Self-Assembly of Nanoscale Supramolecular Truncated Tetrahedra

Manuela Schweiger,[†] Takuya Yamamoto,[†]
Peter J. Stang,*,[†] Dieter Bläser,[‡] and Roland Boese[‡]

Department of Chemistry, University of Utah,
Salt Lake City, Utah 84112, and Institut für Anorganische
Chemie der Universität Duisburg-Essen Fachbereich
Chemie, Campus Essen 45117 Essen, Germany

stang@chem.utah.edu

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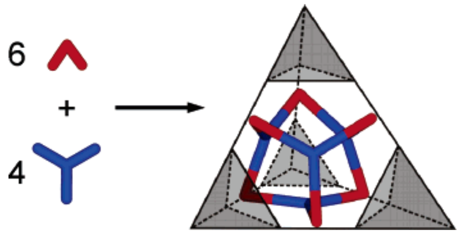
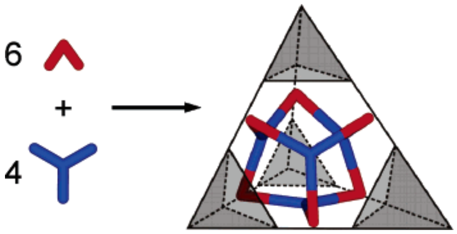


Two nanoscale truncated tetrahedra were synthesized via Pt(II)-mediated self-assembly. The first resulted from the reaction of 3 equiv of *cis*-Pt$(PMe_3)_2(OTf)_2$ and 2 equiv of 1,3,5-tris(4-pyridylethynyl)benzene, giving a truncated tetrahedron with a diameter of approximately 25 Å. The second, analogous structure was obtained by the self-assembly of *cis*-Pt$(PMe_3)_2(OTf)_2$ and 1,3,5-tris(4-pyridyl-*trans*-ethenyl)benzene. These two truncated tetrahedra were crystallized after partially exchanging the counterion to cobalticarborane for the X-ray structural analysis.

Introduction

Self-Assembly utilizing reversible Pt(II)− and Pd(II)−pyridyl coordination allows the systems to self-correct to obtain the thermodynamic products. These products, often highly symmetric polygons and polyhedra, are obtained in single-step reactions with essentially quantitative yields.[1−8] Truncated tetrahedron, the simplest Archimedean solid, has been a popular discrete molecular architecture objective.[9,10] This structural entity can be self-assembled from six ditopic angular units and four tritopic planar linkers having a separation of 120° between their reactive sites (Scheme 1). The ditopic units lie along the edges and the planar linkers span the faces of the truncated tetrahedron. Fujita and co-workers utilized this concept to synthesize several water-soluble truncated tetrahedra.[5,11−25] These assemblies have large cavities that accommodate guest molecules and have been used for catalyses,[5,11,13,23] stereoselective reactions,[19,24] and stabilization of a labile reaction intermediate.[14,17] We wish to synthesize these structural entities in organic solvents, which might allow for applications in organic reactions. Though a variety of organic-soluble truncated tetrahedra were prepared via Pt(II)- and Pd(II)-mediated self-assembly, crystal structures have not been reported.[9]

SCHEME 1. Self-Assembly of a Truncated Tetrahedron from Six Angular Linkers and Four Tritopic Planar Linkers



Herein, we report the self-assembly of two supramolecular truncated tetrahedra containing flexible unsaturated aliphatic hydrocarbon functional groups. These complexes were successfully crystallized by partial counterion exchange to cobalticarborane and analyzed by X-ray crystallography.

Results and Discussion

Self-Assembly of the Truncated Tetrahedra. The cis-square-planar metal unit, *cis*-Pt$(PMe_3)_2(OTf)_2$[26,27] (**1**), was reacted with two tritopic pyridyl units containing the unsaturated hydrocarbon moieties 1,3,5-tris(4-py-

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* To whom correspondence should be addressed.
[†] University of Utah.
[‡] Institut für Anorganische Chemie der Universität Duisburg-Essen Fachbereich Chemie.
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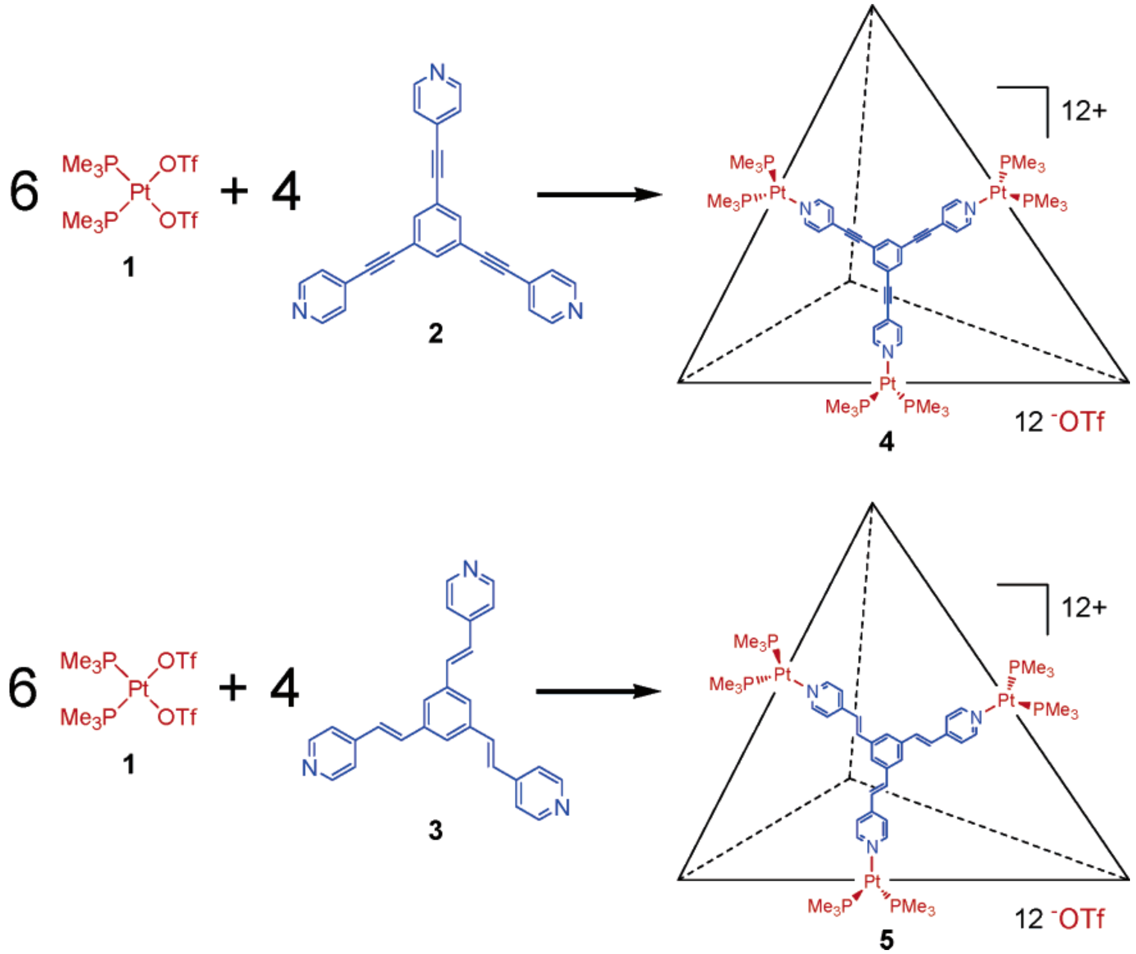
SCHEME 2. Truncated Tetrahedra 4 and 5 Synthesized via Self-Assembly of 1 and Pyridyl Linkers 2 and 3[a]



[a] Only the front faces of the truncated tetrahedra are shown for clarity. The back and bottom faces have the same compositions.

ridylethynyl)benzene[28,29] (**2**) and 1,3,5-tris(4-pyridyl-*trans*-ethenyl)benzene[29,30] (**3**) (Scheme 2). The reaction between 3 equiv of **1** and 2 equiv of **2** under ambient conditions resulted in the formation of the supramolecular truncated tetrahedron **4**. The analogous tetrahedron **5** was obtained from the self-assembly of **1** and **3**.

Multinuclear NMR verified the essentially quantitative formation of each assembly. Singlet resonances in the ^{31}P NMR spectra at −28.8 and −28.2 ppm for **4** and **5**, respectively, were shifted upfield relative to the starting material **1**. On the other hand, pyridyl−Pt(II) coordination caused downfield shifts of the α- and β-pyridyl protons. ^{1}H NMR spectra exhibit only one resonance each from the α- and β-pyridyl protons for **4** and **5**. The multiplicity of the methyl protons in the PMe_3 groups simplified to a doublet from a complicated second-order splitting pattern found in the starting material **1**. These data are consistent with the proposed high symmetry (T_d point group) structure. ESI-MS data supports the proposed structures **4** and **5**. Peaks corresponding to the self-assembled structures minus two to four triflate counterions were found at m/z = 2549.4 [**4** − 2OTf]$^{2+}$, 1649.9 [**4** − 3OTf]$^{3+}$, and 1200.0 [**4** − 4OTf]$^{4+}$; 2560.7 [**5** − 2OTf]$^{2+}$, 1657.3 [**5** − 3OTf]$^{3+}$, and 1205.5 [**5** − 4OTf]$^{4+}$. Numerous fragment peaks were observed due to the high temperature in the device.[18,31,32]

Crystal Structures of 4 and 5. X-ray quality crystals of **4** and **5** were obtained by adding 12 equiv of sodium cobalticarborane to CH_3NO_2 solutions of the assemblies, resulting in partial exchange of cobalticarborane for the triflate anion. Diffusion of Et_2O into these solutions generated single crystals of sufficient size and quality for X-ray diffraction. The crystal structures confirm the truncated tetrahedral geometry of the complexes (Figure 1). The relevant crystallographic parameters are listed in Table 1.

The Pt atoms of the assemblies **4** and **5** adopt a distorted square-planar geometry, coordinating to two PMe_3 and two nitrogen atoms of the pyridyl groups. The mean values

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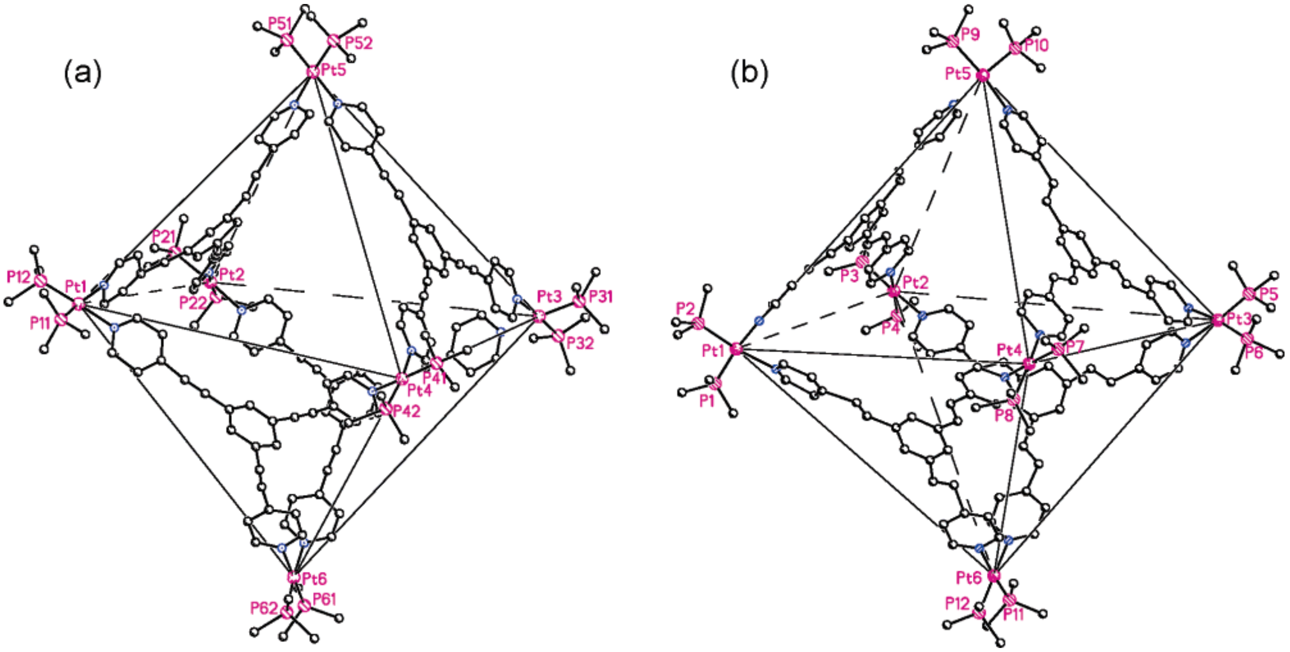

FIGURE 1. Crystal structures of the truncated tetrahedra (a) **4** and (b) **5**. Hydrogen atoms, solvent molecules, and counterions are omitted for clarity.

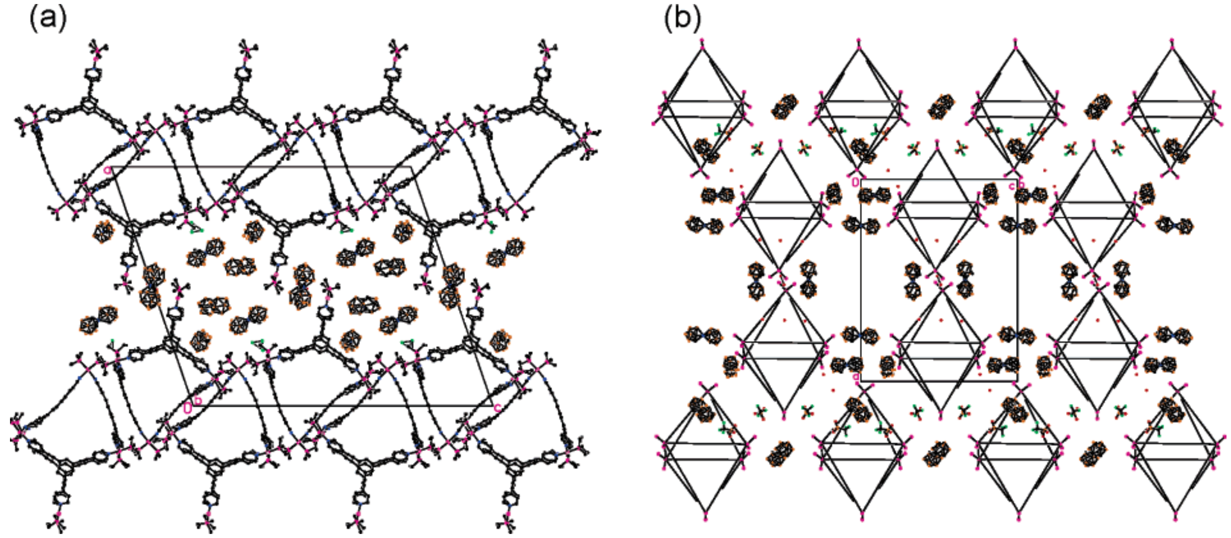

FIGURE 2. (a) Packing diagrams of **4** viewed along *b*-axis. (b) Schematic representation viewed along *c*-axis.

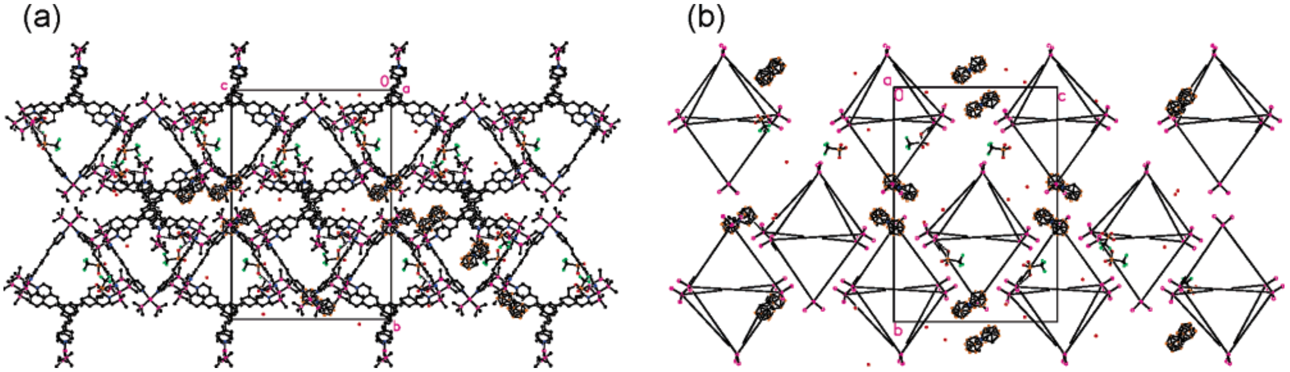

FIGURE 3. (a) Packing diagrams of **5** viewed along *a*-axis. (b) Schematic representation viewed along *a*-axis.

for the square-planar Pt(II) in **4** and **5** are N−Pt−N 83.8, 84.0°; P−Pt−P 95.1, 95.6°; N−Pt−P 90.8, 90.3°, respectively. The edges of the truncated tetrahedron **4** are slightly longer than those of **5** because the ethynyl groups in **4** extend further than *trans*-ethenyl groups in **5**; the mean edge Pt···Pt distances for **4** and **5** are 17.9 and 17.4

TABLE 1. Relevant Crystallographic Parameters of 4 and 5

	4	**5**
formula	$C_{144}H_{168}Pt_6P_{12}N_{12}\cdot 4(CF_3SO_3)\cdot 6(C_4H_{22}B_{18}Co)\cdot 9(H_2O)^c$	$C_{144}H_{192}Pt_6P_{12}N_{12}\cdot 2(CF_3SO_3)\cdot 4(C_4H_{22}B_{18}Co)\cdot 7(H_2O)$
formula weight	6110.66	5175.08
D_{calc}, g cm^{-3}	1.038	0.912
T, K	283(2)	278(2)
λ, Å	0.71073	0.71073
space group	$C2/c$	$P2_1/c$
a, Å	45.53(4)	27.979(4)
b, Å	33.50(4)	43.908(6)
c, Å	54.22(5)	31.316(5)
β, deg	109.04(6)	101.585(3)
V, Å^3	78188(124)	37688(9)
Z	8	4
μ, mm^{-1}	2.498	2.482
final R indices [$I > 2\sigma(I)$]		
R1^a	0.1016	0.1289
wR2^b	0.2730	0.3299
R indices (all data)		
R1^a	0.2579	0.3092
wR2^b	0.3190	0.3804

[a] $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$. [b] $wR2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum(F_o^2)^2]^{1/2}$. [c] Oxygen water atoms O(10), O(11), and O(13) to O(16) are disordered over two sites with SOF 0.5.

Å, respectively. The distances from the centers of the aryl groups to the Pt atoms are also slightly longer for **4** than for **5**; the mean Cent···Pt distances for **4** and **5** are 10.4 and 10.0 Å, respectively. The diagonal Pt···Pt distances in **4** and **5** are 25.2 and 24.5 Å, respectively.

The two crystal structures are not isomorphic as expected from the very slight differences of the size of the cationic clusters. It is obviously the number of the different anions which determine the packing symmetry, probably controlled by the concentration of the anions. Therefore, it is expected that both structures have polymorphs, but with the manifold problems to get the data presented here it was not possible to find any evidence for this assumption. In accordance with the different space groups, the packing of the structures is distinctly different, as demonstrated by Figures 2 and 3. For **4**, chains of cations are separated by a layer of the different anions (Figure 2a), whereas for **5** the arrangement of anions and cations are not so clearly distinguishable (Figure 3a). In Figures 2b and 3b, the different orientation of the truncated tetrahedra is apparent, which requires more space for **4** than for **5** (cell volume difference per formula unit 3.7%) in accordance with the difference in volume of the cations.

Conclusions

Two predesigned nanoscopic, organic-soluble supramolecular truncated tetrahedra **4** and **5** were self-assembled in essentially quantitative yields. These structures possess ethynyl and *trans*-ethenyl groups within each tritopic planar linker, which helps to provide the supramolecules with flexibility as well as direct this research to eventual applications that bear higher order functional groups on the self-assemblies. Partial triflate counterion exchange with cobalticarborane anion aided crystallization of the truncated tetrahedra **4** and **5**.

Experimental Section

Truncated Tetrahedron 4. *cis*-Pt(PMe$_3$)$_2$(OTf)$_2$ (**1**) (30.52 mg, 47.29 μmol; 3 equiv) was dissolved in a mixture of acetone-d_6 (0.5 mL) and CD_3NO_2 (0.7 mL). 1,3,5-Tris(4-pyridylethynyl)benzene (**2**) (12.03 mg, 31.54 μmol; 2 equiv) was dissolved in CD_2Cl_2 (0.5 mL). The two solutions were combined and stirred for 10 min at ambient temperature. After filtration through a glass microfiber, the product was precipitated by addition of Et_2O. Isolated yield: 41.70 mg (93%). ^{1}H NMR (CD_3NO_2, acetone-d_6, and CD_2Cl_2; CD_3NO_2 as an internal standard): δ (ppm) 9.11 (bd, 24H, PyH_α), 7.92 (s, 12H, ArH), 7.75 (bd, 24H, PyH_β), 1.71 (d, J_{H-P} = 11.2 Hz, 108H, P(CH_3)$_3$). ^{13}C NMR (CD_3NO_2, acetone-d_6, and CD_2Cl_2; CD_3NO_2 as an internal standard): δ (ppm) 151.8, 138.6, 136.5, 130.9, 123.9, 97.1, 88.0, 14.6 (m). ^{19}F NMR (CD_3NO_2, acetone-d_6, and CD_2Cl_2): δ (ppm) −77. ^{31}P NMR (CD_3NO_2, acetone-d_6, and CD_2Cl_2): δ (ppm) −28.8 (s, J_{Pt-P} = 3171 Hz). ESI-MS m/z 2549.4 [**4** − 2OTf]$^{2+}$, 1649.9 [**4** − 3OTf]$^{3+}$, 1200.0 [**4** − 4OTf]$^{4+}$. Anal. Calcd for $C_{156}H_{168}F_{36}N_{12}O_{36}P_{12}Pt_6S_{12}\cdot 4CH_3NO_2\cdot CH_3COCH_3$: C, 34.35; H, 3.29; N, 3.93; S, 6.75. Found: C, 34.32; H, 3.33; N, 4.06; S, 6.71. The solid product (5.57 mg, 9.77 × 10^{-1} μmol) was dissolved in CH_3NO_2 (1.0 mL), and sodium cobalticarborane (4.08 mg, 11.8 μmol; 12 equiv) was added. Subsequent diffusion of Et_2O into this solution generated crystals of **4** of sufficient quality for X-ray diffraction studies.

Truncated Tetrahedron 5. *cis*-Pt(PMe$_3$)$_2$(OTf)$_2$ (**1**) (8.34 mg, 12.9 μmol; 3 equiv) was dissolved in CD_3NO_2 (1.7 mL). 1,3,5-Tris(4-pyridyl-*trans*-ethenyl)benzene (**3**) (3.33 mg, 8.59 μmol; 2 equiv) was dissolved in CD_2Cl_2 (1.7 mL). The solutions were combined and stirred for 10 min at ambient temperature. After filtration through a glass microfiber, the product was precipitated by addition of Et_2O. Isolated yield: 11.37 mg (96%). ^{1}H NMR (CD_3NO_2): δ (ppm) 8.83 (bd, 24H, PyH_α), 7.92 (s, 12H, ArH), 7.82 (bd, 24H, PyH_β), 7.63 (d, J = 16.3 Hz, 12H, C=CHAr), 7.34 (d, J = 16.3 Hz, 12H, C=CHPy), 1.71 (d, J_{H-P} = 11.2 Hz, 108H, P(CH_3)$_3$). ^{13}C NMR (CD_3NO_2): δ (ppm) 151.5, 150.6, 138.2, 137. 5, 129.0, 126.0, 126.0, 122.5 (q, OTf, J_{C-F} = 320 Hz), 14.5 (m). ^{19}F NMR (CD_3NO_2): δ (ppm) −78. ^{31}P NMR (CD_3NO_2): δ (ppm) −28.2 (s, J_{Pt-P} = 3111 Hz). ESI-MS m/z 2560.7 [**5** − 2OTf]$^{2+}$, 1657.3 [**5** − 3OTf]$^{3+}$, 1205.5 [**5** − 4OTf]$^{4+}$. Anal. Calcd for $C_{156}H_{192}F_{36}N_{12}O_{36}P_{12}Pt_6S_{12}\cdot 6H_2O$: C, 33.88; H, 3.72; N, 3.04; S, 6.96. Found: C, 33.87; H, 3.75; N, 3.15; S, 6.89. The solid product (5.64 mg, 1.02 μmol) was dissolved in CH_3NO_2 (1.0 mL), and sodium cobalticarborane (4.56 mg, 13.2 μmol; 12 equiv) was added to the solution. Subsequent diffusion of Et_2O generated crystals of **5** of sufficient quality for X-ray diffraction studies.

Crystal Data and Structure Refinement for 4 and 5. For both structures, further cooling was not possible because the crystals gradually lost further diffraction intensity, which was poor at the beginning. The structure solutions were only feasible with many trials, and complete refinements were unstable and could only be performed with groupwise treatment of the anions and cations, respectively, as rigid groups with the first atom as the pivot atom each. In both structures, the cation as well as the cobalticarborane and triflate anions could be assembled, but the electroneutral state cannot be achieved without considering some of the residual electron densities as hydroxyl oxygen atoms and disordered water molecules floating in the remaining cavities of the crystal. Consequently, hydrogen atoms were not determined, and except for Pt, Co and P atoms, isotropic displacement parameters were applied. The residual electron densities down to 1.5 e Å^{-3} were close to the heavy atoms, and the remaining ones were unstable if attributed to partial occupied oxygen atoms. In both structures, the calculated density is too low, indicating that further water molecules reside in voids of the cell.

Acknowledgment. Financial support by the National Science Foundation (CHE-0306720) is gratefully acknowledged.

Supporting Information Available: ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra, tables for angles at the Pt atoms, and edge Pt···Pt and Cent···Pt distances and crystallographic data for compounds **4** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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