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Fluoroalkenyl, fluoroalkynyl and fluoroalkyl phosphines

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ABSTRACT

A review of the methods available for the preparation of monodentate P(III) compounds containing fluoroalkenyl, fluoroalkynyl and fluoroalkyl groups is given. The synthesis, properties and coordination chemistry of some fluoroalkenyl- and fluoroalkynyl-containing phosphines derived from HFC-134a (CF_3CH_2F) and HFC-245fa ($CF_3CH_2CH_2F$) is summarised. The development of the reaction between trimethylsilyl-containing phosphines and R_fI which provides a general method by which bulky fluoroalkyl groups, such as *i*-C_3F_7, *t*-C_4F_9, *c*-C_6F_{11}, can be readily introduced into phosphorus(III) centres is reported. Together these methods provide a way of generating P(III) systems of the type $R_{3-n}P(R_f)_n$ capable of possessing a wide range of steric and electronic properties.

1. Introduction

Phosphorus(III) systems of the type PR_3 are amongst the most widely studied ligand systems in transition metal chemistry, and they, or their derivatives, find applications in a wide range of areas, including functional materials, such as phase-transfer reagents and electrolytes, as organocatalysts, and as ligands in a variety of metal-catalysed C–C bond forming reactions [1]. Part of the reason for their widespread utility is that by varying the R-groups both the steric demand and the electronic properties of PR_3 compounds may be systematically modified.

The number of P(III) systems containing one, or more, perfluorinated substituents (denoted by R_f) is significantly smaller than for their perprotio analogues and this is often because of either limitations in synthetic methodology, or available starting materials. However, where such compounds exist they can show an unusual combination of steric and electronic properties [2]. Typically, when compared with their non-fluorinated analogue, fluorine-containing phosphines possess a greater steric demand (due to the larger size of fluorine compared with hydrogen) whilst electronically the phosphorus centre becomes a poorer σ-donor and a better π-acceptor. Indeed, PF_3 and *tris*(perfluoroalkyl)phosphines, have been considered as bulky mimics of the CO ligand [3].

The most frequently used measure of the size of a phosphine ligand is the solid cone angle that completely encapsulates the ligand in the complex $[Ni(CO)_3P]$ (where P = phosphine ligand) assuming an Ni–P bond length of 2.28 Å proposed by Tolman [4]. Typical values range from ca. 90°, for phosphines with small steric demand such as PH_3, to more than 180° for $P(t\text{-}Bu)_3$ and $P(o\text{-}tolyl)_3$. An alternative measure of the size of a phosphine, called the S'_4 parameter, is the difference between the sum of the C–P–C angles between substituents and the sum of the M–P–C angles [5]. This second measure has the advantage of being easily derived from crystallographic or computational data, but counter-intuitively bulky phosphines possess small S'_4 values.

The electronic properties of phosphines are most frequently described based on the CO stretching frequency value of a phosphine-substituted transition metal carbonyl complex. Originally Tolman's electronic parameter (TEP) was based on the A'_1 symmetry $\nu(CO)$ stretching frequency of a series of $[Ni(CO)_3P]$ complexes (P = P(III) ligand) [4]. This is a single measure of the combined σ and π electronic effect of the phosphine towards the nickel centre [6]; the better the donor the lower the $\nu(CO)$ vibration as a result of increased back-donation into CO π* orbitals, Table 1. However, because of the toxicity and hence difficulty in handling $[Ni(CO)_4]$ a number of alternative metal complexes have been used, including those of the type $[Mo(CO)_5P]$ [7] and $[Rh(CO)ClP_2]$ [8]. Comparison of the values obtained from one complex with those measured for another show similar trends (Fig. 1 (a) and (b)), and the values can be empirically inter-related.

$$\mathrm{TEP} = 1.116\nu(\mathrm{CO})_{\mathrm{Mo}} - 243\,\mathrm{cm}^{-1} \quad (1.1)$$

$$\mathrm{TEP} = 0.226\nu(\mathrm{CO})_{\mathrm{Rh}} + 1621\,\mathrm{cm}^{-1} \quad (1.2)$$

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Table 1
Steric and electronic properties of some monodentate P(III) compounds.[a].

	Phosphine[b]	Cone angle (°)	ν(CO) (cm^{-1}), $Ni(CO)_3P$[c]	ν(CO) (cm^{-1}), $Mo(CO)_5P$	ν(CO) (cm^{-1}), $RhCOClP_2$	^1J(SeP) $R_3P{=}Se$	^1J(PtP) $PtCl_2P_2$	^1J(RhP) $RhCOClP_2$
1	PH_3	87	2083.2		1961			
2	PMe_3	118	2064.1	2071	1967	684	2379	114.7
3	PEt_3	132	2061.7	2069	1958	686	2394	116.1
4	P*i*-Pr_3	160	2059.2		1950		2413	
5	P*n*-Bu_3	132	2060.3	2070	1955	689	2384	115.9
6	P*t*-Bu_3	182	2056.1		1955	712		
7	PPh_3	145	2068.9	2073	1979	731	2637	126.9
8	PBz_3	165	2066.4		1970			
9	PCy_3	170	2056.4		1943	673	2397	
10	P(*o*-Tol)$_3$	194	2066.6	2066	1974	706		
11	P(*p*-Tol)$_3$	145	2066.7	2070	1976	720		
12	$P(NMe_2)_3$	166	2061.9		1964	805		
13	PMe_2Ph	122	2065.3	2071	1968	710		117.7
14	$PMePh_2$	136	2067.0	2073	1974	725		122.4
15	PEt_2Ph	136	2063.7		1964			120.4
16	$PEtPh_2$	140	2066.7	2070	1973		2482	123.3
17	PCy_2Ph	162	2060.6		1964			
18	$PCyPh_2$	153	2064.8		1966	726		
19	PPh_2(*p*-Tol)	145	2068.2		1977	726		
20	$P(CCMe)Ph_2$		*2073*	2075				
21	$P(OMe)_3$	107	2079.5	2080	2014	954		193.9
22	$P(OEt)_3$	109	2076.3	2078			5694	
23	P(O*i*-Pr)$_3$	130	2075.9					
24	$P(OPh)_3$	128	2085.3	2083	2016			
25	$PPh_2(OMe)$	132	2072.0			810		
26	$PPh_2(OEt)$	133	2071.6			796		
27	$PPh_2(OPh)$	139	2074.6					
28	$PPh(OEt)_2$	116	2074.2				4828	
29	$P(CF_3)_3$	137	2107.0	2104				
30	PMe_2CF_3	124	2080.9	2086				
31	PEt_2pfv	152	*2069*		1981	730		128.4
32	P*i*-Pr_2pfv	165	*2069*		1981	766	2673	131.1
33	PCy_2pfv	169	*2069*	2073.1	1979		2654	130.6
34	$PPhpfv_2$	161	*2078*	2084	2002	848	3039	142.3
35	PPh_2pfv	163	*2073*	2077	1989	785		132.5
36	PPh_2cdfv		*2076*	2078			2794	
37	$PPhcdfv_2$		*2081*	2082				
38	P*i*-Pr_2cdfv	173	*2072*	2074			2644	
39	P*i*-Pr_2tfp	156	*2075*	2077				
40	P*i*-Prtfp$_2$		*2084*	2085				
41	P*t*-Butfp$_2$		*2077*	2079			3068	
42	PPh_2tfp		*2075*	2077				
43	$PPhtfp_2$		*2079*	2081				
44	P(*p*-F-Ph)$_3$	145	2071.3	2078	1982	741		
45	P(*p*-Cl-Ph)$_3$	145	2072.8		1984	750		
46	$PPh(C_6F_5)_2$	171	2082.8		2002			136.4
47	$PPh_2(C_6F_5)$	158	2075.9	2080	1982			133
48	$P(C_6F_5)_3$	184	2090.9		2008		3145	155.3
49	$P(C_6H_3CF_3\text{-}3,5)_3$	160	*2073*		2000		2798	134.7
50	$PPh_2C_2F_5$	160	*2078*	2080			2945	
51	$PPh(C_2F_5)_2$		*2088*	2089			4120	
52	PPh_2(*i*-C_3F_7)	161	*2079*	2081		828	2986	
53	$P(C_6H_4CF_3\text{-}4)_3$	145	*2071*		1990			
54	PPh_2Cl	138	2080.7		1993	867		
55	$PPhCl_2$	131	2092.1			935		
56	PCl_3	124	2102.0	2095				
57	PF_3	104	2110.8	2103				

[a] Data taken from Refs. [1,4,7–11].

[b] pfv: perfluorovinyl ($CF{=}CF_2$), cdfv: chlorodifluorovinyl ($CCl{=}CF_2$), tfp: trifluoropropynyl ($C{\equiv}CCF_3$).

[c] Values in italics are the average values calculated using Eqs. (1.1) and (1.2).

The TEP, and related parameters, also provide a measure from which the electronic contribution due to each R-group of a phosphine of type $PR_1R_2R_3$ can be derived, using the formula $\nu(CO) = 2056.1 + \chi(R_1) + \chi(R_2) + \chi(R_3)\ cm^{-1}$ [9]. Electron-donating groups, such as alkyl groups have small $\chi(R)$ values (e.g. $\chi(CH_3) = 2.6$), whilst electron-withdrawing groups have larger values (e.g. $\chi(F) = 18.2$, $\chi(CF_3) = 19.6$). Alternatively, coupling constant information derived from NMR studies may be used as a gauge of the electronic properties of a P(III) ligand. For example ^1J(SeP) from phosphine selenides and ^1J(RhP) from Vaska-type complexes have been used previously [10,11], and correlations between these and TEP exist.

Since the early work of Chatt and Wilkins [12] and Tolman [4,9] rationalising the properties of phosphines there have been many attempts to model and predict the behaviour of these systems. These include attempts to extract information about the stereo-electronic factors that influence the thermodynamics and kinetics of reactions by quantitative analysis of ligand effects (abbreviated as QALE) [13] and attempts to generate a phosphine ligand knowledge database [14]. The approaches used, and their validity

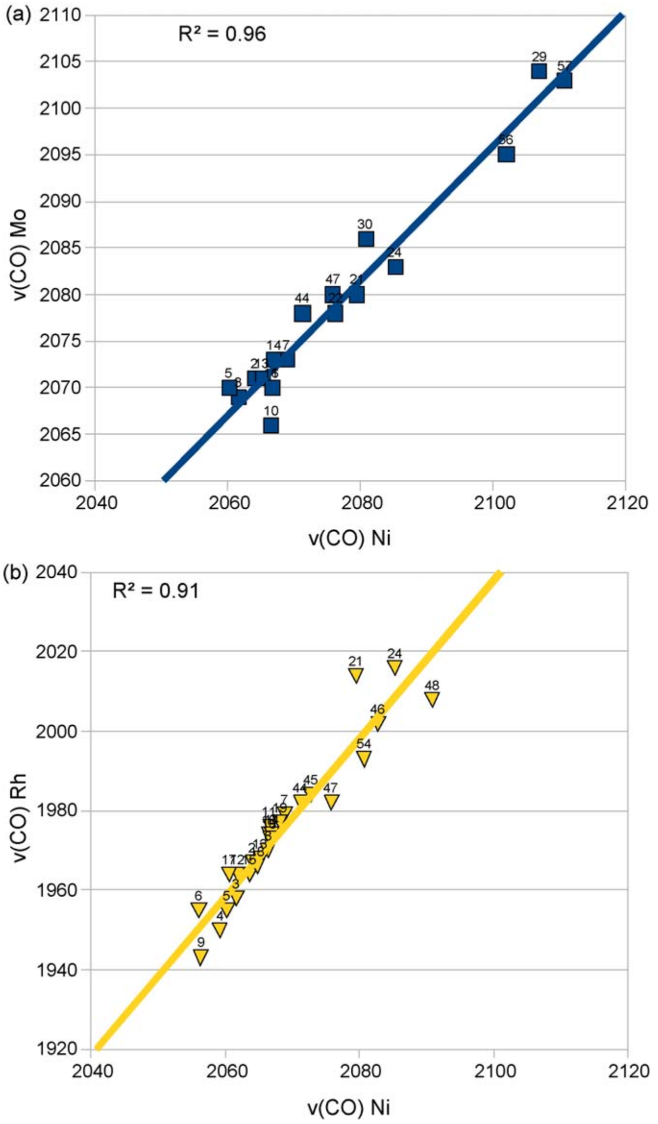


Fig. 1. Correlation between ν(CO) in $[Ni(CO)_3P]$ and (a) $[Mo(CO)_5P]$ and (b) $[Rh(CO)ClP_2]$ (P = monodentate P(III) ligand), the number above each point refers to the entry in Table 1.

has recently been reviewed [15]. What is clear however, from the experimental data is that when electronic and steric information is combined (Fig. 2) a number of interesting features become apparent.

This, and other similar stereoelectronic maps [16], illustrate the fact that traditional PR_3 phosphine ligands (represented by squares) whilst spanning a wide range of steric demands have a much more limited set of electronic properties. When combined with data for phosphites, $P(OR)_3$, phosphinites $PR_2(OR')$, phosphonites, $PR(OR')_2$ (all represented by diamonds) and halo-containing phosphines (triangles) it becomes clear that the upper right part of the stereoelectronic map, which represents sterically demanding, electron-poor P(III) ligand systems is under represented. This is unfortunate since in some cases these are exactly the types of ligands that have demonstrated enhanced reactivity and catalytic properties [17].

The data that exists for organofluorine-substituted phosphine ligands (represented by inverted triangles) shows that these systems offer an opportunity to generate ligands that fill this void, with electronic properties more akin to those of phosphites, but a significantly larger steric demand. As such fluorinated phosphines

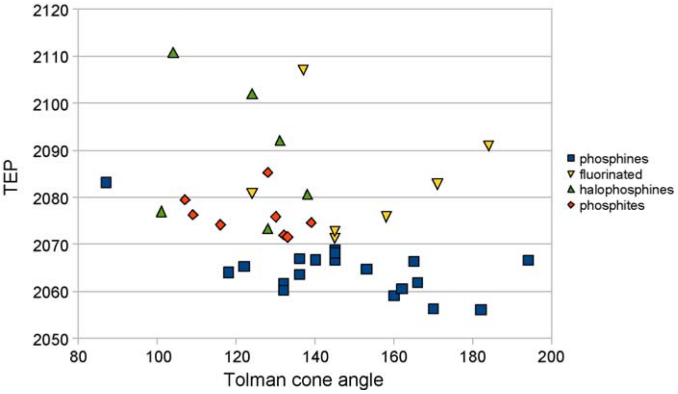


Fig. 2. A stereoelectronic map for monodentate P(III) ligands.

have the potential to provide P(III) ligands with properties which are distinct from both perprotio-phosphines and phosphites [18]. To date the majority of known $PR_{3-n}(R_f)_n$ (n = 1–3) systems contain fluoroaryl substituents, an area which has recently been reviewed [19]. A second family of ligands that have been studied in some detail are those that possess long fluorinated chains, such as $CH_2CH_2(CF_2)_nCF_3$ (n = 5, 7), for use in fluorous-biphase systems [20]. These ligands typically include a non-fluorinated $-C_6H_4-$ or $-CH_2CH_2-$ "spacer" group in order to insulate the phosphorus centre from the electronic effects of the fluorocarbon chain and because of this they resemble non-fluorinated phosphines in both steric and electronic respects.

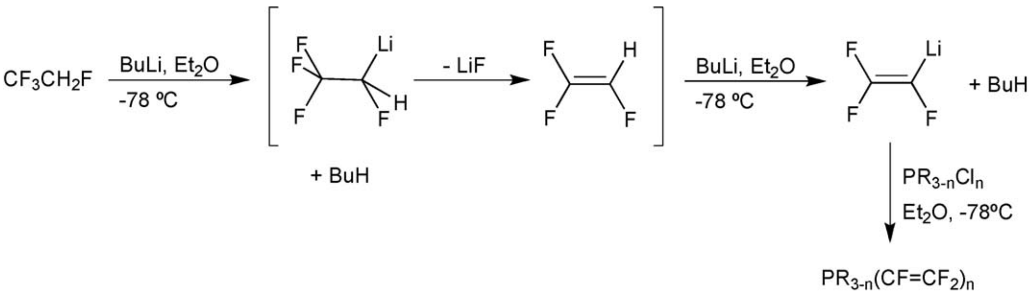
The potential that organofluorine-containing P(III) systems offer to modify the steric demands and electronic properties of traditional systems, coupled with the synthetic challenges that exist in this area of chemistry ensures that this continues to be an actively pursued research area in academia and industry. The remainder of this paper describes work associated with monomeric P(III) systems containing one or more perfluorinated, non-aromatic group.

2. Results and discussion

2.1. Fluoroalkenyl-containing phosphines

Fluoroalkenyl-containing phosphines, such as those containing a perfluorovinyl group, have been known since 1960 [21]. Initially these compounds were prepared by the low temperature reaction of an appropriate chlorophosphine with the Grignard reagent derived from $F_2C{=}CFI$ [22], or $LiCF{=}CF_2$ derived from $CF_2{=}CFBr$ and MeLi [23]; these two methods accounted for the synthesis of perfluorovinyl-containing phosphines of the type $P(CF{=}CF_2)_3$, $PR_{3-n}(CF{=}CF_2)_n$ (n = 1,2; R = Ph, NMe_2, NEt_2, EtO and BuO). More recent approaches have utilised CF_3CH_2F (HFC-134a) as the perfluorovinyl-synthon, as shown in Scheme 1 [24], and have provided perfluorovinyl-containing phosphines with R = Cl, Et, *i*-Pr, Ph, Cy and the P-chiral compound $PPhBu(CF{=}CF_2)$ [25–27]. In an analogous fashion 1-chloro-2,2-difluorovinyl phosphines can be prepared from CF_3CH_2Cl [28].

Shortly after the first reports of perfluorovinyl phosphines a number of their spectroscopic properties, including NMR [29], IR [30] and modes of fragmentation in mass spectrometry experiments [31], were published, along with a limited number of examples of their reactivity. Cowley and Taylor prepared $PCl_{3-n}(CF{=}CF_2)_n$ from the reaction of $P(Me_2N)_{3-n}(CF{=}CF_2)_n$ with HCl, and subsequently converted that to $F_2P(CF{=}CF_2)_n$ by reaction with SbF_3 [32]. Horn and Kolkmann reported that when preparing *tris*(perfluorovinyl)phosphine from PCl_3 and an excess of CF_2CFLi nucleophilic attack of the resulting $P(CF{=}CF_2)_3$ occurred to give a



Scheme 1.

product which was formulated as $(F_2C{=}CF)_2PCF{=}CF{-}CF{=}CF_2$, whilst the reaction of $P(CF{=}CF_2)_3$ with methyl lithium gave $(F_2C{=}CF)_2PCF{=}CFMe$, and with $LiPPh_2$ $(F_2C{=}CF)_2PCF{=}CFPPh_2$ and $P(CF{=}CFPPh_2)_3$ were reported [33]. However, until 1999 there was no coordination chemistry of these P(III) compounds published, and hence little characterisation of their ligand properties. We [27,28], and subsequently others [34], have developed the derivatisation and coordination chemistry of these ligands.

The fluorovinyl phosphines are typically non-malodorous, and generally stable towards water and aerial oxidation, although they can be oxidised to their P(V) analogues, $P(E)R_{3-n}(CF{=}CF_2)_n$ (E = O, S, Se) with hydrogen peroxide, elemental sulfur and selenium respectively [25], or by reaction with Me_3SiN_3 to quantitatively give $Ph_2(CF_2{=}CF)P{=}NSiMe_3$ [35]. Stereospecific replacement of the fluorine *trans*-to the phosphorus centre can also be achieved, for example hydrogen can be introduced by reaction with $LiAlH_4$ or $LiAlH(OBu)_3$, whilst R′Li reagents (R′ = alkyl) result in the incorporation of R′ via an addition elimination reaction [26].

In contrast to the general stability of these phosphines in many of the reactions investigated we found that in studies of the quaternisation of these systems many of the compounds showed poor stability. For example, the reaction of $PPh_2(CF{=}CF_2)$ with methyliodide results in the isolation of a solid product for which neither the NMR spectra or elemental analysis correspond to the anticipated product, $[Ph_2P(CF{=}CF_2)Me]^+I^-$. The $^{31}P\{^1H\}$ NMR spectrum showed a doublet of quartets (*J*PF = 64, 3 Hz) at 22.6 ppm, shifted ca. 50 ppm from the starting phosphine whilst the ^{19}F NMR spectra show the presence of a CF_3 group as a doublet of doublet of doublets at −68.7 ppm and a CFH group as an overlapping doublet of doublet of quartets at −214.4 ppm. Taken together these data suggest the presence of a phosphorus-bound $-CFHCF_3$ group. In a similar fashion the reaction of benzyl bromide with $Ph_2P(CF{=}CF_2)$ resulted in NMR data which was consistent with $[Ph_2P(CFHCF_3)(CH_2Ph)]Br$, the identity of which was subsequently confirmed in the solid state by X-ray diffraction, the resulting structure is shown in Fig. 3.

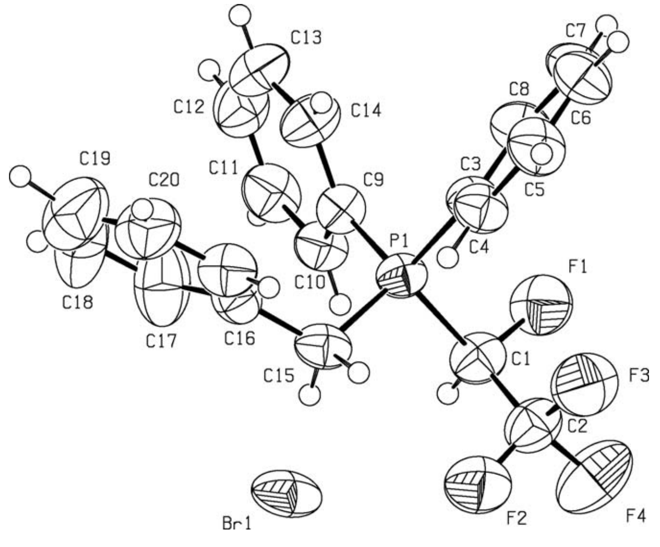


Fig. 3. An ORTEP representation of the solid state structure of $[Ph_2P(CH_2Ph)(CHFCF_3)]Br$. Selected bond lengths: P1-C1 = 1.850(4), P1-C3 = 1.782(3), P1-C9 = 1.794(3), P1-C15 = 1.806(4), C1-C2 = 1.504(6) Å; selected angles: C1-P1-C3 = 108.76(18), C1-P1-C9 = 106.87(18), C1-P1-C15 = 105.88(18), C3-P1-C9 = 108.79(17), C3-P1-C15 = 114.42(17), C9-P1-C15 = 111.79(17)°.

The crystal structure of $[Ph_2P(CFHCF_3)(CH_2Ph)]Br$ shows the presence of the two phenyl, one benzyl and the $CHFCF_3$ group coordinated to the phosphorus centre in an approximately tetrahedral arrangement. The P–C bond lengths to the non-fluorinated groups are within the range 1.782(3)–1.806(4) Å, whilst the $P{-}CHFCF_3$ bond length is significantly longer at 1.850(4) Å and *d*(C1–C2) = 1.504(6) Å. There are no X-ray data for a $CFHCF_3$ group bonded to phosphorus within the CCDC database [36], although carbon and Pd and Pt-based systems have been characterised, the latter being formed by the oxidative addition of CF_3CFHI to $[M(TMEDA)Me_2]$ (M = Pd, Pt) followed by reductive elimination of MeI [37,38]. The most similar quaternary phosphine to have been structurally characterised is $[Ph_2MePCF_2CF_2Br]^+I^-$. MeI in which the average P–Ph bond length is 1.774(6) Å, the $P{-}CF_2CF_2Br$ distance is 1.912(8) Å, and *d*(C–C) of the halogenated fragment is 1.539(4) Å [39].

Since the fluorovinyl phosphines are not water sensitive it is assumed that the anticipated perfluorovinyl-containing phosphonium salt is initially formed, and that this cation is sensitive to nucleophilic attack by adventitious moisture which results in the generation of some HF. This subsequently adds across the vinyllic double bond of another perfluorovinyl phosphonium salt to give the observed $-CFHCF_3$ containing product, in much the same way that HBr was observed to add across the C=C bond of $Ph_2P(O)CF{=}CF_2$ [26]. Further support for this interpretation comes from studies involving other phosphines and organoiodides. The slow reaction between $Ph_2P(CF{=}CF_2)$ and iodobenzene was followed by NMR spectroscopy. After a period of 4 weeks the peaks due to the perfluorovinyl-containing phosphine starting material were reduced in intensity and new mutually coupling signals were observed at 19.1 ppm in the $^{31}P\{^1H\}$ spectrum and in the fluorine NMR spectrum (−79.9, −101.4 and −186.6 ppm) which confirm the presence of a new perfluorovinyl-containing phosphorus species. All the NMR data is consistent with $[Ph_3P(CF{=}CF_2)]^+I^-$, but we cannot be unequivocal of the identity of this species since attempts to isolate it hastened the decomposition. After leaving to stand for a further 8 days the signals due to the starting phosphine were no longer apparent and those of the intermediate species were being replaced by a new signal in both the fluorine and phosphorus NMR spectra indicative of decomposition.

Interestingly, quaternisation of *i*-$Pr_2PCF{=}CF_2$ with methyliodide, according to NMR evidence, proceeds to the anticipated quaternary phosphonium species, but in this case the product appears to be more stable. The $^{31}P\{^1H\}$ NMR spectrum displays a signal at 42 ppm, which is shifted approximately 50 ppm from the starting material. Even after a week in solution there was no sign of decomposition, however, attempts to work-up and isolate the product was unsuccessful due to decomposition. Furthermore, attempts to quaternise the P(III) compounds containing more than one perfluorovinyl group, such as $PhP(CF{=}CF_2)_2$ or *i*-$PrP(CF{=}CF_2)_2$ were completely unsuccessful. These observations are in line with the expected trend in nucleophilicity of these compounds.

The coordination chemistry of these ligands has been investigated in a number of molybdenum, rhodium, palladium, platinum and gold systems [25,27,28,35]. Some of these complexes have been crystallographically characterised, and in those cases it has been possible to estimate the cone angles of the ligands involved. Such studies suggest that the cone angles for the mono-substituted perfluorovinyl phosphines range from ca. 152° for $PEt_2(CF{=}CF_2)$ to 169° for $PCy_2(CF{=}CF_2)$. Interestingly the cone angle for $PhP(CF{=}CF_2)_2$ (161°) appears to be somewhat smaller than that of $PhP(C_6F_5)_2$ (171°) and this is suggested as the reason why $PhP(CF{=}CF_2)_2$ will form a complex with $[Cp^*RhCl(\mu\text{-}Cl)]_2$ but that $PhP(C_6F_5)_2$ does not [40]. It was also shown that intramolecular dehydrofluorinative coupling of rhodium bound pentafluoromethylcyclopentadienyl and perfluorovinyl phosphine ligands can occur. In these reactions the fluorine *cis*- to the phosphorus centre is lost, as HF, as coupling to one of the CH_3 groups of the Cp* ligand occurs. The reaction is not, however, clean and by-products containing CF_3CHF-phosphines, similar to those observed in the quaternisation reactions are also detected.

In order to assess the electronic properties of these ligands two approaches have been used; the first was based on $^1J(PX)$ coupling constants in $P(Se)R_n(CF{=}CF_2)_m$ compounds (*vide supra*) or platinum or rhodium metal complexes whilst the second was based on the $\nu(CO)$ stretching frequencies of $[Mo(CO)_5P]$ and $[RhP_2(CO)Cl]$ (P = monodentate P(III) ligand) complexes. Comparison of the carbonyl stretching frequencies obtained from the rhodium complexes demonstrate that they are poorer donors than non-fluorinated phosphines, e.g. for the complex of $PhP(CF{=}CF_2)_2$ $\nu(CO) = 2002\ cm^{-1}$ which compares with $1979\ cm^{-1}$ for PPh_3, $1996\ cm^{-1}$ for $PhP(C_6F_5)_2$ [40], and $2014\ cm^{-1}$ for $P(OMe)_3$, Table 1. Thus, whilst the perfluorovinyl group appears to have a smaller steric demand than $-C_6F_5$, it appears to possess a comparable electron-withdrawing effect, and this is reflected in the χ values for these groups both of which are ca. 10, which is larger than that found for many OR groups, e.g. $\chi(OEt) = 6.8$.

Whilst the *tris*-substituted compounds $E(CF{=}CF_2)_3$ (E = P, As, Sb) have been prepared before [21], none have been structurally characterised, or assessed as ligands. We were able to prepare all of these materials in good to moderate yields, but we were completely unsuccessful in getting them to coordinate to metal centres. We were equally unsuccessful in obtaining solid state structures of $P(CF{=}CF_2)_3$ and $Sb(CF{=}CF_2)_3$, both of which froze as glassy solids. However, $As(CF{=}CF_2)_3$ could be frozen *in situ* on the diffractometer within a capillary tube to give a crystalline solid, and the data collected were solved to give the representation of the solid state structure shown in Fig. 4. The three As–C distances lie within the range 1.922(4)–1.938(4) Å, whilst the C–F distances show somewhat greater variation, ranging from 1.313(4) to 1.353(4) Å and the average C–As–C bond angle is 96.86(16)°. This constitutes the first structurally characterised perfluorovinyl-containing arsenic compound, and the first example of a neutral homoleptic perfluorovinyl compound of any p-block element. Moreover, the cone angle of this compound is calculated as 189°, which suggests that the corresponding upper limit for $P(CF{=}CF_2)_3$ is 187°, based on a previous comparison of values observed for a series of PR_3 and AsR_3 compounds [41].

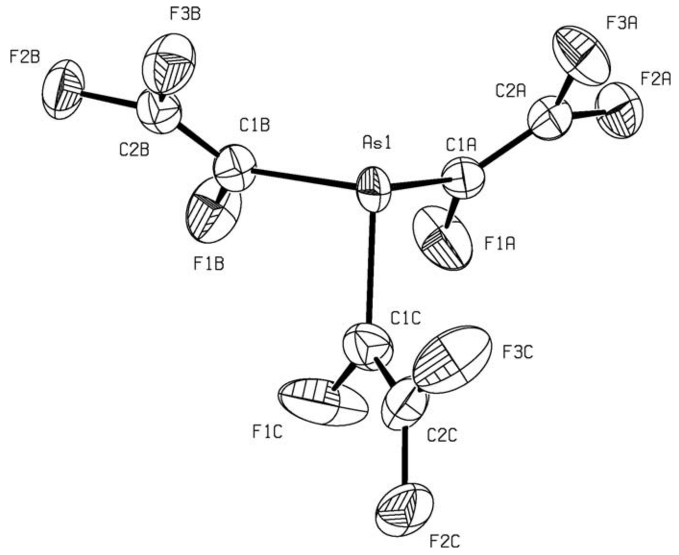


Fig. 4. ORTEP representation of the solid state structure of $As(CF{=}CF_2)_3$. Selected bond lengths: As1-C1a = 1.922(4), As1-C1b = 1.934(3), As1-C1c = 1.938(4), C1a-C2a = 1.301(5), C1a-F1a = 1.349(4) C2a-F2a = 1.314(4), C2a-F3a = 1.316(4) Å; selected angles: C1a-As1-C1b = 97.57(17), C1a-As1-C1c = 96.41(15), C1b-As1-C1c = 96.59(15), As1-C1a-C2a = 122.3(3), C2a-C1a-F1a = 116.5(3), C1a-C2a-F2a = 126.3, C1a-C2a-F3a = 123.6(3), F2a-C2a-F3a = 110.1°.

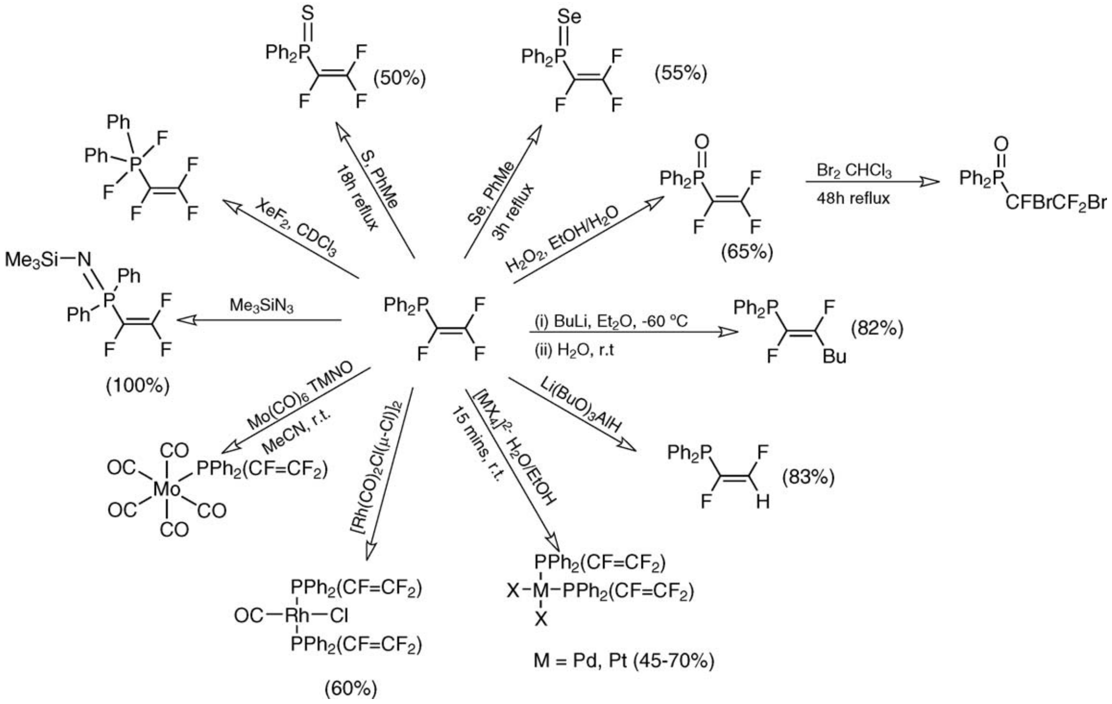
Thus fluoroalkenyl-containing phosphines of the type $PR_{3-n}(CF{=}CF_2)_n$ (n = 1–3) derived from HFC-134a provide a straightforward way of generating a series of P(III) ligands with electronic properties which may be systematically varied by changing n and R. Their electronic properties lie between those of traditional phosphines and phosphites according to measures of their carbonyl stretching frequencies in metal complexes. It is also possible to tailor the steric demand of these systems from ca. 150–170° by modification of the ancillary R-group. The detailed parameters are given in Table 1, and a summary of the reactivity of perfluorovinyl-containing phosphines, exemplified by $Ph_2P(CF{=}CF_2)$, is presented in Scheme 2.

There have been a limited number of studies of more extended perfluorinated alkenyl P(III) systems, to date these have mainly been of the *E*- and *Z*-isomers of $R_2P(CF{=}CFCF_3)$ (R = Me, Et, *t*-Bu, Ph, MeO, EtO, Et_2N) which have been prepared either from the Grignard reagent derived from $CFI{=}CFCF_3$ or by reaction of a $F_2C{=}CFCF_3$ with R_2PH [42]. There are, as far as we are aware, no published reports of the coordination chemistry of these P(III) ligands.

2.2. Fluoroalkynyl-containing phosphines

The simplest fluoroalkynyl-containing P(III) system should be those based on $-C{\equiv}C{-}F$, however, there are no published reports of these compounds, which is not surprising considering the known instability of fluoroalkynes. Indeed, the only known perfluoroalkynyl-containing P(III) compounds are those of $-C{\equiv}C{-}CF_3$ and $-C{\equiv}C{-}C_6F_5$ [43], although a greater range of P(V) species of the type $(RO)_2P(O)(C{\equiv}C{-}R_f)$ (R = Me, Et, *i*-Pr, Ph; $R_f = CF_3$, C_2F_5, C_3F_7, CF_2Cl and CF_2H) have been prepared and their applications and conversions, for example to fluoroalkylated vinylphosphonates, have been studied [44].

A number of synthetic routes to Li(tfp) (tfp = $CCCF_3$) exist based on a variety of starting materials. In 1952 Henne and Nager reported the preparation of the Grignard reagent EtMg(tfp), derived from the metathesis of F_3CCCH and EtMgBr [45], whilst in 1971 Carty et al. obtained the lithium alkynyl reagent by deprotonation of 3,3,3-trifluoropropyne [46]. More recently, because of difficulties in obtaining CF_3CCH a number of alternative routes have been proposed. These include the dechlorination of



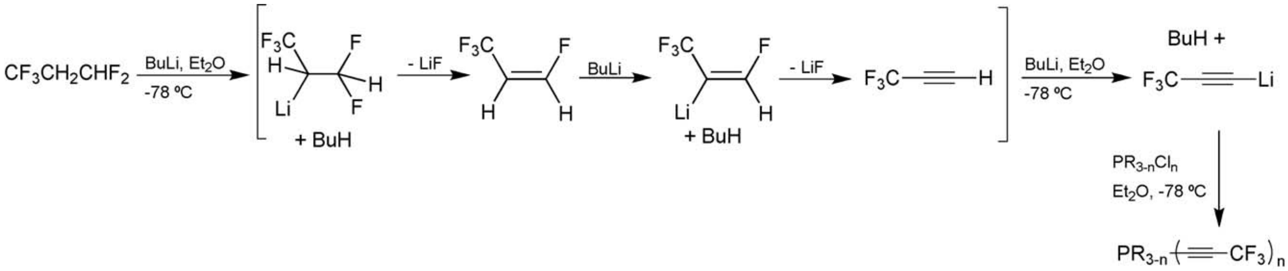
Scheme 2.

$CF_3CCl{=}CCl_2$ with zinc dust in DMF at 100 °C to give $F_3CCCZnCl$ [47], and the generation of Li(tfp) from $F_3CCBr{=}CH_2$ treated with two equivalents of LDA at −78 °C [48]. In 2002 we reported that the commercially available hydrofluorocarbon $CF_3CH_2CHF_2$ (HFC-245fa), on treatment with three equivalents of *n*-butyl lithium, results in $LiC{\equiv}CCF_3$ (Scheme 3) [49], whilst more recently Shimizu et al. published the reaction of 1,1,1-trifluoro-3,3-dichloroacetone with tosyl chloride and triethylamine in DCM to give the enol tosylate which on treatment with two equivalents of *n*-BuLi generates the same lithium reagent [50].

Despite the existence of a number of synthetic routes to Li(tfp) the only trifluoropropenyl-containing phosphorus(III) compounds that have been reported in the literature are Ph_2P(tfp), $(Et_2N)_2P$(tfp), PhP$(tfp)_2$ and P$(tfp)_3$, none of which have been structurally characterised either in isolation or when acting as simple σ-donor ligands towards metal centres. Indeed when coordination studies have been undertaken, with Co, Rh, Pd and Pt metal centres, the phosphines were found to coordinate as bidentate donors. The phosphine would act as a σ donor to one metal centre and as a π donor to a second metal [51]. Subsequent reactions of the metal-bound P(III) systems with amines [52], alcohols [53] and secondary phosphines [54] have been investigated, all of which resulted in coupling of the phosphine ligands with the incoming reagent.

It is because of their bifunctional nature and the versatility they offer in synthesis and coordination chemistry that alkynyl-containing phosphines have attracted attention [55]. The recent application of such systems includes the generation of heterocycles, proposed catalysts for Heck–Mizoroki carbon–carbon cross-coupling reactions [56] and the activation of C–H bonds [57]. There has also been theoretical studies of the electronic structures of a series of phosphoralkynyls, including those containing the $P{-}C{\equiv}CCF_3$ fragment [58].

We were interested to see whether the electron-withdrawing effect of the remote CF_3 group would be transmitted via the C≡C bond to the phosphorus centre and so offer a relatively small, but electronically-poor substituent for phosphines. A number of trifluoropropynyl-containing phosphines were prepared using the method outlined in Scheme 3. Subsequent reaction of these ligands with $[Mo(CO)_6]$ afforded complexes of the type $[Mo(CO)_5P]$ from which the CO stretching frequency was obtained. Interestingly, the data obtained suggests that despite the distance of the CF_3 group from the phosphorus centre the total electronic effects of the ligand are nearly the same as that derived from the perfluorovinyl group. For example, ν(CO) of $[Mo(CO)_5\{Ph_2PC{\equiv}CCF_3\}]$ is observed at 2077 cm^{-1}, the same value as that found for the $Ph_2PCF{=}CF_2$ analogue, whilst for $[Mo(CO)_5\{PhP(C{\equiv}CCF_3)_2\}]$ and $[Mo(CO)_5\{PhP(CF{=}CF_2)_2\}]$ the corresponding values are 2085 and



Scheme 3.

2084 cm^{-1}. However, not surprisingly, the trifluoropropynyl-containing ligand possesses a smaller steric demand, the cone angle of $i\text{-}Pr_2PC{\equiv}CCF_3$ is estimated to be 156°, bigger than that of $i\text{-}Pr_3P$, but 9° smaller than that of perfluorovinyl-containing analogue at 165° [59].

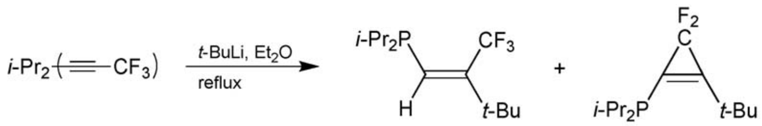
The trifluoropropynyl-containing phosphines are found to be somewhat more reactive than the perfluorovinyl analogues. Thus, unlike for the perfluorovinyl P(III) systems slow decomposition at room temperature is observed for the $-C{\equiv}CCF_3$ phosphines. One other area where the greater reactivity of these compounds becomes obvious is on reaction with alkyl lithium reagents. Previously we have shown that reaction of a main-group trifluoropropynyl compound with *t*-BuLi results in two possible products after work-up, one of which corresponds to an unusual cyclisation process [60]. The reaction of *t*-BuLi with $i\text{-}Pr_2PC{\equiv}CCF_3$ dissolved in ether was studied at a series of different temperatures. Two phosphorus-containing products were evident in the $^{31}P\{^1H\}$ NMR spectra, the proportions of which changed considerably with temperature. When the reaction is carried out at −20 °C, after work-up, the predominant product is characterised as $i\text{-}Pr_2P(Z\text{-}CH{=}CF_3(t\text{-}Bu))$, which arises from the syn-addition of *t*-BuLi across the triple bond with the direction of addition being consistent with both the sterics and electronics of the precursor. But on increasing the temperature the proportion of the second product increased, until by 40 °C it constituted 90% of the isolated material (Scheme 4). The identity of this second product was initially inferred from multinuclear NMR data; the fluorine NMR spectrum displayed a doublet (J(PF) = 4 Hz) at −103.3 ppm whilst the $^{13}C\{^1H\}$ data showed triplets due to coupling with two fluorine nuclei at 106.2 (*J*(CF) = 273 Hz), 122.7 (*J*(CF) = 14 Hz) and 149.2 ppm (*J*(CF) = 10 Hz). These data are consistent with those previously observed for the *gem*-difluorocyclopropene unit obtained in a similar reaction on silicon based systems [60]. Because this cyclisation reaction is not observed for less sterically demanding RLi reagents we have suggested that steric congestion which resulted following the addition of *t*-BuLi across the triple bond resulted in elimination of LiF and concomitant cyclisation. An alternative explanation might be that addition of *t*-BuLi is followed by $LiCF_3$ elimination which decomposes to generate LiF and difluorocarbene which then adds back across the triple bond. We have investigated this reaction in a variety of solvents and over a range of temperatures in an attempt to provide additional information on this unusual process. However, even when a good difluorocarbene acceptor, such as cyclohexene, is used as solvent we have been unable to detect any product from the addition of difluorocarbene to the cyclohexene. We therefore have no evidence against an intramolecular process, but equally we concede that we cannot distinguish this from a process where $LiCF_3$ is produced, decomposes and recombines all within the primary coordination sphere.

Reaction of this unusual P(III) ligand with $[PtI_2(COD)]$ resulted in the formation of a light orange-coloured solid, the phosphorus NMR spectrum of which exhibits a singlet at δ 24.3 ppm, ca. 30 ppm more positive than that of the uncoordinated phosphine, with platinum satellites (^{195}Pt, $I = 1/2$, 33%), $^1J(PtP) = 3453$ Hz. Recrystallization from dichloromethane–hexane resulted in crystals suitable for X-ray diffraction, and the solid-state structure of the product, $[PtI_2\{Pi\text{-}Pr_2(C_3F_2t\text{-}Bu)\}_2]$, is shown in Fig. 5. It confirms, as expected from the magnitude of the platinum–phosphorus coupling constant, a *trans*-arrangement of the ligands around a square-planar platinum centre, with the metal siting on a crystallographic centre of symmetry. The bond lengths and angles observed in this complex are largely unexceptional; the Pt–P bond length is 2.3201(9) Å, which is comparable to of 2.318(2) Å found for *trans*-$[PtI_2(PPh_3)_2]$ [61]. From the data we can determine a cone angle value of 171°, which makes this one of the bulkiest fluorocarbon P(III) ligands we have yet prepared. This is the first structurally characterised example of any phosphorus ligand containing a cyclopropene unit, however, Chen and co-workers have published the structures of two phenyl-substituted *gem*-difluorocyclopropene systems [62,63].

2.3. Fluoroalkyl-containing phosphines

The third class of monodentate organofluorine P(III) compounds – those containing phosphorus-bound perfluoroalkyl groups – is largely restricted to $-CF_3$ and $-CF_2CF_3$ containing compounds. This is because of the limited number of suitable perfluoroalkyl-delivery reagents; perfluoroalkyl Grignard and lithium reagents are thermally unstable (e.g. LiC_2F_5 decomposes above −70 °C) or inaccessible (e.g. $LiCF_3$). A variety of specialised methods have therefore been developed, those that have some generic capabilities include: direct fluorination of PR_3 with F_2 (followed by reduction of the resulting P(V) $P(R_f)_3F_2$ species) [64] and electrochemical fluorination of PR_3 in anhydrous HF [65]. For trifluoromethyl-containing phosphines the principal historical methods have relied on the reaction of perfluoroalkyl transfer agents, such as $Hg(CF_3)_2$, $Cd(CF_3)_2.DME$ or $Te(CF_3)_2$ with PI_3 [66] or heating P_4 with R_fI [67]. Perfluoroethyl-containing phosphines are usually prepared from the reaction of an appropriate chlorophosphine with LiC_2F_5 at low temperature [68].

Because of the limitations in R_f^- delivery reagents a number of alternative methods and starting materials have been investigated. One of the simplest and readily available starting materials to use would be the commercially available perfluoroalkyl iodides. However, unlike their perprotio analogues, these tend to be resistant to S_N1 and S_N2 reactions due to a combination of the polarization of the R_f–I ($C^{\delta-}$–$I^{\delta+}$) bond and steric and lone-pair repulsion from the fluorine substituents. Fortunately, for soft



temp. / ºC			unreacted
40	90	10	0
20	75	14	11
0	55	38	7
-20	7	58	34

Scheme 4.

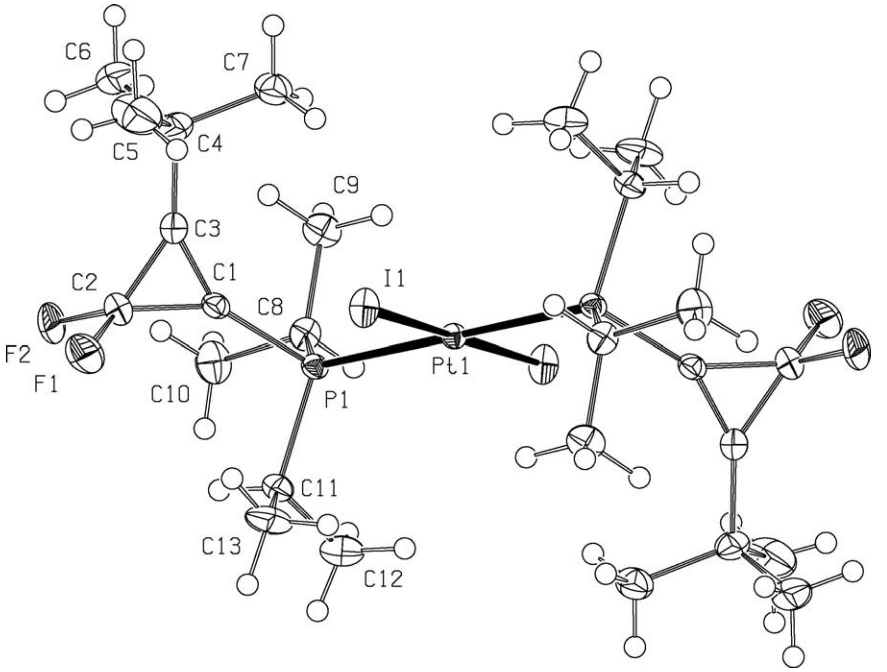


Fig. 5. An ORTEP representation of the solid state structure of *trans*-[$PtI_2\{Pi\text{-}Pr_2(C_2F_3t\text{-}Bu)\}_2$]. Selected bond lengths: Pt1-I1 = 2.6191(3), Pt1-P1 = 2.3201(9), P1-C1 = 1.799(4), P1-C8 = 1.848(4), P1-C11 = 1.841(4), C2-C3 = 1.425(5), C2-F1 = 1.365(4), C2-F2 = 1.376(4) Å; selected angles: I1-Pt1-P1 = 89.53(2), Pt1-P1-C1 = 115.89(13), Pt1-P1-C8 = 117.50(13), Pt1-P1-C11 = 113.80(12), C1-P1-C8 = 99.37(17), C1-P1-C11 = 102.14(17), C8-P1-C11 = 106.09(18), 114.42(17), P1-C1-C2 = 147.0(3), C1-C2-C3 = 55.2(2), C1-C3-C2 = 63.3(3), C1-C2-F1 = 122.7(3), C1-C2-F2 = 122.6(3)°.

nucleophiles, such as those of phosphorus, the $S_{RN}1$ radical–anion chain mechanism is possible. Indeed, Vaillard et al. proposed this for the reaction of Ph_2PNa with n-C_4F_9I or n-$C_6F_{13}I$ in HMPA under photolytic conditions, which yielded, after oxidation, $Ph_2P(O)(n$-$C_4F_9)$ and $Ph_2P(O)(n$-$C_6F_{13})$ in 55–85% yields [69].

We have also investigated this approach as a method of preparing fluoroalkyl-containing phosphines with the emphasis on sterically demanding R_f groups. The addition of i-C_3F_7I to a THF solution of Ph_2PLi (prepared from Ph_2PCl and lithium wire) results in an almost immediate loss of the colour associated with Ph_2PLi. Subsequent addition of hexane followed by filtration, to remove lithium halides, resulted in a low melting point solid, the $^{31}P\{^1H\}$ and ^{19}F NMR spectra of which are shown in Fig. 6. The phosphorus NMR spectrum exhibits an overlapping doublet of septets, and the fluorine NMR spectrum shows a doublet of doublets and a doublet of septets in the ratio of 6:1. These spectra are consistent with the anticipated A_6MX spin-system of $Ph_2P(i$-$C_3F_7)$, and was confirmed as the identity of the product subsequently by elemental analysis and finally a single-crystal X-ray structure [75].

The preparation of lithium phosphides is straightforward either from the reaction of chloro- or dichloro-phosphines with lithium wire in THF, or by cleavage of a P–Ar bond of an aryl-phosphine. By reaction of these phosphides with a number of R_fI compounds it is potentially possible to generate a fairly large library of perfluoroalkyl-containing phosphines. The reaction of Ph_2PLi and i-Pr_2PLi with a variety of R_fI compounds was undertaken, including CF_3I, C_2F_5I, i-C_3F_7I, s-C_4F_9I, t-C_4F_9I and c-$C_6F_{11}I$; the results of these reactions are summarised in Table 2. Unfortunately, the yields of fluoroalkylphosphines prepared in this way tended to be low and so alternative routes have been investigated (Scheme 5).

In 2005 Caffyn and co-workers reported that $P(R_f)_3$ compounds can be obtained from the reaction of Me_3SiR_f with $P(OR)_3$ (R = Ph, p-C_6H_4CN) [70]. Subsequently Togni and co-workers synthesised CF_3-containing phosphines from the reaction of R_2PH or Ph_2PSiMe_3 and CF_3-containing hypervalent iodine compounds [71], Scheme 5. Both of these methods benefit from the commercial availability of trifluoromethyl-containing starting materials such as Me_3SiCF_3. Whilst the first of these methods provides a generic route to $P(R_f)_3$ compounds it relies on the availability of Me_3SiR_f reagents, of which only a few are commercially available. The second procedure offers the possibility of generating a family of $PR_2(CF_3)$ compounds, but is equally difficult to extend to other fluoroalkyl groups. One approach that has been successful for the synthesis of fluoroaryl-containing phosphines involves the reaction of trimethylsilyl-containing phosphanes with polyfluoroarenes [72]. In that reaction, and a similar one reported by Oshima and co-workers on tertiary organofluorides [73], a C–F bond is replaced by a C–P bond and Me_3SiF is generated. A similar approach has been employed for the generation of some perprotio-phosphines and, under transition metal-catalysed conditions, $Ph_2P(CF_2)_nBr$ and $Ph_2P(CF_2)_nPPh_2$ from Ph_2PSiMe_3 and $Br(CF_2)_nBr$ (n = 1 or 2]) [74]. We were surprised to find that this strategy does not appear to have been applied to the synthesis of perfluoroalkyl-containing phosphanes.

The reaction of R_2PSiMe_3 with i-C_3F_7I at −20 °C in hexane, after work-up, resulted in white-coloured solid material, the NMR spectra of which showed the same $^{31}P\{^1H\}$ and ^{19}F signals as those observed for the product of the reaction between i-C_3F_7I with Ph_2PLi. Significantly, the reaction is quicker and the product, $Ph_2P(i$-$C_3F_7)$, could be isolated in yields of more than 70%. Extending this work to a wide range of R_fI compounds ($R_f = CF_3$, C_2F_5, i-C_3F_7, s-C_4F_9, t-C_4F_9, c-C_6F_{11}) allowed for the synthesis of a number of R_2PR_f analogues, as shown in Table 2 [75]. The spectroscopic data for Ph_2PCF_3 [70] and $Ph_2PCF_2CF_3$ [68] agrees with those previously reported. We found that the reactions with primary, short-chain perfluoroalkyl groups were significantly slower than the reactions with the secondary and tertiary iodides, whilst reactions with perfluoroaryliodides and perfluorovinyliodides were unsuccessful after 5 days. We have subsequently investigated a number of variations of the procedure, such as the addition of a fluoride catalyst, replacing the silyl phosphine with Ph_2PH and using perfluoroalkyl chlorides or bromides, instead of

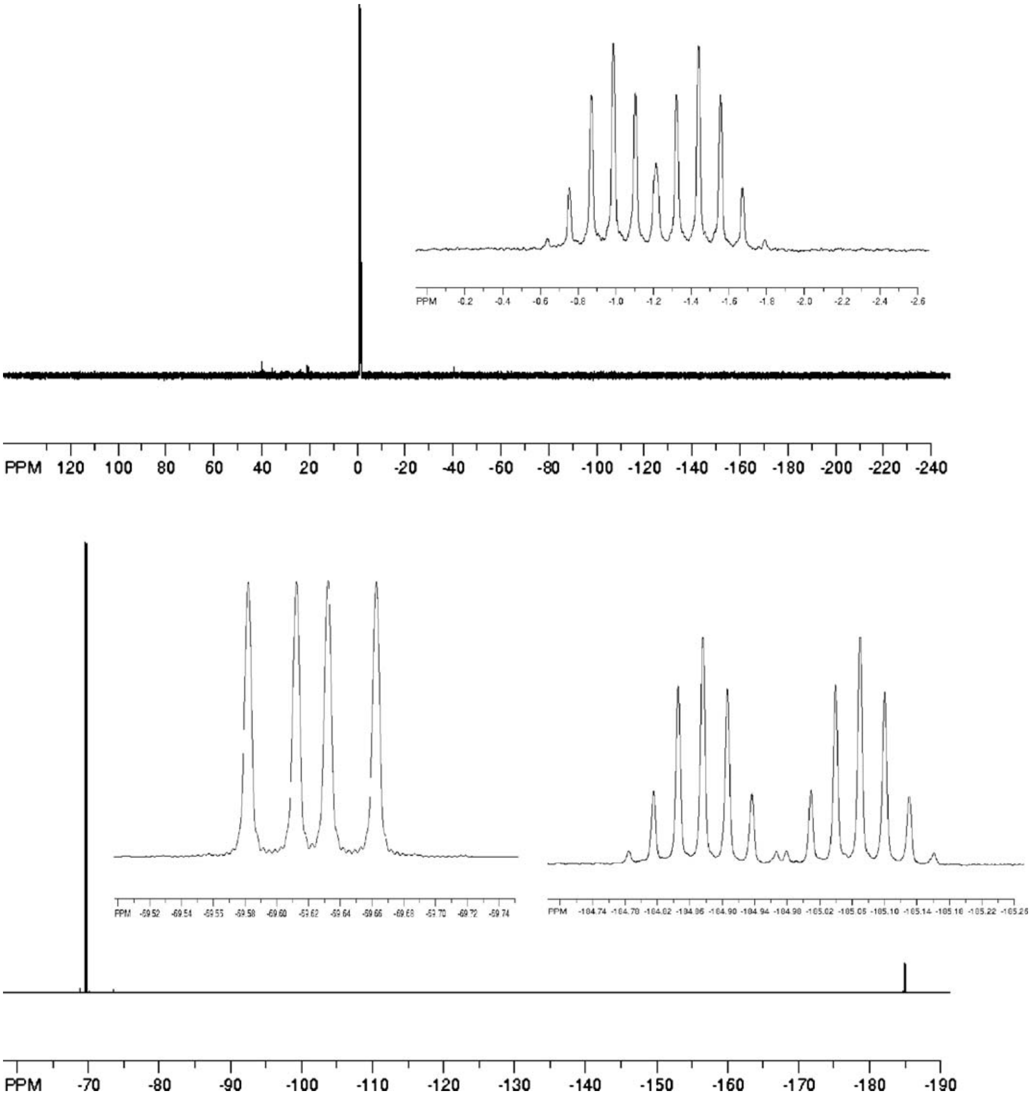


Fig. 6. (a) $^{31}P\{^1H\}$ and (b) ^{19}F NMR spectra of $Ph_2P(i\text{-}C_3F_7)$ in $CDCl_3$ solution, with expansions.

iodides. However, none of these modifications were found to offer any advantage.

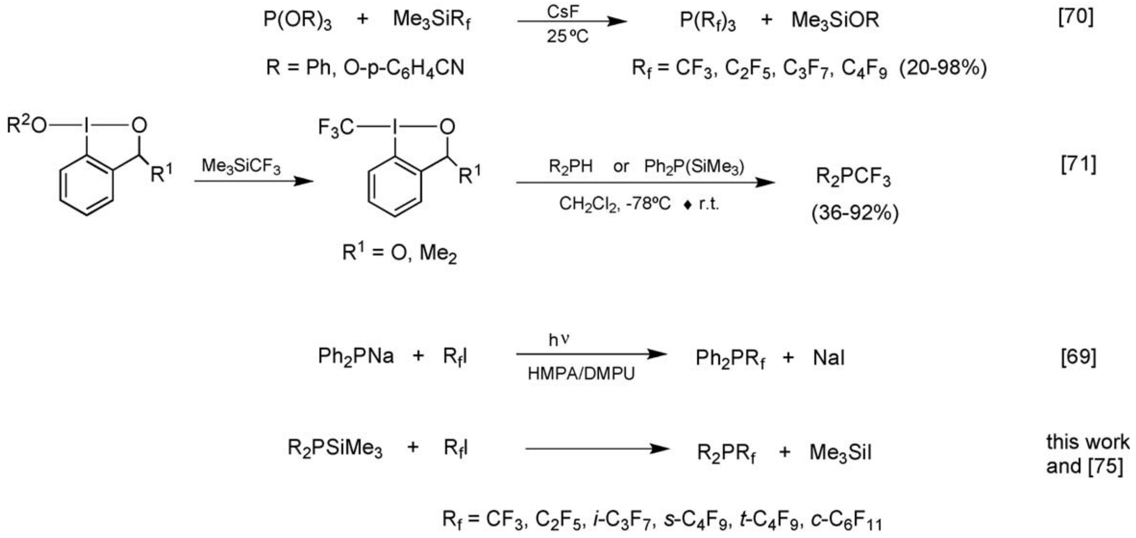
We have undertaken some studies of the reactivity and coordination chemistry of these ligands containing bulky, fluoroalkyl groups. Attempts to quaternise some of these P(III) compounds with benzyl bromide were unsuccessful, presumably because of the reduced nucleophilicity of the phosphorus centre due to the presence of the electron-withdrawing i-C_3F_7 group. However, oxidation to give the P(V) compound occurs readily; thus reaction of $Ph_2P(i\text{-}C_3F_7)$ with elemental selenium in toluene generates the selenide, from which the magnitude of the $^1J(SeP)$ coupling constant (828 Hz) can be obtained. This value is considerably higher than the values obtained for non-fluorinated phosphines, which typically lie in the range 670–730 Hz (Table 1) but is comparable with those for phosphinites (e.g. $Ph_2P(OMe)$ $^1J(SeP) = 810$ Hz) and between that measured for $Ph_2P(CF{=}CF_2)$ (785 Hz) and $PhP(CF{=}CF_2)_2$ (848 Hz) [76].

We were able to obtain an estimate of the steric demand of $Ph_2P(i\text{-}C_3F_7)$ from its molecular structure which, as expected, exhibits a pyramidal geometry at the phosphorus centre. The three P–C bond lengths are 1.828(5), 1.831(5) and 1.899(5) Å, with the longer distance being that to the fluorinated group. There are four other solid state structures of phosphines containing one, or more, perfluorinated groups, they are $PPh_2(C_2F_5)$ [68], $PPh(C_2F_5)_2$ [25], $PPh_2(C_6F_5)$ [77] and $P(C_6F_5)_3$ [78]. The P–C bond distances are similar in all five of these phosphines, but $Ph_2P(i\text{-}C_3F_7)$ appears to be the most sterically demanding mono-substituted phosphine with the sum of the angles around the phosphorus centre being 309.6°, which is larger than that observed in $PPh_2(C_2F_5)$ (304.2°),

Table 2
Selected perfluoroalkyl-containing phosphines prepared from the reaction of R_fI with silyl phosphines and lithium phosphides.

R_fI	Product	$^{31}P\{^1H\}$ NMR (δ, ppm)[a]	Method (yield)
CF_3I	Ph_2PCF_3	2.5	Ph_2SiMe_3 (75%)
C_2F_5I	$Ph_2PC_2F_5$	−1.9	Ph_2SiMe_3 (80%) Ph_2PLi (5%)
	i-$Pr_2P(C_2F_5)$	24.5	i-Pr_2SiMe_3 (52%)
$C_8F_{17}I$	$Ph_2P(C_8F_{17})$	1.1	Ph_2SiMe_3 (85%)
i-C_3F_7I	$Ph_2P(i\text{-}C_3F_7)$	−0.8	Ph_2SiMe_3 (75%) Ph_2PLi (40%)
	i-$Pr_2P(i\text{-}C_3F_7)$	41.7	i-Pr_2PLi (32%)
	$PhMeP(i\text{-}C_3F_7)$	−12.0	$PhMeSiMe_3$ (65%) $PhMePLi$ (36%)
s-C_4F_9I	$Ph_2P(s\text{-}C_4F_9)$	3.7	Ph_2SiMe_3 (56%)
c-$C_6F_{11}I$	$Ph_2P(c\text{-}C_6F_{11})$	−3.4	Ph_2SiMe_3 (48%)
t-C_4F_9I	$Ph_2P(t\text{-}C_4F_9)$	15.2	Ph_2SiMe_3 (30%)
$CF_2{=}CFI$	–		
C_6F_5I	–		

[a] Data taken from Ref. [75].



Scheme 5.

$PPh(C_2F_3)_2$ (299.6°) and $PPh_2(C_6F_5)$ (306.6°) and very similar to that of the *tris*-substituted $P(C_6F_5)_3$ (309.9°). Furthermore, we have recently obtained the first crystal structure of a metal complex of this ligand, which also suggests that the cone angle is slightly larger than $PPh_2(C_2F_5)$ in a comparable complex [76].

3. Conclusions

There is considerable interest in the synthesis and potential applications for bulky, electron-poor phosphines. P(III) systems containing fluorinated groups offer one solution to this problem, particularly in systems in which it is possible to vary the identity of the fluorinated and non-fluorinated groups which allows for the steric demand and electronic properties of the ligands to be modified in a systematic fashion. Methods exist by which such variation can be introduced into fluoroaryl, fluoroalkenyl and fluoroalkynyl based systems using Grignard or lithium reagents of suitable precursors. The replacement of CFCs with HFCs has provided a number of new fluorocarbon building blocks which can be used to readily generate fluoroalkenyl- and fluoroalkynyl-containing phosphines. Such systems are shown to possess steric and electronic properties that place them between traditional phosphines and phosphites.

The reaction of trimethysilyl-containing phosphines with perfluoroalkyliodides offers a convenient route by which the a similar variation may be applied to perfluoroalkyl-containing P(III) compounds. This general synthetic method has been successfully used to introduce secondary, tertiary and perfluorocyclohexyl groups, and as such provides, in many cases for the first time, access to a new range of sterically demanding, electron-poor fluorinated P(III) ligands. We are continuing to investigate the scope of these findings as well as the properties, coordination chemistry and application of these new ligands.

4. Experimental

Reactions were routinely performed under anaerobic conditions in flame-dried glassware, with moisture-sensitive reagents being handled under an argon atmosphere in a dry box (Belle Technologies, UK). Diethyl ether and THF were dried over sodium/benzophenone for ca. 1 day and then freshly distilled prior to use. Hexane was dried over sodium wire for ca. 1 day and then freshly distilled prior to use. CF_3CH_2F was provided by INEOS Fluor and $CF_3CH_2CHF_2$ by Honeywell. CF_3I, C_2F_5I, *i*-C_3F_7I, *s*-C_4F_9I, *t*-C_4F_9I, *cyclo*-$C_6F_{11}I$ (all Apollo Scientific), Li (3.2 mm diameter wire), *n*-BuLi (10 M or 2.5 M in hexanes), *t*-BuLi (1.5 M in pentanes), MeLi (1.6 M in Et_2O) (Acros or Aldrich), Ph_2PCl, *i*-Pr_2PCl, PPh_3, $AsCl_3$, $SbCl_3$, Me_3SiCl and $CDCl_3$ were purchased from commercial vendors and used as supplied. Perfluorovinyl-containing phosphines were prepared as described in the literature [25,27]. $Ph_2P(SiMe_3)$ and *i*-$Pr_2P(SiMe_3)$ were prepared based on literature methods [79,80]. NMR spectra were recorded on Bruker spectrometers operating at 200, 300 or 400 MHz for ^1H and referenced against TMS (^1H and ^{13}C), $CFCl_3$ (^{19}F) and 85% H_3PO_4 (^{31}P). All NMR data are reported using the high frequency positive convention. Infrared spectra were recorded using KBr plates on a Nicolet Nexus FTIR/Raman spectrometer. Elemental analyses were performed by the departmental microanalytical service.

4.1. X-ray crystallography

X-ray data for $[Ph_2P(CH_2Ph)(CHFCF_3)]Br$ and *trans*-$[PtI_2\{Pi\text{-}Pr_2(c\text{-}C_2F_3t\text{-}Bu)\}_2]$ were recorded on a Nonius κ-CCD 4-circle diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The data for all structures were solved by direct methods and subjected to full-matrix least-squares refinement on F^2 using the SHELX-97 program [81]. All non-hydrogen atoms were refined with anisotropic thermal parameters. A crystal of $As(CF{=}CF_2)_3$ was obtained from a sample held in a Pyrex capillary (o.d. 0.38 mm) mounted on a Stöe Stadi-4 diffractometer equipped with an Oxford Cryosystems low temperature device. Crystallization was achieved by first establishing a stable solid–liquid equilibrium at 260 K and then cooling the sample at a rate of 10 K h^{-1}. A data set comprising a full sphere of data to $2\theta = 60°$ was collected at 110 K; an absorption correction was applied using ψ-scans. The structure was solved by placing the As atom at the origin and locating the C and F atoms in a subsequent difference synthesis (CRYSTALS). Data collection and refinement parameters are summarised in Table 3. Molecular representations shown in the figures were generated using Pluton [82]. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 732138–732140. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

Table 3
Crystal data and structure refinement data.

Compound	$[Ph_2P(CH_2PH)(CHFCF_3)]Br$	$As(CF{=}CF_2)_3$	*trans*-$[PtI_2\{Pi\text{-}Pr_2(c\text{-}C_2F_3t\text{-}Bu)\}_2]$
Formula	$C_{21}H_{18}BrF_4P$	C_6AsF_9	$C_{26}H_{46}F_4I_2P_2Pt$
M	457.23	447.46	945.45
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*P*21/*n* (no. 14)	*P*21/*c*	*P*21/*n* (no. 14)
Unit cell parameters			
a (Å)	10.9179(3)	6.6969(8)	9.5442(2)
b (Å)	11.5879(3)	7.2004(8)	16.8766(3)
c (Å)	16.7960(5)	19.599(3)	11.1179(2)
α (Å)	90	90	90
β (°)	104.370(1)	99.633(10)	113.449(1)
γ (°)	90	90	90
V (Å^3)	1776.12(10)	931.7(2)	1642.91(6)
Z	4	4	2
D (g cm^{-3})	1.475	2.267	1.911
μ (Mo Kα) (mm^{-1})	2.112	3.758	6.283
Crystal size (mm)	0.07 × 0.15 × 0.25	0.39 × 0.27 × 0.27	0.20 × 0.20 × 0.20
No. data collected (θ range)	29248 (2.60–27.00)	3258 (3.02–27.52)	16055 (3.10–24.90)
Temperature (K)	293	120	150
F(0 0 0)	920	600	904
Data/restraints/parameters	4096/0/317	2141/0/146	2877/0/253
R_1, $wR_2[I > 2s(I)]$	0.0456, 0.1176	0.0343, 0.0597	0.0204, 0.0466
Maximum, minimum residual electron density (e Å^{-3})	0.41, −0.35	0.567, −0.325	0.80, −1.02

4.1.1. $[Ph_2P(CFHCF_3)Me]I$

$PPh_2(CF{=}CF_2)$ (0.40 g, 1.5 mmol) and iodomethane (0.21 g, 1.5 mmol) were stirred at 46 °C for 7 days in hexane (10 cm^3). After cooling the precipitate which had formed was filtered off to give an off-white product. (0.095 g 15%). Anal. Calcd. for $C_{15}H_{14}PF_4I$: C 42.1%, H 3.3%, I 29.7%. Found: C 43.1%, H 3.21%, I 30.1%. IR (KBr, neat); ν 1263, 1197, 1149 (C–F) cm^{-1}. ^{13}C NMR (75.5 MHz, $CDCl_3$, TMS): δ 130–137 (C_6H_5), 113.9 (m, *C*HF), 8.8 (d, *J*PC = 62 Hz, CH_3). ^{19}F NMR (188.3 MHz, $CDCl_3$, CCl_3F): δ −68.7 (ddd, 3F, *J*FP = 4, *J*FaFb = 16, *J*FaH = 19 Hz, CHFC*F*$_3$), −214.4 (ddq, 1F, *J*FaFb = 16, *J*FbH = 42, *J*FbP = 61 Hz, CH*F*CF$_3$). ^{31}P NMR (81.8 MHz, $CDCl_3$, 85% H_3PO_4) 22.6 (dd, *J*PFb = 61, *J*PFa = 3 Hz).

4.1.2. $[Ph_2P(CFHCF_3)CH_2Ph]Br$

$PPh_2(CF{=}CF_2)$ (1.5 g, 5.6 mmol) and benzyl bromide (0.60 g, 3.5 mmol) were stirred at 46 °C for 7 days in THF (10 cm^3). After cooling the precipitate which had formed was filtered off to give a white solid. (0.85 g 55%). Anal. Calcd. for $C_{21}H_{18}PF_4Br$: C 55.1, H 4.0, Br 17.5%. Found: C 55.7%, H 3.9%, Br 18.2%. IR (KBr, neat); ν 1584 (C=C aromatic), 1197, 1024, 993 (C–F) cm^{-1}. ^{13}C NMR (75.5 MHz, $CDCl_3$, TMS): δ 125.8–136.8 (C_6H_5), 28.0 (d, *J*PC = 41 *C*H$_2$). ^{19}F NMR (188.3 MHz, $CDCl_3$, CCl_3F): δ −68.8 (ddd, 3F, *J*FP = 4, *J*FaH = 6, *J*FaFb = 16 Hz, CHFC*F*$_3$), −214.4 (ddq, 1F, *J*FaFb = 16, *J*FbH = 41, *J*FbP = 57 Hz, CH*F*CF$_3$). ^{31}P NMR (81.8 MHz, $CDCl_3$, 85% H_3PO_4) 25.2 (dd, *J*PFb = 60 Hz, *J*PFa = 3).

4.1.3. $[Ph_3P(CF{=}CF_2)]I$

$PPh_2(CF{=}CF_2)$ (0.40 g, 1.5 mmol) and iodobenzene (0.40 g, 1.9 mmol) in THF (5 cm^3) were stirred at 46 °C for a period of 28 days under a positive pressure of dinitrogen and samples were taken from the reaction mixture periodically for characterisation by NMR spectroscopy (see text). ^{19}F NMR (188.3 MHz, $CDCl_3$, CCl_3F): −79.9 (m, 1F, *J* = 120 Hz, CF=CF*F*), −101.4 (m, 1F, *J* = 120 Hz CF=C*F*F), −186.6 (m, 1F, *J*FP = 50 Hz, C*F*=CF$_2$). ^{31}P NMR (81.8 MHz, $CDCl_3$, 85% H_3PO_4) 19.6 (dm, *J*PFb = 49 Hz).

4.1.4. $[i\text{-}Pr_2P(CF{=}CF_2)Me]I$

i-$Pr_2P(CF{=}CF_2)$ (0.40 g, 1.5 mmol) and iodomethane (0.20 g, 1.4 mmol) in hexane (10 cm^3) were stirred at 46 °C for a period of 28 days under a positive pressure of dinitrogen and samples were taken from the reaction mixture periodically (see text). ^{19}F NMR (188.3 MHz, $CDCl_3$, CCl_3F): −80.1 (dd, 1F, *J*FF = 29, 43 Hz, CF=C*F*$_2$), −105.6 (ddd, 1F, *J*FF = 43, 119 *J*FP = 9 Hz, CF=C*F*$_2$), −189.5 (dd, 1F, *J*FF = 30, 119 Hz, C*F*=CF$_2$). ^{31}P NMR (81.8 MHz, $CDCl_3$, 85% H_3PO_4) 42.0 (d, *J*PFb = 59 Hz).

4.1.5. $As(CF{=}CF_2)_3$

To a three-necked round-bottomed flask, equipped with nitrogen inlet/outlet and magnetic stirrer, maintained at −78 °C, were added CF_3CH_2F (9.3 ml, 110 mmol) and diethyl ether (400 ml) followed by *n*-BuLi (in hexanes, 22.0 ml, 10 M, 220 mmol) at a sufficiently slow rate to ensure that the temperature of the reaction mixture did not increase beyond −70 °C. After 6 h of maintaining this temperature the solution was cooled to −85 C and $AsCl_3$ (2.3 ml, 27.4 mmol) dissolved in Et_2O (40 ml) was added slowly. After leaving the reaction mixture to warm to room temperature overnight hexane (450 ml) was added and the solution was filtered. Removal of the solvents from the filtrate followed by distillation (58 °C, 80 mmHg) resulted in $As(CF{=}CF_2)_3$ as a clear liquid (7.84 g 90%). Anal. Calcd. for C_6F_9As: C 22.6%, F 53.8%, As 23.6%; found C 22.3%, F 53.3%. IR (KBr, neat); ν 1710 (C=C), 1299, 1165, 998 (C–F) cm^{-1}. ^{13}C NMR (75.5 MHz, neat, external $CDCl_3$): 124.1 (dd, *J* = 306, 65 Hz CF=*C*F$_2$), 158.1 (ddd, *J* = 325, 283, 35, *C*F=CF$_2$). ^{19}F NMR (188.3 MHz, neat external CCl_3F): −87.1 (dd, 1F, *J* = 40, 57 Hz), −114.2 (dd, 1F, *J* = 57, 120 Hz), −180.1 (dd, 1F, *J* = 41, 120 C*F*=CF$_2$).

4.1.6. $Sb(CF{=}CF_2)_3$

Using a similar method to that described above using CF_3CH_2F (9.3 ml, 110.3 mmol) in diethyl ether (100 ml), *n*-BuLi (in hexanes, 88 ml, 2.5 M, 220 mmol) and $SbCl_3$ (6.3 g, 27.6 mmol) dissolved in Et_2O (100 ml) resulted, after distillation (42 °C, 10 mmHg) in $Sb(CF{=}CF_2)_3$ as a clear liquid (6.85 g 70%). Anal. Calcd. for C_6F_9Sb: C 19.7%, F 46.9%, Sb 33.4%. Found: C 19.9%, F 46.5%. IR (KBr, neat); ν 1710 (C=C), 1299, 1165, 998 (C–F) cm^{-1}. ^{19}F NMR (188.3 MHz, neat external CCl_3F): δ −82.1 (dd, 1F, *J*FF = 48, 57 Hz), −114.0 (dd, 1F, *J*FF = 57, 132 Hz), −181.0 (dd, 1F, *J*FF = 48, 132 Hz C*F*=CF$_2$).

4.1.7. $i\text{-}Pr_2PCCCF_3$

To a three-necked round-bottom flask equipped with magnetic stirrer and nitrogen inlet and outlet held in a slush bath at −20 °C was added diethyl ether (150 ml) and HFC-245fa (3.6 ml, 37 mmol). *n*-BuLi (42 ml, 2.5 M in hexanes, 105 mmol) was added slowly over a period of 1 h at a sufficiently slow rate to ensure that the internal temperature did not rise above −20 °C. The reaction mixture was maintained at this temperature for a further 1 h. and then cooled to −90 °C. A cold, concentrated solution of chlorodiisopropylphosphine (3.8 ml 24 mmol, in 20 ml ether) was slowly added. The reaction was left to stir overnight and the temperature then raised to 0 °C. Hexane (150 ml) was added and the solution was filtered to remove the precipitated lithium salts. The combined solvents were removed under vacuum and after distillation (39 °C, 10 mmHg) 2.1 g (40%) of *i*-Pr_2PCCCF_3 was collected as a clear liquid. Anal. Calcd. for $C_9H_{14}F_3P$: C 51.4%, H 6.7%, F 27.1%, P 14.7%. Found: C 49.8%, H 6.6%, F 27.3%, P 14.5%. IR (KBr, neat); ν 2960 (CH), 2193 (C═C), 1255, 1140 (C–F) cm^{-1}. ^1H NMR (200.2 MHz, $CDCl_3$): 1.27 (m, CH_3), 2.03 (s, *J* = 5 Hz, CH), $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): 114.1 (q, *J* = 134 Hz CC*C*F3), 91.2 (dq, *J* = 6, 39, C*C*CF3), 89.4 (dq, *J* = 34, 4, *C*CCF3), 24.3 (CH), 19.7 (CH_3). ^{19}F NMR (188.3 MHz, $CDCl_3$, $CFCl_3$): −50.7 (d, *J* PF = 6 Hz, CF_3), $^{31}P\{^1H\}$ (81.8 MHz, $CDCl_3$, 85% H_3PO_4) NMR: −12.4 (q, *J*PF = 6 Hz).

4.1.8. *i-Pr_2P(c-C_2F_3t-Bu)*

In a round-bottom flask fitted with reflux condenser and maintained under a positive pressure of nitrogen was placed diethyl ether (15 ml) and *i*-Pr_2PCCCF_3 (0.423 g, 2.01 mmol) and the solution was brought to reflux. *t*-BuLi (2.7 ml, 1.5 M in pentanes, 4.05 mmol) was added dropwise over 15 min. The solution was allowed to cool down and methanol (2 ml) was added to quench unreacted butyl lithium. Hexane (40 ml) was added and the solution filtered through celite. Removal of the solvents under reduced vacuum produced a mixture of *i*-Pr_2P(*c*-C_2F_3*t*-Bu) and *i*-Pr_2P(CH═CF_3*t*-Bu) as a 91:9 mixture according to fluorine NMR measurements which was used without further purification. IR (KBr, neat); ν 2960 (CH), 1746 (C═C) cm^{-1}. ^1H NMR (200.2 MHz, $CDCl_3$): 1.26 (m, CH_3), 2.07 (s, *J* = 5 Hz, CH), $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): 149.2 (dt, *J* = 3, 10 Hz PC*C*CF2), 122.7 (dt, *J* = 62, 14, P*C*CCF2), 106.2 (dt, *J* = 5, 273, PCC*C*F2), 25.0 (CH), 19.9 (CH_3). ^{19}F NMR (188.3 MHz, $CDCl_3$, $CFCl_3$): −103.3 (d, *J*PF = 4 Hz, CF_2), $^{31}P\{^1H\}$ (81.8 MHz, $CDCl_3$, 85% H_3PO_4) NMR: −5.7 (q, *J*PF = 4 Hz).

4.1.9. *trans-[PtI_2\{Pi-Pr_2(c-C_2F_3t-Bu)\}$_2$]*

A round-bottomed flask was charged with dichloromethane (15 ml), [PtI_2(COD)] (0.272 g, 0.05 mmol) and *i*-Pr_2P(*c*-C_2F_3*t*-Bu) (0.364 g, 0.49 mmol) and the solution was stirred at room temperature for 24 h. Removal of the solvent under vacuum left a light orange powder (38 mg, 80%). Recystallisation from a mixed dichloromethane–hexane solvent system yielded crystals of suitable quality for X-ray diffraction studies. ^1H NMR (200.2 MHz, $CDCl_3$): 1.20 (m, CH_3), 1.87 (s, *J* = 5 Hz, CH), ^{19}F NMR (188.3 MHz, $CDCl_3$, $CFCl_3$): −105.3 (s, *J*PtF = 14 Hz, CF_2), $^{31}P\{^1H\}$ (81.8 MHz, $CDCl_3$, 85% H_3PO_4) NMR: 24.3 (s, *J*PtP = 3453 Hz).

4.1.10. *Typical procedure for reaction of R_2PLi with R_fI*

Under a nitrogen atmosphere a Schlenk flask was charged with THF (5 ml) and Ph_2PCl (0.12 ml, 0.67 mmol) to this was added lithium wire (0.02 g, 2.9 mmol) and the reaction mixture was stirred at room temperature for 1 h. *i*-C_3F_7I (0.1 ml, 0.67 mmol) was syringed into the solution and left to stir at room temperature for 1 h. after which all volatile material was removed under vacuum to yield a viscous pale yellow oil. The oil was passed down a short column, the first fraction which eluted from the column (1:1 hexane:toluene) was collected and the solvent removed to yield 0.10 g (40%) of Ph_2P(*i*-C_3F_7). ^1H NMR ($CDCl_3$, 400.4 MHz): 7.24–7.45 (m, 6H), 7.69–7.82 (m, 4H); ^{19}F NMR ($CDCl_3$, 376 MHz) –69.6 (dd, 6F, ^3J(PF) = 18.5, ^3J(FF) = 11.8 Hz, CF_3), −184.9 (dsept, 1F, ^2J(PF) = 74.0, ^3J(PF) = 11.6, CF) $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz, 85% H_3PO_4): −0.7 (dsept, ^2J(PF) = 73.0, ^3J(PF) = 19.0 Hz) [74].

4.1.11. *Typical procedure for R_2PSiMe_3 reaction with R_fI*

A dried Schlenk vessel maintained under a positive pressure of nitrogen was charged with $Ph_2P(SiMe_3)$ (2.2 ml, 8.5 mmol) and hexane (20 ml). The solution was cooled to −30 °C and *i*-C_3F_7I (1.2 ml, 8.5 mmol) was added over ca. 30 min. The solution was stirred and left to warm to room temperature overnight. MeLi (1.6 M in Et_2O, 5.4 ml, 8.6 mmol) was added to the yellow solution and stirred for ca. 30 min. The resulting precipitate was filtered off under an inert atmosphere and the volatiles were removed under vacuum to yield Ph_2P(*i*-C_3F_7) as a white solid (2.26 g, 75%).

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