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Topospecific Self-Assembly of Mixed-Metal Molecular Hexagons with Diameters of 5.5 nm Using Chiral Control

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Transition metal-mediated self-assembly reactions are one of the most useful and well-explored methods of constructing spatially well-defined molecular rings, helicates, racks, and clusters,[1] The frequent occurrence of the propeller-like $[M(L-L)_3]^{\pm z}$ structural motif in supramolecular chemistry has been exploited to introduce chirality at both the local and global structural level in these assemblies.[2] Herein, we explore the use of preset chirality (at kinetically-inert metal centers) as a tool to direct the formation of cyclic suprastructures as well as the topochemical make-up of these structures.

NMR, thermal, and thermodynamic evidence is presented to support the self-assembly of molecular hexagons of large dimension (>5 nm).[3] Here, the absolute stereochemistry of the six vertice synthons $[(bpy)Ru(tpphz)_2]^{2+}$ (**1**) or $[(bpy)Os(tpphz)_2]^{2+}$ (**2**) (Figure 1), directs the formation of the ring structure and permits topospecific placement of different metals at unique symmetry sites within the ring. Three mixed-metal self-assembly systems are described, each containing six inert transition metal complexes (**1** or **2**) joined by six labile Pd(II) ions. The Ru_6Pd_6 (**3**), Os_6Pd_6 (**4**), and $Ru_3Os_3Pd_6$ (**5**) structures (Figure 1) form due to the torsional restraints imposed by the stereochemistry of **1** or **2** along with the entropic factors which favor rings systems over polymeric structures. As seen in Figure 1, the metals alternate in a Ru−Pd, Os−Pd, and Ru−Pd−Os−Pd fashion for **3**, **4**, and **5**, respectively.

Our chiral synthons are the enantiomers (Δ and Λ) of **1** and **2**.[4] Reaction of these bifunctional synthons with Pd(II) (1:1 ratio)[5] can give rise to either polymeric or cyclic hexagonal structures in which **1** or **2** acts as a 120° vertice of the hexagon (coordinate vector analysis).[6]

Molecular modeling clearly reveals that the formation of an approximately planar hexagonal ring structure, such as **3**, requires the chirality at adjacent vertices to be opposite. This is because the stereochemical "sequence" along a chain of linked chiral centers dramatically affects the chain topology.[7] For example, the macroscopic torsional angle formed by a chain of four such stereogenic centers (i.e., Ru(1)−Ru(2)−Ru(3)−Ru(4)) is fixed when the bridge between units is planar (i.e, tpphz or two tpphz connected by a square planar Pd^{2+})[8] and is strongly dependent on the absolute stereochemistry of the central two sites (Ru(2)−Ru(3)). When they are of opposite chirality, they cancel, giving a fixed torsional angle of either 0° or 180° which are denoted as the *cis* and *trans* torsional isomers, respectively. When Ru(2)−Ru(3) are homochiral, the torsional angle can be either 72° or 108° and therefore cannot form a planar configuration of all four metal centers. Thus, to form a planar ring of six stereogenic centers, an alternating distribution of Λ and Δ configurations is required, and furthermore each torsional isomer within this ring must have the *cis* configuration.

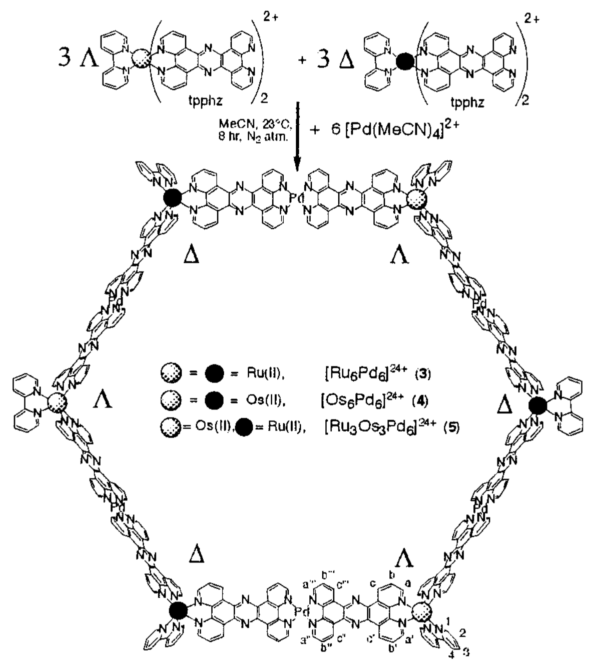

Figure 1. Synthesis and structure of mixed metal hexagons; **3**, **4**, and **5**. Yields are nearly quantitative.

To test this hypothesis, the formation of hexagon **3** was attempted by mixing the racemate of **1** and Pd^{2+} (1 Ru:1 Pd ratio) under self-assembly conditions (see Figure 1). The NMR of the sparingly soluble racemic-**1** (PF_6^- salt) is broad and poorly resolved. However, 30 min after addition of the $[Pd(MeCN)_4](BF_4)_2$, the solution is clear, and the NMR signals are much sharper (see Supporting Information for both NMR spectra). Ultimately the NMR spectrum evolves to give the simplified NMR spectrum, shown in Figure 2(i), which is consistent with quantitative formation of the ring structure **3**. Out of 192 H atoms in structure **3**, only 16 are symmetry-inequivalent (D_{3d}). All 16 are observed. The proton signals were assigned on the basis of the coupling patterns established by a COSY analysis and by comparison with model compounds.[9] The protons para to the imine nitrogens (H_c, $H_{c'}$, $H_{c''}$, and $H_{c'''}$) on the tpphz ligands

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[1] For recent reviews of this extensive field, see: (a) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853. (b) Lehn, J.-M. *Supramolecular Chemistry, Concepts and Perspectives*; VCH: New York, 1995. (c) Fujita, M. *Chem. Soc. Rev.* **1998**, *27*, 417.

[2] Reviews: (a) Provent, C.; Williams, A. F. *Perspectives in Supramolecular Chemistry*; Sauvage, J.-P., Ed.; John Wiley and Sons: New York, 1999; Vol. 5, pp 135−192. (b) Knof, U.; von Zelewsky, A. *Angew. Chem., Int. Ed.* **1999**, *38*, 303. (c) Keene, F. R. *Coord. Chem. Rev.* **1997**, *121*, 159.

[3] Estimated from molecular modeling and X-ray crystallographic data for the dimer $[(bpy)_2Ru(tpphz)Ru(bpy)_2][NO_3]_4$: Bolger, J.; Gourdon, A.; Ishow, E.; Launay, J.-P. *J. Chem. Soc., Chem. Commun.* **1995**, 1799.

[4] Ali, M. M.; MacDonnell, F. M. Manuscript in preparation.

[5] The coordination of two enantiopure $[Ru(bpy)_3]^{2+}$-type complexes to Pd(II) under similar conditions was first reported by: Wärnmark, K.; Thomas, J. A.; Heyke, O.; Lehn, J.-M. *Chem. Commun.* **1996**, 701.

[6] Caulder, D. L.; Raymond, K. N. *J. Chem. Soc., Dalton. Trans.* **1999**, 1185.

[7] (a) Chen, J.; MacDonnell, F. M. *Chem. Commun.* **1999**, 2529. (b) MacDonnell, F. M.; Ali, M. M.; Kim, M.-J. *Comments Inorg. Chem.* **2000**. In press.

[8] Some deviations from square planar geometry are expected due to steric interactions between the phenanthroline 2 and 9 hydrogens. Twists, step, and bow-type distortions are observed in crystal structures of $[Pd(phen)_2]^{2+}$ units (see: Wheman, P.; Kaasjager, V. E.; de Lange, W. G. J.; Hartl, F.; Kamer, P. C. J.; M., v. L. P. W. N. *Organometallics* **1995**, *14*, 3751; Geremia, S.; Randaccio, L.; Mestroni, G.; Milani, B. *J. Chem. Soc. Dalt. Trans.* **1992**, 2117); however, the presence of such distortions would not significantly alter the ability of this system to form ring structures in the manner presented.

[9] (a) Kim, M.-J.; MacDonnell, F. M.; Gimon-Kinsel, M. E.; DuBois, T.; Asgharian, N.; Griener, J. C. *Angew. Chem., Int. Ed.* **2000**, *39*, 615. (b) MacDonnell, F. M.; Kim, M.-J.; Bodige, S. *Coord. Chem. Rev.* **1999**, *185−186*, 535. (c) Bodige, S.; Torres, A. S.; Maloney, D. J.; Tate, D.; Walker, A.; Kinsel, G.; MacDonnell, F. M. *J. Am. Chem. Soc.* **1997**, *117*, 110364. (d) MacDonnell, F. M.; Bodige, S. *Inorg. Chem.* **1996**, *35*, 5758. (e) Bolger, J.; Gourdon, A.; Ishow, E.; Launay, J.-P. *Inorg. Chem.* **1996**, *35*, 2937.

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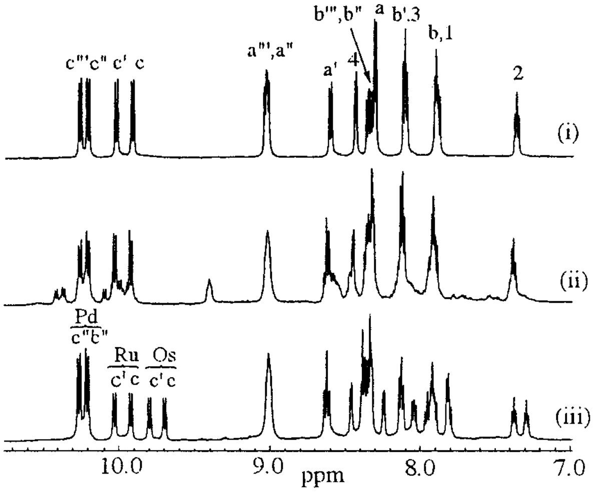

Figure 2. ^{1}H NMR in MeCN-d_3 of (i) rac-**1** and Pd^{2+} after 8 h to give **3**, (ii) Δ-**1** and Pd^{2+} after 8 h, (iii) **5** from Δ-**1** and Λ-**2** and Pd^{2+}.

provide a particularly good handle on the nature of the product. From our previous studies,[9] we know that such hydrogens (those para to the imine nitrogens on a tpphz ligand) appear as doublets shifted downfield to ~9.5−10.5 ppm. Symmetry considerations of **3** lead us to expect four doublets of equal intensity. These doublets are clearly observed at 9.95, 10.03, 10.22, and 10.30 ppm in Figure 2(i).

Next, the same reaction was performed except that pure Δ-[(bpy)Ru(tpphz)$_2$][PF$_6$]$_2$ and [Pd(MeCN)$_4$][BF$_4$]$_2$ (1Ru:1 Pd ratio) were mixed. In this case, the chain topology is defined by torsional angles of approximately 72° and 108° which does not allow formation of a planar cyclic structure. After 2 h, the NMR spectrum shown in Figure 2 (ii) is observed and remained unchanged thereafter. As can be seen, the spectrum is almost as clean as that for **3**; however, six additional small doublets are observed in the "H$_c$" region. We attribute these peaks to tpphz endgroups on a short polymer of Pd^{2+} and Δ-**1**. These endgroup signals correspond to a tpphz which has a {Pd(MeCN)$_2$}$^{2+}$ fragment coordinated to the end or one in which the tpphz coordination site is open. Integration analyses of these peaks relative to intrachain tpphz peaks gives an approximate polymer chain length of 7.7 Ru(II) units.

The determination of the polymer average chain length gives an important indication of the thermodynamics of the resulting systems. It is reasonable to assume that the enthalpic contribution toward the formation of polymer chain versus ring structures will be approximately equal and therefore the product of these reactions will be primarily determined by entropic contributions to the free energy change (in the absence of stereochemical constraints). In the simplest analyses, more six-membered rings may be formed than short polymers of average chain length of 7.7 units.

The polymer versus ring structure was further tested by examining the thermal stability of the two complexes rac-**1**/Pd (ring) and Δ-**1**/Pd (polymer) using variable temperature NMR. When a solution of polymer (Pd^{2+} and Δ-**1**) was heated to 80 °C, the H$_{c''}$ and H$_{c'''}$ signals are halved in intensity relative to H$_c$ and H$_{c'}$, and many new peaks are observed (see Supporting Information). This clearly suggests the rigid, ribbonlike polymer breaks into a mixture of oligomers upon increasing temperature. When a solution of **3** (Pd^{2+} and rac-**1**) was heated to 80 °C, no change was observed in the NMR spectrum, confirming its greater stability as would be expected of a cyclic structure. The hexamer **3** could also be isolated as a solid by slow addition of a saturated NH$_4$PF$_6$ solution in acetonitrile to the concentrated reaction solution to give a deep red precipitate (yield 90%). This precipitate gave NMR identical to the species generated in solution and was characterized by thermal and elemental analysis.[10] Despite extensive effort, attempts to confirm the hexagonal structure by electrospray ionization mass spectrometry (ESI-MS, only short polymeric fragments were observed) or by crystallography have not yet been successful.

The ability of this system to self-assemble is predicated on its ability to organize the opposing stereocenters in an alternating fashion. This element of chiral recognition was used to prepare topologically organized hexagons, such as **5** (containing Ru, Os, and Pd). The ring **5** was obtained from a mixture of Δ-**1**, Λ-**2**, and [Pd(MeCN)$_4$]$^{2+}$ (1:1:2 ratio) in acetonitrile. Product **5** (shown in Figure 1 with D_3 symmetry) is expected to show a total of 32 aromatic proton NMR signals of which 30 are observed (Figure 2(iii)). The tpphz protons furthest from the Ru and Os ions (or closest to the Pd^{2+} centers), H$_{a'',b'',c''}$ and H$_{a''',b''',c'''}$, do not show significantly different chemical shifts when bound to Ru or Os and therefore overlap in the spectrum. However the chemical shifts for H$_{a,b,c}$ and H$_{a'b',c}$ are quite different and are readily assigned upon comparison to **3** and the all Os hexagon, [Os$_6$Pd$_6$]$^{24+}$ (**4**, see Supporting Information) which was prepared from racemic-**2** and Pd^{2+} (1:1).

Hexagon **5** is chiral[11] (D_3 symmetry) and shows topospecific placement of the Os and Ru. In essence, we have used an isostructural replacement scheme of substituting Λ-**2** for Λ-**1**. A similar strategy was recently employed by Breu et al. to place Δ-[Os(bpy)$_3$]$^{2+}$ in specific symmetry sites in a doped crystal of rac-[Ru(bpy)$_3$](PF$_6$)$_2$.[12] In our system, this effect is used to topospecifically organize a molecular species. The high kinetic lability of the Pd^{2+} center allows the various subunits to explore possible structures until ultimately the thermodynamically favored ring structure is obtained.

We have shown that the absolute stereochemistry of a metal complex can have a significant impact on the types of supramolecular structures "allowed" and can be used as a tool to direct the placement of a specific metal or complex within the suprastructure. We continue to explore the role of chirality in organizing higher-order structures.

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Supporting Information Available: Synthetic schemes for **1** and **2**, ^{1}H NMR for **3** and **4**, COSY data for **3**, **4**, and **5** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[10] TGA for **3** indicated a 4% weight loss after heating at 200 °C for 1 h. corresponding to approximately 24H$_2$O of hydration. Anal. Calcd for **3**, C$_{348}$H$_{192}$N$_{84}$Ru$_6$Pd$_6$ P$_{24}$F$_{144}$·24H$_2$O: C 39.04, H 2.26, N 10.99. Found C 38.69, H 2.05, N 10.83. Yield 90%.

[11] Compound **5**. UV−vis (MeCN; λ, nm (ε, M^{-1} cm^{-1} ×10^{-3}, calculated per mol **5**)): 246 (568), 283 (1, 010), 361 (274), 379 (349), 447 (149), 554sh (20.0). CD (MeCN; λ$_{min/max}$ (Mol. CD calculated per mol **5**)): 310 (−43.2), 330 (−26.4), 381 (+9.6), 438 (−34.2), 501 (+57.0).

[12] Breu, J.; Kratzer, C.; Yersin, H. *J. Am. Chem. Soc.* **2000**, *122*, 2548.