

Self-Selected Formation of Single Discrete Supramolecules with Flexible, Bidentate Ligands in the Coordination-Driven Self-Assembly

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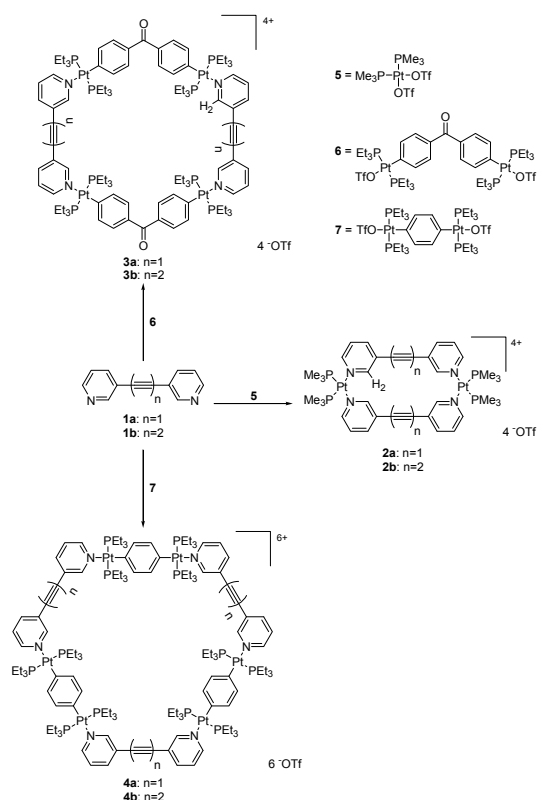
Abstract — Flexible donor ligands like 1,2-bis(3-pyridyl)ethyne or 1,4-bis(3-pyridyl)-1,3-butadiyne self-assemble into discrete 2-D supramolecules instead of infinite networks upon combination with organoplatinum 90, 120, and 180 degree acceptor units. These systems are unique examples of versatile pyridine donors adjusting their bonding directionality to accommodate rigid platinum acceptors in the formation of closed macrocycles. Discrete, nanoscopic 3-D cages are also prepared in high yield via coordination-driven self-assembly from bidentate 3-substituted pyridines and tripod organoplatinum acceptors. Flexible, bidentate 3-substituted pyridine donors and a rigid organopalladium acceptor are also exclusively self-assembled into discrete 2-D macrocycles. Moreover, discrete supramolecules are successfully prepared from ambidentate donor ligands and platinum containing acceptors. Despite the possibility of forming more than one product, ambidentate ligands prefer to self-assemble predominantly into one species. Flexible, ambidentate pyridyl-carboxylate based donor ligands like sodium 3-(3-pyridyl)benzoate, sodium 4-(3-pyridyl)benzoate and potassium 4-(3-pyridyl)ethynylbenzoate self-assemble into discrete [2+2] macrocyclic species instead of infinite networks when combined with a 90 degree organoplatinum acceptor. In each case only one isomeric ensemble is selectively formed in high yield. All products are characterized by electrospray ionization mass spectrometry (ESI-MS), $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectroscopy. They are the first examples of discrete supramolecules incorporating flexible, bidentate donor ligands. Despite their potential versatility, these flexible donors adjust their bonding directionality to accommodate a rigid acceptor in the formation of one discrete ensemble.

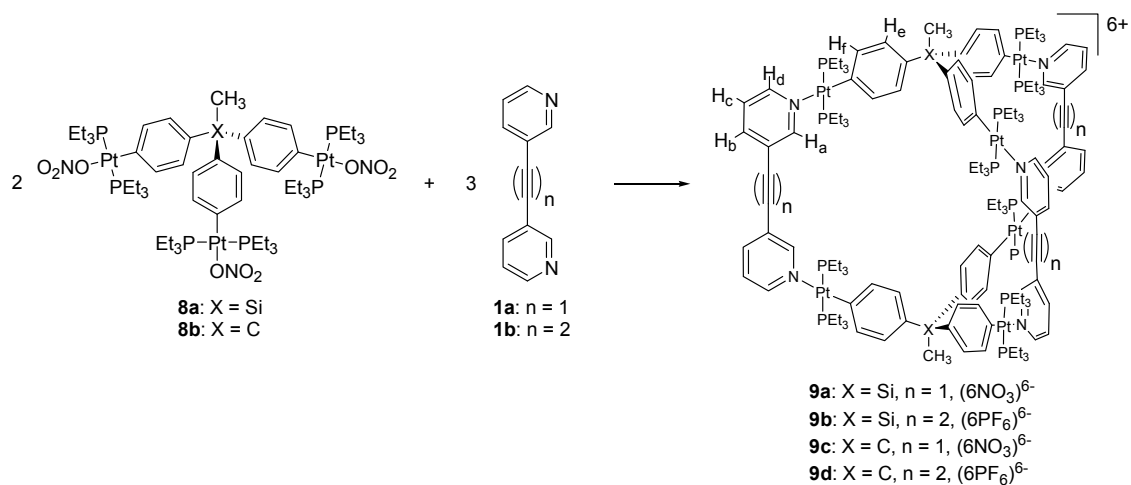
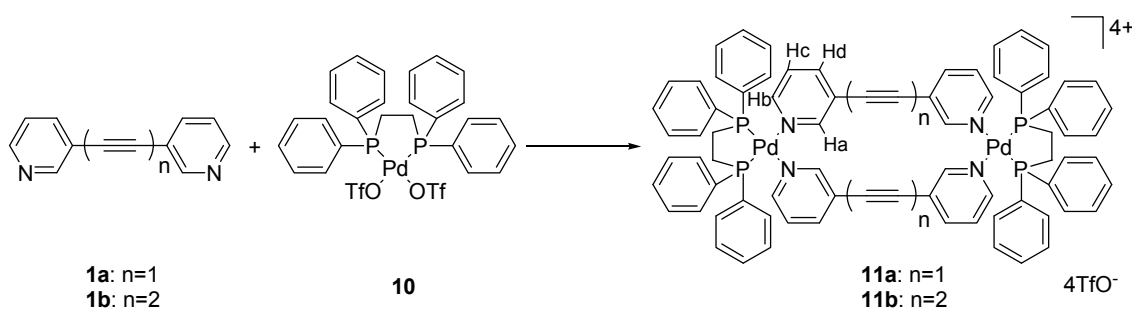
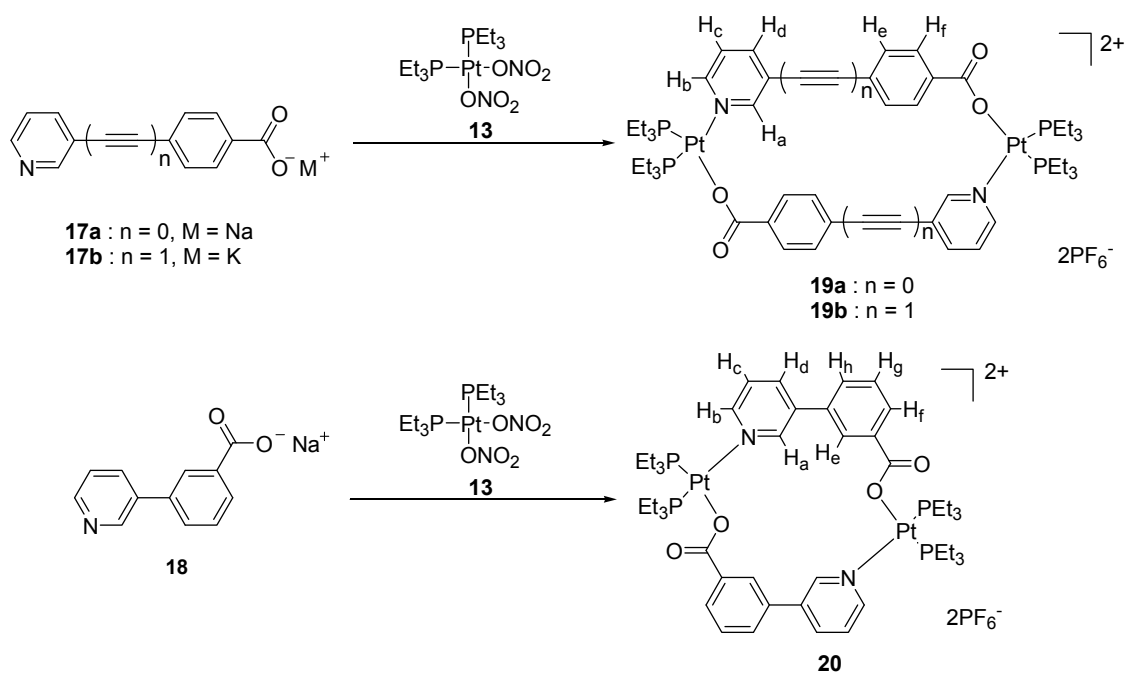
I. INTRODUCTION

During the past decade, coordination-driven self-assembly with Pt^{I} or Pd^{II} acceptors has drawn much attention and been successfully applied for the production of various discrete 2-D or 3-D supramolecules. Well-matched pre-designed donors and metal-containing acceptors have provided discrete self-assemblies in an almost quantitative yield. Exclusive production of discrete ensembles rather than oligomeric or polymeric structures has been unique and interesting outcome in that similar result can not be expected with other synthetic methodologies. This result could be ascribed to the fact that the coordination between metal and ligand is thermodynamically controlled and the formation of discrete entities favors in enthalpy over that of oligomeric

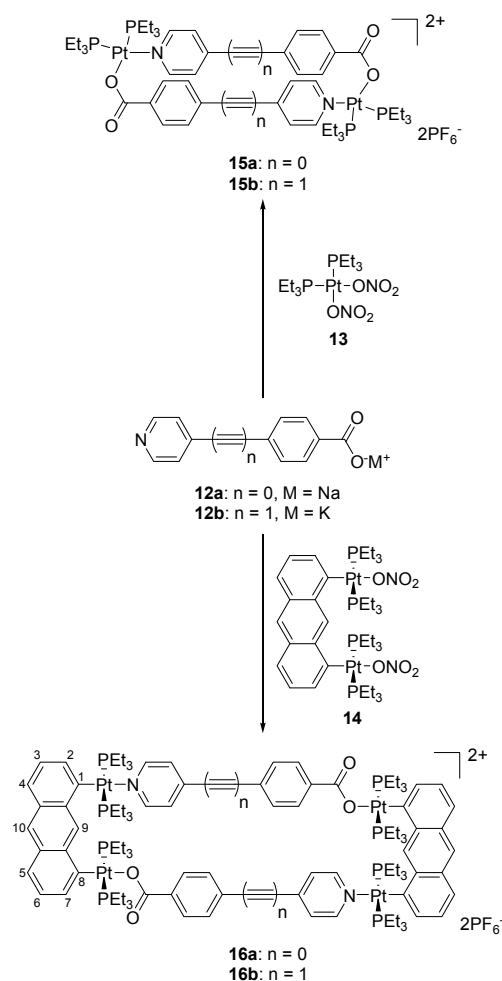
forms. Thus, the right combination of donor and acceptor in the type of their reacting elements and bond angles was crucial for the effective production of discrete self-assemblies.³ Most of the reactions required specific donor and acceptors with fixed-bond angles, and the shape of supramolecular product was decided by the fixed-bond angles used. Only a few flexible ligands in the presence of template molecules self-assembled into discrete entities.⁴ Recently, ligands with variable bond angles were successfully applied without assistance of any template for the synthesis of discrete supramolecules via coordination-driven self-assembly.⁵ Herein, we report the summary of our investigations on the coordination-driven self-assembly of discrete supramolecules between flexible/unsymmetrical donor and Pt/Pd acceptor.

Scheme 1. Self-Assembly of Flexible Ligands 1 with Platinum Acceptors 5 – 7.



Scheme 2. Self-Assembly of Flexible, Pyridyl Ligands **1** with Tripodal Acceptors **8**.Scheme 3. Self-Assembly of Flexible, Pyridyl Ligands **1** with Palladium acceptor **10**.Scheme 5. Self-Assembly of Flexible, Ambidentate Ligands **17**, **18** with Acceptor **13**.

Scheme 4. Self-Assembly of Pyridine-Carboxylates 12 with 90° linker 13 and clip 14.



II. RESULTS AND DISCUSSION

As shown in Scheme 1,^{5a} heating conformationally flexible 3-substituted pyridines 1 with 90° platinum acceptor 5 gave the [2+2] assemblies 2 in quantitative yield. Unexpectedly, two chair-boat type conformers of 2b were detected in the product NMR spectra. Two peaks of nearly equal intensity separated by 0.02 ppm were observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at room temperature. Upon warming of the sample to 80 °C, coalescence of these peaks was observed. The ^1H 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_2 was observed. A possible explanation is the close proximity of neighboring H_2 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. When the flexible pyridines 1 were reacted with 120° platinum linker 6, self-assemblies 3 were formed. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of 3a showed only one signal (14.8 ppm) with the consistent upfield shift from 6. The mass spectrum adds support to the structure. Peaks

attributable to the consecutive loss of triflate anions were observed: $[\text{M-OTf}]^+$ (m/z 2893), $[\text{M-2OTf}]^{2+}$ (m/z 1372) and $[\text{M-3OTf}]^{3+}$ (m/z 865). The former and latter were isotopically resolved and agree very well with the theoretical distribution. On the contrary, the [3+3] assemblies 4 were exclusively made from 1 and linear platinum linker 7. We were also interested in investigating whether 1 could be used to prepare discrete 3-D supramolecules rather than infinite networks.^{5b} The formation of 3-D cages 9 is shown in Scheme 2. They are prepared by heating two equivalents of tritopic unit 8 with three equivalents of bidentate ligand 1 in a 1:1 acetone- d_6 / D_2O medium at 60 °C for 24 hours. Cages 9 are the first examples of discrete 3-D supramolecules formed from flexible 3-substituted pyridines 1 and organoplatinum reagents. Clearly 1 prefer to self-assemble into closed systems despite their ability to vary their bonding directionality. Square planar palladium complexes in which two positions are occupied by strong Pd-P bonds and remaining positions are coordinated by labile triflate anions have been popular acceptors in supramolecular chemistry.⁶ Therefore, we decided to check if flexible, bidentate pyridyl ligands 1 would self-assemble with a rigid organopalladium acceptor 10 into discrete supramolecular structures.^{5d} A CD_3NO_2 solution of ligands 1 and organopalladium 10 was heated at 60 °C for 3 hour, followed by evaporation of solvent with nitrogen gas to give [2+2] supramolecules 11 in almost quantitative yield as shown in Scheme 3. We were also interested in the possibility of self-recognized and self-

selected assembly between unsymmetrical ligands like 12 and rigid Pt acceptors 13-14.^{5c} As shown in Scheme 4, we have successfully prepared discrete macrocycles 15-16 from ambidentate donor ligands 12 and platinum containing acceptors 13-14. The self-assembly processes were all performed in the same general manner. A 1:1 acetone- d_6 / D_2O solution of ligands 12 and a particular organoplatinum 13-14 was heated at 60 °C for up to 2.5 hours, followed by anion exchange with KPF_6 to precipitate the products in high yield. Despite the possibility of forming more than one product, ambidentate ligands 12 prefer to self-assemble predominantly into one species. They are the first examples of discrete supramolecules made from ambidentate ligands via coordination-driven transition-metal-mediated self-assembly. Our attention has moved to investigate self-assembly processes with ambidentate donor ligands that are also conformationally flexible such as sodium 4-(3-pyridyl)benzoate (17a), potassium 4-(3-pyridyl)ethynyl benzoate (17b) and sodium 3-(3-pyridyl)benzoate (18).^{5f} A 1:1 acetone- d_6 / D_2O solution of ligand 17 or 18 and 13 was stirred at 25 °C for 1 hour, followed by anion exchange with KPF_6 to precipitate the [2+2] products 19, 20 in high yield (Scheme 5). The self-assembled macrocycles were initially characterized by $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectroscopy. The $^{31}\text{P}\{^1\text{H}\}$ spectra of each assembly displayed two coupled doublets (19a: 7.20, 2.47 ppm, $^2J_{\text{P-P}} = 21.2$ Hz, Figure 1; 19b: 7.10, 1.59 ppm, $^2J_{\text{P-P}} = 21.0$ Hz; 20: 6.74, 2.18 ppm, $^2J_{\text{P-P}} = 21.2$ Hz) of approximately equal intensity with concomitant ^{195}Pt satellites. The signals near 2 ppm are shifted approximately 5 ppm upfield relative to 13 due to back donation from the platinum centers. These phosphorus nuclei are *trans* to the pyridine ring. In contrast,

coordination of the carboxylate group does not result in the same large ^{31}P chemical shift change. This is attributed to the similarity between the newly formed platinum-carboxylate bond and the Pt-ONO₂ bond of 13. The coupled phosphorus doublets are indicative of two inequivalent phosphorus nuclei bound to the same platinum atom in 19, 20. Despite the possibility of varying bond directionality and formation of different linkage isomers, ligands 17 and 18 prefer to self-assemble into one closed ensemble 19 or 20 each time. In contrast to O-Pt-O and N-Pt-N bond angles formation of an N-Pt-O linkage in these systems facilitates closing of the [2+2] ensemble by orientating the unbound pyridyl and carboxyl termini closer together in space. In addition, the formal charge of +1 on the pyridine nitrogens is more widely separated in 19, 20 relative to their constitutional isomers. They are also the first examples of discrete supramolecules made from conformationally flexible, ambidentate ligands via coordination-driven transition-metal-mediated self-assembly.

III. CONCLUSION

In conclusion, we have described the first discrete supramolecules prepared from organoplatinum or organopalladium reagents and bidentate 3-substituted pyridine donors 1. Despite their ability to vary their bonding directionality, ligands 1 prefer to self-assemble into closed 2-D macrocycles 2-4 and 11 regardless of the geometrical features of the platinum or palladium acceptor. Discrete 3-D cages 9 have been prepared via coordination-driven self-assembly from flexible ligands 1 and tripod organoplatinum acceptors 8. We have also prepared discrete macrocycles 19, 20 from flexible, ambidentate donor ligands 17, 18 and platinum containing acceptor 13. Despite the possibility of varying bond directionality and formation of different linkage isomers, ligands 17, 18 prefer to self-assemble into one closed ensemble each time. They are the first examples of discrete supramolecules made from conformationally flexible, ambidentate ligands via coordination-driven transition-metal-mediated self-assembly. These results provide further evidence of thermodynamic control favoring formation of discrete entities over oligomeric networks, presumably due to the added gain in enthalpy from the additional coordination bond to platinum or palladium in the closed system. Moreover, it has been shown the reversibility in a coordination-driven process and the added gain in enthalpy in the formation of closed system make self-recognition and self-selection possible out of various combinations between donor and acceptor.

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