

**INCORPORATION OF FLEXIBLE  
PYRIDINE -FUNCTIONALIZED  
LIGANDS INTO DISCRETE  
SUPRAMOLECULES VIA  
COORDINATION-DRIVEN SELF-  
ASSEMBLY**

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**Abstract**

Flexible, pyridine-functionalized ligands were self-assembled into discrete supramolecules of differing stoichiometries upon combination with various organoplatinum molecules. They are characterized by electrospray ionization mass spectrometry, <sup>31</sup>P{<sup>1</sup>H} and <sup>1</sup>H NMR. Despite its inherent flexibility, 3-substituted pyridines **1** and di-pyridyl substituted 18-membered diaza-crown ligand **8** prefer to self-assemble into closed systems when reacted with platinum-containing acceptors.

**Keywords:** self-assembly, coordination-driven, transition-metal-mediated, flexible ligands, pyridyl ligands

Coordination-driven transition-metal-mediated self-assembly has been used to prepare a wide variety of two- and three-dimensional discrete supramolecules in recent years. The strategy frequently employed for their preparation involves the combination of rigid starting materials of well-defined shape and bonding directionality. This generally allows a reasonably accurate prediction of the assembled product structure. In contrast, the successful use of flexible building blocks in self-assembling discrete structures is less documented due to the increased chance of numerous reaction pathways and products. When they are used, a

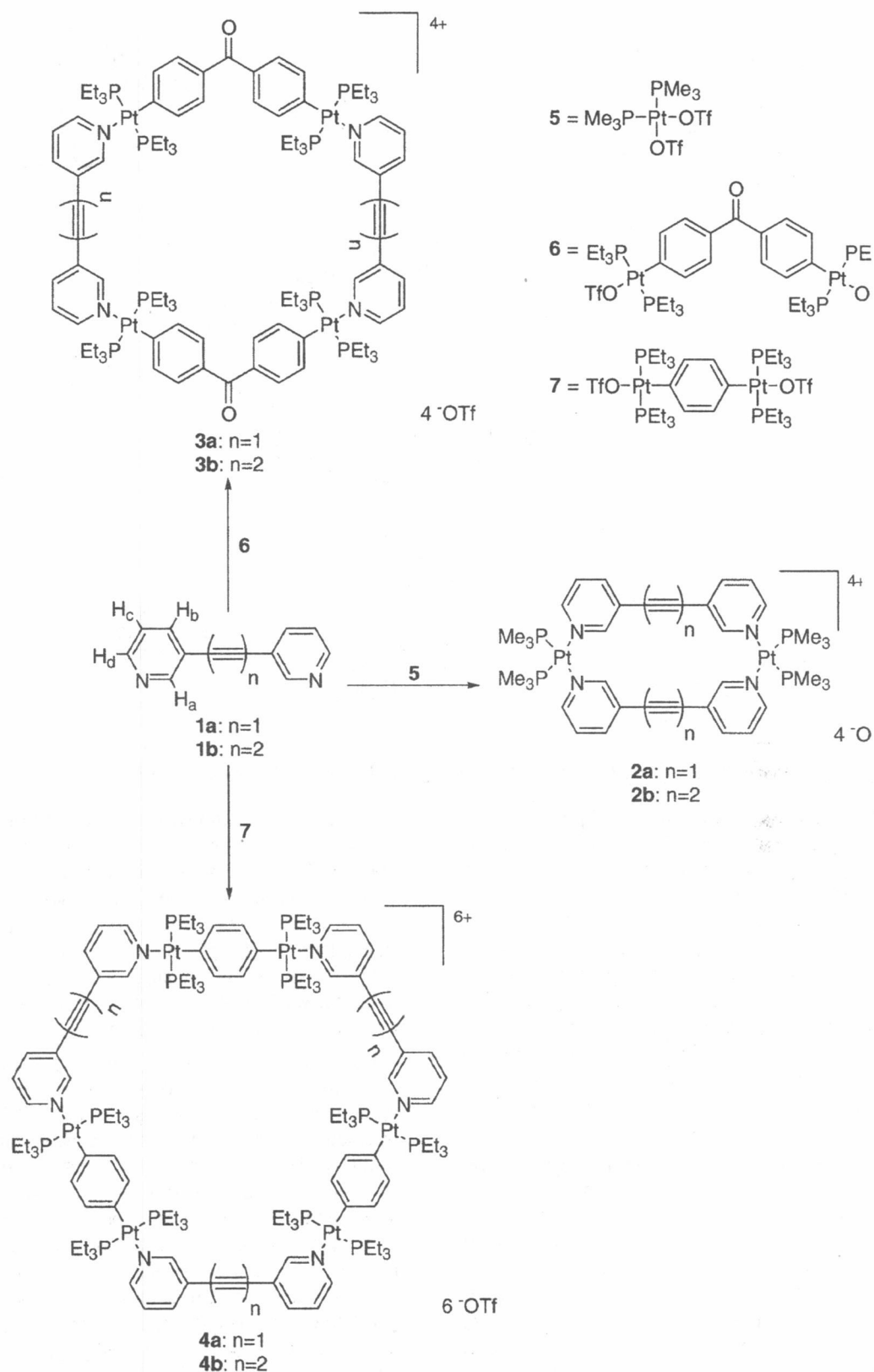
template molecule or ion is often necessary to control the self-assembly outcome. Often, one of the building blocks contains two or more rigid 4-substituted pyridine rings. This type of ligand maintains the same bonding directionality regardless of any rotation of these rings. In contrast, conformationally flexible 3-substituted pyridines **1** are capable of orientating their nitrogen atoms to any dihedral angle between 0 and 180°, thus producing marked structural differences in reaction products.

Macrocyclic crown ether compounds and derivatives as well as their properties and applications have been extensively examined since their discovery in 1967. More recent studies focused on diaza-crown ethers with functionalized heteroaromatic side arms. To date, there are no reports of platinum- or palladium-mediated self-assembly of flexible, pyridyl-substituted diaza-crown ethers into supramolecular species.

We were interested to see if flexible, bidentate ligands **1**, **8** and organoplatinum molecules would self-assemble into closed supramolecular structures or acyclic, infinite oligomers. Herein, we report the results of our investigations. All the products are characterized by electrospray ionization mass spectrometry (ESIMS), <sup>31</sup>P{<sup>1</sup>H} and <sup>1</sup>H NMR.[1-3]

Heating **1a** with 90° platinum acceptor **5** in CD<sub>3</sub>NO<sub>2</sub> for 3.5 hours gave the [2+2] assembly **2a** in quantitative yield.(Scheme 1) The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum showed a single sharp peak at -27.9ppm. This is shifted approximately 8ppm upfield relative to **5** due to back donation from the platinum atoms. In the <sup>1</sup>H NMR, both α-hydrogen nuclei of the pyridine rings experienced downfield shifts (H<sub>a</sub> 1ppm, H<sub>d</sub> 0.3ppm) relative to **1a**. These are consistent with the loss of electron density upon coordination of the pyridine-N. Further evidence was obtained with ESI-MS. The isotopically resolved peak m/z 1501 was assigned as the [M-OTf]<sup>+</sup> species where M represents the intact macrocycle.

Combination of **1b** and **5** under similar conditions gave **2b**. The mass spectrum was similar to **2a**. Unexpectedly, two chair-boat type conformers of **2b** were detected in the product NMR spectra. Two peaks of nearly equal intensity separated by 0.02ppm were observed in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum at room temperature. Upon warming of the sample to 80 °C, coalescence of these peaks was observed. The <sup>1</sup>H NMR spectrum also showed two sets of similar signals at room temperature. At 80 °C, the two phosphine methyl group doublets merge into one signal. Only partial coalescence of H<sub>a</sub> was observed. A possible explanation is the close proximity of neighboring H<sub>a</sub> proton nuclei during conformer interconversion. After cooling back to room temperature the NMR spectra return to their original appearance. X-Ray quality crystals were grown by vapor diffusion of ether into a nitromethane solution of **2b**. The ORTEP picture is of the chair conformer

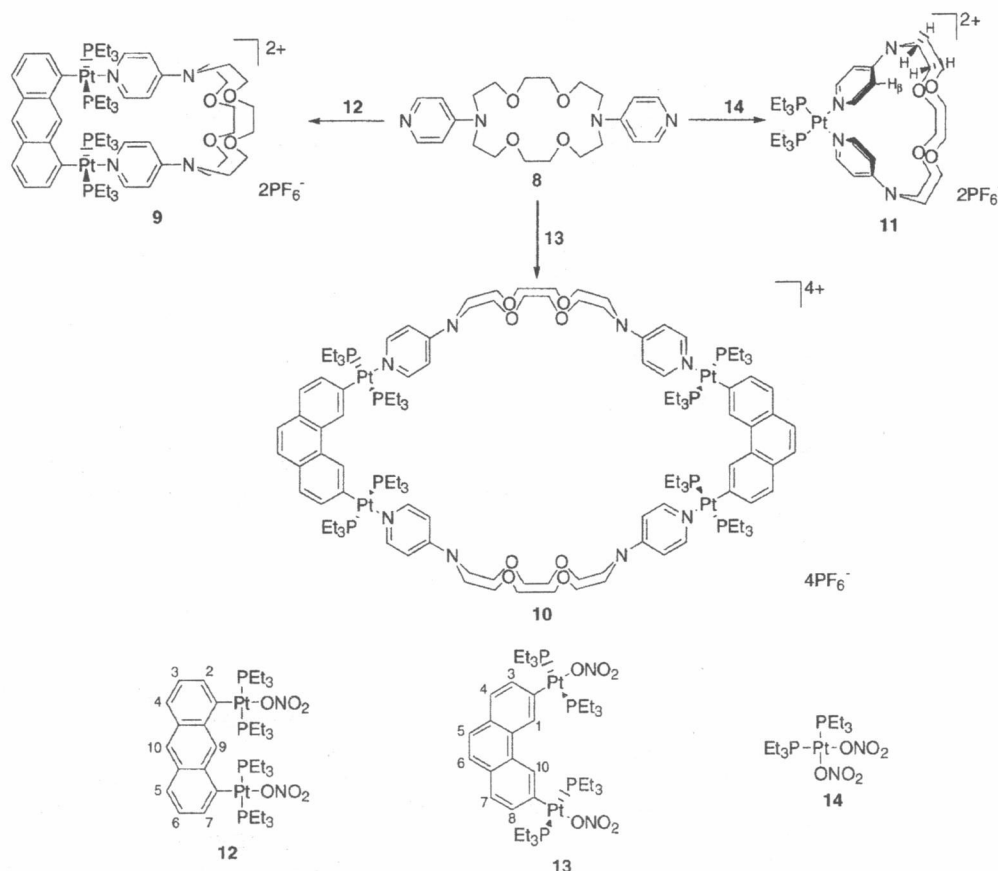


Scheme 1. Self-Assembly of 1 with Organoplatinum Reagents 5-7 into Discrete Assemblies 2-4

which crystallizes preferentially over the boat form. An analogous conformer mixture of **2a** was not observed. The closer proximity of the phosphine groups in a boat conformation of **2a** may make this structure much less energetically favorable than its chair counterpart. Use of the longer ligand **1b** results

in more spatial separation between the phosphine groups in the assembly **2b**. Our observation that each conformer is formed in approximately equal amounts suggests they are much closer in energy.

When **1a** was reacted with  $120^\circ$  platinum linker **6**, self-assembly **3a** was formed. The  $^{31}\text{P}$   $\{^1\text{H}\}$  NMR



Scheme 2. Self-Assembly of **8** with Organoplatinum Reagents **12-14** into Discrete Assemblies **9-11**

spectrum showed only one signal (14.8ppm) with the consistent upfield shift from **6**. In contrast to **2a**, the  $H_a$  signal of **3a** (9.06ppm) experiences a smaller shift to lower field (0.26ppm). The aromatic region of the  $^1H$  spectrum showed small amounts (< 5 %) of by-products. The broadened appearance of these signals suggests they may be of an oligomeric nature. Likewise, larger cycle **3b** was made from **1b** and **6**. Its NMR and mass spectra were similar to **3a**:  $[M-OTf]^+$  ( $m/z$  2940),  $[M-2OTf]^{2+}$  ( $m/z$  1396) and  $[M-3OTf]^{3+}$  ( $m/z$  881) were observed. The isotopically resolved patterns of the former and latter peaks are in excellent agreement with theory.

[3+3] assemblies **4** were made from **1** and linear platinum linker **7**. Both display strong  $^{31}P$  signals (14.6ppm **4a**; 14.9ppm **4b**). Small amounts of by-products give weak shoulder bands on either side of these resonances. These impurities are less evident in the proton NMR spectra, which are fairly similar as expected. One difference is the signals for the aromatic proton nuclei of the linker **7**. Assembly **4a** shows two singlets for these nuclei; **4b** only one. The benzene rings of **4a** must be hindered in their rotation leading to distinct inner and outer nuclei. These signals did not coalesce when the sample was heated to 80 °C.

The synthesis of **8** was achieved by palladium-mediated coupling of commercially available 1,4,10,13-Tetraoxa-7,16-diazacyclooctadecane with

an excess of 4-bromopyridine hydrochloride using the reported conditions. A modest yield (53%) was obtained. The self-assembly of supramolecules **9-11** was performed in the same general manner. (Scheme 2) An acetone- $d_6$  /  $D_2O$  solution of **8** and a particular organoplatinum acceptor **12-14** was heated at 60 °C for up to 16 h. Anion exchange with  $KPF_6$  facilitated straightforward isolation of the assemblies as hexafluorophosphate salts in high yield.

Unexpectedly, the  $^{31}P\{^1H\}$  NMR spectrum of the [1+1] assembly **9** displayed two singlets of approximately equal intensity near 9.40 ppm (assigned to  $PCH_2CH_3$ ) with concomitant  $^{195}Pt$  satellites. Their upfield shift relative to **12** is consistent with back donation from the platinum atoms upon pyridine coordination. When the sample was heated to 80 °C, coalescence of these signals was observed. Changes were also observed in the  $^1H$  spectrum. At room temperature there was a single, well-defined set of anthracene / pyridyl hydrogens while complex signals for the ethyl phosphine and methylene groups of the diaza-crown ring were observed. At 80°C, the ethyl signals simplified dramatically, the methylenes became sharper and more resolved while the pyridine hydrogens broadened significantly. The spectra returned to their original appearance when the sample was cooled back to room temperature. We believe the non-equivalent phosphine groups in **9** are distorted from their ideal position perpendicular to the anthracene

plane at room temperature. At 80°C, increased rotation makes them indistinguishable by NMR. Partial rotation of the pyridine rings also occurs at elevated temperature, as the two distinct sets of  $\alpha$ - and  $\beta$ -hydrogens at room temperature broaden upon heating. In the mass spectrum, peaks assignable to  $[2\text{-PF}_6^-]^+$  ( $m/z = 1600$ ) and  $[2\text{-}2\text{PF}_6^-]^{2+}$  ( $m/z = 727$ ) added support for the structure of **9**. The former was isotopically resolved and is in excellent agreement with the theoretical distribution. No evidence for any larger assemblies was found.

The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of the [2+2] product **10** exhibited a single peak at 15.97 ppm ( $\text{PCH}_2\text{CH}_3$ ) which was flanked by minor impurities. A septet for the  $\text{PF}_6^-$  counterions was centered at -143.1 ppm. The restricted rotation of the pyridine rings was evident in the  $^1\text{H}$  spectrum by two sets of  $\alpha$ -hydrogens. An unidentified by-product was also present (7.01 ppm). In contrast to **9** (and **11**), the appearance of the diaza-crown ring methylene signals in **10** resembled those of **8**. Clearly, the conformation of the 18-membered ring in **10** is more similar to that of **8** rather than in assemblies **9** and **11**. This has marked effects on the  $^1\text{H}$  lineshape. The structure was confirmed using ESIMS.

The [1+1] assembly **11** was formed with little or no by-products. In the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum the phosphines gave rise to a single peak at 2.75 ppm. The chemical shifts of the pyridyl hydrogen nuclei ( $\text{H}_{\alpha\text{-Py}}$  7.92 ppm,  $\text{H}_{\beta\text{-Py}}$  6.76 ppm) were almost unchanged relative to **8** (in  $\text{CD}_3\text{NO}_2$ :  $\text{H}_{\alpha\text{-Py}}$  8.07 ppm,  $\text{H}_{\beta\text{-Py}}$  6.64 ppm). This is in stark contrast to the downfield shift these hydrogens normally exhibit in pyridine-Pt based assemblies. Electron donation from the nitrogen atoms of the diaza-ring must offset the loss of electron density that occurs upon coordination. We have observed similar behavior in a model study with 4-(dimethylamino)pyridine and *cis*-( $\text{PMe}_3$ )<sub>2</sub>Pt(OTf)<sub>2</sub>. The appearance of the diaza-crown methylene signals resembles that of **9** and is characteristic of the highly folded conformation the macrocycle adopts in **11**. Isotopically resolved ESIMS peaks  $[4\text{-PF}_6^-]^+$  ( $m/z = 993$ ) and  $[4\text{-}2\text{PF}_6^-]^{2+}$  ( $m/z = 424$ ) reinforced the structure of **11**. Evidence for higher assemblies was not found.

The formation of the [1+1] products **9** and **11** is entropically favorable over larger supramolecules. This is apparently the dominant factor in their formation despite the introduced ring strain of these two assemblies. In the reaction of **8** and platinum acceptor **13**, a [1+1] product is geometrically impossible thus the formation of the [2+2] species **10**.

In conclusion, we have described the first discrete supramolecules prepared from organoplatinum reagents and bidentate pyridine donors **1**. Despite their ability to vary their bonding directionality, ligands **1** prefer to self-assemble into closed macrocycles **2-4** regardless of the geometrical

features of the platinum acceptor. And the coordination-driven self-assembly of supramolecules **9-11** from a di-pyridyl substituted diaza-crown ring **8** and varying platinum acceptors **12-14** has been described. This work shows for the first time that a conformationally flexible, di-pyridyl substituted 18-membered diaza-crown ring can be incorporated effectively into discrete species of varying size and shape.

#### References

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