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The Preparation, Properties and Gas-Phase Molecular Structure of Difluoro(germylthio)phosphine

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Difluoro(germylthio)phosphine, $PF_2(SGeH_3)$, has been prepared by the reaction of $S(PF_2)_2$ with GeH_3Cl, and has been characterised by i.r., *Raman*, n.m.r. and mass spectroscopy. Cleavage reactions with Cl_2 and HBr, donor reactions of the phosphorus atom and exchange reactions with platinum complexes have been studied. The molecular structure of $PF_2(SGeH_3)$ in the gas phase has been determined by electron diffraction. Principal parameters (r_a) are: r(Ge—S) 225.6(4) pm; r(P—S) 211.5(8) pm; r(P—F) 159.0(9) pm; $<$(GeSP) 99.0(6)°; $<$(SPF) 99.9(4)°; $<$(FPF) 97.0(10)°. The conformation adopted is such that there are short non-bonded F···H contacts, with the PF_2 group twisted 18° from the position in which the FPF angle bisector eclipses the Ge—S bond.

[Keywords: B-*11 NMR; Difluoro(germylthio)phosphine; Electron diffraction,* $PF_2(SGeH_3)$; F-*19 NMR; Germylthiophosphine, difluoro-; Molecular structure,* $PF_2(SGeH_3)$; *Phosphine, difluoro(germylthio)-;* P-*31 NMR]*

Difluor(germylthio)phosphin. Darstellung, Eigenschaften und Molekülstruktur in der Gasphase

$PF_2(SGeH_3)$ wurde über die Reaktion von $S(PF_2)_2$ mit GeH_3Cl dargestellt und mittels IR, *Raman*, NMR and MS charakterisiert. Es wurden Spaltungsreaktionen mit Cl_2 und HBr, Donor-Reaktionen des Phosphor und Austauschreaktionen mit Platinkomplexen untersucht. Die Molekülstruktur von $PF_2(SGeH_3)$ in der Gasphase wurde mittels Elektronendiffraktion bestimmt. Die Hauptparameter (r_a) sind: r(Ge—S) 225,6(4) pm; r(P—S) 211,5(8) pm; r(P—F) 159,0(9) pm; $<$(GeSP) 99,0(6)°; $<$(SPF) 99,9(4)°; $<$(FPF) 97,0(10)°.

Introduction

Although compounds with two or more silyl[1], germyl[2] or difluorophosphino[3] groups bound to a single atom have been known for many years, it is only relatively recently that the first compounds containing

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a difluorophosphino group and a silyl or germyl group bound to a common atom have been reported[4]. Such species are of particular interest for three reasons. In the first place, if delocalisation of lone pairs of electrons on the central atom into vacant d orbitals on neighbouring atoms takes place, there may be expected to be competition between phosphorus and the group IV atoms for the available electrons, which will be reflected in the spectroscopic and structural properties of the compounds. Secondly, the conformations adopted by the molecules are important, and it seems that the most favourable arrangements are stabilised by weak $H \cdots F$ contacts[4]. Finally, they have potential as reagents for bridging between metal atoms in complexes, as substituted fluorophosphines are well known as electron pair donors[5], behaving generally in a similar way to carbon monoxide, whereas silyl and germyl compounds readily undergo oxidative addition reactions to coordinatively unsaturated systems such as square-planar four-coordinate platinum(II)[6] or iridium(I)[7].

So far, the only reports of mixed difluorophosphino—silyl or germyl compounds being isolated have concerned amines[4,8,9]. No similar mixed-substituent oxides have been reported, although the parent symmetrical oxides are well known[1–3]. The only stable mixed derivative of second row elements to have been isolated is 1,1-difluoro-2,2-digermyl-biphosphine[10]. A study of the exchange reactions of disilyl and digermyl derivatives of sulphur, selenium and tellurium with bromodifluorophosphine[11] showed that both silyl or germyl groups could be replaced.

$$Y(MH_3)_2 + PBrF_2 \rightarrow PF_2(YMH_3) + MBrH_3$$

$$PF_2(YMH_3) + PBrF_2 \rightarrow Y(PF_2)_2 + MBrH_3 \quad [M = \mathrm{Si, Ge};\ Y = \mathrm{S, Se, Te}]$$

The two substitutions took place simultaneously, and it seemed that it would be impossible to obtain the mixed intermediates without disproportionation occurring. However, we have now studied the reverse exchanges, using $Y(PF_2)_2$ and MH_3Cl, and find that in one case it is possible to obtain the intermediate, free from either of the symmetrical species, and that disproportionation is very slow. We report here the results of our studies of $PF_2(SGeH_3)$.

Results and Discussion

Preparation of $PF_2(SGeH_3)$

When equimolar amounts of $S(PF_2)_2$ and GeH_3Cl were allowed to react together in the liquid phase at room temperature, an exchange reaction took place, yielding $PF_2(SGeH_3)$. Great care was needed to ensure that the relative quantities of reagents were correct, as the product could not be separated from either $S(PF_2)_2$ or $S(GeH_3)_2$ by trap-to-trap distillation. Similarly, traces of moisture in the vacuum system or of HCl in the GeH_3Cl gave rise to $PF_2H(S)$, which also was inseparable from the desired product.

The observation that the first exchange of GeH_3 for PF_2 went to completion before the second one started was unexpected in view of the results for the reverse process reported earlier[11]. It would appear that $PF_2(SGeH_3)$ is stable with respect to disproportionation, at least for short periods, but that the two stages of the exchange reaction of $S(GeH_3)_2$ with $PBrF_2$ take place at comparable rates.

Vibrational Spectra

Details of the gas-phase i.r. and liquid-phase *Raman* spectra are given in Table 1. These spectra provide strong evidence for the identity of the compound as there are peaks which may be assigned to stretching, deformation and rocking modes of the GeH_3 group, and others in the regions associated with vibrations of the PF_2 group. In addition there are three strong, polarised bands in the *Raman* spectrum, which we assign to the vibrations of the PSGe skeleton. The highest frequency band of this group is at 508 cm^{-1}, compared with 580 and 444 cm^{-1} for the skeletal stretches of $S(PF_2)_2$[12], and 512 cm^{-1} for the P—S stretch in $PF_2(SCH_3)$[13], and so is assigned as the P—S stretch in this case also. The second band, at 425 cm^{-1}, is assigned to be the

Table 1. *Vibrational spectra of* $PF_2(SGeH_3)$

I.r (gas)	*Raman* (liquid)	Assignment
2114 s	2110 s, p	$\nu(GeH_3)$
830 810 s, br	868 m, dp 830 m, dp	$\nu(PF_2)$, $\delta(GeH_3)$
590 m	600 m, dp	$\rho(GeH_3)$
514 s	508 s, p	ν(P—S)
425 s	422 s, p	ν(Ge—S)
	380 s, p	δ, $\omega(PF_2)$
	305 w, dp	$\rho(PF_2)$
	116 s, p	δ(GeSP)

s = strong, m = medium, w = weak, br = broad, p = polarised, dp = depolarised.

Ge—S stretch; equivalent stretches in $S(GeH_3)_2$ are at 408 and 370 cm^{-1} [2]. The third band, at 116 cm^{-1}, must be the skeletal deformation, which comes at 110 cm^{-1} in $S(GeH_3)_2$, but the analogous mode in $S(PF_2)_2$ is at 237 cm^{-1}. There is a band at 125 cm^{-1} in the *Raman* spectrum of the latter compound but it is not polarised, and has been assigned as a torsion of the PF_2 groups.

Table 2. *N.m.r. parameters of* $PF_2(SGeH_3)$ *and some derivatives*

Compound	$PF_2(SGeH_3)$	$L \cdot BH_3'$	$Mo(CO)_4L_2$
$\delta(^1H)$/ppm	4.8	5.8	4.9
$\delta(^1H')$/ppm		1.0	
$\delta(^{11}B)$/ppm^a		-60.6	
$\delta(^{19}F)$/ppm^b	-56.5	-54.1	-15.7
$\delta(^{31}P)$/ppm^c	233.7	193.9	226.6
$^1J(^{31}P\,^{19}F)$/Hz	1280	1255	1201
$^1J(^{11}B\,^1H')$/Hz		102.8	
$^1J(^{31}P\,^{11}B)$/Hz		47	
$^2J(^{31}P\,^1H')$/Hz		16	
$^2J(^{31}P\,^{31}P)$/Hz			45
$^3J(^{31}P\,^1H)$/Hz	12.6	8.7	2.5
$^3J(^{19}F\,^1H')$/Hz		18.2	
$^3J(^{31}P\,^{19}F)$/Hz			3
$^4J(^{19}F\,^1H)$/Hz	3.4	2.0	<2

^{a} Relative to $B(OMe)_3$; ^{b} relative to CCl_3F; ^{c} relative to 85% H_3PO_4.

N.m.r Spectra

The ^1H, ^{19}F and ^{31}P spectra of $PF_2(SGeH_3)$ provide unequivocal evidence of its identity and purity. In particular, the high ^{31}P chemical shift confirms that it is a phosphorus(III) species and not a phosphorus(V) derivative, $S{=}PF_2(GeH_3)$. The n.m.r. parameters are listed in Table 2.

Mass Spectrum

Details of the mass spectrum of $PF_2(SGeH_3)$ are given in Table 3. The multiplicity of germanium isotopes can make analysis of the spectra of GeH_3 derivatives difficult, but in the present case it appears that the groups of peaks centred at 178 and 109 mass units arose predominantly from ions with three hydrogen atoms, while the group at 158 mass units arose from ions with two hydrogens. Thus sequential loss of hydrogen atoms does not occur to any great extent. Breakdown of the parent ion can take place by three distinct routes, involving as the initial step elimination of HF, or cleavage of either P—S of Ge—S bonds. The strength of the peak due to PF_2HS^+ suggests that elimination of GeH_2 is also an important process.

Table 3. *Mass spectrum of* $PF_2(SGeH_3)$

m/e	Relative Abundance	Assignment
178[a]	20	$[PF_2(SGeH_3)]^+$
158[a]	20	$[PF(SGeH_2)]^+$
109[a]	20	$[GeH_3S]^+$
102	100	$[PF_2HS]^+$
101	12	$[PF_2S]^+$
88	5	$[PF_3]^+$
82	25	$[PFS]^+$
69	50	$[PF_2]^+$
63	25	$[PS]^+$
50	5	$[PF]^+$
34	3	$[SH_2]^+$
32	2	$[S]^+$
31	2	$[P]^+$
20	1	$[FH]^+$
metastable		
39.5	weak	$[PF_2S]^+ \rightarrow F_2 + [PS]^+$

Cleavage Reactions of the Ge—S *Bond*

When HCl, HBr and Cl_2 were allowed to react with $PF_2(SGeH_3)$, in each case cleavage of the Ge—S, rather than the P—S, bond took place, with a germanium—halogen bond being formed.

$$PF_2(SGeH_3) + HX \rightarrow GeH_3X + PF_2H(S) \quad [X = Cl, Br]$$

$$PF_2(SGeH_3) + Cl_2 \rightarrow GeH_3Cl + PClF_2(S)$$

It seemed probable that similar reactions could be used to synthesize compounds containing SPF_2 groups and one such reaction was studied. At room temperature chlorodiphenylphosphine gave $S{=}PF_2PPh_2$ as the major product, identified by its n.m.r. parameters [δP 114.0, —1.9 ppm, $^1J_{PF}$ 1,274 Hz, $^2J_{PF}$ 18.3 Hz, $^1J_{PP}$ 366 Hz]. A small amount of $S{=}PPh_2PPh_2$, was also formed [δP 45.1, —13.3 ppm, $^1J_{PP}$ 254 Hz]: this would seem to indicate that some cleavage of the P—S bond also occurs, giving $PPh_2(SGeH_3)$ as an intermediate.

Donor Reactions of $PF_2(SGeH_3)$

On reaction with diborane, $PF_2(SGeH_3)$ behaved as other fluorophosphines, giving a complex in which the phosphorus atom was the donor. There have been several attempts to relate n.m.r. parameters of borane-phosphine complexes to the base strengths of the phosphines[13–15], but the empirical relationships between ^1J ($^{31}P\,^{11}B$) and dative bond strength are useful only for restricted ranges of similar phosphines[14]. The n.m.r. parameters for $GeH_3SPF_2 \cdot BH_3$ (Table 2) show the usual coordination shifts and coupling constants similar to those in related molecules. The $^{31}P\,^{11}B$ coupling is clearly resolved, although it is unresolved in $F_2PSPF_2 \cdot BH_3$, with a coupling constant of 47 Hz, compared with 41 Hz in $PF_2(SCH_3)$[14]. This is consistent with the suggestion[13] that base strength is increased by π-bonding, which is extended in the present case through sulphur to germanium.

A displacement reaction occurred with tetracarbonyl(norbornadiene)molybdenum to form $Mo(CO)_4(PF_2SGeH_3)_2$, identified by its n.m.r. spectra. These were second order, and proton-decoupled spectra were analysed as arising from an $[AX_2]_2$ spin system, with very small long-range XX couplings: the n.m.r. parameters are listed in Table 2. The most noticeable feature is the small ^{31}P coordination shift (7 ppm) compared with that found for $Mo(CO)_4[S(PF_2)_2]$ (78 ppm)[12].

Reactions with Platinum Complexes

In reactions of $PF_2(SGeH_3)$ with four-coordinate Pt(II) complexes, there are three possibilities. The fluorophosphine may displace another ligand: there may be oxidative addition, with a P—S, a Ge—S, or most likely a Ge—H bond adding across the platinum, perhaps followed by elimination: or there may be an exchange reaction, with an SPF_2 or an $SGeH_3$ group displacing another ligand.

In the reaction with *trans*-$PtCl_2(PEt_3)_2$, exchange occurred, giving $GeClH_3$ and *trans*-$PtCl(PEt_3)_2(PF_2S)$, identified by its n.m.r. parameters[16], with small amounts of two other unidentified platinum complexes. Similarly, *trans*-$PtClH(PEt_3)_2$ gave $GeClH_3$ and *trans*-$PtH(PEt_3)_2(PF_2S)$[16], but on standing at room temperature the platinum product slowly gave $PtCl(PEt_3)_2(PF_2S)$. As GeH_4 was not formed at the same time, it would appear that the solvent, chloroform, must be involved in the reaction. A third PF_2S complex, *trans*-$PtI(PEt_3)_2(PF_2S)$, was also formed by an exchange reaction, with *trans*-$PtI_2(PEt_3)_2$. With $[PtH(PEt_3)_3][BPh_4]$, *trans*-$PtH(PEt_3)_2(PF_2S)$ was again formed, together with PEt_3 and $GeClH_3$. The last product is unexpected, and its formation must involve the solvent, dichloromethane. One possible mechanism would involve an unstable triethyl(germyl)phosphonium intermediate, which could react with dichloromethane to give chlorogermane.

Molecular Structure

In the refinements of the structure of $PF_2(SGeH_3)$ it was assumed that the $SGeH_3$ group had local C_3 symmetry, and that the SPF_2 group had local C_s symmetry. With these constraints the molecular geometry was defined by 10 parameters, chosen to be the P—F, P—S, Ge—S and Ge—H bond lengths, the P—S—Ge, S—Ge—H, F—P—F and F—P—S bond angles, and twist angles, which defined the conformation about the Ge—S and P—S bonds. The Ge—S twist angle was zero when one Ge—H bond was *trans* to the P—S bond, and the P—S twist angle was taken to be zero when the FPF bisector was *trans* to the Ge—S bond. Both twist angles were defined to be positive for a clockwise rotation of the GeH_3 or PF_2 group when viewed from Ge or P towards S.

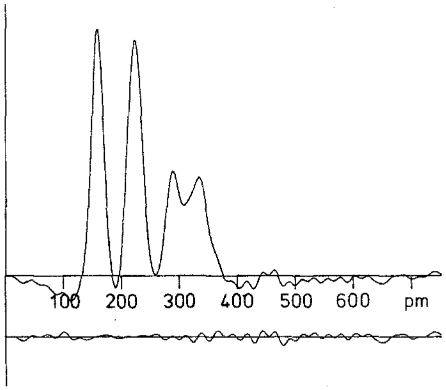

Fig. 1. Radial distribution curve, $P(r)/r$, for $PF_2(SGeH_3)$. Before *Fourier* inversion the data were multiplied by $s \cdot \exp[(-0.00002\, s^2)/(Z_P - f_P)(Z_{Ge} - f_{Ge})]$

The radial distribution curve (Fig. 1) shows four strong peaks. The first one includes contributions from two bonded distances, P—F and Ge—H, and although both distances could be refined, only one amplitude could be included. Similarly, the second peak had P—S, Ge—S and F···F components, and again the geometrical parameters dependent on these (the two bonded distances and the FPF angle) could be refined, but with only one amplitude of vibration. The third peak was attributed to just the S···F atom pairs, and the associated

Table 4. *Least squares correlation matrix multiplied by 100* (only elements greater than 50 are included)

*r*1	*r*2	*r*3	*r*4	<1	<2	<3	*u*1	*u*3	*u*6	*u*7	*k*1	*k*2	
100		54					61						*r*1
	100				51		—51						*r*2
		100		81	—79		61						*r*3
			100										*r*4
				100	—84		59						<1
					100		—63						<2
						100							<3
							100						*u*1
								100			58		*u*3
									100				*u*6
										100			*u*7
											100	63	*k*1
												100	*k*2

amplitude of vibration and the SPF angle both therefore refined easily. The final peak had a major contribution from the Ge···P distance, thus defining the GeSP angle, and substantial shoulders arising from the two Ge···F distances. The positions of these two determine the conformation of the PF_2 group, but it was found that there was considerable uncertainty about the amplitudes of vibration which would refine satisfactorily neither separately nor as a single parameter. The optimum values of both amplitudes of vibration and of the PF_2 twist angle were therefore found by comparing *R* factors with these parameters fixed at various values, and they were not subsequently refined.

The least squares correlation matrix (Table 4) shows several substantial correlations between parameters defining the heavy-atom skeleton, as would be expected, given the many overlapping peaks in the radial distribution curve. However, some of the parameters involving hydrogen did not appear to be strongly correlated with other parameters, but were not well determined. Studies of variations of *R* factors with values of some of these parameters showed that the SGeH angle was $110 \pm 3°$, and that the GeH_3 twist angle was $29 \pm 14°$.

The results of the final refinement, for which R_G was 0.08, are given in Table 5 and the intensity data and final difference curves are shown in Fig. 2. The bond lengths and angles of the PF_2S group are similar to the corresponding parameters for $S(PF_2)_2$[17] and $PF_2(SCH_3)$[18], but the Ge—S distance [225.6 (4) pm] is significantly longer than the equivalent distance in $S(GeH_3)_2$ [220.9 (4) pm][19]. As the expected Ge—S bond length, based on covalent radii derived from structures of ethane[20], dimethylsulphide[21] and methylgermane[22] is 221.3 pm, the present

Table 5. *Molecular parameters for* $PF_2(SGeH_3)$[a]

	Distance/pm	Amplitude/pm
Independent distances		
*r*1 P—S	211.5 (8)	5.6 (8)
*r*2 Ge—S	225.6 (4)	
*r*3 P—F	159.0 (9)	5.7 (5)
*r*4 Ge—H	153.8 (15)	7.1 (fixed)
Dependent distances		
*d*5 F···F	238.3 (14)	6.7 (fixed)
*d*6 S···F	285.7 (13)	8.5 (6)
*d*7 Ge···P	332.6 (17)	12.5 (9)
*d*8 Ge···F	299.5 (18)	22.3 (fixed)
*d*9 Ge···F	350.6 (16)	
Shortest F···H	271.3 (17)	
Independent angles/°		
<1 Ge—S—P	99.0 (6)	
<2 F—P—F	97.0 (10)	
<3 S—P—F	99.9 (4)	
<4 S—Ge—H	110 (3)[b]	
<5 PF_2 twist	161.8 (17)[b]	
<6 GeH_3 twist	29 (14)[b]	

[a] All distances are r_a. Quoted errors are estimated standard deviations obtained in the least squares analysis, increased to allow for systematic errors.

[b] See text.

distance must be regarded as being exceptionally long. As the other bond lengths are towards the high end of their normal ranges, the possibility of an overall scaling error must be considered. The calibration procedure used for wavelength determination involved recording of the diffraction patterns of benzene and of $PF_2(SGeH_3)$ in the same experiment, and analysing the benzene structure using the full procedure normally used for unknown structure determination. The wavelength was then adjusted to bring the C—C distance of benzene to 139.70 pm, thereby eliminating any possible systematic scale error.

The conformation adopted contrasts strikingly with those adopted by other PF_2SR compounds. In $S(PF_2)_2$ the overall symmetry is C_{2v}, with each phosphorus lone pair of electrons eclipsing the further S—P bond[17]. In $PF_2(SCH_3)$ the PF_2 group is twisted 110°, at which point the

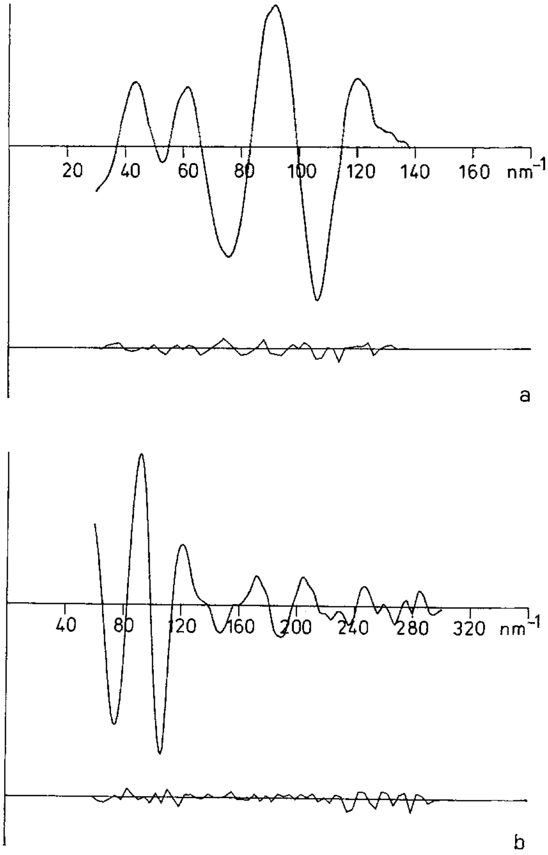

Fig. 2. Observed and final weighted difference molecular intensities for nozzle-to-plate distances of *a* 12.8 and *b* 286 nm

shortest H···F distance is ca. 265 pm[18], close to the sum of the *van der Waals'* radii of hydrogen and fluorine. In the present case the twist angle is 162° and it is possible that the average value is actually 180°, with the observed distortion being caused by a large amplitude torsional vibration. The shortest H···F distance is 271 pm, and thus it seems that in these compounds with no steric crowding, the preferred conformation is one in which a weak fluorine-hydrogen contact is possible. Although the presence of small amounts of a second conformer cannot be ruled out, there is no evidence either from our refinements or from an inspection of the radial distribution curve for the existence of a second form.

Experimental

All volatile compounds were handled on a glass vacuum line fitted with Sovirel greaseless taps. Bis(difluorophosphino)sulphide was prepared from bis(tributylstannyl)sulphide and bromodifluorophosphine[12], and chlorogermane from monogermane and stannic chloride[23]. Other reagents were prepared by published methods or obtained commercially.

Infra-red spectra were recorded in the range 4,000-200 cm^{-1} using a Perkin Elmer 557 spectrometer and *Raman* spectra were obtained using a Cary 83 spectrometer, with 488 nm argon-ion laser excitation. For mass spectra, an AEI MS902 spectrometer was used, and n.m.r. spectra were recorded on Varian XL100 (^{31}P, ^{19}F), HA100 (^{1}H), JEOL FX60 (^{31}P) and Bruker WH360 (^{11}B) spectrometers.

Electron diffraction intensities were recorded photographically on Kodak Electron Image plates using the Cornell/Edinburgh diffraction apparatus[24,25]. Sample and nozzle were maintained at room temperature (293 K) during experiments. Data were collected using two camera distances, 128 mm (3 plates) and 286 mm (3 plates), giving data over a range of 30-300 nm^{-1} in the scattering variable, s. Intensities were obtained in digital form using a Jarrell-Ash double-beam microphotometer[26] with spinning plates. The electron wavelength, 5.779 ± 0.003 pm, was determined from the diffraction pattern of gaseous benzene.

Calculations were performed on an ICL 2970 computer using established data reduction[25] and least-squares refinement[27] programmes. Weighting points used in setting up the off-diagonal weight matrix are given in Table 6, together with scale factors and correlation parameters. In all calculations the complex scattering factors of *Schäfer*, *Yates* and *Bonham*[28] were used.

Table 6. *Weighting functions, correlation parameters and scale factors*

Camera height mm	Δs nm^{-1}	s_{min} nm^{-1}	$sw1$ nm^{-1}	$sw2$ nm^{-1}	s_{max} nm^{-1}	p/h	Scale factor
128.35	4	60	80	280	300	0.20	0.866 (19)
285.56	2	30	38	120	138	0.25	0.854 (17)

Preparation of $PF_2(SGeH_3)$

Chlorogermane (5.0 mmol) was condensed with $S(PF_2)_2$ (5.5 mmol) in a dry glass bulb (ca. 250 ml), and the reagents were then warmed to 209 K for 2 hours. The volatile products were examined by n.m.r. spectroscopy to ascertain the extent of reaction and the exact amount of $GeClH_3$ required to convert the remaining $S(PF_2)_2$ was added. In this way allowance could be made for imbalance of quantities of the reagents, caused by slight impurities, reaction with surface moisture etc. Products were separated by fractional condensation, a *difluoro(germylthio)phosphine* (4.8 mmol, 87% yield) was collected at 209 K. [M.wt. 180.6 (Calc. 178.7); v.p. (273 K) 31.5 mm; m.pt. 199 K]. The other major product was $PClF_2$ (5.0 mmol), with traces of $PF_2H(S)$, GeH_4 and $GeClH_3$.

Reaction with HCl

$PF_2(SGeH_3)$ (2.5 mmol) and HCl (2.5 mmol) were condensed into a glass bulb (250 ml) and warmed to room temperature for 5 min. The products were separated by fractional condensation yielding $GeClH_3$ (2.5 mmol) and $PF_2H(S)$ (2.5 mmol), identified by i.r. and n.m.r. spectroscopy.

Reactions with HBr, Cl_2 *and* $PClPh_2$

In each case 0.2 mmol of each reagent was taken and they were allowed to mix in CCl_3D (0.5 ml) at room temperature. The reactions were monitored by ^1H, ^{19}F and ^{31}P n.m.r. spectroscopy.

Reactions with B_2H_6

$PF_2(SGeH_3)$ (0.4 mmol) and B_2H_6 (0.2 mmol) were condensed in an n.m.r. tube with CCl_3D (0.5 ml) as solvent. N.m.r. spectra were recorded at 273 K. In a second reaction, $PF_2(SGeH_3)$ (0.8 mmol) was condensed in a glass ampoule with B_2H_6 (1.1 mmol), without a solvent. After warming to 195 K for 5 min excess B_2H_6 (0.7 mmol containing a trace of GeH_4) was removed. The combining ratio $PF_2(SGeH_3)$: $B_2H_6 = 2:1$ was thus established.

Reaction with $Mo(CO)_4(C_7H_8)$

$PF_2(SGeH_3)$ (0.4 mmol) was added to an n.m.r. tube containing $Mo(CO)_4(C_7H_8)$ (0.060 g, 0.2 mmol) in CCl_3D, and the solution was warmed to room temperature before ^{31}P, ^{19}F and ^1H n.m.r. spectra were recorded.

Reactions with platinum complexes

In each case the platinum complex (0.2 mmol) was weighed and dissolved in CCl_3D or CCl_2D_2 in an n.m.r. tube, and $PF_2(SGeH_3)$ (0.2 mmol) was added. The progress of reactions was monitored by ^{31}P n.m.r. spectroscopy. When reactions were complete ^{19}F spectra were also recorded.

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