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Recent advances in fluorovinyl-containing compounds

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Abstract

The reaction of the HFC-replacements CF_3CH_2F (HFC-134a) and CF_3CH_2Cl (HCFC-133a) with two equivalents of butyllithium generates, in high yield, the fluorovinyllithium reagents $CF_2{=}CFLi$ and $CF_2{=}CClLi$, respectively. These lithium reagents have been used to synthesise fluorovinyl-containing transition metal and main-group compounds in good yields. The resulting compounds may themselves then be used as stable transfer reagents. Here we report the synthesis of new fluorovinyl-containing organometallic complexes, fluorovinyl-containing phosphine ligands of the type $R_nP(CX{=}CF_2)_{3-n}$ ($n = 1, 2$; $X = Cl, F$) and their complexes. The single crystal X-ray structures of $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(CCl{=}CF_2)]$, *cis*-$[PtBr_2\{PEt_2(CF{=}CF_2)\}_2]$ and *trans*-$[PtCl_2\{PPh_2(CCl{=}CF_2)\}_2]$ are reported. © 2001 Published by Elsevier Science B.V.

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1. Introduction

The range and stability of synthons for the delivery of small perprotio-organic fragments, such as Grignard and organolithium reagents, is not matched in fluoro-organic chemistry. In many cases fluorinated analogues of well-known perprotio-organic reagents are either not available, or where such reagents can be formed they are of limited thermal stability due to the thermodynamically favourable formation of metal fluorides. A case in point is that of C_2-fluorovinyl reagents of the type $–CX{=}CX_2$ where X is a combination of fluorine and or chlorine.

The first fluorovinyl-containing compound, $CF_2{=}CFI$, was reported by Seffl and co-workers in 1956 and they subsequently used this for the preparation of the perfluorovinyl Grignard reagent, $CF_2{=}CFMgI$, at low temperature [1]. The efficiency of this reaction was estimated as ca. 20% based on an analysis of the amount of CF_2CFH formed on hydrolysis of the Grignard reagent. Work by Knunyants et al. on the same system, but utilising lower reaction temperatures resulted in a significant increase in the yield of the Grignard reagent to 70% [2,3]. Subsequent work [4,5] showed that bromotrifluoroethane, which was commercially available, unlike C_2F_3I, could also be used as the starting material for generation of perfluorovinyl Grignard reagents in a similar fashion and this method was used to synthesise a few examples of perfluorovinyl-containing organometallic complexes.

Perfluorovinyllithium was first prepared by Seyferth and co-workers from a transmetallation reaction of tris(perfluorovinyl)phenyltin (prepared from $CF_2{=}CFMgBr$ and $PhSnCl_3$) and phenyllithium in yields of around 65% [6,7,8]. Later work by Tarrant et al. [9] showed that bromotrifluoroethane can be used directly as a precursor for reaction with alkyllithiums and subsequently that the reaction of trifluoroethene with butyllithium at −100°C in diethylether results in yields of around 80% of perfluorovinyllithium [10].

It is possible to generate perfluorovinyl-containing transition metal complexes directly by the reaction of fluoroalkenes such as $CF_2{=}CF_2$ or $CF_2{=}CFCl$ with strong metal-based nucleophiles such as $[Re(CO)_5]^-$, $[Fe(CO)_2(\eta^5\text{-}C_5H_5)]^-$ [11] and $[Rh(CO)_2(PPh_3)_2]^-$ [12]. However, the single method responsible for the generation of the largest number of fluorovinyl organometallic complexes involved inducing a vinyllic rearrangement of a π-bound fluoroethene-based ligand. This method, suitable only for complexes containing coordinatively unsaturated metal centres, involves initial π-coordination of a $CF_2{=}CFX$ ($X = Br, Cl$) or $CF_2{=}CCl_2$ ligand followed by a thermal rearrangement, or one induced by the addition of lithium or silver salts [13]. Using these methods by the mid-1970s, around 70 fluorovinyl-containing metal compounds had been prepared, and of these over half were of the group 10 metals (Ni, Pd, Pt) obtained via the vinyllic rearrangement method. By the same time, there were just seven chlorodifluorovinyl-containing metal com-

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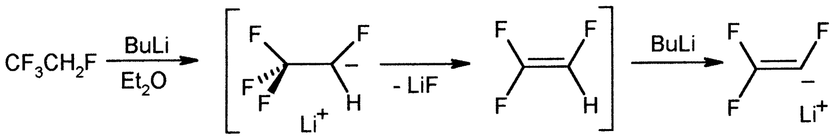

Scheme 1.

pounds, all but one of which was based on the group 10 metals.

More recent methods for the synthesis of fluorovinyl organometallic reagents include the direct reactions between activated metal powders and bromo- or iodo-perfluoroethene in dimethylformamide at, or just above, room temperature demonstrated by Burton, to yield a mixture of mono- and bis-substituted perfluorovinyl-metal compounds in high yields [14].

In 1997, Olah and co-workers reported work which resulted in the synthesis of a trimethylsilyl reagent capable of delivering the perfluorovinyl anion, $Me_3SiCF_2CF_2SiMe_3$. This was obtained by electrocoupling of Me_3SiCF_2Cl and Me_3SiCl in THF solution to give a 75% yield of a mixture dominated by $Me_3SiCF_2CF_2SiMe_3$, but also containing some $Me_3SiCF_2SiMe_3$ [15]. This reagent, in the presence of fluoride sources, produces $Me_3Si(CF{=}CF_2)$ in situ which in the presence of a second equivalent of fluoride acts as a perfluorovinyl anion source.

At about the same time Coe and co-workers showed that the CFC-replacement HFC-134a, CF_3CH_2F, can be used to generate perfluorovinyllithium at low temperature by reaction with two equivalents of a base, such as BuLi [16]. The proposed mechanism is shown in Scheme 1 and although the intermediate compound $CF_2{=}CFH$ is not isolated the mechanism is supported by the interception of $CF_3CHFSnBu_3$ when Bu_3SnCl is added to the reaction mixture.

Formation of the fluorovinyllithium reagent in this way, although still a low temperature reaction, has the advantage that it is based on materials that are now widely commercially available as CFC-replacements. Subsequent work [17] showed that in a similar way the chloro-analogue CF_3CH_2Cl (HCFC-133a) might be used to synthesise the chlorodifluorovinyllithium reagent. In both cases these workers concentrated on the application of this methodology to the synthesis of organic molecules. More recently, we have started to apply these methods for the synthesis of fluorovinyl-containing main-group and transition metal compounds.

2. Fluorovinyl organometallic complexes

When two equivalents of perfluorovinyllithium are reacted with mercury(II) chloride in THF solution a white precipitate of lithium chloride is formed along with bis-perfluorovinyl mercury. The presence of the fluorovinyl moiety in the resulting compound is confirmed by ^{19}F NMR studies which show three mutually-coupled doublets of doublets typical of an AMX spin system [18]. Confirmation of the bis-substituted nature of the product is obtained from the ^{199}Hg NMR spectrum where a triplet of triplets is observed. The isolated liquid product was crystallised at low temperature and X-ray crystallographic data was obtained [19]. Solution of the data recorded at 110 K shows flat, centosymmetric molecules that exhibit stacking of the perfluorovinyl moieties. Despite the first perfluorovinyl-containing organometallic complexes being prepared in the 1960s there is no structural data available for these systems; the data for $Hg(CF{=}CF_2)_2$ therefore represented the first solid state structure for an inorganic perfluorovinyl system. Inspection of the data obtained showed a typical Hg–C distance of 1.998(5) Å; although this is somewhat shorter than that found for $Hg(CF_3)_2$ [2.109(16) Å]. The C=C distance is 1.312(6) Å and three unique C–F bond lengths [1.362(6), 1.286(6) and 1.324(6) Å] are observed. Weak interactions between each of the three fluorines and adjacent mercury centres are also seen, these being 2.964(5), 3.129(5) and 3.523(5) Å. Fig. 1 shows an ORTEP representation of part of the solid state structure, and indicates these intermolecular interactions.

In order to determine whether these interactions are entirely responsible for the three different C–F bond distances gas phase electron diffraction data for $Hg(CF{=}CF_2)_2$ was obtained. Analysis of the data shows that in the gas

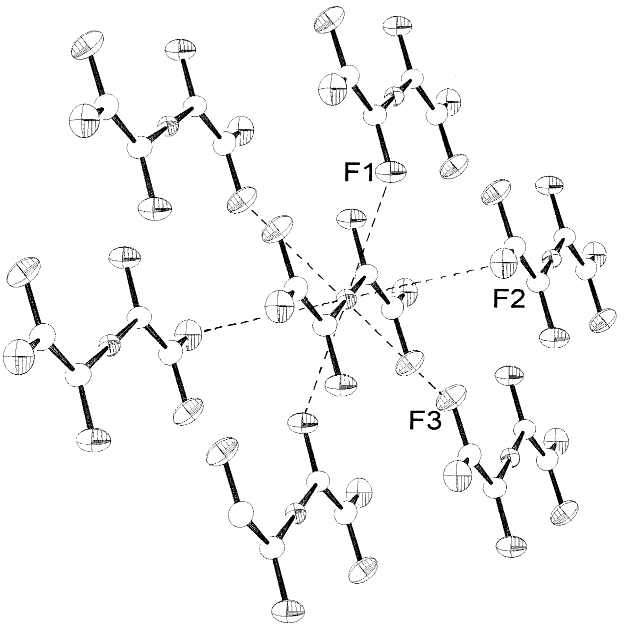

Fig. 1. The packing arrangement of $Hg(CF{=}CF_2)_2$ showing the weak intermolecular Hg···F interactions.

phase free rotation is observed around the Hg–C bonds, but otherwise a similar structural picture emerges. That is, three unique C–F bond distances are determined, with the same ordering of C–F bond lengths in the gas phase and in the solid state. However, in the gas phase the difference between the largest and the smallest C–F distances is smaller (5σ rather than 10σ) than that derived from the X-ray diffraction data. Therefore, the weak Hg···F interactions observed in the solid state structure are undoubtedly responsible, in part, for the observed variation in these distances. Ab initio calculations, performed at the MP2/DZP level, also predict that the three C–F distances should be different, with the unique α-C–F being the longest [19]. In addition, these calculations predict that the planar C_{2h} form is the energy minimum, the true minimum (0.9 kJ/mol lower in energy) exists when the two perfluorovinyl groups are essentially perpendicular ($\Phi = 89°$). However, the low value of the energy barrier is consistent with the observation of free rotation of the fluorovinyl groups at the temperature of the GED experiment (361 K). The data from these experiments is summarised in Table 1.

Table 1
Comparison of bond lengths (Å) and angles (°) obtained for $Hg(CF{=}CF_2)_2$

Parameter	X-ray	GED (r_a)	Theoretical (r_e)[a]
Hg–C1	1.998(5)	2.054(3)	2.066
C1=C2	1.312(6)	1.326(8)	1.343
C1–F1	1.362(6)	1.357(13)	1.373
C2–F2	1.286(6)	1.321(7)	1.327
C2–F3	1.324(6)	1.332(7)	1.338
C2–C1–Hg	125.4(4)	123.9(7)	126.2
F1–C1–Hg	118.4(3)	117.9(11)	117.6
C2–C1–F1	116.3(4)	118.2(6)	116.2
C1–C2–F2	125.4(5)	127.0(5)	126.5
C1–C2–F3	124.2(5)	122.7(7)	122.2
F2–C2–F3	110.4(4)	110.4(10)	111.3
Φ(C=C···C=C)	180	Free rotation	98.2

[a] MP2/DZP level parameters optimised for the C_{2h} geometry.

Using a similar synthetic method, but involving CF_3CH_2Cl rather than CF_3CH_2F results in 1-chloro-2,2-difluorovinyl analogues being prepared. Thus, reaction of the $CF_2{=}CClLi$ reagent with mercury(II) halides in the appropriate ratio provides the mono- and bis-substituted chlorodifluorovinyl mercury compounds. The bis-substituted compound is a liquid under normal conditions, whilst (chlorodifluorovinyl)mercury(II)chloride is solid. X-ray diffraction studies of the latter compound again shows stacking of the fluorovinyl moieties with the distance between neighbouring molecules being ca. 4.24 Å [20]. In this case, however, stacking occurs in an alternate head-to-tail fashion such that regions of ‘fluorous’ and ‘chlorous’ sections are observed in the solid state structure, as shown in Fig. 2. Within each molecule a near-linear geometry is adopted at the mercury atom, Cl1–Hg–Cl = 176.1(8)°, with Hg–Cl and Hg–C distances of 2.325(7) and 2.09(3) Å, respectively.

In this compound the two C–F distances [1.32(4) and 1.37(4) Å] are within experimental limits the same. However, the C=C distance is very short; this may be due to the proximity of Cl to the large mercury atom which dominates the X-ray scattering, alternatively it may be due to librational effects which cannot be corrected for in this case. This was the first chlorodifluorovinyl-containing compound to be structurally characterised and there was, therefore, no data with which to make direct comparisons of the derived distances. However, we note that the three C–Cl distances observed for the trichlorovinyl-containing 3,4,7,8-tetramethyl-1-10-phenanthralene adduct of $Hg(CCl{=}CCl_2)_2$ are all essentially the same [21].

Although the previous methods (see above) have been used to prepare a number of examples of organometallic fluorovinyl complexes the vast majority of these have been of group 10 metals. Many of those compounds which have been synthesised previously may also be obtained conveniently using our one-pot method [22], in addition we have shown that analogous perfluorovinyl and chlorodifluorovinyl-containing organometallic complexes, such as

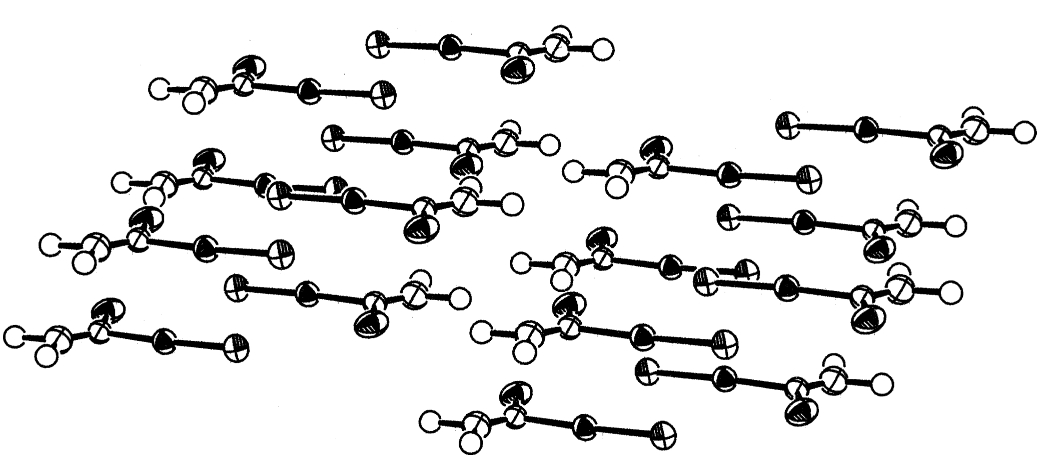

Fig. 2. The packing arrangement of $Hg(CCl{=}CF_2)Cl$ showing the alternating fluorous and chlorous sections (fluorine is denoted by open circles, all other atoms by quadrants).

$[Au(PPh_3)$-$(CF{=}CF_2)]$ and $[Au(PPh_3)(CCl{=}CF_2)]$ may be readily prepared [20]. More importantly, we can also prepare the first examples of early- and mid-transition metal-containing organometallic fluorovinyl complexes in good yields. For example, the reaction of Cp_2TiX_2 with $LiCX{=}CF_2$ ($X = F$, Cl) results in moderate yields of the first examples of early-transition metal-containing perfluorovinyl complexes of the type $Cp_2Ti(CX{=}CF_2)_nX_{2-n}$ [23]. These early-transition metal-containing complexes are generally much less stable than those of late-transition metals and they decompose to generate $CF_2{=}CXH$. Although these species are not sufficiently stable in solution to obtain single crystals limited structural data has been obtained from EXAFS studies [23]. Our work on mid-transition metal complexes has, however, been more successful in yielding structural information. $[CpFe(CO)_2(CX{=}CF_2)]$ may be prepared from the reaction of $[CpFe(CO)_2I]$ with $LiCX{=}CF_2$. The formulation of the resulting complexes are confirmed by multinuclear NMR spectroscopy. In particular the ^{19}F NMR spectrum of the perfluorovinyl-containing complex exhibits three mutually-coupled doublets of doublets whilst the chlorodifluorovinyl-containing complex shows two mutually coupling doublets. These signals are typical of those reported for other, related complexes [20]. Elemental analysis of this complex, as indeed for a number of other fluorovinyl-containing compounds, including those for which single crystal structures have been obtained, yield somewhat unsatisfactory data. In most cases this appears to be due to small amounts of solvent which are very difficult to completely remove, even by repeated distillation or recrystallisation. This situation is most notable for liquid, or oily samples, such as this perfluorovinyl-containing complex which has a melting point (23–26°C) only just above room temperature.

Unfortunately, the low melting point of the perfluorovinyl-containing complex also meant that it was not possible to obtain satisfactory solid state structural data. However, crystals suitable for X-ray diffraction studies were grown for $[CpFe(CO)_2(CCl{=}CF_2)]$ by slow evaporation of the solvents from a dichloromethane/hexane solution. The data obtained shows that there are three independent molecules within the unit cell. The iron atom is situated in the expected three-legged piano-stool arrangement. However, there is also a weak, second, 'ghost' iron atom which is located very near the cyclopentadienyl ring, this presumably arises from a disorder effect. A representation of this solid state structure is shown in Fig. 3, and selected bond lengths and bond angles are given in Table 2. The distances from the iron centre to the carbon atoms of the cyclopentadienyl ring and to the carbonyl ligands are unexceptional, and comparable with those found in related complexes [24–28]. Interestingly, as is observed for $Hg(CF{=}CF_2)_2$, there is a significant variation in the two beta-C–F bond distances. The difference between these two bondlengths [1.308(10) and 1.254(11) Å] corresponds to 5σ, with the C–F bond *trans* to the metal

Table 2
Selected bond lengths (Å) and angles (°) for $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(CCl{=}CF_2)]$

Fe–C8	1.968(8)
Fe–Co_{av}	1.744(5)
C–O_{av}	1.146(6)
C8–C9	1.361(13)
C8–Cl1	1.742(9)
C9–F9*b*	1.308(10)
C2–F9*a*	1.254(11)
Fe–C8–C9	127.4(7)
F9*a*–C9–F9*b*	111.8(9)

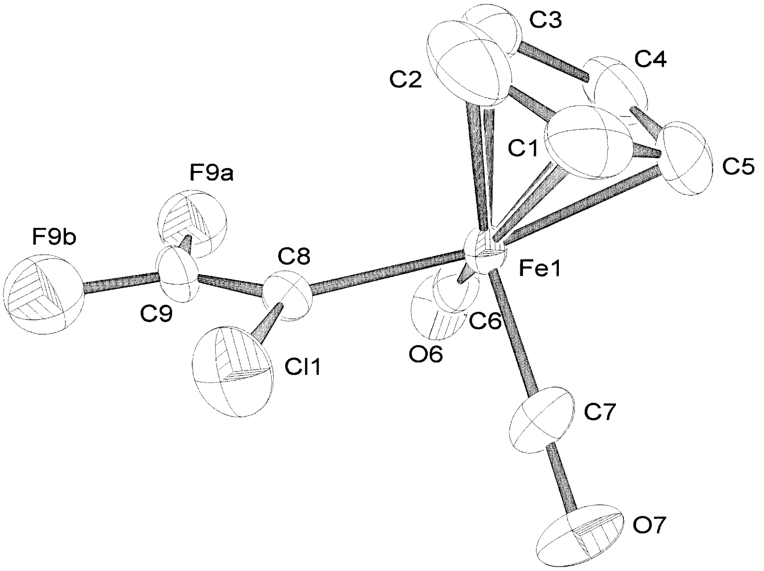

Fig. 3. An ORTEP representation of the molecular structure of $[FeCp(CO)_2(CCl{=}CF_2)]$, thermal ellipsoids are shown at the 30% probability level and hydrogen atoms are omitted for clarity.

being the longer distance; this is the opposite of the situation observed for $Hg(CF{=}CF_2)_2$.

Using this synthetic method, a wide range of main-group and transition metal fluorovinyl-containing complexes has been synthesised. Some of these have been demonstrated to be stable fluorovinyl-delivery agents. For example, compounds of the type $R_3Sn(CCl{=}CF_2)$ will undergo reaction with inorganic halides, such as $HgCl_2$ and $[AuCl(PPh_3)]$ to produce the substituted products $HgCl(CCl{=}CF_2)$ and $[Au(CCl{=}CF_2)(PPh_3)]$, respectively [20].

3. Fluorovinyl-phosphines

Non-metal, main-group fluorovinyl-containing compounds have also been prepared, in particular recent studies have concentrated on fluorovinyl-containing phosphines. Compounds of this type have been reported before; for example, in 1978 Horn et al. reported that $Ph_2P(CF{=}CF_2)$ may be obtained in 1.6% yield from the reaction of $CF_2{=}CFBr$ with methyllithium and then Ph_2PCl [29]. This, and other related fluorovinyl-containing phosphines may also be obtained from CF_3CH_2X starting materials, but the yields are now significantly higher. For example, $Ph_2P(CF{=}CF_2)$ can be obtained in yields greater than 80% from the two-stage, one-pot reaction of CF_3CH_2F with firstly two equivalents of butyllithium and then chlorodiphenyl-phosphine [30]. A range of such phosphines may be obtained based on the variety of commercially available R_2PCl and $RPCl_2$ precursors. The resulting perfluorovinyl-phosphines are mobile, clear liquids which are, generally, air- and thermally-stable, and soluble in a wide range of organic solvents and structural data has been reported for $PhP(CF{=}CF_2)_2$ [30].

An extension of these methods to CF_3CH_2Cl results in the formation of 1-chloro-2,2-difluorovinyl-containing phosphines in moderate to good yields. These materials are also soluble in a wide range of organic solvents and they are air-, moisture- and thermally-stable.

Characterisation of the new phosphines was obtained via the usual range of analytical methods. The ^{19}F NMR spectra of phosphines of the type $R_2P(CCl{=}CF_2)$ exhibit two fluorine signals at ca. −66 and −77 ppm. The first of these appears as a doublet, due to coupling with the other, inequivalent, fluorine nucleus [$J(FF) = 8$ Hz], and the second is a doublet of doublets due to further coupling with the phosphorus nucleus. Because of this the second, lower frequency, signal is assigned to the fluorine nucleus that is *trans* to the phosphorus across the double bond.

A comparison of the ^{31}P NMR chemical shift data obtained for the fluorovinyl-phosphines suggests that the electronic properties of the perfluorovinyl group is similar to that of the C_6F_5 group. A broadly similar conclusion may be drawn from data obtained for complexes which contain perfluorovinyl-phosphines. The electronic properties of the fluorovinyl-phosphines has been investigated by refluxing one equivalent of the phosphine with molybdenum hexacarbonyl to yield complexes of the type $[Mo(CO)_5P]$ and recording the carbonyl stretching frequencies. The data obtained for the complexes with $PPh_n(CX{=}CF_2)_{3-n}$ ($n = 1$, 2; X = F, Cl) is shown in Table 3 and is compared with data for related phosphines. It is clear from this data that the electronic properties of these ligands are more akin to those of traditional phosphites than phosphines, however, the electron withdrawing properties are not as pronounced as those of the trihalophosphines PF_3, PCl_3, PBr_3 or PI_3.

Table 3
The highest frequency $\nu(CO)$ absorptions observed for the complexes $[Mo(CO)_5P]$

Phosphine, P	$\nu(CO)$
PMe_3	2070
PMe_2Ph	2071
$PMePh_2$	2071
PH_3	2072
$PPh_2(CF{=}CF_2)$	2078
$PPh(CF{=}CF_2)_2$	2077
$PPh_2(CCl{=}CF_2)$	2078
$PPh(CCl{=}CF_2)_2$	2082
$P(OEt)_3$	2078
$P(OPh)_3$	2083
PI_3	2087
PBr_3	2093
PCl_3	2095
PF_3	2104

We have undertaken an extensive study of the coordination chemistry of these fluorovinyl-phosphine ligands; in particular we have investigated their coordination chemistry in palladium, platinum, gold and rhodium complexes, and some of this has already been reported [30].

When two equivalents of fluorovinyl-containing phosphines are added to $[K_2PtX_4]$ salts (X = Cl, Br, I) immediate reaction occurs. From the magnitude of the $^1J(^{195}Pt–^{31}P)$ coupling constants obtained from $^{31}P\{^1H\}$ NMR spectroscopic studies the stereochemistry of the complexes may be determined. Values of 3350–3700 Hz for this parameter are typical for the *cis*-$[PtX_2P_2]$ complexes whilst for the less-common *trans*-isomers significantly smaller values (2390–2650 Hz) are expected. When $PEt_2(CF{=}CF_2)$ is added to an ethanolic solution of K_2PtCl_4 a light-coloured oily product is produced, the elemental analysis and ^{31}P NMR data of which shows a doublet at 9.8 ppm with associated platinum satellites [$^1J(PtP) = 3667$ Hz] these data are consistent with the *cis*-isomer of $[PtCl_2\{PEt_2(CF{=}CF_2)\}_2]$. By comparison when the same phosphine is added to a solution of K_2PtI_4 a low melting point solid is formed and the ^{31}P NMR spectrum shows a virtual triplet centred at –0.5 ppm with a $^1J(PtP)$ coupling constant of 2497 Hz. The observation of a virtual triplet in the ^{31}P NMR spectrum, and the magnitude of the phosphorus–platinum coupling constant is indicative of the formation of *trans*-$[PtI_2\{PEt_2(CF{=}CF_2)\}_2]$.

When $PEt_2(CF{=}CF_2)$ is reacted with K_2PtBr_4 in an ethanol/water solvent system a light brown coloured solution is

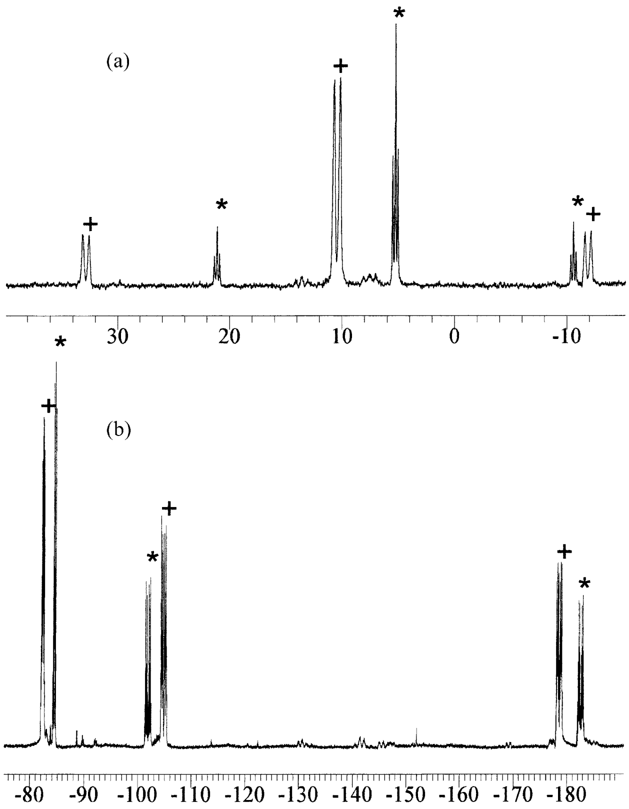

Fig. 4. The (a) ^{31}P and (b) ^{19}F NMR spectra of a solution of *cis*- and *trans*-[$PtBr_2\{PEt_2(CF{=}CF_2)\}_2$] dissolved in $CDCl_3$.

obtained, the $^{31}P\{^1H\}$ NMR spectrum of which shows a doublet [$J(PF) = 44$ Hz] at +10.5 ppm and a virtual triplet at +5.3 ppm, as shown in Fig. 4(a). Both of these signals have attendant platinum satellites from which the magnitude of the $^1J(PtP)$ coupling constants can be determined as 3617 and 2568 Hz, respectively. From these values, and the multiplicity of the resonances we can assign the first signal to a *cis*-isomer and the second to the *trans*-analogue. The ^{19}F NMR spectrum, Fig. 4(b), confirms the existence of two species with the observation of six fluorine signals. Based on intensity and coupling constants measurements we can assign the peaks at −82.3, −104.8 and −178.5 ppm to one species and the peaks at −84.5, −101.9 and −182.5 ppm to the second. The four higher-frequency signals all appear as doublets of doublets by virtue of coupling with the other two inequivalent fluorine nuclei of the fluorovinyl group. The lowest frequency signal for each complex is a doublet of doublets of doublets due to additional coupling to the ^{31}P nucleus, and on this basis the assignment of the fluorine resonances to the *cis*- and *trans*-isomers is made.

Crystals suitable for X-ray diffraction studies were obtained after slow evaporation of the solvent from a sample of the mixture of *cis*- and *trans*-isomers dissolved in dichloromethane. The resulting structure, consists of two independent molecules within the asymmetric unit, but both of the molecules show a *cis*-arrangement of ligands, albeit with slight distortions from idealised square-planar geometry. There are no significant differences in the distances observed in the two molecules and one of them is represented in Fig. 5. Selected bond distances and angles are presented in Table 4; the average Pt–Br distance is 2.467(5) Å and the average Pt–P distance is 2.231(11) Å. There are very few *cis*-[$PtBr_2(PR_3)$] complexes that have been crystallographically characterised with which to make direct comparisons, however, where such complexes do exist, principally for non-fluorine-containing phosphine ligands, the Pt–Br and Pt–P distances are slightly longer [31].

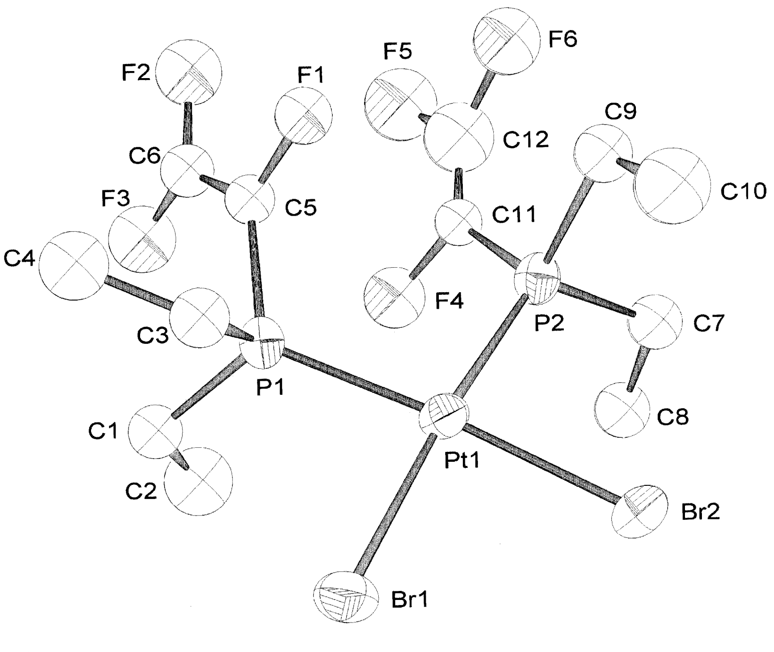

Fig. 5. An ORTEP representation of the molecular structure of *cis*-[$PtBr_2\{PEt_2(CF{=}CF_2)\}_2$], thermal ellipsoids are shown at the 30% probability level and hydrogen atoms are omitted for clarity.

Table 4
Selected bond lengths (Å) and angles (°) for *cis*-[$PtBr_2\{PEt_2(CF{=}CF_2)\}_2$]

Pt1–Br1	2.472(3)
Pt1–Br2	2.463(4)
Pt1–P1	2.238(9)
Pt1–P2	2.228(7)
C5–C6	1.35(6)
C5–F1	1.32(4)
C6–F2	1.29(5)
C6–F3	1.37(5)
C11–C12	1.17(6)
C11–F4	1.41(5)
C12–F5	1.35(7)
C12–F6	1.38(6)
Br1–Pt1–Br2	87.48(11)
P1–Pt1–P2	100.4(3)
P1–C5–C6	128(3)
F2–C6–F3	111(4)

Table 5
Selected bond lengths (Å) and angles (°) for *trans*-[$PtCl_2\{PPh_2(CCl{=}CF_2)\}_2$]

Pt–Cl1	2.303(7)
Pt–P1	2.309(7)
C1–C2	1.29(4)
C1–C12	1.72(3)
C2–F1	1.30(3)
C2–F2	1.26(3)
Cl1–Pt1–P1	87.4(3)
P1–C1–C2	123(2)
F1–C2–F2	108(2)

When $PPh_2(CCl{=}CF_2)$ is reacted with K_2PtCl_4 a lightly-coloured solid is obtained, the $^{31}P\{^1H\}$ NMR spectrum of which shows a singlet at +21 ppm with associated platinum satellite peaks [$^1J(PtP) = 2794$ Hz] which are indicative of a *trans*-isomer. This is unusual; most platinum(II) complexes crystallise as the *cis*-isomer unless very large phosphine or halide ligands are present. The ^{19}F NMR spectrum confirms the presence of the chlorodifluorovinyl moiety with the observation of two mutually-coupled doublets centred at −63.7 and −65.1 ppm [20]. Crystals suitable for X-ray diffraction studies were obtained by slow evaporation of the solvent from a chloroform/hexane layered solution. The unit cell contains two independent molecules one of which is shown in Fig. 6. This is the first published example of a structure containing a chlorodifluorovinyl-phosphine ligand and confirms the presence of the *trans*-arrangement of the ligands. Selected bond lengths are given in Table 5 from which it is apparent that the Pt–Cl and Pt–P distances are essentially the same [2.303(7) and 2.309(7) Å, respectively]. These distances are similar to those found in related complexes, containing either fluorinated- [32,33] or non-fluorinated-phosphine ligands, for example in *trans*-[$PtCl_2(PPh_3)_2$] [34] the Pt–Cl and Pt–P distances are 2.300 and 2.316 Å, respectively.

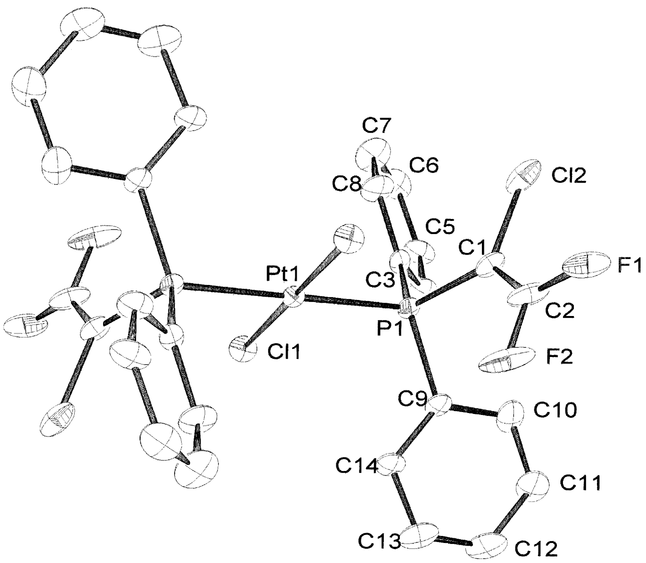

Fig. 6. An ORTEP representation of the molecular structure of *trans*-[$PtCl_2\{PPh_2(CCl{=}CF_2)\}_2$], thermal ellipsoids are shown at the 30% probability level and hydrogen atoms are omitted for clarity.

Interestingly, when the analogous perfluorovinyl-containing phosphine is used the resulting complex is the *cis*- rather than *trans*-isomer [30]. The observation of the *trans*-complex for $PPh_2(CCl{=}CF_2)$ and the *cis*-isomer for $PEt_2(CF{=}CF_2)$ can be understood by consideration of the size of the phosphine ligands; the steric demand of $PPh_2(CCl{=}CF_2)$ is expected to be considerably larger than that of $PEt_2(CF{=}CF_2)$.

Although the fluorovinyl-containing phosphine ligands are stable against oxidation under ambient conditions, it is possible to oxidise them using more forcing conditions. For example, the ^{31}P NMR spectrum of the oily product resulting from the reaction of H_2O_2 with $PPh_2(CCl{=}CF_2)$ showed an intense peak in the ^{31}P NMR spectrum at +36.2 ppm. This can be compared with the resonance for the starting phosphine at −12 ppm. The ^{19}F NMR spectrum confirms the presence of the chlorodifluorovinyl moiety and a peak at 1441 cm^{-1} in the IR spectrum is assigned to the P=O stretching mode. However, in all cases, signals were also observed for some unreacted starting material and it has not yet proved possible to completely separate the phosphine-oxide and phosphine species.

In an attempt to obtain complete oxidation of the chlorodifluorovinyl-phosphine compounds stronger oxidising agents were used. Small-scale reactions were undertaken between $PR_2(CCl{=}CF_2)$ phosphines and XeF_2 in NMR tubes. Thus, when one equivalent of XeF_2 is added to a $CDCl_3$ solution of $PPh_2(CCl{=}CF_2)$ an immediate and vigorous reaction occurs. The phosphorus NMR spectrum of the resulting solution exhibited a triplet ($J = 700$ Hz) of doublets ($J = 17$ Hz) of doublets ($J = 9$ Hz) at −56.2 ppm. This data is consistent with the formation of a phosphorus(V) species of the type R_3PF_2 [35]. The ^{19}F NMR spectrum of the same sample contained three signals which integrated in the approximate ratio of 2:1:1 at −38.7, −72.6

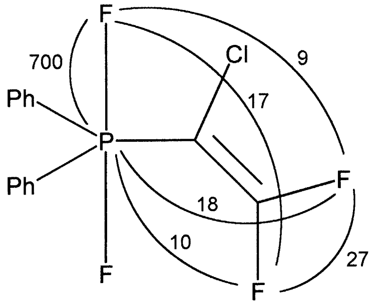

Fig. 7. A representation of the coupling constants (Hz) determined for $F_2PPh_2(CCl{=}CF_2)$.

and −73.8 ppm. The first of these signals is a doublet ($J = 700$ Hz) of doublets of doublets. The magnitude of the coupling is consistent with a $^1J(PF)$ coupling and this signal is therefore assigned to the two terminal P–F nuclei which most likely occupy the axial positions in order to be chemically equivalent. Crystallographic studies of two similar compounds have been undertaken, Ph_3PF_2 [36] and $(C_6F_5)_3PF_2$ [37] both of which have shown that the two fluorides occupy the axial positions in a trigonal bipyramidal arrangement around the phosphorus atom. The other two sets of peaks in the ^{19}F NMR spectrum are both more complicated multiplets and occur in the region for a chlorodifluorovinyl moiety. The signals themselves will arise from overlap of the expected doublets of doublets of triplets, and although it is not possible to unambiguously assign these multiplets to the individual fluorine nuclei, by computer simulation it is possible to reproduce the observed patterns and determine the magnitude of the J(FF) coupling constants. The resulting coupling constants are represented pictorially in Fig. 7. Unfortunately all attempts to isolate the product met with limited success, in all cases a mixture of chlorodifluorovinyl-containing products were recovered which included some of the previously identified phosphine-oxide, which presumably arises from the hydrolysis of the difluoride.

4. Conclusions

In summary, we have demonstrated that the commercially available CFC-replacements may be conveniently used as readily available starting materials for the synthesis of fluorovinyl-containing compounds. Using this one-pot method a variety of main-group and transition metal substituted perfluorovinyl- and chlorodifluorovinyl-containing compounds may be prepared in high yields. This method has resulted in the synthesis of new early-, mid- and late-transition metal complexes, some of which have been crystallographically characterised. The method also provides new high-yielding routes to main-group compounds which are able to act as novel ligand systems. Fluorovinyl-containing phosphorus(III) ligands appear to behave electronically more like phosphites than phosphines and they have a large steric demand. These ligands therefore provide an unusual combination of steric and electronic effects for which there are few analogues and we are continuing to investigate their chemistry and applications.

5. Experimental

5.1. General experimental procedures

HCFC-133a, HFC-134a (both ICI Klea), butyllithium (2.5 M in hexane, Aldrich) and K_2PtCl_4 (Johnson Matthey) were used as supplied after verification of purity. K_2PtX_4 salts (X = Br, I) were prepared from K_2PtCl_4 by reaction with KBr/HBr or KI, respectively. Diethylether and THF were dried by standing over sodium wire for ca. 1 day and subsequently refluxed over sodium/benzophenone under a dinitrogen atmosphere. Hexane was stored over sodium wire prior to use. Fluorine, proton and phosphorus NMR spectra were recorded on solutions of samples on a Bruker DPX200 instrument at 188.3, 200.2 and 81.0 MHz and referenced against $CFCl_3$, Me_4Si and 85% H_3PO_4, respectively, using the high-frequency positive convention. Elemental analyses were performed by the analytical service in the department. IR spectra were recorded on Nicolet PC5 or Nexus instruments. All reactions were carried out under anaerobic and anhydrous conditions, unless otherwise stated. Glassware was flame dried prior to use, and moisture sensitive reagents were handled under an argon atmosphere in a dry box (Belle Technology, UK). All recorded reaction temperatures are uncorrected temperatures measured using an internal thermocouple.

5.1.1. X-ray crystallography

X-ray data were collected either at room temperature or at low temperature on a Nonius MACH3 diffractometer. The data for all the compounds was solved using direct methods (SHELXS [38,39]). The structures were refined by full-matrix least squares on F_o^2, using the program SHELX-97. All data used were corrected for Lorentz-polarisation factors and subsequently for absorption by the psi-scan method. The non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms in the compounds were included in idealised positions and were refined isotropically. Crystallographic data are summarised in Table 6 and (except for structure factors) have been deposited with the Cambridge Crystallographic Database Centre as supplementary publication numbers CCDC 162251-162253. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1E2, UK.[1]

5.1.2. $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(CF{=}CF_2)]$

A 250 ml three-neck flask held at −80°C was equipped with a magnetic stirrer, a rubber septum and a silicon oil

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Table 6
Crystallographic data for the complexes [FeCp(CO)$_2$(CCl=CF$_2$)], *cis*-[PtBr$_2${PEt$_2$(CF=CF$_2$)}$_2$] and *trans*-[PtCl$_2${PPh$_2$(CCl=CF$_2$)}$_2$]

Compound	[FeCp(CO)$_2$(CCl=CF$_2$)]	*Cis*-[PtBr$_2${PEt$_2$(CF=CF$_2$)}$_2$]	*Trans*-[PtCl$_2${PPh$_2$(CCl=CF$_2$)}$_2$]
Formula	$C_9H_5ClF_2F_2FeO_2$	$C_{20}H_{20}Br_2F_6P_2Pt$	$C_{28}H_{20}Cl_4F_4P_2Pt$
M	274.43	791.21	831.27
Crystal system	Monoclinic	Monoclinic	Triclininc
Space group	*P*2(1)/*n*	*P*2(1)/*n*	*P*(−1)
a (Å)	12.109(2)	15.5720(5)	9.9823(10)
b (Å)	9.6180(10)	15.3120(5)	11.7553(10)
c (Å)	26.514(6)	18.2490(11)	13.0586(10)
α, β, γ (°)	90, 101.31(1), 90	90, 112.05(5), 90	98.76(1), 104.38(1), 94.50(1)
U (Å)	3028.0(9)	4033.1(16)	1456.1(2)
Z	12	8	2
D (g/cm^3)	1.806	2.280	1.896
μ(Mo Kα) (mm^{-1})	1.761	9.749	5.339
Crystal size (mm)	0.35 × 0.30 × 0.15	0.20 × 0.20 × 0.20	0.30 × 0.25 × 0.10
No. of data collected (θ range)	5275 (1.57 − 25)	7078 (1.50 − 25.10)	5110 (1.64 − 24.99)
F(0 0 0)	1632	2604	800
Temperature (K)	203(2)	293(2)	293(2)
R1, wR2 [$I > 2\sigma(I)$]	0.0856, 0.2583	0.1038, 0.2016	0.0950, 0.1873
R1 (all data)	0.1257	0.2875	0.2316
Maximum, minimum residual electron density e Å^{-3}	−0.761, 1.056	−2.357, 1.754	−1.191, 0.938

bubbler and maintained under a positive flow of dinitrogen gas. The flask was charged with pre-cooled diethylether (70 ml, −50°C) and liquid HCF 134a (1.00 cm^3, 11.85 mmol) was added. Butyllithium (2.5 M in hexane, 9.5 cm^3, 23.5 mmol) was added slowly to the stirred solution over a 0.5 h period. Once addition of the BuLi was complete the reaction temperature was maintained at −65°C for 2 h to ensure generation of $CF_2 = CF^-Li^+$. After lowering the reaction mixture temperature to −110°C [CpFe(CO)$_2$I] (2.652 g, 8.78 mmol), dissolved in THF (60 ml, −80°C), was added slowly. The reaction was slowly allowed to attain room temperature. The solvent volume was reduced in vacuo to half and hexane (80 ml) was added resulting in the precipitation of lithium salts, from the organic phase. The mixture was allowed to settle before being carefully filtered through a sinter under a dinitrogen atmosphere. The solvent was then removed in vacuo to leave an orange-red oil which was purified by column chromatography using 75:25 toluene:petroleum ether as eluent to yield [CpFe(CO)$_2$(CF=CF$_2$)] as a yellow-orange material (1.53 g, 68% yield); mp 23–6°C; anal. calcd. for $C_9H_5FeF_3O_2$: C, 41.9; H, 1.9; F, 22.1. Found: C, 40.9; H, 1.7; F, 19.9. ^{19}F(CDCl$_3$): δ −84.3 [dd, $J = 101$, 41 Hz], −130.5 [dd, $J = 114$, 101 Hz], −138.5 [dd, $J = 114$, 41 Hz]; ^{1}H(CDCl$_3$): δ 5.06 [m, C$_5$H$_5$]. IR (neat); v 2039 and 1991 (CO), 1707 (C=C), 1235, 1036 and 963 (C–F).

5.1.3. [Fe(η^5-C$_5$H$_5$)(CO)$_2$(CCl=CF$_2$)]

This compound was prepared in a similar method to that described for the perfluorovinyl-analogue using 0.23 cm^3 (2.37 mmol) of CF$_3$CH$_2$Cl, 1.9 cm^3 of BuLi and 0.71 g of [CpFe(CO)$_2$I] and resulted in a yellow-brown coloured product, 0.23 g, 47.1% yield; mp 48–51°C; anal. calcd. for $C_9H_5ClFeF_2O_2$: C, 39.4; H, 1.8; Cl, 12.9. Found: C, 42.9; H, 1.8; Cl, 11.2. ^{19}F(CDCl$_3$): δ −65.4 [d, $J = 65$ Hz], −94.4 [d, $J = 65$ Hz]; ^{1}H(CDCl$_3$): δ 5.04 [m, C$_5$H$_5$]. IR (nujol mull); v 2043 and 1995 (CO), 1692 (C=C), 1208 and 954 (C–F).

5.1.4. Ph$_2$P(CCl=CF$_2$)

Using a similar method to that described above BuLi (65 cm^3 of 2.5 M solution, 163 mmol) was slowly added to a pre-cooled solution of CF$_3$CH$_2$Cl (8.0 cm^3, 80 mmol) in diethylether (100 ml). After 2 h Ph$_2$PCl (13.5 cm^3, 75 mmol) was slowly added and the reaction was allowed to attain room temperature overnight. Hexane (200 cm^3) was added, the lithium salts removed by filtration and the solvents removed under vacuum. Purification of the resulting phosphine was achieved using column chromatography (70–230 nm silica support, 1:1 hexane:toluene eluent) to give 11.2 g, 53% yield of Ph$_2$P(CCl=CF$_2$); anal. calcd. for $C_{14}H_{10}ClF_2P$: C, 59.5; H, 3.6; F, 13.4. Found: C, 58.9; H, 4.0; F, 13.0. ^{19}F(CDCl$_3$): δ −67 [d, $J = 8$ Hz], −77.8 [dd, $J = 78$, 8 Hz]; ^{31}P(CDCl$_3$): δ −12.0 [d, $J = 78$ Hz]. IR (neat); v 3058 (CH), 1690 (C=C), 1284 and 1010 (C–F).

5.1.5. PhP(CCl=CF$_2$)$_2$

Using a similar method to that described above BuLi (53.6 cm^3 of 2.5 M solution, 140 mmol) was added to a pre-cooled solution of CF$_3$CH$_2$Cl (6.4 cm^3, 65 mmol) in diethylether (100 ml). After 2 h PhPCl$_2$ (4.1 cm^3, 32 mmol) was slowly added and the reaction was allowed to attain room temperature overnight. Following work up, as described above, 7.85 g, 40% yield of PhP(CCl=CF$_2$)$_2$ was obtained; anal. calcd. for $C_{10}H_5Cl_2F_4P$: C, 39.6; H, 1.7; F, 25.1. Found: C, 41.3; H, 2.3; F, 23.6. ^{19}F(CDCl$_3$): δ −65.1 [d, $J = 8$ Hz], −76.0 [dd, $J = 72$, 8 Hz]; ^{31}P(CDCl$_3$): δ −18.8 [t, $J = 72$ Hz]. IR (neat); v 3050 (CH), 1699 (C=C), 1292 and 1016 (C–F).

5.1.6. ^{i}Pr$_2$P(CCl=CF$_2$)

Using a similar method to that described for $Ph_2P(CCl{=}CF_2)$ BuLi (16.8 cm^3 of 2.5 M solution, 42 mmol) was added to a pre-cooled solution of CF_3CH_2Cl (1.9 cm^3, 20 mmol) in diethylether (80 cm^3). After 2 h ^{i}Pr$_2$PCl (3.0 cm^3, 19 mmol) was slowly added and the reaction was allowed to attain room temperature overnight. Following work up, as described above, 2.12 g, 52% yield of ^{i}Pr$_2$P(CCl=CF$_2$) was obtained; anal. calcd. for $C_8H_{14}ClF_2P$: C, 44.8; H, 6.6; F, 16.5. Found: C, 45.0; H, 6.9; F, 16.7. ^{19}F(CDCl$_3$): δ -69.1 [d, $J = 8$ Hz], -76.2 [dd, $J = 71$, 8 Hz]; ^{31}P(CDCl$_3$): δ 2 [d, $J = 71$ Hz]. IR (neat); v 2957 (CH), 1687 (C=C), 1278 and 1005 (C–F).

5.1.7. Cis-[PtCl$_2${PEt$_2$(CF=CF$_2$)}$_2$]

$PEt_2(CF{=}CF_2)$ was prepared from PEt_2Cl using the method previously described [30]. K_2PtCl_4 (0.42 g, 1 mmol) was dissolved in 10 cm^3 of water and added to a solution of $PEt_2(CF{=}CF_2)$ (0.34 g 2.1 mmol) in 10 cm^3 of EtOH. The solution was stirred at room temperature for 20 min and the resulting precipitate was filtered off, washed with water and ethanol and dried under vacuum for 1 h. The product was isolated as a light-coloured oil (0.19 g, 32% yield); anal. calcd. for $C_{12}H_{20}Cl_2F_6P_2Pt$: C, 23.8; H, 3.3; Cl, 11.7. Found: C, 24.2; H, 3.2; Cl, 9.9. ^{19}F(CDCl$_3$): δ -82.0 [dd, $J = 51$, 30 Hz], -104.6 [dd, $J = 117$, 51 Hz], -179.2 [ddd, $J = 117$, 43, 30 Hz]; ^{31}P(CDCl$_3$): δ -9.8 [d, 43 Hz, J(PtP) = 3667 Hz]. IR (CHCl$_3$ solution); v 1740 (C=C), 1310, 1159 and 1032 (C–F).

5.1.8. [PtBr$_2${PEt$_2$(CF=CF$_2$)}$_2$]

This compound was prepared in a similar fashion to that described above using K_2PtBr_4 (0.60 g, 1 mmol) and 0.34 g (2.1 mmol) of $PEt_2(CF{=}CF_2)$. The product was isolated as a golden-brown solid (0.10 g, 14.4% yield); mp 58–60°C; anal. calcd. for $C_{12}H_{20}Br_2F_6P_2Pt$: C, 20.7; H, 2.9; Br, 23.0. Found: C, 23.4; H, 2.6; Br, 22.1. IR (CHCl$_3$ solution); n 1742 (C=C), 1314, 1152 and 1032 (C–F). *Cis*-isomer ^{19}F(CDCl$_3$): δ -82.3 [dd, $J = 52$, 29 Hz], -104.8 [dd, $J = 116$, 52 Hz], -178.5 [ddd, $J = 116$, 44, 29 Hz]; ^{31}P(CDCl$_3$): δ 10.5 [d, 44 Hz, J(PtP) = 3617 Hz]. *Trans*-isomer ^{19}F(CDCl$_3$): δ -84.5 [dd, $J = 46$, 32 Hz], -101.9 [dd, $J = 118$, 46 Hz], -182.5 [ddd, $J = 118$, 32, 19 Hz]; ^{31}P(CDCl$_3$): δ 5.3 [vt, 19 Hz, J(PtP) = 2568 Hz].

5.1.9. Trans-[PtI$_2${PEt$_2$(CF=CF$_2$)}$_2$]

This compound was prepared in a similar fashion to that described above using 0.78 g (1 mmol) of K_2PtI_4 and 0.34 g (2.1 mmol) of $PEt_2(CF{=}CF_2)$. The product was isolated as an orange solid (0.35 g, 44% yield); mp 51–2°C; anal. calcd. for $C_{12}H_{20}I_2F_6P_2Pt$: C, 18.3; H, 2.5; I, 32.2. Found: C, 20.7; H, 2.4; I, 29.4. ^{19}F(CDCl$_3$): δ -86.1 [dd, $J = 48$, 32 Hz], -102.5 [dd, $J = 117$, 48 Hz], -180.1 [ddd, $J = 117$, 32, 19 Hz]; ^{31}P(CDCl$_3$): δ -0.5 [vt, 19 Hz, J(PtP) = 2497 Hz]. IR (CHCl$_3$ solution); v 1742 (C=C), 1314, 1150 and 1030 (C–F).

5.1.10. Trans-[PtCl$_2${PPh$_2$(CCl=CF$_2$)}$_2$]

K_2PtCl_4 (0.3 g, 0.723 mmol) was dissolved in 30 cm^3 of EtOH and $PPh_2(CCl{=}CF_2)$ (0.41 g 1.45 mmol) in 5 cm^3 of EtOH was added. The solution was stirred at room temperature for 3 h and the resulting precipitate was filtered off, washed with water and ethanol and dried under vacuum for 1 h. The product was suspended in hexane and stirred with two further drops of phosphine. The isolated product was a light-coloured solid (0.32 g, 53% yield); anal. calcd. for $C_{28}H_{20}Cl_4F_4P_2Pt$: C, 40.5; H, 2.4; Cl, 17.1. Found: C, 40.5; H, 2.2; Cl, 16.9. ^{19}F(CDCl$_3$): δ -63.7 [d, $J = 9$ Hz], -65.1 [d, $J = 9$ Hz]; ^{31}P(CDCl$_3$): δ 21.0 [s, J(PtP) = 2794 Hz]. IR (CHCl$_3$ solution); v 1693 (C=C), 1304 and 1024 (C–F).

5.1.11. OPh$_2$P(CCl=CF$_2$)

In a round-bottomed flask which was equipped with a stirrer was placed $PPh_2(CCl{=}CF_2)$ (1.0 g 3.50 mmol) and acetone (10 cm^3). To this solution was added, dropwise, an aqueous solution of H_2O_2 (1 cm^3 27% w/w). After stirring for 1 h, the acetone was removed under vacuum and the aqueous layer was extracted with toluene (3 × 10 cm^3). The combined toluene extracts were collected and the solvent removed under vacuum to leave an oily white solid. ^{19}F(CDCl$_3$): δ -64.1 [d, $J = 7$ Hz], -69.0 [d, $J = 8$ Hz]; ^{31}P(CDCl$_3$): δ 36 [br s]. IR (neat); v 1759 (C=C), 1441 (P=O), 1259 and 1026 (C–F).

5.1.12. F$_2$Ph$_2$P(CCl=CF$_2$)

An NMR tube fitted with a Young's tap was charged with $Ph_2P(CCl{=}CF_2)$ (0.1 g 0.35 mmol) and $CDCl_3$ in a dry box and small crystals of XeF_2 (0.07 g, 0.40 mmol) were added. After the vigorous reaction had subsided the tube was sealed and spectroscopic data was recorded. ^{19}F(CDCl$_3$): d -38.7 [ddd, $J = 700$, 18, 10 Hz], -72.6 [m, $J = 27$, 16, 10 Hz], -73.8 [m, $J = 27$, 18, 9 Hz]; ^{31}P(CDCl$_3$): d -56.2 [tdd, 700, 17, 9 Hz].

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