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Molecular architecture of cyclic nanostructures: use of co-ordination chemistry in the building of supermolecules with predefined geometric shapes

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Rapid growth and recent breakthroughs in the field of molecular manufacturing have resulted in the development of an entirely new synthetic strategy for the preparation of organized nanostructures. This strategy is based on molecular self-assembly, a phenomenon in which the individual subunits are quickly driven together and held in place by multiple, accurately positioned non-covalent interactions. The use of transition metals and co-ordination-based design allows the formation of a variety of self-organized nanosystems in a few highly convergent synthetic steps. Molecular architecture utilizes the large diversity of available transition metals and their co-ordination chemistry to create complex geometric shapes. This article explores some of its most interesting aspects, beginning with the construction of simple self-assembled structures that have the shapes of various convex polygons, such as squares, rectangles and triangles to more complex assemblages with shapes of polyhedra and three-dimensional nets. An attempt is also made to provide insight on how this strategy can be used to create advanced materials with properties and functions determined by their structure.

1 Introduction

The challenge facing the future of modern nanotechnology is molecular manufacturing, a process that is designed to synthesize advanced materials with specific properties and functions. These are determined by controlling the form, shape and distribution of each individual building block and their precise placement. Such intermolecular control imposes strict requirements on the nature, type and directionality of the bonding forces that operate within the entire aggregated structure. The chemical bonding of the subunits must be relatively weak, thermodynamically stable, yet kinetically labile to allow the self-rearrangement of the subunits within the entire structure, thereby enabling the self-correction of possible defects. Another important requirement is the conformational rigidity of the building blocks in order to reduce entropic factors upon self-organization. This is only an illustrative, not an exhaustive list of important considerations, which has triggered enormous interest and growth in modern supramolecular

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chemistry. A recent novel synthetic protocol in the construction of organized nanoscopic assemblies from multiple building blocks in a single step, namely self-assembly, relies on critical information about the shape and properties of the resulting structure being preprogrammed into each individual building block. Although this approach was initiated by the artificial mimicking of natural receptors that utilize weak hydrogen bonds, it has now resulted in an entirely different 'unnatural' strategy, molecular architecture, that employs transition metals and dative bonding to achieve structurally well defined, highly ordered assemblages. This approach relies on the fact that fewer metal–ligand bonds may be used in place of several hydrogen bonds owing to their greater strength. Another advantage lies in the existence of a large variety of transition metals with different co-ordination numbers, thus facilitating the building of diverse nanoscopic entities with tremendous variations in shapes and sizes. In this article we present an overview of this molecular architecture paradigm and demonstrate the application of transition metals and co-ordination chemistry in the rational design of artificial nanoscopic objects with desired forms and shapes.

What is self-assembly and why is it gaining importance in the construction of complex macromolecules and organized nanosystems? Throughout the evolution of chemistry as a discipline, the preparation of various chemical compounds *via* the stepwise formation of covalent bonds between appropriate precursors has been the most widely used method. Although this method is useful for the synthesis of relatively small organic molecules, it becomes burdensome when applied to the synthesis of large macromolecules or molecular assemblies since it possesses several inherent limitations. Among its serious drawbacks are the inordinate amount of time required for the linear step by step synthesis of complex macromolecules composed of hundreds or even thousands of subunits and the drastic reduction of the overall yield in such a multistep synthetic process. Since most covalent bonds are kinetically inert, even a single assembly error can jeopardize the integrity and functionality of the entire structure. Self-assembly offers some important advantages over stepwise bond formation. Since it proceeds *via* the simultaneous assembly of predetermined building blocks, the resulting synthesis is highly convergent and thus requires fewer steps than the corresponding covalent synthesis. Also, since non-covalent interactions are usually established very rapidly, final product formation is fast and facile. The presence of kinetically labile non-covalent interactions between the constituents results in relatively defect-free assemblies with self-maintained integrity since the usual equilibria between the constituents and the final products contribute to the self-rearrangement of components and correction of defects. Nature has been exploiting these advantages of self-assembly for a long time. Various cell components, such as ribosomes, mitochondria, chromosomes and others, are almost exclusively made *via* self-assembly and non-covalent interactions, such as hydrogen bonds. During their formation the individual components are quickly driven together and held in place by thousands of accurately positioned non-covalent interactions, creating incredibly complex and exquisite patterns of life. In light of this tremendous complexity, it is difficult to imagine how these components could have been created if only covalent forces were in Nature's arsenal.

In marked contrast to biological supramolecules, the design of artificial self-assembling systems is still in its early stages. It requires consideration of many factors, such as type and strength of dative bonds between various components, the symmetry of both the constituents and the entire self-assembled structure, the precise positioning of the co-ordination sites of the components, temperature and solvent polarity, and possibly many others. The first step in solving this complex problem is the development of relatively simple, self-assembling structures of the desired shape and symmetry that mimic at least a single function of an appropriate biomolecule. Such functions may be catalytic, receptive, transportive or others. It is also important for such structures to exhibit some active property that differs from the properties of its constituent components. These tasks are being addressed by supramolecular chemistry, a relatively new field that is concerned with the design and structure of large and complex nanoscale-sized macromolecules.[1] Molecular design is based on the basic principles of 'molecular informatics' in which the structure and function of the final product can be preprogrammed within its individual building blocks, giving the chemist enormous control over the intermolecular bond. Modern supramolecular chemistry[1] emerged from studies of covalent systems, such as cyclophanes, crown ethers, calixarenes and cryptands, although it is now dominated by studies of non-covalent assemblies. In less than a decade the novel motif of transition metals and co-ordination bonds in assemblies has emerged as a strong and viable alternative to hydrogen-bonded aggregates, patterned after natural macromolecules.

2 Principles and Design Strategies

The structural and functional features of self-assembled supramolecular entities result from the information stored in their components and the components' intrinsic properties that are dictated by the presence of functional groups. A simple and general concept for generating ordered structures is based on the recognition-driven spontaneous assembly of complementary subunits. Since transition metals have co-ordination sites with specific geometries that depend upon their electronic structure they can serve as acceptor subunits. These can be linked together *via* donor building blocks that form the rigid frame of the assembled entity. Both of these types of subunits must possess specific geometries and remain multidentate or at least bidentate, *i.e.* they must have at least two co-ordination sites that cannot be capped, to form the desired cyclic structure. For the synthesis to be efficient and convergent, it is important for these building blocks to be readily available. From the above considerations it is obvious that these units can be nitrogen-containing heteroaryls, cyano-substituted aromatic ligands, as well as bis(*o*-catecholates) and some thiocatechols.

The construction of almost any entity that contains a transition metal requires the assessment of the angles between the binding sites of each donor and acceptor subunit. Hence, the subunits can be classified into two types based on the value of this angle: linear subunits that possess these reactive sites with a 180° orientation relative to each other and angular subunits that have other, smaller angles.[2] When these types of building blocks are combined the structure of the resulting species will solely depend on the symmetry and the number of binding sites within each subunit. The symmetry of the resulting assembly will be the combination and spherical distribution of the main symmetry axis of each building block. Thus, monocyclic entities can be built by combining subunits with symmetry axes not higher than twofold, while the construction of polycyclic frameworks requires at least one subunit to possess a symmetry axis higher than twofold.[2] Thus, the shapes of monocyclic entities will resemble convex polygons and those of polycyclic frameworks will resemble canonical polyhedra.

Hence, the assembly of a planar triangle requires the combination of three linear building blocks and three angular ones with a 60° turning angle. A molecular square can be assembled in several different ways, either by combining four linear with four angular building blocks, or by combining two different angular subunits. Molecular pentagons can be built by combining five linear components with five angular ones that possess a 108° angle between their binding sites. Likewise, molecular hexagons can be constructed *via* the combination of six linear components and six angular subunits with a 120° directing

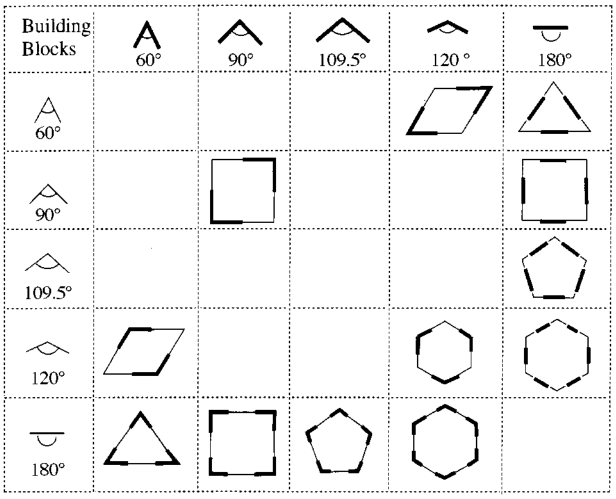


Fig. 1 A combinatorial library of cyclic molecular polygons may be created *via* the systematic combination of building blocks with predetermined angles

angle or *via* the combination of two different types of angular subunits with a 120° angle between the binding sites (Fig. 1).

The design of three-dimensional polyhedra is more complex since it requires the interaction of many more subunits and at least one type of building block to be multidentate with more than two binding sites (Fig. 2).[2] Thus, the preparation of a triangular prism can involve the combination of two tridentate subunits with three linear spacers. If the spacers do not have linear geometry then the formation of a triple helix is expected. Likewise, twelve linear subunits combined with eight tridentate subunits with 90° angles between each of the co-ordinating sites will yield a cube whereas six angular bidentate units in combination with four angular tridentate subunits will result in the shape of an octahedron and so on.

It is important to note that this approach only accounts for the angles between the binding sites within each free subunit and extrapolates them into the final self-assembled entity. Therefore, it can be assumed that the value of the directing angle within each such subunit does not change significantly upon its incorporation into the self-assembled structure. This assumption is based on the initial requirement of conformational rigidity of the subunits. In reality, however, distortions of the binding angle up to several degrees may occur, but in most cases they can be neglected as the weak dative bonding to the transition metals is likely to prevent the formation of highly distorted structures.

3 Cyclic Binuclear Molecular Systems: Polygons, Rectangles and Strands

One of the first cyclic self-assembled host molecules was reported by Maverick *et al.*[3] This work was based on the formation of a cofacial binuclear structure generated from the $Cu(NH_3)_4^{2+}$ complex and a bis(β-diketone) ligand, which on mixing in an aqueous solution generated assembly **1**. The ability of **1** to function as a host was tested by measuring its binding constants with pyridine, pyrazine, quinuclidine and DABCO. For example, DABCO could be selectively bound inside the macrocyclic host over the other potential guests with a binding constant of 220 m^{-1}. The internal co-ordination of DABCO was established by X-ray studies of the inclusion complex. These investigations were among the early observations of the intermolecular co-ordination of bifunctional Lewis bases to binuclear transition metal-based hosts.[3]

Another example of binuclear assemblies with potential receptor abilities is the work of Hartshorn and Steel.[4] They employed polyheteroaryl-substituted arenes in combination with silver(I) salts to prepare binuclear frameworks. When 2 equivalents of 1,4-bis(2-pyridoxy)benzene were allowed to react in acetone with 2 equivalents of silver nitrate assembly **2** was formed, as determined by X-ray crystallographic studies. In this assembly each silver atom is co-ordinated to two pyridine nitrogens and less strongly to a water oxygen. This distorts its geometry to T-shaped with the N–Ag–N′ angle being close to 157°. Another interesting feature of this assembly is the close π–π stacking of the two benzene rings that are coplanar and separated only by 3.33 Å.[4]

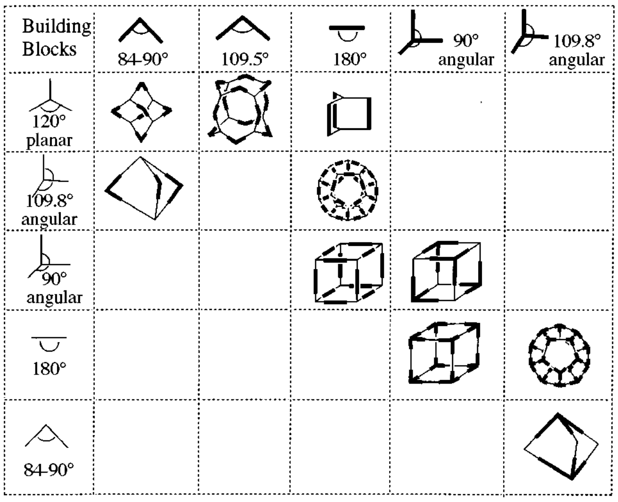
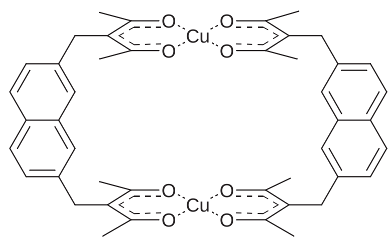


Fig. 2 A part of the combinatorial library of canonical molecular polyhedra

Hannon *et al.*[5] employed an interesting strategy. They incorporated both chelating ligands into the reactive donor unit, thereby eliminating the need for the additional preparation of the transition metal complex and allowing the use of transition metals with multiple, open co-ordination sites. The ligand 4-methylsulfanyl-6-(3-pyridyl)-2,2′-bipyridine acts as a bidentate chelate for one transition metal and as a monodentate binding site for the other. The preparation of assembly **3** was achieved by mixing 1 equivalent of copper(I) salt with 1 equivalent of ligand in acetonitrile. Mass spectrometry and single-crystal X-ray studies allowed the elucidation of its structure. Interestingly, a topologically similar assembly could also be obtained by using an octahedral Group II metal, such as cadmium.

An elegant example of a binuclear structure was prepared by utilizing the copper(I) or zinc(II) 2,2′-bipyridyl co-ordination.[6] Since this type of co-ordination chemistry is well known, it allowed the authors to use two 2,2′-bipyridyls connected to each side of the aromatic spacers, such as 2,2-naphthalene and 2,7-pyrene. Treatment of these ligands with either copper(I) or zinc(II) salts produced the binuclear assemblies **4**. Fast atom bombardment and ES mass spectrometry were used to establish the stoichiometry of these complexes and variable temperature NMR spectra to study their dynamics.

Binuclear triple helicates can be formed by combining the transition metals that prefer octahedral co-ordination, such as iron or Group IVa metals, with three subunits that contain one bidentate binding site at each end. Caulder and Raymond[7] employed this motif to produce highly ordered helical assemblies in solution that are formed from a mixture of predesigned building blocks. The three ligands, **5**–**7** (Scheme 1), contain a systematically increased distance between the binding sites. The reaction of 3 equivalents of any of these ligands with 2 equivalents of trivalent $M(acac)_3$ (M = Fe, Al, Ga) **8** in methanol and KOH results in the formation of triple-helical assemblies **9**–**11** in high yields.[7] The remarkable degree of self-recognition in this self-assembly process is illustrated by the



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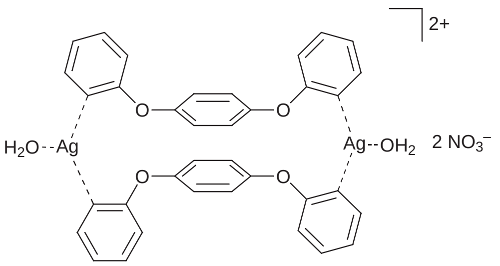

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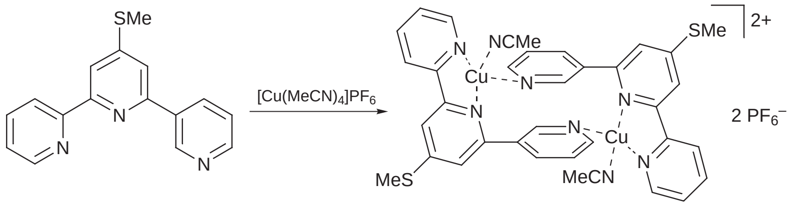

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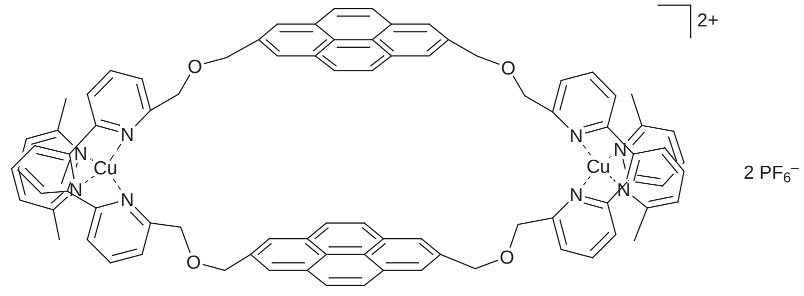

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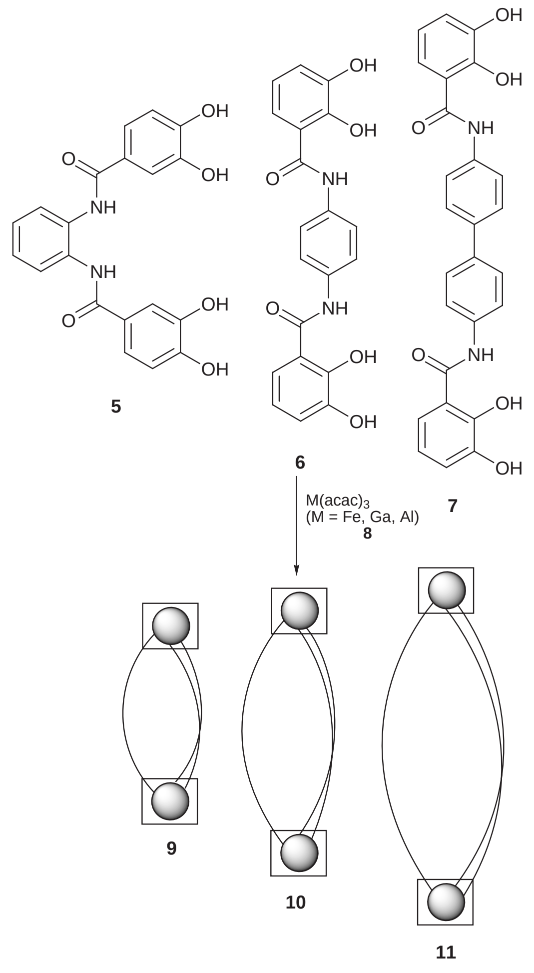
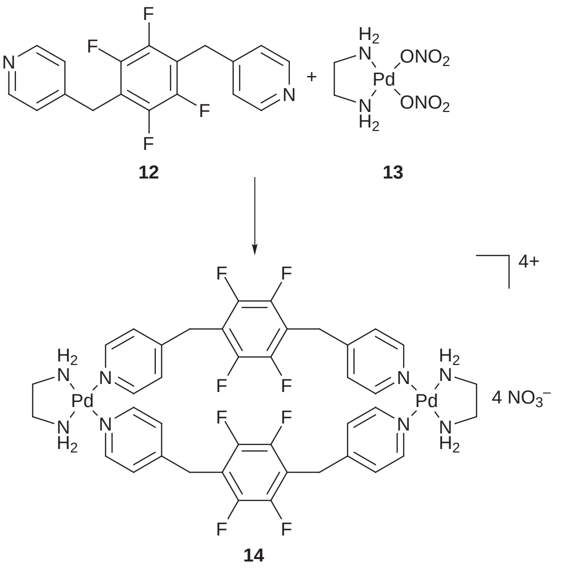


Scheme 1

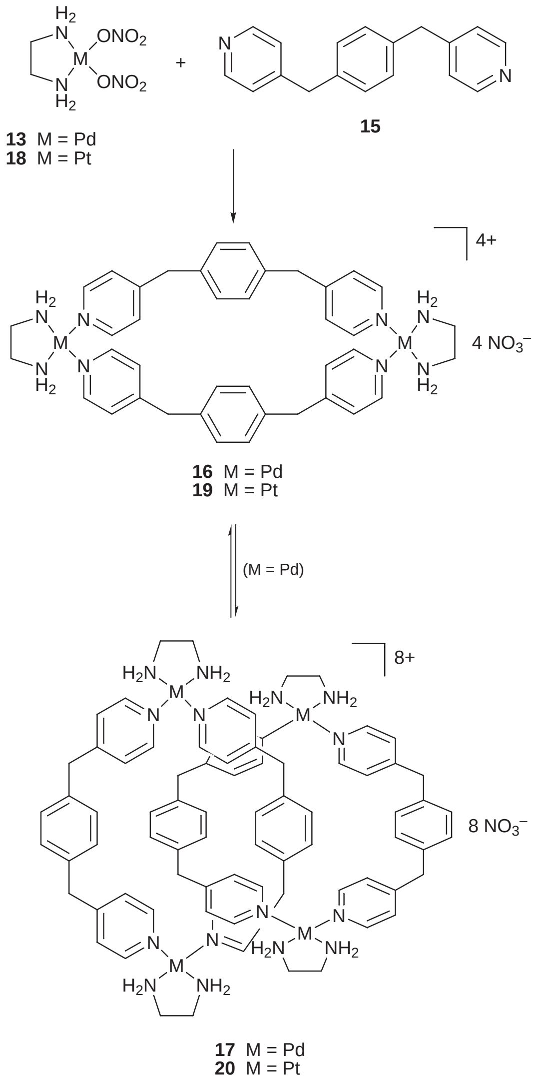
following two examples. When these complexes were prepared in the presence of an excess of ligand NMR spectra only indicated the formation of the final products and the excess of the free ligand remained intact.[7] When mixtures of all three or any two ligands were allowed to react with [Ga(acac)$_3$] **8** under these conditions only complexes containing one type of ligand were formed with no mixed ligands or oligomers formed in solution. Both NMR spectroscopy and electrospray mass spectrometry indicated a mixture of three final helical products in equal amounts with no traces of oligomeric or mixed species. The main reasons for this self-recognition are the high degree of conformational rigidity of each donor subunit combined with different steric requirements due to the different distances between the binding sites in the assembled product.

By introducing additional tetrahedral carbons between the pyridine rings, Fujita *et al.*[8] assembled several water-soluble binuclear macrocycles. When ligand **12** was mixed with an aqueous solution of [Pd(en)(NO$_3$)$_2$] **13** the formation of assembly **14** was observed (Scheme 2). Since it contains the electron-deficient subunit with the perfluorinated phenylene, it was capable of recognizing electron-rich compounds such as naphthalene, in an aqueous medium.[8]

Using a slightly modified subunit, 1,4-bis(4-pyridylmethyl)benzene **15** (Scheme 3), it was possible to prepare the corresponding palladium-based bimetallic species **16**. Its interesting property is the ability to form the catenated dimer **17**.[9] At ambient temperature, the palladium catenane **17** is in equilibrium with its monomeric form **16**, as confirmed by spectroscopic studies. At lower concentrations this equilibrium favors the single-ring assembly but at higher concentrations the catenane is the dominant species. The reaction of a platinum precursor **18** with **15** produced an analogous assembly **19** (Scheme 3). Due to the greater Pt–N bond strength, it is exclusively formed as the monocyclic structure at room temperature. However, when the reaction mixture was heated to 100 °C in the presence of NaNO$_3$, the formation of the catenated dimer **20** was observed

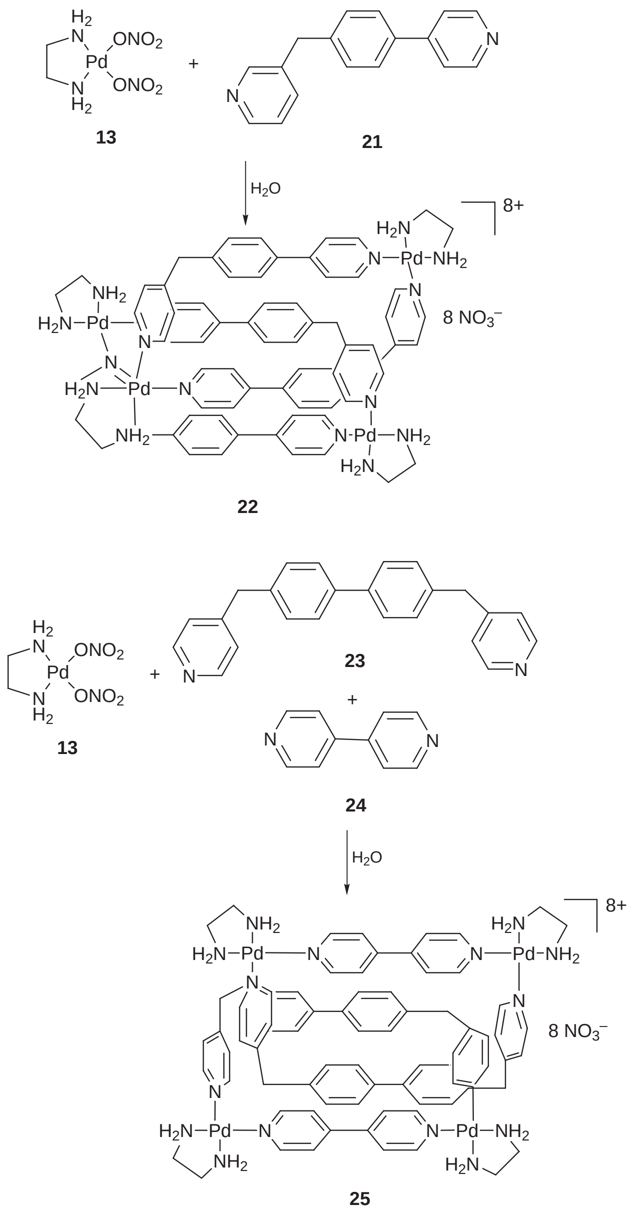


Scheme 2



Scheme 3

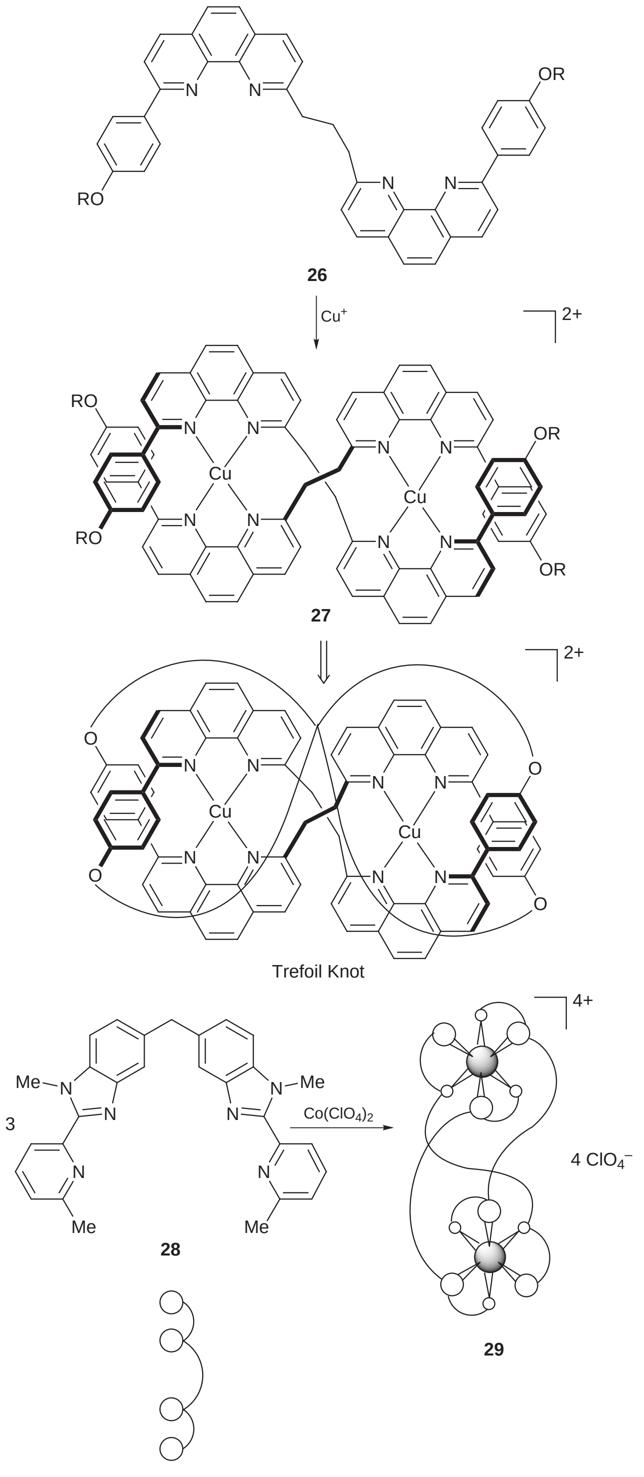
due to the increased lability of the platinum–pyridine bond.[10] The irreversible formation of this catenane can be achieved by cooling the solution to room temperature.



Scheme 4

The self-assembly of molecular rectangles may be accomplished by using modified organic angular subunits.[11] Two types of rectangles were constructed: one which contains two identical angular subunits in combination with [Pd(en)$(NO_3)_2$] **13** and the other composed of this transition metal complex combined with both linear and angular units. When the unsymmetrical angular block **21** was mixed with **13** it quantitatively formed the catenated rectangular assembly **22** (Scheme 4). This molecule is remarkably stable as the dissociation of **22** into its components was not observed even at low concentrations.[11] Reaction of the same palladium complex with two disparate heteroaryls, such as substituted biphenyl **23** and 4,4′-bipyridyl **24** formed catenated assembly **25** (Scheme 4). In the solid state catenane **22** consists of two crystallographically independent structures whereas catenane **25** is a stable single isomer.[11]

The preparation of a double helix can be carried out by utilizing the co-ordination chemistry of four-co-ordinate transition metals, as illustrated in the following two examples. Sauvage and co-workers[12] used functionalized bis(1,10-phenanthroline) **26** which reacted with appropriate copper(I) salts (Scheme 5). The assembly **27**, after being subjected to further chemical transformations, resulted in the formation of a unique trefoil knot.[13] Williams *et al.*[13] prepared a triple-helical binuclear assembly by using octahedral cobalt(II) salts and an organic heterocyclic subunit bis[2-(2′-pyridyl)benzimidazoyl]methane **28**. The product helicate **29** (Scheme 5) was isolated as a per-

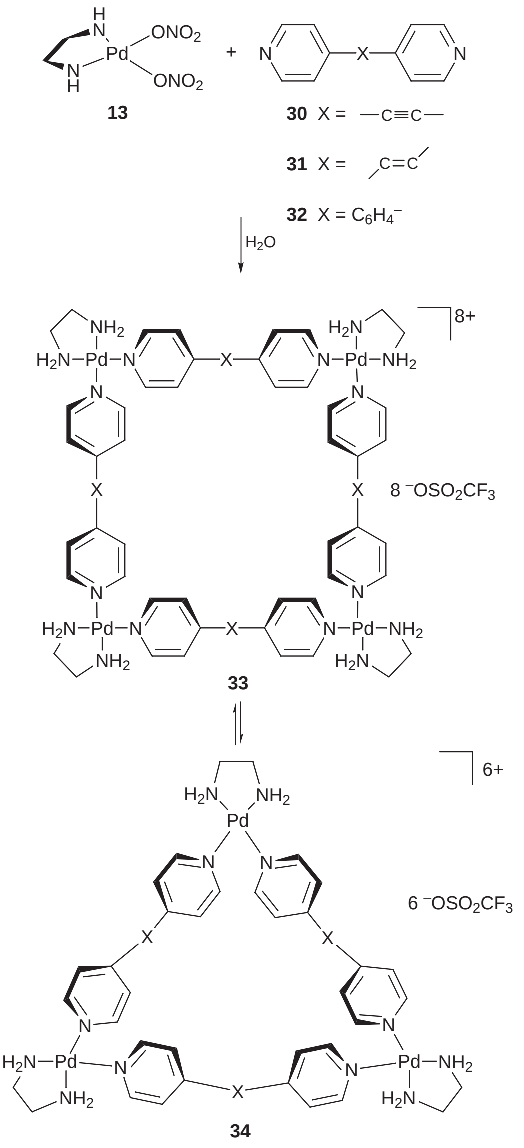


Scheme 5

chlorate salt and its crystal structure indicates an 8 Å separation between the transition metals which are interconnected by three helical strands. The current literature contains hundreds of examples of unique helical assemblies that are prepared by using the co-ordination motif and which, due to the restrictive nature of this article, we were forced to omit. Interested readers may wish to pursue some recent reviews[14] which provide further insights into the chemistry of this interesting class of supramolecular assemblies.

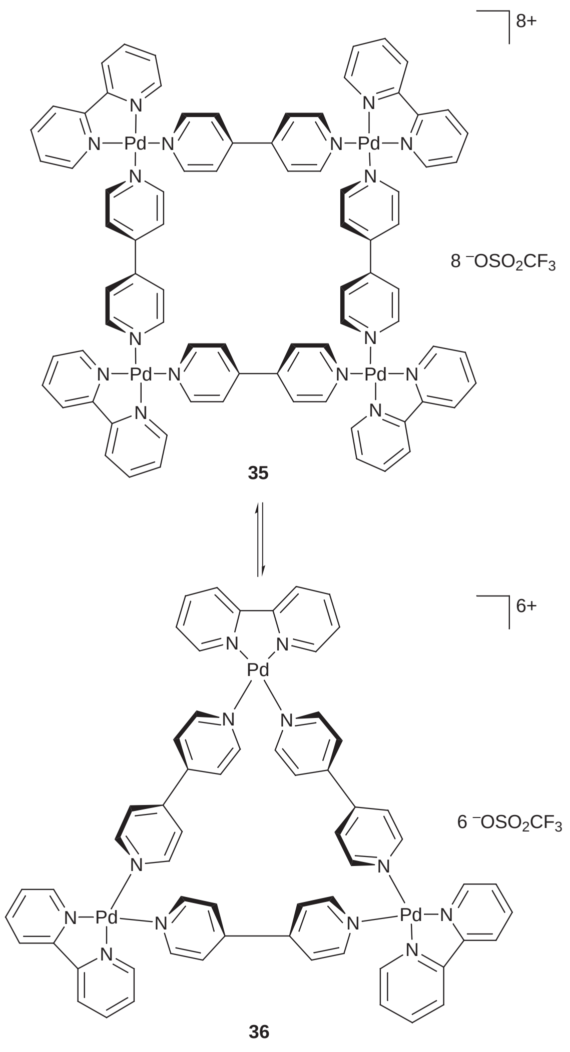
4 Molecular Polygons: Triangles, Squares, Pentagons and Hexagons

Although the *de novo* construction of a molecular triangle seems not to be a very synthetically complicated task, a surprisingly small number of attempts have been reported in the literature. From the general design standpoint, any cyclic combination of three linear building blocks with three angular ones that possess a 60° directing angle should result in a molecular triangle. One possible reason for the relative rarity of such assemblies may be the value of its turning angle, which is quite uncommon and relatively difficult to attain, both in transition metals and organic linking subunits. Fujita *et al.*[15] observed the formation of two types of equilibrium products when [Pd(en)-$(NO_3)_2$] **13** was mixed with selected linear linking components **30**–**32** resulting in molecular squares **33** and additional highly symmetrical assemblies that were assigned as molecular triangles (Scheme 6). A triangular entity **34** dominated the equilibrium products when the linear linking components were extended or were more constitutionally flexible. The assignment of one equilibrium product to the triangle is strongly supported by the effect of concentration on the equilibrium ratio. At higher concentrations this ratio shifts towards the formation of a molecular triangle. This equilibrium results from a thermodynamic balance, where the less strained molecular square is more stable in terms of enthalpy while entropy favors self-assembled entities with fewer number of components, *i.e.* molecular triangles.

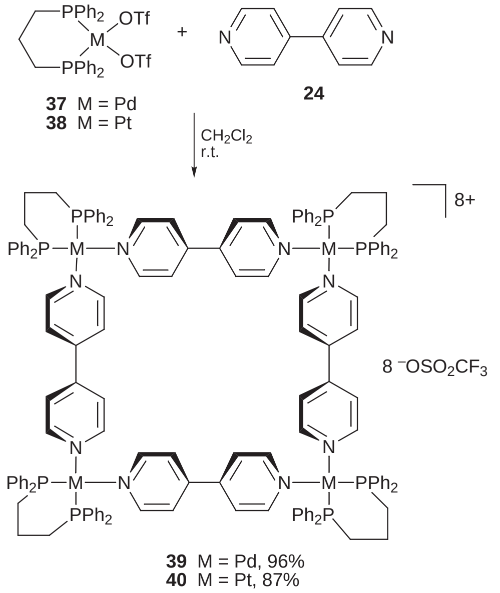


Scheme 6

The presence of steric effects can also play a vital role in the equilibrium shift towards the molecular square or the molecular



Scheme 7



Scheme 8 r.t. = Room temperature

triangle. It was found that, if for instance, the ethylenediamine groups on Pd were replaced with the more sterically demanding 2,2′-bipyridine, the resulting squares **35** were also in equilibrium with the molecular triangles **36** (Scheme 7), probably due to steric repulsion between two subunits.[15]

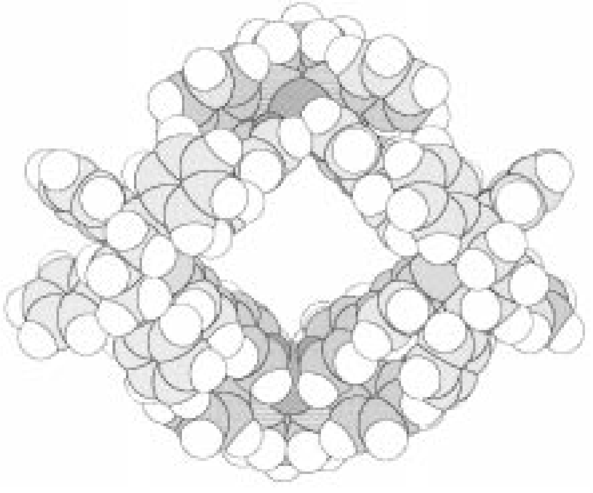
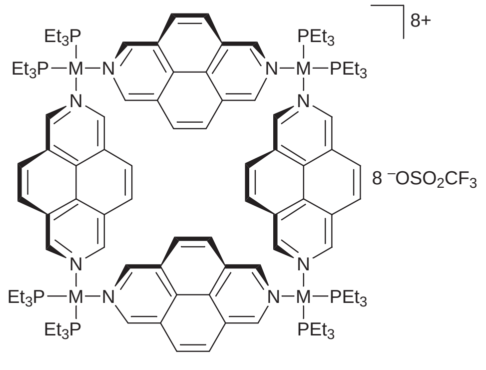


Fig. 3 Space-filling model of molecular square **40**, based on its X-ray coordinates

Self-assembly of molecular squares can be achieved *via* the interaction of four bidentate angular units with four linear components where the angular and linear subunits have a cyclic arrangement. Transition metals with specific geometries and co-ordination numbers are best suited to become angular subunits for these assemblies. Divalent four-co-ordinate complexes of Pd and Pt are square planar species with adjacent bond angles of about 90°. Co-ordination with a bis(phosphane) results in a cyclic chelated complex with a constrained *cis* geometry. If the remaining two adjacent co-ordination sites are occupied by weakly co-ordinated ligands, such as the triflate ion, then on interaction with a linear nitrogen-containing bis(heteroaryl) (*i.e.* with the lone pairs of the nitrogen atoms oriented 180° relative to each other) a square assembly will be formed. Indeed, when bis(phosphane) complexes **37** and **38** reacted with an equivalent amount of 4,4′-bipyridine **24** in dichloromethane at room temperature the resulting species were identified as molecular squares **39** and **40** (Scheme 8) based on multinuclear NMR, physical properties and later by single-crystal X-ray diffraction studies.[16,17] A space-filling model based on the X-ray structure of **40** is shown in Fig. 3. A number of interesting geometric features are worthy of mention. The geometry about the Pt^{II} is square planar with only a slight deviation of the angles from 90°. The shape of the molecule is undoubtedly that of a square despite the deviation from planarity of about 4 Å. This assembly has a large, molecule-sized cavity. There is a high degree of π stacking between the phenyls of the chelated bis(phosphane) and one of the 4,4′-bipyridine rings.[16] This kind of interaction may be responsible for the high stability of squares **39** and **40**. Experiments have shown that it is impossible to prepare and isolate only a ‘corner’ or a ‘side’ of these assemblies. Even with a 100-fold excess of 4,4′-bipyridine in solution only complete squares were formed, with the rest of the free bipyridine left intact. It was also not possible to obtain an isolable intermediate when the reaction was carried out with a large excess of transition metal bis(triflate).

In the last few years various tetranuclear molecular squares have been prepared and reported in the literature by us[3] as well as by Fujita *et al.*,[18] who assembled a water-soluble square **41** from the complex **13** in combination with 4,4′-bipyridyl **24** (Scheme 9). The assemblies **42**–**46** contain various linking subunits, such as 4,4′-bipyridyl, 1,4-dicyanobenzene, 4,4′-dicyano-1,1′-biphenyl, diazapyrene and diazaperylene combined with both chelated and non-chelated bis(phosphines). Molecular squares **47** are built by using ferrocene-containing units.[19] The versatility of this self-assembly strategy also allowed the preparation of a series of multicomponent squares **48**–**51** that



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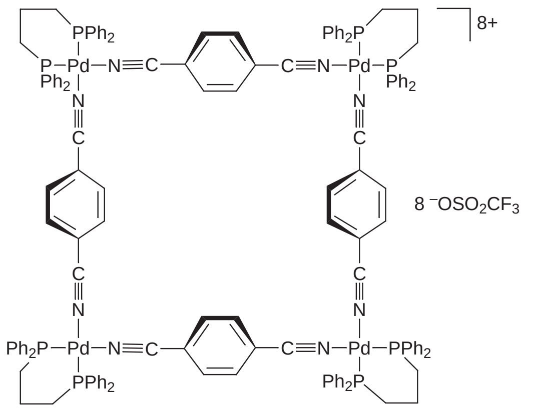

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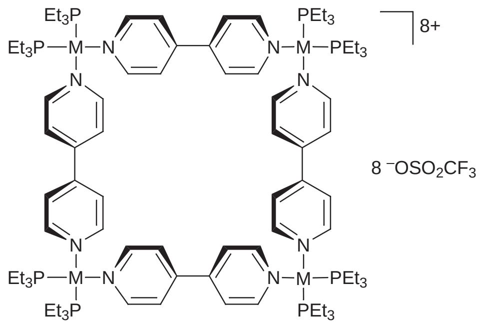

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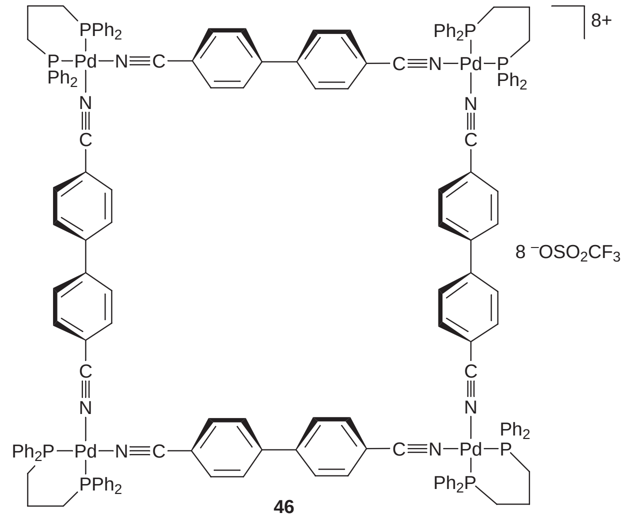

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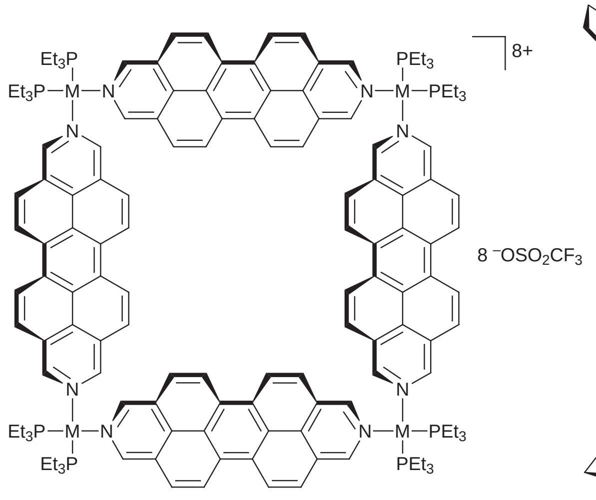

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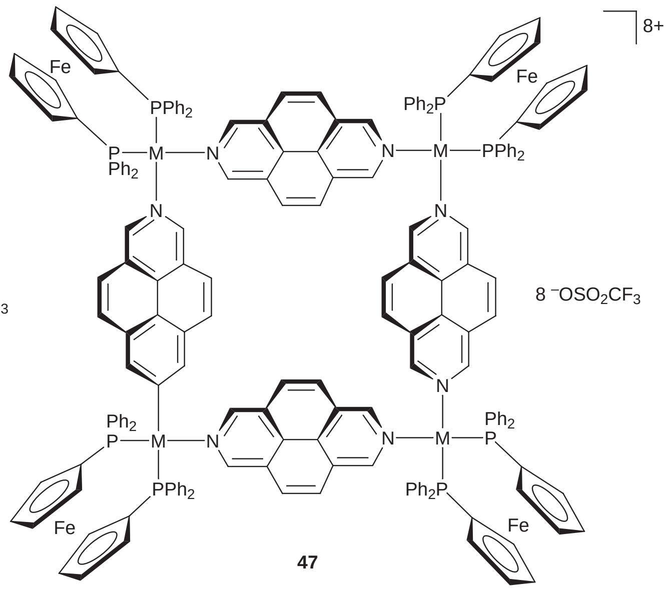
M = Pd, Pt



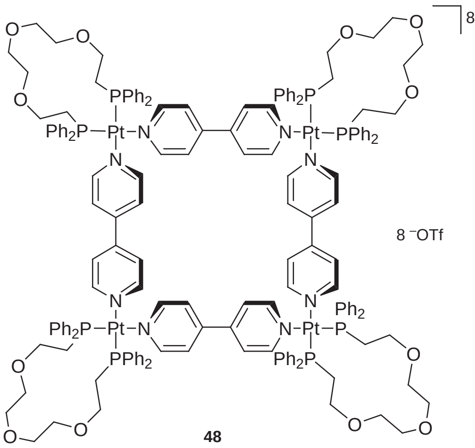
47

contain crown ethers or calixarenes as angular units[20] or squares **52** which contain porphyrins as linear linking components.[21]

The self-assembly of water-soluble squares of similar topology was completed by Fujita *et al.*[18] Their approach utilized the co-ordination of 4,4′-bipyridyl **24** to the ethylenediamine complexes of palladium(II) and platinum(II) dinitrates. Assemblies of this type are soluble in water and serve as hosts for various aromatic guests, such as naphthalene, 1,4-dimethoxybenzene and others.

Hupp and co-workers[22] recently utilized the co-ordination chemistry of octahedral rhenium complexes to prepare an interesting family of luminescent molecular squares. By heating a mixture of [Re(CO)$_5$Cl] and selected ligands **24** and **53**, **54** (Scheme 10) in toluene for 2 d, the resulting assemblies **55**–**57** were isolated in excellent yields. Usual characterization and X-ray crystallographic studies have established the structure of these interesting macrocycles. Molecular squares **55** and **57** were found to be luminescent and have been further subjected to time-resolved luminescence measurements.

All the molecular squares described above were isolated in



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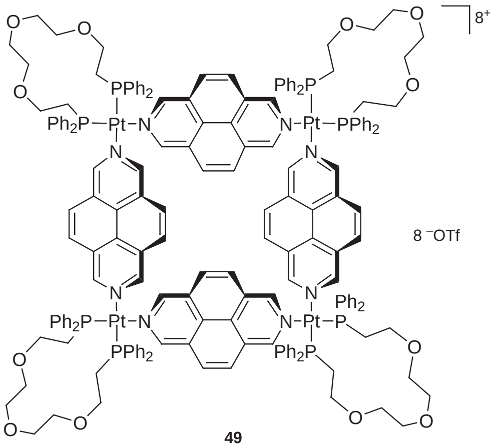

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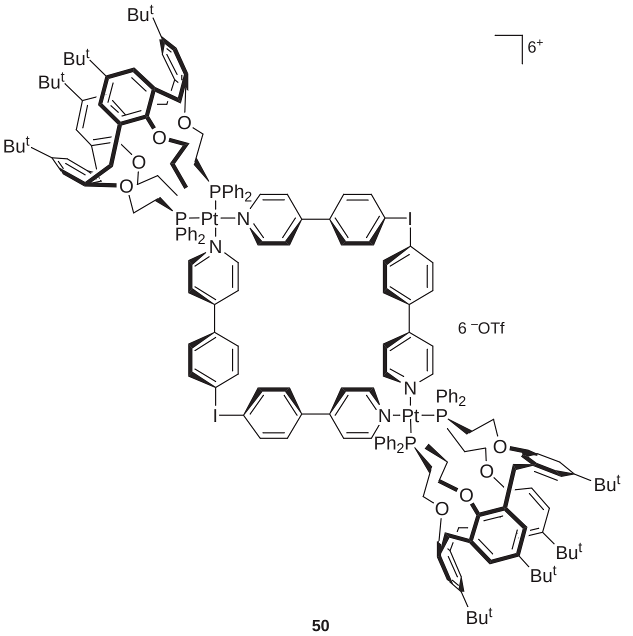

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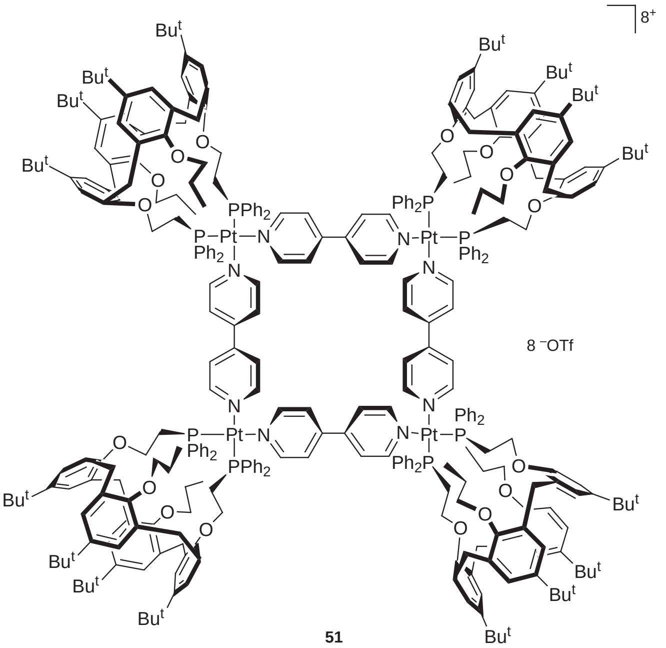

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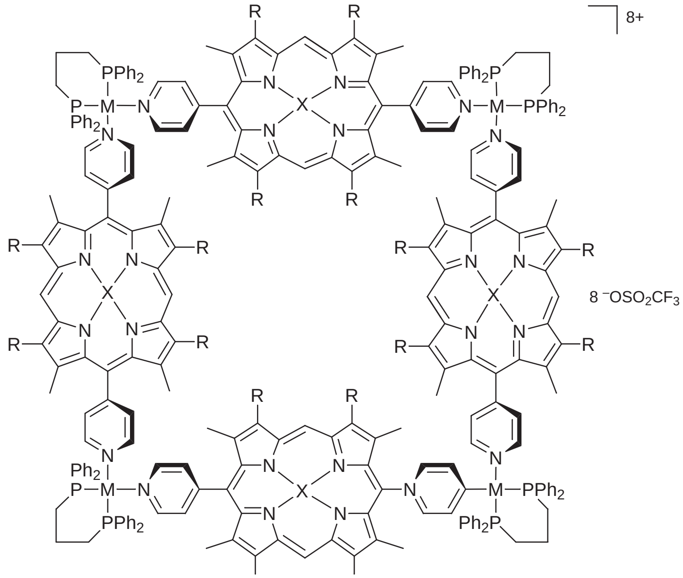
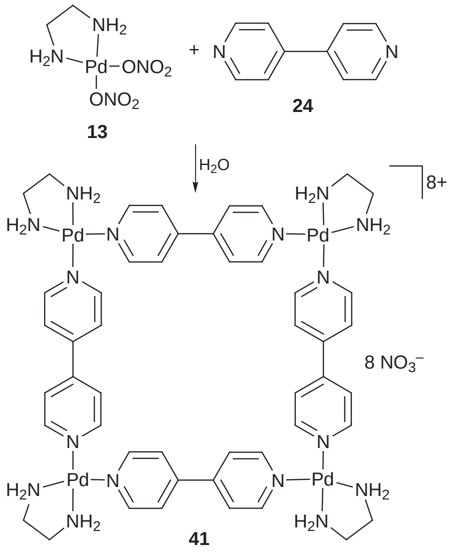


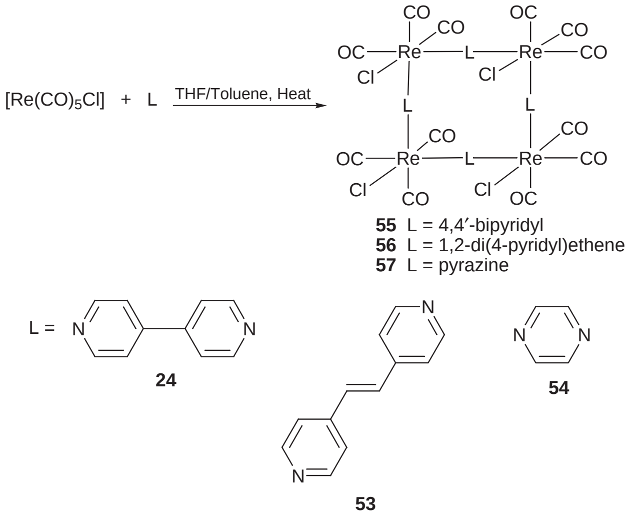
R = n-C_6H_{13} **52** M = Pd, Pt; X = 2H, Zn

high yields as robust, air-stable, microcrystalline solids, which decompose at their melting points. Most of them are prone to crystallize with either solvent of crystallization or water that cannot be removed even by prolonged heating under vacuum.

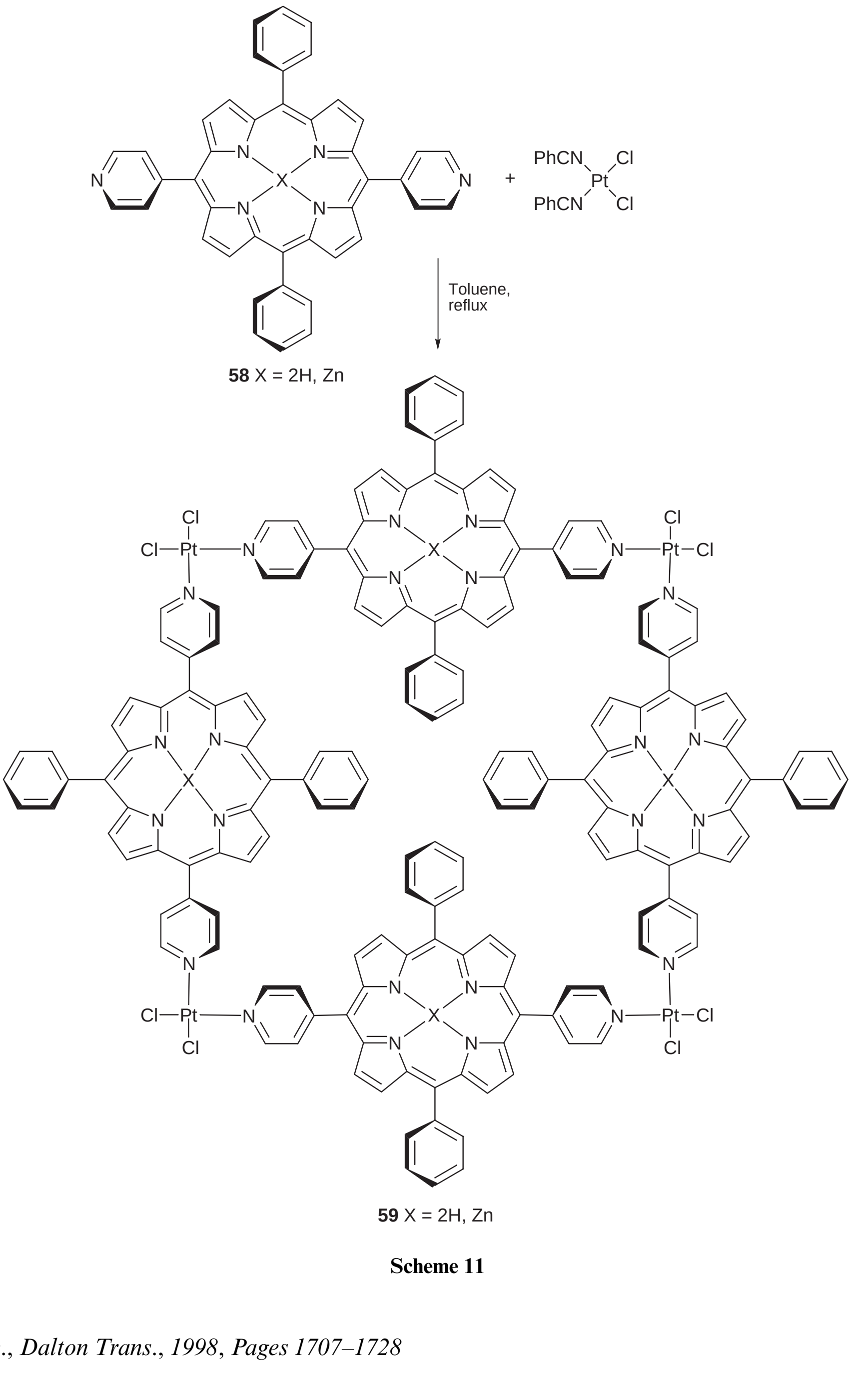
Interesting examples of photoactive, porphyrin-based molecular squares were reported by Drain and Lehn.[23] They prepared tetranuclear assemblies by two different methods. One of them involved the *cis*-[Pt(PhCN)$_2$Cl$_2$] complex as an angular building block which, when combined with the linear porphyrin **58** resulted in molecular square **59** (Scheme 11). Another



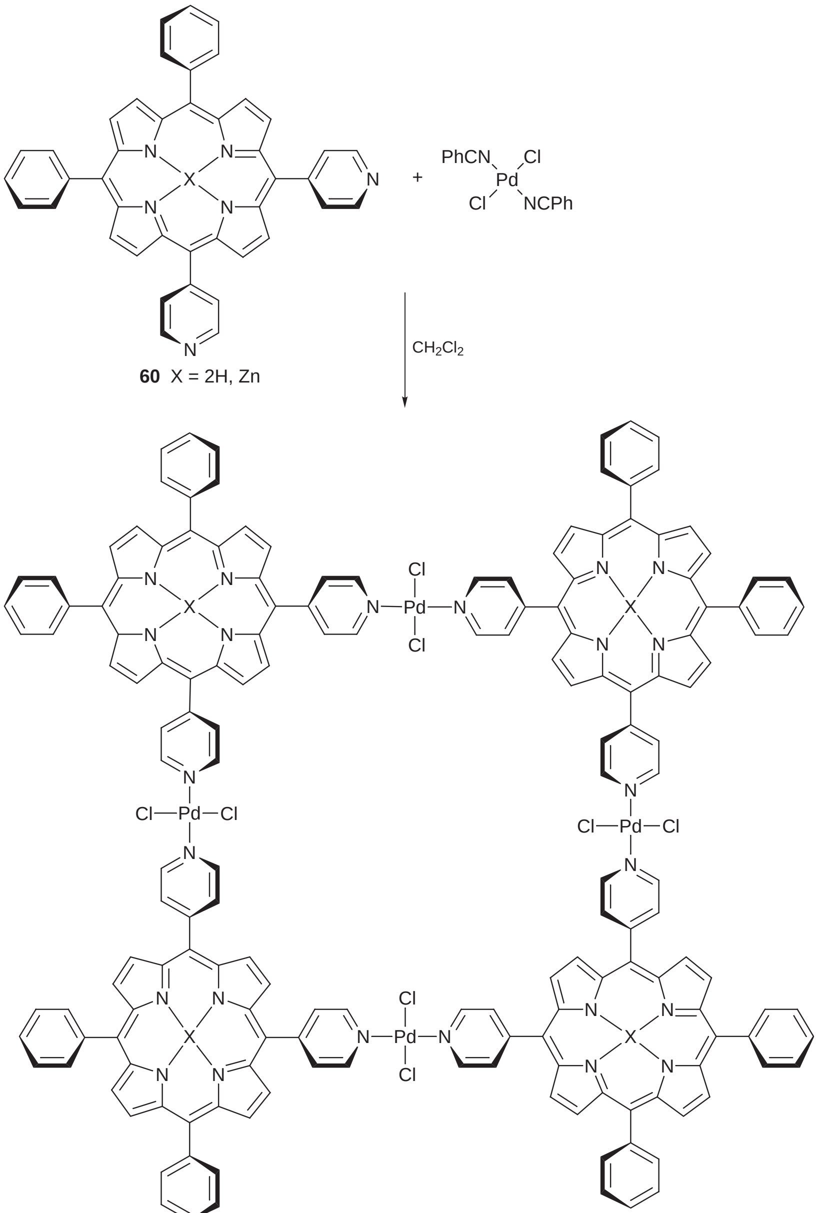
Scheme 9



Scheme 10



Scheme 11



60 X = 2H, Zn

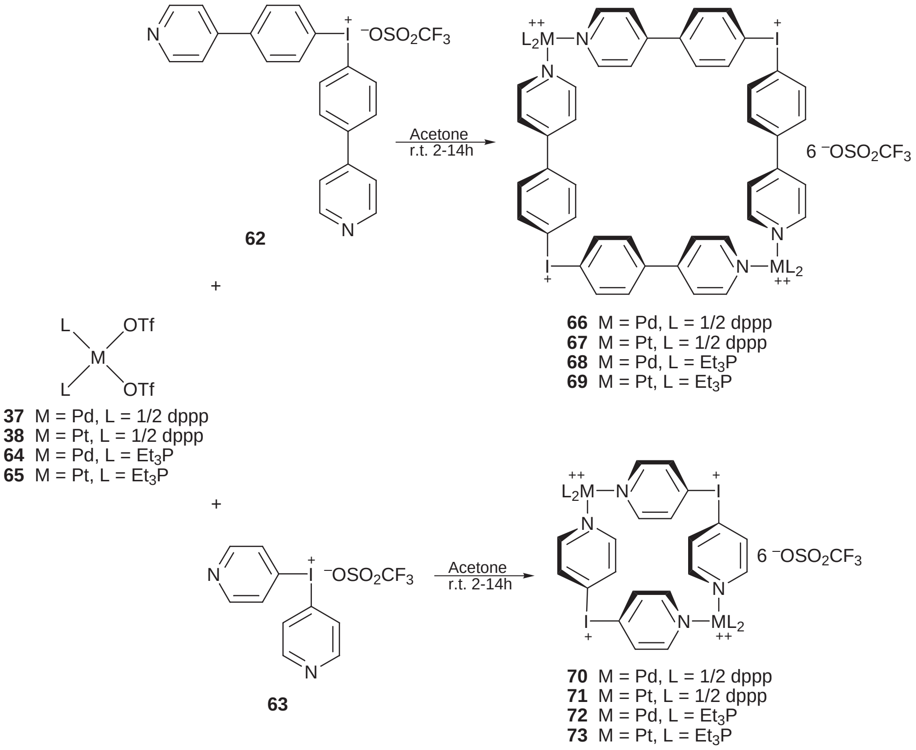
61 X = 2H, Zn

Scheme 12

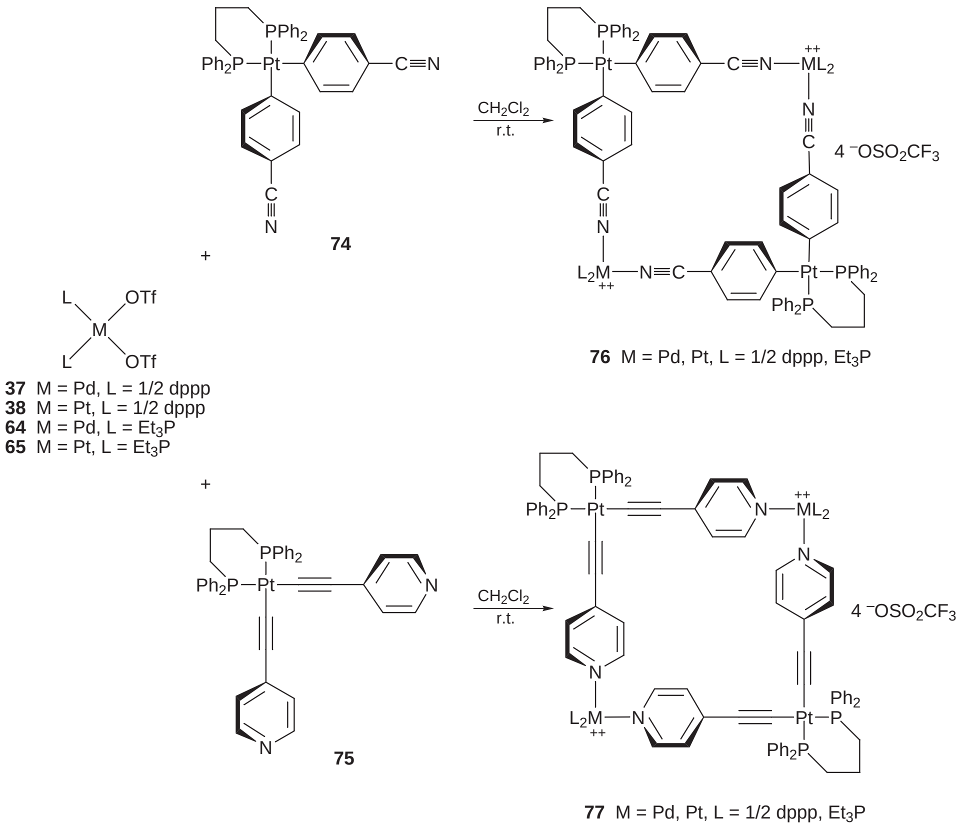
approach utilized 5,10-bis(4′-pyridyl)porphyrins **60** as the angular building block and *trans*-[Pd(PhCN)$_2$Cl$_2$] as the linear linking subunit in the preparation of square **61** (Scheme 12). Both the original squares and their zinc porphyrin complexes were studied by UV/VIS, NMR spectroscopy and mass spectrometry.[23] The luminescence studies, including the fluorescence polarization spectra of these assemblies, confirmed that the electronic interactions in these molecules are greater than those in just the porphyrin subunits or simple porphyrin dimers. The photochemical properties of these assemblies may prove to be a valuable addition in the arsenal of modern photochemistry and provide insights into the structural and physico-chemical properties of some natural photoreceptors.

An interesting type of molecular square can be prepared by utilizing a different strategy: two types of bidentate angular components can be combined in a co-operative manner, resulting in a cyclic polygon. An angular component can be prepared by taking advantage of the T-shaped, pseudo-trigonal bipyramidal geometry of the iodonium moiety with its near 90° angles.[24] The preparation of such iodonium-containing corner units can be easily accomplished in several simple synthetic steps.[25] Since the hypervalent iodine plays the role of one of the 90° turns, only two transition metal centers are present in the resulting square, while two alternating corners are occupied by the hypervalent iodine moiety.[26,27] In the building blocks **62**, **63** (Scheme 13) the lone pairs of the nitrogen atoms are located perpendicular to each other. The interaction of equimolar amounts of these bis(heteroaryl)iodonium triflates with the reactive bis(triflate) complexes of transition metal (Pd^{II} or Pt^{II}) bis(phosphanes) **37**, **38** and **64**, **65** results in the ready formation of the hybrid molecular squares **66**–**73**.[26,27] These assemblies are air-stable microcrystalline solids with high decomposition points. Due to their relatively high polarity, they are soluble in polar organic solvents such as acetone and methanol and only slightly soluble in dichloromethane. The solid state structure of the Et$_3$P–Pd containing square **68** was also confirmed by single-crystal X-ray diffraction studies.[27] As in the case of the previously discussed structure of square **40**, the N–Pd^{II}–N valent angle is less than 90° and is close to 84°, while the C–I–C bond angle opens to 98.7° resulting in the rhomboid shape.

One of the major advantages of modular self-assembly is the ability to vary corner units, and therefore charge density, *via* different oxidation states or transition metals along with the

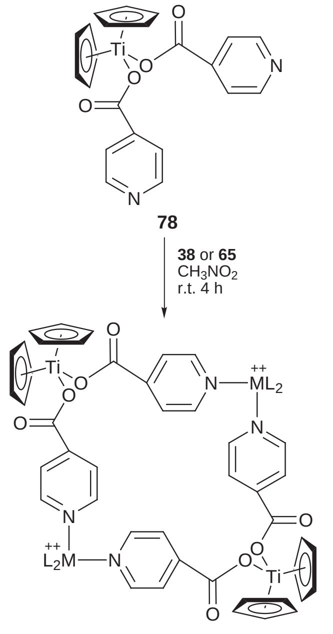


Scheme 13



Scheme 14

cavity size. This feature is quite valuable since it can be fine-tuned by using different connector ligands with the appropriate charge. All these considerations are of importance if the resulting assemblies are to be exploited as possible molecular hosts. The simplest way to prepare mixed neutral–charged or hetero-bimetallic molecular squares is by using the already described palladium(II) and platinum(II) bis(triflate) complexes **37**, **38** and **64**, **65** for the charged portion of the assembly along with specially designed building units which contain the covalently bound and thus neutral, late transition metal bis(phosphane).[28] Reaction of equimolar amounts of these transition metal bis(triflates) in an appropriate solvent with either **74** or **75** (Scheme 14) afforded the mixed heterobimetallic squares **76**, **77** in high isolated yields.[28,29] Mass spectrometry, along with



79 M = Pd, Pt, L = 1/2 dppp, Et$_3$P

Scheme 15

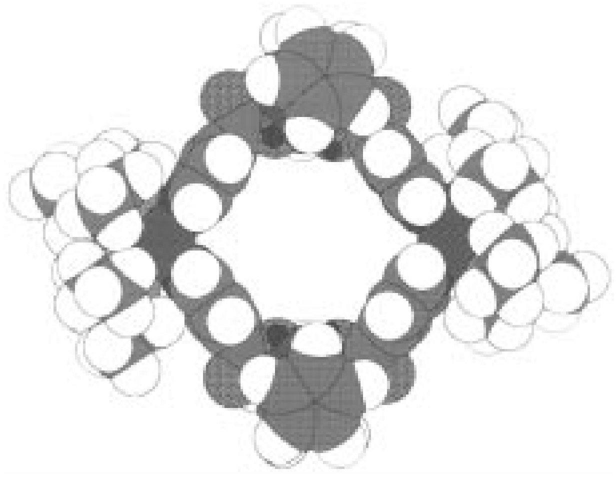
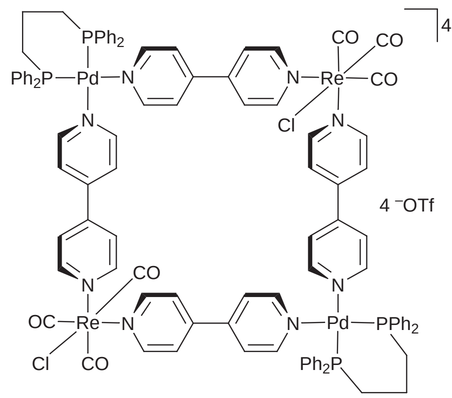


Fig. 4 Space-filling model of molecular square **79** (M = Pd)

other spectroscopic techniques, was successfully used in the characterization of these squares.[30]

Building blocks can be potentially useful if they contain early transition metals, since the incorporation of these metals can allow one further to vary the charge density on each individual subunit as well as the physical dimensions and shapes. Titanocene complexes were chosen as an example of early transition metal modules due to the favorable valent angle between the metal and the attached ligands as well as their rich and versatile chemistry. Interaction of complex **78** with the platinum(II) bis(phosphane) complex **38** or **65** in nitromethane at room temperature for 5 h produced the macrocyclic assemblies **79** (Scheme 15) in excellent yields. Both assemblies were isolated as stable microcrystalline orange solids.[31] They were characterized by a variety of spectroscopic methods, including liquid secondary ion mass spectrometry (LSIMS). These mass spectroscopic data show the doubly charged ion $[M - 2\mathrm{OTf}]^{2+}$ at $m/z = 1002.6$ whose isotope pattern matches the calculated value very closely, thereby confirming the tetranuclear nature of this macrocycle. Unlike all previously discussed assemblies, squares **79** contain relatively flexible oxygen links and are therefore significantly more conformationally flexible. The energy-minimized model of one of these squares is presented in Fig. 4, illustrating the shape and unusual cavity of this interesting macrocyclic assembly. Further examples of modular self-assembly were reported by Hupp and co-workers[32] who prepared the luminescent heterobimetallic molecular square **80**.

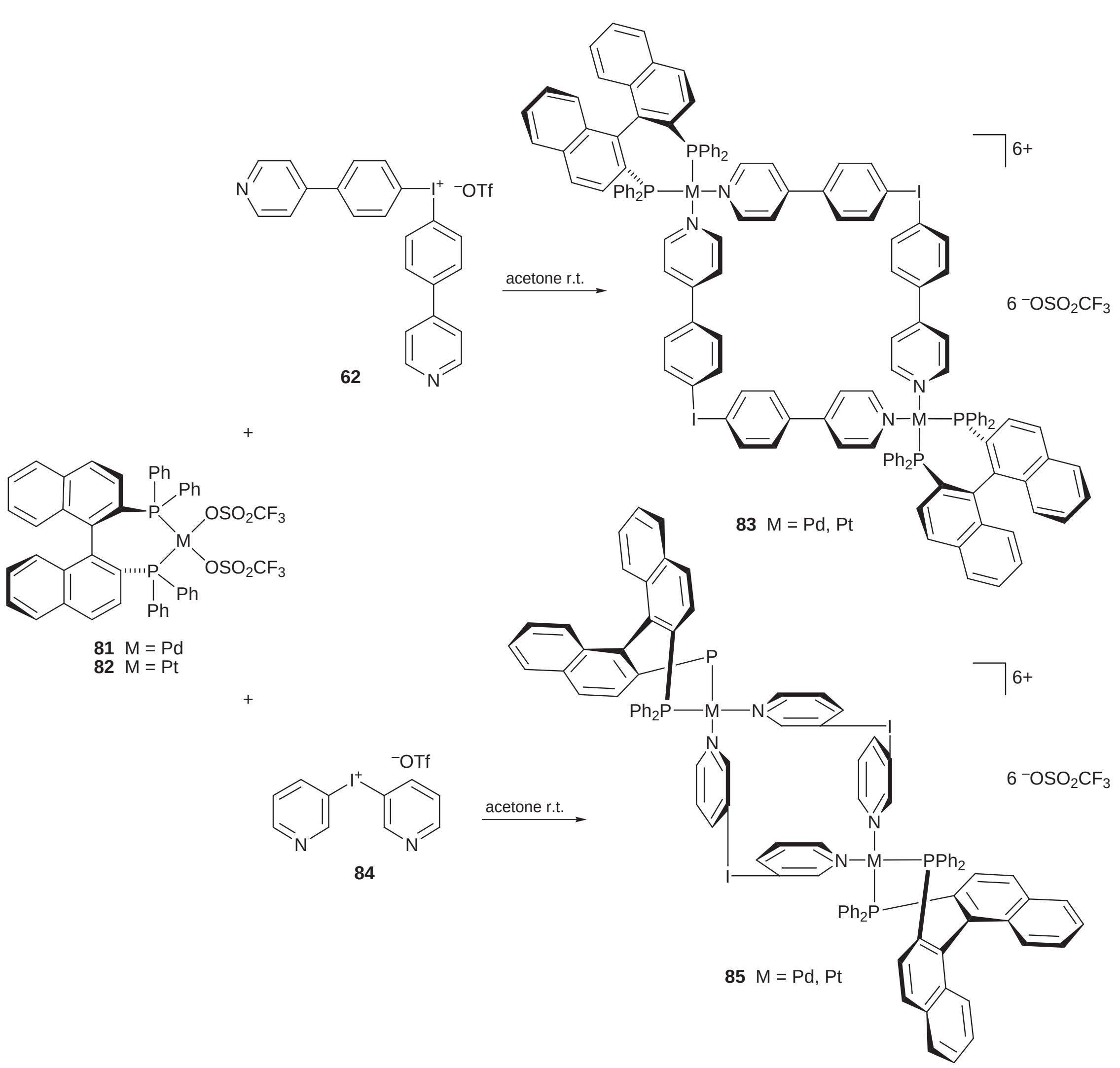


80

Although a variety of naturally occurring biomolecules are chiral and in many instances comprised of a large number of chiral subunits, the understanding of the exact mechanisms of formation of such asymmetric entities is a relatively new field of inquiry. Thus, the design of artificial chiral self-assembled species that mimic some biomolecules represents a formidable challenge. In marked contrast to the chemistry of covalent organic molecules, where asymmetric synthesis may be done routinely, the stereochemical control of non-covalent self-assembly processes is still in its early stages of development.

This task can be addressed by preparing a family of self-assembled, cyclic tetranuclear entities, in which chirality is introduced in several different ways. One possibility is the use of a chiral auxiliary, such as a chiral bis(phosphine), co-ordinated to the transition metal. Another approach can employ diaza-ligands which lack rotation symmetry about their linkage axis, which will result in an overall ‘twist’ of the square, thereby introducing the elements of a cyclic helicate in its assembly. In this situation, however, the formation of several (six for a tetranuclear assembly) stereoisomers is possible. The use of inherently chiral octahedral metal centres is also possible; the separation of the individual enantiomers may be a problem in this case. Finally, very interesting results may be achieved by combining some of the above principles. Thus, a chiral metal auxiliary may be used in conjunction with the elements of helicity or with optically active diaza-ligands, and so on.

Optically active hybrid molecular squares can be prepared *via* the interaction of bis[4-(4′-pyridyl)phenyl]iodonium triflate **62** and [Pd{*R*-(+)-BINAP}(H$_2$O)][OTf]$_2$ **81** or [Pt{*R*-(+)-BINAP}(H$_2$O)][OTf]$_2$ **82** (Scheme 16) [BINAP = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl].[33] In this case, the diaza-ligands of the iodonium species possess rotation symmetry about their linkages and therefore molecular squares **83** are chiral exclusively due to the chiral transition metal auxiliary (BINAP) in the assembly. Another interesting example of chiral hybrid molecular squares was prepared *via* the reaction of bis(3-pyridyl)iodonium triflate **84** and chiral palladium(II) and platinum(II) complexes **81** and **82**. Interaction of a chiral square planar complex of Pd$^{\mathrm{II}}$ or Pt$^{\mathrm{II}}$ with an iodonium precursor where the heterocyclic ring lacks rotation symmetry about its linkages can result in the formation of six diastereomers.[33] However, it was anticipated that the use of a chiral auxiliary such as BINAP would, on self-assembly, reduce the complexity of the stereochemical outcome *via* asymmetric induction. Indeed, when chiral transition metal complexes reacted with bis(3-pyridyl)iodonium triflate in acetone the result was the formation, in excellent isolated yields, of an excess of one of



Scheme 16

each of the preferred diastereomers of assembly **85** (Scheme 16) as assessed by NMR, physical and mass spectrometric data.

The self-assembly of all-metal chiral molecular squares was also carried out using the above-mentioned chiral bis(triflate) complexes of Pd^{II} and Pt^{II} and the C_{2h}-symmetrical diaza-ligands 2,6-diazaanthracene (DAA) **86**, and 2,6-diazaanthracene-9,10-dione (DAAD) **87**.[34] When either **81** or **82** was mixed with DAA in acetone at room temperature, the formation of a single diastereomer of each of the squares **88** was observed (Scheme 17). A space-filling model of the palladium square is presented in Fig. 5. These assemblies, essentially cyclic tetranuclear helicates, possess a large, molecular-size cavity. When DAAD **87** was employed as a connector ligand the reaction mixture consisted of a significant excess of one diastereomeric product, **89**, along with minor amounts of other diastereomers, as demonstrated by ^{31}P NMR spectra. The macrocyclic nature of these species was established by multinuclear NMR and confirmed by mass-spectroscopic data.[34] The interesting fact that both these types of assemblies are formed either as a single diastereomer or a significantly enriched diastereomeric mixture is attributable to a significant degree of asymmetric induction by the chiral bis(phosphane) complexes. In the absence of such induction a mixture of six isomers may be formed.[34] Such a mixture was indeed observed when an achiral transition metal bis(phosphane) complex was used instead of BINAP.[34]

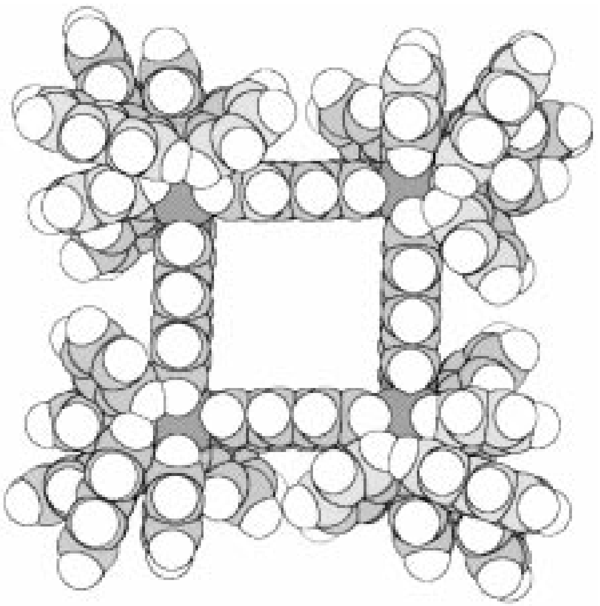
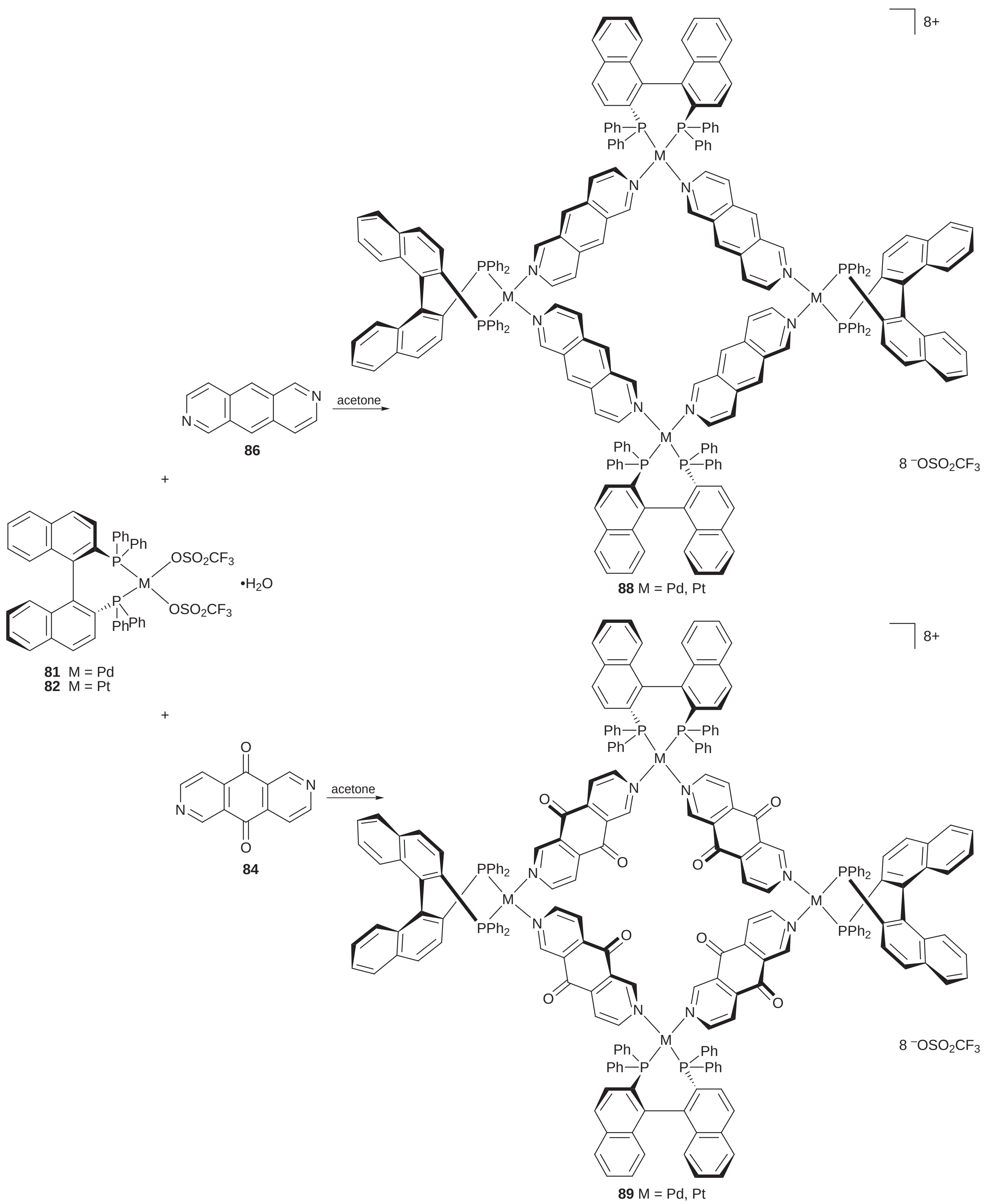


Fig. 5 Molecular model of a chiral square **88** (M = Pd), derived from force-field calculations

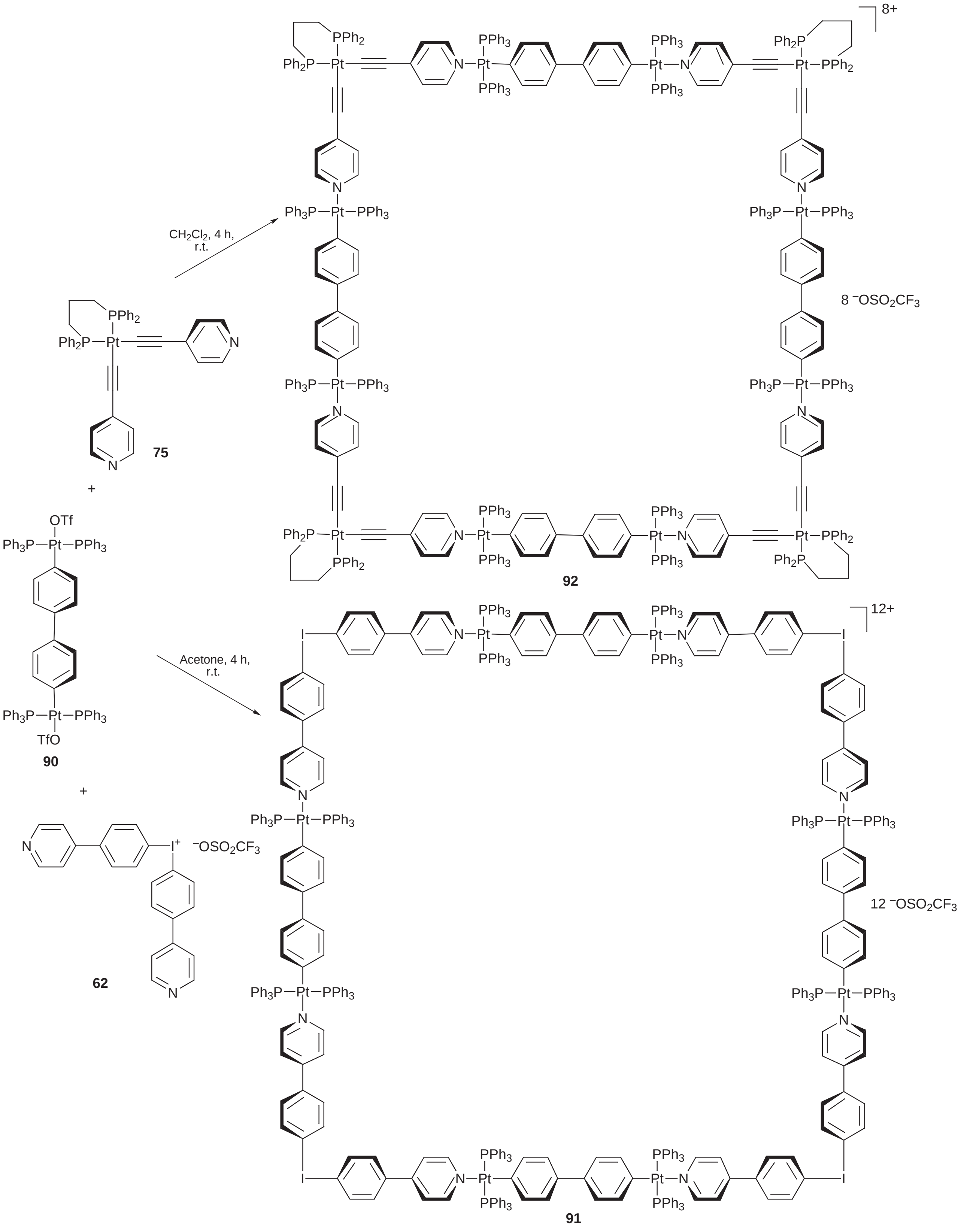
The synthesis of larger organometallic squares was achieved by applying a different self-assembly strategy: the organoplatinum linear linking unit **90** was employed as the sides of the square, while the corners were the already described angular subunits **62** or **75** which possess roughly 90° geometries (Scheme 18).[35] Unit **90** can be prepared from 4,4′-diiodo-



Scheme 17

biphenyl and $[Pt(PPh_3)_4]$ *via* oxidative addition followed by treatment of the resulting product with AgOTf. Self-assembly of both macrocyclic assemblies **91** and **92** was achieved by simply mixing either **62** in acetone or **75** in dichloromethane with **90** (Scheme 18). Both products were isolated in good yields and characterized by a variety of physical and spectroscopic techniques. In addition, the structure of assembly **92** was confirmed both by MALDI (matrix-assisted laser-desorption ionization) and ESI-FTICR (Fourier transform ion cyclotron resonance) mass spectrometric techniques.[35] Both these macrocyclic assemblies belong to the category of ultrafine particles, because of their large size with estimated dimensions of about 3.4 nm along the edge and 4.8 nm across the diagonal for assembly **91** and 3.0 and 4.3 nm for **92**, respectively. In the light of their unique structure, they may become useful in the construction of nanoscale molecular devices.

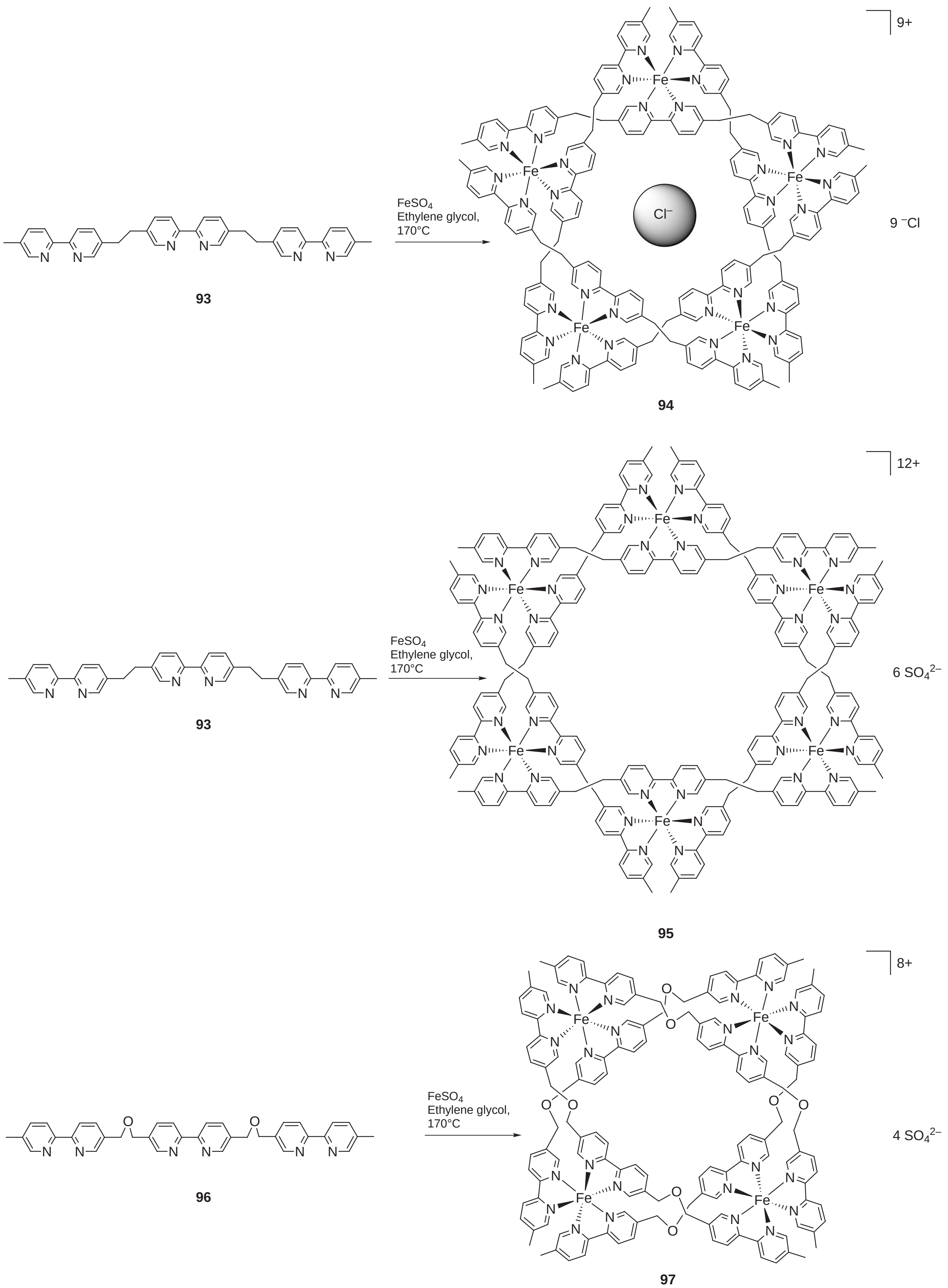
A strikingly different approach was recently developed by Lehn and co-workers.[36] They utilized a template effect to prepare three different types of metallacyclic polygons *via* exactly the same synthetic route. When the tris(2,2′-bipyridine) ligand **93** was added to $FeCl_2$ in ethylene glycol at 170 °C the formation of pentanuclear assembly **94** was detected (Scheme 19).[37]



Scheme 18

When the iron dichloride was replaced with iron sulfate the hexanuclear complex **95** was obtained. It is worth noting that detailed studies of these complexes readily revealed the presence of a chloride ion within the central cavity of the assembly **94**. This ion may ultimately be responsible for the preferred formation of the molecular pentagon in the first reaction.

The replacement of the $(CH_2)_2$ bridge in ligand **93** with the more flexible CH_2OCH_2 had a profound impact on the structure of the resulting assembly. Reaction of **96** with $FeCl_2$ under the above conditions (Scheme 19) resulted in the formation of a tetranuclear assembly **97**.[36] Even when this reaction was repeated with $FeBr_2$, $FeSiF_6$ or $FeSO_4$ it resulted only in the formation of a tetranuclear assembly without even traces of



Scheme 19

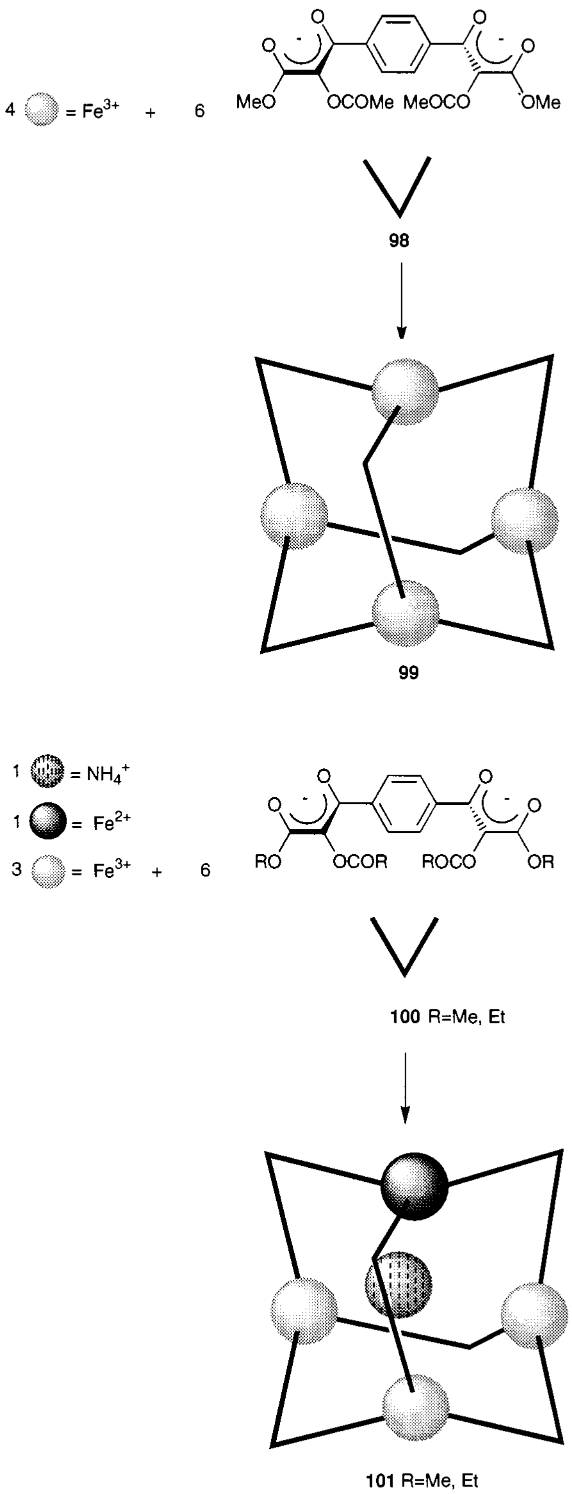
the higher nuclearity metallacycles (Scheme 19). This example demonstrates an interesting and important point: the assembly of a specific architecture results from substrate binding effects, such as interactions with counter ions and ligand-specific features, such as size and flexibility. Some parallels to this can be taken from natural structures, such as proteins. In the case of the latter the self-assembled metallacycle represents a tertiary structure. Each of them is unique in a structural sense, but all share the same secondary structure, *i.e.* co-ordination mode to the iron centers.

5 Three-dimensional Discrete Assemblies: Nanoscopic Polyhedra

If molecular building blocks of various nanostructured materials are to be connected in a three-dimensional fashion, one needs to find rigid three-dimensional molecules which could serve as skeletons, thus providing the core of such nanostructures. Apart from the fact that the overwhelming bulk of molecules are of a flexible chain-like nature, the few rigid and compact cages (cubane, adamantane, dodecahedrane, the norbornanes, and the fullerenes) are very difficult to functionalize in a useful and systematic way as they are extremely inert once synthesized. Their stepwise syntheses often face severe steric problems at one or more steps. Aso, lengthy syntheses and low yields are involved along with the fact that the harsh conditions often employed may be intolerable for many functional groups. Even norbornanes, which are usually assembled in one step by a Diels–Alder cycloaddition reaction, are not totally free from these limitations. Another serious drawback of these organic precursors is their relatively small size. The synthesis of conformationally rigid large cages with multiple functional binding sites by using only the tools of classical synthetic organic chemistry becomes more difficult with the increasing number of carbon atoms in the cage. As any individual molecular building subunit has to be incorporated into the skeleton in a confined, rigid fashion, it usually will have to be attached by at least three bonds. If this building block then provides one additional functional group that will actually appear on its periphery, then in the overall analysis three functional groups have been consumed for the one that has been delivered. If one looks at the totally assembled structure one finds that essentially nothing has been gained in terms of providing more potential functionalization sites which would have been desirable for design and which was the reason why one wanted larger cages in the first place. The functional groups needed for holding together the subunits in the skeleton are lost because usually the atoms in such a bond cannot engage in any further function other than the bond formation itself. Similarly, no additional functionality can be gained by using the sp-hybrid carbons of acetylene, except larger overall dimensions. Hence, the formation of organic, carbon-based nanostructures suffers from the one fundamental unalterable limitation of the carbon atom, its maximum number of valences cannot exceed four. Transition metal-based nanosystems, on the other hand, are free from such limitations because it is relatively easy to find, for each specific task, a suitable metal with a co-ordination number higher than four. Moreover, due to multiple binding sites the resulting cages can be of significantly larger size and can still retain their conformational rigidity.

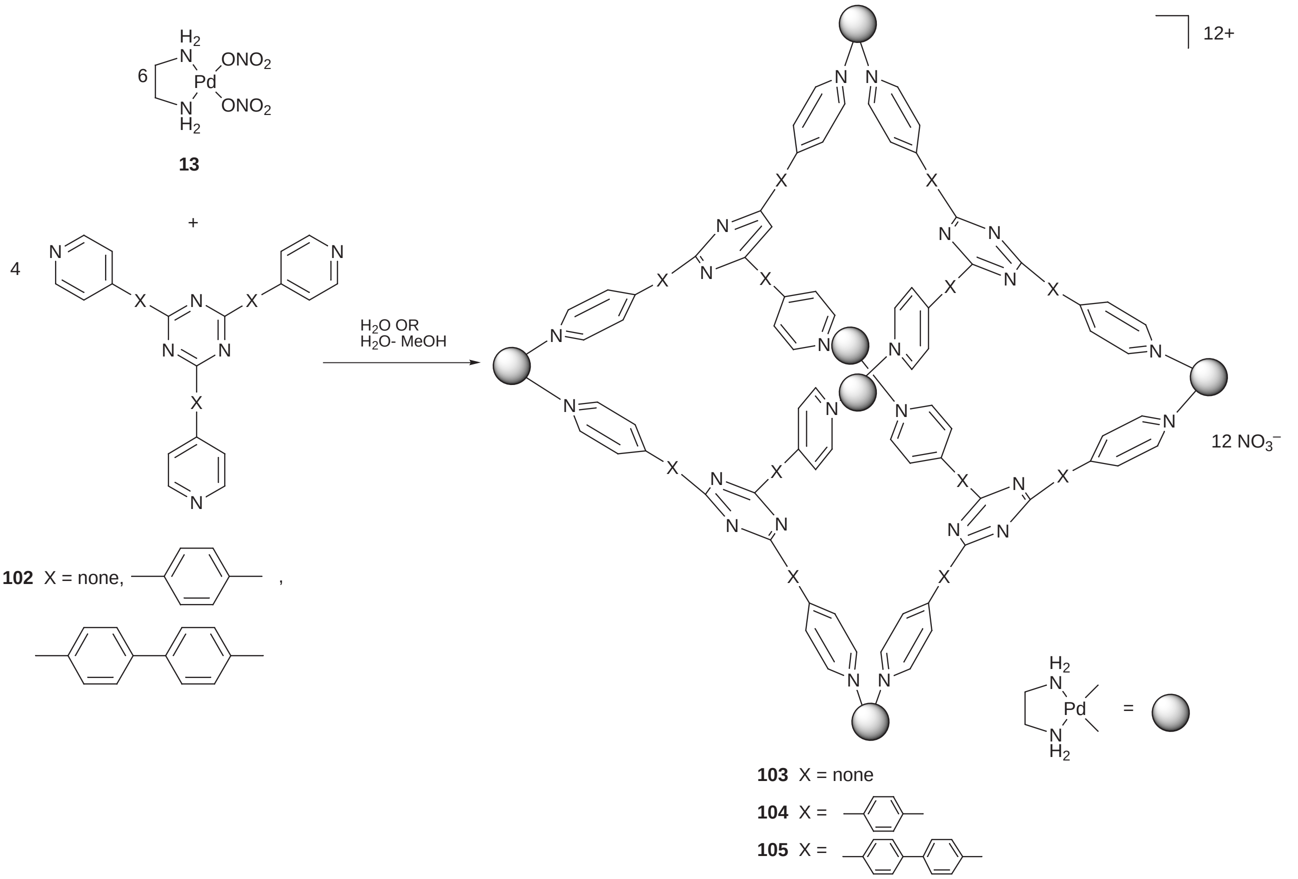
An example of a tetranuclear adamantanoid cage was prepared by Saalfrank *et al.*[38] They used the co-ordination chemistry of trivalent iron complexes that are bound to an anionic ligand **98**. The three-dimensional complex **99** contains four iron atoms interconnected by six anionic subunits in a cyclic manner and has a large, open cavity. Another interesting example involved ligand **100** and mixed-valence iron complexes to prepare cage **101** (Scheme 20).[38] They are formed by self-assembly *via* the reaction of dialkyl malonates with methyllithium and $FeCl_2$ in tetrahydrofuran at low temperatures. Both assemblies are capable of encapsulating ammonium ions, as confirmed by mass spectrometry and X-ray crystallographic studies.[38] The mixed-valence character of both assemblies was also established by studying their Mössbauer spectra and further proven by measurements of cyclic voltammograms. Due to their ability to hold cationic species, these complexes may be found valuable in the design of artificial cages that are capable of encapsulating various alkali metals.

The self-assembly of nanoscopic three-dimensional molecules with the shape of an octahedron was carried out by Fujita *et al.*[39] utilizing ethylenediamine palladium(II) dinitrate



Scheme 20

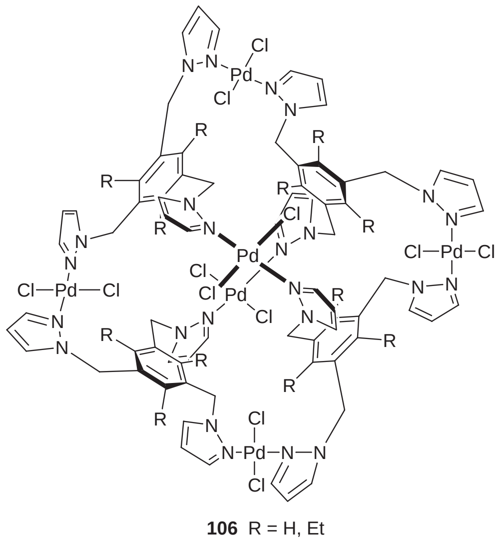
13 in combination with the tridentate aromatic ligands **102**. The near-quantitative yields of assemblies **103**–**105** (Scheme 21) and the high thermodynamic stability of the final products were noted. These assemblies were formed even in the presence of an excess of the transition metal-containing subunit. These water-soluble molecules are capable of encapsulating up to four aliphatic guests of similar symmetry and shape, such as adamantanecarboxylate.[39] The final products were reported to be very stable: when the transition metal complex **13** and the ligand **102** were mixed in a 2 : 1 ratio only the assembly with a 3 : 2 stoichiometry was observed while the excess of free transition metal complex remained intact. The inclusion complex of assembly **103** with adamantanecarboxylate was studied by X-ray crystal-



Scheme 21

lography.[39] Thus, assembly **103** formed a host–guest complex with four molecules of adamantanecarboxylate and no intermediate inclusion complexes with one, two or three guest molecules were observed. This is probably due to allosteric effects: the hydrophobicity of the cavity increases and the complexation between **103** and the guest becomes more effective with increasing number of the guests in the cavity.

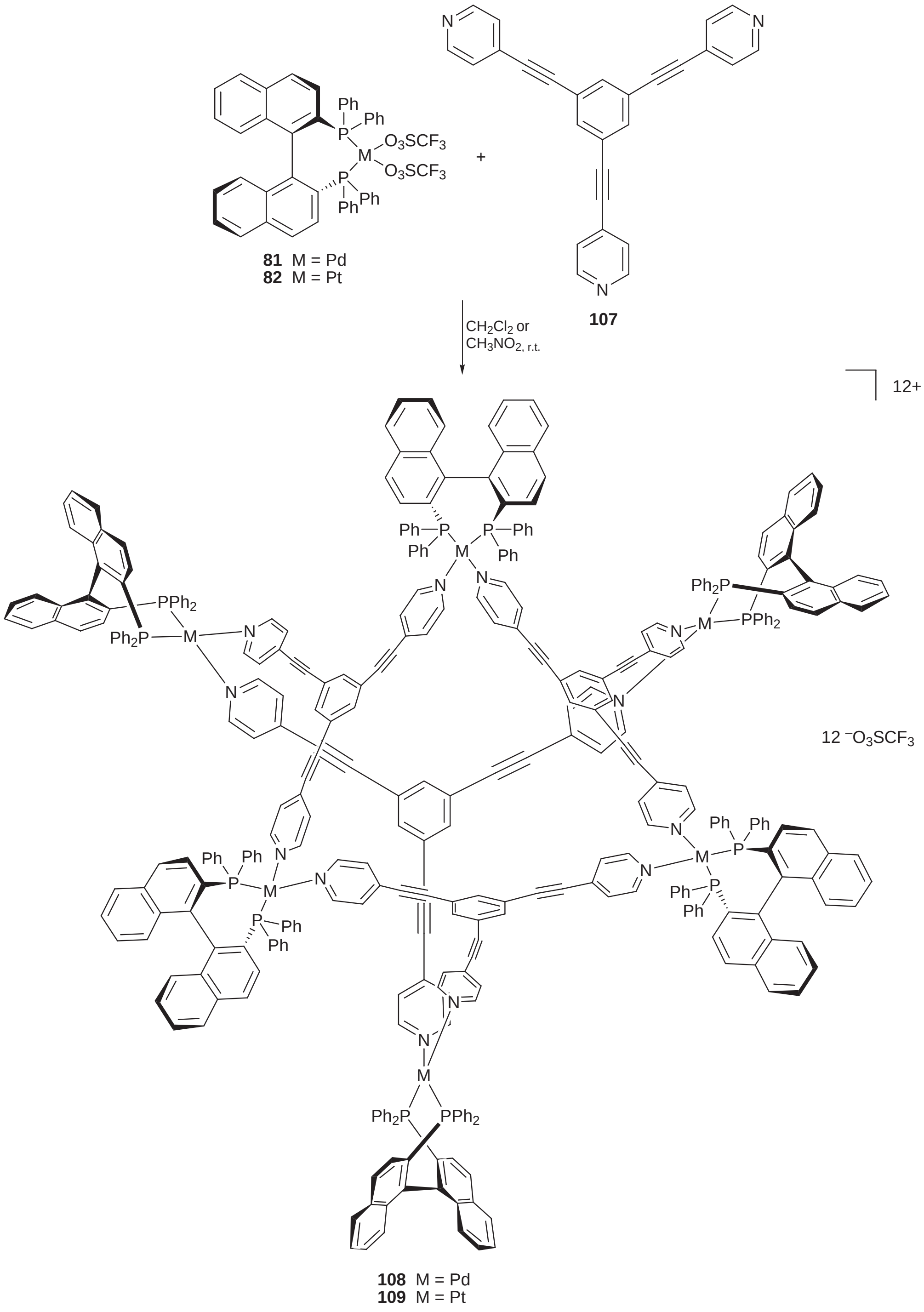
In work reported by Hartshorn and Steel[40] a topologically similar three-dimensional cage **106** was prepared by utilizing the co-ordination chemistry of 1,3,5-triethyl-2,4,6-tris(pyrazol-1-ylmethyl)benzene and the square-planar palladium(II) complexes; NMR studies have confirmed the highly symmetrical nature of **106**. Single crystals of this compound were also analysed by X-ray crystallography. This macromolecule possesses a relatively large cavity: the diagonally opposite palladium atoms are separated by 13–15 Å, thus the cavity size is sufficient to encapsulate relatively large guests.



106 R = H, Et

An example of a chiral three-dimensional structure was also recently reported.[41] The previously mentioned *R*-(+)-BINAP bis(triflate) complexes of Pd^{II} **81** and Pt^{II} **82** were chosen as the bidentate angular units. Since BINAP is conformationally rigid the loss of conformational entropy is minimized on binding to the nitrogen-based ligand. Such a ligand, 1,3,5-tris(4′-pyridylethynyl)benzene **107** was prepared from 1,3,5-tris-triethynylbenzene and 4-bromopyridine *via* the Hagihara cross-coupling. The addition of ligand **107** to a dichloromethane solution of the transition metal bis(triflates) resulted in the self-assembly of the highly symmetrical entities **108**, **109** (Scheme 22) with the stoichiometry of the reactants being 3 : 2 as observed by NMR spectroscopy.[41] The stoichiometry of assembly **108** was also firmly established by mass spectrometry: the ESI-FTICR mass spectrum obtained from a dichloromethane solution resolved the peak centered at $m/z = 1768.19$ with an m/z peak spacing of $\frac{1}{4}$ corresponding to the $[M - 4^{-}\mathrm{OTf}]^{4+}$ ion, corresponding to the cyclic assembly with loss of four triflate counter ions. The observed molecular weight and close match of the calculated and observed isotopic distribution patterns of the 4+ charge state (M 7092.76) are in agreement with the theoretical molecular weight of 7092.89 (error = 13 ppm). Since both molecules belong to the *T*-symmetry group, they are the first examples of highly symmetrical, yet chiral three-dimensional macrocyclic cages prepared by using a rational, co-ordination-directed self-assembly strategy.

The construction of a rigid metallacyclic cage from two pre-organized cavitands and four square-planar transition metal bis(triflates) was also reported recently.[42] When specifically designed tetracyanocavitand **110** reacted with bis(triflates) **37**,



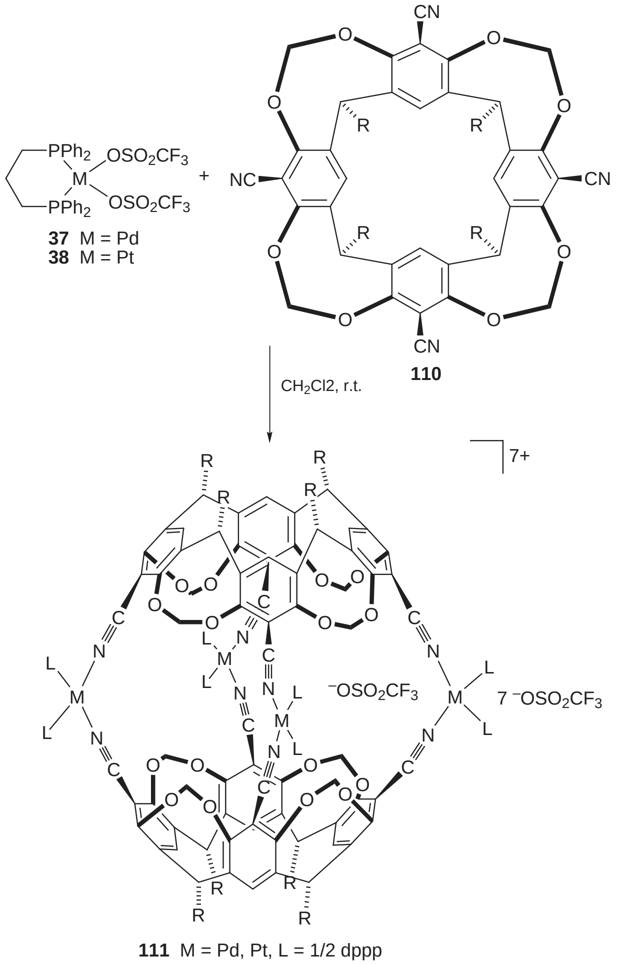
Scheme 22

38 at room temperature they produced rigid dimeric assemblies **111** (Scheme 23). Spectroscopic studies revealed one triflate counter ion being trapped within their rigid three-dimensional cavities.

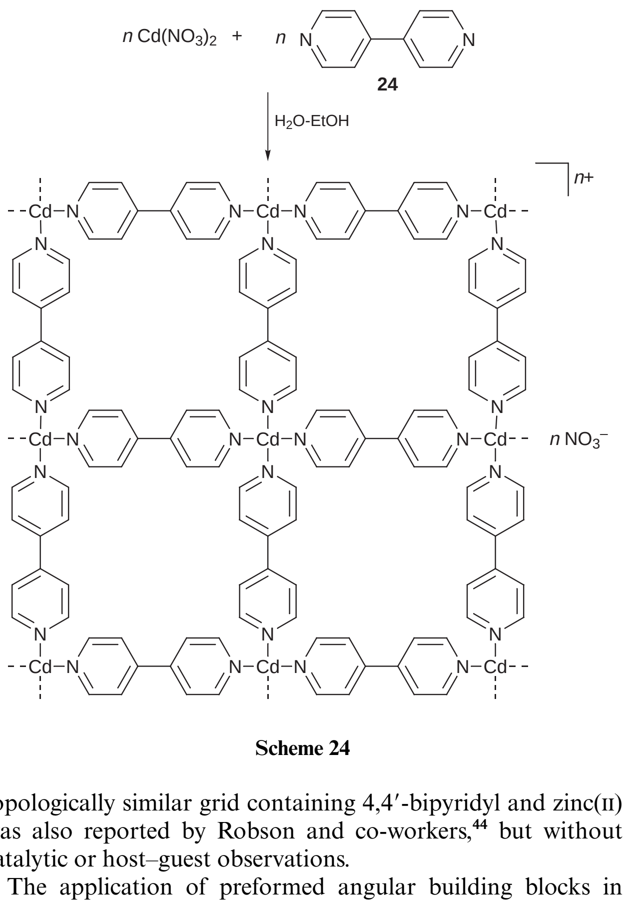
6 Three-dimensional Infinite Assemblies: Nets

The self-assembly of infinite co-ordination networks is of special interest to material science. The materials constructed by utilizing such an approach contain precisely arranged subunits and therefore depending upon the type of subunits and strategy employed, may exhibit interesting optical, magnetic or electronic properties. Construction of such infinite assemblies may be accomplished by applying the experience gained in the preparation of discrete assemblies, if they share the same building blocks.

One example of a molecular grid that contains 4,4′-bipyridine subunits was reported by Fujita *et al.*[43] They used the co-ordination chemistry of divalent cadmium. When two components were mixed in aqueous ethanol solution a two-dimensional grid was formed (Scheme 24). Each metal ion in this structure is surrounded by four 4,4′-bipyridyl molecules; its repeated unit shape and size thus resembles the molecular squares discussed previously. Similar to their discrete parent squares, this grid was shown to encapsulate aromatic guests such as *o*-dibromobenzene with high shape selectivity. Interestingly, unlike the discrete squares, this complex also shows catalytic activity; it accelerated cyanosilylation reactions. A



Scheme 23

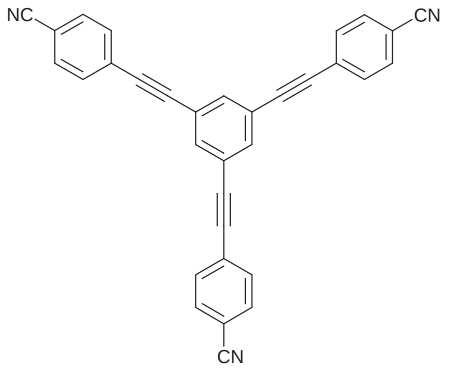


Scheme 24

topologically similar grid containing 4,4′-bipyridyl and zinc(II) was also reported by Robson and co-workers,[44] but without catalytic or host–guest observations.

The application of preformed angular building blocks in combination with cadmium(II) ions to construct infinite self-assembled arrays was also reported.[12] When ligand **15** was mixed in solution with cadmium(II) nitrate it yielded an infinite assembly structurally similar to the discrete assemblies **16** or **19**. This network also demonstrated interesting inclusion properties as was demonstrated by X-ray crystallographic studies of its inclusion complex with *p*-nitroaniline.

Construction of a three-dimensional network using tridentate organic ligands in combination with a silver(I) salt was reported by Moore.[45] These networks have a honeycomb-like structure and utilize a tris(*p*-cyanobenzene)ethynylbenzene linking unit **112** co-ordinated to Ag^I in a triangular planar manner. The two other co-ordination sites of silver are occupied by the triflate counter ions. This network was capable of encapsulating benzene and some other small molecules within its porous structure.[45] The crystals of such assemblies may also exhibit auxetic properties, such as a negative coefficient of thermal expansion, due to the nearly barrierless transition from one type of crystal ordering (honeycomb) into another (flat hexagonal).



112

7 Outlook

As discussed in this article, the molecular architecture paradigm allows the creation of a remarkable variety of artificial self-assembling systems of different shapes and sizes. This self-assembly method is very versatile: it allows the ready formation of a great number of discrete supramolecular species with well defined, predesigned shapes and geometries. The most important advantages of this method are its wide applicability and the large and different number of potentially suitable transition metal complexes and multidentate nitrogen-containing ligands that are available as building units. The excellent product yields that are inherent to such self-assembly processes have been observed in many cases. This method also allows the ready control of the polarity of the assembly and hence its solubility properties *via* controlled formation of charged and neutral macrocycles. Its synthetic versatility is in the possible use of covalent macrocycles as subunits in larger assemblies. Overall, it allows the precise control of the shape of the formed assembly *via* simple variations of the dative bond angles of the transition metal or linker units.

The list of novel assemblies that have been presented in this article is by no means exhaustive. The applicability of the transition metal-mediated self-assembly process, employing co-ordination as the motif, allows the manipulation of the macroscopic properties of materials at the nanoscopic level and the creation of future supramolecular species and nanoscale-sized devices with specific, precisely tuned properties, functions and microenvironments.

Today's manufacturing methods are very crude at the molecular level. Casting, grinding and even lithography move atoms in great statistical numbers. In the future, nanotechnology will allow the development of new 'post-lithographic' manufacturing processes which will allow one to, for example, build materials that are molecular in both size and precision and are interconnected in complex and highly specific patterns. It will be able to put together the fundamental building blocks of nature easily, inexpensively and in almost any arrangement that one desires. This will be essential if we are to continue the revolution in material science beyond the next decade, and will also let one fabricate an entire new generation of products that are stronger, lighter, cleaner and more precise.

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