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Modular Assembly of Hybrid Iodonium–Transition Metal Cationic Tetranuclear Macrocyclic Squares. Single Crystal Molecular Structure of {[(Et₃P)₂Pd(OTf)₂][(NC₅H₄C₆H₄)₂I(OTf)]}₂†

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Abstract: Interaction of bis[4-(4′-pyridyl)phenyl]iodonium triflate and bis(4-pyridyl)iodonium triflate respectively with *cis*-L₂M(OSO₂CF₃)₂ (L = Et₃P, dppp; M = Pt, Pd) in acetone at room temperature results in hybrid iodonium–transition metal cationic tetranuclear macrocyclic squares in good isolated yields (50–100%) via self-assembly. The 4-(4′-pyridyl)phenyl compounds are stable microcrystalline solids as are the Et₃P-chelated 4-pyridyl Pt and Pd squares whereas the dppp-chelated 4-pyridyl molecules are less stable. The single crystal X-ray molecular structure of **5d,** {[(Et₃P)₂Pd(OTf)₂][(NC₅H₄C₆H₄)₂I(OTf)]}₂, shows a planar rhomboid-like geometry, rather than a perfect square, for this macrocyclic ring system.

Introduction

Tetranuclear macrocyclic squares with nearly 90° bond angles have recently emerged[1–8] as interesting new members of the family of supramolecular[9–11] compounds. Two major types of macrocyclic squares are known to date: The first type involves squares based on transition metals[1–6] at the four corners held by chelating ligands as exemplified by **1**. In these molecules
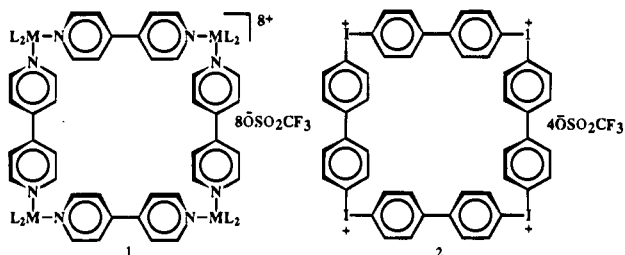
the required 90° bond angles are a consequence of the square planar metal corners.[12] The second class, **2**, involves iodine in

the form of an iodonium species at the four corners[7,8] and covalent C–I bonds. In these species the requisite ~90° angles are the result of the T-shaped, pseudotrigonal, bipyramidal nature[13,14] of the iodonium moiety. Moreover, the chelating transition metal based molecular squares, **1**, are formed by self-assembly, upon simple mixing of the appropriate square-planar metal precursors with the proper bidentate ligands,[15] in accord with the principles of non-covalent synthesis,[16] whereas the iodonium based macrocyclic squares are synthesized[7] by classical covalent synthesis one step at a time.[17]

In this paper we report the preparation, by modular assembly, along with the spectral characterization, properties, and a single crystal molecular structure, of hybrid, main group, iodonium–transition metal macrocyclic squares.[18]

Results and Discussion

cis- and *trans*-L₂MX₂, square planar, Pt(II) and Pd(II) dihalide complexes, with approximately 90° bond angles around the central metal, have been known[19] for over 30 years. Likewise, diaryliodonium salts, Ar₂I⁺X⁻, have been around for over a century.[13] However, the bis-phosphine metal dihalides are generally inert to displacement by weak neutral nucleophiles such as pyridine. It is well-known in organic chemistry that triflates, CF₃SO₃, are some 10⁶ more reactive[20] than halides whereas in organometallic chemistry triflates serve as highly labile, weakly coordinating, ligands.[21,22] Hence, we reasoned

† Dedicated to Academician Nikolai S. Zefirov on the occasion of this 60th birthday.

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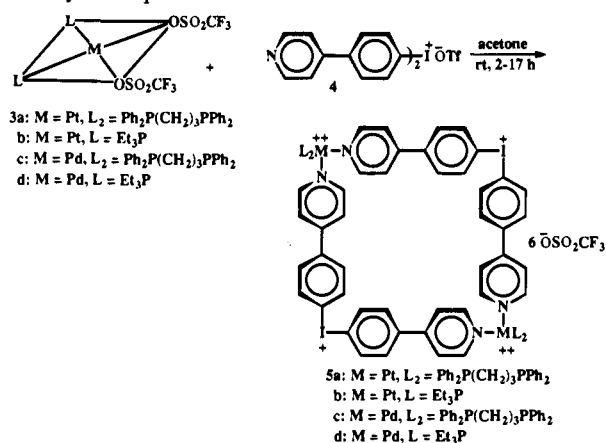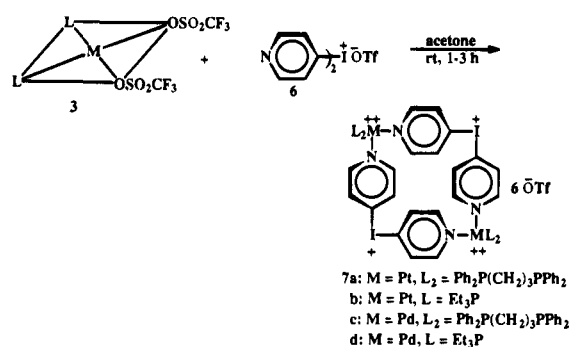
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Scheme 1. Modular Self-Assembly of Hybrid Tetranuclear Macrocyclic Squares

3a: M = Pt, L₂ = Ph₂P(CH₂)₃PPh₂
b: M = Pt, L = Et₃P
c: M = Pd, L₂ = Ph₂P(CH₂)₃PPh₂
d: M = Pd, L = Et₃P

5a: M = Pt, L₂ = Ph₂P(CH₂)₃PPh₂
b: M = Pt, L = Et₃P
c: M = Pd, L₂ = Ph₂P(CH₂)₃PPh₂
d: M = Pd, L = Et₃P

Scheme 2. Modular Self-Assembly of Hybrid Macrocyclic Squares **7**

7a: M = Pt, L₂ = Ph₂P(CH₂)₃PPh₂
b: M = Pt, L = Et₃P
c: M = Pd, L₂ = Ph₂P(CH₂)₃PPh₂
d: M = Pd, L = Et₃P

Table 1. Crystallographic Data for {[(OTf)₂(Et₃P)₂Pd][(4-NC₅H₄C₆H₄)₂I(OTf)]}₂ (**5d**)

molecular formula	$C_{80}H_{112}F_{18}I_2N_4O_{24}P_4Pd_2S_6$
formula wt, g mol⁻¹	2638.656
space group	*C2/c*
space group no.	15
crystal system	monoclinic
a, Å	25.395(8)
b, Å	9.501(3)
c, Å	49.072(10)
β, deg	93.42(2)
cell volume, Å³	11818.35
Z	4
calcd density, g cm⁻³	1.483
crystal size, mm	0.3 × 0.27 × 0.16
abs coeff, cm⁻¹	10.580
radiation	Mo 0.71073 Å
no. of reflcns measured	8988
no. of unique reflcns	8165
no. of observations	4746 ($I < 3.00\delta(I)$)
θ range, deg	2.00 to 46.00
scan technique	*θ/2θ* scan
scan width, deg	0.8000 + 0.3400 tan *θ*
R factor	0.1180
weighted *R* factor	0.1395

that *cis*-L₂M(OTf)₂, M = Pt, Pd, **3**, might serve as a modular template, along with a bis(heteroaryl)iodonium species **4** as the second module, for the self-assembly of the desired hybrid macrocyclic molecular squares.

Indeed, interaction of equimolar amounts of the square-planar *cis*-L₂M(OTf)₂ complexes **3** with the bis[4-(4′-pyridyl)phenyl]-iodonium triflate (**4**) in acetone at room temperature for 2−17 h gave the desired products **5** as outlined in Scheme 1. The formation of the two precursors **3** and **4** requires classical inorganic and organic covalent synthesis, whereas the final step occurs via self-assembly upon simple mixing; therefore we refer to this type of preparation as modular assembly. Likewise, interaction of equimolar amounts of **3** with bis(4-pyridyl)-iodonium triflate (**6**) results in hybrid squares **7** as summarized in Scheme 2.

The hybrid macrocyclic squares **5**, **7b**, and **7c** are stable microcrystalline solids with either water or organic solvents of crystallization, whereas **7a** and **7d** are considerably less stable and decompose soon after formation. Analytically pure **5** are all white whereas **7b** and **7c** are yellow in color. All hybrid squares **5** and **7** are insoluble in water as well as nonpolar organic solvents, slightly soluble in nitromethane and methylene chloride, and soluble in acetone and methanol.

These novel hybrid macrocycles are characterized by analytical and spectral means as summarized in the Experimental Section. The structures of **5b** and **5d** were unambiguously established by single-crystal X-ray diffraction.

In particular, all new compounds have elemental analyses consistent with their respective compositions. Multinuclear NMR and the internal consistency of the spectral data among the related molecular squares anchored to an X-ray determination confirm the tetranuclear square nature of their structure. Moreover, the spectral characteristics of these hybrid macro-

cycles closely track the respective NMR properties of the all-metal[1,15] **1** and the pure iodonium,[7] **2**, molecular squares.

Specifically, as demanded by symmetry, all hybrid molecular squares, in analogy with the all-metal systems **1**, display a single sharp singlet for the equivalent phosphorus atoms in the ³¹P{¹H} NMR spectra, with appropriate Pt satellites for the Pt complexes **5a,b** and **7a,b**. Furthermore, the ³¹P signals of the hybrid squares are shifted downfield by several ppm due to further complexing relative to the precursor *cis*-Pt(II) and Pd(II) complexes **3**. The presence of the ionic triflate counterions is indicated by the ¹⁹F NMR signal, at −78 to −79.5 ppm, as well as the characteristic[21] infrared absorptions in the area of 1160, 1100, and 1030 cm⁻¹.

Particularly valuable and characteristic of the symmetrical tetranuclear macrocyclic square geometry are the respective ¹³C{¹H} and ¹H NMR signals. All ¹³C NMR signals for each molecular square can be assigned and are internally consistent among the related compounds. In the ¹H NMR especially revealing are the proton chemical shifts of the chelating pyridyl and 4-phenylpyridyl rings. For the Et₃P-complexed squares **7**, the α-H relative to the N in the pyridyl ring is shifted downfield by ∼0.4 ppm and the β-H is shifted downfield by ∼0.3 ppm relative to the corresponding protons in the precursor iodonium species **6**, which are themselves shifted by ∼0.3 ppm (H_α) and ∼1.1 ppm (H_β) relative to the pure uncomplexed pyridine protons. In contrast, with the dppp-complexed molecules **5**, the α-proton is shifted downfield by only ∼0.1 ppm and the β-hydrogen actually shifts upfield by ∼0.2 ppm relative to precursor **6**. This effect is due to the shielding provided by the phenyl groups of the dppp moiety. Similar effects can be seen for macrocyclic squares **5**. For the Et₃P-complexed compounds **5b** and **5d** *all* four different types of protons on the two chelating rings are shifted downfield upon formation of the squares relative to the precursor iodonium salt **4**, with the largest shift of ∼0.4 ppm experienced by the hydrogens ortho to the chelating nitrogen. In contrast, for the dppp-complexed systems the two sets of meta hydrogens (meta to the N and I, respectively) are shielded by the dppp phenyls, and therefore are slightly shifted upfield 0.04−0.2 ppm despite chelation, relative to the signals in **4**. Finally, all integrations are in accord with the expected values for the respective squares.

Single-Crystal X-ray Molecular Structure Determinations. As these macrocyclic molecular squares represent a unique type
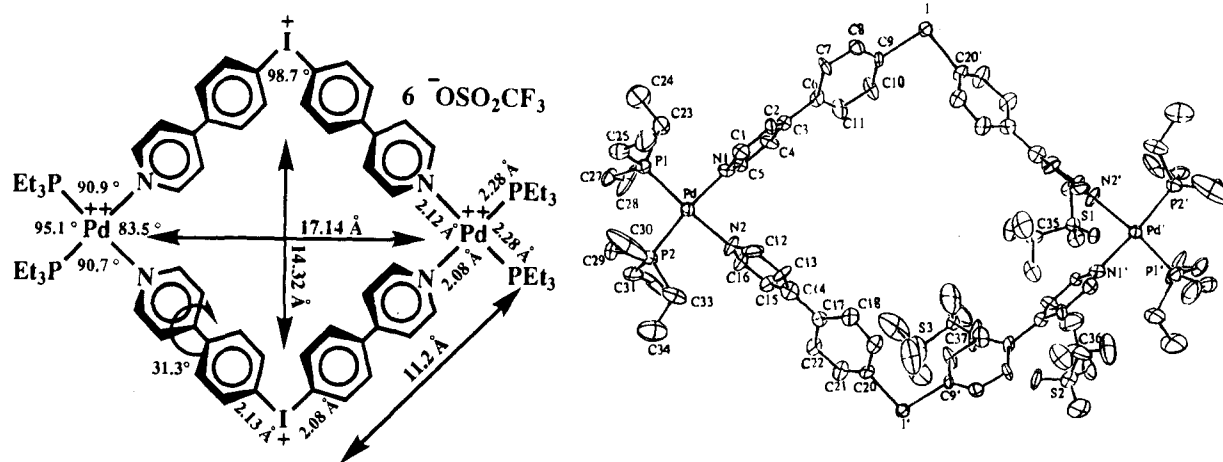
Tetranuclear Macrocyclic Squares

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Figure 1. Summary of the significant geometric features and ORTEP representation of molecular square **5d**.

Table 2. Important Bond Angles (in deg) and Bond Distances (in Å) for Compound **5d**

atom 1—atom 2—atom 3	angles^a	atom 1—atom 2	distances^a
C9—I—C20'	98.7(9)	I—C9	2.08(2)
P1—Pd—P2	95.1(3)	I—C20'	2.13(2)
P1—Pd—N1	90.9(5)	Pd—P1	2.281(7)
P2—Pd—N1	173.4(5)	Pd—P2	2.277(7)
P1—Pd—N2	171.6(6)	Pd—N1	2.08(2)
P2—Pd—N2	90.7(6)	Pd—N2	2.12(2)
N1—Pd—N2	83.5(8)	I—I'	14.31(8)
		Pd—Pd'	17.1(4)
		Pd—I	11.16(3)

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

of molecular architecture, their exact structures, shapes, and size are of considerable inherent interest as well as of practical interest in possible future applications. Hence, we attempted to obtain single crystals and carry out X-ray molecular structure determinations of all macrocyclic squares prepared and described above. To date suitable single crystals were obtained for **5b**, **5d**, and **7c**. Unfortunately, **7c** contained solvents of crystallization which were immediately lost upon mounting and the single crystal collapsed into a powder, despite numerous precautions and different mounting techniques. Likewise, for **5b** large amounts of solvents, coupled with disordered triflates, precluded refining to a satisfactory and acceptable level. Nevertheless, the gross structure and square nature of **5b** were confirmed and established even by this crude structure determination. Fortunately, the structure of **5d** was sufficiently resolved and readily solved. Crystallographic data for **5d** are summarized in Table 1. The numbering diagram, ORTEP representation, and significant geometric features are shown in Figure 1. The important bond distances and angles are given in Table 2.

Examination of these data reveal a number of interesting structural features. The Pd(II) center is square planar but with significant deviations from the ideal 90° angles. The P—Pd—P angle opens up to 95.1° whereas the N—Pd—N bond angle is only 83.5°. The Pd—P and Pd—N bond lengths are normal and comparable[15] to those in the all-metal macrocyclic square. The C—I—C angle opens up to 98.7° compared to the more normal ~90° of diaryl and related iodonium salts.[13,14] The I—C$_{sp^2}$ distances of 2.08 to 2.13 Å are within the expected[13,14] range.

In order to accommodate the larger C—I—C angle and the smaller N—Pd—N angle the molecule, although essentially planar, adopts a rhomboid-like geometry with the Pd-to-Pd
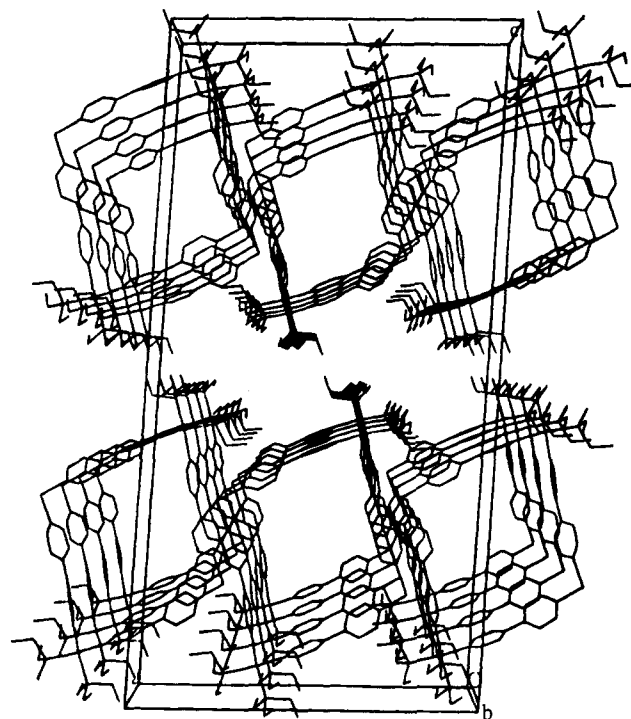

Figure 2. Packing diagram of the molecular square **5d**.

diagonal distance being 17.1 Å whereas the I-to-I diagonal distance is only 14.3 Å. The edge-to-edge Pd-to-I distance is 11.2 Å. This compares to a metal-to-metal diagonal distance of 14.6 Å for the all-metal macrocyclic square[15] with an edge-to-edge distance also of 11.2 Å. As expected, the pyridyl unit is twisted from the phenyl unit around the central C—C bond by a twist angle of approximately 32°.

Especially interesting and revealing is the stacking pattern in the solid state as shown in Figure 2. The cationic squares are stacked along the *B* axis, resulting in long channel-like cavities. The repeating units are 9.5 Å apart as compared to a stacking distance of nearly 16 Å for the all-metal analog.[15] The triflate counterions are below and above the planes of the cations with one triflate each close to the iodonium moiety and the cationic Pd whereas the third one actually is in-between the Pd^{2+} and I$^+$ corners (see Figure 1).

The gross features of the analogous Pt-complex **5b** are identical to the Pd-analog **5d**. The molecule is also planar but a rhomboid rather than a square. Unfortunately triflate disorder and solvent occlusion precluded refinement to a satisfactory level for **5b**.

Finally, it is interesting to compare the geometry of **5d** to the all-metal analog **1** (L_2 = dppp, M = Pt). The all-metal macrocycle is a puckered square[15] whereas the hybrid molecular squares **5** are likewise planar rhomboids and we have no reliable geometric information on the smaller congeners **7**. We are continuing our efforts to grow suitable crystals for exact molecular structure determination of all the above described unique macrocyclic species.

Conclusions

A new class of compounds, cationic, hybrid iodonium–transition metal macrocyclic squares, have been isolated via modular self-assembly of the precursor bis(heteroaryl)iodonium species with the *cis* square-planar Pt(II) and Pd(II) bis-triflate complexes. The larger species **5** are stable whereas the smaller congeners are less stable. This difference is likely due to the greater ability of **5** to accommodate the angle distortions from the ideal 90° of a perfect square than the smaller macrocycles **7**. The X-ray crystal structure establishes molecules **5a–d** as planar rhomboids with an I-to-M distance of around 11 Å on the sides and diagonal distances of M-to-M and I–I around 17 and 14 Å, respectively. The stacking diagram clearly shows a channel in the solid state that is likely to be important and useful for molecular interactions and potential host–guest chemistry. Such studies are under way.

Experimental Section

General Methods: ^{1}H, ^{7}Li, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded on a Varian XL-300 spectrometer at 300, 117, 75, 282, and 121 MHz, respectively. ^{1}H chemical shifts are reported relative to the residual nondeuterated solvent of acetone at δ 2.05 or methanol at δ 3.31. The ^{7}Li chemical shifts are referenced relative to LiCl in CD$_3$OD at δ 0.00. The ^{13}C chemical shifts are referenced relative to CD$_3$COCD$_3$ at δ 29.0 or CD$_3$OD at δ 49.0. The ^{19}F NMR spectra are referenced to CFCl$_3$ (sealed capillary) at δ 0.00 and the ^{31}P chemical shifts are referenced to 85% H$_3$PO$_4$ (sealed capillary) at δ 0.00 in the appropriate solvent. IR spectra were recorded on a Mattson Polaris FT-IR spectrometer, and X-ray data for **5b** and **5d** were collected on a CAD4 diffractometer. Melting points were obtained with a Mel-Temp capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA.

All reactions were performed in oven-dried glassware under an inert atmosphere of dry N$_2$, solvents used during the workup were reagent or HPLC grade unless specified otherwise. Dry (or anhydrous) solvents used for reactions were distilled from the indicated drying agents; CH$_2$Cl$_2$ (CaH$_2$), THF (sodium/benzophenone), Et$_2$O (sodium/benzophenone), toluene (P$_2$O$_5$), and DMF (CaH$_2$) and were stored over molecular sieves (3 Å) if not used right after distillation. Acetone used for the preparation of **5** and **7** was HPLC grade and was stored over molecular sieves (3 Å). *cis*-ML$_2$(OTf)$_2$ (**3**), were prepared as previously described.[1,15] Bis(heteroaryl)iodonium chlorides were prepared according to the published procedure.[23]

Bis[4-(4′-pyridyl)phenyl]iodonium Triflate (4). Bis[4-(4′-pyridyl)phenyl]iodonium chloride[23] (0.300 g, 0.620 mmol) was suspended in 15 mL of dry CH$_2$Cl$_2$ at 0 °C, followed by the addition of excess TMSOTf (5.0 mL, 0.5 solution in CH$_2$Cl$_2$). The reaction mixture was allowed to stir at room temperature overnight. The insoluble material was collected by filtration, washed with CH$_2$Cl$_2$, and dried under nitrogen to yield a yellow solid (0.67 g) of protonated **4**: ^{1}H NMR (CD$_3$COCD$_3$) δ 9.20 (d, 7.0; 4 H, H$_\alpha$-Py), 8.71 (d, 8.8; 4 H, H$_\alpha$-PhI), 8.64 (d, 7.0; 4 H, H$_\beta$-Py), 8.28 (d, 8.9; 4 H, H$_\beta$-PhI), 5.8–4.5 (bs; 14H, NH + H$_2$O); ^{19}F NMR (CD$_3$COCD$_3$) δ −78.3.

The protonated iodonium salt (0.455 g) was suspended in 50 mL of dry CH$_2$Cl$_2$, then a solution of Et$_3$N (0.127 g, 1.26 mmol) in 5 mL of CH$_2$Cl$_2$ was added slowly at room temperature. After stirring for an additional 1.5 h, the insoluble material was collected by filtration, washed with CH$_2$Cl$_2$, and dried under N$_2$ to afford 0.253 g of **4** as a

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tan powder, mp 172 °C dec. (softened at 94 °C): IR (thin film) cm^{-1} 3103, 3019, 1600, 1478 (Ar), 1263, 1160, 1030 (OTf); ^{1}H NMR (CD$_3$OD) δ 8.63 (d, 6.1; 4 H, H$_\alpha$-Py), 8.37 (d, 8.4; 4 H, H$_\alpha$-PhI), 7.92 (d, 8.4; 4 H, H$_\beta$-PhI), 7.73 (d, 6.3; 4 H, H$_\beta$-Py); ^{13}C NMR (CD$_3$OD) δ 151.02 (d, 9.0; C$_\alpha$-Py), 148.36 (s; C$_\gamma$-Py), 143.38 (s; C$_\gamma$-PhI), 137.43 (d, 11.2; C$_\alpha$-PhI), 131.81 (d, 11.6; C$_\beta$-PhI), 123.48 (d, 11.0; C$_\beta$-Py), 121.86 (q, 318.4; CF$_3$), 116.92 (s; C-I); ^{19}F NMR (CD$_3$OD) δ −79.6; ^{7}Li NMR (CD$_3$OD) δ 0.01. Anal. Calcd for C$_{23}$H$_{16}$F$_3$IN$_2$O$_3$S·2(CF$_3$SO$_3$Li)·3.5H$_2$O: C, 31.28; H, 2.42; I, 13.23; N, 2.92; S, 10.00. Found: C, 30.90; H, 2.12; I, 12.84; N, 2.82; S, 9.87. The elemental analysis of compound **4** contains two molecules of triflic acid lithium salt as is also confirmed by ^{7}Li NMR, which cannot be removed by washing with CH$_2$Cl$_2$, therefore, compound **4** was used without further purification. Analytically pure compound **4** containing no lithium triflate can be obtained by recrystallization from a warm mixture of acetonitrile and acetone (1:2.5) and washed with acetone (39% recovered), mp 197–198 °C dec. The ^{1}H, ^{13}C spectral data for analytically pure **4** is identical with material containing LiOTf whereas the ^{19}F is shifted to δ 78.4. Anal. Calcd for C$_{23}$H$_{16}$F$_3$IN$_2$O$_3$S: C, 47.27; H, 2.76; I, 21.72; N, 4.79; S, 5.49. Found: C, 46.90; H, 2.86; I, 21.50; N, 4.71; S, 5.35.

Bis(4-pyridyl)iodonium Triflate (6). To a suspension of bis(4-pyridyl)iodonium chloride[23] (0.202 g, 0.560 mmol) in 30 mL of dry CH$_2$Cl$_2$, was added dropwise at 0 °C a solution of TMSOTf (5.7 ml, 0.5 M in CH$_2$Cl$_2$). After the addition was complete, the reaction mixture was allowed to stir at room temperature for 5 h. Protonated iodonium triflate **6** was isolated in a similar manner described for protonated **4** to yield 0.305 g of an off-white hygroscopic solid: ^{1}H NMR (CD$_3$COCD$_3$) δ 8.92 (d, 6.2; 4 H, H$_\alpha$-Py), 8.55 (d, 6.2; 4 H, H$_\beta$-Py); ^{19}F NMR (CD$_3$COCD$_3$) δ −78.3.

A suspension of this protonated bis(4-pyridyl)iodonium triflate (0.220 g) in 30 mL of dry CH$_2$Cl$_2$ was allowed to react with Et$_3$N (0.092 g, 0.91 mmol) at 0 °C for 5 min and then at room temperature for 20 min. The product was isolated in a similar manner to that of **4** affording 0.196 g of **6** as a tan solid: IR (thin film) cm^{-1} 3086, 1641, 1631 (Ar), 1281, 1264, 1176, 1039 (OTf); ^{1}H NMR (CD$_3$COCD$_3$) δ 8.84 (d, 6.0; 4 H, H$_\alpha$-Py), 8.40 (d, 6.02; 4 H, H$_\beta$-Py); ^{13}C NMR spectrum could not be obtained due to decomposition in acetone; ^{19}F NMR (CD$_3$COCD$_3$) δ −78.2.

{[(OTf)$_2$(dppp)Pt][(NC$_5$H$_4$C$_6$H$_4$)$_2$I(OTf)]}$_2$ (5a), General Method. *cis*-Pt(dppp)(OTf)$_2$ (**3a**) (0.129 g, 0.142 mmol) was added to a suspension of bis[4-(4′-pyridyl)phenyl]iodonium triflate (**4**) (0.078 g, 0.0813 mmol) in 25 mL of acetone at room temperature. A yellow solution resulted almost instantaneously. After stirring at room temperature for 16 h, the trace amount of insoluble material was filtered off and washed with acetone. The filtrate was concentrated to a light brown oil, from which a pale yellow solid of **5a** was obtained quantitatively after trituration with Et$_2$O. An analytically pure sample was obtained by dissolving **5a** in acetone and diffusion with a mixture of Et$_2$O/CHCl$_3$ (4:1) to give pure **5a** as a colorless solid, mp 253–256 °C dec (darkened after 250 °C): IR (thin film) cm^{-1} 3089, 3052, 1617, 1437 (Ar), 1278, 1257, 1162, 1029 (OTf); ^{1}H NMR (CD$_3$COCD$_3$) δ 9.06 (bd, 5.0; 8 H, H$_\alpha$-Py), 8.42 (d, 8.7; 8 H, H$_\alpha$-PhI), 7.88–7.70 (m; 24 H, H$_\beta$-PhI and H$_o$-PhP), 7.53 (d, 6.7; 8 H, H$_\beta$-Py), 7.48–7.34 (m; 24 H, H$_m$ and H$_p$-PhP), 3.49 (bs, 8 H, PCH$_2$), 2.34 (m; 4 H, PCH$_2$CH$_2$); ^{13}C NMR (CD$_3$COCD$_3$) δ 151.76 (s; C$_\alpha$-Py), 149.48 (s; C$_\gamma$-Py), 139.80 (s; C$_\gamma$-PhI), 137.88 (d, 4.1; C$_\alpha$-PhI), 134.13 (bs, C$_o$-PhP), 133.03 (s; C$_p$-PhP), 131.59 (d, 4.1; C$_\beta$-PhI), 130.19 (t, 5.6; C$_m$-PhP), 126.07 (m; C$_{ipso}$-PhP), 125.30 (s; C$_\beta$-Py), 122.23 (q, 320.7; CF$_3$), 117.59 (s; C-I), 21.76 (m; P-CH$_2$), 18.52 (bs; PCH$_2$CH$_2$); ^{31}P NMR (CD$_3$COCD$_3$) δ −13.0 (s, J$_{Pt−P}$ = 3040 Hz); ^{19}F NMR (CD$_3$COCD$_3$) δ −78.0. Anal. Calcd for C$_{104}$H$_{84}$F$_{18}$I$_2$N$_4$P$_4$Pt$_2$O$_{18}$S$_6$·3H$_2$O: C, 41.17; H, 2.99; I, 8.37; N, 1.85; S, 6.34. Found: C, 41.38; H, 2.99; I, 8.33; N, 1.83; S, 6.32.

{[(OTf)$_2$(PEt$_3$)$_2$Pt][(NC$_5$H$_4$C$_6$H$_4$)$_2$I(OTf)]}$_2$ (5b). Reaction of iodonium salt **4** (0.083 g, 0.0866 mmol) with *cis*-Pt(PEt$_3$)$_2$(OTf)$_2$ (**3b**) (0.100 g, 0.137 mmol) in acetone (35 mL) for 2 h as described above in the above general procedure afforded the desired product **5b** as a pale yellow solid quantitatively. An analytically pure sample (white powder) and a single crystal suitable for X-ray analysis of **5b** were obtained by diffusion with a mixture of Et$_2$O/CHCl$_3$ (3:1) into an acetone solution of **5b**, mp 216–219 °C dec (softened at 211 °C): IR (thin film) cm^{-1} 3093, 2980, 1614 (Ar), 1281, 1159, 1032 (OTf); ^{1}H

NMR (CD$_3$OD) δ 9.05 (bd, 5.7; 8 H, H$_\alpha$-Py), 8.37 (d, 8.7; 8 H, H$_\alpha$-PhI), 8.01 (d, 6.7; 8 H, H$_\beta$-Py), 7.94 (d, 8.8; 8 H, H$_\beta$-PhI), 1.89 (quintet, 8.0; 24 H, PCH_2), 1.34 and 1.28 (2t, overlapping, $J = 7.7$ and 7.5; 36 H, PCH$_2$CH_3); ^{13}C NMR (CD$_3$OD) δ 152.19 (s; C$_\alpha$-Py), 151.72 (s; C$_{\gamma'}$-Py), 140.26 (s; C$_{\gamma'}$-PhI), 137.70 (d, 3.5; C$_\alpha$-PhI), 132.07 (d, 3.2; C$_\beta$-Py), 127.07 (d, 4.9; C$_\beta$-PhI), 121.90 (q, 318.6; CF$_3$), 118.38 (s; C-I), 15.95 (m; PCH_2), 8.40 (s; PCH$_2$CH_3); ^{31}P NMR (CD$_3$OD) δ 0.59 (s, J_{Pt-P} = 3060 Hz); ^{19}F NMR (CD$_3$OD) δ −78.5 (s). Anal. Calcd for C$_{74}$H$_{92}$F$_{18}$I$_2$N$_4$O$_{18}$P$_4$Pt$_2$S$_6$·3H$_2$O: C, 33.14; H, 3.68; N, 2.09. Found: C, 33.09; H, 3.61; N, 2.13.

{[(OTf)$_2$(dppp)Pd][(NC$_5$H$_4$C$_6$H$_4$)$_2$I(OTf)]}$_2$ (**5c**). Reaction of iodonium triflate (**4**) (0.120 g, 0.125 mmol) with *cis*-Pd(dppp)(OTf)$_2$ (**3c**) (0.165 g, 0.193 mmol) in acetone (35 mL) at room temperature for 17 h afforded **5c** (0.173 g, 95%) as a pale yellow solid. Further purification similar to that of **5a** gave **5c** as a white solid, mp 228−230 °C dec (darkened after 226 °C); IR (thin film) cm^{-1} 3057, 1613, 1437 (Ar), 1277, 1256, 1156, 1028 (OTf); ^{1}H NMR (CD$_3$COCD$_3$) δ 9.03 (bd, 6.4; 8 H, H$_\alpha$-Py), 8.41 (d, 8.8; 8 H, H$_\alpha$-PhI), 7.87−7.72 (m; 24 H, H$_\beta$-PhI and H$_o$-PhP), 7.47 (d, 6.6; 8 H, H$_\beta$-Py), 7.44−7.32 (m; 24 H, H$_m$ and H$_p$-PhP), 3.38 (bs, 8 H, PCH_2), 2.37 (m; 4 H, PCH$_2$CH_2); ^{13}C NMR (CD$_3$COCD$_3$) δ 151.73 (s; C$_\alpha$-Py), 148.93 (s; C$_{\gamma'}$-Py), 140.18 (s; C$_{\gamma'}$-PhI), 137.35 (s; C$_\alpha$-PhI), 134.09 (t, 5.0; C$_o$-PhP), 133.00 (s; C$_p$-PhP), 131.55 (d, 4.1; C$_\beta$-PhI), 130.30 (t, 5.6; C$_m$-PhP), 126.63 (m; C$_{ipso}$-PhP), 124.77 (s; C$_\beta$-Py), 122.20 (q, 321.2; CF$_3$), 117.34 (s; C-I), 21.78 (m; P-CH_2), 18.50 (bs; PCH$_2$CH_2); ^{31}P NMR (CD$_3$COCD$_3$) δ 8.9 (s); ^{19}F NMR (CD$_3$COCD$_3$) δ −78.0. Anal. Calcd for C$_{104}$H$_{84}$F$_{18}$I$_2$N$_4$P$_4$Pd$_2$O$_{18}$S$_6$·6H$_2$O: C, 42.91; H, 3.32; I, 8.72; N, 1.93; S, 6.61. Found: C, 42.72; H, 3.05; I, 9.02; N, 1.99; S, 6.62.

{[(OTf)$_2$(PEt$_3$)$_2$Pd][(NC$_5$H$_4$C$_6$H$_4$)$_2$I(OTf)]}$_2$ (**5d**). Iodonium triflate (**4**) (0.130 g, 0.136 mmol) and *cis*-Pd(PEt$_3$)$_2$(OTf)$_2$ (**3d**) (0.143 g, 0.222 mmol) were allowed to react in acetone (40 mL) for 2 h affording a crude product which contained two components, compound **5d** being the major product (by ^{1}H NMR). Pure **5d** (0.131 g, 77%) was obtained as needles by slow diffusion of a mixture of Et$_2$O/CHCl$_3$ (4:1) into an acetone solution of **5d**. An analytically pure sample (white powder after losing solvents of crystallization) and a single crystal suitable for X-ray analysis of **5d** were thus obtained, mp 165−167 °C dec: IR (thin film) cm^{-1} 3069, 2975, 1612 (Ar), 1278, 1258, 1159, 1030 (OTf); ^{1}H NMR (CD$_3$OD) δ 9.05 (bd; 8 H, H$_\alpha$-Py), 8.36 (d, 8.7; 8 H, H$_\alpha$-PhI), 7.96 (d, 6.4; 8 H, H$_\beta$-Py), 7.91 (d, 8.7; 8 H, H$_\beta$-PhI), 1.89 (quintet, 7.8; 24 H, PCH_2), 1.38 and 1.32 (2t, overlapping, $J = 7.6$ and 7.5; 36 H, PCH$_2$CH_3); ^{13}C NMR (CD$_3$OD) δ 152.16 (s; C$_\alpha$-Py), 151.25 (s; C$_{\gamma'}$-Py), 140.58 (s; C$_{\gamma'}$-PhI), 137.66 (s; C$_\alpha$-PhI), 132.01 (s; C$_\beta$-Py), 126.53 (s; C$_\beta$-PhI), 121.91 (q, 318.6; CF$_3$), 118.17 (s; C-I), 16.86 (m; PCH_2), 8.64 (s; PCH$_2$CH_3); ^{31}P NMR (CD$_3$OD) δ 29.5 (s); ^{19}F NMR (CD$_3$OD) δ −79.5 (s). Anal. Calcd for C$_{74}$H$_{92}$F$_{18}$I$_2$N$_4$O$_{18}$P$_4$Pd$_2$S$_6$·3H$_2$O: C, 35.49; H, 3.94; I, 10.13; N, 2.24; S, 7.68. Found: C, 35.73; H, 3.97; I, 9.71; N, 2.15; S, 7.52. The same product was also obtained in 81% yield from the reaction of non-lithium triflate-containing iodonium salt **4** (0.018 g, 0.0315 mmol) with *cis*-Pd(PEt$_3$)$_2$(OTf)$_2$ (0.021 g, 0.0315 mmol) in acetone (11 mL) for 2.3 h at room temperature. The spectra (^{1}H NMR, ^{19}F NMR, and ^{31}P NMR) of this compound were identical to those reported above.

{[(OTf)$_2$(dppp)Pt][(NC$_5$H$_4$)$_2$I(OTf)]}$_2$ (**7a**). Reaction of bis(4-pyridyl)iodonium triflate (**6**) (0.110 g, 0.260 mmol) with *cis*-Pt(dppp)-(OTf)$_2$ (**3a**) (0.200 g, 0.220 mmol) in 40 mL of acetone at room temperature for 80 min with workup according to the general procedure afforded 0.202 g (59%) of **7a** as a tan solid. Several attempts at obtaining analytically pure sample led only to decomposition of the product. ^{1}H NMR (CD$_3$COCD$_3$) δ 8.95 (bd, 6.3; H$_\alpha$-Py), 8.20 (bd, 6.6; H$_\beta$-Py), 7.80−7.68 (m; H$_o$-PhP), 7.50−7.35 (m; H$_p$ and H$_m$-PhP),

3.38−3.63 (m; PCH_2), 2.42−2.20 (m; PCH$_2$CH_3); ^{31}P NMR (CD$_3$-COCD$_3$) δ −13.8 (s, J_{Pt-P} = 3074.6).

{[(OTf)$_2$(PEt$_3$)$_2$Pt][(NC$_5$H$_4$)$_2$I(OTf)]}$_2$ (**7b**). Reaction of bis(4-pyridyl)iodonium triflate (**6**) (0.084 g, 0.185 mmol) with *cis*-Pt(PEt$_3$)$_2$-(OTf)$_2$ (**3b**) (0.135 g, 0.185 mmol) in 35 mL of acetone at room temperature for 2 h and workup in accord with the general procedure afforded 0.108 g (50%) of **7b** as a brown powder. An analytically pure sample was obtained by slow diffusion of Et$_2$O/CHCl$_3$ (3:1) into a solution of the product in acetone which gave pale yellow needles which turned to yellow powder after losing solvents of crystallization, mp 184−186 °C dec (darkened after 173 °C): IR (thin film) cm^{-1} 3087, 2981, 1409 (Ar), 1258, 1168, 1032 (OTf); ^{1}H NMR (CD$_3$OD) δ 9.12 (bd, 4.4; 8 H, H$_\alpha$-Py), 8.67 (d, 6.4; 8 H, H$_\beta$-Py), 1.86 (quintet, 7.6; 24 H, P-CH_2), 1.30 and 1.24 (2t, overlapping, $J = 7.6$ and 7.5; 36 H, PCH$_2$CH_3); ^{13}C NMR (CD$_3$OD) δ 154.10 (s; C$_\alpha$-Py), 136.02 (s; C$_\beta$Py), 129.20 (s; C-I), 121.84 (q, 319.7; CF$_3$), 16.01 (m; PCH_2), 8.35 (s; PCH$_2$CH_3); ^{31}P NMR (CD$_3$OD) δ 1.01 (s, J_{Pt-P} = 3097.4); ^{19}F NMR (CD$_3$OD) δ −79.4 (s). Anal. Calcd for C$_{50}$H$_{76}$F$_{18}$I$_2$N$_4$O$_{18}$P$_4$Pt$_2$S$_6$·2H$_2$O: C, 25.45; H, 3.42; N, 2.37. Found: C, 25.39; H, 3.27; N, 2.37.

{[(OTf)$_2$(dppp)Pd][(NC$_5$H$_4$)$_2$I(OTf)]}$_2$ (**7c**). Reaction of bis(4-pyridyl)iodonium triflate (**6**) (0.100 g, 0.230 mmol) with *cis*-Pd(dppp)-(OTf)$_2$ (**3c**) (0.194 g, 0.230 mmol) in 40 mL of acetone at room temperature for 3 h and workup as described above gave **7c**, 0.172 g (60%), as a tan solid. Single crystals (light brown-yellow) were obtained by slow diffusion with a mixture of Et$_2$O/CHCl$_3$ (4:1) into an acetone solution of **7c**, mp 182−183 °C dec: IR (thin film) cm^{-1} 3086, 2961, 1439 (Ar), 1259, 1170, 1030 (OTf); ^{1}H NMR (CD$_3$COCD$_3$) δ 8.94 (bd, 5.8; 8 H, H$_\alpha$-Py), 8.17 (bd, 6.3; 8 H, H$_\beta$-Py), 7.80−7.65 (m; 16 H, H$_o$-PhP), 7.52−7.34 (m; 24 H, H$_p$ and H$_m$-PhP), 3.39 (bs; 8 H, PCH_2), 2.35 (m; 4 H, PCH$_2$CH_3); ^{13}C NMR (CD$_3$COCD$_3$) δ 153.13 (s; C$_\alpha$-Py), 133.86 (bs; C$_o$-PhP), 133.54 (s; C$_\beta$-Py), 133.43 (bs; C$_p$-PhP), 130.64 (t, 5.6; C$_m$-PhP), 127.04 (s; C-I), 125.73 (m; C$_{ipso}$-PhP), 121.86 (q, 320.6; CF$_3$), 21.50 (m; PCH_2), 18.31 (bs; PCH$_2$CH_3); ^{31}P NMR (CD$_3$COCD$_3$) δ 9.34 (s); ^{19}F NMR (CD$_3$COCD$_3$) δ −77.9 (s). Anal. Calcd for C$_{80}$H$_{68}$F$_{18}$N$_4$I$_2$O$_{18}$P$_4$Pd$_2$S$_6$·3H$_2$O: C, 37.65; H, 2.92; I, 9.94; N, 2.20; S, 7.54. Found: C, 37.62; H, 2.91; I, 9.84; N, 2.13; S, 7.48.

{[(OTf)$_2$(PEt$_3$)$_2$Pd][(NC$_5$H$_4$)$_2$I(OTf)]}$_2$ (**7d**). Reaction of bis(4-pyridyl)iodonium triflate (**6**) (0.120 g, 0.280 mmol) with *cis*-Pd(PEt$_3$)$_2$-(OTf)$_2$ (**3d**) (0.178 g, 0.280 mmol) in 40 mL of acetone at room temperature for 2.3 h with workup according to the general procedure afforded 0.398 g of an oily material. This material consisted mainly of product **7d** and solvents as assayed by ^{1}H NMR, even after drying under vacuum at 0.5 mmHg for 10 h at room temperature. Several attempts at purification of the product were unsuccessful and only led to the formation of a black material. ^{1}H NMR of the crude **7d** in acetone-d_6 showed proton chemical shifts at δ 9.33 (bd, 6.7; H$_\alpha$-Py), 8.72 (d, 6.4; H$_\beta$-Py), 2.35−2.15 (m; P-CH_2), 1.45−1.25 (m; PCH$_2$CH_3).

Supporting Information Available: Tables of positional parameters and ESD, anistropic displacement parameters, and an extended list of bond lengths and bond angles for compound **5d** (11 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 the ACS, and can be downloaded from the internet; see any current masthead page for ordering information and internet access instructions.

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