ELSEVIER

Journal of Fluorine Chemistry 100 (1999) 21–34

JOURNAL OF FLUORINE CHEMISTRY

www.elsevier.com/locate/jfluchem

Perfluoroorganoelement chemistry anticipating the 21st century

Alois Haas*

Department of Chemistry, Ruhr-Universität Bochum, FNO 034/036, D-44780 Bochum, Germany

Received 4 March 1999; received in revised form 17 August 1999; accepted 17 August 1999

Abstract

On the basis of the definition of perfluoroorganoelement compounds, their preparation and chemical reactions are described. The element displacement principle is developed and a periodic system of functional groups is provided. On this base R_fE- and functional groups are defined as paraelements. Evidence for this new concepts are provided. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Perfluoroorganoelement; Main group; Transition metals; Element displacement; Periodic system; Functional groups; Biological activities; Adamantanes; Groupelectronegativity; Paraelements

1. Introduction and limiting definitions

In the second half of the last century, a new branch of chemistry emerged: perfluoro- and perfluorohalogeno-organo element compounds.

Intensive investigations in the field of fluorine chemistry, carried out during the Manhattan Project, motivated researchers to stay in this fascinating area and attracted other researchers worldwide. A substantial number of new perfluoro- and perfluorohalogenoorgano compounds became available as synthons, encouraging chemists to develop this new branch of chemistry. The field of perfluorohalogenoorganoelement compounds of the main group elements and later, in a period of steady growth, also of the transition metals expanded continuously. The structural and mechanistic concepts of organic chemistry were combined with modern synthetic approaches from inorganic chemistry.

In a period of about 20 years the number of compounds had increased to such an extent that it became necessary by using comprehensive and precise definitions to establish border lines with respect to inorganic and organic chemistry, bearing in mind the many close associations of both of these areas. Considering this, compounds of the type $(R_f)_xE^mY_{m-x}$ were E is the main group element (excepting O or C), m the oxidation state of E, Y the monofunctional group and R_f is the (a) perfluoroaliphatic radicals such as C_nF_{2n+1}, C_nF_{2n-1}, C_nF_{2n-3}, corresponding polyenes and -ynes, cyclo-C_nF_{2n-1} and unsaturated aliphatic cyclo-radicals, $n = 1, 2, 3\ldots$; (b) perfluorohalogenoaliphatic groups such as $C_nF_{2n+1-i}X_i$, $C_nF_{2n-(1+i)}X_i$, $C_nF_{2n-(3+i)}X_i$, corresponding polyenes and -ynes, cyclo-$C_nF_{2n-(1+i)}X_i$ and unsaturated aliphatic cyclo-groups, $i = 1,2,\ldots$ until one F-atom is left. X = Cl, Br, I, OH...., *not* H; (c) perfluoroaromatic and perfluorohalogenoaromatic moieties, were synthesized and characterized both physically and spectroscopically.

This chemistry has been studied extensively. These limitations are arbitrary and have their origin in the comprehensive summary published in "Gmelin Handbook of Inorganic and Organometallic Chemistry" [1]. It was necessary to establish a border between organic and inorganic chemistry by defining "title compounds" (see [1]) as having no CH bond, but at least one fluorine atom in the perfluorohalogenoorgano moiety. These boundaries are arbitrary and artificial. One is free to include also, to some extent compounds containing CH-bonds into this branch of chemistry, if appropriate. These clear limitations, as well as the precise definitions, organization and the publication of these compounds and their properties in Gmelin's Handbook might be considered as a cornerstone of this field of chemistry. The publication does not include *perfluorohalogeno-organo-oxygen* compounds, which, without any doubt, should have been included. They were omitted because of the vast number of such compounds.

Special features of the perfluorhalogenoorgano group are its chemical inertness, being stable to nucleophilic and elctrophilic attack, and its ability to form strong carbon-

*Tel.: +49-234-332-3004; fax: +49-234-321-4541.
E-mail address: alois.haas@ruhr-uni-bochum.de (A. Haas)

0022-1139/99/$ – see front matter
PII: S0022-1139(99)00203-1

element bonds. Thus substitution of higher valent elements with R_f-moieties reduced their valency depending on their nature by 1, 2 or 3 units when they became substituted by 1, 2 or 3 mono valent R_f-radicals, e.g. $E^{II} \rightarrow R_fE–$ (E = O, S, Se, Te), $E^{III} \rightarrow R_fE= \rightarrow (R_f)_2E–$ (E = N, P, As, Sb, Bi) etc. In this way it became possible to control the reactivity of multivalent elements, e.g. $R_fP=$, $(R_f)_2P–$, $(R_f)_3P^{v}=$, $R_fS–$, $(R_f)_2S^{IV}=$, $R_fGe\equiv$, $(R_f)_2Ge=$, $(R_f)_3Ge–$ and to study the chemical reactivity of a single reactive unit such as $(R_f)_3Ge–$, $(R_f)_2P–$, $R_fS–$ or, if intended, a double reactive unit, e.g. $(R_f)_2Ge=$, $R_fP=$, $(R_f)_2S^{IV}=$. Ideal substituents were CF_3 as an example for an aliphatic and C_6F_5 for an aromatic perfluoroorgano group.

2. Reactions and educts

The first synthesis for CF_3I was published in 1948. It was prepared from CI_4 and IF_5 in 90% yield [2,3]. This important starting material can readily be prepared by a Hunsdiecker reaction. Treating $R_fC(O)OAg$ with I_2 at elevated temperatures yielded R_fI [4,5] according to:

$$R_fC(O)OAg + I_2 \rightarrow R_fI + CO_2 + AgI$$
$$(R_f = CF_3,\ C_2F_5,\ n\text{-}C_3F_7)$$

Manufacturing processes for these educts involve a two step reaction.

$$5\ CF_2{=}CF_2 + IF_5 + 2\ I_2 \xrightarrow{\text{catalyst}} 5C_2F_5I$$
$$C_2F_5I + nCF_2{=}CF_2 \rightarrow CF_3CF_2(CF_2CF_2)_nI$$
$$(n = 2\text{–}4\ [6]).$$

Fluorination of C_6H_6 with CoF_3 yielded octafluorocyclohexadiene, which could be aromatized with hot Fe or Ni forming hexafluorobenzene [7] in good yield. Another route to C_6F_6 was the total fluorination of C_6Cl_6 with KF or NaF in a polar solvent or using KF without a solvent at 450–500°C, yielding 21% C_6F_6, 20% C_6F_5Cl, 14% $C_6F_4Cl_2$ and 12% $C_6F_3Cl_3$ [8–10].

Suitable synthons for the preparation of C_6F_5-element compounds proved to be C_6F_5X (X = Br, I). They were prepared by the halogenation of C_6F_5H with a stirred mixture of Br_2, 20% oleum and anhydrous $AlBr_3$ or I_2 dissolved in 20% oleum in good yields [11]. Another synthesis involved the diazotization of $C_6F_5NH_2$ with $NaNO_2$ in 80% HF and treating the $[C_6F_5N_2]F$ formed with Cu_2Br_2 in hydrobromic acid or adding sulfamic acid and finely ground KI to obtain good yields of C_6F_5Br or C_6F_5I [12], respectively. Ignoring the true chronological order of the development of perfluoroorganoelement chemistry, it should be mentioned that one general method was applicable for the preparation of such compounds: heating CF_3I with non-metals or metals in sealed tubes at about 160–300°C or irradiating the mixture before heating to 120°C [13].

$$CF_3I + E \rightarrow (CF_3)_3E + (CF_3)_2EI + CF_3EI_2$$

(E = P [14–16], As [17,18], Sb [19])

$$CF_3I + S \rightarrow CF_3SSCF_3 + CF_3SSSCF_3\ [20,21]$$

$$CS_2 + IF_5 \xrightarrow{155°C} CF_3SSCF_3\ [22]$$

$$CF_3I + Se \xrightarrow{260\text{–}285°C} CF_3SeCF_3 + CF_3SeSeCF_3\ [23]$$

$$CF_3I + Hg \xrightarrow{h\nu} CF_3HgI \xrightarrow{120°C/Cd/Hg} (CF_3)_2Hg\ [24].$$

Starting materials for the preparation of perfluoroarylelement compounds were Gringard reagents and lithiated synthons.

Using C_6F_5 as a representative ligand for such derivatives, the corresponding educts were prepared according to:

$$C_6F_5X + n\text{-}C_4H_9Li \xrightarrow{-70°C\ \text{to}\ -78°C} C_6F_5Li$$

(X =H [25], Cl [26], Br [27], I [28])

$$C_6F_5Y + Mg\ (\text{activated by } I_2) \rightarrow C_6F_5MgY$$

(Y = Cl [29]; Br [30,31]; I [31]).

These metallated pentafluorophenyl compounds were utilized, among others, in metathetical reactions with element halides to make C_6F_5 substituted element compounds. Replacement of C_6F_5 by other perfluoroaryl groups provided compounds with other radicals [1].

Special methods were used for the synthesis of substances with high synthetic potential, such as $Hg(SCF_3)_2$, CF_3SCl, CF_3SO_2Cl and CF_3SO_3H. Fluorination of Cl_3CSCl with NaF in tetramethylene sulfone at 170–250°C is the best method for synthesizing CF_3SCl in good yields and preparative quantities [32]. Oxidation or chlorination in aqueous solution provided $CF_3S(O)Cl$ [33] or CF_3SO_2Cl [129]. Alkaline hydrolysis of sulfonyl halides is a general method for synthesizing the corresponding perfluoroorganosulfonic acids [34–37]. Among these, CF_3SO_3H (trivial name "triflic acid"; its esters and salts are commonly known as "triflates") is now available commercially and is made on a ton scale. Perfluoroorganosulfonyl fluorides were obtained by electrochemical fluorination of the corresponding organosulfonyl chlorides in anhydrous HF [38].

Perfluorinated azaalkenes are important building blocks for the preparation of perfluororganonitrogen compounds, as having a very varied and diverse chemistry. In addition to many individual targeted synthesis, they are prepared by pyrolysis of the corresponding tertiary amines, heterocycles or copolymers formed from R_fNO and perfluorinated olefins [54,55]. Highly fluorinated alkenes when treated with nitrogen oxides (NO, NO_2, N_2O_3) form compounds like $O_2NCF(R_f)CF(R_f')X$ (X = NO_2, ONO, NO) [56]. Dehydration of amides, such as $R_fCF_2C(O)NH_2$ or $H_2NC(O)(CF)_x$-$C(O)NH_2$ yielded the corresponding CN-substituted derivatives, which are also important starting materials for the development of R_fN-chemistry [57,58]. Of similar importance is the synthesis by electrochemical fluorination. Compounds of the type R_fNF_2, $(R_f)_2NF$, $(R_f)_3N$ or $C_5F_{11}N$ were prepared in this way. Defluorination of $C_5F_{11}N$ yielded perfluorinated di- and tetrahydropyridine as well as pentafluoropyridine [59].

Perfluoroorganooxygen compounds play an important role in fluorine chemistry although oxygen in contrast to S, Se, P, etc. has only the oxidation states +1, –1, –2 in these compounds. Besides a limited number of perfluoroorganocyclo derivatives, which are prepared either by electrochemical fluorination, direct fluorination with F_2 and other fluorinating agents or by specific synthetic procedures, there are a substantial number of linear perfluoroorgano derivatives of oxygen. This field is dominated by substances like R_fOR_f, R_fOOR_f, R_fOX (X = F, Cl), R_fOOF, $(R_f)_2C{=}O$, $R_fC(O)Y$ (Y = OH, halogen) and $(R_f)_2C{=}C{=}O$. Without any doubt perfluoroorganocarboxylic acids are besides, ketones, the most important molecules and some of them like $CF_3C(O)OH$ or $(CF_3)_2CO$ are prepared industrially.

The first derivatives, the hypofluorites, were synthesized mainly by Cady and his group. Fluorination of CO [60,61,65,66] CO_2 [62], COF_2 [61,63] or CH_3OH vapor [61] with F_2 in the presence of a AgF_2 catalyst provided CF_3OF in high yields. Irradiation of CF_3OF yielded CF_3OOCF_3 and reactions with SF_4 gave CF_3OSF_5 [64,67–69], with SO_3 at 245–260°C mainly CF_3OOSO_2F and with SO_2 in the gas [65] and liquid phase [66] a series of esters were obtained. Perfluorocyclopentene added to CF_3OF across the double bond to form perfluoro(methoxycyclopentane) [66]. The hypofluorites $R_fC(O)OF$ ($R_f = CF_3$, C_2F_5) were prepared from $CF_3C(O)OH$ [67,68] or $CF_3CF_2C(O)OH$ and F_2 diluted with N_2 [69]. Meanwhile it was shown that direct fluorination of polyfluorinated alcohols or hexafluoroacetone in the presence of water under mild conditions provided the corresponding hypofluorites [73] according to:

$$\begin{matrix} CF_3CH_2OH & & CF_3CF_2OF \\ CF_3CH_2CH_2OH & & CF_3CF_2CF_2OF \\ & +F_2 \rightarrow & \\ (CF_3)_2CO + H_2O & & (CF_3)_2CFOF \\ (CF_3)COH & & (CF_3)_3COF. \end{matrix}$$

The hypofluorites are strong oxidizing reagents and CF_3OF is commonly used as an electrophilic fluorinating reagent. Probably the best method of preparing fluorooxyperfluoroalkanes are MF (M = K, Rb, Cs) catalyzed addition of F_2 across the C=O bond of perfluorinated ketones [74], e.g.

$$R_fC(O)F + F_2 \rightarrow R_fCF_2OF; \quad R_f = F,\ CF_3,\ C_2F_5$$

$$(CF_3)_2C{=}O + F_2 \rightarrow (CF_3)_2CFOF$$

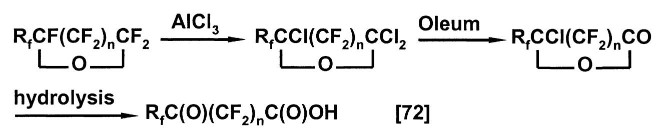
$$FC(O)(CF_2)_nC(O)F + F_2 \rightarrow FO(CF_2)_{n'}OF; \quad n = 2,\ 3;\ n' = 4,\ 5.$$

Replacing F_2 by ClF provided $C_nF_{2n+1}OCl$ (n = 1, 2, 3)...[75].

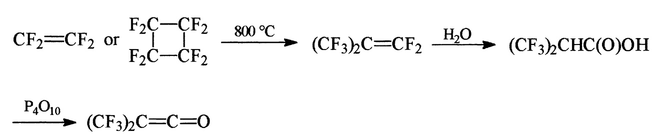
$$(R_f)_2CO + ClF \rightarrow (R_f)_2CFOCl, \quad R_f = F \text{ or } CF_3.$$

Bis(fluorooxy)perfluoroalkanes extended the class of fluoroxy derivatives: the first member of this series $CF_2(OF)_2$ was made by fluorinating $CF_3C(O)ONa$ or $Na_2C_2O_4$ with F_2 [76] or from CO_2 in the presence of CsF [77,78]. Higher members, such as $CF_3CF(OF)_2$ and $(CF_3)_2C(OF)_2$ were synthesized analogously [79].

Perfluorinated ethers were readily prepared in good yields by electrochemical fluorination of ethers [70,71]. In this way $(C_nH_{2n+1})_2O$ was converted into $(C_nF_{2n+1})_2O$ (n = 1–6) [70]. Cyclic ethers $\overline{CH_2(CH_2)_nO}$ gave $\overline{CF_2(CF_2)_nO}$ (n = 1–4)[1] [71]. Treatment of cyclic ethers with $AlCl_3$ gave perfluorocarboxylic acids according to:



Photochemically initiated reactions provided perfluoroorgano peroxides. An elegant synthesis of FC(O)OOC(O)F from CO, O_2 and F_2 at 20°C had an almost 100% yield [80]. This compound was also made in about 50% yield by irradiating a mixture of oxalyl fluoride and oxygen [81]. The fluorination of COF_2 with F_2 under the influence of UV-light yielded 20% CF_3OOCF_3 [82]. In a multistep synthesis an important perfluorinated oxygen containing compound $(CF_3)_2C{=}C{=}O$ [83] was made according to:



It is a versatile building block for the synthesis of many other derivatives.

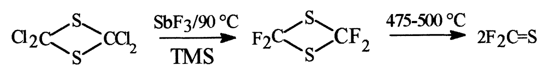
Lagow and coworkers developed a direct fluorination method using diluted F_2 for the preparation of perfluorinated monomeric and polymeric ethers. The crown ethers should be mentioned, which were prepared from 12-crown-4, 15-crown-5 or 18-crown-6 and a varying mixture of helium and F_2, depending on the fluorinated state of the educt starting at –78°C and finishing at 45–60°C to yield the perfluorinated analogs [84].

3. Perfluorinated E=C (p–p) π-sytems

Element-carbon double bonds are stabilized either by steric hindrance using bulky groups or by the highly electronegative perfluorinated group or fluorine (perfluoro-

[1] Additional information on referee's request: only perfluorotetrahydrofurane can be synthesized by this method, due to polymerization of the starting materials in AHF.

effect). One of the first compounds of this type was thiocarbonyl difluoride, the best preparation of which is the fluorination of tetrachloro-1,3-dithietane with SbF_3 and subsequent pyrolysis of the fluorinated product [39,40] according to:



Generally applicable methods are:

1. treatment of mercurials with $(C_2H_5)_2MI$.

$$Hg(ECF_2R_f)_2 + (C_2H_5)_2MI \rightarrow \langle(C_2H_5)_2MECF_2R_f\rangle \rightarrow R_fCF{=}E + (C_2H_5)_2MF,$$

E = Se; R_f = F [41,42], CF_3 [42,43], C_2F_5 [42]; E = Te; R_f = F [44].

2. Pyrolysis of $(CH_3)_3SnECF_2R_f$ according to:

$$(CH_3)_3SnECF_2R_f \xrightarrow{300-500^\circ C/10^{-2}-10^{-3}\ Torr} R'_f(F)C{=}E + (CH_3)_3SnF$$

E = Se, $R_f = CF_3$ [45]; E = Te, R_f = F [46,47], CF_3 [48].

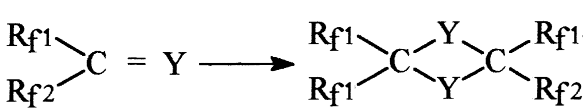
3. Pyrolysis of $(CH_3)_3SnE(X)CF_2R_f$:

$$(CH_3)_3SnE(X)CF_2R_f \xrightarrow[10^{-3}\ Torr]{320-340^\circ C} XE{=}C(F)R_f + (CH_3)_3SnF$$

E = P; X = CF_3, R_f = F [49,50]; X = CF_3, $R_f = CF_3$ [51]; X = C_2F_5, R_f = F [51]X = C_2F_5, $R_f = CF_3$ [52]; E = As; X = CF_3, R_f = F [49,50].

Above 150°C $Hg[N(CF_3)_2]_2$ dissociates in a reversible reaction into $CF_3N{=}CF_2$ and HgF_2 [53].

The highly reactive unsaturated compounds dimerize to the corresponding four membered ring systems according to



When $R_f^1 \# R_f^2$ *cis*-, *trans*-isomers are formed. In some cases polymerization yielded linear di-, tri- and polymeric species. Important, general applicable reactions are Diels-Alder cyclisations mainly [4 + 2] cycloadditions with dienes. Nucleophilic reagents such as HX (X = halogen) alcohols, thiols, amines etc. were added across the double bond, see [1].

4. Element displacement principle

Since the preparation of CF_3IF_2 was published in 1959 [85] a large number of derivatives were synthesized by the fluorination of excess R_fI, dissolved in perfluorohexane with ClF_3, diluted with an inert gas, at – 70 °C yielding R_fIF_2 ($R_f = C_2F_5$, n-C_3F_7, $(CF_3)_2CF$, C_4F_9, C_6F_{13}, $C_{20}F_{21}$) [86]. Other ligands, replacing iodine bonded F, such as, e.g. O, NO_3, ClO_4, $CF_3C(O)O$, OSO_2F, $OTeF_5$, Cl, etc. were also successfully applied. Meanwhile also corresponding compounds with chlorine or bromine as the central atoms including perfluoroorganohalogen derivatives with Cl, Br and I in oxidation state V, and ionic species were described [28]. Very recently perfluoroorganoxenon compounds, such as $(CF_3)_2Xe$ [87] and $[C_6F_5Xe]^+$ salts with varying anions have been prepared [88,89].

The number of perfluorohalogenoorganoelement compounds, synthesized, characterized and studied in the last 50 years is so large, that a simple, convincing and easily understandable concept was needed to organize material. The arrangement, as used in Gmelins Handbook [1], is based on the nature of the organic radical. This means: number of carbon atoms, degree of fluorination, nature of the organic radical, whether linear, cyclic or aromatic, the nature of halogens, as well as the central atom of the functional group, its position in the periodic system and its oxidation state. But this systematization does not provide a basic correlation among the functional groups or a more deeper understanding of their chemical nature. Due to their high group electronegativity radicals like and $CF_3\cdot$ or $CF_3S\cdot$ were considered as "pseudohalogens" [91]. An answer to these and other peculiarities is provided by the element displacement principle. This permits the establishment of an association between perfluorohalogenoorganoelement compounds including the classical pseudohalogens, with main group elements as a basis for the organization of them in a periodic system of functional groups. It is based on Grimm's hydrogen displacement principal [92] and is defined as follows: "coordination of the elements of groups 14–18, subsequently termed base elements, with elements or element groups, termed ligands, forming one, two, three or four covalent bonds result 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. Hereafter, a few examples are given to explain this definition. First of all fluorine — a representative for all other monovalent radicals — is coordinated as a ligand to the second and third row elements starting from carbon and silicon according to Scheme 1. Each group in turn is able to function as a ligand, e.g. using the monovalent CF_3 radical first order derivative moieties are obtained as shown in Scheme 2. If a first order derivative radical, e.g. the monovalent CF_3S-group is applied similarly, second order derivative groups can be deduced (Scheme 3). Continuing this procedure and system of nomenclature gives, in many cases, meaningful and realistic results. It is interesting to note that this principle is not restricted only to monovalent elements or radicals, but can be extended to higher valent elements and groups, e.g. O, S, N, P, CF_3N, CF_3SN etc. If any more of these are used as the ligand, a displacement of two (O, S) or three (N, P) must, of course, result as follows: in Scheme 4. These radicals may also be used as ligands. If =CO, CN or =CS [93] are coordinated, first order derivative groups are obtained according to Scheme 5.

C	N	O	F	Ne	Na
	≡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
	≡SiF	=PF	-SF	ClF	-
		$=SiF_2$	$-PF_2$	SF_2	$[ClF_2]$
			$-SiF_3$	PF_3	$[SF_3]$
				SiF_4	$[PF_4]$

Scheme 1

C	N	O	F	Ne
	$\equiv CCF_3$	$=NCF_3$	$-OCF_3$	$F-CF_3$
		$=C(CF_3)_2$	$-N(CF_3)_2$	$O(CF_3)_2$
			$-C(CF_3)_3$	$N(CF_3)_3$
				$C(CF_3)_4$

Si	P	S	Cl	Ar
	$\equiv SiCF_3$	$=PCF_3$	**$-SCF_3$**	$Cl-CF_3$
		$=Si(CF_3)_2$	$-P(CF_3)_2$	$S(CF_3)_2$
			$-Si(CF_3)_3$	$P(CF_3)_3$
				$Si(CF_3)_4$

Scheme 2

C	N	O	F	Ne
	$\equiv CSCF_3$	$=NSCF_3$	$-OSCF_3$	$FSCF_3$
		$=C(SCF_3)_2$	$-N(SCF_3)_2$	$O(SCF_3)_2$
			$-C(SCF_3)_3$	$N(SCF_3)_3$
				$C(SCF_3)_4$

Si	P	S	Cl	Ar
	$\equiv SiSCF_3$	$=PSCF_3$	$-SSCF_3$	$Cl-SCF_3$
		$=Si(SCF_3)_2$	$-P(SCF_3)_2$	$S(SCF_3)_2$
			$-Si(SCF_3)_3$	$P(SCF_3)_3$
				$Si(SCF_3)_4$

Scheme 3

C	N	O	F	Ne
		=CO	-NO	O=O
			-CN	N≡N
		=CS	-NS	O=S

Scheme 4

At this stage it is necessary to deal with the nomenclature for these "constructed radicals". The name "*pseudo*[2] *elements*" is already used for –OH, NH_2, CH_3 etc. — radicals deduced according to Grimm [92] and for CN, NCO, NCS, N_3 etc. classified experimentally as pseudohalogens by Birkenbach and Kellermann [91] due to their chemical and physical properties. The first moieties OH, NH_2, CH_3 etc. are isoelectronic and isoprotonic to the reference element fluorine; the others are not. They have only the same number of valence electrons and cannot be assigned to a certain halogen, but only to group 17 elements. Additional parameters, such as group electronegativity, chemical properties, physical data allow such tentative assignments. The latter arguments are also valid for the radicals obtained by element displacement. Therefore they should be clearly differentiated conceptually from Grimm's pseudoelements. The name suggested for them was "*paraelements*"[3] [96].

[2] Ψενδο (pseudo) = lie, falsehood, untruth.

[3] παρα (para) = near, secondary.

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

Scheme 5

This formalism can also be extended to addition of an electron (equivalent to a covalent bond) or to loss of electrons. The negative ions are shifted to the right, e.g. $Tl^- \cong Cl$ [94]; $C^- \cong N$; Si^-, Ge^-, $Pb^- \cong P$; Si^{--}, $As^- \cong Se$; $S^- \cong Cl$ [95] and the positive ions to the left, e.g. $C^+ \cong B$; $N^+ \cong C$; $O^+ \cong N$; $Cl^+ \cong S$.

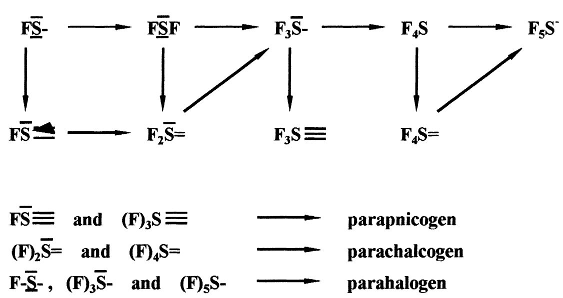
Paraelement formation is not restricted to the examples noted above. Elements of Groups 15–17 have free electron pairs available and consequently are able to form dative coordinate bonds. In this case base and reference element are identical, e.g. O–N, O–S, O–P, OSO.

Elements which are able to expand the outer octet of electrons, e.g. S, Se, Te, P, As, etc. form a new type of paraelements. With fluorine as a ligand sulfur can form the following paraelements:

FS≡ and $(F)_3S$≡ $\rightarrow$ parapnicogen

$(F)_2S$= and $(F)_4S$= $\rightarrow$ parachalcogen

F–S–, $(F)_3S$– and $(F)_5S$– $\rightarrow$ parahalogen.



The groups deduced above are no longer electronically isovalent with their reference element, however they remain topologically isovalent. Thus, all *paraelements* obtained by the procedures described previously, are *isovalent* with their *reference element* and are organized as shown in the periodic system of functional groups.

For perfluorohalogenoorgano main group elements groups this means that not only the perfluorohalogenoorgano radicals but also the reactive functional groups behave like elements and when combined, they form the compounds discussed in this paper. The perfluoroorgano moieties can be obtained by the addition of elements and paraelements, such as, FC≡, F_2C=, O, F_3C–, F, CF_3C≡, $(CF_3)_2C$=, $(CF_3)_3C$–, halogens etc. according to:

$CF_3-+-(CF_2)_n- \rightarrow CF_3(CF_2)_n-$;
$n = 1, 2, 3\ldots$ (alkyls)

FC≡ + =CF_2 $\rightarrow$ CF_2=CF (alkenyls)

FC≡ + ≡C– $\rightarrow$ FC≡C– (alkinyls)

5CF≡ + ≡C– $\rightarrow$ C_6F_5–

CF_3C≡ + 4FC≡ + ≡C– $\rightarrow$ $CF_3C_6F_4$

FC≡ + O $\rightarrow$ FC(O)– (carbonyls)...

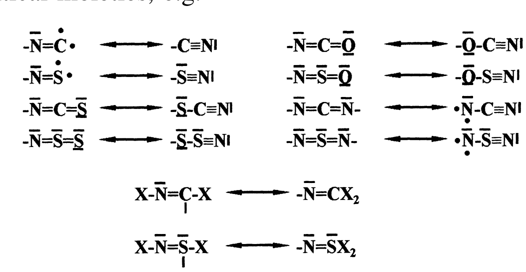
The paraelements deduced as shown in Schemes 1–5 and the radicals described above are the building blocks for the creation of known and unknown perfluorinated organoelement compounds. These principles are arbitrary limitations for this field of chemistry, but are also evidence for its independence.

Is the formalism of the *element displacement*, which provides the periodic system of functional groups, only an intellectual concept or is it a tool which can use existing data to predict the course of unknown reactions, and the existence, properties and structures of new compounds?

One of the applications of the element displacement principle to chemical problems is the equivalence between carbon and sulfur (IV).

5. Comparability of S(IV) and carbon

In a number of unsaturated functional groups containing carbon replacement by an s^2p^3d hybridized sulfur provides identical moieties, e.g.



In the paraelements shown above carbon and sulfur can be exchanged without altering their chemical properties. Only the structures differ, because of the extra electron pair on the sulfur atom. This means, while the carbon containing groups with three or four atoms are linear or planar, the corresponding sulfur paraelements are bent or non-planar. Primary amines react with $SCCl_2$ to isothiocyanates and with S_2Cl_2 in the isomeric form of a thiothionylchloride, N-thiosulfinylimines are formed according to:

RNH_2 + S=CCl_2 $\rightarrow$ RN=C=S [97]

RNH_2 + S=SCl_2 $\rightarrow$ RN=S=S [98]

CF_3SNH_2 + S=SCl_2 $\rightarrow$ CF_3SN=S=S [99].

Both groups show comparable chemical reactions [93]. The isomeric paraelements N=CX_2 and XN=C(X) resemble

N=SX_2 and XN=S(X), respectively. This principle encouraged the successful synthesis of unknown compounds with a R_fS=N(X) unit.

Fluorination and chlorination of $CF_3SN[Si(CH_3)]_2$ yielded $CF_3S(X)$=NX (X = F, Cl) [99] as shown below:

$$CF_3SN[Si(CH_3)_3]_2 + F_2 \overset{-60^\circ C}{\rightarrow} CF_3S(F){=}NF + 2(CH_3)_3SiF$$

$$CF_3SN[Si(CH_3)_3]_2 + Cl_2 \overset{-40^\circ C}{\rightarrow} CF_3S(Cl){=}NSi(CH_3)_3 \overset{Cl_2/-20^\circ C}{\rightarrow} CF_3S(Cl){=}NCl + (CH_3)_3SiCl.$$

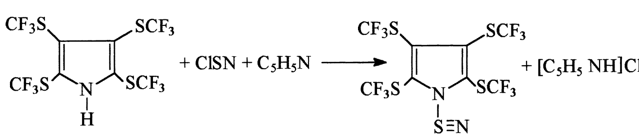
Replacing carbon for sulfur in carbodiamides leads to sulfurdiimides to paraelement units with numerous derivatives. The –N=C=N– group also exists in an isomeric form as cyanamide (=N–C≡N). The corresponding amino thiazyl (=N–S≡N) was not known. Attempts to synthesize such derivatives by condensing R_2NH with ClS≡N resulted in the preparation of RN=S=NR, according to:

$$R_2NH + Cl-S{\equiv}N \rightarrow RN{=}S{=}NR; \quad R = C_6F_5S$$

[100], CF_3S [101], CF_3Se [102]

probably via the formation of R_2N–S≡N as an unstable intermediate, which rearranged to RN=S=NR.

Using tetrakis(trifluoromethylthio)pyrrole as an educt prevents such a rearrangement. As suggested it reacts with Cl–S≡N as shown below to the corresponding thiazyl containing compound.



Contrary to FS≡N, Cl–S≡N and their carbon analogues F–C≡N, ClC≡N that readily cyclise to six membered heterocycles, the product obtained, showed no tendency to trimerize to a trithiazyl derivative. The corresponding N-cyano-tetrakis(trifluoromethylthio)pyrrole prepared from the potassium salt and ClCN has similar chemical properties. Both undergo [4 + 2]-cycloaddition, e.g. with butadiene to yield 3,6-dihydro-1,λ^4,2-thiazine and 3,6-di-hydropyridine derivatives, demonstrating additionally the relationship between –C≡N and –S≡N paraelements [201].

6. Equivalence between elements and paraelements

6.1. CF_3 and fluorine

Impressive similarities between F and the parafluorines CF_3, $(CF_3S)_2N$ are observed. It is known that SF_2 dimerizes to unsymmetrical F_3SSF. Replacing one F-atom by a CF_3 radical in SF_2 giving CF_3SF a complete analogous dimerization [103] is observed, e.g.

$$2F-SF \rightarrow F_3SSF$$

$$2CF_3-SF \rightarrow CF_3S(F_2)SCF_3.$$

Other convincing examples for the equivalency of fluorine and CF_3 are the acid/anhydrofluoride relationship of perfluorinated acids, not dissociating in water. The following equations illustrate this statement:

$$2HOF \rightarrow O{=}O + 2HF \ [103]$$

$$HOCF_3 \rightarrow F_2C{=}O + HF \ [106, 107]$$

$$2H(NF)F \rightarrow FN{=}NF + 2HF \ [104]$$

$$H(NCF_3)CF_3 \rightarrow F_2C{=}NCF_3 + HF \ [108, 109]$$

$$2H(CF_2)Cl \overset{800^\circ C}{\rightarrow} F_2C{=}CF_2 + 2HCl \ [105]$$

$$HC(CF_3)_3 \rightleftharpoons F_2C{=}C(CF_3)_2 + HF \ [110, 111].$$

These examples evidence not only the similarities between F and CF_3, but also between FN=, F_2C=, CF_3N= and $(CF_3)_2C$= with oxygen. Additionally fluorine-like-behavior is also demonstrated by the parafluorines FO–, F_2N–, CF_3O–, $(CF_3)_2N$– and $(CF_3)_3C$– as postulated in Schemes 1 and 2. No direct conversion of CF_3H to CF_2, and hence F_2C=CF_2, or decomposition of $(CF_3)_3CH$ to $(CF_3)_2C$=CF_2 is observed. But in the presence of F^- the addition of HF to $(CF_3)_2C$=CF_2 forming $(CF_3)_3CH$ takes place under normal reaction conditions [110,111].

Some anhydrofluorides add metal fluorides to form salt like compounds:

$$MF + CF_2{=}O \rightarrow MOCF_3 \ (M = K, Rb, Cs) \ [112]$$

$$HgF_2 + 2CF_3N{=}CF_2 \rightarrow Hg[N(CF_3)_2]_2 \ [113]$$

$$HgF_2 + 2(CF_3)_2C{=}CF_2 \rightarrow Hg[C(CF_3)_3]_2 \ [114].$$

6.2. $(CF_3S)_2N$– and fluorine

Even second-order derivative paraelements can show close similarities to the corresponding reference element. A strong case in this respect is the bis(trifluoromethylthio)amino-radical. Because of its high group electronegativity of 3.7 [115], it is considered as a parafluorine. The amine $(CF_3S)_2NH$ is a weak acid, pK_A(in dioxan/water) = 9.99 [116], and it reacts with HgO forming $Hg[N(SCF_3)_2]$ [117]. The ability of the radical to dimerize reversible to $(CF_3S)_2NN(SCF_3)_2$ is comparable with examples like F_2NNF_2 [118] or O_2NNO_2 [119]. The dissociation enthalpies of $(CF_3S)_2NN(SCF_3)_2$ = 32.0 kJ mol^{-1} [120] and of $(CF_3S)_3CC(SCF_3)_3$ = 57.0 kJ mol^{-1} [121] are even lower than that for F_2 = 156.9 kJ mol^{-1} [122]. They dissociate at 20°C:

$$F_2 \rightleftharpoons 2F\cdot$$

$$(CF_3S)_2NN(SCF_3)_2 \rightleftharpoons 2(CF_3S)_2N\cdot$$

$$(CF_3S)_3CC(SCF_3)_3 \rightleftharpoons 2(CF_3S)_3C\cdot$$

Only a small change in the chemical shift of the ^1H NMR-spectrum of $[(CF_3S)_2N]_2CH_2$, $\delta(CH_2)$ = 5.15 ppm, [123] occurs when F is replaced by $(CF_3S)_2N$ in CH_2F_2, $\delta(CH_2) = 5.99$ ppm.

While metathetical reactions between BX_3 (X=Cl, Br) and $(CF_3S)_2NH$ yield only the monosubstituted product $(CF_3S)_2NBX_2$ [124], further halogen replacements occur with $Hg[N(SCF_3)_2]_2$ giving $[(CF_3S)_2N]_2BX$ or $[(CF_3S)_2N]_3B$. Rather surprising and completely unexpected is the formation of the tris-substituted borane from $B(SCF_3)_3$ and $Hg[N(SCF_3)_2]_2$. This reaction is readily understood with the aid of the element displacement principle by applying paraelements. Now the radical CF_3S is a parachlorine (*p*Cl) and $(CF_3S)_2N$ a parafluorine (*p*F). The procedure can be described now by the following reactions

$$2B(SCF_3)_3 + 3Hg[N(SCF_3)_2]_2 \rightarrow 2B[N(SCF_3)_2]_3 + 3Hg(SCF_3)_2$$

or

$$2B(pCl)_3 + 3Hg(pF)_2 \rightarrow 2B(pF)_3 + 3Hg(pCl)_2.$$

This means that the above-described reaction is equivalent to the fluorination of BCl_3 with HgF_2 giving BF_3 and $HgCl_2$ [125]. Analogously $Te(SCF_3)_2$, when treated with $Hg(NSO)_2$ in CS_2, provides $Te(NSO)_2$ and $Hg(SCF_3)_2$ [126] according to:

$$Te(SCF_3)_2 + Hg(NSO)_2 \rightarrow Te(NSO)_2 + Hg(SCF_3)_2$$

or

$$Te(pCl)_2 + Hg(pF)_2 \rightarrow Te(pF)_2 + Hg(pCl)_2.$$

This is an excellent method for the preparation of $Te(NSO)_2$, a widely applicable educt for the preparation of tellurachalcogenonitrogen heterocycles [127].

6.3. CF_3 and chlorine

The halogen like behavior of the CF_3S-group has already been postulated on the basis of its group electronegativity of 2.7 [90]. Many additional examples can be found to substantiate its properties as parachlorine. Replacing chlorine in $OPCl_3$ and $SPCl_3$ yielded the new compounds $CF_3SP(O)Cl_2$ and $CF_3SP(S)Cl_2$. The chemical and physical similarities between these two pairs of compounds are remarkable and are detailed elsewhere [128]. Impressive examples include the hydrolytic reactions of the element–element molecule Cl_2, the element–paraelement compound CF_3SCl and the paraelement–paraelement substance CF_3SSCF_3. The first step of hydrolysis takes place according to:

$$Cl-Cl + H_2O \rightarrow H-Cl + HOCl \text{ [129]}$$

$$CF_3S-Cl + H_2O \rightarrow H-Cl + HOSCF_3 \text{ [129]}$$

$$CF_3S-SCF_3 + H_2O \rightarrow H-SCF_3 + HOSCF_3 \text{ [130]}.$$

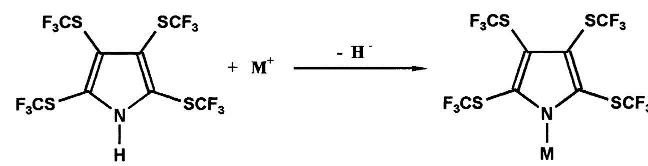
The oxyacid intermediates are not stable and disproportionate as follows:

$$2Cl-OH \rightarrow Cl(O)OH + HCl$$

$$2CF_3S-OH \rightarrow CF_3S(O)OH + HSCF_3 \text{ [129]}.$$

6.4. Tetrakis(trifluoromethylthio)pyrrolyl and chlorine

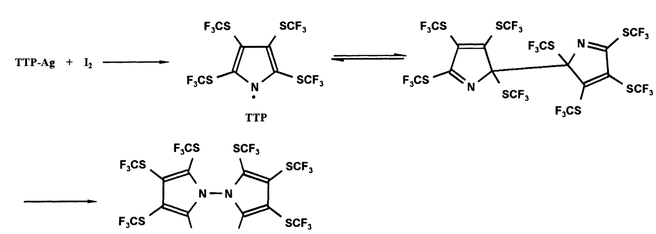
The higher order derivative parahalogen, tetrakis(trifluoromethylthio)pyrrole radical (TTP) is a good paraelement in spite of its size and complexity. Based on its group electronegativity of 2.9 [133] and its chemical properties, chlorine like behavior is observed. The hydrogen derivative (TTP–H) is an acid ($pK_A = 9.2$ water/dioxane) and reacts with various cations forming the corresponding salts:



TTP-H TTP-M

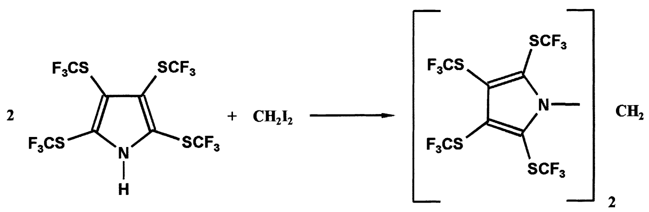
M = Ag [131], K, Na, NH_4, $[(C_5H_5NH]$, $[(CH_3)_3NH]$ [132], Zn, Cu(I), $[C_6H_5)_3(C_2H_5)P]$ $[CC_6H_5)_4As]$, $[(C_6H_5)_4Sb]$, $[(C_2H_5)_3Se]$, $[(C_2H_5)_2I]$ [133].

By treating TTP–Ag with iodine in pentane or by oxidizing TTP–H with PbO_2 in C_6H_6 the TTP radical is formed. This dimerizes at 20°C reversibly to 2,2′,3,3′,4,4′,5,5′-octakis(trifluoromethylthio)-2,2′-bi-2H-pyrrole [134] according to:



On heating the C–C bonded dimer to 120–130°C, the N–N linked compound is formed [134].

The silver and the potassium salts are good educts for the preparation of N-substituted derivatives. Among the numerous compounds synthesized, the pentakis(trifluoromethylthio)pyrrole prepared from TTPAg and CF_3SCl should be mentioned as a better sulfenylating agent than CF_3SCl. While CF_3SCl is able to react with primary, secondary alcohols, secondary amines and C_6H_5SH substituting the acidic hydrogen by a CF_3S-moiety, no substitution takes place in $(CH_3)_3COH$. The pentasubstituted pyrrole reacts not only with the materials mentioned, but also with $(CH_3)_3COH$ yielding $(CH_3)_3COSCF_3$ and TTP–H [132]. Another example for the close relationship between the radical TTP and chlorine is shown in the ^1H NMR spectrum of $(TTP)_2CH_2$, prepared from TTP–H and CH_2I_2 in the presence of concentrated NaOH as shown below:



The unusual chemical shift of $\delta(CH_2) = 6.9$ ppm [133] of the methylene protons is also observed in dihalogenomethanes, e.g. $\delta(CH_2)$ in $CH_2Cl_2 = 5.3$ ppm.

6.5. *Electronegativity as a parameter for assigning paraelements*

The examples provided so far prove that besides the rules for element displacement, there must also be other parameters adjusting a paraelement with a differently coordinated central atom to a reference element in the corresponding main group. While the equivalency between CF_3, $(CF_3S)_2N$ with F or CF_3S with Cl are reasonable, it is not easily understood why TTP, with nitrogen as the central atom, behaves like chlorine. This contradiction, which is mainly observed for higher derivative paraelements, can be solved by the addition of group electronegativity for classifying a paraelement. Although TTP· and $(CF_3S)_2N\cdot$ have identical central atoms, they behave differently. As expected, in many cases $(CF_3S)_2N\cdot$ (group electronegativity 3.7) resembles fluorine and TTP· (group electronegativity 2.9) chlorine. The importance of electronegativity for assigning paraelements can also be shown by comparison of Grimm's pseudoelements OH, NH_2, CH_3 with the corresponding paraelements OF, NF_2, CF_3. The group electronegativities of the two series show this convincingly:

$$OH: 2.78-3.51, \quad OF: 3.8;$$

$$NH_2: 2.47-2.61, \quad NF_2: 3.60-3.64;$$

$$CH_3: 2.27-2.34, \quad CF_3: 3.46-3.55.$$

Although OH, NH_2 and CH_3 are isoprotonic and isoelectronic with fluorine, they are worse replacements than OF, NF_2 and CF_3 which are not isosteric [128].

6.6. *Exchangeability of elements by paraelements in given structures*

It has been shown previously that elements in known structures can be substituted by pseudo- and paraelements without structural changes occurring [93,96,128]. An easily understandable and convincing example, among many other models, is illustrated with the adamantane type structure. Binary element–element adamantane structures are formed for example by phosphorus, arsenic and antimony with oxygen having the formula M_4O_6 (M = P, As, Sb). No nitrogen oxide of this type (N_4O_6) and structure is known. Complete replacing of oxygen by pseudooxygen CH_2, gives $N_4(CH_2)_6$, hexamethylenetetramine, which has an adamantane structure. If in addition nitrogen is also substituted by pseudonitrogen, then $(CH)_4(CH_2)_6$, adamantane is obtained. This example shows that starting even from an unknown binary inorganic compound and replacing elements by derivative moieties lead from inorganic via an intermediate into organic chemistry:

$$(N_4O_6) \rightarrow N_4(CH_2)_6 \rightarrow (CH)_4(CH_2)_6\ [C_{10}H_{16}].$$

It can be shown quite generally that adamantanes are composed from elements of the 15th and 16th group of the periodic table in the ratio 4:6. These may be replaced by pseudo- or/and paraelements without structural change. All adamantanes synthesized so far correspond to this composition [135–137]. Even boron and its higher homologous have in a sp^2-hybridized form three unpaired valance electrons available. The planar geometry of these orbitals are changed to four coordinate tetrahedral form by adding a Lewis base, e.g. $LB\cdot BX_3$ becoming electronically isovalent to MX_3 (M = N, P, As...). The element–paraelement relationship makes it possible to substitute 15th-group elements and derivative radicals for LB·B≡ and in fact 1-boroadamantanes has been synthesized [138]. Following this strategy it was possible to synthesize two basic adamantanes of the formula $(HSi)_4E_6$ by reacting $HSiCl_3$ with $(H_3Si)_2E$ (E = S, Se) [139]. With the aid of the chalcogenating agent $(H_3Si)_2E$ it was also possible to prepare $(CF_3Ge)_4E_6$ and to confirm their expected adamantane structure by X-ray structural analysis [140]. Reacting $C_6F_5SnCl_3$ with $(CH_3)_3SiS\text{-}Si(CH_3)_3$ as the sulfanylating agent yield $(C_6F_5Sn)_4S_6$ with the adamantane structure [141].

7. Perfluorohalogeno compounds of transition- and d^{10}-metals

7.1. *Mercury*

Although CF_3HgI and $(CF_3)_2Hg$ [2,3,24] were among the first precursors synthesized in the field of perfluoroorganoelement chemistry, there was little interest shown in this type of compounds compared with organometallic educts in organic chemistry. Higher homologues were prepared by treating HgF_2 with perfluorohalogenoolefines in HF as a solvent according to:

$$CF_2{=}CF_2 + HgF_2 \rightarrow (CF_3CF_2)_2Hg$$

$$CF_2{=}CCl_2 + HgF_2 \rightarrow (CF_3CCl_2)_2Hg$$

$$CF_3CF{=}CF_2 + HgF_2 \rightarrow [(CF_3)_2CF]_2Hg$$

$$(CF_3)_2C{=}CF_2 + HgF_2 \rightarrow [(CF_3)_3C]_2Hg\ [142].$$

In all cases HgF_2 adds regiospecifically to olefins with more than two carbons to give either secondary or tertiary perfluoroorganomercurials [143–145]. A mixture of HgF_2 and $HgCl_2$ reacted with $CF_3CF{=}CF_2$ in HF to yield $(CF_3)_2CFHgCl$ [146]. An alternative to these syntheses is the replacement of HgF_2 by alkali metal fluorides and mercury halides in an aprotic polar solvent [147,148]. Functionalisation of these "mercurials" is achieved by the preparation of $Hg(SCF_3)_2$ by irradiating CF_3SSCF_3 with mercury in quartz tube [130]. Preparative amounts are generated from CS_2 and HgF_2 in an autoclave at 250°C [149]. It is also formed from $F_2C{=}S$ and HgF_2 at –78°C (18 h) proving that F_2CS was an intermediate in the preparation mentioned previously [150]. Other compounds such as $[(CF_3)_2CFS]_2Hg$, $[(CF_3)_3CS]_2Hg$ [151], $(n\text{-}C_3F_7S)_2Hg$ [152], $[CF_3C(O)S]_2Hg$ [153] and CF_3SHgX ($X = Cl, NO_3$) [154] were also prepared and are used as synthons. Pentafluorobenzenethiol was the educt for the preparation of various metallic derivatives such as $Hg(SC_6F_5)_2$, $Cd(SC_6F_5)_2$, $Zn(SC_6F_5)_2$ and $Ni(SC_6F_5)_2$ [155]. In an almost analogous reaction heating R_fEER_f (E = Se, Te) with excess mercury it was possible to synthesize $(R_fSe)_2Hg$, $R_f = CF_3$, C_2F_5, $n\text{-}C_3F_7$, C_6F_5 [23,156–158]) and $(R_fTe)_2Hg$, $R_f = CF_3$[159], C_2F_5 [160], C_6F_5 [161].

Even though "mercurials" such as $(R_f)_2Hg$, $(R_fX)_2Hg$ and $[(CF_3)_2N]_2Hg$ were known from the very beginning of perfluorohalogenoorganoelement chemistry and were used successfully for developing synthetic routes to establish this branch of chemistry, it is only in the last decade that efforts have been concentrated on the synthesis of fluorinated organometallics.

Meanwhile a variety of precursors became commercially available, which encouraged chemists to investigate the field of perfluorinated organometallics especially of zinc, cadmium, copper, silver, gold and study their preparative potential.

7.2. Zinc

Perfluoroalkyliodide reacts with zinc in ether giving solvated R_fZnI compounds. A good example is the preparation of $n\text{-}C_3F_7ZnI$ or $(CF_3)_2CFZnI$ at 0°C in dilute dioxane solution according to:

$$n\text{-}R_fI + Zn \xrightarrow{\text{dioxane}} R_fZnI \cdot \text{dioxane}; \quad R_f = n\text{-}C_3F_7$$

[162,163], CF_3CF [164].

Solvated bis(perfluoroorganyl)zinc reagents are also formed from R_fI and dialkyzincs in Lewis base solvents,

$$2R_fI + R_2Zn \rightarrow (R_f)_2Zn + 2\,RI;$$
$$R_f = CF_3,\ C_2F_5,\ (CF_3)_2CF,\ C_6F_5.$$

Only CF_3I gives $(CF_3)_2Zn$ in quantitative yields. With C_2F_5I and $n\text{-}C_3F_7I$ contaminated compounds are obtained [165]. A remarkable reaction is observed, when zinc in dimethylformamide (DMF) is treated with CF_2X_2 giving mixtures of CF_3ZnX and $(CF_3)_2Zn$ as shown below:

$$Zn + CF_2X_2 \rightarrow CF_3ZnX + (CF_3)_2Zn;$$
$$X = Cl,\ Br\ [166].$$

An additional synthesis is based on ligand exchange between $(CH_3)_2Zn$ and $(CF_3)_2M$ (M = Hg, Cd) in DMF or pyridine yielding solvated $(CF_3)_2Zn$ [167,168]. Treating zinc atoms with CF_3I makes solvate free CF_3ZnI. It is only stable at low temperature and decomposes above –80°C [169].

7.3. Cadmium

The first perfluoroalkylcadmium compound was prepared in 1971 by ligand exchange reactions in pyridine or diglyme [170] according to:

$$(CF_3)_2Hg + CH_3Cd \rightarrow (CH_3)_2Hg + (CF_3)_2Cd.$$

An excess of $(CF_3)_2Hg$ shifts the equilibrium towards the formation of $(CF_3)_2Cd$. A decade later $(CF_3)_2Cd{\cdot}$glyme was prepared from $(CF_3)_2Hg$ and $(CH_3)_2Cd$ and isolated in a complex form as an air stable white solid [177,178]. Higher homologues are formed in a direct reaction between R_fI and $(CH_3)_2Cd$ in Lewis base solvents, e.g. CH_3CN, pyridine etc.

$$2R_fI + R_2Cd \rightarrow (R_f)_2Cd + 2\,RI$$
$$R_f = CF_3,\ C_2F_5,\ n\text{-}C_3F_7,\ (CF_3)_2CF,\ n\text{-}C_4F_9;$$
$$R = CH_3,\ C_2H_5.$$

These were isolated and characterized as Lewis base adducts [171,172]. In order to avoid the use of highly toxic dialkylcadmiums, $(R_f)_2Cd$, reagents are generated in situ via:

$$R_fI + Cd \xrightarrow{\text{DMF}} (R_f)_2Cd + (R_f)CdI;$$
$$R_f = C_nF_{2n+1},\ n = 1\text{–}8\ [173].$$

The compounds $(C_6F_{13})_2Cd$ and $(C_8F_{17})_2Cd$ are isolated in a pure state as well as an adduct with $(CH_3)_2NC(O)H$, glyme and diglyme by reacting R_fI with $(CH_3)_2Cd$. The procedure takes place in two steps according to:

$$R_fI + (CH_3)_2Cd \rightarrow CH_3CdR_fI + CH_3I$$
$$R_fI + CH_3CdCF_3 \rightarrow (R_fI)_2Cd + CH_3I$$
$$2\,R_fI + (CH_3)_2Cd \rightarrow (R_f)_2Cd + 2CH_3I.$$

When the reaction is carried out in CH_2Cl_2 solvent free colorless solid products are isolated [174]. At –40°C donor free $(CF_3)_2Cd$ has been prepared analogously from CF_3I and $(C_2H_5)_2Cd$ in quantitative yields. At –5°C it eliminates CF_2 and can be used as a low temperature source of CF_2 [175]. A series of $(CF_3)_2CdX^-$ anions are made via:

$$(CF_3)_2Cd + MX \rightarrow M^+[(CF_3)_2CdX]^-$$
$$\rightarrow M_2^+[(CF_3)_2CdX_2]^-;$$
$$M = Cs,\ Rb;\ X = Cl,\ Br,\ I\ [176].$$

7.4. Copper

For the preparation of R_f substituted copper derivatives, three main procedures are available.

1. Reaction of R_fX (X = halogen) with copper powder in Lewis base solvents at elevated temperatures.
2. In situ decarboxylation of $Cu[R_fC(O)O]_n$ in the presence of CuX.
3. Ligand transfer from $(R_f)_2M$ (M = Zn, Cd, Hg) to copper metal or Cu(I) salts.

The reactions between perfluoroalkyl iodides and copper in $(CH_3)_2SO$ at 110–120°C (1–3 h) are generally applicable, according to:

$$R_fI + 2Cu \rightarrow R_fCu + CuI, \quad R_f = C_nF_{2n+1};$$
$n = 1-7$ [179].

Disadvantages of this method are the high temperatures and rather expensive perfluoroalkyl iodides.

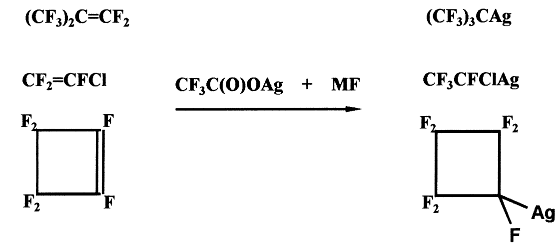
The second procedure provides R_fCu reagents only in situ, and they are used for regiospecific trifluoromethylations of arylhalides, replacing halogen for CF_3. They are made from $R_fC(O)ONa$ and CuI in dipolar aprotic solvents, e.g. N-methylpyrrolidone (NMP). For $R_f = CF_3$ the reaction is carried out at 140–160°C in the presence of an aromatic iodide [180]. Pentafluoroethyl substituted aromatics can be made by using water free solvents such as a mixture of $(CH_3)_2NC(O)H$, toluene and $C_2F_5C(O)ONa$ [181]. Metathetical reactions are applicable for the preparation of R_fCu, according to method 3. Heating $Hg(CF_3)_2$ and copper powder in NMP or dimethylacetamide at 140°C gives CF_3Cu and Cu [182]. A solution of CF_3Cu is formed almost quantitatively from a mixture of CF_3CdX and $(CF_3)_2Cd$ (made from Cd and CF_2BrCl in DMF [166]) and CuY (Y = I, Br, Cl, CN) [183]. Higher homologues are synthesized by oligomerisation of CF_3Cu at 90–100°C in $(CH_3)_2NC(O)H$ according to:

$$CF_3Cu \rightarrow C_nF_{2n+1}Cu; \quad n = 1-15 \text{ [184]}.$$

The stable copper(III) anion $[Cu(CF_3)_4]^-$ is made either by oxidizing $[CdI]^+[Cu(CF_3)_2]^-$ with oxygen, iodine, bromine [185] or by treating $CF_3Cu(I)$ in $(CH_3)_2NC(O)H$ with stoichiometric amounts of XeF_2, I_2, Br_2, Cl_2 or ICl. The complex anion can be isolated and its structure has been confirmed by X-ray structure analysis [186,187].

7.5. Silver and gold

The first perfluoroalkylsilver compounds were synthesized by addition of AgF to $CF_3CF{=}CF_2$ in CH_3CN at 25°C (2 h) yielding $(CF_3)_2CFAg$ [188] or by reacting with $F_2C{=}C{=}CF_2$ forming $CF_3C(Ag){=}CF_2$ [189]. Other suitable solvents are tetraglyme, $(CH_3)_2NC(O)H$ and benzonitrile [188]. Similarly AgF adds to $(CF_3)_2C{=}C{=}O$ forming $(CF_3)_2C(Ag)C(O)F$. Silver fluoride can be replaced by a mixture of $CF_3C(O)OAg$ and MF (M = K, Cs) giving with $CF_3CF{=}CF_2$ in CH_3CN, $(CH_3)_2NC(O)H$ or 1,2-dimethoxyethane $(CF_3)_2CFAg$. Other perfluorinated olefins react according to:



This addition presumably proceeds through a perfluorocarbanion intermediate [190]. Ligand exchange reactions are also used for the preparation of R_fAg reagents. In aprotic polar solvents such as $(CH_3)_2NC(O)H$, $(C_2H_5)_3N$ $(R_f)_2Cd{\cdot}2L$ reacts with $AgNO_3$ to R_fAg, $Cd(NO_3)_2$ and 2L (L = CH_3CN, THF, etc.), $R_f = CF_3$, C_2F_5, n-C_3F_7, $(CF_3)_2CF$, n-C_4F_9. An equilibrium exists between R_fAg and $[Ag(R_f)_2]^-$ that is strongly solvent dependent [191]. The preparation of CF_3Ag must be performed at –35°C, as spontaneous disproportion occurs above –30°C forming Ag^0 and $Ag[Ag(CF_3)_3]$ [192]. The stable complex $(CF_3)_2Cd{\cdot}$glyme is a very good trifluoromethylating reagent and was used among others for the preparation of $(CF_3)_3Au$ [204,205].

In this section also perfluoroorganochalcogeno groups bonded to Cu or Ag should be incorporated (see also Section 7). Important procedures for their preparation are metathetical reactions [193], e.g.

$$AgSCF_3 + CuBr \rightarrow CuSCF_3 + AgBr,$$

cleavage of a chalcogen–chalcogen bond in $(CH_3)_2NC(O)H$, NMP or HMPA as solvent with activated copper powder, e.g.

$$R_fEER_f + 2Cu \rightarrow 2\ R_fECu,$$
$$R_f = CF_3;\ E = S,\ Se;\ R_f = C_6F_5,\ E = Se \text{ [194, 195]}$$

fluorination of CS_2 with AgF at 140°C in an autoclave, e.g.

$$CS_2 + 3AgF \rightarrow CF_3SAg + Ag_2S \text{ [196]}$$

and sulfur insertion in $(CF_3)_3CAg$ yielding $(CF_3)_3CSAg$ [190].

The compounds described in this section proved out to be useful tools for the selective transfer of R_f-groups particularly CF_3-moieties to other metals, and non-metals as well as to organic derivatives providing other new perfluoroorgano substituted element compounds. An extensive summary on this chemistry is provided in [197] and citations therein.

8. Biological activities

Since the synthesis of N-trichloromethylthio-phthalimide and -tetrahydrophthalimide [198], two very active fungicides, intensive efforts were undertaken to prepare more active materials with lower toxicity. This is achieved by replacing chlorine in Cl_3CS by fluorine or other fluorinated radicals and exchanging the organo-imino group. Substituting one Cl for one F showed a specific increase of fungicidal activity, which decreased on further substitution. A maximum of activity was obtained for $(CH_3)_2NSO_2N(SCFCl_2)C_6H_5$ [199].

Two other compounds, the N–$SCCl(X)SCF_3$-phthalimides (X = F, SCF_3), showed excellent fungicidal activities, comparable to those of $(CH_3)_2NSO_2N(SCFCl_2)_2$–$C_6H_5$ [200]. Besides these active compounds containing either Cl_3CSN–, FCl_2CSN or $(CF_3S)_nCl(F_{2-n})CSN$– ($n = 1$, 2) groups, the R_fS-carbon substituted derivatives also showed remarkable activities. A high metabolic activity was shown for the 2,5-disubstituted thiophenes, such as 2,5-$(F_2ClCS)_2$- and 2,5-$(F_3CSO_2)_2$-thiophene. It was demonstrated, that their anorectic activities increases substantially when CF_3S– is replaced by CF_3SO_{2-} moieties but dropped by the F_2ClCS/F_2ClCSO_2 replacement. Among R_fS-substituted pyrroles the highest activity as a fungicide is shown by 2,3,4,5-$(F_3CS)_4$-pyrrole [131]. Biological activities are also observed in some perfluoroalkyl substituted aliphatic compounds. Perfluoroalkylsulfonylurea derivatives such as R_fSO_2–N(H)C(O)NH_2 ($R_f = CF_3$, n-C_4F_9, n-C_8F_{17}) inhibit cholesterol readsorption, lower the triglycerides and show anorectic activities [202] see also [203].

9. Summary and outlook

The author's intention was to summarize briefly a subject, which just started in the late 1940s and by the end of the century has developed into an enormous and important field of chemistry. The compounds and chemical reactions were selected in such a way that they illustrate how these reactive compounds could be used to prepare further compounds. Much effort was spent in the definition of perfluoroorganoelement compounds and their classification. In addition reactions between important, extensively studied moieties and basic elements were provided leading to paraelements. They were inserted into the periodic system yielding the periodic system of functional groups by applying the rules of element displacement.

These principles could support innovation and serve as a basic guide to continue the development of perfluorohalogenoorganoelement chemistry in the 21st century. They might also be useful to develop and prepare new compounds including appropriate syntheses, understanding reaction pathways, forecasting the arrangement of atoms in a molecule and extrapolating physical data. All in all researchers interested in high quality preparative chemistry will find in this field excitement, success and contentment and are invited to participate in the further organization and development of perfluorohalogenoorganoelement chemistry.

Acknowledgements

I would like to thank Prof. Dr. M.E. Peach, Acadia University, Wolfville, New Scotia, Canada, for reading the manuscript and valuable discussions.

References

[1] A. Haas, Gmelin Handbook of Inorganic and Organometallic Chemistry, Perfluorohalogenoorgano Compounds of Main Group Elements, Part 1–9; Suppl. vol. 1–6, 2nd Suppl. vol. 1–3, Springer, Berlin, 1973–1997.
[2] A.A. Banks, H.J. Emeléus, R.N. Haszeldine, V. Kerrigan, J. Chem. Soc. (1948) 2188.
[3] H.J. Emeléus, R.N. Haszeldine, J. Chem. Soc. (1949) 2948.
[4] A.L. Henne, W.G. Finnegan, J. Am. Chem. Soc. 72 (1950) 3806.
[5] R.N. Haszeldine, J. Chem. Soc. (1951) 584.
[6] C. Wakselman, A. Lomtz, Perfluoroalkyl Bromides and Iodides, In: R.E. Banks, B.E. Smart, J.C. Tatlow (Eds.), Organofluorine Chemistry, Plenum Press, New York, 1994, 188.
[7] R.E. Banks, A.K. Barbour, A.E. Tipping, B. Gething, C.R. Patrick, J.C. Tatlow, Nature 183 (1959) 586.
[8] N.N. Vorozhtsov, V.E. Platonov, G.G. Yakobson, Izw. Akad. Nauk SSSR, Ser. Khim. (1963) 1524.
[9] N.N. Vorozhtsov, V.E. Platonov, G.G. Yakobson, Bull. Acad. Sci. USSR, Div. Chem. Sci. (1963) 1389.
[10] N.N. Vorozhtsov, V.E. Platonov, G.G. Yakobson, Zhur. Obshch. Khim. 35 (1965) 1158.
[11] E. Nields, R. Stephens, J.C. Tatlow, J. Chem. Soc. (1959) 166.
[12] G.M. Brooke, E.J. Forbes, R.D. Richardson, M. Stacey, J.C. Tatlow, J. Chem. Soc. (1965) 2088.
[13] H.J. Emeléus, Metallic compounds containing fluorocarbon radicals and organometallic compounds containing fluorine, in: J.H. Simons (Ed.), Fluorine Chemistry, vol. 2, Academic Press, New York, 1954, pp. 321–336.
[14] F.W. Bennett, H.J. Emeléus, R.N. Haszeldine, J. Chem. Soc. (1953) 1565.
[15] L.K. Peterson, A.B. Burg, J. Am. Chem. Soc. 86 (1964) 2587.
[16] H.J. Emeléus, J.D. Smith, J. Chem. Soc. (1959) 375–381.
[17] H.J. Emeléus, R.N. Haszeldine, E.G. Walaschewski, J. Chem. Soc. (1953) 1552.
[18] E.G. Walaschewski, Chem. Ber. 86 (1953) 272.
[19] J.W. Dale, H.J. Emeléus, R.N. Haszeldine, J.H. Moss, J. Chem. Soc. (1957) 3708.
[20] F.W. Bennett, G.A.R. Brandt, H.J. Emeléus, R.N. Haszeldine, Nature 166 (1950) 225.
[21] G.A.R. Brand, H.J. Emeléus, R.N. Haszeldine, J. Chem. Soc. (1952) 2198.
[22] R.N. Haszeldine, J.M. Kidd, J. Chem. Soc. (1953) 3219.
[23] J.W. Dale, H.J. Emeléus, R.N. Haszeldine, J. Chem. Soc. (1958) 2939.
[24] H.J. Emeléus, R.N. Haszeldine, J. Chem. Soc. (1949) 2948, 2953.
[25] R.J. Harper, E.J. Soloski, C. Tamborski, J. Org. Chem. 29 (1964) 2385.
[26] S.C. Cohen, M.L.N. Reddy, D.M. Roe, A.J. Tomlinson, A.G. Massey, J. Organometal. Chem. 14 (1968) 241.
[27] P.L. Coe, R. Stephens, J.C. Tatlow, J. Chem. Soc. (1962) 3227.
[28] D.E. Fenton, A.G. Massey, J. Inorg. Nucl. Chem. 27 (1965) 329.
[29] A.E. Jukes, H. Gilman, J. Organometal. Chem. 17 (1969) 145.
[30] W.J. Pummer, L.A. Wall, J. Res. Natl. Bur. Std. A 63 (1959) 167.
[31] E. Nield, R. Stephens, J.C. Tatlow, J. Chem. Soc. (1959) 166.
[32] C.W. Tullock, D.D. Coffman, J. Org. Chem. 25 (1960) 2016.
[33] C.A. Burton, J.M. Shreeve, Inorg. chem. 16 (1977) 1039.
[34] Minnesota Mining and Manufg. Co., T.J. Brice, P.W. Trott, US Patent 2 732 398, 1956; C.A. (1956) 13982.
[35] R.N. Haszeldine, J.M. Kidd, J. Chem. Soc. (1955) 2901.
[36] J. Burdon, J. Farazmand, M. Stacey, J.C. Tatlow, J. Chem. Soc. (1957) 2574.
[37] T. Gramstad, R.W. Haszeldine, J. Chem. Soc. (1957) 2640 (see also patent in [34]).
[38] Minnesota Mining and Manufg. Co., H-J. Simons, US Patent 2 519 983, 1950; C.A. (1951) 51.

[39] W.J. Middleton, E.G. Howard, W.H. Sharkey, J. Am. Chem. Soc. 83 (1961) 2589.
[40] W.J. Middleton, E.G. Howard, W.H. Sharkey, J. Org. Chem. 30 (1965) 1375.
[41] A. Darmadi, A. Haas, B. Koch, Z. Naturforsch. B 35 (1980) 526.
[42] R. Boese, A. Haas, M. Spehr, Chem. Ber. 124 (1991) 51.
[43] A. Haas, M. Spehr, Chimia 42 (1988) 265.
[44] R. Boese, A. Haas, Ch. Limberg, J. Chem. Soc., Chem. Commun. (1991) 3378.
[45] J. Grobe, D. Le Van, J. Welzel, J. Organomet. Chem. 386 (1990) 321.
[46] A. Haas, Ch. Limberg, Chimia 46 (1992) 72.
[47] R. Boese, A. Haas, Ch. Limberg, J. Chem. Soc., Dalton Trans. (1993) 2547.
[48] J. Beck, A. Haas, W. Herrendorf, H. Heuduk, J. Chem. Soc., Dalton Trans. (1996) 4463.
[49] J. Grobe, D. Le Van, Angew. Chem. 96 (1984) 716.
[50] J. Grobe, D. Le Van, Angew. Chem. Int. Ed. Engl. 23 (1984) 710.
[51] J. Grobe, M. Hegemann, D. Le Van, Z. Naturforsch. B 45 (1990) 148.
[52] J. Grobe, J. Szameitat Z. Naturforsch. B 41 (1986) 974.
[53] J.A. Young, S.N. Tsoukalas, R.D. Dresdner, J. Am. Chem. Soc. 80 (1958) 3604.
[54] H.J. Emeléus, The Chemistry of Fluorine and its Compounds, Academic Press, New York, 1969, pp. 77–91.
[55] I.L. Knunyants, A.F. Gontar, Chem. Rev. 5 (1984) 219–254 (Edit. M.E. Vol'pin).
[56] A.V. Fokin, Yu.N. Studnev, A.I. Rapkin, Chem. Rev. 5 (1984) 1–46 (Edit. M.E. Vol'pin).
[57] H. Gilman, R.G. Jones, J. Am. Chem. Soc. 65 (1943) 1458.
[58] F. Swarts, Bull. Classe Sci. Acad. Roy. Belg. 8 (1922) 343; C.A. (1923) 769.
[59] J.H. Simmons, Trans. Electrochem. Soc. 95 (1949) 47–52.
[60] J.A.C. Allison, G.H. Cady, J. Am. Chem. Soc. 81 (1959) 1089.
[61] K.B. Kellog, G.H. Cady, J. Am. Chem. Soc. 70 (1948) 3986.
[62] J.W. Dale, International Symposium on Fluorine Chemistry, University of Birmingham and The Chemical Society, London, 1959, p. 29.
[63] R.T. Lageman, E.A. Jones, P.J.H. Woltz, J. Chem. Phys. 20 (1952) 1768.
[64] G. Pass, H.L. Roberts, Inorg. Chem. 2 (1963) 1016.
[65] W.P. Van Meter, G.H. Cady, J. Am. Chem. Soc. 82 (1960) 6005.
[66] R.S. Porter, G.H. Cady, J. Am. Chem. Soc. 79 (1957) 5625.
[67] G.H. Cady, K.B. Kellog, J. Am. Chem. Soc. 75 (1953) 2501.
[68] R.D. Stewart, G.H. Cady, J. Am. Chem. Soc. 77 (1955) 6110.
[69] A. Menefee, G.H. Cady, J. Am. Chem. Soc. 76 (1954) 2020.
[70] J.H. Simmons, B.P. 659251 (1951), US Patent 2 500 388, 1950.
[71] E.A. Kauck, J.H. Simmons, US Patent 2 594 272, 1952.
[72] G.V.D. Tiers, J. Am. Chem. Soc. 77 (1955) 4837.
[73] J.H. Prager, P.G. Thompson, J. Am. Chem. Soc. 87 (1965) 230.
[74] M. Lustig, A.R. Pitochelli, J.K. Ruff, J. Am. Chem. Soc. 89 (1967) 2841.
[75] C.J. Schack, W. Maya, J. Am. Chem. Soc. 91 (1969) 2902.
[76] P.G. Thompson, J. Am. Chem. Soc. 89 (1967) 1811.
[77] R.L. Cauble, G.H. Cady, J. Am. Chem. Soc. 89 (1967) 1962.
[78] F.A. Hohorst, J.M. Shreeve, J. Am. Chem. Soc. 89 (1967) 1800.
[79] P.G. Thompson, J.H. Prager, J. Am. Chem. Soc. 89 (1967) 2263.
[80] A. Arvia, P. Aymonino, C. Waldow, H.J. Schumacher, Angew. Chem. 72 (1960) 169.
[81] R. Czerpinski, G.H. Cady, Inorg. Chem. 7 (1968) 169.
[82] P. Aymonino, Proc. Chem. Soc. (1964) 341.
[83] D.C. England, C.G. Krespan, J. Am. Chem. Soc. 88 (1966) 5582.
[84] R.J. Lagow, T.R. Bierschenk, T.J. Juhlke, H. Kawa, in: G.A. Olah, R.D. Chambers, G.K. Surya Prakash (Eds.), Synthetic Fluorine Chemistry, Wiley, New York, 1991, p. 97.
[85] M. Schmeißer, E. Scharf, Angew. Chem. 71 (1959) 524.
[86] C. Rondestredt, J. Am. Chem. Soc. 91 (1969) 3054.
[87] L.J. Turbini, R.E. Ackman, R.J. Lagow, J. Am. Chem. Soc. 101 (1979) 5833.
[88] H.J. Frohn, St. Jakobs, J. Chem. Soc., Chem. Commun. (1989) 625.
[89] D. Naumann, W. Tyrra, J. Chem. Soc., Chem. Commun. (1989) 47.
[90] J.J. Lagowski, Quart. Rev. 8 (1959) 233.
[91] L. Birkenbach, K. Kellermann, Ber. Dtsch. Chem. Ges. 58 (1925) 786.
[92] H.G. Grimm, Z. Electrochem. 31 (1925) 474.
[93] A. Haas, Pure Appl. Chem. 63 (1991) 1577.
[94] E. Zintl, Angew. Chem. 53 (1939) 1.
[95] W. Klemm, E. Bussmann, Z. Anorg. Allg. Chem. 319 (1963) 297.
[96] A. Haas, Chem. Ztg. 106 (1982) 239.
[97] M. Bögemann, S. Petersen, D.E. Schultz, H. Söll, Methoden der Organischen Chemie (Houben-Weil-Müller), 4 Aufl., vol. IX, Thieme, Stuttgart, 1955, p. 790.
[98] D.H.R. Barton, M.J. Robson, J. Chem. Soc., Perkin Trans. I (1974) 1247.
[99] A. Haas, R. Walz, Chem. Ber. 118 (1985) 3248.
[100] A. Golloch, M. Kuss, Z. Naturforsch. B 27 (1972) 1281.
[101] A. Haas, U. Westebbe, Unpublished results.
[102] A. Haas, K. Tebbe, Z. Naturforsch. B 39 (1984) 897.
[103] E.A. Appelman, Acc. Chem. Res. 6 (1973) 113.
[104] E.A. Lawton, D. Pilipovich, R.D. Wilson, Inorg. Chem. 4 (1965) 118.
[105] D.J. Burton, J.L. Hahnfeld, Fluorine Chem. Rev. 8 (1977) 119.
[106] K. Seppelt, Angew. Chem. 89 (1977) 325.
[107] K. Seppelt, Angew. Chem. Int. Ed. 16 (1977) 322.
[108] D.A. Barr, R.N. Haszeldine, J. Chem. Soc. (1955) 2532.
[109] J.H. Young, S.N. Tsoukalas, R.D. Dresdner, J. Am. Chem. Soc. 80 (1958) 3604.
[110] I.L. Knunyants, M.P. Krasuskaya, N.P. Gambaryan, Izv. Akad. Nauk SSSR Ser. Khim. (1965) 723.
[111] I.L. Knunyants, M.P. Krasuskaya, N.P. Gambaryan, Bull. Akad. Sci. USSR Chem. Div. (1965) 702.
[112] M.E. Redwood, C.J. Willis, Can. J. Chem. 43 (1965) 1893.
[113] J.H. Young, S.N. Tsoukalas, R.D. Dresdner, J. Am. Chem. Soc. 80 (1958) 3604.
[114] P.E. Aldrich, E.G. Howard, W.J. Linn, W.J. Middleton, W.H. Sharkey, J. Org. Chem. 28 (1963) 184.
[115] H.E. Borowski, A. Haas, Chem. Ber. 115 (1982) 533.
[116] A. Haas, R. Lorenz, Unpublished results; R. Lorenz, Dissertation, Bochum, 1972.
[117] K.H. Flegler, A. Haas, Chem. Ztg. 100 (1976) 339.
[118] J.P. Freeman, Inorg. Chim. Mta. Rev. 1 (1967) 65.
[119] A.J. Vosper, J. Chem. Soc. A. (1970) 625.
[120] K. Schlosser, S. Steenken, J. Am. Chem. Soc. 105 (1983) 1504.
[121] A. Haas, K. Schlosser, S. Steenken, J. Am. Chem. Soc. 101 (1979) 6282.
[122] J.J. De Corpo, R.P. Steiger, J.L. Franklin, J.L. Margrave, J. Chem. Phys. 53 (1970) 936.
[123] H.E. Borowski, A. Haas, Chem. Ber. 115 (1982) 523.
[124] A. Haas, M. Häberlein, C. Krüger, Chem. Ber. 109 (1976) 1769.
[125] A. Haas, M. Willert-Porada, Chem. Ber. 118 (1985) 1463.
[126] R. Boese, J. Dworak, A. Haas, M. Pryka, Chem. Ber. 128 (1995) 477.
[127] A. Haas, Adv. Heterocycl. Chem. 71 (1998) 115.
[128] A. Haas, Adv. Inorg. Radiochem. 28 (1984) 167.
[129] R.M. Haszeldine, J.M. Kidd, J. Chem. Soc. (1955) 2901.
[130] G.A.R. Brandt, H.J. Emeléus, R.N. Haszeldine, J. Chem. Soc. (1952) 2198.
[131] S. Dorn, P. Eggenberg, M.R.C. Gerstenberger, A. Haas, U. Niemann, P. Zobrist, Helv. Chem. Acta 62 (1979) 1442.
[132] D.M. Ceacarceanu, M.R.C. Gerstenberger, A. Haas, Chem. Ber. 116 (1983) 3325.
[133] A. Haas, T. Maciej, Z. Anorg. Allg. Chem. 524 (1985) 33.
[134] M.R.C. Gerstenberger, A. Haas, B. Kirste, C. Krüger, H. Kurrek, Chem. Ber. 115 (1982) 2540.

[135] H. Stetter, Angew. Chem. 74 (1962) 361.
[136] N.V. Averina, N.S. Zefirov, Aspekki Khimii 45 (1976) 1077.
[137] N.V. Averina, N.S. Zefirov, Russian Chem. Rev. 45 (1976) 544.
[138] B.M. Mikhailov, Pure Appl. Chem. 52 (1980) 691.
[139] A. Haas, R. Hitze, C. Krüger, K. Angermund, Z. Naturforsch. B 39 (1984) 890.
[140] A. Haas, H.J. Kutsch, C. Krüger, Chem. Ber. 120 (1987) 1045.
[141] A. Berwe, A. Haas, Chem. Ber. 120 (1987) 1175.
[142] C.G. Krespan, J. Org. Chem. 25 (1960) 107.
[143] W.T. Miller, M.B. Freedman, J. Am. Chem. Soc. 85 (1963) 180.
[144] P.E. Aldrich, E.G. Howard, W.J. Linn, W.J. Middleton, W.H. Sharkey, J. Org. Chem. 28 (1963) 184.
[145] H. Goldwhite, R.N. Haszeldine, R.N. Mukherjee, J. Chem. Soc. (1961) 3825.
[146] K.J. Klabunde, J.Y.F. Low, M.S. Key, J. Fluorine Chem. 2 (1972/1973) 207.
[147] B.L. Dyatkin, S.R. Sterlin, B.I. Martynov, I.L. Knunyants, Tetrahedron Lett. (1970) 1387.
[148] B.L. Dyatkin, S.R. Sterlin, B.I. Martynov, E.I. Mysov, I.L. Knunyants, Tetrahedron 27 (1971) 2843.
[149] E.H. Man, D.D. Coffman, E.L. Muetterties, J. Am. Soc. 81 (1959) 3575.
[150] A.J. Downs, J. Chem. Soc. (1962) 4361.
[151] B.L. Dyatkin, S.R. Sterlin, B.I. Martynov, I.L. Knunyants, Tetrahedron Lett. (1971) 345.
[152] R.N. Haszeldine, J.M. Kidd, J. Chem. Soc. (1955) 3871.
[153] W.V. Rochat, G.L. Gard, J. Org. Chem. 34 (1969) 4173.
[154] H.J. Emeleus, H. Pugh, J. Chem. Soc. (1960) 1108.
[155] M.E. Peach, Can. J. Chem. 46 (1968) 2699.
[156] H.J. Emeleus, N. Welcman, J. Chem. Soc. (1963) 1268.
[157] N. Wekman, H. Regev, J. Chem. Soc. (1965) 7511.
[158] E. Kostiner, M.L.N. Reddy, D.S. Lerch, A.G. Massey, J. Organomet. Chem. 15 (1968) 383.
[159] J. Kischkewitz, D. Naumann, Z. Anorg. Allg. Chem. 547 (1987) 167.
[160] H.L. Paige, J. Passmore, Inorg. Nucl. Chem. Lett. 9 (1973) 277.
[161] R. Kasemann, D. Naumann, J. Fluorine Chem. 48 (1990) 207.
[162] R.N. Haszeldine, E.G. Walaschewski, J. Chem. Soc. (1953) 3607.
[163] W.T. Miller Jr., E. Bergman, A.H. Fainberg, J. Am. Chem. Soc. 79 (1957) 4159.
[164] R.D. Chambers, W.K.R. Masgrave, J. Savory, J. Chem. Soc. (1962) 1993.
[165] H. Lange, D. Naumann, J. Fluorine Chem. 26 (1984) 435.
[166] D.J. Burton, D.M. Wiemers, J. Am. Chem. Soc. 107 (1985) 5014.
[167] E.K.S. Liu, L.B. Asprey, J. Organomet. Chem. 169 (1979) 249.
[168] E.K.S. Liu, Inorg. Chem. 19 (1980) 266.
[169] K.J. Klabunde, M.S. Key, J.Y.F. Low, J. Am. Chem. Soc. 94 (1972) 999.
[170] B.L. Dyatkin, B.I. Martynov, I.L. Knunyants, S.R. Sterlin, L.A. Fedorov, Z.A. Stumbrevichute, Tetrahedron Lett. (1971) 1345.
[171] H. Lange, D. Naumann, J. Fluorine Chem. 26 (1984) 1.
[172] H. Lange, D. Naumann, J. Fluorine Chem. 41 (1988) 185.
[173] P.L. Heinze, D.J. Burton, J. Fluorine Chem. 29 (1985) 359.
[174] D. Naumann, K. Glinka, W. Tyrra, Z. Anorg. Allg. Chem. 594 (1991) 95.
[175] E. Eujen, B. Hogen, J. Organomet. Chem. 503 (1995) C51.
[176] D. Naumann, W. Tyrra, J. Organomet. Chem. 368 (1989) 131.
[177] L.J. Krause, J.A. Morrison, J. Chem. Soc., Chem. Commun. (1981) 1282.
[178] L.J. Krause, J.A. Morrison, J. Am. Chem. Soc. 103 (1981) 2995.
[179] V.C.R. McLoughlin, J. Thrower, Tetrahedron 25 (1969) 5921.
[180] K. Matsui, E. Tobita, M. Ando, K. Kondo, Chem. Lett. (1981) 1719.
[181] J.N. Freskos, Synth. Commun. 18 (1988) 965.
[182] N.V. Kondratenko, E.P. Vechirko, L.M. Yagupolskii, Synthesis (1980) 932.
[183] D.M. Wiemers, D.J. Burton, J. Am. Chem. Soc. 108 (1986) 832.
[184] J.C. Easdon, Ph. D. Thesis, University of Iowa, 1987.
[185] M.A. Willert-Porada, D.J. Burton, N.C. Baenziger, J. Chem. Soc., Chem. Commun. (1989) 1633.
[186] D. Naumann, T. Roy, K.F. Tebbe, W. Crump, Angew. Chem. 105 (1993) 1555.
[187] D. Naumann, T. Roy, K.F. Tebbe, W. Crump, Angew. Chem. Int. Ed. 105 (1993) 1482.
[188] W.T. Miller Jr., R.J. Burnard, J. Am. Chem. Soc. 90 (1968) 7367.
[189] R.E. Banks, R.N. Haszeldine, D.R. Taylor, G. Webb, Tetrahedron Lett. (1970) 5215.
[190] B.L. Dyatkin, B.I. Martynov, L.G. Martynova, N.G. Kizim, S.R. Sterlin, Z.A. Stumbrevichute, L.A. Fedorov, J. Organomet. Chem. 57 (1973) 423.
[191] D. Naumann, W. Wessel, J. Hahn, W. Tyrra, J. Organomet. Chem. 547 (1997) 79.
[192] W. Dukat, D. Naumann, Rev. Chim. Miner. 23 (1986) 589.
[193] L.M. Yagupolskii, N.V. Kondratenko, V.P. Sambur, Synthesis (1975) 721.
[194] N.V. Kondratenko, A.A. Kolomeytsev, V.I. Popov, L.M. Yagupolskii, Synthesis (1985) 667.
[195] L.M. Yagupolskii, J. Fluorine Chem. 36 (1987) 1.
[196] H.J. Emeleus, D.E. MacDuffie, J. Chem. Soc. (1961) 2597.
[197] D.J. Burton, Z.-Y. Yang, Tetrahedron 48 (1992) 189.
[198] A.R. Kittleson, Sciences (Washington) (1952) 115.
[199] E. Kühle, E. Klauke, F. Grewe, Angew. Chem. 76 (1964) 807.
[200] E. Kühle, A. Haas, W. Klug, F. Grewe, Deutsch. Offenlegungsschrift 1908680, A.G. Farbenfabriken Bayer, 1969/1970; C.A. 73 (1970) 109522.
[201] A. Haas, C. Klare, Chem. Ber. 118 (1985) 4588.
[202] M.R.C. Gerstenberger, A. Haas, H. Pauling, Helvetica Chim. Acta 65 (1982) 490.
[203] A. Haas, L'Actualite Chimique (1987) 183.
[204] R.D. Sanner, J.H. Satcher Jr., M.W. Droege, Organometallics 8 (1989) 1498.
[205] H.K. Nair, J.A. Morrison, J. Organomet. Chem. 376 (1989) 149.