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Ambidentate Ligands Capable of Variable Bond Angles in the Coordination-Driven Self-Assembly of Discrete Pt Macrocycles

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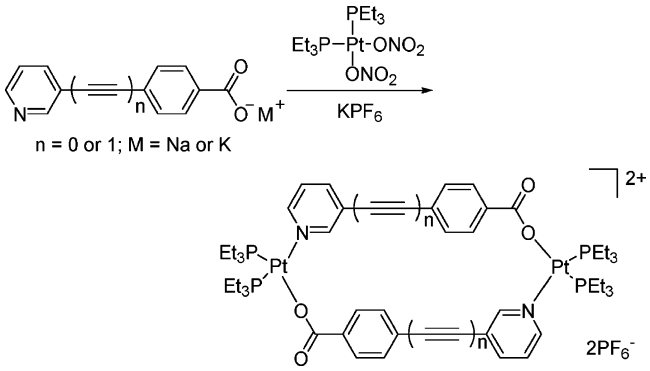

Flexible, ambidentate pyridyl-carboxylate based donor ligands such as sodium 3-(3-pyridyl)benzoate, sodium 4-(3-pyridyl)-benzoate, and potassium 4-(3-pyridyl)ethynylbenzoate self-assemble into discrete [2 + 2] macrocyclic species instead of infinite networks when combined with a 90° platinum-containing 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) and $^{31}P\{^1H\}$ and ^1H NMR spectroscopy. They are the first examples of discrete supramolecules incorporating flexible, ambidentate donor ligands. Despite their potential versatility, these pyridyl-carboxylate donors adjust their bonding directionality to accommodate a rigid platinum acceptor in the formation of one discrete ensemble.

The predesigned combination of homodi- and tridentate pyridyl ligands with platinum and palladium containing acceptors in the synthesis of discrete two- and three-dimensional (2- and 3-D) supramolecules has been investigated extensively.[1−10] More recently, incorporation of oxygen donor molecules into simple Pt-containing polygons was achieved.[11,12] This coordination-driven self-assembly methodology has taken advantage of the inherent rigid bonding, directionality, and symmetry within building blocks to accurately predict the structure of the assembled product. Conversely, conformationally flexible ligands have been seldom utilized in the self-assembly of discrete supramolecules because of the higher number of plausible reaction pathways. In several examples, the presence of template guest molecules or ions during self-assembly was necessary to form distinct entities.[13−17] Recently, we demonstrated that the reaction of 1,2-bis(3-pyridyl)ethyne and 1,4-bis(3-pyridyl)-1,3-butadiyne with a range of organoplatinum and organosilicon linkers led to discrete 2- and 3-D ensembles.[18,19] In addition, we self-assembled distinct architectures from a pyridine-functionalized diaza-crown ether and three organoplatinum reagents without template assistance.[20] A different level of complexity occurs when less symmetrical rigid ambidentate ligands, for example, sodium 4-(4-pyridyl)benzoate, are reacted with organoplatinum acceptors. Although two constitutional isomers due to differences in connectivity are possible, a single isomer was preferentially formed.[21] This led us to investigate self-assembly processes with ambidentate donor ligands that are also conformationally flexible. Sodium 4-(3-pyridyl)benzoate (**1a**), potassium 4-(3-pyridyl)ethynyl benzoate (**1b**), and sodium 3-(3-pyridyl)benzoate (**2**) (shown in Scheme 1) satisfy these requirements. Herein we report that despite the possibility of constitutional isomers and oligomeric networks, the self-assembly of ligands **1** and **2** with platinum-containing acceptor **3** yields predominantly one ensemble.

The self-assembly processes were all performed in the same general manner. A 1:1 acetone-d_6/D_2O solution of ligand **1** or **2** and **3** was stirred at 25 °C for 1 h, followed by anion exchange with KPF_6 to precipitate the [2 + 2] products **4** and **5** in high yield (Scheme 1). The self-assembled macrocycles were initially characterized by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy. The $^{31}P\{^1H\}$ spectra of each assembly displayed two coupled doublets (**4a**: 7.20, 2.47 ppm, $^2J_{P-P} = 21.2$ Hz, Figure 1; **4b**: 7.10, 1.59

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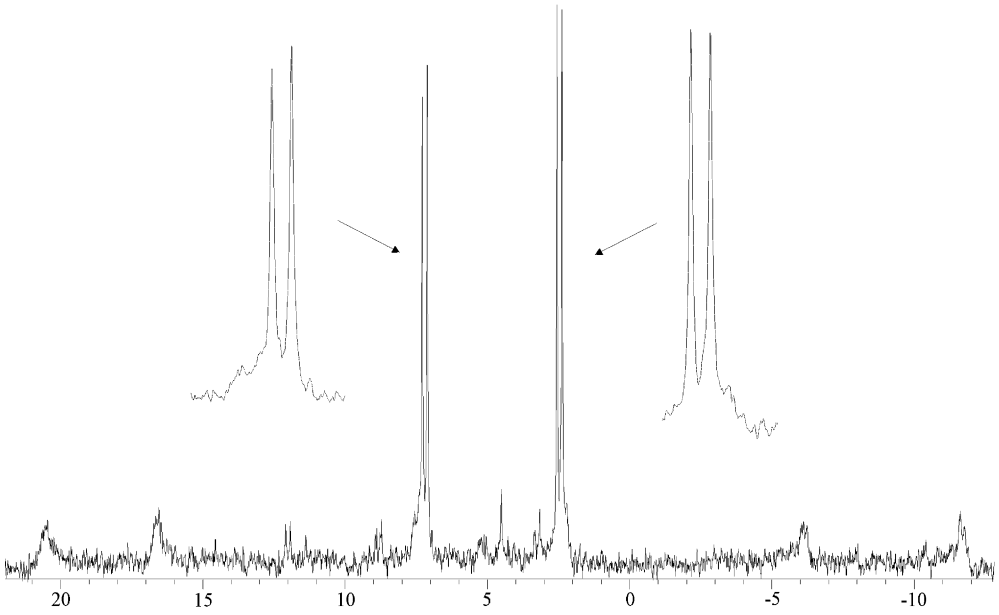
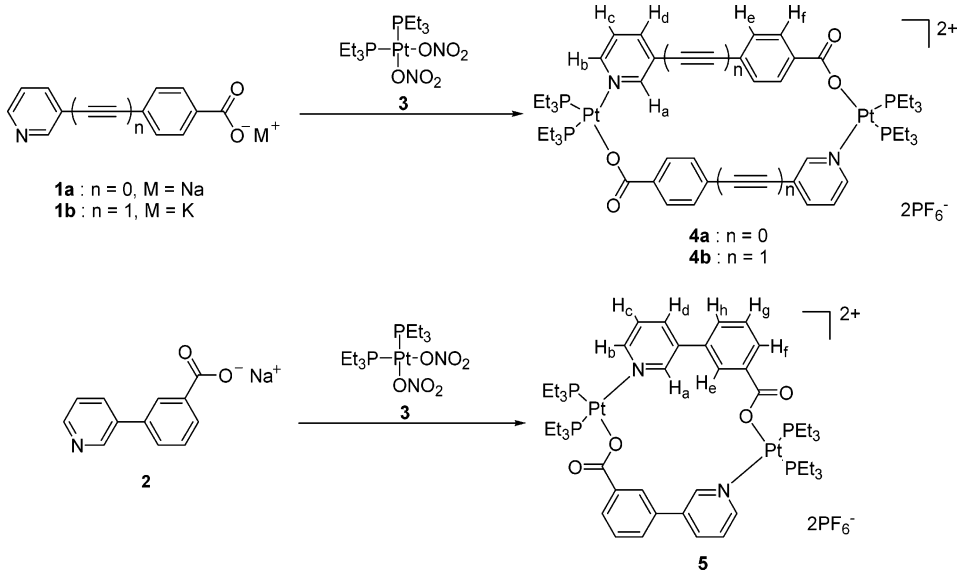


FIGURE 1. ^{31}P NMR spectrum of 4a.

SCHEME 1. Self-Assembly of Flexible, Ambidentate Ligands 1 and 2 with Platinum Acceptor 3



ppm, $^2J_{P-P}$ = 21.0 Hz; **5**: 6.74, 2.18 ppm, $^2J_{P-P}$ = 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 **3** because of 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−ONO_2 bond of **3**.[11,12] The coupled phosphorus doublets are indicative of two inequivalent phosphorus nuclei bound to the *same* platinum atom in **4** and **5**.[21]

In the ^{1}H NMR spectra of **4** and **5**, both α-hydrogen nuclei (H_a and H_b) of the pyridine rings experienced downfield shifts (0.3−0.7 ppm) relative to **1** and **2** (**4a**: Figure 2) consistent with the loss of electron density upon coordination of the pyridine nitrogen atom. Coordination of the carboxylate group did not produce any significant ^{1}H chemical shift change of H_e or H_f in **4** and **5**.

Further evidence for the formation of assemblies **4** and **5** was obtained with ESI-MS (**4a**: Figure 3). All three products displayed similar spectra. A peak corresponding to the intact macrocycle minus one PF_6^- counterion was observed {[**4a**-PF_6^-]$^+$ (*m*/*z* 1403), [**4b**-PF_6^-]$^+$ (*m*/*z* 1451), [**5**−PF_6^-]$^+$ (*m*/*z* 1403)}. The base peaks were assigned to half of the intact cycle {[**4a**/2-PF_6^-]$^+$ (*m*/*z* 629), [**4b**/2-PF_6^-]$^+$ (*m*/*z* 653), [**5**/2-PF_6^-]$^+$ (*m*/*z* 629)}. These were all isotopically resolved and are in excellent agreement with their theoretical distributions. Presumably **4** and **5** readily undergo fragmentation under the electrospray analysis conditions employed.

All reactions gave one predominant species with few byproducts evident in the NMR spectra. Small peaks (<5%) evident in the ^{31}P{^{1}H} spectra could not be assigned. Their sharp appearance suggests they belong to other discrete species rather than oligomeric networks. Because of their relatively weak intensity and lack of discernible ^{1}H NMR signals, we were unable to further characterize them. In addition, we found no

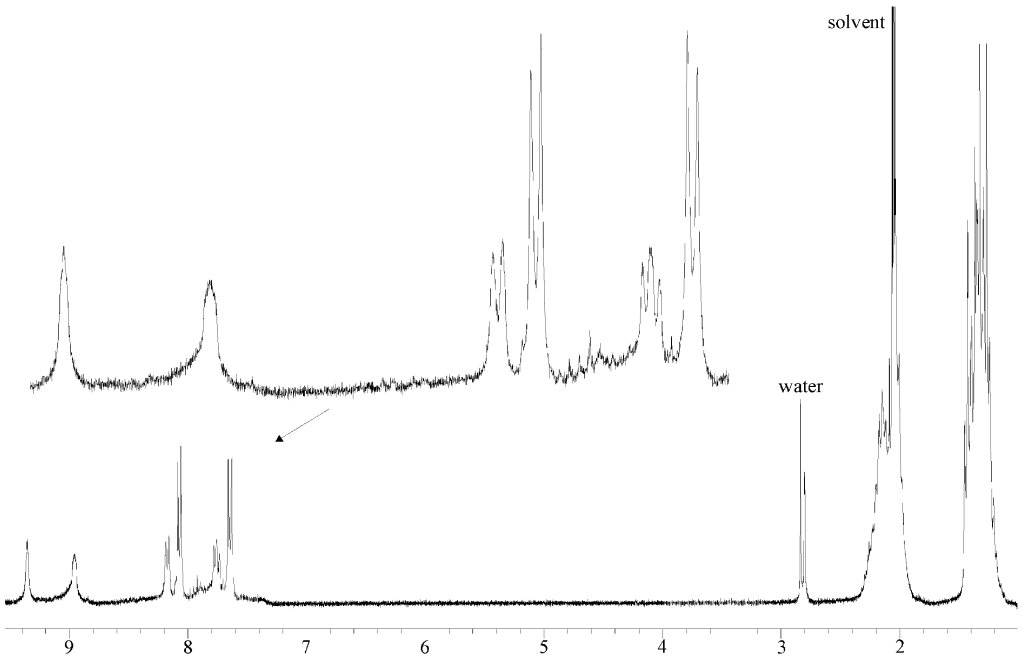


FIGURE 2. ^{1}H NMR spectrum of 4a.

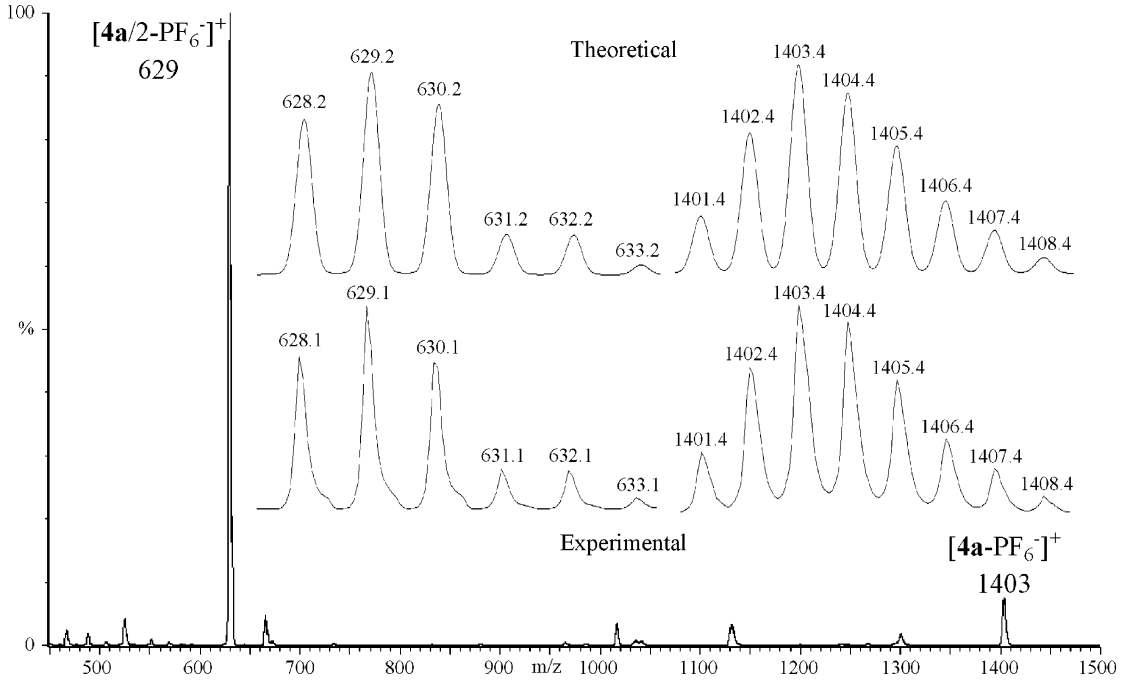


FIGURE 3. ESI-MS spectrum of 4a.

mass spectral evidence for any larger macrocycles. Impurity levels were smaller in reactions with the shorter ligands **1a** and **2** than those of **1b** which reflects a general trend that less flexible ligands produce higher yields of self-assembled products.[18]

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.[21] In addition, the formal charge of +1 on the pyridine nitrogens is more widely separated in **4** and **5** relative to their constitutional isomers.

In conclusion, we have prepared discrete macrocycles **4** and **5** from flexible, ambidentate donor ligands **1** and **2** and platinum containing acceptor **3**. Despite the possibility of varying bond directionality and formation of different linkage isomers, ligands **1** and **2** 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. This provides further evidence of thermodynamic control favoring formation of discrete entities over oligomeric networks, presumably because of the added gain in enthalpy from

the additional coordination bond to platinum in the closed system.

Experimental Section

Methods and Materials. The free acids of ligands **1a**−**b**[22,23] and **2**[22] were synthesized by the published procedures. They were then dissolved in an aqueous solution containing 1 equiv of the appropriate alkali metal hydroxide. Evaporation of the solvent afforded a quantitative recovery of **1** and **2**. The ^{1}H NMR spectra of **1** and **2** were recorded in acetone-d_6 in the presence of a minimum amount of D_2O to aid dissolution. Compound **3**[24] was prepared as reported. ^{1}H and ^{31}P{^{1}H} NMR chemical shifts are reported relative to the residual protons of acetone-d_6 (2.05 ppm) and an external, unlocked sample of H_3PO_4 (0.0 ppm), respectively.

General Procedure for the Preparation of Assemblies 4 and **5**. Platinum acceptor **3** (10 μmol) and ambidentate ligand **1** or **2** (10 μmol) were placed in a 1-dram vial. Acetone-d_6 (0.5 mL) and D_2O (0.5 mL) were added. The vial was sealed with Teflon tape, and the reaction stirred at room temperature for 60 min. Excess KPF_6 was added to precipitate the product, which was collected and washed with water then dried in vacuo.

4a. Yield 93%; mp 228−230 °C dec. ^{1}H NMR (acetone-d_6, 300 MHz): δ 9.35 (br s, 2H, H_a), 8.95 (br s, 2H, H_b), 8.17 (d, ^3J = 8.1 Hz, 2H, H_d), 8.07 (d, ^3J = 8.0 Hz, 4H, H_e or H_f), 7.76 (t, ^3J = 6.4 Hz, 2H, H_c), 7.64 (d, ^3J = 8.2 Hz, 4H, H_f or H_e), 2.10 (m, 24H, PCH_2), 1.33 (m, 36H, PCH_2CH_3). ^{31}P{^{1}H} NMR (acetone-d_6, 121 MHz): δ 7.20 (d, $^2J_{P-P}$ = 21.2 Hz, ^{195}Pt satellites $^1J_{Pt-P}$ = 3259 Hz, PCH_2CH_3), 2.47 (d, $^2J_{P-P}$ = 21.3 Hz,^{195}Pt satellites $^1J_{Pt-P}$ = 3447 Hz, PCH_2CH_3), −142.3 (septet, $^1J_{P-F}$ = 707 Hz, PF_6^-). Anal. Calcd for $C_{48}H_{76}F_{12}N_2O_4P_6Pt_2\cdot H_2O$: C, 36.79; H, 5.02; N, 1.79. Found: C, 36.57; H, 4.93; N, 1.64.

4b. Yield 96%; mp 198−202 °C dec. ^{1}H NMR (acetone-d_6, 300 MHz): δ 9.08 (br s, 2H, H_a), 9.04 (br s, 2H, H_b), 8.18 (d, ^3J = 6.9 Hz, 2H, H_d), 7.74−7.86 (m, 6H, H_c, H_e or H_f), 7.47 (m, 4H, H_e or H_f), 2.10 (m, 24H, PCH_2), 1.33 (m, 36H, PCH_2CH_3). ^{31}P{^{1}H} NMR (acetone-d_6, 121 MHz): δ 7.10 (d, $^2J_{P-P}$ = 21.0 Hz, ^{195}Pt satellites $^1J_{Pt-P}$ = 3259 Hz, PCH_2CH_3), 1.59 (d, $^2J_{P-P}$ = 21.0 Hz,^{195}Pt satellites $^1J_{Pt-P}$ = 3440 Hz, PCH_2CH_3), −142.3 (septet, $^1J_{P-F}$ = 707 Hz, PF_6^-). Anal. Calcd for $C_{52}H_{76}F_{12}N_2O_4P_6Pt_2\cdot H_2O$: C, 38.67; H, 4.87; N, 1.73. Found: C, 38.58; H, 4.77; N, 1.67.

5. Yield 94%; mp 204−208 °C dec. ^{1}H NMR (acetone-d_6, 300 MHz): δ 9.61 (br s, 2H, H_a), 8.92 (m, 2H, H_b), 8.59 (s, 2H, H_e), 8.23 (d, ^3J = 8.1 Hz, 2H, H_d), 7.83 (m, 4H, H_f and H_h), 7.74 (dd, ^3J = 7.9 Hz, ^3J = 5.7 Hz, 2H, H_c), 7.49 (t, ^3J = 7.7 Hz, 2H, H_g), 2.17 (m, 24H, PCH_2), 1.39 (m, 36H, PCH_2CH_3). ^{31}P{^{1}H} NMR (acetone-d_6, 121 MHz): δ 6.74 (d, $^2J_{P-P}$ = 21.2 Hz, ^{195}Pt satellites $^1J_{Pt-P}$ = 3262 Hz, PCH_2CH_3), 2.18 (d, $^2J_{P-P}$ = 21.2 Hz,^{195}Pt satellites $^1J_{Pt-P}$ = 3470 Hz, PCH_2CH_3), −142.7 (septet, $^1J_{P-F}$ = 707 Hz, PF_6^-). Anal. Calcd for $C_{48}H_{76}F_{12}N_2O_4P_6Pt_2\cdot 2H_2O$: C, 36.37; H, 5.09; N, 1.77. Found: C, 36.25; H, 4.94; N, 1.83.

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Supporting Information Available: NMR and mass spectral data for assemblies **4b** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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