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Carbon–fluorine activation by iron(I): organoiron ring transformation promoted by addition of tertiary phosphanes to a perfluorosulfanylvinyldiiron(I) complex

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The perfluorosulfanylvinyldiiron(I) complex [{Fe(CO)$_3$}$_2${μ-C(SMe)(CF$_3$)C(CF$_2$)}] **1** reacted with tertiary phosphanes [L = PPh$_3$ or P(OMe)$_3$] in dichloromethane or chloroform at 60 °C to give high yields of cycloferrathiapentadiene iron clusters. When the nucleophile was PPh$_3$, the salt **2** was obtained: formally, a fluoride-ion transfer between two molecules of **1** generates the anion [{Fe(CO)$_3$}$_2${μ-C(CF$_3$)C(CF$_3$)SMe}]$^-$ and addition of PPh$_3$ at two separate sites produces the counter cation [(Ph$_3$P)(OC)$_2$Fe{μ-CFC(PPh$_3$)C(CF$_3$)SMe}-Fe(CO)$_3$]$^+$. In contrast, with P(OMe)$_3$ the neutral derivative [{Fe(CO)$_3$}$_2${μ-CFC[PO(OMe)$_2$]C(CF$_3$)SMe}] **4** was formed. Thermally induced C−F bond activation is a feature of these reactions. All the reaction products have been characterized by elemental analysis and IR, ^{1}H, ^{19}F, ^{31}P and ^{13}C NMR spectroscopy. The solid-state structure of [(Ph$_3$P)(OC)$_2$Fe{μ-CFC(PPh$_3$)C(CF$_3$)SMe}Fe(CO)$_3$][{Fe(CO)$_3$}$_2${μ-C(CF$_3$)C(CF$_3$)SMe}] **2** has been established by single-crystal X-ray analysis. The Fe−Fe bond in the cation [2.716(2) Å] is appreciably longer than the corresponding bond in the anion [2.570(2) Å]. Possible routes to the formation of **2** and **4** have been investigated. The conversion of **1** into **4** has been shown to involve an intermediate **3** which has been fully characterized by ^{19}F, ^{31}P and ^{13}C NMR spectroscopy.

The differences in bonding and structure between fluorinated organic ligands and their more thoroughly studied hydrocarbon analogues are revealed through different and often novel chemical behaviour. The C−F bonds have higher energies than C−H bonds and are in consequence harder to activate. Despite this, several examples of carbon–fluorine bond activation and functionalization in or by organometallic complexes have been reported in the last few years.[1] Most involve drastic reaction conditions, however, and descriptions of organometallic complexes capable of C−F bond activation under milder conditions have appeared only comparatively recently.[2] For example, we have shown that the C−F bonds in perfluorosulfanylvinyliron(I) complexes can be activated under mild conditions by primary and secondary amines, by thiols and by secondary phosphines PH(X)Y to give molecular complexes containing cycloferrathiapentadiene rings.[3,4] We have extended these investigations, using tertiary phosphanes as the nucleophilic reagent, and now report reactions between the perfluorosulfanylvinyldiiron cluster [{Fe(CO)$_3$}$_2${μ-C(SMe)(CF$_3$)C-(CF$_2$)}][5] **1** and triphenylphosphine or trimethyl phosphite. These reactions provide new examples of facile C−F bond cleavage. Their products, obtained in high yield, are stable diiron(I) metallacycles.

Results and Discussion

Reaction of [{Fe(CO)$_3$}$_2${μ–C(SMe)(CF$_3$)C(CF$_2$)}] with PPh$_3$ and characterization of compound 2

The thermal reaction (1) of compound **1** with triphenylphosphine, in CHCl$_3$ at 60 °C for 12 h, yielded a red solution from which a red solid **2** was obtained on evaporation of the solvent. The solid was characterized by elemental analysis and by ^{1}H, ^{19}F, ^{31}P and ^{13}C-{^{1}H} NMR spectroscopy (Table 1) which showed that **2** was obtained as a mixture of isomers **2a** and **2b** (4 : 1). Pure samples of the major isomer **2a** were obtained by recrystallization. The X-ray analysis of a single crystal of the major isomer **2a** revealed that the complex is a salt of the cation [{Fe$_2$(CO)$_5$(PPh$_3$)}{μ-CFC(PPh$_3$)C(CF$_3$)SMe}]$^+$ with the counter anion [{Fe(CO)$_3$}$_2${μ-C(CF$_3$)C(CF$_3$)SMe]$^-$. The structures of these ions are shown in Fig. 1 and selected distances and angles are given in Table 2.

$$\underset{\mathbf{1}}{2[\{Fe(CO)_3\}_2\{\mu\text{-}C(SMe)(CF_3)C(CF_2\}]} + 2PPh_3 \longrightarrow$$
$$\underset{\mathbf{2}}{[(Ph_3P)(OC)_2Fe\{\mu\text{-}CFC(PPh_3)C(CF_3)SMe\}Fe(CO)_3]\text{-}[\{Fe(CO)_3\}_2\{\mu\text{-}C(CF_3)C(CF_3)SMe\}]} \quad (1)$$

The cation contains a puckered FeSC$_3$ cycloferrathiapentadiene ring with CF and CPPh$_3$ groups α and β to the Fe(2A) iron atom. The Fe(2A)−C(4A)−C(3A)−C(2A) portion of this ring is nearly planar [torsion angle −9.2(8)°] and acts as a ferrabutadiene unit to which the Fe(CO)$_3$ group containing the second iron atom, Fe(1A), is π bonded. The Fe(1A) atom is not connected to the sulfur atom of the cycloferrathiapentadiene ring [Fe(1A)···S(1A) 2.959(2) Å]. The Fe(1A)−Fe(2A) bond length [2.716(2) Å] is noticeably greater than comparable values in unsubstituted diiron molecular complexes which have a cycloferrapentadiene [Fe−Fe ≈ 2.514(1) Å][6] or cycloferrathiapentadiene ring [Fe−Fe ≈ 2.606(2) Å].[3,4,7] Electron release by the PPh$_3$ ligand onto Fe(2A) or the steric crowding induced by the presence of two bulky tertiary phosphine groups (see Fig. 2) may explain this lengthening. The three adjacent C(4A), C(3A), C(2A) atoms are nearly equidistant from Fe(1A) (Fe–C 2.03–2.08 Å). The shortness of the Fe(1A)−C(4A) bond [2.080(7) Å] is noteworthy, since comparable distances in closely related complexes can be much longer, *e.g.* 2.379(4) Å in [{Fe(CO)$_3$}$_2${μ-C(NMe$_2$)CFC(CF$_3$)SMe}].[3] The Fe(2A)−C(4A) bond is also shorter than corresponding bonds in related complexes [1.873(7) Å compared with an average of 1.980(6)[6] and 1.964(8) Å[3,4,7] in diiron compounds with cycloferrapentadiene and cycloferrathiapentadiene rings]. The presence of an electronegative substituent on C(4), and of an electron-releasing phosphine ligand on Fe(2A) *trans* to C(4), are both favourable

Table 1 The NMR data (δ)[a] for compounds **2**–**4**

Complex		
2a	^{1}H	7.96–7.48 (m, 30 H, Ph), 2.04 (s, 3 H, SMe, anion), 1.66 (s, 3 H, SMe, cation)
	^{31}P	51.6 (d, $^3J_{PF}$ = 14.0, PPh$_3$), 24.4 (s, P$^+$Ph$_3$)
	^{19}F	−59.9 (q, J_{FF} = 7.0, CF$_3$, anion), −52.6 (s, CF$_3$, cation), −49.2 (q, J_{FF} = 7.0, CF$_3$, anion), −31.3 (d, $^3J_{PF}$ = 14.0, CF)
	^{13}C-{^{1}H}	224.6 (dd, $^1J_{CF}$ = 341.0, $^2J_{PC}$ = 34.0, CF), 218.2, 214.6 (s, CO, anion), 211.7 [s, Fe(PPh$_3$)(*C*O)$_2$], 210.5 [d, $^2J_{PC}$ = 29.0, Fe(PPh$_3$)(*C*O)$_2$], 206.0 [br, Fe (CO)$_3$], 130–120 (m, CF$_3$ and Ph), 101.2 (q, $^2J_{CF}$ = 41.0, *C*CF$_3$, anion), 83.0 (dm, $^1J_{PC}$ = 60.0, CP$^+$), 51.8 (m, *C*CF$_3$, cation), 51.0 (q, $^2J_{CF}$ = 37.0, ECF$_3$, anion), 33.6 (s, SMe, anion), 31.8 (s, SMe, cation)
2b	^{1}H	8.0–7.4 (m, Ph), 2.30 (s, 3 H, SMe, cation), 2.04 (s, 3 H, SMe, anion)
	^{31}P	62.8 (s, PPh$_3$), 24.4 (s, P$^+$Ph$_3$)
	^{19}F	−59.9 (q, J_{PF} = 7.0, CF$_3$, anion), −50.8 (s, CF$_3$, cation), −49.2 (q, J_{FF} = 7.0, CF$_3$, anion), −25.2 (s, CF)
3	^{31}P	−56.2 [d, $^1J_{PF}$ = 835.0, PF(OMe)$_3$]
	^{19}F	−57.7 (s, CF$_3$), −50.5 (s, CF), −26.3 (d, $^1J_{PF}$ = 835.0 PF)
	^{13}C-{^{1}H}[b]	221.1 [d, $^1J_{CF}$ = 350.0, CF], 209.0 (d, $^3J_{CF}$ = 8.0, CO), 207.9 (d, $^3J_{CF}$ = 10.0, CO), 205.9 (d, $^3J_{CF}$ = 3.0, CO), 125.9 (q, $^1J_{CF}$ = 272.0, CF$_3$), 97.4 (ddd, $^1J_{PC}$ = 225.0, $^2J_{CF}$ = 10.0, 44.0, CP), 55.9 [br, P(OMe)$_3$], 53.0 (m, *C*CF$_3$), 32.8 (s, SCH$_3$)
4	^{1}H	3.95 (d, 3 H, J_{PH} = 2.5, OMe), 3.85 (d, 3 H, J_{PH} = 2.5, OMe), 2.0 (s, 3 H, SMe)
	^{31}P-{^{1}H}	16.08 [s, P(OMe)$_3$]
	^{19}F	−56.0 (s, CF$_3$), −36.1 (s, CF)
	^{13}C-{^{1}H}	226.7 (d, $^1J_{CF}$ = 356.0, CF), 207.8 (d, $^3J_{CF}$ = 7.5, CO), 207.0 (br, 3CO), 206.7 (d, $^3J_{CF}$ = 11.5, CO), 205.3 (d, $^3J_{CF}$ = 3.0, CO), 125.7 (q, $^1J_{CF}$ = 273.5, CF$_3$), 82.8 (dd, $^1J_{PC}$ = 179.0, $^2J_{CF}$ = 10.0, CP), 54.0 (d, $^2J_{PC}$ = 6.0, OCH$_3$), 53.5 (d, $^2J_{PC}$ = 6.0, OCH$_3$), 50.4[c] (dq, $^2J_{CF}$ = 35.0, $^3J_{CF}$ = 12.5, *C*CF$_3$), 33.8 (s, SCH$_3$)

[a] Unless otherwise stated spectra are recorded in CDCl$_3$ at 298 K; *J* in Hz. [b] Recorded at 273 K. Resonances assigned to three Fe(CO)$_3$ carbon atoms are not observed at 273 K due to coalescence. [c] ^{13}C-{^{31}P}.

Table 2 Selected distances (Å) and angles (°) in [(Ph$_3$P)(OC)$_2$Fe{μ-CFC(PPh$_3$)C(CF$_3$)SMe}Fe(CO)$_3$][{Fe(CO)$_3$}$_2${μ-C(CF$_3$)C(CF$_3$)SMe}] **2**

(*a*) Cation

Fe(1A)–Fe(2A)	2.716(2)	Fe(1A)–C(2A)	2.027(7)	P(1A)–C(11)	1.797(5)	P(1A)–C(21)	1.801(4)
Fe(1A)–C(3A)	2.038(7)	Fe(1A)–C(4A)	2.080(7)	P(1A)–C(31)	1.804(4)	P(1A)–C(3A)	1.841(7)
Fe(1A)–C(6A)	1.778(10)	Fe(1A)–C(7A)	1.788(10)	P(2A)–C(41)	1.840(4)	P(2A)–C(51)	1.846(4)
Fe(1A)–C(8A)	1.787(10)	Fe(2A)–P(2A)	2.330(2)	P(2A)–C(61)	1.847(4)	F(4A)–C(4A)	1.380(7)
Fe(2A)–C(4A)	1.873(7)	Fe(2A)–S(1A)	2.261(2)	C(1A)–C(2A)	1.515(10)	C(2A)–C(3A)	1.452(9)
Fe(2A)–C(9A)	1.702(10)	Fe(2A)–C(10A)	1.791(9)	C(3A)–C(4A)	1.432(9)		
S(1A)–C(2A)	1.785(7)	S(1A)–C(5A)	1.818(8)				

C(6A)–Fe(1A)–C(8A)	91.5(4)	C(6A)–Fe(1A)–C(7A)	98.0(4)	C(21)–P(1A)–C(3A)	113.3(3)	C(31)–P(1A)–C(3A)	112.6(3)
C(8A)–Fe(1A)–C(7A)	98.6(4)	C(6A)–Fe(1A)–Fe(2A)	173.0(3)	C(41)–P(2A)–C(51)	102.5(3)	C(41)–P(2A)–C(61)	104.3(3)
C(8A)–Fe(1A)–Fe(2A)	93.3(3)	C(7A)–Fe(1A)–Fe(2A)	86.3(3)	C(51)–P(2A)–C(61)	102.3(2)	C(41)–P(2A)–Fe(2A)	114.0(2)
C(9A)–Fe(2A)–C(10A)	95.0(4)	C(9A)–Fe(2A)–C(4A)	97.3(3)	C(51)–P(2A)–Fe(2A)	113.0(2)	C(61)–P(2A)–Fe(2A)	118.8(2)
C(10A)–Fe(2A)–C(4A)	90.4(3)	C(9A)–Fe(2A)–S(1A)	95.5(3)	C(3A)–C(2A)–C(1A)	126.8(6)	C(3A)–C(2A)–S(1A)	116.0(5)
C(10A)–Fe(2A)–S(1A)	168.9(3)	C(4A)–Fe(2A)–S(1A)	84.8(2)	C(1A)–C(2A)–S(1A)	111.9(6)	C(3A)–C(2A)–Fe(1A)	69.5(4)
C(9A)–Fe(2A)–P(2A)	95.9(3)	C(10A)–Fe(2A)–P(2A)	88.4(2)	C(1A)–C(2A)–Fe(1A)	121.6(6)	S(1A)–C(2A)–Fe(1A)	101.6(3)
C(4A)–Fe(2A)–P(2A)	166.7(2)	S(1A)–Fe(2A)–P(2A)	93.93(8)	C(4A)–C(3A)–C(2A)	107.6(6)	C(4A)–C(3A)–P(1A)	120.1(5)
C(9A)–Fe(2A)–Fe(1A)	144.9(3)	C(10A)–Fe(2A)–Fe(1A)	96.9(3)	C(2A)–C(3A)–P(1A)	131.6(5)	C(4A)–C(3A)–Fe(1A)	71.2(4)
C(4A)–Fe(2A)–Fe(1A)	49.9(2)	S(1A)–Fe(2A)–Fe(1A)	72.32(6)	C(2A)–C(3A)–Fe(1A)	68.6(4)	P(1A)–C(3A)–Fe(1A)	133.2(4)
P(2A)–Fe(2A)–Fe(1A)	117.21(7)	C(2A)–S(1A)–C(5A)	104.2(4)	F(4A)–C(4A)–C(3A)	112.3(6)	F(4A)–C(4A)–Fe(2A)	121.6(5)
C(2A)–S(1A)–Fe(2A)	94.0(2)	C(5A)–S(1A)–Fe(2A)	112.9(3)	C(3A)–C(4A)–Fe(2A)	125.8(5)	F(4A)–C(4A)–Fe(1A)	122.5(5)
C(11)–P(1A)–C(21)	108.8(3)	C(11)–P(1A)–C(31)	106.3(3)	C(3A)–C(4A)–Fe(1A)	68.1(4)	Fe(2A)–C(4A)–Fe(1A)	86.6(3)
C(21)–P(1A)–C(31)	108.0(3)	C(11)–P(1A)–C(3A)	107.5(3)				

(*b*) Anion

Fe(1B)–C(2B)	1.982(8)	Fe(1B)–C(3B)	1.907(8)	Fe(2B)–C(10B)	1.762(10)	Fe(2B)–C(11B)	1.791(11)
Fe(1B)–C(6B)	1.756(11)	Fe(1B)–C(7B)	1.766(10)	S(1B)–C(2B)	1.783(9)	S(1B)–C(5B)	1.804(8)
Fe(1B)–C(8B)	1.785(11)	Fe(2B)–S(1B)	2.313(2)	C(1B)–C(2B)	1.501(12)	C(2B)–C(3B)	1.423(10)
Fe(2B)–C(3B)	1.984(8)	Fe(2B)–C(9B)	1.810(10)	C(3B)–C(4B)	1.465(12)	Fe(1B)–Fe(2B)	2.570(2)

C(6B)–Fe(1B)–C(7B)	90.5(5)	C(6B)–Fe(1B)–C(8B)	102.8(4)	C(9B)–Fe(2B)–Fe(1B)	105.2(3)	C(3B)–Fe(2B)–Fe(1B)	47.4(2)
C(7B)–Fe(1B)–C(8B)	100.6(4)	C(6B)–Fe(1B)–Fe(2B)	163.5(4)	S(1B)–Fe(2B)–Fe(1B)	76.10(7)	C(2B)–S(1B)–C(5B)	105.8(4)
C(7B)–Fe(1B)–Fe(2B)	96.9(3)	C(8B)–Fe(1B)–Fe(2B)	90.4(3)	C(2B)–S(1B)–Fe(2B)	76.7(3)	C(5B)–S(1B)–Fe(2B)	107.4(3)
C(10B)–Fe(2B)–C(11B)	94.1(4)	C(10B)–Fe(2B)–C(9B)	92.3(4)	C(3B)–C(2B)–C(1B)	129.2(8)	C(3B)–C(2B)–S(1B)	107.7(6)
C(11B)–Fe(2B)–C(9B)	100.7(4)	C(10B)–Fe(2B)–C(3B)	93.7(4)	C(1B)–C(2B)–S(1B)	113.8(7)	C(3B)–C(2B)–Fe(1B)	65.8(5)
C(11B)–Fe(2B)–C(3B)	106.3(4)	C(9B)–Fe(2B)–C(3B)	151.8(4)	C(1B)–C(2B)–Fe(1B)	124.5(7)	S(1B)–C(2B)–Fe(1B)	106.4(4)
C(10B)–Fe(2B)–S(1B)	165.2(3)	C(11B)–Fe(2B)–S(1B)	97.1(3)	C(2B)–C(3B)–C(4B)	127.1(8)	C(2B)–C(3B)–Fe(1B)	71.4(5)
C(9B)–Fe(2B)–S(1B)	95.0(3)	C(3B)–Fe(2B)–S(1B)	73.9(2)	C(4B)–C(3B)–Fe(1B)	135.8(7)	C(2B)–C(3B)–Fe(2B)	96.8(5)
C(10B)–Fe(2B)–Fe(1B)	89.6(3)	C(11B)–Fe(2B)–Fe(1B)	153.7(3)	C(4B)–C(3B)–Fe(2B)	125.9(7)	Fe(1B)–C(3B)–Fe(2B)	82.7(3)

to Fe(2A)→C(4A) back donation. The bridging role adopted by C(4) relative to the two iron atoms implies significant μ-carbene character and is unusual for diiron compounds having cycloferrapentadiene[6] or cycloferrathiapentadiene[3,4,7] rings. It is, however, consistent with the ^{13}C NMR spectrum of **2a** which shows a low-field resonance for the C(4) carbon atom at δ 224.6.

The anion of compound **2a** contains a dinuclear Fe$_2$(CO)$_6$ unit (Fig. 1) linked by a bridging organic group derived from the perfluorosulfanylvinyl ligand in **1** by a fluoride attack on the CF$_2$ carbon atom, the fluorovinyl function being thereby transformed into the C(4B) trifluoromethyl group. The structure of the anion is based on a Fe(2B)–S(1B)–C(2B)–C(3B) cycloferrathiabutene ring which is linked to Fe(1B) by an iron–iron bond and through C(2B) and C(3B). The C(3B) carbon atom may be regarded as a bridging carbene, the Fe(1B)–C(3B)

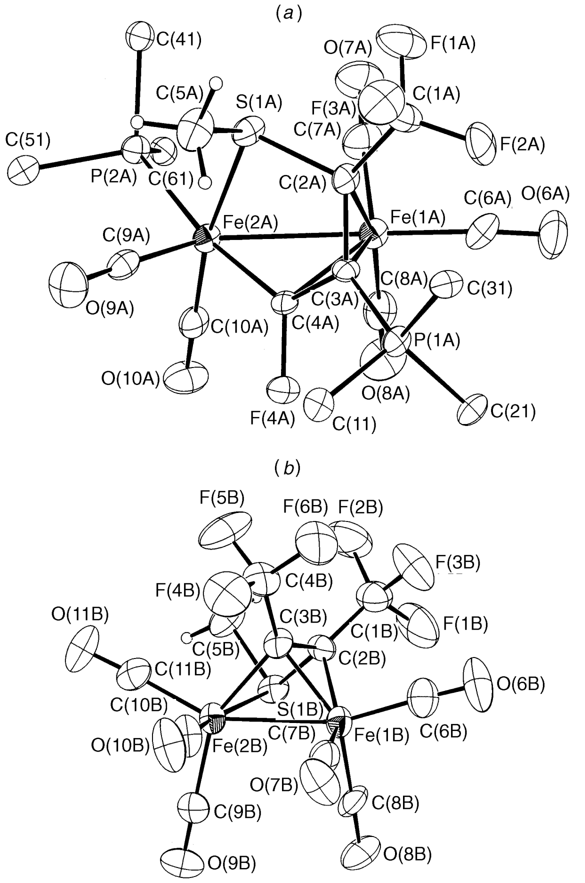


Fig. 1 Views of (*a*) $[\{Fe_2(CO)_5\}(PPh_3)\}\{\mu\text{-}CFC(PPh_3)C(CF_3)SMe\}]^+$ and (*b*) $[\{Fe(CO)_3\}_2\{\mu\text{-}C(CF_3)C(CF_3)SMe\}]^-$ in compound **2a**. Only *ipso* phenyl carbon atoms are shown. Hydrogen atoms are represented by spheres of arbitrary radius and other atoms by 30% probability ellipsoids

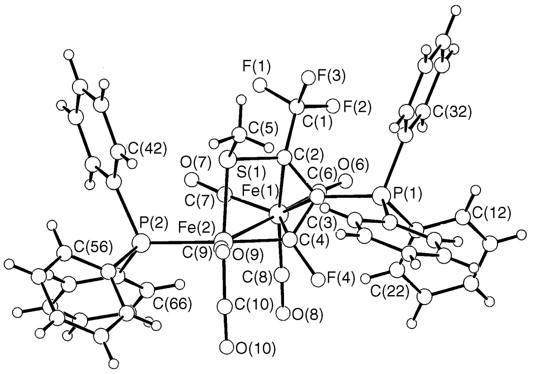


Fig. 2 The $[\{Fe_2(CO)_5\}(PPh_3)\}\{\mu\text{-}CFC(PPh_3)C(CF_3)SMe\}]^+$ cation showing the numbering of all the non-hydrogen atoms. Carbon atoms in phenyl rings $n = 1$–6 are numbered C(*n*1)–C(*n*6) in sequence, starting at the *ipso*-carbon atom. For clarity only C(*n*2) or C(*n*6) is labelled and for non-phenyl ring atoms the terminal A is omitted from the atom name

and Fe(2B)–C(3B) distances [1.907(8) and 1.984(8) Å] are within the range typical of iron–carbene bonds.[3,4,8]

The longest C–F bond in compound **2** is that between C(4A) and F(4A) [1.380(7) Å compared with 1.31(1)–1.35(1) Å], possibly reflecting the presence of an intramolecular hydrogen bond (see Fig. 2): C(22)···F(4A) 3.030(7), H(22)···F(4A) 2.2 Å, C(22)–H(22)···F(4A) 131° (assuming C–H 1.08 Å). Otherwise the distances in both the cation and anion are unexceptional.[9]

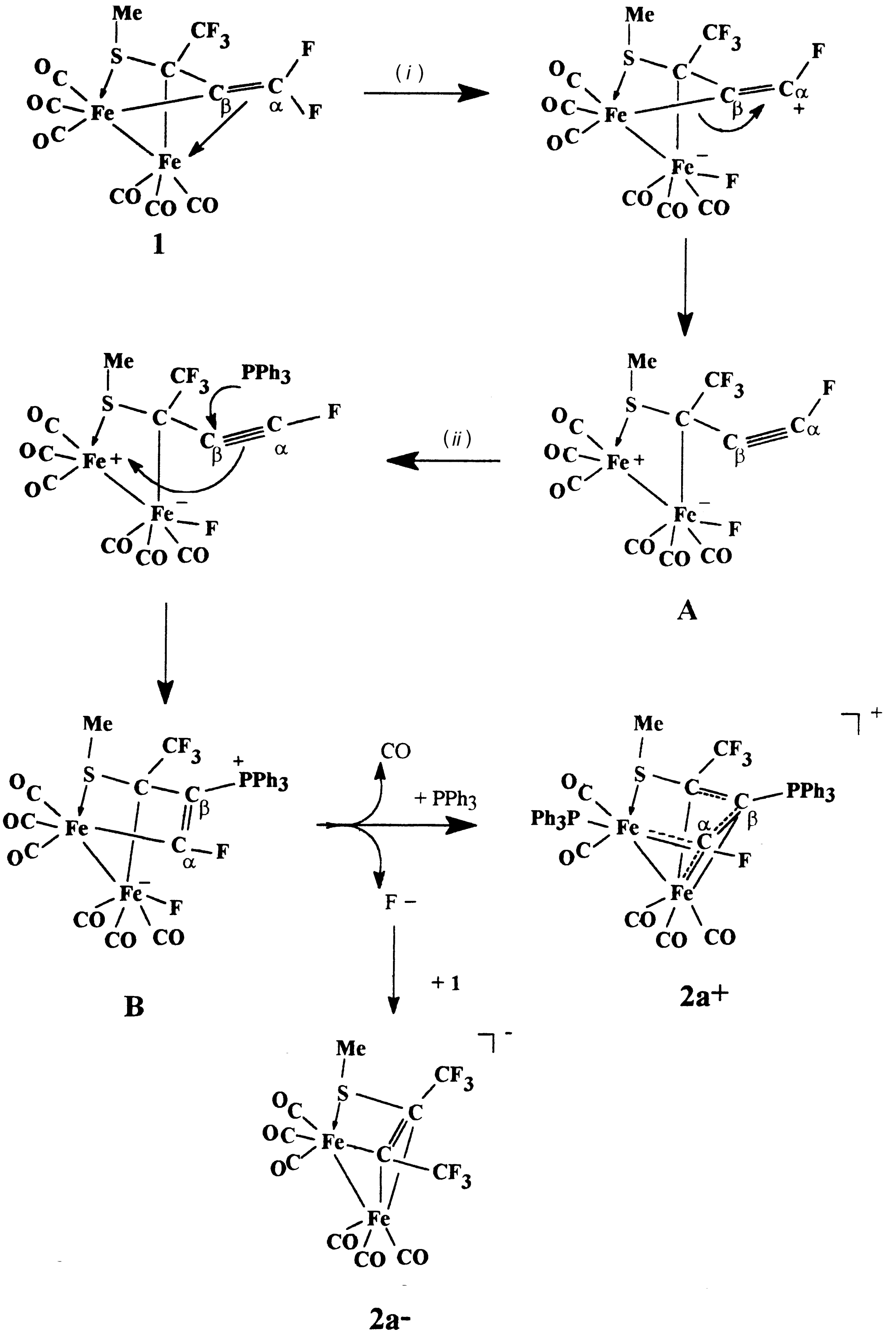
Crystals of compound **2a** were dissolved in cold $CDCl_3$ and the resulting solution was heated; NMR spectroscopy indicated no change up to 270 K but on further heating **2a** was partly converted into **2b**. The spectral patterns of **2b** (Table 1) were derived by subtracting from the ^1H, ^{31}P and ^{19}F NMR spectra of **2** the peaks pertaining to **2a**. The spectra of the two isomers are similar; indeed, the ^1H and ^{19}F spectra of the anions of **2a** and **2b** are indistinguishable. This indicates for **2b** a cluster framework similar to that in **2a**, and suggests that the isomers interconvert by CO and PPh_3 ligand exchange on Fe(2A).

Formation of compound **2** thus involves a C–F bond cleavage followed by an unusual external fluorine migration. The driving force of the reaction is not as expected elimination of hydrogen fluoride, but formation of the stable anion $[\{Fe(CO)_3\}_2\{\mu\text{-}C(CF_3)C(CF_3)SMe\}]^-$. If the reasoning used by Mott and Carty[10] to determine the polarity of an acetylide fragment is applicable to a perfluorovinyl fragment, $C_\beta{=}C_\alpha F_2$, we conclude that C_α is more electrophilic than C_β in **1** since its ^{13}C NMR spectrum at −54 °C gives $\delta(C_\beta) - \delta(C_\alpha) = 128.7 - 156.0 = -27.3$. As the phosphine nucleophile attacks C_β rather than C_α it would appear that the reaction involves a precursor in which C_β is more electrophilic than C_α so that the polarization of the C_β–C_α bond is inverted relative to **1**. A pathway consistent with this (Scheme 1) involves α elimination of a fluorine atom in **1** to give the dinuclear μ-perfluorosulfanylalkyne complex **A**. Subsequent regioselective nucleophilic attack by the triphenylphosphine at C_β followed by rearrangement gives **B**. Replacement of CO by phosphine then yields the cation $[\{Fe_2(CO)_5(PPh_3)\}\{\mu\text{-}CFC(PPh_3)C(CF_3)SMe\}]^+$. Such a replacement at an iron centre incorporated into a cycloferrapentadiene ring is unusual. The $CFC(PPh_3)C(CF_3)SMe$ ligand of the precursor **B** may act as an attracting group, allowing release of the carbonyl which is *trans* to the CF group.

Reaction of $[\{Fe(CO)_3\}_2\{\mu\text{-}C(SMe)(CF_3)C(CF_2)\}]$ with $P(OMe)_3$ and characterization of compounds 3 and 4

Two equivalents of trimethyl phosphite were allowed to react in a Schlenk tube at 60 °C for 1 h with a solution of $[\{Fe(CO)_3\}_2\{\mu\text{-}C(SMe)(CF_3)C(CF_2)\}]$ in CH_2Cl_2. On evaporation of the solvent complex **4** was obtained in *ca.* 85% yield and no other product could be isolated. The organometallic cluster **4** was characterized spectroscopically. The observation of the molecular ion in its mass spectrum, together with six successive CO-loss peaks, indicated that a dinuclear complex had been formed. The ^{19}F and ^{13}C NMR spectra confirm that the formation of **4** from **1** involves rupture of a C–F bond. The ^{19}F spectrum consists of two singlets with an intensity ratio of 1:3, indicating the presence of CF and CF_3 groups. The ^{13}C NMR spectrum also shows a doublet ($J = 356$ Hz) at δ 226.7 characteristic of a CF group. Complex **4** and the cation of **2a** show similar ^{13}C NMR patterns of four resonances for the carbon atoms of the cycloferrathiapentadiene ring region (Table 1) which indicates unambiguously that they have the same basic structure (Scheme 2). The presence of a $P(O)(OMe)_2$ group in **4** is evident from the NMR spectra: thus, the ^1H spectrum shows two doublets ($J = 2.5$ Hz) at δ 3.95 and 3.85 characteristic of two OMe groups. The IR spectrum in the ν(PO) region is particularly informative: there are three absorption bands, one corresponding to a P=O (1250s cm^{-1}) and two to P–O–C (1060m and 1040s cm^{-1}).

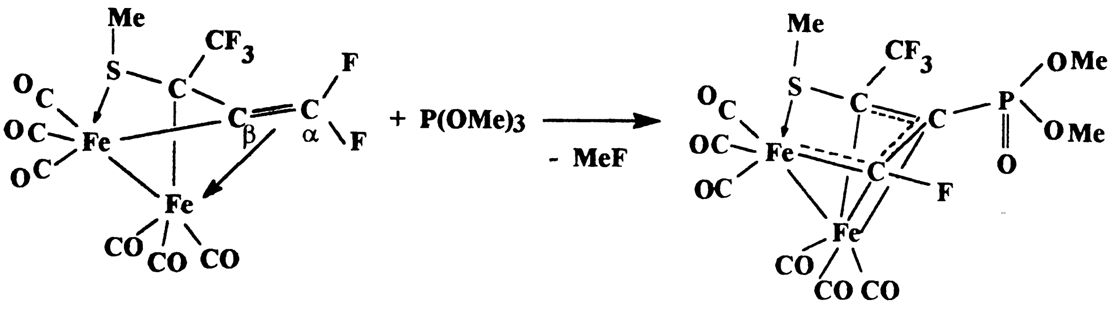
In order to understand the mechanism by which complex **4** was formed, we have monitored the reaction of **1** with an excess of trimethyl phosphite in $CDCl_3$ at 60 °C by NMR. After a few minutes complex **1** wholly disappeared and an intermediate **3** was obtained and characterized by NMR spectroscopy. Intermediate **3** was stable in solution, and only when the solvent was removed by evaporation it was transformed into **4**. When the reaction was conducted at lower temperatures (273 to 303 K) no intermediate other than **3** was detected in solution. Compound **3** displays a $^{13}C\text{-}\{^1H\}$ NMR pattern very similar to that of **4** and



Scheme 1 Possible pathway to the formation of $[(Ph_3P)(OC)_2Fe\{\mu\text{-}CFC(PPh_3)C(CF_3)SMe\}Fe(CO)_3][\{Fe(CO)_3\}_2\{\mu\text{-}C(CF_3)C(CF_3)SMe\}]$ **2**. (*i*) α Elimination of F; (*ii*) nucleophilic attack of PPh_3 at C_β

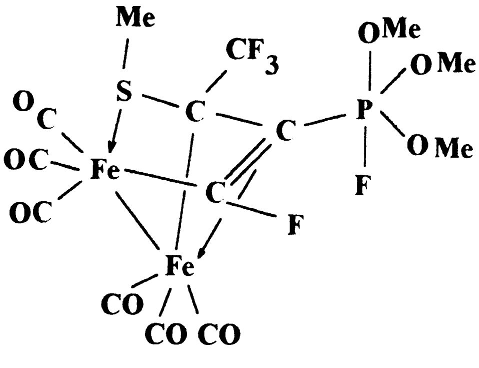
the cation of **2a** (Table 1), suggesting strongly that it too contains a cycloferrathiapentadiene ring π bonded to a $Fe(CO)_3$ unit. The presence of a $PF(OMe)_3$ unit is evident from its NMR spectra. The ^{19}F spectrum exhibits three resonances (relative intensities 3:1:1), two being singlets assigned to the CF_3 and CF groups and the third a doublet. The coupling constant for the doublet ($J = 835$ Hz) indicates the presence of a phosphorus-bound fluorine atom. This is confirmed by the ^{31}P NMR spectrum which shows a doublet at δ −56.2 with a coupling constant characteristic of a P–F group.

Complex **3** was the sole intermediate detected during the formation of **4**. The mechanism by which a C–F bond in **1** was cleaved to give successively **3** and **4** is uncertain, but since **3** and the cation of **2a** have similar structures we would suggest that this reaction proceeds like (1) *via* a zwitterionic intermediate of type **B** (Scheme 3). Removing the solvent favours elimination



1 4

Scheme 2 Synthesis and proposed structure of complex **4**



3

of methyl fluoride to give **4** and this may be the driving force for the reaction.

Conclusion

We have demonstrated that co-ordination of the difluorovinyl ligand by the diiron residue present in $[\{Fe(CO)_3\}_2\{\mu\text{-}C(SMe)(CF_3)C(CF_2)\}]$ **1** facilitates its reaction with nucleophiles. The vinylic C−F bonds are readily activated by tertiary phosphanes L under mild conditions. The products of these reactions depend on L but are always obtained in high yield. The reactions proceed with C−F bond activation and organo-iron ring expansion to produce the ionic species $[(Ph_3P)(OC)_2Fe\{\mu\text{-}CFC(PPh_3)C(CF_3)SMe\}Fe(CO)_3][\{Fe(CO)_3\}_2\{\mu\text{-}C(CF_3)C(CF_3)SMe\}]$ **2** when L is triphenylphosphine, and the molecular cluster $[\{Fe(CO)_3\}_2\{\mu\text{-}CFC[PO(OMe)_2]C(CF_3)SMe\}]$ **4** when L is trimethyl phosphite. It appears that the reactions do not proceed *via* direct nucleophilic attack or simple fluoride dissociation but involve as a key step the migration of a fluoride ion to the metal centre.

Experimental

The NMR spectra (^1H, ^{13}C, ^{19}F, ^{31}P), in $CDCl_3$ solution, were recorded on either a Bruker AC 300 or DRX 400 spectrometer and were referenced to $SiMe_4$ (^1H, ^{13}C), $CFCl_3$ (^{19}F) and $H_3(PO_4)$ (^{31}P). Infrared spectra were recorded on a Perkin-Elmer 1430 spectrophotometer from dichloromethane solutions for the ν(CO) region or from KBr discs in other spectral regions, mass spectra on a GC/MS Ribermag R10-10 spectrometer at the Laboratoire de Biochimie, Faculté de Médecine (Brest). Chemical analyses were performed either by the Océanographie Chimique Laboratory or by the Spectroscopie Atomique Laboratory at the University of Brest.

The reactions were performed under either argon or nitrogen using standard Schlenk techniques and solvents were deoxygenated and dried by standard methods. The bimetallic complex $[\{Fe(CO)_3\}_2\{\mu\text{-}C(SMe)(CF_3)C(CF_2)\}]$ **1** was prepared as described previously.[5] All other reagents were commercial grade and were used as obtained. Yields are with respect to the starting cluster **1** for the preparations of **2** and **4**.

Reactions of compound 1

With PPh_3. A solution of compound **1** (282 mg, 0.6 mmol) and PPh_3 (157.2 mg, 0.6 mmol) in $CHCl_3$ (5 cm^3) was heated in a Schlenk tube to 60 °C for 12 h [when an excess of phosphine (5 equivalent) was added, the reaction was complete within 1 h]. After filtration through cotton-wool and evaporation of the solvent, the residue was washed with pentane–CH_2Cl_2 (9 : 1, 10 cm^3) to give **2** as a red powder which was crystallized from a CH_2Cl_2–hexane mixture. Yield: *ca.* 396 mg, 92% (Found: C, 47.8; H, 2.6; Fe, 14.9. $C_{57}H_{36}F_{10}Fe_4O_{11}P_2S_2$ requires C, 47.7; H, 2.5; Fe, 15.5%). IR (CH_2Cl_2, cm^{-1}): ν(CO) 2065, 2038, 2018, 1982, 1960, 1938 and 1904.

With $P(OMe)_3$. (*a*) *In a Schlenk tube.* A solution of compound **1** (47 mg, 0.1 mmol) and an excess of $P(OMe)_3$ (24.8 mg, 0.2 mmol) in CH_2Cl_2 was heated in a Schlenk tube to 60 °C for 1 h. After evaporation of the solvent the residue was chromatographed on a silica gel column. Elution with CH_2Cl_2–diethyl ether (19 : 1) gave a yellow band containing **4**. Crystallization from CH_2Cl_2–pentane (3 : 7) gave yellow crystals. Yield: *ca.* 48 mg, 85% (Found: C, 28.1; H, 1.7; Fe, 19.7. $C_{13}H_9F_4Fe_2O_9PS$ requires C, 27.9; H, 1.6; Fe, 19.9%). Mass spectrum: *m/z* 560, M^+; 532, 504, 476, 448, 420, 392, $[M - nCO]^+$ (n = 1–6); 298, $[M - 2CO\text{-}FeF_2]^+$. IR (cm^{-1}): (CH_2Cl_2) ν(CO) 2090s, 2050s, 2025s, 2015(sh); (KBr pellet) ν(P=O) 1250s, ν(P−O−C) 1060m, 1040s, ν(C−F) 1215s, 1150s, 1125s and 1090s.

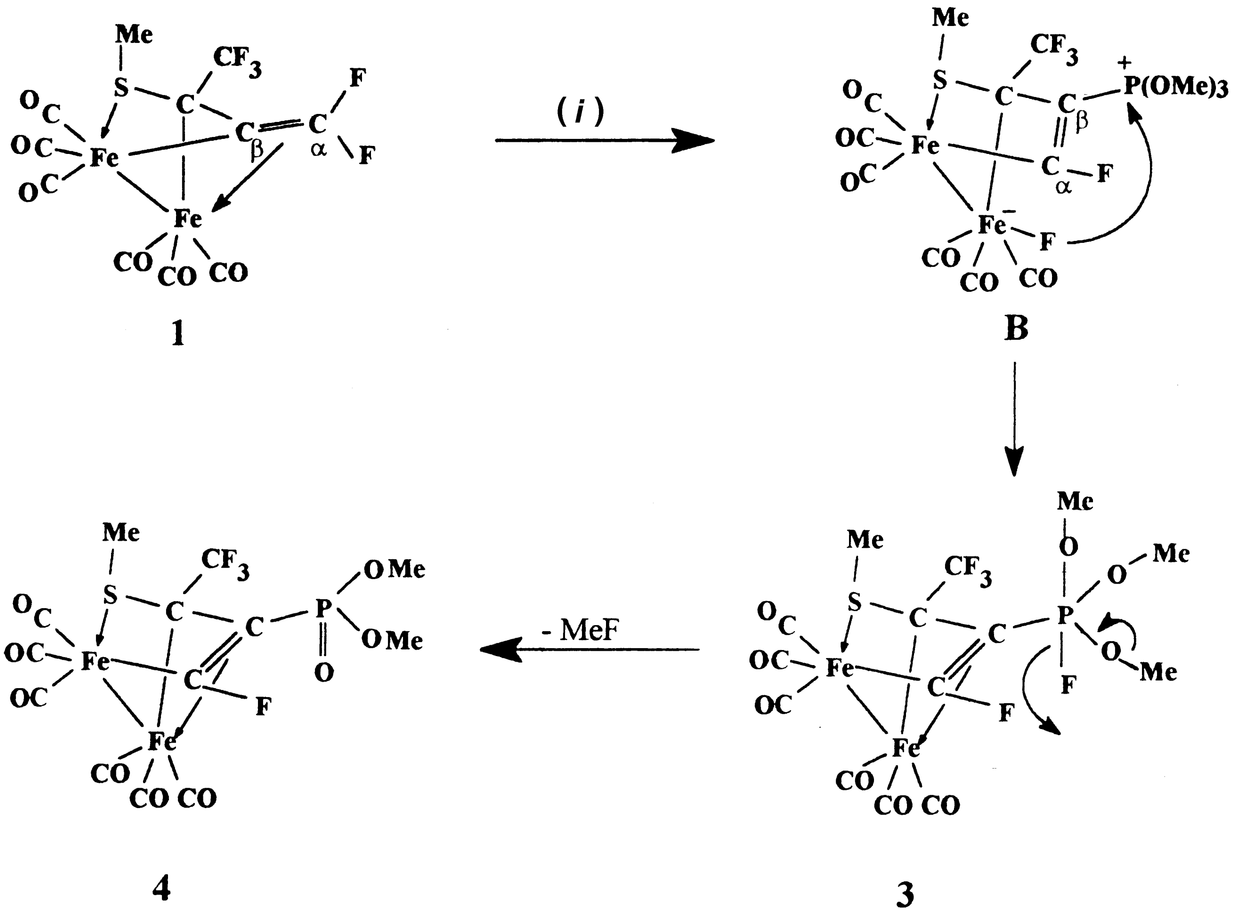
(*b*) *In a NMR tube.* A $CDCl_3$ solution of compound **1** (47 mg, 0.1 mmol) and $P(OMe)_3$ (24.8 mg, 0.2 mmol) was introduced in a NMR tube and heated at 60 °C. The reaction was monitored by NMR spectroscopy (^{19}F, ^{31}P). After a few minutes complex **1** disappeared and the intermediate **3** was characterized by NMR spectroscopy. Removal of the solvent by evaporation transformed **3** quantitatively into **4**.

Crystallography

Measurements of compound **2** were made at room temperature on an Enraf-Nonius diffractometer with graphite-monochromatized Mo-Kα radiation, $\lambda = 0.710\,73$ Å, using a red crystal of dimensions 0.23 × 0.10 × 0.08 mm.

Crystal data. $C_{57}H_{36}F_{10}Fe_4O_{11}P_2S_2$, $M = 1436.32$, triclinic, space group $P\bar{1}$, $a = 12.824(1)$, $b = 14.198(2)$, $c = 16.117(1)$ Å, $\alpha = 85.71(1)$, $\beta = 86.27(1)$, $\gamma = 84.85(1)°$, $U = 2909.4(5)$ Å^3, $Z = 2$, $F(000) = 1444$, $D_c = 1.640$ g cm^{-3}, μ(Mo-Kα) = 1.20 mm^{-1}.

Structure analysis. The cell constants were determined by a least-squares treatment of the setting angles of 20 reflections with $8.1 < \theta < 15.3°$. The intensities were measured from continuous ω–2θ scans. The mean of the intensities of three stand-



Scheme 3 Possible pathway to the formation of $[\{Fe(CO)_3\}_2\{\mu\text{-}CFC[PO(OMe)_2]C(CF_3)SMe\}]$ **4**. (*i*) (*a*) α Elimination of F, (*b*) nucleophilic attack by $P(OMe)_3$ at C_β

ard reflections, remeasured every 2 h, decreased by 11% during the experiment. Of 8050 unique reflections with h −14 to 14, k −15 to 0, l −17 to 17 and θ(Mo-Kα) < 23°, 3703 had $I > 2\sigma(I)$ and 2201 were measured twice ($R_{int} = 0.067$). The intensities were corrected for crystal decomposition and Lorentz-polarization effects but not for absorption or extinction.

The structure was solved by direct methods[11] and was refined on F^2 by full-matrix least squares using SHELXL 93 with $w = 1/[\sigma^2(F_o^2) + (0.0588P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$.[12,13] Adjustment of 705 parameters converged to $R_1[I > 2\sigma(I)] = 0.060$, $wR2 = 0.131$. Phenyl rings were refined as rigid hexagons of side 1.38 Å. Anisotropic displacement parameters were refined for all non-H atoms and H atoms rode on their parent C atoms with $U(\mathrm{H}) = pU_{eq}(\mathrm{C})$ where $p = 1.2$ for phenyl and 1.5 for methyl hydrogen atoms. A single orientation parameter was refined for each methyl group. Neutral atom scattering factors and anomalous dispersion corrections were taken from ref. 14.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/427.

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