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Perfluoropropenyl-containing phosphines from HFC replacements.

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A series of new perfluoropropenyl-containing phosphines of the type $R_{3-n}P(E\text{-}CF{=}CFCF_3)_n$ (R = Ph, iPr, n = 1, 2; R = tBu, n = 2) have been prepared from the reaction of the hydrofluoroolefin *Z*-$CF_3CF{=}CFH$ (HFO-1225ye) with base and the appropriate chlorophosphine, while reaction with $Cl_2PCH_2CH_2PCl_2$ gave $(CF_3CF{=}CF)_2PCH_2CH_2P(CF{=}CFCF_3)_2$, the first example of a bidentate perfluoroalkenyl-containing phosphine. An alternative route to these phosphines based on the room- or low-temperature deprotonation of $CF_3CF_2CH_2F$ (HFC-236ea) gives mainly the *E*- isomer, but also a small amount of the *Z*- isomer, the ratio of which depends on the reaction temperature. All of the phosphines could be readily oxidised with either H_2O_2 or urea.H_2O_2, and the phosphine selenides $R_{3-n}P(Se)(E\text{-}CF{=}CFCF_3)_n$ (R = Ph, n=1,2; R = iPr, n=1; R = tBu, n=2) were also prepared. The steric and electronic properties of these ligands were determined based on their platinum(II), palladium(II) and molybdenum carbonyl complexes. The crystal structures of $(CF_3CF{=}CF)_2PCH_2CH_2P(CF{=}CFCF_3)_2$, $(CF_3CF{=}CF)_2P(O)CH_2CH_2P(O)(CF{=}CFCF_3)_2$, $iPr_2P(Se)(CF{=}CFCF_3)_2$, *trans*-$[PtCl_2\{Ph_{(3-n)}P(E\text{-}CF{=}CFCF_3)_n\}_2]$ (n = 1 or 2), *trans*-$[PdCl_2\{R_2P(E\text{-}CF{=}CFCF_3)\}_2]$ (R = Ph, iPr) and $[Mo(CO)_4\{(CF_3CF{=}CF)_2PCH_2CH_2P(CF{=}CFCF_3)_2\}]$ are reported.

Introduction

Phosphines are one of the largest and most successful classes of ligands for transition metals, with a huge range of applications including catalysis, where the right ligand can dramatically increase yields, reduce waste and improve selectivity. The inclusion of one or more fluorinated groups in a tertiary phosphine offers a means of controllably modifying both the steric and electronic properties of phosphines so that they become more sterically demanding, with reduced σ-donation and better π-acceptance properties, and generally more oxidatively stable than their perprotio-analogues.[1] Metal based catalysts containing mono- and bidentate fluorinated phosphines have demonstrated success as catalysts for processes such as ethylene dimerisation, hydrogenation, Baeyer-Villiger oxidations and asymmetric alkylations.[2] While recent work using a mixture of computational modelling and experimental work, has shown that a bidentate fluorinated phosphine systems is one of the few that can induce $ArCF_3$ reductive elimination from a Pd(II) centre, even if possessing a small bite angle by virtue of F...F repulsive interactions.[3]

Despite a recent renaissance in fluoroalkyl-phosphine work,[4] there still exists many different methods, rather than a universal approach, to generate phosphines with fluoroalkyl substituents; an area which has been reviewed recently.[5] Fluoroaryl-substituted systems are more established, and can be prepared via organolithium and Grignard reagents,[6] and some of these ligands are commercially available, albeit at relatively high cost.[7] The replacement of CFCs with "greener" HFCs which are non ozone depleting offered a route to fluoroalkenyl and fluoroalkynyl systems from commercially readily available hydrofluorocarbon (HFC) starting materials. Thus, perfluorovinyl-containing phosphines have been generated by us, and others, in high yields from the reaction of the commercially available CFC-replacement HFC-134a (CF_3CH_2F) with two equivalents of base at low temperature.[8]

Hydrofluoroolefins (HFOs) have now been identified as replacements for HFCs in air conditioning and related applications because HFOs, whilst still non ozone depleting, possess atmospheric lifetimes in the order of days (rather than years for HFCs) and so have very reduced global warming potentials. It is thus timely to investigate whether the HFOs that are being commercialised can be used as potentially cheap, readily available starting materials for the synthesis of phosphines and the properties that such ligands might possess.

One of the HFOs being developed is HFO-1225ye, *Z*-$CF_3CF{=}CFH$ from which it should be possible to generate perfluoropropenyl-containing phosphines. Surprisingly, there are very few examples of these systems. The first perfluoropropenyl (pfp) containing phosphine was reported in 1969 in a Russian patent describing the preparation of $(CF_3)_2C{=}CFPR_2$ (R = iPr, nBu) and $(CF_3)CF{=}CFP(nBu)_2$ by reaction of lithium phosphides with perfluoroalkenes.[9] Subsequently the reaction of hexafluoropropene with Me_2PH was reported to generate a mixture of *trans*- and *cis*-$(CF_3)CF{=}CFPMe_2$; the *trans*-isomer being unambiguously identified by the presence of a large (144 Hz) F-F coupling constant. In the dark the *trans*- isomer was the favoured product (95%) while under UV photolysis conditions a somewhat lower yield of the *trans*-isomer (70%) was

detected. However, it was not possible to separate the two products by GLC.[10] In 1985 the *trans*- (*Z*) isomer alone was isolated in 36% yield from the reaction of hexafluoropropene with Me_2PH.[11] Subsequently this methodology was extended to the reaction with Et_2PH, Et_3P and t-Bu_3P.[12] In all three cases the *Z*-isomers of $R_2PCF{=}CF(CF_3)$ were proposed, based on the observation of a large F-F coupling constant (144-156 Hz) typical of a *trans*-^3JFF coupling across a double bond. Interestingly, in that work, it was also reported that the perfluoropropenyl-containing phosphines could not be oxidised to form the P(V) oxides or sulfides under standard conditions, although reaction with SF_4 did yield $R_2P(F)_2CF{=}CF(CF_3)$. Subsequently the Grignard reagent derived from $CF_3CF{=}CFI$ was reacted with suitable precursors to give *Z*-$(CF_3)CF{=}CFPR_2$ (R = OEt, NEt_2),[12] *Z*-$(CF_3)CF{=}CFPiPr_2$, *Z*-$(CF_3)CF{=}CFP(OMe)(NMe_2)$ and *Z*-$(CF_3)CF{=}CFP(OEt)(NEt_2)$.[14]

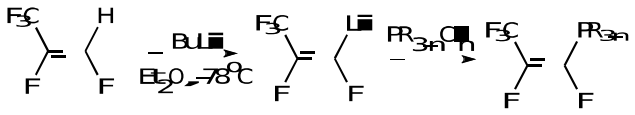
All of the above perfluoropropenyl-containing phosphines were found to contain the *Z*-isomer of the fluorocarbon, and none of the phosphines bear more than one perfluoropropenyl group. Furthermore, what little chemistry has been investigated suggests that these materials are particularly stable towards oxidation, and, significantly, thus far no coordination chemistry of these systems has been reported. It is also noteworthy that no bidentate perfluoroalkenyl-containing phosphines have been reported to date, in particular since the transition metal complexes containing the related phosphine $(CF_3CF_2)_2PCH_2CH_2(CF_2CF_3)_2$, pfepe, have demonstrated interesting catalytic activity.[2]

Here we report the generation of a series of new perfluoropropenyl-containing phosphines, focussing particularly on the previously unisolated *E*-isomer, by extending our previous work on the preparation of metallic main-group compounds containing the perfluoropropenyl group derived from HFC and HFO (hydrofluoroolefin) precursors such as *Z*-$CF_3CF{=}CFH$.[15] which are becoming the preferred replacements for HFCs due to the high global warming potential of HFCs compared with HFOs.

Results and Discussion

The deprotonation of *Z*-$CF_3CF{=}CFH$ can be effectively undertaken in cold ether solutions using either n-BuLi or, more preferably, LDA as a base, to form the thermally unstable lithium intermediate *Z*-$LiCF{=}CFCF_3$, scheme 1. Subsequent reaction, at low temperature, with Ph_2PCl, followed by work up and column chromatography yielded compound **1** as a stable liquid product in reasonable yield. The $^{31}P\{^1H\}$ NMR spectrum of **1** shows a widely separated quartet (J = 58.2 Hz) of doublet (7.7 Hz) of doublets (4.1 Hz) at *ca*. -19 ppm, as shown in figure 1, and the ^{19}F NMR spectrum shows three signals, at *ca*. -64, -125 and -133 ppm in the ratio 3:1:1. Whilst assignment of the signal at -64 ppm to the CF_3 group is trivial based on the position and intensity of the peak, assignment of the two single fluorine environments in the ^{19}F NMR spectrum is less obvious, and is made on the basis of the P-F and C-F coupling constants, which were derived from modelling the NMR spectra using the program SpinWorks,[16] and by comparison with previously reported data for perfluoropropenyl systems.[15] The assignment of the geometry of the product as the *E*-isomer is suggested by the lack of a large *trans*-F-F coupling being observed, which would be present in the *Z*-isomer, and was subsequently confirmed by crystallographic studies (see below).

The appearance of the ^{31}P NMR spectrum as a widely spaced quartet of doublet of doublets (figure 1) means that the largest P-F coupling is observed to the three fluorine nuclei of the CF_3 group, rather than to either of the other single fluorine nuclei, ie the magnitude of $^4J(PCF_3)$ is greater than either $^2J(PF_a)$ or $^3J(PF_b)$. This we ascribe to lone-pair assisted through-space coupling as has been observed in some other phosphorus(III) compounds.[8b,17]



Scheme 1 Preparation of *E*-perfluoropropenyl phosphines from HFC-1225ye

$LiCF{=}CFCF_3$, prepared at low temperature, was also reacted with the chlorophosphines $R_{(3-n)}PCl_n$ (R = Ph, iPr, n = 1, 2) in a similar way to generate a series of mono- and bis-substituted perfluoropropenyl (pfp) phosphines (**1**-**4**) as summarised in Table 1.

We were also able to prepare the tetra-substituted bidentate phosphine $(CF_3CF{=}CF)_2PCH_2CH_2P(CF{=}CFCF_3)_2$, from the low temperature reaction of an excess of $LiCF{=}CFCF_3$ with $Cl_2PCH_2CH_2PCl_2$. This is in contrast to previous work within our group when attempts to prepare the perfluorovinyl-containing analogue have failed. In this case however, not only is the product readily formed without any partially-substituted impurities, it crystallises on purification into thin colourless plates, and was therefore structurally characterised by single crystal X-ray analysis. Although the quality of the X-ray data was somewhat lower than might normally be anticipated (R_1 = 10.8%) it is sufficiently good to allows us to confirm the *E*-geometry of the perfluoropropenyl fragments, fig 2. The crystallographic parameters for this, and all of the compounds studied, are listed in Table 4.

This is the first reported structure of a bidentate phosphine ligand bearing perfluorinated alkyl or alkenyl groups, although the structure of $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$ is known.[6b] The central C-C and P-C bond distances are similar in both structures, d(C-C) = 1.520(8) and 1.528(11) Å and d(C-P) = 1.825(9) Å and 1.840(4) Å in $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$ and **6** respectively.

Despite **6** being a highly symmetric molecule its NMR spectra are complicated, because every spin-active nucleus is either chemically or magnetically inequivalent, resulting in complex, but symmetric, signals in the ^{31}P, ^{19}F and ^1H NMR spectra. While a full interpretation has not been undertaken, it is evident from the ^{19}F NMR spectrum that there are no large F-F couplings observed, thus supporting the presence of the

E- rather than *Z*-isomer in solution and the solid state.

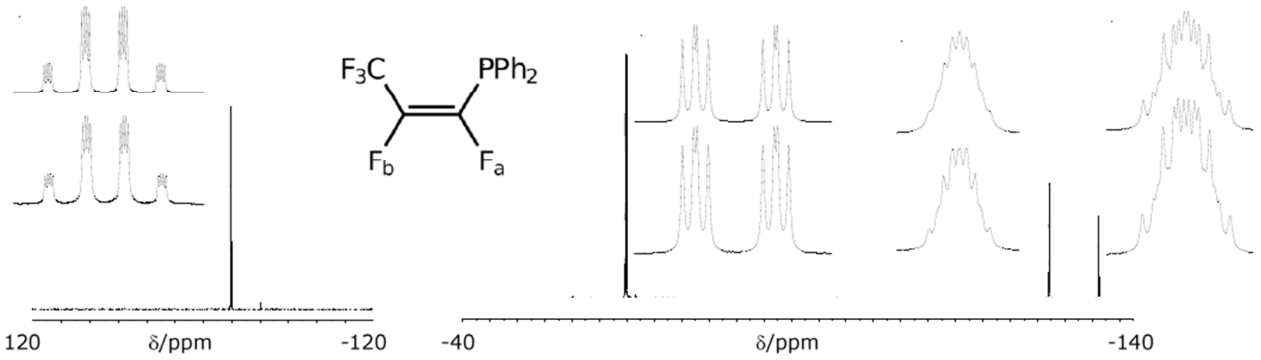


Fig. 1 $^{31}P\{^{1}H\}$ and ^{19}F NMR spectra of $Ph_2P(E\text{-}CF{=}CFCF_3)$ with expansions of each signal and simulated spectra (above).

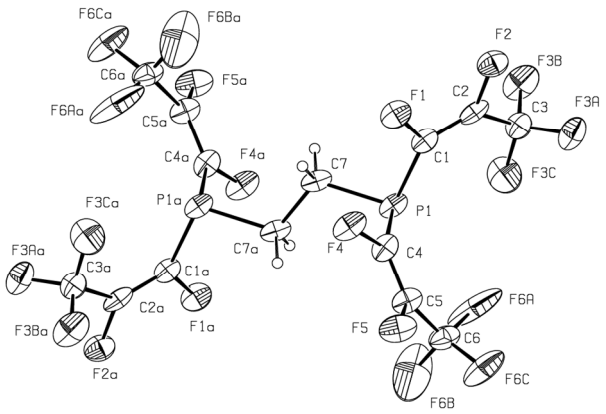
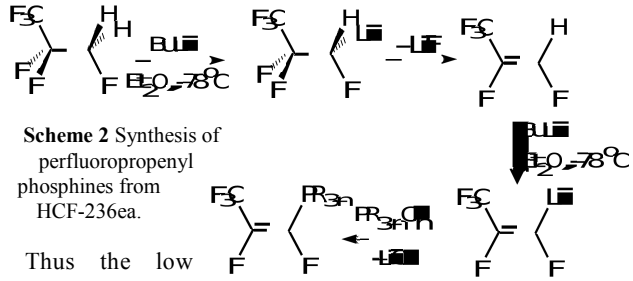


Fig. 2 ORTEP representation of $(CF_3CF{=}CF)_2PCH_2CH_2P(CF{=}CFCF_3)_2$, 6. Selected distances (Å) and angles (°): P1-C1 1.793(9), P1-C4 1.810(8), P1-C7 1.825(9), C1-F1 1.351(10), C4-F4 1.353(10), C1-C2 1.338(13), C4-C5 1.334(13), C2-F2 1.334(10), C5-F5 1.326(10), C2-C3 1.506(13), C5-C6 1.493(13), C3-F3A 1.286(10), C3-F3B 1.336(12), C3-F3C 1.350(12), C6-F6A 1.285(13), C6-F6B 1.233(16), C6-F6C 1.281(12), C7-C7a 1.528(11). C1-P1-C4 97.1(4), C1-P1-C7 99.1(4), C4-P1-C7 98.1(4), P1-C1-F1 119.6(6), P1-C4-F4 118.6(6), P1-C1-C2 128.3(7), P1-C4-C5 125.8(7), C1-C2-F2 122.9(8), C4-C5-F5 121.0(8), P1-C7-C7a 111.6(6).

Unfortunately attempts to prepare $P(E\text{-}CF{=}CFCF_3)_3$ were unsuccessful; on addition of a diluted solution of PCl_3 to $LiCF{=}CFCF_3$ extensive decomposition of the perfluoropropenyllithium reagent was observed, as indicated by a rapid darkening of the ether solution. We were also unable to generate any significant amount of $tBuP(CF{=}CFCF_3)_2$ from the low-temperature reaction of $LiCF{=}CFCF_3$ with $tBuPCl_2$. Reasoning that in this case, because unreacted chlorophosphine was detected, more reactive conditions may be required for such a sterically inhibited chlorophosphine, we investigated a room-temperature variation of this reaction, similar to that reported by Burton previously for HFC-134a (CF_3CH_2F) reactions.[18]

Addition of LDA to a room-temperature mixture of $CF_3CF{=}CFH$ and $tBuPCl_2$ dissolved in ether, in a flask fitted with a dry ice condenser, should result in the $LiCF{=}CFCF_3$ generated reacting immediately with the chlorophosphine present *in situ*. We were pleased to find that after work-up of such a reaction a perfluoropropenyl-containing phosphine was indeed obtained, the identity of which was determined from multi-nuclear NMR studies and elemental analysis, as $tBuP(E\text{-}CF{=}CFCF_3)_2$, **5**.

We also investigated a route to perfluoropropenyl phosphines based on the reaction of HFC-236ea, $CF_3CF_2CH_2F$, with base, which by analogy with the two-step deprotonation and concomitant LiF elimination reaction of HFC-134a (CF_3CH_2F) with two equivalents of a base to generate trifluorovinyllithium, should also generate the perfluoropropenyllithium reagent, scheme 2.



Scheme 2 Synthesis of perfluoropropenyl phosphines from HCF-236ea.

Thus the low temperature reaction of HFC-236ea with BuLi followed by the addition of iPr_2PCl resulted, after work-up, in the generation of two peaks in the phosphorus NMR spectrum at -2 and -4 ppm in the ratio 90:10. Similarly the fluorine NMR spectrum exhibited two sets of three mutually coupled signals in the same relative proportion. This suggested that two different perfluoropropenyl-containing products had been formed in this reaction. The more intense signals in the ^{31}P and ^{19}F NMR spectra can be assigned to **3**, by comparison with the data obtained from the reaction of HFC-1125ye. The second set of peaks showed similar signals and coupling patterns, except for the presence of a large J(FF) coupling constant of *ca*. 150 Hz, in the ^{19}F NMR spectrum. A coupling constant of this magnitude is typical of a *trans*-CF=CF- coupling, and we therefore assign the weaker signals to the *Z*-isomer, ie $iPr_2P(Z\text{-}CF{=}CFCF_3)$, **3z**.

Table 1 Characterising data for $CF=CFCF_3$-containing phosphines.

Number	Compound	Isolated Yield	$\delta^{31}P$/ppm (J/Hz)	$\delta^{19}F_{CF3}$/ppm (J/Hz)	$\delta^{19}F_{Fa}$/ppm (J/Hz)	$\delta^{19}F_{Fb}$/ppm (J/Hz)	%C (calc)	%H (calc)	%P (calc)
1	$Ph_2P(E\text{-}CF=CFCF_3)$	75%	-19.6 (58,8,4)	-63.8 (58,11, 8)	-125.7 (8,5,4)	-132.8 (11,8,5)	58.9 (56.9)	3.4 (3.2)	9.7 (9.8)
2	$PhP(E\text{-}CF=CFCF_3)_2$	85%	-39.2 (59,10,10)	-64.8 (59, 10, 5)	-122.8 (10,5,0.2)	-129.6 (10,10,0.2)	39.4 (38.9)	1.8 (1.4)	9.2 (8.4)
3	$iPr_2P(E\text{-}CF=CFCF_3)$	72%	-2.0 (52,4,3)	-63.8 (52,11,8)	-124.0 (9,6,4)	-134.1 (11,5,4)	43.5 (42.1)	5.7 (5.1)	12.5 (13.7)
3z	$iPr_2P(Z\text{-}CF=CFCF_3)$	a	-4.0 (71,6, 2)	-67.2 (21,11,2)	-141.5 (151,21,6)	-156.3 (151,71,11)	a	a	a
4	$iPr(E\text{-}CF=CFCF_3)_2$	66%	-34.0 (65,14,8)	-64.6 (65,10,5)	-126.7 (14,10)	-139.1 (8,5)	32.1 (31.2)	2.1 (2.0)	9.2 (9.1)
5	$tBuP(E\text{-}CF=CFCF_3)_2$ [c]	50%	-23.5 (56,12,10)	-64.1 (56,11,6)	-121.0 (12,6,0.2)	-127.9 (11,10,0.2)	34.3 (33.1)	2.6 (2.4)	8.8 (7.2)
6	$(E\text{-}CF_3CF=CF_2)_2PCH_2CH_2P(E\text{-}CF=CFCF_3)_2$	35%	-44.2 (m)	-65.1 (m)	-126.9 (m)	-128.4 (m)	27.4 (27.4)	1.0 (0.7)	b

[a] *Z*-isomer formed as a minor product in a mixture containing *E*- and *Z*-isomers, see text, and not isolated. [b] not determined. [c] prepared from room temperature reaction, see text.

Repeating this reaction at room temperature resulted in formation of the same two products, except that now the ratio of *E*- to *Z*-isomers was 79:21, indicating that the proportion of the *Z*-isomer formed is greater in the room temperature reaction compared with that carried out at -78 °C. This presumably arises from the greater thermal energy allowing for rotation about the central C-C bond in the lithiated intermediate, prior to LiF elimination (scheme 2), so resulting in a greater mixture of the two possible organolithium reagents, *E*- and *Z*-$LiCF=CFCF_3$. This in turn results in a greater mixture of *E*- and *Z*-perfluoropropenyl phosphines. We found that the phosphines **1**-**4** and **6** could all be formed in a similar way using HFC-136ea, however the requirement to use less base and the formation of a single isomer meant that HFO-1225ye was generally our preferred starting material over HFC-236ea.

Because, even at room temperature, the amount of Z-isomer formed was low we were unable to isolate sufficient of these materials, so here we only report our subsequent studies of the *E*-isomers of the perfluoropropenyl-containing phosphines.

Oxidation Studies

The unexpected, previously reported, stability of $Me_2P(Z\text{-}CF=CFCF_3)$ towards oxidation, as described above, lead us to initially investigate the oxidation chemistry of our new phosphines. Addition of a few drops of H_2O_2 to an NMR tube containing a $CDCl_3$ solution of $Ph_2P(E\text{-}CF=CFCF_3)$ resulted in a reduction in intensity of the $^{31}P\{^1H\}$ NMR signals due to the starting phosphine, and the appearance of a new signal at 20.0 ppm. The change in the chemical shift of *ca*. 40 ppm is consistent with that observed for oxidation of other phosphines to the corresponding phosphine oxide, for example Ph_3P to $Ph_3P(O)$: $\Delta\delta$ = 34.8 ppm[19] and $Ph_2P(CF=CF_2)$ to $Ph_2P(O)(CF=CF_2)$: $\Delta\delta$ = 46 ppm.[8] Significantly, this signal is now observed as a doublet (JPF = 56 Hz) due to coupling with one of the single fluorine nuclei, instead of coupling to the CF_3 group, presumably as a consequence of the lone pair on phosphorus no longer being available because oxidation has occurred, and so only through-bond coupling is observed.

Extending this reaction to the other phosphines we found that, unlike the previous report, **1**-**6** could be readily converted to their respective oxides (**7**-**12**) by reaction with either aqueous hydrogen peroxide or urea.H_2O_2. In the case of **12** confirmation of the identity of the oxidised product as $(E\text{-}CF_3CF=CF)_2P(O)CH_2CH_2P(O)(E\text{-}CF=CFCF_3)_2$ was obtained from an X-ray structure determination of crystals grown by slow evaporation of the solvent from a chloroform solution. Although the diffraction by the thin plates was weak it was possible to obtain a solution to the data (R = 9.3%), and this is represented in fig. 3.

Comparing the structural data obtained for compound **6** and its oxide, **12**, there is a lengthening of the bonds between phosphorus and the perfluoropropenyl groups on oxidation and a concomitant reduction in the P-CH_2 distances, however in both cases these are only just significant at the 3σ level. More noteworthy is the change in bond angles around the phosphorus centre which increase from an average C-P-C value of 98.1(4) in **6** to 105.3(5)° in the oxide, **12**.

To date all of our fluoroalkenyl phosphine oxides have been made by preparing the P(III) compound and then oxidising it, however an alternative single-step synthetic strategy based on reaction of a suitable P(V) precursor, such as $Ph_2P(O)Cl$ with $CF_3CF=CFLi$ should also result in $Ph_2P(O)(E\text{-}CF=CFCF_3)$. Indeed, we found that when this reaction was carried out at low temperature compound **7** was prepared, but only in a moderate isolated yield (29%). Extending this reaction to phenyl phosphonic dichloride ($PhP(O)Cl_2$) gave 35% of, **8**, $PhP(O)(E\text{-}CF=CFCF_3)_2$. Thus it would appear that the oxides can be prepared directly from suitable P(V) starting materials, but in both of these cases the yields are relatively poor, and a

number of unidentified by-products were also generated, which could not easily be separated by column chromatography. This disadvantage, and the low yield suggests that currently the more traditional, two-step process to the perfluoroalkenyl phosphine oxides is the preferable route.

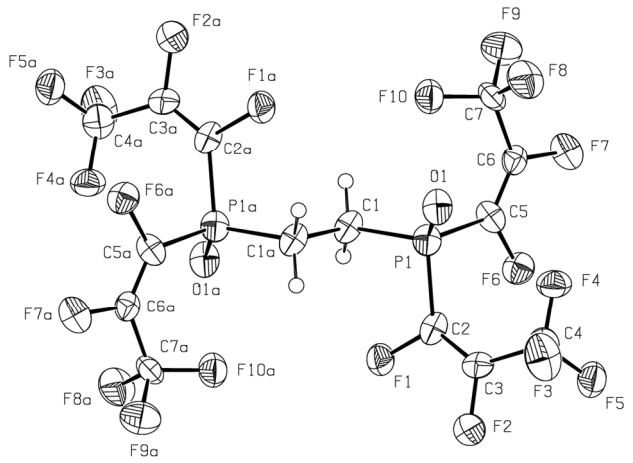


Fig. 3 ORTEP representation of (*E*-$CF_3CF{=}CF)_2P(O)CH_2CH_2P(O)$(*E*-$CF{=}CFCF_3)_2$, **12**. Selected distances (Å) and angles (°): P1-O1 1.479(6), P1-C1 1.785(10), P1-C2 1.838(10), P1-C5 1.843(11), C2-F1 1.363(11), C5-F6 1.348(12), C2-C3 1.302(15), C5-C6 1.284(15), C3-F2 1.337(12), C6-F7 1.353(12), C3-C4 1.528(16), C6-C7 1.503(15), C4-F3 1.311(12), C4-F4 1.316(13), C4-F5 1.337(14), C7-F8 1.348(12), C7-F9 1.314(13), C7-F10 1.319(15), O1-P1-C1 115.1(5), O1-P1-C2 114.0(4), O1-P1-C5 111.0(4), C1-P1-C2 103.6(5), C1-P1-C5 108.7(5), C2-P1-C5 103.6(5), P1-C2-C3 130.3(8), P1-C2-F1 112.9(7), C2-C3-C4 128.6(9), C2-C3-F2 120.6(9)

In addition to forming the oxides of our new phosphines we were also able to prepare the selenides of **1-3** by heating a toluene solution of the appropriate phosphine with elemental selenium. Unfortunately, in the case of **5** the selenide was produced, along with other unidentifiable by-products, while we were not able to generate the selenides of **4** and **6**, even after extended reaction periods, or using alternative methods.[20] It would appear that either elemental selenium is not a sufficiently powerful oxidant, or that the phosphorus centres are too sterically crowded for incorporation of selenium (r_{cov} = 120 pm) rather than oxygen (r_{cov} = 66 pm).[21]

The $^{31}P\{^1H\}$ NMR spectra of selenides **13-16** show a shift of ca. 50 – 70 ppm to higher frequency compared with the starting phosphine. These signals are accompanied by selenium satellites (^{77}Se, 7.58% *I* = ½) from which $|^1J(PSe)|$ values ranging from *ca*. 760 to 970 Hz were obtained, with the larger values being observed for the *bis*-substituted phosphines. A comparison of these values with those reported for other phosphines is shown in Table 2. From these data, which have previously been used as a measure of the electronic properties of phosphines,[22] it is clear that the perfluoropropenyl group has a similar, but slightly less withdrawing effect than the perfluorovinyl group. Thus, the magnitude of the P=Se coupling constant in $Ph_2P(Se)$(*E*-$CF{=}CFCF_3$) is *ca*. 20 Hz less than that of $Ph_2P(Se)(CF{=}CF_2)$, whereas for the di-isopropyl analogues the value for the perfluoropropenyl system is *ca*. 30 Hz greater than that for the perfluorovinyl analogue. This suggests that the CF_3-for-F replacement results in only a small change in the electronic properties of the resulting phosphines. In any case, the values lie between those found for typical tertiary phosphine selenides (e.g. $Se{=}PPh_3$, 729 Hz,[20] $Se{=}P(iPr)_3$, 678 Hz[23]) and those of phosphites (e.g. $Se{=}P(OPh)_3$, 1039 Hz, $Se{=}P(OiPr)_3$, 924 Hz)[24].

Table 2 $^{31}P\{^1H\}$ NMR data for some $R_{(3-n)}P(Se)$(*E*-$CF{=}CFCF_3)_n$ compounds.

Phosphine Selenide	$\delta^{31}P$/ppm ($^1J_{PSe}$/Hz)	Ref.
$Ph_2P(Se)$(*E*-$CF{=}CFCF_3$), **13**	35.5 (763)	a
$PhP(Se)$(*E*-$CF{=}CFCF_3)_2$, **14**	28.8 (832)	a
$iPr_2P(Se)$(*E*-$CF{=}CFCF_3$), **15**	61.5 (799)	a
$tBuP(Se)$(*E*-$CF{=}CFCF_3)_2$, **16**	17.0 (967)	a
$Ph_3P(Se)$	35.0 (729)	20
$i\text{-}Pr_3P(Se)$	69.6 (678)	23
$Ph_2P(Se)(CF{=}CF_2)$	22.2 (785)	8
$PhP(Se)(CF{=}CF_2)_2$	4.5 (848)	8
$iPr_2P(Se)(CF{=}CF_2)$	55.9 (766)	8
$(PhO)_3P(Se)$	58.5 (1039)	24
$(iPrO)_3P(Se)$	66.6 (924)	24

[a] this work.

For one of the selenides, $iPr_2P(Se)(CF{=}CFCF_3)$, **15**, crystals suitable for X-ray diffraction work were obtained by slow evaporation of the solvent from a dichloromethane solution. The data obtained from the colourless triclinic crystals resulted in the structure shown in fig. 4.

The compound adopts the expected four-coordinate geometry around the phosphorus centre, and confirms the formation of the anticipated product. Surprisingly, there are no previously reported crystal structures for any tertiary phosphine selenide containing a fluorinated group of any type. The closest published structure to that of **15** is $iPr_2P(S)CF{=}CF_2$.[8] In both the perfluoropropenyl selenide and the perfluorovinyl sulfide compounds the chalcogen-P-C bond angles are similar, all being greater than the idealised tetrahedral value, while the C-P-C angles are all smaller. The P=Se bond length (2.1059(16) Å) is a little shorter than that found in $iPr_3P(Se)$, d(P=Se) = 2.1244(9) Å.[25] The internal bondlengths of the perfluoropropenyl fragment are much as anticipated based on the hybridisation of the carbon centres,[26] and as previously reported for the only other structurally characterised main-group systems, $Ph_3Sn(CF{=}CFCF_3)$ and $Ph_3Ge(CF{=}CFCF_3)$.[15] The extended packing of the molecules results in fluorinated and non-fluorinated parts of the molecules aggregating, Fig. 3(b), but there are no particularly short intermolecular interactions observed.

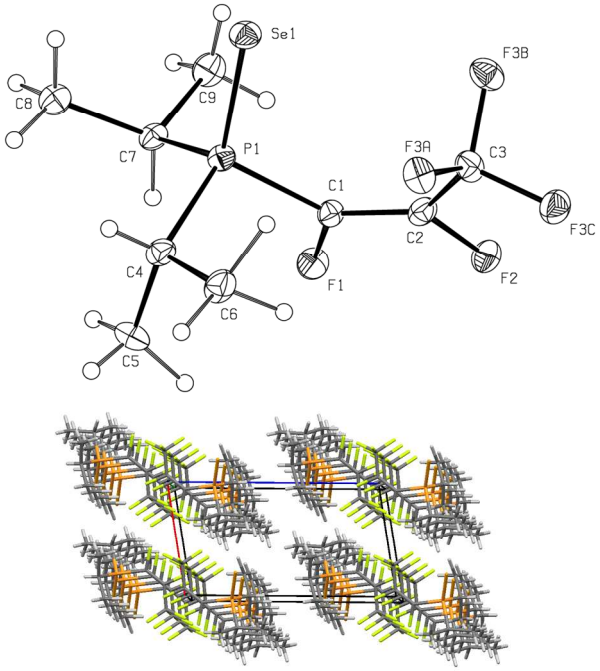


Fig. 4 (a) ORTEP representation of $iPr_2P(Se)(E\text{-}CF{=}CFCF_3)$, **15**. Selected distances (Å) and angles (°): P1-Se1 = 2.1059(16), P1-C1 = 1.845(6), P1-C4 = 1.827(6), P1-C7=1.836(6), C1-C2 = 1.336(9), C1-F1 = 1.349(7), C2-F2 = 1.342(7), C3-F3A = 1.325(7), C3-F3B = 1.348(6), C3-F3C = 1.344(7); Se1-P1-C1 = 114.69(19), Se1-P1-C4 = 114.6(2), Se1-P1-C7 = 113.20(19), C1-P1-C4 = 104.8(2), C1-P1-C7 = 101.2(3), C4-P1-C7 = 107.2(3). (b) packing diagram viewed down the *b*-axis.

Coordination Chemistry

Because there is no known coordination compounds for any perfluoropropenyl-containing phosphine we undertook a study of their basic coordination chemistry in order to assess the electronic and steric properties of the new phosphines. The reaction of K_2PtCl_4 with $PPh_2(E\text{-}CF{=}CFCF_3)$, **1**, in ethanol/water at room temperature resulted in the formation of a red solid. The $^{31}P\{^1H\}$ NMR spectrum of this solid showed a single, broad, peak at 18.8 ppm with attendant platinum satellites (^{195}Pt, 33%, I = ½) from which |J(PtP)| was determined to be 2780 Hz. This is considerably less than that reported for the *cis*-isomers of related complexes, such as *cis*-$[PtCl_2\{PPh_2(CF{=}CF_2)\}_2]$, 3698 Hz[27] and *cis*-$[PtCl_2\{PPh(CF{=}CF_2)_2\}_2]$, 3711 Hz, but closer to that found for *trans*-$[PtCl_2\{PPh(CF{=}CF_2)_2\}_2]$ (3039 Hz),[28] suggesting a *trans*-arrangement of the two phosphine ligands in this complex. Similar NMR data were obtained from the products of the reaction between K_2PtCl_4 and **2** and **3**, which were also assigned on the basis of their analytical data to the complexes *trans*-$[PtCl_2\{PPh(E\text{-}CF{=}CFCF_3)_2\}_2]$, **18**, and *trans*-$[PtCl_2\{PiPr_2(E\text{-}CF{=}CFCF_3)\}_2]$, **19**, respectively. Further evidence for the formation of these products, as *trans*-isomers, comes ultimately from a crystallographic study.

Crystals suitable for X-ray crystallography of **17** and **18** were obtained by slow solvent evaporation of their dichloromethane solutions. Complex **17** crystallised in the $P\bar{1}$ space group, while **18** was monoclinic, $P2_1/n$. Unfortunately, in the case of **18** the data collection was restricted due to icing problems at ca. 70%; although the data are sufficient to confirm the connectivities and the chemical nature of the complex, the derived distances should be treated with some caution. The resulting structures are shown in fig. 5. In both cases *trans*-square planar platinum(II) bis-phosphine dichloride complexes were formed, in accord with the solution-phase NMR data. This is in contrast to the analogous complex of the smaller perfluorovinyl phosphine, $Ph_2P(CF{=}CF_2)$, ligand, which was found to preferentially form the *cis*-isomer,[27] but similar to that found for $Ph_2P(C_2F_5)$.[29] In both structures a slightly distorted square-planar geometry is observed (**17**: Cl1-Pt1-P1 = 92.59(8)°, Cl1-Pt1-P2 = 89.13(8)°, **18**: Cl1-Pt1-P1 = 93.87(15)°) with asymmetry in the Pt-P and Pt-Cl distances also observed for **17**, although there are no obvious intra- or intermolecular interactions to account for these. However, in general the Pt-P and Pt-Cl distances are consistent with those found in the related perfluorovinyl,[28] pentafluoroethyl,[29] and *iso*-heptafluoropropyl[4b] systems, being intermediate between the Pt-P distances observed in perprotio phosphines, such as PPh_3, PBz_3, PCy_3[30] and fully fluorinated systems, such as $P(C_6F_5)_3$.[31]

In the solid state structures of both **17** and **18** interactions less than the sum of the van der Waals' radii are observed between fluorine and hydrogen atoms of the phosphine ligands of adjacent molecules. In the case of **17**, the complex of ligand **1**, two such interactions arise, one between an ortho-hydrogen of one ring and the fluorine on the α-carbon of the perfluoropropenyl group of an adjacent molecule. A slightly longer interaction is observed between the para-hydrogen of one phenyl ring and one of the CF_3 fluorines, whilst an F...F distance of 2.813(9) Å (0.127 Å less than the sum of the van der Waals radii) is observed between the α-F and one of the CF_3 fluorines. For the complex derived from ligand **2** only one short interaction is observed, this occurs between the para-hydrogen of the phenyl ring and one of the terminal CF_3 fluorines of one of the perfluoropropenyl groups. The reverse interaction is observed on the other side of the molecule, such that a ribbon of complexes is generated.

The reactions of K_2PdCl_4 with ligands **1** and **3** were also undertaken, resulting in complexes **20** and **21** which are assigned as the analogous square-planar *trans*-bis-phosphine palladium dichloride complexes based on their spectroscopic and analytical data. For both of these complexes, we were able to grow crystals suitable for structurally characterisation. In both cases triclinic, $P\bar{1}$ crystals resulted from which the structures shown in figure 6 were obtained. Both complexes exhibit very similar Pd-P and Pd-Cl distances (2.2971(12) Å vs 2.2868(10) Å for **20** and 2.326(2) vs 2.310(3) Å for **21**). These are comparable to the distances found in most of the other, albeit limited number, of *trans*-palladium *bis* chloride *bis* phosphine complexes in which the phosphine is either partially or fully fluorinated, such as *trans*-$[PdCl_2\{PR_2(CF{=}CF_2)\}_2]$ R = iPr, Cy,[28] *trans*-$[PdCl_2\{P(NMe_2)_2(C_6F_4CF_3\text{-}4)\}_2]$,[32] although they do not show quite as large a difference in these two parameters as was observed in *trans*-$[PdCl_2\{P(C_6F_5)_3\}_2]$.[33]

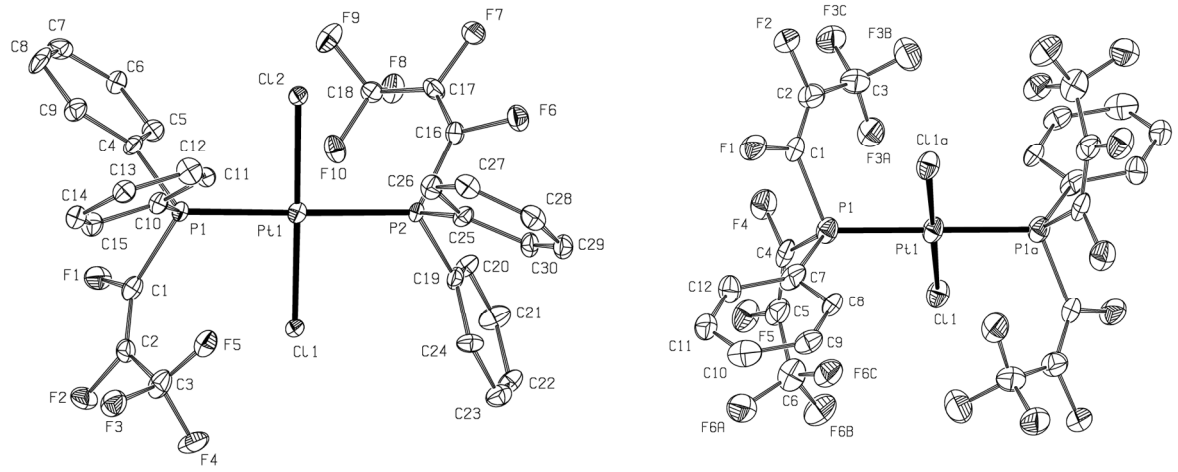


Fig. 5 ORTEP representation of *trans*-[$PtCl_2\{PPh_2(E\text{-}CF{=}CFCF_3)\}_2$], **17**, and *trans*-[$PtCl_2\{PPh(E\text{-}CF{=}CFCF_3)_2\}_2$], **18**, hydrogen atoms not shown for clarity. Selected distances (Å) and angles (°) for **17**: Pt1-P1 = 2.097(2), Pt1-P2 = 2.311(2), Pt1-Cl1 = 2.303(2), Pt1-Cl2 = 2.322(2), P1-C4 = 1.808(10), P1-C10 = 1.823(10), P2-C19 = 1.815(10), P2-C25 = 1.824(10), P1-C1 = 1.818(11), P2-C16 = 1.848(10), C1-C2 = 1.316(15), C16-C17 = 1.328(14), C1-F1 = 1.367(11), C16-F6 = 1.353(11), C2-F2 = 1.371(10), C17-F7 = 1.355(12), C2-C3 = 1.491(15), C17-C18 = 1.481(14), C3-F3 = 1.330(14), C3-F4 = 1.354(14), C3-F5 = 1.311(13), C18-F8 = 1.350(11), C18-F9 = 1.337(12), C18-F10 = 1.320(12), Cl1-Pt1-P1 = 92.59(8), Cl1-Pt1-P2 = 89.13(8), Pt1-P1-C1 = 114.8(4), Pt1-P2-C16 = 117.2(3), Pt1-P1-C4 = 112.8(3), Pt1-P1-C10 = 116.1(3), Pt1-P2-C19 = 119.7(3), Pt1-P2-C25 = 110.7(3), C1-P1-C4 = 100.1(5), C1-P1-C10 = 104.1(5), C4-P1-C10 = 107.4(5), C16-P2-C19 = 100.9(4), C16-P2-C25 = 99.9(4), C19-P2-C25 = 106.1(5). **18**: Pt1-P1 = 2.286(4), Pt1-Cl1 = 2.308(4), P1-C1 = 1.859(15), P1-C4 = 1.847(18), P1-P7 = 1.795(15), C1-F1 = 1.337(16), C4-F4 = 1.311(18), C1-C2 = 1.30(2), C4-C5 = 1.35(2), C2-F2 = 1.37(2), C5-F5 = 1.38(2), C2-C3 = 1.47(2), C5-C6 = 1.43(3), C3-F3A = 1.30(2), C3-F3B = 1.35(2), C3-F3C = 1.34(2), C6-F6A = 1.34(2), C6-F6B = 1.35(2), C6-F6C = 1.32(2), Cl1-Pt1-P1 = 93.87(15), Pt1-P1-C1 = 112.0(5), Pt1-P1-C4 = 117.7(5), Pt1-P1-C7 = 115.8(6), C1-P1-C4 = 100.0(7), C1-P1-C7 = 103.5(7), C4-P1-C7 = 105.8(7).

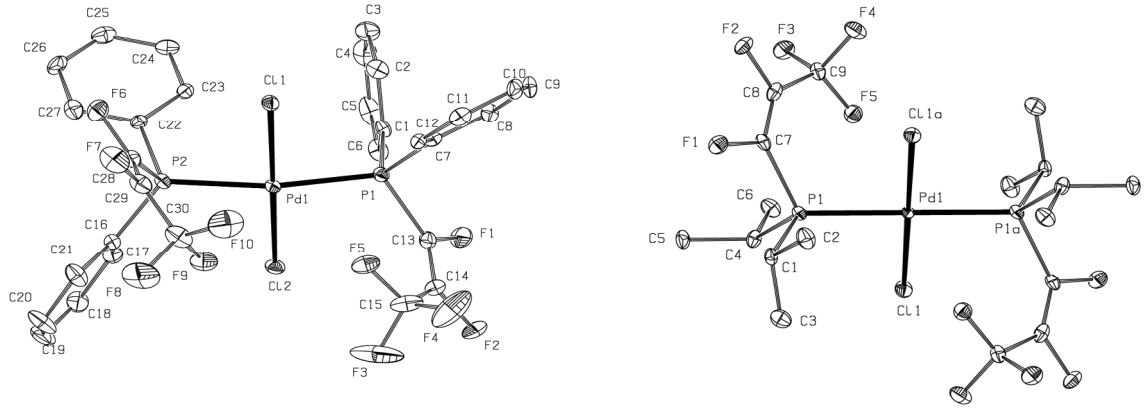


Fig. 6 ORTEP representation of of *trans*-[$PdCl_2\{PPh_2(E\text{-}CF{=}CFCF_3)\}_2$], **20**, and *trans*-[$PdCl_2\{PiPr_2(E\text{-}CF{=}CFCF_3)\}_2$], **21**, hydrogen atoms not shown for clarity. Selected distances (Å) and angles (°) for **20**: Pd1-P1 = 2.2954(12), Pd1-P2 = 2.2987(12), Pd1-Cl1 = 2.2913(10), Pd1-Cl2 = 2.2823(10), P1-C1 = 1.805(5), P1-C7 = 1.815(4), P2-C16 = 1.822(4), P2-C22 = 1.816(5), P1-C13 = 1.834(5), P2-C28 = 1.833(5), C13-C14 = 1.315(8), C28-C29 = 1.312(8), C13-F1 = 1.351(5), C28-F6 = 1.346(5), C14-F2 = 1.342(6), C29-F7 = 1.351(5), C14-C15 = 1.474(9), C29-C30 = 1.491(8), Cl1-Pd1-P1 = 90.05(4), Cl1-Pd1-P2 = 86.28(4), Pd1-P1-C1 = 101.92(15), Pd1-P1-C7 = 123.32(16), Pd1-P1-C13 = 117.11(15), Pd1-P2-C16 = 122.55(16), Pd1-P2-C22 = 108.25(15), Pd1-P2-C28 = 110.80(15), C1-P1-C7 = 105.7(2), C1-P1-C13 = 106.6(2), C7-P1-C13 = 100.9(2), C16-P2-C22 = 104.4(2), C16-P2-C28 = 105.6(2), C16-P2-C22 = 104.4(2). **21**: Pd1-P1 = 2.326(2), Pd1-Cl1 = 2.310(3), P1-C1 = 1.856(9), P1-C4 = 1.848(10), P1-C7 = 1.853(9), C7-F1 = 1.336(10), C7-C8 = 1.316(12), C8-F2 = 1.357(10), C8-C9 = 1.510(12), C9-F3 = 1.348(11), C9-F4 = 1.316(11), C9-F5 = 1.327(10), Cl1-Pd1-P1 = 88.36(8), Pd1-P1-C1 = 110.3(3), Pd1-P1-C4 = 120.4(3), Pd1-P1-C7 = 114.5(3), C1-P1-C4 = 105.3(4), C1-P1-C7 = 100.8(4), C4-P1-C7 = 103.5(4).

Once again, a number of distances less than the sum of the respective van der Waals radii are observed. For complex **20**, which is the palladium-containing analogue of **17**, similar interactions are observed between an ortho-hydrogen of one ring and the α-fluorine of the perfluoropropenyl group of an adjacent molecule. F...F interactions between adjacent α-fluorines (2.740(3) Å, 0.200 Å less than twice the van der Waals radius of fluorine) and between fluorines of adjacent CF_3 groups (2.702(5) Å, 0.238 Å less twice r_{vdw} for fluorine) are also apparent. For complex **21** pairing occurs due to mutual Cl...H (2.83 Å) and $F_2...F_2$ (2.820(7) Å) contacts.

These platinum and palladium complexes represent the first

reported coordination compounds of any perfluoropropenyl-containing phosphine ligand and also the first to be structurally characterised. We therefore used the Tolman command of the Olex2 program[34] to make estimates of the Tolman cone angles for these new ligands. For **1**, values of 162 and 161° were obtained from **17** and **20**, whilst for the *bis*-perfluoropropenyl and di-isopropyl substituted ligands **2** and **3**, larger values of 179 and 171° respectively were obtained. These can be compared with those previously reported for the analogous perfluorovinyl-containing phosphines.[28] In the case of $Ph_2P(CF=CF_2)$ the Tolman cone angle is essentially the same (163°) as that determined for $Ph_2P(E\text{-}CF=CFCF_3)$. Whilst the value for $iPr_2P(CF=CF_2)$ (165°) is 6° less than that of $iPr_2P(E\text{-}CF=CFCF_3)$, however the biggest difference is found for the *bis*-substituted phosphines $PhP(CF=CF_2)_2$ (161°) and $PhP(E\text{-}CF=CFCF_3)_2$ (179°), where the replacement of two fluorines on the β-carbon with two CF_3 groups clearly has a very significant impact on the steric demand of phosphine **2**, to the point that this ligand has a similar Tolman cone angle to that of $P(tBu)_3$ or PCy_3.[1]

While we were unable to coordinate ligand **6** to platinum or palladium metal centres using the methods described above, we were more successful in reacting **6** with $Mo(CO)_6$ under thermal conditions, which resulted in a complex that analysed as $[Mo(CO)_4\{(E\text{-}CF_3CF=CF)_2PCH_2CH_2P(E\text{-}CF=CFCF_3)_2\}]$, **22.** Although other $Mo(CO)_4$-containing complexes of bidentate phosphines possessing fluorinated groups, such as $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$ (dfppe), $(CF_3CF_2)_2PCH_2CH_2P(CF_2CF_3)_2$ (dfepe)[35] and $(C_6H_3F_2\text{-}2,6)_2PCH_2CH_2P(C_6H_3F_2\text{-}2,6)_2$[36] have been reported before, a search of the crystallographic database reveals that none of them have been structurally characterised. We were therefore pleased to obtain crystals of complex **22**, by slow evaporation of the solvent from an chloroform solution, suitable for X-ray diffraction studies.

The structure obtained for **22** is shown in fig. 7. This is the first such data for a molybdenum tetracarbonyl complex of any fluorinated bidentate phosphine, although X-ray structural data for a number of Pd, Pt, Fe, Ru, Ir and Rh complexes of $(R_f)_2PCH_2CH_2P(R_f)_2$, R_f = CF_3, C_2F_5, C_6F_5, have been reported before, as have the structures of $[(\eta^6\text{-}C_6H_5Me)Mo\{(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2\}L]$ (L = N_2 or py)[37] and $[(\eta^5\text{-}C_5H_5)Mo\{(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2\}(CO)Cl]$.[38] The data confirm the identity of the complex and shows the anticipated *cis*-coordination of the bidentate phosphine. The molecule possesses a mirror plane so that the two sides of the ligand are equivalent. The perfluoropropenyl groups point away from each other to minimise the steric repulsion between them. The resulting P-Mo-P bite angle is 80.69(4)°, which is *ca*. 4° smaller than the average bite angle for previously studied transition metal complexes of the dfmpe, dfepe and dfppe bidentate ligands of 84.5°.[39] Only for $[(\eta^6\text{-}C_6H_5Me)Mo\{(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2\}L]$ (L = N_2 or py) systems have smaller bite angles been recorded, and those complexes also exhibited significantly shorter Mo-P distances (2.319 – 2.347 Å) than is observed here, 2.4438(11) Å.[37]

A number of contacts less than the sum of the respective van der Waals radii are present in the solid state. In this case the interactions are between the fluorines of adjacent CF_3 groups, which at 2.684(4) Å is 0.256 Å less than twice r_{vdw} for fluorine (2.94 Å), and between the α-fluorine and one of the CF_3 fluorines (2.803(5) Å).

The presence of CO ligands in this complex means that the electronic properties of ligand **6** can be compared with related bidentate ligands. Although four IR-active stretching modes are expected for $Mo(CO)_4(PP)$ (PP= bidentate phosphine ligand) complexes, based on them adopting idealised C_{2v} geometry, in ours, and some other fluorinated systems it is not possible to resolve all four signals.[40] The highest frequency CO stretching mode for this system, and some other ligands are listed in Table 3. These data suggest that the electronic properties of **6** lie between those of $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$ and $(R_f)_2PCH_2CH_2P(R_f)_2$ (R_f = CF_3 or C_2F_5). It is interesting to note that all of these systems result in higher CO stretching frequencies than those found for phosphite-substituted analogues.

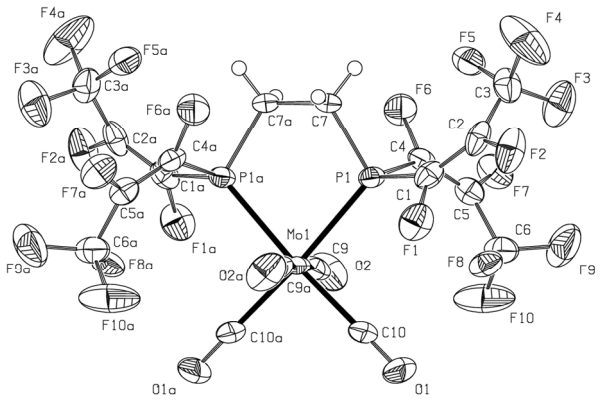


Fig. 7 ORTEP representation of $[Mo(CO)_4\{(E\text{-}CF_3CF=CF)_2PCH_2CH_2P(E\text{-}CF=CFCF_3)_2\}]$, **22**. Selected distances (Å) and angles (°): Mo1-P1 = 2.4438(11), Mo1-C9 = 2.043(5), Mo1-C10 = 2.019(5), C9-O2 = 1.143(7), C10-O1 = 1.134(6), P1-C7 = 1.846(4), C7-C7a = 1.1.541(5), P1-C1 = 1.841(4), C1-F1 = 1.348(5), C1-C2 = 1.327(6), C2-F2 = 1.350(5), C2-C3 = 1.491(7); P1-Mo1-P1a = 80.69(4), Mo1-P1-C7 = 110.25(13), Mo1-P1-C4 = 116.89(13), Mo1-P1-C1 = 119.87(15), C1-P1-C4 = 103.3(2), P1-C1-C2 = 134.3(4), P1-C1-F1 = 110.2(3), F1-C1-F2 = 115.5(4).

Table 3 Highest frequency IR-active carbonyl stretching mode for $[Mo(CO)_4(PP)]$, PP = bidentate phosphine ligand.

PP	ν(CO)/cm^{-1}	Ref.
$(CF_3)_2PCF_2CF_2P(CF_3)_2$	2082	40
$(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$, dfepe	2064	35
$(CF_3)_2PCH_2CH_2P(CF_3)_2$, dfmpe	2063	40
$(E\text{-}CF_3CF=CF)_2PCH_2CH_2P(E\text{-}CF=CFCF_3)_2$, **6**	2051	a
$(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$, dfppe	2041	35
$(MeO)_2PCH_2CH_2P(OMe)_2$	2033	41
$(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$, dppe	2020	42
$(C_2H_5)_2PCH_2CH_2P(C_2H_5)_2$, depe	2012	42

[a] this work.

We also prepared the molybdenum pentacarbonyl phosphine complex from the reaction of $[(MeCN)Mo(CO)_5]$ with ligand **1**. The highest frequency ν(CO) stretching mode for this complex was observed at 2078.8 cm^{-1}, which can be compared with values of ca. 2080 cm^{-1} for the corresponding complexes of $Ph_2P(i\text{-}C_3F_7)$, $Ph_2P(C_2F_5)$ and $Ph_2P(CF_3)$ and 2077 cm^{-1} for the analogous complex of $Ph_2P(CF{=}CF_2)$.[4,2,8]

Irrespective of whether a comparison is made of either the ν(CO) absorption position of the $[Mo(CO)_5P]$ complexes, or the $^1J(PSe)$ or $^1J(PtP)$ coupling constants of the phosphine selenides or *trans*-$[PtCl_2P_2]$ complexes (P = phosphine) a very similar order is shown for the electronic properties of the fluorinated phosphine ligands. For the monodentate phosphines the perfluoropropenyl group has a similar electronic effect to the perfluorovinyl group. In the case of the bidentate ligand, **6**, there are currently fewer pieces of comparative data, but it would appear to offer electronic properties between those of the commercially available $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$ and (the more difficult to synthesise) bidentate phosphines, such as $(R_f)_2PCH_2CH_2P(R_f)_2$ (R_f = CF_3 or C_2F_5), but with a smaller bite angle, making this a very unusual combination which we intend to investigate further.

Conclusions

The reaction of HFC-1225ye (Z-$CF_3CF{=}CFH$) with one equivalent of base, in ether at low temperature, generates the thermally unstable $CF_3CF{=}CFLi$ reagent, which on reaction with $R_{(3\text{-}n)}PCl_n$ (n = 1, R = Ph, iPr; n=2, R = Ph, iPr) and $Cl_2PCH_2CH_2PCl_2$ gave a series of *E*-$CF_3CF{=}CF_2$-containing phosphines. For chlorophosphines containing a sterically more demanding group, such as $tBuPCl_2$, it was found necessary to use a room-temperature variation of the reaction in order for success. The same products could also be obtained from the reaction of chlorophosphines with $CF_3CF{=}CFLi$ derived from HFC-236ea ($CF_3CF_2CH_2F$) and two equivalents of base, but in this case both *E* and *Z* isomers are produced. The *E* isomer was always preferred, but the proportion of *Z* isomer is greater for the room-temperature reactions.

The perfluoropropenyl-containing phosphines appear to undergo the types of chemistry anticipated for electronically neutral and electron-poor phosphines. They are generally stable towards aerial oxidation, but can be chemically oxidised; this is in contrast to what has been reported before. They also form a range of coordination complexes. In all cases these are new complexes. Based on measurement of the CO stretching frequencies of metal carbonyl complexes, and the $^1J(PSe)$ and $^1J(PtP)$ coupling constants of the phosphine selenides and *trans*-bis chloride bis phosphine complexes, electronically these phosphines act as donors similar to perfluorovinyl-containing phosphines, whilst X-ray derived data suggest that some of the perfluoropropenyl-containing phosphines are considerably more sterically demanding. Thus these phosphines continue to populate an area in the stereoelectronic profile for which there are few alternatives.

Surprisingly, the bidentate phosphine, **6**, can be readily prepared, which is in stark contrast to the perfluorovinyl analogue, and so offers the first bidentate perfluoroalkenyl ligand. Despite the presence of four perfluoropropenyl substitutents, the bite angle of the only complex formed to date is relatively small. This further demonstrates that by incorporating a combination of fluorinated and non-fluorinated groups fine-tuning of the steric and electronic properties of ligands can be effected, which in turn may influence the behaviour of catalytic systems.

Experimental

All ligand synthesis reactions were carried out under an inert atmosphere of dinitrogen in oven dried glassware. All non-chlorinated solvents were dried over sodium wire prior to use. $CF_3CF_2CH_2F$ and $CF_3CF{=}CHF$ were obtained from INEOS Fluor. Commercial phosphorus, palladium and platinum starting materials were used as supplied after verification of their purity. ^1H, ^{19}F and $^{31}P\{^1H\}$ NMR spectra were recorded on Bruker Avance spectrometers operating at 400.132, 376.461 and 161.967 MHz respectively. All samples were recorded as $CDCl_3$ solutions and peak positions are quoted in ppm relative to residual proton signals (^1H) or external $CFCl_3$ and 85% H_3PO_4, using the high frequency positive convention. Coupling constants are given in Hz. Elemental analyses were performed by the School of Chemistry microanalytical service.

X-ray crystallography

Details of the structure analyses carried out are summarised in table 4. Measurements for the complexes were made on crystals prepared by slow solvent evaporation on Nonius FR590, Bruker APEX2 and Oxford Instruments XCalibur2 diffractometers using Mo K_α radiation. X-ray structural data solution was by direct methods and refined against F^2 using SHELX.[43] All non-H atoms were modelled with anisotropic displacement parameters, H-atoms were placed in idealised positions and refined with isotropic thermal parameters. The computer packages MERCURY[44] and PLUTON[45] were used to investigate the extended structures and to produce graphical representations used in the figures. Olex2[34] was used to determine Tolman cone angles for the phosphines. CCDC 1402987-1402994 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of $Li(CF{=}CFCF_3)$

Diethyl ether solutions of $Li(CF{=}CFCF_3)$ may be prepared from the low-temperature reaction of either *Z*-$CF_3CF{=}CFH$ with one equivalent of base, or from the reaction of $CF_3CF_2CH_2F$, HFC-236ea with two equivalents of base. These two methods are described below for a 20 mmol scale preparation.

(a) Reaction of *Z*-$CF_3CF{=}CFH$ (HFO-1225ye)

A 3-necked round–bottom flask equipped with a magnetic stirrer, inlet and outlet for nitrogen gas, was held in a pre-cooled ethanol slush bath at -85 °C. Diethyl ether (150 ml)

was added along with *Z*-CF_3CF=CFH (2.9 ml, 30 mmol). A solution of LDA [prepared from n-BuLi (8 ml, 2.5 M, 20 mmol), iPr_2NH (2.8 ml, 20 mmol) in 20 ml of THF] was added to this solution. The solution was stirred for 1h at a temperature between -80 and -85 °C.

(b) Reaction of $CF_3CF_2CH_2F$ (HFC-236ea)

A 3-necked round–bottom flask was equipped with a magnetic stirrer, an inlet and outlet for nitrogen gas, and held in a pre-cooled ethanol slush bath at -85 °C. Diethyl ether (150 ml) was added along with $CF_3CF_2CH_2F$, HFC-236ea (3.8 ml, 30 mmol). A solution of LDA [made from n-BuLi, (16 ml, 2.5 M, 40 mmol), and $^{i}Pr_2NH$ (5.6 ml, 40 mmol) in THF, 30 ml] was added to the continuously stirred solution and the mixture was allowed to react for 90 min while maintaining a temperature between -80 to -85 °C.

Synthesis of $Ph_2P(CF=CFCF_3)$, 1.

A 20 mmol diethyl ether solution of Li(CF=$CFCF_3$), prepared as described above, was cooled to -95 °C, to this was added a solution of Ph_2PCl (2.1 ml, 12 mmol) dissolved in diethyl ether (20 ml) slowly over 15 min. whilst maintaining the temperature below -95 °C. The reaction was allowed to attain room temperature and then worked up by addition of hexane (150 ml) to precipitate the inorganic salts. After filtration through a sinter, the filtrate was concentrated by rotary evaporation to afford the crude product. Purification was by column chromatography on silica with hexane and toluene (1:1) eluent. Yield 2.7 g (75%). Anal. Calcd for $C_{15}H_{10}F_5P$: C: 57.0%, H: 3.2%, P: 9.8% found C: 58.9%, H: 3.4%, P: 9.7%. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ: -19.6 (d,d,q, $J(PCF_3)$ = 58.2 Hz, $J(PF_b)$ = 7.7 Hz $J(PF_a)$ = 4.1 Hz), ^{19}F NMR ($CDCl_3$, 20 °C) δ: -63.8 (d,d,d, $J(PCF_3)$ = 58.0 Hz, $J(CF_3F_b)$ = 10.5 Hz, $J(CF_3F_a)$ = 8.2 Hz, 3F, CF_3), -125.7 (q,d,d, $J(F_aCF_3)$ = 8.2 Hz, $J(F_aF_b)$ = 5.0 $J(PF_a)$ = 4.1 Hz, 1F, CF_a), -132.8 (q,d,d, $J(F_bCF_3)$ = 10.5 Hz, $J(PF_b)$ = 7.7 Hz, $J(F_bF_a)$ = 5.0 Hz, 1F, CF_b), ^1H NMR ($CDCl_3$, 20 °C) δ: 7.3-7.7 (m, 10H, ArH).

Synthesis of $PhP(CF=CFCF_3)_2$, 2.

A 20 mmol diethyl ether solution of Li(CF=$CFCF_3$), prepared as described above, was cooled to -95 °C and a solution of $PhPCl_2$ (1.2 ml, 9 mmol) dissolved in diethyl ether (20 ml) was added slowly over a 30 min period, so as to maintain a temperature of -95 °C. The solution was allowed to attain room temperature overnight and then worked up by addition of hexane (150 ml) to precipitate the inorganic salts. After filtration through a sinter, the filtrate was concentrated by rotary evaporation to afford the crude product. Purification was by column chromatography using hexane and toluene (1:1) as eluent to give 3.05 g (85%). Anal. Calcd for $C_{12}H_5F_{10}P$: C: 38.9, H: 1.4, P: 8.4% found C: 39.4, H: 1.8, P: 9.2%. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ: -39.2 (sept,t,t, $J(PCF_3)$ = 59.0 Hz, $J(PF_b)$ = 10.47 Hz $J(PF_a)$ = 9.9 Hz), ^{19}F NMR ($CDCl_3$, 20 °C) δ: -64.8 (d,d,d,d $J(CF_3P)$ = 59.0, $J(CF_3F_b)$ = 10.5, $J(CF_3F_a)$ = 5.0 Hz, J = 5.2 Hz, 3F, CF_3), -122.8 (d,q,d, $J(F_aP)$ = 9.9, $J(F_aCF_3)$ = 5.0 Hz, $J(F_aF_b)$ = 0.15 Hz, 1F, CF_a), -129.6 (d,q,d $J(F_bCF_3)$ = 10.5, $J(F_bP)$ = 10.0 Hz, $J(F_bF_a)$ = 0.15 Hz, 1F, CF_b), ^1H NMR ($CDCl_3$, 20 °C) δ: 7.37 (m, 2H, ArH), 7.42 (m 2H, ArH), 7.55 (m, 1H, ArH).

Preparation of $iPr_2P(CF=CFCF_3)$, 3.

A 20 mmol diethyl ether solution of Li(CF=$CFCF_3$), prepared as described above, was cooled to -95 °C and a solution of iPr_2PCl (1.6 ml, 10 mmol) dissolved in diethyl ether (25 ml) was added slowly over 20 min. whilst maintaining the low temperature. After allowing the solution to slowly warm to room temperature and workup, the crude product was passed down a silica column (hexane eluent) to give 1.8 g (72%). Anal. Calcd for $C_9H_{14}F_5P$: C: 43.6, H: 5.7, P: 12.5% found C: 42.1, H: 5.1, P: 13.7 %. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ: -2 .0 ppm (q,d,d, $J(PCF_3)$ = 52.0 Hz, J (PF_b) = 4.0 Hz, $J(PF_a)$ = 3.5 Hz, ^{19}F NMR ($CDCl_3$, 20 °C) δ: -63.8 ppm (d,d,d, $J(CF_3P)$ = 52.0 Hz, $J(CF_3F_b)$ = 11.0 Hz, $J(CF_3F_a)$ = 8.1 Hz, 3F, CF_3) -124.0 ppm (m, 1F, F_a) -134.1 (q,d,d, $J(F_bCF_3)$ = 11.1 Hz, (F_bF_a) = 5.1 Hz, $J(F_bP)$ = 4.0 Hz, 1F, F_b), ^1H NMR ($CDCl_3$, 20 °C) δ: 0.78 ppm (t, J = 7.0 Hz, 12H, CH_3), 1.18 ppm, (m, J= 8.2 Hz, 2H, CH).

Synthesis of iPr_2P(*Z*-$CF=CFCF_3$), 3z.

To 3-necked round–bottom flask equipped with a magnetic stirrer, dry-ice/acetone condenser, inlet and outlet for nitrogen gas, was added $CF_3CF_2CH_2F$, HFC-236ea (0.8 ml, 6.0 mmol), iPr_2PCl (0.6 ml, 4 mmol) and diethyl ether (150 ml). A solution of LDA (n-BuLi, 3.2 ml, 2.5 M, 8 mmol, iPr_2NH 1.1 ml, 8 mmol, THF 20 ml) was added to this solution drop-wise over 15 min. After stirring for a further 30 min. hexane was added (150 ml) to precipitate the inorganic salts, which were removed by filtration through a sinter. The filtrate was concentrated by rotary evaporation to afford the crude product, which contained a mixture of *E* and *Z* isomers (see text). This was purified by column chromatography on silica with hexane and toluene (1:1) eluent. Data for *E*-isomer as above. Data for *Z*-isomer: $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ: -4.0 (d,d,d, $J(PF_b)$ = 71.0 Hz, $J(PF_a)$ = 6.0 Hz, $J(PCF_3)$ = 2 Hz), ^{19}F NMR ($CDCl_3$, 20 °C) δ: -67.2 (d, d, d, $J(CF_3F_a)$ = 21.4 Hz, $J(CF_3F_b)$ = 10.6 Hz, $J(CF_3P)$ = 2.0 Hz, 3F, CF_3), -141.5 (d,q,d, $J(F_aF_b)$ = 151.2, $J(F_aCF_3)$ = 21.4, $J(F_aP)$ = 6.0, 1F, F_a), -156.3 (d,d,q, $J(F_bF_a)$ = 151.0 Hz, J(PF) = 71.0 Hz, $J(F_bCF_3)$ = 10.6 Hz, 1F, F_b).

Preparation of $iPrP(CF=CFCF_3)_2$, 4.

A 15 mmol diethyl ether solution of Li(CF=$CFCF_3$) was prepared based on the methods described above. The solution was cooled to -95 °C and $iPrPCl_2$ (0.6 ml, 5 mmol) dissolved in diethyl ether (25 ml) was added slowly over 20 min. After work up and purification (column, hexane eluent) 1.10 g (66%) of **4** was obtained as an oil. Anal. Calcd for $C_9H_7F_{10}P$, C 32.2, H: 2.1, P: 9.2% found: C: 31.2, H: 2.0, P: 9.1%. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ: -34.0 ppm (sept, t, t,) $J(PCF_3)$ = 65.5 Hz, $J(PF_a)$ = 13.5 Hz, $J(PF_b)$ = 7.7 Hz. ^{19}F NMR ($CDCl_3$, 20 °C) δ: -64.6 ppm (q,d,d, $J(CF_3P)$ = 65.5 Hz, $J(CF_3F_a)$ = 10.0 Hz, $J(CF_3F_b)$ = 5.0 Hz, 3F, CF_3), -126.7 (d,q $J(F_aP)$ = 13.5, $J(F_aCF_3)$ = 10.0 Hz, 1F, F_a), -139.05 ppm (d,q, $J(F_bP)$ = 7.7 Hz, $J(F_bCF_3)$ = 5.0 Hz, 1F, F_b), ^1H NMR ($CDCl_3$, 20 °C) δ: 1.05 ppm (m, 6H, CH_3), 2.10 ppm (sept, 1H, CH).

Synthesis of $tBuP(CF=CFCF_3)_2$, 5.

To 3-necked round–bottom flask equipped with a magnetic

stirrer, dry-ice/acetone condenser, inlet and outlet for nitrogen gas, was added Z-CF_3CF=CHF, HFC-1225ye (2.9 ml, 30 mmol), $tBuPCl_2$ (1.7 g, 5 mmol) and diethyl ether (150 ml). A solution of LDA (n-BuLi, 9.6 ml, 2.5 M, 24 mmol, iPr_2NH 3.4 ml, 25 mmol, THF 20 ml) was added slowly over 30 min. via a septum directly into the stirred solution. The reaction was left to stire for 15 mins. then worked up by addition of hexane (150 ml) to precipitate the inorganic salts. After filtration through a sinter, the filtrate was concentrated by rotary evaporation to afford the crude product. Purification was by column chromatography on silica with hexane and toluene (1:1) to give 0.9 g (50%) of **5**. Anal. Calcd for $C_{10}H_9F_{10}P$: C: 34.3, H: 2.6, P: 8.8 % found C: 33.1, H: 2.4, P: 7.2 %. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ: -23.5 (sept,d,d $J(PCF_3)$ = 56.0 Hz, $J(PF_a)$ = 12.5 Hz $J(PF_b)$ = 10.0 Hz), ^{19}F NMR ($CDCl_3$, 20 °C) δ: -64.1 (d,d,d, $J(CF_3P)$ = 56.0 Hz, $J(CF_3F_b)$ = 10.6 Hz, $J(CF_3F_a)$ = 5.6 Hz, 6F, CF_3), -121.0 (d,q,d, $J(F_aP)$ = 12.5 Hz, $J(F_aCF_3)$ = 5.6, $J(F_aF_b)$ = 0.2 Hz, 2F, F_a), -127.9 (q,d,d, $J(F_bCF_3)$ = 10.8 Hz, $J(F_bP)$ = 9.8 Hz, $J(F_bF_a)$ = 0.2 Hz, 2F, F_b), ^1H NMR ($CDCl_3$, 20 °C) δ: 0.8 (m, 9H, CH_3).

Synthesis of $(CF_3CF{=}CF)_2PCH_2CH_2P(CF{=}CFCF_3)_2$, 6.

A 50 mmolar diethyl ether solution of Li(CF=$CFCF_3$) was prepared based on the method described above. The solution was cooled to -95 °C and a concentrated cold solution of $Cl_2PCH_2CH_2PCl_2$ (1.7 ml, 10 mmol) dissolved in Et_2O (25 ml) was added drop wise whilst maintaining the solution temperature below -90 °C. The reaction was allowed to attain room temperature slowly and then worked up by addition of hexane (150 ml) to precipitate the inorganic salts. After filtration through a sinter, the filtrate was concentrated by rotary evaporation to afford the crude product which was purified by column chromatography on silica, with a 1:1 toluene/hexane (1:1) to give 2.18 g (35%) of the pure product as a colourless solid. Anal. Calcd for $C_{14}H_4F_{10}P_2$: C: 27.4 %, H: 0.7 %, found C: 27.4 %, H: 1.0 %. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ: -44.2 (m, 2P), ^{19}F NMR ($CDCl_3$, 20 °C) δ: -65.1 (m, 12F, CF_3), -126.9 (m, 4F), -128.4 (br.s, 4F). IR, ν/cm^{-1}: 1675, 1345, 1186, 1099. Mass Spec. (APCI) 614.1 (50%, M^+), 293.0 (50 %, $(CF{=}CFCF_3)_2P^+$), ^1H NMR ($CDCl_3$, 20 °C) δ: 2.2(m, 4H).

NMR-scale synthesis of $R_2P(O)(E\text{-}CF{=}CFCF_3)$

The small-scale preparation of phosphine oxides of compounds **1**-**5** were undertaken in NMR tubes containing a solution of each phosphine dissolved in $CDCl_3$ to which was added a few drops of H_2O_2 (aqueous solution, 30 vol %) or a few crystals of urea.H_2O_2.

$Ph_2P(O)(E\text{-}CF{=}CFCF_3)$, 7: $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ: 20.0 ppm (d,d $J(PF_a)$ = 56.0 Hz, $J(PF_b)$ = 7.7 Hz), ^{19}F NMR ($CDCl_3$, 20 °C) δ: -64.6 ppm (d,d, $J(CF_3F_b)$ = 10.5 Hz, $J(CF_3F_a)$ = 7.6 Hz, 3F, CF_3), -131.4 ppm (d,q,d, $J(F_aP)$ = 56.0 Hz, $J(F_aCF_3)$ = 7.6 Hz, $J(F_aF_b)$ = 5.8 Hz, 1F, F_a) -132.0 (q,d,d, $J(F_bCF_3)$ = 10.5 Hz, $J(F_bP)$ = 7.7 Hz, $J(F_bF_a)$ = 5.8 Hz, 1F, F_b), ^1H NMR ($CDCl_3$, 20 °C) δ: 7.8 - 7.6 (m, ArH).

$PhP(O)(E\text{-}CF{=}CFCF_3)_2$, 8: $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ: 9.6 ppm (t,t, $J(PF_b)$ = 63.5 Hz, $J(PF_a)$ = 4.8 Hz) ^{19}F NMR ($CDCl_3$, 20 °C) δ: -66.1 ppm (d,d, $J(CF_3F_a)$ = 10.9 Hz, $J(CF_3F_b)$ = 6.9 Hz, 6F, CF_3) -128.4 ppm (m, 2F, F_a), -136.4 (q,m, $J(F_bP)$ = 63.5 Hz, 2F, F_b). ^1H NMR ($CDCl_3$, 20 °C) δ: 7.7 - 7.5 (m, ArH).

$iPr_2P(O)(E\text{-}CF{=}CFCF_3)$, 9: $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ: 51.0 ppm (d,m, $J(PF_b)$ = 42.7 Hz), ^{19}F NMR ($CDCl_3$, 20 °C) δ: -64.0 ppm (d,d, $J(CF_3F_b)$ = 8.2 Hz, $J(CF_3F_a)$ = 9.5 Hz, 3F, CF_3), -130.5 ppm (q,m, $J(F_aCF_3)$ = 9.5 Hz, 1F, F_a), -140.0 (d,q, $J(F_bP)$ = 42.7 Hz, $J(F_bCF_3)$ = 8.2 Hz, 1F, F_b), ^1H NMR ($CDCl_3$, 20 °C) δ: 2.3 (m, J=1.7 Hz, 2H, CH), 1.2 (m, 12H, CH_3).

$iPrP(O)(E\text{-}CF{=}CFCF_3)_2$, 10: $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ: 45.7 ppm (t,m $J(PF_b)$ = 56.0 Hz), ^{19}F NMR ($CDCl_3$, 20 °C) δ: -63.8 ppm (d,d, $J(CF_3F_a)$ = 10.8 Hz, $J(CF_3F_b)$ = 3.3 Hz, 6F, CF_3), -124.0 ppm (m, 2F, F_a) -137.0 (d,m $J(F_bP)$ = 56.0 Hz, 2F, F_b) ^1H NMR ($CDCl_3$, 20 °C) δ: 2.8 (m, J=1.7 Hz, 1H, CH), 1.2 (m, 6H, CH_3).

$tBuP(O)(E\text{-}CF{=}CFCF_3)_2$, 11: $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ: 27.4 ppm (t,m, $J(PF_b)$ = 51.2 Hz), ^{19}F NMR ($CDCl_3$, 20 °C) δ: -64.8 ppm (d,d,d, J = 9.8, 8.0, 1.5 Hz, 6F, CF_3) -125.9 ppm (q, $J(F_aCF_3)$ = 9.8 Hz, 2F, F_a), -138.0 (d,m $J(F_bP)$ = 51.2 Hz, 2F, F_b) ^1H NMR ($CDCl_3$, 20 °C) δ: 0.82 (m, 9H, CH_3).

$(E\text{-}CF_3CF{=}CF)_2P(O)CH_2CH_2P(O)(E\text{-}CF{=}CFCF_3)_2$, 12: $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ: 16.7 (m, 2P), ^{19}F NMR ($CDCl_3$, 20 °C) δ: -56.8 (br.s, 12F, CF_3), -124.0 (br.s, 4F, CF_a), -142.0 (br.d, $J(PF)$ = 60.9 Hz, 4F, CF_b), ^1H NMR ($CDCl_3$, 20 °C) δ: 1.3-1.4 (m, 2H), 1.7-1.8 (m, 2H).

Synthesis of $Ph_2P(O)(E\text{-}CF{=}CFCF_3)$, 7, via $Ph_2P(O)Cl$

A 3-necked round–bottom flask was equipped with a magnetic stirrer, an inlet and outlet for nitrogen gas, and held in a pre-cooled acetone slush bath at -90 °C. Et_2O (150 ml) was added along with $CF_3CF_2CH_2F$, HFC-236ea (3.8 ml, 30 mmol). A solution of LDA made from n-BuLi, (16 ml, 2.5 M, 40 mmol), and iPr_2NH (5.6 ml, 40 mmol) in THF (20 ml) was added to the continuously stirred solution and the mixture was allowed to stir for 1 hour while maintaining a temperature between -80 to -85 °C. After 1 h the reaction was cooled to -95 °C and diphenyl phosphorylchloride (2.8 ml, 15 mmol) dissolved in diethyl ether (20 ml) was added slowly over a 30 min period. The solution was allowed to attain room temperature overnight and then worked up by addition of hexane (150 ml) to precipitate the inorganic salts. After filtration through a sinter, the filtrate was concentrated by rotary evaporation to afford 1.4 g (29 %) of the product as a liquid. NMR data recorded were in agreement with **7** prepared in an NMR tube.

Synthesis of $PhP(O)(E\text{-}CF{=}CFCF_3)_2$, 8, via $PhP(O)Cl_2$

A 3-necked round–bottom flask was equipped with a magnetic stirrer, an inlet and outlet for nitrogen gas, and held in a pre-cooled ethanol slush bath at -90 °C. Et_2O (150 ml) was added along with $CF_3CF_2CH_2F$, HFC-236ea (3.8 ml, 20 mmol). A solution of LDA made from n-BuLi, (16 ml, 2.5 M, 40 mmol), and iPr_2NH (5.6 ml, 40 mmol) in THF (20 ml) was added to the continuously stirred solution and the mixture was allowed to stir for 1 hour while maintaining a temperature between -80 to -85 °C. After 1 hour the reaction was cooled to -95 °C and phenyl phosphonic dichloride (1.0 ml, 7 mmol) dissolved in Et_2O (20 ml) was added slowly over a 30 minutes period. The solution was allowed to attain room temperature overnight and then worked up by addition of hexane (150 ml) to precipitate

the inorganic salts. After filtration through a sinter, the filtrate was concentrated by rotary evaporation to afford the product as a liquid 0.95 g (35 %). NMR data agree with those recorded for **8** prepared in an NMR tube.

Synthesis of $Ph_2P(Se)(E\text{-}CF{=}CFCF_3)$, 13.

A solution of $Ph_2(E\text{-}CF{=}CFCF_3)$ (0.075 g, 0.2 mmol) was dissolved in toluene (20 ml). Selenium (0.06 g, 0.4 mmol) was added and the solution was refluxed for 2 days. After cooling to room temperature the mixture was filtered and the solvent removed under vacuum to give 0.04 g (45 %) of a yellow oil. Anal. Calcd for $C_{15}H_{10}F_5PSe$ C: 45.5, H: 2.5, P: 7.8%, found C: 46.2, H: 2.1, P: 7.0%. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ: 35.5 ppm (d,d, J(SeP) = 763 Hz, J(PF_a) = 59.4 Hz, J (PF_b)= 9.0 Hz). ^{19}F NMR ($CDCl_3$, 20 °C) δ: -65.1 (d,d, J(CF_3F_b) = 20.2 Hz, J(CF_3F_a) = 5.9 Hz), -121 ppm (d,q, J(F_aP) = 59.4 Hz, J(F_aCF_3) = 5.9 Hz, 1F, F_a), -149 ppm (q,d, J(F_bCF_3) = 20.2 Hz, J(F_bP) = 9.0 Hz, 1F, F_b). ^1H NMR ($CDCl_3$, 20 °C) δ: 7.4 – 7.5 ppm, 10H, ArH).

Synthesis of $PhP(Se)(E\text{-}CF{=}CFCF_3)_2$, 14.

Powdered elemental selenium (0.06 g, 0.8 mmol) was added to a solution of $PhP(E\text{-}CF{=}CFCF_3)_2$ (0.15 g, 0.4 mmol) in toluene (10 ml). The solution was refluxed for 3 days, after which time the excess of selenium was removed by filtration, and the volatiles removed in vacuo to give the title compound as an amber liquid, 0.07 g, (40%). Anal. Calcd for $C_{12}H_5F_{10}PSe$ C 32.1, H 1.1, P 6.9%, found C: 31.5, H: 1.1, P: 6.2%. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ: 28.8 (t,t, J(PSe) = 832 Hz, J(PF_a) = 55.2 Hz, J(PF_b) = 3.5 Hz). ^{19}F NMR ($CDCl_3$, 20 °C) δ: -63.6 (d,d, J(CF_3F_a) = 3.5 Hz, J(CF_3F_b) = 23.5 Hz, 6F, CF_3), -121.0 ppm (d,d,q, J(F_aP) = 55.2 Hz, J(F_aF_b) = 6.3 Hz, J(F_aCF_3) = 3.5 Hz, 2F, F_a), -134.0 (q,d,d J(F_bCF_3) = 23.5 Hz, J(F_bF_a) = 6.3 Hz, J(F_bP) = 3.5 Hz, 2F, F_b). ^1H NMR ($CDCl_3$, 20 °C) δ: 7.4 - 7.8 (m, ArH).

Synthesis of $iPr_2P(Se)(E\text{-}CF{=}CFCF_3)$, 15.

$iPr_2P(E\text{-}CF{=}CFCF_3)$ (0.15 g, 0.6 mmol) was dissolved in toluene (20 ml). Selenium (0.06 g, 0.8 mmol) was added and the solution was refluxed for 1 week, after which time the excess of selenium was removed by filtration and the solvent removed under vacuum to give the product as a solid, 0.08 g (40%). Anal. Calcd for $C_9H_{14}F_5PSe$ C, 33.0; H: 4.3; P: 9.5%, found C: 32.7, H: 5.1, P: 8.4 %. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ: 61.5 (d,d, J(PSe) = 799 Hz, J(PF_a) = 50 Hz, J(PF_b) = 10.0 Hz). ^{19}F NMR ($CDCl_3$, 20 °C) δ: -62.5 (d,d,d, J(CF_3F_a) = 3.5 Hz, J(CF_3F_b) = 11.6 Hz, 3F, CF_3), -128.1 ppm (d,d,q J(F_aP) = 50.0 Hz J(F_aF_b) = 3.6 Hz, J(F_aCF_3) = 3.5 Hz, 1F, F_a), -133.0 (q,d,d J(F_bCF_3) = 11.5 Hz, J(F_bP) = 10.0 Hz, J(F_bF_a) = 3.6 Hz, 1F, F_b). ^1H NMR ($CDCl_3$, 20 °C) δ: 2.9 (m, J=1.7 Hz, 1H, CH), 1.2 (m, 6H, CH_3).

Synthesis of $tBuP(Se)(E\text{-}CF{=}CFCF_3)_2$, 16.

Powdered elemental selenium (0.06 g, 0.8 mmol) was added to a solution of $tBuP(E\text{-}CF{=}CFCF_3)_2$ (0.15 g, 0.4 mmol) in toluene (60 ml). The solution was refluxed for 7 days, and then cooled and filtered to remove the excess of selenium. After evaporation of the solvent the product was isolated in combination with unreacted starting material and another unidentifiable compound from which it could not be separated. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ: 17.0 (d, J(PF_a) = 67 Hz J(PSe) = 967 Hz).

Synthesis of *trans*-$[PtCl_2\{Ph_2P(E\text{-}CF{=}CFCF_3)\}_2]$, 17

K_2PtCl_4 (0.10 g, 0.24 mmol) was dissolved in water (10 ml), to this solution was added to an ethanolic solution (10 ml) of $Ph_2P(E\text{-}CF{=}CFCF_3)$ (0.125 g, 0.4 mmol). The solution was stirred at room temperature for 2 days before filtration of the product. The precipitate was washed with water and ice-cold ethanol, (3 x 5 ml) and dried in vacuo for 1 h, to give a red solid, yield 0.09g, (42%), mpt 187-189 °C. Anal. Calcd for $C_{30}H_{20}Cl_2F_{10}P_2Pt$ C: 40.1, H: 2.2, P: 6.9, found: C: 39.0, H: 1.7, P: 6.5 %. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ: 18.8 ppm (br.m, J(PPt) = 2780 Hz) ^{19}F NMR ($CDCl_3$, 20 °C) δ: -66.2 (d,d,t, J= 6.6, 12.0, 18.3 Hz, 3F, CF_3), -121.1 (q, J = 6.6 Hz, 1F, F_a), -136.3 (q, J= 12.0 Hz 1F, F_b), ^1H NMR ($CDCl_3$, 20 °C) δ: Ar-H δ 7.85 (m, 2H, ArH), 7.45(m, 1H, ArH), 7.4 (m, 2H, ArH).

Synthesis of *trans*-$[PtCl_2\{PhP(E\text{-}CF{=}CF(CF_3))_2\}_2]$, 18

To one equivalent of K_2PtCl_4 (0.10 g, 0.24 mmol) dissolved in water (10 ml) was added to a stirred ethanolic solution (10 ml) of two equivalents of $PhP(E\text{-}CF{=}CFCF_3)_2$ (0.15 g, 0.4 mmol) at room temperature. The solution was stirred for 4 days before filtration of the product, which was washed with water and ethanol, and dried in vacuo for 2 h to give an orange yellow solid, 0.11 g (50%), mpt 124 °C. Anal. Calcd for $C_{24}H_{10}Cl_{2}F_{20}P_2Pt$ C: 28.6, H: 1.0, P: 6.2, found C: 27.4 H: 0.8, P: 5.9 %. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ: 16.6 ppm (br. J(PPt) = 3324 Hz). ^{19}F NMR ($CDCl_3$, 20 °C) δ: -66.54 (m, J(CF_3P) = 5.3 Hz, J(CF_3F_b) = 17.6 Hz, 12F, CF_3), -124.2 (m, 4F, F_a), -128.3 (q, J(F_bCF_3) = 17.5 Hz, 4F, F_b). ^1H NMR ($CDCl_3$, 20 °C) δ: 7.45 (m, J= 13.5 Hz, ArH) 7.65 (m, J= 8.0 Hz, ArH).

Synthesis of *trans*-$[PtCl_2\{iPr_2P(CF{=}CFCF_3)\}_2]$, 19

One equivalent of K_2PtCl_4 (0.127g 0.3 mmol) dissolved in water (5 ml) was added to stirred ethanolic solution (5 ml) of $iPr_2P(E\text{-}CF{=}CFCF_3)$ (0.15 g, 0.6 mmol) at room temperature. The solution was stirred for 4 hours to give an oily crude product which was extracted from the ethanolic solution by shaking with portions of chloroform (3 x 20 ml) which were combined and the solvent removed in vacuo to yield the complex, 0.08g (40%). Anal. Calcd for $C_{18}H_{28}Cl_2F_{10}P_2Pt$ C: 28.4, H: 3.7, P: 8.1, Found: C: 27.8, H: 2.7, P: 7.7 %. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ: 36.35 (br. m, ^1J(PtP) = 3082 Hz). ^{19}F NMR ($CDCl_3$, 20 °C) δ: -65.8 (m, J(CF_3F_a) = 2.0 Hz, 6F, CF_3), -128.2 (m, 2F, F_a), -132 (q, J(CF_3F_b) = 2.0 Hz, 2F, F_b). ^1H NMR ($CDCl_3$, 20 °C) δ: 1.2 (m, CH_3), 3.5 (m, CH).

Synthesis of *trans*-$[PdCl_2\{Ph_2P(CF{=}CFCF_3)\}_2]$, 20

$Ph_2P(E\text{-}CF{=}CFCF_3)$ (0.2 g, 0.6 mmol) was dissolved in ethanol (5 ml), and added dropwise to a solution of $K_2[PdCl_4]$ (0.10 g, 0.3 mmol) in water (5 ml) and stirred for 2 days. The mixture was filtered, and the filtrate washed with ethanol (2 x 5 ml) to yield a yellow solid mpt 136-7 °C, yield, 0.18g (75%). Anal. Calcd for $C_{30}H_{20}Cl_2F_{10}P_2Pd$ C: 44.5, H: 2.5, P: 7.7. Found C: 45.5, H: 2.9, P: 7.3%. $^{31}P\{^1H\}$ NMR ($CDCl_3$,

20 °C) δ: 22.0 ppm (m). ^{19}F NMR ($CDCl_3$, 20 °C) δ: -66.2 (m, 6F, CF_3), -121.0 (m, 2F, F_a), -136.0 (m, 2F, F_b). ^{1}H NMR ($CDCl_3$, 20 °C) δ: 7.0 (m, 20H, ArH)

Synthesis of *trans*-[$PdCl_2${iPr_2P(*E*-CF=$CFCF_3$)}$_2$], 21

iPr_2P(*E*-CF=CFCF)$_3$ (0.2 g, 0.8 mmol) was dissolved in ethanol (10 ml) and added dropwise to a solution of $K_2[PdCl_4]$ (0.10 g, 0.3 mmol) in water (10 ml) and stirred for 2 days. The mixture was filtered, and the filtrate washed with ethanol (2 x 5 ml) to yield a yellow solid mpt 142-4 °C. Yield 0.10 g (50%). Anal. Calcd for $C_{18}H_{28}Cl_2F_{10}P_2Pd$ C: 32.1, H: 4.2, P: 9.2. Found C: 32.5, H 4.2, P: 8.8 %. ^{31}P{^{1}H} NMR ($CDCl_3$, 20 °C) δ: -1.6 ppm (m). ^{19}F NMR ($CDCl_3$, 20 °C) δ: -67.7 (m, 6F, CF3), -148.0 (m, 2F, F_a), -153.4 (m, 2F, F_b). ^{1}H NMR ($CDCl_3$, 20 °C) δ: 1.2 (m, CH_3), 4.15 (sept, 2H, CH).

Synthesis of [$Mo(CO)_4${(*E*-CF_3CF=CF)$_2$$PCH_2CH_2$P(*E*-CF=$CFCF_3$)$_2$}] , 22

6 (1.0 g, 1.63 mmol) and $Mo(CO)_6$ (0.5 g, 1.89 mmol) were placed in a one-necked round-bottom flask with a stirrer. Octane (50 ml) was added and the reaction heated at reflux for 8 hours in an oil bath. After cooling to room temperature, the mixture was filtered and concentrated on a rotary evaporator to yield a solid material (0.54 g, 40 %). Anal. Calcd for $C_{18}H_4F_{20}MoO_4P_2$: C, 26.3; H, 0.5. Found: C, 27.0; H, 0.9 %. ^{31}P{^{1}H} NMR ($CDCl_3$, 20 °C) δ: 60.0 (t, J(PF) = 99.1 Hz, 2P), ^{19}F NMR ($CDCl_3$, 20 °C) δ: -66.6 (s, 12F, CF_3), -128.3 (s, 4F, CF), -133.7 (t,m, 4F,CF). ν(CO)/cm^{-1} : 2051, 1946. Mass Spec. (APCI)

Synthesis of [$Mo(CO)_5${Ph_2P(*E*-CF=$CFCF_3$)}] , 23.

$Mo(CO)_6$ (0.3 g, 1.14 mmol) was dissolved in MeCN (20 ml), and $Me_3NO.2H_2O$ (0.126 g, 1.14 mmol) was added. After stirring under a static vacuum for 1 hour, with occasional re-evacuation, a solution of **1** (0.36 g, 1.14 mmol) in MeCN (5 ml) was added and the mixture allowed to stir overnight. The solution was passed down a short silica column (toluene eluent) affording the title compound as a viscous material, 0.1 g (17%). Anal. Calcd for $C_{20}H_{10}F_5MoO_5P$: C, 43.5; H: 1.8; P: 5.6%. Found: C, 43.8; H, 2.0; P, 6.1%. ^{31}P{^{1}H} NMR ($CDCl_3$, 20 °C) δ: 40.6 ppm (d,d, J(PF_b) = 7.3 Hz, J(PF_a)= 57 Hz). ^{19}F NMR ($CDCl_3$, 20 °C) δ: -70.6 (d,d, J(CF_3P) = 3.5 Hz, J(CF_3F_b) = 11.0 Hz, 12F, CF_3), -146.0 ppm (m, J(F_aP) = 57.2 Hz, J(F_aF_b) = 20.0 Hz, 4F, F_a), -152.0 ppm (d,d,q, J(F_bCF_3) = 11.0 Hz, J(F_bF_a) = 20.0 Hz, J(F_bP) = 7.3 Hz. ^{1}H NMR ($CDCl_3$, 20 °C) δ: 7.5-7.8 ppm (m). ν(CO)/cm^{-1} 2079, 1940.

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Notes and references

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Table 4. Crystallographic data for $(CF_3CF=CF)_2PCH_2CH_2P(CF=CFCF_3)_2$, **6**, $(CF_3CF=CF)_2P(O)CH_2CH_2P(O)(CF=CFCF_3)_2$, **12**, $iPr_2P(Se)(CF=CFCF_3)$, **15**, *trans*-$[PtCl_2\{PPh_2(CF=CFCF_3)\}_2]$, **17**, *trans*-$[PtCl_2\{PPh(CF=CFCF_3)_2\}_2]$, **18**, *trans*-$[PdCl_2\{PPh_2(CF=CFCF_3)\}_2]$, **20**, *trans*-$[PdCl_2\{PiPr_2(CF=CFCF_3)\}_2]$, **21**, and $[Mo(CO)_4\{(CF_3CF=CF)_2PCH_2CH_2P(CF=CFCF_3)_2\}]$, **22**.

	6	**12**	**15**	**17**	**18**	**20**	**21**	**22**
Formula	$C_{14}H_4F_{20}P_2$	$C_{14}H_4F_{20}O_2P_2$	$C_9H_{14}F_5PSe$	$C_{30}H_{20}Cl_2F_{10}P_2Pt$	$C_{24}H_{10}Cl_2F_{20}P_2Pt$	$C_{30}H_{20}Cl_2F_{10}P_2Pd$	$C_{18}H_{28}Cl_2F_{10}P_2Pd$	$C_{18}H_4F_{20}MoO_4P_2$
Formula weight	614.11	646.11	327.13	898.39	1006.25	809.70	673.64	822.09
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	*C*2/*c*	*C*2/*c*	*P*1	*P*1	$P2_1/n$	*P*1	*P*1	*C*2/*c*
a (Å)	22.171(6)	24.566(16)	6.9690(7)	10.5209 (2)	11.5370(15)	10.9856 (4)	8.147 (4)	10.222 (1)
b (Å)	5.9138(11)	5.0981(8)	7.7290(7)	11.6030(3)	9.1420 (13)	15.4755 (5)	8.856 (4)	13.9344 (7)
c (Å)	15.967(3)	16.835(4)	12.4730(16)	14.0370 (4)	14.762 (2)	16.1213 (5)	9.608(4)	18.7749 (17)
α (°)	90	90	77.095(14)	106.030(1)	90	62.762 (3)	77.301 (9)	90
β (°)	106.437(19)	103.70(2)	78.880(5)	90.450 (1)	100.526 (5)	81.225 (3)	77.160 (7)	100.202 (9)
γ (°)	90	90	73.227(9)	109.124 (1)	90	75.555 (15)	75.285 (8)	90
V (Å^3)	2008.0(8)	2048.4(8)	621.04(12)	1546.89 (7)	1530.8 (4)	2357.45 (15)	643.8 (5)	2632.0 (4)
Z	4	4	2	2	2	3	1	4
T / K	100 (2)	150 (2)	100 (2)	100 (2)	100 (2)	100 (2)	100 (2)	150 (2)
D_c (g cm^{-3})	2.031	2.095	1.749	1.929	2.183	1.711	1.737	2.075
Crystal size (mm)	0.01 × 0.04 × 0.15	0.05 × 0.08 × 0.20	0.12 × 0.12 × 0.12	0.06 x 0.10 x 0.15	0.08 × 0.08 × 0.14	0.10 × 0.10 × 0.20	0.02 × 0.10 × 0.17	0.01 × 0.04 × 0.10
μ (mm^{-1})	0.401	0.406	3.185	4.894	5.002	0.943	1.130	0.789
2θ range (°)	7.2 → 57	6.6 → 52.0	6.2 → 51.0	5.8 → 52.0	6.6 → 51.0	5.4 → 52.8	4.4 → 52.8	7.2 → 52.0
Total reflections	6946	6352	6746	11650	4379	16029	3652	5541
Unique reflections (R_{int})	2288 (0.131)	2018 (0.259)	2143 (0.122)	6055 (0.074)	1989 (0.122)	9504 (0.047)	2548 (0.121)	2595 (0.043)
Observed reflections [I > 2σ(I)]	877	625	1731	4631	1475	5787	1700	1964
Parameters	163	172	145	407	224	610	155	204
Final *R* indices $I > 2\sigma(I)$]	R_1 0.1082, wR_2 0.3558	R_1 0.0932, wR_2 0.2112	R_1 0.0561, wR_2 0.1532	R_1 0.0535, wR_2 0.1372	R_1 0.0701, wR_2 0.1584	R_1 0.0394, wR_2 0.0733	R_1 0.0656, wR_2 0.1443	R_1 0.0544, wR_2 0.0963
Max., min. Δρ (eÅ^{-3})	0.95, -0.68	0.52, -0.46	0.68, -1.13	4.74, -2.30	1.78, -1.29	0.88, -0.49	1.87, -1.66	0.60, -0.48
Goodness of fit on F^2	0.98	0.94	1.11	1.05	1.04	0.88	0.88	1.06

From HFC replacements $CF_3CF_2CH_2F$ and *Z*-$CF_3CF{=}CFH$ new *E*-perfluoropropenyl phosphine ligands are prepared, including the first perfluoroalkenyl bidentate phosphine, (*E*-$CF_3CF{=}CF)_2PCH_2CH_2$(*E*-$CF{=}CFCF_3)_2$.