

Transition-metal-directed assembly of well-defined organic architectures possessing large voids: from macrocycles to [2]catenanes

Makoto Fujita, Katsuyuki Ogura

Department of Applied Chemistry, Faculty of Engineering, Chiba University, 1-33 Yayoicho, Inageku, Chiba 263, Japan

Received 8 February 1995; in revised form 19 July 1995

Contents

Abstract	249
1. Introduction	250
2. Spontaneous self-assembly of macrocyclic polynuclear complexes	251
2.1. Macrocyclic tetranuclear group 10 metal (Ni(II), Pd(II), Pt(II)) complexes	251
2.2. Macrocyclic dinuclear Pd(II) complexes	254
2.3. Ability of macrocyclic Pd(II) complexes for molecular recognition	255
3. Guest-induced assembly of a 3-D Pd(II) trinuclear complex: induced-fit molecular recognition	256
4. Quantitative self-assembly of [2]catenanes	258
4.1. Synthesis, structure, and thermodynamic behavior of [2]catenanes	258
4.2. Irreversible formation of catenane from two molecular rings	260
5. Future outlook	262
Acknowledgments	262
References	263

Abstract

This paper discloses coordination approaches to well-defined organic structures including macrocycles, a three-dimensional cage-like compound, and [2]catenanes. These supramolecules self-assembled from (en)Pd(NO₃)₂ (**1**, en = ethylenediamine) and appropriate polypyridyl-substituted ligands. Treatment of **1** with 4,4'-bipyridine (**2**), for example, gave the macrocyclic tetranuclear Pd(II) complex [(en)Pd(μ-**2**)]₄(NO₃)₈ quantitatively, while macrocyclic dinuclear Pd(II) complexes were assembled from **1** and flexible ligands such as PyCH₂CH₂Py (Py = 4-pyridyl). From the tridentate ligand 1,3,5-(PyCH₂)₃C₆H₃ and **1** in 2:3 ratio, however, a three-dimensional cage-like compound was assembled in high yields only in the presence of certain types of guest molecules, providing an entire model for 'induced-fit.' The coordination approach made it possible to interlock two apparently continuous molecular rings: i.e. a macrocycle assembled from **1** and 1,4-(PyCH₂)₂C₆H₄ was found to exist in equilibrium with

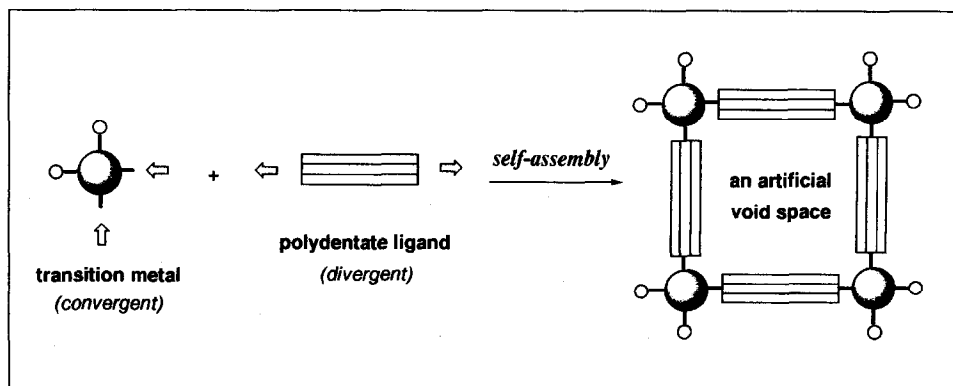
its catenated dimer, and a polar medium strongly pushed the equilibrium toward the catenane up to a greater than 99:1 ratio.

Keywords: Self-assembly; Supramolecules; Macrocycles; Catenanes; Cage compounds; Palladium complexes

1. Introduction

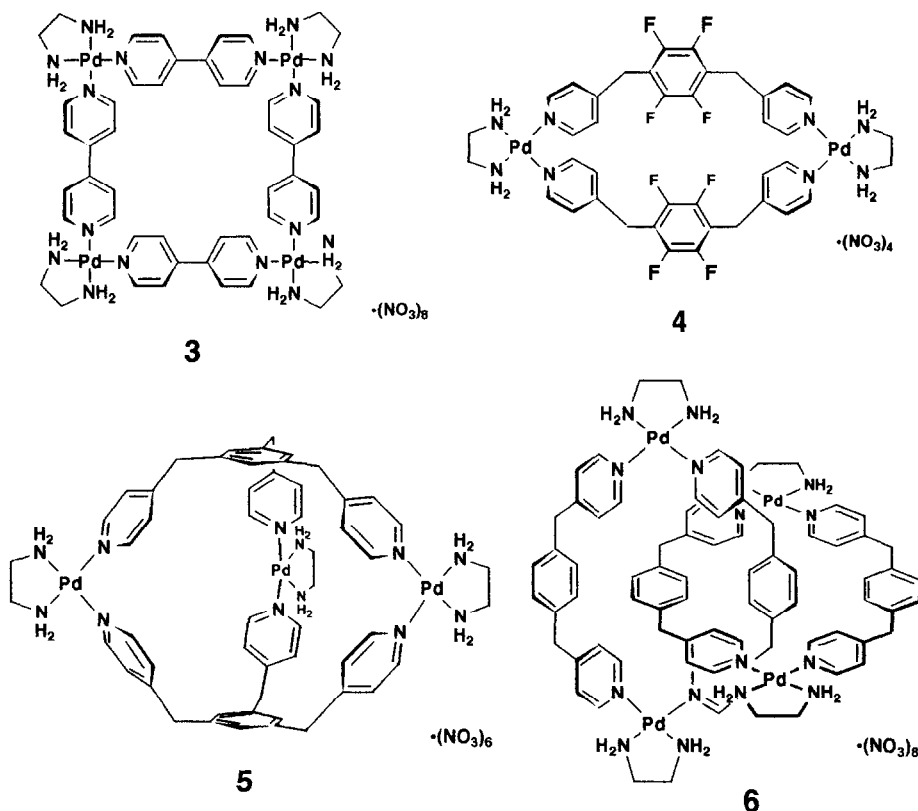
Supramolecular self-assembly [1] through metal-coordination has recently shown remarkable potential for the construction of well-defined architectures such as helices [2,3], grids [4], boxes [5], rods [6], tubes [7], and so on [8]. Since 1990, we have been studying the self-assembly of macrocyclic and related structures and their supramolecular functions [9]. Despite the remarkable potential utility [10], the common use of macrocycles in organic chemistry has been extremely limited, mainly due to difficulties encountered in their synthesis. If macrocycles themselves were accessible via a self-assembly process, the synthetic problem would be solved; this idea prompted us to study the supramolecular assembly of macrocycles. Prior to this study, several macrocyclic complexes containing transition metals in their backbones have been reported [11,12]. For example, Shaw and others reported the formation of macrocyclic iridium(I), platinum(II), and palladium(II) complexes [11]. However, these complexes are not designed as host compounds, and thus no binding data were reported so far for these complexes. More recently, Maverick et al. prepared macrocyclic dinuclear complexes composed of Cu(II) and a bridging ligand having two bis(β -diketone) coordination sites and an aromatic spacer [12]. When the aromatic spacer is a 1,7-naphthyl, the macrocycle selectively recognized DABCO in the cavity [13,14].

Our basic concept for the transition metal-based assembly of macrocycles is shown in Scheme 1. Coordination of divergent bridged ligands on protected transition metals gives rise to the self-assembly of closed molecules as a result of thermodynamic equilibration. Along with this concept, we have already prepared macrocyclic tetra-



Scheme 1: The basic concept of the present study.

and dinuclear complexes such as **3** and **4** [9], a three-dimensional (3-D) cage (**5**) [15], and [2]catenanes (**6**) [16]. This strategy is characterized by the use of protected transition metal (en)Pd²⁺ (en = ethylenediamine) on which pyridine-based, very simple ligands are converged at an included right angle. This feature makes our strategy contrast strikingly with the general strategy of metal-directed assembly, in which naked and divergent metals are combined with more complicated convergent ligands containing, e.g. 2,2'-bpy (bpy = bipyridyl) or acetylacetonate units.

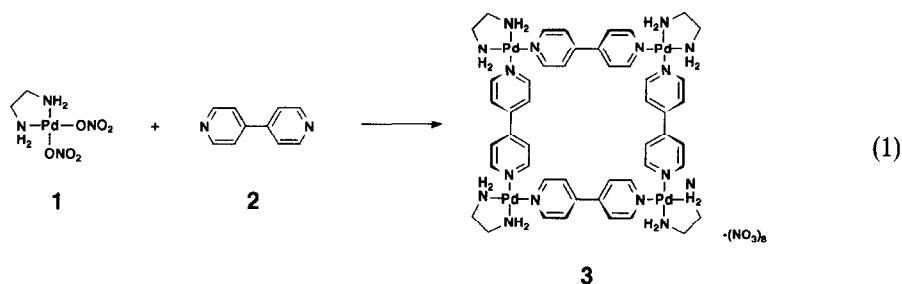


2. Spontaneous self-assembly of macrocyclic polynuclear complexes

2.1. Macrocyclic tetranuclear group 10 metal (Ni(II), Pd(II), Pt(II)) complexes

According to the concept shown in Scheme 1, we designed and first synthesized the macrocyclic tetranuclear complex $[(\text{en})\text{Pd}(4, 4'\text{-bpy})]_4(\text{NO}_3)_8$ (**3**) [9a]. This compound was obtained by a very simple procedure: mixing of the cis-protected Pd(II) complex $(\text{en})\text{Pd}(\text{NO}_3)_2$ (**1**) and an equivalent molar amount of 4,4'-bpy in ethanol–water at room temperature followed by addition of ethanol precipitated pure **3** as a pale yellow powder (NMR yield: 100%; isolated yield: 91%, Eq. (1)).

The structural determination of **3** was based on ^1H and ^{13}C NMR, electrospray mass spectroscopy, and elemental analysis. Related tetranuclear macrocycles having protected Pd(II) or Pt(II) at every corner have been reported recently [17].



It is clear that the macrocycle assembles under thermodynamic control because the Pd(II)–pyridine coordinate bond is reversible. Thus, as far as the ratio of **1** to **2** was kept at 1:1, macrocycle **3** assembled quantitatively regardless of the reaction conditions (concentration, temperature, or order of the addition of the components). The thermodynamic stability of **3** is interpreted in terms of ‘complementary molecular recognition’ among eight components (four Pd(II) plus four bpy units). Namely, each bpy molecule or (en)Pd unit is recognized by an ideal recognition-site formed by the remaining seven components.

The behavior of platinum(II) in the macrocyclization of an analogous Pt(II) system was quite different from those of the palladium(II) system [9b]. In contrast to the Pd(II) complex, treatment of (en)Pt(NO₃)₂ (**7**) with 4,4'-bpy did not give the desired macrocycle **8** but afforded an intractable mixture of oligomeric products (Fig. 1(a)). As ligand dissociation (or substitution) on platinum is much slower than that on palladium [18], this undesirable result is explained by the formation of kinetically distributed products. On heating the mixture at 100 °C, however, the spectrum became simpler and converged to that of **8** (Figs. 1(b), 1(c)). This spectral change is attributable to the conversion of the kinetic products to the thermodynamic products. After the conversion was almost complete, **8** was isolated as a pure material (81%). In our initial experiment, more than 4 weeks were required to give **8** as an

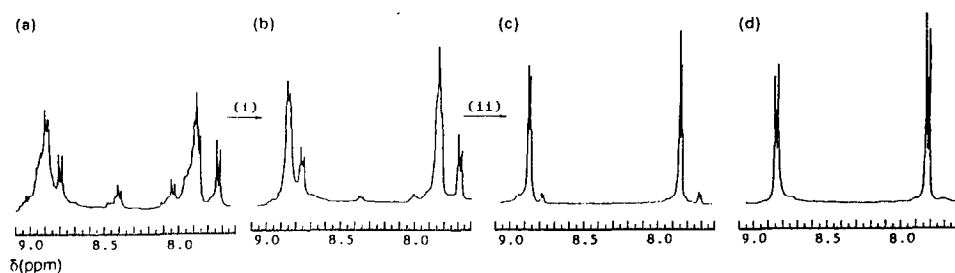
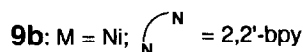
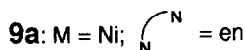
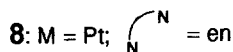
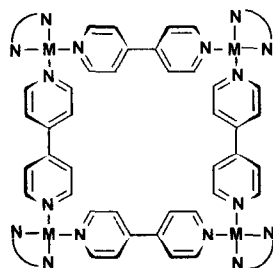


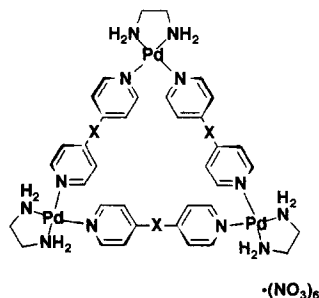
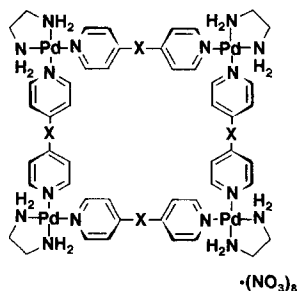
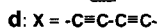
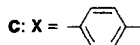
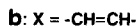
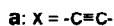
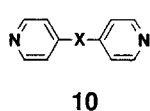
Fig. 1. (a)–(c) Spectroscopic observation of the assembly of **9**. Conditions are as follows: (i) room temperature, 1 week; then 100 °C, 1 week; (ii) 100 °C, 4 weeks. (d) The spectrum of **9** after isolation.

almost pure component. However, the reaction period could be reduced by the employment of 4,4'-bpy·2HNO₃ instead of 4,4'-bpy itself or by the addition of NaNO₃ (1–5 M), and the convergence to **8** at 100 °C was respectively completed within a week or even a day. In the supramolecular self-assembly, there are few examples of the monitoring of the assembly process because the equilibrium in the metal-directed assembly is usually very rapid. In our experiment, however, the dynamic assembling process was successfully observed.

Results using (en)Ni²⁺ were quite comparable with those using (en)Pd²⁺, although NMR data could not be obtained owing to the paramagnetic property of Ni(II) ions. Thus, treatment of [(diamine)Ni(H₂O)₂]SO₄·2H₂O (diamine=en or 2,2'-bpy) with 4,4'-bpy (1–2 mol equiv) in methanol at room temperature afforded a pale blue powder (86% and 90% respectively) whose elemental analysis was consistent with the formula of **9**. The structure of these products must be terminated or cyclized because the composition of the products was reproducible regardless of the amount of 4,4'-bpy employed in these reactions (1–2 mol equiv), implying the quantitative self-assembly of **9**.

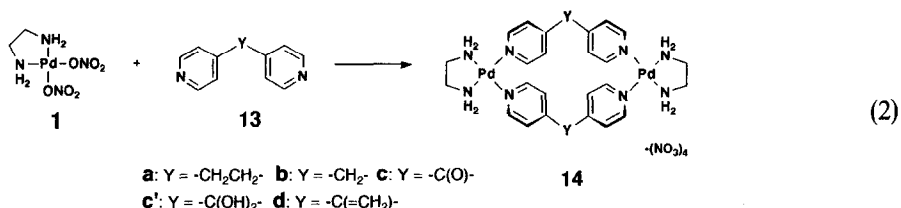


Analogs of **3** with larger voids were accessible from ligands **10a–d**. However, the assembly of **11** was accompanied by the formation of a by-product that is most probably assigned as cyclic trimer **12** because it also has the same composition ((en)Pd(II):ligand=1:1) and qualitatively showed the same NMR as **11**. Though less favored in enthalpy, trimer **12** is more favored in entropy because it assembles from fewer components. As **11** and **12** are under thermodynamic equilibration, the ratio of **11** to **12** increased with increasing concentration. For example, the ratios **11a**:**12a** (net Pd(II) concentration (mM)) are as follows: 92:8 (80), 89:11 (40), 87:13 (20), 82:18 (8).



2.2. Macrocyclic dinuclear Pd(II) complexes

Besides tetranuclear macrocyclic complexes, a variety of mono-, di-, and trinuclear macrocycles have been reported during the recent years [13]. Nevertheless, protected transition metals such as **1** have never been examined for the assembly of these complexes. Thus, we next examined the combination of **1** and flexible bidentate ligands **13a–c**. Contrary to our anticipation that flexible components would give linear oligomers, we observed the self-assembly of dinuclear Pd(II) complexes **14a**, **14b** and **14c'** (Eq. (2)) [9d,f]. The structures of **14a** and **14c'** (ClO₄ salt) were determined by crystallography (Figs. 2 and 3) while that of **14b** was deduced from FABMS and NMR.



The structure of **14c'** is quite unique because diaryl ketone ligand **13c** is hydrated on complexation. The appearance of a quaternary carbon at the expense of a carbonyl carbon in ¹³C NMR showed that this macrocycle also existed in solution as the hydrated form. Thus, reduction of an sp² angle at the carbonyl to an sp³ angle by hydration is probably essential to the assembly of **14c'**, otherwise significant ring strain arises in the cyclic structure. In fact, ligand **13d**, whose Py-C(sp²)-Py angle

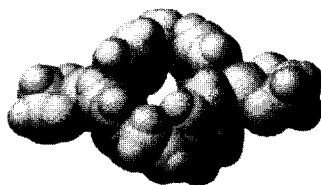


Fig. 2. Crystal structure of **14a**. (NO₃⁻ omitted.)

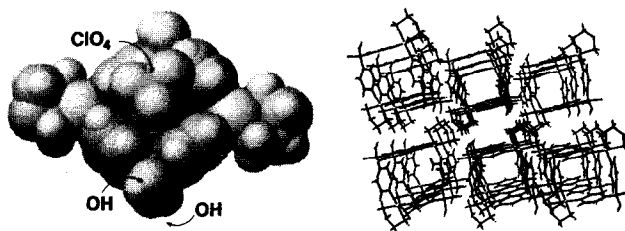
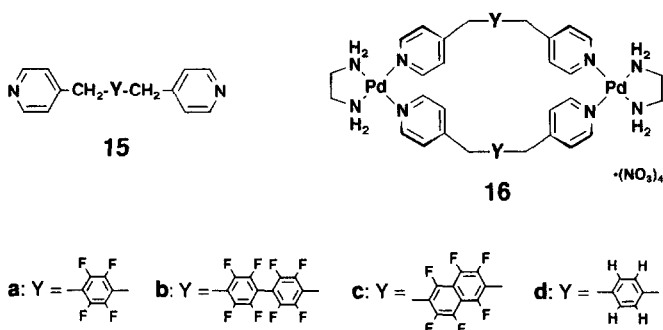


Fig. 3. Left: molecular structure of **14c'** (ClO₄ salt, ClO₄ omitted). Right: crystal packing of **14c'** (ClO₄ salt). Only macrocyclic frameworks are shown.

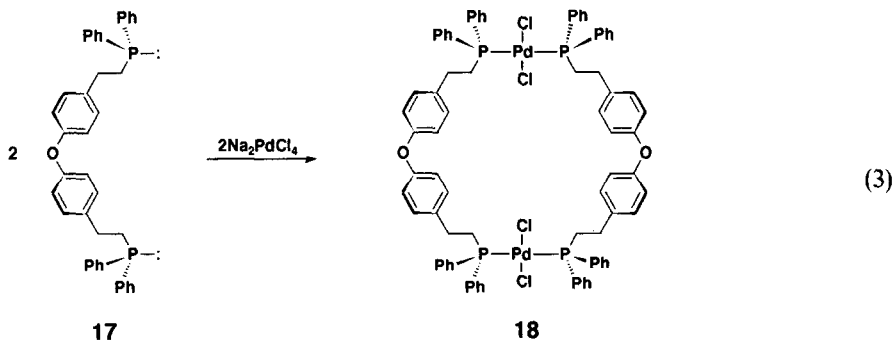
(Py = 4-pyridyl) does not vary, gave a mixture of corresponding dimeric and trimeric macrocycles.

Besides unusual hydration, the crystallography suggested the potential ability of **14c'** for molecular recognition of small (anionic) molecules because two ClO_4^- ions are clathrated above and below the cavity. Microchannels observed in the crystal packing are also worth noting (Fig. 3).

To expand and functionalize the cavity, ligands having fluorinated aromatic rings **15a–c** were examined. Again, we observed the self-assembly of the dinuclear Pd(II) macrocycle **16a–c** (**16a** = **4**) [9d,f]. The yield of **16a** was quantitative. In contrast, **16b** and **16c** were shown to exist in equilibrium with linear oligomers though the equilibrium ratio could be shifted overwhelmingly toward the macrocycles by diluting the solution or replacing an aqueous solvent with methanol. The structures of **15** and **16** were determined based on satisfactory FABMS, NMR, and elemental analysis.



Macrocyclic dinuclear Pd(II)–diphosphine complex **18** also assembled in a high yield from diphosphine ligand **17** and Na_2PdCl_4 (Eq. (3)) [9e].



2.3. Ability of macrocyclic Pd(II) complexes for molecular recognition

Some of the macrocycles discussed above have voids large enough to accommodate organic molecules therein. In fact, we observed their remarkable ability for molecular recognition in aqueous media. Table 1 summarizes the association constants for various neutral guests and our macrocycles [9c,d,f]. Some binding data of other self-assembling hosts have been reported.

Table 1

Association constants (1 mol^{-1}) between various neutral guests and various hosts (25°C , D_2O)

Guest	3	8	11b	16a	16b	16d
1,3,5-Trimethoxybenzene	750		420	2500		
<i>p</i> -Dimethoxybenzene	330	260	130	2680	96	201
<i>m</i> -Dimethoxybenzene	580	550		1560		
<i>o</i> -Dimethoxybenzene	30	20		1300		
<i>p</i> -Di(methoxymethyl)benzene	10			560		
<i>p</i> -Dicyanobenzene				80		200
<i>p</i> -Dinitrobenzene	0			30		
1,4-Dimethoxycyclohexane	0			0		
<i>N</i> -(2-naphthyl)acetamide	1800			15		

The most significant results show specific recognition of electron-rich aromatic guests by **16a** having a fluorinated aromatic function. For example, *p*-dimethoxybenzene (**17**) was recognized ($K_a = 2680 \text{ l mol}^{-1}$) to be more than 30 times stronger than *p*-dicyanobenzene ($K_a = 80 \text{ l mol}^{-1}$). In striking contrast, the non-fluorinated counterpart **16d** did not show any specificity in the recognition of aromatic guests **17** and **18** ($K_a = 200$ and 201 l mol^{-1} respectively). This marked difference proved that the specific recognition of electron-rich guests by **16a** is obviously caused by the fluoroaromatic rings. Although strong affinity between aromatics and fluoroaromatics has been shown since the discovery of a stable benzene–hexafluorobenzene (1:1) adduct in 1960 [19], molecular recognition with fluorinated cyclophanes still remains unexplored [20], partly due to synthetic difficulty in linking fluoroaromatic units into a macrocyclic skeleton [21]. We could emphasize that, in addition to the solution of the synthetic problem, the specific recognition of the electron density of the guest aromatics is achieved through the assembly of **16a** and its use as a host.

Other important aspects derived from the results of Table 1 are as follows. First, the recognition is not ascribed to the coordination on the metal but to interaction in the cavity because the nature of the central metals (Pd or Pt) had little influence on the recognition (compare **3** with **8**). Second, good geometrical fit of the cavity with the guests is, of course, conditional. For example, *N*-(2-naphthyl)acetamide is not associated with **16a** effectively but is strongly recognized by the large cavity of **3**; MM2 calculation suggested exothermic host–guest contact in the complexation of **16a** with **17** ($\Delta H(\text{calc}) = \Delta_f H_{16a \cdot 17} - (\Delta_f H_{16a}) + \Delta_f H_{17} = -14.7 \text{ kcal mol}^{-1}$, $K_a(\text{obs}) = 2780 \text{ l mol}^{-1}$) (Fig. 4). In addition, by having too small cavities, macrocycles **14a–d** did not recognize any organic molecules

3. Guest-induced assembly of a 3-D Pd(II) trinuclear complex: induced-fit molecular recognition

Since the development of cryptands opened the door to the chemistry of 3-D receptors, various cage-like molecules with a 3-D void have been prepared. The

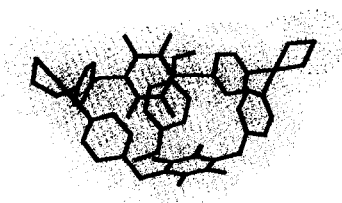


Fig. 4. An MM2 (CACHe, ver. 3.5) optimized structure of the **16a-17** complex.

concept of supramolecular self-assembly has again realized the spontaneous generation of the 3-D systems. The strategy shown in Scheme 1 is next expanded to a 3-D system [15,22]. We designed the self-assembly of a 3-D cage-like complex **5** from **1** and tridentate ligand **19** (Eq. (4)). Our initial result was quite disappointing; an intractable mixture of oligomeric products was obtained. However, we found that appropriate guests induced the assembly of the desired cage-like complex **5**. Interestingly, this guest-induced assembly process could be monitored by a time-dependent ^1H NMR measurement (Fig. 5). Thus, after addition of sodium (*p*-methoxyphenyl)acetate (**20**) to the reaction mixture derived from **1** and **19**, the oligomers gradually disappeared and the signals of **5** became stronger, accompanying the upfield shifting of the guest signals (a and b). The assembly of **5** was completed within several hours, and the isolated yield of the **5-20** complex (ClO_4 salt) was 94%.

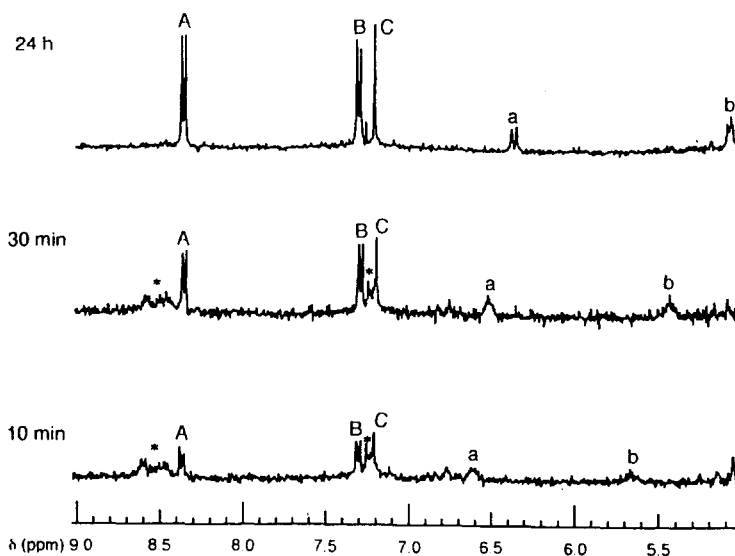
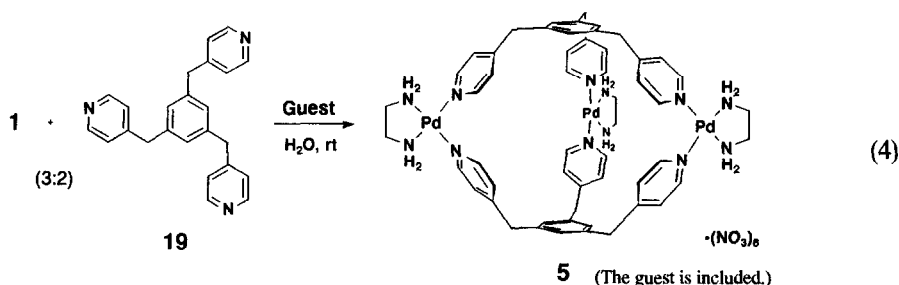
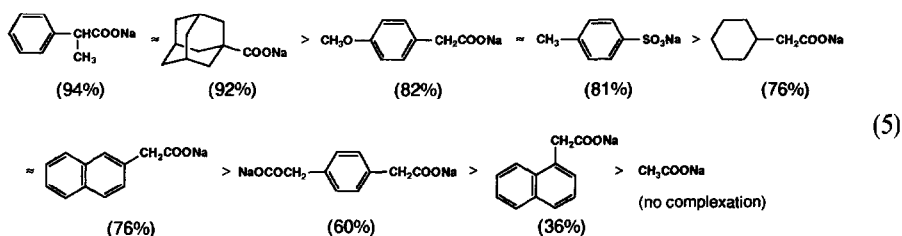


Fig. 5. Spectroscopic observation of guest-induced assembly of **5**. Spectra were collected at 10 min, 30 min, and 24 h after the addition of **20**·Na to an oligomeric mixture arising from **1** and **19** in D_2O ($[\mathbf{1}]_0 = 3.6 \text{ mM}$, $[\mathbf{19}]_0 = 2.4 \text{ mM}$, $[\mathbf{20}] = 1.2 \text{ mM}$). Signals A, B, and C refer to aromatic protons of **5** (A: PyH_a , B: PyH_b , C: ArH), while signals a and b correspond to aromatic protons of **20**. Complicated signals appearing at δ 7.1–7.3 and 8.4–8.7 (indicated by asterisks) are attributed to oligomeric components.

The structure of **5** was deduced mainly from NMR, electrospray mass spectrum, and elemental analysis.



NMR titration experiments showed 1:1 host–guest complexation between **5** and various organic carboxylates. Besides anionic hosts, a neutral hydrophobic guest such as *p*-xylene was also effective. In contrast, the less hydrophobic neutral guest **17** hardly induced the organization of the host. The ability of guests to induce the organization of **5** was qualitatively evaluated by comparing NMR yields of **5** self-assembling in the presence of the guests under a set of conditions ($[\text{Pd}^{2+}] = 3 \text{ mM}$, $[\text{guest}] = 1.5 \text{ mM}$, D_2O , 25°C); the order of the efficiency is shown in Eq. (5), where the values in parentheses show the NMR yields of **5**. Significant upfield shifts of guest signals up to about 3 ppm were observed when the guests effectively induced the organization of **5**.



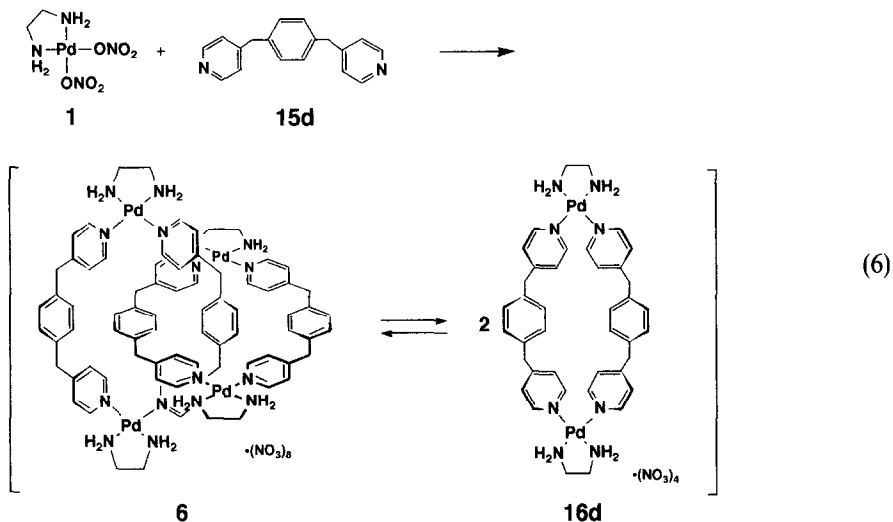
It is particularly interesting that the spontaneous manner in which the framework of **5** assembles only in the presence of specific guests can be regarded as a model for ‘induced-fit’.

4. Quantitative self-assembly of [2]catenanes

4.1. Synthesis, structure, and thermodynamic behavior of [2]catenanes

Catenane chemistry has recently expanded rapidly, partly in expectation of serving molecular-scale devices [23–25]. A Grignard catenane involving an Ar–Mg–Ar linkage was reported by Bickelhaupt and co-workers in 1993 [26]. We found that

[2]catenane **6** assembled together with monomer ring **16d** from **1** and ligand **15d** (Eq. (6)) [16]. The structure of **6** was first deduced mainly from ESI-MS, NMR, and elemental analysis. Quite recently, the crystallographic study of Pt(II) complex **22**, which is analogous to **6**, confirmed the catenated structure [27] (Fig. 6). As Pd–N bonds are reversible, a rapid equilibrium was observed between **6** and **16d**. While the equilibrium lay toward **16d** at a lower concentration (less than 2 mM), **6** became an overwhelmingly dominant component at a higher concentration (greater than 50 mM) (Table 2).



We suggest that the assembly of catenane **6** is promoted by 'double molecular recognition,' in which two molecules of **16d** bind each other in their cavities. That is, double molecular recognition can produce approximately double the magnitude of ΔG , making the structure of **6** stable enough to assemble quantitatively at high concentration. Such an interpretation is consistent with a remarkable medium effect that enables the modulation of the equilibrium ratio **6**:**16d** in the range $>99: <1$

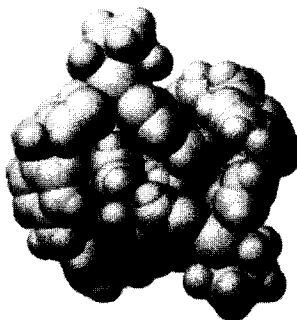


Fig. 6. Crystal structure of catenane **22** (NO_3^- omitted).

Table 2

Concentration effects on the equilibrium ratios between catenane **6** and monomer **16d**^a

Conc. Pd(II) (mM)	6 : 16d	Conc. Pd(II) (mM)	6 : 16d
1	<1: >99	10	59:41
2	11:89	20	75:25
5	38:62	50	90:10

^a Measured in D₂O at room temperature.

Table 3

Medium effects on the equilibrium ratios between catenane **6** and monomer **16d**^a

Medium	Guest ^b	6 : 16d
1.0 M NaNO ₃ –D ₂ O	—	>99: <1
0.2 M NaNO ₃ –D ₂ O	—	95:5
0.05 M NaNO ₃ –D ₂ O	—	86:17
D ₂ O	—	59:41
D ₂ O	0.5 ^c	27:73
D ₂ O	2.0 ^c	12:88
D ₂ O–CD ₃ OD (7:3)	—	9:91
D ₂ O–CD ₃ OD (5:5)	—	<1: >99

^a Measured at 10 mM/Pd. ^b Sodium (4-methoxyphenyl)acetate. ^c Mol equiv to Pd(II).

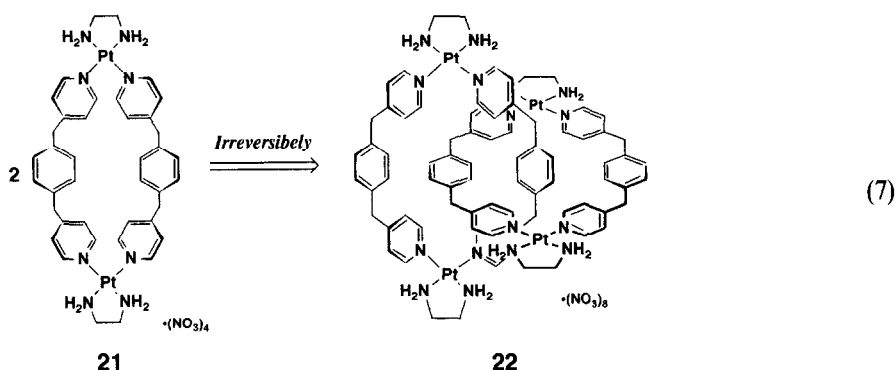
to <1: >99 (Table 3). Thus, the employment of a more polar media (D₂O solution of NaNO₃) increased the proportion of **6** up to greater than 99%, even at a low concentration, most probably owing to enhanced hydrophobic interaction in the catenane formation. In contrast, the proportion of **6** diminished with a less polar media (CD₃OD–D₂O). Selective stabilization of **16d** by adding **20**, a specific guest for **16d**, also reduced the ratio **6**:**16d**.

Quite recently, self-assembled catenanes containing Fe(II) and Ag(I) were reported [28]. Related interlocking systems are self-assembled rotaxanes containing transition metals [29].

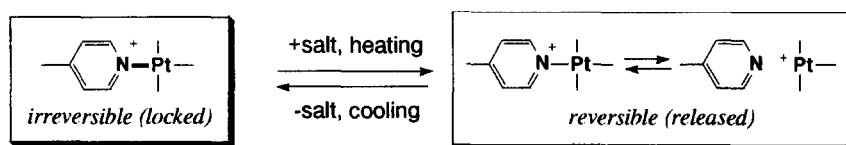
4.2. Irreversible formation of catenane from two molecular rings

As discussed above, the utilization of the labile nature of a palladium(II)–pyridine (Pd(II)–Py) coordinate bond has realized the quantitative self-assembly of [2]catenane **6** from two complete molecular rings **16d**. This tricky molecular action is ascribed to the dissociation of the Pd(II)–Py bonds that causes a rapid equilibrium between **16d** and **6**. However, the presence of the equilibrium means that [2]catenane **6** once formed easily dissociates into two separate rings. If the labile coordinate bond can be frozen after the catenane assembles, a complete catenane that never dissociates into two rings is obtained. Such a one-way formation of a catenane was

achieved in a platinum(II) counterpart system (Eq. (7)) using the concept of ‘molecular lock’ [27].



The concept of ‘molecular lock’ stems from the exploitation of the ephemeral nature of the Pt(II)–Py bond. This bond can be likened to a lock because it is irreversible (‘locked’) under ordinary conditions but becomes reversible (‘released’) in highly polar media at high concentration (Scheme 2). Thus, Fig. 7 illustrates the overall one-way transformation of **21** into **22** using the molecular lock. Initially, a molecular ring is on the lock (A). The lock is then released by adding a salt (NaNO₃) and heating at 100 °C (B), allowing the self-assembly of a catenated framework within 12 h (C). Finally, this framework is locked by removing the salt and cooling (D). This chemical manipulation of molecular rings could be followed by ¹H NMR (Fig. 8).



Scheme 2: Schematic presentation of the concept ‘molecular lock’.

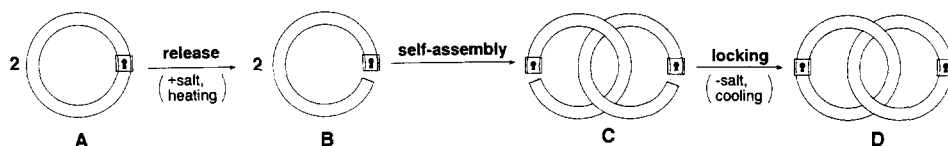


Fig. 7. Schematic presentation of the procedure for the irreversible formation of a catenane from two complete rings using the molecular lock.

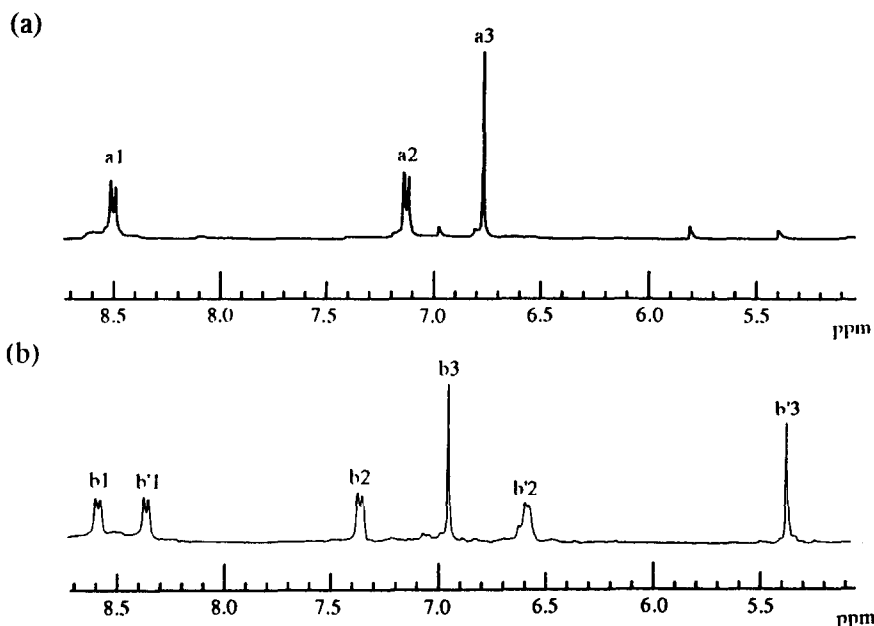


Fig. 8. Spectroscopic observation of transfer of **21** into **22** by releasing the molecular lock. Molecular ring **21** (10 mM) was heated at 100 °C in D₂O solution of NaNO₃ (5 M). (a) After 0 h; signals a1, a2, and a3 are assigned as the PyHa, PyHb, C₆H₄ protons of **21** respectively. (b) After 24 h; signals b and b' refer to the outside and inside ligands of **22** respectively.

5. Future outlook

As discussed above, we and others have been showing the remarkable potentials of metal directed-assembly of organic architectures—from macrocycles to [2]catenanes [30]. It is difficult to construct these molecular structures by organic synthesis, in which the molecules are made up atom-by-atom by chemical reactions. In this sense, the extension of the present study could provide alternate organic synthesis. However, the most challenging subject for us is further development of our chemistry from 'alternative' to only 'methods' for the construction of ultimately defined architectures. We continue to challenge ourselves toward this final goal, as many chemists are now doing with their own concepts and strategies.

Acknowledgments

We wish to thank all co-workers who by their efforts and knowledge have contributed to the success of our research.

References

- [1] (a) J.-M. Lehn, *Angew. Chem. Int. Ed. Engl.*, 27 (1988) 89. (b) J.-M. Lehn, *Angew. Chem. Int. Ed. Engl.*, 29 (1990) 1304. (c) V. Balzani, and L. DeCola (Eds.), *Supramolecular Chemistry*, Kluwer, The Netherlands, 1992.
- [2] (a) J.-M. Lehn, A. Rigault, J. Siegel, J. Harrowfield and B. Chevrier, *Proc. Natl. Acad. Sci. USA*, 84 (1987) 2565. (b) J.-M. Lehn and A. Rigault, *Angew. Chem. Int. Ed. Engl.*, 27 (1988) 1095.
- [3] (a) For a review of double or triple helical complexes: E.C. Constable, *Tetrahedron*, 48 (1992) 10013. (b) E.C. Constable, M.D. Ward and D.A. Tocher, *J. Am. Chem. Soc.*, 112 (1990) 1256. (c) E.C. Constable, R. Chotalia and D.A. Tocher, *J. Chem. Soc. Chem. Commun.*, (1992) 771. (d) A.F. Williams, C. Piguet and G. Bernardinelli, *Angew. Chem. Int. Ed. Engl.*, 30 (1991) 1490. (e) R. Kramer, J.-M. Lehn, A. DeCian and J. Fischer, *Angew. Chem. Int. Ed. Engl.*, 32 (1993) 703. (f) T.W. Bell and H. Jousselein, *Nature*, 367 (1994) 441.
- [4] (a) M.-T. Youinou, N. Rahmouni, J. Fischer and J.A. Osborn, *Angew. Chem. Int. Ed. Engl.*, 31 (1992) 733. (b) P.N.W. Baxter, J.-M. Lehn, J. Fischer, M.-T. Youinou, *Angew. Chem. Int. Ed. Engl.*, 33 (1994) 2284.
- [5] A cylindrical Cu(I) hexanuclear complex: P. Baxter, J.-M. Lehn and A. DeCian, *Angew. Chem. Int. Ed. Engl.*, 32 (1993) 69. (b) A related Cu(I) trinuclear complex: E. Leize, A.V. Dorselaer, R. Kramer and J.-M. Lehn, *J. Chem. Soc. Chem. Commun.*, (1993) 990.
- [6] X. Delaigue, M.W. Hosseini, E. Leize, S. Kieffer and A.V. Doreeslaer, *Tetrahedron Lett.*, 34 (1993) 7561.
- [7] R. Fuchs, N. Habermann and P. Klufers, *Angew. Chem. Int. Ed. Engl.*, 32 (1993) 852.
- [8] (a) L. Fabbrizzi and A. Poggi, *Transition Metals in Supramolecular Chemistry*, Kluwer, Dordrecht, 1994. (b) M. Fujita, in J.-M. Lehn (Ed.), *Comprehensive Supramolecular Chemistry*, Vol. 9, Pergamon, Oxford, 1995, Chapter 5.
- [9] (a) M. Fujita, J. Yazaki and K. Ogura, *J. Am. Chem. Soc.*, 112 (1990) 5645. (b) M. Fujita, J. Yazaki and K. Ogura, *Chem. Lett.*, (1991) 1031. (c) M. Fujita, J. Yazaki, K. Ogura, *Tetrahedron Lett.*, 32 (1991) 5589. (d) M. Fujita, S. Nagao, M. Iida, K. Ogata and K. Ogura, *J. Am. Chem. Soc.*, 115 (1993) 1574. (e) M. Fujita, J. Yazaki, T. Kuramochi and K. Ogura, *Bull. Chem. Soc. Jpn.*, 66 (1993) 1837. (f) M. Fujita, M. Aoyagi and K. Ogura, *Inorg. Chim. Acta.*, in press.
- [10] For recent reviews on chemistry of macrocycles: (a) F. Diederich, *Angew. Chem. Int. Ed. Engl.*, 27 (1988) 362. (b) H.-J. Schneider, *Angew. Chem. Int. Ed. Engl.*, 30 (1991) 1417. (c) F. Diederich, *Cyclophanes*, Monographs in Supramolecular Chemistry 2, The Royal Society of Chemistry, London, 1991.
- [11] (a) F.C. March, R. Mason, K.M. Thomas and B.L. Shaw, *J. Chem. Soc. Chem. Commun.*, (1975) 584. (b) A.J. Pryde, B.L. Shaw and B. Weeks, *J. Chem. Soc. Chem. Commun.*, (1973) 947. (c) A.R. Sanger, *J. Chem. Soc. Chem. Commun.*, (1975) 893. (d) N.A. Al-Salem, H.D. Empsall, R. Markham, B.L. Shaw and B. Weeks, *J. Chem. Soc. Dalton Trans.*, (1979) 1972. (e) W.E. Hill, J.G. Taylor, C.P. Falshaw, T.J. King, B. Beagley, D.M. Tonge, R.G. Pritchard and C.A. McAuliffe, *J. Chem. Soc. Dalton Trans.*, (1986) 2289. (f) R.J. Puddephatt, *Chem. Soc. Rev.*, 12 (1983) 99. (g) P.M. Stricklen, E.J. Volcko and J.G. Verkade, *J. Am. Chem. Soc.*, 105 (1983) 2494.
- [12] (a) A.W. Maverick and F.E. Klavetter, *Inorg. Chem.*, 23 (1984) 4129. (b) A.W. Maverick, S.C. Buckingham, Q. Yao, J.R. Bradbury and G.G. Stanley, *J. Am. Chem. Soc.*, 108 (1986) 7430. (c) J.R. Bradbury, J.L. Hampton, D.P. Martone and A.W. Maverick, *Inorg. Chem.*, 28 (1989) 2392. (d) A.W. Maverick, M.L. Ivie, J.H. Waggenspack and F.R. Fronczek, *Inorg. Chem.*, 29 (1990) 2403.
- [13] Metal-directed assembly of macrocyclic complexes (after 1990): (a) Y. Kobuke, Y. Sumida, M. Hayashi and H. Ogoshi, *Angew. Chem. Int. Ed. Engl.*, 30 (1991) 1496. (b) Y. Kobuke and Y. Satoh, *J. Am. Chem. Soc.*, 114 (1992) 789. (c) S.I. Al-Resayes, P.B. Hitchcock and J.F. Nixon, *J. Chem. Soc. Chem. Commun.*, (1991) 78. (d) P. Scrimin, P. Tecilla, U. Tonellato and N. Vignaga, *J. Chem. Soc. Chem. Commun.*, (1991) 449. (e) L.G. Mackay, H.L. Anderson and J.K.M. Sanders, *J. Chem. Soc. Chem. Commun.*, (1992) 43. (f) A.W. Schwabacher, J. Lee and H. Lei, *J. Am. Chem. Soc.*, 114 (1992) 7597. (g) K.L. Cole, M.A. Farran and K. Deshayes, *Tetrahedron Lett.*, 33 (1992) 599. (h) E.C. Constable, R.P.G. Henney, P.R. Raithby and L.R. Sousa, *Angew. Chem. Int. Ed.*

- Engl., 30 (1991) 1363. (i) S. Ruttimann, G. Bernardinelli and A.F. Williams, *Angew. Chem. Int. Ed. Engl.*, 32 (1993) 392.
- [14] Metal-templated synthesis of macrocycles: S. Anderson, H.L. Anderson and J.K.M. Sanders, *Acc. Chem. Res.*, 26 (1993) 469 and references cited therein. Also, see: L.G. Mackay, R.S. Wylie and J.K.M. Sanders, *J. Am. Chem. Soc.*, 116 (1994) 3141.
- [15] M. Fujita, S. Nagao and K. Ogura, *J. Am. Chem. Soc.*, 117 (1995) 1649.
- [16] M. Fujita, F. Ibukuro, H. Hagihara and K. Ogura, *Nature*, 367 (1994) 720.
- [17] (a) H. Rauter, E.C. Hillgeris, A. Erxleben and B. Lippert, *J. Am. Chem. Soc.*, 116 (1994) 616. (b) P.J. Stang and D.H. Cao, *J. Am. Chem. Soc.*, 116 (1994) 4981. (c) P.J. Stang and J.A. Whiteford, *Organometallics*, 13 (1994) 3776. (d) P.J. Stang and V.V. Zhdankin, *J. Am. Chem. Soc.*, 115 (1993) 9808.
- [18] F. Basolo, J. Chatt, H.B. Gray, R.G. Pearson, B.L. Shaw, *J. Chem. Soc.*, (1971) 2207.
- [19] (a) C.R. Prttrick and G.S. Prossor, *Nature*, 187 (1966) 1021. (b) J.H. Williams, J.K. Cockcroft and A.N. Fitch, *Angew. Chem. Int. Ed. Engl.*, 31 (1992) 1655. (c) M.R. Battaglia, A.D. Buckingham and J.H. Williams, *Chem. Phys. Lett.*, 78 (1981) 421. (d) J.A. Ripmeester, D.A. Wright, C.A. Fyfe and R.K. Boyd, *J. Chem. Soc., Faraday Trans. 2*, 74 (1978) 1164. (e) E. Bartsch, H. Bertagnolli and P. Chieux, *Ber. Bunsenges. Phys. Chem.*, 90 (1986) 34.
- [20] I. Ojima and H.B. Kwon, *J. Am. Chem. Soc.*, 110 (1988) 5617.
- [21] Perfluorinated crown ethers: (a) W. Lin, W. Bailey and R. Lagow, *J. Chem. Soc. Chem. Commun.* (1985) 1350. (b) J. Brodbelt, S. Maleknia, C.-C. Liou and R. Lagow, *J. Am. Chem. Soc.*, 113 (1991) 5913. (c) C.-Y. Guo, R.L. Kirchmeier and J.M. Shreeve, *J. Am. Chem. Soc.*, 113 (1991) 9000.
- [22] Cage-like compounds: (a) F. Evmeyer and F. Vögtle, in J.L. Atwood, J.E.D. Davies and D.D. MacNicol (Eds.), *Inclusion Compounds*, Vol. 4, Academic Press, London, 1991, Chapter 6, pp. 263–282. (b) C. Seel, F. Vögtle, *Angew. Chem. Int. Ed. Engl.*, 31 (1992) 528. (c) Y. Murakami, O. Hayashida, Y. Nagai, *J. Am. Chem. Soc.*, 116 (1994) 2611.
- [23] J.-P. Sauvage (Ed.), *New J. Chem. (special issue)*, 17 (1993) 617.
- [24] Recent development of highly efficient catenane synthesis: (a) C.O. Dietrich-Buchecker and J.-P. Sauvage, *Chem. Rev.* 87 (1987) 795. (b) J.-P. Sauvage, *Acc. Chem. Res.*, 23 (1990) 319. (c) P.L. Anelli, P.R. Ashton, R. Ballardini, V. Balzani, M. Delgado, T. Fandolfi, T.T. Goodnow, A.E. Kaifer, D. Philp, M. Pietraszkiewicz, L. Prodi, M.V. Reddington, A.M.Z. Slawin, N. Spencer, J.F. Stoddart, C. Vicent and D.J. Williams, *J. Am. Chem. Soc.*, 114 (1992) 193 and references cited therein.
- [25] (a) C.A. Hunter, *J. Am. Chem. Soc.*, 114 (1992) 5303. (b) F. Vögtle, W.M. Muller, U. Muller, M. Bauer and K. Rissanen, *Angew. Chem. Int. Ed. Engl.*, 32 (1993) 1295. (c) D. Armspach, P.R. Ashton, C.P. Moore, N. Spencer, J.F. Stoddart, T.J. Wear and D.J. Williams, *Angew. Chem. Int. Ed. Engl.*, 32 (1993) 854. (d) D.B. Amabilino, P.R. Ashton, A.S. Reder, N. Spencer, J.F. Stoddart, *Angew. Chem. Int. Ed. Engl.* 33 (1994) 1286. (e) J.-F. Nierengarten, C.O. Dietrich-Buchecker and J.-P. Sauvage, *J. Am. Chem. Soc.*, 116 (1994) 375. (f) A. Livoreil, C.O. Dietrich-Buchecker, J.-P. Sauvage, *J. Am. Chem. Soc.*, 116 (1994) 375.
- [26] G.J.M. Gruter, F.J.J. de Kanater, P.R. Markies, T. Nemoto, O.S. Akkerman and F. Bickelhaupt, *J. Am. Chem. Soc.*, 115 (1993) 375.
- [27] M. Fujita, F. Ibukuro, K. Yamaguchi and K. Ogura, *J. Am. Chem. Soc.*, 117 (1995) 4175.
- [28] C. Piguet, G. Bernardinelli, A.F. Williams and B. Bocquet, *Angew. Chem. Int. Ed. Engl.*, 34 (1995) 582.
- [29] (a) H. Ogino, *J. Am. Chem. Soc.*, 103 (1981) 1303. (b) H. Ogino, *New. J. Chem.*, 17 (1993) 683. (c) R.S. Wylie and D.H. Macartney, *J. Am. Chem. Soc.*, 114 (1992) 3136.
- [30] Related works not involved in this article: (a) M. Fijita, Y.J. Kwon, S. Washizu and K. Ogura, *J. Am. Chem. Soc.*, 116 (1994) 1151. (b) M. Fujita, Y.J. Kwon, M. Miyazawa and K. Ogura, *J. Chem. Soc. Chem. Commun.*, (1994) 1977. (c) M. Fujita, Y.J. Kwon, O. Sasaki, K. Yamaguchi and K. Ogura, *J. Am. Chem. Soc.*, 117 (1995) 4175. (d) M. Fujita, D. Oguro, M. Miyazawa, H. Oka, K. Yamaguchi and K. Ogura, *Nature*, 378 (1995) 469.