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Molecular Paneling via Coordination: Guest-Controlled Assembly of Open Cone and Tetrahedron Structures from Eight Metals and Four Ligands

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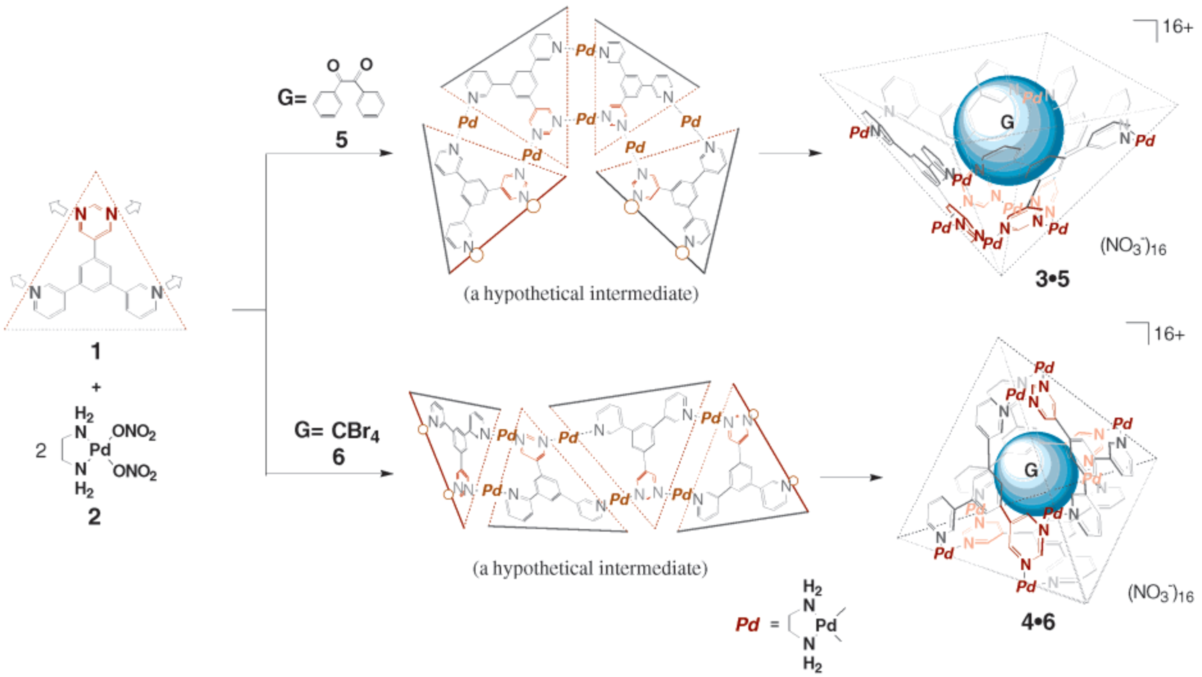
Triangular exo-polydentate ligands have been frequently employed for the metal-directed assembly of coordination polyhedra.[1−4] By linking triangles at their corners or edges, a family of polyhedral structures can in principle be engaged at will. Here, we design a triangular panel-like ligand with four donor sites on the two edges of the triangle (two donor sites on each edge): namely, compound **1** in Scheme 1. Having two-point binding sites on its two edges, this triangular unit is expected to assemble into edge-sharing polyhedral entity upon complexation with (en)Pd$(NO_3)_2$ (**2**), which is a versatile 90° coordination unit for metal-directed assembly. Whereas previous triangular ligands all possess C_3 symmetry,[1−4] panel **1** is C_2-symmetric and hence can be linked in two different ways: parallel and antiparallel links. Interestingly, these two options were perfectly controlled by the guests.[5] We show that some large guests induce the parallel link of the triangles leading to open cone (tetragonal pyramidal) structure **3**, whereas antiparallel link is selected by some small tetrahedral guests giving closed tetrahedron structure **4** (Scheme 1). Both assemblies have the same M_8L_4 composition and, therefore, constitute a dynamic receptor library[6,7] from which each receptor is selected by its optimal guests.

The quantitative assembly of M_8L_4 open cone **3** was induced by large guest molecules such as dibenzoyl (**5**). Thus, ligand **1** (0.025 mmol) and guest **5** (0.25 mmol) were suspended in the aqueous solution (2.5 mL) of **2** (0.05 mmol). After the mixture was stirred for 24 h at ambient temperature, excess **5** was filtered off and the resulting solution was analyzed by NMR and ESI-MS, which clearly evidenced the formation of open cone **3** accommodating one molecule of **5**. In ESI-MS, some of the major peaks were assigned as $[\mathbf{3}\cdot(\mathbf{5})_m\cdot(NO_3)_{16-n}]^{n+}$ $m = 0-2$, $n = 3,4$],[8] and no peaks could be found for other cone structures (e.g., M_6L_3 and $M_{10}L_5$ types, etc.). NMR displayed eight proton signals, which stems from ligand **1** located on a C_2-symmetric environment, in good agreement with the structure of **3**. The accommodation of **5** in the cone-shaped cavity of **3** was strongly suggested by the outstanding upfield shifts of signals of **5** in D_2O. The host−guest ratio was estimated to be 1:1 by NMR integration ratio. After the aqueous solution was allowed to stand at room temperature for 1 week, a colorless precipitate was obtained, which was washed with small portions of water and dried in vacuo to give **3·5** complex in 78%.[9] The same 1:1 complexes were also obtained with other bulky guests such as 1,2-diphenyl-1,2-ethanediol and 1,1′-ferrocenedicarboxylic acid.

The combination of components **1** and **2** enjoys another way of molecular paneling: the antiparallel link of adjacent ligands leading to tetrahedral coordination assembly **4** (Scheme 1). This was achieved in an efficient fashion by using small template molecules such as CBr_4 (**6**). Thus, the reaction of **1** (0.048 mmol) and **2** (0.106 mmol) in the presence of **6** (0.48 mmol, suspended) in D_2O (5.0 mL) resulted in the selective formation of **4·6** complex. Obviously, **6** templated the assembly of **4** and was efficiently entrapped within the framework of **4**. In fact, the entrapped **6** was observed at −26.9 ppm in ^{13}C NMR when ^{13}C-enriched **6** was employed. The antiparallel link of the ligands in **4** was strongly supported by the observation of NOE between the adjacent ligands, which was not observed in **3**. The complex was isolated as a colorless precipitate in 93% yield by adding a large amount of EtOH and the **4·6** stoichiometry was confirmed by elemental analysis.[9] The selective formation of tetrahedron **4** was also observed with similar small guests such as $CHCl_3$ and $CBrCl_3$.

The structure of **4·6** complex was finally determined by an

Scheme 1



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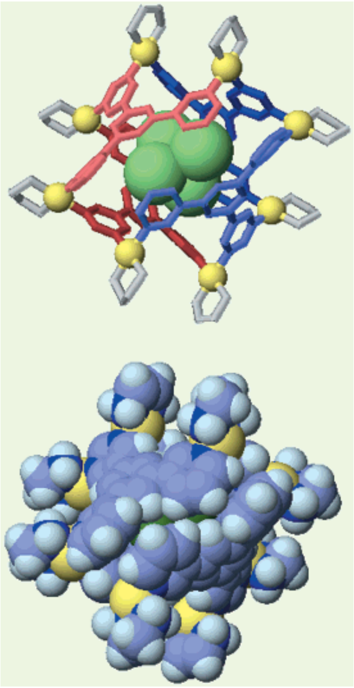


Figure 1. Crystal structure of **4·6**. Top: ball and cylindrical representation; bottom: Space-filling representation.

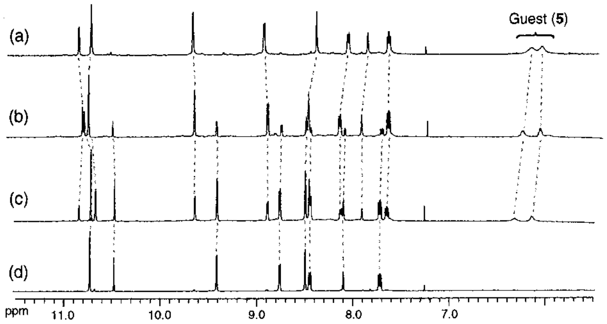
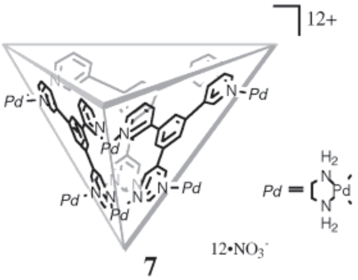


Figure 2. The ^{1}H NMR monitoring of reorganization process from **3·5** to **4·6** via guest exchange. (a) **3·5** complex in D_2O; (b−d) After the addition of excess amount of **6** at 25 °C ((b) 3 h, (c) 8 h, (d) 24 h). Note that free **5** is immiscible in water and, after guest exchange, becomes invisible in the spectrum.

X-ray crystallographic analysis (Figure 1).[10] The single crystal was obtained by standing the aqueous solution of **4·6** at ambient temperature for 3 days. As expected, the crystal structure of **4·6** displayed the antiparallel junction of ligands. The whole tetrahedral structure is somewhat distorted in such a way that efficient host−guest interaction and aromatic contact between the ligands are gained. As a result, the 12-component assembly makes a closed shell framework in which the guest molecule is completely insulated (Figure 1, bottom).

In the absence of guests at 25 mM concentration, **1** and **2** were assembled into a 3:2 mixture of two products, and the minor product was identified as **3**. The proportion of the major product increased at lower concentrations, indicating that this product is composed of fewer components than **3**. Since its NMR is qualitatively the same to that of **3**, the major product was tentatively assigned as an M_6L_3 trimeric open cone structure (**7**).[11]



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Being generated under thermodynamic control, three complexes **3**, **4**, and **7** are interconvertable with each other by guest addition or exchange via remarkably effective reorganization processes. Trimeric cone **7** (in the mixture of **3** and **7**) was converted upon the addition guest such as **5** to tetrameric cone **3** within 24 h. The addition of **6** to the mixture of **3** and **7** resulted in the disappearance of both complexes and reorganization into **4·6** complex within a day. Once assembled open cone **3·5** was transformed into **4·6** complex upon the addition of excess amount of **6** within 24 h (Figure 2) via guest exchange.

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Supporting Information Available: Preparation and physical properties of **1**, **3·5** and **4·6**, NMR spectra of **3·5**, **4·6** complexes (^{1}H, ^{13}C, HH COSY, NOESY, and CH COSY), and the mixture of complexes **3** and **7** (^{1}H and HH COSY); detailed crystallographic data of **4·6** complex (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Satisfactory NMR, ESI-MS, and elemental analysis data were obtained. See Supporting Information.

(10) Crystal data of **4·6**: see Supporting Information.

(11) The equilibration 3·**3** ⇆ 4·**7** shifts toward **7** at low concentrations. NMR data of **3** and **7** (from the mixture of **3** and **7**): see Supporting Information.