A generic route to fluoroalkyl-containing phosphanes[†]

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The reaction of trimethylsilyl-containing phosphanes with perfluoroiodoalkanes provides a general and convenient route to perfluoroalkyl-containing phosphanes.

Phosphorus(III) ligand systems of the type PR₃ are amongst the most widely studied and utilised in transition metal chemistry, and they, or their metal complexes, find applications in areas such as materials, drugs, organocatalysts and a variety of C-C bond forming reactions.¹ When one, or more, of the substituents are perfluorinated (denoted by R_f) an unusual combination of steric and electronic properties can result.² Whilst a range of fluoroaryl-phosphanes are known,³ the only perfluoroalkyl phosphanes to have been studied in detail are those containing the $-CF_3^4$ and $-CF_2CF_3^5$ groups. This limitation in phosphorus (and other element) organofluorine chemistry largely arises because of a limited number of suitable perfluoroalkyl-delivery reagents; perfluoroorganic Grignard and lithium reagents are frequently unstable (e.g. LiC_2F_5 is reported to decompose above $-70 \degree C^5$) or inaccessible (e.g. LiCF₃). Thus fluoroalkyl phosphanes have been prepared by a variety of specialised methods, including direct fluorination of PR_3 with F_2 (followed by reduction of the resulting P(v)species),⁶ electrochemical fluorination of PR₃ in anhydrous HF,⁷ the reaction of heavy metal transfer agents with PI₃,⁸ or reaction of CF₃I with P₄.9

In 2005, Caffyn and co-workers published a method for the synthesis of $P(R_f)_3$ compounds, based on the reaction of Me_3SiR_f with $P(OR)_3$ (R = Ph, $p-C_6H_4CN$).¹⁰ Subsequently Togni *et al.* reported that CF₃-containing phosphanes may be prepared from Ph_2PH or Ph_2PSiMe_3 and CF₃-containing hypervalent iodine compounds.¹¹ Both of these methods benefit from the commercial availability of Me_3SiCF_3 , unfortunately other Me_3SiR_f reagents are more difficult to obtain.

Trimethylsilyl-containing phosphanes have been used, often under transition metal catalysed conditions, to prepare perprotio-phosphanes¹² and to generate the fluorine-containing phosphanes, $Ph_2P(CF_2)_nBr$ and $Ph_2P(CF_2)_nPPh_2$, from Ph_2PSiMe_3 and $Br(CF_2)_nBr$ ($n = 1^{13}$ or 2^{14}) and fluoroaryl-phosphanes from polyfluoroarenes.^{14,15} It is surprising that a similar strategy has not yet been successfully applied to the synthesis of perfluoroalkyl-containing phosphanes.

The NMR-scale reactions of a series of primary, secondary and tertiary R_fI compounds with Ph₂PSiMe₃ were undertaken.‡

UK M13 9PL. E-mail: alan.brisdon@manchester.ac.uk; Fax: +44 (0)161 275 4598; *Tel:* +44 (0)161 306 4459 Thus, CF₃I was added to a solution of Ph₂PSiMe₃ in CDCl₃ and the course of the reaction was followed using ¹⁹F and ³¹P{¹H} NMR spectroscopy. The phosphorus resonance due to Ph₂PSiMe₃, at -56.7 ppm, decreased in intensity and was slowly replaced by a quartet (J = 73.8 Hz) centred at 2.5 ppm. Similarly, the ¹⁹F NMR spectrum of the reaction mixture showed replacement of the peak due to CF₃I at -5.2 ppm¹⁶ with a doublet signal (J = 73.8 Hz) at -55.1 ppm. These spectroscopic data are consistent with those previously reported for Ph₂PCF₃.¹¹ The principal by-product of the reaction was identified as Me₃SiI from ¹H and ²⁹Si NMR studies ($\delta_{\rm H}$ 0.8 ppm, $\delta_{\rm Si}$ 9.7 ppm¹⁷).

When other perfluoroalkyliodides were investigated, Table 1, we similarly observed a consumption of the starting materials and new signals in the ${}^{31}P{}^{1}H{}$ and ${}^{19}F{}$ NMR spectra consistent with R_f-containing phosphines. For $Ph_2P(CF_3)$ and $Ph_2P(C_2F_5)$ these data are consistent with those previously reported. Whilst for the new compounds unequivocal assignment is possible based on the complex, largely first order, NMR patterns observed in the mutually coupled fluorine and phosphorus NMR spectra. Particularly noteworthy is the reaction with $t-C_4F_9I$. Although this reaction was not as clean as many of the others, some $(CF_3)_3CH$ and $(CF_3)_2C = CF_2$ being observed by known decomposition routes,¹⁸ it is to the best of our knowledge the first report of a phosphine containing a tertiary perfluoroalkyl group being prepared. Calculations performed by others suggest that such ligands should possess unusual and interesting steric and electronic properties.²

Replacement of Ph_2PSiMe_3 with *i*- Pr_2PSiMe_3 or the P-chiral PhMePSiMe_3 starting materials was also successful, which suggests that this method may be applied to a number of trimethylsilyl-containing phosphane starting materials. However, no significant reaction was observed to occur over a period of 5 days when either CF_2 —CFI or C_6F_5I was used.

On a preparative scale the reaction of i-C₃F₇I with Ph₂PSiMe₃ at -20 °C results in an immediate reaction, after addition of MeLi to facilitate removal of Me₃SiI as volatile Me₄Si, and work-up a white, low-melting point solid was isolated. NMR data (¹H, ¹³C, ¹⁹F, ³¹P) and elemental analysis confirmed the compound to be Ph₂P(i-C₃F₇), **4**, furthermore, by slow cooling of the molten solid, we were able to obtain single-crystals suitable for X-ray analysis.§

The molecular structure of **4** (Fig. 1), as expected, exhibits a pyramidal geometry at the phosphorus centre with the P–C bond length to the fluorinated fragment, 1.899(5) Å, being longer than the average distance to the non-fluorinated groups, 1.830(5) Å. These distances are consistent with the other four X-ray structures of phosphanes containing one, or more, perfluorinated groups that have been reported

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$R_{\rm f}I$	R ₂ in R ₂ PSiMe ₃	Time for R_2PSiMe_3 consumption ^{<i>a</i>}	³¹ P{ ¹ H} NMR δ (ppm)	Product, yield ^b
CF ₃ I	Ph ₂	6 days	2.5	Ph ₂ PCF ₃ , 1, 75%
C_2F_5I	Ph ₂	5 days	-1.9	Ph ₂ PC ₂ F ₅ , 2 , 80%
$C_8F_{17}I$	Ph ₂	6 days	1.1	$Ph_2P(C_8F_{17}), 3, 85\%$
i-C ₃ F ₇ I	Ph_2	30 min	-0.8	$Ph_2P(i-C_3F_7), 4, 75\%$
s-C ₄ F ₉ I	Ph_2	30 min	3.7	$Ph_2P(s-C_4F_9)$, 5, 56%
$c-C_6F_{11}I$	Ph_2	30 min	-3.4	$Ph_2P(c-C_6F_{11}), 6, 48\%$
$t-C_4F_9I$	Ph_2	30 min	15.2	$Ph_2P(t-C_4F_9), 7, 30\%$
CF ₂ =CFI	Ph_2	_	_	
C ₆ F ₅ I	Ph_2	_	_	_
C ₂ F ₅ I	$i - Pr_2$	2 h	24.5	$i-\Pr_2 P(C_2F_5), 8, 52\%$
i-C ₃ F ₇ I	PhMe	30 min	-12	PhMeP $(i-C_3F_7)$, 9, 65%
^a At room tem	perature. ^b Typical NMR	t yields based on integration against an integration	ernal standard.	

before—PPh₂(C₂F₅),⁵ PPh(C₂F₃)₂,¹⁹ PPh₂(C₆F₅)²⁰ and P(C₆F₅)₃.²¹ The P–C distances observed for **4** are similar to those found in the related fluoroalkyl phosphane PPh₂(C₂F₅) [d(P–CF) = 1.891(3) and d(P–C)av. = 1.834(3) Å]. Significantly, although not surprisingly when compared with structures of metal-bound *n*-fluoroalkyl and *i*-C₃F₇-containing complexes,²² the sum of the angles around the phosphorus centre is larger in **4**, which contains a bulky perfluoroisopropyl group, (309.6°), than is observed in PPh₂(C₂F₅) (306.6°) and similar to that of P(C₆F₅)₃ (309.9°).

We have investigated a number of modifications to our procedure; including the addition of fluoride catalysts, using perfluoroalkyl bromides or chlorides, instead of iodides, and replacement of Ph_2PSiMe_3 with Ph_2PH . None of these were found to be as successful. We have also investigated the reaction between $PhP(SiMe_3)_2$ and $P(SiMe_3)_3$ with R_fI , but they were rapid and exothermic, resulting in a mixture of products.

The observation of much faster reactions between R_fI and Ph_2PSiMe_3 for tertiary and secondary perfluoroalkyliodides compared with primary analogues lead us to initially consider a radical mechanism. However, the addition of radical traps and radical initiators does not appear to significantly effect the outcome, or rate, of these transformations; we were also



Fig. 1 An ORTEP representation of the molecular structure of $Ph_2P(i-C_3F_7)$, 4, thermal ellipsoids are shown at 30% probability level. Selected distances: P1–C1, 1.899(5); P1–C4, 1.828(5); P1–C10, 1.831(5); C1–F1, 1.400(5); C1–C2, 1.539(6), C1–C3, 1.531(7) Å. Selected angles: C1–P1–C4, 102.9(2)°; C1–P1–C10, 103.6(2)°; C4–P1–C10, 103.1(2)°.

unable to observe any signals from in situ EPR studies which, taken together, suggests that the rate determining step is not radical-based. Whilst nucleophilic substitution would explain the observed products, and the enhanced rate of reaction of C₂F₅I with *i*-Pr₂PSiMe₃ compared with that of Ph₂PSiMe₃, multinuclear (³¹P, ¹⁹F, ²⁹Si and ¹H) NMR studies, carried out on a variety of reaction stoichiometries, suggest that the mechanism is more complicated. In the slower reactions-those of the straight chain perfluoroalkyl iodides-in situ monitoring via NMR spectroscopy shows a significant peak due to Ph₂PPPh₂ in the ³¹P{¹H} NMR spectra ($\delta_P = -15$ ppm). Interestingly, in related work, such as the reactions of Ph₂PSiMe₃ with CBr₄¹⁴ (Ph₂P)₂PSiMe₃ with BrCF₂CF₂Br²³ and Ph₂PH with CCl₄²⁴ Ph₂PPPh₂ was also identified as a significant product or key intermediate. We therefore propose that a similar process is occurring here; initially R₂PSiMe₃ is converted to R₂PPR₂ which then reacts with $R_f I$ to produce $R_2 P R_f$ and $R_2 P I$. The R₂PI so formed can react with R₂PSiMe₃ to generate further R₂PPR₂ and Me₃SiI. Some support for the latter sequence of reactions comes from the separate reaction of Ph₂PPPh₂ with R_fI, which produces both Ph₂PR_f and Ph₂PI. Furthermore, Ph₂PI ($\delta_{\rm P} = 38 \text{ ppm}^{25}$) and R_iSiMe₃ ($\delta_{\rm Si} = 4.2 \text{ ppm}, {}^{2}J({\rm SiF}) =$ 38 Hz, $R_f = CF_3$; 11.6 ppm, ²J(SiF) = 21.5 Hz, $R_f = i-C_3F_7$) are also identified as intermediates in these reactions by NMR spectroscopy. We are continuing to investigate the mechanism of this reaction as well as its scope.

In conclusion, we have demonstrated that the reaction of trimethylsilyl-substituted phosphanes with perfluoroalkyliodides results in the facile generation of perfluoroalkyl-containing phosphanes. The reaction is rapid for phosphanes containing a secondary, tertiary or cycloperfluoroalkyl group, however, for n-fluoroalkyl systems the reaction is slower. This method provides, for the first time, a method by which a number of new, sterically demanding, electron-poor fluorinated P(III) ligands may be accessed from readily-available starting materials.

Notes and references

[‡] NMR scale experiments were carried out on a 0.4 mmol scale by dissolving the appropriate trimethylsilylphosphane in 0.75 cm³ of CDCl₃, and then adding a slight excess of R_I under anaerobic conditions. Spectra were recorded [Bruker DPX 200 (¹H, ¹⁹F and ³¹P at 200.131, 188.310 and 81.014 MHz) or Bruker AVANCE III 400 (¹H, ¹⁹F and ³¹P at 400.131, 376.498 and 161.976 MHz) spectrometers and referenced to external TMS, CFCl₃ and 85% H₃PO₄, respectively] immediately and then periodically until no further sign of reaction occurred.

*Ph*₂*PCF*₃ (1). ³¹P NMR δ = 2.5 [q, ²*J*(PF) = 73.8 Hz], ¹⁹F NMR δ = -55.1 [d, ²*J*(PF) = 73.8 Hz]. ¹H NMR δ = 7.7–7.4 (m), literature (CDCl₃), δ _P 2.8 [²*J*(PF) = 73.5 Hz], δ _F -55.0 [*J* = 73 Hz]. ¹¹

(CDCl₃), $\delta_{\rm p} 2.8 \left[{}^2J(\rm PF) = 73.5 \, \rm Hz \right]$, $\delta_{\rm F} -55.0 \, [J = 73 \, \rm Hz]$.¹¹ $Ph_2PCF_3CF_3(2)$, ${}^{31}{\rm P} \, \rm NMR \, \delta = -1.9 \, [tq, {}^2J(\rm PF) = 56.8, {}^3J(\rm PF) = 16.7 \, \rm Hz]$, ${}^{15}{\rm F} \, \rm NMR \, \delta = -81.0 \, [3F, \, dt, {}^3J(\rm PF) = 16.7, {}^3J(\rm FF) = 3.0 \, \rm Hz$, $\rm CF_3$], $-113.0 \, [2F, \, dq, {}^2J(\rm PF) = 56.8, {}^3J(\rm FF) \, 3.0, \, \rm CF_2$], ${}^{1}{\rm H} \, \rm NMR \, \delta = 7.7-7.4 \, (m)$, literature (C₆D₆), $\delta_{\rm P} -1.4 \, [J = 58, \, 17]$, $\delta_{\rm F} -80.7 \, [J = 16.5, \, 3.1], -112.6 \, [J = 57.0, \, 3.1 \, \rm Hz]$.^{5a}

 $Ph_2PC_8F_{17}$ (3). $\delta_{\rm P}$ 1.1 [m, ${}^2J({\rm PF})$ = 56.0 Hz], $\delta_{\rm F}$ -81.7 [t, $J({\rm FF})$ = 7.8 Hz, 35, CF₃], -109.4 [dt, ${}^2J({\rm PF})$ = 56.0, $J({\rm FF})$ = 13.3, 2F, PCF₂], -122.1 [m, 2F], -122.6 [m, 6F], -123.5 [m, 2F], -127.0 [m, 2F]. $\delta_{\rm H}$ 7.7-7.4 (m).

 $\begin{array}{l} \delta_{\rm Fd} - 114.5 \ {\rm ppm} \ (1{\rm F}, \ {\rm dddqq}, \ {}^1J({\rm F_dF_c}) = \ 295.6 \ {\rm Hz}, \ {}^3J({\rm F_dP}) = \ 44.6 \ {\rm Hz}, \\ {}^3J({\rm F_dF_b}) = \ 11.9 \ {\rm Hz}, \ {}^4J({\rm F_dF_a}) = \ 5.5 \ {\rm Hz}, \ {}^3J({\rm F_dF_c}) = \ 0.6 \ {\rm Hz}, \\ {\rm PCF}({\rm C}F_3)({\rm CFFCF_3})), \ \delta_{\rm Fb} - 183.4 \ {\rm ppm} \ (1{\rm F}, \ {\rm dqdq}, \ {}^2J({\rm F_bP}) = \ 78.0 \ {\rm Hz}, \\ {}^3J({\rm F_bF_a}) = \ 12.1 \ {\rm Hz}, \ {}^3J({\rm F_bF_c}) = \ 12.0 \ {\rm Hz}, \ {}^4J({\rm F_bF_c}) = \ 12.0, \\ {}^3J({\rm F_bF_d}) = \ 11.9 \ {\rm Hz}, \ {\rm PCF}({\rm CF_3})({\rm CF_2{\rm CF_3}})). \ \delta_{\rm H} \ 7.7-7.4 \ ({\rm m}). \end{array}$

 $\begin{array}{l} J(\mathrm{Fb}\mathrm{Fa}) &= 12.1 \ \mathrm{Hz}, \ J(\mathrm{Fb}\mathrm{Fc}) &= 12.0 \ \mathrm{Hz}, \ J(\mathrm{Fb}\mathrm{Fc}) &= 12.0, \\ {}^{3}J(\mathrm{Fb}\mathrm{Fd}) &= 11.9 \ \mathrm{Hz}, \ \mathrm{PCF}(\mathrm{CF}_3)(\mathrm{CF}_2\mathrm{CF}_3)). \ \delta_\mathrm{H} \ 7.7-7.4 \ \mathrm{(m)}. \\ Ph_2P(c^-C_6F_{11}) \ (\mathbf{6}) \ \delta_\mathrm{P} &= -3.4 \ \mathrm{ppm} \ (\mathrm{td}, \ {}^{3}J(\mathrm{PF}_{2ax}) &= 84.0 \ \mathrm{Hz}, \\ {}^{2}J(\mathrm{PF}_1) &= 68.0 \ \mathrm{Hz}). \ \delta_\mathrm{F} \ -110.5 \ (\mathrm{2F}, \ {}^{3}J(\mathrm{PF}) &= 84.0 \ \mathrm{Hz}, \ {}^{2}J(\mathrm{FF}) &= \\ 298.3 \ \mathrm{Hz}, \ \mathrm{F}_{2a,6a}), \ -122.6 \ (\mathrm{2F}, \ \mathrm{d}, \ {}^{2}J(\mathrm{FF}) &= 280.0 \ \mathrm{Hz}, \ \mathrm{F}_{3a,5a}), \ -124.4 \\ \mathrm{ppm} \ (\mathrm{IF}, \ \mathrm{d}, \ {}^{2}J(\mathrm{FF}) &= 288.8 \ \mathrm{Hz}, \ \mathrm{F}_{4a}) \ -124.5 \ (\mathrm{2F}, \ \mathrm{d}, \ {}^{2}J(\mathrm{FF}) &= 298.3 \\ \mathrm{Hz}, \ \mathrm{F}_{2e,6e}), \ -138.2 \ (\mathrm{2F}, \ \mathrm{d}, \ {}^{2}J(\mathrm{FF}) &= 280.0 \ \mathrm{Hz}, \ \mathrm{F}_{3e,5e}), \ -142.0 \ (\mathrm{IF}, \ \mathrm{d}, \ {}^{2}J(\mathrm{FF}) &= 285.5 \ \mathrm{Hz}, \ \mathrm{F}_{4e}), \ \mathrm{and} \ -185.8 \ (\mathrm{IF}, \ \mathrm{m}, \ {}^{2}J(\mathrm{PF}) &= 68.0 \ \mathrm{Hz}, \ \mathrm{F1a}). \\ \delta_\mathrm{H} \ 7.7-7.4 \ (\mathrm{m}). \end{array}$

 $Ph_2PC(CF_3)_3$ (7). δ_P 15.2 (dectet, ${}^3J(PF) = 12.3$ Hz), δ_F -60.0 (d, ${}^3J(PF) = 12.2$ Hz). δ_H 7.7-7.4 (m).

 $i \cdot Pr_2 P C_2 F_5$ (8). δ_P 24.5 (tq, ${}^2J(PF) = 41.7$, ${}^3J(PF) = 14.8$ Hz), $\delta_F - 82.4$ (dt, ${}^3J(PF) = 14.8$, ${}^3J(PF) = 2.9$ Hz), -111.7 (dq, ${}^2J(PF) = 41.7$, ${}^3J(PF) = 2.9$ Hz). δ_H 1.16 (6H, m, CH₃), 2.2 (1H, dsept, ${}^2J(PH) = 2.4$, ${}^3J(HH) = 7.1$ Hz, CH).

 $\begin{array}{l} PhMePCF(CF_3)_2 \ (9). \ \delta_{\rm P} - 12.0 \ (dsept, \ ^2J({\rm PF}) \ = \ 61.1, \ ^3J({\rm PF}) \ = \ 16.4 \ {\rm Hz}) \ \delta_{\rm F} - 70.2 \ [ddq, \ ^2J({\rm PF}) \ = \ 16.4, \ ^3J({\rm FF}) \ = \ 11.2, \ ^4J({\rm FF}) \ = \ 9.3 \ {\rm Hz}, \\ {\rm CF_3]}, \ -71.2 \ [ddqq, \ ^2J({\rm PF}) \ = \ 16.4, \ ^3J({\rm FF}) \ = \ 11.2, \ ^4J({\rm FF}) \ = \ 9.3, \\ {}^5J({\rm FH}) \ = \ 1.5 \ {\rm Hz}, \ {\rm CF_3]}, \ -190.3 \ [dsept, \ ^2J({\rm PF}) \ = \ 61.1, \ ^3J({\rm FF}) \ = \ 11.0, \\ {\rm CF} \ \delta_{\rm H} \ 7.28 - 7.40 \ (6{\rm H, m}), \ 1.63 \ (3{\rm H, d}, \ ^2J({\rm PH}) \ = \ 6.0 \ {\rm Hz}, \ {\rm CH_3}). \end{array}$

Synthesis of $Ph_2P(i-C_3F_7)$ (4): A dried Schlenk vessel was charged with $Ph_2P(SiMe_3)$ (2.2 cm³, 8.5 mmol) and dry hexane (20 cm³). The solution was cooled to -30 °C and $i-C_3F_7I$ (1.2 cm³, 8.5 mmol) was added slowly over *ca*. 30 minutes. The solution was warmed to room temperature overnight. MeLi (1.6 M in Et₂O, 5.4 cm³, 8.6 mmol) was added to the yellow solution and stirred for 30 minutes. The resulting white precipitate was filtered off under an inert atmosphere (N₂) and the volatiles removed under vacuum to yield **4** as a white solid (2.26 g, 75%). Elemental analysis C: 50.88, H: 2.71, P: 8.04%, C₁₃H₁₀F₇P requires: C: 50.84, H: 2.85, P: 8.75%. δ_P –0.8 [dsept, ²/(PF) = 74.0, ³/(PF) = 18.0 Hz] δ_F –69.6 [dd, ³/(PF) = 18.0, ³/(FF) = 11.9 Hz, CF₃], –184.9 [dsept, ²/(PF) = 74.0, ³/(PF) = 11.9, CF] δ_H 7.24–7.45 (6H, m), 7.69–7.82 (4H, m)].

§ Crystal data for 4: (C₁₅H₁₀F₇P): $M_r = 354.12$; crystal size = 0.15 × 0.15 × 0.15 mm³; monoclinic, space group $P2_1/c$, a = 8.9091(2), b = 26.2430(6), c = 6.3928(1) Å, $\beta = 99.406(1)^\circ$, V = 1474.55(5) Å, Z = 4, $\rho_{calcd} = 1.595$ g cm⁻³, $\mu = 0.257$ mm, $\lambda = 0.71073$ Å, 150(2) K, $2\theta_{max} = 51^\circ$, 2736 reflections collected, 208 parameters and 0 restraints, GOF on $F^2 = 1.082$, final *R* indices for $I > 2\sigma(I)$, w $R_2 = 0.2181 R_1 = 0.0796$. Data were collected on a Nonius κ -CCD 4-circle diffractometer, and were corrected for Lorentz, polarisation and absorption using the multi-scan method. The X-ray structural data

were solved by direct methods, with full-matrix least-squares refinement on F^2 using the SHELXL program.²⁶ Non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were placed in idealised locations.

- 1 See for example: D. W. Allen, Organophosphorus Chem., 2006, 35, 1.
- 2 See for example: K. D. Cooney, T. R. Cundari, N. W. Hoffman, K. A. Pittard, M. D. Temple and Y. Zhao, J. Am. Chem. Soc., 2003, **125**, 4318.
- 3 C. L. Pollock, G. C. Saunders, E. Smyth and V. I. Sorokin, *J. Fluorine Chem.*, 2008, **129**, 142.
- 4 H. J. Emeleus and J. D. Smith, *J. Chem. Soc.*, 1958, 527; A. B. Burg and W. Mahler, *J. Am. Chem. Soc.*, 1958, **80**, 2334.
- 5 (a) R. G. Peters, B. L. Bennett, R. C. Schnabel and D. M. Roddick, *Inorg. Chem.*, 1997, **36**, 5962; (b) J. D. Palcic, P. N. Kapoor, D. M. Roddick and R. G. Peters, *Dalton Trans.*, 2004, 1644.
- 6 J. J. Kampa, J. W. Nail and R. J. Lagow, Angew. Chem., Int. Ed. Engl., 1995, 34, 1241.
- 7 V. Y. Semenii, V. A. Stepanov, N. V. Ignat'ev, G. G. Furin and L. M. Yagupolskii, *Zh. Obshch. Khim.*, 1985, 55, 2716; N. Ignat'ev and P. Sartori, *J. Fluorine Chem.*, 2000, 103, 57.
- 8 E. A. Ganja, C. D. Ontiveros and J. A. Morrison, *Inorg. Chem.*, 1988, 27, 4535.
- 9 F. W. Bennett, G. R. A. Brandt, H. J. Emeleus and R. N. Haszeldine, *Nature*, 1950, **166**, 225; F. W. Bennett, H. J. Emeleus and R. N. Haszeldine, *J. Chem. Soc.*, 1953, 1565.
- 10 M. B. Murphy-Jolly, L. C. Lewis and A. J. M. Caffyn, Chem. Commun., 2005, 4479.
- 11 P. Eisenberger, I. Kieltsch, N. Armanino and A. Togni, *Chem. Commun.*, 2008, 1575.
- 12 J. K. Stille, J. Org. Chem., 1987, 52, 748; V. S. Chan, R. G. Bergman and F. D. Troste, J. Am. Chem. Soc., 2007, 129, 15122; S. E. Vaillard, C. Muck-Lichtenfeld, S. Grimme and A. Studer, Angew. Chem., Int. Ed., 2007, 46, 6533.
- 13 M. Fild, P. G. Jones and K. Ruhnau, J. Fluorine Chem., 1991, 54, 387; M. L. Clarke, A. G. Orpen, P. G. Pringle and E. Turley, *Dalton Trans.*, 2003, 4393.
- 14 H.-G. Horn and H. J. Lindner, Chem.-Ztg., 1988, 112, 195.
- 15 L. I. Goryunov, J. Grobe, V. D. Shteingarts, B. Krebs, A. Lindemann, E.-U. Wrthwein and C. Mck-Lichtenfeld, *Chem.-Eur. J.*, 2000, 6, 4612; L. I. Goryunov, V. D. Shteingarts, J. Grobe, B. Krebbs and M. U. Triller, *Z. Anorg. Allg. Chem.*, 2002, 628, 1770.
- 16 D. Naumann and J. Kischkewitz, J. Fluorine Chem., 1990, 47, 283.
- 17 M. Sako, T. Kihara, K. Okada, Y. Ohtani and H. Kawamoto, J. Org. Chem., 2001, 66, 3610.
- 18 A. Probst, K. Raab, K. Ulm and K. von Werner, J. Fluorine Chem., 1987, 37, 223.
- 19 K. K. Banger, R. P. Banham, A. K. Brisdon, W. I. Cross, G. Damant, S. Parsons, R. G. Pritchard and A. Sousa-Pedrares, *J. Chem. Soc., Dalton Trans.*, 1999, 427.
- 20 O. B. Shawkataly, M.-L. Chong, H.-K. Fun and K. Sivakumar, Acta Crystallogr., Sect. C, 1996, 52, 1725.
- 21 A. Karipides and C. M. Cosio, *Acta Crystallogr., Sect. C*, 1989, 45, 1743.
- 22 R. P. Hughes, J. S. Overby, A. Williamson, K.-C. Lam, T. E. Concolino and A. L. Rheingold, *Organometallics*, 2000, 19, 5190.
- 23 I. Kovacs, E. Matern and G. Fritz, Z. Anorg. Allg. Chem., 1996, 622, 935.
- 24 P. Majewski, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1998, **134**, 399.
- 25 E. Vincent, L. Verdonck and G. P. Van der Kelen, J. Mol. Struct., 1980, 65, 239.
- 26 G. M. Sheldrick, SHELXS97, University of Göttingen, Germany.