

The synthesis and chemistry of fluorovinyl-containing phosphines and the single crystal X-ray structure of $\text{SPPr}_2^i(\text{CF}=\text{CF}_2)$

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The first perfluorovinyl alkyl-containing phosphines of the type $\text{PR}_2(\text{CF}=\text{CF}_2)$ ($\text{R} = \text{Et}$, $i\text{Pr}$, Cy) are reported. The reactivity of these air- and moisture-stable materials has been explored, both at the phosphorus centre and at the fluorovinyl moiety. When $\text{PR}_2(\text{CX}=\text{CF}_2)$ ($\text{X} = \text{F}$, Cl) is reacted with LiAlH_4 a mixture of $\text{PR}_2(\text{CX}=\text{CFH})$ isomers and other defluorinated materials are produced, but the reaction with $\text{LiAlH}(\text{OBu}^t)_3$ affords the single products $Z\text{-PR}_2(\text{CF}=\text{CFH})$ or $E\text{-PR}_2(\text{CCl}=\text{CFH})$, respectively, in high yields. Reaction of the fluorovinyl alkyl phosphines with hydrogen peroxide, elemental sulfur or selenium yields fluorovinyl-containing phosphine oxides, sulfides and selenides, respectively. The phosphine sulfide $\text{SPPr}_2^i(\text{CF}=\text{CF}_2)$ is the first perfluorovinyl phosphorus(v) compound to be characterised crystallographically and it exhibits an unusually short [1.9358(9) Å] $\text{P}=\text{S}$ bond. Reaction of fluorovinyl phosphines with XeF_2 results in compounds of the type $\text{F}_2\text{PR}_2(\text{CF}=\text{CF}_2)$, identified on the basis of multinuclear NMR studies. These compounds decompose in the presence of moisture to yield the respective phosphine oxides. Reaction of $\text{OPPh}_2(\text{CF}=\text{CF}_2)$ with Br_2 results in bromine addition across the double bond to give $\text{OPPh}_2(\text{CFBrCF}_2\text{Br})$.

Introduction

There is considerable interest in the synthesis and chemistry of phosphorus(III) compounds containing fluorinated organic fragments, in part due to their utility as ligands that exhibit a combination of steric and electronic parameters for which there are few analogues in traditional, hydrocarbon-phosphine chemistry.¹ Equally significant is the widespread use of related vinyl-containing phosphines as versatile building blocks in synthetic organic chemistry.² Historically, the first important fluorocarbon-containing phosphine was $\text{P}(\text{CF}_3)_3$, prepared from the reaction between CF_3I and elemental phosphorus, or CF_3 sources and PCl_3 .³ Amongst the numerous synthetic methods available, the most prevalent approach to perfluoroalkyl and perfluoroaryl phosphines has relied upon Grignard or lithium reagents derived from chloro-, or more usually, bromofluorocarbons. This route has been widely used for the synthesis of poly- and pentafluorophenyl-substituted phosphines^{4,5} and, more recently, for perfluoroalkyl systems.^{6,7} However, the number of reported examples of phosphines containing fluorocarbon groups is still small compared to hydrocarbon analogues; in particular, there is a dearth of examples of phosphines containing fluorovinyl groups. Vinyl phosphines of the type $\text{P}(\text{CH}=\text{CH}_2)_3$, $\text{PR}(\text{CH}=\text{CH}_2)_2$ and $\text{PR}_2(\text{CH}=\text{CH}_2)$ are well-known⁸ and some, for example with $\text{R} = \text{Ph}$, are commercially available. Following the reports of vinyl phosphines, Knunyants and co-workers prepared $\text{P}(\text{CF}=\text{CF}_2)_3$, $\text{P}(\text{NEt}_2)_3-x(\text{CF}=\text{CF}_2)_x$ ($x = 1, 2$), the halophosphines $\text{PCl}_{3-x}(\text{CF}=\text{CF}_2)_x$ and $\text{PF}_{3-x}(\text{CF}=\text{CF}_2)_x$ ($x = 1, 2$),⁹ and $(\text{CF}_2=\text{CF})\text{P}(\text{O})(\text{OEt})_2$ from the unstable Grignard reagent $\text{CF}_2=\text{CFMgBr}$, obtained from $\text{CF}_2=\text{CFBr}$ and elemental Mg .¹⁰ Subsequently, Cowley and Taylor reported the dimethylamino analogues, $\text{P}(\text{NMe}_2)_{3-x}(\text{CF}=\text{CF}_2)_x$ ($x = 1, 2$)¹¹ and, in 1978, two phenyl perfluorovinyl phosphines,

$\text{PPh}_{3-x}(\text{CF}=\text{CF}_2)_x$ ($x = 1, 2$), were prepared by Horn and co-workers in yields ranging from 2 to 21%.¹²

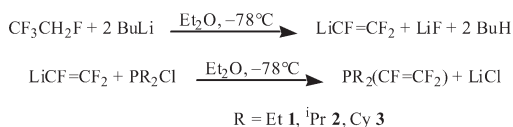
It is not now possible to rely upon chloro- and bromofluorocarbons as sources of fluoro-organo Grignard and lithium reagents, given the reduced availability of these materials, as a result of their ozone-depleting properties. More recent work has thus applied alternative methodologies such as the use, by Ichikawa *et al.*, of 2,2,2-trifluoroethyl triflate in the synthesis of 2,2-difluorovinyl phosphine derivatives.¹³ We have previously reported an improved synthesis for the phosphines $\text{PPh}_{3-x}(\text{CF}=\text{CF}_2)_x$ ($x = 1, 2, 3$) and their chloride analogues $\text{PCl}_2(\text{CF}=\text{CF}_2)$ and $\text{PCl}(\text{CF}=\text{CF}_2)_2$, in high yields and purity, *via* the generation, *in situ*, of perfluorovinyl lithium from the commercially available CFC replacement $\text{CF}_3\text{CH}_2\text{F}$ (HFC-134a) and BuLi .¹⁴ We have now extended this approach to the synthesis of the first alkyl perfluorovinyl phosphines, of the type $\text{PR}_2(\text{CF}=\text{CF}_2)$ and $\text{PRR}'(\text{CF}=\text{CF}_2)$. In view of the wide potential for steric and electronic control afforded by alkyl phosphines we have also investigated derivatisation of these and related phosphines of the type $\text{PR}_2(\text{CF}=\text{CF}_2)$ where $\text{R} = \text{alkyl}$, aryl . We thus report the synthesis and characterisation of a range of fluoro-organo phosphorus(III) and phosphorus(V) compounds

Results and discussion

Synthesis of alkyl perfluorovinyl phosphines

The low-temperature reaction of perfluorovinyl lithium, generated from $\text{CF}_3\text{CH}_2\text{F}$ and two equivalents of $n\text{-BuLi}$,^{15,16} with the appropriate alkylchlorophosphines affords, after workup and distillation, the dialkyl perfluorovinyl phosphines, 1–3 (see Scheme 1), as colourless liquids, in good yields (60–80%). Similarly, the addition of PhBuPCL , prepared from PhPCl_2 and BuLi , to a solution of perfluorovinyl lithium results in the synthesis of the *P*-chiral phosphine $\text{PhBuP}(\text{CF}=\text{CF}_2)$ (4), albeit in somewhat lower yield.

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

Together, these constitute the first examples of perfluorovinyl-substituted phosphines containing alkyl groups. All of these compounds have proven to be air- and moisture-stable for many months, like the previously reported phenyl counterparts.¹⁴ This is in contrast to the properties of alkyl-substituted vinyl phosphines, and alkyl phosphines in general, which are much more sensitive to oxidation.¹⁷

Unambiguous identification of all pure products was obtained by a combination of elemental analysis, IR and multinuclear (¹H, ¹⁹F, ³¹P{¹H} and ¹³C{¹H}) NMR spectroscopy. The ¹⁹F NMR spectra of the alkylperfluorovinyl phosphines **1** to **4** each exhibit three sets of doublets of doublets at *ca.* −86, −110 and −185 ppm, consistent with the expected AMX spin system for the perfluorovinyl moiety, with additional coupling to the phosphorus nucleus. These resonances were assigned to the *trans*, *cis* and geminal fluorine nuclei, respectively, of the perfluorovinyl group, by comparison with previously recorded data.^{11,12,14,18,19} The ³¹P{¹H} NMR spectra of **1** to **4** each exhibit a resonance dominated by one large PF coupling of *ca.* 55 Hz and two smaller magnitude couplings. The larger coupling constant is also observed for the ¹⁹F NMR resonance corresponding to the fluorine nucleus *cis* to the phosphorus centre. Although the anticipated magnitude of bond-mediated couplings in a vinyl group is $J(\text{PF}_{\text{trans}}) > J(\text{PF}_{\text{cis}})$, we observe a large $J(\text{PF}_{\text{cis}})$ coupling constant, which is consistent with lone-pair-assisted through-space coupling.²⁰

The approximate ³¹P NMR chemical shifts of tertiary phosphines can be predicted using the empirical formula:²¹

$$\delta = -62 + \sum_{i=1}^3 \sigma_{\text{P}}$$

where σ_{P} is a constant for a given alkyl or aryl group attached to the phosphorus centre. This relationship has not previously been applied to fluorovinyl systems; however, based upon the data reported herein we conclude that for the CF=CF₂ group $\sigma_{\text{P}} = -3$ and $+5$ for the CCl=CF₂ group.¹⁸ We note that while σ_{P} values for most alkyl and aryl substituents are positive, the negative value for the CF=CF₂ group is consistent with those for other highly fluorinated, electron-withdrawing groups, such as C₆F₅, where $\sigma_{\text{P}} = -5$.

The ¹³C{¹H} NMR spectra of **1** to **4** show the expected peaks due to the alkyl groups as well as two complex multiplets at *ca.* 127 and 160 ppm, which are assigned to the α- and β-perfluorovinyl resonances, respectively, on the basis of $J(\text{CF})$ magnitudes.

Reactivity of perfluorovinyl phosphines

Reactions with *n*-butyl lithium. Previously, it has been reported that when an excess of CF₂=CFLi is present during the preparation of perfluorovinyl-containing phosphines, nucleophilic attack occurs, to generate species of the type PR₂(CF=CF-CF=CF₂).¹² We have found no evidence for this, despite routinely using an excess of CF₂=CFLi in order to ensure high yields. However, we have previously reported that carbolithiation of group 14 perfluorovinyl compounds with RLi (R = Me, ^{*n*}Bu, ^{*i*}Bu, Ph), occurs readily to afford new difluorovinyl-based products.²² In view of this success, we have now extended this work to phosphorus derivatives. Thus, when PPh₂(CF=CF₂) is reacted with ^{*n*}BuLi at −90 °C

an oil (**5**) results. The ¹⁹F NMR spectrum of **5** exhibits two doublet of doublet of triplet resonances at −132.7 and −159.1 ppm, with a large, mutual $J(\text{FF})$ coupling of 141 Hz. The ³¹P{¹H} NMR spectrum of **5** displays a doublet of doublets at −27.1 ppm, which is only slightly shifted from that of the parent phosphine (−26.2 ppm), while the ¹H NMR spectrum shows four signals associated with the butyl group, one of which exhibits coupling to the two fluorine nuclei ($J = 23$ and 10 Hz). The NMR data is consistent with a 1,2-difluorovinyl-containing compound, also confirmed by the ¹³C{¹H} NMR spectrum; while the presence of a large, typically *trans*, $^3J(\text{FF})$ coupling,¹⁹ identifies the product as *Z*-PPh₂(CF=CFBu). The higher frequency ¹⁹F NMR resonance (−132.7 ppm) is assigned to the fluorine nucleus *cis* to phosphorus on the basis of a large $J(\text{PF})$ coupling (89 Hz) and a coupling of 23 Hz to the proximate butyl protons. The lower frequency resonance (−159.1 ppm) is therefore assigned to the geminal fluorine nucleus, which exhibits much smaller $J(\text{PF})$ (5 Hz) and $J(\text{FH})$ (10 Hz) couplings.

The exclusive formation of the *Z* isomer of **5** contrasts with recently reported work on the similar nonfluorinated systems, PPh₂(CH=CHR) [R = Ph, *p*-tolyl, *p*-NO₂C₆H₄ and CH₂CH(Ph)CH₃].²³ In these compounds both *E* and *Z* isomers were obtained, with *cis*-PPh₂(CH=CHR) typically being predominant. However, the dominance of the *trans* isomer of **5** concurs with our previous work on related group 14 compounds.²² The preference for this isomer can be explained by consideration of the intermediate species formed during carbolithiation. Nucleophilic attack would be favoured at the β-carbon, since this is expected to be the more electron-deficient centre. Additionally, the resulting intermediate carbanion on the α-carbon centre would be the least destabilised by + π effects from the adjacent fluorine atoms. The *trans* arrangement of the large PPh₂ and Bu groups minimises steric repulsions, thus subsequent syn elimination of LiF would give rise to the observed *Z* isomer.²⁴

Reaction with hydride reagents. There are no readily available CFC replacements that easily allow for the facile generation of hydrofluorovinyl ligands directly from lithium reagents and relatively few such compounds have been reported previously. However, such phosphines should be accessible *via* reaction of perfluorovinyl compounds with nucleophilic sources of hydride. We have thus explored the reactions of PPh₂(CF=CF₂) and PPh₂(CCl=CF₂) with LiAlH₄, which in each case resulted in the isolation of a number of species. The ³¹P{¹H} NMR spectrum obtained from the reaction of PPh₂(CF=CF₂) and LiAlH₄ indicates the presence of two major products, characterised by a multiplet at −27.5 ppm (dd, $J = 74, 8$ Hz) and a singlet at −39 ppm, in an approximately 1:1 ratio. The resonance at −27.5 ppm is consistent with formation of a 1,2-difluorovinyl-substituted phosphine. The geometry of this product is assigned as *Z*-PPh₂(CF=CFH) (**6**) on the basis of the magnitudes of coupling constants observed in the ¹⁹F and ¹H NMR spectra. This interpretation is also consistent with the data recorded after LiAlH₄ is reacted with group 14 perfluorovinyl compounds.²² The lower frequency signal observed in the ³¹P NMR spectrum is assigned to PPh₂PH on the basis of literature data,²⁵ confirmed by acquisition of a proton-coupled ³¹P NMR spectrum, where this resonance appears as a doublet of quintets ($J = 218, 7$ Hz). It therefore appears that the excess of LiAlH₄ used in these reactions, required to ensure complete consumption of the starting phosphine, causes cleavage of the phosphorus-perfluorovinyl P–C bond, resulting in Ph₂PH as a significant by-product. We note that no resonances consistent with PhPH(CF=CF₂) were observed, which suggests that the P–C bond to the perfluorovinyl group is preferentially cleaved under these conditions. A number of lower intensity signals

are also observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (see Experimental). These include *E*- $\text{PPh}_2(\text{CF}=\text{CFH})$, the identity of which was confirmed by the corresponding ^{19}F and ^1H NMR resonances, which appear in regions typical of *cis*- $\text{CF}=\text{CFH}$ substituted compounds of phosphorus²⁶ and sulfur.²⁷

Exclusive production of *Z*- $\text{PPh}_2(\text{CF}=\text{CFH})$, **6**, with no attendant P–C bond cleavage can, however, be achieved if $\text{PPh}_2(\text{CF}=\text{CF}_2)$ is reacted with $\text{LiAlH}(\text{O}i\text{Bu})_3$ in place of LiAlH_4 . The formation of a single isomer allows for identification of the vinylic resonance in the ^1H NMR spectrum (7.6 ppm), the chemical shift of which is typical for a proton attached to an electron-deficient fluorovinyl system, and is consistent with observations for related silicon, germanium and tin compounds.^{22,28–30} The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **6** displays resonances between 126 and 132 ppm, assigned to the aromatic carbons, and two doublet of doublet of doublets at 149.7 and 152.8 ppm. The former is assigned as the β -vinyl carbon and the latter as the α -vinyl carbon, on the basis of the DEPT-135 spectrum and magnitude of the $J(\text{PC})$ and $J(\text{CF})$ coupling constants.

The analogous reactions of $\text{PPh}_2(\text{CCl}=\text{CF}_2)$ with hydride reagents have also been explored, with comparable results. Thus, with LiAlH_4 several species were again observed, *E*- $\text{PPh}_2(\text{CCl}=\text{CFH})$ and Ph_2PH being the major products, formed in admixture with trace species, which include $\text{PPh}_2(\text{CH}=\text{CF}_2)$ ¹³ and *E*- $\text{PPh}_2(\text{CH}=\text{CFH})$. The presence of both of these species is consistent with displacement of the geminal chlorine atom being more facile than the corresponding fluorine atom of $\text{PPh}_2(\text{CF}=\text{CF}_2)$. Once again, use of the milder hydride reagent $\text{LiAlH}(\text{O}i\text{Bu})_3$ results in isolation of *E*- $\text{PPh}_2(\text{CCl}=\text{CFH})$, **7** without the presence of by-products.

Perfluorovinylphosphine chalcogenides

Oxidation of perfluorophosphines. The stability of perfluorovinyl phosphines towards aerial oxidation has prompted us to study this aspect of their behaviour in some detail and to this end a series of reactions was undertaken (see Scheme 2). Oxidation reactions were performed with H_2O_2 , elemental sulfur and elemental selenium. The reactions with hydrogen peroxide were effected at 0 °C, whilst those with sulfur or selenium powder required prolonged periods of reflux in toluene, with an excess of the powdered element.

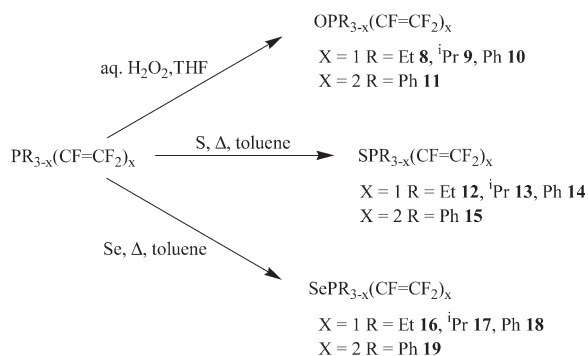
The progress of the oxidation reactions was monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy; in each case the resonances assigned to the starting phosphines were replaced by a new peak, observed at higher frequencies of between 45 and 75 ppm, and assigned to the $\text{E} = \text{PR}_{3-x}(\text{CF}=\text{CF}_2)_x$ species ($\text{E} = \text{O}, \text{S}, \text{Se}$), the chemical shifts being consistent with those reported for 4-coordinate phosphorus(v) compounds.³¹ The rates of conversion were highly dependant upon the groups bound to phosphorus; in general, oxidation of $\text{PR}_2(\text{CF}=\text{CF}_2)$

is more rapid when R is an alkyl group than when R = Ph. Oxidation with hydrogen peroxide is typically complete after 30 min, whilst longer reaction times are needed for the selenides (2 to 3 h) and sulfides (6 to 24 h). In contrast, complete oxidation of $\text{PPh}(\text{CF}=\text{CF}_2)_2$ could not be obtained, even with hydrogen peroxide. This illustrates the increased stability of the phosphorus centre towards oxidation upon substitution of a second electron-withdrawing perfluorovinyl group and is consistent with previous reports of the oxidation of $\text{P}(\text{CF}_3)_3$ and $\text{P}(\text{C}_6\text{F}_5)_3$ with elemental sulfur,³² where complete conversion to the phosphine sulfides required temperatures of 160–200 °C for up to 8 days. Generally the phosphine selenides are somewhat less stable than the sulfides or oxides, especially $\text{SePEt}_2(\text{CF}=\text{CF}_2)$, which decomposed completely over a period of a few hours, thus precluding satisfactory elemental analysis.

In all cases retention of the perfluorovinyl group in the final product was confirmed by ^{19}F NMR spectroscopy, signals for the products being shifted only slightly from the starting phosphines, although significant changes were observed in $J(\text{PF})$ coupling constants. This is to be expected since there is a change in oxidation state and angles around the phosphorus centre in the phosphorus(v) species as compared to the free phosphines. Additionally, the absence of a lone pair on the phosphorus atom in **8** to **19** results in a reduction in the magnitude of the $^3J(\text{PF}_{\text{cis}})$ coupling constant for all the phosphorus(v) compounds, compared to the parent phosphines.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the phosphine selenides show additional low-intensity satellite peaks, due to coupling to the spin-active selenium nucleus (^{77}Se , 7.58%, $I = \frac{1}{2}$) from which absolute values for $^1J(\text{SeP})$ of between 730 and 848 Hz are obtained. These values lie intermediate between those observed for trialkyl and triaryl phosphine selenides (680 to 735 Hz) and trialkyl phosphite selenides (over 900 Hz).³³ The magnitude of the phosphorus-selenium coupling constant is dependent on the electronic characteristics of the compound rather than there being any strong correlation between the steric demand of the phosphine, as measured by its cone angle. For example, the P–Se coupling constant for SePCy_3 (cone angle 170°) is 673 Hz, whilst that for SePMe_3 (cone angle 118°) is little different at 684 Hz.³⁴ However, the presence of electron-withdrawing substituents attached to the phosphorus centre does have a significant effect, as displayed by the increase in $J(\text{SeP})$ coupling from SePPh_3 (736 Hz)³⁵ to $\text{SePPh}_2(\text{CF}=\text{CF}_2)$ (785 Hz) and $\text{SePPh}(\text{CF}=\text{CF}_2)_2$ (848 Hz). Coupling to the spin-active selenium nuclei was sometimes also resolved in the ^{19}F NMR spectrum, with satellites most often observed to the F_{cis} nucleus.

In general the products of these reactions were isolated as oily materials; however, in the case of $\text{SPPr}_2^i(\text{CF}=\text{CF}_2)$, **13**, small X-ray quality crystals slowly developed. Compound **13** adopts the anticipated 4-coordinate geometry around phosphorus (Fig. 1); selected bond distances and angles are summarised in Table 1.



Scheme 2 Oxidations of perfluorovinyl phosphines with H_2O_2 , S and Se.

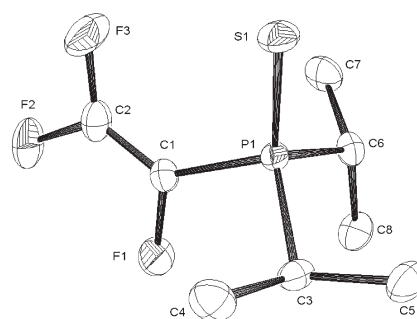
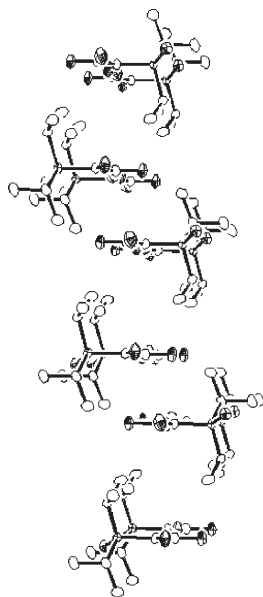


Fig. 1 The molecular structure of $\text{SPPr}_2^i(\text{CF}=\text{CF}_2)$, **13** (thermal ellipsoids are plotted at 30% level and hydrogens have been removed for clarity).

Table 1 Selected bond lengths (Å) and angles (°) for $\text{SPPr}_2(\text{CF}=\text{CF}_2)$, **13**

P(1)–S(1)	1.9358(9)	C(1)–C(2)	1.298(3)
P(1)–C(1)	1.809(2)	C(1)–F(1)	1.353(3)
P(1)–C(3)	1.810(2)	C(2)–F(2)	1.310(3)
P(1)–C(6)	1.820(2)	C(2)–F(3)	1.301(3)
C(1)–P(1)–S(1)	113.46(8)	C(1)–P(1)–C(3)	101.92(11)
C(3)–P(1)–S(1)	114.13(8)	C(1)–P(1)–C(6)	103.95(11)
C(6)–P(1)–S(1)	113.49(8)	C(3)–P(1)–C(6)	108.82(11)

The three S–P–C angles are all greater than the idealised tetrahedral angle, while the three C–P–C angles are all somewhat smaller. The P=S bond length [1.9358(9) Å] is shorter than that typically found in trialkyl or triaryl phosphine sulfides: SPCy_3 [$d(\text{P}=\text{S}) = 1.966(2)$ Å],³⁶ SPPPh_3 [$d(\text{P}=\text{S}) = 1.950(3)$ Å]³⁷ and $\text{SPPPh}_2(\text{CH}=\text{CH}_2)$ [$d(\text{P}=\text{S}) = 1.953(7)$ Å].³⁸ The observed distance is, however, consistent with that found in the limited number of crystallographically characterised sulfides of phosphines possessing fluoro-organo groups: $\text{SPPPh}_2(\text{CF}_2\text{Br})$ [$d(\text{P}=\text{S}) = 1.9348(11)$ Å],³⁹ $\text{SPMe}_2(p\text{-C}_6\text{F}_4\text{H})$ [$d(\text{P}=\text{S}) = 1.943(2)$ Å], $\text{SPMe}_2(p\text{-C}_6\text{F}_4\text{Cl})$ [$d(\text{P}=\text{S}) = 1.945(1)/1.936(1)$ Å] and $\text{SPMe}_2(p\text{-C}_5\text{F}_4\text{N})$ [$d(\text{P}=\text{S}) = 1.937(1)$ Å].⁴⁰ The three C–F distances in **13** show some variation, as previously observed for $\text{PPh}(\text{CF}=\text{CF}_2)_2$.¹⁴ In both compounds the C $_{\alpha}$ –F bond is the longest, although there are no particularly short intra- or intermolecular interactions to account for this. In the extended structure, stacks of molecules exhibit interlaced perfluorovinyl groups in a fluorinated “zipper-like” arrangement in the *b* direction (Fig. 2). In this way the perfluorovinyl groups of the molecules of two adjacent stacks sit one above another, resulting in fluorocarbon and hydrocarbon domains within the crystal.



Oxidation with XeF_2 . Oxidative fluorination of phosphines to give R_3PF_2 species has been achieved with a variety of reagents, including SF_4 ,⁴¹ NF_3O ,⁴² COF_2 ,⁴³ F_2 ,⁴⁴ XeF_2 ⁴⁵ and also *via* electrochemical methods.⁴⁶ Of these the use of XeF_2 has a number of advantages to offer, including its ease of handling, short reaction times and gaseous xenon being the by-product. Therefore, the reaction of the perfluorovinyl phosphines $\text{PR}_{3-x}(\text{CF}=\text{CF}_2)_x$ ($x = 1$, R = Et, **1**; *i*Pr, **2**; Cy, **3**; Ph; $x = 2$, R = Ph), $\text{Z-PPh}_2(\text{CF}=\text{CFH})$, **6**, and $\text{E-PPh}_2(\text{CCl}=\text{CFH})$, **7**, with xenon difluoride were undertaken. Under an inert atmosphere, crystals of XeF_2 were added to

solutions of the phosphines, dissolved in CDCl_3 in an NMR tube, which resulted in an immediate, exothermic reaction with liberation of xenon. Fig. 3 shows the ^{19}F NMR spectra of solutions containing $\text{PEt}_2(\text{CF}=\text{CF}_2)$, before and after addition of XeF_2 . It is clear that, following the initial addition of XeF_2 (Fig. 3(b)), four new multiplets are observed, in addition to those of the parent phosphine (labelled *), three of which are observed in regions characteristic of a perfluorovinyl moiety (–81, –97 and –180 ppm), though with additional couplings. The fourth resonance appears at *ca.* –43 ppm and displays a large doublet coupling suggestive of a $^1\text{J}(\text{PF})$ interaction. On further addition of XeF_2 (Fig. 3(c)), these four resonances become the dominant species. Due to the complexity of these resonances the final chemical shifts and coupling constants were determined by modelling the observed spectra against the spin system of $\text{F}_2\text{PET}_2(\text{CF}=\text{CF}_2)$ using the programs MestRe-C⁴⁷ and Spin.⁴⁸ The quality of the fit between the calculated and observed spectra (shown in Fig. 4) allows confidence in our assignment of the NMR spectrum of this species.

The perfluorovinyl phosphorus(v) difluorides **20** to **24** have all been characterised in this way, as have the products from the reactions of $\text{PPh}_2(\text{CX}=\text{CFH})$ (X = F, Cl) with XeF_2 to yield compounds **25** and **26**. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra recorded for **20** to **26** all show a large triplet-based resonance between –19.6 and –66.6 ppm, as the result of a large $^1\text{J}(\text{PF})$ coupling, the magnitude of which varies between 654 and 739 Hz. The chemical shifts for all these compounds are found in the region typical for five-coordinate phosphorus(v) species. All compounds of this stoichiometry have previously been assigned as trigonal bipyramidal, with the fluoride ligands occupying axial positions, and the NMR data for **20** to **26** is consistent with this formulation; in all cases equivalence of the two terminal P–F fluorides is evident.

This work represents the first report of perfluorovinyl-containing phosphorus(v) species of stoichiometry R_3PF_2 and compliments the data for $(\text{CF}_2=\text{CF})\text{PF}_4$ and $(\text{CF}_2=\text{CF})_2\text{PF}_3$, which have been previously described.⁴⁹ It has proven impossible to isolate **20** to **26** in their pure form, due to their propensity to decompose in the presence of moisture to the respective phosphine oxides, as determined by $^{31}\text{P}\{^1\text{H}\}$ and ^{19}F NMR spectroscopy. This is also consistent with the reported tendency of $(\text{CF}_2=\text{CF})\text{PF}_4$ to hydrolyse to $(\text{CF}_2=\text{CF})\text{POF}_2$.⁵⁰

Addition of dihalogens

The reactions of the phosphines **1** to **3** and $\text{PPh}_2(\text{CF}=\text{CF}_2)$ with X_2 (X = Cl, Br, I) and SO_2Cl_2 have been explored. However, a mixture of products is obtained, as indicated by $^{31}\text{P}\{^1\text{H}\}$ NMR studies, due to competition between halogenation of the double bond and oxidation of the phosphorus centre. In order to preclude the latter, reaction of the phosphine oxide, $\text{OPPh}_2(\text{CF}=\text{CF}_2)$, **10**, was explored. Reflux of a chloroform solution of dibromine and $\text{OPPh}_2(\text{CF}=\text{CF}_2)$ resulted in a change in the colour of the solution from red-brown to yellow. The ^{19}F NMR spectrum of the resulting yellow oil (**27**) displayed three signals at –50.6, –53.0 and –132.4 ppm (as shown in Fig. 5). This is consistent with the addition of bromine across the double bond to generate a 1,2-dibromo-trifluoroethyl moiety.

The two resonances associated with the β -fluorine nuclei (F_b , F_b') are observed in close proximity, with a large mutual coupling constant (170 Hz), due to diastereotopism at the β -carbon centre. This results in a marked departure of these resonances from first-order behaviour. Notwithstanding, all couplings are clearly resolved and correlate well with those observed for the unique α -fluorine (F_a) resonance (23 and 18 Hz). The F_b' resonance (–53.0 ppm) additionally exhibits a further doublet coupling of 3 Hz. Coupling of a similar magnitude is also observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum,

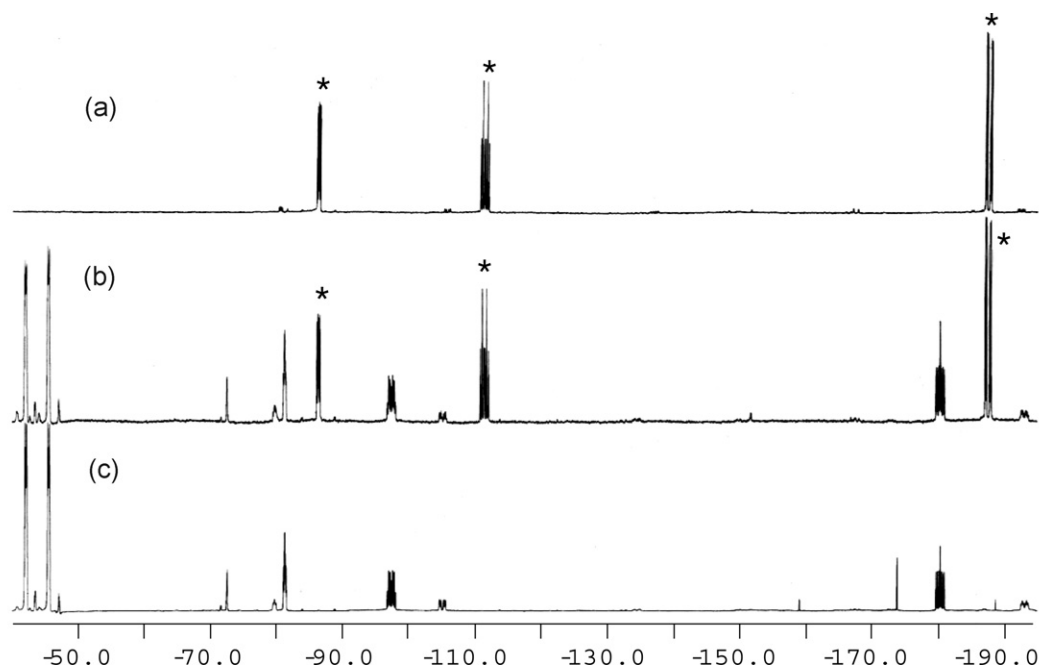


Fig. 3 ^{19}F NMR spectra of $\text{PEt}_2(\text{CF}=\text{CF}_2)$ (a), $\text{PEt}_2(\text{CF}=\text{CF}_2)$ and 0.6 equiv. XeF_2 (b) and $\text{PEt}_2(\text{CF}=\text{CF}_2)$ and 1.1 equiv. XeF_2 (c).

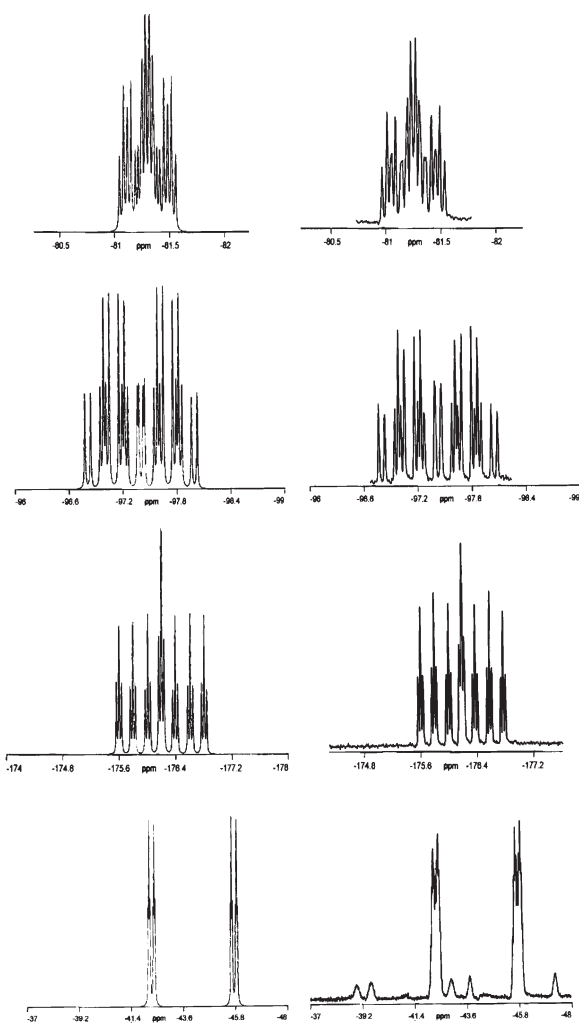


Fig. 4 Calculated (left) and observed (right) ^{19}F NMR signals due to $\text{F}_2\text{PEt}_2(\text{CF}=\text{CF}_2)$.

suggesting this to be a $^3J(\text{PF}_{\text{b}}')$ interaction. Significantly, no such coupling is observed to F_{b} and we therefore suggest that the observed interaction is dipolar-mediated and thus localised due to hindered rotation around the C–C bond. Variable temperature NMR studies would seem to support this suggestion, the coupling being lost at elevated temperatures.

The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **27** displays four aromatic resonances between 127.5 and 133.9 ppm and two further multiplets at 104.4 and 120.5 ppm. The resonance at 104.4 ppm appears as an overlapping doublet of doublet of doublets, with one large $^1J(\text{CF})$ coupling of 283.9 Hz, and is thus assigned to the α -carbon of the CFBrCF_2Br group. The apparent triplet multiplicity of this resonance arises due to coupling to the two diastereotopic fluorine nuclei [$^2J(\text{CF}_{\text{b}}) = ^2J(\text{CF}_{\text{b}}') = 32.8$ Hz]; the remaining doublet coupling (63.7 Hz) is assigned as a $^1J(\text{CP})$ interaction. The β -carbon resonance (120.5 ppm) exhibits two large $^1J(\text{CF})$ couplings (313.9 Hz twice) and smaller interactions to the α -fluorine and phosphorus nuclei.

Conclusion

In conclusion, we have generated a range of new fluorovinyl-substituted phosphines and have demonstrated methods of derivatising these compounds stereospecifically to generate

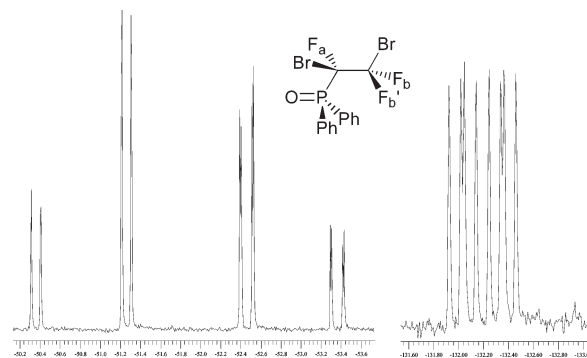


Fig. 5 Sections of the ^{19}F NMR spectrum of $\text{OPPh}_2(\text{CFBrCF}_2\text{Br})$, **27**.

new difluorovinyl phosphines in high yields. We have studied the oxidation of fluorovinyl-substituted phosphines in detail and report the first crystal structure of a phosphorus(v) perfluorovinyl compound, $\text{SPPr}_2(\text{CF}=\text{CF}_2)$ **13**.

Experimental

General methods and materials

Syntheses of the tertiary phosphines **1** to **4** were carried out under an inert atmosphere of argon or nitrogen in flame-dried glassware. Diethyl ether and THF were dried over sodium wire for *ca.* 24 h and subsequently refluxed over sodium/benzophenone under a nitrogen atmosphere. CF_3CFH_2 (HFC-134a, Ineos Fluor), BuLi (2.5 M in hexanes, Acros), PEt_2Cl , PPR_2Cl and PCy_2Cl (Aldrich) were used as supplied after verification of purity. $\text{PPh}_2(\text{CF}=\text{CF}_2)$, $\text{PPh}(\text{CF}=\text{CF}_2)_2$ ¹⁴ and $\text{PPh}_2(\text{CCl}=\text{CF}_2)$ ¹⁸ were prepared as described previously. ^{19}F , $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectra were recorded on a Bruker DPX200 spectrometer operating at 188.3, 81.8 and 200.1 MHz, respectively. Peak positions are quoted relative to external CFCl_3 , 85% H_3PO_4 and TMS, respectively, using the high frequency positive convention. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (reference TMS) were recorded on a Bruker DPX 400 spectrometer, operating at 100.5 MHz. Infrared and Raman spectra were recorded on a Nicolet-Nexus FT-IR/Raman spectrometer with OMNIC 5 software. Elemental analyses were performed by the Departmental Microanalytical Service.

X-Ray crystallography

Measurements for **13** were made on a Nonius MACH3 CAD4 diffractometer, using graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). All the data obtained was corrected for Lorentz, polarisation and absorption using the psi-scan method. X-Ray structural data solution was by direct methods and refined against F^2 using SHELXTL⁵¹ or SHELX-97⁵² 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.⁵³ Crystal data for $\text{SPPr}_2(\text{CF}=\text{CF}_2)$: $\text{C}_8\text{H}_{14}\text{F}_3\text{PS}$, $M = 230.22$, triclinic, space group $P-1$, $a = 6.6533(10)$, $b = 8.881(2)$, $c = 9.771(2)$ Å, $\alpha = 82.31(2)^\circ$, $\beta = 74.07(2)^\circ$, $\gamma = 86.98(2)^\circ$, $U = 550.09(19)$ Å³, $Z = 8$, $D_c = 1.390$ Mg m⁻³, $\mu(\text{Mo-K}\alpha) = 0.435$ mm⁻¹, crystal size $0.25 \times 0.25 \times 0.10$ mm³, $F(000) = 240$, $T = 203(2)$ K, max/min transmission = $0.9578/0.8990$; 2115 reflections measured (2.18° to 24.97° θ range), 1931 unique [$R(\text{int}) = 0.0109$], which were used in all calculations. The final $R1 = 0.0323$, $wR2 = 0.0744$, $R1$ (all data) was 0.0472. Max/min residual electron density = $+0.239$ and -0.226 e Å⁻³, respectively.†

Syntheses

$\text{PEt}_2(\text{CF}=\text{CF}_2)$, 1. A three-neck round-bottom flask equipped with magnetic stirrer, and argon inlet and outlet, was held in an ethanol slush bath (-80°C) and diethyl ether (50 cm^3) was added. The temperature was lowered to *ca.* -100°C and liquid HFC-134a (1.00 cm^3 , 0.012 mol) introduced. Two equivalents of *n*-BuLi (9.49 cm^3 , 0.024 mol) were added slowly, maintaining the temperature below -80°C . After addition of the BuLi the temperature was raised and maintained between -55°C and -65°C for 2 h. The temperature was then lowered to -90°C and a concentrated, cold solution of PEt_2Cl (1.44 cm^3 , 0.012 mol) dissolved in diethyl ether (50 cm^3) was added dropwise, maintaining the solution

temperature below -90°C . The reaction was left at -78°C for 2 h, after which time it was allowed to attain ambient temperature overnight. Subsequent addition of hexane (100 cm^3) resulted in the precipitation of lithium salts, which were removed by filtration. The resulting organic phase was dried over anhydrous MgSO_4 and filtered. Distillation of the crude product under vacuum ($56-60^\circ\text{C}$, 10 mm Hg), afforded **1** as a clear liquid (1.266 g , 62.8%). (Found: C, 42.3 ; H, 5.3% . $\text{C}_6\text{H}_{10}\text{F}_3\text{P}$ requires C, 42.4 ; H, 5.9%). ν/cm^{-1} (neat): 1734 ($\text{C}=\text{C}$), 1298 ($=\text{CF}_2$ asym), 1132 ($=\text{C}-\text{F}$), 1042 ($=\text{CF}_2$ sym). δ_{P} : -32.3 [ddd, $^3J(\text{PF}_1) = 5\text{ Hz}$, $^3J(\text{PF}_2) = 53\text{ Hz}$], $\delta_{\text{F1 trans}}$: -86.6 [ddd, $^2J(\text{F}_1\text{F}_2) = 54\text{ Hz}$, $^3J(\text{PF}_1) = 5\text{ Hz}$, $^3J(\text{F}_1\text{F}_3) = 30\text{ Hz}$], $\delta_{\text{F2 cis}}$: -111.6 [ddd, $^2J(\text{F}_1\text{F}_2) = 54\text{ Hz}$, $^3J(\text{F}_2\text{F}_3) = 124\text{ Hz}$, $^3J(\text{PF}_2) = 53\text{ Hz}$], $\delta_{\text{F3 gem}}$: -187.7 [ddd, $^3J(\text{F}_1\text{F}_3) = 30\text{ Hz}$, $^3J(\text{F}_2\text{F}_3) = 124\text{ Hz}$], δ_{H} : 1.58 [dq, (CH_2), $^2J(\text{PH}) = 21.6\text{ Hz}$, $^3J(\text{HH}) = 7.5\text{ Hz}$], 1.13 [dt, (CH_3), $^3J(\text{PH}) = 16.5\text{ Hz}$, $^3J(\text{HH}) = 7.5\text{ Hz}$], $\delta_{\text{C ethyl}}$: 15.1 [s, (CH_2), br], 8.7 [d, (CH_3), $^2J(\text{PC}) = 13.5\text{ Hz}$], $\delta_{\text{C } \alpha\text{-vinyl}}$: 127.3 [dddd, $^1J(\text{PC}) = 51.2\text{ Hz}$, $^2J(\text{CF}) = 6.8$, 47.3 Hz , $^1J(\text{CF}) = 289.8\text{ Hz}$], $\delta_{\text{C } \beta\text{-vinyl}}$: 158.8 [dddd, $^2J(\text{PC}) = 29.9\text{ Hz}$, $^2J(\text{CF}) = 43.5\text{ Hz}$, $^1J(\text{CF}) = 282.0$, 304.2 Hz].

$\text{PPR}_2(\text{CF}=\text{CF}_2)$, 2. Synthesis was in an analogous manner to **1**, using HFC-134a (3.50 cm^3 , 0.042 mol), BuLi (33.2 cm^3 , 0.083 mol) and PPR_2Cl (6.28 cm^3 , 0.042 mol) in 100 cm^3 diethyl ether. Workup and distillation at $65-68^\circ\text{C}$ (10 mm Hg) resulted in **2** as a clear liquid (8.025 g , 87%). (Found: C, 48.2 ; H, 7.4 ; F, 29.1% . $\text{C}_8\text{H}_{14}\text{F}_3\text{P}$ requires C, 48.5 ; H, 7.1 ; F, 28.8%). ν/cm^{-1} (neat): 1728 ($\text{C}=\text{C}$), 1294 ($=\text{CF}_2$ asym), 1129 ($=\text{C}-\text{F}$), 1036 ($=\text{CF}_2$ sym). δ_{P} : -7.7 [ddd, $^3J(\text{PF}_1) = 4\text{ Hz}$, $^3J(\text{PF}_2) = 53\text{ Hz}$, $^2J(\text{PF}_3) = 7\text{ Hz}$], $\delta_{\text{F1 trans}}$: -86.5 [ddd, $^2J(\text{F}_1\text{F}_2) = 53\text{ Hz}$, $^3J(\text{PF}_1) = 4\text{ Hz}$, $^3J(\text{F}_1\text{F}_3) = 29\text{ Hz}$], $\delta_{\text{F2 cis}}$: -110.7 [ddd, $^2J(\text{F}_1\text{F}_2) = 53\text{ Hz}$, $^3J(\text{F}_2\text{F}_3) = 126\text{ Hz}$, $^3J(\text{PF}_2) = 53\text{ Hz}$], $\delta_{\text{F3 gem}}$: -178.9 [ddd, $^3J(\text{F}_1\text{F}_3) = 29\text{ Hz}$, $^3J(\text{F}_2\text{F}_3) = 126\text{ Hz}$, $^2J(\text{PF}_3) = 7\text{ Hz}$], δ_{H} : 0.92 [br], 1.10 [br], $\delta_{\text{C alkyl}}$: 18.6 [s], 18.7 [d, $J(\text{PC}) = 13.5\text{ Hz}$], 20.6 [br], $\delta_{\text{C } \alpha\text{-vinyl}}$: 127.4 [dddd, $^1J(\text{PC}) = 54.1\text{ Hz}$, $^2J(\text{CF}) = 8.7$, 46.4 Hz , $^1J(\text{CF}) = 291.7\text{ Hz}$], $\delta_{\text{C } \beta\text{-vinyl}}$: 159.7 [dddd, $^2J(\text{PC}) = 29.9\text{ Hz}$, $^2J(\text{CF}) = 43.6\text{ Hz}$, $^1J(\text{CF}) = 281.0$, 304.2 Hz].

$\text{PCy}_2(\text{CF}=\text{CF}_2)$, 3. Prepared as for **1**, using HFC-134a (2.50 cm^3 , 0.030 mol), BuLi (23.7 cm^3 , 0.059 mol) and PCy_2Cl (6.55 cm^3 , 0.030 mol) in 100 cm^3 diethyl ether. Workup and purification by column chromatography (50:50 toluene-hexane) resulted in **3** as a clear liquid (6.04 g , 72%). (Found: C, 59.9 ; H, 7.1 ; P, 10.1% . $\text{C}_{14}\text{H}_{22}\text{F}_3\text{P}$ requires C, 60.4 ; H, 8.0 ; P, 11.2%). δ_{P} : -16.2 [ddd, $^3J(\text{PF}_1) = 5\text{ Hz}$, $^3J(\text{PF}_2) = 54\text{ Hz}$, $^2J(\text{PF}_3) = 8\text{ Hz}$], $\delta_{\text{F1 trans}}$: -86.4 [ddd, $^2J(\text{F}_1\text{F}_2) = 30\text{ Hz}$, $^3J(\text{PF}_1) = 5\text{ Hz}$, $^3J(\text{F}_1\text{F}_3) = 29\text{ Hz}$], $\delta_{\text{F2 cis}}$: -110.5 [ddd, $^2J(\text{F}_1\text{F}_2) = 30\text{ Hz}$, $^3J(\text{F}_2\text{F}_3) = 127\text{ Hz}$, $^3J(\text{PF}_2) = 54\text{ Hz}$], $\delta_{\text{F3 gem}}$: -177.3 [ddd, $^3J(\text{F}_1\text{F}_3) = 29\text{ Hz}$, $^3J(\text{F}_2\text{F}_3) = 127\text{ Hz}$, $^2J(\text{PF}_3) = 8\text{ Hz}$], δ_{H} : 1.82 [br], 1.29 [br].

$^n\text{BuPhP}(\text{CF}=\text{CF}_2)$, 4. $^n\text{BuPhP}\text{Cl}$ was prepared by the slow addition of $^n\text{BuLi}$ (5.6 cm^3 , 0.014 mol) to a cold (-100°C) solution of PhPCl_2 (2.5 cm^3 , 0.014 mol) in diethyl ether (100 cm^3) under a nitrogen atmosphere. The reaction mixture was allowed to attain ambient temperature and the precipitated LiCl removed by filtration. The solvent was reduced to 20 cm^3 under vacuum and the resulting material reacted with $\text{CF}_2=\text{CFLi}$, as described for **1**, using HFC-134a (1.2 cm^3 , 0.014 mol), BuLi (11.2 cm^3 , 2.5 M , 0.028 mol) in 100 cm^3 diethyl ether. Workup and purification by column chromatography (chloroform), followed by distillation (141°C , 65 mm Hg), resulted in **4** as a clear liquid (0.95 g , 28%). (Found: C, 52.6 ; H, 5.2 ; P, 10.3% . $\text{C}_{12}\text{H}_{14}\text{F}_3\text{P} \cdot 0.33\text{CHCl}_3$ requires C, 51.8 ; H, 5.1 ; P, 10.8%). δ_{P} : -37.0 [ddd, $^3J(\text{PF}_1) = 4\text{ Hz}$, $^3J(\text{PF}_2) = 55\text{ Hz}$, $^3J(\text{PF}_3) = 8\text{ Hz}$], $\delta_{\text{F1 trans}}$: -82.9 [ddd, $^2J(\text{F}_1\text{F}_2) = 41\text{ Hz}$, $^3J(\text{PF}_1) = 4\text{ Hz}$, $^3J(\text{F}_1\text{F}_3) = 12\text{ Hz}$],

† CCDC reference number 232752. See <http://www.rsc.org/suppdata/nj/b3/b316099h/> for crystallographic data in .cif or other electronic format.

$\delta_{F_2 \text{ cis}}$: -106.5 [ddd, $^2J(F_1F_2)$ = 41 Hz, $^3J(F_2F_3)$ = 125 Hz, $^3J(PF_2)$ = 55 Hz], $\delta_{F_3 \text{ gem}}$: -176.8 [ddd, $^3J(F_1F_3)$ = 12 Hz, $^3J(F_2F_3)$ = 125 Hz, $^2J(PF_3)$ = 8 Hz], δ_H : 0.92 [br], 1.10 [br], $\delta_C \text{ alkyl}$: 14.0 [s], 22.3 [s], 24.2 [s], 28.2 [s] $\delta_C \alpha\text{-vinyl}$: 127.4 [dddd], $^1J(PC)$ = 54.1 Hz, $^2J(CF)$ = 8.7, 46.4 Hz, $^1J(CF)$ = 291.7 Hz], $\delta_C \beta\text{-vinyl}$: 159.5 [dddd], $^2J(PC)$ = 33.4 Hz, $^2J(CF)$ = 43.6 Hz, $^1J(CF)$ = 283.0, 337.9 Hz].

Z-PPh₂(CF=CFBu), 5. PPh₂(CF=CF₂) (0.5 g, 1.88×10^{-3} mol) was dissolved in 100 cm³ of ether and cooled to -90 °C, whereupon *n*-BuLi (1.5 cm³, 3.00×10^{-3} mol) was added dropwise, resulting in a colour change from yellow to brown. After allowing the solution to warm to -60 °C, ice/water (100 cm³) was added and the mixture left to stand until all the ice had melted; the organic soluble material was then extracted into diethyl ether (4 × 50 cm³). Removal of the solvent yielded a brown oil that was purified by column chromatography (eluent 1:1 hexane-toluene) to afford **5** as a brown oil (0.470 g, 82%). (Found: C, 71.0; H, 6.5; F, 12.1%. C₁₈H₁₉F₂P requires C, 71.0; H, 6.3; F, 12.5%). ν/cm^{-1} (neat): 3056 (C-H arom), 2964, 2928, 2874 (C-H alkyl), 1670 (C=C), 1132, 1091 (C-F). δ_P : -27.1 [dd, $^3J(PF)$ = 89 Hz, $^2J(PF)$ = 5 Hz], $\delta_{F \text{ cis}}$: -132.7 [ddt, $^3J(FF)$ = 141 Hz, $^3J(PF)$ = 89 Hz, $^3J(FH_a)$ = 23 Hz], $\delta_{F \text{ gem}}$: -159.1 [dtd, $^3J(FF)$ = 141 Hz, $^4J(FH_a)$ = 10 Hz, $^2J(PF)$ = 5 Hz], $\delta_H \text{ butyl Ha}$: 2.5 [ddt, $^3J(FH_a)$ = 23 Hz, $^4J(FH_a)$ = 10 Hz, $^3J(H_aH_b)$ = 7.5 Hz], δ_{Hb} : 1.6 [tt, $^3J(H_aH_b)$ = 7.5 Hz, $^3J(H_bH_c)$ = 7.5 Hz], δ_{Hc} : 1.4 [tq, $^3J(H_bH_c)$ = 7.5 Hz, $^3J(H_cH_d)$ = 7.5 Hz], δ_{Hd} : 1.0 [t, $^3J(H_cH_d)$ = 7.5 Hz], δ_{Cd} : 14.0 [s], δ_{Cc} : 22.4 [s], δ_{Ca} : 27.4 [dd, $^2J(CF)$ = 23 Hz, $^3J(CF)$ = 2 Hz], δ_{Cb} : 28.1 [s], $\delta_C \text{ meta}$: 128.9 [d, $^3J(PC)$ = 6.6 Hz], $\delta_C \text{ para}$: 129.4 [s], $\delta_C \text{ ortho}$: 133.8 [d, $^2J(PC)$ = 19.4 Hz], $\delta_C \alpha\text{-vinyl}$: 149.1 [dddd, $^1J(PC)$ = 51.2 Hz, $^2J(CF)$ = 42.5 Hz, $^1J(CF)$ = 287.0 Hz], $\delta_C \beta\text{-vinyl}$: 164.9 [ddd, $^2J(PC)$ = 19.3 Hz, $^2J(CF)$ = 46.4 Hz, $^1J(CF)$ = 251.1 Hz].

Reaction of PPh₂(CF=CF₂) with LiAlH₄. PPh₂(CF=CF₂) (2.0 g, 7.52×10^{-3} mol) was dissolved in diethyl ether (50 cm³) and cooled to -80 °C, whereupon freshly powdered LiAlH₄ (1.14 g, 0.030 mol) was added, the resulting solution being allowed to return to room temperature overnight. Dry hexane (100 cm³) was added and the solution filtered to yield a pale yellow filtrate that was dried over MgSO₄, re-filtered and the solvent removed *in vacuo* to yield a mixture of the following species. Major products: Z-PPh₂(CF=CFH), **6** (see following reaction for details); Ph₂PH: δ_P -39.0 [dq, $^1J(PH)$ = 218 Hz, $^3J(PH)$ = 7 Hz], δ_H 5.37 [d, $^1J(PH)$ = 218 Hz]. Minor products: PPh₂(CF=CH₂):⁵⁴ δ_P -9.5 [d, $^2J(PF)$ = 40.4 Hz], δ_F -96.2 [ddd, $^3J(HF)$ = 20.4, 50.9 Hz, $^2J(PF)$ = 40.4 Hz], $\delta_H \text{ trans}$ 5.45 [ddd, $^2J(HH)$ = 2.6 Hz, $^3J(HH)$ = 20.4 Hz, $^3J(PH)$ = 23.4 Hz], $\delta_H \text{ cis}$ 5.03 [ddd, $^2J(HH)$ = 2.6 Hz, $^3J(HF)$ = 50.9 Hz, $^3J(PH)$ = 6.4 Hz]; E-PPh₂(CF=CFH): δ_P -19.9 [dd, $^2J(PF)$ = 10.5 Hz, $^3J(PF)$ = 32.9 Hz], $\delta_F \text{ trans}$ -134.3 [ddd, $^3J(FF)$ = 19 Hz, $^3J(PF)$ = 33 Hz, $^2J(HF)$ = 74 Hz], $\delta_F \text{ gem}$ -141.3 [ddd, $^3J(PF)$ = 10.5 Hz, $^3J(FF)$ = 19 Hz, $^3J(HF)$ = 17 Hz], $\delta_H \text{ cis}$ 6.86 [ddd, $^2J(HF)$ = 74 Hz, $^3J(HF)$ = 17 Hz, $^3J(PH)$ = 4 Hz]; Z-PPh₂(CH=CFH): δ_P -9.8 [d, $^3J(PF)$ = 58.6 Hz], δ_F -125.3 [ddd, $^3J(HF)$ = 18 Hz, $^2J(HF)$ = 70 Hz, $^3J(PF)$ = 56 Hz]; PhPH₂: δ_P -121.0 [tt, $^1J(PH)$ = 199 Hz, $^3J(PH)$ = 7 Hz]; PPh₂(CH=CF₂) (see reaction of PPh₂(CCl=CF₂) with LiAlH₄); PPh₂(CH=CH₂):⁵⁵ δ_P -11.4 [s]

Z-PPh₂(CF=CFH), 6. PPh₂(CF=CF₂) (0.95 g, 3.57×10^{-3} mol) was dissolved in THF (50 cm³) and freshly powdered LiAlH(OBu^t)₃ (1.81 g, 7.14×10^{-3} mol) was added at ambient temperature; the mixture was stirred overnight. The reaction was quenched with water and the product extracted with 40-60° petroleum ether (2 × 20 cm³), dried over MgSO₄, re-filtered and solvent removed *in vacuo* to yield **6** as a pale

yellow oil, after purification by column chromatography (eluent 1:1 hexane-toluene) (0.73 g, 83%). (Found: C, 67.6; H, 4.3; P, 12.0%. C₁₄H₁₁F₂P requires C, 67.8; H, 4.5; P, 12.5%). ν/cm^{-1} (neat): 3074, 3057 (C-H vinyl), 1647 (C=C), 1151, 1105 (C-F). δ_P : -27.5 [dd, $^3J(PF)$ = 74 Hz, $^2J(PF)$ = 8 Hz], $\delta_F \text{ cis}$: -159.8 [ddd, $^3J(FF)$ = 144 Hz, $^3J(PF)$ = 74 Hz, $^3J(FH)$ = 77 Hz], $\delta_F \text{ gem}$: -163.9 [ddd, $^3J(FF)$ = 144 Hz, $^3J(FH)$ = 6 Hz, $^2J(PF)$ = 8 Hz], $\delta_H \text{ vinyl}$: 7.59 [ddd, $^3J(PH)$ = 12 Hz, $^3J(FH)$ = 77 Hz, $^3J(FH)$ = 6 Hz], $\delta_H \text{ aromatic}$: 7.51 [m, br], 7.40 [m, br], $\delta_C \text{ ipso}$: 126.8 [d, $^1J(PC)$ = 81 Hz], $\delta_C \text{ meta}$: 126.9 [d, $^3J(PC)$ = 7 Hz], $\delta_C \text{ para}$: 127.6 [s], $\delta_C \text{ ortho}$: 131.7 [d, $^2J(PC)$ = 20 Hz], $\delta_C \beta\text{-vinyl}$: 149.7 [ddd, $^1J(CF)$ = 253 Hz, $^2J(CF)$ = 61 Hz, $^2J(PC)$ = 19 Hz], $\delta_C \alpha\text{-vinyl}$: 152.7 [ddd, $^1J(CF)$ = 293 Hz, $^2J(CF)$ = 44 Hz, $^1J(PC)$ = 38 Hz].

Reaction of PPh₂(CCl=CF₂) with LiAlH₄. PPh₂(CCl=CF₂) (1.0 g, 3.54×10^{-3} mol) was reacted with LiAlH₄ (0.54 g, 0.014 mol) using the same method outlined above for PPh₂(CF=CF₂) to yield a mixture of the following species. Major products: E-PPh₂(CCl=CFH), **7** (see following reaction for details); Ph₂PH (see above). Minor products: PPh₂(CCl=CH₂): δ_P -32.8 [s], $\delta_H \text{ trans}$ 6.6 [dd, $^2J(HH)$ = 2.4 Hz, $^3J(PH)$ = 11 Hz], $\delta_H \text{ cis}$ 6.4 [dd, $^2J(HH)$ = 2.4 Hz, $^3J(PH)$ = 28 Hz]; Z-PPh₂(CCl=CFH): δ_P -4.3 [d, $^3J(PF)$ = 24 Hz], $\delta_F \text{ trans}$ -99.6 [dd, $^3J(PF)$ = 24 Hz, $^2J(HF)$ = 80 Hz]; E-PPh₂(CH=CFH): δ_P -26.9 [d, $^3J(PF)$ = 17 Hz], δ_F -95.2 [ddd, $^3J(HF)$ = 21 Hz, $^2J(HF)$ = 86 Hz, $^3J(PF)$ = 17 Hz], $\delta_H \text{ cis}$ 6.90 [ddd, $^3J(HH)$ = 11.7 Hz, $^2J(HF)$ = 86 Hz, $^3J(PH)$ = 6 Hz], $\delta_H \text{ gem}$ 6.11 [dd, $^3J(HH)$ = 11.7 Hz, $^3J(HF)$ = 21 Hz]; PPh₂(CH=CF₂):¹³ δ_P -33.3 [d, $^3J(PF)$ = 45 Hz]

E-PPh₂(CCl=CFH), 7. PPh₂(CCl=CF₂) (1.02 g, 3.61×10^{-3} mol) was dissolved in THF (50 cm³) and LiAlH(OBu^t)₃ (1.83 g, 7.20×10^{-3} mol) added. Following workup, as for **6** above, resulted in isolation of **7** as a pale yellow oil, after purification by column chromatography (eluent 1:1 hexane-toluene) (0.591 g, 62%). (Found: C, 63.4; H, 4.3; Cl, 14.8%. C₁₄H₁₁ClFP requires C, 62.5; H, 4.2; Cl, 13.4%). δ_P : -14.5 [d, $^3J(PF)$ = 84 Hz], δ_F : -106.5 [dd, $^3J(PF)$ = 84 Hz, $^2J(FH)$ = 82 Hz], $\delta_H \text{ vinyl}$: 7.35 [dd, $^3J(PH)$ = 12 Hz, $^2J(FH)$ = 82 Hz], $\delta_H \text{ aromatic}$: 7.51 to 7.40 [m, br], $\delta_C \text{ ipso}$: 127.0 [d, $^1J(PC)$ = 79 Hz], $\delta_C \text{ meta}$: 126.9 [d, $^3J(PC)$ = 7.7 Hz], $\delta_C \text{ para}$: 127.7 [s], $\delta_C \text{ ortho}$: 131.8 [d, $^2J(PC)$ = 20.3 Hz], $\delta_C \beta\text{-vinyl}$: 155.0 [dd, $^1J(CF)$ = 275 Hz, $^2J(PC)$ = 19 Hz], $\delta_C \alpha\text{-vinyl}$: 119.0 [dd, $^2J(CF)$ = 26 Hz, $^1J(PC)$ = 55 Hz].

OPR_{3-x}(CF=CF₂)_x (x = 1, R = Et, **8; R = ⁱPr, **9**; R = Ph, **10**; x = 2, R = Ph, **11**).** The synthesis of OPEt₂(CF=CF₂) (**8**) is typical. PEt₂(CF=CF₂) (0.178 g, 0.001 mol) was dissolved in THF (5 cm³) and an excess of 27% w/w H₂O₂ (10.5 cm³) was added at 0 °C (ice bath). The mixture was stirred for 20 to 30 min and the progress of the reaction checked by ³¹P{¹H} NMR spectroscopy. Water (15 cm³) and chloroform (20 cm³) were added to the reaction mixture and OPEt₂(CF=CF₂) was extracted into the organic phase, which was dried with MgSO₄. After filtration the solvent was removed to yield **8** as a clear liquid.

8. (0.077 g, 41%). (Found: C, 37.0; H, 5.4; F, 28.7%. C₆H₁₀F₃PO requires C, 38.7 H, 5.4; F, 30.6%). δ_P : 45.8 [dd, $^3J(PF_2)$ = 10 Hz, $^2J(PF_3)$ = 45 Hz], $\delta_{F1 \text{ trans}}$: -81.8 [dd, $^2J(F_1F_2)$ = 45 Hz, $^3J(F_1F_3)$ = 30 Hz], $\delta_{F2 \text{ cis}}$: -106.7 [ddd, $^2J(F_1F_2)$ = 45 Hz, $^3J(F_2F_3)$ = 119 Hz, $^3J(PF_2)$ = 10 Hz], $\delta_{F3 \text{ gem}}$: -192.3 [ddd, $^3J(F_1F_3)$ = 30 Hz, $^3J(F_2F_3)$ = 119 Hz, $^2J(PF_3)$ = 45 Hz]. ν/cm^{-1} (neat): 1738 (C=C), 1318 (=CF₂ asym), 1165 (=C-F), 1069 (=CF₂ sym).

9. (0.119 g, 55%). (Found: C, 45.2; H, 6.8; F, 26.2%. C₈H₁₄F₃PO requires C, 44.9; H, 6.5; F, 26.6%). δ_P 53.4

[dd, $^3J(\text{PF}_2) = 10$ Hz, $^2J(\text{PF}_3) = 34$ Hz], $\delta_{\text{F1 trans}} -80.3$ [dd, $^2J(\text{F}_1\text{F}_2) = 43$ Hz, $^3J(\text{F}_1\text{F}_3) = 30$ Hz], $\delta_{\text{F2 cis}} -105.7$ [ddd, $^2J(\text{F}_1\text{F}_2) = 43$ Hz, $^3J(\text{F}_2\text{F}_3) = 119$ Hz, $^3J(\text{PF}_2) = 10$ Hz], $\delta_{\text{F3 gem}} -189.5$ [ddd, $^3J(\text{F}_1\text{F}_3) = 30$ Hz, $^3J(\text{F}_2\text{F}_3) = 119$ Hz, $^2J(\text{PF}_3) = 34$ Hz]. ν/cm^{-1} (neat): 1732 (C=C), 1314 (=CF₂ asym), 1204 (P=O), 1156 (=C-F), 1063 (=CF₂ sym).

10. (0.183 g, 65%). (Found: C, 59.5; H, 3.5; F, 19.9%. C₁₄H₁₀F₃PO requires C, 59.6; H, 3.5; F, 20.2%). $\delta_{\text{P}}: 19.8$ [ddd, $^3J(\text{PF}_1) = 6$ Hz, $^3J(\text{PF}_2) = 11$ Hz, $^2J(\text{PF}_3) = 49$ Hz], $\delta_{\text{F1 trans}} -79.9$ [ddd, $^3J(\text{PF}_1) = 6$ Hz, $^2J(\text{F}_1\text{F}_2) = 38$ Hz, $^3J(\text{F}_1\text{F}_3) = 28$ Hz], $\delta_{\text{F2 cis}} -101.4$ [ddd, $^2J(\text{F}_1\text{F}_2) = 38$ Hz, $^3J(\text{F}_2\text{F}_3) = 120$ Hz, $^3J(\text{PF}_2) = 11$ Hz], $\delta_{\text{F3 gem}} -186.6$ [ddd, $^3J(\text{F}_1\text{F}_3) = 28$ Hz, $^3J(\text{F}_2\text{F}_3) = 120$ Hz, $^2J(\text{PF}_3) = 49$ Hz]. ν/cm^{-1} (CH₂Cl₂): 1734 (C=C), 1323 (=CF₂ asym), 1173 (=C-F), 1072 (=CF₂ sym).

11. Complete conversion to the phosphine oxide was not obtained, data characteristic of **11** is given below. $\delta_{\text{P}}: 8.4$ [ttt, $^3J(\text{PF}_1) = 10$ Hz, $^3J(\text{PF}_2) = 11$ Hz, $^2J(\text{PF}_3) = 56$ Hz], $\delta_{\text{F1 trans}} -77.3$ [ddd, $^3J(\text{PF}_1) = 10$ Hz, $^2J(\text{F}_1\text{F}_2) = 31$ Hz, $^3J(\text{F}_1\text{F}_3) = 30$ Hz], $\delta_{\text{F2 cis}} -99.4$ [ddd, $^2J(\text{F}_1\text{F}_2) = 31$ Hz, $^3J(\text{F}_2\text{F}_3) = 121$ Hz, $^3J(\text{PF}_2) = 11$ Hz], $\delta_{\text{F3 gem}} -192.4$ [ddd, $^3J(\text{F}_1\text{F}_3) = 30$ Hz, $^3J(\text{F}_2\text{F}_3) = 121$ Hz, $^2J(\text{PF}_3) = 56$ Hz]. ν/cm^{-1} (CH₂Cl₂): 1734 (C=C), 1333 (=CF₂ asym), 1200 (P=O), 1181 (=C-F), 1071 (=CF₂ sym).

SPR_{3-x}(CF=CF₂)_x (x = 1, R = Et, **12; R = ⁱPr, **13**; R = Ph, **14**; x = 2, R = Ph, **15**).** Perfluorovinyl phosphine sulfides were synthesised by refluxing the phosphine with a large excess of sulfur, the synthesis of **14** being typical. PPh₂(CF=CF₂) (0.710 g, 2.67 × 10⁻³ mol) was dissolved in toluene (15 cm³) and an excess of sulfur (0.193 g, 6 × 10⁻³ mol) was added. The solution was refluxed for 18 h, with additional 0.2 g portions of sulfur added every 3 h. After the reaction was judged to have gone to completion (³¹P{¹H} NMR spectroscopy), the solvent was removed and the residue purified by column chromatography using 50:50 toluene-ether as eluent. The solvent was removed to give **14** as a yellow oil.

12. (0.208 g, 38%). $\delta_{\text{P}}: 47.2$ [dd, $^3J(\text{PF}_2) = 10$ Hz, $^2J(\text{PF}_3) = 37$ Hz], $\delta_{\text{F1 trans}} -80.0$ [dd, $^2J(\text{F}_1\text{F}_2) = 39$ Hz, $^3J(\text{F}_1\text{F}_3) = 32$ Hz], $\delta_{\text{F2 cis}} -101.3$ [ddd, $^2J(\text{F}_1\text{F}_2) = 39$ Hz, $^3J(\text{F}_2\text{F}_3) = 123$ Hz, $^3J(\text{PF}_2) = 10$ Hz], $\delta_{\text{F3 gem}} -184.4$ [ddd, $^3J(\text{F}_1\text{F}_3) = 32$ Hz, $^3J(\text{F}_2\text{F}_3) = 123$ Hz, $^2J(\text{PF}_3) = 37$ Hz]. ν/cm^{-1} (neat): 1737 (C=C), 1318 (=CF₂ asym), 1150 (=C-F), 1065 (=CF₂ sym), 592 (P=S).

13. (0.290 g, 47%), mp 32 °C. (Found: C, 41.3; H, 7.1; P, 13.2; S, 13.3%. C₈H₁₄F₃PS requires C, 41.7; H, 6.1; P, 13.5; S, 13.9%). $\delta_{\text{P}}: 63.6$ [dd, $^3J(\text{PF}_2) = 10$ Hz, $^2J(\text{PF}_3) = 28$ Hz], $\delta_{\text{F1 trans}} -79.1$ [dd, $^2J(\text{F}_1\text{F}_2) = 37$ Hz, $^3J(\text{F}_1\text{F}_3) = 32$ Hz], $\delta_{\text{F2 cis}} -101.4$ [ddd, $^2J(\text{F}_1\text{F}_2) = 37$ Hz, $^3J(\text{F}_2\text{F}_3) = 122$ Hz, $^3J(\text{PF}_2) = 10$ Hz], $\delta_{\text{F3 gem}} -181.4$ [ddd, $^3J(\text{F}_1\text{F}_3) = 32$ Hz, $^3J(\text{F}_2\text{F}_3) = 122$ Hz, $^2J(\text{PF}_3) = 28$ Hz]. ν/cm^{-1} (nujol): 1730 (C=C), 1318 (=CF₂ asym), 1146 (=C-F), 1061 (=CF₂ sym), 600 (P=S).

14. (0.390 g, 49%). (Found: C, 56.2; H, 3.5; P, 10.2; S, 10.9%. C₁₄H₁₀F₃PS requires C, 56.4; H, 3.4; P, 10.4; S, 10.7%). $\delta_{\text{P}}: 32.5$ [ddd, $^3J(\text{PF}_1) = 4$ Hz, $^3J(\text{PF}_2) = 12$ Hz, $^2J(\text{PF}_3) = 46$ Hz], $\delta_{\text{F1 trans}} -80.3$ [ddd, $^3J(\text{PF}_1) = 4$ Hz, $^2J(\text{F}_1\text{F}_2) = 34$ Hz, $^3J(\text{F}_1\text{F}_3) = 30$ Hz], $\delta_{\text{F2 cis}} -97.4$ [ddd, $^2J(\text{F}_1\text{F}_2) = 34$ Hz, $^3J(\text{F}_2\text{F}_3) = 122$ Hz, $^3J(\text{PF}_2) = 12$ Hz], $\delta_{\text{F3 gem}} -178.0$ [ddd, $^3J(\text{F}_1\text{F}_3) = 30$ Hz, $^3J(\text{F}_2\text{F}_3) = 122$ Hz, $^2J(\text{PF}_3) = 46$ Hz]. ν/cm^{-1} (neat): 1728 (C=C), 1317 (=CF₂ asym), 1106 (=C-F), 1060 (=CF₂ sym), 645 (P=S).

15. Conversion of PPh(CF=CF₂)₂ was incomplete. $\delta_{\text{P}}: 17.4$ [ttt, $^3J(\text{PF}_1) = 6$ Hz, $^3J(\text{PF}_2) = 13$ Hz, $^2J(\text{PF}_3) = 50$ Hz], $\delta_{\text{F1 trans}} -77.7$ [ddd, $^3J(\text{PF}_1) = 6$ Hz, $^2J(\text{F}_1\text{F}_2) = 31$ Hz, $^3J(\text{F}_1\text{F}_3) = 31$ Hz], $\delta_{\text{F2 cis}} -97.4$ [ddd, $^2J(\text{F}_1\text{F}_2) = 31$ Hz, $^3J(\text{F}_2\text{F}_3) = 122$ Hz, $^3J(\text{PF}_2) = 13$ Hz], $\delta_{\text{F3 gem}} -183.0$ [ddd, $^3J(\text{F}_1\text{F}_3) = 31$ Hz, $^3J(\text{F}_2\text{F}_3) = 122$ Hz, $^2J(\text{PF}_3) = 50$ Hz].

SePR_{3-x}(CF=CF₂)_x (x = 1, R = Et, **16; R = ⁱPr, **17**; R = Ph, **18**; x = 2, R = Ph, **19**).** Perfluorovinyl phosphine selenides were synthesised by a similar method as the sulfides **12** to **15**. For example, PPr₂(CF=CF₂) (0.85 g, 4.30 × 10⁻³ mol) was refluxed with selenium (0.455 g, 5.70 × 10⁻³ mol) in 20 cm³ toluene for 3 h. After this period the excess selenium was filtered off and the solvent removed to yield **17** as a brown liquid.

16. (0.418 g, 39%). $\delta_{\text{P}}: 33.4$ [dd, $^1J(\text{SeP}) = 730$ Hz, $^3J(\text{PF}_2) = 10$ Hz, $^2J(\text{PF}_3) = 34$ Hz], $\delta_{\text{F1 trans}} -79.9$ [dd, $^2J(\text{F}_1\text{F}_2) = 38$ Hz, $^3J(\text{F}_1\text{F}_3) = 32$ Hz], $\delta_{\text{F2 cis}} -99.8$ [ddd, $^2J(\text{F}_1\text{F}_2) = 38$ Hz, $^3J(\text{F}_2\text{F}_3) = 123$ Hz, $^3J(\text{PF}_2) = 10$ Hz], $\delta_{\text{F3 gem}} -182.9$ [ddd, $^3J(\text{F}_1\text{F}_3) = 32$ Hz, $^3J(\text{F}_2\text{F}_3) = 123$ Hz, $^2J(\text{PF}_3) = 34$ Hz]. ν/cm^{-1} (neat): 1736 (C=C), 1316 (=CF₂ asym), 1144 (=C-F), 1065 (=CF₂ sym).

17. (0.536 g, 45%). (Found: C, 39.6; H, 5.9; F, 6.7%. C₈H₁₄F₃PSe requires C, 34.7; H, 5.1; F, 11.2%). $\delta_{\text{P}}: 55.9$ [dd, $^1J(\text{SeP}) = 766$ Hz, $^3J(\text{PF}_2) = 10$ Hz, $^2J(\text{PF}_3) = 24$ Hz], $\delta_{\text{F1 trans}} -79.7$ [dd, $^2J(\text{F}_1\text{F}_2) = 33$ Hz, $^3J(\text{F}_1\text{F}_3) = 32$ Hz], $\delta_{\text{F2 cis}} -98.5$ [ddd, $^4J(\text{SeF}) = 28$ Hz, $^2J(\text{F}_1\text{F}_2) = 33$ Hz, $^3J(\text{F}_2\text{F}_3) = 124$ Hz, $^3J(\text{PF}_2) = 10$ Hz], $\delta_{\text{F3 gem}} -179.6$ [ddd, $^3J(\text{F}_1\text{F}_3) = 32$ Hz, $^3J(\text{F}_2\text{F}_3) = 124$ Hz, $^2J(\text{PF}_3) = 24$ Hz]. ν/cm^{-1} (neat): 1732 (C=C), 1316 (=CF₂ asym), 1144 (=C-F), 1059 (=CF₂ sym), 550 (P=Se).

18. (0.835 g, 56%). (Found: C, 48.0; H, 2.7; F, 8.1%. C₁₄H₁₀F₃PSe requires C, 48.7; H, 2.9; F, 9.0%). $\delta_{\text{P}}: 22.2$ [ddd, $^1J(\text{SeP}) = 785$ Hz, $^3J(\text{PF}_1) = 3$ Hz, $^3J(\text{PF}_2) = 12$ Hz, $^2J(\text{PF}_3) = 46$ Hz], $\delta_{\text{F1 trans}} -80.4$ [ddd, $^2J(\text{F}_1\text{F}_2) = 33$ Hz, $^3J(\text{F}_1\text{F}_3) = 30$ Hz, $^3J(\text{PF}_1) = 3$ Hz], $\delta_{\text{F2 cis}} -96.3$ [ddd, $^4J(\text{SeF}) = 18$ Hz, $^2J(\text{F}_1\text{F}_2) = 33$ Hz, $^3J(\text{F}_2\text{F}_3) = 123$ Hz, $^3J(\text{PF}_2) = 12$ Hz], $\delta_{\text{F3 gem}} -176.6$ [ddd, $^3J(\text{SeF}) = 3$ Hz, $^3J(\text{F}_1\text{F}_3) = 30$ Hz, $^3J(\text{F}_2\text{F}_3) = 123$ Hz, $^2J(\text{PF}_3) = 46$ Hz]. ν/cm^{-1} (neat): 1726 (C=C), 1317 (=CF₂ asym), 1144 (=C-F), 1058 (=CF₂ sym), 582 (P=Se).

19. Complete conversion of starting material was not achieved even after extended periods of reaction. $\delta_{\text{P}}: 4.5$ [ttt, $^1J(\text{SeP}) = 848$ Hz, $^3J(\text{PF}_1) = 5$ Hz, $^3J(\text{PF}_2) = 13$ Hz, $^2J(\text{PF}_3) = 47$ Hz], $\delta_{\text{F1 trans}} -78.6$ [ddd, $^2J(\text{F}_1\text{F}_2) = 33$ Hz, $^3J(\text{F}_1\text{F}_3) = 32$ Hz, $^3J(\text{PF}_1) = 5$ Hz], $\delta_{\text{F2 cis}} -96.9$ [ddd, $^2J(\text{F}_1\text{F}_2) = 33$ Hz, $^3J(\text{F}_2\text{F}_3) = 124$ Hz, $^3J(\text{PF}_2) = 13$ Hz], $\delta_{\text{F3 gem}} -181.2$ [ddd, $^3J(\text{F}_1\text{F}_3) = 33$ Hz, $^3J(\text{F}_2\text{F}_3) = 124$ Hz, $^2J(\text{PF}_3) = 47$ Hz]. ν/cm^{-1} (neat): 1741 (C=C), 1312 (=CF₂ asym), 1159 (=C-F), 1048 (=CF₂ sym), 599 (P=Se).

F₂PR_{3-x}(CF=CF₂)_x (x = 1, R = Et, **20; R = ⁱPr, **21**; R = Cy, **22**; R = Ph, **23**; x = 2, R = Ph, **24**), **F₂PPh₂(CF=CFH)**, **25**, and **F₂PPh₂(CCl=CFH)**, **26**.** All reactions were performed on a NMR tube scale in a dry box with addition of XeF₂, in portions, to one equivalent of the phosphine dissolved in CDCl₃. The reactions were exothermic with evolution of xenon gas. The products were identified using ¹⁹F and ³¹P{¹H} NMR spectroscopy.

20. $\delta_{\text{P}}: -23.6$ [tddd, $^3J(\text{PF}_1) = 13$ Hz, $^3J(\text{PF}_2) = 12$ Hz, $^2J(\text{PF}_3) = 77$ Hz, $^1J(\text{PF}_4) = 654$ Hz], $\delta_{\text{F1 trans}} -81.3$ [dddt, $^3J(\text{PF}_1) = 13$ Hz, $^2J(\text{F}_1\text{F}_2) = 32$ Hz, $^3J(\text{F}_1\text{F}_3) = 37$ Hz, $^4J(\text{F}_1\text{F}_4) = 7$ Hz], $\delta_{\text{F2 cis}} -97.4$ [dtdd, $^3J(\text{PF}_2) = 12$ Hz, $^2J(\text{F}_1\text{F}_2) = 32$ Hz, $^3J(\text{F}_2\text{F}_3) = 113$ Hz, $^4J(\text{F}_2\text{F}_4) = 39$ Hz], $\delta_{\text{F3 gem}} -180.4$ [dddt, $^2J(\text{PF}_3) = 77$ Hz, $^3J(\text{F}_1\text{F}_3) = 37$ Hz, $^3J(\text{F}_2\text{F}_3) = 113$ Hz, $^3J(\text{F}_3\text{F}_4) = 7$ Hz], $\delta_{\text{F4 P-F}} -43.9$ [dddt, $^1J(\text{PF}_4) = 654$ Hz, $^4J(\text{F}_1\text{F}_4) = 7$ Hz, $^4J(\text{F}_2\text{F}_4) = 39$ Hz, $^3J(\text{F}_3\text{F}_4) = 7$ Hz].

21. $\delta_{\text{P}}: -19.6$ [tddd, $^3J(\text{PF}_1) = 13$ Hz, $^3J(\text{PF}_2) = 12$ Hz, $^2J(\text{PF}_3) = 72$ Hz, $^1J(\text{PF}_4) = 690$ Hz], $\delta_{\text{F1 trans}} -80.7$ [dddt, $^3J(\text{PF}_1) = 13$ Hz, $^2J(\text{F}_1\text{F}_2) = 28$ Hz, $^3J(\text{F}_1\text{F}_3) = 39$ Hz, $^4J(\text{F}_1\text{F}_4) = 9$ Hz], $\delta_{\text{F2 cis}} -95.5$ [dtdd, $^3J(\text{PF}_2) = 12$ Hz, $^2J(\text{F}_1\text{F}_2) = 28$ Hz, $^3J(\text{F}_2\text{F}_3) = 111$ Hz, $^4J(\text{F}_2\text{F}_4) = 45$ Hz], $\delta_{\text{F3 gem}} -176.7$ [dddt, $^2J(\text{PF}_3) = 72$ Hz, $^3J(\text{F}_1\text{F}_3) = 39$ Hz, $^3J(\text{F}_2\text{F}_3) = 111$ Hz, $^3J(\text{F}_3\text{F}_4) = 9$ Hz], $\delta_{\text{F4 P-F}} -62.1$ [dddt,

$^1J(\text{PF}_4) = 690 \text{ Hz}$, $^4J(\text{F}_1\text{F}_4) = 9 \text{ Hz}$, $^4J(\text{F}_2\text{F}_4) = 45 \text{ Hz}$, $^3J(\text{F}_3\text{F}_4) = 9 \text{ Hz}$].

22. δ_{P} : -25.6 [tddd, $^3J(\text{PF}_1) = 13 \text{ Hz}$, $^3J(\text{PF}_2) = 12 \text{ Hz}$, $^2J(\text{PF}_3) = 71 \text{ Hz}$, $^1J(\text{PF}_4) = 684 \text{ Hz}$], $\delta_{\text{F1 trans}}$: -79.8 [dddt, $^3J(\text{PF}_1) = 13 \text{ Hz}$, $^2J(\text{F}_1\text{F}_2) = 28 \text{ Hz}$, $^3J(\text{F}_1\text{F}_3) = 39 \text{ Hz}$, $^4J(\text{F}_1\text{F}_4) = 10 \text{ Hz}$], $\delta_{\text{F2 cis}}$: -95.3 [dtdd, $^3J(\text{PF}_2) = 12 \text{ Hz}$, $^2J(\text{F}_1\text{F}_2) = 28 \text{ Hz}$, $^3J(\text{F}_2\text{F}_3) = 110 \text{ Hz}$, $^4J(\text{F}_2\text{F}_4) = 45 \text{ Hz}$], $\delta_{\text{F3 gem}}$: -176.7 [dddt, $^2J(\text{PF}_3) = 71 \text{ Hz}$, $^3J(\text{F}_1\text{F}_3) = 39 \text{ Hz}$, $^3J(\text{F}_2\text{F}_3) = 110 \text{ Hz}$, $^3J(\text{F}_3\text{F}_4) = 9 \text{ Hz}$], $\delta_{\text{F4 P-F}}$: -60.3 [dddt, $^1J(\text{PF}_4) = 684 \text{ Hz}$, $^4J(\text{F}_1\text{F}_4) = 10 \text{ Hz}$, $^4J(\text{F}_2\text{F}_4) = 45 \text{ Hz}$, $^3J(\text{F}_3\text{F}_4) = 9 \text{ Hz}$].

23. δ_{P} : -62.8 [tddd, $^3J(\text{PF}_1) = 17 \text{ Hz}$, $^3J(\text{PF}_2) = 13 \text{ Hz}$, $^2J(\text{PF}_3) = 78 \text{ Hz}$, $^1J(\text{PF}_4) = 707 \text{ Hz}$], $\delta_{\text{F1 trans}}$: -80.1 [dddt, $^3J(\text{PF}_1) = 17 \text{ Hz}$, $^2J(\text{F}_1\text{F}_2) = 29 \text{ Hz}$, $^3J(\text{F}_1\text{F}_3) = 33 \text{ Hz}$, $^4J(\text{F}_1\text{F}_4) = 8 \text{ Hz}$], $\delta_{\text{F2 cis}}$: -95.7 [dtdd, $^3J(\text{PF}_2) = 13 \text{ Hz}$, $^2J(\text{F}_1\text{F}_2) = 29 \text{ Hz}$, $^3J(\text{F}_2\text{F}_3) = 112 \text{ Hz}$, $^4J(\text{F}_2\text{F}_4) = 41 \text{ Hz}$], $\delta_{\text{F3 gem}}$: -178.2 [dddt, $^2J(\text{PF}_3) = 78 \text{ Hz}$, $^3J(\text{F}_1\text{F}_3) = 33 \text{ Hz}$, $^3J(\text{F}_2\text{F}_3) = 112 \text{ Hz}$, $^3J(\text{F}_3\text{F}_4) = 7 \text{ Hz}$], $\delta_{\text{F4 P-F}}$: -50.1 [dddt, $^1J(\text{PF}_4) = 707 \text{ Hz}$, $^4J(\text{F}_1\text{F}_4) = 8 \text{ Hz}$, $^4J(\text{F}_2\text{F}_4) = 41 \text{ Hz}$, $^3J(\text{F}_3\text{F}_4) = 7 \text{ Hz}$].

24. δ_{P} : -66.6 [tttt, $^3J(\text{PF}_1) = 18 \text{ Hz}$, $^3J(\text{PF}_2) = 15 \text{ Hz}$, $^2J(\text{PF}_3) = 88 \text{ Hz}$, $^1J(\text{PF}_4) = 739 \text{ Hz}$], $\delta_{\text{F1 trans}}$: -75.5 [dddt, $^3J(\text{PF}_1) = 18 \text{ Hz}$, $^2J(\text{F}_1\text{F}_2) = 18 \text{ Hz}$, $^3J(\text{F}_1\text{F}_3) = 39 \text{ Hz}$, $^4J(\text{F}_1\text{F}_4) = 9 \text{ Hz}$], $\delta_{\text{F2 cis}}$: -92.7 [dtdd, $^3J(\text{PF}_2) = 15 \text{ Hz}$, $^2J(\text{F}_1\text{F}_2) = 18 \text{ Hz}$, $^3J(\text{F}_2\text{F}_3) = 112 \text{ Hz}$, $^4J(\text{F}_2\text{F}_4) = 46 \text{ Hz}$], $\delta_{\text{F3 gem}}$: -180.6 [dddt, $^2J(\text{PF}_3) = 88 \text{ Hz}$, $^3J(\text{F}_1\text{F}_3) = 39 \text{ Hz}$, $^3J(\text{F}_2\text{F}_3) = 112 \text{ Hz}$, $^3J(\text{F}_3\text{F}_4) = 6 \text{ Hz}$], $\delta_{\text{F4 P-F}}$: -56.5 [dttt, $^1J(\text{PF}_4) = 739 \text{ Hz}$, $^4J(\text{F}_1\text{F}_4) = 9 \text{ Hz}$, $^4J(\text{F}_2\text{F}_4) = 46 \text{ Hz}$, $^3J(\text{F}_3\text{F}_4) = 6 \text{ Hz}$].

25. δ_{P} : -61.0 [tdd, $^3J(\text{PF}_1) = 5 \text{ Hz}$, $^2J(\text{PF}_2) = 100 \text{ Hz}$, $^1J(\text{PF}_3) = 697 \text{ Hz}$], $\delta_{\text{F1 cis}}$: -154.8 [dtdd, $^3J(\text{PF}_1) = 5 \text{ Hz}$, $^3J(\text{F}_1\text{F}_2) = 131 \text{ Hz}$, $^4J(\text{F}_1\text{F}_3) = 31 \text{ Hz}$, $^2J(\text{HF}_2) = 74 \text{ Hz}$], $\delta_{\text{F2 gem}}$: -168.8 [dddt, $^2J(\text{PF}_2) = 100 \text{ Hz}$, $^3J(\text{F}_1\text{F}_2) = 131 \text{ Hz}$, $^3J(\text{F}_2\text{F}_3) = 6 \text{ Hz}$, $^3J(\text{HF}_3) = 7 \text{ Hz}$], $\delta_{\text{F3 P-F}}$: -48.9 [dddt, $^1J(\text{PF}_3) = 697 \text{ Hz}$, $^4J(\text{F}_1\text{F}_3) = 31 \text{ Hz}$, $^3J(\text{F}_2\text{F}_3) = 6 \text{ Hz}$].

26. δ_{P} : -49.3 [td, $^3J(\text{PF}_1) = 26 \text{ Hz}$, $^1J(\text{PF}_2) = 703 \text{ Hz}$], $\delta_{\text{F1 cis}}$: -154.8 [ddt, $^3J(\text{PF}_1) = 26 \text{ Hz}$, $^4J(\text{F}_1\text{F}_2) = 8 \text{ Hz}$, $^2J(\text{HF}_2) = 79 \text{ Hz}$], $\delta_{\text{F2 P-F}}$: -39.4 [dd, $^1J(\text{PF}_2) = 703 \text{ Hz}$, $^4J(\text{F}_1\text{F}_2) = 8 \text{ Hz}$].

OPPh₂(CFBrCF₂Br), 27. OPPh₂(CF=CF₂) (0.235 g, $8.33 \times 10^{-4} \text{ mol}$) was dissolved in chloroform (10 cm^3) and a solution of bromine in CHCl₃ (2.12 cm^3 , $0.417 \text{ mol dm}^{-3}$, $8.84 \times 10^{-4} \text{ mol}$) was added. The solution was refluxed for 48 h, after which time the deep red solution had lightened to yellow. The solution was concentrated *in vacuo* to yield OPPh₂(CFBrCF₂Br), **27**, as a yellow-brown oil. (0.350 g, 95%). (Found: C, 38.4; H, 2.6; P, 6.8%. C₁₄H₁₀F₃Br₂PO requires C, 38.0; H, 2.3; P, 7.0%). δ_{P} : 27.3 [dd, $^2J(\text{PF}_a) = 61 \text{ Hz}$, $^3J(\text{PF}_b) = 3 \text{ Hz}$], δ_{Fa} : -132.4 [ddd, (CFBrCF₂Br), $^2J(\text{PF}_a) = 61 \text{ Hz}$, $^3J(\text{F}_a\text{F}_b) = 23 \text{ Hz}$, $^3J(\text{F}_a\text{F}_c) = 18 \text{ Hz}$], δ_{Fb} : -50.6 [dd, (CFBrCF₂Br), $^3J(\text{F}_a\text{F}_b) = 23 \text{ Hz}$, $^2J(\text{F}_b\text{F}_c) = 170 \text{ Hz}$], δ_{Fc} : -53.0 [ddd, (CFBrCF₂Br), $^3J(\text{PF}_b) = 3 \text{ Hz}$, $^3J(\text{F}_a\text{F}_c) = 18 \text{ Hz}$, $^2J(\text{F}_b\text{F}_c) = 170 \text{ Hz}$], δ_{Ca} : 104.4 [dddt, (CFBrCF₂Br), $^2J(\text{CF}_b) = ^2J(\text{CF}_c) = 32.8 \text{ Hz}$, $^1J(\text{CP}) = 63.7 \text{ Hz}$, $^1J(\text{CF}_a) = 283.9 \text{ Hz}$], δ_{Cb} : 120.5 [dddt, (CFBrCF₂Br), $^2J(\text{CP}) = 5.8 \text{ Hz}$, $^2J(\text{CF}_a) = 32.8 \text{ Hz}$, $^1J(\text{CF}_b) = ^1J(\text{CF}_c) = 313.9 \text{ Hz}$], $\delta_{\text{C ipso}}$: 127.5 [d, $^1J(\text{PC}) = 69.5 \text{ Hz}$], $\delta_{\text{C meta}}$: 129.2 [dd, $^3J(\text{PC}) = 12.6 \text{ Hz}$, $^5J(\text{CF}) = 1.9 \text{ Hz}$], $\delta_{\text{C para}}$: 132.7 [d, $^4J(\text{PC}) = 8.7 \text{ Hz}$], $\delta_{\text{C ortho}}$: 133.9 [dd, $^2J(\text{PC}) = 7.7 \text{ Hz}$, $^4J(\text{CF}) = 2.9 \text{ Hz}$].

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References

- D. M. Roddick and R. C. Schnabel, in *Inorganic Chemistry: Towards the 21st Century*, ACS Symposium Series 555, ed. J. S. Thrasher, ACS, Washington, D.C., 1994, ch. 27; W. Levason, in *The Chemistry of Organophosphorus Compounds*, ed. F. R. Hartley, Wiley, New York, 1990, vol. 1, ch. 15.
- E. Zbiral, in *Organophosphorus Reagents in Organic Synthesis*, ed. J. I. G. Cadogan, Academic Press, New York, 1979, p. 223.
- F. W. Bennet, G. R. A. Brandt, H. J. Emel us and R. N. Haszeldine, *J. Chem. Soc.*, 1953, 1565; A. B. Burg, W. Mahler, A. J. Bilbo, C. P. Haber and D. L. Herring, *J. Am. Chem. Soc.*, 1957, **79**, 247.
- M. Fild, O. Glemser and G. Cristoph, *Angew. Chem., Int. Ed. Engl.*, 1964, **3**, 801.
- L. A. Wall, R. E. Donadio and W. J. Pummer, *J. Am. Chem. Soc.*, 1960, **82**, 4846.
- M. F. Ernst and D. M. Roddick, *Inorg. Chem.*, 1989, **28**, 1624.
- R. G. Peters, B. L. Bennett, R. C. Schnabel and D. M. Roddick, *Inorg. Chem.*, 1997, **36**, 5962.
- See, for example: L. Maier, D. Seyferth, F. G. A. Stone and E. G. Rochow, *J. Am. Chem. Soc.*, 1957, **79**, 5884; M. S. Holt, J. H. Nelson and N. W. Alcock, *Inorg. Chem.*, 1986, **25**, 2288; L. P. Barthel-Rosa, V. J. Catalano and J. H. Nelson, *J. Chem. Soc., Chem. Commun.*, 1995, 1629; L. P. Barthel-Rosa, V. J. Catalano, K. Maitra and J. H. Nelson, *Organometallics*, 1996, **15**, 3924.
- I. L. Knunyants, R. N. Sterlin, R. D. Yatsenko and L. N. Pinkina, *Izv. Akad. Nauk. SSSR. Otd. Khim. Nauk.*, 1960, 1991.
- I. L. Knunyants, E. J. Perova and V. V. Tuleneva, *Dokl. Akad. Nauk. SSSR*, 1959, **121**, 576.
- A. H. Cowley and M. W. Taylor, *J. Am. Chem. Soc.*, 1969, **91**, 1929.
- H. G. Horn, R. Kontges, H. C. Marsmann and F. Kolkman, *Z. Naturforsch., B: Anorg. Chem. Org. Chem.*, 1978, **33**, 1422.
- J. Ichikawa, H. Jyono, S. Yonemaru, T. Okauchi and T. Minami, *J. Fluorine Chem.*, 1999, **97**, 109.
- K. K. Banger, R. P. Banham, A. K. Brisdon, W. I. Cross, G. Damant, S. Parsons, R. G. Pritchard and A. Sousa-Pedares, *J. Chem. Soc., Dalton Trans.*, 1999, 427.
- J. Burdon, P. L. Coe, I. B. Haslock and R. L. Powell, *Chem. Commun.*, 1996, 49.
- K. K. Banger, A. K. Brisdon and A. Gupta, *Chem. Commun.*, 1997, 139.
- See, for example: K. D. Berlin and G. B. Butler, *J. Org. Chem.*, 1961, **26**, 2537; R. Rabinowitz and J. Pellon, *J. Org. Chem.*, 1961, **26**, 4623; D. J. Peterson, *J. Org. Chem.*, 1966, **31**, 950.
- N. A. Barnes, A. K. Brisdon, M. J. Ellis and R. G. Pritchard, *J. Fluorine Chem.*, 2001, **112**, 35.
- J. M. Emsley, L. Phillips and V. Wray, *Fluorine Coupling Constants*, Pergamon Press, Oxford, 1977.
- R. H. Contreas, M. C. Ruiz de Azua and C. G. Giribet, *Magn. Reson. Chem.*, 1986, **24**, 675; H. O. Gavarini and M. A. Natiello, *J. Comput. Chem.*, 1987, **8**, 265; H. Poleschner, M. Heydenreich and R. Radeaglia, *Magn. Reson. Chem.*, 1999, **37**, 333.
- Handbook of Phosphorus-31 Nuclear Magnetic Resonance Data*, ed. J. C. Tebb, CRC Press, Boca Raton, FL, USA, 1991.
- A. K. Brisdon, I. R. Crossley, R. G. Pritchard and J. E. Warren, *Inorg. Chem.*, 2002, **41**, 4748.
- M. Taillefer, H. J. Cristau, A. Fruchier and V. Vicente, *J. Organomet. Chem.*, 2001, **624**, 307.
- S. Martin, R. Sauvetre and J.-F. Normant, *J. Organomet. Chem.*, 1984, **264**, 155.
- R. Batchelor and T. Birchall, *J. Am. Chem. Soc.*, 1982, **104**, 674.
- R. N. Haszeldine, D. R. Taylor and E. White, *J. Fluorine Chem.*, 1978, **11**, 441.
- C. De Tollenare and L. Ghosez, *Tetrahedron*, 1997, **53**, 17127.
- A. D. Beveridge, H. C. Clark and J. T. Kwon, *Can. J. Chem.*, 1966, **44**, 179; M. Aktar and H. C. Clark, *Can. J. Chem.*, 1968, **46**, 633; M. Aktar and H. C. Clark, *Can. J. Chem.*, 1968, **46**, 2165.
- S. A. Fontana, C. R. Davis, Y.-B. He and D. J. Burton, *Tetrahedron*, 1996, **52**, 37.
- L. Xue, L. Lu, S. D. Pedersen, Q. Liu, R. M. Narake and D. J. Burton, *J. Org. Chem.*, 1997, **62**, 1064.
- ³¹P{¹H} NMR Spectroscopy in Stereochemical Analysis*, eds. J. G. Verkade and L. D. Quin, VCH, New York, 1987.
- H. J. Emel us and J. M. Miller, *J. Inorg. Nucl. Chem.*, 1966, **28**, 662; R. C. Dobbie, L. F. Doty and R. G. Cavell, *J. Am. Chem. Soc.*, 1968, **90**, 2015.

- 33 E. Krawczyk, A. Skowrońska and J. Michalski, *J. Chem. Soc., Perkin Trans. 2*, 2000, 1135 and references therein.
- 34 J. A. Davies, S. Dutramez and A. A. Pinkerton, *Inorg. Chem.*, 1991, **30**, 2380; W. McFarlane and D. S. Rycroft, *J. Chem. Soc., Dalton Trans.*, 1973, 2162.
- 35 R. P. Pinell, C. A. Mergerle, S. L. Marrat and P. A. Kroan, *J. Am. Chem. Soc.*, 1973, **95**, 977.
- 36 K. A. Kerr, P. M. Boorman, B. S. Miesener and J. G. H. Van Roode, *Can. J. Chem.*, 1977, **55**, 3081.
- 37 P. W. Coddling and K. A. Kerr, *Acta Crystallogr., Sect. B*, 1978, **34**, 3785.
- 38 K. M. Pietrusiewicz, M. Kuznikowski, W. Wiczorek and A. Brandi, *Heteroat. Chem.*, 1992, **3**, 37.
- 39 P. G. Jones, *Acta Crystallogr., Sect. C*, 1996, **52**, 1793.
- 40 L. I. Goryunov, J. Grobe, V. D. Shteingarts, A. Lindemann, E.-U. Würthweld and C. Mück-Lichtenfeld, *Chem.-Eur. J.*, 2000, **6**, 4612.
- 41 C. A. Tolman, W. C. Seidel and L. W. Gosser, *J. Am. Chem. Soc.*, 1960, **82**, 6176.
- 42 O. D. Gupta, R. L. Kirchmeier and J. M. Shreeve, *Inorg. Chem.*, 1990, **29**, 573.
- 43 O. D. Gupta and J. M. Shreeve, *J. Chem. Soc., Chem. Commun.*, 1984, 416.
- 44 I. Ruppert and V. Bastian, *Angew. Chem., Int. Ed. Eng.*, 1977, **16**, 718.
- 45 K. Alam and A. F. Janzen, *J. Fluorine Chem.*, 1987, **36**, 179; J. A. Gibson, R. K. Marat and A. F. Janzen, *Can. J. Chem.*, 1975, **53**, 3044.
- 46 N. Ignatiev and P. Sartori, *J. Fluorine Chem.*, 2000, **103**, 57.
- 47 J. C. Cobas, J. Crucas and F. J. Sardina, *MestRe-C 2.3*, Departamento de Química Orgánica, , Universidade de Santiago de Compostela, Santiago de Compostela, Spain, 2000.
- 48 I. D. Gay, *SPIN* Version 2.0, 1996.
- 49 A. H. Cowley and M. W. Taylor, *J. Am. Chem. Soc.*, 1969, **91**, 1934.
- 50 K. W. Sharp and I. Schwager, *Inorg. Chem.*, 1976, **15**, 1697.
- 51 G. M. Sheldrick, *SHELXTL*, Siemens Analytical X-ray Instruments, Madison, WI, USA, 1995.
- 52 G. M. Sheldrick, *SHELXS-97, Program for solution of crystal structures*, University of Göttingen, Germany, 1997; G. M. Sheldrick, *SHELXL-97, Program for refinement of crystal structures*, University of Göttingen, Germany, 1997.
- 53 L. J. Farrugia, *ORTEP-3 for Windows*, University of Glasgow, Glasgow, UK, 1997.
- 54 T. Hanamoto, Y. Kiguchi, K. Shindo, M. Matsuoka and M. Kando, *Chem. Commun.*, 1999, 151.
- 55 J. A. Rahn, M. S. Holt, M. O'Neil-Johnson and J. H. Nelson, *Inorg. Chem.*, 1988, **27**, 1316.