

Molecular Architecture via Coordination: Self-Assembly of Pseudo-hexagonal $A^2_3X^2_3$ -Macrocycles

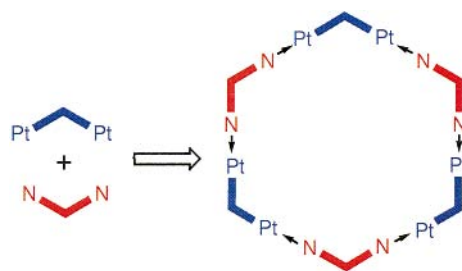
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Received October 11, 1999

ABSTRACT



The interaction of two complementary ditopic building blocks, each incorporating 120° angles between the active coordination sites, in methylene chloride at room temperature results in the spontaneous self-assembly of platinum-based assemblies of hexagonal shape.

The field of biomimetic inorganic chemistry first evolved from the observation of nucleation and growth of biologically relevant calcareous morphologies.¹ With the rapidly developing concepts in template synthesis, self-assembly, and molecular recognition, chemists are now able to synthesize materials with complex forms on the basis of biological design principles.² One of the most common arrangements of biological morphology is the hexagonal pattern, found in the skeletons of diatoms and radiolaria and in the honeycomb of the bee.³ Likewise, in carbon-based chemistry, the hexagonal shape is familiar from benzene to graphite, polycondensed aromatic hydrocarbons, nanotubes, and fullerenes.⁴ Since the coordination-driven self-assembly methodology⁵ offers an alternative to the biological and classical covalent motifs, we have extended our research to

include the rational design of platinum-based macrocycles with a hexagonal shape. According to the “molecular library” model⁶ and the “symmetry interaction” model,⁷ discrete hexagonal entities of the type $A^2_6L^2_6$ can be rationally assembled via the combination of six shape defining and directing corner units A^2 (offering two coordination sites which enclose a 120° angle) with six appropriate linear linker units L^2 .⁸ An alternative route for the assembly of hexagonal systems involves the combination of two complementary

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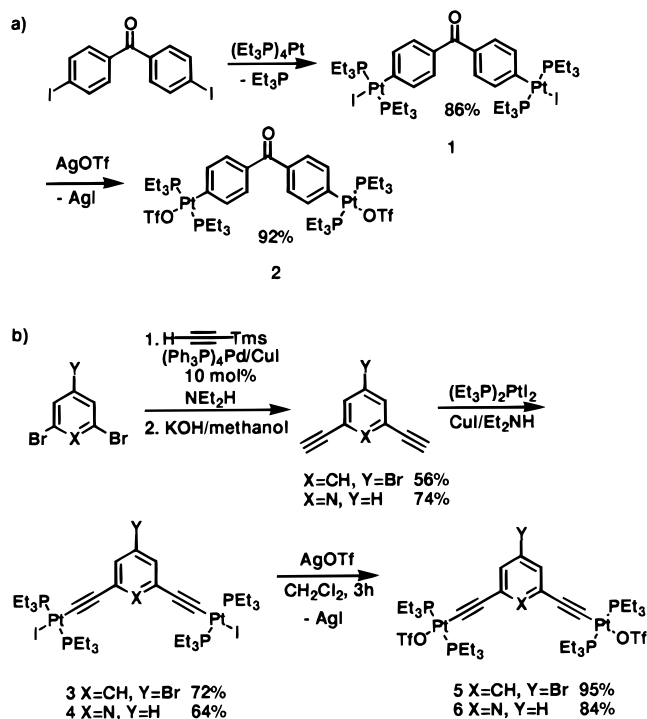
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ditopic building blocks A^2 and X^2 , each incorporating 120° angles between the active coordination sites, allowing for the construction of essentially unexplored ring systems of the type $A^2_3X^2_3$. So far only two examples of this type of macrocycles are described as minor products in the formation of rhomboid-like structures, but these were not isolated and properly characterized.⁹ Therefore, the complexes herein described represent the first fully characterized $A^2_3X^2_3$ ring systems.

For the synthesis of suitable platinum-containing 120° building blocks, two different approaches were applied as outlined in Scheme 1.

Scheme 1. Synthesis of 120° Corner Units

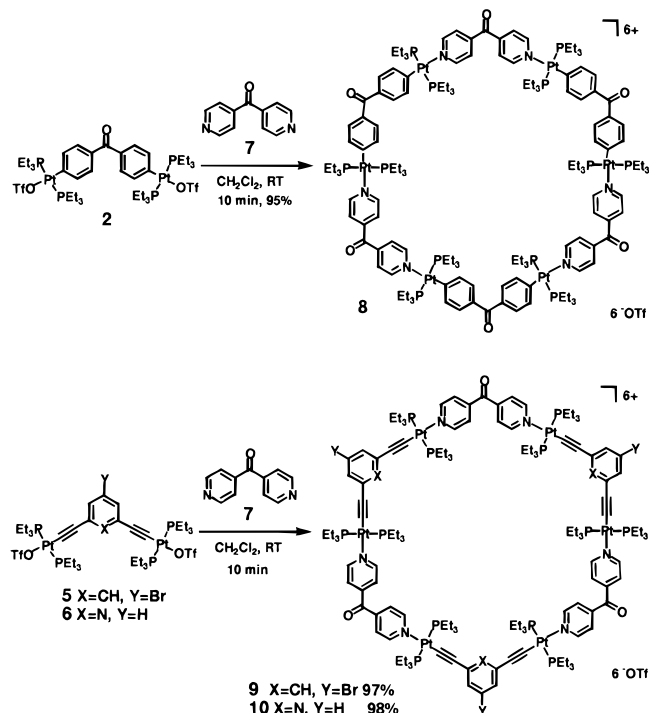


The double oxidative addition of 4,4'-diiodobenzophenone with tetrakis(triethylphosphine)platinum(0) yielded the bis-platinum compound **1**. Subsequent reaction with AgOTf gave the bistriflate salt **2** in good yield. The copper-catalyzed reaction¹⁰ of *trans*-diiodobis(triethylphosphine)platinum(II) with 2,6-bis(ethynyl)pyridine or 3,5-bis(ethynyl)bromobenzene, derived via Hagihara coupling of (trimethylsilyl)acetylene and the corresponding dibromoarene, yielded compounds **3** and **4**. Subsequent halogen abstraction with AgOTf resulted in the isolation of the bistriflate salts **5** and **6** in good yield.

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Slow addition of bis(4-pyridyl)ketone **7** to an equimolar solution of compound **2**, **5**, or **6** in methylene chloride at room temperature resulted in the spontaneous formation of the hexagonal assemblies **8**, **9**, and **10**, respectively (Scheme 2).

Scheme 2. Self-assembly of Molecular Hexagons



All three complexes have been fully characterized by analytical and spectroscopic means. The elemental analyses are consistent with the expected 1:1 stoichiometry. Particularly diagnostic for these assemblies are the 1H and $^{31}P\{^1H\}$ spectra. Upon coordination of the pyridyl groups of **7**, characteristic downfield shifts in the proton NMR spectra were observed for the α - as well as the β -protons in all three cases.^{9,11} While the β -protons showed a more dramatic shift (0.4–0.6 ppm), the α -protons shifted only slightly (0.1–0.2 ppm) due to electron density transfer from the pyridyl group to the metal.

Consequently, an increased back-bonding from the metal to the phosphine ligands resulted in an upfield shift of the triethylphosphine methylene resonances of about 0.2 ppm. In the ^{31}P NMR spectra, all three compounds showed sharp singlets with ^{195}Pt satellites. Furthermore, the coordination of the pyridyl ligands was accompanied by an upfield shift of the phosphorus resonance of 6.4 ppm for **8**, 5.4 ppm for **9**, and 5.9 ppm for **10**. The $^{13}C\{^1H\}$ NMR spectra of all three compounds were in accordance with the expectations.

Since all three assemblies **8–10** possessed carbonyl functionalities, IR measurements also provided a useful tool for monitoring and characterization. Upon coordination, the C–O stretching bands of the bis(4-pyridyl)ketone units shifted to longer wavenumbers by 15–18 cm^{-1} . In addition,

the carbonyl function of the organometallic subunit **2** experienced a similar shift of 25 cm^{-1} to higher wavenumbers.

As an illustrative example of the versatility of electrospray mass spectrometry in determining the exact molecular weight and the isotopic distribution pattern of highly charged systems,¹² the ESMS spectrum of compound **9** is discussed. The derived spectrum showed several characteristic peaks, which were assigned to the trimeric structure of **9**. The three observed peaks ($m/z = 2173$ (calcd 2174) $[M - 2\text{OTf}]^{2+}$, 1400 (calcd 1399) $[M - 3\text{OTf}]^{3+}$, 1012 (calcd 1013) $[M - 4\text{OTf}]^{4+}$) belonged to species resulting from a consecutive loss of three triflate counterions from the +2 charge state to the +4 charge state. In addition, the spectrum contained signals for liberated building block **5** minus one triflate counterion and several other peaks for single and multi-charged fragments of **9**. Aside from the peak at $m/z = 1400$, which is characteristic for every $n:n$ stoichiometric composition of building blocks **5** and **7** minus n triflate counterions, no indications for the presence of dimeric (2:2) or tetrameric (4:4) compositions were detected. The electrospray mass spectra of compounds **8** and **10** show a similar fragmentation pattern. Therefore, formation of smaller, more strained rhombus-like structures or larger, entropically disfavored octagonal systems can be excluded.

Since no suitable crystals for single-crystal analysis could be obtained to date, a molecular model of compound **10** was generated from force-field simulations (Figure 1) to assess

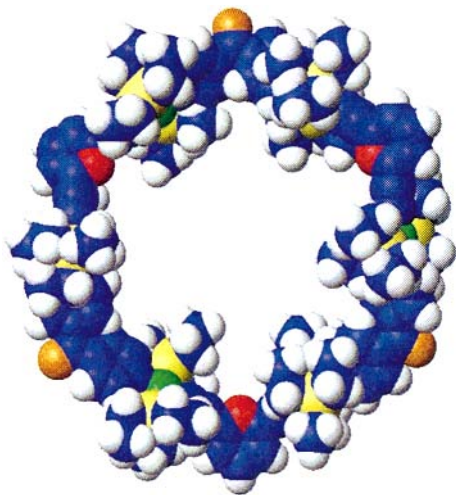


Figure 1. Space-filling model of hexagon **10** derived from ESFF simulations.

the geometric features of this assembly.¹³ The minimum structure of **10** revealed a chairlike rather than planar hexagonal conformation, caused by a slight inward bending of the acetylene units. Given that **10** possesses three accessible uncoordinated nitrogen atoms with C_3 symmetry, it should be possible to bind a complementary guest molecule within its cavity.¹⁴ Therefore, the size of the cavity of **10** was assessed by measuring the distance between the uncoordinated pyridine-nitrogen atoms ($\sim 15\text{ \AA}$ taking the van der Waals radii of nitrogen into account). Several D_{3h} symmetrical guest molecules with suitable end groups, capable of interacting with the pyridyl nitrogen atoms, may be used in host-guest and templating experiments that are under investigation.

In conclusion, the formation of the hexagonal-shaped systems **8–10** shows again the versatility of the coordination driven self-assembly process as a rapid method to synthesize macrocyclic, highly symmetrical compounds from simple building units. In addition, introduction of functional groups may offer symmetrical anchor points for specific guest molecules.

Acknowledgment. We thank the National Science Foundation (CHE-9818472), the National Institute of Health (5R01GM57052), and the Petroleum Research Fund for support and the Alexander von Humboldt Foundation for a Feodor Lynen Fellowship to M.S. and S.L., respectively.

Supporting Information Available: General experimental procedures and characterization data for compounds **1–6** and **8–10**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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