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Intermediates and anion effects in the activation of carbon–fluorine bonds by η^5-pentamethylcyclopentadienylrhodium halide complexes; crystal structure of $[\{\eta^5\text{-}C_5Me_3[CH_2C_6F_4P(C_6F_5)CH_2]_2\text{-}1,3\}RhBr]^+\cdot Br^-$

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Abstract

The reaction between $[(\eta^5\text{-}C_5Me_5)RhBr(\mu\text{-}Br)]_2$ and the diphosphine, $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$ (dfppe), in benzene proceeded via the intermediate cation $[(\eta^5\text{-}C_5Me_5)RhBr(dfppe)]^+$, which underwent C–F and C–H bond activation and C–C bond formation to give sequentially $[\{\eta^5\text{-}C_5Me_4CH_2C_6F_4P(C_6F_5)CH_2CH_2P(C_6F_5)_2\}RhBr]^+$ and then $[\{\eta^5\text{-}C_5Me_3[CH_2C_6F_4P(C_6F_5)CH_2]_2\text{-}1,3\}RhBr]^+$, as evidenced by mass spectrometry and NMR spectroscopy. The bromide salt of the final product (**4c**) has been structurally characterized by X-ray diffraction. Compound **4c** crystallizes in the triclinic space group $P\bar{1}$ with $a = 10.616(1)$, $b = 13.904(2)$, $c = 14.911(1)$ Å, $\alpha = 66.86(1)$, $\beta = 86.38(1)$, $\gamma = 84.72(1)°$ and $Z = 2$. Refinement gave final $R1$ and $wR2$ $[I = 2\sigma(I)]$ values of 0.0581 and 0.1641, respectively, for 6837 unique reflections. In contrast to the BF_4^- salt, the Cl^- and BPh_4^- salts of cation $[(\eta^5\text{-}C_5Me_5)RhCl(dfppe)]^+$ undergo reaction upon thermolysis in benzene to give the cation $[\{\eta^5\text{-}C_5Me_3[CH_2C_6F_4P(C_6F_5)CH_2]_2\text{-}1,3\}RhCl]^+$. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: C–F bond activation; C–H bond activation; C–C bond formation; Rhodium; 1,2-Bis{bis(pentafluorophenyl)phosphino}ethane

1. Introduction

As part of a programme to develop the synthetic utility of C–F bond activation in the synthesis of organometallic complexes we have been studying the intriguing reaction between the metal complexes $[(\eta^5\text{-}C_5Me_4R)MCl(\mu\text{-}Cl)]_2$ (M = Rh, Ir; R = H, Me, Et) and the diphosphine $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$ (dfppe). We have reported that dfppe reacts with $[(\eta^5\text{-}C_5Me_5)RhCl(\mu\text{-}Cl)]_2$ under mild conditions in benzene or ethanol to afford, in quantitative yield, the cationic complex $[LRhCl]^+$ (**1**[1], **L** = $\eta^5\text{-}C_5Me_3[CH_2C_6F_4P(C_6F_5)CH_2]_2\text{-}1,3$; Fig. 1) in which two aryl C–F bonds and two pentamethylcyclopentadienyl C–H bonds have been cleaved and two C–C bonds have been formed (Eq. (1)) [1,2].

$$\tfrac{1}{2}[(\eta^5\text{-}C_5Me_5)RhCl(\mu\text{-}Cl)]_2 + \text{dfppe} \rightarrow [LRhCl]^+\cdot X^- + 2HF \quad (1)$$

$(X^- = Cl^-$ **1a**, $X^- = BF_4^-$ **1b**)

The reaction exhibits complete regiospecificity: only one *ortho* C–F bond of each $P(C_6F_5)_2$ moiety and C–H bonds of methyl groups exclusively in a 1,3 disposition are activated. Further, remarkable regioselectivity was observed in the reaction between $[(\eta^5\text{-}C_5Me_4H)RhCl(\mu\text{-}Cl)]_2$ and dfppe, in which a racemic mixture of the chiral-at-metal cation $[\{\eta^5\text{-}C_5HMe_2\text{-}2,4\text{-}[CH_2C_6F_4P(C_6\text{-}$

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[1] For salts, the number refers to the cation and the letter indicates the anion: **a** = Cl⁻, **b** = BF_4^-, **c** = Br^-, **d** = BPh_4^-, **e** = PF_6^-.

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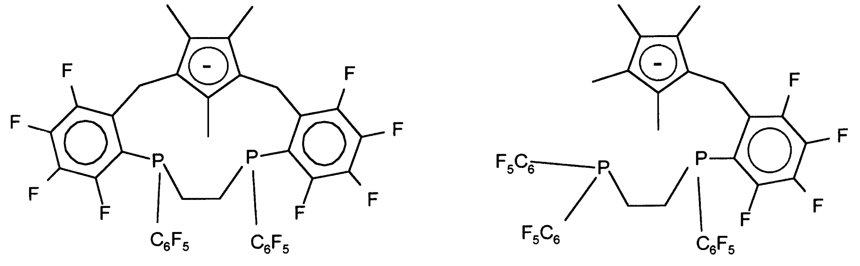
$F_5)CH_2]_2$-1,3}RhCl]$^+$ was formed selectively in high yield [3]. In order to extend the scope of such reactivity it is important to understand the mechanism of reaction (1) and related reactions.

Reaction (1) is complete in refluxing benzene or ethanol after a few hours, but also occurs at room temperature and in dichloromethane, albeit more slowly. In ethanol two intermediate cations have been identified, and it has been established that the reaction proceeds via cation **2**, which undergoes C–F and C–H bond activation and C–C bond formation with loss of HF to give the singly activated cation [**L**′RhCl]$^+$ (**3**, **L**′ = η^5-$C_5Me_4CH_2C_6F_4P(C_6F_5)CH_2CH_2P(C_6F_5)_2$, Fig. 1) and then **1** (Scheme 1) [2]. Furthermore, the tetrafluoroborate salt of **2** (**2b**), prepared independently, undergoes reaction on thermolysis in ethanol to yield **1b** via **3b** (Eq. (2)) [2].

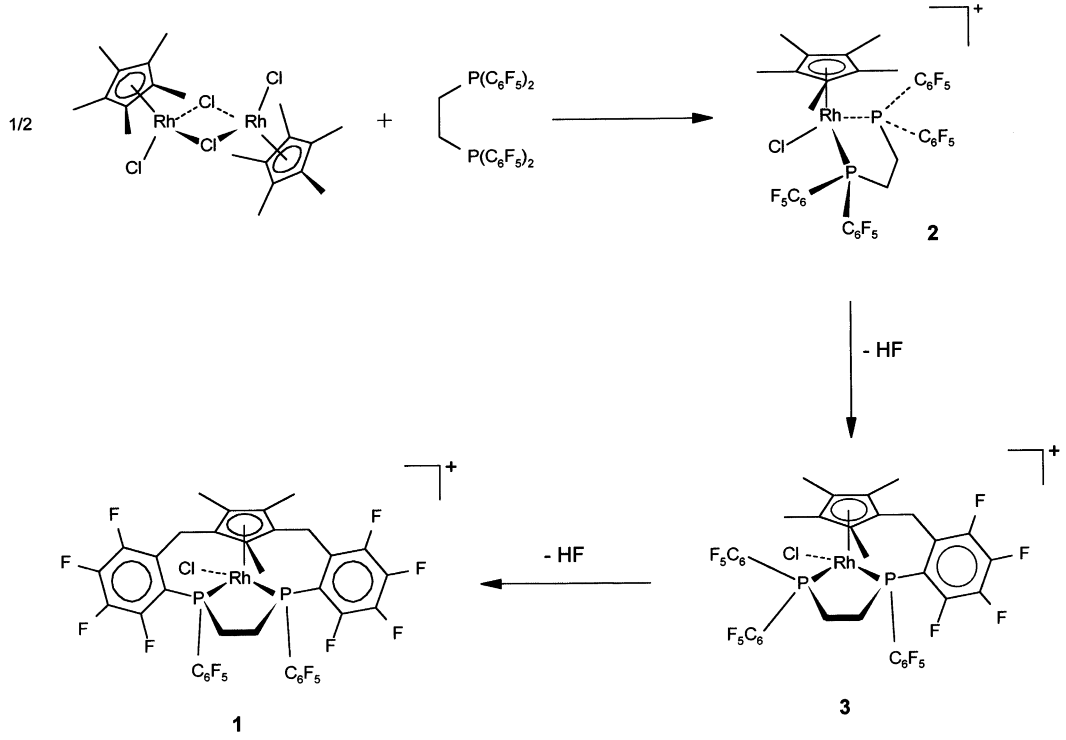
$$\underset{\textbf{(2b)}}{[(\eta^5\text{-}C_5Me_5)RhCl(dfppe)]^+ \cdot BF_4^-} \rightarrow \underset{\textbf{(1b)}}{[LRhCl]^+ \cdot BF_4^-} + 2HF \qquad (2)$$

Similar observations were noted for reactions involving (η^5-C_5Me_5)IrCl [2] and (η^5-C_5Me_4Et)RhCl species [3] in ethanol. However, there is no evidence to support this sequence for the reaction in benzene. Subsequent in situ NMR spectroscopic studies, performed on the reaction between [(η^5-C_5Me_5)RhCl(μ-Cl)]$_2$ and dfppe in C_6D_6, have failed to detect the presence of either **2** or **3**. (Spectroscopic data indicate that the cations [(η^5-C_5Me_4H)RhCl(dfppe)]$^+$ and [{η^5-$C_5Me_3HCH_2C_6F_4$-$P(C_6F_5)CH_2CH_2P(C_6F_5)_2$}RhCl]$^+$ are present in the final product mixture of the reaction between [(η^5-C_5Me_4H)RhCl(μ-Cl)]$_2$ and dfppe in benzene [3], but their presence may indicate their existence as by-products and not as intermediates.) Furthermore, **2b** does

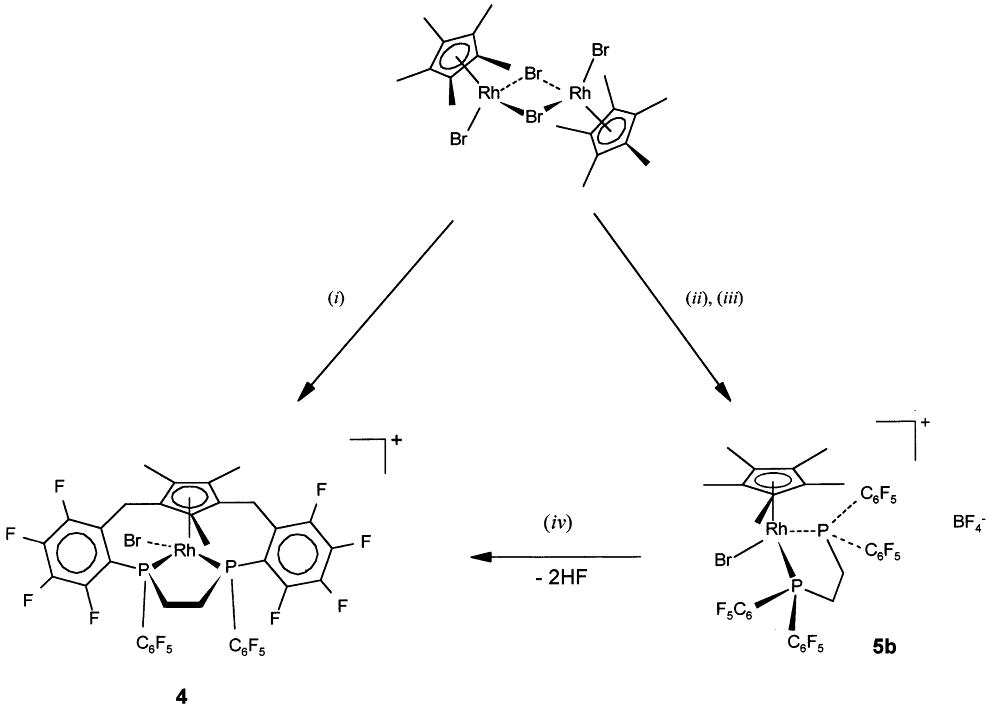


L **L**′

Fig. 1. Ligands **L** and **L**′.



Scheme 1.



Scheme 2. (i) dfppe, C_6H_6, reflux 5 days; (ii) NH_4BF_4, MeOH; (iii) dfppe, CH_2Cl_2; (iv) EtOH, reflux.

not undergo reaction on thermolysis in benzene and other aprotic solvents such as dichloromethane or dry acetone [2]. Clearly the solvent exerts a strong influence in these reactions. We were interested in determining whether reaction (1) proceeds by a different mechanism in benzene to that in ethanol and whether the anion also exerts a large effect in this reaction.

Our previous studies into the mechanism and scope of these reactions have concentrated on variation of the metal [2] and the cyclopentadienyl ligand [3,4]. Here, we report the effect of changing the halide ligand, which has allowed the determination of the intermediates in the reactions between $[(\eta^5\text{-}C_5Me_4R)\text{-}RhX(\mu\text{-}X)]_2$ and dfppe in benzene, and the effect of the anion on the thermolysis of $[(\eta^5\text{-}C_5Me_5)\text{-}RhCl(dfppe)]^+\cdot X^-$.

2. Results and discussion

*2.1. Synthesis and characterization of $[LRhBr]^+\cdot BF_4^-$ (**4b**) and $[(\eta^5\text{-}C_5Me_5)RhBr(dfppe)]^+\cdot BF_4^-$ (**5b**)*

The reaction between $[(\eta^5\text{-}C_5Me_5)RhBr(\mu\text{-}Br)]_2$ and dfppe proceeded in refluxing benzene with activation of two C–F and C–H bonds and the formation of two C–C bonds to afford a mixture of the salts $[LRhBr]^+\cdot X^-$, $X^- = Br^-$ or BF_4^- (Scheme 2). The complex was characterized by mass spectrometry and multinuclear NMR spectroscopies of the tetrafluoroborate salt, **4b**, which was formed by anion metathesis of the product and isolated in moderate yield and also by an X-ray diffraction study of a crystal of bromide salt, **4c**, which was crystallized from the crude product mixture. The spectroscopic data are entirely consistent with the formulation of **4b** and similar to those of **1a** [1]. Unfortunately it was not possible to obtain elemental analysis of **4b** due to traces of other products with similar solubilities from which it could not be separated.

The tetrafluoroborate salt of the postulated intermediate bromo-diphosphine cation, $[(\eta^5\text{-}C_5Me_5)\text{-}RhBr(dfppe)]^+\cdot BF_4^-$ (**5b**), was prepared in good yield by addition of dfppe to a solution of $[(\eta^5\text{-}C_5Me_5)RhBr(\mu\text{-}Br)]_2$ and NH_4BF_4 in methanol. Salt **5b** was characterized by elemental analysis, mass spectrometry and multinuclear NMR spectroscopies. The ^1H-, ^{19}F- and $^{31}P\{^1H\}$-NMR spectra show only minor differences to those of the chloride analogue **2b** [2]. For example, the phosphorus resonance of **5b** is shifted to lower frequency by only 1.1 ppm. As with **2b**, thermolysis of **5b** in ethanol induces C–F and C–H bond activation/C–C bond formation and the diactivated product **4b** was obtained almost quantitatively after 4.5 h (Scheme 2).

Attempts to prepare the iodo analogues of **4b** and **5b** from $[(\eta^5\text{-}C_5Me_5)RhI(\mu\text{-}I)]_2$ were unsuccessful. Presumably, the larger size of iodide (covalent radius: 1.33 Å [5]) in comparison with chloride (0.99 Å) and bromide (1.14 Å) prevents coordination of the bulky dfppe ligand. Simple molecular modelling supports this hypothesis.

2.2. Crystal structure of $[LRhBr]^+ \cdot Br^-$ (4c)

Crystals of **4c** suitable for single-crystal X-ray diffraction study were obtained by slow evaporation of solvent from an acetone solution of the crude product of the reaction between $[(\eta^5\text{-}C_5Me_5)RhBr(\mu\text{-}Br)]_2$ and dfppe. The crystallographic data, atomic coordinates and selected distances and angles are given in Tables 1–3, respectively. The cation has a potential mirror plane [through Rh(1), Br(1) and the C_5 ring centroid], but in the crystal the PCH_2 methylene carbon atoms and the terminal pentafluorophenyl rings are twisted away from an ideal conformation, presumably to reduce steric interactions between the *ortho*-F atoms F(12) and F(32). [Distance F(12)···F(32) is 2.601 Å, which would be ca. 2.26 Å in the idealized, untwisted conformation]. The atoms involved in this twisted conformation are 50% disordered between the two possible twist directions, thus maintaining the near mirror symmetry of the cation. These distortions appear to be completely accommodated by movement of only two of the carbons attached to phosphorus, and there is no hint of disorder in the third attached carbons [C(21) and C(41)]. There are indications of solvent molecules in the crystal which could not be fully identified, the strongest residual density was modelled by a single oxygen atom, presumably of water.

Table 1
Crystallographic data for $[LRhBr]^+ \cdot Br^-$ (**4c**)

Formula	$C_{36}H_{17}Br_2F_{18}P_2Rh.O$
Formula weight	1132.17
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	10.616(1)
b (Å)	13.904(2)
c (Å)	14.911(1)
α (°)	66.86(1)
β (°)	86.38(1)
γ (°)	84.72(1)
V (Å^3)	2014.4(4)
Z	2
$F(000)$	1096
D_{calc} (g cm^{-3})	1.867
Crystal size (mm)	$0.63 \times 0.54 \times 0.41$
Radiation (λ (Å))	Mo–K_α (0.71073)
Monochromator	Graphite
μ (Mo–K_α) (mm^{-1})	2.601
T (K)	190(2)
Scan method	ω
h, k, l Ranges	-1 to 12, -15 to 15, -17 to 17
2θ limits (°)	5.04–50.00
Total reflections	8045
Unique reflections	6837 ($R_{int} = 0.0238$)
Observed reflections $[F_o = 4\sigma(F_o)]$	5302
Absorption correction method	Semi-empirical based on ψ-scans
Max and min transmission	0.9547, 0.7108
Restraints	12
Variables	507
R_1, wR_2 $[I = 2\sigma(I)]$	0.0581, 0.1641
R_1, wR_2 (all data)	0.0794, 0.1783
Weighting scheme	$w = 1/[\sigma^2(F_o)^2 + 0.09P^2 + 11.55P]$ [a]
$(\Delta/\sigma)_{max}$	0.25
Max, min $\Delta\rho$ (eÅ^{-3})	2.472, -0.882
Goodness of fit on F^2	1.076

[a] $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

The structure (Fig. 2) is similar to that of the tetrafluoroborate salt of the chloride analogue **1b** [1]. The Rh–C_5(centroid) distance is the same as that of **1b**. The two Rh–P distances are identical within experimental error and similar to those of **1b**. The Rh–Br distance of 2.5018(10) Å is ca. 0.12 Å longer than the Rh–Cl distance of **1b** (2.380(3) Å) consistent with the larger size of bromide relative to chloride. The P–Rh–P angle is 86.94(7)°, consistent with that of **1b**. The C_5(centroid)–Rh–Br angle of 122.5(2)° is ca. 4° more acute, and the two P–Rh–Br angles of 94.43(6) and 93.81(6)° are more obtuse than the analogous angles of **1b** (126.1(1), 90.6(1) and 93.0(1)°, respectively). Presumably, the differences in the angles between **4c** and **1b** arise because of the larger size of the bromide ligand compared with the chloride ligand.

2.3. Reaction between $[(\eta^5\text{-}C_5Me_5)RhBr(\mu\text{-}Br)]_2$ and dfppe in benzene

The reaction of dfppe with $[(\eta^5\text{-}C_5Me_5)RhBr(\mu\text{-}Br)]_2$ is similar to that with the chloride analogue [1,2], but proceeded at a far slower rate. This afforded a convenient opportunity to carry out investigations of the reaction mixture at various times throughout the reaction. This was achieved by stopping the reflux, allowing the mixture to cool and removing the benzene by rotary evaporation to allow characterization of the solids by mass spectrometry and multinuclear NMR spectroscopies in $CDCl_3$. After characterization, the mixture was redissolved in benzene and reflux continued.

The ^{19}F- and ^{31}P{^{1}H}-NMR spectra after 6 h indicate that dfppe was the predominant phosphorus and fluorine containing species in the mixture. The ^{31}P-NMR and mass spectra indicate the presence of the bromo-diphosphine cation **5** and the diactivated product cation **4**. The mass spectrum also contained small peaks at 1057 and 1055 suggesting the presence of the singly activated cation $[\mathbf{L'}RhBr]^+$ (**6**). After 26 h the spectral data indicated that virtually no dfppe remained and that cation **5** was the predominant species. After 48 h the ^{31}P{^{1}H}-NMR spectrum displays two more doublets of multiplets at δ 83.8 and 57.9 with $^1J_{Rh-P}$ 143 and 128 Hz, respectively, in equal intensity. Comparison of these data with those of singly activated **3b** [2] indicate that these can be assigned to cation **6**. The relative proportion of **5** had diminished and no dfppe remained. After 122 h at reflux, and addition of

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) with estimated standard deviations in parentheses for the non-hydrogen atoms of $[\mathbf{L}RhBr]^+ \cdot Br^-$ (**4c**)

Atom	x	y	z	$U_{(eq)}$
Rh(1)	3696(1)	6989(1)	7165(1)	24(1)
Br(1)	4567(1)	8441(1)	5717(1)	45(1)
Br(2)	847(1)	5047(1)	1521(1)	55(1)
P(1)	2071(2)	6801(2)	6358(1)	27(1)
P(2)	2356(2)	8080(2)	7625(1)	28(1)
C(1)	4533(7)	6282(6)	8604(5)	33(2)
C(10)	6598(8)	7169(7)	7784(7)	47(2)
C(11)	2047(2)	7383(2)	5044(2)	13(3)
C(11A)	2489(3)	9456(2)	7104(1)	18(3)
C(12)	1290(2)	8286(2)	4528(2)	29(3)
C(12A)	1651(2)	10174(2)	6444(2)	42(4)
C(13)	1440(3)	8774(2)	3516(2)	37(4)
C(13A)	1917(3)	11220(2)	5990(2)	50(5)
C(14)	2347(3)	8361(2)	3021(2)	29(3)
C(14A)	3021(3)	11549(2)	6196(2)	52(5)
C(15)	3104(3)	7458(2)	3537(2)	21(5)
C(15A)	3859(3)	10830(2)	6856(2)	47(4)
C(16)	2954(3)	6969(2)	4548(2)	25(6)
C(16A)	3593(3)	9784(2)	7310(2)	31(4)
C(2)	3742(7)	5563(6)	8471(5)	32(2)
C(21)	1755(7)	5462(6)	6560(5)	30(2)
C(22)	2522(7)	4564(6)	7060(5)	30(2)
C(23)	2082(8)	3596(6)	7221(6)	36(2)
C(24)	950(9)	3490(6)	6882(6)	39(2)
C(25)	210(8)	4367(7)	6371(6)	38(2)
C(26)	629(8)	5332(6)	6220(6)	36(2)
C(3)	4311(7)	5316(6)	7667(5)	31(2)
C(31)	2876(3)	9510(2)	6964(1)	37(4)
C(31A)	2422(2)	7519(2)	4976(2)	32(3)
C(32)	2389(2)	10201(2)	6074(2)	32(4)
C(32A)	2068(2)	8579(2)	4491(1)	34(3)
C(33)	2669(3)	11250(2)	5696(2)	35(4)
C(33A)	2257(3)	9060(2)	3486(1)	36(4)
C(34)	3436(3)	11608(2)	6208(2)	29(3)
C(34A)	2801(3)	8480(2)	2966(1)	37(4)
C(35)	3923(3)	10916(2)	7099(2)	41(4)
C(35A)	3155(3)	7420(2)	3451(2)	46(8)
C(36)	3643(3)	9867(2)	7477(2)	48(5)
C(36A)	2965(3)	6939(2)	4456(2)	31(6)
C(4)	5404(7)	5883(6)	7321(5)	30(2)
C(41)	2279(7)	7849(6)	8917(5)	30(2)
C(42)	3134(7)	7163(6)	9624(6)	30(2)
C(43)	2872(8)	7021(6)	10579(6)	37(2)
C(44)	1852(9)	7498(8)	10875(6)	44(2)
C(45)	1064(9)	8195(8)	10207(7)	46(2)
C(46)	1291(8)	8366(7)	9241(6)	40(2)
C(5)	5540(7)	6488(6)	7896(6)	34(2)
C(51)	567(26)	7181(18)	6920(18)	21(5)
C(51A)	767(36)	7714(27)	7523(23)	41(8)
C(52)	727(37)	8076(21)	7239(21)	26(6)
C(52A)	667(30)	7459(21)	6633(20)	27(6)
C(6)	4378(8)	6659(7)	9420(6)	41(2)
C(7)	2661(8)	5022(6)	9125(6)	38(2)
C(8)	3888(8)	4512(6)	7348(6)	37(2)
C(9)	6335(8)	5811(7)	6561(6)	43(2)
F(12)	419(2)	8683(2)	5004(2)	40(2)
F(12A)	586(2)	9857(2)	6245(2)	57(3)
F(13)	713(3)	9641(2)	3021(2)	59(3)
F(13A)	1109(3)	11912(2)	5354(2)	90(5)
F(14)	2491(4)	8830(2)	2049(2)	53(4)
F(14A)	3278(4)	12557(2)	5759(2)	83(5)
F(15)	3974(3)	7060(2)	3061(2)	29(2)
F(15A)	4924(3)	11147(3)	7055(3)	90(5)
F(16)	3681(3)	6102(2)	5044(2)	30(3)
F(16A)	4401(3)	9092(2)	7947(2)	48(3)
F(23)	2791(5)	2702(4)	7703(4)	50(1)
F(24)	588(5)	2536(4)	7039(4)	54(1)
F(25)	−904(5)	4295(5)	6037(4)	57(1)
F(26)	−140(5)	6168(4)	5700(4)	49(1)
F(32)	1653(2)	9858(2)	5581(2)	44(3)
F(32A)	1544(2)	9138(2)	4993(2)	45(2)
F(33)	2201(4)	11914(2)	4841(2)	53(3)
F(33A)	1916(3)	10082(2)	3018(1)	58(3)
F(34)	3705(4)	12616(2)	5845(2)	55(4)
F(34A)	2983(4)	8944(2)	1997(1)	48(3)
F(35)	4660(4)	11260(3)	7591(2)	65(4)
F(35A)	3679(3)	6862(2)	2950(2)	47(3)
F(36)	4111(4)	9203(2)	8332(2)	59(4)
F(36A)	3307(3)	5917(2)	4923(2)	42(3)
F(43)	3658(5)	6370(4)	11281(3)	51(1)
F(44)	1611(5)	7269(5)	11840(4)	60(2)
F(45)	53(6)	8676(6)	10477(4)	71(2)
F(46)	495(5)	9070(4)	8594(4)	52(1)
O(1)	−582(8)	6640(7)	9512(6)	78(2)

NH_4BF_4, the ^{19}F- and ^1H-NMR spectra recorded indicate that the diactivated product **4b** was the major species, and that only small quantities of other compounds, including **5b** and **6b**, were also present. The ^{19}F-NMR spectrum displays more resonances than can be accounted for by the presence of **4b**, **5b** and **6b** alone, and it is therefore inferred that the reaction is not as clean as between $[(\eta^5\text{-}C_5Me_5)RhCl(\mu\text{-}Cl)]_2$ and dfppe. The identities of the by-products are, as yet, not known.

The data clearly establish that the reaction between $[(\eta^5\text{-}C_5Me_5)RhBr(\mu\text{-}Br)]_2$ and dfppe in benzene proceeds via formation of the bromo-diphosphine cation **5**, followed by sequential C–F and C–H bond activation with concomitant C–C bond formation to form the singly activated **6** and finally the di-activated product **4**. This reaction scheme is analogous to the reaction between $[(\eta^5\text{-}C_5Me_5)RhCl(\mu\text{-}Cl)]_2$ and dfppe in ethanol (Scheme 1). Although there is no direct evidence, it is reasonable to assume that the reaction between $[(\eta^5\text{-}C_5Me_5)RhCl(\mu\text{-}Cl)]_2$ and dfppe in benzene proceeds via cations **2** and **3**. The lack of a reaction on thermolysis of **2b** in benzene may, therefore, be inferred to be due to the effect of the anion. To test this hypothesis it was proposed to synthesize the chloride, tetraphenylborate and hexafluorophosphate salts of cation **2** and investigate any reaction occurring on thermolysis in benzene.

Table 3
Selected interatomic distances (Å) and angles (°) for $[LRhBr]^+\cdot Br^-$ (**4c**)

Bond lengths			
Rh(1)–P(1)	2.256(2)	Rh(1)–P(2)	2.257(2)
Rh(1)–Br(1)	2.5018(10)	Rh(1)–Cp*[a]	1.829(7)
P(1)–C(52A)	1.79(3)	P(1)–C(11)	1.803(3)
P(1)–C(21)	1.824(8)	P(1)–C(51)	1.89(3)
P(1)–C(31A)	1.933(3)	P(2)–C(11A)	1.775(3)
P(2)–C(41)	1.823(8)	P(2)–C(51A)	1.84(4)
P(2)–C(52)	1.86(4)	P(2)–C(31)	1.955(3)
C(51)–C(52)	1.52(5)	C(51A)–C(52A)	1.51(5)
Rh(1)–C(1)	2.187(7)	Rh(1)–C(3)	2.192(7)
C(1)–C(6)	1.497(11)	C(3)–C(8)	1.488(11)
C(6)–C(42)	1.508(11)	C(8)–C(22)	1.526(11)
C(41)–C(42)	1.419(10)	C(21)–C(22)	1.391(10)
Bond angles			
P(1)–Rh(1)–P(2)	86.94(7)	P(1)–Rh(1)–Br(1)	94.43(6)
P(2)–Rh(1)–Br(1)	93.81(6)	Cp*–Rh(1)–Br(1)	122.5(2)
Cp*–Rh(1)–P(1)	124.9(2)	Cp*–Rh(1)–P(2)	124.7(2)
C(11)–P(1)–Rh(1)	121.03(13)	C(21)–P(1)–Rh(1)	116.7(2)
C(31A)–P(1)–Rh(1)	107.97(12)	C(51)–P(1)–Rh(1)	107.2(9)
C(52A)–P(1)–Rh(1)	109.1(11)	C(11A)–P(2)–Rh(1)	121.07(13)
C(41)–P(2)–Rh(1)	117.0(2)	C(51A)–P(2)–Rh(1)	104.9(13)
C(52)–P(2)–Rh(1)	110.2(11)	C(31)–P(2)–Rh(1)	108.96(12)
C(52A)–P(1)–C(21)	109.4(10)	C(11)–P(1)–C(21)	99.5(2)
C(11)–P(1)–C(51)	111.4(8)	C(21)–P(1)–C(51)	99.0(8)
C(52A)–P(1)–C(31A)	106.3(8)	C(21)–P(1)–C(31A)	106.9(2)
C(11A)–P(2)–C(41)	100.2(3)	C(11A)–P(2)–C(51A)	113.0(10)
C(41)–P(2)–C(51A)	98.7(11)	C(41)–P(2)–C(52)	108.1(11)
C(41)–P(2)–C(31)	104.8(3)	C(52)–P(2)–C(31)	107.2(8)
C(52)–C(51)–P(1)	112(2)	C(51)–C(52)–P(2)	113(2)
C(52A)–C(51A)–P(2)	112(3)	C(51A)–C(52A)–P(1)	114(2)
C(3)–Rh(1)–P(1)	92.0(2)	C(1)–Rh(1)–P(2)	92.0(2)
C(22)–C(21)–P(1)	125.7(6)	C(42)–C(41)–P(2)	125.2(6)
C(21)–C(22)–C(8)	127.0(7)	C(41)–C(42)–C(6)	126.3(7)
C(3)–C(8)–C(22)	120.5(6)	C(1)–C(6)–C(42)	121.3(7)
C(8)–C(3)–Rh(1)	128.8(5)	C(6)–C(1)–Rh(1)	128.2(5)

[a] Cp* denotes the centroid of the cyclopentadienyl ring.

2.4. Syntheses and thermolyses of $[(\eta^5\text{-}C_5Me_5)RhCl(dfppe)]^+\cdot X^-$ ($X^- = Cl^-$ **2a**, BPh_4^- **2d**, PF_6^- **2e**)

In an attempt to prepare $[(\eta^5\text{-}C_5Me_5)RhCl(dfppe)]^+\cdot Cl^-$ (**2a**) by anion metathesis, **2b** was twice treated with an excess of NH_4Cl in acetone at room temperature (Scheme 3). The ^1H-, ^{19}F- and $^{31}P\{^1H\}$-NMR spectra showed the orange product of the attempted metathesis to be a mixture comprising predominantly chloro-diphosphine cation **2** together with activated cations **3**, **1** and some uncomplexed dfppe. The ^{19}F-NMR spectrum reveals the presence of BF_4^-, but in significantly less than stoichiometric quantity. The mixture was found to be almost completely soluble in benzene, which **2b** is not, suggesting that the desired chloride salt, **2a**, was the major product. Thus, it appears that the metathesis has been at least partially successful, but that C–F and C–H bond activating and C–C bond forming reactions have also occurred to a small extent. That these reactions have occurred in a solvent in which **2b** undergoes no reaction, even under prolonged reflux [2], strongly suggests that substitution of the tetrafluoroborate for chloride facilitates the reaction under mild conditions.

The syntheses of $[(\eta^5\text{-}C_5Me_5)RhCl(dfppe)]^+\cdot X^-$ ($X^- = BPh_4^-$ **2d**, $X^- = PF_6^-$, **2e**) were attempted using a similar route to the preparation of the tetrafluoroborate salt **2b** [2] (Scheme 3). For **2d**, $[(\eta^5\text{-}C_5Me_5)RhCl(\mu\text{-}Cl)]_2$ was treated with two equivalents of $NaBPh_4$, followed by addition of dfppe. For **2e**, an excess of KPF_6 was used. The NMR spectroscopic and mass spectrometric data indicate that **2d** and **2e** had been formed, but were components of mixtures also containing activated cations **1** and **3**. The tetraphenylborate salt **2d** constituted ca. 90% and the hexafluorophosphate salt **2e** considerably less of the respective mixtures. The positive ion FAB mass spectra of both mixtures show the presence of **2** and [**2** − Cl], and the negative ion FAB mass spectra confirm the presence of BPh_4^- in **2d** and PF_6^- in **2e**. The ^1H-, ^{19}F- and $^{31}P\{^1H\}$-NMR spectra, recorded in $(CD_3)_2CO$, were similar to those of **2b** [2], but the ^{19}F-NMR spectrum lacked resonances due to BF_4^-. The ^1H-NMR spectrum of **2d** also contained three resonances between δ 6.5 and 7.5 assigned to BPh_4^- and the ^{19}F- and $^{31}P\{^1H\}$-NMR spectra of **2e** also included doublet and septet resonances, respectively, assigned to PF_6^-. The elemental analyses of both salts could not be obtained due to their contamination by significant amounts of **1** and **3**, from which they could not be separated. Preparations of **2b**, if not performed with care, occasionally produce small quantities of activated cations **1** and **3**, but very much less than produced in the syntheses of **2d** and **2e**. These observations are consistent with the anion exerting a large influence on the reactions. Hexafluorophosphate and tetraphenylborate appear to render the C–F and C–H activation of cation **2** more facile relative to tetrafluoroborate.

Thermolysis of the mixture containing **2a** in benzene for 11 h gave a yellow solution. The ^1H-, ^{19}F- and $^{31}P\{^1H\}$-NMR spectra indicated that the product of thermolysis was the diactivated cation **1**, contaminated by traces of uncomplexed dfppe and cations **2** and **3**. The ^{19}F-NMR spectrum showed that BF_4^- was present in an almost stoichiometric quantity. The increase in the relative amount of this anion on thermolysis is indicative of C–F and C–H bond activation occurring to produce HF, which reacts with the borosilicate glass reaction vessel to form BF_4^- [2].

Thermolysis of **2d** in benzene for 5 h gave a purple solution, which yielded a purple oil on removal of the solvent. The NMR spectra indicated that C–F and C–H

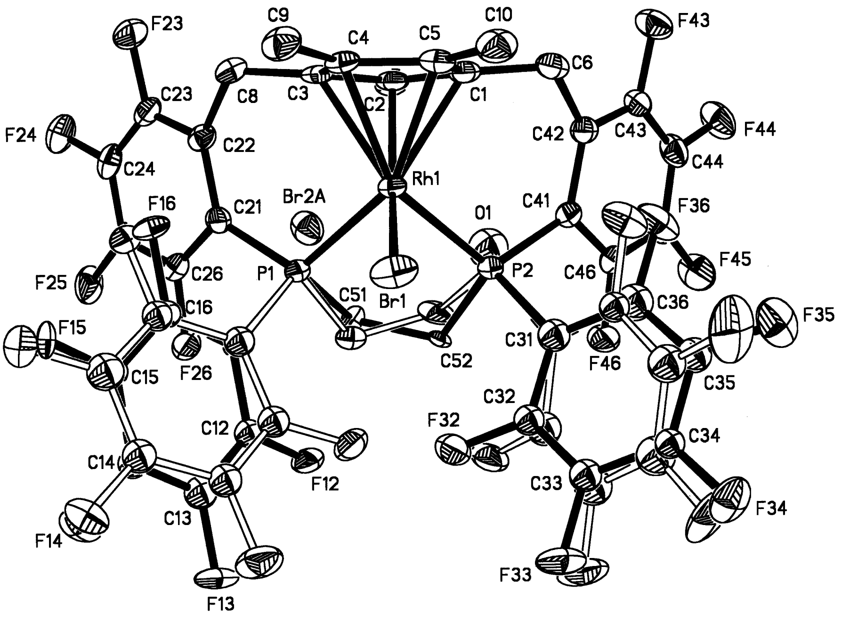
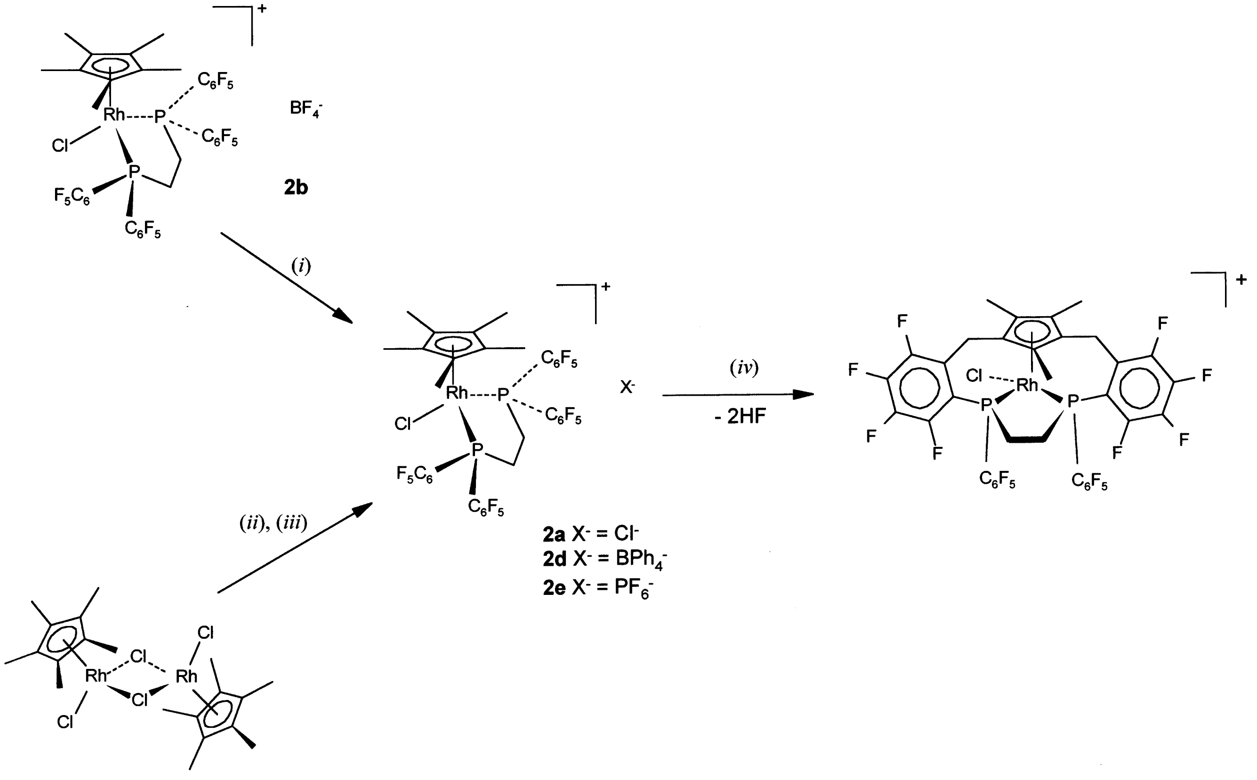


Fig. 2. Molecular structure of $[LRhBr]^+ \cdot Br^-$ (**4c**). Displacement ellipsoids are shown at the 35% probability level. All hydrogen atoms are omitted for clarity. The disordered site names are derived from their pseudo-mirror-related partners, e.g. C(12A) is opposite C(12) and close to C(32).

bond activation/C–C bond formation had taken place to form cation **1**. The ^{1}H-NMR spectrum showed the presence of BPh_4^-, but was complicated by many other signals due to aromatic hydrogen atoms. No attempt was made to identify the additional species, but it is presumed that the HF formed in this reaction cleaves one or more of the B–C bonds of BPh_4^-. Since **2e** was very impure the thermolysis was not attempted.

The results of these reactions, together with the evidence presented in Section 2.3, confirms the hypothesis



Scheme 3. (i) NH_4Cl, $(CH_3)_2CO$; (ii) $NaBPh_4$ (**2d**) or KPF_6 (**2e**), MeOH; (iii) dfppe, CH_2Cl_2; (iv) C_6H_6, reflux.

that the anion is having a large effect in determining whether the C–F and C–H bond activating reaction occurs. Reaction (1), which involves Cl^- as the anion, occurs in aprotic, non-polar solvents, such as benzene, toluene and dichloromethane (ε_r 2.274, 2.379 at 25°C and 9.08 at 20°C, respectively [6]), as well as the protic, polar solvent ethanol (ε_r 24.30 at 25°C [6]). Reaction (2) does not occur in aprotic, non-polar solvents, such as benzene, nor in the aprotic, polar solvent dry acetone (ε_r 20.7 at 25°C [6]), to only a small extent in the more polar acetontirile (ε_r 37.5 at 20°C [6]), but occurs readily in ethanol [2]. However, on substitution of the anion from BF_4^- to Cl^- or BPh_4^- the reaction occurs readily in benzene. These observations suggest that the Coulombic interaction between the cation and anion is not the predominant factor in inhibiting reaction (1) since the ion pairs should be dissociated to a greater extent in acetonitrile than in ethanol. It is clear that BF_4^- exerts a different influence than the other anions on the reaction, and that a protic solvent is necessary to facilitate reaction (1). Anion effects in the reactions of cationic $[(\eta^5\text{-}C_5R_5)Rh]$ species have been observed previously, but are thought to arise due to differences in coordination of the anions to the metal. For example, in CH_3NO_2 at 80°C benzene can be displaced from $[(\eta^5\text{-}C_5Me_4Et)Rh(\eta^6\text{-}C_6H_6)]^{2+}\cdot 2PF_6^-$ by methanol, whereas $[(\eta^5\text{-}C_5Me_4Et)Rh(\eta^6\text{-}C_6H_6)]^{2+}\cdot 2BF_4^-$ shows no reaction after 48 h [7]. However, it is improbable that the differences in reactivity of $[(\eta^5\text{-}C_5Me_5)\text{-}RhCl(dfppe)]^+\cdot X^-$ are due to coordination of the anion to the metal. Even if an intermediate such as $[(\eta^5\text{-}C_5Me_5)Rh(dfppe)]^{2+}$ is formed the metal will coordinate chloride preferentially to the bulkier and more weakly coordinating anions. We are currently carrying out further investigations to understand more fully the mechanism of these intriguing reactions and why tetrafluoroborate exerts such an effect.

3. Conclusion

In conclusion we have demonstrated that formation of the cation $[\mathbf{L}RhCl]^+$, **4**, from $[(\eta^5\text{-}C_5Me_5)RhBr(\mu\text{-}Br)]_2$ and dfppe proceeds via the bromo-diphosphine cation **5** and then the singly activated cation $[\mathbf{L'}RhCl]^+$, **6**, with concomitant formation of HF in both ethanol and benzene. This corroborates mechanistic data obtained for reaction (1) in ethanol and suggests that the mechanism is identical in benzene. We have also determined that the lack of reaction observed on thermolysis of **2b** in both non-polar and polar aprotic solvents can ascribed to the influence of the tetrafluoroborate anion, since substitution for chloride or tetraphenylborate leads to the facile formation of cation **1** in benzene.

4. Experimental

4.1. General procedures

^1H-, ^{19}F- and ^{31}P-NMR spectra were recorded on Bruker AM300, DPX300 or ARX250 spectrometers. ^1H-NMR spectra were referenced using the residual protio solvent resonance relative to tetramethylsilane (δ 0), ^{19}F- and ^{31}P-NMR spectra externally to $CFCl_3$ (δ 0) and 85% H_3PO_4 (δ 0), respectively, using the high frequency positive convention. ^{19}F-NMR spectra of salts containing BF_4^-, the fluorine atoms of which have a relatively high value of T_1, were recorded with a relaxation delay of 10 s. All chemical shifts (δ) are quoted in ppm and coupling constants in Hz. Abbreviations used in multiplicities are: s, singlet; d, doublet; t, triplet; m, multiplet; br denotes a signal broadened due to a fluxional process. Elemental analyses were performed by Butterworths Ltd. Positive and negative ion FAB mass spectra were obtained on a Kratos Concept 1H mass spectrometer using *m*-nitrobenzyl alcohol as matrix.

4.2. Reagents

$(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$ (Fluorochem) and $[(\eta^5\text{-}C_5Me_5)RhCl(\mu\text{-}Cl)]_2$ (Aldrich) were used as supplied. $[(\eta^5\text{-}C_5Me_5)RhX(\mu\text{-}X)]_2$ (X = Br or I) was prepared as described [8].

4.3. Preparations

4.3.1. Preparation of $[LRhBr]^+\cdot BF_4^-$ (**4b**)

A slurry of $[(\eta^5\text{-}C_5Me_5)RhBr(\mu\text{-}Br)]_2$ (0.080 g, 0.10 mmol) and dfppe (0.150 g, 0.20 mmol) in benzene (60 cm^3) was refluxed under nitrogen for 122 h. The solvent was removed by rotary evaporation to afford an orange–yellow solid, which was extracted into methanol (70 cm^3) and filtered. NH_4BF_4 (1.00 g, 9.54 mmol) was added and the solution left for 2 h. The solvent was removed by rotary evaporation and the product extracted into dichloromethane (100 cm^3) and filtered. The solvent was removed by rotary evaporation to yield an orange solid, which was washed with chloroform (60 cm^3) to yield 0.035 g of the yellow product **4b**, which was washed with light petroleum and dried. A further 0.025 g was obtained on concentration of the chloroform washings and addition of light petroleum. Yield, 0.060 g, 27%. ^1H [CD_2Cl_2, 300.14 MHz]: 4.47 (dm, $^2J_{H-H'}$ 18.3, 2H, $CHH'C_6F_4$), 3.76 (m, 2H, PCH_2), 3.65 (d, $^2J_{H-H'}$ 18.3, 2H, $CHH'C_6F_4$), 3.03 (m, 2H, PCH_2), 2.17 (d, $^4J_{P-H}$ 7.6, 6H, 4- and 5-CH_3), 1.04 (s, 3H, 2-CH_3). ^{19}F [CD_2Cl_2, 282.41 MHz]: −117.1 (s, 2F, C_6F_4), −134.65 (s, 2F), −127.60 (br s, 2F, F_{ortho}), −132.80 (br s, 2F, F_{ortho}), −143.44 (dt, J_{F-F} 20.4, 10.4, 2F), −144.72 (t, $^3J_{F-F}$

21.6, 2F), −152.26 (t, $^3J_{F\text{–}F}$ 21.6, 2F), −152.99 and −153.04 (1:4) (4F, BF_4^-), −158.43 (br s, 4F, F_{meta}). $^{31}P\{^1H\}$ [CD_2Cl_2, 121.50 MHz]: 68.5 (dm, $^1J_{Rh\text{–}P}$ 142 Hz). FAB MS *m*/*z*: 1038, 1036 ($[M-BF_4+H]^+$), 956 ($[M-BF_4-Br]^+$).

4.3.2. *Preparation of* $[(\eta^5\text{-}C_5Me_5)RhBr(dfppe)]^+\cdot BF_4^-$ *(5b)*

The salt NH_4BF_4 (0.600 g, 5.72 mmol) was added to $[(\eta^5\text{-}C_5Me_5)RhBr(\mu\text{-}Br)]_2$ (0.084 g, 0.11 mmol) in methanol (50 cm^3) and the mixture stirred for 10 min. Dfppe (0.16 g, 0.21 mmol) in dichloromethane (10 cm^3) was added and the mixture stirred for 3 h. The solvents were removed by rotary evaporation and the product extracted into dichloromethane (80 cm^3). The solution was filtered and concentrated by rotary evaporation to 40 cm^3. Addition of light petroleum precipitated **5b** as a yellow microcrystalline solid, which was filtered off and washed with light petroleum and dried. Yield 0.185 g (62%). ^1H [$(CD_3)_2CO$, 300.14 MHz]: 3.50 (m, 4H, CH_2), 1.82 (t, $^4J_{P\text{–}H}$ 4.85, CH_3). ^{19}F [$(CD_3)_2CO$, 282.41 MHz]: −124.20 (br s, 4F, F_{ortho}), −127.43 (dm, $^3J_{F\text{–}F}$ 12.4, 4F, F_{ortho}), −144.95 (m, 2F, F_{para}), −146.25 (m, 2F, F_{para}), −150.87 and −150.93 (1:4) (4F, BF_4^-), −158.32 (m, 4F, F_{meta}), −160.32 (m, 4F, F_{meta}). $^{31}P\{^1H\}$ [$(CD_3)_2CO$, 121.50 MHz]: 34.0 (dm, $^1J_{Rh\text{–}P}$ 151 Hz). FAB MS *m*/*z*: 1077, 1075 ($[M-BF_4]^+$), 996 ($[M-BF_4-Br]^+$). Anal. Found: C, 38.3; H, 1.6. $C_{36}H_{19}BBrF_{24}P_2Rh$. Calc.: C, 38.65; H, 1.7%.

4.3.3. *Preparation of* $[(\eta^5\text{-}C_5Me_5)RhCl(dfppe)]^+\cdot Cl^-$ *(2a)*

The salt NH_4Cl (1.0 g, 9.54 mmol) was added to **2b** (0.100 g, 0.11 mmol) in acetone (150 cm^3) and water (20 cm^3). The mixture was left at room temperature for 30 min, then filtered. The filtrate was concentrated by rotary evaporation to yield a yellow emulsion, which was extracted with CH_2Cl_2. After drying over anhydrous $MgSO_4$, the CH_2Cl_2 extract was filtered and the solvent removed by rotary evaporation to give a yellow solid, which contained significant amounts of tetrafluoroborate. The solid was treated with NH_4Cl as above and the process repeated. The resultant yellow solid was a mixture comprising predominantly cation **2**, and also **1** and **3** with dfppe and small amounts of BF_4^-. Yield ca. 0.08 g. The impure nature of the product precluded characterization by elemental analysis and characterization is based on NMR spectroscopic data by comparison with **2b**. ^1H [($CDCl_3$, 300.01 MHz]: 2.56 (m, 4H, CH_2), 1.56 (t, $^4J_{P\text{–}H}$ 4.6, CH_3). ^{19}F [$CDCl_3$, 282.26 MHz]: −125.68 (br s, 4F, F_{ortho}), −128.51 (dm, $^3J_{F\text{–}F}$ 10.2, 4F, F_{ortho}), −141.87 (t, $^3J_{F\text{–}F}$ 20.2, 2F, F_{para}), −143.85 (t, $^3J_{F\text{–}F}$ 20.5, 2F, F_{para}), −158.28 (m, 4F, F_{meta}), −159.68 (m, 4F, F_{meta}). $^{31}P\{^1H\}$ [$CDCl_3$, 121.45 MHz]: 30.5 (dm, $^1J_{Rh\text{–}P}$ 152 Hz).

4.3.4. *Preparation of* $[(\eta^5\text{-}C_5Me_5)RhCl(dfppe)]^+\cdot BPh_4^-$ *(2d)*

Salt **2d** was prepared as for **5b** from $[(\eta^5\text{-}C_5Me_5)RhCl(\mu\text{-}Cl)]_2$ (0.125 g, 0.20 mmol), two equivalents of $NaBPh_4$ (0.165 g, 0.48 mmol) and dfppe (0.32 g, 0.42 mmol). The product was obtained as an orange solid, contaminated by cations **1** and **3** from which it could not be separated. Characterization is based on the spectroscopic data and by comparison with **2b**. Yield 0.30 g (ca. 55%). ^1H [$(CD_3)_2CO$, 300.14 MHz]: 7.33 (m, 8H, BPh_4), 6.91 (m, 8H, BPh_4), 6.76 (t, *J* 7.2, 4H, *para*-BPh_4), 3.40 (m, 4H, CH_2), 1.72 (t, $^4J_{P\text{–}H}$ 4.8, CH_3). ^{19}F [$(CD_3)_2CO$, 282.41 MHz]: −124.48 (br s, 4F, F_{ortho}), −127.47 (dm, $^3J_{F\text{–}F}$ 13.9, 4F, F_{ortho}), −144.77 (m, 2F, F_{para}), −146.03 (m, 2F, F_{para}), −158.20 (m, 4F, F_{meta}), −160.28 (m, 4F, F_{meta}). $^{31}P\{^1H\}$ [$(CD_3)_2CO$, 121.50 MHz]: 35.3 (dm, $^1J_{Rh\text{–}P}$ 151 Hz). FAB MS *m*/*z*: 1031 ($[M-BPh_4]^+$), 996 ($[M-BPh_4-Cl]^+$), 319 (BPh_4^-).

4.3.5. *Preparation of* $[(\eta^5\text{-}C_5Me_5)RhCl(dfppe)]^+\cdot PF_6^-$ *(2e)*

The salt **2e** was prepared as for **5b** from $[(\eta^5\text{-}C_5Me_5)RhCl(\mu\text{-}Cl)]_2$ (0.09 g, 0.15 mmol), KPF_6 (0.91 g, 4.9 mmol) and dfppe (0.23 g, 0.30 mmol). The product was obtained as a yellow powder, highly contaminated by cations **1** and **3** from which it could not be separated. Characterization is based on the spectroscopic data and by comparison with **2b**. Yield 0.21 g (ca. 60%). ^1H [$(CD_3)_2CO$, 300.14 MHz]: 3.40 (m, 4H, CH_2), 1.74 (t, $^4J_{P\text{–}H}$ 4.8, CH_3). ^{19}F [$(CD_3)_2CO$, 282.41 MHz]: −71.78 (d, $^1J_{P\text{–}F}$ 706.6, PF_6^-), −124.47 (br s, 4F, F_{ortho}), −127.52 (dm, $^3J_{F\text{–}F}$ 13.9, 4F, F_{ortho}), −144.82 (tm, $^3J_{F\text{–}F}$ 21.0, 2F, F_{para}), −146.21 (m, 2F, F_{para}), −158.24 (m, 4F, F_{meta}), −160.29 (m, 4F, F_{meta}). $^{31}P\{^1H\}$ [$(CD_3)_2CO$, 121.50 MHz]: 35.1 (dm, $^1J_{Rh\text{–}P}$ 155 Hz, dfppe), −138.8 (sept, $^1J_{P\text{–}F}$ 706.6, PF_6^-). FAB MS *m*/*z*: 1031 ($[M-PF_6]^+$), 996 ($[M-PF_6-Cl]^+$), 145 (PF_6^-).

4.3.6. *X-ray crystal structure determination*

Crystals of salt **4c** suitable for X-ray structure determination were grown from acetone. The structure was determined at low temperature on a Siemens P4 diffractometer. Crystallographic data are presented in Table 1 and atomic coordinates and isotropic displacement parameters are given in Table 2. Accurate unit cell parameters were determined by least-squares refinement of the optimised setting angles of 39 reflections in the range $5 \leq \theta \leq 12.5°$. Three standard check reflections, monitored every 97 reflections, indicated no crystal decay. The data were corrected for absorption, Lorentz and polarization effects.

The structure was solved by direct methods using the PATT option of SHELXTL-PC [9] and refined by full matrix least squares on F^2. The disordered C_6F_5 rings were modelled as idealized planar rings (C–C 1.39, C–F 1.34 Å) and refined as rigid groups with individual atom anisotropic displacement parameters. Hydrogen atoms were included in calculated positions (C–H 0.99 Å) and refined by a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters. An analysis of the weighting scheme over $|F_0|$ and $(\sin\theta)/\lambda$ was satisfactory.

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