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Cyclic Ether Induced Asymmetric Cyclopalladation: Synthesis and Structural Characterization of Enantiopure Bis(μ-acetato)-Bridged Dimers of Planar Chiral Cyclopalladated Ferrocenylimines and Their Derivatives

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Enantiopure bis(μ-acetato)-bridged planar chiral cyclopalladated products $[\overline{\mathrm{Pd}\{(\eta^5\text{-}C_5H_3\text{-}CR{=}N}CH_2\overline{CHCH_2CH_2CH_2O})Fe(\eta^5\text{-}C_5H_5)\}(\mu\text{-}OAc)]_2$ (R = H, Me) have been obtained by asymmetric cyclopalladation of the corresponding chiral ferrocenylimines with palladium(II) acetate and sodium acetate in methanol at room temperature with a high level of diastereoselectivity (product ratio *syn*-(+)-(R_p,*R*,*R*,R_p):*syn*-(−)-(S_p,*R*,*R*,S_p) ≈ *syn*-(−)-(S_p,*S*,*S*,S_p):*syn*-(+)-(R_p,*S*,*S*,R_p) ≈ 9:1). One or both acetato groups can be readily substituted by other anionic ligands to yield novel mixed-bridge or bis(μ-anion)-bridged planar chiral dimers of ferrocene derivatives. The first *cis*-type *syn*-(R_p,S_p) cyclopalladated dimer of ferrocenylimine has been obtained. The diphenylacetylene insertion reaction of a variety of anion-bridged planar chiral dimeric cyclopalladated derivatives of ferrocene has also been investigated. The absolute configurations of bis(μ-acetato)-, bis(μ-halogeno)-, (μ-1κ*S*:2κ*N*)-(μ-1κ*N*:2κ*S*)-thiocyanato-, and (μ-1κ*O*:2κ*N*)-(μ-1κ*N*:2κ*O*)-nitrito-bridged planar chiral dimers and bis(diphenylacetylene) insertion products have been elucidated by single-crystal X-ray analysis.

Introduction

Despite the critical importance of chiral cyclopalladated dimers in catalysis,[1] materials chemistry,[2] optical resolution,[3] the determination of enantiomeric excess[4] and absolute configuration of chiral compounds,[5] and studies on antitumor activity,[6] as well as the promotion of asymmetric Diels−Alder reactions,[1a,d,e] enantiopure cyclopalladated derivatives of ferrocene are scarce.[7−16]

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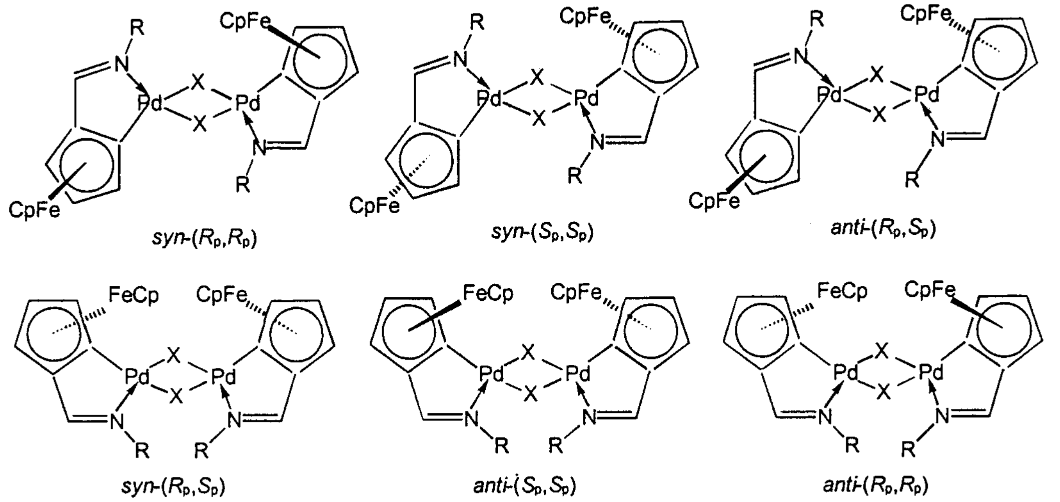

Figure 1. Possible diastereomers of dianion-bridged dimers of planar chiral cyclopalladated ferrocenylimine.

In 1979, Sokolov[7] et al. reported the first single-crystal X-ray structure of a planar chiral cyclopalladated monomer of ferrocene. During the last two decades, cyclopalladated derivatives of ferrocene have been studied extensively.[17,18] Some optically active cyclopalladated derivatives of ferrocene have been obtained, but their absolute configurations have only been determined by means of independent chemical correlations with two previously studied ferrocene derivatives.[8] Recently, the absolute configurations of several planar chiral halogeno-bridged dimers or Lewis base coordinated monomers have been elucidated by X-ray single-crystal analyses.[9−16] As shown in Figure 1, there are six possible diastereomeric bis(μ-anion)-bridged dimers of a planar chiral cyclopalladated ferrocenylimine that differ in regard to their planar chiralities, *cis*/*trans* relationship of the pair of coordinating nitrogen atoms, or *syn*/*anti* arrangement of the ferrocenyl moieties. The arrangement of the pair of coordinating nitrogen atoms is *trans* in three of them, namely *syn*-(R_p,R_p), *syn*-(S_p,S_p), and *anti*-(R_p,S_p), and *cis* in the other three, namely *syn*-(R_p,S_p), *anti*-(S_p,S_p), and *anti*-(R_p,R_p). López[9] et al. reported the X-ray single-crystal structure of *anti*-(S_p,S_p)-(+)-[$Pd\{(\eta^5-C_5H_3CH(CH_3)N(CH_3)_2Fe(\eta^5-C_5H_5)\}$-($\mu$-Cl)]$_2$ in 1996. In our recent studies, the *syn*-(R_p,R_p)-, *syn*-(S_p,S_p)-, and *anti*-(R_p,S_p)-type dimers have been obtained and characterized by X-ray crystallography.[14] Hitherto the remaining two dimers, *syn*-(R_p,S_p) and *anti*-(R_p,R_p), have not been isolated due to their unstable configuration caused by steric repulsion between the *cis*-related imino R groups. In this paper we present a simple and highly stereoselective synthesis of enantiopure bis(μ-acetato)-bridged planar chiral cyclopalladated ferrocenylimines and the first evidence of a *syn*-(R_p,S_p)-type dimer. Novel mixed-bridge and bis(μ-anion)-bridged planar chiral dimers of ferrocene have been obtained by anion exchange reactions. Their absolute configurations and diphenylacetylene insert reaction are also reported.

Results and Discussion

Ligand Synthesis. The optically pure ferrocenylimines (−)-(*R*)-**1a**, (+)-(*S*)-**1a**, (−)-(*R*)-**1b** and (+)-(*S*)-**1b** were obtained as orange plates in 59−75% yield from the reaction between acylferrocene and (−)-(*R*)-tetrahydrofurfurylamine or (+)-(*S*)-tetrahydrofurfurylamine in benzene. For these systems the presence of molecular sieves (5 Å) was needed to enforce favorable displacement of the equilibria, as the chiral ferrocenylimines readily decomposed in the purification procedure using column chromatography. ^{1}H NMR and ^{13}C{^{1}H} NMR spectra in CDCl$_3$ of the compounds (−)-(*R*)-**1a**, (+)-(*S*)-**1a**, (−)-(*R*)-**1b**, and (+)-(*S*)-**1b** provide useful information about their structure and behavior in solution (see Experimental Section).

Asymmetric Cyclopalladation of Ferrocenylimines (−)-(*R*)-1a, (+)-(*S*)-1a, (−)-(*R*)-1b, and (+)-(*S*)-1b with Palladium Acetate and Sodium Acetate. Asymmetric cyclopalladation of the ferrocenylimines (−)-(*R*)-**1a**, (+)-(*S*)-**1a**, (−)-(*R*)-**1b** and (+)-(*S*)-**1b** with $Pd(OAc)_2$ and $NaOAc{\cdot}3H_2O$ in MeOH gave a mixture of cyclopalladated compounds (Scheme 1). Chromatographic separation of each mixture yielded two bis(μ-acetato)-bridged diastereomers, [$Pd\{(\eta^5-C_5H_3CR{=}NCH_2CHCH_2CH_2CH_2O)Fe(\eta^5-C_5H_5)\}(\mu-OAc)$]$_2$ (R = H, *syn*-

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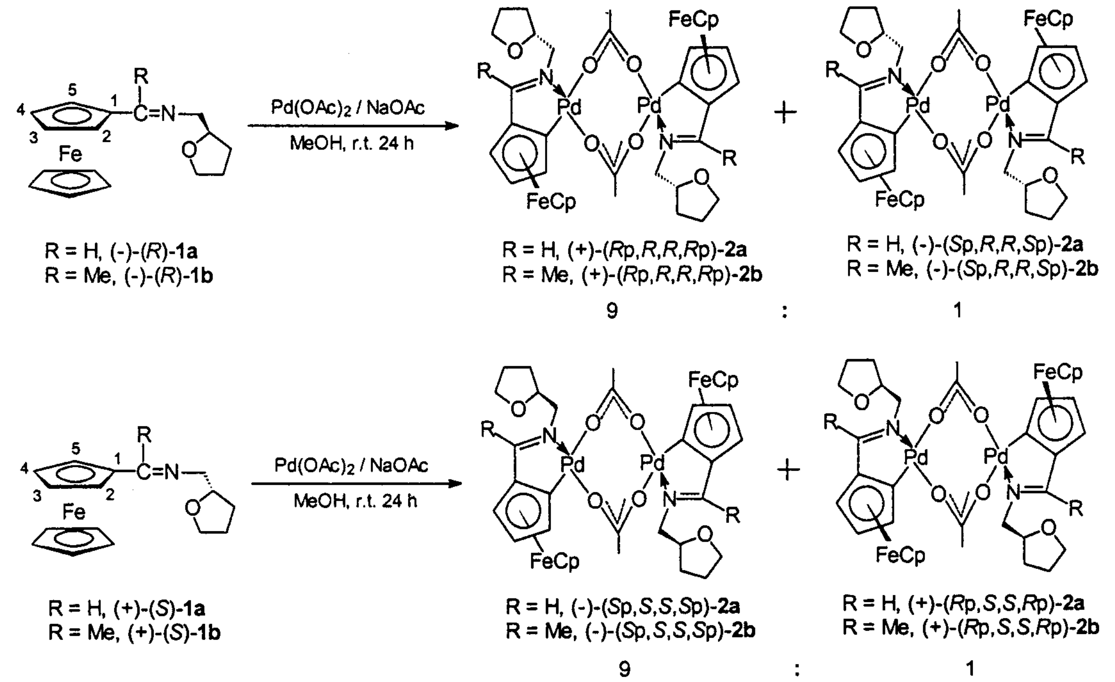
Scheme 1. Asymmetric Cyclopalladation of Ferrocenylimines



(+)-$(R_\mathrm{p},R,R,R_\mathrm{p})$-**2a** and *syn*-(−)-$(S_\mathrm{p},R,R,S_\mathrm{p})$-**2a** for (−)-$(R)$-**1a**; *syn*-(−)-$(S_\mathrm{p},S,S,S_\mathrm{p})$-**2a** and *syn*-(+)-$(R_\mathrm{p},S,S,R_\mathrm{p})$-**2a** for (+)-$(S)$-**1a**; R = Me, *syn*-(+)-$(R_\mathrm{p},R,R,R_\mathrm{p})$-**2b** and *syn*-(−)-$(S_\mathrm{p},R,R,S_\mathrm{p})$-**2b** for (−)-$(R)$-**1b**; *syn*-(−)-$(S_\mathrm{p},S,S,S_\mathrm{p})$-**2b** and *syn*-(+)-$(R_\mathrm{p},S,S,R_\mathrm{p})$-**2b** for (+)-$(S)$-**1b**), in ca. 60% yield at a high level of diastereoselectivity (product ratio *syn*-(+)-$(R_\mathrm{p},R,R,R_\mathrm{p})$-**2**:*syn*-(−)-$(S_\mathrm{p},R,R,S_\mathrm{p})$-**2** ≈ *syn*-(−)-$(S_\mathrm{p},S,S,S_\mathrm{p})$-**2**:*syn*-(+)-$(R_\mathrm{p},S,S,R_\mathrm{p})$-**2** ≈ 9:1).

Cyclopalladation is usually carried out in acetic acid, one of the standard solvents. However, a complex reaction mixture is obtained when cyclopalladation of ferrocenylimines is carried out in this solvent due to the acid sensitivity of imine, which causes difficulty in purification. We found that cyclopalladation of this kind of imine with $Pd(OAc)_2$ and $NaOAc{\cdot}3H_2O$ in MeOH (nonacidic medium) at room temperature gives planar chiral compounds of ferrocene in good yield with a high level of stereoselectivity.

The interrelationship of all enantiopure planar chiral compounds was elucidated by ^1H NMR and single-crystal X-ray analysis. It is noted that the ^1H NMR spectra in $CDCl_3$ of enantiomers are similar but obviously quite different from those of their diastereomers. The ^1H NMR spectra of *syn*-(+)-$(R_\mathrm{p},R,R,R_\mathrm{p})$-**2a**, *syn*-(−)-$(S_\mathrm{p},R,R,S_\mathrm{p})$-**2a**, *syn*-(−)-$(S_\mathrm{p},S,S,S_\mathrm{p})$-**2a**, *syn*-(+)-$(R_\mathrm{p},S,S,R_\mathrm{p})$-**2a**, *syn*-(+)-$(R_\mathrm{p},R,R,R_\mathrm{p})$-**2b**, *syn*-(−)-$(S_\mathrm{p},R,R,S_\mathrm{p})$-**2b**, *syn*-(−)-$(S_\mathrm{p},S,S,S_\mathrm{p})$-**2b**, and *syn*-(+)-$(R_\mathrm{p},S,S,R_\mathrm{p})$-**2b** show the *trans* arrangement of the ligands in all acetato-bridged cyclopalladated compounds, with the acetato-bridge methyl groups appearing as only singlets at 2.03, 2.01, 2.03, 2.07, 2.09, 2.07, and 2.06 ppm, respectively (the *cis* arrangement of the ligands in the complex shows the methyl groups appearing as two singlets).[19] In the ^1H NMR spectra of the free ligands (−)-(R)-**1a**, (+)-(S)-**1a**, (−)-(R)-**1b**, and (+)-(S)-**1b**, chemical shifts are 4.12−4.13 ppm for the unsubstituted cyclopentadienyl protons and 4.27 (H^3, H^4) and 4.70 (H^2, H^5) ppm for substituted cyclopentadienyl protons. However, the signals due to substituted cyclopentadienyl protons in cyclopalladated compounds split into three signals (4.19, 4.28, and 4.39 ppm for *syn*-(+)-$(R_\mathrm{p},R,R,R_\mathrm{p})$-**2a**, *syn*-(−)-$(S_\mathrm{p},S,S,S_\mathrm{p})$-**2a**, *syn*-(+)-$(R_\mathrm{p},R,R,R_\mathrm{p})$-**2b**, and *syn*-(−)-$(S_\mathrm{p},S,S,S_\mathrm{p})$-**2b**; 4.17, 4.21, and 4.22 ppm for *syn*-(−)-$(S_\mathrm{p},R,R,S_\mathrm{p})$-**2a,** *syn*-(+)-$(R_\mathrm{p},S,S,R_\mathrm{p})$-**2a**, *syn*-(−)-$(S_\mathrm{p},R,R,S_\mathrm{p})$-**2b**, and *syn*-(+)-$(R_\mathrm{p},S,S,R_\mathrm{p})$-**2b**), among which H^3, H^5, and H^4 all shifted upfield. However, chemical shifts for the unsubstituted cyclopentadienyl protons for all cyclopalladated compounds are 4.21−4.26 ppm, which shifted downfield by ca. 0.10−0.13 ppm. One of the most relevant differences observed in the $^{13}C\{^1H\}$ NMR spectra of free ligands and those of their cyclopalladated complexes is the splitting of the resonance due to the C^3, C^4 pair of carbon atoms, since the formation of the metallacycle causes a decrease in the symmetry of the substituted cyclopentadienyl ring. The signals from the cyclopalladated carbon atoms appear between 100 and 103 ppm, corresponding to a 30−33 ppm downfield shift from the signals of the parent ferrocenylimines, probably due to Pd−C back-bonding.[20] The diastereoselectivity of the ortho-palladation reaction can be explained by the cyclic ether induction model shown in Figure 2, assuming prior coordination by the oxygen atom of the tetrahydrofurfuryl group, a process often encountered in asymmetric synthesis.[21−23]

Synthesis of *cis*-Planar Chiral Cyclopalladated *μ*-Chloro *μ*-Acetato Mixed-Bridge Dimer. Asymmetric cyclopalladation of chiral ferrocenylimine (+)-(S)-**1a** with Na_2PdCl_4 and NaOAc gives the major product *syn*-(−)-$(S_\mathrm{p},S,S,S_\mathrm{p})$-**4a** and the minor product

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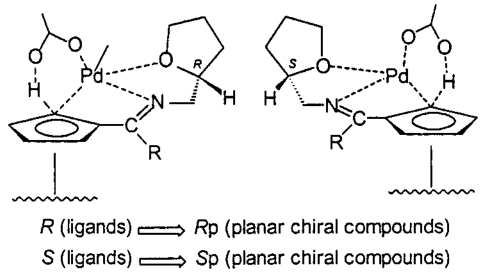
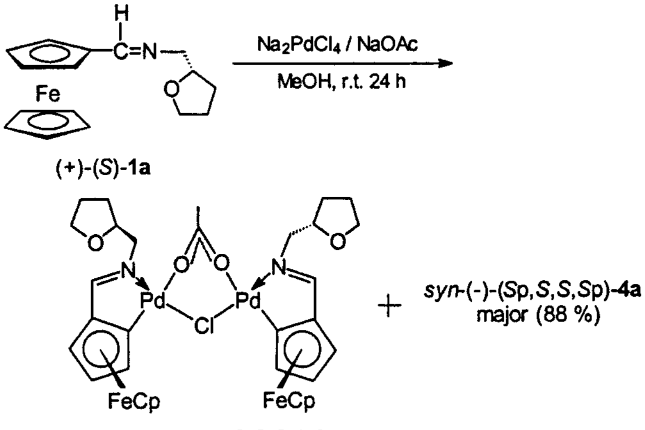


Figure 2. Model accounting for the stereoselectivity of ortho palladation of ferrocenylimines.

Scheme 2. Synthesis of the *cis*-Planar Chiral Cyclopalladated Derivative of Ferrocenylimine *syn*-(−)-(R_p,*S*,*S*,S_p)-3.



syn-(-)-(*R*p,*S*,*S*,*S*p)-3
minor (12 %)

syn-(−)-(R_p,*S*,*S*,S_p)-**3** (*syn*-(−)-(S_p,*S*,*S*,S_p)-**4a**:*syn*-(−)-(R_p,*S*,*S*,S_p)-**3** = 6.3:1) (Scheme 2). To our knowledge, the latter is the first example among the three possible *cis* structures[14] of a dimeric planar chiral ferrocenylimine. Formation of the *μ*-chloro *μ*-acetato mixed bridges under these reaction conditions also provides evidence of the mechanism of cyclopalladation catalyzed by sodium acetate, because the bis(*μ*-acetato) bridge is readily converted into a bis(*μ*-chloro) bridge but not vice versa.

NMR spectra and microanalysis confirmed the formulation of *syn*-(−)-(R_p,*S*,*S*,S_p)-**3,** and X-ray analysis established its absolute configuration. The signal due to unsubstituted cyclopentadienyl protons is 4.24 ppm, which is shifted downfield by 0.12 ppm, and the chemical shifts for substituted cyclopentadienyl protons are 4.15, 4.31, and 4.37 ppm, respectively. The signal of H^3 shifted upfield by 0.12 ppm, and those of H^4 and H^5 shifted downfield by 0.05 and 0.33 ppm in comparison with the free ligands. The signal from the cyclopalladated carbon atoms appears at 99.8 ppm, corresponding to a 29.8 ppm downfield shift from the signals of the parent ferrocenylimines, probably due to Pd−C backbonding.[20]

Synthesis of *cis*-Planar Chiral Cyclopalladated Bis(*μ*-anion)-Bridged Dimers. Bis(*μ*-acetato)-bridged planar chiral cyclopalladated dimers dissolve in methanol and readily react with MA (A = Cl, Br, I, NO_2, and SCN) at MA:Pd_2-complex molar ratios in the range of 2−5, to form a series of bis(*μ*-anion)-bridged planar chiral dimers by substitution of the acetato groups.

Formation of Bis(*μ*-halogeno)-Bridged Planar Chiral Dimers. Bis(*μ*-halogeno)-bridged planar chiral cyclopalladated derivatives of ferrocenylimines were prepared by the treatment of bis(*μ*-acetato)-bridged dimers with LiCl, LiBr, and KI in methanol at room temperature for 15 min, respectively. Chemical shifts for substituted cyclopentadienyl protons of bis(*μ*-halogeno)-bridged dimers are 4.25, 4.33, and 4.40 ppm, respectively. Moreover, the signals due to unsubstituted cyclopentadienyl protons all shifted downfield by ca. 0.40 ppm at 4.55 ppm in comparison with their free ligands. In all spectra of cyclopalladated compounds, H^3 and H^4 shifted upfield and H^5 downfield.

Formation of Bis(*μ*-nitrito)- or Bis(*μ*-thiocyanato)-Bridged Planar Chiral Dimers. Although many bis(*μ*-halogeno)-bridged cyclopalladated derivatives of ferrocene have been synthesized, there has as yet been no report on any bis(*μ*-nitrito)- or bis(*μ*-thiocyanato) analogue. We have found that bis(*μ*-acetato)-bridged planar chiral cyclopalladated derivatives of ferrocene can readily react with $NaNO_2$ or KSCN in methanol at room temperature to give the bis(*μ*-nitrito)- or bis(*μ*-thiocyanato)-bridged dimers $[Pd\{(\eta^5\text{-}C_5H_3CR{=}NCH_2CHCH_2\text{-}CH_2CH_2O)Fe(\eta^5\text{-}C_5H_5)\}(\mu\text{-}X)]_2$ (X = NO_2, R = H, *syn*-(+)-(R_p,*R*,*R*,R_p)-**6a**, *syn*-(−)-(S_p,*S*,*S*,S_p)-**6a**; X = NO_2, R = Me, *syn*-(+)-(R_p,*R*,*R*,R_p)-**6b**, *syn*-(−)-(S_p,*S*,*S*,S_p)-**6b**; X = SCN, R = H, *syn*-(+)-(R_p,*R*,*R*,R_p)-**7a**, *syn*-(−)-(S_p,*S*,*S*,S_p)-**7a**; X = SCN, R = Me, *syn*-(+)-(R_p,*R*,*R*,R_p)-**7b**, *syn*-(−)-(S_p,*S*,*S*,S_p)-**7b**), respectively, with very high yield and no changes of configuration during the reaction process (Scheme 3).

Microanalysis indicated that all the compounds are dimeric cyclopalladated complexes. Chemical shifts for the substituted cyclopentadienyl protons of bis(*μ*-nitrito)-bridged dimers *syn*-(+)-(R_p,*R*,*R*,R_p)-**6a**, *syn*-(−)-(S_p,*S*,*S*,S_p)-**6a**, *syn*-(+)-(R_p,*R*,*R*,R_p)-**6b**, and *syn*-(−)-(S_p,*S*,*S*,S_p)-**6b** are ca. 4.21, 4.29, and 4.34 ppm, respectively, but those of bis(*μ*-thiocyanato)-bridged dimers *syn*-(+)-(R_p,*R*,*R*,R_p)-**7a**, *syn*-(−)-(S_p,*S*,*S*,S_p)-**7a**, *syn*-(+)-(R_p,*R*,*R*,R_p)-**7b**, and *syn*-(−)-(S_p,*S*,*S*,S_p)-**7b** are ca. 4.27, 4.41, and 4.45 ppm, respectively. Moreover, the signals due to unsubstituted cyclopentadienyl protons of bis(*μ*-nitrito)-bridged dimers shifted downfield by 0.27 ppm at 4.39 ppm and those of bis(*μ*-thiocyanato)-bridged dimers shifted much more downfield by 0.57 ppm at 4.69 ppm. In all spectra of cyclopalladated compounds, H^3 shifted upfield and H^4 and H^5 downfield.

Diphenylacetylene Insertion Reactions of Bis(*μ*-anion)-Bridged Planar Chiral Dimers. Diphenylacetylene insertion reactions of the bis(*μ*-halogeno)-bridged dimers have been investigated widely. In general, the reaction is controlled not only by the three important variables (i) the nature of the donor atom in the palladacyclic substrate, (ii) the nature of the substituents on the alkyne, and (iii) the size of the chelate ring in the cyclopalladated substrate and the presence or absence of additional heteroatoms within the chelate ring[24] but also by (iv) the nature of the remaining ligands bound to palladium(II), as shown in this work. Diphenylacetylene insertion reactions of the bis(*μ*-chloro) and bis(*μ*-bromo)-bridged analogues have been reported in our previous studies.[11,16] Here we present a

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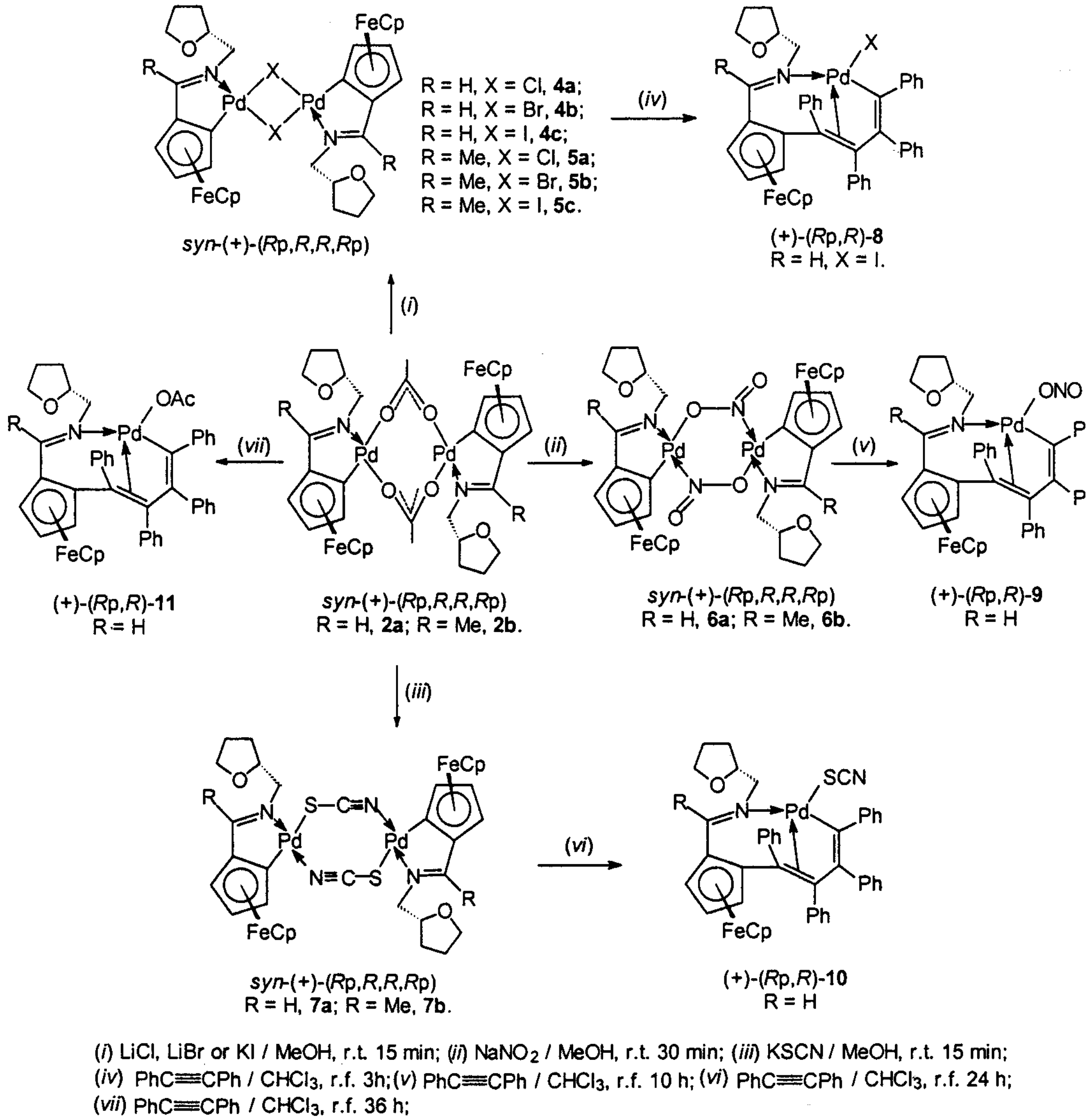
(24) Davies, J. A. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G., Wilkinson, G., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 9, p 321.

Scheme 3. Preparation of *trans* Bis(μ-anion)-Bridged Planar Chiral Cyclopalladated Derivatives of Ferrocene and Their Alkyne-Insertion Reactions[a]



(*i*) LiCl, LiBr or KI / MeOH, r.t. 15 min; (*ii*) $NaNO_2$ / MeOH, r.t. 30 min; (*iii*) KSCN / MeOH, r.t. 15 min;
(*iv*) PhC≡CPh / $CHCl_3$, r.f. 3h; (*v*) PhC≡CPh / $CHCl_3$, r.f. 10 h; (*vi*) PhC≡CPh / $CHCl_3$, r.f. 24 h;
(*vii*) PhC≡CPh / $CHCl_3$, r.f. 36 h;

[a] Their enantiomers are obtained under the same conditions.

comparative study including the bis(μ-iodo)-, bis(μ-acetato)-, bis(μ-nitrito)-, and bis(μ-thiocyanato)-bridged dimers.

The bis(μ-halogeno)-bridged dimers readily react with diphenylacetylene,[11,16] but the bis(μ-nitrito)-, bis(μ-thiocyanato)-, and bis(μ-acetato)-bridged dimers appear to be much less reactive (see Experimental Section), presumably because the reaction is controlled by the electronic effect of anion bridges. The replacement of a hydrogen atom by a methyl group is expected to modify the electron donor nature of the metalated ligand. The bis(μ-anion)-bridged cyclopalladated dimers containing Schiff bases derived from acetylferrocene (R = Me) might be expected to undergo bis insertion of alkynes more easily than their analogues with R = H containing identical bridging groups. However, no electron-releasing effect of the methyl group was found in the reaction. The ^1H NMR spectra of the four bis(diphenylacetylene) insertion compounds are similar: the signals due to unsubstituted cyclopentadienyl protons are 4.11, 4.10, 4.20, and 4.19 ppm for (+)-(R_p,R)-**8**, (+)-(R_p,R)-**9**, (+)-(R_p,R)-**10**, and (+)-(R_p,R)-**11**, respectively, and chemical shifts for the substituted cyclopentadienyl protons are 4.20, 4.38, and 4.58 ppm for (+)-(R_p,R)-**8**, 4.20, 4.38, and 4.58 ppm for (+)-(R_p,R)-**9**, 4.29, 4.36, and 4.59 ppm for (+)-(R_p,R)-**10,** and 4.28, 4.36, and 4.42 ppm for (+)-(R_p,R)-**11**. In addition to this information, the existence of a multiplet between 6.61 and 7.47 ppm indicates that the bis(diphenylacetylene) insertion compound is obtained.

Crystal and Molecular Structures of *syn*-(−)-(S_p,S,S,S_p)-2a, *syn*-(+)-(R_p,S,S,R_p)-2a·CH_2Cl_2, and *syn*-(+)-(R_p,R,R,R_p)-2b. X-ray analysis has established the absolute planar chiralities of the ferrocenyl moieties on the basis of the (−)-(R)-tetrahydrofurfurylamine, (+)-(S)-tetrahydrofurfurylamine marker in the compounds *syn*-(−)-(S_p,S,S,S_p)-**2a** (Figure 3), *syn*-(+)-(R_p,S,S,R_p)-**2a**·CH_2Cl_2 (Figure 4), and *syn*-(+)-(R_p,R,R,R_p)-**2b**. *syn*-(−)-(S_p,S,S,S_p)-**2a** and syn-(+)-(R_p,R,R,R_p)-**2b** are nearly like a pair of enantiomers, except that the hydrogens H(11A) and H(27A) are replaced by methyl groups. *syn*-(−)-(S_p,S,S,S_p)-**2a** and *syn*-(+)-(R_p,S,S,R_p)-**2a**·CH_2Cl_2 are diastereomers. In all cases, the acetate groups force the two square planes of each palladium atom to have

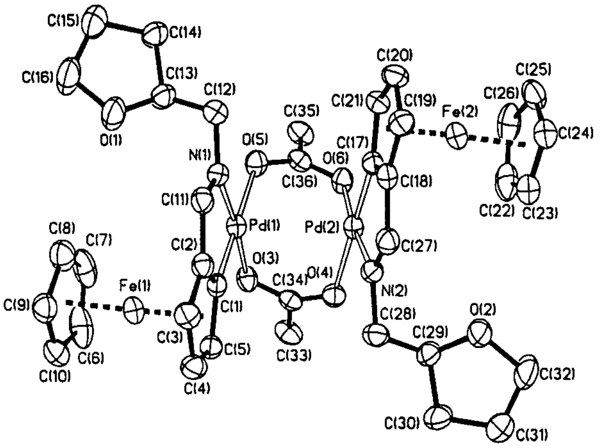


Figure 3. Molecular structure (30% thermal ellipsoids) and absolute configuration of the bis(μ-acetato)-bridged planar chiral dimer *syn*-(−)-(S_p,*S*,*S*,S_p)-**2a** with atom-numbering scheme.

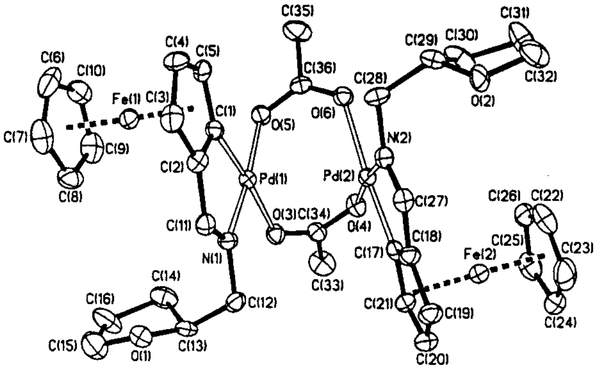


Figure 4. Molecular structure (30% thermal ellipsoids), atom-numbering scheme, and absolute configuration of the bis(μ-acetato)-bridged planar chiral dimer *syn*-(+)-(R_p,*S*,*S*,R_p)-**2a** as its 1:1 adduct with CH_2Cl_2.

a relatively small dihedral angle between the planes N(1)−Pd(1)−C(1) and O(3)−Pd(1)−O(5) (tilt angle: 3.1° for *syn*-(−)-(S_p,*S*,*S*,S_p)-**2a**, 3.1° for *syn*-(+)-(R_p,*S*,*S*,R_p)-**2a**·CH_2Cl_2, and 5.6° (molecule A) and 2.2° (molecule B) for *syn*-(+)-(R_p,*R*,*R*,R_p)-**2b**), resulting in the molecule adopting a clam-like shape. The angle between the two planes defined by Pd(1), Pd(2), O(3), O(4) and Pd(1), Pd(2), O(5), O(6), respectively, is 90.0° in *syn*-(−)-(S_p,*S*,*S*,S_p)-**2a**, 83.1° in *syn*-(+)-(R_p,*S*,*S*,R_p)-**2a**·CH_2Cl_2, and 91.2° (molecule A) and 86.6° (molecule B) in *syn*-(+)-(R_p,*R*,*R*,R_p)-**2b**. The angle between the two planes of the palladacycles is 26.3° in *syn*-(−)-(S_p,*S*,*S*,S_p)-**2a**, 32.2° in *syn*-(+)-(R_p,*S*,*S*,R_p)-**2a**·CH_2Cl_2, and 17.0° (molecule A) and 17.8° (molecule B) in *syn*-(+)-(R_p,*R*,*R*,R_p)-**2b**. The angle in *syn*-(+)-(R_p,*S*,*S*,R_p)-**2a**·CH_2Cl_2 is significantly larger than those in *syn*-(−)-(S_p,*S*,*S*,S_p)-**2a** and *syn*-(+)-(R_p,*R*,*R*,R_p)-**2b**. As a consequence, the distances Pd(1)···Pd(2) in *syn*-(−)-(S_p,*S*,*S*,S_p)-**2a** and *syn*-(+)-(R_p,*R*,*R*,R_p)-**2b** (1.84 Å) are shorter than that in *syn*-(+)-(R_p,*S*,*S*,R_p)-**2a**·CH_2Cl_2 (2.94 Å). All of these Pd(1)···Pd(2) distances are regarded as nonbonding; the covalent radius of square-planar Pd(II) has been estimated as approximately 1.31 Å.[25] The cyclopentadienyl rings are each planar and nearly parallel to each other (tilt angle: 2.7° for *syn*-(−)-(S_p,*S*,*S*,S_p)-**2a**, 2.8° (molecule A) and 2.4° (molecule B) for *syn*-(+)-(R_p,*R*,*R*,R_p)-**2b**, and 0.7° for *syn*-(+)-(R_p,*S*,*S*,R_p)-**2a**·CH_2Cl_2), and the two rings involved in the bicyclic system formed by fusion of the palladacycle with the ferrocenyl C_5H_3 moiety are approximately coplanar, the relevant dihedral angle being 2.3° for *syn*-(−)-(S_p,*S*,*S*,S_p)-**2a**, 5.0° (molecule A) and 3.9° (molecule B) for *syn*-(+)-(R_p,*R*,*R*,R_p)-**2b**, and 1.5° for *syn*-(+)-(R_p,*S*,*S*,R_p)-**2a**·CH_2Cl_2.

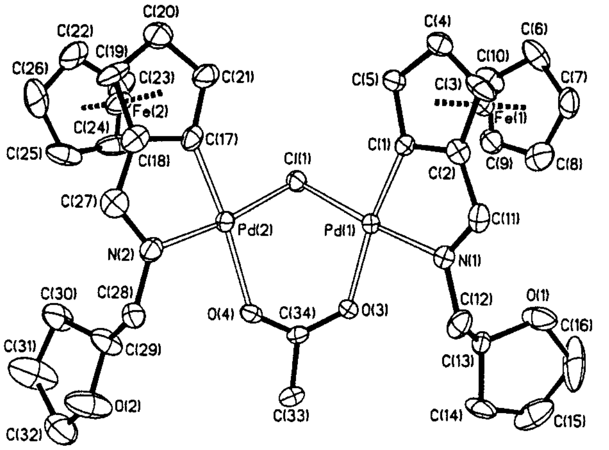


Figure 5. Molecular structure (30% thermal ellipsoids) and absolute configuration of the μ-chloro μ-acetato mixed-bridge dimer *syn*-(−)-(R_p,*S*,*S*,S_p)-**3** with atom-numbering scheme.

The Pd−N bond lengths are normal; however, all Pd−C bond lengths (1.926(3) Å in *syn*-(−)-(S_p,*S*,*S*,S_p)-**2a**, 1.940(2) Å in *syn*-(+)-(R_p,*R*,*R*,R_p)-**2b**, and 1.949(2) Å in *syn*-(+)-(R_p,*S*,*S*,R_p)-**2a**·CH_2Cl_2) are substantially shorter than the predicted value of 2.05 Å.[20] This suggests some multiple-bond character in Pd−C linkages due to metal-to-ligand back-bonding.[20] The Pd−O bonds, Pd(1)−O(3) and Pd(1)−O(6), having nitrogen atoms in *trans* positions, are significantly shorter (2.040(3), 2.030(2) Å for *syn*-(−)-(S_p,*S*,*S*,S_p)-**2a**, 2.019(3), 2.038(3) Å for *syn*-(+)-(R_p,*R*,*R*,R_p)-**2b**, and 2.061(2), 2.048(4) Å for *syn*-(+)-(R_p,*S*,*S*,R_p)-**2a**·CH_2Cl_2) than those (Pd(1)−O(4) and Pd(1)−O(5)) showing a *trans* relationship with respect to the ferrocenyl carbon (2.165(3), 2.162(2) Å for *syn*-(−)-(S_p,*S*,*S*,S_p)-**2a**, 2.141(2), 2.164(2) Å for *syn*-(+)-(R_p,*R*,*R*,R_p)-**2b**, and 2.142(1), 2.148(2) Å for *syn*-(+)-(R_p,*S*,*S*,R_p)-**2a**·CH_2Cl_2), as a consequence of the different *trans* influences of both atoms.[26,27]

Crystal and Molecular Structures of *syn*-(−)-(*R*_p,*S*,*S*,*S*_p)-3. X-ray analysis has established the absolute planar chiralities of the ferrocenyl moieties. The asymmetric unit in the crystal structure of *syn*-(−)-(R_p,*S*,*S*,S_p)-**3** contains two independent molecules (designated A and B) that are nearly alike, and only molecule A is shown (Figure 5). The pair of coordinating N atoms bears a *cis* relationship, and each palladium atom in the metallacycle is in a slightly distorted square-planar coordination environment. With reference to the mean planes of the palladacycles, the pair of ferrocenyl groups takes a *syn* arrangement. The angle between the two planes of the palladacycles is 99.8° (molecule A) and 98.6° (molecule B), being significantly

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(25) Churchill, M. R.; Wasserman, H. J.; Young, G. J. *Inorg. Chem.* **1980**, *19*, 762.

(26) Garcia-Ruano, J. L.; López-Solera, I.; Masaguer, J. R.; Navarro-Ranninger, C.; Rodriguez, J. H.; Martinez-Carrera, S. *Organometallics* **1992**, *11*, 3013.

(27) Caygill, G. B.; Steel, P. J. *J. Organomet. Chem.* **1987**, *327*, 115.

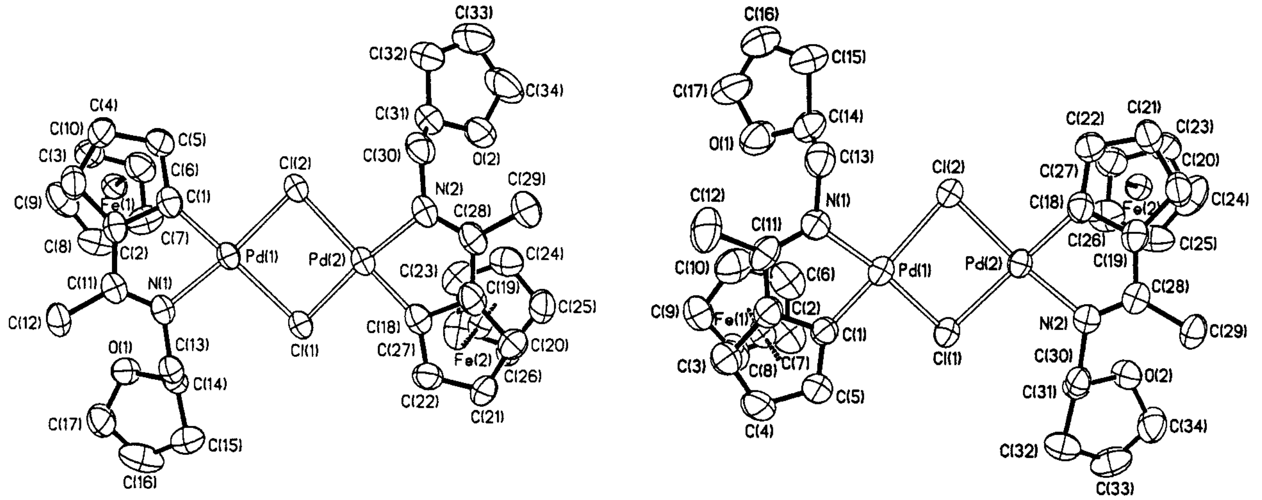

Figure 6. Molecular structures (30% thermal ellipsoids) and absolute configurations of the pair of bis(μ-chloro)-bridged enantiomers *syn*-(+)-(R_p,R,R,R_p)-**5a** (left) and *syn*-(−)-(S_p,S,S,S_p)-**5a** (right) with atom-numbering schemes.

larger than that in bis(μ-acetato)-bridged dimers. Consequently, the distance between the palladium atoms (3.213(1) Å for molecule A; 3.197(1) Å for molecule B) is much longer than that (2.84−2.94 Å) in bis(μ-acetato)-bridged dimers, resulting in the molecule adopting a half-opened book shape. The cyclopentadienyl rings are each planar and nearly parallel to each other (tilt angle: 2.3° (molecule A) and 2.2° (molecule B)), and the two rings involved in the bicyclic system formed by fusion of the palladacycle with the ferrocenyl C_5H_3 moiety are approximately coplanar, the relevant dihedral angle being 2.5° (molecule A) and 3.0° (molecule B).

The Pd−N bond lengths are normal; however, all Pd−C bond lengths (1.984(2), 1.987(2) Å (molecule A) and 1.956(2), 1.937(2) Å (molecule B)) are substantially shorter than the predicted value of 2.05 Å.[20] This is suggestive of some multiple-bond character in the Pd−C linkages due to metal-to-ligand back-bonding.[20] Due to the *cis* structure the Pd−O bonds (2.091(2), 2.155(3) Å (molecule A) and 2.109(2), 2.131(2) Å (molecule B)) are similar to each other, as are the Pd−Cl bonds (2.321(1), 2.330(1) Å (molecule A) and 2.327(1), 2.327(1) Å (molecule B)).

Crystal and Molecular Structures of *syn*-(+)-(R_p,R,R,R_p)-4a, *syn*-(−)-(S_p,S,S,S_p)-4a, *syn*-(+)-(R_p,R,R,R_p)-4b, *syn*-(+)-(R_p,R,R,R_p)-5a, and *syn*-(−)-(S_p,S,S,S_p)-5a. With reference to the mean plane of the Pd and X atoms, the pair of ferrocenyl groups takes a *cis* arrangement in all the compounds (Figure 6). The Pd_2X_2 ring is significantly folded (the angle between the two planes defined by the atoms Pd(1), X(1), X(2) and Pd(2), X(1), X(2) is 29.3° for *syn*-(−)-(S_p,S,S,S_p)-**4a**, 29.1° for *syn*-(+)-(R_p,R,R,R_p)-**4a**, 38.5° for *syn*-(−)-(S_p,S,S,S_p)-**5a**, 38.3° for *syn*-(+)-(R_p,R,R,R_p)-**5a**, and 28.0° for *syn*-(+)-(R_p,R,R,R_p)-**4b**). Each palladium atom in the metallacycle is in a slightly distorted square-planar coordination environment. In all structures, the two cyclopentadienyl rings are each planar and nearly parallel to each other (tilt angle: 3.3° for *syn*-(−)-(S_p,S,S,S_p)-**4a**, 1.4° for *syn*-(+)-(R_p,R,R,R_p)-**4a**, 1.3° for *syn*-(−)-(S_p,S,S,S_p)-**5a**, 2.7° for *syn*-(+)-(R_p,R,R,R_p)-**5a**, and 2.0° for *syn*-(+)-(R_p,R,R,R_p)-**4b**) and the two rings involved in the bicyclic system formed by fusion of the palladacycle with the ferrocenyl C_5H_3 moiety are approximately coplanar, the relevant dihedral angle being 7.9° for *syn*-(−)-(S_p,S,S,S_p)-**4a**, 3.5° for *syn*-(+)-(R_p,R,R,R_p)-**4a**, 4.7° for *syn*-(−)-(S_p,S,S,S_p)-**5a**, 3.8° for *syn*-(+)-(R_p,R,R,R_p)-**5a**, and 2.6° for *syn*-(+)-(R_p,R,R,R_p)-**4b**.

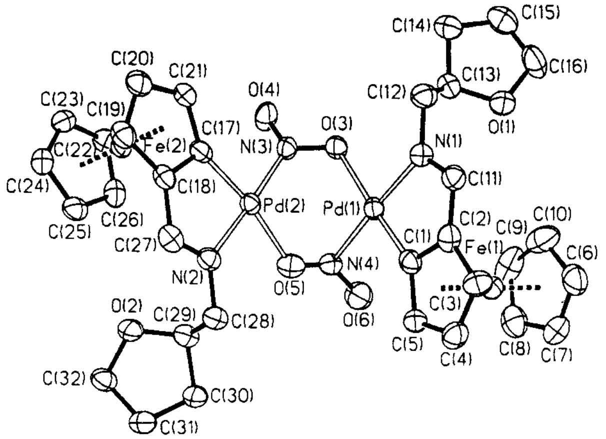

Figure 7. Molecular structure (30% thermal ellipsoids) and absolute configuration of the bis(μ-nitrito)-bridged dimer *syn*-(+)-(R_p,R,R,R_p)-**6a** with atom-numbering scheme.

Crystal and Molecular Structures of *syn*-(+)-(R_p,R,R,R_p)-6a. X-ray analysis established the absolute planar chiralities of the two ferrocenyl moieties and the (μ-1κO:2κN)-(μ-1κN:2κO) bonding mode of the pair of nitrito groups (Figure 7). The nitrito oxygen atom is *cis* to the imino nitrogen atom in the slightly distorted square-planar coordination environment around each palladium atom. The deviations (in Å) from the least-squares plane defined by the atoms Pd(1), C(1), N(1), O(3), and N(4) are as follows: Pd(1), −0.024; C(1), 0.009; N(1), 0.003; O(3), 0.008; N(4), 0.003. In the structure the two cyclopentadienyl rings are each planar and nearly parallel to each other (tilt angle: 2.0°), and the two rings involved in the bicyclic system formed by fusion of the palladacycle with the ferrocenyl C_5H_3 moiety are approximately coplanar, the relevant dihedral angle being 2.6°. The Pd(1)−N(4)−O(5)−Pd(2) and Pd(1)−O(3)−N(3)−Pd(2) rings are markedly folded, and the angle between the two planes is 107.6°. The angle between the two planes of the palladacycles is 82.9°,

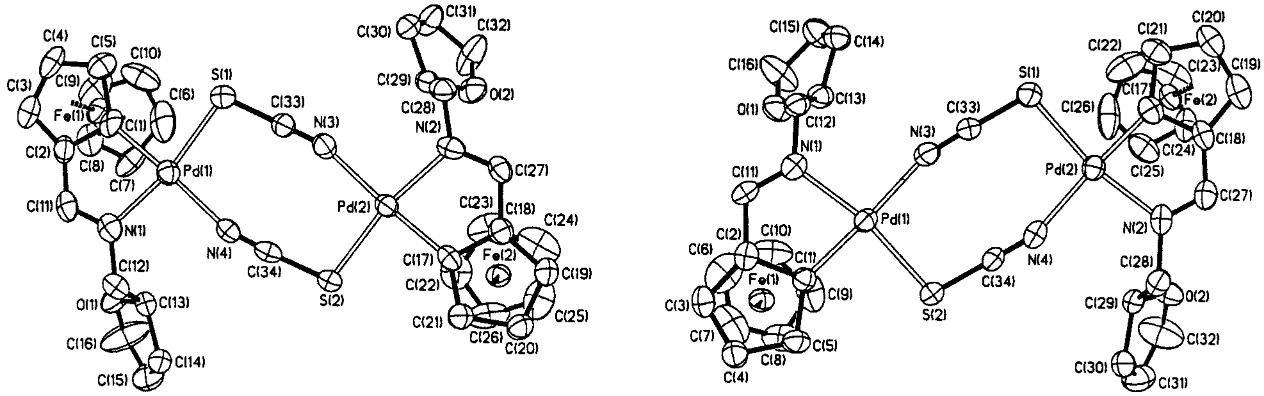

Figure 8. Molecular structures (30% thermal ellipsoids) and absolute configurations of the pair of bis(μ-thiocyanato)-bridged enantiomers *syn*-(+)-(R_p,R,R,R_p)-**7a** (left) and *syn*-(−)-(S_p,S,S,S_p)-**7a** (right) with atom-numbering schemes.

Table 1. Crystal Data for *syn*-(−)-(S_p,S,S,S_p)-2a, *syn*-(+)-(R_p,S,S,R_p)-2a·CH_2Cl_2, *syn*-(−)-(R_p,S,S,S_p)-3, and *syn*-(+)-(R_p,R,R,R_p)-5a

	syn-(−)-(S_p,S,S,S_p)-**2a**	*syn*-(+)-(R_p,S,S,R_p)-**2a**·CH_2Cl_2	*syn*-(−)-(R_p,S,S,S_p)-**3**	*syn*-(+)-(R_p,R,R,R_p)-**5a**
		Crystal Parameters		
formula	$C_{36}H_{42}Fe_2N_2O_6Pd_2$	$C_{37}H_{44}Cl_2Fe_2N_2O_6Pd_2$	$C_{34}H_{39}ClFe_2N_2O_4Pd_2$	$C_{34}H_{40}Cl_2Fe_2N_2O_2Pd_2$
fw	933.2	1008.1	899.6	904.1
shape (color)	block (red)	prism (red)	prism (red)	prism (red)
size, mm	0.22 × 0.15 × 0.15	0.30 × 0.20 × 0.15	0.29 × 0.20 × 0.15	0.20 × 0.15 × 0.15
cryst syst	orthorhombic	hexagonal	monoclinic	hexagonal
space group	$P2_12_12_1$	$P3_2$	$P2_1$	$P6$
a, Å	11.461(1)	11.026(1)	11.959(2)	24.414(1)
b, Å	11.474(1)	11.026(1)	22.106(3)	24.414(1)
c, Å	28.106(3)	27.253(2)	13.080(2)	10.506(1)
β, deg			104.76(1)	
γ, deg		120		120
V, Å^3	3696(1)	2870(1)	3344(1)	5423(1)
Z	4	3	4	6
F(000)	1856	1518	1800	2712
D(calcd), g cm^{-3}	1.659	1.750	1.787	1.661
μ(Mo Kα), mm^{-1}	1.772	1.855	2.029	1.945
		Data Collection		
scan type	21 oscillation photos	ω-scans with 0.3° per frame	ω-scans with 0.3° per frame	20 oscillation photos
2θ range, deg	$3 < 2\theta < 55$	$4.26 < 2\theta < 52.04$	$3.52 < 2\theta < 56.72$	$3 < 2\theta < 55$
no. of rflns coll	6077	7423	35 046	6402
no. of indep rflns	5314 (R_{int} = 6.02%)	5046 (R_{int} = 0.00%)	16 115 (R_{int} = 4.42%)	6037 (R_{int} = 5.19%)
		Refinement		
R1[a]	0.0531	0.0379	0.0395	0.0536
wR2[b]	0.1128	0.0650	0.0744	0.1385
weighting scheme[c]	a = 0.0483, b = 0.0000	a = 0.0156, b = 0.0000	a = 0.0353, b = 0.0000	a = 0.0950, b = 0.0000
no. of params refined	435	462	740	399
S (GOF)[d]	1.079	0.877	0.880	1.067
Flack params	0.45(2)	0.04(1)	0.07(2)	0.50(2)
max, mean Δ/σ	−0.069, 0.002	−0.144, 0.011	0.194, 0.020	−0.132, 0.026
$\Delta\rho_{max}$, e Å^{-3}	0.389, −1.169	0.515, −0.423	0.733, −0.412	1.076, −0.476

[a] $R1 = \Sigma|F_o| - |F_c|/\Sigma|F_o|$. [b] $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$. [c] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = (F_o^2 + 2F_c^2)/3$. [d] GOF $= S = \{[\Sigma w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$.

which is significantly larger than the tilt angles of bis(μ-acetato)-bridged dimers. As a consequence, the nonbonding distance Pd(1)···Pd(2) is 3.089 Å, which falls outside the range (2.84−2.96 Å) of dimeric cyclopalladated compounds in the literature.[25,26]

Crystal and Molecular Structures of *syn*-(+)-(R_p,R,R,R_p)-7a·$^1/_2$$CH_2Cl_2$ and *syn*-(−)-(S_p,S,S,S_p)-7a·$^1/_2$$CH_2Cl_2$. The molecular structures and absolute configurations of the pair of bis(μ-thiocyanato)-bridged enantiomers *syn*-(+)-(R_p,R,R,R_p)-**7a**·$^1/_2$$CH_2Cl_2$ and *syn*-(−)-(S_p,S,S,S_p)-**7a**·$^1/_2$$CH_2Cl_2$ are shown in Figure 8. Selected bond lengths and bond angles are listed in Table 4. The two palladium atoms are bound to two thiocyanato groups in the (μ-1κS:2κN)-(μ-1κN:2κS) mode. The two thiocyanato groups have a nearly linear configuration (the angles S(1)−C(37)−N(5) and S(2)−C(38)−N(6) are 178.1(5) and 176.2(6)° for *syn*-(+)-(R_p,R,R,R_p)-**7a**·$^1/_2$$CH_2Cl_2$ and 178.3(3) and 179.1(3)° for *syn*-(−)-(S_p,S,S,S_p)-**7a**·$^1/_2$$CH_2Cl_2$), and the two palladacycles are approximately coplanar, the relevant dihedral angle being 170.2° for *syn*-(+)-(R_p,R,R,R_p)-**7a**·$^1/_2$$CH_2Cl_2$ and 169.9° for *syn*-(−)-(S_p,S,S,S_p)-**7a**·$^1/_2$$CH_2Cl_2$. This makes the distance between the palladium atoms much longer (5.591 Å for *syn*-(+)-(R_p,R,R,R_p)-**7a**·$^1/_2$$CH_2Cl_2$ and 5.604 Å for syn-(−)-(S_p,S,S,S_p)-**7a**·$^1/_2$$CH_2Cl_2$) than that (2.83−3.50 Å) of their bis(μ-anion)-bridged analogues reported here. The palladium atoms and the bridge-ligand atoms form a slightly distorted eight-membered planar ring. The deviations (in Å) from the least-squares plane defined by the atoms Pd(1), Pd(2), S(1), S(2), C(33), C(34), N(3), and N(4) are as follows: Pd(1), −0.008; Pd(2), −0.016; S(1), 0.006; S(2), 0.028; C(33), 0.014; C(34),

Table 2. Crystal Data for *syn*-(+)-(R_p,R,R,R_p)-6a, *syn*-(−)-(S_p,S,S,S_p)-7a·$^1/_2$CH$_2$Cl$_2$, and (+)-(R_p,R)-8

	syn-(+)-(R_p,R,R,R_p)-**6a**	*syn*-(−)-(S_p,S,S,S_p)-**7a**·$^1/_2$CH$_2$Cl$_2$	(+)-(R_p,R)-**8**
Crystal Parameters			
formula	$C_{32}H_{36}Fe_2N_4O_6Pd_2$	$C_{34.5}H_{36}ClFe_2N_4O_2Pd_2S_2$	$C_{44}H_{38}FeINOPd$
fw	897.2	962.7	885.9
shape (color)	prism (red)	prism (red)	prism (red)
size, mm	0.25 × 0.15 × 0.20	0.45 × 0.35 × 0.20	0.20 × 0.15 × 0.15
cryst syst	monoclinic	monoclinic	orthorhombic
space group	$P2_1$	$C2$	$P2_12_12_1$
a, Å	10.217(1)	20.649(4)	10.407(2)
b, Å	12.940(1)	12.472(2)	17.177(3)
c, Å	12.906(1)	14.664(3)	20.811(4)
β, deg	93.81(1)	104.15(3)	
V, Å^3	1702(1)	3662(1)	3720(1)
Z	2	4	4
F(000)	896	1920	1768
D(calcd), g cm^{-3}	1.750	1.746	1.582
μ(Mo Kα), mm^{-1}	1.922	1.967	1.738
Data Collection			
scan type	60 oscillation photos	25 oscillation photos	65 oscillation photos
2θ range, deg	$3 < 2\theta < 55$	$3 < 2\theta < 55$	$3 < 2\theta < 55$
no. of rflns coll	5676	5607	5734
no. of indep rflns	5502 (R_{int} = 3.44%)	5037 (R_{int} = 5.45%)	4887 (R_{int} = 6.17%)
Refinement			
R1[a]	0.0619	0.0531	0.0617
wR2[b]	0.1750	0.1381	0.1401
weighting scheme[c]	$a = 0.1080$, $b = 1.4461$	$a = 0.0731$, $b = 0.0000$	$a = 0.0964$, $b = 0.0000$
no. of params refined	417	431	443
S (GOF)[d]	1.091	1.035	1.017
Flack params	0.33(2)	0.51(2)	0.44(2)
max, mean Δ/σ	−0.074, 0.005	0.051, 0.006	−0.009, 0.001
$\Delta\rho_{max}$, e Å^{-3}	0.732, −0.897	0.560,−0.538	0.610, −0.956

[a] $R1 = \sum F_o - F_c/\sum F_o$. [b] $wR2 = \{[\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]\}^{1/2}$. [c] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = (F_o^2 + 2F_c^2)/3$. [d] GOF $= S = \{[\sum w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$.

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) of *syn*-(−)-(S_p,S,S,S_p)-2a, *syn*-(+)-(R_p,S,S,R_p)-2a·CH$_2$Cl$_2$, *syn*-(−)-(R_p,S,S,S_p)-3, and *syn*-(+)-(R_p,R,R,R_p)-5a

syn-(−)-(S_p,S,S,S_p)-**2a**		*syn*-(+)-(R_p,S,S,R_p)-**2a**·CH$_2$Cl$_2$		*syn*-(−)-(R_p,S,S,S_p)-**3**		*syn*-(+)-(R_p,R,R,R_p)-**5a**	
Pd(1)−C(1)	1.926(3)	Pd(1)−C(1)	1.955(2)	Pd(1)−C(1)	1.984(2)	Pd(1)−C(1)	1.916(4)
Pd(2)−C(17)	1.936(4)	Pd(2)−C(17)	1.949(2)	Pd(1)−N(1)	2.055(2)	Pd(1)−N(1)	2.058(2)
Pd(1)−N(1)	2.044(3)	Pd(1)−N(1)	2.019(2)	Pd(1)−O(3)	2.091(2)	Pd(1)−Cl(2)	2.339(1)
Pd(2)−N(2)	2.040(3)	Pd(2)−N(2)	2.021(2)	Pd(1)−Cl(1)	2.321(1)	Pd(1)−Cl(1)	2.475(1)
Pd(1)−O(3)	2.040(3)	Pd(1)−O(3)	2.148(2)	Pd(2)−C(17)	1.987(2)	Pd(2)−C(18)	1.921(4)
Pd(1)−O(5)	2.162(2)	Pd(1)−O(5)	2.031(2)	Pd(2)−N(2)	2.046(2)	Pd(2)−N(2)	2.062(2)
Pd(2)−O(4)	2.165(3)	Pd(2)−O(4)	2.041(1)	Pd(2)−O(4)	2.155(2)	Pd(2)−Cl(1)	2.329(1)
Pd(2)−O(6)	2.030(2)	Pd(2)−O(6)	2.142(1)	Pd(2)−Cl(1)	2.330(1)	Pd(2)−Cl(2)	2.475(1)
O(1)−C(16)	1.390(6)	O(1)−C(15)	1.411(2)	O(1)−C(16)	1.376(6)	O(1)−C(17)	1.420(6)
O(1)−C(13)	1.420(5)	O(1)−C(13)	1.432(3)	O(1)−C(13)	1.417(4)	O(1)−C(14)	1.418(4)
O(2)−C(32)	1.419(6)	O(2)−C(29)	1.419(2)	O(2)−C(32)	1.402(5)	O(2)−C(34)	1.315(6)
O(2)−C(29)	1.423(5)	O(2)−C(31)	1.427(3)	O(2)−C(29)	1.422(4)	O(2)−C(31)	1.377(6)
O(3)−C(34)	1.264(4)	O(3)−C(34)	1.214(3)	O(3)−C(34)	1.277(3)	N(1)−C(11)	1.264(4)
O(4)−C(34)	1.242(4)	O(4)−C(34)	1.279(2)	O(4)−C(34)	1.218(3)	N(2)−C(28)	1.313(5)
O(5)−C(36)	1.241(4)	O(5)−C(36)	1.281(2)	N(1)−C(11)	1.249(4)	C(2)−C(11)	1.432(5)
O(6)−C(36)	1.255(4)	O(6)−C(36)	1.244(2)	N(2)−C(27)	1.285(4)	C(19)−C(28)	1.421(6)
C(1)−Pd(1)−N(1)	80.9(1)	C(1)−Pd(1)−N(1)	81.7(1)	C(1)−Pd(1)−N(1)	79.59(8)	C(1)−Pd(1)−N(1)	80.4(1)
C(17)−Pd(2)−N(2)	80.2(1)	C(17)−Pd(2)−N(2)	80.9(1)	C(17)−Pd(2)−N(2)	82.68(9)	C(18)−Pd(2)−N(2)	81.3(1)
O(3)−Pd(1)−O(5)	87.8(1)	O(5)−Pd(1)−O(3)	93.6(1)	O(3)−Pd(1)−Cl(1)	93.40(6)	Cl(1)−Pd(2)−Cl(2)	87.8(1)
O(6)−Pd(2)−O(4)	88.1(1)	O(4)−Pd(2)−O(6)	94.1(1)	O(4)−Pd(2)−Cl(1)	96.25(6)	N(1)−Pd(1)−Cl(1)	98.5(1)
C(1)−Pd(1)−O(3)	93.7(1)	C(1)−Pd(1)−O(5)	90.7(1)	Pd(1)−Cl(1)−Pd(2)	87.41(3)	N(2)−Pd(2)−Cl(2)	100.0(1)
N(1)−Pd(1)−O(5)	97.6(1)	N(1)−Pd(1)−O(3)	94.1(1)	C(34)−O(3)−Pd(1)	127.1(2)	C(1)−Pd(1)−Cl(2)	93.6(1)
C(17)−Pd(2)−O(6)	94.0(1)	C(17)−Pd(2)−O(4)	90.6(1)	C(34)−O(4)−Pd(2)	131.9(2)	C(18)−Pd(2)−Cl(1)	91.5(1)
N(2)−Pd(2)−O(4)	97.8(1)	N(2)−Pd(2)−O(6)	94.5(1)	C(11)−N(1)−Pd(1)	117.6(2)	Pd(2)−Cl(1)−Pd(1)	86.0(1)
C(11)−N(1)−Pd(1)	115.6(3)	C(11)−N(1)−Pd(1)	115.7(2)	C(27)−N(2)−Pd(2)	113.3(2)	Pd(1)−Cl(2)−Pd(2)	85.8(1)
C(27)−N(2)−Pd(2)	116.4(3)	C(27)−N(2)−Pd(2)	116.1(2)	C(2)−C(1)−Pd(1)	113.1(1)	C(11)−N(1)−Pd(1)	116.8(2)
C(2)−C(1)−Pd(1)	114.3(3)	C(2)−C(1)−Pd(1)	111.8(2)	C(1)−C(2)−C(11)	114.7(2)	C(28)−N(2)−Pd(2)	115.4(2)
C(18)−C(17)−Pd(2)	114.9(3)	C(18)−C(17)−Pd(2)	114.2(2)	N(1)−C(11)−C(2)	114.9(2)	N(1)−C(11)−C(2)	113.7(3)
C(1)−C(2)−C(11)	113.4(3)	C(11)−C(2)−C(1)	115.4(2)	C(18)−C(17)−Pd(2)	111.7(1)	N(2)−C(28)−C(19)	114.3(3)
C(17)−C(18)−C(27)	112.7(4)	C(17)−C(18)−C(27)	113.0(2)	C(17)−C(18)−C(19)	108.0(1)	C(19)−C(18)−Pd(2)	113.3(3)
N(1)−C(11)−C(2)	115.6(4)	N(1)−C(11)−C(2)	115.3(2)	C(17)−C(18)−C(27)	114.5(2)	C(2)−C(1)−Pd(1)	113.3(3)
N(2)−C(27)−C(18)	115.7(3)	N(2)−C(27)−C(18)	115.6(2)	N(2)−C(27)−C(18)	117.6(3)	C(11)−C(2)−C(1)	115.5(3)
O(4)−C(34)−O(3)	126.4(4)	O(3)−C(34)−O(4)	127.6(2)	O(4)−C(34)−O(3)	126.0(3)	C(28)−C(19)−C(18)	115.5(3)

−0.022; N(3), −0.006; N(4), 0.004 for *syn*-(+)-(R_p,R,R,R_p)-**7a**·$^1/_2$CH$_2$Cl$_2$ and Pd(1), 0.016; Pd(2), −0.004; S(1), 0.009; S(2), −0.032; C(33), −0.007; C(34), 0.009; N(3), 0.004; N(4), 0.023 for *syn*-(−)-(S_p,S,S,S_p)-**7a**·$^1/_2$CH$_2$Cl$_2$.

Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) of *syn*-(+)-(R_p,R,R,R_p)-6a, *syn*-(−)-(S_p,S,S,S_p)-7a·$^1/_2$CH$_2$Cl$_2$, and (+)-(R_p,R)-8

syn-(+)-(R_p,R,R,R_p)-**6a**		*syn*-(−)-(S_p,S,S,S_p)-**7a**·$^1/_2$CH$_2$Cl$_2$		(+)-(R_p,R)-**8**	
Pd(1)−C(1)	1.906(4)	Pd(1)−C(1)	1.957(3)	Pd(1)−C(20)	1.974(4)
Pd(1)−N(1)	2.053(3)	Pd(1)−N(1)	2.068(3)	Pd(1)−C(18)	2.148(4)
Pd(1)−N(4)	2.079(3)	Pd(1)−N(3)	2.099(3)	Pd(1)−N(1)	2.162(4)
Pd(1)−O(3)	2.173(3)	Pd(1)−S(2)	2.309(1)	Pd(1)−I(1)	2.666(1)
Pd(2)−C(17)	1.957(4)	Pd(2)−C(17)	1.965(4)	Pd(1)−Y[a]	2.056
Pd(2)−N(3)	2.000(4)	Pd(2)−N(2)	2.072(3)	O(1)−C(13)	1.425(6)
Pd(2)−N(2)	2.061(4)	Pd(2)−N(4)	2.108(3)	O(1)−C(16)	1.439(7)
Pd(2)−O(5)	2.176(3)	Pd(2)−S(1)	2.318(1)	C(13)−C(14)	1.544(7)
O(1)−C(16)	1.373(8)	S(1)−C(33)	1.648(4)	N(1)−C(11)	1.272(6)
O(1)−C(13)	1.409(6)	S(2)−C(34)	1.649(4)	C(1)−C(2)	1.435(7)
O(2)−C(29)	1.404(5)	O(1)−C(16)	1.358(6)	C(1)−C(11)	1.405(6)
O(2)−C(32)	1.415(6)	O(1)−C(13)	1.423(5)	C(2)−C(17)	1.482(6)
O(3)−N(3)	1.279(4)	O(2)−C(32)	1.357(5)	C(17)−C(18)	1.428(6)
O(4)−N(3)	1.232(5)	O(2)−C(29)	1.437(5)	C(18)−C(19)	1.530(6)
N(1)−C(11)	1.254(6)	N(3)−C(33)	1.152(4)	C(19)−C(20)	1.320(6)
N(2)−C(27)	1.243(5)	N(4)−C(34)	1.150(5)		
C(1)−Pd(1)−N(1)	81.4(2)	C(1)−Pd(1)−N(1)	80.6(1)	C(20)−Pd(1)−N(1)	161.6(2)
C(17)−Pd(2)−N(2)	81.4(2)	C(17)−Pd(2)−N(2)	80.7(1)	C(20)−Pd(1)−I(1)	100.5(1)
N(4)−Pd(1)−O(3)	90.34(1)	C(1)−Pd(1)−N(3)	176.2(1)	N(1)−Pd(1)−I(1)	94.9(1)
N(3)−Pd(2)−O(5)	92.8(2)	C(17)−Pd(2)−N(4)	176.0(1)	C(11)−N(1)−Pd(1)	125.7(3)
N(3)−O(3)−Pd(1)	111.8(2)	N(1)−Pd(1)−S(2)	169.1(1)	C(12)−N(1)−Pd(1)	115.6(3)
N(4)−O(5)−Pd(2)	114.0(3)	N(2)−Pd(2)−S(1)	168.3(1)	C(11)−C(1)−C(2)	128.6(4)
C(11)−N(1)−Pd(1)	114.2(3)	N(3)−Pd(1)−S(2)	95.0(1)	C(1)−C(2)−C(17)	129.5(4)
C(27)−N(2)−Pd(2)	114.4(3)	N(4)−Pd(2)−S(1)	96.1(1)	N(1)−C(11)−C(1)	126.3(5)
O(4)−N(3)−O(3)	114.0(3)	C(34)−S(2)−Pd(1)	103.0(1)	C(18)−C(17)−C(2)	120.4(4)
O(5)−N(4)−O(6)	120.6(4)	C(33)−S(1)−Pd(2)	102.4(1)	C(17)−C(18)−C(19)	114.3(4)
O(3)−N(3)−Pd(2)	119.6(3)	C(11)−N(1)−Pd(1)	114.7(2)	C(20)−C(19)−C(18)	104.6(4)
O(5)−N(4)−Pd(1)	124.1(3)	C(27)−N(2)−Pd(2)	116.2(2)	C(19)−C(20)−Pd(1)	100.8(3)
C(2)−C(1)−Pd(1)	113.4(3)	C(33)−N(3)−Pd(1)	164.1(3)	C(20)−Pd(1)−Y[a]	73.9
C(11)−C(2)−C(1)	113.5(4)	C(34)−N(4)−Pd(2)	161.5(3)	N(1)−Pd(1)−Y[a]	97.6
C(17)−C(18)−C(27)	115.2(3)	C(2)−C(1)−Pd(1)	114.0(2)	I(1)−Pd(1)−Y[a]	150.1
N(1)−C(11)−C(2)	117.3(4)	N(3)−C(33)−S(1)	178.3(3)		
N(2)−C(27)−C(18)	117.0(4)	N(4)−C(34)−S(2)	179.1(3)		

[a] The midpoint of the C(17)−C(18) double bond is referred to as Y.

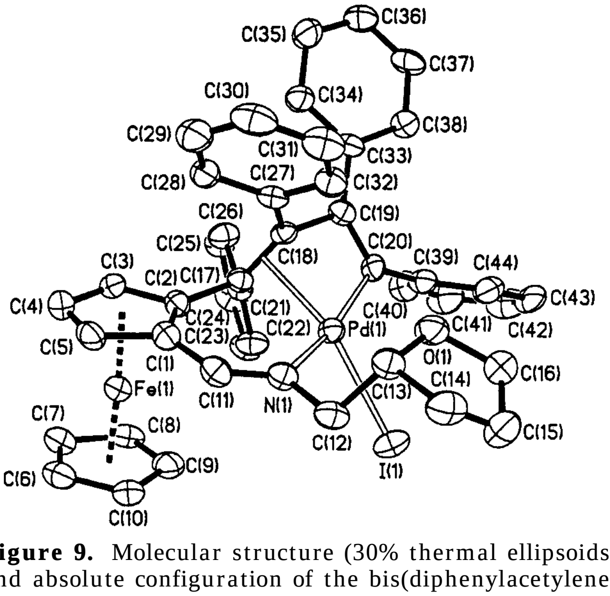

Figure 9. Molecular structure (30% thermal ellipsoids) and absolute configuration of the bis(diphenylacetylene) insertion compound (+)-(R_p,R)-**8** with atom-numbering scheme.

The two rings involved in the bicyclic system formed by fusion of the palladacycle with the eight-membered bridge ring are approximately coplanar, the relevant dihedral angle being 3.3° for *syn*-(+)-(R_p,R,R,R_p)-**7a**·$^1/_2$CH$_2$Cl$_2$ and 2.2° for *syn*-(−)-(S_p,S,S,S_p)-**7a**·$^1/_2$CH$_2$Cl$_2$.

Crystal and Molecular Structures of (+)-(R_p,R)-8. A perspective drawing of the representative molecular structure of (+)-(R_p,R)-**8** is presented in Figure 9. Selected bond lengths and bond angles are presented in Table 4. The palladium atom has effectively square-planar coordination, being bound to an iodine atom, the imino nitrogen atom, the terminal carbon atom C(20) of the η^3-butadienyl fragment, and the midpoint of the C(17)═C(18) double bond (hereafter referred to as Y) (Figure 2 and Table 4). The two cyclopentadienyl rings are each planar and nearly parallel to each other (tilt angle: 2.8°). The Pd−N bond length (2.162(4) Å) is clearly longer than those (ca. 2.05 Å) of related five-membered metallacycles containing a Pd−C$_{sp^2}$(ferrocene) σ-bond (see *syn*-(+)-(R_p,R,R,R_p)-**4a**, *syn*-(−)-(S_p,S,S,S_p)-**4a**, *syn*-(+)-(R_p,R,R,R_p)-**4b**, *syn*-(+)-(R_p,R,R,R_p)-**5a,** and *syn*-(−)-(S_p,S,S,S_p)-**5a**). The N(1)−C(11) bond length (1.272 Å) is shorter than those (1.30 Å) of related five-membered metallacycles.

Experimental Section

General Methods. ^{1}H NMR and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker DPX 300 instrument using CDCl$_3$ (99.8%) and SiMe$_4$ as solvent and internal standard. Optical rotations were measured in chloroform solution within a 1 dm cell at 25 °C with a Perkin-Elmer Model 341 polarimeter. Melting points were determined on a Regeltrafo F Thermogeräte 7950 instrument. Elemental analyses were performed by MEDAC Ltd of the Department of Chemistry at Brunel University. Ferrocenecarboxaldehyde, acetylferrocene, sodium tetrachloropalladate(II), and palladium acetate were obtained from Strem Chemicals, Inc. (−)-(R)-Tetrahydrofurfurylamine, (+)-(S)-tetrahydrofurfurylamine, and 5 Å molecular sieves were purchased from Aldrich. All were used as received. Benzene was dried over sodium metal and boiled at reflux under a nitrogen atmosphere until it gave a blue coloration with Ph_2CO and was then distilled.

Preparation of (η^5-$C_5H_4CR{=}NCH_2CHCH_2CH_2CH_2O$)Fe($\eta^5$-$C_5H_5$) (R = H, (−)−(*R*)-1a or (+)−(*S*)-1a; R = Me, (−)-(*R*)-1b or (+)-(*S*)-1b). Acetylferrocene (10 mmol) and (−)-(*R*)-tetrahydrofurfurylamine or (+)-(*S*)-tetrahydrofurfurylamine (1.01 g, 10 mmol) were dissolved in dry benzene (100 mL). The flask containing the reaction mixture was connected to a condenser equipped with a Dean−Stark apparatus. The red solution was refluxed on an oil bath about 6 h. The hot solution was carefully transferred into a Schlenk tube, in which 5 Å molecular sieves (3.0 g) were introduced. The mixture was refluxed for 5−6 h. Then the hot solution was carefully filtered and the filtrate reduced to dryness. Addition of *n*-hexane to the oily material and cooling at −20 °C produced yellow platelike crystals. Yield: 2.23 g (75%), 2.11 g (71%), 1.67 g (59%), and 1.81 g (64%), respectively. Characterization data for (−)-(*R*)-**1a:** mp 63.0−64.0 °C; $[\alpha]_D^{20}$ −25.1 (*c* 1.0, $CHCl_3$); ^1H NMR (selected data): δ 3.70 (m, 2H, NCH_2), 3.90 (d, *J* = 7.2 Hz, 3H, $CHOCH_2$), 4.12 (s, 5H, C_5H_5), 4.27 [s, 2H, H^3, H^4 (C_5H_4)], 4.71 [s, 2H, H^2, H^5 (C_5H_4)], 8.06 (s, 1H, CH=N); $^{13}C\{^1H\}$ NMR (selected data) δ 68.7 (N−CH_2), 69.7 (C_5H_5), 70.2 [C^2, C^5 (C_5H_4)], 70.9 [C^3, C^4 (C_5H_4)], 163.3 (C=N). Anal. Calcd for $C_{16}H_{19}FeNO$: C, 64.66; H, 6.44; N, 4.71. Found: C, 64.26; H, 6.56; N, 4.81. Characterization data for (+)-(*S*)-**1a:** mp 63.5−64.0 °C; $[\alpha]_D^{20}$ +25.8 (*c* 1.0, $CHCl_3$); ^1H NMR (selected data) δ 3.70 (m, 2H, NCH_2), 3.89 (d, *J* = 6.9 Hz, 3H, $CHOCH_2$), 4.12 (s, 5H, C_5H_5), 4.26 [s, 2H, H^3, H^4 (C_5H_4)], 4.70 [s, 2H, H^2, H^5 (C_5H_4)], 8.06 (s, 1H, CH=N); $^{13}C\{^1H\}$ NMR (selected data): δ *68*.5 (N−CH_2), 69.6 (C_5H_5), 70.2 [C^2, C^5 (C_5H_4)], 71.1 [C^3, C^4 (C_5H_4)], 163.5 (C=N). Anal. Calcd for $C_{16}H_{19}FeNO$: C, 64.66; H, 6.44; N, 4.71. Found: C, 64.51; H, 6.27; N, 4.76. Characterization data for (−)-(*R*)-**1b**: mp 55.0−56.0 °C; $[\alpha]_D^{20}$ −40.9 (*c* 1.0, $CHCl_3$); ^1H NMR (selected data) δ 2.18 (s, 6H, $CH_3C{=}N$), 3.71 (m, 2H, NCH_2), 3.88 (d, *J* = 6.0 Hz, 3H, $CHOCH_2$), 4.13 (s, 5H, C_5H_5), 4.28 [s, 2H, H^3, H^4 (C_5H_4)], 4.71 [s, 2H, H^2, H^5 (C_5H_4)]; $^{13}C\{^1H\}$ NMR (selected data) δ 68.9 (N−CH_2), 69.8 (C_5H_5), 70.5 [C^2, C^5 (C_5H_4)], 71.1 [C^3, C^4 (C_5H_4)], 163.8 (C=N). Anal. Calcd for $C_{17}H_{21}FeNO$: C, 65.61; H, 6.80; N, 4.50. Found: C, 65.28; H, 6.91; N, 4.62. Characterization data for (+)-(*S*)-**1b:** mp 55.0−56.0 °C; $[\alpha]_D^{20}$ +40.5 (*c* 1.0, $CHCl_3$); ^1H NMR (selected data) δ 2.16 (s, 6H, $CH_3C{=}N$), 3.71 (m, 2H, NCH_2), 3.89 (d, *J* = 5.4 Hz, 3H, $CHOCH_2$), 4.13 (s, 5H, C_5H_5), 4.26 [s, 2H, H^3, H^4 (C_5H_4)], 4.71 [s, 2H, H^2, H^5 (C_5H_4)]; $^{13}C\{^1H\}$ NMR (selected data) δ 68.9 (N−CH_2), 69.9 (C_5H_5), 70.4 [C^2, C^5 (C_5H_4)], 71.0 [C^3, C^4 (C_5H_4)], 163.8 (C=N). Anal. Calcd for $C_{17}H_{21}FeNO$: C, 65.61; H, 6.80; N, 4.50. Found: C, 65.46; H, 6.57; N, 4.38.

Preparation of [Pd{(η^5-$C_5H_3CR{=}NCH_2CHCH_2CH_2CH_2O$)Fe($\eta^5$-$C_5H_5$)}($\mu$-OAc)]$_2$ (R = H, *syn*-(+)-(R_p,*R*,*R*,R_p)-2a, *syn*-(−)-(S_p,*R*,*R*,S_p)-2a, *syn*-(−)-(S_p,*S*,*S*,S_p)-2a, *syn*-(+)−(R_p,*S*,*S*,R_p)-2a; R = Me, *syn*-(+)-(R_p,*R*,*R*,R_p)-2b, *syn*-(−)-(S_p,*R*,*R*,S_p)-2b, *syn*-(−)-(S_p,*S*,*S*,S_p)-2b, *syn*-(+)-(R_p,*S*,*S*,R_p)-2b). The ferrocenylimine (−)-(*R*)-**1a** (or (+)-(*S*)-**1a**, (−)-(*R*)-**1b**, or (+)-(*S*)-**1b**) (1.0 mmol) was added to a methanolic (30 mL) solution containing $Pd(OAc)_2$ (0.22 g, 1.0 mmol) and NaOAc·$3H_2O$ (0.14 g, 1.0 mmol), and this mixture was stirred at room temperature for 24 h. The resulting reaction mixture was dried under high vacuum. The product was extracted into chloroform and passed through an SiO_2 column using $CHCl_3$/MeOH (9.5:0.5) as eluent. The first red fraction (ca. 90−95%) was *syn*-(+)-(R_p,*R*,*R*,R_p)-**2** or *syn*-(−)-(S_p,*S*,*S*,S_p)-**2**. The second red fraction (ca. 5−10%) was *syn*-(−)-(S_p,*R*,*R*,S_p)-**2** or *syn*-(+)-(R_p,*S*,*S*,R_p)-**2**. Concentration of the eluted solution produced *syn*-(+)-(R_p,*R*,*R*,R_p)-**2a** (or *syn*-(−)-(S_p,*R*,*R*,S_p)-**2a**, *syn*-(−)-(S_p,*S*,*S*,S_p)-**2a**, *syn*-(+)-(R_p,*S*,*S*,R_p)-**2a**, *syn*-(+)-(R_p,*R*,*R*,R_p)-**2b**, *syn*-(−)-(S_p,*R*,*R*,S_p)-**2b**, *syn*-(−)-(S_p,*S*,*S*,S_p)-**2b**, or *syn*-(+)-(R_p,*S*,*S*,R_p)-**2b**, respectively), which was recrystallized from dichloromethane/*n*-hexane (1:3) as red plates. Total yield: 0.21 g (46%), 0.19 g (41%), 0.23 g (49%), and 0.20 g (43%), respectively. Characterization data for *syn*-(+)-(R_p,*R*,*R*,R_p)-**2a**: $[\alpha]_D^{20}$ +2989.6 (*c* 1.0 in $CHCl_3$); ^1H NMR (selected data) δ 2.03 (s, 6H, CH_3CO_2), 3.25 (d, 4H, *J* = 7.5 Hz, NCH_2), 3.74 (m, 6H, $CHOCH_2$), 4.19 [d, *J* = 1.5 Hz, 2H, H^3 (C_5H_3)], 4.28 [d, *J* = 2.4 Hz, 2H, H^4 (C_5H_3)], 4.39 [s, 2H, H^5 (C_5H_3)], 4.25 [s, 10H, C_5H_5)], 7.88 (s, 2H, HC=N); $^{13}C\{^1H\}$ NMR (selected data) δ 26.4 (CH_3CO_2), 68.7 [C^4 (C_5H_3)], 71.2 (C_5H_5), 75.4 [C^3 (C_5H_3)], 78.0 [C^5 (C_5H_3)], 99.8 [C^1 (C_5H_3)], 175.0 (C=N). Anal. Calcd for $C_{36}H_{42}Fe_2N_2O_6Pd_2$: C, 46.83; H, 4.59; N, 3.04. Found: C, 46.45; H, 4.61; N, 3.46. Characterization data for *syn*-(−)-(S_p,*R*,*R*,S_p)-**2a**: $[\alpha]_D^{20}$ −370.1 (*c* 1.0 in $CHCl_3$); ^1H NMR (selected data) δ 2.01 (s, 6H, CH_3CO_2), 3.24 (d, 4H, *J* = 4.5 Hz, NCH_2), 3.74 (m, 6H, $CHOCH_2$), 4.17 [d, *J* = 2.1 Hz, 2H, H^3 (C_5H_3)], 4.21 [d, *J* = 2.1 Hz, 2H, H^4 (C_5H_3)], 4.22 [s, 2H, H^5 (C_5H_3)], 4.26 [s, 10H, C_5H_5)], 7.82 (s, 2H, HC=N); $^{13}C\{^1H\}$ NMR (selected data) δ 23.2 (CH_3CO_2), 69.6 [C^4 (C_5H_3)], 71.5 (C_5H_5), 75.3 [C^3 (C_5H_3)], 78.1 [C^5 (C_5H_3)], 99.8 [C^1 (C_5H_3)], 178.1 (C=N). Anal. Calcd for $C_{36}H_{42}Fe_2N_2O_6Pd_2$: C, 46.83; H, 4.59; N, 3.04. Found: C, 46.52; H, 4.39; N, 3.28. Characterization data for *syn*-(−)-(S_p,*S*,*S*,S_p)-**2a**: $[\alpha]_D^{20}$ −2980.9 (*c* 1.0 in $CHCl_3$); ^1H NMR (selected data) δ 2.03 (s, 6H, CH_3CO_2), 3.22 (d, 4H, *J* = 5.7 Hz, NCH_2), 3.74 (m, 6H, $CHOCH_2$) 4.17 [d, *J* = 2.1 Hz, 2H, H^3 (C_5H_3)], 4.27 [d, *J* = 2.1 Hz, 2H, H^4 (C_5H_3)], 4.38 [s, 2H, H^5 (C_5H_3)], 4.22 [s, 10H, C_5H_5)], 7.83 (s, 2H, HC=N); $^{13}C\{^1H\}$ NMR (selected data) δ 26.3 (CH_3CO_2), 68.3 [C^4 (C_5H_3)], 71.0 (C_5H_5), 75.8 [C^3 (C_5H_3)], 78.2 [C^5 (C_5H_3)], 100.1 [C^1 (C_5H_3)], 175.5 (C=N). Anal. Calcd for $C_{36}H_{42}Fe_2N_2O_6Pd_2$: C, 46.83; H, 4.59; N, 3.04. Found: C, 46.51; H, 4.78; N, 2.98. Characterization data for *syn*-(+)-(R_p,*S*,*S*,R_p)-**2a**: $[\alpha]_D^{20}$ +376.1 (*c* 1.0 in $CHCl_3$); ^1H NMR (selected data) δ 2.03 (s, 6H, CH_3CO_2), 3.25 (d, 4H, *J* = 3.6 Hz, NCH_2), 3.76 (m, 6H, $CHOCH_2$), 4.17 [d, *J* = 2.7 Hz, 2H, H^3 (C_5H_3)], 4.20 [d, *J* = 2.1 Hz, 2H, H^4 (C_5H_3)], 4.25 [s, 2H, H^5 (C_5H_3)], 4.25 [s, 10H, C_5H_5)], 7.85 (s, 2H, HC=N); $^{13}C\{^1H\}$ NMR (selected data) δ 23.6 (CH_3CO_2), 69.8 [C^4 (C_5H_3)], 71.5 (C_5H_5), 75.4 [C^3 (C_5H_3)], 78.3 [C^5 (C_5H_3)], 100.1 [C^1 (C_5H_3)], 178.7 (C=N). Anal. Calcd for $C_{36}H_{42}Fe_2N_2O_6Pd_2$: C, 46.83; H, 4.59; N, 3.04. Found: C, 46.73; H, 4.27; N, 2.89. Characterization data for *syn*-(+)-(R_p,*R*,*R*,R_p)-**2b**: $[\alpha]_D^{20}$ +1727.1 (*c* 1.0 in $CHCl_3$); ^1H NMR (selected data) δ 2.07 (s, 6H, CH_3CO_2), 2.15 (s, 6H, $CH_3C{=}N$), 3.41 (d, 4H, *J* = 7.5 Hz, NCH_2), 3.75 (m, 6H, $CHOCH_2$), 4.16 [d, *J* = 2.4 Hz, 2H, H^3 (C_5H_3)], 4.20 [s, 10H, C_5H_5)], 4.25 [d, *J* = 2.4 Hz, 2H, H^4 (C_5H_3)], 4.35 [s, 2H, H^5 (C_5H_3)]; $^{13}C\{^1H\}$ NMR (selected data) δ 26.3 (CH_3CO_2), 68.3 [C^4 (C_5H_3)], 71.5 (C_5H_5), 75.1 [C^3 (C_5H_3)], 78.0 [C^5 (C_5H_3)], 100.3 [C^1 (C_5H_3)], 188.1 (C=N). Anal. Calcd for $C_{38}H_{46}Fe_2N_2O_6Pd_2$: C, 47.98; H, 4.87; N, 2.95. Found: C, 47.57; H, 4.88; N, 2.89. Characterization data for *syn*-(−)-(S_p,*R*,*R*,S_p)-**2b**: $[\alpha]_D^{20}$ −583.7 (*c* 1.0 in $CHCl_3$); ^1H NMR (selected data) δ 2.09 (s, 6H, CH_3CO_2), 2.15 (s, 6H, $CH_3C{=}N$), 3.29 (d, 4H, *J* = 3.0 Hz, NCH_2), 3.76 (m, 6H, $CHOCH_2$), 4.15 [d, *J* = 2.1 Hz, 2H, H^3 (C_5H_3)], 4.23 [d, *J* = 1.5 Hz, 2H, H^4 (C_5H_3)], 4.28 [s, 2H, H^5 (C_5H_3)], 4.26 [s, 10H, C_5H_5)]; $^{13}C\{^1H\}$ NMR (selected data) δ 26.6 (CH_3CO_2), 69.0 [C^4 (C_5H_3)], 71.2 (C_5H_5), 75.3 [C^3 (C_5H_3)], 78.3 [C^5 (C_5H_3)], 100.3 [C^1 (C_5H_3)], 188.6 (C=N). Anal. Calcd for $C_{38}H_{46}Fe_2N_2O_6Pd_2$: C, 47.98; H, 4.87; N, 2.95. Found: C, 47.82; H, 4.61; N, 3.12. Characterization data for *syn*-(−)-(S_p,*S*,*S*,S_p)-**2b**: $[\alpha]_D^{20}$ −1743.2 (*c* 1.0 in $CHCl_3$); ^1H NMR (selected data) δ 2.07 (s, 6H, CH_3CO_2), 2.15 (s, 6H, $CH_3C{=}N$), 3.42 (d, 4H, *J* = 6.9 Hz, NCH_2), 3.75 (m, 6H, $CHOCH_2$), 4.16 [d, *J* = 2.1 Hz, 2H, H^3 (C_5H_3)], 4.21 [s, 10H, C_5H_5)], 4.26 [d, *J* = 2.4 Hz, 2H, H^4 (C_5H_3)], 4.37 [s, 2H, H^5 (C_5H_3)]; $^{13}C\{^1H\}$ NMR (selected data) δ 26.0 (CH_3CO_2), 68.5 [C^4 (C_5H_3)], 71.5 (C_5H_5), 75.1 [C^3 (C_5H_3)], 78.2 [C^5 (C_5H_3)], 100.1 [C^1 (C_5H_3)], 188.0 (C=N). Anal. Calcd for $C_{38}H_{46}Fe_2N_2O_6Pd_2$: C, 47.98; H, 4.87; N, 2.95. Found: C, 48.09; H, 4.57; N, 2.99. Characterization data for *syn*-(+)-(R_p,*S*,*S*,R_p)-**2b**: $[\alpha]_D^{20}$ +602.5 (*c* 1.0 in $CHCl_3$); ^1H NMR (selected data) δ 2.06 (s, 6H, CH_3CO_2), 2.14 (s, 6H, $CH_3C{=}N$), 3.31 (d, 4H, *J* = 2.4 Hz, NCH_2), 3.76 (m, 6H, $CHOCH_2$), 4.16 [d, *J* = 2.1 Hz, 2H, H^3

(C_5H_3)], 4.22 [d, $J = 1.5$ Hz, 2H, H^4 (C_5H_3)], 4.31 [s, 2H, H^5 (C_5H_3)], 4.27 [s, 10H, C_5H_5]; $^{13}C\{^1H\}$ NMR (selected data) δ 26.5 (CH_3CO_2), 69.5 [C^4 (C_5H_3)], 71.4 (C_5H_5), 75.4 [C^3 (C_5H_3)], 78.6 [C^5 (C_5H_3)], 100.0 [C^1 (C_5H_3)], 188.5 (C═N). Anal. Calcd for $C_{38}H_{46}Fe_2N_2O_6Pd_2$: C, 47.98; H, 4.87; N, 2.95. Found: C, 47.53; H, 4.70; N, 2.72.

Preparation of *syn*-(−)−(R_p,*S*,*S*,S_p)-$[Pd\{(\eta^5\text{-}C_5H_3CR{=}NCH_2CHCH_2CH_2CH_2O)Fe(\eta^5\text{-}C_5H_5)\}]_2(\mu\text{-}Cl)(\mu\text{-}OAc)$ (*syn*-(−)−(R_p,*S*,*S*,S_p)-3). The ferrocenylimine (+)-(*S*)-**1a** (0.30 g, 1.0 mmol) was added to a methanolic (30 mL) solution containing Na_2PdCl_4 (0.30 g, 1.0 mmol) and $NaOAc{\cdot}3H_2O$ (0.14 g, 1.0 mmol). The resulting mixture was stirred at room temperature for 24 h. The mixture was eluted through a column of SiO_2 with 10:1 chloroform/*n*-hexane. Concentration of the eluted solution of two successive red bands produced *syn*-(−)-(S_p,*S*,*S*,S_p)-**4a** (0.19 g, 44%) and *syn*-(−)-(R_p,*S*,*S*,S_p)-**3** (0.06 g, 7%) in that order, which were recrystallized from dichloromethane/*n*-hexane (1:3) as red plates (product ratio ≈ 6.3:1). Characterization data for *syn*-(−)-(R_p,*S*,*S*,S_p)-**3**: $[\alpha]_D^{20}$ −726.0 (*c* 1.0 in $CHCl_3$); ^1H NMR (selected data) δ 2.02 (s, 6H, CH_3CO_2), 3.24 (d, 4H, $J = 2.1$ Hz, NCH_2), 3.76 (m, 6H, $CHOCH_2$), 4.15 [d, $J = 2.7$ Hz, 2H, H^3 (C_5H_3)], 4.31 [d, $J = 2.1$ Hz, 2H, H^4 (C_5H_3)], 4.37 [s, 2H, H^5 (C_5H_3)], 4.24 [s, 10H, C_5H_5], 7.85 (s, 2H, *H*C═N); $^{13}C\{^1H\}$ NMR (selected data) δ 26.4 (CH_3CO_2), 66.5 [C^4 (C_5H_3)], 71.2 (C_5H_5), 68.4 [C^3 (C_5H_3)], 78.0 [C^5 (C_5H_3)], 99.8 [C^1 (C_5H_3)], 175.0 (C═N). Anal. Calcd for $C_{34}H_{39}ClFe_2N_2O_4Pd_2$: C, 45.39; H, 4.37; N, 3.11. Found: C, 45.61; H, 4.26; N, 2.98.

General Method for Preparation of Bis(μ-anion)-Bridged Planar Chiral Cyclopalladated Derivatives of Ferrocenylimines. *syn*-(+)-(R_p,*R*,*R*,R_p)-**2a** (or *syn*-(+)-(R_p,*R*,*R*,R_p)-**2b**, *syn*-(−)-(S_p,*S*,*S*,S_p)-**2a**, or *syn*-(−)-(S_p,*S*,*S*,S_p)-**2b**) (0.2 mmol) was dissolved in 30 mL of methanol, and a solution of MA ($NaNO_2$, LiCl, LiBr, KI, or KSCN) (1.0 mmol) in 10 mL of methanol was added to the above solution with stirring at room temperature. The reaction mixture became cloudy. The deep red suspension was stirred at room temperature for 15−30 min and dried under high vacuum. The product was extracted into chloroform and isolated as a red solid *via* column chromatography (silica 60 and chloroform as eluent). The solid was subsequently recrystallized from dichloromethane by addition of *n*-hexane. Subsequently it was found that changing the MA:Pd_2-acetato complex molar ratio to 2:1 yielded the same disubstituted product.

Preparation of $[Pd\{(\eta^5\text{-}C_5H_3CR{=}NCH_2CHCH_2CH_2CH_2O)Fe(\eta^5\text{-}C_5H_5)\}(\mu\text{-}X)]_2$ (R = H, X = Cl, *syn*-(+)-(R_p,*R*,*R*,R_p)-4a, *syn*-(−)-(S_p,*S*,*S*,S_p)-4a; R = H, X = Br, *syn*-(+)-(R_p,*R*,*R*,R_p)-4b, *syn*-(−)-(S_p,*S*,*S*,S_p)-4b; R = H, X = I, *syn*-(+)-(R_p,*R*,*R*,R_p)-4c, *syn*-(−)-(S_p,*S*,*S*,S_p)-4c; R = Me, X = Cl, *syn*-(+)-(R_p,*R*,*R*,R_p)-5a, *syn*-(−)-(S_p,*S*,*S*,S_p)-5a; R = Me, X = Br, *syn*-(+)-(R_p,*R*,*R*,R_p)-5b, *syn*-(−)-(S_p,*S*,*S*,S_p)-5b; R = Me, X = I, *syn*-(+)-(R_p,*R*,*R*,R_p)-5c, *syn*-(−)-(S_p,*S*,*S*,S_p)-5c). These compounds were prepared according to the procedure described above using LiCl, LiBr, or KI as starting materials in a reacting time of 15 min. Yield: 0.15−0.19 g (85−90%). Characterization data for *syn*-(+)-(R_p,*R*,*R*,R_p)-**4a**: $[\alpha]_D^{20}$ +389.2 (*c* 1.0 in $CHCl_3$); ^1H NMR (selected data) δ 3.13 (d, 4H, $J = 6.3$ Hz, NCH_2), 3.76 (m, 6H, $CHOCH_2$) 4.25 [d, $J = 2.1$ Hz, 2H, H^3 (C_5H_3)], 4.33 [d, $J = 2.1$ Hz, 2H, H^4 (C_5H_3)], 4.39 [s, 2H, H^5 (C_5H_3)], 4.50 [s, 10H, C_5H_5)], 7.79 (s, 2H, *H*C═N); $^{13}C\{^1H\}$ NMR (selected data) δ 69.0 [C^4 (C_5H_3)], 71.7 (C_5H_5), 74.8 [C^3 (C_5H_3)], 78.1 [C^5 (C_5H_3)], 97.8 [C^1 (C_5H_3)], 175.4 (C═N). Anal. Calcd for $C_{32}H_{36}Cl_2Fe_2N_2O_2Pd_2$: C, 43.87; H, 4.14; N, 3.20. Found: C, 43.56; H, 4.37; N, 3.21. Characterization data for *syn*-(−)-(S_p,*S*,*S*,S_p)-**4a**: $[\alpha]_D^{20}$ −384.8 (*c* 1.0 in $CHCl_3$); ^1H NMR (selected data) δ 3.10 (d, 4H, $J = 6.3$ Hz, NCH_2), 3.77 (m, 6H, $CHOCH_2$) 4.25 [d, $J = 2.4$ Hz, 2H, H^3 (C_5H_3)], 4.35 [d, $J = 2.1$ Hz, 2H, H^4 (C_5H_3)], 4.38 [s, 2H, H^5 (C_5H_3)], 4.50 [s, 10H, C_5H_5)], 7.79 (s, 2H, *H*C═N); $^{13}C\{^1H\}$ NMR (selected data) δ 68.8 [C^4 (C_5H_3)], 71.5 (C_5H_5), 74.8 [C^3 (C_5H_3)], 78.0 [C^5 (C_5H_3)], 97.9 [C^1 (C_5H_3)], 175.3 (C═N). Anal. Calcd for $C_{32}H_{36}Cl_2Fe_2N_2O_2Pd_2$: C, 43.87; H, 4.14; N, 3.20. Found: C, 43.69; H, 4.49; N, 3.36. Characterization data for *syn*-(+)-(R_p,*R*,*R*,R_p)-**4b**: $[\alpha]_D^{20}$ +1799.3 (*c* 1.0 in $CHCl_3$); ^1H NMR (selected data) δ 3.10 (d, 4H, $J = 3.3$ Hz, NCH_2), 3.72 (m, 6H, $CHOCH_2$). 4.22 [d, $J = 2.4$ Hz, 2H, H^3 (C_5H_3)], 4.36 [d, $J = 2.1$ Hz, 2H, H^4 (C_5H_3)], 4.42 [s, 2H, H^5 (C_5H_3)], 4.56 [s, 10H, C_5H_5)], 7.74 (s, 2H, *H*C═N); $^{13}C\{^1H\}$ NMR (selected data) δ 68.7 [C^4 (C_5H_3)], 71.0 (C_5H_5), 74.2 [C^3 (C_5H_3)], 78.1 [C^5 (C_5H_3)], 97.9 [C^1 (C_5H_3)], 176.4 (C═N). Anal. Calcd for $C_{32}H_{36}Br_2Fe_2N_2O_2Pd_2$: C, 39.83; H, 3.76; N, 2.90. Found: C, 40.12; H, 3.89; N, 3.06. Characterization data for *syn*-(−)-(S_p,*S*,*S*,S_p)-**4b**: $[\alpha]_D^{20}$ −1812.0 (*c* 1.0 in $CHCl_3$); ^1H NMR (selected data) δ 3.12 (d, 4H, $J = 2.1$ Hz, NCH_2), 3.73 (m, 6H, $CHOCH_2$) 4.22 [d, $J = 2.1$ Hz, 2H, H^3 (C_5H_3)], 4.38 [d, $J = 2.7$ Hz, 2H, H^4 (C_5H_3)], 4.44 [s, 2H, H^5 (C_5H_3)], 4.56 [s, 10H, C_5H_5)], 7.75 (s, 2H, *H*C═N); $^{13}C\{^1H\}$ NMR (selected data) δ 68.9 [C^4 (C_5H_3)], 71.1 (C_5H_5), 74.3 [C^3 (C_5H_3)], 78.1 [C^5 (C_5H_3)], 98.2 [C^1 (C_5H_3)], 176.6 (C═N). Anal. Calcd for $C_{32}H_{36}Br_2Fe_2N_2O_2Pd_2$: C, 39.83; H, 3.76; N, 2.90. Found: C, 39.69; H, 3.72; N, 3.18. Characterization data for *syn*-(+)-(R_p,*R*,*R*,R_p)-**3c**: $[\alpha]_D^{20}$ +980.5 (*c* 1.0 in $CHCl_3$); ^1H NMR (selected data) δ 3.10 (d, 4H, $J = 3.3$ Hz, NCH_2), 3.72 (m, 6H, $CHOCH_2$) 4.22 [d, $J = 2.4$ Hz, 2H, H^3 (C_5H_3)], 4.36 [d, $J = 2.1$ Hz, 2H, H^4 (C_5H_3)], 4.42 [s, 2H, H^5 (C_5H_3)], 4.56 [s, 10H, C_5H_5)], 7.74 (s, 2H, *H*C═N); $^{13}C\{^1H\}$ NMR (selected data) δ 68.7 [C^4 (C_5H_3)], 71.0 (C_5H_5), 74.2 [C^3 (C_5H_3)], 78.1 [C^5 (C_5H_3)], 97.9 [C^1 (C_5H_3)], 176.4 (C═N). Anal. Calcd for $C_{32}H_{36}Fe_2I_2N_2O_2Pd_2$: C, 36.29; H, 3.43; N, 2.65. Found: C, 36.59; H, 3.17; N, 2.49. Characterization data for *syn*-(−)-(S_p,*S*,*S*,S_p)-**4c**: $[\alpha]_D^{20}$ −966.3 (*c* 1.0 in $CHCl_3$); ^1H NMR (selected data) δ 3.12 (d, 4H, $J = 3.0$ Hz, NCH_2), 3.73 (m, 6H, $CHOCH_2$) 4.25 [d, $J = 2.1$ Hz, 2H, H^3 (C_5H_3)], 4.37 [d, $J = 1.8$ Hz, 2H, H^4 (C_5H_3)], 4.42 [s, 2H, H^5 (C_5H_3)], 4.55 [s, 10H, C_5H_5)], 7.76 (s, 2H, *H*C═N); $^{13}C\{^1H\}$ NMR (selected data) δ 68.8 [C^4 (C_5H_3)], 71.2 (C_5H_5), 74.5 [C^3 (C_5H_3)], 78.5 [C^5 (C_5H_3)], 98.1 [C^1 (C_5H_3)], 176.4 (C═N). Anal. Calcd for $C_{32}H_{36}Fe_2I_2N_2O_2Pd_2$: C, 36.29; H, 3.43; N, 2.65. Found: C, 36.29; H, 3.59; N, 2.26. Characterization data for *syn*-(+)-(R_p,*R*,*R*,R_p)-**5a**: $[\alpha]_D^{20}$ +820.9 (*c* 1.0 in $CHCl_3$); ^1H NMR (selected data) δ 3.17 (d, 4H, $J = 1.2$ Hz, NCH_2), 3.38 (s, 6H, H_3CC═N), 3.67 (m, 6H, $CHOCH_2$) 4.26 [d, $J = 2.1$ Hz, 2H, H^3 (C_5H_3)], 4.39 [d, $J = 3.0$ Hz, 2H, H^4 (C_5H_3)], 4.44 [s, 2H, H^5 (C_5H_3)], 4.58 [s, 10H, C_5H_5)]; $^{13}C\{^1H\}$ NMR (selected data) δ 68.9 [C^4 (C_5H_3)], 71.4 (C_5H_5), 75.6 [C^3 (C_5H_3)], 78.2 [C^5 (C_5H_3)], 98.8 [C^1 (C_5H_3)], 176.9 (C═N). Anal. Calcd for $C_{34}H_{40}Cl_2Fe_2N_2O_2Pd_2$: C, 45.17; H, 4.46; N, 3.10. Found: C, 44.92; H, 4.29; N, 3.48. Characterization data for *syn*-(−)-(S_p,*S*,*S*,S_p)-**5a**: $[\alpha]_D^{20}$ −811.1 (*c* 1.0 in $CHCl_3$); ^1H NMR (selected data) δ 3.19 (d, 4H, $J = 2.1$ Hz, NCH_2), 3.33 (s, 6H, H_3CC═N), 3.65 (m, 6H, $CHOCH_2$) 4.25 [d, $J = 1.5$ Hz, 2H, H^3 (C_5H_3)], 4.40 [d, $J = 3.0$ Hz, 2H, H^4 (C_5H_3)], 4.46 [s, 2H, H^5 (C_5H_3)], 4.56 [s, 10H, C_5H_5)]; $^{13}C\{^1H\}$ NMR (selected data) δ 68.9 [C^4 (C_5H_3)], 71.3 (C_5H_5), 75.8 [C^3 (C_5H_3)], 78.1 [C^5 (C_5H_3)], 98.9 [C^1 (C_5H_3)], 176.5 (C═N). Anal. Calcd for $C_{34}H_{40}Cl_2Fe_2N_2O_2Pd_2$: C, 45.17; H, 4.46; N, 3.10. Found: C, 45.38; H, 4.51; N, 3.09. Characterization data for *syn*-(+)-(R_p,*R*,*R*,R_p)-**5b**: $[\alpha]_D^{20}$ +1528.4 (*c* 1.0 in $CHCl_3$); ^1H NMR (selected data) δ 3.23 (d, 4H, $J = 2.1$ Hz, NCH_2), 3.36 (s, 6H, H_3CC═N), 3.63 (m, 6H, $CHOCH_2$), 4.25 [d, $J = 2.1$ Hz, 2H, H^3 (C_5H_3)], 4.38 [d, $J = 2.7$ Hz, 2H, H^4 (C_5H_3)], 4.44 [s, 2H, H^5 (C_5H_3)], 4.57 [s, 10H, C_5H_5)]; $^{13}C\{^1H\}$ NMR (selected data) δ 68.6 [C^4 (C_5H_3)], 71.0 (C_5H_5), 75.6 [C^3 (C_5H_3)], 78.0 [C^5 (C_5H_3)], 98.7 [C^1 (C_5H_3)], 176.8 (C═N). Anal. Calcd for $C_{34}H_{40}Br_2Fe_2N_2O_2Pd_2$: C, 41.12; H, 4.06; N, 2.82. Found: C, 41.45; H, 4.09; N, 2.53. Characterization data for *syn*-(−)-(S_p,*S*,*S*,S_p)-**5b**: $[\alpha]_D^{20}$ −1526.2 (*c* 1.0 in $CHCl_3$); ^1H NMR (selected data) δ 3.22 (d, 4H, $J = 2.1$ Hz, NCH_2), 3.34 (s, 6H, H_3CC═N), 3.66 (m, 6H, $CHOCH_2$) 4.24 [d, $J = 2.7$ Hz, 2H, H^3 (C_5H_3)], 4.39 [d, $J = 2.7$ Hz, 2H, H^4 (C_5H_3)], 4.44 [s, 2H, H^5 (C_5H_3)], 4.56 [s, 10H, C_5H_5)]; $^{13}C\{^1H\}$ NMR (selected data) δ 68.9 [C^4 (C_5H_3)], 71.2 (C_5H_5), 75.8 [C^3 (C_5H_3)], 78.1 [C^5 (C_5H_3)], 98.9 [C^1 (C_5H_3)], 176.6 (C=N). Anal. Calcd for $C_{34}H_{40}Br_2Fe_2N_2O_2Pd_2$: C, 41.12; H, 4.06; N, 2.82. Found: C, 41.05; H, 3.83; N, 2.94. Characterization data for *syn*-(+)-(R_p,R,R,R_p)-**5c**: $[\alpha]_D^{20}$ +1027.6 (*c* 1.0 in $CHCl_3$); ^1H NMR (selected data) δ 3.20 (d, 4H, $J = 2.7$ Hz, NCH_2), 3.32 (s, 6H, H_3CC=N), 3.67 (m, 6H, $CHOCH_2$) 4.26 [d, $J = 2.1$ Hz, 2H, H^3 (C_5H_3)], 4.40 [d, $J = 2.7$ Hz, 2H, H^4 (C_5H_3)], 4.46 [s, 2H, H^5 (C_5H_3)], 4.59 [s, 10H, C_5H_5)]; $^{13}C\{^1H\}$ NMR (selected data) δ 69.5 [C^4 (C_5H_3)], 71.5 (C_5H_5), 75.9 [C^3 (C_5H_3)], 78.1 [C^5 (C_5H_3)], 99.2 [C^1 (C_5H_3)], 176.8 (C=N). Anal. Calcd for $C_{34}H_{40}Fe_2I_2N_2O_2Pd_2$: C, 37.57; H, 3.71; N, 2.58. Found: C, 3.53; H, 3.37; N, 2.23. Characterization data for *syn*-(−)-(S_p,S,S,S_p)-**5c**: $[\alpha]_D^{20}$ −1034.6 (*c* 1.0 in $CHCl_3$); ^1H NMR (selected data) δ 3.22 (d, 4H, $J = 2.4$ Hz, NCH_2), 3.36 (s, 6H, H_3CC=N), 3.68 (m, 6H, $CHOCH_2$), 4.25 [d, $J = 2.1$ Hz, 2H, H^3 (C_5H_3)], 4.41 [d, $J = 2.7$ Hz, 2H, H^4 (C_5H_3)], 4.49 [s, 2H, H^5 (C_5H_3)], 4.60 [s, 10H, C_5H_5)]; $^{13}C\{^1H\}$ NMR (selected data) δ 69.9 [C^4 (C_5H_3)], 71.7 (C_5H_5), 76.0 [C^3 (C_5H_3)], 78.2 [C^5 (C_5H_3)], 99.8 [C^1 (C_5H_3)], 176.8 (C=N). Anal. Calcd for $C_{34}H_{40}Fe_2I_2N_2O_2Pd_2$: C, 37.57; H, 3.71; N, 2.58. Found: C, 37.53; H, 3.68; N, 2.73.

Preparation of [Pd{(η^5-C_5H_3CR=$NCH_2CHCH_2CH_2CH_2$O)Fe(η^5-C_5H_5)}(μ-NO_2)]$_2$ (R = H, *syn*-(+)-(R_p,R,R,R_p)-6a, *syn*-(−)-(S_p,S,S,S_p)-6a; R = Me, *syn*-(+)-(R_p,R,R,R_p)-6b, *syn*-(−)-(S_p,S,S,S_p)-6b). Red blocks of *syn*-(+)-(R_p,R,R,R_p)-**6a**, *syn*-(−)-(S_p,S,S,S_p)-**6a**, *syn*-(+)-(R_p,R,R,R_p)-**6b**, and *syn*-(−)-(S_p,S,S,S_p)-**6b** were prepared according to the procedure described above using $NaNO_2$ as starting material and 30 min of reaction time. The yield was 0.14−0.16 g (80−90%). Characterization data for *syn*-(+)-(R_p,R,R,R_p)-**6a**: $[\alpha]_D^{20}$ +3020.2 (*c* 1.0 in $CHCl_3$); ^1H NMR (selected data) δ 3.21 (d, 4H, $J = 6.3$ Hz, NCH_2), 3.73 (m, 6H, $CHOCH_2$), 4.21 [d, $J = 1.5$ Hz, 2H, H^3 (C_5H_3)], 4.29 [d, $J = 2.4$ Hz, 2H, H^4 (C_5H_3)], 4.34 [s, 2H, H^5 (C_5H_3)], 4.39 [s, 10H, C_5H_5)], 7.90 (s, 2H, HC=N); $^{13}C\{^1H\}$ NMR (selected data) δ 69.1 [C^4 (C_5H_3)], 71.4 (C_5H_5), 75.3 [C^3 (C_5H_3)], 78.5 [C^5 (C_5H_3)], 100.3 [C^1 (C_5H_3)], 180.2 (C=N). Anal. Calcd for $C_{32}H_{36}Fe_2N_4O_6Pd_2$: C, 42.84; H, 4.04; N, 6.25. Found: C, 42.95; H, 4.27; N, 6.28. Characterization data for *syn*-(−)-(S_p,S,S,S_p)-**6a**: $[\alpha]_D^{20}$ −3031.6 (*c* 1.0 in $CHCl_3$); ^1H NMR (selected data) δ 3.23 (d, 4H, $J = 6.0$ Hz, NCH_2), 3.71 (m, 6H, $CHOCH_2$), 4.23 [d, $J = 2.1$ Hz, 2H, H^3 (C_5H_3)], 4.29 [d, $J = 2.1$ Hz, 2H, H^4 (C_5H_3)], 4.35 [s, 2H, H^5 (C_5H_3)], 4.40 [s, 10H, C_5H_5)], 7.88 (s, 2H, HC=N); $^{13}C\{^1H\}$ NMR (selected data) δ 69.0 [C^4 (C_5H_3)], 71.3 (C_5H_5), 75.5 [C^3 (C_5H_3)], 78.6 [C^5 (C_5H_3)], 100.0 [C^1 (C_5H_3)], 180.3 (C=N). Anal. Calcd for $C_{32}H_{36}Fe_2N_4O_6Pd_2$: C, 42.84; H, 4.04; N, 6.25. Found: C, 42.54; H, 4.09; N, 6.61. Characterization data for *syn*-(+)-(R_p,R,R,R_p)-**6b**: $[\alpha]_D^{20}$ +1729.7 (*c* 1.0 in $CHCl_3$); ^1H NMR (selected data) δ 3.23 (s, 6H, H_3CC=N), 4.27 [t, $J = 2.1$, 2H, H^3 (C_5H_3)], 4.31 (s, 10H, C_5H_5), 4.46 [t, $J = 2.4$ Hz, 2H, H^4 (C_5H_3)], 4.70 [s, 2H, H^5 (C_5H_3)]; $^{13}C\{^1H\}$ (selected data) δ 67.0 [C^4 (C_5H_3)], 70.2 [C^3 (C_5H_3)], 71.7 [C^5 (C_5H_3)], 75.8 (C_5H_5), 100.3 [C^1 (C_5H_3)], 188.0 (C=N). Anal. Calcd for $C_{34}H_{40}Fe_2N_4O_6Pd_2$: C, 44.16; H, 4.36; N, 6.06. Found: C, 44.22; H, 4.56; N, 6.15. Characterization data for *syn*-(−)-(S_p,S,S,S_p)-**6b**: $[\alpha]_D^{20}$ −1712.3 (*c* 1.0 in $CHCl_3$); ^1H NMR (selected data) δ 3.22 (s, 6H, H_3CC=N), 4.27 [t, $J = 2.1$ Hz, 2H, H^3 (C_5H_3)], 4.30 (s, 10H, C_5H_5), 4.46 [t, $J = 2.4$ Hz, 2H, H^4 (C_5H_3)], 4.73 [s, 2H, H^5 (C_5H_3)]; $^{13}C\{^1H\}$ (selected data) δ 67.2 [C^4 (C_5H_3)], 70.3 [C^3 (C_5H_3)], 71.7 [C^5 (C_5H_3)], 75.6 (C_5H_5), 99.8 [C^1 (C_5H_3)], 188.3 (C=N). Anal. Calcd for $C_{34}H_{40}Fe_2N_4O_6Pd_2$: C, 44.16; H, 4.36; N, 6.06. Found: C, 44.08; H, 4.29; N, 6.27.

Preparation of [Pd{(η^5-C_5H_3CR=$NCH_2CHCH_2CH_2CH_2$O)Fe(η^5-C_5H_5)}(μ-SCN)]$_2$ (R = H, *syn*-(+)-(R_p,R,R,R_p)-7a, *syn*-(−)-(S_p,S,S,S_p)-7a; R = Me, *syn*-(+)-(R_p,R,R,R_p)-7b, *syn*-(−)-(S_p,S,S,S_p)-7b). These compounds were prepared according to the procedure described above using KSCN as starting material in a reaction over 15 min. Yield: 0.15−0.17 g (82−93%). Characterization data for *syn*-(+)-(R_p,R,R,R_p)-**7a**: $[\alpha]_D^{20}$ +3306.1 (*c* 1.0 in $CHCl_3$); ^1H NMR (selected data) δ 3.24 (d, 4H, $J = 2.1$ Hz, NCH_2), 3.75 (m, 6H, $CHOCH_2$), 4.27 [d, $J = 2.1$ Hz, 2H, H^3 (C_5H_3)], 4.41 [d, $J = 2.7$ Hz, 2H, H^4 (C_5H_3)], 4.45 [s, 2H, H^5 (C_5H_3)], 4.69 [s, 10H, C_5H_5)]; $^{13}C\{^1H\}$ NMR (selected data) δ 68.7 [C^4 (C_5H_3)], 72.3 (C_5H_5), 74.7 [C^3 (C_5H_3)], 78.1 [C^5 (C_5H_3)], 90.7 [C^1 (C_5H_3)], 176.8 (C=N). Anal. Calcd for $C_{34}H_{36}Fe_2N_4O_2Pd_2S_2$: C, 44.32; H, 3.94; N, 6.08. Found: C, 44.25; H, 4.12; N, 6.26. Characterization data for *syn*-(−)-(S_p,S,S,S_p)-**7a**: $[\alpha]_D^{20}$ −3337.4 (*c* 1.0 in $CHCl_3$); ^1H NMR (selected data) δ 3.22 (d, 4H, $J = 2.4$ Hz, NCH_2), 3.76 (m, 6H, $CHOCH_2$), 4.26 [d, $J = 2.7$ Hz, 2H, H^3 (C_5H_3)], 4.42 [d, $J = 2.4$ Hz, 2H, H^4 (C_5H_3)], 4.46 [s, 2H, H^5 (C_5H_3)], 4.69 [s, 10H, C_5H_5)]; $^{13}C\{^1H\}$ NMR (selected data) δ 68.8 [C^4 (C_5H_3)], 72.3 (C_5H_5), 74.9 [C^3 (C_5H_3)], 78.1 [C^5 (C_5H_3)], 90.9 [C^1 (C_5H_3)], 176.9 (C=N). Anal. Calcd for $C_{34}H_{36}Fe_2N_4O_2Pd_2S_2$: C, 44.32; H, 3.94; N, 6.08. Found: C, 44.61; H, 3.57; N, 6.23. Characterization data for *syn*-(+)-(R_p,R,R,R_p)-**7b**: $[\alpha]_D^{20}$ +1729.0 (*c* 1.0 in $CHCl_3$); ^1H NMR (selected data) δ 3.21 (d, 4H, $J = 1.8$ Hz, NCH_2), 3.36 (s, 6H, H_3CC=N), 3.74 (m, 6H, $CHOCH_2$), 4.22 [d, $J = 2.1$ Hz, 2H, H^3 (C_5H_3)], 4.43 [d, $J = 2.1$ Hz, 2H, H^4 (C_5H_3)], 4.47 [s, 2H, H^5 (C_5H_3)], 4.71 [s, 10H, C_5H_5)]; $^{13}C\{^1H\}$ NMR (selected data) δ 68.9 [C^4 (C_5H_3)], 72.6 (C_5H_5), 75.3 [C^3 (C_5H_3)], 78.0 [C^5 (C_5H_3)], 92.5 [C^1 (C_5H_3)], 176.2 (C=N). Anal. Calcd for $C_{36}H_{40}Fe_2N_4O_2Pd_2S_2$: C, 45.54; H, 4.25; N, 5.90. Found: C, 45.68; H, 4.29; N, 6.16. Characterization data for *syn*-(−)-(S_p,S,S,S_p)-**7b**: $[\alpha]_D^{20}$ −1740.3 (*c* 1.0 in $CHCl_3$); ^1H NMR (selected data) δ 3.20 (d, 4H, $J = 1.5$ Hz, NCH_2), 3.37 (s, 6H, H_3CC=N), 3.76 (m, 6H, $CHOCH_2$), 4.25 [d, $J = 3.0$ Hz, 2H, H^3 (C_5H_3)], 4.44 [d, $J = 1.8$ Hz, 2H, H^4 (C_5H_3)], 4.48 [s, 2H, H^5 (C_5H_3)], 4.72 [s, 10H, C_5H_5)]; $^{13}C\{^1H\}$ NMR (selected data) δ 69.1 [C^4 (C_5H_3)], 72.9 (C_5H_5), 75.3 [C^3 (C_5H_3)], 78.2 [C^5 (C_5H_3)], 92.5 [C^1 (C_5H_3)], 176.8 (C=N). Anal. Calcd for $C_{36}H_{40}Fe_2N_4O_2Pd_2S_2$: C, 45.54; H, 4.25; N, 5.90. Found: C, 45.27; H, 4.53; N, 5.72.

Preparation of [PdX(η^5-C_5H_3{η^3-(PhC=C(Ph)(Ph)C=CPh)}CH=$NCH_2CHCH_2CH_2CH_2$O)Fe(η^5-C_5H_5)] (X = I, (+)-(R_p,R)-8; X = NO_2, (+)-(R_p,R)-9; X = SCN, (+)-(R_p,R)-10; X = OAc, (+)-(R_p,R)-11). A 0.15 mmol portion of *syn*-(+)-(R_p,R,R,R_p)-**4c** (or *syn*-(+)-(R_p,R,R,R_p)-**6a**, *syn*-(+)-(R_p,R,R,R_p)-**7a**, or *syn*-(+)-(R_p,R,R,R_p)-**2a**) was dissolved in 30 mL of $CHCl_3$, and then PhC≡CPh (0.14 g, 0.8 mmol) was added. The mixture was refluxed for 3−36 h (3 h for *syn*-(+)-(R_p,R,R,R_p)-**4c**, 10 h for *syn*-(+)-(R_p,R,R,R_p)-**6a**, 24 h for *syn*-(+)-(R_p,R,R,R_p)-**7a**, and 36 h for *syn*-(+)-(R_p,R,R,R_p)-**2a**), allowed to evaporate to ca. 5 mL, and isolated via column chromatography (silica 60, chloroform as eluent). The red solid was subsequently recrystallized as red needles from dichloromethane/*n*-hexane. Yield: 0.14 g (53%) for (+)-(R_p,R)-**8**, 0.19 g (68.3%) for (+)-(R_p,R)-**9**, 0.14 g (53%) for (+)-(R_p,R)-**10**, and 0.21 g (75.3%) for (+)-(R_p,R)-**11**. Characterization data for (+)-(R_p,R)-**8**: $[\alpha]_D^{20}$ +392.8 (*c* 1.0, $CHCl_3$); ^1H NMR (selected data) δ 3.21 (d, 4H, $J = 2.1$ Hz, NCH_2), 3.69 (m, 6H, $CHOCH_2$), 4.11 (s, 5H, C_5H_5), 4.20 [t, $J = 1.8$ Hz, 1H, H^3 (C_5H_3)], 4.38 [d, $J = 1.5$ Hz, 1H, H^5 (C_5H_3)], 4.58 [d, $J = 2.1$ Hz, 1H, H^4 (C_5H_3)], 6.61−7.44 (m, 20H, aromatic), 7.73 (s, 2H, HC=N); $^{13}C\{^1H\}$ NMR (selected data) δ 72.2 [C^4 (C_5H_3)], 72.9 [C^3 (C_5H_3)], 75.6 [C^5 (C_5H_3)], 78.1 (C_5H_5), 110.6 [C^1 (C_5H_3)], 126.6, 127.1, 128.1, 128.4, 133.0, 135.5, 138.1, 140.8, 145.8 (Ph and =C), 167.3 (C=N). Anal. Calcd for $C_{44}H_{38}FeINOPd$: C, 59.65; H, 4.32; N, 1.58. Found: C, 59.32; H, 4.56; N, 1.81. Characterization data for (+)-(R_p,R)-**9**: $[\alpha]_D^{20}$ +443.9 (*c* 1.0, $CHCl_3$); ^1H NMR (selected data) δ 3.21 (d, 4H, $J = 1.2$ Hz, NCH_2), 3.69 (m, 6H, $CHOCH_2$), 4.10 (s, 5H, C_5H_5), 4.20 [t, $J = 1.5$ Hz, 1H, H^3 (C_5H_3)], 4.38 [d, $J = 1.8$ Hz, 1H, H^5 (C_5H_3)], 4.58 [d, $J = 2.1$ Hz, 1H, H^4 (C_5H_3)], 6.61−7.46 (m, 20H, aromatic), 7.64 (s, 2H, HC=N); $^{13}C\{^1H\}$ NMR (selected data) δ 72.2 [C^4 (C_5H_3)], 72.6 [C^3 (C_5H_3)], 75.5 [C^5 (C_5H_3)], 78.1 (C_5H_5), 110.1 [C^1 (C_5H_3)], 126.5, 127.1, 128.2, 128.4, 133.1, 135.5, 138.2, 140.5, 145.6 (Ph and =C), 167.8 (C=N). Anal. Calcd for $C_{44}H_{38}FeN_2O_3Pd$: C, 65.64; H, 4.76; N, 3.48.

Found: C, 65.49; H, 4.65; N, 3.72. Characterization data for (+)-(R_p,R)-**10**: $[\alpha]_D^{20}$ +579.5 (c 1.0, $CHCl_3$); ^{1}H NMR (selected data) δ 3.21 (d, 4H, J = 1.5 Hz, NCH_2), 3.70 (m, 6H, C*H*OC*H*$_2$), 4.20 (s, 5H, C_5H_5), 4.29 [t, J = 1.8 Hz, 1H, H^3 (C_5H_3)], 4.36 [d, J = 1.8 Hz, 1H, H^5 (C_5H_3)], 4.59 [d, J = 1.8 Hz, 1H, H^4 (C_5H_3)], 6.62−7.45 (m, 20H, aromatic), 7.65 (s, 2H, *H*C=N); ^{13}C{^{1}H} NMR (selected data) δ 72.3 [C^4 (C_5H_3)], 72.7 [C^3 (C_5H_3)], 75.7 [C^5 (C_5H_3)], 78.1 (C_5H_5), 110.3 [C^1 (C_5H_3)], 126.7, 127.2, 128.1, 131.9, 135.4, 137.0, 138.1, 140.7, 145.8 (Ph and =C), 167.3 (C=N). Anal. Calcd for $C_{44}H_{38}FeN_2OPdS$: C, 66.14; H, 4.69; N, 3.43. Found: C, 66.05; H, 4.82; N, 3.53. Characterization data for (+)-(R_p,R)-**11**: $[\alpha]_D^{20}$ +443.9 (c 1.0, $CHCl_3$); ^{1}H NMR (selected data) δ 3.31 (d, 4H, J = 1.8 Hz, NCH_2), 3.69 (m, 6H, C*H*OC*H*$_2$), 4.19 (s, 5H, C_5H_5), 4.28 [t, J = 2.1 Hz, 1H, H^3 (C_5H_3)], 4.36 [d, J = 2.4 Hz, 1H, H^5 (C_5H_3)], 4.42 [d, J = 2.1 Hz, 1H, H^4 (C_5H_3)], 6.57−7.47 (m, 20H, aromatic), 7.74 (s, 2H, *H*C=N); ^{13}C{^{1}H} NMR (selected data) δ 71.2 [C^4 (C_5H_3)], 73.0 [C^3 (C_5H_3)], 75.8 [C^5 (C_5H_3)], 78.1 (C_5H_5), 109.5 [C^1 (C_5H_3)], 126.6, 127.4, 128.1, 132.0, 135.0, 136.9, 138.3, 140.3, 145.8 (Ph and =C), 175.8 (C=N). Anal. Calcd for $C_{46}H_{41}FeNO_3Pd$: C, 67.53; H, 5.05; N, 1.71. Found: C, 67.44; H, 4.92; N, 1.53.

Crystallographic Studies. Crystallographic data for *syn*-(−)-(S_p,S,S,S_p)-**2a**, syn-(+)-(R_p,R,R,R_p)-**2b**, *syn*-(+)-(R_p,R,R,R_p)-**4a**, *syn*-(−)-(S_p,S,S,S_p)-**4a**, *syn*-(+)-(R_p,R,R,R_p)-**4b**, *syn*-(+)-(R_p,R,R,R_p)-**5a**, *syn*-(−)-(S_p,S,S,S_p)-**5a**, *syn*-(+)-(R_p,R,R,R_p)-**6a**, *syn*-(+)-(R_p,R,R,R_p)-**7a**·$^1/_2CH_2Cl_2$, *syn*-(−)-(S_p,S,S,S_p)-**7a**·$^1/_2CH_2Cl_2$, and (+)-(R_p,R)-**8** measured on a MSC/Rigaku RAXIS IIC imaging-plate diffractometer are summarized in Tables 1 and 2. Intensities were collected at 294 K using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) from a rotating-anode generator operating at 50 kV and 90 mA ($2\theta_{\min}$ = 3°, $2\theta_{\max}$ = 55°, 2−5° oscillation frames in the range of 0−180°, exposure 8 min. per frame).[28] A self-consistent semiempirical absorption correction based on Fourier coefficient fitting of symmetry-equivalent reflections was applied using the ABSCOR program.[29] Crystallographic data for *syn*-(+)-(R_p,S,S,R_p)-**2a**·CH_2Cl_2 and *syn*-(−)-(R_p,S,S,S_p)-**3** were measured on a Bruker SMART-CCD diffractometer (ω-scans with 0.3° per frame, $4.26 < 2\theta < 52.04$ for *syn*-(+)-(R_p,S,S,R_p)-**2a**·CH_2Cl_2 and $3.52 < 2\theta < 56.72°$ for *syn*-(−)-(R_p,S,S,S_p)-**3**) using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å).

The crystal structures of all compounds were solved by direct phase determination, and all the non-hydrogen atoms were refined anisotropically. The dichloromethane solvate molecule in *syn*-(+)-(R_p,S,S,R_p)-**2a**·CH_2Cl_2 is located in a general position with full site occupancy for its component atoms. The dichloromethane solvate molecules in both *syn*-(+)-(R_p,R,R,R_p)-**7a**·$^1/_2CH_2Cl_2$ and *syn*-(−)-(S_p,S,S,S_p)-**7a**·$^1/_2CH_2Cl_2$ are located in a special position with half site occupancy for their component atoms. Hydrogen atoms were all generated geometrically (C−H bond lengths fixed at 0.96 Å), assigned appropriate isotropic thermal parameters, and allowed to ride on their parent carbon atoms. Full-matrix least-squares refinement on F^2 was performed on an IBM-compatible 486 PC with the SHELXTL-PC program package.[30] Although in most cases the Flack parameter[31] failed to give a clear indication of the absolute structure in the X-ray analysis, the known chiralities of (−)-(R)-tetrahydrofurfurylamine and (+)-(S)-tetrahydrofurfurylamine as starting synthetic materials ensured the correct assignment of the absolute configurations of all diastereomers. The final R1 and wR2 indices and other refinement parameters are presented in Tables 1 and 2, and Tables 3 and 4 give selected bond distances and angles.

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Supporting Information Available: Tables of final atomic coordinates, all bond distances and angles, hydrogen coordinates, and anisotropic thermal parameters for *syn*-(−)-(S_p,S,S,S_p)-**2a**, *syn*-(+)-(R_p,S,S,R_p)-**2a**·CH_2Cl_2, *syn*-(+)-(R_p,R,R,R_p)-**2b**, *syn*-(−)-(R_p,S,S,S_p)-**3**, *syn*-(+)-(R_p,R,R,R_p)-**4a**, *syn*-(−)-(S_p,S,S,S_p)-**4a**, *syn*-(+)-(R_p,R,R,R_p)-**4b**, *syn*-(+)-(R_p,R,R,R_p)-**5a**, *syn*-(−)-(S_p,S,S,S_p)-**5a**, *syn*-(+)-(R_p,R,R,R_p)-**6a**, *syn*-(+)-(R_p,R,R,R_p)-**7a**·$^1/_2CH_2Cl_2$, *syn*-(−)-(S_p,S,S,S_p)-**7a**·$^1/_2CH_2Cl_2$, and (+)-(R_p,R)-**8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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