[3] J.-P. Simonato, J. Pecaut, L. L. Pape, J.-L. Oddou, C. Jeandey, M. Shang, W. R. Scheidt, J. Wojacynski, S. Wolowiec, L. Latos-Grazynski, J.-C. Marchon, *Inorg. Chem.* **2000**, *39*, 3978–3987.

[4] T. Ikeue, T. Saitoh, T. Yamaguchi, Y. Ohgo, M. Nakamura, M. Takahashi, M. Takeda, *Chem. Commun.* **2000**, 1989–1990.

[5] D. R. Evans, C. A. Reed, *J. Am. Chem. Soc.* **2000**, *122*, 4660–4667.

[6] Abbreviations: oetpp, T*i*PrP, and TEtP are dianions of 2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetraphenylporphyrin, *meso*-tetraisopropylporphyrin, and *meso*-tetraethylporphyrin, respectively. dmap: 4-dimethylaminopyridine; py: pyridine; 4-CNpy: 4-cyanopyridine; HIm: imidazole; 2-MeIm: 2-methylimidazole.

[7] J. Sams, T. B. Tsin in *The Porphyrins*, *Vol. IV* (Ed.: D. Dolphin), Academic Press, New York, **1979**, pp. 425–478.

[8] K. D. Hodges, R. G. Wollmann, S. L. Kessel, D. N. Hendrickson, D. G. Van Derveer, E. K. Barefield, *J. Am. Chem. Soc.* **1979**, *101*, 906–917.

[9] W. O. Koch, V. Schünemann, M. Gerdan, A. X. Trautwein, H.-J. Krüger, *Chem. Eur. J.* **1998**, *4*, 686–691.

[10] EPR measurements: **1:** $g = 2.79, 2.35, 1.63$ ($S = 1/2$); $g = 3.25$ ($S = 1/2$). **2:** $g = 3.06, 2.14, 1.42$ ($S = 1/2$). **3:** $g = 3.39, 2.08$ ($S = 1/2$). **4**: $g = 4.28, 3.80, 2.08$ ($S = 3/2$).

[11] The signals corresponding to the *meso* carbon atoms were assigned unambiguously by the use of *meso*-^{13}C-enriched complexes. The α-pyrrole and *ipso*-phenyl signals were assigned on the basis of their coupling with the *meso* carbon atom of the labeled complexes.

[12] High-spin and low-spin complexes show *meso* signals at $\delta = 500-600$ and $50-100$, respectively, at room temperature.[13] Some low-spin complexes with the less common $(d_{xz}, d_{yz})^4(d_{xy})^1$ electronic configuration exhibit the signals further downfield ($\delta = 700-800$).[14]

[13] "Physical Bioinorganic Chemistry Series 1": H. Goff in *Iron Porphyrin, Part I* (Eds.: A. B. P. Lever, H. B. Gray), Addison-Wesley, Reading, **1983**, pp. 237–281.

[14] T. Ikeue, Y. Ohgo, T. Saitoh, M. Nakamura, H. Fujii, M. Yokoyama, *J. Am. Chem. Soc.* **2000**, *122*, 4068–4076.

[15] The large downfield shifts of the α- and β-pyrrole signals are consistent with the occupancy of unpaired electrons in both the d_{xz} and d_{yz} orbitals; the unpaired electrons in these orbitals are transferred to the pyrrole carbon atoms by a d_π-$3e_g$ interaction. Since the $3e_g$ orbital has zero electron density at the *meso* carbon atom, the large upfield shift of the *meso* signal is ascribed to the spin polarization from the neighboring α-pyrrole carbon atom.[14]

[16] The extent of the upfield shift of the *meso* carbon atom is not necessarily proportional to the $S = 3/2$ contribution. The large difference in the shifts of the *meso* carbon atoms between **4** and **5** ($\Delta\delta = 186$ at 223 K) could be the indication that the d_π-$3e_g$ interaction in **4** is much stronger than that in **5** as a result of the difference in the nature of the axial ligands.

[17] Although the X-ray crystal structures of **4** and $[Fe^{III}(TiPrP)(4\text{-}CNpy)_2]ClO_4$ are not available at present, a preliminary result has shown that saddled **3** has much longer Fe–N(axial ligand) bonds than ruffled $[Fe^{III}(TEtP)(2\text{-}MeIm)_2]Cl$; the average bond lengths are 2.203(3) and 2.02(1) Å, respectively. Y. Ohgo, T. Ikeue, M. Nakamura, unpublished results.

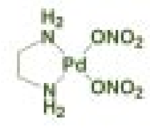
[18] K. M. Barigia, M. D. Berber, J. Fajer, C. J. Medforth, M. W. Renner, K. M. Smith, *J. Am. Chem. Soc.* **1990**, *112*, 8851–8857.

[19] R.-J. Cheng, P.-Y. Chen, P.-R. Gau, C.-C. Chen, S.-M. Peng, *J. Am. Chem. Soc.* **1997**, *119*, 2563–2569.

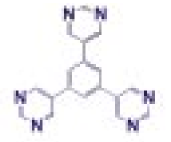
Molecular Paneling by Coordination: An $M_{15}L_6$ Hexahedral Molecular Capsule having Clefts for Reversible Guest Inclusion

Kazuhiko Umemoto, Hitoshi Tsukui,
Takahiro Kusukawa, Kumar Biradha, and
Makoto Fujita*

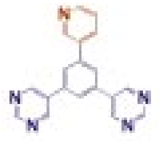
The construction of three-dimensional (3D) molecular structures by linking two-dimensional (2D), planar organic components through metal coordination provides a new concept that is termed molecular paneling.[1] A family of 2D components are coordinated by transition metals to give rise to various hollow 3D polyhedral structures.[2–8] The triangular *exo*-hexadentate ligand **2** has been recently shown to give $M_{18}L_6$ hexahedral coordination capsule **4** by linking together with Pd^{II} building block **1**.[4b] This coordination capsule has a very stable closed-shell structure which makes it difficult to encapsulate guest molecules. We have designed another molecular panel **3**, which is similar to **2** but misses one binding site, to prepare a hexahedral capsule with more



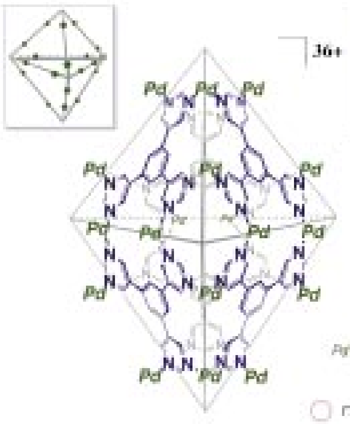
1



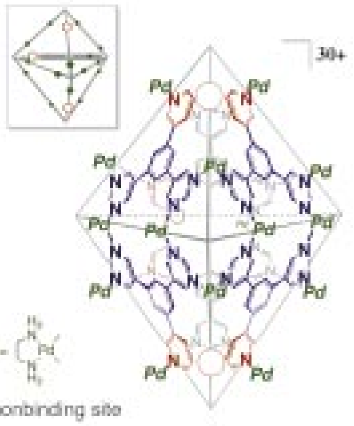
2



3



4



5

---

[*] Prof. Dr. M. Fujita,[+] H. Tsukui, Dr. T. Kusukawa, Dr. K. Biradha
Department of Applied Chemistry
Graduate School of Engineering, Nagoya University
Chikusaku, Nagoya 464-8603 (Japan)
Fax: (+81) 52-789-3199
E-mail: mfujita@apchem.nagoya-u.ac.jp

Dr. K. Umemoto
The Graduate University for Advanced Studies
Myodaiji, Okazaki 444-8585 (Japan)

[+] Prof. Fujita is responsible for the Core Research for Evolutional Science and Technology (CREST) project of the Japan Science and Technology Corporation (JST).

Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.

flexibility that would allow guest encapsulation and release. We show that, despite the lack of one binding site, ligand **3** is assembled into a unique $M_{15}L_6$ hexahedral structure **5** without the formation of any other positional isomers. An important finding is that capsule **5** can encapsulate/exchange guest molecules reversibly through the clefts at the nonbinding sites of the capsule.[9]

When ligand **3**[10] was treated with Pd^{II} complex **1** in D_2O at room temperature for 24 h we obtained a complex NMR spectrum (Figure 1), from which the presence of 39 proton signals was confirmed in the aromatic region. The observed 39 protons correspond to the total number of protons of three ligands, which suggested the assembly of a $(3\,L)_n$-type entity. Since the only possible $(3\,L)_n$ structure is a hexahedron, we proposed an $M_{15}L_6$ composition with a hexahedral framework. All the protons were fully assigned for three symmetrically ligands by H–H relay COSY and NOESY experiments.[11] Furthermore, through-space correlation by NOESY experiments made the connectivity of the six ligands clear. As a consequence, the structure was assigned as **5**. It is remarkable that, of the many possible structures, only a single isomer of a hexahedral structure was assembled from 21 small components (15 metals and 6 ligands) and fully assigned by NMR techniques alone.

The complex **5** was isolated as a colorless precipitate in 83 % yield by adding a large amount of EtOH to the reaction mixture. The elemental analysis of **5** was consistent with a formula of $C_{144}H_{198}N_{90}O_{90}Pd_{15}\cdot 25\,H_2O$.

The hexahedral structure of **5** was unambiguously determined by an X-ray crystallographic analysis of a single crystal of **5** (Figure 2). As expected, the crystal structure of **5** displayed the hexahedral $M_{15}L_6$ assembly with two nonbinding sites located around the apical corners and another one situated on the equatorial corner (Figure 2a–c). As a result, ligand **3** is placed in three different environments. In the X-ray structure 28 out of the 30 nitrate anions of **5** were found: five existed inside the capsule and the remaining were outside.

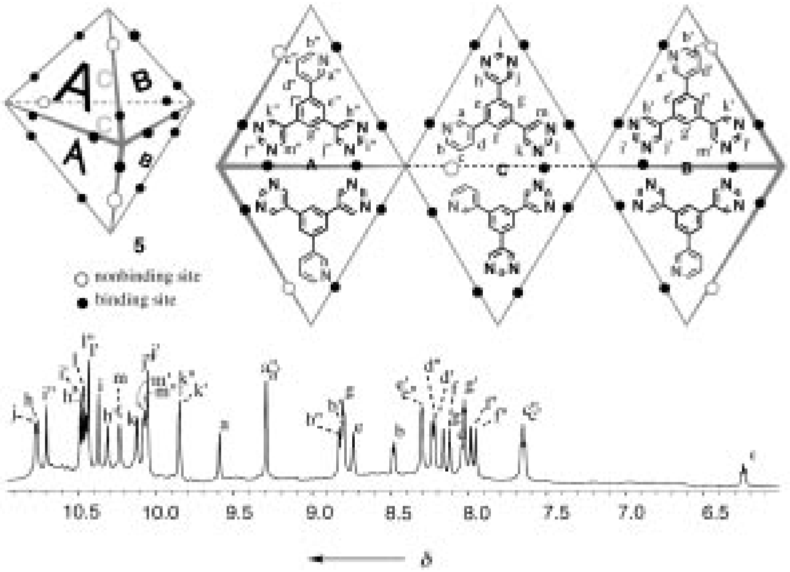


Figure 1. ^1H NMR spectra showing the formation of hexahedral capsule **5** (500 MHz, D_2O, TMS as external standard).

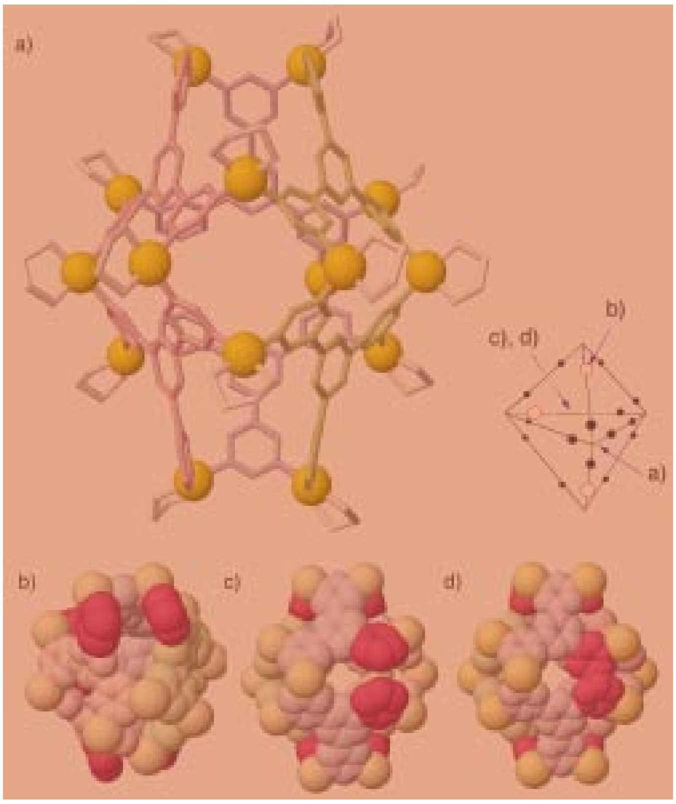


Figure 2. The crystal structure of **5**. Although two crystallographically independent structures **5a** and **5b** are found in the solid state, only structure **5a** is represented, except in (d). In (b)–(d), the ancillary ethylenediamine ligands on the Pd ions are omitted for clarity. The nonbinding sites are emphasized with red-colored 3-pyridyl groups. a) The ball and cylindrical representation of the front view; b) a view from an apical direction; c) a view from the back side; d) the same view of structure **5b**.

Interestingly, the X-ray analysis of capsule **5** showed the presence of two crystallographically independent structures (**5a** and **5b**) for capsule **5**. The difference between **5a** and **5b** is that a 3-pyridyl group at the equatorial site flips outward in **5a** but inward in **5b** (Figure 2c, d). The large upfield shift of H_c at $\delta = 6.3$ is most probably the result of the inward flipping of the 3-pyridyl group bearing H_c and suggests that structure **5b** is dominant in solution.

The size and the shape of complex **5** are almost the same as those of **4**. However, the striking feature of capsule **5** is the presence of three clefts at nonbinding sites. The clefts at the two apical sites are relatively large (3.5–5.0 Å) but the cleft at the equatorial site is almost closed. Thus, the capsule may encapsulate small molecules through the apical clefts (Figure 2b).[9i] In fact, the encapsulation of CBr_4 was observed when this guest was suspended in a solution of **5** in D_2O at room temperature. The facile complexation was completed within 10 min, as monitored by ^1H and ^{13}C NMR spectroscopy (Figure 3). The chemical shifts of the host were significantly changed and, moreover, the entrapped CBr_4 was observed at $\delta = -26.9$ in the ^{13}C NMR spectrum. The host–guest ratio was estimated to be 1:2 by inverse-gated ^1H-decoupling ^{13}C NMR spectroscopy.[12] Guest encapsulation was also observed

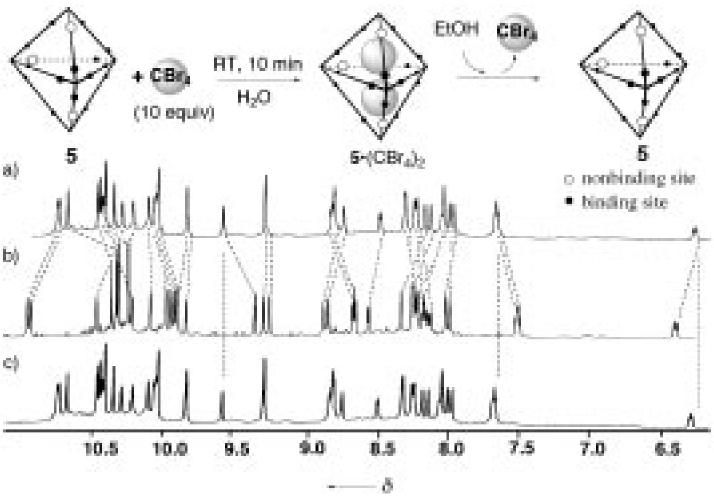


Figure 3. ^{1}H NMR spectra showing the reversible encapsulation of guests by **5** (500 MHz, D_2O, TMS as an external standard); a) complex **5**; b) complex **5**$\cdot(CBr_4)_2$ formed upon the addition of 10 equivalents CBr_4 (suspended); c) the spectrum after the addition of excess EtOH.

with similar small molecules such as CH_2Br_2 and $CHCl_3$. The formation of hydrophobic interactions in the capsule should be the driving force for encapsulation. Thus, the addition of ethanol to the aqueous solution of **5**$\cdot(CBr_4)_2$ induced the decapsulation of CBr_4, as monitored by NMR spectroscopy (Figure 3c).[13]

Experimental Section

5: Ligand **3** (7.9 mg, 0.025 mmol) was suspended in an aqueous solution (0.7 mL) of **1** (20.3 mg, 0.07 mmol) and left to stand for 24 h at room temperature. The addition of a large amount of EtOH to the mixture precipitated **5** as a colorless powder (22.1 mg, 83 %). M.p. 240 °C (decomp); ^{1}H NMR (500 MHz, D_2O, 25 °C): $\delta = 2.90-3.15$ (m, 30 H), 6.24 (dd, $J = 5.3$, 6.1 Hz, 1 H), 7.65 (dd, $J = 5.3$, 6.1 Hz, 2 H), 7.95 (s, 1 H), 7.98 (s, 1 H), 8.02 (s, 1 H), 8.03 (d, $J = 6.1$ Hz, 1 H), 8.12 (s, 1 H), 8.16 (s, 1 H), 8.22 (d, $J = 6.1$ Hz, 2 H), 8.30 (s, 2 H), 8.48 (d, $J = 5.3$ Hz, 1 H), 8.73 (s, 1 H), 8.80 (s, 1 H), 8.81 (d, $J = 5.3$ Hz, 2 H), 9.29 (s, 2 H), 9.59 (s, 1 H), 9.85 (s, 2 H), 10.05 (s, 2 H), 10.06 (s, 1 H), 10.07 (s, 1 H), 10.12 (s, 1 H), 10.23 (s, 1 H), 10.31 (s, 1 H), 10.37 (s, 1 H), 10.43 (s, 2 H), 10.45 (s, 1 H), 10.46 (s, 1 H), 10.48 (s, 1 H), 10.69 (s, 1 H), 10.75 (s, 1 H), 10.76 (s, 1 H); ^{13}C NMR (125 MHz, D_2O, 25 °C): $\delta = 47.4$ (CH), 47.6 (CH), 47.7 (CH), 124.6 (CH), 125.0 (CH), 125.5 (CH), 126.3 (CH), 126.6 (CH), 127.0 (CH), 127.1 (CH), 127.9 (CH), 128.0 (CH), 128.4 (CH), 128.8 (CH), 129.2 (CH), 130.5 (Cq), 131.1 (Cq), 131.6 (Cq), 131.7 (Cq), 131.9 (Cq), 132.3 (Cq), 134.8 (Cq), 135.0 (Cq), 135.2 (Cq), 135.3 (Cq), 136.0 (Cq), 136.8 (Cq), 136.9 (Cq), 137.3 (Cq), 137.4 (Cq), 137.6 (Cq), 137.7 (Cq), 137.9 (Cq), 138.5 (CH), 138.6 (CH), 139.0 (CH), 149.4 (CH × 2), 149.6 (CH), 150.7 (CH), 150.8 (CH × 2), 158.5 (CH), 158.7 (CH), 158.8 (CH), 158.9 – 159.0 (CH × 4), 159.8 – 160.3 (CH × 9), 160.6 (CH), 160.9 (CH); IR (KBr) 3480, 3210, 3100, 1610, 1431, 1380, 1080, 840, 725 cm^{-1}. Elemental analysis calcd for $C_{144}H_{198}N_{90}O_{90}Pd_{15}\cdot 25H_2O$: C 25.91, H 3.74, N 18.88; found: C 25.93, H 3.81, N 18.94.

X-ray structural analysis of **5**: The single crystal was obtained by the slow diffusion of methanol into an aqueous solution of **5** at 20 °C for 7 days. A single crystal of **5** ($0.20 \times 0.15 \times 0.15$ mm^3) was mounted onto a glass fiber. All measurements were made on a charge-coupled device (CCD) plate area detector with graphite monochromated $Mo_{K\alpha}$ radiation. The data were collected at 173(2) K. Crystal data for **5**: $C_{144}H_{198}N_{90}O_{90}Pd_{15}\cdot 57.5H_2O\cdot 1.5MeOH$, $M_r = 7309.91$, triclinic, space group $P1$, $a = 26.503(3)$, $b = 30.887(3)$, $c = 35.743(4)$ Å, $\alpha = 85.468(2)$, $\beta = 85.735(2)$, $\gamma = 89.850(2)°$, $V = 29086(6)$ Å^3, $\rho_{calcd} = 1.669$ mg m^{-3}, $Z = 4$, $F(000) = 14816$, $\mu(Mo_{K\alpha}) = 1.016$ mm^{-1}, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, 189592 reflections measured, 131409 observed ($I > 2\sigma(I)$), number of variables 6859, $R_1 = 0.0867$, $wR_2 = 0.2189$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-159454. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Received: March 26, 2001 [Z16848]

---

[1] For a review, see M. Fujita, K. Umemoto, M. Yoshizawa, N. Fujita, T. Kusukawa, K. Biradha, *Chem. Commun.* **2001**, 509 – 518.

[2] a) R. W. Saalfrank, A. Stark, K. Peters, H. G. von Schnering, *Angew. Chem.* **1988**, *100*, 878 – 880; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 851 – 853; b) R. W. Saalfrank in *Molecular Self-Assembly: Organic Versus Inorganic Approaches*, *Vol. 96* (Ed.: M. Fujita), Springer, Berlin, **2000**, chap. 2, pp. 149 – 176.

[3] a) P. Baxter, J.-M. Lehn, A. DeCian, J. Fischer, *Angew. Chem.* **1993**, *105*, 92 – 95; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 69 – 72; b) P. N. W. Baxter, J.-M. Lehn, G. Baum, D. Fenske, *Chem. Eur. J.* **1999**, *5*, 102 – 112; c) P. N. W. Baxter, J.-M. Lehn, B. O. Kneisel, G. Baum, D. Fenske, *Chem. Eur. J.* **1999**, *5*, 113 – 120.

[4] a) M. Fujita, D. Oguro, M. Miyazawa, H. Oka, K. Yamaguchi, K. Ogura, *Nature* **1995**, *378*, 469 – 471; b) N. Takeda, K. Umemoto, K. Yamaguchi, M. Fujita, *Nature* **1999**, *398*, 794 – 796; c) K. Umemoto, K. Yamaguchi, M. Fujita, *J. Am. Chem. Soc.* **2000**, *122*, 7150 – 7151.

[5] a) C. Brückner, R. E. Powers, K. N. Raymond, *Angew. Chem.* **1998**, *110*, 1937 – 1940; *Angew. Chem. Int. Ed.* **1998**, *37*, 1837 – 1840; b) D. L. Caulder, K. N. Raymond, *Acc. Chem. Res.* **1999**, *32*, 975 – 982.

[6] a) P. J. Stang, B. Olenyuk, D. C. Muddiman, R. D. Smith, *Organometallics* **1997**, *16*, 3094 – 3096; b) B. Olenyuk, J. A. Whiteford, A. Fechtenkötter, P. J. Stang, *Nature* **1999**, *398*, 796 – 799; c) S. Leininger, B. Olenyuk, P. J. Stang, *Chem. Rev.* **2000**, *100*, 853 – 908.

[7] C. M. Hartshorn, P. J. Steel, *Chem. Commun.* **1997**, 541 – 542.

[8] B. F. Abrahams, S. J. Egan, R. Robson, *J. Am. Chem. Soc.* **1999**, *121*, 3535 – 3536.

[9] Molecular capsules: a) D. J. Cram, J. M. Cram, *Container Molecules and Their Guests*, Royal Society of Chemistry, Cambridge, **1994**; b) P. Timmerman, W. Verboom, F. C. J. M. van Veggel, J. P. M. van Duynhoven, D. N. Reinhoudt, *Angew. Chem.* **1994**, *106*, 2437 – 2440; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2345 – 2348; c) L. R. MacGillivray, J. L. Atwood, *Nature* **1997**, *389*, 469 – 472; d) M. M. Conn, J. Rebek, Jr., *Chem. Rev.* **1997**, *97*, 1647 – 1668; e) T. Heinz, D. M. Rudkevich, J. Rebek, Jr., *Nature* **1998**, *394*, 764 – 766; f) J. J. Gonzalez, P. Prados, J. de Mendoza, *Angew. Chem.* **1999**, *111*, 546 – 549; *Angew. Chem. Int. Ed.* **1999**, *38*, 525 – 528; g) A. Ikeda, M. Yoshimura, H. Udzu, C. Fukuhara, S. Shinkai, *J. Am. Chem. Soc.* **1999**, *121*, 4296 – 4297; h) M. Ziegler, J. L. Brumaghim, K. N. Raymond, *Angew. Chem.* **2000**, *112*, 4285 – 4287; *Angew. Chem. Int. Ed.* **2000**, *39*, 4119 – 4121; i) N. Cuminetti, M. H. K. Ebbing, P. Prados, J. de Mendoza, E. Dalcanale, *Tetrahedron Lett.* **2001**, *42*, 527 – 530; j) R. Warmuth, J. Yoon, *Acc. Chem. Res.* **2001**, *34*, 95 – 105.

[10] Ligand **3** was prepared by the Suzuki – Miyaura coupling of 3,5-pyrimidylboronic acid pinacol ester and 3,5-dibromo-1-(3-pyridyl)-benzene. Satisfactory spectral and analytical data were obtained. For the details, see the Supporting Information.

[11] For example, 13 protons $H_a - H_m$ should exist on the same ligand because of the following observations: 1) protons of each ring are correlated by relay COSY experiments; 2) the core C_6H_3 ring is correlated with other heteroaromatic rings of the same ligand by NOESY experiments.

[12] a) M. L. Martin, G. J. Martin, J. J. Delpuech, *Practical NMR Spectroscopy*, Heyden, London, **1984**, chap. 9, pp. 350 – 376; b) E. D. Becker, *High Resolution NMR*, Academic Press, New York, **1980**, chap. 12; c) C. H. Sotak, C. L. Dumoulin, G. C. Levy, *Top. Carbon-13 NMR Spectrosc.* **1984**, 91 – 121; d) L. D. Field, S. Sternhell, *Analytical NMR*, Wiley, Chichester, **1989**, chap. 3, pp. 41 – 63.

[13] For the synthesis and physical properties of **5**$\cdot(CBr_4)_2$, see the Supporting Information.