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Ambidentate Pyridyl-carboxylate Ligands in the Coordination-Driven Self-Assembly of 2D Pt Macrocycles: Self-Selection for a Single Isomer

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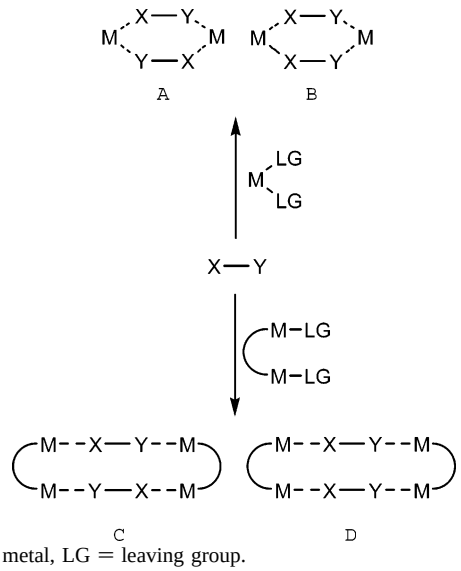
Abstract: The coordination-driven self-assembly of discrete 2D macrocyclic species from ambidentate pyridyl-carboxylate-based donor ligands and platinum-containing acceptors is presented. All these species are characterized by electrospray ionization mass spectrometry (ESIMS), multinuclear NMR, and in one example, X-ray crystallography. In each case only one isomeric assembly is selectively formed in high yield, despite the potential for more than one product as a consequence of differences in connectivity.

Introduction

The rational design and self-assembly of large discrete supramolecules from simple precursors has been extensively studied.[1−12] In particular, the coordination bonding motif of pyridyl-based ligands with platinum and palladium acceptors has proven very useful for constructing a wide array of architectures. Recently, rigid oxygen donor linkers were incorporated into neutral 2D Pt-containing macrocycles.[13,14] Most assemblies prepared to date are highly symmetrical in nature as they are built from simple homodi- and tridentate pyridine-containing donors and metal acceptors. In fact, we are aware of only one example of a molecular square incorporating an ambidentate ligand, 4-isonicotinate (**1a**).[15] The hydrogen-bond-mediated self-assembly of discrete and polymeric arrays from bis-platinum complexes containing nicotinamide and nicotinic and isonicotinic acids was also reported recently.[16] The chemistry of some elongated derivatives of **1a**, namely sodium 4-(4-pyridyl)benzoate (**1b**), potassium 4-(4-pyridylethynyl)benzoate (**1c**), and their free acids, is limited to studies on crystal engineering,[17] supramolecular self-assembly on metal surfaces,[18,19] and amorphous glass substrates in high vacuum.[20] One problem inherent in the design of lower symmetry discrete self-assembled species containing this type of ligand is the possibility of linkage isomerism. The result is a larger number of potential products, constitutional isomers that differ only in connectivity. The simplest approach is the combination of an ambidentate ligand (X−Y) with a homotopic bidentate acceptor in a 1:1 ratio (Scheme 1), where only two cyclic products (**A**/**B** or **C**/**D**) are possible in each case.

Scheme 1. Combination of Bidentate Metal Acceptors with Ambidentate Ligand X−Y Can Give Isomeric Cyclic Products **A**−**D**[a]



[a] M = metal, LG = leaving group.

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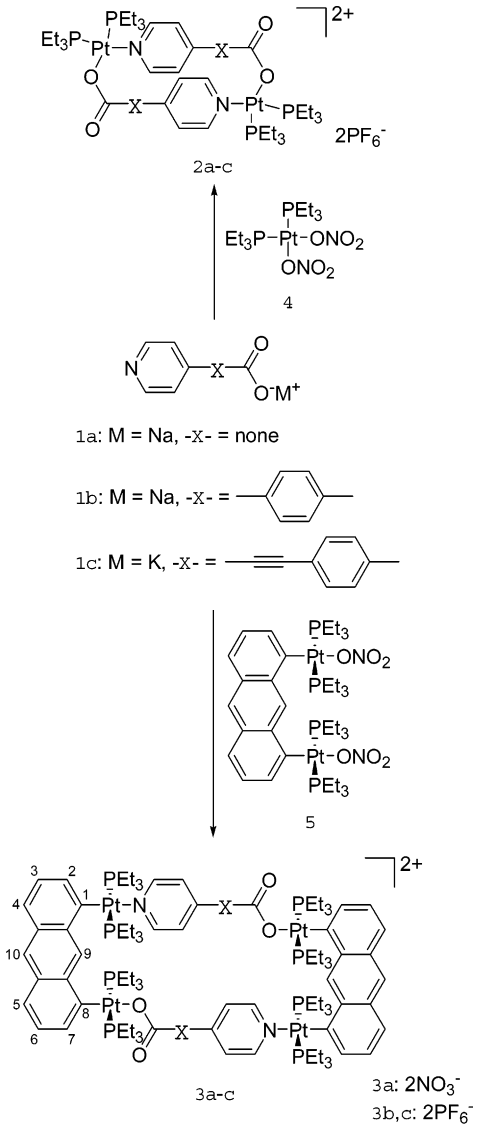
Scheme 2. Self-Assembly of Pyridyl-carboxylates **1** with 90° Linker **4** and Clip **5**



We were interested in the self-assembly outcome between ambidentate ligands **1** and platinum-containing acceptors **4** and **5** (shown in Scheme 2). Particularly interesting is the question of self-recognition and self-selection for one or the other of the two possible constitutional isomers. Herein we report that, despite the possibility of product mixtures, essentially a single ensemble is formed in high yield in each case.

Results and Discussion

The self-assembly processes were all performed in the same general manner. A 1:1 acetone-d_6/D_2O solution of ligand **1** and a particular organoplatinum **4** or **5** was either stirred at room temperature (**4**) or heated at 60 °C (**5**) for up to 2.5 h, followed by anion exchange with KPF_6 (except **3a**) to precipitate the products **2** and **3** in high yield.

NMR spectroscopy was initially used to characterize the ensembles. The $^{31}P\{^1H\}$ NMR spectra of **2** displayed two coupled doublets (**2a**, 6.65, 2.05 ppm, $^2J_{P-P} = 21.2$ Hz; **2b**, 6.79, 1.84 ppm, $^2J_{P-P} = 21.6$ Hz, Figure 1; **2c**, 7.47, 2.15 ppm, $^2J_{P-P} = 21.4$ Hz) of approximately equal intensity with concomitant ^{195}Pt satellites. The signals near 2 ppm are shifted approximately 4 ppm upfield relative to **4** 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 a large ^{31}P chemical shift change. Assemblies **2**, which are representative of topology **A** (Scheme 1), contain two inequivalent (and thus coupled) phosphorus nuclei bound to the same platinum atom. This is consistent with our data. The other possible macrocyclic product **B** also possesses two inequivalent phosphorus nuclei; these are bound to different platinum atoms. The $^{31}P\{^1H\}$ NMR spectrum of this species would show two *uncoupled* signals with shifts and intensities similar to what is observed. In the ^1H NMR spectra of **2**, a multiplet near 8.9 ppm for the pyridine hydrogens adjacent to the nitrogen nucleus is shifted approximately 0.5 ppm to lower field relative to **1**, consistent with the loss of electron density that occurs upon coordination.

The $^{31}P\{^1H\}$ NMR spectra of **3** gave two sharp singlets (**3a**, 12.77, 7.38 ppm; **3b**, 13.00, 8.00 ppm; **3c**, 12.43, 7.70 ppm) of equal intensity with concomitant ^{195}Pt satellites. The upfield shift of the signals near 8 ppm relative to **5** shows they are bound to the platinum nucleus coordinated to the pyridine rings. In this case, the ^{31}P NMR data are insufficient for distinguishing the products **3** (topology **C** in Scheme 1) from their isomeric relatives **D**. This problem was initially solved by examination of the ^1H NMR spectra. One unique feature of assemblies **3** is the presence of an inversion center in the middle of the molecule. Consequently, **3** has only one type of H_9 and H_{10} anthracene proton nuclei, while isomer **D** has two types. The ^1H NMR spectrum reveals one signal each for H_9 (**3a**, 9.83 ppm; **3b**, 10.06 ppm; **3c**, 9.95 ppm, Figure 2) and H_{10} (**3a**, 8.31 ppm; **3b**, 8.39 ppm, part of multiplet; **3c**, 8.38 ppm). Given the sharpness of these signals and good spectral resolution, we are confident they do *not* represent an accidental equivalence of both H_9 and H_{10} nuclei for isomer **D**. Two sets of doublets corresponding to the pyridyl hydrogens highlighted the restricted rotation of these rings once the macrocycle is formed, thus creating different inner and outer environments, consistent with previous observations in related systems.[21]

X-ray crystallography confirmed that the NMR assignment of **3** was indeed topology **C**. Diffraction-quality single crystals of **3a** were grown by vapor diffusion of hexane into a chloroform solution of the assembly. Crystallographic data and refinement parameters are listed in Table 1. Although the isonicotinate moieties show significant disorder in the rectangle **3a**, there is no doubt as to their head-to-tail orientation (Figure 3a). Three molecules of disordered $CHCl_3$ per unit cell were also found.

The packing pattern of **3a** in the solid state is also shown in Figure 3. When viewed along the *b* axis (Figure 3b), the isonicotinate moieties from neighboring rectangles are superimposed and are separated by 14.8 Å. A system of channels is also obvious. One nitrate anion is located halfway between the charged platinum nuclei of two adjacent ensembles, while the other can be found in the middle of each channel. The assemblies are arranged in an intercalating fashion so that the closest anthracene groups are approximately 8.7 Å apart. Each individual rectangle shows significant deviation from planarity (Figure 3c).

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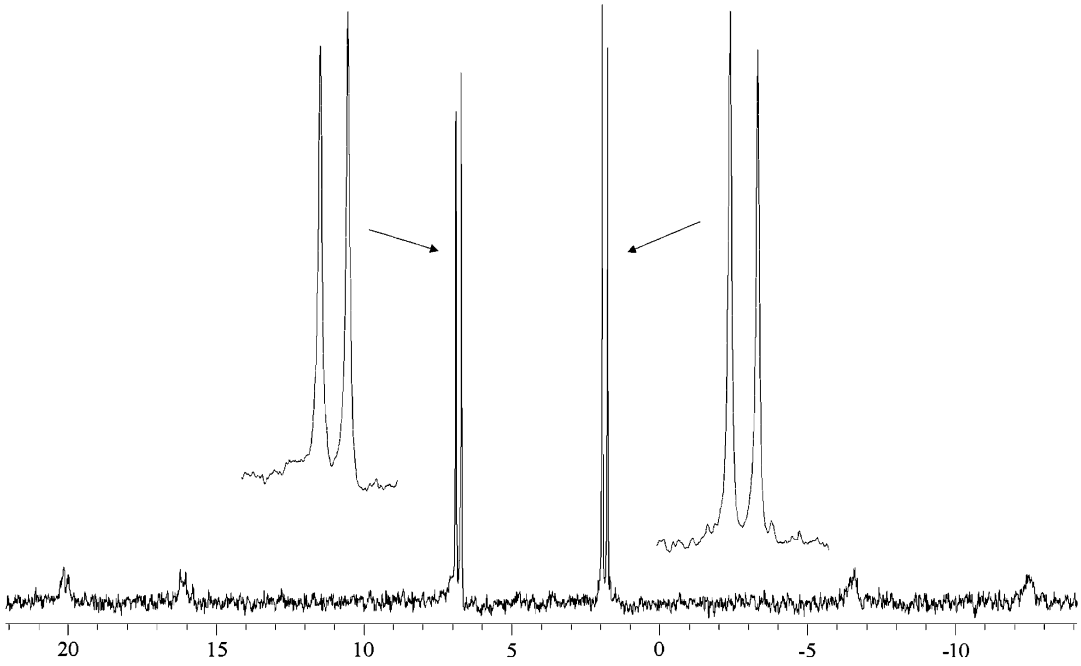

Figure 1. ^{31}P NMR spectrum of **2b**.

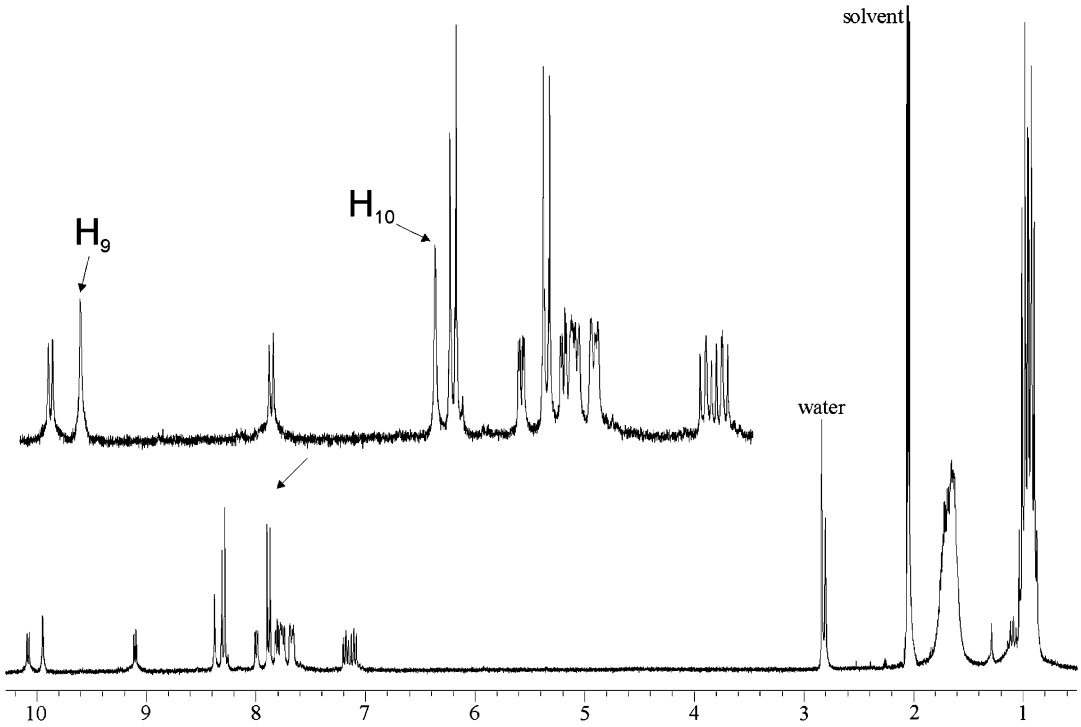

Figure 2. ^{1}H NMR spectrum of **3c**.

Further evidence for the structures of **2** and **3** was obtained with electrospray ionization mass spectrometry (ESIMS). Ensembles **2a**,**b** and **3a**,**b** were analyzed as their nitrate salts, whereas **2c** and **3c** were analyzed as the hexafluorophosphate salts after anion exchange. For **2**, peaks were observed corresponding to the intact structure minus one counterion: [**2a** − NO_3^-]$^+$ (*m*/*z* 1169), [**2b** − NO_3^-]$^+$ (*m*/*z* 1321), and [**2c** − PF_6^-]$^+$ (*m*/*z* 1451). In the case of **3**, peaks were found attributable to the consecutive loss of counterions: [**3a** − NO_3^-]$^+$ (*m*/*z* 2384), [**3a** − $2NO_3^-$]$^{2+}$ (*m*/*z* 1161); [**3b** − NO_3^-]$^+$ (*m*/*z* 2535), [**3b** − $2NO_3^-$]$^{2+}$ (*m*/*z* 1237); and [**3c** − PF_6^-]$^+$ (*m*/*z* 2666, Figure 4), [**3c** − $2PF_6^-$]$^{2+}$ (*m*/*z* 1261). These were all isotopically resolved and are in excellent agreement with their theoretical distributions.

All reactions gave one predominant species with few minor byproducts evident in the NMR spectra. There are two small peaks (<5%) near 14 and 9 ppm in the $^{31}P\{^1H\}$ NMR spectra of **3** which we were unable to assign. Their sharp appearance suggests they are not oligomeric in nature. They may belong to isomeric assembly **D**.

Formation of isomer **B** is highly unfavorable with regard to strain energy. The ideal N−Pt−N bond angle is approximately

Table 1. Crystallographic Data and Refinement Parameters for **3a**

formula	$C_{91}H_{147}Cl_9N_4O_{10}P_8Pt_4$
formula weight	2804.30
temp (K)	150(1)
λ (Å)	0.71073
crystal system	triclinic
space group	$P\bar{1}$
a (Å)	13.1654(2)
b (Å)	14.8448(2)
c (Å)	16.6288(3)
α (deg)	70.9567(6)
β (deg)	69.6170(7)
γ (deg)	74.8414(14)
V (Å^3)	2839.31(8)
Z	1
D_{calc} (g/cm^3)	1.640
μ (mm^{-1})	5.287
F(000)	1386
reflections collected	20964
independent reflections	13409
max and min trans	0.4178 and 0.2999
$R1$ [$I > 2\sigma(I)$]	0.0815
w$R2$	0.2272

90°. Due to the rigidity of **1**, this angle, or anything close to it, is virtually impossible to obtain in the closed system **B**. We illustrate this by using the MM2 force field simulation[22] to optimize some intermediates which may be involved in the formation of **2b** and its isomer **B** (Figure 5). Structures **E** and **F** are precursors to **B**. They are formed when 2 equiv of **1b** bond to a single platinum atom via their pyridyl (**E**) or carboxyl (**F**) termini. The largest distance between the carboxyl oxygen atoms is 14.7 Å in the case of **E**, while in **F** 7.5 Å separates the pyridine nitrogens. The analogous gap in **G** (with one pyridyl and one carboxyl group bound to the same platinum) is only 4.5 Å. Our experimental results show that in these systems closed structures are preferred over oligomers. Of the three intermediates **E**−**G**, **G** has the best arrangement of uncoordinated termini to form a closed macrocycle upon reaction with a second platinum center and does not experience the same repulsive forces that presumably occur in **E** and **F** as two ends of similar polarity approach each other in space. Charge distribution is also a factor in the orientation **1b** adopts as it approaches an intermediate structure comprised of a single unit of **1b** spanning two platinum nuclei. In this case, the head-to-tail orientation of the **1b** units (topology **A**) maximizes the charge separation as the closed assembly **2b** forms. We believe these intermediate geometries and polarity considerations are the major reasons why **2** is selectively formed instead of **B**. Clearly, the formal charge of 1+ on the pyridine nitrogens is more widely separated in the closed macrocycles **2** and **3** than in their isomers **B** and **D**.

Several unsuccessful attempts were made at synthesizing open-chain intermediates **E** and **F** to examine the possible stepwise formation of products. When **4** was reacted with **1b** (either 2.2 equiv or in excess), ill-defined product mixtures resulted (NMR) from which no simple product could be isolated. This was also true when the free acid of **1b** (M = H$^+$) was used. Reaction of clip **5** with **1b** (similar stoichiometries) resulted in polymer formation. However, when excess free acid **1b** (M = H$^+$) was used, the ^{31}P{^{1}H} NMR spectrum displayed one predominant peak at 8.8 ppm consistent with an open-chain structure composed of one clip **5** with two pyridine-bound ligands **1b**. Unfortunately, the workup was complicated by excess **1b** (M = H$^+$) and decomposition of the product before it could be isolated.

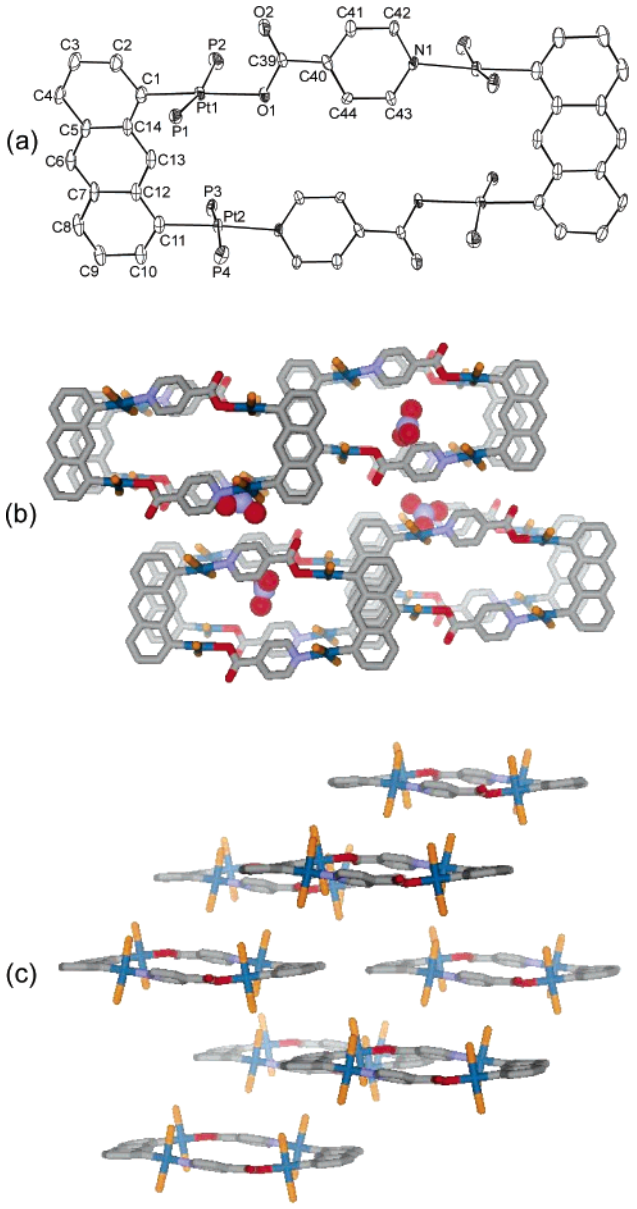

Figure 3. (a) ORTEP drawing (30% probability ellipsoids) of **3a**. (b) Packing diagram when viewed along the b axis. (c) Another orientation highlights the nonplanarity of each ensemble. Solvent molecules, hydrogen atoms, and the phosphine ethyl groups are omitted from all illustrations for clarity. Nitrate anions are shown in (b) only as CPK models.

In conclusion, we have prepared discrete macrocycles **2** and **3** from ambidentate donor ligands **1** and platinum-containing acceptors **4** and **5**. Despite the possibility of forming multiple products that differ only in connectivity, ambidentate ligands **1** and acceptors **4** and **5** prefer to self-assemble predominantly into one closed species. They are another important example of the relatively few discrete supramolecules made from ambidentate ligands via coordination-driven transition-metal-mediated self-assembly. These results also provide further insights into the coordination driven self-assembly process. Moreover, they demonstrate that ambidentate ligands can be used in the self-assembly of discrete metallacycles with some

(22) *CS Chem3D Ultra 7.0.0*; CambridgeSoft Corp., 2001.

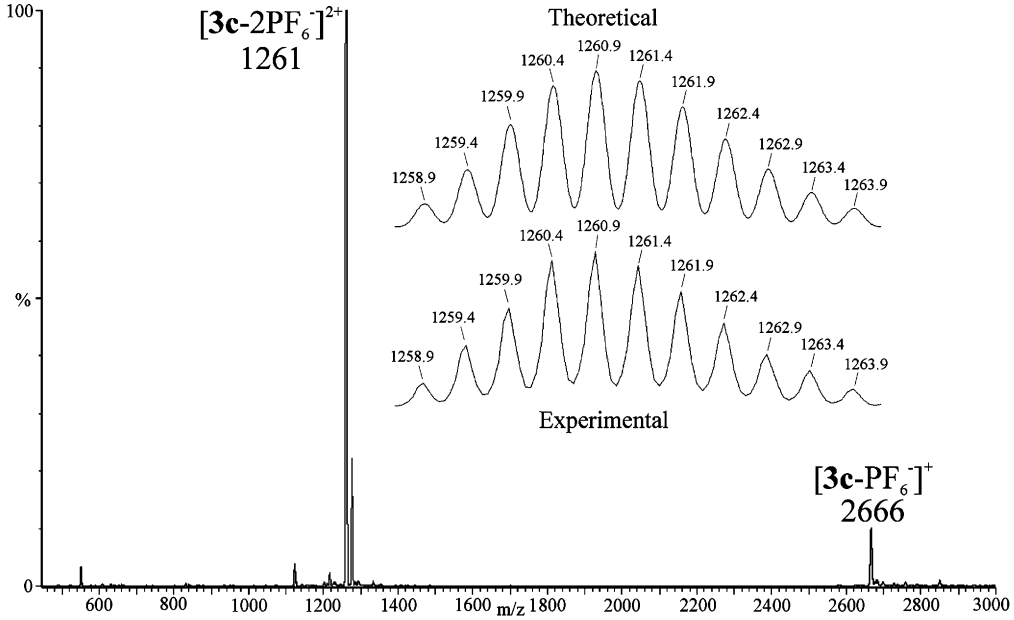

Figure 4. ESIMS of **3c**.

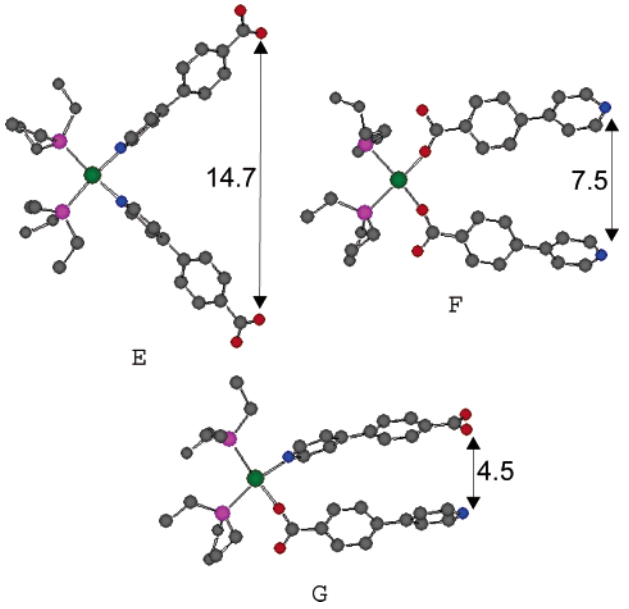

Figure 5. Possible intermediates leading to **2b** optimized with the MM2 force field simulation.[22] All distances are in Å. Atom key: green, Pt; pink, P; blue, N; red, O; gray, C. Hydrogens are omitted for clarity.

predictability as a consequence of preferred self-recognition due to charge separation as well as strain.

Experimental Section

Methods and Materials. Isonicotinic acid was purchased from Aldrich. The free acid of **1c**[20] was synthesized by the published procedure. These acids were dissolved in an aqueous solution containing 1 equiv of the appropriate alkali metal hydroxide. Evaporation of the solvent afforded a quantitative recovery of **1**. Ligand **1b**[23] and organoplatinum compounds **4**[24] and **5**[21] were prepared as reported. Deuterated solvents were purchased from Cambridge Isotope Laboratories. All NMR spectra were recorded on a Varian Unity 300 spectrometer. ^{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. ESI mass spectra were recorded on a Micromass Quattro II triple-quadrupole mass spectrometer with Micromass MassLynx operating system. Elemental analyses were performed by Atlantic Microlab, Norcross, GA.

X-ray Data Collection, Structure Solution, and Refinement. A yellow prism-shaped crystal of **3a** (0.30 × 0.25 × 0.20 mm) was mounted on a glass fiber with traces of viscous oil and then transferred to a Nonius KappaCCD diffractometer equipped with Mo Kα radiation (λ = 0.71073 Å). Ten frames of data were collected at 150(1) K with an oscillation range of 1 deg/frame and an exposure time of 20 s/frame.[25] Indexing and unit cell refinement were based on all observed reflection from those 10 frames. The structure was solved by a combination of direct and heavy-atom methods using SIR 97.[26] All of the non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were assigned isotropic displacement coefficients U(H) = 1.2U(C) or 1.5U(Cmethyl), and their coordinates were allowed to ride on their respective carbons using SHELXL97.[27] The weighting scheme employed was $w = 1/[\sigma^2(F_o^2) + (0.1462P)^2 + 26.9617P]$, where $P = (F_o^2 + 2F_c^2)/3$. Scattering factors were taken from the *International Tables for Crystallography*, Volume C.[28,29] The disordered assembly is sitting on an inversion center.

General Procedure for the Preparation of Assemblies 2 and 3. The platinum acceptor (**4**, 9 μmol; **5**, 5 μmol) and ambidentate ligand **1** (1 equiv) 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 2 h (**4**) or heated in an oil bath at 60 °C for 2.5 h (**5**). NMR spectroscopy was used to follow the progress of the reaction. In all cases (except **3a**) excess KPF_6 was added

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to precipitate the product, which was collected, washed with water, and then dried in vacuo.

2a: yield 92%; ^{1}H NMR (acetone-d_6/D_2O, 300 MHz) δ 8.89 (m, 4H, $H_{\alpha-Py}$), 7.79 (m, 4H, $H_{\beta-Py}$), 1.98 (m, 24H, PCH_2), 1.26 (m, 36H, PCH_2CH_3); ^{31}P{^{1}H} NMR (acetone-d_6/D_2O, 121 MHz) δ 6.65 (d, $^2J_{P-P}$ = 21.2 Hz, ^{195}Pt satellites $^1J_{Pt-P}$ = 3208 Hz, PCH_2CH_3), 2.05 (d, $^2J_{P-P}$ = 21.3 Hz,^{195}Pt satellites $^1J_{Pt-P}$ = 3511 Hz, PCH_2CH_3), −142.7 (septet, $^1J_{P-F}$ = 707 Hz, PF_6^-). Anal. Calcd for $C_{36}H_{68}F_{12}N_2O_4P_6Pt_2$: C, 30.95; H, 4.91; N, 2.01. Found: C, 31.06; H, 5.00; N, 2.02.

2b: yield 97%; ^{1}H NMR (acetone-d_6, 300 MHz) δ 8.93 (m, 4H, $H_{\alpha-Py}$), 7.95 (d, ^3J = 5.8 Hz, 4H, $H_{\beta-Py}$), 7.81 (d, ^3J = 8.6 Hz, 4H, H_{phenyl}), 7.75 (d, ^3J = 8.6 Hz, 4H, H_{phenyl}), 2.06 (m, 24H, PCH_2), 1.33 (m, 36H, PCH_2CH_3); ^{31}P{^{1}H} NMR (acetone-d_6, 121 MHz) δ 6.79 (d, $^2J_{P-P}$ = 21.6 Hz, ^{195}Pt satellites $^1J_{Pt-P}$ = 3238 Hz, PCH_2CH_3), 1.84 (d, $^2J_{P-P}$ = 21.3 Hz, ^{195}Pt satellites $^1J_{Pt-P}$ = 3468 Hz, PCH_2CH_3), −142.7 (septet, $^1J_{P-F}$ = 707 Hz, PF_6^-). Anal. Calcd for $C_{48}H_{76}F_{12}N_2O_4P_6Pt_2$: C, 37.22; H, 4.95; N, 1.81. Found: C, 37.57; H, 5.09; N, 1.73.

2c: yield 95%; ^{1}H NMR (acetone-d_6, 300 MHz) δ 8.97 (m, 4H, $H_{\alpha-Py}$), 7.79 (m, 4H, H_{phenyl}), 7.71 (dd, ^3J = 6.7 Hz, ^4J = 1.0 Hz, 4H, $H_{\beta-Py}$), 7.51 (m, 4H, H_{phenyl}), 2.05 (m, 24H, PCH_2), 1.32 (m, 36H, PCH_2CH_3); ^{31}P{^{1}H} NMR (acetone-d_6, 121 MHz) δ 7.47 (d, $^2J_{P-P}$ = 21.4 Hz, ^{195}Pt satellites $^1J_{Pt-P}$ = 3228 Hz, PCH_2CH_3), 2.15 (d, $^2J_{P-P}$ = 21.5 Hz,^{195}Pt satellites $^1J_{Pt-P}$ = 3446 Hz, PCH_2CH_3), −142.7 (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, 38.44; H, 4.79; N, 1.67.

3a: yield 94%; ^{1}H NMR (acetone-d_6/D_2O, 300 MHz) δ 9.83 (s, 2H, H_9), 9.72 (d, ^3J = 5.5 Hz, 2H, $H_{\alpha-Py}$), 9.18 (d, ^3J = 5.4 Hz, 2H, $H_{\alpha'-Py}$), 8.38 (m, 4H, $H_{\beta-Py}$), 8.31 (s, 2H, H_{10}), 7.69−7.59 (m, 8H, $H_{2,4,5,7}$), 7.13 (t, ^3J = 6.9 Hz, 2H, H_3 or H_6), 7.06 (t, ^3J = 6.9 Hz, 2H, H_6 or H_3), 1.51 (m, 48H, PCH_2), 0.87 (m, 72H, PCH_2CH_3); ^{31}P{^{1}H} NMR (acetone-d_6/D_2O, 121 MHz) δ 12.77 (s, ^{195}Pt satellites, $^1J_{Pt-P}$ = 2855 Hz, COO−Pt−PCH_2CH_3), 7.38 (s, ^{195}Pt satellites, $^1J_{Pt-P}$ = 2686 Hz, Py−Pt−PCH_2CH_3). Anal. Calcd for $C_{88}H_{144}N_4O_{10}P_8Pt_4 \cdot 3H_2O$: C, 42.27; H, 6.05; N, 2.24. Found: C, 42.04; H, 5.75; N, 2.21.

3b: yield 93%; ^{1}H NMR (acetone-d_6, 300 MHz) δ 10.06 (s, 2H, H_9), 9.96 (d, ^3J = 6.1 Hz, 2H, $H_{\alpha-Py}$), 9.14 (d, ^3J = 5.8 Hz, 2H, $H_{\alpha'-Py}$), 8.39 (m, 8H, $H_{\beta-Py}$, H_{10} and H_{phenyl}), 8.03 (d, ^3J = 8.3 Hz, 4H, H_{phenyl}), 7.92 (d, ^3J = 6.2 Hz, 2H, $H_{\beta'-Py}$), 7.78−7.67 (m, 8H, $H_{2,4,5,7}$), 7.19 (t, ^3J = 7.6 Hz, 2H, H_3 or H_6), 7.12 (t, ^3J = 7.6 Hz, 2H, H_6 or H_3), 1.68 (m, 48H, PCH_2), 0.98 (m, 72H, PCH_2CH_3); ^{31}P{^{1}H} NMR (acetone-d_6, 121 MHz) δ 13.00 (s, ^{195}Pt satellites, $^1J_{Pt-P}$ = 2910 Hz, COO−Pt−PCH_2CH_3), 8.00 (s, ^{195}Pt satellites, $^1J_{Pt-P}$ = 2699 Hz, Py−Pt−PCH_2CH_3), −142.7 (septet, $^1J_{P-F}$ = 707 Hz, PF_6^-). Anal. Calcd for $C_{100}H_{152}F_{12}N_2O_4P_{10}Pt_4$: C, 43.45; H, 5.54; N, 1.01. Found: C, 43.21; H, 5.53; N, 0.96.

3c: yield 97%; ^{1}H NMR (acetone-d_6, 300 MHz) δ 10.08 (d, ^3J = 5.7 Hz, 2H, $H_{\alpha-Py}$), 9.95 (s, 2H, H_9), 9.10 (d, ^3J = 5.7 Hz, 2H, $H_{\alpha'-Py}$), 8.38 (s, 2H, H_{10}), 8.30 (m, 4H, H_{phenyl}), 8.00 (dd, ^3J = 5.7 Hz, ^4J = 1.8 Hz, 2H, $H_{\beta-Py}$), 7.88 (m, 4H, H_{phenyl}), 7.81 (dd, ^3J = 5.7 Hz, ^4J = 1.8 Hz, 2H, $H_{\beta'-Py}$), 7.76−7.67 (m, 8H, $H_{2,4,5,7}$), 7.18 (dd, ^3J = 8.2 Hz, ^3J = 7.0 Hz, 2H, H_3 or H_6), 7.11 (dd, ^3J = 8.0 Hz, ^3J = 6.8 Hz, 2H, H_6 or H_3), 1.67 (m, 48H, PCH_2), 0.95 (m, 72H, PCH_2CH_3); ^{31}P{^{1}H} NMR (acetone-d_6, 121 MHz) δ 12.43 (s, ^{195}Pt satellites, $^1J_{Pt-P}$ = 2915 Hz, COO−Pt−PCH_2CH_3), 7.70 (s, ^{195}Pt satellites, $^1J_{Pt-P}$ = 2695 Hz, Py−Pt−PCH_2CH_3), −142.7 (septet, $^1J_{P-F}$ = 707 Hz, PF_6^-). Anal. Calcd for $C_{104}H_{152}F_{12}N_2O_4P_{10}Pt_4 \cdot H_2O$: C, 44.13; H, 5.48; N, 0.99. Found: C, 43.88; H, 5.44; N, 0.97.

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Supporting Information Available: NMR and mass spectral data for assemblies **2** nd **3** (PDF); X-ray crystallographic data of **3a** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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