

# Asymmetric fluoro-organomercurials. Part 2. The synthesis and characterisation of the fluorovinyl-mercurials $\text{RHgCX}=\text{CF}_2$ ( $\text{R} = \text{Ph}$ , $\text{Fc}$ ; $\text{X} = \text{F}$ , $\text{Cl}$ ): 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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## Abstract

The asymmetric fluorovinyl mercurials  $\text{RHgCX}=\text{CF}_2$  ( $\text{R} = \text{Ph}$ ,  $\text{Fc}$ ;  $\text{X} = \text{F}$ ,  $\text{Cl}$ ) have been prepared from  $\text{RHgCl}$  and  $\text{LiCX}=\text{CF}_2$ , the later being derived from the reaction of  $\text{HFC-134a}$ ,  $\text{CF}_3\text{CH}_2\text{F}$  ( $\text{X} = \text{F}$ ) or  $\text{HCFC-133a}$ ,  $\text{CF}_3\text{CH}_2\text{Cl}$  ( $\text{X} = \text{Cl}$ ) 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  $\text{Hg-C}$  distances and extensive intramolecular  $\text{Hg}\cdots\text{F}$  and  $\text{Hg}\cdots\eta^2\text{-arene}$  interactions are observed.

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## 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  $\text{PhHgCF}_3$  and  $\text{Hg}(\text{CF}_3)_2$  which are formed by mercury insertion in  $\text{C-X}$  ( $\text{X} = \text{halogen}$ ) 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  $\text{RHgC}\equiv\text{CCF}_3$  ( $\text{R} = \text{Me}$ ,  $n\text{-Bu}$ ,  $t\text{-Bu}$ ,  $\text{Ph}$ ,  $\text{Fc}$ ) [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

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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  $\text{RHg}(\text{CX}=\text{CF}_2)$  ( $\text{R} = \text{Ph}$ ,  $\text{Fc}$ ;  $\text{X} = \text{F}$ ,  $\text{Cl}$ ) 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**,  $\text{Fc}$  **4**) were prepared by the low temperature ( $-78^\circ\text{C}$ ) reaction of the appropriate organomercurihalides  $\text{RHgCl}$  ( $\text{R} = \text{Ph}$ ,  $\text{Fc}$ ), with an excess of the lithium reagents  $\text{LiCX}=\text{CF}_2$  ( $\text{X} = \text{F}$ ,  $\text{Cl}$ ), which are generated in situ from  $\text{HFC-134a}$  ( $\text{CF}_3\text{CH}_2\text{F}$ ) and  $\text{HCFC-133a}$  ( $\text{CF}_3\text{CH}_2\text{Cl}$ ), 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
<b>1</b>	Ph	F
<b>2</b>	Fc	F
<b>3</b>	Ph	Cl
<b>4</b>	Fc	Cl

Nonetheless, the identities of all four materials were readily established on the basis of multinuclear ( $^{19}\text{F}$ ,  $^{13}\text{C}\{^1\text{H}\}$ ) NMR spectroscopic studies. In each case, the  $^{19}\text{F}$  NMR spectra exhibit a characteristic set of mutually coupling resonances associated with the trifluorovinyl  $\text{AMX}$  (**1** and **2**) or 1-chloro-2,2-difluorovinyl  $\text{AB}$  (**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  $^{13}\text{C}$  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  $^{19}\text{F}$  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**,  $\text{Fc}$  **2**;  $\text{X} = \text{Cl}$ ,  $\text{R} = \text{Ph}$  **3**,  $\text{Fc}$  **4**)

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

the magnitudes of  $^{19}\text{F}$ – $^{19}\text{F}$  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  $^{19}\text{F}$  NMR resonance corresponds to the fluorine centre *trans* to the metal/metalloid, based upon the comparable magnitudes of  $\text{M}$ – $^{19}\text{F}$  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  $^{13}\text{C}$  NMR resonances is in each case unequivocal, being based upon the observation of two large  $J_{\text{CF}}$  coupling constants for the  $\text{CF}_2$  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

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