Available online at www.sciencedirect.com
SCIENCE DIRECT®
Polyhedron 23 (2004) 2659–2664
POLYHEDRON
www.elsevier.com/locate/poly

# Intramolecular dehydrofluorinative coupling of pentamethylcyclopentadienyl and phosphine ligands in iridium complexes

Ronan M. Bellabarba, Graham C. Saunders *

*School of Chemistry, Queen's University Belfast, David Keir Building, Belfast BT9 5AG, UK*

Received 13 April 2004; accepted 20 May 2004
Available online 15 July 2004

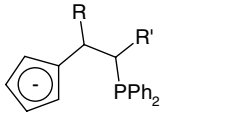
Dedicated to Prof. Malcolm Green FRS for his guidance and inspiration

**Abstract**

Cationic iridium(III) complexes of bifunctional $\eta^5,\kappa P$-Cp–P and trifunctional $\eta^5,\kappa P,\kappa L$-Cp–PL ligands may be conveniently prepared by intramolecular dehydrofluorinative carbon–carbon coupling. The iridium(III) complex $[(\eta^5\text{-}C_5Me_5)IrCl(dfppe)]BF_4$ (dfppe = $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$) undergoes rapid dehydrofluorinative coupling on addition of proton sponge to produce $[\{\eta^5,\kappa P,\kappa P\text{-}C_5Me_3[CH_2C_6F_4\text{-}2\text{-}P(C_6F_5)CH_2]_2\text{-}1,3\}IrCl]BF_4$. The reaction requires less than the stoichiometric quantity of proton sponge and also occurs on addition of $Bu^n_4NF$. The cationic phosphine–thioether complex $[(\eta^5\text{-}C_5Me_5)IrCl\{\kappa P,\kappa S\text{-}(C_6F_5)_2PC_6H_4SMe\text{-}2\}]BF_4$ undergoes rapid dehydrofluorinative coupling to $[\{\eta^5,\kappa P,\kappa S\text{-}C_5Me_4CH_2C_6F_4\text{-}2\text{-}P(C_6F_5)C_6H_4SMe\text{-}2\}IrCl]BF_4$ on treatment with proton sponge. NMR studies indicate that on treatment with proton sponge the cations $[(\eta^5\text{-}C_5Me_5)IrCl(CNR)\{PPh_2(C_6F_5)\}]^+$ (R = Ph or $^t$Bu) undergo coupling to give $[(\eta^5,\kappa P\text{-}C_5Me_4CH_2C_6F_4\text{-}2\text{-}PPh_2)IrCl(CNR)]^+$, but at a much slower rate and less cleanly than for the cations containing chelating ligands. The neutral compound $[(\eta^5\text{-}C_5Me_5)IrCl_2\{PPh_2(C_6F_5)\}]$ does not undergo coupling, indicating that a positive charge is necessary for the reaction. The results are analogous to those for rhodium complexes.

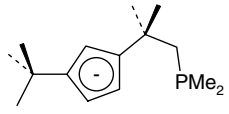

## 1. Introduction

Transition metal complexes of chelating bifunctional $\eta^5,\kappa P$-cyclopentadienyl–phosphine (Cp–P) or trifunctional $\eta^5,\kappa P,\kappa L$-cyclopentadienyl–phosphine-donor (Cp–PL) ligands can possess benefits over the analogous complexes of the unlinked ligands. Enhancement of stability [1–4], reactivity [5,6] and regio and stereo-selectivity in their reactions [7] has been reported, and configurational stability is expected for chiral-at-metal complexes of Cp–PL ligands [8]. Despite the benefits relatively few complexes of Cp–P ligands, and even fewer of Cp–PL ligands, have been reported, primarily due to the lack of convenient synthetic routes [9,10]. Nonetheless a number of rhodium complexes of Cp–P and Cp–PL ligands have been reported [4–6,9,11–14]. In contrast the number of complexes of iridium is limited to those of the Cp–P ligands **1** [15,16] and **2** [17], and **3** [18].

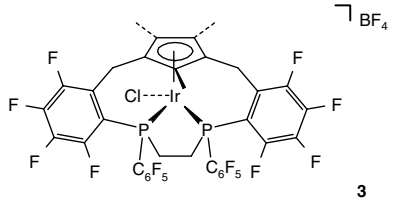



**1**

R = H, R' = H or *cyclo*-$C_6H_{11}$
R = Ph, R' = H




**2**

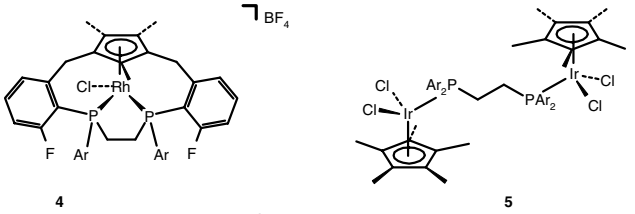



**3**

* Corresponding author. Tel.: +44-28-90374682; fax: +44-28-90382117/+44-28-90273333.
*E-mail address:* g.saunders@qub.ac.uk (G.C. Saunders).

0277-5387/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2004.05.014

We have demonstrated that intramolecular dehydrofluorinative carbon–carbon coupling provides a convenient route to cationic rhodium complexes of Cp–P and Cp–PL ligands [12]. The coupling of the pentamethylcyclopentadienyl and fluorophenylphoshphines of cationic complexes of the formula $[(\eta^5\text{-}C_5Me_5)\ RhXL\{PR_2(C_6F_5)\}]^+$ (X = Cl or Br, L = 2-electron donor ligand) may be performed by addition of less than one equivalent of 1,8-bis(dimethylamino)naphthalene (proton sponge) or fluoride ions. The reaction is rapid and quantitative for complexes in which the phosphine is part of a chelating ligand, as in a diphosphine or a phosphine-thioether, but considerably slower for complexes of monodentate phosphines. Alternatively, for cations containing chelating phosphines, heating a solution of the salt in an appropriate solvent yields the coupled product, although not always cleanly [18,19]. The preparation of the complexes of trifunctional cyclopentadienyl–diphosphine ligands containing two linkages has also been accomplished by heating a slurry of a 2:1 mixture of the diphosphine and $[(\eta^5\text{-}C_5Me_5)RhCl(\mu\text{-}Cl)]_2$ in benzene or ethanol [18,20]. The last method has also been found to yield **3** from $[(\eta^5\text{-}C_5Me_5)IrCl(\mu\text{-}Cl)]_2$ and $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$ (dfppe) [18]. A mechanism involving formation of an $\eta^4$-fulvene by loss of a proton from the pentamethylcyclopentadienyl ligand and intramolecular nucleophilic attack of the methylene carbon on an *ortho* C–F bond has been proposed for cationic rhodium(III) and cobalt(III) complexes [12,21]. The similarity of the chemistry of analogous rhodium(III) and iridium(III) pentamethylcyclopentadienyl complexes suggests that intramolecular dehydrofluorinative carbon–carbon coupling would also provide a convenient route to Cp–P and Cp–PL complexes of iridium. In support $\eta^4$-fulvene complexes of iridium have been proposed as nucleophilic intermediates in a number of reactions [22–26] and $[(\eta^4\text{-}C_5Me_4CH_2)IrMe(dppe)]$ has been structurally characterized [27]. However, some differences in reactivity between analogous complexes of iridium and rhodium have been observed. One apposite example is provided by the reactions between $[(\eta^5\text{-}C_5Me_5)MCl(\mu\text{-}Cl)]_2$ and $(C_6H_3\ F_2\text{-}2,6)_2PCH_2CH_2P(C_6H_3F_2\text{-}2,6)$, which yielded the coupled product **4** and the uncoupled bimetallic compound **5** [19]. Therefore, we set out to examine whether the coupling reactions that occur for the cationic rhodium complexes also occur for the analogous complexes of iridium. Here, the results of our study are reported.




**4** **5**

Ar = $C_6H_3F_2$-2,6

## 2. Experimental

### 2.1. Physical measurements

The $^1H$, $^{19}F$ and $^{31}P$ NMR spectra were recorded using a Bruker DPX300 spectrometer. $^1H$ (300.01 MHz) were referenced internally using the residual protio solvent resonance relative to $SiMe_4$ ($\delta$ 0), $^{19}F$ (282.26 MHz) externally to $CFCl_3$ ($\delta$ 0) and $^{31}P$ (121.45 MHz) externally to 85% $H_3PO_4$ ($\delta$ 0). All spectra were recorded in $CDCl_3$ at 300 K. Data are given as chemical shifts ($\delta$) using the high frequency positive convention, [relative intensity, multiplicity, *J*/Hz, assignment], s, singlet; d, doublet; t, triplet; m, multiplet; br, broad. The IR spectra were recorded on a Perkin–Elmer RX I Fourier transform spectrometer. Mass spectra were recorded on a VG Autospec X series mass spectrometer. Elemental analyses were carried out by A.S.E.P., The School of Chemistry, Queen's University Belfast.

### 2.2. Materials

The compounds $[(\eta^5\text{-}C_5Me_5)IrCl(\mu\text{-}Cl)]_2$, sodium tetrafluoroborate and proton sponge (Aldrich) were used as supplied. The salt $[(\eta^5\text{-}C_5Me_5)IrCl(dfppe)]BF_4$ [18] and phenylisonitrile [28] were prepared as described. The phosphines $P(C_6F_5)_3$ and $PPh_2(C_6F_5)$ [29] were prepared from $PCl_3$ and $Ph_2PCl$ as described for similar compounds [30].

### 2.3. $(C_6F_5)_2PC_6H_4SMe$-2 (**6**)

A solution of $Bu^nLi$ in hexane (3.0 $cm^3$, 1.6 M) was added to $MeSC_6H_4Br$-2 (1.10 g, 5.4 mmol) in diethyl ether at 0 °C. After stirring for 1 h the solution was added over 10 min to $P(C_6F_5)_3$ (3.12 g, 5.8 mmol) in diethyl ether (100 $cm^3$) at 0 °C to give a black solution. After stirring for a further 5 min water (100 $cm^3$) was added. The organic layer was washed with water (100 $cm^3$). The aqueous layer and washings were extracted with 1:2 ethyl acetate/chloroform (200 $cm^3$). The combined organic extracts were dried over magnesium sulfate. Filtration and removal of the solvent by rotary evaporation yielded a brown oil comprising $P(C_6F_5)_3$, (**6**) and $(C_6F_5)P(C_6H_4SMe\text{-}2)_2$. Compound **6** was obtained by distillation by kugelrohr at 130–140 °C and 0.03 mm Hg. Yield 0.120 g (4.2%).

### 2.4. $[(\eta^5\text{-}C_5Me_5)IrCl\{\kappa P,\ \kappa S\text{-}(C_6F_5)_2PC_6H_4SMe\text{-}2\}]BF_4$ (**7**)

Sodium tetrafluoroborate (0.164 g, 1.5 mmol) was added to $[(\eta^5\text{-}C_5Me_5)IrCl(\mu\text{-}Cl)]_2$ (0.175 g, 0.22 mmol) and **6** (0.216 g, 0.44 mmol) in dichloromethane (30 $cm^3$) and methanol (30 $cm^3$), and the mixture stirred for 90 min. The solvent was removed by rotary evaporation

and the product extracted into dichloromethane. The extract was filtered and the solvent removed by rotary evaporation to give the product as a yellow solid. Yield 0.351 g (87%). *Anal.* Calc. for $C_{29}H_{22}BClF_{14}PIrS$ (**7**): C, 37.0; H, 2.4. Found: C, 36.9; H, 2.2%. $^1$H NMR: $\delta$ 8.55 (1H, m, $C_6H_4$), 8.10 (2H, m, $C_6H_4$), 7.98 (1H, m, $C_6H_4$), 3.14 (3H, s, SMe), 1.78 (15H, s, Me). $^{19}$F NMR: −122.50 (1F, br s, $F_o$), −127.32 (1F, br s, $F_o$), −127.55 (1F, br s, $F_o$), −131.76 (1F, br s, $F_o$), −141.99 (1F, br s, $F_p$), −144.65 (1F, br s, $F_p$), −153.59 (0.8F, s, $^{10}BF_4^-$), −153.64 (3.2F, s, $^{11}BF_4^-$), −155.14 (1F, br s, $F_m$), −157.24 (1F, br s, $F_m$), −158.41 (1F, br s, $F_m$), −160.61 (1F, br s, $F_m$). $^{31}P\{^1H\}$ NMR: 5.4 (s).

### 2.5. [{$\eta^5$,κP,κS-$C_5Me_4CH_2C_6F_4$-2-P($C_6F_5$)$C_6H_4$SMe-2}IrCl]$BF_4$ (**8**)

Proton sponge (0.041 g, 0.19 mmol) was added to **7** (0.129 g, 0.14 mmol) in dichloromethane (40 cm$^3$) and the solution left at ambient temperature for 48 h. The solution was washed with water (50 cm$^3$), dilute hydrochloric acid (50 cm$^3$) and water (50 cm$^3$), and dried over magnesium sulfate. Filtration and removal of the solvent by rotary evaporation gave the product as a yellow solid, which was dried in vacuo. Yield 0.084 g (66.5%). *Anal.* Calc. for $C_{29}H_{21}BClF_{13}PIrS$ (**8**): C, 37.9; H, 2.3. Found: C, 40.05; H, 2.6%. Repeated washing and drying in vacuo failed to give satisfactory analysis ($N < 0.1$%). LSIMS: 831 ($[M-BF_4]^+$) [Found: 831.02980 $C_{29}H_{21}ClF_9^{193}IrPS$ requires 831.02759]. $^1$H NMR: $\delta$ 8.14 (1H, m, $C_6H_4$), 7.97 (1H, m, $C_6H_4$), 7.74 (1H, m, $C_6H_4$), 7.66 (1H, m, $C_6H_4$), 4.58 [1H, dd, $^2J$(HH) 17.9, $^4J$(PH) 7.6, $CH_2$], 3.05 [1H, d, $^2J$(HH) 17.9, $CH_2$], 2.65 (3H, s, SMe), 2.34 [3H, d, $^4J$(PH) 6.5, $CH_3$], 1.87 [3H, d, $^4J$(PH) 2.2, $CH_3$], 1.82 [3H, d, $^4J$(PH) 2.9, $CH_3$], 1.69 (3H, s, $CH_3$). $^{19}$F NMR: $\delta$ −119.47 (1F, m), −128.81 (1F, m), −133.22 (1F, m), −133.52 (1F, m), −142.81 (1F, m), −146.05 [1F, t $^3J$(FF) 20.7], 151.97 [1F, t $^3J$(FF) 22.0, $F_p$], −153.77 (0.8F, s, $^{10}BF_4^-$), −153.83 (3.2F, s, $^{11}BF_4^-$), −158.85 (2H, m). $^{31}P\{^1H\}$ NMR: $\delta$ 31.9 (s).

### 2.6. [($\eta^5$-$C_5Me_5$)$IrCl_2${$PPh_2$($C_6F_5$)}] (**9**)

A mixture of [($\eta^5$-$C_5Me_5$)IrCl(μ-Cl)]$_2$ (0.112 g, 0.14 mmol) and $Ph_2P(C_6F_5)$ (0.099 g, 0.28 mmol) in dichloromethane/methanol (50 cm$^3$) was left at ambient temperature for 2 h. The solvent was removed by rotary evaporation affording the product as an orange solid, which was recrystallized from dichloromethane. Yield 0.160 g (76.1%). *Anal.* Calc. for $C_{28}H_{27}Cl_2F_5PIr$ (**9**): C, 44.8; H, 3.4. Found: C, 44.5; H, 3.1%. $^1$H NMR: $\delta$ 7.81 (4H, m, $C_6H_5$), 7.41 (6H, m, $C_6H_5$), 1.44 [15H, d, $^4J$(PH) 2.5, Me]. $^{19}$F NMR: $\delta$ −120.06 (2F, m, $F_o$), −148.52 [1F, t, $^3J(F_mF_p)$ 19.8, $F_p$], −160.22 (2F, m, $F_m$). $^{31}P\{^1H\}$ NMR: −1.7 (s).

### 2.7. [($\eta^5$-$C_5Me_5$)IrCl(CNPh){$PPh_2$($C_6F_5$)}]$BF_4$ (**10a**)

Sodium tetrafluoroborate (0.110 g, 1.00 mmol) in methanol (30 cm$^3$) was added to **9** (0.100 g, 0.13 mmol) and phenylisonitrile (0.108 g, 1.05 mmol) in dichloromethane/methanol (30 cm$^3$), and the mixture stirred for 2 h. The solvent was removed by rotary evaporation and the product extracted into dichloromethane. Concentration by rotary evaporation and addition of hexane precipitated the product as a yellow solid. Yield 0.070 g (59.1%). *Anal.* Calc. for $C_{35}H_{30}BClF_9IrNP.0.5CH_2Cl_2$ (**10a**): C, 44.7; H, 3.9; N, 1.5. Found: C, 45.15; H, 3.15; N, 1.75%. $\nu$(N≡C) 2181 cm$^{-1}$. $^1$H NMR: $\delta$ 7.85 (2H, m), 7.33 – 7.54 (11H, m), 6.86 (2H, m), 5.30 (1H, s, $CH_2Cl_2$), 1.80 [15H, d, $^4J$(PH) 2.7, Me]. $^{19}$F NMR: $\delta$ −124.67 (2F, m, $F_o$), −143.55 (1H, br s, $F_p$), −153.68 (0.8F, s, $^{10}BF_4^-$), −153.74 (3.2F, s, $^{11}BF_4^-$), −156.93 (2F, br s, $F_m$). $^{31}P\{^1H\}$ NMR: $\delta$ 9.4 (s).

### 2.8. [($\eta^5$-$C_5Me_5$)IrCl($CNBu^t$){$PPh_2$($C_6F_5$)}]$BF_4$ (**10b**)

Compound **9** (0.060 g, 0.08 mmol), $^t$butylisonitrile (0.009 cm$^3$, 0.08 mmol) and sodium tetrafluoroborate (0.109 g, 1.00 mmol) were treated as for **10a**. Yield 0.045 g (63.6%). *Anal.* Calc. for $C_{33}H_{34}BClF_9IrNP$ (**10b**): C, 44.8; H, 3.9; N, 1.6. Found: C, 44.5; H, 3.9; N, 1.75%. LSIMS: 798 ($[M-BF_4]^+$), 763 ($[M-BF_4-Cl]^+$) [Found: 798.16367 $C_{33}H_{34}BClF_9^{193}IrNP$ requires 798.16670]. $\nu$(N≡C) 2199 cm$^{-1}$. $^1$H NMR: $\delta$ 7.79 (2H, m), 7.37 −7.63 (8H, m), 1.72 [15H, d, $^4J$(PH) 2.6, Me], 1.29 (9H, s, $^t$Bu). $^{19}$F NMR: $\delta$ −124.71 (2F, m, $F_o$), −144.04 (1H, br s, $F_p$), −153.87 (0.8F, s, $^{10}BF_4^-$), −153.96 (3.2F, s, $^{11}BF_4^-$), −157.22 (2F, br s, $F_m$). $^{31}P\{^1H\}$ NMR: $\delta$ −9.0 (s).

### 2.9. [($\eta^5$,κP-$C_5Me_4CH_2C_6F_4$-2-$PPh_2$)IrCl(CNPh)]$BF_4$ (**11a**)

Proton sponge (0.005 g, 0.023 mmol) was added to **10a** (0.057 g, 0.063 mmol) in dichloromethane (15 cm$^3$). After 7 days dichloromethane (85 cm$^3$) was added and the solution washed with water (3 × 50 cm$^3$) and dried over magnesium sulfate. Filtration and removal of the solvent by rotary evaporation gave an oily brown solid, which was washed with diethyl ether (10 cm$^3$) and dried in vacuo. Yield 0.045 g (80.7%). *Anal.* Calc. for $C_{35}H_{29}BClF_8IrNP$ (**11a**): C, 47.5; H, 3.3; N, 1.6. Found: C, 49.4; H, 3.9; N, 1.9%. Repeated washing and drying in vacuo failed to give satisfactory analysis. LSIMS: 798 ($[M-BF_4]^+$), 763 ($[M-BF_4-Cl]^+$) [Found: 798.12522 $C_{35}H_{29}ClF_4^{193}$ IrNP requires 798.12917]. $\nu$(N≡C) 2180 cm$^{-1}$. $^1$H NMR: $\delta$ 7.05–7.82 (15H, m, $C_6H_5$), 3.85 [1H, dd, $^2J$(HH) 16.9, $^4J$(PH) 4.8, $CH_2$], 3.64 [1H, dd, $^2J$(HH) 16.9, $^4J$(PH) 4.8, $CH_2$], 2.30 [3H, d, $^4J$(PH) 4.0, $CH_3$], 1.90 [3H, d, $^4J$(PH) 4.3, $CH_3$], 1.73 [3H, d, $^4J$(PH) 4.4, $CH_3$], 1.51

(3H, s, $CH_3$). $^{19}F$ NMR: $\delta$ −118.64 (1F, m), −136.29 (1F, m), −145.78 (1F, m), −152.30 (1F, m), −153.05 (0.8F, s, $^{10}BF_4^-$), −153.11 (3.2F, s, $^{11}BF_4^-$). $^{31}P\{^1H\}$ NMR: $\delta$ 5.6 (s).

### 2.10. *[($\eta^5$,κP-$C_5Me_4CH_2C_6F_4$-2-$PPh_2$)IrCl(CNBu$^t$)]$BF_4$ (**11b**)*

A sample was obtained from the reaction between **10b** and proton sponge in an NMR tube. There was insufficient sample for elemental analysis. LSIMS: 778 ($[M-BF_4]^+$), 743 ($[M-BF_4-Cl]^+$) [Found: 778.16394 $C_{33}H_{33}ClF_4^{193}IrNP$ requires 778.160471]. $\nu$(N≡C) 2197 $cm^{-1}$. $^{19}F$ NMR: $\delta$ −120.71 (1F, m), −136.76 (1F, m), −146.35 (1F, m), −152.45 (1F, m), −153.20 (0.8F, s, $^{10}BF_4^-$), 153.25 (3.2F, s, $^{11}BF_4^-$). $^{31}P\{^1H\}$ NMR: $\delta$ 5.1 (s). Important $^1H$ NMR resonances are given in Section 3 (vide infra).

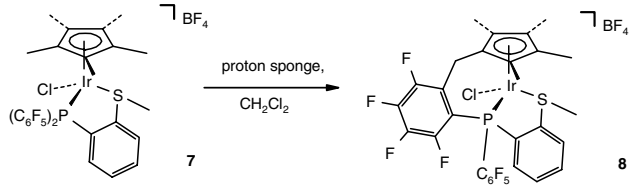
## 3. Results and discussion

An in situ NMR experiment in $CDCl_3$ revealed that the salt [($\eta^5C_5Me_5$)IrCl(dfppe)]$BF_4$ underwent rapid intramolecular dehydrofluorinative carbon–carbon coupling in the presence of less than one equivalent of proton sponge to give **3** [18]. As for the rhodium analogue, the fluoride generated as the by-product acted as a base. An in situ NMR experiment confirmed that the coupling occurred rapidly on addition of tetrabutylammonium fluoride to [($\eta^5$-$C_5Me_5$)IrCl(dfppe)]$BF_4$ in acetone. In contrast [($\eta^5$-$C_5Me_5$)IrCl{κP,κP-[($C_6H_3F_2$-2,6)$_2PCH_2$]$_2$}]$BF_4$ [20] did not undergo any reaction in the presence of proton sponge in $CDCl_3$ at ambient temperature over 24 h. This observation is consistent with the lack of a coupling reaction of this salt in refluxing ethanol and also when [($\eta^5$-$C_5Me_5$)IrCl(μ-Cl)]$_2$ and ($C_6H_3F_2$-2,6)$_2PCH_2CH_2P$($C_6H_3F_2$-2,6) are heated in benzene. The rhodium analogue [($\eta^5$-$C_5Me_5$)RhCl{κP,κP-[($C_6H_3F_2$-2,6)$_2PCH_2$]$_2$}]$BF_4$ also did not undergo a reaction with proton sponge. This salt also underwent no reaction in refluxing ethanol, but dehydrofluorinative carbon–carbon coupling was observed in the reaction between [($\eta^5$-$C_5Me_5$)RhCl(μ-Cl)]$_2$ and ($C_6H_3F_2$-2,6)$_2PCH_2CH_2P$($C_6H_3F_2$-2,6) in benzene [20].

We wished to attempt the coupling reaction with an iridium complex of the phosphine-thioether ($C_6F_5$)$_2$ $PC_6H_4SMe$-2, (**6**), which possesses only one phosphine functionality. Compound **6** has been prepared by the reaction between $MeSC_6H_4Li$ and ($C_6F_5$)$_2PBr$ [12], but following the observation that when a mixture of ($C_6F_5$)PPhCl and ($C_6F_5$)PPhBr was treated with an excess of $MeSC_6H_4Li$-2 the phosphine $PhP(C_6H_4SMe2)_2$ was formed, consistent with previous reports of P–$C_6F_5$ bond cleavage by Grignard reagents [31], it was decided to investigate whether **6** could be prepared from $P(C_6F_5)_3$. Addition of one equivalent of $MeSC_6H_4Li$-2 to $P(C_6F_5)_3$ in diethyl ether at 0 °C gave a black solution, consistent with the formation of $C_6F_5Li$. Following hydrolysis a brown oil was isolated which was shown by NMR spectroscopy to contain $P(C_6F_5)_3$, (**6**) and $(C_6F_5)P(C_6H_4SMe\text{-}2)_2$ in roughly equal amounts. Although the result confirms that the P–$C_6F_5$ bond can be readily cleaved by organolithium reagents, the reaction is not selective. Further, separating these phosphines proved difficult, although slightly impure **6** was obtained in ca. 4% yield by distillation by kugelrohr at 130–140 °C and 0.03 mm Hg. Thus this method of preparing **6** is inferior to that we have reported previously [12].

Treatment of [($\eta^5$-$C_5Me_5$)IrCl(μ-Cl)]$_2$ with **6** in the presence of an excess of sodium tetrafluoroborate yielded the salt [($\eta^5$-$C_5Me_5$)IrCl{κP,κS-($C_6F_5$)$_2PC_6H_4SMe$-2}]$BF_4$, **7**. The $^1H$ and $^{19}F$ NMR spectra of **7** are similar to those of the rhodium analogue [11,12]. The $^{19}F$ NMR spectrum exhibits 10 resonances in addition to those of tetrafluoroborate. Each fluorine atom of the cation is unique due to hindered rotation about the P–$C_6F_5$ bonds. The $^{31}P\{^1H\}$ spectrum exhibits a singlet at $\delta$ 5.4, which is to a lower frequency of the doublet resonance of the rhodium analogue ($\delta$ 30.2). This difference is consistent with differences observed between rhodium and iridium analogues of similar compounds [18,20]. There are two stereogenic centres in the cation: the iridium and sulfur atoms. However only one set of resonances is seen in the NMR spectra, in particular there is only one thiomethyl hydrogen resonance, at $\delta$ 3.14, strongly suggesting that only one pair of enantiomers are present in solution. It is expected that the $R_{Ir}R_S$ and $S_{Ir}S_S$ pair, in which the methyl group is *trans* to the pentamethylcyclopentadienyl ligand would be the thermodynamically and kinetically preferred products for steric reasons. It is not known whether the exclusive existence of one pair of enantiomers is as a result of kinetics of coordination of the thioether or whether the other stereoisomers are formed and isomerize rapidly. This process can occur by dissociation and re-coordination of the labile thioether or by inversion at coordinated sulfur, which is presumed to have a low activation barrier. In support of the latter, the pyramidal inversion at the sulfur of $PPh(C_6H_4SMe\text{-}2)_2$, κP,κS-coordinated to palladium, has a free energy of activation, $\Delta G^{\ddagger}$, of 40–60 kJ $mol^{-1}$ [32].

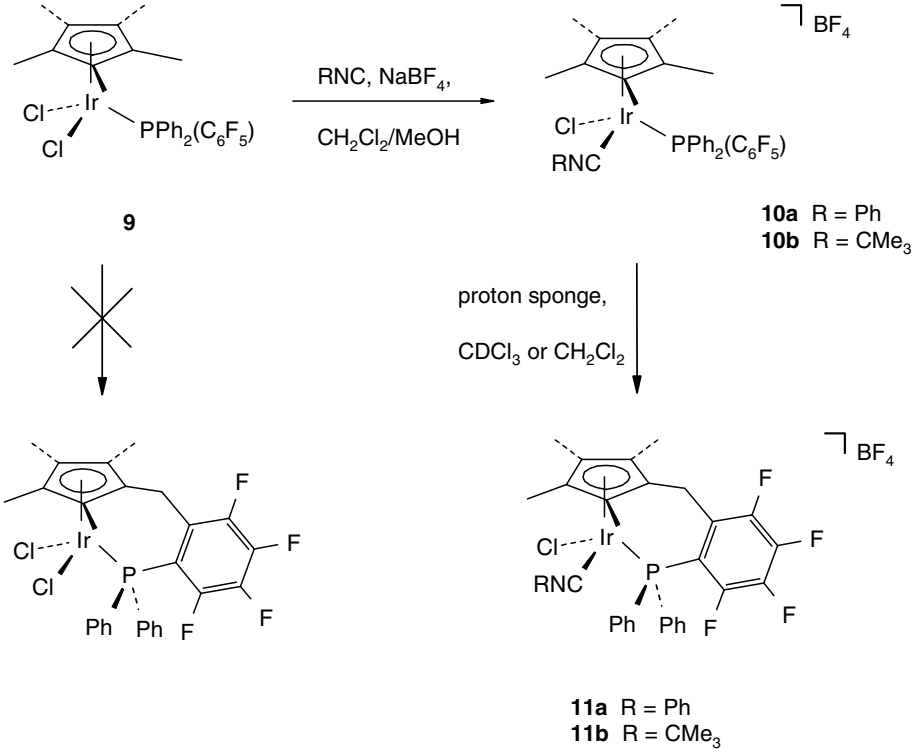
An in situ NMR spectroscopic study revealed that on treatment with proton sponge **7** underwent rapid intramolecular dehydrofluorinative coupling to give salt **8** (Scheme 1), which was isolated in 67% yield from a preparative scale reaction. The $^1H$ and $^{19}F$ NMR spectra of **8** are similar to those of the rhodium analogue [11,12] and the $^{31}P\{^1H\}$ spectrum exhibits a singlet at $\delta$ 31.9. The shift of the phosphorus resonance to higher frequency on coupling of the phosphine to the pen-




Scheme 1.

tamethylcyclopentadienyl ligand is consistent with previous observations [12,18,20]. The $^{1}$H spectroscopic studies show NOE correlation between the thiomethyl hydogen atoms and one aromatic hydrogen, but not between the thiomethyl and pentamethylcyclopentadienyl hydrogen atoms, suggesting that the thiomethyl group is *trans* to the cyclopentadienyl ring, as for the rhodium analogue [11,12]. The cation of **8** contains three stereogenic centres: the iridium, sulfur and phosphorus atoms. In rhodium complexes of Cp–PL ligands the configurations at the metal and phosphorus are fixed relative to each other by the ligand's geometry such that the non-ligating substituent of the phosphine and the halide are on the same side of the plane defined by the metal and phosphorus atoms and the cyclopentadienyl centroid [12]. Presumably the same argument is valid for **8**. This, together with the exclusively *trans* disposition of the thiomethyl and pentamethylcyclopentadienyl groups, leads to the existence of only the $R_{Ir}R_{S}S_{P}$ and $S_{Ir}S_{S}R_{P}$ pair of enantiomers.

Treatment of $[(\eta^5\text{-}C_5Me_5)IrCl(\mu\text{-}Cl)]_2$ with $PPh_2(C_6F_5)$ yielded the neutral complex $[(\eta^5\text{-}C_5Me_5)IrCl_2\{PPh_2(C_6F_5)\}]$ (**9**). Consistent with the rhodium analogue, compound **9** underwent no reaction with proton sponge. The cationic iridium complexes $[(\eta^5\text{-}C_5Me_5)IrCl(CNR)\{PPh_2(C_6F_5)\}]BF_4$ (**10a** R = phenyl; **10b** R = *t*-butyl) were prepared by treatment of **9** with the appropriate isonitrile in the presence of an excess of sodium tetrafluoroborate (Scheme 2). The $^{1}$H and $^{19}$F NMR spectra of **10a** are similar to those of the rhodium analogue [12] and the $^{31}P\{^{1}H\}$ NMR spectrum exhibits a singlet at $\delta$ −9.1. The $^{19}$F and $^{31}P\{^{1}H\}$ NMR spectral properties of **10b** are similar to those of **10a**. In situ NMR studies indicate **10a** and **10b** undergo slow reactions in the presence of proton sponge. The NMR data are fully consistent with intramolecular dehydrofluorinative coupling to give **11a** and **11b**. In particular, the $^{19}$F NMR spectra show four resonances in addition to those of tetrafluoroborate with values of $\delta$ similar to those of the rhodium analogue (−119.22, −136.07, −145.54 and −152.01 [12]). Both $^{31}P\{^{1}H\}$ NMR spectra exhibit a singlet resonance at ca. $\delta$ 5. The shift of ca. 15 ppm to higher frequency on coupling is similar to that of 18.3 ppm observed in the rhodium analogue of **11a** [12]. The $^{1}$H NMR spectrum of **11a** exhibits the two expected methylene resonances at $\delta$ 3.85 (dd) and 3.64 (dd), and four methyl resonances at $\delta$ 2.30 (d), 1.90 (d), 1.73 (d) and 1.51 (s), which are at similar chemical shifts to those of the rhodium analogue ($\delta$ 2.08, 1.82, 1.71 and 1.52).




Scheme 2.

Although methylene resonances at $\delta$ 3.75 (m) and 3.46 (m), and two methyl resonances at $\delta$ 2.18 (d) and 1.85 (d) are evident in the $^1$H NMR spectrum of **11b**, the other resonances are obscured by other products and the proton sponge resonances. The reaction of **10a** is reasonably clean, but that of **10b** is not and **11b** is produced in ca. 50% yield. The identities of **11a** and **11b** were confirmed by mass spectrometry. The values of $\nu$(N≡C) for **11a** and **11b** were identical within experimental error to those of **10a** and **10b** respectively. The coupling reaction of **10a** was also performed on a preparative scale giving **11a** as a yellow–brown solid in 81% yield.

## 4. Conclusion

The intramolecular dehydrofluorinative coupling of pentamethylcyclopentadienyl and pentafluorophenylphosphine ligands can be accomplished in cationic iridium complexes by treatment with less than one equivalent of proton sponge. The fluoride generated as the byproduct is sufficient to facilitate the reaction. The reaction occurs slowly for complexes of monophosphines to give bifunctional $\eta^5$,κP-Cp–P ligands, but is more successful for complexes of chelating phosphine ligands, which give trifunctional $\eta^5$,κP,κL-Cp–PL ligands rapidly. The reported reactions are identical to those of the rhodium analogues.

## Acknowledgements

We thank the E.P.S.R.C. for support (to R.M.B.), the Royal Society of Chemistry for a *Grant for International Authors* (to G.C.S.) and Prof. R.P. Hughes for helpful discussion.

## References

[1] T.-F. Wang, C.Y. Lai, J. Organomet. Chem. 546 (1997) 179.
[2] M.D. Fryzuk, S.H.S. Mao, M.J. Zaworotko, L.R. MacGillivray, J. Am. Chem. Soc. 115 (1993) 5336.
[3] B.E. Bosch, G. Erker, R. Fröhlich, O. Meyer, Organometallics 16 (1997) 5449.
[4] E.C. McConnell, D.E. Foster, P. Pogorzelec, A.M.Z. Slawin, D.J. Law, D.J. ColeHamilton, J. Chem. Soc., Dalton Trans. (2003) 510.
[5] Y. Kataoka, Y. Iwato, A. Shibahara, T. Yamagata, K. Tani, Chem. Commun. (2000) 841.
[6] Y. Kataoka, A. Shibahara, T. Yamagata, K. Tani, Organometallics 20 (2001) 2431.
[7] K. Onitsuka, N. Dodo, Y. Matsushima, S. Takahashi, Chem. Commun. (2001) 521.
[8] H. Brunner, C. Valerio, M. Zabel, New J. Chem. 24 (2000) 275.
[9] H. Butenschön, Chem. Rev. 100 (2000) 1527.
[10] J. Vogelsgang, A. Frick, G. Huttner, P. Kircher, Eur. J. Inorg. Chem. (2001) 949.
[11] R.M. Bellabarba, M. Nieuwenhuyzen, G.C. Saunders, J. Chem. Soc., Dalton Trans. (2001) 512.
[12] R.M. Bellabarba, M. Nieuwenhuyzen, G.C. Saunders, Organometallics 21 (2002) 5726.
[13] R.M. Bellabarba, M. Nieuwenhuyzen, G.C. Saunders, Organometallics 22 (2003) 1802.
[14] M. Nieuwenhuyzen, G.C. Saunders, J. Organomet. Chem. 595 (2000) 292.
[15] I. Lee, F. Dahan, A. Maisonnat, R. Poilblanc, Organometallics 13 (1994) 2743.
[16] A. Doppiu, U. Englert, V. Peters, A. Salzer, Inorg. Chim. Acta 357 (2004) 1773.
[17] T.A. Mobley, R.G. Bergman, J. Am. Chem. Soc. 120 (1998) 3253.
[18] M.J. Atherton, J. Fawcett, J.H. Holloway, E.G. Hope, A. Karaçar, D.R. Russell, G.C. Saunders, J. Chem. Soc., Dalton Trans. (1996) 3215.
[19] M.J. Atherton, J. Fawcett, J.H. Holloway, E.G. Hope, D.R. Russell, G.C. Saunders, J. Organomet. Chem. 582 (1999) 163.
[20] J. Fawcett, S. Friedrichs, J.H. Holloway, E.G. Hope, V. McKee, M. Nieuwenhuyzen, D.R. Russell, G.C. Saunders, J. Chem. Soc., Dalton Trans. (1998) 1477.
[21] R.P. Hughes, D.C. Lindner, A.L. Rheingold, G.P.A. Yap, Organometallics 15 (1996) 5678.
[22] J.A. Miguel-Garcia, H. Adams, N.A. Bailey, P.M. Maitlis, J. Chem. Soc., Chem. Commun. (1990) 1472.
[23] J.A. Miguel-Garcia, H. Adams, N.A. Bailey, P.M. Maitlis, J. Organomet. Chem. 413 (1991) 427.
[24] J.A. Miguel-Garcia, H. Adams, N.A. Bailey, P.M. Maitlis, J. Chem. Soc., Dalton Trans. (1992) 131.
[25] O.V. Gusev, S. Sergeev, I.M. Saez, P.M. Maitlis, Organometallics 13 (1994) 2059.
[26] J.R. Fulton, T.A. Hanna, R.G. Bergman, Organometallics 19 (2000) 602.
[27] D.S. Glueck, R.G. Bergman, Organometallics 9 (1990) 2862.
[28] J.H. Rigby, S. Laurent, J. Org. Chem. 63 (1998) 6742.
[29] R.D.W. Kemmitt, D.I. Nichols, R.D. Peacock, J. Chem. Soc. A (1968) 2149.
[30] A.H. Cowley, M. Cushner, M. Fild, J.A. Gibson, Inorg. Chem. 14 (1975) 185.
[31] S.A. Sicree, C. Tamborski, J. Fluor. Chem. 59 (1992) 269.
[32] E.W. Abel, J.C. Dormer, D. Ellis, K.G. Orrell, V. Šik, M.B. Hursthouse, M.A. Mazid, J. Chem. Soc., Dalton Trans. (1992) 1073.