Molecular Architecture: Coordination as the Motif in the Rational Design and Assembly of Discrete Supramolecular Species—Self-Assembly of Metallacyclic Polygons and Polyhedra

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Abstract: A simple, general systematic strategy has been developed for the rational design by self-assembly of diverse metallacyclic polygons and polyhedra using coordination as the motif. The methodology is illustrated by the self-assembly of various molecular squares, molecular hexagons, and 3D species, new members of the family of abiotic supramolecular entities. The design features and some advantages of the coordination motif are discussed.

Keywords: chirality · coordination · metallacycles · self-assembly · supramolecular chemistry

Introduction

Supramolecular chemistry and self-assembly are at the frontiers of the molecular sciences, as evidenced by the intense interest and the near-exponential growth of publications in this area in just the last decade.[1] Although contemporary supramolecular chemistry has its roots in the classical covalent macrocycles such as crown ethers, cyclophanes, cyclodextrins, calixarenes, cryptands, spherands, and so on, it is currently heavily dominated by the biomimetic motif of weak interactions, amongst others hydrogen bonding, hydrophilic–hydrophobic interactions, π–π-stacking, electrostatic, and Van der Waals forces. The great versatility and power of this bio-derived motif is illustrated by the recent, elegant investigation of nanoporous molecular sandwiches by Ward et al.,[2] the synthesis of self-organized nanostructures by Stupp and coworkers,[3] the rosette aggregates[1e] and the two- and three-dimensional self-assembly of mesoscale objects by Whitesides and coworkers,[4] the three-dimensional tennis-ball-like capsules of Rebek,[5] the ordered hydrogen-bonded arrays of Hamilton[6] and Zimmerman,[7] the dipyridine-based aggregates of Wuest,[8] the cagelike hydrogen-bonded dimers of Lehn[9] and Gokel,[10] and many others.

A completely different approach to the formation of abiotic supramolecular species, by spontaneous self-assembly of precursor building blocks under appropriate conditions, involves the coordination motif, that is, the use of transition metals, multidentate ligands and dative bonding to drive and direct the self-assembly process. Although this methodology has been successfully and fairly extensively employed in the formation of metal helicates,[11] oligomeric chains,[12] step-ladders,[12] grids,[12] some rings and cages,[12] and most recently dendrimers,[13] it has not been systematically used in the construction of discrete, predesigned, metallacyclic polygons and polyhedra with well-defined shapes and sizes.

Discussion

Concepts, principles, and strategy: The precoding associated with the preferred coordination numbers and geometries of transition metal complexes as well as the shapes and geometries of di- and polydentate ligands and considerations of topology and symmetry is inherent in the coordination-based motif for the construction of supramolecular metallacyclic convex polygons and canonical polyhedra. In other words, the appropriate subunits are programmed with the information required for proper error-free self-assembly, at least in principle, into the desired supramolecular structure with correct shape, size, stereochemistry, symmetry, and so on.

Any convex polygon or canonical polyhedron can be constructed with just two simple types of building blocks: 1) linear units (**L**) containing reactive sites with a 180° orientation relative to each other and 2) various angular units (**A**) possessing binding sites with other desirable (required) angular orientations, as illustrated in Figures 1 and 2. The shape of any individual two-dimensional polygon is solely determined by the value of the turning angles within its angular components. Thus, a triangle requires the engineering of three 60° turns, a square the engineering of four 90° turns, a pentagon 108° and a hexagon 120° turns. Hence, a simple system of descriptors can be easily devised to both describe and design any molecular polygon, as illustrated in Figure 1. For example, a planar molecular triangle requires three 60°

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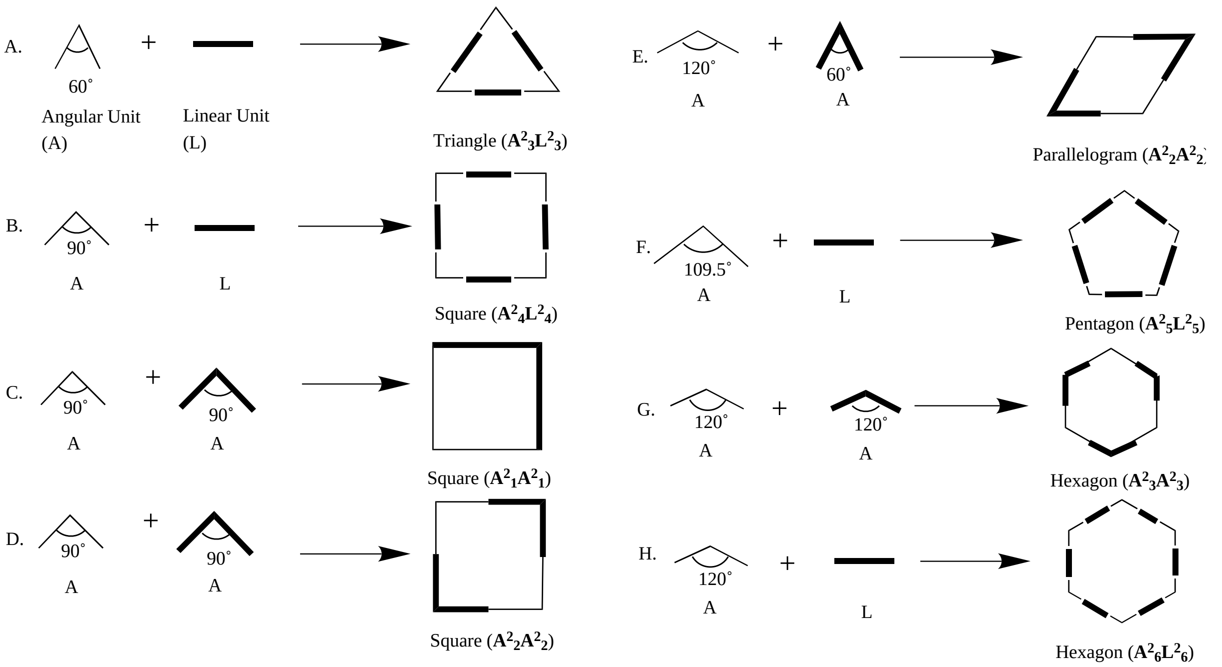

Figure 1. Some of the possible combinations of the two types of building blocks necessary for construction of convex polygons or canonical polyhedra, linear units **L** and various angular units **A**.

bidentate angular binding units ($\mathbf{A}_3^2$) and three bidentate linear linking units ($\mathbf{L}_3^2$); the combination of four bidentate 90° units ($\mathbf{A}_4^2$) with four bidentate linear linkers ($\mathbf{L}_4^2$) gives a molecular square and so on. In other words the designator **A** indicates an appropriate angular binding unit, the superscript the denticity of the unit and the subscript the number required of a particular angular building block for the design of a specific polygon; likewise for the linear linker units **L**. From topological considerations it is obvious that there are variations on this theme, as illustrated for the different squares (B, C, D), parallelogram (E), as well as hexagons (G, H) in Figure 1. Of course, for proper self-assembly to occur, the building units must follow each other in proper, incommensurate order and remain multidentate (i.e., they cannot be capped) in order to form the desired predesigned metallacyclic molecular polygon.

The design and formation of three-dimensional canonical polyhedra are somewhat more complex: they require at least one type of linker that has more than two coordination binding sites. For example, the combination of three bidentate linear linkers ($\mathbf{L}_3^2$) with two tridentate angular binding units ($\mathbf{A}_2^3$) should yield a trigonal prism, whereas eight tridentate angular components ($\mathbf{A}_8^3$) in combination with twelve linear bidentate linkers ($\mathbf{L}_{12}^2$) will result in a cube, as illustrated in Figure 2 J and L. Likewise, in this simple notation an $\mathbf{A}_8^3\mathbf{L}_{12}^2$ system with planar tridentate linkers is a cuboctahedron, an Archimedean semiregular polyhedron (M in Figure 2). Similarly, twenty tridentate tetrahedral (109°) angular binding units ($\mathbf{A}_{20}^3$) in combination with thirty bidentate linear linkers ($\mathbf{L}_{30}^2$) describe a dodecahedron.

Preparation of angular (A) and linear (L) building units: For any self-assembly process to be efficient and convergent it is important to have easily available preprogrammed building

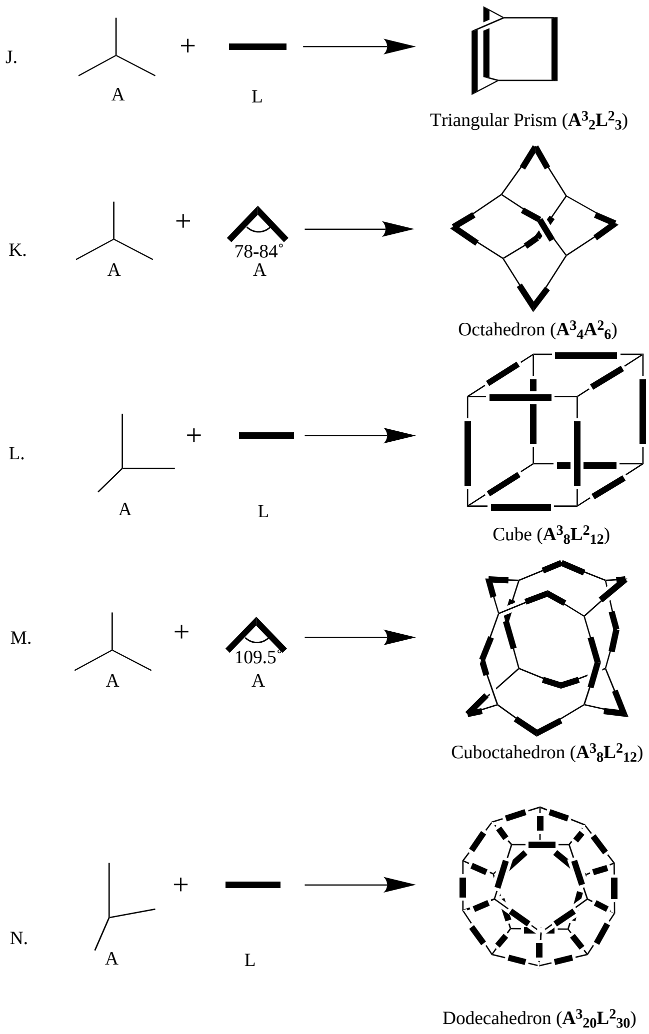

Figure 2. Three-dimensional combinations of **A** and **L** units.

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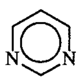
units. From the concepts and strategy described above it is obvious that both the angular (**A**) as well the linear (**L**) binding units may be either di- or polydentate nitrogen or other appropriate lone-pair-bearing organic ligands or appropriately functionalized organometallic complexes. Simple, commercially available angular as well as linear units include compounds **1**–**5**. Others, such as **3** ($n=1,2$) and **6**–**10** are readily made in a couple of easy steps by standard organic protocols such as cross-coupling methodologies [for **3** ($n=1,2$), **6**, **7**] or other well-established procedures. Organometallic angular (**A**) or linear (**L**) binding units can be easily made[14] from readily available halides by a double oxidative addition, metathesis, process as illustrated in Scheme 1.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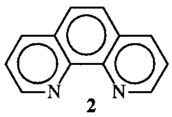
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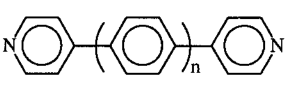
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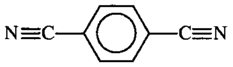
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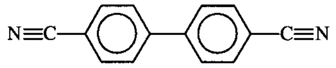
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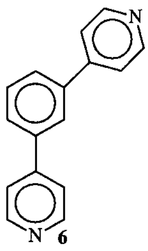
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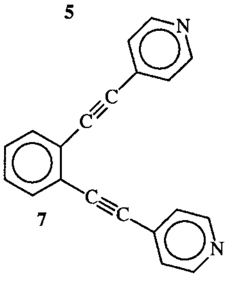
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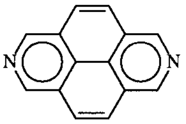
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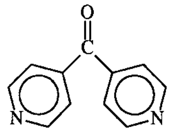
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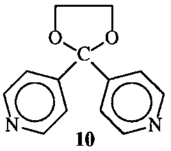
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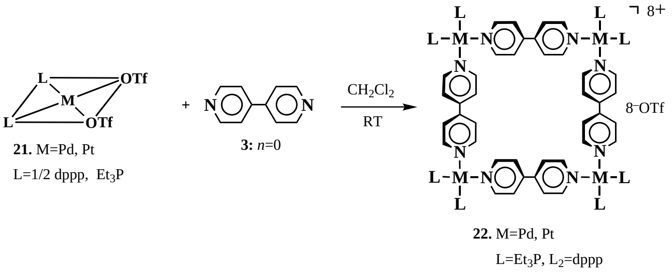
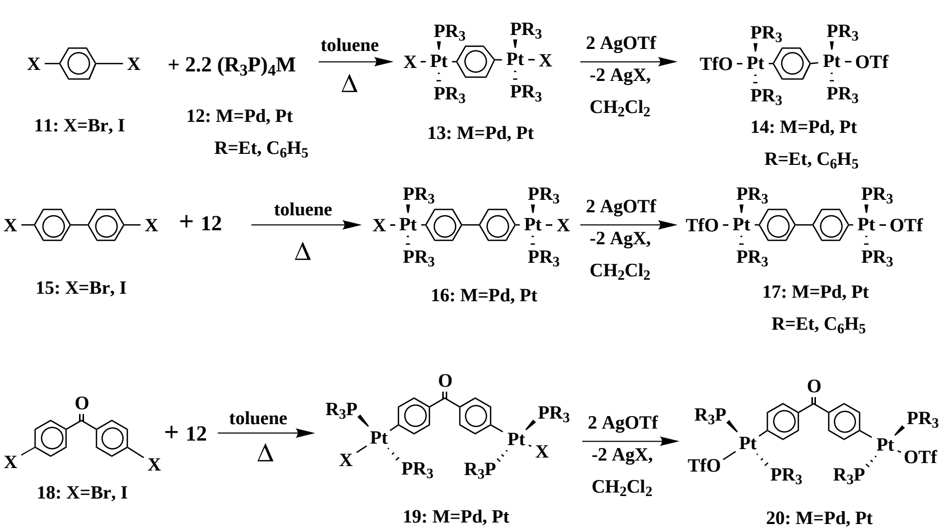
Self-assembly of molecular squares: As depicted in Figure 1, the design and assembly of molecular squares require 90° angular binding units in conjunction with bidentate linear building blocks. The square-planar Group 10 metals *cis*-tetracoordinated by two adjacent weakly coordinating reactive ligands, such as triflates, and two ancillary ligands (**21**) together with linear linkers like **3**, **4**, **5**, and **8** are ideal building units, preprogrammed for self-assembly into molecular squares. Indeed, simple mixing of **21** with 4,4′-bipyridine [bipy, **3** ($n=0$)] in CH_2Cl_2 at room temperature affords, in a matter of minutes, the desired molecular squares **22** in near-quantitative isolated yields,[15] as summarized in Scheme 2.



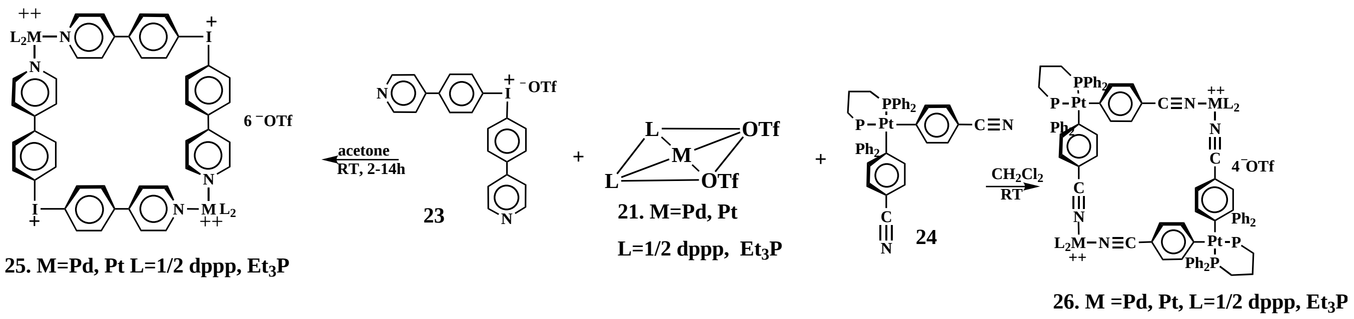
Scheme 2. Self-assembly of squares containing square-planar metal complexes.

Likewise, simple mixing of **4**, **5**, and **8** with **21** (in the case of **4** and **5** M = Pd only) gives the appropriate molecular squares in excellent isolated yields.[15a] Similar results were first reported by Fujita, Ogura and coworkers,[16] who used the water-soluble [(*cis*-en)M(ONO_2)$_2$] and bipy (**3**) as building units for self-assembly in water. In fact, Fujita and Ogura's water-soluble molecular squares and related supramolecular systems[17] nicely complement our own supramolecular assemblies, soluble in organic solvents (CH_2Cl_2, $CHCl_3$, CH_3NO_2, CH_3OH, acetone). More recently, a luminescent, mixed Re/Pd square was prepared employing the same methodology by Hupp and coworkers.[18]

Use of the pseudotrigonal bipyramidal T-shaped bis(heteroaryl)iodonium triflate **23** or the *cis*-Pt unit **24**, two different types of angular building units, in conjunction with **21** afforded the hybrid molecular squares **25**[19] and the mixed neutral/charged squares **26**,[20] respectively, in >95% isolated yields, as summarized in Scheme 3. These molecular squares are variants of squares illustrated in Figure 1B. Likewise, the titanocene-based square **28**,[21] made via **27**, represents an interesting A_4^2 system with four bidentate self-complementary angular building units (Scheme 4). Mixed Ti/Pt mo-



Scheme 1. Double oxidative addition metathesis to yield organometallic **A** or **L** binding units.

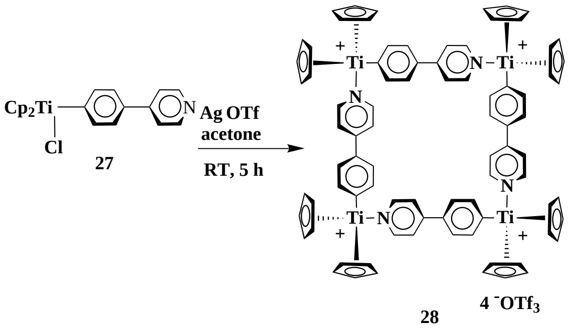


Scheme 3. Two possible reactions of **21** with angular building units, bis(heteroaryl)iodonium triflate **23** or the *cis*-Pt unit **24**.

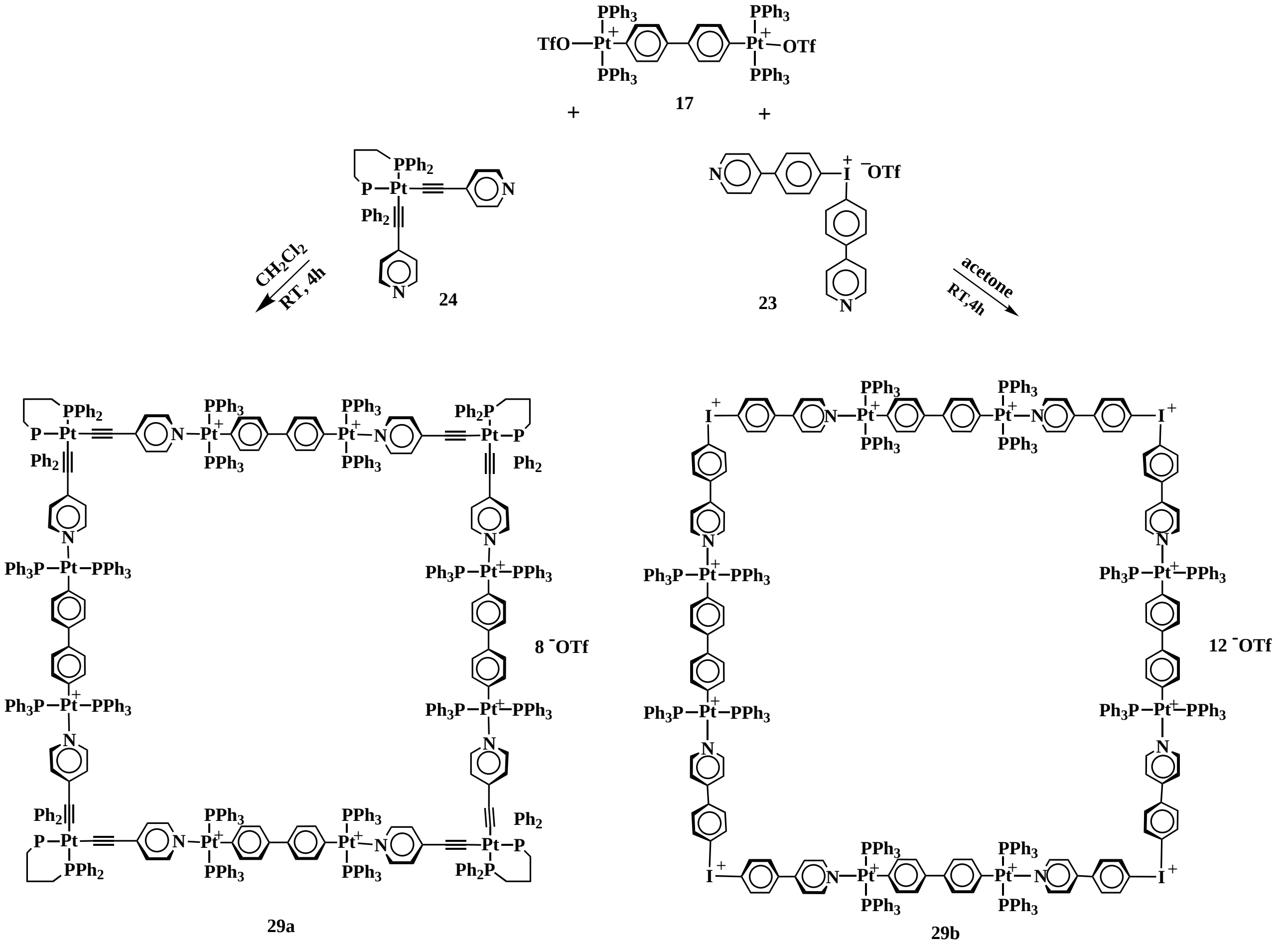
lecular squares are also accessible by this self-assembly protocol.[22]

The versatility and power of this coordination motif is illustrated by the ability to vary size from squares with cavities of a few angstroms to ones with nm-size cavities as illustrated in Scheme 5.[23]

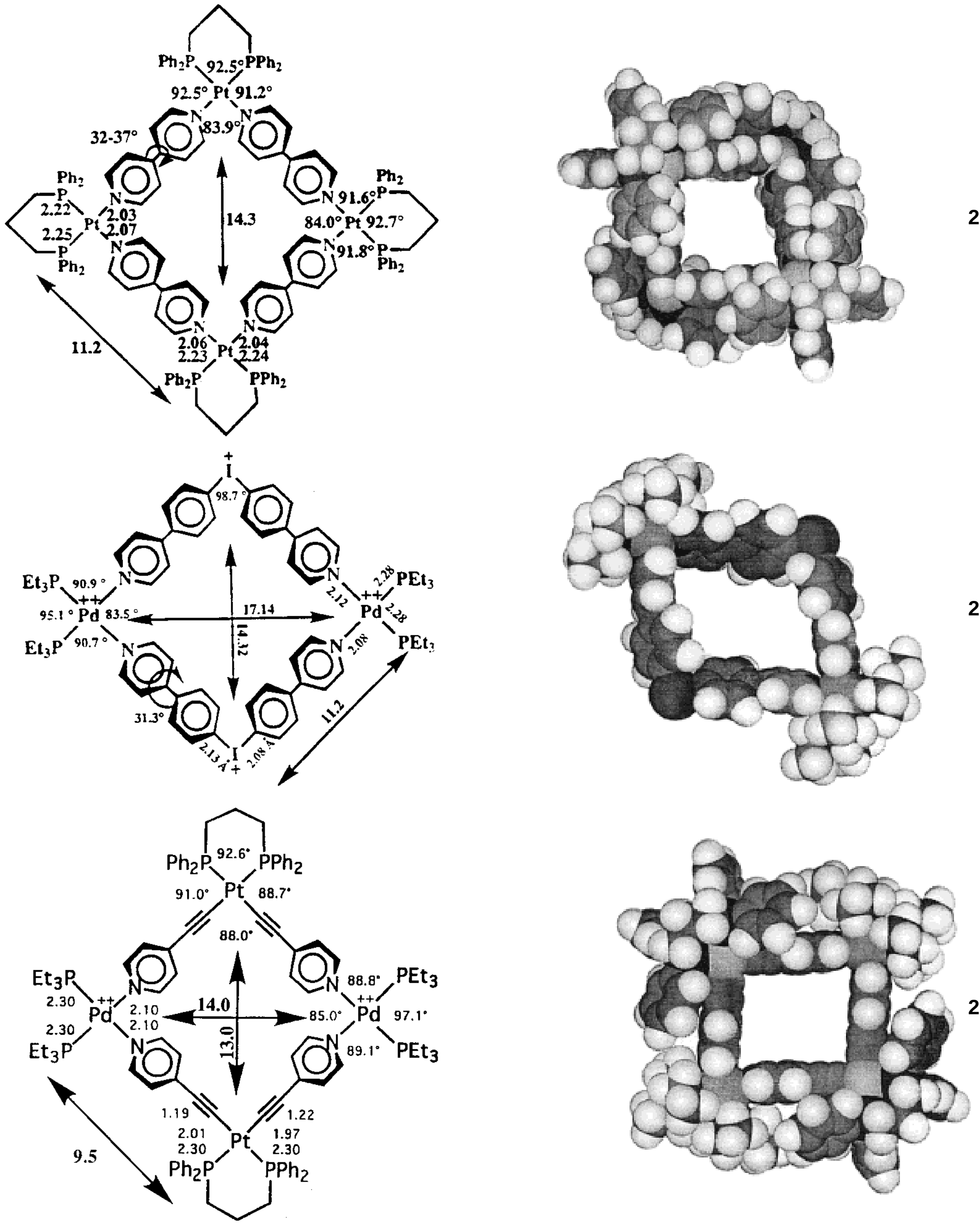
The shapes and molecular dimensions determined from X-ray data[15a,19a,20a] of some of these molecular squares are summarized in Figure 3, along with space-filling models based upon the structural data. Squares **22** and **26** are near-perfect squares, although **22** is not planar but puckered in order to accommodate the 84° turn angles as opposed to the ideal 90°



Scheme 4. Synthesis of the titanocene-based square **28**.



Scheme 5. Squares with nm-size cavities.



22

25

26

Figure 3. Crystallographic data (left) and space-filling models (right) of molecular squares **22**, **25**, and **26**.

of a perfect planar square. Species **25** is a rhomboid rather than a square.

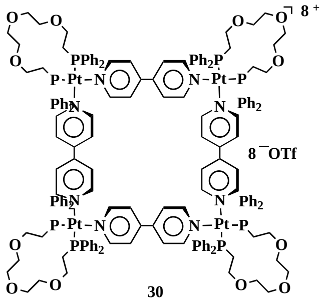
This simple methodology also allows the marriage of classical covalent macrocycles with molecular squares. For example, molecular squares containing both metallacrowns (**30** and **31**) and metallacalixarenes (**32** and **33**) have been prepared by self-assembly using this methodology.[24] Likewise, ferrocene chemistry can be combined with molecular squares, as exemplified by **34**.[25]

Chiral molecular squares: Chirality is one of the unique features of both macroscopic and microscopic objects. Chirality is essential for life as we know it and hence pervades biological systems. The ability to readily incorporate chirality into nonbiological supramolecular species and an understanding of chiral self-assembly processes is a critical aspect of this developing field.

There are at least five different ways of rationally designing and preparing chiral supramolecular species by spontaneous self-assembly of building units comprising transition metal complexes and organic multidentate ligands as part of the coordination motif. These are:

1) use of an appropriate metal complex bearing a chiral ancillary ligand;
2) use of an inherently chiral octahedral metal complex;
3) use of an optically active atropisomeric diazaheterocycle (such as properly substituted 4,4′-bipyridine, bisquinolines etc.) as linker ligands;
4) helicity or twist as a consequence of diaza linker ligands that lack rotational symmetry about the bis linkage axis;
5) combinations of any of these four methods.

As chiral auxiliaries are more readily available than either chiral atropisomeric bidentate ligands or inherently chiral optically active metal complexes, a logical place to start was



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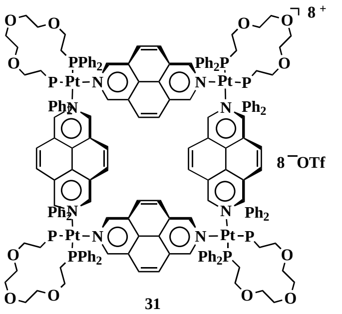

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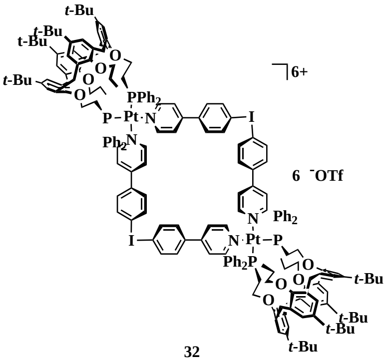

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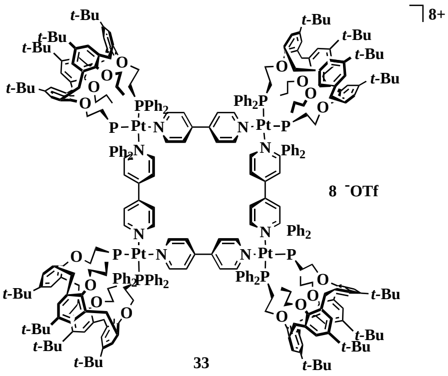

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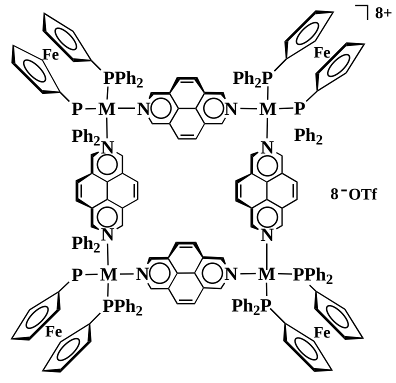


34. M=Pd, Pt

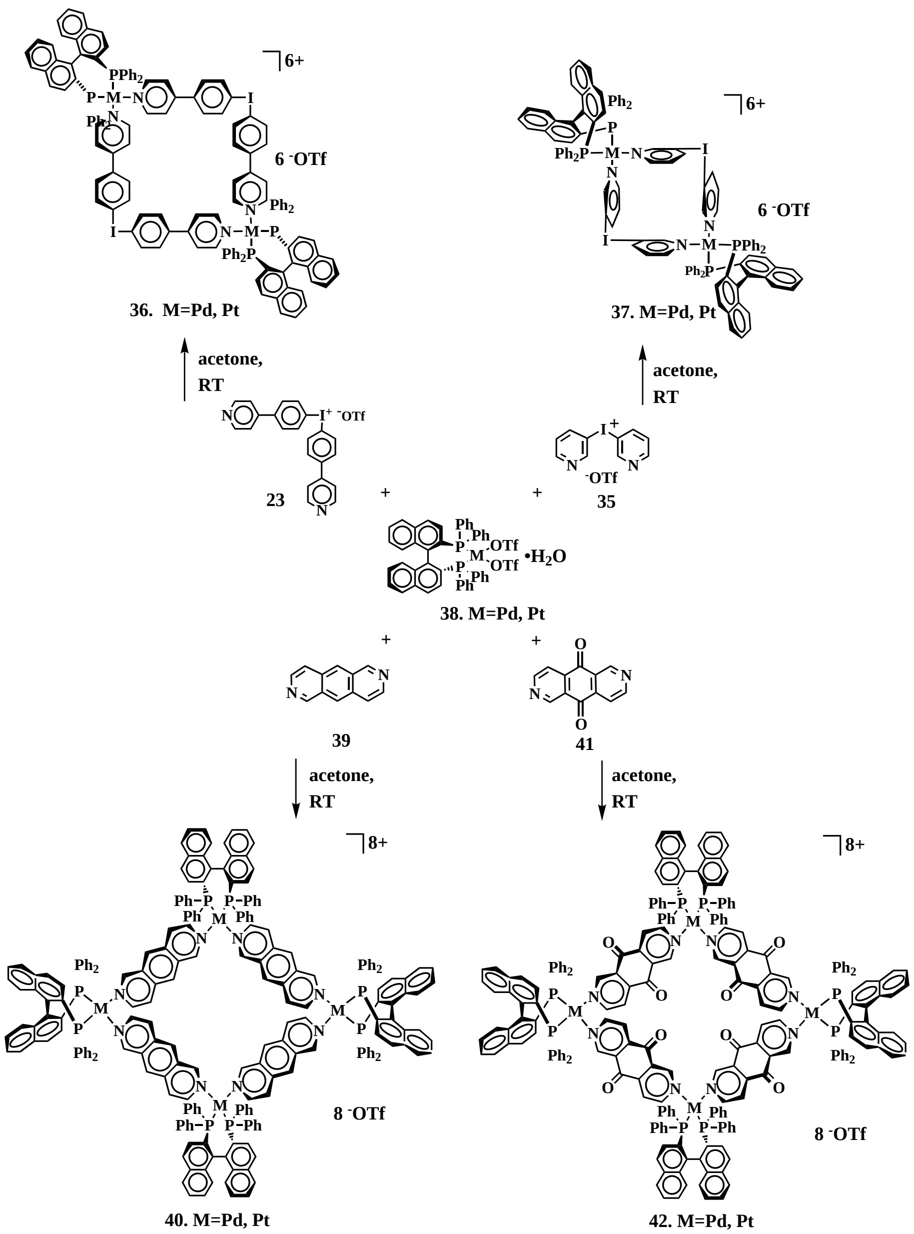
approach 1) and use of a commercially available chiral auxiliary. The results are summarized in Scheme 6 and Figure 4. Specifically, interaction of either bisheteroaryliodonium units **23** or **35** with the BINAP/bistriflate complexes **38** gave chiral molecular squares **36** and **37**, where the optical activity is solely due to the chiral auxiliary BINAP ligands.[26] In contrast, squares **40** and **42** illustrate both helicity (twist) and the use of a chiral auxiliary. In particular, the interaction of either of the diazaligands diazaanthracene (**39**, DAA) or diazaanthracenedione (**41**, DAD) lacking rotational symmetry about their linkage axis with a chiral metal complex such as **38** can, in principle, result in six possible diastereoisomers due to twist (helicity), as illustrated in Figure 4. In fact, with DAD with Pt-**38** an 84% *de* was observed, while with Pd-**38** the *de* was 79%. In other words, there is asymmetric induction by the chiral auxiliary that preferentially selects for one major diastereomer out of the six possible ones. Even more interesting, only a single diastereoisomer, again out of the six possible, was observed in the reaction of **38** with DAA (**39**), according to ^{31}P NMR.[26] This is a truly remarkable reaction, as the single diastereoisomer is formed by spontaneous self-assembly upon simple mixing of the two components in acetone!

Self-assembly of molecular hexagons: As stated at the outset, the self-assembly methodology using coordination as the motif and appropriate angular (**A**) and linear (**L**) polydentate building units is in principle completely general for the formation of polygons and polyhedra. The brief description of the diverse molecular squares investigated to date amply illustrates both the versatility and depth of this approach. To further illustrate the generality of this methodology for the self-assembly of discrete supramolecular species we next examined the formation of molecular hexagons and 3D assemblies.

In our simple descriptive system (Figures 1 and 2) a molecular hexagon is a $\mathbf{A}_6^2\mathbf{L}_6^2$ species with six 120° angular and six linear units properly joined together. Indeed, as summarized in Scheme 7, two isoelectronic isostructural molecular hexagons **42** and **43**, each with a M_r of 12433 Da, readily form in high isolated yields by simple mixing of the appropriate precursors.[27] This is a rather remarkable reaction, as twelve individual units have to come together in an incommensurate correct order. A molecular pentagon can likewise be formed by spontaneous self-assembly of **10** with **17**.[28]

3D Assemblies: To date, two discrete, related polyhedra, both octahedra of the $\mathbf{A}_6^2\mathbf{A}_4^3$ type, obtained by the coordination of self-assembly strategy, have been reported. Using their water-soluble $[(en)Pd(ONO_2)_2]$ building unit (**44**) and the tridentate ligand **45** Fujita, Ogura and coworkers[29] assembled the octahedron **46** (Scheme 8) and examined its host–guest chemistry with adamantane carboxylate as well as adamantane itself. With **47** as the requisite tridentate binding ligand, Stang and Olenyuk[30] recently reported the related optically active octahedral assembly **48** (Scheme 9). A unique feature of these chiral 3D metallacyclic polyhedra is that they belong to the *T*-symmetry point group, which has so far only been observed in a very few covalent organic molecules.[30]

Design features and some advantages of the coordination motif: It is evident that the coordination motif offers some unique design features and advantages for the construction by spontaneous self-assembly of discrete metallamacrocyclic polygons and polyhedra, new members of the family of supramolecular species. These include:



Scheme 6. Routes to chiral supramolecular squares.

1) high rational design predictability based upon two simple types of building units, angular (**A**) and linear (**L**) building units;
2) predictable and considerable variation of shape and size by simple variation of the size of the building units;
3) large number and diversity of possible transition metal complexes and multidentate binding units;
4) bond energies in the range of 15–30 kcal mol^{-1} per interaction that fall between those of the strong covalent bonds in classical macrocycles and the weak interactions (hydrogen bonding, π–π-stacking, electrostatic and Van der Waals interactions, etc.);
5) excellent product yields inherent in the self-assembly process;
6) ready control of the oxidation and charge states of the desired macrocycles;
7) easy access to chiral metallamacrocyclic supramolecular systems with controlled stereochemistry;
8) ability to create both organic- or water-soluble aggregates, and so on, and so on.

Conclusions

A simple system has been devised, developed, and exploited for the creation of a new class of abiotic supramolecular species, namely metallacyclic polygons and polyhedra. The methodology employs coordination as the motif and takes advantage of dative bonding between transition metal complexes and di- and polydentate binding ligands to drive and direct the self-assembly process. It is important to state that the emphasis on molecular squares is only a start but clearly illustrative of the generality, diversity, and power of this simple methodology. In this brief description emphasis was placed on concepts and principles as well as illustrative examples. In fact the real challenges, as in all of contemporary

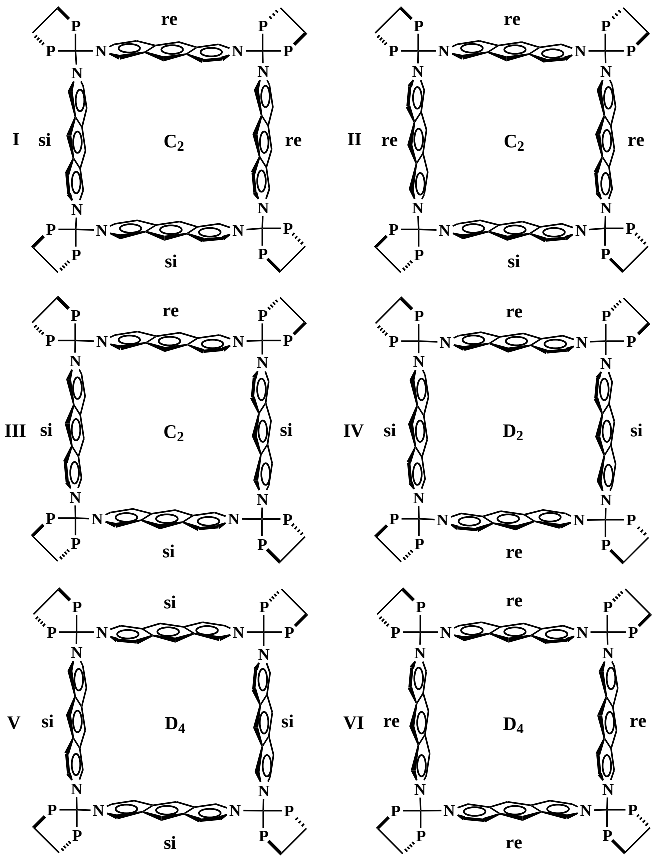
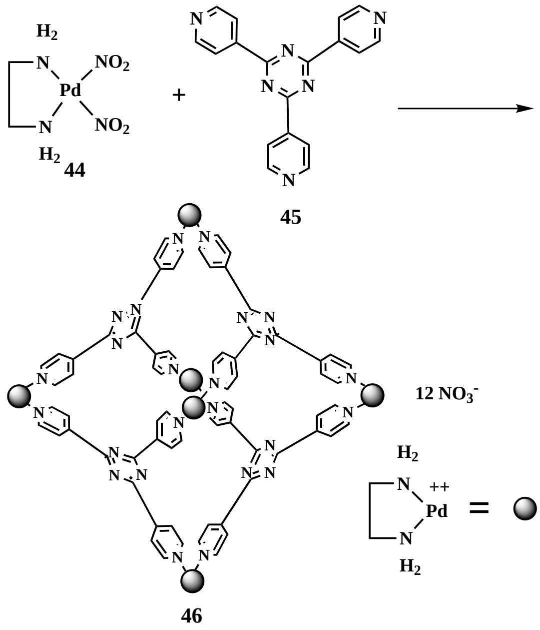


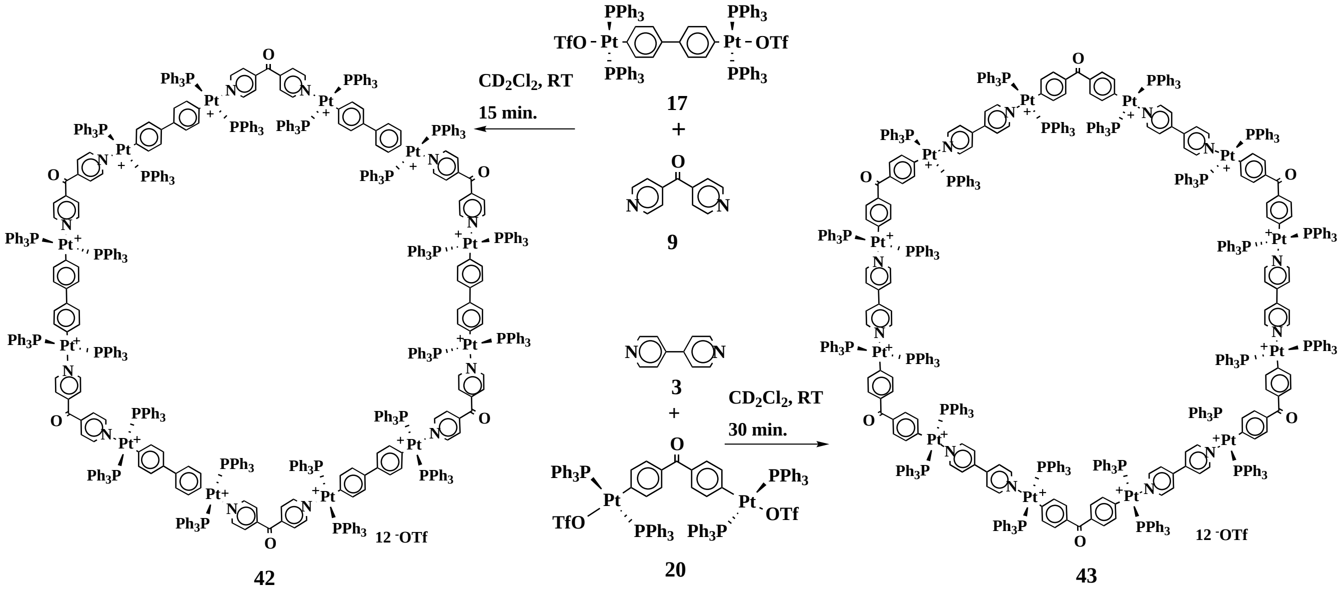
Figure 4. Chiral supramolecular squares.

supramolecular chemistry, are the proper characterization and structure determination of the species observed. This challenge increases with the complexity of the supramolecular species, from simple polygons (triangles and squares) to complex polyhedra (cuboctahedron, dodecahedron, etc.).

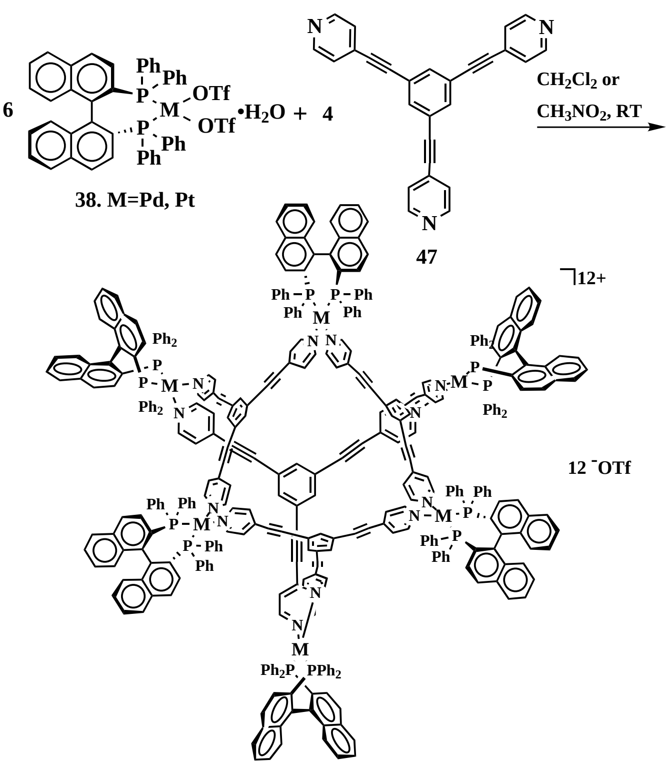
It is evident that the coordination motif can be combined with classical covalent macrocycles, as already illustrated, as well as the hydrogen-bonding motif for the design of even more elaborate, complex and sophisticated supramolecular species with well-defined shapes, form and size. In architectural terms the development of the coordination motif is only in the Romanesque period, with the Gothic, Baroque, Rococo and modern periods yet to come. The beauty, elegance, and sophistication of synthetic supramolecular entities is limited only by the boundless imagination of chemists—the modern equivalent of architects—and the practical considerations of the available techniques for the proper characterization and structure determination of the resulting products. Furthermore, as in nature, use and function will derive and follow from structure. The next century is likely to see hitherto unthinkable nanoscale devices and molecular machinery, as



Scheme 8. Self-assembly of the octahedron **46** (Fujita, Ogura et al.).



Scheme 7. Formation of the isoelectronic molecular hexagons **42** and **43**.



48. M=Pd, Pt

Scheme 9. Self-assembly of the octahedron **48** (Stang and Olenyuk).

well as many new materials with unique unfamiliar properties. We hope that the concepts and ideas expressed herein will ultimately play some small role in facilitating these developments.[31]

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