

# Carbon–fluorine bond activation by iron(I). C–F bond cleavage induced by addition of phosphines or thiols to a perfluorovinylidiron complex

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## Abstract

The reaction of phosphines PXYH (X = Y = Ph, *i*-Pr; X = Ph, Y = H) or ethanethiol with the perfluorovinyl compound  $[(\text{Fe}(\text{CO})_2)_2\{\mu\text{-C}(\text{SMe})(\text{CF}_3)_2\text{CCF}_2\}]$  (**1**) proceeds with cleavage of one C–F bond and gives rise to unusual ligand transformations. The multicenter processes involved lead to new diiron complexes  $[(\text{Fe}(\text{CO})_2)_2\{\mu\text{-C}(\text{SMe})(\text{CF}_3)_2\text{C}(\text{PXY})\text{CF}\}]$  (X = Y = Ph, **2a**; X = Y = *i*-Pr, **2b**; X = Ph, Y = H, **2c**) and  $[(\text{Fe}(\text{CO})_2)_2\{\mu\text{-C}(\text{SMe})(\text{CF}_3)_2\text{C}(\text{SEt})\text{CF}\}]$  (**3**). Mechanisms for these reactions are proposed. The fluxional behavior of **2a** and **3** has been investigated by variable-temperature <sup>13</sup>C NMR spectroscopy. The molecular structure of **2a** has been established by a single-crystal X-ray diffraction study. The Fe<sub>2</sub>(CO)<sub>6</sub> core contains an Fe–Fe bond of 2.633(1) Å bridged by the six-electron donor C(SMe)(CF<sub>3</sub>)<sub>2</sub>C(PPh<sub>2</sub>)CF ligand. **2a** crystallizes in the triclinic space group P $\bar{1}$  with *a* = 9.019(2), *b* = 9.550(2), *c* = 18.583(3) Å,  $\alpha$  = 101.06(2),  $\beta$  = 92.53(2),  $\gamma$  = 116.48(2)°, *R* = 0.0419 for 3984 reflections.

**Keywords:** C–F activation; Iron cluster; Sulphur; Fluorine; Carbene; Carbonyl

## 1. Introduction

The large dissociation energies of C–F bonds in fluorocarbons [1] are frequently used to explain the low reactivity of these compounds. However, when a fluorocarbon interacts with transition metal centers activation and, ultimately, cleavage of the robust C–F bonds may occur [2]. Although the activation of the C–F bonds of coordinated ligands is now well-established [3], most reports are concerned with the oxidative addition of aromatic C–F bonds to transition metals [4]; similar processes involving perfluorocarbon chains have been less explored. We have recently shown [5] that the reaction of RR'NH with the iron(I) complex  $[(\text{Fe}(\text{CO})_2)_2\{\mu\text{-C}(\text{SMe})(\text{CF}_3)_2\text{CCF}_2\}]$  **1** depends on the amine: reactions of primary amines proceed with cleavage of two C–F bonds in **1** to give **a** (Scheme 1),

whereas with secondary amines fluorine migration and C–F bond rupture afford, via monosubstituted species **e**, diiron complexes **b** stabilised by novel electroneutral six-electron donor ligands. The 1,2 migration of fluorine along the carbon chain of the ligand which accompanies these C–F bond cleavages is particularly noteworthy.

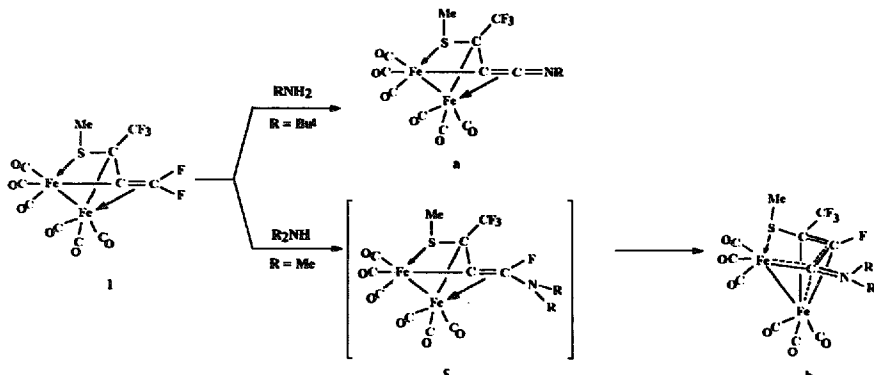
To illustrate further the ability of perfluorovinyl metallic complexes to undergo carbon–fluorine bond cleavage, we describe here the reactions of  $[(\text{Fe}(\text{CO})_2)_2\{\mu\text{-C}(\text{SMe})(\text{CF}_3)_2\text{CCF}_2\}]$  **1** with phosphines and thiols.

## 2. Results and discussion

### 2.1. Synthetic studies and spectroscopic characterization

The reaction of  $[(\text{Fe}(\text{CO})_2)_2\{\mu\text{-C}(\text{SMe})(\text{CF}_3)_2\text{CCF}_2\}]$  **1** [6] with diaryl or dialkylphosphines PXYH (X = Y =

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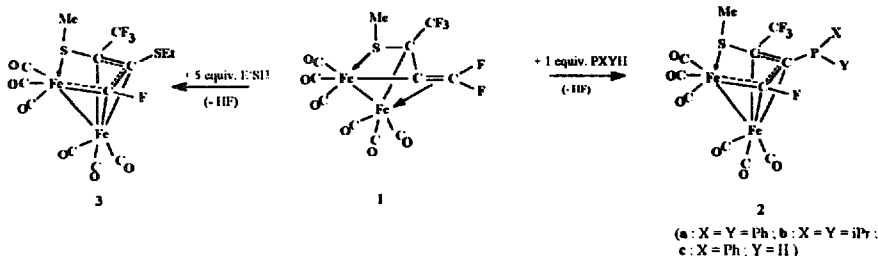


Scheme 1.

Ph, *i*-Pr) under argon in dichloromethane at room temperature for 3 h afforded the diiron complexes **2** (Scheme 2). After recrystallization from hexane–CH<sub>2</sub>Cl<sub>2</sub> complexes **2** were isolated in 97% yield as orange-red crystals. The corresponding reaction with phenylphosphine (X = Ph, Y = H) in CDCl<sub>3</sub> was complete in ca. 45 min at 55 °C and gave a 3:2 mixture of the diastereoisomers **2c**<sub>1</sub> and **2c**<sub>2</sub>. Under similar conditions **1** and ethanethiol produced in good yield (95%) the crystalline complex **3** in which SET takes the place of the phosphino substituent in **2**.

The new complexes **2** and **3** have been characterized

by various spectroscopic methods (<sup>1</sup>H, <sup>31</sup>P, <sup>19</sup>F and <sup>13</sup>C NMR, and IR), elemental analysis, and mass measurements. The spectroscopic data and assignments (Table 1) will not be further discussed, except where their interpretation is not straightforward. The structures for the new compounds are shown in Scheme 2. The NMR spectra of **2b**, **2c** and **3** are almost identical to those of **2a**, consistent with a similar basic structure. All the complexes exhibit low-field <sup>13</sup>C NMR resonances at about δ 220 (d, *J*<sub>C–F</sub> ≅ 350 Hz) which are typical of species containing a carbon atom with a single fluoro substituent. The C(F) resonance is significantly shifted



Scheme 2.

## Notes to Table 1:

<sup>a</sup> Chemical shifts (δ) measured in CDCl<sub>3</sub> at 293 K unless otherwise stated by footnote c.

<sup>b</sup> Hydrogen-1 decoupled.

<sup>c</sup> In CD<sub>2</sub>Cl<sub>2</sub>.

<sup>d</sup> Phosphorus-31 decoupled.

Table I  
 NMR data for complexes (δ)<sup>a</sup>

Complex	<sup>1</sup> H	<sup>31</sup> P	<sup>19</sup> F	<sup>13</sup> C <sup>b</sup>
2a	7.9-7.4 (m, 10H, 2C <sub>6</sub> H <sub>5</sub> ), 1.62 (s, 3H, SC H <sub>3</sub> )	-8.40 (dq, <sup>4</sup> J <sub>F-P</sub> = 51 Hz, <sup>3</sup> J <sub>F-P</sub> = 12 Hz)	-53.36 (d, <sup>2</sup> J <sub>F-P</sub> = 51 Hz, C F <sub>3</sub> ), -36.88 (d, <sup>3</sup> J <sub>F-P</sub> = 12 Hz, C F)	225.2 (dq, J <sub>C-F</sub> = 351.5 Hz, <sup>4</sup> J <sub>C-F</sub> = 1.5 Hz, CF), 209 (br, Fe <sub>2</sub> (CO) <sub>3</sub> ), 208.85 (d, <sup>3</sup> J <sub>C-F</sub> = 8 Hz, CO), 207.7 (d, <sup>2</sup> J <sub>C-F</sub> = 11 Hz, CO), 206.5 (d, <sup>1</sup> J <sub>C-F</sub> = 4 Hz, CO), 136-128.5 (2 C <sub>6</sub> H <sub>5</sub> ), 126.9 (q, J <sub>C-F</sub> = 275 Hz, CF <sub>3</sub> ), 94.4 (dd, <sup>2</sup> J <sub>C-P</sub> = 15 Hz, J <sub>C-P</sub> = 60 Hz, C-P), 53.7 (ddq, <sup>3</sup> J <sub>C-F</sub> = 13 Hz, <sup>2</sup> J <sub>C-P</sub> = 25 Hz, <sup>1</sup> J <sub>C-F</sub> = 35 Hz, C-CF <sub>3</sub> ), 33.0 (s, SCH <sub>3</sub> ) <sup>c</sup>
2b	2.66 (m, 1H, PC H), 2.38 (m, 1H, PC H), 1.94 (s, 3H, S Me), 1.33 (m, 12H, C H <sub>2</sub> )	18.40 (dq, <sup>4</sup> J <sub>F-P</sub> = 48 Hz, <sup>3</sup> J <sub>F-P</sub> = 11 Hz)	-53.86 (d, <sup>4</sup> J <sub>F-P</sub> = 48 Hz, C F <sub>3</sub> ), -40.60 (d, <sup>3</sup> J <sub>F-P</sub> = 11 Hz, C F)	224.8 (d, J <sub>C-F</sub> = 349 Hz, C-F), 208.6 (d, <sup>3</sup> J <sub>C-F</sub> = 8 Hz, CO), 208 (br, 3CO), 207.6 (d, <sup>2</sup> J <sub>C-F</sub> = 12 Hz, CO), 206.25 (d, <sup>1</sup> J <sub>C-F</sub> = 3 Hz, CO), 126.3 (q, J <sub>C-F</sub> = 274 Hz, CF <sub>3</sub> ), 93.3 (dd, <sup>2</sup> J <sub>C-F</sub> = 18 Hz, J <sub>C-P</sub> = 67 Hz, C-P), 53.5 (ddq, <sup>2</sup> J <sub>C-F</sub> = 34 Hz, <sup>3</sup> J <sub>C-F</sub> = 13 Hz, <sup>1</sup> J <sub>C-P</sub> = 23 Hz, C-CF <sub>3</sub> ), 33.2 (s, SCH <sub>3</sub> ), 25.5 (dd, J <sub>C-P</sub> = 16.5 Hz, <sup>4</sup> J <sub>C-F</sub> = 3.5 Hz, PC H), 24.9 (dd, J <sub>C-P</sub> = 17 Hz, <sup>4</sup> J <sub>C-P</sub> = 8 Hz, PC H), 22.2 (d, <sup>2</sup> J <sub>C-P</sub> = 25 Hz, CH <sub>3</sub> ), 22.0 (d, <sup>1</sup> J <sub>C-P</sub> = 20.5 Hz, CH <sub>3</sub> ), 20.2 (d, <sup>2</sup> J <sub>C-P</sub> = 14.5 Hz, CH <sub>3</sub> ), 19.7 (d, <sup>1</sup> J <sub>C-P</sub> = 10.5 Hz, CH <sub>3</sub> )
2c <sub>1</sub>	7.78 (m, 2H, C <sub>6</sub> H <sub>5</sub> ), 7.35 (m, 3H, C <sub>6</sub> H <sub>5</sub> ), 5.67 (dq, 1H, J <sub>H-P</sub> = 230 Hz, <sup>3</sup> J <sub>H-F</sub> = 4 Hz, PH), 1.33 (s, 3H, SC H <sub>3</sub> )	-71.1 (dq, <sup>3</sup> J <sub>F-P</sub> = 34 Hz, <sup>4</sup> J <sub>F-P</sub> = 39 Hz)	-53.97 (dd, <sup>4</sup> J <sub>F-P</sub> = 39 Hz, <sup>3</sup> J <sub>F-P</sub> = 4 Hz, C F <sub>3</sub> ), -44.64 (d, <sup>3</sup> J <sub>F-P</sub> = 34 Hz, C F)	219.7 (d, J <sub>C-F</sub> = 349 Hz, C-F), 209.1-205.4 (CO), 135.3-128.7 (C <sub>6</sub> H <sub>5</sub> ), 126.3 (q, J <sub>C-F</sub> = 274 Hz, CF <sub>3</sub> ), 90.5 (d, J <sub>C-F</sub> = 18.7 Hz, CP) <sup>d</sup> , 52.9 (dq, <sup>3</sup> J <sub>C-F</sub> = 11.7 Hz, <sup>2</sup> J <sub>C-F</sub> = 35.5 Hz, C-CF <sub>3</sub> ) <sup>d</sup> , 33.4 (s, SCH <sub>3</sub> )
2c <sub>2</sub>	7.7 (m, 2H, C <sub>6</sub> H <sub>5</sub> ), 7.35 (m, 3H, C <sub>6</sub> H <sub>5</sub> ), 5.08 (ddq, 1H, J <sub>H-P</sub> = 228 Hz, <sup>3</sup> J <sub>H-F</sub> = 2 Hz, <sup>4</sup> J <sub>H-F</sub> = 9.5 Hz, P-H), 1.52 (s, 3H, SC H <sub>3</sub> )	-65.7 (dq, <sup>3</sup> J <sub>F-P</sub> = 42 Hz, <sup>4</sup> J <sub>F-P</sub> = 8 Hz)	-55.02 (dd, <sup>4</sup> J <sub>F-P</sub> = 8 Hz, <sup>3</sup> J <sub>F-P</sub> = 2 Hz, C F <sub>3</sub> ), -45.57 (dd, <sup>4</sup> J <sub>F-P</sub> = 42 Hz, <sup>3</sup> J <sub>F-P</sub> = 9.5 Hz, C F)	224.9 (d, J <sub>C-F</sub> = 348 Hz, CF), 209.1-205.4 (CO), 135.3-128.7 (C <sub>6</sub> H <sub>5</sub> ), 126.4 (q, J <sub>C-F</sub> = 273 Hz, CF <sub>3</sub> ), 91.95 (d, J <sub>C-F</sub> = 15.7 Hz, CP) <sup>d</sup> , 51.0 (dq, <sup>2</sup> J <sub>C-F</sub> = 35 Hz, <sup>3</sup> J <sub>C-F</sub> = 11.5 Hz, C-CF <sub>3</sub> ) <sup>d</sup> , 33.81 (s, SCH <sub>3</sub> )
3	3.09, 2.91 (ABX <sub>3</sub> , 2H, J <sub>A-B</sub> = 12 Hz, J <sub>A-X</sub> = 7.5 Hz, C H <sub>2</sub> ), 1.94 (s, 3H, SC H <sub>3</sub> ), 1.44 (t, 3H, J <sub>H-H</sub> = 7.5 Hz, CH <sub>2</sub> CH <sub>3</sub> )		-58.63 (s, C F <sub>3</sub> ), -53.91 (s, C F)	220.65 (dq, J <sub>C-P</sub> = 351.5 Hz, <sup>4</sup> J <sub>C-F</sub> = 1.8 Hz, CF), 208.4 (d, <sup>3</sup> J <sub>C-F</sub> = 8 Hz, CO), 208.2 (s, br, Fe(2)(CO)), 207.55 (d, <sup>2</sup> J <sub>C-F</sub> = 10 Hz, CO), 205.8 (d, <sup>1</sup> J <sub>C-F</sub> = 5 Hz, CO), 126.1 (q, J <sub>C-F</sub> = 274 Hz, CF <sub>3</sub> ), 94.8 (d, J <sub>C-F</sub> = 15 Hz, CSEt), 53.4 (dq, <sup>2</sup> J <sub>C-F</sub> = 35 Hz, <sup>3</sup> J <sub>C-F</sub> = 8 Hz, C-CF <sub>3</sub> ), 34.0 (s, SCH <sub>3</sub> ), 31.5 (s, CH <sub>2</sub> -CH <sub>3</sub> ), 14.9 (s, CH <sub>2</sub> -CH <sub>3</sub> )

to low field from that of the amino-compound **b** (Scheme 1;  $\delta$  120 ppm). This indicates that the carbon bearing the fluorine atom bridges the two iron atoms, a conclusion confirmed by X-ray analysis of the diethyl ether solvate of **2a**. The  $^{19}\text{F}$  NMR spectra of the complexes **2** and **3** contain two fluorine signals in a 3:1 area ratio, consistent with the presence of a  $\text{CF}_3$  group at highest field and a single fluorine atom, which confirms that one of the C–F bonds in **1** has been cleaved.

As shown by NMR spectroscopy, the phenylphosphino complex **2c** exists in solution as interconverting diastereoisomers (Scheme 3). The  $2c_1:2c_2$  ratio depends on the solvent: less polar solvents favor the  $2c_1$  isomer (e.g.  $2c_1:2c_2 = 1.5:1$  in  $\text{CDCl}_3$  but 1.25:1 in a mixture of  $\text{CDCl}_3$  and  $\text{CH}_3\text{CN}$ ). The two isomers can be distinguished by the magnitudes of the P–F and H–F coupling constants observed in their  $^{31}\text{P}$ ,  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectra (Table 1).

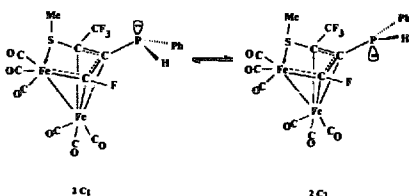
Variable-temperature  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of complexes **2a** and **3** were recorded. It appears that the line shapes in the carbonyl region of these spectra are temperature-dependent and clearly indicate averaging of the low-temperature resonances with increasing temperature, implying that fluxional processes are operative in solution. The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **3** in the CO region between 200 and 373 K is presented in Fig. 1 as an example. At 200 K the spectra of **2a** and **3** are similar and both show three doublets and three broad singlets of equal intensity. On the basis of X-ray structural data for **2a** (see below; Fig. 2) and by assuming that the Fe–C(7)F distances in solution are comparable with those in the solid state [e.g. Fe(1)–C(7)F = 1.918(3) Å, Fe(2)–C(7)F = 2.073(3) Å], we tentatively assign the resonances which have the largest coupling constants to the three CO groups which are coordinated to the Fe(1) atom. The three singlets are then attributed to the carbonyls which are attached to Fe(2). As the temperature increases, a broadening of the three signals assigned to the carbonyls bound to Fe(2) is observed and these collapse at 272 K and 245 K for **2a** and **3** respectively. At higher temperatures a broadening of the three doublets [ $\text{Fe}(1)(\text{CO})_3$ ] occurs before they collapse at about 350 K to a broad resonance. Above 350 K, sharpening of the resonances occurs, leading to the

high-temperature spectra at 373 K, which consists of a singlet at about 208.5 and a broad singlet at about 207.3 in an integral ratio of 1:1. All the line-shape changes throughout the temperature range were found to be completely reversible. Experiments using a wide range of concentrations of the complexes were conducted to confirm that the fluxional processes are intramolecular. The above observations imply that all the carbonyl ligands take part in local CO exchange processes on the two iron atoms.

The activation barriers of the observed dynamic processes are estimated from the chemical shift difference  $\Delta\nu$  and the coalescence temperature [7] (see Table 2). The values of the energy barriers associated with site exchange are low. They are of the order expected for localized scrambling of the carbonyls on metal atoms [8]. The observed exchange behavior can be understood in terms of two-stage ligand motion processes. That of lower-energy consists of movements at Fe(2) involving local CO exchange. The higher-energy process concerns CO movements at Fe(1).

## 2.2. Solid state structure of $\{[\text{Fe}(\text{CO})_3]_2[\mu\text{-C}(\text{SMe})(\text{CF}_3)\text{C}(\text{P Ph}_2)\text{CF}]\}_2 \mathbf{2a}$

X-ray analysis of **2a** (Fig. 2, Table 3) reveals that its structure consists of a dinuclear  $\text{Fe}_2(\text{CO})_6$  unit stabilized by an iron–iron bond [Fe(1)–Fe(2) 2.633(1) Å] and by a bridging organic group derived formally from the vinylic ligand in **1** by loss of a fluorine atom from C(7) and addition of a diphenylphosphino group to C(8). The Fe(1)–C(8) linkage in **1** is replaced by a bond between Fe(1) and C(7), the Fe(1)–C(7) distance [1.918(3) Å] being ca 0.06 Å shorter than values typical of Fe–C (carbene) bonds [9]. Fe(1) and the three carbon atoms C(7), C(8) and C(9) are all attached to Fe(2) and are nearly coplanar [Fe(1)–C(7)–C(8)–C(9) 10.0(4)°]. There is extensive electron delocalization along the Fe(1)–C(7)–C(8)–C(9) chain, as shown by the sequence of distances 1.918(3), 1.408(4) and 1.456(4) Å. Fe(2) is slightly closer to C(9) than it is to C(7) and C(8), these Fe(2)–C bond lengths [2.073(3), 2.079(3) and 2.019(3) Å] being comparable to the accepted mean values [2.068 Å and 2.082 Å] for terminal and central  $\text{C}(\eta^3\text{-allyl})\text{-Fe}$  distances [10]. The bridging ligand donates a total of six electrons and each iron atom can therefore be assigned the 18-electron count implied by the structural diagram in Scheme 2: Fe(1) receives two electrons from S(1) and one from C(7) and Fe(2) one each from C(7), C(8) and C(9). This view implies that Fe(2) is  $\pi$ -bonded to a butadiene-like  $\text{Fe}(1)\text{C}_3$  unit. Such a system would be expected to deform easily and relative rotation of the ferrabutadiene and  $\text{Fe}(2)(\text{CO})_3$  groups may then explain the lower energy ligand motion process observed in the NMR spectra (see above). The Fe(1)–C(CO) bonds (mean length 1.809 Å) are, if



Scheme 3.

anything, slightly weaker than the Fe(2)–C(CO) bonds (mean 1.795 Å) and therefore do not help to explain why local CO exchange occurs more readily at Fe(2).

The intramolecular Fe(2)···S(1) separation in **2a** [2.992(1) Å], though short, is clearly non-bonding [cf. Fe(1)–S(1) 2.266(1) Å].

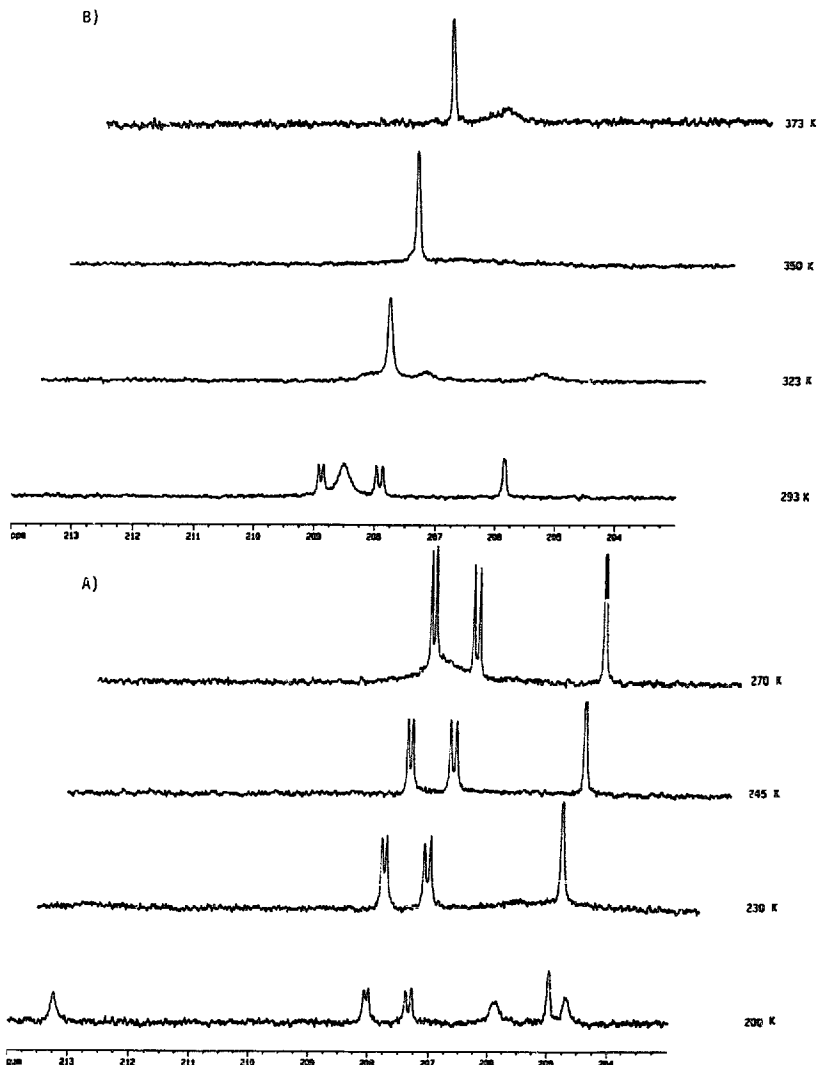


Fig. 1. Variable-temperature  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra in the carbonyl region of **3**: (A) in  $\text{CD}_2\text{Cl}_2$ ; (B) in  $\text{toluene-}d_6$ .

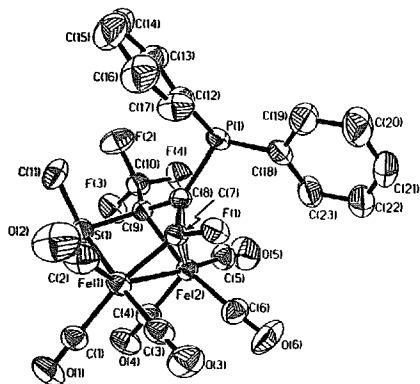


Fig. 2. View of a molecule of complex **2a**. Hydrogen atoms are omitted and 50% probability ellipsoids are displayed.

### 2.3. Possible mechanisms of formation of products

Attempts to investigate the mechanism of these reactions were made by NMR spectroscopy at low temperature. In contrast to the reaction of **1** with  $\text{Me}_2\text{NH}$ , where the intermediate fluoro-amino-vinyl compound  $[[\text{Fe}(\text{CO})_3]_2\{\mu\text{-C}(\text{SMe})(\text{CF}_2)\text{CCF}(\text{NMe}_2)\}]$  could be characterised at  $-50^\circ\text{C}$  [5],<sup>1</sup> when **1** reacted with phosphine no intermediates were observed; presumably they are short-lived species, not present in large enough quantities to be detected by NMR techniques. However, by analogy with the mechanism proposed for the reaction of **1** with dimethylamine [5], we suggest here a similar zwitterionic fluoro-Fe(2) intermediate, **A**, in the formation of **2**. This mechanism, which is outlined in Scheme 4, is based on the availability of a vacant coordination site on Fe(2) in **1**. This center could act as an internal Lewis acid in the  $\alpha$ -elimination of fluoride to generate **A**. Internal rearrangement affords the zwitterionic acetylenic intermediate **B** which is then activated towards attack at the  $\beta$ -carbon atom by the phosphine  $\text{PXYH}$  [11], giving successively **C** and **D**. Subsequent elimination of HF affords complex **2**.

The possibility that the  $\text{CF}_2$  group in **1** undergoes direct nucleophilic attack by the phosphine has been considered and rejected because **1** does not react with

Table 2  
Dynamic  $^{13}\text{C}$  NMR data

Compounds	Resonance	$T_c$ (K) <sup>a</sup>	$\Delta\nu^b$ (Hz)	$\Delta G^\ddagger$ <sup>c</sup> (kJ mol <sup>-1</sup> )
<b>2a</b>	Fe(2)-(CO) <sub>3</sub>	272	422.5	50.6
	Fe(1)-(CO) <sub>3</sub>	355	296	68.1
<b>3</b>	Fe(2)-(CO) <sub>3</sub>	245	573	45.1
	Fe(1)-(CO) <sub>3</sub>	350	204	68.1

<sup>a</sup> Coalescence temperature.

<sup>b</sup> Frequency difference between resonances of exchanging groups in low temperature limit.

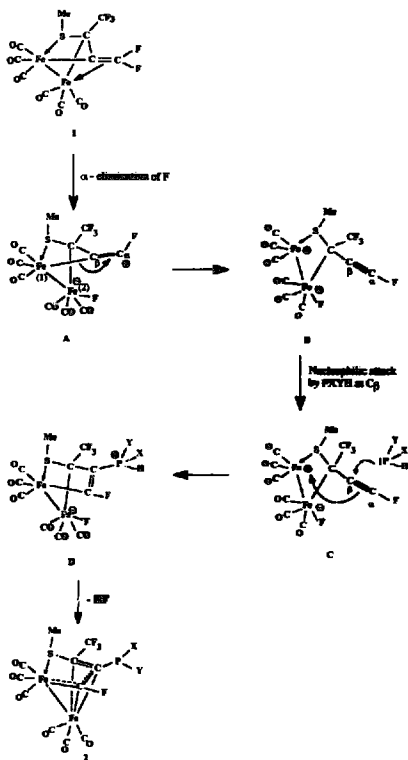
<sup>c</sup> Highest error limit:  $\pm 0.8$  kJ mol<sup>-1</sup>.

strong nucleophiles such as  $\text{NaNH}_2$ , a surprising result given the presence of sodium ion and the known stability of NaF. The involvement of the iron atoms in the activation of the  $\text{C}(\text{CF}_3)\text{C}=\text{CF}_2$  fluorovinyl ligand of **1** is also supported by the failure of  $\text{PPh}_2\text{H}$  to cleave the

Table 3  
Selected bond lengths (Å) and angles (deg) in **2a**

Bond lengths			
Fe(1)-Fe(2)	2.633(1)	Fe(2)-C(4)	1.788(4)
Fe(1)-C(1)	1.835(4)	Fe(2)-C(5)	1.797(4)
Fe(1)-C(2)	1.792(5)	Fe(2)-C(6)	1.800(4)
Fe(1)-C(3)	1.801(4)	Fe(2)-C(7)	2.073(3)
Fe(1)-C(7)	1.918(3)	Fe(2)-C(8)	2.079(3)
Fe(1)-S(1)	2.266(1)	Fe(2)-C(9)	2.019(3)
C(7)-C(8)	1.408(4)	C(8)-C(9)	1.456(4)
C(7)-Fe(1)	1.367(4)	C(8)-P(1)	1.859(3)
C(9)-C(10)	1.504(5)	C(9)-S(1)	1.786(3)
C(10)-Fe(2)	1.335(4)	P(1)-C(12)	1.827(4)
Bond angles			
C(2)-Fe(1)-C(3)	93.0(2)	C(4)-Fe(2)-C(5)	96.0(2)
C(2)-Fe(1)-C(1)	99.3(2)	C(4)-Fe(2)-C(6)	100.2(2)
C(3)-Fe(1)-C(1)	91.9(2)	C(5)-Fe(2)-C(6)	90.4(2)
C(2)-Fe(1)-C(7)	100.5(2)	C(4)-Fe(2)-C(9)	99.8(2)
C(3)-Fe(1)-C(7)	90.0(2)	C(5)-Fe(2)-C(9)	97.7(2)
C(1)-Fe(1)-C(7)	160.0(2)	C(6)-Fe(2)-C(9)	157.4(2)
S(1)-Fe(1)-Fe(2)	74.9(1)	C(7)-Fe(2)-C(9)	69.0(1)
C(4)-Fe(2)-C(7)	128.1(2)	C(4)-Fe(2)-C(8)	138.9(2)
C(5)-Fe(2)-C(7)	134.8(2)	C(5)-Fe(2)-C(8)	101.9(2)
C(6)-Fe(2)-C(7)	90.4(2)	C(6)-Fe(2)-C(8)	116.1(2)
C(9)-Fe(2)-C(8)	41.6(1)	C(12)-P(1)-C(18)	105.1(2)
C(7)-Fe(2)-C(8)	39.6(1)	C(12)-P(1)-C(8)	96.0(2)
C(4)-Fe(2)-Fe(1)	82.1(1)	C(18)-P(1)-C(8)	104.9(2)
C(5)-Fe(2)-Fe(1)	173.9(1)	P(1)-C(7)-C(8)	115.1(3)
C(6)-Fe(2)-Fe(1)	95.7(1)	F(1)-C(7)-Fe(1)	121.2(2)
C(7)-Fe(2)-Fe(1)	46.2(1)	C(8)-C(7)-Fe(1)	123.5(2)
C(8)-Fe(2)-Fe(1)	76.2(1)	F(1)-C(7)-Fe(2)	124.4(2)
C(9)-Fe(2)-Fe(1)	77.0(1)	C(8)-C(7)-Fe(2)	70.4(2)
C(9)-S(1)-C(11)	104.3(2)	Fe(1)-C(7)-Fe(2)	82.5(1)
C(9)-S(1)-Fe(1)	92.0(1)	C(7)-C(8)-C(9)	108.0(3)
C(11)-S(1)-Fe(1)	110.2(2)	C(7)-C(8)-Fe(2)	69.9(2)
S(1)-C(9)-Fe(2)	103.5(2)	C(8)-C(8)-Fe(2)	67.0(2)
C(7)-C(8)-P(1)	129.9(2)	C(8)-C(9)-C(10)	124.0(3)
C(9)-C(8)-P(1)	121.5(2)	C(8)-C(9)-S(1)	114.8(2)
P(1)-C(8)-Fe(2)	135.6(2)	C(8)-C(9)-Fe(2)	71.4(2)
		C(10)-C(9)-Fe(2)	123.4(2)

<sup>1</sup> The fluoro-amino vinyl intermediate  $[[\text{Fe}(\text{CO})_3]_2\{\mu\text{-C}(\text{SMe})(\text{CF}_2)\text{CCF}(\text{NMe}_2)\}]$  has been characterized by NMR at  $-50^\circ\text{C}$ :  $^{19}\text{F}$  (THF- $d_6$ )  $\delta$  -19.05 (s, CF), -63.34 (s, CF<sub>2</sub>);  $^{13}\text{C}$  (H) (THF- $d_6$ )  $\delta$  215.4 (s, 3 CO), 212.0, 209.9, 207.7 (s, CO), 182.1 (d,  $J_{\text{C-F}}$  = 287.5 Hz, CF), 125.9 (q,  $J_{\text{C-F}}$  = 275.7 Hz, CF<sub>2</sub>), 73.1 (d,  $J_{\text{C-F}}$  = 19 Hz, C=CF), 48.6 (q, C-CF<sub>2</sub>), 42.5, 39.7 (s, N-CH<sub>3</sub>), 33.3 (s, SCH<sub>3</sub>).



Scheme 4.

C–F bonds in dichlorodifluoroethylene which also contains the C=CF<sub>2</sub> group.

An alternative mechanism involving dissociation of fluoride from C<sub>α</sub> which could be stabilized by carbene formation has been examined. Indeed, carbene intermediates do show electrophilic reactivity at the carbene center and react with nucleophilic reagents as shown previously by Shriver and coworkers [12] and Roper and coworkers [13]. Transient carbenes might be formed in the reaction of perfluoroalkyl carbonyl compounds with Lewis acidic halides. In order to verify the possibility of carbene formation as intermediate during the course of the reaction of 1 with phosphines, we have added Me<sub>3</sub>SiCl to 1. No reaction was observed, rendering any pathway involving a carbene intermediate less likely.

### 3. Experimental section

#### 3.1. General procedures

All experiments were carried out under an inert argon atmosphere using Schlenk techniques. Solvents were freshly distilled from sodium–benzophenone prior to use. The bimetallic complex  $[[\text{Fe}(\text{CO})_2]_2(\mu\text{-C}(\text{SMe})(\text{CF}_3)\text{CCF}_2)]$  1 was prepared as described previously [6]. All other reagents were commercial grade and were used as-obtained.

Infrared spectra were obtained with a Perkin–Elmer 1430 spectrophotometer. The mass spectra were measured on a GC/MS Hewlett Packard 5595 C. NMR spectra (<sup>1</sup>H, <sup>31</sup>P, <sup>19</sup>F, <sup>13</sup>C) in CDCl<sub>3</sub> or CD<sub>2</sub>Cl<sub>2</sub> solution were recorded on a Jeol FX 100, a Bruker AC 300 or a Bruker DRX 400 and were referenced to Me<sub>4</sub>Si, H<sub>3</sub>(PO<sub>4</sub>), CCl<sub>4</sub> and Me<sub>4</sub>Si respectively. Chemical analyses were performed by the ‘Centre de Microanalyses du CNRS de Lyon’.

#### 3.2. Synthesis of $[[\text{Fe}(\text{CO})_2]_2(\mu\text{-C}(\text{SMe})(\text{CF}_3)\text{C}(\text{PPh}_2)\text{CF})]$ 2a and $[[\text{Fe}(\text{CO})_2]_2(\mu\text{-C}(\text{SMe})(\text{CF}_3)\text{C}(\text{P}-i\text{-Pr}_2)\text{CF})]$ 2b

$[[\text{Fe}(\text{CO})_2]_2(\mu\text{-C}(\text{SMe})(\text{CF}_3)\text{CCF}_2)]$  1 (235 mg, 0.5 mmol) and PX<sub>2</sub>Y [X = Y = Ph (93 mg), *i*-Pr (59 mg), 0.5 mmol] were stirred at room temperature in dichloromethane (10 ml) for 3 h. The solvent was then removed and the residue chromatographed on deoxygenated silica gel. Elution with hexane–dichloromethane (5.6:1) afforded a yellow–orange band which gave complexes 2a or 2b as orange–red solids (97% yield).

2a. Anal. Found: C, 43.3; Fe, 17.8; P, 4.9. C<sub>23</sub>H<sub>13</sub>F<sub>4</sub>Fe<sub>2</sub>O<sub>6</sub>PS. Calc.: C, 43.4; Fe, 17.5; P, 4.9%. Mass spectrum, *m/z* 636 (M<sup>+</sup>), other peaks, M<sup>+</sup> – *x*(CO) (*x* = 1–6). IR (hexane),  $\nu(\text{CO})$  2080, 2041, 2020, 2002, 1990(sh) cm<sup>-1</sup>.

2b. Anal. Found: C, 36.1; H, 2.9. C<sub>17</sub>H<sub>11</sub>F<sub>4</sub>Fe<sub>2</sub>O<sub>6</sub>PS. Calc.: C, 35.9; H, 3.0%. Mass spectrum, *m/z* 568. IR (hexane),  $\nu(\text{CO})$  2084, 2044, 2021, 2004, 1925(sh) cm<sup>-1</sup>.

#### 3.3. Synthesis of $[[\text{Fe}(\text{CO})_2]_2(\mu\text{-C}(\text{SMe})(\text{CF}_3)\text{C}(\text{PPhPh})\text{CF})]$ 2c

A similar procedure was used to synthesize 2c, except that the reaction was carried out in CDCl<sub>3</sub> at 55 °C. After removal of the solvent the mixture was chromatographed on deoxygenated silica gel, and the two diastereoisomers 2c<sub>1</sub> and 2c<sub>2</sub> were eluted with hexane–CH<sub>2</sub>Cl<sub>2</sub> (5.6:1) (2c: 100% yield).

2c. Anal. Found: C, 36.4; Fe, 20.1; P, 5.5. C<sub>17</sub>H<sub>9</sub>F<sub>4</sub>Fe<sub>2</sub>O<sub>6</sub>PS. Calc.: C, 36.5; Fe, 19.9; P, 5.5. IR

(hexane),  $\nu(\text{CO})$  2084, 2045, 2023, 2008, 1998(sh)  $\text{cm}^{-1}$ .

### 3.4. Synthesis of $[(\text{Fe}(\text{CO})_3)_2\{\mu\text{-C}(\text{SMe})\text{-}(\text{CF}_3)_2\text{C}(\text{SEt})\text{CF}\}]_3$

Diiron complex **1** (141 mg, 0.3 mmol) and 5 equiv. of ethanethiol (93 mg) were stirred in  $\text{CH}_2\text{Cl}_2$  (10 ml) at 55°C for 14 h. Compound **3** was isolated (95% yield) by column chromatography on deoxygenated silica gel using a 5.6:1 hexane–dichloromethane solvent mixture.

**3**. Anal. Found: C, 31.1; Fe, 21.9; S, 12.3.  $\text{C}_{13}\text{H}_8\text{F}_4\text{Fe}_2\text{O}_6\text{S}_2$ . Calc.: C, 30.5; Fe, 21.8; S, 12.5. Mass spectrum,  $m/z$  512 ( $\text{M}^+$ ), other peaks,  $\text{M}^+ - x(\text{CO})$  ( $x = 1-6$ ). IR (hexane),  $\nu(\text{CO})$  2084, 2043, 2020, 2004, 1998(sh)  $\text{cm}^{-1}$ .

### 3.5. X-ray analysis of $[(\text{Fe}(\text{CO})_3)_2\{\mu\text{-C}(\text{SMe})\text{-}(\text{CF}_3)_2\text{C}(\text{PPH}_2)\text{CF}\}]_2$

Measurements were made at room temperature on an Enraf–Nonius diffractometer with graphite-monochromatized Mo K $\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$ , using an orange-red crystal of dimensions  $0.3 \times 0.16 \times 0.05 \text{ mm}$ .

#### 3.5.1. Crystal data

$\text{C}_{23}\text{H}_{13}\text{F}_4\text{Fe}_2\text{O}_6\text{PS} \cdot 0.5\text{Et}_2\text{O}$ ,  $M = 673.15$ , triclinic, space group  $P1$ ,  $a = 9.019(2)$ ,  $b = 9.550(2)$ ,  $c = 18.583(3) \text{ \AA}$ ,  $\alpha = 101.06(2)$ ,  $\beta = 92.53(2)$ ,  $\gamma = 116.48(2)^\circ$ ,  $V = 1390.6(5) \text{ \AA}^3$ ,  $Z = 2$ ,  $F(000) = 678$ ,  $D_{\text{calc}} = 1.608 \text{ g cm}^{-3}$ ,  $\mu(\text{Mo K}\alpha) = 1.24 \text{ mm}^{-1}$ .

#### 3.5.2. Structure analysis

The cell constants were determined by a least squares treatment of the setting angles of 20 reflections with  $20.0 < \theta < 20.5^\circ$ . The intensities were measured from continuous  $\omega/2\theta$  scans. Scan speeds were adjusted to give  $\sigma(I)/I < 0.03$ , subject to a maximum count time of 60 s. The mean of the intensities of three standard reflections, remeasured every 2 h, varied by  $< 1\%$  during the experiment. The structure is based on the intensities of 6379 unique reflections with  $h - 11$  to 11,  $k - 12$  to 12,  $l 0$  to 24 and  $\theta(\text{Mo K}\alpha) < 27.5^\circ$ ; of these 3984 have  $I > 2\sigma(I)$  and 426 were measured twice ( $R_{\text{int}} = 0.055$ ). The intensities were corrected for Lp effects but allowance for absorption, extinction or crystal decay was judged unnecessary.

The structure was solved by direct methods [14] and was refined on  $F^2$  by full-matrix least squares using SHELXL-93 with  $w = 1/[\sigma^2(F_{\text{obs}}^2) + (0.0693P)^2]$  where  $P = (F_{\text{obs}}^2 + 2F_{\text{calc}}^2)/3$  [15].

Adjustment of 351 parameters (Table 4) converged at  $R_1[I > 2\sigma(I)] = 0.042$ ,  $wR_2 = 0.128$ . Anisotropic displacement parameters were refined for all non-H atoms except the atoms of a disordered diethyl ether solvate molecule which lies with its central oxygen atom on an

Table 4

Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **2a**

	x	y	z	$U_{\text{eq}}^a$
Fe(1)	766(1)	1995(1)	8557(1)	37(1)
Fe(2)	-2352(1)	296(1)	8756(1)	34(1)
S(1)	-109(1)	3835(1)	9003(1)	41(1)
P(1)	-4275(1)	1101(1)	7224(1)	40(1)
F(1)	-1402(3)	-1(3)	7194(1)	45(1)
F(2)	-3381(3)	4230(3)	8728(2)	72(1)
F(3)	-3092(3)	3505(3)	9723(1)	63(1)
F(4)	-5033(3)	1879(3)	8835(1)	60(1)
O(1)	3008(4)	2928(4)	9969(2)	65(1)
O(2)	3165(5)	3968(5)	7707(2)	101(1)
O(3)	1351(4)	-768(4)	8008(2)	72(1)
O(4)	-855(4)	1166(4)	10309(1)	62(1)
O(5)	-5779(4)	-1323(4)	9075(2)	85(1)
O(6)	-2491(5)	-2867(4)	8240(2)	82(1)
C(1)	2145(5)	2584(5)	9435(2)	45(1)
C(2)	2252(5)	3203(6)	8039(3)	60(1)
C(3)	1123(5)	286(5)	8227(2)	49(1)
C(4)	-1388(4)	834(4)	9697(2)	43(1)
C(5)	-4474(5)	-662(5)	8940(2)	52(1)
C(6)	-2415(5)	-1638(5)	8447(2)	51(1)
C(7)	-1239(4)	1024(4)	7851(2)	35(1)
C(8)	-2563(4)	1417(4)	7931(2)	34(1)
C(9)	-2253(4)	2414(4)	8675(2)	33(1)
C(10)	-3440(5)	2999(4)	8988(2)	44(1)
C(11)	371(6)	5272(5)	8429(3)	63(1)
C(12)	-2953(5)	2632(5)	6756(2)	47(1)
C(13)	-3196(6)	3993(5)	6818(2)	59(1)
C(14)	-2164(8)	5264(6)	6529(3)	82(2)
C(15)	-912(8)	5179(7)	6169(3)	89(2)
C(16)	-655(7)	3850(7)	6092(3)	82(2)
C(17)	-1661(6)	2583(6)	6380(2)	60(1)
C(18)	-4804(4)	-832(4)	6586(2)	44(1)
C(19)	-4860(7)	-1020(6)	5836(2)	68(1)
C(20)	-5461(8)	-2530(6)	5362(3)	87(2)
C(21)	-6017(7)	-3862(6)	5634(3)	75(1)
C(22)	-5979(7)	-3712(6)	6376(3)	79(2)
C(23)	-5403(6)	-2220(5)	6847(2)	67(1)
O(1E)	0	0	5000	201(4)
C(1E) <sup>b</sup>	-300(33)	710(30)	4427(14)	179(9)
C(1E) <sup>b</sup>	-1465(34)	-772(33)	4461(16)	186(9)
C(2E) <sup>b</sup>	-1426(22)	242(22)	3999(9)	109(4)
C(3E) <sup>b</sup>	1938(26)	-862(27)	3907(12)	142(6)

<sup>a</sup>  $U_{\text{eq}}$  is defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

<sup>b</sup> These atoms have site occupancy factors of 0.5.

inversion center. Solvate H-atoms were not included but other H-atoms rode on their parent C atoms with  $U = 0.080 \text{ \AA}^2$ . Neutral atom scattering factors and anomalous dispersion corrections were taken from Ref. [16].

## 4. Supporting information available

Tables of atomic coordinates and anisotropic displacement parameters, a complete geometry listing, and structure factor tables (21 pp.). Ordering information is available on any current masthead page.



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