

Some aspects of fluorine chemistry in Göttingen

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Abstract

The review gives a short summary of some developments in fluorine chemistry in Göttingen. A major part covers sulphur-nitrogen-fluorine compounds and their derivatives. Furthermore the chemistry of organometallic fluorides of main group and transition elements is described. Fluorine containing compounds of group 4 and group 13 are good candidates for catalysis and material science. © 1999 Elsevier Science S.A. All rights reserved.

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In his widely read book *Le Fluor et ses Composés*, published in 1900, Henri Moissan described how he produced fluorine for the first time in 1886 and demonstrated that it is an element with an extraordinary high reactivity. It was clear from the outset, therefore, that this element challenges chemists to work with it. This is one of the two reasons why I started to practise Fluorine Chemistry. The other stems from the long tradition of Fluorine Chemistry in Göttingen.

Due to the rapid development of science in the early 1900s, the University of Göttingen founded a Faculty of Mathematics and Science in 1922. This incorporated the Chemistry Department, which up to that time had been part of the Faculty of Medicine. Otto Wallach (1889–1915), Adolf Windaus (1915–1944), and Hans Brockmann (1945–1972) were the outstanding organic chemists of the time. Gustav Tammann (1908–1929), Arnold Eucken (1929–1950) and Wilhelm Jost (1953–1971) became the pioneers of an excellent school of physical chemistry. The chair of inorganic chemistry was held by Richard Zsigmondy (1908–1929), Hans von Wartenberg (1933–1948) and, later on, by Oskar Glemser (1952–1979). Fluorine chemistry in Göttingen was started by von Wartenberg, promoted strongly by Glemser, and is now my field of endeavour.

1. The von Wartenberg era



Hans von Wartenberg [1] was a chemist blessed with excellent experimental skills, who openly declared that he liked particularly tricky experimental problems. This special mentality strongly influenced his choice of research topics. His research publications (more than 150 papers) reveal that he did not specialize in only one field but was an ‘universal chemist’, working in physical, organic and inorganic areas of his subject. His Ph.D. thesis, completed in Berlin in 1902, describes research on oxyhalides of mercury; he then became a co-worker of Walter Nernst, who at that time was professor of Physical Chemistry in Göttingen.

His stay in Göttingen at that time was not very long because Nernst left the university in 1905 and went to Berlin taking his young co-worker with him.

During his time with Nernst, von Wartenberg designed and constructed electrical equipment containing platinum and porcelain or iridium components for use in thermochemical studies on inorganic compounds at temperatures up to 1300°C or 2000°C, respectively. His work in this area

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continued throughout his research career, the final piece involving determination in 1959 of the heats of formation of La_2O_3 and $\text{La}(\text{OH})_3$.

In 1913 von Wartenberg moved from Berlin to the University of Danzig, where he first became a full professor of Physical Chemistry, and later (1916) full professor of Inorganic Chemistry. It was in Danzig that he commenced his pioneering researches on fluorine and its compounds, his major interest being in the thermochemistry of inorganic fluorides; and by 1921 he had conducted his first experiments using elemental fluorine, generated electrolytically using a cell based on the technical procedure developed by Moissan and Ruff.

In 1932 von Wartenberg was offered the chair of Inorganic Chemistry at the University of Göttingen; he accepted, and thus became the successor to Tammann and Zsigmondy. With the financial support of the Rockefeller Foundation, the then-existing Institute of Inorganic Chemistry was enlarged and renovated, providing him with enough space to expand his research interests. Unfortunately his work was interrupted in 1936 when, due to the political situation, he was forced to retire and leave the Institute. At the same time the chair he held was abolished, hence for about 10 years Inorganic Chemistry was no longer viewed as an important discipline in the Chemistry Department. However, von Wartenberg's work was not stopped completely but only interrupted, because his colleague R.W. Pohl offered him some rooms in the Institute of Physics where he was able to continue to do some experiments. Inevitably, his research output decreased, but not its quality. During the years of his forced retirement he confirmed that $\text{KF} \cdot 3 \text{HF}$, which had been proposed earlier (1925–1927) by Lebeau and Damiens as an electrolyte in fluorine cells, was a definite compound. Moreover, for the first time he obtained pure white CuF_2 and used it in calorimetric studies on copper fluorides, observing that this compound dissociates at its melting point, giving CuF and F_2 ; on cooling, the CuF disproportionated into CuF_2 and Cu . Furthermore, he measured the heat of formation of AgF_2 and succeeded in preparing colourless crystals of PbF_4 , CeF_4 and BiF_5 . Finally, he produced CrF_3 , CrF_4 and CrF_5 from chromium metal and fluorine.

After the end of World War II (1945) von Wartenberg was reinstated to his former position at Göttingen, and retired normally in 1948. Even after his retirement he worked regularly in his laboratory and always came up with new and often surprising results. Like many great scientists von Wartenberg was quite a character. For example, he liked to sit in a rocking chair and move to and fro while speaking to his co-workers and colleagues. Since he always spoke with a very low voice, those listening to him had to move with him, back and forth. So people coming out of his laboratory after sessions of some 20 or 30 min were always sick!

The successor to the chair of inorganic chemistry was Oskar Glemser, who came to Göttingen in 1951.

2. Oskar Glemser's reign

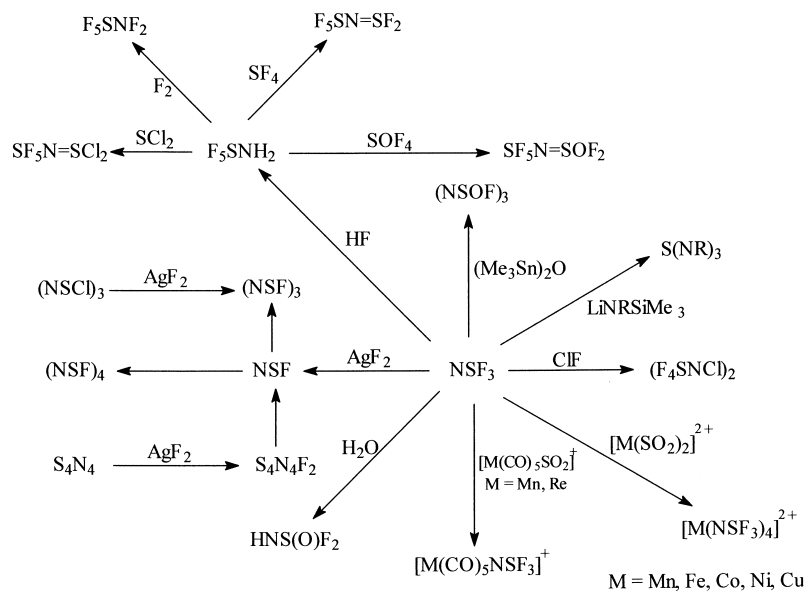


Oskar Glemser graduated from the University of Stuttgart and then moved to the Technische Hochschule in Aachen in 1939. There he discovered new metal oxides and hydroxides of nickel, molybdenum and tungsten. In Göttingen, influenced by von Wartenberg, he changed his research field and began to work with inorganic fluorides sulphur-nitrogen-fluorine compounds and various non-metal and metal fluorides. Since that time, Fluorine Chemistry remained the major research pre-occupation for Glemser and many of his co-workers.

Shortly after Glemser's arrival in Göttingen, von Wartenberg showed him a fluorine generator which he had constructed, and said that he could use it to produce F_2 for experiments such as the direct fluorination of S_4N_4 (tetrasulfur tetranitride, an orange-yellow solid)¹. However this nitride reacted explosively with pure F_2 or even F_2 diluted with N_2 . So a procedure involving AgF_2 (made using F_2) as the fluorinating agent was developed. Thiacyl fluoride ($\text{N}=\text{SF}$) and a number of other sulphur-nitrogen-fluorine compounds were obtained. This was the beginning of a long research period for Glemser in the field of Fluorine Chemistry, with NSF and NSF_3 proving to be key substances in the promotion of his group's researches. The highlights of Glemser's sulphur-nitrogen-fluorine chemistry are compiled in Scheme 1. The exceptional properties of fluorinated compounds in comparison to those of other halides, and the idea of applying them as insecticides or pesticides, prompted many chemists to work in this field [2–4].

Oskar Glemser, now in his 88th year, has received many honours (Member of the Akademie der Wissenschaften in Göttingen, the Österreichische Akademie der Wissenschaften in Vienna, the Deutsche Akademie der Naturforscher 'Leopoldina' in Halle, the Centro di Logica e Scienze Comparete in Bologna, the New York Academy of Science, and the American Association for the Advancement of Science; Associate Member of the Jozef Stefan Institute in

¹Working with elemental fluorine in those early days was a very dangerous task, made worse by the fact that at the time the Institute was more than 100 years old and had wooden floors and partly old equipment. The only more or less safe place was a solid stone building where Friedrich Wöhler accomplished his famous chemistry in the last century (it was said that even Wöhler did experiments with hydrogen fluoride). Later on, in the Fluorine Chemistry period, this building was called the 'witches kitchen'. The 'witches' (young enthusiastic students) more than once produced big explosions, which resulted in fires, injuries and cauterisations, and it is said that one doctor close by earned a fortune during the 'elemental fluorine period'.



Scheme 1. Highlights of Glemser's N-S-F research.

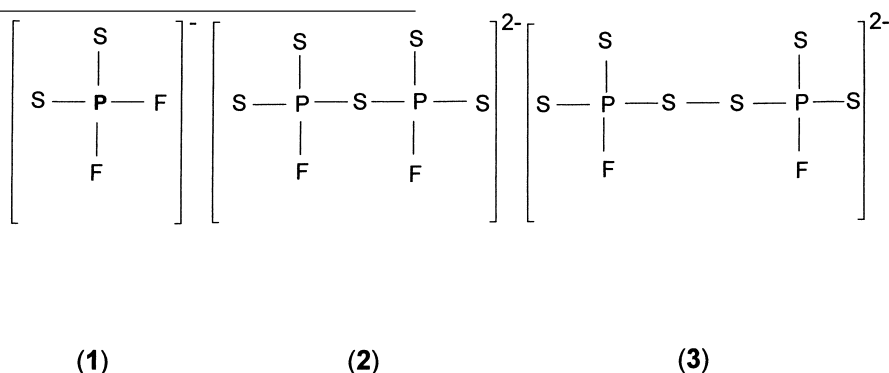
Ljubljana). He retired in 1979 but is still working with a small group of researchers. One of the most important events in Glemser's career as a fluorine chemist was the 2nd European Symposium on Fluorine Chemistry, which was held in the 100-year-old building at the University of Göttingen in 1968 (the Department of Chemistry did not move to a new modern building outside the old city until 1972); some 200 fluorine chemists from all over the world attended. In 1970 he received the Liebig Denknünze and was the President of the German Chemical Society in 1976–77 and President of the inorganic division of IUPAC (1969–73).

3. Accomplishments of Herbert Roesky's group



After receiving a Diploma in Chemistry from Göttingen in 1961, I started working for a Ph.D. in Glemser's group, using elemental fluorine and metals such as chromium, manganese, lead, bismuth and rhenium in an autoclave or in a fluidized bed to generate the corresponding fluorides in high oxidation states [5–9]. Since fluorine was not commercially available in Germany then, we had to prepare it using the well-known electrochemical process. I still remember the frequent explosions we had when the cell was first turned on due to the water content of the HF we used.

After finishing my Ph.D. work I took up a postdoctoral position (1963–1966) in Göttingen and at DuPont's Experimental Station in Wilmington, where, under the supervision of Earl Muetterties, I was asked to work in aluminium chemistry. However, I had enough freedom to develop my own chemistry in the phosphorus-fluorine field, and prepared a new class of thiosphosphates from alkali-metal fluorides and P_4S_{10} which contained anions 1–3 [10,11].



Caesium difluorodithiophosphate can also be prepared in almost quantitative yield via the reaction $2 \text{SPF}_3 + 2 \text{CsF} \rightarrow \text{CsS}_2\text{PF}_2 + \text{CsPF}_6$ using acetonitrile as a solvent. Studies on $(\text{S}_2\text{PF}_2)_2$, prepared from CsS_2PF_2 and bromine, and the corresponding acid $\text{HSP}(\text{S})\text{F}_2$ have revealed the existence of a large class of metal chelates whose distinguishing features are relatively high volatility and unusual reactivity. Established examples of this class include mono-chelates of Cu(I), Ag(I), bis-chelates of divalent Mn, Fe, Co, Ni, Pd, Zn, Cd, and Hg and tris-chelates of trivalent Cr and Co [12]. Volatile derivatives of Ni, Co, Mn, Cr, Zn, and Cd have been prepared using $\text{R}(\text{F})\text{P}(\text{S})\text{SH}$ ($\text{R} = \text{Me}, \text{Et}$) and the metals as starting materials [13,14].

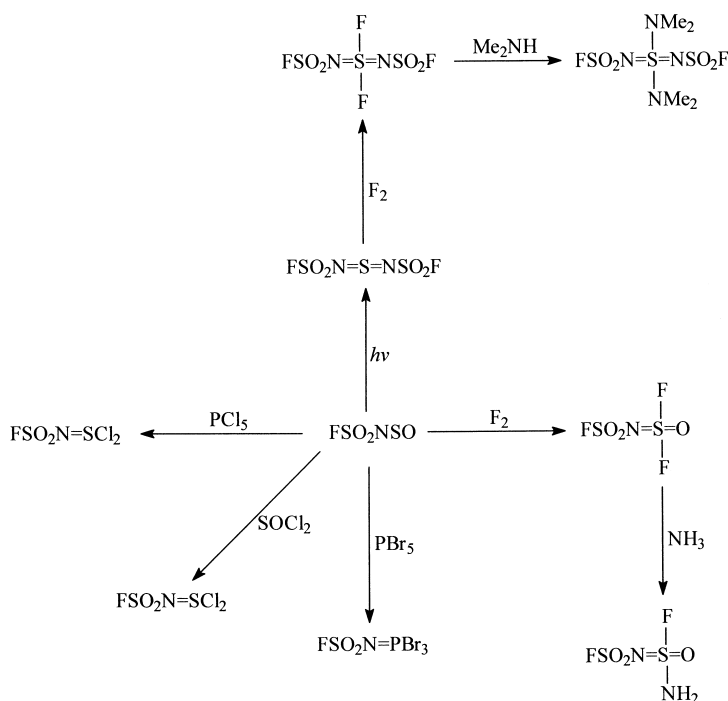
The thiophosphoryl halides SPF_3 and SPFCl_2 can be converted to the corresponding amides $\text{S}=\text{PF}_2\text{NH}_2$ and $\text{S}=\text{PFCINH}_2$ [15,16], which have a broad chemistry; e.g., SPF_2NH_2 has been used to obtain $\text{SPF}_2\text{N}=\text{PF}_3$ and numerous analogues ($\text{SPF}_2\text{N}=\text{PF}_2\text{X}$, where $\text{X} = \text{Br}, \text{NH}_2$, or OH), $\text{SPF}_2\text{N}=\text{PCl}_3$, $\text{SPF}_2\text{N}=\text{NPF}_2\text{N}=\text{PCl}_3$, $\text{SPF}_2\text{N}=\text{PCl}_2\text{N}=\text{PCl}_3$, $\text{SPF}_2\text{N}=\text{PF}_2\text{N}=\text{C}=\text{NSiMe}_3$ [17–20]. In this connection it is worth mentioning that the first $-\text{N}=\text{PBr}_3$ compound was obtained from FSO_2NSO and PBr_5 ; FSO_2NSO , prepared from FSO_2NH_2 and SOCl_2 , turned out to be a versatile compound for preparing FSO_2N -derivatives (Scheme 2) [21–27]. Furthermore, the availability of the tetraza compound $\text{FSO}_2\text{N}=\text{S}(\text{NMe}_2)_2=\text{NSO}_2\text{F}$ enabled work on the chemistry of aza analogues of sulfate to be initiated.

Subsequently these types of reaction were extended to $\text{CF}_3\text{SO}_2\text{NSO}$, prepared from $\text{CF}_3\text{SO}_2\text{NH}_2$ and SOCl_2 [28,29]. The most prominent derivatives obtained were

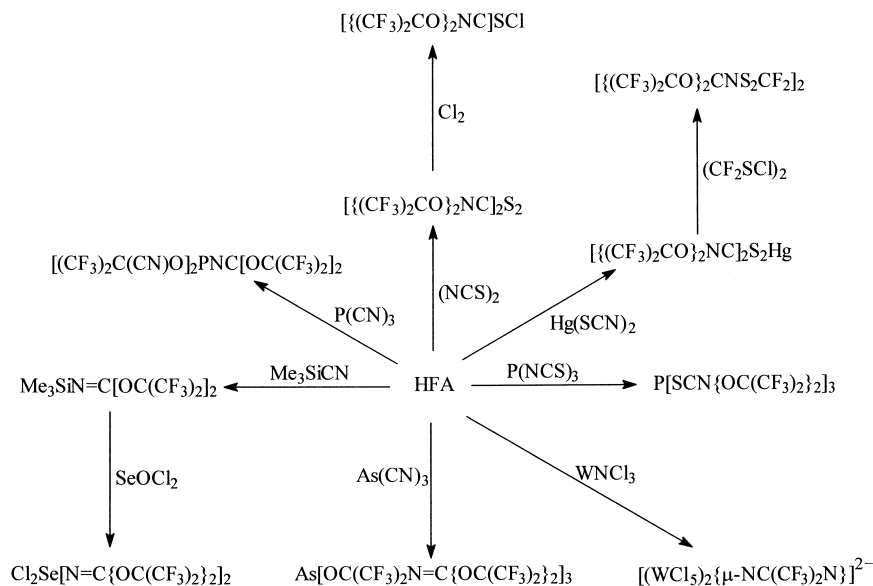
$\text{CF}_3\text{SO}_2\text{N}=\text{SF}_2=\text{NSO}_2\text{CF}_3$, $\text{CF}_3\text{SO}_2\text{N}=\text{PCl}_3$, $\text{CF}_3\text{SO}_2\text{N}=\text{SF}_2\text{O}$, $\text{CF}_3\text{SO}_2\text{NHSO}_2\text{F}$ and $\text{CF}_3\text{SO}_2\text{N}=\text{PBr}_3$.

In 1970 I moved with 10 very good students from Göttingen to Frankfurt, where I held a Chair in Inorganic Chemistry for nearly 10 years. In the following years we demonstrated the use of tin-nitrogen compounds for the preparation of nitrogen-containing derivatives based on the facile formation and cleavage of Sn-N bonds [30]. (This type of cleavage reaction was later frequently copied by other groups.) For example $\text{CF}_3\text{SO}_2\text{NSO}$ was found to react with $(\text{Me}_3\text{Sn})_3\text{N}$ to give $\text{CF}_3\text{SO}_2\text{N}(\text{SnMe}_3)_2$ and Me_3SnNSO [31], while the cyclotriphosphazene $\text{P}_3\text{N}_3\text{F}_6$ and $(\text{Me}_3\text{Sn})_3\text{N}$ gave $\text{P}_3\text{N}_3\text{F}_5\text{N}(\text{SnMe}_3)_2$, accompanied by elimination of Me_3SnF [32,33]. From there, $\text{P}_3\text{N}_3\text{F}_5\text{N}=\text{S}=\text{O}$, $\text{P}_4\text{N}_4\text{F}_6(\text{NSO})_2$ and $\text{P}_3\text{N}_3\text{F}_5\text{NCO}$ were synthesised via treatment of the corresponding P-N-F compounds with SOCl_2 , and used as starting materials for the preparation of various derivatives, such as $\text{P}_3\text{N}_3\text{F}_5\text{NSNP}_3\text{N}_3\text{F}_5$ [34], $\text{P}_4\text{N}_4\text{F}_6\text{N}_2\text{S}$ [35–38], and $\text{P}_3\text{N}_3\text{F}_5\text{N}_3\text{S}_3$ [39].

In Frankfurt, at the beginning of the 1970s, we isolated the perfluoroalkanesulfinic acids $\text{CF}_3\text{S}(\text{O})\text{OH}$ and $n\text{-C}_4\text{F}_9\text{S}(\text{O})\text{OH}$, the first members of their class to be prepared. They were obtained as stable (in glass at room temperature) colourless liquids following treatment of their hydrazinium salts (from $2 \text{R}_F\text{SO}_2\text{F} + 5 \text{N}_2\text{H}_4 \rightarrow 2 \text{R}_F\text{SO}_2[\text{N}_2\text{H}_5]^+ + \text{N}_2 + 2[\text{N}_2\text{H}_5]^+\text{F}^-$; $\text{R}_F = \text{CF}_3, n\text{-C}_4\text{F}_9$) with concentrated sulfuric acid [40,41]. Also during that decade we showed that $(\text{FSO}_2\text{NSO}_2)_2$ and $(\text{CF}_3\text{SO}_2\text{NSO}_2)_2$ form the 1:1 adducts $\text{FSO}_2\text{N}=\text{SO}_2\text{S}_4\text{N}_4$ and $\text{CF}_3\text{SO}_2\text{N}=\text{SO}_2\text{py}$ with S_4N_4 and pyridine, respectively [42–44]. Comparable adducts were obtained with FSO_2NCO [45]. A 10- and a



Scheme 2. Syntheses based on FSO_2NSO .



Scheme 3. Reactions of hexafluoroacetone (HFA).

Table 1
Hexafluoroarsenate complexes [52–75] (*highlights of the series)

[Zn(OS ₃ N ₂) ₆][AsF ₆] ₂	[Ag][Ag ₂ (CH ₂ O) ₆][AsF ₆] ₃
[Cd(OS ₃ N ₂) ₆][AsF ₆] ₂	[Ag(OCH ₂ CH ₂) ₈][AsF ₆]
[Ag(OS ₃ N ₂) ₂][AsF ₆]	[Ag ₂ (Ph ₂ S ₂) ₄][AsF ₆] ₂
[Zn(S ₂ N ₂ CO) ₆][AsF ₆] ₂	[Ag ₂ (Ph ₂ Se) ₄][AsF ₆] ₂
[Zn{S(NSO) ₂ } ₂][AsF ₆] ₂	[Ag(1,3-C ₄ H ₈ O ₂) ₃][AsF ₆]
*[Ag(S ₈)]AsF ₆	[Ag{(CN) ₂ } ₂] _n [AsF ₆] _n
*[Ag(S ₄ N ₄ O ₂) ₄][AsF ₆]	[PhPH ₂ Ag{μ-(PhPH) ₂ } ₂][AsF ₆] ₂
[Ag ₄ {S(NSO) ₂ } ₉][AsF ₆] ₄	*[Ag{S _n (CN) ₂ }] _n [AsF ₆] _n (n = 3, 4)
[Zn{P(O=P(OC ₂ H ₅) ₂) ₃ } ₂][AsF ₆] ₂	*[Ag(NCS) ₂] _n [AsF ₆] _n
[Ag ₂ {(CH ₂ S) ₃ } ₅][AsF ₆] ₂	

12-membered sulphur-nitrogen ring was isolated using the CF₃SO₂ group as an electron-withdrawing substituent, namely (CF₃SO₂NS)₄S₂ and (CF₃SO₂NS₂)₄, respectively [46–48]. Smaller S-N rings such as FSO₂N₃S₃ and CF₃SO₂N₃S₃ were prepared from S₃N₂O and FSO₂NSO and CF₃SO₂NSO, respectively, via the elimination of SO₂ [49]. The analogous phosphorus-containing compound P₃N₃F₅N₃S₃ was prepared in high yield from P₃N₃F₅N(SnMe₃)₂ and S₃N₂Cl₂ [50,51].

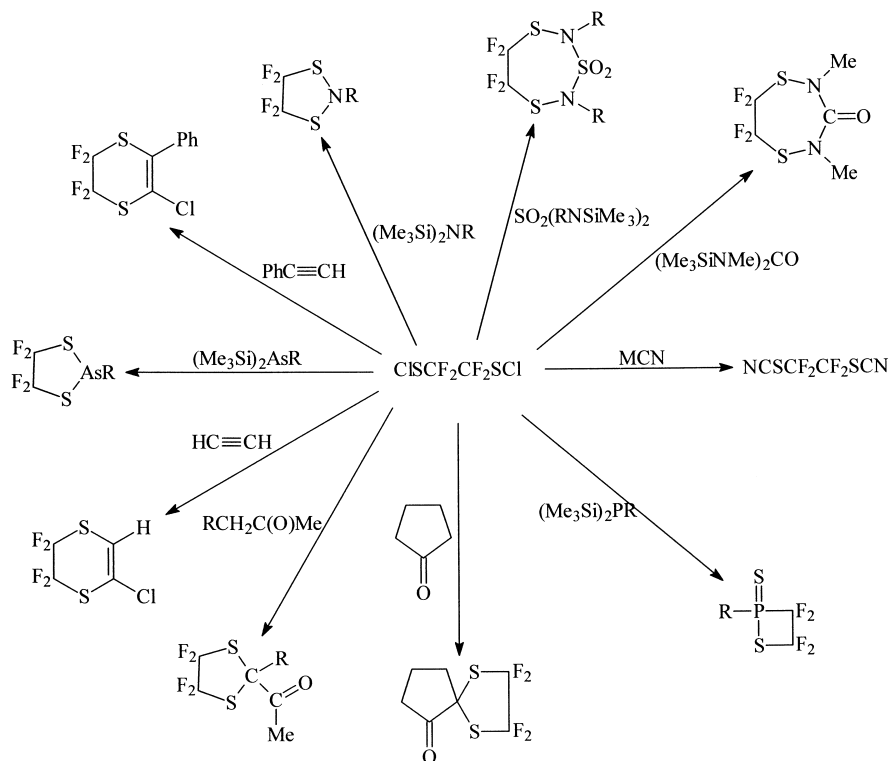
In the 1980s we developed some extensive co-ordination chemistry using AsF₆⁻ salts, preferentially of Ag⁺, Zn²⁺ and Cd²⁺. These systems are soluble in liquid SO₂ and easily form adducts with ligands having soft donors according to Pearson's principle. The complexes isolated are listed in Table 1 [52–75], the highlights of this series being the silver complexes of S₈, cyanogen and thiocyanogen. The cyanogen and thiocyanogen complexes form two- and one-dimensional polymers, which are the prototypes of recent materials research using CN-containing starting materials. The geometry around the silver cation was found to be linear, square planar and tetrahedral, respectively. The S₈ complex [Ag(S₈)₂][AsF₆] is the only co-ordination compound of S₈ reported so far.

3.1. Studies on hexafluoroacetone and tetrafluoro-1,2-ethanedisulphenyl dichloride

My researches on carbon-fluorine systems have focused on reactions involving hexafluoroacetone (HFA), tetrafluoro-1,2-ethanedisulphenyl dichloride, or 1,3,5-tris(trifluoromethyl)benzene. Results of work on reactions between hexafluoroacetone and CN- or SCN-compounds of main group and transition elements are summarised in Scheme 3; cyclization reactions involving the CN-moiety are catalysed by base, preferentially triethylamine. Of particular interest are the adducts of HFA with (SCN)₂ and Hg(SCN)₂, which are precursors for various new compounds containing six-membered rings [76–84]. Moreover, it was found that the dimer of hexafluorothioacetone reacts with nitriles of germanium, phosphorus, and arsenic to yield comparable insertion products [85,86] (Scheme 3).

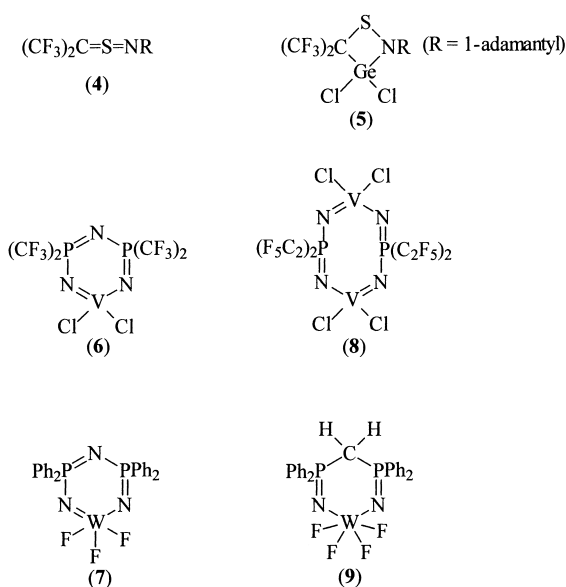
Tetrafluoro-1,2-ethanedisulphenyl dichloride was used extensively for the preparation of fluorine-containing heterocycles (Scheme 4) [87–89]. Of special interest are the reactions with cyclic ketones which result in the formation of spirocyclic ring systems via substitution of the activated hydrogens alpha to the carbonyl group. Furthermore, cleavage reactions involving reagents containing Si-N, As-Si and P-Si- bonds leads to various heterocycles [90–94] (Scheme 4).

A definite highlight from our development of sulphur-nitrogen chemistry was the synthesis of stable thione S-imides containing trifluoromethyl groups (**4**, R = 1-adamantyl or 1,1,3,3-tetramethylbutyl). Prepared from (CF₃)₂CClSCl and Me₃SiN(H)R, with subsequent metallation and elimination of the metal chloride, these thione S-imides undergo [2–4]-cycloaddition reactions with norbornene [95], and combine with dichlorogermylene at room temperature to yield [5–8] cycloadducts (e.g. **5**, R = 1-



Scheme 4. Reactions of tetrafluoro-1,2-ethanedisulfonyl dichloride.

adamantyl) [96] in which the bond angles of the four-membered CSN₂Ge ring are all close to 90°.



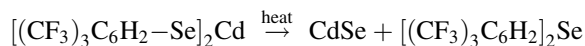
3.2. Chemistry without borders between main group and transition metal chemistry

This concept was used in a particularly elegant fashion in the synthesis of transition metal-containing phosphazenes. The (NPCl₂)_x compounds date back to 1834 and were first

made by Liebig, Wöhler, and Rose [97,98] by reactions of NH₃ or NH₄Cl with PCl₅, a method which is still used on both laboratory and industrial scales. In the past, researchers have concentrated mainly on substitution reactions of the chlorine atoms bonded to phosphorus. Our approach, however, has been different. We have replaced one, two or three of the phosphorus atoms in the cyclotri- and cyclotetra-phosphazenes by transition metal atoms, as exemplified by products **6–9** [99].

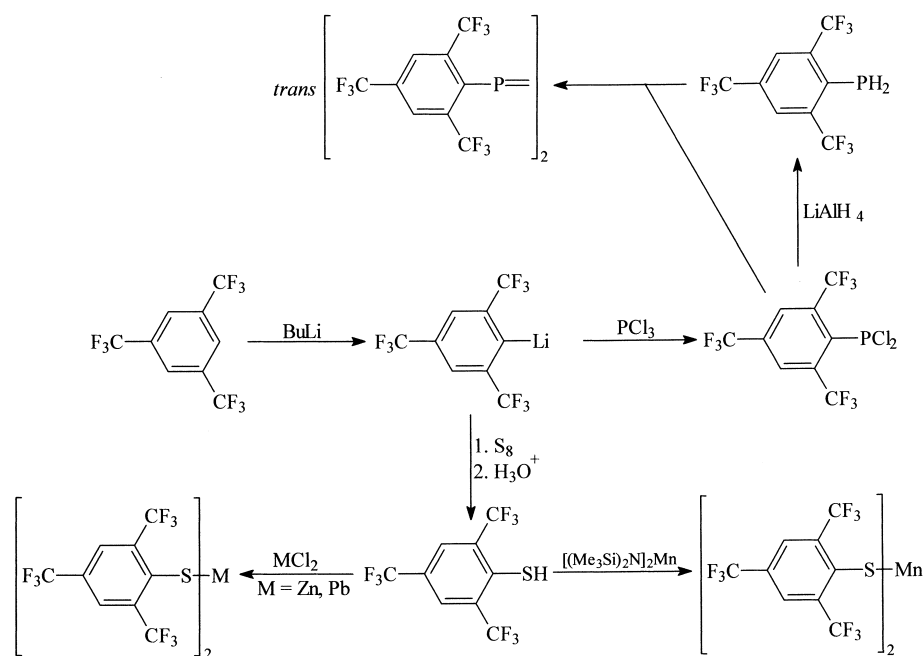
3.3. 2,4,6-Tris(trifluoromethyl)phenyl derivatives

Another area of research that is being actively investigated by my group concerns the development of highly volatile single-source precursors for the preparation of main group and transition metal based thin films by MOCVD processes. Mention should be made of the successful preparation of CdSe films using 2,4,6-tris(trifluoromethyl)phenyl as a ligand [100,101]:



The reaction of Cd[N(SiMe₃)₂]₂ with two equivalents of Ar_FSeH [Ar_F = 2,4,6-(CF₃)₃C₆H₂] afforded the starting material in good yield [102].

Moreover, the 2,4,6-(CF₃)₃C₆H₂ ligand was found capable of stabilizing species otherwise unstable or even unknown under ambient conditions. Obviously, steric crowding, electron-withdrawal, and agostic fluorine inter-



Scheme 5. Synthesis of 2,4,6-tris(trifluoromethyl)phenyl derivatives.

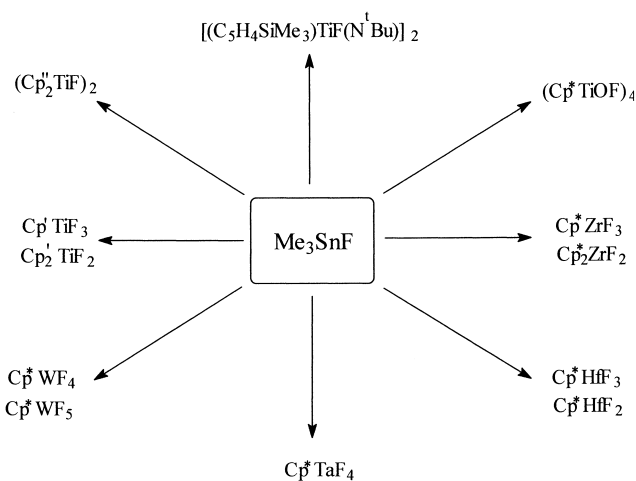
actions stemming from the CF_3 groups enhance the stabilities of the compounds. Some of the 2,4,6-tris(trifluoromethyl)phenyl compounds we have synthesized are shown in Scheme 5 [102–109].

3.4. Organometallic fluorides of main groups and transition elements

The term organometallic fluoride is used for compounds having both a metal-fluorine and a metal-carbon bond (C–M–F). Compounds of this type have a very polar metal-fluorine bond, often resulting in fluorine bridge formation, and a more covalent rather weak carbon-metal bond that is easily cleaved by oxidative fluorinating agents. This problem has been overcome to a large extent by the introduction of new fluorinating agents.

3.4.1. Trimethyltin fluoride

In recent years we have introduced Me_3SnF as a fluorinating agent for the preparation of group 4–6 and group 13–15 fluorides. It is easy to make from Me_3SnCl and sodium fluoride, and many starting materials used in the preparation of organometallic fluorides are readily available and conveniently handled as the chloro or bromo derivatives. Consequently, halide metathesis, using Me_3SnF in a stoichiometric amount, has proved to be one of the most reliable routes to the corresponding fluorides. Moreover, the resulting Me_3SnCl can be easily removed from the crude product, in vacuo, and recycled. The insolubility of Me_3SnF in weakly co-ordinating solvents, in combination with the high volatility of Me_3SnCl , makes this an ideal fluorinating system.



($\text{Cp}' = \text{C}_5\text{H}_4\text{Et}$; $\text{Cp}'' = \text{C}_5\text{H}_4\text{Me}$; $\text{Cp}^* = \text{C}_5\text{Me}_5$)

Scheme 6. Examples of organometallic fluorides prepared by treating the corresponding chlorides with Me_3SnF .

3.4.2. Preparation and reactions of group 4 cyclopentadienyl derivatives

Owing to the higher solubility of the fluorides in organic solvents, substituted cyclopentadienyl compounds of Group 4 were preferred substrates. Moreover, these systems give crystalline materials suitable for investigation by X-ray techniques. Scheme 6 shows a number of compounds made using Me_3SnF and reveals that mono- and bis-cyclopentadienyl derivatives as well as Ti(III) compounds can be prepared. Mixed fluoro-chloro group 4 compounds can be obtained by treating Cp^*MF_3 ($\text{Cp}^* = \text{C}_5\text{Me}_5$, $\text{M} = \text{Zr}, \text{Hf}$) with Me_3SiCl , and compounds of composition $\text{Cp}^*\text{MF}_2\text{Cl}$

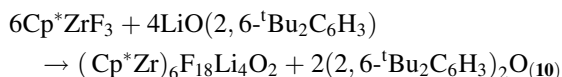
have been generated in almost quantitative yield. Products obtained by the reduction of Cp*TiF₃ are shown below (Eqs. 1–5).



Reduction of Cp*TiF₃ and Cp₂TiF₂ using group 1, 2 and 13 metals has led to the structural characterisation of several 'molecular solids' which show a wide range of metal fluoride environments. Furthermore (Cp₂TiF)₃(AlF₃) demonstrates the symbiosis between organometallic systems and Werner co-ordination compounds. The products in Eqs. 1–5 above are soluble in organic solvents due to the wrapping of the inorganic core by the organic ligands [110].

Of particular interest are the reactions of Cp*TiF₃ and Cp*ZrF₃ with AlMe₃. Methylation of Cp*TiF₃ with 2 equivalents of AlMe₃ gives Cp*TiMe₂F at room temperature and the reduced product Cp*₂Ti₂(μ-F)₈Al₄Me₈ at elevated temperature, with the release of methane. The single crystal structure of the latter product shows an octahedral metal core of Ti₂Al₄ with the two Ti atoms occupying trans positions [111]. Treatment of Cp*ZrF₃ with a molar equivalence of AlMe₃ results in selective exchange of fluorine for methyl, yielding [Cp*Zr(Me)F₃AlMe₂]₂. However, methane gas evolution is observed when Cp*ZrF₃ is treated with an excess of AlMe₃, yielding a fluorine-free cluster core of composition Zr₃Al₆C₇.

An interesting product (**10**) has been isolated from the following reaction:



This intercalated lithium oxide is another example of a trapped molecular solid surrounded by soluble Cp*ZrF₃ molecules.

3.5. Aluminium-fluorine compounds

The great differences in melting points and solubilities of AlCl₃ (subl. 183°C; m.p. 193°C at 1700 mbar) and AlF₃ (subl. 1272°C; m.p. 1290°C) indicate the problems associated with the preparation of organoaluminium fluorides.

While monofluorides R₂AlF (R = alkyl, aryl) have been known for many years, compounds of the type RAlF₂ have been mentioned only in the patent literature. Recently, however, we were able to prepare (Me₃Si)₃CAIF₂ from (Me₃Si)₃CAIME₂·THF and Me₃SnF. The initial product isolated was the solvate (Me₃Si)₃CAIF₂·THF, which lost THF in vacuo to afford the THF-free aluminium difluoride in the form of its trimer (Me₃Si)₃CAIF₂. This contains a

puckered six-membered ring which has been characterised by X-ray single crystal structure analysis and contains alternating aluminium and fluorine atoms; the aluminium atoms have distorted tetrahedral geometry with terminal fluorine atoms. The trimer [(Me₃Si)₃CAIF₂]₃ has been used to gain access to the novel anions [(Me₃Si)₃CAIF₃][−] and [(Me₃Si)₃CAIF₂]₂F[−].

Of particular interest is the oxidative addition of Ph₂SiF₂ to (Cp*Al)₄ leading to [(Cp*AlF)₂SiPh₂]₂. This product is a rare example of a structurally-characterised compound containing an eight-membered Al₄F₄ ring, and an unprecedented example of one possessing an Al-Si-Al bridge [112].

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