Design and Study of Synthetic Chiral Nanoscopic Assemblies. Preparation and Characterization of Optically Active Hybrid, Iodonium−Transition-Metal and All-Transition-Metal Macrocyclic Molecular Squares

Bogdan Olenyuk, Jeffery A. Whiteford, and Peter J. Stang*

Contribution from the Department of Chemistry, The University of Utah, Salt Lake City, Utah 84112

Received May 1, 1996[⊗]

Abstract: The synthesis and characterization of various optically active nanoscale-size tetranuclear assemblies held together by coordination bonds is described. Interaction of bis[4-(4′-pyridyl)phenyl]iodonium triflate and bistriflates of chiral transition metal (Pd(II) or Pt(II)) bisphosphines resulted in the formation of chiral hybrid iodonium-transition metal molecular squares. Restricted rotation of the coordinated bis[4-(4′-pyridyl)phenyl]iodonium moiety was detected in these squares and investigated by using variable-temperature NMR. The preparation of chiral hybrid squares which possess the elements of helicity (twist) in the assembly was accomplished using the above bisphosphines and bis(3-pyridyl)iodonium triflate. Interaction between the bistriflates of chiral (*R*(+)-BINAP or *S*(−)-BINAP)) transition metal (Pd(II) or Pt(II)) bisphosphines and a diaza ligand with C_{2h} symmetry, 2,6-diazaanthracene (DAA) or 2,6-diazaanthracene-9,10-dione (DAAD), in acetone at ambient temperature results in chirality-directed assembly of a single stable diastereomer or highly enriched diastereomeric mixtures of optically active macrocyclic molecular squares. The stereochemical outcome of such self-assembly at the full combinatorial level was investigated as well by the use of achiral Pd(II) or Pt(II) bisphosphine complexes.

Introduction

The self-assembly of chiral supramolecular entities is common in vivo. Various biomolecules that are subunits of large multicomponent assemblies typically possess the ability to enter into a large number of precisely positioned noncovalent interactions which drive the self-organization process and maintain the structural and stereochemical integrity of the assembly. In contrast, the design and preparation of chiral artificial self-assembling systems is a relatively new endeavor which represents a formidable challenge.[1,2] In recent years, various chiral helical arrays were synthesized, by employing hydrogen bonds,[3] hydrophobic interactions,[4] or transition metal coordination[5] as the self-assembly motif. Considerably less is known, however, about self-assembly of *discrete cyclic* chiral species held together by noncovalent interactions. Whereas asymmetric synthesis of organic compounds is well established, the control of stereochemistry in noncovalent synthesis remains virtually unexplored.

Molecular squares are examples of discrete cyclic assemblies, where 90° angles are used to achieve a well-defined shape.[6] This feature, combined with their conformational rigidity, make molecular squares promising targets for the study of stereoselective self-assembly. Chirality in these macrocycles can be achieved via at least four ways: (1) by use of a chiral auxiliary, such as a chiral bisphosphine, coordinated to the transition metal; (2) using optically active C_2-symmetrical diaza ligands as connectors (unfortunately, there is no known example of chiral (atropoisomeric) 4,4′-bipyridines to date, although there is a large number of known atropoisomeric bis-aryls);[7] (3) by employing diaza ligands which lack a rotation symmetry about their linkage axis that will result in an overall "twist" of the square, thereby introducing the elements of helicity in its assembly (in this situation, however, the formation of several (six for a tetranuclear assembly) stereoisomers is possible); and (4) by combination of the above principles. Thus, a chiral metal

[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1996.

(1) Lehn, J.-M. *Supramolecular Chemistry: Concepts and Perspectives;* VCH: New York, 1995.

(2) Cram, D. J.; Cram, J. M. *Container Molecules and Their Guests;* The Royal Society of Chemistry: Cambridge, UK, 1994.

(3) (a) Gulik-Krzywicki, T.; Fouquey, C.; Lehn, J.-M. *Proc. Natl. Acad. Sci. U.S.A.* **1993**, *90*, 163. (b) Geib, S. J.; Vincent, C.; Fan, E.; Hamilton, A. D. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 119. (c) Hanessian, S.; Gomtsyan, A.; Simard, M.; Roelens, S. *J. Am. Chem. Soc.* **1994**, *116*, 4495.

(4) (a) Osterman, D. G.; Kaiser, E. T. *J. Cell. Biol.* **1985**, *29*, 57. (b) Kaiser, E. T.; Kezdy, F. J. *Science* **1984**, *223*, 249.

(5) (a) Lehn, J.-M.; Sauvage, J. P.; Ziessel, R.; Piccinni-Leopardi, C.; Germain, G.; Declerq, J. P.; Van Meerssche, M. *Nouv. J. Chim.* **1983**, *7*, 413. (b) Lehn, J.-M.; Rigault, A.; Siegel, J.; Harrowfield, J.; Chevrier, B.; Moras, D. *Proc. Natl. Acad. Sci. U.S.A.* **1987**, *84*, 2565. (c) Lehn, J.-M.; Rigault, A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1095. (d) Garrett, T. M.; Koert, U.; Lehn, J.-M.; Rigault, A.; Meyer, D.; Fischer, J. *J. Chem. Soc., Chem. Commun.* **1990**, 557. (e) Kert, U.; Harding, M. M.; Lehn, J.-M. *Nature* **1990**, *346*, 339. (f) Constable, E. C.; Ward, M. D.; Tocher, D. A. *J. Am. Chem. Soc.* **1990**, *112*, 1256. (g) Constable, E, C.; Elder, S. M.; Healy, J. A.; Ward, M. D.; Tocher, D. A. *J. Am. Chem. Soc.* **1990**, *112*, 4590. (h) Zarges, W.; Hall. J.; Lehn, J.-M.; Bolm, C. *Helv. Chim. Acta* **1991**, *74*, 1843. (i) Constable, E. C.; Walker, J. V. *J. Chem. Soc., Chem. Commun.* **1992**, 884. (j) Potts, K. T.; Keshavarz-K. M.; Tham, F. S.; Abruna, H. D.; Arana, C. R. *Inorg. Chem.* **1993**, *32*, 4422, 4436, 4450, 5477. (k) Piguet, C.; Bunzli, J. C. G.; Bernadinelli, G.; Hopfgartner, G.; Williams, A. F. *J. Am. Chem. Soc.* **1993**, *115*, 8197 and references therein. (l) Carboniere, L. J.; Bernardinelli, G.; Piguet, C.; Sargeson, A. M.; Williams, A. F. *J. Chem. Soc., Chem. Commun.* **1994**, 1419. (m) Bell, T. W.; Jousselin, H. *Nature* **1994**, *367*, 441. (n) Ohata, N.; Masuda, H.; Yamauchi, O. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 531.

(6) (a) Stang, P. J.; Olenyuk, B.; Fan, J.; Arif, A. M. *Organometallics* **1996**, *15*, 904. (b) Stang, P. J.; Chen. K.; Arif, A. M. *J. Am. Chem. Soc.* **1995**, *117*, 8793. (c) Stang, P. J.; Cao, D. H.; Saito, S.; Arif, A. M. *J. Am. Chem. Soc.* **1995**, *117*, 6273. (d) Stang, P. J.; Chen, K. *J. Am. Chem. Soc.* **1995**, *117*, 1667. (e) Drain, C. M.; Lehn, J.-M. *J. Chem. Soc., Chem. Commun.* **1994**, 2313. (f) Stang, P. J.; Whiteford, J. A. *Organometallics* **1994**, *13*, 3776. (g) Stang, P. J.; Cao, D. H. *J. Am. Chem. Soc.* **1994**, *116*, 4981. (h) Fujita, M.; Kwon, Y. J.; Washizu, S.; Ogura, K. *J. Am. Chem. Soc.* **1994**, *116*, 1151. (i) Rauter, H.; Hillgeris, E. C.; Erxleben, A.; Lippert, B. *J. Am. Chem. Soc.* **1994**, *116*, 616. (j) Fujita, M.; Nagao, S.; Iida, M.; Ogura, K. *J. Am. Chem. Soc.* **1993**, *115*, 1574. (k) Fujita, M.; Yazaki, J.; Ogura, K. *J. Am. Chem. Soc.* **1990**, *112*, 5645.

(7) Eliel, E.; Wilen, S. *Stereochemistry of Organic Compounds;* Wiley: New York, 1994.

S0002-7863(96)01444-8 CCC: $12.00

auxiliary may be used in conjunction with the elements of helicity or with optically active diaza ligands, etc. In this paper we report the self-assembly driven synthesis of chiral tetranuclear molecular squares and demonstrate the role of asymmetric induction in the assembly of these highly symmetrical chiral macromolecules as well as the preparation of a unique family of hybrid iodonium−transition-metal based molecular squares, employing principles 1, 3, and 4 above.

Results and Discussion

Chirality via a Coordinated Transition Metal Auxiliary: Modular Self-Assembly of Optically Active Hybrid, Iodonium−Transition Metal Macrocyclic Molecular Squares. Hybrid molecular squares represent a family of unique macrocyclic assemblies, because they are the first example of aggregates, where a hypervalent main group element is incorporated as a shape-defining unit.[6b,d] Due to its pseudo-trigonal-bipyramidal geometry the carbon−iodine−carbon bond angle of iodonium compounds is close to 90°. Moreover, since the iodonium moiety is relatively flexible with respect to deformation of this angle, by assuming a value from approximately 87° to 98° it can accommodate a variety of shapes in the resulting assemblies. To date, the only known iodine-containing assemblies are the rhomboid-shaped hybrid molecular squares reported recently.[6b] Hence, these species are ideal candidates for stereochemical investigation of supramolecular species by self-assembly.

Among the various chiral bisphosphines, 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP) has been known for over a decade.[8] It has been extensively utilized as a chiral transition metal chelator with a variety of applications in chiral catalysis. Most important, its Pd(II) and Pt(II) complexes are significantly more rigid in conformation than are other chiral transition metal bisphosphine chelators such as 2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane (DIOP), or 2,4-bis(diphenylphosphino)pentane (BDPP). BINAP was also found to exhibit a high degree of asymmetric induction in the formation of covalent platinum complexes with monosubstituted bis-aryls.[9] Furthermore, we have already prepared the BINAP Pd(II) and Pt(II) bistriflate complexes[10] that are suitable building blocks for the self-assembly of chiral molecular squares.

Optically active hybrid molecular squares are formed by intreracting bis(4-(4′-pyridyl)phenyl)iodonium triflate **1** and [Pd(*R*(+)-BINAP)(H_2O)][OTf]$_2$ (**2**) or [Pt(*R*(+)-BINAP)(H_2O)][OTf]$_2$ (**3**) (Scheme 1). Since in this case the diaza ligands of the iodonium species possess rotation symmetry about their linkages no "twists" in the assembly are present and molecular squares **4** and **5** are chiral exclusively due to the chiral transition-metal auxiliary (BINAP) in the assembly. Although this represents the simplest possible *chiral* hybrid molecular square, one of the interesting features of these species is that they are excellent model compounds where the possible restricted rotation of the coordinated pyridine moiety may be easily detected and investigated by variable-temperature NMR. Since both **4** and **5** posses D_2 symmetry, with one of the symmetry axes across the plane of the transition metals, if free rotation of the pyridine ligands is restricted, the hydrogens on the pyridine rings are diastereotopic and may be detected by ^{1}H NMR. As

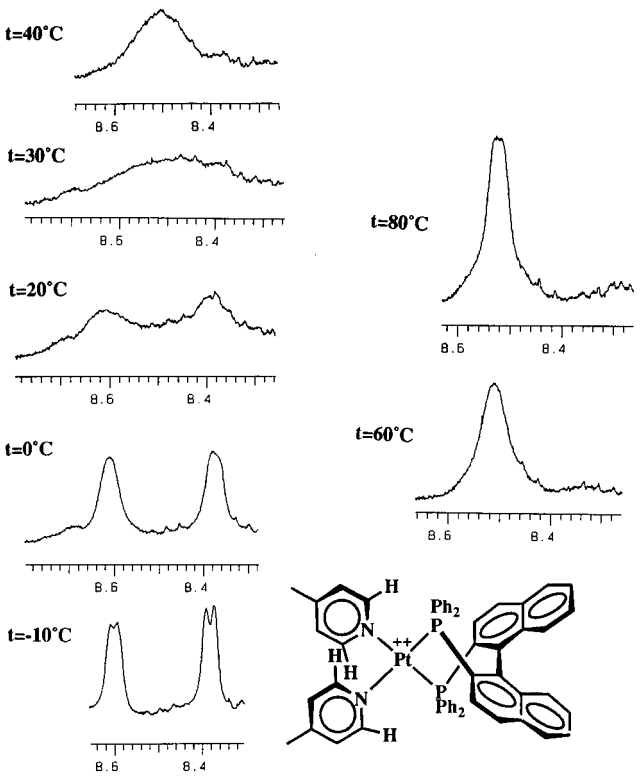
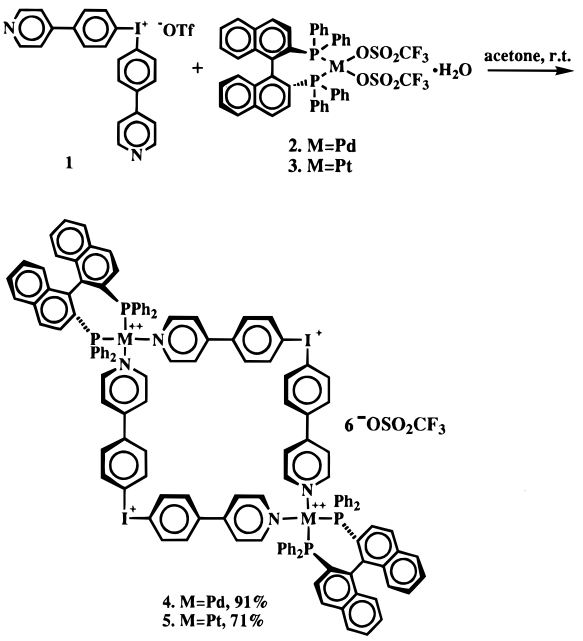


Figure 1. Variable-temperature ^{1}H NMR spectra of molecular square **5**, indicating the coalescence of α-pyridyl protons at elevated temperatures.

Scheme 1



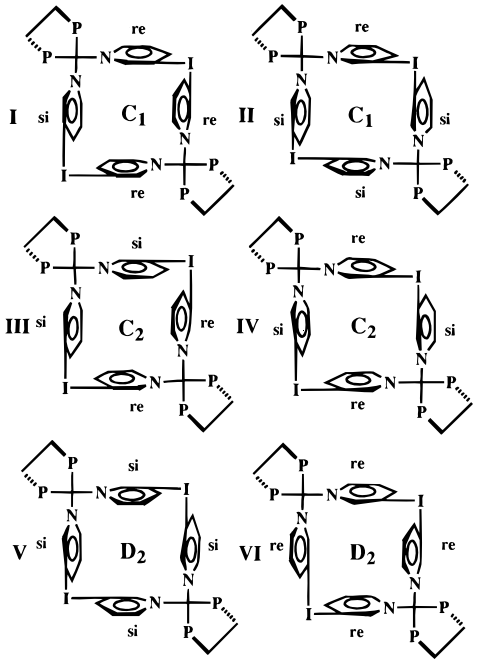
the β-pyridyl hydrogens are obscured by the BINAP signals the α-protons were chosen for the survey. Variable-temperature NMR (Figure 1) demonstrated the coalescence of these protons and allowed us to estimate the rotational barriers of the pyridine rings in these chiral molecular squares as 12.9 kcal/mol for **4** and 15.0 kcal/mol for **5**. It is clear that the palladium analog **4** has a lower barrier to rotation than the platinum square **5** despite their great similarity in structure. This interesting effect was also noted in the variable-temperature study of the simple monomeric chiral complexes of [M(*R*(+)-BINAP)(isoquinoline)$_2$][OTf]$_2$ (M = Pd, Pt),[10] but it is the first such observation for any chiral supramolecular asembly.

(8) (a) Miyashita, A.; Yasuda, A.; Takaya, H.; Torimi, K.; Ito, T.; Souchi, T.; Noyori, R. *J. Am. Chem. Soc.* **1980**, *102*, 7932. (b) Takaya, H.; Mashima, K.; Koyano, K.; Yagi, M.; Kumobayashi, H.; Taketomi, T.; Akutagawa, S.; Noyori, R. *J. Org. Chem.* **1986**, *51*, 629.

(9) Brown, J. M.; Pérez-Torrente, J. J.; Alcock, N. W. *Organometallics* **1995**, *14*, 1195.

(10) Stang, P. J.; Olenyuk, B.; Arif, A. M. *Organometallics* **1995**, *14*, 5281.

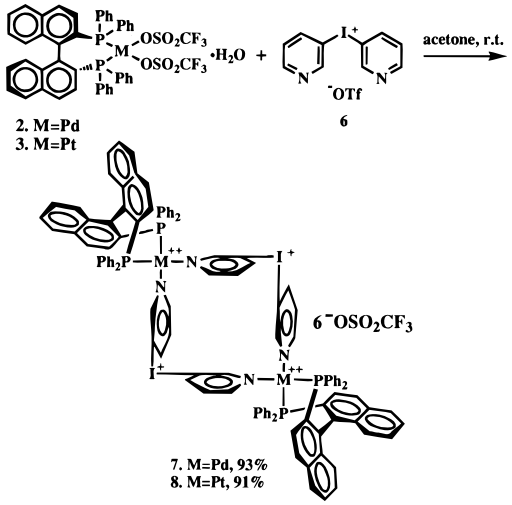
Chart 1



If hybrid chiral molecular squares with elements of helicity (twist) are to assemble, the coordinated heterocycle has to be restricted in rotation about the metal−nitrogen bond. Moreover, it requires an iodonium precursor where the heterocyclic ring lacks the rotation symmetry about its linkages: the nitrogen lone pair and the carbon−iodine bond. Although a number of such iodonium salts are feasible, the known bis(3-pyridyl)-iodonium chloride[11] is the simplest and most useful. However, in order to prevent the unwanted coordination of the chloride ion to the transition metal, the bis(3-pyridyl)iodonium chloride has to be converted to the triflate salt by treatment with Me_3-SiOTf, followed by subsequent deprotonation with triethylamine, as detailed in the Experimental Section.

Analysis of the problem reveals that interaction of a chiral square planar Pd(II) or Pt(II) complex with an iodonium precursor where the heterocyclic ring lacks rotation symmetry about its linkages can result in the formation of six diastereomers as displayed in Chart 1. Should all these isomers form in nearly equal amounts the ^{31}P NMR spectrum of the overall product mixture is expected to be very complicated. This is a consequence of the fact that the C_1-symmetrical structures **I** and **II** are both expected to contribute two singlets and AB-type doublets, structures **III** and **IV** with C_2 symmetry contribute a singlet and one AB-type doublet, whereas the D_2-symmetrical structures **V** and **VI** contribute two separate singlets in the ^{31}P NMR. However, we anticipated that use of a chiral auxiliary, such as BINAP, will reduce the complexity of the stereochemical outcome via asymmetric induction upon the self-assembly process. Indeed, interaction of the chiral Pd(II) and Pt(II) bisphosphine complexes **2** and **3** with bis(3-pyridyl)iodonium triflate **6** in acetone results in an excess of one each of the preferred diastereomers of $[Pd(R(+)\text{-BINAP})(C_{10}H_8N_2I)]_2[OTf]_6$ (**7**) and $[Pt(R(+)\text{-BINAP})(C_{10}H_8N_2I)]_2[OTf]_6$ (**8**) as assessed by NMR (Scheme 2), in a matter of minutes, in excellent isolated yields. The ^{31}P spectra of both **7** and **8** exhibit a high-field shift relative to the precursors **2** and **3** as a consequence of the nitrogen coordination to the transition metal. However, in the case of square **8**, probably due to the relative conformational flexibility of the iodonium moiety, significant amounts of the other diastereomers are formed as well (Figure 2). Hence, in this case, only a modest degree of asymmetric induction is achieved by the two chiral transition-metal centers in the self-assembly of these hybrid molecular squares. Liquid secondary ion (LSI) mass spectra of **7** indicate the presence of the $[M-{}^{-}OTf]^{+}$ ion with an *m/z* ratio of 2770. For square **8**, hovewer, it was possible to detect only doubly-charged ion $[M-2{}^{-}OTf]^{2+}$ with an *m/z* of 1398 and to unambiguously establish its charge state (+2). These data as well as a close match of calculated and measured isotopic patterns of these ions confirm predicted molecular weights for **7** and **8**, proving that these products exist as [2 + 2] assemblies. In the absence of X-ray or other definite structural data it is not possible to ascertain precisely which diastereoisomer is preferentially formed. However, the observation of a singlet in the ^{31}P NMR spectrum as a *major* signal indicates stereoisomers **V** or **VI** as the likely candidates. One possible structure was derived from MM2 calculations (Figure 3). As a consequence of the restricted rotation of the coordinated pyridine ligands about the metal−nitrogen bonds, both the Pd(II) square **7** and its Pt(II) analog **8** are conformationally relatively rigid. The structures in Chart 1, in fact, represent their "frozen" conformers. In analogy with molecular squares **4** and **5**, where the Pt compound **5** is conformationally rigid at room temperature, one would predict that **8** is also rigid whereas **7** should be less so. To our surprise, a variable-temperature study of the ^{31}P NMR spectrum of **7** between −30 and +40 °C revealed no detectable line broadening or other changes. Perharps the greater steric strain in the smaller square **7** compared to **4** might account for this lack of rotation around the Pd−N bond.

Scheme 2



These chiral hybrid molecular squares are robust (though hygroscopic) microcrystalline solids with high decomposition points. They are remarkably soluble in polar organic solvents, such as acetone, nitromethane, or methanol, despite their relatively large charge and molecular weight. An indication of the thermodynamic stability of these species is the fact that they readily form even from the protonated bis(3-pyridyl)iodonium salt and remain intact in the presence of triflic acid.

Self-Assembly of Diastereomeric Mixtures of Hybrid Squares Using Achiral Bisphoshines. In the absence of asymmetric induction, with the achiral metal bisphosphines $[Pd(cis\text{-}Et_3P)_2][OTf]_2$, (**9**), $[Pt(cis\text{-}Et_3P)_2][OTf]_2$ (**10**), and **6** under the above self-assembly conditions (Scheme 3), a diastereomeric mixture of products $[Pd(cis\text{-}Et_3P)_2(C_{10}H_8N_2I)]_2[OTf]_6$ (**11**) and $[Pt(cis\text{-}Et_3P)_2(C_{10}H_8N_2I)]_2(OTf)_6$ (**12**) is expected (Chart 2). The six possible isomers depicted in Chart 2 are similar to those in

(11) Stang, P. J.; Olenyuk, B.; Chen, K. *Synthesis* **1995**, 937.

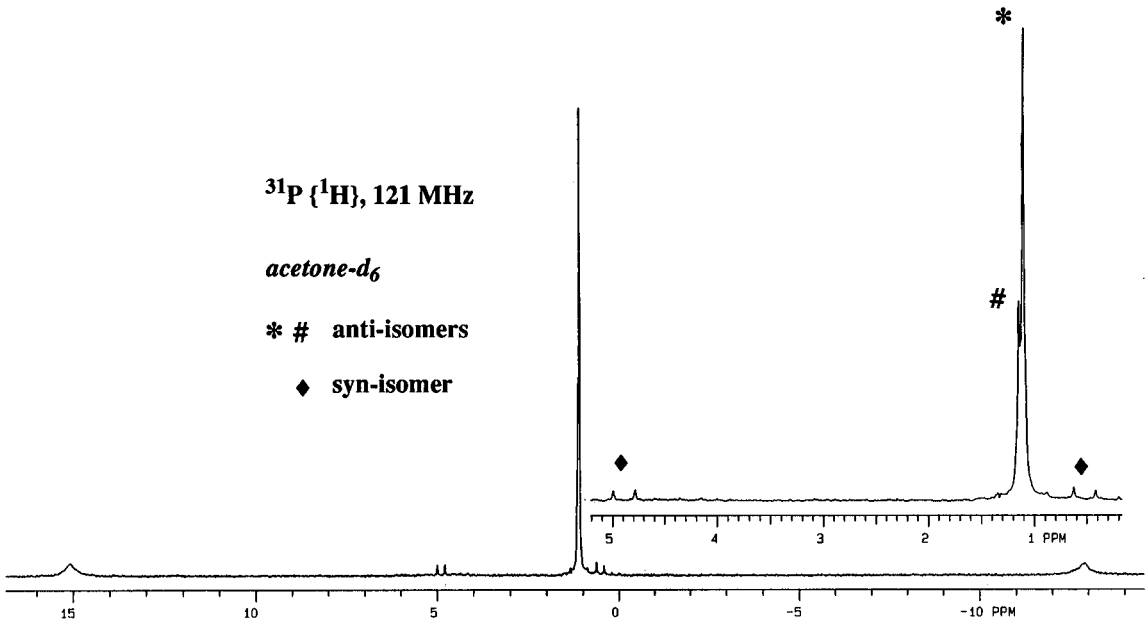


Figure 2. ^{31}P $\{^1H\}$ NMR spectrum of molecular square **8**, indicating the presence of other diastereomers.

Scheme 3

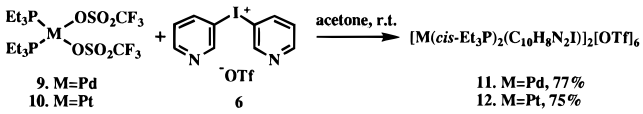


Chart 2

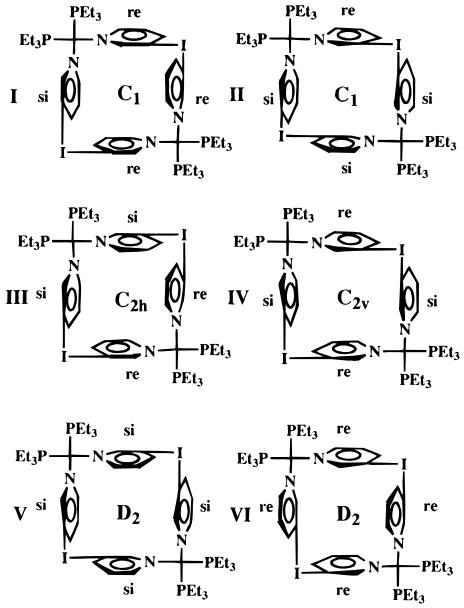


Chart 1, except that due to the presence of an *achiral* bisphosphine some have different symmetries. The analysis of these structures with respect to their predicted ^{31}P NMR spectra results in the following: structures **I** and **II** are chiral but enantiomers of each other so the ^{31}P NMR spectrum of each square should consist of two singlets. However, as enantiomers the two sets of signals for each square are of course identical. Squares **III** and **IV** are achiral and each should have a separate singlet. Structures **V** and **VI** are also chiral but enantiomers of each other and hence should possess only one singlet. Hence, if all possible isomers are formed by self-asembly, a total of five singlets should be observed in the ^{31}P spectrum in accord with the symmetries of the individual squares in Chart 2.

The NMR spectra of **11** indicate that it exists as a mixture of cyclic and linear oligomers. The lines in the ^1H spectrum of this product are significantly broadened and its ^{31}P NMR spectrum consists of a broad signal of linear oligomer along with the sharp singlet of the cyclic assembly. For square **12**, however, the experimental ^1H and ^{31}P spectra indicate the presence of only cyclic products and once again show restricted rotation of the pyridine ligands around the Pt−N bond as well as formation of a mixture of cyclic diastereomeric products. Interestingly, the ^{31}P NMR spectrum of **12** contains *only* two singlets in a ratio of 1:8. This unexpected result is likely due to the very small chemical shift differences betweeen the ^{31}P NMR signals of the *cis*-coordinated Et_3P of the different stereoisomers and hence they are accidentally equivalent. Because the two singlets have markedly different intensities this explanation is more plausible than selective formation of a single isomer of **I** or **II**. However, the possible formation of some individual diastereoisomers in excess cannot be completely ruled out.

Chiral All-Transition-Metal Macrocyclic Molecular Squares. The self-assembly of the all-metal chiral molecular squares was carried out[12] with use of the chiral BINAP Pd(II) and Pt(II) bistriflate monohydrate complexes **2** and **3** and the C_{2h}-symmetrical diaza ligands, 2,6-diazaanthracene (DAA, **13**) and 2,6-diazaanthracene-9,10-dione[13] (DAAD, **14**). When [Pd(*R*(+)-BINAP)(H_2O)][OTf]$_2$ **(2)** or [Pt(*R*(+)-BINAP)(H_2O)][OTf]$_2$ **(3)** is mixed with DAA in acetone at room temperature, the formation of a single diastereomer each of squares **15** and **16** is observed, as assessed by NMR. The singlet in the ^{31}P NMR is indicative of the exclusive formation of only one highly symmetrical chiral product (Scheme 4). The absolute stereochemistry of **15** and **16**, as shown in Scheme 4, was assigned based upon the known[9] X-ray structures of chiral BINAP transition-metal bis-aryls in combination with MM2 force field calculations. We realize that in the absence of X-ray structures for **15** and **16**, some degree of uncertainty still remains in this assignment.

In contrast, when DAAD was employed as a connector ligand (Scheme 5), the reaction mixture consists of a significant excess of one diastereomeric product, **17** or **18**, respectively, along

(12) Stang, P. J.; Olenyuk, B. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 732.

(13) European Patent Application 0394846 A2.

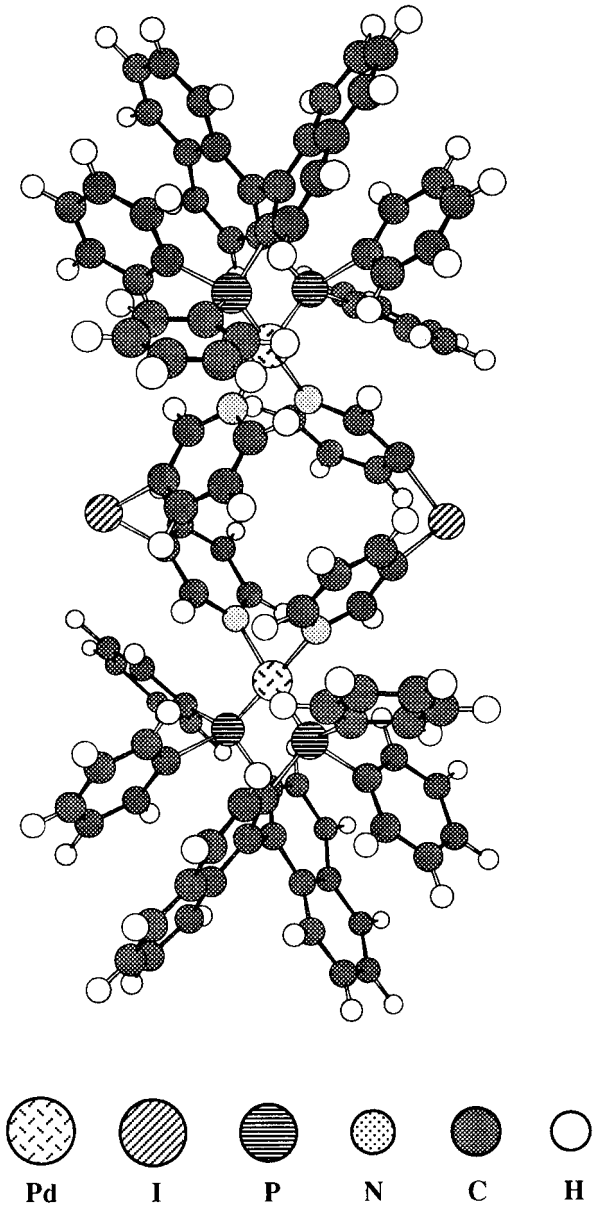
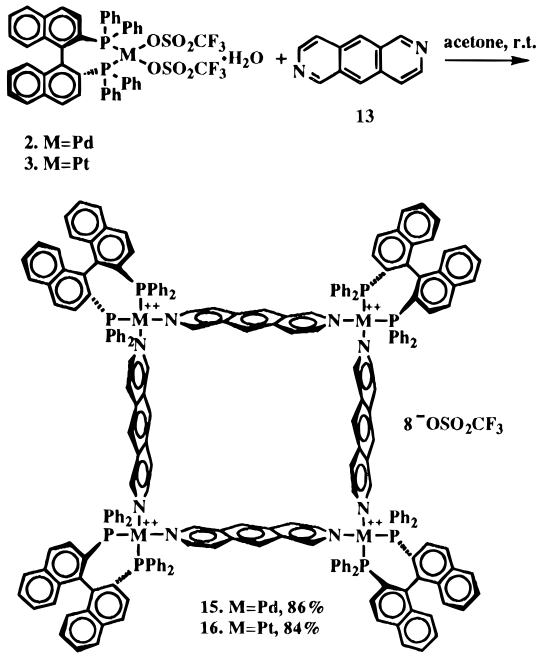


Figure 3. Ball-and-stick model of square **7**, derived from the MM2 calculations.

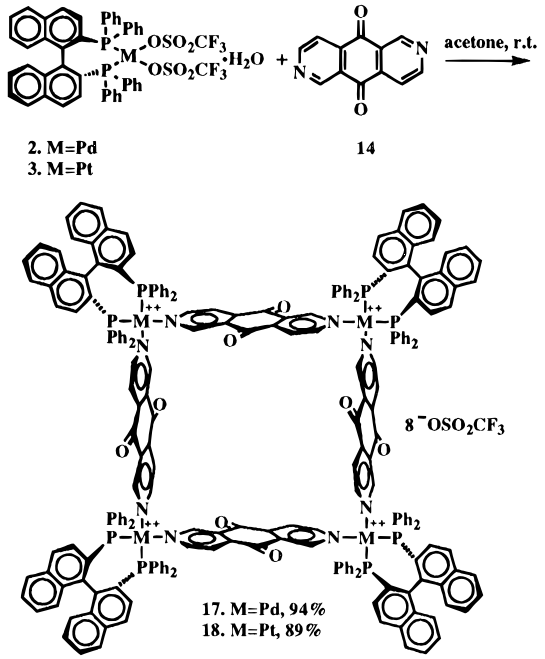
with minor amounts of other diastereomers, as demonstrated by the ^{31}P NMR spectra of **17** and **18**, displayed in Figure 4. Integration of the individual expanded ^{31}P spectrum gives a diastereomeric excess (de) of 81% for **17** and 72% for **18**. The macrocyclic nature of these species is established by multinuclear NMR and confirmed by mass-spectral data. The electrospray mass spectrum of molecular square **18** showed the presence of the doubly-charged $[M-2^{-}OTf]^{2+}$ and quadruply-charged $[M-4^{-}OTf]^{4+}$ ions with *m/z* ratios of 2503 and 1178, respectively. These ions correspond to the cyclic tetramer with loss of two and four triflate anions.

In comparison to hybrid squares **7** and **8** the all-metal squares are formed in signifigantly greater diastereomeric excess and are conformationally much more rigid. When variable-temperature experiments were performed with the Pd(II)-containing square **15**, no free rotation of the coordinated DAA ligand was detected in the temperature range from −80 to +80 °C. A similar observation holds for the Pd square **17**. These observations are consistent with the fact that the four-metal-center architecture in these all-metal squares **15**−**18** contributes to a considerably higher degree to both asymmetric induction and the impedance of the diaza ligand to free rotation than the two-metal-center system of **7** and **8**. Simply put, for significant conformational rigidity the C_{2h}-symmetrical connector ligands must be restricted in rotation by two, *not* just one, coordinated metal centers.

Scheme 4



Scheme 5



As expected, by use of the opposite enantiomers (*S*(−)-BINAP) of chiral Pd(II) and Pt(II) bisphosphine complexes, namely **19** and **20**, the opposite enantiomers of chiral molecular squares, $[Pd(S(-)\text{-BINAP})(DAAD)]_4[OTf]_8$ (**21**) and $[Pt(S(-)\text{-BINAP})(DAAD)]_4[OTf]_8$ (**22**), were obtained (Scheme 6). Products **21** and **22** have identical NMR and UV−vis spectra to **17** and **18**, but opposite signs of optical rotation. The circular dichroism (CD) spectra of squares **17**, **18**, **21**, and **22** (Figure 5) confirm the expected enantiomeric relationships.

Self-Assembly of Diastereomeric Mixtures of All-Transition-Metal Macrocyclic Molecular Squares with Achiral Bisphosphine Ligands and Diaza Ligands DAA and DAAD.

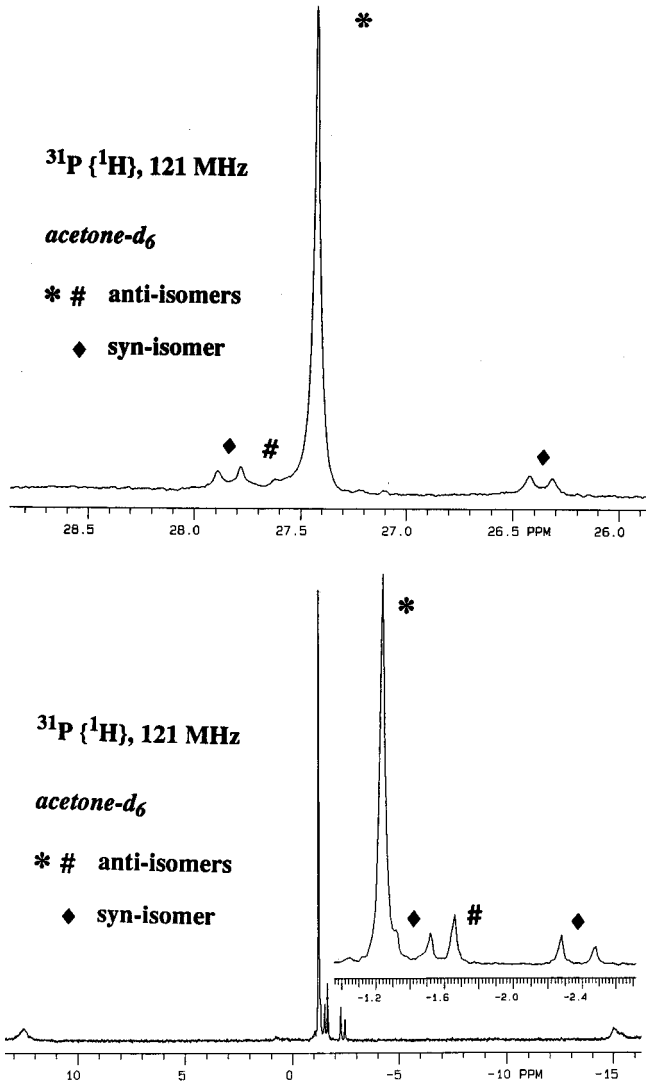


Figure 4. ^{31}P $\{^1H\}$ NMR spectra of molecular squares **17** (top) and **18** (bottom).

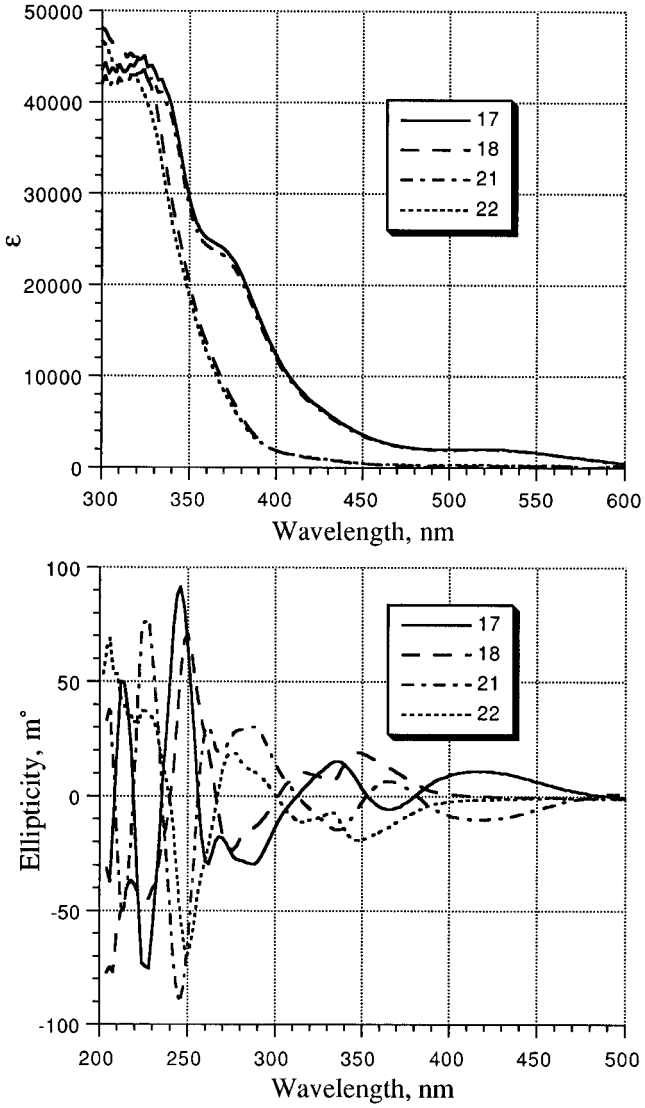
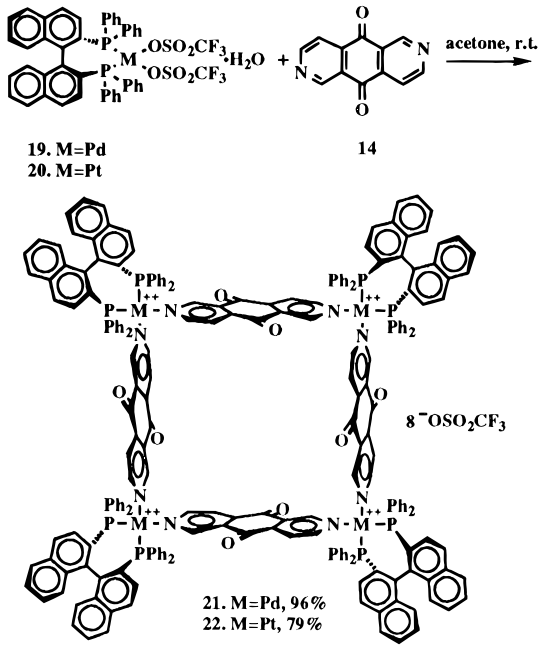


Figure 5. Absorbance (top) and CD spectra (bottom) of 6.0×10^{-5} M solutions of chiral squares **17**−**18** and **21**−**22** in methanol.

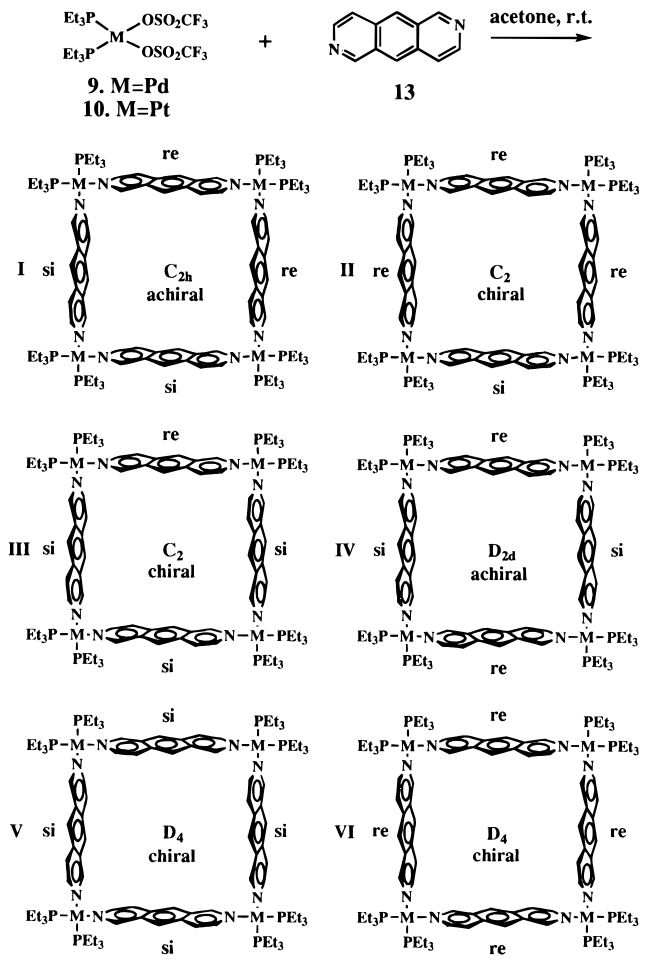
Scheme 6



It is known[10] that when achiral bisphosphine is used in the formation of *mononuclear* Pd(II) and Pt(II) complexes with diaza ligands which lack a rotation symmetry about the metal−nitrogen bond the formation of diastereomeric mixtures occurs due to the restricted rotation of these diaza ligands about the metal−nitrogen coordination bonds. This mixture reveals itself in the ^{31}P spectrum as a set of two singlets, one representing a syn-isomer, and the other an indistinguishable pair of enantiomeric anti-isomers.[10] In order to explore the stereochemistry of self-assembly of all-metal squares at the full combinatorial level we also prepared molecular squares with the achiral transition-metal bisphosphines [Pd(*cis*-$Et_3P)_2$][$OTf]_2$, (**9**) and [Pt(*cis*-$Et_3P)_2$][$OTf]_2$, (**10**) and the diaza ligand **13**. In the absence of asymmetric induction once again six diastereomers are possible (Chart 3). Moreover, unlike the iodonium squares **11** and **12**, the all-metal assemblies are expected to be significantly more rigid in conformation, just like their chiral analogs **15**−**18** and **21**−**22**.

Indeed, the products of this reaction (Chart 3) indicated a complex mixture, with a large number of peaks in the ^{31}P NMR and overlapping signals in the ^1H NMR, which made analyses very difficult as it is impossible by NMR to unambiguously assign the signals for each individual square **I**−**VI**. However, in combination, the total number of signals in the ^{31}P NMR is consistent with the formation of the six isomers (Chart 3).

Chart 3



Careful analysis of this chart reveals a number of interesting features. Square **I** is achiral, since it possesses a plane of symmetry. Its ^{31}P spectrum, thus, must contain two singlets, since two groups of nonequivalent phosphorus atoms are present. Squares **II** and **III** are both chiral and are enantiomers of each other. Therefore, their ^{31}P NMR are identical and contain two signals as well. Structure **IV** is achiral and its ^{31}P spectrum should contain only one singlet. Finally, squares **V** and **VI** are also enantiomers, so their ^{31}P NMR spectra are identical with a singlet as well. At the present time, we do not know which of these signals if any accidentally coincide, but in the absence of accidental equivalence there should be six singlets in the ^{31}P spectrum.

The phosphorus atoms in the bisphosphine around the transition metal are very sensitive to the orientation of the coordinated unsymmetrically substituted diaza ligands. Thus syn-oriented ligands give rise to a different signal in the ^{31}P NMR spectrum than those which are anti-oriented with respect to the square plane of the transition metal.[10] In these all-metal assemblies the four metal centers with the coordinated bisphosphines are relatively far apart to influence each other sterically or electronically. Hence, it might be possible to determine the structure, where the orientation of the connector ligand alone, not the overall symmetry of the individual assembly, is a major factor which dictates the chemical shift difference in the ^{31}P NMR.

When [Pd(*cis*-$Et_3P)_2$][OTf]$_2$, (**9**) or [Pt(*cis*-$Et_3P)_2$][OTf]$_2$, (**10**) respectively, were mixed with DAAD (**14**, Scheme 7), the ^{31}P NMR spectra of the products **23** and **24** show *only* two signals for the diastereomeric mixture **24** and three signals for the Pd analog **23** with ratios close to 1:1.4 and 1:1:1, respectively. If

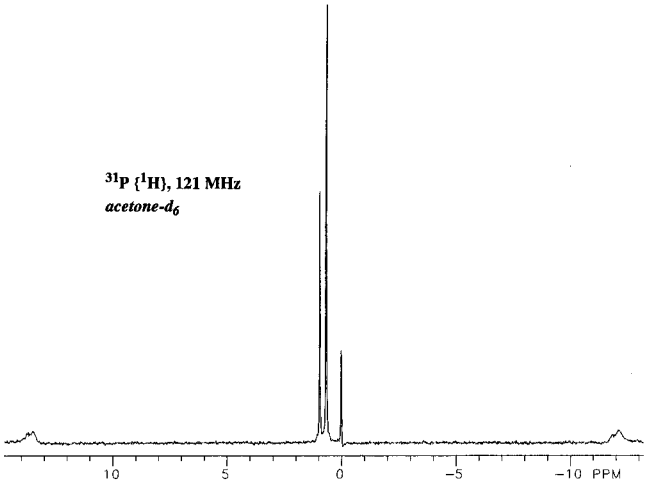
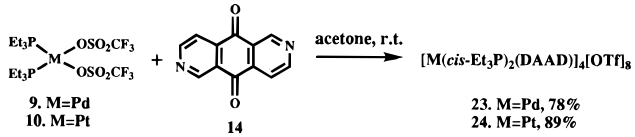


Figure 6. ^{31}P NMR spectrum of molecular square **24**. The signal at 0 ppm represents H_3PO_4 (external standard).

Scheme 7



we disregard the overall symmetry of the molecules in Chart 3 and focus only on the orientation of the ligands with respect to each square plane of the metal center then the anti-orientation (si−si or re−re corners) to syn-orientation (re−si or si−re corners) ratio should be 7:5. Since each individual corner contributes to the ^{31}P NMR signal the ratio of the intensities of these signals should also be 7:5 or 1.4:1. This predicted ratio, compared to the integrated experimental ratio in the ^{31}P spectrum of **24** (Figure 6), is indicative that a diastereomeric mixture of **I**−**VI** is present in solution, rather than just an individual square. In contrast, as seen from the ^{31}P NMR of **23** in this case although we cannot disregard the overall symmetry of the squares, it is still possible to predict a similar spectrum if some of the signals are accidentally equivalent. Despite the fact that it is not possible by NMR alone to establish which orientation gives rise to a specific ^{31}P NMR signal in either **23** or **24**, all the data taken into account from the all-metal squares allow one to deduce a relationship between the symmetry of the chiral squares **15**−**18** and **21**−**22** and their ^{31}P NMR spectra; namely that it is *possible* to distinguish between the different diastereomers by simply using NMR and that only D_4-symmetrical species **15**−**18** and **21**−**22** will display a singlet in ^{31}P NMR spectrum.

Conclusion

This paper represents a first step in the design and study of discrete cyclic chiral supramolecular assemblies based on noncovalent interactions. We prepared and examined by using different spectroscopic techniques two new classes of these asemblies: chiral hybrid iodonium-transition-metal and all-metal tetranuclear molecular squares. The modest number of chiral centers, two for hybrid assemblies and four for the all-metal systems, allowed us to investigate their topology in a more elaborate and complete fashion.

Due to asymmetric induction by the chiral bisphosphine auxiliary chelated to the transition-metal center and restricted rotation of the diaza ligands, which lack a rotation symmetry about the nitrogens, we prepared a varitety of chiral molecular squares that possess the elements of moleclular helicity (twist). Thus, interaction between reactive chiral transition metal

(Pd(II) or Pt(II)) bisphosphine (*R*(+)-2,2′-bis(diphenylphosphine)-1,1′-binaphthyl (*R*(+)-BINAP) or *S*(−)-2,2′-bis(diphenylphosphine)-1,1′-binaphthyl (*S*(−)-BINAP)) bistriflates and the diaza ligand 2,6-diazaanthracene (DAA), in acetone at ambient temperature, results in the chirality-directed assembly of a single stable diastereomer of an optically active macrocyclic molecular square. The use of 2,6-diazaanthracene-9,10-dione (DAAD) under these conditions results in the formation of significantly enriched diastereomeric mixtures of the molecular squares, with carbonyl groups as useful functionalities. Use of the opposite enantiomer of the chiral BINAP transition metal bistriflates led to the formation of the mirror image products. The stereochemical outcome of chirality-directed self-assembly at the full combinatorial level was also established by employing achiral bisphosphine complexes of Pd(II) and Pt(II) bistriflates and the above diaza ligands.

The preparation of chiral hybrid iodonium−transition-metal molecular squares was accomplished by using bis(3-pyridyl)-iodonium triflate which does not possess rotation symmetry about the heterocycle ring linkages. By using enantiomerically pure complexes of *R*(+)-BINAP Pd(II) and Pt(II) bistriflates it was possible to reduce the strereochemical variability to the formation of a preferred diastereomer of the hybrid molecular square in a significant diastereomeric excess. The interaction of bis[4-(4′-pyridyl)phenyl]iodonium triflate, where the nitrogen lone pair and iodonium moiety are located on the same axis, and chiral BINAP Pd(II) and Pt(II) bistriflates resulted in the formation of chiral hybrid molecular squares where the chirality is due strictly to the chiral BINAP auxiliary coordinated to the transition metal. The restricted rotation of the coordinated phenylpyridine moiety in these squares was investigated by variable-temperature NMR.

These chiral supramolecular assemblies represent an interesting and unique opportunity to study and manipulate stereochemistry at the nanoscopic level and to create supramolecular species with specific, precisely-tuned shapes and microenvironments, which depend upon numerous carefully controlled interactions between the constituent components. While this work is still in its infancy, progress in this rapidly growing field will contribute to understanding some of the most interesting aspects of modern supramolecular chemistry.

Experimental Section

General Information. Schlenk techniques along with dry N_2 were employed although the products may be handled in air. IR spectra were recorded on a Mattson Polaris FT-IR spectrophotometer. UV spectra were obrained using a Hewlett-Packard UV−vis spectrophotometer. Circular dichroism (CD) spectra were recorded on an Aviv 60DS CD spectrophotometer. Optical rotations were measured on a Perkin-Elmer 241MC polarimeter. NMR spectra were recorded on Varian XL-300 or Unity-300 spectrometers. ^{1}H NMR spectra were recorded at 300 MHz, and all chemical shifts (δ) are reported downfield in ppm relative to tetramethylsilane (Me_4Si) as an internal standard (0.0 ppm) or the proton resonance resulting from incomplete deuteration of the deuterated acetone (2.05 ppm), nitromethane (4.33 ppm), or methanol (3.31 ppm). Proton decoupled ^{13}C NMR spectra were recorded at 75 MHz in acetone-d_6, and all chemical shifts (δ) are reported downfield in ppm relative to the carbon resonance of the methyl group of deuterated acetone (29.8 ppm), nitromethane (62.3 ppm), or methanol (49.0 ppm). ^{31}P{^{1}H} NMR spectra were recorded at 121 MHz, and all chemical shifts (δ) are reported downfield 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 downfield relative to external $CFCl_3$ at 0.00 ppm. The signals due to water of crystallization in the ^{1}H NMR are omitted. Isomer A denotes the diastereomer or NMR-equivalent enantiomeric pair, which is present in the greatest amount, whereas isomer B refers to the diastereomer or NMR-equivalent enantiomeric pair, which is present in the smallest amount, as indicated by the peak ratios in the ^{1}H and ^{31}P NMR. Microanalyses were performed by Atlantic Microlab Inc., Norcross, GA. Melting points were obtained with a Mel-Temp capillary melting point apparatus and are not corrected.

Materials. Solvents were purified as follows: CH_2Cl_2 was purified by literature procedure[14] and distilled over CaH_2; Et_2O was purified by literature procedure[14] and distilled over Na/benzophenone; Spectrograde acetone was used without further purification. All solvents were freeze−thaw−pump degassed twice before use.

All commercial reagents were ACS reagent grade. The precursors, bis(4-(4′-pyridyl)phenyl)iodonium triflate (**1**),[6b] [Pd(*R*(+)-BINAP)(H$_2$O)][OTf]$_2$ (**2**),[10] and [Pt(*R*(+)-BINAP)(H$_2$O)][OTf]$_2$ (**3**),[10] [Pd(*cis*-Et$_3$P)$_2$][OTf]$_2$ (**9**),[6c] and [Pd(*cis*-Et$_3$P)$_2$][OTf]$_2$ (**10**)[6c] along with 2,6-diazaanthracene (DAA, **13**),[13] and 2,6-diazaanthracene-9,10-dione (DAAD, **14**),[13] were prepared according to literature methods. [Pd(*S*(−)-BINAP)][Cl]$_2$ and [Pt(*S*(−)-BINAP)][Cl]$_2$ were prepared by a modified literature procedure.[15]

[Pd(*R*(+)-BINAP)(C$_{22}$H$_{16}$N$_2$I)]$_2$[OTf]$_6$ (4). A 25-mL Schlenk flask was charged with 29 mg (0.050 mmol) of bis(4-(4′-pyridyl)phenyl)-iodonium triflate (**1**) and 8 mL of acetone. To this, 52 mg (0.050 mmol) of [Pd(*R*(+)-BINAP)(H$_2$O)][OTf]$_2$ (**2**) was added and the solution was stirred at room temperature for 20 min. The solution was reduced in volume to 2 mL, and diethyl ether was added, and the yellow precipitate was collected, washed with a minimum amount of diethyl ether, and dried in vacuo. Yield: 75 mg (91%), mp 252−254 °C dec. $[\alpha]_D$ +311° (c 0.0205, acetone, 20 °C). ^{1}H NMR (acetone-d_6): 8.74 (br s, 8H, py H$_\alpha$), 8.35 (d, J = 8.7, PhI H$_\alpha$), 8.01 (overlap of m, 8H, BINAP), 7.86 (m, 16H, BINAP), 7.76 (d, J = 8.7, 8H, PhI H$_\beta$), 7.55 (t, J = 7.6, 4H, BINAP), 7.40 (br d, J = 1.2, 8H, py H$_\beta$), 7.33 (s, 16H, BINAP), 7.13 (overlap of m, 16H, BINAP), 6.52 (d, J = 8.4, 4H, BINAP). ^{13}C NMR (acetone-d_6): 152.9 (s), 149.2 (s), 141.1 (t), 139.9 (s), 137.3 (s), 135.7 (s), 134.1 (t), 132.6 (s), 132.5 (s), 131.4 (s), 131.2 (t), 130.0 (t), 129.8 (s), 128.2 (s), 127.9 (s), 125.6 (t), 124.4 (s), 121.3 (q), 120.0 (t), 117.2 (s). ^{31}P NMR (acetone-d_6): 27.7 (s). ^{19}F NMR (acetone-d_6): −76.4 (s, OTf). IR (neat, cm^{-1}): 1250, 1157, 1028 (all OTf). Anal. Calcd for $C_{138}H_{96}N_4P_4I_2S_6F_{18}O_{18}Pd_2\cdot 3H_2O$: C, 50.58; H, 3.14; N, 1.71; S, 5.87. Found: C, 50.63; H, 3.18; N, 1.68; S, 5.77.

[Pt(*R*(+)-BINAP)(C$_{22}$H$_{16}$N$_2$I)]$_2$[OTf]$_6$ (5). To the solution of 29 mg (0.050 mmol) of bis(4-(4′-pyridyl)phenyl)iodonium triflate (**1**) in 20 mL of acetone was added 57 mg (0.049 mmol) of [Pt(*R*(+)-BINAP)(H$_2$O)][OTf]$_2$ (**3**) and the resulting mixture was stirred at room temperature for 20 min. Diethyl ether was then added and the white precipitate was filtered, washed with diethyl ether, and dried in vacuo. Yield: 60 mg (71%), mp 258−260 °C dec. $[\alpha]_D$+168° (*c* 0.0055, CH_3NO_2, 20 °C). ^{1}H NMR (acetone-d_6): 8.85 (br s, 4H, diastereotopic py H$_\alpha$), 8.75 (br s, 4H, diastereotopic py H$_\alpha$), 8.36 (d, J = 8.7, PhI H$_\alpha$), 8.02−7.91 (overlap of m, 8H, BINAP), 7.83 (m, 16H, BINAP), 7.79 (d, J = 8.7, 8H, PhI H$_\beta$), 7.52 (t, J = 7.6, 4H, BINAP), 7.50 (br s, 4H, diastereotopic py H$_\beta$), 7.46 (br s, 4H, diastereotopic py H$_\beta$), 7.32 (s, 16H, BINAP), 7.15 (t, J = 8.0, 8H BINAP), 7.08 (t, J = 5.9, 8H, BINAP), 6.52 (d, J = 8.8, 4H, BINAP). ^{13}C NMR (CD_3NO_2): 153.2 (br s), 150.8 (s), 141.7 (t), 140.9 (s), 137.7 (s), 136.2 (s), 134.6 (t), 133.3 (s), 133.2 (s), 132.3 (s), 131.6 (t), 130.5 (t), 129.6 (s), 128.8 (s), 128.6 (s), 128.0 (s), 126.2 (s), 124.8 (t), 121.3 (q), 120.3 (t), 116.4 (s). ^{31}P NMR (CD_3NO_2): 1.14 (s, ^{195}Pt satellites, $^1J_{P-Pt}$ = 3291 Hz). ^{19}F NMR (CD_3NO_2): −76.4 (s, OTf). IR (neat, cm^{-1}): 1281, 1259, 1159, 1029 (OTf). Anal. Calcd for $C_{138}H_{96}N_4P_4I_2S_6F_{18}O_{18}Pt_2\cdot 3H_2O$: C, 47.98; H, 2.98; N, 1.62; S, 5.57. Found: C, 47.74; H, 3.05; N, 1.60; S, 5.55.

Bis(3-pyridyl)iodonium Triflate (6). The white heterogeneous suspension of 0.86 g (2.69 mmol) of bis(3-pyridyl)iodonium chloride[11] in 50 mL of CH_2Cl_2 was treated with 20 mL of a 0.5 M solution of Me_3SiOTf in CH_2Cl_2 at 0 °C. The mixture was warmed up to room temperature and further stirred for 12 h. The precipitate was filtered under N_2 and dried in vacuo. This product was suspended in 50 mL

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

(15) The reaction between Pd(cod)Cl$_2$ or Pt(cod)Cl$_2$ (cod = cyclooctadiene) and *S*(−)-BINAP in CH_2Cl_2 for 20 min at room temperature provided [Pd(*S*(−)-BINAP)][Cl]$_2$ and [Pt(*S*(−)-BINAP)][Cl]$_2$ in 84% and 93% yields, respectively.

of CH_2Cl_2 and 0.98 g of Et_3N in 15 mL of CH_2Cl_2 were added. The mixture was stirred at room temperature for 30 min, filtered, washed with CH_2Cl_2, and dried in vacuo. Yield: 1.09 g (94%), mp 168−172 °C dec. ^{1}H NMR (CD_3OD): 9.31 (d, J = 2.2, 2H, H-2), 8.86 (dd, J = 4.4, 2.2, 2H, H-6), 8.72 (dd, J = 8.0, 2.2, 2H, H-4), 7.63 (dd, J = 8.0, 4,4, 2H, H-5). ^{13}C NMR (CD_3OD): 154.0 (s, C-2), 152.8 (s, C-6), 145.7 (s, C-4), 128.9 (s, C-5), 121.4 (q, J = 320, OTf), 117.2 (s, C_{ipso}-I). ^{19}F NMR (CD_3OD): −76.4 (s, OTf). IR (neat, cm^{-1}): 1598, 1471, 1279, 1245, 1171, 1149, 1027. MS (FAB, *m/z*): 283 (51) [M−$^-$OTf]$^+$.

[Pd(*R*(+)-BINAP)($C_{10}H_8N_2I$)]$_2$[OTf]$_6$ (7). Bis(3-pyridyl)iodonium triflate (**6**, 29 mg, 0.068 mmol) was dissolved in 8 mL of acetone. To this clear solution was added 71 mg (0.068 mmol) of [Pd(*R*(+)-BINAP)(H_2O)][OTf]$_2$ (**2**) and the solution was stirred at room temperature for 20 min. The solvent was reduced in volume to 1 mL. Diethyl ether−pentane (2:1) mixture was then added, following by formation of a white precipitate, which was collected, washed with the diethyl ether−pentane mixture, and dried in vacuo. Yield: 96 mg (93%), mp 218−221 °C dec. [α]$_D$ +141° (*c* 0.0152, acetone, 20 °C). ^{1}H NMR (acetone-d_6): 9.24 (bs, 8H, overlap of py H-2 and H-6), 8.78 (d, J = 8.5, 4H, py H-4), 8.10−7.81 (m, 8H, BINAP), 7.90−7.70 (overlap of m, 16H, BINAP), 7.65−7.55 (overlap of m, 8H, py H-5+BINAP), 7.50 (s, 16H, BINAP), 7.15−6.90 (overlap of m, 16H, BINAP), 6.44 (d, 4H, J = 8.6, BINAP). ^{13}C NMR (acetone-d_6): 156.7 (s), 156.2 (s), 148.0 (s), 136.1 (s), 135.9 (s), 135.3 (s), 134.7 (s), 134.2 (s), 133.0 (s), 131.6 (overlap of s), 130.7 (overlar of s), 130.2 (s), 130.0 (s), 129.7 (s), 129.3 (s), 128.6 (s), 128.0 (s), 125.2 (s), 124.5 (s), 123.8 (t), 121.4 (q), 119.0 (t), 114.0 (s). ^{31}P NMR (acetone-d_6): 26.0 (s). ^{19}F NMR (acetone-d_6): −75.4 (s, OTf). IR (neat, cm^{-1}): 1249, 1160, 1093, 1028 (all OTf) . Anal. Calcd for $C_{114}H_{80}N_4P_4I_2S_6F_{18}O_{18}Pd2{\cdot}4H_2O$: C, 45.78; H, 2.97; N, 1.87; S, 6.43. Found: C, 45.72; H, 3.02; N, 1.80; S,6.45.

[Pt(*R*(+)-BINAP)($C_{10}H_8N_2I$)]$_2$[OTf]$_6$ (8). To a solution of 15 mg (0.035 mmol) of bis(3-pyridyl)iodonium triflate (**6**) in 5 mL of acetone was added, 40 mg (0.035 mmol) of [Pt(*R*(+)-BINAP)(H_2O)][OTf]$_2$ (**3**) and the mixture was stirred at room temperature for 30 min. The solution was reduced in volume to ca. 0.5 mL and pentane was added, and the white precipitate was filtered, washed with pentane, and dried in vacuo. Yield: 50 mg (91%), mp 232−234 °C dec. [α]$_D$ +99° (*c* 0.0101, acetone, 20 °C). ^{1}H NMR (acetone-d_6): 9.71 (s, 4H, py H-2, isomer B), 9.39 (s, 4H, py H-2, isomer A), 9.28 (d, J = 4.8, 4H, py H-6, isomer A), 8.89 (d, J = 4.8, 4H, py H-6, isomer B), 8.85 (d, J = 8.5, 4H, py H-4, isomer A), 8.47 (d, J = 8.5, 4H, py H-4, isomer B), 8.09 (d, J = 9.7, 4H, BINAP, isomer B), 8.01 (d, J = 9.7, 4H, BINAP, isomer A), 7.90−7.60 (overlap of m, 32H, BINAP, isomers A+B), 7.58−7.40 (overlap of m, 48H, py H-5+BINAP, isomers A+B), 7.15−6.90 (overlap of m, 32H, BINAP, isomers A+B), 6.44 (d, J = 8.6, 4H, BINAP, isomer A), 6.34 (d, J = 8.6, 4H, BINAP, isomer B). ^{13}C NMR (acetone-d_6): 156.9 (s), 156.7 (s), 156.6 (s), 154.0 (s), 153.7 (s), 149.0 (s), 148.6 (s), 148.5 (s), 141.2 (t), 135.6 (s), 135.4 (s), 135.0 (s), 134.6 (s), 134.5 (s), 133.8 (t), 133.3 (t), 132.6 (s), 131.2 (s), 130.8 (s), 130.4 (s), 130.1 (s), 122.6 (s), 129.2 (s), 128.9 (s), 128.2 (s), 123. 8 (s), 123.8 (s), 123.4 (s), 123.0 (s), 122.6 (s), 121.3 (q), 119.5 (s), 119.2 (s), 118.5 (s), 118.3 (s), 115.3 (s), 114.9 (s), 111.8 (s). ^{31}P NMR (acetone-d_6): 1.15 (s, ^{195}Pt satellites, J_{Pt-P} = 3378 Hz, isomer B), 1.11 (s, ^{195}Pt satellites, J_{Pt-P} = 3378 Hz, isomer B), 2.80 (dd, J = 527, 28, ^{195}Pt satellites, J_{Pt-P} = 3378 Hz, syn-isomer). ^{19}F NMR (acetone-d_6): −75.1 (s, OTf). IR (neat, cm^{-1}): 1250, 1152, 1027 (all OTf). Anal. Calcd for $C_{114}H_{80}N_4P_4I_2S_6F_{18}O_{18}Pt_2{\cdot}3H_2O$: C, 43.47; H, 2.75; N, 1.78; S, 6.11. Found: C, 43.45; H, 2.79; N, 1.76; S, 6.05.

[Pd(*cis*-Et_3P)$_2$($C_{10}H_8N_2I$)]$_2$[OTf]$_6$ (11). The solution of 15 mg (0.035 mmol) of bis(3-pyridyl)iodonium triflate (**6**) in 8 mL of acetone was treated with 22 mg (0.034 mmol) of [Pd(*cis*-Et_3P)$_2$][OTf]$_2$ (**9**) and the solution was stirred at room temperature for 10 min. The solvent was reduced in volume to 1 mL in vacuo. Diethyl ether was then added, and the precipitate was filtered, washed with diethyl ether, and dried in vacuo. Yield: 29 mg (77%), ^{1}H NMR (acetone-d_6): 10.0 (bs, 4H, py H-2), 9.63 (bd, 4H, py H-6), 9.37 (bs, 4H, py H-4), 8.35 (bm, 4H, py H-5), 2.08 (m, 24H, PCH_2CH$_3$), 1.35 (m, 36H, PCH$_2$CH_3). ^{31}P NMR (acetone-d_6): 34.9 (s), 35.9 (br m). ^{19}F NMR (acetone-d_6): −76.6 (s, OTf). IR (neat, cm^{-1}): 1259, 1152, 1102, 1028 (all OTf). Anal. Calcd for $C_{50}H_{76}N_4P_4I_2S_6F_{18}O_{18}Pd_2{\cdot}4H_2O$: C, 27.07; H, 3.82; N, 2.53; S, 8.67. Found: C, 27.05; H, 3.96; N, 2.38; S, 8.62.

[Pt(*cis*-Et_3P)$_2$($C_{10}H_8N_2I$)]$_2$[OTf]$_6$ (12). To a solution of 60 mg (0.14 mmol) of bis(3-pyridyl)iodonium triflate (**6**) in 50 mL of acetone was added 101 mg (0.138 mmol) of [Pt(*cis*-Et_3P)$_2$][OTf]$_2$ (**10**) and the solution was stirred at room temperature for 1 h. The solution was reduced in volume to 10 mL and diethyl ether was added, and the white precipitate was filtered, washed, with diethyl ether and dried in vacuo. Yield: 122 mg (75%), mp 218−224 °C dec. ^{1}H NMR (acetone-d_6): 10.24 (s, 4H, py H-2, isomer A), 9.92 (s, 4H, py H-2, isomer B), 9.80 (d, J = 5.1, 4 H, py H-6, isomer B), 9.69 (d, J = 5.1, 4 H, py H-6, isomer A), 9.35 (d, J = 8.3, 8 H, py H-4, isomers A+B), 8.40 (dd, J = 8.3, 5.1, 4 H, py H-5, isomer B), 7.93 (dd, J = 8.3, 5.1, 4 H, py H-5, isomer A), 2.20 (m, 24H, PCH_2CH$_3$, isomer B), 1.98 (m, 12H, PCH_2CH$_3$, isomer A), 1.83 (m, 12H, PCH_2CH$_3$, isomer A), 1.31 (m, 72H, PCH$_2$CH_3, isomers A+B). ^{13}C NMR (acetone-d_6): 156.6 (s, py C-2, isomer A), 155.8 (s, py C-2, isomer B), 155.3 (s, py C-6, isomer A), 155.0 (s, py C-6, isomer B), 150.0 (s, py C-4, isomer A), 149.2 (s, py C-4, isomer B), 132.7 (s, py C-5, isomer B), 132.1 (s, py C-5, isomer A), 121, 3 (q, J = 319, OTf), 118.4 (s, py C_{ipso}-I, isomer B), 115.1 (s, py C_{ipso}-I, isomer A), 15.4 (m, PCH_2CH$_3$, isomers A+B), 8.3 (s, PCH$_2$CH_3, isomer A), 8.2 (s, PCH$_2$CH_3, isomer A), 8.0 (S, PCH$_2$CH_3, isomer B). ^{31}P NMR (acetone-d_6): 2.28 (s, ^{195}Pt satellites, $^1J_{P-Pt}$ = 3116 Hz), 1.73 (s, ^{195}Pt satellites, $^1J_{P-Pt}$ = 3108 Hz). ^{19}F NMR (acetone-d_6): −75.6 (s, OTf). IR (neat, cm^{-1}): 1221, 1153, 1102, 1023 (all OTf). Anal. Calcd for $C_{50}H_{76}N_4P_4I_2S_6F_{18}O_{18}Pt_2{\cdot}3H_2O$: C, 25.26; H, 3.48; N, 2.36; S, 8.09. Found: C, 25.38; H, 3.54; N, 2.22; S, 7.97.

[Pd(*R*(+)-BINAP)(DAA)]$_4$[OTf]$_8$ (15). To a solution of 3.4 mg (0.019 mmol) of 2,6-diazaantracene (**13**) in 8 mL of dry acetone was added 19 mg (0.019 mmol) of [Pd(R(+)-BINAP)][OTf]$_2$ (**2**) and the solution was stirred under nitrogen for 30 min. Diethyl ether was then added and the precipitate was collected, washed with diethyl ether, and dried in vacuo. Yield: 19.2 mg (86%), mp 268−270 °C dec. [α]$_D$ +441° (*c* 0.015, acetone, 20 °C). ^{1}H NMR (acetone-d_6): 9.71 (s, 8H, DAA H-1 and H-5), 8.66 (d, J = 6.8, DAA H-3 and H-7), 8.34 (s, 8H, DAA H-9 and H-10), 8.16 (t, J = 9.0, 8H, BINAP), 8.06 (t, J = 7.6, 8H, BINAP), 7.87 (m, 16H, BINAP+DAA H-4 and H-8), 7.55 (t, J = 8.0, 8H, BINAP), 7.44 (d, J = 6.6, 8H, BINAP), 7.14 (m, 24H, BINAP), 6.87 (t, J = 7.3, 8H, BINAP), 6.46 (d, J = 8.5, 8H, BINAP). ^{13}C NMR (acetone-d_6): 160.2 (s), 141.3 (t), 140.2 (s), 135.7 (overlap of m), 134.2 (t), 132.7 (s), 132.5 (s), 131.6 (s), 131.1 (t), 130.2 (m), 130.0 (s), 129.8 (s), 129.5 (s), 129.4 (s), 128.2 (s), 127.8 (s), 127.7 (s), 125.0 (t), 124.9 (s), 121.3 (q), 120.2 (t). ^{31}P NMR (acetone-d_6): 27.42 (s). ^{19}F NMR (acetone-d_6): −75.7 (s, OTf). IR (neat, cm^{-1}): 1259, 1159, 1097, 1029 (all OTf). Anal. Calcd for $C_{232}H_{160}N_8S_8P_8O_{24}F_{24}Pd_4{\cdot}3H_2O$: C, 57.06; H, 3.43; N, 2.29; S, 5.25. Found: C, 56.94; H, 3.44; N, 2.31; S, 5.28.

[Pt(*R*(+)-BINAP)(DAA)]$_4$[OTf]$_8$ (16). To a solution of 8.2 mg (0.046 mmol) of 2,6-diazaanthracene (**13)** in 10 mL of acetone was added 43.2 mg (0.0379 mmol) of [Pt(R(+)-BINAP)][OTf]$_2$ (**3**) and the solution was stirred under nitrogen for 5 h. Diethyl ether was added resulting in the formation of a precipitate which was collected, washed with diethyl ether, and dried in vacuo. Yield: 42.0 mg (84%), mp 365−367 °C dec. [α]$_D$ +237° (*c* 0.0082, acetone, 20 °C). ^{1}H NMR (acetone-d_6): 9.86 (s, 8H, DAA H-1 and H-5), 8.66 (d, J = 6.4, DAA H-3 and H-7), 8.47 (s, 8H, DAA H-9 and H-10), 8.13 (t, J = 10.0, 8H, BINAP), 8.07 (t, J = 7.7, 8H, BINAP), 7.86 (m, 16H, BINAP+DAA H-4 and H-8), 7.51 (t, J = 7.9, 8H, BINAP), 7.19−7.07 (m, 32H, BINAP), 6.87 (t, J = 7.4, 8H, BINAP), 6.45 (d, J = 8.5, 8H, BINAP). ^{13}C NMR (acetone-d_6): 160.5 (s), 141.2 (t), 140.7 (s), 135.7 (t), 135.6 (s), 134.2 (t), 132.5 (s), 131.7 (s), 131.0 (t), 130.3 (s), 129.7 (s), 129.1(s), 128.1 (s), 127.4 (t), 125.6 (s), 123.4 (t), 123.0 (t), 121.3 (q), 120.2 (t). ^{31}P NMR (acetone-d_6): 0.63 (s, ^{195}Pt satellites, J_{Pt-P} = 3277 Hz). ^{19}F NMR (acetone-d_6): −75.3 (s, OTf). IR (neat, cm^{-1}): 1248, 1152, 1092, 1028 (all OTf). Anal. Calcd for $C_{232}H_{160}N_8S_8P_8O_{24}F_{24}Pt_4{\cdot}6H_2O$: C, 52.65; H, 3.28; N, 2.12; S, 4.85. Found: C, 52.39; H, 3.47; N, 2.15; S, 4.96.

[Pd(*R*(+)-BINAP)(DAAD)]$_4$[OTf]$_8$ (17). To a solution of 22.4 mg (0.107 mmol) of 2,6-diazaantracene-9,10-dione (**14**) in 12 mL of dry acetone was added 105 mg (0.102 mmol) of [Pd(*R*(+)-BINAP)][OTf]$_2$ (**2**) and the solution was stirred under nitrogen for 1 h. Diethyl ether was then added and the yellow precipitate was collected and washed with diethyl ether and the product was dried in vacuo. Yield: 118.2 mg (94%), mp 254−256 °C dec. [α]$_D$ +395° (*c* 0.05, acetone, 20 °C).

^{1}H NMR (acetone-d_6): 9.46 (d, J = 4.8, 8H, DAAD), 8.89 (s, 8H, DAAD), 8.20 (t, J = 9.0, 8H, BINAP), 8.12−8.01 (m, 8H, BINAP), 7.86 (m, 16H, BINAP), 7.65 (d, J = 5.3, 8H, BINAP), 7.57 (t, J = 7.0, 8H, BINAP), 7.33 (t, J = 6.0, 16H, BINAP), 7.28−6.92 (m, 24H, BINAP), 6.43 (d, J = 8.7, 8H, BINAP). ^{13}C NMR (acetone-d_6): 178.0 (s), 155.8 (s), 152.2 (s), 150.3 (s), 141.3 (t), 138.9 (s), 135.9 (s), 135.6 (s), 135.4 (s), 135.2 (s), 134.2 (s), 132.9 (s), 131.3 (s), 130.4 (t), 130.1 (s), 129.1 (s), 128.5 (s), 127.9 (s), 124.9 (t), 123.1 (t), 122.5 (s), 121.3 (q), 119.8 (t). ^{31}P NMR (acetone-d_6): 27.43 (s). ^{19}F NMR (acetone-d_6): −75.6 (s, OTf). IR (neat, cm^{-1}): 1695 (C═O), 1245, 1149, 1027 (all OTf). Anal. Calcd for $C_{232}H_{152}N_8S_8P_8F_{24}O_{32}Pd_4\cdot 3H_2O$: C, 55.69; H, 3.18; N, 2.24; S, 5.13. Found: C, 55.69; H, 3.22; N, 2.27; S, 5.07.

[Pt(*R*(+)-BINAP)(DAAD)]$_4$[OTf]$_8$ (18). To a solution of 19.3 mg (0.0918 mmol) of 2,6-diazaantracene-9,10-dione (**14**) in 8 mL of dry acetone was added 87.1 mg (0.0764 mmol) of [Pt(*R*(+)-BINAP)][OTf]$_2$ (**3**) and the solution was stirred under nitrogen for 3 h. Addition of diethyl ether afforded an off-white precipitate, which was collected, washed with diethyl ether, and dried in vacuo. Yield: 92.1 mg (89%), mp 320−322 °C dec. $[\alpha]_D$ +154° (*c* 0.011, CH_3NO_2, 20 °C). ^{1}H NMR (acetone-d_6): 9.50 (d, J = 5.0, 8H, DAAD), 9.06 (s, 8H, DAAD), 8.30−8.03 (m, 16H, BINAP), 7.83 (m, 16H, BINAP), 7.74 (d, J = 6.0, 8H, BINAP), 7.51 (t, J = 7.3, 8H, BINAP), 7.32 (t, J = 6.8, 16H, BINAP), 7.22 (t, J = 7.1, 8H, BINAP), 7.17−6.98 (m, 16H, BINAP), 6.40 (d, J = 8.6, 8H, BINAP). ^{13}C NMR (acetone-d_6): 177.6 (s), 155.8 (s), 156.4 (s), 152.7 (s), 141.4 (t), 138.9 (s), 139.2 (s), 135.8 (s), 135.6 (s), 135.5 (s), 134.3 (s), 133.0 (s), 132.9 (s), 131.4 (t), 130.3 (s), 130.2 (s), 129.8 (s), 129.2 (s), 128.4 (s), 128.1 (s), 127.6 (s), 124.5 (t), 123.9 (s), 123.6 (s), 123.5 (t), 121.3 (q), 119.9 (t). ^{31}P NMR (acetone-d_6): −1.25 (s, ^{195}Pt satellites, J_{Pt-P} = 3340 Hz, major *anti*-isomer), −1.65 (s, ^{195}Pt satellites, J_{Pt-P} = 3340 Hz, minor *anti*-isomer), −1.90 (dd, J = 24, 115, ^{195}Pt satellites, J_{Pt-P} = 3340 Hz, *syn*-isomer). ^{19}F NMR (acetone-d_6): −75.3 (s, OTf). IR (neat, cm^{-1}): 1695 (C═O), 1250, 1152, 1092, 1028 (OTf). Anal. Calcd for $C_{232}H_{152}N_8S_8P_8F_{24}O_{32}Pt_4\cdot 4H_2O$: C, 51.83; H, 3.00; N, 2.08; S, 4.77. Found: C, 51.68; H, 2.98; N, 2.21; S, 4.73.

[Pd(*S*(−)-BINAP)(H$_2$O)][OTf]$_2$ (19). [Pd(*S*(−)-BINAP)][Cl]$_2$[15] (orange powder, 100 mg, 0.125 mmol) was placed into a 50-mL Schlenk flask equipped with a stir bar and dissolved in CH_2Cl_2 (5 mL). Then, 80.3 g (0.312 mmol) of AgOTf was added, and the resulting solution was allowed to stir 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 1 mL in vacuo. The diethyl ether was added and the yellow precipitate was collected and washed with ether. The solid was collected and dried in vacuo. Yield 108 mg (84%), mp 191−193 °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, OTf). IR (neat, cm^{-1}): 1294, 1162, 1104, 1026 (all OTf). Anal. Calcd for $C_{46}H_{34}P_2S_2F_6O_7Pd$: C, 52.86; H, 3.28; S, 6.13. Found: C, 53.21; H, 3.42; S, 5.96.

[Pt(*S*(−)-BINAP)(H$_2$O)][OTf]$_2$ (20). A 100-mL Schlenk flask equipped with a stir bar was charged with 0.350 g (0.390 mmol) of [Pt(*S*(−)-BINAP)][Cl]$_2$[15] 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 allowed to stir under nitrogen for 5 days at room temperature. The precipitated AgCl 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 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 NMR (CD_2Cl_2): 4.40 (s, ^{195}Pt satellites, $^1J_{P-Pt}$ = 4023 Hz). ^{19}F NMR (CD_2Cl_2): −76.6 (s, OTf). IR (neat, cm^{-1}): 1288, 1170, 1096, 1027 (all OTf). Anal. Calcd for $C_{46}H_{34}P_2S_2F_6O_7Pt$: C, 48.73; H, 3.02; S, 5.65. Found: C, 48.71; H, 3.12; S, 5.58.

[Pd(*S*(−)-BINAP)(DAAD)]$_4$[OTf]$_8$ (21). A 25-mL Schlenk flask was charged with 4.59 mg (0.0218 mmol) of 2,6-diazaantracene-9,10-dione (**14**) and 5 mL of dry acetone. To this solution was added 22.5 mg (0.0215 mmol) of [Pd(*S*(−)-BINAP)(H_2O)][OTf]$_2$ (**19**) and the solution was stirred at room temperature for 20 min. After addition of diethyl ether, the yellow precipitate was collected, washed with a minimum amount of diethyl ether, and dried in vacuo. Yield: 25.6 mg (96%), mp 256−260 °C dec. $[\alpha]_D$ −390° (*c* 0.0098, acetone, 20 °C). The ^{1}H and ^{31}P NMR spectra of **21** were identical to those of **17**.

[Pt(*S*(−)-BINAP)(DAAD)]$_4$[OTf]$_8$ (22). To a solution of 3.22 mg (0.0153 mmol) of 2,6-diazaantracene-9,10-dione (**14**) in 8 mL of dry acetone was added 15.9 mg (0.0137 mmol) of [Pt(*S*(−)-BINAP)(H_2O)][OTf]$_2$ (**20**) and the solution was stirred under nitrogen for 3 h. Diethyl ether was added resulting in the formation of an off-white precipitate, which was collected, washed with diethyl ether, and dried in vacuo. Yield: 14.4 mg (79%), mp 320−322 °C dec. $[\alpha]_D$ −151° (*c* 0.005, CH_3NO_2, 20 °C). The ^{1}H and ^{31}P NMR spectra of **22** were identical to those of **18**.

[Pd(*cis*-Et$_3$P)$_2$(DAAD)]$_4$[OTf]$_8$ (23). A solution of 10 mg (0.048 mmol) of DAAD **14** in 15 mL of dry nitromethane was treated with 30 mg (0.047 mmol) of [Pd(*cis*-$Et_3P)_2$][OTf]$_2$ (**9**). The solution was stirred at room temperature for 10 min, then reduced in volume to 2 mL. Diethyl ether was added and the yellow precipitate was collected, washed with diethyl ether, and dried in vacuo. Yield: 31 mg (78%), mp 240−245 °C dec. ^{1}H NMR (CD_3NO_2): 9.56 (s, 4H), 9.53 (s, 4H), 9.52 (s, 4H), 9.45 (s, 8H), 9.38 (s, 4H), 9.36 (s, 8H), 8.21 (d, J = 8.8, 8H), 8.12 (d, J = 8.8, 8H), 8.11 (d, J = 8.8, 8H), 1.97 (m, 96H), 1.33 (m, 144H). ^{31}P NMR (CD_3NO_2): 38.27 (s), 37.89 (s), 37.85 (s). ^{19}F NMR (CD_3NO_2): −76.8 (s, OTf). IR (neat, cm^{-1}): 1701 (C═O), 1260, 1154, 1029 (all OTf). Anal. Calcd for $C_{104}H_{144}N_8P_8S_8F_{24}O_{32}Pd_4\cdot 4H_2O$: C, 35.93; H, 4.41; N, 3.22; S, 7.38. Found: C, 35.96; H, 4.23; N, 3.23; S, 7.27.

[Pt(*cis*-Et$_3$P)$_2$(DAAD)]$_4$[OTf]$_8$ (24). A 50-mL Schlenk flask was charged with 21 mg (0.10 mmol) of DAAD **14** and 30 mL of dry nitromethane. To this solution was added 70 mg (0.096 mmol) of [Pt(*cis*-$Et_3P)_2$][OTf]$_2$ (**10**) and the solution was stirred at room temperature for 10 min. The solvent was reduced in volume in vacuo and diethyl ether was then added. The white precipitate was collected, washed with diethyl ether, and dried in vacuo. Yield: 80.1 mg (89%), mp 252−258 °C dec. ^{1}H NMR (CD_3OD): 9.76 (s, 4H), 9.70 (s, 4H), 9.56 (s, 8H), 9.48 (d, J = 8.8, 8H), 9.36 (d, J = 8.8, 8H), 8.28 (d, J = 8.8, 8H), 8.16 (d, J = 8.8, 8H), 1.92 (m, 96H), 1.30 (m, 144H). ^{13}C NMR (CD_3OD): 178.1 (s), 155.4 (s), 150.3 (s), 149.9 (s), 141.1 (s), 140.5 (s), 140.1 (s), 131.4 (s), 131.0 (s), 125.0 (s), 15.3 (t, J = 38), 7.2 (s). ^{31}P NMR (CD_3OD): 0.94 (s, ^{195}Pt satellites, $^1J_{P-Pt}$ = 3092 Hz), 0.66 (s, ^{195}Pt satellites, $^1J_{P-Pt}$ = 3092 Hz). ^{19}F NMR (CD_3OD): −76.4 (s, OTf). IR (neat, cm^{-1}): 1709 (C═O), 1260, 1156, 1029 (all OTf). Anal. Calcd for $C_{104}H_{144}N_8P_8S_8F_{24}O_{32}Pt_4\cdot 3H_2O$: C, 32.76; H, 3.97; N, 2.94; S, 6.73. Found: C, 32.75; H, 4.15; N, 2.84; S, 6.51.

Acknowledgment. This article is dedicated to Professor Nelson J. Leonard on the occasion of his 80th birthday. A University of Utah Graduate Research Fellowship to Bogdan Olenyuk is gratefully acknowledged. We thank the National Cancer Institute of NIH (ROCA16903), NSF (CHE-9002690), University of Utah Institutional Funds Committee for financial support, and Johnson−Matthey for the generous loan of platinum salts.

Supporting Information Available: Calculated and observed isotopic distribution data for LSIMS of compounds **7** and **8** and ES mass spectra of **18** (5 pages). See any current masthead page for ordering and Internet access instructions.

JA961444R