

Asymmetric fluoro-organomercurials. Part 2. The synthesis and characterisation of the fluorovinyl-mercurials $\text{RHgCX}=\text{CF}_2$ ($\text{R} = \text{Ph}$, Fc ; $\text{X} = \text{F}$, Cl): The single crystal X-ray structures of $\text{PhHgCF}=\text{CF}_2$, $\text{FcHgCF}=\text{CF}_2$ and $\text{FcHgCCl}=\text{CF}_2[\text{Fc}(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)]^\star$

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Received 17 November 2006; received in revised form 16 January 2007

Available online 26 January 2007

Abstract

The asymmetric fluorovinyl mercurials $\text{RHgCX}=\text{CF}_2$ ($\text{R} = \text{Ph}$, Fc ; $\text{X} = \text{F}$, Cl) have been prepared from RHgCl and $\text{LiCX}=\text{CF}_2$, the later being derived from the reaction of HFC-134a , $\text{CF}_3\text{CH}_2\text{F}$ ($\text{X} = \text{F}$) or HCFC-133a , $\text{CF}_3\text{CH}_2\text{Cl}$ ($\text{X} = \text{Cl}$) and $n\text{-BuLi}$. All the complexes have been fully characterised by spectroscopic methods and, apart from $\text{PhHgCCl}=\text{CF}_2$, the compounds are sufficiently stable to be investigated by single-crystal X-ray diffraction, making this the first report of structurally characterised asymmetric fluorovinyl mercurial complexes of the type $\text{RHg}(\text{CX}=\text{CF}_2)$. In the solid state all of the structurally characterised complexes demonstrate asymmetric Hg-C distances and extensive intramolecular $\text{Hg}\cdots\text{F}$ and $\text{Hg}\cdots\eta^2\text{-arene}$ interactions are observed.

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Keywords: Fluorovinyl; Organofluorine; Mercury; Synthesis; X-ray structure; $\text{Hg}\cdots\eta^2$ interactions

1. Introduction

Since the first documented study of an organomercurial, by Frankland in 1852 [2], these materials have become one of the most widely studied classes of organometallic compound, and have found widespread utility as synthetic reagents, in spite of their inherent toxicity. In recent years much of the interest in these complexes has focussed on their physico-chemical properties and applications, such as optical and NLO materials, chemosensing, molecular recognition and supramolecular assembly. In the solid state structures of these materials extensive mercury-centred packing interactions are frequently observed and these are ascribed to the acidic character of the mercury(II) centre. Nowhere is this more evident than in the research into heavily fluorinated organomercurials [3], inspired by the

synergy between an acidic mercury(II) centre and the electron-withdrawing effects imparted by perfluorocarbon fragments. This has resulted in the development of poly-functional, supramolecular Lewis acidic systems [4], capable of catalytic activity [5].

In spite of such topicality the literature contains relatively few examples of organomercurials containing ‘small’ perfluorinated organic fragments ($\text{C}_1\text{--C}_3$). Historically, those that have been reported are frequently trifluoromethyl-based systems, such as PhHgCF_3 and $\text{Hg}(\text{CF}_3)_2$ which are formed by mercury insertion in C-X ($\text{X} = \text{halogen}$) bonds [6], halogen exchange reactions [7] or decarboxylation of fluorocarboxylates [8]. There are even fewer cases of small, unsaturated perfluorocarbons. Indeed, prior to our recent report of the compounds $\text{RHgC}\equiv\text{CCF}_3$ ($\text{R} = \text{Me}$, $n\text{-Bu}$, $t\text{-Bu}$, Ph , Fc) [1] only seven such materials were known, viz.: $\text{Hg}(\text{C}\equiv\text{CCF}_3)_2$ [9,10], $\text{Hg}(\text{CF}=\text{CF}_2)_2$ [11], $\text{BrHg}(\text{CF}=\text{CF}_2)$ [11a,11b], $\text{Hg}(\text{C}(\text{CF}_3)=\text{CF}_2)_2$ [12], $\text{ClHg}(\text{CF}=\text{CF}_2)$ [13], $\text{Hg}(\text{CCl}=\text{CF}_2)_2$ [13], $\text{ClHg}(\text{CCl}=\text{CF}_2)$ [13] and $(\text{CH}_2=\text{CH})\text{Hg}(\text{CF}=\text{CF}_2)$ [14], most of

[☆] For Part 1, see Ref. [1].

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which are prepared using Grignard or organolithium reagents. Of these only two, $\text{ClHg}(\text{CF}=\text{CF}_2)$ [13] and $\text{Hg}(\text{CF}=\text{CF}_2)_2$ [15], have been structurally characterised. We have sought to enhance the range of known asymmetric mercurials comprising the trifluorovinyl ($\text{CF}=\text{CF}_2$) and 1-chloro-2,2-difluorovinyl ($\text{CCl}=\text{CF}_2$) moieties. Here we report the syntheses of the compounds $\text{RHg}(\text{CX}=\text{CF}_2)$ ($\text{R} = \text{Ph}$, Fc ; $\text{X} = \text{F}$, Cl) and an investigation of the solid state structures of $\text{PhHg}(\text{CF}=\text{CF}_2)$, $\text{FcHg}(\text{CF}=\text{CF}_2)$ and $\text{FcHg}(\text{CCl}=\text{CF}_2)$.

2. Results and discussion

2.1. Synthesis and characterisation

The compounds $\text{RHg}(\text{CX}=\text{CF}_2)$ ($\text{X} = \text{F}$, $\text{R} = \text{Ph}$ **1**, $(\text{C}_5\text{H}_5)\text{Fe}(\text{C}_5\text{H}_4)(\text{Fc})$ **2**; $\text{X} = \text{Cl}$, $\text{R} = \text{Ph}$ **3**, Fc **4**) were prepared by the low temperature (-78°C) reaction of the appropriate organomercurihalides RHgCl ($\text{R} = \text{Ph}$, Fc), with an excess of the lithium reagents $\text{LiCX}=\text{CF}_2$ ($\text{X} = \text{F}$, Cl), which are generated in situ from HFC-134a ($\text{CF}_3\text{CH}_2\text{F}$) and HCFC-133a ($\text{CF}_3\text{CH}_2\text{Cl}$), respectively, as previously described [16,13]. In this way the compounds **1**, **2** and **4** were obtained, after non-aqueous work-up, in good yields, as high purity crystalline solids, which exhibit good stability under ambient conditions and can be stored for prolonged periods in the exclusion of light. In contrast, compound **3** ($\text{PhHgCCl}=\text{CF}_2$), though similarly accessible, has proven more difficult to obtain in pure form, being frequently formed in admixture with unidentified impurities, and it tends to decompose, with deposition of elemental mercury, over a period of days in the solid state or hours in solution.

Compound	R	X
1	Ph	F
2	Fc	F
3	Ph	Cl
4	Fc	Cl

Nonetheless, the identities of all four materials were readily established on the basis of multinuclear (^{19}F , $^{13}\text{C}\{^1\text{H}\}$) NMR spectroscopic studies. In each case, the ^{19}F NMR spectra exhibit a characteristic set of mutually coupling resonances associated with the trifluorovinyl AMX (**1** and **2**) or 1-chloro-2,2-difluorovinyl AB (**3** and **4**) spin systems, each with attendant mercury satellites. Moreover, in addition to the aromatic fragments, the vinylic carbon centres are clearly apparent from the ^{13}C NMR spectra, observed as complex multiplet resonances due to coupling with three (**1** and **2**) or two (**3** and **4**) fluorine nuclei. Selected spectroscopic data for the fluorovinyl moieties are summarised in Table 1.

For the trifluorovinyl systems **1** and **2**, assignment of individual ^{19}F NMR resonances to the respective nuclei is trivial and based upon previously established trends in

Table 1

Selected NMR spectroscopic data for compounds $\text{RHgCX}=\text{CF}_2$ ($\text{X} = \text{F}$, $\text{R} = \text{Ph}$ **1**, Fc **2**; $\text{X} = \text{Cl}$, $\text{R} = \text{Ph}$ **3**, Fc **4**)

Compound	δ (J/Hz)
$\text{PhHgCF}=\text{CF}_2$ (1)	δ_{F} -90.7 (dd, 77.9, 36.4, J_{HgF} 142.8, F_{trans}) -125.2 (dd, 107.8, 77.9, J_{HgF} 41.6, F_{cis}) -185.2 (dd, 107.8, 36.4, J_{HgF} 620.7, F_{gem}) δ_{C} 163.6 (C, ddd, 312.0, 263.0, 32.0, C_{β}) 153.2 (C, ddd, 292.0, 92.0, 6.0, C_{α})
$\text{FcHgCF}=\text{CF}_2$ (2)	δ_{F} -91.1 (dd, 79.2, 37.0, J_{HgF} 153.2, F_{trans}) -125.8 (dd, 109.1, 79.2, J_{HgF} 42.8, F_{cis}) -185.0 (dd, 109.1, 37.0, J_{HgF} 650.6, F_{gem}) δ_{C} 170.1 (C, ddd, 290.7, 91.8, 4.8, C_{α}) 163.7 (C, ddd, 312.9, 262.7, 32.8, C_{β})
$\text{PhHgCCl}=\text{CF}_2$ (3)	δ_{F} -75.5 (d, 42.9, J_{HgF} 148.0, F_{trans}) -87.2 (d, 42.9, J_{HgF} 132.5, F_{cis}) δ_{C} 160.2 (C, dd, 310.0, 270.0 C_{β}) 120.2 (C, dd, 87.0, 7.0, C_{α})
$\text{FcHgCCl}=\text{CF}_2$ (4)	δ_{F} -75.9 (d, 41.6, J_{HgF} 189.7, F_{trans}) -87.6 (d, 41.6, J_{HgF} 135.1, F_{cis}) δ_{C} 160.3 (C, dd, 310.0, 269.4 C_{β}) 122.0 (C, dd, 85.9, 6.8, C_{α})

the magnitudes of ^{19}F – ^{19}F coupling constants within the $\text{CF}=\text{CF}_2$ group [17]; viz.: $J_{\text{trans}} > J_{\text{gem}} > J_{\text{cis}}$. Thus, the lower frequency resonances (ca. -185 ppm) are in each case assigned to the unique fluorine centre lying *geminal* to mercury, the remaining signals being attributed to those centres *cis* (ca. -125 ppm) and *trans* (ca. -90 ppm) to the metal. These assignments are consistent with the majority of previously reported trifluorovinyl compounds, but they do contrast the case of $\text{Hg}(\text{CF}=\text{CF}_2)_2$, where the fluorine nucleus *cis* to mercury is observed to resonate at the lower frequency [15].

Assignment of the 1-chloro-2,2-difluorovinyl resonances is, however, less obvious, given the absence of a third, mutually coupling homo-nucleus. We have previously discussed this for both transition metal [18] and main-group [19] derivatives, and have concluded that the lower frequency ^{19}F NMR resonance corresponds to the fluorine centre *trans* to the metal/metalloid, based upon the comparable magnitudes of M – ^{19}F satellite couplings within trifluorovinyl and 1-chloro-2,2-difluorovinyl homologues. Application of the same arguments here results, unusually, in the assignment of the resonances, $\delta_{\text{trans}} > \delta_{\text{cis}}$, however, this is consistent with that reported previously for $\text{Hg}(\text{CCl}=\text{CF}_2)_2$ and $\text{ClHg}(\text{CCl}=\text{CF}_2)$ [13]. Assignment of the fluorovinyl ^{13}C NMR resonances is in each case unequivocal, being based upon the observation of two large J_{CF} coupling constants for the CF_2 centre.

2.2. Structural characterisation

While the propensity of $\text{PhHgCCl}=\text{CF}_2$ (**3**) for decomposition (vide supra) has precluded crystallographic study, compounds **1**, **2** and **4** have all proven more amenable; X-ray quality single crystals being readily obtained by evaporation of dichloromethane/hexane solutions. In each

case, solution of the diffraction data reveals largely anticipated molecular geometries, though with appreciable disorder in the fluorovinyl group; as has been observed previously in other ‘heavy-element’ fluorovinyl compounds [13, 17,20]. Thus, in **1** the $\text{HgCF}=\text{CF}_2$ unit is resolved across two equally populated sites, as shown in Fig. 1, which are related by a crystallographic twofold rotation axis. The plane of the $\text{CF}=\text{CF}_2$ unit is tilted at an angle of 46° with respect to the aromatic ring. For the ferrocenyl derivative **2**, a similar disorder is observed within the perfluorovinyl section of the molecule, Fig. 2, but in this case with relative site occupancies of 2:1 and the $\text{CF}=\text{CF}_2$ unit is co-planar with the Cp rings. The situation for compound **4** is that the $\text{CCl}=\text{CF}_2$ group is essentially co-planar with the Cp rings and while a single site exists for the mercury centre the $\text{CCl}=\text{CF}_2$ fragment shows disorder across two sites with relative occupancies of 2:1, in a similar way to the perfluorovinyl analogue. Additionally a small percentage (2%) of the molecules are resolved with the entire $\text{HgCCl}=\text{CF}_2$ unit on the alternative cyclopentadienyl ring. Selected molecular structure parameters are summarised in Tables 2 and 3.

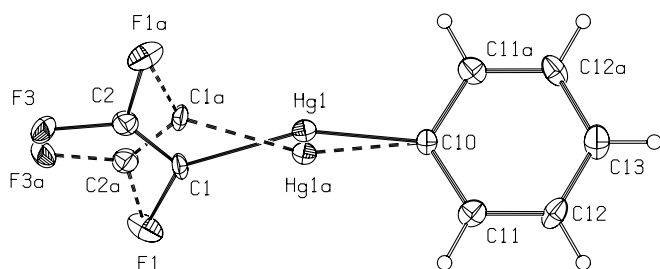


Fig. 1. Illustration of the molecular structure of $\text{PhHgCF}=\text{CF}_2$ (**1**), with thermal ellipsoids set at the 30% probability level, showing the disorder of the $\text{Hg}(\text{CF}=\text{CF}_2)$ unit. In each case one F atom of the perfluorovinyl group is symmetry generated.

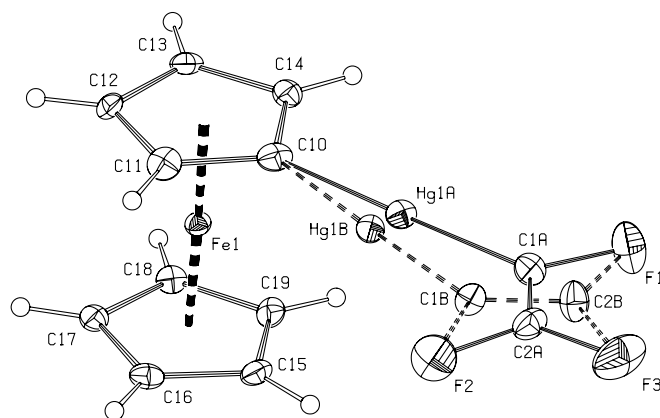


Fig. 2. ORTEP representation of the molecular structure of $\text{FcHgCF}=\text{CF}_2$ (**2**), with thermal ellipsoids set at the 30% probability level. The disordered sites (Hg1A , C1A , C2A) and (Hg1B , C1B , C2B) are occupied in the ratio 2:1. The numbering scheme is transposable to $\text{FcHgCCl}=\text{CF}_2$ (**4**), but with C1I in place of F1 and a single site for Hg1 .

Table 2

Selected bond distances (Å) and angles ($^\circ$) for $\text{PhHgCF}=\text{CF}_2$ (**1**) with estimated standard deviations in parenthesis

Hg1–C1	2.169(14)	C1–F1	1.415(14)
Hg1–C10	2.040(9)	C2–F2	1.394(14)
C1–C2	1.27(2)	C2–F3	1.37(2)
C10–Hg1–C1	155.3(4)/178.8(4)	C1–C2–F2	128.2(16)
Hg1–C1–C2	117.2(11)	C1–C2–F3	120.5(16)
Hg1–C1–F1	132.4(9)	F1–C1–C2	110.3(13)
		F2–C2–F3	111.1(15)

Table 3

Selected bond distances (Å) and angles ($^\circ$) for $\text{FcHgCF}=\text{CF}_2$ (**2**) and $\text{FcHgCCl}=\text{CF}_2$ (**4**) with estimated standard deviations in parenthesis

	$\text{FcHgCF}=\text{CF}_2$ (2)	$\text{FcHgCCl}=\text{CF}_2$ (4)
Hg1–C1	2.083(12)	2.119(7)
Hg1–C10	2.061(6)	2.053(5)
C1–C2	1.256(12)	1.286(10)
C1–X	1.362(11) (X = F1)	1.686(9) (X = Cl)
C2–F2	1.415(13)	1.312(10)
C2–F3	1.361(12)	1.351(8)
C10–Hg1–C1	178.9(3)	174.5(3)
Hg1–C1–C2	127.7(8)	118.1(6)
Hg1–C1–X	119.8(7) (X = F1)	122.9(4) (X = Cl)
C1–C2–F2	120.6(10)	128.5(7)
C1–C2–F3	122.9(11)	123.7(7)
X–C1–C2	112.4(10) (X = F1)	119.0(6) (X = Cl)
F2–C2–F3	116.4(8)	107.1(6)

These disorder effects result in larger uncertainties in the parameters obtained for the fluorovinyl parts of the molecules, and thus detailed discussion of the internal geometries of these fragments is of limited utility, although some features are noteworthy. In each of the characterised complexes the Hg–fluorovinyl distance is greater than the Hg–hydrocarbon distance. This asymmetry in the Hg–C distances is most marked in complex **1** with $\Delta r = 0.129$ Å.

For compound **1**, the disorder allows for two crystallographically viable conformations, which differ in the $\text{Ph-Hg-C}_{\text{vinyl}}$ angle, being either near linear [$\angle\text{C-Hg-C}$ $178.8(4)^\circ$] or significantly ‘bent’ [$\angle\text{C-Hg-C}$ $155.3(4)^\circ$] at the mercury(II) centre. Whilst some deviation from linearity has been noted in the related fluoroalkynyl mercurials $\text{RHgC}\equiv\text{CCF}_3$ (R = Ph, Fc) [1] and, indeed, would seem prolific in mercury–alkynyl chemistry, the extent is considerable smaller, and such effects have proven far less prevalent amongst vinylic systems; presumably a consequence of the reduced capacity for $\pi(\text{C}=\text{C}) \rightarrow \text{Hg}$ interactions over their alkynyl analogues. Indeed, there is negligible evidence for such interactions in any of the present compounds (vide infra), or indeed the previously reported $\text{ClHgCCl}=\text{CF}_2$ [13] or $\text{Hg}(\text{CF}=\text{CF}_2)_2$ [15], which taken together with the conformations observed for **2** and **4** would seem to mitigate against a ‘bent’ geometry. It is, however, noted that the influence of the ferrocenyl fragment upon molecular packing cannot be quantified, and in lieu of further, appropriate, examples a definitive conclusion cannot be unequivocally reached.

A shortening of the C=C bond, relative to the averaged distance for $Csp^2=Csp^2$ [1.299 Å] [21], appears to be present in all three structures. This has been observed in nearly all structurally characterised fluorovinyl compounds, and has been attributed to librational effects [15], which become more pronounced with increasing mass of the metal/metalloid fragment. The C=C distances [$d(C=C)$ 1.27(2) Å **1**; 1.256(12) Å **2**; 1.286(10) Å **4**] are amongst the shorted yet observed for any fluorovinyl compound. However, it should be cautioned that the combination of libration and disorder in **1**, **2** and **4** cannot be readily deconvoluted.

In view of the prevalence of mercuriophilic interactions that has been reported for related organofluoro mercury(II) systems, we were interested in the extended structures of these materials. In the solid state the extended structure of **1** consists of sheets of alternating but offset “head-to-tail” molecules in the *b*-direction. The offset is such that each mercury centre is adjacent to F1 of two neighbouring perfluorovinyl units to produce Hg···F1 distances of 3.023 Å, and results in a planar four-coordinate arrangement around the mercury(II) centre (F1···Hg···F1' = 174.9°). Such a distance is considerably less than the sum of the van der Waals radii (3.58 Å) of mercury [22] and fluorine [23]. More significantly, these Hg···F distances are shorter than those found in the cyclotrimeric tetrafluoro-*o*-phenylenemercury systems [4d,24]. Additional contacts exist within the layers between the *ortho*-hydrogens (H11) of the arene ring and F1 of adjacent molecules, $d(H···F) = 2.595(8)$ Å, which is slightly less than the sum of the van der Waals radii (2.67 Å). While there are no obvious Hg···Hg interactions, with the shortest such distance being over 5 Å, the average mercury position is located above C12–C13–C12' of the phenyl ring of an adjacent molecule at a distance of 3.438(9) Å.

In the other perfluorovinyl system, FcHgCF=CF₂ (**2**) once again “head-to-tail” packing is observed. H···F contacts of a similar length to that found in **1** exist between F2 and one Cp hydrogen (H11) [$d(H···F) = 2.595(3)$ Å]. These are augmented by interactions between F1 and F2 and the mercury centre of a neighbouring molecule with distances of 3.035(4) and 3.404(5) Å, respectively. Once again no particularly short Hg···Hg interactions are observed, but the mercury centre is located above the mid-point of the C11–C12 bond, the distance between the mercury ion and the mid-point of this bond is 3.235(6) Å.

Complexes **2** and **4** are related except that in **2** a fluorovinyl group is present whilst in **4** a 1-chloro-2,2-difluorovinyl group exists. Not unexpectedly, the solid-state structure of **4** shows a similar structural motif to **2**, although a number of small perturbations are apparent. The Hg···F1 interaction observed in complexes **1** and **2** is no longer present, and is not replaced by any notable Hg···Cl interactions; by comparison, the Hg···F2 interaction is seen for **4**, as it is for **1** and **2**, with $d(Hg···F2) = 3.150(5)$ Å. Additional weak interactions are observed between F3···H13, $d = 2.662$ Å, and Cl···H14, $d = 2.793(5)$ Å. A more significant change in the molecular stacking becomes obvious

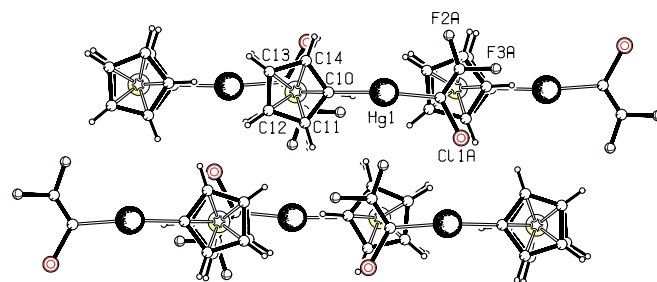


Fig. 3. Representation of the extended structure of FcHgCCl=CF₂ (**4**) looking down the ferrocenyl ligands. Only the principal component is shown for clarity.

when the structure is viewed down the Cp–Fe–Cp axes, Fig. 3, the chlorodifluorovinyl group of one molecule now sits parallel and directly above the Cp ring of another molecule, at a distance of 3.756 Å.

It appears that in all three complexes the solid state structure consists of layers of the organomercurial complexes in which Hg···F and H···F interactions are important. Additionally mercury–arene interactions are apparent. For molecules **1** and **4** these interactions are weak, while for complex **2** the Hg···η²-arene distance of 3.235(6) Å makes this one of the more significant such interactions observed to date and comparable to that recently recorded for the fluorophenyl-containing triazene-polymeric complex, {Hg[NNN(PhF)₂]₂}_n [25]. A search of the Cambridge Crystallographic database revealed 416 datasets for compounds exhibiting Hg···π-system distances less than 4 Å. Within this set of data the average distance was 3.706 Å and the shortest such distance observed is 3.117 Å [26]. As anticipated the presence of an electron-withdrawing fluorovinyl group on the mercury centre does appear to enhance these interactions. It is also interesting to note that in these fluorovinyl-containing complexes, unlike the related systems containing trifluoropropynyl ligands, there are no indications of any mercuriophilic interactions, with most of the Hg···Hg distances observed in the fluorovinyl systems being over 5 Å and the shortest 4.895(9) Å in complex **4**, which contrasts with 4.088 Å in FcHgCCCCF₃ [1].

3. Conclusions

We have reported the synthesis of four new asymmetric mercurial compounds of the type RHgCX=CF₂. Where X = F and X = Cl, R = Fc the compounds are stable and have been isolated, fully characterised and their solid state structures determined by single X-ray crystallography. All of the structures exhibit some degree of disorder of the fluorovinyl substituent, typically across two sites, notwithstanding this these are amongst the first examples of asymmetric fluorovinyl organomercury complexes to be structurally characterised. No evidence for mercuriophilic interactions was observed, however, significant Hg···F and Hg···π interactions are present in all three of the structurally characterised complexes. The former is most signif-

icant in $\text{PhHgCF}=\text{CF}_2$ (**1**) where $d(\text{Hg}\cdots\text{F}) = 3.023 \text{ \AA}$ and the latter in $\text{FcHgCF}=\text{CF}_2$ (**2**) where the $\text{Hg}\cdots\eta^2\text{-arene}$ distance is $3.235(6) \text{ \AA}$.

4. Experimental

Caution! Alkyl-mercurials are highly toxic and prone to disproportionation; fluorinated derivatives are potentially volatile. Extreme care is necessary when handling all products and their solutions.

Reactions were performed in well-ventilated fume hoods, using standard inert atmosphere techniques. Diethyl ether was dried over sodium wire for ca. 1 day prior to use. The compounds $\text{CF}_3\text{CH}_2\text{F}$ (HFC-134a), $\text{CF}_3\text{CH}_2\text{Cl}$ (HCFC-133a) (Ineos/ICI Klea), *n*-BuLi (2.5 M in hexane, Acros), FcHgCl and PhHgCl (Aldrich) were used as supplied. NMR spectra (CDCl_3) were recorded on Bruker DPX200 (^{19}F , 188.310 MHz with respect to CFCl_3) or DPX400 (^{13}C , Dept-135, 100.555 MHz; ^1H 400.4 MHz, with respect to SiMe_4) spectrometers. Infrared (CHCl_3 , KBr plates) and Raman spectra were recorded on a Nicolet Nexus FTIR/Raman spectrometer. Elemental analyses were performed by the departmental microanalytical service.

4.1. X-ray crystallography

X-ray data for compounds **1**, **2** and **4** were recorded on a Nonius κ -CCD 4-circle diffractometer using Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 120(2) K; solved using direct methods and subject to full-matrix least-squares refinement on F^2 using SHELX-97 [27]. Absorption correction

was by the multi-scan method. Non-hydrogen atoms were refined with anisotropic thermal parameters, while hydrogen atoms were included in idealised positions. Geometric analyses and figures were generated using PLATON [28]. Data collection and refinement parameters are summarised in Table 4.

4.2. Preparation of $\text{PhHgCF}=\text{CF}_2$ (**1**)

Typically, in a flask shielded from light, a stirred ethereal solution (100 cm^3) of HFC-134a (0.50 cm^3 , 5.93 mmol) was treated, under N_2 , with *n*-BuLi (4.50 cm^3 , 11.25 mmol), at $-78 \text{ }^\circ\text{C}$. After 2 h, PhHgCl (0.869 g, 2.78 mmol) in ether (40 cm^3) was added, whilst maintaining $-78 \text{ }^\circ\text{C}$, then the mixture held at $-60 \text{ }^\circ\text{C}$ and stirred overnight. The reaction was allowed to attain ambient temperature then hexane (160 cm^3) was added to precipitate the inorganics; the settled mixture was filtered through Celite[®] and the filtrate concentrated in vacuo to afford **7** as a yellow solid. Yield: 0.788 g, 79%. Anal. Calc. for **1**: C, 26.8; H, 1.4; F, 15.9. Found: C, 27.1; H, 1.4; F, 15.5%. δ_{F} , δ_{C} see Table 1, also δ_{C} 160.5 [m, C], 136.3 [s, CH, J_{HgC} 92.0 Hz], 128.1 [s, CH, J_{HgC} , 19.0 Hz], 127.9 [s, CH, J_{HgC} 124.0 Hz]. δ_{H} 7.6–7.3 (m). $\nu_{\text{max}}/\text{cm}^{-1}$ 1716 (C=C str.), 1269, 1105, 1001 (C–F str.).

4.3. $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{HgCF}=\text{CF}_2)](\text{2})$

From HFC-134a (0.36 cm^3 , 4.27 mmol), *n*-BuLi (3.40 cm^3 , 8.50 mmol), FcHgCl (0.907 g, 2.15 mmol). Product obtained as an orange solid. Yield: 0.937 g, 93%. Anal. Calc. for **2**: C, 31.0; H, 1.9; F, 12.2. Found: C, 31.1; H, 1.8; F, 11.9%. δ_{F} , δ_{C} see Table 1, also δ_{C} 90.3 [ddd, C, J_{CF} 10.6,

Table 4
Crystallographic data for compounds **1**, **2** and **4**

Compound	$\text{PhHgCF}=\text{CF}_2$ (1)	$\text{FcHgCF}=\text{CF}_2$ (2)	$\text{FcHgCCl}=\text{CF}_2$ (4)
Formula	$\text{C}_8\text{H}_5\text{F}_3\text{Hg}$	$\text{C}_{12}\text{H}_9\text{F}_3\text{FeHg}$	$\text{C}_{12}\text{H}_9\text{ClF}_2\text{FeHg}$
Molecular weight	358.71	466.63	483.08
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$ (No. 15)	$P21/c$ (No. 14)	$P21/c$ (No. 14)
Unit cell parameters			
a (Å)	9.8805(3)	9.9708(2)	10.2910(4)
b (Å)	13.1590(5)	11.8840(2)	11.8042(4)
c (Å)	6.8458(2)	9.7195(2)	10.2242(3)
α (°)	90	90	90
β (°)	112.545(2)	103.9840(10)	107.1270(10)
γ (°)	90	90	90
V (Å ³)	822.05(5)	1117.56(4)	1186.93(7)
Z	4	4	4
D_{calc} (g cm^{-3})	2.898	2.773	2.702
λ (Mo $\text{K}\alpha$) (mm^{-1})	18.709	15.028	14.361
Crystal size (mm)	$0.01 \times 0.03 \times 0.24$	$0.03 \times 0.10 \times 0.14$	$0.07 \times 0.10 \times 0.10$
Habit	Lath	Blade	Plate
Color	Colourless	Orange	Colourless
Number of data (θ range, °)	936 (4.47–27.46)	2548 (3.14–27.48)	2663 (3.01–27.47)
Parameters refined	75	183	209
$F(000)$	640	856	888
R_1 , wR_2 [$I > 2\sigma(I)$]	0.0527, 0.1209	0.0366, 0.0944	0.0417, 0.1048
Maximum and minimum density ($\text{e } \text{Å}^{-3}$)	2.131 and 3.651	1.883 and 1.697	1.612 and 3.071

5.8, 1.5], 73.2 [s, CH, J_{HgC} 148.7 Hz], 69.7 [s, CH, J_{HgC} , 120.7 Hz], 66.7 [s, CH, J_{HgC} 38.8 Hz]. δ_{H} 4.5 (br. m., J_{HGH} 16.8 Hz, 2H), 4.3 (s, J_{HGH} 11.3 Hz, 5H), 4.1 (br. m., J_{HGH} 37.1 Hz, 2H). $\nu_{\text{max}}/\text{cm}^{-1}$ 1714 (C=C str.), 1270, 1105, 1000 (C–F str.).

4.4. *PhHgCCL=CF₂* (**3**)

From HCFC-133a (0.85 cm³, 9.96 mmol), *n*-BuLi (7.70 cm³, 19.25 mmol), PhHgCl (2.500 g, 7.98 mmol). Product obtained as a yellow solid. Yield: 2.634 g, 88%. M.p. 110 °C. Anal. Calc. for **3**: C, 25.6; H, 1.3; Cl, 9.5. Found: C, 24.5; H, 1.1; Cl, 7.1%. δ_{F} , δ_{C} see Table 1, also δ_{C} 161.1 [d, C, J_{CF} 6.0 Hz], 137.7 [s, CH, J_{HgC} 94.0 Hz], 129.6 [s, CH, J_{HgC} , 22.0 Hz], 129.4 [s, CH, J_{HgC} 130.0 Hz]. δ_{H} 7.6–7.3 (m).

4.5. $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{HgCCL=CF}_2)]$ (**4**)

From HFC-133a (0.45 cm³, 5.28 mmol), *n*-BuLi (3.75 cm³, 9.34 mmol), FcHgCl (1.701 g, 4.04 mmol). Product obtained as an orange solid. Yield: 1.735 g, 89%. Anal. Calc. for **4**: C, 29.8; H, 1.9; Cl, 7.3. Found: C, 29.9; H, 1.9; Cl, 7.5%. δ_{F} , δ_{C} see Table 1, also δ_{C} 90.5 [dd, C, J_{CF} 6.5, 1.5], 73.1 [s, CH, J_{HgC} 152.6 Hz], 69.7 [s, CH, J_{HgC} , 123.6 Hz], 66.8 [s, CH]. δ_{H} 4.5 (br. m., J_{HGH} 16.0 Hz, 2H), 4.3 (s, 5H), 4.1 (br. m., J_{HGH} 37.4 Hz, 2H). $\nu_{\text{max}}/\text{cm}^{-1}$ 1687 (C=C str.), 1250, 984 (C–F str.).

Acknowledgements

We thank the Engineering and Physical Sciences Research Council (EPSRC) and UMIST for financial support, ICI Klea and Ineos Fluor for donation of HFC-134a and HCFC-133a. We acknowledge the EPSRC for support of the UMIST NMR (GR/L52246) and FT-IR/Raman (GR/M30135) facilities, a Research Equipment Initiative grant for X-ray equipment, and also for access to the Chemical Database Service at Daresbury. We thank the EPSRC National Crystallographic Service, Department of Chemistry, University of Southampton, for data collections for compounds **1** and **2**.

Appendix A. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Database. CCDC 627595, 627596 and 627597 contain the supplementary crystallographic data for **4**, **1** and **2**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2007.01.030](https://doi.org/10.1016/j.jorganchem.2007.01.030).

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