First Resolution of a Free Fluorophosphine Chiral at Phosphorus. Resolution and Reactions of Free and Coordinated (±)-Fluorophenylisopropylphosphine

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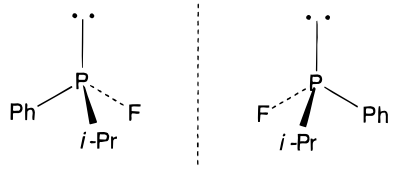
The trivalent fluorophosphine (±)-PFPh(*i*-Pr), (±)-**1**, has been prepared by halogen exchange of the corresponding chlorophosphine with sodium fluoride in hot sulfolane. The neat fluorophosphine rapidly decomposes by *equilibrium redox disproportionation* into $PF_3Ph(i\text{-}Pr)$ and (*R**,*R**)/(*R**,*S**)-Ph(*i*-Pr)PPPh(*i*-Pr), but in benzene, (±)-**1** has considerable thermodynamic stability. The resolution of (±)-**1** was achieved by a fractional crystallization of the diastereomers (R,R_P)- and (R,S_P)-chloro[1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C,N*](fluorophenylisopropylphosphine)palladium(II), (R,R_P)- and (R,S_P)-**5**, whereby the less soluble (R,R_P) diastereomer selectively crystallized in 64% yield in a typical second-order asymmetric transformation. Optically pure (*S*)-(−)-**1**, $[\alpha]_D^{20}$ −210 (*c* 0.59, C_6H_6), was liberated from (R,R_P)-**5** with (*R**,*S**)-1,2-phenylenebis(methylphenylphosphine). The optically active phosphine in benzene racemizes over 6 h without significant redox disproportionation. The methoxyphosphine (±)-P(OMe)Ph(*i*-Pr), (±)-**9**, was also resolved by the method of metal complexation. Thus, fractional crystallization of (R,R_P)- and (R,S_P)-chloro[1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C,N*](methoxyphenylisopropylphosphine)palladium(II), (R,R_P)- and (R,S_P)-**8**, followed by liberation of the respective optically active methoxyphosphines from the separated diastereomers with 1,2-bis(diphenylphosphino)ethane, gave (*R*)-(+)- and (*S*)-(−)-**9** of 92% and 96% ee, respectively. The barrier to unimolecular inversion for (±)-**9** was determined to be >82.9 ± 0.5 kJ mol^{-1} by variable temperature ^{1}H NMR spectroscopy. The substitution of fluoride in (R,R_P)-**5** by methoxide proceeds with predominant inversion of the configuration at phosphorus to give (R,R_P)- and (R,S_P)-**8** with (R,S_P)/(R,R_P) = $^1/_5$. The crystal structures of (R,R_P)-**5** and (R,R_P)-**8** have been determined: (R,R_P)-**5** ($C_{23}H_{28}ClFNPPd$) crystallizes in the orthorhombic space group $P2_12_12_1$ with a = 9.967(2) Å, b = 10.998(4) Å, c = 21.324(3) Å, Z = 4, and R = 0.031; (R,R_P)-**8** ($C_{24}H_{31}ClNOPPd$) crystallizes in the space group $P2_12_12_1$ with a = 10.444(3) Å, b = 12.146(3) Å, c = 19.047(2) Å, Z = 4, and R = 0.026.

Introduction

Following the first resolution of a simple acyclic tertiary phosphine in 1961,[1,2] the question arose as to the suitability for resolution of other simple trivalent phosphorus compounds, especially halogenophosphines of the type PXR^1R^2, which would be valuable intermediates for subsequent syntheses in optically active form. Calculations of pyramidal inversion barriers for compounds of this type indicated that configurational stability at phosphorus increased with attachment of electronegative substituents, for example chlorine or especially fluorine atoms.[3] Nevertheless, the first reported attempts at synthesizing optically active fluoro- and chlorophosphines of the type PXR^1R^2 from optically active compounds of the type $P(NR_2)$-R^1R^2 by cleavage of the amino group with appropriate acyl halides, hydrogen chloride, or phosphorus trichloride were unsuccessful.[4] In 1992, however, it was reported that (*S*)-(−)-[P(SMe)Cl(*t*-Bu)Ph]CF_3SO_3 of 63% optical purity could be desulfurized with tris(dimethylamino)phosphine at −70 °C to give (*S*)-(+)-PCl(*t*-Bu)Ph of 49.4% optical purity before purification.[5] The chlorophosphine lost its optical activity over 20 h in the polarimeter cell (conditions not specified). In other work it was shown that (±)-PClMePh or (±)-AsFMePh could be resolved in certain iron(II) complexes, but the phosphine or arsine could not be liberated from the metal in these complexes.[6] Here we report that (±)-PFPh(*i*-Pr), (±)-**1**, can be readily resolved by the separation of diastereomers of certain optically active palladium(II) complexes containing the phosphine, and that free (*S*)-(−)-**1** can be liberated in optically pure form from the less soluble diastereomer. The methoxyphosphine (±)-P(OMe)Ph(*i*-Pr) was also prepared and independently resolved. The stereochemistry of the substitution of the fluoride by methoxide in coordinated (±)-**1** has been investigated. A preliminary account of part of this work has been published.[7]



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

Results and Discussion

(a) Synthesis and Resolution of (±)-Fluorophenylisopropylphosphine ((±)-1). On the basis of the literature procedure for the synthesis of $PF(t\text{-}Bu)_2$,[8] (±)-**1** was isolated in 55% yield

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

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(2) Pietrusiewicz, K. M.; Zablocka, M. *Chem. Rev.* **1994**, *94*, 1375.
(3) Baechler, R. D.; Mislow, K. *J. Am. Chem. Soc.* **1971**, *93*, 773.
(4) Horner, H.; Jordan, M. *Phosphorus Sulfur Relat. Elem.* **1980**, *8*, 235.
(5) Omelańczuk, J. *J. Chem. Soc., Chem. Commun.* **1992**, 1718. Hägele, G.; Kückelhaus, W.; Tossing, G.; Seega, J. *J. Chem. Soc., Dalton Trans.* **1987**, 795.
(6) Salem, G.; Shaw, G. B.; Willis, A. C.; Wild, S. B. *J. Organomet. Chem.* **1993**, *444*, 147. Salem, G.; Shaw, G. B.; Willis, A. C.; Wild, S. B. *Ibid.* **1993**, *455*, 185.
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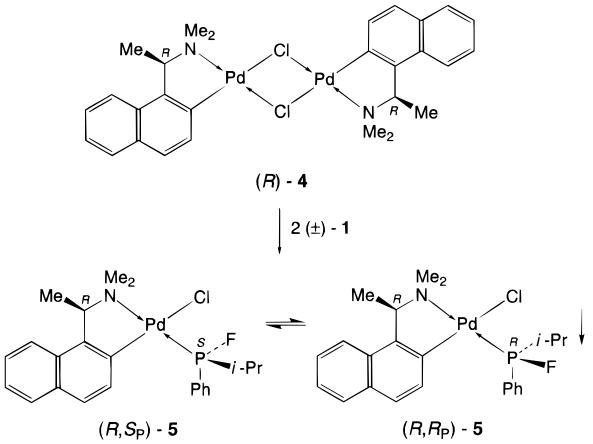
Scheme 1



by heating a mixture of (±)-PClPh(*i*-Pr)[9] and sodium fluoride in sulfolane and distillation in vacuo with collection at −196 °C (eq 1). The $^{31}P\{^1H\}$ NMR spectrum of a benzene solution

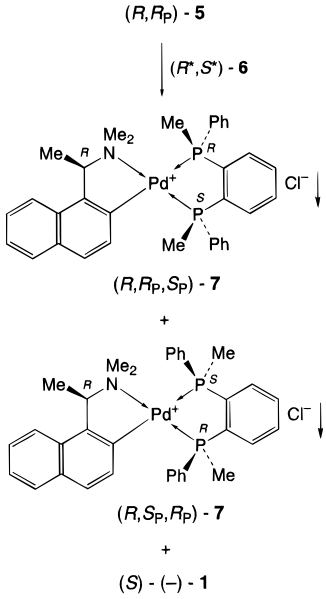
$$(\pm)\text{-PClPh}(i\text{-Pr}) \xrightarrow{\text{NaF}} \underset{(\pm)\text{-}\mathbf{1}}{(\pm)\text{-PFPh}(i\text{-Pr})} \qquad (1)$$

of the freshly thawed distillate at 25 °C indicated 86% of (±)-**1**, along with a number of minor impurities including the redox disproportionation product **2**. A neat sample of (±)-**1**, after 16 h at 25 °C, had almost completely disproportionated into **2** and (*R**,*R**)/(*R**,*S**)-**3**. Thus, (±)-**1** is considerably less stable than PF(*t*-Bu)$_2$, which showed no evidence of decomposition when heated at 150 °C for 100 h, even in the presence of a trace of sodium fluoride.[8] It is noteworthy, however, that the redox disproportionation of (±)-**1** is slowed down dramatically in benzene. After 20 months, a solution of (±)-**1** in benzene-d_6 had disproportionated according to eq 2, but a trace (ca. 1%) of (±)-**1** was still evident in the $^{31}P\{^1H\}$ NMR spectrum of the solution, suggesting an equilibrium between the trivalent fluorophosphine and the redox disproportionation products (eq 2).

$$3\ (\pm)\text{-}\mathbf{1} \rightleftharpoons \underset{\mathbf{2}}{\text{PF}_3\text{Ph}(i\text{-Pr})} + \underset{(R^*,R^*)/(R^*,S^*)\text{-}\mathbf{3}}{\text{Ph}(i\text{-Pr})\text{P}-\text{PPh}(i\text{-Pr})} \qquad (2)$$

The reaction of 2 equiv (±)-**1** with (*R*)-**4**·CH_2Cl_2[10] in dichloromethane produced the pair of diastereomeric complexes (*R*,*R*P)- and (*R*,*S*P)-**5**[11] in almost equal amounts (Scheme 1), as evidenced by a sharp doublet at δ_P 185.14 ppm ($^1J(PF) = 927.8$ Hz) and a broad doublet at δ_P 181.36 ppm ($^1J(PF) = 937.5$ Hz) in the $^{31}P\{^1H\}$ NMR spectrum. Interestingly, the intensity of the resonance at δ_P 185.14 ppm increased to 75% over 18 h, whereupon it remained constant at this equilibrium value. Consistent with this observation, removal of solvent, followed by dissolution of the residue in diethyl ether and subsequent filtration to remove a small quantity of solid impurity, gave a colorless solution from which the diastereomer having δ_P 185.14 ppm was obtained in 64% combined yield in a typical second-order asymmetric transformation.[13] The final mother liquor was found to contain both diastereomers in the equilibrium 75:25 ratio. In pure form, (*R*,*R*P)-**5** is kinetically stable in dichloromethane-d_2. The interconversion between (*R*,*R*P)- and (*R*,*S*P)-**5** could be caused by ligand exchange involving traces of (±)-**1** or its decomposition products with one or both of the diastereomers and subsequent intermolecular racemization and recoordination of the fluorophosphine. The configurationally homogeneous product having δ_P 185.14 ppm, colorless prisms, readily soluble in dichloromethane and benzene, moderately soluble in diethyl ether, was identified as (*R*,*R*P)-**5** by X-ray crystallography (see below).

Scheme 2



(b) Liberation of (*S*)-(−)-Fluorophenylisopropylphosphine ((*S*)-(−)-1). The liberation of optically pure (*S*)-(−)-**1** from (*R*,*R*P)-**5**[14] was effected by treatment of the complex with achiral (*R**,*S**)-1,2-$C_6H_4(PMePh)_2$ (**6**)[15] in benzene (Scheme 2). The displacement proceeds with retention of configuration at phosphorus to give homochiral (*S*)-(−)-**1**, as verified by the quantitative repreparation of the starting complex (*R*,*R*P)-**5** from the free ligand and (*R*)-**4**·CH_2Cl_2 in a rapid quenching experiment (Scheme 1). A solution of (*S*)-(−)-**1** having $[\alpha]_D^{20}$ −210 (*c* 0.59, C_6H_6) was obtained within 30 min of liberation, the minimum period required to remove (*R*,*R*P,*S*P)- and (*R*,*S*P,*R*P)-**7** and to prepare an accurate sample of the phosphine for polarimetry. Significantly, however, although the specific rotation of the solution increased to zero within 6 h (presumably by intermolecular fluorine exchange, perhaps involving the phosphenium fluoride as intermediate[4,5]), the $^{31}P\{^1H\}$ NMR spectrum of a sample taken from the same solution showed no discernible disproportionation into **2** and (*R**,*R**)/(*R**,*S**)-**3** over this period. With 1,2-bis(diphenylphosphino)ethane (dppe), the displacement of (*S*)-(−)-**1** from (*R*,*R*P)-**5** was too slow for the observation of optical activity in the liberated fluorophosphine.

(c) Synthesis and Resolution of (±)-Methoxyphenylisopropylphosphine ((±)-9). The methoxyphosphine (±)-**9** was isolated as a colorless liquid in 67.8% yield by treatment of a solution of (±)-PClPh(*i*-Pr) in *n*-hexane with an excess of a mixture of triethylamine and methanol in the same solvent at −78 °C, followed by filtration, removal of the solvent from the filtrate, and distillation of the residue in vacuo.

(8) Fild, M.; Schmutzler, R. *J. Chem. Soc. A* **1970**, 2359. Stelzer, O.; Schmutzler, R. *Inorg. Synth.* **1978**, *18*, 173.
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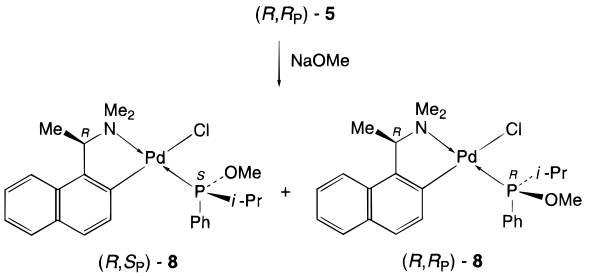
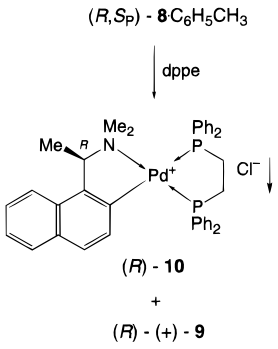
(10) Martin, J. W. L.; Stephens, F. S.; Weerasuria, K. D. V.; Wild, S. B. *J. Am. Chem. Soc.* **1988**, *110*, 4346.
(11) For clarity the heteroatom is specified in the Cahn−Ingold−Prelog (CIP)[12] descriptors of compounds containing two or more different chiratopic atoms.
(12) Cahn, R. S.; Ingold, C.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 385.
(13) Turner, E. E.; Harris, M. M. *Q. Rev. Chem. Soc.* **1947**, *1*, 299.
(14) The apparent inversion that takes place on liberation of the phosphine is a consequence of the CIP rules.[12]
(15) Roberts, N. K.; Wild, S. B. *J. Am. Chem. Soc.* **1979**, *101*, 6254.

Scheme 3



Scheme 4



Reaction of 2 equiv (±)-**9** with (*R*)-**4**·CH_2Cl_2 in dichloromethane produced an equimolar mixture of the pair of diastereomeric complexes (*R*,R_P)-**8** and (*R*,S_P)-**8**, according to the intensities of the two singlets at δ_P 137.79 and 141.38 ppm in the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture. Removal of the solvent from the reaction mixture, followed by treatment of the residue with diethyl ether, concentration, and filtration, afforded a colorless solid and a pale yellow mother liquor. Recrystallization of the solid from dichloromethane−diethyl ether afforded the pure diastereomer having δ_P 141.38 ppm in 43% yield, whereas the pure diastereomer having δ_P 137.79 ppm was isolated from the mother liquor as the *1-toluene solvate* in 37% yield by removal of the solvent followed by four consecutive recrystallizations of the residue from hot toluene−*n*-hexane. The isomer having δ_P 141.38 ppm was identified as (*R*,R_P)-**8** by X-ray crystallography (see below); accordingly, the diastereomer having δ_P 137.79 ppm has the (*R*,S_P) configuration.

(d) Isolation of (*R*)-(+)- and (*S*)-(−)-9. The liberation of (*R*)-(+)-**9** from configurationally homogeneous (*R*,S_P)-**8**·$C_6H_5CH_3$ was effected by treatment of the complex in dichloromethane with 1,2-bis(diphenylphosphino)ethane (dppe) (Scheme 4). Optically active (*R*)-(+)-**9** was isolated as a colorless liquid in 58% yield with $[\alpha]_D^{20}$ +310 (*c* 0.47, CH_2Cl_2) by the addition of *n*-hexane, concentration of the mixture, filtration, removal of the solvent under reduced pressure, and recondensation of the residue at −78 °C and 7.5×10^{-6} mmHg. Treatment of a solution of the recondensed product in dichloromethane-d_2 with (*R*)-**4**·CH_2Cl_2 gave (*R*,S_P)-**8** and (*R*,R_P)-**8** in the ratio of (*R*,S_P)/(*R*,R_P) = 96/4, as determined by $^{31}P\{^1H\}$ NMR spectroscopy. Thus (*R*)-(+)-**9** was isolated in 92% ee. Similarly, (*S*)-(−)-**9** was liberated from (*R*,R_P)-**8** in 57% yield having $[\alpha]_D^{20}$ −317 (*c* 0.60, CH_2Cl_2) (96% ee).

The degree of racemization of (+)- and (−)-**9** during liberation, albeit small, was unexpected and the application of similar conditions to those used for the liberation of optically pure (*S*)-(−)-**1** did not lead to an improvement in the optical purity of the enantiomers of (±)-**9**. Once liberated, however, free (*R*)-(+)- and (*S*)-(−)-**9** were configurationally stable, as indicated by the invariance of the $^{31}P\{^1H\}$ NMR spectra of samples of the free phosphine in dichloromethane after 5 min, 1 d, and 2 d, when quenched with (*R*)-**4**·CH_2Cl_2.

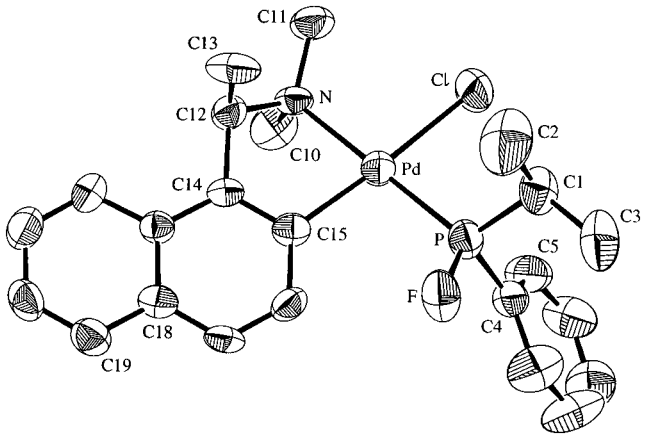


Figure 1. ORTEP view of (*R*,R_P)-**5** showing atom-labeling scheme of selected non-hydrogen atoms. Thermal ellipsoids enclose 50% probability levels.

In the ^1H NMR spectrum of (±)-**9** in 1,2-xylene-d_{10} at 128 °C the isopropyl *methyl* resonances were still observed as two doublets of doublets, which was implicit of chiratopic phosphorus at the elevated temperature. Therefore unimolecular inversion at phosphorus is slow on the NMR time scale under these conditions. If 128 °C is taken as the lower limit for the coalescence that would result from faster inversion, it can be calculated from the NMR data that the upper limit for the rate constant for intramolecular inversion at phosphorus in (±)-**9** at this temperature is 131.3 s^{-1}. Applying Eyring's equation to these data, the minimum value for the free energy of activation for inversion at phosphorus in (±)-**9** is 82.9 ± 0.5 kJ mol^{-1} at 128 °C.

(e) Reaction of (*R*,R_P)-5 with Sodium Methoxide. Due to rather rapid racemization in the free form, derivatizations of resolved (±)-**1** were carried out on the coordinated ligand. Thus, treatment of a benzene solution of (*R*,R_P)-**5** with an excess of freshly prepared sodium methoxide in methanol followed by removal of the solvents in vacuo, dissolution of the residue in dichloromethane, and flash chromatography of the solution on silica afforded the corresponding methoxyphosphine complex (*R*,S_P)/(*R*,R_P)-**8** with (*R*,S_P)/(*R*,R_P) = 5/1, as indicated by the intensities of the two singlets in the $^{31}P\{^1H\}$ NMR spectrum at δ_P 137.79 and 141.38 ppm (Scheme 3). (Treatment of (*R*,R_P)-**5** with an excess of an equimolar mixture of triethylamine and methanol, however, resulted in very slow conversion of the complex into (*R*,S_P)-**8** and (*R*,S_P)-**8**, together with considerable epimerization at phosphorus in the starting complex.) Thus, the substitution of fluoride in (*R*,R_P)-**5** by methoxide proceeds with predominant inversion at the fluorophosphine-*P* stereocenter.

(f) Crystal and Molecular Structures of (*R*,R_P)-5 and (*R*,R_P)-8. The molecular structures of (*R*,R_P)-**5** and (*R*,R_P)-**8** are depicted in Figures 1 and 2, respectively. Crystal data for the two complexes are given in Table 1. The most important bond distances and angles for (*R*,R_P)-**5** and (*R*,R_P)-**8** are given in Tables 2 and 3, respectively. Compound (*R*,R_P)-**5** is the first alkylarylfluorophosphine complex to be isolated, and the structure determination performed is the first to our knowledge on an organo(fluoro)phosphine palladium complex. The P−F distance in (*R*,R_P)-**5** is slightly longer than the P−F bonds in

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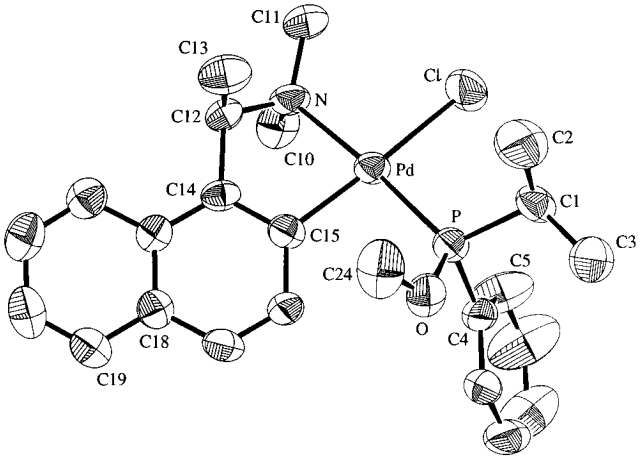

Figure 2. ORTEP view of (*R*,*R*P)-**8** showing atom-labeling scheme of selected non-hydrogen atoms. Thermal ellipsoids enclose 50% probability levels.

Table 1. Crystallographic Data for Compounds (*R*,*R*P)-**5** and (*R*,*R*P)-**8**

	(*R*,*R*P)-**5**	(*R*,*R*P)-**8**
formula	$C_{23}H_{28}ClFNPPd$	$C_{24}H_{31}ClNOPPd$
mol wt	510.31	522.34
cryst syst	orthorhombic	orthorhombic
space group	$P2_12_12_1$	$P2_12_12_1$
a, Å	9.967(2)	10.444(3)
b, Å	10.998(4)	12.146(3)
c, Å	21.324(3)	19.047(2)
V, Å^3	2337.3(7)	2416.2(4)
Z	4	4
cryst dimens, mm	0.20 × 0.16 × 0.13	0.32 × 0.27 × 0.20
d_{calcd}, g cm^{-3}	1.450	1.436
μ, cm^{-1}	9.93	9.60
X-ray radiation[a]	Mo Kα (λ = 0.710 69 Å)	Mo Kα (λ = 0.710 69 Å)
diffractometer	Rigaku AFC6S	Philips PW 1100/20
T, °C	25.0	23.0
no. of unique data	1923	2456
no. of data used[b]	1528	2096
no. of variables	253	262
R[c]	0.031	0.026
R_w[c]	0.020	0.029
GOF[c]	2.09	1.54
F(000)	1040	1072

[a] Graphite monochromator. [b] $I > 3\sigma(I)$. [c] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2\}^{1/2}$; $GOF = \{\sum w(|F_o| - |F_c|)^2/(\text{no. ref.} - \text{no. var.})\}^{1/2}$.

Table 2. Selected Bond Distances and Angles for (*R*,*R*P)-**5**

	Distances (Å)		
Pd−P	2.215(3)	Pd−Cl	2.397(2)
Pd−N	2.126(7)	Pd−C(15)	2.012(7)
P−C(1)	1.819(10)	P−C(4)	1.786(9)
P−F	1.589(5)	N−C(10)	1.50(1)
N−C(11)	1.474(10)	N−C(12)	1.49(1)
C(12)−C(14)	1.51(1)	C(14)−C(15)	1.38(1)
	Angles (deg)		
P−Pd−Cl	88.08(10)	Cl−Pd−N	92.9(2)
N−Pd−C(15)	81.0(3)	C(15)−Pd−P	98.1(3)
P−Pd−N	178.4(2)	Cl−Pd−C(15)	173.2(2)
Pd−P−C(1)	115.0(3)	Pd−P−C(4)	115.3(3)
Pd−P−F	117.1(2)	Pd−N−C(10)	108.8(6)
Pd−N−C(11)	115.9(6)	Pd−N−C(12)	106.2(5)
N−C(12)−C(14)	107.8(7)	C(12)−C(14)−C(15)	116.9(8)
C(14)−C(15)−Pd	113.7(6)		

similar diarylfluorophosphine complexes of platinum,[16] however, and very similar to the corresponding distances in *trans*-[$NiBr_2$-{$PF(t\text{-}Bu)_2$}$_2$],[17] where the P−F bonds are shortened by 0.04 Å upon complexation.[18] (*R*,*R*P)-**8** appears to be the first transition metal complex of an alkylalkoxyphenylphosphine to be characterized by X-ray structural analysis. The P−O distance in (*R*,*R*P)-**8** of 1.604(4) Å compares closely with the corresponding distance in other (alkoxyphosphine)palladium(II) complexes, and the Pd−P distance is also unexceptional.[19] In both (*R*,*R*P)-**5** and (*R*,*R*P)-**8**, the coordination geometry around the palladium is slightly distorted from square-planar with the phosphine ligand being situated trans to the dimethylamino group, which is typical for such complexes.[20] Characteristic of complexes containing the ortho-palladated 1-[(1-dimethylamino)ethyl]naphthalene fragment, the 5-membered metallacyclic rings in (*R*,*R*P)-**5** and (*R*,*R*P)-**8** each adopt the δ-envelope conformation, which forces the benzylic methyl group [C(13)] in each complex into the axial disposition due to the unfavorable steric interactions between the equatorial benzylic methyl group and H(22) of the naphthalene residue.[10,20,21] The interplanar angles between Pd−N−C(12) and C(12)−C(14)−C(15)−Pd are 37.52 and 39.59° for (*R*,*R*P)-**5** and (*R*,*R*P)-**8**, respectively.

Table 3. Selected Bond Distances and Angles for (*R*,*R*P)-**8**

	Distances (Å)		
Pd−P	2.227(1)	Pd−Cl	2.398(1)
Pd−N	2.155(4)	Pd−C(15)	1.997(4)
P−C(1)	1.820(6)	P−C(4)	1.816(6)
P−O	1.604(4)	O−C(24)	1.428(9)
N−C(10)	1.485(7)	N−C(11)	1.474(7)
N−C(12)	1.497(7)	C(12)−C(14)	1.504(7)
C(14)−C(15)	1.386(7)		
	Angles (deg)		
P−Pd−Cl	92.51(6)	Cl−Pd−N	92.2(1)
N−Pd−C(15)	80.4(2)	C(15)−Pd−P	95.0(1)
P−Pd−N	175.2(1)	Cl−Pd−C(15)	169.2(1)
Pd−P−C(1)	115.4(2)	Pd−P−C(4)	111.1(2)
Pd−P−O	120.1(2)	Pd−N−C(10)	106.6(3)
Pd−N−C(11)	116.8(3)	Pd−N−C(12)	104.9(3)
N−C(12)−C(14)	108.2(4)	C(12)−C(14)−C(15)	116.0(5)
C(14)−C(15)−Pd	114.8(4)		

Conclusion. Despite rapid equilibrium redox disproportionation in the neat state, (±)-PFPh(*i*-Pr) in benzene has considerable thermodynamic stability and can be readily resolved in diastereomeric palladium(II) complexes from which the optically pure (*S*)-(−) fluorophosphine can be liberated with retention of the configuration at phosphorus. The methoxyphosphine (±)-P(OMe)Ph(*i*-Pr) was resolved by a similar procedure, giving the configurationally stable (*R*)-(+) and (*S*)-(−) enantiomers in 92 and 96% ee, respectively. Substitution of fluoride by methoxide in the coordinated fluorophosphine proceeds with predominant inversion at phosphorus.

Experimental Section

Manipulations involving air-sensitive compounds were performed under a nitrogen atmosphere with use of the Schlenk technique. Diethyl ether, *n*-hexane, and toluene were freshly distilled from sodium

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benzophenone ketyl and dichloromethane from calcium hydride, respectively, and stored under nitrogen. (±)-Chlorophenylisopropylphosphine,[9] resolving agent (*R*)-**4**·CH_2Cl_2,[10] and (*R**,*S**)-1,2-C_6H_4(PMePh)$_2$ (**6**)[15] were prepared according to published procedures.

^{1}H, ^{31}P and ^{19}F NMR spectra were recorded in the solvents specified at 23 °C on a Varian VXR 300S spectrometer operating at 299.94, 121.42, and 282.20 MHz, respectively. ^{13}C{^{1}H} NMR spectra were recorded in the solvents specified at 23 °C on a Varian XL 200E or VXR 300S spectrometer operating at 50.31 and 75.43 MHz, respectively. The NMR spectra were referenced to Me_4Si (^{1}H, ^{13}C), $CFCl_3$ (^{19}F), or external 85% aqueous H_3PO_4 (^{31}P) with downfield shifts being positive. Optical rotations were measured in a Perkin-Elmer Model 241 polarimeter in a 1-dm cell at 20 °C. Mass spectra were recorded on a VG Micromass 7070F double-focusing mass spectrometer. Fast atom bombardment (FAB) mass spectra were recorded on a VG Analytical ZAB-2SEQ mass spectrometer (ionization: 30 keV Cs^+ ions) in a matrix of 3-nitrobenzyl alcohol. Elemental analyses were carried out by staff within the Research School of Chemistry.

(±)-Fluorophenylisopropylphosphine (±)-1. A mixture of chlorophenylisopropylphosphine (11.75 g, 63.0 mmol) and sodium fluoride (14.36 g, 342.0 mmol) in sulfolane (120 mL) was heated with stirring at 140 °C for 80 min. The product, bp 93 °C (14 mmHg), was collected at −196 °C. Yield: 6.09 g (55%). ^{1}H NMR (CD_2Cl_2): δ 0.91 (ddd, ^3J(HP) = 15.6 Hz, ^3J(HH) = 6.9 Hz, ^4J(HF) = 1.2 Hz, 3 H, CH_3), 1.21 (ddd, ^3J(HP) = 13.5 Hz, ^3J(HH) = 6.9 Hz, ^4J(HF) = 1.2 Hz, 3 H, CH_3), 1.94−2.14 (m, 1 H, C*H*Me$_2$), 7.44−7.62 (m, 5 H, C_6H_5). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75,43 MHz): δ 15.30 (dd, ^2J(CP) = 19.2 Hz, ^3J(CF) = 5.5 Hz, CH_3), 16.85 (dd, ^2J(CP) 15.3 Hz, ^3J(CF) = 2.7 Hz, CH_3), 34.09 (dd, ^1J(CP) = 21.4 Hz, ^2J(CF) = 12.1 Hz, CH), 128.71 (dd, ^3J(CP) = 7.7 Hz, ^4J(CF) = 1.7 Hz, ArC-*m*), 129.64 (dd, ^2J(CP) = 23.1 Hz, ^3J(CF) = 8.2 Hz, ArC-*o*), 130.66 (s; ArC-*p*), 140.66 (dd, ^1J(CP) = 29.1 Hz, ^2J(CF) = 10.5 Hz, ArC-*ipso*). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 183.10 (d, ^1J(PF) = 855.3 Hz) (ca. 86%). ^{19}F NMR ($CDCl_3$): δ −208.44 (dd, ^1J(FP) = 857.5 Hz, ^3J(FH) = 13.7 Hz). A sample of (±)-**1** after 16 h at 25 °C had the following ^{31}P{^{1}H} NMR spectrum in CD_2Cl_2: δ −13.182 (td, $^1J(PF_{ax})$ = 849.8 Hz, $^1J(PF_{eq})$ = 979.6 Hz) (**2**), −8.98 (s), −15.30 (s) [(*R**,*R**)/(*R**,*S**)-**3**].

[*SP*-4-4]-Chloro[(*R*)-1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C,N*][(*R*)-fluorophenylisopropylphosphine]palladium(II) ((*R*,R_P)-5). A solution of (*R*)-**4**·CH_2Cl_2 (7.67 g, 10.0 mmol) in dichloromethane (200 mL) was added over 5 min to a solution of (±)-**1** (4.07 g of 86% purity, 20.3 mmol) in the same solvent (100 mL). After the mixture was stirred for 18 h the solvent was removed from the reaction mixture in vacuo and the residue was dissolved in diethyl ether (400 mL). The solution was filtered and concentrated to ca. 60 mL, whereupon a colorless microcrystalline solid precipitated. The crude product was washed with 25 mL of cold diethyl ether and dried in vacuo. The mother liquor by concentration yielded additional product. Three recrystallizations of the combined crude material from diethyl ether gave the pure product as pale yellow prisms: mp 182 °C; yield 6.65 g (64%); $[\alpha]_D^{20}$ +35.2 (*c* 0.88, CH_2Cl_2). Anal. Calcd for $C_{23}H_{28}$ClFNPPd: C, 54.1; H, 5.5; Cl, 7.0; F, 3.7; N, 2.7. Found: C, 54.0; H, 5.6; Cl, 7.1; F, 3.5; N, 2.6. ^{1}H NMR ($CDCl_3$): δ 1.00 (dd, ^3J(HP) = 14.3 Hz, ^3J(HH) = 7.1 Hz, 3 H, CH*Me*$_2$), 1.68 (dd, ^3J(HP) = 20.3 Hz, ^3J(HH) = 7.4 Hz, 3 H, CH*Me*$_2$), 1.97 (d, ^3J(HH) = 6.3 Hz, 3 H, CH*Me*), 2.58 (d, ^4J(HP) = 1.8 Hz, 3 H, NMe), 2.90 (d, ^4J(HP) = 3.9 Hz, 3 H, NMe), 2.92−3.06 (m, 1 H, C*H*Me$_2$), 4.31 (d of quart., ^4J(HP) = 6.8 Hz, ^3J(HH) = 6.3 Hz, 1 H, C*H*Me), 7.20−8.20 (m, 11 H, ArH). ^{13}C{^{1}H} NMR (50.31 MHz, $CDCl_3$): δ 14.95 (dd, ^2J(CP) = 6.0 Hz, ^3J(CF) = 3.1 Hz, CH*Me*$_2$), 18.27 (d, ^2J(CP) = 4.2 Hz, CH*Me*$_2$), 23.64 (s; CH*Me*), 34.28 (dd, ^1J(CP) = 28.5 Hz, ^2J(CF) = 12.5 Hz, *C*HMe$_2$), 47.66 (d, ^3J(CP) = 2.7 Hz, NMe), 50.93 (d, ^3J(CP) = 3.3 Hz, NMe), 72.60 (d, ^3J(CP) = 3.5 Hz, *C*HMe), 123.09−148.94 (aromatics). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 185.14 (d, ^1J(PF) 927.8 Hz). ^{19}F NMR ($CDCl_3$): δ −185.08 (dd, ^1J(FP) 927.8 Hz, ^3J(FH) 24.4 Hz). MS (70 eV): 511.1 amu [M^+].

(*S*)-(−)$_{589}$-Fluorophenylisopropylphosphine ((*S*)-(−)-1). A solution of (*R**,*S**)-1,2-C_6H_4(PMePh)$_2$ (**6**) (67.5 mg, 209.4 μmol) in benzene (1 mL) was added to a stirred solution of (*R*,R_P)-**5** (106.8 mg, 209.3 μmol) in the same solvent (1 mL). The mixture was diluted immediately with benzene (4 mL) and centrifuged to give a colorless solution of (*S*)-(−)-**1**, $[\alpha]_D^{20}$ −210 (*c* 0.59, C_6H_6), and a sediment of (*R*,R_P,*S*,$_P$)/(*R*,*S*,$_P$,R_P)-**7**. Treatment of the solution with (*R*)-**4**·CH_2Cl_2 regenerated quantitatively (*R*,R_P)-**5**, as determined by ^{31}P{^{1}H} NMR spectroscopy.

(±)-Methoxyphenylisopropylphosphine ((±)-9). A mixture of methanol (4.69 g, 135.3 mmol) and triethylamine (13.25 g, 130.9 mmol) in *n*-hexane (150 mL) was added dropwise to a stirred solution of (±)-chlorophenylisopropylphosphine (18.13 g, 97.2 mmol) in the same solvent (200 mL) at −78 °C. At room temperature, the triethylammonium chloride was filtered off and washed with *n*-hexane (2 × 75 mL). Removal of the solvent from the filtrate under reduced pressure followed by distillation of the residue in vacuo afforded the desired product as a colorless liquid: bp 40 °C (0.2 mmHg); yield 11.96 g (67.6%). Anal. Calcd for $C_{10}H_{15}$OP: C, 65.9; H, 8.3; P, 17.0. Found: C, 65.5; H, 8.5; P, 16.7. ^{1}H NMR (C_6D_6): δ 0.87 (dd, ^3J(HP) = 15.0 Hz, ^3J(HH) = 7.5 Hz, 3 H, CH*Me*$_2$), 1.11 (dd, ^3J(HP) = 13.5 Hz, ^3J(HH) = 7.2 Hz, 3 H, CH*Me*$_2$), 1.79 (d of sept., ^3J(HH) = 7.2 Hz, ^2J(HP) = 0.6 Hz, 1 H, C*H*Me$_2$), 3.35 (d, ^3J(HP) = 13.2 Hz, 3 H, OMe), 7.08−7.60 (m, 5 H, ArH). ^{13}C{^{1}H} NMR (C_6D_6, 75.43 MHz): δ 16.48 (d, ^2J(CP) = 17.6 Hz, CH*Me*$_2$), 17.34 (d, ^2J(CP) = 14.3 Hz, CH*Me*$_2$), 32.73 (d, ^1J(CP) = 12.1 Hz, C*H*Me$_2$), 57.01 (d, ^2J(CP) = 19.8 Hz, OMe), 128.30 (d, ^3J(CP) = 6.6 Hz, ArC-*m*), 129.30 (s, ArC-*p*), 130.21 (d, ^2J(CP) = 20.8 Hz, ArC-*o*), 141.83 (d, ^1J(CP) = 27.4 Hz, ArC-*ipso*). ^{31}P{^{1}H} NMR (C_6D_6): δ 133.28 (s). MS: *m*/*e* 182.1 amu [M^+].

[*SP*-4-4]-Chloro[(*R*)-1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C,N*][(*R*)-methoxyphenylisopropylphosphine]palladium(II) and [*SP*-4-4]-Chloro[(*R*)-1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C,N*]-[(*S*)-methoxyphenylisopropylphosphine]palladium(II)−1-Toluene ((*R*,R_P)-8 and (*R*,S_P)-8·$C_6H_5CH_3$). A solution of (±)-**9** (4.89 g, 26.8 mmol) in dichloromethane (100 mL) was added to a solution of (*R*)-**4**·CH_2Cl_2 (10.01 g, 13.1 mmol) in the same solvent (350 mL). After stirring of the mixture at room temperature for 1 h, the solvent was removed in vacuo. Treatment of the residue with diethyl ether (300 mL) and concentration of the mixture to ca. 60 mL, afforded a colorless solid, which was separated, washed with diethyl ether (3 × 25 mL), and dried in vacuo. (The mother liquor was reserved for the subsequent isolation of the (*R*,S_P) diastereomer.) The solid was dissolved in dichloromethane (27 mL), and diethyl ether (100 mL) was added as a top layer. After 8 h, additional diethyl ether (100 mL) was added, and the mixture was stored over night at room temperature. Crystalline, pale yellow (*R*,R_P)-**8** deposited, which was separated and washed with diethyl ether and dried in vacuo: mp 231 °C dec; yield 5.87 g (43%); $[\alpha]_D^{20}$ −33.8 (*c* 1.00, CH_2Cl_2). Anal. Calcd for $C_{24}H_{31}$ClNOPPd: C, 55.2; H, 6.0; Cl, 6.8; N, 2.7. Found: C, 55.2; H, 6.3; Cl, 6.9; N, 2.7. ^{1}H NMR (CD_2Cl_2): δ 0.87 (dd, ^3J(HP) = 14.4 Hz, ^3J(HH) = 7.5 Hz, 3 H, CH*Me*$_2$), 1.60 (dd, ^3J(HP) = 18.6 Hz, ^3J(HH) = 9.0 Hz, 3 H, CH*Me*$_2$), 1.97 (d, ^3J(HH) = 6.3 Hz, 3 H, CH*Me*), 2.54 (d, ^4J(HP) = 1.8 Hz, 3 H, NCH_3), 2.81 (septet, ^3J(HH) = 7.2 Hz, 1 H, C*H*Me$_2$), 2.89 (d, ^4J(HP) = 3.6 Hz, 3 H, NMe), 3.44 (d, ^3J(HP) = 12.0 Hz, 3 H, OMe), 4.32 (d of quart., ^3J(HH) = ^4J(HP) = 6.0 Hz, 1 H, C*H*Me), 7.10−8.18 (m, 11 H, ArH). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75.43 MHz): δ 15.45 (d, ^2J(CP) = 4.4 Hz, CH*Me*$_2$), 19.58 (d, ^2J(CP) = 3.3 Hz, CH*Me*$_2$), 23.70 (s, *C*HMe), 35.13 (d, ^1J(CP) = 28.6 Hz, *C*HMe$_2$), 47.72 (s, NMe), 50.58 (d, ^3J(CP) = 3.2 Hz, NMe), 58.71 (s, OMe), 72.62 (d, ^3J(CP) = 2.2 Hz, *C*HMe), 123.53−149.99 (ArC). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 141.38 (s). FAB-MS: *m*/*e* 522.9 amu [M^+]. The solvent was removed from the original mother liquor in vacuo. Four recrystallizations of the residue from a hot mixture of toluene (15 mL) and *n*-hexane (100 mL) afforded (*R*,S_P)-**8**·$C_6H_5CH_3$ as pale yellow needles, which were washed with *n*-hexane and dried in vacuo: mp 89 °C; yield 5.90 g (37%); $[\alpha]_D^{20}$ −67.7 (*c* 1.00, CH_2Cl_2). Anal. Calcd for $C_{31}H_{39}$ClNOPPd: C, 60.6; H, 6.4; Cl, 5.8; N, 2.3. Found: C, 60.4; H, 6.6; Cl, 5.5; N, 2.1. ^{1}H NMR (CD_2Cl_2): δ 0.92 (dd, ^3J(HP) = 13.2 Hz, ^3J(HH) = 6.9 Hz, 3 H, CH*Me*$_2$), 1.14 (dd, ^3J(HP) = 20.7 Hz, ^3J(HH) = 7.2 Hz, 3 H, CH*Me*$_2$), 1.98 (d, ^3J(HH) = 6.3 Hz, 3 H, CH*Me*), 2.33 (s, 3 H, Ph*Me*), 2.58 (d, ^4J(HP) = 2.1 Hz, 3 H, NMe), 2.91 (d, ^4J(HP) = 3.6 Hz, 3 H, NMe), 3.34 (d of sept., ^2J(HP) = 10.5 Hz, ^3J(HH) = 6.9 Hz, 1 H, C*H*Me$_2$), 4.05 (d, ^3J(HP) = 13.5 Hz, 3 H, OMe), 4.32 (d of quart., ^3J(HH) = ^4J(HP) = 6.2 Hz, 1 H, C*H*Me), 6.82−7.74 (m, 11 H, ArH). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75.43 MHz): δ 15.29 (d, ^2J(CP) = 5.5 Hz, CH*Me*$_2$), 16.54 (d, ^2J(CP) = 7.7 Hz, CH*Me*$_2$), 21.49 (s, Ph*Me*), 23.88 (s, *C*HMe), 30.10 (d, ^1J(CP) = 29.6 Hz, *C*HMe$_2$), 47.81 (d, ^3J(CP)

= 2.2 Hz NMe), 50.48 (d, ^3J(CP) = 3.3 Hz, NMe), 57.73 (s, OCH_3), 72.60 (d, ^3J(CP) = 3.3 Hz, *C*HMe), 123.55−151.13 (ArC). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 137.79 (s). FAB-MS: *m/e* 523.1 amu [M^+].

(*R*)-(+)$_{589}$-Methoxyphenylisopropylphosphine ((*R*)-(+)-9). A solution of (*R*,S_P)-**8**·$C_6H_5CH_3$ (4.81 g, 7.8 mmol) in dichloromethane (35 mL) was added dropwise at room temperature to a stirred solution of dppe (3.43 g, 8.6 mmol) in the same solvent (40 mL). After 2 h, *n*-hexane (100 mL) was added and the reaction mixture was concentrated to ca. 50 mL under reduced pressure. The mixture was filtered and the solid was washed with *n*-hexane (3 × 10 mL). Removal of solvent from the filtrate, followed by recondensation of the residue into a trap at −78 °C at 7.5 × 10^{-6} mmHg, afforded (*R*)-(+)-**9** as a colorless liquid: yield 0.82 g (57.5%); $[\alpha]_D^{20}$ +310 (*c* 0.47, CH_2Cl_2) (92% ee). Anal. Calcd for $C_{10}H_{15}OP$: C, 65.9; H, 8.3. Found: C, 66.3; H, 8.7. ^1H and $^{31}P\{^1H\}$ NMR: identical with those for (±)-**9**. Treatment of a solution of (*R*)-(+)-**9** in CD_2Cl_2 with (*R*)-**4**·CH_2Cl_2 afforded (*R*,S_P)-**8**/(*R*,R_P)-**8** = 96/4, as determined by $^{31}P\{^1H\}$ spectroscopy.

(*S*)-(−)$_{589}$-Methoxyphenylisopropylphosphine ((*S*)-(−)-9). The isolation of this enantiomer from (*R*,R_P)-**8** was carried out in the same manner as that described for the (*R*)-(+) enantiomer, but with use of (*R*,R_P)-**8** (3.65 g, 7.0 mmol) and dppe (3.43 g, 8.6 mmol): yield 0.73 g (57.3%); $[\alpha]_D^{20}$ −317 (*c* 0.60, CH_2Cl_2) (96% ee). Anal. Calcd for $C_{10}H_{15}OP$: C, 65.9; H, 8.3. Found: C, 65.8; H, 8.6. ^1H and $^{31}P\{^1H\}$ NMR: identical with those for (±)-**9**. Treatment of a solution of this product in CD_2Cl_2 with (*R*)-**4**·CH_2Cl_2 afforded a mixture of (*R*,R_P)-**8**/(*R*,S_P)-**8** = 98/2, as determined by $^{31}P\{^1H\}$ spectroscopy.

Treatment of (*R*,R_P)-5 with Sodium Methoxide. A solution of sodium methoxide (71 mg, 1.3 mmol) in methanol (5 mL) was added dropwise to a stirred solution of (*R*,R_P)-**5** (290 mg, 0.6 mmol) in benzene (10 mL). The solvent was removed from the mixture. Flash chromatography of the residue on silica with dichloromethane, followed by removal of the solvent from the eluate under reduced pressure, afforded a pale yellow solid. The $^{31}P\{^1H\}$ NMR spectrum of the solid in CD_2Cl_2 indicated (*R*,S_P)-**8**/(*R*,R_P)-**8** = 5/1.

Crystal Structure Analyses. Crystal data for (*R*,R_P)-**5** and (*R*,R_P)-**8** are given in Table 1. For (*R*,R_P)-**5** the data set was collected using ω scans of (1.40 + 0.34 tan θ)° with a scan speed of 2.0° min^{-1}. For (*R*,R_P)-**8** the data set was collected using $\omega-2\theta$ scans of (1.00 + 0.35 tan θ)° with a scan speed of 2.0° min^{-1} in ω. In both cases stationary background counts were recorded on each side of every reflection. The intensities of three representative reflections were measured periodically. Whereas no significant decrease in intensity during data collection was observed for (*R*,R_P)-**5**, a decay correction of 2% was applied for (*R*,R_P)-**8**. Data were also corrected for absorption (transmission ranges: 0.86−0.91 for (*R*,R_P)-**5** and 0.782−0.841 for (*R*,R_P)-**8**) and for Lorentz and polarization effects. The structures were solved by heavy atom Patterson methods and expanded using Fourier techniques.[22] The hydrogen atoms were included in calculated positions (r_{C-H} = 0.95 Å, with methyl hydrogen atoms being staggered with respect to adjacent groups) and not refined. The absolute configurations were assigned on the basis of the known configuration of the (*R*)-1-[1-(dimethylamino)ethyl]naphthalene[10] precursor and by analysis of pairs of Friedel opposites. The maximum and minimum peaks in the final difference Fourier map corresponded to +0.37 and −0.46 e $Å^{-3}$ for (*R*,R_P)-**5** and to +0.27 and −0.33 e $Å^{-3}$ for (*R*,R_P)-**8**. All calculations for (*R*,R_P)-**5** were performed using teXsan.[23] For (*R*,R_P)-**8**, however, data reduction was performed using Xtal[24] and for the refinement teXsan[23] was employed. Atomic scattering factors for neutral atoms were taken from ref 25, and real and imaginary dispersion terms were taken from ref 26. Selected interatomic distances and angles (*R*,R_P)-**5** and (*R*,R_P)-**8** are given in Tables 2 and 3, respectively.

Supporting Information Available: For (*R*,R_P)-**5** and (*R*,R_P)-**8**, tables of bond distances and angles, atomic coordinates and equivalent isotropic displacement parameters for non-hydrogen atoms, thermal parameters for non-hydrogen atoms, calculated hydrogen atom parameters, least-squares planes, and selected torsion angles and ORTEP diagrams showing complete numbering of non-hydrogen atoms. (36 pages). Ordering information is given in every current masthead page.

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