Toward Self-Assembled Surface-Mounted Prismatic Altitudinal Rotors. A Test Case: Molecular Rectangle
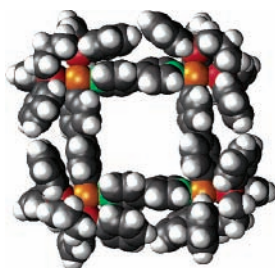
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ABSTRACT

A self-assembly path toward prismatic molecular rotors based on transversely reactive terminally metalated molecular rods and pyridine-terminated star connectors is outlined. The concept is tested on the assembly of the biphenyl rod $[Ph_2P(CH_2)_3PPh_2Pt^+\text{-}C_6H_4\text{-}C_6H_4\text{-}Pt^+[Ph_2P(CH_2)_3\text{-}PPh_2]$ and 4,4′-bipyridyl into a molecular rectangle, fully characterized by NMR and MS, including diffusion-ordered NMR and collision-induced dissociation MS.

For some time,[1] this laboratory has been developing a molecular assembly kit of rods[2] and star-shaped connectors[3–5] analogous to elements of the children's "Tinkertoy"[6] construction set. They have been used to assemble surface-mounted structures[7] and simple molecular rotors whose

dipolar rotor can be flipped by the electric field of an STM (scanning tunneling microscope) tip.[8]

We next wish to find out whether surface-mounted altitudinal (axle parallel to surface) molecular rotors could be driven by fluid flow parallel to the surface. Rotators with large paddles would offer advantages, but the rotor axle then needs to be located farther away from the surface than has been the case so far. It appears to us that molecules consisting of edges of regular prisms, particularly trigonal and tetragonal, might be a suitable choice. Two edges of the prism would be adsorbed on the surface, and one or two other edges would represent axles carrying rotors to be driven by the flow. This motivated an effort to develop an approach to prototype prismatic rotors of the type presented in Figure 1,

(1) (a) Kaszynski, P.; Michl, J. *J. Am. Chem. Soc.* **1988**, *110*, 5225. (b) Michl, J.; Kaszynski, P.; Friedli, A. C.; Murthy, G. S.; Yang, H. C.; Robinson, R. E.; McMurdie, N. D.; Kim, T. In *Strain and Its Implications in Organic Chemistry*; NATO ASI Ser. 273; de Meijere, A., Blechert, S., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1989; p 463. (c) Kaszynski, P.; Friedli, A. C.; Michl, J. *J. Am. Chem. Soc.* **1992**, *114*, 601.

(2) Schwab, P. F. H.; Levin, M. D.; Michl, J. *Chem. Rev.* **1999**, *99*, 1863.

(3) Schöberl, U.; Magnera, T. F.; Harrison, R. M.; Fleischer, F.; Pflug, J. L.; Schwab, P. F. H.; Meng, X.; Lipiak, D.; Noll, B. C.; Allured, V. S.; Rudalevige, T.; Lee, S.; Michl, J. *J. Am. Chem. Soc.* **1997**, *119*, 3907.

(4) Harrison, R. M.; Brotin, T.; Noll, B. C.; Michl, J. *Organometallics* **1997**, *16*, 3401.

(5) Schwab, F. H.; Noll, B. C.; Michl, J. *J. Org. Chem.* **2002**, *67*, 5476.

(6) Tinkertoy is a trademark of Playskool, Inc., Pawtucket, RI 02862 and designates a children's toy construction set consisting of straight wooden sticks and other simple elements insertable into spool-like connectors.

(7) Magnera, T. F.; Michl, J. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4788.

(8) Zheng, X.; Mulcahy, M. E.; Horinek, D.; Galeotti, F.; Magnera, T. F.; Michl, J. *J. Am. Chem. Soc.* **2004**, *126*, 4060.
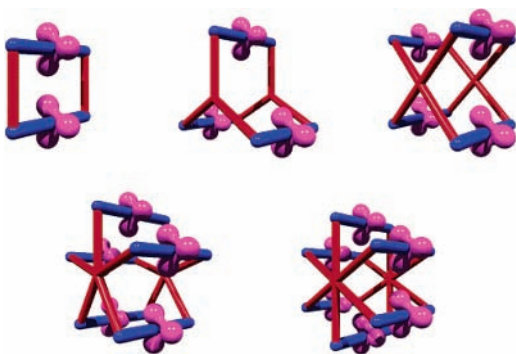
Figure 1. Prototypes of prismatic altitudinal rotors. The purple triple lobes stand for rotators (e.g. triptycene). The blue rods terminate in a metal carrying a transverse ligation site and the red rods terminate in an axially directed ligand.

which would ultimately be provided with functionalities designed to attach two of the prism edges to a surface such as gold or quartz.

The logical way to such large and relatively rigid prism skeletons is transition metal mediated, coordination driven self-assembly,[9–11] well-known to produce highly symmetric structures, such as polygonal macrocycles and polyhedral boxes.[10,12] The prism skeletons of Figure 1 are of lower symmetry and require an ability to prepare molecular rectangles.[13,14] Avoiding the formation of a mixture of small and large squares from chemically equivalent rods of different lengths is hard.[15] The use of metal centers carrying two distinct cis-disposed sites for assembly seems preferable, but such structures are rare.[16]

(9) (a) Baxter, P. N. W.; In *Comprehensive Supramolecular Chemistry*; Lehn, J. M., Chair, E., Atwood, J. L., Davis, J. E. D., MacNichol, D. D., Vogtle, F., Eds.; Pergamon Press: Oxford, UK, 1996; Vol. 9, Chapter 5, p 165. (b) Lehn, J.-M.; Ball, P. *New Chem.* **2000**, 300. (c) Fujita, M. *Chem. Soc. Rev.* **1998**, *27*, 417. (d) Balzani, V.; Gomez-Lopez, M.; Stoddart, J. F. *Acc. Chem. Res.* **1998**, *31*, 405. (e) Cotton, F. A.; Lin, C.; Murillo, C. A. *Acc. Chem. Res.* **2001**, *34*, 759.

(10) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853.

(11) Caulder, D. L.; Raymond, K. N. *Acc. Chem. Res.* **1999**, *32*, 975.

(12) Swiegers, G. F.; Malefetse, T. J. *Chem. Rev.* **2000**, *100*, 3483.

(13) (a) Sommer, R. D.; Rheingold, A. L.; Goshe, A. J.; Bosnich, B. *J. Am. Chem. Soc.* **2001**, *123*, 3940. (b) Manimaran, B.; Rajendran, T.; Lu, Y.-L.; Lee, G.-H.; Peng, S.-M.; Lu, K.-L. *J. Chem. Soc., Dalton Trans.* **2001**, 515. (c) Suzuki, H.; Tajima, N.; Tatsumi, K.; Yamamoto, Y. *Chem. Commun.* **2000**, 1801. (d) Rajendran, T.; Manimaran, B.; Lee, F.-Y.; Lee, G.-H.; Peng, S.-M.; Wang, C. M.; Lu, K.-L. *Inorg. Chem.* **2000**, *39*, 2016. (e) Yan, H.; Suss-Fink, G.; Neels, A.; Stoeckli-Evans, H. *J. Chem. Soc., Dalton Trans.* **1997**, 4345. (f) Benkstein, K. D.; Hupp, J. T.; Stern, C. L. *Inorg. Chem.* **1998**, *37*, 5404. (g) Woessner, S. M.; Helms, J. B.; Shen, Y.; Sullivan, B. P. *Inorg. Chem.* **1998**, *37*, 5406. (h) Benkstein, K. D.; Hupp, J. T.; Stern, C. L. *Angew. Chem., Int. Ed.* **2000**, *39*, 2891. (i) Su, C.-Y.; Cai, Y.-P.; Chen, C.-L.; Smith, M. D.; Kaim, W.; zur Loye, H.-C. *J. Am. Chem. Soc.* **2003**, *125*, 8595.

(14) Kuehl, C. J.; Mayne, C. L.; Arif, A. M.; Stang, P. J. *Org. Lett.* **2000**, *2*, 3727.

(15) (a) Slone, R. V.; Benkstein, K. D.; Bélanger, S.; Hupp, J. T.; Guzei, I. A.; Rheingold, A. L. *Coord. Chem. Rev.* **1998**, *171*, 221. (b) Caulder, D. L.; Raymond, K. N. *Angew. Chem., Int. Ed.* **1997**, *36*, 1440. (c) Kramer, R.; Lehn, J.-M.; Marquis-Rigult, A. *Proc. Natl. Acad. Sci. U.S.A.* **1993**, *90*, 5394.

(16) (a) Baxter, P. N.; Lehn, J.-M.; DeCian, A.; Fischer, J. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 69. (b) Hasenknopf, B.; Lehn, J.-M.; Baum, G.; Fenske, D. *Proc. Natl. Acad. Sci. U.S.A.* **1996**, *93*, 1397. (c) Baxter, P. N.; Lehn, J.-M.; Kneisel, B. O.; Fenske, D. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1978.

Directed assembly of low-symmetry systems such as trigonal prisms has been addressed by the "Symmetry Interaction"[11] and "Molecular Library"[10] models.[17] We have adopted the latter, which is based on the use of directional building blocks. For instance, a "molecular clip", carrying two coordination sites rigidly facing in the same direction, has been used with linear ditopic ligands to assemble rectangles, and with trigonal tritopic ligands to assemble trigonal prisms.[14,18,19]

We wish to produce the self-assembled prisms of Figure 1 from star-shaped connectors carrying a radially directed ligand at each arm end (shown in orange) and rotator paddle-wheel carrying rods whose termini carry a metal atom with a transversely directed active site (shown in purple and blue). The association of the connector ligands with the metal is to be reversible, whereas the attachment of the metal to the rod is to be covalent and permanent.

The simplest test case, employing a two-armed star connector, is a rectangle ("digonal prism"). The requirement of nearly free rotation for the rotator makes it difficult to fix the dihedral angle between the transverse directions of the terminal coordination sites on the rod. The organometallic rods thus will be less effective as shape-defining units than Stang's clips.[14,18,19] His initial attempt to prepare a rectangle using such a nearly free rotatable organometallic rod yielded only polymers.[18] More recently, he has been successful in assembling hexagons and prisms from nearly freely rotatable rods terminated with transversely directed ligands and an organometallic clip with radially directed metal coordination sites.[20] This is exactly complementary to our intended approach, which requires the use of nearly freely rotating biphenyl-based rods terminated in the $-PtdpppNO_3$ (dppp $= Ph_2P(CH_2)_3PPh_2$) substituents (**1**), which carry a transversely directed metal coordination site. Combination with 4,4′-bipyridyl as a digonal star connector with radially directed ligands (Scheme 1) should then yield our first target structure, the molecular rectangle **2** (Figure 2).

Scheme 1. Self-Assembly of Molecular Rectangle **2**
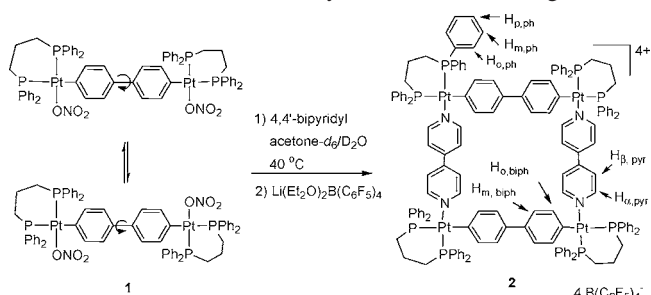
A suspension obtained from 4,4′-bipyridyl and **1**, prepared according to Scheme 1S (Supporting Information) in acetone-

(17) (a) Stang, P. J. *Chem. Eur. J.* **1998**, *4*, 19. (b) Caulder, D. L.; Raymond, K. N. *J. Chem. Soc., Dalton Trans.* **1999**, 1185. (c) Holliday, B. J.; Mirkin, C. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 2022. (d) Fujita, M.; Umemoto, K.; Yoshizawa, M.; Fujita, N.; Kusukawa, K.; Biradha, K. *Chem. Commun.* **2001**, 509.
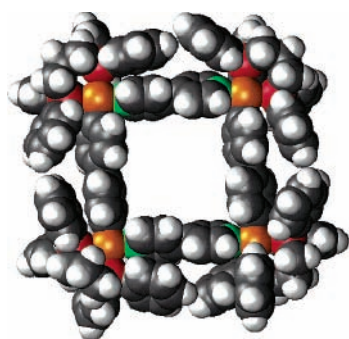
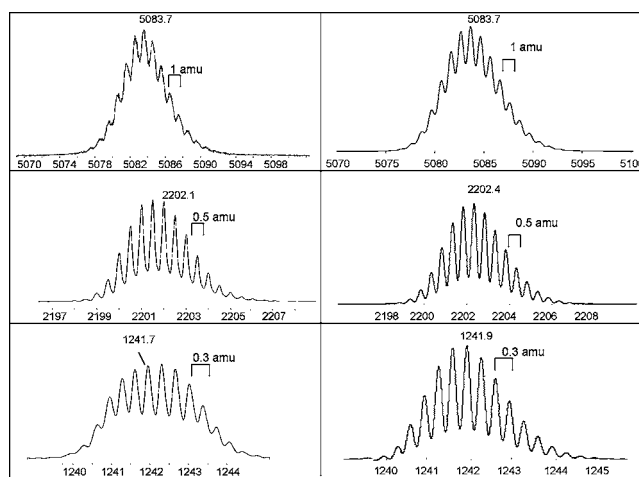**Figure 2.** Optimized (UFF)[21] structure of molecular rectangle, **2**.

Figure 3. Observed (left) and calculated (right) isotopic distribution patterns of **2**: $[M - 1B(C_6F_5)_4]^+$, $[M - 2B(C_6F)_4]^{2+}$, and $[M - 3B(C_6F_5)_4]^{3+}$.

d_6/D$_2$O, slowly dissolved upon heating. Product **2** was precipitated by addition of LiB(C$_6$F$_5$)$_4$, chosen for the low nucleophilicity of its anion, expected[18] to impart kinetic stability to **2**. We were unable to grow X-ray diffraction quality crystals, but the composition, structure, and purity of the product were determined beyond reasonable doubt by a combination of multinuclear NMR, ESI-MS-CID, and elemental analysis.

The NMR spectra do not change from −90 to 100 °C. They have been fully assigned and fit the presence of a single type of square-planar Pt atom carrying the dppp ligand and two distinct rods in cis orientation. Only one type of biphenyl rod and one type of bipyridyl rod are present, and it follows that the product is a ring of alternating biphenyl and bipyridyl units linked via Pt$^+$(dppp) cations. Only one signal is present for each ortho and meta ^{1}H and ^{13}C atom in each aromatic ring, demonstrating the equivalence of the two termini of each rod, and the absence of exo−endo differentiation of rod edges, attributed to rapid twisting equilibration.

The ^{195}Pt NMR spectrum reveals one type of resonance appearing as a doublet of doublets, $J_{P-Pt} = 3629$ and 1535 Hz, consistent with Pt satellites observed in the ^{31}P spectra. The ^{31}P{^{1}H} NMR spectrum indicates two inequivalent ^{31}P nuclei as two doublets ($J_{PP} = 24$ Hz), one at 2.9 ppm, cis to pyridine (determined by NOE), with ^{195}Pt satellites ($J_{PPt} = 1538$ Hz), and another of equal intensity at −7.7 ppm, trans (NOE) to pyridine ($J_{PPt} = 3646$ Hz). The ^{1}H NMR spectrum shows a single set of α pyridine protons at 8.2 ppm. The signals of the β protons are obscured under a set of signals from biphenyl at 6.8 ppm but have been revealed and assigned through 2-dimensional correlation experiments. Compared to the free ligand, the pyridyl signals show an upfield shift, Δδ 0.0.6 ppm, attributed to shielding by the dppp phenyl rings (Figure 2) as has been reported for similar systems.[21] The ^{13}C NMR spectrum revealed C$_{ipso}$ of biphenyl

(18) Kuehl, C. J.; Huang, S. D.; Stang, P. J. *J. Am. Chem. Soc.* **2001**, *123*, 9634.

(19) Kuehl, C. J.; Yamamoto, T.; Seidel, S. R.; Stang, P. J. *Org. Lett.* **2002**, *4*, 913.

(20) (a) Chi, K.-W.; Addicott, C.; Arif, A. M.; Das, N.; Stang, P. J. *J. Org. Chem.* **2003**, *68*, 9798. (b) Chi, K.-W.; Addicott, C.; Kryschenko, Y. K.; Stang, P. J. *J. Org. Chem.* **2004**, *69*, 964.

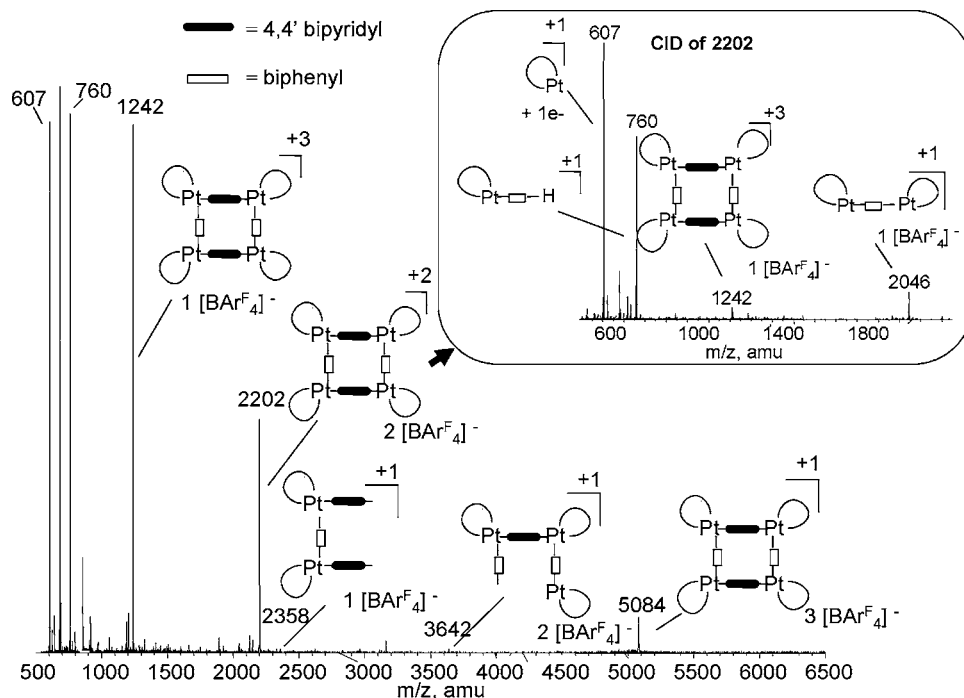(21) Stang, P. J.; Danh, C. H. *J. Am. Chem. Soc.* **1994**, *116*, 4981.

as a doublet of doublets, $J_{P-C} = 99$ and 8 Hz. No coupling was observed to ^{195}Pt, probably because the ^{195}Pt satellites were below the noise level. An HMBC experiment established one ^{1}H multiple-bond correlation to C$_{ipso}$ at 6.41 ppm, thus allowing us to assign ^{1}H$_{m,biph}$. One single-bond ^{13}C correlation to ^{1}H$_{m,biph}$ was observed at 125.9 ppm by HSQC, allowing the assignment of C$_{m,biph}$. The ^{1}H$_{m,biph}$ signal is correlated to only one ^{1}H signal at 6.80 ppm, allowing the assignment of ^{1}H$_{o,biph}$ (6.80 ppm). One single-bond ^{13}C correlation to ^{1}H$_{o,biph}$ was observed by HSQC leading to the assignment of C$_{o,biph}$ (135.6 ppm). The ^{1}H$_{o,biph}$ signal was correlated to both C$_{o,biph}$ and another quaternary carbon at 135.0 ppm assigned as C$_{p,biph}$. The C$_{p,biph}$ signal is not correlated to any other ^{1}H signals. All ^{1}H and ^{13}C signals of the bipyridyl portion of the rectangle were assigned similarly.

NOE has been used to examine group proximity. To eliminate the possible loss of NOE correlations due to rotational correlation times approaching $1/\omega_0$, the rotating frame ROESY experiment was utilized. Figure 1S (Supporting Information) shows that it revealed NOEs from bipyridyl to both adjacent phosphine phenyls and biphenyl, specifically from H$_{\alpha,pyr}$ to H$_{\beta,pyr}$, H$_{o,biph}$, H$_{o,ph}$, and weakly to H$_{m,ph}$. An NOE was also observed from H$_{\beta,pyr}$ to H$_{m,ph}$. These results support the expected cis arrangement of biphenyl and bipyridyl and leave no doubt that the product has a molecular structure consisting of biphenyl and bipyridyl units alternating in a ring.

The size of the macrocyclic ring was determined by diffusion-ordered NMR (DOSY) with ^{1}H detection. Since the diffusion constant of the CHDCl$_2$ peak from the solvent varied with sample composition, only the relative values of the reduced molecular masses are meaningful. The values found were 455 g/mol for **1** and 3.3 times higher, 1492 g/mol, for **2**. The values expected are 1491 g/mol for **1** and 5763 g/mol for **2**, in a ratio of 1:3.9. The ratio agrees well, particularly if one considers that the B(C$_6$F$_5$)$_4^-$ anions need not be ion-paired with the cation all the time. If the

Figure 4. ESI-MS of **2** and CID of the peak at *m/z* 2202.

macrocycle had a hexagonal structure with three rods of each kind, the expected ratio would be 1:5.8, and with larger rings the discrepancy would be even bigger. We conclude on the basis of the integrated NMR evidence that the self-assembled macrocycle has the rectangular structure **2**.

To confirm the structural assignment, the electrospray ionization mass spectrum of the product was obtained. It showed $[M - B(C_6F_5)_4]^+$, $[M - 2B(C_6F_5)_4]^{2+}$, and $[M - 3B(C_6F_5)_4]^{3+}$ peaks at the values of *m/z* 5083.6, 2201.6, and 1242.0, respectively, expected for **2**, with the anticipated isotopic distribution patterns (Figure 3). The $[M - 4B(C_6F_5)_4]^{4+}$ peak was not observed, but two fragment peaks observed also support the structure **2** (Figure 4): One is at *m/z* 2358 with a spacing of $\Delta m = 1$ amu and corresponds to the cleavage of two Pt–N bonds and the loss of one side of the rectangle, a Pt-terminated biphenyl. The other corresponds to the loss of one Pt center and a bipyridyl and addition of a proton at *m/z* 3642, but its resolution is insufficient for independent charge state determination.

Collision-induced dissociation (CID) on the *m/z* 2202 ion $[M - 2B(C_6F_5)_4]^{2+}$ confirmed structure **2** (Figure 4). A peak at *m/z* 1242 corresponds to $[M - 3B(C_6F_5)_4]^{3+}$, a peak at *m/z* 2046, with spacing of $\Delta m = 1$, corresponds to $[1 - 1B(C_6F_5)_4]^+$, a peak with a spacing of $\Delta m = 1$ at *m/z* 760 corresponds to one Pt corner with one biphenyl rod, and a peak with a spacing of $\Delta m = 1$ at *m/z* 607 corresponds to one Pt corner.

In conclusion, the evidence that **2** has been assembled is overwhelming. This structure is not the first self-assembled molecular rectangle with metal atoms in the corners, but it has unique features important for our overall plan. Its corners consist of metal atoms carrying one covalently and one coordinatively attached rod, permitting a facile differentiation of the rectangle sides, and it contains a nearly freely internally rotating organometallic rod with transverse directions of the terminal coordination sites, a necessity for the proposed approach to prismatic altitudinal rotors. This bodes well for the preparation of the prisms shown in Figure 1 from rotator-carrying rods terminated in metal atoms with a transversely directed active site, combined with pyridine-terminated star-shaped connectors such as those that we have already synthesized.[4,5] The issues of kinetic stability of the prismatic rotors and their attachment to a surface remain to be addressed.

Supporting Information Available: Full experimental details for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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