Exchange Reactions of Bromodifluorophosphine with Silyl and Germyl Derivatives of the Group VI Elements

By **D. E. J. Arnold, J. S. Dryburgh, E. A. V. Ebsworth,** and **D. W. H. Rankin,*** Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ

The reactions of PF_2X (X = Cl or Br) with $(MH_3)_2Y$ (M = Si or Ge; Y = O, S, Se, or Te) have been studied by n.m.r. spectroscopy. When X = Br and Y = S, Se, or Te, reaction occurs at room temperature to give the species MH_3YPF_2, $(PF_2)_2Y$, and MH_3Br. ^{19}F and ^1H N.m.r. and double-resonance techniques have been used to determine the chemical shifts (^1H, ^{19}F, ^{31}P, and ^{77}Se) and coupling constants (including relative signs) of the products. The PF_2Se– and PF_2Te– compounds have exceptionally low ^{31}P chemical shifts. The ^{19}F spectrum of $(PF_2)_2Se$ has been studied over a wide range of temperatures, and $^2J(PP)$ and both $^4J(FF)$ values are found to be strongly temperature-dependent. The ^1H spectrum of SiH_3TePF_2 is also temperature-dependent.

THERE have been a number of studies of exchange reactions involving substituted silyl and germyl compounds.[1-3] In general these have shown that in the equilibrium state the more electronegative groups are preferentially bound to silicon, but that kinetic factors may make some exchanges extremely slow.[3] It is possible that this preference is associated with the tendency of atoms with lone pairs of electrons to indulge in π-bonding to a greater extent with silicon than with germanium. Our structural studies of fluorophosphine derivatives have suggested that bonds from phosphorus to nitrogen or oxygen have properties similar to those of bonds from silicon or germanium to nitrogen or oxygen.[4-6] We have, therefore, made a study of the reactions of a series of silyl and germyl Group VI derivatives with chloro- and bromo-difluorophosphine, to see whether chemical evidence would confirm or contradict our conclusions based on structural evidence.

EXPERIMENTAL

All manipulations of volatile materials were carried out in a conventional Pyrex vacuum system, with Apiezon L and N greases on taps and ground-glass joints. Tellurium compounds were handled in a grease-free section, with polytetrafluoroethylene taps. Bromo- and chloro-difluorophosphine were prepared from hydrogen bromide or chloride and dimethylaminodifluorophosphine.[7] Silyl and germyl compounds of elements of Group VI were obtained by use of reactions (1)—(5). Purities were checked by i.r. spectroscopy.

$$(SiH_3)_2Y + H_2O \longrightarrow (SiH_3)_2O + H_2Y \quad (Y = S \text{ and } Se) \qquad (1)$$

$$(SiH_3)_3N + 2H_2Y \longrightarrow NH_4{}^+YSiH_3{}^- + (SiH_3)_2Y \quad (Y = S, Se, \text{ and } Te) \text{ (ref. 8)} \qquad (2)$$

$$2SiH_3Br + K_2Y \longrightarrow (SiH_3)_2Y + 2KBr \quad (Y = S, Se, \text{ and } Te) \text{ (refs. 9 and 10)} \qquad (3)$$

$$2GeH_3Br + Pb(OH)_2 \longrightarrow (GeH_3)_2O + H_2O + PbBr_2 \quad \text{(ref. 11)} \qquad (4)$$

$$2GeH_3Br + (SiH_3)_2Y \longrightarrow (GeH_3)_2Y + 2SiH_3Br \quad (Y = S, Se, \text{ and } Te) \text{ (refs. 3 and 9)} \qquad (5)$$

Reactions were studied in a 1 : 1 mixture of cyclohexane and CCl_3F as solvent. Usually 0·2 mmol of the Group VI compound in *ca.* 0·7 ml of solvent was treated at room temperature with 0·2—0·7 mmol of the fluorophosphine (the amount of the latter used depending on which products were to be studied) for periods of from a few minutes up to several weeks.

N.m.r. spectra were recorded on a Varian Associates HA100 spectrometer operating at 100 MHz (^1H) or 94·075 MHz (^{19}F), the probes of which were double-tuned to accept a second radiofrequency provided by a Schlumberger frequency synthesizer.[12] Although the circuits were designed for ^1H–{^{19}F} and ^{19}F–{^1H} double resonance, satisfactory results have been obtained with irradiating frequencies of *ca.* 40·5 MHz, and 19·1 MHz in ^1H–{^{31}P}, ^{19}F–{^{31}P}, and ^{19}F–{^{77}Se} spin-tickling experiments.

Although the spectrometer and irradiation frequencies are derived from independent crystal sources, we find the relative frequencies to be stable to within a few parts in 10^8 during several months. Consequently, by comparing irradiation frequencies for the same nucleus in different compounds, we have been able to determine chemical shifts for ^{31}P and ^{77}Se, without the need for continuous monitoring of the spectrometer operating frequency.

Estimated standard deviations of quoted chemical shifts are 0·01(^1H), 0·1(^{19}F), or 0·5(^{31}P,^{77}Se) p.p.m. Errors in coupling constants are of the order of 2% of the value quoted.

RESULTS AND DISCUSSION

During the early stages of this work, a number of observations were made which influenced the choice of starting materials and conditions for subsequent reactions. The most important of these was that chlorodifluorophosphine exchanged with the germyl Group VI derivatives only slowly, with the result that mixed products, most of which are unstable during long periods at room temperature, could only be obtained in low con-

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centrations. With the silyl compounds, reactions were fast, but expected products, other than silyl chloride, were not observed. Consequently, the results reported here all concern exchange reactions of bromodifluorophosphine.

Secondly, it was observed that with sulphur, selenium, and tellurium derivatives, relative exchange rates were Si > Ge and Te > Se > S. Moreover, the equilibria were such that, if sufficient bromodifluorophosphine was present, all the silyl starting materials were apparently consumed, whereas some germyl compounds remained. At no time could high concentrations of the mixed MH_3YPF_2 species be obtained.

Thirdly, the disilyl ether exchange reaction was found to be slow, even with bromodifluorophosphine, only small amounts of silyl bromide being formed in 24 h, whereas digermyl ether reacted too quickly for the spectra of the starting materials to be observed. Neither oxygen system gave peaks which could be assigned to mixed MH_3OPF_2 species, and although MH_3Br was formed, yields of bis(difluorophosphino) ether were much lower than expected; trifluorophosphine appeared instead.

Finally, the reactions gave unstable products. The sulphur and selenium systems precipitated small amounts of yellow solids on standing, and the tellurium systems precipitated much metallic tellurium very rapidly. These solid products did not appear to interfere with the recording of n.m.r. spectra.

These observations, although only qualitative, do include some important results. Most important, they show that the tendency is, in fluorophosphine–silyl exchanges, for the more electronegative atoms to be bound to silicon, whereas in fluorophosphine–germyl systems the electronegative atoms tend to be bound to phosphorus. This is consistent with the idea that in these and other fluorophosphine derivatives, the PF_2 group is a π-electron acceptor intermediate in strength between the silyl and germyl groups.[4] If this also explains why some reactions go rapidly and to completion while others do not, then one would expect chlorodifluorophosphine to react to a greater extent than bromodifluorophosphine with the silyl derivatives, but to a lesser extent with the germyl ones. This is to a certain extent substantiated experimentally. With the germyl compounds reactions were slow, as shown by the rate of formation of germyl chloride, and the products, most of which are unstable, decomposed as rapidly as they were formed, and so were not observed in the n.m.r. spectra. With the silyl compounds, silyl chloride was formed in a few minutes, and the reactions apparently went to completion. However further reactions occurred giving insoluble products.

Some of the details of the more important experiments with bromodifluorophosphine are in Table 1. In addition to the products listed there, small amounts of $(PF_2)_2O$ and YPF_2H (Y = S or Se) were also formed if traces of water were present.

TABLE 1

Reactions of $(MH_3)_2Y$ and PF_2Br

Reagents PF_2Br^+	Molar ratio $PF_2Br : (MH_3)_2Y$	Reaction time/s	$(MH_3)_2Y$ remaining/%	Observed products			Others
				MH_3Br	MH_3YPF_2	$(PF_2)_2Y$	
$(SiH_3)_2O$	2·5 : 1	80,000	65	✓		✓	
	3·5 : 1	80,000	55	✓		✓	
$(GeH_3)_2O$	2 : 1	600	0	✓		✓	OPF_2H
	1 : 1	600	0	✓			PF_3
$(SiH_3)_2S$	1·8 : 1	2000	60	✓	✓	✓	
	1·8 : 1	50,000	30	✓	✓	✓	SiH_3F
$(GeH_3)_2S$	2·5 : 1	7000	100				
	2·5 : 1	180,000	80	✓	✓	✓	
$(SiH_3)_2Se$	2·5 : 1	25,000	15	✓	✓	✓	
	3 : 1	4000	30	✓	✓	✓	
	3 : 1	8000	0	✓	✓	✓	
$(GeH_3)_2Se$	2·5 : 1	8000	90	✓			
	2·5 : 1	200,000	60	✓	✓	✓	
$(SiH_3)_2Te$	1 : 1	2000	65	✓	✓	✓	Te
$(GeH_3)_2Te$	2 : 1	5000	70	✓			Te

Reactions involving germyl and silyl ethers gave only bis(difluorophosphino) ether and the appropriate halide, and no mixed species. GeH_3TePF_2 was not observed. As the germyl exchanges were slow, and decomposition of fluorophosphine–tellurium compounds was rapid, the products of this reaction, other than germyl bromide, were not observable in the n.m.r. spectra.

Chemical Shifts.—Chemical shifts for all the Group VI species studied are in Table 2. The interpretation of chemical shifts is difficult and may be misleading. Nevertheless, a number of noteworthy trends are apparent in the shifts listed.

There is a downfield shift in the proton resonances when one $-MH_3$ group in $(MH_3)_2Y$ is replaced by a $-PF_2$ group. This shift, for a given element Y, is roughly the same when M is Ge as when it is Si, but it varies with Y in the order Te > Se > S. The downfield shifts probably reflect the electron-withdrawing character of the $-PF_2$ groups. The variations in the shift could be due to changes in the geometry of the molecules, as the extent of intramolecular hydrogen bonding, in a five-membered ring (I) would be very dependent on the precise bond lengths and valence angles in the compound.

^{19}F Chemical shifts increase in the order $O < S < Se < Te$, and it is also noticeable that for any one element Y, $\delta(SiH_3YPF_2) \sim \delta(GeH_3YPF_2) < \delta(PF_2YPF_2)$.

The first of the trends is very similar to that found for the difluorohalogenophosphines,[13,14] and may be attributed simply to electronegativity differences. Such differences do not account for the second observed relationship, for which there is no obvious rationalisation.

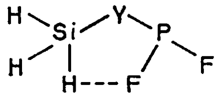
TABLE 2

Chemical shifts

Compound	$\tau(^1H)$	$\delta(^{19}F)$ [a]	$\delta(^{31}P)$ [b]	$\delta(^{77}Se)$ [c]
$(SiH_3)_2O$	+5·44			
$(GeH_3)_2O$	+4·72			
$(PF_2)_2O$		+36·7	−111 [d]	
$(SiH_3)_2S$	+5·71			
SiH_3SPF_2	+5·65	+57·3	−229·5	
$(GeH_3)_2S$	+5·40			
GeH_3SPF_2	+5·32	+57·1	−232·0	
$(PF_2)_2S$		+64·3	−219·4	
$(SiH_3)_2Se$	+5·98			+666·0
SiH_3SePF_2	+5·83	+59·6	−255·4	n.o.
$(GeH_3)_2Se$	+5·82			+611·5
GeH_3SePF_2	+5·70	+59·5	−258·9	n.o.
$(PF_2)_2Se$ [e]		+66·4	−246·9	−700·8
$(SiH_3)_2Te$	+6·41			
SiH_3TePF_2	+6·06	+68·5	−297·0	
$(GeH_3)_2Te$	+6·48			
$(PF_2)_2Te$		+72·6	−295·8	

N.o., Not observed.

[a] P.p.m. to high field of CCl_3F. [b] P.p.m. to high field of 85% H_3PO_4. [c] P.p.m. to high field of Me_2Se. [d] R. W. Rudolf, R. C. Taylor, and R. W. Parry, *J. Amer. Chem. Soc.*, 1966, **88**, 3729. [e] Measured at 193 K. All other spectra recorded at 300 K.



(I)

Phosphorus chemical shifts are useful in that they confirm that the compounds studied are derivatives of trico-ordinate phosphorus.[15] Variations are much as would be expected, with the shifts decreasing as the associated ^{19}F shifts increase.[16] All the shifts are lower than those in the corresponding simple difluorohalogenophosphines, with the consequence that those in the tellurium compounds are lower than any reported previously. Clearly, the phosphorus atoms are in some extreme environment: the multiplicity of explanations of phosphorus chemical shifts [17] makes it impossible for us at this stage to explain fully the nature of the bonding in these compounds.

The selenium shifts are also difficult to interpret, this time because of the lack of comparable data in the literature. However, it seems probable that simple electronegativity effects can account for the observed shifts. We are now studying the effects of substitution on the chemical shifts (^{77}Se and ^{125}Te) of a variety of selenium and tellurium compounds, and hope to be able to rationalise the present results more fully.

Coupling Constants.—The observed coupling constants for the mixed Group VI derivatives MH_3YPF_2 are in Table 3. The magnitudes of the directly bonded phosphorus–fluorine coupling constants increase with increasing electronegativity of the third atom bonded to phosphorus, in the usual manner.[18] The three-bond coupling, J(PYMH), is found to be positive [it being assumed that ^1J(PF) is negative [19,20]] in each compound studied, and to be larger in compounds with lighter elements Y and M. The positive sign is as expected for a three-bond coupling, and the trend in magnitude is also consistent with trends observed in other silyl and germyl derivatives of the Group VI elements.[21] However, on the basis that reduced coupling constants are usually negative over even, but positive over odd, numbers of bonds, the fluorine–hydrogen coupling in each of these molecules should be negative. In each case it is positive. This may be accounted for, at least in part, by the possibility of direct interaction between hydrogen atoms on silicon or germanium, and the fluorine atoms bonded to phosphorus, as described above. Such direct interaction might well provide a positive contribution to the four-bond coupling.

TABLE 3

Coupling constants for MH_3YPF_2

Compound	T/K	^1J(PF)/Hz	^3J(PH)/Hz	^4J(FH)/Hz
SiH_3SPF_2	300	−1298	+13·3	+2·7
GeH_3SPF_2	300	−1285	+11·8	+3·4
SiH_3SePF_2	300	−1286	+11·6	+2·9
GeH_3SePF_2	300	−1287	+11·2	+3·3
SiH_3TePF_2	203		11·4	3·0
	233		10·1	2·9
	273		9·6	2·7
	300	−1253	+9·3	+2·8

TABLE 4

Coupling constants for $(PF_2)_2Y$

Compd.	T/K	^1J(PF)/ Hz	^3J(PF)/ Hz	$\frac{\vert ^2J(PP)\vert}{Hz}$	$\frac{\vert ^4J(FF)\vert}{Hz}$	$\frac{\vert ^2J(FY)\vert}{Hz}$
$(PF_2)_2O$	300	−1365	+14	5	0	
$(PF_2)_2S$	300	−1303	+28	274	8·5, 2·5	
$(PF_2)_2Se$	293	−1305	+21	232	8·8, 2·8	39
	273	−1300	+25	249	9·3, 1·8	36
	253	−1301	+24	264	10·0, 1·5	36
	233	−1297	+25	281	10·5, 1·5	35
	213	−1293	+26	300	11·4, 0·9	35
	193	−1299	+35	316	12·0, 0·0	36
	173	−1297	+28	336	12·5, 0·0	36
$(PF_2)_2Te$	300	(1244) [a]	n.o.	n.o.	n.o.	n.o.

n.o., not observed.

[a] $\vert ^1J(PF) + ^3J(PF)\vert$

Coupling constants for the bis(difluorophosphino)-Group VI derivatives are in Table 4. The ^{19}F spectrum of $(PF_2)_2S$ and its temperature-dependence have been described.[22] We have studied the temperature-variation

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[14] R. W. Rudolph, J. G. Morse, and R. W. Parry, *Inorg. Chem.*, 1966, **5**, 1464.

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[21] C. Glidewell, D. W. H. Rankin, and G. M. Sheldrick, *Trans. Faraday Soc.*, 1967, **65**, 1409.

[22] R. W. Rudolph and R. A. Newmark, *J. Amer. Chem. Soc.*, 1970, **92**, 1195.

of the ^{19}F spectrum of $(PF_2)_2Se$ in detail, and Table 4 includes the parameters determined at each of seven temperatures. Absolute temperatures quoted may be up to 5 K in error, but relative values should be correct to within 1 K. The spectra (Figure 1) are of the second order, and have been analysed, on the assumption that $|^1J(PF) - {}^3J(PF)| \gg |^2J(PP)| \gg |^4J(FF)|, |^4J(FF)'|$, by the method of Harris *et al.*[23] The parameters in the oxygen compound are remarkable in that all couplings across the oxygen atom are small compared with similar couplings in the sulphur, selenium, and tellurium compounds. In particular, $^2J(PP)$ is only 5 Hz compared with over 200 Hz in the other compounds and *ca.* 400 Hz in some $(PF_2)_2NR$ compounds. Also, no four-bond fluorine–fluorine coupling is evident, whereas all other $(PF_2)_2X$ compounds studied show two different couplings, averaging *ca.* 6 Hz.

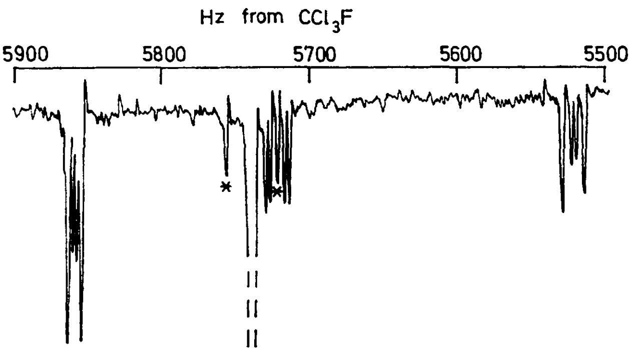

FIGURE 1 Low-field half of the ^{19}F n.m.r. spectrum of $(PF_2)_2Se$ at 173 K; $^{*77}Se$ satellites

These parameters distinguishing $(PF_2)_2O$ most dramatically from the other bis(difluorophosphino)-compounds are also those that change most significantly with temperature in $(PF_2)_2Se$. The parameters for this compound listed in Table 4 have been expressed (by least-squares fitting) as simple polynomial functions of temperature. The results (Table 5) have been used in obtaining Figure 2, which shows how the various line positions in one half of the spectrum change with temperature. These positions have been extrapolated outside the temperature range studied experimentally.

TABLE 5

Temperature-dependence of n.m.r. parameters of $(PF_2)_2Se$

$\phi(F) = 69{\cdot}05(8) - 0{\cdot}009(1)T$ p.p.m.
$^1J(PF) = -1284{\cdot}7(74) - 0{\cdot}061(31)T$ Hz
$^3J(PF) = 44{\cdot}2(78) - 0{\cdot}077(33)T$ Hz
$|^2J(PP)| = 525{\cdot}2(152) - 1{\cdot}238(133)T + 0{\cdot}00081(29)T^2$ Hz
$|^4J(FF)| = 4{\cdot}0(7) - 0{\cdot}022(3)T$ Hz
$|^4J(FF)'| = 18{\cdot}1(3) - 0{\cdot}032(1)T$ Hz
$|^2J(SeF)| = 36(1)$ Hz

Estimated standard deviations are given in parentheses; T refers to absolute temperature.

Although changes could be caused by movements of the positions of equilibria, it seems probable that the variations in these parameters, and in those for SiH_3-$TePF_2$ (Table 3), are caused by conformational changes within the molecules, with the long-range couplings between various atoms being affected by the interactions between the lone pairs of electrons, which are present on every atom in the molecules. The wide POP angle (over 140° in the gas phase) and staggered conformation of the PF_2 groups in bis(difluorophosphino) ether[6] result in fairly small interactions between the lone pairs on the phosphorus atoms, and between the remote pairs of fluorine atoms. However in the sulphur, selenium, and tellurium compounds and in the amines, the PF_2 groups can be much closer together, with consequent greater direct interaction. In addition to this, conformational changes with temperature will be possible in the Group VI compounds, where such changes might well be hindered by the presence of an alkyl or aryl group in the amines. Such an interpretation must be speculative. Since further structural work will be invaluable in understanding the behaviour of these compounds we are investigating ways of preparing them pure: the present reaction method is unsuitable as it gives several products of similar volatility.

Thus the extents to which these reactions proceed, and the various n.m.r. parameters of the products, give much information about the nature of the bonding in these compounds. One important question remains: why are these compounds apparently stable as phosphorus(III) derivatives, whereas other, similar, compounds revert to the phosphorus(V) forms? Thus species such as F_2PSH[24] and Me_2PSMe[25] are more stable in their phosphorus(V) forms, whereas F_2PSSiH_3 and $(CF_3)_2PSH$[26] exist exclusively with phosphorus(III). One possibility is that the stability of a particular form may be increased by intramolecular hydrogen bonding,

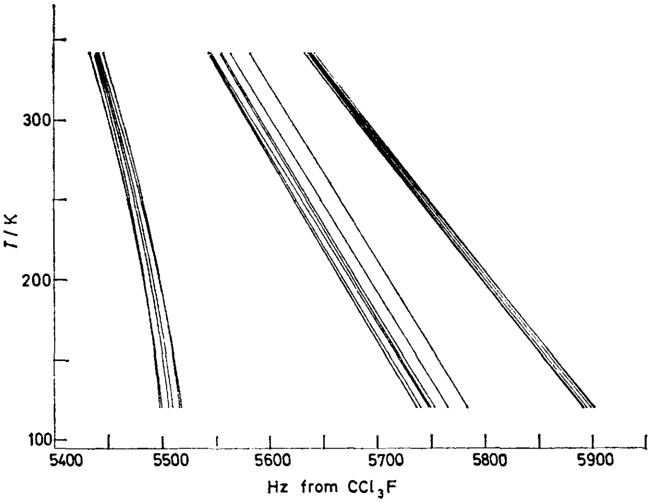

FIGURE 2 Variation of the positions of lines in the low-field half of the ^{19}F n.m.r. spectrum of $(PF_2)_2Se$ with temperature

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[23] R. K. Harris, J. R. Woplin, R. E. Dunmur, M. Murray, and R. Schmutzler, *Ber. Bunsenges. phys. Chem.*, 1972, **76**, 44.

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readily possible in the last two cases, where four bonds separate the fluorine and hydrogen atoms. An alternative explanation, for the silyl and germyl derivatives, is that these groups, when attached to phosphorus, reduce the electron density there by delocalisation of the lone pair of electrons, if present, into their vacant *d* orbitals. This mechanism has been suggested to account for the low base strength of trisilylphosphine,[27] and would certainly decrease the probability of forming phosphorus(V) silyl (or germyl) derivatives. In addition there is the possibility of some additional stabilisation of the phosphorus(III) forms by $(p \longrightarrow d)\pi$-interactions in the silicon–sulphur bonds. Further information is required to enable the structure-determining factors to be identified.

[2/1205 *Received*, 26*th May*, 1972]

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[27] C. Glidewell and E. A. V. Ebsworth, *J. Chem. Soc.* (*A*), 1969, 352.