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Solution and Solid State Studies of a Triangle–Square Equilibrium: Anion-Induced Selective Crystallization in Supramolecular Self-Assembly

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We report that an equilibrium mixture of triangular and square supramolecular species results when the flexible, ditopic donor unit, *trans*-bis(4-pyridyl)ethylene, is reacted with the ditopic acceptor unit, *cis*-$(Me_3P)_2Pt(OTf)_2$, in a one-to-one ratio. Both products are characterized in solution, by way of multinuclear NMR, and in the solid state, via X-ray crystallography. The effects of water and anions, cobalticarborane versus triflate, on the equilibrium are probed. The selective crystallization of either of the two species can be accomplished via the appropriate choice of solvents and ratio of anions present in the system. The dominant species in solution is not always consistent with the most prevalent species in the solid state.

Introduction

Transition-metal-mediated, coordination-driven self-assembly has allowed for the synthesis of a host of predesigned macrocycles and cages.[1] Since nearly the inception of this field, however, there have been certain instances in which the stoichiometric combination of ~90° corners with linear linking units has led to a mixture of two, highly symmetrical products, instead of the anticipated supramolecular square.[2] This phenomenon has been postulated as an equilibrium between both square and triangular entities in solution, yet the first example which crystallographically proves the existence of such an equilibrium has only recently been reported.[2f] These systems have been a topic of interest in recent years due in part to their deviation from the directional-bonding approach[1f,j] and, more importantly, due to the insight that they may provide into the mechanism of self-assembly. Interestingly, bimetallic loops have also been produced under similar circumstances when bent or highly flexible linking subunits have been employed.[1k,2k,m]

Herein, we report a triangle–square equilibrium based upon a ditopic ~90° acceptor unit, *cis*-$(Me_3P)_2Pt(OTf)_2$ **1**, and flexible building block, *trans*-bis(4-pyridyl)ethylene **2**. In addition, we probe its dependence on water and anions and describe a method for the selective crystallization of the two species, allowing for a high degree of control over the final outcome of the reaction.[2f,3,4] Both products in the equilibrium are characterized by way of X-ray crystallography and in solution via multinuclear NMR.

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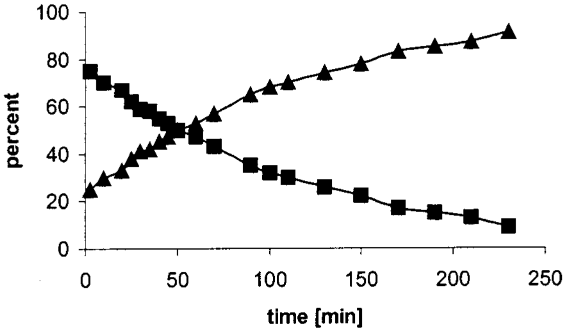
Chart 1. Observation of the Percent Square **3** (Squares) and Triangle **4** (Triangles) vs Time in Achieving Equilibrium



Experimental Section

NMR spectra were recorded on a Varian XL-300 or a Unity 300 spectrometer. ^1H chemical shifts are reported relative to the residual hydrogens of d_6-nitromethane (4.33 ppm). ^{19}F and ^{31}P chemical shifts are reported relative to unlocked, external samples of $CFCl_3$ (0.0 ppm) and H_3PO_4 (0.0 ppm), respectively.

All reagents were purchased from Aldrich, except for *cis*-$(Me_3P)_2Pt(OTf)_2$ **1**, which was prepared according to literature methods.[5]

[*cis*-$(Me_3P)_2Pt(OTf)_2$]$_4$[*trans*-bis(4-pyridyl)ethylene]$_4$ (Square 3). A solution of 1.41 mg (0.0077 mmol) of *trans*-bis(4-pyridyl)ethylene **2** in 0.3 mL of CD_3NO_2 was added to 5.00 mg (0.0077 mmol) of *cis*-$(Me_3P)_2Pt(OTf)_2$ **1** dissolved in 0.3 mL of CD_3NO_2. The combined assembly was quantitative via multinuclear NMR, leading to a mixture of square **3** and triangle **4** in a ratio of 9:91. The solution was transferred to a small test tube, and 5 μL of D_2O was added. Diffusion of diethyl ether into the test tube yielded large, colorless crystals. After essentially quantitative crystallization of the material, the solvent was removed carefully via pipet, the residue was dried for about 1 min under a flow of nitrogen, and the crystals were redissolved in 0.6 mL of CD_3NO_2. The equilibration process was monitored via ^1H NMR. After 2 min 45 s, the ratio of square to triangle was 75:25. After 4 h, equilibrium was reached, with a ratio of 8:92 (square to triangle, Chart 1). **Square 3:** ^1H NMR (CD_3NO_2, 300 MHz) δ 8.91 (d, $H_{\alpha pyr}$), 7.85 (d, $H_{\beta pyr}$), 7.54 (s, $H_{=}$), 1.62 (d, $J_{P-H} = 11.4$ Hz, $P-CH_3$); $^{31}P\{^1H\}$ NMR (CD_3NO_2, 121 MHz) δ −27.98 (s, ^{195}Pt satellites, $J_{Pt-P} = 3123$ Hz); ^{19}F NMR (CD_3NO_2, 282 MHz) δ −78.8. **Triangle 4**: ^1H NMR (CD_3NO_2, 300 MHz) δ 8.82 (d, $H_{\alpha pyr}$), 7.73 (d, $H_{\beta pyr}$), 7.43 (s, $H_{=}$), 1.72 (d, $J_{P-H} = 11.4$ Hz, $P-CH_3$); $^{31}P\{^1H\}$ NMR (CD_3NO_2, 121 MHz) δ −28.03 (s, ^{195}Pt satellites, $J_{Pt-P} = 3123$ Hz); ^{19}F NMR (CD_3NO_2, 282 MHz) δ −78.8.

[*cis*-$(Me_3P)_2Pt(OTf)_{4/3}$(cobalticarborane)$_{2/3}$]$_3$[*trans*-bis(4-pyridyl)ethylene]$_3$ (Triangle 5). A solution of 2.83 mg (0.016 mmol) of *trans*-bis(4-pyridyl)ethylene **2** in 0.3 mL of CD_3NO_2 was added to 10.03 mg (0.016 mmol) of *cis*-$(Me_3P)_2Pt(OTf)_2$ **1** dissolved in 0.3 mL of CD_3NO_2. The combined assembly was quantitative via multinuclear NMR, leading to a mixture of square **3** and triangle **4** in a ratio of 10:90. The solution was titrated, by way of NMR monitoring, with $NaCoB_{18}C_4H_{22}$ (0.01 mmol) in CD_3NO_2 solution to obtain a ratio of two cobalticarborane anions to each triangle **5**. The solvent was removed under a flow of nitrogen, and the residue was washed three times with deionized water to remove the excess sodium triflate. The remaining yellow solid was dried in vacuo and redissolved in about 0.3 mL of CD_3NO_2. Yellow crystals were grown by diffusion of diethyl ether into the resultant solution. After essentially quantitative crystallization of the material (colorless solvent), the solvent was removed carefully via pipet, the residue was dried for about 1 min under a flow of nitrogen, and the crystals were redissolved in 0.6 mL of CD_3NO_2. The equilibration process was monitored via ^1H NMR. After 2 min, no square could be detected. After 45 min, 5% square could be detected.

Table 1. Crystallographic Parameters for Compounds **3** and **5**

	3	**5**
formula	$C_{86}H_{130}F_{24}N_{14}O_{36}P_8Pt_4S_8$	$C_{72}H_{148}B_{36}Co_2F_{12}N_8O_{19}P_6Pt_3S_4$
M	3676.64	3064.33
T/K	200(1)	170(1)
syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a/Å	11.5726(16)	17.8621(4)
b/Å	17.160(3)	18.1176(4)
c/Å	21.568(4)	24.7289(5)
α/deg	80.901(7)	79.2671(14)
β/deg	74.906(10)	72.8745(12)
γ/deg	87.888(13)	62.5075(13)
V/Å^3	4083.2(12)	6772.3(3)
Z	1	2
μ/mm^{-1}	3.686	3.531
R1 ($I > 2\sigma(I)$)	0.0948	0.0805
GOF	1.032	1.082

X-ray Crystallography. The crystals were mounted on a glass fiber with traces of viscous oil and then transferred to a Nonius KappaCCD diffractometer equipped with Mo Kα radiation (λ = 0.71073 Å). Ten frames of data were collected at 200(1) K for **3** and 170(1) K for **5** with an oscillation range of 1 deg/frame and an exposure time of 20 s/frame.[6] Indexing and unit cell refinement, based on all observed reflection from those 10 frames, indicated the lattice type and space group. All reflections were indexed, integrated, and corrected for Lorentz, polarization, and absorption effects using DENZO-SMN and SCALEPAC.[7] Postrefinement of the unit cell gave its final parameters, which were used in the final least squares refinement of the structure. See Table 1 for selected crystallographic parameters.

The structure was solved by a combination of direct methods and heavy atom using SIR 97.[8] All of the non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were assigned isotropic displacement coefficients U(H) = 1.2U(C) or 1.5U(Cmethyl), and their coordinates were allowed to ride on their respective carbons using SHELXL97.[9] Scattering factors were taken from the *International Tables for Crystallography*, Volume C.[10,11]

Along with its eight triflate anions, square **3** shows the presence of six nitromethane molecules enclathrated within the crystal lattice per macrocycle. Both the anions and solvent molecules in **3** exhibit disorder. The lattice of **5** includes four triflate and two cobalticar-

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(3) (a) Hasenknopf, B.; Lehn, J.-M.; Boumediene, N.; Dupont-Gervais, A.; van Dorsselaer, A.; Kneisel, B.; Fenske, D. *J. Am. Chem. Soc.* **1997**, *119*, 10956−10962. (b) Hasenknopf, B.; Lehn, J.-M.; Kneisel, B. O.; Baum, G.; Fenske, D. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1838−1840.

(4) (a) Campos-Fernández, C. S.; Clérac, R.; Dunbar, K. R. *Angew. Chem., Int. Ed.* **1999**, *38*, 3477−3479. (b) Campos-Fernández, C. S.; Clérac, R.; Koomen, J. M.; Russell, D. H.; Dunbar, K. R. *J. Am. Chem. Soc.* **2001**, *123*, 773−774. (c) Vilar, R.; Mingos, D. M. P.; White, A. J. P.; Williams, D. J. *Angew. Chem., Int. Ed.* **1998**, *37*, 1258−1261. (d) Fleming, J. S.; Mann, K. L. V.; Carraz, C.-A.; Psillakis, E.; Jeffery, J. C.; McCleverty, J. A.; Ward, M. D. *Angew. Chem., Int. Ed.* **1998**, *37*, 1279−1281.

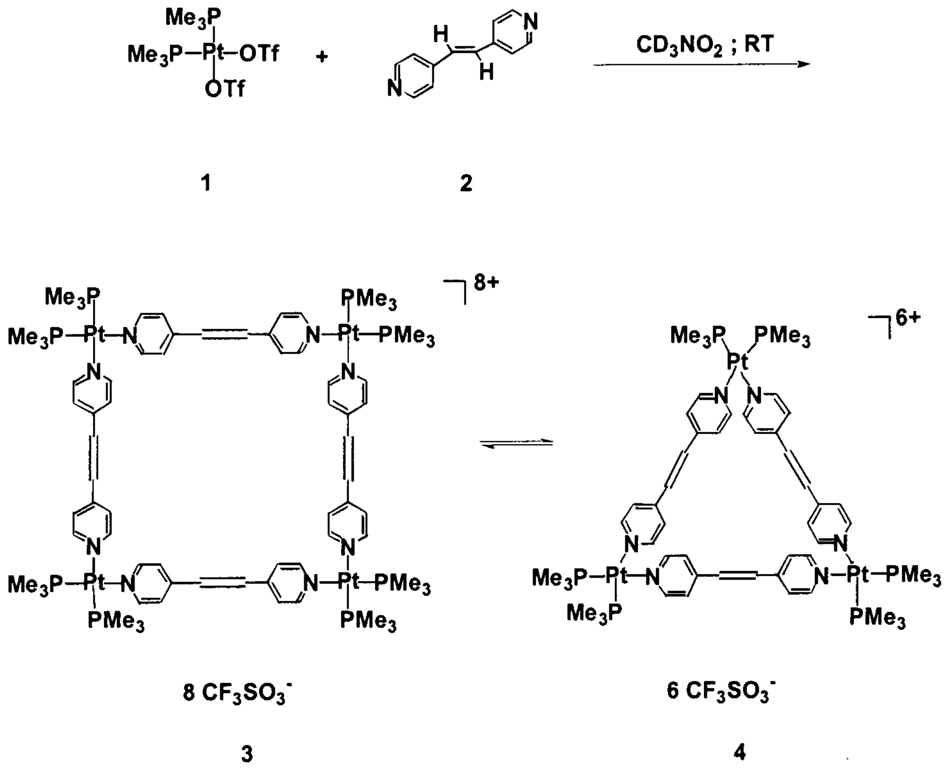
(5) (a) Schweiger, M.; Seidel, S. R.; Arif, A. M.; Stang, P. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 3467−3469. (b) Leung, W.-H.; Chim, J. L. C.; Wong, W.-T. *J. Chem. Soc., Dalton Trans.* **1996**, 3153−3154.

(6) COLLECT Data Collection Software. Nonius B.V. 1998.

(7) Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307−326.

(8) SIR97 (Release 1.02): A program for automatic solution and refinement of crystal structure. A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliteni, G. Polidori, and R. Spagna.

Scheme 1. Reaction of Acceptor Unit **1** and Donor Unit **2** Leads to an Equilibrium Mixture of Square **3** and Triangle **4**



borane counterions, two nitromethane molecules, two waters, and one molecule of diethyl ether for each triangle. Disorder is present in the nitromethane, diethyl ether, and triflate molecules in the unit cell of **5**.

Results and Discussion

cis-$(Me_3P)_2Pt(OTf)_2$ **1**, a ditopic ~90° acceptor unit with an apparent propensity toward making triangular species,[5a] is reacted stoichiometrically with *trans*-bis(4-pyridyl)ethylene **2** in deuterated nitromethane. Ditopic, donor linker **2** is employed due to its increased flexibility over more rigid building blocks, such as 4,4′-dipyridyl, giving it the potential for bringing closer together in energy the two products of any square–triangle equilibrium that may exist.[2g] Monitoring of the reaction via $^{31}P\{^{1}H\}$ and ^{1}H NMR shows a 2-fold set of signals with similar splitting patterns and indicates the presence of two highly symmetrical species, a square **3** and a triangle **4**, in solution (Scheme 1).

Slow diffusion of diethyl ether into the reaction mixture leads to the formation of colorless, highly solvent dependent crystals suitable for X-ray crystal structure analysis. The resulting species is that of square **3**, which crystallizes in the triclinic space group $P\bar{1}$. The Pt–N linkages are all ~2.1 Å, and each N–Pt–N bond angle falls within the range of ~84–87° (Figure 1). These values are in agreement with related supramolecular squares in the literature.[1f]

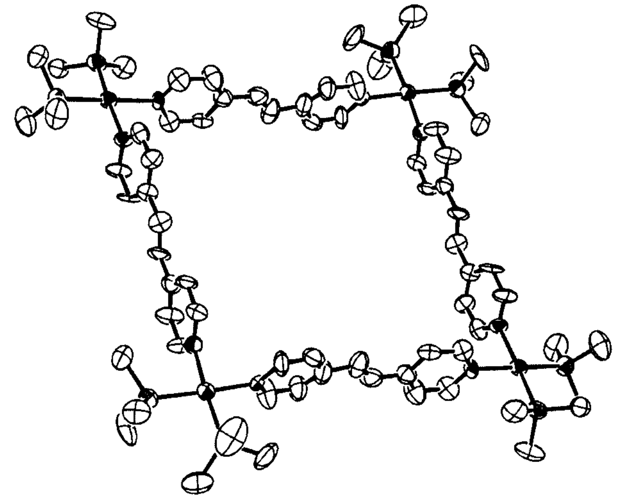


Figure 1. ORTEP plot of square **3** (anions, solvent, and hydrogens omitted for clarity).

The solid state structure coupled with NMR experiments[12] allows for the reasonable assignment of the square and triangle signals in the NMR spectra. With this, the original, precrystallization reaction mixture is found to comprise only 11% square **3** and 89% triangle **4**. Immediately upon redissolution in nitromethane, however, the solid resulting from the complete crystallization of the products shows 54%

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(9) SHELX97 [Includes SHELXS97, SHELXL97, CIFTAB]: Sheldrick, G. M. (1997). Programs for Crystal Structure Analysis (Release 97-2). University of Göttingen, Germany.

(10) Maslen, E. N.; Fox, A. G.; O'Keefe, M. A. In *International Tables for Crystallography: Mathematical, Physical and Chemical Tables*; Wilson, A. J. C., Ed.; Kluwer: Dordrecht, The Netherlands, 1992; Vol. C, Chapter 6, pp 476–516.

(11) Creagh, D. C.; McDauley, W. J. In *International Tables for Crystallography: Mathematical, Physical and Chemical Tables*; Wilson, A. J. C., Ed.; Kluwer: Dordrecht, The Netherlands, 1992; Vol. C, Chapter 4, pp 206–222.

(12) Taking the NMR spectra immediately after redissolving the crystalline material, and before equilibrium can be fully reestablished, allows for the assignment of the two species.

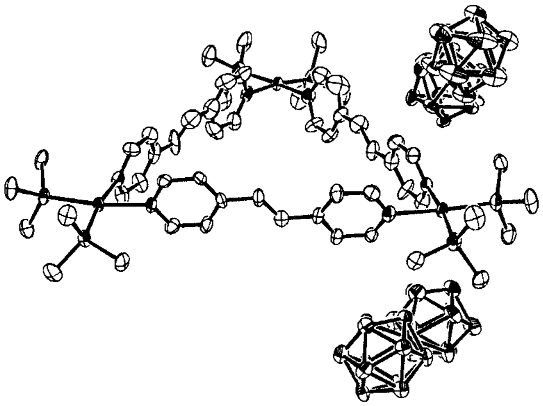

Figure 2. ORTEP plot of triangle **5** and two cobalticarborane anions (solvent, hydrogens, and triflate anions omitted for clarity).

square **3** and 46% triangle **4**, and takes over 16 h to re-achieve its initial equilibrium values. The fact that square **3** crystallizes out preferentially over triangle **4**, even though it is not the most favored assembly in solution, points to the fact that crystal packing forces must play a significant role in determining the solid state structure.

Surprisingly, when the reaction is repeated under the same conditions but in the presence of ∼5 μL of D_2O, the precrystallization solution has a similar ratio of square **3** (9%), but the amount present in the preequilibrium, redissolved crystalline batch increases to 75%. In addition, the rate of achieving equilibrium upon redissolving the crystallized material in nitromethane is augmented significantly, taking only about 4 h. This is most likely due to residual water being present in this new batch, whereas in the initial batch no water was present, as evidenced by the crystal structure. Coupled with the above observation from this experiment, this tends to indicate that water has an accelerating effect on reaching equilibrium. The process of realizing this steady state can be observed, and the results are depicted in Chart 1.[13]

In order to explore the effects of the counterion on the system, the reaction can be carried out in the presence of an excess of a substantially larger anion, such as cobalticarborane ($CoB_{18}C_4H_{22}^-$). When this is done, and X-ray quality crystals are grown via slow diffusion of diethyl ether into a nitromethane solution of **1** and **2** that has had excess sodium cobalticarborane added to it, an unexpected result occurs. The X-ray data reveals that the solid state structure of the product is that of a triangle (**5**), where only two of the six triflates have exchanged with two cobalticarboranes, instead of the square that is seen in the purely triflate batch (Figure 2).

As with square **3**, triangle **5** crystallizes in the triclinic space group $P\bar{1}$ and also has Pt−N bond lengths of ∼2.1 Å. In contrast, the N−Pt−N bond angles of **5** are somewhat smaller, falling in the range of ∼82−83°. The overall similarity of the two structures, particularly the nearness of the vertex angles, however, tends to indicate that any strain incurred in making the smaller triangle over the larger square is delocalized throughout the flexible linkers that constitute the framework of the assembly and does not contribute significantly to the end product in the solid state. This is further substantiated by the noticeably more bowed nature of the pyridyl linkers in triangle **5** compared to square **3**.[14]

This result also shows the importance of the anion in self-assembly reactions that occur under thermodynamic control. In changing a portion of the anions from the small triflates to the large cobalticarboranes, the crystalline form of the self-assembly itself can be transformed from one species to another. This allows for the selective tuning of the solid state properties of the system.

In order to further study the specific product for which the X-ray structure was obtained, a *representative* batch of triangle **5** is prepared and crystallized in which two triflates are exchanged exactly for two cobalticarboranes.[15] The resulting orange crystals show 100% triangle **5** immediately after redissolution in nitromethane. After approximately 45 min, equilibrium is reached, and 95% triangle **5**, with only ∼5% of the corresponding square species (**6**), is found.[13]

In conclusion, this work represents one of the few[2f−l] instances in which both products in a square−triangle equilibrium of this sort are characterized in the solid state as well as in solution. In addition, this work allows for the selective, anion-induced crystallization of either of the aggregates in high yield (75% for **3** and 100% for **5**), and thus a tuning of the crystalline properties of the resultant material is realized. Moreover, it must be underscored that the solid state structure of any thermodynamically controlled system may not necessarily be identical to that present in the solution and that care must be exercised in the appropriate assignment of both.

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Supporting Information Available: Crystallographic data for **3** and **5**. NMR data for **3**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Determination of the relative percentages of square **3** (**6**) and triangle **4** (**5**) is based on ^{1}H NMR integration.

(14) A referee suggests that the distinction, both in the solution and in the solid state, between the square and triangle species before and after anion exchange may be due in part to the outer coordination sphere influence of the larger cobalticarborane anions forcing a smaller bite angle at the platinum center, thereby favoring triangle **5**.

(15) Stoichiometry controlled and monitored via ^{1}H NMR integration.