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# Syntheses, structure characterisation and X-ray studies of some mono, di- and tri-substituted cluster complexes of $Ru_3(CO)_{12}$ substituted by bulky fluorinated phosphine ligands

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#### ABSTRACT

Five trinuclear substituted complexes of the type  $Ru_3(CO)_{11}L$ ,  $Ru_3(CO)_{10}L_2$  and  $Ru_3(CO)_{9}L_3$  were synthesised by the reaction of  $Ru_3(CO)_{12}$  with fluorine substituted phosphine ligands, { $P(C_6H_4F-m)_3$  and  $P(C_6H_4F-m)_3$  $p_{3}$ , using the radical anion catalysed method. The structures of the resulting clusters were elucidated by means of elemental analyses and spectroscopic methods, which included IR, <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectroscopy. X-ray crystallographic studies of four of the complexes were carried out. In all the complexes, the ligand occupies an equatorial position due to steric reasons, and coordination of the ligand is observed only at the phosphorus atom. In the two monosubstituted complexes,  $Ru_3(CO)_{11}P(C_6H_4F-m)_3$ and  $Ru_3(CO)_{11}P(C_6H_4F-p)_3$ , the effect of substitution resulted in an increase in the Ru-Ru distances. Out of the three Ru-Ru bonds, the one which is cis to the ligand is noticeably longer than the other two. The asymmetric unit of the disubstituted complex  $Ru_3(CO)_{10}{P(C_6H_4F-p)_3}_2$  is composed of two molecules, A and B. As expected, the two phosphorus ligands are equatorially bonded to two different ruthenium atoms. The asymmetric unit of the trisubstituted complex is composed of one molecule of  $Ru_3(CO)_9{P(C_6H_4F-m)_3}_3$  and one disordered solvent molecule. The structure consists of one triangular ruthenium complex in which each of the phosphorus ligands is equatorially bonded to three different ruthenium atoms. In the structure, disorder of the fluorine atoms is observed. Bond parameters, especially bond lengths and bond angles, are correlated to the structure and also are compared with the literature data of similar compounds.

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#### 1. Introduction

The chemistry of metal carbonyl clusters has always attracted researchers' interest, not only from the synthetic angle but also because of their application in catalysis [1]. The thermal reaction of  $Ru_3(CO)_{12}$  with  $PR_3$  in general leads to the mono, di- and tri-substituted derivatives, i.e., { $Ru_3(CO)_{11}(PR_3)$ }, { $Ru_3(CO)_{10}(PR_3)_2$ }, and { $Ru_3(CO)_9(PR_3)_3$ } [2]. An earlier method reported by Bruce et al. was the displacement method, whereby the complex  $Ru_3(-CO)_{11}(CNBu^t)$  was made to react with CO or a ligand containing P, As or Sb as a donor element, by displacing CO or  $CNBu^t$  [3]. The usefulness of this process has been successively demonstrated for synthesising monosubstituted complexes of  $Os_3(CO)_{12}$  by the reaction of  $Os_3(CO)_{11}(MeCN)$  with  $PR_3$  [4,5]. For the direct synthesis of mono, di- and tri-substituted clusters of Ru<sub>3</sub>(CO)<sub>12</sub>, trimethylamine oxide-induced carbonyl substitution [6], bis(triphenylphosphine)iminium salt-catalysed carbonyl substitution [7] and radical anion catalysed ligand substitution [8a,b] methods have been developed. However, we prefer the radical anion method, as developed by Bruce et al., to synthesise derivatives of the type Ru<sub>3</sub>(CO)<sub>12-n</sub>L<sub>n</sub> [n = 1, 2, 3, 4], substituted by tertiary phosphines, phosphites, arsines and isocyanides [9a,b]. Substitution of CO by a more bulky ligand results in the latter occupying the sterically least demanding site, which in all cases is the equatorial site.

Phosphine ligands have found extensive use in the formation of many complexes of ruthenium over the years. It has been observed that the substitution of phosphine ligands for carbonyls may increase the catalytic activity for hydrogenation–isomerization reactions of linear dienes [10]. Homogeneous hydrogenation of diphenylacetylene in the presence of  $Ru_3(CO)_9L_3$  has also been studied [11]. While complexes of many phosphine substituted  $Ru_3(CO)_{12}$  have been studied by Bruce et al., and they summarised that it proved difficult to obtain X-ray quality crystals of the series



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of complexes  $Ru_3(CO)_{12-n}L_n$ , in which the CO group is progressively substituted by the same phosphine ligand [12].

Some examples of n = 1-3 and n = 1-4 have been reported, but substitution by bulky phosphines makes it increasingly more difficult. Recently, the synthesis, structural characterisation and X-ray studies of some monosubstituted complexes of the type Ru<sub>3</sub>(-CO)<sub>11</sub>L have been studied in our laboratory [13]. To further our interest on the substituted triangle ruthenium clusters, we report the synthesis and characterisation of Ru<sub>3</sub>(CO)<sub>11</sub>P(C<sub>6</sub>H<sub>4</sub>F-*m*)<sub>3</sub> (**1**), Ru<sub>3</sub>(CO)<sub>9</sub>{P(C<sub>6</sub>H<sub>4</sub>F-*m*)<sub>3</sub>} (**2**), Ru<sub>3</sub>(CO)<sub>11</sub>P(C<sub>6</sub>H<sub>4</sub>F-*p*)<sub>3</sub> (**3**), Ru<sub>3</sub>(-CO)<sub>10</sub>{P(C<sub>6</sub>H<sub>4</sub>F-*m*)<sub>3</sub>} (**4**) and Ru<sub>3</sub>(CO)<sub>9</sub>{P(C<sub>6</sub>H<sub>4</sub>F-*p*)<sub>3</sub>} (**5**). X-ray diffraction studies of complexes **1–4** were carried out, however a similar study of complex **5** was not undertaken as attempts to obtain suitable single crystals for X-ray studies were not successful.

It has been observed that the introduction of non-CO ligands in general to  $Ru_3(CO)_{12}$  result in the lengthening of the Ru–Ru bond. The effect was more prominent in the two monosubstituted complexes **1** and **3**. A disorder of the fluorine atoms has been observed in the two complexes (**1** and **2**) where  $P(C_6H_4F-m)_3$  has been used as the ligand. In light of other published reports on substituted clusters of  $Ru_3(CO)_{12}$  with phosphine ligands, this study enables us to make a detailed comparison on the molecular geometries which results from substitution of CO.

#### 2. Experimental

#### 2.1. Chemicals, starting materials and spectroscopic measurements

All the syntheses were carried out using standard Schlenk techniques under an atmosphere of oxygen-free nitrogen.  $Ru_3(CO)_{12}$ (Aldrich),  $P(C_6H_4F-m)_3$  and  $P(C_6H_4F-p)_3$  (Maybridge Chem. Co. Ltd., UK) were used as received. Tetrahydrofuran was distilled from sodium benzophenone ketyl under an oxygen-free nitrogen atmosphere. The radical anion method was used for the syntheses of the complexes [14]. AR grade solvents were used for crystallisation. Florisil (100-200 mesh, Acros) was used as the stationary phase for column chromatography. Preparative TLC was carried out on glass plates,  $20 \times 20$  cm, using Silica gel 60GF<sub>254</sub> (Merck). Hexane and dichloromethane of AR grades were used for elution during column chromatography and preparative TLC. Elemental analyses were performed using a Perkin-Elmer model 2400 LS Series II C, H, N analyser, USA. Melting points of the compounds were performed in open capillaries using a SMP1 melting point apparatus, UK and were uncorrected. IR spectra were recorded with a Perkin-Elmer System 2000 FTIR spectrometer in a NaCl solution cell (0.1 mm). Deuterated chloroform was used as a solvent for <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR studies. These NMR studies were carried out on a Bruker B2H 400 FT-NMR spectrometer using 5 mm tubes. The <sup>1</sup>H and <sup>13</sup>C NMR shifts were referenced to TMS and <sup>31</sup>P NMR shifts were referenced to 85% H<sub>3</sub>PO<sub>4</sub>. All the complexes were synthesised by the reaction between  $Ru_3(CO)_{12}$  and a stoichiometric amount of the appropriate ligand. The resulting complexes were separated by chromatographic techniques and then isolated in the pure form. All the complexes were characterised by microanalyses and their spectral studies.

#### 2.2. Synthesis of the metal complexes

#### 2.2.1. Synthesis of $Ru_3(CO)_{11}P(C_6H_4F-m)_3$ (1)

 $Ru_3(CO)_{12}$  (100 mg, 0.16 mmol) and  $P(C_6H_4F-m)_3$  (52 mg, 0.17 mmol) in 10 ml dry deoxygenated THF were heated in an oil bath and warmed to 40 °C to dissolve the  $Ru_3(CO)_{12}$ . Sodium benzophenone ketyl solution (5 drops) was added dropwise via syringe, which immediately turned the reaction solution red. After completion of the reaction (monitored by TLC), the solvent was re-

moved under reduced pressure to give an oily mass. Thin layer chromatography showed the presence of two spots, one of them being a trace amount of the starting material, Ru<sub>3</sub>(CO)<sub>12</sub>. This was identified by its IR v(CO) spectrum with that of an authentic sample. The major orange band was separated by column chromatography and characterised. Yield: 97.5 mg (67%), m.p. 147–149 °C. Anal. Calc. for Ru<sub>3</sub>C<sub>29</sub>H<sub>12</sub>O<sub>11</sub>F<sub>3</sub>P: C, 37.55; H, 1.30. Found: C, 37.59; H, 1.28%. IR (cyclohexane), v(CO): 2099(m), 2049(m), 2017(s) and 1988(m) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.05–7.55 (m, 12H, Ph); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  37.3 (s, P ligand). Crystals suitable for X-ray crystallography were grown by solvent/solvent diffusion of *n*-hexane/dichloromethane at 10 °C.

#### 2.2.2. Synthesis of $Ru_3(CO)_9\{P(C_6H_4F-m)_3\}_3$ (2)

Compound **2** was prepared in a similar way to compound **1**, by reacting Ru<sub>3</sub>(CO)<sub>12</sub> and P(C<sub>6</sub>H<sub>4</sub>F-*m*)<sub>3</sub> in a 1:3 ratio. TLC of the reaction showed three bands. The major red-purple band was separated by preparative thin layer chromatography ( $R_{\rm f}$ : 0.32, hexane:dichloromethane 70:30) and characterised. Yield: 87.7 mg (62%), m.p. 166–168 °C. *Anal.* Calc. for Ru<sub>3</sub>C<sub>63</sub>H<sub>36</sub>O<sub>9</sub>F<sub>9</sub>F<sub>3</sub>: C, 50.31; H, 2.41. Found: C, 50.27; H, 2.39%. IR (cyclohexane),  $\iota$ (CO): 2058(m), 2041(m), 1989(s) and 1980(s) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.05–7.55 (m, Ph); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  117.8–164.5 (m, Ph), 204.2 (m, CO); <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  39.2 (s, P ligand). Crystals suitable for X-ray crystallography were grown by solvent/solvent diffusion of *n*-hexane/dichloromethane at 10 °C.

#### 2.2.3. Synthesis of $Ru_3(CO)_{11}P(C_6H_4F-p)_3$ (3)

Ru<sub>3</sub>(CO)<sub>12</sub> (100 mg, 0.16 mmol) and P(C<sub>6</sub>H<sub>4</sub>F-*p*)<sub>3</sub> (52 mg, 0.17 mmol) were reacted in a similar way to compound **1**. Thin layer chromatography showed the presence of two spots, one of them being a trace amount of the starting material, Ru<sub>3</sub>(CO)<sub>12</sub>. The major orange band was separated by column chromatography and characterised. Yield: 94.0 mg (64.8%), m.p. 154–156 °C. Anal. Calc. for Ru<sub>3</sub>C<sub>29</sub>H<sub>12</sub>O<sub>11</sub>F<sub>3</sub>P: C, 37.55; H, 1.30. Found: C, 37.58; H, 1.32%. IR (cyclohexane), t(CO): 2099(m), 2059(w), 2048(m), 2017(s) and 1988(s) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.1–7.5 (m, 12H, Ph); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  116.4–166.1 (m, Ph), 204.4 (m, CO); <sup>31</sup>P NMR (CDCl<sub>3</sub>)  $\delta$  34.2 (s, P ligand). Crystals suitable for X-ray crystal-lography were grown by solvent/solvent diffusion of *n*-hexane/ dichloromethane at 10 °C.

#### 2.2.4. Synthesis of $Ru_3(CO)_{10}\{P(C_6H_4F-p)_3\}_2$ (4)

Compound **4** was prepared in a similar way to compound **1**, by reacting Ru<sub>3</sub>(CO)<sub>12</sub> and P(C<sub>6</sub>H<sub>4</sub>F-*p*)<sub>3</sub> in a 1:2 molar ratio. Separation of the products was done by preparative TLC which showed three bands. The major red band was separated ( $R_f$ : 0.44, hexane:dichloromethane 78:22) and characterised. Yield: 79.0 mg (52%), m.p. 178–179 °C. Anal. Calc. for Ru<sub>3</sub>C<sub>46</sub>H<sub>24</sub>O<sub>10</sub>F<sub>6</sub>P<sub>2</sub>: C, 45.44; H, 1.99. Found: C, 45.41; H, 1.97%. IR (cyclohexane), v(CO): 2079(m), 2057(m), 2021(s) and 1997(s). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.05–7.55 (m, 24H, Ph); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  34.2 (s, P ligand). Crystals suitable for X-ray crystallography were grown by solvent/solvent diffusion of *n*-hexane/dichloromethane at 10 °C.

#### 2.2.5. Synthesis of $Ru_3(CO)_9\{P(C_6H_4F-p)_3\}_3$ (**5**)

Compound **5** was prepared in a similar way to compound **1**, by reacting  $Ru_3(CO)_{12}$  and  $P(C_6H_4F-p)_3$  in a 1:3 ratio. TLC of the reaction showed three bands. The major red-purple band was separated by preparative thin layer chromatography ( $R_f$ : 0.34, hexane:dichloromethane 68:32) and characterised. Yield: 94.6 mg (67%), m.p. 169–171 °C. Anal. Calc. for  $Ru_3C_{63}H_{36}O_9F_9F_3$ : C, 50.31; H, 2.41. Found: C, 50.32; H, 2.42%. IR (cyclohexane),  $\iota$ (CO) 2059(m), 2045(w), 2018(w)1988(s) and 1974(s) cm<sup>-1</sup>.

<sup>1</sup>HNMR (CDCl<sub>3</sub>):  $\delta$  7.05–7.50 (m, Ph); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  116.0–164.5 (m, Ph), 204.0 (m, CO); <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  36.4 (s, P ligand). All attempts to grow suitable single crystals of this compound for X-ray diffraction studies were not successful.

#### 2.3. X-ray structural determination

Determination of cell constants and data collection were carried out at 100.0(1) K using the Oxford Cryosystem Cobra low-temperature attachment with Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) on a Bruker SMART APEX2 CCD area-detector diffractometer equipped with a graphite monochromator [15]. The data were reduced using SAINT [15]. A semi-empirical absorption correction was applied to the data using SADABS [15]. The structure was solved by direct methods and refined against  $F^2$  by full-matrix least-squares using SHELXTL [16]. Hydrogen atoms were placed in calculated positions. Crystal data and experimental details of the structure determinations are listed in Table 1. All hydrogen atoms were positioned geometrically and refined using a riding model with C–H = 0.93–0.97 Å and  $U_{iso}(H) = 1.2$  or  $1.5U_{eq}(C)$ . Details of all hydrogen bonding geometries are listed in Table 2.

#### 3. Results and discussion

#### 3.1. Synthesis and characterisation

The microanalyses of all the compounds agreed well with the proposed molecular formula for all the reported compounds, within the experimental errors. The isolation of a number of substituted derivatives of Ru<sub>3</sub>(CO)<sub>12</sub> has enabled definite information on v(CO) frequencies, and the degree of substitution can be easily established from IR spectroscopic studies [8b]. Individual bands, however, may vary slightly in relative intensity and their position. The <sup>1</sup>H NMR spectra of compounds **1–5** showed a multiplet around  $\delta$  7.0–7.6 ppm, characteristic of phenyl groups. The <sup>13</sup>C NMR spectra of all the clusters exhibited prominent signals in the range  $\delta$ 

Table 1

Crystal data and structure refinement parameters for 1-4.

115–166 ppm, characteristic of phenyl carbons. The longer range was due to the carbons attached to the electronegative fluorine atoms, which were downfield, and these aromatic carbons were observed in the range  $\delta$  160–166 ppm. The carbonyl carbons in all the five clusters showed a multiplet, as a single broad peak. The broadness of the single peak in the <sup>13</sup>C NMR suggests that the carbonyl ligands of the triruthenium clusters are fluxional in solution. A similar observation was made by Lam et al. when they investigated the reaction of 2-indolylphosphines with Ru<sub>3</sub>(CO)<sub>12</sub> [17]. <sup>31</sup>P NMR spectra of the two monosubstituted clusters showed single signals at  $\delta$  37.3 and 34.2 ppm for clusters **1** and **3** respectively. For the disubstituted cluster  $Ru_3(CO)_{10}{P(C_6H_4F-p)_3}_2$ , **4**, a single signal was expected in the <sup>31</sup>P spectrum as both the ligands are in identical chemical environments, however due to background noise. splitting of the signal is observed at  $\delta$  34.2, whereas a single signal is observed for the tri-substituted cluster complexes 2 and 5, as all the phosphorus atoms in these complexes are in the same environment.

#### 3.2. X-ray crystal structural analysis

## 3.2.1. Molecular structures of $Ru_3(CO)_{11}P(C_6H_4F-m)_3$ (1) and $Ru_3(CO)_{11}P(C_6H_4F-p)_3$ (3)

The crystal structures of both the monosubstituted complexes **1** and **3** have been determined. The ORTEP plot of  $Ru_3(CO)_{11}P(C_6H_4F-m)_3$  is shown in Fig. 1. The ORTEP plot of  $Ru_3(CO)_{11}P(C_6H_4F-p)_3$ , **3**, is shown in Fig. 3. Both the clusters contain a triangular arrangement of three ruthenium atoms. The coordination of the ligand was only observed at the phosphorus atom and all ligands occupy equatorial sites. In  $Ru_3(CO)_{12}$ , the average Ru–Ru separations is 2.852 Å [18], one of the three Ru–Ru bonds being slightly longer than the other two Ru–Ru bonds. The longest Ru–Ru bond in  $Ru_3(CO)_{12}$  is 2.859 Å. In the two monosubstituted complexes **1** and **3**, the longest Ru–Ru bond is the one which is cis to the ligand. For cluster **1**, it is 2.905(3) Å and for cluster **3**, the longest Ru–Ru bond is 2.876(3) Å. The uneven increase in the length of the metal–metal

Compound	1	2	3	4
Empirical formula	C <sub>29</sub> H <sub>12</sub> F <sub>3</sub> O <sub>11</sub> PRu <sub>3</sub>	C63H36F9O9P3Ru3/C6H14	C <sub>29</sub> H <sub>12</sub> F <sub>3</sub> O <sub>11</sub> PRu <sub>3</sub>	C46H24F6O10P2Ru3
Formula weight	927.57	1590.21	927.57	1215.80
<i>T</i> (K)	296(2)	100.0(1)	100.0(1)	296(2)
$\lambda$ (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	triclinic	monoclinic	orthorhombic
Space group	C2/c	ΡĪ	$P2_1/c$	Pccn
Unit cell dimensions				
a (Å)	22.3380(2)	12.6885(3)	13.8320(2)	22.6851(2)
b (Å)	16.6337(2)	14.4056(3)	12.1783(2)	22.8971(2)
c (Å)	17.5209(2)	18.3377(4)	22.4851(3)	17.7814(2)
α (°)	90	74.038(1)	90	90
β(°)	104.363(1)	83.077(1)	126.740(1)	90
γ (°)	90	82.258(1)	90	90
$V(Å^3)$	6306.65(12)	3180.97(12)	3035.24(9)	9236.07(15)
Ζ	8	2	4	8
$D_{\text{calc}}$ (Mg m <sup>-3</sup> )	1.954	1.660	2.030	1.749
F(0 0 0)	3584	1588	1792	4768
Absorption coefficient (mm <sup>-1</sup> )	1.545	0.863	1.606	1.119
Crystal size (mm)	$0.12 \times 0.26 \times 0.34$	$0.17 \times 0.30 \times 0.55$	$0.11 \times 0.20 \times 0.22$	$0.05\times0.17\times0.32$
$\theta$ Range (°)	1.5-35.1	1.9-32.5	1.9–30.2	1.3-27.5
Reflections collected/unique	71 046/13 964	102 284/22 807	38 310/8911	99 811/10 611
R <sub>int</sub>	0.047	0.038	0.045	0.075
Data/restraints/parameters	13 964/0/434	22 807/5/897	8911/0/424	10 611/0/605
Goodness-of-fit on $F^2$	1.02	1.10	1.06	1.05
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0401$	$R_1 = 0.0471$	$R_1 = 0.0321$	$R_1 = 0.0650$
	$wR_2 = 0.0951$	$wR_2 = 0.1193$	$wR_2 = 0.0570$	$wR_2 = 0.1456$
R indices (all data)	$R_1 = 0.0847$	$R_1 = 0.0674$	$R_1 = 0.0512$	$R_1 = 0.0991$
	$wR_2 = 0.1135$	$wR_2 = 0.1397$	$wR_2 = 0.0635$	$wR_2 = 0.1677$
Largest difference in peak and hole (e $Å^{-3}$ )	–0.49 and 1.54	–2.89 and 2.89	-0.73 and 0.75	-1.04 and 3.44

Table 2	
Hydrogen-bonding geometry (Å	, °)

D–H···A	Distance (Å) D–H	Distance (Å) H····A	Distance (Å) D···A	Angle (°) D–H···A
Complex <b>1</b> C15–H15A⋯O10 <sub>i</sub> Symmetry codes: (i) 1/2 – x,	0.93 1/2 - y, -z	2.59	3.514(6)	174
Complex <b>2</b> C8-H8A $\cdots$ F3A <sub>i</sub> C16-H16A $\cdots$ F8A <sub>ii</sub> C50-H50A $\cdots$ F1A <sub>iii</sub> Symmetry codes: (i) 1 - x, 1	0.93 0.93 0.93 - y, 2 - z; (ii) 2 - x, 1 - y, 2-z; (iii)	2.43 2.36 2.54 2 - x, -y, 2 - z	3.062(6) 3.285(8) 3.221(6)	125 169 130
Complex <b>3</b> C9−H9A…F1 <sub>i</sub> Symmetry codes: (i) 2 − x, 1/	0.93 /2 + y, 1/2 - z	2.48	3.113(4)	126
Complex <b>4</b> C12−H12B···O1B C14−H14A···O1B <sub>i</sub> Symmetry codes: (i) 1/2 + x,	0.93 0.93 -y, 3/2-z	2.59 2.59	3.451(8) 3.389(9)	155 144



Fig. 1. The ORTEP diagram of complex 1 with 10% probability of ellipsoids for non-H atoms. Only the major disorder component is shown.

bonds in comparison with those in  $Ru_3(CO)_{12}$  can be attributed to the steric effect induced by the bulky substituent. Thus the Ru–Ru separations in both complexes have ranges of 2.842(3)-2.905(3) Å. In the monosubstituted complexes of a similar type synthesised by Bruce et al., the Ru–Ru separations have ranges of 2.839-2.920 Å [9a].

In clusters **1** and **3**, the Ru–P bond lengths are 2.364(7) and 2.349(7) Å respectively which are slightly shorter compare to the Ru–P bond length of 2.380(6) Å observed for  $Ru_3(CO)_{11}(PPh_3)$ , in which the P atom is similarly bonded equatorially to the ruthenium cluster [19]. In the complexes, the ligand is approximately trans to one of the Ru–Ru bonds. The Ru–Ru–P angles in the complexes are 103.1(19)° for complex **1** and 113.3(2)° for complex **3**.

As observed in  $Ru_3(CO)_{12}$ , the bonds from the metal atoms to the axial CO ligands are longer compared to the bonds to the equatorial CO groups [20]. In the previously reported structures of  $Ru_3(-CO)_{11}L$ , the  $Ru-CO_{(ax)}$  distances are longer than the  $Ru-CO_{(eq)}$  distances, the average value of Ru-CO(ax) being 1.939(4) and 1.938(3) Å for clusters **1** and **3** and the average  $Ru-CO_{(eq)}$  value being 1.908(4) and 1.917(3) Å for the two complexes, in the same order. In Ru<sub>3</sub>(CO)<sub>12</sub>, the equatorial Ru-C-O moieties are almost linear (the average Ru-C-O angle is 178.9°) while the axial Ru-C-O moieties are slightly bent (average value, 172.9°) [20]. The reason for this distortion is attributed to the van der Waals repulsion between the oxygen atoms. In the monosubstituted complexes, the equatorial CO groups are essentially linear (the average value for cluster **1** is 177.9° and for cluster **3**, it is 177.1°), while the axial CO groups are slightly bent (average value for cluster 1 is 173.0° and for cluster 3, it is 174.2°). These observations are consistent with the previously published observations of monosubstituted triruthenium cluster complexes [9a]. In Ru (CO)<sub>12</sub>, the average axial OC-Ru-CO angles are 178.3° and the average equatorial OC-Ru-CO angles are 104.1°. In the two monosubstituted complexes reported here, the average axial OC-Ru-CO angles are 175.3° and



**Fig. 2.** The ORTEP diagram of complex **2** with 10% probability of ellipsoids for non-H atoms. Only the major disorder component is shown. The disordered hexane solvent is omitted for clarity.



Fig. 3. The <code>ortep</code> diagram of complex 3 with 50% probability of ellipsoids for non-H atoms.

171.8° for clusters **1** and **3**, whereas the average equatorial OC–Ru– CO angles are 101.6° and 101.4° for the two clusters in the same order. These observations are also in line with previously published reports on monosubstituted complexes [9a].

In complex **1**, the dihedral angles between the three phosphinesubstituted benzene rings are  $85.94(19)^\circ$ ,  $78.7(2)^\circ$  and  $68.72(19)^\circ$ . One of the fluorine atoms is disordered over two positions with refined site occupancies of 0.511(6) and 0.489(6). In complex **3**, the dihedral angles between the three phosphine-substituted benzene rings are  $63.53(17)^\circ$ ,  $63.72(19)^\circ$  and  $86.84(16)^\circ$ .

#### 3.2.2. Molecular structure of $Ru_3(CO)_9{P(C_6H_4F-m)_3}_3$ (2)

The crystal structure of complex **2** has been determined. The OR-TEP plot of  $Ru_3(CO)_9{P(C_6H_4F-m)_3}_3$  is shown in Fig. 2. The asymmetric unit consists of one triruthenium complex and one disordered hexane solvent molecule The three tris{(m-fluorophenyl)phosphine} ligands take up positions that are as far apart as possible, each occupying an equatorial site. The structure consists of a triangular  $Ru_3$  core with three nearly equal Ru-Ru bonds which posses an average bond length of 2.883 Å. This is close to the average value of 2.873 Å observed for  $Ru_3(CO)_9(PPh_3)_3$  in which the P atoms are similarly bonded equatorially to the ruthenium cluster [21]. The average Ru-Ru distance of 2.883 Å is slightly longer (0.031 Å) than found in Ru<sub>3</sub>(CO)<sub>12</sub>, where the corresponding distance is 2.852 Å [18]. The nine carbonyl ligands are all terminal, six occupying the two axial positions on the Ru atoms, while the other three are alternating with the phosphine ligands in one of the two equatorial positions of each ruthenium atom. The Ru-P distances are typical of ruthenium complexes of this type, with an average bond length of 2.337 Å. The three phosphorus atoms make P-Ru-Ru angles of 165.7(2)°, 167.5(2)° and 170.2(2)°. The equatorial Ru-C distances [average 1.890 Å] are slightly shorter than the equatorial Ru–C bond distances of Ru<sub>3</sub>(CO)<sub>12</sub>, which averages 1.924 Å. As expected, upon phosphine substitution, these Ru-C bond distances are slightly shortened relative to those in  $Ru_3(CO)_{12}$ . The Ru–C–O<sub>(eq)</sub> angles are slightly deviated from linear (average value 176.0°), while the average  $Ru-C-O_{(ax)}$  angle is slightly bent, with a value of 173.8°. The hexane molecule is disordered over two positions with refined site occupancies of 0.555(7)and 0.445(7). Seven out of the nine fluorine atoms are disordered over two positions. The dihedral angles between the three phosphine-substituted benzene rings at the P1 atom are 53.8(2)°, 77.4(2)° and 89.60(19)°, at the P2 atom are 55.47(18)°, 80.48(19)° and 86.03(17)°, and at P3 atom are 49.90(19)°, 73.68(19)° and 88.84(19)°.

#### 3.2.3. Molecular structure of $Ru_3(CO)_{10}\{P(C_6H_4F-p)_3\}_2$ (4)

The ORTEP plot of cluster **4** is shown in Fig. 4. The asymmetric unit of  $Ru_3(CO)_{10}{P(C_6H_4F-p)_3}_2$  consist of two-half molecules (A and B) of the triruthenium complex. The Ru2A and Ru2B atoms lie across a two-fold rotation axis. The structure is composed of a triangle of ruthenium atoms with the two phosphine ligands equatorially bonded to two different ruthenium atoms. The two phosphine ligands take up positions as far apart as possible. The two phosphine ligands are approximately trans to the same Ru-Ru bond, with P-Ru-Ru bond angles of 172.5° and 171.5(5) ° for molecules A and B. While the P1-Ru1-Ru2 bond angles are 115.6 and  $114.5(4)^{\circ}$  for both the molecules, in the same order. There is no noticeable lengthening of the Ru-Ru bond cis to the ligand, and the Ru-Ru distances are very close to each other. As observed in  $Ru_3(CO)_{12}$  [18], the Ru-CO<sub>(ax)</sub> bonds are longer than the Ru-CO<sub>(eq)</sub> bonds. The Ru-CO<sub>(eq)</sub> bonds on the metal atom bearing the phosphine ligands show the shortest M-CO separations. The Ru-P separations are identical to those of analogous complexes [22,23]. It has been observed that Ru-C-O<sub>(ax)</sub> angles on the metal atoms that do not bear phosphine ligands have bent significantly from linearity. These Ru-C-O<sub>(ax)</sub> angles are 167.2(8)° and 168.5(8)° for molecules A and B respectively. The P-Ru-Ru-P dihedral angles are



**Fig. 4.** The ORTEP diagram of complex **4** with 20% probability of ellipsoids for non-H atoms, only one molecule of the asymmetric unit is shown. The other molecule is of a similar conformation. The atoms with suffix AA or C are symmetry generated.



**Fig. 5.** Comparative study of the rotation about the  $Ru(CO)_4$  unit from the plane of the  $Ru_3$  triangle.

108.9° and 107.3° for molecules A and B respectively. The dihedral angles between the three phosphine-substituted benzene rings are  $64.2(4)^{\circ}$ ,  $79.8(5)^{\circ}$  and  $80.0(4)^{\circ}$  in molecule A, whereas these angles are  $82.2(4)^\circ$ ,  $64.7(4)^\circ$  and  $80.7(4)^\circ$  in molecule B. In compounds 1– **3**, the dihedral angles of the Ru<sub>3</sub> plane with the Ru–Ru–C plane are (Ru1-Ru3-C28) 81.42(13)°, (Ru1-Ru3-C63) 78.61(9)° and (Ru1-Ru3-C28) 72.81(13)°, respectively. However in compound 4, these dihedral angles are (Ru1A-Ru2A-C22A) 65.8(2)° and (Ru1B-Ru2B-C22B) 63.8(3)° in molecules A and B respectively. The twisting of the  $Ru(CO)_4$  unit in cluster **4** is most likely due to the steric hindrance of the fluorine substituted on the phenyl ring of the phosphine ligand (Fig. 5).

#### 4. Conclusion

Some substituted triruthenium cluster carbonyl complexes were synthesised using fluorine substituted phosphine ligands. In all the cluster complexes reported, the ligands occupy equatorial positions, and coordination of the ligands is only at the phosphorus atom. Due to the steric effect of the ligand, one of the metal-metal bonds is noticeably longer in the two monosubstituted complexes. The <sup>13</sup>C NMR spectra of all the complexes showed a single broad peak for CO instead of a multiplet, indicating the fluxional behaviour of the CO ligands in solution. In the complex Ru<sub>3</sub>- $(CO)_{11}P(C_6H_4F-m)_3$ , there is a disorder of one of the fluorine atoms. Complex  $Ru_3(CO)_9{P(C_6H_4F-m)_3}_3$  shows disorder of the solvent molecule as well as the fluorine atoms. In the complex Ru<sub>3</sub>- $(CO)_{10}{P(C_6H_4F-p)_3}_2$ , twisting of the Ru(CO)<sub>4</sub> unit is observed, probably due to the presence of electronegative fluorine atoms substituted on the phenyl ring of the phosphine ligand.

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#### **Appendix A. Supplementary material**

CCDC 784933, 784934, 784935 and 784936 contain the supplementary crystallographic data for 1, 2, 3 and 4. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/ retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk

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