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The synthesis and single-crystal X-ray structures of palladium(II) and platinum(II) complexes of the difluorovinyl and 1-chloro-2-fluorovinyl-substituted phosphines, PPh_2(*Z*-CF=CFH) and PPh_2(*E*-CCl=CFH)

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Dedicated to Russ Hughes on the occasion of receiving the ACS award for Creative Work in Fluorine Chemistry.

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ABSTRACT

The coordination chemistry of the fluorovinyl substituted phosphines PPh_2(*Z*-CF=CFH) and PPh_2(*E*-CCl=CFH) with K_2MX_4 (M = Pd, Pt; X = Cl, Br, and I) salts has been investigated resulting in the first reported palladium(II) and platinum(II) complexes of phosphines containing partially fluorinated vinyl groups. The complexes have been characterised by a combination of multinuclear [^{1}H, ^{13}C{^{1}H}, ^{19}F, ^{31}P{^{1}H}] NMR spectroscopy, and IR/Raman spectroscopy. The single-crystal X-ray structures of *trans*-[$PdX_2\{PPh_2(CF{=}CFH)\}_2$], X = Cl (**1**), Br (**2**), I (**3**), *trans*-[$PdCl_2\{PPh_2(CCl{=}CFH)\}_2$] (**4**), *cis*-[$PtX_2\{PPh_2(CF{=}CFH)\}_2$], X = Cl (**5**), Br (**6**), *trans*-[$PtI_2\{PPh_2(CF{=}CFH)\}_2$] (**7**), and both *cis*- and *trans*-[$PtCl_2\{PPh_2(CCl{=}CFH)\}_2$] (**8**), have been determined. Results obtained from spectroscopic and crystallographic data suggest that replacement of a β-fluorine by hydrogen, whilst reducing the steric demand of the ligand, has little effect on the electronic character of the ligand. The presence of a proton in the vinyl group results in short proton–halide secondary interactions in the solid state (d(H···X) = 2.72(3) for **1**, and 2.92(5) Å for **2**) forming an infinite chain ribbon motif.

1. Introduction

Phosphines are amongst the most widely studied ligand systems, in part because of the ability to modify their steric and electronic properties [1], which can be used to fine-tune the reactivity of metal complexes, such as was shown in a series of (η^3-cyclopropenyl)iron complexes [2]. Whilst there is a wide range of traditional (non-fluorinated) phosphines there are considerably fewer containing perfluorinated groups. Where such ligands have been prepared, it has been demonstrated that they are typically poorer σ-donors and better π-acceptors, as a result of the fluorinated fragment [3]. Where the solvency effects arising from the presence of an organofluorine group is desired, but not the attendant electronic influence, a spacer group is included, as is practised for fluorous ligands of the type $PPh_2(C_6H_4C_6F_{13})_3$ and $PPh_2(CH_2CH_2C_6F_{13})$ [4]. In between these two approaches lies the use of partially fluorinated phosphines which contain a mixture of fluorinated and non-fluorinated substituents or partially fluorinated groups. A number of such systems are known, most frequently based on aromatic systems, such as, for example, $P(2,6\text{-}C_6H_3F_2)_3$, and their coordination chemistry has been investigated [5]. Whilst ligands containing a combination of perfluoro and perprotio groups are well established, apart from fluoroaryl systems and fluorous ligands of the type described above, there are very few studies of the coordination chemistry of phosphines containing partially fluorinated groups.

We have previously reported on the coordination chemistry of phosphine ligands containing trifluorovinyl (–CF=CF_2) or 1-chlorodifluorovinyl (–CCl=CF_2) fragments [6–9]. Complexes of these ligands show that the CF=CF_2 group imparts electronic properties onto the phosphine ligand which are similar to C_6F_5 substituted phosphines, as evidenced by a comparison of the ν(CO) frequencies of *trans*-[$RhCl(CO)\{PPh_2(R_F)\}_2$] complexes (R_F = CF=CF_2, C_6F_5) [9]. However, it appears that the CF=CF_2 group displays a greater steric flexibility than the C_6F_5 group. We have separately shown that partial hydrodefluorination of the vinyl groups in ligands such as $PPh_2(CF{=}CF_2)$ and $PPh_2(CCl{=}CF_2)$ may be achieved by reaction with $LiAlH(O\text{-}t\text{-}Bu_3)$, to give PPh_2(*Z*-CF=CFH) and PPh_2(*E*-CCl=CFH) [10], where in both cases, specifically, the β-fluorine atom *trans* to phosphorus is replaced by hydrogen. In this way it is envisaged that it should be possible to fine-tune the steric and electronic properties of fluorovinyl-containing phosphines to lie between the analogous vinyl- and trifluorovinyl-substituted phosphines. Furthermore, we have observed a number of

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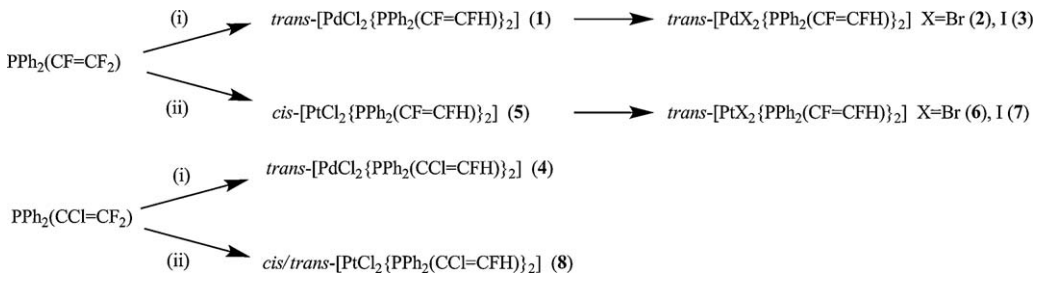

Scheme 1.

interesting structural features in complexes of fluorovinyl-containing ligands. These include the formation of hydrogen bonds between the β-fluorine *trans* to phosphorus and one of the cyclohexyl protons in $[PdCl_2\{P(C_6H_{11})_2(CF{=}CF_2)\}_2]$ [9], the aggregation of fluorovinyl fragments to give a highly unusual 1:2 *cis:trans*-mixture of $[PtCl_2\{PiPr_2(CF{=}CF_2)\}_2]$ in the solid state and the observation of M···Cl secondary interactions in chlorodifluorovinyl-containing complexes [9]. For these reasons we have been interested in assessing the properties of partially fluorinated vinyl ligands of this type. Here we report, work from Professor Russell Hughes' *alma mater* concerning the first palladium(II) and platinum(II) complexes of *trans*-1,2-difluorovinyl and 1-chloro-2-fluorovinyl-containing phosphines.

2. Results and discussion

Complexation of $PPh_2(CF{=}CFH)$ and $PPh_2(CCl{=}CFH)$ to palladium and platinum centres was achieved by reaction of two equivalents of the appropriate phosphine with either K_2PdCl_4 or K_2PtCl_4 to produce the chloride complexes **1**, **4**, **5**, and **8**. Bromide and iodide analogues of **1** and **4** were prepared by metathesis of the chloride complex with an excess of KBr or KI, (see Scheme 1). These complexes are the first reported examples of Pd and Pt complexes of phosphines containing the partially fluorinated vinyl groups, CF=CFH or CCl=CFH.

In all cases, the $^{31}P\{^1H\}$ NMR spectra of the complexes exhibit resonances shifted 25–40 ppm to higher frequencies compared to the free ligands ($PPh_2(CF{=}CFH)$, δP: −27.5, $PPh_2(CCl{=}CFH)$, δP: −14.5) [10]. The $^{31}P\{^1H\}$ NMR spectra of the palladium complexes $[PdX_2\{PPh_2(CF{=}CFH)\}_2]$, X = Cl **1**, Br **2** and I **3**, all appear as "virtual" triplets with couplings indicative of a *trans* arrangement of the phosphine ligands. This is assigned as $0.5|^2J(PF) + {}^4J(PF)|$, arising from coupling to the fluorine nucleus on the α-carbon by comparison with our previous work on related trifluorovinyl-substituted phosphines [8,9]. Thus, on complexation no coupling is observed to the fluorine on the β-carbon centre. Further support for this interpretation comes from the $^{31}P\{^1H\}$ NMR spectrum of $PPh_2(CCl{=}CFH)$, which is observed as a doublet due to coupling with fluorine, but upon reaction with K_2PdCl_4 to give *trans*-$[PdCl_2\{PPh_2(CCl{=}CFH)\}_2]$, **4**, results in a singlet, because the ligand does not possesses fluorine on the α-carbon.

The ^{19}F NMR spectra of the complexes of $PPh_2(CF{=}CFH)$ display two multiplets, as shown in Fig. 1 for *trans*-$[PdCl_2\{PPh_2(CF{=}CFH)\}_2]$, **1**. The two multiplets exhibit a large (*ca.* 140 Hz) mutual coupling, indicative of a *trans*-arrangement of the two fluorine atoms across the double bond [10–12]. This is about 20 Hz larger than that observed for related $CF{=}CF_2$ systems [6–9]. The signal at −150 ppm also exhibits coupling ($^2J(FH)$ = 75 Hz) to the single proton, and so this signal is assigned to the β-fluorine. The presence of the distinctive virtual triplet $0.5|^2J(PF) + {}^4J(PF)|$ coupling pattern and a

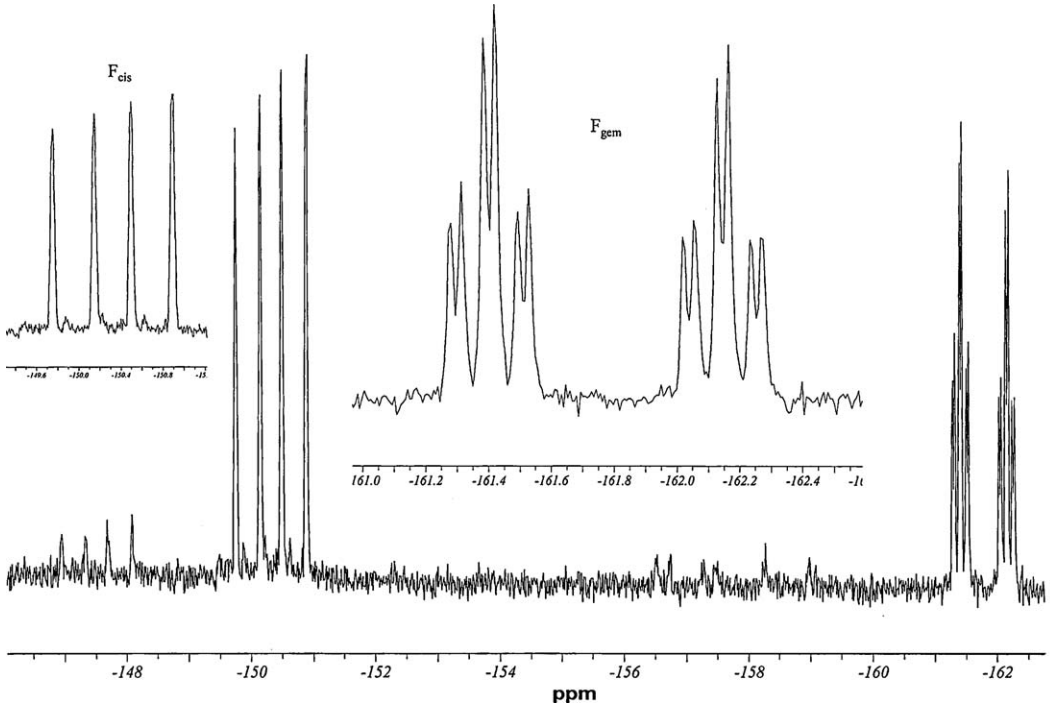

Fig. 1. ^{19}F NMR spectrum of *trans*-$[PdCl_2\{PPh_2(CF{=}CFH)\}_2]$, **1**.

smaller F–H coupling constant (7 Hz) on the signal at *ca.* −160 ppm, is used to assign this as the α-fluorine resonance. The ^{19}F NMR spectrum of the coordinated chlorodifluorovinyl-substituted ligand, for example in $[PdCl_2\{PPh_2(CCl{=}CFH)\}_2]$, **4**, appears as a doublet at −95.2 ppm, with a $^2J(FH)$ coupling of 79 Hz. Assignment of the configuration of **4** as the anticipated *trans*-square planar complex can be made by examination of the $^{13}C\{^1H\}$ NMR spectrum where all P-C couplings appear as virtual triplets, as is the case in the $^{13}C\{^1H\}$ NMR spectra of **1**–**4**. In addition, the Raman spectra of **1**–**4** all display one ν(Pd–X) band, consistent with the predictions for a *trans*-geometry. We were unable to find any evidence of the production of *cis*-isomers, which are known for palladium(II) complexes of the analogous $PPh_2(CH{=}CH_2)_2$ ligand [13–17].

Assignment of the stereochemistry of the square planar platinum complexes **5**–**8** was also made on the basis of $^{31}P\{^1H\}$ NMR spectroscopic data. Firstly, the *trans*-isomers exhibit virtual triplets whilst the *cis*-isomers appear as doublets with an apparent *J*(PF) coupling approximately twice as large as that observed for the *trans*-complexes, e.g. $^2J(PF) = 46$ Hz (*cis*-**6**), $0.5|^2J(PF) + {}^4J(PF)| = 22$ Hz (*trans*-**6**). Additionally, the magnitude of the $^1J(PtP)$ coupling (^{195}Pt, $I = 1/2$, 33%) in these systems is diagnostic, with values above 3000 Hz being previously observed for *cis*-complexes, compared with <2800 Hz for *trans*-complexes. Thus, for complex **5** a single $^{31}P\{^1H\}$ resonance is observed with $^1J(PtP) = 3692$ Hz, which allows us to assign the complex as *cis*-$[PtCl_2\{PPh_2(CF{=}CFH)\}_2]$. The magnitude of the Pt–P coupling constant is very similar to that of *cis*-$[PtCl_2\{PPh_2(CF{=}CF_2)\}_2]$, $^1J(PtP) = 3698$ Hz, [6] but somewhat higher than that observed for the analogous $PPh_2(CH{=}CH_2)$-containing complex, $^1J(PtP) = 3633$ Hz, [18] which suggests that $PPh_2(CF{=}CFH)$ is electronically quite similar to $PPh_2(CF{=}CF_2)$.

In contrast, the bromide, **6**, and iodide, **7** (both analogues of **5**) are formed as a mixture of both isomers. In the case of **6** the *trans*-isomer is present only in trace amounts (≈5%), but for the iodide analogue **7** it is the major component (*cis:trans* ratio 25:75). Thus the proportion of *cis*-isomer generated decreases in the order Cl > Br > I. These observations contrast with the platinum iodide complexes of $PPh_2(CF{=}CF_2)$, and $PPh_2(CCl{=}CF_2)$, both of which do not form *cis*-isomers, but instead result in the formation of dimeric, iodide-bridged complexes of the type $[PtI(\mu\text{-}I)(PR_3)]_2$ [8]. However, this possibility can be discounted here on the basis of the $^1J(PtP)$ coupling constant, which is much larger (typically 3800–3900 Hz) in those dimeric complexes. For $[PtI_2\{PPh_2(CF{=}CFH)\}_2]$, **6**, the observed value of 3470 Hz is more consistent with a *cis*-monomer, being a little larger than that reported for *cis*-$[PtI_2\{PPh_2(CH{=}CH_2)\}_2]$ (3433 Hz) [18]. No sign of any solution-state isomerisation was observed for **6** or **7** as solutions of the complexes were monitored over a number of weeks by $^{31}P\{^1H\}$ NMR spectroscopy.

The product of the reaction of K_2PtCl_4 with two equivalents of $PPh_2(CCl{=}CFH)$ yields a complex of formulation $[PtCl_2\{PPh_2(CCl{=}CFH)\}_2]$, **8**, which is also shown by $^{31}P\{^1H\}$ NMR studies to exist as a mixture of isomers, however, unlike **6** and **7** isomerisation is observed in solution, as shown in Fig. 2. The initial $^{31}P\{^1H\}$ NMR spectrum displays a singlet at +21.4 ppm with $^1J(PtP) = 2787$ Hz, this is therefore assigned as the *trans*-isomer; the magnitude of the PtP coupling constant being very similar to that observed for the analogous complex *trans*-$[PtCl_2\{PPh_2(CCl{=}CF_2)\}_2]$ (2794 Hz) [7]. Over a period of days this signal is slowly replaced with a resonance at 13.4 ppm ($^1J(PtP) = 3731$ Hz), indicative of the *cis*-isomer.

All the platinum complexes display ^{19}F and $^{13}C\{^1H\}$ NMR spectra similar to the palladium complexes **1**–**4**, but with additional platinum satellites. In the ^{19}F NMR spectra of the $PPh_2(CF{=}CFH)$ complexes **5**–**7** *J*(PtF) couplings of around 86 and 40–45 Hz are observed to the *gem*- and *cis*-fluorine nuclei respectively. This latter coupling is lower (*ca.* 28 Hz) for the isomers of the $PPh_2(CCl{=}CFH)$ complex **8**. Platinum satellites were more difficult to resolve in the $^{13}C\{^1H\}$ NMR spectra due to the low intensity of the α-vinyl carbon signal in particular. Virtual *J*(PF) and *J*(PC) triplet couplings are observed for, and used to identify, the *trans*-isomers that were formed.

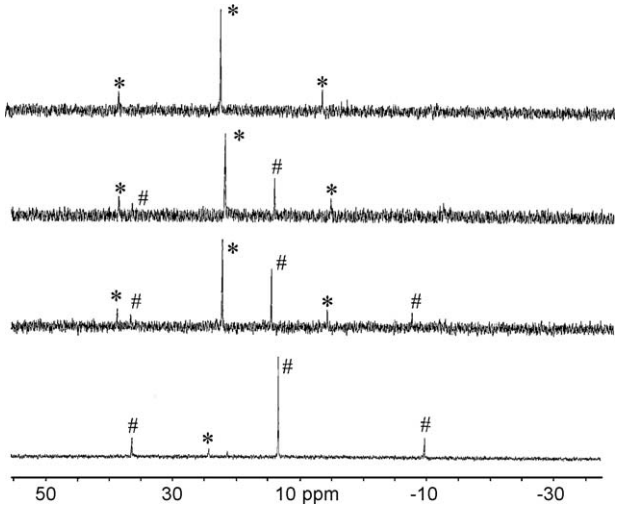

Fig. 2. $^{31}P\{^1H\}$ NMR spectra of *trans*- to *cis*-isomerisation of $[PtCl_2\{PPh_2(CCl{=}CFH)\}_2]$ in $CDCl_3$ solution over a 7-day period (* = *trans*-$[PtCl_2\{PPh_2(CCl{=}CFH)\}_2]$ and # = *cis*-$[PtCl_2\{PPh_2(CCl{=}CFH)\}_2]$).

2.1. X-ray diffraction studies

Crystals of complexes **1**–**8** suitable for single-crystal X-ray diffraction studies were grown via slow evaporation of layered CH_2Cl_2:hexane solutions, and the molecular structures are shown in Figs. 3–5. In all cases the complexes display the anticipated square planar geometry around the metal centre and the C=C and C–F distances of the difluorovinyl compounds are largely as expected compared with previous systems [6,9,11,23]. The structural data obtained from complexes **4** and **8** represent the first for any compound containing the CCl=CFH group, although comparisons can be made with the related complex *trans*-$[PtCl_2\{PPh_2(CCl{=}CF_2)\}_2]$ [7].

All of the palladium complexes adopt a *trans*-geometry (in agreement with the solution-phase spectroscopic data), with the palladium atom sitting on a cystallographic centre of symmetry. Complexes **3** and **4** both contain two independent molecules in the unit cell. The metal–phosphorus bond lengths in the majority of the complexes are slightly shorter than is typically observed for similar systems containing non-fluorinated groups, for example, *d*(Pd–P) in *trans*-$[PdCl_2\{PPh_2(CF{=}CFH)\}_2]$, **1**, is 2.3195(6) Å, compared with 2.3284(5) Å in the corresponding diphenylvinylphosphine complex [17]. The Pd–P bond length of **1** is also shorter than in the two independent molecules of *trans*-$[PdCl_2\{PPh_2(CCl{=}CFH)\}_2]$, **4**, Pd1–P1: 2.3268(10) Å, Pd21–P21: 2.3219(10) Å. In both cases these changes are consistent with steric and electronic considerations. Whilst this represents, as far as we are aware, the first structural data for a metal complex containing a CCl=CFH group, it is noteworthy that the Pd–P bond lengths for **4** are comparable to that reported (2.322(1) Å) for *trans*-$[PdCl_2\{PPh_2(CH{=}CClCF_3)\}_2]$, the only other structurally characterised complex containing a partially fluorinated alkenyl substituent [19].

X-ray crystallographic data for $[PtCl_2\{PPh_2(CF{=}CFH)\}_2]$, **5,** confirmed a *cis*-orientation of the phosphine ligands, with Pt–P bond lengths of 2.2426(15) and 2.2449(15) Å, slightly longer than was observed in *cis*-$[PtCl_2\{PPh_2(CF{=}CF_2)\}_2]$, *d*(Pt–P) = 2.234(3) and 2.228(3) Å [6]. For the bromide and iodide analogues **6** and **7** the crystals grown were of the major isomer in the component

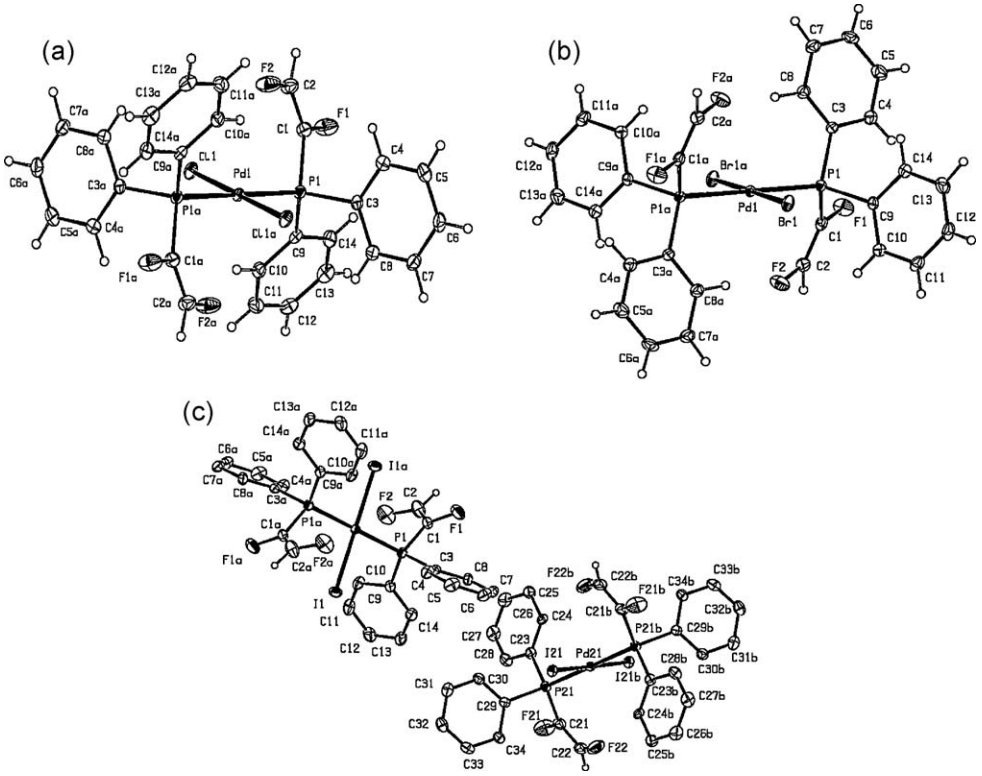

Fig. 3. Molecular structure of *trans*-[$PdX_2\{PPh_2(CF{=}CFH)\}_2$] (X = Cl, **1**; Br, **2**; I, **3**) complexes Thermal ellipsoids are shown at the 30% probability level. Selected bond lengths [Å] and angles [°]: (a) **1**, Pd1–P1 2.3195(6), Pd1–Cl1 2.2904(6), C1–C2 1.306(4), C1–F1 1.363(4), C2–F2 1.340(3), Cl1–Pd1–P1 88.31(2), Cl1–Pd1–P#1 91.69(2), (symmetry operation used to generate equivalent atoms: $-x+1, -y+1, -z+2$) (b) **2**, Pd1–P1 2.3137(8), Pd1–Br1 2.4271(3), C1–C2 1.309(5), C1–F1 1.356(3), C2–F2 1.345(4), Br1–Pd1–P1 92.24(2), Br1–Pd1–P#1 87.76(2), (symmetry operation used to generate equivalent atoms: $-x+1, -y, -z$). (c) **3**, Pd1–P1 2.3179(12), Pd1–I1 2.6012(3), Pd21–P21 2.3266(11), Pd21–I21 2.6059(3), C1–C2 1.309(5), C21–C22 1.317(8), C1–F1 1.356(3), C2–F2 1.345(4), C21–F21 1.360(6), C22–F22 1.336(7), I1–Pd1–P1 87.54(3), I1–Pd1–P#1 92.46(3), I21–Pd21–P21 91.96(3), I21–Pd21–P21#2 88.04(3), (symmetry operation used to generate equivalent atoms: #1: $-x+2, -y+1, -z+1$; #2: $-x+1, -y, -z+1$).

mixture, i.e. the *cis*-isomer for **6** and the *trans*-isomer for **7**. The *cis*-complexes **5** and **6** both displayed some deviation from ideal square planar geometry, e.g. Cl2–Pt1–P2: 169.98(5)° for **5**. The iodide complex *trans*-[$PtI_2\{PPh_2(CF{=}CFH)\}_2$], **7**, is unusual as it does not have an inversion centre at the metal atom, (Fig. 4(c)), which results in asymmetry in the Pt–I distances, Pt–I1: 2.6288(7) Å, Pt–I2: 2.5949(7) Å (difference = 0.0339 Å) although the Pt–P bonds are essentially the same, Pt–P1: 2.311(2) Å, Pt–P2: 2.310(3) Å. It might be noteworthy that the substituents of the phosphines in the solid state are orientated such that both the CF=CFH subunits are located on the same side of the P–Pt–P axis with the four phenyl groups on the other side. A similar conformation has been observed for the complex *trans*-[$PdI_2\{PPh_2(CH{=}CH_2)\}_2$] [17], although in that case there is no asymmetry in the Pd–I bond lengths (2.5938(4) and 2.5939(4) Å). The related platinum complex *trans*-[$PtCl_2\{PPh_2(2\text{-}C_6H_4C_6F_{13})\}_2$] also displays this type of ligand conformation; in that case it was suggested that this was due to the additional number of F···F interactions set up by this orientation of the ligands [20]. However, this appears not to be the case for **7** as there are no particularly short F···F interactions in the extended structure.

Just as in solution, where we were able to observe both the *cis*- and *trans*-isomers of [$PtCl_2\{PPh_2(CCl{=}CFH)\}_2$], **8**, we were also able to obtain, by varying the method of crystallisation, single crystals of both isomers. The *trans*-isomer was formed when a layered CH_2Cl_2:hexane solution was allowed to rapidly evaporate to dryness, whilst slow concentration of a CH_2Cl_2 solution of the complex led to crystals of the *cis*-isomer, which also incorporated one molecule of solvent in the unit cell. A comparison of the two structures shows that in the *cis*-isomer the Pt–P bonds [Pt–P1: 2.2359(17), Pt–P2: 2.2587(7) Å] are significantly shorter than in the *trans*-isomer [Pt–P1: 2.3089(8) Å]. Conversely, the Pt–Cl bonds are longer for the *cis*-isomer, [Pt–Cl1: 2.3617(17), Pt–Cl_2: 2.3386(17) Å] than for the *trans*-complex [Pt–Cl1: 2.3029(3) Å]. These trends are anticipated, based on the relative *trans* influence of phosphine and chloride ligands (P > Cl). The observed Pt–P and Pt–Cl bond lengths in *trans*-[$PtCl_2\{PPh_2(CCl{=}CFH)\}_2$] **8**, (2.3089(8) and 2.3029(8) Å respectively) are almost identical to those observed for *trans*-[$PtCl_2\{PPh_2(CCl{=}CF_2)\}_2$], where *d*(Pt–P) = 2.309(7) Å, and *d*(Pt–Cl) = 2.303(7) Å [7]. Similarly, in the *cis*-isomer of **8** the average Pt–P distance (2.2473(5) Å) is essentially the same as that observed in *cis*-[$PtCl_2\{PPh_2(CF{=}CFH)\}_2$], **5**, (2.2437(6) Å), which suggests that the electronic properties of these ligands are quite similar.

A comparison of the steric bulk of the different fluorovinyl phosphines in the *cis*-[$PtCl_2L_2$] system was undertaken using the symmetric deformation constant (S_4') as a measure of the size of the ligand. S_4', as defined by Orpen and co-workers [21], is the sum of the three M–P–C angles minus the sum of the three C–P–C angles; i.e. phosphines with greater steric bulk should exhibit lower S_4' values. The average S_4' value are 30.7° for *cis*-[$PtCl_2\{PPh_2(CF{=}CF_2)\}_2$], 31.8° for **5**, and 29.0° for **8**, thus the size of the three ligands decreases along the series $PPh_2(CCl{=}CFH) > PPh_2(CF{=}CF_2) > PPh_2(CF{=}CFH)$. This suggests that replacement of the β-fluorine atom *trans* to the phosphorus by a hydrogen atom has little effect on the electronic properties of the ligand, but a reduction in the steric footprint of the ligand. In contrast, the inclusion of an α-chlorine increases the size of the ligand relative to both the $CF{=}CF_2$ and CF=CFH groups.

2.2. Structural features of the fluorovinyl subunit

We have previously observed a number of well-defined secondary interactions in the crystal structures of the transition

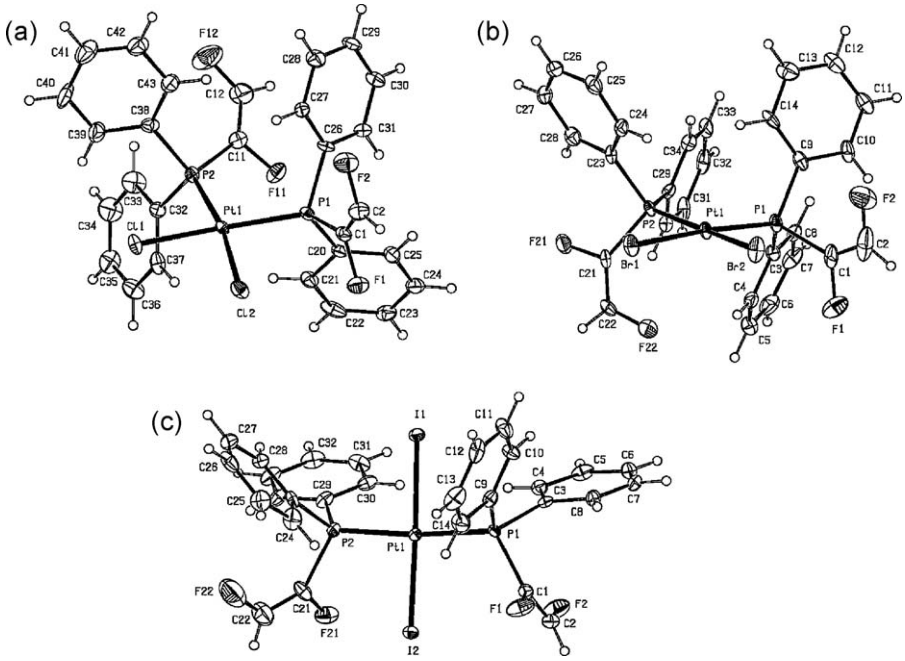

Fig. 4. Molecular structure of $[PtX_2\{PPh_2(CF{=}CFH)\}_2]$ (X = Cl, **5**; Br, **6**; I, **7**). Thermal ellipsoids are shown at the 30% probability level. Selected bond lengths [Å] and angles [°]: (a) **5**, Pt1–P1 2.2426(15), Pt1–P2 2.2449(15), Pt1–Cl1 2.3348(16), Pt1–Cl2 2.3380(15), C1–C2 1.297(8), C11–C12 1.300(9), C1–F1 1.385(6), C2–F2 1.326(7), C11–F11 1.367(7), C12–F12 1.313(9), P1–Pt1–P2 100.13(6), Cl2–Pt1–P1 89.39(3), Cl2–Pt1–P2 169.98(5), Cl1–Pt1–P1 176.00(5), Cl1–Pt21–P2 83.61(6), Cl1–Pt1–Cl2 86.96(6). (b) **6**, Pt1–P1 2.251(3), Pt1–P2 2.257(2), Pt1–Br1 2.4699(11), Pt1–Br2 2.4588(11), C1–C2 1.233(19), C21–C22 1.312(14), C1–F1 1.447(14), C2–F2 1.33(2), C21–F21 1.365(10), C22–F22 1.345(11), P1–Pt1–P2 97.57(9), Br2–Pt1–P1 90.88(7), Br2–Pt1–P2 170.63(7), Br1–Pt1–P1 175.29(8), Br1–Pt21–P2 85.55(7), Br1–Pt1–Br2 86.28(4). (c) **7**, Pt1–P1 2.311(2), Pt1–P2 2.310(3), Pt1–I1 2.6288(7), Pt1–I2 2.5949(7), C1–C2 1.284(15), C21–C22 1.295(16), C1–F1 1.367(12), C2–F2 1.341(13), C21–F21 1.354(13), C22–F22 1.371(17), P1–Pt1–P2 173.27(9), I2–Pt1–P1 92.49(6), I2–Pt1–P2 92.66(7), I1–Pt1–P1 87.01(6), I1–Pt21–P2 87.47(7), I1–Pt1–I2 174.85(3).

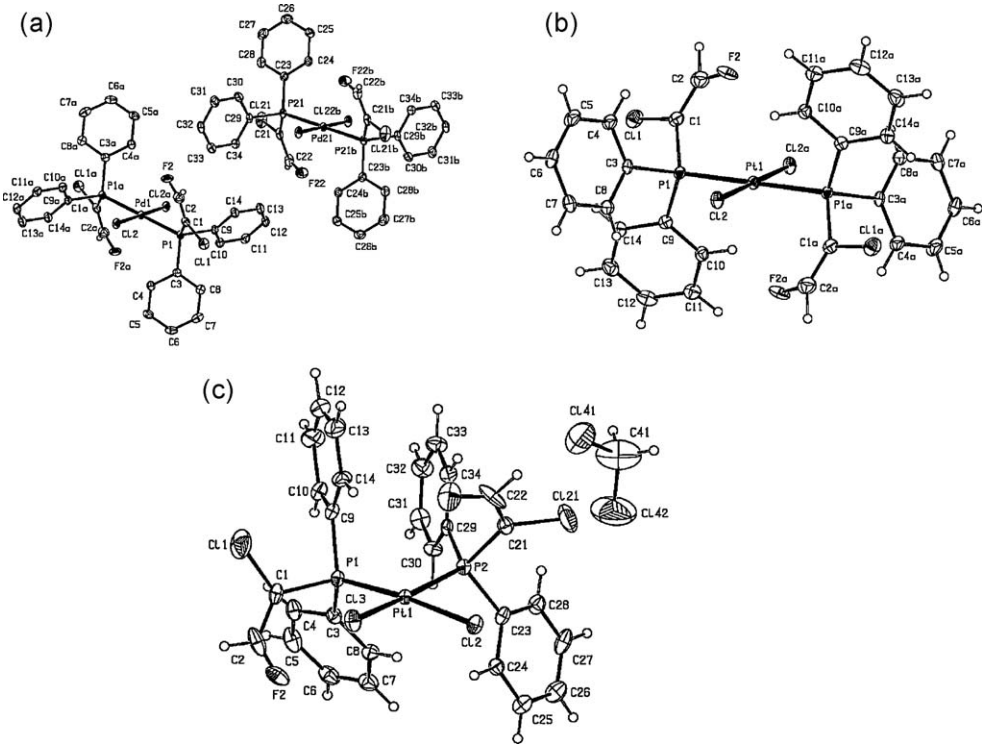

Fig. 5. Molecular structure of complexes **4** and **8**. Thermal ellipsoids are shown at the 30% probability level. Selected bond lengths [Å] and angles [°]:
(a) *trans*-$[PdCl_2\{PPh_2(CCl{=}CFH)\}_2]$ **4**, Pd1–P1 2.3268(10), Pd1–Cl2 2.2940(9), Pd21–P21 2.3219(10), Pd21–Cl22 2.2959(9), C1–C2 1.292(6), C21–C22 1.359(7), C1–Cl1 1.763(5), C2–F2 1.328(6), C21–Cl21 1.744(5), C22–F22 1.273(6), Cl2–Pd1–P(1) 88.57(3), Cl2–Pd1–P#1 91.43(3), Cl22–Pd21–P21 91.03(3), Cl22–Pd21–P21#2 88.97(3), (symmetry operation used to generate equivalent atoms: #1: $-x+2, -y+2, -z+2$; #2: $-x+2, -y+1, -z+1$). (b) *trans*-$[PtCl_2\{PPh_2(CCl{=}CFH)\}_2]$ **8**-*trans*, Pt1–P1 2.3089(8), Pt1–Cl2 2.3029(8), C1–C2 1.290(6), C1–Cl1 1.779(4), C2–F2 1.272(5), Cl2–Pt1–P1 90.97(3), Cl2–Pt1–P#1 89.03(3), (symmetry operation used to generate equivalent atoms: #1: $-x+1, -y+1, -z+1$). (c) *cis*-$[PtCl_2\{PPh_2(CCl{=}CFH)\}_2].CH_2Cl_2$. **8**-*cis*, Pt1–P1 2.2359(17), Pt1–P2 2.2587(17), Pt1–Cl2 2.3617(17), Pt1–Cl3 2.3386(17), C1–C2 1.356(12), C1–Cl1 1.767(8), C2–F2 1.114(12), C21–C22 1.315(11), C21–Cl21 1.749(7), C22–F22 1.244(10), P1–Pt1–P2 96.16(6), Cl2–Pt1–P1 174.52(6), Cl2–Pt1–P2 85.75(6), Cl3–Pt1–P1 91.15(6), Cl3–Pt1–P2 169.81(6), Cl2–Pt1–Cl3 87.62(6).

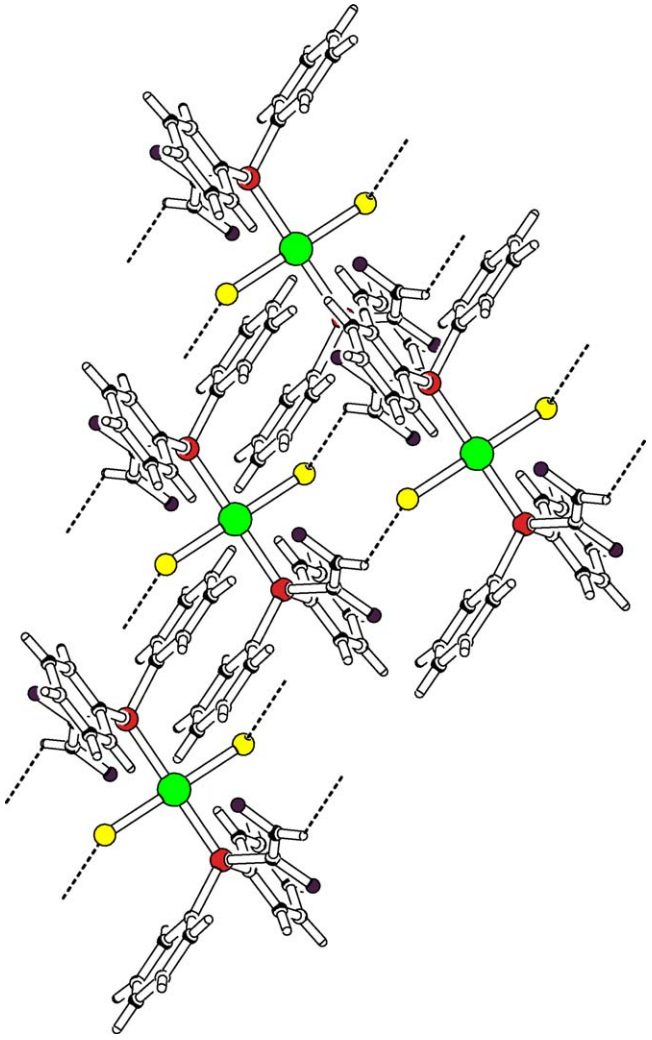

Fig. 6. Platon representation of the intermolecular Cl···H interactions in the solid-state structure of *trans*-[$PdCl_2\{PPh_2(CF{=}CFH)\}_2$] **1**.

metal complexes of trifluorovinyl phosphines. Frequently, (especially for *trans*-square planar complexes), the fluorovinyl group bound to each ligand lies perpendicular to the PdP_2X_2 plane and bends back towards the metal atom, setting up a short intramolecular interaction between the fluorine atom *cis* to phosphorus and the metal centre. Furthermore, the extended structures of trifluorovinyl phosphine complexes often adopt crystal packing motifs which favour the formation of fluorophillic and fluorophobic regions in the extended structure [9].

Most of the complexes of the mixed hydrofluorovinyl phosphines exhibit a similar interaction between the metal and the fluorine *cis* to phosphorus (F2) with the M–F2 distance being more than 0.5 Å shorter than the sum of the van der Waal radii. In contrast, complexes **5** and **7** do appear not to exhibit these interactions because of the relative orientation of the fluorovinyl groups. Many of the complexes also exhibit intermolecular hydrogen bonding from the vinyl proton to the halide ligand of an adjacent molecule, e.g. H3···Cl1a = 2.72(3) Å for **1**, and H2···Br1a = 2.92(5) Å for **2**. These interactions are shown in Fig. 6 for complex **1**. The vinyl–halide interactions result in the formation of an infinite chain of complexes, reinforced by extensive π-stacking, with a short Cg···Cg interaction of 3.799(18) Å for **1**, whilst the shortest Cg···Cg distance observed for **2** is 4.285(2) Å. Short F···H interactions are also present, e.g. F2···H4 = 2.54(3) Å for **1** and F2···H8 = 2.5(4) Å for **2**.

Table 1
Intramolecular metal–fluorine interactions.

Complex	M···F interaction, Å[a]
trans-[$PdCl_2\{PPh_2(CF{=}CFH)\}_2$] **1**	3.0935(18)
trans-[$PdBr_2\{PPh_2(CF{=}CFH)\}_2$] **2**	3.224(3)
trans-[$PdI_2\{PPh_2(CF{=}CFH)\}_2$] **3**	3.209(3)
(Two molecules in unit cell)	Not observed
trans-[$PdCl_2\{PPh_2(CCl{=}CFH)\}_2$] **4**	3.194(2)
(Two molecules in unit cell)	2.996(3)
cis-[$PtCl_2\{PPh_2(CF{=}CFH)\}_2$] **5**	Not observed
cis-[$PtBr_2\{PPh_2(CF{=}CFH)\}_2$] **6**	3.224(6)
trans-[$PtI_2\{PPh_2(CF{=}CFH)\}_2$] **7**	Not observed
trans-[$PtCl_2\{PPh_2(CCl{=}CFH)\}_2$] **8**	3.270(3)
cis-[$PtCl_2\{PPh_2(CCl{=}CFH)\}_2$] **8**	3.077(5)

[a] Compared to sum of van der Waal radii of both Pd and F, and Pt and F of 3.77 Å.

The majority of the palladium complexes **1**–**4** display short Pd···F interactions, Table 1, the only exception being one of the two independent molecules of **3**. (where the CF=CFH unit is twisted away from the metal centre). The platinum complexes **5**–**8** do not exhibit this feature with such regularity, for example *cis*-[$PtBr_2\{PPh_2(CF{=}CFH)\}_2$] **6** and the *cis*-isomer of [$PtCl_2\{PPh_2(CCl{=}CFH)\}_2$] **8** are orientated such that only one of the two fluorovinyl units is able to set up an interaction, whilst the other is twisted away from the metal centre, whereas the orientation of the fluorovinyl subunits in *cis*-[$PtCl_2\{PPh_2(CF{=}CFH)\}_2$] **5** does not allow the close approach necessary to set up the interaction. Similarly, the orientation of the fluorovinyl groups in the non-centrosymmetric *trans*-[$PtI_2\{PPh_2(CF{=}CFH)\}_2$] **7** results in no particularly short interactions.

3. Conclusions

The synthesis of a series of palladium(II) and platinum(II) complexes of the mixed hydrofluorovinyl phosphines, PPh_2(*Z*-CF=CFH) and PPh_2(*E*-CCl=CFH) have provided data which allow us to assess the steric and electronic properties of these phosphines, relative to both their fully fluorinated, and non-fluorinated analogues. Metal–phosphorus bond lengths are shorter than observed for analogous $PPh_2(CH{=}CH_2)$ systems, but similar to distances seen in $PPh_2(CF{=}CF_2)$, suggesting similar π-acid character to the trifluorovinyl phosphines. A comparison of the steric bulk (by S_4' values) on *cis*-[$PtCl_2L_2$] systems suggest the size of the phosphines decreases in the order $PPh_2(CCl{=}CFH) > PPh_2(CF{=}CF_2) > PPh_2(CF{=}CFH)$. The extended structures of these complexes indicate that these systems show much less tendency to exhibit fluorous congregation than is observed for trifluorovinyl-containing analogous systems, instead a number of short intermolecular non-classical hydrogen-bonding interactions occur between the vinyl proton and a metal-bound halide.

4. Experimental

4.1. Reagents and physical measurements

The ligands $PPh_2(CF{=}CFH)$ and $PPh_2(CCl{=}CFH)$ were synthesised as previously reported via the reaction of $PPh_2(CF{=}CF_2)$ or $PPh_2(CCl{=}CF_2)$ respectively with $LiAlH(O\text{-}t\text{-}Bu)_3$ [10]. K_2PdCl_4 and K_2PtCl_4 (Johnson Matthey) were used as supplied. Elemental analyses were performed by the Chemistry microanalytical service. Infrared spectra were recorded as nujol mulls held between KBr plates on a Nicolet PC-5 FTIR spectrometer, whist Raman spectra were recorded as solid samples on a Nicolet–Nexus combined FT-IR/FT-Raman spectrometer. ^{19}F (188.3 MHz), and $^{31}P\{^1H\}$ (81.8 MHz) NMR spectra were recorded on a Bruker

DPX200 spectrometer, and ^{1}H (399.9 MHz), and $^{13}C\{^{1}H\}$ (100.5 MHz) NMR spectra were recorded on a Bruker DPX400 spectrometer. Peak positions are quoted relative to external TMS [$^{1}H/^{13}C$], $CFCl_3$ [^{19}F], and 85% H_3PO_4 [^{31}P] using the high frequency positive convention.

4.2. Crystallographic details

Details of the structure analyses carried out on compounds **1–8** are summarised in Table 2. Measurements were made on crystals prepared by slow solvent evaporation of CH_2Cl_2/hexane solutions

Table 2
Crystallographic data for complexes **1–8**.

	1	2	3	4
Empirical formula	$C_{28}H_{22}F_4Cl_2P_2Pd$	$C_{28}H_{22}F_4Br_2P_2Pd$	$C_{28}H_{22}F_4I_2P_2Pd$	$C_{28}H_{22}F_2Cl_4P_2Pd$
fw	673.70	762.62	856.60	706.60
Colour, habit	Yellow, prism	Orange, block	Dark orange, plate	Orange, plate
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	*P*-1 (no. 2)	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)	*P*-1 (no. 2)
Crystal size	0.23 mm × 0.21 mm × 0.20 mm	0.25 mm × 0.20 mm × 0.20 mm	0.23 mm × 0.23 mm × 0.08 mm	0.25 mm × 0.10 mm × 0.05 mm
Unit cell dimensions	a = 7.8745(2) Å, α = 72.1000(10)°	a = 8.9584(2) Å, α = 90.07°	a = 9.5372(2) Å, α = 90°	a = 7.4820(2) Å, α = 94.221(2)°
	b = 9.5419(2) Å, β = 71.6310(10)°	b = 15.4686(5) Å, β = 101.853(2)°	b = 18.7291(3) Å, β = 90.3370(10)°	b = 11.8011(4) Å, β = 103.335(2)°
	c = 10.3767(2) Å, γ = 89.4180(10)°	c = 10.1840(3) Å, γ = 89.80°	c = 16.1555(3) Å, γ = 90°	c = 16.2582(6) Å, γ = 95.380(2)°
Volume	700.88(3) Å^3	1381.14(7) Å^3	2885.70(9) Å^3	1383.94(8) Å^3
T	150(2) K	150(2) K	150(2) K	150(2) K
Z	1	2	4	2
$D_{calcd.}$	1.596 mg/m^3	1.834 mg/m^3	1.972 mg/m^3	1.696 mg/m^3
λ	1.71073 Å	0.71073 Å	0.71073 Å	1.71073 Å
μ(Mo-Kα)	1.010 mm^{-1}	3.725 mm^{-1}	2.936 mm^{-1}	1.204 mm^{-1}
F(000)	336	744	1632	704
θ range	3.38–27.46°	2.76–27.39°	2.51–30.00°	1.29–27.44°
No. of reflections	15,146 (3183 unique)	8584 (3117 unique)	56,936 (8404 unique)	11,334 (6178 unique)
$R1/wR2$	0.0339/0.0563	0.0336/0.0586	0.0536/0.0907	0.0466/0.1087
$R1/wR2$ (all data)	0.0503/0.0614	0.0548/0.0644	0.1180/0.1104	0.0732/0.1217
Largest diff. peak and hole	0.398 and −0.545 eÅ^{-3}	0.454 and −0.837 eÅ^{-3}	1.004 and −1.351 eÅ^{-3}	1.756 and −0.895 eÅ^{-3}

	5	6	7	8-*trans*
Empirical formula	$C_{28}H_{22}F_4Cl_2P_2Pt$	$C_{28}H_{22}F_4Br_2P_2Pt$	$C_{28}H_{22}F_4I_2P_2Pt$	$C_{28}H_{22}F_2Cl_4P_2Pt$
fw	762.39	851.31	945.29	795.29
Colour, habit	Colourless, prism	Pale yellow, prism	Yellow, plate	Yellow, block
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Triclinic
Space group	*C*2/c (no. 15)	$P2_1/c$ (no. 14)	*Pbna* (no. 60)	*P*-1 (no. 2)
Crystal size	0.25 mm × 0.20 mm × 0.03 mm	0.25 mm × 0.20 mm × 0.15 mm	0.30 mm × 0.15 mm × 0.05 mm	0.15 mm × 0.10 mm × 0.10 mm
Unit cell dimensions	a = 15.525 (10) Å, α = 90°	a = 14.9442(6) Å, α = 90°	a = 9.80520(10) Å, α = 90°	a = 7.60230(10) Å, α = 70.9310(10)°
	b = 9.205(3) Å, β = 92.57(3)°	b = 10.7238(4) Å, β = 97.4910(10)°	b = 18.6363(3) Å, β = 90°	b = 9.7680(2) Å, β = 79.5490(10)°
	c = 38.307(9) Å, γ = 90°	c = 17.3847(8) Å, γ = 90°	c = 30.9521(4) Å, γ = 90°	c = 10.3021(2) Å, γ = 74.8480(10)°
Volume	5469(4) Å^3	2762.3(2) Å^3	5655.96(13) Å^3	694.04(2) Å^3
T	203(2) K	150(2) K	150(2) K	150(2) K
Z	8	4	8	1
$D_{calcd.}$	1.852 mg/m^3	2.047 mg/m^3	2.220 mg/m^3	1.903 mg/m^3
λ	1.71073 Å	0.71073 Å	0.71073 Å	1.71073 Å
μ(Mo-Kα)	5.488 mm^{-1}	8.133 mm^{-1}	7.302 mm^{-1}	5.586 mm^{-1}
F(000)	2944	1616	3520	384
θ range	2.13–25.02°	3.03–27.52°	2.18–27.32°	2.60–31.90°
No. of reflections	4996 (4805 unique)	22,745 (6249 unique)	35,163 (6323 unique)	8713 (4748 unique)
$R1/wR2$	0.0488/0.1072	0.0588/0.1093	0.0526/0.1221	0.0343/0.0675
$R1/wR2$ (all data)	0.0888/0.1248	0.1398/0.1351	0.0936/0.1421	0.0379/0.0695
Largest diff. peak and hole	2.768 and −1.302 eÅ^{-3}	2.334 and −2.951 eÅ^{-3}	2.204 and −2.313 eÅ^{-3}	1.866 and −1.704 eÅ^{-3}

8-*cis* CH_2Cl_2	
Empirical formula	$C_{29}H_{24}F_2Cl_6P_2Pt$
fw	880.21
Colour, habit	Colourless, plate
Crystal system	Orthorhombic
Space group	*P*na21 (no. 33)
Crystal size	0.08 mm × 0.15 mm × 0.20 mm
Unit cell dimensions	a = 17.9232(4) Å, α = 90°
	b = 11.3727(2) Å, β = 90°
	c = 15.8439(3) Å, γ = 90°
Volume	3229.54(11) Å^3
T	223(2) K
Z	4
$D_{calcd.}$	1.810 mg/m^3
λ	1.71073 Å
μ(Mo-Kα)	4.972 mm^{-1}
F(000)	1704
2θ range	3.20–27.50°
No. of reflections	22,421 (7001 unique)
$R1/wR2$	0.0350/0.0677
$R1/wR2$ (all data)	0.0644/0.0756
Largest diff. peak and hole	1.06 and −1.19 eÅ^{-3}

of the complexes on a Nonius FR590 diffractometer. All the data obtained from the complexes were corrected for Lorentz-polarisation factors and subsequently for absorption using the psi-scan method. X-ray structural data solution was by direct methods and refined against F^2 using SHELXTL [22] or SHELX-97 [23] with H atoms in idealised positions. All non-H atoms were modelled with anisotropic displacement parameters. The asymmetric units shown in the figures were produced using Platon [24]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). Any request to the CCDC for this material should quote the full literature citation and the reference numbers 771751–771759.

General method of synthesis for palladium(II) and platinum(II) complexes **1**–**8**: one equivalent of K_2PdCl_4 or K_2PtCl_4 dissolved in water (10 cm^3) is added to a stirred solution of two equivalents of the appropriate phosphine dissolved in ethanol (10 cm^3). The mixture was stirred for 15 min after which time the desired product precipitated out. This was filtered off, washed with a little water and dried under vacuum for 1 h. The bromo- and iodo-analogues were prepared by metathesis of the appropriate chloride complex with a four-fold excess of KBr, or KI at room temperature in 1:1 water:ethanol overnight. All the complexes were re-crystallised from CH_2Cl_2:hexane.

trans-[$PdCl_2${PPh_2(CF=CFH)}$_2$], 1. Yellow solid, mp. 169–71 °C, yield = 75%. Found: C, 51.5: H, 3.8: Cl, 11.4: P, 8.8. $C_{28}H_{22}F_4Cl_2P_2Pd$ requires C, 49.9: H, 3.3: Cl, 10.5: P, 9.2. Raman (cm^{-1}) 303 ν(Pd–Cl). IR (nujol, cm^{-1}): 1654 ν(C=C), 1157, 1095 ν(C–F). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ: +2.6 [vt, $0.5|^2J(PF) = {}^4J(PF)| = 21$]. ^{19}F NMR ($CDCl_3$): δ: −150.6 (*cis*) [dd, $^3J(FF) = 140$, $^2J(HF) = 75$], −161.8 (*gem*) [dvtd, $^3J(FF) = 140$, $0.5|^2J(PF) + {}^4J(PF)| = 21$, $^3J(HF) = 7$]. ^1H NMR ($CDCl_3$): δ: 7.95–7.45 [m, Ar + CF=CFH]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ: 123.8 [Ci, vt, $0.5|^1J(PC) + {}^3J(PC)| = 27$], 127.4 [Cm, vt, $0.5|^3J(PC) + 5J(PC)| = 5.8$], 130.5 [Cp, s], 134.0 [Co, vt, $0.5|^2J(PC) + {}^4J(PC)| = 6.8$], 145.9 [CF=CFH, ddvt, $^1J(CF) = 270.4$, $^2J(CF) = 38.6$, $0.5|^1J(PC) + {}^3J(PC)| = 26.1$], 150.0 [CF=CFH, ddvt, $^1J(CF) = 261.7$, $^2J(CF) = 59.9$, $0.5|^2J(PC) + {}^4J(PC)| = 6.8$].

trans-[$PdBr_2${PPh_2(CF=CFH)}$_2$], 2. Orange solid, mp. 174–6 °C, yield = 71%. Found: C, 43.7: H, 2.6: Br, 14.6: P, 8.2. $C_{28}H_{22}F_4Br_2P_2Pd$ requires C, 44.1: H, 2.9: Br, 14.9: P, 8.1. Raman (cm^{-1}) 191 ν(Pd–Br). IR (nujol, cm^{-1}): 1651 ν(C=C), 1143, 1097 ν(C–F). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ: +10.0 [vt, $0.5|^2J(PF) + {}^4J(PF)| = 19$]. ^{19}F NMR ($CDCl_3$): δ: −149.8 (*cis*) [dd, $^3J(FF) = 140$, $^2J(HF) = 74$], −160.5 (*gem*) [dvtd, $^3J(FF) = 140$, $0.5|^2J(PF) + {}^4J(PF)| = 19$, $^3J(HF) = 6$]. ^1H NMR ($CDCl_3$): δ: 7.89–7.82, 7.55–7.41 [m, Ar], 7.65 [CF=CFH, dd, $^2J(HF) = 74$, $^3J(HF) = 6$]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ: 125.0 [Ci, vt, $0.5|^1J(PC) + {}^3J(PC)| = 27$], 127.2 [Cm, vt, $0.5|^3J(PC) + {}^5J(PC)| = 4.8$], 130.4 [Cp, s], 134.2 [Co, vt, $0.5|^2J(PC) + {}^4J(PC)| = 6.8$], 147.3 [CF=CFH, ddvt, $^1J(CF) = 271.4$, $^2J(CF) = 38.6$, $0.5|^1J(PC) + {}^3J(PC)| = 26.1$], 149.3 [CF=CFH, ddvt, $^1J(CF) = 260.8$, $^2J(CF) = 59.9$, $0.5|^2J(PC) + {}^4J(PC)| = 5.8$].

trans-[PdI_2{PPh_2(CF=CFH)}$_2$], 3. Chocolate-brown solid, mp. 160 °C (dec), yield = 64%. Found: C, 39.5: H, 2.5: I, 29.3: P, 7.2. $C_{28}H_{22}F_4I_2P_2Pd$ requires C, 39.3: H, 2.5: I, 29.7: P, 7.2. Raman (cm^{-1}) 141 ν(Pd–I). IR (nujol, cm^{-1}): 1657 ν(C=C), 1140, 1090 ν(C–F). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ: −2.0 [vt, $0.5|^2J(PF) + {}^4J(PF)| = 18$]. ^{19}F NMR ($CDCl_3$): δ: −148.0 (*cis*) [dd, $^3J(FF) = 139$, $^2J(HF) = 73$], −158.3 (*gem*) [dvtd, $^3J(FF) = 139$, $0.5|^2J(PF) + {}^4J(PF)| = 18$, $^3J(HF) = 7$]. ^1H NMR ($CDCl_3$): δ: 7.85–7.40 [m, Ar + CF=CFH]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ: 127.8 [Ci, vt, $0.5|^1J(PC) + {}^3J(PC)| = 27.0$], 127.0 [Cm, vt, $0.5|^3J(PC) + {}^5J(PC)| = 5.8$], 130.3 [Cp, s], 134.3 [Co, vt, $0.5|^2J(PC) + {}^4J(PC)| = 6.8$], 148.4 [CF=CFH, ddvt, $^1J(CF) = 260.8$, $^2J(CF) = 60.9$, $0.5|^2J(PC) + {}^4J(PC)| = 5.8$], 149.8 [CF=CFH, ddvt, $^1J(CF) = 271.4$, $^2J(CF) = 36.7$, $0.5|^1J(PC) + {}^3J(PC)| = 27.0$].

trans-[$PdCl_2${PPh_2(CCl=CFH)}$_2$], 4. Pale yellow solid, mp. 185 °C (dec), yield = 82%. Found: C, 48.3: H, 2.8: Cl, 19.8: P, 8.6. $C_{28}H_{22}F_2Cl_4P_2Pd$ requires C, 47.6: H, 3.1: Cl, 20.1: P, 8.8. Raman (cm^{-1}) 302 ν(Pd–Cl). IR (nujol, cm^{-1}): 1613 ν(C=C), 1134, 1092 ν(C–F), 826 ν(C–Cl). $^{31}P\{^1H\}$ NMR (CDCl3): δ: +22.8 [s]. ^{19}F NMR ($CDCl_3$): δ: −95.2 [d, $^2J(HF) = 79$]. ^1H NMR ($CDCl_3$): δ: 7.86–7.40 [m, Ar], 7.30 [CCl=CFH, d, $^2J(HF) = 79$]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ: 112.6 [CCl=CFH, dvt, $^2J(CF) = 27.0$, $0.5|^1J(PC) + {}^3J(PC)| = 21.3$], 126.1 [Ci, vt, $0.5|^1J(PC) + {}^3J(PC)| = 27$], 128.6 [Cm, vt, $0.5|^3J(PC) + {}^5J(PC)| = 5.8$], 131.8 [Cp, s], 135.8 [Co, vt, $0.5|^2J(PC) + {}^4J(PC)| = 6.8$], 157.1 [CCl=CFH, dvt, $^1J(CF) = 281.0$, $0.5|^2J(PC) + {}^4J(PC)| = 3.9$].

cis-[$PtCl_2${PPh_2(CF=CFH)}$_2$], 5. White solid, yield = 94%. Found: C, 44.4: H, 2.7: F, 9.7. $C_{28}H_{22}F_4Cl_2P_2Pt$ requires C, 44.7: H, 2.9: F, 10.0. Raman (cm^{-1}) 321, 301 ν(Pt–Cl). IR (nujol, cm^{-1}): 1653 ν(C=C), 1153, 1141, 1121, 1098 ν(C–F). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ: +3.8 [d, $^2J(PF) = 47$, $^1J(PtP) = 3692$]. ^{19}F NMR (CD_2Cl_2): δ: −146.3 (*cis*) [dd, $^3J(FF) = 138$, $^2J(HF) = 74$, $^4J(PtF) = 44$], −156.2 (*gem*) [ddd, $^3J(FF) = 138$, $^2J(PF) = 47$, $^3J(HF) = 8$, $^3J(PtF) = 86$]. ^1H NMR (CD_2Cl_2): δ: 7.83–7.25 [m, Ar = CCl=CFH]. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ: 125.1 [Ci, d, $^1J(PC) = 69.5$], 129.1 [Cm, d, $^3J(PC) = 12.6$], 132.9 [Cp, s], 135.7 [Co, d, $^2J(PC) = 11.6$], 145.8 [CF=CFH, ddd, $^1J(CF) = 264.6$, $^2J(CF) = 74.3$, $^1J(PC) = 35.7$], 151.4 [CF=CFH, ddd, $^1J(CF) = 263.6$, $^2J(CF) = 61.8$, $^2J(PC) = 10.6$].

cis-/trans-[$PtBr_2${PPh_2(CF=CFH)}$_2$], 6 (ratio 95:5). White solid, mp. 129–32 °C, yield = 65%. Found: C, 39.8: H, 2.6: P, 7.8. $C_{28}H_{22}F_4Br_2P_2Pt$ requires C, 39.5: H, 2.6: P, 7.3. Raman (cm^{-1}) 218, 199 ν(Pt–Br). IR (nujol, cm^{-1}): 1651 ν(C=C), 1155, 1134, 1120, 1095 ν(C–F). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): *cis*-isomer: δ: +2.7 [d, $^2J(PF) = 46$, $^1J(PtP) = 3632$], *trans*-isomer: +9.9 [vt, $0.5|^2J(PF) + {}^4J(PF)| = 22$, $^1J(PtP)$ = not resolved]. ^{19}F NMR (CD_2Cl_2): *cis*-isomer: δ: −147.4 (*cis*) [dd, $^3J(FF) = 138$, $^2J(HF) = 74$, $^4J(PtF) = 45$], −156.4 (*gem*) [ddd, $^3J(FF) = 138$, $^2J(PF) = 46$, $^3J(HF) = 7$, $^3J(PtF) = 86$], *trans*-isomer: −150.3 (*cis*) [dd, $^3J(FF) = 139$, $^2J(HF) = 73$, $^4J(PtF) = 39$], −160.7 (*gem*) [dvtd, $^3J(FF) = 139$, $0.5|^2J(PF) + {}^4J(PF)| = 22$, $^3J(HF) = 8$, $^3J(PtF) = 85$]. ^1H NMR (CD_2Cl_2): δ: 7.95–7.35 [m, Ar + CF=CFH].

cis-/trans-[PtI_2{PPh_2(CF=CFH)}$_2$], 7 (ratio 25:75). Yellow solid, yield = 73%. Found: C, 35.3: H, 2.5: P, 7.3. $C_{28}H_{22}F_4I_2P_2Pt$ requires C, 35.6: H, 2.3: P, 6.6. Raman (cm^{-1}) 148 ν(Pt–I). IR (nujol, cm^{-1}): 1656 ν(C=C), 1144, 1096 ν(C–F). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): *cis*-isomer: δ: −0.6 [d, $^2J(PF) = 45$, $^1J(PtP) = 3470$], *trans*-isomer: +1.9 [vt, $0.5|^2J(PF) + {}^4J(PF)| = 20$, $^1J(PtP) = 2638$]. ^{19}F NMR (CD_2Cl_2): *cis*-isomer: δ: −147.3 (*cis*) [dd, $^3J(FF) = 140$, $^2J(HF) = 74$, $^4J(PtF) = 45$], −155.6 (*gem*) [ddd, $^3J(FF) = 140$, $^2J(PF) = 45$, $^3J(HF) = 8$, $^3J(PtF) = 86$], *trans*-isomer: −150.1 (*cis*) [dd, $^3J(FF) = 138$, $^2J(HF) = 74$, $^4J(PtF) = 45$], −159.4 (*gem*) [dvtd, $^3J(FF) = 138$, $0.5|^2J(PF) + {}^4J(PF)| = 20$, $^3J(HF) = 7$, $^3J(PtF) = 86$]. ^1H NMR (CD_2Cl_2): δ: 7.90–7.35 [m, Ar + CF=CFH]. $^{13}C\{^1H\}$ NMR: (CD_2Cl_2): *trans*-isomer: δ: 126.5 [Ci, vt, $0.5|^1J(PC) + {}^3J(PC)| = 27.8$], 127.4 [Cm, vt, $0.5|^3J(PC) + {}^5J(PC)| = 5.8$], 130.5 [Cp, s], 134.6 [Co, vt, $0.5|^2J(PC) + {}^4J(PC)| = 6.8$], 150.1 [CF=CFH, ddvt, $^1J(CF) = 261.6$, $^2J(CF) = 60.3$, $0.5|^2J(PC) + {}^4J(PC)| = 5.8$], 150.4 [CF=CFH, ddvt, $^1J(CF) = 270.4$, $^2J(CF) = 35.7$, $0.5|^1J(PC) + {}^3J(PC)| = 27.0$].

cis-/trans-[$PtCl_2${PPh_2(CCl=CFH)}$_2$], 8. Pale yellow solid, mp. 160 °C (dec), yield = 83%. Found: C, 42.3: H, 2.6: Cl, 18.3: P, 7.7. $C_{28}H_{22}F_2Cl_4P_2Pt$ requires C, 42.3: H, 2.8: Cl, 17.9: P, 7.8. Raman (cm^{-1}) *trans*-isomer: 330 ν(Pt–Cl), *cis*-isomer: 318, 295 ν(Pt–Cl). IR (nujol, cm^{-1}): 1657 ν(C=C), 1142, 1117, 1097 ν(C–F), 822 ν(C–Cl). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): *cis*-isomer: δ: +13.4 [s, $^1J(PtP) = 3731$], *trans*-isomer: +21.4 [s, $^1J(PtP) = 2787$]. ^{19}F NMR (CD_2Cl_2): *cis*-isomer δ: −93.5 [d, $^2J(HF) = 79$, $^4J(PtF) = 28$], *trans*-isomer: −95.5 [d, $^2J(HF) = 79$, $^4J(PtF) = 29$]. ^1H NMR (CD_2Cl_2): δ: 8.00–7.40 [m, Ar], 7.06 (*cis*-isomer) [CCl=CFH, d, $^2J(HF) = 79$]. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): (*cis*-isomer) δ: 112.1 [CCl=CFH, dd, $^2J(CF) = 25.1$, $^1J(PC) = 58.9$], 125.7 [Ci, d, $^1J(PC) = 67.6$, $^2J(PtC) = 32.8$], 128.8 [Cm, d, $^3J(PC) = 13.4$], 132.8 [Cp, s], 136.4 [Co, d, $^2J(PC) = 11.4$], 155.5 [CCl=CFH, d, $^1J(CF) = 283.9$].

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References

[1] See for example:
(a) J.H. Downing, M.B. Smith, in: J.A. McCleverty, T.J. Meyer (Eds.), Comprehensive Coordination Chemistry II, Elsevier Ltd., Oxford, UK, 2004 (Chapter 1.12);
(b) D.W. Allen, Organophosphorus Chem. 35 (2006) 1.
[2] R.P. Hughes, J.M.J. Lambert, J.L. Hubbard, Organometallics 5 (1986) 797–804.
[3] See for example:
(a) S. Jeulin, S. Duprat de Paule, V. Ratovelomanana-Vidal, J.P. Genet, N. Champion, P. Dellis, Angew. Chem. Int. Ed. 43 (2004) 320–325;
(b) J.D. Palcic, P.N. Kapoor, D.M. Roddick, R.G. Peters, Dalton Trans. (2004) 1644–1647;
(c) R.A. Baber, M.L. Clark, K.M. Heslop, A.C. Marr, A.G. Orpen, P.G. Pringle, A. Wards, D.E. Zambrano-Williams, Dalton Trans. (2005) 1079–1085;
(d) R.B. DeVashe, J.M. Spruell, D.A. Dixon, G.A. Broker, S.T. Griffin, R.D. Rogers, K.H. Shaughnessy, Organometallics 24 (2005) 962–971;
(e) R. Wursche, T. Debaerdemaeker, M. Klinga, B. Rieger, Eur. J. Inorg. Chem. (2000) 2063–2070;
(f) E. Rivard, A.D. Sutton, J.C. Fettinger, P.P. Powers, Inorg. Chim. Acta 360 (2007) 1278–1286;
(g) K.K. Banger, A.K. Brisdon, C.J. Herbert, H.A. Ghaba, I.S. Tidmarsh, J. Fluorine Chem. 130 (2009) 1117–1129.
[4] See for example:
(a) I.T. Horvath, J. Rabai, Science 266 (1994) 72;
(b) V. Herrera, P.J.F. de Rege, I.T. Horvath, T. Le Husebo, R.P. Hughes, Inorg. Chem. Commun. 1 (1998) 197–199;
(c) E.G. Hope, A.M. Stuart, J. Fluorine Chem. 100 (1999) 75;
(d) A.P. Dobbs, M.R. Kimberley, J. Fluorine Chem. 118 (2002) 3;
(e) P. Bhattacharyya, D. Gudmunsen, E.G. Hope, R.D.W. Kemmitt, D.R. Paige, A.M. Stuart, J. Chem. Soc. Perkin Trans. 1 (1997) 3609.
[5] C. Corcoran, J. Fawcett, S. Friedrichs, J.H. Holloway, E.G. Hope, D.R. Russell, G.C. Saunders, A.M. Stuart, J. Chem. Soc. Dalton Trans. (2000) 161.
[6] K.K. Banger, R.P. Banham, A.K. Brisdon, W.I. Cross, G. Damant, S. Parsons, R.G. Pritchard, A. Sousa-Pedares, J. Chem. Soc. Dalton Trans. (1999) 427.
[7] N.A. Barnes, A.K. Brisdon, M.J. Ellis, W.I. Cross, R.G. Pritchard, J. Fluorine Chem. 112 (2001) 35.
[8] N.A. Barnes, A.K. Brisdon, J.G. Fay, R.G. Pritchard, J.E. Warren, Inorg. Chim. Acta 358 (2005) 2543.
[9] N.A. Barnes, A.K. Brisdon, W.I. Cross, C. Herbert, R.G. Pritchard, G. Sadiq, Dalton Trans. (2008) 101–114.
[10] N.A. Barnes, A.K. Brisdon, F.R.W. Brown, W.I. Cross, I.R. Crossley, C. Fish, J.V. Morey, R.G. Pritchard, L. Sekhri, New J. Chem. (2004) 828.
[11] A.K. Brisdon, I.R. Crossley, R.G. Pritchard, J.E. Warren, Inorg. Chem. 41 (2002) 4748.
[12] (a) A.D. Beveridge, H.C. Clark, J.T. Kwon, Can. J. Chem. 44 (1966) 179;
(b) M. Aktar, H.C. Clark, Can. J. Chem. 46 (1968) 633;
(c) M. Aktar, H.C. Clark, Can. J. Chem. 46 (1968) 2165;
(d) S.A. Fontana, C.R. Davis, Y.B. He, D.J. Burton, Tetrahedron 52 (1996) 37;
(e) L. Xue, L. Lu, S.D. Pedersen, Q. Liu, R.M. Narake, D.J. Burton, J. Org. Chem. 62 (1997) 1064.
[13] J.A. Rahn, M.S. Holt, M. O'Neil-Johnson, J.H. Nelson, Inorg. Chem. 27 (1988) 1316.
[14] N.W. Alcock, W.L. Wilson, J.H. Nelson, Inorg. Chem. 32 (1993) 3193.
[15] X.L.R. Fontaine, D.P. Markham, B.L. Shaw, J. Organomet. Chem. 391 (1990) 123.
[16] S.J. Coles, P. Faulds, M.B. Hursthouse, D.G. Kelly, G.C. Ranger, A.J. Toner, N.M. Walker, J. Organomet. Chem. 586 (1999) 234.
[17] M.B. Hursthouse, D.G. Kelly, M.E. Light, A.J. Toner, Can. J. Chem. 78 (2000) 1073.
[18] J.A. Rahn, L. Baltusis, J.H. Nelson, Inorg. Chem. 29 (1990) 750.
[19] N.J. Taylor, S.E. Jacobson, A.J. Carty, Inorg. Chem. 14 (1975) 2648.
[20] B. Croxtall, J. Fawcett, E.G. Hope, A.M. Stuart, J. Chem. Soc. Dalton Trans. (2002) 491.
[21] B.J. Dunne, R.B. Morris, A.G. Orpen, J. Chem. Soc. Dalton Trans. (1991) 653.
[22] G.M. Sheldrick, SHELXTL, Siemans Analytical X-ray instruments, Madison, WI, 1995.
[23] G.M. Sheldrick, SHELX-97, Institut fur Anorganische Chemie der Universitat Göttingen, Göttingen, Germany, 1998.
[24] A.L. Spek, PLATON, a multipurpose crystallographic tool, Utrecht University, Utreht, The Netherlands, 2005.