

Supramolecular chemistry and molecular design: Self-assembly of molecular squares

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Abstract: Coordination is used as the motif for the construction of discrete supramolecular species. The formation of a wide variety of molecular squares *via* self-assembly, along with their structure determination, including X-ray molecular structure, is discussed.

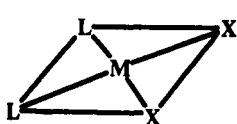
Introduction

Modern supramolecular chemistry has been described as organized polymolecular systems held together by noncovalent interactions and represents one of the major frontiers in the chemical sciences.^{1–5} At present the field is dominated by the hydrogen bonding motif that mimics biological systems and the classical covalent macrocyclics such as crown ethers, cyclophanes, cyclodextrins, calixarenes, etc., that represent the roots of the field.^{6,7} Much less is known about the use of coordination and transition metals as a motif for the assembly of supramolecular species.

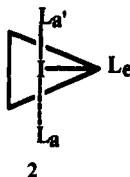
Herein we describe the use of transition metals and coordination as the motif for the construction of discrete supramolecular species with well-defined shapes and geometry. Specifically, we discuss methodology for the preparation of diverse molecular squares *via* self-assembly, along with the characterization, including X-ray molecular structure, of these novel species.

Results and Discussions

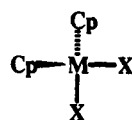
The construction of a square requires the ability to engineer 90° turns. Hence, the self-assembly of molecular squares needs but two building blocks: (a) units that provide approximately 90° and provide the corners and hence shape and (b) units that connect the 90° corners. Building blocks that provide ~90° angles include the tetracoordinate square planar Ni-triad metals in the cis-geometry **1**, the pseudo-trigonal bipyramidal iodonium species⁸ **2**, as well as distorted tetrahedral systems as exemplified by the metallocenes **3**. As connectors, appropriate bidentate ligands with the proper spacial orientation, such as 4,4'-bipyridine (bipy), 1,4-dicyanobenzene etc. may be employed.



1: M = Pt, Pd
X = OTf, ONO₂
L = Et₃P, 1/2 Ph₂P(CH₂)₃PPh₂



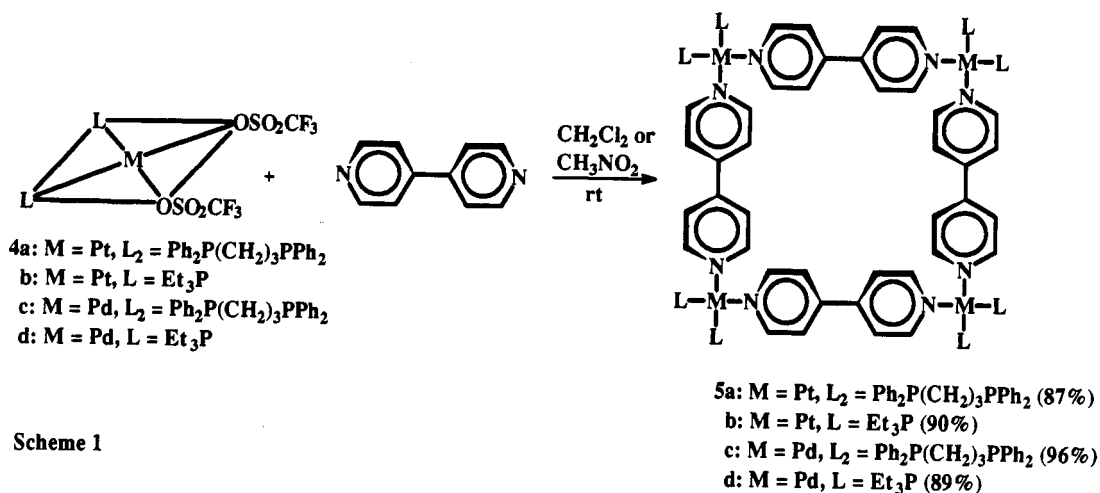
2



3: M = Ti, Zr
X = OTf

Indeed, simple mixing of the cis-Pt and Pd bistriflate complexes **4** with such bidentate ligands as 4,4'-bipyridine,^{2,7} diazapyrene, diazaperylene and dicyanobenzene in solvents such as CH₂Cl₂, CH₃NO₂, and acetone results⁹ in the formation of cationic tetranuclear macrocyclic molecular squares **5** *via* self-assembly, in excellent isolated yields, as illustrated in Scheme 1.

Likewise, simple mixing of **4** with the bisaryliodonium salt **6** in acetone affords¹⁰ the hybrid macrocyclic squares **7** as shown in Scheme 2. The product molecular squares **5** and **7** are remarkably stable microcrystalline solids that are soluble in common organic solvents like CH₂Cl₂, CH₃NO₂, CH₃OH and acetone despite their charges and relatively high molecular weights.



All molecular squares were characterized by spectral and physical means along with X-ray structural data in selected cases.^{9,10} Multinuclear NMR data (¹H, ¹⁹F, ³¹P, ¹³C) as well as elemental analyses results are all consistent with the proposed structures.^{9,10} A particularly characteristic signature for molecular squares is the single, sharp signal in the ³¹P spectrum, consistent with the symmetry requirements of these unique macrocycles. Further proof of structure is provided by Liquid Secondary Ion Mass Spectrometry (LSIMS) and single crystal X-ray molecular structure determination for selected squares.

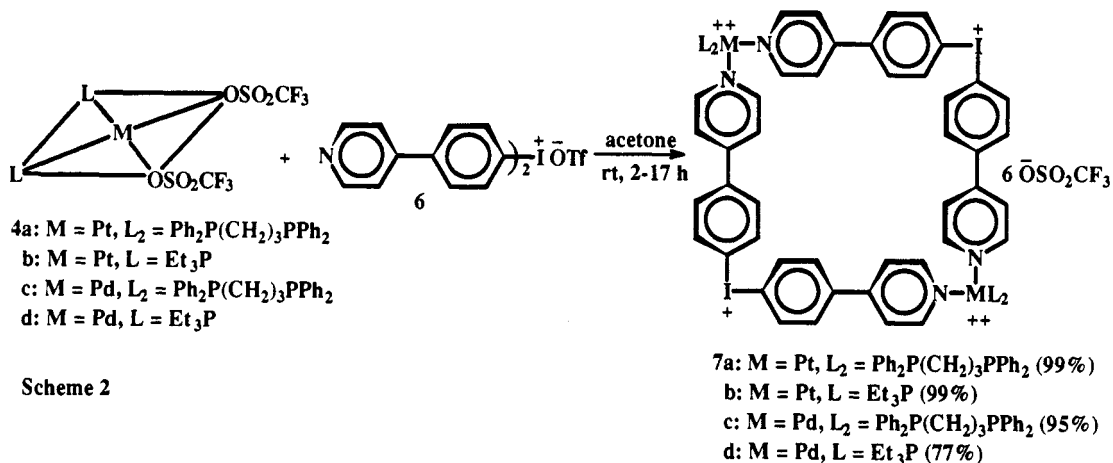


Fig.1 displays selected structural parameters, a space filling model (based upon the X-ray data) and the crystal packing diagram¹⁰ for molecular square 7d. The X-ray data reveal a planar structure with the geometry of a rhomboid. Particularly interesting are the channels and cavity revealed by the stacking diagram, where the cationic units stack 9.5Å on top of each other along the B-axis.

A number of interesting variations on the above theme have also been explored. Interaction of 4 with the neutral, square planar cyanophenyl Pt-complex 8 yields,¹¹ mixed neutral-charged and heterobimetallic molecular squares 9 (Scheme 3). Similarly, reaction of ferrocenyl diaqua complex 10 with the bis-aryliodonium salt 6 affords the hybrid macrocyclic squares 11 that combine ferrocene with molecular squares (Scheme 4).

The structure of 11b was unambiguously established by LSIMS. Fig. 2 displays the calculated (top) and experimental (bottom) isotopic distribution pattern of the (M-OTf)⁺ parent ion of 11b. The close match

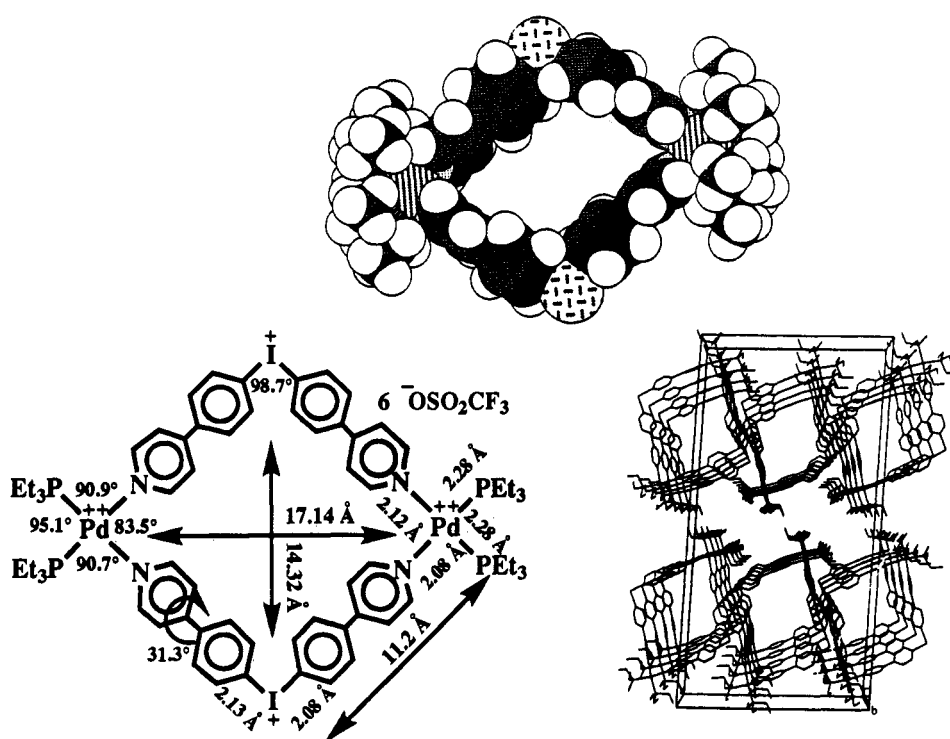
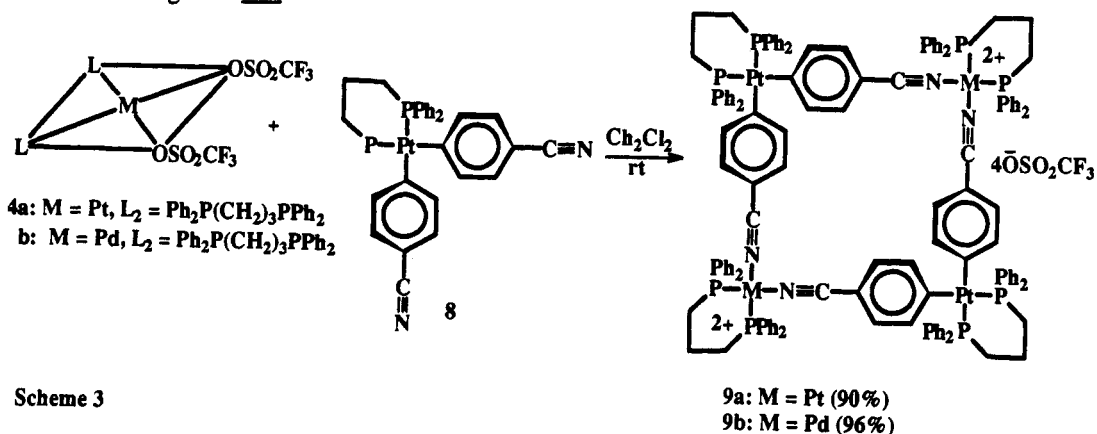


Fig. 1

between the experimental and calculated data leave no doubt about the tetrameric nature and correct molecular weight of **11b**.



Related, but water soluble, molecular squares were obtained by Fujita and coworkers¹² by use of ethylenediamine instead of phosphines as ligands and use of nitrate anions rather than triflates to balance the charges. Fujita's molecular squares and related species were also formed by self-assembly in mixtures of water/ethanol. Rhenium based¹³ as well as W and Cr-based¹⁴ molecular squares have also been reported.

More recently we¹⁵ have combined calixarenes as well as crown ethers with molecular squares that resulted in species analogous to **11** but with crown ethers and calixarenes rather than ferrocene at the edges.

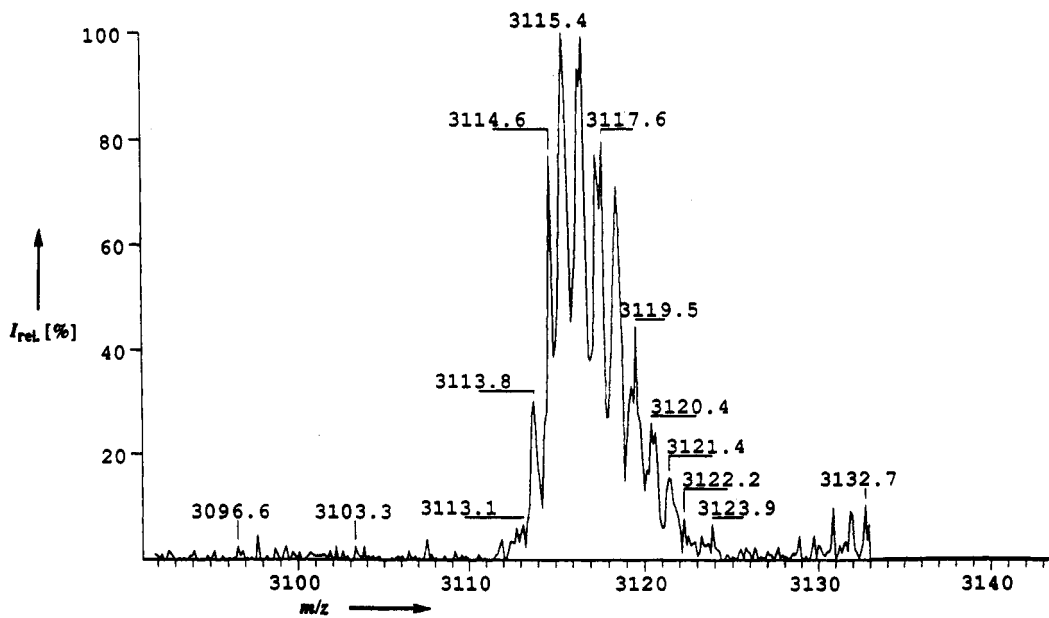
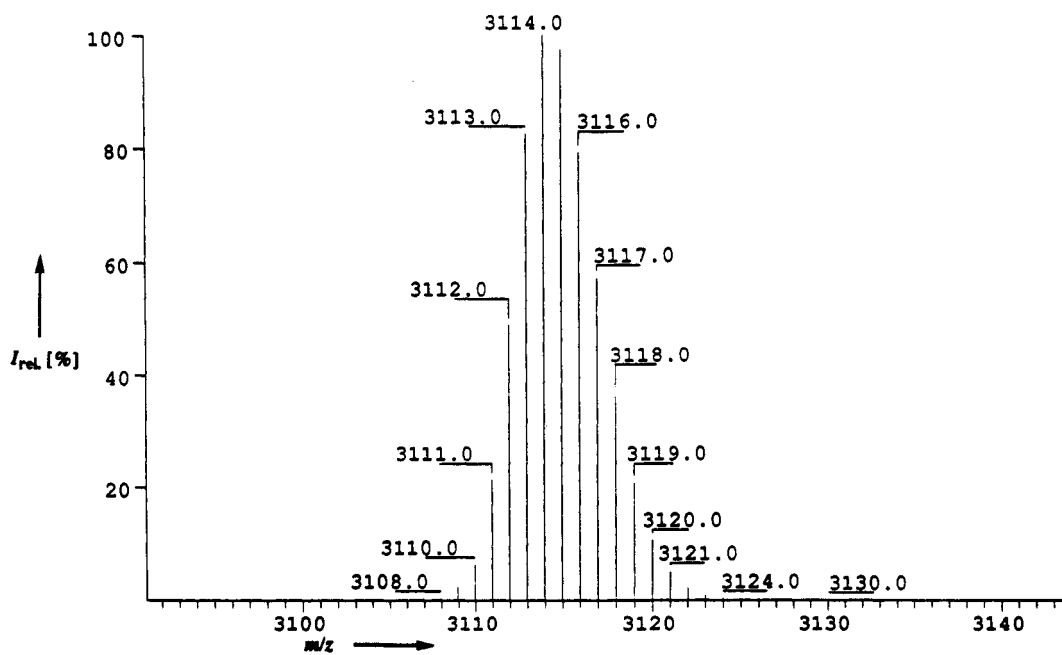
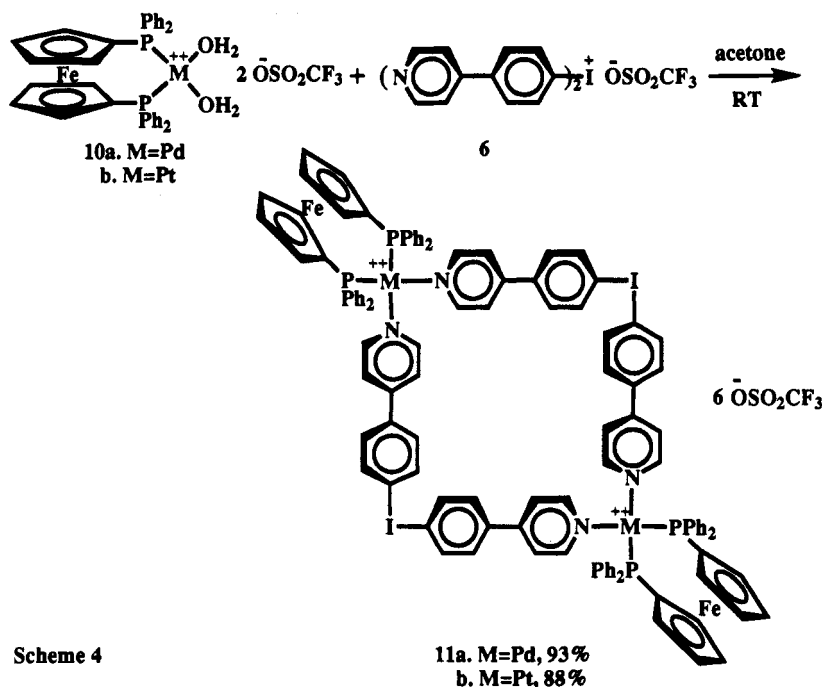
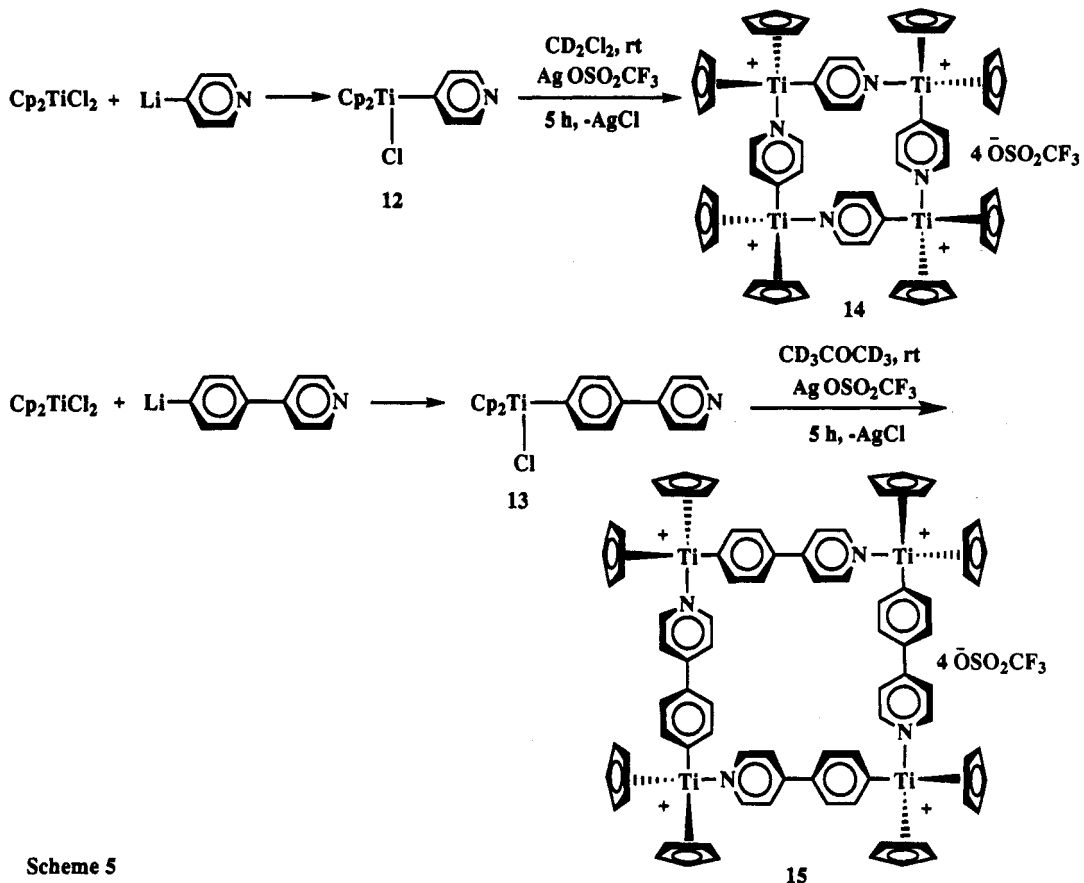


Fig. 2



Scheme 4

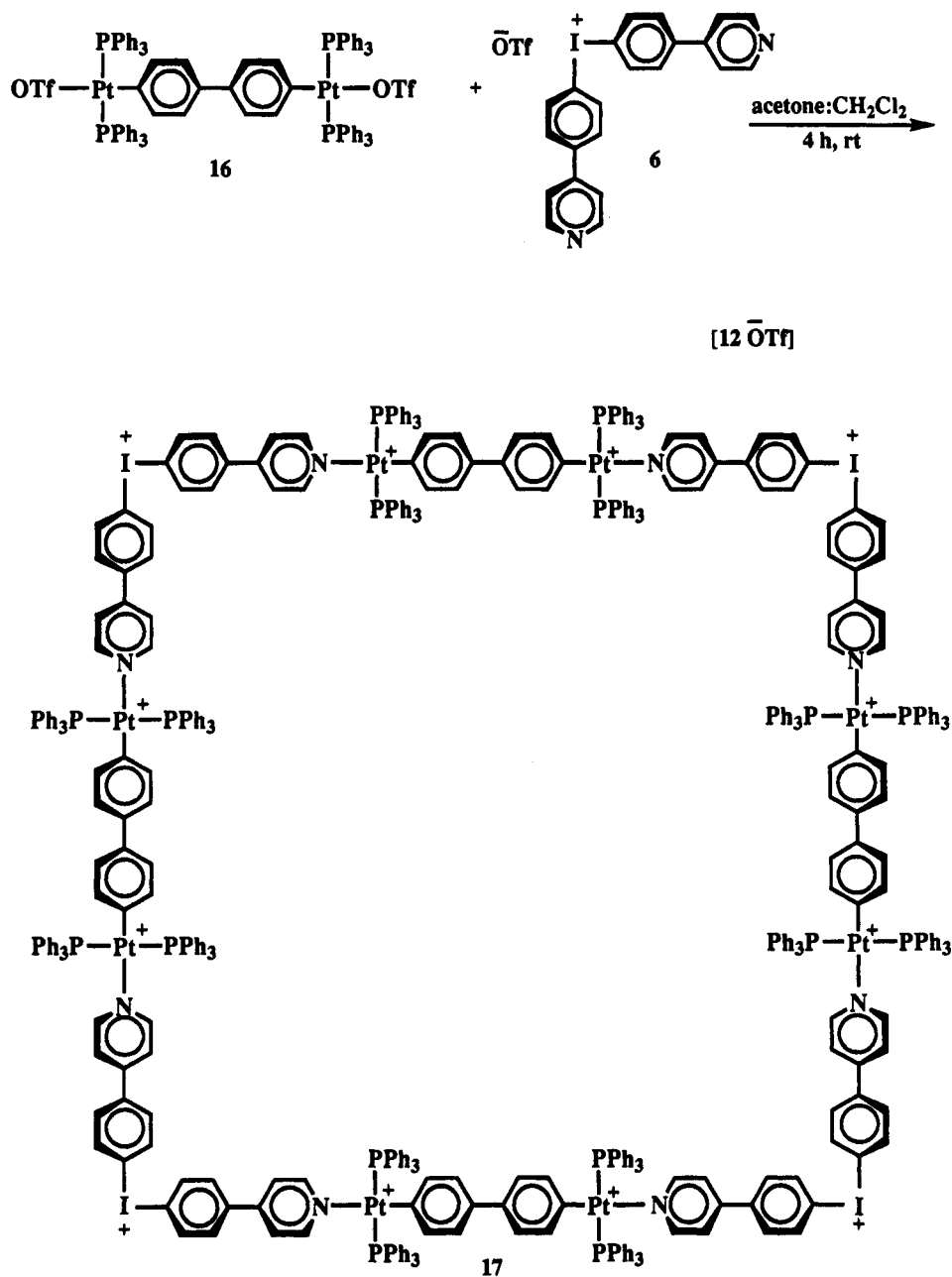
Early transition metal based molecular squares can be obtained by use of titanocene. X-ray structural data established that $\text{Cp}_2\text{Ti}(\text{NC}_4\text{H}_4)_2$ ¹⁶ and $\text{Cp}_2\text{Ti}(\text{OSO}_2\text{CF}_3)_2$ ¹⁷ possess a distorted tetrahedral geometry



Scheme 5

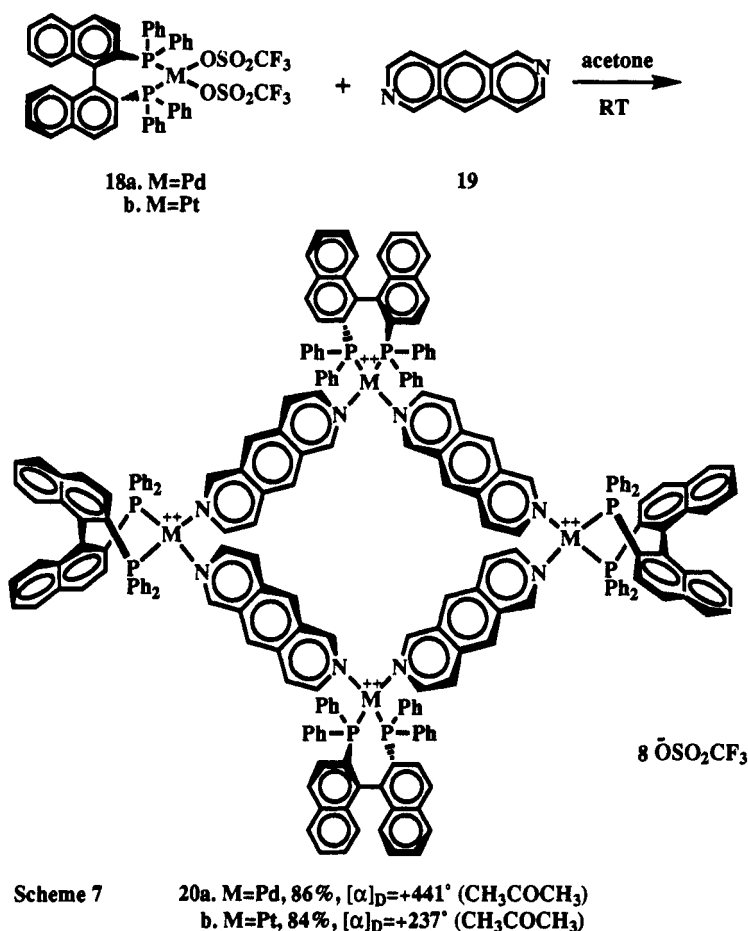
with N-Ti-N and O-Ti-O bond angles of nearly 90° . Hence, we prepared¹⁸ precursors 12 and 13, as shown, and self-assembled the Ti-based macrocyclic molecular squares 14 and 15 (Scheme 5) by interaction with AgOTf in CD_2Cl_2 and acetone. Unfortunately, unlike the late transition metal and hybrid molecular squares that are robust, the Ti-based ones 14 and 15 are very unstable and impossible to isolate pure.¹⁸

Most recently we have been able to prepare both nanoscale¹⁹ as well as chiral²⁰ molecular squares. Interaction of the bis-platinum-bis triflate complex 16 as a linker with the bisaryliodonium species 6 providing the 90° corners afforded¹⁹ the nanoscale molecular square 17 (Scheme 6).



Scheme 6

Reaction of the BINAP complex **18** with 2,6-diazaanthracene **19** gave²⁰ the chiral molecular squares **20** *via* self-assembly (Scheme 7). This last reaction is particularly remarkable as a single diastereomer is formed *via* self-assembly out of a total combinatorial possibility of six diastereomers. Similar results were obtained by using 2,6-diazaanthracene-9,10-dione as a connecting ligand. However, in this case the asymmetric induction gave a diastereomeric excess of only 81% (Pd) and 72% (Pt) of the respective chiral molecular squares. Asymmetric induction by the chiral BINAP auxiliary in **18** and restricted rotation^{20,21} about the M-N chelation bond, along with the noncentrosymmetric connector ligands that provide the element of helicity (twist) in **20** are critical for the formation of these novel chiral molecular species by self-assembly.



Scheme 7

20a. M=Pd, 86%, $[\alpha]_D^{25} = +441^\circ$ (CH_3COCH_3)
b. M=Pt, 84%, $[\alpha]_D^{25} = +237^\circ$ (CH_3COCH_3)

Conclusions

We have developed a remarkable construction kit, based upon coordination and transition metals as the motif, for the ready preparation, *via* self-assembly, of a wide variety of molecular squares with tunable cavity sizes. This field of molecular architecture is only in its infancy. These principles and techniques can be adopted and used for the formation of other molecular assemblies with diverse shapes, such as triangles, rectangles, pentagons and hexagons. Moreover, the principles are applicable to the construction of three dimensional (3D) entities as well as dendrimers *via* self-assembly. Furthermore, the architecture may be enriched by combining the motifs of coordination with hydrogen-bonding. Upon reflection it becomes obvious that with a little imagination almost an infinite variety and type of molecular structures, aggregates etc. may be relatively easily assembled using these concepts and techniques. As a matter of

fact the real challenge in this field is not so much the construction of new and unique molecular assemblies even with great complexity and beauty, but the proper and full characterization of the species obtained by currently available techniques. At present it is not trivial to obtain either accurate molecular weights or X-ray structural data on the more complex species and spectral data often does not allow unambiguous distinction between several possible molecular aggregates formed by self-assembly. The picture is further complicated by both solubility limitations as well as solution dynamics of the more complex (larger, 3D, dendrimeric etc.) species. However, these are challenges not insurmountable obstacles.

Finally, the ultimate long-range goals of this research are the denovo design of new materials with desired properties and functions as well as possible nanoscale assemblies for applications in information storage, nonlinear optics, artificial photosynthetic devices etc. More immediate and practical goals include insight into self-assembly, noncovalent interactions, molecular recognition phenomena, host-guest interactions, potential catalyses etc. Both we⁹ and Fujita¹² have demonstrated host-guest interactions in solution between electron rich guests and all metal cationic macrocyclic squares.

Acknowledgement

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