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Articles

Intramolecular Dehydrofluorinative Coupling of the Asymmetric Diphosphine $Ph_2PCH_2CH_2PPh(C_5F_4N\text{-}4)$ and Pentamethylcyclopentadienyl Ligands in a Rhodium Complex

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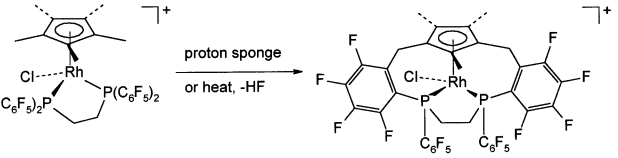
The tetrafluoropyridyl-substituted diphosphine $Ph_2PCH_2CH_2PPh(C_5F_4N\text{-}4)$ (**1**) has been prepared in three steps from dppe. Comparison of the spectroscopic properties between *trans*-$[RhCl(CO)\{PPh_2(C_5F_4N\text{-}4)\}_2]$ and analogous complexes of other fluorinated triaryl phosphines reveals the lower basicity of tetrafluoropyridylphosphines relative to pentafluorophenylphosphines. The reaction between $[Cp^*RhCl(\mu\text{-}Cl)]_2$ and **1** in the presence of $[BF_4^-]$ yielded racemic diastereoisomers of [Cp*RhCl(**1**)][BF_4]. In the $S_{Rh}R_P$ and $R_{Rh}S_P$ pair of enantiomers the Cp* and tetrafluoropyridyl groups have a *cis* disposition about the Rh−P bond, and in the $S_{Rh}S_P$ and $R_{Rh}R_P$ pair the groups are *trans*. In situ NMR experiments reveal that the *cis* pair, in which the Cp* and tetrafluoropyridyl groups are close, underwent rapid dehydrofluorinative C−C coupling to give the respective enantiomers of $[\{\eta^5,\kappa P,\kappa P\text{-}C_5Me_4CH_2\text{-}2\text{-}C_5F_3N\text{-}4\text{-}PPhCH_2\text{-}CH_2PPh_2\}RhCl][BF_4]$ (**6**·[BF_4]). The *trans* pair did not undergo coupling, but isomerized to the *cis* pair on heating in ethanol. The reaction between $[Cp^*RhCl(\mu\text{-}Cl)]_2$ and **1** in refluxing benzene afforded **6**·[BF_4] in 64% yield after anion metathesis. The structures of $OPPh_2(C_5F_4N\text{-}4)$, the *cis* isomer of [Cp*RhCl(**1**)][BF_4], and one enantiomer of **6**·[BF_4], which crystallizes as a conglomerate, have been determined by single-crystal X-ray diffraction.

Introduction

We have been developing intramolecular dehydrofluorinative C−C coupling as a convenient route to complexes of trifunctional hybrid $\eta^5,\kappa P,\kappa P$-cyclopentadienyl-diphosphine ligands.[1−3] To date we have concentrated on $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$ (dfppe) as the diphosphine ligand, which yields products containing cyclic trifunctional ligands with two linkages between the cyclopentadienyl and phosphine moieties (Cp═PP ligands), such as $\eta^5,\kappa P,\kappa P\text{-}C_5Me_3\{CH_2\text{-}2\text{-}C_6F_4P(C_6F_5)CH_2\}_2\text{-}1,3$ (Scheme 1). The products obtained from chelating diphosphine ligands with only one bis(pentafluorophenyl)phosphine moiety will contain ligands with a single linkage between the cyclopentadienyl and phosphine moieties (Cp−PP ligands). A three-legged piano stool complex of one of these ligands would contain a stereogenic metal atom by virtue of the four different groups coordinated to the metal. Chiral-at-metal piano stool complexes $[(\eta^5\text{-}C_5R_5)MX(P_2)]^{n+}$ (R = H or Me, X = one-electron donor ligand, P_2 = diphosphine or related ligand) can serve as stoichiometric reagents or precursors to Lewis acid catalyts for stereoselective organic transformations.[4−6] However, these complexes suffer from the disadvantage that, under certain conditions, they undergo epimerization at the metal, with the loss of chiral information at the metal leading to a loss of stereoselectivity in reactions.[5−7] Coupling of the cyclopentadienyl and diphosphine ligands is expected to confer configurational stability on a complex. Mechanisms for inversion at the metal can be devised, but these are expected to involve

Scheme 1



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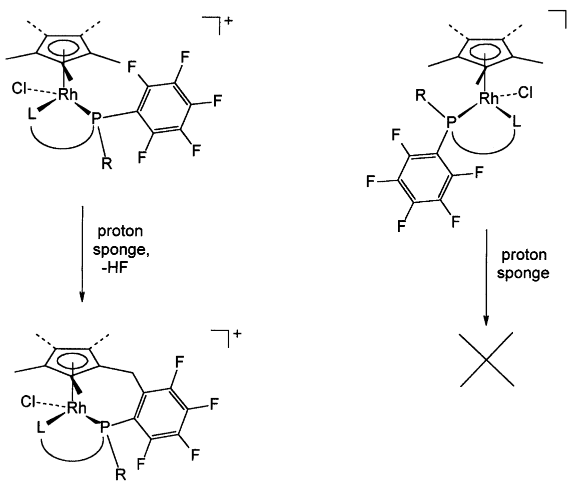
10.1021/om020874p CCC: $25.00

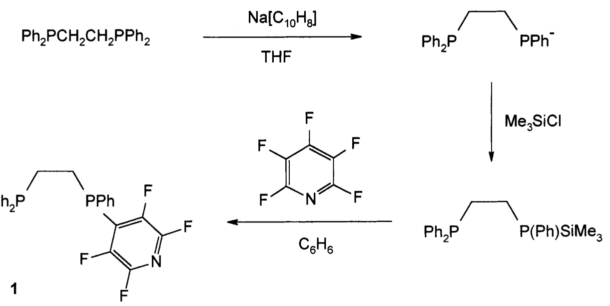
Scheme 2



processes with high activation energies: dissociation of both κ-ligating fragments of the chelating ligand, inversion at the phosphorus atom and recoordination, or dissociation of the cyclopentadienyl and phosphine, inversion at the phosphorus atom, and recoordination.[3] Although the asymmetric phosphine ligands $(C_6F_5)_2P-L$, where L is a ligating fragment, such as a thioether or a non-fluorinated phosphine moiety, would yield chiral-at-metal complexes, these would be formed as a racemic mixture. One method of controlling the stereochemistry at the metal center would be through the use of an enantiopure $(C_6F_5)RP-L$ ligand. Although initial coordination of this ligand would result in diastereoisomers, intramolecular dehydrofluorinative C−C coupling can give only one enantiomer of the product (Scheme 2).[8] If the L moiety is sufficiently labile, then the diastereoisomers can isomerize readily and the product may be formed in 100% yield; if the L group is nonlabile, then a yield dependent on the ratio of diastereoisomers would be expected. We are interested in synthesizing diphosphines of the type $R_2PCH_2CH_2PRAr_F$, where Ar_F is a suitable fluorinated aromatic group, and coupling these to Cp* ligands in order to generate configurationally stable, chiral-at-metal complexes of Cp−PP ligands.

Recently it has been reported that trimethylsilylphosphines react with polyfluoroaromatic compounds, producing phosphines bearing a polyfluoroaromatic substituent and trimethylsilyl fluoride.[9,10] The driving force for the reaction is the high enthalpy of Si−F bond formation. The reaction is particularly successful for pentafluoropyridine. Although our studies of dehydrofluorinative coupling have concentrated on pentafluorophenylphosphines, tetrafluoropyridyl-substituted phosphines should be no less amenable to intramolecular dehydrofluorinative C−C coupling, which is postulated to occur by nucleophilic attack at an *ortho* carbon of the pentafluorophenyl group.[1,2,11] For the coupling reaction involving $R_2P(C_5F_4N\text{-}4)$ nucleophilic attack will be at a carbon *meta* to the nitrogen. The rate of nucleophilic substitution of a *meta* fluorine of pentafluoropyridine is ca. 10 times more rapid than that of a fluorine atom of hexafluorobenzene.[12] Furthermore, since the nitrogen atom of pentafluoropyridine is virtually nonbasic,[13] it is likely that that of $R_2P(C_5F_4N\text{-}4)$ is similarly unreactive. Thus, the tetrafluoropyridyl-substituted diphosphine $Ph_2PCH_2CH_2PPh(C_5F_4N\text{-}4)$ (**1**) was envisaged to be ideal for our study because of the expected convenience of preparation by the reaction between $Ph_2PCH_2CH_2PPhSiMe_3$ and pentafluoropyridine and the enhanced rate of nucleophilic substitution of an *ortho* fluorine atom (*meta* to nitrogen) over dfppe.

Scheme 3



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Here we demonstrate the potential of intramolecular dehydrofluorinative carbon−carbon coupling to generate desirable configurationally stable, chiral-at-metal complexes of Cp−PP ligands through the use of an asymmetric diphosphine. The preparation of the tetrafluoropyridyl-substituted diphosphine $Ph_2PCH_2CH_2PPh(C_5F_4N\text{-}4)$ and its coupling to an η^5-pentamethylcyclopentadienyl ligand to yield a racemic Cp−PP rhodium complex are reported.

Results and Discussion

The three-step synthesis of diphosphine **1** is outlined in Scheme 3. A dark green solution of sodium naphthalide in THF was added to $Ph_2PCH_2CH_2PPh_2$ (dppe) and the mixture left at room temperature until a dark red solution containing $Na[Ph_2PCH_2CH_2PPh]$ and NaPh had developed by P−C(Ph) bond cleavage.[14] An excess of Me_3SiCl was added, causing the immediate disappearance of the color as $Ph_2PCH_2CH_2PPhSiMe_3$, $PhSiMe_3$, and NaCl were formed. Treatment of pentafluoropyridine with $Ph_2PCH_2CH_2PPhSiMe_3$ in benzene at room temperature gave diphosphine **1**, which was purified by column chromatography and obtained as a white solid in 50% yield. Unfortunately **1** was contaminated by a small amount of unreacted dppe (ca. 2%), from which it could not be separated. The phosphine $Ph_2P(C_5F_4N\text{-}4)$, **2**,[10] was also obtained, showing that $P-CH_2$ bond cleavage had also occurred in the reaction between dppe and sodium naphthalide, yielding Ph_2P^- then Ph_2PSiMe_3 on treatment with Me_3SiCl. Charac-

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terization of **1** was based on NMR spectroscopy and mass spectrometry. The resonance of the PPh_2 phosphorus atom occurs at δ −11.3, which is similar to that of δ −12.5 for dppe.[15] The resonance of the $PPh(C_5F_4N\text{-}4)$ phosphorus atom occurs at δ −20.3 and shows a coupling to two fluorine atoms of 19 Hz. The value of δ is similar to those of **2** (δ −18.9),[10] $PPh_2(C_6F_5)$ (δ −24.7),[16] and $PPh_2(C_6H_3F_2\text{-}2,6)$ (δ −27.7),[17] but the P−F coupling is roughly half that of these monophosphines (30, 38, and 42.2 Hz, respectively). The three-bond P−P coupling of 40 Hz is similar to that of 47.2 Hz found for $(C_6H_3F_2\text{-}2,6)_2PCH_2CH_2P(C_6H_3F_2\text{-}2,6)_2$.[18] Despite contamination by dppe, **1** was found to be amenable to further reaction.

The tetrafluoropyridyl group is more electron-withdrawing than pentafluorophenyl,[12] and so phosphines bearing the former might be expected to be less basic than those bearing the latter. To assess the electronic effect of the tetrafluoropyridyl substituent on phosphines, we sought to compare the spectroscopic properties of the rhodium complexes *trans*-$[RhCl(CO)(P)_2]$, where P = **2**, $Ph_2P(C_6F_5)$, and $Ph_2P(C_6H_3F_2\text{-}2,6)$. The value of the cone angle, θ, for $Ph_2P(C_6H_3F_2\text{-}2,6)$[17] has been shown to be almost identical to that of $Ph_2P(C_6F_5)$ (158°),[19] and the similarity of the respective P−C, PC−C, and C−F distances and C−C(P)−C and PC−C−F angles of $[Cp^*RhClL][BF_4]$ for L = **1** (vide infra), dfppe,[20] and $(C_6H_3F_2\text{–}2,6)_2PCH_2CH_2P(C_6H_3F_2\text{-}2,6)_2$[18] suggests a cone angle for **2** similar to that of $Ph_2P(C_6F_5)$ and $Ph_2P(C_6H_3F_2\text{-}2,6)$. Thus, these phosphines exert similar steric effects on the complex and differences between the values of $\nu(C{\equiv}O)$ can be ascribed to the differences in the electronic properties of the phosphines. Complex **3** was prepared in 80% yield by treatment of $[Rh(\mu\text{-}Cl)(CO)_2]_2$ with **2**. The $^{31}P\{^1H\}$ NMR spectrum exhibits a doublet at δ_P 27.8 with a coupling, $^1J_{RhP}$, of magnitude 110 Hz. These data are comparable with those of the analogous complexes of $Ph_2P(C_6F_5)$ (δ_P 24.0, $^1J_{RhP}$ = 133 Hz)[21] and $Ph_2P(C_6H_3F_2\text{-}2,6)$ (δ_P 18.7, $^1J_{RhP}$ = 133 Hz).[17] The IR spectrum of **3** exhibits $\nu(C{\equiv}O)$ at 1993 cm^{-1}. This is higher than those of the complexes of $PPh_2(C_6F_5)$ (1982 cm^{-1})[21] and $PPh_2(C_6H_3F_2\text{-}2,6)$ (1967 cm^{-1})[17] and is consistent with the poorer donor ability of **2** compared to these phosphines, which are poorer donors than PPh_3.[22] The data suggest that, as expected, the $PPh(C_5F_4N\text{-}4)$ functionality of diphosphine **1** is less basic than the PPh_2 functionality.

During this study we found that on exposure to air for several weeks phosphine **2**, a pale yellow oil, deposited colorless crystals of $OPPh_2(C_5F_4N\text{-}4)$, **4**.[10] Phosphine oxide **4** was characterized by mass spectrometry and NMR spectrometry. (Although **4** has been prepared previously, only the ^{31}P NMR data were reported.[10]) In addition the structure of **4** was determined by single-crystal X-ray diffraction. There are two molecules in the asymmetric unit; the structure of one is shown in Figure 1. Crystal and refinement data are given in Table 1, and selected bond distances and angles of **4** are given in Table 2. The two molecules of **4** possess identical bond distances and angles with the exception of the P=O distances, which differ by at least 0.01 Å, and the $O{=}P{-}C_5F_4N$ and $C(Ph){-}P{-}C_5F_4N$ angles. The mean P=O distance of 1.454(3) Å is significantly shorter than that of 1.474 Å reported for $OPPh_2(C_6F_5)$ (no esd's are given for this structure)[23] and that of 1.487(3) Å for $OPPh_3$.[24] The molecule of **4** with the longer P=O bond has a smaller $O{=}P{-}C_5F_4N$ angle by ca. 3°. The $C{-}P{-}C(C_5F_4N)$ angles differ slightly, with a range of ca. 3°, between the two molecules but are consistent with those of 105.1(2)° and 106.8(2)° for $SPMe_2(C_5F_4N)$.[9] The $P{-}C_5F_4N$ distance is the same as in $SPMe_2(C_5F_4N)$. The P−C(Ph) distances and the C−C distances of the phenyl rings are consistent with those of $OPPh_3$ (1.795(5)−1.804(5) and 1.341(9)−1.398(8) Å, respectively)[24] and $OPPh_2(C_6F_5)$ (means of 1.796 and 1.378 Å, respectively).[23] The two pairs of O−P−C(Ph) angles for each molecule are identical and consistent with those of $OPPh_3$ (111.8(2)−113.3(2)°). The C(Ph)−P−C(Ph) angles are consistent with the three identical C(Ph)−P−C(Ph) angles of $OPPh_3$ (106.4(2)°).[24]

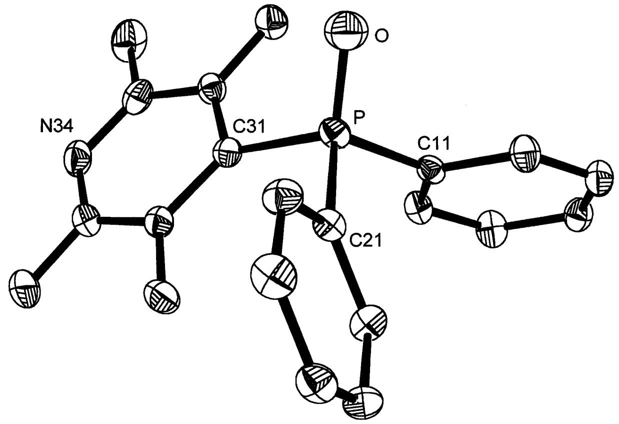

Figure 1. Structure of one of the independent molecules of $OPPh_2(C_6F_5N\text{-}4)$ (**4**) (molecule A). Thermal ellipsoids are at the 30% probability level. Hydrogen atoms are omitted for clarity.

Treatment of $[Cp^*RhCl(\mu\text{-}Cl)]_2$ with diphosphine **1** in the presence of sodium tetrafluoroborate yielded a ca. 1:1 mixture of racemic diastereoisomers of $[Cp^*RhCl(\mathbf{1})][BF_4]$, **5a**, and **5b** in ca. 50% yield (Scheme 4). In the $S_{Rh}R_P$ and $R_{Rh}S_P$ pair of enantiomers the Cp* and tetrafluoropyridyl groups have a *cis* disposition on the Rh−P bond of the $RhP_2(CH_2)_2$ ring (**5a**), and in the $S_{Rh}S_P$ and $R_{Rh}R_P$ pair the groups are *trans* (**5b**). Chelating diphosphines are not expected to be labile and interconversion of **5a** and **5b** is not expected to be rapid at room temperature, which is confirmed by studies of the reaction of the mixture with proton sponge (vide infra); thus the ratio of **5a** to **5b** is a consequence of the

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Table 1. Crystal Data and Structure Refinement for Compounds 4, 5b·0.5CH$_2$Cl$_2$, and 6·[BF$_4$]

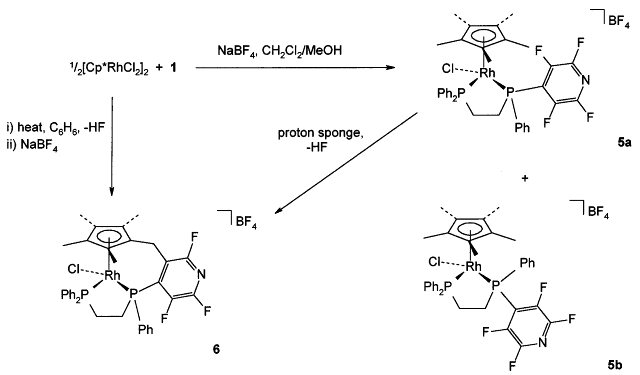
	4	**5b**·0.5CH$_2$Cl$_2$	**6**·[BF$_4$] [a]
formula	$C_{17}H_{10}F_4NOP$	$C_{35.5}H_{35}BCl_2F_8NP_2Rh$	$C_{35}H_{33}BClF_7P_2Rh$
fw	351.23	874.21	811.73
cryst dimens, mm	0.42 × 0.24 × 0.10	0.48 × 0.24 × 0.20	0.24 × 0.18 × 0.10
T, K	153(2)	153(2)	153(2)
cryst syst	monoclinic	monoclinic	orthorhombic
space group	*P*2(1)/*c*	*P*2(1)/*n*	$P2_12_12_1$
unit cell dimens			
a, Å	18.1475(15)	8.6204(7)	9.7712(10)
b, Å	9.5981(8)	23.2170(19)	14.9173(16)
c, Å	19.1255(15)	18.0923(15)	22.791(3)
β, deg	114.107(2)	102.1340(10)	90
U, Å^3	3040.8(7)	3540.1(5)	3321.9(6)
Z	8	4	4
calc density, g cm^{-3}	1.534	1.640	1.623
F(000)	1424	1764	1640
θ, deg	1.23−28.89	1.45−28.31	0.93−28.95
abs coeff, mm^{-1}	0.229	0.795	0.758
total data	7179	8049	7914
unique data, R_{int}	3258, 0.0865	7065, 0.0559	4312, 0.1347
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0517 wR2 = 0.1230	R1 = 0.0343 wR2 = 0.0841	R1 = 0.0588 wR2 = 0.1221
R indices (all data)	R1 = 0.1314 wR2 = 0.1566	R1 = 0.0401 wR2 = 0.0866	R1 = 0.1393 wR2 = 0.1648
GoF on F^2	0.859	1.047	0.943
largest diff peak and hole, e Å^{-3}	0.482, −0.467	0.547, −0.830	0.802, −1.711

[a] Flack parameter 0.03(5).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 4

	molecule A	molecule B
P=O	1.441(3)	1.467(2)
P−C(C_5F_4N)	1.832(3)	1.836(3)
P−C(Ph)	1.792(3), 1.798(3)	1.788(3), 1.798(3)
C−F (*ortho*-P)	1.343(4), 1.343(4)	1.344(4), 1.346(4)
C−F (*meta*-P)	1.336(4), 1.340(4)	1.339(4), 1.341(4)
C−N	1.293(4), 1.312(5)	1.301(4), 1.303(4)
C−C(C_5F_4N)	1.375(4)−1.394(4)	1.370(5)−1.393(4)
C−C(Ph)	1.367(5)−1.389(5)	1.371(5)−1.397(4)
O−P−C(C_5F_4N)	113.02(15)	110.27(14)
O−P−C(Ph)	112.19(15), 113.23(15)	112.67(15), 113.94(14)
C−P−C(C_5F_4N)	105.40(15), 106.37(15)	104.06(15), 108.46(15)
C(Ph)−P−C(Ph)	106.01(15)	106.96(15)
O−P−C−C(C_5F_4N)	45.9, −130.1	−48.9, 128.3
O−P−C−C(Ph)	51.0, −128.2	−44.1, 136.2
	31.8, −147.4	−27.0, 149.6

Scheme 4



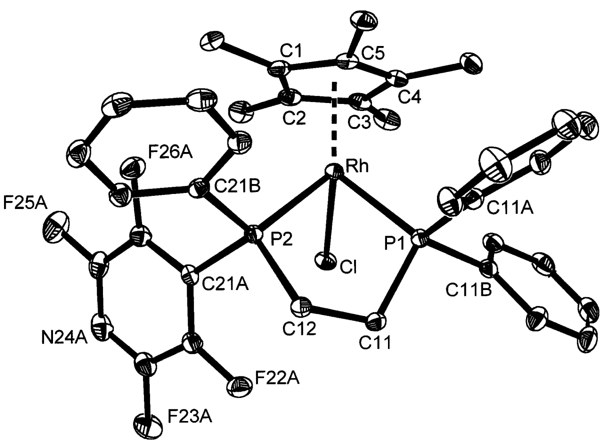


Figure 2. Structure of the $S_{Rh}S_P$ enantiomer of the cation of [Cp*RhCl{$Ph_2PCH_2CH_2PPh(C_5F_4N$-4)}][BF$_4$] (**5b**). Thermal ellipsoids are at the 30% probability level. Hydrogen atoms are omitted for clarity.

kinetics of the coordination of **1** to the [Cp*RhCl]$^+$ fragment. The PPh$_2$ phosphorus resonances of **5a** and **5b** occur at similar chemical shifts, δ 70.5 and 66.8, respectively, and both exhibit coupling to rhodium of ca. 130 Hz. The PPh(C_5F_4N-4) phosphorus resonances are at lower frequency, with that of **5a** (δ 58.2) lower than that of **5b** (δ 64.6). (The assignments of the resonances of **5a** and **5b** are based on the reaction of the mixture with proton sponge, vide infra.) The lower frequency of the *cis* isomer resonance is consistent with the spectra of *cis*- and *trans*-[Cp*RhCl{*κP*,*κS*-(C_6F_5)Ph-PC$_6$H$_4$SMe-2}][BF$_4$].[8] The two-bond P−P coupling differs considerably between the two isomers. The value for **5a** (11 Hz) is less than half that of **5b** (26 Hz). The ^{19}F NMR spectrum shows the expected four resonances, two at ca. δ −88 and two at ca. δ −130 assigned to two pairs of *meta*(P) and *ortho*(P) flourine atoms, respectively, in addition to those resonances assigned to [BF$_4^-$].

Although an attempt to separate **5a** and **5b** by fractional crystallization on the bulk scale was unsuccessful, a crystal of **5b** was isolated and the structure of this isomer determined by single-crystal X-ray diffraction. Both the $S_{Rh}S_P$ and $R_{Rh}R_P$ enantiomers were present in the unit cell. The structure of the $S_{Rh}S_P$ enantiomer is shown in Figure 2, crystal and refinement data are given in Table 1, and selected bond distances and angles are given in Table 3. The Cp†−Rh distance is consistent with those of similar [Cp*RhCl(P$_2$)]$^+$ salts.[6,18,20] The Rh−P distances of **5b** are identical to

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 5b

$Cp^{\dagger}-Rh$	1.867(2)	$Rh-P(1)$	2.3154(6)
$Rh-P(2)$	2.3165(6)	$Rh-Cl$	2.4009(5)
mean $C-CH_3$	1.489(4)	$C(11)-C(12)$	1.524(3)
$P(1)-C(11)$	1.834(2)	$P(2)-C(12)$	1.841(2)
$P(1)-C(11A)$	1.832(2)	$P(1)-C(11B)$	1.820(2)
$P(2)-C(21A)$	1.833(2)	$P(2)-C(21B)$	1.815(2)
$Cp^{\dagger}-Rh-Cl$	120.9(1)	$Cp^{\dagger}-Rh-P(1)$	131.4(1)
$Cp^{\dagger}-Rh-P(2)$	131.6(1)	$P(1)-Rh-P(2)$	84.54(2)
$P(1)-Rh-Cl$	86.46(2)	$P(2)-Rh-Cl$	86.952(19)
$Rh-P(1)-C(11)$	106.53(7)	$Rh-P(1)-C(11A)$	118.12(7)
$Rh-P(1)-C(11B)$	117.42(8)	$C(11)-P(1)-C(11A)$	107.78(11)
$C(11)-P(1)-C(11B)$	104.01(10)	$C(11A)-P(1)-C(11B)$	101.88(10)
$Rh-P(2)-C(12)$	109.65(7)	$Rh-P(2)-C(21A)$	110.87(7)
$Rh-P(2)-C(21B)$	119.83(7)	$C(12)-P(2)-C(21A)$	108.39(10)
$C(12)-P(2)-C(21B)$	101.83(10)	$C(21A)-P(2)-C(21B)$	105.50(10)

the shorter Rh−P distance of $[Cp^*RhCl\{Ph_2PCH_2CH(Me)PPh_2\}]^+$[6] and significantly shorter than those of $[Cp^*RhCl(dfppe)]^+$ and $[Cp^*RhCl\{(C_6H_3F_2\text{-}2,6)_2PCH_2CH_2P(C_6H_3F_2\text{-}2,6)_2\}]^+$ (2.329(1)−2.362(1) Å).[18,20] The shorter distance in **5b** is consistent with the lower steric demand of **1** in comparison to diphosphines in which fluorine atoms occupy all the *ortho* aryl positions. However, it is noted that the Rh−Cl distance of **5b** is longer than those of other $[Cp^*RhCl(P_2)]^+$ salts (2.385(1)−2.393(1) Å).[6,18,20] The P−Rh−P angle is identical to that of the non-fluorinated diphosphine cation $[Cp^*RhCl\{Ph_2PCH_2CH(Me)PPh_2\}]^+$ and slightly larger than those of the $[Cp^*RhCl(dfppe)]^+$ and $[Cp^*RhCl\{(C_6H_3F_2\text{-}2,6)_2PCH_2CH_2P(C_6H_3F_2\text{-}2,6)_2\}]^+$ (83.00(5)° and 84.05(8)°, respectively).[18,20] The Cp* ligand is distorted from C_5 symmetry about the $Cp^{\dagger}$−Rh axis. The C(1)−C(2) and C(3)−C(4) bonds (1.418(3) and 1.422(3) Å, respectively), which are approximately *trans* to P(1) and P(2), respectively, are significantly shorter than the three other internal C−C ring bonds (1.443(3)−1.446(4) Å). Further, the Rh−C(5) bond (2.184(2) Å), approximately *trans* to chloride, is ca. 0.03 Å shorter than Rh−C(2) and Rh−C(3) (2.225(2) and 2.231(2) Å, respectively), which are themselves significantly shorter than Rh−C(1) and Rh−C(4) (2.263(2) and 2.249(2) Å, respectively). The data are suggestive of slight ring slippage from η^5 to $\eta^2,\eta^2,\kappa C$ coordination of Cp*.

In situ NMR studies of the reaction between proton sponge and the mixture of **5a** and **5b** in $CDCl_3$ at room temperature revealed that **5a** underwent rapid dehydrofluorinative C−C coupling to give $[\{\eta^5,\kappa P,\kappa P\text{-}C_5Me_4CH_2\text{-}2\text{-}C_5F_3N\text{-}4\text{-}PPhCH_2CH_2PPh_2\}RhCl][BF_4]$, **6**·$[BF_4]$, whereas, as expected, **5b**, in which the tetrafluoropyridyl group is distant to the pentamethylcyclopentadienyl ligand, showed no reaction (Scheme 4). This result was confirmed by a preparative scale reaction which yielded a mixture of **5b** and **6**·$[BF_4]$. Attempts to separate **6**·$[BF_4]$ from this mixture were unsuccessful. Since the salt $[Cp^*RhCl\{Ph_2PCH_2CH(Me)PPh_2\}][BF_4]$ has been reported to undergo epimerization on heating in polar solvents,[6] and $[Cp^*RhCl(dfppe)][BF_4]$ is known to undergo dehydrofluorinative coupling on thermolysis in refluxing ethanol,[20] we reasoned that when heated in ethanol **5b** in the mixture would isomerize to **5a**, which would undergo dehydrofluorinative coupling to give **6**·$[BF_4]$, thereby providing a method to produce the product free of **5b**. The mixture of **5b** and **6**·$[BF_4]$ was heated in ethanol for 13 h, after which time the $^{31}P\{^1H\}$ and ^{19}F NMR spectrum indicated the presence of **5b** and **6**·$[BF_4]$ in a ratio of ca. 1:2 and a small amount of **5a**, but also the presence of small amounts of unidentified phosphorus- and fluorine-containing compounds. The data confirm the hypothesis that isomerization does occur in ethanol at elevated temperature, but that this method does not produce pure **6**·$[BF_4]$. The formation of impurities has been noted in the thermolysis of other $[(\eta^5\text{-}C_5M_4R)RhX(dfppe)]^+$ salts in ethanol.[25,26]

It has been noted that salts of $[\{\eta^5,\kappa P,\kappa P\text{-}C_5HMe_2\text{-}3,4\text{-}[CH_2\text{-}2\text{-}C_6F_4P(C_6F_5)CH_2]_2\text{-}1,2\}RhX]^+$ (X = Br or Cl) are precipitated from the reaction between $[(\eta^5\text{-}C_5Me_4H)RhX(\mu\text{-}X)]_2$ and dfppe in refluxing benzene.[25] Although the precipitates are a mixture of halide and tetrafluoroborate salts, they are free of contamination by starting materials and salts of the intermediate cations $[(\eta^5\text{-}C_5Me_4H)RhCl(dfppe)]^+$ and $[\{\eta^5,\kappa P,\kappa P\text{-}C_5HMe_3CH_2\text{-}2\text{-}C_6F_4P(C_6F_5)CH_2CH_2P(C_6F_5)_2\}RhX]^+$. Thus the reaction between $[Cp^*RhCl(\mu\text{-}Cl)]_2$ and **1** in refluxing benzene was attempted in the expectation that **6**·Cl might be obtained as a precipitate free from **5a** and **5b**. Heating a slurry of $[Cp^*RhCl(\mu\text{-}Cl)]_2$ and **1** in benzene under reflux for 9 h yielded a yellow precipitate and an orange solution, which were readily separated by filtration. NMR spectroscopy revealed the precipitate to comprise the cation $[\{\eta^5,\kappa P,\kappa P\text{-}C_5Me_4CH_2\text{-}2\text{-}C_5F_3N\text{-}4\text{-}PPhCH_2CH_2PPh_2\}\text{-}RhCl]^+$ as the only phosphorus- and hydrogen-containing species. Presumably the product was present predominantly as the chloride salt, **6**·Cl, but the ^{19}F NMR spectrum also shows the presence of small amounts of tetrafluoroborate (<2%) and hexafluorosilicate (<5%), which are formed by the reaction of the byproduct HF with the borosilicate glass vessel.[20] The salt **6**·Cl was readily converted to **6**·$[BF_4]$ by anion metathesis with $NaBF_4$ in methanol, giving an overall isolated yield of 64%. The $^{31}P\{^1H\}$ NMR spectrum of **6**·$[BF_4]$ exhibits two mutually coupled phosphorus resonances at δ 78.3 and 67.0 assigned to $PPh(C_5F_3N)CH_2C_5Me_4$ and PPh_2, respectively. The higher frequencies relative to the respective resonances of **5a** are consistent with the coupling of Cp* and phosphines in other complexes.[3,8,20] Both resonances exhibit coupling to rhodium of ca. 130 Hz, which is consistent with those of **5a**, as is the two-bond P−P coupling of 16 Hz. As expected the ^{19}F NMR spectrum exhibits three multiplet resonances (δ −72.39, −85.82, and −134.09) in addition to those of $[BF_4^-]$. The ^1H NMR spectrum contains two mutually coupled resonances at δ 3.98 and 3.24, the former of which is also coupled to phosphorus, which are assigned to the nonequivalent hydrogen atoms of the methylene bridge between the cyclopentadienyl ring and the trifluoropyridyl group. Three multiplet resonances at δ 3.47, 3.26, and 2.97, integrating for one, one, and two hydrogen atoms, respectively, are assigned to the ethylene backbone of the diphosphine moiety. The four methyl resonances occur as three doublets at δ 1.91, 1.20, and 0.23 and a doublet of doublets at δ 1.66. The chloride salt of **6** gave similar NMR spectra with small shifts of δ and changes in coupling constant. The differences in the

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(25) (a) Atherton, M. J.; Holloway, J. H.; Hope, E. G.; Saunders, G. C. *J. Organomet. Chem.* **1998**, *558*, 209. (b) Nieuwenhuyzen, M.; Saunders, G. C. *J. Organomet. Chem.* **2000**, *595*, 292.

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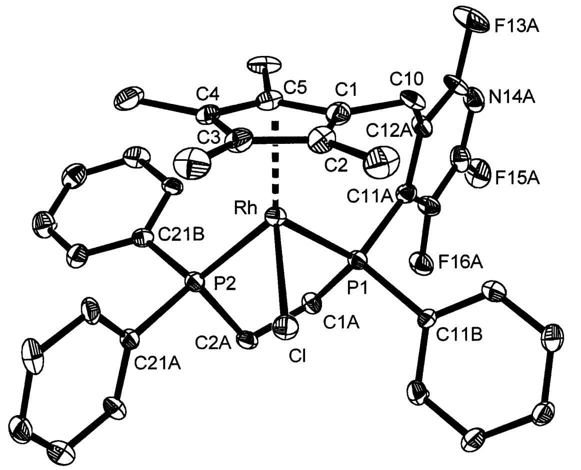

Figure 3. Structure of the $S_{Rh}R_P$ enantiomer of the cation of [{η^5,κP,κP-$C_5Me_4[CH_2$-2-C_5F_3N-4-$PPhCH_2CH_2PPh_2$}-RhCl][BF_4] (**6**·[BF_4]). Thermal ellipsoids are at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 6·[BF$_4$]

$Cp^{\dagger}$−Rh	1.851(9)	Rh−P(1)	2.272(2)
Rh−P(2)	2.312(2)	Rh−Cl	2.368(2)
mean C−CH_3	1.498(12)	C(1)−C(10)	1.509(12)
C(10)−C(12A)	1.518(13)	C(1A)−C(2A)	1.558(11)
P(1)−C(1A)	1.818(8)	P(2)−C(2A)	1.819(8)
P(1)−C(11A)	1.819(8)	P(1)−C(21A)	1.821(8)
P(2)−C(11B)	1.802(8)	P(2)−C(21B)	1.818(8)
$Cp^{\dagger}$−Rh−Cl	121.9(3)	$Cp^{\dagger}$−Rh−P(1)	126.0(3)
$Cp^{\dagger}$−Rh−P(2)	134.0(3)	P(1)−Rh−P(2)	86.12(8)
P(1)−Rh−Cl	90.17(8)	P(2)−Rh−Cl	84.85(8)
Rh−P(1)−C(1A)	108.7(3)	Rh−P(1)−C(11A)	113.4(3)
Rh−P(1)−C(11B)	118.5(3)	C(1A)−P(1)−C(11A)	105.8(4)
C(1A)−P(1)−C(11B)	107.8(4)	C(11A)−P(1)−C(11B)	101.9(4)
Rh−P(2)−C(2A)	105.8(3)	Rh−P(2)−C(21A)	115.7(3)
Rh−P(2)−C(21B)	120.0(3)	C(2A)−P(2)−C(21A)	105.2(4)
C(12)−P(2)−C(21B)	105.1(4)	C(21A)−P(2)−C(21B)	103.7(4)

NMR spectra between the two salts are not as great as have been observed in Cp═PP rhodium complexes.[3,18,20,25]

Salt **6**·[BF_4] crystallized as a conglomerate from acetone, and the structure of one enantiomer was determined by single-crystal X-ray diffraction (Figure 3). Crystal and refinement data are given in Table 1, and selected bond distances and angles are given in Table 4. The $Cp^{\dagger}$−Rh distance is shorter than in **5b** and is consistent with that of 1.842(2) Å found for the only other structurally characterized [(Cp−PP)RhX]$^+$ salt, [{η^5,κP,κP-$C_5Me_4CH_2$-2-$C_6F_4P(C_6F_5)CH_2CH_2P(C_6F_5)_2$}-RhCl][$BF_4$].[8] The Rh−$PPh(C_5F_3NCH_2C_5Me_4)$ distance is identical to that of the Rh−$P(C_6F_5)(C_5F_4CH_2C_5Me_4)$ distance of [{η^5,κP,κP-$C_5Me_4CH_2$-2-$C_6F_4P(C_6F_5)CH_2$-$CH_2P(C_6F_5)_2$}RhCl][BF_4] and consistent with those of double-linked [(Cp═PP)RhX]$^+$ salts (2.256(2)−2.283(3) Å),[26,27] The Rh−PPh_2 distance is similar to the Rh−$P(C_6F_5)_2$ distance of [{η^5,κP,κP-$C_5Me_4CH_2$-2-C_6F_4P-$(C_6F_5)CH_2CH_2P(C_6F_5)_2$}RhCl][$BF_4$] (2.3306(11) Å) and consistent with those of [Cp*RhCl(P_2)]$^+$ salts (2.314(2)−2.362(2) Å).[6,18,20] The $Cp^{\dagger}$−Rh−$PPh(C_5F_3NCH_2C_5Me_4)$ angle is identical to the $Cp^{\dagger}$−Rh−$P(C_6F_5)(C_5F_4CH_2C_5$-$Me_4)$ angle of [{η^5,κP,κP-$C_5Me_4CH_2$-2-$C_6F_4P(C_6F_5)CH_2$-$CH_2P(C_6F_5)_2$}RhCl][BF_4] and consistent with those of salts of [(Cp═PP)RhX]$^+$ (122.2(1)−126.3(1)°). The $Cp^{\dagger}$−Rh−PPh_2 angle is identical to the $Cp^{\dagger}$−Rh−$P(C_6F_5)_2$ of [{η^5,κP,κP-$C_5Me_4CH_2$-2-$C_6F_4P(C_6F_5)CH_2CH_2P(C_6F_5)_2$}-RhCl][$BF_4$] and consistent with those of salts of [Cp*RhCl(P_2)]$^+$ (130.98(5)−135.5(13)°). The Rh−Cl distance is considerably shorter than that of **5b** and is similar to that of [{η^5,κP,κP-$C_5Me_3[CH_2$-2-$C_6F_4P(C_6F_5)$-$CH_2]$-1,3}RhCl][BF_4] (2.380(3) Å).[27] The P−Rh−P angle is ca. 2° larger than that of **5b** and similar to those of [(Cp═PP)RhX]$^+$ and [(Cp−PP)RhCl]$^+$ salts (86.94(7)−87.9(1)°).[6,26,27] No distortion of the C_5 ring from C_5 symmetry about the $Cp^{\dagger}$−Rh axis is evident: with the exception of Rh−C(4) (2.261(8) Å) the Rh−C distances are the same within 3σ (2.198(8)−2.243(9) Å); likewise all five internal ring C−C distances are the same (1.420(12)−1.461(12) Å). Unfortunately the nature of the crystals did not permit manual separation of the enantiomers.

The red benzene filtrate obtained from the reaction between [Cp*RhCl(μ-Cl)]$_2$ and **1** yielded a red solid on evaporation of the solvent. The $^{31}P\{^1H\}$ NMR spectrum exhibited at least six resonances in the range δ 50−80 with couplings to rhodium of 120−160 Hz. The predominant of these are doublets at δ 79.5 (dm, $^1J_{RhP}$ = 147 Hz) and 66.3 (dd, $^1J_{RhP}$ = 134 Hz, $^2J_{PP}$ = 16 Hz), which are assigned to **6**·Cl. Other doublets are consistent with cations of formulation [Cp*RhCl(**1**)]$^+$ (the cations of **5a** and **5b**). The ^{19}F NMR spectrum is consistent with the presence of **6**·Cl and [Cp*RhCl(**1**)]$^+$, but also shows the presence of other fluorine-containing compounds as well as [SiF_6^{2-}] and [BF_4^-]. In addition the $^{31}P\{^1H\}$ spectrum exhibits a broad resonance between δ_P 27 and 40, and the ^{19}F NMR spectrum exhibits resonances at δ −89.85 and −123.87. These data are consistent with the neutral compound [$(Cp^*RhCl_2)_2$-{μ,κP,κP-$Ph_2PCH_2CH_2PPh(C_5F_4N$-4)}] (vide infra).

The reaction between [Cp*RhBr(μ-Br)]$_2$ and dfppe in benzene proceeded via the cation [Cp*RhBr(dfppe)]$^+$,[26] and it is presumed that the reaction between [Cp*RhCl(μ-Cl)]$_2$ and **1** in benzene proceeds via the chloride salts of the cations of **5a** and **5b**. From the synthesis of **5a** and **5b** it might be expected that the *cis* and *trans* isomers would be formed in ca. 1:1 ratio, although under thermodynamic control the *trans* isomer might predominate because of the greater steric crowding in the *cis* isomer. Assuming no isomerization of the cation of **5b** to that of **5a**, the maximum yield of **6**·[BF_4] would be 50%. The higher yield of **6**·[BF_4] obtained strongly suggests that epimerization of the chloride salt of **5b** to **5a** did occur. This is in contrast to the epimerization of [Cp*RhCl{$Ph_2PCH_2CH(Me)PPh_2$}][BF_4], which has been reported to occur only in polar solvents.[6] However, it is noted that the presence of chloride ions accelerated the rate of epimerization. A number of mechanisms for the isomerization can be proposed, involving either dissociation of one or both of the phosphine functionalities or chloride dissociation/coordination or coordination/dissociation.[8] To confirm the intermediacy of the cation **5a** and the isomerization of the cation of **5b** to that of **5a**, and to attempt to elucidate the mechanism for this, an NMR study of the reaction was undertaken.

The ^1H, ^{19}F, and $^{31}P\{^1H\}$ NMR spectra of a mixture [Cp*RhCl(μ-Cl)]$_2$ and **1** in a 1:2 ratio were recorded in

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C_6D_6. At room temperature a red solution and a red solid, presumably [Cp*RhCl(μ-Cl)]$_2$, which is sparingly soluble in benzene, were present. The $^{31}P\{^1H\}$ NMR spectrum contains resonances at δ 44.9 (dd) and −6.76 (dt), with a mutual coupling of 46 Hz. The former resonance also shows coupling to rhodium ($^1J_{RhP} = 144$ Hz) and the latter to two fluorine atoms ($^3J_{PF} = 20$ Hz). There is also a broad resonance or collection of resonances between δ 40 and 50. The ^{19}F NMR spectrum shows two sets of resonances with integrations in a 1:2 ratio: δ −90.70 and −124.18, both of which show slight broadening, and multiplets at δ −92.18 and −133.00. The ^1H NMR spectrum exhibits resonances that can be assigned to phenyl rings (δ 6.8−8.2) and the ethylene backbone (δ 2.0−3.6) of coordinated **1** and three doublet resonances at δ 1.11, 1.04, and 1.02 with couplings of ca. 3 Hz and integrations in a ratio of ca. 1:4:1 assigned to Cp* hydrogen atoms. Additionally a low-intensity singlet at δ 1.35, assigned to [Cp*RhCl(μ-Cl)]$_2$, is present. No change in the appearance of the mixture or the spectra was observed after 72 h at room temperature. The species responsible for these resonances were identified from the spectra of mixtures of varying ratios of [Cp*RhCl(μ-Cl)]$_2$ and **1** in $C_6D_6/CDCl_3$ (3:7), in which both reagents and all products are soluble. For a sample containing <1 equiv of **1** the ^1H NMR spectrum showed the presence of [Cp*RhCl(μ-Cl)]$_2$ (δ 1.73) and contained two doublets at δ 1.50 and 1.42 with couplings, $^4J_{PH}$, of 3.8 and 3.4 Hz, respectively, and integrations in a ratio of 1:1. The ^{19}F NMR contains two major resonances at δ −89.48 and −123.56, accounting for >90% of the total integration, and the $^{31}P\{^1H\}$ NMR spectrum exhibits a broad resonance or collection of resonances between δ 30 and 40. On cooling to −20 °C, the $^{31}P\{^1H\}$ NMR spectrum (recorded at 202.47 MHz) exhibits only two doublets of doublet resonances at δ 38.0 and 34.9 with couplings to rhodium, $^1J_{RhP}$, of 157 and 142 Hz, with a mutual coupling of 20 Hz. These data are similar to those of the compound [(Cp*RhCl$_2$)$_2$\{μ,κP,κP-Ph$_2$PCH$_2$CH(Me)PPh$_2$\}] (at −50 °C and 121.4 MHz: δ 38.3, $^1J_{RhP} = 145$ Hz, δ 30.5, $^1J_{RhP} = 143$ Hz, $^3J_{PP} = 18$ Hz).[6] It is argued that the fluxionality of this compound arises from hindered rotation about the Rh−PPh$_2$CH(Me) bond and rotation about the Rh−PPh$_2$CH$_2$ bond being slowed at low temperature. Different resonances were observed for [Cp*RhCl(μ-Cl)]$_2$ and **1** in a 1:2 ratio. The ^1H NMR spectrum shows a doublet at δ 0.99 with a coupling, $^4J_{PH}$, of 3.5 Hz, as well as resonances consistent with the ethylene and phenyl groups of coordinated **1**. The ^{19}F spectrum exhibits two multiplet resonances at δ −92.39 and −132.80. The ^{31}P NMR spectrum exhibits a doublet of doublets at δ 31.4 with a coupling to rhodium, $^1J_{RhP}$, of 140 Hz and a doublet of triplets at δ −20.0 with a coupling to fluorine, $^3J_{PF}$, of ca. 20 Hz with a mutual coupling of 45 Hz. These data are comparable to those of [Cp*RhCl$_2$\{κP-Ph$_2$PCH$_2$CH(Me)PPh$_2$\}] (δ 34.7, $^1J_{RhP} = 141$ Hz, δ −16.4, $^3J_{PP} = 25$ Hz).[6] Addition of [Cp*RhCl(μ-Cl)]$_2$ to this mixture leads to the appearance in the spectra of the resonances observed in the spectra of the mixture containing <1 equiv of **1**. These data are consistent with [(Cp*RhCl$_2$)$_2$\{μ,κP,κP-Ph$_2$PCH$_2$CH$_2$PPh(C$_5$F$_4$N-4)\}], **7**, and [Cp*RhCl$_2$\{κP-Ph$_2$PCH$_2$CH$_2$PPh(C$_5$F$_4$N-4)\}], **8**, formed from [Cp*RhCl(μ-Cl)]$_2$ and **1** in a 1:1 ratio and 1:2 ratio, respectively. The data also show that the tetrafluoropyridyl-substituted phosphine group is readily displaced by the more strongly donating non-fluorinated phosphine group, which is consistent with the lack of observation of the isomer of **8** [Cp*RhCl$_2$\{κP-(C$_5$F$_4$N-4)PhPCH$_2$CH$_2$PPh$_2$\}]. Thus an equilibrium between **7** and **8**, dependent on the relative proportions of [Cp*RhCl(μ-Cl)]$_2$ and **1**, is established rapidly. This was confirmed by NMR spectra after addition of more **1** to the mixture. The data also show that neither phosphine group of **1** is labile on the NMR time scale. The similarity of the NMR data with those of the mixture in C_6D_6, allowing for the effects of solvent on δ, strongly suggests that **7** and **8** are those present in the benzene solution at room temperature (in a 1:2 ratio). Over time the spectra of the mixture in $C_6D_6/CDCl_3$ developed resonances consistent with the cations of **5a** and **5b** in a ratio of ca. 1:1. The presence of these cations in a mixture of benzene and chloroform but not in benzene at room temperature is presumably a consequence of the greater polarity of chloroform. Addition of an excess of [Cp*RhCl(μ-Cl)]$_2$ to this mixture immediately increased the amount of **7** relative to **8**, but had no effect on the amounts of cations of **5a** and **5b**, even over several hours. Heating this solution at 60 °C for 9.5 h had little effect on the proportions of the cations of **5a** and **5b** relative to **7**. These observations show that neither phosphine group of **1** can be readily displaced from the cations [Cp*RhCl(**1**)]$^+$ up to 60 °C. The spectra also revealed that a small amount of **6**·Cl (<5%) had been formed under these conditions.

An NMR tube containing a mixture of [Cp*RhCl(μ-Cl)]$_2$ and **1** in a ca. 1:2 ratio in C_6D_6 with a small amount $CDCl_3$ added in an attempt to keep the intermediates and products in solution was heated at 70 °C, and at 2−3 h intervals the spectra were recorded (at 25 °C). The occurrence of reaction was evident after 2.5 h from the presence of resonances assigned to **6**·Cl in the $^{31}P\{^1H\}$ and ^{19}F NMR spectra. After 13 h, the solution was lighter in color and a small amount of yellow precipitate was present. The spectra showed the presence of **7**, **8**, the cations of **6** and **5b**, and the anions [BF$_4^-$] and [SiF$_6^{2-}$]. The resonances of **8** decreased in intensity with time until after 21.5 h they were no londer observed. The resonances of **7** were observed throughout the experiment. The reaction was continued for 45 h, at which time no changes in the spectra were observed and a significant amount of yellow precipitate was present. The spectra of the product mixture, obtained by removal of the solvent under reduced pressure, were recorded in $CDCl_3$, in which it was completely soluble, giving an orange-red solution. The $^{31}P\{^1H\}$ and ^1H NMR spectra indicated the presence of three major phosphorus- and fluorine-containing species: the cations of **6** and **5b**, in a ratio of ca. 3:1, and **7**. The lack of observation of resonances of the cation of **5a** does not preclude its intermediacy, since the intramolecular dehydrofluorinative coupling to give **6** may be too rapid for there to be a sufficient concentration of **5a** for observation by NMR. In support of this, [Cp*RhCl(dfppe)]$^+$ was not observed in the reaction between [Cp*RhCl(μ-Cl)]$_2$ and dfppe in benzene, but [Cp*RhBr(dfppe)]$^+$ was observed in the reaction between [Cp*RhBr(μ-Br)]$_2$ and dfppe, in which the dehydrofluorinative coupling is much slower.[26] Unfortunately the data are insufficient to aid the elucidation of the mechanism of the isomerization of the cation of **5b** to that of **5a**.

Conclusions

The asymmetric tetrafluoropyridyl-substituted diphosphine **1** can be conveniently prepared from dppe in moderate yield. Comparison of $\nu(C{\equiv}O)$ for the complexes *trans*-[RhCl(CO)P_2] between P = $PPh_2(C_5F_4N\text{-}4)$ (**2**) and P = $PPh_2(C_6F_5)$ and $PPh_2(C_6H_3F_2\text{-}2,6)$ indicates that the effect of the tetrafluoropyridyl group is to decrease the basicity of the phosphine. The tetrafluoropyridyl-substituted phosphine moiety of **1** is less basic than those of dppe. Diphosphine **1** can be linked to a Cp* ligand in a cationic rhodium(III) complex by intramolecular dehydrofluorinative carbon−carbon coupling to give a cationic complex of a Cp−PP ligand, **6**. The reaction is best carried out by treating [Cp*RhCl(μ-Cl)]$_2$ with **1** in refluxing benzene, since diastereoisomers, which are not readily separated, are formed by the reaction between [Cp*RhCl(μ-Cl)]$_2$ and **1** in the presence of [BF_4^-], and only one undergoes the coupling reaction on treatment with proton sponge. Although racemic **1** leads to racemic **6**, the reaction shows the potential of this methodology to provide a convenient route to nonracemic, configurationally stable, chiral-at-metal complexes from nonracemic chelating phosphines.

Experimental Section

General Considerations. [Cp*RhCl(μ-Cl)]$_2$ and dppe (Aldrich) were used as supplied. Pentafluoropyridine (Lancaster) was stored over $MgSO_4$. Me_3SiCl (Aldrich) was purified by distillation in vacuo and stored under dinitrogen over Na_2CO_3. The preparations of **1** and **2** were performed under dinitrogen using THF and benzene dried by distillation under dinitrogen from potassium and storage over molecular sieves (4A). No precautions to exclude air or moisture were taken for the other preparations.

The ^{1}H, ^{19}F, and ^{31}P NMR spectra were recorded using Bruker DPX300 or DRX500 spectrometers. ^{1}H NMR spectra (300.01 or 500.13 MHz) were referenced internally using the residual protio solvent resonance relative to $SiMe_4$ (δ 0), ^{19}F (282.26 MHz) externally to $CFCl_3$ (δ 0), and ^{31}P (121.45 or 202.47 MHz) externally to 85% H_3PO_4 (δ 0). All chemical shifts are quoted in δ (ppm), using the high-frequency positive convention, and coupling constants in Hz. The IR spectrum was recorded on a Perkin-Elmer RX I Fourier transform spectrometer. EI and LSIMS mass spectra were recorded on a VG Autospec X series mass spectrometer. Elemental analyses were carried out by ASEP, The School of Chemistry, Queen's University Belfast.

$Ph_2PCH_2CH_2PPh(C_5F_4N)$ (1). Sodium naphthalide in THF (150 cm^3), prepared from naphthalene (1.64 g, 13.0 mmol), was added to dppe (2.00 g, 5.0 mol) and the solution left at room temperature for 72 h until a deep red solution had formed. Me_3SiCl (ca. 1.2 g, 13 mmol) was added, resulting in an immediate loss of color. The volatiles were removed under reduced pressure to give a pale yellow oil. Benzene (100 cm^3) was added and the extract filtered and added to pentafluoropyridine (ca. 0.85 g, 5 mmol). The reaction mixture was left at ambient temperature for 20 h, during which time the solution darkened. The solvent was removed under reduced pressure and the resulting oil chromatographed on deactivated neutral alumina (6% H_2O). Naphthalene was eluted with hexane, phosphine **2** with dichloromethane/hexane (1:9), and diphosphine **1** with dichloromethane/hexane (1:1). Recrystallization from methanol/dichloromethane gave **1** as a white solid. Yield: 1.19 g (51%). ^{1}H ($CDCl_3$): δ 7.52 (m, 2H, C_6H_5), 7.39 (m, 13H, C_6H_5), 2.50 (m, 2H, CH_2), 2.11 (m, 2H, CH_2). ^{19}F ($CDCl_3$): δ −91.87 (m, 2F, F_{meta-P}), −132.96 (m, 2F, $F_{ortho-P}$). $^{31}P\{^{1}H\}$ ($CDCl_3$): δ −11.3 (d, $^{3}J_{PP}$ = 40 Hz), −20.25 (dt, $^{3}J_{PP}$ = 40 Hz, $^{3}J_{PF}$ = 19 Hz). EIMS, m/z (rel int): 471 M^+ (24), 393 $[M - C_6H_5 - H]^+$ (47), 335 $[M - 2C_6H_5 + F]^+$(21), 183 $[H_2PC_5F_4N]^+$ (77), 151 $[C_5F_4N + H]^+$ (70). HRMS: calcd for $C_{25}H_{19}F_4NP_2$, 471.09289; found M^+, 471.09272.

$PPh_2(C_5F_4N\text{-}4)$ (2). Phosphine **2** was prepared as described.[10] ^{1}H ($CDCl_3$): δ 7.43 (m, 10H, C_6H_5). ^{19}F ($CDCl_3$): δ −91.46 (m, 2F, F_{meta-P}), −131.40 (m, 2F, $F_{ortho-P}$). $^{31}P\{^{1}H\}$ ($CDCl_3$): δ −18.9 (t, $^{3}J_{PF}$ = 30 Hz). EIMS, m/z (rel int): 335 M^+ (96), 183 $[H_2PC_5F_4N]^+$ (99). HRMS: calcd for $C_{17}H_{10}F_4NP$, 335.04870; found M^+, 335.04936.

***trans*-[RhCl(CO){$PPh_2(C_5F_4N\text{-}4)$}$_2$] (3).** A slurry of [Rh(μ-Cl)(CO)$_2$]$_2$ (0.036 g, 0.093 mmol) and **2** (0.139 g, 0.41 mmol) in dichloromethane (20 cm^3) was stirred for 3 h, after which time the solvent was removed by rotary evaporation and the resulting solid washed with hot hexane (50 cm^3) to afford **3** as a yellow solid. Yield: 0.127 g (82%). ^{1}H ($CDCl_3$): δ 6.8−7.9 (20H, m, C_6H_5). ^{19}F ($CDCl_3$): δ −90.22 (m, 2F, F_{meta-P}), −127.91 (m, 2F, $F_{ortho-P}$). $^{31}P\{^{1}H\}$ ($CDCl_3$): δ 27.8 (d, $^{1}J_{RhP}$ = 110 Hz). Anal. Calcd for $C_{35}H_{20}ClF_8N_2OP_2Rh$: C, 50.23; H, 2.41; N, 3.35. Found: C, 50.19; H, 2.44; N, 3.11. IR (KBr, cm^{-1}): $\nu(C{\equiv}O)$ 1993 (s).

$OPPh_2(C_5F_4N\text{-}4)$ (4). Crystals of **4** were deposited from **2** on exposure to air over several weeks. ^{1}H ($CDCl_3$): δ 7.72 (m, 4H), 7.64 (m, 2H), 7.55 (m, 4H). ^{19}F ($CDCl_3$): δ −88.84 (m, 2F, F_{meta-P}), −131.00 (m, 2F, $F_{ortho-P}$). $^{31}P\{^{1}H\}$ ($CDCl_3$): δ 21.8 (s).[8] HRMS: calcd for $C_{17}H_{10}F_4NOP$, 351.04362; found M^+, 351.04481.

[Cp*RhCl{$Ph_2PCH_2CH_2PPh(C_5F_4N)$}][$BF_4$] (5). A slurry of [Cp*RhCl(μ-Cl)]$_2$ (0.069 g, 0.11 mmol), **1** (0.101 g, 0.23 mmol), and $NaBF_4$ (ca. 0.44 g, 4 mmol) in dichloromethane (20 cm^3) and methanol (40 cm^3) was stirred for 1 h, after which time the solvent was removed by rotary evaporation. The product was extracted into dichloromethane (2 × 50 cm^3), the solution filtered, and the solvent removed from the filtrate by rotary evaporation to yield the product, a mixture of **5a** and **5b** (ca. 1:1), as an orange solid. 0.086 g (47%) A sample for analysis was obtained by recrystallization from dichloromethane. The assignments of the NMR resonances were made by studying the reaction of the mixture with proton sponge. **5a**: ^{1}H ($CDCl_3$): δ 7.3−7.7 (m, 13H), 7.03 (dd, J = 11.5, 7.4 Hz, 2H), 3.15 (m, 1H, PCH_2), 2.77 (m, 3H, PCH_2), 1.47 (ddd, $^{4}J_{PH}$ = 10.2 Hz, $^{4}J_{Ph}$ = 3.4 Hz, $^{3}J_{RhH}$ = 3.4 Hz, 15H, Me). ^{19}F ($CDCl_3$): δ −88.07 (m, 2F, F_{meta-P}), −129.46 (m, 2F, $F_{ortho-P}$), −154.18 (0.8F, s, [$^{10}BF_4^-$]), −154.23 (3.2F, s, [$^{11}BF_4^-$]). $^{31}P\{^{1}H\}$ ($CDCl_3$): δ 70.5 (dd, $^{1}J_{RhP}$ = 126 Hz, $^{3}J_{PP}$ = 11 Hz, PPh_2), 58.2 (dm, $^{1}J_{RhP}$ = 137 Hz, $PPh(C_5F_4N)$). **5b**: ^{1}H ($CDCl_3$): δ 7.3−7.7 (m, 15H), 3.47 (m, 1H, PCH_2), 3.15 (m, 1H, PCH_2), 2.44 (m, 1H, PCH_2), 2.26 (m, 1H, PCH_2), 1.20 (m, 15H, Me). ^{19}F ($CDCl_3$): δ −88.10 (br s, 2F, F_{meta-P}), −129.86 (br s, 2F, $F_{ortho-P}$), −154.18 (0.8F, s, [$^{10}BF_{4-}$]), −154.23 (3.2F, s, [$^{11}BF_4^-$]). $^{31}P\{^{1}H\}$ ($CDCl_3$): δ 66.8 (dd, $^{1}J_{RhP}$ = 134 Hz, $^{2}J_{PP}$ = 26 Hz, PPh_2), 64.6 (ddm, $^{1}J_{RhP}$ = 140 Hz, $^{3}J_{PP}$ = 26 Hz, $PPh(C_5F_4N)$). LSIMS, m/z (rel int): 744 M^+ (54), 709 $[M - Cl]^+$ (22). HRLSIMS: calcd for $C_{35}H_{34}ClF_4NP_2Rh$, 744.08462; found M^+, 744.08437. Anal. Calcd for $C_{35}H_{34}BClF_8NP_2Rh\cdot 0.25CH_2Cl_2$: C, 49.64; H, 4.08; N, 1.64. Found: C, 49.64; H, 4.12; N, 1.37.

[{$\eta^5,\kappa P,\kappa P$-$C_5Me_4[CH_{2-}$2-C_5F_3N-4-$P(C_6F_5)CH_2CH_2PPh_2$}-RhCl][BF_4] (6·[BF_4]). A slurry of [Cp*RhCl(μ-Cl)]$_2$ (0.108 g, 0.17 mmol) and **1** (0.150 g, 0.34 mmol) in benzene (60 cm^3) was heated under dinitrogen for 9 h. The resulting yellow precipitate of **6**·Cl was filtered off, washed with hexane (2 × 20 cm^3), and dried in vacuo. The solid was dissolved in methanol (60 cm^3), and $NaBF_4$ (ca. 0.2 g) added. The mixture was stirred for 3 h, then filtered. The solvent was removed from the filtrate by rotary evaporation. The product was extracted into dichloromethane (2 × 80 cm^3), and the combined extracts were dried over $MgSO_4$. After filtration the solvent was removed by rotary evaporation, yielding **6**·[BF_4] as a yellow solid, which was dried in vacuo. Yield: 0.173 g (64%). ^{1}H (CD_2Cl_2): δ 7.53 (m, 10H, C_6H_5), 7.37 (m, 1H, C_6H_5), 7.28 (m, 2H, C_6H_5), 6.64 (m, 2H, C_6H_5), 3.98 (dd, 1H, $^4J_{PH} = 16.3$ Hz, $^2J_{HH} = 16.3$ Hz, $C_5C\mathit{H}H'C_5F_3N$), 3.47 (m, 1H, PCH_2), 3.26 (m, 1H, PCH_2), 3.24 (d, 1H, $^2J_{HH} = 16.3$ Hz, $C_5CH\mathit{H'}C_5F_3N$), 2.97 (m, 2H, PCH_2), 1.91 (d, 3H, $^4J_{PH} = 5.4$ Hz, Me), 1.66 (dd, 3H, $^4J_{PH} \approx {}^4J_{PH} \approx 5.2$ Hz, Me), 1.20 (d, 3H, $^4J_{PH} = 7.7$ Hz, Me), 0.23 (d, 3H, $^4J_{PH} = 2.1$ Hz, Me). ^{19}F (CD_2Cl_2): δ −72.39 (m, 1F), −85.82 (m, 1F), −134.09 (m, 1F), −153.55 (0.8F, s, [$^{10}BF_4^-$]), −153.60 (3.2F, s, [$^{11}BF_4^-$]). $^{31}P\{^1H\}$ (CD_2Cl_2): δ 78.3 (dm, $^1J_{RhP} = 129$ Hz, PPh(C_5F_3N)), 67.0 (dd, $^1J_{RhP} = 130$ Hz, $_3J_{PP} = 16$ Hz, PPh_2). LSIMS, *m/z* (rel int): 724 M$^+$ (100), 689 [M − Cl]$^+$ (22). HRLSIMS: calcd for $C_{35}H_{33}ClF_3NP_2Rh$, 724.07839; found M$^+$, 724.07686. Anal. Calcd for $C_{35}H_{33}BClF_7NP_2Rh\cdot0.5CH_2Cl_2$: C, 49.92; H, 4.01; N, 1.64. Found: C, 49.98; H, 3.93; N, 1.42.

X-ray Crystallography. Crystals of **4** were deposited from neat **2**. Crystals of **5b** and **6**·[BF_4] were grown from dichloromethane/ethanol and acetone, respectively. Crystal data are listed in Table 1. Diffraction data were collected on a Bruker SMART diffractometer using the SAINT-NT[28] software with graphite-monochromated Mo Kα radiation. A crystal was mounted on the diffractometer at low temperature, ca. 120 K. Lorentz and polarization corrections were applied. Empirical absorption corrections were applied using SADABS.[29] The structures were solved using direct methods and refined with the program package SHELXTL version 5,[30] and the non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atom positions were added, and idealized positions and a riding model with fixed thermal parameters ($U_{ij} = 1.2U_{eq}$ for the atom to which they are bonded (1.5 for CH_3)) were used for subsequent refinements. The function minimized was $\sum[w(|F_o|^2 - |F_c|^2)]$ with reflection weights $w^{-1} = [\sigma^2\,|F_o|^2 + (g1P)^2 + (g2P)]$ where $P = [\max\,|F_o|^2 + 2|F_c|^2]/3$. Additional material available from the Cambridge Crystallographic Data Centre comprises relevant tables of atomic coordinates, bond lengths and angles, and thermal parameters (CCDC numbers: **4** 194821, **5b** 194822, **6**·[BF_4] 194823)

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Supporting Information Available: A listing of atomic coordinates, anisotropic displacement parameters, bond distances, and bond angles for **4**, **5b**·0.5CH_2Cl_2, and **6**·[BF_4]. This material is available free of charge via the Internet at http://pubs.acs.org.

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