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Synthesis and Characterization of a Metallocycle-Based Molecular Shuttle

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Kinetically stable metallocycle-based molecular shuttles of [2]rotaxanes **4a** and **4b**, along with [3]-rotaxanes **5a** and **5b**, have been prepared using the rhenium(I)-bridged metallocycle **2** and the dumbbell components containing two stations, **3a** and **3b**. The rotaxanes were self-assembled by hydrogen bonding interactions upon heating a $Cl_2CHCHCl_2$ solution containing their components at 70 °C. Each rotaxane was isolated in pure form by silica gel chromatography under ordinary laboratory conditions and fully characterized by elemental analysis and various spectroscopic methods. The ^{1}H NMR signals for the amide NH and the methylene $-(CH_2)_4-$ of the station were considerably changed when occupied by the metallocycle. In [2]rotaxane **4b**, which has a larger naphthyl spacer, the occupied and unoccupied stations gave widely separated signals in the ^{1}H NMR spectroscopy at room temperature, but averaged signals of two stations were observed in [2]rotaxane **4a**, which has a smaller phenyl spacer. This is attributed to the shuttling of the metallocycle between two stations. The coalescence temperature experiment gave a shuttling rate of $\sim$670 s^{-1} at 19 °C in $CDCl_3$, corresponding to an activation free energy ($\Delta G^{\ddagger}$) of 13.3 kcal/mol. With respect to the relative position of the chloride in the rhenium(I) center, two diastereomers are possible in the [2]rotaxane and three diastereomers are possible in the [3]rotaxane. In fact, the rotaxanes exist as diastereomeric mixtures in nearly equal amounts of all possible diastereomers on the basis of the amide NH signals of the station in the ^{1}H NMR spectroscopy.

Introduction

Molecular shuttles[1] are a kind of rotaxane[2] comprised of two distinct molecular components, a macrocycle and a dumbbell-shaped linear component. The macrocycle can move reversibly from one station to another on the dumbbell component, due to the absence of direct covalent bond between the two components. A variety of molecular shuttles have been reported for the past decade, and all of them were prepared using organic macrocycles.[3,4]

Recently, we prepared a new molecular shuttle **1**[5] containing an osmate ester macrocycle,[6] which is the first example of metallocycle-based molecular shuttle.

Unfortunately, shuttle **1** is kinetically labile and exists only in an equilibrium mixture with its components in solution due to the weak nature of the $Os^{VI}-N$ coordi-

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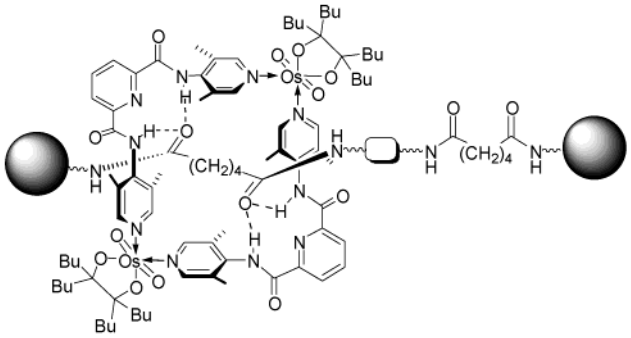

1

native bond. Furthermore, the shuttling kinetics could not be determined quantitatively because shuttle **1** simultaneously conducted two different dynamic processes with similar rates: reversible disassembly and reassembly between **1** and its constituents as well as internal shuttling of the metallocycle between two stations. The rate of the former process is directly related to the strength of the coordinative bond in the metallocycle and to the kinetic stability[7] of the molecular shuttle. With this in mind, using the rhenium-bridged metallocycle,[8] we here prepared new kinetically stable molecular shuttles of [2] rotaxanes **4a** and **4b**, along with the corresponding [3]rotaxanes **5a** and **5b**. The high stabilities of these rotaxanes allow us not only to isolate them in pure form by silica gel chromatography under ambient conditions but also to determine quantitatively the shuttling kinetics of molecular shuttle **4a**.

Results and Discussion

Synthesis. Metallocycle **2**[9] was prepared in 93% yield by heating a 1:1 mixture of the precursor bispyridyl ligand[6b] and $Re(CO)_5Cl$ in 1,1,2,2-tetrachloroethane at 100 °C for 2 h. The molecular shuttle of [2]rotaxane **4a** was prepared by heating either a mixture of metallocycle **2** and dumbbell **3a**[5] (Scheme 1) or directly a mixture of $Re(CO)_5Cl$, the ligand, and dumbbell **3a** in 1,1,2,2-tetrachloroethane at 70 °C. The major driving force for the formation of the rotaxane is a hydrogen-bonding interaction between the carbonyl oxygen of the adipamide station and the amide NH of the metallocycle. The reaction was therefore performed in a minimum amount of a relatively nonpolar solvent, 1,1,2,2-tetrachloroethane, to increase the yield of the rotaxane. The reaction did not occur at room temperature but proceeded in a reasonable rate at ~70 °C. Under these conditions, [3]rotaxane **5a**, where both stations are occupied by the metallocycle **2**, was also formed (Scheme 1). For example, heating a $Cl_2CHCHCl_2$ solution of **2** (0.4 M) and **3a** (0.2 M) for 6 h provided [2]rotaxane **4a** and [3]rotaxane **5a** in 37 and 10% isolated yields, respectively. On the other hand, a 1:1:1 mixture of $Re(CO)_5Cl$, ligand, and **3a** in $Cl_2CHCHCl_2$ (each 0.2 M) gave **4a** and **5a** in 20 and 7% isolated yields, respectively. The relative distribution of the [2]rotaxane and the [3]rotaxane depends on the molar ratio of the reactants and on the reaction conditions.

For comparisons of spectroscopic properties and shuttling dynamics, we also prepared in the same way rotaxanes **4b** and **5b**, which contain the bulkier naphthyl spacer instead of the phenyl group between two adipamide stations.

Spectroscopic Properties. The FAB-mass analyses were consistent with the structures of the [2]rotaxanes and the [3]rotaxanes. For example, the mass spectrum of [2]rotaxane **4a** showed peaks of $[MH]^+$ (m/z = 2599, 10%) and $[M - Cl]^+$ (m/z = 2563, 3%), along with fragments of [metallocycle − Cl]$^+$ and [dumbbell]$^+$. The other [2]rotaxane, **4b**, gave a mass spectral pattern similar to that of **4a**. In addition, the [3]rotaxanes, **5a** and **5b**, gave $[M]^+$ peaks at m/z = 3734 (1%) and 3785 (3%), respectively, in the FAB mass spectra. Under ionization conditions, loss of one metallocycle **2** from the [3]rotaxanes leads to the [2]rotaxanes, and consequently spectral patterns of the [3]rotaxanes at lower m/z regions were similar to those of the corresponding [2]rotaxanes (see Supporting Information).

As shown in Figure 1, the ^{1}H NMR spectra gave definitive evidence for the structures of [2]rotaxanes **4a** and **4b** and [3]rotaxanes **5a** and **5b**. Some important observations are as follows. First, two NH signals of metallocycle **2** in all four rotaxanes were shifted downfield ($\Delta\delta$ = 1.3 and 1.6 ppm) relative to those of free **2**, as the result of hydrogen bond formation. Second, the ^{1}H NMR signals for the methylene units $-(CH_2)_4-$ of the adipamide stations appeared at approximately 0.9 and 0.2 ppm in [3]rotaxanes **5a** and **5b** (Figure 1b,f), while those in free dumbbell **3** appeared at 2.1 and 1.6 ppm (Figure 1d,h). These large upfield shifts are direct evidence for the location of metallocycle **2** on the adipamide station of the dumbbell component. Third, in [2]rotaxane **4b** with a naphthyl spacer, the methylene signals were split into and appeared at two different regions: at 2.1 and 1.6 ppm for the unoccupied station and at 0.9 and 0.2 ppm for the occupied station (Figure 1g). On the other hand, the same signals in [2]rotaxane **4a** containing a smaller phenyl spacer were broadened out at temperatures around room temperature (Figure 1c), but at lower temperatures (< 0 °C), the signals become similar to those of **4b** (see Supporting Information). Finally, the signals for the amide NH[a] of the dumbbell components were considerably broadened in [2]rotaxane **4a**, while sharp NH signals between 5.2 and 6.3 ppm were observed for other rotaxanes **4b**, **5a**, and **5b** (about which more will be discussed later). The last

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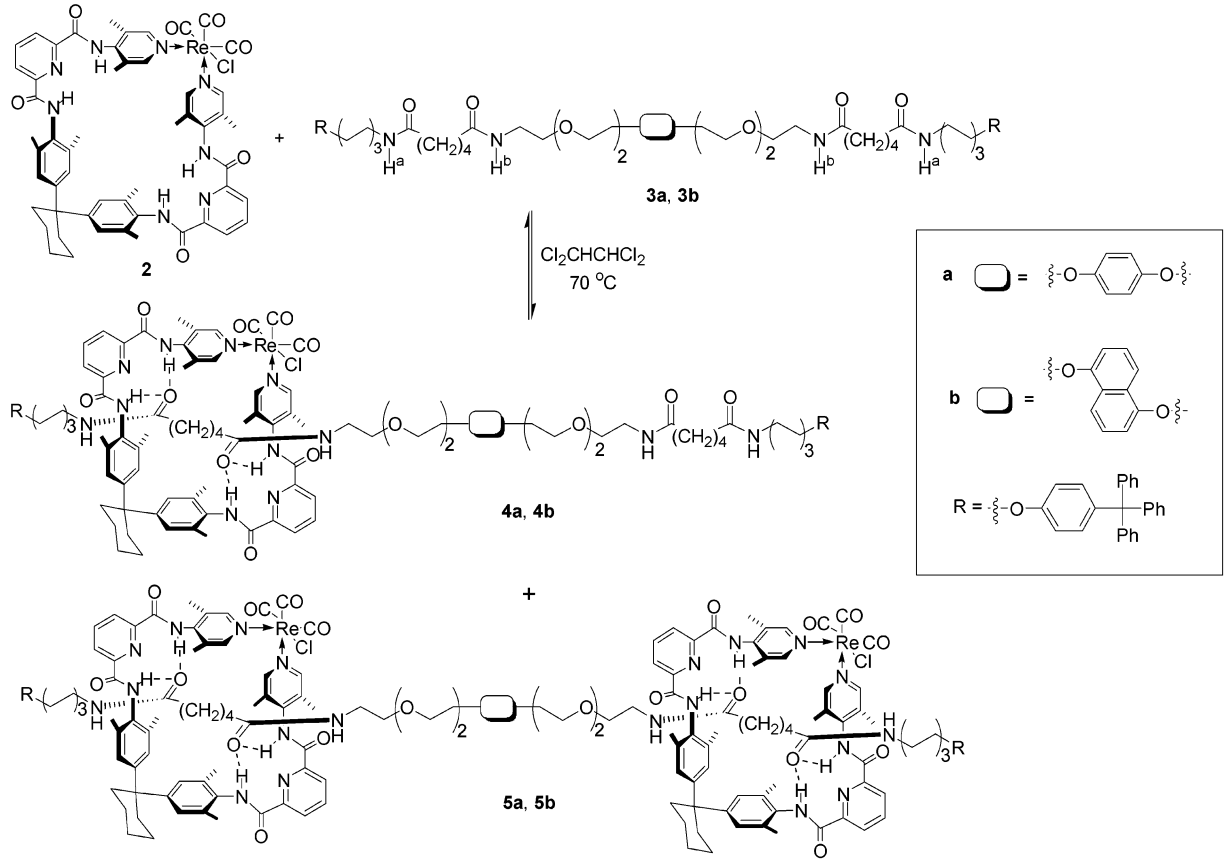
SCHEME 1. Synthesis of [2]- and [3]rotaxanes



two observations must be associated with the shuttling of the metallocycle between two stations.

Shuttling Kinetics. There are two possible ways for the metallocycle to move on from one station to the other in the [2]rotaxanes (Figure 2). One is the internal shuttling of the macrocycle (route 1), and the other is the disassembly of the rotaxane into the molecular components followed by their reassembly into the rotaxane (route 2). The latter route is practically negligible around room temperature on the basis of the following observations. Rotaxanes **4a**, **4b**, **5a**, and **5b** could be isolated in pure form by silica gel column chromatography under ordinary laboratory conditions as mentioned earlier. Furthermore, there was no sign of decomposition of the rotaxanes in $CDCl_3$ at least for 1 week at 23 ± 2 °C in the ^{1}H NMR spectroscopy. However, when the temperature was increased > 50 °C, the signals corresponding to the disassembled metallocycle and dumbbell slowly appeared in the ^{1}H NMR spectroscopy (see Supporting Information).

The internal shuttling can occur only when the size of the spacer between two stations is smaller than the cavity size of the metallocycle. The CPK molecular models have demonstrated that the phenyl group is sufficiently small to allow for the shuttling of the metallocycle, but the naphthyl group is sterically bulkier and interferes significantly with the shuttling. The ^{1}H NMR spectra of [2]rotaxanes **4a** and **4b** illustrated well the size effect on the shuttling (Figure 3). [2]Rotaxane **4b**, having a bulkier naphthyl spacer, showed completely separated signals[10] for the methylene $-(CH_2)_4-$ and amide NH of the occupied and unoccupied stations in $CDCl_3$ at room temperature (Figure 3a). On the other hand, the corresponding signals of **4a**, having a smaller phenyl spacer, were highly broad and nearly disappeared on the baseline because of the fast, reversible shuttling of the metallocycle between two stations (Figure 3b). As the temperature was lowered, the signals initially disappeared, split into two sets of broad signals, and eventually looked similar to those in **4b** (see Supporting Information). From the coalescence of the amide NH signals that were not overlapped with other signals, the shuttling rate of the metallocycle in **4a** was calculated to be approximately 670 s^{-1} at 19 °C in $CDCl_3$, corresponding to an activation free energy ($\Delta G^{\ddagger}$) of 13.3 kcal/mol.[11]

Diastereomeric Relationship of Rotaxanes. In the rhenium(I) center of the metallocycle **2**, the chloride and one of carbonyls exist in a trans relationship.[12] As a consequence, two diastereomeric [2]rotaxanes are possible as shown in Figure 4a. This can be noticed in the ^{1}H NMR spectra of the [2]rotaxane **4b** (Figure 3a). Each of the amide NH^a and NH^b signals of the occupied station was split into two sets of broad singlets (in fact, weakly coupled triplets) and appeared at 6.29 and 6.18 ppm and

(10) Signals became broadened but not coalesced as the temperature was raised to 50 °C, above which temperature [2]rotaxane **4b** began to disassemble into its molecular components. Therefore, the shuttling rate of **4b** could not be determined.

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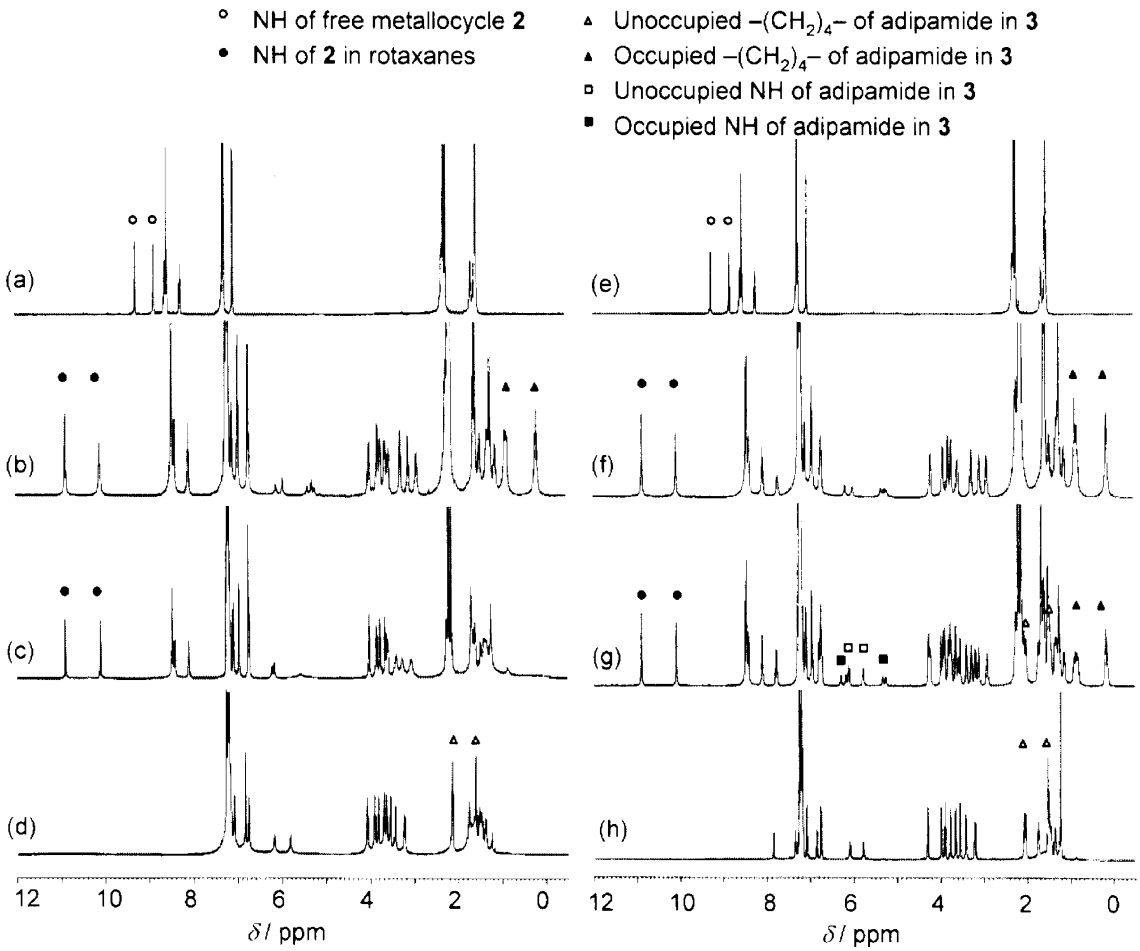

FIGURE 1. ^{1}H NMR spectra (500 MHz, $CDCl_3$, 25 °C) of (a) metallocycle **2**, (b) [3]rotaxane **5a**, (c) [2]rotaxane **4a**, (d) dumbbell **3a**, (e) metallocycle **2**, (f) [3]rotaxane **5b**, (g) [2]rotaxane **4b**, and (h) dumbbell **3b**. (○) NH of free metallocycle **2**. (●) NH of **2** in rotaxanes. (△) Unoccupied $-(CH_2)_4-$ of adipamide in **3**. (▲) Occupied $-(CH_2)_4-$ of adipamide in **3**. (□) Unoccupied NH of adipamide in **3**. (■) Occupied NH of adipamide in **3**.

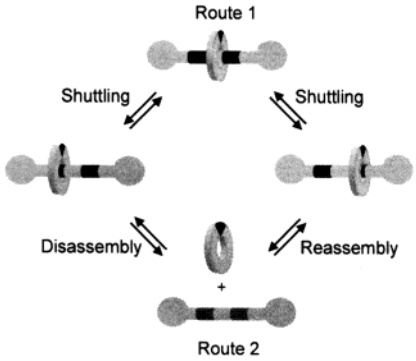

FIGURE 2. Two possible routes for the movement of the metallocycle from one station to another in [2]rotaxane.

5.32 and 5.25 ppm, respectively.[13] The nearly equal intensities of the signals imply a lack of preferential formation of one diastereomer over the other.

Similarly, three diastereomers of the [3]rotaxanes are possible with respect to the relative direction of the chloride: *in*−*in*, *out*−*out*, and *in*−*out* (equivalent to *out*−*in*) (Figure 4b). In the *in*−*in* and *out*−*out* diasteomers, both chlorides (one from each metallocycle) are positioned on the same side (either to the inside spacer or to the outside stopper of the dumbbell). These

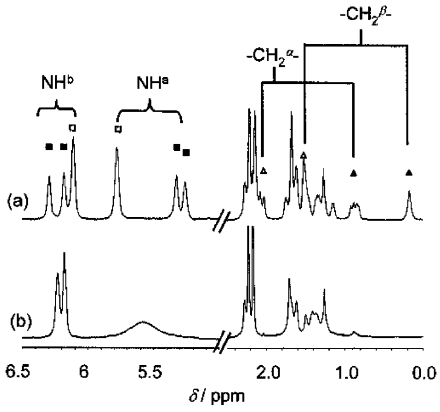

FIGURE 3. Partial ^{1}H NMR spectra (500 MHz, $CDCl_3$, 25 °C) for the amide NH and $-(CH_2)_4-$ regions of the stations in (a) [2]rotaxane **4b** and (b) [2]rotaxane **4a**. (△) Unoccupied $-(CH_2)_4-$ of adipamide in **3b**. (▲) Occupied $-(CH_2)_4-$ of adipamide in **3b**. (□) Unoccupied NH of adipamide in **3b**. (■) Occupied NH of adipamide in **3b**.

(13) Corresponding signals of the unoccupied station were not separated from each other possibly because of the large distance from the rhenium center.

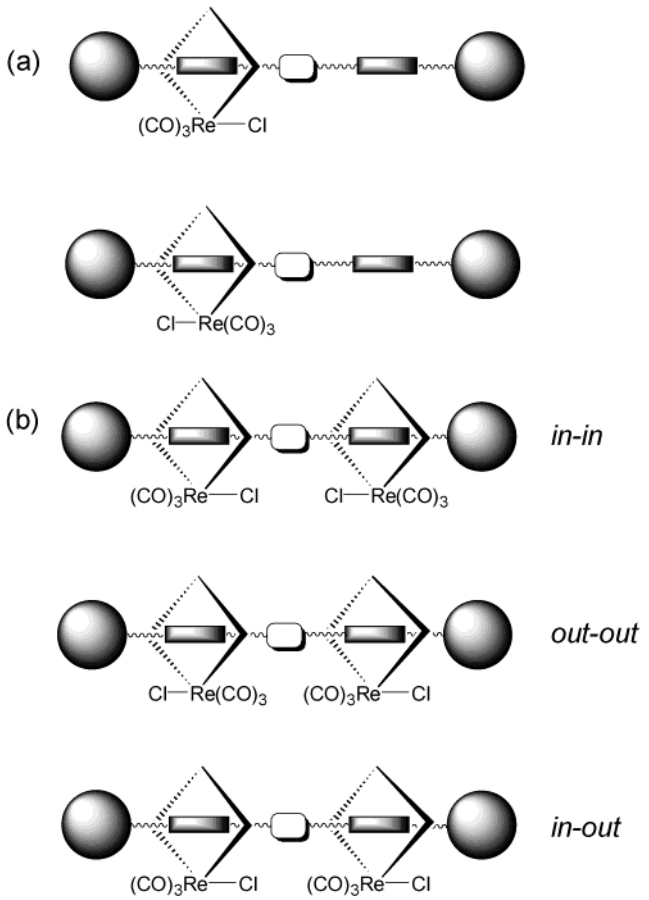

FIGURE 4. Schematic representation for possible diastereomers of (a) [2]rotaxane and (b) [3]rotaxane.

diastereomers can be considered as *meso* [3]rotaxanes, and the NH signals of both stations are expected to have identical chemical shifts. One the other hand, in the *in*−*out* (or *out*−*in*) diastereomer, the chloride of one metallocycle is directed to the spacer and that of the other is directed to the stopper. In this diastereomer, two stations are not equivalent in terms of chemical shift and will give separate signals in the ^{1}H NMR spectroscopy. The diastereomeric relationship of [3]rotaxanes **5a** and **5b** may be recognized in the NH^a resonance of the dumbbell component, which appeared as broad singlets at three or four different positions between 5.2 and 5.4 ppm with almost equal intensities (Figure 5).

Conclusion

Kinetically stable molecular shuttles of [2]rotaxanes, along with [3]rotaxanes, have been prepared on the basis of the rhenium (I)-bridged metallocycle. Especially in the molecular shuttle of the [2]rotaxane, having a smaller phenyl spacer, the metallocycle shuttles back and forth between two adipamide stations with a rate constant of ~670 s^{-1} at 19 °C in $CDCl_3$. This metallocycle-based shuttle is possibly a candidate for the construction of molecular-level machines or devices, considering that transition metals generally display more diverse photophysical and electrochemical properties than organic molecules.[14]

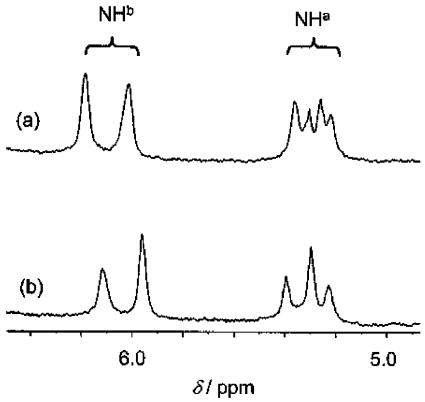

FIGURE 5. Partial ^{1}H NMR spectra (500 MHz, $CDCl_3$, 25 °C) of the amide NH regions in (a) [3]rotaxane **5b** and (b) [3]rotaxane **5a**

Experimental Section

Synthesis of [2]Rotaxane 4a and [3]Rotaxane 5a. Method A. A solution of dumbbell **3a** (80 mg, 0.055 mmol) and metallocycle **2** (124 mg, 0.11 mmol, 2 equiv) in 1,1,2,2-tetrachloroethane (0.27 mL) was heated with stirring at 70 °C for 6 h. After cooling to room temperature, the reaction mixture was directly purified by silica gel column chromatography (MeOH/CH_2Cl_2 = 1:18 for **4a**, EtOAc/CH_2Cl_2 = 2:3 for **5a**) to give [2]rotaxane **4a** (52 mg, 37%) and [3]rotaxnane **5a** (21 mg, 10%) as white solids.

Method B. A solution of the precursor bispyridyl ligand (24 mg, 0.029 mmol), $Re(CO)_5Cl$ (10 mg, 0.029 mmol, 1 equiv), and dumbbell **3a** (43 mg, 0.029 mmol, 1 equiv) in 1,1,2,2-tetrachloroethane (0.14 mL) was heated at 70 °C for 12 h. The column chromatography gave [2]rotaxane **4a** (15 mg, 20%) and [3]rotaxane **5a** (8 mg, 7%) as white solids.

[2]Rotaxane 4a. ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.90 (s, 2H; NH), 10.10 (s, 2H; NH), 8.48−8.47 (m, 6H), 8.41 (d, J = 7.6 Hz, 2H), 8.10 (t, J = 7.6 Hz, 2H), 7.25−7.16 (m, 30 H), 7.09 (d, J = 8.2 Hz, 4H), 6.97 (s, 4H), 6.76−6.73 (m, 8H), 6.23 and 6.18 (m, 2H; NH^b, two diastereomers), 5.58 (br s, 2H; NH^a), 4.03 (br s, 4H), 3.86 (br s, 4H), 3.78 (br s, 4H), 3.67−3.60 (m, 8H), 3.41 (br s, 4H), 3.27 (br s, 4H), 3.07 (br s, 4H), 2.27 (br s, 4H), 2.22 (s, 12H), 2.16 (s, 12H),1.70−1.36 (m, 38 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 195.2, 193.1, 173.3, 173.1, 162.4, 161.9, 157.2, 153.3, 153.2, 152.9, 149.5, 148.6, 148.1, 147.3, 145.8, 139.7, 139.2, 139.1, 135.6, 133.2, 132.4, 131.7, 131.3, 127.6, 126.7, 126.1, 126.0, 125.5, 115.8, 113.4, 70.9, 70.6, 70.5, 70.0, 69.7, 68.3, 67.7, 45.0, 39.9, 39.5, 36.3, 36.2, 35.4, 29.9, 29.8, 29.7, 29.4, 27.0, 26.5, 26.0, 24.3, 23.0, 19.1, 16.1. IR (KBr): 3258, 2024, 1921, 1885, 1688, 1645 cm^{-1}. FAB-MS m/z (%): 2598.7 (10) $[MH]^+$, 2562.7 (3), $[M - Cl]^+$. Anal. Calcd for $C_{145}H_{162}ClN_{12}O_{19}Re$: C, 67.02; H, 6.28; N, 6.47. Found: C, 67.10; H, 6.47; N, 6.55.

[3]Rotaxane 5a. ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.88 (s, 4H; NH), 10.10−10.08 (m, 4H; NH), 8.47−8.46 (m, 12H), 8.40 (d, J = 7.5 Hz, 4H), 8.09 (t, J = 7.6 Hz, 4H), 7.24−7.17 (m, 30H), 7.10 (d, J = 8.5 Hz, 4H), 6.97 (s, 8H), 6.74−6.72 (m, 8H), 6.12 and 5.96 (m, 2H; NH^b, three diastereomers), 5.39, 5.30 and 5.23 (m, 2H, NH^a, three diastereomers), 4.00 (m, 4H), 3.92−3.40 (m, 16H), 3.29 (br s, 4H), 3.11 (br s, 4H), 2.92 (m, 4H), 2.26 (br s, 8H), 2.21 (s, 24H), 2.16 (s, 24H), 1.61 (br s, 16H), 1.48−1.13 (m, 12H), 0.91−0.87 (m, 8H), 0.19 (br s, 8H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 195.0, 192.8, 173.3, 173.2,

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173.1, 173.0, 162.1, 161.6, 156.9, 156.8, 152.8, 152.7, 149.3, 148.3, 147.9, 147.0, 145.5, 139.5, 139.0, 139.2, 139.1, 139.0, 135.4, 133.0, 132.2, 131.5, 131.1, 127.4, 126.4, 125.8, 125.7, 125.3, 115.7, 113.2, 70.6, 70.4, 70.3, 69.8, 69.7, 69.1, 69.0, 68.1, 67.4, 67.3, 44.8, 39.9, 39.8, 39.4, 36.0, 35.9, 34.4, 34.3, 34.2, 29.7, 29.5, 29.3, 29.1, 26.7, 26.2, 25.8, 25.7, 23.2, 23.1, 23.0, 22.9, 22.8, 18.9, 15.8. IR (KBr): 3260, 2024, 1920, 1884, 1693, 1646 cm^{-1}. FAB-MS *m*/*z* (%): 3734.0 (1) $[M]^+$. Anal. Calcd for $C_{198}H_{214}Cl_2N_{20}O_{26}Re_2$: C, 63.70; H, 5.78; N, 7.50. Found: C, 63.74; H, 5.97; N, 7.47.

Synthesis of [2]Rotaxane 4b and [3]Rotaxane 5b. [2]-Rotaxane **4b** and [3]rotaxane **5b** were synthesized using dumbbell **3b** instead of **3a** under the same conditions described for the preparation of **4a** and **5a**. Method A gave **4b** and **5b** in 37 and 18% yields, respectively, and method B provided **4b** and **5b** in 30 and 11% yields, respectively.

[2]Rotaxane 4b. ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.88 (s, 2H; NH), 10.08 (s, 2H; NH), 8.48−8.46 (m, 6H), 8.41 (d, J = 7.6 Hz, 2H), 8.10 (t, d, J = 7.7 Hz, 2H), 7.80−7.76 (m, 2H), 7.24−7.17 (m, 32H), 7.11−7.07 (m, 4H), 6.95 (s, 4H), 6.80−6.74 (m, 6H), 6.29 and 6.18 (m, 1H; occupied NH^b, two diastereomers), 6.11 (s, 1H; unoccupied NH^b), 5.78 (s, 1H; unoccupied NH^a), 5.32 and 5.25 (m, 1H; occupied NH^a, two diastereomers), 4.26−4.23 (m, 4H), 3.98−3.90 (m, 6H), 3.82−3.77 (m, 6H), 3.65−3.54 (m, 6H), 3.40 (m, 2H), 3.28 (m, 2H), 3.19 (m, 2H), 3.11 (m, 2H), 2.92 (m, 2H), 2.26−2.02 (m, 32H), 1.74−1.13 (m, 26H), 0.92−0.79 (m, 4H), 0.17 (br s, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 195.0, 194.9, 192.8, 192.7, 173.3, 173.2, 173.1. 173.0, 172.8, 172.7, 162.1, 161.6, 157.0, 156.8, 156.7, 154.4, 154.3, 154.2, 154.1, 154.0, 152.7, 149.2, 148.3, 147.9, 147.0, 145.5, 139.5, 139.0, 138.9, 138.8, 135.4, 132.9, 132.2, 131.5, 131.1, 127.4, 126.7, 126.6, 126.4, 125.8, 125.7, 125.3, 125.1, 114.8, 114.7, 114.4, 114.2, 113.2, 105.8, 70.9, 70.8, 70.5, 70.4, 70.3, 69.8, 69.7, 69.2, 69.1, 69.0, 68.0, 67.6, 67.4, 67.3, 64.3, 44.7, 39.9, 39.8, 39.4, 39.1, 36.2, 36.0, 35.9, 35.8, 35.1, 35.0, 34.3, 34.2, 29.7, 29.5, 29.4, 29.3, 29.2, 29.1, 26.7, 26.2, 25.8, 25.0, 24.7, 23.2, 23.1, 22.9, 22.8, 22.7, 18.8, 15.8. IR (KBr): 3301, 2024, 1921, 1886, 1689, 1650 cm^{-1}. FAB-MS *m*/*z* (%): 2649.5 (5) $[MH]^+$, 2612.5 (1.5) $[M - Cl]^+$. Anal. Calcd for $C_{149}H_{164}ClN_{12}O_{19}Re$: C, 67.57; H, 6.24; N, 6.35. Found: C, 67.47; H, 6.59; N, 6.09.

[3]Rotaxane 5b. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.87 (s, 4H; NH), 10.08 (s, 4H; NH), 8.45(br s, 12H), 8.40 (d, J = 7.2 Hz, 4H), 8.08 (t, J = 7.2 Hz, 4H), 7.73 (m, 2H), 7.24−7.17 (m, 32H), 7.10 (d, J = 8.3 Hz, 4H), 6.94 (s, 8H), 6.77−6.73 (m, 6H), 6.18 and 6.01 (m, 2H; NH^b, three diastereomers), 5.36, 5.30, 5.26 and 5.21 (m, 2H; NH^a, three diastereomers), 4.22 (m, 4H), 3.93 (br s, 4H), 3.81−3.74 (m, 8H), 3.59 (m, 4H), 3.27 (br s, 4H), 3.09 (br s, 4H), 2.92 (br s, 4H), 2.25 (br s, 8H), 2.18 (s, 24H), 2.13 (s, 24H), 1.57 (s, 12H), 1.48−1.13 (m, 16H), 0.89−0.84 (m, 8H), 0.15 (br s, 8H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 195.0, 192.9, 173.2, 173.0, 162.1, 161.6, 156.8, 152.6, 152.3, 149.2, 148.3, 147.9, 147.0, 145.5, 139.5, 135.4, 132.9, 132.2, 131.5, 131.1, 127.4, 126.4, 125.8, 125.2, 113.2, 105.8, 70.8, 70.4, 69.8, 69.1 69.0, 68.0, 67.3, 39.9, 39.4, 36.0, 34.3, 34.2, 29.7, 29.5, 29.3, 29.1, 26.7, 26.2, 25.8, 23.1, 22.8, 18.8, 15.8. IR (KBr): 3275, 2024, 1920, 1885, 1685, 1648 cm^{-1}. FAB-MS *m*/*z* (%): 3784.9 (3) $[M]^+$. Anal. Calcd for $C_{202}H_{216}Cl_2N_{20}O_{26}Re_2$: C, 64.13; H, 5.75; N, 7.40. Found: C, 64.28; H, 6.15; N, 7.30.

Determination of Shuttling Rate Constant. For [2]-rotaxane **4a**, the averaged NH signals of the occupied and unoccupied stations were observed in ^{1}H NMR spectroscopy at room temperature due to fast, reversible shuttling of the metallocycle between two stations. When a $CDCl_3$ solution containing **4a** (2 mM) was cooled below 15 °C, the shuttling slowed and the peaks were separated (see Supporting Information). The coalescence temperature (T_c) and the difference in hertz between two signals ($\Delta\nu$) were 19 °C and 301 Hz, respectively. The rate constant (k) and activation barrier ($\Delta G^{\ddagger}$) were calculated to be ~670 s^{-1} and 13.3 kcal/mol, respectively, on the basis of the equations shown below.[11]

$$k = 2.22\Delta\nu$$

$$k = \chi \times \frac{k_B T}{h} e^{-\Delta G^{\ddagger}/RT}$$

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Supporting Information Available: FAB-mass spectra of all rotaxanes and temperature-dependent ^{1}H NMR spectra of [2]rotaxanes **4a** and **4b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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