

Wanda Śliwa

*Pedagogical University, Częstochowa*

## PLATINUM (IV) COMPLEXES OF PYRIDINES AND PLATINUM SUPRAMOLECULAR ASSEMBLIES

**Abstract:** Syntheses and reactivity of platinum (IV) complexes of pyridines and of platinum supramolecular assemblies are presented. In the first part examples of platinum (IV) complexes are described. In the second part molecular squares, so platinum-iodonium as well as all-platinum species are shown, along with examples of dendrimers.

### Introduction

Platinum (IV) complexes and platinum supramolecular assemblies deserve an attention so from the theoretical as practical point of view [1-3]. Pyridines and related compounds form easily complexes with transition metal ions and often serve as ligands. Transition metal directed self-assembly *via* coordination is an important topic in supramolecular chemistry.

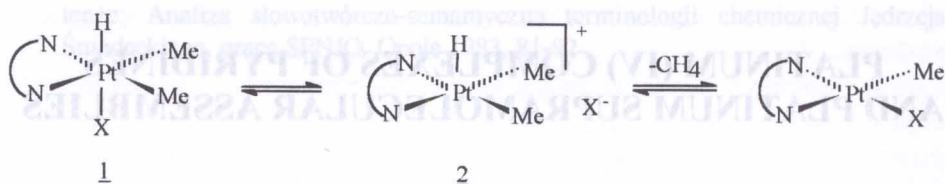
Platinum complexes of pyridines are widely investigated in the aspect of formation of supramolecular structures, host-guest chemistry, molecular recognition and catalysis. The photochromism and chemiluminescence of these species are promising for application in microelectronics; their catalytic properties are useful in biochemistry and biotechnology.

In the review some examples of Pt (IV) complexes of pyridines are presented along with supramolecular assemblies of fascinating shape - molecular squares and dendrimers.

Platinum molecular squares of variable cavities, formed by self - assembly are a subject of many works concerning host-guest interactions and biomimetic investigations. The chemistry of organoplatinum dendrimers is developing intensively, some of them show interesting catalytic properties.

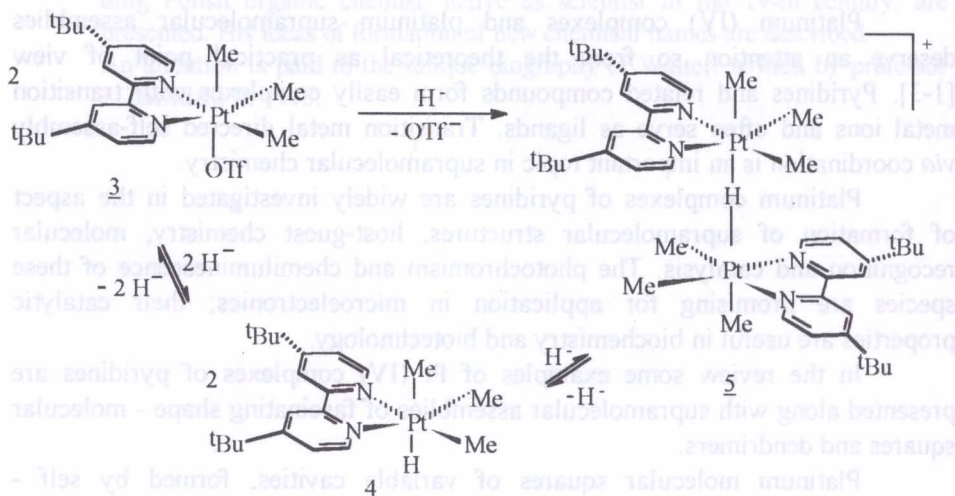
## Platinum(IV) complexes

Numerous platinum (IV) complexes of pyridines are known [4]; as examples may serve methyl (hydrido) platinum(IV) complexes  $[\text{PtHXM}_2\text{NN}]$  1, (where  $X = \text{halo}, \text{TfO}, \text{CF}_3\text{COO}$ , and  $\text{NN}$  = a bidentate nitrogen ligand); these species decompose by the dissociation of the ligand  $X$  *trans* to the hydride to form a five - coordinate intermediate 2 which then undergoes the reductive elimination of methane [5].



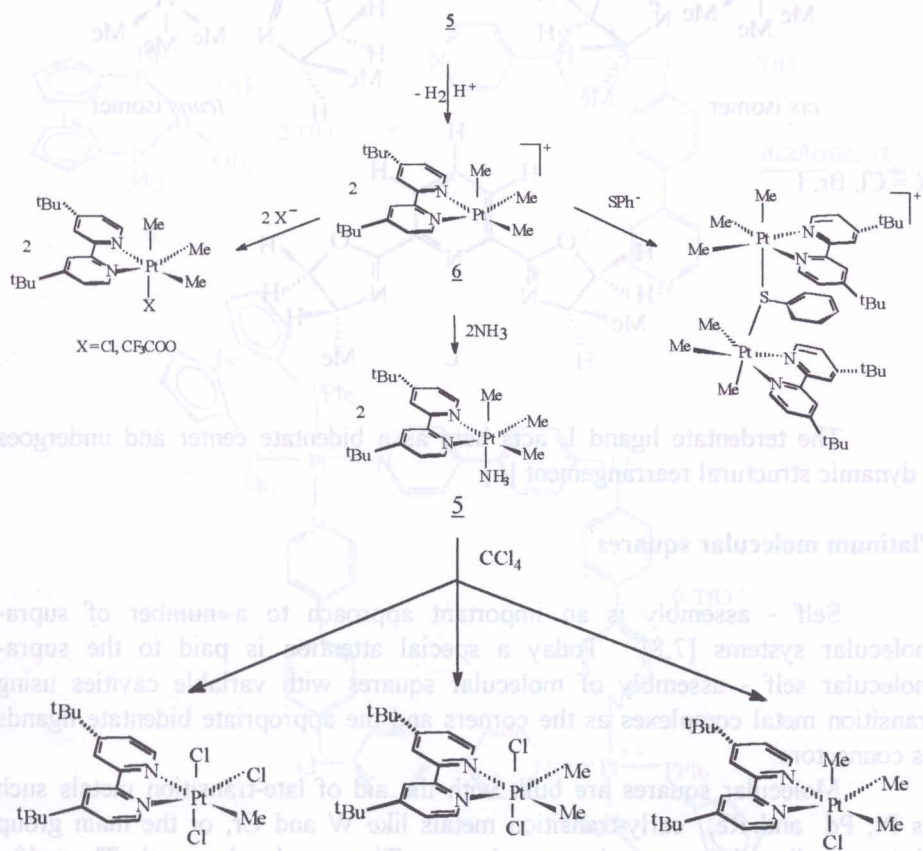
However complexes of the type  $[\text{PtHMe}_3(\text{NN})\text{X}]$  in which the group  $X$  cannot easily dissociate do not undergo the reductive elimination of methane [5].

The reaction of *fac*- $[\text{PtMe}_3(\text{TfO})(\text{bu}_2\text{bpy})]$  3 with  $\text{NaBH}_4$  leading to 4 proceeds *via* the cationic intermediate  $[\text{Pt}_2(\mu\text{-H})\text{Me}_6(\text{bu}_2\text{bpy})_2]^+$  5, the first example of a ( $\mu$ -hydrido) platinum(IV) complex. The complex 5 can be isolated as a  $\text{BPh}_4^-$  salt; it is indefinitely stable at room temperature and is stable in solution in common organic solvents [5].



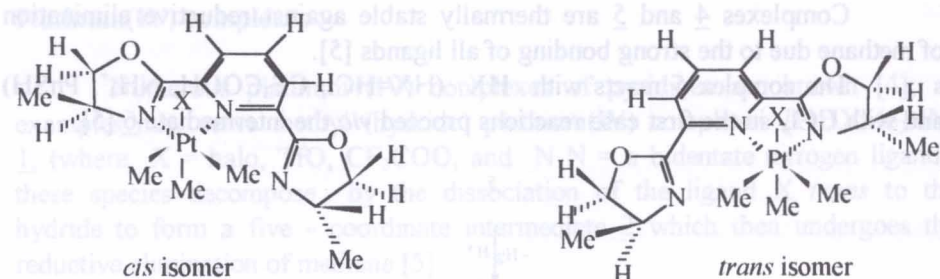
Complexes 4 and 5 are thermally stable against reductive elimination of methane due to the strong bonding of all ligands [5].

The complex 5 reacts with  $HX$  ( $HX=HCl$ ,  $CF_3COOH$ ,  $NH_4^+$ ,  $PhSH$ ) and with  $CCl_4$ ; in the first case reactions proceed *via* the intermediate 6 [5].

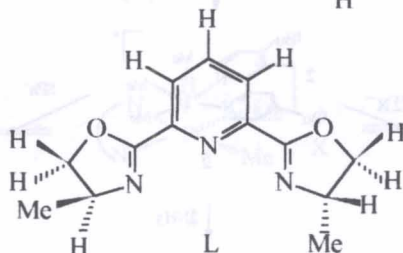


In the investigation of the stereochemistry of „chiral - at - ligand” complexes, following *fac*- $[PtXMe_3L]$  species ( $X=Cl$ ,  $Br$ ,  $I$ ) have been obtained as *cis*- and *trans*-isomers, from halogenotrimethylplatinum(IV) and 2,6-bis[4-(S)-methyloxazolin-2-yl]pyridine *L* [6].





X = Cl, Br, I



The terdentate ligand L acts here as a bidentate center and undergoes a dynamic structural rearrangement [6].

### Platinum molecular squares

Self - assembly is an important approach to a number of supramolecular systems [7,8]. Today a special attention is paid to the supramolecular self - assembly of molecular squares with variable cavities using transition metal complexes as the corners and the appropriate bidentate ligands as connectors.

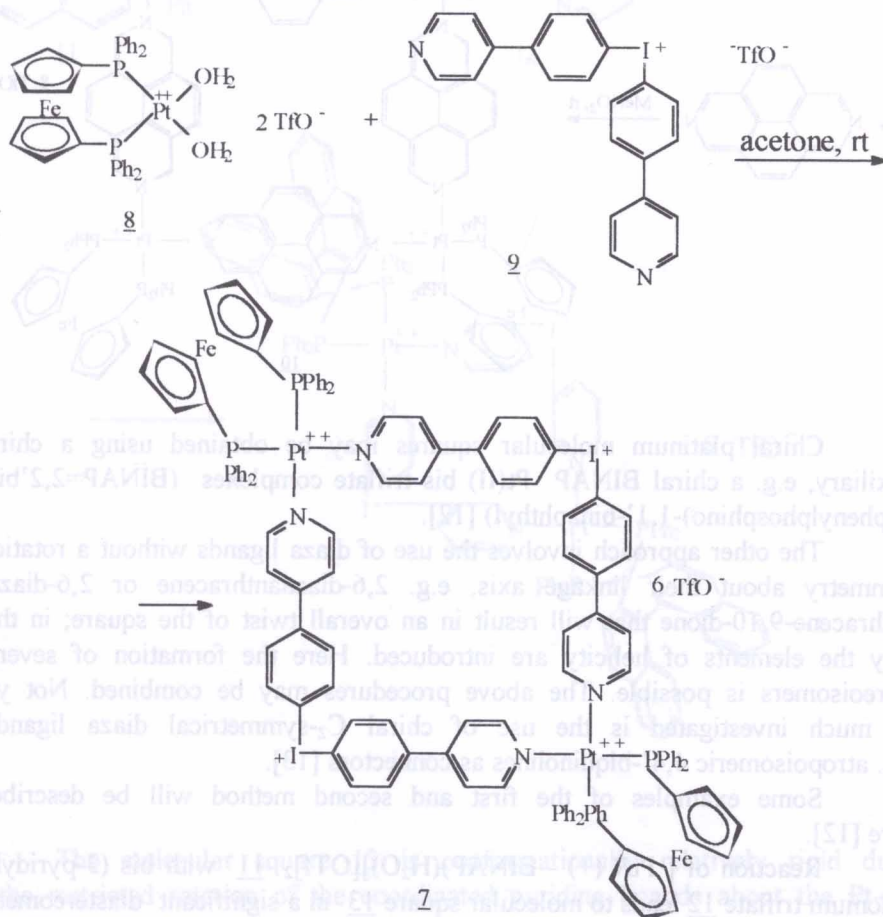
Molecular squares are built with the aid of late-transition metals such as Pt, Pd and Re, early-transition metals like W and Cr, or the main group element iodine; however other metals, e.g. Ti may also be used. The self - assembly of molecular squares mediated by protected, square - planar platinum complexes of pyridines is a topic of numerous works [10].

Two types of platinum molecular squares can be distinguished:

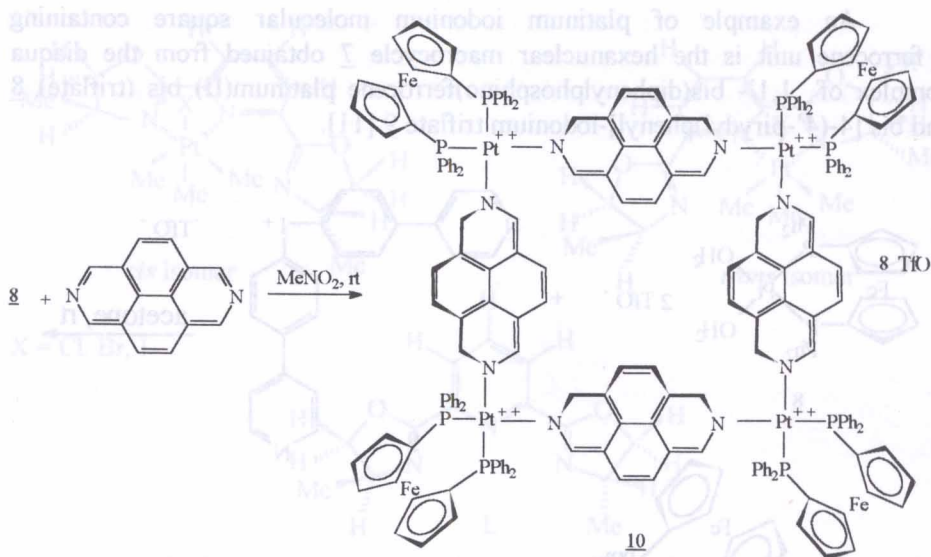
- 1) platinum - iodonium molecular squares, i.e. hybrid systems with alternating platinum and hypervalent iodine at the corners
- 2) all-platinum molecular squares, i.e. tetranuclear platinum systems.

Platinum molecular squares are rigid species of a high air and thermal stability; they are obtained in simple procedures, at room temperature, in excellent yields, due to self - assembly. Having in view the large number of suitable Pt complexes and bidentate ligands and their ready synthesis, platinum molecular squares are very interesting new species promising in the study of host-guest interactions and of their other not yet known behaviour.

An example of platinum iodonium molecular square containing a ferrocene unit is the hexanuclear macrocycle 7 obtained from the diaqua complex of 1,1'-bis(diphenylphosphino)ferrocene platinum(II) bis (triflate) 8 and bis [4-(4'-pyridyl)phenyl]-iodonium triflate 9 [11].



An example of all-platinum molecular square is the octanuclear macrocycle 10 formed in the reaction of 8 with 2,7-diazapyrene [11].



Chiral platinum molecular squares may be obtained using a chiral auxiliary, e.g. a chiral BINAP  $\text{Pt}(\text{II})$  bis triflate complexes (BINAP=2,2'-bis(diphenylphosphino)-1,1'-binaphthyl) [12].

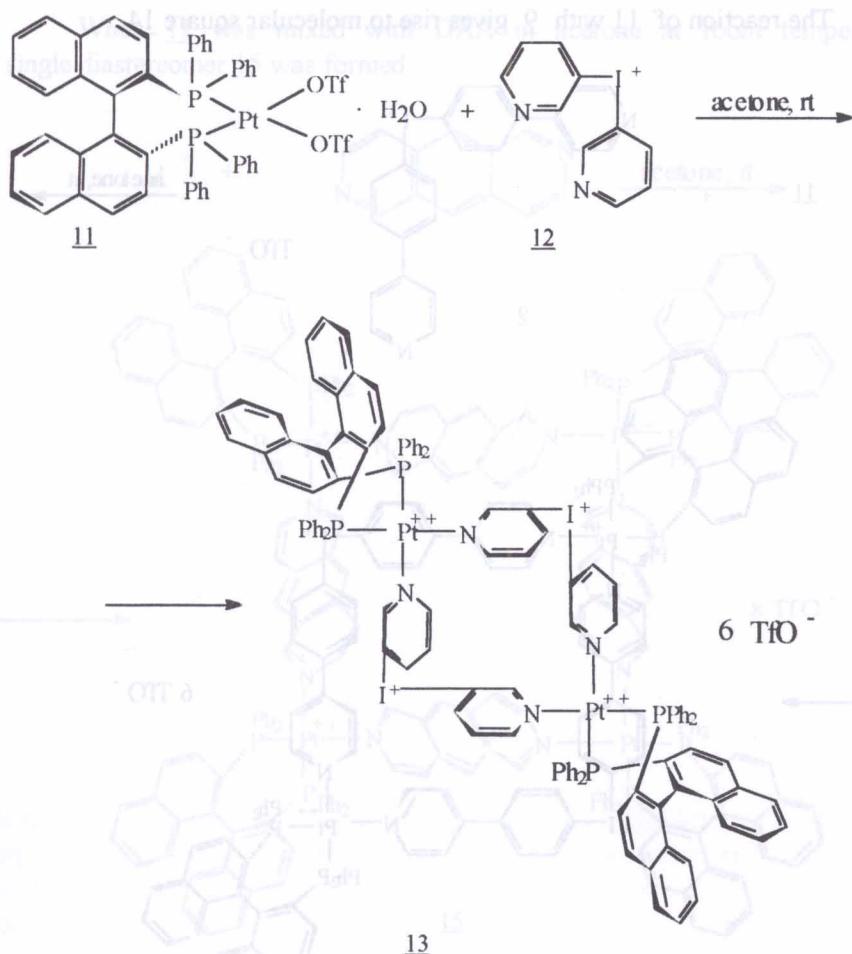
The other approach involves the use of diaza ligands without a rotation symmetry about their linkage axis, e.g. 2,6-diazaanthracene or 2,6-diazaanthracene-9,10-dione that will result in an overall twist of the square; in this way the elements of helicity are introduced. Here the formation of several stereoisomers is possible. The above procedures may be combined. Not yet so much investigated is the use of chiral  $\text{C}_2$ -symmetrical diaza ligands, e.g. atropisomeric 4,4'-biquinolines as connectors [13].

Some examples of the first and second method will be described here [12].

Reaction of  $[\text{PtR}^+(\text{BINAP})(\text{H}_2\text{O})][\text{OTf}]_2$  **11** with bis (3-pyridyl)-iodonium triflate **12** leads to molecular square **13** in a significant diastereomeric excess.

Two types of platinum molecular squares can be distinguished: 1) platinum - ferrocene molecular squares, 2) platinum - diaza molecular squares. An example of all-platinum molecular squares is the macrocyclic 10-formyl-1,1'-bis(2,6-diazaanthracene-9,10-dione) **14** with 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl **15**.

Platinum molecular squares are a rigid species of a square planar geometry. They are obtained by the reaction of a platinum(II) complex with a diaza ligand. Having a large number of suitable Pt complexes and diaza ligands, the synthesis of suitable Pt molecular squares is very interesting. The study of the properties of these complexes is the subject of ongoing research.

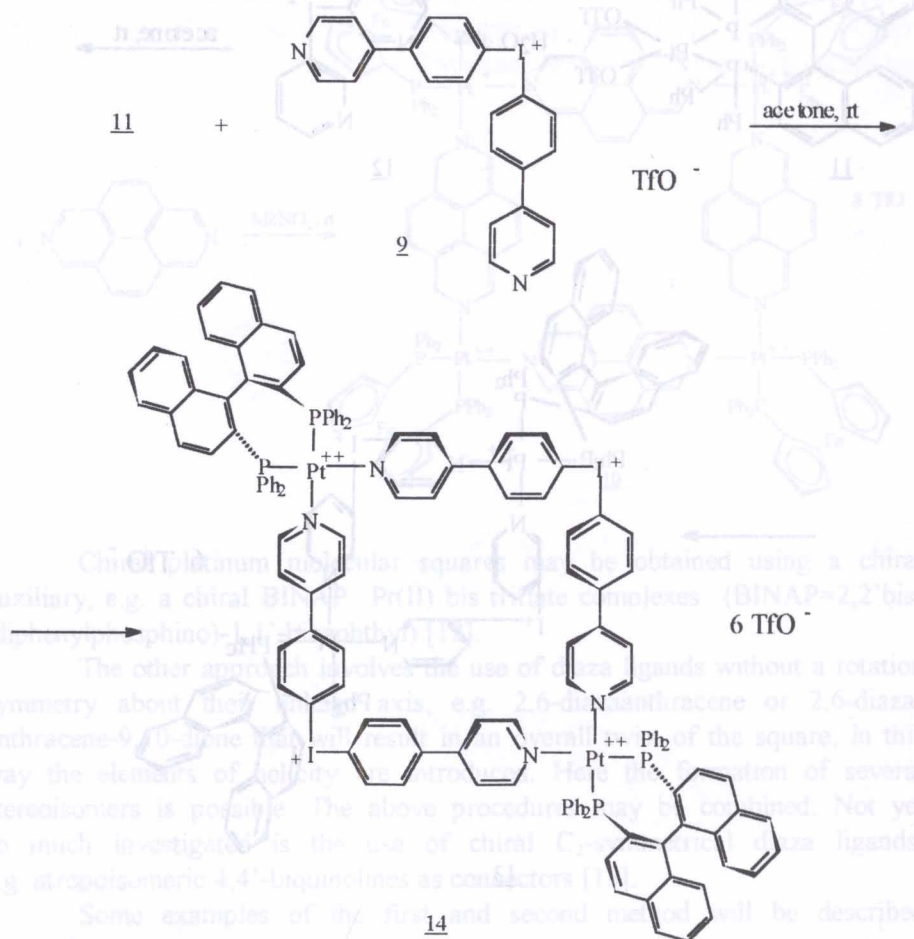


The molecular square **13** is conformationally relatively rigid due to the restricted rotation of the coordinated pyridine ligands about the Pt-N bonds [12].

However, when DAAD was used as a connector ligand, a significant increase in molecular rigidity was observed. Tetranuclear all-platinum molecular squares that are chiral due to the restricted rotation of the coordinated pyridine ligands about the Pt-N bonds [12]. The products are conformationally rigid because of the restricted rotation about the Pt-N bond and the orthogonal situation of ligands to the Pt coordination plane [14].



The reaction of 11 with 9 gives rise to molecular square 14.



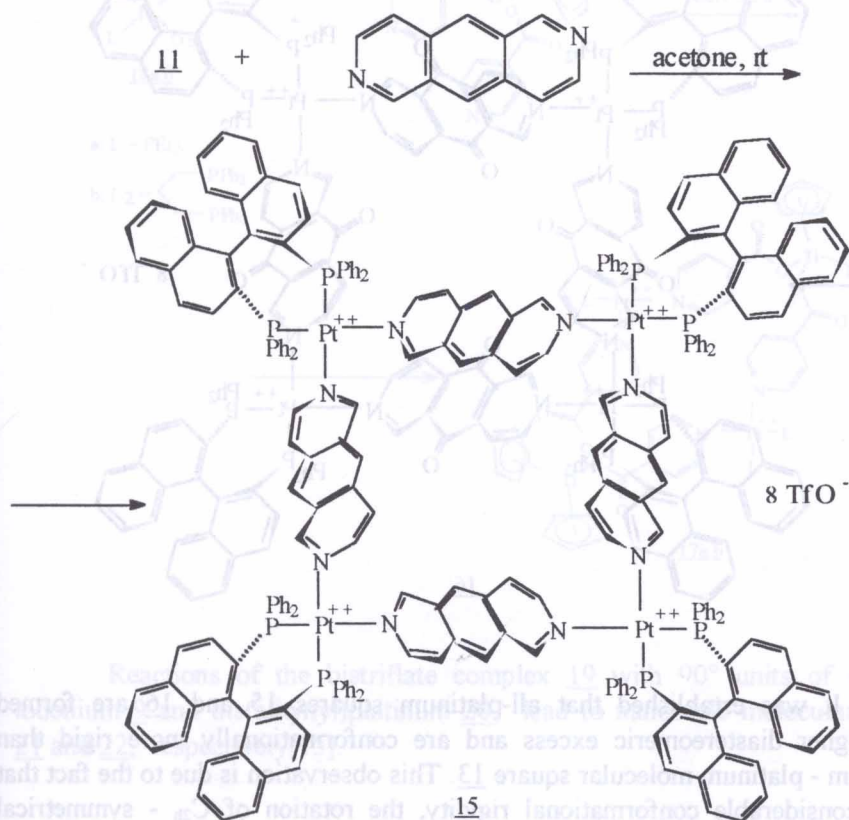
No twists in the assembly occur, since the diaza ligands of 9 have rotation symmetry about their linkages; molecular square 14 is chiral due exclusively to the chiral platinum auxiliary, i.e. BINAP [12].

Tetranuclear all-platinum molecular squares that are chiral due to molecular helicity have been obtained by self - assembly between 11 and achiral bidentate diaza ligands -  $\text{C}_{2h}$  symmetrical 2,6-diazaanthracene (DAA) and 2,6-diazaanthracene-9,10-dione (DAAD).

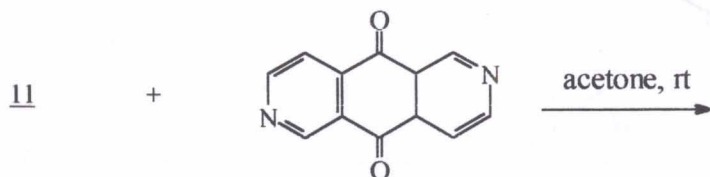
The products are conformationally rigid because of the restricted rotation about the Pt-N bond and the orthogonal situation of ligands to the Pt coordination plane [14].

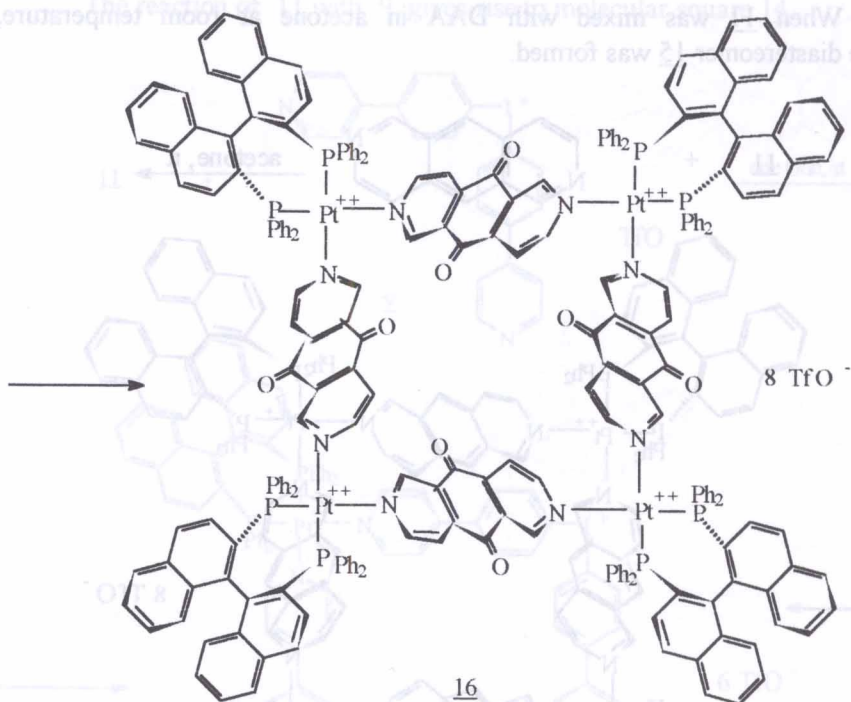


When **11** was mixed with DAA in acetone at room temperature, a single diastereomer **15** was formed.



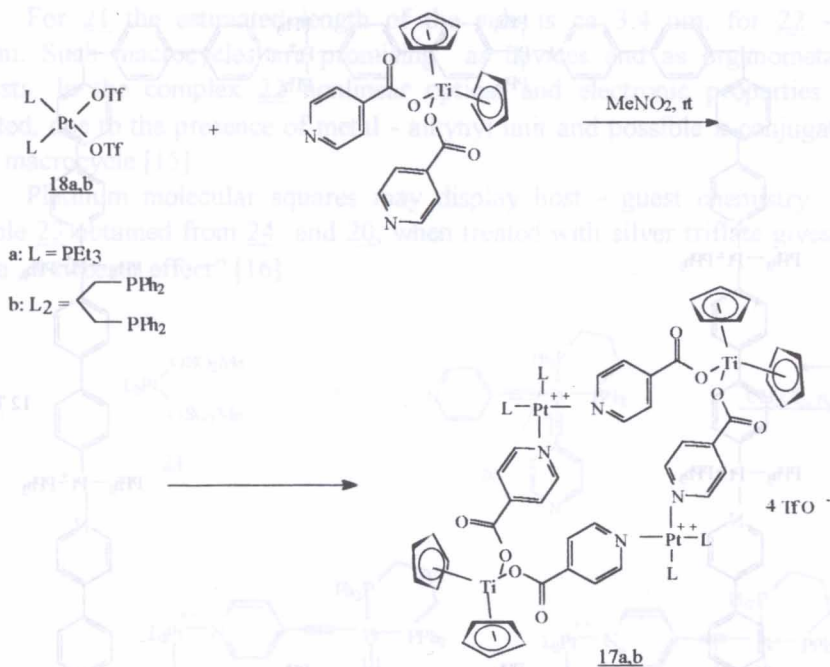
However, when DAAD was used as a connector ligand, a significant excess of one diastereomer of **16** (de=72%) was produced along with minor amounts of other diastereomers. The molecular square **16** is interesting due to the presence of carbonyl groups as useful functionalities [14].



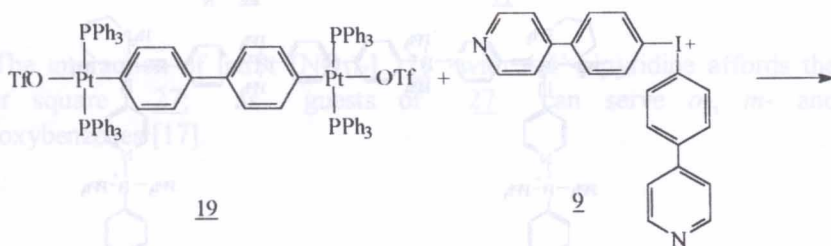


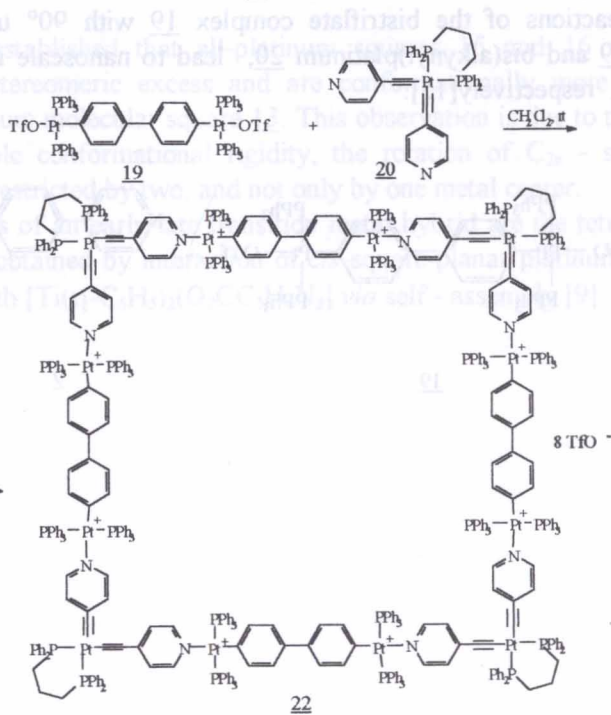
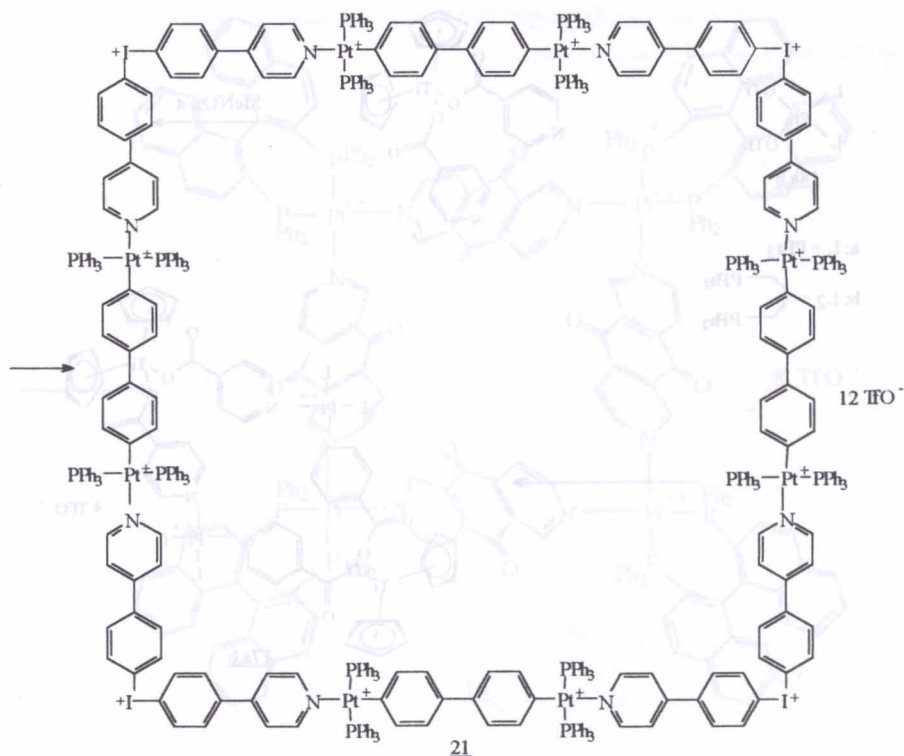
It was established that all-platinum squares 15 and 16 are formed in a higher diastereomeric excess and are conformationally more rigid than iodonium - platinum molecular square 13. This observation is due to the fact that for a considerable conformational rigidity, the rotation of  $C_{2h}$  - symmetrical ligands must be restricted by two, and not only by one metal center.

Examples of an early-late transition metal hybrid are the tetramolecular macrocycles 17 obtained by interaction of *cis*-square-planar platinum bistriflate complexes 18 with  $[Ti(\eta-C_5H_5)_2(O_2CC_5H_4N_2)]$  via self - assembly [9].



Reactions of the bistriflate complex 19 with 90° units of bis(aryl)iodonium 9 and bis(alkynyl)platinum 20, lead to nanoscale molecular squares 21 and 22, respectively[15].

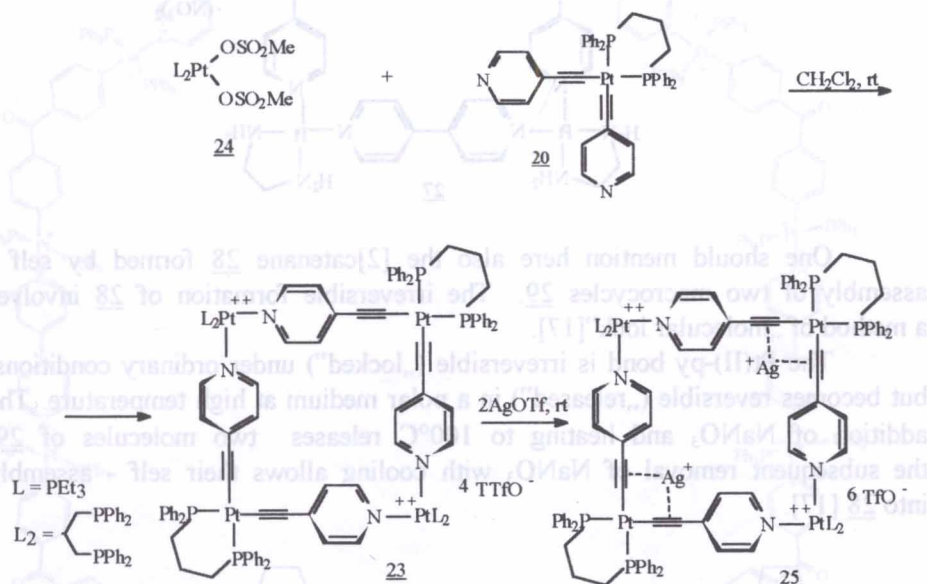






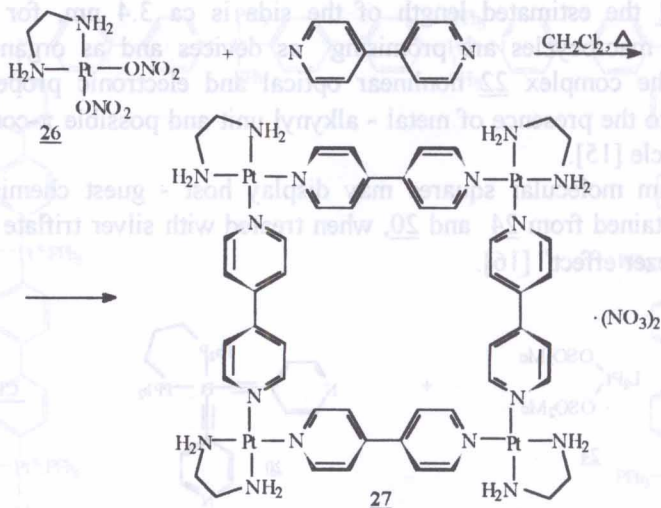
For 21 the estimated length of the side is ca 3.4 nm, for 22 - ca 3.0 nm. Such macrocycles are promising as devices and as organometallic catalysts. In the complex 22 nonlinear optical and electronic properties are expected, due to the presence of metal - alkynyl unit and possible  $\pi$ -conjugation of the macrocycle [15].

Platinum molecular squares may display host - guest chemistry. For example 23 obtained from 24 and 20, when treated with silver triflate gives 25 via the „ $\pi$ -tweezer effect” [16].



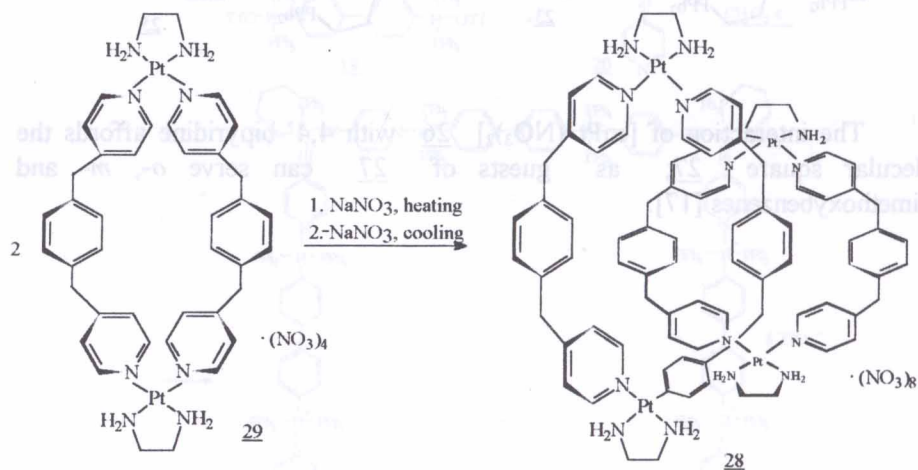
The interaction of  $[enPt(NO_3)_2]$  26 with 4,4'-bipyridine affords the molecular square 27; as guests of 27 can serve *o*-, *m*- and *p*-dimethoxybenzenes [17].

In the search for nanoscopic assemblies, three dimensional structures containing in their framework platinum complexes of pyridine recently have been reported [10].

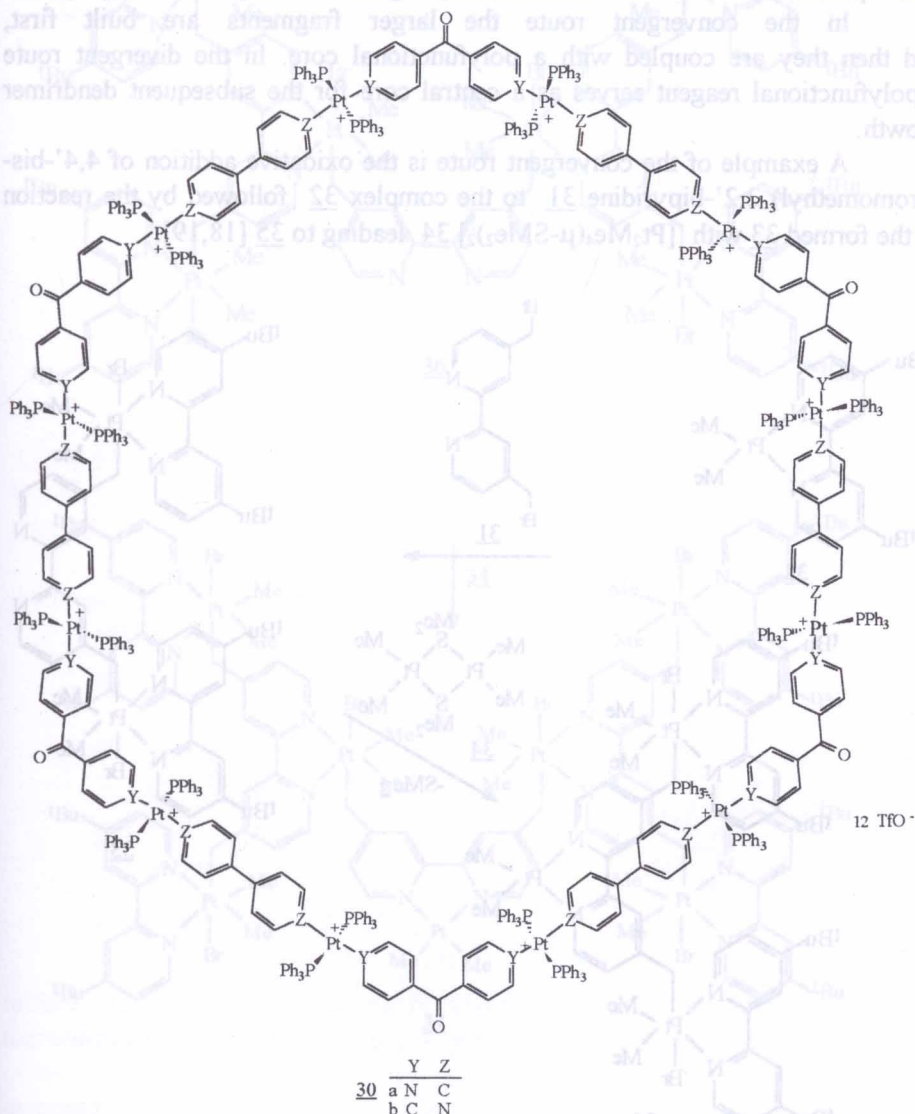


One should mention here also the [2]catenane **28** formed by self-assembly of two macrocycles **29**. The irreversible formation of **28** involves a method of „molecular lock” [17].

The Pt(II)-py bond is irreversible („locked”) under ordinary conditions, but becomes reversible („released”) in a polar medium at high temperature. The addition of  $\text{NaNO}_3$  and heating to  $100^\circ\text{C}$  releases two molecules of **29**; the subsequent removal of  $\text{NaNO}_3$  with cooling allows their self-assembly into **28** [17].



Besides molecular squares also molecular hexagons of the type 30a,b are known. These macrocycles of the inside diameter equal to 3 nm and the outside diameter of about 5 nm have the cavity large enough to enclose three  $C_{60}$  units [10].



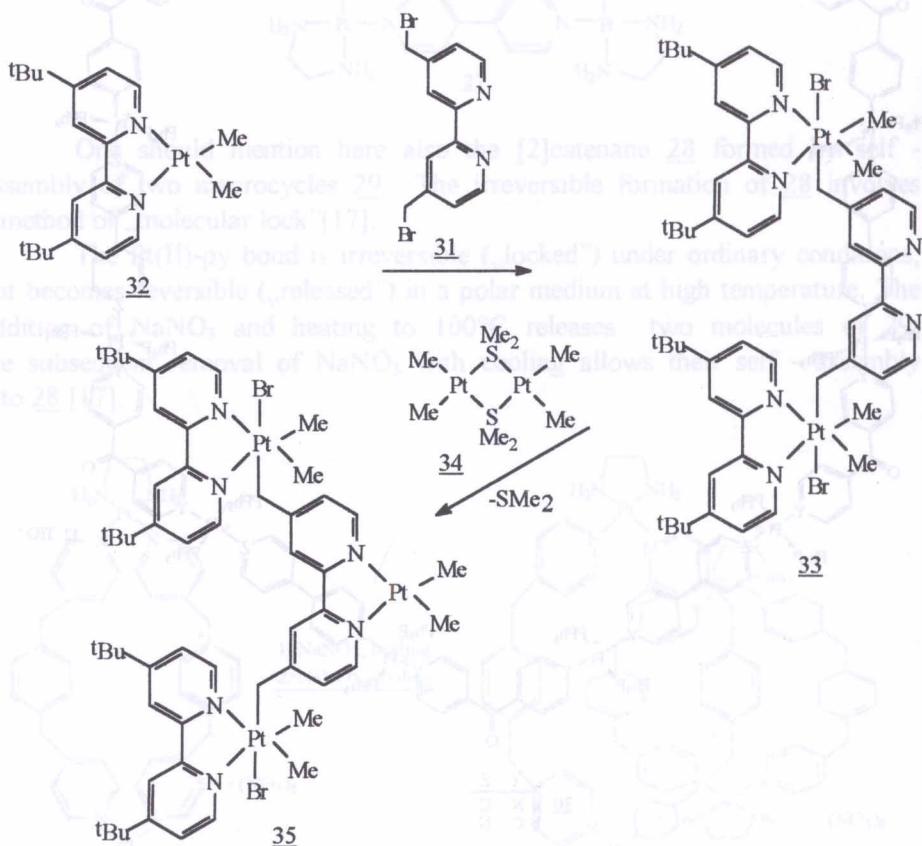
In the search for nanoscopic assemblies, three - dimensional structures containing in their framework platinum complexes of pyridine recently have been reported [10].

## Platinum dendrimers

The area of dendrimers is intensively studied. A convenient approach to these species is the oxidative addition; convergent or divergent routes are used.

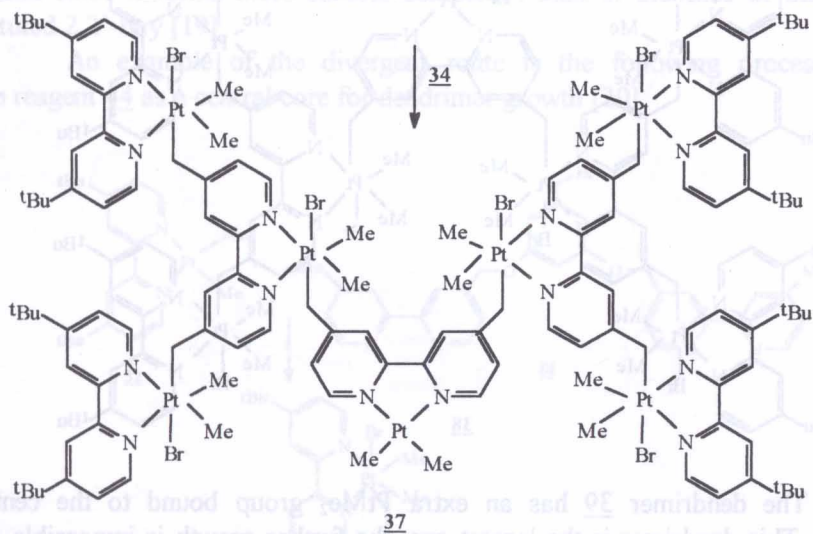
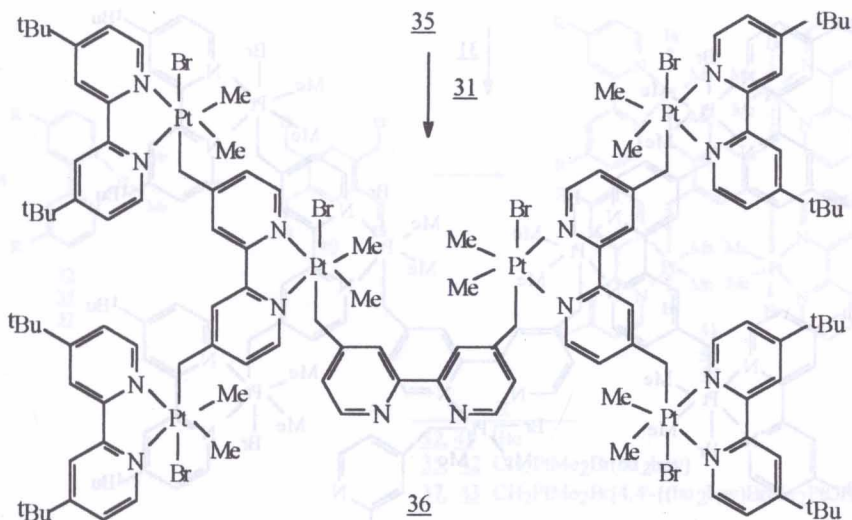
In the convergent route the larger fragments are built first, and then they are coupled with a polyfunctional core. In the divergent route a polyfunctional reagent serves as a central core for the subsequent dendrimer growth.

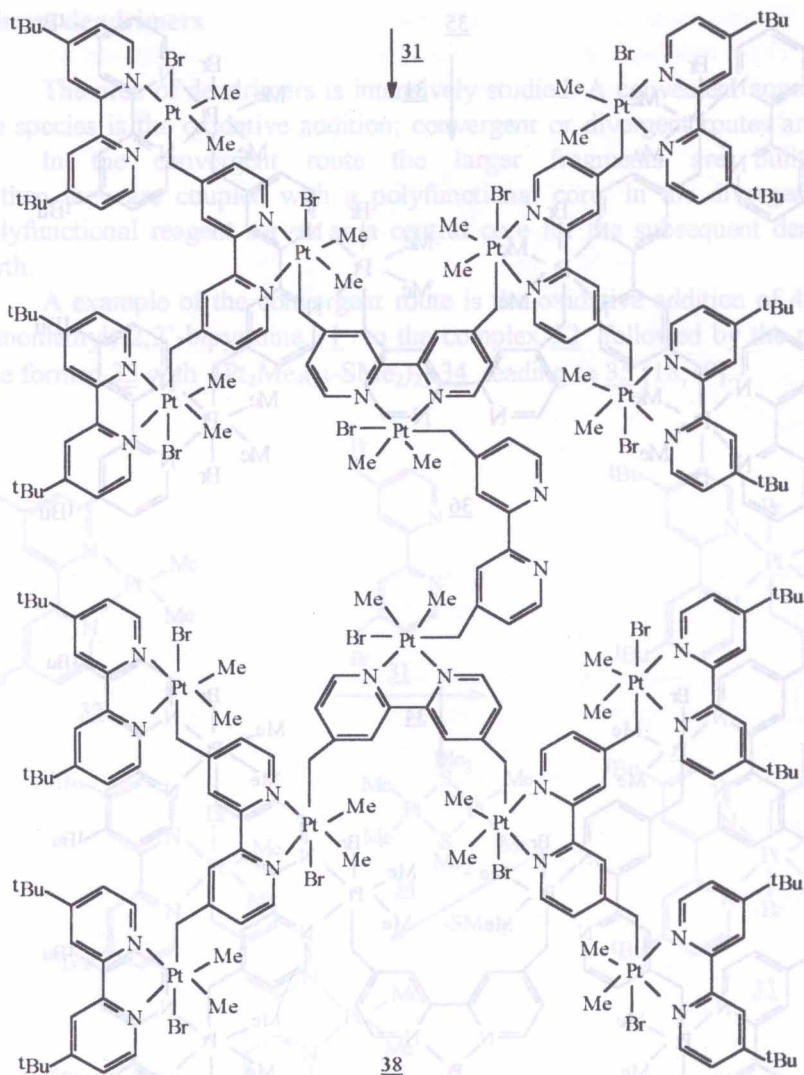
An example of the convergent route is the oxidative addition of 4,4'-bis-(bromomethyl) 2,2'-bipyridine **31** to the complex **32** followed by the reaction of the formed **33** with  $[\text{Pt}_2\text{Me}_4(\mu\text{-SMe}_2)_2]$  **34** leading to **35** [18,19].



Repetition of this procedure gives dendrimers containing 6, 7 and 14 platinum atoms, i.e. **36**, **37** and **38**, respectively [18].

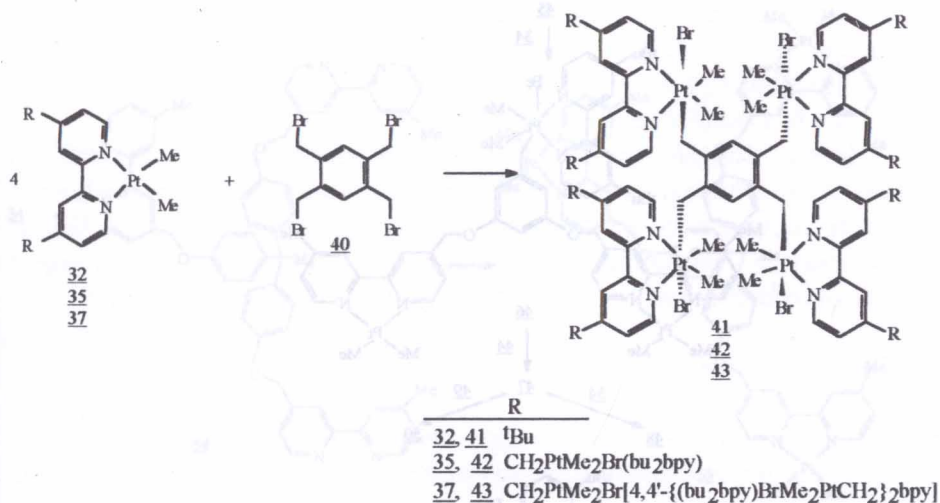






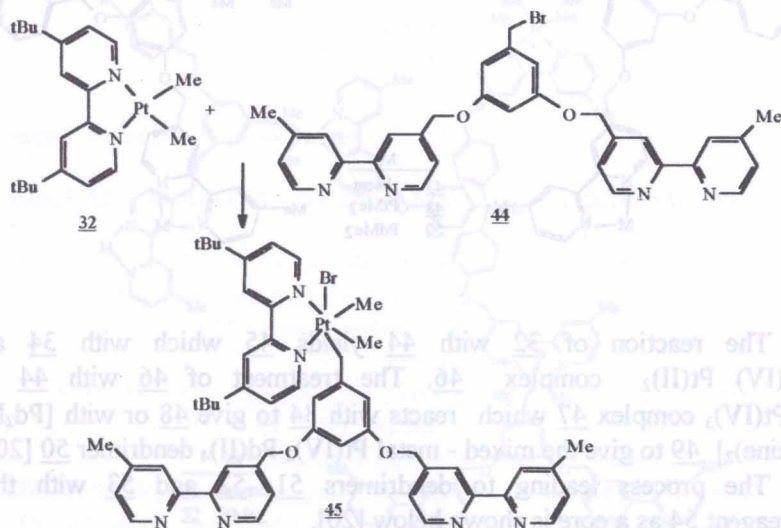
The dendrimer **39** has an extra PtMe<sub>2</sub> group bound to the central diimine. This dendrimer is the largest one; the further growth is impossible due to steric reasons.

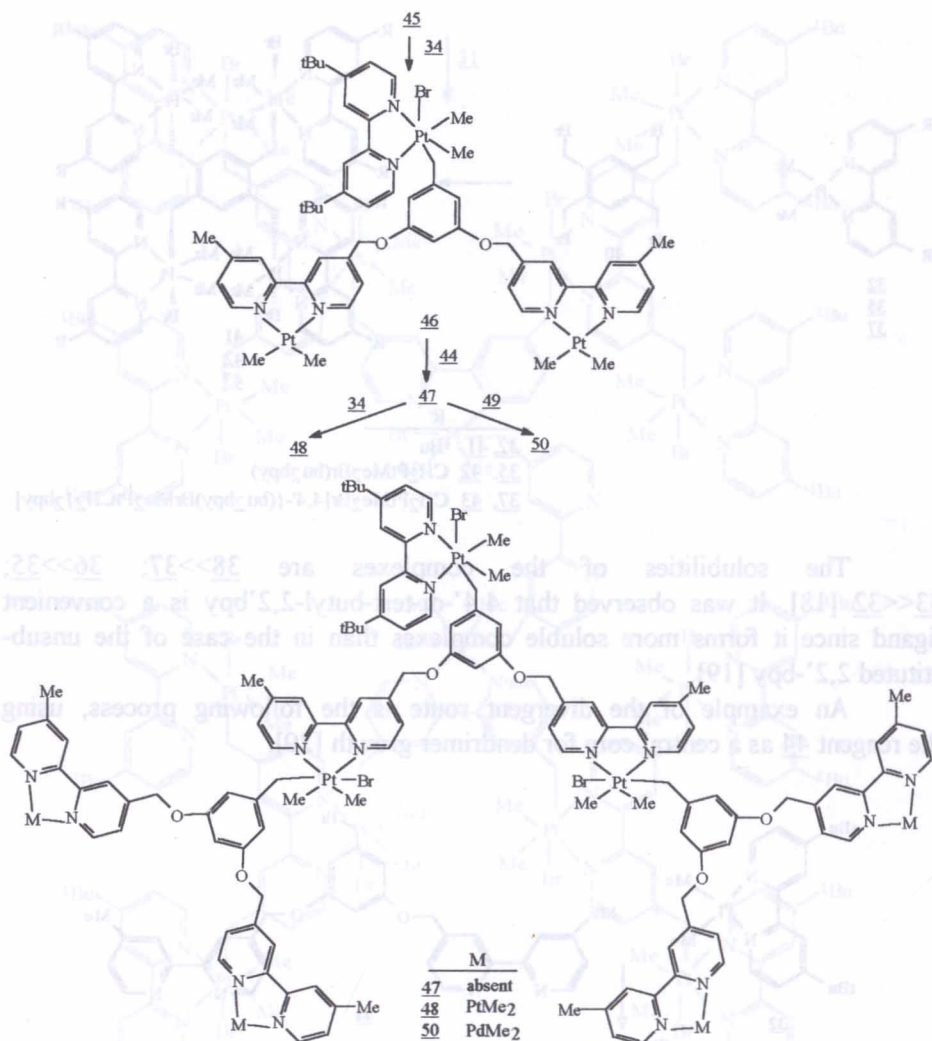
The reaction of complexes **32**, **35** and **37** containing 1, 3 and 7 platinum atoms, respectively, with tetrafunctional 1,2,4,5-tetrakis(bromomethyl)benzene **40** affords dendrimers with 4, 12 and 28 platinum atoms, i.e. **41**, **42** and **43**.



The solubilities of the complexes are **38** > **37**; **36** > **35**; **33** < **32** [18]. It was observed that 4,4'-di-*tert*-butyl-2,2'-bpy is a convenient ligand since it forms more soluble complexes than in the case of the unsubstituted 2,2'-bpy [19].

An example of the divergent route is the following process, using the reagent **44** as a central core for dendrimer growth [20].





The reaction of 32 with 44 yields 45 which with 34 affords the Pt(IV) Pt(II)<sub>2</sub> complex 46. The treatment of 46 with 44 results in the Pt(IV)<sub>3</sub> complex 47 which reacts with 34 to give 48 or with [Pd<sub>2</sub>Me<sub>4</sub>(μ-pyridazine)<sub>2</sub>] 49 to give the mixed - metal Pt(IV)<sub>3</sub> Pd(II)<sub>4</sub> dendrimer 50 [20].

The process leading to dendrimers 51, 52 and 53 with the use of the reagent 54 as a core is shown below [20].





The interaction of 34 with 54 yields the complex 55 which by treatment with 44 gives the compound 51. The reaction of 51 with 34 or 49 leads to dendrimers 52 or 53, respectively. Complexes 52 and 53 are sparingly soluble, this fact being a limit to further growth [20].

In the divergent routes shown here the solubility decreases with the increase of the dendrimer size, while in the convergent routes shown earlier the solubilities increase with the dendrimer size; in this case the growth is limited by steric reasons. Having this in view, the use of a mixed convergent-divergent route seems to be the most convenient approach to platinum dendrimers [20].

### Concluding remarks

Platinum (IV) complexes of pyridines, and especially nanostructures are promising in the design of new, tailor - made materials; investigation in this area is developing rapidly.

Such species, mostly of a beautiful, highly symmetrical shape are of interest e.g. in the construction of nanoscale devices, in catalysis and in chiral recognition.

### REFERENCES

1. P.J. Stang, *Chem. Eur. J.*, 1998, **4**, 19
2. B. Olenyuk, A. Fechtenkötter, P.J. Stang, *J. Chem. Soc., Dalton Trans.*, 1998, 1707
3. P.J. Stang, D.H. Cao, K. Chen, G.M. Gray, D.C. Muddiman, R.D. Smith, *J. Am. Chem. Soc.*, 1997, **119**, 5163
4. L. M. Rendina, R.J. Puddephatt, *Chem. Rev.*, 1997, **97**, 1735
5. G.S. Hill, J.J. Vittal, R.J. Puddephatt, *Organometallics*, 1997, **16**, 1209
6. P.J. Heard, C. Jones, *J. Chem. Soc., Dalton Trans.*, 1997, 1083
7. J. M. Tour, *Chem. Rev.*, 1996, **96**, 537
8. D. Philp, J.F. Stoddart, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1154
9. P.J. Stang, N.E. Persky, *Chem. Commun.*, 1997, 77
10. P.J. Stang, B. Olenyuk, *Acc. Chem. Res.* 1997, **30**, 502
11. P.J. Stang, B. Olenyuk, J. Fan, A.M. Arif, *Organometallics*, 1996 **15**, 904
12. B. Olenyuk, J.A. Whiteford, P.J. Stang, *J. Am. Chem. Soc.*, 1996, **118**, 82
13. M. Slany, P.J. Stang, *Synthesis*, 1996, 1019
14. P.J. Stang, B. Olenyuk, *Angew. Chem. Int. Ed. Engl.*, 1996, **35**, 732
15. J. Manna, J.A. Whiteford, P.J. Stang, D.C. Muddiman, R.D. Smith, *J. Am. Chem. Soc.*, 1996, **118**, 8731

16. J.A. Whiteford, C. V. Lu, P.J. Stang, *J. Am. Chem. Soc.*, 1997, **119**, 2524
17. M. Fujita, K. Ogura, *Bull. Chem. Soc. Jpn.*, 1996, **69**, 1471
18. S. Achar, J.J. Vittal, R.J. Puddephatt, *Organometallics*, 1996, **15**, 43
19. G.-X. Liu, R.J. Puddephatt, *Inorg. Chim. Acta*, 1996, **251**, 319
20. G.-X. Liu, R.J. Puddephatt, *Organometallics*, 1996, **15**, 5257

Marian Mielniczak<sup>1</sup>Jerzy Peszek<sup>2</sup>Wanda Śliwa<sup>2</sup>

Wanda Śliwa

<sup>1</sup> Common School, Bohemia<sup>2</sup> Pedagogical University, Cracow

### Kompleksy Pt(IV) ze związkami pirydynowymi oraz pokrewne układy supramolekularne

**Streszczenie:** Opisano syntezy i reaktywność kompleksów Pt(IV) ze związkami pirydynowymi oraz pokrewnych układów supramolekularnych. W pierwszej części przedstawiono przykłady kompleksów Pt(IV). W drugiej części scharakteryzowano cząsteczkowe kwadraty zawierające jony platyny i jodu, lub jedynie jony platyny, oraz podano przykłady dendrymerów.

**Abstract:** For three N-oxides of isomeric methyl- 1,3- and 4,6- diazaphenanthrenes (daps) 4-6 as well as for three model species, i.e. N-oxides of unsubstituted daps 7-9 the geometry optimization and calculation of electronic structure are presented.

The UV spectroscopy results of considered compounds are compared with those of parent daps 1-3.

Isomeric 1,3-, 1,6- and 4,6-diazaphenanthrenes (dap) 1-3, respectively, a topic of our research are interesting for their reactivity<sup>1</sup>, physicochemical properties<sup>2</sup> and biological activities<sup>3,4</sup>.

