# Dynamic Assembly of Coordination Boxes from (en)Pd(II) Unit and a Rectangular Panel-Like Ligand: NMR, CSI-MS, and X-ray Studies

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The simple combination of square planar coordination geometry of Pd(II) or Pt(II) with pyridine-based ligands offers an efficient method for the self-assembly of nanometer-sized frameworks such as macrocycles, cages, catenanes, tubes, and capsules.[1] To expand the structures of pyridyl-coordinated Pd(II) complexes into more rigid and bigger coordination frameworks, one can replace a mono-coordinating 4-pyridyl group by a doubly ligating 3,5-bis-(3-pyridyl)phenyl unit. According to this idea, 4,4′-bipyridine,
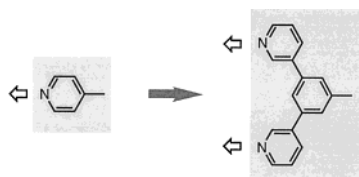
which is the simplest pyridine-based bridging ligand, is modified into tetradentate ligand **1**). This ligand is expected to take a panel-like conformation and, on complexation with (en)Pd(NO$_3$)$_2$ (**2**), assemble into large discrete box structures such as **3**$^{12+}$ and **4**$^{16+}$ in analogy to the assembly of trinuclear and tetranuclear cyclic complexes from **2** and 4,4′-bipyridine.[2,3] Here we report that these expected box structures are efficiently formed in a *dynamic* fashion. Namely, the boxes are in equilibrium and smoothly

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(1) Reviews: (a) Fujita, M. *Chem. Soc. Rev.* **1998**, *27*, 417. (b) Biradha, K.; Fujita, M. In *Advances in Supramolecular Chemistry;* Gokel, G. W., Ed.; JAI Press Inc.: Connecticut, 2000; Vol. 6, p 1. (c) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853.
(2) 4,4′-Bipyridine-based coordination boxes: (a) Fujita, M.; Yazaki, J.; Ogura, K. *J. Am. Chem. Soc.* **1990**, *112*, 5645. (b) Stang, P. J.; Cao, D. H. *J. Am. Chem. Soc.* **1994**, *116*, 4981. (c) Slone, R. V.; Hupp, J. T.; Stern, C. L.; Albrecht-Schmitt, T. E. *Inorg. Chem.* **1996**, *35*, 4096.
(3) Coordination boxes with other ligands: (a) Stang, P. J.; Olenyuk, B. *Acc. Chem. Res.* **1997**, *30*, 502. (b) Stang, P. J. *Chem. Eur. J.* **1998**, *4*, 19. (c) Fujita, M.; Sasaki, O.; Mitsuhashi, T.; Fujita, T.; Yazaki, J.; Yamaguchi, K.; Ogura, K. *J. Chem. Soc., Chem. Commun.* **1996**, 1535. (d) Rauter, H.; Mutikainen, I.; Blomberg, M.; Lock, C. J. L.; OmarOchoa, P.; Freisinger, E.; Randaccio, L.; Chiarparin, E.; Lippert, B. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1296. (e) Hanan, G. S.; Volkmer, D.; Schubert, U. S.; Lehn, J.-M.; Baum, G.; Fenske, D. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1843. (f) Duan, C.-Y.; Liu, Z.-H.; You, X.-Z.; Xue, F.; Mak, T. C. W. *Chem. Commun.* **1997**, 381. (g) Li, J.; Zeng, H.; Chen, J.; Wang, Q.; Wu, X. *Chem. Commun.* **1997**, 1213. (h) Cotton, F. A.; Daniels, L. M.; Lin, C.; Murillo, C. A. *J. Am. Chem. Soc.* **1999**, *121*, 4538. (i) Bonar-Law, R. P.; McGrath, T. D.; Singh, N.; Bickley, J. F.; Steiner, A. *Chem. Commun.* **1999**, 2457. (j) Bu, X.-H.; Morishita, H.; Tanaka, K.; Biradha, K.; Furusho, S.; Shionoya, M. *Chem. Commun.* **2000**, 971.
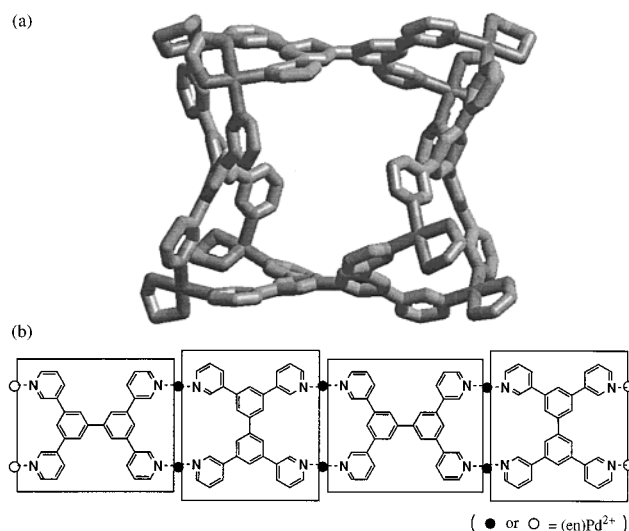
Figure 1. (a) X-ray structure of coordination box **6**$^{16+}$. (b) The linkage connectivity in **6**$^{16+}$ involving two conformations (A and B).

interconvertable. Coldspray ionization mass spectroscopy (CSI-MS), which was developed recently by some of us,[4] is found to be very effective to study both kinetic and thermodynamic products in the assembly process (Scheme 1).

Scheme 1
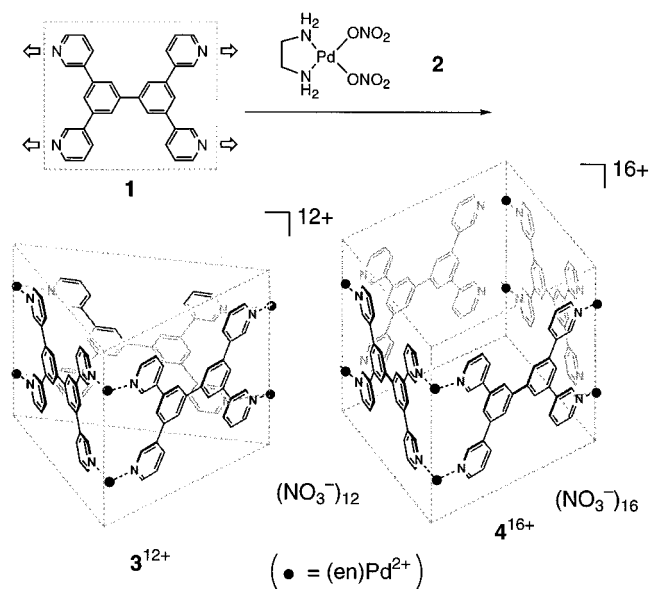
Treatment of **2** (1.25 × 10^{-2} mmol) with ligand **1** (0.62 × 10^{-2} mmol) at 50 °C for 4 d in D$_2$O−CD$_3$OD (1:1, 0.5 mL) gave rise to one major product, which was assigned as tetrameric box **4**$^{16+}$ by CSI-MS after being isolated as PF$_6$ salt in 88% yield (prominent peaks at *m/z* = 1688.8 [**4**·13PF$_6$]$^{3+}$ and 1230.8 [**4**·12PF$_6$]$^{4+}$). In ^{1}H NMR, a set of six protons was observed in consistent with the *D*$_{4h}$ structure of **4**$^{16+}$.

In addition to box **4**$^{16+}$, uncharacterized minor products were also detected in ^{1}H NMR. Being in equilibrium, all of the products constituted a dynamic library of box structures from a single ligand.[5] From the library, we found that two box structures, both

(4) Cold ESI-MS is a sort of electrospray ionization (ESI) MS operated under low temperature: Sakamoto, S.; Fujita, M.; Kim, K.; Yamaguchi, K. *Tetrahedron* **2000**, *56*, 955.
(5) Lehn, J.-M. *Chem. Eur. J.* **1999**, *5*, 2455.
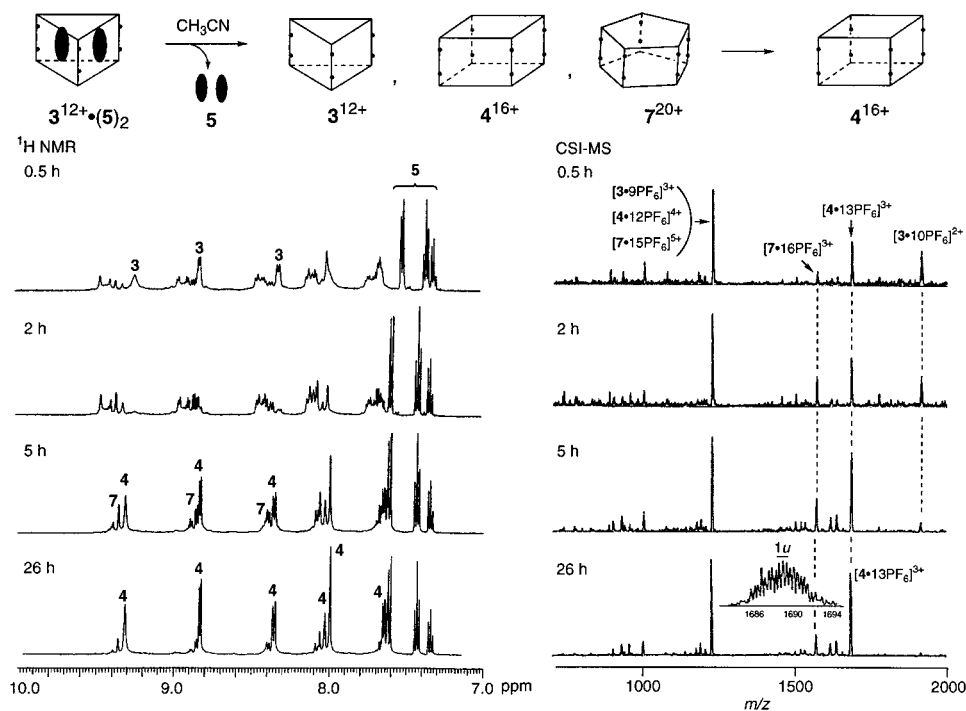
Figure 2. ^{1}H NMR (500 MHz, CD$_3$CN, aromatic region) and CSI-MS (CH$_3$CN) showing the conversion of 3^{12+} into 4^{16+} at the concentration of 6.7 mg/mL. CSI-MS conditions: accel volt, 5.0 kV; needle volt, 2.2 kV; orifice volt, 150 V; spray temp, −20 °C.

of which were very minor products under normal conditions, were quantitatively formed by the following two methods.

The first method is to use an organic template. When biphenyl (**5**) was added as a template, trimeric 3^{12+} was formed quantitatively.[6] Thus, template **5** (2.0×10^{-2} mmol) was suspended in the reaction mixture of **2** (2.0×10^{-2} mmol) and **1** (1.0×10^{-2} mmol) in D$_2$O (1.0 mL) at 80 °C. After 7 h, the mixture became an almost clear solution and, after filtration, ^{1}H NMR spectrum showed a set of six signals for trimeric complex 3^{12+} and another set of three signals for **5** in aromatic region (see Supplementary Information). The biphenyl protons were significantly upfield shifted probably due to inclusion in the deep cavity of 3^{12+}. The structure was strongly supported by conventional ESI-MS measurement which displayed five peaks at m/z = 1502.9, 982.1, 720.8, 564.3, and 460.3 corresponding to the cations [$3\cdot10NO_3$]$^{2+}$, [$3\cdot9NO_3$]$^{3+}$, [$3\cdot8NO_3$]$^{4+}$, [$3\cdot7NO_3$]$^{5+}$, and [$3\cdot6NO_3$]$^{6+}$. The integration of the ^{1}H NMR signals showed the enclathration of two biphenyl molecules in the cavity of trimeric prism 3^{12+}. The host−guest complex was precipitated by adding an excess amount of NH$_4$PF$_6$ to the reaction solution and was isolated as a pure PF$_6$ salt in 53% yield. Elemental analysis agreed with the formula of $3\cdot12(PF_6)\cdot2(\mathbf{5})\cdot2H_2O$.

The second method to select a single box structure from the library is crystallization.[7] When THF vapor was slowly diffused into the H$_2$O−CH$_3$CN solution of **1** and **2** for a few weeks, a single-crystal suitable for diffraction study was obtained. X-ray diffraction experiments showed the formation of unexpected tetrameric box 6^{16+}, which has the same composition as 4^{16+} but different linkage connectivity (Figure 1).[8] In the ^{1}H NMR of 3^{12+}

and 4^{16+}, the proposed planer conformation of ligand **1**, shown in Scheme 1, was supported by the observation of strong NOE (PyH_a−ArH_f and PyH_d−ArH_e). However, the solid structure 6^{16+} involved two conformations (Figure 1b). The formation of this linkage is possibly ascribed to a packing effect and unknown equilibrium brought by THF diffusion[9].

The dynamic behavior of the coordination boxes in solution was simultaneously monitored by ^{1}H NMR and CSI-MS.[10] Combination of these two methods was shown to be quite effective to study the dynamic assembly process. Thus, clathrate complex $3\cdot12(PF_6)\cdot2(\mathbf{5})\cdot2H_2O$ was dissolved in CH$_3$CN or CD$_3$CN. In this media, guest **5** was immediately liberated, leaving empty 3^{12+}. Interestingly, the analysis of the reorganizing process from 3^{12+} into 4^{16+} showed the presence of pentamer 7^{20+} as a kinetic intermediate (Figure 2). After 0.5 h, trimeric prism 3^{12+} was observed with some uncharacterized components by NMR, whereas CSI-MS clearly showed the formation of 3^{12+}, 4^{16+}, and pentamer 7^{20+}. After 2 h, components were hardly analyzed by NMR, but CSI-MS showed the increase of 4^{16+} and 7^{20+} and the decrease of 3^{12+}. After 5 h, both NMR and CSI-MS displayed two major components, which were easily assigned as 4^{16+} and 7^{20+} by comparing the spectra. After 26 h, the only major component is tetrameric box 4^{16+} as confirmed by both methods.

Supporting Information Available: Experimental procedures and spectroscopic characterization of ligand **1**, tetramer 4^{16+}, and trimer 3^{12+}, and the details of the X-ray diffraction study of 6^{16+} (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) Guest-templated assembly: (a) Anderson, S.; Anderson, H. L.; Sanders, J. K. M. *Acc. Chem. Res.* **1993**, *26*, 469. (b) Fujita, M.; Nagao, S.; Ogura, K. *J. Am. Chem. Soc.* **1995**, *117*, 1649. (c) Bilyk, A.; Harding, M. M. *J. Chem. Soc., Chem. Commun.* **1995**, 1697.

(7) Baxter, P. N. W.; Lehn, J.-M.; Rissanen, K. *Chem. Commun.* **1997**, 1323.

(8) Crystallographic data of **6**: See Supporting Information.

(9) Attempts to obtain the NMR of pure 6^{16+} were unsuccessful because of its rapid isomerization in D$_2$O−CD$_3$OD into more stable solution structures.

(10) ESI-MS and ^{1}H NMR observation of kinetic and thermodynamic products in the metal-directed self-assembly: Hasenknopf, B.; Lehn, J.-M.; Boumediene, N.; Leize, E.; Dorsselaer, A. V. *Angew. Chem., Int. Ed.* **1998**, *37*, 3265.