

# Self-Assembly of [2]Catenanes Containing Metals in Their Backbones

MAKOTO FUJITA<sup>†</sup>

Coordination Chemistry Laboratories, Institute for Molecular Science, Myodaiji, Okazaki 444, Japan

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## Introduction

Linked or not linked? Chemists have been asking themselves this question when they consider chainlike molecules composed of two rings which are not linked chemically but nevertheless cannot be separated from each other.<sup>1</sup> Such molecules are termed catenanes<sup>1,2</sup> (*catena* = chain in Latin) and have long intrigued chemists not only because of their unique structures but also as a result of their potential, explored recently, as molecular-scale devices.<sup>3</sup>

Earlier catenane syntheses were based on statistical methods. For example, Wassermann's first catenane synthesis<sup>4</sup> was achieved through the statistical threading of a macrocycle onto a molecular thread followed by ring closure. A nonstatistical catenane synthesis was first developed in 1983 by Sauvage, who employed molecular assembly around a Cu(I) template for achieving a high-yield synthesis of a catenane.<sup>5</sup> Another approach, using organic templating, was developed by Stoddart in 1989, who showed that an organic rectangular molecular box containing quaternary alkylated 4,4'-bipyridine has a remarkable ability to bind  $\pi$ -electron-rich aromatic systems through efficient aromatic contact.<sup>6</sup> This principle was successfully applied to a high-yield synthesis of a catenane.<sup>7</sup> More recently, amide hydrogen bonds were shown to template catenane formation effectively.<sup>8–11</sup> While the methods disclosed above afforded wholly organic catenanes, an inorganic catenane involving carbon–magnesium bonds was first reported in 1993.<sup>12</sup> However, this Grignard catenane was not isolated because of its instability, and the structure was deduced from NMR spectroscopy only.

In 1994, we encountered a novel formation of a [2]catenane during a study on the metal-directed self-assembly of coordination macrocycles.<sup>13</sup> Whereas previous catenane syntheses have taken a synthetic step of the threading of a ring onto a thread, followed by linking the

ends of the thread, our approach involves the self-assembly of catenanes from two preformed molecular rings as shown in Scheme 1. In this Account, we describe our recent studies on self-assembling catenanes incorporating transition metals in their backbones.<sup>14</sup> The discussion will be focused on the rational design, self-assembly, mechanistic aspects, and chemical manipulations of the transition metal-linked catenanes.

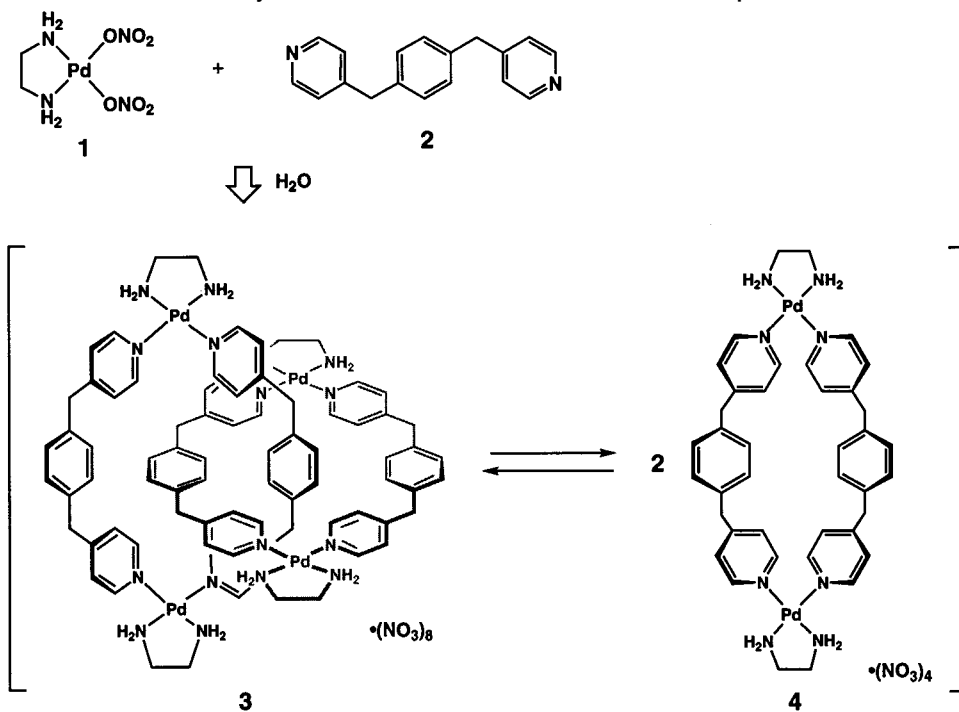
## Spontaneous Generation of a Catenane from Two Preformed Rings: Molecular Magic Rings

In biological systems, DNA large rings are frequently catenated and topoisomerase II catalyzes the dissociation and catenation of DNA rings. Recently, a biological method by the use of DNA ligase to close DNA rings was applied to a quite unique approach to a family of topologically interesting systems (e.g., cube, octahedron, and Borromean rings).<sup>15</sup> It seems quite difficult to mimic such a biological transformation in an artificial system. However, we found that the [2]catenane **3** and its component macrocycle **4** self-assembled by just combining Pd(NO<sub>3</sub>)<sub>2</sub>(en) (**1**) and the pyridine-based bridging ligand **2** in an aqueous solution (Scheme 1). Since the pyridine–Pd(II) coordinate bond forms reversibly, we observed a rapid equilibrium between these two species. Due to the presence of this equilibrium, the ratio between the catenane **3** and the monomer macrocycle **4** could be controlled by simply adjusting the concentration of the species. At higher concentrations, the ratio shifts so that two molecules produce one molecule according to the Le Chatelier principle and the catenane **3** becomes the overwhelmingly dominant species above 50 mM concentration (Scheme 1). The NMR spectrum (Figure 1) of **3** is characteristic of the catenane structure: two inequivalent PyCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Py units are observed which are assignable to the inside and outside units of **3**; the inside phenylene protons are markedly high-field-shifted, appearing at  $\delta = 5.3$  ppm because of facing the aromatic rings of another ring. In addition to satisfactory NMR data, the electrospray ionization mass spectrum (ESI-MS) also supported the molecular weight of **3**. Finally, the solid structure of **3** was confirmed by the X-ray crystallographic analysis (Figure 2) of the platinum analogue **5**.<sup>16</sup>

We suggest that the self-assembly of the catenane **3** is explained in terms of a *double-molecular recognition* process in which two molecules of **4** bind each other in their cavities. Such a process produces approximately double the magnitude of  $\Delta G$ , making the structure of **3** stable enough to assemble quantitatively at high concentrations. This interpretation is consistent with a remarkable medium effect that enables the modulation of the equilibrium ratio **3**:**4** in the range of >99:1 to <1:99 (Table 1). Thus, the employment of a more polar medium (D<sub>2</sub>O solution of NaNO<sub>3</sub>) increased the ratio of **3** up to >99% even at low concentrations because of enhanced hydrophobic interactions accompanying the catenane formation

Makoto Fujita is Associate Professor at the Institute for Molecular Science (IMS) in Okazaki, Japan. He received his Ph.D. degree from the Tokyo Institute of Technology in 1987, started his career in 1988 at Chiba University, and moved to his current position in 1997. He is a recipient of the Progress Award in Synthetic Organic Chemistry, Japan, and is currently a leader of the CREST (Core Research for Evolutional Science and Technology) project of the Japan Science and Technology Corporation. His research interests include the self-assembly of metal-linked nanostructures (macrocycles, cages, catenanes, networks, etc.) and their functionalization.

<sup>†</sup> E-mail: mfujita@ims.ac.jp. Fax: 81-564-55-5245. Phone: +81-564-55-7250.

Scheme 1. Self-Assembly of [2]Catenane 3: Concentration Effects on the Equilibrium Ratio of 3:4<sup>a</sup>

|                         |              |          |               |
|-------------------------|--------------|----------|---------------|
| <b>1 mM<sup>b</sup></b> | <b>&lt;1</b> | <b>:</b> | <b>&gt;99</b> |
| <b>2 mM</b>             | <b>11</b>    | <b>:</b> | <b>89</b>     |
| <b>5 mM</b>             | <b>38</b>    | <b>:</b> | <b>62</b>     |
| <b>10 mM</b>            | <b>59</b>    | <b>:</b> | <b>41</b>     |
| <b>20 mM</b>            | <b>75</b>    | <b>:</b> | <b>25</b>     |
| <b>50 mM</b>            | <b>91</b>    | <b>:</b> | <b>9</b>      |

<sup>a</sup> Measured in D<sub>2</sub>O at room temperature. <sup>b</sup> Net concentration of Pd(II).

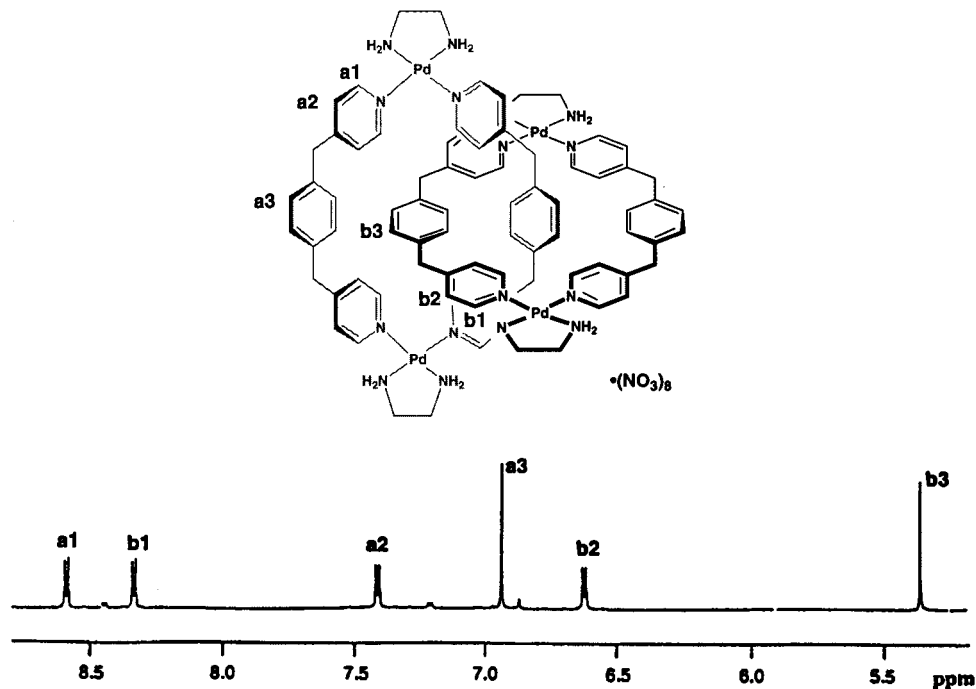


FIGURE 1. <sup>1</sup>H NMR (aromatic region) of the catenane 3.

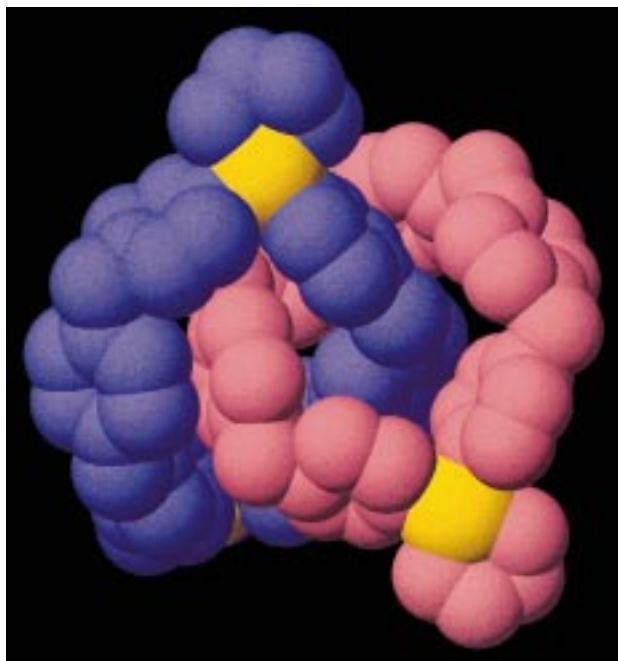


FIGURE 2. X-ray crystal structure of the catenane 5.

**Table 1. Medium Effects on the Equilibrium Ratio of 3 and 4<sup>a</sup>**

| medium                                     | guestb/mol equiv | 3:4     |
|--|------------------|---------|
| 1.0 M NaNO <sub>3</sub> /D <sub>2</sub> O  |                  | >99: <1 |
| 0.2 M NaNO <sub>3</sub> /D <sub>2</sub> O  |                  | 95:5    |
| 0.05 M NaNO <sub>3</sub> /D <sub>2</sub> O |                  | 86:14   |
| D <sub>2</sub> O                           |                  | 59:41   |
| D <sub>2</sub> O                           | 0.5              | 27:73   |
| D <sub>2</sub> O                           | 2.0              | 12:88   |
| D <sub>2</sub> O-CD <sub>3</sub> OD (7:3)  |                  | 9:91    |
| D <sub>2</sub> O-CD <sub>3</sub> OD (5:5)  |                  | <1: >99 |

<sup>a</sup> Measured at 10 mM, room temperature. <sup>b</sup> Sodium *p*-methoxyphenylacetate.

(runs 1–3). In contrast, the ratio of 3 diminishes in a less polar medium (CD<sub>3</sub>OD–D<sub>2</sub>O, runs 7 and 8). Selective stabilization of 4 by adding sodium (*p*-methoxyphenyl)acetate, a specific guest for 4, also reduces the ratio 3:4.

### Designer Catenanes: Quantitative Formation of Catenanes from Rectangular Molecular Boxes

As discussed above, the driving force for the self-assembly of catenane 3 is the efficient aromatic contact between the two monomer rings. Therefore, we designed a rectangular molecular box 6 containing Pd(II)–pyridine co-

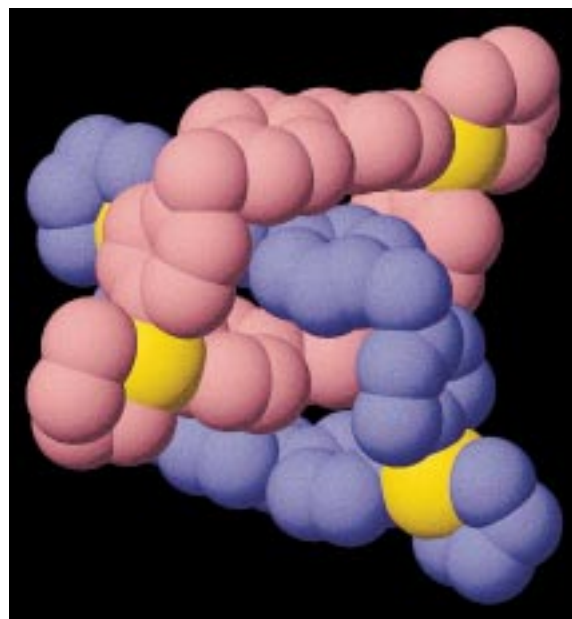
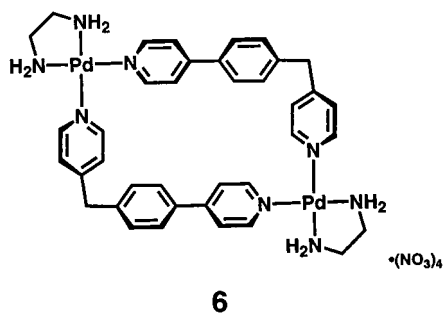
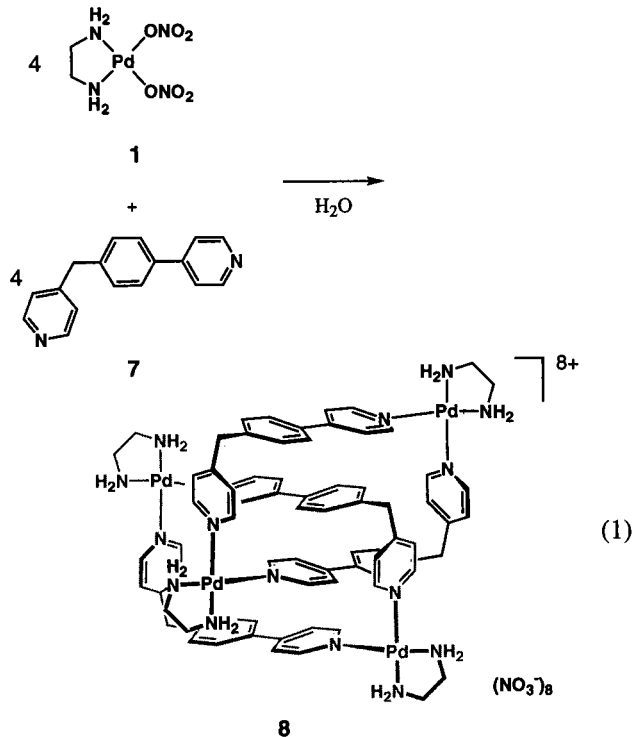


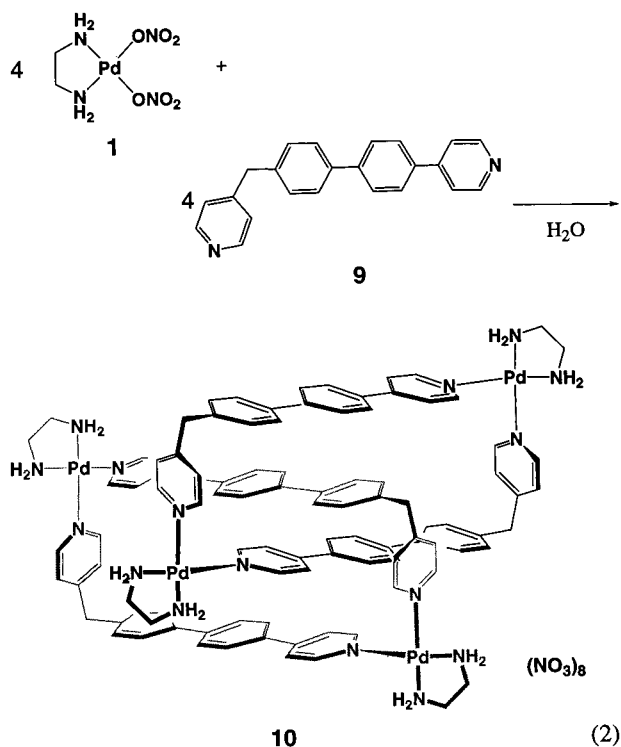
FIGURE 3. X-ray crystal structure of the catenane 8.

ordination bonds. A force field calculation predicted that this box would have an appropriate interplanar separation (ca. 3.5 Å) in the cavity. Therefore, two molecules of the inorganic box 6 are expected to be linked to a catenane dimer. In fact, when 1 and the ligand 7 were combined, we observed the formation of a single component which could be assigned to the catenane 8 (eq 1).<sup>17</sup>



The structure of 8 was determined by an X-ray diffraction study (Figure 3), as well as by careful examination of NMR spectra and ESI-MS.<sup>18</sup> From the crystal structure, we note the very efficient stacking of four aromatic rings, a feature that stabilizes the catenane structure signifi-

cantly. In fact, the stability of **8** in a solution is remarkable. The dissociation of the catenane into component rings is not observed, even at low concentration or in a less polar medium ( $D_2O-CD_3OD$ , 1:1). It is noteworthy that the observation of the molecular weight of **8** by ESI-MS shows that the catenane is still stable at MS concentrations ( $<0.1$  mM). The structure of the catenane **8** is such that it exhibits topological chirality:<sup>19</sup> i.e., the clockwise and anticlockwise interlocking of the second rings onto the first ring gives rise to the enantiomers of **8**. Due to this chirality, otherwise equivalent pairs of protons on the same aromatic rings became nonequivalent. The observation of topological chirality is reliable evidence for the solution structure of the catenane. The crystal structure also shows that the catenane framework is very tight. However, we expanded the cavity successfully by inserting an additional phenylene ring into the ligand framework. Thus, we observed the quantitative self-assembly of a relatively flexible catenane **10** from **1** and the ligand **9** (eq 2).<sup>20</sup> Again, an interplanar separation of ca. 3.5 Å seems essential to afford an efficient stacking of the four aromatic systems in the catenated structure.



### Selective Formation of Catenanes from Three Species—Eight Components

We have also achieved the self-assembly of a catenane in a three-species–eight-component system. Three compounds, namely **1**, **11**, and **12**, present in aqueous solution in a 2:1:1 stoichiometry self-assemble quantitatively into the catenane **13**, which can be isolated in a very high yield (94%) as a pure form (eq 3). The structure of **13** was confirmed by X-ray analysis (Figure 4), ESI-MS, and NMR spectroscopies, which also showed that the catenane

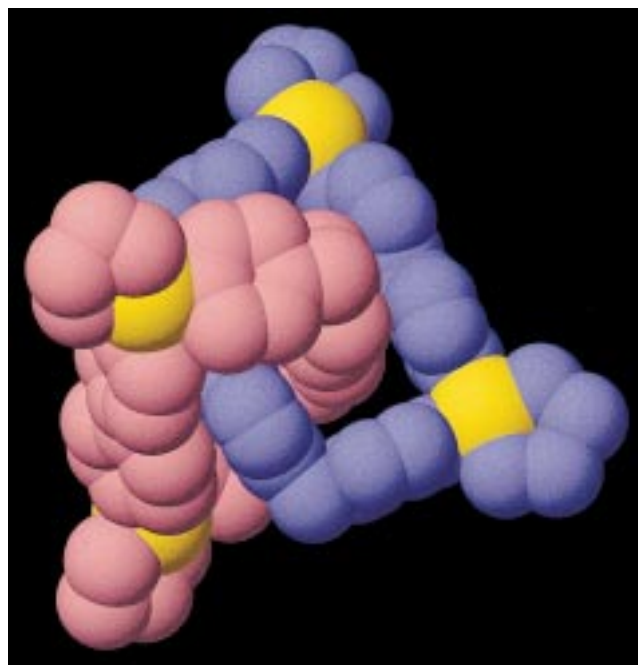
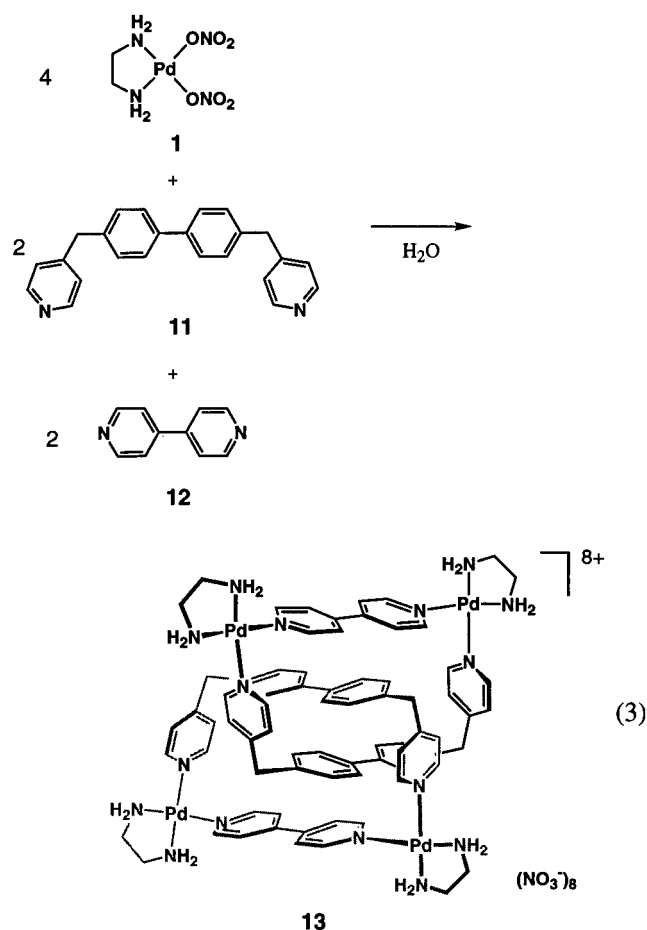


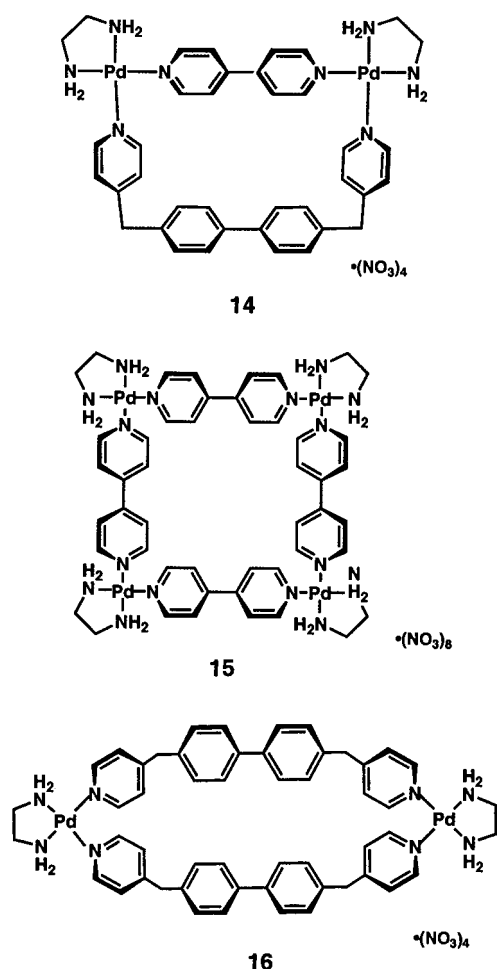
FIGURE 4. X-ray crystal structure of the catenane **13**.

consisted of only one isomer both in the solution and in the solid.



It is noteworthy that the remarkable thermodynamic stability of the catenane **13** overcomes the combination problem which arises in the self-assembly of larger sets

of components.<sup>21</sup> At least, the formation of three-component macrocycles **14**–**16** is possible because their

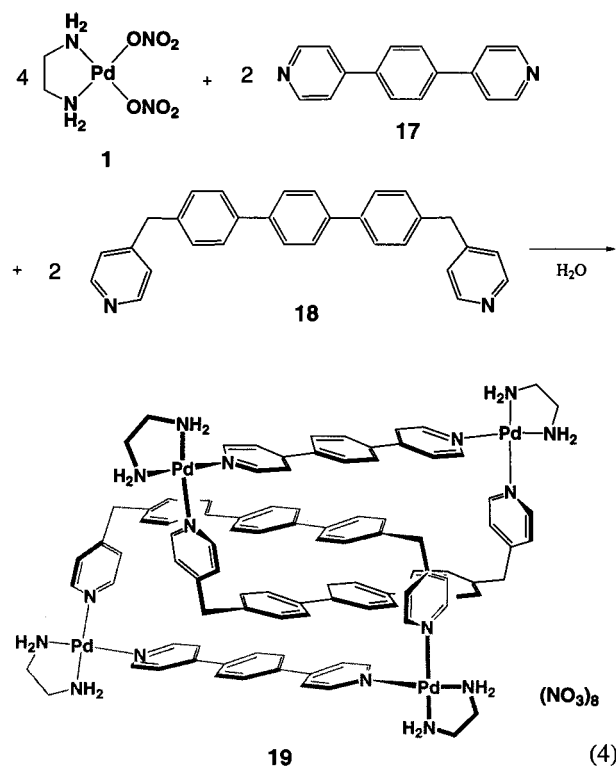


thermodynamic stability is comparable. Nevertheless, the catenane **13** self-assembles as the sole product. This result shows that, having an ideal van der Waals separation (3.5 Å) in its framework, only the rectangular box **14** can be stabilized by filling its own cavity with another copy of itself.

The more flexible, expanded catenane **19** was obtained in a quantitative yield through self-assembly of **1** with the ligands **17** and **18** (eq 4). The structure was deduced from an ESI-MS study.<sup>20</sup>

### Prediction of the Self-Assembly of Catenanes by Force Field Calculations

Since self-assembly proceeds under thermodynamically controlled conditions, we can predict approximately the self-assembly of the catenanes from their component rings by force field calculations.<sup>20</sup> In addition to the ligands shown in the above sections, we also examined ligands **20** and **21** which are the methylene homologues of **2**; however, they did not self-assemble into catenanes upon treatment with **1**. The reason was clarified very easily from

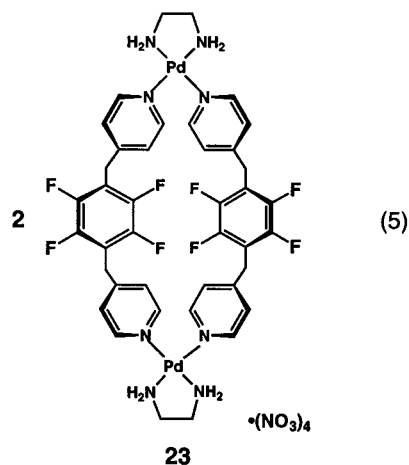
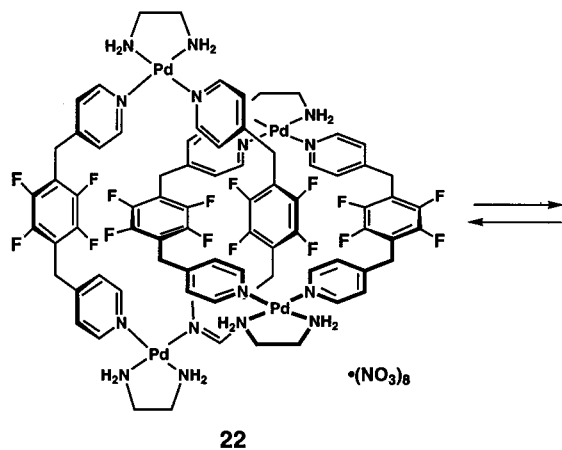


force field calculations, as shown in Table 2: we found that the coordination rings are catenated if the ring has an ideal interplane separation in their optimized conformations, whereas catenation does not take place if the macrocycles possess no voids in their cavities because of the flexibility of the ligands. These results also emphasize that the existence of an appropriate interplanar separation is essential to the self-assembly of catenanes.

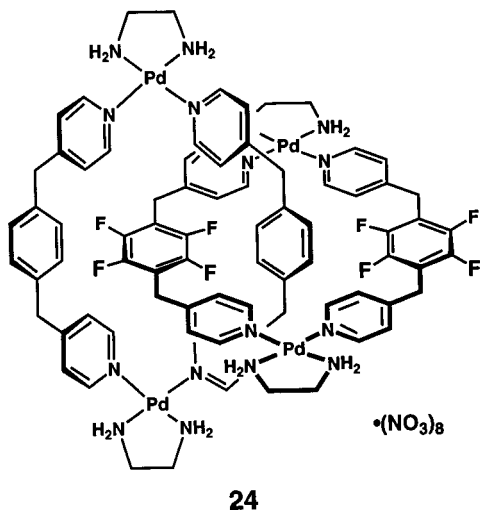
### Electronic Effects in the Self-Assembly of Catenanes

To study electronic interactions between the two rings of **3** in the catenation, its fluorinated analogue **22** was prepared. When we examined the complexation at higher concentrations, it was found that the fluorinated macrocycle **23** is also in equilibrium with the [2]catenane **22** though the equilibrium ratio tends to shift toward **23** (eq 5).<sup>22</sup> The ratios of **23** to **22** [mM/Pd] are as follows: >95: <5 [1]; 93:7 [2]; 84:16 [5]; 68:32 [10].

The catenane **3** is apparently more effectively assembled than **22**. For example, the catenane-to-monomer ratio at 10 mM/Pd was 59:41 for **3**:**4**, whereas it was 32:68 for **22**:**23**. This difference is most probably due to attractive edge-to-face or CH– $\pi$  interactions<sup>23</sup> present in the catenane **3**. In fact, such interactions are found in the crystal structure of a platinum incorporated catenane **5** (Figure 1): we can observe efficient edge-to-face aromatic contacts between two phenylene units or a phenylene and a pyridine ring. This interaction works effectively in the catenated structure of **3** whereas it does not operate in the structure of **22** which has no C–H bonds on the phenylene ring.



We also examined the selective formation of the mixed catenane **24** from three species, **1**, **2**, and  $\text{PyCH}_2\text{C}_6\text{F}_4\text{CH}_2\text{-Py}$ . However, there seemed to be no selectivity in the



formation of a special combination such as **24** possessing an alternative contact of  $\text{C}_6\text{H}_4$  and  $\text{C}_6\text{F}_4$  rings. The complete scrambling of two ligands shows that donor-acceptor type interactions are not important in this system.

### Mechanism of the Rapid Interconversion: Möbius Strip Mechanism

The equilibrium between the catenane **3** and the monomer ring **4** is so rapid that any attempts to observe the

transfer process from one to another have to date been unsuccessful. It is interesting, however, that careful mechanistic considerations of the rapid interconversion led us to propose a "Möbius strip mechanism",<sup>24</sup> which involves a molecular topology reminiscent of the well-known Möbius strip.<sup>25</sup>

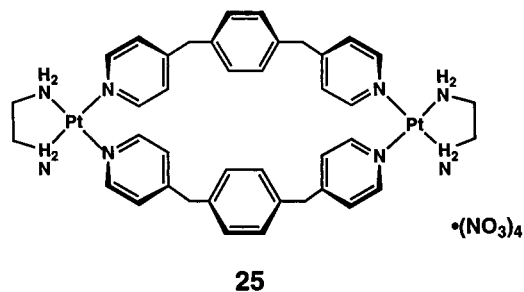
For the catenane formation in our system, the most reasonable explanation involves dissociation of a ring, threading another ring on the thread, and reconnection of the ends of the thread (Scheme 2a). However, the careful consideration of NMR spectra, as well as a few additional experiments, gave us the following two significant insights into the mechanism: (i) An intermediate must be involved in the interconversion between **3** and **4**. (ii) Reversible coordinative bonds must be involved in both rings. These facts strongly support an alternative Möbius strip mechanism that involves two sequential ligand exchanges between two molecular rings concomitant with a twisting of the rings around each other (Scheme 2b).<sup>24</sup>

### Irreversible Interlock of Molecular Rings

Catenane **3**, once formed, is quite apt to dissociate into two monomer rings because there is a rapid equilibrium between the catenane **3** and the monomer ring **4**. If the labile coordinative bond can be frozen after the catenane assembles, one could obtain a catenane that never dissociates into two rings.

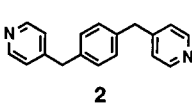
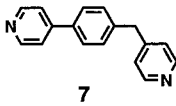
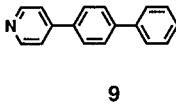
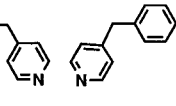
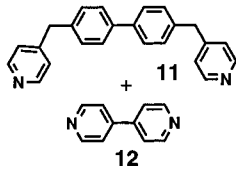


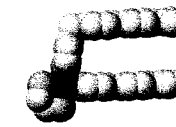


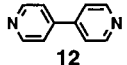
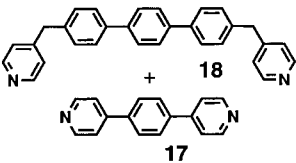
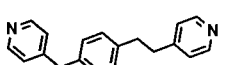
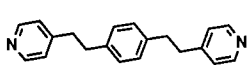
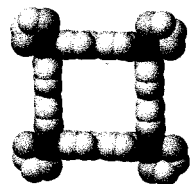
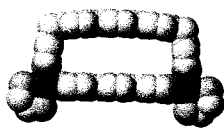


Such a one-way formation of a catenane was achieved in the analogous platinum(II) system by employing the concept of a "molecular lock", which exploits the dual character of a platinum(II)-pyridine (Pt(II)-Py) coordinative bond.<sup>16</sup> This bond can be likened to the lock since it is irreversible ("locked") under the ordinary conditions, but becomes reversible ("released") in highly polar media at elevated temperatures (Scheme 3). Incorporation of the molecular lock into a macrocyclic backbone makes it possible to interlock *irreversibly* two molecular rings according to the schematic sequence in Figure 5b. Initially, a molecular ring is on the lock (A). Then, the lock is released by adding a salt and heating (B) to allow the self-assembly of a catenated framework (C). Finally, this framework is locked by removing the salt and cooling (D).

Thus, sodium nitrate was added to an aqueous solution of the molecular ring **25**, and the solution was heated at 100 °C. Then, the equilibrium between **25** and its cat-

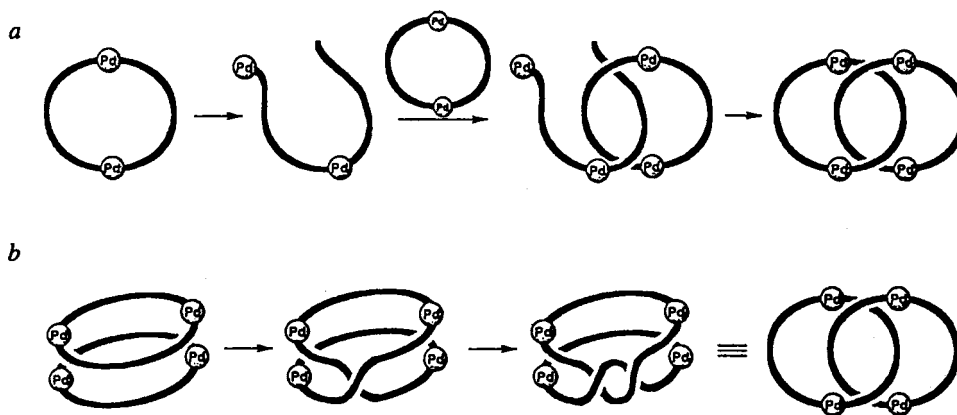


enated dimer **5** is directed by the polar media toward the catenane. After self-assembling in a high yield, catenane

Table 2. Prediction of the Catenane Formation Based on Force Field Calculation<sup>a</sup>

|            |   |   |  |   |   |
|------------|---|---|--|---|---|
| Ligand(s)  |  |  |   |   |  |
| macrocycle |  |  |   |   |  |
| cavity     | yes   | yes   | yes  | no  | yes   |
| catenation | yes   | yes   | yes  | no  | yes   |
| Ligand(s)  |  |  |  |  |   |
| macrocycle |  |  |  |  |   |
| cavity     | yes, but too large  | yes   | no   | no  |   |
| catenation | no  | yes   | no   | no  |   |

<sup>a</sup> MM2 parameters supplied by CAChe system (Ver. 3.5, Sony/Tektronix) were employed for the refinement.

Scheme 2. Possible Mechanisms for the Rapid Slippage of Two Molecular Rings: (a) a Conventional Mechanism; (b) a Transmetalation Mechanism<sup>a</sup>

<sup>a</sup> Note that these schemes present only the topology of the pathways. Thus, the second transmetalation in mechanism b may happen between any Pd–N bonds.

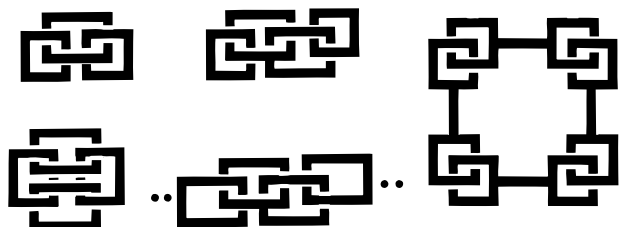


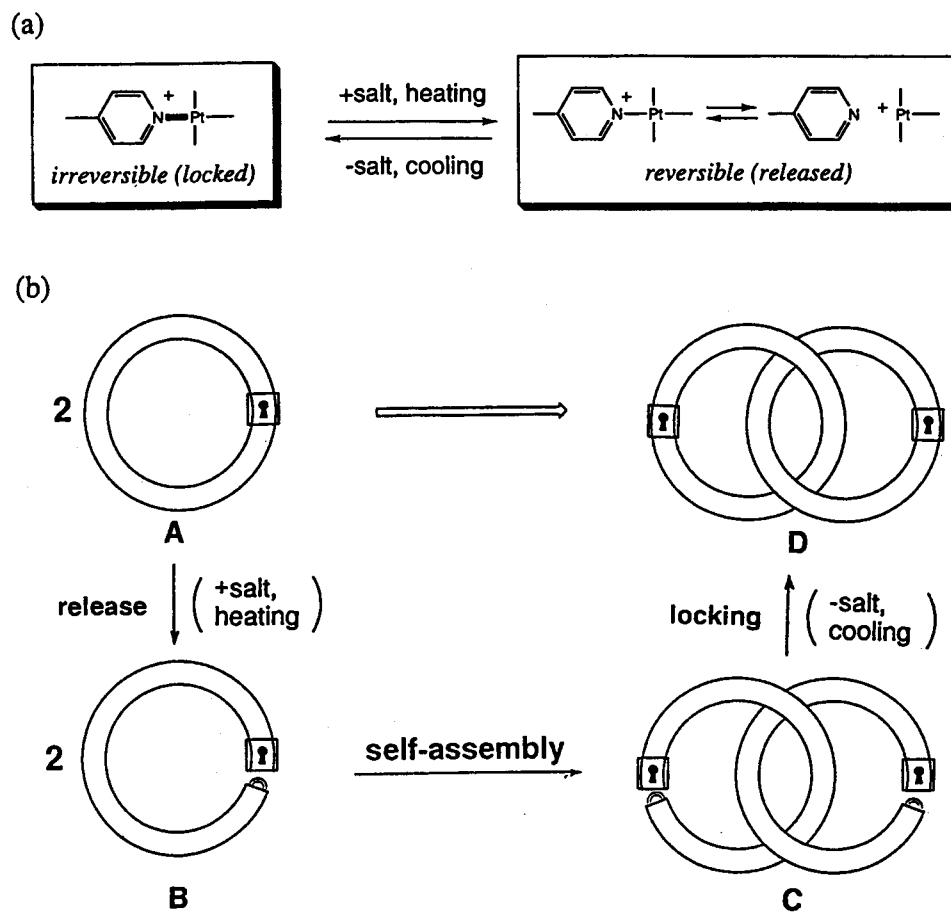
FIGURE 5. Schematic presentation of the construction of nanostructures by metal-directed catenation.

5 was isolated as the ClO<sub>4</sub> salt in a reasonable yield. It was confirmed that the catenane 5 thus obtained does not dissociate into two rings in aqueous solution because its framework has been locked.

### Conclusion and Perspective

In this Account, we have shown a very simple, designable, and highly efficient catenane synthesis through transition metal-directed self-assembly. Our results demonstrated

Scheme 3. Schematic Representation of a "Molecular Lock": (a) Dual Character of a Pt(II)–Py Coordinate Bond; (b) Irreversible Formation of a Catenane from Two Complete Rings by Using the Molecular Lock



that *catenanes can be thermodynamically more stable than monomer rings*. This very simple but remarkable principle has not been recognized during the past decades due to the lack of pathways from macrocycles to catenanes in covalent bond chemistry. However, the reversibility of coordinative bond formation enables macrocycles to be transformed into catenanes as a result of momentary bond cleavage. Thus, we have demonstrated the unique behavior of coordination rings in which two rings spontaneously interlock into catenanes. In this self-assembly strategy, it is remarkable that catenane formation is controlled only by the thermodynamics of the system: we need not consider the reaction conditions or the order of events in the synthesis, but should only design catenane frameworks so that large stabilization can be achieved by weak interactions. Such thermodynamic aspects can be roughly estimated by simple force field calculations. Therefore, we can predict the self-assembly of catenanes by modeling and molecular mechanics calculations.

Future applications of the metal-directed assembly of catenanes should also be considered. Current interests in the application of catenanes are focused on their dynamic motion,<sup>26,27</sup> functionalization,<sup>28</sup> and applications to multi-ring systems.<sup>29–31</sup> In addition, the self-assembly of catenane may be applicable to nanotechnology. Nowadays, extensive studies have begun on the construction of nanoscale molecules, in both chemistry and physics.<sup>31</sup>

One of the most efficient ways to construct nanostructures is to interconnect molecular building blocks. We propose that large building blocks with metal-containing ring portions are easily linked together by catenation to give nanoscale structures. Toward this goal, we are currently investigating the construction of nanostructures such as those schematically shown in Figure 5 as a result of the self-assembly of catenated frameworks.

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