

# The synthesis and crystallographic characterisation of the complexes $[\text{RuX}(\text{CO})(\eta^2\text{-C,N-C}_6\text{H}_5\text{C(H)NC}_6\text{H}_4\text{-4Me})(\text{PPh}_3)_2] \cdot \text{CHCl}_3$ (X = Cl, Br, I, F): Evidence for competing $\text{Ru-X} \cdots \text{Cl-CHCl}_2$ and $\text{Ru-X} \cdots \text{HCCl}_3$ interactions in the solid state

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## Abstract

Treatment of  $[\text{RuCl}(\text{CO})\{\eta^2\text{-C,N-C}_6\text{H}_4\text{C(H)=NC}_6\text{H}_4\text{-4-Me}\}(\text{PPh}_3)_2]$  **2-Cl** with  $\text{Ag}[\text{BF}_4]$  in acetone/ $\text{CH}_2\text{Cl}_2$  gives the cationic complex  $[\text{Ru}\{\text{O}=\text{C}(\text{CH}_3)_2\}(\text{CO})\{\eta^2\text{-C,N-C}_6\text{H}_4\text{C(H)=NC}_6\text{H}_4\text{-4-CH}_3\}(\text{PPh}_3)_2][\text{BF}_4]$  (not isolated) which then reacts with  $\text{NaX}$  (X = F, Br, I) to afford the new compounds  $[\text{RuX}(\text{CO})\{\eta^2\text{-C,N-C}_6\text{H}_4\text{C(H)=NC}_6\text{H}_4\text{-4-CH}_3\}(\text{PPh}_3)_2]$  (X = F, Br, I) **2-F**, **2-Br**, and **2-I**. All of the new compounds have been characterised by elemental analysis (C, H, and N),  $^1\text{H}$ ,  $^{13}\text{C}$ - $\{^1\text{H}\}$ ,  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy and infrared spectroscopy. The infrared data support the hypothesis of that the fluoride ligand is the strongest halogen  $\pi$ -donor to the metal centre. In addition, the compounds **2-Br**· $1.5\text{CHCl}_3$ , **2-Cl**· $\text{CHCl}_3$ , **2-I**· $1.5\text{CHCl}_3$  have been characterised by single crystal X-ray diffraction studies: **2-Cl** shows a rare example of a  $\text{Ru-Cl} \cdots \text{ClCHCl}_2$  interaction, whereas **2-Br** and **2-I** show the expected  $\text{Ru-X} \cdots \text{HCCl}_3$  hydrogen bond interactions.

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## 1. Introduction

There was an initial reluctance to accept the possibility of the hydrogen bond, from its first mention in 1902 [1], based upon the chemical dogma that hydrogen has a valence of 1 [2]. The hydrogen bond first reached the main stream in Pauling's book: the nature of the chemical bond [3] in which the electrostatic nature of the interaction was emphasised. In 1960, Pimentel and McClellan modified the definition of a hydrogen bond to: a hydrogen bond is said to exist when: (1) there is evidence of a bond and (2) there is evidence that this bond sterically involves a hydrogen atom involved in a bond

to another atom [4]. Conventionally, hydrogen bonds involved hydrogen atom interactions with electronegative elements and donor groups such as N–H, O–H, halogen–H, with conventional acceptors based upon the same atoms in different hybridisation states [5]. Non-conventional interactions recognise the potential of, for example, C–H, P–H, M–H systems, to act as donors and  $\pi$ -systems (aryl, acetylenic) and C–F, for example, to act as acceptors. These and other secondary intermolecular interactions that influence solid state structures are currently of much interest, with hydrogen bonding of particular note, due to its importance in biological systems [6], non-covalent synthesis [7], crystal engineering [8], catalysis [9,10], and anion recognition [11] to name but a few. A recent review of hydrogen bonding in the solid state has also recently appeared [12]. In

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addition to the hydrogen bond it has been recognised [13] that the halogens, Cl, Br, and I, may also interact with electronegative atoms via weak secondary interactions. The nature of these interactions has been subject to much debate. It has been shown, that covalently bound halogen atoms do not occupy spherical volumes in space but are ellipsoidal due to the anisotropic distribution of electron density about their nucleus [14,15]. This leads to a non-uniform van der Waals radius that is shorter in the C–X bond direction. This so-called polar flattening has been used to explain why there are close intermolecular halogen···halogen contacts. Allen et al have shown, however, that intermolecular contacts between the halogen (Cl, Br, and I) and the electronegative (O, N) atoms can exist [16] and strong intermolecular halogen···halogen interactions have been, for example, reported for chlorinemonofluoride [17].

Based on methodology developed by Roper and Wright [18], we recently reported [19,20] the preparation of some cycloruthenated azobenzene containing complexes of the type  $[\text{RuX}(\text{CE})(\eta^2\text{-C}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_5)(\text{PPh}_3)_2]$  (X = Cl, Br, I; E = O, S) and subsequently extended the methodology to the preparation [21] of complexes of the type  $[\text{RuCl}(\text{CO})\{\eta^2\text{-C}_6\text{H}_4\text{C}(\text{H})=\text{NC}_6\text{H}_4\text{-4-R}\}(\text{PPh}_3)_2]$  **1-Cl**, **2-Cl**, **3-Cl**, **4-Cl** (R = NMe<sub>2</sub>, Me, I, NO<sub>2</sub>) which contain cycloruthenated 2-(phenylimino)phenyl ligands, Fig. 1. The structural and spectro-

scopic characteristics of these compounds afforded evidence for a *cis*-push–pull effect between the halide ligand and the CO ligand, which is moderated by the cyclometallated ligand. This effect was clearly shown by comparison of the solid state structures (X-ray) and <sup>13</sup>C–{<sup>1</sup>H} NMR data obtained for **1-Cl**, **2-Cl**, **3-Cl**, **4-Cl** with that obtained from previous studies concerned with the tautomeric process undergone by *ortho*-hydroxyazobenzene and *ortho*-hydroxyphenyliminophenyl Schiff bases [22–24], Fig. 1. The effect was shown to be dependent on the *para*-substituent of the phenyl-imino ring. We were then interested to see if the magnitude of the effect could be moderated by the  $\pi$ -donor strength of the halogen ligand. Recently, we reported the preparation and crystallographic characterisation of **4-F**, **4-Cl**, **4-Br**, and **4-I**···CHCl<sub>3</sub> and observed Ru–X···CHCl<sub>3</sub> interactions in the solid state [25]. What was most interesting in this series of compounds was that **4-Cl** and **4-Br** displayed a competing Ru–X···ClCHCl<sub>2</sub> interaction. Perusal of crystallographic databases showed that there was evidence for this kind of interaction although it had not been fully discussed before. Herein, we report that by changing the remote substituent of the cycloruthenated phenylimino ring the weak interactions between the Ru–X bond and the chloroform of crystallisation are significantly modified. A preliminary communication of this work has appeared [26].

## 2. Results and discussion

The compounds  $[\text{RuX}(\text{CO})\{\eta^2\text{-C}_6\text{H}_4\text{C}(\text{H})=\text{NC}_6\text{H}_4\text{-4-CH}_3\}(\text{PPh}_3)_2]$  (X = Br, F, I) **2-Br**, **2-F**, **2-I** were prepared, in essentially quantitative yield by treatment of **2-Cl** with a stoichiometric amount of Ag[BF<sub>4</sub>] followed by, after filtration to remove AgCl, a slight excess of NaX (X = F, Br, I). The new compounds **2-F**, **2-Br**, **2-I** were all characterised by elemental analysis (C, H and N) and infrared spectroscopy, Table 1, <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy, Table 2, <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy, Table 3, see Fig. 2 for the numbering scheme. Compounds, **2-Cl**, **2-Br** and **2-I** have also been characterised by single crystal X-ray diffraction studies, see Table 4 for data collection and processing parameters, Table 5 for selected bond lengths (Å), angles (°), Table 6 for hydrogen-bond data, ORTEP [27] representations of the molecular structures of **2-Br** and **2-I** are presented as Figs. 3 and 4, respectively (both the structures have the same numbering scheme). Fig. 5 shows the ORTEP representation of **2-Cl** [26] for comparison. All of the structures are best considered as octahedral about a central ruthenium atom with two PPh<sub>3</sub> ligands mutually *trans* and axial with the orthometallated imine, carbonyl and halide ligands in the equatorial plane. All of the solid state structures show a close approach, within the sum of the van der Waals radii [28], of a CHCl<sub>3</sub> of

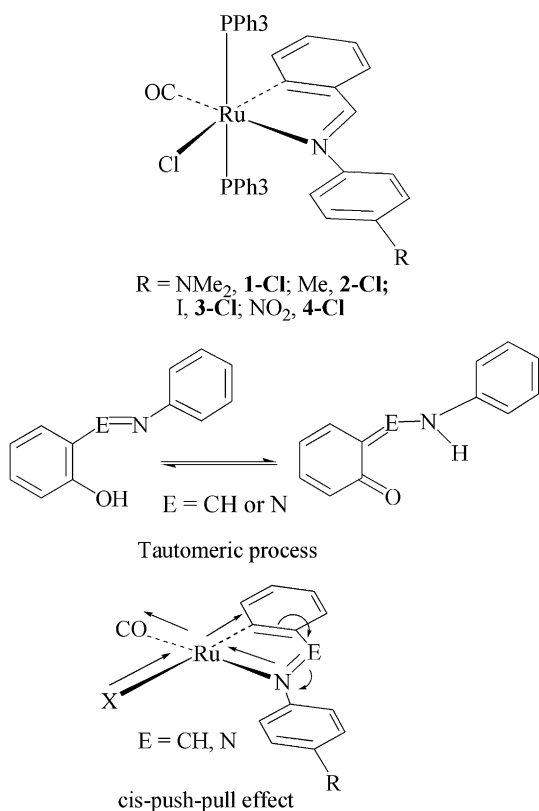


Fig. 1. The analogy between the *cis*-push pull effect and the tautomerisation in *ortho*-hydroxy Schiff bases.

Table 1  
Physical, analytical<sup>a</sup> and infrared<sup>b</sup> data for **2-F–2-I**

Compound	Color	Yield (%)	Microanalytical data (%)			IR (cm <sup>-1</sup> )
			C	H	N	CO(s)
<b>2-F</b> [Ru(F)(CO){η <sup>2</sup> -C,N-C <sub>6</sub> H <sub>4</sub> C(H)=NC <sub>6</sub> H <sub>4</sub> -4-Me}(PPh <sub>3</sub> ) <sub>2</sub> ]·CH <sub>2</sub> Cl <sub>2</sub>	Yellow	64	61.5 (60.7)	4.9 (5.3)	1.4 (1.6)	1921
<b>2-Cl</b> [Ru(Cl)(CO){η <sup>2</sup> -C,N-C <sub>6</sub> H <sub>4</sub> C(H)=NC <sub>6</sub> H <sub>4</sub> -4-Me}(PPh <sub>3</sub> ) <sub>2</sub> ]·0.75CH <sub>2</sub> Cl <sub>2</sub>	Yellow	96	65.4 (65.9)	5.2 (4.7)	1.4 (1.5)	1934
<b>2-Br</b> [Ru(Br)(CO){η <sup>2</sup> -C,N-C <sub>6</sub> H <sub>4</sub> C(H)=NC <sub>6</sub> H <sub>4</sub> -4-Me}(PPh <sub>3</sub> ) <sub>2</sub> ]·0.75CH <sub>2</sub> Cl <sub>2</sub>	Yellow	91	61.4 (61.7)	4.8 (4.4)	1.2 (1.4)	1936
<b>2-I</b> [Ru(I)(CO){η <sup>2</sup> -C,N-C <sub>6</sub> H <sub>4</sub> C(H)=NC <sub>6</sub> H <sub>4</sub> -4-Me}(PPh <sub>3</sub> ) <sub>2</sub> ]·0.75CH <sub>2</sub> Cl <sub>2</sub>	Yellow	93	59.3 (60.1)	4.8 (4.4)	1.2 (1.4)	1936

<sup>a</sup> Calculated values in parentheses.

<sup>b</sup> Spectra recorded as Nujol mulls between KBr discs, s = strong.

Table 2  
<sup>31</sup>P{<sup>1</sup>H} NMR and proton data<sup>a</sup> for compounds **2-F–2-I**

Compound	<sup>31</sup> P (δ)	<sup>1</sup> H (δ)
<b>2-F</b>	27.5, 27.3, d, <i>J</i> <sub>PF</sub> = 13.5	7.95 (t, <i>J</i> <sub>HP</sub> = 1.9, 1H, CH=N); 7.50–6.5 (m, 36H, aryl-H); 6.43 (t, <i>J</i> <sub>HH</sub> = 7.5, 1H, aryl-H); 6.12 (m, 1H, aryl-H); 2.15 (s, 3H, CH <sub>3</sub> )
<b>2-Cl</b>	28.6	7.90 (t, <i>J</i> <sub>HP</sub> = 1.85, 1H, CH=N); 7.43–6.89 (m, 30H, aryl-H); 6.64 (d, <i>J</i> <sub>HH</sub> = 7.5, 1H, aryl-H); 6.54 (d, <i>J</i> <sub>HH</sub> = 8.4, 2H, aryl-H); 6.43 (t, <i>J</i> <sub>HH</sub> = 7.1, 1H, aryl-H); 6.14 (d, <i>J</i> <sub>HH</sub> = 8.3, 2H, aryl-H); 6.08 (m, 1H, aryl-H); 5.22 (s, 1.5H, CH <sub>2</sub> Cl <sub>2</sub> ); 2.15 (s, 3H, CH <sub>3</sub> )
<b>2-Br</b>	28.1	7.90 (t, <i>J</i> <sub>HP</sub> = 2.26, 1H, CH=N); 7.40–6.92 (m, 30H, aryl-H); 6.62 (d, <i>J</i> <sub>HH</sub> = 7.5, 1H, aryl-H); 6.54 (d, <i>J</i> <sub>HH</sub> = 8.3, 2H, aryl-H); 6.43 (t, <i>J</i> <sub>HH</sub> = 7.5, 1H, aryl-H); 6.06 (m, 3H, aryl-H); 5.21 (s, 1.5H, CH <sub>2</sub> Cl <sub>2</sub> ); 2.9 (s, 3H, CH <sub>3</sub> )
<b>2-I</b>	27.1	7.87 (t, <i>J</i> <sub>HP</sub> = 1.8, 1H, CH=N); 7.37–6.92 (m, 31H, aryl-H); 6.76 (d, <i>J</i> <sub>HH</sub> = 7.6, 1H, aryl-H); 6.57 (d, <i>J</i> <sub>HH</sub> = 8.3, 2H, aryl-H); 6.47 (t, <i>J</i> <sub>HH</sub> = 7.1, 1H, aryl-H); 6.12 (t, d, <i>J</i> <sub>HH</sub> <sup>1</sup> 7.3, <i>J</i> <sub>HH</sub> <sup>2</sup> 1.5, 1H, aryl-H); 6.00 (d, <i>J</i> <sub>HH</sub> = 8.3, 2H, aryl-H); 5.23 (s, 1.5H, CH <sub>2</sub> Cl <sub>2</sub> ); 2.10 (s, 3H, CH <sub>3</sub> )

The <sup>13</sup>C–{<sup>1</sup>H} NMR spectra were assigned with the aid of DEPT 135 spectra substituent effects [33] and the data previously reported [21] for **1-Cl**, **2-Cl**, **3-Cl**, **4-Cl** and are consistent with the formulation of **2-F**, **2-Cl**, **2-Br** and **2-I**.

<sup>a</sup> Spectra recorded in CDCl<sub>3</sub> 293 K; coupling constants (*J*) in Hz; s = singlet, d = doublet, t = triplet.

crystallisation close to the Ru–X bond. For **2-Cl** the orientation of the CHCl<sub>3</sub> molecule gives rise to a Ru–Cl(1)··Cl(2)CHCl<sub>3</sub> interaction: Cl(1)··Cl(2) 3.419(1); Cl(2)–C(52) 1.720(2) Å; Cl(1)··Cl(2)–C(52) 164.35(11)°. This clearly differs from that observed for **4-Cl** where the competing Ru–Cl··HCCl<sub>3</sub> and Ru··ClCHCl<sub>2</sub> interactions were evident [25].

For **2-Br** there is no evidence of a Ru–Br··ClCHCl<sub>2</sub> interaction which was seen, as well as a Ru–Br··HCCl<sub>3</sub> interaction, in the crystal structure of **4-Br** [25]. For **2-I**, the originally expected Ru–X··HCCl<sub>3</sub> interaction is observed again as it was for **4-I**. See Table 6 for the dimensions of these interactions. These structures of **2-Br** and **2-I** were obtained at higher temperatures than for **4-Br** and **4-I** and a second orientation of the CHCl<sub>3</sub> close to the Ru–X group is also seen. It too has the C–H bond pointing towards the Ru–X moiety. This suggests as the temperature is raised the chloroform begins to move within the cavity and that these interactions are weak. A full discussion of these Ru–X··ClCHCl<sub>2</sub> and Ru–X··HCCl<sub>3</sub> including full database searches has been described elsewhere [25]. In addition to these interactions, a full Platon analysis [29] showed the presence of a number of other weak solid state interactions in **2-Cl**, **2-Br** and **2-I**: see Table 6. For example, four intramolecular aryl C–H hydrogen bonds to the Ru–X moiety are observed for all of the compounds completing an essen-

tially octahedral coordination sphere about the halide ion. It is clear, from the structure of **2-Cl**, **2-Br** and **2-I** and those previously reported for **4-F**, **4-Cl**, **4-Br** and **4-I**, that the Ru–X moiety readily engages in hydrogen or halogen bond interactions and that the interactions are weak and (qualitatively) of comparable energy. What is not immediately obvious is why changing a remote substituent on the cycloruthenated 2-phenylimino ring changes the relative proportions of each orientation for **2-Cl** and **4-Cl** and **2-Br** and **4-Br**.

The infrared spectra (Table 1) for **2-F**, **2-Cl**, **2-Br**, **2-I** all show a single strong ν(CO) band between 1921 (**2-F**) and 1936 cm<sup>-1</sup> (**2-I**). In a previous report [21] describing the synthesis of [RuCl(CO){η<sup>2</sup>-C,N-C<sub>6</sub>H<sub>4</sub>C(H)=NC<sub>6</sub>H<sub>4</sub>-4-R}(PPh<sub>3</sub>)<sub>2</sub>] (R = NMe<sub>2</sub>, Me, I, NO<sub>2</sub>) **1-Cl**, **2-Cl**, **3-Cl**, **4-Cl** we were able to correlate the metallated carbon <sup>13</sup>C–{<sup>1</sup>H} resonance with the Hammett σ<sup>+</sup> parameter [30] which confirmed that the remote *para*-substituent influenced the *cis*-push pull effect, Fig. 1; however, the trend in ν(CO) stretching frequencies was consistent with the <sup>13</sup>C{<sup>1</sup>H} NMR data, but not conclusive due to the narrow frequency separation across the series of 6 cm<sup>-1</sup>. For compounds **2-F**, **2-Cl**, **2-Br**, **2-I**, where the expected π-donor strength of the halide follows the trend F > Cl > Br > I with a constant *para*-substituent (CH<sub>3</sub>), the ν(CO) decreases across the series I > Br > Cl > F. This observation is consistent with the

Table 3  
 $^{13}\text{C}\{^1\text{H}\}$  NMR data<sup>a</sup> for **2-F–2-I**

Compound	CO	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13	C14	C15	Others
<b>2-F</b>	206.8	188.04	140.8	129.5	119.6	130.0	143.3	172.9	147.5	124.3	127.7	134	133.2	134.1	127.4	128.9	20.8CH <sub>3</sub>
	<i>t</i> , <i>J</i> = 10.6	<i>t</i> , <i>J</i> = 9.6									<i>t</i> , <i>J</i> = 21.2		<i>t</i> , <i>J</i> = 4.8	<i>t</i> , <i>J</i> = 4.7			
<b>2-Cl</b>	206.9	188.3	140.8	129.5	119.7	130.0	143.6	172.8	147.5	124.4	127.7	135.2	133.2	134.1	127.4	128.9	20.9CH <sub>3</sub>
	<i>t</i> , <i>J</i> = 10.2	<i>t</i> , <i>J</i> = 9.4									<i>t</i> , <i>J</i> = 21.1		<i>t</i> , <i>J</i> = 5.1	<i>t</i> , <i>J</i> = 4.4			
<b>2-Br</b>	207.5	188.4	140.5	129.2	119.5	130.0	143.0	172.9	147.3	124.7	127.3	135.0	133.1	133.9	127.1	128.6	20.5CH <sub>3</sub>
	<i>t</i> , <i>J</i> = 10.6	<i>t</i> , <i>J</i> = 10.6									<i>t</i> , <i>J</i> = 21.2		<i>t</i> , <i>J</i> = 4.8	<i>t</i> , <i>J</i> = 3.9			
<b>2-I</b>	207.2	190.0	141.1	130.1	120.4	130.8	144.1	173.9	148.1	125.2	127.9	135.8	133.9	134.8	127.6	129.3	21.2CH <sub>3</sub>
	<i>t</i> , <i>J</i> = 11.6	<i>t</i> , <i>J</i> = 12.5									<i>t</i> , <i>J</i> = 21.2		<i>t</i> , <i>J</i> = 4.8	<i>t</i> , <i>J</i> = 3.9			

<sup>a</sup> Spectra recorded in CDCl<sub>3</sub> at 298 K; all resonances singlets unless otherwise stated; all *J* = PC.

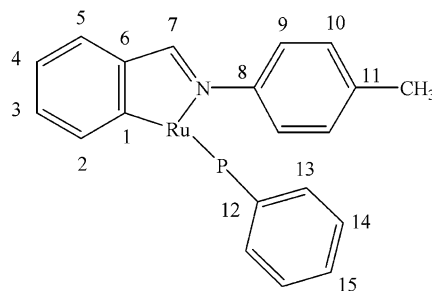


Fig. 2. Numbering scheme for  $^{13}\text{C}\{^1\text{H}\}$  NMR data.

fluoride ligand being the strongest  $\pi$ -donor, Table 1, (note: the wavenumber separation across the whole series is  $17\text{ cm}^{-1}$ ). This observation is also consistent with that reported for the *para*-NO<sub>2</sub> series [25]. It should also be remembered that the orthogonal halide p-orbital will be involved in *cis*- $\pi$ -donation to the CO ligand, in this case mediated by a metal  $d\pi$  orbital, not the cyclometalated ligand [31]. This trend in the observed  $\nu(\text{CO})$  values observed for **2-F**, **2-Cl**, **2-Br**, **2-I** must therefore be a result of both processes. Other evidence for this trend in  $\pi$ -donor strength for the halides ( $\text{F} > \text{Cl} > \text{Br} > \text{I}$ ) to transition metal centres has been noted previously [32].

The compounds **2-Cl**, **2-Br**, **2-I** all show the expected singlet resonance in their  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra Table 1, whereas for **2-F** a doublet is observed with  $J_{\text{PF}} = 13.5\text{ Hz}$ . The resonance position is little perturbed on halogen exchange.

The  $^1\text{H}$  NMR data are consistent with the formulation of **2-F**, **2-Cl**, **2-Br**, **2-I**. All the compounds show a triplet resonance for the imine CH proton (coupling to the mutually *trans* phosphine ligands). The presence of solvents of crystallisation is often seen in the  $^1\text{H}$  NMR spectra due to the propensity of these compounds to entrain solvent in the crystal lattice. For example, recrystallisation [21] of **2-Cl** from CH<sub>2</sub>Cl<sub>2</sub> and EtOH afforded **4-Cl**·1.5CH<sub>2</sub>Cl<sub>2</sub>, indeed the rapidity of recrystallisation process can affect the amount of solvent incorporated and microanalytical data needs to be correlated with the NMR data. This is equally true for compounds **1-Cl**, **2-Cl** and **3-Cl** [21].

### 3. Experimental

General considerations: All solvents, except alcohols, were dried by refluxing over an appropriate drying agent: toluene, Na; CH<sub>2</sub>Cl<sub>2</sub>, P<sub>4</sub>O<sub>10</sub>; hexane, NaK; and distilled prior to use. [RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub>] [34] and [RuCl(CO){ $\eta^2$ -*C,N*-C<sub>6</sub>H<sub>4</sub>CH=NC<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>}(PPh<sub>3</sub>)<sub>2</sub>] [21] were prepared according to literature procedures. All other chemicals were obtained from commercial sources and used as received except for RuCl<sub>3</sub>, which was loaned by Johnson Matthey. Infrared spectra were recorded as nujol mulls between KBr plates on a

Table 4  
Crystal data, data collection and refinement details for **2-Br** and **2-I**

	<b>2-Cl</b> ·CHCl <sub>3</sub>	<b>2-Br</b> ·1.5CHCl <sub>3</sub>	<b>2-I</b> ·1.5CHCl <sub>3</sub>
Empirical formula	C <sub>52</sub> H <sub>43</sub> Cl <sub>4</sub> NOP <sub>2</sub> Ru	C <sub>52.50</sub> H <sub>43.50</sub> Cl <sub>4.50</sub> BrNOP <sub>2</sub> Ru	C <sub>52.50</sub> H <sub>43.50</sub> Cl <sub>4.50</sub> INOP <sub>2</sub> Ru
Formula weight	1002.68	1106.83	1153.82
<i>T</i> (K)	150(2)	200(2)	293(2)
Crystal size (mm <sup>3</sup> )	0.07 × 0.10 × 0.25	0.20 × 0.20 × 0.10	0.18 × 0.18 × 0.10
λ(Mo Kα) (Å)	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	<i>Pna</i> 2 <sub>1</sub>	<i>P</i> 12 <sub>1</sub> / <i>n</i>	<i>P</i> 12 <sub>1</sub> / <i>n</i>
Unit cell dimensions			
<i>a</i> (Å)	26.1033(4)	10.9757(3)	11.07400(10)
<i>b</i> (Å)	15.7843(2)	26.9003(7)	27.0900(4)
<i>c</i> (Å)	11.0025(2)	16.2598(4)	6.5050(2)
β(°)	90	90.0330(10)	91.3150(10)
<i>V</i> (Å <sup>3</sup> )	4533.28(12)	4800.7(2)	4950.11(10)
<i>Z</i>	4	4	4
<i>d</i> (calcd) (Mg/m <sup>3</sup> )	1.469	1.531	1.548
<i>F</i> (000)	2048	2236	2308
2θ Range (°)	3.0–25.0	2.27–27.09	2.91–25.08
Total reflections collected	27759	33015	31357
Independent reflections	7456	8897	8623
<i>R</i> <sub>int</sub>	0.043	0.0470	0.0559
Completeness to θ (%)	100	84.2	98.10
Data/restraints/parameters	6984/2/725	8897/14/586	8623/14/584
Goodness-of-fit	1.027	1.045	1.075

Table 5  
Selected bond lengths (Å) and angles (°) for **2-Cl**, **2-Br**, **2-I**

	<b>2-Cl</b>	<b>2-Br</b>	<b>2-I</b>
Ru(1)–X	2.5110(6)	2.6638(6)	2.8416(4)
Ru(1)–C(1)	2.063(2)	2.056(5)	2.055(3)
Ru(1)–N(1)	2.2321(17)	2.240(4)	2.242(3)
Ru(1)–C(15)	1.812(2)	1.829(6)	1.817(4)
C(15)–O(1)	1.166(3)	1.162(7)	1.155(5)
C(7)–N(1)	1.1302(3)	1.307(7)	1.288(5)
C(1)–Ru(1)–X	169.93(6)	169.86(15)	170.92(10)
C(1)–Ru(1)–N(1)	78.47(8)	78.30(19)	78.24(13)
N(1)–Ru(1)–C(15)	167.19(9)	167.4(2)	167.47(14)
N(1)–Ru(1)–X	91.52(5)	91.87(12)	93.09(7)
C(15)–Ru(1)–X	101.24(7)	100.56(17)	99.32(11)
C(15)–Ru(1)–C(1)	88.80(9)	89.4(2)	89.44(15)
X–Ru(1)–P(1)	88.41(2)	89.85(4)	89.61(2)
X–Ru(1)–P(2)	89.06(2)	90.41(4)	90.84(2)
P(1)–Ru(1)–P(2)	173.37(2)	173.12(5)	173.57(3)

Nicolett 5PC spectrometer. <sup>1</sup>H NMR (200.2 MHz) and <sup>31</sup>P{<sup>1</sup>H} NMR (81.3 MHz) were recorded on a Bruker DPX200 spectrometer and <sup>13</sup>C{<sup>1</sup>H} NMR (100.55 MHz) were recorded on a Bruker DPX400 spectrometer. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were referenced to CHCl<sub>3</sub> (δ = 7.26) and CHCl<sub>3</sub> (δ = 77.0) and <sup>31</sup>P{<sup>1</sup>H} NMR were referenced externally to 85% H<sub>3</sub>PO<sub>4</sub> (δ = 0.0). Elemental analyses were performed by the Microanalytical service, Department of Chemistry, UMIST; solvates of crystallisation were confirmed by repeated elemental analysis and confirmed by <sup>1</sup>H NMR. The syntheses of all complexes were carried out under a dinitrogen atmosphere using standard Schlenk

techniques. Work-ups were generally carried out in the open unless otherwise stated.

### 3.1. Synthesis of [RuF(CO){η<sup>2</sup>-C,N-C<sub>6</sub>H<sub>4</sub>CH=NC<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>}(PPh<sub>3</sub>)<sub>2</sub>]·2CHCl<sub>3</sub> **2-F**

To [RuCl(CO){η<sup>2</sup>-C,N-C<sub>6</sub>H<sub>4</sub>CH=NC<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>}(PPh<sub>3</sub>)<sub>2</sub>] (0.1 g, 0.11 mmol) dissolved in CH<sub>2</sub>Cl<sub>2</sub> acetone (10 mL, 1:1) under a stream of dry N<sub>2</sub> was added Ag[BF<sub>4</sub>] (0.022 g, 0.11 mmol). After 20 min, the solution was filtered to remove AgCl and NaF (0.05 g, 1.2 mmol) dissolved in H<sub>2</sub>O (0.2 mL) was added followed by enough EtOH to generate a homogeneous solution. After 20 min, the organic solvent was removed under reduced pressure precipitating crude **4-F**. Collection by filtration and recrystallization from CHCl<sub>3</sub> afforded **2-F**·2CH<sub>2</sub>Cl<sub>2</sub> (0.078 g, 64%). Compounds **2-Br** and **2-I** were prepared in an analogous fashion see Table 1 for physical and analytical data.

*X-ray crystallography:* All of the crystals were grown by the slow evaporation of chloroform from a 20-mg sample initially dissolved 0.5 mL in a lightly capped 5 mm NMR tube. All measurements were carried out on a Nonius Kappa CCD diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 150 K for **2-Cl**, at the National Crystallographic Service, University of Southampton, England and **2-Br** and **2-I** at The Department of Chemistry University of Manchester at 200 and 293 K, respectively. The structures were solved using direct methods using SHELXL97 [35] and subjected to full matrix-least-squares refinement on *F*<sup>2</sup>. Additionally for **2-Br**, and **2-I** the lattice CHCl<sub>3</sub>

Table 6  
Intramolecular hydrogen-bond data, distances (Å) and angles (°) for **2-Cl**, **2-Br**, **2-I**

Compound	Interaction	D–H	H···A	D···A	D–H–A
<b>2-Cl</b>	C(13)–H(13)···Cl(1)	0.89(2)	2.76(2)	3.298(2)	120.0(3)
	C(33)–H(33)···Cl(1)	0.89(2)	2.78(2)	3.581(2)	150.2(4)
	C(47)–H(47)···Cl(1)	0.97(3)	2.55(2)	3.344(2)	139.2(3)
	C(17)–H(17)···Cl(1)	0.95(3)	2.92(2)	3.437(4)	113.6(4)
<b>2-Br</b>	C(17)–H(17)···Br(1)	0.95(3)	2.78(3)	3.499(3)	133.0(4)
	C(39)–H(39)···Br(1)	0.95(2)	2.77(3)	3.660(2)	157.2(4)
	C(9)–H(9)···Br(1)	0.95(2)	2.98(2)	3.414(3)	108.9(4)
	C(47)–H(47)···Br(1)	0.95(2)	2.94(3)	3.514(4)	120.2(4)
	C(52)–H(52a)···Br(1)	1.00(2)	2.95(2)	3.481(4)	148.1(4)
<b>2-I</b>	C(17)–H(17)···I(1)	0.93(3)	2.95(3)	3.598(4)	128.0(3)
	C(39)–H(39)···I(1)	0.93(3)	2.90(3)	3.786(4)	160.0(4)
	C(9)–H(9)···I(1)	0.93(2)	3.15(3)	3.556(5)	108.3(4)
	C(47)–H(47)···I(1)	0.93(3)	3.11(2)	3.627(3)	116.8(3)
	C(52)–H(52a)···I(1)	0.98(3)	2.98(2)	3.789(4)	151.5(3)

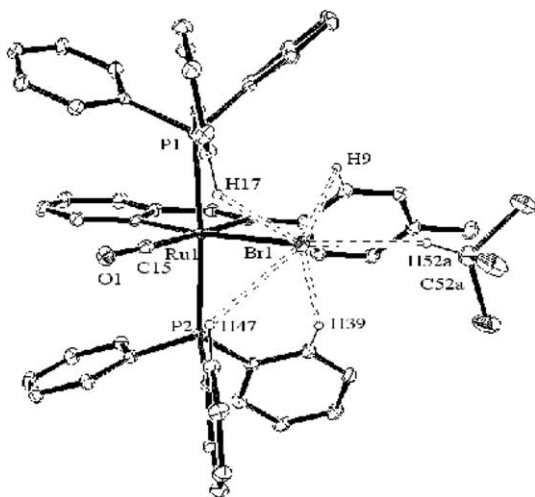


Fig. 3. ORTEP representation of **2-Br** showing the weak secondary interactions.

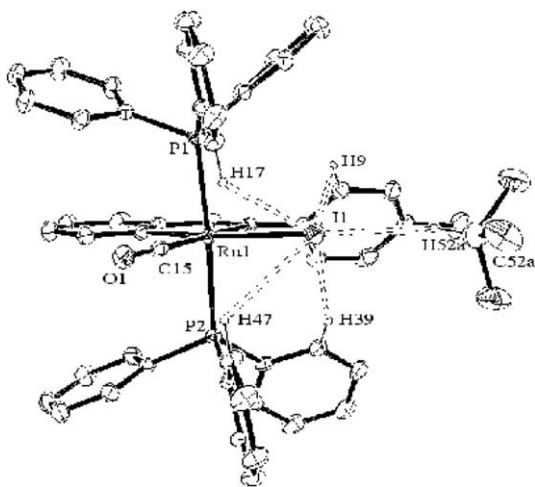


Fig. 4. ORTEP representation of **2-I** showing the weak secondary interactions.

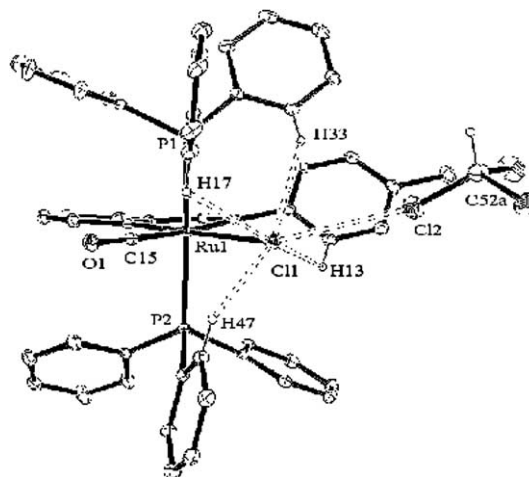


Fig. 5. ORTEP representation of **2-Cl** showing the weak secondary interactions.

is disordered about a crystallographic inversion point and was also modelled using geometric restraints, but in this case the atomic site occupancies were set to 0.5. A preliminary report containing the structure of **2-Cl** has appeared [26]. The crystallographic details are presented in Table 4. Crystallographic data for the structural analysis (CIF) has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 204733 for **2-Cl**, CCDC No. 266250 for **2-Br** and CCDC No. 266251 for **2-I**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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