

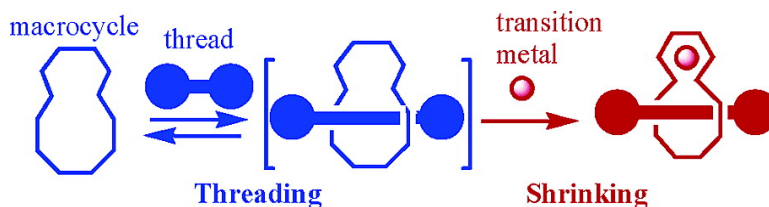
Communication

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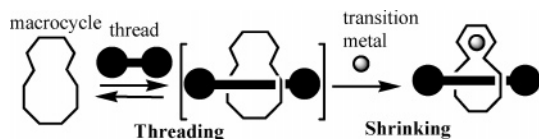
## Threading-Followed-by-Shrinking Protocol for the Synthesis of a [2]Rotaxane Incorporating a Pd(II)–Salophen Moiety

Il Yoon, Mamiko Narita,<sup>†</sup> Toshimi Shimizu, and Masumi Asakawa\*

Nanoarchitectonics Research Center, National Institute of Advanced Industrial Science and Technology (AIST),  
Tsukuba Central 5, 1-1-1 Higashi, Tsukuba Ibaraki 305-8565, Japan

Received June 16, 2004; E-mail: masumi-asakawa@aist.go.jp

Rotaxanes and catenanes have attracted a considerable amount of interest in recent years because a number of them function as molecular motors and molecular switches.<sup>1</sup> Although rotaxanes have been prepared from many different building blocks, the number of synthetic methods for their construction remains limited. [2]-Rotaxanes are most conveniently prepared using template-directed syntheses such as clipping,<sup>2</sup> threading-followed-by-stoppering,<sup>3</sup> and slipping<sup>4</sup> methods. In this communication, we report a new synthetic method (Figure 1), which we name “threading-followed-by-



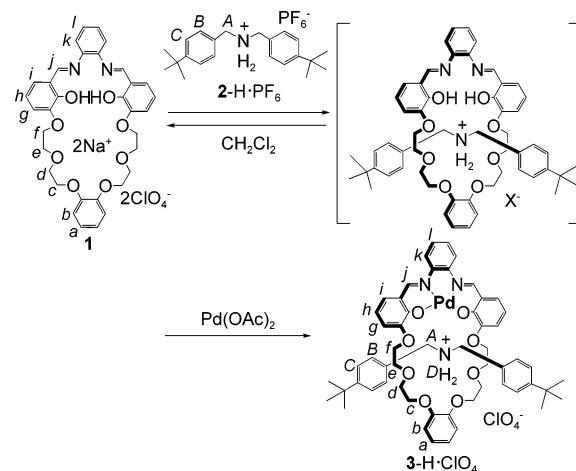
**Figure 1.** Synthesis of a [2]rotaxane using a threading-followed-by-shrinking method.

shrinking”, that involves threading a rodlike unit through a macrocycle and then shrinking the free space within the macrocycle through coordination between its salophen [*N,N'*-*o*-phenylenebis(salicylidene-iminato) dianion] moiety and a transition metal. Recently, Leigh et al. reported the synthesis of [2]rotaxanes, based on octahedral and square-planar metal complexes formed by thread-macrocycle-metal assemblies incorporating transition-metal ions; the metal coordination in these systems occurs through binding of both the thread and macrocycle components to the metal ion, and these rotaxanes are formed effectively upon mixing of the components in what is, essentially, a threading-followed-by-stoppering approach.<sup>5</sup> Our protocol for [2]rotaxane formation differs conceptually in a number of areas: the metal ion is stabilized through square-planar coordination, the shrinking process involves metal ion coordination by the macrocycle only (i.e., the threadlike unit does not coordinate to the metal ion), and the macrocycle is not interlocked by the thread in the absence of the metal ion.

Recently, we synthesized the bis-compartmental sodium perchlorate-crown ether complex **1**, which incorporates a salophen moiety, and its transition-metal complex.<sup>6</sup> Salophens are tetradentate ligands that react with transition-metal ions to form square-planar complexes<sup>7</sup> whose versatile properties are of interest to applications in areas such as molecular recognition,<sup>8</sup> metalcatalysis,<sup>9</sup> and electron transfer.<sup>6,10</sup> We introduced the salophen moiety as a unit to control the size of the macrocycle within rotaxanes, which may, in addition, have potential for use as catalysts.

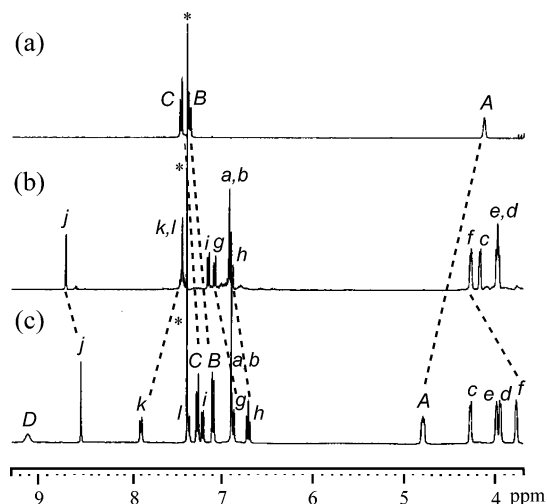
The interaction of **1** with the secondary dialkylammonium salt **2**–H·PF<sub>6</sub><sup>4b</sup> forms a pseudorotaxane intermediate in a reversible self-assembly process; the addition of palladium acetate afforded the rotaxane **3**–H·ClO<sub>4</sub> in reasonable yield (30%) after counterion

**Scheme 1**



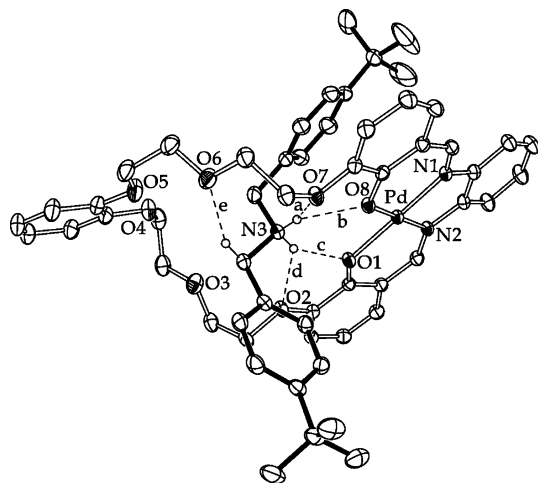
exchange (Scheme 1). We have characterized **3**–H·ClO<sub>4</sub> fully through NMR and IR spectroscopic, mass spectrometric, and elemental and X-ray crystallographic analyses.

The <sup>1</sup>H NMR spectrum of **3**–H·ClO<sub>4</sub> (Figure 2c), together with its 2D (ROESY and COSY) NMR spectra (Supporting Information), provides good evidence for the formation of the rotaxane. Figure 2c indicates that the signal of the CH<sub>2</sub>N<sup>+</sup> (A) protons in the thread has shifted downfield significantly, relative to that of the free thread (Figure 2a), as a result of the formation of [C–H···O] hydrogen bonds<sup>11</sup> (Figure 3). In addition, the signal of one proton (k) of the salophen unit in the macrocycle also underwent a significant downfield shift relative to that of the free macrocycle (Figure 2b);



**Figure 2.** <sup>1</sup>H NMR spectra of (a) **2**–H·PF<sub>6</sub>, (b) **1**, and (c) **3**–H·ClO<sub>4</sub> in CDCl<sub>3</sub>/CD<sub>3</sub>CN (5:1) at 25 °C. The signal labeled with an asterisk represents CHCl<sub>3</sub>.

<sup>†</sup> Current address: Toyota Central R&D Labs., Inc., 41-1, Aza Yokomichi, Oaza Nagakute, Nagakute-cho, Aichi-gun, Aichi-Ken, 480-1192, Japan.



**Figure 3.** Molecular structure of  $3\text{-H}\cdot\text{ClO}_4$  (ORTEP, 30% thermal probability ellipsoids) displaying the intercomponent  $[\text{N}^+\text{-H}\cdots\text{O}]$  and  $[\text{C}\text{-H}\cdots\text{O}]$  hydrogen bonds. Hydrogen atoms, except for those involved in H-bonds, have been omitted for clarity. Hydrogen bond geometries  $\{-[\text{X}\cdots\text{O}], [\text{H}\cdots\text{O}]\}$  distances (Å), and  $[\text{X}\text{-H}\cdots\text{O}]$  angles (deg): (a) 3.010, 2.187, 151.8; (b) 2.823, 2.120, 134.2; (c) 2.835, 2.015, 150.8; (d) 3.067, 2.346, 137.1; (e) 3.384, 2.476, 157.8.

this shift may be attributable to the deshielding effect of the aromatic rings of the thread in the rotaxane (Figure S4). In contrast, the signal for proton *f* of the oligoether ring shifted relatively upfield, which we attribute to the shielding effect of the aromatic units in the thread that arises from the bent conformations of the components (Figure 3). In addition, the signals of some protons in the salophen (*h*, *g*, *j*; Figure 2c) and aromatic units in the thread (*B*, *C*; Figure 2c) have shifted upfield relative to those signals in the free components, which suggests the existence of  $\pi\text{-}\pi$  stacking interactions.<sup>12</sup> Moreover, the interlocked nature of  $3\text{-H}\cdot\text{ClO}_4$  is suggested by the ROESY spectrum (Supporting Information), which displays cross-peaks between the signals of the protons of the ether linkages in the macrocycle (*c-f*) and those of both the  $\text{CH}_2\text{N}^+$  (*A*) and aromatic (*C*) groups of the thread.

We obtained orange-colored single crystals of  $3\text{-H}\cdot\text{ClO}_4$  suitable for X-ray analysis upon vapor diffusion of diethyl ether into an acetonitrile solution of  $3\text{-H}\cdot\text{ClO}_4$ .<sup>13</sup> The crystal structure of  $3\text{-H}\cdot\text{ClO}_4$  (Figure 3) confirms the encircling of the macrocycle about the molecular axle of the thread. Stabilization of the [2]rotaxane is achieved through a combination of (a)  $[\text{N}^+\text{-H}\cdots\text{O}]$ <sup>14</sup> and  $[\text{C}\text{-H}\cdots\text{O}]$ <sup>14b,d</sup> hydrogen bonds between the oxygen atoms of the macrocycle and the  $\text{NH}_2^+$  and benzylic  $\text{CH}_2\text{N}^+$  units of the secondary dialkylammonium ion and (b)  $\pi\text{-}\pi$  stacking interactions<sup>14</sup> between aromatic rings (Supporting Information). The packing of the [2]-rotaxane is stabilized by pairs of  $[\text{C}\text{-H}\cdots\pi]$  interactions<sup>14a,c</sup> (a and b in Figure S4) between one proton of an aromatic ring of the salophen unit in one rotaxane and an aromatic ring of the thread in another and between one proton of a  $\text{CH}_2\text{O}$  unit in one rotaxane and an aromatic ring of the salophen in another. The  $[\text{N}^+\text{-H}\cdots\text{O}]$ <sup>14</sup> and  $[\text{C}\text{-H}\cdots\text{O}]$ <sup>14b,d</sup> hydrogen bonding distances (2.823–3.384 Å) are comparable with those of related compounds.<sup>14</sup> The palladium atom exists in a distorted square-planar array that is very similar to one that we have described previously<sup>6</sup> (Figure S3). The Pd(II) $\cdots\pi$  distances (3.477 and 3.733 Å) are longer than the sum of the van der Waals radii (3.25–3.30 Å).<sup>15</sup> In summary, we have successfully self-assembled and characterized the [2]rotaxane  $3\text{-H}\cdot\text{ClO}_4$  incorporating a crown ether-like macrocycle containing a palladium(II)–salophen moiety. In particular, we have demonstrated a new protocol for the synthesis of [2]rotaxanes—the threading-

followed-by-shrinking method—that we believe will be useful for the construction of additional mechanically interlocked molecules.

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**Supporting Information Available:** Experimental procedures and spectroscopic data for  $3\text{-H}\cdot\text{ClO}_4$  (PDF, CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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