (Supporting Information: CCDC No.: 684329; Fig. S3). That is, the counterions play important role in the formation of the present labile metallacyclization. Of course, the aromatic 1H NMR of [(tmeda)Pd(L)]3(NO3)6 is significantly different form that of [(tmeda)Pd(L)]2(PF6)4 in acetone (Supporting Information), indicating that [(tmeda)-Pd(L)]3(NO3)6 is cyclotrimer rather than cyclodimer in the solution.

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(NO3)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-frozen 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. Even though the
mechanism of hydrogelation is not clear at this stage, electrostatic interaction through NO₃⁻ 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 hydrogels. 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, but the T species is unprecedented in the catenation. Indeed, the most significant difference between D and T, as established by the ¹H NMR spectra, may be ascribed to the molecular motion. That is, CD is rigid whereas CT is fluorescent 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 hydrophobic NO₃⁻, electrostatic interaction, and the fluxional motion. Another important factor in both catenation and hydrogelation is solvent effects. T in a mixture of D₂O and MeOH-d₄ 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 complex molecules 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 complex molecules 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 °C 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.

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Supporting Information. FAB mass data of [(en)Pd(L)]³⁺(NO₃)₆ (Fig. S1) and [(tmeda)Pd(L)]³⁺(NO₃)₆ (Fig. S2); X-ray crystal structure of [(tmeda)Pd(L)]²⁺(PF₆)₄ (Fig. S3); ¹H NMR of [(tmeda)Pd(L)]³⁺(NO₃)₆ (a) and [(tmeda)Pd(L)]³⁺(PF₆)₄ (b) in aceton-d₆ (Fig. S4); ¹H NMR spectra of [(tmeda)Pd(L)]³⁺(NO₃)₆ along with addition of NaNO₃ (Fig. S5). Crystallographic data for [(tmeda)Pd(L)]²⁺(PF₆)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.

References