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Intramolecular dehydrofluorinative coupling of η^6-arene and fluoroarylphosphine ligands in ruthenium complexes

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ABSTRACT

NMR studies of reactions between a series of arene ruthenium(II) fluoroarylphosphine complexes and Proton Sponge have revealed the necessary conditions for intramolecular dehydrofluorinative ligand coupling. The complex must be cationic, and the phosphine need have only one fluoroaryl substituent. The reaction is rapid and clean for [(η^6-toluene)RuCl(dfppe)]BF_4, [(η^6-mesitylene)RuCl{$(C_6F_5)_2PC_6H_4S$-Me}]BF_4 and the diastereomer of [(η^6-toluene)RuCl{$Ph_2PC_2H_4PPh(C_5F_4N$-4)}]BF_4 in which the tetrafluoropyridyl substituent is close to the η^6-arene. [(η^6-*p*-cymene)RuCl(dfppe)]BF_4 reacts in the presence of Proton Sponge to give a mixture of unidentified compounds. The neutral complex [(η^6-toluene)$RuCl_2${$Ph_2P(C_6F_5)$}] and the diastereomer of [(η^6-toluene)RuCl{$Ph_2PC_2H_4PPh(C_5F_4N$-4)}]BF_4 in which the tetrafluoropyridyl substituent is distant to the η^6-arene do not undergo reaction.

1. Introduction

We have developed intramolecular dehydrofluorinative carbon–carbon coupling as a methodology to couple cyclopentadienide and phosphine ligands in cationic rhodium [1–3] and iridium [4] complexes. The reaction, which proceeds on thermolysis or addition of base, is presumed to involve deprotonation of a methyl substituent of the cylopentadienide ring and nucleophilic attack at the *ortho* position of a fluoroaryl substituent of a phosphine. The method provides a convenient route to complexes of tridentate tethered η^5,κP-cyclopentadieneide-phosphine ligands, which can be difficult to access by other routes [5]. Although tethered η^6,κP-arene–phosphine ligands are more readily accessible by other methods [6–20], intramolecular coupling of ligands is still attractive for reasons of enhanced regio- and stereo-selectivity. A small number of intramolecular coupling reactions that afforded complexes of η^6,κP-arene–phosphine ligands have been reported [21–23]. Prompted by the isoelectronic relationship between the fragments [(η^5-C_5R_5)Rh]$^+$ and [(η^6-arene)Ru]$^+$, we set out to investigate whether intramolecular dehydrofluorinative coupling could be extended to arene ruthenium complexes. We have already communicated the coupling reaction in the arene ruthenium complex [(η^6-$C_6H_3Me_3$-1,3,5)RuCl(dfppe)]BF_4 (dfppe = $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$), **1**, which proceeded stepwise on addition of the stoichiometric quantity of Proton Sponge, but not on thermolysis, to generate **2** then **3** (Scheme 1) [24]. Here we report further studies into the intramolecular dehydrofluorinative coupling of arene and phosphine ligands in ruthenium complexes. The coupling reaction was assessed by *in situ* NMR experiments on a range of cationic complexes containing different arene and phosphine ligands and on a neutral complex. This strategy has proved useful for assessing the analogous reaction with η^5-cyclopentadienide rhodium complexes of polyfluoroaryl- [2] and trifluorovinyl-phopshines [25].

2. Results and discussion

The salts [(η^6-toluene)RuCl(dfppe)]BF_4, **4**, and [(η^6-*p*-cymene)RuCl(dfppe)]BF_4, **5**, were prepared by treatment of the appropriate $[ArRuCl_2]_2$ complex with dfppe in the presence of an excess of tetrafluoroborate, and obtained in moderate to high yields as orange microcrystalline solids. An attempt to prepare [(η^6-hexamethylbenzene)RuCl(dfppe)]BF_4 was unsuccessful, presumably because the steric requirement of the hexamethylbenzene ligand precludes coordination of the bulky dfppe. The $^{31}P\{^1H\}$ spectra of **4** and **5** display resonances at δ 47.2 and 52.3 respectively, consistent with that of **1** (δ 46.8) [24]. The ^{19}F NMR spectrum of **4**, recorded in deutero-chloroform at 282 MHz, displays seven resonances in addition to those of tetrafluoroborate: Two broad resonances and a doublet with a ratio of integration of 2:2:4 assigned to the *ortho* fluorine atoms, two triplet resonances assigned to the *para* fluorine atoms, and two

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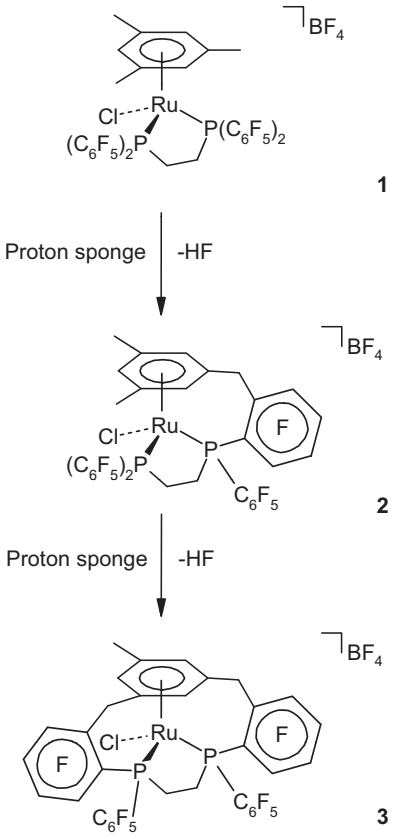


Scheme 1.

multiplet resonances of equal integration assigned to the *meta* fluorine atoms. The data are consistent with the expected two pairs of equivalent pentafluorophenyl substituents, but also indicate hindered rotation about the P–C bonds of one pair. The ^{19}F NMR spectrum of **5**, recorded in deutero-acetone at 282 MHz, is similar to that of **4**, except that the resonances assigned to the *meta* fluorine atoms are a multiplet and two broad resonances with a ratio of integration of 4:2:2. From a variable temperature ^{19}F NMR study of **5** a value of the energy barrier to rotation, $\Delta G^{\ddagger}$, of 56 ± 4 kJ mol^{-1} was calculated [26]. Broadening of the resonance of the *ortho* fluorine atoms of the other pair of pentafluorophenyl groups was observed below 213 K, but it was not possible to reach the coalescence temperature and calculate $\Delta G^{\ddagger}$ for rotation about these P–C bonds.

The structure of **4** (Fig. 1) has been determined by a single-crystal X-ray diffraction study. Crystallographic data are given in Table 1. Selected bond distances and angles are given in Table 2. The geometry around ruthenium is similar to that in [(η^6-*p*-cymene)RuCl(dppe)]BF_4 [27], with some slight differences in distances and angles. In particular the Ru–Cl distance is significantly shorter in **4** (2.398(2) *cf.* 2.430(1) Å).

NMR tube experiments revealed that on addition of Proton Sponge **4** and **5** underwent rapid reactions. ^{31}P{^{1}H} and ^{19}F NMR spectroscopy revealed that in deutero-acetone salt **4** gave the coupled product **6** cleanly (Scheme 2). The ^{31}P{^{1}H} NMR spectrum comprises two mutually coupled resonances at δ 48.4 and 73.7. By comparison with the spectrum of **2** [24] these resonances are assigned to the untethered and tethered phosphorus atoms respectively. The change of the chemical shift on coupling, $\Delta\delta_P$, of 26.5 ppm is consistent with that observed for **2** and **3**, and also on coupling of cyclopentadienide and phosphine ligands in rhodium complexes [2]. The ^{19}F spectrum contains eleven signals in addition to those of tetrafluoroborate. Three are assigned to the

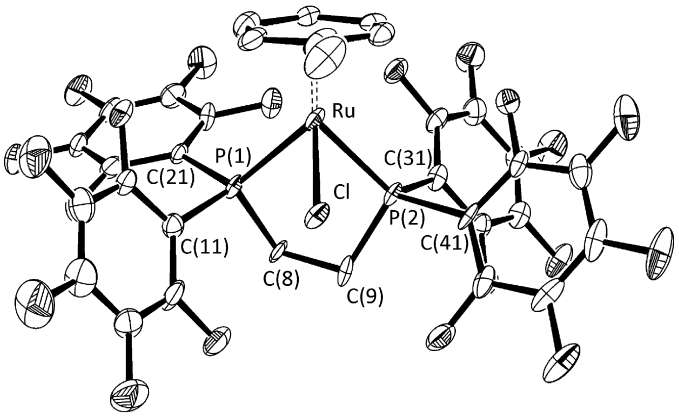


Fig. 1. Structure of the cation of [(η^6-toluene)RuCl(dfppe)]BF_4, **4**.Thermal ellipsoids are at the 50% level. Hydrogen atoms are omitted for clarity.

bridging tetrafluorophenyl group, three to *ortho* fluorine atoms of the pentafluorophenyl groups (integrating 1:1:4), and two to *meta* fluorine atoms of the pentafluorophenyl groups (integrating 2:4). The remaining three are assigned to the *para* fluorine atoms of the pentafluorophenyl groups and one fluorine atom of the tetrafluorophenyl tether (integrating 1:1:2 with the resonance of one *para* fluorine atom coincident with another or the C_6F_4 resonance). Unfortunately the presence of Proton Sponge and its protonated product obscured many of the resonances of **6** in the ^{1}H NMR spectrum, but repeating the reaction in deutero-dimethyl sulphoxide allowed these data to be obtained. The two hydrogen atoms of the methylene group of the η^6-arene give rise to doublet resonances at δ 4.69 and 3.54 with a mutual coupling of 18.3 Hz, consistent with those in **2** and **3**. ^{31}P{^{1}H} and ^{19}F NMR spectroscopy revealed that the reaction between **5** and Proton Sponge gave a complicated mixture of compounds. The ^{31}P{^{1}H} NMR spectrum display at least eight resonances. Unfortunately it was not possible to identify any of the products of the reaction.

Treatment of [(η^6-mesitylene)$RuCl_2$]$_2$ with $(C_6F_5)_2PC_6H_4SMe$-2 in the presence of an excess of tetrafluoroborate gave **7** in 53% yield. No complex was formed with the potentially bidentate ligand $(C_6F_5)_2PC_6H_4OMe$-2, as was found for [(η^5-C_5Me_5)RhCl $_2$]$_2$

Table 1
Crystallographic data for [(η^6-toluene)RuCl(dfppe)]BF_4·CH_2Cl_2 (**4**·CH_2Cl_2).[a]

Formula	$C_{33}H_{12}BClF_{24}P_2Ru\cdot CH_2Cl_2$
Formula weight	1158.62
Crystal system	Monoclinic
Space group	$P2_1/n$
a, Å	8.4907(12)
b, Å	22.457(3)
c, Å	20.904(3)
β,°	97.164(3)
V, Å^3	3954.9(10)
Z	4
D_c (g cm^{-3})	1.946
Crystal size (mm^3)	$0.42 \times 0.18 \times 0.08$
μ (mm^{-1})	0.823
θ range (°)	$1.34 \rightarrow 25.00$
Total reflections	14815
Unique reflections (R_{int})	6810 (0.1405)
Observed reflections [$I > 2\sigma(I)$]	3742
Parameters	587
Final *R* indices [$I > 2\sigma(I)$]	R_1 0.0561, $wR_2 = 0.110$
R indices (all data)	$R_1 = 0.1201$, $wR_2 = 0.1412$
Weighting scheme	$w = 1/[\sigma^2(F_o)^2 + \{0.0545(F_o^2 + 2F_c^2)/3\}^2]$
Max., min. $\Delta\rho$ (eÅ^{-3})	1.017, −0.971
Goodness of fit on F^2	0.952

[a] Estimated standard deviations are given in parentheses. Data were collected at 153(2) K with graphite monochromated radiation ($\lambda = 0.71073$ Å).

Table 2
Selected bond distances (Å) and angles (°) for [(η^6-toluene)RuCl(dfppe)]BF_4·CH_2Cl_2 (**4**·CH_2Cl_2).[a]

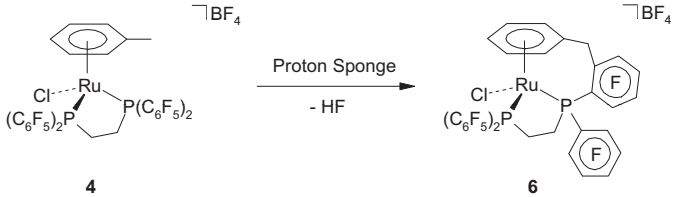
Ar*–Ru	1.751(8)	Ru–Cl	2.398(2)
Ru–P(1)	2.334(2)	Ru–P(2)	2.347(2)
P(1)–C(8)	1.834(7)	P(1)–(11)	1.827(7)
P(1)–C(21)	1.830(7)	P(2)–C(9)	1.827(7)
P(1)–C(31)	1.842(8)	P(1)–C(41)	1.836(7)
Mean C–C (η^6-C_6)	1.414(11)	Mean C–F	1.348(8)
Ar*–Ru–Cl	123.3(2)	Ar*–Ru–P(1)	130.7(2)
Ar*–Ru–P(2)	135.9(2)	Cl–Ru–P(1)	84.68(7)
Cl–Ru–P(2)	79.38(7)	P(1)–Ru–P(2)	83.50(7)
Ru–P(1)–C(8)	109.4(2)	Ru–P(1)–C(11)	108.6(2)
Ru–P(1)–C(21)	124.1(2)	C(8)–P(1)–C(11)	110.8(3)
C(8)–P(1)–C(21)	100.5(3)	C(11)–P(1)–C(21)	102.9(3)
Ru–P(2)–C(9)	106.4(2)	Ru–P(2)–C(31)	127.1(3)
Ru–P(2)–C(41)	111.9(2)	C(9)–P(2)–C(31)	102.5(3)
C(9)–P(2)–C(41)	98.2(3)	C(31)–P(2)–C(41)	109.8(3)

[a] Estimated standard deviations are given in parentheses. Ar* represents the centroid of the η^6-C_6 ring.

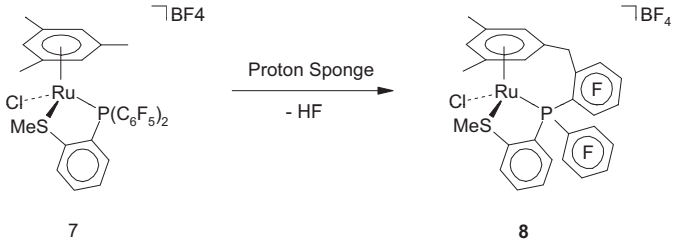
[2]. It is presumed that the anisole oxygen atom is not a suitable donor ligand to bond to ruthenium(II) and rhodium(III) sufficiently strongly, and that monodentate phosphines bearing two pentafluorophenyl substituents are too bulky to coordinate. The ^{19}F NMR spectrum of **7** displays four resonances assigned to the *ortho* fluorine atoms, indicating hindered rotation about both P–C bonds, as was observed for [(η^5-C_5Me_5)RhCl{(C_6F_5)$_2$PC_6H_4SMe-2}]BF_4 [2].

An NMR tube experiment in deutero-chloroform revealed that on addition of an excess of Proton Sponge **7** underwent rapid intramolecular dehydrofluorinative ligand coupling to give **8** (Scheme 3). A shift of δ_P of 20 ppm to 63.8 ppm was observed, and the ^{19}F NMR spectrum displays the expected nine resonances of the aryl fluorine atoms, including those at δ −120.91, −134.62, −143.71 and −151.48 which are assigned to the tetrafluorophenyl group and are consistent with those of [(η^5,κP,κS-$C_5Me_4CH_2C_6F_4$-2-P(C_6F_5)C_6H_4SMe-2}RhCl]$^+$ (δ −119.73, −134.35, −142.43 and −151.54). The ^{1}H NMR spectrum was consistent with the formulation of **8**, displaying in particular three resonances between δ 5.5 and 6.2 assigned to the non-equivalent arene hydrogen atoms, a doublet of doublet resonance at δ 4.80 assigned to one methylene hydrogen atom, and two singlet resonances at *ca.* 2.5 assigned to the non-equivalent methyl groups. Unfortunately the resonance of the other methylene hydrogen atom is obscured by those of protonated Proton Sponge. Although no attempt to isolate salt **8** was made, the mass spectrum of the crude product, after evaporation of the solvent, confirmed the formulation of the cation of **8**. The ^{31}P and ^{19}F NMR spectra indicated a mixture of **7** and **8** when less than one equivalent of Proton Sponge was used.

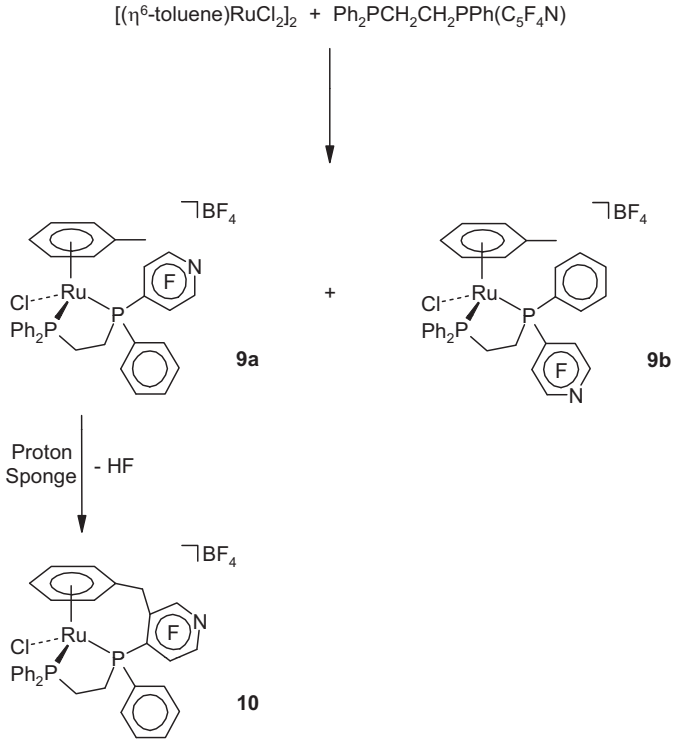
Treatment of [(η^6-toluene)$RuCl_2$]$_2$ with $Ph_2PCH_2CH_2PPh(C_5F_4$N-4)[28] in the presence of an excess of tetrafluoroborate gave **9** in 65% yield. The NMR spectra indicated that **9** was formed as a *ca.* 1:1 mixture of diastereomers differing in the relative positions of the η^6-arene ligand and the tetrafluoropyridyl substituent (Scheme 4). The ^{31}P{^{1}H} NMR spectrum displays four doublet resonances between δ 70 and 80, two of which also show coupling to multiple fluorine atoms (Fig. 2). The ^{19}F NMR spectrum displays four



Scheme 2.



Scheme 3.



Scheme 4.

resonances in addition to those of tetrafluoroborate, one of which, assigned to the fluorine atoms *ortho* to phosphorus of **9a** (*vida infra*), is broad and indicative of hindered rotation about the P–C. From a variable temperature ^{19}F NMR study in deutero-acetone at 282 MHz a value of the energy barrier to rotation, $\Delta G^{\ddagger}$, of 47 ± 3 kcal mol^{-1} was calculated [26]. Only slight broadening of the resonances of **9b** was observed at 223 K, but it was not possible to reach the coalescence temperature and calculate $\Delta G^{\ddagger}$ for rotation about the P–C bond.

An NMR tube experiment revealed that on addition of an excess of Proton Sponge to **9** in deutero-dimethylsulphoxide **9a** underwent intramolecular dehydrofluorinative ligand coupling to give **10** (Scheme 4). A shift of δ_P of 20 ppm to 89.2 was observed, and the ^{19}F NMR spectrum displays three trifluoropyridyl resonances at δ −91.95 (1F, m), −115.86 (1F, m), −140.03 (1F, m) (Fig. 2). Unfortunately the ^{1}H NMR spectrum was complicated by the presence of **9b** and protonated Proton Sponge, and no meaningful data for **10** could be obtained. Diastereomer **9b** did not react even over an extended period. The observations are consistent with the reaction of the analogous rhodium complex [(η^5-C_5Me_5)RhCl{$Ph_2PCH_2CH_2PPh(C_5F_4$N-4)}]BF_4 [28].

It has been established that for η^5-cyclopentadienyl rhodium complexes to undergo intramolecular dehydrofluorinative ligand coupling they must be cationic. In order to determine whether it is also necessary for η^6-arene ruthenium to be cationic to undergo

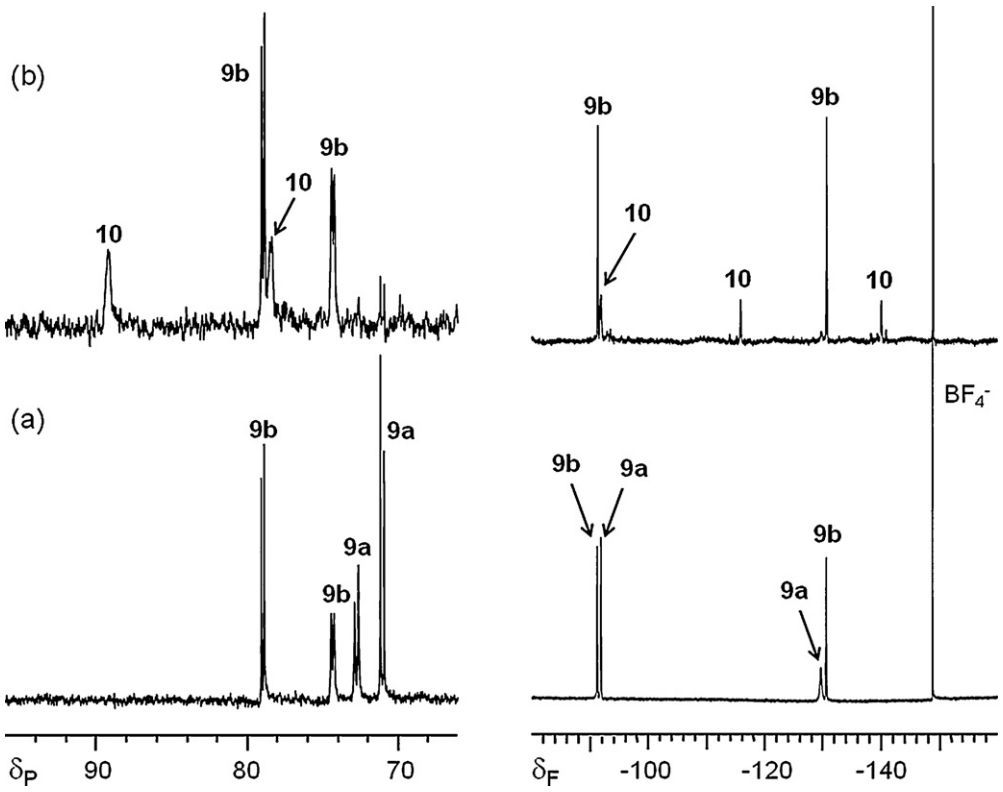


Fig. 2. $^{31}P\{^{1}H\}$ and ^{19}F NMR spectra of **9** (a) before and (b) after the addition of Proton Sponge.

the reaction the neutral complex [(η^6-toluene)$RuCl_2${$Ph_2P(C_6F_5)$}], **11**, was investigated. *In situ* NMR studies revealed that on addition of Proton Sponge no reaction occurred, even over an extended period.

3. Conclusions

Intramolecular dehydrofluorinative carbon–carbon coupling provides a method of preparing ruthenium(II) complexes of tethered η^6-arene–phosphine ligands. It has been established that the reaction occurs rapidly in the presence of the stoichiometric amount of Proton Sponge, and does not on thermolysis [24]. NMR studies have revealed that it is necessary for complex to be cationic. We suggest that in neutral complexes the acidity of the hydrogen atoms of methyl substituents is not sufficient for reaction, but the presence of the positive charge increases the acidity enough to facilitate the reaction. Only one polyfluoroaryl substituent is necessary, but this must be sufficiently close to the η^6-arene ligand, as in **4**, **7** and **9a**.

4. Experimental

4.1. Instrumentation

^{1}H, ^{19}F and ^{31}P NMR spectra were recorded using Bruker DPX300 or DRX300 spectrometers. ^{1}H (300.01 MHz) NMR spectra were referenced internally using the residual protio solvent resonance relative to $SiMe_4$ (δ 0), ^{19}F (282.26 MHz) externally to $CFCl_3$ (δ 0) and ^{31}P (121.45 MHz) externally to 85% H_3PO_4 (δ 0). All chemical shifts are quoted in δ (ppm), using the high frequency positive convention, and coupling constants in Hz. LSIMS mass spectra was 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. No precautions to exclude oxygen and water were taken in the preparations. NMR tube reactions were performed under nitrogen using tubes fitted with Young's taps. A solution of the appropriate ruthenium complex and Proton Sponge estimated in deuterated solvent was degassed in the NMR tube. If insufficient Proton Sponge was present then more was added and the sample degassed again.

4.2. Materials

The compounds $NaBF_4$, dfppe and Proton Sponge (Aldrich) were used as supplied. The complex [(η^6-toluene)$RuCl_2]_2$ was prepared from $RuCl_3.xH_2O$ and methylcyclohexadiene [29,30]. The complex [(η^6-mesitylene)$RuCl_2]_2$ was prepared by heating [(η^6-*p*-cymene)$RuCl_2]_2$ in mesitylene as described for the preparation of the hexamethylbenzene analogue [31]. The phosphines $(C_6F_5)_2PC_6H_4SMe$-2 [2], $(C_6F_5)_2PC_6H_4OMe$-2 [2] and $Ph_2PCH_2CH_2PPh(C_5F_4N$-4) [28] were prepared as described.

4.3. Preparation of [(η^6-toluene)RuCl(dfppe)]BF_4 (4)

The salt $NaBF_4$ (0.232 g, 2.11 mmol) in methanol (20 ml) was added to [(η^6-toluene)$RuCl]_2$ (0.062 g, 0.117 mmol) and dfppe (0.177 g, 0.233 mmol) in dichloromethane (30 ml), and the mixture stirred for 2 h. The solvent was removed by rotary evaporation, and the product extracted into dichloromethane (50 ml). The insoluble white salts were filtered off and the solvent removed from the filtrate by rotary evaporation to yield the product as an orange solid, which was recrystallized from dichloromethane/hexane and dried *in vacuo*. The product crystallized with one equivalent of dichloromethane. Yield: 0.117 g (43%). Anal. Calcd. for $C_{33}H_{12}BClF_{24}P_2Ru{\cdot}CH_2Cl_2$: C, 35.3; H, 1.2. Found C, 35.3; H, 1.1%. LSIMS: 987 (57) ([M−BF_4]$^+$), 952 (5) ([*M*−BF_4–Cl]$^+$). HRLSIMS: $C_{33}H_{12}{}^{35}ClF_{20}P_2{}^{102}Ru$ requires 986.88407; found: [*M*−BF_4]$^+$ 986.88425. ^{1}H NMR ($CDCl_3$): δ 6.28 (2H, *m*, H_{meta}), 6.20 (2H, *d*, $^{3}J_{HH}$ = 5.8 Hz, H_{ortho}), 5.30 (2H, *s*, CH_2Cl_2), 5.25 (1H, *t*,

$^3J_{HH}$ = 5.5 Hz, H_{para}), 3.14 (4H, *m*, PCH_2), 2.21 (3H, *s*, CH_3). ^{19}F NMR ($CDCl_3$): δ −125.64 (2F, *br s*, F_{ortho}), −129.86 (2F, *br s*, F_{ortho}), −130.48 (4F, *d*, $^3J_{FF}$ = 17 Hz, F_{ortho}), −142.64 (2F, *t*, $^3J_{FF}$ = 21 Hz, F_{para}), −144.43 (2F, *t*, $^3J_{FF}$ = 21 Hz, F_{para}), −154.33 (0.8F, *s*, $^{10}BF_4^-$), −154.37 (3.2F, *s*, $^{11}BF_4^-$), −155.94 (4F, *m*, F_{meta}), −158.39 (4F, *m*, F_{meta}). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 47.2 (*s*).

4.4. Preparation of [(η^6-*p*-cymene)RuCl(dfppe)]BF_4 (5)

[(η^6-*p*-cymene)$RuCl_2$]$_2$ (0.045 g, 0.073 mmol), dfppe (0.110 g, 0.145 mmol) and $NaBF_4$ (0.201 g, 1.83 mmol) were treated as for **4**. Yield: 0.147 g (90%). Anal. Calcd. for $C_{36}H_{18}BClF_{24}P_2Ru$: C, 38.75; H, 1.6. Found C, 39.4; H, 1.9%. ^1H NMR ((CD_3)$_2$CO): δ 6.67 (2H, *d*, $^3J_{HH}$ = 5.8 Hz, C_6H_4), 6.51 (2H, *d*, $^3J_{HH}$ = 5.8 Hz, C_6H_4), 3.42 (4H, *m*, CH_2), 2.60 [1H, *sept*, $^3J_{HH}$ = 6.9 Hz, $CH(CH_3)_2$], 1.67 (3H, *s*, CH_3), 1.09 [6H, *d*, $^3J_{HH}$ = 6.9 Hz, $CH(CH_3)_2$]. ^{19}F NMR ((CD_3)$_2$CO): δ −124.10 (2F, *br s*, F_{ortho}), −126.82 (2F, *br s*, F_{ortho}), −127.81 (4F, *d*, $^3J_{FF}$ = 19 Hz, F_{ortho}), −145.84 (2F, *t*, $^3J_{FF}$ = 20 Hz, F_{para}), −147.26 (2F, *t*, $^3J_{FF}$ = 20 Hz, F_{para}), −150.83 (0.8F, *s*, $^{10}BF_4^-$), −150.89 (3.2F, *s*, $^{11}BF_4^-$), −158.35 (4F, *m*, F_{meta}), −160.09 (2F, *br s*, F_{meta}), −160.82 (2F, *br s*, F_{meta}). $^{31}P\{^1H\}$ ((CD_3)$_2$CO): δ 52.3 (*m*).

4.5. Reaction between [(η^6-toluene)RuCl(dfppe)]BF_4 (4) and Proton Sponge

The reaction between **4** and Proton Sponge was performed in deutero-acetone and in deutero-dimethylsulphoxide. ^1H NMR ((CD_3)$_2$SO): δ 7.03 (1H, *m*, η^6-C_6H_5), 6.96 (1H, *m*, η^6-C_6H_5), 6.78 (2H, *m*, η^6-C_6H_5), 5.21 (1H, *m*, η^6-C_6H_5), 4.69 (1H, *d*, $^2J_{HH}$ = 18.3 Hz, $C_6CHH'C_6F_4$), 4.05 (2H, *m*, PCH_2), 3.88 (2H, *m*, PCH_2), 3.54 (1H, *d*, $^2J_{HH}$ = 18.3 Hz, $C_6CHH'C_6F_4$). ^{19}F NMR ((CD_3)$_2$CO): δ −121.57 (1F, *s*, C_6F_4), −122.95 (1F, *br s*, F_{ortho}), −126.82 (1F, *br s*, F_{ortho}), −130.53 (4F, *m*, F_{ortho}), −138.11 (1F, *s*, C_6F_4), −148.38 (1F, *m*, F_{para} or C_6F_4), −148.63 (1F, *m*, F_{para} or C_6F_4), −150.05 (2F, *m*, F_{para} and C_6F_4 or F_{para}), −152.21 (0.8F, *s*, $^{10}BF_4^-$), −152.26 (3.2F, *s*, $^{11}BF_4^-$), −156.57 (1F, *m*, C_6F_4), −159.13 (2F, *m*, F_{meta}), −160 to −165 (4F, *br m*, F_{meta}). $^{31}P\{^1H\}$ NMR ((CD_3)$_2$CO): δ 73.7 (*m*, PC_6F_4), 48.8 [*dm*, $^2J_{PP}$ = 21 Hz, $P(C_6F_5)_2$].

4.6. Preparation of [(η^6-mesitylene)RuCl{(C_6F_5)$_2$$PC_6H_4$SMe-2}]$BF_4$ (7)

[(η^6-mesitylene)$RuCl_2$]$_2$ (0.073 g, 0.125 mmol), (C_6F_5)$_2$$PC_6H_4$SMe-2 (0.104 g, 0.213 mmol) and $NaBF_4$ (0.200 g, 1.82 mmol) were treated as for **4**. The yellow product was washed with hot cyclohexane (250 ml) and diethyl ether (2× 25 ml), and dried *in vacuo*. Yield: 0.111 g (53%). Anal. Calcd. for $C_{28}H_{19}BClF_{14}PRuS$: C, 40.4; H, 2.3. Found C, 40.6; H, 2.6%. HRLSIMS: $C_{28}H_{19}{}^{35}ClF_{10}P^{102}RuS$ requires 744.95174; found: [*M*−BF_4]$^+$ 744.95330. ^1H NMR ($CDCl_3$): δ 7.93 (1H, *dd*, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 4.1 Hz, C_6H_4), 7.69 (1H, *m*, C_6H_4), 7.53 (2H, *m*, C_6H_4), 5.60 [3H, *s*, $C_6H_3(CH_3)_3$], 3.06 (3H, *s*, SMe), 2.20 [9H, *s*, $C_6H_3(CH_3)_3$]. ^{19}F NMR ($CDCl_3$): δ −123.48 (1F, *br s*, F_{ortho}), −124.44 (1F, *br s*, F_{ortho}), −127.23 (1F, *br s*, F_{ortho}), −132.73 (1F, *br s*, F_{ortho}), −142.53 (1F, *t*, $^3J_{FF}$ = 20 Hz, F_{para}), −145.30 (1F, *t*, $^3J_{FF}$ = 20 Hz, F_{para}), −152.45 (0.8F, *s*, $^{10}BF_4^-$), −152.50 (3.2F, *s*, $^{11}BF_4^-$), −155.53 (2F, *br s*, F_{meta}), −159.07 (1F, *br s*, F_{meta}), −160.04 (1F, *br s*, F_{meta}). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 43.8 (m). LSIMS: 745 (100) ([*M*−BF_4]$^+$), 710 (5) ([*M*−BF_4–Cl]$^+$), 695 (7) ([M−BF_4–Cl–CH_3]$^+$).

4.7. Reaction between [(η^6-mesitylene)RuCl{(C_6F_5)$_2$$PC_6H_4$SMe-2}]$BF_4$ (7) and Proton Sponge

The reaction between **7** and Proton Sponge was performed in deutero-chloroform. HRLSIMS: $C_{28}H_{18}{}^{35}ClF_9P^{102}RuS$ requires 724.94551; found: [*M*−BF_4]$^+$ 724.94264. ^1H NMR ($CDCl_3$): δ 7.3–7.7 (4H, C_6H_4), 6.12 (1H, *s*, C_6H_3), 5.91 (1H, *s*, C_6H_3), 5.47 (1H, *s*, C_6H_3), 4.80 (1H, *dd*, $^2J_{HH}$ = 18.5 Hz, $^4J_{PH}$ = 3.5 Hz, C*H*H′), 2.66 (3H, *s*, Me), 2.54 (3H, *s*, Me), 2.14 (3H, *s*, Me) (the resonance of the other methylene hydrogen atom is obscured by those of protonated Proton Sponge). ^{19}F NMR ($CDCl_3$): δ −120.91 (1F, *m*, C_6F_4), −129.36 (1F, *br s*, F_{ortho}), −132.69 (1F, *br s*, F_{ortho}), −134.62 (1F, *m*, C_6F_4), −143.71 (1F, *m*, C_6F_4), −146.64 (1F, *t*, $^3J_{FF}$ = 20 Hz, F_{para}), −151.48 (1F, *m*, C_6F_4), −152.29 (0.8F, *s*, $^{10}BF_4^-$), −152.34 (3.2F, *s*, $^{11}BF_4^-$), −159.28 (1F, *m*, F_{meta}), −159.96 (1F, *m*, F_{meta}). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 63.8 (*m*). LSIMS: 725 (100) ([*M*−BF_4]$^+$), 690 (15) ([*M*−BF_4–Cl]$^+$), 675 (22) ([*M*−BF_4–Cl–CH_3]$^+$).

4.8. Preparation of [(η^6-toluene)RuCl{$Ph_2PCH_2CH_2PPh(C_5F_4N$-4)}]BF_4 (9)

[(η^6-toluene)$RuCl_2$]$_2$ (0.068 g, 0.128 mmol), $Ph_2PCH_2CH_2PPh$ (C_5F_4N-4) (0.120 g, 0.255 mmol) and $NaBF_4$ (0.202 g, 1.84 mmol) were treated as for **4**. Yield: 0.130 g (65%). Anal. Calcd. for $C_{32}H_{27}BClNF_8P_2Ru$: C, 48.9; H, 3.5; N 1.8. Found C, 48.2; H, 3.2; N 1.2%. LSIMS: 700 (100) ([*M*−BF_4]$^+$), 665 (14) ([*M*−BF_4–Cl]$^+$). HRLSIMS: $C_{32}H_{27}{}^{35}ClNF_4P_2{}^{102}Ru$ requires 700.03159; found: [*M*−BF_4]$^+$ 700.02869. ^1H NMR ((CD_3)$_2$SO): δ 7.98 (2H, *m*, PPh), 7.86 (4H, *m*, PPh), 7.50–7.80 (18H, *m*, Ph), 7.47 (2H, *m*, Ph), 7.38 (2H, *m*, Ph), 7.15 (2H, *m*, Ph), 6.74 (1H, *d*, $^3J_{HH}$ = 6.1 Hz, η^6-C_6H_5Me), 6.45 (1H, *d*, $^3J_{HH}$ = 6.3 Hz, η^6-C_6H_5Me), 6.36 (1H, *d*, $^3J_{HH}$ = 6.1 Hz, η^6-C_6H_5Me), 6.15–6.34 (4H, *m*, η^6-C_6H_5Me), 5.90 (1H, *m*, η^6-C_6H_5Me), 5.38 (1H, *t*, $^3J_{HH}$ = 5.3 Hz, η^6-C_6H_5Me), 5.03 (1H, *t*, $^3J_{HH}$ = 5.5 Hz, η^6-C_6H_5Me), 3.53 (2H, *br m*, PCH_2), 3.22 (2H, *br m*, PCH_2), 2.83 (2H, *m*, PCH_2), 2.33–2.67 (2H, *m*, PCH_2), 2.13 (3H, *s*, C_6H_5Me), 2.00 (3H, *s*, C_6H_5Me). ^{19}F NMR ((CD_3)$_2$SO): δ −91.15 (2F, *m*, $F_{meta\text{-}P}$ **9b**), −91.79 (2F, *m*, $F_{meta\text{-}P}$ **9a**), −129.58 (2F, *br s*, $F_{ortho\text{-}P}$ **9a**), −130.47 (2F, *m*, $F_{ortho\text{-}P}$ **9b**), −148.68 (1.6F, *s*, BF_4^-), −148.74 (6.4F, *s*, BF_4^-). $^{31}P\{^1H\}$ NMR ((CD_3)$_2$SO): δ 79.0 (*d*, $^2J_{PP}$ = 22 Hz, PPh_2 **9b**), 74.3 [*dm*, $^2J_{PP}$ = 22 Hz, PPh(C_5F_4N) **9b**], 72.7 [*dm*, $^2J_{PP}$ = 30 Hz, PPh(C_5F_4N) **9a**], 71.1 (*d*, $^2J_{PP}$ = 30 Hz, PPh_2 **9a**).

4.9. Reaction between [(η^6-toluene)RuCl{$Ph_2PCH_2CH_2PPh(C_5F_4N$-4)}]BF_4 (9) and Proton Sponge

The reaction between **9** and Proton Sponge was performed in deutero-dimethylsulphoxide. ^{19}F NMR ((CD_3)$_2$SO): δ −91.95 (1F, *m*), −115.86 (1F, *m*), −140.03 (1F, *m*), −148.86 (0.8F, *s*, $^{10}BF_4^-$), −148.91 (3.2F, *s*, $^{11}BF_4^-$). $^{31}P\{^1H\}$ NMR ((CD_3)$_2$SO): δ 89.2 (*dm*, $^2J_{PP}$ = 14 Hz, PC_5F_3N), 78.5 (*dm*, $^2J_{PP}$ = 14 Hz, PPh_2).

4.10. Preparation of [(η^6-toluene)RuCl{$Ph_2P(C_6F_5)$}] (11)

A mixture of [(η^6-toluene)$RuCl_2$]$_2$ (0.087 g, 0.165 mmol) and $Ph_2P(C_6F_5)$ (0.113 g, 0.320 mmol) were dissolved in dichloromethane (40 ml). After 2 h hexane (20 ml) was added and the solvent was allowed to evaporate, yielding **11** as a brown microcrystalline solid containing equivalent of dichloromethane. Yield: 0.100 g (51%). Anal. Calcd. for $C_{25}H_{18}Cl_2F_5PRu{\cdot}CH_2Cl_2$: C, 46.5; H, 2.9. Yield Found C, 46.2; H, 2.8%. HRLSIMS: $C_{25}H_{18}{}^{35}Cl_2F_5P^{102}Ru$ requires 615.94868; found: [*M*]$^+$ 615.94954. ^1H NMR ($CDCl_3$): δ 7.84 (4H, *m*, PPh), 7.41 (6H, *m*, PPh), 5.36 (2H, *m*, η^6-C_6H_5), 5.31 (2H, *m*, η^6-C_6H_5), 5.14 (1H, *s*, CH_2Cl_2), 4.85 (1H, *m*, η^6-C_6H_5), 2.31 (3H, *d*, $^4J_{PH}$ = 1.0 Hz, CH_3). ^{19}F NMR ($CDCl_3$): δ −121.47 (2F, *m*, F_{ortho}), −147.93 (1F, *t*, $^3J_{FF}$ = 20 Hz, F_{para}), −159.21 (2F, *m*, F_{meta}). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 18.9 (*t*, $^3J_{PF}$ = 6 Hz). LSIMS: 616 (33) (M^+), 581 (64) ([*M*−Cl]$^+$), 545 (100) ([M−2Cl]$^+$).

4.11. X-ray crystallography

A crystal of **4**·CH_2Cl_2 was obtained by slow evaporation of solvent from a solution of **4** in dichloromethane and hexane. Crystal data are listed in Table 1. Diffraction data were collected on

a Bruker SMART diffractometer using the SAINT-NT [32] software with graphite-monochromated Mo-K_α radiation. Lorentz and polarization corrections were applied. Empirical absorption corrections were applied using SADABS [33]. The structure was solved by direct methods and refined with the program package SHELXTL version 5 [34]. The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atom positions were added in idealized positions and a riding model with fixed thermal parameters (*Uij* = 1.2 Ueq for the atom to which they are bonded (1.5 for CH_3)) was used for subsequent refinements. The function minimized was $\Sigma[w(|F_o|^2 - |F_c|^2)]$ with reflection weights $w^{-1} = [\sigma^2 |Fo|^2 + (g1P)^2 + (g2P)]$ where $P = [\max|F_o|^2 + 2|F_c|^2]/3$. CCDC 810245 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

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