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FULL PAPER

Synthesis and co-ordination chemistry of perfluorovinyl phosphine derivatives. Single crystal structures of $PPh(CF{=}CF_2)_2$, *cis*-$[PtCl_2\{PPh_2(CF{=}CF_2)\}_2]$ and $[\{AuCl[PPh_2(CF{=}CF_2)]\}_2]$

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Reaction of perfluorovinyllithium, derived from CF_3CH_2F, with chloro-substituted phosphines generated perfluorovinylphosphines of the type $PPh_m(CF{=}CF_2)_n$ and $P(CF{=}CF_2)_nCl_m$ ($n + m = 3$) in high yields. A low-temperature crystal structure determination of the air- and moisture-stable compound $PPh(CF{=}CF_2)_2$ provided the first reported structural data for any perfluorovinyl-containing material. There is considerable variation in the C–F bond distances [1.310(4), 1.321(4), 1.353(3) Å] within the perfluorovinyl group in the phosphine. The co-ordination chemistry of these ligands has been investigated *via* the synthesis of examples of late transition-metal complexes. The results of single crystal structural determinations of *cis*-$[PtCl_2\{PPh_2(CF{=}CF_2)\}_2]$ and $[\{AuCl[PPh_2(CF{=}CF_2)]\}_2]\cdot 0.5CH_2Cl_2$ are reported. In both of these molecules short metal–phosphorus distances [$d(\text{Pt–P})_{av} = 2.231(3)$ and $d(\text{Au–P})_{av} = 2.217(2)$ Å] are observed compared with typical distances for similar phosphine complexes. A comparison of the electronic properties of these ligands with those of other phosphines, halogenophosphines and phosphites was made on the basis of a spectroscopic investigation of the carbonyl stretching frequencies of the complexes $[Mo(CO)_5\{PPh_m(CF{=}CF_2)_n\}]$ ($n + m = 3$).

Introduction

Tertiary organophosphine compounds are probably the most widely studied ligand systems in inorganic chemistry.[1] One reason for this widespread use is the ease with which changes to the electronic and steric properties of the ligands can be induced by altering the organic fragments attached to the phosphorus centre. Such variation is frequently confined to simple alkyl and aryl substitution, however there has recently been renewed interest in phosphine ligands containing perfluorinated organic fragments.[2] Part of this interest has arisen from the potential these ligands have in solubilising metal complexes in fluorous solvents, for example by incorporating long fluorocarbon 'ponytails' on the phosphines.[3] However, in order that the presence of the fluorocarbon fragment does not significantly alter the electronic properties of the phosphorus donor it has, so far, proved important that a short section of the alkyl chain closest to the phosphorus is non-fluorinated. By contrast studies of phosphines containing direct P–F linkages such as $PF_{3-x}R_x$ ($R = CF_3$ or Ph)[4] show that these ligands act as strong π acceptors with PF_3 acting as an analogue of CO.[5] When fluoroorganic groups are present the phosphines are still good π acceptors, but have a larger, and controllable, steric demand; the number of examples of such compounds is more limited. To date much of the interest has been in fluoroarylphosphines[6] such as $P(C_6F_5)_3$ and related systems; this is, in part, because they, or suitable precursors, are commercially available. More significantly, in a number of cases metal complexes containing these ligands have shown examples of activation of the strong C–F bonds in the phosphine ligand.[7]

Simple fluoroalkyl systems such as $P(CF_3)_3$,[8] $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$[9] and, very recently, $PPh(C_2F_5)_2$[10] have been prepared and are generally limited by the availability of straightforward preparative methods. As a consequence there are relatively few fluoroalkylphosphine ligands and little co-ordination chemistry known for them. Even for the very simplest organofluorophosphine, $P(CF_3)_3$, only a relatively few complexes are known, such as $[M(CO)_{n-x}\{(CF_3)_3P\}_x]$ (M = Ni, $n = 4$, $x = 1$–3;[11] M = Fe, $n = 5$, $x = 1$–3[12]) and one example of a platinum complex.[13]

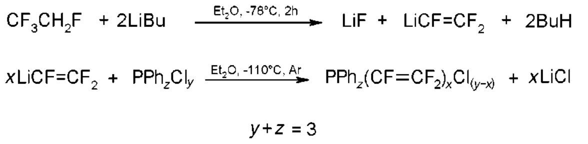
The synthesis of a few examples of phosphines containing fluorovinyl moieties has been reported, including in the early 1960s the synthesis and spectroscopic properties of compounds of the type $P(CF{=}CF_2)_xR_y$ (R = alkyl; $x + y = 3$).[14] Most of these materials were synthesized *via* the thermally unstable perfluorovinyl Grignard reagent obtained from $CF_2{=}CFX$ (X = Cl or Br). In 1978 Horn *et al.*[15] reported the synthesis of perfluorovinylphosphine compounds by the reaction of C_2F_3Br with methyllithium followed by reaction with chlorophosphines. However, these perfluorovinyl systems were obtained only in very low yields (<2% in some cases) and no structural data or studies of their co-ordination chemistry were reported. In fact the halogenofluorocarbons such as $CF_2{=}CFX$ (X = Cl or Br) which in the past have been precursors to these compounds are now difficult to obtain because of their potentially harmful effect on the ozone layer.

Recently we reported the synthesis of inorganic perfluorovinyl compounds *via* the perfluorovinyllithium intermediate $CF_2{=}CF^-Li^+$ **1** resulting from the treatment of the chlorofluorocarbon replacement HFC 134a, CF_3CH_2F, with 2 equivalents of LiBu.[16] We have shown that this route is wide ranging and high yielding and can be used to generate a number of main group and transition metal perfluorovinyl compounds by the reaction of metal halides with the transfer reagent **1**. Here we report an extension of this route to the synthesis of perfluorovinylphosphines resulting in their structural characterisation and an investigation of their co-ordination chemistry.

Results and discussion

The slow addition of 2 equivalents of *n*-butyllithium to a diethyl ether solution of CF_3CH_2F at −78 °C results in the formation of the thermally unstable $CF_2{=}CF^-Li^+$ reagent **1** in good yields. Following a series of experiments under a variety of conditions it appears that at −78 °C a reaction time of *ca.* 2 h results in essentially complete conversion of CF_3CH_2F into $CF_2{=}CF^-Li^+$ without any appreciable decomposition of the generated lithium reagent. Compound **1** generated in this way is stable in diethyl ether or THF solution for up to 24 h at low temperatures with only minor decomposition being noted, but raising the temperature to −45 °C results in immediate and complete decomposition of **1** resulting in a dark coloured, viscous solution.

Generation of reagent **1** from CF_3CH_2F is assumed to proceed *via* a two step mechanism which can be viewed simplistically as involving deprotonation of the HFC with subsequent elimination of 1 equivalent of lithium fluoride to yield trifluoroethene which is deprotonated by the second equivalent of base to generate **1** (Scheme 1). Support for this mechanism has come from the interception of the intermediate tetrafluoroethyllithium species by reaction with tributyltin chloride to generate $CF_3CFHSnBu_3$.[17]



Scheme 1 Reaction scheme for the two-stage, one-pot synthesis of perfluorovinylphosphines.

Perfluorovinylphosphine compounds are obtained by allowing a cold, concentrated diethyl ether or THF solution to react with the appropriate chlorophosphine compound (*e.g.* $PClPh_2$, $PPhCl_2$ and PCl_3) whilst maintaining the reactor temperature at −100 °C. Prior to working up the reaction samples were withdrawn from the organic phase and monitored by multinuclear NMR studies to determine the degree of substitution and extent of reaction. The ^{19}F NMR spectra of these solutions clearly demonstrate that the HFC has been consumed since the complex multiplet signals at δ −64.9 and −226.5 due to CF_3CH_2F[18] have been replaced by three sets of doublets of doublets of doublets within the chemical shift regions typical of those previously recorded for perfluorovinyl complexes.[19] After allowing the reaction mixture slowly to attain room temperature overnight hexane was added resulting in the precipitation of the alkali-metal salts which were removed by filtration. The resulting organic solvents were dried and removed under vacuum to leave a crude product from which, by distillation under reduced pressure, the colourless, liquid perfluorovinylphosphines are obtained in high yield. For the majority of perfluorovinyl complexes the final yields are around 70%, based on the amount of chlorophosphine used, however for the tris-substituted perfluorovinylphosphine the final yields were very much lower. This, in part, appears to be due to the large amount of heat evolved on reaction of PCl_3 with **1**, which results in localised heating of the reaction mixture and decomposition.

By varying the stoichiometric ratios of phosphines PPh_2Cl, $PPhCl_2$ and PCl_3 to reagent **1** the compounds $PPh_2(CF{=}CF_2)$, $PPh(CF{=}CF_2)_2$, $PPh(CF{=}CF_2)Cl$, $P(CF{=}CF_2)Cl_2$, $P(CF{=}CF_2)_2Cl$ and $P(CF{=}CF_2)_3$ were prepared. Those materials without P–Cl bonds are air- and moisture-stable liquids and show no appreciable signs of decomposition even after extended periods in solution. Indeed many of the reactions of these phosphines may be carried out in aqueous solution. The materials with P–Cl bonds were, however, as expected moisture sensitive and their reactions have not yet been investigated to the same extent.

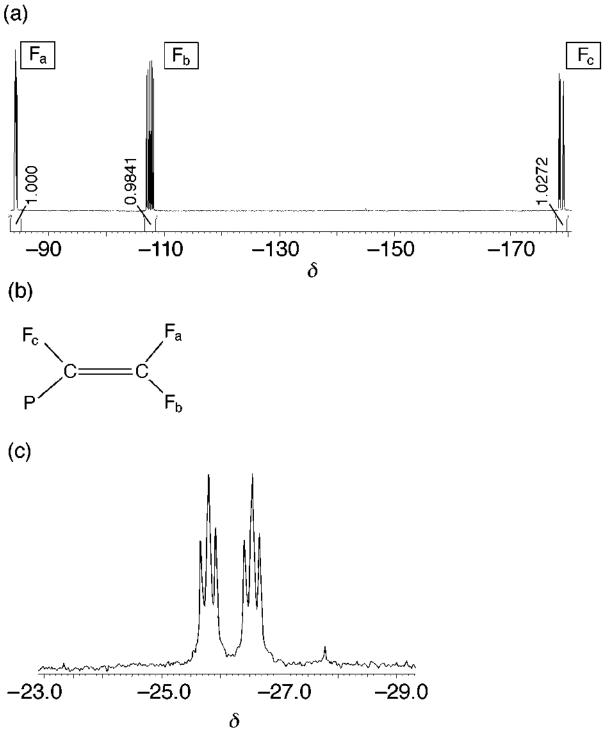


Fig. 1 (a) The ^{19}F NMR spectrum recorded for a solution of $PPh_2(CF{=}CF_2)$ in $CDCl_3$, (b) the labelling system used for NMR spectroscopic data for the perfluorovinyl moiety and (c) the $CDCl_3$ solution-phase ^{31}P NMR spectrum.

Unambiguous identification of all of the products was obtained by a combination of elemental analysis, IR and multinuclear (^1H, ^{19}F, ^{31}P and ^{13}C) NMR spectroscopy as outlined in Table 1. The ^{19}F NMR spectra of all these compounds exhibit doublets of doublets of doublets for each of the three inequivalent fluorine nuclei of the perfluorovinyl ligand in distinct regions typical of an AMX spin system, as shown in Fig. 1(a). By comparison with data previously obtained for perfluorovinyl complexes[19] and the magnitude of typical coupling constants observed in fluoroolefins (20–90 Hz for *gem*, 30–60 Hz for *cis* and 110–130 Hz for *trans* couplings[20]) the signals within the regions δ −78 to −85, −95 to −110 and −168 to −185 are assigned to F_a, F_b and F_c [Fig. 1(b)] respectively.

By virtue of the one relatively large magnitude P–F coupling constant the extent of perfluorovinyl substitution can readily, and simply, be determined from ^{31}P-{^1H} NMR studies. The spectra obtained for solutions of a mono-perfluorovinyl-substituted phosphine such as $PPh_2(CF{=}CF_2)$ or $P(CF{=}CF_2)Cl_2$ display a basic doublet structure due to coupling between the phosphorus nucleus and the fluorine nucleus, F_b. Additional fine structure is visible on each of the components of the doublet due to coupling with the remaining non-equivalent fluorine nuclei. In the case of $PPh_2(CF{=}CF_2)$ however, due to similar coupling constants, overlapping of peaks occurs to produce a doublet of triplets, such as that shown in Fig. 1(c). In a similar way the ^{31}P NMR spectra of bis-substituted compounds such as $PPh(CF{=}CF_2)_2$ and $P(CF{=}CF_2)_2Cl$ display a signal with a basic triplet appearance and that of the tris-substituted compound, $P(CF{=}CF_2)_3$, is based on a 1 : 3 : 3 : 1 quartet. We note that under the routine conditions used for recording NMR spectra we were not able to detect through-phosphorus coupling corresponding to $^4J_{FF}$, or more distant, coupling.

The infrared spectra of neat samples of the perfluorovinylphosphines are dominated by four strong absorptions. The C=C absorption is observed around 1710–1750 cm^{-1} and is typical of systems in which the carbon–carbon double bond is substituted

Table 1 Characterising data

	Analysis (%)						$\delta(^{31}P)$ (J/Hz)[a]	$\delta(^{19}F)$ (J/Hz)[a]		
Compound	C	H	P	F	Cl		F_a	F_b	F_c
$PPh_2(CF{=}CF_2)$	63.8	4.1	11.5	21.1	—	−26.2 (dt)	−84.3 (ddd)	−107.6 (ddd)	−178.6 (ddd)
	(63.2)	(3.8)	(11.7)	(21.4)		(10, 61)	(10, 30, 46)	(46, 61, 125)	(11, 30, 125)
$PPh(CF{=}CF_2)_2$	44.8	2.1	11.0	41.9	—	−51.5 (ttt)	−83.6 (ddd)	−106.1 (ddd)	−176.5 (ddd)
	(44.4)	(1.9)	(11.5)	(42.2)		(12, 12, 57)	(12, 29, 42)	(42, 57, 120)	(12, 29, 120)
$P(CF{=}CF_2)_3$	[b]					−76.5 (m)	−82.1 (ddd)	−105.9 (ddd)	−175.5 (ddd)
						(12, 12, 57)	(12, 35, 43)	(43, 57, 121)	(12, 35, 121)
$P(CF{=}CF_2)_2Cl$	15.1	—	13.5	49.5	15.1	−59.5 (ttt)	−81.2 (ddd)	−103.9 (ddd)	−181.2 (ddd)
	(15.5)		(13.6)	(49.9)	(15.5)	(5, 9, 54)	(9, 32, 48)	(48, 54, 121)	(5, 32, 121)
$P(CF{=}CF_2)Cl_2$	13.3	—	16.6	30.8	38.3	−40.8 (ddd)	−82.9 (ddd)	−103.7 (ddd)	−186.4 (ddd)
	(13.1)		(16.9)	(31.1)	(38.8)	(7, 17, 84)	(7, 32, 39)	(39, 84, 123)	(17, 32, 123)
2 *cis*-$[PtCl_2\{PPh_2(CF{=}CF_2)\}_2]$	27.8	1.7	9.7	18.1	—	4.2 (m)	−80.8 (m)	−94.0 (m)	−173.5 (m)
	(27.1)	(1.6)	(10.0)	(18.4)		J(Pt–P) = 3698			
3a $[\{AuCl[PPh_2(CF{=}CF_2)]\}_2]$	34.0	2.2	6.1	11.2	—	12.4 (m)	−78.1 (m)	−95.8 (m)	−179.9 (m)
	(33.7)	(2.0)	(6.2)	(11.4)					
3b $[AuCl\{PPh(CF{=}CF_2)_2\}]$	24.0	1.2	6.1	22.2	—	−7.8 (m)	−76.0 (m)	−95.8 (m)	−180.5 (m)
	(23.9)	(1.0)	(6.2)	(22.7)					
4a $[Mo(CO)_5\{PPh_2(CF{=}CF_2)\}]$	45.0	1.8	6.3		—	30.8 (d)	−82.5 (dd)	−98.2 (dd)	−170.6 (ddd)
	(45.4)	(2.0)	(6.2)			$J(P\text{–}F_c) = 56$	(32, 43)	(43, 118)	(32, 56, 118)
4b $[Mo(CO)_5\{PPh(CF{=}CF_2)_2\}]$	35.9	1.2	—	24.0	—	21.1 (t)	−80.0 (dd)	−97.6 (dd)	−173.6 (ddd)
	(35.6)	(1.0)		(22.5)		$J(P\text{–}F_c) = 64$	(32, 40)	(40, 116)	(32, 64, 116)

[a] The multiplicity of signals is denoted by d = doublet, t = triplet, m = multiplet, *etc.*; |J(FF)| and |J(PF)| values are quoted but their assignment is not explicitly given in most cases. [b] The high volatility of this compound precluded satisfactory elemental analysis. Mass spectrometric analysis gave *m/z* (M^+) as 274.

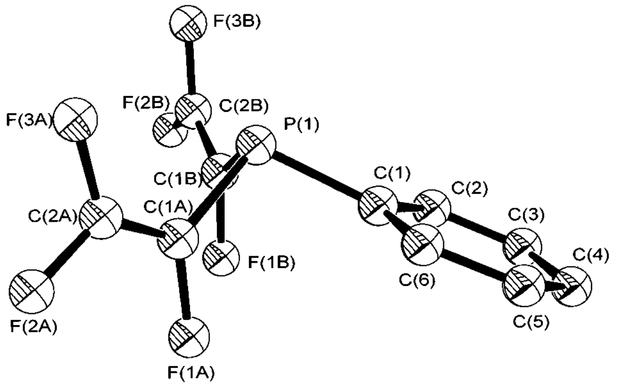


Fig. 2 Molecular structure of compound $PPh(CF{=}CF_2)_2$ showing the atom labelling scheme adopted. Thermal ellipsoids are drawn at the 30% probability level and hydrogen atoms are omitted for clarity.

Table 2 Selected bond lengths (Å) and angles (°) for $PPh(CF{=}CF_2)_2$

P(1)–C(1A)	1.809(3)	C(1A)–F(1A)	1.353(3)
P(1)–C(1B)	1.807(3)	C(2A)–F(2A)	1.321(4)
P(1)–C(1)	1.830(3)	C(2A)–F(3A)	1.310(4)
C(1A)–C(2A)	1.318(4)		
C(1B)–P(1)–C(1A)	98.45(14)	P(1)–C(1A)–F(1A)	120.6(2)
C(1B)–P(1)–C(1)	100.93(14)	C(1A)–C(2A)–F(2A)	124.2(3)
C(1A)–P(1)–C(1)	100.26(13)	C(1A)–C(2A)–F(3A)	124.9(3)
P(1)–C(1A)–C(2A)	123.5(3)		

with strongly electron-withdrawing groups.[21] The three C–F stretching modes are observed as intense absorptions at *ca.* 1350, 1150 and 1050 cm^{-1}.

To date no structural data have been reported for any inorganic perfluorovinyl compound. Attempts were made to grow crystals of these phosphines by freezing them in sealed glass capillaries in a stream of cold nitrogen. Unfortunately most of the materials resulted in glassy solids, but for $PPh(CF{=}CF_2)_2$ it was possible to obtain crystals suitable for X-ray diffraction studies. The asymmetric unit contains two unique molecules both of which show the expected pyramidal geometry around the phosphorus atom and typical P–C and C=C bond lengths,[22] Fig. 2. As anticipated the P–C bond lengths to the more electronegative perfluorovinyl groups are shorter than that between the phosphorus and phenyl carbon. There do not appear to be any particularly significant differences between like distances and angles of the two different molecules within the symmetric unit. There is, however, some variation in the C–F bond lengths of the perfluorovinyl moiety [for example, 1.353(3), 1.321(4) and 1.310(4) Å; Table 2], although there appear to be no especially significant intermolecular interactions to account for these. The longest C–F distance is the unique α-C–F bond which we note is consistent with that found in structural studies on perfluoroalkyl-bound moieties. Preliminary density functional calculations on a related perfluorovinyl compound[23] suggest that the α-carbon atom is appreciably more positively charged than the β-carbon which would result in a stronger ionic contribution to the C_β–F bonds than in the C_α–F one. Atomic overlap population calculations also suggest that there are more electrons involved in bonding within the C_β–F bonds than in the C_α–F linkage. Calculation of the cone angle of this phosphine according to Tolman's method,[24] based on our structural data, yields a value of *ca.* 172°. This, however, is likely to be an upper limit since on co-ordination the C–P–C angle usually decreases and the substituents rearrange or intermesh to minimise their steric requirements.[1]

Despite the fact that a few examples of Group 15 perfluorovinyl derivatives have been prepared before, they do not appear to have been isolated in sufficient quantities for their co-ordination chemistry to be investigated. We have, therefore, carried out reactions with these perfluorovinyl phosphines in order to generate some typical late-transition metal complexes. Unfortunately only reactions with $PPh_2(CF{=}CF_2)$ or $PPh(CF{=}CF_2)_2$ proved to be consistently successful; in most other cases the phosphine was recovered after work-up. The reaction of an excess of $PPh_2(CF{=}CF_2)$ with K_2PtCl_4 in water over 1 d results in the formation of a white precipitate of *cis*-$[PtCl_2\{PPh_2(CF{=}CF_2)\}_2]$ **2**. The phosphorus NMR spectrum of this new complex in $CDCl_3$ exhibits a single multiplet at δ +4.2, a shift to higher frequency of *ca.* 30 ppm compared with the value of δ −26.2 for the 'free' ligand. Associated with the multiplet are satellites due to coupling with the spin active ^{195}Pt nucleus [$I = \frac{1}{2}$, 33%, $^1J(Pt\text{–}P) = 3698$ Hz]. The magnitude of the Pt–P coupling constant is somewhat larger than that observed

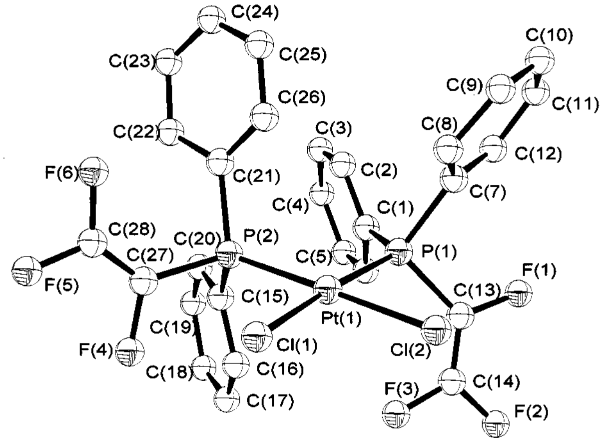


Fig. 3 Molecular structure of compound **2**. Details as in Fig. 2.

Table 3 Selected bond lengths (Å) and angles (°) for compound **2**

Pt(1)–P(1)	2.234(3)	P(1)–C(13)	1.792(12)
Pt(1)–P(2)	2.228(3)	C(13)–C(14)	1.31(2)
Pt(1)–Cl(1)	2.315(3)	C(13)–F(1)	1.354(14)
Pt(1)–Cl(2)	2.343(3)	C(14)–F(2)	1.296(14)
P(1)–C(1)	1.811(10)	C(14)–F(3)	1.315(14)
P(1)–C(7)	1.813(11)		
P(1)–Pt(1)–P(2)	95.25(10)	Cl(1)–Pt(1)–Cl(2)	87.43(11)
P(2)–Pt–Cl(1)	90.73(11)	Pt(1)–P(1)–C(1)	122.4(4)
P(1)–Pt(1)–Cl(1)	174.00(10)	Pt(1)–P(1)–C(7)	112.6(4)
P(2)–Pt–Cl(2)	178.09(11)	Pt(1)–P(1)–C(13)	110.4(4)
P(1)–Pt(1)–Cl(2)	86.59(10)		

in many other bis(phosphine)platinum dichloride complexes, although less than that found in some analogous bis(phosphite) complexes, *e.g. cis*-$[PtCl_2\{P(OMe)_3\}_2]$ ^1J(Pt–P) = 3908 Hz.[25] The ^{19}F NMR spectrum of the co-ordinated phosphine shows a small shift of *ca.* 5 ppm to higher frequency in the position of each set of peaks. This represents the first reported example of a perfluorovinyl-containing phosphine ligand bound to any metal centre. The complex appeared to be quite stable with no visual sign or spectroscopically detected decomposition apparent over a number of weeks even when left in solution.

Recrystallisation of the complex from a mixed dichloromethane–hexane solvent system produced a number of colourless crystals suitable for analysis by single-crystal X-ray diffraction, Fig. 3. The crystal packing consists of discrete neutral molecules separated by the normal van der Waals contacts. The complex displays a *cis* configuration of the phosphine ligands and a slight distortion from planar co-ordination geometry, Table 3. The Pt–P bond distances of 2.228(3) and 2.234(3) Å [average 2.231(3) Å] are shorter than those found in most other crystallographically characterised *cis*-platinum(II) dichloride bis(phosphine) complexes.[26] For example in *cis*-$[PtCl_2(PPh_3)_2]$ the platinum–phosphorus bond lengths are 2.251(2) and 2.265(2) Å [average 2.258(2) Å] and in the related perprotiovinyl complex *cis*-$[PtCl_2\{PPh(C_2H_3)_2\}_2]$ they are 2.248(1) and 2.243(2) Å [average 2.246(2) Å].[27] The Pt–Cl distances in complex **2** [2.315(3) and 2.343(3), average 2.329(3) Å] are also short by comparison with the range of distances found in related phosphine systems. For comparison in *cis*-$[PtCl_2(PPh_3)_2]$ and in *cis*-$[PtCl_2\{PPh(C_2H_3)_2\}_2]$ the Pt–Cl distances are 2.333(2) and 2.355(2) [average 2.344(2) Å] and 2.354(1) and 2.368(2) Å [average 2.361(2) Å] respectively.[27] However, shorter platinum–phosphorus distances are observed for *cis*-$[PtCl_2P_2]$ complexes when the phosphorus donor is a phosphite, *e.g. cis*-$[PtCl_2\{P(OMe)_3\}_2]$, *d*(Pt–P)$_{av}$ = 2.174(3) Å, or a phosphine possessing P–F bonds such as PF_2R (R = ^{t}Bu, adamantyl or *o*-$MeOC_6H_4$) or PF_3.[28] It would, therefore, appear that the distances observed for complex **2** are more akin to those found in phosphite- rather than phosphine-containing platinum(II) dichloride complexes. This is consistent with the large magnitude of the Pt–P coupling constant noted previously. It has been suggested that there is an inverse relationship between the magnitude of ^1J(Pt–P) and the Pt–P distance; our complex also appears to fit this correlation.[24,25] The short Pt–P and Pt–Cl bond distances observed from complex **2** are presumably a reflection of the electronic properties of the ligand rather than any steric factors (which would give rise to longer rather than shorter distances) and as such is consistent with the behaviour expected when a phosphine ligand contains electron-withdrawing substituents.[29]

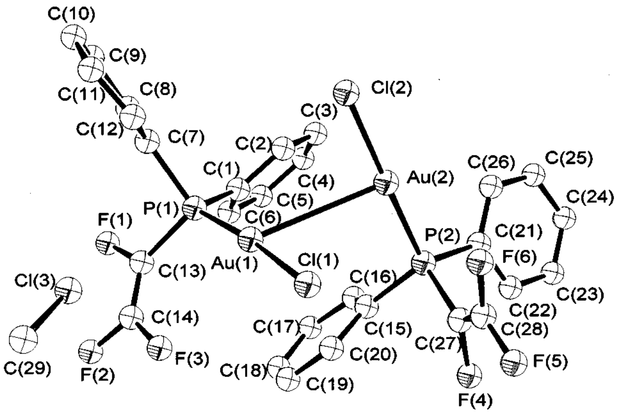


Fig. 4 Molecular structure of compound **3a**. Details as in Fig. 2.

The reactions between phosphines $PPh_2(CF{=}CF_2)$ and $PPh(CF{=}CF_2)_2$ and sodium tetrachloroaurate(III) were also investigated. Although these resulted in the formation of new complexes the most successful preparative route involved reaction of the phosphine with an intermediate thiodiethanol complex[30] rather than with the tetrachloroaurate. This is not surprising since the direct reaction of the phosphine with sodium tetrachloroaurate(III) requires an excess of the phosphine to reduce the gold complex, in so doing resulting in oxidation of the phosphine. In view of the air stability of these phosphines such a reaction is not favourable. The resulting monochloromonophosphine gold(I) complexes were characterised by a combination of elemental analyses and spectroscopic methods and these data are summarised in Table 1. Co-ordination of the phosphine is confirmed by a change in the phosphorus chemical shift, which in both cases is around δ 40 (δ −26.2 for free phosphine $PPh_2(CF{=}CF_2)$ to δ +12.4 for the complex **2a** and δ −7.8 for $[AuCl\{PPh(CF{=}CF_2)_2\}]$ compared with δ −51.5 for $PPh(CF{=}CF_2)_2$). The large shifts to higher frequency for the ^{31}P resonances on co-ordination are accompanied by small shifts to higher frequency in the position of the ^{19}F NMR signals.

Although complexes of both (perfluorovinyl)diphenylphosphine and bis(perfluorovinyl)phenylphosphine were prepared only those of the former yielded crystals suitable for structure determination. Solution of the data, shown in Fig. 4, resulted in a dimeric structure $[\{AuCl[PPh_2(CF{=}CF_2)]\}_2]$ for the complex with a molecule of solvent (CH_2Cl_2) shared between two dimers located at a special position within the unit cell. The dimer consists of two mutually perpendicular and nearly linear Cl–Au–P units [Cl(1)–Au(1)–Au(2)–P(2) 98.6(1), Cl(1)–Au(1)–P(1) 177.36(8) and Cl(2)–Au(2)–P(2) 177.65(8)°; Table 4] that are connected by a short Au–Au bond distance of 3.1945(5) Å. The vast majority of the structurally characterised bis-phosphine gold halide complexes are monomeric, unless bidentate phosphine ligands are involved.[26] The exceptions to this are found in gold(I) complexes containing fairly small phosphines, *e.g.* bis[(dimethylphenylphosphine)halogenogold(I)][31] [*d*(Au–Au) = 3.104(2)–3.230(2) Å, cone angle 122°] and bis[iodo(trimethylphosphine)gold(I)][32] [*d*(Au–Au) = 3.168(1) Å, cone angle 99°]. In these complexes, and compound **3a**, the Au–Au distances lie

Table 4 Selected bond lengths (Å) and angles (°) for compound **3a**

Au(1)–P(1)	2.216(2)	C(13)–C(14)	1.294(12)
Au(2)–P(2)	2.218(2)	C(13)–F(1)	1.336(9)
Au(1)–Cl(1)	2.288(2)	C(14)–F(2)	1.307(10)
Au(2)–Cl(2)	2.278(2)	C(14)–F(3)	1.306(10)
Au(1)–Au(2)	3.1945(5)	C(27)–C(28)	1.277(13)
P(1)–C(1)	1.801(8)	C(27)–F(4)	1.351(10)
P(1)–C(7)	1.808(8)	C(28)–F(5)	1.315(11)
P(1)–C(13)	1.799(9)	C(28)–F(6)	1.333(12)
P(1)–Au(1)–Cl(1)	177.36(8)	Au(1)–P(1)–C(7)	114.9(3)
P(1)–Au(1)–Au(2)	104.87(5)	Au(1)–P(1)–C(13)	112.7(3)
P(2)–Au(2)–Cl(2)	177.65(8)	Cl(1)–Au(1)–Au(2)–Cl(2)	98.6(1)
Cl(1)–Au(1)–Au(2)	77.59(5)	P(1)–C(13)–C(14)	129.3(7)
Cl(2)–Au(2)–Au(1)	84.44(6)	P(1)–C(13)–F(1)	115.3(6)
Au(1)–P(1)–C(1)	115.6(3)	F(2)–C(14)–F(3)	109.8(8)

Table 5 Observed ν(CO) absorptions for selected Mo(CO)$_5$L complexes

	$\tilde{\nu}$/cm^{-1}			
Phosphine, L	A$_1$	E	A$_1$	Ref.
PPh$_2$(CF=CF$_2$), complex **4a**	2077	1956	1989	This work
PPh(CF=CF$_2$)$_2$, complex **4b**	2084	1965	1988	This work
PMe$_3$	2070	1937	1947	35
PMe$_2$Ph	2071	1938	1947	35
PMePh$_2$	2071	1938	1947	35
PPh$_3$	2072	1939	1942	35
P(OEt)$_3$	2078	1945	1959	36
P(OPh)$_3$	2083	1958	1965	37
PI$_3$	2087	1979	1981	37
PBr$_3$	2093	1982	1991	37
PCl$_3$	2095	1985	1999	36
PF$_3$	2104	1990	2012	36

between that found in the Au$_2$ molecule (2.47 Å) and twice the gold van der Waals radius (3.60 Å).[33] The Au–P distances for complex **3a** are 2.216(2) and 2.218(2) Å [average 2.217(2) Å] which are considerably shorter than that observed in the monomeric structure for [AuCl(PPh$_3$)] [*d*(Au–P) = 2.235(3) Å], which is typical of the average Au–P distance of 2.236 Å for all such structures containing trialkyl- and triaryl-phosphines.[26] However, the Au–P distances are not quite as short as those found in phosphite and fluorophosphine complexes, such as [AuCl{P(OPh)$_3$}] [*d*(Au–P) = 2.192(5) Å] and in the air-sensitive chloro[(2,5-dimethylphenyl)difluorophosphine]gold(I) complex [*d*(Au–P) = 2.188(2) Å].[34] The gold–chlorine distances in complex **3a**, 2.288(2) and 2.278(2) Å [average 2.282(2) Å], are, in contrast, not significantly shorter than that observed in chloro(triphenylphosphine)gold(I) [*d*(Au–Cl) = 2.279(3) Å]. In fact there appears to be relatively little variation of the gold–chloride distances in these types of complexes even when phosphite and fluorophosphine ligands are present. For example in chloro(triphenyl phosphite)gold(I) and chloro[(2,5-dimethylphenyl)difluorophosphine]gold(I) the gold–chloride distances are 2.273(5) and 2.281(3) Å respectively.[34] Once again there is some variation in the C–F distances of the perfluorovinyl ligand in the co-ordinated phosphine and these follow a similar trend to those observed in the other perfluorovinylphosphine structures.

Although it did not prove possible to obtain structural data for the non-co-ordinated monosubstituted perfluorovinylphosphines from which cone angle estimates could be made the structural data for the gold and platinum complexes allow an estimate for this parameter to be made for phosphine PPh$_2$(CF=CF$_2$) as 135°.

In view of the short metal–phosphorus bond distances observed for the crystallographically characterised complexes a comparison of the electronic properties of these ligands with other phosphorus donors was undertaken *via* the synthesis of phosphine-substituted molybdenum carbonyl complexes. Addition of a slight excess of ligand PPh$_2$(CF=CF$_2$) or PPh(CF=CF$_2$)$_2$ to a refluxing toluene solution of [Mo(CO)$_6$] followed by separation *via* column chromatography resulted in analytically pure [Mo(CO)$_5$L] (**4a** and **4b**) as lightly coloured, oily materials which were characterised by elemental analysis, IR and NMR spectroscopies. Reactions carried out with ligand P(CF=CF$_2$)$_3$ did not result in complex formation, according to IR data, and mixtures of products were obtained when reactions with ligands P(CF=CF$_2$)$_2$Cl and P(CF=CF$_2$)Cl$_2$ were undertaken.

On co-ordination of the phosphine to the metal centre a shift (δ −26.2 to 30.8 and −51.5 to 21.1 respectively for **4a** and **4b**) and a simplification of the ^{31}P NMR signal is observed. For example, the ^{31}P NMR spectrum of PPh$_2$(CF=CF$_2$) consists of a doublet of triplets, Fig 1(a), which on co-ordination to yield **4a** simplifies to a doublet due to a loss of the coupling to F$_a$ and F$_b$. These changes in ^{31}P NMR parameters are reflected in the ^{19}F NMR spectrum which now consists of doublets of doublets for the signals due to the F$_a$ and F$_b$ nuclei and a doublet of doublets of doublets for nucleus F$_c$. Unfortunately attempts to crystallise the oily products obtained from these reactions were unsuccessful.

For the monosubstituted complexes, assuming local C_{4v} symmetry, three infrared-active carbonyl stretching modes are anticipated of symmetry 2A$_1$ + E and the observed infrared spectra are consistent with this expectation. The three observed peaks differed quite significantly in intensity and half-width. The most intense, and broadest, peak is assigned to the E mode, in line with the assignments made in related systems.[35–37] The two A$_1$ modes are therefore assigned to the two other weaker and sharper absorptions.

The carbonyl stretching frequencies obtained from infrared spectra for toluene solutions of complexes **4a** and **4b** are compared with those obtained for other phosphine-substituted complexes in Table 5. The position of the highest frequency A$_1$ vibrational mode is most often used as a measure of the electronic properties of the ligand.[10] As can be seen from the data presented in Table 5 the typical position of this absorption for alkyl and aryl phosphine-substituted molybdenum pentacarbonyl complexes is within the range 2070 to 2075 cm^{-1}. For phosphites this increases to 2078–2085 cm^{-1} and is even higher for PI$_3$, PBr$_3$, PCl$_3$ and PF$_3$ ligands. There is relatively little data available for fluorocarbon phosphine ligands, but for [Mo(CO)$_5${PPh(C$_2$F$_5$)$_2$}] the highest A$_1$ mode absorption is observed at 2089 cm^{-1}[10] and for PMe(CF$_3$)$_2$ 2094 cm^{-1}.[38] The carbonyl absorptions observed for complexes **4a** and **4b** at 2077 and 2084 cm^{-1} respectively lie in a rather similar position to those found for the analogous phosphite-containing complexes. This result is perhaps not unexpected in view of the distances observed in the crystal structure of both the platinum(II) and gold(I) complexes which are more consistent with those found in related phosphite- rather than the phosphine-containing analogues.

As has previously been observed for other fluorocarbon phosphines there is strong preference for mono- over di- or tri-substituted complexes.[10] Although it was possible thermally to substitute two carbonyl ligands when using a large excess of the phosphine this did not proceed cleanly, instead resulting in a mixture of mono- and di-substituted products. We were unable to produce any trisubstituted complexes *via* this method.

In conclusion, alkylperfluorovinylphosphines may be obtained in high yields and purity from the reaction of CF$_3$CH$_2$F (HFC-134a) with 2 equivalents of LiBu at low temperature followed by the addition of chlorophosphines. These materials are non-malodorous, air- and moisture-stable and extremely soluble in a wide range of organic solvents. An investigation of the co-ordination chemistry of these ligands suggests from single crystal data and from infrared vibrational

Table 6 Crystallographic data for compounds $PPh(CF{=}CF_2)_2$, **2** and **3a**

	$PPh(CF{=}CF_2)_2$	*cis*-$[PtCl_2\{PPh_2(CF{=}CF_2)\}_2]$ **2**	$[\{AuCl[PPh_2(CF{=}CF_2)]\}_2]\cdot 0.5CH_2Cl_2$ **3a**
Formula	$C_{10}H_5F_6P$	$C_{28}H_{20}Cl_2F_6P_2Pt$	$C_{29.5}H_{21}Au_2Cl_3F_6P_2$
M	270.11	798.37	1039.68
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$C2/c$
a/Å	7.486(2)	11.083(3)	20.1903(14)
b/Å	26.719(7)	15.162(2)	9.8220(15)
c/Å	10.717(3)	16.668(3)	31.974(4)
β/°	90.22(3)	100.231(14)	103.493(9)
U/Å^3	2143.5(9)	2756.6(3)	6165.7(12)
Z	8	4	8
D_c/g cm^{-3}	1.674	1.924	2.240
μ(Mo-Kα)/mm^{-1}	0.312	5.459	9.926
Crystal size/mm	0.40 × 0.27 × 0.27	0.35 × 0.30 × 0.02	0.35 × 0.35 × 0.25
No. data collected (θ range/°)	8581 (2.72–25.00)	4843 (1.83–25.02)	5591 (2.07–24.99)
F(000)	1072	1536	3880
Maximum, minimum transmission	—	1.0, 0.79	1.0, 0.83
T/K	120(2)	146(2)	203(2)
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0419, 0.1048	0.0467, 0.1157	0.0373, 0.0768
$R1$ (all data)	0.0712	0.0947	0.0559
Maximum, minimum residual electron density/e Å^{-3}	0.347, −0.237	2.178, −1.425	1.336 and −1.126

studies that they appear to possess electronic properties similar to those of traditional phosphite ligands.

Experimental

All reactions were carried out under dinitrogen in flame-dried glass. Diethyl ether and THF were dried over sodium wire for *ca.* 1 d and subsequently refluxed over sodium–benzophenone under a nitrogen atmosphere. The compounds CF_3H_2CF (ICI Klea), LiBu (2.5 M in hexanes, Acros), PPh_2Cl (Lancaster), $PPhCl_2$, PCl_3 and $[Mo(CO)_6]$ (all Aldrich) were used as supplied after verification of their purity by spectroscopic methods. Fluorine, phosphorus and proton NMR spectra were recorded on a Bruker AC200 spectrometer operating at 188.296, 81.83 and 200.13 MHz respectively. Peak positions are quoted relative to external $CFCl_3$, 85% H_3PO_4 and $SiMe_4$ using the high frequency positive convention. Carbon NMR spectra were recorded on a Bruker AC300 spectrometer operating at 75.47 MHz and referenced to external $SiMe_4$. Infrared spectra were recorded as Nujol mulls or of samples dissolved in a suitable hydrocarbon solvent held between KBr on a Nicolet PC-5 FTIR spectrometer. Elemental analyses were performed by this Department's microanalytical service.

X-Ray crystallography

Many of the details of the structure analyses carried out on compounds $PPh(CF{=}CF_2)_2$, **2** and **3a** are summarised in Table 6. Measurements for compounds **2** and **3a** were made on crystals prepared by slow solvent evaporation, on a Rigaku AFC6S and Nonius MAC3 CAD4 diffractometer respectively. The crystal of $PPh(CF{=}CF_2)_2$ was grown at low temperature at the University of Edinburgh. A stable solid–liquid equilibrium was established on a sample held in a glass capillary at 248 K. Reduction of the temperature to 247.5 K overnight led to steady crystal growth. Data for this compound were collected on a Stoe Stadi-4 diffractometer equipped with an Oxford cryosystems low temperature device. The data obtained from the two heavy-atom complexes were corrected for Lorentz-polarisation and absorption using the ψ-scan method. X-Ray structural data solution was by direct methods and refined against F^2 using SHELXTL[39] or SHELXL97[40] with H atoms in ideal positions. All non-H atoms were modelled with anisotropic displacement parameters. The asymmetric units shown in the figures were produced using ORTEP 3 for Windows.[41]

CCDC reference number 186/1264.

See http://www.rsc.org/suppdata/dt/1999/427/ for crystallographic files in .cif format.

Syntheses

$PPh_2(CF{=}CF_2)$. To a 3-neck round-bottom flask equipped with magnetic stirrer, inlet and outlet for argon, and held in an ethanol slush bath, was added precooled (−78 °C) diethyl ether (200 cm^3). The temperature of the flask and its contents was lowered to *ca.* −100 °C and liquid HFC-134a (5.74 cm^3, 0.068 mol) introduced. Two equivalents of LiBu^n (2.5 M in hexane, 54.40 cm^3, 0.136 mol) were added slowly over 15 min. An internal thermocouple was used to ensure that during addition the temperature of the solution remained below −80 °C. After complete addition the temperature was raised and maintained between −55 and −65 °C for 2 h. The reaction mixture was then cooled to −90 °C and a concentrated cold solution of chlorodiphenylphosphine (10.14 cm^3, 0.068 mol dissolved in 50 cm^3 diethyl ether) added dropwise whilst maintaining the solution temperature below −90 °C. The reaction was left at −78 °C for 2 h after which it was allowed to attain room temperature overnight. Addition of 100 cm^3 of hexane resulted in the precipitation of lithium salts which were removed by filtration. The resulting organic phase was dried over anhydrous $MgSO_4$ overnight. Distillation of the crude product under vacuum (112 °C, 10 mmHg) resulted in $PPh_2(CF{=}CF_2)$ as a clear liquid. Yield 14.5 g, 80%. $\tilde{\nu}$/cm^{-1} (neat) 3045 (C–H), 1725 (C=C), 1300 (C–F), 1135 (C–F) and 1100 (C–F). $\delta(^{13}C)$ ($CDCl_3$) 159 (1C, m, $\mathit{C}F_2{=}CF$) and 131 (1C, m, $CF_2{=}\mathit{C}F$).

$PPh(CF{=}CF_2)_2$. In an analogous method HFC-134a (9.40 cm^3, 55.90 mmol) was treated with LiBu (10 M, 22.36 cm^3, 223.5 mmol) in 400 cm^3 of diethyl ether at −78 °C. After *ca.* 2 h the solution was cooled to −100 °C and a precooled solution of $PPhCl_2$ (7.60 cm^3, 111.70 mmol) dissolved in diethyl ether (50 cm^3) slowly added. Work-up and distillation at 77 °C resulted in 20.4 g, 67% of pure $PPh(CF{=}CF_2)_2$. $\tilde{\nu}$/cm^{-1} (neat) 3040 (C–H), 1740 (C=C), 1720 (C=C), 1315 (C–F), 1170 (C–F) and 1050 (C–F). $\delta(^{13}C)$ ($CDCl_3$) 160 (1C, m, $\mathit{C}F_2{=}CF$) and 127 (1C, m, $CF_2{=}\mathit{C}F$).

$P(CF{=}CF_2)_3$. In an analogous method HFC-134a (2.15 cm^3, 25.48 mmol) was treated with LiBu (10 M, 5.01 cm^3, 50.96 mmol) in 100 cm^3 of diethyl ether at −78 °C. After *ca.* 2 h the solution was cooled to −100 °C and a precooled solution of

PCl$_3$ (0.64 cm^3, 7.28 mmol) dissolved in diethyl ether (5 cm^3) very slowly added. Work-up and distillation at 54 °C resulted in 0.48 g, 24% yield of pure P(CF=CF$_2$)$_3$. *m*/*z* (GC-MS) 274 (M$^+$, 30%), 193 ([M − C$_2$F$_3$]$^+$, 100%) and 112 ([M − 2C$_2$F$_3$]$^+$, 65%).

P(CF=CF$_2$)Cl$_2$. In an analogous method to that described, HFC-134a (2.15 cm^3, 25.48 mmol) was treated with LiBu (10 M, 5.01 cm^3, 50.96 mmol) in 100 cm^3 of diethyl ether at −78 °C. After *ca.* 2 h the solution was cooled to −100 °C and a precooled solution of PCl$_3$ (0.64 cm^3, 7.28 mmol) dissolved in 5 cm^3 diethyl ether very slowly added. Work-up and distillation at 70 °C resulted in 0.85 g (64% yield) of pure P(CF=CF$_2$)Cl$_2$.

P(CF=CF$_2$)$_2$Cl. In an analogous method HFC-134a (2.15 cm^3, 25.48 mmol) was treated with LiBu (10 M, 5.01 cm^3, 50.96 mmol) in 100 cm^3 of diethyl ether at −78 °C. After *ca.* 2 h the solution was cooled to −100 °C and a precooled solution of PCl$_3$ (0.64 cm^3, 7.28 mmol) dissolved in 5 cm^3 diethyl ether very slowly added. Work-up and distillation at 54 °C resulted in 0.80 g (48% yield) of pure P(CF=CF$_2$)$_2$Cl. $\tilde{\nu}$/cm^{-1} (neat) 1730 (C=C), 1320 (C–F), 1160 (C–F) and 1035 (C–F). δ(^{13}C) (CDCl$_3$) 159 (1C, m, CF$_2$=CF) and 126 (1C, m, CF$_2$=CF).

***cis*-[PtCl$_2${PPh$_2$(CF=CF$_2$)}$_2$] 2.** To a solution of potassium tetrachloroplatinate(II) (1.0 g, 2.41 mmol) in water (50 cm^3) was added (perfluorovinyl)diphenylphosphine (1.14 g, 4.3 mmol) and stirred overnight. A mixture of a pink-tan and white precipitate was formed. The mixture was heated on a steam-bath until the pink precipitate dissolved, and a layer of white solid formed. The solid was filtered off, washed with water, crushed in a mortar and dried under vacuum. The dried solid was then suspended in 10 cm^3 of pentane containing 2 drops of PPh(CF=CF$_2$) and stirred for *ca.* 15 min to ensure that any *trans* isomer that may have formed isomerises to the less soluble *cis* form. The mixture was then filtered, and the white solid dried under vacuum to remove the excess of phosphine. Yield 0.70 g, 36%.

[{AuCl[PPh$_2$(CF=CF$_2$)]}$_2$] 3a. Sodium tetrachloroaurate(III) dihydrate (0.394 g, 1 mmol) dissolved in water (20 cm^3) was added dropwise over 30 min to a stirred solution of thiodiethanol (0.367 g, 3 mmol) held at 0 °C. A yellow precipitate was formed initially which redissolved on stirring. Eventually the yellow colour of the mixture was discharged. A solution of the PPh$_2$(CF=CF$_2$) (0.266 g, 1 mmol dissolved in 40 cm^3 of chloroform) was then added dropwise over 45 min with stirring. The resulting colourless mixture was stirred for 1 h during which time it was allowed to warm to room temperature. The chloroform layer was then separated and the remaining aqueous phase extracted with 20 cm^3 of chloroform. The organic layers were combined before being removed by rotary evaporator to leave behind a white solid. The product was refrigerated overnight to allow for further precipitation. A white powder was recovered and dried under vacuum. Yield 0.304 g, 61%.

[AuCl{PPh(CF=CF$_2$)$_2$}] 3b. Using a similar method to that described for the synthesis of complex **3a**, sodium tetrachloroaurate(III) dihydrate (0.394 g, 1 mmol) dissolved in water (20 cm^3) was added dropwise over 30 min to a stirred solution of thiodiethanol (0.367 g, 3 mmol) held at 0 °C. A yellow precipitate was formed initially which redissolved on stirring. A solution of PPh(CF=CF$_2$)$_2$ (0.270 g, 1 mmol dissolved in 40 cm^3 of chloroform) was then added dropwise over 45 min with stirring. The resulting colourless mixture was stirred for 1 h during which time it was allowed to warm to room temperature. The chloroform layer was separated and the remaining aqueous phase extracted with 20 cm^3 of chloroform. The organic layers were combined and the solvents removed on a rotary evaporator to leave behind a white solid. The product was refrigerated overnight resulting in a white powder which was dried under vacuum. Yield 0.241 g, 48%.

[Mo(CO)$_5${PPh$_2$(CF=CF$_2$)}] 4a. To a solution of molybdenum hexacarbonyl (0.262 g, 0.99 mmol) in toluene (30 cm^3) was added perfluorovinyldiphenylphosphine (0.260 g, 0.98 mmol). After refluxing under nitrogen for 2 h the reaction mixture was filtered to yield an almost colourless solution. Removal of the solvent under vacuum resulted in 0.28 g (56%) of an oily material. $\tilde{\nu}$/cm^{-1} (toluene) 2077 (CO), 1956 (CO), 1989 (CO), 1726 (C=C), 1310 (C–F), 1141 (C–F) and 1049 (C–F).

[Mo(CO)$_5${PPh(CF=CF$_2$)$_2$}] 4b. To a solution of molybdenum hexacarbonyl (0.137 g, 0.52 mmol) in toluene (30 cm^3) was added bis(perfluorovinyl)phenylphosphine (0.139 g, 0.51 mmol). After refluxing under nitrogen for 3 h the reaction mixture was passed down a column eluted with toluene to yield a greeny yellow solution. Removal of the solvents under vacuum resulted in 0.122 g (47% yield) of a dark oily material. $\tilde{\nu}$/cm^{-1} (toluene) 2084 (CO), 1965 (CO), 1988 (CO), 1719 (C=C), 1313 (C–F), 1159 (C–F) and 1049 (C–F).

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