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Coordination-Driven Assembly of Molecular Rectangles via an Organometallic “Clip”

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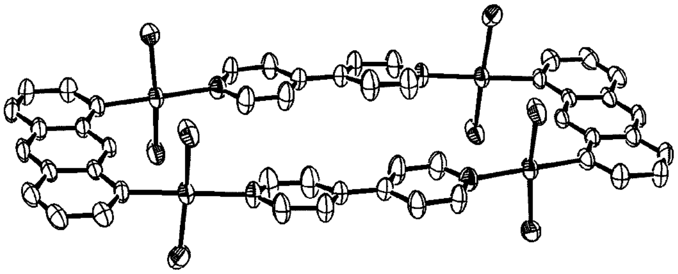
ABSTRACT



The combination of linear dipyridyl ligands with a new type of modular building unit, based upon a 1,8-platinum-functionalized anthracene, leads to the self-organization of rectangular frameworks. X-ray crystallography confirms the cyclic structure of the supramolecular cationic complexes. Spectral assignments were provided by 2D NOESY ^{1}H NMR experiments.

The formation of discrete supramolecular entities driven and held together through metal coordination has remained an intense area of study for the past decade. An attractive feature of this methodology is the rational design of diverse structures of predetermined shape, size, and functionality based on symmetry considerations.[1] The construction and characterization of macrocyclic species has been particularly successful, facilitated by the inherent simplicity of rings over three-dimensional systems. Typically comprising a backbone of difunctionalized aromatic ligands joined through transition metals, these inorganic cyclophanes have demonstrated the ability to act as hosts for small organic molecules in both aqueous[2] and nonpolar media.[3]

Of the various types of macrocycles reported to date, tetranuclear “molecular squares” have dominated the literature. Other high-symmetry structures, such as triangles, pentagons, and hexagons, have also been made.[1a]

As lower symmetry hosts can ultimately be expected to show enhanced guest selectivity, they represent a logical next step in the development of this area. Despite their relative simplicity, molecular rectangles[4] are much less common.

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Fujita first assembled dimetallic rectangular systems used in catenane syntheses by the use of cleverly designed flexible organic ligands.[5] More recently, a series of related tetrametallic systems have appeared.[6] The most noteworthy were built by Hupp and co-workers from doubly bridged dimetallic rhenium and manganese units.[3c,6d]

Since mixed-ligand species[7] are rarely observed, i.e., the combination of metals with different length ligands usually leads to complexes containing only one type of ligand,[8] the difficulty in the construction of rectangular structures lies in the necessity of designing a building unit with two parallel coordination sites facing in the same direction.

Presented here is a *ligand-directed* approach to molecular rectangles based upon a double-oxidative addition strategy. 1,8-Bis(*trans*-Pt(PEt_3)$_2$(NO_3))anthracene (**1**, Figure 1),[9] derived from 1,8-dichloroanthracene,[10] possesses two labile coordination sites rigidly directed in a nearly parallel fashion—a molecular "clip." We envisioned that such an arrangement, when combined with an appropriate ligand, would offer ready entry into a variety of new two- and three-dimensional architectures. Here we report the self-assembly reactions and characterization of the newest members of a family of molecular rectangles.

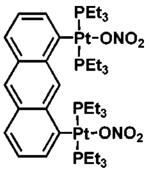

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Figure 1. Molecular "clip" **1**.

When **1** was combined with an equimolar amount of 4,4′-bipyridyl in an acetone-d_6/D_2O mixture, a pale yellow suspension resulted which, upon gentle heating, gradually dissolved (2 h) to give a bright orange homogeneous solution. $^{31}P\{^1H\}$ NMR (121.4 MHz) analysis of the reaction solution showed the quantitative formation of a single, highly symmetrical species (**2a**, Figure 2) by the appearance of a sharp singlet with concomitant ^{195}Pt satellites, shifted 6.0 ppm upfield ($-\Delta\delta$) relative to **1** ($\Delta^1J_{PPt} = -208$ Hz).

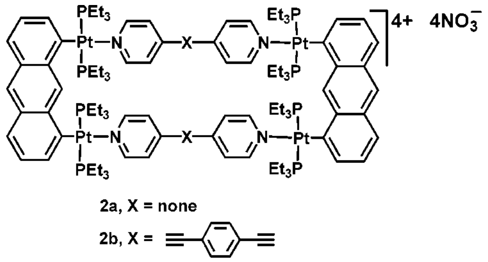

Figure 2. Molecular rectangles **2a**,**b**.

Also diagnostic were the significant downfield shifts of the pyridyl signals ($\Delta\delta \sim 0.5$ ppm) in the ^1H NMR (300 MHz) spectrum, associated with the loss in electron density upon coordination by the nitrogen lone pair to the metal center. However, the most noteworthy feature was that these two sets of signals from the pyridyl protons—equivalent in free 4,4′-bpy—became inequivalent in the assembled structure. The nature of this distinction was revealed in the crystal structure of **2a**.[11]

Antecedently, the product was isolated by precipitation with KPF_6 and then collected on a frit, washed with water, and dried. Crystals of **2a** were then grown by vapor diffusion of diethyl ether into an acetonitrile solution of the complex. Each unit contains two disordered solvent molecules, although the crystals were not found to be solvent dependent. Shown in the ORTEP representation (Figure 3), the structure of **2a** is not a perfect rectangle but is somewhat bowed in the middle, probably due to the steric demands of the triethylphosphines which push the platinum atoms slightly

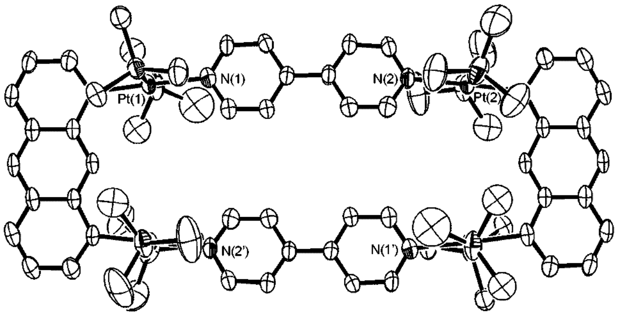

Figure 3. ORTEP of **2a** with hydrogens and counterions omitted for clarity. The solvent molecules and the methyl groups from the triethylphosphines are also excluded. Thermal ellipsoids are drawn to 30% probability.

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(4) Here metal-containing species is understood. For examples of organic molecular rectangles, see: (a) Odell, B.; Reddington, M. V.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1547. (b) Ashton, P. R.; Odell, B.; Reddington, M. V.; Slawin, A. M. Z.; Stoddart, J. F.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1550. (c) Büchner, M.; Geuder, W.; Gries, W.-K.; Hünig, S.; Koch, M; Poll, T. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1553. (d) Geuder, W.; Hünig, S.; Suchy, A. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 489.

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apart. Furthermore, the entire aromatic framework appears to be nearly coplanar with an unusually small dihedral angle ($\phi \cong 9°$) between the pyridyl planes of the 4,4′-bipyridines. Pyridyl planes in bridging 4,4′-bpy ligands are commonly twisted by anywhere from 25 to 35°, so as to reduce interaction of the ligand's 3,3′ and 5,5′ protons.[6b] In rectangle **2a**, the planar arrangement is presumably related to the rotational barriers found around platinum−nitrogen heteroaryl bonds.[12]

Although these effects are less likely to reveal themselves in metal complexes of higher symmetry, in **2a** we observe their influence with marked clarity due to the adjacent ligand positioning imposed by **1**. Consequently, the pyridyl protons pointed toward the inside of the complex experience an environment different from those on the periphery. Specific ^{1}H NMR assignments for the inner and outer pyridyl protons (Figure 4) were established by NOESY NMR (500 MHz). It should be noted that in the course of our two-dimensional spectroscopic studies of **2a**, at 26 °C we observed exchange between **1** and 4,4′-bpy with the nitrate salt of **2a**. By preparing the hexafluorophosphate salt of **2a** and carrying out the experiment at −40 °C in CD_2Cl_2, this exchange was suppressed, leaving the NOE's as shown in Figure 4. The strong NOE's from H_b to H_d, H_c to H_f, H_e to H_g, H_g to H_i, and H_i to H_h are all consistent with the crystal structure. The weaker NOE from H_a to H_b establishes the orientation of the 4,4′-bpy ligands.

The overall dimensions of the rectangle, defined by the metal corners, are 5.56 × 11.31 Å. As no solvent molecules or counterions were located within the cavity, nor did any channels exist in the crystal packing, **2a** was not expected to be capable of any host−guest interactions.

However, to demonstrate the versatility of **1** as a useful building block, a larger molecular rectangle was synthesized, **2b**, where the bridging ligands used were 4,4″-dipyridyl-1′,4′-diethynylbenzene.[13] We reasoned that this ligand would have the advantage of two freely rotating central rings, which may then offer potential for aromatic guest inclusion. The synthesis of **2b** has so far been confirmed by ^{1}H and ^{31}P-{^{1}H} NMR. Analogous to **2a**, the pyridyl protons are inequivalent, but with the central ring proton resonance appearing as a sharp singlet, indicating free rotation at ambient temperature. Preliminary experiments with aromatic

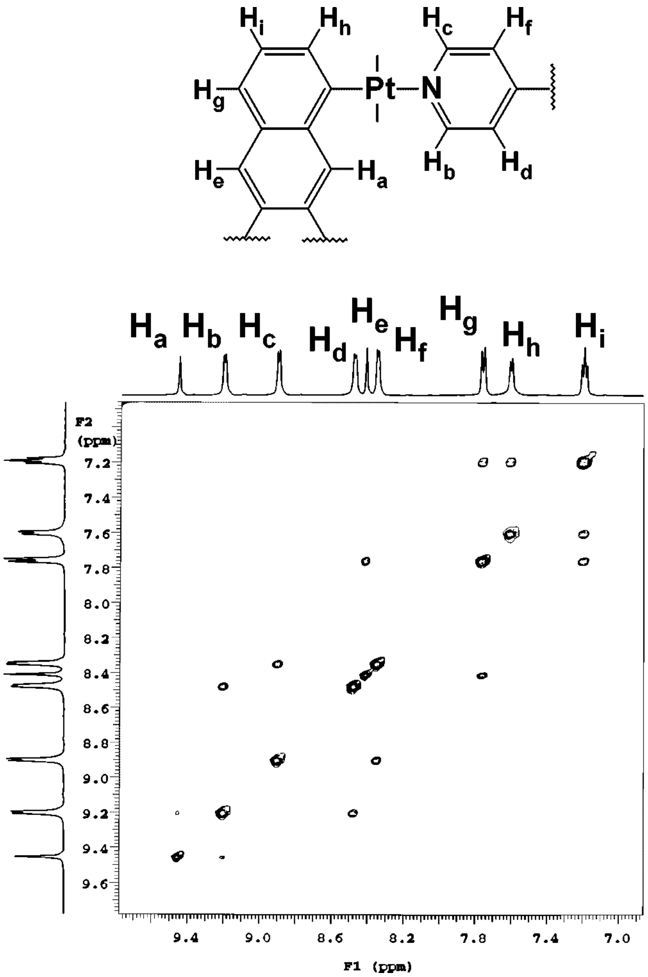

Figure 4. ^{1}H NMR NOESY spectrum (500 MHz) of the aromatic region of the hexafluorophosphate salt of **2a** in CD_2Cl_2 at −40 °C.

guests are now being conducted, the details of which will be the subject of future reports, including mechanistic insights, spectroscopic studies, and the extension of this structural motif to three-dimensional architectures.

Acknowledgment. We thank the National Institute of Health (5R01GM57052) for financial support.

Supporting Information Available: General experimental procedures and characterization data for compounds **1**, **2a**, and **2b** including crystal data, structure refinement details, and SHELXL file for **2a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[11] Crystal data: **2a**, monoclinic, space group $P2_1/c$ (No. 14), a = 20.0273(4) Å, b = 15.2535(2) Å, c = 21.7461(5) Å, β = 112.737(1)°, V = 6126.9(2) Å^3, Z = 2, D_c = 1.677 g/cm^3, final R value 0.061 for 20145 unique reflections, goodness of fit 1.057.

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