Periodic system of functional groups: formalism only or heuristic principles

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Abstract – The element displacement principle provides a concept for the recognition of new radicals with element–like behaviour. It also allows the correlation of classical pseudohalogens with perfluoroorgano–element groups. Radicals derived in this way have the same valence–electron structure as the reference element and are termed "paraelements". They represent functional groups which can be incorporated without difficulty into the existing periodic system. The application of this heuristic principle to current research problems such as the comparability of S(IV) with carbon, CF_3 or $(CF_3S)_2N$ with fluorine and CF_3S with chlorine is presented. The substitution of elements in known structures e.g. adamantanes with paraelements is discussed along with methods of preparation for new adamantane analogues.

The element–like behaviour of such different radicals as CH; CH_2, NH; OH, NH_2, CH_3 (called pseudoelements) are understood by Grimm's hydrogen displacement principle (ref. 1). They are isoprotonic and isoelectronic with their reference element; CH corresponds to nitrogen, CH_2 and NH to oxygen, and OH, NH_2, CH_3 to fluorine. However the halogen–like behaviour of CN, SCN, NCS, OCN, NCO, N_3 (ref. 2), or CF_3, CF_3S (ref.3) (called pseudohalogens) is not understood. These are neither isoelectronic nor isoprotonic with halogens.

A correlation between the different radicals pseudoelements and pseudohalogens cannot be recognized. Therefore one has to answer the following questions:

a) What are the logical, causal connections between pseudohalogens with halogens and pseudoelements with pseudohalogens?

b) Are these element–like properties purely accidental, and are these restricted only to the above mentioned radicals?

c) Is there a concept which is able to prove that these groups belong together?

d) Is it possible to deduce new element like radicals by means of such a concept, or will they only accidentally be discovered by experience?

There are many unanswered questions. However, the answer is simple and comprehensive and is formulated in the concept of element displacement (ref. 4).

The concept is based on Grimm's hydrogen–displacement principle and is defined as follows. "Coordination of the elements of Groups IV to VIII – subsequently termed base elements – with elements or element groups – termed ligands – forming one, two, three, or four covalent bonds results in a shift of one, two, three, or four places to the right (higher atomic number) within a period of the periodic system. This process is termed the element displacement principle". Examples my help to understand this definition. As a representative for all other monovalent elements fluorine is used since it is isogeometric with hydrogen and, therefore, an ideal ligand to demonstrate this principle.

C	N	O	F	Ne	Na	(Note a)
	$\equiv$CF	=NF	-OF	F_2	–	
		=CF_2	-NF_2	OF_2	–	
			-CF$_3$	NF_3	–	
				CF_4	[NF_4]	

Si	P	S	Cl	Ar	K
	$\equiv$SiF	=PF	-SF	ClF	–
		=SiF_2	PF_2	SF_2	[ClF_2]
			-SiF_3	PF_3	[SF_3]
				SiF_4	[PF_4]

The groups obtained by fluorine displacement are different from Grimm's pseudoelements obtained by hydrogen displacement, because they are neither isoelectronic nor isoprotonic with their reference atoms. Therefore, they should be clearly differentiated from them conceptually. It is suitable to call these and other radicals obtained in a similar manner "paraelements" (Note b). Each paraelement in turn is able to function as a ligand. Thus, e.g., using the halogen–like CF_3 radical, the first–order derivative paraelements shown below are obtained.

C	N	O	F	Ne
	$\equiv$CCF$_3$	=NCF$_3$	-OCF$_3$	CF_3-F
		=C(CF_3)$_2$	-N(CF_3)$_2$	(CF_3)$_2$O
			-C(CF_3)$_3$	(CF_3)$_3$N
				(CF_3)$_4$C

Si	P	S	Cl	Ar
	$\equiv$SiCF$_3$	=PCF$_3$	**-SCF$_3$**	CF_3-Cl
		=Si(CF_3)$_2$	-P(CF_3)$_2$	(CF_3)$_2$S
			-Si(CF_3)$_3$	(CF_3)$_3$P
				(CF_3)$_4$Si

If first–order derivative paraelements themselves are used as ligands, this system of nomenclature leads to second–order derivative para–elements, e.g., using CF_3S. This procedure can be continued in many cases with meaningful results.

C	N	O	F	Ne
	$\equiv$CSCF$_3$	=NSCF$_3$	-OSCF$_3$	CF_3SF
		=C(SCF_3)$_2$	-N(SCF_3)$_2$	(CF_3S)$_2$O
			-C(SCF_3)$_3$	(CF_3S)$_3$N
				(CF_3S)$_4$C

Si	P	S	Cl	Ar
	$\equiv$SiSCF$_3$	=PSCF$_3$	-SSCF$_3$	CF_3SCl
		=Si(SCF_3)$_2$	-P(SCF_3)$_2$	(CF_3S)$_2$S
			-Si(SCF_3)$_3$	(CF_3S)$_3$P
				(CF_3S)$_4$Si

(Note a) Paraelements of this group are only stable as cations.

(Note b) παρα (para): near, secondary

Which sort of paraelements do we obtain with ligands like oxygen, sulfur, or nitrogen? When any one of these is used as the ligand; a displacement of two or three groups must, of course, result as follows.
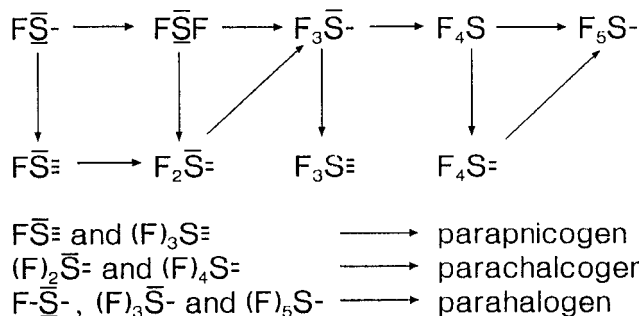
C	N	O	F	Ne
		=CO	-NO	O=O
			-CN	N≡N
		=CS	-NS	O=S

C	N	O	F	Ne
		C=CO	**NCO**	OCO
	CCN	NCN	**OCN**	FCN
		C=CS	**NCS**	OCS

These resulting paraelements may also appear as ligands. If, for example, the CO, CN, or CS groups are coordinated, first–order derivative paraelements are obtained as shown above. All classical pseudohalogens can be deduced in this way. A base element and the corresponding paraelement have the same number of valence electrons. This means that covalent electron pairs held in common by base atom and ligand are assigned to the base atom. Therefore, it becomes electronically isovalent with the reference element. Analogously, addition of an electron to an element (equivalent to a covalent bond) forms an ion which is shifted in the same direction, e.g., $Tl^{-} \triangleq C$ in $(NaTl)_n$ (ref. 5); $C^{-} \triangleq N$; $Si^{-} \triangleq P$ in $Na_4(Si_4)^{4-}$, Ge^{-}, $Pb^{-} \triangleq P$; Si^{2-}, $As^{-} \triangleq Se$; O^{-}, $S^{-} \triangleq Cl$ (ref. 6). A shift to the left side of the periodic system is achieved by loss of electrons, e.g., $C^{+} \triangleq B$, $N^{+} \triangleq C$, $O^{+} \triangleq N$, $Cl^{+} \triangleq S$.

The possibility of paraelement formation is not exhausted with above examples, because elements of Groups V – VII have free electron pairs and consequently are able to form coordinate bonds: The number of valence electrons on the central atom being unchanged, base and reference element are identical, e.g.

$$\overline{|O|}{:}\overline{N}{\cdot} \qquad \overline{|O|}{:}\overline{S}{\cdot} \qquad \overline{|O|}{:}\overline{P}{\cdot} \qquad \overline{|O|}{:}\overline{S}{\cdot} \atop \overline{|O|}$$

Elements of the third to fifth periods are also capable to octett expansion. New paraelements result in this way which have not been mentioned so far. Thus when fluorine is a ligand sulfur can form the following paraelements:

$$F\overline{\underline{S}}{-} \longrightarrow F\overline{\underline{S}}F \longrightarrow F_3\overline{S}{-} \longrightarrow F_4S \longrightarrow F_5S{-}$$

$$F\overline{\underline{S}}{\equiv} \longrightarrow F_2\overline{S}{=} \qquad F_3\overline{S}{\equiv} \qquad F_4S{=}$$

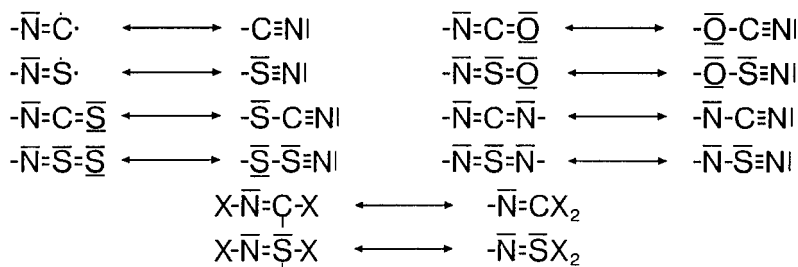|		
$F\overline{S}{\equiv}$ and $(F)_3S{\equiv}$	⟶	parapnicogen
$(F)_2\overline{S}{=}$ and $(F)_4S{=}$	⟶	parachalcogen
$F{-}\overline{\underline{S}}{-}$, $(F)_3\overline{S}{-}$ and $(F)_5S{-}$	⟶	parahalogen

An analogous behaviour is found for the other elements, e.g., phosphorous, arsenic, selenium, etc. Paraelements of this sort are no longer electronically isovalent with their reference elements; they do, however, remain topological isovalent. Thus, the criterion of isovalence is common to all paraelements.

This is in short the formalism of **element displacement** which provides the periodic system of functional groups. These rules however are only applicable to main groups elements. A link between these and transition metals was provided by R. Hoffmann (ref. 6a). His "Isolobal Concept" published in 1982 provides a relationship between molecular fragments which are neither isoelectronic nor isostructural but whose frontier orbitals have comparable symmetry, similar energy and therefore resembling bonding properties with the same number of unpaired electrons e.g. $CH_3 \triangleq Co(CO)_4$, $CH_2 \triangleq Fe(CO)_4$, $CH \triangleq Cr(CO)_3$.

But which heuristic impulses and conclusions can a preparative chemist derive from such an empirically found, but intellectual concept of element displacement? Can one forecast the pathway of an unknown reaction? Is it possible to predict existence, properties and structures of new compounds based on available knowledge?

In the following I would like to talk about applications of the element displacement principle to recent chemical problems, e.g. the equivalency between carbon and sulfur–IV.

Such an interesting relationship between carbon and s^2p^3d hybridized sulfur can be observed in a number of unsaturated functional groups containing carbon and sulfur.

$$-\overline{N}=\dot{C}- \longleftrightarrow -C\equiv N| \qquad -\overline{N}=C=\underline{O} \longleftrightarrow -\underline{O}-C\equiv N|$$

$$-\overline{N}=\dot{S}- \longleftrightarrow -\overline{S}\equiv N| \qquad -\overline{N}=\overline{S}=\underline{O} \longleftrightarrow -\underline{O}-\overline{S}\equiv N|$$

$$-\overline{N}=C=\underline{S} \longleftrightarrow -\overline{S}-C\equiv N| \qquad -\overline{N}=C=\overline{N}- \longleftrightarrow -\overline{N}-C\equiv N|$$

$$-\overline{N}=\overline{S}=\underline{S} \longleftrightarrow -\underline{S}-\overline{S}\equiv N| \qquad -\overline{N}=\overline{S}=\overline{N}- \longleftrightarrow -\overline{N}-\overline{S}\equiv N|$$

$$X-\overline{N}=\underset{|}{C}-X \longleftrightarrow -\overline{N}=CX_2$$

$$X-\overline{N}=\underset{|}{\overline{S}}-X \longleftrightarrow -\overline{N}=\overline{S}X_2$$
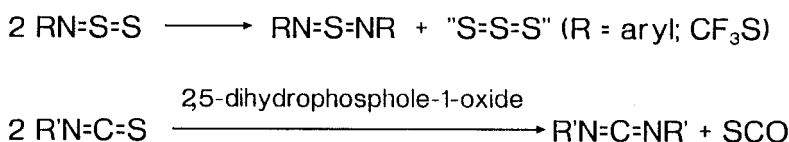
In these paraelements carbon and sulfur can be exchanged without altering their chemical properties significantly. The main difference between them is caused by the extra electron pair at the sulfur atom which gives rise to bent or nonplanar structures. While the carbon–containing paraelements are linear or planar, the corresponding sulfur analogues are bent or nonplanar.

Let's consider the equivalency between the two paraelements, isothiocyanate and N-(thiosulfinylamine). They are prepared by condensation of primary amines with thiophosgene (ref. 4b) or disulfurdichloride (ref. 7). It is assumed that in this reactions S_2Cl_2 acts in its isomeric structure thiothionyldichloride resembling as expected thiophosgene.

$$RNH_2 + S=CCl_2 \longrightarrow RN=C=S + 2 HCl$$
$$RNH_2 + S=SCl_2 \longrightarrow RN=S=S + 2 HCl \text{ (R = aryl-) (ref. 7)}$$
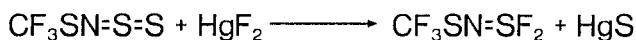$$CF_3SNH_2 + S=SCl_2 \longrightarrow CF_3SN=S=S + 2 HCl \text{ (ref. 8)}$$
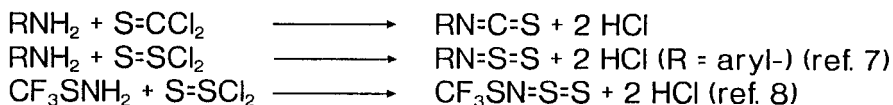
After many unsuccessful attempts it was finally possible to synthesize CF_3SNSS (ref. 8) from the amine and S_2Cl_2 in the presence of quinoline in CS_2 solution. With other amines in different solvents only decomposition products are obtained. N-(thiosulfinylamines) are very reactive compounds and decompose to $RN=S=NR$ and sulfur (ref. 7,8). Some isothiocyanates behave similarly. In the presence of 2,5-dihydrophosphol-1-oxide they condense to $RN=C=NR$ (ref. 9) according to
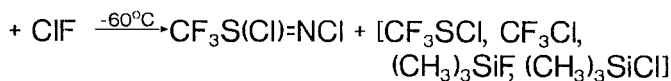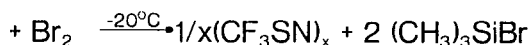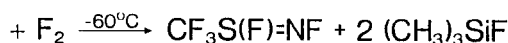
$$2 RN=S=S \longrightarrow RN=S=NR + \text{"}S=S=S\text{"} \text{ (R = aryl; } CF_3S)$$

$$2 R'N=C=S \xrightarrow{\text{2,5-dihydrophosphole-1-oxide}} R'N=C=NR' + SCO$$

As a result of the reaction with the catalyst, SCO rather than S=C=S (which is similar to the unstable "S=S=S"), is formed. Equivalency is also observed in the chlorination and fluorination
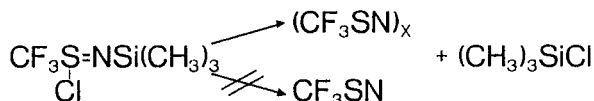
reactions, as shown below (ref. 4b)

$$CF_3SN=S=S + Cl_2 \longrightarrow CF_3SN=SCl_2 \longrightarrow CF_3SCl + (ClSN)_3$$

$$CF_3SN=S=S + HgF_2 \longrightarrow CF_3SN=SF_2 + HgS$$

The two isomeric paraelements $-N=CX_2$ and $XN=C(X)-$ resemble formally their sulfur analogues $-N=SX_2$ and $XN=S(X)$. While compounds of the type $R_fN=CX_2$, $R_fN=SX_2$, and $R_fC(X)=NX$ are already known, so far no substances of the type $R_fS(X)=NX$ with $R_f \neq X$ (X = halogen) have been described. The reactions which normally lead to $XN=C(X)R_f$ fluorination of isocyanurates, e.g. $(CF_3CN)_3$ (ref. 10) or halogenation of R_fCN [X = F (ref. 11,12), X=Cl (ref. 13)] are not applicable to the S-N system due to the lack of the corresponding starting materials. Their successful preparation was achieved via oxidative halogenation:
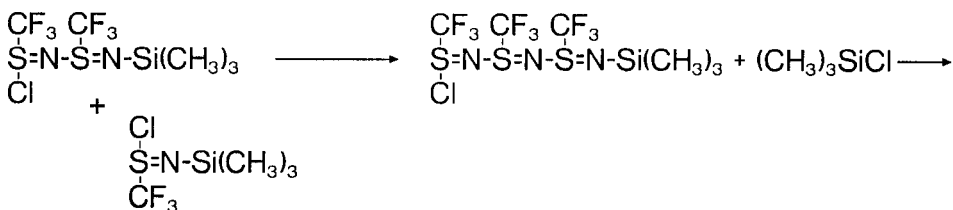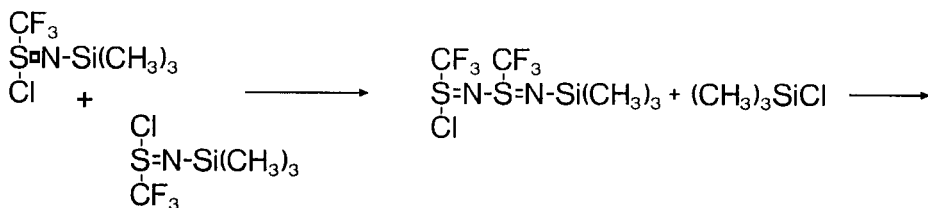
$$+ F_2 \xrightarrow{-60^{\circ}C} CF_3S(F)=NF + 2 (CH_3)_3SiF$$

$$+ Cl_2 \xrightarrow{-40^{\circ}C} CF_3S(Cl)=NSi(CH_3)_3 \xrightarrow[-20^{\circ}C]{Cl_2} CF_3S(Cl)=NCl$$
$$+ 2 (CH_3)_3SiCl$$

$$CF_3SN[Si(CH_3)_3]_2$$

$$+ Br_2 \xrightarrow{-20^{\circ}C} 1/x(CF_3SN)_x + 2 (CH_3)_3SiBr$$

$$+ ClF \xrightarrow{-60^{\circ}C} CF_3S(Cl)=NCl + [CF_3SCl, CF_3Cl,$$
$$(CH_3)_3SiF, (CH_3)_3SiCl]$$

No reaction occured with iodine (ref. 8).

The monohalogenated $CF_3S(Cl)=NSi(CH_3)_3$ is unstable at room temperature and decomposes to yield the $(CF_3SN)_x$ polymer and $(CH_3)_3SiCl$ as shown below:

$$\begin{array}{c} \nearrow (CF_3SN)_X \\ CF_3S=NSi(CH_3)_3 + (CH_3)_3SiCl \\ \;\;\,\overset{|}{Cl} \searrow CF_3SN \end{array}$$

This observation raised a different problem. Is monomeric CF_3SN an intermediate in this procedure?

All attempts to prove the formation of monomeric CF_3SN as an intermediate are unsuccessfull. Decomposition in the presence of dienes of different types such as butadiene, cyclobutadiene, hexachlorocyclopentadiene and tetraphenylcyclopentadienone give no addition products of CF_3SN. The dienes are recovered quantitatively. These observations are consistent with inter– instead of intramolecular condensation for $CF_3S(Cl)=NSi(CH_3)_3$. A reaction scheme, illustrating this process is proposed below.

$$\begin{array}{l} \overset{|}{CF_3} \\ S=N-Si(CH_3)_3 \\ \overset{|}{Cl} \;\; + \\ \overset{|}{Cl} \\ S=N-Si(CH_3)_3 \\ \overset{|}{CF_3} \end{array} \longrightarrow \begin{array}{l} CF_3 \; CF_3 \\ \overset{|}{S}=N-\overset{|}{S}=N-Si(CH_3)_3 + (CH_3)_3SiCl \longrightarrow \\ \overset{|}{Cl} \end{array}$$

$$\begin{array}{l} CF_3 \; CF_3 \\ \overset{|}{S}=N-\overset{|}{S}=N-Si(CH_3)_3 \\ \overset{|}{Cl} \;\;\; + \\ \overset{|}{Cl} \\ S=N-Si(CH_3)_3 \\ \overset{|}{CF_3} \end{array} \longrightarrow \begin{array}{l} CF_3 \; CF_3 \; CF_3 \\ \overset{|}{S}=N-\overset{|}{S}=N-\overset{|}{S}=N-Si(CH_3)_3 + (CH_3)_3SiCl \longrightarrow \\ \overset{|}{Cl} \end{array}$$
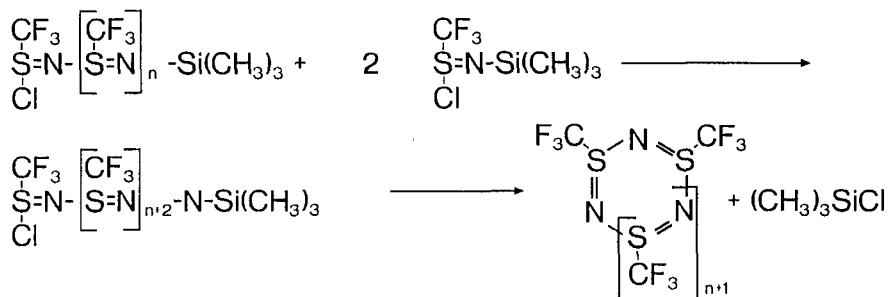
Because neither chlorine nor trimethylsilyl, both possible end groups in a chain polymer, can be detected by elemental analysis, it is concluded that $(CF_3SN)_x$ is cyclic in nature, possible with rings of different size, (ref. 14).

Another method to generate CF$_3$SN is the controlled thermal decomposition of CF$_3$SN$_3$, synthesized from CF$_3$SCl and (CH$_3$)$_3$SiN$_3$ (ref. 15). The materials obtained are N$_2$ and a rather unstable $(CF_3SN)_x$ which on standing changes its melting point and decomposes on heating to CF$_3$SSCF$_3$ and N$_2$. The final product obtained after storing the mixture for a few days at 25°C shows an ^{19}F–NMR–signal similar to that of the polymer obtained from CF$_3$S(Cl)=NSi(CH$_3$)$_3$. In the decomposition of CF$_3$SN$_3$ an intermolecular condensation can be ruled out, so that CF$_3$SN must be an intermediate. In the presence of hexachlorocyclopentadiene, CF$_3$SN$_3$ decomposes and low yields of a white solid containing CF$_3$SN and C$_5$Cl$_6$ units in a 1:1 ratio are obtained. Surprisingly, the chemical shift in the ^{19}F–NMR–spectrum [δ(CF$_3$)=-51.6] appears in a region where normally trifluoromethylthioamino (CF$_3$SN=) groups resonate. This raises some doubt whether the product obtained is formed by a (4+2) cyclo addition reaction. The presence of a discrete CF$_3$SN group is confirmed by single crystal X–ray diffraction analysis. The adduct C$_5$Cl$_6$·CF$_3$SN is found to have a thioketimine structure shown in Fig. 1
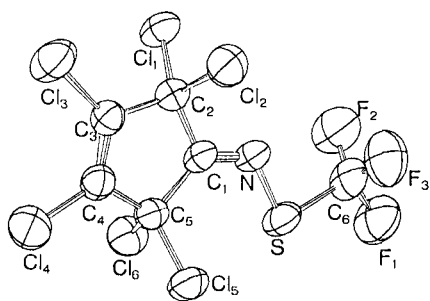

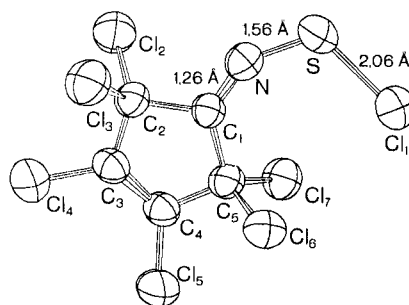Fig. 1. Molecular structure of hexachloro-3-cyclopentenylidenaminotrifluormethylsulfide

Fig. 2. Molecular structure of hexachloro-3-cyclopentenylidenaminosulfanyl chloride

These results prove convincingly that the intermediate CF$_3$SN does not react with C$_5$Cl$_6$ as a thiazyl but as a "nitrene", presumably via an unstable (2+1) cycloaddition intermediate rearranging to the final product according to

Scheme 1
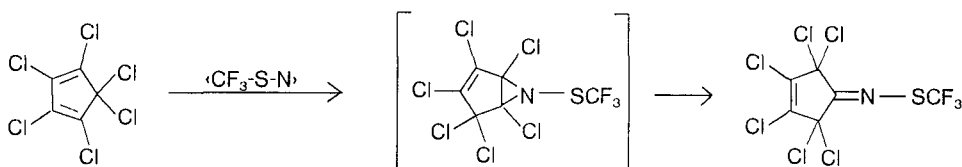
Alternative reaction pathways can be excluded. Since it could be demonstrated that under these conditions C$_5$Cl$_6$ does not react with (CH$_3$)$_3$SiN$_3$ (ref. 16).

A second independent synthesis for $CF_3SN=C_5Cl_6$ supports the proposed mechanism. Generally nitrenes are also produced by oxidation of primary amines (ref. 17). When a mixture of CF_3SNH_2, C_5Cl_6 and $Pb(CH_3COO)_4$ is refluxed in dichloromethane, 5.4 %. $CF_3SN=C_5Cl_4$ is formed in addition to $(CF_3S)_2NH$ and $(CF_3SN)_x$. These results confirm the formation of CF_3SN as a nitrene intermediate in the reaction.

These observations raise the question how ClSN and FSN interact with C_5Cl_6. When ClSN – prepared by heating of $Cl_3S_3N_3$ in toluene – is reacted with C_5Cl_6 at 130°C (3h) a 1:1 adduct is formed in 38 % yield. An X–ray structural analysis of the yellow crystals showed an identical ketimino structure shown in Fig.2.

Hexachloro-3-cyclopentenylideniminosulfanyl chloride is probably formed similarly to $CF_3SN=C_5Cl_6$ according to
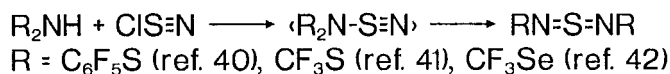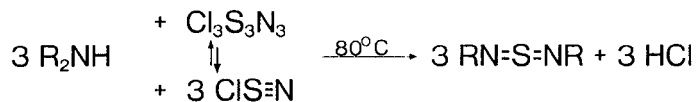
Scheme 2
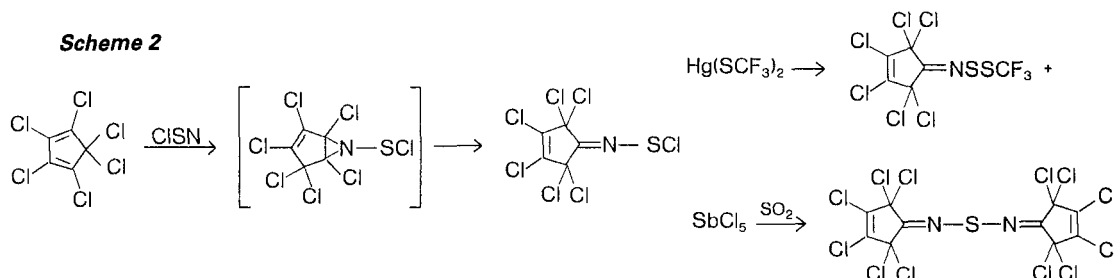
Its reactivity is comparable to other sulfanyl chlorides. Again it is evident that ClSN reacts as a nitrene. The reactions of FSN with C_5Cl_6 are found to be somewhat more complicated. In analogy to the chemical behaviour of CF_3SN and ClSN, it is expected that FSN forms with C_5Cl_6 the corresponding sulfanyl fluoride C_5Cl_6NSF. However, it is known that such compounds are very reactive and, therefore, it can be expected that such a molecule may not be isolatable (ref. 18). Indeed the reaction of FSN with C_5Cl_6 (molar ratio 2:1) in SO_2 at 20°C gives C_5Cl_6NSCl in 20 % yield. In addition, partial fluorinated derivatives of C_5Cl_6 are formed according to the ^{19}F NMR spectra. The formation of the sulfanyl chloride can be explained as follows.

Scheme 3
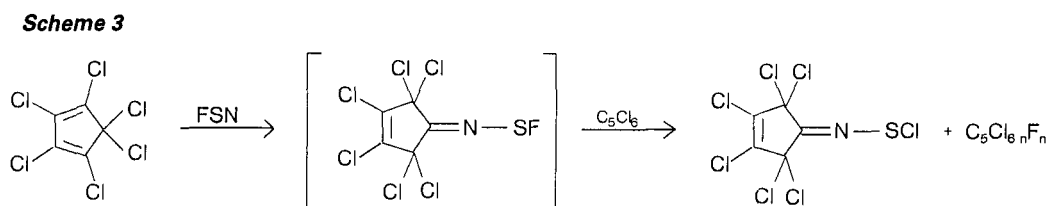
If this procedure is carried out at 75°C in a stainless steel autoclave C_5Cl_6NSNSO is formed (ref. 16) according to

Scheme 4
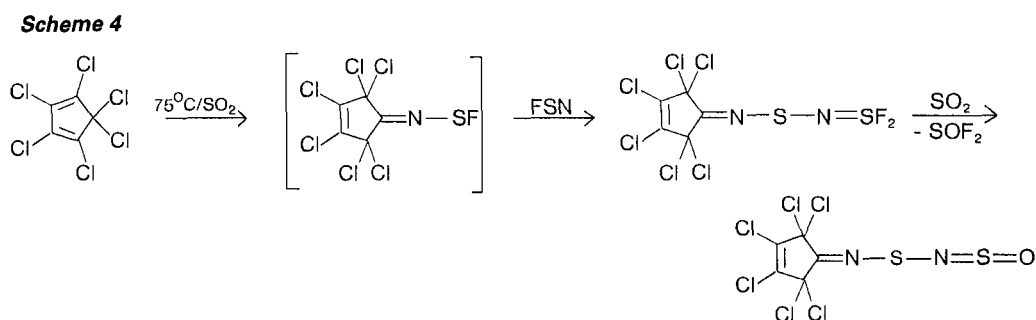
Another paraelement pair, -N=C=N- and -N=S=N⁻ seem to have a lot in common. A large number of their organic and perfluoroorganoderivatives are known. The carbodiimide group exists also in an isomeric form as cyanoamide (=N-C≡N). Up to now the corresponding isomer, =N-S≡N, is not known. The only evidence for such a group to exist is the reaction of secondary amines with $Cl_3S_3N_3$ in boiling CCl_4 in the presence of pyridine.

$$3 \ R_2NH \quad \begin{array}{c} + \ Cl_3S_3N_3 \\ \updownarrow \\ + \ 3 \ ClS\equiv N \end{array} \quad \xrightarrow{\ 80^\circ C\ } \quad 3 \ RN=S=NR + 3 \ HCl$$

$$R_2NH + ClS\equiv N \longrightarrow \langle R_2N\text{-}S\equiv N \rangle \longrightarrow RN=S=NR$$
$$R = C_6F_5S \ (ref. \ 40), \ CF_3S \ (ref. \ 41), \ CF_3Se \ (ref. \ 42)$$

At elevated temperatures $Cl_3S_3N_3$ pyrolyzes to give ClSN, which condenses with the imine to form $R_2NS\equiv N$ as an intermediate. This rearranges immediately to the stable compound RN=S=NR. There might be a chance to isolate a molecule with an N-S≡N group provided an imine is found with stable element–nitrogen bonds, incapable of rearranging under the reaction conditions. Tetrakis(trifluoromethylthio)pyrrol might fulfill these requirements and react with $Cl_3S_3N_3$ to give the wanted substance. If rearrangement occurs, ring opening has to take place. When reacting the substituted pyrrole with $Cl_3S_3N_3$ in refluxing CCl_4 in the presence of pyridine, a light yellow substance can be isolated and purified by sublimation in vacuo. On standing it changes colour continuously, ending with deep purple, without changing its physical properties. On subliming an aged sample in vacuo, a light yellow material is recovered almost quantitatively. Analytical and spectroscopic investigations show that the product is the suggested molecule, which is formed according to :

Scheme 5
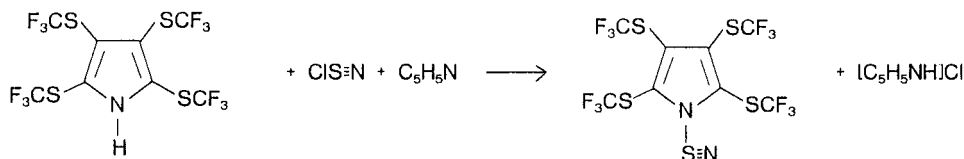
Molecular weight determinations prove that the product is monomeric and shows no tendency to trimerize to a trithiazyl ring. Such cyclizations are observed for FSN and ClSN, and are comparable with those of FCN and ClCN. The corresponding cyanoderivative obtained from the potassium salt and ClCN demonstrates similarities between -C≡N and -S≡N paraelements. Both compounds undergo (4+2) cyclo addition to yield 3,6-dihydro-1,λ^4,2-thiazine and 3,6-dihydropyridine derivatives (ref. 19) according to :

Scheme 6

$$Z = C, S$$
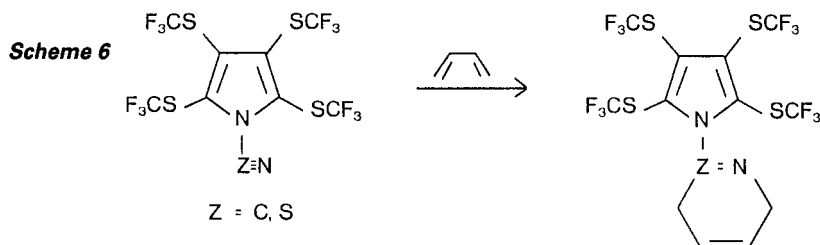
Another imine with a stable element–nitrogen bond incapable of rearranging might be $(CF_3)_2C=NH$. The lithium salt reacts with ClSN at 70°C in CCl_4 to give a mixture, which on fractional condensation at −35 to −65°C produces a deep green liquid. On standing at 20°C the colour changes to brown. After additional fractionation the liquid turns green again and when kept in a sealed tube in vacuo for several weeks an almost complete sublimation occurs, yielding colourless crystals. Their structure, determined by single crystal X–ray diffraction analysis,

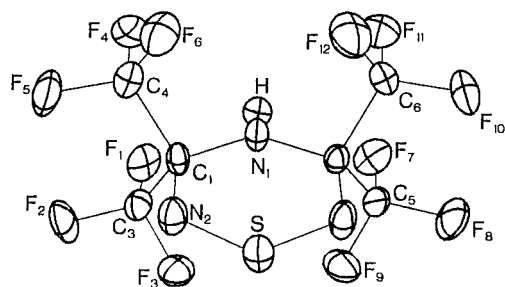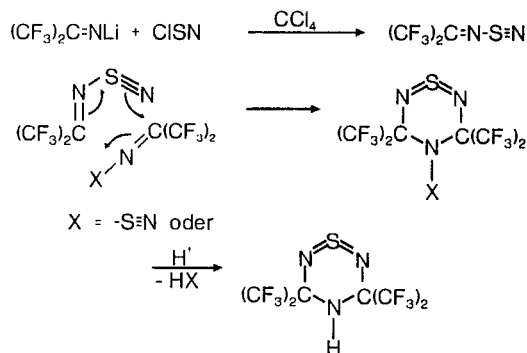suggests a six membered ring arrangement shown in Figure 3. A scheme for its formation might be as follows:

Fig. 3. A perspective drawing of S[NC(CF₃)₂]₂NH with 20 % probability thermal ellipsoids

Scheme 7

$(CF_3)_2C=NLi + ClSN \xrightarrow{CCl_4} (CF_3)_2C=N-S\equiv N$

The course of this reaction is completely mysterious, especially the formation of the NH function. A systematic investigation of this reaction showed that $(CF_3)_2C=NLi$ and $Cl_3S_3N_3$ form in CH_2Cl_2 at 80°C (24 h) in situ the ring, $(CF_3)_2C=N-S_x-N=C(CF_3)_2$ (x=1,2), and small amounts of $(CF_3)_2C(Cl)N=S=NC(Cl)(CF_3)_2$. The product distribution depends on the purity of $Cl_3S_3N_3$. If it is made from disulphur dichloride and ammonium chloride with subsequent chlorination of the intermediate thiodithiazyl dichloride (ref. 20), $Cl_3S_3N_3$ contains sometimes ammonium chloride which is responsible for the formation of the NH group in the ring. When $(CF_3)_2C=NLi$ is reacted with $Cl_3S_3N_3$ – made from tetrasulphur–tetranitride and sulphuryl dichloride (ref. 21) only $(CF_3)_2C=N-S_x-N=C(CF_3)_2$ (x=1,2) is formed. Addition of ammonium chloride to the reaction mixture produces the ring $S[NC(CF_3)_2]_2NH$ in yields of up to 11.7 %. It is also formed when thiodithiazyl dichloride is reacted with $(CF_3)_2C=NLi$. In addition $(CF_3)_2C=N-S-S-N=C(CF_3)_2$ is obtained in the ratio 5:1. Condensation of $(CF_3)_2C(Cl)N=S=N-C(CF_3)_2Cl$ with ammonium chloride or ammonia at 100°C (18h) could not be accomplished. The results prove quite clearly that $(CF_3)_2C=N-S\equiv N$ is an intermediate in the formation of $S[NC(CF_3)_2]_2NH$. With thiazyl fluoride $(CF_3)_2C=NLi$ forms at 70 to 80°C only $(CF_3)_2C=N-S_x-N=C(CF_3)_2$ (x=1,2) but in the presence of cesium fluoride additionally $(CF_3)_2C=N-S-N=S=NCF(CF_3)_2$ is obtained (ref. 22) according to:

$$\longrightarrow (CF_3)_2C=N-S_x-N=C(CF_3)_2 \quad (x = 1,2)$$

$$(CF_3)_2C=NLi + FSN$$

$$\xrightarrow{CsF} (CF_3)_2C=N-S-N=S=NCF(CF_3)_2 +$$
$$(CF_3)_2C=N-S_x-N=C(CF_3)_2$$
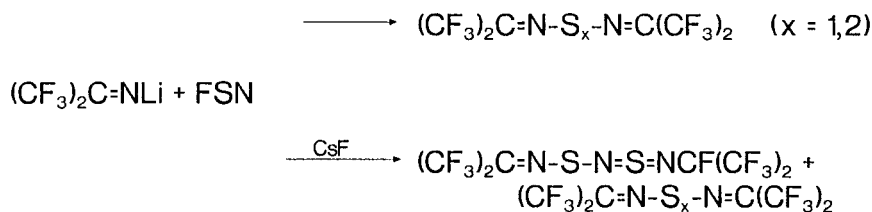
Formation of 3,6-dihydro-1-[2,3,4,5-tetrakis(trifluoromethylthio)-1-pyrrolyl]-1,λ^4,2-thiazine and of 3,3,5,5-tetrakis(trifluoromethyl)-4H-1,λ^4,2,4,6-thiatriazine by (4+2) cycloaddition of a thiazyl with dienes are contradicting reactions of X–S≡N (X=CF₃, Cl, F) and hexachloro–cyclobutadiene. It was also stated by NMR–spectroscopical arguments that F–S≡N and hexafluorobutadiene form by (4+2) cycloaddition heptafluoro-3,6-dihydro-1,λ^4,2-thiazine (A) which on treating with $(CH_3)_3SiCl$ is converted to 1-chloro-hexafluoro-3,6-dihydro-1,λ^4,2-thiazine (B) (ref. 43). The later is also formed from hexafluorobutadiene and $Cl_3S_3N_3$ at 20°C (14 days) in good yields and is fluorinated by KF to A. X–ray structure determination confirmed

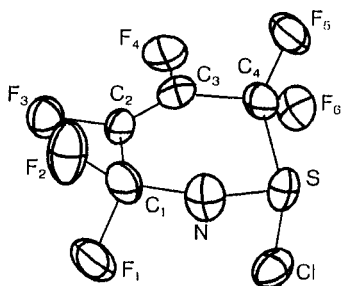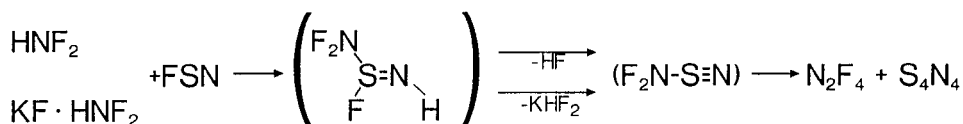for B unambiguously the six membered ring structure shown in Fig. 4 (ref. 44).

Fig. 4. Molecular structure of 1-chloro-hexafluoro- 3,6,-dihydro-1,λ^4,2-thiazine

The reactions studied so far prove that X-S≡N (X=CF₃, Cl, F) react with hexachlorocyclobutadiene as a "nitrene" but X'-S≡N (X'= F, (CF₃)₂C≡N, (CF₃S)₄C₄N-) react with hexafluorobutadiene or butadiene as a "thiazyl". The following mesomeric structures explain these different behaviour best.
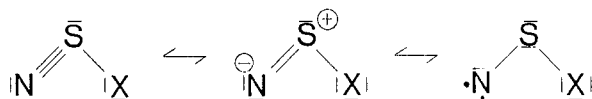
A completely different type of reaction is observed between HNF₂ or KF·HNF₂ respectively and FSN. Reaction takes place presumable through an addition – elimination mechanism leading to the unstable intermediate F₂N-S≡N which decomposes:

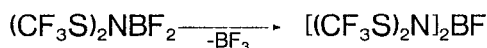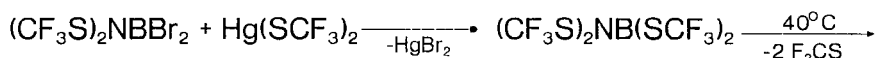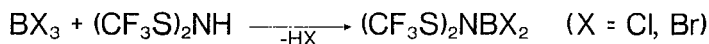$$\begin{matrix} HNF_2 \\ \\ KF \cdot HNF_2 \end{matrix} +FSN \longrightarrow \left(\begin{matrix} F_2N \\ S \equiv N \\ F \quad\quad H \end{matrix} \right) \xrightarrow[-KHF_2]{-HF} (F_2N\text{-}S\equiv N) \longrightarrow N_2F_4 + S_4N_4$$

Carbon–sulphur exchangeability raises the question of the existence of (CF₃)₂S=N-S≡N. When (CF₃)₂S=NH is reacted with FSN in CH₂Cl₂/CD₂Cl₂ the formation of (CF₃)₂S=N-S≡N can be assumed according to ¹⁹F- and ¹⁴N–NMR measurements. The unstable intermediate decomposes to the final products CF₃SCF₃, S₄N₄ and nitrogen (ref. 22).

EQUIVALENCE BETWEEN (CF₃S)₂N- AND FLUORINE

The bis(trifluoromethylthio)amino radical must be considered as a second–order derivative parafluorine and its high group electronegativity of 3.7 (ref. 23) supports this classification. The hydrogen derivative (CF₃S)₂NH is a weak acid –pK_D (in dioxan/water) = 9.99 (ref. 24) – and with HgO the compound Hg[N(SCF₃)₂]₂ (ref. 25) is formed. Similarly to F₂NNF₂ (ref. 26), O₂NNO₂ (ref. 27), and (CF₃S)₃CC(SCF₃)₃, (ref. 28), its dimer (CF₃S)₂NN(SCF₃)₂, (ref. 29), dissociates at 20°C like a halogen to 2 (CF₃S)₂N; K₁ = 4 ± 2·10⁻⁶ M at 25°C, H_diss. = 32 ± 2 kJ·mol⁻¹ (7.7 kcal mol⁻¹).

In the ¹H–NMR spectrum of (CF₃S)₂NCH₂N(SCF₃)₂, prepared from (CF₃S)₂NH and HC(O)H at 0°C (0.5 h) in the presence of 100 % H₂SO₄, δ(CH₂) is found to be 5.15 and compares well with δ(CH₂) = 5.99 in CH₂F₂, (ref. 30). In boron trihalides, (CF₃S)₂N is able to replace halogens, forming [(CF₃S)₂N]ₙBX₃₋ₙ. Only monosubstitution to (CF₃S)₂NBX₂ is observed when BCl₃ or BBr₃ react with (CF₃S)₂NH. The corresponding (CF₃S)₂NBF₂ can only be made by thermal decomposition of (CF₃S)₂NB(SCF₃)₂ at 40°C. It is not very stable and above 60°C gives off BF₃, forming [(CF₃S)₂N]₂BF, (ref. 31).

$$BX_3 + (CF_3S)_2NH \xrightarrow[-HX]{} (CF_3S)_2NBX_2 \quad (X = Cl, Br)$$

$$(CF_3S)_2NBBr_2 + Hg(SCF_3)_2 \xrightarrow[-HgBr_2]{} (CF_3S)_2NB(SCF_3)_2 \xrightarrow[-2 F_2CS]{40°C}$$

$$(CF_3S)_2NBF_2 \xrightarrow[-BF_3]{} [(CF_3S)_2N]_2BF$$

Further substitution of BX_3 (X = Cl, Br) is only achievable in the reaction of stoichiometrical amounts of $(CF_3S)_2NBX_2$ and $Hg[N(SCF_3)_2]_2$, giving $[(CF_3S)_2N]_2BX$. A complete exchange takes place when excess $Hg[N(SCF_3)_2]_2$ reacts with BBr_3, yielding $B[N(SCF_3)_2]_3$ in 93 % yield. When BCl_3 is used instead of BBr_3 the yield drops to 55 % at $80^{\circ}C$. Completely unexpected is the formation of the trisaminoborane from $B(SCF_3)_3$ and the mercurial

$$(CF_3S)_2NBX_2 \quad + \quad \longrightarrow [(CF_3S)_2N]_2BX$$
$$(X = Cl, Br; \text{ ratio } 2:1)$$
$$BX_3 \quad + Hg[N(SCF_3)_2]_2 \longrightarrow B[N(SCF_3)_2]_3$$
$$B(SCF_3)_3 \quad + \quad \longrightarrow B[N(SCF_3)_2]_3 + Hg(SCF_3)_2$$

In order to understand the reactions of $(CF_3S)_2NH$ or $Hg[N(SCF_3)_2]_3$ with BX_3 (X = F, Cl, Br, SCF_3) it is necessary to consider the radicals CF_3S as parachlorine (pCl) and $(CF_3S)_2N$ as parafluorine (pF) according to the element displacement principle. With BF_3 and $H(pF) \triangleq [(CF_3S)_2NH]$ or $Hg(pF)_2 \triangleq (Hg[N(SCF_3)_2]_2)$ no reaction takes place. Similarly no metathetical exchange occurs between BF_3 and HF or HgF_2. But BCl_3 and BBr_3 react with $H(pF)$ to give monosubstituted boranes in agreement with HF fluorinations of BX_3 (X=Cl, Br). The only difference between $(pF)BX_2$ and FBX_2 is that the former are more stable than the mixed boron halides and the reaction with $H(pF)$ stops after monosubstitution. When $Hg(pF)_2$ is used, according to reaction conditions, mono–, di–, and trisubstituted boranes are formed with BX_3. In addition, the reaction between $Hg[N(SCF_3)_2]_2$ and $B(SCF_3)_3$ is in agreement with the preparation of BF_3 from BCl_3 and HgF_2 according to:

$$2B(pCl)_3 + 3Hg(pF)_2 \longrightarrow 2B(pF)_3 + 3Hg(pCl)_2$$
$$(CF_3S)_2N = pF; CF_3S = pCl$$

Decreasing yields going from BBr_3, $B(SCF_3)_3$, to BCl_3 at $25^{\circ}C$ are in good agreement with known reactivities of BX_3 and also show that parachlorine (CF_3S) is more reactive than Cl in this metathesis (ref. 32).

INTERCHANGEABILITY OF ELEMENTS AND PARAELEMENTS IN KNOWN STRUCTURES

Elements and paraelements can be exchanged without structural alterations. Of the many examples, this exchangeability is demonstrated for molecules with adamantane structures. Phosphorus, arsenic, and antimony form oxides with the formula E_4O_6 (E = P, As, Sb) which have the adamantane structure. An analogous nitrogen compound, N_4O_6 with a corresponding structure is unknown and N_2O_3 is stable only at low temperature. If, oxygen is replaced by a pseudooxygen unit such as, e.g., CH_2, hexamethylenetetramine $N_4(CH_2)_6$ is obtained. Further replacement of N by CH leads to adamantane $(CH)_4(CH_2)_6$ itself. Consequently it is possible to replace elements in an unknown inorganic compound, as N_4O_6 by elementlike groups such as CH_2 or CH to obtaining $N_4(CH_2)_6$ and the organic molecule $(CH)_4(CH_2)_6$.

It has been generally established that compounds with the adamantane structure are formally made up of elements of Groups 15 and 16 in the ratio 4 : 6. These may be replaced either completely or in part by the corresponding pseudo– or paraelements. Accordingly, adamantane $(CH)_4(CH_2)_6$ consists of four pseudonitrogen and six pseudooxygen atoms. All substances with an adamantane structure so far synthesized correspond to this composition (ref. 33,34). Only recently was it possible to synthesize two basic adamantanes of the formula $(HSi)_4S_6$ and $(HSi)_4Se_6$. They are made by reacting $HSiCl_3$ with $(H_3Si)_2E$ (E = S, Se) at $20^{\circ}C$ (14 days) according to:

$$(H_3Si)_2E + HSiCl_3 \xrightarrow{AlCl_3} (HSi)_4E_6 + H_3SiCl$$

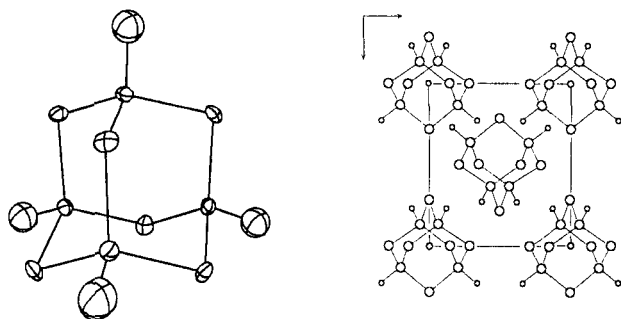Fig. 5. Structure of (HSi)$_4$S$_6$ and its packing diagram.
Projection on a, c along –b.

Fig. 6. Molecular structure of
(CF$_3$Ge)$_4$S$_6$ and (CF$_3$Ge)$_4$Se$_6$

An X–ray structure determination proves the expected adamantane structure for (HSi)$_4$S$_6$ and spectroscopic investigations left no doubt that (HSi)$_4$Se$_6$ has the same structure. The molecular structure of the silathiaadamantane (ref. 35) is shown in Fig. 5.

These sulfenylation and selenination reactions using the corresponding silyl compound are also applied for the preparation of germanium adamantanes. According to reaction conditions presented below it is possible to synthesize the corresponding trifluoromethylgermanium adamantanes.

$$4\ CF_3GeCl_3 + 6\ (H_3Si)_2E \longrightarrow (CF_3Ge)_4E_6 + 12\ H_3SiCl$$
$$E = S,\ in\ CS_2\ at\ 80°C\ (7d).$$
$$E = Se,\ in\ n\text{-hexane at } 110°C\ (4d).$$
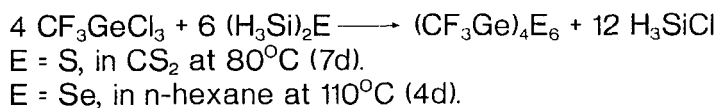
They crystallize in regular octahedrons and their expected structures are confirmed by X–ray structural analyses presented in Fig. 6.

In addition spectroscopic investigations prove that both compounds have adamantane structures.

The structures of tin–sulphur compounds of the general formula (RSnS$_{1.5}$)$_x$ are still an unsolved problem. Only for (CH$_3$Sn)$_4$S$_6$ an adamantan structure is proved (ref. 37). Very little is known about the others, named "organotinsequisulfides", with a suitable stoichiometry. Because of their physical properties it was suggested that they form polymers, (ref. 38). In order to improve their solubility it was essential to synthesize molecules with large organic substituents R.

Organotrichlorostannanes are used as starting materials. As sulfenylating agents either (CH$_3$)$_3$SiSSi(CH$_3$)$_3$ or Na$_2$S·9H$_2$O are used depending on the stability of RSnCl$_3$. The following reactions were carried out

$$4\ RSnCl_3 + 6\ (CH_3)_3SiSSi(CH_3)_3 \dashrightarrow (RSn)_4S_6 + 12\ (CH_3)_3SiCl$$
$$R = 3\text{-F·C}_6H_4,\ C_6F_5$$
$$4\ R'SnCl_3 + 6\ Na_2S \longrightarrow (R'Sn)_4S_6 + 12\ NaCl$$
$$R' = 2,4,6\text{-(CH}_3)_3\text{·C}_6H_2,\ 1\text{-naphthyl},\ 4\text{-CH}_3\text{·C}_6H_4,$$
$$4\text{-CH}_3O\text{·C}_6H_4,\ 4\text{-F·C}_6H_4,\ 3\text{-F·C}_6H_4.$$
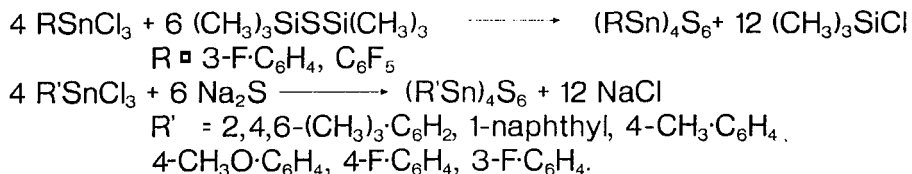
Their structure are elucidated by determining the intensity ratio of geminal [119]Sn– [117]Sn couplings. In case of equal relaxation times for two isotopes – this is almost accomplished for [119]Sn and [117]Sn –, molecules of the type R$_3$SnSSnR$_3$, (R$_2$SnS)$_3$ and (RSn)$_4$S$_6$ shall provide in their ^{119}Sn NMR spectra the splitting pattern (singulet plus two side bands) shown in Fig. 7 with different intensities according to the number of geminal tin atoms in the molecule. For compounds of composition (RSn)$_4$S$_6$ structures A and B have to be considered. In case of B the coupling constants J(Sn$_1$ – Sn$_2$) and J(Sn$_1$ – Sn$_4$) must be different.
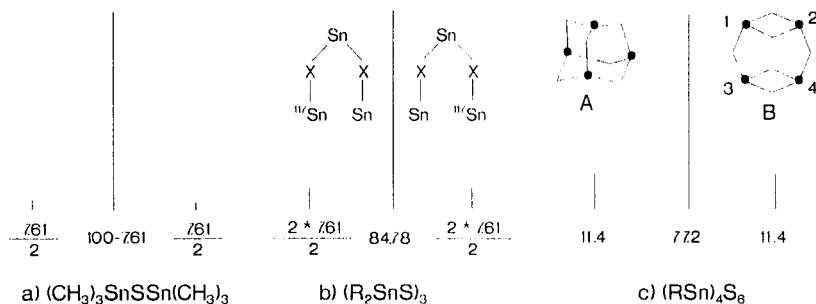
Fig. 7.
Theoretical splitting pattern
and intensity distribution for
a,b and c

a) (CH₃)₃SnSSn(CH₃)₃   b) (R₂SnS)₃   c) (RSn)₄S₆

If R contains an NMR active substituent, splitting of the signals takes place which provides additional information for elucidating structures. This is convincingly demonstrated for the series [(4-CH₃-C₆H₄)₂SnS]₃, [(4-F-C₆H₄)₂SnS]₃ and (4-F-C₆H₄Sn)₄S₆. Their spectra are presented in Fig. 8.

a) [(4-CH₃C₆H₄)₂SnS]₃   b) [(4-FC₆H₄)₂SnS]₃   c) (4- FC₆H₄Sn)₄S₆
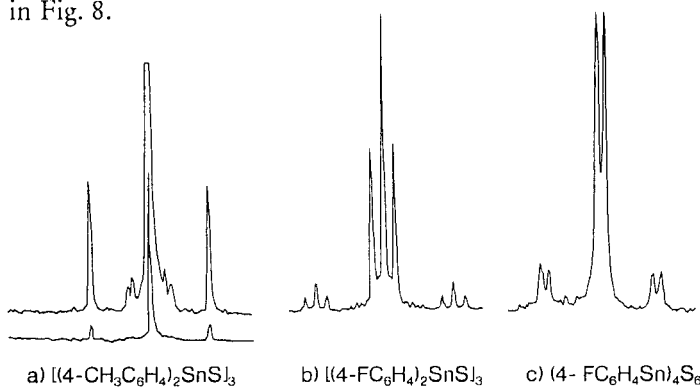
Fig. 8. Broadband-¹H-decoupled ¹¹⁹Sn-NMR spectra of a,b and c
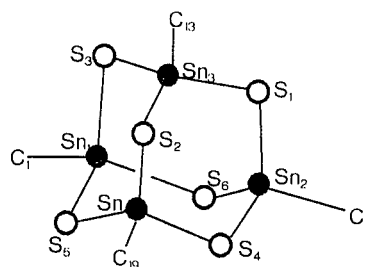
Fig. 9. Structure of (C₆F₅Sn)₄S₆ (C₆F₅ ≙ C)

The intensities measured for the compounds synthesized, except the ones with R = 2,4,6-(CH₃)₃-C₆H₂, 4 -CH₃O-C₆H₄ and C₆F₅ are in good agreement with the calculated values. This leaves little doubt about the adamantane structures for (RSn)₄S₆ in solution. An X–ray structure determination proved for (C₆F₅Sn)₄S₆ the same geometry, Fig. 9.

These results prove quite clearly that "organotinsesquisulphides" have an adamantan structure as demanded by the element displacement principle, (ref. 39).

ELECTRONEGATIVITIES

Paraelements, derived from element displacement, exhibit chemical properties which are largely determined by the coordinated central element and which resemble those of neighbours on the right within a period in the periodic system. Thus, e.g., CF₃ resembles fluorine and CF₃S resembles chlorine. Such an assignment is very difficult for higher order derivative paraelements, e.g., (CF₃S)₂N and (CF₃SC)₄N·[tetrakis(trifluoromethylthio)-pyrrolyl]. Both compounds have nitrogen as the base element but (CF₃S)₂N is a parafluorine (pF) and (CF₃SC)₄N a parachlorine (pCl). The chemical properties of these paraelements, as shown, confirm these assignments. Group electronegativities might be one criterion that might help to solve such problems, e.g., the members of the series OII, NII₂, and CII₃ have chemically much less in common with fluorine than OF, NF₂, and CF₃, although the former are isoelectronic and isoprotonic with fluorine and the others only electronically isovalent. The group electronegativities of the two series show this quite convincingly as they differ by at least one unity. Group electronegativities of fluorinated paraelements which have been determined experimentally may be placed between those of fluorine and bromine, giving the following sequence: F (4.0); OF (3.8); OOF (3.8); (CF₃S)₂N (3.7); CF₃OO (3.7); CF₃ (3.3); CF₃SNII- (3.2); Cl (3.0); (CF₃SC)₄N. (2.9); CF₃S (2.7); Br (2.8). This shows that incorporation of paraelements in the periodic system smoothes out sudden changes in the properties of elements in going over from one period to the next, (ref. 4).

A final comment remains to be made: paraelements are in all instances molecular moieties while elements describe atomic building blocks. Both paraelements and elements display very similar features and, as this summary has shown, both have very closely related reaction chemistry. The molecular nature of paraelements allows for an additional feature, observed only for paraelements, namely the ability to undergo dissociation, addition, condensation and elimination reactions under appropriate conditions. The element displacement principle discussed here does not permit predictions of such reactivities by comaprison to reference elements, where such reactions are generally not observed. The concept provides nevertheless a valuable approach with predictive value, when attention is focussed solely on reactions bonding and structures situations common to both paraelements and reference elements.

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