Intramolecular Dehydrofluorinative Coupling of η^5-Pentamethylcyclopentadienyl and Pentafluorophenylphosphine Ligands in Rhodium Complexes

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Received July 29, 2002

The rhodium(III) complex [Cp*RhCl(dfppe)]BF_4, **1**, undergoes rapid stepwise intramolecular dehydrofluorinative carbon−carbon coupling on addition of proton sponge to produce [{η^5,κP,κP-C_5Me_3[$CH_2C_6F_4$-2-P(C_6F_5)CH_2]$_2$-1,3}RhCl]BF_4. The reaction requires less than the stoichiometric quantity of proton sponge and also occurs on addition of Bu^n_4NF or in the presence of polymer-supported fluoride. NMR studies of reactions between a series of complexes and proton sponge have revealed the necessary conditions for intramolecular dehydrofluorinative coupling in pentamethylcyclopentadienyl rhodium(III) phosphine complexes. The complex must be cationic, and the phosphine, which can be either part of a chelating ligand or monodentate need have only one pentafluorophenyl substituent. The reaction is rapid where Cp* and C_6F_5 are held in close proximity. The compounds [Cp*RhCl{(C_6F_5)$_2$PC_6H_4SMe-2}]BF_4, **7**, and the diastereoisomer of [Cp*RhCl{(C_6F_5)PhPC_6H_4SMe-2}]BF_4, **11a**, in which Cp* and C_6F_5 are *cis*, undergo rapid coupling on treatment with proton sponge. The diastereoisomer of [Cp*RhCl{(C_6F_5)PhPC_6H_4SMe-2}]BF_4, in which Cp* and C_6F_5 are *trans*, undergoes isomerization to **11a** at a much slower rate than that of coupling. Cationic complexes of monodentate phosphines, in which there is rotation about the Rh−P bond, undergo coupling on addition of proton sponge, but at a much slower rate than for **1**, **7**, and **11a**. The structures of [{η^5,κP,κP-$C_5Me_4CH_2C_6F_4$-2-P(C_6F_5)CH_2CH_2P(C_6F_5)$_2$}RhCl]BF_4, [{η^5,κP,κS-$C_5Me_4CH_2C_6F_4$P(C_6F_5)C_6H_4SMe}RhCl]BF_4, and [Cp*$RhCl_2${PEt_2(C_6F_5)}] have been determined by single-crystal X-ray diffraction.

Introduction

Cyclopentadienyl and phosphine ligands are two of the most common and important classes of ligand employed in organometallic chemistry. The coupling of these two ligand types in chelating bi- or trifunctional ligands is of current interest, since the resulting hybrid cyclopentadienyl-phosphine ligands are expected to affect metal reactivity differently from the separated ligands and endow the complexes with enhanced regio- and stereoselectivities in their reactions.[1] For a number of cases these expectations have been realized. For example, zirconium complexes of trifunctional cyclopentadienyl-diphosphines have been isolated, the unlinked cyclopentadienide phosphine analogues of which are either unknown or unstable;[2] [{η^5,κP-indenyl-CH_2CH_2-PPh_2}RhMe(CO)]BF_4 reacts with 1-phenylpropyne at room temperature, affording [{η^5,κP-indenyl-CH_2CH_2-PPh_2}RhMe{C(Ph)═C(Me)C(Me)═O}]BF_4, whereas under the same conditions [(η^5-indenyl)RhMe(CO)(PPh_3)]BF_4 does not react;[3] and the high diastereoselectivity shown by [{η^5,κP-C_5H_2($CO_2CH_2CH_2PPh_2$)MeR-2,4}Ru-$(NCMe)_2$]PF_6 in its ligand substitution reactions with phosphines and phosphites is in contrast to the low diastereoselectivity shown by [{η^5-C_5H_2(CO_2Et)MeR-2,4}Ru$(NCMe)_2${$P(OMe)_3$}]PF_6.[4] Despite the advantages offered by these ligands, the number of reports of complexes of chelating hybrid cyclopentadienyl-phosphine ligands is somewhat limited.[1] One reason for this scarcity is the lack of convenient syntheses. Three synthetic approaches to complexes of these hybrid ligands can be envisaged: (i) prior synthesis of the hybrid ligand followed by coordination to the metal; (ii) coordination of both functionalities of the hybrid ligand to the metal followed by intramolecular coupling; (iii) coordination of one functionality of the hybrid ligand to the metal followed by intermolecular coupling to the second functionality and subsequent chelation. The first strategy is the most commonly adopted route, but suffers from the disadvantage that ligand syntheses are often elaborate, involving multiple steps, and consequently poor overall yields are obtained.[1] The second approach provides a method of overcoming this problem. Since the two functionalities are held in close proximity by coordination to the metal, high yields coupled with high regioselectivities are expected. Despite the appeal

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(1) Butenschön, H. *Chem. Rev.* **2000**, *100*, 1527.

(2) (a) Fryzuk, M. D.; Mao, S. H. S.; Zaworotko, M. J.; MacGillivray, L. R. *J. Am. Chem. Soc.* **1993**, *115*, 5336. (b) Bosch, B. E.; Erker, G.; Fröhlich, R.; Meyer, O. *Organometallics* **1997**, *16*, 5449. (c) Wang, T.-F.; Lai, C.-Y. *J. Organomet. Chem.* **1997**, *546*, 179

(3) Kataoka, Y.; Iwato, Y.; Shibahara, A.; Yamagata, T.; Tani, K. *J. Chem. Soc., Chem. Commun.* **2000**, 841.

(4) Onitsuka, K.; Dodo, N.; Matsushima, Y.; Takahashi, S. *J. Chem. Soc., Chem. Commun.* **2001**, 521.

10.1021/om020612n CCC: $22.00
Publication on Web 11/21/2002

of this approach, there are very few reports of intramolecular reactions leading to complexes of hybrid cyclopentadienyl-phosphine ligands. The reaction of decafluorodiazabenzene with [CpRuMe(PPh_3)$_2$] produces the hybrid cyclopentadienyl-phosphine ligand complex [(η^5,κP-$C_5H_4C_6H_4PPh_2$)Ru(κC^1,κN^2-$C_6F_4N{=}NC_6F_5$] in moderate yield,[5] Nelson and co-workers have reported that the rhodium complex cation [Cp*RhCl($PPh_2CH{=}CH_2$)$_2$]$^+$ undergoes radical or base-promoted hydroalkylation to give a mixture of the 1,2 and 1,3 isomers of [{η^5,κP,κP-$C_5Me_3(CH_2CH_2CH_2PPh_2)_2$}RhCl]$^+$ in 35% and 42% yield, respectively,[6,7] and we have reported that in refluxing ethanol the salts [(η^5-C_5Me_4R)MX(dfppe)]BF_4 (M = Rh, X = Cl or Br, R = H, Me or Et; M = Ir, X = Cl, R = Me; dfppe = $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$) undergo dehydrofluorinative C−C coupling to give [{η^5,κP,κP-C_5Me_2R-[$CH_2C_6F_4$-2-$P(C_6F_5)CH_2$]$_2$}MX]BF_4 in virtually quantitative yield.[8−13] Although not definitely established, it is probable that the reaction between [Cp*RhCl(μ-Cl)]$_2$ and $(C_6H_3F_2$-2,6$)_2PCH_2CH_2P(C_6H_3F_2$-2,6$)_2$[14] and that between [(η^5-$C_5Me_4CF_3$)RhCl(μ-Cl)]$_2$ and $Ph_2PCH{=}CH_2$ to give [{η^5,κP-$C_5Me_3(CO_2Et)$-2-$CH_2CH_2CH_2PPh_2$}$RhCl_2$][7] also occur by coordination of the phosphine and subsequent intramolecular reaction, rather than being genuine examples of the third type of synthetic approach to hybrid cyclopentadienide-phosphine ligands. There are reports of complexes of other hybrid cyclopentadienyl-phosphorus(III) ligands formed by intramolecular reactions, namely, the cyclopentadienyl-phosphite complex [{η^5,κP-$C_5H_4C_6H_4OP(OPh)_2$}FeI{$P(OPh)_3$}][15] and the cyclopentadienyl-phosphide complexes [{η^5,κP-C_5Me_4-$CH_2PCH(SiMe_3)_2P(SiMe_3)$}Fe(CO)$_2$], [{$\eta^5$,$\kappa P$-$C_5Me_4CH{=}C(NMe_2)PN(CO_2R)NHCO_2R$}Fe(CO)$_2$], and [{$\eta^5$,$\kappa P$-$C_5$-$Me_4CH{=}C(NMe_2)PHX$}Fe(CO)$_2$] (X = $Cr(CO)_5$ or CpRh(CO)).[16] As far as we are aware, there are no incontrovertible examples of the third synthetic approach.

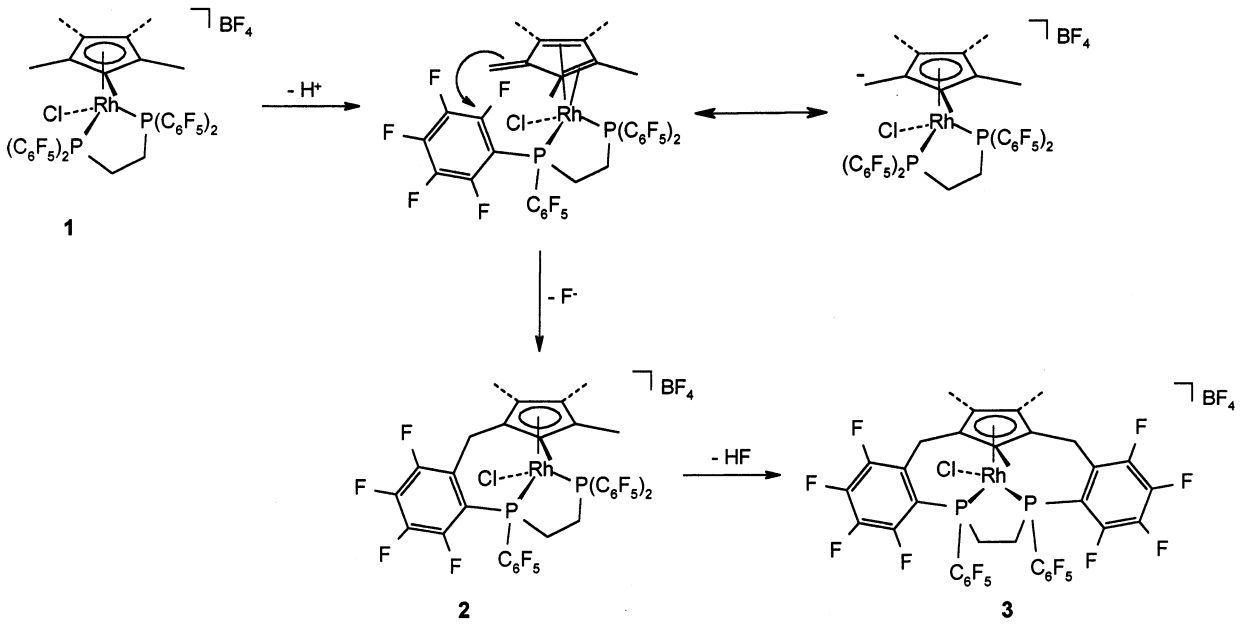
Here we describe dehydrofluorinative carbon−carbon coupling as a convenient synthetic route to rhodium complexes of bi- and trifunctional hybrid cyclopentadienide-phosphine ligands, suggest a possible mechanism for the reaction, and report the necessary conditions for such coupling to occur. Part of this work has been communicated.[12,17]

Results and Discussion

Intramolecular Dehydrofluorinative Ligand Coupling of [Cp*RhCl(dfppe)]BF_4. It has been established that in refluxing ethanol [Cp*RhCl(dfppe)]BF_4, **1**, undergoes stepwise dehydrofluorinative carbon−carbon coupling to give [{η^5,κP,κP-$C_5Me_4CH_2C_6F_4$-2-$P(C_6F_5)CH_2CH_2P(C_6F_5)_2$}RhCl]$BF_4$, **2**, then [{$\eta^5$,$\kappa P$,$\kappa P$-$C_5Me_3[CH_2C_6F_4$-2-$P(C_6F_5)CH_2]_2$-1,3}RhCl]$BF_4$, **3** (Scheme 1).[8] We have since found that treatment of **1** with 2 equiv of the strong, non-nucleophilic base 1,8-bis(dimethylamino)naphthalene (proton sponge) at room temperature also yields **3** in quantitative yield. An NMR tube experiment in $CDCl_3$ indicated that the reaction is very rapid and had reached completion within 15 min. We suggest that the mechanism of this reaction involves initial formation of an η^4-fulvene complex, or equivalent zitterionic carbanion, by loss of a pentamethylcyclopentadienyl proton, followed by nucleophilic attack of the methylene carbon atom at the *ortho* position of the pentafluorophenyl group (Scheme 1). In support of this mechanism it has previously been established that the methylene carbon atoms of η^4-fulvene rhodium complexes are nucleophilic[18] and that polyfluorinated arenes are susceptible to nucleophilic attack.[19] This mechanism has previously been proposed by Hughes and co-workers for the similar dehydrofluorinative C−C coupling reaction between the pentamethylcyclopentadienyl and perfluorobenzyl ligands of [Cp*Co($CF_2C_6F_5$)(PMe_3)(CO)]$^+$.[20] It has been proposed that proton sponge can also act as a single-electron donor,[21] and the possibility of a mechanism involving proton sponge acting in this way was also considered. However, two observations militate against such a mechanism. First, the salt [C_8H_6-$(NMe_2)_2H$]BF_4, characterized by single-crystal X-ray diffraction,[22] was obtained on addition of $NaBF_4$ to the reaction mixture, and second the reaction does not require the stoichiometric quantity of proton sponge to proceed to completion. An attempt to prepare **2** by treatment of **1** with 1 equiv of proton sponge gave **3** quantitatively. Even a ratio of 1:0.1 **1**:proton sponge produced predominantly **3** along with some **2**. Although the two products could not be separated, a single crystal of **2** was obtained from the mixture, allowing the structure of this intermediate to be determined (vide

(5) (a) Bruce, M. I.; Gardner, R. C. F.; Goodall, B. L.; Stone, F. G. A.; Doedens, R. J.; Moreland, J. A. *J. Chem. Soc., Chem. Commun.* **1974**, 185. (b) Bruce, M. I.; Gardner, R. C. F.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1976**, 81.
(6) Barthel-Rosa, L. P.; Catalano, V. J.; Nelson, J. H. *J. Chem. Soc., Chem. Commun.* **1995**, 1629.
(7) Barthel-Rosa, L. P.; Catalano, V. J.; Maitra, K.; Nelson, J. H. *Organometallics* **1996**, *15*, 3924.
(8) Atherton, M. J.; Fawcett, J.; Holloway, J. H.; Hope, E. G.; Karaçar, A.; Russell, D. R.; Saunders: G. C. *J. Chem. Soc., Dalton Trans.* **1996**, 3215.
(9) Atherton, M. J.; Fawcett, J.; Holloway, J. H.; Hope, E. G.; Russell, D. R.; Saunders, G. C. *J. Organomet. Chem.* **1999**, *582*, 163.
(10) Atherton, M. J.; Fawcett, J.; Holloway, J. H.; Hope, E. G.; Martin, S. M.; Russell, D. R.; Saunders: G. C. *J. Organomet. Chem.* **1998**, *555*, 67.
(11) (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.
(12) Bellabarba, R. M.; Nieuwenhuyzen, M.; Saunders, G. C. *J. Chem. Soc., Dalton Trans.* **2001**, 512.
(13) Bellabarba, R. M.; Nieuwenhuyzen, M.; Saunders, G. C. *Inorg. Chim. Acta* **2001**, *323*, 78.
(14) Fawcett, J.; Friedrichs, S.; Holloway, J. H.; Hope, E. G.; McKee, V.; Nieuwenhuyzen, M.; Russell, D. R.; Saunders, G. C. *J. Chem. Soc., Dalton Trans.* **1998**, 1477.
(15) Adrianov, V. G.; Chapovskii, Y. A.; Simeon, V. A.; Struchkov, Y. *J. Chem. Soc., Chem. Commun.* **1968**, 282.
(16) (a) Weber, L.; Kirchhoff, R.; Boese, R.; Stammler, H.-G.; Neumann B. *Organometallics* **1993**, *12*, 731. (b) Weber, L.; Kirchhoff, R.; Boese, R. *Chem. Ber.* **1993**, *126*, 1963. (c) Weber, L.; Kaminski, O.; Boese, R.; Bläser, D. *Organometallics* **1995**, *14*, 820. (d) Weber, L.; Kirchhoff, R.; Quasdorff, B.; Stammler, H.-G.; Neumann, B. *J. Organomet. Chem.* **1997**, *529*, 329. (e) Weber, L.; Quasdorff, B.; Stammler, H.-G.; Neumann, B. *Chem. Eur. J.* **1998**, *4*, 469. (f) Weber, L.; Scheffer, M. H.; Stammler, H.-G.; Neumann, B. *Inorg. Chim. Acta* **1999**, *291*, 311.
(17) Bellabarba, R. M.; Saunders: G. C. *J. Fluorine Chem.* **2001**, *112*, 139.
(18) (a) Gusev, O. V.; Rubeshov, A. Z.; Miguel-Garcia, J. A.; Maitlis, P. M. *Mendeleev Commun.* **1991**, 121. (b) Gusev, O. V.; Sergeev, S.; Saez, I. M.; Maitlis, P. M. *Organometallics* **1994**, *13*, 2059.
(19) (a) Chambers, R. D. *Fluorine in Organic Chemistry*; J. Wiley & Sons: New York, 1973; Chapter 9. (b) Kobrina, L. S. *Fluorine Chem. Rev.* **1974**, *7*, 1. (c) Brooke, G. M. *J. Fluorine Chem.* **1997**, *87*, 1.
(20) Hughes, R. P.; Lindner, D. C.; Rheingold, A. L.; Yap, G. P. A. *Organometallics* **1996**, *15*, 5678.
(21) Hughes, R. P.; Kovacik, I.; Lindner, D. C.; Smith, J. M.; Willemsen, S.; Zhang, D.; Guzei, I. A.; Rheingold, A. L. *Organometallics* **2001**, *20*, 3190.
(22) Wozniak, K.; Krygowski, T. M.; Kariuki, B.; Jones, W.; Grech, E. *J. Mol. Struct.* **1990**, *240*, 111.

Scheme 1



infra). The production of **3** from **1** using significantly less than the stoichiometric quantity can be explained by fluoride ion, generated by the reaction, acting as the base. In support of this explanation an NMR tube reaction between stoichiometric amounts of **1** and Bu^n_4NF in $(CD_3)_2CO$ also yielded **3** quantitatively. Furthermore, **3** was obtained in high yield from treatment of **1** with polymer-supported fluoride in CH_2Cl_2.

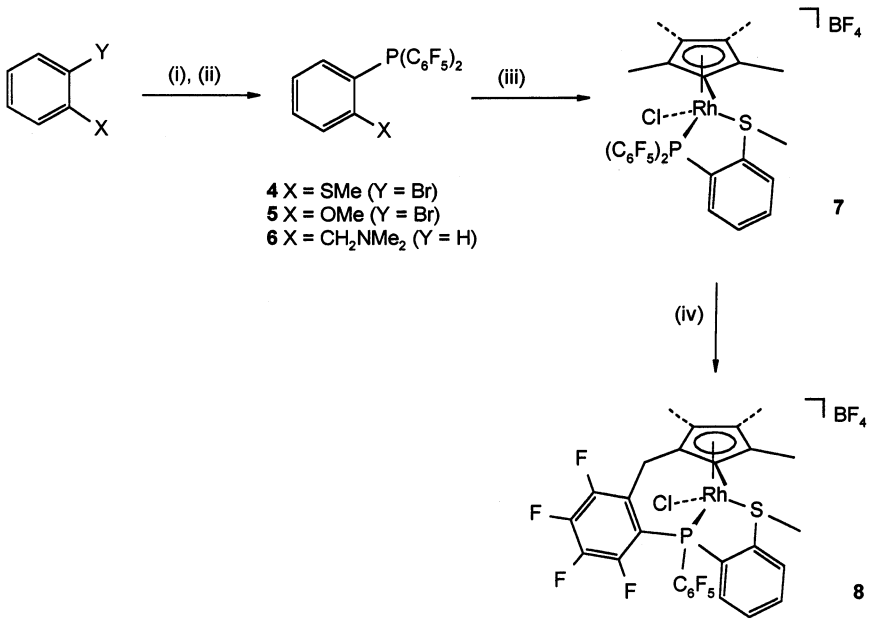
The concept of an intramolecular dehydrofluorinative carbon−carbon coupling reaction coupling two functionalities by a mechanism involving loss of a proton and nucleophilic attack by the resulting methylene carbon at an *ortho* carbon of a pentafluorophenyl substituent of a phosphine provides a simple, rational method for the synthesis of transition metal complexes of other hybrid cyclopentadienyl-phosphine ligands. The reaction in Scheme 1 involves a cationic rhodium complex of a chelating diphosphine in which both phosphorus atoms bear two pentafluorophenyl substituents. We wished to determine the criteria for intramolecular dehydrofluorinative coupling between Cp* and phosphines in rhodium(III) complexes by answering the following questions: (i) is it necessary for the complex to be cationic? (ii) is it necessary to use a chelating diphosphine, or can other types of chelating ligand undergo coupling? (iii) is it necessary for the phosphorus atom to bear two pentafluorophenyl groups, or will phosphines bearing only one pentafluorophenyl substituent undergo coupling? and (iv) is it necessary to use chelating ligands, or will monodentate phosphines undergo coupling? To answer these questions, we chose to investigate reactions between the following rhodium(III) complexes and proton sponge: (i) cationic complexes of chelating ligands bearing only one bis(pentafluorophenyl)phosphine moiety $[Cp^*RhCl\{(C_6F_5)_2P-L\}]^+$, (ii) a cationic complex of a chelating phosphine ligand bearing only one pentafluorophenyl substituent, $[Cp^*RhCl\{(C_6F_5)RP-L\}]^+$, (iii) neutral complexes of monodentate phosphines, $[Cp^*RhCl_2\{PR_{3-x}(C_6F_5)_x\}]$, and (iv) cationic complexes of monodentate phosphines, $[Cp^*RhCl\{PR_{3-x}(C_6F_5)_x\}L]^+$ (L = two-electron donor).

In situ NMR experiments have proved useful in establishing the reaction of **1** with proton sponge and the intermediacy of **2** in the transformation **1** → **3**,[8] since the products containing coupled Cp* and phosphine ligands possess very different NMR spectroscopic properties from the starting materials. In particular, δ_P for **3** is at a higher frequency than that of **1** (by ca. 40 ppm), and the ^1H NMR spectrum of **1** shows a triplet resonance assigned to the Cp* hydrogen atoms, whereas **3** shows two resonances for the hydrogen atoms of the three methyl groups. The ^1H NMR spectra of the expected products of intramolecular dehydrofluorinative coupling in the complexes $[Cp^*RhCl\{(C_6F_5)_{2-x}R_xP-L\}]^+$ and $[Cp^*RhClL\{PR_{3-x}(C_6F_5)_x\}]^+$ should contain four methyl resonances, each integrating as three hydrogen atoms, by virtue of the stereogenic metal center, as is found for the tetramethylcyclopentadienyl complexes $[(\eta^5\text{-}C_5Me_4H)RhCl(CNC_6H_{11})PPh_{3-x}(C_6F_5)_x]BF_4$ ($x = 0$ or 1),[23] and that from the coupling in the complexes $[Cp^*RhCl_2\{PR_{3-x}(C_6F_5)_x\}]$ should contain two methyl resonances each integrating for six hydrogen atoms. The presence of products of coupling in complexes of phosphines bearing only one pentafluorophenyl group should be readily discernible from the presence of four resonances in their ^{19}F spectra, in addition to those of BF_4, rather than the three associated with pentafluorophenyl groups. Thus, the NMR spectra should provide definitive evidence as to whether the coupling of the Cp* and phosphine ligands has occurred, and we therefore decided to investigate the reactions between the rhodium complexes and proton sponge by in situ NMR experiments.

Synthesis and Intramolecular Dehydrofluorinative Ligand Coupling Study of $[Cp^*RhCl\{(C_6F_5)_2P-L\}]^+$. The bifunctional phosphine-thioether compound $(C_6F_5)_2PC_6H_4SMe$-2 (**4**) was prepared in 80% yield by treating $(C_6F_5)_2PBr$ with $Li[C_6H_4SMe]$, formed by addition of ^nBuLi to 2-bromothioanisole. The similar phosphine-anisole and phosphine-amine com-

(23) FitzGerald, Á. M.; Nieuwenhuyzen, M.; Saunders, G. C. *J. Organomet. Chem.* **1999**, *584*, 206.

Scheme 2[a]



[a] (i) Bu^{n}Li, Et_2O; (ii) $(C_6F_5)_2PCl$; (iii) $NaBF_4$, CH_2Cl_2/MeOH; (iv) proton sponge, CH_2Cl_2.

Table 1. NMR Data for the Products of the Reactions between 7, 11, 14a−c, and Proton Sponge

starting material	product	δ_P ($^1J_{RhP}$/Hz)	$\Delta\delta_P$	δ_H of C_5Me_4 ($^4J_{PH}$/Hz)	δ_F of C_6F_4
7[a]	**8**	58.6 (150)	+28.4	2.17 d (8.9), 1.95 d (3.5), 1.65 s, 1.52 s	−119.73, −134.35, −142.43, −151.54
11[b]	**12**	53.6 (141)	+16.1[c]	2.08 d (6.7), 1.82 d (4.5), 1.34 s, 1.30 s	−125.24, −139.91, −149.93, −156.39
14a[d]	**15a**	40.9 (133)	+18.3	2.08 d (5.1), 1.82 d (6.2), 1.71 s, 1.52 s	−119.22, −136.07, −145.54, −151.82
14b[a]	**15b**	41.7 (132)	+19.5	2.12 d (4.6), 1.86 d (6.6), 1.78 s, 1.32 s	−120.61, −137.09, −146.30, −152.01
14c[a]	**15c**	59.0 (130)	+24.1	2.09 d (4.9), 1.85 d (5.6), 1.70 s, 1.45 s	−125.64, −136.22, −146.71, −153.13

[a] Performed in $CDCl_3$. [b] Performed in $(CD_3)_2CO$. [c] Relative to **11a**. [d] Performed in CD_2Cl_2.

pounds $(C_6F_5)_2PC_6H_4OMe$-2 (**5**) and $(C_6F_5)_2PC_6H_4CH_2$-NMe-2 (**6**) were prepared similarly in 90 and 70% yields, respectively. Compounds **4** and **5** were isolated as white powders and **6** was isolated as a pale yellow oil, and all were characterized by mass spectrometry and multinuclear NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectra of all three compounds comprise a quintet at ca. δ −57, with phosphorus−fluorine coupling of 35−40 Hz. These data are similar to those of $PhP(C_6F_5)_2$.[24]

Treatment of $[Cp^*RhCl(\mu\text{-}Cl)]_2$ with **4** in the presence of an excess of tetrafluoroborate afforded $[Cp^*RhCl(\mathbf{4})]BF_4$ (**7**) as a yellow oil in 79% yield (Scheme 2). Attempts to crystallize **7** were unsuccessful, and characterization is based on the NMR data and subsequent reaction. The $^{31}P\{^1H\}$ NMR spectrum of **7** comprises a doublet of multiplets at δ 30.2 with a rhodium−phosphorus coupling of 174 Hz, similar to that of **1**, which comprises a doublet of multiplets at δ 35.1 with a coupling of 150 Hz.[8] The ^{19}F NMR spectrum of **7**, recorded at 298 K and 282 MHz, contains 10 resonances in addition to those due to BF_4^-, indicating that there is hindered rotation about the P−C bonds since all the fluorine atoms of the $P(C_6F_5)_2$ moiety are unique. No attempts were made to determine the stereochemistry at sulfur of **7**, and the conformation suggested in Scheme 2, giving rise to the $R_{Rh}R_S$ and $S_{Rh}S_S$ pair of enantiomers, is based on arguments for compound **8** (vide infra). In contrast to **4**, neither **5** nor **6** coordinated to the Cp*RhCl fragment.

An NMR tube experiment revealed that on addition of proton sponge, **7** underwent a similarly rapid and clean dehydrofluorinative carbon−carbon coupling as **1**, to form **8** (Scheme 2). The NMR data are entirely consistent with coupling of the Cp* and phosphine ligands (Table 1). The ^{31}P NMR spectrum showed a resonance with coupling to rhodium at δ 58.6, the ^1H NMR spectrum contained four resonances assigned to the four unique methyl groups between δ 0 and 2.5, each integrating for three hydrogen atoms, and the resonances in the ^{19}F spectrum integrated for 13 atoms rather than the 14 of **7**. Confirmation of the identity of the product of the coupling reaction, **8**, was obtained by characterization of a sample prepared in 92% by a preparative scale reaction, including a single-crystal X-ray structure determination (vide infra). The ^1H NMR spectrum of **8** contained, in addition to the four methyl resonances, three resonances between δ 7.5 and 8.1, assigned to the four aromatic hydrogen atoms, and two resonances showing mutual coupling at δ 4.36 and 3.30, each integrating for one hydrogen atom. The resonance at δ 4.36 also shows coupling to phosphorus. These two resonances are assigned to the nonequivalent hydrogen atoms of the methylene group which links the Cp* and C_6F_4 group and are consistent with resonances observed for **3**.[8] The hydrogen atoms of the thiomethyl group give a singlet resonance at δ 2.60. Compound **8** can exist as four stereoisomers: the geometry of the cation leads to only two possibilities of the stereochemistry at rhodium and phosphorus, $R_{Rh}S_P$ and $S_{Rh}R_P$, but for each there

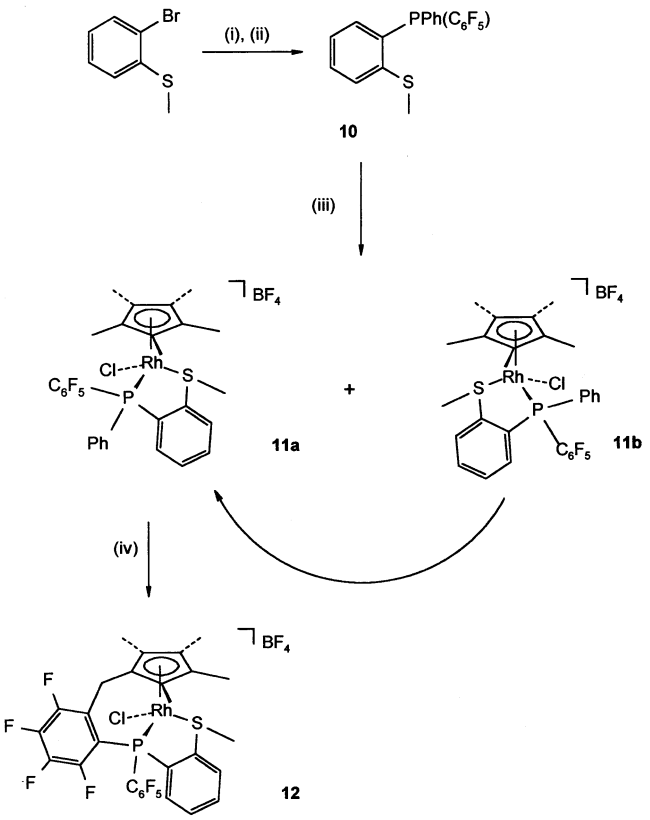
(24) Nichols, D. I. *J. Chem. Soc. A* **1969**, 1471.

are two possibilities of the stereochemistry at sulfur. ^{1}H spectroscopic studies reveal that there is no NOE correlation between the thiomethyl and Cp* hydrogen atoms, although NOE correlation between the thiomethyl and two of the aromatic hydrogen atoms is observed. This observation suggests that just two of the possible stereoisomers, the enantiomers $R_{Rh}R_SS_P$ and $S_{Rh}S_SR_P$, are present in solution. This is in agreement with the X-ray structure (vide infra). In these enantiomers the Cp* and methyl groups are *trans* groups on the five-membered $RhSC_2P$ ring, and this is expected to be the sterically favored conformation. The possibility of the singlet resonance arising from the averaging of resonances from diastereoisomers was examined by variable-temperature ^{1}H NMR spectroscopy. Down to 228 K, the lowest temperature at which spectra were recorded, no change in the resonance was observed, and we suggest that the stereochemistry at the sulfur in **8** (and also in the compounds **7**, **11a**, **11b**, and **12**) is such that the Cp* and methyl group are *trans*.

Synthesis and Intramolecular Dehydrofluorinative Ligand Coupling Study of [Cp*RhCl{(C_6F_5)RP−L}]$^+$. The reaction between $PhPCl_2$ and C_6F_5MgBr in diethyl ether produced a mixture of $PhP(C_6F_5)Cl$ (**9a**) and $PhP(C_6F_5)Br$ (**9b**) as a colorless solid.[25] The mixture was characterized by NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum, which has not been reported previously, shows two triplets at δ 57.3 and 41.1, both with coupling constants, $^3J_{PF}$, of 49 Hz. By analogy with the $^{31}P\{^1H\}$ NMR spectra of $(C_6F_5)_2PX$ and $(C_6F_5)PX_2$, in which the resonances for chlorides are at higher frequency to those of the respective bromides,[26] the former resonance is assigned to **9a** and the latter to **9b**. The ^{19}F NMR spectrum supports the presence of two compounds. Although the *meta* and *para* fluorine resonances are coincident for the two compounds, the *ortho* fluorine resonances occur at δ −129.13 for **9a** and −127.53 for **9b**. The ratio of **9a** to **9b** was determined to be 1:3 from these spectra. Treatment of the mixture of **9a** and **9b** with $Li[C_6H_4SMe]$ gave the bifunctional phosphine-thioether compound $PhP(C_6F_5)C_6H_4SMe$-2 (**10**) in ca. 50% yield. The $^{31}P\{^1H\}$ NMR spectrum of **10** comprises a triplet at δ −32.6 with a value of $^3J_{PF}$ of 37 Hz, comparable with the data for $Ph_2P(C_6F_5)$.[24]

Treatment of $[Cp^*RhCl(\mu\text{-}Cl)]_2$ with compound **10** in the presence of an excess of tetrafluoroborate yielded a mixture of two isomers of [Cp*RhCl(**10**)]BF_4 in ca. 1:1 ratio (Scheme 3). The isomers were fully characterized by multinuclear spectroscopy, and subsequent reaction (vida infra), as **11a** and **11b**. If, as suggested for **8**, the Cp* and methyl groups are *trans* groups on the $RhSC_2P$ ring, then the isomers are racemic diastereoisomers, differing in the relative positions of the Cp* and C_6F_5 groups. In **11a** these groups are *cis* and in **11b** *trans*. The NMR data indicate that the relative proportions of **11a** and **11b** are 43 and 57%, respectively. Although the ratio is consistent with the greater steric congestion in **11a**, it is not known whether the mixture is in equilibrium or the ratio is a consequence of the kinetics of the coordination of **10** to the $[Cp^*RhCl]^+$ fragment. Although **11b** can isomerize to **11a** (vide infra), and

Scheme 3[a]



[a] (i) Bu^{n}Li, Et_2O; (ii) $(C_6F_5)PhPBr/Cl$; (iii) $NaBF_4$, CH_2Cl_2/MeOH; (iv) proton sponge.

presumably the reverse can occur, the rate of isomerization is slow and the equilibrium may not have been established before the solid was isolated nor in the NMR tube. The $^{31}P\{^1H\}$ NMR spectrum exhibits two doublet resonances at δ 37.5 and 55.6, both with coupling to rhodium of ca. 145 Hz. The former resonance is assigned to **11a** and is similar to that of **1** (δ_P 35.1, $^1J_{RhP}$ = 151 Hz).[8] The latter resonance is assigned to **11b** and is comparable to that of $[Cp^*RhCl(dppe)]BF_4$ (δ_P 66.2, $^1J_{RhP}$ = 151 Hz).[27] Both **11a** and **11b** show three resonances in addition to those due to BF_4^- in the ^{19}F NMR spectrum.

The reaction between proton sponge and the mixture of **11a** and **11b** was performed in $(CD_3)_2CO$ in an NMR tube at room temperature. A rapid reaction was observed by $^{31}P\{^1H\}$ NMR spectroscopy, which showed a decrease in intensity of the doublet resonance of **11a** and the appearance of a new doublet at δ 53.6 with a coupling to rhodium of 141 Hz. The ^{1}H and ^{19}F NMR spectra also showed a decrease in intensity of the resonances assigned to **11a** and the presence of new resonances (Table 1) consistent with coupling of the Cp* and phosphine ligands to give **12** (Scheme 3). In addition to the resonances assigned to C_5Me_4, the ^{1}H NMR spectrum possesses mutually coupled resonances at δ 4.33 and 3.49 characteristic of the nonequivalent hydrogen atoms of the methylene group. The former resonance appears as a triplet due to coupling to phosphorus of the same magnitude as the H−H coupling (17.2 Hz). The latter resonance is a doublet. The

(25) (a) Fild, M.; Glemser, O.; Hollenberg, I. *Z. Naturforsch., Teil B* **1966**, *21*, 920. (b) Cowley, A. H.; Cushner, M.; Fild, M.; Gibson, J. A. *Inorg. Chem.* **1975**, *14*, 1851.

(26) Ali, R.; Dillon, K. B. *J. Chem. Soc., Dalton Trans.* **1990**, 2593.

(27) Hope, E. G.; Kemmitt, R. D. W.; Stuart, A. M. *J. Chem. Soc., Dalton Trans.* **1998**, 3765.

thiomethyl resonance occurs at δ 3.02 Over time a decrease in the intensity of the resonances assigned to **11b** and a concomitant increase in the intensity of those of **12** was observed. The relative integrations of the resonances assigned to **11a**, **11b**, and **12** were ca. 1:3:2 after 3.5 h, ca. 0:1:3 after 19 h, ca. 0:1:5 after 28 h, and ca. 0:1:10 after 50 h. Only resonances assigned to **12** and byproducts were observed after 144 h. The NMR data are consistent with a rapid coupling of the Cp* and phosphine ligands of **11a** and a relatively slow isomerization of **11b** to **11a**. Possible mechanisms of the isomerization include (i) dissociation of the thioether group rotation about the Rh−P bond and recoordination, (ii) dissociation of the phosphine, rotation about the Rh−S bond, and recoordination, (iii) dissociation of the ligand **10** and recoordination to give **11a**, (iv) dissociation of chloride and recoordination from the opposite face of the Cp*Rh(**10**) fragment,[28] (v) dissociation of chloride from one cation and attack at another cation of **11b** *trans* to the coordinated chloride, followed by dissociation of the appropriate chloride,[29] and (vi) dissociation of the phosphine, inversion at phosphorus, and recoordination (Scheme 4). Mechanisms (i)−(v) result in inversion of chirality only at rhodium, whereas mechanism (vi) results in inversion of chirality only at phosphorus. The isomerization of [Cp*RhCl(*R*-Ph_2PCHMeCH_2PPh_2)]Cl, which occurs only at elevated temperature, was proposed to occur by mechanism (v).[29] The largest difference in coordination about rhodium between **11b** and [Cp*RhCl(*R*-Ph_2PCHMeCH_2PPh_2)]Cl is the presence of an Rh−S bond in the former instead of the Rh−P bond of the latter. We suggest that it is this difference that accounts for the difference in isomerization rates at room temperature and reason that (i) is the dominant mechanism of isomerization of **11b**. If the other mechanisms are important, then the isomerization of **11b** might be expected to occur only under conditions similar to that of [Cp*RhCl(*R*-Ph_2PCHMeCH_2PPh_2)]Cl.

Synthesis and Intramolecular Dehydrofluorinative Ligand Coupling Study of Cp*RhCl$_2${PR_2-(C_6F_5)}. The neutral monodentate phosphine complex [Cp*$RhCl_2${PPh_2(C_6F_5)}] (**13a**) has been described previously.[10] The new complex [Cp*$RhCl_2${PEt_2(C_6F_5)}] (**13b**) was prepared from [Cp*RhCl(μ-Cl)]$_2$ and PEt_2(C_6F_5) (Scheme 5). The $^{31}P\{^1H\}$ NMR spectrum of **13b** possesses a doublet of triplets resonance, arising from coupling to rhodium and the *ortho* fluorine atom, at higher frequency by ca. 10 ppm than the resonances of **13a** (δ_P 18.8)[10] and [(η^5-C_5Me_4H)$RhCl_2${PPh_2(C_6F_5)}] (δ_P 21.4).[23] The coupling to rhodium is ca. 145 Hz for all three compounds. The formulation of **13b** was confirmed by single-crystal X-ray diffraction (vide infra). Neither **13a** nor **13b** underwent a reaction with proton sponge, even over prolonged periods.

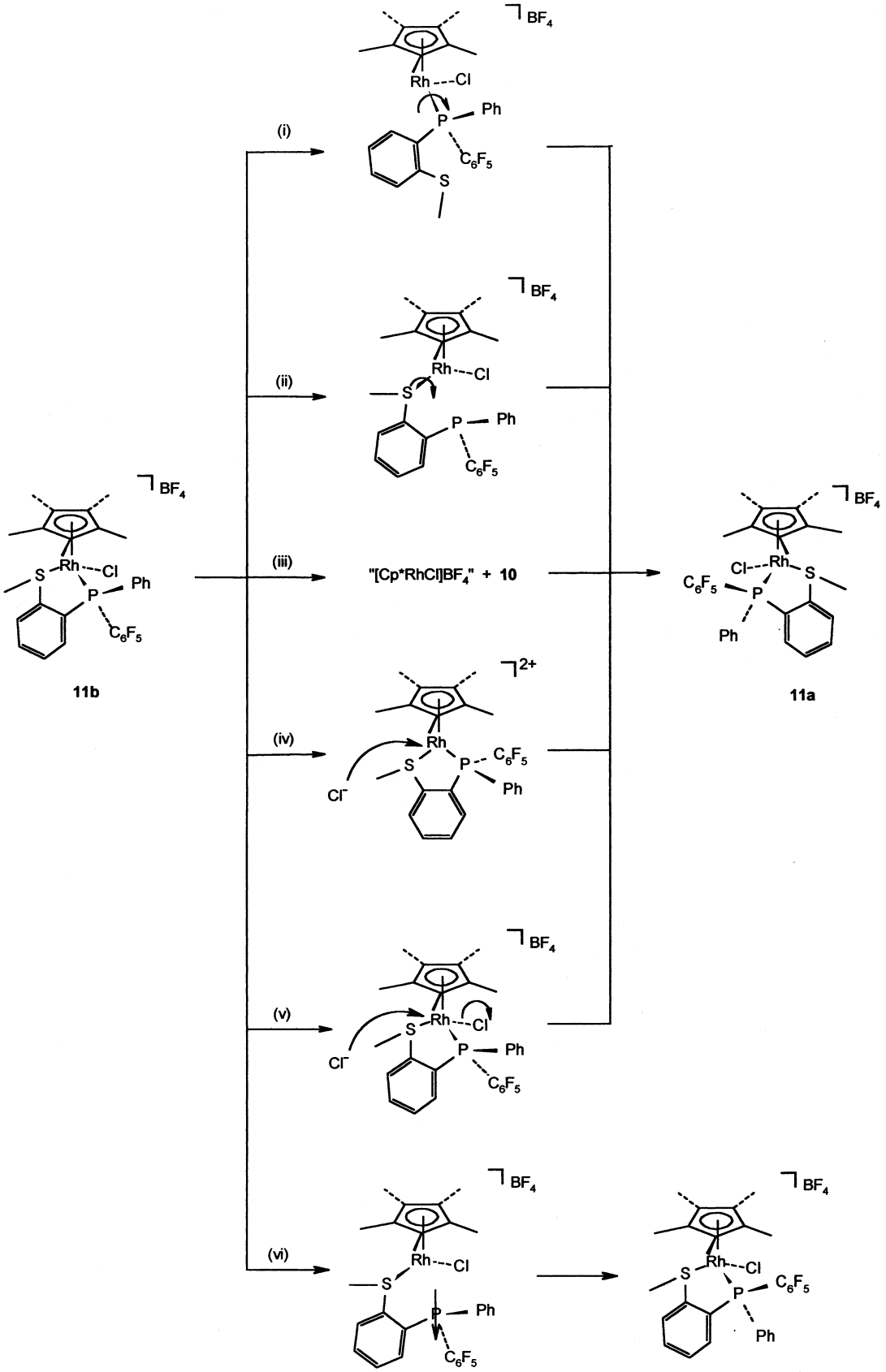
We have previously established that phosphines containing two or more phenyl rings bearing two *ortho* fluorine substituents are too bulky to coordinate to the Cp*$RhCl_2$ fragment,[10,30] and compounds of formulation [Cp*$RhCl_2${$PR(C_6F_5)_2$}] could not be prepared.

Synthesis and Intramolecular Dehydrofluorinative Ligand Coupling Study of [Cp*RhCl{PR'_2-(C_6F_5)}L]$^+$. Attempts to prepare the bis(phosphine) complex cations [Cp*$RhCl${$PR_2(C_6F_5)$}$_2$]$^+$ were unsuccessful, presumably for steric reasons. Salts of the cations [Cp*$RhCl${$R_2P(C_6F_5)$}(CNR′)]$^+$ (R = phenyl, R′ = phenyl **14a** or cyclohexyl, **14b**; R = ethyl, R′ = *cyclo*hexyl, **14c**) were prepared by treatment of [Cp*$RhCl_2$-{$PR_2(C_6F_5)$}] with an excess of sodium tetrafluoroborate and the appropriate isonitrile (Scheme 5). The salt **14a** was obtained as an orange solid, but **14b** and **14c** were obtained as yellow oils, which, despite repeated attempts, failed to produce solid products and elemental analyses could not be obtained. Characterization of these two salts was based on the NMR spectroscopic data and comparisons with **14a** and similar compounds.[23,30] The $^{31}P\{^1H\}$ NMR spectra show doublet resonances at ca. δ 22 for **14a** and **14b** and δ 34.9 for **14c**. All three show coupling to rhodium of ca. 130 Hz, and that of **14c** also to fluorine of 11 Hz. The small shifts of δ_P to higher frequency on going from [Cp*$RhCl_2${PR_2-(C_6F_5)}] to [Cp*$RhCl${$PR_2(C_6F_5)$}(CNR′)]$^+$ are consistent with those of the tetramethylcyclopentadienyl analogues.[23]

NMR tube experiments revealed that on addition of proton sponge, **14a**−**c** underwent dehydrofluorinative carbon−carbon coupling to form **15a**−**c** (Scheme 5). The NMR data are entirely consistent with coupling of the Cp* and phosphine ligands (Table 1). The ^{31}P NMR spectra showed resonances, with coupling to rhodium of ca. 130 Hz, at ca. 20 ppm higher frequency than the starting materials. The resonance of **15c** also shows a 6 Hz coupling to one fluorine atom. The ^1H NMR spectra contained four resonances assigned to the four unique methyl groups between δ 1 and 2.5. The methylene hydrogen resonances of **15b** appear as two doublets of doublets at δ 3.64 and 3.30 with a mutual coupling of 16.0 Hz and couplings to phosphorus of 11.8 and 5.6 Hz, respectively. For **15a** and **15c** only one methylene resonance is observed; the other is presumably obscured by broad resonances due to protonated proton sponge at 2.6−3.0 ppm. That of **15a** appears as a triplet at δ 3.64 with a coupling of 8.1 Hz to phosphorus and the other methylene hydrogen, and that of **15c** appears as a doublet at δ 3.87 with a coupling of 8.3 Hz. The rates of the reactions for **14a**−**14c** are considerably slower than those for **1**, **7**, and **11a**. In each case the ratio of starting material to product was ca. 1:1 after 24 h. The reactions of **14b** and **14c** were clean, and the spectra indicated that **15b** and **15c** were formed almost quantitatively after 68 and 45 h, respectively. In contrast the reaction between **14a** and proton sponge gave varying amounts of other fluorine- and phosphorus-containing compounds depending on the solvent. In chloroform at least three other phosphorus- and fluorine-containing compounds were formed in significant amounts (10−30% of the total product), although in dichloromethane the formation of these other products was significantly reduced. The slower rates of dehydrofluorinative carbon−carbon coupling for **14a**−**c** in comparison to **1**, **7**, and **11a** can be explained by rotation about the Rh−P bond in the former group of compounds. In **1**, **7**, and **11a** the

(28) Davies, D. L.; Fawcett, J.; Garratt, S. A.; Russell, D. R. *Organometallics* **2001**, *20*, 3029.
(29) Carmona, D.; Lahoz, F. J., Oro, L. A.; Lamata, M. P.; Viguri, F.; San José, E. *Organometallics* **1996**, *15*, 2961.
(30) Corcoran, C.; Friedrichs, S.; Fawcett, J.; Holloway, J. H.; Hope, E. G.; Russell, D. R.; Saunders, G. C.; Stuart, A. M. *J. Chem. Soc., Dalton Trans.* **2000**, 161.

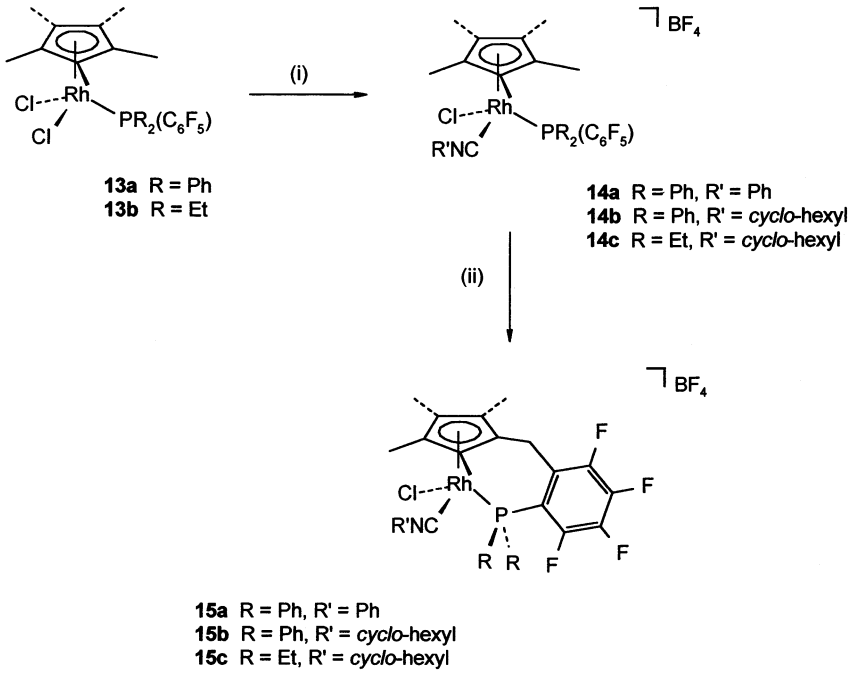
Scheme 4



two reacting groups are held in close proximity, which is not the case for **14a**−**c**. The slow rate of the reaction would also allow the possibility of intermolecular reactions with, for example, solvent and lead to nonquantitative formation of the ligand-coupled product, as observed for **14a**.

X-ray Diffraction Studies of 2, 8, and 13b. The structures of compounds **2**, **8**, and **13b** were determined

Scheme 5[a]



[a] (i) R′NC, $NaBF_4$, CH_2Cl_2/MeOH; (ii) proton sponge.

Table 2. Crystal and Structure Refinement Data

	2·2$CHCl_3$	**8**·3$CHCl_3$	**13b**
formula	$C_{36}H_{16}BClF_{23}P_2Rh.2CHCl_3$	$C_{29}H_{21}BClF_{13}PRhS.3CHCl_3$	$C_{20}H_{25}Cl_2F_5PRh$
M	1337.35	1186.76	565.18
T, K	153(2)	153(2)	153(2)
cryst syst	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a, Å	12.2595(8)	11.6484(9)	8.267(4)
b, Å	14.1355(9)	11.7516(10)	35.806(19)
c, Å	14.7311(10)	17.7351(14)	8.288(4)
α, deg	86.1140(10)	93.233(2)	90
β, deg	69.5290(10)	102.5490(10)	116.566(8)
γ, deg	75.0530(10)	112.3060(10)	90
U, Å^3	2310.0(3)	2166.3(3)	2194(2)
Z	2	2	4
D_{calc}, g cm^{-3}	1.923	1.819	1.768
λ, Å	0.71073	0.71073	0.71073
μ, mm^{-1}	0.969	1.179	1.150
θ_{max}, deg	28.73	28.66	22.50
cryst dimens, mm^3	0.38 × 0.28 × 0.24	0.48 × 0.31 × 0.19	0.35 × 0.28 × 0.20
no. of reflns collected	20235	14538	9676
no. of ind reflns	10397 (R_{int} = 0.0683)	8998 (R_{int} = 0.0521)	2860 (R_{int} = 0.1421)
no. of obsd reflns [$I > 2\sigma(I)$]	6753	6357	1508
R1, wR2 [$I > 2\sigma(I)$]	0.0507, 0.1011	0.0470, 0.1100	0.0916, 0.2242
R1, wR2 (all data)	0.0830, 0.1144	0.0701, 0.1204	0.1511, 0.2564
goodness-of-fit	0.926	0.935	0.953
largest Δ*ρ*, e Å^{-3}	1.182, −1.015	0.728, −0.674	2.860, −1.110

by single-crystal X-ray diffraction. The crystal and structure refinement data are given in Table 2.

Both **2** and **8** are racemic, and in both structures the two enantiomers are contained within the unit cell. The structure of the $R_{Rh}S_P$ cation of **2** is shown in Figure 1, and that of the $R_{Rh}R_SS_P$ enantiomer of the cation of **8** is shown in Figure 2.

A number of structural changes occur on coupling Cp* and phosphine ligands through a tetrafluorophenylene bridge. There is a reduction in the Cp†−Rh (Cp† represents the centroid of the C_5 ring) and Rh−P distances and the Cp†−Rh−P and P−Rh−P angles, but there is little effect on the Rh−Cl distance. The Cp†−Rh distances of the coupled products **2**, **3** (1.837(1) Å),[31] and the bromo analogue of **3** (1.829(7) Å)[9] are identical within experimental error, but significantly shorter than that of **1**, which is identical to those of salts of [Cp*RhCl(P_2)]$^+$, where P_2 = $(C_6H_3F_2$-2,6$)_2PCH_2CH_2P(C_6H_3F_2$-2,6$)_2$ (1.868(4) Å)[14] and *R*-$Ph_2PCH(Me)CH_2PPh_2$ (1.873(2) Å).[29] The Cp†−Rh of **8** is considerably shorter than those of **2** and **3**, which is presumably due to the difference between coordination to phosphine and thioether. The mean Rh−C distances of [Cp*RhCl(thioether)]$^+$ compounds range from 2.15 to 2.17 Å,[32] that of **8** is 2.185 Å, and those of **1**[31] and **2** are 2.22 and 2.21 Å, respectively. The Rh−P distances for uncoupled phosphines range from 2.33 to 2.36 Å, whereas those for the coupled

(31) Atherton, M. J.; Fawcett, J.; Holloway, J. H.; Hope, E. G.; Karaçar, A.; Russell, D. R.; Saunders, G. C. *J. Chem. Soc., Chem Commun.* **1995**, 191.

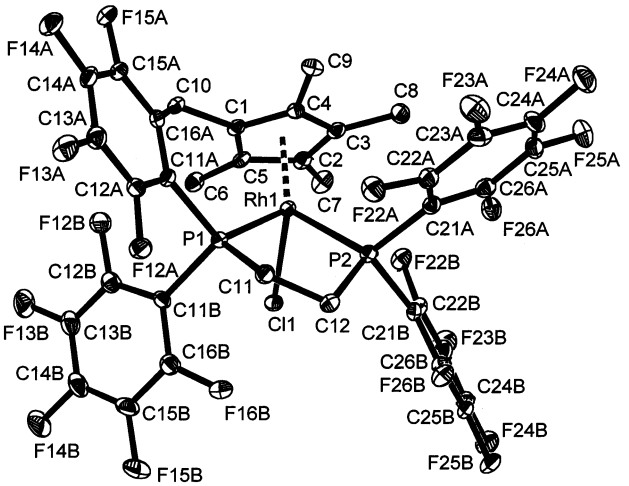


Figure 1. Structure of the $R_{Rh}S_P$ enantiomer of the cation of $[\{\eta^5,\kappa P,\kappa P\text{-}C_5Me_4CH_2C_6F_4\text{-}2\text{-}P(C_6F_5)CH_2CH_2P(C_6F_5)_2\}\text{-}RhCl]BF_4$ (**2**). Thermal ellipsoids are at the 30% probability level. Hydrogen atoms are omitted for clarity. Cp†−Rh(1) 1.842(4) Å; Rh(1)−P(1) 2.2726(11) Å; Rh(1)−P(2) 2.3306(11) Å; Rh(1)−Cl(1) 2.3879(10) Å; C(1)−C(10) 1.505(5) Å, C−CH_3(mean) 1.491(6) Å; P(1)−C(11A) 1.825(4) Å; P(1)−C(11B) 1.831(4) Å; P(1)−C(11) 1.831(4) Å; P(2)−C(21A) 1.837(4) Å; P(2)−C(21B) 1.838(4) Å; P(2)−C(12) 1.847(4) Å; Cp†−Rh(1)−P(1) 124.2(1)°; Cp†−Rh(1)−P(2) 132.6(1)°; Cp†−Rh(1)−Cl(1) 123.5(1)°; P(1)−Rh−P(2) 87.18(4)°; P(1)−Rh−Cl(1) 88.38(4)°; P(2)−Rh−Cl(1) 87.73(4)°.

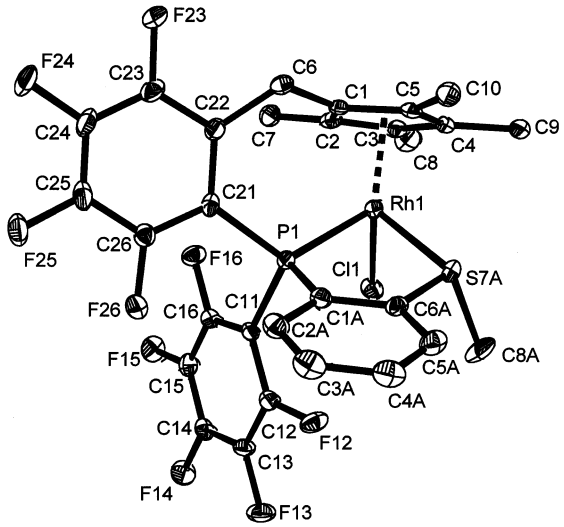


Figure 2. Structure of the $R_{Rh}R_SS_P$ enantiomer of the cation of $[\{\eta^5,\kappa P,\kappa S\text{-}C_5Me_4CH_2C_6F_4\text{-}2\text{-}P(C_6F_5)C_6H_4SMe\}\text{-}RhCl]BF_4$ (**8**). Thermal ellipsoids are at the 30% probability level. Hydrogen atoms are omitted for clarity. Cp†−Rh(1) 1.815(4) Å; Rh(1)−P(1) 2.2540(10) Å; Rh(1)−S(7A) 2.3502(10) Å; Rh(1)−Cl(1) 2.3719(11) Å; C(1)−C(6) 1.496(5) Å; C−CH_3(mean) 1.498(6) Å; P(1)−C(11) 1.825(4) Å; P(1)−C(21) 1.825(4) Å; P(1)−C(1A) 1.818(4) Å; S(7A)−C(6A) 1.793(4) Å; S(7A)−C(8A) 1.801(4) Å; Cp†−Rh−P(1) 126.6(1)°; Cp†−Rh−S(7A) 121.7(1)°; Cp†−Rh−Cl(1) 124.4(1)°; P(1)−Rh(1)−S(7A) 86.10(4)°; P(1)−Rh(1)−Cl(1) 93.19(4)°; Cl(1)−Rh(1)−S(7A) 94.71(4)°.

phosphines are considerably shorter, 2.25 to 2.28 Å. The Rh−Cl distance is the same within experimental error for **1**−**3** and **8**. The Cp†−Rh−P angles are >130° for uncoupled phosphines, but are significantly smaller for coupled phosphines (<127°). Both groups show a range of ca. 3−4°. The P−Rh−P angle of **1** is ca. 3° smaller than those of **2** and **3**, which are similar. The Rh−P distance and Cp†−Rh−P and P−Rh−P angles are consistent with those of similar uncoupled[14,29] and coupled compounds.[9] The Rh−S distance of **8** is significantly shorter than those found in $[Cp^*RhCl(thioether)]^+$ compounds (2.3645(9) to 2.4164(19) Å),[32] all of which comprise aliphatic thioethers, and this may be a consequence of the phenylene backbone of the phosphine-thioether moiety rather than coupling of the phosphine to the Cp* ligand.

The cyclopentadienyl ring of **2** shows distortion from a symmetrical η^5-C_5 ring toward an η^3,η^2-enyl-ene[33] form with the central atom of the enyl moiety attached to the tetrafluorobenzyl group. The Rh−C(1), Rh−C(4), and Rh−C(5) distances, ranging from 2.163(4) to 2.184(4) Å, are significantly shorter than the Rh−C(2) and Rh−C(3) distances (2.256(4) and 2.270(4) Å), which are approximately *trans* to P(1). Consistent with this distortion, the C(2)−C(3) (ene) distance (1.412(6) Å) is significantly shorter than the C(3)−C(4) distance (1.453(5) Å), although within 3σ of the C(2)−C(5) distance (1.444(5) Å). The enyl C(1)−C(4) and C(1)−C(5) distances are within 3σ of all other internal C−C ring distances. A similar distortion of the cyclopentadienyl ring is found in **8**. The Rh−C(3) and Rh−C(4) distances (*trans* to phosphine) of 2.241(4) and 2.219(4) Å, respectively, are up to 0.1 Å longer than Rh−C(1), Rh−C(2), and Rh−C(5) (2.134(4) to 2.171(4) Å), and the C(3)−C(4) (ene) distance (1.399(6) Å) is ca. 0.4 Å shorter than C(2)−C(3) and C(4)−C(5). The enyl C(1)−C(2) distance is within 3σ of all other internal C−C ring distances. The other enyl bond distance, C(1)−C(5), is longer than C(3)−C(4) but within experimental error of the others.

The structure of **13b** is shown in Figure 3. The complex shows the expected three-legged piano stool geometry about rhodium. The C_5 ring is symmetrical with identical Rh−C, C−C, and C−CH_3 distances. The mean Rh−C, Rh−P, and Rh−Cl distances lie within the ranges of those of other Cp^*RhCl_2(phosphine) complexes (2.17−2.20, 2.29−2.38, and 2.36−2.42 Å, respectively).[34] The three Cl−Rh−X (X = P or Cl) angles of **13b** are less than 90°, which is in contrast to other Cp^*RhCl_2-(phosphine) complexes, in which at least one Cl−Rh−X angle is greater than 90°. However, the angles are all within the range found for similar complexes (84.8−

(32) (a) Bell, M. N.; Blake, A. J.; Schröder, M.; Stephenson, T. A. *J. Chem. Soc., Chem. Commun.* **1986**, 471. (b) Albrecht, M.; Scheiring, T.; Sixt, T.; Kaim, W. *J. Organomet. Chem.* **2000**, *596*, 84. (c) Valderama, M.; Contreras, R.; Arancibia, V.; Boys, D. *J. Organomet. Chem.* **2001**, *620*, 256.

(33) (a) Dahl, L. F.; Wei, C. H. *Inorg. Chem.* **1963**, *2*, 713. (b) Bennett, M. J.; Churchill, M. R.; Gerloch, M.; Mason, R. *Nature* **1964**, *201*, 1318. (c) Mingos, D. M. P.; Minshall, P. C.; Hursthouse, M. B.; Malik, K. M. A.; Willoughby, S. D. *J. Organomet. Chem.* **1979**, *181*, 169. (d) Rigby, W.; Lee, H. B.; Bailey, P. M.; McCleverty, J. A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1979**, 387.

(34) (a) Dapporto, P.; Stoppioni, P.; Maitlis, P. M. *J. Organomet. Chem.* **1982**, *236*, 273. (b) Brost, R. D.; Bruce, G. C.; Grundy, S. L.; Stobart, S. R. *Inorg. Chem.* **1993**, *32*, 5195. (c) Keim, W.; Kraneburg, P.; Dahmen, G.; Deckers, G.; Englert, U.; Linn, K.; Spaniol, T. P.; Raabe, G.; Krüger, C. *Organometallics* **1994**, *13*, 3085. (d) Han, X.-H.; Yamamoto, Y. *J. Organomet. Chem.* **1988**, *561*, 157. (e) Fawcett, J.; Hope, E. G.; Kemmitt, R. D. W.; Paige, D. R.; Russell, D. R.; Stuart, A. M. *J. Chem. Soc., Dalton Trans.* **1998**, 3751. (f) Ma, J.-F.; Yamamoto, Y. *J. Organomet. Chem.* **1999**, *574*, 148. (g) Vézina, M.; Gagnon, J.; Villeneuve, K.; Drouin, M.; Harvey, P. D. *J. Chem. Soc., Chem. Commun.* **2000**, 1073. (h) Yamamoto, Y.; Sugawara, K. *J. Chem. Soc., Dalton Trans.* **2000**, 2896. (i) Durran, S. E.; Smith, M. B.; Slawin, A. M. Z.; Steed, J. W. *J. Chem. Soc., Dalton Trans.* **2000**, 2771.

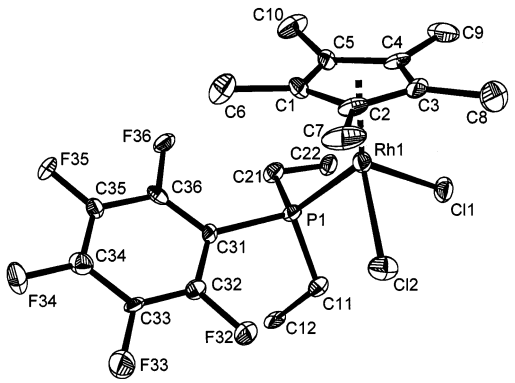


Figure 3. Structure of $[Cp^*RhCl_2\{PEt_2(C_6F_5)\}]$ (**13b**). Thermal ellipsoids are at the 30% probability level. Hydrogen atoms are omitted for clarity. Cp†−Rh(1) 1.82(2) Å; Rh(1)−P(1) 2.310(5) Å; Rh(1)−Cl(1) 2.402(4) Å; Rh(1)−Cl(2) 2.389(5) Å; Rh−C (mean) 2.180(16) Å; P(1)−C(11) 1.825(16) Å; P(1)−C(21) 1.837(16) Å; P(1)−C(31) 1.880(15) Å; Cp†−Rh(1)−P(1) 132.2(5)°; Cp†−Rh(1)−Cl(1) 123.6(5)°; Cp†−Rh(1)−Cl(2) 123.1(5)°; P(1)−Rh(1)−Cl(1) 87.25(15)°; P(1)−Rh(1)−Cl(2) 89.36(15)°; Cl(1)−Rh(1)−Cl(2) 88.44(17)°; Rh(1)−P(1)−C(11) 115.1(5)°; Rh(1)−P(1)−C(21) 117.2(6)°; Rh(1)−P(1)−C(31) 115.4(5)°; C(11)−P(1)−C(21) 103.1(7)°; C(11)−P(1)−C(31) 101.8(7)°; C(21)−P(1)−C(31) 102.2(7)°.

93.9°) and the sum of these angles for **13b**, 265.0(5)°, is similar to that found for $Cp^*RhCl_2PPh_2CH_2CH(C_6H_4\text{-}CO_2Me\text{-}4)C_6H_3(OMe\text{-}2)(OH\text{-}6)$, 265.5(6)°.[34h] The Cp†−Rh−P angle is ca. 9° larger than the Cp†−Rh−Cl angles, which is consistent with the greater bulk of the phosphine group in comparison to chloride. In comparison, the Cp†−Rh−P and Cp†−Rh−Cl angles of the triarylphosphine complex $Cp^*RhCl_2P\{C_6H_4(CF_2)_5CF_3\text{-}4\}_3$ are respectively ca. 2.5° larger and 1−3° smaller.[34e] The phosphine group of **13b** possesses pseudo-C_3 symmetry about the Rh−P axis with similar Rh−P−C and C−P−C angles and P−C distances that are identical within experimental error.

Conclusions

Intramolecular dehydrofluorinative carbon−carbon coupling provides a convenient method of preparing rhodium(III) complexes of hybrid cyclopentadienide-phosphine ligands. Results of studies of this reaction for **1**, which forms **2** then **3**, are consistent with a mechanism proposed by Hughes and co-workers for a cobalt(III) complex.[20] Loss of a proton from the Cp* ligand affords an η^4-fulvene complex or equivalent carbanion-containing zwitterion, which contains a nucleophilic methylene carbon (carbanion) which attacks a pentafluorophenyl group at an *ortho* position, leading to loss of fluoride and formation of a carbon−carbon bond. The reaction occurs rapidly in the presence of proton sponge, which acts as a base, and also fluoride, which is generated by the reaction. Thus reaction occurs on addition of much less than the stoichiometric quantity of proton sponge.

NMR studies have revealed the necessary conditions for the intramolecular dehydrofluorinative coupling of Cp* and phosphine ligands of rhodium(III) complexes. The complex must be cationic. We suggest that in neutral complexes the acidity of the hydrogen atoms of the Cp* complex is not sufficient for reaction, but the presence of the positive charge increases the acidity enough to facilitate the reaction. It is necessary for the phosphine to bear only one pentafluorophenyl group. The reaction is rapid (within 15 min) in complexes where a pentafluorophenyl group is held close to the Cp* ligand. This occurs in complexes of chelating ligands with a $P(C_6F_5)_2$ functionality (**1**, **7**) and that with a $PPh(C_6F_5)$ functionality where the pentafluorophenyl group is in a *cis* arrangement with the Cp* about the Rh−P bond (**11a**). Where only a *trans* arrangement of pentafluorophenyl and Cp* exists (as in **11b**) the presence of a labile group in the chelating ligand can allow isomerization to a complex with a *cis* arrangement followed by intramolecular coupling to occur. Thus, the coupling of Cp* to ligands such as $(C_6F_5)PhPC_6H_4SMe\text{-}2$ (**10**) leads to only one product. Coupling between Cp* and monodentate phosphines occurs at a much slower rate than reactions involving chelating ligands. This is a consequence of rotation about the Rh−P bond, which allows the pentafluorophenyl group to be distant to the Cp* ligand.

Experimental Section

General Procedures. The preparations of **4**, **5**, **6**, **9a** and **9b**, and **10** were carried out under dinitrogen using standard Schlenk line techniques and diethyl ether dried by distillation from sodium/benzophenone under dinitrogen. $PhPCl_2$ and Ph_2PCl (Aldrich) were distilled under dinitrogen before use. For all other preparations and NMR tube reactions no special precautions were taken and reagent grade solvents were used as supplied. The compounds $[Cp^*RhCl(\mu\text{-}Cl)]_2$, $NaBF_4$, proton sponge, polymer-supported fluoride (fluoride on Amberlyst A-26), 2-bromothioanisole, 2-bromoanisole, *N*,*N*-dimethylbenzylamine, Et_2PCl (Aldrich), and C_6F_5Br (Fluorochem) were used as supplied. $(C_6F_5)_2PBr$,[26] **13a**,[10] and PhNC[35] were prepared as described. $PPh_2(C_6F_5)$[36] and $PEt_2(C_6F_5)$[37] were prepared from Ph_2PCl and Et_2PCl, respectively, as described for similar compounds.[25] The ^1H, ^{19}F, and ^{31}P NMR spectra were recorded using Bruker DPX300 and 500 spectrometers. ^1H NMR (300.13 and 500.13 MHz) were referenced internally using the residual protio solvent resonance relative to $SiMe_4$ (δ 0), ^{19}F NMR (282.26 MHz) externally to $CFCl_3$ (δ 0), and ^{31}P NMR (121.45 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 are in Hz. EI mass spectra were recorded on a VG Autospec X series mass spectrometer. Elemental analyses were carried out by A.S.E.P., The School of Chemistry, Queen's University Belfast.

$(C_6F_5)_2PC_6H_4SMe\text{-}2$, 4. A solution of Bu^nLi in hexane (1.5 cm^3, 1.6 M) was added to 2-bromothioanisole (0.50 g, 2.4 mmol) in diethyl ether (50 cm^3) at 0 °C. After stirring for 1 h the solution was added dropwise to $(C_6F_5)_2PBr$ (1.07 g, 2.4 mmol) at 0 °C. The solution was allowed to warm to room temperature overnight. Water (ca. 2 cm^3) was added, and the volatiles were removed under reduced pressure. The product was obtained as a white solid on recrystallization from methanol. Yield: 0.82 g (80%). ^1H NMR ($CDCl_3$): δ 7.44 (m, 2H, C_6H_4), 7.20 (m, 1H, C_6H_4), 7.08 (m, 1H, C_6H_4), 2.51 (s, 3H, Me). ^{19}F ($CDCl_3$): δ −129.15 (m, 4F, *o*-C_6F_5), −149.40 (t, $^3J_{FF}$ = 21.2 Hz, 2F, *p*-C_6F_5), −160.30 (m, 4F, *m*-C_6F_5). ^{31}P ($CDCl_3$): δ −57.4 (quintet, $^3J_{PF}$ = 37 Hz). MS(EI) *m*/*z*: 487 (25%, $[M - H]^+$), 472 (100%, $[M - CH_4]^+$); found for $[M - H]^+$ 486.97691. $C_{19}H_6F_{10}PS$ requires 486.97682.

(35) Rigby, J. H.; Laurent, S. *J. Org. Chem.* **1998**, *63*, 6742.
(36) Kemmitt, R. D. W.; Nichols, D. I.; Peacock, R. D. *J. Chem. Soc. A* **1968**, 2149.
(37) Fild, M.; Glemser, O.; Hollenberg, I. *Naturwissenschaften* **1965**, *52*, 590.

$(C_6F_5)_2PC_6H_4OMe$-2, 5. Compound **5** was prepared similarly to $Ph_2PC_6H_4OMe$-2[38] from 2-bromoanisole (0.33 cm^3, 2.6 mmol) and $(C_6F_5)_2PBr$ (1.15 g, 2.6 mmol). Yield: 0.97 g (90%). ^1H NMR ($CDCl_3$): δ 7.43 (m, 1H, C_6H_4), 6.95 (m, 3H, C_6H_4), 3.83 (s, 3H, OMe). ^{19}F ($CDCl_3$): δ −129.95 (m, 4F, *o*-C_6F_5), −150.11 (t, $^3J_{FF}$ = 19.8 Hz, 2F, *p*-C_6F_5), −160.78 (m, 4F, *m*-C_6F_5). ^{31}P ($CDCl_3$): δ −57.0 (quintet, $^3J_{PF}$ = 36 Hz). MS(EI) *m*/*z*: 472 (87%, M^+), 365 (100%, $[M - C_6H_4OCH_3]^+$); found for M^+ 472.00897. $C_{19}H_7F_{10}PO$ requires 472.00749.

$(C_6F_5)_2PC_6H_4CH_2NMe_2$-2, 6. Compound **6** was prepared as described for **4** from *N*,*N*-dimethylbenzylamine (0.15 cm^3, 1.0 mmol) and $(C_6F_5)_2PBr$ (0.445 g, 1.0 mmol). Yield: 0.35 g (70%). ^1H NMR ($CDCl_3$): δ (m, 2H, C_6H_4), 7. ^{19}F ($CDCl_3$): δ −130.51 (m, 4F, *o*-C_6F_5), −151.84 (t, $^3J_{FF}$ = 21.2 Hz, 2F, *p*-C_6F_5), −161.48 (m, 4F, *m*-C_6F_5). ^{31}P ($CDCl_3$): δ −56.5 (quintet, $^3J_{PF}$ = 39.5 Hz). MS(EI) *m*/*z*: 499 (51%, M^+); found for M^+ 499.05579. $C_{21}H_{12}F_{10}NP$ requires 499.05477.

[Cp*RhCl{$(C_6F_5)_2PC_6H_4SMe$-2}]BF_4, 7. [{RhCl(μ-Cl)(η^5-C_5Me_5)}$_2$] (0.14 g, 0.22 mmol), **4** (0.28 g, 0.44 mol), and $NaBF_4$ (0.11 g, 1 mmol) were treated as for the synthesis of [Cp*RhCl(dfppe)][BF_4].[8] Salt **5** was obtained as an orange oil. Yield: 0.40 g (79%). Repeated attempts at recrystallization failed to give solid product, and elemental analysis could not be obtained. Characterization is based on the NMR spectroscopic data and comparison with similar compounds.[8] ^1H NMR ($CDCl_3$): δ 7.95 (m, 1H, C_6H_4), 7.73 (m, 1H, C_6H_4), 7.65 (m, 1H, C_6H_4), 7.54 (m, 1H, C_6H_4), 3.08 (s, 3H, SMe), 1.76 (d, J_{PH} = 4.7 Hz, 15H, Cp*). ^{19}F ($CDCl_3$): δ −122.05 (m, 1F, *o*-C_6F_5), −126.75 (m, 1F, *o*-C_6F_5), −127.47 (m, 1F, *o*-C_6F_5), −131.36 (m, 1F, *o*-C_6F_5), −141.96 (t, 1F, $^3J_{FF}$ = 19.8 Hz, *p*-C_6F_5), −144.39 (t, 1F, $^3J_{FF}$ = 19.8 Hz, *p*-C_6F_5), −153.69 (s, 0.8F, $^{10}BF_4^-$), −153.74 (s, 3.2F, $^{11}BF_4^-$), −154.74 (m, 1F, *m*-C_6F_5), −156.91 (m, 1F, *m*-C_6F_5), −157.84 (m, 1F, *m*-C_6F_5), −160.31 (m, 1F, *m*-C_6F_5). ^{31}P ($CDCl_3$): δ 30.2 (dm, $^1J_{RhP}$ = 174 Hz).

[{η^5,κP,κS-$C_5Me_4CH_2C_6F_4P(C_6F_5)C_6H_4SMe$}RhCl]$BF_4$, 8. Salt **7** (0.4 g, 0.35 mmol) in chloroform (50 cm^3) was treated with proton sponge (0.08 g, 0.35 mmol). The mixture was stirred for 30 min, and $NaBF_4$ (0.10 g, 0.9 mol) and water (ca. 20 cm^3) were added. The organic layer was separated and the solvent removed under reduced pressure. The resulting orange oil was washed with diethyl ether (2 × 50 cm^3) and dried in vacuo. Yield: 0.36 g (92%). Crystals for analysis and X-ray diffraction were grown from chloroform. ^1H NMR ($CDCl_3$): δ 8.08 (m, 1H, C_6H_4), 7.80 (m, 2H, C_6H_4), 7.71 (m, 1H, C_6H_4), 4.36 (dd, J_{PH} = 17.2, $^2J_{HH}$ = 17.2, Hz, 1H, CH_2), 3.03 (d, $^2J_{HH}$ = 17.2 Hz, 1H, CH_2), 2.60 (s, 3H, SMe), 2.17 (d, J_{PH} = 8.9 Hz, 3H, Me), 1.95 (d, J_{PH} = 3.5 Hz, 3H, Me), 1.65 (m, 3H, Me), 1.52 (s, 3H, Me). ^{19}F ($CDCl_3$): δ −119.73 (m, 1F), −126.32 (m, 1F), −132.89 (m, 1F), −134.35 (m, 1F), −142.43 (m, 1F), −145.50 (t, 1F, $^3J_{FF}$ = 19.8 Hz, *p*-C_6F_5), −151. 54 (m, 1F) −153.27 (s, 0.8F, $^{10}BF_4^-$), −153.33 (s, 3.2F, $^{11}BF_4^-$), −158.50 (m, 2F, *m*-C_6F_5). ^{31}P ($CDCl_3$): δ 58.6 (dm, $^1J_{Rh-P}$ = 150 Hz). Anal. Calcd for $C_{29}H_{21}BClF_{13}PRhS\cdot 2.5CHCl_3$: C, 33.57; H, 2.10. Found: C, 33.47; H, 2.07.

$(C_6F_5)PhPX$ (X = Cl or Br), 9. A 1:3 ratio of $PPh(C_6F_5)Cl$, **9a**, and $PPh(C_6F_5)Br$, **9b**, was prepared from $PhPCl_2$ and C_6F_5-MgBr in diethyl ether as described.[25] A ratio of 1:3 of **9a** to **9b** was determined by ^{31}P and ^{19}F NMR spectroscopy. ^1H ($CDCl_3$): 7.65 (2H, m), 7.40 (3H, m). ^{19}F ($CDCl_3$): −127.53 [2F, m, F_{ortho} **9b**, 75%], −129.13, F_{ortho} **9a**, 25%], −147.39 (1F, m, F_{para}), −160.36 (2F, m, F_{meta}). $^{31}P\{^1H\}$ ($CDCl_3$): 57.3 [t, $^3J_{PF}$ = 49 Hz, **9a**, 25%], 41.1 [t, $^3J_{PF}$ = 49 Hz, **9b**, 75%].

$(C_6F_5)PhPC_6H_4SMe$-2, 10. Compound **10** was prepared as for described for **4** from 2-bromothioanisole (0.50 g, 2.4 mmol) and a 1:3 mixture of **9a** and **9b** (0.83 g, 2.4 mmol). The product was purified by chromatography on a neutral deactivated alumina using 2:1:1 hexane/toluene/diethyl ether as eluant. Yield: 0.455 g (48%). ^1H NMR ($CDCl_3$): δ 7.53 (m, 5H), 7.35 (m, 2H), 7.10 (m, 1H), 6.98 (m, 1H), 2.48 (s, 3H, Me). ^{19}F (282.4 MHz, $CDCl_3$): δ −128.30 (m, 2F, *o*-C_6F_5), −150.69 (t, $^3J_{FF}$ = 20.0 Hz, 1F, *p*-C_6F_5), −160.95 (m, 2F, *m*-C_6F_5). ^{31}P ($CDCl_3$): δ −32.6 (t, $^3J_{PF}$ = 37 Hz).

[Cp*RhCl{$(C_6F_5)PhPC_6H_4SMe$-2}]BF_4, 11. [Cp*RhCl(μ-Cl)]$_2$ (0.14 g, 0.22 mmol), **10** (0.175 g, 0.44 mmol), and $NaBF_4$ (0.11 g, 1.0 mmol) were treated as for the preparation of **7**. A mixture of 43% **11a** and 57% **11b** was obtained as an orange microcrystalline solid containing 0.33 molecule of dichloromethane. Yield: 0.35 g (100%). ^1H NMR [$(CD_3)_2CO$]: δ 7.4−8.2 (m, 9H, C_6H_4 and C_6H_5), 5.56 (s, 0.66H, CH_2Cl_2), 3.09 (s, 1.3H, SMe **11a**), 2.96 (s, 1.7H, SMe **11b**), 1.73 (d, J_{PH} = 4.1 Hz, 6.45H, Cp* **11a**), 1.66 (d, J_{PH} = 4.0 Hz, 8.55H, Cp* **11b**). ^{19}F [$(CD_3)_2CO$]: δ −125.34 (d, J = 16.3 Hz, 1.1F, *o*-C_6F_5 **11b**), −127.58 (br s, 0.9F, *o*-C_6F_5 **11a**), −148.99 (m, 0.4F, *p*-C_6F_5 **11a**), −150.79 (m, 0.6F, *p*-C_6F_5 **11b**), −152.95 (s, 0.8F, $^{10}BF_4^-$), −153.00 (s, 3.2F, $^{11}BF_4^-$), −161.51 (m, 0.9F, *m*-C_6F_5, **11a**), −163.31 (m, 1.1F, *m*-C_6F_5 **11b**). ^{31}P (121.5 MHz, $(CD_3)_2CO$): δ 55.6 (dm, $^1J_{RhP}$ = 143 Hz, **11b**), 37.5 (dm, $^1J_{RhP}$ = 146 Hz, **11a**). Anal. Calcd for $C_{29}H_{27}BClF_9PSRh\cdot 0.33CH_2Cl_2$: C, 44.76; H, 3.54. Found: C, 44.85; H, 3.46.

[Cp*RhCl$_2${$PEt_2(C_6F_5)$}], 13b. $PEt_2(C_6F_5)$ (0.082 g, 0.32 mmol) in dichloromethane (20 cm^3) was added to [Cp*RhCl(μ-Cl)]$_2$ (0.10 g, 0.16 mmol) in methanol (10 cm^3) and the mixture stirred for 1 h under nitrogen. The volatiles were removed under reduced pressure, and the red solid was washed with hexane and recrystallized from hot toluene to give 0.13 g of **13b**. Yield: 70%. Crystals for analysis and X-ray diffraction studies were grown from chloroform. ^1H NMR ($CDCl_3$): δ 2.38 (m, 4H, CH_2), 1.39 (d, $^4J_{PH}$ 3.7 Hz, 15H, Cp*), 1.05 (dt, $^3J_{PH}$ 16.8 Hz, $^3J_{HH}$ 7.4 Hz, 6H, CH_2CH_3). ^{19}F ($CDCl_3$): δ −129.82 (t, $^3J_{FF}$ 16 Hz, 2F, *o*-C_6F_5), −153.25 (t, $^3J_{FF}$ = 20 Hz, 1F, *p*-C_6F_5), −163.87 (m, 2F, *m*-C_6F_5). ^{31}P ($CDCl_3$): δ 33.9 (dt, $^1J_{RhP}$ = 148 Hz, $^3J_{PF}$ = 15.5 Hz). Anal. Calcd for $C_{20}H_{25}Cl_2F_5PRh$: C, 42.50; H, 4.46. Found: C, 42.46; H, 4.38.

[Cp*RhCl{$PPh_2(C_6F_5)$}$(CNPh)$]BF_4, 14a. Salt **14a** was prepared as described for [(η^5-C_5Me_4H)RhCl{$PPh_2(C_6F_5)$}-(CNC_6H_{11})]BF_4[23] from **13a**, prepared in situ from [Cp*RhCl$_2$]$_2$ (0.200 g, 0.330 mmol) and $PPh_2(C_6F_5)$ (0.236 g, 0.670 mmol) using phenylisonitrile (0.066 g, 0.640 mmol), and obtained as an orange solid containing 0.5 molecule of dichloromethane. Yield: 0.500 g, 88%. ^1H NMR ($CDCl_3$): δ 7.86 (2H, m, C_6H_5), 7.42 (11H, m, C_6H_5), 6.91 (2H, d, J = 7.5 Hz, C_6H_5), 5.30 (s, 1H, CH_2Cl_2), 1.75 (15H, d, J_{PH} = 4.2 Hz, Cp*). ^{19}F ($CDCl_3$): δ −124.15 (2F, m, *o*-F), −143.86 (1F, m, *p*-F), −153.81 (0.8F, s, $^{10}BF_4^-$), −153.86 (3.2F, s, $^{11}BF_4^-$), −157.24 (2F, m, *m*-F). $^{31}P\{^1H\}$ ($CDCl_3$): δ 22.6 (dm, $^1J_{RhP}$ = 130 Hz). Anal. Calcd for $C_{35}H_{30}BClF_9NPRh\cdot 0.5CH_2Cl_2$: C, 49.68; H, 3.64; N, 1.63. Found: C, 49.55; H, 3.57; N, 1.49.

[Cp*RhCl{$PPh_2(C_6F_5)$}(CNC_6H_{11})]BF_4, 14b. Complex **13a** (0.110 g, 0.170 mmol) was treated with $NaBF_4$ (0.022 g, 0.200 mmol) and cyclohexylisonitrile (0.022 g, 0.200 mmol) as described for the preparation of [(η^5-C_5Me_4H)RhCl{PPh_2-(C_6F_5)}(CNC_6H_{11})]BF_4.[23] The product was obtained as a yellow oil in virtually quantitative yield. Repeated recrystallization failed to give solid product, and elemental analysis could not be obtained. Characterization is based on the NMR spectroscopic data and comparison with similar compounds.[23] ^1H NMR ($CDCl_3$): δ 7.77 (2H, m, C_6H_5), 7.47 (8H, m, C_6H_5), 4.17 (1H, m, CNCH), 2.05 (2H, m, C_6H_{11}), 1.67 (15H, d, J_{PH} = 4.2 Hz, Cp*), 1.61 (8H, m, C_6H_{11}). ^{19}F ($CDCl_3$): δ −123.79 (2F, br, *o*-F), −144.21 (1F, br, *p*-F), −153.91 (0.8F, s, $^{10}BF_4^-$), −153.96 (3.2F, s, $^{11}BF_4^-$), −157.38 (2F, br, *m*-F). $^{31}P\{^1H\}$ ($CDCl_3$): δ 22.19 (dm, $^1J_{RhP}$ = 129 Hz).

[Cp*RhCl{$PEt_2(C_6F_5)$}(CNC_6H_{11})]BF_4, 14c. Complex **13b** (0.17 g, 0.3 mmol), cyclohexylisocyanide (0.036 g, 0.33 mmol), and $NaBF_4$ (0.11 g, 1 mmol) were treated as described for the preparation of [(η^5-C_5Me_4H)RhCl{$PPh_2(C_6F_5)$}(CNC_6H_{11})]BF_4.[23] The product was obtained as a yellow oil. Repeated recrystallizations failed to give solid product, and elemental analysis could not be obtained. Characterization is based on the NMR

(38) Blin, J.; Braunstein, P.; Fischer, J.; Kickelbick, G.; Knorr, M.; Morise, X.; Wirth, T. *J. Chem. Soc., Dalton Trans.* **1999**, 2159.

spectroscopic data and comparison with similar compounds.[23] Yield: 0.18 g (83%). ^{1}H NMR ($CDCl_3$): δ 4.17 (1H, m, CNCH), 2.53 (4H, m, PCH_2), 2.09 (2H, m, C_6H_{11}), 1.85 (2H, m, C_6H_{11}), 1.72 (15H, d, J_{PH} = 3.9 Hz, Cp*), 1.45 (6H, m, C_6H_{11}), 1.32 (3H, dt, $^3J_{PH}$ = 18.7 Hz, $^3J_{HH}$ = 7.3 Hz, PCH_2CH_3), 1.16 (3H, dt, $^3J_{PH}$ = 17.4 Hz, $^3J_{HH}$ = 7.6 Hz, PCH_2CH_3). ^{19}F ($CDCl_3$): δ −128.86 (2F, m, *o*-C_6F_5), −144.86 (1F, t, $^3J_{FF}$ = 19.5 Hz, *p*-C_6F_5), −153.99 (0.8F, s, $^{10}BF_4^-$), −154.05 (3.2F, s, $^{11}BF_4^-$), −157.20 (2F, m, *m*-C_6F_5). ^{31}P ($CDCl_3$): δ 34.9 (dt, $^1J_{RhP}$ = 130 Hz, $^3J_{PF}$ = 11 Hz).

X-ray Crystallography. Crystals of **2**, **8**, and **13b** were obtained from chloroform. Crystal data are listed in Table 2. Diffraction data were collected on a Bruker SMART diffractometer using the SAINT-NT[39] 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.[40] The structures were solved using direct methods and refined with the program package SHELXTL,[41] 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 $w^{-1} = [\sigma^2|Fo|^2 + (g1P)^2 + (g2P)]$ 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: **2** 190808, **8** 155415, **13b** 190807).

Acknowledgment. We are grateful to Prof. R. P. Hughes, Prof. D. S. Glueck, and Dr P. Bhattacharyya for helpful discussions. We thank the E.P.S.R.C. for support (to R.M.B.).

Supporting Information Available: A listing of atomic coordinates, anisotropic displacement parameters, and bond distances and bond angles for **2**·2$CHCl_3$, **8**·3$CHCl_3$, and **13b**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020612N

(39) *SAINT-NT*; Bruker AXS Inc.: Madison, WI, 1998.
(40) Sheldrick, G. M. *SADABS*; University of Göttingen: Germany 1996.
(41) Sheldrick, G. M. *SHELXTL*; Bruker AXS Inc.: Madison, WI, 1998.