

A systematic method of promoting an aryl fluoride to coordinate to ruthenium(II)

Sarath D. Perera, Bernard L. Shaw

School of Chemistry, University of Leeds, Leeds LS2 9JT, UK

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Abstract

The phosphino hydrazone $Z\text{-PPh}_2\text{CH}_2\text{C}(\text{Bu}^i)=\text{NNH}_2$ (**1**) condenses with 2,6-difluorobenzaldehyde to give $Z,E\text{-PPh}_2\text{CH}_2\text{C}(\text{Bu}^i)=\text{N}-\text{N}=\text{CH}(\text{C}_6\text{H}_3\text{F}_2-2,6)$ (**2a**), which reacts rapidly with the labile ruthenium(II) complex $[\text{RuCl}_2(\text{PPh}_3)_3]$ to give *mer,trans*- $[\text{RuCl}_2(\text{PPh}_3)\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^i)=\text{N}-\text{N}=\text{CH}(\text{C}_6\text{H}_3\text{F}_2-2,6)\}]$ (**3a**). In the $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of **3a** the fluorines are coupled equally to P_A but are not coupled to P_B . In the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, P_A is coupled equally to both fluorines, i.e. there is a dynamic system with both fluorines coordinated to ruthenium in turn and coupled to P_A , $^2J(\text{P}_A\text{F})=68$ Hz. Similar condensations of **1** with other fluorine-substituted benzaldehydes, viz. pentafluorobenzaldehyde, 2-chloro-6-fluorobenzaldehyde, 2-fluorobenzaldehyde, 2,3-difluorobenzaldehyde, gave mixed azine phosphines. In each case these mixed azine phosphines when treated with $[\text{RuCl}_2(\text{PPh}_3)_3]$, displaced two triphenylphosphines to give tridentate chelates showing fluorine coordination to ruthenium. Proton, $^{31}\text{P}\{^1\text{H}\}$ and $^{19}\text{F}\{^1\text{H}\}$ NMR data are given and discussed.

Keywords: Ruthenium complexes; Tridentate ligand complexes; Aryl fluoride complexes

1. Introduction

The halogen of an organic halide or halocarbon is a relatively weak donor atom compared with other donor atoms such as nitrogen, phosphorus, sulfur etc. The first example of halogen coordination from an organic halide was with 1,2-di-iodobenzene, which chelates to iridium(III) in $[\text{IrH}_2(\text{PPh}_3)_2(\text{C}_6\text{H}_4\text{I}_2-1,1')]\text{SbF}_6$, and was prepared by displacing two acetone ligands from $[\text{IrH}_2(\text{PPh}_3)_2(\text{O}=\text{CMe}_2)_2]\text{SbF}_6$ [1]. It was later found that methyl iodide would not displace acetone but $[\text{IrH}_2(\text{PPh}_3)_2(\text{IME})_2]\text{SbF}_6$ could be prepared by hydrogenating $[(\text{cod})\text{Ir}(\text{PPh}_3)_2]\text{SbF}_6$ in the presence of an excess of MeI [2]. Various ways of synthesising halocarbon-metal complexes have been devised, and the subject was reviewed in 1990 [3]. Other recent publications on organic halide-metal complexes are with Re(I) [4], Fe(II) [5], Ru(II) [5], Pt(II) [6] and Mo(II) [7].

Fluorocarbon-metal complexes in which fluorine is coordinated to the metal are rare [3]. Probably the first example of an aryl fluoride-metal interaction comes from the crystal structure of $[\text{NBu}_4]_2[\text{Pt}_2\text{Ag}_2\text{Cl}_4(\text{C}_6\text{F}_5)_4]$ although the authors commented that the Ag-F interaction "does not approach true bond formation" [8]. Another example of coordination of an aryl fluoride,

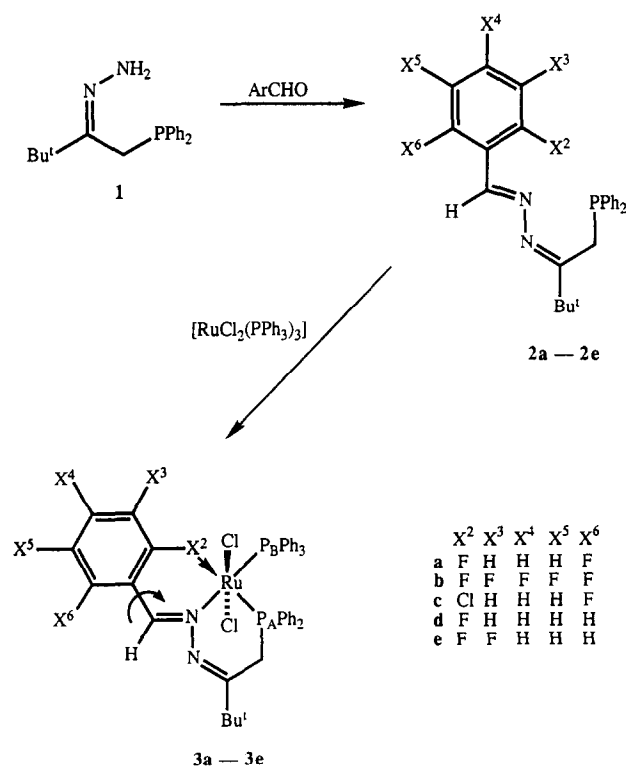
based on a crystal structure determination, is with pentafluorophenyl thiolate complex of ruthenium(III), viz. $[\text{Ru}(\text{PMe}_2\text{Ph})_2(\text{C}_6\text{F}_5\text{S}-\text{S})_2(\text{C}_6\text{F}_5\text{S}-\text{S},\text{F})]$ [9]. The first example of interaction in solution was $[\text{IrH}_2(\text{PPh}_3)_2(8\text{-fluoroquinoline})][\text{SbF}_6]$ [10] which showed spin-spin coupling between fluorine and the hydride ligand in *trans* position, $^2J(\text{FH trans})=95$ Hz, whilst $^2J(\text{FH cis})\sim 0$ Hz. Another example in solution involved a Zr-F-C bridge [11]. Molybdenum complexes of the type $[\text{MoCl}(\text{CO})_3\{o\text{-XC}_6\text{H}_4\text{N}=\text{CH}(\text{C}_6\text{H}_3\text{Cl}_2-o)\}]$ showed coordination of halogen to molybdenum(II) (when X=Cl, Br or I), but attempts to prepare the analogous aryl fluoride complex (X=F) were unsuccessful [7].

We report here a new method of generating fluorine atom coordination based on our phosphino hydrazone $Z\text{-PPh}_2\text{CH}_2\text{C}(\text{Bu}^i)=\text{NNH}_2$ (**1**) [12]. Hydrazones are very nucleophilic and generally condense with aldehydes or ketones to give azines. These condensations are frequently rapid and go to completion. We anticipated therefore that $Z\text{-PPh}_2\text{CH}_2\text{C}(\text{Bu}^i)=\text{NNH}_2$ (**1**) would condense with 2,6-difluorobenzaldehyde to give a mixed azine phosphine $\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^i)=\text{N}-\text{N}=\text{CH}(\text{C}_6\text{H}_3\text{F}_2-2,6)$ (**2a**) of Z,E -configuration since the $\text{C}_6\text{H}_3\text{F}_2$ moiety is much more sterically demanding than H. Moreover, the mixed azine phosphine **2a** would be expected to

chelate to a metal through phosphorus and CH=N nitrogen to give a six-membered chelate ring, and therefore one would hope to force one of the two fluorine substituents (in the 2,6-positions) to be in close proximity to the metal and possibly coordinate to it. We have found this strategy to work very well with some ruthenium(II) complexes for which we get fluorine–ruthenium interaction and describe our results here.

2. Results and discussion

Treatment of the phosphino hydrazone **1** with 2,6-difluorobenzaldehyde in ethanol gave the hoped for mixed azine phosphine **2a** in 60% yield as a yellow crystalline solid. Further details are given in Section 3 as are elemental analytical and mass spectral data for this and other new compounds described in this paper. The various syntheses and reactions are summarised in Scheme 1. $^{31}\text{P}\{^1\text{H}\}$ NMR and $^{19}\text{F}\{^1\text{H}\}$ NMR data are given in Table 1 and proton NMR data (Table 2) were determined by recording both ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra. We reasoned that the labile complex $[\text{RuCl}_2(\text{PPh}_3)_3]$ [13,14], which is believed to show agostic interaction between an *ortho*-C–H bond and ruthenium(II), should undergo displacement of some of the PPh_3 ligands readily on treatment with an azine phosphine, such as **2a**, and we have found this to be the case. Treatment of $[\text{RuCl}_2(\text{PPh}_3)_3]$ with **2a** in hot ben-



Scheme 1.

Table 1
 $^{31}\text{P}\{^1\text{H}\}$ NMR data ^a and $^{19}\text{F}\{^1\text{H}\}$ NMR data ^b

	$\delta(\text{P}_A)$	$\delta(\text{P}_B)$	$^2J(\text{PP})$	$^2J(\text{P}_A\text{F})$	$\delta(\text{F})$
1	-22.6(s)				
2a	-11.9(s)				-111.9(s)
2b	-11.6(s)				^c
2c	-11.6(s)				-108.9(s)
2d	-10.7(s)				-120.9(s)
2e	-10.9(s)				-140.0(d), -146.0(d) ^d
3a ^e	84.6(dt)	45.0(d)	38	68	-128.9(d) ^f
3b	85.2(dt)	41.9(d)	39	54	
3c	78.3(dd)	41.5(d)	39	51	-124.8(d) ^g
3d ^e	81.2(dd)	45.2(d)	37	44	-125.6(d) ^h
3e	79.9(dd)	45.3(d)	37	11	-137.3(d), -143.1(dd) ⁱ

^a Recorded at 36.2 MHz, chemical shifts $\delta(\text{P})$ are in ppm relative to 85% H_3PO_4 , J values are in Hz, solvent CDCl_3 unless otherwise stated, s=singlet, d=doublet, dd=doublet of doublets, dt=doublet of triplets.

^b Recorded at 84.26 MHz, chemical shifts $\delta(\text{F})$ are in ppm relative to CFCl_3 , solvent CDCl_3 , m=multiplet tt=triplet of triplets.

^c -141.3 (2F, m), -153.2 [1F, tt, $^3J(\text{FF})=21$, $^4J(\text{FF})=3$ Hz] and -163.6 (2F, m).

^d $^3J(\text{FF})=20$ Hz.

^e In CD_2Cl_2 .

^f $^2J(\text{P}_A\text{F})=68$ Hz.

^g $^2J(\text{P}_A\text{F})=50$ Hz.

^h $^2J(\text{P}_A\text{F})=42$ Hz.

ⁱ $^3J(\text{FF})=20$ Hz and $^2J(\text{P}_A\text{F})=10$ Hz.

zene (60 °C) for ~1 min gave the *mer,trans*-ruthenium(II) complex $[\text{RuCl}_2(\text{PPh}_3)\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^1)=\text{N}-\text{N}=\text{CH}(\text{C}_6\text{H}_3\text{F}_2-2,6)\}]$ (**3a**) in 76% yield. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of this complex showed a doublet of triplets for P_A , $\delta(\text{P}_A)=84.6$ ppm with $^2J(\text{P}_A\text{P}_B)=38$ and $^2J(\text{P}_A\text{F})=68$ Hz, and a doublet for P_B . The $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum showed only one doublet fluorine resonance at -128.9 ppm with $^2J(\text{P}_A\text{F})=68$ Hz and $^2J(\text{P}_B\text{F})\sim 0$ Hz for both fluorines. The coupling constant $^2J(\text{P}_A\text{P}_B)$ of 38 Hz shows that these two phosphorus ligands are mutually *cis* [15]. The CH_2 protons are equivalent and coupled only to P_A , $^2J(\text{P}_A\text{H})=14.4$ Hz (Table 2), as shown by selective decoupling of P_A . Interestingly, the $\text{HC}=\text{N}$ proton is coupled to P_B , $^4J(\text{P}_B\text{H})=6.8$ Hz, but not to P_A . Since the CH_2 protons are chemically equivalent, this suggests that the chloride ligands are mutually *trans*, and in agreement with this, there is a strong single IR band at 320 cm^{-1} typical of a *trans*-Cl–Ru–Cl moiety [15]. $^{13}\text{C}\{^1\text{H}\}$ NMR data (see Section 3) for the $\text{C}_6\text{H}_3\text{F}_2$ moiety of **3a** are as follows: C^1 appeared as a triplet at 111.7 ppm with $^2J(\text{FC})=13$ Hz; C^2 and C^6 are chemically equivalent and appeared as a doublet of doublets at 159.8 ppm with $^1J(\text{FC})=252$ Hz and $^3J(\text{FC})$ or $^3J(\text{PC})=6.5$ Hz; C^3 and C^5 are also chemically equivalent and appeared as a doublet of doublets at 112.3 ppm with $^2J(\text{FC})=23.5$ Hz and $^4J(\text{FC})$ or $^4J(\text{PC})=2.7$ Hz and C^4 appeared as a triplet at 133.6 ppm with $^3J(\text{FC})=11.7$ Hz. Even at -50 °C, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (Fig. 1) does not

Table 2
Proton NMR data ^a

	$\delta(\text{Bu}^a)$	$\delta(\text{CH}_2\text{P})$	$\delta(\text{CH}=\text{N})$
1	0.98 (9H, s)	3.10 [2H, d, $^2J(\text{PH})$ 2.2]	
2a	1.29 (9H, s)	3.55 [2H, d, $^2J(\text{PH})$ 2.2]	7.89 (1H, s)
2b	1.30 (9H, s)	3.50 [2H, d, $^2J(\text{PH})$ 2.0]	7.79 (1H, s)
2c	1.29 (9H, s)	3.53 [2H, d, $^2J(\text{PH})$ 2.2]	8.01 (1H, s)
2d	1.24 (9H, s)	3.50 [2H, d, $^2J(\text{PH})$ 2.7]	8.24 (1H, s)
2e	1.25 (9H, s)	3.49 [2H, d, $^2J(\text{PH})$ 2.4]	8.16 (1H, s)
3a^b	0.72 (9H, s)	3.38 [2H, d, $^2J(\text{P}_A\text{H})$ 14.4]	8.84 [1H, d, $^4J(\text{P}_B\text{H})$ 6.8]
3b	0.72 (9H, s)	3.33 [2H, d, $^2J(\text{P}_A\text{H})$ 14.5]	8.78 [1H, d, $^4J(\text{P}_B\text{H})$ 6.4]
3c	0.74 (9H, s)	3.34 [2H, d, $^2J(\text{P}_A\text{H})$ 14.0]	8.80 [1H, d, $^4J(\text{P}_B\text{H})$ 6.8]
3d^b	0.74 (9H, s)	3.42 [2H, d, $^2J(\text{P}_A\text{H})$ 14.9]	9.13 [1H, d, $^4J(\text{P}_B\text{H})$ 6.6]
3e	0.75 (9H, s)	3.40 [2H, d, $^2J(\text{P}_A\text{H})$ 14.8]	9.27 [1H, d, $^4J(\text{P}_B\text{H})$ 6.6]

^a Recorded at 100 MHz, chemical shifts are in ppm relative to SiMe₄, *J* values are in Hz, solvent CDCl₃ unless otherwise stated, s=singlet, d=douplet.

^b In CD₂Cl₂.

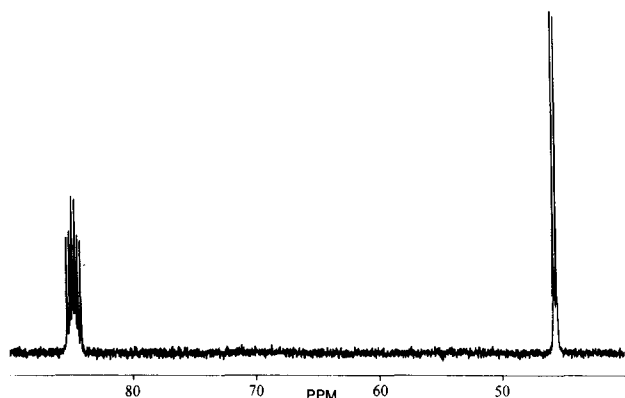


Fig. 1. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3a** in CDCl₃ at 161.9 MHz and 223 K.

change, indicating that the two *ortho*-fluorines are coordinated to ruthenium in turn, and rotation around the aryl–C bond is rapid on the NMR timescale.

Similarly, pentafluorobenzaldehyde condensed with **1** to give **2b** which reacted rapidly with [RuCl₂(PPh₃)₃] to give **3b**, in which both *ortho*-fluorines are coordinated to ruthenium in turn; characterising data are given in Section 3 and Tables 1 and 2. We have also made the mixed azine phosphine **2c** from 2-chloro-6-fluorobenzaldehyde. This with [RuCl₂(PPh₃)₃] gave **3c**. $^{31}\text{P}\{^1\text{H}\}$ NMR data for **3c** showed that P_A is coupled to the fluorine $\delta(\text{P}_A)=78.3$ (dd), $^2J(\text{P}_A\text{F})=51$ and $^2J(\text{P}_A\text{P}_B)=39$ Hz. It is generally considered that the order of donor ability of halogen atoms in halocarbons is I > Br > Cl > F [3], but in the case of **3c** the coupling between P_A and F is 50 Hz similar to the other *ortho*-fluoro-substituted benzaldehydes, suggesting that coordination of fluorine and chlorine takes place in turn due to the rapid rotation around the aryl–C bond and perhaps in this case coordination of F is stronger than Cl; even at –50 °C $J(\text{P}_A\text{F})$ is still ~50 Hz. We also made the mixed azine phosphines **2d** and **2e**, from

2-fluorobenzaldehyde and 2,3-difluorobenzaldehyde, and their ruthenium(II) complexes **3d** and **3e**, respectively. In each case coordination of fluorine to ruthenium was observed; characterising data are given in Section 3 and Tables 1 and 2.

Thus condensation of the phosphino hydrazone **1** with *ortho*-fluorobenzaldehydes gives mixed azine phosphines of type **2**, which when complexed to ruthenium, show coordination of the *ortho*-fluorine(s) with rapid rotation around the fluoroaryl–carbon bond. Other halo-substituted aldehydes (or ketones) could probably be condensed with **1** and the resultant azine could complex to a metal showing halogen coordination to metal. We have shown that the mixed azine phosphines, derived from non-halogen-substituted benzaldehydes, when treated with [RuCl₂PPh₃]₃ similarly displaced two PPh₃ ligands, and resultant complexes showed agostic interactions (C–H–Ru) between ruthenium and *ortho*-hydrogens [16]. It is possible that in compounds **3d** and **3e** some interaction between Ru and an *ortho*-hydrogen is also occurring.

3. Experimental

All reactions were carried out in an inert atmosphere of dry nitrogen or dry argon. IR spectra were recorded using a Perkin-Elmer model 457 grating spectrometer. NMR spectra were recorded using a JEOL FX-90Q spectrometer (operating frequencies for ¹H, ¹⁹F and ³¹P of 89.5, 84.26 and 36.2 MHz), a JEOL FX-100 spectrometer (operating frequencies for ¹H and ³¹P of 99.5 and 40.25 MHz) or a Bruker AM400 spectrometer (operating frequencies for ¹H, ³¹P and ¹³C of 400.13, 161.9 and 100.6 MHz). ¹H and ¹³C chemical shifts are relative to tetramethylsilane, ³¹P shifts are relative to 85% phosphoric acids, ¹⁹F shifts are relative to CFCl₃ and all coupling constants are in Hz. Electron impact

(EI) and fast atom bombardment (FAB) mass spectra were recorded using a VG Autospec spectrometer with 8 kV acceleration, and m/z values are quoted for ^{102}Ru .

3.1. Preparation of phosphine ligands

$Z\text{-PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{NNH}_2$ (**1**) was prepared according to our published procedure [10].

Preparation of $Z,E\text{-PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=N-N=\text{CH}(\text{C}_6\text{H}_3\text{-F}_2\text{-2,6})$ (**2a**)

2,6-Difluorobenzaldehyde (0.20 g, 0.15 mmol, 1.40 mmol) was added to a solution of $Z\text{-PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{NNH}_2$ (**1**) (0.4 g, 1.35 mmol) in ethanol ($\sim 4\text{ cm}^3$) and the resultant yellow solution was cooled to $-30\text{ }^\circ\text{C}$. The required mixed azine phosphine **2a** was obtained as a pale yellow crystalline solid (0.35 g, 62%). *Anal.* Found: C, 71.0; H, 6.1; N, 6.5. *Calc.* for $\text{C}_{25}\text{H}_{25}\text{F}_2\text{N}_2\text{P}$: C, 71.05; H, 5.9; N, 6.65%. m/z (EI): 422 (M^+) and 365 ($M-\text{Bu}^t$).

Similarly, the following mixed azine phosphines were prepared and isolated as yellow crystalline solids.

Preparation of $Z,E\text{-PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=N-N=\text{CH}(\text{C}_6\text{F}_5)$ (**2b**)

Yield 62%. *Anal.* Found: C, 63.15; H, 4.75; N, 5.65. *Calc.* for $\text{C}_{25}\text{H}_{22}\text{F}_5\text{N}_2\text{P}$: C, 63.0; H, 4.65; N, 5.9%. m/z (EI): 476 (M^+) and 419 ($M-\text{Bu}^t$).

Preparation of $Z,E\text{-PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=N-N=\text{CH}(\text{C}_6\text{H}_3\text{-Cl-2,F-6})$ (**2c**)

Yield 56%. *Anal.* Found: C, 68.5; H, 5.85; Cl, 7.95; N, 6.45. *Calc.* for $\text{C}_{25}\text{H}_{25}\text{ClF}_2\text{N}_2\text{P}$: C, 68.4; H, 5.75; Cl, 8.1; N, 6.4%. m/z (EI): 437 ($M-1$) and 381 ($M-\text{Bu}^t$).

Preparation of $Z,E\text{-PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=N-N=\text{CH}(\text{C}_6\text{H}_4\text{-F-2})$ (**2d**)

Yield 81%. *Anal.* Found: C, 73.85; H, 6.25; N, 7.15. *Calc.* for $\text{C}_{25}\text{H}_{26}\text{FN}_2\text{P}$: C, 74.25; H, 6.5; N, 6.9%. m/z (EI): 404 (M^+) and 347 ($M-\text{Bu}^t$).

Preparation of $Z,E\text{-PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=N-N=\text{CH}(\text{C}_6\text{H}_3\text{-F}_2\text{-2,3})$ (**2e**)

Yield 71%. *Anal.* Found: C, 71.05; H, 6.0; N, 6.45. *Calc.* for $\text{C}_{25}\text{H}_{25}\text{F}_2\text{N}_2\text{P}$: C, 71.05; H, 5.9; N, 6.65%. m/z (EI): 423 ($M+1$) and 365 ($M-\text{Bu}^t$).

3.2. Preparation of ruthenium(II) complexes

$\text{Mer,trans-[RuCl}_2(\text{PPh}_3)\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=N-N=\text{CH}(\text{C}_6\text{H}_3\text{F}_2\text{-2,6})\}]$ (**3a**)

$[\text{RuCl}_2(\text{PPh}_3)_3]$ [12] (80 mg, 0.083 mmol) and the azine phosphine **2a** (36 mg, 0.085 mmol) were warmed ($\sim 60\text{ }^\circ\text{C}$) in benzene ($\sim 2\text{ cm}^3$) for 1 min. The resulting cherry red solution was concentrated to a low volume ($\sim 0.5\text{ cm}^3$). The addition of cyclohexane ($\sim 1.5\text{ cm}^3$)

to the residue gave the *mer,trans*-ruthenium(II) complex **3a** as red microcrystals (54 mg, 76%). *Anal.* Found: C, 62.35; H, 5.25; Cl, 7.75; N, 3.15. *Calc.* for $\text{C}_{43}\text{H}_{40}\text{Cl}_2\text{F}_2\text{N}_2\text{P}_2\text{Ru}\cdot 0.75\text{C}_6\text{H}_6$: C, 62.3; H, 4.9; Cl, 7.75; N, 3.05%. m/z (FAB): 856 (M^+), 821 ($M-\text{Cl}$) and 785 ($M-\text{Cl}-\text{HCl}$). $\nu(\text{Ru}-\text{Cl})$ 320 cm^{-1} . $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CD_2Cl_2), δ_{C} (ppm): 27.3 [3C, s, CMe_3], 32.6 [1C, d, $^1J(\text{P}_{\text{A}}\text{C})$ 24.4, CH_2], 40.0 [1C, d, $^3J(\text{P}_{\text{A}}\text{C})$ 1.8, CMe_3], 111.7 [1C, t, $^2J(\text{FC})$ 13.0, C^1], 112.3 [2C, dd, $^2J(\text{FC})$ 23.5, $^4J(\text{FC})$ or $^4J(\text{PC})$ 2.7, C^3 and C^5], 127.5 [6C, d, $^3J(\text{P}_{\text{B}}\text{C})$ 9.5, C_{meta}], 127.6 [4C, d, $^3J(\text{P}_{\text{A}}\text{C})$ 10.5, C_{meta}], 129.5 [3C, d, $^4J(\text{P}_{\text{B}}\text{C})$ 2.1, C_{para}], 130.6 [2C, d, $^4J(\text{P}_{\text{A}}\text{C})$ 2.2, C_{para}], 133.6 [1C, t, $^3J(\text{FC})$ 11.7, C^4], 133.6 [3C, d, $^1J(\text{P}_{\text{B}}\text{C})$ 42.6, C_{ipso}], 134.3 [2C, d, $^1J(\text{P}_{\text{A}}\text{C})$ 51.2, C_{ipso}], 134.6 [4C, d, $^2J(\text{P}_{\text{A}}\text{C})$ 9.2, C_{ortho}], 135.4 [6C, d, $^2J(\text{P}_{\text{B}}\text{C})$ 9.6, C_{ortho}], 153.6 (1C, s, $\text{HC}=\text{N}$), 159.8 [2C, dd, $^1J(\text{FC})$ 252.0, $^3J(\text{FC})$ or $^3J(\text{PC})$ 6.5, C^2 and C^6], 174.3 (1C, s, $\text{Bu}^t\text{C}=\text{N}$).

The following *mer,trans*-ruthenium(II) complexes were prepared similarly.

$\text{Mer,trans-[RuCl}_2(\text{PPh}_3)\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=N-N=\text{CH}(\text{C}_6\text{F}_5)\}]$ (**3b**)

Yield 64%. *Anal.* Found: C, 59.8; H, 4.45; Cl, 6.9; N, 2.6. *Calc.* for $\text{C}_{43}\text{H}_{37}\text{Cl}_2\text{F}_5\text{N}_2\text{P}_2\text{Ru}\cdot 1.0\text{C}_6\text{H}_6$: C, 59.5; H, 4.4; Cl, 7.15; N, 2.85%. m/z (FAB): 910 (M^+), 874 ($M-\text{HCl}$), 839 ($M-\text{Cl}-\text{HCl}$). $\nu(\text{Ru}-\text{Cl})$ 315 cm^{-1} .

$\text{Mer,trans-[RuCl}_2(\text{PPh}_3)\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=N-N=\text{CH}(\text{C}_6\text{H}_3\text{Cl-2,F-6})\}]$ (**3c**)

Yield 84%. *Anal.* Found: C, 59.05; H, 4.4; N, 3.0. *Calc.* for $\text{C}_{43}\text{H}_{40}\text{Cl}_3\text{FN}_2\text{P}_2\text{Ru}$: C, 59.15; H, 4.6; N, 3.2%. m/z (FAB): 872 (M^+), 837 ($M-\text{Cl}$), 801 ($M-\text{Cl}-\text{HCl}$). $\nu(\text{Ru}-\text{Cl})$ 315 cm^{-1} .

$\text{Mer,trans-[RuCl}_2(\text{PPh}_3)\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=N-N=\text{CH}(\text{C}_6\text{H}_4\text{F-2})\}]$ (**3d**)

Yield 69%. *Anal.* Found: C, 63.55; H, 4.95; Cl, 7.8; N, 3.15. *Calc.* for $\text{C}_{43}\text{H}_{41}\text{Cl}_2\text{FN}_2\text{P}_2\text{Ru}\cdot 0.75\text{C}_6\text{H}_6$: C, 63.55; H, 5.1; Cl, 7.9; N, 3.1%. m/z (FAB): 838 (M^+), 802 ($M-\text{HCl}$) and 767 ($M-\text{Cl}-\text{HCl}$). $\nu(\text{Ru}-\text{Cl})$ 315 cm^{-1} .

$\text{Mer,trans-[RuCl}_2(\text{PPh}_3)\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=N-N=\text{CH}(\text{C}_6\text{H}_3\text{F}_2\text{-2,3})\}]$ (**3e**)

Yield 83%. *Anal.* Found: C, 60.1; H, 4.6; Cl, 8.1; N, 3.05. *Calc.* for $\text{C}_{43}\text{H}_{40}\text{Cl}_2\text{F}_2\text{N}_2\text{P}_2\text{Ru}$: C, 60.3; H, 4.7; Cl, 8.25; N, 3.25%. m/z (FAB): 856 (M^+), 820 ($M-\text{HCl}$), 785 ($M-\text{Cl}-\text{HCl}$). $\nu(\text{Ru}-\text{Cl})$ 320 cm^{-1} .

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