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Journal of Fluorine Chemistry 128 (2007) 943–951
JOURNAL OF FLUORINE CHEMISTRY
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Pentamethylcyclopentadienyl rhodium(III) trifluorovinyl phosphine complexes and attempted intramolecular dehydrofluorinative coupling of pentamethylcyclopentadienyl and trifluorovinyl phosphine ligands

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Received 30 January 2007; received in revised form 3 April 2007; accepted 3 April 2007
Available online 7 April 2007

Abstract

The trifluorovinyl phosphine complexes $[Cp^*RhCl_2\{PR_{3-x}(CF{=}CF_2)_x\}]$ (**1** $x = 1$, **a** R = Ph, **b** Pr^i, **c** Et; **2** $x = 2$, R = Ph) have been prepared by treatment of $[Cp^*RhCl(\mu\text{-}Cl)]_2$ with the relevant phosphine. The salt $[Cp^*RhCl(CNBu^t)\{PPh_2(CF{=}CF_2)\}]BF_4$, **3**, was prepared by addition of Bu^tNC to **1a** in the presence of $NaBF_4$. The salt $[Cp^*RhCl\{\kappa P,\kappa S\text{-}(CF_2{=}CF)PPh(C_6H_4SMe\text{-}2)\}]BF_4$ was prepared as a mixture of *cis* (**5a**) and *trans* (**5b**) isomers by treatment of $[Cp^*RhCl(\mu\text{-}Cl)]_2$ with the phosphine-thioether $(CF_2{=}CF)PPh(C_6H_4SMe\text{-}2)$, **4**, in the presence of $NaBF_4$. The structures of **1a–c** and **5a** have been determined by single-crystal X-ray diffraction. Intramolecular dehydrofluorinative carbon–carbon coupling between pentamethylcyclopentadienyl and trifluorovinylphosphine ligands of **1a**, **3** and **5** has been attempted. No reaction was observed on treatment of the neutral complex $[Cp^*RhCl_2\{PPh_2(CF{=}CF_2)\}]$, **1a**, with proton sponge, however, **5a** underwent dehydrofluorinative coupling to yield $[\{\eta^5,\kappa P,\kappa S\text{-}(C_5Me_4CH_2CF{=}CF)PPh(C_6H_4SMe\text{-}2)\}RhCl]BF_4$, **6**. Other reactions, in particular addition of HF across the vinyl bonds of **5**, occurred leading to a mixture of products. The cation of **3** underwent similar reactions.

Keywords: Trifluorovinylphosphines; Rhodium; Pentamethylcyclopentadienyl; C–F bond cleavage; Dehydrofluorinative carbon–carbon coupling

1. Introduction

In contrast to fluorinated aryl and alkyl phosphines [1–10], fluoroalkenylphosphines have received relatively little attention [11–13]. Following the development of a convenient synthetic route to $[CF_2{=}CF]^-Li^+$ from the readily available HFC-134a (CF_3CH_2F), and subsequent syntheses of trifluorovinylphosphines $R_{3-x}P(CF{=}CF_2)_x$ [14–16], a number of complexes of trifluorovinylphosphines with molybdenum [15], platinum [15,17] and gold [15] have been reported over the past decade.

The trifluorovinyl substituent is known to be susceptible to nucleophilic attack [16,18], with substitution of the fluorine atom *trans* to the phosphorus atom, which allows the opportunity for functionalizing the phosphine. One attractive possibility is the intramolecular coupling of metal-bound cyclopentadienyl and trifluorovinylphosphine ligands. Rhodium complexes of chelating bi- and tri-functional cyclopentadienyl–phosphine ligands have been synthesized by intramolecular dehydrofluorinative carbon–carbon coupling [19–24]. These ligands contain a three-carbon atom linkage between the cyclopentadienyl ring and the phosphorus atom. To date the complexes synthesized by this method have been restricted to those in which two of the carbon atoms in the linkage are part of a fluoroaromatic group: tetrafluorophenyl [19–21,24], fluorophenyl [22] or trifluoropyridyl [23]. The coupling occurs on addition of proton sponge to the salts $[Cp^*RhCl(PL)]^+$ (PL = chelating fluoroarylphosphine) or $[Cp^*RhCl_L(P)]^+$, or by heating a benzene solution of $[Cp^*RhCl(\mu\text{-}Cl)]_2$ and PL. The reaction is postulated to proceed

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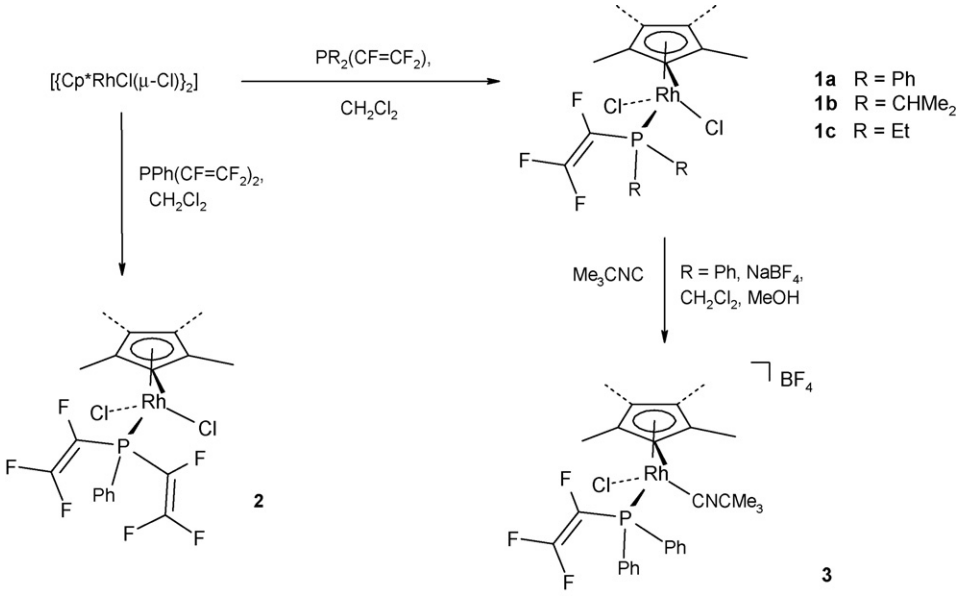
doi:10.1016/j.jfluchem.2007.04.003



Scheme 1.

by generation of a nucleophilic *exo* methylene carbon atom by loss of a proton from the pentamethylcyclopentadienyl ring of the cation and subsequent attack at the *ortho* position of a fluoroarene [19,25]. If this mechanism is correct then the trifluorovinyl group would be suitable as a substituent leading to a three-carbon atom linkage in which two of the carbon atoms are part of an alkene.

Here we report rhodium piano stool complexes comprising trifluorovinylphosphines and an investigation into the intramolecular coupling of η^5-pentamethylcyclopentadienyl to phosphine and phosphine–thioether ligands bearing trifluorovinyl substituents.

2. Results and discussion

2.1. Synthesis and characterization

Cleavage of the chloride bridges of the rhodium(III) dimer $[Cp^*RhCl(\mu\text{-}Cl)]_2$ with two equivalents of the trifluorovinyl phosphines $PR_2(CF{=}CF_2)$ (R = Ph [15], Pr^i [16], Et [16]), afforded deep orange to red complexes of formula $[Cp^*RhCl_2\{PR_2(CF{=}CF_2)\}]$ (R = Ph **1a**, Pr^i **1b**, Et **1c**) in *ca.* 50% yield (Scheme 1). Complexation of the phosphines is confirmed by the $^{31}P\{^1H\}$ NMR spectra (Table 1), which exhibit doublet resonances with coupling constants of *ca.*

Table 1
$^{31}P\{^1H\}$ and $^{19}F\{^1H\}$ NMR spectroscopic data for compounds **1–7**

	δ_P	$^1J_{RhP}$ (Hz)	$\Delta\delta_P$	$^2J_{PFg}$ (Hz)	$^3J_{PFt}$ (Hz)	$^3J_{PFc}$ (Hz)	δ_{Ft}	δ_{Fc}	δ_{Fg}	$^2J_{FtFc}$ (Hz)	$^3J_{FgFt}$ (Hz)	$^3J_{FgFc}$ (Hz)
1a	21.2	149	47.4	73	8	10	−82.1	−98.9	−174.2	39	29	116
1b	35.7	147	43.4	29	11	8	−87.7	−104.0	−176.8	56	32	113
1c	24.8	147	57.1	40	10	10	−85.4	−104.9	−182.0	54	31	114
2	13.7	152	65.5	75	–	–	−79.9	−97.3	−176.1	32	29	117
3[a]	27.8	142	54.0	84	0	8	−79.5	−98.1	−174.5	36	31	117
4	−34.2	–	–	19	9	58	−84.9	−106.8	−177.8	44	30	124
5a[b]	39.0	144	73.2	76	–	–	−79.3	−97.1	−174.8	40	31	119
5b[b]	44.3	141	78.5	107	–	–	−76.7	−94.0	−174.5	[c]	[c]	118
6[d]	44.0	132	–	<5	<5	–	−89.2	–	−154.7[e]	–	<5	–
7	56.1	125	–	38	0	–	−66.0[f,g]	–	−204.5[g,h]	–	14	–
	52.9	147	–	25	0	–	−69.2[f,g]	–	−204.1[g,h]	–	14	–

Recorded in $CDCl_3$. F*t*, F*c* and F*g* represent the fluorine atoms *trans*, *cis* and *geminal* to phosphorus, respectively.

[a] ^{19}F NMR (282.26 MHz, $CDCl_3$): $\delta_F(BF_4) = -153.07$ (0.8F, s, $^{10}BF_4^-$), −153.12 (3.2F, s, $^{11}BF_4^-$).

[b] ^{19}F NMR (282.26 MHz, $CDCl_3$): $\delta_F(BF_4) = -153.64$ (0.8F, s, $^{10}BF_4^-$), −153.70 (3.2F, s, $^{11}BF_4^-$).

[c] The coupling constants could not be obtained due to the low intensity of the resonances.

[d] ^{19}F NMR (282.26 MHz, $CDCl_3$): $\delta_F(BF_4) = -153.10$ (0.8F, s, $^{10}BF_4^-$), −153.20 (3.2F, s, $^{11}BF_4^-$).

[e] *cf. trans*-$Ph_2PCF{=}CFBu^n$ δ_F: −159.1 ($^2J_{PF}$ = 5 Hz) [16].

[f] CF_3. *cf.* $[(PhCH_2)Ph_2P(CHFCF_3)]^+$: δ −68.8 ($^3J_{FF}$ = 16 Hz, $^3J_{HF}$ = 6 Hz, $^3J_{PF}$ = 4 Hz) [27].

[g] Coupling to hydrogen evident in the ^{19}F NMR spectrum.

[h] CHF. The integration for each resonances is 1/3 of that for the respective CF_3 resonance. *cf.* $[(PhCH_2)Ph_2P(CHFCF_3)]^+$: δ −214.4 (CHF, $^2J_{HF}$ = 41 Hz, $^2J_{PF}$ = 57 Hz, $^3J_{FF}$ = 16 Hz) [27].

150 Hz, which are typical for rhodium complexes of formula [Cp*RhCl$_2$(PR$_3$)] that contain fluoro-organo substituted phosphines. The values of δ_P are shifted to higher frequencies by 43–57 ppm to those of the non-coordinated ligands. This coordination chemical shift ($\Delta\delta_P$) is somewhat larger than that usually observed (*ca*. 35 ppm) for [Cp*RhCl$_2$(PR$_3$)] systems where PR$_3$ contains non-fluorinated groups, for example, $\Delta\delta_P$ for [Cp*RhCl$_2${PPh$_2$(CH=CH$_2$)}] is 37.8 ppm [26]. It is however noted that complexes of other fluoro-organo substituted phosphines also display large $\Delta\delta_P$ values, for example $\Delta\delta_P$ for [Cp*RhCl$_2${PPh$_2$(C$_6$F$_5$)}] is 45.1 ppm [21]. In each complex coupling of the phosphorus atom to the three fluorine nuclei is also observed. The largest coupling is between phosphorus and the geminal fluorine atom. This is in contrast to the non-coordinated ligands for which the largest coupling is between phosphorus and the *cis* fluorine atom [15,16]. The ^{19}F NMR spectra of **1a**–**c** each display three doublet of doublet of doublet resonances at δ_F *ca*. −85, −100 and −180, assigned to the fluorine atoms respectively *trans*, *cis* and *geminal* to the phosphorus atom. The magnitude of the *trans* three-bond coupling between the *cis* and *geminal* fluorine atoms (*ca*. 115 Hz) is considerably larger than those of the other two fluorine–fluorine couplings (30–60 Hz). The identities of the complexes were confirmed by single-crystal X-ray diffraction studies (Figs. 1–3). Crystallographic data are presented in Table 2. There are two independent molecules with similar geometry in the unit cell of complex **1a**, and the structure of complex **1c** exhibits disorder with two sites for each chlorine atom and the phosphorus atom, resulting in two sites for all atoms bonded to the phosphorus centre. All three structures possess large thermal parameters which preclude detailed comparison of bond lengths and angles (Table 3), but the connectivity and piano-stool geometry are clear, and it is noted that the Cp*–Rh, Rh–P and Rh–Cl distances and Cp*–Rh–Cl, Cp*–Rh–P, P–Rh–Cl and Cl–Rh–Cl angles are consistent with those of other

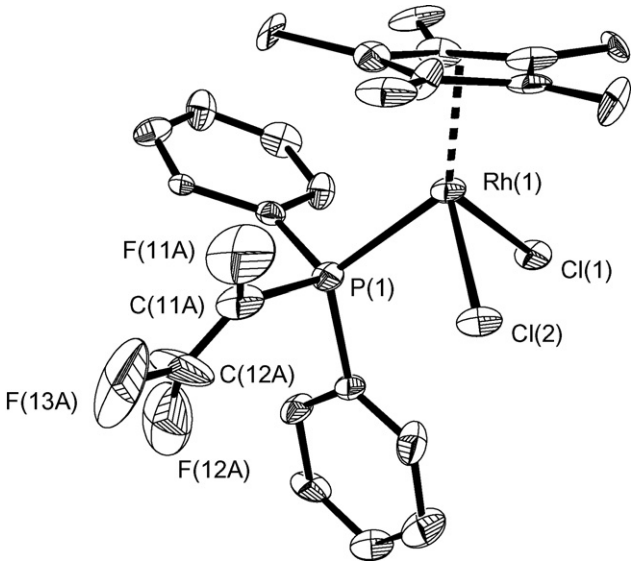


Fig. 1. Structure of molecule A of [Cp*RhCl$_2${PPh$_2$(CF=CF$_2$)}] **1a**. Thermal ellipsoids are at the 30% probability level. Hydrogen atoms are omitted for clarity.

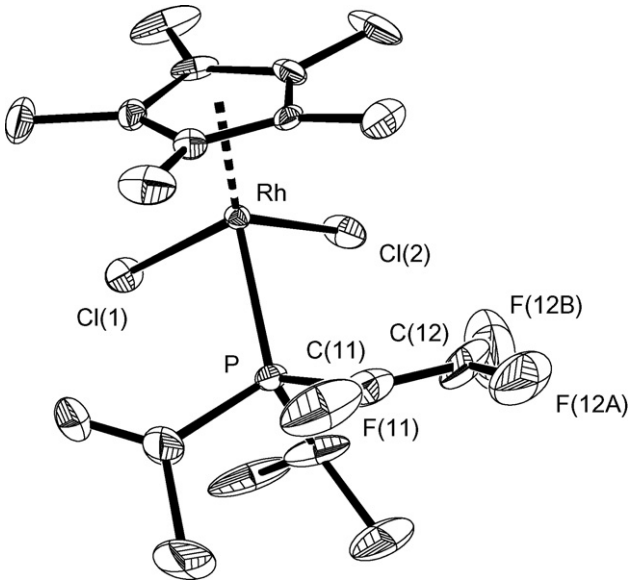


Fig. 2. Structure of [Cp*RhCl$_2${PPr$^i_2$(CF=CF$_2$)}] **1b**. Thermal ellipsoids are at the 10% probability level. Hydrogen atoms are omitted for clarity.

[Cp*RhCl$_2$(phosphine)] complexes [19] and the distances and angles of the trifluorovinyl group are similar to those of *cis*-[PtCl$_2${PPh$_2$(CF=CF$_2$)}$_2$] and [AuCl{PPh$_2$(CF=CF$_2$)}]$_2$ [15].

Cleavage of the chloride bridges of [Cp*RhCl(μ-Cl)]$_2$ with two equivalents of the trifluorovinyl phosphine PPh(CF=CF$_2$)$_2$ [15] produced the orange complex [Cp*RhCl$_2${PPh(CF=CF$_2$)$_2$}] **2** in 58.5% yield (Scheme 1). This is in contrast to the non-complexation of the analogous pentafluorophenyl phosphine PPh(C$_6$F$_5$)$_2$ [19], strongly suggesting that the CF=CF$_2$ group is

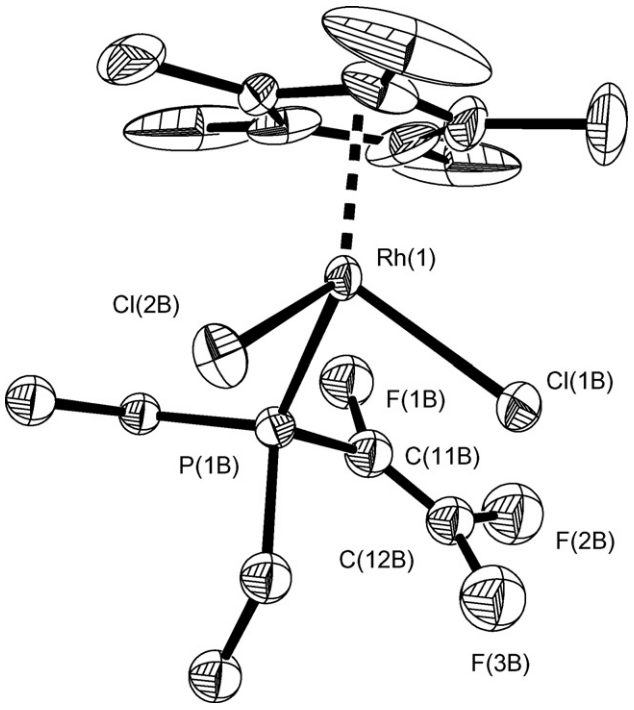


Fig. 3. Structure of [Cp*RhCl$_2${PEt$_2$(CF=CF$_2$)}] **1c**. Thermal ellipsoids are at the 30% probability level. Only one of each pair of disordered sites is shown. Hydrogen atoms are omitted for clarity.

Table 2
Crystallographic data for [Cp*RhCl$_2${PPh$_2$(CF=CF$_2$)}] (**1a**), [Cp*RhCl$_2${PPr$^i_2$(CF=CF$_2$)}] (**1b**), [Cp*RhCl$_2${PEt$_2$(CF=CF$_2$)}] (**1c**) and *cis*-[Cp*RhCl{κP,κS-(CF$_2$=CF)PPhC$_6$H$_4$SMe-2}]BF$_4$ (**5a**)

	1a	**1b**	**1c**	**5a**
Formula	$C_{24}H_{25}Cl_2F_3PRh$	$C_{18}H_{29}Cl_2F_3PRh$	$C_{16}H_{25}Cl_2F_3PRh$	$C_{25}H_{27}BClF_7PRhS$
Formula weight	575.22	507.19	479.14	672.67
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	8.705(8)	8.268(2)	8.309(2)	10.033(5)
b (Å)	18.312(17)	35.068(2)	33.122(6)	10.503(5)
c (Å)	15.076(14)	8.512(2)	8.080(2)	26.096(12)
β (°)	98.611(15)	117.71(2)	117.35(2)	99.180(8)
V (Å^3)	2376(4)	2185.2(7)	1975.1(8)	2714(4)
Z	4	4	4	4
T (K)	153(2)	293(2)	293(2)	153(2)
D_c (g cm^{-3})	1.608	1.542	1.611	1.646
Crystal size (mm)	0.20 × 0.14 × 0.08	0.30 × 0.30 × 0.03	0.30 × 0.30 × 0.03	0.45 × 0.23 × 0.18
μ (mm^{-1})	1.044	1.123	1.2	0.926
2θ range (°)	2.74 → 50.00	4.64 → 50.00	5.96 → 50.00	3 → 50.00
Total reflections	21717	4094	3464	24849
Unique reflections (R_{int})	8307 (0.0922)	3827 (0.0289)	3459 (0.0927)	4767 (0.0622)
Observed reflections [$I > 2\sigma(I)$]	5546	2262	2099	4261
Parameters	569	235	235	340
Final R indices [$I > 2\sigma(I)$]	R_1 0.0963, wR_2 0.1512	R_1 0.0679, wR_2 0.1588	R_1 0.0753, wR_2 0.1818	R_1 0.1136, wR_2 0.2747
R indices (all data)	R_1 0.2206, wR_2 0.2674	R_1 0.1280, wR_2 0.1947	R_1 0.1289, wR_2 0.2097	R_1 0.1205, wR_2 0.2772
Weighting scheme	$w = 1/[\sigma^2(F_o^2)+ \{0.0889(F_o^2+2F_c^2)/3\}^2+ 49.5539(F_o^2+2F_c^2)/3]$	$w = 1/[\sigma^2(F_o^2)+ \{0.0926(F_o^2+2F_c^2)/3\}^2+ 5.6174(F_o^2+2F_c^2)/3]$	$w = 1/[\sigma^2(F_o^2)+ \{0.1152(F_o^2+2F_c^2)/3\}^2]$	$w = 1/[\sigma^2(F_o^2)+ \{0.0103(F_o^2+2F_c^2)/3\}^2+ 130.8878(F_o^2+2F_c^2)/3]$
Max., min. $\Delta\rho$ (eÅ^{-3})	1.613, −2.259	0.851, −0.990	0.875, −0.885	3.142, −1.555
Goodness of fit on F^2	1.120	1.007	1.041	1.216
Flack parameter	−0.01(9)	–	–	–

Estimated standard deviations are given in parentheses. Data were collected with graphite monochromated Mo Kα radiation (λ = 0.71073 Å).

Table 3
Selected bond distances (Å) and angles (°) for [Cp*RhCl$_2${PPh$_2$(CF=CF$_2$)}] (**1a**), [Cp*RhCl$_2${PPr$^i_2$(CF=CF$_2$)}] (**1b**) and [Cp*RhCl$_2${PEt$_2$(CF=CF$_2$)}] (**1c**)

	1a		**1b**	**1c**	
	Molecule A	Molecule B			
Cp*–Rh	1.809(2)	1.811(2)	1.813(4)	1.797(12)	
Rh–P	2.313(6)	2.316(5)	2.3317(8)	2.421(6)	2.162(6)
Rh–Cl	2.400(5), 2.419(6)	2.396(6), 2.427(5)	2.3966(11), 2.3663(13)	2.381(7), 2.396(5)	2.363(7), 2.440(5)
P–C(C_2F_3)	1.768(19)	1.803(18)	1.802(4)	1.85(2)	1.83(3)
P–C	1.81(2), 1.860(19)	1.76(2), 1.78(2)	1.775(6), 1.863(5)	1.82(2), 1.78(2)	1.82(3), 1.78(2)
(P)C=C(F_2)	1.23(3)	1.23(3)	1.320(9)	1.26(3)	1.26(4)
C–F_{gem}	1.50(2)	1.46(2)	1.479(9)	1.37(3)	1.36(3)
C–F_{cis}	1.27(2)	1.37(2)	1.424(7)	1.31(4)	1.32(3)
C–F_{trans}	1.38(3)	1.295(19)	1.177(11)	1.34(4)	1.33(3)
Cp*–Rh–P	133.1(6)	133.2(6)	131.6(8)	130.4(5)	132.9(5)
Cp*–Rh–Cl	122.3(6), 121.5(6)	122.6(6), 120.9(5)	123.1(8), 121.8(8)	125.7(5), 126.7(5)	120.8(5), 130.4(5)
P–Rh–Cl	85.54(19), 87.8(2)	85.6(2), 89.06(19)	89.79(3), 90.42(4)	86.0(2), 81.9(2)	90.4(2), 88.3(3)
Cl–Rh–Cl	95.6(2)	94.3(2)	87.97(5)	92.2(3)	90.7(3)
Rh–P–C(C_2F_3)	110.0(7)	109.8(7)	111.92(15)	114.0(8)	112.3(8)
Rh–P–C	111.1(7), 120.9(7)	113.9(6), 121.8(7)	118.06(18), 114.04(15)	117.7(7), 114.3(7)	120.4(8), 115.6(8)
P–C=C	133.3(16)	137.8(16)	127.2(6)	130(2)	132(2)
P–C–F_{gem}	120.0(15)	111.2(12)	112.0(4)	112.3(15)	112.3(17)
C=C–F_{cis}	121(3)	121.4(16)	117.3(5)	127(3)	125(3)
C=C–F_{trans}	122(2)	130(2)	107.5(7)	122(3)	123(3)
F_{cis}–C–F_{trans}	117(3)	108.7(18)	134.5(6)	111(2)	111(2)

Estimated standard deviations are given in parentheses. Cp* represents the centroid of the C_5 ring. There is disorder in complex **1c** with 50% occupancy of two sites for the chlorine atoms and all the atoms of the phosphine.

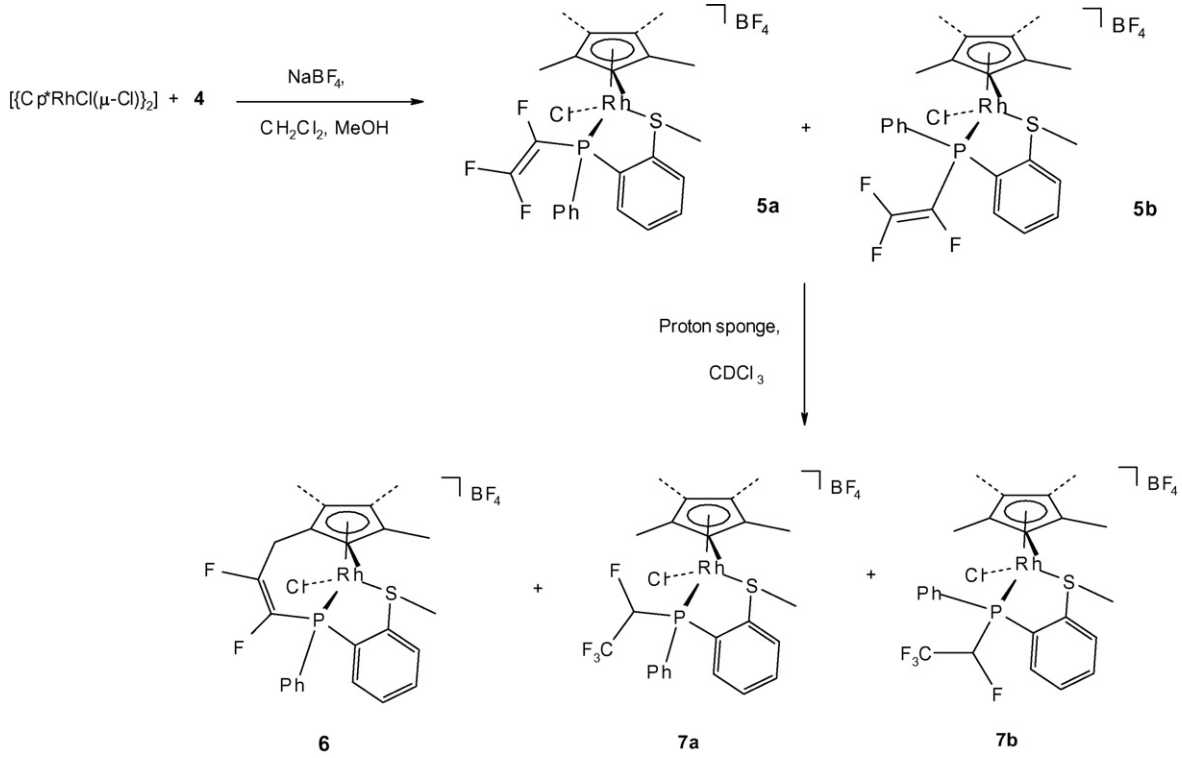
less sterically demanding than the C_6F_5 group. Complex **2** was characterized by elemental analysis and multinuclear NMR spectroscopy. The ^{31}P and ^{19}F NMR spectroscopic data (Table 1) are consistent with those of **1a–c**, although the resonances are broader, presumably due to hindered rotation about the Rh–P and P–C_2F_3 bonds, which obscures some of the phosphorus–fluorine coupling.

The yellow salt [Cp*RhCl(CNBu^t){PPh_2(CF=CF_2)}]BF_4, **3**, was prepared in almost quantitative yield by addition of a stoichiometric amount of *tert*-butylisonitrile to **1a** in the presence of an excess of sodium tetrafluoroborate (Scheme 1). (Treatment of **1a** with an excess of *tert*-butylisonitrile lead to displacement of the phosphine.) The NMR spectra of **3** were similar to those of **1a** except for additional resonances arising from the *tert*-butylisonitrile ligand and tetrafluoroborate anion in the ^1H and ^{19}F NMR spectra, respectively.

The phosphine-thioether (CF$_2$=CF)PPh(C$_6$H$_4$SMe-2), **4**, was prepared in 14.5% yield by the addition of [CF_2=CF]$^-$Li$^+$ [15] to (MeSC$_6$H$_4$-2)PPhCl, prepared *in situ* from MeSC$_6$H$_4$Li and $PPhCl_2$, in diethyl ether at low temperature. The identity of **4** was confirmed by mass spectrometry and multinuclear NMR spectroscopy. The $^{31}P\{^1H\}$ and ^{19}F NMR spectroscopic data (Table 1) are similar to those of $Ph_2P(CF{=}CF_2)$ [15]. The salt [Cp*RhCl{κP,κS-(CF$_2$=CF)PPh(C$_6$H$_4$SMe-2)}]BF_4, **5**, was prepared as a mixture of isomers by treatment of [Cp*RhCl(μ-Cl)]$_2$ with **4** in the presence of an excess of sodium tetrafluoroborate (Scheme 2). Salt **5** contains three stereogenic centres, at rhodium, phosphorus and sulfur, giving rise to four pairs of enantiomers. The NMR spectral data indicate the presence of two geometric isomers, presumably two pairs of enantiomers, in the ratio of *ca.* 8 to 1. NOE experiments indicate that, as for [Cp*RhCl{κP,κS-(C$_6$F$_5$)PPh(C$_6$H$_4$SMe-2)}]BF_4 [19], only those isomers in which the thioether methyl group is *trans* to the pentamethylcyclopentadienyl ligand are observed. The two pairs of enantiomers, **5a** and **5b**, differ in the relative positions of the trifluorovinyl group and pentamethylcyclopentadienyl ligand. The $^{19}F\{^1H\}$-HOESY NMR spectrum shows a correlation between the α-fluorine atom and the pentamethylcyclopentadienyl ligand of the major pair of isomers, **5a**, but not for the minor pair, **5b**, strongly suggesting that in the major isomers the trifluorovinyl group and pentamethylcyclopentadienyl ligand are *cis* in **5a**. This disposition is confirmed by the rapid reaction of **5a** on addition of proton sponge (*vide infra*). The identity of **5a** was confirmed by a single-crystal X-ray diffraction study (Fig. 4). Crystallographic data are presented in Table 2. Unfortunately the quality of the data does not allow detailed comparison of bond lengths and angles (Table 4) with other [Cp*RhCl(PS)]$^+$ complexes, but the connectivity and piano-stool geometry are clear.

2.2. Attempted dehydrofluorinative carbon–carbon coupling

It has been found that dehydrofluorinative coupling between pentamethylcyclopentadienyl and polyfluoroarylphosphines occurs only in cations, and most cleanly and rapidly in complexes of chelating phosphine ligands [19]. In order to determine whether dehydrofluorinative coupling can occur in trifluorovinyl complexes, and, if so, its scope, the salts **5**, which contains a chelating trifluorovinylphosphine, and **3**, which contains a monodentate trifluorovinylphosphine, and the



Scheme 2.

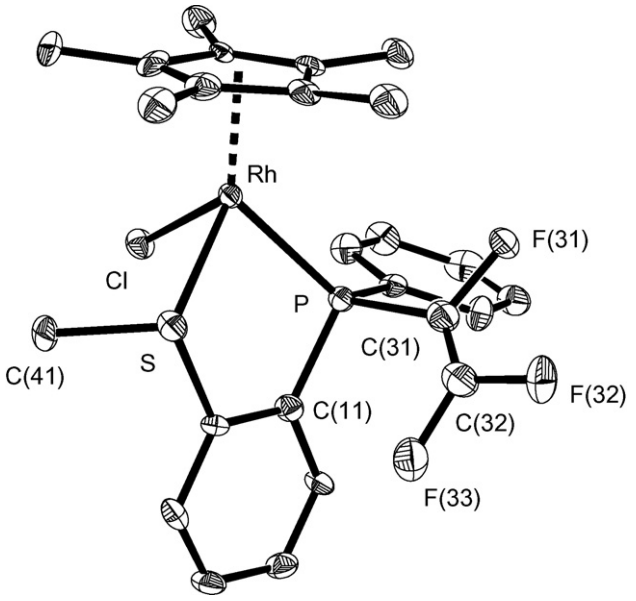


Fig. 4. Structure of the $S_{Rh}S_SR_P$ stereoisomer of the cation of *cis*-[Cp*RhCl{κP,κS-(CF_2═CF)$PPhC_6H_4SMe$-2}]BF_4 **5a**. Thermal ellipsoids are at the 30% probability level. Hydrogen atoms are omitted for clarity.

neutral complex **1a** were chosen for study. Repeated trial reactions between the selected complexes and proton sponge were monitored by *in situ* ^1H, $^{19}F\{^1H\}$, ^{19}F and $^{31}P\{^1H\}$ NMR spectroscopy. The products were also analysed by high-resolution mass spectrometry.

Addition of proton sponge to **5** led to the rapid disappearance of resonances assigned to the *cis* isomer **5a** and the appearance of many new resonances in the ^1H, $^{19}F\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra indicating a mixture of products. The ^1H NMR spectra were far from simple with overlapping and coincident resonances, and further complicated by resonances arising from proton sponge, and so were not informative regarding the identity of the products. The $^{19}F\{^1H\}$, ^{19}F and $^{31}P\{^1H\}$ NMR spectra were simpler and, in combination with the mass spectral data, allowed the tentative identification of the product of dehydrofluorinative coupling, **6**, and *cis* and *trans* isomers of **7**, the product arising from HF addition across the vinyl bond of **5** (Table 1, Scheme 2). The identification of **6** is supported by comparison of the data for the geminal fluorine resonance with those of *trans*-Ph_2PCF═$CFBu^n$ (Table 1) [16]. The identification of the two isomers of **7** was supported by comparison of the ^{19}F NMR spectral data with those of $[(PhCH_2)Ph_2P(CHFCF_3)]^+$ (Table 1) [27].

Table 4
Selected bond distances (Å) and angles (°) for *cis*-[Cp*RhCl{κP,κS-(CF_2═CF)$PPhC_6H_4SMe$-2}]BF_4 (**5a**)

Cp*–Rh	1.820(14)	Rh–P	2.303(4)
Rh–S	2.366(4)	Rh–Cl	2.409(4)
P–C(C_6H_4SMe)	1.774(15)	P–C(C_6H_5)	1.811(14)
S–C(Me)	1.800(16)	P–C(C_2F_3)	1.847(17)
C═C	1.27(2)	C–F_{gem}	1.358(18)
C–F_{cis}	1.306(19)	C–F_{trans}	1.33(2)
Cp*–Rh–P	131.1(4)	Cp*–Rh–S	127.6(4)
Cp*–Rh–Cl	122.4(4)	P–Rh–S	82.83(14)
P–Rh–Cl	90.27(14)	S–Rh–Cl	89.34(14)
Rh–P–C(C_6H_4SMe)	105.6(5)	Rh–P–C(C_6H_5)	120.8(5)
Rh–P–C(C_2F_3)	115.6(5)	Rh–S–C(Me)	109.0(6)
P–C═C	130.8(14)	P–C–F_{gem}	110.7(11)
C═C–F_{cis}	127.5(17)	C═C–F_{trans}	122.9(16)
F_{cis}–C–F_{trans}	109.3(15)		

Estimated standard deviations are given in parentheses. Cp* represents the centroid of the C_5 ring.

An attempt was made to verify the assignment of **7a** and **7b** by an *in situ* NMR experiment in which **5**, in chloroform, was treated with wet Bu_4^nNF in tetrahydrofuran, as a mild source of HF. A rapid reaction producing a complicated mixture was evident, with the resonances assigned to **5** disappearing and several new resonances being observed in the $^{19}F\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra. The $^{19}F\{^1H\}$ NMR spectrum indicates the addition of HF across the vinyl bond, but the $^{31}P\{^1H\}$ NMR spectrum indicates that the major products result from dissociation of the phosphine ligand.

The reaction between $[Cp^*RhCl(\mu\text{-}Cl)]_2$ and **4** in refluxing benzene yielded a more complicated mixture of products than that between **5** and proton sponge. The mass spectral and NMR spectroscopic data indicated that the cation of **6** was formed, but the other products could not be identified. Attempts to separate the products by fractional crystallization were unsuccessful.

Addition of proton sponge to **3** led to the disappearance of its resonances and the appearance of numerous signals consistent with a reaction giving a mixture of products. Consistent with reactions of cationic rhodium complexes of chelating and monodentate phosphines [19] the reaction was slower than for **5**. None of these were positively identified, but the ^{19}F NMR spectrum displays resonances similar to those of **6** and **7** in addition to many others.

Complex **1a** was found not to undergo intramolecular dehydrofluorinative coupling on treatment with proton sponge, even over prolonged periods, which is consistent with the lack of reaction previously found for the neutral complex $[Cp^*RhCl_2\{PPh_2(C_6F_5)\}]$ [19].

3. Conclusion

Intramolecular dehydrofluorinative coupling has been achieved between the pentamethylcyclopentadienyl ligand and trifluorovinyl substituents of phosphines in cationic rhodium complexes. However, a mixture of products containing alkene and alkane linkages resulted due to addition of hydrogen fluoride across the vinyl double bond.

4. Experimental

4.1. Instrumentation

The ^1H, ^{13}C, ^{19}F and ^{31}P NMR spectra were recorded using Bruker DPX300 or DPX200 spectrometers. ^1H (300.01 or 200.20 MHz) were referenced internally using the residual protio solvent resonance relative to $SiMe_4$ (δ 0), ^{13}C (50.29 MHz) externally to $SiMe_4$ (δ 0), ^{19}F (282.26 or

188.31 MHz) externally to $CFCl_3$ (δ 0) and ^{31}P (121.45 or 81.03 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 hertz. IR spectra were recorded on Perkin-Elmer RX I or Nicolet Nexus Fourier transform spectrometers. Raman spectra were recorded on a Nicolet Nexus Fourier transform spectrometer. EI and LSIMS 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 and Chemical Engineering, Queen's University Belfast, and by the Microanalytical Service, U.M.I. S.T.

4.2. Materials

The compounds *tert*-butylisonitrile, sodium tetrafluoroborate, proton sponge (Aldrich) and CF_3CH_2F (ICI Klea) were used as supplied. $PPhCl_2$ (Aldrich) was distilled under reduced pressure and stored under dinitrogen. The compounds $[Cp^*RhCl(\mu\text{-}Cl)]_2$ [28], $PPh_2(CF{=}CF_2)$ [15], $PPh(CF{=}CF_2)_2$ [15] and $MeSC_6H_4Br$-2 [29] were prepared as previously described. Diethyl ether was dried by storage over sodium wire. The preparation of phosphine-thioether **4** was performed under dinitrogen.

4.3. Preparations

4.3.1. *[Cp*RhCl$_2${PPh$_2$(CF=CF$_2$)}] (**1a**)*

$[Cp^*RhCl(\mu\text{-}Cl)]_2$ (0.142 g, 0.23 mmol) was added to a solution of $PPh_2(CF{=}CF_2)$ (0.123 g, 0.46 mmol) in dichloromethane (15 cm^3) under argon. The orange-brown solid dissolved rapidly to give a blood red solution, which was stirred for 2 h at ambient temperature. The solvent was removed *in vacuo* and the product washed with petroleum ether (bp 40–60 °C, 2 × 5 cm^3) and dried *in vacuo*. Yield 0.054 g (40.7%). Anal. Calcd for $C_{24}H_{25}F_3Cl_2PRh$: C, 50.1; H, 4.3; Cl, 12.3. Found C, 50.3; H, 4.5; Cl, 12.2%. LSIMS: 539 ($[M - Cl]^+$). HRSIMS: $C_{24}H_{25}ClF_3PRh$ requires 539.03896; found: $[M - Cl]^+$ 539.03763. ^1H NMR ($CDCl_3$): δ = 7.82–7.96 (4H, m, C_6H_5), 7.42–7.62 (6H, m, C_6H_5), 1.46 (15H, d, $^4J_{PH}$ = 3.7 Hz, C_5Me_5). Raman (cm^{-1}): 280, 197 ν(Rh–Cl). IR (nujol, cm^{-1}): 1727 ν(C=C), 1306, 1144, 1049 ν(C–F).

4.3.2. *[Cp*RhCl$_2${PPr$^i_2$(CF=CF$_2$)}] (**1b**)*

$[Cp^*RhCl(\mu\text{-}Cl)]_2$ (0.155 g, 0.26 mmol) and $PPr^i_2(CF{=}CF_2)$ (0.101 g, 0.51 mmol) were treated as in 4.3.1. Yield 0.066 g (50%). Anal. Calcd for $C_{18}H_{19}F_3Cl_2PRh$: C, 42.6; H, 5.7; Cl, 14.0. Found C, 42.5; H, 6.0; Cl, 14.0%. ^1H NMR ($CDCl_3$): δ = 3.12 [2H, m, 2H, C*H*(CH_3)$_2$], 1.61 (15H, d, br, C_5Me_5), 1.37 (12H, m, CH(C*H*$_3$)$_2$). Raman (cm^{-1}): 283, 199 ν(Rh–Cl). IR (nujol, cm^{-1}): 1728 ν(C=C), 1302, 1150, 1030 ν(C–F).

4.3.3. *[Cp*RhCl$_2${PEt$_2$(CF=CF$_2$)}] (**1c**)*

$[Cp^*RhCl(\mu\text{-}Cl)]_2$ (0.248 g, 0.41 mmol) and $PEt_2(CF{=}CF_2)$ (0.138 g, 0.81 mmol) were treated as in 4.3.1. Yield 0.099 g (50.3%). Anal. Calcd for $C_{16}H_{25}F_3Cl_2PRh$: C, 40.1; H, 5.2; Cl, 14.8. Found C, 40.4; H, 5.4; Cl, 14.6%. ^1H NMR ($CDCl_3$): δ = 2.38 (4H, m, C*H*$_2$CH$_3$), 1.67 (15H, d, $^4J_{PH}$ = 3.7 Hz, C_5Me_5), 1.18 (6H, dt, $^3J_{PH}$ = 17.1 Hz, $^3J_{HH}$ = 7.5 Hz, CH_2CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 8.2 (d, $^2J_{PC}$ = 4.8 Hz, CH_2CH_3), 9.5 [s, $C_5(CH_3)_5$], 14.8 (d, $^1J_{PC}$ = 28.0 Hz, *C*H$_2$CH$_3$), 99.6 (dd, J_{PC} = 2.9 Hz, J_{RhC} = 6.8 Hz, C_5), 125.7 (dddd, $^1J_{PC}$ = 55.0, $^1J_{CF}$ = 255.9 Hz, $^2J_{CF}$ = 41.5, 10.6 Hz, *C*F=CF$_2$), 158.8 (dddd, $^2J_{PC}$ = 13.5, $^1J_{CF}$ = 305.2, 284.9 Hz, $^2J_{CF}$ = 41.5 Hz, CF=*C*F$_2$). Raman (cm^{-1}): 283, 199 ν(Rh–Cl). IR (nujol, cm^{-1}): 1732 ν(C=C), 1304, 1152, 1049 ν(C–F).

4.3.4. *[Cp*RhCl$_2${PPh(CF=CF$_2$)$_2$}] (**2**)*

$[Cp^*RhCl(\mu\text{-}Cl)]_2$ (0.178 g, 0.29 mmol) and $PPh(CF{=}CF_2)_2$ (0.159 g, 0.59 mmol) were treated as in 4.3.1. Yield 0.098 g (58.5%). Anal. Calcd for $C_{20}H_{20}F_6Cl_2PRh$: C, 41.5; H, 3.5; Cl, 12.3. Found C, 41.4; H, 3.6; Cl, 12.6%. ^1H NMR ($CDCl_3$): δ = 7.75–7.82 (2H, m, C_6H_5), 7.45–7.57 (3H, m, C_6H_5), 1.66 (15H, s br, C_5Me_5). Raman (cm^{-1}): 272, 195 ν(Rh–Cl). IR (nujol, cm^{-1}): 1730 ν(C=C), 1310, 1169, 1053 ν(C–F).

4.3.5. *[Cp*RhCl(CNCMe$_3$){PPh$_2$(CF=CF$_2$)}]BF$_4$ (**3**)*

Tert-butylisonitrile (0.02 cm^3, 0.18 mmol) in dichloromethane (1 cm^3) was added to **1a** (0.105 g, 0.18 mmol) and sodium tetrafluoroborate (0.295 g, 2.69 mmol) in 1:1 dichloromethane/methanol (40 cm^3) with rapid stirring. After 30 min the solvent was removed by rotary evaporation and the product extracted with dichloromethane (50 cm^3 × 2). The solution was filtered and the solvent removed by rotary evaporation to give **3** as an orange solid. The product was triturated with hexane (10 cm^3) and dried *in vacuo*. Yield 0.125 g (96.3%). A sample for analysis was recrystallized from dichloromethane. Anal. Calcd for $C_{29}H_{34}BCl_2F_7NPRh\cdot(1/2)CH_2Cl_2$: C, 47.1; H, 4.7; N, 1.9. Found C, 47.3; H, 5.0; N 2.2%. LSIMS: 622 ($[M - BF_4]^+$), 587 ($[M - BF_4 - Cl]^+$), 539 ($[M - BF_4 - CNBu^t]^+$), 356 ($[M - BF_4 - PPh_2(CF{=}CF_2)]^+$). HRSIMS: $C_{29}H_{34}ClF_3NPRh$ requires 622.11245; found $[M - BF_4]^+$ 622.11972. ^1H NMR ($CDCl_3$): δ = 7.4–7.9 (10H, m, C_6H_5), 1.63 (15H, d, $^4J_{PH}$ = 3.9 Hz, C_5Me_5), 1.31 (9H, s, ^{t}BuNC). IR (KBr, cm^{-1}): ν(N≡C) 2206 cm^{-1}.

4.3.6. *(CF$_2$=CF)PPh(C$_6$H$_4$SMe-2) (**4**)*

A solution of $Li[C_6H_4SMe]$, prepared from $MeSC_6H_4Br$-2 (2.28 g, 0.011 mol) and ^{n}BuLi (4.2 cm^3 of a 2.5 M solution in hexanes, 0.011 mol) in diethyl ether (100 cm^3), at 0 °C was added during 40 min to $PPhCl_2$ (1.3 cm^3, 1.7 g, 0.01 mol) in diethyl ether (10 cm^3) at 0 °C affording a pale yellow solution and a white solid. The mixture was stirred at 0 °C for 1 h and allowed to warm to ambient temperature. The mixture was cooled to −78 °C and added portionwise during 1 h to a solution of $Li[CF{=}CF_2]$, prepared from ^{n}BuLi (18 cm^3 of a 2.5 M solution in hexanes, 0.045 mol) and an excess of CF_3CH_2F in diethyl ether (100 cm^3), at −85 °C. The temperature was maintained at −75 to −80 °C during the addition. The reaction mixture was allowed to warm to ambient temperature overnight affording a pale brown solution and a white solid. Hexane (200 cm^3) was added and the solution filtered. The solvent was removed from the filtrate by rotary

evaporation to yield a brown oil, which was slurried in toluene/hexane (1:1) and filtered through a column of silica (5 cm). The silica was washed with toluene/hexane (1:1) (500 cm^3). The filtrate and washings were combined and the solvent removed by rotary evaporation to give a yellow-brown oil, which deposited colourless crystals of $PPh(C_6H_4SMe\text{-}2)_2$ [29] which were filtered off. The filtrate was distilled by Kugelrohr under reduced pressure. $PPh(CF{=}CF_2)_2$ [15] was removed by distillation at 40–50 °C at 0.1 mmHg. A pale yellow oil, comprising **4** and unreacted $BrC_6H_4SMe\text{-}2$, was collected between 70 and 130 °C at 0.04 mmHg. $BrC_6H_4SMe\text{-}2$ was removed by distillation at 70–95 °C at 0.04 mmHg, leaving **4** as a yellow oil. Yield 0.454 g (14.5%). EIMS: 312 (M^+), 297 ($[M - CH_3]^+$). HRMS: $C_{15}H_{12}F_3PS$ requires 312.03495; found M^+ 312.03600. ^1H NMR ($CDCl_3$): $\delta = 7.46$ (2H, m, C_6H_5 or C_6H_4), 7.32 (11H, m, C_6H_5 and C_6H_4), 7.13 (1H, m, C_6H_4), 2.34 (3H, s, SCH_3).

4.3.7. *[Cp*RhCl{κP,κS-(CF$_2$=CF)PPh(C$_6$H$_4$SMe-2)}]BF$_4$ (**5**)*

A mixture of $[Cp^*RhCl(\mu\text{-}Cl)]_2$ (0.105 g, 0.17 mmol), **4** (0.115 g, 0.37 mmol) and sodium tetrafluoroborate (0.180 g, 1.65 mmol) was treated as for the preparation of $[Cp^*RhCl\{\kappa P,\kappa S\text{-}(C_6F_5)_2PC_6H_4SMe\text{-}2\}]BF_4$ [19]. The product was obtained as yellow crystals from chloroform. Yield 0.163 g (71.3%). Anal. Calcd for $C_{25}H_{27}BClF_7PRhS$: C, 44.6; H, 4.05. Found C, 46.8; H, 4.3% (repeated recrystallization failed to provide satisfactory analysis). LSIMS: 585 ($[M - BF_4]^+$), 550 ($[M - BF_4 - Cl]^+$). HRSIMS: $C_{25}H_{27}ClF_3PRhS$ requires 585.02668; found $[M - BF_4]^+$ 585.02535. **5a major**: ^1H NMR ($CDCl_3$): $\delta = 7.92$ (2H, m), 7.82 (1H, m), 7.67 (4H, m), 7.55 (2H, m), 3.11 (3H, s, SCH_3), 1.86 (15H, d, $^4J_{PH} = 4.1$ Hz, $C_5(CH_3)_5$). **5b minor**: ^1H NMR ($CDCl_3$): $\delta = 3.05$ (3H, s, Me), 1.84 (15H, d, $^4J_{PH}$ *ca.* 5 Hz, $C_5(CH_3)_5$). The resonances of the hydrogen atoms of the aryl groups of **5b** are obscured by those of **5a**.

4.3.8. *NMR reactions between proton sponge and **1a**, **3** and **5***

In a typical reaction the complex (*ca.* 0.020 g) was dissolved in $CDCl_3$ in an NMR tube and the ^1H, ^{19}F and $^{31}P\{^1H\}$ NMR spectra recorded. Proton sponge (*ca.* 0.010 g) was added and the spectra recorded immediately. Subsequent spectra were recorded over 2 weeks. The solvent was removed from the product mixture formed from **5** and mass spectra recorded. $^{19}F\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopic data are presented in Table 1. **6** LSIMS: 565 (M^+), 529 ($[M - Cl]^+$). HRSIMS: $C_{25}H_{26}ClF_2PRhS^+$ requires 565.0204; found M^+ 565.0177. **7** LSIMS: 605 (M^+), 569 ($[M - Cl]^+$). HRSIMS: $C_{25}H_{28}ClF_4PRhS^+$ requires 605.03290; found M^+ 605.03233.

4.3.9. *Reaction between [Cp*RhCl(μ-Cl)]$_2$ and **4** in benzene*

A slurry of $[Cp^*RhCl(\mu\text{-}Cl)]_2$ (0.085 g, 0.14 mmol) and **4** (0.090 g, 0.29 mmol) in benzene (60 cm^3) was refluxed for 14 h. The solvent was removed by rotary evaporation to give an oily solid, which was triturated with cyclohexane (20 cm^3) and recrystallized from acetone. 0.17 g of a complicated mixture of products was obtained as a red solid. Attempts to separate the products by fractional crystallization were unsuccessful.

4.4. X-ray crystallography

Crystals of **1a** and **5a** were grown from $CHCl_3$ and CH_2Cl_2, respectively and **1b** and **1c** from mixed dichloromethane–hexane solutions. Diffraction data (Table 1) were collected on a Bruker SMART (**1a**, **5a**) or a Nonius MACH3 (**1b**, **1c**) diffractometer using the SAINT-NT [30] software with graphite-monochromated Mo Kα radiation using φ/ω scans. Lorentz and polarization corrections were applied. Crystal stabilities were monitored via recollection of the first set of frames. There were no significant variations (<±1%). Empirical absorption corrections were applied using SADABS [31]. The structures were solved using direct methods and refined with the SHELXTL programme package [32]. The non-hydrogen atoms of **1a**, **1b** and **5a** and Rh(1), Cl(1A), Cl(1B), Cl(2A), Cl(2B), P(1A), P1(B), C(1), C(2), C(3), C(4), C(5), C(6), C(7), C(8), C(9) and C(10) of **1c** were refined with anisotropic thermal parameters. The other non-hydrogen atoms of **1c** were refined with isotropic parameters. Hydrogen-atom positions were located from difference Fourier maps and then fully refined. The function minimised was $\Sigma[w(|F_o|^2 - |F_c|^2)]$ with reflection weights $w^{-1} = [\sigma^2|F_o|^2 + (g_1P)^2 + (g_2P)]$ where $P = [\max|F_o|^2 + 2|F_c|^2]/3$. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 634089 (**1a**), 634090 (**1b**), 634091 (**1c**) and 634092 (**5**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

We thank ICI Klea for supplying CF_3CH_2F and I.R. Crossley for helpful discussion.

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