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THE PREPARATION AND CHARACTERISATION OF SOME NEW CF_3Se- DERIVATIVES

C.J. MARSDEN

Department of Chemistry, Southampton University, Southampton
SO9 5NH (Gt. Britain)

SUMMARY

The preparation and characterisation of CF_3SePF_2, $CF_3SeSi(CH_3)_3$ and $CF_3SeTl(CH_3)_2$ are described. The vibrational and n.m.r. spectra of these compounds are presented and discussed.

INTRODUCTION

CF_3Se- compounds were first prepared nearly twenty years ago,[1] and since that time new derivatives have been reported slowly but steadily. It has been shown that CF_3SeCl reacts with acidic hydrogen atoms such as those in dimethylamine[2] or acetone,[3] that it reacts with a series of AgX salts forming a series of pseudo-halides,[4] that it adds across the double bond of ethylene,[3] and that it is oxidised by ozone giving $CF_3Se(O)Cl$.[5] CF_3Se- can act as a briding 3-electron donor ligand towards transition metal carbonyl species.[6,7] $Hg(SeCF_3)_2$ reacts with $(CF_3)_2PI$ abstracting iodine atoms.[8] This paper describes the preparation of three new CF_3Se- derivatives which it is hoped are of particular chemical and structural interest. The new compounds are CF_3SePF_2, $CF_3SeSiMe_3$ and $CF_3SeTlMe_2$.

EXPERIMENTAL

(a) CF_3SePF_2

0.76 g PF_2I [9] (3.6 mmole) were distilled onto 0.90 g $Hg(SeCF_3)_2$ [1] (1.8 mmole). After 30 minutes at -45°C, the volatile products were removed. Fractionation gave a clear liquid passing through a -45°C trap but retained at -96°C. Gas phase molecular weight measured as 214, calculated 217. V.p. 33 cm Hg at 25°C. Raman spectrum of solid residue (wt. 0.82 g, calculated for 1.8 mmole HgI_2 0.82 g) showed only HgI_2.

N.m.r. spectrum apparently first-order. ^{19}F chemical shifts $CF_{\underline{3}}$ 23.48 ppm, $PF_{\underline{2}}$ 69.93 ppm, both to high field of CCl_3F, in $(CD_3)_2CO$ solution, roughly 50% by volume.

Coupling constants:

^1J (P - F)	1297.5 Hz	^3J (P .. F)	22.0 Hz
^4J (F .. F)	5.0 Hz	^1J (^{77}Se - P)	345.5 Hz
^2J (^{77}Se .. $PF_{\underline{2}}$)	46 Hz	^2J (^{77}Se .. $CF_{\underline{3}}$)	18 Hz
^1J (^{13}C - F)	335 Hz		

(b) $CF_3SeSi(CH_3)_3$

0.49 g Me_3SiI (2.5 mmole) were added to a stirred solution of 0.63 g $Hg(SeCF_3)_2$ (1.3 mmole) in 12 ml dry ether at room temperature. Volatile products removed after stirring for 30 minutes. After repeated fractionation, the sample retained by a trap at -45°C gave gas-phase molecular weight of 225 (calculated for $CF_3SeSiMe_3$ 221). V.p. of this sample 2.1 cm Hg at 24°C. N.m.r. spectroscopy showed trace, about 5%, of Me_3SiI remaining. Raman spectrum of solid residue (wt. 0.60 g, calculated for 1.3 mmole HgI_2 0.59 g) showed only HgI_2.

N.m.r. data: ^{19}F chemical shift 22.79 ppm to high field of CCl_3F, in 10% solution by volume in CCl_3F. ^1H chemical shift 9.50 τ.

(c) $CF_3SeTl(CH_3)_2$

0.052 g $TlMe_3$ (0.21 mmole) was mixed with excess CF_3SeH and maintained at -45°C. 4.5 ml (at STP) of permanent gas were evolved during several hours. Solid residue weighed 0.0786 g (calculated for 0.21 mmole $CF_3SeTlMe_2$, 0.0798 g). AT STP, 0.21 mmole ideal gas occupies 4.8 ml.

N.m.r. data: ^{19}F chemical shift 12.6 ppm to high field of CCl_3F, in solution in pyridine. ^{1}H chemical shift 8.71 τ. ^{2}J (Tl .. H) 383 Hz.

A standard pyrex vacuum system was used equipped with "Rotaflo" greaseless taps. Pressures were measured using a sensitive glass spiral gauge as a null-point instrument The procedures used for obtaining vibrational and n.m.r. spectra have been described in the preceding paper. The infrared spectrum of solid $CF_3SeTlMe_2$ was recorded from a sample prepared in situ on the window of a low-temperature cell. The spectrum was recorded at room temperature.

RESULTS AND DISCUSSION

The reaction between PF_2I [9] and $Hg(SeCF_3)_2$ at -45°C yields CF_3SePF_2 according to the following equation:

$$2PF_2I + Hg(SeCF_3)_2 \rightarrow 2CF_3SePF_2 + HgI_2$$

PF_2Br does not react under these conditions, and was recovered quantitatively. CF_3SePF_2 is a colourless volatile liquid at room temperature, of limited thermal stability even in the gas phase. One of the decomposition products was shown to be PF_3, identified by its infrared spectrum, but the other products were not identified. CF_3SePF_2 has been characterised by its n.m.r. and vibrational spectra, by the determination of its molecular weight in the gas phase, and from consideration of the stoichiometry of the reaction leading to its formation.

The n.m.r. spectrum is first order. The ^{19}F spectrum consists of a doublet of triplets in the CF_3 region, and a doublet of quartets in the PF_2 region. The ^{31}P spectrum shows a triplet of quartets. ^{13}C satellites were seen in the fluorine spectra, and ^{77}Se satellites in both the fluorine and phosphorus spectra. The coupling constants measured are given in the Experimental Section.

In order to determine the relative signs of the three coupling constants ^{1}J (P – F), ^{3}J (P .. F) and ^{4}J (F .. F), two decoupling ("spin-tickling") experiments were performed. The first examined the changes in the central quartet of the phosphorus spectrum, while irradiatin at a frequency corresponding to the lower-field PF_2 quartet. It was found that irradiation of the high-frequency region of the PF_2 quartet produces maximum perturbation of the high frequency side of the ^{31}P quartet, and vice versa. The two coupling constants ^{3}J(P .. F) and ^{4}J(F ..F) are thus shown to be of the same sign.

The second decoupling experiment examined separately the changes produced in the two outer phosphorus quartets whilst the irradiating frequency swept through the whole CF_3 region. The irradiating frequency required to produce maximum perturbation in the lowest frequency ^{31}P quartet was higher than for the highest frequency quartet. Within one ^{31}P quartet, a higher frequency of irradiation produced the maximum perturbation of the lowest frequency line than was required for the highest frequency line. These observations establish that the lower side of the CF_3 quartet, and the ^{1}J (P – F) and ^{4}J (F . . F) coupling constants are shown to be of opposite sign. It is generally agreed that the ^{1}J (P – F) coupling constant is negative;[10] these studies determine, therefore, that both the ^3J (P .. F) and ^4J (F .. F) coupling constants in CF_3SePF_2 are positive.

The results for CF_3SePF_2 can be compared with those obtained recently[11] for $(PF_2)_2Se$. In this latter compound ^3J(P .. F) was observed to be 21 Hz, virtually identical with the 22 Hz recorded here, even though the interactions are transmitted through different bonds. In $(PF_2)_2Se$, ^4J (F .. F) was found to be 8.8 and 2.8 Hz, while a single value of 5 Hz is determined for CF_3SePF_2. In both compounds, ^3J(P .. F) and ^4J (F .. F) are found to be positive. While this is expected for a three-bond coupling constant, those over four bonds are generally found to be negative. This apparent anomaly may well be accounted for by a direct interaction between the fluorine atoms across the molecule, providing a positive contribution to ^4J (F .. F).

The vibrational spectra observed for CF_3SePF_2 are presented in Table 1. The highest possible molecular symmetry is $\underline{C}_s$, making a complete assignment of the eighteen fundamental vibrations a formidable task. However, based on the assignments of CF_3SeH,[12] and PF_2Br[13], a tentative assignment can be made of many of the observed bands to group frequencies, which are named assuming local symmetries of $\underline{C}_{3v}$ and $\underline{C}_s$ for the CF_3Se- and $-SePF_2$ groups, respectively. The low-frequency region is too complex for this treatment, however, and is left unassigned.

The new compound $CF_3SeSiMe_3$ has been prepared by the reaction of Me_3SiI with $Hg(SeCF_3)_2$ in solution in diethyl ether at -45°C. Me_3SiCl does not react under these conditions. $CF_3SeSiMe_3$ is a colourless liquid of low volatility at room temperature. It has been characterised by a study of its vibrational and n.m.r. spectra, by the determination of its gas-phase molecular weight, and by a consideration of the stoichiometry of its formation.

TABLE 1

Vibrational Spectra of CF_3SePF_2

Raman (liquid) cm^{-1}		Infrared (gas) cm^{-1}		Tentative Assignment
		2275	w	1172 +1112 = 2284
		1900	vw	1172 + 750 = 1922
		1850	vw,br	1112 + 750 = 1862
		1665	w	1112 + 548 = 1660
		1440	vw	1112 + 337 = 1449
		1390	w	1112 + 290 = 1402
		1278	w,br	750 + 548 = 1298
		1172	vs	C-F stretch asym
		1112	vs	C-F stretch sym
		1077	m	750 + 337 = 1087
		980	m	850 + 133 = 983
		928	w	
		850	vs	P-F stretch asym
837	p w			P-F stretch sym
745	p m	750	m	CF_3 def sym
		665	w,br	450 + 223 = 673
545	dp w	548	mw	CF_3 def asym
444	p m	450	s	FPF bend
413	p m	415	w	
396	dp,sh,vw	395	sh,w	
375	p,s	388	s	Se-P stretch
335	p m	337	mw	C-Se stretch
291	dp,w	290	mw	CF_3 rock
223	p s			
210	p vs			
144	w			
133	w			
119	vw			

Abbreviations:

s	strong	br	broad	asym	asymmetric
m	medium	sh	shoulder	p	polarized
w	weak	def	deformation	dp	depolarized
v	very	sym	symmetric		

Its vibrational spectra are presented in Table 2, where a tentative assignment is given of most of the observed bands to group frequencies of the $SiMe_3$ and $SeCF_3$ moieties, assuming local $\underline{C}_{3v}$ symmetry for both. The frequencies and polarization data observed for $CF_3SeSiMe_3$ are so similar to a superposition of the appropriate bands of Me_3SiI,[14] $(SiH_3)_2Se$[15]

TABLE 2

Vibrational Spectra of $CF_3SeSiMe_3$

Raman (liquid) cm^{-1}				Infrared (gas) cm^{-1}		Tentative Assignment
2963	dp	w	br	2970	m	C-H stretch asym
2902	p	m		2910	w	C-H stretch sym
1417		w,br		1415	w	CH_3 def asym
1265		vw,br		1260	m	CH_3 def sym
				1140	vs	C-F stretch asym
1100	p	vw,br		1110	vs	C-F stretch sym
				1080	s	745 + 344 = 1089
840		vw,br		855	vs	CH_3 rock
764	dp	w,br		763	m	CH_3 rock
743	p	m		745	m	CF_3 def sym
706	dp	w		700	w	C-Si stretch asym
660		vw				
631	p	s		630	m	C-Si stretch sym
535	dp	w,vbr				CF_3 def asym
367	p	s		370	m	Se-Si stretch
344	p	m				C-Se stretch
300	p	m		300	w	CF_3 rock
				285	w	
237	dp	m				SiC_3 def asym
208	p	m				SiC_3 def sym
170	dp	m				SiC_3 rock
121		w				C-Se-Si bend
81		w				

Abbreviations as in Table 1.

and CF_3SeH,[12] that the reasonably complete assignment in Table 2 seems justified. The vibrations of the $SiMe_3$ and $SeCF_3$ groups appear fairly independent of each other. While this observation may be initially surprising for a large molecule of very low symmetry containing many atoms of similar mass, it is plausible that mechanical coupling between the $SeCF_3$ and $SiMe_3$ groups is limited, due to the probable nearness to 90^o of the C-Se-Si and C-Si-Se bond angles.

$CF_3SeSiMe_3$ was prepared as a potential precursor to the compound $CF_2 = Se$, as yet unknown. A sample of $CF_3SeSiMe_3$ was passed several times in vacuo through a tube heated to 200^o. Trace amounts of the anticipated byproduct, Me_3SiF, were detected, but infrared and mass spectroscopic studies gave no hard evidence for the formation of $CF_2 = Se$. Similar experiments on CF_3SeSiH_3 also failed to give $CF_2 = Se$.[16]

The new compound $CF_3SeTl(CH_3)_2$ has been prepared by the reaction of CF_3SeH with $TlMe_3$ at -45^oC, according to the equation:

$$CF_3SeH \ + \ Tl(CH_3)_3 \ \rightarrow \ CF_3SeTl(CH_3)_2 \ + \ CH_4$$

It is a white solid at room temperature, of low thermal stability. Its characterization rests on the stoichiometry of its formation, and its n.m.r. and infrared spectra. Trimethyl thallium is known to react with acids HX, giving Me_2TlX derivatives,[17] and it was of interest to determine whether CF_3SeH is a sufficiently strong acid for this reaction to be possible. Dimethyl thallium halides have structures best described as "largely ionic", in that linear Me_2Tl groups exist in layers, the thallium surrounded by four halogen atoms.[18]

However, $Me_2TlSeMe$, and related compounds containing donor sulphur, oxygen or nitrogen atoms, are known to be dimeric in solution,[19] and thus it was intriguing to discover whether the electronegative

CF_3 group would change the structure of Me_2TlSeY (Y = CH_3 or CF_3) towards that of the halide derivatives.

Unfortunately the low stability of $CF_3SeTlMe_2$ has prevented the gathering of conclusive evidence on this point. The compound is instantly turned brown by addition of methanol, and the solution in pyridine, used to record n.m.r. data, decomposed significantly during three hours at room temperature. The ^{19}F spectra of this solution contained only a one peak at lower field than any reported so far for CF_3Se derivatives. This is consistent with the attachment of CF_3Se- to an electropositive group such as $TlMe_2$. The ^1H spectra of this solution showed, apart from peaks attributable to the solvent pyridine, only two peaks of equal intensity, 383 Hz apart. This is a typical $^2(Tl .. H)$ coupling constant for Me_2TlX derivatives. These observations indicate strongly that $CF_3SeTlMe_2$ had been formed, as does the observed stoichiometry of the reaction (see Experimental section).

TABLE 3

Infrared Spectrum of Solid $CF_3SeTlMe_2$

Frequency cm^{-1}		Tentative Assignment	Frequency cm^{-1}		Tentative Assignment
3000	w	C-H stretch asym	785	vs	CH_3 rock
2925	mw	C-H stretch sym	740	s	CF_3 def sym
1390	mw	CH_3 def asym	545	m	CF_3 def asym
1273	m	CH_3 def sym	476	sh	Tl-C stretch
1180	ms	C-F stretch asym	450	s	
1045	vs	C-F stretch sym	425	sh	
			343	w	C-Se stretch

Abbreviations as in Table 1.

It proved impossible to record Raman spectra of the compound, since it decomposed visibly even in the relatively weak beam of a He-Ne laser. The infrared spectrum of the solid, set out in Table 3, was recorded from a sample prepared in situ on the window of a low-temperature cell. The assignment of the observed bands to group vibrations is tentative, based on the spectra of CF_3SeH and of $Tl(CH_3)_3$.[20] The presence of three bands in the infrared spectrum which can plausibly be attributed to Tl-C stretching modes suggests that the compound does not contain linear, isolated $TlMe_2$ groups as found in Me_2Tl- halides. However, it is well known that deductions from solid spectra are liable to error, since vibrational coupling between different molecules in the same unit cell may give rise to more bands than predicted on the basis of single molecules. Unfortunately, therefore, it seems prudent to regard the structure of $CF_3SeTlMe_2$ as undetermined by the results presented here.

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REFERENCES

1. J. W. Dale and H. J. Emeleus, J. Chem. Soc., (1958) 2939.
2. M. J. Dunn and H. J. Emeleus, J. Inorg. Nucl. Chem., 27 (1965) 752.
3. N. N. Yarovenko, V. N. Shemania and G. B. Gasieva, Zhur. Obschei. Khim., 29 (1959) 942.
4. N. Welcman and M. Wulf, Israel J. Chem., 6 (1968) 37.
5. R. Paetzold and E. Wolfram, Z. Anorg. Allg. Chem., 353 (1967) 167.

6. J. Grobe, J. E. Helgerud and H. Stierand, Z. Anorg. Allg. Chem., 371 (1969) 123.

7. C. J. Marsden and G. M. Sheldrick, J. Organomet. Chem., 40 (1972) 175.

8. H. J. Emeleus, K. J. Packer and N. Welcman, J. Chem. Soc., (1962) 2529.

9. Inorganic Syntheses, X, 153.

10. W. MacFarlane, Quart. Rev. Chem. Soc., 23 (1969) 187 and references therein

11. D. E. J. Arnold, J. S. Dryburgh, E. A. V. Ebsworth and D. W. H. Rankin, J. Chem. Soc. Dalton Transactions, (1972) 2518.

12. C.J. Marsden, J. Fluor. Chem., 5 (1975) 401.

13. Inorganic Syntheses, X, 147.

14. J. Goubeau and H. Sommer, Z. Anorg. Allg. Chem., 289 (1957) 1.

15. E. A. V. Ebsworth, R. Taylor and L. A. Woodward, Trans. Farad. Soc., 55 (1959) 211.

16. E. A. V. Ebsworth, H. J. Emeleus and N. Welcman, J. Chem. Soc., (1962) 2290

17. A. G. Lee and G. M. Sheldrick, J. Organomet. Chem., 17 (1969) 481.

18. H. M. Powell and D. M. Crowfoot, Z. Krist., 87 (1934) 370.

19. A. G. Lee, "The Chemistry of Thallium", Elsevier, 1971, p.201 and references therein.

20. A. G. Lee, personal communication.