

Molecular Architecture via Coordination: Self-Assembly of Nanoscale Platinum Containing Molecular Hexagons

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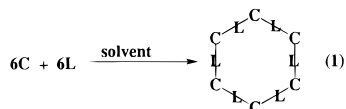
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Molecular architecture deals with the design, construction, structure, and stereochemistry of large, complex molecular species with interesting properties.¹ Supramolecular chemistry,^{2,3} organized polymolecular systems held together by non-covalent interactions,⁴ is a specially important part of molecular architecture at the frontiers of modern chemical sciences. Recently transition metal based coordination has emerged as a new motif in the construction of unique supramolecular species with well defined shapes and geometries. To date this methodology has primarily been applied to the formation of diverse molecular squares.^{5–11}

In nature the hexagon represents the most common pattern throughout biological morphology from simple diatoms to the honeycomb of the bee.¹² Likewise, in classical covalent, chemistry the hexagonal shape is familiar from benzene itself through the diverse polycondensed aromatic hydrocarbons to C₆₀. In contrast we are not aware of any supramolecular species with the shape of a simple hexagon. Hence, in this Communication we wish to report the first examples of hitherto unknown molecular hexagons formed via self-assembly using coordination as the motif.

A rational design strategy and formation of molecular hexagons requires the following: (a) shape defining and directing corner units **C** with approximately 120° bond angles; (b) appropriate linkers, **L**; and (c) proper self-assembly of the corners, **C**, with linkers, **L**, as schematically illustrated in eq 1.



Suitable corner units **C** include the known¹³ bispyridyl ketone **1** as well as the Pt complex **2**, and appropriate linkers **L** include the commercially available 4,4'-bipyridine **3** and the known^{6b,14} bis-Pt(II) complex **4**.

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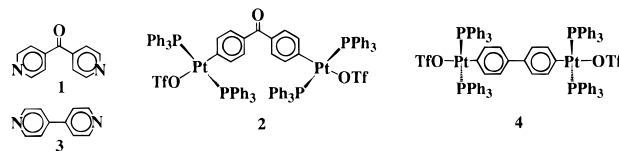
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Corner unit **2**¹⁵ is readily available via triflate metathesis of the diiodide¹⁴ obtained by double oxidative addition of (Ph₃P)₄-Pt to 4,4'-diiodobenzophenone, prepared analogously to the literature procedure¹³ employed in the synthesis of bis(4-pyridyl)ketone.

Addition of equal molar amounts of a CD₂Cl₂ solution of linker **3** to corner **2** dissolved in CD₂Cl₂ at room temperature followed by stirring for 30 min results in quantitative formation (as observed by ¹H and ³¹P NMR) of the desired molecular hexagon **5**.¹⁶ Likewise, for the assembly of **6** the solid metal linker **4** was simply added to a solution of ketone **1** in CD₂Cl₂ at room temperature and stirred for 15 min resulting in the isoelectronic, isostructural hexagon **6**¹⁶ as summarized in Scheme 1. Both complexes **5** and **6** are remarkably stable, soluble solids.

The characterization and structure determination of these unique, cationic, nanoscale, molecular hexagons rests upon the following: (a) principles of supramolecular chemistry and self-assembly; (b) spectral and physical data; and (c) analogy to related molecular squares. Specifically, it is well recognized^{17,18} in self-assembly processes that enthalpy favors formation of

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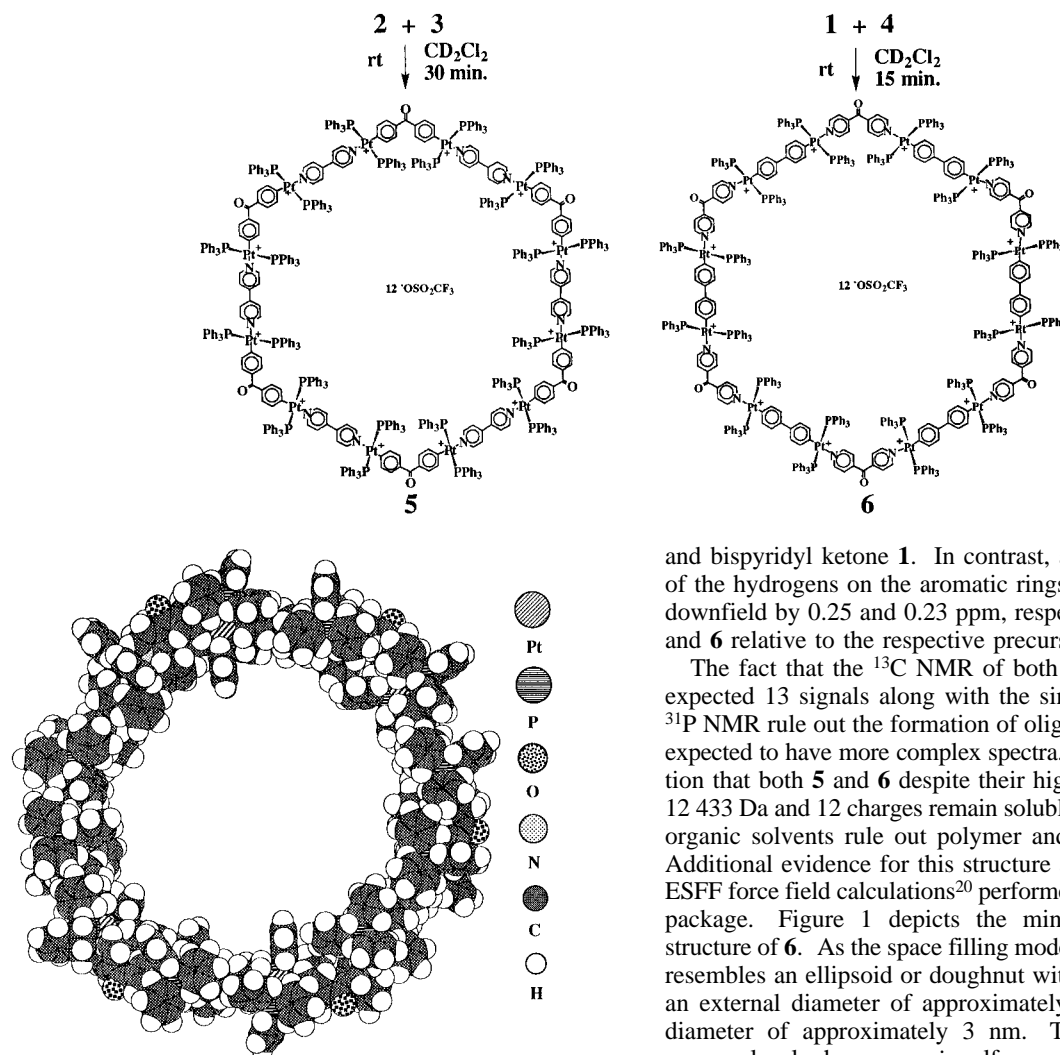
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(15) For **2**: Yield: 85%; mp 240–242 °C dec; IR (thin film; CD₂Cl₂; cm⁻¹) 3055 (C–H), 1968, 1907, 1813 (Ar), 1635 (C=O), 1438, 1481 (Ar), 1286, 1247, 1181, 1098 (OTf); ¹H NMR (CD₂Cl₂) δ 7.52 (m, 24H, H_o-P), 7.39 (t, 12H, ³J_{HH} = 7.2 Hz, H_p-P), 7.31 (m, 24H, H_m-P), 6.59 (d, 4H, ³J_{HH} = 8.2 Hz, ³J_{HPT} = 56 Hz, H_o-Pt), 6.26 (d, 4H, ³J_{HH} = 8.2 Hz, H_m-Pt), 131.3 (s, C_p-P), 129.2 (s, C_m-Pt), 129.1 (t, J_{CP} = 28.8 Hz, C_p-P), 128.7 (t, J_{CP} = 5.3 Hz, C_m-P), not observed (OTf); ³¹P{¹H} NMR (CD₂Cl₂) δ 28.1 (s, ¹J_{PPT} = 3159 Hz); ¹⁹F{¹H} NMR (CD₂Cl₂) δ -78.3 (s). FAB-MS m/z (rel intensity) 1768 (M – OTf⁺, 100%), 1506 (M – OTf – PPh₃⁺, 62%). Anal. Calcd for C₈₇H₆₈F₆O₇Pa₂S₂Pt₂: C, 54.49 H, 3.57. Found: C, 54.0; H, 3.59.

(16) For **5**: mp 278–283 °C dec; IR (thin film; CD₂Cl₂; cm⁻¹) 3061 (C–H), 1646 (C=O), 1435 (Ar), 1264, 1181, 1099 (OTf); ¹H NMR (500 MHz; CD₂Cl₂) δ 8.27 (d, 24H, ³J_{HH} = 6.0 Hz, H_o-Py), 7.42 (m, 144H, H_p-P), 7.36 (t, 72H, ³J_{HH} = 7.2 Hz, H_p-P), 7.32 (m, 144H, H_m-P), 6.90 (m, 24H, ³J_{HH} = 6.0 Hz, H_b-Py), 6.84 (d, 24H, ³J_{HH} = 8.2 Hz, H_o-Pt), 6.32 (d, 4H, ³J_{HH} = 8.2 Hz, H_m-Pt); ¹³C{¹H} NMR (125.7 MHz; CD₂Cl₂) δ 196.52 (s, C=O), 153.31 (s, C_o-Py), 144.91 (br s, C_o-Py), 138.57 (s, C_p-P), 137.44 (s, C_o-Pt), 134.68 (t, ²J_{CP} = 5.7 Hz, C_o-PPh₃), 132.91 (s, C_p-Pt), 131.63 (s, C_p-PPh₃), 129.39 (t, ³J_{CP} = 5.2 Hz, C_m-PPh₃), 128.99 (s, C_m-Pt), 127.55 (t, ¹J_{CP} = 28.7 Hz, C_p-PPh₃), 124.31 (s, C_p-Py), 121.88 (q, ¹J_{CF} = 322 Hz, OTf); ³¹P{¹H} NMR (CD₂Cl₂) δ 22.1 (s, ¹J_{PPT} = 2995 Hz); ¹⁹F{¹H} NMR (CD₂Cl₂) δ -78.4 (s). Anal. Calcd for C₅₈₂H₄₅₆F₃₆N₁₂O₄₂P₂₄S₁₂Pt₁₂: C, 56.18; H, 3.69; N, 1.35; Found: C, 55.15; H, 3.69; N, 1.30. For **6**: Yield: 82%; mp 246–248 °C dec; IR (CCl₄) 3061, 3008 (Ar), 1685 (CO), 1262, 1151, 1098, 1030 (OTf) cm⁻¹; ¹H NMR (CD₂Cl₂) δ 8.48 (d, 24H, ³J_{H-H} = 5.1 Hz, H_{app}), 7.44–7.28 (m, 360H, P-H_om_p), 6.85 (d, 24H, ³J_{H-H} = 5.4 Hz, H_{pp}), 6.69 (d, 24H, ³J_{H-H} = 7.5 Hz, Pt-H_o), 6.37 (d, 24H, ³J_{H-H} = 7.8 Hz, Pt-H_m); ¹³C{¹H} NMR (CD₂Cl₂) δ 189.8 (s, CO), 153.9 (s, C_{app}), 141.2 (s, C_{pp}), 137.8 (s, Pt-C_o), 136.6 (s, Pt-C_p), 134.7 (t, ²J_{CP} = 6 Hz, P-C_o), 131.4 (s, P-C_p), 129.2 (t, ³J_{CP} = 5 Hz, P-C_m), 127.7 (t, J_{CP} = 28 Hz, P-C_{ipso}), 126.6 (m, Pt-C_{ipso}), 126.4 (s, Pt-C_m), 125.3 (s, C_{pp}), 121.8 (q, J_{CF} = 322 Hz, C_{OTf}); ³¹P{¹H} NMR (CD₂Cl₂) δ 23.0 (s, J_{P-Pt} = 3043 Hz); ¹⁹F{¹H} NMR (CD₂Cl₂) δ -76. Anal. Calcd for C₅₈₂H₄₅₆O₄₂S₁₂P₂₄F₃₆Pt₁₂N₁₂·2H₂O: C, 56.02; H, 3.72; N, 1.35; S, 3.08. Found: C, 55.57; H, 3.81; N, 1.27; S, 3.09.

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Scheme 1. Synthesis of Macrocycles **5** and **6****Figure 1.** Space-filling model of **6**, obtained from ESFF simulations.

macrocycles over oligomerization (but not necessarily polymerization) because of the greater number of energetically favorable interactions (in this case dative bonding) per unit building block in the closed system vs oligomers of the same size (i.e., number of units). Moreover, entropy favors a macrocycle with the minimum number of subunits since the energy cost for the loss of degrees of freedom for the components of the assembly will be less in the system with the smaller number of units.¹⁸ For 2D assemblies made with building units with $\sim 120^\circ$ bond angles these conditions are best met by a molecular hexagon.

Indeed, all spectral data are consistent with a molecular hexagon as is the elemental analysis. In particular, symmetry demands that in both **5** and **6** all the phosphorous atoms be equal and hence have but a sharp singlet in the ^{31}P NMR, as is observed.¹⁵ In analogy with our molecular squares^{6–8} the ^{31}P signals in **5** and **6** are high-field shifted by ~ 6 ppm relative to the signals in the respective precursors **2** and **4**, upon complexation with the aza-heterocycles. In both hexagons **5** and **6** in the ^1H NMR signals of the hydrogens α to the chelating nitrogen are shifted upfield by 0.44 and 0.35 ppm, respectively, relative to the precursors **3** and **1**. Likewise, the signals of the hydrogens β to the chelating nitrogen are also shifted upfield by 0.65 and 0.74 ppm, respectively, for **5** and **6** compared to bipyridine **3**

and bispyridyl ketone **1**. In contrast, as expected, the signals of the hydrogens on the aromatic rings α to the Pt are shifted downfield by 0.25 and 0.23 ppm, respectively, for hexagons **5** and **6** relative to the respective precursors **2** and **4**.

The fact that the ^{13}C NMR of both **5** and **6** show only the expected 13 signals along with the single sharp signal in the ^{31}P NMR rule out the formation of oligomers as they would be expected to have more complex spectra. Likewise, the observation that both **5** and **6** despite their high molecular weights of 12 433 Da and 12 charges remain soluble in CH_2Cl_2 , and similar organic solvents rule out polymer and oligomer formation.¹⁹ Additional evidence for this structure assignment comes from ESFF force field calculations²⁰ performed with the Biosym/MSI package. Figure 1 depicts the minimum energy, derived structure of **6**. As the space filling model indicates the molecule resembles an ellipsoid or doughnut with a circular cavity with an external diameter of approximately 5 nm and an internal diameter of approximately 3 nm. The formation of these supramolecular hexagons *via* self-assembly, using the coordination motif, is truly remarkable as 12 individual building units (six each of the corners **C** and linkers **L**) have to come together in the proper sequence and manner.

In summary, use of $\sim 120^\circ$ shape defining corner units and appropriate linkers results in the formation via coordination and self-assembly of hitherto unknown, cationic molecular hexagons. Both the assembly process as well as the exact structure and chemistry of these novel supramolecular species are under active investigation and will be the subject of future reports.

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Supporting Information Available: Experimental procedures for the formation of **2**, **4**, **5**, and **6**. IR, ^{31}P , ^1H , and ^{13}C NMR of hexagons **5** and **6** (12 pages). See any current masthead page for ordering and Internet access instructions.

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