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Strategy for Preparing Molecular Cylinders with Synthetically Programmable Structural Parameters

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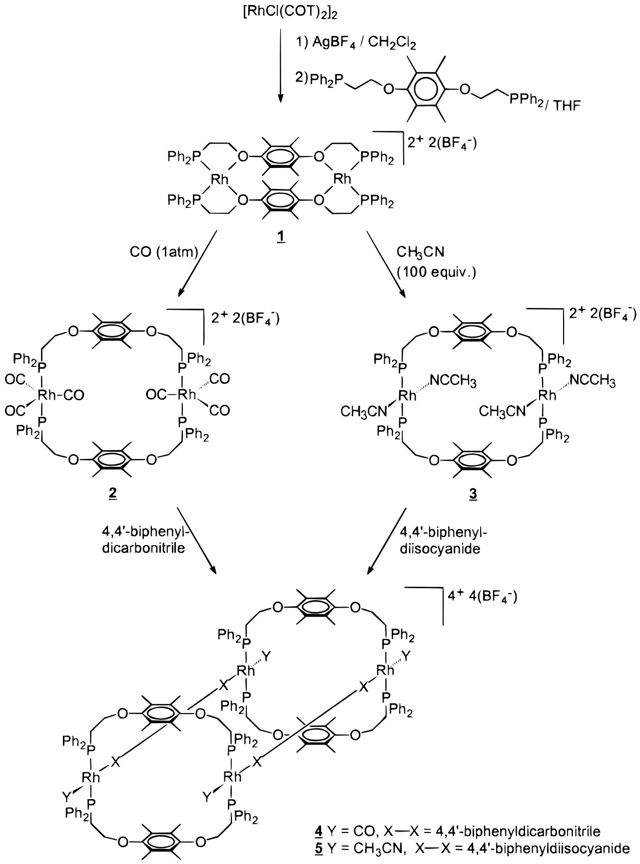
In recent years, significant progress has been made in reaction development as it applies to the preparation of two and three-dimensional structures;[1−4] however, researchers in this field are still a long way from being able to design and synthesize geometric structures in a totally predictable fashion. With regard to inorganic structures, the pioneering work of Fujita[1] and others[2] has made it possible to fabricate a wide variety of tetranuclear square structures by reacting rigid linker molecules with metal complexes with chemically available *cis*-coordination sites. We recently developed an approach that allows one to use structurally flexible hemilabile ligands to prepare binuclear intermediates that can be opened into expanded ring structures. In this synthetic strategy, the hemilabile ligands are designed to react with late transition metals to form condensed structures **1** that are held together by both strong (M−P) and weak (M−O) bonds[3] (e.g., **1** in Scheme 1). The weak bonds in the condensed intermediate can be broken easily with small molecules (e.g., CO) that form stronger bonds with the metal centers, which result in the formation of expanded ring structures, **2** or **3**, Scheme 1. With these methods, it is now becoming possible to design and synthesize ring, square, and rectangular structures with a great degree of control over structural parameters.

Although there have been some impressive advances, methods for preparing structures such as cylinders, boxes, cages, ladders, grids, and other three-dimensional structures[4] have lagged behind those for preparing two-dimensional systems. Herein, we report a novel and general method for preparing cylindrical structures in high yield, which is based upon a combination of simple flexible hemilabile ligands, rigid linker ligands, readily available metal precursors, and our "weak-link approach" to the synthesis of binuclear macrocycles. This strategy, which is outlined in Scheme 1, utilizes phosphinoalkyl ether hemilabile ligands and their predictable coordination chemistry with late transition metals[5] to control the stepwise synthesis of a cylinder through the initial formation of preconceived thermodynamically stable intermediates. The weak-link approach reported in this manuscript breaks the cylinder formation process into the following two discreet high-yield steps: (1) the formation of bimetallic rings which function as ends for the cylinders and (2) the linking of two rings via bifunctional ligands. Importantly, these initial proofs of concept may be extended to a wide array of hemilabile ligands and metals, thereby providing a general route to multifunctional molecular cylinders with synthetically programmable structural parameters (diameter, height, interior hydrophobicity, metal binding functionality, redox activity, and optical activity).

Scheme 1



Square planar Rh(I) compounds with two *trans*-phosphine ligands and *trans* σ-donating and π-accepting ligands are a common motif in organometallic chemistry.[6] We have taken advantage of this observation and the extensive literature base revolving around hemilabile ligands[5] to develop two new synthetic routes to molecular cylinders. The basic strategy involves introducing a condensed macrocycle such as **1** to a ring opening ligand such as CO or acetonitrile to form intermediate macrocycles **2** and **3**, respectively, Scheme 1. Note that **2** and **3** can be synthesized in one-pot directly from a hemilabile phosphinoalkyl ether ligand and Rh(I) precursor without isolating intermediate **1**; therefore, we consider this to be the first step in the two-step process of synthesizing these cylindrical structures. The characterization of compound **2** has been reported elsewhere,[3] and the characterization of **3** is based upon a comparison of its ^{31}P

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NMR spectrum with that for known mononuclear analogues.[7] Without isolation, compounds **2** and **3** are reacted with bifunctional linking ligands 4,4′-biphenyldicarbonitrile and 4,4′-biphenyldiisocyanide.[8] In the case of **2**, a molecular cylinder **4** is formed immediately in quantitative yield as determined by FTIR, ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy, (see Supporting Information). For example, the ^{31}P{^{1}H} NMR spectrum of **4** exhibits a single resonance at δ 20.7 (d, $J_{\mathrm{Rh-P}} = 112.4$ Hz), which is assigned to the eight magnetically equivalent P atoms. The FTIR spectrum of **4** exhibits a single ν_{CN} band at 2258 cm^{-1} and a single ν_{CO} band at 2011 cm^{-1}. The ν_{CN} band is shifted to higher energy by 27 cm^{-1} as compared with the free ligand. These data rule out unsymmetrical structures and structures with monodentate 4,4′-biphenyldicarbonitrile ligands.

Intermediate **3** reacts with 4,4′-biphenyldiisocyanide in CH_2Cl_2 to form initially an insoluble precipitate which over the course of several days forms one soluble product, molecular cylinder **5**. Compound **5** is a more durable cylinder than **4** as evidenced by its ability to maintain its structure under the electrospray mass spectrometry conditions used to study **4**.[9] Like **4**, compound **5** has been characterized by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy, both of which are consistent with the proposed structural formulation for **5** (see Supporting Information).

X-ray quality single crystals of the $B(C_6F_5)_4^-$ salt of **5** were grown by diffusion of pentane into a saturated CH_2Cl_2 solution of (**7**) 4[$B(C_6F_5)_4^-$].[10] The solid-state structure of **5**, which is consistent with our solution formulation of it, clearly shows two bimetallic rings linked together via two 4,4′-biphenyldiisocyanide ligands, Figure 1. Each Rh(I) center exhibits square planar geometry with two *trans*-phosphine ligands and *trans*-isocyanide and acetonitrile ligands. The Rh(I) metal centers on a ring that comprise the cylinder ends are separated by 11.74 Å, and the Rh(I) metal centers spanned by the bridging 4,4′-biphenyldiisocyanide ligands are separated by 16.01 Å. Measuring the volume of the cylinder is difficult due to the open walls of the structure, but the area of the rectangular void space defined by the four Rh(I) metal centers is ca. 190 Å^2, and the total free volume of the cylindrical cavity is approximately 1100 Å^3. No $B(C_6F_5)_4$ anions are located within the cavity of the cylinder which is large enough to easily accommodate a molecule the size of C_{70}.

Although **5** is an impressive and aesthetically pleasing structure, the significance of the discoveries reported herein does not revolve around the isolation and crystallographic characterization of a molecular cylinder but rather a potentially general and simple strategy for the preparation of such structures with synthetically tunable dimensions. This novel synthetic route will give us a powerful and rational way for preparing meso- and macroscopic pore structures that have significant implications and utility in catalysis, sensing, and separations technologies.

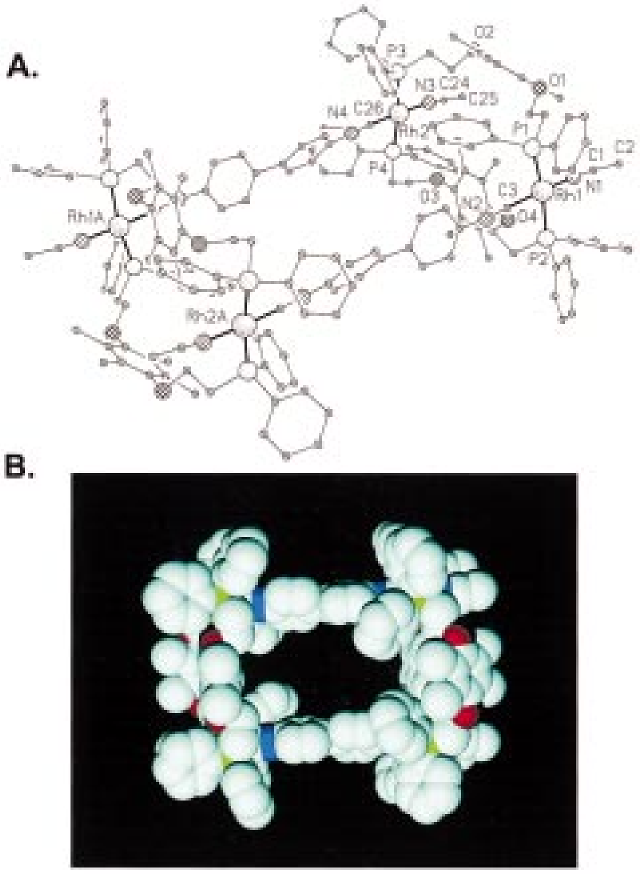

Figure 1. Two plots of X-ray crystal structure of (**5**) {$(C_{47}H_{27}N_2O_2P_2Rh)[B(C_6F_5)_4]$}$_4\cdot 10CH_2Cl_2$: (A) Ball and stick model showing the connectivity of the cylinder and (B) space-filling model showing the cavity within the cylinder (side view). Color scheme is as follows: Rh (yellow); P (green); O (red); N (blue); C (light blue). Hydrogen atoms, solvent, and $B(C_6F_5)_4^-$ anions are omitted for clarity. Selected bond distances and angles in (Å) and (deg): Rh(1)−Rh(2) = 11.24; Rh(1)−Rh(2a) = 16.01; Rh(1)−P(1) = 2.333(3); Rh(1)−P(2) = 2.327(3); Rh(1)−N(1) = 2.073(8); Rh(1)−C(3) = 1.857(11); Rh(2)−P(3) = 2.322(3); Rh(2)−P(4) = 2.332(3); Rh(2)−N(3) = 2.080(9); Rh(2)−C(26) = 1.884(11); C(3)−Rh(1)−N(1) = 178.2(4); N(1)−Rh(1)−P(2) = 90.4(2); N(1)−Rh(1)−P(1) = 92.8(2); C(3)−Rh(1)−P(2) = 88.3(3); C(3)−Rh(1)−P(1) = 88.6(3); P(2)−Rh(1)−P(1) = 174.72(10); C(26)−Rh(2)−N(3) = 177.2(4); C(26)−Rh(2)−P(3) = 89.0(3); N(3)−Rh(2)−P(3) = 93.8(2); C(26)−Rh(2)−P(4) = 86.9(3); N(3)−Rh(2)−P(4) = 90.3(2); P(3)−Rh(2)−P(4) = 170.42(11). Numbers in parentheses are errors in the last digits.

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Supporting Information Available: Synthesis of **4** and **5**, characterization of **4** and **5**, X-ray structural data for **5**, including a summary of crystallographic parameters, atomic coordinates, bond distances and angles, anisotropic thermal parameters, H atom coordinates, and three ORTEP diagrams of the one cation and two unique anions (22 pages, print/PDF). An X-ray crystallographic file, in CIF format, for **5** is available through the Web only. See any current masthead page for ordering information and Web access instructions.

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(9) Molecular cylinder **5** loses all four CH_3CN ligands under ESMS conditions. Molecular cylinder **4** is held together by the cyano groups of the 4,4′-biphenyldicarbonitrile ligands, which are likely to have bond strengths similar to the CH_3CN ligands of **5**. This is why no peaks were observed that correspond to the parent ion of **4** in its mass spectrum. For more information on ESMS, see: (a) Henderson, W.; McIndoe, J. S.; Nicholson, B. K.; Dyson, P. J. *J. Chem. Soc., Dalton Trans.* **1998**, 519. (b) Lofthagen, M.; Siegel, J. S.; Hackett, M. *Tetrahedron* **1995**, *51*, 6195. (c) Colton, R.; Dagostino, A.; Traeger, J. C. *Mass Spectrom. Rev.* **1995**, *2*, 79.

(10) Yellow crystals of {$(C_{47}H_{27}N_2O_2P_2Rh)[B(C_6F_5)_4]$}$_4\cdot 10CH_2Cl_2$, fw = 6912.32, grown from CH_2Cl_2, belonged to the triclinic space group *P*-1: $a = 17.01270(2)$, $b = 20.3437(4)$, $c = 24.4755(4)$ Å, $\alpha = 82.6712(4)$, $\beta = 86.6043(12)$, $\gamma = 81.0029(9)°$, $V = 8347.4(3)$ Å^3, $Z = 1$, $T = 198(2)$ K, $R(F) = 9.00\%$, $R(wF^2) = 22.76\%$ for 10 230 observed independent reflections ($4.0 \leq 2\theta \leq 52.0°$). A Siemans P4 diffractometer with a SMART/CCD detector was used to collect 34 513 reflections. The data were empirically corrected for absorption by DIFABS.[11] The metal atoms were located from a Patterson projection, and the structure was refined by blocked-matrix methods. The cation resides on an inversion center. All of the phenyl rings were fixed as rigid planar groups to maintain a reasonable data-to-parameter ratio. Ten molecules of CH_2Cl_2, in a range of ordered and disordered forms, are also contained in the unit cell. The solvent molecules were fixed as tetrahedra with 1.79 Å C−Cl distances. One of the five unique CH_2Cl_2 molecules has chlorine atoms disordered over two positions, 70/30. The solvent molecules were refined isotropically. All other non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were treated as idealized contributions. All software and sources of the scattering factors are contained in the SHELXTL (5.3) program library (G. Sheldrick, Siemens XRD, Madison, WI).

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