Tetrametallic rectangular box complexes assembled from heteroligated macrocycles†

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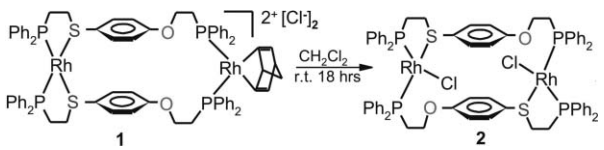
The reaction of a heteroligated Rh(I) bimetallic macrocycle with rigid ditopic ligands (1,4-dicyanobenzene, 4-4′-dicyanobiphenyl, or dipyridyl terminated salen ligand 5) results in the formation of tetrametallic rectangular box complexes.

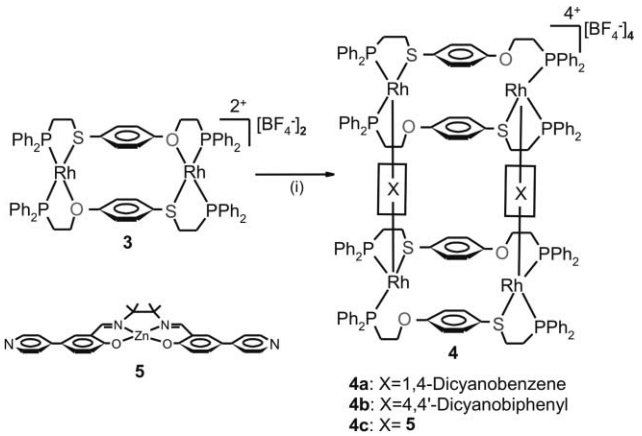
Over the past decade, supramolecular chemistry has evolved beyond simple macrocycles to involve more complex two- and three-dimensional architectures such as cylinders, squares, and prisms.[1–14] Often times the strategies used to generate such structures result in architectures with multiple metal centers, each forming a specific domain of the larger structure.[1–14] These centers, in certain cases, can be used to control the recognition properties of the supramolecular entity and to realize multifunctionality in catalysis and chemical sensing.[15–17] Indeed, we recently demonstrated a new class of allosteric catalysts based upon tetrametallic macrocycles and trimetallic tweezers that mimic allosteric enzymes and can be used in novel signal amplification systems in the context of chemical sensing.[17,18]

The Weak-Link Approach (WLA) to macrocycle synthesis allows one to predictably construct a variety of structurally flexible, three-dimensional geometries in nearly quantitative yields.[1,19,20] Recently we discovered an unusual and interesting outersphere to innersphere halide-induced ligand rearrangement process for bisphosphine Rh(I) olefin complexes resulting in heteroligated Rh coordination environments (eqn (1)).[21–24] For example, upon abstraction of the chlorides from complex **2** with $AgBF_4$, condensed complex **3** is formed in near-quantitative yield (Scheme 1).[23] Recently, we have discovered that this reaction can be used in the context of a binuclear precursor **3** and ditopic ligands to prepare a novel class of tetrametallic rectangular box complexes **4a–c**.



(1)

An important aspect of this strategy is the use of the heteroligated macrocyclic ends **3** within complex **4** that allow one to selectively control the chemistry at one coordination site of each metal center in the formation of the ditopic walls. The Rh(I) coordination environment in complex **3** contains strong metal–P bonds, intermediate strength metal–S bonds and relatively weaker metal–O bonds. Therefore, one can selectively cleave the Rh–O bonds using a variety of functional groups such as pyridines, nitriles, isonitriles, halides, and carbon monoxide, leaving the stronger Rh–S and Rh–P links intact. Thus, we have a number of functionalities at our disposal that can be incorporated into rigid organic molecules to create bridging ligands that act as building blocks to assemble multiple units of **3**. The ability to manipulate a single coordination site at each Rh center in complex **3** allows us to avoid by-products, such as polymeric multimetallic species, that would likely form with a complex containing multiple available coordination sites. Therefore, the design of higher ordered architectures such as the observed multimetallic rectangular box complexes can be targeted and synthesized in a predictable fashion.



Scheme 1 Reagents and solvents: (i) 1 equiv of **3** and 1 equiv of corresponding bridging ligand X in CH_2Cl_2 at r.t. for 10 min.

A variety of ditopic rigid ligands with nitrile or pyridine functionalities can be easily prepared using literature methods and subsequently used to assemble the tetrametallic rectangular box complexes.[25] For example, the addition of one equiv of 1,4-dicyanobenzene to a methylene chloride solution containing one equiv of **3** selectively cleaves the weak Rh–O bond and allows for the formation of complex **4a** (Scheme 1). The $^{31}P\{^1H\}$ NMR spectrum of the cationic "condensed" macrocycle **3** exhibits resonances at δ 74.1 (dd, J_{P-P} = 41 Hz, J_{Rh-P} = 201 Hz) and δ 51.0 (dd, J_{P-P} = 41 Hz, J_{Rh-P} = 170 Hz) while the product, complex **4a**, exhibits resonances at δ 67.3 (dd, J_{P-P} = 41 Hz, J_{Rh-P} = 166 Hz) and δ 26.7 (dd, J_{P-P} = 42 Hz, J_{Rh-P} = 164 Hz) indicative of inequivalent phosphine atoms in the η^2-PCH_2CH_2S chelates and the η^1-PCH_2CH_2O ligands.[21–24] Similarly, addition of one equiv of

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† Electronic supplementary information (ESI) available: Additional ORTEP diagram of **4a**. Experimental procedures and spectral data for all new compounds **4a–c**. See DOI: 10.1039/b609931a

4,4′-dicyanobiphenyl to **3** results in tetrametallic rectangular box complex **4b** with resonances at δ 69.3 (dd, J_{P-P} = 42 Hz, J_{Rh-P} = 169 Hz) and δ 32.2 (dd, J_{P-P} = 41 Hz, J_{Rh-P} = 164 Hz), assigned to the two pairs of inequivalent P atoms in the η^2-PCH_2CH_2S chelates and the η^1-PCH_2CH_2O ligands.[21–24]

Rectangular box complexes with catalytic functionality located within the side walls of the structure can be prepared by using ditopic rigid ligands that are comprised of a catalytic moiety. For example, complex **4c**, which contains a (salen)Zn group in the backbone of each ditopic bridging ligand, was synthesized in quantitative yield from the addition of one equiv of the zinc salen pyridyl-terminated bridging ligand **5** to a CH_2Cl_2 solution containing **3** (Scheme 1). Complex **4c** exhibits resonances in the $^{31}P\{^1H\}$ NMR spectrum at δ 70.7 (dd, J_{P-P} = 42 Hz, J_{Rh-P} = 156 Hz) and δ 37.9 (dd, J_{P-P} = 42 Hz, J_{Rh-P} = 175 Hz), and all data are consistent with its proposed formulation.

Further evidence for the proposed rectangular box structures was obtained from a single crystal X-ray structure analysis of complex **4a** (Fig. 1).[26,27] Diffraction quality crystals were grown from a concentrated solution of **4a** in CH_2Cl_2 layered with pentane. Crystals were grown over a two day period and were deep red in color. The Rh(I) centers exhibit square planar geometries with N1–Rh1–S1 and N1–Rh1–P2 angles of 85.7(15)° and 89.0(15)°, respectively. In addition, each Rh(I) coordination environment contains *cis*-phosphine ligands and *trans*-sulfur/cyano ligands. The distance between the centroids of the benzene rings of each bridging 1,4-dicyanobenzene ligand is 3.55 Å while the distance along this ligand from Rh1–Rh3 is 11.99 Å. The torsion angle between the same centroids about N1 and N3 is 55.9° and about N2 and N4 is 51.0°. Indeed, a side view of the structure shows that the bridging dicyano ligands are aligned in a cofacial manner with one another but rotated 55.9° (see ESI†). The Rh1–Rh2 distance is 8.76 Å. The area of the rectangle formed by the four Rh atoms/corners is approximately 110 Å^2.

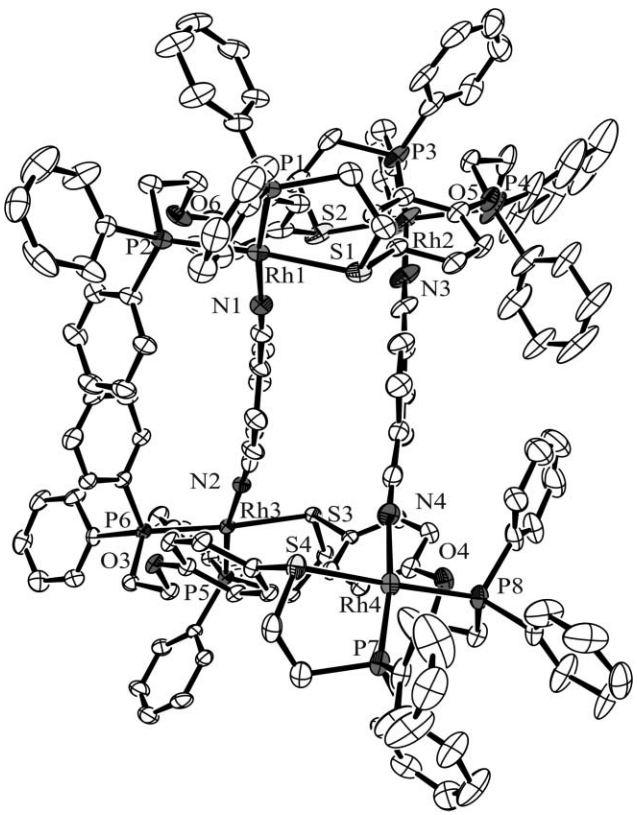

Fig. 1 ORTEP diagram of **4a** $\{(C_{152}H_{136}N_4O_4P_8S_4Rh_4)\ [B_4F_{16}]\}\cdot 3\ CH_2Cl_2\cdot 1\frac{1}{2}\ CH_3(CH_2)_3CH_3$ with thermal ellipsoids drawn to 30% probability. Hydrogen atoms, solvent molecules, and counterions have been omitted for clarity.

In conclusion, this manuscript demonstrates how one can use heteroligated complexes as novel building blocks where a single coordination site at each Rh center can be used to template the assembly of higher ordered multimetallic architectures. The ability to incorporate a wide variety of functional groups in the ditopic walls, ranging from complex chromophores to catalyst precursors, should make this chemistry and these structures attractive to researchers interested in building a variety of functional supramolecular materials.

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26 Crystallographic details for **4a**·3 CH_2Cl_2; $C_{162.5}H_{160}B_4Cl_6F_{16}N_4O_4P_8Rh_4S_4$, CCDC 615031, M = 3580.52, red block, Bruker Smart 1000 CCD (Mo Kα radiation), T = 153(2) K, Triclinic, space group P-1, a = 17.6443(14) Å, b = 21.5365(17) Å, c = 24.3009(19) Å, α = 73.6160(10)°, β = 75.7640(10)°, γ = 88.2150(10)°, V = 8580.0(12) Å^3, Z = 2, D_{calc} = 1.386 g cm^{-3}, μ(Mo Kα) = 0.663 mm^{-1}, 79 001 measured reflections, 39 961 independent reflections [R_{int} = 0.0446], θ_{max} = 28.82°, R_1 = 0.0987, $wR2$ = 0.2883, GOF = 1.192 [$I > 2\sigma(I)$]. The BF_4 with B4 is constrained to BF_4 with B1. A group anisotropic displacement parameter was refined for the constrained BF_4 which was necessary owing to disorder of the counterion. CCDC 615031. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b609931a.

27 The proposed structural model was refined with contributions from some of the solvate molecules removed from the diffraction data using the bypass procedure in PLATON (SPEK, 1990). The electron count from the "squeeze" model was 265 and the total potential solvent accessible area volume was 922.1 Å^3.

