# Palladium(II) and Palladium(0) Complexes of BINAP(O) (2-(Diphenylphosphino)-2′-(diphenylphosphinyl)-1,1′-binaphthyl)

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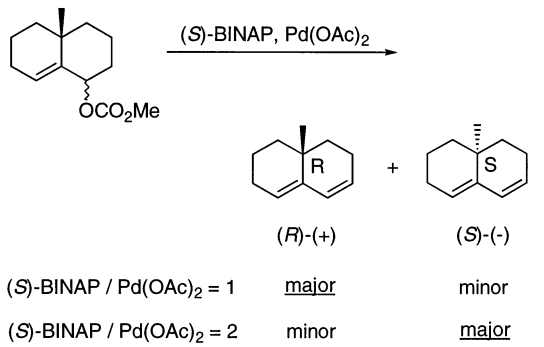
The coordination organopalladium chemistry of 2-(diphenylphosphino)-2′-(diphenylphosphinyl)-1,1′-binaphthyl (BINAP(O)) was found to be totally different from that of other phosphine−phosphine oxide ligands, as well as of BINAP. The reaction of $[(MeCN)_2PdCl_2]$ with BINAP(O) (1 equiv) afforded $[(BINAP(O))PdCl_2]$ (**1**), in which BINAP(O) is P,O-chelated to Pd in the solid state (X-ray) and in solution (NMR). Treatment of **1** with free BINAP(O) led to the reversible formation of a P,P-bonded nonchelate, $[(BINAP(O))_2PdCl_2]$ (**2**), which could not be isolated due to the equilibrium being strongly shifted toward **1**. Reduction of **1** with $LiBH_4$ in the presence of BINAP(O) afforded a new zerovalent Pd complex $[(BINAP(O))_2Pd]$ (**3**), in which both BINAP(O) ligands are P-bonded to Pd and one provides $\eta^2$-arene coordination via the C=C bond adjacent to the phosphinyl group (X-ray). Oxidative addition of PhI to **3** led cleanly to [(BINAP(O))Pd(Ph)I] (**4**; Ph trans to O; X-ray) which was also prepared by the reaction of $[Pd_2(dba)_3]$ with BINAPO and PhI. The ultrasound-promoted I/F exchange reaction of [(BINAPO)Pd(Ph)I] with AgF afforded [(BINAP(O))Pd(Ph)F] (**5**), which was decomposed thermally to produce a mixture of P−F and C−P reductive elimination products.



## Introduction

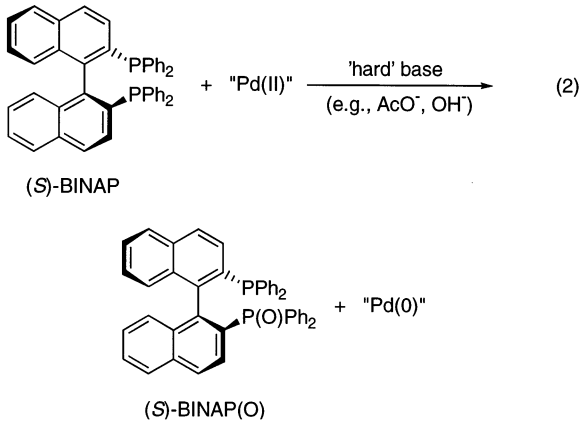
In 1996, Shimizu, Yamamoto, and co-workers reported[1] their remarkable observation of chirality reversal depending on the (*S*)-BINAP to $Pd(OAc)_2$ catalyst ratio used for the enantioselective elimination reaction of a 6,6-membered bicyclic allylic carbonate. At a ligand to Pd ratio of 1, the *R* product dominated, whereas an increase in the ratio to 2 resulted in the formation of mostly the *S* isomer (eq 1).




(1)

| | (*R*)-(+) | (*S*)-(-) |
|---|---|---|
| (*S*)-BINAP / $Pd(OAc)_2$ = 1 | major | minor |
| (*S*)-BINAP / $Pd(OAc)_2$ = 2 | minor | major |

A series of additional experiments indicated[1] that the effect was likely due to the facile Pd(II)/P(III) → Pd(0)/P(V) redox process,[2] also reported[3] for BINAP (eq 2). The stoichiometry of reaction 2 shows that at the BINAP to Pd(II) ratio of 1 the catalyst formed in situ would derive from BINAP monoxide, BINAP(O), and Pd(0) generated in equimolar quantities. If an extra 1 equiv of BINAP is used (i.e. BINAP/Pd(II) = 2) active catalyst would be somehow composed of a 1:1:1 blend of Pd(0), BINAP(O), and more strongly chelating, unreacted BINAP.




(2)

† Contribution No. 8359.

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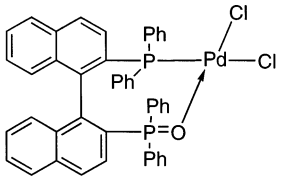
Clearly, a 1:1 mixture of BINAP and $Pd(OAc)_2$ can produce catalytically active Pd(0) complexes of BINAP(O) which possess properties that are totally different from those of Pd(0) BINAP catalysts, even to the extent of reversal of chirality induced. While the organometallic and coordination chemistry of BINAP complexes of palladium is quite well developed,[4] very little is known about their BINAP(O) analogues.[5] The Pd BINAP(O) species generated in situ (eq 2) must have been involved as intermediates in various catalytic reactions, though in many cases this fact has not been fully realized. In this paper we report the synthesis and characterization of a series of new BINAP(O) complexes of Pd(II) and Pd(0). These complexes exhibit interesting coordination modes that differ considerably from those commonly observed for Pd derivatives of other hemilabile mixed phosphine−phosphine oxide ligands.

## Results and Discussion

Treatment of $[(MeCN)_2PdCl_2]$ with 1 equiv of (*R*)- or (*S*)-BINAP(O)[6] in toluene or $CH_2Cl_2$−benzene under reflux resulted in quantitative formation of [(BINAP(O))$PdCl_2$] (**1**) (eq 3). A P,O-chelate structure for (*S*)-**1**

$$[(MeCN)_2PdCl_2] + (R)\text{- or } (S)\text{-BINAP(O)} \xrightarrow[-2MeCN]{\Delta} \quad (3)$$

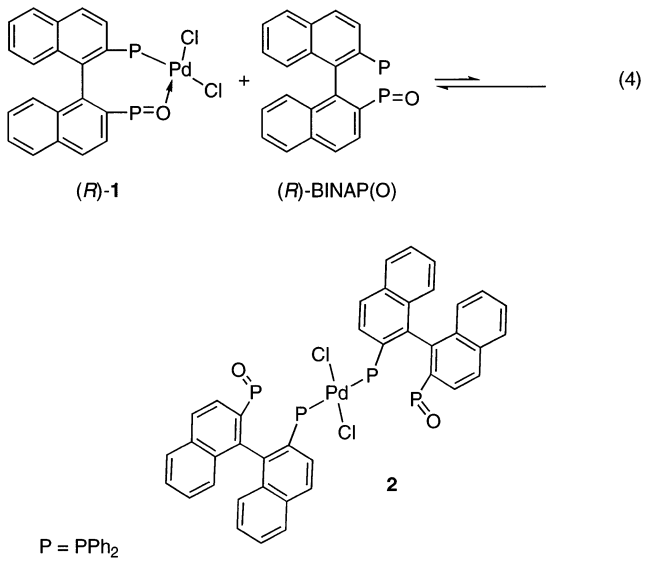



(*R*)- or (*S*)-**1**

in the solid state and in solution was established by X-ray analysis (Figure 1) and NMR data, respectively.[7]

Two sharp singlets at 22.8 and 48.5 ppm were observed in the $^{31}P$ NMR spectrum of **1**. The strong downfield shift for the P═O resonance (vs 27.5 ppm for free BINAP(O)) pointed to P═O−Pd coordination, whereas the sharpness of the peaks indicated that **1** is inert on the NMR time scale (20 °C).

Unexpectedly, addition of 1 equiv of (*R*)-BINAP(O) to (*R*)-**1** in $CH_2Cl_2$ led to a mixture of (*R*)-**1**, (*R*)-BINAP(O) ($^{31}P$ NMR: −14.6 and 27.5 ppm), and a new Pd complex ($^{31}P$ NMR: singlets at 26.3 and 32.7 ppm). On the basis of the $^{31}P$ NMR data, the new complex was formulated as [((*R*)-BINAP(O))$_2PdCl_2$] (**2**), with only P-coordination of both BINAP(O) ligands to Pd. Further experiments with various (*R*)-**1** to (*R*)-BINAP(O) ratios and different degrees of dilution revealed that all three species were in equilibrium (eq 4) which readily established within the time of mixing, while being slow on the NMR time scale. The formation of **2** is disfavored by the equilibrium (4), which is strongly shifted toward (*R*)-**1** and (*R*)-BINAP(O). Thus, even when a 4-fold excess of (*R*)-BINAP(O) was used ([(*R*)-**1**] = $0.8 \times 10^{-2}$ M; [(*R*)-BINAP(O)] = $3.2 \times 10^{-2}$ M before equilibrium) the equilibrated mixture exhibited only ca. 40% conversion of the (*R*)-**1** to **2**. Integration of the three pairs of the $^{31}P$ NMR signals (see the Experimental Section) allowed for calculation of $K_{eq}$ at 20.7 $M^{-1}$.




The reluctance of **1** to form **2** upon addition of BINAP(O) was unexpected, given the fact that monoxides of other bidentate phosphines, such as dppmO, dppeO, dpppO, dppbO, and dppfcO, are not prone to P,O-coordination to Pd(II), forming exclusively analogues of **2** upon treatment of Pd(II) chloro derivatives with 2 equiv of the ligand.[8,9] Both the rigidity of the BINAP framework and steric hindrance can provide a rationale for the favored P═O−Pd coordination and uncommon position of the equilibrium (4).

A comparison of geometry parameters of (*S*)-**1** (Figure 1) and those reported[4b] for its BINAP analogue [((*R*)-BINAP)$PdCl_2$] reveal much difference between the two.

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(5) (a) To the best of our knowledge, only one fully characterized Pd BINAP(O) complex has been reported, [BINAP(O)PdL], where L = cyclometalated *N*,*N*-dimethyl-(*S*)-1-(1-naphthyl)ethylamine.[5b] (b) Gladiali, S.; Pulacchini, S.; Fabbri, D.; Manassero, M.; Sansoni, M. *Tetrahedron: Asymmetry* **1998**, *9*, 391.

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(7) For a similar Pt complex, see: Gladiali, S.; Alberico, E.; Pulacchini, S.; Kollàr, L. *J. Mol. Catal. A* **1999**, *143*, 155.

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(9) The platinum analogue of **2**, [((*S*)-BINAP(O))$_2PtCl_2$], has been generated and characterized in solution.[7] The isolation and stability of this Pt complex have not been reported.[7]

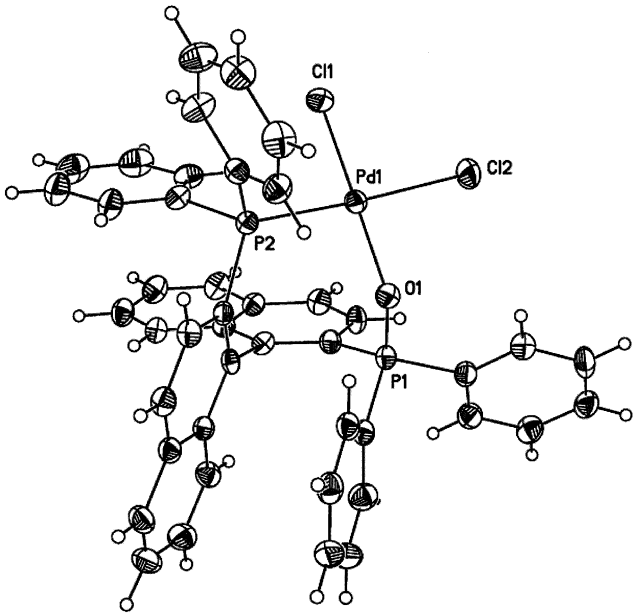



**Figure 1.** ORTEP plot of [((*S*)-BINAP(O)-$\kappa^2P,O$)$PdCl_2$] ((*S*)-**1**), with thermal ellipsoids drawn to the 50% probability level. Selected bond lengths (Å) and angles (deg): Pd(1)−O(1), 2.080(2); Pd(1)−P(2), 2.249(1); Pd(1)−Cl(1), 2.268(1); Pd(1)−Cl(2), 2.353(1); P(1)−O(1), 1.517(2); O(1)−Pd(1)−P(2), 91.16(6); O(1)−Pd(1)−Cl(1), 175.44(6); P(2)−Pd(1)−Cl(1), 86.98(3); O(1)−Pd(1)−Cl(2), 88.99(6); P(2)−Pd(1)−Cl(2), 173.15(3); Cl(1)−Pd(1)−Cl(2), 92.36(3).

The molecule of (*S*)-**1** is square planar with the sum of bond angles at Pd exceeding 359° and the O(1)−Pd−Cl(1) and P(2)−Pd−Cl(2) angles being 175.44(6) and 173.15(3)°, respectively. In contrast, the geometry around the metal in [((*R*)-BINAP)$PdCl_2$] is severely distorted, with the Cl atoms situated below and above the $P_2Pd$ plane and the sum of coordination angles at Pd being only 367.3(2)°.[4b] Thus, formal insertion of an oxygen atom in one of the Pd−P bonds of [(BINAP)$PdCl_2$] makes the chelating ligand more flexible, alleviating steric strain in the coordination sphere and allowing the molecule to reach the desired planarity. In (*S*)-**1**, the Pd−Cl bond trans to P (2.353(1) Å) is within the expected range[4b] and is much longer than the Pd−Cl bond trans to O (2.268(1) Å), indicating the weaker trans influence of the phosphynyl ligand.

Due to the apparent, yet not recognized, importance of BINAP(O) complexes of zerovalent Pd in catalysis (see above), it was particularly interesting to isolate and characterize such species, as well as to study their ability to undergo oxidative addition. Reduction of **1** with excess $LiBH_4$ in the presence of BINAP(O) afforded an air-sensitive, crystalline reddish brown material which analyzed as [(BINAP(O))$_2$Pd] (**3**). Two unresolved resonances were observed in the $^{31}P$ NMR spectrum of **3** (benzene-$d_6$) at room temperature, at 22.2 ppm ($\Delta\nu_{1/2}$ = 50 Hz) and 28.5 ppm ($\Delta\nu_{1/2}$ = 500 Hz). Addition of excess PhI to this NMR sample resulted in a rapid color change to greenish yellow and concomitant replacement of the two broad resonances with four 1:1:1:1 sharp singlets at −13.5, 14.2, 26.5, and 36.7 ppm. The most upfield and second downfield resonances were from free BINAP(O), whose presence was also confirmed by TLC. The other two signals (14.2 and 36.7 ppm) were from [BINAP(O)Pd(Ph)I] (**4**), which was eventually isolated

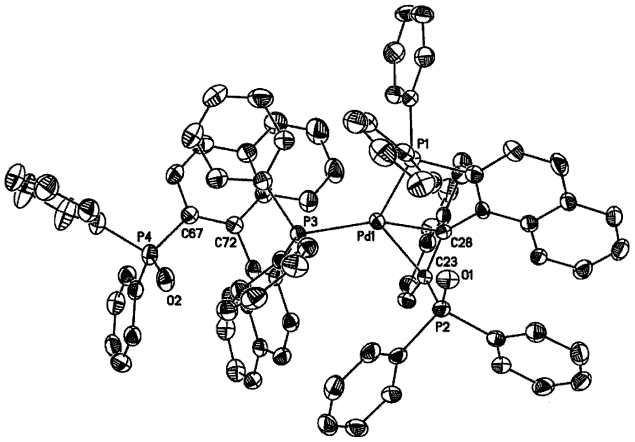
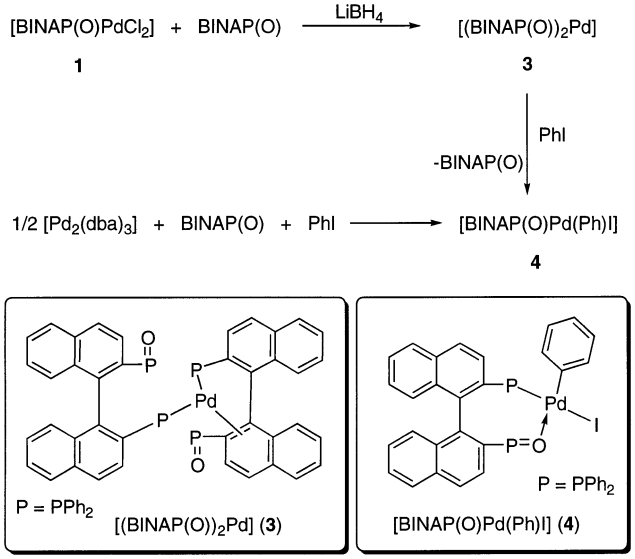



**Figure 2.** ORTEP plot of [((*R*)-BINAP(O))$_2$Pd] ((*R*)-**3**), with thermal ellipsoids drawn to the 50% probability level.

**Scheme 1**




from a similar experiment and fully characterized by analytical, NMR, and X-ray diffraction data (see below). Both (*R*)- and (*S*)-**4** could be more conveniently prepared by reacting [$Pd_2$(dba)$_3$] with PhI and BINAP(O) (1 equiv/Pd). All transformations involving the formation of **3** and **4** are shown in Scheme 1.

X-ray analysis of [((*R*)-BINAP(O)$_2$)$_2$Pd] ((*R*)-**3**; 1:1 hexane solvate), revealed its remarkable structure (Figure 2), in which both BINAP(O) ligands are bonded to Pd through the P centers, while one of the two is also $\pi$-coordinated to the metal via the aromatic C=C bond bearing the naphthyl and phosphinyl groups. While well-characterized $\eta^2$-arene complexes of Pd(II) are not uncommon,[10−13] their Pd(0) analogues are extremely rare. Earlier this year, as our work was in progress, a communication from Buchwald's group appeared, reporting an X-ray structure of a complex of Pd(0) intramolecularly $\pi$-coordinated to a phenanthrene moiety.[14] To the best of our knowledge, (*R*)-**3** is the only other structurally characterized $\eta^2$-arene complex of zerovalent palladium.

Like complexes of the type $P_2$M(olefin) (M = Pd(0), Pt(0)),[15,16] (*R*)-**3** is trigonal planar (Y-shaped) with the P−Pd−P angle being 117.6° and the interplanar angle between P(1)PdP(3) and C(23)PdC(28) being 142.8°. Considerable back-donation from the metal is mani-

fested by the geometry parameters of the coordinated arene in (*R*)-**3** (Figure 3). The $\pi$-coordinated bond C(23)−C(28) (1.447(4) Å) is longer than the analogous noncoordinated bond C(67)−C(72) (1.395(4) Å) of the other BINAP(O) ligand, which is bonded to Pd only through the P atom (Figures 2 and 3). As a result of partial rehybridization of C(23) and C(28) toward $sp^3$, both of the substituents P(2) and C(18) at the $\pi$-donating C═C bond deviate from the mean plane C(23)−C(28) by 0.62 and 0.64 Å, respectively. In contrast, the deviations of the ring-forming carbon atoms from the plane are minor, not exceeding 0.02 Å.

The nonplanarity of a coordinated olefin (Figure 3) can be quantified by the Ittel−Ibers parameters $\alpha$, $\beta$, and $\beta'$.[16] For (*R*)-**3**, the parameter $\alpha$, defined as the angle between the normal lines to planes C(18)C(28)C(27) and P(2)C(23)C(24), is calculated at 40.7°. This value is lower than the 55−61° found[15] in a series of Pd(0) complexes of tetracyanoethylene, a much stronger $\pi$-acid. Both the $\beta$ and $\beta'$ parameters are defined as the other two angles of the triangle formed by C(23), C(28), and the point of intersection of the two normals described above. Thus, the angles $\beta$ and $\beta'$ between C(23)−C(28) and the normal lines to planes C(18)C(28)C(27) and P(2)C(23)C(24) are calculated at 66.3 and 73.0°, correspondingly. It was interesting to compare (*R*)-**3** with the recently reported[11a] structure of $[(MOP)Pd(allyl)]^+$, where MOP = 2-methoxy-2′-(diphenylphosphino)-1,1′-binaphthyl is bound to Pd via the P atom and the Ar,MeO-disubstituted aromatic C═C bond. Using the reported[11a] structural data for $[(MOP)Pd(allyl)]^+$, we calculated its $\eta^2$-arene angle parameters at $\alpha = 31.2$, $\beta = 69.5$, and $\beta' = 78.8$°. The $\alpha$ angle in $[(MOP)Pd(allyl)]^+$ (a Pd(II) complex; 31.2°) is noticeably more acute than in (*R*)-**3** (a Pd(0) complex; 40.7°), in accord with much stronger back-donation expected from zerovalent palladium.

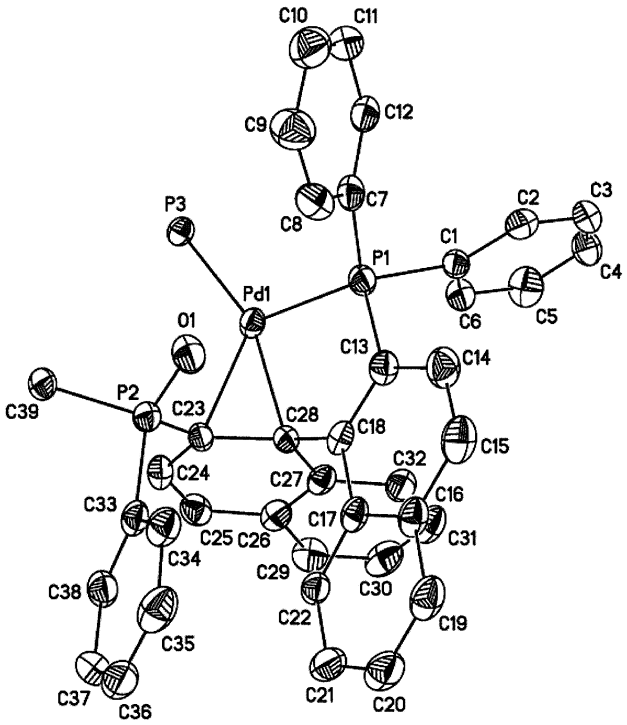



**Figure 3.** ORTEP plot of $[((R)\text{-BINAP(O)})_2Pd]$ ((*R*)-**3**), with thermal ellipsoids drawn to the 50% probability level, showing the P,$\eta^2$-arene coordination of BINAP(O). All atoms of the second BINAP(O), except for coordinated P, are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)−C(28), 2.160(3); Pd(1)−C(23), 2.228(3); Pd(1)−P(1), 2.290(1); Pd(1)−P(3), 2.343(1); C(28)−Pd(1)−C(23), 38.47(11); C(28)−Pd(1)−P(1), 84.57(9); C(23)−Pd(1)−P(1), 114.76(9); C(28)−Pd(1)−P(3), 157.86(9); C(23)−Pd(1)−P(3), 122.71(8); P(1)−Pd(1)−P(3), 117.57(3).

The average Pd−C bond distance, 2.19 Å (Pd−C(23) = 2.228(3) Å and Pd−C(28) = 2.160(3) Å), is longer than the values previously determined for Pd(0) olefin complexes, 2.04−2.13 Å.[15−19] The Pd−P bond distances of 2.290(1) and 2.343(1) Å for Pd−P(1) and Pd−P(3), correspondingly, are in the expected range.[15] No $\pi$-stacking interactions were detected in the structure of (*R*)-**3**.

Clearly, the structure of $[(BINAP(O))_2Pd]$ is unusual, being totally different from that of $[(BINAP)_2Pd]$, in which all four P centers are coordinated to the metal.[20] It is not surprising, therefore, that reactions catalyzed by Pd(0) complexes of BINAP may result in a stereochemical outcome that is different from that of analogous reactions conducted in the presence of Pd(0) catalysts stabilized by BINAP(O) of the same enantiomeric configuration.[1]

As mentioned above, the oxidative addition of PhI to **3** resulted in the formation of a 1:1 mixture of free BINAP(O) and [(BINAP(O))Pd(Ph)I] (**4**) (Scheme 1). Only these two products could be observed in the reaction mixture by $^{31}P$ NMR spectroscopy (see above). Therefore, in contrast to $[(BINAP(O))PdCl_2]$ (**1**) (eq 4), **4** does not react with BINAP(O) to give an observable product. Furthermore, the $^{31}P$ NMR data indicate that

(10) For examples of some $\eta^2$- and $\eta^4$-arene complexes of Pd(II), see: (a) Ossor, H.; Pfeffer, M.; Jastrzebski, J. T. B. H.; Stam, C. H. *Inorg. Chem.* **1987**, *26*, 1169. (b) Wehman, E.; van Koten, G.; Jastrzebski, J. T. B. H.; Ossor, H.; Pfeffer, M. *J. Chem. Soc., Dalton Trans.* **1988**, 2975. (c) Dupont, J.; Pfeffer, M.; Rotteveel, M. A.; De Cian, A.; Fischer, J. *Organometallics* **1989**, *8*, 1116. (d) Pfeffer, M. *Recl. Trav. Chim. Pays-Bas* **1990**, *109*, 567. (e) Li, C. S.; Cheng, C. H.; Liao, F. L.; Wang, S. L. *J. Chem. Soc., Chem. Commun.* **1991**, 710. (f) Sommovigo, M.; Pasquali, M.; Leoni, P.; Braga, D.; Sabatino, P. *Chem. Ber.* **1991**, *124*, 97. (g) DuPont, J.; Pfeffer, M.; Theurel, L.; Rotteveel, M. A.; de Cian, A.; Fischer, J. *New J. Chem.* **1991**, *15*, 551. (h) Li, C. S.; Jou, D. C.; Cheng, C. H. *Organometallics* **1993**, *12*, 3945. (i) Liu, C. H.; Li, C. S.; Cheng, C. H. *Organometallics* **1994**, *13*, 18. (j) Duan, J.-P.; Cheng, C.-H. *J. Chin. Chem. Soc.* **1994**, *41*, 749. (k) Kannan, S.; James, A. J.; Sharp, P. R. *J. Am. Chem. Soc.* **1998**, *120*, 215. (l) Casas, J. M.; Fornies, J.; Martinez, F.; Rueda, A. J.; Tomas, M.; Welch, A. J. *Inorg. Chem.* **1999**, *38*, 1529. (m) Reddy, K. R.; Surekha, K.; Lee, G.-H.; Peng, S.-M.; Liu, S.-T. *Organometallics* **2001**, *20*, 5557. (n) Catellani, M.; Mealli, C.; Motti, E.; Paoli, P.; Perez-Carreno, E.; Pregosin, P. S. *J. Am. Chem. Soc.* **2002**, *124*, 4336.

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(13) Soon after preparation of this paper, another paper appeared, describing P,O,$\eta^2$ bonding of BINAP(O) to Ru: Cyr, P. W.; Rettig, S. J.; Patrick, B. O.; James, B. R. *Organometallics* **2002**, *21*, 4672.

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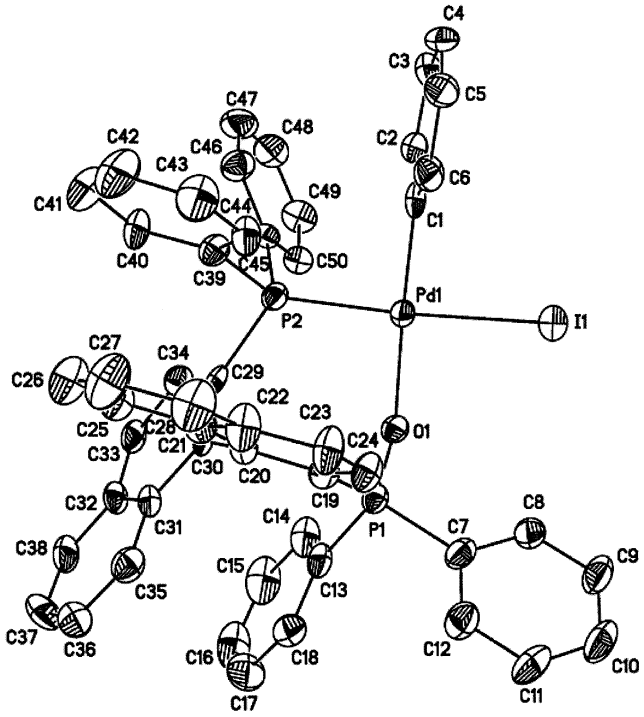
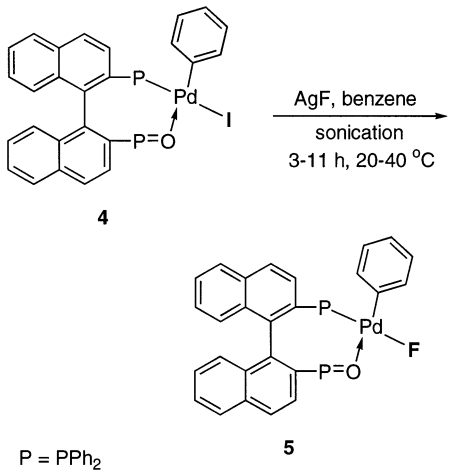



**Figure 4.** ORTEP drawing of [((*R*)-BINAP(O)-$\kappa^2$*P,O*)Pd(Ph)I] ((*R*)-**4**), with thermal ellipsoids drawn to the 50% probability level. Selected bond lengths (Å) and angles (deg): I(1)−Pd(1), 2.609(1); Pd(1)−C(1), 2.011(8); Pd(1)−O(1), 2.182(4); Pd(1)−P(2), 2.271(2); P(1)−O(1), 1.502(5); C(1)−Pd(1)−O(1), 173.4(3); C(1)−Pd(1)−P(2), 90.0(2); O(1)−Pd(1)−P(2), 91.82(14); C(1)−Pd(1)−I(1), 86.5(2); O(1)−Pd(1)−I(1), 91.53(13); P(2)−Pd(1)−I(1), 176.25(5).

**4** exists as a single isomer in solution. Because tertiary phosphines and $\sigma$-aryls are both electron-rich, strongly trans-influencing ligands, it was proposed that, in the observed isomer of **4**, the $\sigma$-phenyl is trans to oxygen rather than phosphorus of the chelating BINAP(O).[21] Indeed, this geometry was confirmed by X-ray analysis of (*R*)-**4**.

The molecule of (*R*)-**4** is square planar, with both the phosphino and phosphinyl groups coordinated to Pd and the $\sigma$-Ph trans to less electron-donating oxygen (Figure 4). The planarity of (*R*)-**4** is manifested by the coordination angles around Pd, varying in the narrow range 86.5(2)−91.8(2)°. Furthermore, the deviations of the five atoms from the mean plane defined by I(1)Pd(1)P(2)O(1)C(1) are minor, being 0.026, 0.059, 0.028, −0.053, and −0.060 Å, respectively. The Pd−C bond distance of 2.011(8) Å is within the range of 1.94−2.08 Å for 42 reports of mononuclear $\sigma$-phenyl Pd(II) complexes found in the Cambridge Crystallographic Database (CSD version 5.23 of April 2002). Because the longest reported Pd−Ph bonds (2.04-2.08 Å) are trans to most strongly trans-influencing phosphine[22] or $\sigma$-C[23] ligands, the observed geometry of (*R*)-**4** is not surprising.[21b] Being trans to the phosphine, the Pd−I bond (2.609(1) Å) is slightly longer than the average value calculated for various reported Pd(II) iodo complexes (2.597 Å) yet shorter than the Pd−I bond trans to Ph in $[(Ph_3P)_2Pd(Ph)I]$.[24] In accord with the strong trans influence of $\sigma$-Ph, the Pd−O bond in (*R*)-**4** (2.182(4) Å) is considerably longer than in (*S*)-**1** (2.080(2) Å). In contrast, the Pd−P bond (2.271(2) Å) is shortened, being trans to the phosphinyl group rather than a phosphine.[24] In general, all trends with the Pd−O, Pd−P, Pd−C, and Pd−halogen bond distances of (*R*)-**4** are similar to those previously reported for the structure of [(dppmO-$\kappa^2$*P,O*)Pd(Me)Cl].[21a] The dihedral angle between the Pd coordination plane and the $\sigma$-Ph ring is 79.3°, deviating noticeably from the ideal value of 90°. This deviation is possibly dictated by the need to alleviate filled−filled repulsions[25] via push−pull interactions of the negatively charged oxygen with $\pi^*$ of the $\sigma$-aryl through Pd.[24]

Our longstanding interest in the chemistry of organopalladium fluoride complexes[26,27] prompted us to attempt I/F exchange on **4** in order to synthesize [(BINAP(O))Pd(Ph)F]. Treatment of (*S*)-**4** with AgF in dry benzene under sonication[26,27a−e,g] cleanly produced [((*S*)-BINAP(O))Pd(Ph)F]((*S*)-**5**) (eq 5). The $^{31}$P NMR




spectrum of (*S*)-**5** exhibited two 1:1 resonances, a singlet at 40.2 ppm from the coordinated phosphinyl group and a doublet at 30.5 ppm from the phosphine trans to the F, as follows[27g] from the large coupling constant $J_{P-F}$ = 179.7 Hz (vs 10−20 Hz for cis-$J_{P-F}$).[27a,b,g] A doublet at −215.7 ppm with the same coupling constant of 179.7 Hz was observed in the $^{19}$F NMR spectrum of (*S*)-**5**. The

(21) (a) A similar dppmO complex, [(dppmO-$\kappa^2$*P,O*)Pd(Me)Cl], with the methyl trans to oxygen has been structurally characterized: Brassat, I.; Englert, U.; Keim, W.; Keitel, D. P.; Killat, S.; Suranna, G.-P.; Wang, R. *Inorg. Chim. Acta* **1998**, *280*, 150. (b) A known phenomenon recently referred to as *transphobia*: Vicente, J.; Arcas, A.; Bautista, D.; Jones, P. G. *Organometallics* **1997**, *16*, 2127 (includes a structurally characterized C,N-cyclometalated dppmO-$\kappa^2$*P,O* Pd complex). Vicente, J.; Abad, J.-A.; Frankland, A. D.; Ramírez de Arellano, M. C. *Chem. Eur. J.* **1999**, *5*, 3066. Vicente, J.; Abad, J.-A.; Hernandez-Mata, F. S.; Jones, P. G. *J. Am. Chem. Soc.* **2002**, *124*, 3848.

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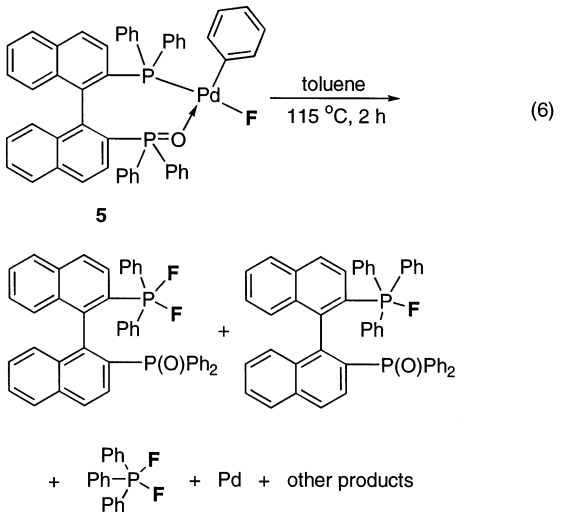
geometry of (*S*)-**5** seemed ideally suited for C−F reductive elimination of PhF from Pd, a key step of the highly desired, yet not realized, catalytic fluorination of haloarenes.[26]

We have previously demonstrated[26,27e,g] that the thermal decomposition of (*σ*-phenyl)palladium fluoride complexes stabilized by tertiary phosphines involves P−F and P−C rather than the needed C−F reductive elimination. The selectivity observed was thought to be due, at least in part, to the geometry of those fluorides *trans*-[$(R_3P)_2$Pd(Ph)F], in which the F and Ph are trans, while both are cis to the phosphines. On the contrary, in (*S*)-**5** the F ligand is trans to P and cis to the *σ*-phenyl (eq 5), a geometry that one would expect to favor C−F and suppress P−F reductive elimination. Nonetheless, the thermal decomposition of (*S*)-**5** did not furnish fluorobenzene but rather produced a mixture of products that obviously emerged from C−P and P−F reductive elimination processes (eq 6).




(6)

The fluorine-containing products were not isolated from the complex reaction mixture but rather identified by their $^{19}$F and $^{31}$P NMR data, using previously reported[27e] assignments (for detailed NMR data, see the Experimental Section). It is noteworthy that the ease of thermal decomposition at 115 °C in toluene decreases noticeably in the order **5** (2 h) > [$(Ph_3P)_2$Pd(Ph)F] (16 h)[27e] > [$(Me_3P)_2$Pd(Ph)F] (72 h).[27g] This order parallels the apparent lability $P(Ph)_2O$ > $Ph_3P$ > $Me_3P$ on the metal, which provides additional support to a mechanism that may involve dissociation of a neutral ligand from Pd prior to reductive elimination.[27e] Dissociation of the phosphinyl group from Pd in **5** would result in a tricoordinate species, from which C−P and P−F reductive elimination is preferred.

## Conclusion

This paper describes a series of new complexes of Pd(II) and Pd(0) with BINAP(O), a chiral phosphine−phosphine oxide ligand. These complexes display coordination modes and properties that are markedly different from those of analogous Pd derivatives of other phosphine−phosphine oxide ligands and BINAP. The particularly uncommon [$(BINAP(O))_2$Pd] (**3**) is a rare example of a structurally characterized $\eta^2$-arene Pd(0) complex, in which the $\pi$-bonded aromatic C=C bond is the one that is most sterically hindered, bearing the phosphinyl and aryl substituents. The considerable difference between BINAP and BINAP(O) complexes of both zerovalent palladium and organopalladium(II) bears important implications for catalysis. It has been reported before[3] that, under certain conditions, added BINAP/Pd(II) catalyst is easily and cleanly converted to BINAP(O) and Pd(0). In the presence of a base, this process can rapidly occur under very mild conditions, i.e. minutes at room temperature.[6b] Upon coming together, the BINAP(O) and Pd(0) produce catalytically active BINAP(O) species (such as **3**) which, being structurally very different from BINAP Pd(0) species, can change the catalytic reaction profile considerably, up to complete reversal of product chirality.[1,28]

## Experimental Section

NMR spectra were obtained with a Bruker Avance DPX 300 spectrometer. Reactions involving Pd(0) complexes and the Pd(II) fluoride complex were carried out under nitrogen using glovebox or Schlenk techniques. Both (*R*)- and (*S*)-BINAP(O) were prepared as described in the literature.[6] All other chemicals were purchased from Aldrich and Strem and used as received. For NMR studies of **3** and **5**, deuterated solvents were dried using standard procedures and stored in a glovebox over freshly calcined molecular sieves (4 Å). The ultrasound-promoted synthesis of **5** was carried out with an Aquasonic 50HT ultrasound bath.

**[((*R*)-BINAP(O)-$\kappa^2$*P,O*)PdCl$_2$] ((*R*)-1).** The entire procedure was performed in air. A mixture of (*R*)-BINAP(O) (205 mg; 0.32 mmol) and [$(MeCN)_2PdCl_2$] (83 mg; 0.32 mmol) was dissolved in warm dichloromethane (5 mL), and this solution was then evaporated to leave a dark orange oil. Stirring this oil with benzene (3 mL) under reflux for 30 min produced a yellow solid which was separated by filtration, recrystallized from $CH_2Cl_2$−ether (twice), and dried under vacuum. The yield of (*R*)-**1**·$^1/_3CH_2Cl_2$ was 259 mg (96%). Anal. Calcd for $C_{44}H_{32}Cl_2OP_2Pd\cdot{}^1/_3CH_2Cl_2$: C, 63.1; H, 3.9. Found: C, 62.8; H, 3.6. $^1$H NMR ($CD_2Cl_2$, 20 °C): $\delta$ 6.1−8.4 (multiplets). $^{31}$P NMR ($CD_2Cl_2$, 20 °C): $\delta$ 22.8 (s, 1P, $PPh_2$); 48.3 (s, 1P, $P(O)Ph_2$).

**[((*S*)-BINAP(O)-$\kappa^2$*P,O*)PdCl$_2$] ((*S*)-1).** The entire procedure was performed in air. A stirred mixture of [$(MeCN)_2PdCl_2$] (205 mg; 0.79 mmol) and toluene (10 mL) was brought to gentle boiling. To this mixture was added a solution of (*S*)-BINAP(O) (507 mg; 0.79 mmol) in warm toluene (5 mL). The mixture was stirred under reflux for 30 min and then cooled to room temperature. The orange solid was separated by filtration, recrystallized from $CH_2Cl_2$−ether (twice), and dried under vacuum. The yield of (*S*)-**1**·$^1/_3CH_2Cl_2$ was 620 mg (93%). Anal. Calcd for $C_{44}H_{32}Cl_2OP_2Pd\cdot{}^1/_3CH_2Cl_2$: C, 63.1; H, 3.9. Found: C, 63.4; H, 3.7. $^1$H NMR ($CD_2Cl_2$, 20 °C): $\delta$ 6.1−8.4 (multiplets). $^{31}$P NMR ($CD_2Cl_2$, 20 °C): $\delta$ 22.8 (s, 1P, $PPh_2$); 48.3 (s, 1P, $P(O)Ph_2$).

**Reaction of [((*R*)-BINAP(O)-$\kappa^2$*P,O*)PdCl$_2$] ((*R*)-1) with (*R*)-BINAP(O).** A solution of [((*R*)-BINAP(O)-$\kappa^2$*P,O*)$PdCl_2$] ((*R*)-**1**: 5.9 mg; $7.2 \times 10^{-3}$ mmol) and (*R*)-BINAP(O) (18.5 mg; $2.9 \times 10^{-2}$ mmol) in $CH_2Cl_2$ (0.9 mL) was placed in a standard 5 mm NMR tube and analyzed by $^{31}$P NMR at 20 °C (number of transients 1). The NMR spectrum displayed three pairs of singlets, from (*R*)-**1** (22.8 and 48.5 ppm), (*R*)-BINAP(O) (−14.6 and 27.5 ppm), and [((*R*)-$BINAP(O))_2PdCl_2$] (**2**) (26.3 and 32.7 ppm), in a 1:5.9:0.8 molar ratio. This ratio did not change after the measurement was repeated in 30 min. On the basis of these data, $K_{eq}$ was calculated at 20.7 L mol$^{-1}$.

(28) Very recently, it was reported that in some asymmetric Suzuki cross-coupling reactions, the chirality reversal depending on the Pd(OAc)$_2$ to (*R*)-BINAP ratio might be due to phenomena other than the formation of BINAP(O) (eq 2). See: Castanet, A.-S.; Colobert, F.; Broutin, P.-E.; Obringer, M. *Tetrahedron: Asymmetry* **2002**, *13*, 659.

**Table 1. Selected Crystallographic Data for (*S*)-1, (*R*)-3, and (*R*)-4**

| param | [((*S*)-BINAP(O))PdCl$_2$] ((*S*)-**1**) | [((*R*)-BINAP(O))$_2$Pd] ((*R*)-**3**) | [((*R*)-BINAP(O))Pd(Ph)I] ((*R*)-**4**·C$_6$H$_{14}$) |
|---|---|---|---|
| empirical formula | $C_{44}H_{32}Cl_2OP_2Pd$ | $C_{88}H_{64}O_2P_4Pd$ | $C_{37.33}H_{34}I_{0.67}O_{0.67}P_{1.33}Pd_{0.67}$ |
| fw | 815.94 | 1383.67 | 690.14 |
| crystal size, mm | 0.25 × 0.24 × 0.12 | 0.10 × 0.04 × 0.03 | 0.19 × 0.02 × 0.01 |
| crystal system | monoclinic | triclinic | hexagonal |
| space group | $P2_1$ | $P1$ | $P6_5$ |
| temp, K | 173 | 173 | 173 |
| *a*, Å | 11.940(3) | 11.956(1) | 29.934(6) |
| *b*, Å | 11.711(3) | 12.809(1) | 29.934(6) |
| *c*, Å | 13.548(3) | 13.422(1) | 11.858(5) |
| α, deg | | 63.105(2) | |
| *β*, deg | 108.328(4) | 78.267(2) | |
| *γ*, deg | | 68.287(2) | |
| *V*, Å$^3$ | 1798.4(7) | 1701.5(3) | 9202(5) |
| *Z* | 2 | 1 | 9 |
| calcd density, g cm$^{-3}$ | 1.507 | 1.350 | 1.121 |
| $\mu$(Mo), cm$^{-1}$ | 79 | 42 | 89 |
| 2$\theta$ range, deg | 3.16−56.64 | 3.40−56.56 | 2.72−52.72 |
| abs cor | SADABS | none | SADABS |
| no. of rflns collected | 30 552 | 22 836 | 63 593 |
| no. of unique rflns used in refinement ($I > 4\sigma(I)$) | 8555 | 15 230 | 12 147 |
| no. of params refined | 451 | 856 | 552 |
| data to param ratio | 18.97 | 17.79 | 22.01 |
| R1, % | 3.5 | 4.1 | 5.2 |
| wR2, % | 7.2 | 7.0 | 12.3 |
| goodness of fit | 1.06 | 0.93 | 1.03 |



**[((*R*)-BINAP(O))$_2$Pd] ((*R*)-3).** The entire procedure was performed under $N_2$. To a mixture of [((*R*)-BINAP(O)-$\kappa^2$*P,O*)-PdCl$_2$] ((*R*)-**1**: 100 mg; 0.12 mmol), (*R*)-BINAP(O) (80 mg; 0.12 mmol), benzene (10 mL), and water (1.5 mL) was added $LiBH_4$ (20 mg; 0.9 mmol). The mixture was vigorously stirred at room temperature for 6 h, until all solids had dissolved and a dark red-brown solution formed. The mixture was evaporated and the residue carefully dried under vacuum. The dark solid was extracted first with 7 mL and then with 5 mL of benzene. The combined extracts were filtered through Celite, reduced in volume to ca. 3 mL, and treated with hexanes (5 mL, in portions). After 2 h the red-brown crystals were separated, washed with hexanes, and dried under vacuum. The yield of (*R*)-**3** was 145 mg (85%). Anal. Calcd for $C_{88}H_{64}O_2P_4Pd$: C, 76.4; H, 4.7. Found: C, 76.1; H, 4.7. $^{31}$P NMR ($C_6D_6$, 20 °C): $\delta$ 22.2 (br s, 2P, $PPh_2$); 28.5 (br s, 2P, $P(O)Ph_2$).

**[((*S*)-BINAP(O))$_2$Pd] ((*S*)-3).** Under conditions of the previous experiment, (*S*)-**3** was prepared in 73% yield (185 mg) from [((*S*)-BINAP(O)-$\kappa^2$*P,O*)PdCl$_2$] (150 mg), (*S*)-BINAP(O) (117 mg), and $LiBH_4$ (30 mg) in a benzene (10 mL)−water (1 mL) biphasic system.

**[((*R*)-BINAP(O)-$\kappa^2$*P,O*)Pd(Ph)I] ((*R*)-4).** The reaction was carried out under $N_2$. The isolation and purification steps were performed in air. To a stirred mixture of (*R*)-BINAP(O) (805 mg; 1.26 mmol), iodobenzene (520 mg; 2.55 mmol), and methanol (20 mL) was added [$Pd_2(dba)_3$] (580 mg; 0.63 mmol). After vigorous stirring at room temperature for 1 day, the original purple-red color was gone and a thick grayish slurry was obtained. The precipitate was filtered, thoroughly washed with methanol, dried, and redissolved in $CH_2Cl_2$. The dichloromethane solution was filtered through a silica gel plug, which was then washed with $CH_2Cl_2$ (TLC control). The combined dichloromethane solutions were reduced in volume to ca. 5−10 mL and treated with ether (50 mL). After 12 h the pale yellow solid was filtered, washed with hexanes, and dried under vacuum. The yield of (*R*)-**4**·$^1/_4CH_2Cl_2$ was 875 mg (72%). Anal. Calcd for $C_{50}H_{37}IOP_2Pd\cdot{}^1/_4CH_2Cl_2$: C, 62.2; H, 3.9. Found: C, 62.1; H, 3.4. $^1$H NMR ($CD_2Cl_2$, 20 °C): $\delta$ 6.3−8.4 (multiplets). $^{31}$P NMR ($CD_2Cl_2$, 20 °C): $\delta$ 15.5 (s, 1P, $PPh_2$); 37.8 (s, 1P, $P(O)Ph_2$).

**[((*S*)-BINAP(O)-$\kappa^2$*P,O*)Pd(Ph)I] ((*S*)-4).** The reactions were carried out under $N_2$. The isolation and purification steps were performed in air.

(a) To a stirred mixture of (*S*)-BINAP(O) (590 mg; 0.92 mmol), iodobenzene (380 mg; 1.86 mmol), and benzene (15 mL) was added [$Pd_2(dba)_3$] (403 mg; 0.44 mmol). After vigorous stirring at room temperature for 3 h, the original purple-red color was gone and much grayish precipitate formed. After addition of methanol (30 mL) and stirring for 1 h the precipitate was filtered, washed with methanol, dried, and redissolved in $CH_2Cl_2$. The dichloromethane solution was filtered through Celite, reduced in volume to ca. 10 mL, and treated with hexanes (30 mL). After 12 h the pale yellow solid was filtered, washed with hexanes, and dried under vacuum to produce 610 mg of the product as tiny yellowish needles. Evaporation of the benzene−MeOH mother liquors and washing the residue with MeOH (15 mL) produced an additional quantity of (*S*)-**4**, which was purified by recrystallization from $CH_2Cl_2$−hexanes as described above. The second crop amounted to 165 mg of the product. The total yield of (*S*)-**4**·$^1/_4CH_2Cl_2$ was 775 mg (91%). Anal. Calcd for $C_{50}H_{37}IOP_2Pd\cdot{}^1/_4CH_2Cl_2$: C, 62.2; H, 3.9. Found: C, 62.3; H, 3.5. $^1$H NMR ($CD_2Cl_2$, 20 °C): $\delta$ 6.3−8.4 (multiplets). $^{31}$P NMR ($CD_2Cl_2$, 20 °C): $\delta$ 15.5 (s, 1P, $PPh_2$); 37.8 (s, 1P, $P(O)Ph_2$).

(b) Iodobenzene (150 mg; 0.74 mmol) was added to a mixture of [((*S*)-BINAP(O))$_2$Pd], (*S*)-**3** (150 mg; 0.11 mmol), and benzene (2 mL). After the mixture was stirred for 2 h, the volatiles were removed under vacuum, and the residue was stirred with ethanol (3 mL) for 30 min. The fluffy needles of the product were separated by filtration, washed with cold (5−10 °C) EtOH (3 × 1 mL), dried, and recrystallized from $CH_2Cl_2$−hexanes. The yield of (*S*)-**4** was 91 mg (88%). The material was identical with the sample of (*S*)-**4** prepared using the [$Pd_2(dba)_3$] method (see above).

**[((*S*)-BINAP(O)-$\kappa^2$*P,O*)Pd(Ph)F] ((*S*)-5).** The synthesis and isolation were performed under anhydrous conditions.

(a) In a drybox, a standard 5 mm NMR tube was charged with [((*S*)-BINAP(O)-$\kappa^2$*P,O*)Pd(Ph)I] ((*S*)-**4**: 40 mg; 0.04 mmol), AgF (25 mg; 0.20 mmol), and benzene (1 mL). The tube was sealed with a rubber septum, brought out, and sonicated with occasional shaking at 20−40 °C. After 1 h 15 min, $^{31}$P NMR analysis indicated 70% conversion to [((*S*)-BINAP(O)-$\kappa^2$*P,O*)-Pd(Ph)F] ((*S*)-**5**). The sonication was resumed and continued for an additional 1.5 h, after which the exchange was complete. $^{31}$P NMR: $\delta$ 30.5 (d, $J_{P-F}$ = 179.7 Hz, 1P, $PPh_2$); 40.2 (s, 1P,

P(O)$Ph_2$). $^{19}$F NMR, $\delta$: −215.7 (d, $J_{P-F}$ = 179.7 Hz). No other signals were observed in the NMR spectra.

(b) In a drybox, a 25 mL round-bottom Schlenk flask was charged with [((*S*)-BINAP(O)-$\kappa^2$*P*,*O*)Pd(Ph)I] ((*S*)-**4**: 300 mg; 0.31 mmol), AgF (120 mg; 0.94 mmol), and benzene (8 mL). The flask was sealed with a rubber septum, brought out, and sonicated, with stirring, at 20−40 °C for 10 h. $^{31}$P NMR analysis indicated 100% conversion. In drybox, the solution was filtered through Celite. The solids were extracted with warm benzene (3 × 3 mL) and filtered through the same Celite plug. The combined benzene filtrates were reduced in volume to ca. 5 mL, treated with ether (10 mL), and left at room temperature overnight. The solid was separated, recrystallized from hot benzene−hexanes, and dried under vacuum. The yield of (*S*)-**5**·$C_6H_6$ was 209 mg (72%). Anal. Calcd for $C_{50}H_{37}FOP_2Pd\cdot C_6H_6$: C, 73.2; H, 4.7. Found: C, 73.3; H, 4.3. $^1$H NMR (toluene-$d_8$, 20 °C): $\delta$ 6.2−9.2 (multiplets). $^{31}$P NMR (toluene-$d_8$, 20 °C): $\delta$ 30.5 (d, $J_{P-F}$ = 179.7 Hz, 1P, $PPh_2$); 40.2 (s, 1P, P(O)$Ph_2$). $^{19}$F NMR (toluene-$d_8$, 20 °C): $\delta$ −215.7 (d, $J_{P-F}$ = 179.7 Hz).

**Thermal Decomposition of [((*S*)-BINAP(O)-$\kappa^2$*P*,*O*)Pd(Ph)F] ((*S*)-5).** In a drybox, a standard 5 mm NMR tube was charged with [((*S*)-BINAP(O)-$\kappa^2$*P*,*O*)Pd(Ph)F] ((*S*)-**5**: 40 mg) and toluene-$d_8$ (0.7 mL), sealed with a rubber septum, brought out, and heated at 115 °C (oil bath) for 2 h. Palladium metal formation was observed. The sample was analyzed by $^{19}$F and $^{31}$P NMR spectroscopy. No fluorobenzene was present in the sample ($^{19}$F NMR). On the basis of the NMR data and previous assignments[27e] three products were identified. (1) $Ph_3PF_2$: $^{19}$F NMR $\delta$ −39.6 (d, $J_{P-F}$ = 666 Hz); $^{31}$P NMR $\delta$ −56.1 (t, $J_{P-F}$ = 666 Hz). (2) 1-(2-$Ph_2$(O)P$C_{10}H_6$)-1′-(2′-$C_{10}H_6PPh_2F_2$): $^{19}$F NMR $\delta$ −34.2 (d, $J_{P-F}$ = 684 Hz); $^{31}$P NMR $\delta$ −50.4 (t, $J_{P-F}$ = 684 Hz). (3) 1-(2-$Ph_2$(O)P$C_{10}H_6$)-1′-(2′-$C_{10}H_6PPh_3F$): $^{19}$F NMR $\delta$ 8.2 (d, $J_{P-F}$ = 658 Hz); $^{31}$P NMR $\delta$ −65.4 (d, $J_{P-F}$ = 658 Hz). Structural formulas of the products are presented in eq 6.

**X-ray Diffraction Studies.** A Bruker SMART 1K CCD diffractometer (Mo Kα radiation) was used for X-ray analysis at −100 °C of all three complexes. In all cases, SADABS correction was applied. The structures were solved by direct methods and refined by full-matrix least squares on $F^2$. All non-hydrogen atoms were refined anisotropically, while all of the hydrogen atoms were idealized using a riding model. A summary of the crystallographic data is presented in Table 1. For full details of the X-ray studies, see the Supporting Information.

**Supporting Information Available:** Full details of the X-ray crystallographic studies of (*S*)-**1**, (*R*)-**3**, and (*R*)-**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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