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Fluorovinyl organometallic compounds — an historical review and some recent advances

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Abstract

This review describes the historically important routes to fluorovinyl organometallic species of the type M-(CX=CX$_2$), where M is a main-group or transition-metal element and one, or more, of the substituent atoms, X, is fluorine, the others being either other halogens, or hydrogen. A number of newer synthetic methods are described which have resulted in the preparation of a wider range of examples of such compounds. The structure, spectrocopy, properties, reactivity and future prospects for this class of compounds are described. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Fluorovinyl; Organometallic; Synthesis; Structure; Spectroscopy; Reactivity

1. Introduction

The replacement of hydrogen for fluorine in organic fragments results in moieties that are sterically larger than their perprotio analogues, and which possess very different electronic characteristics [1]. These factors are reflected in significantly different physical and chemical properties for related C–H and C–F containing compounds and in no area is this more obvious than in the field of organometallic chemistry [2].

While there exists a large arsenal of reagents available for the introduction of alkyl and related perprotio groups onto metal centres, this situation is not matched either in range, or stability, of reagents for the synthesis of metal-fluorocarbon species. For example whilst the first metal-methyl compound — methyl mercury — was prepared in 1852 it was not until 1949 that the first fluoroorganometallic, IHgCF$_3$, was reported [3].

Although there have been a number of recent reviews of the synthesis and chemistry of CF$_3$-containing organometallics most of the reviews of fluorovinyl systems are now somewhat outdated [4,5]. During the last few years a number of significant advances have been made in this area resulting in renewed interest in these systems. This paper reviews the historically important developments and recent advances in the study of fluorovinyl compounds of the type M–CX=CX$_2$ where at least one of the substituent atoms, X, is fluorine, the others being either fluorine, other halogens or hydrogen, and M is a main-group or transition-metal element.

2. Synthetic methods

2.1. Grignard reagents

The first fluorovinyl-containing compound, CF$_2$=CFI, was prepared by Seffl in 1956 and this was subsequently used in the preparation of the perfluorovinyl Grignard reagent, CF$_2$=CFMgI, at low temperature [6]. The efficiency of this reaction was estimated as ca. 20% based on an analysis of the amount of CF$_2$CHF formed on hydrolysis of the Grignard reagent. Subsequent work by Knunyants [7,8] on the same system, but utilising lower reaction temperatures, resulted in a significant increase in the yield of the Grignard to 70%. Both he and Stone [9] found that bromotrifluoroethane, which was commercially available, unlike C$_2$F$_3$I, could also be used as the starting material for generation of perfluorovinyl-Grignard reagents in a similar fashion. This method was used to synthesise some of the earliest examples of perfluorovinyl-containing compounds, including a few organometallic complexes [10,11] (Table 1).

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Table 1
Fluorovinyl complexes prepared between 1959 and 1978

Compound	Reagents	Method[a]	Yield	Reference
$Me_3N\cdot Al(CF{=}CF_2)_3$	$Hg(CF{=}CF_2)_2 + Me_3N\cdot AlH_3$	O		[67]
$Ge(CF{=}CF_2)_4$	$CF_2{=}CFBr + GeCl_4$	G	–	[56]
$Me_2Ge(CF{=}CF_2)$	$CF_2{=}CFBr + Me_2GeCl_2$	G	–	[53]
$Et_3Ge(CF{=}CF_2)$	$CF_2{=}CFBr + Et_3GeCl$	G	–	[68]
$Ph_3Ge(CF{=}CF_2)$	$CF_2{=}CFBr + Ph_3GeCl$	G	–	[68]
$Sn(CF{=}CF_2)_4$	$CF_2{=}CFI + SnCl_4$	G	31	[10]
$Me_nSn(CF{=}CF_2)_{4-n}$	$CF_2{=}CFBr + Me_nSnCl_{4-n} (n = 2, 3)$	G, Li	65, 64	[9,12]
$Et_nSn(CF{=}CF_2)_{4-n}$	$CF_2{=}CFBr + Et_nSnCl_{4-n}$ $(n = 1, 2, 3)$	Li	80,40	[9,11]
$Bu_nSn(CF{=}CF_2)_{4-n}$	$CF_2{=}CFBr + Bu_nSnCl_{4-n}$ $(n{=}1, 2, 3)$	G	56–72	[10,11]
$Ph_nSn(CF{=}CF_2)_{4-n}$	$CF_2{=}CFIBr + Ph_nSnCl_{4-n}$ $(n = 1, 2, 3)$	G	45–72	[10,11]
$(CH_2{=}CH)_2Sn(CF{=}CF_2)_2$	$CF_2{=}CFBr + (CH_2{=}CH)_2SnCl_2$	G	46	[9,10]
$As(CF{=}CF_2)_3$	$CF_2{=}CFI + AsCl_3$	G	–	[7,8]
$Sb(CF{=}CF_2)_3$	$CF_2{=}CFI + SbCl_3$	G	–	[7,8]
$Bi(CF{=}CF_2)_3$	$CF_2{=}CFI + BiCl_3$	G	–	[7,8]
$Hg(CF{=}CF_2)_2$	$CF_2{=}CFI/Br + HgCl_2$	G, Li	–, 52	[7,8,15]
$Hg(CF{=}CF_2)Br$	$Hg(CF{=}CF_2)_2 + HgBr_2$	O	46	[7,8]
$[Mn(CO)_5(CF{=}CFH)]$	$CF_2{=}CFH + Me_3SnMn(CO)_5$	O	–	[57]
$[Re(CO)_5(CF{=}CF_2)]$	$CF_2{=}CF_2 + Na[Re(CO)_5]$	N	63	[24]
$[Re(CO)_2Cp(CF{=}CF_2)]$	$CF_2{=}CF_2 + Na[Re(CO)_2Cp]$	N	20	[24]
$[Fe(CO)_4I(CF{=}CF_2)]$	$CF_2{=}CFI + Fe_2(CO)_9$	UV	3	[26,27]
$[Fe(CO)_2Cp(CF{=}CF_2)]$	$CF_2{=}CF_2 + Na[Fe(CO)_2Cp]$	N	20	[24]
$[Ru(CO)_2Cl(CF{=}CF_2)(PMe_2Ph)_2]$	$CF_2{=}CFCl + [Ru(CO)_3(PMe_2Ph)_2]$	UV	50	[26,27]
$[Rh(CF{=}CF_2)(CO)_2(PPh_3)_2]$	$CF_2{=}CFCl + Na[Rh(CO)_2(PPh_3)_2]$	N	44	[25]
$[Ni(PEt_3)_2(CF{=}CF_2)_2]$	$CF_2{=}CFBr + [Ni(PEt_3)_2Cl_2]$	G	25	[20]
$[Ni(PEt_3)_2(CF{=}CF_2)Cl]$	$CF_2{=}CFBr + [Ni(PEt_3)_2Cl_2]$	G	68	[20]
$[Ni(PPh_3)_2Cl(CCl{=}CF_2)]$	$CCl_2{=}CF_2 + [Ni(PPh_3)_2(C_2H_4)]$	V	63	[35,36]
$[Ni(PPh_3)_2Cl(CF{=}CFCl)]$	$CFCl{=}CFCl + [Ni(PPh_3)_2(C_2H_4)]$	V	87	[35,36]
$[Ni(PMePh_2)_2(CF{=}CF_2)Cl]$	$CF_2{=}CFCl + [Ni(PMePh_2)_2(C_2H_4)]$	V	89	[35,36]
$[Ni(PMePh_2)_2(CCl{=}CF_2)Cl]$	$CF_2{=}CCl_2 + [Ni(PMePh_2)_2(C_2H_4)]$	V	–	[35,36]
$[Ni(PPh_3)_2(CF{=}CF_2)Cl]$	$CF_2{=}CFCl + [Ni(PPh_3)_2(C_2H_4)]$	V	64	[35,36]
$[Ni(PPh_3)_2(CF{=}CF_2)Br]$	$CF_2{=}CFBr + [Ni(PPh_3)_2(C_2H_4)]$	V	87	[35,36]
$[Ni(AsMe_2Ph)_2(CF{=}CF_2)Cl]$	$CF_2{=}CFCl + [Ni(AsMe_2Ph)_4]$	V	64	[35,36]
$[Ni(AsMe_2Ph)_2(CF{=}CFCl)Cl]$	$CFCl{=}CFCl + [Ni(AsMe_2Ph)_4]$	V	90	[35,36]
$[Ni(AsMe_2Ph)_2(CCl{=}CF_2)Cl]$	$CF_2{=}CCl_2 + [Pd(AsMe_2Ph)_4]$	V	60	[35,36]
$[Pd(Bu^tNC)_2(CF{=}CF_2)Cl]$	$CF_2{=}CFCl + [Pd(Bu^tNC)_2]$	V	40	[32]
$[Pd(Bu^tNC)_2(CF{=}CF_2)Br]$	$CF_2{=}CFBr + [Pd(Bu^tNC)_2]$	V	45	[32]
$[Pd(PEt_3)_2(CF{=}CF_2)_2]$	$CF_2{=}CFBr + [Pd(PEt_3)_2Cl_2]$	Li	55	[20]
$[Pd(PEt_3)_2(CF{=}CF_2)Cl]$	$CF_2{=}CFCl + [Pd(PEt_3)_4]$	V	80	[31]
$[Pd(PEt_3)_2(CF{=}CF_2)Br]$	$CF_2{=}CFBr + [Pd(PEt_3)_4]$	V	90	[31]
$[Pd(PEt_3)_2(CF{=}CF_2)Br]$	$CF_2{=}CFBr + [Pd(PEt_3)_2Cl_2]$	G, Li	33, 40	[20]
$[Pd(AsMe_2Ph)_2(CF{=}CF_2)Cl]$	$CF_2{=}CFCl + [Pd(AsMe_2Ph)_4]$	V	71	[32]
$[Pt(Bu^tNC)_2(CF{=}CF_2)Cl]$	$CF_2{=}CFCl + [Pt_3(Bu^tNC)_6]$	V	–	[71]
$[Pt(Bu^tNC)_2(CF{=}CF_2)Br]$	$CF_2{=}CFBr + [Pt_3(Bu^tNC)_6]$	V	45	[71]
$[Pt(PEt_3)_2(CF{=}CF_2)_2]$	$CF_2{=}CFBr + [Pt(PEt_3)_2Cl_2]$	Li	–	[20]
$[Pt(PEt_3)_2(CF{=}CF_2)Cl]$	$CF_2{=}CF_2 + [Pt(PEt_3)_2HCl]$	O	20	[37]
$[Pt(PEt_3)_2(CF{=}CF_2)Br]$	$CF_2{=}CFBr + [Pt(PEt_3)_2Cl_2]$	G	40	[20]
$[Pt(PEt_3)_2(CF{=}CFH)Cl]$	$CF_2{=}CFH + [Pt(PEt_3)_2HCl]$	O	–	[37]
$[Pt(PEt_3)_2(CF{=}CF_2)(CO)][ClO_4]$	$CFCl{=}CF_2 + [Pt(PEt_3)_4] + CO + NaClO_4$	V	74	[32]
$[Pt_2(PEt_3)_2(CF{=}CF_2)_2Br_2]$	$CF_2{=}CFBr + [Pt_2(PEt_3)_2Br_4]$	Li	49	[20]
$[Pt(PMePh_2)_2(CF{=}CF_2)Br]$	$CF_2{=}CFBr + [Pt(PMePh_2)_4]$	V	67, 93	[30,31]
$[Pt(PMePh_2)_2(CF{=}CF_2)Cl]$	$CF_2{=}CFCl + [Pt(PMePh_2)_4]$	V	90	[31]
$[Pt(PMePh_2)_2(CF{=}CFCl)Cl]$	$CFCl{=}CFCl + [Pt(PMePh_2)_4]$	V	75	[28]
$[Pt(PMePh_2)_2(CF{=}CF_2)OAc]$	$CF_2{=}CFBr + [Pt(PMePh_2)_4] + AgOAc$	V	80	[31]
$[Pt(PMePh_2)_2(CF{=}CF_2)SCN]$	$CFBr{=}CF_2 + [Pt(PMePh_2)_4] + KSCN$	V	60	[33]
$[Pt(PMePh_2)_2(CF{=}CF_2)NO_2]$	$CFBr{=}CF_2 + [Pt(PMePh_2)_4] + KNO_2$	V	55	[33]
$[Pt(PPh_3)_2(CF{=}CF_2)Cl]$	$CF_2{=}CFCl + [Pt(PPh_3)_4]$	V	60	[29]
$[Pt(PPh_3)_2(CF{=}CF_2)Br]$	$CF_2{=}CFBr + [Pt(PPh_3)_4]$	V	95	[29]
$[Pt(PPh_3)_2(CF{=}CF_2)I]$	$CF_2{=}CF_2 + [Pt(PPh_3)_4] + LiI$	V	55	[34]
$[Pt(PPh_3)_2(CF{=}CF_2)OAc]$	$CF_2{=}CFCl + [Pt(PPh_3)_4] + AgOAc$	V	90	[32]
$[Pt(PPh_3)_2(CF{=}CF_2)SCN]$	$CFBr{=}CF_2 + [Pt(PPh_3)_4] + KSCN$	V	55	[33]
$[Pt(PPh_3)_2(CF{=}CF_2)NO_2]$	$CFBr{=}CF_2 + [Pt(PPh_3)_4] + KNO_2$	V	25	[33]
$[Pt(PPh_3)_2(CF{=}CF_2)NO_3]$	$CFBr{=}CF_2 + [Pt(PPh_3)_4] + KNO_3$	V	30	[33]

Table 1 (*Continued*)

$[Pt(PPh_3)_2(CF{=}CF_2)(CO_2CF_3)]$	$CFBr{=}CF_2 + [Pt(PPh_3)_4] + KCO_2CF_3$	V	50	[32]
$[Pt(PPh_3)_2(CF{=}CF_2)(acac)]$	$CFBr{=}CF_2 + [Pt(PPh_3)_4] + Kacac$	V	25	[32]
$[Pt(PPh_3)_2(CF{=}CF_2)CN]$	$CFBr{=}CF_2 + [Pt(PPh_3)_4] + AgCN$	V	70	[32]
$[Pt(PPh_3)_2(CF{=}CF_2)NCS]$	$CFBr{=}CF_2 + [Pt(PPh_3)_4] + AgNCS$	V	60	[32]
$[Pt(PPh_3)_2(CF{=}CF_2)SnMe_3]$	$Me_3SnCF{=}CF_2 + [Pt(PPh_3)_3]$	O	75	[66]
$[Pt(AsPh_3)_2(CF{=}CF_2)Cl]$	$CF_2{=}CFCl + [Pt(AsPh_3)_4]$	V	91	[34]
$[Pt(AsPh_3)_2(CF{=}CF_2)Br]$	$CF_2{=}CFBr + [Pt(AsPh_3)_4]$	V	87	[34]

[a] G = Grignard reagent, Li = lithium reagent, N = metal-based nucleophilic attack of a fluoroalkene, UV = u.v. photolysis, V = vinyllic rearrangement, O = other methods, see text.

2.2. Lithium reagents

Early attempts to synthesise perfluorovinyllithium by the reaction of perfluorovinyl halides with elemental lithium were unsuccessful [6], however, perfluorovinyllithium was obtained in 1962 via transmetallation reactions using perfluorovinyl compounds prepared from the Grignard reagent. Seyferth [12] reported that ligand exchange between tris-(perfluorovinyl)phenyltin (prepared from $CF_2{=}CFMgBr$ and $PhSnCl_3$) and phenyllithium, at low temperature, produced perfluorovinyllithium in yields of around 65%. Perfluorovinyllithium prepared by this method was used to expand the number of perfluorovinyl-containing complexes [13,14]. Subsequent work by Tarrant [15] demonstrated that contrary to an earlier report [16] fluoroolefins, such as bromotrifluoroethane, can be used directly as fluorovinyl precursors by reaction with alkyllithium reagents (Scheme 1).

$$CF_2{=}CFBr + RLi \longrightarrow CF_2{=}CFLi + RBr$$

Scheme 1

Subsequent reaction of the lithium reagent obtained via this route was used to prepare a number of perfluorovinyl-containing organometallic compounds (Table 1). This method was also used to prepare examples of other fluorovinyl lithium compounds such as $LiCF{=}CClF$ (from $CFCl{=}CFCl$) [17,18], $LiCCl{=}CF_2$ (from $CCl_2{=}CF_2$ [19] or $CBrCl{=}CF_2$) [20] and $LiCF{=}CH_2$ from $BrFC{=}CH_2$ [21]. It is also possible to produce fluorovinyl species by proton abstraction of a suitably substituted alkene with strong bases such as butyllithium at low temperature, as shown in Scheme 2.

$$CF_2{=}CFH + BuLi \longrightarrow CF_2{=}CFLi + BuH$$

Scheme 2

In this way $LiCF{=}CCl_2$ [22], $LiCCl{=}CF_2$, $LiCCl{=}CFCl$ and $LiCH{=}CF_2$ [21] are obtained from $CHF{=}CCl_2$, $CHCl{=}CF_2$, $CHCl{=}CFCl$ and $CH_2{=}CF_2$, respectively. It is worth noting that generally the use of diethylether as solvent for these reactions is preferred over that of THF, due to greater thermal stability of the resulting lithium species. However, the successful generation of some fluorovinyllithium species requires the reaction to be carried out in THF rather than ether, this is because in ether a competitive reaction resulting in alkyl-substitution at the CF_2-group is more important [23].

The stability of fluorovinyl Grignard and lithium reagents is very much lower than that of their perprotio analogues and has been the subject of a number of investigations. Tarrant studied the stability of perfluorovinyllithium at 0°C, −27°C and −78°C and concluded that it is stable for around 1 h at low temperature. Seyferth [14] suggested that decomposition arises from initial loss of lithium fluoride generating difluoroacetylene which, in the presence of an excess of phenyllithium, results in diphenylacetylene. However, Tarrant proposed, on the basis of the concentration dependence of decomposition, that an intermolecular mechanism is responsible [21].

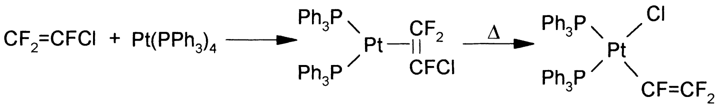
Most importantly, the availability of fluorovinyllithium species, albeit of limited stability resulted in the synthesis of a number of inorganic perfluorovinyl-containing compounds (Table 1) with yields generally higher than those obtained from Grignard reagents. These reagents also provided an important nucleophilic source of the fluorovinyl anion which have been extensively used in synthetic organic chemistry (see later).

2.3. Direct reaction with metal complexes

Perfluorovinyl-containing metal-complexes can be generated by attack of fluoroalkenes such as $CF_2{=}CF_2$ or $CF_2{=}CFCl$ with nucleophilic complexes such as $Na[Re(CO)_5]$, $Na[Re(CO)_2(\eta^5\text{-}C_5H_5)]$ [24] and $Na[Rh(CO)_2(PPh_3)_2]$ [25]. However, the weaker nucleophiles such as $[Mn(CO)_5]^-$, $[Fe(CO)_4]^{2-}$ and $[Co(CO)_4]^-$ do not appear to generate perfluorovinyl complexes under similar conditions [24]. One of the few iron-containing fluorovinyl compounds $[(CF_2{=}CF)Fe(CO)_4I]$ is generated, albeit in yields of ca. 3% as one of a number of products, by the direct reaction of $CF_2{=}CFI$ with $[Fe_2(CO)_9]$ under UV irradiation [26,27].

2.4. Vinyllic rearrangements

The single method responsible for the generation of the largest number of transition metal-containing fluorovinyl-complexes involves a vinyllic rearrangement of a π-bound fluoroethene ligand as shown in Scheme 3 [28].



Scheme 3

Using this method, which is applicable to thermally-stable complexes which contain coordinatively unsaturated metal centres, a large number of platinum, nickel and palladium perfluorovinyl derivatives have been obtained. Studies have shown that the use of CF_2=CFBr is favoured over CF_2=CFCl since complexes containing the former alkene do not require such high temperatures for thermal rearrangement [29]. Thus $[Pt(Ph_3P)_2(\eta^2\text{-}CF_2{=}CFCl)]$ generates *trans*-$[Pt(Ph_3P)_2(CF{=}CF_2)Cl]$ in 60% yield whilst the analogous π-coordinated CF_2=CFBr-containing starting material generates 95% of the bromide product. Other studies showed that, not surprisingly, the nature of the metal centre, the ancillary ligands and the solvent used effects the degree of conversion [29–33]. It was also discovered that the addition of silver salts significantly increased the rate of rearrangement in benzene/ethanol solutions, presumably resulting from halide abstraction [34].

Work by Green and Parker [28] on the mechanism of the vinyllic rearrangement suggested that a dissociative, S_N1-type process, involving a tight ion pair is responsible. During their study they also reported the synthesis of one of the few compounds containing a fluorovinyl group other than CF_2=CF–, $[PtCl(CF{=}CFCl)(PMePh_2)_2]$. Kemmitt and co-workers [34] showed that carbonatobis(triphenylarsine)-platinum(II) is a good starting material for such reactions and that on reaction with tetrafluoroethylene or trifluoroethylene in ethanol at 40°C the π-bound acetylene complexes are formed which rearrange, on extended heating, to generate the corresponding fluorovinyl complexes $[PtCl(CF{=}CF_2)(AsPh_3)_2]$. However, when bromotrifluoroethylene is used the intermediate complex is not isolated and the vinyl complex is generated directly. This work also demonstrated that the analogous, but less reactive, triphenylphosphine-containing complexes can be forced to undergo a vinyllic rearrangement if LiI is added prior to heating resulting in the formation of LiF.

Later studies proposed a S_N2-type mechanism for the $\pi \rightarrow \sigma$ rearrangement and further evidence for this interpretation was obtained by a series of reactions which, when carried out in the presence of additional ligands, resulted in a number of analogous platinum perfluorovinyl complexes incorporating these ligands [32,33].

A limited number of reactions have been conducted in attempts to generate chlorine-containing fluorovinyls. In these reactions the intermediate π-bound fluoro-alkene complex is not usually isolated and high yields are obtained. For example, displacement of ethylene from $[(PPh_3)_2Ni(\eta^2\text{-}C_2H_4)]$ by $CCl_2{=}CF_2$ or CClF=CClF in ether is followed by a spontaneous rearrangement to generate $[(PPh_3)_2NiCl(CCl{=}CF_2)]$ and a *cis–trans*-mixture of $[(PPh_3)_2NiCl(CF{=}CFCl)]$, respectively [35,36]. Despite the ease of this reaction there are very few examples of metal complexes containing mixed chloro-fluorovinyl ligands.

An alternative way of generating perfluorovinyl organometallics was demonstrated by Clark and Tsang [37] who showed that when a fluoro-alkene reacts with a metal hydride a perfluorovinyl-containing complex may be obtained. Thus *trans*-$[(PEt_3)_2PtHCl]$ reacts with $CF_2{=}CF_2$ and CF_2=CHF to generate the *trans*-complexes $[(PEt_3)_2PtCl(CF{=}CFX)]$ X = F and X = H, respectively, although not in high yields. It was proposed that the first stage of the reaction involves coordination of the alkene to the metal centre as a π-bound ligand which is followed by rearrangement and elimination of HF to generate the perfluorovinyl complex. An alternative method of generating hydrofluorovinyl ligands was demonstrated in the reaction of dimethyl tin hydrides with methylperfluorovinyl tin compounds under UV irradiation. This resulted in a scrambling of the vinyl substituents yielding a mixture of tin compounds containing —CF=CF_2 and *cis*- and *trans*-CF=CFH ligands [38].

Table 1 lists the organometallic fluorovinyl-containing complexes obtained from the methods outlined above. These methods effectively account for all fluorovinyl complexes obtained up to 1978. It is interesting to note that the vast majority (ca. 90%) of these materials contain the perfluorovinyl ligand as opposed to chlorine- or hydrogen-substituted fluorovinyl species. It is also noteworthy that nearly all the publications are limited to reporting the synthesis and spectroscopic characterisation of these complexes. Over the last 10 years, there has been renewed interest in fluorovinyl-containing species and in particular their application in organic systems [39–41] which has resulted in a number of advances in this area as described below.

2.5. Activated metal powder methods

Of the newer methods, one of the most intriguing is the direct reaction between activated metal powders and bromo- or iodo-perfluoroethene in DMF at, or just above, room temperature demonstrated by Burton [42], Scheme 4, to yield stable perfluorovinyl-cadmium or zinc reagents [43] in very high yields. Although frequently a mixture of mono- and bis-substituted compounds are produced, and the materials are hydrolytically sensitive, they have the advantage of thermal stability over lithium and Grignard reagents and they have been used in a number of organic transformations such as alkylations, coupling and acylation reactions [44].

$$CF_2{=}CFI + M \xrightarrow[DMF]{RT} CF_2{=}CFMI + (CF_2{=}CF)_2M \qquad (M = Cd, Zn)$$

Scheme 4

Interestingly when the same reaction is carried out with activated copper, the metal reagent is not produced. However, perfluorovinylcopper may be prepared quantitatively via a transmetallation reaction between a perfluorovinylcadmium or zinc reagent and copper(I)halides [45].

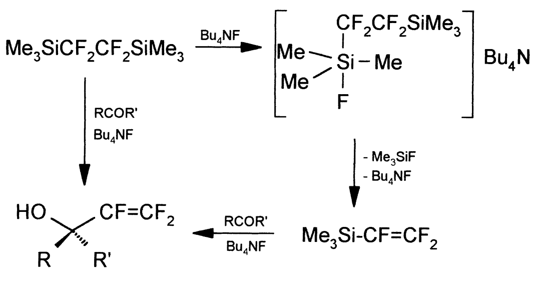
2.6. *Silyl reagents*

Recent work by Olah and co-workers [46] has resulted in the synthesis of a stable trimethylsilyl reagent, $Me_3SiCF_2CF_2SiMe_3$, capable of delivering the perfluorovinyl anion. This material is generated by electrocoupling of Me_3SiCF_2Cl and Me_3SiCl in THF solution to give a 75% yield of a mixture dominated by $Me_3SiCF_2CF_2SiMe_3$, but also containing some $Me_3SiCF_2SiMe_3$. In the presence of TBAF (tetrabutylammonium fluoride), $Me_3Si(CF{=}CF_2)$ is generated in situ which acts as a perfluorovinyl anion source towards, for example, carbonyl compounds, as illustrated in Scheme 5.

A similar type of reaction, although requiring higher reaction temperatures and resulting in mixed products is observed for the analogous reagent $PhMe_2SiCF_2CF_2SiPhMe_2$ [47].

2.7. *CFC-replacement methods*

In 1996, Coe and co-workers [48] reported that HFC-134a, a CFC replacement, can be used to generate perfluorovinyllithium at low temperature by reaction with two equivalents of a base, such as BuLi. The proposed mechanism is shown in Scheme 6 and although the intermediate compound $CF_2{=}CFH$ is not isolated the mechanism is supported by the interception of $CF_3CHFSnBu_3$ when Bu_3SnCl is added after the first stage of reaction.



Scheme 5

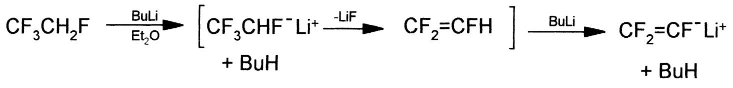
Formation of the fluorovinyllithium reagent in this way, although still a low temperature reaction, has the advantage that it is based on a material that is widely commercially available as a CFC-replacement. This is in contrast to the earlier routes which relied on substituted fluoroalkenes which are becoming progressively more difficult to obtain or C_2F_4 which has an attendant risk of explosion if not handled correctly.

Perfluorovinyllithium generated by this method has been used to synthesise a number of perfluorovinyl-containing organic species. Since then we have used the same route to obtain a range of perfluorovinyl-containing organometallic species, including those based on late-transition metal and main-group elements such as $Me_3Sn(CF{=}CF_2)$, $Hg(CF{=}CF_2)_2$, $[Mn(CO)_5(CF{=}CF_2)]$, $[FeCp(CO)_2(CF{=}CF_2)]$ and $[Pt(PR_3)_2Cl_{n-2}(CF{=}CF_2)_n]$ ($n = 1, 2$) [49] and the first examples of early transition-metal complexes of the type $Cp_2MX_{2-n}(CF{=}CF_2)_n$ ($M = Ti, Zr$; $X = F, Cl$; $n = 1, 2$), Scheme 7 [50].

It is possible to extend this method to the reaction of HCFC-133a (CF_3CH_2Cl) with two equivalents of butyllithium to generate 1-chloro-2,2-difluorovinyllithium in good yields [51]. Once again this route has provided a new method for the synthesis of organometallic complexes of this ligand — an area which is conspicuous by its current dearth. Prior to 1998 there were just 3 organometallic complexes containing the $CF_2{=}CCl^-$ group reported in the literature, (Table 1) these are all of the type $[Ni(CCl{=}CF_2)ClL_2]$ where $L = PPh_3$, $PMePh_2$ and $AsMe_2Ph$. We have prepared, using HCFC-133a as the fluorovinyl precursor, examples of chlorodifluorovinyl-complexes of titanium, zirconium, iron, nickel, palladium, gold and mercury in a fashion analogous to that shown in Scheme 7. These complexes constitute the first significant number of such materials to be generated and their properties are currently under investigation [52].

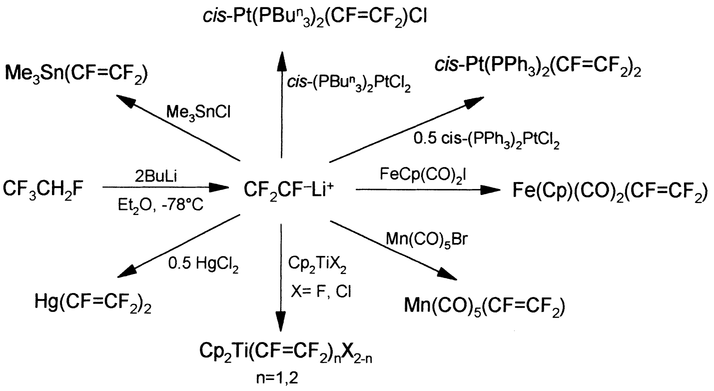
3. Structure and spectroscopy

There have been a number of spectroscopic studies, in particular NMR studies, of perfluorovinyl-containing complexes [37,38,53]. The signals observed in the ^{19}F NMR spectra of these complexes usually appear as simple AMX patterns due to the relative magnitude of the coupling constants and the chemical shifts of the three inequivalent



$$CF_3CH_2F \xrightarrow[Et_2O]{BuLi} \left[\underset{+\,BuH}{CF_3CHF^-Li^+} \xrightarrow{-LiF} CF_2{=}CFH \right] \xrightarrow{BuLi} \underset{+\,BuH}{CF_2{=}CF^-Li^+}$$

Scheme 6



Scheme 7

fluorine nuclei. In many cases where the metal also possesses one or more magnetically-active nuclei additional coupling is observed, e.g. [(PR$_3$)$_2$PtCl(CF=CF$_2$)] [37], Hg(CF=CF$_2$)$_2$ [54]. In fact analysis of the NMR data for a series of [PtL(CF=CF$_2$)(PEt$_3$)$_2$] complexes has been used to determine the *cis*- and *trans*-influence of ligand L [55]. The ^{19}F NMR spectra of chlorodifluorovinyl-containing complexes exhibit two doublets within the chemical shift ranges −65 to −82 ppm and −80 to −99 ppm and a ^{2}J(FF) coupling constant of magnitude between 35 and 75 Hz [52].

There have also been a number of reports of vibrational spectroscopic studies. The infra-red spectrum of CF$_2$=CF-containing complexes exhibit four, distinctive, strong absorptions between: 1730 and 1695, 1330 and 1275, 1180 and 1120, and 1050 and 970 cm^{-1} which have been assigned as ν(C=C), ν_{as}(=CF$_2$), ν(CF) and ν_s(CF$_2$), respectively [56]. For complexes containing the CF$_2$=CCl ligand ν(C=C) is typically observed between 1700 and 1670 cm^{-1}, while the two ν(=CF$_2$) modes are to be found around 1210 and 960 cm^{-1} [52].

Until very recently there was only one published structural characterisation of a fluorovinyl-organometallic complex and no data for any perfluorovinyl-containing complexes. The lone set of data, determined in 1967, is for 1,2-difluorovinyl-pentacarbonylmanganese, [Mn(CO)$_5$-(CF=CFH)], which was obtained from the reaction of [Me$_3$SnMn(CO)$_5$] with CF$_2$=CFH [57]. In this complex the C=C distance was determined to be 1.28(4) Å and the two C–F distances as 1.46(3) and 1.50(3) Å. It was not until 1998 that any further reports of single-crystal structural data for fluorovinyl-containing compounds appeared. We have recently published the low-temperature structure of the perfluorovinyl-containing phosphine ligand, Ph$_2$P(CF=CF$_2$) and of metal complexes containing a related ligand, i.e. *cis*-[PtCl$_2${PPh$_2$(CF=CF$_2$)}$_2$] and [{AuCl[PPh$_2$(CF=CF$_2$)]}$_2$] [58]. Interestingly all the three of C–F bond lengths of the perfluorovinyl moiety are different in the free ligand [1.353(3), 1.321(4) and 1.310(4) Å], although there appears to be no especially significant intermolecular interactions to account for these variations. There is also a similar variation in the C–F distances in the two complexes. Since then we have obtained structural data for a number of organometallic complexes containing this and related chlorodifluorovinyl ligands using both extended X-ray absorption fine structure (EXAFS) spectroscopy and single crystal X-ray diffraction work.

Studies of the structure of early-transition metal perfluorovinyl-containing complexes, such as Cp$_2$Ti(CF=CF$_2$)$_n$X$_m$ ($n + m = 2$; X = F, Cl), have been limited to Ti K-edge EXAFS studies. This is because these materials are too reactive in solution to allow crystals suitable for X-ray diffraction to be obtained. Analysis of the data yielded titanium–carbon bond distances of 2.033(12) and 2.050(18) Å in Cp$_2$Ti(CF=CF$_2$)$_2$ and Cp$_2$Ti(CF=CF$_2$)F, respectively. These distances are similar to 2.03 Å, the sum of the covalent radii for Ti(IV) (1.36 Å) and sp^2 hybridised carbon (0.67 Å) which suggests, not surprisingly, that the perfluorovinyl group is bound in a simple σ-fashion and that there is no obvious π-delocalisation even though the metal is electron poor [50].

The first single-crystal data for a perfluorovinyl-organometallic compound was obtained for Hg(CF=CF$_2$)$_2$ after crystallisation at low temperature. Subsequently supporting experiments were conducted via gas-phase electron-diffraction studies and that data have been compared with ab initio calculations carried out at the MP2/DZP level [59]. In the solid-state, considerable variation in the C–F bond lengths of the perfluorovinyl ligand are again observed [1.362(6), 1.286(6) and 1.324(6) Å]. In the gas phase, the differences between the different C–F distances are smaller [1.357(13), 1.321(7) and 1.332(7) Å], but still significant and the molecule appears to undergo essentially free-rotation around the Hg–C bonds. The *ab initio* calculations suggest that a shallow energy minimum exists when the torsional angle C=C…C=C is 98°.

We have also obtained the first solid-state structures of chlorodifluorovinyl-containing metal complexes, for example HgCl(CCl=CF$_2$) prepared from the reaction of CF$_2$=CClLi with HgCl$_2$ [60] is shown in Fig. 1 and compared with that of Hg(CF=CF$_2$)$_2$.

Structural data for other examples of perfluorovinyl and chlorodifluorovinyl-containing transition-metal complexes

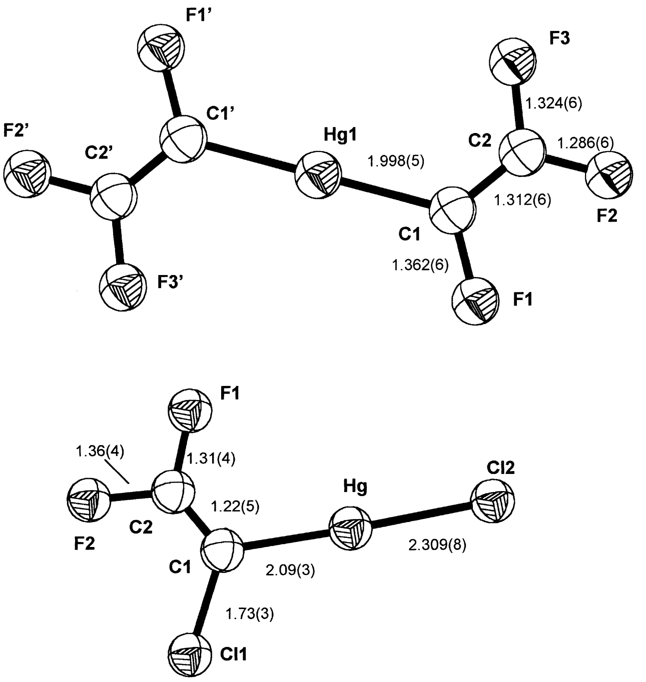


Fig. 1. The molecular structures of $Hg(CF{=}CF_2)_2$ and $Hg(CCl{=}CF_2)Cl$ as determined by single crystal X-ray diffraction at 100 and 293 K, respectively.

has been obtained, including the two analogous gold complexes $[AuPR_3(CX{=}CF_2)]$ ($X = F$, Cl) [61]. Once again there is a variation in the C–F bond lengths of the fluorovinyl ligands which have been observed in all of the crystal structures obtained to date. In every case, the longest C–F distance is the unique α-C–F bond which is consistent with that found in structural studies on metal-bound perfluoroalkyl moieties. Attempts to rationalise this variation have been based on density functional calculations for $Hg(CF{=}CF_2)_2$. These suggest that the alpha-carbon atom is appreciably more positively charged than the beta-carbon which would result in a stronger ionic contribution to the C_β–F bonds than in the C_α–F one. Atomic overlap population calculations also suggest that there are more electrons involved in bonding within the C_β–F bonds than in the C_α–F linkage [62].

4. Properties and reactivity

Studies of the chemistry and reactivity of perfluorovinyl-containing complexes are very limited. It was recognised quite early on that $CF_2{=}CFH$ is generated as the major decomposition product when perfluorovinyl complexes are left in protic solvents for an extended period of time. Similarly decomposition of other fluorovinyl-containing complexes result in the generation of $CX_2{=}CXH$. However, the stability of perfluorovinyl complexes compared with their perprotio-analogues is not clear-cut. In some cases perfluorovinyl-containing metal complexes appear to exhibit enhanced thermal and oxidative stabilities when compared with their vinyl analogues. Thus, for example, whilst $Cp_2Ti(CH{=}CH_2)_2$ rearranges in solution at ca. −30°C to generate a metallacyclobutane [63,64]. $Cp_2Ti(CF{=}CF_2)_2$ decomposes only slowly in solution and is stable as a solid indefinitely. This trend is not, however, uniform, $Hg(CF{=}CF_2)_2$ is reasonably stable towards both air and moisture, but it does slowly decompose unless kept cold, while $Hg(CH{=}CH_2)_2$, by comparison, is air- and moisture-stable. Similarly $Sn(CF{=}CF_2)_4$ is both air- and moisture-sensitive whilst $Sn(CH{=}CH_2)_4$ is neither.

There is a similar lack of consistency for other fluorovinyl compounds. $Et_3Si(CCl{=}CF_2)$ is reported as being unstable, and forming Et_3SiF [65], whilst a recent report of $Me_3Si(CCl{=}CF_2)$ describes the material as being stable at room temperature [51]. From our work on transition-metal perfluorovinyl and chlorodifluorovinyl complexes we observe that chlorodifluorovinyl materials tend to be less stable than their perfluorovinyl analogues. However, because of the limited number of compounds prepared of other fluorovinyl complexes it is not yet possible to generalise further.

One use of organometallic fluorovinyl complexes is as fluorovinyl transfer reagents. In this respect the perfluorovinyltin compounds appear to act as better exchange reagents than the analogous vinyltin materials and these compounds have therefore been used to generate a few examples of organometallic compounds, these include the synthesis of perfluorovinyllithium [11] and $[Pt(PPh_3)_2(CF{=}CF_2)SnMe_3]$ [66]. Conversely while divinylmercury has been used fairly widely as a vinyl-transfer reagent it would appear that bis(perfluorovinyl)mercury is not generally useful in this context, although it has been used to generate the only known perfluorovinyl aluminium compounds [67] and $HgX(CF{=}CF_2)$ $X = Br$, Cl [7,8] via metathesis reactions (Scheme 8).

The study of reactions of metal-coordinated fluorovinyl groups is very limited. Seyferth [68] investigated the reactions of $Et_3SiCF{=}CF_2$ with compounds such as Br_2, HBr, $CBrCl_3$ and CCl_4; in many cases addition across the double bond of the perfluorovinyl group was observed, to varying degrees, although attack of the silicon-ethyl bond also occurred. Because of the increased reactivity of $Sn(CF{=}CF_2)_4$ over that of $Sn(CH{=}CH_2)_4$ studies of insertion into the metal-fluorocarbon bond has been undertaken on this system [69]. Infrared spectroscopic studies suggested

$$Me_3NAlH_3 + Hg(CF{=}CF_2)_2 \longrightarrow Me_3NAl(CF{=}CF_2)_2H \xrightarrow{Hg(CF=CF_2)_2} Me_3NAl(CF{=}CF_2)_3$$

Scheme 8

$$Sn(CF{=}CF_2)_4 + SO_2 \xrightarrow{60^{\circ}C,\ 1d} (CF_2{=}CF)_2Sn(O_2SCF{=}CF_2)_2$$

Scheme 9

that tetrakis(perfluorovinyl)tin will react with SO_2 by insertion into the M–C bond, to yield a perfluoroethenesulfinate species, Scheme 9.

However, the yield was low (<5%) and for mixed ligand tetraorganotin compounds such as $[Ph_3Sn(C_6F_5)]$ and $[Ph_2Sn(CF{=}CF_2)_2]$, insertion was observed to take place preferentially into the tin-phenyl bond.

Attempts to polymerise perfluorovinyl-containing species have been reported [70]. For example, perfluorovinylsilanes undergo polymerisation to yield air-stable, silicon-containing, polymeric materials which exhibit conductivity.

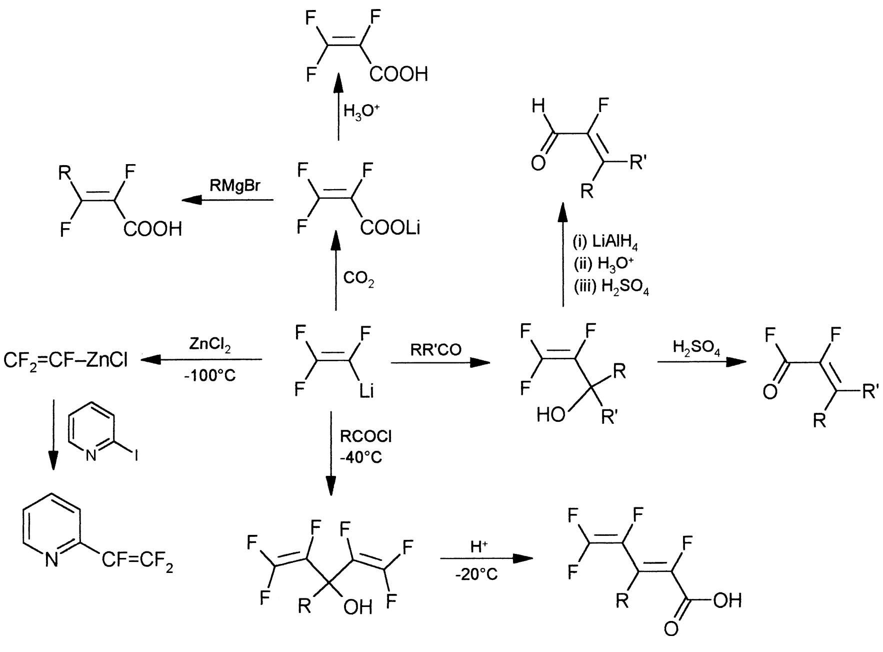
However, to date, the single, major use of metal-based fluorovinyl complexes is as transfer reagents in organic synthesis. This is true for Grignard [7,8], and particularly, vinyl-lithium [15,17–19,21–23,48,51,72,73], copper, zinc and cadmium reagents [44], and to a lesser extent, silyl- [46,47] and stannane- [74] reagents. Scheme 10 illustrates some typical, reactions of the perfluorovinyl-nucleophile as derived from, for example, the lithium reagent. These reactions can be subdivided into insertion, substitution and nucleophilic attack of carbonyl groups. Of particular interest in the last class of reaction is the frequent difficulty in isolating the alcoholic product due to the ease with which allylic rearrangements occur either on warming or under acidic conditions [72,73].

Similar types of reactivity have been observed for other fluorovinyllithium reagents (for example, hydrogen-containing analogues) and these too have proved to be of some synthetic utility [75,76].

5. Future prospects

To date much of the work undertaken in the study of organometallic fluorovinyl complexes has been confined to the perfluorovinyl systems. Even though a reasonable number of compounds of this type have been reported, the majority are simple group-10 metal-containing complexes. This is unfortunate since most of the more interesting chemistry would be anticipated for fluorovinyl complexes of the earlier transition metals. Recent advances have resulted in new methods for the synthesis of these materials and studies of the reactivity and applications for these compounds are called for. With one exception, it has only very recently been possible to obtain structural data for metal-fluorovinyl compounds and these have exhibited some interesting characteristics which require further theoretical studies. It is also noticeable that there has been relatively little attention paid to vinyl systems containing a mixture of fluoro/chloro and fluoro/hydrido substituents, this is despite the potential here for transfer reagents in organic synthesis for which there are few alternatives and which may result in compounds of some utility. Indeed it has already been demonstrated that fluorovinyl substitution into uracil [77] and uridine [78] systems give rise to active materials. The potential fluorovinyl ligands offer in modification of the steric, electronic and physical properties of metal centres is large and may well result in systems of importance in catalytic applications. There are also many possibilities for modification and incorporation of fluorovinyl systems in a wide variety of polymeric materials.

It has, in the past, been suggested that the synthesis, properties and chemistry of the fluorovinyl ligand are well understood. However, it should be clear that until very



Scheme 10

recently data has only been available for a relatively small number of compounds of principally one fluorovinyl ligand coordinated to a handful of elements. New compounds, methodology and applications continue to be published and it is likely that this is an area in which there will be continued, and renewed, interest both from the academic and industrial standpoints.

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