Self-Assembly, Chiroptical Properties, and Host−Guest Chemistry of Chiral Pt−Pt and Pt−Pd Tetranuclear Macrocycles. Circular Dichroism Studies on Neutral Guest Inclusion Phenomena

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Abstract: The synthesis, characterization, and circular dichroism (CD) spectra of optically active mixed, neutral-charged Pt/Pt and Pt/Pd macrocyclic complexes are described as well as the CD spectra of their corresponding precursors. Interaction between the chiral monomers (*R*(−)-DIOP or *S*(+)-DIOP) of *cis*-Pt(DIOP)(4-ethynylpyridine)$_2$ and the bistriflates of chiral (*R*(+)-BINAP or *S*(−)BINAP)) Pt(II) or Pd(II) bisphosphines or *cis*-Pd(PEt$_3$)$_2$(OSO$_2$CF$_3$)$_2$, in CH$_2$Cl$_2$ at room temperature results in the formation of cyclic, chiral molecular squares in 84−99% yields via self-assembly. CD studies and optical rotation of the chiral macrocycles and their corresponding precursors reveal that the chiroptical properties are mainly determined by the BINAP moiety. The host−guest chemistry of the chiral 4-ethynylpyridine tetramers with silver triflate and the capture of neutral guests via the resulting square Lewis acid/base receptors have been monitored by CD.

Introduction

The advent[1] and rapid development of supramolecular chemistry increasingly focuses upon the methods that might improve aspects of molecular architecture, organization, and self-assembly. The desire to design and create microenvironments with interesting chemical, electronic, and optical properties, as well as specific features to aid (a) selective guest binding, (b) transport of bound guest, (c) catalysis of reactions, and (d) molecular recognition resulted in the development of inorganic and organometallic macrocycles accessible in high yield via the self-assembly methodology.[2,3] So far, a variety of well-defined shapes and geometries of this class of supramolecular species have been realized; besides (achiral) cationic,[4−6] anionic,[7] and neutral[8] systems, a number of chiral transition-metal-based

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infinite structures and smaller chiral systems, such as helices and helicates,[9] have been reported. A considerable amount of attention has been given to natural biological systems.[3f] In particular, it is important to understand the function of chiral elements in supramolecular structures in an effort to unravel the intricacies of biological systems and the subtle functions respective chiral components introduce.

Among the various synthetic chiral moieties available, bisphosphines such as 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP) and its derivatives have been most extensively utilized as a chiral transition-metal-chelating reagent in asymmetric catalysis reactions.[10,11] Specifically, they are known to have superior chirality recognition and induction abilities.[12] This conformationally flexible bidentate ligand, possessing only an axial element of chirality, can accommodate a wide variety of transition metals. The BINAP Pd(II) and Pt(II) bistriflate complexes[13] are fairly pliant and have been shown to be suitable building blocks for the preparation of chiral macrocyclic molecular squares.[5j] Axially dissymmetric BINAP possesses C_2 symmetry, which is a significant feature for asymmetric induction processes, first shown by Kagan's DIOP (2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)-butane) in conjugation with the Rh-catalyzed asymmetric hydrogenation.[10c,14,15]

Circular dichroism (CD) has been shown to be a powerful tool for analytical applications and the study of biological systems[16] and has been used extensively for studying substrate binding in biological systems[17] and inclusion phenomena in cyclodextrins.[18] However, its use in studying chiral, synthetic systems and molecular recognition phenomena of chiral hosts has been limited.[19]

There are at least five ways of introducing chirality into molecular squares:[5c] (1) transition metal complexes with chiral chelated ligands; (2) chiral linear linking units; (3) inherently chiral octahedral metal centers; (4) helicity (twist); (5) combinations of ways 1−4. Previously, we have reported the preparation of all transition metal and mixed Pt and Pd−iodonium, fully charged, cationic systems and the asymmetric induction resulting in these complexes using metal centers with chiral chelating ligands and helicity.[5j,k] After observing several interesting properties in these systems, we decided to explore neutral-charged chiral systems to allow more control of chiral component combinations and identify the most useful components for inclusion phenomena monitoring using chiral chelated ligands. In this paper, we report the synthesis of new chiral tetranuclear molecular squares using the simplest approach that of a chiral chelating ligand, to access chirality. We then focus on the study of the resulting chiroptical properties of the chiral assemblies. Optical rotation and CD spectra of the chiral starting material are reported; their set of intrinsic properties is being compared to those of the resulting macrocycles. The coordination of silver via π-interaction with the acetylenes is detected by CD, as well as the capture of diheteroatomic aromatic guests by the resulting Lewis acid/base receptors.

Results and Discussion

The synthesis of monomeric subunits containing 1,3-bis(diphenylphosphino)propane and 4-ethynylpyridine has been described previously.[5d] In a similar fashion, the synthesis of the neutral chiral monomers **1** and **2** was accomplished. 4-Ethynylpyridine was prepared via cross-coupling of 4-bromopyridine with trimethylsilylacetylene and treatment with K_2CO_3 in a methanol/THF (1:1) solution at room temperature. After deprotonation of 2 equiv of 4-ethynylpyridine with *tert*-butyllithium in THF at −78 °C and immediate addition of 1 equiv of DIOP−Pt(II)Cl_2, the desired DIOP-substituted monomers were obtained, purified by column chromatography, and isolated in 54% and 58% yield, respectively (Scheme 1).

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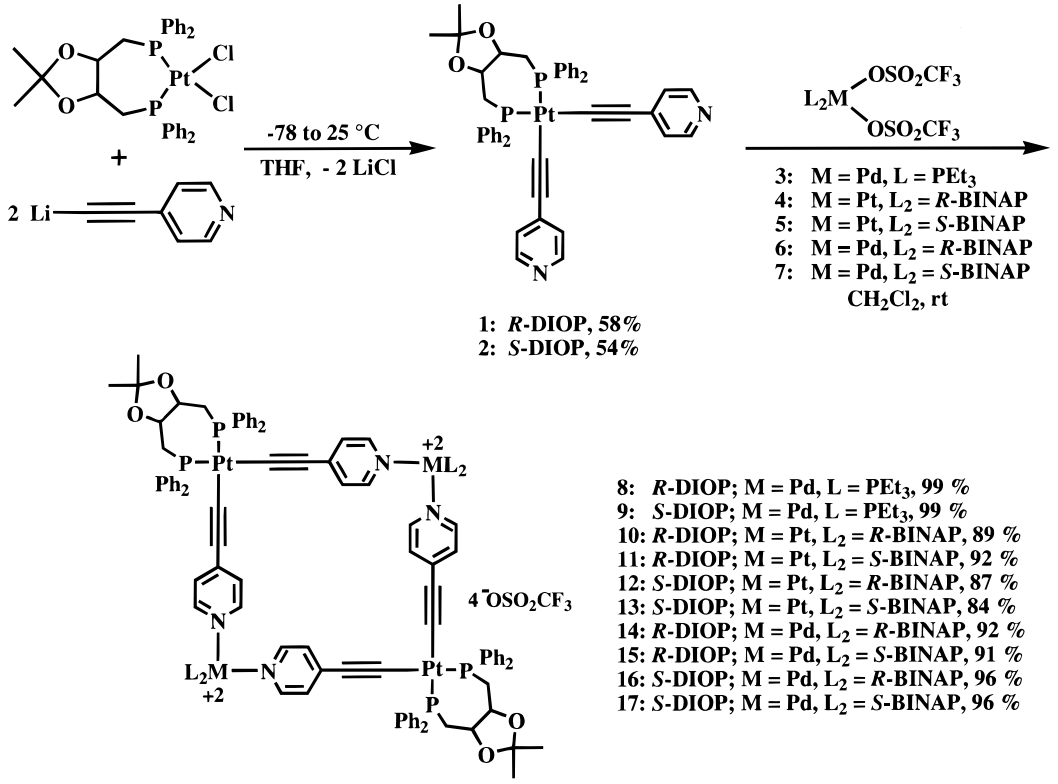
Scheme 1



Optically active neutral-charged supramolecular squares were prepared by self-assembly of **1** and **2**, respectively, with equimolar amounts of the bistriflate complexes of bis-triethylphosphine Pd(II) **3**, BINAP Pt(II) **4** or **5**, or BINAP Pd(II) **6** or **7**, respectively, in CH_2Cl_2 at room temperature (Scheme 1). The complete conversion to the tetranuclear complexes **8** and **9**, via self-assembly, required about 10 min, while **10**−**13** and **14**−**17** required about 2 h and 30 min, respectively, and resulted in stable, microcrystalline solids in excellent yields. These macrocyclic complexes were fully characterized by analytical and spectral means as described in the Experimental Section. The $^{31}P\{^1H\}$ NMR spectra of **8**−**17** each display two singlets, shifted by −0.9 to 0.8 ppm for the phosphorus on the (neutral) Pt−DIOP moiety, 9.1−24.2 ppm for the phosphorus on the Pd(II) triethylphosphine, and 1.2−1.5 ppm for the Pt(II) BINAP, respectively, relative to the precursors **1**−**7**.

Particularly diagnostic for the formation of the tetranuclear complexes **8**−**17** are the respective ^1H NMR data. The ^1H NMR signal for the α-pyridyl protons is shifted upfield by 0.2 ppm, and for the *β*-pyridyl protons, the signal is shifted upfield by 0.5 ppm relative to the precursors **1** and **2**. The pyridyl protons display broad singlets due to restricted rotation about the Pt−N chelation bond at room temperature.[5j] Integration of the proton signals is in accordance with the requirements for **8**−**17**. The ^{19}F NMR spectra display characteristic singlets for ionic $CF_3SO_3^-$ at −76 ppm.

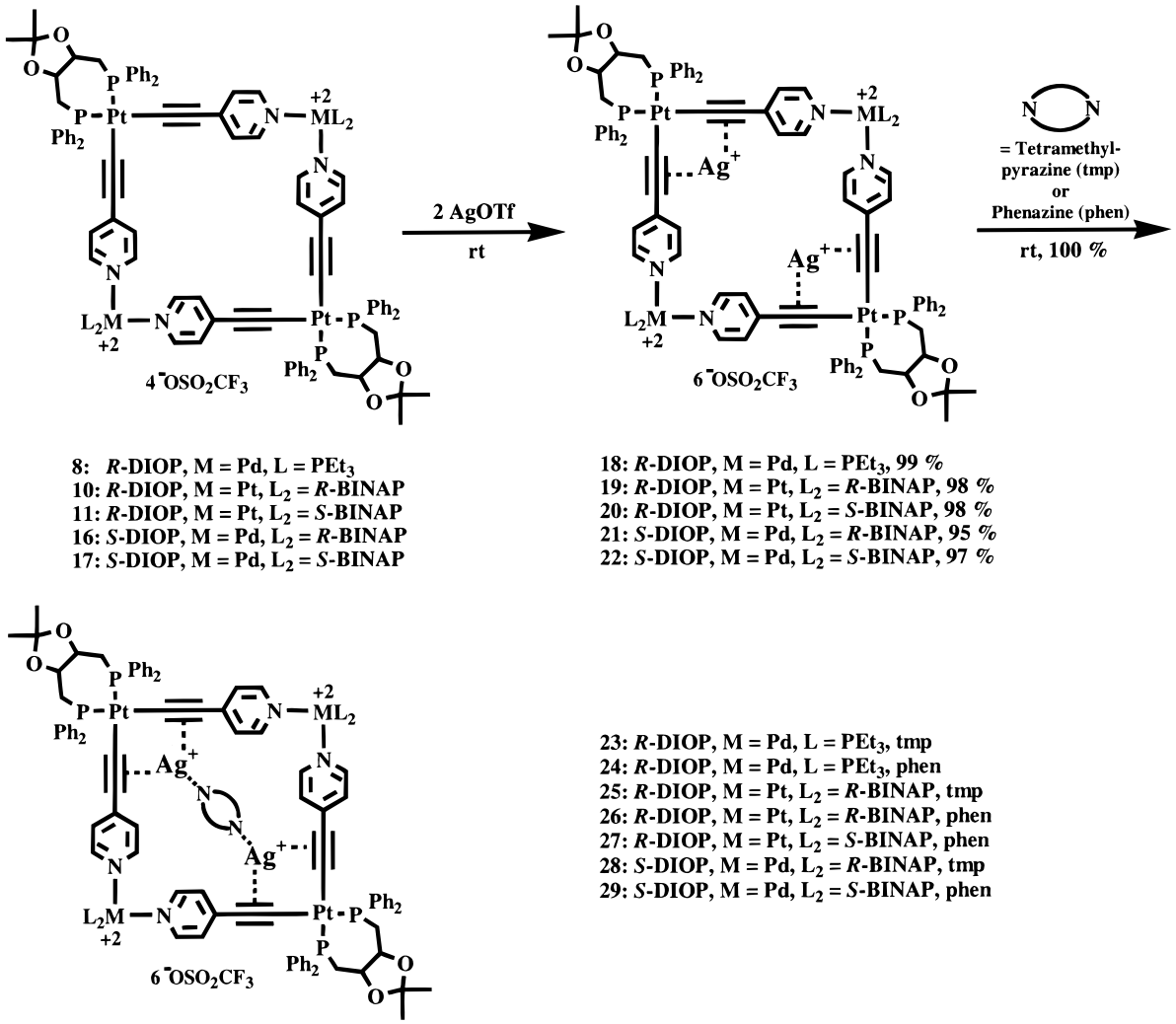
Addition of 2 equiv of silver triflate to macrocycles **8**, **10**, **11**, **16**, and **17** resulted in the expected silver complexes **18**−**22** via the "*π*-tweezer effect" (Scheme 2). Similar nonchiral silver analogues have been previously described, and the 2:1 stoichiometry has been proven by NMR, IR, EA, and FABMS.[5a] The formation of the silver complexes was complete in ca. 10 min and monitored by $^{31}P\{^1H\}$ NMR, which displayed two singlets that shifted 1.6−3.9 ppm upfield (with a coupling constant increase of 141−226 Hz) for the phosphorus on the neutral corner whereas the charged corner phosphorus shifted very little (0.1−0.9 ppm) with no significant change of the coupling constant, relative to the corresponding free square. This is not surprising since the *π*-electrons coordinated to the silver atom are a considerable distance from the charged metal center phosphines relative to the neutral metal center phosphines.

Similarly, the IR spectra of the silver complexes showed notable differences when comparing the C≡C stretches of **8**, **10**, **11**, **16**, and **17** versus those of silver complexes **18**−**22.** A shift to smaller wavenumbers was observed in each of the complexes ranging from 28 to 52 cm^{-1}, which agrees with previously reported silver tetramer complexes.[5a,d,e]

Capture of neutral guests, tetramethypyrazine, or phenazine, via coordination to the *π*-coordinated silver atoms at the respective neutral corners (two silver atoms per macrocyclic tetramer), was accomplished by simple addition of 1 equiv of the guest, resulting in complexes **23**−**29** (Scheme 2). Correlation to a nonchiral system previously reported, which was confirmed by X-ray crystallography, provided insight for the monitoring of inclusion complex formation.[5a] Guest inclusion was complete within ca. 5 min as monitored by $^{31}P\{^1H\}$ NMR at room temperature. As expected, a singlet resulted for the phosphorus on the neutral corners and a singlet for the phosphorus of the charged corners of the macrocycle. Shifts of −0.2 to +1.4 ppm were observed upon guest coordination to the silver atoms for the neutral DIOP corner with a coupling constant change of +11 to −33 Hz. The charged BINAP corner phosphorus shifted less, as expected, ranging from −0.2 to +0.1 ppm with a coupling constant increase of 3−30 Hz, relative to the starting silver containing precursors **18**−**22**.

The C≡C stretch in the IR was again diagnostic for host−guest complex formation ranging from a decrease of 2 cm^{-1} for complex **28** to an increase to larger wavenumbers of 28 cm^{-1} for complex **24**, upon neutral guest coordination, relative to silver complexes **21** and **18**, respectively. All other data are described in the Experimental Section and will not be discussed further, since the study focused on the utility of circular

Scheme 2



8: ***R*****-DIOP, M = Pd, L = PEt_3**
10: ***R*****-DIOP, M = Pt, L_2 =** ***R*****-BINAP**
11: ***R*****-DIOP, M = Pt, L_2 =** ***S*****-BINAP**
16: ***S*****-DIOP, M = Pd, L_2 =** ***R*****-BINAP**
17: ***S*****-DIOP, M = Pd, L_2 =** ***S*****-BINAP**

18: ***R*****-DIOP, M = Pd, L = PEt_3, 99 %**
19: ***R*****-DIOP, M = Pt, L_2 =** ***R*****-BINAP, 98 %**
20: ***R*****-DIOP, M = Pt, L_2 =** ***S*****-BINAP, 98 %**
21: ***S*****-DIOP, M = Pd, L_2 =** ***R*****-BINAP, 95 %**
22: ***S*****-DIOP, M = Pd, L_2 =** ***S*****-BINAP, 97 %**

23: ***R*****-DIOP, M = Pd, L = PEt_3, tmp**
24: ***R*****-DIOP, M = Pd, L = PEt_3, phen**
25: ***R*****-DIOP, M = Pt, L_2 =** ***R*****-BINAP, tmp**
26: ***R*****-DIOP, M = Pt, L_2 =** ***R*****-BINAP, phen**
27: ***R*****-DIOP, M = Pt, L_2 =** ***S*****-BINAP, phen**
28: ***S*****-DIOP, M = Pd, L_2 =** ***R*****-BINAP, tmp**
29: ***S*****-DIOP, M = Pd, L_2 =** ***S*****-BINAP, phen**

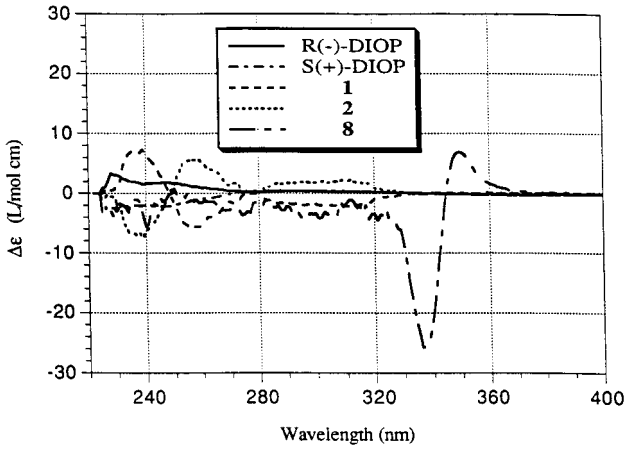


Figure 1. CD spectra of *R*(−)-DIOP, *S*(+)-DIOP, Pt(*R*(−)-DIOP)(4-ethynylpyridine)$_2$ **1**, Pt(*S*(+)-DIOP)(4-ethynylpyridine)$_2$ **2** and of the chiral square **8**.

dichroism for the observation of neutral guest inclusion via coordination in organometallic tetranuclear complexes.

Circular Dichroism Studies

The CD spectra of the noncoordinated bidentate diphosphines *R*(−)-DIOP, *S*(+)-DIOP, *R*(+)-BINAP, and *S*(−)-BINAP are provided in Figures 1 and 2, respectively. The molar ellipticities in the CD spectra give rise to much less intense Cotton effects for the most characteristic bands of DIOP (Figure 1), relative to BINAP (Figure 2). This behavior is reflected by the much larger specific optical rotation of BINAP (*R*, $[\alpha]_D$ +143.7°; *S*, $[\alpha]_D$ −139.1°) in comparison to DIOP (*R*, $[\alpha]_D$ −26.5°; *S*, $[\alpha]_D$ +27.7°).

Coordination of the chelating ligands to Pt centers causes considerable changes in the CD spectra displayed in Figure 1 (**1** and **2**) and Figure 2 (bistriflates of *R*(+)-BINAP and *S*(−)-BINAP **4**−**7**). The small Cotton effects for neutral DIOP monomers **1** and **2** are negative and positive, respectively, in accordance with the sign of the measured chirality (*R*, −3.4°; *S*, +2.6°) with an apparent Davydov splitting of ca. 13 nm.[16d,20]

Interestingly, the characteristic bands between 230 and 270 nm for the monomers **1** and **2** disappear upon self-assembled formation of the chiral tetramers **8** and **9**. In contrast, a clear large negative Cotton effect was observed for **8** (maximum at 336 nm), while a smaller positive Cotton effect was observed with an absorption maximum at 349 nm (Figure 1).

This anomalous dispersion corresponded to the 322 nm vibrational structure of the UV spectra, which was centered at the turning point for the observed negative Cotton effect. As expected, the opposite enantiomer, tetramer **9**, which possesses an *S*-chiral center, had an antipodal Cotton effect, and the CD

(20) (a) Harada, N.; Nakanishi, K. *Acc. Chem. Res.* **1972**, *5*, 257−263 and references therein. (b) Davydov, A. S. *Theory of Molecular Excitons*; McGraw-Hill: New York, 1962.

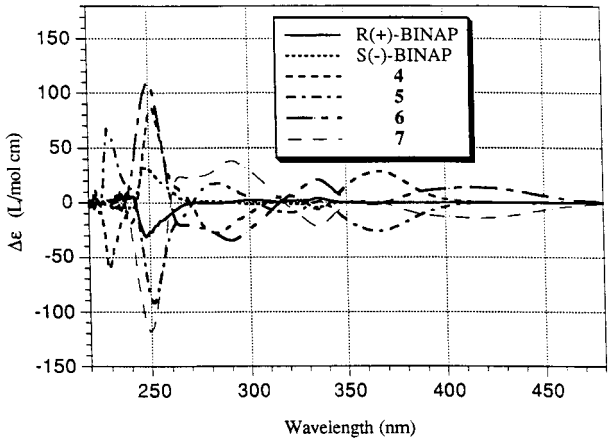


Figure 2. CD spectra of *R*(+)-BINAP, *S*(−)-BINAP, [Pt(*R*(+)-BINAP)(H_2O)][OTf]$_2$ **4**, [Pt(*S*(−)-BINAP)(H_2O)][OTf]$_2$ **5**, and of the corresponding [Pd(BINAP)(H_2O)][OTf]$_2$ complexes **6** (*R*(+)-BINAP) and **7** (*S*(−)-BINAP).

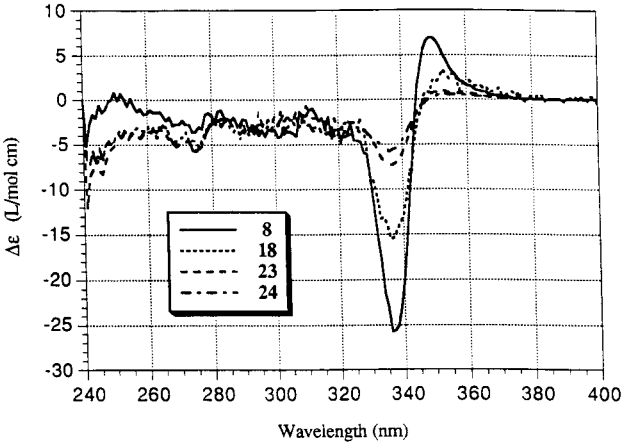


Figure 3. CD spectra of the chiral squares **8**, the AgOTf complex **18** and the tetramethylpyrazine and phenazine complexes **23** and **24**.

spectrum represents an accurate mirror image in both the form and intensity of the signals.

This large Cotton effect is probably a result of orbital overlap perturbation upon coordination of the neutral Pt(DIOP)(4-ethynylpyridine)$_2$ monomer **1** or **2** with the corresponding Pd(II) bistriflate triethylphosphine, resulting in the conformationally more rigid tetramers **8** and **9** and subsequently a change in the orbital overlap efficiency.[20a]

Most importantly, Figure 3 shows the Cotton effect decrease and absorption intensity decrease upon coordination of 2 equiv of silver triflate resulting in complex **18** ($\Delta\epsilon = -15$ L/(mol cm) at 336 nm). This change of intensity upon coordination of silver in the formation of **18** qualitatively correlates to a large binding constant as expected for a π-coordinated salt complex.[21] Subsequent coordination of guests tetramethylpyrazine or phenazine, resulting in inclusion complexes **23** and **24**, respectively, continued to decrease the absorption intensity and Cotton effect ($\Delta\epsilon = -7$ and -6 L/(mol cm) at 336 nm, respectively). Small blue shifts in the UV spectra (11 and 1 nm, respectively) were also observed, indicating further delocalization of electron density afforded by the neutral guests and silver complexation.[22] Observation of the significant changes in the CD spectra of the

(21) Yano, S.; Nakagoshi, M.; Teratani, A.; Kato, M.; Onaka, T.; Iida, M.; Tanase, T.; Yamamoto, Y.; Uekusa, H.; Ohashi, Y. *Inorg. Chem.* **1997**, *36*, 4187−4194.

(22) Hendrickson, J. B.; Cram, D. J.; Hammond, G. S. *Organic Chemistry*; McGraw-Hill: New York, 1970; Chapter 7, pp 246−256.

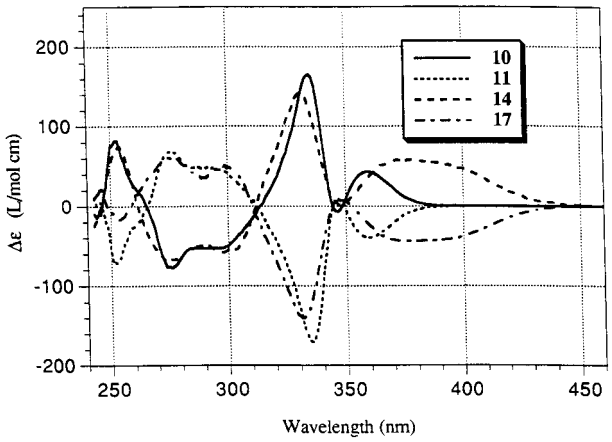


Figure 4. CD spectra of the chiral squares **10**, **11**, **14** and **17**.

simple systems **23** and **24** prompted us to examine more complex DIOP/BINAP systems (vide supra).

While the molar ellipticities for DIOP showed only changes between 230 and 330 nm upon formation of **1** and **2**, the Cotton effects of the conformationally more rigid BINAP systems were approximately double, relative to the noncoordinated diphosphines, which corresponds with the observed specific optical rotation. In parallel with the simple triethyl phosphine/DIOP macrocycles **8** and **9**, the more complicated DIOP/BINAP systems **10**−**17** resulted in an intensity decrease of the band at lower wavelengths (ca. 250 nm) and gave rise to larger Cotton effects between 320 and 350 nm upon macrocycle formation (Figure 4).

The CD spectra of the chiral macrocycles **14** (*R*-BINAP/*R*-DIOP) and **17** (*S*-BINAP/*S*-DIOP) are provided in Figure 4 and confirm the mirror image relationship. Not surprisingly, the presence of four chiral elements in each macrocycle gives rise to large Cotton effects and high specific optical rotations. The Pt/Pt systems **10**−**13** and the Pt/Pd tetramers **14**−**17** are easily distinguishable by the absorption differences between 350 and 440 nm (**10**−**13**, 350−380 nm; **14**−**17**, 350−440 nm).

The enantiomeric relationship between *R*-BINAP and *S*-BINAP substituted systems is shown by the mirror image relationship between the CD spectra of **10** and **11** (both *R*-DIOP substituted, but opposite BINAP enantiomers) that are provided in Figure 4. By comparing the CD spectra of **10** and **11**, we can conclude that the chiroptical properties appear to be dominated by the BINAP systems and are not significantly affected by the DIOP. According to the dominating effect of BINAP, the CD spectra of **11** (*S*-BINAP/*R*-DIOP) and **17** (*S*-BINAP/*S*-DIOP) show only differences associated with the bands characteristic of the BINAP moiety.

As expected, the coordination of 2 equiv of silver triflate resulted in notable changes in the CD observed in the comparison of the free Pt/Pt tetramers **10** and **11** vs the corresponding silver complexes **19** and **20** shown in Figure 5. Specifically, the most intense band maxima shift by about 15 nm (from 335 to ca. 320 nm) and by about 12 nm (from ca. 347 to ca. 335 nm), respectively. Coordination of silver triflate to the Pt/Pd tetramers **16** and **17** causes a change in the shape of the most prominent bands between 260 and 350 nm as well as a decrease in the molar ellipticity, $\Delta\epsilon$ (L/(mol cm)) (Figure 6).

Subsequent coordination of the guests tetramethylpyrazine and phenazine to the silver complexes **19**−**22** resulting in **25**−**29** (Figures 7 and 8) gave little change in the CD spectra. However, inclusion of the respective guests to the Pt/Pt silver complexes **19** and **20**, resulting in host−guest complexes **25**−

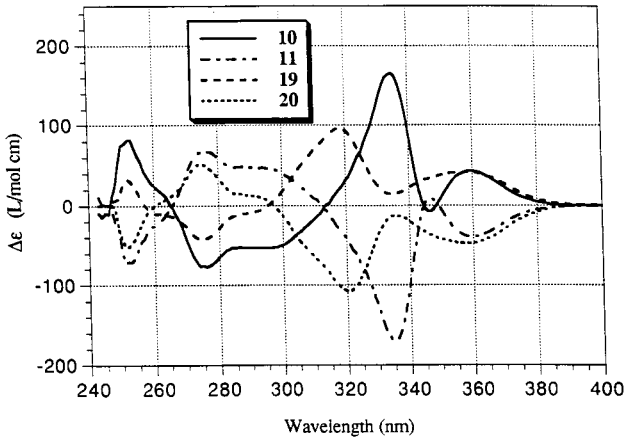


Figure 5. CD spectra of the chiral squares **10**, **11** and their AgOTf complexes **19** and **20**.

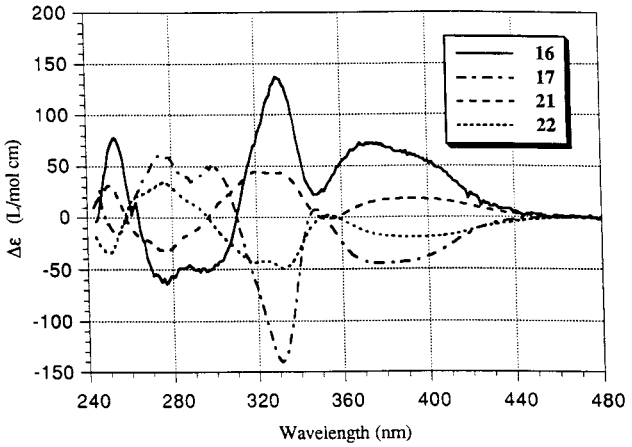


Figure 6. CD spectra of the chiral squares **16**, **17** their AgOTf complexes **21** and **22**.

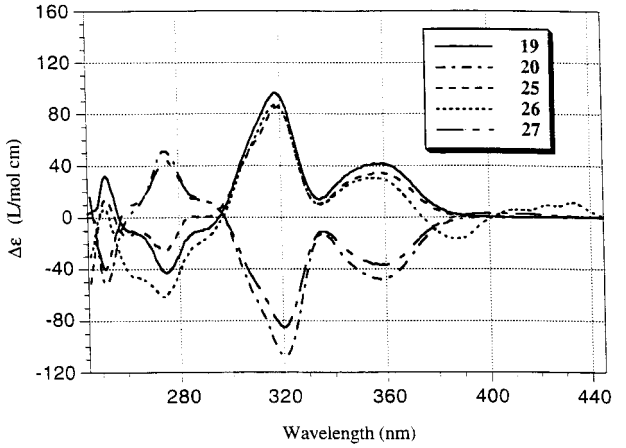


Figure 7. CD spectra of the AgOTf complexes **19**, **20** and the tetramethylpyrazine and phenazine complexes **25**−**27**.

27, gave a large band intensity decrease (ca. 15−20 L/(mol cm)). This is also the case for the Pt/Pd neutral guest complexes **28** and **29**; however, the molar ellipticity changes were slightly more pronounced. It is well-known that a dative Pd−N bond is considerably weaker than a Pt−N dative bond.[5m] This probably allows for a larger change in macrocycle periphery upon guest coordination, thus resulting in larger geometry changes for the chiral moiety and giving rise to larger changes in the CD spectra. In general, for the neutral guest containing systems **25**−**29**, the largest effects in the CD spectra were observed with the phenazine complexation.

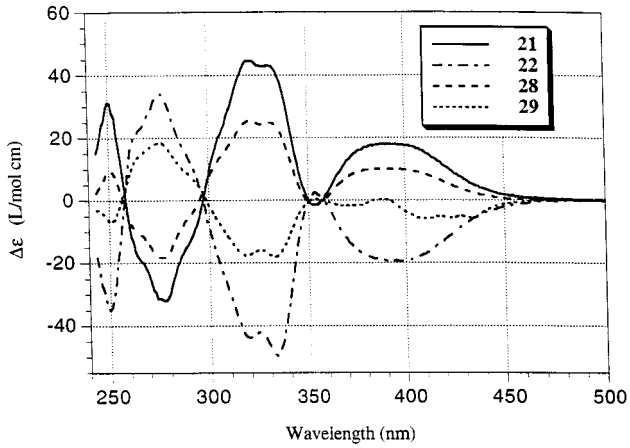


Figure 8. CD spectra of the AgOTf complex **21**, **22** and the tetramethylpyrazine and phenazine complexes **28** and **29**.

Conclusions

Ten different air stable, chiral, neutral-charged Pt/Pt and Pt/Pd complexes were prepared in excellent yields via self-assembly from readily available precursors. Five silver complexes **18**−**22** were prepared by addition of 2 equiv of silver triflate, resulting in stable Lewis acid/base receptors. Addition of heteroatom-containing, neutral aromatic guests, tetramethylpyrazine or phenazine, afforded stable inclusion complexes **23**−**29** in essentially quantitative yields. NMR spectroscopy, circular dichroism (CD), and UV spectroscopy were used to observe tetramer formation, silver coordination, and guest inclusion. Significant Cotton effects and antipodal Cotton effects of the corresponding chiral enantiomer were observed for the formation of the modularly self-assembled macrocycles. The UV absorption maxima correspond to the CD turning point for the observed Cotton effects. The coordination of silver was readily monitored by a significant change in the intensity and shape of the CD absorption bands. It was demonstrated that the DIOP moiety was most useful when used in conjuction with the achiral triethyl phosphine palladium bistriflate. However, the BINAP moiety allowed for the observation of larger Cotton effects, which proved particularly useful for monitoring the formation of the chiral tetramers as well as the inclusion of neutral guests. The utility of CD for the observation of stoichiometric addition of respective guests to the Lewis acid/base receptors, resulting in inclusion phenomena, was demonstrated by a subsequent decrease in the absorption intensities and a variation of the signal shape. Circular dichroism proved to be a valuable tool for providing evidence of inclusion phenomena in Lewis acid/base designed host−guest receptor systems.

Experimental Section

General Methods. Schlenk techniques along with dry N_2 were employed, although the products may be handled in air. Melting points are uncorrected and were obtained using a Mel-Temp capillary melting point apparatus. Infrared spectra were recorded as CCl_4 mulls on a Mattson Polaris FT-IR spectrometer. UV spectra were obtained using a Hewlett-Packard UV−vis spectrophotometer. Circular dichroism (CD) spectra were recorded on an Aviv 62ADS CD spectrometer. Standard solutions in CH_2Cl_2 were prepared by weighing out the material on a Satorius microbalance followed by dilution to appropriate volumes. Further dilution gave the desired concentration (2.5×10^{-5} M).

Optical rotations were measured on a Perkin-Elmer 241MC polarimeter. All NMR spectra were recorded on a Varian Unity 300 or a Varian VXR 500 spectrometer. The ^{1}H NMR spectra were recorded

at 300 MHz, and chemical shifts are reported relative to the residual protonated solvent peaks of CD_2Cl_2 δ 5.32. The ^{13}C NMR spectra were recorded at 125 MHz, ^1H decoupled, and reported relative to CD_2Cl_2 δ 54.0. The ^{19}F NMR spectra were recorded at 282 MHz, and chemical shifts were reported relative to external $CFCl_3$ δ 0.0 (sealed capillary) in CD_2Cl_2. The ^{31}P NMR spectra were recorded at 121 MHz, ^1H decoupled, and reported relative to external 85% H_3PO_4 (sealed capillary) in CD_2Cl_2. The signals due to water of crystallization in the ^1H NMR are omitted.

Mass spectra were obtained with a Finnigan MAT 95 mass spectrometer with a Finnigan MAT ICIS II operating system under positive fast atom bombardment (FAB) conditions at 8 keV. 3-Nitrobenzyl alcohol was used as a matrix in CH_2Cl_2 as a solvent; polypropylene glycol and cesium iodide were used as a reference for peak matching. Microanalyses were performed by Atlantic Microlabs, Atlanta, GA.

Materials. Commercial reagents were ACS reagent grade and used without further purification. Reagent grade methylene chloride was dried by distillation over CaH_2. Diethyl ether and THF were distilled from Na/benzophenone. The methylene chloride used in spectroscopy was spectrophotometric grade. *tert*-Butyllithium (1.5 M) in pentane was purchased from Fisher Scientific, *R*(+)-BINAP (98%), *S*(−)-BINAP (97%), *R*(−)-DIOP (99.5%), and *S*(+)-DIOP (99.5%) were purchased from Strem Chemicals. The precursors, 4-ethynylpyridine,[23] $[Pd(PEt_3)_2(H_2O)][OTf]_2$ (**3**),[5m] [Pt(*R*(+)-BINAP)(H_2O)][OTf]$_2$ (**4**),[5j] [Pt(*S*(−)-BINAP)(H_2O)][OTf]$_2$ (**5**),[5j] [Pd(*R*(+)-BINAP)(H_2O)][OTf]$_2$ (**6**),[5j] and [Pd(*S*(−)-BINAP)(H_2O)][OTf]$_2$ (**7**),[5j] were prepared according to literature methods. [Pt(*R*(−)-DIOP)][Cl]$_2$ and [Pt(*S*(+)-DIOP)][Cl]$_2$ were prepared by a modified literature procedure.[24]

Optical Rotation and CD Data for Precursors. *R*(+)-BINAP. $[\alpha]_D$ +143.7 ± 0.1° (*c* 0.015, CH_2Cl_2, 20 °C). CD (CH_2Cl_2), λ ($\Delta\epsilon$) [nm (L mol^{-1} cm^{-1})], 239 (+9.5), 248 (−31.5), 274 (+0.1), 301 (+2.4), 315 (+0.3), 336 (+4.1).

***S*(−)-BINAP.** $[\alpha]_D$ −139.1 ± 0.1° (*c* 0.015, CH_2Cl_2, 20 °C). CD (CH_2Cl_2), λ ($\Delta\epsilon$) [nm (L mol^{-1} cm^{-1})], 239 (−9.3), 247 (+31.7), 274 (+0.3), 300 (−1.9), 316 (+0.1), 335 (−4.4).

***R*(−)-DIOP.** $[\alpha]_D$ −26.5 ± 0.1° (*c* 0.015, CH_2Cl_2, 20 °C). CD (CH_2Cl_2), λ ($\Delta\epsilon$) [nm (L mol^{-1} cm^{-1})], 228 (+3.4), 247 (+1.9), 294 (+0.5).

***S*(+)-DIOP.** $[\alpha]_D$ +27.7 ± 0.2° (*c* 0.015, CH_2Cl_2, 20 °C). CD (CH_2Cl_2) λ, ($\Delta\epsilon$) [nm (L mol^{-1} cm^{-1})], 227 (−3.1), 246 (−2.2), 281 (+0.6).

[Pt(*R*(+)-BINAP)(H_2O)][OTf]$_2$ (4). $[\alpha]_D$ +192.6 ± 0.2° (*c* 0.015, CH_2Cl_2, 20 °C). CD (CH_2Cl_2), λ ($\Delta\epsilon$) [nm (L mol^{-1} cm^{-1})], 230 (−60.8), 252 (+85.3), 283 (−28.1), 320 (+6.6), 335 (−6.2), 367 (+28.2).

[Pt(*S*(−)-BINAP)(H_2O)][OTf]$_2$ (5). $[\alpha]_D$ −198.3 ± 0.1° (*c* 0.015, CH_2Cl_2, 20 °C). CD (CH_2Cl_2), λ ($\Delta\epsilon$) [nm (L mol^{-1} cm^{-1})], 229 (+67.1), 252 (−91.9), 285 (+17.8), 319 (−9.3), 336 (+1.0), 366 (−26.5).

[Pd(*R*(+)-BINAP)(H_2O)][OTf]$_2$ (6). $[\alpha]_D$ +435.4 ± 0.1° (*c* 0.015, CH_2Cl_2, 20 °C). CD (CH_2Cl_2), λ ($\Delta\epsilon$) [nm (L mol^{-1} cm^{-1})], 249 (+109.9), 267 (−20.6), 291 (−34.9), 335 (+21.0), 361 (−2.1), 415 (+13.9).

[Pd(*S*(−)-BINAP)(H_2O)][OTf]$_2$ (7). $[\alpha]_D$ −413.76 ± 0.1° (*c* 0.015, CH_2Cl_2, 20 °C). CD (CH_2Cl_2), λ ($\Delta\epsilon$) [nm (L mol^{-1} cm^{-1})], 249 (−118.5), 265 (+23.9), 291 (+38.2), 334 (−21.3), 360 (1.83), 416 (−14.1).

General Procedure for the Preparation of *cis*-Pt(DIOP)(4-ethynyl-pyridine)$_2$ (1, 2). A solution of *tert*-BuLi (1.5 M, pentane, 2.10 mmol) was added via syringe to a solution of 4-alkynylpyridine (238 mg, 2.31 mmol) in 100 mL of THF at −78 °C under argon. Platinum(II)dichloride(DIOP) (803 mg, 1.05 mmol) was immediately added all at once at −78 °C. The cold bath was removed, and the reaction mixture was allowed to warm to 25 °C on its own and stirred for 5 h in the absence of light, followed by solvent removal via rotary evaporation at ambient temperature. The residue was extracted with $CHCl_3$ (5 × 40 mL). The solvent was removed via rotary evaporation, and the extract was subjected to column chromatography (silicagel, CH_2Cl_2/MeOH = 19:1). The solvent was reduced in volume to 2 mL, and diethyl ether (5 mL) was added. The white precipitate was collected, washed with diethyl ether (3 × 5 mL), and dried at 60 °C in vacuo.

***cis*-Pt(*R*(−)-DIOP)(4-ethynylpyridine)$_2$ (1).** Yield: 547 mg (58%). mp 226−228 °C (dec). IR (CCl_4) 3050, 3035 (Ar), 2979 (CH_3), 2939 (CH_2), 2121 (CC) cm^{-1}. UV−vis (CH_2Cl_2) λ_{max} = 308 nm, ϵ = 2.4 × 10^4 L cm^{-1} mol^{-1}. $[\alpha]_D$ −3.4 ± 0.2° (*c* 0.015, CH_2Cl_2, 20 °C). CD (CH_2Cl_2), λ ($\Delta\epsilon$) [nm (L mol^{-1} cm^{-1})], 239 (+7.3), 257 (−5.6), 276 (+0.25), 312 (−2.4). ^1H NMR (CD_2Cl_2) δ 8.20 (d, 4H, $^3J_{HH}$ = 6.1 Hz), 7.79−7.61 (m, 8H), 7.50−7.42 (m, 12H), 6.60 (d, 4H, $^3J_{HH}$ = 6.1 Hz), 3.94 (s, br, 2H), 3.21 (m, 2H), 2.62 (m, 2H), 1.16 (s, 6H). ^{13}C {^1H} NMR (CD_2Cl_2) δ 149.5 ($C_{\alpha pyr}$), 135.6 ($C_{ipsopyr}$), 134.9, 133.2 (Pt−P−C_o), 133.0, 130.5 (Pt−P−C_{ipso}), 132.1, 131.3 (Pt−P−C_p), 129.3, 129.0 (Pt−P−C_m), 125.8 ($C_{\beta pyr}$), 112.8 (q, CC−Pt_α, $^2J_{P-C(cis)}$ = 21.1 Hz, $^2J_{P-C(trans)}$ = 148.5 Hz), 109.4 (s, OCO), 107.8 (t, CC−Pt_β, $^2J_{P-C}$ = 17.1 Hz), 77.4 (t, O*C*HCH$_2$, $^2J_{P-C}$ = 5.6 Hz), 31.5−31.2 (m, OCH*C*H$_2$), 27.0 (CH_3). ^{31}P {^1H} NMR (CD_2Cl_2) δ 2.5 (s, J_{Pt-P} = 2252 Hz). Anal. Calcd for $C_{45}H_{40}O_2P_2PtN_2$: C, 60.20; H, 4.49; N, 3.12. Found: C, 60.12; H, 4.52; N, 3.04.

***cis*-Pt(*S*(+)-DIOP)(4-ethynylpyridine)$_2$ (2).** Yield: 509 mg (54%). mp 231−233 °C (dec). IR (CCl_4) 3056, 3039 (Ar), 2986 (CH_3), 2939 (CH_2), 2119 (CC) cm^{-1}. UV−vis (CH_2Cl_2) λ_{max} = 308 nm, ϵ = 2.4 × 10^4 L cm^{-1} mol^{-1}. $[\alpha]_D$ +2.6 ± 0.1° (*c* 0.015, CH_2Cl_2, 20 °C). CD (CH_2Cl_2), λ ($\Delta\epsilon$) [nm (L mol^{-1} cm^{-1})], 239 (−7.4), 258 (−5.6), 276 (−0.2), 309 (+2.3). ^1H NMR (CD_2Cl_2) δ 8.20 (d, 4H, $^3J_{HH}$ = 6.1 Hz), 7.82−7.58 (m, 8H), 7.52−7.40 (m, 12H), 6.60 (d, 4H, $^3J_{HH}$ = 6.3 Hz), 3.94 (s, br, 2H), 3.21 (m, 2H), 2.62 (m, 2H), 1.16 (s, 6H). ^{13}C {^1H} NMR (CD_2Cl_2) δ 149.4 ($C_{\alpha pyr}$), 135.5 ($C_{ipsopyr}$), 134.9, 133.2 (Pt−P−C_o), 132.9, 130.5 (Pt−P−C_{ipso}), 132.1, 131.3 (Pt−P−C_p), 129.3, 129.0 (Pt−P−C_m), 125.7 ($C_{\beta pyr}$), 112.8 (q, CC−Pt_α, $^2J_{P-C(cis)}$ = 21.1 Hz, $^2J_{P-C(trans)}$ = 148.8 Hz), 109.4 (s, OCO), 107.8 (t, CC−Pt_β, $^2J_{P-C}$ = 17.1 Hz), 77.4 (t, O*C*HCH$_2$ $^2J_{P-C}$ = 5.9 Hz), 31.4−31.1 (m, OCH*C*H$_2$, CH), 27.0 (CH_3). ^{31}P {^1H} NMR (CD_2Cl_2) δ 2.5 (s, J_{Pt-P} = 2248 Hz). Anal. Calcd for $C_{45}H_{40}O_2P_2PtN_2$: C, 60.20; H, 4.49; N, 3.12. Found: C, 60.45; H, 4.58; N, 3.04.

General Procedure for the Preparation of Cyclobis[[*cis*-Pt(DIOP)(4-ethynylpyridine)$_2$]][*cis*-Pd^{2+}(PEt$_3$)$_2$($^-$OSO$_2$CF$_3$)$_2$]] (8, 9). To a 7 mm NMR tube 20.0 mg (0.022 mmol) of Pt(DIOP)(4-ethynylpyridine)$_2$ (**1** or **2**) and 14.3 mg (0.022 mmol) of Pd^{2+}(PEt$_3$)$_2$($^-$OSO$_2$CF$_3$)$_2$ were added. In a nitrogen atmosphere glovebag, 750 μL of acetone-d_6 were added at room temperature, and the mixture was capped and shaken for 5 min and monitored by ^{31}P {^1H} NMR. The solution was transferred to a 2 mL vial, followed by solvent removal with a stream of dry nitrogen and dried in vacuo.

Cyclobis[[*cis*-Pt(*R*(−)-DIOP)(4-ethynylpyridine)$_2$][*cis*-Pd^{2+}(PEt$_3$)$_2$($^-$OSO$_2$CF$_3$)$_2$]] (8). Yield: 34.2 mg (99%). mp 198−205 °C (dec). IR (CCl_4) 3056 (Ar), 2979 (CH_3), 2938 (CH_2), 2116 (CC) cm^{-1}. UV−vis (CH_2Cl_2) λ_{max} = 322 nm, ϵ = 12.6 × 10^4 L cm^{-1} mol^{-1}. $[\alpha]_D$ −5.7 ± 0.1° (*c* 0.015, CH_2Cl_2, 20 °C). CD (CH_2Cl_2), λ ($\Delta\epsilon$) [nm (L mol^{-1} cm^{-1})], 229 (−4.3), 237 (−1.0), 240 (−5.6), 252 (+0.7), 277 (−3.3), 283 (−1.2), 301 (−4.2) 312 (−1.0), 336 (−25.8), 349 (+6.9). ^1H NMR (acetone-d_6) δ 8.72 (m, 4H), 7.83−7.60 (m, 8H), 7.60−7.40 (m, 12H), 6.76 (m, 4H), 4.09 (s, br, 2H), 3.33 (m, 2H), 2.86 (m, 2H), 1.95 (m, 24H), 1.34 (m, 36H), 1.17 (s, 12H). ^{13}C {^1H} NMR (acetone-d_6) δ 150.3 ($C_{\alpha pyr}$), 140.4 ($C_{ipsopyr}$), 135.1, 133.8 (Pt−P−C_o), 133.0, 131.1 (Pt−P−C_{ipso}), 132.6, 131.8 (Pt−P−C_p), 129.6, 129.4 (Pt−P−C_m), 129.0 ($C_{\beta pyr}$), 124.0 (q, CC−Pt_α), 122.4 (q, $^1J_{C-F}$ = 322 Hz, OTf), 106.9 (t, CC−Pt_β, $^2J_{P-C}$ = 15.8 Hz), 109.5 (s, OCO), 77.7 (t, O*C*HCH$_2$P, $^2J_{P-C}$ = 5.9 Hz), 27.0 (CH_3), 16.6 (m, Pd−P−*C*H$_2$CH$_3$), 8.4 (bs, Pd−P−CH$_2$*C*H$_3$). ^{31}P {^1H} NMR (acetone-d_6) δ 31.7 (s), 3.4 (s, J_{Pt-P} = 2257 Hz). ^{19}F NMR (acetone-d_6) δ −75 (s, OTf). FAB LRMS, *m*/*z* 2926.5 (M−OTf).

Cyclobis[[*cis*-Pt(*S*(+)-DIOP)(4-ethynylpyridine)$_2$][*cis*-Pd^{2+}(PEt$_3$)$_2$($^-$OSO$_2$CF$_3$)$_2$]] (9). Yield: 34.3 mg (99%). mp 200−205 °C (dec). IR (CCl_4) 3057 (Ar), 2977 (CH_3), 2939 (CH_2), 2117 (CC) cm^{-1}. UV−

(23) (a) Ciana, L. D.; Haim, A. *J. Heterocycl. Chem.* **1984**, 607−608. (b) Takahashi, S.; Kuroyama, Y.; Sonogahira, K.; Hagihara, N. *Synthesis* **1980**, 627−630.

(24) The reaction between *R*(−)-DIOP or *S*(+)-DIOP and Pt(COD)Cl$_2$ (COD = cyclooctadiene) for 15 min at room temperature provided [Pt(*R*(−)-DIOP)][Cl]$_2$ and [Pt(*S*(+)-DIOP)][Cl]$_2$ in 91% and 93% yields, respectively.

vis (CH_2Cl_2) λ_{max} = 321 nm, $\epsilon = 10.7 \times 10^4$ L cm^{-1} mol^{-1}. $[\alpha]_D$ +5.9 ± 0.1° (*c* 0.015, CH_2Cl_2, 20 °C). CD (CH_2Cl_2), λ ($\Delta\epsilon$) [nm (L mol^{-1} cm^{-1})], 230 (3.8), 239 (−1.8), 241 (+6.2), 252 (−0.6), 277 (+3.5), 283 (+1.1), 301 (+4.5), 313 (+1.2), 336 (+26.1), 349 (−7.0). ^{1}H NMR (acetone-d_6) δ 8.73 (d, 4H, $^3J_{HH}$ = 6.1 Hz), 7.85−7.60 (m, 8H), 7.60−7.40 (m, 12H), 6.77 (d, 4 H, $^3J_{HH}$ = 6.3 Hz), 4.09 (s, br, 2H), 3.32 (m, 2H), 2.86 (m, 2H), 1.95 (m, 24H), 1.34 (m, 36H), 1.17 (s, 12H). ^{13}C {^{1}H} NMR (acetone-d_6) δ 150.3 ($C_{\alpha pyr}$), 140.4 ($C_{ipsopyr}$), 135.1, 133.8 (Pt−P−C_o), 133.0, 131.1 (Pt−P−C_{ipso}), 132.6, 131.8 (Pt−P−C_p), 129.6, 129.4 (Pt−P−C_m), 129.0 ($C_{\beta pyr}$), 124.0 (q, CC−Pt$_\alpha$), 122.4 (q, $^1J_{C-F}$ = 322 Hz, OTf), 109.4 (s, OCO), 106.9 (t, CC−Pt$_\beta$, $^2J_{P-C}$ = 15.8 Hz), 77.7 (t, O*C*HCH$_2$P, $^2J_{P-C}$ = 5.9 Hz), 27.0, (CH_3) 16.6 (m, Pd−P-*C*H$_2$CH$_3$), 8.4 (bs, Pd−P−CH$_2$*C*H$_3$). ^{31}P {^{1}H} NMR (acetone-d_6) δ 31.7 (s), 3.4 (s, J_{Pt-P} = 2257 Hz). ^{19}F NMR (acetone-d_6) δ −75 (s, OTf). Anal. Calcd for $C_{118}H_{140}F_{12}N_4O_{16}P_8Pd_2Pt_2S_4 \cdot 5C_3D_6O$: C, 47.35; H, 5.26; N, 1.66; S, 3.80. Found: C, 47.36; H, 5.02; N, 1.73; S, 3.51.

General Procedure for the Preparation of Cyclobis[[*cis*-Pt(DIOP)(4-ethynylpyridine)$_2$][*cis*-Pt^{2+}(BINAP)($^-$OSO$_2$CF$_3$)$_2$]] (10−13). To a solution of 18.0 mg (0.020 mmol) of Pt(DIOP)(4-ethynylpyridine)$_2$ (**1**, **2**) in 3.0 mL of CH_2Cl_2 was added 22.7 mg (0.020 mmol) of [Pt(BINAP)(H_2O)][OTf]$_2$ (**4**, **5**), and the mixture was stirred under nitrogen at room temperature for 2 h. The solution was reduced in volume to ca. 0.5 mL. Diethyl ether was then added, and the precipitate was collected, washed with diethyl ether, and dried in vacuo.

Cyclobis-[[*cis*-Pt(*R*(−)-DIOP)(4-ethynylpyridine)$_2$][*cis*-Pt^{2+}(*R*(+)-BINAP)($^-$OSO$_2$CF$_3$)$_2$]] (10). Yield: 36 mg (89%). mp 338−340 °C (dec). IR (CCl_4) 3052, 3041 (Ar), 2986 (CH_3), 2934 (CH_2), 2119 (CC), 1256, 1154, 1100, 1029 (all OTf) cm^{-1}. UV−vis (CH_2Cl_2) λ_{max} = 330 nm, $\epsilon = 6.63 \times 10^4$ L cm^{-1} mol^{-1}. $[\alpha]_D$ +188.9 ± 0.4° (*c* 0.009, CH_2Cl_2, 20 °C). CD (CH_2Cl_2), λ ($\Delta\epsilon$) [nm (L mol^{-1} cm^{-1})], 253 (+82.1), 276 (−78.0), 335 (+165.8), 346 (−7.3), 359 (+42.9). ^{1}H NMR (CD_2Cl_2) δ 8.01 (bd, 8H), 7.83−7.78 (m, 12H), 7.75−7.54 (m, 28H), 7.51−7.41 (m, 32H), 7.16 (t, 12H, *J* = 6.8 Hz), 7.08−6.97 (m, 16H), 6.42 (d, 4H, $^3J_{HH}$ = 8.5 Hz), 6.17 (bd, 8H), 3.82 (bs, 4H), 3.19 (bm, 4H), 2.58 (bm, 4H), 1.13 (s, 12H). ^{13}C {^{1}H} NMR (CD_2Cl_2) δ 150.3 ($C_{\alpha pyr}$), 140.5 (t), 139.5 ($C_{ipsopyr}$), 136.8 (s), 135.4 (s), 135.0 (s), 134.9, 133.6 (Pt−P−C_o), 133.0 (s), 132.8 (s), 132.6, 131.7 (Pt−P−C_p), 132.0 (s), 130.6 (s), 129.5, 129.0 (Pt−P−C_m), 129.3 ($C_{\beta pyr}$), 129.2 (s), 128.8 (s), 128.4 (s), 127.8 (s), 127.6 (s), 127.4 (t), 124.4 (t), 123.8 (s), 123.7 (s), 122.8 (s), 121.8 (q, $^1J_{C-F}$ = 320 Hz, OTf), 124.1 (q, CC−Pt$_\alpha$), 109.6 (s, OCO), 106.4 (t, CC−Pt$_\beta$, $^2J_{P-C}$ = 15.4 Hz), 77.2 (t, O*C*HCH$_2$, $^2J_{P-C}$ = 5.8 Hz), 31.2−30.9 (m, OCH*C*H$_2$), 26.9 (CH_3). ^{31}P {^{1}H} NMR (CD_2Cl_2) δ 2.9 (s, J_{Pt-P} = 3242 Hz), 1.9 (s, J_{Pt-P} = 2266 Hz). ^{19}F NMR (CD_2Cl_2) δ −76 (s, OTf). Anal. Calcd for $C_{182}H_{144}F_{12}N_4O_{16}P_8Pt_4S_4 \cdot 2H_2O$: C, 53.80; H, 3.67; N, 1.38; S, 3.16. Found: C, 53.42; H, 3.58; N, 1.37; S, 3.04.

Cyclobis-[[*cis*-Pt(*R*(−)-DIOP)(4-ethynylpyridine)$_2$][*cis*-Pt^{2+}(*S*(−)-BINAP)($^-$OSO$_2$CF$_3$)$_2$]] (11). Yield: 37 mg (92%). mp 329−331 °C (dec). IR (CCl_4) 3062, 3036 (Ar), 2986 (CH_3), 2934 (CH_2), 2122 (CC), 1256, 1154, 1101, 1030 (all OTf) cm^{-1}. UV−vis (CH_2Cl_2) λ_{max} = 332 nm, $\epsilon = 6.69 \times 10^4$ L cm^{-1} mol^{-1}. $[\alpha]_D$ −199.9 ± 0.3° (*c* 0.014, CH_2Cl_2, 20 °C). CD (CH_2Cl_2), λ ($\Delta\epsilon$) [nm (L mol^{-1} cm^{-1})], 251 (−72.7), 276 (+67.7), 335 (−170.8), 347 (+8.8), 360 (−39.8). ^{1}H NMR (CD_2Cl_2) δ 8.01 (bd, 8H), 7.82−7.74 (m, 12H), 7.70−7.51 (m, 28H), 7.47−7.39 (m, 32H), 7.13 (t, 12H, *J* = 7.1 Hz), 7.08−6.93 (m, 16H), 6.42 (d, 4H, $^3J_{HH}$ = 8.3 Hz), 6.13 (bd, 8H), 3.94 (bs, 4H), 3.09 (bm, 4H), 2.62 (bm, 4H), 1.11 (s, 12H). ^{13}C {^{1}H} NMR (CD_2Cl_2) δ 150.3 ($C_{\alpha pyr}$), 140.5 (t), 139.5 ($C_{ipsopyr}$), 135.4 (s), 135.1 (s), 134.3, 133.6 (Pt−P−C_o), 133.4 (s), 132.8 (s), 132.5 (s), 131.9 (Pt−P−C_p), 132.0 (s), 130.6 (s), 129.3, 129.1 (Pt−P−C_m), 129.2 ($C_{\beta pyr}$), 129.1 (s), 128.8 (s), 128.4 (s), 127.7 (s), 127.6 (s), 127.4 (t), 124.3 (t), 124.1 (q, CC−Pt$_\alpha$), 123.8 (s), 123.7 (s), 122.9 (s), 121.8 (q, $^1J_{C-F}$ = 321 Hz, OTf), 109.5 (s, OCO), 106.2 (t, CC−Pt$_\beta$, $^2J_{P-C}$ = 15.2 Hz), 77.1 (t, O*C*HCH$_2$, $^2J_{P-C}$ = 6.1 Hz), 30.5−30.1 (m, OCH*C*H$_2$), 26.9 (CH_3). ^{31}P {^{1}H} NMR (CD_2Cl_2) δ 3.1 (s, J_{Pt-P} = 3269 Hz), 1.8 (s, J_{Pt-P} = 2262 Hz). ^{19}F NMR (CD_2Cl_2) δ −76 (s, OTf). Anal. Calcd for $C_{182}H_{144}F_{12}N_4O_{16}P_8Pt_4S_4 \cdot 2H_2O$: C, 53.80; H, 3.67; N, 1.38; S, 3.16. Found: C, 53.32; H, 3.63; N, 1.44; S, 3.15.

Cyclobis-[[*cis*-Pt(*S*(+)-DIOP)(4-ethynylpyridine)$_2$][*cis*-Pt^{2+}(*R*(+)-BINAP)($^-$OSO$_2$CF$_3$)$_2$]] (12). Yield: 35 mg (87%). mp 337−340 °C (dec). IR (CCl_4) 3062, 3037 (Ar), 2987 (CH_3), 2933 (CH_2), 2118 (CC), 1255, 1154, 1100, 1030 (all OTf) cm^{-1}. UV−vis (CH_2Cl_2) λ_{max} = 332 nm, $\epsilon = 6.60 \times 10^4$ L cm^{-1} mol^{-1}. $[\alpha]_D$ +193.9 ± 0.2° (*c* 0.010, CH_2Cl_2, 20 °C). CD (CH_2Cl_2), λ ($\Delta\epsilon$) [nm (L mol^{-1} cm^{-1})], 252 (+79.2), 276 (−71.6), 335 (+179.8), 347 (−8.0), 360 (+41.9). ^{1}H NMR (CD_2Cl_2) δ 8.01 (bd, 8H), 7.82−7.74 (m, 12H), 7.70−7.50 (m, 28H), 7.48−7.39 (m, 32H), 7.13 (t, 12H, *J* = 6.8 Hz), 7.08−6.93 (m, 16H), 6.42 (d, 4H, $^3J_{HH}$ = 8.8 Hz), 6.13 (bd, 8H), 3.93 (bs, 4H), 3.09 (bm, 4H), 2.62 (bm, 4H), 1.11 (s, 12H). ^{13}C {^{1}H} NMR (CD_2Cl_2) δ 150.3 ($C_{\alpha pyr}$), 140.5 (t), 139.5 ($C_{ipsopyr}$), 135.3 (s), 135.0 (s), 134.3, 133.4 (Pt−P−C_o), 133.6 (s), 133.0 (s), 132.8 (s), 132.4, 131.8 (Pt−P−C_p), 132.0 (s), 130.6 (s), 130.5 (Pt−P−C_{ipso}), 129.3, 129.1 (Pt−P−C_m), 129.3 ($C_{\beta pyr}$), 129.2 (s), 128.8 (s), 128.7 (s), 127.8 (s), 127.6 (s), 127.4 (t), 124.3 (t), 124.1 (q, CC−Pt$_\alpha$), 123.8 (s), 123.7 (s), 122.8 (s), 121.8 (q, $^1J_{C-F}$ = 322 Hz, OTf), 109.4 (s, OCO), 106.3 (t, CC−Pt$_\beta$, $^2J_{P-C}$ = 15.8 Hz), 77.1 (t, O*C*HCH$_2$, $^2J_{P-C}$ = 5.2 Hz), 30.5−30.2 (m, OCH*C*H$_2$), 26.9 (CH_3). ^{31}P {^{1}H} NMR (CD_2Cl_2) δ 3.1 (s, J_{Pt-P} = 3257 Hz), 1.7 (s, J_{Pt-P} = 2262 Hz). ^{19}F NMR (CD_2Cl_2) δ −76 (s, OTf). Anal. Calcd for $C_{182}H_{144}F_{12}N_4O_{16}P_8Pt_4S_4 \cdot 2H_2O$: C, 53.80; H, 3.67; N, 1.38; S, 3.16. Found: C, 53.51; H, 3.75; N, 1.40; S, 3.18. FAB LRMS, *m*/*z* 1863.7 (M −2OTf).

Cyclobis-[[*cis*-Pt(*S*(+)-DIOP)(4-ethynylpyridine)$_2$][*cis*-Pt^{2+}-(*S*(−)BINAP)($^-$OSO$_2$CF$_3$)$_2$]] (13). Yield: 34 mg (84%). mp 340−342 °C (dec). IR (CCl_4) 3064, 3036 (Ar), 2987 (CH_3), 2933 (CH_2), 2112 (CC), 1255, 1153, 1100, 1030 (all OTf) cm^{-1}. UV−vis (CH_2Cl_2) λ_{max} = 332 nm, $\epsilon = 6.63 \times 10^4$ L cm^{-1} mol^{-1}. $[\alpha]_D$ −184.2 ± 0.4° (*c* 0.012, CH_2Cl_2, 20 °C). CD (CH_2Cl_2), λ ($\Delta\epsilon$) [nm (L mol^{-1} cm^{-1})], 252 (−90.5), 276 (+80.1), 334 (−167.5), 346 (+4.9), 360 (−45.5). ^{1}H NMR (CD_2Cl_2) δ 8.01 (bd, 8H), 7.83−7.78 (m, 12H), 7.75−7.54 (m, 28H), 7.51−7.41 (m, 32H), 7.15 (t, 12H, *J* = 7.0 Hz), 7.08−6.96 (m, 16H), 6.42 (d, 4H, $^3J_{HH}$ = 8.8 Hz), 6.16 (bd, 8H), 3.82 (bs, 4H), 3.19 (bm, 4H), 2.58 (bm, 4H), 1.13 (s, 12H). ^{13}C {^{1}H} NMR (CD_2Cl_2) δ 150.3 ($C_{\alpha pyr}$), 140.5 (t), 139.5 ($C_{ipsopyr}$), 136.7 (s), 135.3 (s), 135.1 (s), 134.9, 133.6 (Pt−P−C_o), 132.9 (s), 132.8 (s), 132.6, 131.7 (Pt−P−C_p), 132.0 (s), 130.6 (s), 129.5, 129.0 (Pt−P−C_m), 129.3 ($C_{\beta pyr}$), 129.2 (s), 128.8 (s), 129.7 (s), 127.8 (s), 127.6 (s), 127.4 (t), 124.4 (t), 124.0 (q, CC−Pt$_\alpha$), 123.8 (s), 123.7 (s), 122.2 (s), 121.8 (q, $^1J_{C-F}$ = 321 Hz, OTf), 109.6 (s, OCO), 106.2 (t, CC−Pt$_\beta$, $^2J_{P-C}$ = 15.3 Hz), 77.2 (t, O*C*HCH$_2$, $^2J_{P-C}$ = 5.4 Hz), 31.2−30.8 (m, OCH*C*H$_2$), 26.9 (CH_3). ^{31}P {^{1}H} NMR (CD_2Cl_2) δ 3.2 (s, J_{Pt-P} = 3248 Hz), 2.1 (s, J_{Pt-P} = 2268 Hz). ^{19}F NMR (CD_2Cl_2) δ −76 (s, OTf). Anal. Calcd for $C_{182}H_{144}F_{12}N_4O_{16}P_8Pt_4S_4 \cdot 2H_2O$: C, 53.80; H, 3.67; N, 1.38; S, 3.16. Found: C, 53.44; H, 3.58; N, 1.42; S, 3.18.

General Procedure for the Preparation of Cyclobis[[*cis*-Pt(DIOP)(4-ethynylpyridine)$_2$][*cis*-Pd^{2+}(BINAP)($^-$OSO$_2$CF$_3$)$_2$]] (14−17). To a solution of 18.0 mg (0.020 mmol) of Pt(DIOP)(4-ethynylpyridine)$_2$ (**1**, **2**) in 3.0 mL of CH_2Cl_2 was added 20.9 mg (0.020 mmol) of [Pd(BINAP)(H_2O)][OTf]$_2$ (**6**, **7**), and the mixture was stirred under nitrogen at room temperature for 30 min. The solution was reduced in volume to ca. 0.5 mL. Diethyl ether was then added, and the precipitate was collected, washed with diethyl ether, and dried in vacuo.

Cyclobis[[*cis*-Pt(*R*(−)-DIOP)(4-ethynylpyridine)$_2$][*cis*-Pd^{2+}(*R*(+)-BINAP)($^-$OSO$_2$CF$_3$)$_2$]] (14). Yield: 35.4 mg (92%). mp 248−250 °C (dec). IR (CCl_4) 3063 (Ar), 2970 (CH_3), 2939 (CH_2), 2111 (CC), 1251, 1151, 1098, 1029 (all OTf) cm^{-1}. UV−vis (CH_2Cl_2) λ_{max} = 334 nm, $\epsilon = 6.77 \times 10^4$ L cm^{-1} mol^{-1}. $[\alpha]_D$ +301.7 ± 0.2° (*c* 0.015, CH_2Cl_2, 20 °C). CD (CH_2Cl_2), λ ($\Delta\epsilon$) [nm (L mol^{-1} cm^{-1})], 254 (74.6), 274 (−71.8), 287 (−50.5), 296 (−59.1), 331 (141.9), 348 (0.8), 374 (58.1). ^{1}H NMR (CD_2Cl_2) δ 7.96 (d, 8H, $^3J_{HH}$ = 4.6 Hz), 7.84−7.82 (m, 12H), 7.72−7.53 (m, 28H), 7.48−7.41 (m, 32H), 7.16 (t, 12H, *J* = 6.9 Hz), 7.08−6.99 (m, 16H), 6.41 (d, 4H, $^3J_{HH}$ = 8.5 Hz), 6.14 (d, 8H, $^3J_{HH}$ = 5.9 Hz), 3.83 (bs, 4H), 3.17 (bm, 4H), 2.58 (bm, 4H), 1.12 (s, 12H). ^{13}C {^{1}H} NMR (CD_2Cl_2) δ 150.1 ($C_{\alpha pyr}$), 140.5 (t), 138.9 ($C_{ipsopyr}$), 136.6 (s), 135.3 (t), 135.2 (s), 134.8, 133.7 (Pt−P−C_o), 132.7 (Pt−P−C_{ipso}), 133.0 (s), 132.9 (s), 132.5, 131.7 (Pt−P−C_p), 132.2 (s), 132.0 (s), 130.7 (s), 129.9 (s), 129.4, 129.0 (Pt−P−C_m), 129.3 ($C_{\beta pyr}$), 128.0 (s), 127.8 (s), 127.7 (s), 127.5 (t), 124.7 (q, CC−Pt$_\alpha$), 124.3 (t), 122.7 (s), 121.8 (q, $^1J_{C-F}$ = 321 Hz, OTf), 120.0 (s), 119.5 (s), 109.6 (s, OCO), 106.2 (t, CC−Pt$_\beta$, $^2J_{P-C}$ = 15.6 Hz), 77.2 (t, O*C*HCH$_2$, $^2J_{P-C}$ = 5.1 Hz), 31.1−30.9 (m, OCH*C*H$_2$), 26.9 (CH_3). ^{31}P {^{1}H} NMR

CD_2Cl_2) δ 27.4 (s), 2.1 (s, J_{Pt-P} = 2265 Hz). ^{19}F NMR (CD_2Cl_2) δ −76 (s, OTf). Anal. Calcd for $C_{182}H_{144}F_{12}N_4O_{16}P_8Pd_2Pt_2S_4 \cdot 4H_2O$: C, 55.73; H, 3.91; N, 1.43; S, 3.27. Found: C, 55.33; H, 3.79; N, 1.39; S, 3.11. FAB LRMS, *m/z* 1774.8 (M−2OTf).

Cyclobis[[*cis*-Pt(*R*(−)-DIOP)(4-ethynylpyridine)$_2$][*cis*-Pd^{2+}(*S*(−)-BINAP)($^-$OSO$_2$CF$_3$)$_2$]] (15). Yield: 35 mg (91%). mp 275 °C (dec). IR (CCl_4) 3056 (Ar), 2118 (CC), 1253, 1154, 1100, 1029 (all OTf) cm^{-1}. UV−vis (CH_2Cl_2) λ_{max} = 336 nm, $\epsilon = 6.68 \times 10^4$ L cm^{-1} mol^{-1}. $[\alpha]_D$ −311.1 ± 0.1° (*c* 0.015, CH_2Cl_2, 20 °C). CD (CH_2Cl_2), λ ($\Delta\epsilon$) [nm (L mol^{-1} cm^{-1})], 254 (−76.5), 278 (+61.0), 284 (+47.1), 294 (+52.1), 330 (−134.2), 347 (−21.4), 376 (−70.5). ^1H NMR (CD_2Cl_2) δ 7.95 (d, 8H, $^3J_{HH}$ = 4.4 Hz), 7.84−7.82 (m, 12H), 7.71−7.53 (m, 28H), 7.49−7.39 (m, 32H), 7.13 (t, 12H, *J* = 7.1 Hz), 7.08−6.95 (m, 16H), 6.41 (d, 4H, $^3J_{HH}$ = 8.8 Hz), 6.13 (d, 8H, $^3J_{HH}$ = 5.6 Hz), 3.92 (bs, 4H), 3.10 (bm, 4H), 2.62 (bm, 4H), 1.11 (s, 12H). ^{13}C {^1H} NMR (CD_2Cl_2) δ 150.1 ($C_{\alpha pyr}$), 140.5 (t), 138.9 ($C_{ipsopyr}$), 136.7 (s), 135.3 (t), 135.2 (s), 134.4, 133.7 (Pt−P−C_o), 133.3 (s), 132.4, 131.8 (Pt−P−C_p), 132.2 (s), 132.0 (s), 130.7 (s), 129.8 (s), 129.4 ($C_{\beta pyr}$), 129.3, 129.0 (Pt−P−C_m), 129.0 (s), 128.9 (s), 128.0 (s), 127.8 (s), 127.7 (s), 127.5 (t), 124.7 (q, CC−Pt$_\alpha$), 124.3 (t), 122.6 (s), 121.8 (q, $^1J_{C-F}$ = 321 Hz, OTf), 120.0 (s), 109.4 (s, OCO), 106.2 (t, CC−Pt$_\beta$, $^2J_{P-C}$ = 15.4 Hz), 77.1 (t, O*C*HCH$_2$, $^2J_{P-C}$ = 5.2 Hz), 31.5−31.2 (m, OCH*C*H$_2$), 26.9 (CH_3). ^{31}P {^1H} NMR (CD_2Cl_2) δ 27.4 (s), 1.9 (s, J_{Pt-P} = 2261 Hz). ^{19}F NMR (CD_2Cl_2) δ −76 (s, OTf). Anal. Calcd for $C_{182}H_{144}F_{12}N_4O_{16}P_8Pd_2Pt_2S_4 \cdot 4H_2O$: C, 55.73; H, 3.91; N, 1.43; S, 3.27. Found: C, 55.18; H, 3.74; N, 1.42; S, 3.39.

Cyclobis[[*cis*-Pt(*S*(+)-DIOP)(4-ethynylpyridine)$_2$][*cis*-Pd^{2+}(*R*(+)-BINAP)($^-$OSO$_2$CF$_3$)$_2$]] (16). Yield: 37 mg (96%). mp 268−270 °C (dec). IR (CCl_4) 3051 (Ar), 2971 (CH_3), 2933 (CH_2), 2113 (CC), 1254, 1152, 1099, 1029 (all OTf) cm^{-1}. UV−vis (CH_2Cl_2) λ_{max} = 334 nm, $\epsilon = 6.75 \times 10^4$ L cm^{-1} mol^{-1}. $[\alpha]_D$ +333.3 ± 0.1° (*c* 0.015, CH_2Cl_2, 20 °C). CD (CH_2Cl_2), λ ($\Delta\epsilon$) [nm (L mol^{-1} cm^{-1})], 253 (+77.8), 277 (−64.2), 284 (−48.8), 293 (−53.2), 330 (+137.3), 347 (+21.8), 375 (+72.25). ^1H NMR (CD_2Cl_2) δ 7.95 (d, 8H, $^3J_{HH}$ = 4.2 Hz), 7.84−7.82 (m, 12H), 7.72−7.53 (m, 28H), 7.49−7.37 (m, 32H), 7.13 (t, 12H, *J* = 6.8 Hz), 7.08−6.98 (m, 16H), 6.41 (d, 4H, $^3J_{HH}$ = 8.8 Hz), 6.13 (d, 8H, $^3J_{HH}$ = 6.1 Hz), 3.91 (bs, 4H), 3.10 (bm, 4H), 2.58 (bm, 4H), 1.11 (s, 12H). ^{13}C {^1H} NMR (CD_2Cl_2) δ 150.1 ($C_{\alpha pyr}$), 140.5 (t), 138.9 ($C_{ipsopyr}$), 137.0 (s), 135.3 (s), 135.2 (s), 134.5, 133.7 (Pt−P−C_o), 134.4 (s), 133.2 (s), 133.0 (s), 132.4, 131.8 (Pt−P−C_p), 132.2 (s), 132.0 (s), 130.7 (s), 129.9 (s), 129.4, 129.0 (Pt−P−C_m), 129.3 ($C_{\beta pyr}$), 128.9 (s), 128.5 (s), 128.0 (s), 127.7 (s), 127.2 (t), 124.7 (q, CC−Pt$_\alpha$), 124.3 (t), 121.8 (q, $^1J_{C-F}$ = 322 Hz, OTf), 120.0 (s), 109.4 (s, OCO), 106.1 (t, CC−Pt$_\beta$, $^2J_{P-C}$ = 15.4 Hz), 77.1 (t, O*C*HCH$_2$, $^2J_{P-C}$ = 5.7 Hz), 31.2−30.9 (m, OCH*C*H$_2$), 26.9 (CH_3). ^{31}P {^1H} NMR (CD_2Cl_2) δ 27.4 (s), 1.9 (s, J_{Pt-P} = 2261 Hz). ^{19}F NMR (CD_2Cl_2) δ −76 (s, OTf). Anal. Calcd for $C_{182}H_{144}F_{12}N_4O_{16}P_8Pd_2Pt_2S_4 \cdot 4H_2O$: C, 55.73; H, 3.91; N, 1.43; S, 3.27. Found: C, 55.43; H, 3.76; N, 1.43; S, 3.22.

Cyclobis[[*cis*-Pt(*S*(+)-DIOP)(4-ethynylpyridine)$_2$][*cis*-Pd^{2+}(*S*(−)-BINAP)($^-$OSO$_2$CF$_3$)$_2$]] (17). Yield: 37 mg (92%). mp 276−278 °C (dec). IR (CCl_4) 3052 (Ar), 2971 (CH_3), 2111 (CC), 1253, 1151, 1099, 1029 (all OTf) cm^{-1}. UV−vis (CH_2Cl_2) λ_{max} = 332 nm, $\epsilon = 6.65 \times 10^4$ L cm^{-1} mol^{-1}. $[\alpha]_D$ −322 ± 0.1° (*c* 0.015, CH_2Cl_2, 20 °C). CD (CH_2Cl_2), λ ($\Delta\epsilon$) [nm (L mol^{-1} cm^{-1})], 254 (−17.2), 274 (+60.5), 289 (+34.8), 297 (+49.4), 331 (−140.8), 348 (+7.3), 380 (−44.6). ^1H NMR (CD_2Cl_2) δ 7.96 (d, 8H, $^3J_{HH}$ = 4.2 Hz), 7.84−7.82 (m, 12H), 7.71−7.53 (m, 28H), 7.48−7.42 (m, 32H), 7.16 (t, 12H, *J* = 6.8 Hz), 7.08−7.01 (m, 16H), 6.41 (d, 4H, $^3J_{HH}$ = 8.6 Hz), 6.13 (d, 8H, $^3J_{HH}$ = 5.6 Hz), 3.83 (bs, 4H), 3.16 (bm, 4H), 2.56 (bm, 4H), 1.12 (s, 12H). ^{13}C {^1H} NMR (CD_2Cl_2) δ 150.1 ($C_{\alpha pyr}$), 140.5 (t), 138.9 ($C_{ipsopyr}$), 136.7 (s), 135.3 (s), 135.2 (s), 134.8, 133.7 (Pt−P−C_o), 133.0 (s), 132.9 (s), 132.5, 131.7 (Pt−P−C_p), 132.2 (s), 132.0 (s), 130.7 (s), 129.8 (s), 129.4, 129.0 (Pt−P−C_m), 129.3 ($C_{\beta pyr}$), 128.9 (s), 128.0 (s), 127.8 (s), 127.7 (s), 127.5 (t), 124.7 (q, CC−Pt$_\alpha$), 125.1 (s), 124.3 (t), 121.8 (q, $^1J_{C-F}$ = 322 Hz, OTf), 120.0 (s), 109.6 (s, OCO), 106.2 (t, CC−Pt$_\beta$, $^2J_{P-C}$ = 15.4 Hz), 77.2 (t, O*C*HCH$_2$, $^2J_{P-C}$ = 5.1 Hz), 31.2−30.8 (m, OCH*C*H$_2$), 26.9 (CH_3). ^{31}P {^1H} NMR (CD_2Cl_2) δ 27.5 (s), 2.1 (s, J_{Pt-P} = 2264 Hz). ^{19}F NMR (CD_2Cl_2) δ −75 (s, OTf). Anal. Calcd for $C_{182}H_{144}F_{12}N_4O_{16}P_8Pd_2Pt_2S_4 \cdot 4H_2O$: C, 55.73; H, 3.91; N, 1.43; S, 3.27. Found: C, 55.49; H, 3.76; N, 1.47; S, 3.51.

Procedure for the Preparation of Cyclobis[[*cis*-Pt(*R*(+)-DIOP)(4-ethynyl-pyridine)$_2$][Pd^{2+}(PEt$_3$)$_2$($^-$OSO$_2$CF$_3$)$_2$]]·2AgOTf (18). To a solution of square **8** (34.3 mg, 0.011 mmol, 750 μL of acetone-d_6) in a 5 mm NMR tube, 5.7 mg (0.022 mmol) of silver triflate was added at room temperature, and the mixture was shaken for 5 min and monitored by ^{31}P {^1H} NMR (reaction complete in 10 min). The solution was transferred to a 2 mL vial, followed by solvent removal with a stream of dry nitrogen, and dried in vacuo.

Cyclobis[[*cis*-Pt(*R*(+)-DIOP)(4-ethynylpyridine)$_2$][*cis*-Pd^{2+}(PEt$_3$)$_2$($^-$OSO$_2$CF$_3$)$_2$]]·2AgOTf (18). Yield: 39.9 mg (99%). mp 175−180 °C (dec). IR (CCl_4) 3056 (Ar), 2981 (CH_3), 2940 (CH_2), 2087 (CC), 1255, 1158, 1029 (OTf) cm^{-1}. UV−vis (CH_2Cl_2) λ_{max} = 311 nm, $\epsilon = 6.6 \times 10^4$ L cm^{-1} mol^{-1}. CD (CH_2Cl_2), λ ($\Delta\epsilon$) [nm (L mol^{-1} cm^{-1})], 276 (−5.3), 282 (−2.3), 336 (−15.5), 353 (+3.32). ^1H NMR (acetone-d_6) δ 8.80 (d, 4H, $^3J_{HH}$ = 4.8 Hz), 7.80−7.65 (m, 8H), 7.55−7.38 (m, 12H), 6.97, 6.88 (d, 4H), 4.16 (s, br, 2H), 3.39 (m, 2H), 2.90 (m, 2H), 1.94 (m, 24H), 1.33 (m, 36H), 1.19 (s, 12H). ^{13}C {^1H} NMR (acetone-d_6) δ 150.5 ($C_{\alpha pyr}$), 137.5 ($C_{ipsopyr}$), 134.8, 133.8 (Pt−P−C_o), 131.9, 130.5(Pt−P−C_{ipso}), 132.8, 132.1(Pt−P−C_p), 129.8, 129.7 (Pt−P−C_m), 129.1 ($C_{\beta pyr}$), 125.3 (q, CC−Pt$_\alpha$), 122.2 (q, $^1J_{C-F}$ = 321 Hz, OTf), 109.6 (s, OCO), 108.7 (t, CC−Pt$_\beta$, $^2J_{P-C}$ = 16.3 Hz), 77.4 (t, O*C*HCH$_2$, $^2J_{P-C}$ = 5.3 Hz), 27.0 (CH_3), 16.5 (m, Pt−P-*C*H$_2$CH$_3$), 8.4 (bs, Pt−P−CH$_2$*C*H$_3$). ^{31}P {^1H} NMR (acetone-d_6) δ 31.8 (s), 1.8 (s, J_{Pt-P} = 2398 Hz). ^{19}F NMR (acetone-d_6) δ −75 (s, OTf).

General Procedure for the Preparation of the AgOTf Complexes (19−22). To a solution of square (0.01 mmol; 40.3 mg of **10** and **11**, 38.5 mg of **16** and **17**, respectively) dissolved in 750 μL of CD_2Cl_2 in a 5 mm NMR tube at 25 °C was added 2 equiv (5.1 mg, 0.02 mmol) of AgOTf in one portion, and then the reaction mixture was shaken. The solvent was removed under a stream of nitrogen, followed by drying in vacuo.

Cyclobis[[*cis*-Pt(*R*(−)-DIOP)(4-ethynylpyridine)$_2$][*cis*-Pt^{2+}(*R*(+)-BINAP)($^-$OSO$_2$CF$_3$)$_2$]]·2AgOTf (19). Yield: 44.5 mg (98%). mp 216−218 °C (dec). IR (CCl_4) 3056, 3029 (Ar), 2989 (CH_3), 2932 (CH_2), 2069 (CC), 1258, 1171, 1101, 1026 (all OTf) cm^{-1}. UV−vis (CH_2Cl_2) λ_{max} = 298 nm, $\epsilon = 8.7 \times 10^4$ L cm^{-1} mol^{-1}. CD (CH_2Cl_2), λ ($\Delta\epsilon$) [nm (L mol^{-1} cm^{-1})], 252 (+32.6), 275 (−43.4), 318 (+96.5), 335 (+13.9), 359 (+42.0). ^1H NMR (CD_2Cl_2) δ 8.21 (bd, 8H), 7.84−7.75 (m, 12H), 7.73−7.55 (m, 28H), 7.48−7.15 (m, 32H), 7.08 (t, 12H, *J* = 7.3 Hz), 7.03−6.78 (m, 16H), 6.41 (d, 4H, $^3J_{HH}$ = 8.7 Hz), 6.13 (bd, 8H), 4.01 (bs, 4H), 3.15 (bm, 4H), 2.77 (bm, 4H), 1.16 (s, 12H). ^{13}C {^1H} NMR (CD_2Cl_2) δ 151.7 ($C_{\alpha pyr}$), 140.7 (t), 138.3 ($C_{ipsopyr}$), 136.8 (s), 135.3 (s), 135.1 (s), 135.0, 133.6 (Pt−P−C_o), 134.5 (s), 133.9 (s), 133.0 (s), 132.9 (s), 132.6, 129.9 (Pt−P−C_p), 132.2 (s), 130.7 (s), 130.1 (t), 130.0 (s), 129.6, 128.8 (Pt−P−C_m), 129.3 ($C_{\beta pyr}$), 127.7 (s), 127.6 (s), 127.3 (t), 125.7 (q, CC−Pt$_\alpha$), 124.0 (s), 123.5 (s), 123.0 (s), 120.8 (q, $^1J_{C-F}$ = 320 Hz, OTf), 110.0 (s, OCO), 107.6 (t, CC−Pt$_\beta$, $^2J_{P-C}$ = 15.9 Hz), 76.4 (t, O*C*HCH$_2$, $^2J_{P-C}$ = 4.8 Hz), 30.0−29.5 (m, OCH*C*H$_2$), 26.8 (CH_3). ^{31}P {^1H} NMR (CD_2Cl_2) δ 2.1 (s, J_{Pt-P} = 3277 Hz), −1.9 (s, J_{Pt-P} = 2490 Hz). ^{19}F NMR (CD_2Cl_2) δ −74 (s, OTf). Anal. Calcd for $C_{184}H_{144}Ag_2F_{18}N_4O_{22}P_8Pt_4S_6 \cdot 4H_2O$: C, 47.90; H, 3.32; N, 1.21; S, 4.17. Found: C, 47.88; H, 3.31; N, 1.19; S, 4.10.

Cyclobis[[*cis*-Pt(*R*(−)-DIOP)(4-ethynylpyridine)$_2$][*cis*-Pt^{2+}(*S*(−)-BINAP)($^-$OSO$_2$CF$_3$)$_2$]]·2AgOTf (20). Yield: 44.6 mg (98%). mp 248−250 °C (dec). IR (CCl_4) 3055, 3032 (Ar), 2990 (CH_3), 2932 (CH_2), 2070 (CC), 1284, 1163, 1101, 1023 (all OTf) cm^{-1}. UV−vis (CH_2Cl_2) λ_{max} = 298 nm, $\epsilon = 10.1 \times 10^4$ L cm^{-1} mol^{-1}. CD (CH_2Cl_2), λ ($\Delta\epsilon$) [nm (L mol^{-1} cm^{-1})], 252 (−52.6), 275 (+51.2), 321 (−108.3), 336 (−12.8), 358 (−48.5). ^1H NMR (CD_2Cl_2) δ 8.17 (bd, 8H), 7.83−7.72 (m, 12H), 7.70−7.52 (m, 28H), 7.49−7.17 (m, 32H), 7.06 (t, 12H, *J* = 6.8 Hz), 7.03−7.01 (m, 16H), 6.41 (d, 4H, $^3J_{HH}$ = 8.8 Hz), 6.36 (bd, 8H), 4.04 (bs, 4H), 3.14 (bm, 4H), 2.78 (bm, 4H), 1.14 (s, 12H). ^{13}C {^1H} NMR (CD_2Cl_2) δ 150.0 ($C_{\alpha pyr}$), 140.6 (t), 137.5 ($C_{ipsopyr}$), 136.8 (s), 135.4 (s), 135.1 (s), 134.6, 133.5 (Pt−P−C_o), 133.1 (s), 132.7 (s), 132.3, 131.8 (Pt−P−C_p), 132.2 (s), 131.9 (s), 130.4 (s), 130.2 (s), 130.0 (s), 129.5, 128.9 (Pt−P−C_m), 129.3 ($C_{\beta pyr}$), 129.0 (s), 127.8 (s), 127.7 (s), 127.3 (t), 125.1 (q, CC−Pt$_\alpha$), 124.0 (s), 123.3 (s), 122.1 (s), 120.9 (q, $^1J_{C-F}$ = 322 Hz, OTf), 109.9 (s, OCO), 107.7 (t, CC−Pt$_\beta$, $^2J_{P-C}$ = 15.7 Hz), 76.5 (t, O*C*HCH$_2$, $^2J_{P-C}$ = 5.3 Hz), 30.2−29.8 (m, OCH*C*H$_2$), 26.8 (CH_3). ^{31}P {^1H} NMR (CD_2Cl_2) δ 2.2 (s, J_{Pt-P} = 3280 Hz), −2.2 (s, J_{Pt-P} = 2489 Hz). ^{19}F NMR (CD_2Cl_2) δ −75 (s, OTf).

Anal. Calcd for $C_{184}H_{144}Ag_2F_{18}N_4O_{22}P_8Pt_4S_6 \cdot 4H_2O$: C, 47.90; H, 3.32; N, 1.21; S, 4.17. Found: C, 47.85; H, 3.31; N, 1.22; S, 4.13.

Cyclobis[[*cis*-Pt(*S*(+)-DIOP)(4-ethynylpyridine)$_2$][*cis*-Pd^{2+}(*R*(+)-BINAP)($^-$OSO$_2$CF$_3$)$_2$]]·2AgOTf (21). Yield: 41.5 mg (95%). mp 218−220 °C (dec). IR (CCl_4) 3054, 3031 (Ar), 2999 (CH_3), 2933 (CH_2), 2072 (CC), 1282, 1162, 1100, 1022 (all OTf) cm^{-1}. UV−vis (CH_2Cl_2) $\lambda_{max} = 296$ nm, $\epsilon = 7.7 \times 10^4$ L cm^{-1} mol^{-1}. CD (CH_2Cl_2), λ ($\Delta\epsilon$) [nm (L mol^{-1} cm^{-1})], 250 (+31.3), 277 (−32.1), 320 (+44.5), 352 (−1.6), 392 (+18.0). ^{1}H NMR (CD_2Cl_2) δ 8.09 (d, 8H, $^3J_{HH}$ = 4.6 Hz), 7.88−7.85 (m, 12H), 7.74−7.53 (m, 28H), 7.51−7.19 (m, 32H), 7.07 (t, 12H, J = 6.8 Hz), 7.05−7.10 (m, 16H), 6.42 (d, 4H, $^3J_{HH}$ = 19.7 Hz), 6.40 (d, 8H, $^3J_{HH}$ = 5.8 Hz), 4.01 (bs, 4H), 3.17 (bm, 4H), 2.79 (bm, 4H), 1.16 (s, 12H). ^{13}C {^{1}H} NMR (CD_2Cl_2) δ 150.2 ($C_{\alpha pyr}$), 140.5 (t), 138.8 ($C_{ipsopyr}$), 135.4 (s), 135.1 (s), 135.0, 133.6 (Pt−P−C_o), 134.6 (s), 133.7 (t), 133.0 (s), 132.9 (s), 132.6, 132.2 (Pt−P−C_p), 130.7 (t), 130.0 (t), 129.5, 128.8 (Pt−P−C_m), 129.3 ($C_{\beta pyr}$), 129.2 (s), 128.4 (s), 127.7 (s), 127.5 (s), 127.3 (t), 125.4 (q, CC−Pt$_\alpha$), 124.1 (s), 124.0 (s), 123.5 (s), 122.9 (s), 120.7 (q, $^1J_{C-F}$ = 319 Hz, OTf), 110.0 (s, OCO), 108.9 (t, CC−Pt$_\beta$, $^2J_{P-C}$ = 15.8 Hz), 76.4 (t, O*C*HCH$_2$, $^2J_{P-C}$ = 5.4 Hz), 29.8−29.3 (m, OCH*C*H$_2$), 26.7 (CH_3). ^{31}P {^{1}H} NMR (CD_2Cl_2) δ 27.3 (s), −2.1 (s, J_{Pt-P} = 2486 Hz). ^{19}F NMR (CD_2Cl_2) δ −75 (s, OTf). Anal. Calcd for $C_{184}H_{144}Ag_2F_{18}N_4O_{22}P_8Pd_2Pt_2S_6 \cdot 4H_2O$: C, 49.82; H, 3.45; N, 1.26; S, 4.34. Found: C, 49.63; H, 3.46; N, 1.21; S, 4.28.

Cyclobis[[*cis*-Pt(*S*(+)-DIOP)(4-ethynylpyridine)$_2$][*cis*-Pd^{2+}(*S*(−)-BINAP)($^-$OSO$_2$CF$_3$)$_2$]]·2AgOTf (22). Yield: 42.2 mg (97%). mp 220−222 °C (dec). IR (CCl_4) 3057, 3026 (Ar), 2995 (CH_3), 2932 (CH_2), 2070 (CC), 1285, 1168, 1101, 1021 (all OTf) cm^{-1}. UV−vis (CH_2Cl_2) $\lambda_{max} = 294$ nm, $\epsilon = 9.42 \times 10^4$ L cm^{-1} mol^{-1}. CD (CH_2Cl_2), λ ($\Delta\epsilon$) [nm (L mol^{-1} cm^{-1})], 250 (−35.1), 276 (+34.2), 319 (−43.8), 333 (−49.5), 353 (+2.4), 390 (−19.51). ^{1}H NMR (CD_2Cl_2) δ 8.10 (d, 8H, $^3J_{HH}$ = 4.8 Hz), 7.86−7.85 (m, 12H), 7.74−7.56 (m, 28H), 7.51−7.13 (m, 32H), 7.07 (t, 12H, J = 7.1 Hz), 7.05−7.10 (m, 16H), 6.41 (d, 4H, $^3J_{HH}$ = 18.7 Hz), 6.39 (d, 8H, $^3J_{HH}$ = 6.2 Hz), 3.99 (bs, 4H), 3.22 (bm, 4H), 2.75 (bm, 4H), 1.19 (s, 12H). ^{13}C {^{1}H} NMR (CD_2Cl_2) δ 150.4 ($C_{\alpha pyr}$), 140.6 (t), 137.9 ($C_{ipsopyr}$), 135.4 (s), 134.9, 133.7 (Pt−P−C_o), 133.0 (s), 132.9 (s), 132.6, 131.7 (Pt−P−C_p), 132.4 (s), 130.8 (s), 130.6 (s), 129.9, 129.0 (Pt−P−C_m), 129.7 (s), 129.4 ($C_{\beta pyr}$), 129.2 (s), 128.9 (s), 128.4 (s), 127.9 (s), 127.9 (s), 127.7 (s), 127.2 (t), 125.3 (q, CC−Pt$_\alpha$), 124.9 (t), 123.9 (s), 120.7 (q, $^1J_{C-F}$ = 322 Hz, OTf), 119.7 (s), 110.0 (s, OCO), 109.2 (t, CC−Pt$_\beta$, $^2J_{P-C}$ = 15.3 Hz), 76.4 (t, O*C*HCH$_2$, $^2J_{P-C}$ = 5.3 Hz), 29.7−29.2 (m, OCH*C*H$_2$), 26.8 (CH_3). ^{31}P {^{1}H} NMR (CD_2Cl_2) δ 27.2 (s), −1.8 (s, J_{Pt-P} = 2488 Hz). ^{19}F NMR (CD_2Cl_2) δ −74 (s, OTf). Anal. Calcd for $C_{184}H_{144}Ag_2F_{18}N_4O_{22}P_8Pd_2Pt_2S_6 \cdot 4H_2O$: C, 49.82; H, 3.45; N, 1.26; S, 4.34. Found: C, 49.66; H, 3.37; N, 1.28; S, 4.31.

General Procedure for the Preparation of Cyclobis[[*cis*-Pt(DIOP)(4-ethynylpyridine)$_2$][Pd^{2+}(PEt$_3$)$_2$($^-$OSO$_2$CF$_3$)$_2$]]·2AgOTf·guest (23, 24). To a solution of silver complex **18** (40.0 mg, 0.011 mmol, 750 μL of acetone-d_6) in a 5 mm NMR tube, 0.011 mmol of tetramethylpyrazine or phenazine was added at room temperature, and the mixture was shaken for 5 min and monitored by ^{31}P {^{1}H} NMR (reaction complete in 10 min). The solution was transferred to a 2 mL vial, followed by solvent removal with a stream of dry nitrogen, and dried in vacuo.

Cyclobis[[*cis*-Pt(*R*(+)-DIOP)(4-ethynylpyridine)$_2$][*cis*-Pd^{2+}(PEt$_3$)$_2$-($^-$OSO$_2$CF$_3$)$_2$]]·2AgOTf·tetramethylpyrazine (23). Yield: 40.7 mg (99%). mp 195−200 °C (dec). IR (CCl_4) 3061 (Ar), 2980 (CH_3), 2939 (CH_2), 2093 (CC), 1253, 1156, 1029 (OTf) cm^{-1}. UV−vis (CH_2Cl_2) $\lambda_{max} = 300$ nm, $\epsilon = 9.3 \times 10^4$ L cm^{-1} mol^{-1}. CD (CH_2Cl_2), λ ($\Delta\epsilon$) [nm (L mol^{-1} cm^{-1})], 269 (−5.3), 275 (−5.7), 291 (−3.8), 317 (−3.6), 336 (−7.3), 353 (+1.0). ^{1}H NMR (acetone-d_6) δ 8.76 (d, 4H, $^3J_{HH}$ = 5.1 Hz), 7.80−7.65 (m, 8H), 7.55−7.38 (m, 12H), 7.04, 6.89 (d, 4H), 4.22 (s, br, 2H), 3.39 (m, 2H), 2.94 (m, 2H), 2.41 (tmp, s, 12H) 1.87 (m, 24H), 1.30 (m, 36H), 1.22 (s, 12H). ^{13}C {^{1}H} NMR (acetone-d_6) δ 150.9 ($C_{\alpha pyr}$), 150.2 (tmp), 137.4 ($C_{ipsopyr}$), 134.9, 133.8 (Pt−P−C_o), 131.9, 130.7 (Pt−P−C_{ipso}), 132.7, 132.1 (Pt−P−C_p), 129.7 (Pt−P−C_m), 128.7 ($C_{\beta pyr}$), 122.2 (q, $^1J_{C-F}$ = 321 Hz, OTf), 109.6 (s, OCO), 109.1 (t, CC−Pt$_\beta$, $^2J_{P-C}$ = 25.0 Hz), 77.4 (t, O*C*HCH$_2$, $^2J_{P-C}$ = 5.2 Hz), 27.0 (CH_3), 23.3 (s, tmp), 16.4 (m, Pd−P-*C*H$_2$CH$_3$), 8.4 (bs, Pd−P−CH$_2$*C*H$_3$). ^{31}P {^{1}H} NMR (acetone-d_6) δ 31.4 (s), 1.6 (s, J_{Pt-P} = 2392 Hz). ^{19}F NMR (acetone-d_6) δ −75 (s, OTf). Anal. Calcd for $C_{128}H_{152}F_{18}N_6O_{22}P_8Pt_2Pd_2S_6 \cdot 3H_2O$: C, 43.12; H, 4.47; N, 2.36; S, 5.39. Found: C, 43.25; H, 4.52; N, 2.10; S, 4.91.

Cyclobis[[*cis*-Pt(*R*(+)-DIOP)(4-ethynylpyridine)$_2$][*cis*-Pd^{2+}(PEt$_3$)$_2$-($^-$OSO$_2$CF$_3$)$_2$]]·2AgOTf·phenazine (24). Yield: 41.5 mg (99%). mp 180−185 °C (dec). IR (CCl_4) 3058 (Ar), 2980 (CH_3), 2940 (CH_2), 2097 (CC), 1251, 1155, 1027 (OTf) cm^{-1}. UV−vis (CH_2Cl_2) λ_{max} = 310 nm, $\epsilon = 8.6 \times 10^4$ L cm^{-1} mol^{-1}. CD (CH_2Cl_2), λ ($\Delta\epsilon$) [nm (L mol^{-1} cm^{-1})], 269 (−5.0), 275 (−5.8), 321 (−5.0), 336 (−5.9). ^{1}H NMR (acetone-d_6) δ 8.52 (d, 4H), 8.49 (phenazine-β, m, 4H), 7.98 (phenazine-γ, m, 4H, $^3J_{HH}$ = 10.1 Hz), 7.82−7.65 (m, 8H), 7.55−7.38 (m, 12H), 6.98, 6.79 (d, 4H), 4.26 (s, br, 2H), 3.41 (m, 2H), 2.99 (m, 2H), 1.83 (m, 24H), 1.26 (m, 36H), 1.24 (s, 12H). ^{13}C {^{1}H} NMR (acetone-d_6) δ 150.4 ($C_{\alpha pyr}$), 143.0 (phenazine-α), 137.1 ($C_{ipsopyr}$), 134.9, 133.9 (Pt−P−C_o), 133.8 (phenazine-β), 131.8, 130.7 (Pt−P−C_{ipso}), 132.7, 132.1(Pt−P−C_p), 129.8 (phenazine-γ), 129.7 (Pt−P−C_m), 128.6 ($C_{\beta pyr}$), 122.2 (q, $^1J_{C-F}$ = 321 Hz, OTf), 109.8 (m, CC−Pt$_\beta$), 109.7 (s, OCO), 77.4 (t, O*C*HCH$_2$P, $^2J_{P-C}$ = 5.4 Hz), 27.0 (CH_3) 16.4 (m, Pd−P−*C*H$_2$CH$_3$), 8.4 (bs, Pd−P−CH$_2$*C*H$_3$). ^{31}P {^{1}H} NMR (acetone-d_6) δ 31.4 (s), 1.7 (s, J_{Pt-P} = 2409 Hz). ^{19}F NMR (acetone-d_6) δ −75 (s, OTf). Anal. Calcd for $C_{132}H_{148}F_{18}N_6O_{22}P_8Pt_2Pd_2S_6 \cdot 5H_2O$: C, 43.49; H, 4.37; N, 2.31; S, 5.28. Found: C, 43.20; H, 4.52; N, 2.12; S, 4.91.

General Procedure for the Preparation of Cyclobis[[*cis*-Pt(DIOP)(4-ethynylpyridine)$_2$][*cis*-Pt^{2+}(BINAP)($^-$OSO$_2$CF$_3$)$_2$]]·2AgOTf·guest (25−27) and Cyclobis[[*cis*-Pt(DIOP)(4-ethynylpyridine)$_2$][*cis*-Pd^{2+}(BINAP)($^-$OSO$_2$CF$_3$)$_2$]]·2AgOTf·guest (28, 29). To a solution of silver triflate complexes **19**−**22** (36.3 mg of **19** and **20**, 34.9 mg of **21** and **22**) dissolved in 750 μL of CD_2Cl_2 in a 5 mm NMR tube was added 1 equiv of tetramethylpyrazine (1.09 mg, 0.008 mmol) or phenazine (1.44 mg, 0.008 mmol) in one portion at 25 °C, and the reaction mixture was shaken. The solvent was removed under a stream of nitrogen, followed by solvent removal in vacuo.

Cyclobis[[*cis*-Pt(*R*(−)-DIOP)(4-ethynylpyridine)$_2$][*cis*-Pt^{2+}(*R*(+)-BINAP)($^-$OSO$_2$CF$_3$)$_2$]]·2AgOTf·tetramethylpyrazine (25). Yield: 37.4 mg (100%). mp 227−229 °C (dec). IR (CCl_4) 3057, 3024 (Ar), 2988 (CH_3), 2935 (CH_2), 2079 (CC), 1259, 1171, 1025, (all OTf) cm^{-1}. UV−vis (CH_2Cl_2) λ_{max} = 296 nm, $\epsilon = 11.3 \times 10^4$ L cm^{-1} mol^{-1}. CD (CH_2Cl_2), λ ($\Delta\epsilon$) [nm (L mol^{-1} cm^{-1})], 252 (+14.4), 274 (−26.5), 319 (+85.5), 334 (+10.3), 359 (+34.6). ^{1}H NMR (CD_2Cl_2) δ 8.17 (bd, 8H), 7.94−7.76 (m, 12H), 7.72−7.50 (m, 28H), 7.47−7.13 (m, 32H), 7.08 (t, 12H, J = 7.2 Hz), 7.03−6.85 (m, 16H), 6.41 (d, 4H, $^3J_{HH}$ = 8.8 Hz), 6.05 (bd, 8H), 3.93 (bs, 4H), 3.19 (bm, 4H), 2.83 (bm, 4H), 2.34 (tmp, s, 12H), 1.17 (s, 12H). ^{13}C {^{1}H} NMR (CD_2Cl_2) δ 150.9 ($C_{\alpha pyr}$), 150.2 (tmp), 140.5 (t), 138.5 ($C_{ipsopyr}$), 135.3 (s), 135.1 (s), 134.5, 133.6 (Pt−P−C_o), 133.2 (s), 132.9 (s), 132.6, 129.5 (Pt−P−C_p), 132.4 (s), 132.2 (s), 130.7 (s), 130.0 (t), 129.7 (s), 129.5, 128.8 (Pt−P−C_m), 129.4 (s), 129.3 (s), 128.8 (s), 128.7 ($C_{\beta pyr}$), 127.6 (s), 127.4 (s), 125.8 (s), 123.7 (q, CC−Pt$_\alpha$), 123.3 (s), 121.2 (q, $^1J_{C-F}$ = 320 Hz, OTf), 119.7 (s), 110.0 (s, OCO), 112.2 (t, CC−Pt$_\beta$, $^2J_{P-C}$ = 15.2 Hz), 76.7 (t, O*C*HCH$_2$, $^2J_{P-C}$ = 5.0 Hz), 30.6−30.2 (m, OCH*C*H$_2$), 26.9 (CH_3), 21.7 (s, tmp). ^{31}P {^{1}H} NMR (CD_2Cl_2) δ 2.2 (s, J_{Pt-P} = 3284 Hz), −0.5 (s, J_{Pt-P} = 2457 Hz). ^{19}F NMR (CD_2Cl_2) δ −75 (s, OTf). Anal. Calcd for $C_{192}H_{156}Ag_2F_{18}N_6O_{22}P_8Pt_4S_6 \cdot 4H_2O$: C, 48.55; H, 3.48; N, 1.77; S, 4.05. Found: C, 48.53; H, 3.51; N, 1.66; S, 3.94.

Cyclobis[[*cis*-Pt(*R*(−)-DIOP)(4-ethynylpyridine)$_2$][*cis*-Pt^{2+}(*R*(+)-BINAP)($^-$OSO$_2$CF$_3$)$_2$]]·2AgOTf·phenazine (26). Yield: 37.7 mg (100%). mp 228−230 °C (dec). IR (CCl_4) 3058 (Ar), 2989 (CH_3), 2933 (CH_2), 2071 (CC), 1252, 1166, 1029, (all OTf) cm^{-1}. UV−vis (CH_2Cl_2) λ_{max} = 298 nm, $\epsilon = 10.0 \times 10^4$ L cm^{-1} mol^{-1}. CD (CH_2Cl_2), λ ($\Delta\epsilon$) [nm (L mol^{-1} cm^{-1})], 252 (+7.1), 274 (−61.8), 319 (+87.1), 334 (+9.8), 356 (+30.7), 388 (−16.7), 434 (11.6). ^{1}H NMR (CD_2Cl_2) δ 8.39 (phenazine-β, m, 4H), 8.18 (d, 8H, $^3J_{HH}$ = 4.6 Hz), 8.00 (phenazine-γ), 7.85−7.83 (m, 12H), 7.78−7.54 (m, 28H), 7.51−7.14 (m, 32H), 7.06 (t, 12H, J = 7.1 Hz), 7.03−7.01 (m, 16H), 6.50 (d, 4H, $^3J_{HH}$ = 18.8 Hz), 6.41 (d, 8H, $^3J_{HH}$ = 5.7 Hz), 3.86 (bs, 4H), 3.32 (bm, 4H), 2.70 (bm, 4H), 1.19 (s, 12H). ^{13}C {^{1}H} NMR (CD_2Cl_2) δ 150.9 ($C_{\alpha pyr}$), 144.1 (phenazine-α), 140.5 (t), 138.5 ($C_{ipsopyr}$), 135.2 (s), 135.1 (s), 134.5, 133.6 (Pt−P−C_o), 134.2 (s), 133.5 (phenazine-β), 133.2 (s), 132.4, 129.4 (Pt−P−C_p), 132.2 (s), 130.7 (s), 130.6 (s), 130.4 (s), 130.3 (s), 129.8 (s), 129.5 (phenazine-γ), 129.5, 128.8 (Pt−P−C_m), 129.3 (s), 128.7 ($C_{\beta pyr}$), 127.9 (s), 127.6 (s), 127.3 (s), 125.7 (t), 123.8 (q,

CC−Pt_α), 123.4 (s), 121.0 (q, $^1J_{C-F}$ = 320 Hz, OTf), 119.2 (s), 112.0 (t, CC−Pt_β, $^2J_{P-C}$ = 15.0 Hz), 110.2 (s, OCO), 76.6 (t, O*C*HCH$_2$, $^2J_{P-C}$ = 4.9 Hz), 31.0−30.5 (m, OCH*C*H$_2$), 26.9 (CH$_3$). ^{31}P {^{1}H} NMR (CD_2Cl_2) δ 2.1 (s, J_{Pt-P} = 3265 Hz), −0.9 (s, J_{Pt-P} = 2481 Hz). ^{19}F NMR (CD_2Cl_2) δ −75 (s, OTf). Anal. Calcd for $C_{196}H_{152}Ag_2F_{18}N_6O_{22}P_8Pt_4S_6\cdot 4H_2O$: C, 49.11; H, 3.36; N, 1.75; S, 4.01. Found: C, 48.91; H, 3.28; N, 1.62; S, 4.01.

Cyclobis[[*cis*-Pt(*R*(−)-DIOP)(4-ethynylpyridine)$_2$][*cis*-Pt^{2+}(*S*(−)-BINAP)($^-$OSO$_2$CF$_3$)$_2$]]·2AgOTf·phenazine (27). Yield: 37.7 mg (100%). mp 226−228 °C (dec). IR (CCl_4) 3057 (Ar), 2988 (CH$_3$), 2934 (CH$_2$), 2082 (CC), 1287, 1166, 1029, (all OTf) cm^{-1}. UV−vis (CH_2Cl_2) λ_{max} = 298 nm, $\epsilon = 8.7 \times 10^4$ L cm^{-1} mol^{-1}. CD (CH_2Cl_2), λ ($\Delta\epsilon$) [nm (L mol^{-1} cm^{-1})], 252 (+14.4), 274 (−26.5), 319 (+85.5), 334 (+10.3), 359 (+34.6). ^{1}H NMR (CD_2Cl_2) δ 8.35 (phenazine-β, m, 4H), 8.14 (d, 8H, $^3J_{HH}$ = 4.7 Hz), 8.01 (phenazine-γ, m, 4H), 7.86−7.83 (m, 12H), 7.72−7.55 (m, 28H), 7.52−7.14 (m, 32H), 7.05 (t, 12H, J = 7.1 Hz), 7.03−7.00 (m, 16H), 6.41 (d, 4H, $^3J_{HH}$ = 18.5 Hz), 6.31 (d, 8H, $^3J_{HH}$ = 6.5 Hz), 4.09 (bs, 4H), 3.02 (bm, 4H), 2.81 (bm, 4H), 1.10 (s, 12H). ^{13}C {^{1}H} NMR (CD_2Cl_2) δ 151.0 ($C_{\alpha pyr}$), 144.8 (phenazine-α), 140.6 (t), 138.5 ($C_{ipsopyr}$), 135.2 (s), 135.1 (s), 134.6, 133.7 (Pt−P−C_o), 133.6 (phenazine-β), 132.9 (s), 132.8 (s), 132.8, 132.0 (Pt−P−C_p), 132.6 (s), 132.5 (s), 132.4 (s), 132.2 (s), 129.9 (s), 129.8 (s), 129.4 (s), 129.3 (s), 129.2 (s), 129.5 (phenazine-γ), 129.4, 128.9 (Pt−P−C_m), 128.8 (s), 128.7 ($C_{\beta pyr}$), 127.6 (s), 127.4 (s), 125.8 (s), 124.1 (q, CC−Pt_α), 120.9 (q, $^1J_{C-F}$ = 321 Hz, OTf), 111.6 (t, CC−Pt_β, $^2J_{P-C}$ = 15.1 Hz), 109.7 (s, OCO), 76.5 (t, O*C*HCH$_2$, $^2J_{P-C}$ = 5.0 Hz), 30.2−29.8 (m, OCH*C*H$_2$), 26.7 (CH$_3$). ^{31}P {^{1}H} NMR (CD_2Cl_2) δ 2.2 (s, J_{Pt-P} = 3291 Hz), −2.3 (s, J_{Pt-P} = 2470 Hz). ^{19}F NMR (CD_2Cl_2) δ −75 (s, OTf). Anal. Calcd for $C_{196}H_{152}Ag_2F_{18}N_6O_{22}P_8Pt_4S_6\cdot 4H_2O$: C, 49.11; H, 3.36; N, 1.75; S, 4.01. Found: C, 48.92; H, 3.30; N, 1.83; S, 3.95.

Cyclobis[[*cis*-Pt(*S*(+)-DIOP)(4-ethynylpyridine)$_2$][*cis*-Pd^{2+}(*R*(+)-BINAP)($^-$OSO$_2$CF$_3$)$_2$]]·2AgOTf·tetramethylpyrazine (28). Yield: 36.0 mg (100%). mp 214−218 °C (dec). IR (CCl_4) 3058 (Ar), 2989 (CH$_3$), 2933 (CH$_2$), 2070 (CC), 1285, 1166, 1025, (all OTf) cm^{-1}. UV−vis (CH_2Cl_2) λ_{max} = 294 nm, $\epsilon = 10.8 \times 10^4$ L cm^{-1} mol^{-1}. CD (CH_2Cl_2), λ ($\Delta\epsilon$) [nm (L mol^{-1} cm^{-1})], 250 (+9.5), 277 (−18.4), 320 (+25.4), 326 (+24.1), 330 (+24.9), 353 (−1.6), 393 (+10.0). ^{1}H NMR (CD_2Cl_2) δ 8.07 (d, 8H, $^3J_{HH}$ = 4.8 Hz), 7.94−7.90 (m, 12H), 7.86−7.65 (m, 28H), 7.51−7.14 (m, 32H), 7.07 (t, 12H, J = 7.9 Hz), 7.04−7.01 (m, 16H), 6.42 (d, 4H, $^3J_{HH}$ = 18.5 Hz), 6.36 (d, 8H, $^3J_{HH}$ = 6.1 Hz), 4.09 (bs, 4H), 3.09 (bm, 4H), 2.83 (bm, 4H), 2.34 (s, 12H, tmp), 1.13 (s, 12H). ^{13}C {^{1}H} NMR (CD_2Cl_2) δ 151.0 ($C_{\alpha pyr}$), 150.4 (tmp), 140.5 (t), 138.6 ($C_{ipsopyr}$), 135.4 (s), 135.1, 133.3 (Pt−P−C_o), 133.9 (s), 133.7 (t), 133.5 (s), 132.9 (s), 132.8, 132.3 (Pt−P−C_p), 132.5 (s), 130.8 (t), 129.6, 128.8 (Pt−P−C_m), 129.5 (s), 129.4 (s), 128.9 (s), 128.6 ($C_{\beta pyr}$), 128.3 (t), 127.8 (s), 127.7 (t), 127.4 (t), 125.7 (s), 124.5 (q, CC−Pt_α), 123.9 (s), 120.9 (q, $^1J_{C-F}$ = 319 Hz, OTf), 109.7 (s, OCO), 119.8 (s), 109.8 (t, CC−Pt_β, $^2J_{P-C}$ = 15.6 Hz), 76.4 (t, O*C*HCH$_2$, $^2J_{P-C}$ = 5.8 Hz), 29.5−29.0 (m, OCH*C*H$_2$), 26.7 (CH$_3$), 21.7 (s, tmp). ^{31}P {^{1}H} NMR (CD_2Cl_2) δ 27.4 (s), −2.4 (s, J_{Pt-P} = 2481 Hz). ^{19}F NMR (CD_2Cl_2) δ −77 (s, OTf). Anal. Calcd for $C_{192}H_{156}Ag_2F_{18}N_6O_{22}P_8Pd_2Pt_2S_6\cdot 4H_2O$: C, 50.44; H, 3.62; N, 1.84; S, 4.21. Found: C, 50.40; H, 3.64; N, 1.83; S, 4.35.

Cyclobis[[*cis*-Pt(*S*(+)-DIOP)(4-ethynylpyridine)$_2$][*cis*-Pd^{2+}(*S*(−)-BINAP)($^-$OSO$_2$CF$_3$)$_2$]]·2AgOTf·phenazine (29). Yield: 36.3 mg (100%). mp 236−238 °C (dec). IR (CCl_4) 3059, 3013 (Ar), 2990 (CH$_3$), 2934 (CH$_2$), 2074 (CC), 1286, 1166, 1028, (all OTf) cm^{-1}. UV−vis (CH_2Cl_2) λ_{max} = 294 nm, $\epsilon = 9.1 \times 10^4$ L cm^{-1} mol^{-1}. CD (CH_2Cl_2), λ ($\Delta\epsilon$) [nm (L mol^{-1} cm^{-1})], 251 (−7.2), 276 (+18.4), 318 (−17.7), 326 (−16.1), 333 (−18.2), 354 (+0.4), 370 (−1.9), 389 (+0.3), 434 (−5.8). ^{1}H NMR (CD_2Cl_2) δ 8.34 (phenazine-β, m, 4H), 8.10 (d, 8H, $^3J_{HH}$ = 4.8 Hz), 8.03 (phenazine-γ, m, 4H, $^3J_{HH}$ = 9.9 Hz), 7.87−7.84 (m, 12H), 7.73−7.54 (m, 28H), 7.50−7.14 (m, 32H), 7.07 (t, 12H, J = 7.1 Hz), 7.05−7.02 (m, 16H), 6.41 (d, 4H, $^3J_{HH}$ = 18.5 Hz), 6.30 (d, 8H, $^3J_{HH}$ = 5.8 Hz), 3.91 (bs, 4H), 3.26 (bm, 4H), 2.74 (bm, 4H), 1.19 (s, 12H). ^{13}C {^{1}H} NMR (CD_2Cl_2) δ 150.6 ($C_{\alpha pyr}$), 143.0 (phenazine-α), 140.5 (t), 138.5 ($C_{ipsopyr}$), 135.4 (s), 135.0, 133.7 (Pt−P−C_o), 134.2 (phenazine-β), 133.8 (s), 133.2 (s), 132.7 (t), 132.6, 131.8 (Pt−P−C_p), 132.4 (s), 130.8 (s), 130.1 (s), 129.8 (s), 129.6 (s), 129.5, 128.7 (Pt−P−C_m), 129.4 (phenazine-β), 128.9 ($C_{\beta pyr}$), 128.6 (s), 127.9 (s), 127.7 (t), 127.4 (s), 125.8 (s), 125.0 (s), 124.6 (q, CC−Pt_α), 124.0 (s), 121.0 (q, $^1J_{C-F}$ = 319 Hz, OTf), 119.2 (s), 111.2 (t, CC−Pt_β, $^2J_{P-C}$ = 15.5 Hz), 110.0 (s, OCO), 76.5 (t, O*C*HCH$_2$, $^2J_{P-C}$ = 5.4 Hz), 30.2−29.7 (m, OCH*C*H$_2$), 26.8 (CH$_3$). ^{31}P {^{1}H} NMR (CD_2Cl_2) δ 27.2 (s), −1.1 (s, J_{Pt-P} = 2482 Hz). ^{19}F NMR (CD_2Cl_2) δ −75 (s, OTf). Anal. Calcd for $C_{196}H_{152}Ag_2F_{18}N_6O_{22}P_8Pd_2Pt_2S_6\cdot 4H_2O$: C, 51.00; H, 3.49; N, 1.82; S, 4.17. Found: C, 49.95; H, 3.51; N, 1.82; S, 4.20.

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