

Articles

Combining Ferrocenes and Molecular Squares: Self-Assembly of Heterobimetallic Macrocyclic Squares Incorporating Mixed Transition Metal Systems and a Main Group Element. Single-Crystal X-ray Structure of $[\text{Pt}(\text{dppf})(\text{H}_2\text{O})_2][\text{OTf}]_2$

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Received October 3, 1995⁵

The preparation of the reactive diaqua complexes of (bis(diphenylphosphino)ferrocene)-palladium(II) and -platinum(II) bis(triflates) and the X-ray crystal structure of $[\text{Pt}(\text{dppf})(\text{H}_2\text{O})_2][\text{OTf}]_2$ (dppf = 1,1'-bis(diphenylphosphino)ferrocene) are reported. Interaction of these complexes with 2,7-diazapyrene produced novel octanuclear square-shaped metallomacrocycles. Modular self-assembly of $[\text{Pd}(\text{dppf})(\text{H}_2\text{O})_2][\text{OTf}]_2$ and $[\text{Pt}(\text{dppf})(\text{H}_2\text{O})_2][\text{OTf}]_2$ with bis-[4-(4'-pyridyl)phenyl]iodonium triflate results in the facile formation of hexanuclear macrocyclic squares with alternating iodonium–late transition metals (Pd(II) or Pt(II)) at the corners and ferrocene complex as the chelating unit.

Introduction

The design and study of various metal-containing macrocycles is one of the most active and interesting areas in modern supramolecular chemistry.^{1,2} Molecular squares, a new family of conformationally rigid metallomacrocycles with nearly 90° turns, have the potential to become interesting targets for various investigations of host–guest interactions and inclusion phenomena as well as biomimetic studies. The preparation of most of these compounds requires reactive transition metal complexes with nearly 90° bond angles, as demanded by their rectangular geometry, and aza-containing heterocycles which, upon coordination to the transition metal centers, will form the sides of the square. To date, there are two major types of squares, incorporating transition metals: (1) all-metal systems³ and (2) hybrid species, with alternating hypervalent iodine and transition metals at the corners.⁴

1,1'-Bis(diphenylphosphino)ferrocene, a member of a family of ferrocenylphosphines, has been known for over a decade and extensively employed as a chelating agent

for transition metal complexes with interesting properties and geometric features. It was extensively studied and used as a ligand in the ruthenium-, rhodium-, and palladium-catalyzed hydrogenation of olefins⁵ and nickel- and palladium-catalyzed Grignard cross-coupling reactions⁶ and as a ligand for catalytic olefin reduction.⁷ Our primary goal, therefore, was to establish its applicability in the preparation of the reactive Pd(II) and Pt(II) complexes, suitable for the self-assembly of macrocyclic squares. Also, since to date only bis(triflates) of the transition metal bis(phosphines) and, sometimes, their mono aqua complexes were used for self-assembly in organic solvents, it was of particular interest to ascertain the possible use of diaqua complexes of the transition metal bis(triflates) in self-assembly, since these diaqua complexes exhibit high air and thermal stability, in contrast to some hygroscopic anhydrous bis(triflates).⁸

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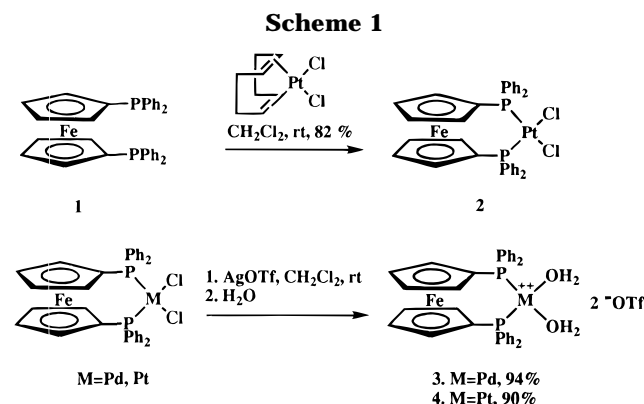
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Results and Discussion

Synthesis of Diaqua Complexes of Transition Metal Bis(triflates). The general protocol for the preparation of various transition metal bis(triflates) involves reaction of the transition metal dihalide with silver triflate in an appropriate organic solvent. When the bis(triflate) products are treated with exactly 2 equiv of water or, in some cases, simply exposed to air, they readily form stable diaqua complexes: (1,1'-bis(diphenylphosphino)ferrocene)palladium(II) and -platinum(II) complexes were prepared this way and spectroscopic data confirmed the formation of the diaqua complexes (Scheme 1). The low-field shift of the signal in the ^{31}P spectrum of **3**, relative to that of **1** in the palladium complex, and the high-field shift in the phosphine region of **4**, relatively to **2**, as well as the presence of water signals in the ^1H spectrum clearly indicated water coordination to the transition metals, which was confirmed by x-ray data.

X-ray Crystal Structure of 4. Slow evaporation of a dichloromethane solution of **4** provided x-ray quality crystals, suitable for structure determination. The ORTEP diagram of complex **4** is presented in Figure 1. The centroids of the ferrocene unit are located essentially in the Pt(II) coordination plane, with a P(1)–Pt–P(2) angle of 97.3° (Table 1). The angle between platinum and the two coordinated water molecules is 86° , thereby manifesting the suitability of this compound for the preparation of molecular squares.

Self-Assembly of Macrocyclic, Ferrocene-Containing Octanuclear Molecular Squares. Interaction of 2,7-diazapyrene^{3a} with the diaqua complexes of 1,1'-bis(diphenylphosphino)ferrocene palladium(II) and platinum(II) bis(triflates) **3** and **4** in nitromethane at room temperature provided molecular squares **5** and **6** in high isolated yields (Scheme 2). These compounds are air-stable, albeit hygroscopic, microcrystalline solids with high decomposition points. They are readily soluble in polar organic solvents, such as acetone, methanol, or nitromethane, and essentially insoluble in less polar solvents, such as ether. As demanded by their geometry, both squares display a sharp singlet for the equivalent phosphorous atoms in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra, with appropriate Pt satellites for the Pt square **6**. The ^{31}P signals are shifted downfield relative to that of the precursors **3** and **4**. The presence of the ionic triflate counterions is indicated by the single signal in the ^{19}F NMR between -74 and -78 ppm and the characteristic infrared absorption spectra, as detailed in the Experimental Section.

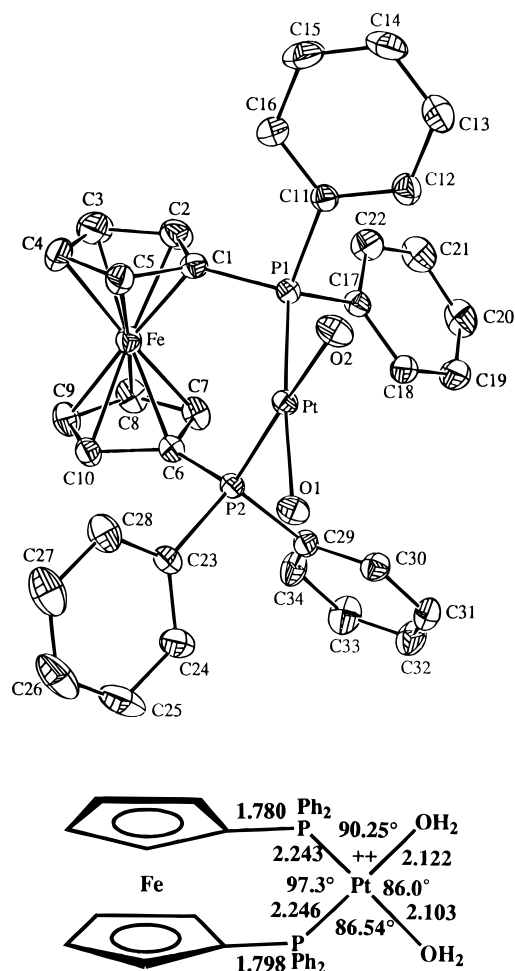


Figure 1. ORTEP diagram and summary of important geometric features of cationic part of complex **4**.

Table 1. Important Bond Angles (deg) and Bond Distances (Å) for [Pt(dppf)(H₂O)₂][OTf]₂ (4**)**

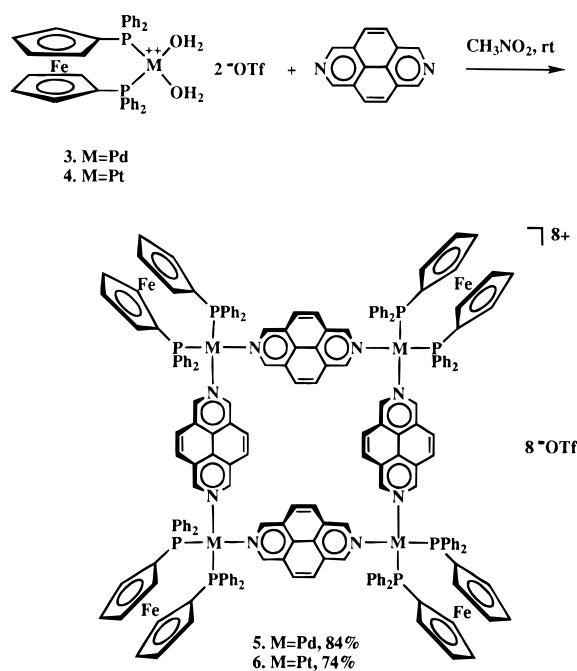
	angle ^a		dist ^a	
O(2)–Pt–O(1)	86.0(2)	Pt–P(1)	2.243(2)	
O(2)–Pt–P(1)	90.25(14)	Pt–P(2)	2.246(2)	
O(1)–Pt–P(1)	174.72(14)	Pt–O(1)	2.122(4)	
O(2)–Pt–P(2)	172.17(14)	Pt–O(2)	2.103(5)	
O(1)–Pt–P(2)	86.54(13)	Fe–C(1)	1.996(7)	
P(1)–Pt–P(2)	97.37(7)	Fe–C(6)	2.012(1)	

^a Numbers in parentheses are estimated standard deviations in the least significant digits.

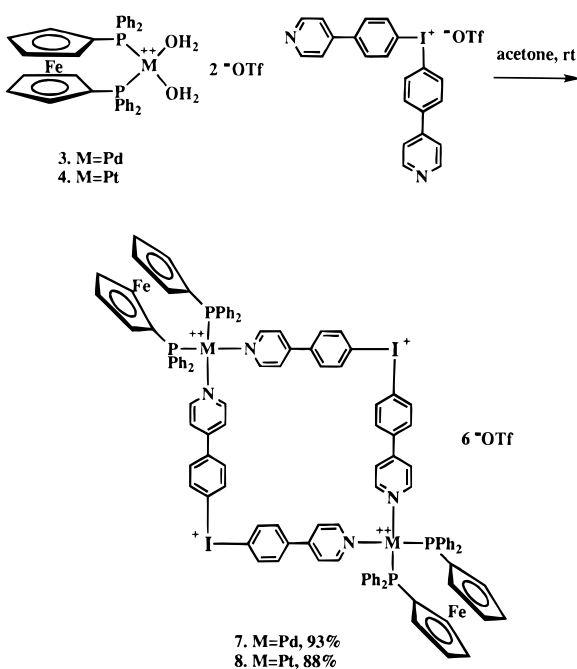
Preparation of Macrocyclic Hexanuclear Molecular Squares. Reaction of complexes **3** and **4** with bis[4-(4'-pyridyl)phenyl]iodonium triflate⁴ in acetone at room temperature provided the predicted desired squares **7** and **8** in a matter of minutes, in excellent isolated yields (Scheme 3). The ^{31}P spectra of both products exhibit high-field shifts, indicative of nitrogen coordination to the transition metal. Interestingly, this reaction is also accompanied by a change of the absorbance spectra of both compounds (Figure 2). When the nitrogen of the heteroaryl replaces the weakly donating water ligands, a series of red shifts is observed in the UV–vis spectrum. This can also be followed visually, due to the change of color of the solutions upon complexation.

Conclusion. A new class of ferrocene-containing macrocyclic molecular squares is prepared, *via* self-assembly of the reactive diaqua complexes of the mixed transition metal bis(triflates) and a coordinating ligand,

Scheme 2



Scheme 3



such as 2,7-diazapyrene or a heteroaryl iodonium moiety. This establishes the suitability of the transition metal diaqua complexes for self-assembly of macrocyclic molecular squares, as well as the usefulness of the ferrocenylphosphine complexes as auxiliary systems for such self-assembly. This combination of several ferrocene-late transition metal systems suggests that it may be fruitful to look at the redox chemistry of these species. Moreover, these molecules provide an important link between the chemistry of ferrocenes, the quintessential transition metal species, and molecular squares, the latest member of the family of supra-molecular assemblies.

Experimental Section

General Methods. All reactions were conducted under a dry nitrogen atmosphere using Schlenk techniques; however,

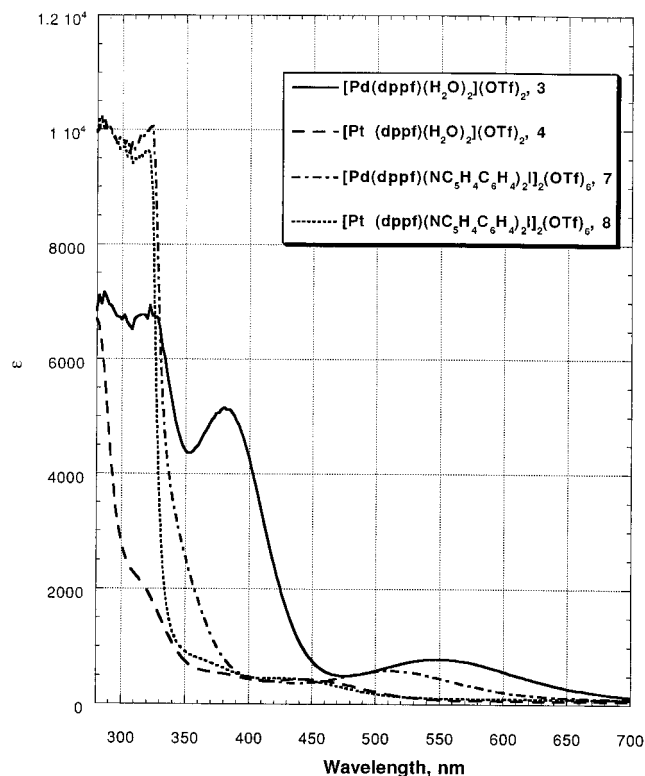


Figure 2. Absorbance spectra of compounds **3** and **4** and molecular squares **7** and **8**.

the products may be handled in air. NMR spectra were recorded on a Varian XL-300 or Unity-300 spectrometer. ^1H spectra were recorded at 300 MHz, and all chemical shifts (δ) are reported in ppm relative to tetramethylsilane (Me_4Si) as an internal standard (0.0 ppm) or the proton resonance resulting from incomplete deuteration of the NMR solvent: CD_2Cl_2 (5.32 ppm), acetone- d_6 (2.05 ppm), or CD_3NO_2 (4.33 ppm). ^{13}C spectra were recorded at 75 MHz, and all chemical shifts (δ) are reported in ppm relative to the carbon resonance of the deuterated NMR solvent: CD_2Cl_2 (53.8 ppm), acetone- d_6 (28.0 ppm), or CD_3NO_2 (62.8 ppm). ^{31}P spectra were recorded at 121 MHz, and all chemical shifts (δ) are reported in ppm relative to external 85% H_3PO_4 at 0.00 ppm. ^{19}F spectra were recorded at 282 MHz, and all chemical shifts are reported relative to external CFCl_3 at 0.00 ppm. Coupling constants J are in Hz. IR spectra were recorded on a Mattson Polaris FT-IR spectrophotometer. Absorbance spectra were measured on a Hewlett-Packard UV-vis spectrophotometer. Microanalyses were performed by Atlantic Microlab Inc., Norcross, GA. Melting points were obtained with a Mel-Temp capillary melting point apparatus and were uncorrected. The water signals in the ^1H spectrum were omitted. Abbreviations: br, broad; H_o, ortho-proton; H_m, meta-proton; H_p, para-proton; C_i, ipso-carbons; C_o, ortho-carbons; C_m, meta-carbons; C_p, para-carbons.

Materials. Solvents were purified as follows: CH_2Cl_2 was purified according to the literature procedure⁹ and distilled over CaH_2 ; Et_2O was purified by the literature procedure⁹ and distilled over Na/benzophenone ; CD_2Cl_2 was vacuum transferred from CaH_2 .

All commercial reagents were ACS reagent grade. 1,1'-Bis(diphenylphosphino)ferrocene and silver triflate were obtained from Aldrich and were used as received. The precursor, $[\text{Pd}(\text{dppf})\text{Cl}_2]$, was prepared according to the literature method.¹⁰

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(10) Reaction of $\text{Pd}(\text{cod})\text{Cl}_2$ with 1,1'-bis(diphenylphosphino)ferrocene provided $[\text{Pd}(\text{dppf})\text{Cl}_2]$ in 90% yield. See also ref 6a for another method of preparation of this complex.

[Pt(dppf)Cl₂] (2). A 50-mL Schlenk flask was charged with 0.183 g (0.330 mmol) of 1,1'-bis(diphenylphosphino)ferrocene, 0.112 g (0.300 mmol) of Pt(cod)Cl₂ (cod = cyclooctadiene), and 20 mL of CH₂Cl₂. The yellow solution was stirred at room temperature for 10 min, transferred into a 25-mL flask, and reduced in volume to 2 mL. Diethyl ether was then added, resulting in the formation of a yellow precipitate, which was collected and dried in vacuo, to yield 0.211 g (82%). Mp = 340–342 °C dec. ¹H NMR (CD₂Cl₂): 7.90–7.83 (m, 8H, H_o-PhP), 7.54–7.40 (m, 12H, H_p, H_m-PhP), 4.40 (s, 4H, H_α-ferr), 4.22 (s, 4H, H_β-ferr). ¹³C NMR (CD₂Cl₂): 135.3 (t, J = 5.5, C_o-PhP), 131.7 (s, C_p-PhP), 131.4 (t, J = 34, C_i-PhP), 128.4 (t, J = 5.7, C_m-PhP), 76.3 (t, J = 5.2, C_α-ferr), 74.5 (t, J = 3.2, C_β-ferr), 73.2 (t, J = 35.3, C_i-ferr). ³¹P NMR (CD₂Cl₂): 15.5 (s, ¹⁹⁵Pt satellites, J = 3766). IR (neat, cm⁻¹): 3044, 1480, 1435 (Ar). Anal. Calcd for C₃₄H₂₈P₂FePtCl₂·2H₂O: C, 47.68; H, 3.77. Found: C, 47.78; H, 3.51.

[Pd(dppf)(H₂O)₂][OTf]₂ (3). To a dark-red solution of 0.452 mg (0.588 mmol) of [Pd(dppf)Cl₂] in 40 mL of CH₂Cl₂ was added 0.428 g (1.67 mmol) of AgOTf, and the mixture was stirred for 18 h at room temperature. The white precipitate was filtered off, and the solution was allowed to stir in air for 10 min. The solution was transferred into a 100-mL flask and reduced in volume to 2 mL. Diethyl ether was then added, and the green precipitate was collected, washed with diethyl ether, and dried in vacuo. Yield: 0.552 g (94%). Mp = 198–200 °C dec. ¹H NMR (CD₂Cl₂): 7.95–7.74 (m, 8H, dppf Ph H_o), 7.74–7.62 (m, 8H, dppf Ph H_p), 7.60–7.46 (m, 8H, dppf Ph H_m), 4.67 (s, 4H, H_o-ferr), 4.63 (s, 4H, H_β-ferr). ¹³C NMR (CD₂Cl₂): 134.7 (t, J = 6.2, C_o-PhP), 133.8 (s, C_p-PhP), 129.9 (t, J = 6.2, C_m-PhP), 128.0 (t, C_i-PhP), 122.2 (q, J = 319, OTf), 78.6 (t, J = 5.9, C_α-ferr), 76.4 (t, J = 4.4, C_β-ferr), 69.8 (t, J = 37.8, C_i-ferr). ³¹P NMR (CD₂Cl₂): 51.1 (s). ¹⁹F NMR (CD₂Cl₂): -79.2 (s, OTf). IR (neat, cm⁻¹): 1437 (Ar), 1300, 1228, 1168, 1028 (OTf). Anal. Calcd for C₃₆H₃₂P₂FePdO₈S₂F₆: C, 43.46; H, 3.24; S, 6.44. Found: C, 43.57; H, 3.27, S, 6.45.

[Pt(dppf)(H₂O)₂][OTf]₂ (4). A 50-mL Schlenk flask was charged with 0.380 g (0.444 mmol) of [Pt(dppf)Cl₂] and 40 mL of CH₂Cl₂ to give an orange solution. To this was added 0.834 g (3.24 mmol) of AgOTf, and the mixture was stirred at room temperature for 3 days. The precipitate was filtered off, and the filtrate was stirred in air for 10 min and then reduced in volume to 2 mL. After addition of diethyl ether, the orange precipitate was filtered off, washed with ether, and dried in vacuo. Yield: 0.434 g (90%). Mp = 192–193 °C dec. ¹H NMR (CD₂Cl₂): 7.79–7.63 (m, 12H, dppf Ph H_o and H_p), 7.56–7.48 (m, 8H, dppf Ph H_m), 4.65 (s, 4H, H_α-ferr), 4.48 (s, 4H, H_β-ferr). ¹³C NMR (CD₂Cl₂): 134.4 (t, J = 5.6, C_o-PhP), 133.6 (s, C_p-PhP), 129.8 (t, J = 6.0, C_m-PhP), 127.4–126.4 (t, C_i-PhP), 122.6 (q, J = 319, OTf), 77.3 (t, J = 5.9, C_α-ferr), 76.2 (t, J = 4.7, C_β-ferr), 68.0 (t, J = 42.0, C_i-ferr). ³¹P NMR (CD₂Cl₂): 11.1 (s, ¹⁹⁵Pt satellites, J = 4195 Hz). ¹⁹F NMR (CD₂Cl₂): -79.1 (s, OTf). IR (neat, cm⁻¹): 1436 (Ar), 1265, 1174, 1028 (OTf). Anal. Calcd for C₃₆H₃₂P₂FePtO₈S₂F₆: C, 39.90; H, 2.60; S, 5.92. Found: C, 39.95; H, 3.00, S, 6.00.

[Pd(dppf)(2,7-diazapyrene)]₄[OTf]₈ (5). The solution of 3.60 mg (0.0176 mmol) of 2,7-diazapyrene in 1.2 mL of dry nitromethane was allowed to react with 16.1 mg (0.0168 mmol) of [Pd(dppf)(H₂O)₂][OTf]₂ (3) for 20 min at room temperature. Addition of the diethyl ether resulted in a pink solid, which was washed with ether and dried in vacuo. Yield of 5: 16.6 mg (84%). Mp = 290–292 °C. ¹H NMR (CD₃NO₂): 9.26 (d, J = 2, 16H, H_α-diazp), 7.91 (m, 32H, dppf H_o), 7.71 (s, 16H, H_γ-diazp), 7.56 (m, 16H, dppf Ph H_p), 7.43 (m, 32H, dppf Ph H_m), 4.92 (s, 16H, H_α-ferr), 4.79 (s, 16H, H_β-ferr). ¹³C NMR (CD₃NO₂): 146.7 (s, C_α-diazp), 135.6 (t, dppp Ph C_o), 134.6 (s, dppp Ph C_p), 131.0 (s, dppp Ph C_m), 129.8 (s, C_γ-diazp), 128.6 (s, C_i-diazp), 128.0 (t, J = 53, dppp Ph C_i), 125.3 (s, C_β-diazp), 121.3 (q, J = 319, OTf), 78.8 (t, C_α-ferr), 77.6 (t, C_β-ferr), 68.4 (t, J = 54, C_i-ferr). ³¹P NMR (CD₃NO₂): 38.51 (s). ¹⁹F NMR (CD₃NO₂): -74.6 (s, OTf). IR (neat, cm⁻¹): 1437 (Ar), 1283,

1252, 1163, 1102, 1029 (OTf). Anal. Calcd for C₂₀₀H₁₄₄-P₈N₈Fe₄Pd₄O₂₄S₈F₂₄·4H₂O: C, 50.84; H, 3.24; N, 2.37; S, 5.43. Found: C, 51.06; H, 3.20; N, 2.45; S, 5.33.

[Pt(dppf)(2,7-diazapyrene)]₄[OTf]₈ (6). To a solution of 2.70 mg (0.0132 mmol) of 2,7-diazapyrene in 1 mL of dry nitromethane was added 13.4 mg (0.0128 mmol) of [Pt(dppf)(H₂O)₂][OTf]₂ (4), and the resulting orange solution was stirred at room temperature for 20 min. Diethyl ether was then added, resulting in the formation of an orange precipitate, which was filtered off, washed with diethyl ether, and dried in vacuo to yield 11.8 mg of 6 (74%). Mp = 310–314 °C dec. ¹H NMR (CD₃NO₂): 9.29 (d, J = 0.3, 16H, H_α-diazp), 7.90 (m, 32H, dppf H_o), 7.76 (s, 16H, H_γ-diazp), 7.52 (m, 16H, dppf Ph H_p), 7.41 (m, 32H, dppf Ph H_m), 4.91 (s, 16H, H_α-ferr), 4.75 (s, 16H, H_β-ferr). ¹³C NMR (CD₃NO₂): 146.9 (s, C_α-diazp), 135.6 (t, dppp Ph C_o), 134.5 (s, dppp Ph C_p), 131.0 (s, dppp Ph C_m), 129.1 (s, C_γ-diazp), 129.0 (s, C_i-diazp), 127.6 (t, J = 58, dppp Ph C_i), 125.3 (s, C_β-diazp), 121.3 (q, J = 319, OTf), 77.8 (t, C_α-ferr), 77.5 (t, C_β-ferr), 67.9 (t, J = 64, C_i-ferr). ³¹P NMR (CD₃NO₂): 8.36 (s, ¹⁹⁵Pt satellites, J_{Pt-P} = 3432). ¹⁹F NMR (CD₃NO₂): -74.6 (s, OTf). IR (neat, cm⁻¹): 1437 (Ar), 1278, 1255, 1157, 1097, 1029 (OTf). Anal. Calcd for C₂₀₀H₁₄₄P₈-N₈Fe₄Pt₄O₂₄S₈F₂₄·4H₂O: C, 47.29; H, 3.01; N, 2.21; S, 5.05. Found: C, 47.22; H, 2.99; N, 2.14; S, 4.97.

{[Pd(dppf)(NC₅H₄C₆H₄)₂][OTf]₃}₂ (7). A 25-mL Schlenk flask was charged with 21.3 mg (0.0365 mmol) of bis(4-phenylpyridine)iodonium triflate and 5 mL of acetone. To this heterogeneous mixture was added, 35.0 mg (0.0352 mmol) of [Pd(dppf)(H₂O)₂][OTf]₂ (3), and the resulting deep purple solution was stirred at room temperature for 20 min and then reduced in volume to 1 mL. Diethyl ether was added, and the resulting purple solid was collected and dried in vacuo. Yield: 52.5 mg (93%). Mp = 224–226 °C dec. ¹H NMR (acetone-*d*₆): 8.92 (br d, J = 3.3, 8H, H_α-Py), 8.44 (d, J = 8.5, 8H, H_α-PhI), 8.06–7.98 (m, 16H, dppf Ph H_o), 7.81 (d, J = 8.5, 8H, H_β-PhI), 7.78–7.62 (m, 24H, dppf Ph H_m + H_p), 7.49 (d, J = 5.4, 8H, H_β-Py), 4.93 (s, 8H, H_α-ferr), 4.84 (s, 8H, H_β-ferr). ¹³C NMR (acetone-*d*₆): 151.8 (s, C_α-Py), 149.5 (s, C_γ-Py), 140.0 (s, C_γ-PhI), 137.3 (s, C_α-PhI), 135.1 (t, J = 6.6, C_o-PhP), 133.8 (s, C_p-PhP), 131.7 (s, C_β-PhI), 130.7 (t, J = 11.8, C_m-PhP), 128.5 (t, J = 28, C_i-PhP), 125.2 (s, C_β-Py), 122.2 (q, J = 319, OTf), 117.2 (s, C-I), 78.1 (t, J = 6, C_α-ferr), 76.7 (t, J = 4.6, C_β-ferr), 68.6 (t, J = 39.8, C_i-ferr). ³¹P NMR (acetone-*d*₆): 38.7 (s). ¹⁹F NMR (acetone-*d*₆): -77.6 (s, OTf). IR (neat, cm⁻¹): 1611, 1435 (Ar), 1279, 1251, 1157, 1027 (OTf). Anal. Calcd for C₁₁₈H₈₈P₄N₄Fe₂Pd₂O₁₈S₆F₁₈·6H₂O: C, 44.36; H, 3.15, N, 1.75; S, 6.62. Found: C, 43.92; H, 2.95; N, 1.93; S, 6.05.

{[Pt(dppf)(NC₅H₄C₆H₄)₂][OTf]₃}₂ (8). To a heterogeneous mixture of 10.0 mg (0.0171 mmol) of bis(4-phenylpyridine)iodonium triflate and 2 mL of acetone was added 17.9 mg (0.0165 mmol) of [Pt(dppf)(H₂O)₂][OTf]₂ (3), and the yellow solution was stirred at room temperature for 20 min. Diethyl ether was added, and the resulting yellow precipitate was collected and dried in vacuo. Yield: 24.5 mg (88%). Mp = 235–236 °C dec. ¹H NMR (acetone-*d*₆): 8.89 (br d, J = 4.9, 8H, H_α-Py), 8.38 (d, J = 8.7, 8H, H_α-PhI), 7.93 (m, 16H, dppf H_o), 7.76 (d, J = 8.7, 8H, H_β-PhI), 7.69–7.53 (m, 24H, dppf Ph H_m and H_p), 7.46 (d, J = 5.0, 8H, H_β-Py), 4.86 (s, 8H, H_α-ferr), 4.75 (s, 8H, H_β-ferr). ¹³C NMR (acetone-*d*₆): 151.8 (s, C_α-Py), 150.1 (s, C_γ-Py), 139.7 (s, C_γ-PhI), 137.5 (s, C_α-PhI), 135.3 (t, J = 5.5, C_o-PhP), 133.8 (s, C_p-PhP), 131.8 (s, C_β-PhI), 130.6 (t, J = 5.6, C_m-PhP), 127.8 (t, J = 32, C_i-PhP), 125.7 (s, C_β-Py), 122.2 (q, J = 319, OTf), 117.5 (s, C-I), 77.2 (t, J = 6.0, C_α-ferr), 76.7 (t, J = 4.6, C_β-ferr), 68.6 (t, J = 39, C_i-ferr). ³¹P NMR (acetone-*d*₆): 7.7 (s, ¹⁹⁵Pt satellites, J_{Pt-P} = 3402 Hz). ¹⁹F NMR (acetone-*d*₆): -77.7 (s, OTf). IR (neat, cm⁻¹): 1613, 1437 (Ar), 1271, 1253, 1160, 1028 (OTf). Anal. Calcd for C₁₁₈H₈₈P₄N₄Fe₂Pt₂O₁₈S₆F₁₈: C, 43.42; H, 2.72; N, 1.72; S, 5.89. Found: C, 43.77; H, 2.93; N, 1.66; S, 5.65.

X-ray Crystallographic Analysis of 4. An X-ray quality crystal was grown by the slow evaporation of a dichloromethane solution of 4. An orange prism, 0.36 × 0.36 × 0.29

Table 2. Crystal Data and Structure Refinement for [Pt(dppf)(H₂O)₂][OTf]₂ (4**)**

empirical formula	C ₃₆ H ₃₂ F ₆ FeO ₈ P ₂ PtS ₂
fw	1083.62
temp	291(2) K
wavelength	0.710 73 Å
cryst system	monoclinic
space group	<i>P2₁/n</i>
unit cell dimens	<i>a</i> = 12.292(2) Å, α = 90° <i>b</i> = 17.988(4) Å, β = 97.76(2)° <i>c</i> = 18.098(3) Å, γ = 90°
cell vol	3965.2(13) Å ³
<i>Z</i>	4
<i>D</i> (calcd)	1.815 Mg/m ³
abs coeff	4.154 mm ⁻¹
<i>F</i> (000)	2128
cryst size	0.36 × 0.36 × 0.29 mm
θ range for data collection	2.02–24.96°
index ranges	0 ≤ <i>h</i> ≤ 14, 0 ≤ <i>k</i> ≤ 21, –21 ≤ <i>l</i> ≤ 21
reflcs colcd	7306
indepdt reflcs	6960 [<i>R</i> (int) = 0.0161]
abs corr	semiempirical from ψ -scans
max and min transm	99.88 and 78.80
refinement method	full-matrix least-squares on <i>F</i> ²
data/restraints/params	6960/236/517
goodness-of-fit on <i>F</i> ²	1.019
final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> 1 = 0.0306, <i>wR</i> 2 = 0.0713
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0613, <i>wR</i> 2 = 0.0795
largest diff peak and hole	1.085 and –1.169 e [–] Å ^{–3}

mm, was glued to a glass fiber and mounted for data collection on Enraf-Nonius CAD4 diffractometer. Cell constants and data collection parameters are presented in Table 2. The unit cell parameters were obtained by a least-squares refinement of 25 centered reflections in the range of $21 < 2\theta < 28^\circ$. The space group was determined from systematic absences (*h*0*l*, *h* + *l* = 2*n*; 0*k*0, *k* = 2*n*) and subsequent least-squares refinement. The data were collected by the θ – 2θ scan

technique, with variable scanning rate, using monochromatic Mo 0.710 73 Å radiation. Standard reflections showed no decay for the crystal during data collection. Lorentz and polarization corrections, and an empirical absorption correction based upon a series of ψ scans, were applied to the data. Intensities of equivalent reflections were averaged.

The structure was solved by the standard heavy-atom technique with the MolEN/VAX package. Non-hydrogen atoms were refined with anisotropic thermal parameters. Data were weighted using a non-Poisson scheme. All hydrogen atoms were calculated and added to the structure factor calculations. Scattering factors, and $\Delta f'$ and $\Delta f''$ values, were taken from the literature.¹¹ All least-squares refinements were done using SHELXL-93. There is a disorder in the crystal exhibited by one of the triflate anions.

Acknowledgment. We thank the National Science Foundation for financial support and Johnson-Matthey for the generous loan of PtCl₂.

Supporting Information Available: Crystal structure data for **4** including tables of calculated positional parameters and *U* values for the hydrogen atoms, non-hydrogen positional and thermal parameters, complete bond lengths and bond angles, and general displacement parameter expressions (10 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

OM950781Q

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