Inorg. Chem. **2004**, *43*, 5335–5338

Inorganic Chemistry
Article

Self-Recognition in the Coordination Driven Self-Assembly of 2-D Polygons

Chris Addicott,* Neeladri Das, and Peter J. Stang*

Department of Chemistry, University of Utah, 315 South 1400 East, Salt Lake City, Utah 84112

Received May 24, 2004

Self-recognition in the transition-metal-mediated self-assembly of some 2-D polygons is presented. Prolonged heating of two or three organoplatinum reagents with 4,4′-dipyridyl in aqueous acetone results in the predominant formation of a rectangle, triangle, and/or square. All mixtures are characterized with NMR and electrospray ionization mass spectrometry (ESIMS). Despite the potential for ill-defined oligomeric products, these mixed ligand systems prefer to self-assemble into discrete species.

Introduction

The preparation of numerous, discrete 2- and 3-D supramolecular complexes via coordination-driven self-assembly has been achieved in the past decade.[1−12] This was often accomplished by the combination of an organic donor with a metal acceptor, where one or both reagents possessed well-defined bonding directionality leading to a single, highly symmetrical product. A more complex situation in self-assembly arises when more than two starting materials are mixed together in one vessel. Will an ordered system of discrete supramolecules or an oligomeric product mixture result?

In 1993, Lehn and co-workers[13] found that mixing several oligo-bipyridine strands containing different numbers of binding sites with Cu(II) ions resulted in the selective formation of double helicates without significant crossover. They also showed that a double and triple helicate were exclusively formed from a mixture of Cu(I) and Ni(II) ions and two differently substituted tris-bipyridine ligands. Another self-recognition phenomenon based on the distance between two coordination sites within a ligand was later observed by Raymond[14] in the preparation of homoleptic helicates from a bis(catecholamide) ligand mixture and Ga(III) ions. Since then, more reports of self-recognition in helicate systems have appeared based on flexible catecholic ligands[15] and alkali metals.[16] Enantiomeric self-recognition processes in which homochiral tetrahedral clusters[17] and simpler M_2L_2 supramolecules[18−20] are formed from racemic ligands and transition metals have also been reported.

To date many of the systems reported have been 3-D in nature. They generally contain building blocks which are more restricted in bonding directionality and/or flexibility (relative to 2-D ensembles), lessening the likelihood of open-chained products. Herein, we report on our own self-recognition observations in the self-assembly of 2-D supramolecular polygons from 4,4′-dipyridyl and mixtures of organoplatinum acceptors [Scheme 1]. Despite the possibility for open chain oligomers, we demonstrate that closed macrocycles containing one type of organoplatinum material are strongly preferred.

Results and Discussion

When molecular clip **1**, phenanthrene linker **2**, and 4,4′-dipyridyl **4** are combined in a 2:3:5 ratio and heated at 55−60 °C for 123 h in aqueous acetone, rectangle **5** and triangle

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* To whom correspondence should be addressed. E-mail: stang@chem.utah.edu; addicot@chem.utah.edu (C.A.).

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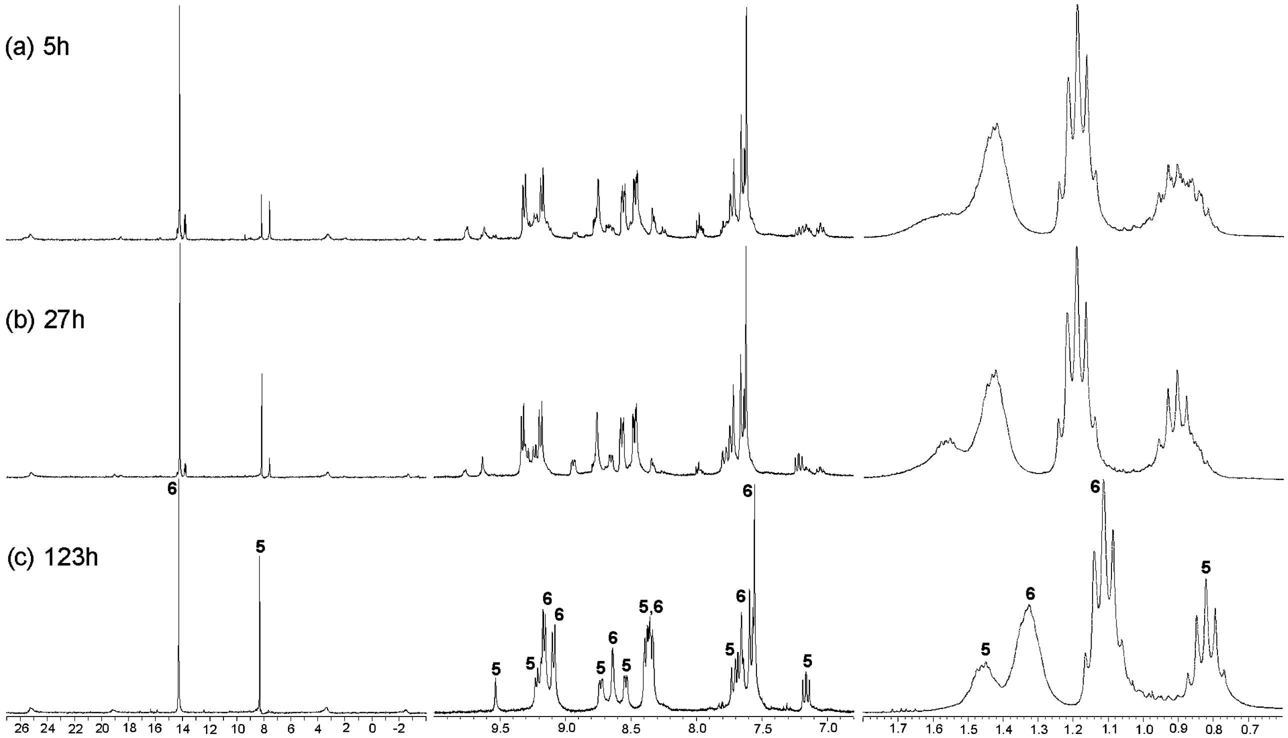
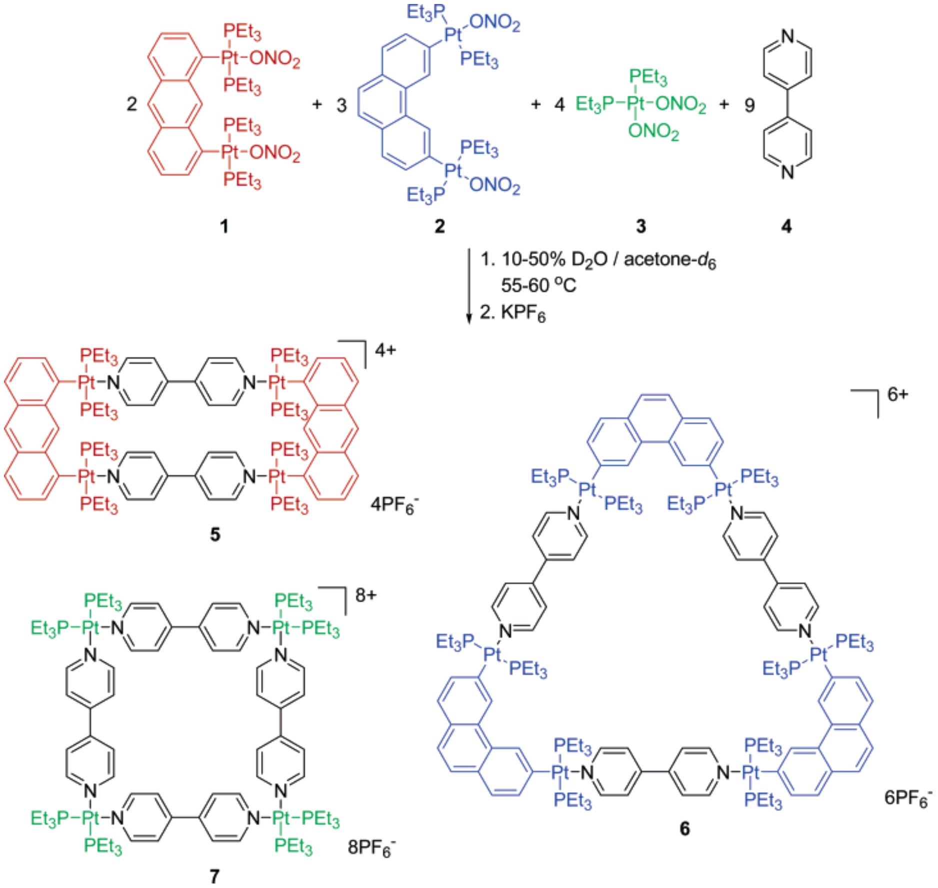


Figure 1. $^{31}P\{^1H\}$ (left) and ^1H (center and right) NMR spectra recorded at various time intervals during the formation of rectangle **5** and triangle **6**.

Scheme 1. Combination of Organoplatinum Linkers **1**−**3** with 4,4′-bipyridine **4** Leads to Discrete Polygons **5**−**7**



6 are the sole products formed [reaction A, Table 1]. NMR spectroscopy was used to follow the self-assembly progress. After 5 h, the $^{31}P\{^1H\}$ spectrum shows peaks at 8.28 and 14.29 ppm with concomitant ^{195}Pt satellites for the nitrate salts of **5** and **6**, respectively [Figure 1a]. Both are flanked by unassignable resonances which slowly disappear upon extended heating [Figure 1c]. The ^1H spectra also simplify during this time. Anion exchange with KPF_6 affords the

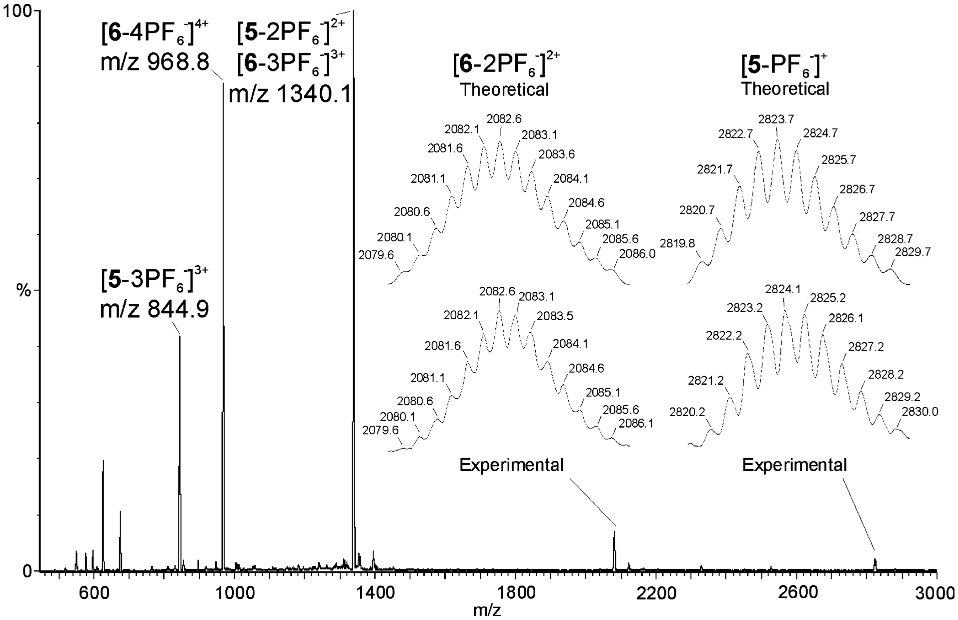


Figure 2. ESIMS of reaction A product mixture containing **5** and **6**.

Table 1. Building Block Combinations and Their Respective Products

reaction	building blocks		products
A	**1** + **2** + **4**	→	**5** + **6**
B	**1** + **3** + **4**	→	**5** + **7**
C	**2** + **3** + **4**	→	**6** + **7**
D	**1** + **2** + **3** + **4**	→	**5** + **6** + **7**

assemblies as hexafluorophosphate salts, the ESI mass spectrum of which is shown in Figure 2. Isotopically resolved peaks of the intact macrocycles centered at *m/z* 2824.1 [**5** − PF_6^-]$^+$ and *m/z* 2082.6 [**6** − $2PF_6^-$]$^{2+}$ confirm the structure of each polygon. Larger peaks at *m/z* 1340.1 ([**5** − $2PF_6^-$]$^{2+}$ and [**6** − $3PF_6^-$]$^{3+}$), *m/z* 968.8 [**6** − $4PF_6^-$]$^{4+}$, and *m/z* 844.9 [**5** − $3PF_6^-$]$^{3+}$ were also assigned.

Heating **1**, **3**, and **4** in a 2:4:6 ratio under similar conditions results in rectangle **5** and square **7** as the major products [reaction B]. The $^{31}P\{^1H\}$ spectrum [Figure S1] displays two large peaks at 8.31 (**5**) and 1.59 ppm (**7**). Smaller peaks near 9.70, 7.70, and 1.20 ppm remain even after prolonged heating. The latter was reduced in intensity upon PF_6^- exchange and 7.70 ppm disappeared. In the ^1H spectrum [Figure S2], well-defined sets of resonances for **5** and **7** are observed among minor amounts of impurity in the aromatic region. The mass spectrum [Figure S3] exhibits peaks corresponding to the consecutive loss of PF_6^- ions from **5**: *m/z* 2824.1 [**5** − PF_6^-]$^+$, *m/z* 1340.1 [**5** − $2PF_6^-$]$^{2+}$, and *m/z* 844.9 [**5** − $3PF_6^-$]$^{3+}$. Evidence for square **7** is shown by a weaker, but isotopically resolved, peak at *m/z* 1024.8 assigned to [**7** − $3PF_6^-$]$^{3+}$.

Triangle **6** and square **7** are the predominant products formed from a mixture of **2**, **3**, and **4** in a 3:4:7 ratio [reaction C]. Both NMR spectra show only minor impurities [Figures S4−S5] and could be partially improved after PF_6^- anion exchange. Mass spectral evidence left no doubt concerning the product composition: *m/z* 1340.1 [**6** − $3PF_6^-$]$^{3+}$, *m/z* 968.8 [**6** − $4PF_6^-$]$^{4+}$, and *m/z* 1024.8 [**7** − $3PF_6^-$]$^{3+}$ were identified [Figure S6].

Finally, all three organoplatinum materials **1**−**3** were heated with **4** in the appropriate ratio to give assemblies **5**−**7** [reaction D]. The $^{31}P\{^1H\}$ and ^1H NMR spectra [Figures S7−S8] show assemblies **5**−**7** to be the major products. The ESI mass spectrum [Figure S9] of the hexafluorophosphate salts confirms the structure of all three ensembles.

In all cases, the NMR data are consistent with that reported previously for **5**,[21] **6**,[22] and the triflate salt of **7**.[23] However, extended reaction times (121−135 h) are necessary in our experiments to reduce the number of products. These are much longer than those required for the individual assemblies (up to 15 h). Indeed, after several hours we observe **5**−**7** in conjunction with other unknown species. Prolonged heating always simplified the NMR spectra. Apparently, our systems are able to self-correct themselves to produce the thermodynamically most stable macrocycles **5**−**7**, although sometimes small amounts of mixed ligand species remained.

In conclusion, we have demonstrated that mixtures of two or three organoplatinum reagents **1**−**3** and 4,4′-dipyridyl **4** undergo self-recognition to give discrete polygons **5**−**7** as the dominant products. This work represents one of the few examples of self-recognition in a 2-D system.

Experimental Section

Methods and Materials. Organoplatinum compounds **1**,[21] **2**,[22] and **3**[24] were prepared as previously reported.

General Procedure. A solution of 4,4′-dipyridyl **4** (2.03 mg, 13.0 μmol [reactions A−C] or 3.00 mg, 19.2 μmol [reaction D]) in acetone-d_6 (0.4 mL) was added dropwise with stirring to a 1- or 2-dram vial containing the appropriate ratio of organoplatinum reagents **1**−**3** in aqueous acetone-d_6 (0.8 mL in the case of reactions

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A−C, 1.6 mL for reaction D). The vial was sealed with Teflon tape and immersed in an oil bath at 55−60 °C for 121−135 h. The yellow solution was periodically transferred to an NMR tube for analysis. After no further changes to the NMR spectra, excess KPF_6 and H_2O were added to precipitate the assemblies as hexafluorophosphate salts. They were washed with H_2O and dried in vacuo. All reactions were essentially quantitative by NMR. However, the isolated yields were slightly lower than expected because of repeated NMR transfers to monitor reaction progress and minor losses which occurred during workup as well as small amounts (3−6%) of undefined products. Samples for ESIMS were prepared in acetone.

Reaction A. Yield of combined products **5** + **6**, 75%. ^{1}H NMR (20% D_2O/acetone-d_6, 300 MHz) **5**: δ 9.53 (s, 2H, H_9), 9.22 (d, $^{3}J = 5.8$ Hz, 4H, $H_{\alpha-Py}$), 9.17 (m, 4H, $H_{\alpha'-Py}$), 8.73 (d, $^{3}J = 5.9$ Hz, 4H, $H_{\beta-Py}$), 8.54 (d, $^{3}J = 5.9$ Hz, 4H, $H_{\beta'-Py}$), 8.36 (s, 2H, H_{10}), 7.72 (d, $^{3}J = 8.2$ Hz, 4H, $H_{4,5}$), 7.65 (m, 4H, $H_{2,7}$), 7.16 (t, $^{3}J = 7.7$ Hz, 4H, $H_{3,6}$), 1.45 (m, 48H, PCH_2), 0.82 (m, 72H, PCH_2CH_3). For **6**: δ 9.16 (d, $^{3}J = 5.6$ Hz, 6H, $H_{\alpha-Py}$), 9.09 (d, $^{3}J = 5.7$ Hz, 6H, $H_{\alpha'-Py}$), 8.64 (s, 6H, $H_{1,10}$), 8.39 (dd, $^{3}J = 5.9$ Hz, $^{4}J = 1.9$ Hz, 6H, $H_{\beta-Py}$), 8.34 (dd, $^{3}J = 5.9$ Hz, $^{4}J = 1.9$ Hz, 6H, $H_{\beta'-Py}$), 7.67 (d, $^{3}J = 8.2$ Hz, 6H, $H_{3,8}$), 7.58 (d, $^{3}J = 8.2$ Hz, 6H, $H_{4,7}$), 7.56 (s, 6H, $H_{5,6}$), 1.33 (m, 72H, PCH_2), 1.11 (m, 108H, PCH_2CH_3). $^{31}P\{^{1}H\}$ NMR (20% D_2O/acetone-d_6, 121 MHz) **5**: 8.28 (^{195}Pt satellites, $^{1}J_{Pt-P} = 2630$ Hz). For **6**: δ 14.29 (^{195}Pt satellites, $^{1}J_{Pt-P} = 2658$ Hz).

Reaction B. Yield of combined products **5** + **7**, 72%. ^{1}H NMR (50% D_2O/acetone-d_6, 300 MHz) **5**: δ 9.51 (s, 2H, H_9), 9.19 (d, $^{3}J = 6.0$ Hz, 4H, $H_{\alpha-Py}$), 9.15 (d, $^{3}J = 6.0$ Hz, 4H, $H_{\alpha'-Py}$), 8.65 (d, $^{3}J = 6.0$ Hz, 4H, $H_{\beta-Py}$), 8.48 (d, $^{3}J = 6.0$ Hz, 4H, $H_{\beta'-Py}$), 8.34 (s, 2H, H_{10}), 7.70 (d, $^{3}J = 8.6$ Hz, 4H, $H_{4,5}$), 7.64 (d, $^{3}J = 6.4$ Hz, 4H, $H_{2,7}$), 7.15 (t, $^{3}J = 7.7$ Hz, 4H, $H_{3,6}$), 1.43 (m, 48H, PCH_2), 0.80 (m, 72H, PCH_2CH_3). For **7**: δ 8.87 (d, $^{3}J = 5.3$ Hz, 16H, $H_{\alpha-Py}$), 7.94 (d, $^{3}J = 6.8$ Hz, 16H, $H_{\beta-Py}$), 1.84 (m, 48H, PCH_2), 1.16 (m, 72H, PCH_2CH_3). $^{31}P\{^{1}H\}$ NMR (50% D_2O/acetone-d_6, 121 MHz) **5**: δ 8.31 (^{195}Pt satellites, $^{1}J_{Pt-P} = 2634$ Hz). For **7**: 1.59 (^{195}Pt satellites, $^{1}J_{Pt-P} = 3072$ Hz).

Reaction C. Yield of combined products **6** + **7**, 80%. ^{1}H NMR (10% D_2O/acetone-d_6, 300 MHz) **6**: δ 9.25 (d, $^{3}J = 5.9$ Hz, 6H, $H_{\alpha-Py}$), 9.14 (d, $^{3}J = 5.9$ Hz, 6H, $H_{\alpha'-Py}$), 8.70 (s, 6H, $H_{1,10}$), 8.49 (dd, $^{3}J = 5.9$ Hz, $^{4}J = 2.0$ Hz, 6H, $H_{\beta-Py}$), 8.42 (dd, $^{3}J = 6.0$ Hz, $^{4}J = 1.9$ Hz, 6H, $H_{\beta'-Py}$), 7.70 (d, $^{3}J = 8.3$ Hz, 6H, $H_{3,8}$), 7.62 (d, $^{3}J = 8.1$ Hz, 6H, $H_{4,7}$), 7.59 (s, 6H, $H_{5,6}$), 1.38 (m, 72H, PCH_2), 1.16 (m, 108H, PCH_2CH_3). For **7**: δ 9.01 (d, $^{3}J = 4.8$ Hz, 16H, $H_{\alpha-Py}$), 8.06 (d, $^{3}J = 6.7$ Hz, 16H, $H_{\beta-Py}$), 1.92 (m, 48H, PCH_2), 1.16 (m, 72H, PCH_2CH_3). $^{31}P\{^{1}H\}$ NMR (10% D_2O/acetone-d_6, 121 MHz) **6**: δ 14.60 (^{195}Pt satellites, $^{1}J_{Pt-P} = 2666$ Hz). For **7**: 1.56 (^{195}Pt satellites, $^{1}J_{Pt-P} = 3082$ Hz).

Reaction D. Yield of combined products **5** + **6** + **7**, 73%. ^{1}H NMR (20% D_2O/acetone-d_6, 300 MHz) **5**: δ 9.60 (s, 2H, H_9), 9.27 (m, 4H, $H_{\alpha'-Py}$), 9.22 (d, $^{3}J = 5.8$ Hz, 4H, $H_{\alpha-Py}$), 8.87 (d, $^{3}J = 5.8$ Hz, 4H, $H_{\beta-Py}$), 8.62 (d, $^{3}J = 5.8$ Hz, 4H, $H_{\beta'-Py}$), 8.44 (s, 2H, H_{10}), 7.77 (d, $^{3}J = 8.4$ Hz, 4H, $H_{4,5}$), 7.71 (m, 4H, $H_{2,7}$), 7.20 (t, $^{3}J = 7.6$ Hz, 4H, $H_{3,6}$), 1.53 (m, 48H, PCH_2), 0.88 (m, 72H, PCH_2CH_3). For **6**: δ 9.27 (d, $^{3}J = 6.1$ Hz, 6H, $H_{\alpha-Py}$), 9.16 (d, $^{3}J = 5.8$ Hz, 6H, $H_{\alpha'-Py}$), 8.72 (s, 6H, $H_{1,10}$), 8.51 (dd, $^{3}J = 6.2$ Hz, $^{4}J = 2.1$ Hz, 6H, $H_{\beta-Py}$), 8.44 (m, 6H, $H_{\beta'-Py}$), 7.71 (d, $^{3}J = 8.4$ Hz, 6H, $H_{3,8}$), 7.63 (d, $^{3}J = 8.2$ Hz, 6H, $H_{4,7}$), 7.60 (s, 6H, $H_{5,6}$), 1.39 (m, 72H, PCH_2), 1.17 (m, 108H, PCH_2CH_3). For **7**: δ 9.04 (d, $^{3}J = 4.8$ Hz, 16H, $H_{\alpha-Py}$), 8.08 (d, $^{3}J = 6.7$ Hz, 16H, $H_{\beta-Py}$), 1.93 (m, 48H, PCH_2), 1.17 (m, 72H, PCH_2CH_3). $^{31}P\{^{1}H\}$ NMR (20% D_2O/acetone-d_6, 121 MHz) **5**: 8.51 (^{195}Pt satellites, $^{1}J_{Pt-P} = 2636$ Hz). For **6**: δ 14.55 (^{195}Pt satellites, $^{1}J_{Pt-P} = 2667$ Hz). For **7**: 1.45 (^{195}Pt satellites, $^{1}J_{Pt-P} = 3076$ Hz).

Acknowledgment. Financial support from the National Science Foundation (CHE-0306720) and the National Institute of Health (5R01GM57052) is gratefully acknowledged. We thank Dr. Yury K. Kryschenko for providing platinum acceptor **2**.

Supporting Information Available: NMR and mass spectral data for assembly mixtures **5** + **7**, **6** + **7**, and **5**−**7**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC049326P