Notes

Molecular Engineering. Part 13. Formation of Hemicarcerand Dimer by Metal Coordination

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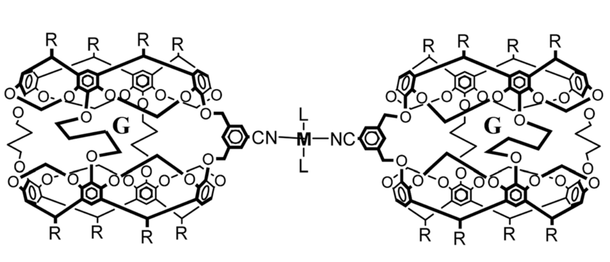
Container molecules such as carcerand,[1] hemicarcerand,[2] and self-assembled molecular capsule[3] have been characterized as molecular scavengers, molecular storages, molecular reactors and controlled-releasing systems. Various heterobridged hemicarceplexes in which the fourth bridging unit differs from the other three bridging units were reported by Cram *et al.*[4] and the fourth bridging unit has been used to adopt an additional binding site[4d] or to connect with another hemicarcerand to obtain covalently linked dimeric hemicarceplexes.[5]

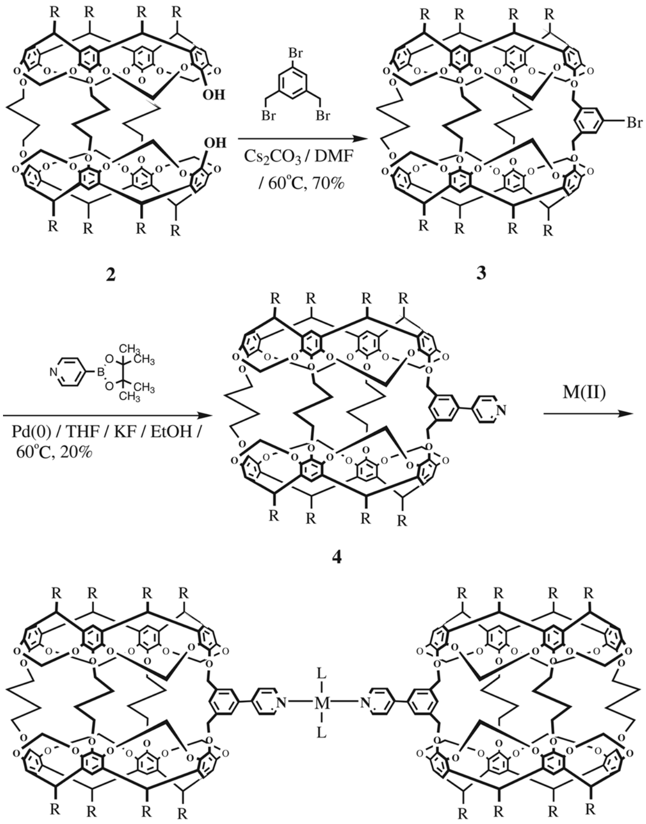
The characteristics of container molecules can be accumulated when they are assembled to highly ordered supramolecular systems. Dimeric container system could duplex the functions of monomeric container molecule and a well-ordered multiple container system would result in a new high density information storage system.[6]

Metal coordination has become an important synthetic strategy for the self-assembly of high-ordered and well-defined supramolecular architectures because it allows well defined geometry, coordination number, and a range of binding strengths.[7] Recently the interesting guest's size and shape selectivities of cyanohemicarcerand **1** was reported.[8] But the stability of Pd(II) or Pt(II)-coordinated dimeric assembly **1**-ML_2-**1** was too weak to be observed by ^{1}H NMR spectrometry.[8] Here we report on the synthesis of hemicarcerand **4** which has a metal coordinating *p*-pyridylphenyl unit on a pillar and its formation of dimeric self-assemblies **5a** and **5b** by Pd(II) and Pt(II)-coordination, respectively.



Dimeric Assembly **1**-ML_2-**1**

As shown in Scheme 1, diol **2**[8] was reacted under the dilution condition with α,α′-dibromo-5-bromo-*m*-xylene in



5a : $ML_2 = PdCl_2$
5b : $ML_2 = PtCl_2$

Scheme 1. Synthesis of Pd(II) or Pt(II)-coordinated dimeric hemicarcerands **5a** and **5b** (R = heptyl).

a mixture of Cs_2CO_3 and DMF at 60 °C to afford bromohemicarcerand **3** in 70% yield after chromatographic purification (hexane : $CHCl_3$ = 2 : 1) and recrystallization (CH_3OH). The Suzuki coupling reaction between bromohemicarcerand **3** and 4-pyridineboronic acid pinacol cyclic ester gave pyridinohemicarcerand **4** in 20% yield. Hemicarcerands **3** and **4** were characterized by ^{1}H NMR, FAB+ Mass spectra, and elementary analyses.

Metal-coordinated dimeric container molecular systems **5a** and **5b** were formed using $Pd(DMSO)_2Cl_2$ or *cis*-

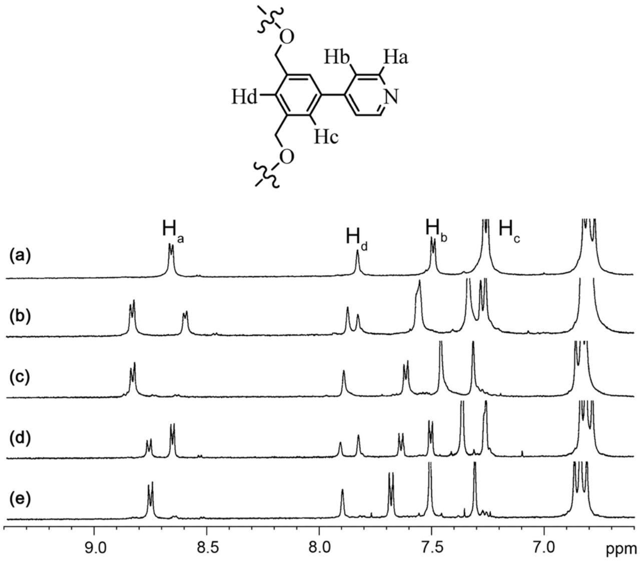


Figure 1. [1]H NMR spectral variation of Hemicarcerand **4** in $CDCl_3$ at 25 °C by Metal Complex addition; (a) free **4**, (b) 0.25 eq $Pd[(DMSO)_2Cl_2]$, (c) 0.50 eq $Pd[(DMSO)_2Cl_2]$, (d) 0.25 eq *cis*-$Pt[(CH_3CN)_2Cl_2]$, and (e) 0.50 eq *cis*-$Pt[(CH_3CN)_2Cl_2]$.

Table 1. Summary of the chemical shift changes upon addition of metal complexes, $Pd[(DMSO)_2Cl_2]$ for dimer **5a** and *cis*-$Pt[(CH_3CN)_2Cl_2]$ for dimer **5b**

Eq of Metal Complex	Chemical shift (ppm)							
	H_a		H_b		H_c		H_d	
	5a	**5b**	**5a**	**5b**	**5a**	**5b**	**5a**	**5b**
None	8.65		7.48		7.24		7.82	
0.25 eq	8.83	8.75	7.55	7.63	7.28	7.26	7.87	7.90
	8.59	8.65		7.50	7.26		7.83	7.82
0.5 eq	8.83	8.75	7.58	7.68	7.28	7.31	7.88	7.90
$\Delta\delta$ ($\delta_5 - \delta_4$)	+0.18	+0.10	+0.10	+0.20	+0.04	+0.07	+0.06	+0.08

$Pt[CH_3CN]_2Cl_2]$. Figure 1 and Table 1 show the chemical shifts changes of hemicarcerand **4** in $CDCl_3$ at 25 °C upon addition of $Pd(DMSO)_2Cl_2$ or *cis*-$Pt[(CH_3CN)_2Cl_2]$, respectively. The peaks for H_a (8.65 ppm), H_b (7.48 ppm), H_c (7.24 ppm), and H_d (7.82 ppm) of free hemicarcerand **4** tend to split into two sets of peaks by 0.25 eq. metal complex which correspond to those of hemicarcernd **4** and dimer **5** (Fig. 1, (b) and (d)). Those two peaks for each H_a, H_b, H_c, and H_d then became one peaks by 0.50 eq. metal complex (Fig. 1, (c) and (e)), which confirms that hemicarcerand **4** and metal complex bind in 2 : 1 ratio to form a stable dimeric assembly **5**. No further split or shift was observed by more than 0.50 eq. of metal complex.

Table 1 summarizes the chemical shift changes upon addition of metal complexes. The change of chemical shifts upon complexation decrease in order of those of $H_a > H_b > H_d$, and $> H_c$ for dimer **5a** and those of $H_b > H_a > H_d$, and $> H_c$ for dimer **5b** due to the strong metal coordination of pyridyl ligand to metal.

The formation of dimeric hemicarcerand **5** suggests that a hemicarcerand with four metal-ligands on each four pillars, which is being developed, would form 2-D net-work of container molecules by metal coordination.

Experimental Section

Bromohemicarcerand 3. A mixture of diol **2** (450 mg, 0.21 mmol) and Cs_2CO_3 (409 mg, 1.25 mmol) in degassed DMF was stirred at 60 °C for 20 min under Ar gas and added 1-bromo-3,5-bis(bromomethyl)benzene (93 mg, 0.27 mmol), then stirred at 60 °C fot 2 days. The mixture was cooled to room temperature and filtered through celite. The residue was partitioned in CH_2Cl_2 and 3 N HCl. The organic layer was washed with 3 N HCl twice, water, brine, and then dried over $MgSO_4$. The solvent was evaporated under vacuum. The residue was purified by silica gel column chromatography with a mixture of CH_2Cl_2/Hexane (1 : 1) as a mobile phase and the product was recrystallized in MeOH (343 mg, 70%): [1]H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, 24H, CH_3), 1.26-1.43 (m, 80H, $(CH_2)_5$), 1.90-1.94 (m, 12H, CH2$(CH_2)_2$-CH2), 2.18 (m, 16H, ArHCH_2), 3.81 (t, 4H, unsym. OCH_2), 3.91-3.96 (m, 8H, sym. OCH_2), 4.15-4.18 (d, J = 8.0, 8H, inner. OCH_2O), 4.70 (t, J = 4.0, 8H, *CH* methine), 4.93 (s, 4H, Ar*CH*O), 5.64-5.83 (d, J = 8.0, 8H, outer OCH_2O), 6.76-6.86 (m, 8H, Ar*H*), 7.13 (s, 2H, Ar*H*), 7.66 (s, 1H, Ar*H*); Anal. Calcd for $C_{140}H_{183}BrO_{24}$·5MeOH·3Hexane; C, 71.23; H, 8.98. Found; C, 71.15; H, 9.00.

Pyridinohemicarcerand 4. Under Ar atmosphere, hemicarcerand **3** (100 mg, 0.043 mmol), 4-pyridineboronic acid pinacol cyclic ester (22.0 mg, 0.11 mmol) and $Pd(PPh_3)_4$ were added to a argon-saturated mixture of THF (55.0 mL), 2 M KF (55.0 mL), and EtOH (30.0 mL). The mixture was refluxed for 5 days. After cooling to room temperature and evaporation of solvent, the residue was dissolved in CH_2Cl_2 and water. The organic layer were washed with water and brine, and then dried over $MgSO_4$. After concentration, the residue was purified by silica gel column chromatography with a mixture of EtOAc/Hexane (1 : 7) as a mobile phase and recrystallized in EtOH (20.0 mg, 20%): FAB+ MS m/z 2326.1 ($[M+1]^+$); [1]H NMR (400 MHz, $CDCl_3$) 0.91 (t, 24H, CH_3), 1.26-1.44 (m, 80H, $(CH_2)_5$), 1.91 (m, 12H, CH_2-$(CH_2)_2CH_2$), 2.19 (m, 16H, ArHCH_2), 3.91 (t, 4H, unsym. OCH_2), 3.97 (m, 8H, sym. OCH_2), 4.19 (d, J = 4.0, 8H, inner OCH_2O), 4.71 (t, J = 8.0, 8H, *CH* methine), 5.06 (s, 4H, Ar*CH*O), 5.68-5.85 (d, J = 8.0, 8H, outer OCH_2O), 6.78-6.83 (m, 8H, Ar*H*), 7.50 (d, J = 4.0, 2H, NCH*CH*), 7.83 (s, 1H, Ar*H*), 8.68 (d, J = 8.0, 2H, N*CH*); Anal. Calcd for $C_{145}H_{187}NO_{24}$·EtOAc·3Hexane·4EtOH; C, 73.52; H, 9.20; N, 0.49. Found; C, 73.38; H, 9.02; N, 0.18.

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