Fluorine as a structure-directing element in organometallic fluorides: discrete molecules, supramolecular self-assembly and host–guest complexation †

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Although formally monovalent (in the classical sense) fluorine can behave as mono-, di-, tri- or tetra-connective and can be encrypted as a guest in host–guest complexes. The broad limits of valence bonds, spanning the range from below 90° to 180° (linearity) and a strong tendency to form bi-, tri- and even tetra-metallic bridges, allows the formation of cyclic and cage compounds of very different compositions and structures. The emerging field of organometallic fluorides is a promising area of research.

1 Introduction

Fluorine, the first member of the halogen family, is expected to be monocovalent or to form mono anions. Being the most electronegative element, fluorine forms very polar, strong chemical bonds with the non-metals and metalloids and/or ionic compounds with the electropositive metals. Its binary inorganic

† Dedicated to Professor F. Albert Cotton.

Herbert W. Roesky was born in 1935 in Laukischken. He studied chemistry at the University of Göttingen, Germany, where he obtained his Diploma in 1961 and doctoral degree in 1963. After one year of postdoctoral work at DuPont in Wilmington, DE, he made his habilitation at the University of Göttingen. In 1971 he became full professor in Frankfurt/Main, and since 1980 he has been a full professor and director of the Institute of Inorganic Chemistry at the University of Göttingen. He has been a visiting professor at Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, Tokyo Institute of Technology, and Kyoto University and also frontiers lecturer at Texas A&M University at College Station, University of Texas at Austin and University of Iowa at Iowa City. He is a member of the Academy of Sciences at Göttingen, the New York Academy of Sciences, the Academy of Scientists 'Leopoldina' in Halle, and the Academia Europaea in London. He served as the vice-president of the German Chemical Society during 1995, and in the period from 1996 to 1998 he was the speaker of Wöhler Vereinigung für Anorganische Chemie. He has received many awards, e.g. the Dr.h.c.(honoris causa) of Bielefeld, Brünn, and Bucharest Universities, Alfred-Stock-Memorial Award, the French Alexander-von-Humboldt award. In 1998 he obtained the Grand Prix de la Maison de la Chimie and very recently (1999), the ACS award for creative work in fluorine chemistry. More than 750 publications, articles, patents, and books document his research activity in the areas of inorganic chemistry and materials science.

Ionel Haiduc is professor at "Babes-Bolyai" University, in Cluj-Napoca, Romania. He obtained his PhD in Moscow with Professor K. A. Andrianov with a thesis on organosilicon chemistry, was a Fulbright Postdoctoral Fellow with Professor Henry Gilman at Iowa State University (1966–1968) and with Professor R. Bruce King at the University of Georgia, Athens, Georgia (1971–1972). He was visiting Professor at Instituto de Quimica, Universidad Nacional Autonoma de Mexico (1993–1994), University of Texas at El Paso (1997) and Universidad de Santiago de Compostela, Spain (1998). He received a Humboldt Fellowship for a research visit to Universität Magdeburg, Germany (1997) and the Gauss Professorship of the Akademie der Wissenschaften in Göttingen, Germany (1998). He also received visiting grants from the National Science Foundation (USA, 1992), European Community (Spain, 1993) and British Council (United Kingdom, 1995) and a NATO Cooperative Research Grant (United Kingdom, 1997). He has authored or co-authored several books (including The Chemistry of Inorganic Ring Systems, *1970,* The Chemistry of Inorganic Homo- and Heterocycles, *1987,* Basic Organometallic Chemistry, *1985,* Organometallics in Cancer Chemotherapy, *1989, 1990 and* Supramolecular Organometallic Chemistry, *1999 in press) and more than 250 research papers and several chapters in some multi-authored books. His interests cover inorganic ring systems, Main Group organometallic and coordination chemistry, organophosphorus and organoarsenic ligands and supramolecular organometallic chemistry. He participated in an extensive international collaboration with colleagues from the United Kingdom, Germany, Spain, Mexico, Belgium, United States of America, Brazil, Canada and France, which resulted in numerous joint publications. After the anti-communist revolution in Romania (December 1989) he was elected and served as Rector (President) of "Babes-Bolyai" University (1990–1993), and in 1998 was elected vice-president of the Romanian Academy.*
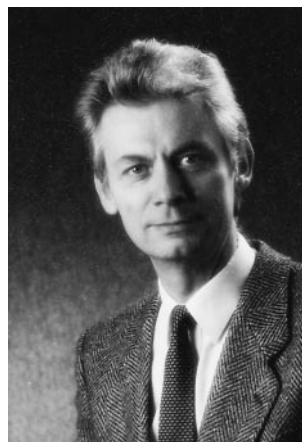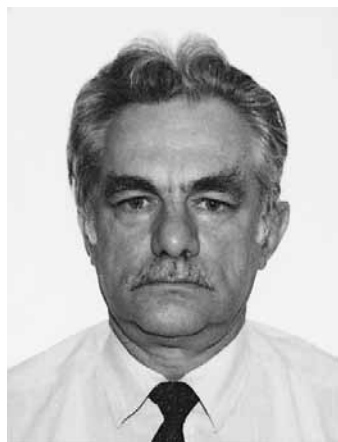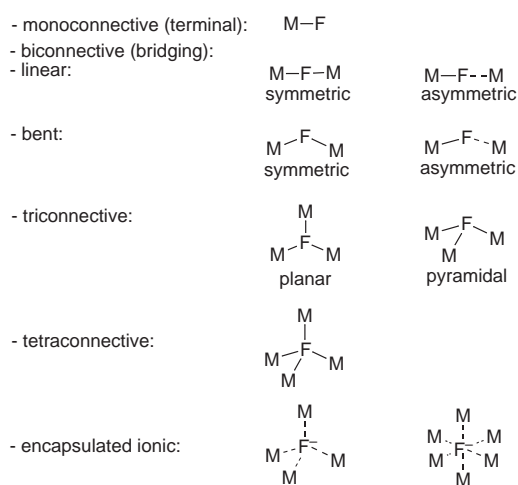
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compounds are either molecular fluorides EF_n or insoluble solids (in which F^- anions alternate with metal cations to form usually tridimensional networks). Between these two extremes, there are some associated compounds, such as tetrameric, cyclic transition metal pentafluorides, $[MF_5]_4$ (M = Nb, Ta, Mo) and polymeric antimony pentafluoride, $[SbF_5]_n$, in which the fluorine atoms form bridges,[1] thus showing that in covalent bonds, the fluorine retains some Lewis base (donor) properties, resulting in an increase of its connectivity. We will use throughout this article the term *connectivity* to describe the number of links to other atoms, to avoid any implications about the nature of the bonds (covalent, coordinative, ionic or secondary interactions).

Until relatively recently, organometallic chemists avoided fluorine for several reasons. One of them was probably the fact that alkyl and aryl fluorides, unlike other halides, do not react directly with active metals, such as magnesium to give Grignard reagents, or lithium, to give organolithium reagents, both extremely useful precursors in organometallic syntheses. The exchange of other halogens for fluorine was generally hampered by the lack of convenient reagents. With a few early exceptions, only in recent years have organometallic fluorides entered the stage and became an attractive field of research. Main group,[2] d-block element[3] and f-element[4] organometallic fluorides are covered by some recent reviews.

During recent years, not only have a large number of organometallic fluorides been synthesised, but numerous molecular and crystal structures have been determined by X-ray diffraction. An overview of the known structures of organometallic fluorides reveals the fact that fluorine plays an important role as a structure directing element, and its bonding patterns are much more diversified than one would expect from a mono-covalent element. These patterns can be classified according to the connectivity of fluorine and its role in the molecular architecture of organometallic fluorides. Thus the following types can be distinguished (Scheme 1):

- monoconnective (terminal): M—F
- biconnective (bridging):
- linear:

     M—F—M   M—F‑‑M
     symmetric   asymmetric

- bent:

     symmetric   asymmetric

- triconnective:

     planar   pyramidal

- tetraconnective:

- encapsulated ionic:

Scheme 1

(a) *Monoconnective* fluorine, forming 'terminal' polar covalent bonds.

(b) *Biconnective* fluorine, forming symmetric or asymmetric bridges, which can be linear or bent.

(c) *Triconnective* fluorine, in either a pyramidal or planar geometrical arrangement.

(d) *Tetraconnective* fluorine, mostly tetrahedral.

(e) *Ionic* fluorine *encapsulated* in cage-like hosts.

All these sub-units may serve as building blocks for a broad diversity of chemical architectures.

The similarity of bonding modes of fluorine with those known for a dicovalent element, oxygen, is striking. Oxygen forms similar building blocks. There is, however, a difference.

Oxygen forms two covalent bonds, but in the case of fluorine, only one of the bonds can be described as covalent, the second and successive ones are coordinative bonds. Sometimes the coordinative bond character is maintained, leading to asymmetric bridges, but bond equalisation may occur and in the symmetric bridge the two bonds are the result of mixing covalent and coordinative bonds. The consequence will be an increase in the interatomic distance, in comparison with the terminal (monoconnective) M–F bonds. When fluorine becomes tri- or tetra-connective the contribution of coordinative bond character is still higher, and some further lengthening of the M–F bonds may be expected.

The consequences of the diversity in connectivity patterns of fluorine will be discussed further. Monoconnective fluorine leads to the formation of discrete molecules, in which it is just another monovalent substituent. The formation of bridges between fluorine as donor and various atoms as acceptors, results in intermolecular self-assembly, with formation of cyclic and cage supermolecules or supramolecular arrays. Thus, the chemistry of organometallic fluorides steps into the field of supramolecular chemistry.

Since reference was made to supramolecular chemistry, perhaps it is useful to remember some definitions and concepts which will be used throughout this article in the presentation of organometallic fluorides. Supramolecular chemistry is '*the chemistry of molecular assemblies and of the intermolecular bond*'. It is '*the chemistry beyond the molecule*' and deals with '*organised entities of higher complexity that result from the association of two or more chemical species held together by intermolecular forces*'.[5,6] There are two types of subjects in supramolecular chemistry: (a) the *supramolecular assemblies* or systems, also called supramolecular arrays, i.e. '*polymolecular entities that result from the spontaneous association of a large undefined number of components*', and (b) *supermolecules or supramolecular arrays i.e. 'well-defined discrete oligomolecular species that result from the intermolecular association of a few components*'.[7]

Chemical bonds in fluorine chemistry are not limited to covalence. Very important are the *coordinative bonds*. In addition to normal covalent bonds, E–F, which are formed by pairing of the free p-electron of the fluorine atom, with an electron of the partner element, the monocovalent fluorine can participate in additional coordinative bonds, F→E, formed by donation of an electron pair from fluorine to an acceptor atom, thus forming an M–F→M bridge. There is a general tendency to assume that the two-electron bonds between a certain pair of atoms are identical, regardless of the origin of electrons (*i.e.* covalent and coordinative), but it has been pointed out that a distinction between the two types should be made.[8,9] In practise, however, it is often impossible to differentiate between the two bonding modes.

The normal covalent and coordinative bonds differ in several major aspects: (a) the nature of the fragments formed when the bonds are broken; (b) the nature of the bond rupture process and (c) the magnitude of the bond cleavage enthalpy. The normal covalent bond ruptures homolytically and the neutral species formed are free radicals; the coordinative bond rupture proceeds in general heterolytically, with the formation of neutral diamagnetic molecules.

When an electron pair donor and an acceptor site are present in the same molecule, and the molecular compound is coordinatively unsaturated, intermolecular association may occur with formation of cyclic (or polymeric) species. This frequently occurs in organometallic compounds,[10] including fluorides. The process is called *self-assembly*. Self-assembly is defined as *a spontaneous association of molecules under equilibrium conditions into stable aggregates held together by non-covalent forces.*[11] The resulting species is a *supermolecule* (see above).

Numerous monomeric organometallic fluoride molecules are able to self-assemble into cyclic supermolecules or sometimes

into supramolecular polymeric arrays. However, most of the compounds characterized in the following sections are not under equilibrium conditions.

2 Discrete molecules

2.1 Monoconnective fluorine (terminal bonds)

There are some organometallic compounds containing one or more fluorine atoms singly bonded to a central metal atom as single, covalent, terminal bonds in discrete, unassociated molecules. This monoconnective fluorine bonding is not particularly interesting, but the terminal covalent bonds are useful in estimating the standard M–F bond lengths. Table 1 contains a list of terminal M–F bond lengths measured in a number of organometallic compounds. They can serve for comparisons with M–F interatomic distances in bridging fluorine units.

2.2 Dinuclear compounds with bridging fluorine

The simplest consequence of biconnective binding of fluorine is the formation of dinuclear compounds with fluorine bridging two identical or different metal atoms. As shown above, there are four types of bridges, because both symmetric and asymmetric, linear and bent geometries are possible. When the two atoms bridged by fluorine are different, asymmetry is most likely. A particular case of fluorine bridging results from the coordination of some fluoro anions, such as $[BF_4]^-$, $[PF_6]^-$, $[AsF_6]^-$ or $[SbF_6]^-$, which have the reputation of being weakly coordinating anions.[59,60] However, they can be attached to metal atoms through M–F–E (E = B, P, As, Sb) bridges, showing that even in non-metal covalent compounds some terminal E–F bonds retain donor capacity.

2.2.1 Symmetric linear bridges. A linear symmetric bridge (Scheme 2) was first identified in dialuminium anions $[R_3Al–F–$
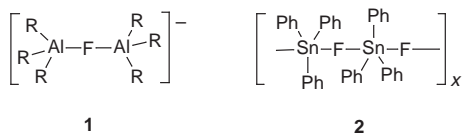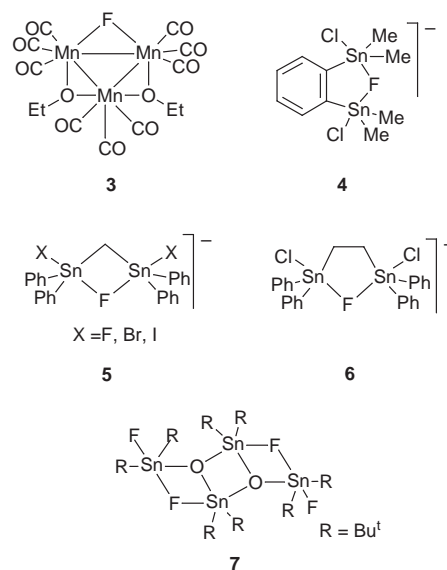
Scheme 2

$AlR_3]^-$ **1** (R = Me, Et) by X-ray diffraction analysis of a compound initially formulated as KF·2AlEt$_3$,[61] and later found also in K[Me$_3$Al(µ-F)AlMe$_3$]·C$_6$H$_6$.[62] The Al–F–Al bond angle is 180° in both compounds, and the Al–F bond lengths are 1.820(3) Å in the ethyl derivative and 1.782(2) Å in the methyl derivative, significantly longer than terminal Al–F bonds (ca. 1.65 Å). The linear anion [Me$_3$Al–F–AlMe$_3$]$^-$ is isoelectronic but not isostructural with the bent molecule of hexamethyl-disiloxane, Me$_3$Si–O–SiMe$_3$ [Si–O–Si 148.8(1)°].[63] Only hexa-phenyldisiloxane, Ph$_3$Si–O–SiPh$_3$, is linear.[64]

A linear fluorine bridge is present in triphenyltin fluoride, which is a rod-like polymer [Ph$_3$Sn(µ-F)]$_x$ **2**, with identical Sn–F interatomic distances of 2.1458(3) Å.[65] Similar linear (rod-like) structures are those of [(PhCH$_2$)$_3$Sn(µ-F)]$_x$[66] and [(Me$_3$SiCH$_2$)$_3$-Sn(µ-F)]$_x$ (2.565 Å).[67] In other triorganotin fluorides the Sn–F–Sn bridges are asymmetric and bent (see below).

2.2.2 Symmetric bent bridges. Symmetric bent bridges seem to be imposed by metal–metal bonds, leading to the formation of a three-membered ring (Scheme 3). Thus, in [Mn$_3$-(CO)$_9$(µ-OEt)$_2$(µ-F)] **3** the fluorine bridge connecting two manganese atoms of a Mn$_3$ cluster is symmetric (within experimental error) but bent [Mn–F 1.93(2) and 1.97(2) Å; Mn–F–Mn 93(1)°].[68]

Other examples of basically symmetric bridges are provided by the fluoride complex of o-bis(chlorodimethyl-

Scheme 3

stannyl)benzene, $[o\text{-}(ClMe_2Sn)_2C_6H_4\cdot F)]^-$ **4**, [with Sn–F–Sn 119.56(13)°, Sn–F 2.139(3) and 2.213(3) Å],[69] or of a complex µ$_3$-oxo-tris(dimethyltin)bis(salicyladoximate) [Sn–F 2.231(8) and 2.185(7) Å],[70] and in the fluoride complexes of bis(halogeno-diphenylstannyl)-methane **5** and -ethane **6**, [{(CH$_2$)$_n$(SnPh$_2$-X)$_2$}F]$^-$, [n = 1, X = F, bridging Sn–F 2.249(2) and 2.204(2) Å, terminal Sn–F 1.995(2) and 2.004(2) Å; n = 1, X = Br, bridging Sn–F 2.212(5) and 2.274(5) Å; n = 1, X = I, bridging Sn–F 2.231(4) and 2.248(4) Å; n = 2, X = Cl, bridging Sn–F 2.178(4) and 2.197(4) Å],[71] and in the dimeric difluorodistannoxanes, [(FSnBu$^t_2$)$_2$O]$_2$ **7**.[72]

2.2.3 Asymmetric linear bridges. Several dinuclear compounds with asymmetric M–F···M bridges are known and are illustrated in Scheme 4. In tricyclohexyltin fluoride **8**, which is
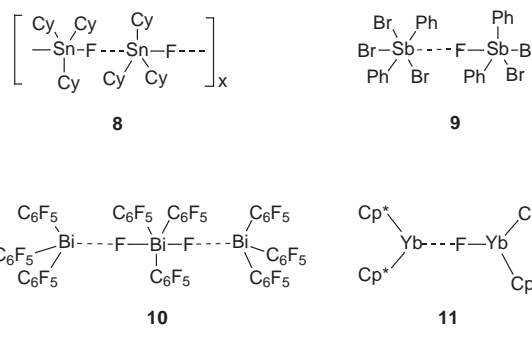
Scheme 4

a polymeric supramolecular array in the solid state, [Cy$_3$Sn(µ-F)]$_x$, the fluorine bridge is linear and asymmetric with Sn–F 2.051(10) and 2.303(10) Å.[73]

Another asymmetric linear bridge is observed in the antimony compound Ph$_2$SbBr$_2$(µ-F)SbPh$_2$Br$_3$ **9** [Sb–F 2.077(7) Å and Sb···F 2.343(7) Å, Sb–F···Sb 174.74(7)°].[74] The asymmetry in this compound may result from the association of two sub-units with differing substituents and coordination

Table 1 Interatomic distances in terminal M–F bonds

	M–F distance/Å	Compound	Ref.
Al–F	1.653(2)	$AlF_2N(2,6-Pr^i_2C_6H_3)(SiPr^iMe_2)$	12
	1.666(2)		
Ga–F	1.838(3)	$[GaF(Mes)_2(Bu^tNH_2)]$	13
Ge–F	1.804(4)	$[Me_4N][GeF_2(CF_3)_3]$	14
(5-coordinate Ge)	1.815(4)		
Ge–F	1.824(2)	$K_2[GeF_4(CF_3)_2\text{-}cis]$	15
(6-coordinate Ge)	1.833(2)		
Sn–F	1.957(2)	$SnF(Mes)_3$	16
(4-coordinate Sn)			
Sn–F	1.956(6)	$SnF_3\{C[C_6H_3(OMe)_2\text{-}2,6]_3\}$	17
(4-coordinate Sn)	1.948(7)		
	1.975(6)		
Sn–F	1.965(8)	$SnFPh_2C(SiMe_3)_3$	18
(4-coordinate Sn)	1.965(2)	$SnFMe_2C(SiMe_2Ph)_3$	18
Sn–F	2.041(5)	$[Et_4N][SnFMe_2(OC_6H_4S\text{-}2)]$	19
(5-coordinate Sn)	2.049(5)	$[SnFBu^t_2(\mu\text{-}OH)]_2$	20
Sn–F	2.126(3)	$[NH_4]_2[SnF_4Me_2\text{-}trans]$	21
(6-coordinate Sn)	2.121(5)		
	2.135(4)		
Ti–F	1.823(1)	$[TiF(C_5Me_4Et)(OSiBu^t_2O)]_2$	22
	1.815(2)	$[TiF(C_5H_4Me)(OSiBu^t_2O)]_2$	22
	1.832(2)	$TiF_2\{C_5H_3(SiMe_3)_2\text{-}1,3\}_2$	23
	1.838(2)	$TiF_2\{C_5H_4(SiMe_3)\}\{C_5H_2(SiMe_3)_3\text{-}1,2,4\}$	23
	1.838(3)	$TiF(Cp)_2\{OC_5(CF_3)_4\}$	24
	1.836(2)	$[TiF(C_5Me_4Et)(NSnMe_3)]_2$	25
	1.845(5)	$[TiF(\mu\text{-}O)(C_5Me_5)]_4$	26
	1.856(2)	$TiF_2(Cp^*)[(Me_3SiN)_2CC_6H_4(OMe)\text{-}4]$	27
	1.807(4)	$TiF_2(Cp^*)NPPh_3$	27
	1.870(5)	$\{TiF_2(Cp^*)NPPh_2\}_2C_2H_2$	27
	1.845(4)	$Ti^{III}F(Cp^*)_2$	28
	1.838(4)		
Zr–F	1.98(1)	$ZrF_2(Cp)_2$	29
	2.212(6)	$ZrF_2\{C_5H_3(SiMe_3)_2\}_2$	30
	2.012(3)	$ZrF(Cl)(C_5Me_4Et)_2$	31
	1.991(3)		
	2.182(2)	$ZrF(Cl)(Cp^*)\{N(SiMe_3)C_6H_3Pr^i_2\text{-}2,6\}$	32
	1.946(3)	$ZrF_2\{N(SiMe_3)C_6H_3Pr^i_2\text{-}2,6\}_2$	33
	1.944(3)		
	1.948(3)		
	1.960(3)		
V–F	1.760(4)	$VF_2O(NPPh_3)$	25
	1.755(4)		
	2.002(2)	$[FP(NEt_2)_3][VF(Mes)_3]$	34
Nb–F	1.920(8)	$[NbF_2(C_5Me_4Et)_2][PF_6]$	35
	1.906(8)		
	1.910(2)	$[NbF(C_5H_4Me)(CH_2SiMe_3)] [PF_6]$	36
	2.199(5)	$[NbF(C_5H_4SiMe_3)(Ph_2HCCNPh)][PF_6]$	37
	1.960(2)	$[Et_3NH][TaF_5(Cp^*)]$	38
	1.970(2)		
	1.931(2)		
	1.933(2)		
Ta–F	1.924(4)	$TaF_4(Cp^*)$	39
	1.906(4)		
	1.925(12)	$[TaF_2(Cp^*)_2][BF_4]$	39
	1.874(12)		
	2.059(13)	$TaF_4(Cp^*)\cdot HNPPh_3$	40
	2.016(11)		
	2.059(13)		
	1.807(13)		
	1.906(4)	$TaF_3(Cp^*)\{OC(Ph)CHC(Ph)O\}$	41
	1.918(3)		
	1.924(4)		
	1.901(3)	$TaF_3(Cp^*)\{(Me_3SiN)_2CC_6H_4(OMe)\text{-}4\}$	42
	1.910(3)		
	1.947(3)		
Mo–F	1.981(4)	$[MoF(PhCCH)(dppe)_2][BF_4]$	43
	2.055(3)	$[NEt_4][MoF(CO)_2(S_2CNEt_2)]$	44
W–F	1.925(1)	$WF_5(Cp^*)$	45
	1.87(2)		
	1.90(2)		
	1.87(2)		
	1.91(2)		
	1.858(5)	$WF_5\{NS(O)Me_2\}$	46
	1.855(5)		
	1.915(8)		

Table 1 (*Contd.*)

	M–F distance/Å	Compound	Ref.
	1.880(5)	$WF_4\{NS(O)Me_2\}_2$	46
	1.919(6)		
	1.857(6)		
	1.964(6)		
	2.044(3)	$WF(H)(C_6H_5Me)(dmpe)$	47
Re–F	2.134(3)	$[ReF(CCH_2CBu^t)(dppe)_2][BF_4]$	48
	1.97(1)	$[ReF(CO)(NO)(PPh_3)_3]$	49
Ru–F	2.011(4)	$[RuF_2(CO)_2(PPh_3)_2]$	50
Ir–F	1.998(3)	$[IrF(CO)_2(PEt_3)_2\{C(O)F\}][BF_4]$	51
	2.069(4)	$IrF(Ph)(PMe_3)(C_5Me_4Et)$	52
	2.089(4)	$IrF(Cl)(CO)(NSF_2)(PPh_3)_2$	53
	2.21(4)	$[IrF(CO)(PPh_3)_2(NH=NC_6H_3CF_3-2)][BF_4]$	54
Pd–F	2.085(3)	$PdF(Ph)(PPh_3)_2$	55
Pt–F	2.03(1)	$PtF(PPh_3)_2\{CH(CF_3)_2\}$	56
Yb–F	2.015(4)	$YbF(Cp^*)_2 \cdot Et_2O$	57
	2.026(2)	$YbF(Cp^*)_2 \cdot THF$	57
U–F	2.106(12)	$UF(Cp)_3$	58

geometries: a square pyramidal Ph_2SbBr_3 molecule as acceptor and a trigonal bipyramidal Ph_2SbBr_2F molecule as donor.

The bismuth compound $(C_6F_5)_3Bi(\mu\text{-}F)_2 \cdot 2Bi(C_6F_5)_3$ **10** is formed by association of a trigonal bipyramidal $(C_6F_5)_3BiF_2$ sub-unit with two trigonal pyramidal (becoming distorted tetrahedral) $Bi(C_6F_5)_3$ molecular sub-units, and the bridges are asymmetric [Bi–F 2.088(8) Å and Bi···F 2.759(8) Å].[75] The origin of asymmetry of the bridge in $(C_5Me_5)_2Yb^{II}\text{-}(\mu\text{-}F)Yb^{III}(C_5Me_5)_2$ **11** seems to be due to the different oxidation states of the metal. In the linear Yb–F···Yb bridge the interatomic distances are Yb^{III}–F 2.084(2) Å and Yb^{II}···F 2.317(2) Å.[76]

A peculiar case of a heterometallic bridge observed in $[Cp^*TiO(\mu\text{-}F)AlMe_3]_4$ **12** should be mentioned. In this compound, the terminal Ti–F bonds of the parent ring compound $[Cp^*Ti(O)F]_4$ connect $AlMe_3$ molecules through strong F–Al bonds, forming basically symmetric linear bridges: Ti–F 1.9593(13), 1.9728(13), Al–F 1.8960(14), 1.8894(14) Å, Al–F–Ti 175.90(8)° and 175.62(8)°.[77]

It seems that the asymmetry of the fluorine bridges can be caused by the steric demand of the groups attached to the metal (like in tricyclohexyltin fluoride) or by the non-equivalence of the molecular sub-units connected through the bridge. The non-equivalence may be due to different substitution, different oxidation states and/or different coordination geometries of the metal centres. The fluorine atom is very flexible in terms of its bonding capabilities and adapts its bridging behaviour to each particular case.

2.2.4 Asymmetric bent bridges. Some asymmetric bent fluorine bridges are illustrated in Scheme 5. An early crystal structure determination of trimethyltin fluoride suggested a polymeric structure **13** with an asymmetric bent Sn–F···Sn bridge (Sn–F 2.2 and 2.6 Å, Sn–F···Sn not reported).[78] The fluorine atoms are said to be disordered. In view of the importance of trimethyltin fluoride as a key compound in organometallic fluoride chemistry it would be useful to redetermine its crystal structure at low temperature.

A clearly unsymmetric Sn–F···Sn bridge was found in the compound $N(CH_2CH_2CH_2)_3SnF \cdot H_2O$ **14**, which is a tetramer held together by tin–fluorine bonds [intramolecular Sn–F 2.115(6), intermolecular Sn···F 2.797(6) Å, Sn–F···Sn angle 151.4(2)°], weak tin–oxygen bonds [Sn···O 3.180(8) Å] and hydrogen bonds (O–H···F).[79]

The rhenium carbonyl fluoride $Re(CO)_5F \cdot ReF_6$ **15** contains two independent molecules in the crystal, both with bent (but slightly different) Re–F···Re bridges: Re–F 1.98, Re···F 2.13, terminal Re–F 1.78–1.93(3) Å, Re–F···Re 142.0(1.4)°, and Re–F 1.95(2), Re···F 2.20(2), terminal Re–F 1.84–1.88(3) Å, Re–F···Re 138.8(1.2)°.[80]
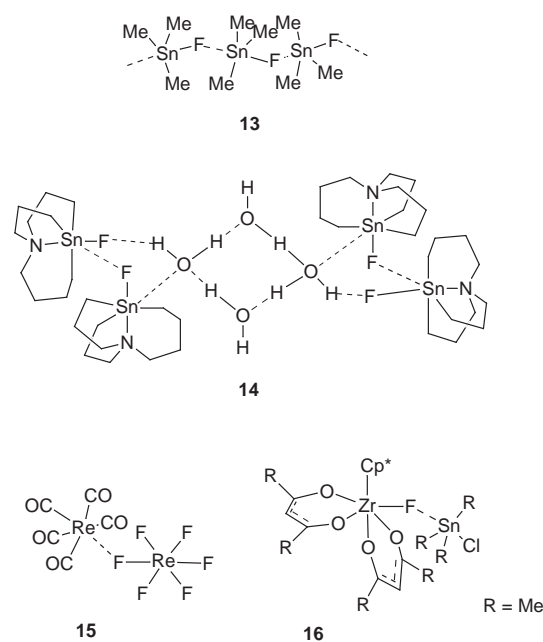
Scheme 5

When the metal atoms connected by a fluorine bridge are different the asymmetry is not a surprise. It seems that the bending of the bridge is also to be expected. Thus, in $[Cp^*Zr(acac)_2\text{-}(\mu\text{-}F)SnMe_3Cl]$ **16** there is a normal, short Zr–F bond [2.030(2)] and a long Sn···F bond [2.462(2) Å]. The bending angle of the Zr–F···Sn bridge is 146.0(1)°.[81]

2.2.5 The case of weakly coordinating fluoro anions. The weakly coordinating anions, being good leaving groups, are important in synthesis and catalysis, since they are readily replaced by more powerful donor ligands or by reacting substrates.[60] Anions such as $[BF_4]^-$, $[PF_6]^-$, $[AsF_6]^-$ and $[SbF_6]^-$ fall into this category. They are present in numerous organometallic compounds as discrete anions, but in certain cases they can coordinate to coordinatively unsaturated metal centers,[59] by forming asymmetric linear or bent M···F–E bridges (M = metal, E = B, P, As, Sb). It is remarkable that the coordination of these anions may display various patterns. Thus, tetrafluoroborate can coordinate as monodentate monoconnective **17**, monodentate triconnective **18**, chelating **19** or bridging **20**; a monodentate biconnective coordination **21** still awaits discovery (Scheme 6).

Monodentate monoconnective type coordination is found in $[Ph_3PCH_2SnBu^t_2F(FBF_3)]$ **22**, $[Ph_3PC(=CH_2)SnBu^t_2F(FBF_3)]$

Table 2 Weakly coordinating anions with M···F–E bridge

Compound	Bond	M···F distance/Å	···F–E (bridging)/Å	E–F (terminal)/Å	M···F–E angle/°	Ref.
Tetrafluoroborates			F–B	B–F		
22	Sn···F					
	bridging	2.782(3)	1.393(7)	1.347(7)	141.9(3)	82
	terminal	2.027(3)		1.338(9)		
				1.324(7)		
23	Sn···F					
	bridging	2.853(4)	1.394(4)	1.382(4)	n.a.	82
	terminal	1.972(2)		1.344(5)		
				1.325(5)		
24	W···F	2.168(7)	1.500(14)	1.316(18)–1.386(16)	104.1(1)	83
25	W···F	2.15(2)	1.45(5)	1.28(5)–1.43(5)	141(2)	84
26	Ir···F	2.272(3)	1.448(6)	1.329(9)–1.340(8)	125.7(3)	85
27	Pd···F	2.355(5)	1.336(7)	1.315(8)–1.419(9)	141.9(4)	86
28	Re···F	2.138(7)	1.503(2)	1.395(16)		87
		2.146(7)		1.338(13)		
Hexafluorophosphates			F–P	P–F		
29	W···F	2.187(10)	1.733(11)	1.550(13)–1.585(13)	142.4(6)	83
30	Ag···F	2.668(4)	1.562(17)	1.505(18)	n.a.	88
				1.508(13)		
Hexafluoroarsenates			F–As	As–F		
31	Ti···F	2.00(1)	1.80(1)	1.64(1)–1.66(1)	178.0(5)	89
32	V···F	2.03(1)	1.78(1)	1.63(1)–1.67(1)	173.2(5)	90
Hexafluoroantimonates			F–Sb	Sb–F		
33a	W···F	2.169(11)	1.954(11)	1.855(12)–1.878(12)	147.2(6)	83
33b	W···F	2.186(3)	1.979(3)	1.832(4)–1.68(4)	138.9(2)	83

n.a. = not available
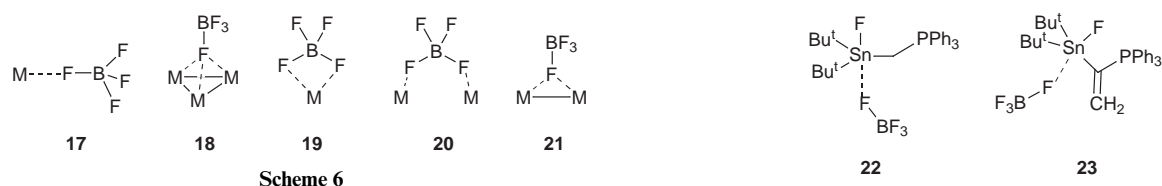
Scheme 6

23,[82] [W(NO)(CO)$_3$(PMe$_3$)(FBF$_3$)] **24**,[83] [WH(CO)$_3$(PCy$_3$)-(FBF$_3$)] **25**,[84] [IrH(PPh$_3$)$_2$(CO)(Cl)(FBF$_3$)] **26**,[85] and [Pd{η^2-C$_5$Et$_5$)C(Et)CH$_2$C$_9$H$_6$N}(FBF$_3$)] **27**.[86] The compounds are shown in Scheme 7. Bond distances and bond angles are collected in Table 2.

The monodentate triconnective mode **18** is rare, and has been found only in the anion [Re$_3$H$_2$(CO)$_9$(FBF$_3$)]$^{2-}$ **28** (tetraethylammonium salt) [Re–F 2.138(7), 2.146(7), bridging B–F 1.503(21), terminal B–F 1.395(16), 1.338(13) Å].[87] The chelating mode **19** has been observed in [(Mes)$_2$In][BF$_4$], where in fact double chelating leads to the formation of a polymeric, supramolecular structure (see Section 3.3). The biconnective bridging mode **20**, leading to cyclic or polymeric supramolecular assemblies, is also illustrated in Section 3.3. The hexafluorophosphate anion coordinates as monodentate monoconnective in [W(PMe$_3$)(CO)$_3$(NO)(FPF$_5$)] **29**,[83] and the chelating mode in [{2,4,6-Bu$^t_3$C$_6$H$_2$NC}$_2$Ag(F$_2$PF$_4$)] **30** (Scheme 8).[88]

Hexafluoroarsenate coordinates as monoconnective, forming a basically linear bridge in Cp$_2$Ti(FAsF$_5$)$_2$ **31** [Ti···F–As 178.0(5)°],[89] and in Cp$_2$V(FAsF$_5$)$_2$ **32** [V···F–As 173.2(5)°].[90]

The coordination of [SbF$_6$]$^-$ is also monoconnective in [W(PMe$_2$Ph)(CO)$_3$(NO)(FSbF$_5$)] **33a** and [W(PCy$_3$)(CO)$_3$(NO)-(FSbF$_5$)] **33b**.[83]

It is apparent that the weakly coordinating anions prefer soft metal centers in low oxidation states (with the simultaneous presence of π-acceptor ligands)[59] and the coordination is favoured when the coordination center is a bent metallocenium cation, with ample vacant space for the incoming anion. When the metal center is coordinatively saturated, the [EF$_n$]$^-$ anions do not coordinate and occur as discrete species, compensating the positive charge of a complex.

27   R = Et
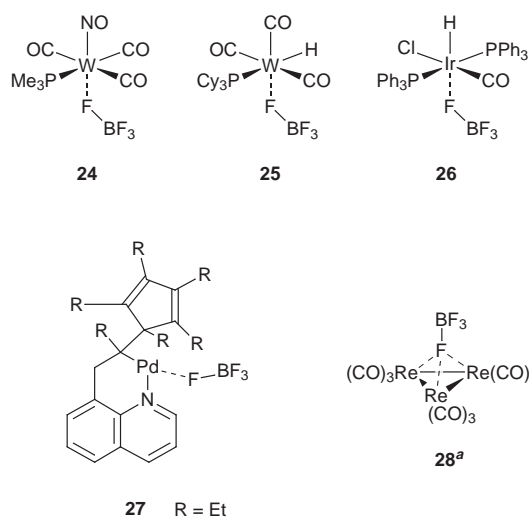
Scheme 7 ^{a} Hydrogen atoms and charge are omitted.

3 Supramolecular self-assembly

Fluorine bridging can be the source of a broad variety of complex structures which can be described as supramolecular. Molecules that contain simultaneously donor fluorine sites and acceptor (coordinatively or electronically) unsaturated metal sites, self-assemble into oligomeric supermolecules or polymeric supramolecular arrays. The simplest are the cyclic supermolecules followed by cages and host–guest architectures. In the latter, fluorine can be both the principal component of a

Scheme 8

29   30   31   32

33 a   PR₃ = PMe₂Ph
   b   PR₃ = PCy₃

Scheme 9

34   35   36   37   38   39   40   41   42   43   44

Cp' = C₅H₄Me   Cp# = C₅H₄Pr^i
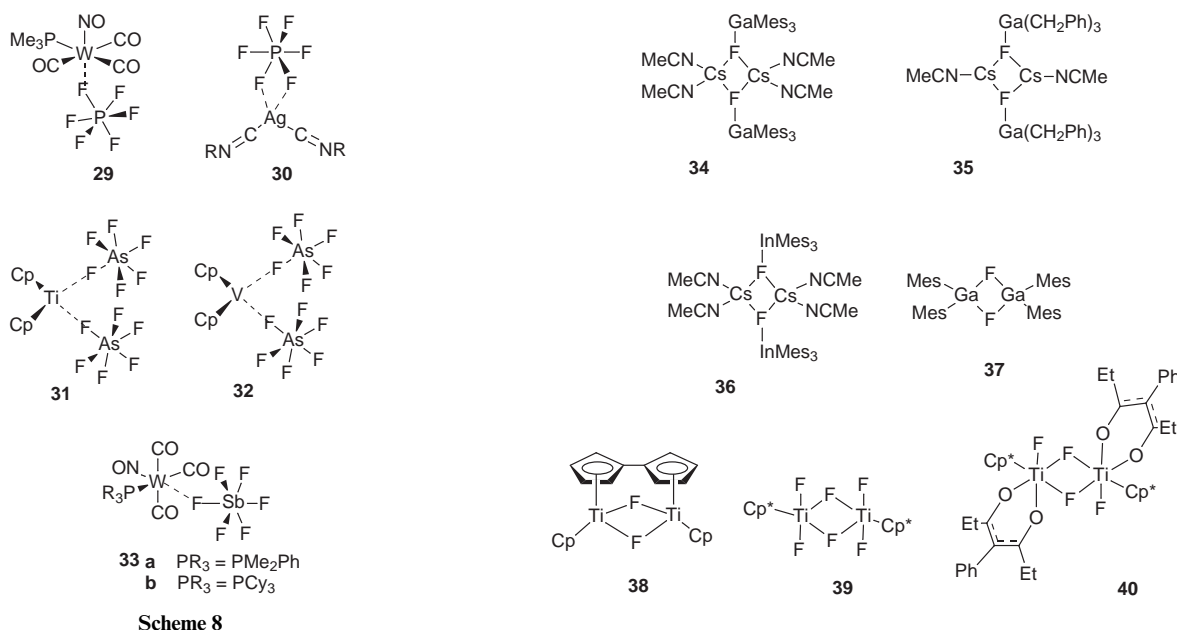
complex host molecule (acting as donor) or can be the host in a molecule of appropriate structure.

The bending of the fluorine bridge allows cyclisation. The formation of four-, six- or eight-membered rings is the pre-requisite for the fulfillment of specific geometric requirements, in terms of bond angles and steric crowding. Biconnective fluorine can display a wide range of bond angles, from small values required for the formation of four-membered rings, to wide angles allowed by non-planar eight-membered rings. Therefore, a broad variety of monocyclic structures are possible, depending to a great extent on the steric crowding of the metal site. Large, bulky organic substituents at the metal sites favour the formation of small, four-membered rings. With less crowded metal sites trimeric (six-membered) rings and tetrameric (eight-membered) rings can be formed. The four-, six- and eight-membered M_nF_n rings (n = 2, 3 and 4) will also be found as building blocks of polycyclic cages.

Triconnective fluorine, with non-planar distribution of the three M–F bonds, provides the Gaussian curvature required for closing of spatial objects, and thus, polycyclic cages can be formed. There are a large number of such cages with triconnective oxygen and nitrogen atoms at the corners of various polycyclic cages, *e.g.* in metallasiloxanes, aluminium and gallium phosphonates, aluminium–nitrogen or tin–oxygen cages, to cite only a few examples. The development of a rather similar chemistry of cages containing triconnective fluorine is in full swing now, and many fascinating new structures can be expected.

3.1 Four-membered rings, M₂F₂

The number of known dimeric supermolecules based on four-membered M₂F₂ rings is already quite impressive. A selection of such compounds is illustrated in Schemes 9 and 10 and molecular parameters (bond lengths and bond angles) are collected in Table 3. In all these compounds the basic skeleton is a four-membered rhomboidal ring with slightly unsymmetric bond lengths and acute bond angles at the metal site and bond angles slightly larger than 90° at fluorine. In certain cases, the M₂F₂ ring is spanned by a chelating bridge, *e.g.* acetate **43** and **44**.

Four-membered rings are formed both in very ionic compounds like caesium organofluorometalates, *e.g.* [Cs(μ-F)Ga-(Mes₃)(MeCN)₂]₂ **34** (Mes = 1,3,5-trimethylbenzene), [Cs(μ-F)-(MeCN)Ga(CH₂Ph)₃]₂ **35** or [Cs(μ-F)In(Mes)₃(MeCN)₂]₂ **36** in which Cs₂F₂ rather than Ga₂F₂ or In₂F₂ rings are present[91] and in strongly covalent compounds like [(Mes)₂Ga(μ-F)]₂·THF **37** which contains Ga₂F₂ rings.[92] A large number of
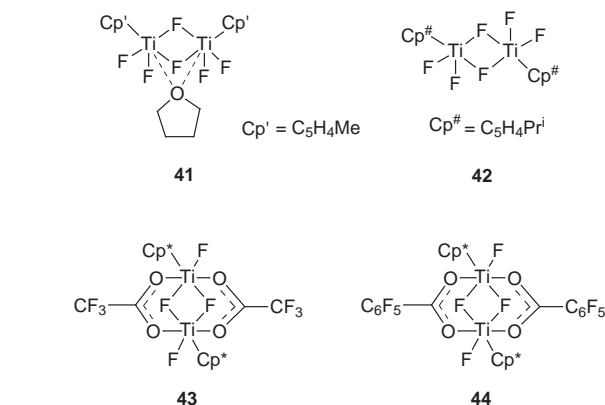
compounds contain the Ti₂F₂ ring **38–45**,[93] but similar rings containing zirconium **47, 48**,[94,95] niobium **49**,[96] tantalum **50**,[97] molybdenum **51, 52**,[98] tungsten **53**[99] and even mercury **54**[100] are known.

3.2 Six-membered rings, M₃F₃

Six-membered rings of varying conformations and with large M–F–M bond angles (in the range between 130 and 153°) and small F–M–F bond angles (in the range between 85 and 93°) are known in some organometallic fluorides (Scheme 11). The six-membered Al₃F₃ ring in [F₂AlN(SiMe₃)(C₆H₃Pr^i₂-2,6)]₃ **55**, is planar,[101] whereas in [F₂AlC(SiMe₃)₃]₃ **56** the six-membered ring displays a flat-boat conformation.[102] A distorted boat conformation is also displayed by the six-membered In₃F₃ ring in [(Mes)₂InF]₃ **57**,[13] whereas in [Cp₂ScF]₃ **58**[103] and in [(Bu^tC₅H₄)₂SmF]₃ **59** the rings are basically planar.[104] It seems that the ring conformation is imposed by the steric requirements of the organic groups and the remarkable flexibility of the M–F–M bond angles can accommodate very different organometallic building units for self-assembly into a cyclic, trimeric structure. Important molecular parameters are collected in Table 4.

The structures of self-assembled organometallic fluoride trimers are reminiscent of the numerous six-membered metal–oxygen rings [*e.g. cyclo*-trititanoxanes **60**[105,106] and *cyclo*-trizirconoxanes **61**[107]] (Scheme 12) which are also known to display a variety of conformations. The bond angles at oxygen are, however, not so wide open in the six-membered rings mentioned and they tend to stay closer to the ideal value of 120°.

A bicyclic system, consisting of two fused six-membered

Table 3 M–F bond lengths and bond angles in M_2F_2 four-membered rings

	Compound	M–F bridging/Å	M–F terminal/Å	Endocyclic M–F–M/°	Angles F–M–F/°	Exocyclic M–F–M′/°	Ref.
34	Cs–F	2.880(5) 3.207(6)	1.903(5)	93.6(1)	86.4(1)	109.7 156.4	91
35	Cs–F	2.838(2) 2.872(2)	1.864(2)	95.15(7)	84.5(6)	119.8 132.9	91
36	Cs–F	2.852(2) 3.040(2)	2.113(2)	97.74(5)	82.26(5)	109.41(7) 152.75(9)	91
37	Ga–F	1.947(2)		101.1(2)	78.9(1)		92
38	Ti–F	2.046(4) 2.047(4)		101.4(2) 101.5(2)	75.9(2) 75.9(2)		93(a)
39	Ti–F	2.002(3) 2.021(3)	1.822(3)	110.0(1)	70.0(1)		27
40	Ti–F	1.940(2) 2.170(3)	1.833(3)	109.9(1)	70.1(1)		27
41	Ti–F	2.022(2) 2.030(2)	1.829(2) 1.820(2)	105.31(7) 104.28(7)	72.21(6)		93(b)
42	Ti–F	2.015(1) 2.028(1)	1.821(2) 1.815(2)	110.20(7)	69.80(7)	93.08(8)	93(c)
43	Ti–F	1.976(1) 2.083(1)	1.822(1)	107.59(6)	72.41(6)	151.36(6) 78.96(5)	93(d)
44	Ti–F	2.072(2) 1.985(2)	1.829(2)	107.18(7)	72.82(7)	151.36(8) 79.83(7)	93(d)
45	Ti–F	2.097(2) 1.974(2)		n.a.	75.6(1)		93(e)
46	Ga–F Ti–F	1.912(2) 2.106(2)		n.a. n.a.	78.4(1) (FGaF) 70.0(1) (FTiF)		93(e)
47	Zr–F	2.145(2)	1.967(3) 1.985(2) 1.964(3)	n.a.	88.6(1)		94
48	Zr–F	2.142(7) 2.147(4) 2.145(4) 2.137(4)		108.2(2) 108.7(2)	71.49(13) 71.64(13)		95
49	Nb–F	2.040(3) 2.178(3)	1.945(3) 1.906(3) 1.896(3)	110.5(1)	69.5(1)		96
50	Ta–F	2.044(5) 2.195(6)	1.900(5) 1.901(5) 1.909(8)	112.1(2) 111.8(2)	68.2(2) 67.9(2)		97
51	Mo–F	2.206(5) 2.151(4) 2.095(6)		97.1(1) 97.1(2)	70.1(2) 68.8(2)		98(a)
52	Mo–F	2.148(9) 2.156(8) 2.13(1) 2.15(1)		103.0(4) 102.1(4)	69.8(4) 70.5(4)		98(b)
53	W–F	2.126(4) 2.146(3) 2.127(4) 2.077(3) 2.124(3) 2.126(3)		97.7(1) 99.8(2) 98.3(1)	68.6(1) 69.1(1) 68.1(1) 69.1(1) 69.9(1) 67.7(2)		98(c)
54	Hg–F	2.395(7) 2.418(7)		97.6(2)	82.4(2)		99

rings, is present in the chromium compound $[Cr_4(Cp^*)_4(\mu\text{-}F)_5\text{-}Cl_2]PF_6$ **62**. Two views of the bicyclic cation are illustrated in Scheme 13.[108] Alternatively, the bicyclic system can be also described as an eight-membered Cr_4F_4 ring spanned by a transannular fluorine bridge. This structure is analogous to that of a borate anion $[B_4O_5(OH)_4]^{2-}$ (borax) **63**.

A polymeric array **64** made up of Sn_3F_3 rings [terminal Sn–F 2.026(3), bridging Sn–F 2.147(1), 2.272(2) and 2.115(3) Å, F–Sn–F 85.7(2)–90.5(2) in the ring, and 175.7(1)–180° between rings, Sn–F–Sn 150.1(2), 151.6(2)° in the ring] is found in the compound $\{[NEt_4][Me_2Sn_2F_5]\}_x$, which contains six-coordinate tin (Scheme 14).[109]

3.3 Eight-membered rings, M_4F_4

There are several eight-membered rings self-assembled through fluorine bridges (illustrated idealised in Scheme 15). Molecular parameters are listed in Table 5. The first eight-membered rings

based upon fluorine bridging have been identified in some inorganic pentafluorides such as $[MoF_5]_4$[110] and $[RuF_5]_4$.[111] Probably the first organometallic cyclic tetramer was the metal carbonyl compound $[Ru(CO)_3F(\mu\text{-}F)]_4$ **65**, containing a non-planar eight-membered ring with non-linear Ru–F bridges (Ru–F–Ru 145°, compared with 132° in $[RuF_5]_4$) and both bridging (Ru–F 2.04 Å) and terminal (Ru–F 1.99 Å) metal–fluorine bonds.[112]

In a mixed valence ytterbium(II,III) fluoride, $(Cp^*)_6Yb_4(\mu\text{-}F)_4$ **66**, the non-planar eight-membered ring contains two $(Cp^*)_2\text{-}Yb^{III}$ and two $(Cp^*)Yb^{II}$ building units, connected by non-linear fluorine bridges (Yb–F–Yb 160.0 and 157.3°).[113]

A rather unusual self-assembled ring containing tetrafluoro-borate bridges is found in the (pentamethylcyclopentadienyl)-lead tetrafluoroborate, $[(Cp^*)Pb(BF_4)]_2$ **67**, better formulated as $[(Cp^*)Pb(\mu\text{-}F)_2BF_2]_2$. It contains rather long Pb–F bonds [2.831(9) and 2.934(8) Å] which could be described as secondary bonds; the bridges are bent at fluorine [B–F–Pb 111.2(7)

Table 4 Six-membered M_3F_3 rings

Compound	Ring	M–F bond in ring/Å	M–F–M/°	F–M–F/°	Ref.
55	Al_3F_3 planar[a]	1.770(2)–1.788(2)	134.3(2) 144.61(13)	91.93(11) 93.25(14)	101
56	Al_3F_3 flat boat[b]	1.795(4)–1.815(4)	144.6(2) 145.2(2) 130.3(2)	91.40(17) 90.57(18) 91.96(18)	102
57	In_3F_3 distorted boat	2.095(5)–2.140(5)	141.6(3) 133.9(3) 134.5(3)	85.8(2) 86.0(2) 85.1(2)	13
58	Sc_3F_3	2.026(8)–2.063(8)	153.5(4) 153.9(5) 152.9(4)	86.6(2) 86.2(3) 86.7(3)	103
59	Sm_3F_3 almost planar	2.234(6)–2.259(2)	157.2(3) 152.7(5)	84.9(3) 82.8(3)	104
62	two Cr_3F_3 fused rings (butterfly)	1.943(5)–1.972(5)	136.1(3)–140.8(3)	90.0(2)–93.2(2)	108

[a] Terminal Al–F 1.634(3)–1.642(2) Å (exocyclic). [b] Terminal Al–F 1.657–1.681 Å (exocyclic).

Scheme 10

Scheme 11

Scheme 12
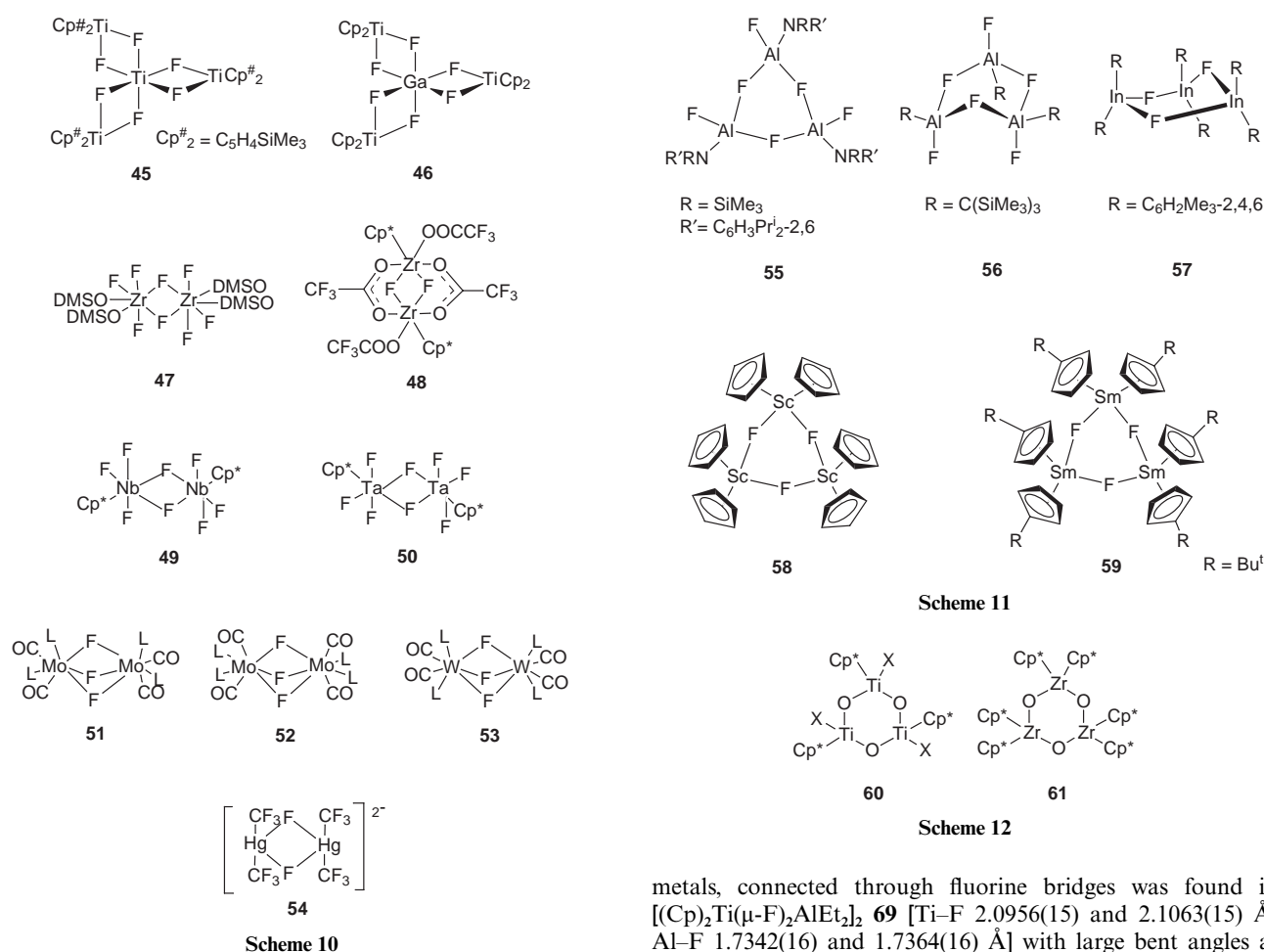
and 163.1(8)°]. The B–F interatomic distances are short [1.370(16) and 1.380(16) Å] as expected for normal covalent bonds.[114]

The tetrameric structure of dimethylaluminium fluoride, $[Me_2Al(\mu\text{-}F)]_4$ **68**, has been established by electron diffraction in the vapor phase,[115] confirming molecular weight determinations in solution.[116] The Al_4F_4 ring is non-planar [Al–F–Al 148(2), F–Al–F 94(2)°] with Al–F 1.808(8) Å, longer than terminal Al–F bonds illustrated in Table 1, and shorter than the bridge in $K[Et_3Al–F–AlEt_3]$ [1.820(3) Å].[61]

A non-planar eight-membered ring containing two different metals, connected through fluorine bridges was found in $[(Cp)_2Ti(\mu\text{-}F)_2AlEt_2]_2$ **69** [Ti–F 2.0956(15) and 2.1063(15) Å; Al–F 1.7342(16) and 1.7364(16) Å] with large bent angles at fluorine [Al–F–Al 160.13(9), Al–F–Ti 169.08(10)°] and small bent angles at the metals [F–Al–F 100.18(8) and F–Ti–F 78.53(7)°].[117]

Diorganoaluminium fluorides $[R_2AlF]_n$ [$n = 3$ **70** and $n = 4$ **71**] are isoelectronic with diorganosiloxanes $[R_2SiO]_n$ [e.g. R = Me, $n = 3$ **72** and $n = 4$ **73**][118] and the similarity of their cyclic structures (Scheme 16) is striking. Trimeric and tetrameric organometallic oxides, e.g. $[(Cp)_2Zr(\mu\text{-}O)]_3$, $[(Cp^*)TiMe(\mu\text{-}O)]_4$ or $[(Cp^*)TiBr(\mu\text{-}O)]_4$ are also topologically similar to the cyclic fluorides.[119]

The mixed tetranuclear compound, cis-$[\{(Cp^*)MeHf(\mu_2\text{-}F)\text{-}AlMe_2\}(\mu_2\text{-}F)_2]_2$ **74** contains an eight-membered ring contour,

Table 5 Eight-membered M_4F_4 rings

Compound	Ring	Bond	M–F bond in ring/Å	M–F–M/°	F–M–F/°	Ref.
65	Ru_4F_4	Ru–F (bridge)	2.04(7)	145		112
		Ru–F (exocyclic)	1.99(7)			
66	Yb_4F_4	Yb–F		160.0(2)	91.9(1)	113
				157.3(2)	105.9(1)	
67	$Pb_2F_4B_2$	Pb–F	2.831(9)	B–F–Pb	F–Pb–F	114
			2.901(9)	111.2(7)	108.9(11)	
			2.934(8)	163.1(8)	108.7(10)	
		B–F	1.370(16)			
			1.371(17)		F–B–F (in ring)	
			1.380(16)		108.9(11)	
			1.382(16)		108.7(10)	
68	Al_4F_4	Al–F	1.808(4)	148(2)	94(2)	115
69	$Al_2F_4Ti_2$	Al–F	1.7342(16)	Al–F–Al	F–Al–F	117
			1.7364(16)	160.13(9)	100.18(8)	
		Ti–F	2.0956(15)	Al–F–Ti	F–Ti–F	
			2.1063(15)	169.08(10)	78.53(7)	

[a] Electron diffraction study.

62[a]

63
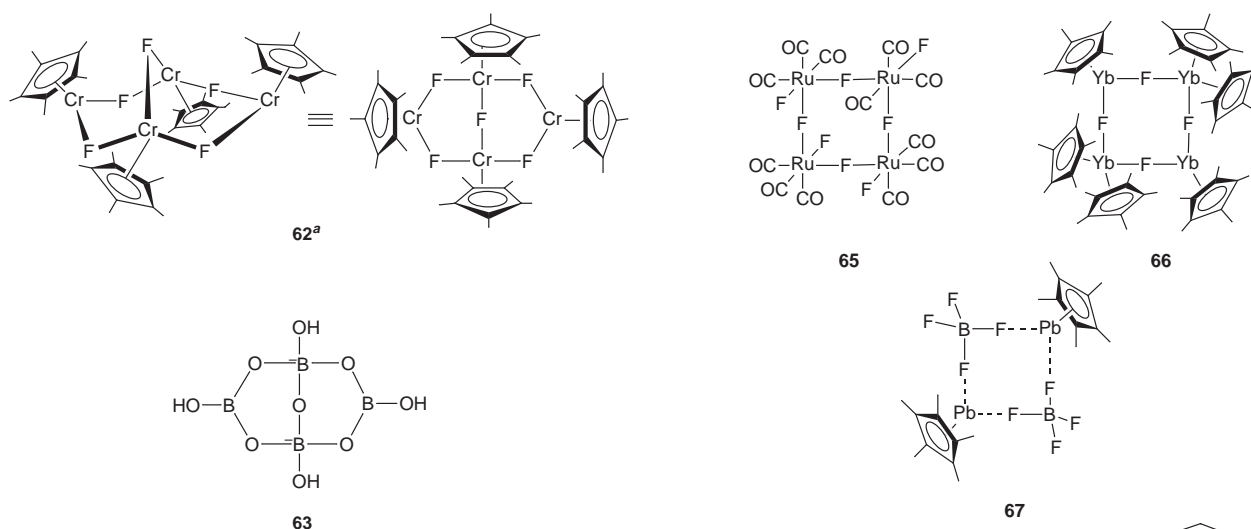
Scheme 13   [a] Cl atoms and PF_6^- are omitted.

R = Me

64

Scheme 14

65

66

67

68

69
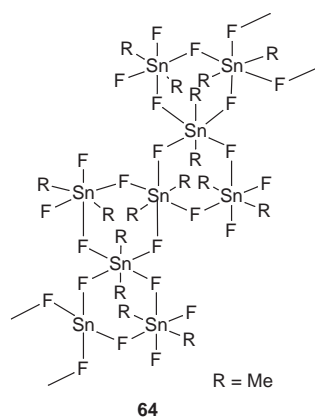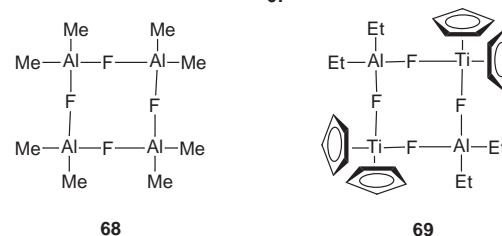
Scheme 15

$Al_2Hf_2F_4$, spanned by two transannular Hf–F–Hf bridges [Hf–F 2.100(7)–2.145(7), Al–F 1.776(8) Å, Hf–F–Hf 112.5(3) and Hf–F–Al 139.9(4) and F–Hf–F 96.1(4) and 152.2(3)°].[120] Alternatively, the structure can be regarded as a tricyclic system, since two six-membered rings Hf_2AlF_3 can also be distinguished as building sub-units, and the $Hf_2(\mu_2\text{-}F)_2$ group can be considered as a four-membered ring (Scheme 17). A similar zirc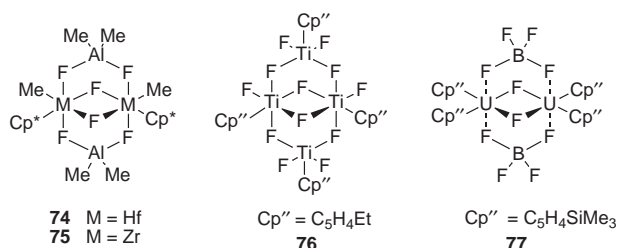onium compound **75** [Zr–F 2.111(3)–2.179(3), Al–F 1.776(4)–1.786(4) Å, Zr–F–Zr 111.67(12), Zr–F–Al 140.2(2), F–Zr–F 67.48(11)°] is also known.[121]

The tetrameric compound $[(EtMe_4C_5)TiF_3]_4$ **76** contains an eight-membered ring Ti_4F_4 with two transannular Ti–F–Ti bridges that close a Ti_2F_2 four-membered ring. The terminal Ti–F bonds [1.832(3) Å] are shorter than the bridging Ti–F bonds [2.057(3) and 2.019(3) Å in the Ti_2F_2 ring]. The bond angles are Ti–F–Ti 108.7(1) and 110.9(1)° and F–Ti–F 70.2(1)° (in the Ti_2F_2 ring).[27] The same type of self-assembled polycyclic structure, with weakly coordinating tetrafluoroborate, has been observed in the uranium complex $[\{Cp''_2U(\mu\text{-}F)(\mu\text{-}F_2BF_2)\}_2]$ [where $Cp'' = C_5H_3(SiMe_3)_2$ **77**].[122] This type of architecture has oxygen-bridged counterparts, *e.g.* in organotin **78**[123] and organoantimony **79**[124] chemistry.

Eight-membered ring skeletons are also present in the tetranuclear compounds $[Cp^*ZrF_3]_4$ **80a**, $[Cp^*ZrF_2Br]_4$ **80b**, $[Cp^*-ZrF_2Cl]_4$ **80c**, $[Cp^*ZrFCl_2]_4$ **80d** and $[\{(Cp^*)_2Zr_2(\mu\text{-}F)_2(\mu\text{-}Cl)\text{-}$
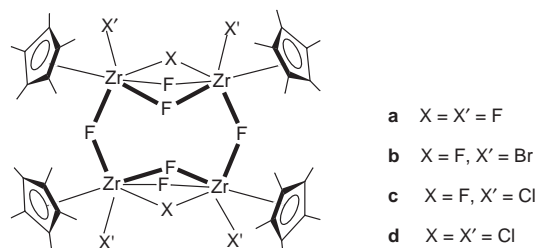
(R₂AlF)₃ **70**

(R₂AlF)₄ **71**

(R₂SiO)₃ **72**

(R₂SiO)₄ **73**

Scheme 16

74 M = Hf
75 M = Zr

Cp″ = C₅H₄Et
76

Cp‴ = C₅H₄SiMe₃
77

78

R = Ph
79

Scheme 17

80

a   X = X′ = F

b   X = F, X′ = Br

c   X = F, X′ = Cl

d   X = X′ = Cl

81

Scheme 18

82   a   M = Ga, R = Prⁱ
         b   M = In, R = Prⁱ

83   M = Si, R = Me

84

85

R = C(SiMe₃)₃
L = THF

86
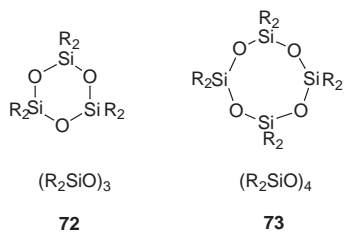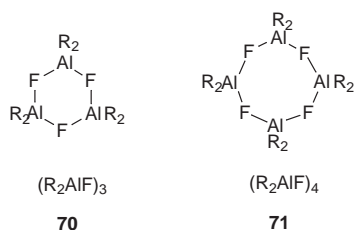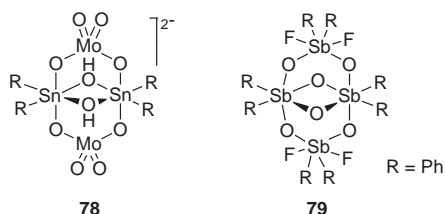
Scheme 19

Cl₂}(μ-F)]₂, and also in [Cp*HfF₃]₄ **81**. In these compounds two of the M–F–M bridges are tripled by two additional M–X–M bridges (X = F, Cl, Br) (Scheme 18).[31,93b,125]

3.4 Polycyclic cages

The cyclic units, M_2F_2, M_3F_3 and M_4F_4 can be combined in space, in various ways as building units to form polycyclic cages. This allows self-assembly of organometallic fluoride molecules into more complex architectures. The formation of polycyclic cages requires triconnectivity of fluorine atoms, with M–F–M bond angles smaller than 120°, to ensure the convexity needed for the cage corners. Tetraconnective fluorine atoms can also occupy corners of a cage; in this case an external side group is attached to fluorine.

3.4.1 Cubane cages. Bond angles of 90° or values close to this afford cubane cages, which can be regarded as the products of stacking two four-membered M_2F_2 rings (Scheme 19). Such a small value for the M–F–M bond angle is possible, as it seems more likely in highly polar or ionic M–F bonds. As a result, tetrameric caesium trialkylfluorometalates, [Cs{(R₃M)F}]₄ (M = Ga, In) **82** form heterocubane structures, based upon a Cs_4F_4 skeleton, rather than a M_4F_4 cubane or ring (as may have been expected). The MR₃ fragments are side groups. Two iso-structural compounds [Cs{(R₃M)F}]₄ with M = Ga, In and R = Prⁱ, have been structurally characterised.[126] The Cs–F–Cs bond angles, at the corners of the cube, are 99.43(5) in the gallium compound and 101.02(6)° in the indium compound; the bonds to external side groups have Cs–F–Ga 118.25(9) and Cs–

F–In 116.99(7)°, *i.e.* larger than tetrahedral values. The F–Cs–F bond angles are small, 79.70(6) in the gallium compound, and 77.77(5)° in the indium compound. Thus, the cubes are rather distorted. The Cs–F distances in the two compounds differ: 2.924(2) in the gallium compound and 2.889(2) Å in the indium compound, probably because of the increasing ionic character of the M–F bonds on going from gallium to indium, which leads to stronger ionic Cs–F interactions. Anyway, the Cs–F interatomic distances are shorter than in crystalline CsF (3.005 Å). It is remarkable that the two fluorine structures are similar to that of an oxygen compound, tetrameric [KOSiMe₃]₄ **83**.[127]

Other cubane clusters are present in [Mn₄F_x(OH)₄₋ₓ(CO)₁₂] **84** [Mn–F–Mn 102.4(1), F–Mn–F 76.1(1)°, Mn–F 2.052(3) Å],[128] [ReF(CO)₃]₄ **85** [Re–F–Re 102.6(3), 102.9(4) and

105.8(4)°; F–Re–F 74.9(2), 74.7(2) and 73.0(2)°, Re–F av. 2.200(5) Å][129] and [RhF(C$_2$H$_4$)(C$_2$F$_4$)]$_4$ [rather distorted, with Rh–F 2.073(2)–2.334(2) Å, Rh–F–Rh 95.20(8)–111.92(9)°].[130]

Large cubane cages, with the fluorine bridges on the edges and metal atoms in the corners, can be formed by self-assembly of eight-membered rings. An example is [Li{F$_3$AlC(SiMe$_3$)$_3$}·THF]$_4$ **86** which contains an Al$_4$Li$_4$F$_{12}$ distorted cubane skeleton.[131]

3.4.2 Other cages. Various types of cages are illustrated in Scheme 20. An unprecedented cage, containing Al–Si bonds **87**,

87

88

R = Mes

89

R = C$_6$H$_2$Pr$^i_3$-2,4,6
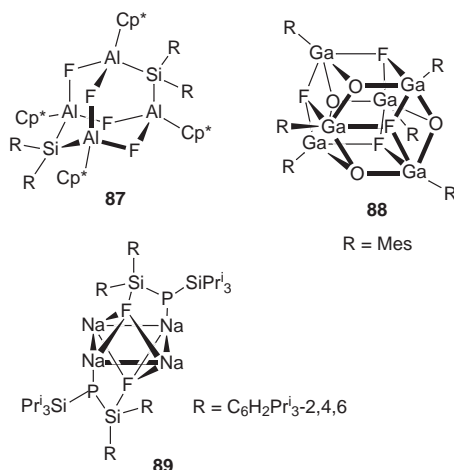
Scheme 20

formed in the reaction of [Cp*Al]$_4$ with Ph$_2$SiF$_2$ contains only μ-F bridges [Al–F 1.843(1) and 1.848(1) Å, Al–F–Al 149.0(1)°, F–Al–F 88.3(1)°], with two Al–Si–Al bridges.[132]

A gallium oxofluoride cage **88**, made of Ga$_2$OF four-membered rings is the molecular skeleton of [(Mes)$_6$Ga$_6$F$_4$O$_4$]·THF and all fluorine atoms form triconnective bridges [Ga–F 1.973(3)–2.521(3) Å, Ga–F–Ga 84.5(1), 86.5(1), 88.0(1) and 90.3(1)°].[92a] Oxo analogues with the same topology are [(Mes)$_6$Ga$_6$(OH)$_4$O$_4$],[92b] and [Bu$^t_6$Al$_6$(OH)$_4$O$_4$],[92c] suggesting that fluorine and oxygen (as OH groups in this case) can be mutually replaceable.

An intriguing Na$_4^{2+}$ cluster **89** forms three Na–F bonds [2.284(3), 2.395(3) and 2.210(3) Å] to a tetraconnective fluorine atom attached to silicon, in the compound Na$_4$[Pr$^i_3$Si–P–SiR$_2$F]$_2$. The Na–F–Na bond angles are 86.35(10) and 83.75(11)°. This intensely yellow compound was formed in a reaction between FR$_2$SiPHSiPr$^i_3$ and NaN(SiMe$_3$)$_2$.[133]

A complex cage, containing Yb$_2$F$_2$, Yb$_3$F$_3$ and Yb$_4$F$_4$ rings and three different bridging modes of fluorine, forms the skeleton of the compound [Cp*$_6$Yb$_5$(μ$_4$-F)(μ$_3$-F)$_2$(μ-F)$_6$].[134]

3.5 Supramolecular polymeric arrays

Some caesium fluorometalates, such as Cs[Me$_3$GaF] **90**, form ladder-like chain (ribbon) supramolecular polymeric arrays, containing tetraconnective fluorine.[138] A similar ribbon structure with dangling R$_2$GaF groups is found in [Cs{(PhCH$_2$)$_2$-GaF$_2$}]$_x$ (Scheme 21).[135] The structure of [Cs{(Mes)GaF$_3$}]$_x$ contains a [CsF]$_x$ layer with the (Mes)Ga sub-units connected to caesium atoms through three Ga–F bonds in GaF$_2$Cs rings [Ga–F 1.784(7) and 1.807(4) and Cs···F 2.910(7)–3.229(5) Å], displaying a broad range of Cs–F–Cs and Cs–F–Ga bond angles.[136]

In the indium compound [(Pr$^i_2$InF)$_2$(CsF·3MeCN)] the structure **91** is based on double chains containing triconnective fluorine [In–F 2.121(5)–2.607(5) Å, In–F–In 100.6(2)–151.2(2)°].[137] More complex supramolecular arrays are present in Cs[Me$_3$AlF], based upon tetraconnective fluorine and Cs$_2$F$_2$ rings interconnected in puckered layers.[138] As mentioned

90

R = Pr^i
L = MeCN

91

R = Mes

92
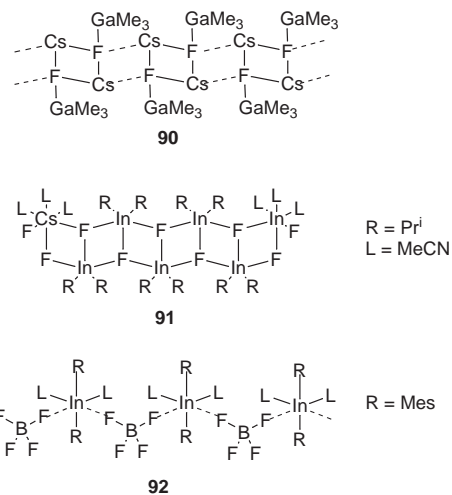
Scheme 21

above, tetrafluoroborate bridging leads to the formation of supramolecular polymeric arrays. Thus, double chelating in [In(Mes)$_2$][BF$_4$] produces a chain structure **92**[139] and simple bridging of the type in **20** (Scheme 6) leads to the formation of bent chain-like arrays in [InPr$^i_2$(THF)$_2$][BF$_4$] [In···F–B 173.8(7) and 155.0(7), F···In···F 120.4(2)°].[140]

4 Host–guest complexation

4.1 Encapsulated fluorine ions

The fluorine anion can be encrypted in various cage structures (Scheme 22). The simplest is an organotin macrobicyclic host in

93

94 R = Ph, Me

95

Cp′ =C$_5$H$_4$SiMe$_3$

96

NRR′ = N(C$_6$H$_3$Pr$^i_2$–2,6)(SiMe$_3$)
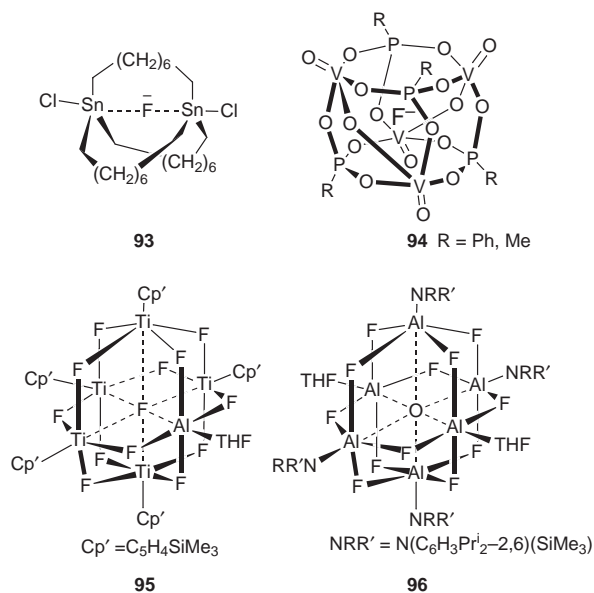
Scheme 22

the anion [ClSn{(CH$_2$)$_6$}$_3$SnCl·F]$^-$ **93**. The tin–fluorine distances are 2.12(4) and 2.28(4) Å, and these values are in the range expected for coordinative tin–fluorine bonds.[141] The inclusion of the fluorine anion changes the conformation of the host by changing the coordination geometry of the tin atoms from distorted tetrahedral [Cl–Sn–C 103(1), 103(1) and 99.1(1)°; C–Sn–C 106(1), 117(2) and 125(2)° in the free cryptand] to trigonal bipyramidal [Cl–Sn–C 84(1), 100(1) and 83(1)°; C–Sn–C 120(2), 123(2) and 116(2)°; Cl–Sn–F 173(1)° in the host–guest complex].

The encapsulation of fluorine has an obvious templating effect in the formation of vanadatophosphonates **94**. Thus, under the directing effect of fluorine the tetranuclear

host–guest complexes [NBu$^n_4$][V$_4$O$_6$(μ_4-F)(PhPO$_3$)$_4$] [V$\cdots$F 2.412(4), 2.427(3), 2.477(4), 2.414(4) Å],[142] [PEt$_4$][V$_4$O$_6$(μ_4-F)-(PhPO$_3$)$_4$] [V$\cdots$F 2.443(3), 2.412(3), 2.454(4) and 2.445(3) Å] and [PEt$_4$][V$_4$O$_6$(μ_4-F)(MePO$_3$)$_4$] [V$\cdots$F 2.486(4), 2.528(4), 2.403(3) 2.392(4) Å][143] are formed from appropriate precursors.

The structure directing role of fluorine is underlined by the fact that in the presence of Cl$^-$ anion as templating agent, octaphosphonato host–guest complexes, *e.g.* [V$_6$O$_6$(O$_3$-POSiMe$_3$)$_8$Cl], [(V$_8$O$_{16}$){V$_4$O$_4$(H$_2$O)$_{12}$}(PhPO$_3$)$_8$Cl$_2$]$^{2-}$,[144] and [V$_6$O$_6$(PhPO$_3$)$_8$Cl]$^-$,[145] are formed. There is also evidence that the metal–fluorine polycyclic cages may act as hosts for various anions, which can be encapsulated into the cage, to form host–guest complexes. The host can be a fluorine anion F$^-$, an oxygen anion O^{2-}, and possibly others. The future may provide some pleasant surprises in this respect.

In some compounds fluorine displays a large coordination number, being six-coordinated and encapsulated in a polycyclic metal–fluorine cage 95. This is the case for [{(C$_5$H$_4$SiMe$_3$)-TiF$_2$}$_5$AlF$_2$(μ_6-F)(THF)]. The distances from the encapsulated fluorine to the surrounding metal atoms [Ti$\cdots$F av. 2.643(3), range 2.542(3)–2.670(3), Al$\cdots$F 1.850 Å] are significantly longer than the biconnective bonds in the μ-bridges of the cage [Ti–F av. 2.024(3), range 1.985(3)–2.089(3) Å, and Al–F av. 1.785(3), range 1.780(3)–1.793(3) Å].[146] The structure is similar to one with an oxygen ion encapsulated into a similar aluminium–oxygen–fluorine cage, in the compound [{(2,6-Pr$^i_2$C$_6$H$_3$)(SiMe$_3$)AlF$_2$}$_4${AlF$_2$(THF)}$_2$O] 96.[12]

The same type of cages with encapsulated O^{2-} anions are characteristic for hexamolybdates and hexatungstates, [M$_6$O$_{19}$]$^{2-}$ (M = Mo, W)[147] and organometallic oxides, such as [CpTiMo$_5$O$_{18}$]$^{3-}$ (M = Mo, W), [Cp*Mo$_6$O$_{18}$]$^-$, [Cp$_2$W$_6$O$_{17}$] and other related compounds.[148]

4.2 Organometallic fluoride cages as guests for metal cations

Organometallic fluorine cages are able to incorporate alkali metal and alkaline earth metal fluorides, formed *in situ* during the reduction of organometallic fluorides with the active metal. Such structures are illustrated in Scheme 23. A host–guest complex, [K(THF)$_2${(Me$_3$Si)$_3$CAlF$_2$(μ-F)F$_2$AlC(SiMe$_3$)$_3$}]$_2$ 97 based on incorporation of potassium cations in a sandwich formed with two RF$_2$Al(μ-F)AlRF$_2$ blocks, is relatively simple, since it contains only biconnective fluorine atoms in heterometallic asymmetric bridges.[102] The Al–F distances in the Al–F–Al bridges are 1.821(2) and 1.817(2) Å, longer than the Al–F distances in the Al–F$\cdots$K bridges [1.672(2)–1.677(2) Å]. The Al–F–Al angle is 126.2(1)° and two sets of values are observed for the Al–F$\cdots$K angles [118.7(1), 107.6(1) and 144.8(1), 147.3(1)°].

Alkali metal host–guest complexes of organotitanium fluorides, M$^+$[M′{(Cp*Ti)$_2$F$_7$}$_2$]$^-$ (M = Na, PPh$_4$, M′ = Na, K) 98a[149] and a calcium complex [Ca{(C$_5$Me$_4$Et)$_2$Ti$_2$F$_7$}$_2$] 98b,[150] are sandwiches in which the active metal cation is intercalated between two (Cp*Ti)$_2$F$_7$ moieties, in a manner which is reminiscent of crown ether complexation.

The compound [(Cp*TiF$_2$)$_{12}$(TiF$_3$)$_2$(NaF)$_{18}$·6THF] has a very complex supramolecular structure, incorporating the equivalent of 18 NaF molecules. In the calcium fluoride complex [Ca{(Cp*)$_3$Ti$_3$F$_7$}$_2$]·2THF 99, the metal cation is sandwiched between (Cp*Ti)$_3$F$_7$ cyclic subunits. Like in the solid CaF$_2$, the calcium cation is eight-coordinate.[151]

A heterometallic cage compound [{(Mes)InF$_2$}$_{10}$MgF$_2$] 100 is made up of two {(Mes)InF$_2$}$_5$ fragments held together by four μ-F bridges and incorporates a guest 'molecule' of MgF$_2$ in the cavity. The cage contains both biconnective μ-F (In–F 2.08–2.12 Å) and triconnective μ_3-F (In–F 2.22–2.24 Å) bridges.[137] The magnesium atom is six-coordinate (distorted octahedron) and each indium atom displays tetragonal pyramidal geometry. Six-membered In$_3$F$_3$ and eight-membered In$_4$F$_4$ fused rings are readily identified as building sub-units of the cage.
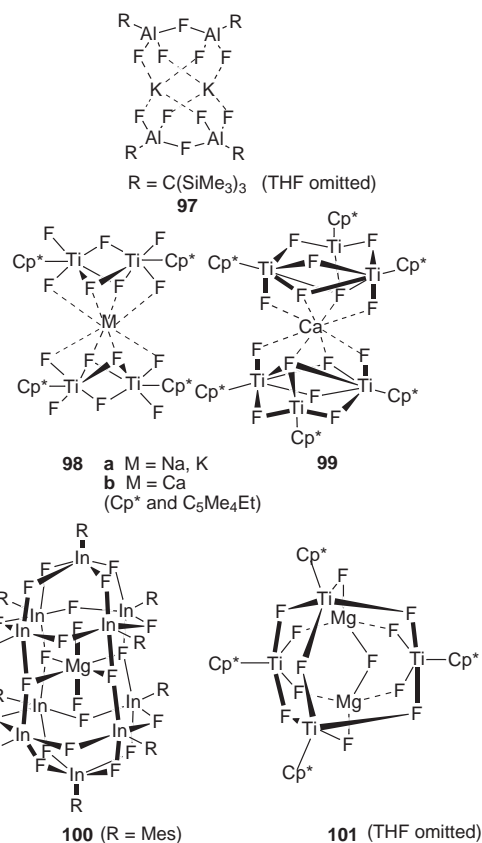
Scheme 23

The compound [(Cp*TiF$_2$)$_4$(MgF$_2$)$_2$]·7THF 101 can be regarded as a magnesium fluoride host–guest complex, although the identity of the MgF$_2$ 'molecules' is lost in the structure of the cage. It is easy to distinguish the six-membered rings TiMg$_2$F$_3$, Ti$_2$MgF$_3$ and TiF$_3$ as structural elements of the cage. Incorporation of sodium fluoride, formed *in situ*, into organometallic fluoride cages, leads to the formation of a more intricate architecture, as found in [(Cp*TiF$_2$)$_6$(NaF)$_7$·2.5THF]. The formation of these species results in solubilisation of highly insoluble ionic solids in organic solvents, in a pseudo-molecular form, protected by lipophilic organic groups.[152] Similarly, compounds such as (Cp*ZrF$_3$)$_6$Li$_4$O$_2$ represent intercalation of a metal oxide into a fluorometalate cage.[153]

The incorporation of six caesium ions into an aluminophosphonate supramolecular structure (Scheme 24) also con-
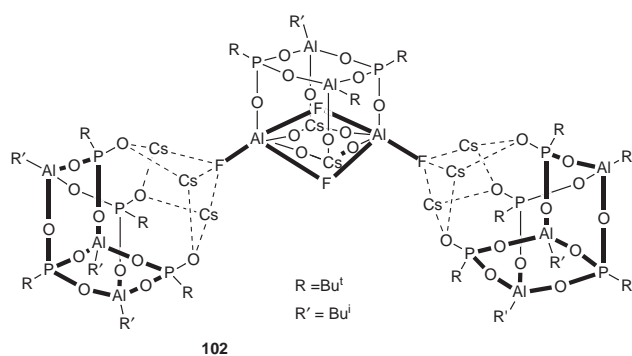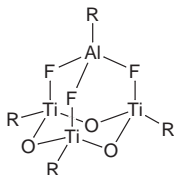

Scheme 24

taining an Al$_2$F$_2$ cyclic sub-unit 102, occurs in a compound of composition [Cs$_3$(THF)$_3$(μ_4-F)(AlBu^i)$_3$(O$_3$PBu^t)$_4$]$_2$[(Bu^{i}Al)$_2$Al$_2$-(μ-F)$_2$(O$_3$PBu^t)$_4$], self-assembled from the very simple synthons Cs[FAlBu$^i_3$] and Bu^{t}PO$_3$H$_2$ in THF.[154] It illustrates the complexity of architectures which can be obtained by involving fluorine as the structure directing element.
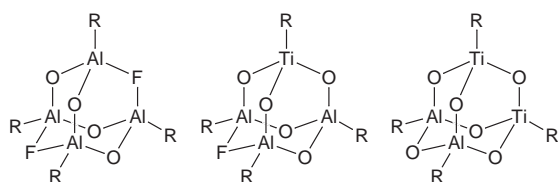
Selected neutral adamantane cages:
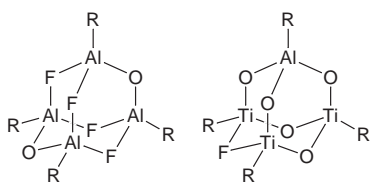
Selected cationic (2+) adamantane cage:

Selected anionic (2–) adamantane cages:

Scheme 25

5 Conclusions and outlook

1. Although monovalent (in the classical sense) fluorine can form more than one bond to other atoms (usually metals) and may appear as mono-, di-, tri- and tetra-connective in organometallic fluorides, the high degree of ionic character of most metal–fluorine bonds is probably the major factor which determines this behaviour.

2. In some cases fluoro anions such as $[BF_4]^-$, $[PF_6]^-$, $[AsF_6]^-$ and $[SbF_6]^-$, can behave as weakly coordinating ligands, although in most cases (not covered in this review) they tend to be discrete species that simply compensate the positive charge of a cationic complex.

3. The biconnective bridging mode of fluorine leads to supramolecular self-assembly into ring and chain polymeric structures. Four-, six- (planar and non-planar) and eight-membered rings are known and more can be expected.

4. The non-planar triconnective binding mode of fluorine allows it to occupy corners of self-assembled polycyclic cages. The smallest are the cubane structures (requiring M–F–M bond angles close to 90°) and these are observed mainly in alkali metal organometallic fluorides. Larger M–F–M bond angles provide a convexity (or Gaussian curvature) leading to larger cages. The tri- and tetra-connective binding mode can also produce double-chain (ladder-like) supramolecular polymeric arrays.

5. Polycyclic cages of organometallic fluorides can encapsulate metal cations or even molecular fragments of solid state fluorides, leading to a particular type of inorganic–organometallic host–guest complex ('molecular solids').

6. The fluoride anion can be encapsulated as a guest in organometallic cryptands or in organometallic fluoride cages, acting as hosts, due to electrostatic interactions. In such cases the fluoride anion displays (in known examples) coordination numbers two, four or six.

7. There is a topological analogy between fluorine and oxygen, which suggests that many fluoro analogues of known organometallic oxo rings and cages, as well as mixed fluoro–oxo organometallic rings and cages can be envisaged. One can speculate that if RM^{III} and RM^{IV} building blocks are considered as possible synthons for adamantane and cubane type

supermolecules, neutral, anionic and cationic species can be anticipated. A selection of such structures, imagined with RAl (R = alkyl, aryl) and RTi (R = substituted or unsubstituted η^5-cyclopentadienyl) building units are illustrated in Schemes 25 and 26. Some can be realistic synthetic targets.
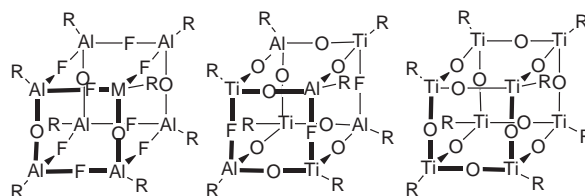
Scheme 26   Charges not indicated.

8. The molecular and supramolecular chemistry of organometallc fluorides presents itself as an attractive area of research, with very promising perspectives of unusual compositions and structures, resulting from the broad diversity of bonding patterns of fluorine.

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