

Synthesis, Structure and Complexation Ability of Novel Metalloreceptors Containing Two Pincer Complexes of Palladium(II)

Tatsuya Nabeshima,^{*,[a]} Daisuke Nishida,^[a] Shigehisa Akine,^[a] and Toshiyuki Saiki^[a]

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Metalloreceptors **1a** and **1b** were synthesized by palladation of 42- and 54-membered crown ethers that have two SCS-pincer ligand moieties. The X-ray crystallographic analysis reveals that the metalloreceptor **1b** has a folded structure in which the two pincer-Pd moieties are stacked in a parallel manner. The metalloreceptor **1b** recognizes the aromatic bi-

dentate guests 4,4'-bipyridine, pyrazine, and pyrimidine and binds to them in a bridging fashion to form the corresponding bimacrocyclic 1:1 complex.

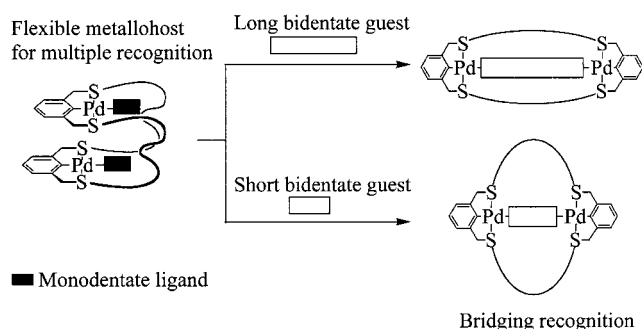
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Metalloreceptors have recently attracted much attention in supramolecular chemistry because the physical and chemical properties of the metal center can be applied in guest binding, sensing, and regulation of molecular functions.^[1] In particular, the coordination of various ligands to metals is very useful for the formation of a stable supramolecular system.^[2–6] Combination of the coordinate bonding and other intermolecular interactions provides a strong and selective recognition.

Complexes between Pd and pincer ligands are useful as they provide a nice coordination site for host-guest interaction.^[7] For example, crown ethers containing a Pd center inside the ring and molecular recognition have been reported.^[8–10] Cooperative binding of the Pd unit and the crown ether moiety to nucleobases such as cytosine and adenine was observed in this system.^[11,12] However, a host molecule containing several pincer complexes as a binding site has not been synthesized although this type of host is very interesting as a multi-point receptor.

Here we report the synthesis, structure and molecular recognition ability of large macrocyclic hosts **1**, which contain two pincer complexes of Pd^{II}. The metallohosts are expected to bind bidentate guests of different sizes in the cavity because the framework of these hosts is flexible so as to cause induced-fit recognition (Scheme 1).

Metallohosts **1** containing the two Pd centers were prepared according to Scheme 2. Diols **2a**^[13] and **2b**^[14] were treated with *p*-toluenesulfonyl chloride to afford **3a** and **3b** in 80% and 63% yield, respectively. Reaction of dithiol **4**^[15] with **3a**, **3b** in the presence of K₂CO₃ afforded diols **5a**, **5b**,



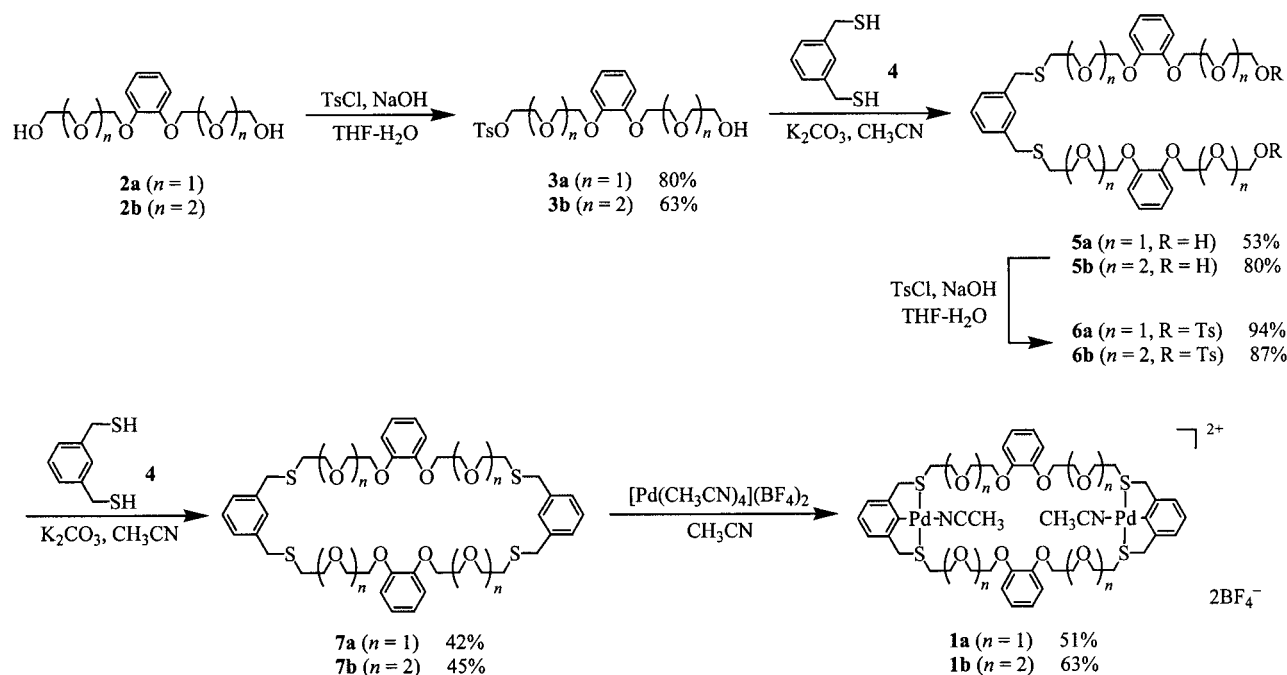
Scheme 1. Recognition of bidentate guests in a bridging fashion

and the following tosylation gave **6a**, **6b**. The ditosylates **6a** and **6b** were then treated with **4** under high dilution conditions to give crown ethers **7a** and **7b** in 42% and 45% yield, respectively. Metallation of **7** with [Pd(CH₃CN)₄](BF₄)₂^[16] yielded metallohosts **1a**, **1b**.

All spectroscopic data are consistent with the formula of **1** (see Exp. Sect.). Palladation of **7** caused broadening of the ¹H NMR signals, probably due to the enhanced rigidity of the structure, which restricts the free rotation of the methylene group. On metallation, downfield shifts of the signals for the SCH₂CH₂ protons (e.g. δ = 2.60 for **7b**, δ = 3.32 for **1b**, Figure 1) and the benzyl protons is observed. This is elucidated by the decreased electron-density of these protons. ESI-MS for **1b** gave signals at *m/z* = 614.1 (C₅₂H₇₀O₁₂S₄Pd₂, [1b–2BF₄–2CH₃CN]²⁺) and *m/z* = 1247.2 (C₅₂H₇₀FO₁₂S₄Pd₂, [1b–2BF₄–2CH₃CN+F]⁺), (the F[–] anion was obtained from decomposition of the BF₄[–] anion during the ESI-MS measurements). In addition, the X-ray crystallographic analysis clarified the structure of **1b** (Figure 2). The two complex moieties exhibit square-planar geometry at Pd, with three donor atoms provided by the rigid SCS chelate. The Pd–S distances are in

^[a] Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan
Fax: (internat.) +81-29-853-6503
E-mail: nabesima@chem.tsukuba.ac.jp

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 Scheme 2. Synthesis of metallohosts **1**

the range between 2.334 Å and 2.286 Å. The two aromatic rings, which bind the palladium atoms, are stacked. The distance between the mean planes of the benzene rings (3.4 Å) suggests the existence of π - π interactions. Furthermore, the palladium atoms are located in closely proximity of the sulfur atoms. The distance between Pd2–S2 (3.371 Å) is shorter than the sum of van der Waals radii for sulfur and palladium (3.43 Å). Two CH₃CN molecules coordinate to Pd₂, and the Pd1–N1 and Pd2–N2 distances are 2.105 Å and 2.092 Å, respectively.

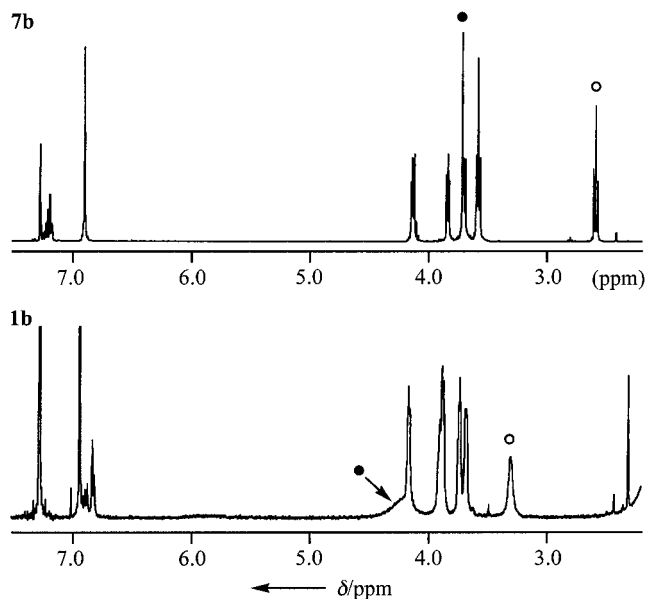


Figure 1. ¹H NMR spectral changes of **7b** upon palladation (400 MHz, CDCl₃); SCH₂CH₂O and benzyl protons are indicated with open and filled circles, respectively

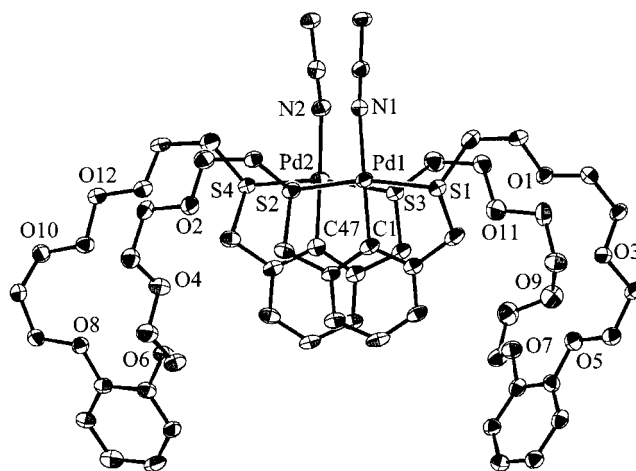


Figure 2. Crystal structure of **1b**; thermal ellipsoids are drawn at 30% probability level; the minor component of the disordered atoms, counter anions, and hydrogen atoms are omitted for clarity

The interaction between **1b** and 4,4'-bipyridine was evaluated by ¹H NMR spectroscopy (Figure 3). Signals of free **1b** disappear when 1.0 equiv. of 4,4'-bipyridine is added, and no change is observed in the presence of excess ligand. This result supports the 1:1 complexation between **1b** and 4,4'-bipyridine in a bridging fashion as illustrated in Scheme 1. ESI-MS also supports the 1:1 complexation. A mixture of **1b** and 4,4'-bipyridine gives a signal at $m/z = 692.1$ (calcd. for C₆₂H₇₈N₂O₁₂S₄Pd₂, [**1b**–2BF₄–2CH₃CN+4,4'-bipyridine]²⁺). In addition, the absorbance of **1b** at 304 nm increases until 1.0 equivalent of 4,4'-bipyridine is added (Figure 4). All the experiments described above indicate the 1:1 complexation between **1b** and 4,4'-

bipyridine. Pyrazine and pyrimidine as bidentate ligands also give rise to 1:1 complexation, as seen by ^1H NMR spectroscopic experiments, although the distances involving the ligating nitrogen atoms of pyrazine and pyrimidine are much shorter than that of 4,4'-bipyridine.

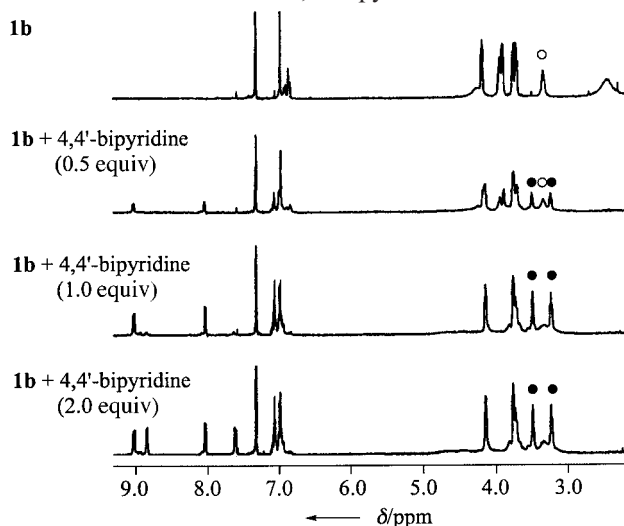


Figure 3. ^1H NMR spectral changes of **1b** upon addition of 4,4'-bipyridine (400 MHz, CDCl_3 , $[\text{1b}] = 2.0 \text{ mM}$); signals for free and complexed **1b** are indicated with open and filled circles, respectively

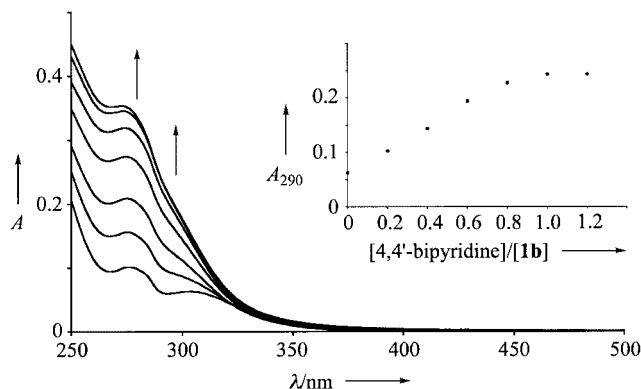


Figure 4. UV/Vis spectral changes of **1b** upon addition of 4,4'-bipyridine (CHCl_3 , $[\text{1b}] = 1.0 \times 10^{-5} \text{ M}$)

Complexation of **1b** with these bidentate ligands should give two small cavities which are almost half as large as that of **1b** (Scheme 1). The change in cavity size is very interesting, because this strategy may be most useful to regulate recognition ability of artificial receptors.^[17–19]

In conclusion, we have prepared metallohosts **1** bearing two Pd centers inside the cavity, and studied the structure and guest-binding ability of **1b** in detail by ^1H , ^{13}C NMR spectroscopy or X-ray crystallographic analysis. We are currently investigating this bridging strategy to control molecular recognition.

Experimental Section

Synthesis of 1a: A solution of $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$ (302 mg, 0.680 mmol) in acetonitrile (10 mL) was added to a solution of

crown ether **7a** (271 mg, 0.322 mmol) in acetonitrile (20 mL), and the mixture was stirred for 2 h at room temperature. The mixture was refluxed for 13 h, and then the solvent was evaporated. The residue was dissolved in dichloromethane (20 mL) and filtered. The filtrate was concentrated and dried in vacuo to afford **1a** (215 mg, 51%) as a yellow solid, which was further purified by recrystallization from acetonitrile to give pale yellow crystals. ^1H NMR (400 MHz, CD_3CN): $\delta = 3.30$ (br. s, 8 H), 3.80 (t, $J = 4.2 \text{ Hz}$, 8 H), 3.90 (br. t, 8 H), 4.12 (t, $J = 4.2 \text{ Hz}$, 8 H), 4.29 (br. t, 8 H), 6.77 (d, $J = 7.6 \text{ Hz}$, 4 H), 6.90–6.99 (m, 10 H) ppm. ^{13}C NMR (100 MHz, CD_3CN): $\delta = 40.00$, 46.78 (br.), 69.20, 70.54 ($\times 2$, CH_2), 114.78, 122.39, 123.96, 126.65 (CH), 149.49, 151.65 (br.), 156 (br., C) ppm. ESI-MS: m/z found 1071.1 $[\text{1a}-2\text{BF}_4-2\text{CH}_3\text{CN}+\text{F}]^+$. $\text{C}_{48}\text{H}_{60}\text{B}_2\text{F}_8\text{N}_2\text{O}_8\text{Pd}_2\text{S}_4$: calcd. C 44.09, H 4.62, N 2.14; found C 43.78, H 4.57, N 2.28.

Synthesis of 1b: **1b** was prepared from **7b** (319 mg, 0.315 mmol) and $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$ (302 mg, 0.680 mmol) in 63% yield by a procedure similar to that for **1a**. **1b**: yellow oil. ^1H NMR (400 MHz, CDCl_3): $\delta = 3.32$ (br. s, 8 H), 3.67–3.69 (m, 8 H), 3.73–3.75 (m, 8 H), 3.86–3.89 (m, 8 H), 3.90–3.92 (m, 8 H), 4.16 (t, $J = 4.0 \text{ Hz}$, 8 H), 4.18 (br., 8 H), 6.79 (d, $J = 7.0 \text{ Hz}$, 4 H), 6.85 (t, $J = 7.0 \text{ Hz}$, 2 H), 6.92 (s, 8 H) ppm. ^{13}C NMR (100 MHz, CD_3CN): $\delta = 39.68$, 46.35, 69.40, 70.50 ($\times 2$), 71.29, 71.38 (CH_2), 115.09, 122.40, 124.01, 126.65 (CH), 149.62, 151.72, 156.59 (C) ppm. ESI-MS: m/z found 1247.2 $[\text{1b}-2\text{BF}_4-2\text{CH}_3\text{CN}+\text{F}]^+$. $\text{C}_{56}\text{H}_{76}\text{B}_2\text{F}_8\text{N}_2\text{O}_{12}\text{Pd}_2\text{S}_4\cdot\text{CHCl}_3$: calcd. C 42.70, H 4.84, N 1.75; found C 42.30, H 5.06, N 2.08.

X-ray Crystallographic Analysis of 1b:^[20] Pale yellow crystals ($0.3 \times 0.15 \times 0.1 \text{ mm}$) were obtained after oily **1b** was allowed to stand at room temperature. $\text{C}_{56}\text{H}_{76}\text{B}_2\text{F}_8\text{N}_2\text{O}_{12}\text{Pd}_2\text{S}_4$, $M = 1483.85$. Intensity data were collected at 130 K on a Rigaku R-Axis Rapid diffractometer with Mo- K_α radiation ($\lambda = 0.71069 \text{ \AA}$). Reflection data were corrected for Lorentz and polarization factors, and for absorption using the multi-scan method. Crystal system, triclinic, $a = 13.2731(12) \text{ \AA}$, $b = 14.4368(16) \text{ \AA}$, $c = 18.1120(19) \text{ \AA}$, $\alpha = 71.267(4)^\circ$, $\beta = 71.424(3)^\circ$, $\gamma = 86.580(3)^\circ$, $V = 3112.0(6) \text{ \AA}^3$, space group $P\bar{1}$, $Z = 2$, $\mu(\text{Mo}-K_\alpha) = 0.797 \text{ mm}^{-1}$, $D_{\text{calcd.}} = 1.584 \text{ g/cm}^3$, $2\theta_{\text{max}} = 52^\circ$, collected reflections 25108, unique reflections 12053 ($R_{\text{int}} = 0.0719$). The structure was solved by Patterson methods (DIRDIF-99)^[21] and refined by full-matrix least-squares on F^2 using SHELXL 97.^[22] The non-hydrogen atoms were refined anisotropically except for the minor component of disordered sulfur atoms (S4 and S6). Hydrogen atoms were idealized by using the riding models. Occupancy factor involving the disordered sulfur atoms was refined to be 0.888(3) for S3 and S5, and 0.112(3) for S4 and S6. $R_1 = 0.0618$ [$I > 2\sigma(I)$], $wR_2 = 0.1537$ (all data), GOF (F^2) = 1.036 for 786 parameters.

Acknowledgments

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