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[15] Crystal data for **2**: $[C_{72}H_{108}Ag_{14}Cl]OH$, $M_r = 2536.2$, rhombohedral, space group $R\bar{3}$ (no. 148), $a = 22.438(2)$, $c = 15.601(2)$ Å, $V = 6802(1)$ Å^3, $Z = 3$ (S_6-symmetric), $\rho_{calcd} = 1.858\ g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 3.01\ mm^{-1}$, $T = 293$ K, colorless prisms; 2618 independent measured reflections, refinement on F^2, $R_1 = 0.063$, $wR_2 = 0.144$, 1375 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 50°$], 156 parameters.

[16] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-163113 (**2**) and CCDC-163114 (**4**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[18] Crystal data for **4**: $[C_{72}H_{108}Ag_{14}Br]OH$, $M_r = 2580.7$, rhombohedral, space group $R\bar{3}$ (no. 148), $a = 22.441(2)$, $c = 15.595(1)$ Å, $V = 6802(1)$ Å^3, $Z = 3$ (S_6-symmetric), $\rho_{calcd} = 1.890\ g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 3.42\ mm^{-1}$, $T = 293$ K, colorless prisms; 2596 independent measured reflections, refinement on F^2, $R_1 = 0.054$, $wR_2 = 0.114$, 1359 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 50°$], 186 parameters.[16]

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[20] The X-ray structures of the chloride-containing cage compound formed by using a range of different synthetic routes and available counteranions have been determined. In all instances the structures were isomorphous and had unit cell volumes that differed at most by only about 40 Å^3, that is, by less than 0.6%.

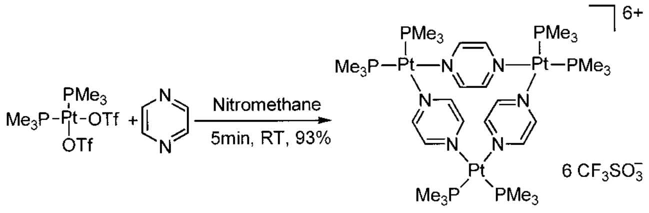
[21] The crystalline samples of **3** and **4** used for the structure determinations were uniform by simple visual inspection. However, it was found consistently that within the same sample some of the material was indeed composed of single crystals (from which the X-ray structures were obtained), whereas the remaining crystalline material was not suitable for X-ray analysis since no resolvable diffraction pattern could be obtained. This observation is consistent with the suggestion that **3** and **4** are mixtures of $[Ag_{14}(C{\equiv}CtBu)_{12}X]BF_4$ and $[Ag_{14}(C{\equiv}CtBu)_{12}X]OH$ (X = Cl, Br), from which only the OH^--containing compounds give crystals suitable for X-ray analyses.

The Self-Assembly of an Unexpected, Unique Supramolecular Triangle Composed of Rigid Subunits**

Manuela Schweiger, S. Russell Seidel, Atta M. Arif, and Peter J. Stang*

In recent years, coordination-driven self-assembly has been employed in the synthesis of a large assortment of supramolecular entities.[1] Among the many members of this family are a wide array of two-dimensional systems, such as rhomboids, squares, pentagons, and hexagons, and three-dimensional systems, such as truncated tetrahedra, adamantanoids, cuboctahedra, dodecahedra, and a variety of other cages.[2] In contrast, only a relatively small number of self-assembled triangles exist in the literature.[3–6] Typically, they have been either the product of rational design, where the outcome of the reaction is dictated by the relative ratios of preprogrammed building blocks, or have been in equilibrium mixtures with larger entities, such as squares. The latter usually results when flexible and/or larger subunits are employed, allowing the formation of multiple species.

Herein, we report a novel, self-assembled, unexpected supramolecular triangle **3** formed from the stoichiometric reaction of ditopic platinum acceptor unit **1**[7] and ditopic donor unit pyrazine (**2**) in nitromethane (Scheme 1).



1 **2** **3**

Scheme 1. Formation of self-assembled triangle **3** from rigid subunits **1** and **2**. $^-$OTf = triflate = $CF_3SO_3^-$.

Pyrazine (**2**) is the smallest, and hence most rigid, linear aromatic linker available for self-assembly processes, while platinum corner **1**, with its two bonding sites oriented approximately 90° to one another, is also quite compact. Based solely on these considerations, the combination of **1** and **2** would be predicted to yield a square as the final aggregate, but triangle **3** instead results. This distinctive occurrence, where inflexible linkers lead to unexpected products, is rare[8] in the field of discrete molecular assembly, and we attribute it to both entropy considerations and the unique electronics incurred by having two platinum centers attached to each pyrazine ring.

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The assembly was monitored by multinuclear NMR spectroscopy, which revealed a highly symmetrical product as the predominant species in solution. Single crystals suitable for X-ray structure analysis (Figure 1)[9] were grown by diffusing diethyl ether into **3** in nitromethane.

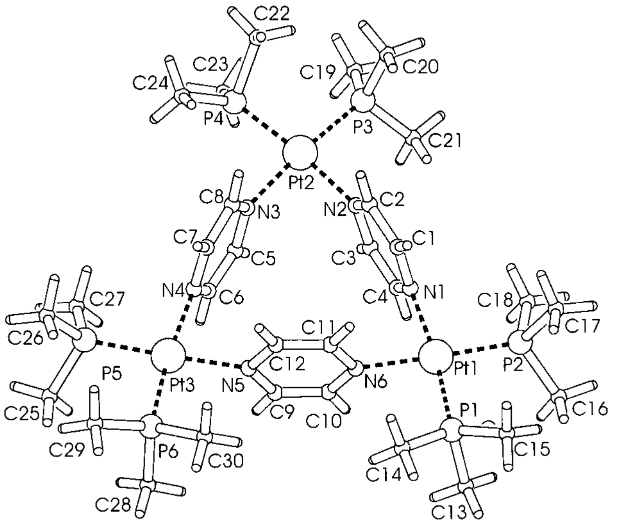

Figure 1. PLUTON plot of supramolecular triangle **3**. Solvent and counterions omitted for clarity. Selected bond lengths [Å] and angles [°]: Pt1-N1 2.13(2), Pt1-N6 2.11(2), Pt2-N2 2.12(2), Pt2-N3 2.14(2), Pt3-N5 2.12(2), Pt3-N4 2.13(2); N1-Pt1-N6 81.9(9), N2-Pt2-N3 83.2(8), N4-Pt3-N5 82.1(9).

The cross-ring distances from each platinum center to the centroid of the opposing pyrazine unit are within the range of 6.4–6.5 Å. Surprisingly, despite the strain present in **3**, the coordination geometry about the platinum atoms is not distorted enough from their ideal 90° angle to account for the triangular assembly (N-Pt-N angles range from 81.9(9)° to 83.2(8)°). Instead, a considerable portion of the tension generated from creating the smaller species is concentrated in the Pt–N connections themselves. While the pyrazine moieties are not noticeably bent (N-centroid(pyrazine)-N angles are all ~179°), the bonds are significantly distorted (centroid(pyrazine)-N-Pt angles range from 167–171°) from their ideal value of 180°.

The triangles stack in staggered columns, with an inter-ring, Pt–Pt distance of 15.6 Å (Figure 2). Interestingly, each ensemble has two triangular arrays of triflate anions aligned above and below the plane of the assembly, with their oxygen atoms pointing toward the positively charged platinum centers. As a consequence, the trifluoromethyl groups of the counterions are positioned diametrically, indicating the formation of a hydrophobic buffer between negatively charged sulfonate groups.

Adjacent columns are offset with respect to one another, leading to sheets in which each assembled system is surrounded by six trigonal anion clusters of alternating, opposite orientation (Figure 3). Disordered nitromethane molecules are interspersed throughout the lattice at various locations, yet, due to the small size of the cavity, never reside within a ring.

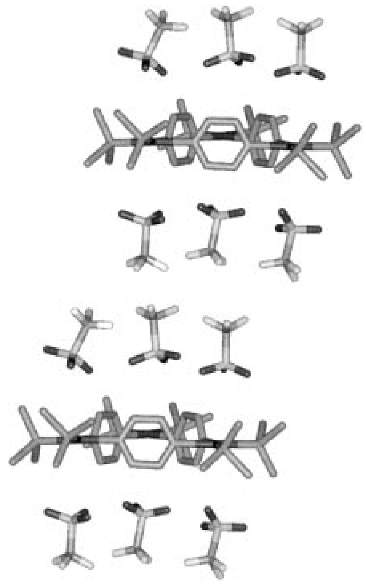

Figure 2. Stacking of **3** into staggered columns (side view; stick representation; dark portions of triflate anions represent oxygen atoms, light portions represent fluorine atoms). Protons omitted for clarity.

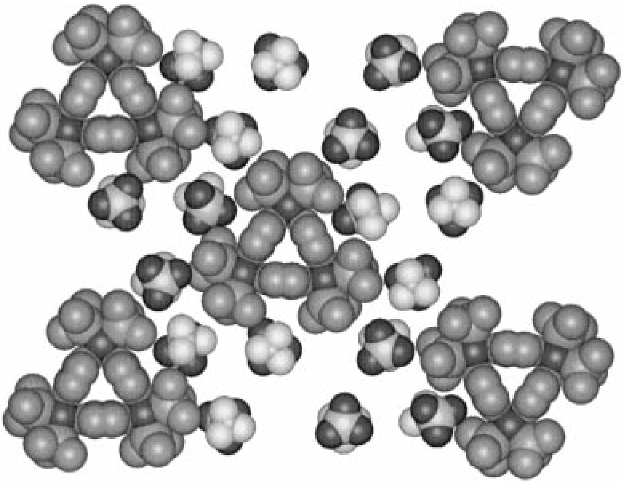

Figure 3. Top view, Van der Waals representation of a single sheet (dark portions of triflate anions represent oxygen atoms, light portions represent fluorine atoms). Protons and solvent omitted for clarity.

In conclusion, we herein report the formation and characterization of a unique, self-assembled, supramolecular aggregate formed from platinum subunit **1** and pyrazine (**2**). By all accounts, with **2** being the most rigid, linear aromatic linker conceivable and **1** being quite compact itself, the most logical outcome of this reaction should be a square. It is not; it is a triangle. This result, which we believe to be due to a combination of entropy factors and the electronic effects of having two platinum centers per pyrazine unit, suggests that there are likely limitations and exceptions to the coordination-directed synthetic strategy of "rational design".[2e]

Experimental Section

A solution of **2** (0.62 mg, 0.0077 mmol) in CD_3NO_2 (0.3 mL) was added to **1** (5.00 mg, 0.0077 mmol) dissolved in CD_3NO_2 (0.3 mL). Multinuclear NMR shows an instantaneous and quantitative reaction. At very high concentrations a second by-product (<5%) could be observed, which is most likely attributable to a square. The solvent was removed under a stream of N_2, and the resulting white precipitate was dried in vacuo (yield 93%). ^1H NMR (CD_3NO_2, 300 MHz): $\delta = 9.41$ (s, 2H; H_{pyr}), 1.79 (d, $J_{P,H} = 11.4$ Hz, 9H; P-CH_3); $^{31}P\{^1H\}$ NMR (CD_3NO_2, 121 MHz): $\delta = -25.6$ (s, ^{195}Pt satellites, $J_{Pt,P} = 3269$ Hz); ^{19}F NMR (CD_3NO_2, 282 MHz): $\delta = -78.1$; $^{13}C\{^1H\}$ NMR (CD_3NO_2, 75 MHz): $\delta = 151.8$ (s, C_{pyr}), 122.2 (q, $J_{C,F} = 319$ Hz, OTf), 14.7 (m, P-CH_3).

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[9] Crystal structure analysis of **3** at 200(1) K: $C_{36}H_{66}F_{18}N_6O_{18}P_6Pt_3S_6 \cdot 3\,CH_3NO_2$, $M_r = 2359.53$, colorless prism, $0.25 \times 0.23 \times 0.15$ mm^3, monoclinic space group $P2_1/c$, $a = 15.584(3)$, $b = 24.021(4)$, $c = 23.542(4)$ Å, $\beta = 105.146(6)^\circ$, $V = 8506(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.842$ Mg m^{-3}, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å, $\mu = 5.287$ mm^{-1}). Data were collected on a Nonius KappaCCD diffractometer in the range $1.23 < \theta < 23.28^\circ$. A total of 16528 measured reflections, 10142 unique, 6426 with $F_o^2 = 4\sigma(F_o^2)$ were used to refine 636 parameters to $R1(wR2) = 0.1134(0.2669)$, $GOF = 1.111$, F^2 refinement in SHELXL97. A multiscan absorption correction gave min. and max. transmission factors of 0.5044 and 0.3516. The residual peaks in the final difference map ranged from -1.832 to $+2.339$ e Å^{-3}.[10]

[10] Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-163666.

Microencapsulated Palladium Catalysts: Allylic Substitution and Suzuki Coupling Using a Recoverable and Reusable Polymer-Supported Palladium Catalyst[**]

Ryo Akiyama and Shū Kobayashi[*]

While palladium catalysts find wide-spread utility in a variety of transformations in organic synthesis,[1] they are expensive, air-sensitive, and cannot be recovered in many cases. Immobilized palladium catalysts have been expected to solve these problems, and several polymer-supported palladium catalysts have been developed for allylic substitution,[2, 9a,b,e] oligomerization,[2c, 3, 4] decarboxylation,[2d] hydrogenation,[4, 9g] isomerization,[5] telomerization,[6] Suzuki coupling,[7, 9c,d,h] and the Mizoroki – Heck reaction,[4c, 8, 9f,h] etc. In most of these cases, however, recovery and reuse of the polymer catalysts have not been satisfactory.[9] Recently, we developed novel polymer-supported catalysts, microencapsulated scandium trifluoromethanesulfonate (MC Sc(OTf)$_3$)[10] and osmium tetroxide (MC OsO$_4$).[11] Our work has demonstrated a new method for immobilizing catalysts onto polymers based on physical envelopment by the polymers and on electronic interaction between the π electrons of the benzene rings of the polystyrene-based polymers and vacant orbitals of the catalysts. We now apply this new technology to immobilizing palladium catalysts. Herein, we describe the use of microencapsulated triphenylphosphane palladium for allylic substitution and Suzuki coupling. In both cases, the catalysts were recovered quantitatively and reused. Moreover, valuable information on the structure of microencapsulated catalysts was obtained.

Preparation of microencapsulated triphenylphosphane palladium was as follows:[12] polystyrene (1.0 g, M_w ca. 280000) was dissolved in cyclohexane (20 mL) at 40 °C, and to this solution was added tetrakis(triphenylphosphane)palladium(0) ([Pd(PPh$_3$)$_4$] 0.20 g) as a core ([Pd(PPh$_3$)$_4$] was dissolved). The mixture was stirred for 1 h at this temperature (and changed from brown to black), then slowly cooled to 0 °C. Coacervates (phase separation) were found to envelop the core dispersed in the medium, and hexane (30 mL) was added to harden the capsule walls. The mixture was left to stand at room temperature for 12 h, and the catalyst capsules were then washed with acetonitrile several times and dried at room temperature for 24 h. Three equivalents of triphenylphosphane (PPh$_3$) were recovered from the washings and one equivalent of PPh$_3$ remained in the catalyst capsules. We measured ^{31}P swollen-resin magic angle spinning (SR-MAS)

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