

Synthesis and Characterization of Cationic Palladium (6,6'-Dimethoxybiphenyl-2,2'-diyl)bis(diphenylphosphine) Complexes

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For compounds of the type [(MeO-BIPHEP)PdX₂] (where MeO-BIPHEP is (6,6'-dimethoxybiphenyl-2,2'-diyl)bis(diphenylphosphine) and X is an anion with low coordination ability) one or both anions X, depending on their nature, are displaced in an outer coordination sphere due to water coordination. The compounds are easily reduced in methanolic solution. With the diaquo complex [(S-MeO-BIPHEP)Pd(H₂O)₂](OTf)₂ as starting material, the formation of the dimeric palladium(I) complex [(S-MeO-BIPHEP)Pd]₂(OTf)₂ is observed. In contrast, under CO pressure, the μ -hydrido μ -carbonyl binuclear palladium(I) complex [(S-MeO-BIPHEP)Pd(μ -H)(μ -CO)Pd(S-MeO-BIPHEP)]OTf is formed. The molecular structures of [(S-MeO-BIPHEP)Pd(H₂O)(THF)](OTf)₂ and [(S-MeO-BIPHEP)Pd(OTfa)₂] were determined by X-ray diffraction.

In recent years cationic palladium(II) complexes have attracted a great deal of attention in organometallic chemistry, particularly due to their catalytic reactions and to their application in the self-assembly of various metallamacrocycles. In the field of catalysis, the most important process which deserves mention is the copolymerization of olefins with carbon monoxide;^{1–3} this is even more so if the possibility of extending the copolymerization process to functionalized olefin substrates is taken into account.^{4,5} Other useful applications, reported in the literature, include the carbonylation of olefinic substrates to form aldehydes,^{6,7} monoesters,⁸ ketones,^{9–12} and diesters,^{13–17} the water-gas shift reaction,¹² and the carbonylation of other

substrates such as nitroaromatics¹⁸ and alkylphenyliodonium salts.¹⁹ Furthermore, oxidations,²⁰ different types of rearrangements,^{21,22} dimerization (of methyl acrylate),^{23,24} acetalization and transacetalization,²⁵ hydration,²⁶ and carbon–carbon bond-forming reactions, such as the Heck^{27,28} and aldol reactions,²⁹ have been catalyzed by cationic palladium complexes.

An important aspect of the chemistry of such complexes is related to the coordination of water.³⁰ In fact, the aquo complexes can give the binuclear μ -hydroxo species **2** (Scheme 1),^{31–36} which could lead to palladium hydride species in the presence of reducing agents (e.g. when CO is present, CO₂ is formed).^{11,34,37,38} Palladium

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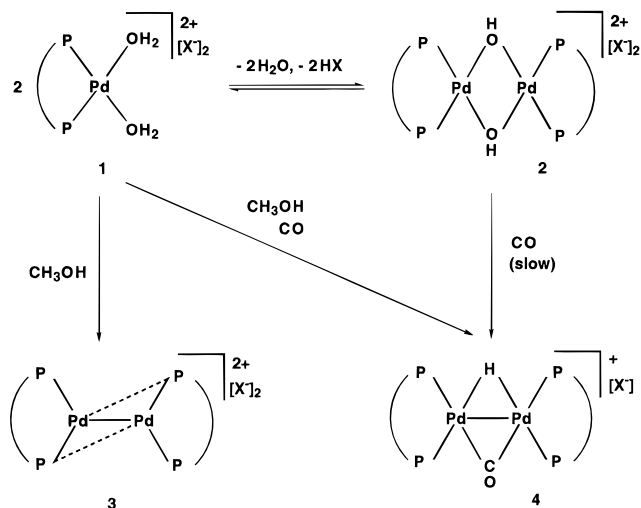
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Scheme 1

Table 1. ^{31}P NMR and Conductivity Data for **1a–d**

complex	^{31}P NMR ^a	conductivity Λ_M^b
$\{[(S)\text{-MeO-BIPHEP}\}\text{Pd}(\text{H}_2\text{O})_2](\text{OTf})_2$ (1a)	33.7	157
$\{[(S)\text{-MeO-BIPHEP}\}\text{Pd}(\text{H}_2\text{O})_2](\text{BF}_4)_2$ (1b)	33.3	171
$\{[(S)\text{-MeO-BIPHEP}\}\text{Pd}(\text{H}_2\text{O})(\text{OTs})\}\text{OTs}$ (1c)	30.7	55
$\{[(S)\text{-MeO-BIPHEP}\}\text{Pd}(\text{OTfa})_2$ (1d)	27.5	4

^a δ (ppm) in CDCl_3 . ^b In a 10^{-3} M acetone solution ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$).

hydrides are believed to be part of the catalytic cycle in most of the aforementioned reactions.

In view of the growing interest in cationic palladium complexes containing chiral atropisomeric diphosphine ligands, both for highly enantioselective catalytic reactions^{14–16,29,39} and for the self-organizing assembly of high-molecular weight species,⁴⁰ we report here the preparation of some palladium(II) complexes of the MeO-BIPHEP ligand (MeO-BIPHEP is (6,6'-dimethoxybiphenyl-2,2'-diyl)bis(diphenylphosphine)) with different anions as well as their characterization in solution and, for two of them, in the solid state. Furthermore, their reactivity under conditions relevant to carbonylation catalysis is discussed.

With $\{[(S)\text{-MeO-BIPHEP}\}\text{PdCl}_2\}$ as starting material,¹⁶ the addition of the corresponding silver salts AgX ($\text{X}^- = \text{OTf}^-, \text{BF}_4^-, \text{OTs}^-, \text{OTfa}^-$) in tetrahydrofuran or acetone led to the formation of the complexes **1** as yellow microcrystalline solids. Table 1 shows the ^{31}P NMR data and the conductivity in a 10^{-3} M acetone solution of the complexes. The reported composition of the complexes is based on those data as well as on elemental analysis and ^1H NMR data.

All manipulations were carried out under a dry nitrogen atmosphere using Schlenk techniques and dried solvents; however, with the exception of the trifluoroacetate compound **1d**, the aquo complex was isolated. A possible source of water may be the silver salt, which was used, as purchased, for the synthesis. This was already observed for the preparation of cationic aquocarbonylmanganese and -rhenium complexes with weakly coordinating anions.⁴¹ The high hygroscopicity of anhydrous palladium bis(triflates) containing atrop-

isomeric diphosphine ligands has been described recently.⁴² Moreover, it was observed that the high binding constant of water to palladium can lead to displacement of ligands even if water is present at an impurity level.²⁸

The cation–anion separation of the complexes **1** corresponds to that expected for the various anions on the basis of their σ -donor strength reported in the literature.⁴³ The stoichiometry of **1** is also supported by conductivity measurements showing increased values of conductivity Λ_M with decreasing coordination ability of the anion. This shows that cationic complexes must be present in acetone solution for **1a–c**. In contrast, the low value of Λ_M for **1d** indicates that almost no dissociation of the trifluoroacetate anions from the palladium center takes place.

All complexes mentioned in Table 1 showed only one ^{31}P NMR signal at room temperature. A ^{31}P NMR variable-temperature study of **1a** showed no line broadening down to -80 °C. Attempts to recognize the anisochronicity of the two phosphorus atoms of **1c** through low-temperature NMR spectroscopy failed. However, the singlets of the methyl protons belonging to the tosylate anion and to the methoxy substituent of the MeO-BIPHEP ligand at room temperature split into two signals with a ratio of $\sim 2:1$ at -80 °C (2.17, 2.31 ppm and 3.40, 3.51 ppm). Correspondingly, the ^{31}P NMR spectrum contains two signals at 29.89 and 33.81 ppm in the same ratio of $\sim 2:1$. The less intense set of signals might be due to the diaquo complex, as indicated by comparison of the NMR data. The species corresponding to the second set of signals must, therefore, contain coordinated tosylate anions as reported for **1c** in Table 1. However, whether the signals are due to $\{[(S)\text{-MeO-BIPHEP}\}\text{Pd}(\text{OTs})_2\}$ or to a still dynamic equilibrium at -80 °C between $\{[(S)\text{-MeO-BIPHEP}\}\text{Pd}(\text{OTs})_2\}$ and $\{[(S)\text{-MeO-BIPHEP}\}\text{Pd}(\text{OTs})(\text{H}_2\text{O})\}(\text{OTs})$ is not obvious. An equilibrium between the coordination of water (present at an impurity level), the solvent (THF), and a triflate anion toward a cationic aryl-(diphosphine)palladium(II) fragment has been reported recently.²⁸ A rapid exchange of THF and water was observed that could be slowed down at -98 °C. The corresponding complex with coordinated triflate, however, has not been observed. Analogously, we observed that complex **1a** crystallized out from a THF solution with exchange of one water molecule as $\{[(S)\text{-MeO-BIPHEP}\}\text{Pd}(\text{H}_2\text{O})(\text{THF})\}(\text{OTf})_2$.

In an attempt to determine the conductivity of **1a–d** in methanol, a color change of the solutions from yellow to red was observed. The rate of the development of the red color was enhanced by increasing the temperature. The conductivity Λ_M of **1d** after stirring a 10^{-3} M methanolic solution for 30 min is $64 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ as compared to $4 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ in acetone (see Table 1). A methanolic solution of **1a** was heated overnight at 50 °C. The ^{31}P NMR spectrum showed the appearance of an AA'XX' pattern as well as the original singlet of unreacted **1a** ($\sim 60\%$). The red color and the NMR data imply the formation of the dimeric palladium(I) complex $\{[(S)\text{-MeO-BIPHEP}\}\text{Pd}\}_2(\text{OTf})_2$, to which structure **3** (Scheme 1; P-P = (S)-MeO-BIPHEP, X = OTf) is

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ascribed in analogy to a recently described similar binuclear Pd(I) compound.⁴⁴ Attempts to isolate **3** through crystallization were unsuccessful.

The fact that the reduction of palladium occurs but carbonyl complexes do not form, as was expected,^{45–47} prompted us to study this reaction in the presence of carbon monoxide, i.e. under conditions in which compounds **1** are catalyst precursors for carbonylation reactions. The NMR spectra show that, after 20 h at 50 °C under a CO pressure of 50 bar, about half of **1a** is transformed into the μ -hydrido μ -carbonyl binuclear palladium(I) complex $[\{(S)\text{-MeO-BIPHEP}\}\text{Pd}(\mu\text{-H})(\mu\text{-CO})\text{Pd}\{(S)\text{-MeO-BIPHEP}\}]\text{OTf}$ (**4**; Scheme 1; P-P = (S)-MeO-BIPHEP, X = OTf). **4** represents a dynamic system at room temperature as analogous compounds.^{45–47} Thus, the ¹H NMR spectrum exhibits a quintet for the bridging hydride centered at -5.22 ppm with a ²J_{PH} coupling of 44 Hz at 25 °C changing into a triplet of triplets at -50 °C (²J_{PH(trans)} = 92 Hz and ²J_{PH(cis)} = 6 Hz). On the other hand, the ³¹P NMR spectrum shows a broad signal at room temperature at 22 ppm, which splits into two doublets at 25.22 and 19.92 ppm (J_{PP} = 37 Hz) at -40 °C. The IR spectrum of **4** shows a strong band at 1835 cm⁻¹ in accordance with the literature.^{46,47}

The oxidation of methanol by palladium(II) complexes has been observed to occur over a π -bonded palladium(II) formaldehyde hydride complex, which eventually decarbonylates to form a Pd(0) carbonyl compound.⁴⁶ Thus, the formation of **3** in the absence of carbon monoxide could imply that, in the present reaction, the decarbonylation of formaldehyde is not favored.⁴⁶ On the other hand, in the presence of carbon monoxide, the palladium hydride intermediate can be stabilized by CO, thereby forming **4** through combination with an unsaturated Pd(0) intermediate.

Suitable single crystals for X-ray structure determinations were obtained by vapor diffusion of *n*-pentane into 10⁻⁵ M THF solutions of **1a** and **1d** at room temperature. Selected crystallographic data are summarized in Table 2, and ORTEP diagrams of $[\{(S)\text{-MeO-BIPHEP}\}\text{Pd}(\text{H}_2\text{O})(\text{THF})](\text{OTf})_2$ and $[\{(S)\text{-MeO-BIPHEP}\}\text{Pd}(\text{OTfa})_2]$ with the atom-numbering scheme are displayed in Figures 1 and 2, respectively. Both compounds crystallize in the orthorhombic space group *P*2₁2₁2₁ as yellow platelets. Two cis positions are occupied by the (S)-MeO-BIPHEP ligand for both compounds. In $[\{(S)\text{-MeO-BIPHEP}\}\text{Pd}(\text{OTfa})_2]$ the trifluoroacetate anions are directly coordinated to the palladium atom, whereas in $[\{(S)\text{-MeO-BIPHEP}\}\text{Pd}(\text{H}_2\text{O})(\text{THF})](\text{OTf})_2$ the triflates act as counteranions. In the latter case the other two cis positions in the first coordination sphere of the palladium are occupied by one molecule of water and one of THF.

In both compounds the seven-membered heterometallic ring involving the (S)-MeO-BIPHEP ligand adopts a skew(v) boat conformation with δ absolute configuration.^{48,49} This correlation between the absolute

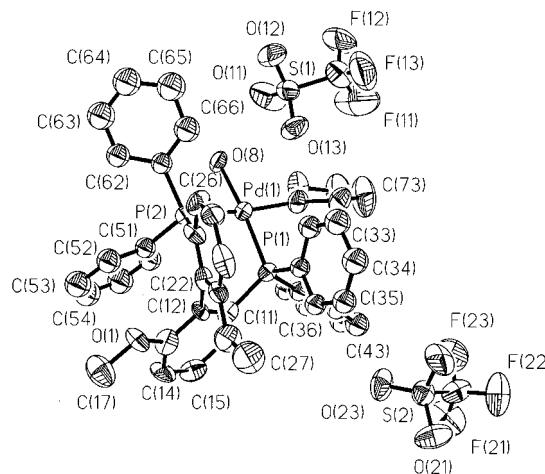


Figure 1. ORTEP diagram of $[\{(S)\text{-MeO-BIPHEP}\}\text{Pd}(\text{H}_2\text{O})(\text{THF})](\text{OTf})_2$.

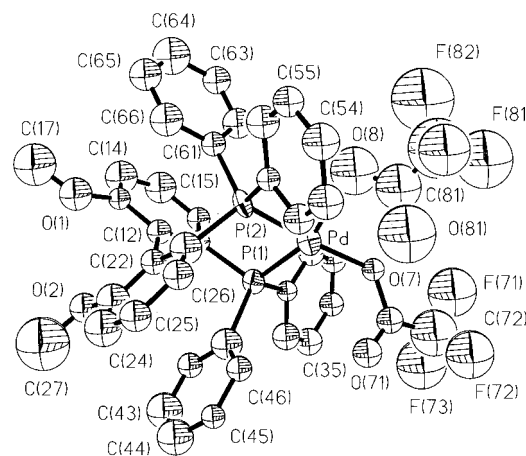


Figure 2. ORTEP diagram of $[\{(S)\text{-MeO-BIPHEP}\}\text{Pd}(\text{OTfa})_2]$.

configuration of the chiral diphosphine and the conformation of the chelating seven-membered ring corresponds to that reported in the sole X-ray structure of a compound containing the MeO-BIPHEP ligand.⁵⁰ In that compound, the *R* enantiomeric ligand formed a seven-membered ring including a palladium atom with a λ skew(v) boat conformation.

The least-squares planes of the two phenyl rings of the biphenyl system in MeO-BIPHEP exhibit an interplanar angle θ of 71.1° for $[\{(S)\text{-MeO-BIPHEP}\}\text{Pd}(\text{H}_2\text{O})(\text{THF})](\text{OTf})_2$ and 71.4° for $[\{(S)\text{-MeO-BIPHEP}\}\text{Pd}(\text{OTfa})_2]$. These values are similar to the 70.3° angle reported for θ of the above-mentioned palladium complex bearing the (*R*)-MeO-BIPHEP ligand and an ortho-metalated dimethyl(α -methylbenzyl)amine.⁵⁰ Moreover, the quasi-axial phenyl rings of the diphenylphosphino groups possess a roughly parallel orientation with apparent π - π stacking interactions with respect to one phenyl ring of the biphenyl system. The interplanar angles of the best-squares planes of 18.6 and 23.2° are slightly higher than the values of 12.4 and 14.1° reported for the aforementioned ortho-metalated palladium complex.⁵⁰

In both complexes the Pd(II) has a distorted-square-planar coordination. While in $[\{(S)\text{-MeO-BIPHEP}\}\text{Pd}(\text{H}_2\text{O})(\text{THF})](\text{OTf})_2$ the oxygen atoms O(7) and O(8) are

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Table 2. Experimental Data for the X-ray Diffraction Study of $\{[(S)\text{-MeO-BIPHEP}\}\text{Pd}(\text{H}_2\text{O})(\text{THF})\}(\text{OTf})_2$ and $\{[(S)\text{-MeO-BIPHEP}\}\text{Pd}(\text{OTfa})_2\}$

	$\{[(S)\text{-MeO-BIPHEP}\}\text{Pd}(\text{H}_2\text{O})(\text{THF})\}(\text{OTf})_2$	$\{[(S)\text{-MeO-BIPHEP}\}\text{Pd}(\text{OTfa})_2\}$
mol formula	$\text{C}_{44}\text{H}_{40}\text{F}_6\text{O}_{10}\text{P}_2\text{PdS}_2$	$\text{C}_{42}\text{H}_{32}\text{F}_6\text{O}_6\text{P}_2\text{Pd}$
mol wt	1075.2	915.0
cryst dimens (mm)	$0.1 \times 0.2 \times 0.4$	$0.1 \times 0.1 \times 0.3$
data collectn T (°C)	20	20
cryst syst	orthorhombic	orthorhombic
space group	$P2_12_12_1$	$P2_12_12_1$
a (Å)	10.994(2)	13.856(14)
b (Å)	11.453(2)	13.929(15)
c (Å)	36.307(7)	21.12(3)
V (Å ³)	4571.6(15)	4077(9)
Z	4	4
D_{calcd} (g cm ⁻³)	1.562	1.491
abs coeff (cm ⁻¹)	6.48	6.07
$F(000)$	2184	1848
diffractometer	Siemens R3m/V	Syntex P21
radiation	Mo K α (graphite monochrom); $\lambda = 0.71073$ Å	
scan range, 2θ (deg)	3.0–40.0	3.0–40.0
scan type	$2\theta-\theta$	$2\theta-\theta$
no. of indep data collected	2446	2179
no. of obsd rflns (n_h)	1988	1149
abs cor	N/A	N/A
no. of params refined (n_r)	467	174
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0000F^2$	$w^{-1} = \sigma^2(F) + 0.0000F^2$
R	0.0449	0.0852
R_w	0.0450	0.0651
GOF	3.04	2.42

Table 3. Selected Bond Distances and Angles

	$\{[(S)\text{-MeO-BIPHEP}\}\text{Pd}(\text{H}_2\text{O})(\text{THF})\}(\text{OTf})_2$	$\{[(S)\text{-MeO-BIPHEP}\}\text{Pd}(\text{OTfa})_2\}$
Bond Distances (Å)		
Pd–P(1)	2.248(4)	2.256(13)
Pd–P(2)	2.256(4)	2.240(12)
Pd–O(7)	2.130(12)	2.076(20)
Pd–O(8)	2.147(9)	2.239(31)
Bond Angles (deg)		
P(1)–Pd–P(2)	90.7(2)	92.9(4)
P(1)–Pd–O(7)	91.8(3)	93.5(6)
P(2)–Pd–O(8)	91.6(3)	80.8(8)
O(7)–Pd–O(8)	87.1(4)	93.3(9)
O(7)–Pd–P(2)	173.4(3)	173.6(6)
O(8)–Pd–P(1)	169.4(3)	156.7(9)

situated above and below the P(1)–Pd–P(2) plane with distances of 0.23(1) and 0.39(1) Å, respectively, only O(8) of one trifluoroacetate ligand is positioned 0.85(1) Å outside the P(1)–Pd–P(2) plane in $\{[(S)\text{-MeO-BIPHEP}\}\text{Pd}(\text{OTfa})_2\}$. The relatively strong deviation of O(8) in the latter case resulted in a elongated Pd–O(8) bond length.

Relevant bond lengths and angles for both structures are reported in Table 3. The palladium–phosphorus distances are similar for both complexes, and the values of 2.240–2.256 Å are in the normal range for *cis*-chelated phosphorus at a palladium(II) center.^{30,51–54} The Pd–OH₂ distance in **1a** of 2.147 Å is comparable

with the corresponding bond length in related Pd–OH₂ complexes.^{30,51}

Different bond lengths Pd–O were observed for the coordinated trifluoroacetate anions in $\{[(S)\text{-MeO-BIPHEP}\}\text{Pd}(\text{OTfa})_2\}$. As already mentioned, O(8) is out of the P(1)–Pd–P(2) plane having the longer distance. Therefore, the angles P(2)–Pd–O(8) and O(8)–Pd–P(1) differ remarkably with respect to the corresponding angles P(1)–Pd–O(7) and O(7)–Pd–P(2). The bite angles of the MeO–BIPHEP ligand in both crystal structures with values of 90.7 and 92.9° are similar to the 91.7° angle reported by Schmid *et al.*⁵⁰

The coordinated O(8) water molecule in $\{[(S)\text{-MeO-BIPHEP}\}\text{Pd}(\text{H}_2\text{O})(\text{THF})\}(\text{OTf})_2$ forms intermolecular hydrogen bonds to two oxygen atoms of two different triflate anions. The distances of Pd–O(11) and Pd–O(22) are 2.74(1) and 2.72(1) Å, respectively. A similar hydrogen-bonding pattern was recently observed for the monoquo and diaquo cationic palladium(II) complexes bearing the chelating DPPP diphosphine ligand.³⁰ Hydrogen bonding seems to be a common feature in aquo–transition-metal complexes⁵⁵ due to its importance in the stabilization of the solid-state structure of these molecules.^{56,57}

Particularly noteworthy are the nonbonding interactions in $\{[(S)\text{-MeO-BIPHEP}\}\text{Pd}(\text{H}_2\text{O})(\text{THF})\}(\text{OTf})_2$ between the palladium center and an oxygen atom of an uncoordinated triflate anion. Thus, a Pd–O(13) distance of about 3.35(1) Å was observed.

Recently, Seebach *et al.* established the existence of two categories of transition-metal complexes containing chelating bis(diphenylphosphino) ligands by superimposing a large number of X-ray structures: one has approximate C_2 symmetry with respect to the two diphenylphosphino groups, and the other has C_1 symmetry.⁵⁸ Both $\{[(S)\text{-MeO-BIPHEP}\}\text{Pd}(\text{H}_2\text{O})(\text{THF})\}(\text{OTf})_2$ and $\{[(S)\text{-MeO-BIPHEP}\}\text{Pd}(\text{OTfa})_2\}$ belong to the former class, having two of the four phosphorus–phenyl rings oriented quasi-axially and the other two phenyl groups quasi-equatorially with respect to the P(1)–Pd–P(2) plane. Note that the quasi-axial rings are at the rear, while the quasi-equatorial phenyl groups are pushed toward the palladium center.

A schematic superimposition of the two structures, as shown in Figure 3, revealed virtually identical conformations in the solid state of the $\{[(S)\text{-MeO-BIPHEP}\}\text{Pd}\}$ fragments.

The steric requirement of the quasi-equatorial phenyl groups around the coordination sphere of the metal in addition to the rigidity of the axially dissymmetric biphenyl system is believed to be responsible for the very high enantioface discrimination observed in the formation of optically active dimethyl 2-phenylbutanedioate¹⁴ and optically active dimethyl 2-oxo-3-phenyl-pentanedioate.¹⁵ If we take into account the possible interactions of the substituent of the olefin substrate during the insertion into a [Pd]–COOCH₃ bond and the secondary

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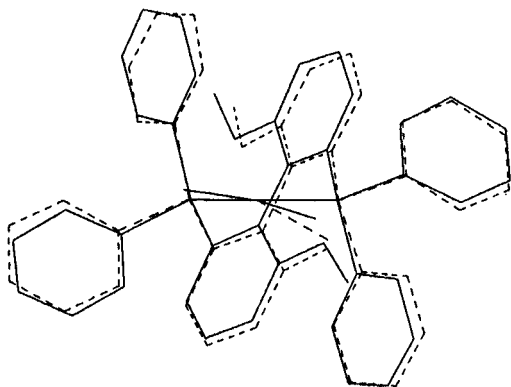


Figure 3. Schematic superposition of the $\{[(S)\text{-MeO-BIPHEP}\}\text{PdO}_2\}$ fragments of the two crystal structures.

insertion established for styrene^{59,60} as the substrate, the prevailing formation of the *l* enantiomer (with respect to the absolute configuration of the ligand) can be rationalized.

Experimental Section

Starting Materials. Silver tetrafluoroborate (AgBF_4), silver trifluoromethanesulfonate (AgSO_3CF_3 or AgOTf), silver *p*-toluenesulfonate ($\text{AgCH}_3\text{C}_6\text{H}_4\text{SO}_3$ or AgOTs), silver trifluoroacetate ($\text{AgCF}_3\text{CO}_2/\text{AgOTfa}$), and MeOH (crown cap) were obtained from Fluka. $\{[(S)\text{-MeO-BIPHEP}\}\text{PdCl}_2\}$ was prepared according to the literature.¹⁶

General Procedures. All reactions and manipulations were carried out under a purified nitrogen atmosphere using either Schlenk techniques or a glovebox (MBraun MB 150BG-I). ^1H and ^{13}C NMR data were reported with tetramethylsilane and 85% H_3PO_4 as the standard. THF was distilled over sodium/benzophenone ketyl and acetone over Drierite (Fluka product) prior to use.

Preparation of $\{[(S)\text{-MeO-BIPHEP}\}\text{Pd}(\text{H}_2\text{O})_2\}(\text{OTf})_2$ (1a**).** A solution of AgOTf (0.632 g, 2.46 mmol) in THF (25 mL) was added dropwise in the dark to a solution of $\{[(S)\text{-MeO-BIPHEP}\}\text{PdCl}_2\}$ (0.936 g, 1.23 mmol) in THF (125 mL). The reaction mixture was stirred for 2 h at room temperature. The precipitated AgCl was filtered off on Celite and washed twice with THF (15 mL). The filtrate was concentrated to a total volume of about 30 mL by evaporation under reduced pressure. Pentane was added to initiate crystallization, which was completed within 24 h at 4 °C. The yellow precipitate was filtered off and dried under reduced pressure. The crude product was recrystallized from THF/hexane. Yield: 77% (0.971 g, 0.95 mmol). ^1H NMR (300 MHz, CDCl_3 , 25 °C): δ 3.51 (s, 6H, OCH_3), 4.05 (s, 4H, H_2O), 6.58–6.60 (m, 2H), 6.79–6.86 (m, 2H), 7.02–7.09 (m, 2H), 7.37–7.88 (m, 20H, H_{arom}). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.02 MHz, CDCl_3 , 25 °C): δ 33.4. Anal. Calcd for $\text{C}_{40}\text{H}_{36}\text{P}_2\text{O}_{10}\text{F}_6\text{S}_2\text{Pd}$ (1023.4): C, 46.95; H, 3.55. Found: C, 46.74; H, 3.63. Suitable single crystals for X-ray structure determination were obtained by vapor diffusion of *n*-pentane into a THF solution of **1a** at room temperature.

Preparation of $\{[(S)\text{-MeO-BIPHEP}\}\text{Pd}(\text{H}_2\text{O})_2\}(\text{BF}_4)_2$ (1b**).** A solution of AgBF_4 (0.111 g, 0.58 mmol) in acetone (20 mL) was added in the dark to a solution of $\{[(S)\text{-MeO-BIPHEP}\}\text{PdCl}_2\}$ (0.218 g, 0.29 mmol) in acetone (60 mL). The reaction mixture was stirred for 2 h at room temperature. The precipitated AgCl was filtered off on Celite and washed twice with acetone (5 mL). The filtrate was concentrated to a total volume of about 25 mL by evaporation under reduced pressure. Diethyl ether was added to initiate crystallization, which was

completed after 24 h at 4 °C. The yellow precipitate was filtered off and dried under reduced pressure. The crude product was recrystallized from acetone/*n*-pentane. Yield: 86% (0.225 g, 0.25 mmol). ^1H NMR (300 MHz, CDCl_3 , 25 °C): δ 2.8 (s, 4H, H_2O), 3.51 (s, 6H, OCH_3), 6.57–6.60 (m, 2H), 6.84–6.90 (m, 2H), 7.02–7.08 (m, 2H), 7.40–7.92 (m, 20H, H_{arom}). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.02 MHz, CDCl_3 , 25 °C): δ 33.3. Anal. Calcd for $\text{C}_{38}\text{H}_{36}\text{P}_2\text{O}_4\text{F}_8\text{B}_2\text{Pd}$ (898.7): C, 50.79; H, 4.04. Found: C, 50.55; H, 4.25.

Preparation of $\{[(S)\text{-MeO-BIPHEP}\}\text{Pd}(\text{H}_2\text{O})(\text{OTs})(\text{OTs})$ (1c**).** The procedure is the same as that for **1a**, except that AgOTs (0.293 g, 1.05 mmol) dissolved in THF (50 mL) was stirred for 5 h with $\{[(S)\text{-MeO-BIPHEP}\}\text{PdCl}_2\}$ (0.399 g, 0.525 mmol) in THF (150 mL) to give a yellow solid of **1c**. Yield: 87% (0.481 g, 0.458 mmol). ^1H NMR (200 MHz, CDCl_3 , 25 °C): δ 2.22 (s, 6H, PhCH_3), 3.44 (s, 6H, OCH_3), 4.54 (s, 2H, H_2O), 6.45–6.49 (m, 2H), 6.71–6.85 (m, 6H), 6.92–7.02 (m, 2H), 7.26–8.03 (m, 24H, H_{arom}). $^{31}\text{P}\{^1\text{H}\}$ NMR (81.02 MHz, CDCl_3 , 25 °C): δ 30.7. Anal. Calcd for $\text{C}_{52}\text{H}_{48}\text{P}_2\text{O}_9\text{S}_2\text{Pd}$ (1049.5): C, 59.51; H, 4.61. Found: C, 59.65; H, 4.74.

Preparation of $\{[(S)\text{-MeO-BIPHEP}\}\text{Pd}(\text{OTfa})_2\}$ (1d**).** The same procedure as described for **1a** was applied, except that AgOTfa (0.385 g, 1.74 mmol) in THF (20 mL) and $\{[(S)\text{-MeO-BIPHEP}\}\text{PdCl}_2\}$ (0.662 g, 0.87 mmol) dissolved in THF (100 mL) led to **1d** as a yellow solid. Yield: 84% (0.664 g, 0.73 mmol). ^1H NMR (200 MHz, CDCl_3 , 25 °C): δ 3.43 (s, 6H, OCH_3), 6.42–6.46 (m, 2H), 6.74–6.83 (m, 2H), 6.93–7.01 (m, 2H), 7.26–7.97 (m, 20H, H_{arom}). $^{31}\text{P}\{^1\text{H}\}$ NMR (81.02 MHz, CDCl_3 , 25 °C): δ 27.5. Anal. Calcd for $\text{C}_{42}\text{H}_{32}\text{P}_2\text{O}_6\text{F}_6\text{Pd}$ (915.1): C, 55.13; H, 3.52; F, 12.46. Found: C, 54.86; H, 3.74; F, 12.54. Single crystals suitable for X-ray structure determination were obtained by vapor diffusion of *n*-pentane into a THF solution of **1d** at room temperature.

Reaction of **1a with Methanol.** A solution of **1a** (0.067 g, 0.065 mmol) was stirred in methanol (3 mL) under a nitrogen atmosphere at 50 °C for 12 h. The red residue obtained after evaporation was dried *in vacuo* for 12 h. The ^1H NMR spectrum shows the formation of $\{[(S)\text{-MeO-BIPHEP}\}\text{Pd}_2(\text{OTf})_2\}$ (**3**) in 35% yield based on the integration of the methoxy signals of the MeO-BIPHEP ligand, in addition to **1a** (60%) and 5% of a complex as yet unidentified. The latter shows a singlet at 23.6 ppm in the ^{31}P NMR (81.02 MHz, CD_2Cl_2 , 25 °C) and a singlet at 4.03 ppm in the ^1H NMR (200 MHz, CD_2Cl_2 , 25 °C) for the methoxy groups. Selected data for **3** (simulated with PANIC from Bruker Spectrospin AG): $^{31}\text{P}\{^1\text{H}\}$ NMR (81.02 MHz, CD_2Cl_2 , 25 °C) δ_{A} 29.76, δ_{X} 5.80, $J_{\text{AA'}}$ = 226.3 Hz, $J_{\text{XX'}}$ = 9.5 Hz, J_{AX} = -57.1 Hz, $J_{\text{AX'}}$ = 125.8 Hz; ^1H NMR (500 MHz, CD_2Cl_2 , 25 °C) δ 3.06 (s, 3H, OCH_3), 3.29 (s, 3H, OCH_3).

Reaction of **1a with Methanol in the Presence of Carbon Monoxide.** A solution of **1a** (0.087 g, 0.085 mmol) in methanol (12 mL) was transferred under a nitrogen atmosphere into a 150 mL steel autoclave. The autoclave was heated to 50 °C under a CO pressure of 50 bar for 20 h. After the gas was released, the resulting red solution was evaporated *in vacuo*, and the red residue was dried overnight. The NMR spectra show the formation of **4** as well as unreacted **1a** (50%). Selected data for **4**: ^1H NMR (200 MHz, CD_2Cl_2 , 25 °C) δ -5.22 ppm ($^2J_{\text{PH}}$ = 44 Hz); ^1H NMR (200 MHz, CD_2Cl_2 , -50 °C) δ -5.22 ppm ($^2J_{\text{PH}}(\text{trans})$ = 92 Hz, $^2J_{\text{PH}}(\text{cis})$ = 6 Hz); ^{31}P NMR (81.02 MHz, CD_2Cl_2 , 25 °C) δ 22 ppm; ^{31}P NMR (81.02 MHz, CD_2Cl_2 , -40 °C): δ 19.92 ppm (d, J_{PP} = 37 Hz), 25.22 (d, J_{PP} = 37 Hz); IR (ν_{CO}) 1835 cm^{-1} .

X-ray Crystallographic Studies of $\{[(S)\text{-MeO-BIPHEP}\}\text{Pd}(\text{H}_2\text{O})(\text{THF})(\text{OTf})_2\}$ and $\{[(S)\text{-MeO-BIPHEP}\}\text{Pd}(\text{OTfa})_2\}$. Data were measured with variable scan speed to ensure constant statistical precision on the collected intensities. One standard reflection was measured every 120 reflections; no significant variation was detected. The structures were solved by direct methods and refined by full-matrix least squares using anisotropic displacement parameters for all non-hydrogen atoms. The contribution of the hydrogen atoms in

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their idealized positions (riding model with fixed isotropic U) was taken into account but not refined. All calculations were carried out by using the Siemens SHELXTL PLUS system.

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Supporting Information Available: Tables of crystal data and refinement details, all bond distances and angles, and anisotropic displacement coefficients for the non-carbon atoms of [(S) -MeO-BIPHEP}Pd(H₂O)(THF)](OTf)₂ and [(S) -MeO-BIPHEP}Pd(OTfa)₂] (18 pages). Ordering information is given on any current masthead page.

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