Diastereomeric Square-Planar Platinum(II) and Palladium(II) Complexes Due to Restricted Rotation about the Chelated M–N Heteroaryl Bond

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Received June 14, 1995[⊗]

The reaction of 3-bromopyridine, quinoline, or isoquinoline with *cis*-M(L)$_2$(OTf)$_2$ (M = Pd, Pt; L = triethylphosphine, $^1/_2$ 1,3-bis(diphenylphosphino)propane (dppp) or $^1/_2$ (*R*)-(+)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl ((*R*)-(+)-BINAP)) results in the formation of diastereomeric, square-planar, cationic complexes, which exhibit restricted rotation about the metal–nitrogen heteroaryl bond. All complexes were characterized by routine physical and spectroscopic methods, of which ^{31}P{^{1}H} NMR spectroscopy was most valuable. Only the complexes [Pd(dppp)(isoquinoline)$_2$][OTf]$_2$ (**14**), [Pt(dppp)(isoquinoline)$_2$][OTf]$_2$ (**15**), and [Pd((*R*)-(+)-BINAP)(isoquinoline)$_2$][OTf]$_2$ (**22**) were found to be dynamic at ambient temperature on the NMR time scale. Variable-temperature studies of the ^{31}P{^{1}H} NMR spectra of these compounds were performed. The X-ray crystal structure of [Pt(dppp)(quinoline)$_2$][OTf]$_2$ (**19**) in one of its stereoisomeric (syn) forms is reported. [Pd((*R*)-(+)-BINAP)(isoquinoline)$_2$][OTf]$_2$ (**22**) and [Pt((*R*)-(+)-BINAP)(isoquinoline)$_2$][OTf]$_2$ (**23**) exhibit three distinct rotamers at −20 °C and ambient temperature, respectively. The role of asymmetric induction of the chiral bis-phosphine ligand on the stereoisomeric ratio of the rotamers of **22** and **23** is discussed.

Introduction

The square-planar, tetracoordinated complexes of divalent palladium and platinum are a most diverse group of organometallic compounds whose unique properties have found a vast number of applications, from natural product synthesis to chemotherapy. This includes catalytic hydroformylation,[1] carbonylation,[2] the Heck reaction,[3] transition-metal-mediated coupling,[4] and C–H bond activation.[5] One of the most recent applications is the self-assembly of the various metallamacrocycles[6] and metallacalixarenes.[7] Although many of these reactions involve the interaction between reactive metal bis-phosphines and different heteroaryls, studies of the stereochemistry of cationic Pd(II) and Pt(II) bis-phosphine complexes, implementing unsymmetrically substituted heterocycles, have not yet been made to date.

The effect of restricted rotation in covalent complexes of Pd, Pt, and Ni has been the subject of several investigations, which shed some light on this interesting phenomenon.[8] The growing interest in this area is manifested by the recent development of several chiral bis-phosphine Pd and Pt complexes with covalently bound iodo aryls and bis-aryls (**1-5**; Chart 1) as well as their potential applications.[9]

Considering all these facts, our objectives were (1) to investigate the stereochemistry of noncovalent, cationic complexes of Pd and Pt, where the chelating M–N bond is considerably weaker as compared to the corresponding covalent systems, (2) to find the influence of nonchelating ligands in the *cis* arrangement on the impedance of free rotation, and (3) to determine the factors which influence both the isomeric ratio and the possibility of preferential formation of one of the diastereomers, especially with the chiral metal system. Also, the degree of rotational freedom for different types of heterocycles was of interest.

Results and Discussion

Synthesis of Cationic Complexes of Heteroaryls with Pt(II) and Pd(II) Bis-Phosphines. Among a variety of the reactive complexes of metal bis-phosphines, the triflates are probably the most versatile group, because triflate ligands have long been recognized as labile leaving groups which can be utilized for many organometallic transformations.[10] The precursors, achiral *cis*-M(L)$_2$(OTf)$_2$ (**6–9**; M = Pd, Pt; L = triethylphosphine, $^1/_2$ 1,3-bis(diphenylphosphino)propane (dppp); Scheme 1) were prepared from the corre-

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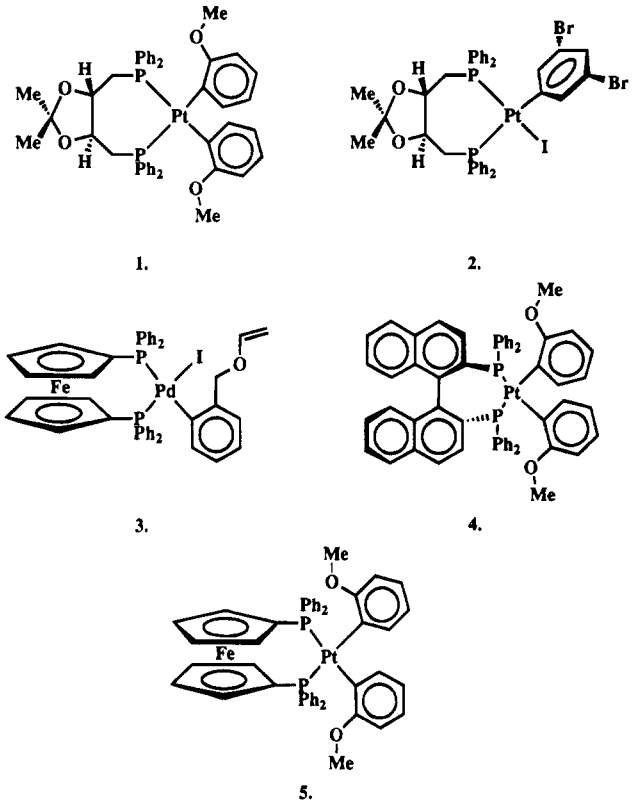
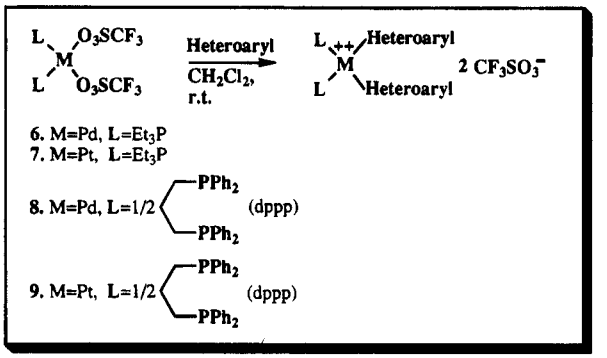
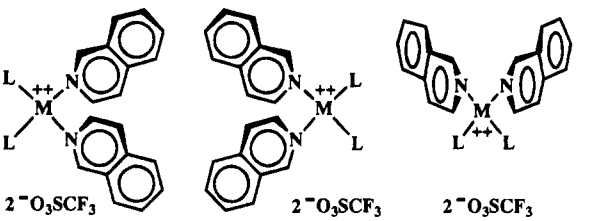
Chart 1

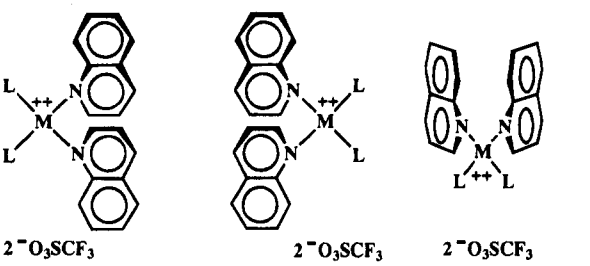


Scheme 1

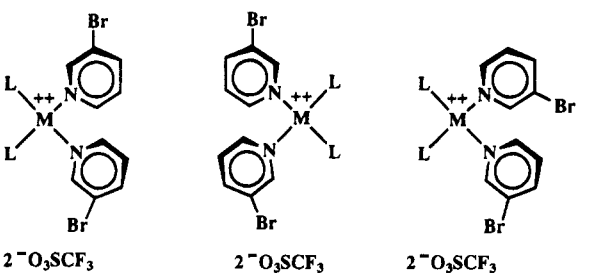




12. M=Pd, L=Et_3P, 3 h, 88%
13. M=Pt, L=Et_3P, 5 h, 89%
14. M=Pd, L=1/2 dppp, 3 h, 89%
15. M=Pt, L=1/2 dppp, 5 h, 84%



16. M=Pd, L=Et_3P, 3h, 84%
17. M=Pt, L=Et_3P, 3 h, 79%
18. M=Pd, L=1/2 dppp, 5 h, 83%
19. M=Pt, L=1/2 dppp, 5 h, 89%



20. M=Pt, L=Et_3P, 3 h, 81%
21. M=Pt, L=1/2 dppp, 5 h, 91%

sponding *cis*-$M(L)_2Cl_2$ by halide abstraction with AgO-Tf.[11] The chiral (*R*)-(+)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl ((*R*)-(+)-BINAP)[12] metal triflates **10** and **11** were prepared by employing a similar procedure (Scheme 2); however, their stable monohydrates were elaborated, as an alternative to highly hygroscopic anhydrous triflates.[13] Three heterocycles were chosen: quinoline, where the ortho influence of the annelated benzene ring is most effective in terms of impedance of free rotation, isoquinoline, where the influence of this ring is less significant, and 3-bromopyridine, where the remotely located bromine can only cause a minimal effect on the rotational freedom of the heterocycle ring, and so the interactions of its α-hydrogens with the phosphine group may play the major role in the possible restriction of free rotation. The achiral complexes **12**–**21** were prepared by the reaction of the appropriate heterocycle with the metal bis-phosphine triflates (Scheme 1) or with their monoaqua complexes (**22** and **23**; Scheme 2) in dichloromethane at ambient temperature. These products are air-stable, albeit hygroscopic, microcrystalline solids, with one or two water molecules often retained in the crystals. For the metal complexes of dppp and (*R*)-(+)-BINAP, the decomposition points are very high, whereas the nonchelated bis-phosphine compounds with *cis*-Et_3P ligands generally melt without decomposition at a relatively low temperature.

NMR Studies of the Complexes. ^{31}P NMR spectroscopy is an excellent tool for the observations of these interesting compounds. At room temperature, achiral bis-phosphine complexes **12**, **13** and **16**–**21** show two sharp distinct peaks in the phosphine region, indicating the presence of the one syn (meso) and two undistinguishable anti isomers (*dl* pair), and a barrier to rotation of at least 70 kJ mol^{-1}. Except for complex **12**, which has a coalescence temperature slightly above ambient

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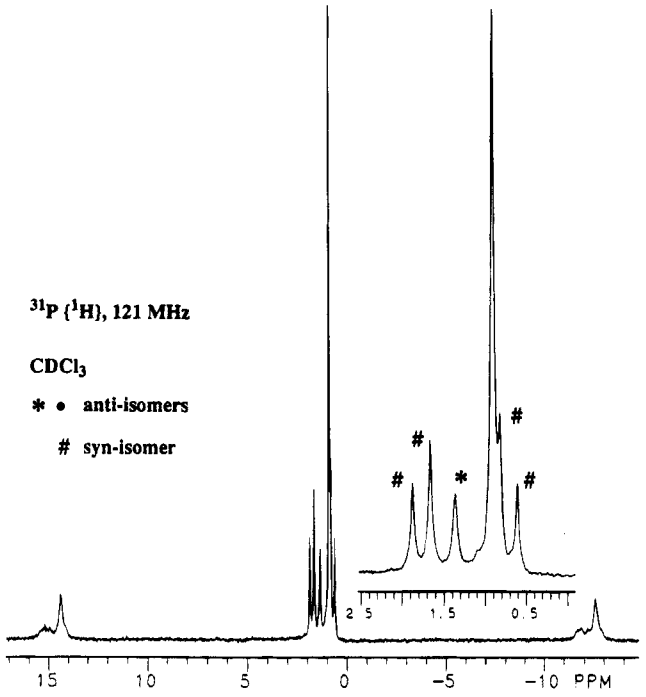
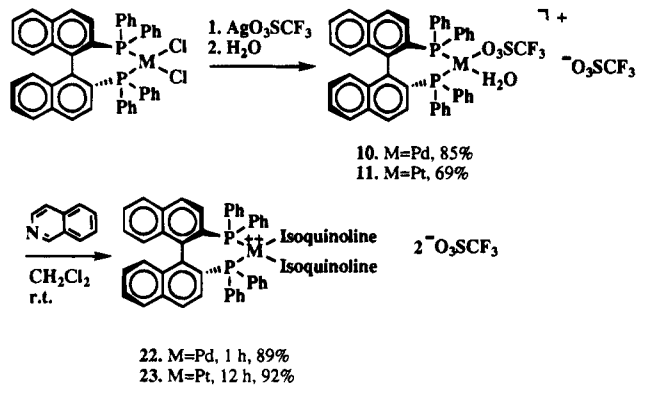


Figure 1. ^{31}P NMR spectrum of compound **23**.

Scheme 2



and a broadened proton spectrum, the ^1H spectra of the others also exhibit two distinct groups of multiplets. Models indicate a low relative free energy for each rotamer but a high barrier to their interconversion. In the course of the synthetic studies it was apparent that the stoichiometric ratio of products of these isomers depends on the type of solvent used to perform the reaction. For example, if the preparation of complex **19** was carried out in CH_2Cl_2, the ^{31}P spectrum of the product shows two peaks for the respective anti and syn isomers in an approximate 0.90:1 ratio. When a $CHCl_3$–CH_2Cl_2 (1:1) mixture was employed, this isomer ratio changed to approximately 1:3. Complexes **14**, **15**, and **22** have a single peak in the ^{31}P spectrum at ambient temperature and significantly broadened lines in the ^1H NMR spectra, thereby indicating lower coalescence barriers. The ^{31}P spectrum of complex **23** contains two singlets and an AB-type doublet of doublets, thereby manifesting the presence of one unsymmetrical (syn) and two C_2-symmetrical (anti) diastereomers (*dl* pair) (Figure 1). The same observation was made for complex **22** at temperatures below −20 °C. The ratio of these isomers indicates a significant preference of one stereoisomeric anti form over the others. This interesting effect, analogous to the observed enantiomeric preference in the neutral covalent bis-aryl complexes of Pt with chiral BINAP and DIOP ligands,[9] is the first such observation for the cationic complexes of Pd(II) and Pt(II).

Variable-temperature ^{31}P NMR studies of **14**, **15**, and **22** were performed, and examples are presented in Figure 2. Above the coalescence temperatures, which are about 0 °C for **14** and 20 °C for **22**, sharp peaks appeared in the spectrum. The ^{31}P spectrum of **15** is analogous to that of complex **14** except for the higher coalescence barrier. Interestingly, the palladium complexes are found to interconvert more readily than their platinum analogs. This can be demonstrated clearly with the chiral complexes **22** (Pd) and **23** (Pt). The Pd complex coalesces at about 0 °C, whereas the Pt complex is above coalescence and its ^{31}P spectrum exhibits signals of all three stereoisomeric forms at room temperature.

X-ray Structure of [Pt(dppp)(quinoline)$_2$][OTf]$_2$ (19). Slow crystallization by the vapor diffusion of diethyl ether into a chloroform solution of the mixture of isomers **19** at room temperature provided X-ray-quality crystals, which were used for the structure determination. A summary of significant features of the structure is presented in Figure 3. The quinoline rings are in the syn configuration, positioned approximately perpendicular to the Pt coordination plane. This result is not unexpected, because our earlier X-ray observations of several pyrazine complexes[6,11] as well as published X-ray structures of pyridine complexes of Pd[14] show that a nitrogen-coordinated heteroaryl ligand possesses an electronic and steric preference for orthogonality to the coordination plane of the transition metal. Both Pt–P bonds are virtually of identical length, as are both Pt–N bonds (Table 1), which suggests the presence of an apparent plane of symmetry that crosses the molecule perpendicularly to the Pt coordination plane. The ^{31}P NMR spectrum of analytically pure **19** shows two peaks at −15.7 and −13.8 ppm and, according to ^1H NMR, a ratio of diastereomers of approximately 1:3. After recrystallization, the ratio in the recrystallized material changed to about 1:7, thereby indicating the absence of equilibration in solution. Hence, it can be implied, although not proven, that the X-ray structure represents the major isomer, which interestingly is the syn form. This syn stereochemistry is opposite to that of other known structures of covalent platinum bis-aryl complexes, where crystallographic analysis shows the anti form in the solid state.[15]

Conclusion

The reaction of selected (achiral chelated, achiral nonchelated, and chiral chelated) Pd(II) or Pt(II) triflates with 3-bromopyridine, quinoline, or isoquinoline complexes results in the formation of diastereomeric, square-planar, cationic complexes. Restricted rotation about the chelated metal–nitrogen heteroaryl bond in these complexes was detected and investigated by

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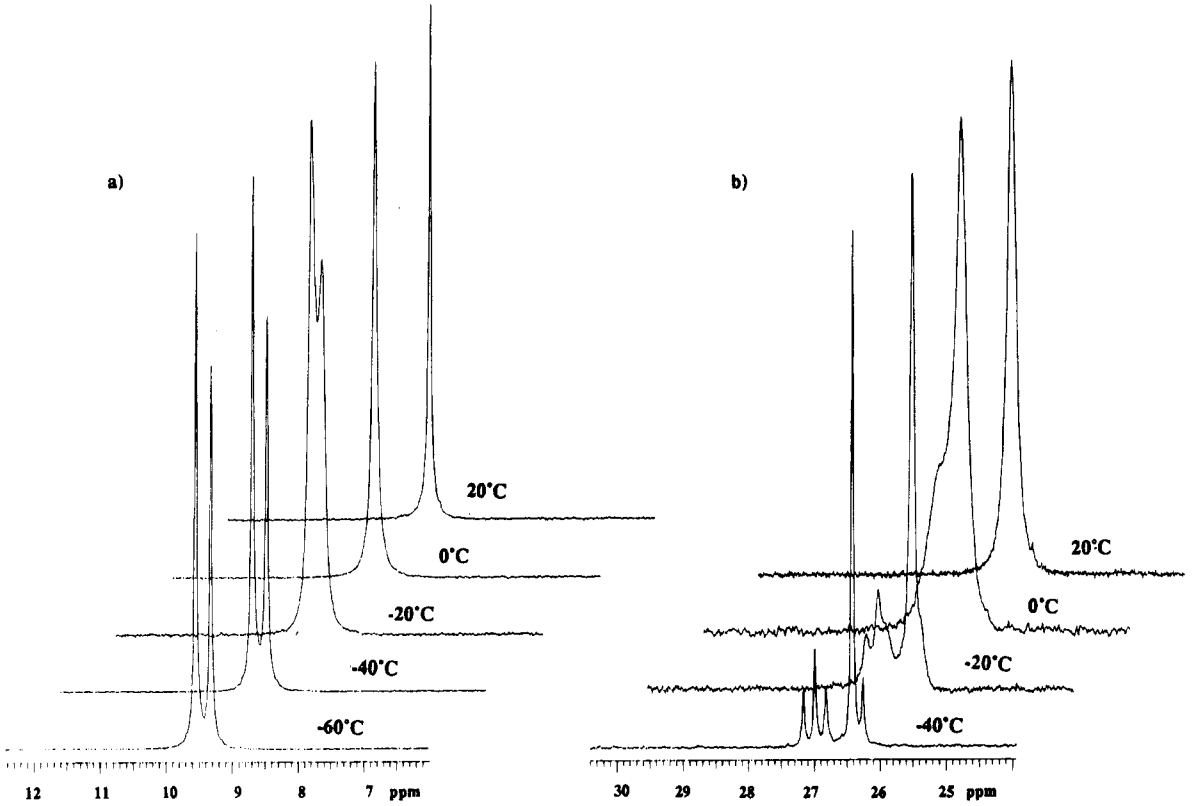

Figure 2. Variable-temperature ^{31}P NMR spectra of compounds **14** (a) and **22** (b).

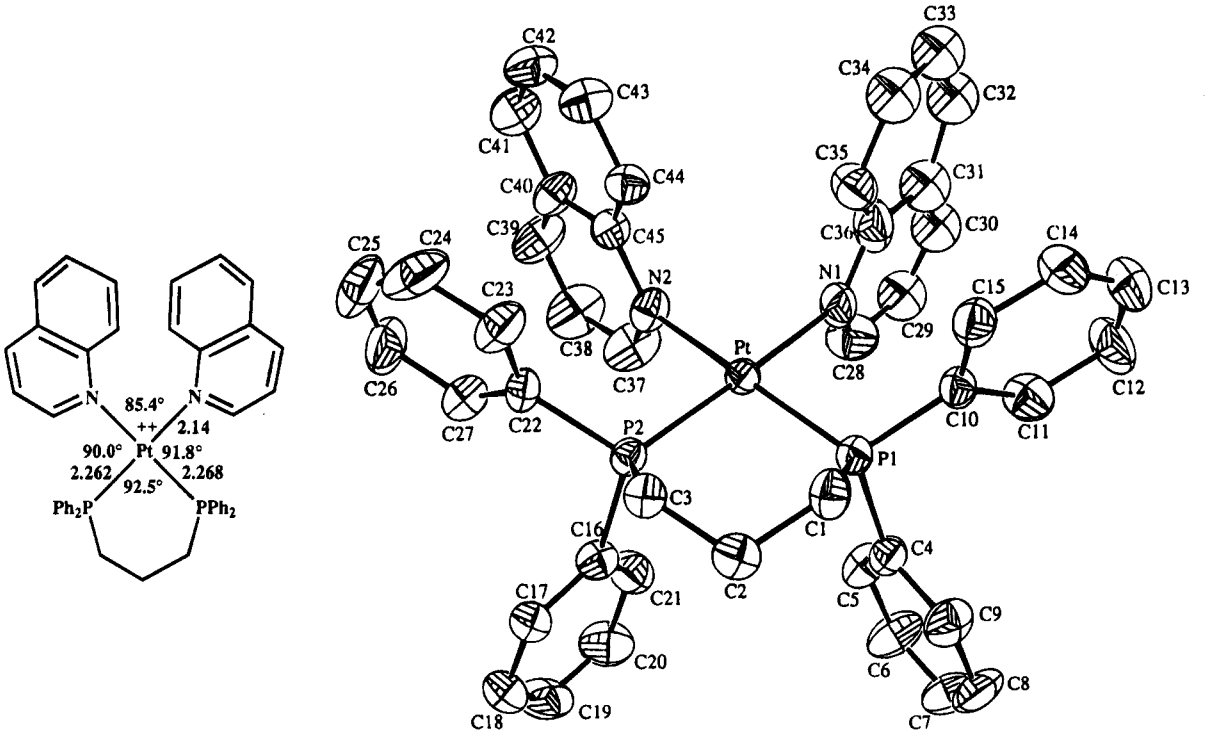

Figure 3. ORTEP diagram and selected bond lengths and bond angles of the cationic part of complex **19**.

different physical and spectroscopic means. The complexes [Pd(dppp)(isoquinoline)$_2$][OTf]$_2$ (**14**), [Pt(dppp)(isoquinoline)$_2$][OTf]$_2$ (**15**), and [Pd((*R*)-(+)-BINAP)(isoquinoline)$_2$][OTf]$_2$ (**22**) were found to be dynamic on the NMR time scale, whereas others exhibited multiple signals indicative of isomers in the $^{31}P\{^1H\}$ spectra at ambient temperature. The hindrance to free rotation was found to be most effective for the *cis*-triethylphosphine complexes. Among the heteroaryls, as expected, the quinoline complexes were found to undergo the slowest interconversion. The observation of restricted rotation in the complexes of 3-bromopyridine with achiral platinum bis-phosphines shows that the presence of an α-substituent in the heteroaryl group or an annelated ring is not a necessary condition for the free rotation restriction. On the basis of the X-ray crystal structure of [Pt(dppp)(quinoline)$_2$][OTf]$_2$ (**19**) and the analysis of its NMR data it can be implied that the

Table 1. Important Bond Angles (deg) and Bond Distances (Å) for *syn*-[Pt(dppp)(quinoline)$_2$][OTf]$_2$ (19)

atom 1	atom 2	atom 3	angle[a]	atom 1	atom 2	distance[a]
P1	Pt	P2	92.5(1)	Pt	P1	2.268(3)
P1	Pt	N1	91.8(3)	Pt	P2	2.262(3)
P1	Pt	N2	175.5(3)	Pt	N1	2.14(1)
P2	Pt	N1	174.7(4)	Pt	N2	2.14(1)
P2	Pt	N2	90.0(3)	P1	C1	1.81(1)
N1	Pt	N2	85.4(5)	P2	C3	1.83(1)

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

major components of the Pd(II) and Pt(II) complexes **18** and **19** are in the syn configuration. In contrast, the spectroscopic data of chiral Pd(II) and Pt(II) complexes of (*R*)-(+)-BINAP strongly suggest that the major isomers are one of the C_2-symmetric anti forms. The latter indicates the critical role of asymmetric induction by the chiral bis-phosphine ligand on the formation of these complexes.

Experimental Section

General Methods. All reactions were conducted under a dry nitrogen atmosphere using Schlenk techniques even though the products can be handled in air. IR spectra were recorded on a Mattson Polaris FT-IR spectrophotometer. NMR spectra were recorded on a Varian XL-300 or Unity-300 spectrometer. ^{1}H NMR 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) or CD_3OD (3.31 ppm). ^{13}C NMR 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_3OD (49.0 ppm) or CD_2Cl_2 (53.8 ppm). ^{31}P NMR 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 NMR spectra were recorded at 282 MHz, and all chemical shifts are reported relative to external $CFCl_3$ at 0.00 ppm. The water signals in ^{1}H NMR were omitted, except for the compound **10**. All *J* values are reported in Hz. Microanalyses were performed by Atlantic Microlab Inc., Norcross, GA. Melting points were obtained with a Mel-Temp capillary melting point apparatus and were not corrected. Abbreviations: br m, broad multiplet; br s, broad singlet, isoq, isoquinoline; quin, quinoline, 3-Br-py, 3-bromopyridine; dppp, 1,3-bis(diphenylphosphino)propane; 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. Isomer A denotes the diastereomer or NMR-equivalent enantiomeric pair, which is present in the greater amount, whereas isomer B refers to the diastereomer or NMR-equivalent enantiomeric pair, which is present in the lower amount, as indicated by the peak ratios in the ^{1}H and ^{31}P NMR. Isomer C indicates an assymmetical syn isomer in chiral bis-phosphine complexes **22** and **23**.

Materials. Solvents were purified as follows: CH_2Cl_2 and $CHCl_3$ were purified by literature procedures[16] and distilled over CaH_2; Et_2O was purified by literature procedures[16] and distilled over Na/benzophenone; CD_2Cl_2 was vacuum-transferred from CaH_2. All solvents were freeze–thaw–pump-degassed twice before use.

All commercial reagents were ACS reagent grade. 3-Bromopyridine, isoquinoline, quinoline, silver triflate, (*R*)-(+)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl ((*R*)-(+)-BINAP), and [Pd((*R*)-(+)-BINAP)][Cl]$_2$ were obtained from Aldrich and were all used as received. The precursors **6** and **7**, along with **8** and **9**, were prepared according to literature methods;[11] [Pt((*R*)-(+)-BINAP)][Cl]$_2$ was prepared by a modified literature procedure.[17]

[Pd((*R*)-(+)-BINAP)(H$_2$O)][OTf]$_2$ (10). The orange powder [Pd((*R*)-(+)-BINAP)][Cl]$_2$ (0.300 g, 0.375 mmol) was placed into a 50-mL Schlenk flask equipped with a stirbar and dissolved in CH_2Cl_2 (25 mL). Then, 0.240 g (0.938 mmol) of AgOTf was added, and the resulting solution was stirred under nitrogen for 20 h at room temperature. The precipitate was filtered, and the filtrate was transferred into a 50 mL flask and reduced in volume to 5 mL in vacuo. Then, 0.007 g (0.390 mmol) of distilled water was added, followed by the addition of diethyl ether. The yellow precipitate was collected and washed with ether. The filtrate was reduced in volume to 5 mL, and additional material was collected as above. Combined solids were dissolved in 10 mL of CH_2Cl_2, and the solution was evaporated to dryness in vacuo at 35–40 °C. The solid was collected and further dried in vacuo: yield of **10** 0.338 g (85%); mp 190–193 °C dec. ^{1}H NMR (CD_2Cl_2): 7.90 (dd, 4H, J = 7.6, 12.2), 7.75–7.56 (m, 14H), 7.49 (dd, 4H, J = 8.3, 15.0), 7.14 (t, 2H, J = 7.4), 6.98 (t, 2H, J = 7.4), 6.85 (br m, 4H), 6.63 (d, 2H, J = 8.7) (BINAP), 4.65 (br s, 2H) (H_2O). ^{31}P{^{1}H} NMR (CD_2Cl_2): 36.53 (s). ^{19}F NMR (CD_2Cl_2): −76.6 (s, 2 CF_3SO_3). IR (neat, cm^{-1}): 1294, 1162, 1104, 1026 (all OTf). Anal. Calcd for $C_{46}H_{34}P_2S_2F_6O_7Pd$: C, 52.9; H, 3.28; S, 6.13. Found: C, 53.2; H, 3.42; S, 5.96.

[Pt((*R*)-(+)-BINAP)(H$_2$O)][OTf]$_2$ (11). A 100-mL Schlenk flask equipped with a stirbar was charged with 0.350 g (0.390 mmol) of [Pt((*R*)-(+)-BINAP)][Cl]$_2$ and 50 mL of CH_2Cl_2. To this colorless solution was added 0.709 g (2.76 mmol) of AgOTf, and the resulting mixture was stirred under nitrogen for 4 days at room temperature. The white precipitate was filtered, and the filtrate was transferred into a 50-mL flask and reduced in volume to 10 mL. Then, 0.007 g (0.390 mmol) of distilled water was added, followed by the addition of diethyl ether. The white precipitate was collected, washed with ether, and dried in vacuo: yield of **11** 0.315 g (69%); mp 232–234 °C dec. ^{1}H NMR (CD_2Cl_2): 7.81–7.58 (m, 18H), 7.50 (dd, 4H, J = 7.8, 14.1), 7.20 (t, 2H, J = 7.2), 7.02 (t, 2H, J = 7.2), 6.85 (br m, 4H), 6.71 (d, 2H, J = 8.0) (BINAP). ^{31}P{^{1}H} NMR (CD_2Cl_2): 4.40 (s, ^{195}Pt satellites, $^1J_{P-Pt}$ = 4023 Hz). ^{19}F NMR (CD_2Cl_2): −76.6 (s, 2 CF_3SO_3). IR (neat, cm^{-1}): 1288, 1170, 1096, 1027 (all OTf). Anal. Calcd for $C_{46}H_{34}P_2S_2F_6O_7Pt$: C, 48.7; H, 3.02; S, 5.65. Found: C, 48.7; H, 3.12; S, 5.58.

***cis*-[Pd(Et$_3$P)$_2$(isoquinoline)$_2$][OTf]$_2$ (12).** A 50-mL Schlenk flask equipped with a stirbar was charged with 0.116 g (0.898 mmol) of isoquinoline and CH_2Cl_2 (10 mL). *cis*-Pd(Et$_3$P)$_2$(OTf)$_2$ (0.128 g, 0.200 mmol) was added, and the resulting colorless mixture was stirred under nitrogen for 3 h at ambient temperature. The solution was transferred *via* syringe into a 50-mL flask and reduced in volume to ca. 2 mL. Diethyl ether was then added, resulting in the formation of a white precipitate, which was collected, washed with diethyl ether (10 mL), and dried in vacuo: yield of **12** 0.158 g (88%); mp 79–81 °C. ^{1}H NMR (CD_2Cl_2): 10.21 (br s, 4H, isoq H-1, isomers A and B), 9.03 (br s, 4H, isoq H-3, isomers A and B), 8.35 (br s, 4H, isoq H-8, isomers A and B), 7.72 (br s, 12H, overlap of isoq H-5, H-6, and H-4, isomers A and B), 7.69 (br s, 4H, isoq H-7, isomers A and B), 1.82 (m, 24H, PCH_2CH$_3$, isomers A and B), 1.32 (m, 36H, PCH$_2$$CH_3$, isomers A and B). ^{13}C{^{1}H} NMR (CD_2Cl_2): 155.5 (s, isoq C-1, isomers A and B), 141.8 (s, isoq C-3, isomers A and B), 136.2 (s, isoq C-10, isomers A and B), 134.0 (s, isoq C-6, isomers A and B), 129.5 (overlap of s, isoq C-9, C-8, and C-7, isomers A and B), 126.6 (s, isoq C-5, isomers A and B), 124.8 (s, isoq C-4, isomers A and B), 121.3 (q, OTf, J_{C-F} = 319 Hz, isomers A and B), 16.6 (t, PCH_2CH$_3$, J_{C-P} = 28 Hz, isomers A and B), 8.2 (s, PCH$_2$$CH_3$, isomers

(16) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals;* Pergamon Press: Oxford, U.K., 1988.

(17) The reaction between Pt(cod)Cl$_2$ (cod = cyclooctadiene) and (*R*)-(+)-BINAP in CH_2Cl_2 for 30 min at room temperature provided Pt((*R*)-(+)-BINAP)Cl$_2$ in 93% yield. Also, see ref 1b for the recent synthesis of this complex.

A and B). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 26.38 (s, isomer A), 26.10 (s, isomer B). ^{19}F NMR (CD_2Cl_2): −76.3 (s, 2 CF_3SO_3). IR (neat, cm^{-1}): 1260, 1150, 1030 (all OTf). Anal. Calcd for $C_{32}H_{44}N_2P_2S_2F_6O_6Pd$: C, 42.7; H, 4.93; N, 3.12; S, 7.13. Found: C, 43.1; H, 5.18; N, 2.95; S, 6.68.

***cis*-[Pt(Et_3P)$_2$(isoquinoline)$_2$][OTf]$_2$ (13).** A 50-mL Schlenk flask equipped with a stirbar was charged with 0.058 g (0.45 mmol) of isoquinoline and CH_2Cl_2 (15 mL). *cis*-Pt(Et_3P)$_2$(OTf)$_2$ (0.131 g, 0.180 mmol) was then added. The resulting mixture was stirred under nitrogen for 5 h at ambient temperature. The solution was transferred *via* syringe into a 50-mL flask and reduced in volume to 5 mL in vacuo. Diethyl ether was added, resulting in the formation of a white precipitate, which was collected and washed with diethyl ether (ca. 10 mL) and dried in vacuo: yield 0.159 g of **13** (89%); mp 88−89 °C. ^1H NMR (CD_2Cl_2): 10.24 (s, 2H, isoq H-1, isomer A), 10.18 (s, 2H, isoq H-1, isomer B), 9.13 (d, 2H, J = 5.7, isoq H-3, isomer A), 9.02 (d, 2H, J = 5.4, isoq H-3, isomer B), 8.44 (d, 2H, J = 9.0, isoq H-8, isomer A), 8.40 (d, 2H, J = 11.0, isoq H-8, isomer B), 7.90 (d, 2H, J = 6.6, isoq H-5, isomer A), 7.87 (d, 2H, J = 9.9, isoq H-5, isomer B), 7.82 (m, 8H, overlap of isoq H-6 and H-4, isomers A and B), 7.74 (t, 4H, J = 6.0, isoq H-7, isomers A and B), 1.79 (m, 24H, PCH_2-CH_3, isomers A and B), 1.31 (m, 36H, PCH_2CH_3, isomers A and B). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 155.83 (s, isoq C-1, isomer A), 155.75 (s, isoq C-1, isomer B), 142.02 (s, isoq C-3, isomer A), 141.95 (s, isoq C-3, isomer B), 136.67 (s, isoq C-10, isomer A), 136.63 (s, isoq C-10, isomer B), 134.84 (s, isoq C-6, isomer A), 134.79 (s, isoq C-6, isomer B), 130.32 (s, isoq C-9, isomer A), 130.29 (s, isoq C-9, isomer B), 130.27 (s, isoq C-8, isomer A), 130.24 (s, isoq C-8, isomer B), 130.08 (s, isoq C-7, isomer A), 130.05 (s, isoq C-7, isomer B), 126.87 (s, isoq C-5, isomers A and B), 125.86 (s, isoq C-4, isomer A), 125.76 (s, isoq C-4, isomer B), 121.3 (q, OTf, J_{C-F} = 319 Hz, isomers A and B), 15.75 (t, PCH_2CH_3, J_{C-P} = 32 Hz, isomers A and B), 8.13 (s, PCH_2CH_3, isomers A and B). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 0.47 (s, ^{195}Pt satellites, $^1J_{P-Pt}$ = 3089 Hz, isomer A), 0.21 (s, ^{195}Pt satellites, $^1J_{P-Pt}$ = 3089 Hz, isomer B). ^{19}F NMR (CD_2Cl_2): −77.7 (s, 2 CF_3SO_3). IR (neat, cm^{-1}): 1257, 1149, 1029 (all OTf). Anal. Calcd for $C_{32}H_{44}N_2P_2S_2F_6O_6Pt\cdot H_2O$: C, 38.2; H, 4.61; N, 2.79; S, 6.37. Found: C, 38.4; H, 4.59; N, 2.84; S, 6.45.

[Pd(dppp)(isoquinoline)$_2$][OTf]$_2$ (14). A 50-mL Schlenk flask equipped with a stirbar was charged with 0.116 g (0.898 mmol) of isoquinoline and CH_2Cl_2 (5 mL). Then, 0.331 g (0.405 mmol) of Pd(dppp)(OTf)$_2$ was added, and the resulting colorless mixture was stirred under nitrogen for 3 h at ambient temperature. To this solution was added pentane, resulting in the formation of a white precipitate, which was collected and washed with 5 mL of pentane and dried in vacuo: yield of **14** 0.389 g (89%); mp 276 °C dec. ^1H NMR (CD_2Cl_2, broadened lines, due to rapid interconversion between A and B): 9.63 (br s, 4H, isoq H-1, isomers A and B), 9.01 (br m, 4H, isoq H-3, isomers A and B), 7.88 (br m, 8H, isoq H-8 and H-5, isomers A and B), 7.65 (t, 4H, J = 7.0, isoq H-6 isomers A and B), 7.52 (d, 4H, isoq H-4 isomers A and B), 7.40 (br m, 40H, dppp Ph, isomers A and B), 7.10 (br m, 4H, isoq H-7 isomers A and B), 3.22 (br m, 8H, dppp PCH_2CH_2, isomers A and B), 2.28 (br m, 4H, dppp PCH_2CH_2, isomers A and B). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 155.3 (s, isoq C-1, isomers A and B), 141.5 (s, isoq C-3, isomers A and B), 135.5 (s, isoq C-10, isomers A and B), 133.4 (s, isoq C-6, isomers A and B), 132.3 (m, dppp Ph, isomers A and B), 132.2 (m, dppp Ph + isoq C-9, isomers A and B), 129.5 (br s, dppp Ph C_p, isomers A and B), 129.1 (s, isoq C-8, isomers A and B), 128.6 (s, isoq C-7, isomers A and B), 126.2 (s, isoq C-5, isomers A and B), 125.8 (br s, dppp C_i, isomers A and B), 123.7 (s, isoq C-4, isomers A and B), 121.3 (q, OTf, J_{C-F} = 319 Hz, isomers A and B), 22.8 (t, dppp PCH_2-CH_2, J_{C-P} = 32 Hz, isomers A and B), 18.0 (s, dppp PCH_2CH_2, isomers A and B). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 9.53 (s). ^{19}F NMR (CD_2Cl_2): −77.5 (s, 2 CF_3SO_3). IR (neat, cm^{-1}): 1252, 1158, 1104, 1030 (all OTf). Anal. Calcd for $C_{47}H_{40}N_2P_2S_2F_6O_6Pd\cdot H_2O$: C, 51.6; H, 3.87; N, 2.56; S, 5.86. Found: C, 51.6; H, 3.86; N, 2.61; S, 5.85.

[Pt(dppp)(isoquinoline)$_2$][OTf]$_2$ (15). A 50-mL Schlenk flask equipped with a stirbar was charged with 0.116 g (0.898 mmol) of isoquinoline and 5 mL of CH_2Cl_2. A solution of 0.163 g (0.180 mmol) of Pt(dppp)(OTf)$_2$ in 20 mL of CH_2Cl_2 was added *via* syringe, and the resulting mixture was stirred under nitrogen for 5 h at ambient temperature. The solution was transferred *via* syringe into a 50-mL flask and reduced in volume to ca. 1 mL on a rotary evaporator. A diethyl ether−pentane mixture (1:10) was added, resulting in the formation of a white precipitate, which was collected and washed with pentane. The filtrate was reduced in volume to 5 mL, and the additional product was isolated as above. The precipitates were combined, dissolved in CH_2Cl_2, and evaporated to dryness in vacuo at 35−40 °C. The white microcrystalline product was further dried in vacuo: yield of **15** 0.175 g (84%); mp 270−272 °C dec. ^1H NMR (CD_2Cl_2, broadened lines, due to rapid interconversion between isomers A and B): 9.70 (br s, 4H, isoq H-1, isomers A and B), 8.95 (br m, 4H, isoq H-3, isomers A and B), 7.95 (br m, 8H, isoq H-8 and H-5, isomers A and B), 7.75 (t, 4H, J = 11.0, isoq H-6 isomers A and B), 7.55 (d, 4H, J = 6.8, isoq H-4 isomers A and B), 7.35 (br m, 40H, dppp Ph, isomers A and B), 7.05 (br m, 4H, isoq H-7 isomers A and B), 3.35 (br m, 8H, dppp PCH_2CH_2, isomers A and B), 2.20 (br t, 4H, dppp PCH_2CH_2, isomers A and B). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 155.5 (s, isoq C-1, isomers A and B), 141.6 (s, isoq C-3, isomers A and B), 135.7 (s, isoq C-10, isomers A and B), 133.9 (s, isoq C-6, isomers A and B), 133.3 (m, dppp Ph, isomers A and B), 132.2 (m, dppp Ph + isoq C-9, isomers A and B), 129.4 (s, isoq C-8, isomers A and B), 129.36 (br s, dppp Ph C_p, isomers A and B), 128.9 (s, isoq C-7, isomers A and B), 126.3 (s, isoq C-5, isomers A and B), 124.5 (s, isoq C-4, isomers A and B), 124.4 (t, dppp C_i, isomers A and B), 121.3 (q, OTf, J_{C-F} = 319 Hz, isomers A and B), 21.88 (t, dppp PCH_2CH_2, J_{C-P} = 36 Hz, isomers A and B), 18.0 (s, dppp PCH_2CH_2, isomers A and B). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): −11.86 (s, ^{195}Pt satellites, $^1J_{P-Pt}$ = 3032 Hz). ^{19}F NMR (CD_2Cl_2): −76.6 (s, 2 CF_3SO_3). IR (neat, cm^{-1}): 1250, 1155, 1101, 1027 (all OTf). Anal. Calcd for $C_{47}H_{40}N_2P_2S_2F_6O_6Pt\cdot H_2O$: C, 47.8; H, 3.58; N, 2.37; S, 5.42. Found: C, 47.7; H, 3.63; N, 2.34; S, 5.47.

***cis*-[Pd(Et_3P)$_2$(quinoline)$_2$][OTf]$_2$ (16).** A 25-mL Schlenk flask equipped with a stirbar was charged with 0.116 g (0.898 mmol) of quinoline and CH_2Cl_2 (10 mL). To this was added 0.128 g (0.200 mmol) of *cis*-Pd(Et_3P)$_2$(OTf)$_2$, and the resulting colorless solution was stirred under nitrogen for 3 h at ambient temperature. The solution was transferred *via* syringe into a 50-mL flask and reduced in volume to ca. 2 mL in vacuo. Diethyl ether was added, and the white precipitate was collected and washed with diethyl ether and dried in vacuo: yield 0.146 g of **16** (84%); mp 50−52 °C. ^1H NMR (CD_2Cl_2): 9.79 (br s, 2H, quin H-2, isomer B), 9.51 (br s, 2H, quin H-2, isomer A), 9.12 (br s, 2H, quin H-4, isomer A), 8.87 (br s, 2H, quin H-4, isomer B), 8.32−8.05 (br m, 4H, quin H-7 and H-5, isomer A), 7.85−7.70 (br m, 4H, quin H-7 and H-5, isomer B), 7.50−7.30 (br m, 8H, quin H-6, H-3, isomers A and B), 1.83 (m, 24H, PCH_2CH_3, isomers A and B), 1.28 (m, 36H, PCH_2CH_3, isomers A and B). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 154.9 (s, quin C-2, isomer A), 154.4 (s, quin C-2, isomer B), 145.1 (s, quin C-9, isomer B), 144.9 (s, quin C-9, isomer A), 141.3 (s, quin C-4, isomers A and B), 134.4 (s, quin C-8, isomer A), 133.7 (s, quin C-8, isomer B), 129.9 (s, quin C-10, isomers A and B), 129.7 (s, quin C-7, isomers A and B), 129.4 (s, quin C-5, isomers A and B), 127.7 (s, quin C-6, isomer B), 127.1 (s, quin C-6, isomer A), 123.6 (s, quin C-3, isomer B), 123.1 (s, quin C-3, isomer A), 121.3 (q, OTf, J_{C-F} = 319 Hz, isomers A and B), 16.8 (t, PCH_2CH_3, J_{C-P} = 28 Hz, isomers A and B), 8.6 (s, PCH_2CH_3, isomers A and B). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 27.71 (s, isomer A), 27.51 (s, isomer B). ^{19}F NMR (CD_2Cl_2): −76.4 (s, 2 CF_3SO_3). IR (neat, cm^{-1}): 1281, 1143, 1031 (all OTf). Anal. Calcd for $C_{32}H_{44}N_2P_2S_2F_6O_6Pd$: C, 42.7; H, 4.93; N, 3.12; S, 7.13. Found: C, 42.4; H, 5.14; N, 3.10; S, 7.02.

***cis*-[Pt(Et$_3$P)$_2$(quinoline)$_2$][OTf]$_2$ (17).** A 50-mL Schlenk flask equipped with a stirbar was charged with 0.116 g (0.898 mmol) of quinoline and CH_2Cl_2 (15 mL). *cis*-Pt(Et$_3$P)$_2$(OTf)$_2$ (0.131 g, 0.180 mmol) was added, and the resulting mixture was stirred under nitrogen for 3 h at ambient temperature. The solution was transferred *via* syringe into a 50-mL flask and reduced in volume to ca. 2 mL on a rotary evaporator. Diethyl ether was added, and the solution was stored for 1 h at −20 °C. The white precipitate was collected and washed with diethyl ether (ca. 10 mL) and dried in vacuo: yield of **17** 0.141 g (79%); mp 142−144 °C. ^{1}H NMR (CD_2Cl_2): 9.89 (s, 2H, quin H-2), isomer B), 9.64 (s, 2H, quin H-2, isomer A), 9.34 (d, 2H, J = 8.8, quin H-4, isomer A), 9.10 (d, 2H, J = 8.5, quin H-4, isomer B), 8.38 (t, 2H, J = 8.0, quin H-7, isomer A), 8.31 (d, 2H, J = 8.1, quin H-5, isomer A), 8.19 (t, 2H, J = 7.2, quin H-7, isomer B), 7.94 (d, 2H, J = 8.1, quin H-5, isomer B), 7.84 (t, 2H, J = 8.0, quin H-6, isomer A), 7.79 (dd, 2H, J = 10.1, 4.0, quin H-3, isomer A), 7.66 (t, 2H, J = 7.2, quin H-6, isomer B), 7.58 (dd, 2H, J = 8.4, 5.6, quin H-3, isomer B), 1.86 (m, 24H, P*CH*$_2$CH$_3$, isomers A and B), 1.28 (m, 36H, PCH$_2$*CH*$_3$, isomers A and B). ^{13}C{^{1}H} NMR (CD_2Cl_2): 155.2 (s, quin C-2, isomer A), 154.5 (s, quin C-2, isomer B), 145.0 (s, quin C-9, isomer B), 144.9 (s, quin C-9, isomer A), 141.9 (s, quin C-4, isomers A and B), 134.8 (s, quin C-8, isomer A), 133.9 (s, quin C-8, isomer B), 130.4 (s, quin C-10, isomer A), 130.3 (s, quin C-10, isomer B), 130.0 (s, quin C-7, isomer B), 129.7 (s, quin C-7, isomer A), 129.6 (s, quin C-5, isomer A), 129.5 (s, quin C-5, isomer B), 127.0 (s, quin C-6, isomer B), 126.3 (s, quin C-6, isomer A), 124.0 (s, quin C-3, isomer B), 123.4 (s, quin C-3, isomer A), 121.3 (q, OTf, J_{C-F} = 319 Hz, isomers A and B), 15.98 (t, P*CH*$_2$CH$_3$, J_{C-P} = 30 Hz, isomers A and B), 8.25-(s, PCH$_2$*CH*$_3$, isomers A and B). ^{31}P{^{1}H} NMR (CD_2Cl_2): −0.28 (s, ^{195}Pt satellites, $^1J_{P-Pt}$ = 3099 Hz, isomer A), −0.75 (s, ^{195}Pt satellites, $^1J_{P-Pt}$ = 3099 Hz, isomer B). ^{19}F NMR (CD_2Cl_2): −77.8 (s, 2 C*F*$_3$SO$_3$). IR (neat, cm^{-1}): 1258, 1148, 1030 (all OTf). Anal. Calcd for $C_{32}H_{44}N_2P_2S_2F_6O_6Pt\cdot H_2O$: C, 38.2; H, 4.61; N, 2.79; S, 6.37. Found: C, 38.2; H, 4.56; N, 2.83; S, 6.44.

[Pd(dppp)(quinoline)$_2$][OTf]$_2$ (18). A 25-mL Schlenk flask equipped with a stirbar was charged with 0.116 g (0.898 mmol) of quinoline and 10 mL of CH_2Cl_2. Pd(dppp)(OTf)$_2$ (0.147 g, 0.180 mmol) was then added, and the resulting colorless solution was stirred under nitrogen for 5 h at room temperature. The solution was transferred *via* syringe into a 50-mL flask and reduced in volume to ca. 2 mL in vacuo. Diethyl ether was added to the residue, resulting in the formation of a white precipitate, which was collected and washed with diethyl ether. The product was dried in vacuo: yield of **18** 0.161 g (83%); mp 296−298 °C dec. ^{1}H NMR (CD_2Cl_2): 10.20 (m, 2H, quin H-2, isomer A), 9.86 (m, 2H, quin H-2, isomer B), 9.35 (d, 2H, J = 8.1, quin H-8, isomer B), 9.21 (d, 2H, J = 8.1, quin H-8, isomer A), 8.26 (m, 2H, quin H-7, isomer B), 8.07 (br m, 6H, overlap of quin H-4 and dppp, isomer A), 7.95 (m, 6H, quin H-7 and dppp, isomer A), 7.83 (d, 2H, J = 8.1, quin H-4, isomer B), 7.65−7.48 (m, 18H, quin H-5 and H-3, isomer A, H-6, isomer B, dppp, isomer B), 7.40 (m, 4H, quin H-6, isomer A, dppp, isomer A), 7.30−7.20 (m, 4H, quin H-5 and H-3, isomer B), 7.09 (m, 8H, dppp, isomer B), 7.02 (m, 4H, dppp, isomer A), 6.70 (t, 2H, J = 7.5, dppp, isomer A), 6.59 (t, 4H, J = 7.5, dppp, isomer A), 4.09 (m, 2H, dppp P*CH*$_2$, isomer A), 3.39 (m, 4H, dppp P*CH*$_2$, isomer B), 2.84 (m, 3H, dppp P*CH*$_2$ and dppp PCH$_2$C*H*, isomer A), 2.36 (m, 2H, dppp PCH$_2$*CH*$_2$, isomer B), 1.91 (m, 1H, dppp PCH$_2$C*H*, isomer A). ^{13}C{^{1}H} NMR (CD_2Cl_2): 155.0, 153.3, 144.6, 144.1, 140.2, 139.9 (all singlets, quin, isomers A and B), 134.5 (m), 133.6 (s), 133.4 (s), 133.0 (m), 132.7 (s), 132.6 (s), 132.2 (s), 131.3 (t, J = 10), 131.0 (s), 130.3 (t, J = 10), 129.8 (s), 129.7 (t, J = 10), 129.3 (s), 129.2 (t, J = 10), 129.0 (s), 128.7 (s), 128.6 (s), 128.5 (s), 128.2 (t, J = 10), 128.1 (dppp and quin, isomers A and B), 126.7 (t, J = 25, dppp C$_i$, isomer A), 126.1 (t, J = 25, dppp C$_i$, isomer B), 123.2, 122.5 (both singlets, quinoline, isomers A and B), 121.3 (q, OTf, J_{C-F} = 319 Hz, isomers A and B), 21.7 (t, J = 20, dppp PCH$_2$CH$_2$, isomer B), 20.8 (t, J = 20, dppp P*CH*$_2$-CH$_2$, isomer A), 17.8 (s, dppp PCH$_2$*CH*$_2$, isomers A and B). ^{31}P{^{1}H} NMR (CD_2Cl_2): 6.88 (s, isomer A), 8.38 (s, isomer B). ^{19}F NMR (CD_2Cl_2): −77.5 (s, 2 C*F*$_3$SO$_3$). IR (neat, cm^{-1}): 1249, 1154, 1028 (all OTf). Anal. Calcd for $C_{47}H_{40}N_2P_2S_2F_6O_6Pd\cdot H_2O$: C, 51.6; H, 3.87; N, 2.56; S, 5.86. Found: C, 51.5; H, 3.85; N, 2.61; S, 5.93.

Table 2. Crystallographic Data for *syn*-[Pt(dppp)(quinoline)$_2$][OTf]$_2$ (19)

molecular formula	$C_{47}H_{40}N_2P_2S_2F_6O_6Pt$
fw	1164.009
space group	$P2_1/a$
space group no.	14
cryst syst	monoclinic
a, Å	17.615(3)
b, Å	16.111(3)
c, Å	18.979(3)
β, deg	103.71(2)
cell vol, Å^3	5232.75
Z	4
calcd density, g cm^{-3}	1.477
cryst size, mm	0.35 × 0.29 × 0.17
abs coeff, cm^{-1}	29.094
radiation	Mo, 0.710 73 Å
no. of rflns measured	8825
no. of unique rflns	8184
no. of observns	5073 ($I < 3.00\sigma(I)$)
2θ range, deg	4.0−48.0
scan technique	$\theta-2\theta$ scan
scan width, deg	0.8000 + 0.3400 tan θ
R factor	0.0529
weighted R factor	0.0607

[Pt(dppp)(quinoline)$_2$][OTf]$_2$ (19). A 50-mL Schlenk flask equipped with a stirbar was charged with 0.140 g (1.084 mmol) of quinoline, 5 mL of $CHCl_3$, and 10 mL of CH_2Cl_2. To this solution was added 0.163 g (0.180 mmol) of Pt(dppp)(OTf)$_2$, and the resulting mixture was stirred under nitrogen for 10 h at ambient temperature. The solution was transferred *via* syringe into a 50-mL flask and reduced in volume to 5 mL on a rotary evaporator. Diethyl ether was then added, and the white precipitate was collected and washed with diethyl ether and dried in vacuo: yield 0.185 g of **19** (89%). Crystallization from CH_2Cl_2−ether solution afforded analytically pure product: mp 322 °C dec. ^{1}H NMR (CD_2Cl_2): 10.24 (m, 2H, quin H-2, isomer A), 9.85 (m, 2H, quin H-2, isomer B), 9.56 (d, 2H, J = 8.0, quin H-8, isomer B), 9.37 (d, 2H, J = 8.0, quin H-8, isomer A), 8.36 (m, 2H, quin H-7, isomer B), 8.10 (br m, 6H, overlap of quin H-4 and dppp, isomer A), 8.02 (m, 6H, quin H-7 and dppp, isomer A), 7.87 (d, 2H, J = 8.0, quin H-4, isomer B), 7.68−7.62 (m, 8H, quin H-5, isomer A, dppp, isomer B), 7.56−7.48 (m, 12H, quin H-3, isomer A, quin H-6, isomer B, dppp, isomer B), 7.45 (m, 4H, quin H-6, isomer A, dppp, isomer A), 7.29 (m, 4H, quin H-5 and H-3, isomer B), 7.05 (m, 8H, dppp, isomer B), 6.98 (m, 4H, dppp, isomer A), 6.69 (t, 2H, J = 7.5, dppp, isomer A), 6.57 (t, 4H, J = 7.5, dppp, isomer A), 4.18 (m, 2H, dppp P*CH*$_2$, isomer A), 3.47 (m, 4H, dppp P*CH*$_2$, isomer B), 3.20−2.70 (m, 3H, dppp P*CH*$_2$ and dppp PCH$_2$C*H*, isomer A), 2.40 (m, 2H, dppp PCH$_2$*CH*$_2$, isomer B), 1.98−1.80 (m, 1H, dppp PCH$_2$C*H*, isomer A). ^{13}C{^{1}H} NMR (CD_2Cl_2): 155.2, 153.4, 144.8, 144.0, 140.7, 140.5 (s, quinoline, isomers A and B), 134.5 (m), 134.1 (s), 133.3 (s), 133.1 (s), 133.0 (m), 132.5 (s), 132.1 (s), 131.2 (t, J = 12), 131.1(s), 130.1 (t, J = 12), 129.6 (t, J = 12), 129.5 (s), 129.0 (s), 128.9 (t, J = 12), 128.8 (s), 128.4 (s), 128.0 (t, J = 12), 127.5 (dppp and quin, isomers A and B), 125.5 (t, J = 25, dppp C$_i$, isomer A), 125.0 (t, J = 25, dppp C$_i$, isomer B), 123.5, 122.7 (both singlets, quinoline, isomers A and B), 121.3 (q, OTf, J_{C-F} = 319 Hz, isomers A and B), 20.8 (t, J = 20, dppp PCH$_2$CH$_2$, isomer B), 20.5 (t, J = 20, dppp P*CH*$_2$CH$_2$, isomer A), 17.8 (s, dppp PCH$_2$*CH*$_2$, isomers A and B). ^{31}P{^{1}H} NMR (CD_2Cl_2): −15.71 (s, ^{195}Pt satellites, $^1J_{P-Pt}$ = 3032 Hz, isomer A), −13.80 (s, ^{195}Pt satellites, $^1J_{P-Pt}$ = 3032 Hz, isomer B). ^{19}F NMR (CD_2Cl_2): −77.4 (s, 2 C*F*$_3$SO$_3$). IR (neat, cm^{-1}): 1252, 1155, 1101, 1030

Table 3. Positional Parameters and Isotropic Thermal Factors (Å²) for Compound 19

atom	x	y	z	B^a	atom	x	y	z	B^a
Pt	0.25026(3)	−0.00857(3)	0.21767(3)	3.717(8)	C31	0.255(1)	0.262(1)	0.266(1)	8.1(4)*
S1	0.7642(3)	0.0425(5)	0.4984(3)	10.6(2)	C32	0.281(1)	0.329(2)	0.227(1)	11.8(7)*
S2	0.2926(3)	0.0650(4)	0.9804(3)	9.8(1)	C33	0.304(2)	0.325(2)	0.169(1)	13.1(8)*
P1	0.1258(2)	−0.0065(2)	0.1494(2)	4.15(7)	C34	0.298(1)	0.251(1)	0.132(1)	10.5(6)*
P2	0.2688(2)	−0.1411(2)	0.1863(2)	3.82(7)	C35	0.2770(9)	0.1749(9)	0.1609(8)	6.4(4)
N1	0.2394(7)	0.1141(7)	0.2571(7)	6.3(3)	C36	0.257(1)	0.1842(9)	0.227(1)	7.9(5)
N2	0.3641(5)	−0.0078(7)	0.2891(5)	5.2(2)	C37	0.3707(9)	−0.030(1)	0.3568(7)	7.3(4)
C1	0.1076(8)	−0.0668(9)	0.0668(7)	5.3(3)	C38	0.443(1)	−0.033(1)	0.4082(8)	8.9(6)
C2	0.1310(8)	−0.1582(8)	0.0768(7)	5.0(3)	C39	0.5064(8)	−0.010(1)	0.3870(9)	8.1(5)
C3	0.2184(7)	−0.1721(8)	0.0943(6)	4.3(3)	C40	0.5024(7)	0.017(1)	0.3191(7)	5.5(3)
C4	0.0558(7)	−0.0393(8)	0.1985(7)	4.5(3)	C41	0.5695(9)	0.042(1)	0.2961(8)	7.0(4)
C5	0.0736(8)	−0.045(1)	0.2723(8)	6.2(4)	C42	0.5637(9)	0.065(1)	0.231(1)	8.0(5)
C6	0.0164(9)	−0.064(1)	0.3104(8)	7.6(5)	C43	0.4929(9)	0.063(1)	0.1788(9)	6.9(4)
C7	−0.0566(9)	−0.077(1)	0.2744(9)	8.1(5)	C44	0.4261(8)	0.0395(8)	0.1981(7)	5.2(3)
C8	−0.0777(8)	−0.071(1)	0.201(1)	7.9(5)	C45	0.4312(7)	0.0167(8)	0.2685(7)	5.2(3)
C9	−0.0226(9)	−0.053(1)	0.1637(8)	6.5(4)	C46	0.844(2)	0.015(2)	0.465(2)	6.6(7)*
C10	0.0943(7)	0.0942(8)	0.1167(7)	4.5(3)	C47	0.352(2)	0.015(2)	0.938(1)	5.8(6)*
C11	0.0497(9)	0.144(1)	0.1513(8)	6.6(4)	F1	0.823(1)	0.014(1)	0.394(1)	9.3(5)*
C12	0.023(1)	0.2246(9)	0.124(1)	8.5(5)	F2	0.898(3)	−0.026(3)	0.503(2)	13(1)*
C13	0.039(1)	0.2523(9)	0.064(1)	7.6(5)	F3	0.881(2)	0.082(2)	0.473(2)	14.2(9)*
C14	0.082(1)	0.207(1)	0.0301(9)	7.4(4)	F4	0.420(1)	−0.008(2)	0.985(1)	11.3(6)*
C15	0.1102(8)	0.1258(9)	0.0536(8)	5.9(4)	F5	0.333(2)	−0.072(2)	0.935(2)	13.6(8)*
C16	0.2422(7)	−0.2188(8)	0.2452(6)	4.5(3)	F6	0.369(1)	0.045(1)	0.883(1)	8.5(5)*
C17	0.2453(8)	−0.3017(8)	0.2303(8)	5.3(3)	O1	0.707(1)	−0.031(2)	0.483(1)	9.3(7)*
C18	0.2294(9)	−0.3599(9)	0.2763(9)	6.8(4)	O2	0.7869(7)	0.0481(8)	0.5727(7)	9.1(3)*
C19	0.212(1)	−0.336(1)	0.3399(9)	8.6(5)	O3	0.768(2)	0.139(3)	0.472(2)	13(1)*
C20	0.208(1)	−0.256(1)	0.3565(9)	7.5(5)	O4	0.2826(7)	0.0208(8)	1.0404(6)	8.8(3)*
C21	0.2257(9)	−0.1962(9)	0.3082(9)	6.3(4)	O5	0.262(2)	0.138(2)	0.957(2)	10.9(8)*
C22	0.3695(7)	−0.1626(8)	0.1899(7)	4.3(3)	O6	0.216(3)	0.014(3)	0.930(2)	11(1)*
C23	0.4011(8)	−0.147(1)	0.1326(9)	6.9(4)	F1′	0.916(2)	0.029(2)	0.497(1)	12.6(7)*
C24	0.4795(9)	−0.164(1)	0.137(1)	9.6(5)	F2′	0.852(2)	−0.062(2)	0.472(2)	13.6(8)*
C25	0.5268(9)	−0.195(1)	0.201(1)	10.6(5)	F4′	0.410(3)	0.065(3)	0.986(2)	13(1)*
C26	0.4962(9)	−0.209(1)	0.257(1)	8.8(6)	F5′	0.381(2)	−0.045(2)	0.950(1)	12.4(7)*
C27	0.4164(9)	−0.194(1)	0.2499(9)	7.1(4)	F6′	0.313(2)	0.000(3)	0.870(2)	12(1)*
C28	0.223(1)	0.121(1)	0.3232(9)	7.8(5)	O1′	0.710(2)	0.033(2)	0.453(2)	11.6(8)*
C29	0.222(1)	0.199(1)	0.361(1)	11.0(6)*	O4′	0.233(1)	0.106(1)	0.932(1)	8.3(6)*
C30	0.235(1)	0.263(1)	0.327(1)	10.0(6)*	O5′	0.362(2)	0.133(2)	1.014(2)	11.7(9)

[a] Starred values denote atoms refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

(all OTf). Anal. Calcd for $C_{47}H_{40}N_2P_2S_2F_6O_6Pt\cdot H_2O$: C, 47.8; H, 3.58; N, 2.37; S, 5.42. Found: C, 47.5; H, 3.47; N, 2.35; S, 5.36.

***cis*-[Pt(Et$_3$P)$_2$(3-bromopyridine)$_2$][OTf]$_2$ (20).** A 25-mL Schlenk flask equipped with a stirbar was charged with 0.071 g (0.446 mmol) of 3-bromopyridine and CH_2Cl_2 (5 mL). Then, 0.148 g (0.203 mmol) of *cis*-Pt(Et$_3$P)$_2$(OTf)$_2$ was added, and the resulting solution was stirred under nitrogen for 3 h at ambient temperature. The mixture was transferred *via* syringe into a 25-mL flask and reduced in volume to 2 mL on a rotary evaporator. Pentane was added, and the mixture was stored at −20 °C for 30 min. The white precipitate was collected and washed with pentane. Drying in vacuo afforded 0.173 g of **20** (81%). The compound melted at 168−170 °C. ^{1}H NMR (CD_2Cl_2): 9.52 (s, 2H, 3-Br-py H-2, isomer B), 9.45 (d, J = 6.5, 2H, 3-Br-py H-6, isomer B), 9.42 (s, 2H, 3-Br-py H-2, isomer A), 9.34 (d, J = 5.3, 2H, 3-Br-py H-6, isomer A), 8.05 (d, J = 8.4, 4H, 3-Br-py H-4, isomers A and B), 7.55 (dd, J = 11.3, 8.8, 4H, 3-Br-py H-5, isomers A and B), 1.77 (m, 24H, P*CH*$_2$CH$_3$, isomers A and B), 1.27 (m, 36H, PCH$_2$*CH*$_3$, isomers A and B). ^{13}C{^{1}H} NMR (CD_2Cl_2): 152.2 (s, 3-Br-py C-2, isomer B), 151.9 (s, 3-Br-py C-2, isomer A), 150.6 (s, 3-Br-py C-6, isomer B), 150.4 (s, 3-Br-py C-6, isomer A), 144.2 (s, 3-Br-py C-4, isomers A and B), 129.0 (s, 3-Br-py C-5, isomers A and B), 124.2 (s, 3-Br-py C-3, isomers A and B), 121.3 (q, OTf, J_{C-F} = 319 Hz, isomers A and B), 15.9 (t, P*CH*$_2$CH$_3$, J_{C-P} = 39 Hz, isomers A and B), 8.0 (s, PCH$_2$*CH*$_3$, isomers A and B). ^{31}P{^{1}H} NMR (CD_2Cl_2): −1.24 (s, ^{195}Pt satellites, $^1J_{P-Pt}$ = 3160 Hz, isomer A), −1.38 (s, ^{195}Pt satellites, $^1J_{P-Pt}$ = 3160 Hz, isomer B). ^{19}F NMR (CD_2Cl_2): −77.8 (s, 2 *CF*$_3$SO$_3$, isomers A and B). IR (neat, cm^{-1}): 1270, 1158, 1102, 1031 (all OTf). Anal. Calcd for $C_{24}H_{38}P_2S_2N_2F_6O_6Pt$: C, 27.6; H, 3.66; N, 2.68; S, 6.13. Found: C, 27.9; H, 3.85; N, 2.58; S, 5.83.

[Pt(dppp)(3-bromopyridine)$_2$][OTf]$_2$ (21). A 50-mL Schlenk flask equipped with a stirbar was charged with 0.142 g (0.899 mmol) of 3-bromopyridine and CH_2Cl_2 (25 mL). Then, 0.163 g (0.180 mmol) of Pt(dppp)(OTf)$_2$ in 20 mL of CH_2Cl_2 was added, resulting in the formation of a white heterogeneous mixture, which was stirred under nitrogen for 5 h at ambient temperature. The mixture was filtered, the precipitate was collected, and a colorless filtrate was transferred *via* syringe into a 50-mL flask and reduced in volume to 5 mL in vacuo. Diethyl ether was added, resulting in the formation of a white precipitate, which was collected. Both precipitates were combined and washed with diethyl ether (ca. 10 mL). The product was dried in vacuo: yield of **21** 0.201 g (91%); mp 308−310 °C dec. ^{1}H NMR (CD_3OD): 9.02 (br s, 2H, 3-Br-py H-2, isomers A and B), 8.78 (br m, 2H, 3-Br-py H-6, isomers A and B), 7.89 (d, 2H, J = 5.1, 3-Br-py H-4, isomer A), 7.82 (d, 2H, J = 5.0, 3-Br-py H-4, isomer B), 7.66 (br m, 16H, dppp Ph H$_o$, isomers A and B), 7.46 (br m, 24H, dppp H$_m$+H$_p$, isomers A and B), 7.35 (t, 2H, J = 6.2, 3-Br-py H-5, isomer B), 7.27 (t, 2H, J = 6.5, 3-Br-py H-5, isomer A), 3.35 (br m, 8H, dppp P*CH*$_2$CH$_2$, isomers A and B), 2.25 (br m, 4H, dppp PCH$_2$*CH2*, isomers A and B). ^{13}C{^{1}H} NMR (CD_3OD): 152.8 (s, 3-Br-py C-2, isomer A), 151.7 (s, 3-Br-py C-2, isomer B), 149.9 (s, 3-Br-py C-6, isomer A), 148.4 (s, 3-Br-py C-6, isomer B), 144.9 (s, 3-Br-py C-4, isomer A), 142.3 (s, 3-Br-py C-4, isomer B), 134.1 (br m, dppp Ph C$_o$+C$_p$, isomers A and B), 130.9 (br s, dppp Ph C$_m$, isomers A and B), 129.4 (s, 3-Br-py C-5, isomer A), 129.0 (s, 3-Br-py C-5, isomer B), 126.6 (t, dppp C$_i$, isomers A and B), 124.5 (s, 3-Br-py C-3, isomers A and B), 121.3 (q, OTf, J_{C-F} = 319 Hz, isomers A and B), 22.5 (t, dppp P*CH*$_2$CH$_2$, isomers

A and B), 18.8 (s, PCH_2CH_2, isomers A and B). $^{31}P\{^1H\}$ NMR (CD_3OD): −11.24 (s, ^{195}Pt satellites, $^1J_{P-Pt}$ = 3036 Hz, isomer B), −11.44 (s, ^{195}Pt satellites, $^1J_{P-Pt}$ = 3036 Hz, isomer A). ^{19}F NMR (CD_3OD): −77.4 (s, 2 CF_3SO_3). IR (neat, cm^{-1}): 1254, 1158, 1104, 1028 (all OTf). Anal. Calcd for $C_{39}H_{34}P_2N_2Br_2S_2O_6F_6Pt\cdot H_2O$: C, 37.8; H, 2.93; N, 2.26; S, 5.17. Found: C, 37.9; H, 2.89; N, 2.20; S, 5.19.

[Pd((*R*)-(+)-BINAP)(isoquinoline)$_2$][OTf]$_2$ (22). A 10-mL Schlenk flask equipped with a stirbar was charged with 0.040 g (0.038 mmol) of Pd((*R*)-(+)-BINAP)$(OTf)_2$ and 1 mL of CH_2Cl_2. A solution of 0.014 g (0.108 mmol) of isoquinoline in 1 mL of CH_2Cl_2 was added, and the yellow solution was stirred under nitrogen for 1 h at ambient temperature. Slow addition of a diethyl ether−pentane (1:10) mixture afforded the product as a yellow precipitate, which was collected and washed with a minimum of diethyl ether-pentane: yield of **22** 0.044 g (89%); mp 282 °C dec. ^1H NMR (CD_2Cl_2): 9.51 (s, 2H), 8.72 (br s, 4H) (isoq), 8.07 (m, 4H), 7.90 (m, 4H), 7.80 (m, 4H), 7.73 (d, 2H, J = 7.8), 7.64 (t, 2H, J = 7.3), 7.53 (d, 4H, J = 7.8), 7.46 (t, 2H, J = 7.8) (BINAP and isoq), 7.29 (br m, 4H), 7.06 (br d, 8H, J = 7.2), 6.87 (br m, 4H), 6.42 (d, 2H, J = 7.8) (BINAP). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 156.5, 142.2, 140.3 (isoq), 135.5, 135.0, 133.4, 131.8, 131.4, 130.3, 129.6, 129.3, 128.9, 128.7, 128.6, 127.6, 127.3, 127.2, 126.1, 125.1 (BINAP and isoq), 124.6 (C_i, BINAP), 124.1 (BINAP), 123.5 (isoq), 121.3 (q, OTf, J_{C-F} = 319 Hz), 120.0, 119.2 (BINAP). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 25.70 (s). ^{19}F NMR (CD_2Cl_2): −76.2 (s, 2 CF_3SO_3). IR (neat, cm^{-1}): 1252, 1152, 1091, 1029 (all OTf). Anal. Calcd for $C_{64}H_{46}N_2P_2S_2F_6O_6Pd\cdot 3H_2O$: C, 57.4; H, 3.91; N, 2.09; S, 4.79. Found: C, 57.6; H, 3.70; N, 2.17; S, 4.88.

[Pt((*R*)-(+)-BINAP)(isoquinoline)$_2$][OTf]$_2$ (23). A 10-mL Schlenk flask equipped with a stirbar was charged with 0.050 g (0.044 mmol) of Pt((*R*)-(+)-BINAP)$(OTf)_2$ and CH_2Cl_2 (1 mL). A solution of 0.028 g (0.217 mmol) of isoquinoline in 1 mL of CH_2Cl_2 was added, and the combined solution was stirred under nitrogen for 12 h at room temperature. A diethyl ether−pentane mixture was added, and the product was collected and washed with diethyl ether−pentane and dried in vacuo: yield of **23** 0.057 g (92%); mp 368−370 °C dec. ^1H NMR (CD_2Cl_2): 9.59 (br s, 2H), 8.78 (br m, 2H), 8.51 (br m, 2H) (all isoq), 8.09−7.82 (m, 8H), 7.80−7.64 (m, 8H) (both BINAP), 7.56 (m, 4H), 7.41 (t, 2H, J = 7.0), 7.33 (d, 2H, J = 6.3) (isoq), 7.04 (m, 10H), 6.77 (t, 2H, J = 7.6) (BINAP), 6.44 (d, 2H, J = 8.7), 6.38 (d, 2H, J = 8.7) (BINAP, isomers A and B). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 156.8, 156.5, 142.6, 142.3 (all isoq), 135.6, 135.1, 134.9, 134.8, 134.0, 133.4, 131.7, 131.4, 130.3, 129.8, 129.4, 129.2, 129.1, 128.8, 128.6, 127.6, 127.4, 127.2, 126.1 (BINAP and isoq), 124.5, 124.4 (isoq), 124.2, 123.9 (C_i, BINAP), 121.3 (q, OTf, J_{C-F} = 319 Hz), 119.6, 119.3 (BINAP). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 1.38 (s, ^{195}Pt satellites, $^1J_{P-Pt}$ = 4095 Hz, isomer C), 1.24 (dd, J = 129 Hz, 26 Hz, ^{195}Pt satellites, $^1J_{P-Pt}$ = 4095 Hz, isomer B), 0.90 (s, ^{195}Pt satellites, $^1J_{P-Pt}$ = 4095 Hz, isomer A). ^{19}F NMR (CD_2Cl_2): −77.0 (s, 2 CF_3SO_3). IR (neat, cm^{-1}): 1256, 1152, 1100, 1029 (all OTf). Anal. Calcd for $C_{64}H_{46}N_2P_2S_2F_6O_6Pt\cdot 2H_2O$: C, 54.5; H, 3.57; N, 1.99; S, 4.55. Found: C, 54.55; H, 3.65; N, 1.77; S, 4.18.

X-ray Crystallographic Analysis of 19. X-ray-quality crystals were grown by the slow vapor diffusion of Et_2O into a $CHCl_3$ solution of **19** at ambient temperature. A colorless plate, 0.35 × 0.29 × 0.17 mm, was glued onto a glass fiber and mounted for data collection on an Enraf-Nonius CAD4 diffractometer. The crystal and data collection information is presented in Table 2. The unit cell parameters were obtained by a least-squares refinement of 25 centered reflections in the range 24 < 2θ < 28°. The space group was determined from systematic absences ($h0l$, $h + l = 2n$; $0k0$, $k = 2n$) and subsequent least-squares refinement. The data were collected by the $\theta-2\theta$ scan technique, with variable scanning rate, using monochromatic Mo (0.710 73 Å) radiation. A total of 8184 unique reflections were measured in the range 4.0 < 2θ < 48.0°, of which 5073 were considered observed. 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.[18] Positional parameters and isotropic thermal factors for non-hydrogen atoms are presented in Table 3. There is a disordered water molecule in the lattice and some disorder exhibited by one of the triflate anions.

Acknowledgment. We thank the National Science Foundation (Grant No. CHE-9101767) for financial support.

Supporting Information Available: Crystal structure data for **19**, including a table of calculated positional parameters for the hydrogen atoms, extended lists of bond lengths and bond angles, and a table of general displacement parameter expressions (8 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.

OM950455A

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