Activation and Functionalization of Vinylic C−F Bonds by Transition Metal Compounds: The Factors Determining Reactions between Nucleophiles and a (Perfluorovinyl)diiron(I) Complex; Syntheses of Diiron Derivatives Containing New C−N, C−S, C−H and C−O Bonds

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The reactions between alcohols ROH (R = Me, Et) and $RR(OH)_2$ (RR = CH_2–CH_2) and the [perfluoro(sulfanyl)vinyl]-diiron complex [{$Fe(CO)_3$}$_2${μ-C(SMe)(CF_3)$C_\beta C_\alpha F_2$}] (**1**) in THF at room temperature involve substitution at the C_α atom to give new (alkoxymethylene)thiaferracyclobutadiene compounds [{$Fe(CO)_3$}$_2${μ-S(Me)C(CF_3)$C_\beta C_\alpha$(OR)$_2$}] [R = Me (**2a**), Et (**2b**); RR = CH_2CH_2 (**2c**)]. Treatment of **1** with aniline and (methoxycarbonyl)hydrazine, bases of intermediate strength according to Pearson, produces α,β-substituted thiaferracyclopentadiene [{$Fe(CO)_3$}$_2${μ-S(Me)C(CF_3)C_β(NHR)C_α-(NHR)}] [R = Ph (**5a**), NHC(O)OMe (**5b**)] complexes. It is suggested that these compounds form through initial nucleophilic attack at C_α to give the zwitterionic intermediate [{$Fe(CO)_3$}$_2${μ-S(Me)C(CF_3)CC(NRH)$_2$}] (**f**). Thermally induced C–F bond activation is a feature of these reactions. When **1** reacts with thioamides containing three "hard" competitive primary and secondary amine functions and one "soft" thione function, the nucleophile first attacks at C_α through a secondary amine and, in a second step, at C_β through the thiol function to give α,β adducts [{$Fe(CO)_3$}$_2${μ-S(Me)C(CF_3)C_βSC(=NR^2)N(R^1)C_α(C_β–C_α)}] [R^1 = NH_2, R^2 = CH_3 (**6a**); R^1 = CH_3, R^2 = H (**6b**); R^1 = R^2 = CH_3 (**6c**)] possessing novel iminothiazolidine systems fused to the five-membered metallacyclic ring. Treatment of **1** with acetylhydrazine, which has three "hard" nucleophilic functions, results in the formation of the compound [{$Fe(CO)_3$}$_2${μ-S(Me)C(CF_3)C(H)$C_{(10)}$NNC(Me)O($C_{(10)}$–O)}] (**7a**), in which an oxadiazole function is fused to the thiaazaferracyclohexene ring. The position of the fluorine substituent on the $C_\alpha C_\beta C_\gamma$($CF_3$)S(Me) ring of ferracyclopentadiene complexes has been found to be the essential factor determining the specific activation of the C–F bond. A single fluoro substituent attached to the β-carbon atom of the chain can be activated by nucleophiles to give α,β adducts [{$Fe(CO)_3$}$_2${μ-S(Me)C(CF_3)C_β(X)C_α(NRR′)}] [X = OR″, R = R′ = R″ = Me (**3a**); X = OR″, R = R″ = Me, R′ = C(O)NMe_2 (**3b**); X = SR″ (**4**)]. In contrast, complexes in which a single fluorine atom is linked to the α-carbon atom do not undergo C–F bond cleavage reactions. X-ray structures of compounds **2a**, **3b**, **5a**, **5b**, **6a** and **7a** are reported.

Introduction

C−F activation reactions induced by transition metal compounds are of salient importance in organometallic chemistry. They are involved in many of the catalytic transformations that result in the formation of new carbon−heteroatom bonds and they are an essential feature of the synthesis of partially fluorinated molecules.[1] The recent upsurge of interest in (perfluorovinyl)metal complexes also stems from the observation that the chemical properties of these compounds differ substantially from those of their hydrocarbon analogues.[2] Although vinyl fluorides are normally inert, in some cases they undergo unexpected C−F cleavage reactions with nucleophilic agents to give either substituted vinyl derivatives[2] or new organofluorine compounds with unusual functional groups.[3,4]

In this context we have previously described the reaction between the [perfluoro(sulfanyl)vinyl]diiron(I) compound [{$Fe(CO)_3$}$_2${μ-C(SMe)(CF_3)$C_\beta C_\alpha F_2$}] (**1**) and primary and secondary amines, thiols, phosphanes and tertiary phosphanes. Analysis of the reaction products showed that soft nucleophiles (phosphanes, tertiary phosphanes, thiols) react at C_β to give thiaferracyclopentadiene compounds of types **D**, **E** or **F**[4b,4c] (Scheme 1), whereas hard nucleophiles (primary and secondary amines) react at C_α to give either monofluorothiaferracyclopentadiene complexes of type **A** when stoichiometric amounts of nucleophile are used, or thiaferracyclobutene compounds of type **C** when excess nucleophile is employed[4a,4d] (Scheme 1). These results imply

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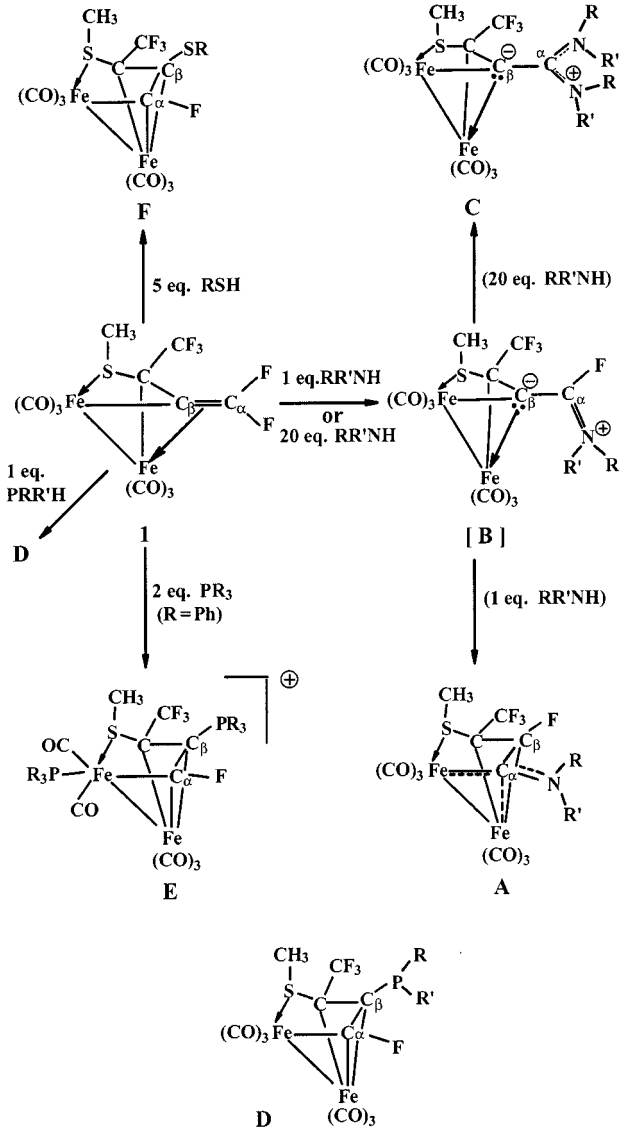
that soft nucleophiles activate only one C−F bond whereas hard bases activate both C−F bonds, resulting either in a 1,2-transfer of F onto C_β or in further addition of nucleophile.



Scheme 1

Perhaps our most striking result from these earlier studies of the reactions of nucleophiles with **1** was that the C−F activation step depended on whether the attacking nucleophile was hard or soft.[4] We have therefore become interested in reactions between **1** and such nucleophiles as alcohols and aniline. These are still hard bases according to Pearson's concept,[5] but are nevertheless thought to be softer than most aliphatic amines. We have also investigated the addition of multifunctional amines to **1**, in order to see whether the reaction of the iron compound with one function influences the reactivity of the others. Moreover, as an extension of our earlier studies of the reactions between nucleophiles and **1**,[4] we have investigated the dependence of the C−F bond activation on the position of the fluorine atoms in the carbon chain of the vinylic ligand.[6] Here we report these various reactions and the characterisation of the resulting products.

Results and Discussion

Analytical data and mass, infrared and multinuclear (^{1}H, ^{19}F and ^{13}C) NMR spectroscopic data for all new compounds discussed in this paper are given in Table 1. Selected bond lengths for **2a**, **3b**, **5a**, **5b**, **6a** and **7a** are compared in Table 2. All these structures contain rather similar $Fe_2(CO)_6$ units, in which the single Fe−Fe bond is bridged in various ways by a six-electron donor $MeSC(CF_3)C_\beta C_\alpha$ ligand. Apart from **7a**, the Fe−Fe distances are in the narrow 2.60−2.65 Å range, with a mean of 2.634 Å. Further spectroscopic and structural details are presented in the Exp. Sect. and in figure captions.

1. Reactions between [{Fe(CO)$_3$}$_2${μ-C(SMe)(CF$_3$)C−CF$_2$}] (1) and Alcohols ROH (R = CH$_3$, C$_2$H$_5$) and RR(OH)$_2$ (RR = CH$_2$−CH$_2$)

Synthesis and Spectroscopic Characterisation

The reactions between **1** and alcohols depend markedly on the solvent. Treatment of **1** with a large excess of alcohol in THF at room temperature results in the quantitative formation of the (alkoxymethylene)thiaferracyclobutene compounds **2** (Scheme 2). When the reaction is carried out in CH_2Cl_2, it is necessary to heat the solution to 60 °C to obtain the same products. The regiochemistry observed in the reaction is consistent with the known hard base character of alcohols: they are expected to react at C_α like amines,[4d] which are even harder nucleophiles than alcohols.

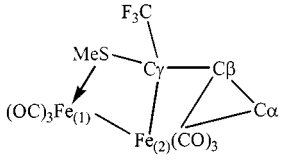
The molecular structure of **2a** was established by X-ray diffraction (see below). It is clearly apparent from the NMR spectroscopic data in Table 1 that complexes **2a** and **2b** have the same basic structure. Both mass spectra have molecular ions corresponding to replacement of the two fluorine atoms of **1** by two alkoxide groups. The ^{13}C NMR spectra of **2a**, **2b** and the parent complex **1** are very similar, each showing two resonances at $\delta \approx 120$ and 160 in the range expected for vinylic carbon atoms σ- and π-bonded to metal atoms. The mass spectrum of **2c** shows a molecular ion peak corresponding to a complex in which two fluorine atoms have been replaced by one molecule of ethylene glycol. The most significant difference between **2c** and **2a** or **2b** occurs in the ^{13}C NMR spectra, and particularly in the region associated with the carbon atom (C_β) directly bound to the two iron atoms. The $^{13}C_\beta$ signal of **2c** appears at $\delta = 85.6$, whereas those of **2a** and **2b** occur at $\delta = 124.0$ and 116.2, respectively, indicating a difference in the bridging mode of the vinyl ligand. However, the ^{13}C NMR spectra of **2c** and **C**[4d] (Table 1) are very similar, strongly suggesting that **2c** in solution adopts mainly the zwitterionic form depicted in Scheme 2, whereas **2a** and **2b** adopt a neutral structure closely related to that of the parent compound **1**. The highfield shifting of the C_β resonance of **2c**

Table 1. Comparison of selected NMR chemical shift data (δ)[a] for neutral (**1**, **2a**, **b**) and zwitterionic (**2c**, [**f**], [**B**] and [**C**]) thiaferracyclobutene, thiaferracyclopentadiene (**3−6** and **A**) and thiaazaferracyclohexene (**7**) derivatives

Compd.	^{19}F			^{13}C{^{1}H}					
	CF_3	CF	SCH_3	C_β	C_α	CO [Fe(1)]	CO [Fe(1)]	CO [Fe(1)]	CO [Fe(2)]
1[c],[d]	−58.7 (d)	−59.2 (m) −81.2 (m)	32.5 (s)	127.7 (d)	152.6 (dd)				
2a	−57.9 (s)		32.4 (s)	124.0 (s)	161.8 (s)		209.5 (s)		210.3 (s, br)
2b	−57.6 (s)		32.4 (s)	116.2 (s)	165.4 (s)		209.9 (s)		211.0 (s, br)
2c	−58.8 (s)		32.4 (s)	85.6 (s)	171.9 (s)		211.7 (s)		210.0 (s, br)
[**f**][c]	−63.2 (s)		32.8 (s)	95.6 (s)	176.9 (s)	204.7 (s)	206.3 (s)	210.6 (s)	208.5 (s, br)
[**B**][c]	−63.35 (s)	−19.05 (s)	33.3 (s)	73.1 (d)	182.1 (d)	207.7 (s)	209.9 (s)	212.0 (s)	215.4 (s, br)
C[e][f]	−62.85 (s)		31.4 (s)	89.7 (s)	177.3 (s)		213.8 (s)		215.4 (s, br)
5a	−57.5 (s)		34.9 (s)	91.6 (s)	202.0 (q, $^4J_{CF}$ = 2)	206.5 (s)	208.6 (s)	210.5 (s)	210.1 (s, br)
5b	−56.6 (s)		34.7 (s)	93.5 (s)	210.7 (q, $^4J_{CF}$ = 2)	204.9 (s)	210.0 (s)	210.4 (s)	210.0 (s, br)
6a	−58.7 (s)		35.2 (s)	89.0 (s)	184.0 (s)	205.3 (s)	209.0 (s)	210.5 (s)	209.1 (s, br)
6b	−59.1 (s)		34.9 (s)	92.8 (s)	183.2 (s)	204.7 (s)	209.9 (s)	210.1 (s)	208.6 (s, br)
6c	−59.0 (s)		34.9 (s)	91.6 (s)	184.1 (s)	204.7 (s)	210.2 (s)	210.3 (s)	208.8 (s, br)
A[e][g]	−59.2 (d)	−152.65 (q)	34.4 (s)	120.0 (d)	190.75 (d)	205.0 (s)	210.7 (s)	211.2 (s)	210.2 (s, br)
3a	−58.4 (s)		34.5 (s)	122.5 (s)	189.1 (q, $^4J_{CF}$ = 2)	207.2 (s)	210.7 (s)	211.0 (s)	210.4 (s, br)
3b	−58.7 (s)		33.2 (s)	102.0 (s)	198.6 (q, $^4J_{CF}$ = 1.5)	205.2 (s)	210.8 (s)	211.5 (s)	210.5 (s, br)
F[h][i]	−58.6 (s)	−53.9 (s)	34.0 (s)	94.8 (d)	220.6 (q)	205.8 (d)	207.5 (d)	208.4 (d)	208.2 (s, br)
4a	−55.5 (s)		34.2 (s)	88.5 (s)	205.7 (s)	206.9 (s)	210.1 (s)	210.8 (s)	210.9 (s)
4b	−55.3 (s)		33.0 (s)	71.5 (s)	212.9 (m)	205.6 (s)	210.5 (s)	210.7 (s)	210.0.(s)
4c	−56.4 (s)		33.1 (s)	78.5 (s)	206.4 (m)	210.6 (s)	210.8 (s)	211.5 (s)	209.9 (s, br)
4d	−55.2 (s)		33.1 (s)	71.3 (s)	212.9 (q, $^4J_{CF}$ = 2)	205.6 (s)	210.5 (s)	210.9 (s)	210.0 (s, br)
4e	−54.9 (s)		33.3 (s)	65.4 (s)	206.3 (q, $^4J_{CF}$ = 2)	205.7 (s)	211.4 (s)	211.5 (s)	210.0 (s, br)
7a	− 62.6		30.1 (s)	24.4 (s)	175.9 (s)	198.3 (s)	211.1 (s)	215.6 (s)	207.6 (s) 214.0 (s, br) 219.4 (s, br)
7b	−62.4 (s)		25.4 (d^3, J_{CP} = 8)	24.8 (s)	176.5 (s)		216.2 (d, $^2J_{CP}$ = 7.5)[b]	219.6 (d, $^2J_{CP}$ = 2)[b]	207.9 (s, br)[b] 214.1 (s, br)[b] 222.8 (s, br)[b]
7c	−62.5 (s)		26.8 (d^3, J_{CP} = 6.5)	24.5 (s)	176.6 (s)		215.0 (d, $^2J_{CP}$ = 11.5)	220.4 (d, $^2J_{CP}$ = 4.5)	213.4 (s, br) 222.5 (s, br)

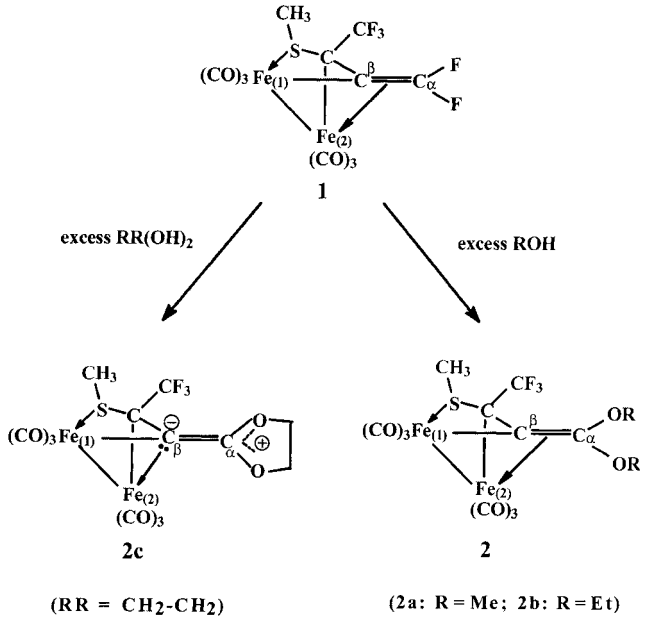
[a] Measured in $CDCl_3$ solution at 293 K unless stated otherwise, J in Hz. [b] At 240 K. [c] At 233 K. [d] From ref.[6] [e] From ref.[4d] [f] R−R′ = $(CH_2)_4$. [g] R = R′ = Me. [h] R = C_2H_5. [i] From ref.[4c]

Table 2. Selected bond lengths [Å] in $[Fe_2(CO)_6\{\mu\text{-}C_\alpha{-}C_\beta{-}C_\gamma(SMe)CF_3\}]$ complexes; Fe−CO distances are in the 1.763(6)−1.820(3) Å range, with a mean of 1.791 Å; except for **2a** the asymmetric unit of each structure contains two crystallographically independent molecules which are structurally indistinguishable



	2a	**3b**	**3b**	**5a**	**5a**	**5b**	**5b**	**6a**	**6a**	**7a**	**7a**	**Mean**
Fe1−C_β	1.963(2)											
Fe1−N										1.974(2)	1.964(2)	
Fe1−C_α		2.000(6)	1.997(6)	1.978(5)	1.966(5)	1.934(5)	1.947(5)	1.947(7)	1.936(7)			1.963
Fe1−S	2.307(1)	2.257(2)	2.246(2)	2.259(2)	2.276(2)	2.267(2)	2.266(2)	2.280(2)	2.282(2)	2.282(1)	2.276(1)	2.271
Fe−Fe	2.600(1)	2.649(1)	2.646(1)	2.634(1)	2.633(1)	2.651(1)	2.647(1)	2.640(2)	2.640(1)	2.794(1)[a]	2.799(1)[a]	2.634
Fe2−C_γ	2.039(2)	1.999(6)	2.016(6)	2.010(5)	2.008(5)	2.011(6)	2.000(6)	2.028(7)	2.028(7)	1.986(3)	1.983(3)	2.010
Fe2−C_β	1.973(2)	2.040(6)	2.043(5)	2.050(5)	2.064(5)	2.036(5)	2.026(5)	2.072(7)	2.060(7)	2.061(3)	2.063(3)	2.044
Fe2−C_α	2.347(2)	2.347(6)	2.397(5)	2.328(6)	2.335(5)	2.285(5)	2.292(5)	2.238(7)	2.229(7)			2.301
$C_\alpha{-}C_\beta$	1.384(3)	1.415(8)	1.428(8)	1.409(7)	1.440(7)	1.431(7)	1.430(7)	1.418(9)	1.416(9)	1.440(4)	1.424(4)	1.421
$C_\beta{-}C_\gamma$	1.441(3)	1.431(8)	1.469(8)	1.459(7)	1.441(7)	1.446(8)	1.440(8)	1.432(9)	1.442(9)	1.455(4)	1.463(4)	1.447
$C_\gamma{-}C_\delta$	1.501(3)	1.497(9)	1.499(9)	1.496(8)	1.487(7)	1.505(9)	1.500(8)	1.504(10)	1.500(11)	1.493(4)	1.489(4)	1.496

[a] Not included in the calculation of the mean.



Scheme 2. Synthesis and proposed structures of complexes **2**

relative to that of **2a** and **2b** may be a consequence of the presence of negative charge on this carbon in **2c**.

Single-Crystal X-ray Analysis of 2a

Crystals suitable for X-ray diffraction were grown from a solution of **2a** in dichloromethane and hexane at −20 °C. The molecular structure of **2a** (Figure 1, Table 2) is broadly consistent with that deduced from the spectra (Scheme 2, Table 1). It is formally derived from **1** by replacement of both fluoro substituents by methoxide groups to give a six-electron donor $MeSC_\gamma(CF_3)C_\beta C_\alpha(OMe)_2$ ligand. This process obviously involves the cleavage of two C−F bonds. Iron atom Fe(1) is incorporated in an $Fe(1)S(1)C_\gamma C_\beta$ thiaferracyclobutene ring, linking to Fe(2) through a normal Fe−Fe bond. Fe(2) interacts weakly with C_α [Fe(2)−C(10) 2.347(2) Å], strongly with C_β [Fe(2)−C(9) 1.973(2) Å] and slightly less strongly with C_γ [Fe(2)−C(8) 2.039(2) Å]. Atom Fe(2) and the $C_\gamma-C_\beta-C_\alpha$ chain define a rather distorted (π-allyl)Fe substructure; this view is consistent with the $C_\delta-C_\gamma-C_\beta-C_\alpha$ and other torsion angles (Figure 1, caption) and with the $C_\alpha-C_\beta$ and $C_\beta-C_\gamma$ distances [1.384(3) and 1.441(3) Å], which may reflect the asymmetry in the Fe(2)−C distances [for comparison, average Fe−C(allyl) and C−C(allyl) distances are 2.07 and 1.404 Å and C−C bond lengths of 1.369(9) − 1.391(4) Å have been reported in μ_2-η^1:η^2-vinyl derivatives[7a,8]]. The Fe−C distances in **2a** are also broadly in agreement with those that we found in the C=C=CN*t*Bu derivative [{Fe(CO)$_3$}$_2$-{μ-C_β[C(CF$_3$)(SMe)]C_α(N*t*Bu)}] [Fe(2)−C_β 2.004(4), Fe(1)−C_β 1.970(3), Fe(2)−C_α 2.465(4) Å[4a]]. Finally, we note that C_β is nearly equidistant from the two metal atoms and that both Fe−C_β distances are within the range typical of iron−carbene bonds.[4b,4c,7b] The ^{13}C NMR spectrum of **2a** in solution shows a highfield resonance for the C_β carbon atom at δ = 124.0, in sharp contrast with the bridging C_α carbon atoms of thiaferracyclopentadiene compounds, which have carbene-like character and which give rise to lowfield resonances at δ ≈ 224.[4b,4c]

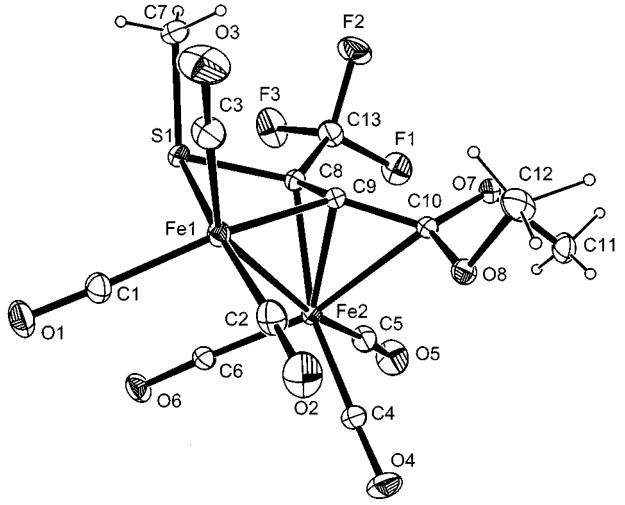


Figure 1. Molecular structure and numbering scheme of compound **2a** in the crystal; here and elsewhere 20% probability ellipsoids are shown for non-hydrogen atoms; selected bond lengths [Å] and angles [°]: O(7)−C(10) 1.352(3), O(7)−C(11) 1.437(3), O(8)−C(10) 1.356(3), O(8)−C(12) 1.446(3); C(8)−C(9)−C(10)−O(7) 38.8, C(8)−C(9)−C(10)−O(8) −161.7(2), and C(13)−C(8)−C(9)−C(10) −43.9(3)

Fluxional Behaviour of Compound 2 and Mechanistic Considerations

Spectroscopic data indicate that **2** is present as a single species in solution (Table 1 and Exp. Sect.). The fluxional solution behaviour of the ligands in **2a** and **2c** was examined by variable temperature $^{13}C\{^1H\}$ NMR studies, and typical results for **2a** in the OMe region between 195 and 270 K are presented in Figure 2. Limiting ^{13}C NMR spectra in the methyl or methylene regions consistent with structures **2a** and **2c** were obtained at 195 and 183 K, respectively. Two resonances in each spectrum are visible at these temperatures, indicating that the two OCH_3 (**2a**) and the two OCH_2 groups (**2c**) are inequivalent. As the temperature is raised from 183 to 270 K, these two signals broaden and coalesce into a single resonance, at 230 K (δ ≈ 59.3) for **2a** and 270 K (δ ≈ 68.9) for **2c**, the chemical shift of which is the weighted average of those of the two methyl or methylene groups in the limiting spectra. The activation barriers of the observed dynamic processes, estimated from the chemical shift difference ($\Delta\nu$) and coalescence temperature (T_c [9]) of the OCH_3 and CH_2 signals, are presented in Table 3. The most obvious route to high-temperature equivalence of the two OCH_3 or OCH_2 groups is rotary motion around the $C_\alpha-C_\beta$ axis. However, rotation about such a multiple bond [$C_\alpha-C_\beta$ 1.384(3) Å in **2a**] would seem at first sight to require an activation energy higher than those estimated for **2a** and **2c** (Table 3). A more elaborate explanation for the fluxionality involves a flip of the π-allyl system from Fe(2) to Fe(1). This would require simultaneous transfer of the Fe(1)−S bond to Fe(2) and of the Fe(2)−C_α and

Fe(2)−C_γ bonds to Fe(1). Both Fe−C_β bonds are conserved, so that C_β momentarily has sp^3 hybridisation (Scheme 3), which permits free rotation about C_α−C_β and averaging of the OR groups attached to C_α, as well as of the CO environments at Fe(1) and Fe(2).

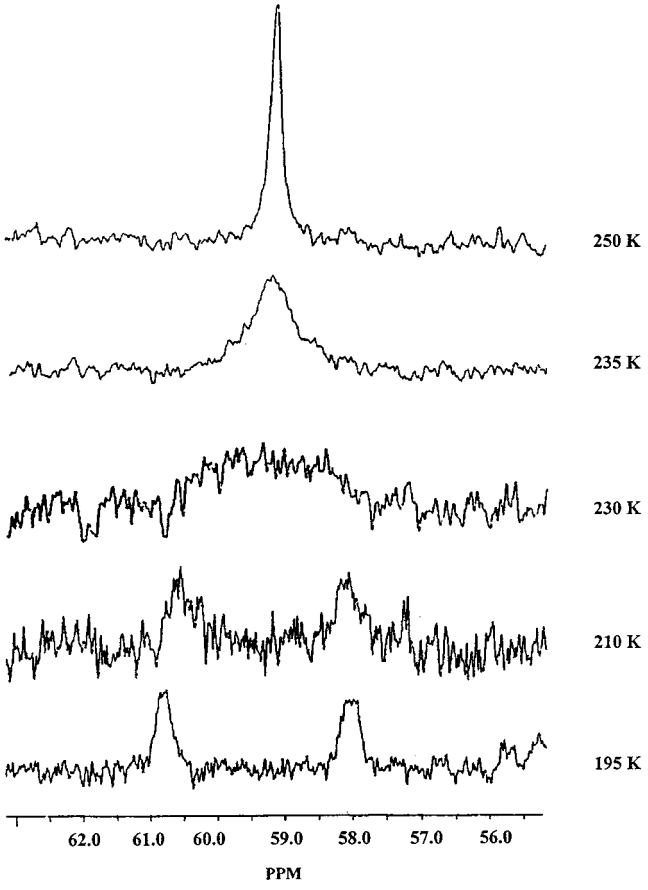
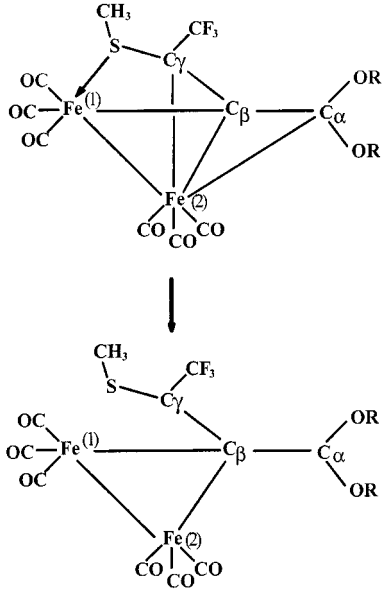


Figure 2. Variable-temperature $^{13}C\{^1H\}$ NMR spectra in the methyl region of **2a** in CD_2Cl_2

The $^{13}C\{^1H\}$ NMR spectra of **2a** and **2c** in the carbonyl region are also temperature-dependent; the low-temperature resonances are averaged as the temperature is increased. The spectrum of **2c** in the CO region between 183 and 298 K is presented in Figure 3 as an example. At 183 K, the spectra of **2a** and **2c** both show six singlets of equal intensity, but three of them are broad. On the basis of previous data for the parent fluorovinyl complex **1**,[6] we tentatively assign the broad resonances to the CO groups coordinated to Fe(1) and the three sharper singlets to the carbonyl groups attached to Fe(2). As the temperature is increased, the three signals assigned to the carbonyl groups bound to Fe(1) broaden still further and finally collapse at 213 and 250 K for **2c** and **2a**, respectively. At still higher temperatures, the signals for the three Fe(2)-bound carbonyl groups broaden and collapse, at about 240 K for **2a** and 270 K for **2c**, to a single broad resonance. Above 270 K the lines again sharpen, producing high-temperature spectra that consist of two singlets at 298 K. All these changes were found to be reversible. These observations indicate that all the carbonyl ligands take part in local CO exchange processes on the two iron atoms. The low values of the energy barriers associated with these site exchanges (Table 3) are roughly of the order expected for localised scrambling of the carbonyl groups on metal atoms.[10] The observed exchange of carbonyl groups at Fe(1) involves scission of only two bonds, whereas localised exchange at Fe(2) requires the rupture of at least three. Since Fe(2) is bonded to both C_α and C_β, it is perhaps to be expected that the energy barriers associated with scrambling of the R substituents in C_β−$C_\alpha(OR)_2$ and those associated with carbonyl exchange at Fe(2) are very similar (Table 3). It is also worth noting



Scheme 3

Table 3. Dynamic $^{13}C\{^1H\}$ NMR spectroscopic data

Compd.	Resonance	T_c [K][a]	Δν [Hz][b]	$\Delta G^{\ddagger}_{T_c}$ [kJ mol^{-1}][c]
2a	$C_\alpha(OCH_3)_2$	230	203	44.1
	$Fe(1)(CO)_3$	250	193	48.3
	$Fe(2)(CO)_3$	240	442	44.6
2c	$C_\alpha(O-CH_2-CH_2-O)$	270	188	52.4
	$Fe(1)(CO)_3$	213	450	39.3
	$Fe(2)(CO)_3$	270	332	51.1

[a] Coalescence temperature. [b] Frequency difference between resonances of exchanging groups at low-temperature limit. [c] Highest error limit: ± 1 kJ mol^{-1}.

that the higher-energy process concerns CO movement at Fe(1) in **2a** but at Fe(2) in **2c**, which may indicate that the coordination modes of the $C_\beta-C_\alpha(OR)_2$ ligands to the iron atoms differ in **2a** and **2c**.

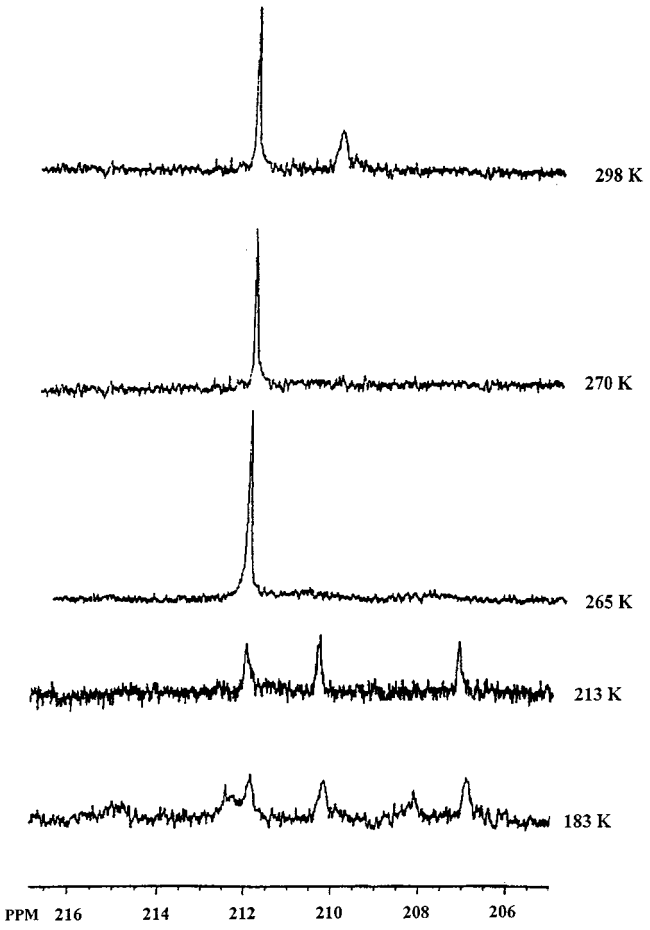
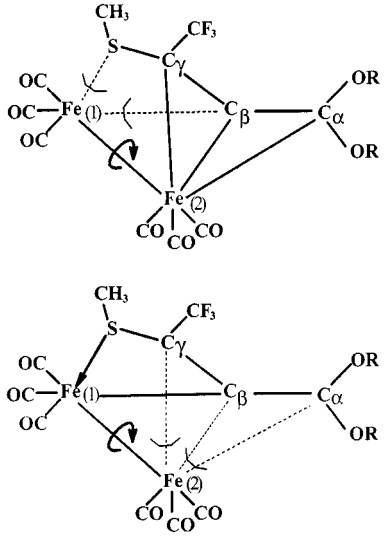


Figure 3. Variable-temperature $^{13}C\{^1H\}$ NMR spectra in the carbonyl region of **2c**, in CD_2C1_2



As mentioned above, the reactions between **1** and excess alcohol depend critically on the conditions; both the nature of the alcohol and that of the solvent greatly influence the reaction rates. Thus, in THF at room temperature, the reactions of **1** with methanol, ethanol and ethylene glycol were complete in 2, 3 and 5 h, respectively. The same reactions in dichloromethane were very slow at room temperature and heating was necessary to provide acceptable yields of **2**. Evidently, the solvent is involved in the mechanism of the reaction between **1** and a large excess of alcohol. Monitoring of the reaction of **1** with 40 equiv. of methanol in $[D_8]$THF by ^{19}F NMR at room temperature showed the gradual disappearance of **1** and the formation of several fluoro intermediates, **2a** being the last in this sequence. As the reaction proceeded, several fluoro complexes were present together in solution, giving rise to complicated ^{19}F NMR patterns from which it was difficult to identify the intermediates. Since the reaction depends markedly upon the nature of the solvent, it probably involves a transient, THF-containing intermediate. There is evidence that such a species plays a role in the reaction between **1** and Me_2NH.[4d]

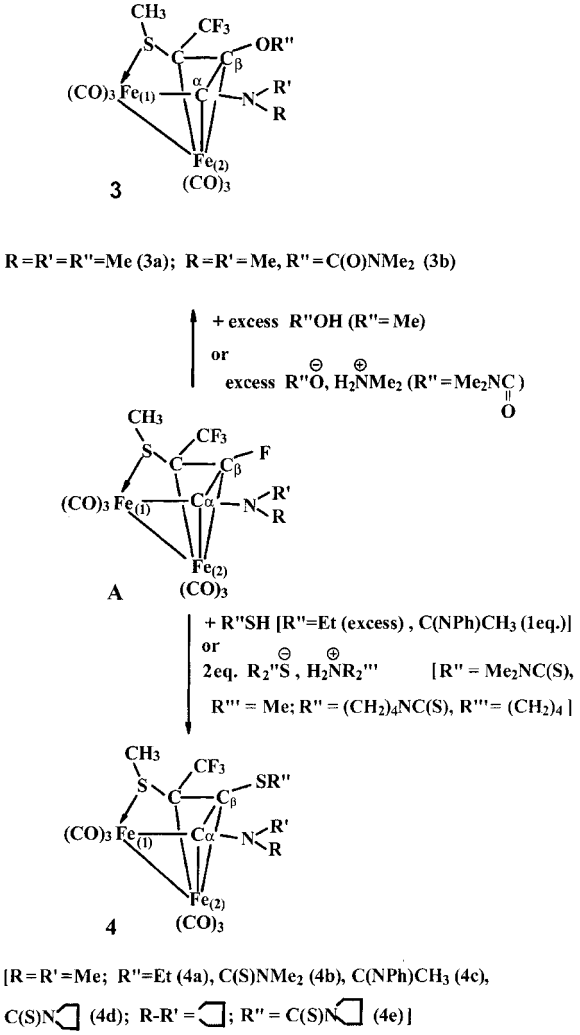
2. Reactions between Monofluorothiaferracyclopentadiene Compounds of Types A, D and F and Nucleophiles

Synthesis and Spectroscopic Characterisation of Complexes 3 and 4

We have previously shown that hard nucleophiles (Nu) such as amines react with the (perfluorovinyl)diiron complex **1**, $[\{Fe(CO)_3\}_2\{\mu\text{-}CC(SMe)(CF_3)C_\beta C_\alpha F_2\}]$, by attack at C_α, activating both vinylic C−F bonds, to give only α adducts containing either a thiaferracyclopentadiene $Fe(1)C_\alpha(Nu)C_\beta(F)C(CF_3)S(Me)$ ring (compounds of type **A**) or a thiaferracyclobutene $Fe(1)S(Me)C(CF_3)C_\beta\text{-}\{C_\alpha(NRR')_2\}$ ring.[4d] In contrast, soft nucleophiles (Nu) (phosphanes, tertiary phosphanes, thiols) react only at C_β, activating only one vinylic C−F bond to give β adducts containing a thiaferracyclopentadiene $Fe(1)C_\alpha(F)C_\beta(Nu)\text{-}CCF_3)S(Me)$ ring (compounds of type **D** or **F**).[4c] It was therefore of interest to see how hard and soft nucleophiles activate the C−F bonds in monofluoro complexes of types **A**, **D** and **F**.

Accordingly, the aminofluorothiaferracyclopentadiene complex **A** (R = R′ = Me) in dichloromethane was treated with large excesses of either methanol or dimethylammonium dimethylcarbamate. The alkoxythiaferracyclopentadiene complexes **3a** and **3b** were formed quantitatively as red or orange microcrystalline solids, respectively (Scheme 4). Soft nucleophiles, such as thiols and dialkylammonium dialkyldithiocarbamates, also react with **A** in dichloromethane to afford high yields of new complexes **4a**−**4e** as orange or red crystalline solids (Scheme 4). Evidently, addition of both hard and soft nucleophiles to **A** results in activation and cleavage of the $C_\beta-F$ bond.

However, treatment of **D** and **F** with nucleophiles, both soft (thiols, phosphanes) and hard (methanol, primary and secondary amines), in dichloromethane produced no reac-



Scheme 4. Synthesis and proposed structures of complexes **3**−**4**

tion (Scheme 5). It thus appears that the vinylic C−F bond is unreactive towards nucleophiles when the fluorine atom is bound to C_α of a *mono*fluorothiaferracyclopentadiene derivative.

It is clearly apparent from the NMR spectroscopic data in Table 1 that the product compounds **3** have the same basic structure as their parent complex **A**. The ^{19}F and ^{13}C NMR spectra are consistent with the formation of **3** from **A** by rupture of the C_β−F bond and replacement of the fluorine atom by an alkoxy group. The $^{13}C\{^1H\}$ NMR spectra contain quadruplets indicative of coupling to a CF_3 group at δ = 189.1 (**3a**) and 198.6 (**3b**); these chemical shifts and the very small $^{13}C-^{19}F$ coupling constant, $^4J_{C,F}$ = 2 Hz, are consistent with the carbon atom responsible being positioned α to Fe(1) in the Fe(1)$C_\alpha C_\beta C_\gamma(CF_3)$S(Me) ring. The assignments of the other quaternary carbon atoms of the thiaferracyclopentadiene ring were then made on the basis of their observed $^{13}C-^{19}F$ coupling constants and chemical shifts. In the highfield regions of **3a** and **3b**, quadruplets at δ = 54.0 ($^2J_{C,F}$ = 34 Hz) and 51.9 ($^2J_{C,F}$ = 35 Hz) were found for the carbon atoms of the $C(CF_3)$ unit. The singlet resonances at δ = 122.5 (**3a**) and 102.0 (**3b**) are attributable to C_β, since a similar chemical shift was observed for the C_β atom (δ = 120.0) in the parent complex **A**. Signals due to the methoxide group were observed at δ = 59.9 in the ^{13}C NMR spectrum and δ = 3.66 in the ^1H NMR spectrum of **3a**. A lowfield resonance at δ = 154.7 in the ^{13}C NMR spectrum of **3b** was assigned to the carbonyl group of the dimethylcarbamoyl unit; the medium band at $\tilde{\nu}$ = 1725 cm^{-1} in the IR spectrum of **3b** is consistent with this attribution.

All compounds **4** may easily be identified from their mass and NMR spectra and elemental analyses. The upper parts of their mass spectra are characterised by the molecular ion peak $[M]^+$ and ion peaks of the sequence $[M^+ - nCO]$ (n = 1−6). The close similarities between the NMR spectra of **4** and those of complex **F**[4c] (Table 1) strongly suggest that all six compounds contain the same Fe(1)C(X)C(SR)$C(CF_3)$S(Me) ring (X = F or NRR′) π-bonded to an $Fe(CO)_3$. It is worth noting that in the ^{13}C NMR spectra the signals of the β-carbon atoms of the thiolato complexes **4** appeared at higher field ($\Delta\bar{\delta}$ = 37) than the corresponding signals from the alkoxo compounds **3**. This highfield shift is consistent with linkage of C_β to the "soft" polarizable sulfur atom rather than the "hard" oxygen nucleophile. In the lowfield part of the $^{13}C\{^1H\}$ NMR spectra of **4b**, **4d** and **4e**, resonances typical of the thiocarbamate groups occur at δ = 197.3, 192.6 and 194.9, respectively.

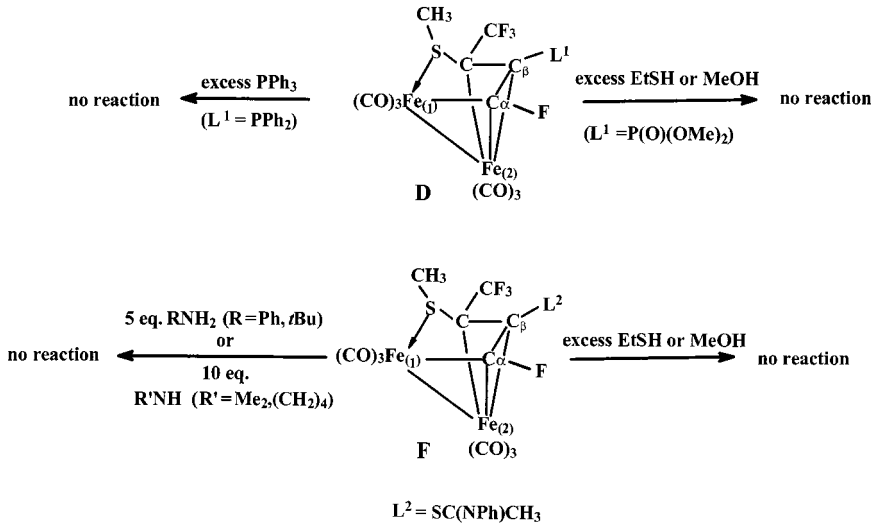
Single-Crystal X-ray Analysis of 3b

The solid-state structure of **3b** (Table 2, Figure 4) fully confirms the conclusions drawn from the solution spectra and is qualitatively similar to that of the parent complex **A**[4a] in that it contains a metallated, butadiene-like Fe(1)=C_α(11)−C_β(10)=C_γ(8) unit π-bonded to Fe(2), the Fe(2)−C_α bond being especially weak. However, as in the parent complex, there is extensive electron delocalization along the Fe(1)=C_α−C_β=C_γ chain, as shown by the sequence of distances [2.000(6), 1.415(8) and 1.431(8)/1.997(6), 1.428(8) and 1.469(8) Å] in the two independent molecules. The Fe(1)−C_α bonds in **3b** are the longest in Table 2, suggesting that C_α here has only a small amount of carbene-like character;[4b,4c,7] this is consistent with the comparatively highfield resonance (δ = 198.6) attributable to this carbon atom in the $^{13}C\{^1H\}$ NMR spectrum. The $C_\alpha-C_\beta-C_\gamma-C_\delta$ torsion angles in **3b** [−171.0(6) and −168.9(6)°] are typical of the values in thiaferracyclopentadiene complexes and contrast with that in **2a** [−43.9(3)°], which presumably resembles the value in the parent complex **1.**

3. Reactions between Compound 1 and Primary Aromatic and Multifunctional Amines

Synthesis of Complexes 5

We have shown that C−F bonds in **1** can be activated by primary[4a] and secondary[4b] monoamines, which have similar basicities according to Pearson.[5] These reactions



Scheme 5. Reaction of **D** and **F** species with nucleophiles

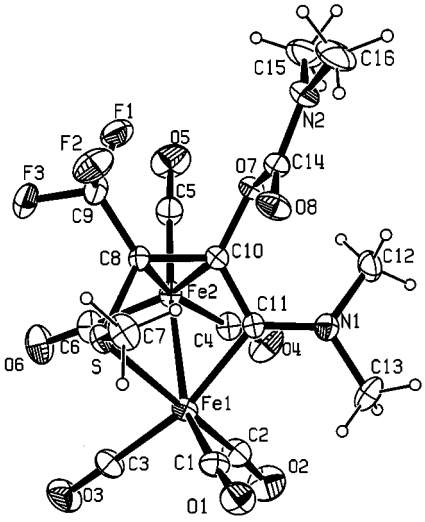
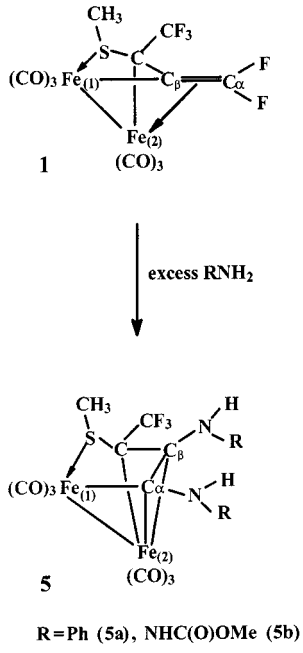


Figure 4. The structure of one of the two independent molecules of **3b** in the crystal; throughout this paper a common atom numbering system has been used for crystallographically independent molecules; selected bond lengths [Å] and angles [°]: O(7)−C(14) 1.369(8)/1.377(7), O(7)−C(10) 1.418(7)/1.405(6), O(8)−C(14) 1.217(8)/1.198(7), N(1)−C(11) 1.356(8)/1.345(7), N(1)−C(13) 1.448(8)/1.450(9), N(1)−C(12) 1.477(9)/1.478(8), N(2)−C(14) 1.332(9)/1.341(8), N(2)−C(15) 1.469(11)/1.441(9), N(2)−C(16) 1.462(10)/1.453(9); C(14)−O(7)−C(10)−C(11) 80.3(8)/75.2(8), C(12)−N(1)−C(11)−C(10) 20.8(10)/19.0(9), C(11)−C(10)−C(8)−C(9) −171.0(6)/−168.9(6)



Scheme 6. Synthesis and proposed structures of complexes **5b**

give rise to substitution patterns that markedly depend on the strength of the attacking nucleophile in the carbon chain of the complex. We therefore decided to investigate the reaction between **1** and both aniline, a base of medium strength according to Pearson,[5] and also (methoxycarbonyl)hydrazine, $H_2NNHC(=O)OMe$, which contains potentially competitive primary and secondary amine functions. Compound **1** was treated with excess quantities (3−4 equiv.) of either aniline or (methoxycarbonyl)hydrazine in dichloromethane at room temperature. The α,β adducts **5a** and **5b** were formed as orange, microcrystalline solids in high yields (Scheme 6).

Elemental analysis, together with mass and NMR spectroscopy, indicated that the reaction of **1** with (methoxycarbonyl)hydrazine paralleled that with aniline. Both reactions gave thiaferracyclopentadiene products of the type $[\{Fe(CO)_3\}_2\{\mu\text{-}C(SMe)(CF_3)C(NHR)C(NHR)\}]$. Thus, in these reactions the (methoxycarbonyl)hydrazine behaves as a primary amine.

Single-crystal X-ray Analyses of Compounds 5a and 5b

The structures of **5a** and **5b** (Figures 5 and 6, Table 2) are based on an $Fe(1)S(1)C_\gamma C_\beta C_\alpha$ thiaferracyclopentadiene ring. The butadiene-like $Fe(1)=C_\alpha-C_\beta=C_\gamma$ unit π-bonds to

the $Fe(2)(CO)_3$ group. The bridging organic group is thus derived formally from the vinylic ligand in **1** through the loss of two fluorine atoms from C_α and the addition of a single NHR group to both C_α and C_β. Several diiron complexes containing the same $[\{(OC)_3Fe(1)S(Me)C_\gamma(CF_3)C_\beta(R^2)C_\alpha(R^1)\}Fe(2)(CO)_3]$ skeleton have now been characterised; they include **3b**, **6a**, and $[\{Fe(CO)_3\}_2\{\mu\text{-}C(SMe)(CF_3)C(PPh_2)CF\}]$ (**D**),[4c] as well as **5a** and **5b**. Some structural features characteristic of this group (see Table 2) are worth noting:

(a) The $Fe(1)S(Me)C_\gamma(CF_3)C_\beta C_\alpha$ rings are distorted envelopes with S at the flap, the S−Me bond axial, and the $C-CF_3$ bond equatorial, so that the $C_\alpha-C_\beta-C_\gamma-CF_3$ torsion angle is close to 180° (range 169−176°).

(b) Where possible, conjugation is maximised across $C_\alpha-R^1$ but minimised across $C_\beta-R^2$; in **5a**, for example, the C−C−N−Ph torsion angles are close to 180° across C7−N1, permitting π-overlap, but close to 90° across C8−N2, precluding it. This is consistent with the shortness of the C7−N1 bonds (1.35 Å) compared those across C8−N2 (1.41 Å). It can be argued that similar effects operate in **3b** and **5b**.

(c) Corresponding bond lengths are remarkably constant, except for the $Fe(1)-C_\alpha$ and $Fe(2)-C_\alpha$ distances (Table 2). Both of these bonds shorten as the substituent at C_α becomes more electron-withdrawing along the series NMe_2 (**3b**) < NHPh (**5a**) < $NHNHCO_2Me$ (**5b**) < $N(NH_2)R$ (**6a**) < F [**D**: $Fe(1)-C_\alpha$ = 1.918(3), $Fe(2)-C_\alpha$ = 2.073(3) Å]. The weak $Fe(2)-C_\alpha$ bonds shorten by 0.28 Å across this series. This can be explained in terms of the occurrence of two alternative structures, shown for **5a** in Scheme 7. Electron release by the substituent at C_α should stabilise the zwitterionic form **II** at the expense of the thiaferracyclopentadiene structure **I**, weakening $Fe(2)-C_\alpha$ but also discouraging $Fe(1)\rightarrow C_\alpha$ back-donation.

The structural features of the recently reported σ-η^3-allylic complex $[\{Fe(CO)_3\}(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1(P):\eta^3(C)\text{-}(C)(Ph)C(Ph)C(H)C(=CH_2)PPh_2\}]$[11] are similar to those of the compounds discussed here.

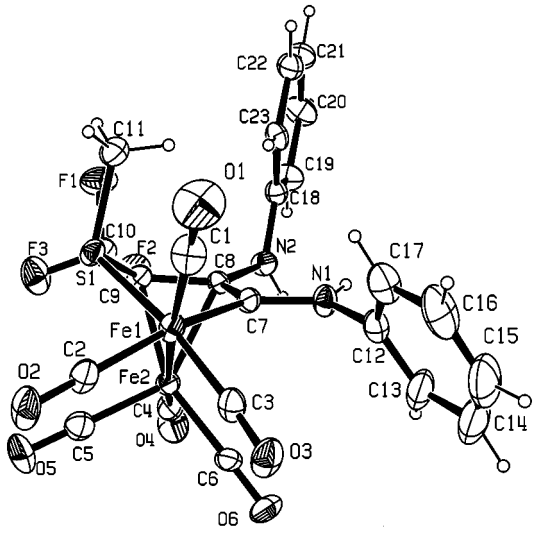


Figure 5. Molecular structure and numbering scheme of compound **5a** in the crystal; only one of the two independent molecules is shown; selected bond lengths [Å] and angles [°]: N(1)−C(7) 1.353(6)/1.353(6), N(1)−C(12) 1.420(8)/1.421(7), N(2)−C(18) 1.407(7)/1.412(6), N(2)−C(8) 1.443(6)/1.422(6), C(7)−C(8)−N(2)−C(18) −82.6(6)/−97.0(6), C(8)−C(7)−N(1)−C(12) −175.8(5)/− 172.1(6), C(7)−C(8)−C(9)−C(10) 172.2(5)/172.1(5)

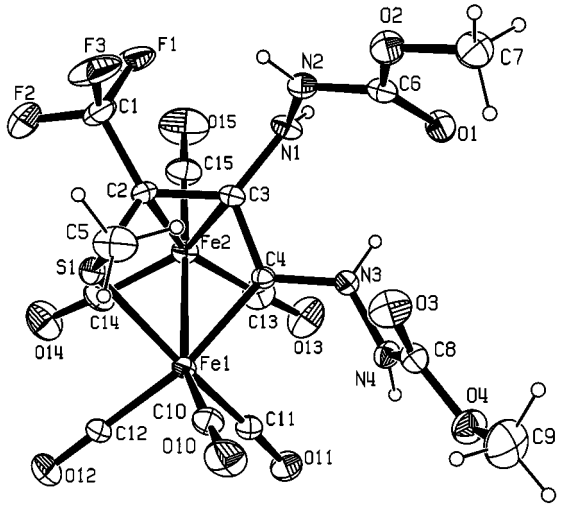
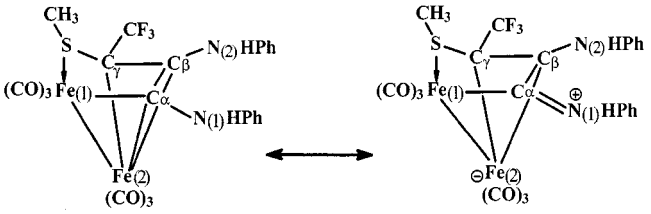


Figure 6. Molecular structure and numbering scheme of compound **5b** in the crystal; only one of the two independent molecules is shown; selected bond lengths [Å] and angles [°]: O(1)−C(6) 1.204(7)/1.202(7), O(2)−C(6) 1.336(7)/1.338(7), O(2)−C(7) 1.451(9)/1.429(9), O(3)−C(8) 1.197(8)/1.197(8), O(4)−C(8) 1.319(8)/1.349(8), O(4)−C(9) 1.447(11)/1.437(11), N(1)−N(2) 1.411(7)/1.405(8), N(1)−C(3) 1.440(7)/1.435(7), N(2)−C(6) 1.348(8)/1.351(9), N(3)−C(4) 1.370(7)/1.365(7), N(3)−N(4) 1.388(7)/1.383(7), N(4)−C(8) 1.371(8)/1.361(8); C(4)−C(3)−N(1)−N(2) −90.0(6)/−86.3(7), C(3)−C(4)−N(3)−N(4) 164.9(5)/168.0(5), C(4)−C(3)−C(2)−C(1) 173.2(6)/171.5(6)

Spectroscopic Characterisation of Complexes 5 and Mechanistic Considerations

The solid-state structures of **5a** and **5b** have definitively been shown to persist in solution by IR and NMR spectroscopy (see Table 1 and Exp. Sect.). The IR spectra in CH_2Cl_2 show four ν(CO) bands in the 2075−1950 cm^{-1} range, corresponding to the Fe-bound terminal carbonyl groups, along with a characteristic band at 1720 cm^{-1} (**5b**), which confirms the presence of the $NHNHC(O)OCH_3$ group. The ^{19}F and ^{13}C NMR spectra are also consistent with the structures proposed for **5a** and **5b**. In particular, the ^{19}F NMR spectra of **5a** and **5b** no longer contain the vinylic CF resonances typical of **1**, but do retain the peaks due to the CF_3 group. In the $^{13}C\{^1H\}$ NMR spectra, the quadruplets assigned to the metallated carbon atoms (C_α) appear at δ = 202.0 (**5a**) and 210.7 (**5b**), with C−F coupling constants (^4J) of about 2 Hz. These resonances are shifted to high field relative to that seen for the closely related phosphanyl complex $[\{Fe(CO)_3\}_2\{\mu\text{-}C_\alpha(F)C_\beta(PPh_2)\text{-}C_\gamma(CF_3)S(CH_3)\}]$ (**D**),[4c] indicating that C_α possesses a less carbene-like character in **5a** and **5b** than in the phosphanyl complex, in conformity with the trends in $Fe-C_\alpha$ bond lengths discussed in the preceding section. Atom C_β gives rise to singlets at δ = 91.6 for **5a** and δ = 93.5 for **5b**, and atom C_γ to quadruplets at δ = 53.4 for **5a** and δ = 52.5 for



Scheme 7

5b, with C−F coupling constants (^2J) of about 33 Hz. The ^{1}H NMR spectra show lowfield resonances at δ = 8.50 (**5a**) and 9.46 (**5b**), characteristic of iminium protons, along with peaks at δ = 4.60 (**5a**) and 4.64 (**5b**), corresponding to the amino protons. In addition, the ^{1}H NMR spectrum of **5b** contains two broad singlets at δ = 6.55 and 6.85, attributable to the amino protons α to the methoxycarbonyl group. Thus, the ^{1}H NMR spectroscopic data clearly indicate that there is an iminium group at $C_α$ but an amino group at $C_β$ in **5a** and **5b**; in solution it is possible that there is an increased contribution from **II** to the overall structure (Scheme 7).

The reactions producing **5a** and **5b** were carried out at low temperature in order to detect possible intermediates. In the event, only one intermediate was found when either aniline or methyl hydrazinocarboxylate reacted with **1**. The reaction between **1** and aliphatic amines[4d] involves the initial formation of a stable fluoro−zwitterionic intermediate [**B**] (see Scheme 1). However, when **1** reacts with excess aniline (3 equiv.) or methyl hydrazinocarboxylate (4 equiv.), instead of [**B**] the only intermediate detected was the doubly substituted species [**f**] (Scheme 8). After 5 h, the relative amounts of [**f**], **1** and **5** were 47, 29 and 24%, respectively. The ^{19}F and ^{13}C{^{1}H} patterns of [**f**] are similar to those of neutral (alkoxymethylene)thiaferracyclobutene compounds (such as **2a**, **2b**; see Table 1) and to those of zwitterionic (diaminomethylene)thiaferracyclobutene derivatives such as **C**. Now, these species are mainly differentiated from one another by the $C_β$ atom resonances, which occur at δ = 70.0−90.0 for the zwitterionic complexes and at δ = 115.0−130.0 for neutral species (see Table 1). In view of this, a zwitterionic structure is proposed for [**f**], which has a chemical shift of δ = 95.6 for the $C_β$ atom (Scheme 8). Conversion of **f** into the final product requires the transfer of one amido group from $C_α$ to $C_β$. This probably occurs through a double intramolecular migration, from $C_α$ to the metal ion and from there to $C_β$, as postulated in Scheme 8.

4. Reactions between Compound 1 and Multifunctional Thioamines

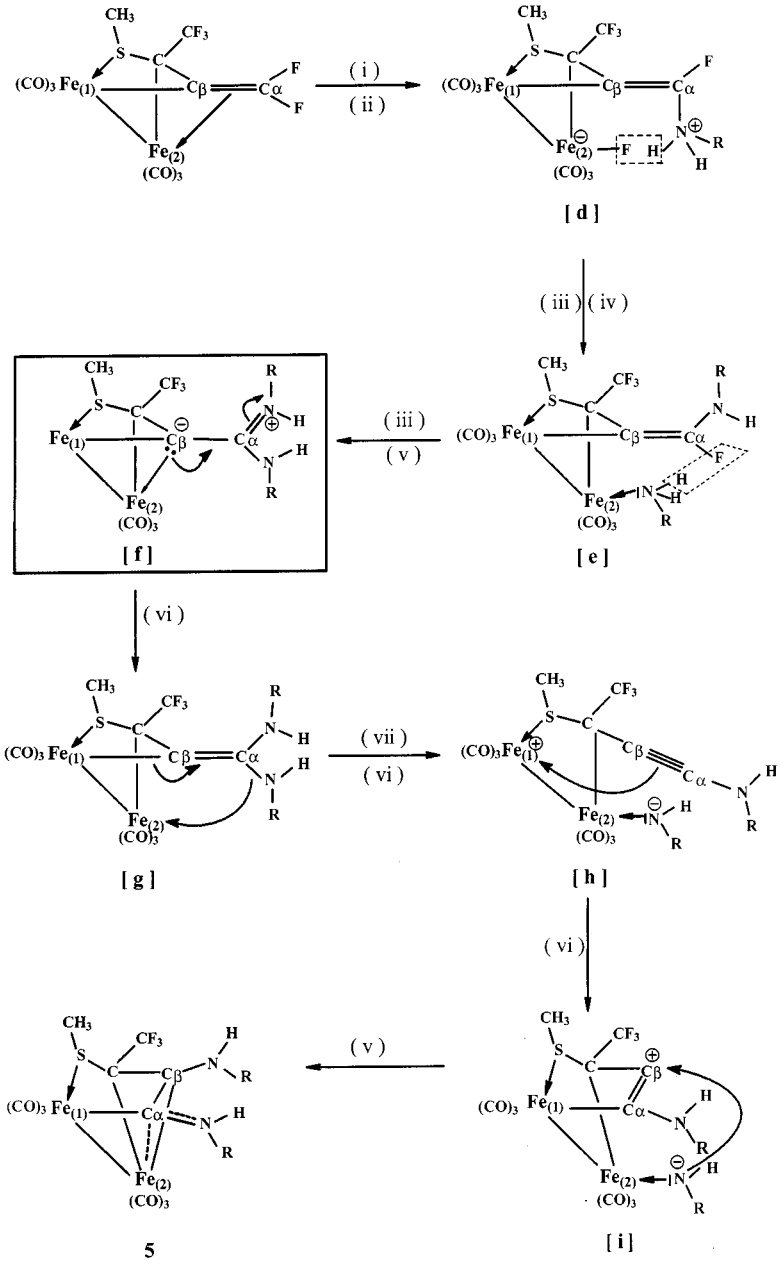
Synthesis and Characterisation of Complexes 6

In the preceding section it was shown that methoxycarbonylhydrazine, although it contains three "hard" and potentially competitive base functions (carbonyl, primary amine and secondary amine), acts only as a primary amine to cleave both C−F bonds of **1**. We speculated that the choice of the nucleophile might be pivotal to the regiochemistry of the C−F activation. We therefore treated **1** with three thioamines containing competitive "hard" amine and "soft" thione functions, namely, MeNHC(S)NHR, R = NH_2, H and Me.

Treatment of **1** with equimolar amounts of 4-methyl-3-thiosemicarbazide in tetrahydrofuran at room temperature resulted in the formation, in high yields, of the N-α,S-β adduct **6a** (Scheme 9). Similar results were obtained with methyl- and dimethylthioureas; complexes **6b** and **6c** were isolated as orange powders (Scheme 9). All the complexes have been characterised by ^{1}H NMR, ^{19}F NMR, ^{13}C NMR and IR spectroscopy and by mass spectrometry and microanalysis (see Table 1 and Exp. Sect.) and, in addition, complex **6a** has been the subject of a single-crystal X-ray diffraction study.

It is immediately apparent from examination of the spectroscopic data that all the complexes **6** have the same basic structure. The close similarity of their ^{13}C NMR spectra with those of compounds **4** (see Table 1) strongly suggests that **4** and **6** contain similar five-membered rings [$FeC_α(NR)C_β(SR)C(CF_3)S(CH_3)$]. The ^{19}F NMR spectra showed only single trifluoromethyl resonances at δ ≈ − 59.0, confirming that the two vinylic C−F bonds had been cleaved. The ^{1}H NMR spectrum of **6a** displayed three singlets in a 2:3:3 ratio, two at δ = 4.67 and 3.18 corresponding to the amino[12] and the methylimino[13] groups, respectively, and the more upfield line (δ = 1.87) to the SMe ligand.[4d] The ^{1}H NMR spectrum of **6b** differs from that of **6c** only by the presence, in a 1:3 ratio, of a lowfield signal at δ = 7.59 for the C=NH imino group in **6b** versus a higher field peak at δ = 3.15 assignable to the methylimino function in **6c**.[14] Otherwise, complexes **6b** and **6c** showed similar ^{1}H NMR patterns, in particular they displayed two signals at δ ≈ 3.7 and 1.9, which were assigned to the methylamino[14] and SMe[4d] groups, respectively. The ^{1}H NMR spectroscopic data clearly indicated the presence in **6** of a $R^1NC(=NR^2)S$ unit (R^1 = NH_2 or CH_3, and R^2 = H or CH_3) derived from the parent thioamine, as depicted in Scheme 9. This was confirmed by the ^{13}C NMR spectra, in which typical C=N resonances were observed at δ ≈ 160, and by the IR spectra in which strong C=N stretching bands were seen at ca. 1625 cm^{-1}. To complete the characterisation, an X-ray diffraction study of **6a** was undertaken.

The structure of **6a** (Figure 7) is derived from **1** through the loss of two fluorine atoms from $C_α$; a new ring is formed by attachment of a hard N-donor function of the thioamide to $C_α$ and of the softer thione S atom to $C_β$. As in **3** and **5**, the Fe(1) atom is now bound to $C_α$, completing a $Fe(1)C_αC_βC(CF_3)S(CH_3)$ metallacycle. The short Fe(1)−$C_α$ bonds [1.947(7) and 1.936(7) Å] imply that $C_α$ has some carbene-like character,[4b,4c,7] and this conclusion is confirmed by the highfield resonance (δ = 205.3) attributable to this carbon atom in the ^{13}C{^{1}H} NMR spectrum. The C(4)N(1)C(5)S(2)C(3) heterocycle formed by coupling

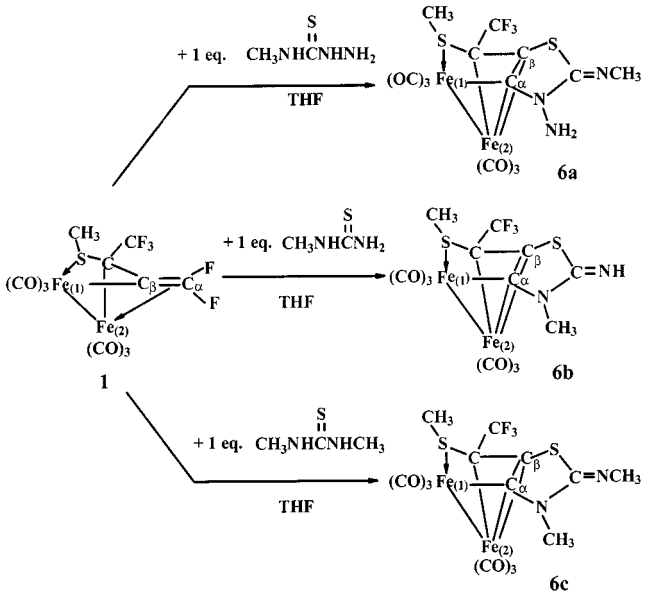


Scheme 8. Possible pathway to the formation of diaminothiaferracyclopentadiene derivatives **5**: (i) α-elimination of F; (ii) nucleophilic attack of RNH_2 at C_α; (iii) − HF; (iv) + RNH_2; (v) amino migration; (vi) internal rearrangement; (vii) α-elimination of NHR

of the 4-methyl-3-thiosemicarbazide to the coordinated $CCC(CF_3)SMe$ ligand is coplanar within ±0.03Å. The shortness of the C(5)−N(3) bonds [1.268(8) and 1.242(8) Å] compared to the C(13)−N(3) distances [1.471(9) and 1.469(9) Å] is consistent with the presence of a localised C(5)=N(3) double bond. The S(2)−C bond lengths (Figure 7, caption) suggest bonds of unit order, while the C_α−N(1) distances [1.382(8) and 1.361(8) Å], though longer than corresponding bonds in **5a** or **5b**, imply some multiple character.

Similar structural examples of diiron or diruthenium thiametallacyclic μ-C(R)C(R)C(R)S(R′) or phosphametallacyclic μ-C(R)C(R)C(R)P(R′)$_2$ ligands include [{$Fe(CO)_3$}$_2$-{μ-C(OEt)C(H)C(Ph)S(*t*Bu)}] (**I**)[15], [{$Fe(CO)_3$}$_2$(μ-C(Ph)-C(R)C(R′)P(Ph)$_2$}] (**J**)[16], [{$Ru_2(CO)_5X_2$}{μ-C(C_2H_5)-C(R)C(R′)S(C_2H_5)} (**K**)[17], as well as the complexes **3**−**5** and **A**, **D**−**F** that we have described previously.[4] The conformations of the μ-C(R)−C(R)−C(R)−X′(R_n) ligands [X′ = S (n = 1), P (n = 2)] in the complexes described by other authors[15−17] are very similar to those we have found in **6** and its close relatives.

Although two isomers, **6a$_1$** and **6a$_2$** (Scheme 10), could result from the reaction between 4-methyl-3-thiosemicarbazide and **1**, depending on whether the $NH(NH_2)$ or NHMe secondary amine function attacked the C_α atom, only one isomer is actually observed.



Scheme 9. Synthesis and proposed structures of complexes **6**

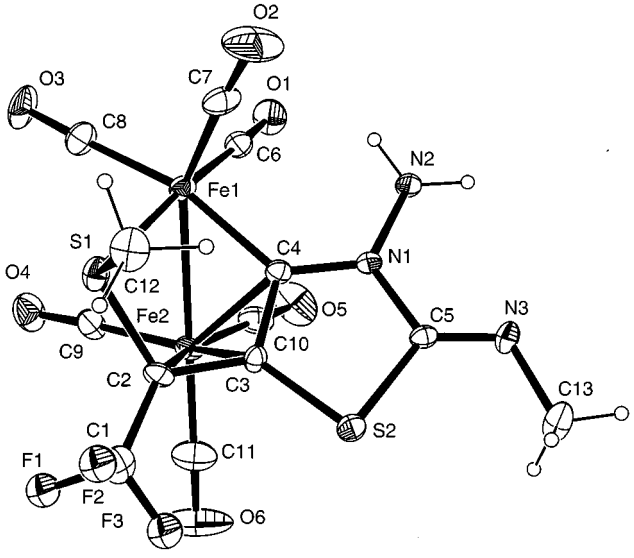
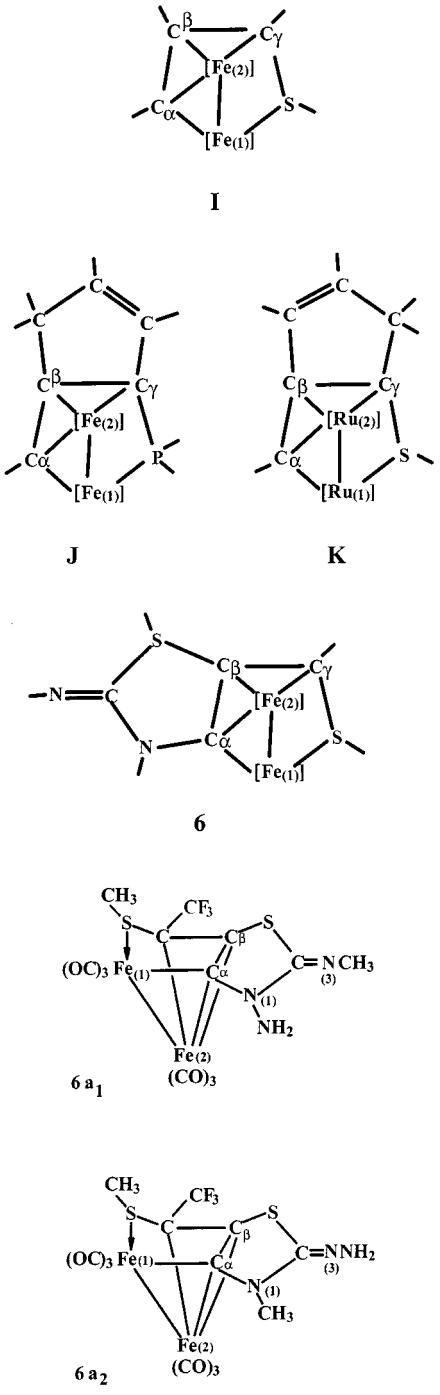


Figure 7. Molecular structure and numbering scheme of compound **6a** in the crystal; only one of the two independent molecules is shown; selected bond lengths [Å] and angles[°]: S(2)−C(3) 1.768(7)/1.762(7), S(2)−C(5) 1.776(7)/1.785(7), N(1)−C(4) 1.382(8)/1.361(8), N(1)−N(2) 1.397(7)/1.404(7), N(1)−C(5) 1.399(8)/1.407(8), N(3)−C(5) 1.268(8)/1.242(8), N(3)−C(13) 1.471(9)/1.469(9); C(4)−C(3)−C(2)−C(1) −176.3(7)/−175.9(7)

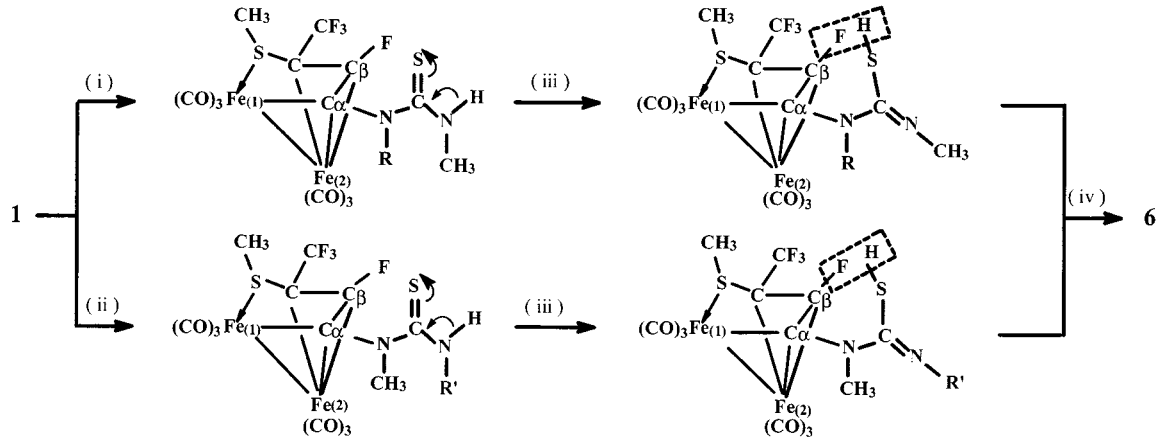


Scheme 10

The crystallographic study favours structure **6a$_1$**, but supporting evidence is desirable at this point, since **6a$_1$** and **6a$_2$** differ only in the positions of isoelectronic CH_3 and NH_2 groups. Accordingly, a ^{1}H-^{13}C 2D HMBC experiment was performed at room temperature. The carbon atom (δ = 159.4) of the imino group correlated ($^3J_{CH}$) with the hydrogen atoms of the methyl group (δ = 3.18), whereas the C_α atom (δ = 184.0) showed a correlation ($^3J_{CH}$) with the low-field resonance (δ = 4.61) due to the protons of the NH_2 group. This coupling pattern clearly showed that the amino group was attached to the nitrogen atom [N(1)], which was bound to C_α (**6a$_1$**). Similar experiments were undertaken for **6b** and revealed that the methyl group (δ = 3.71) correlated ($^3J_{CH}$) with both C_α (δ = 183.2) and the carbon atom of the imino group (δ = 166.0), thereby confirming the structure depicted in Scheme 9.

Mechanistic Considerations

It is likely that similar mechanisms are involved in the formation of **6a**−**6c**, and so we shall give only an illustrative



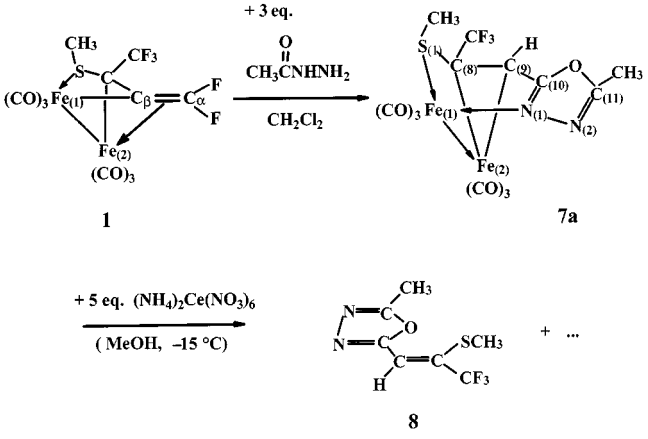
Scheme 11. Possible pathway to the formation of aminothiothiaferracyclopentadiene derivatives **6**: (i) nucleophilic attack of $CH_3-NH-C(S)-NHR$ at C_α; (ii) nucleophilic attack of $CH_3-NH-C(S)-NHR'$ (R′ = H, CH_3) at C_α; (iii) tautomerisation reaction; (iv) HF elimination

discussion of the pathway to **6a** (Scheme 11). Investigation of the reaction between **1** and 1 equiv. of thiosemicarbazide by NMR spectroscopy at low temperature did not result in the characterisation of any intermediate. However, the formation of **6a** is likely to resemble the well-established processes that produce the related thiaferracyclopentadiene derivatives of types **A**[4d] and **F**.[4c] Compound **6a** has some features in common with **A** and **F**, and all three complex types are obtained from the same parent compound **1**. The NH_2 function is preserved unchanged in **6a**, while the secondary amine and thiol functions of the thiosemicarbazide bind to the C_α and C_β atoms of **1**, respectively. If the thiol function initiated the attack, the expected product would be a ferracyclopentadiene intermediate of type **F**,[4c] which we have shown to be totally unreactive towards nucleophiles in Section 2 above. It is more likely then that **1** first reacts through a secondary amine function of the thiosemicarbazide to form a thiaferracyclopentadiene adduct of type **A**,[4d] which, as shown in Section 2, can give rise to intramolecular $C_\beta-F$ activation through a thione function tautomer of the coordinated 4-methyl-3-thiosemicarbazide, ultimately to afford complex **6a** (Scheme 11). A similar pathway to **6b** and **6c** is also summarized in Scheme 11. The main feature of these reactions is the successive activation of two C−F bonds by a nucleophile with both "hard" and "soft" functional groups, resulting in the formation of a five-membered heteroorganic ring fused to the cycloferrathiopentadiene unit.

5. Reactions between Compound 1 and Multifunctional Amides

Reaction between Compound 1 and Acetylhydrazine: Synthesis and Characterisation of Complex 7a

Since the perfluorovinyl complex **1** reacts with thioamides containing both "hard" and "soft" nucleophilic functions to give **6**, we also decided to investigate the behaviour of **1** toward multifunctional reagents containing only "hard" nucleophilic groups. On treatment of **1** with 3 equiv. of acetylhydrazine in CH_2Cl_2 at room temperature, the α,β adduct **7a** was formed (Scheme 12). It was isolated as red solid in 98% yield and has been characterised by ^1H NMR, ^{19}F NMR, ^{13}C NMR and IR spectroscopy and by mass spectrometry and microanalysis (see Table 1 and Exp. Sect.), as well as by a single-crystal X-ray diffraction study.



Scheme 12. Synthesis and proposed structures of compounds **7a** and **8**

Though the nucleophiles involved in the formation of **6a** and of **7a** are exact analogues, the molecular structure of **7a** (Figure 8, Table 2) is novel, differing significantly from that of **6a**. It consists of a dinuclear $Fe_2(CO)_6$ unit stabilized by an Fe−Fe bond and by a bridging organic group. This is derived *formally* from the vinylic ligand in **1** through the substitution of two fluorine atoms at C_α by O and N atoms of the deprotonated nucleophile and protonation of C_β. The result is a *six*-membered $Fe(1)-N(1)=C_\alpha(10)-C_\beta(9)=C(8)-S(1)$ metallacycle. There is extensive electron delocalization along the $Fe(1)-N(1)-C(10)-C(9)-C(8)$ chains, as shown by the bond length sequences [1.974(2), 1.288(3), 1.440(4) and 1.455(4) Å in molecule I and 1.964(2), 1.297(3), 1.424(4) and 1.463(4) Å in molecule II]. The

$Fe(2)(CO)_3$ unit is attached to the metallacycle through a π-interaction with the C(9)−C(8) double bond and through a direct bond to Fe(1). The Fe(1)−Fe(2) distances are long [2.794(1) and 2.799(1) Å], not unexpectedly since Fe(2) bridges across the six-membered Fe(1)-metalla ligand; shorter Fe−Fe distances of 2.591(1) and 2.643(1) Å are found in $[\{Fe(CO)_3\}_2\{\mu\text{-}S(Me)C(CF_3)C(CN\textit{t}Bu)\}]$ and $[\{Fe(CO)_3\}_2\{\mu\text{-}S(Me)C(CF_3)C(F)C(NMe_2)\}]$,[4a] in which the second $Fe(CO)_3$ group is attached to four- and five-membered ferracyclic bridging groups, respectively.

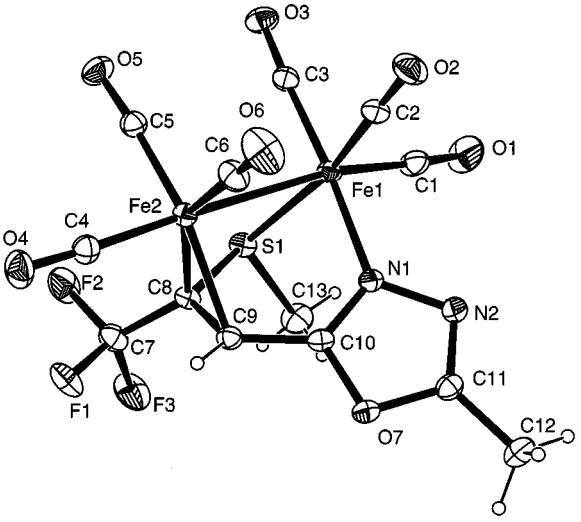


Figure 8. Molecular structure and numbering scheme of compound **7a** in the crystal; only one of the two independent molecules is shown; selected bond lengths [Å] and angles [°]: O(7)−C(10) 1.351(3)/1.359(3), O(7)−C(11) 1.368(3)/1.377(3), N(1)−C(10) 1.288(3)/1.297(3), N(1)−N(2) 1.401(3)/1.403(3), N(2)−C(11) 1.290(4)/1.282(4); C(4)−C(3)−C(2)−C(1) 140.3(3)/142.4(3)

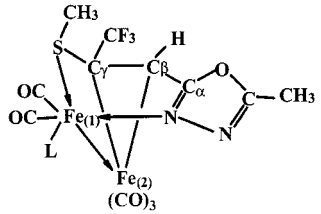
Compound **7a** contains a planar 1,3,4-oxadiazole ring formed by cyclisation of the amide nucleophile with the vinylic C_α carbon atom of **1**. The shortness of the C(10)−N(1) and C(11)−N(2) bonds [1.282(4)−1.297(3) Å] indicates some multiple character.

The solution spectra of **7a** are consistent with the solid-state structure. Four strong to medium IR bands between 2072 and 1950 cm^{-1} can be attributed to carbonyl ν(CO) stretching vibrations. A single highfield signal (δ = −66.65) in the ^{19}F NMR spectrum, typical of a trifluoromethyl resonance, provided the first indication that both C−F bonds in **1** had been cleaved. In the $^{13}C\{^1H\}$NMR spectrum, the carbon atom of the trifluoromethyl group appeared as a quadruplet at δ = 128.6 ($^1J_{C,F}$ = 274 Hz). The assignments of the three carbon atoms of the thiaazaferracyclohexene ring were made on the basis of the observed ^{13}C-^{19}F coupling constants and chemical shifts. The highfield resonances at δ = 44.6 (quadruplet; $^2J_{C-F}$ = 36.5 Hz) and 24.4 (singlet) are attributable to C(8) and C(9). The chemical shifts of these two carbon atoms suggest that they form a $C(sp^3)-C(sp^3)$ single bond rather than a $C(sp^2)=C(sp^2)$ double bond; the C(8)−C(9) distances [1.455(4) and 1.463(4) Å] lie at the upper end of the range for alkenes π-bonded to transition metal ions. The lowfield signals at δ = 175.9 and 163.0 are typical of imino-substituted carbon atoms and are attributable to C(10) and C(11). The carbonyl region contains three singlets at δ = 198.3, 211.1 and 215.6 and three broader singlets at δ = 207.6, 211.0 and 219.4, which correspond to the $Fe(1)(CO)_3$ and $Fe(2)(CO)_3$ fragments, respectively. In the ^1H NMR spectrum there are three singlets at δ = 1.87, 2.49 and 2.86 with intensities in an integral ratio of 3:3:1. The first two resonances can be assigned to the C(12) oxadiazole and S−C(13) methyl groups and the third to the methine proton attached to C(9) of the bridging heteropolycarbon fragment.

Reactions between Compound 7a and Phosphanes and between Compound 7a and Oxidants

An attempt to liberate the bridging heteropolycarbon ligand of **7a** by treatment with an excess of either phosphane (PPh_2Me) or phosphite [$P(OMe)_3$] in CH_2Cl_2 at 60 °C was unsuccessful. However, it resulted in a carbonyl substitution reaction that gave high yields of the complexes $[\{Fe(CO)_2L\}\{\mu S(Me)C(CF_3)CHC_\alpha NNC(CH_3)O(C_\alpha\text{−}O)\}\text{-}\{Fe(CO)_3\}]$ [**7b**: L = PPh_2Me; **7c**: L = $P(OMe)_3$] as red solids. All complexes other than **7a** described in this work showed marked reluctance to undergo carbonyl substitution reactions. Microanalyses of **7b** and **7c** indicated that the two complexes had similar compositions. The mass spectrum of **7c** revealed a single molecular ion peak and fragmentation peaks corresponding to the sequential loss of five carbonyl ligands.

On the basis of the close similarity of their spectroscopic data (see Table 1), structures similar to **7a** are postulated for **7b** and **7c**, with phosphane bound to the iron atom Fe(1) as shown in Scheme 13. The ^{31}P NMR spectra each display only one signal, at δ = 29.12 (**7b**) and at 157.73 (**7c**), corresponding to the terminal PPh_2Me and $P(OMe)_3$ ligands, respectively.[16] The $^{13}C\{^1H\}$ NMR spectra of **7b** and **7c** contain only five distinct resonances in the carbonyl region, two doublets at δ ≈ 215.5 and 220.0, and three broad singlets at δ = 208.2−222.8. The singlets are associated with the $Fe(2)(CO)_3$ group and the two doublets with the carbonyl groups of the $Fe(1)L(CO)_2$ unit. The magnitude of $^2J_{C,P}$ (7.5−2.0 Hz) is consistent with a *cis* arrangement of the phosphane and carbonyl groups. In other respects, the magnitude of the splitting of the methyl resonance of the thiolato group ($^3J_{C,P}$ = 8 and 6.5 Hz) confirms that the phosphane ligand is located at Fe(1) and is *trans* to the SMe



7b (L = PPh_2Me)

7c (L = $P(OMe)_3$)

Scheme 13

groups. The replacement of one carbonyl group in **7a** by an electron-releasing phosphane ligand to give **7b** or **7c** is accompanied by a shift of the resonances of the remaining carbonyl groups attached to Fe(1) to lower field compared with those attached to Fe(2). This observation confirms that the substitution reaction operated at Fe(1).

In a further attempt to decoordinate the bridging heteropolycarbon ligand, **7a** was treated at low temperature with excess ceric salt in methanol. The reaction resulted in the formation of **8** as a white solid in high yields (Scheme 12). The product was fully characterised by mass spectrometry and NMR spectroscopy (see Exp. Sect.). The mass spectrum exhibited a molecular ion, and sequential losses of methyl and oxadiazole fragments. The characterising NMR spectroscopic data of **8** were closely related to those of the parent heteropolycarbon ligand of **7a** and the ^{1}H, ^{19}F and ^{13}C NMR spectra showed the expected pattern of peaks for a 2-methyl-5-(3,3,3-trifluoro-2-methylthio-2-propenyl)-1,3,4-oxadiazole compound. Though unsubstituted and 2,5-dialkyl-1,3,4-oxadiazoles have long been known,[17] compound **8** has not previously been reported.

Conclusion

These investigations have shown that the (perfluorovinyl)-diiron complex [{$Fe(CO)_3$}$_2${μ-C(SMe)(CF_3)$C_\beta C_\alpha F_2$}] (**1**) reacts readily and cleanly with nucleophiles to give novel organometallic compounds through unusual C−F cleavage processes. This work confirms and extends our previous conclusion[4] that the pattern of reactivity depends strongly on the "hardness" or softness" of the nucleophile used in the reactions. Reactions between **1** and "hard" amines involve two C−F cleavages and migration of a fluorine atom from C_α to C_β to give exclusively α adducts with formation of Fe(1)−C_α(NR_2)−C_β(F)−C(CF_3)−S(Me) rings,[4d] while nucleophiles such as alcohol and aniline, thought to be less hard than aliphatic amines, afford either μ_2-η^1:η^2-vinyl complexes, [{Fe $(CO)_3$}$_2${μ-C(SMe)(CF_3)$C_\beta C_\alpha$($OR)_2$}] (**2**), or α,β adducts **5**, containing Fe(1)−C_α(NHR)−C_β-(NHR)−C(CF_3)−S(Me) rings. X-ray analysis of **2a** (R = Me) indicates that the μ_2-η^1:η^2-vinyl ligand [C(SMe)(CF_3)$C_\alpha C_\beta F_2$] present in **1** is maintained in **2** in the form of a dialkoxyvinyl ligand [C(SMe)(CF_3)$C_\beta C_\alpha$($OR)_2$], whereas X-ray analysis of **5** (R = Ph) demonstrates the transformation of the ligand in **1** into a new polycarbon [C(SMe)(CF_3)C_β(NHR)C_α(NHR)] chain by the action of aniline. The mechanisms proposed to account for the formation of complexes **2** and **5** both imply a double C−F bond cleavage. When **1** reacts with a thioamide containing three "hard" primary and secondary amine functions and one "soft" thiol function, the nucleophile attacks first at C_α with its secondary amine, while its primary amine function takes no part in the reaction. In a second step, the thiol function of the nucleophile attacks at C_β to give α,β adducts **6**, each containing a novel iminothiazolidine ring [C(SMe)(CF_3)C_βSC(=NR)N(R′)C_α(C_β−C_α)] fused to the five-membered metallacycle. Formation of the imino-thiazolidine ligand in **6** implies C−N and C−S couplings. When the nucleophile reacting with **1** contains only "hard" functions, namely a primary and secondary amine and a carbonyl group, the reaction involves attack by the primary amine and the carbonyl functions at C_α; two C−F bond cleavages and a 1,3-hydrogen shift from the nitrogen atom to the β-carbon atom of the vinyl ligand gives **7**. Compound **7** contains a thiaazaferracyclohexene ring to which is fused an oxadiazole fragment formed through a cyclisation reaction. Finally, it should be remarked that, while β-fluoro substituents on the $C_\alpha C_\beta C_\gamma$($CF_3$)S(Me) chain of thiaferracyclopentadiene (type **A**) complexes are readily activated by nucleophiles, α-fluoro substituents in compounds of type **D** and **F** are not cleaved by nucleophiles under the same conditions.

Experimental Section

General: All reactions were performed by Schlenk techniques under argon or nitrogen, and solvents were deoxygenated and dried by standard methods. Column chromatography was carried out with silica gel purchased from SDS and deoxygenated before use. The starting materials **1**,[18] **A**,[4d] **D**[4c] and **F**[4c] were prepared as described in the literature. All other reagents were purchased commercially. Yields are with respect to the starting clusters for the preparation of all the products. Infrared spectra were recorded with a Perkin−Elmer 1430 spectrophotometer on dichloromethane or hexane solutions. The mass spectra were measured with a GC/MS Hewlett−Packard 5595C or a GC/MS Ribermag R10−10 spectrometer at the "Laboratoire de Biochimie", Faculté de Médecine (Brest, France). Chemical analyses were performed by the "Centre de Microanalyses du CNRS de Lyon" or the "Laboratoire de Spectroscopie Atomique" at the University of Brest. The NMR spectra (^{1}H, ^{13}C, ^{19}F, ^{31}P), in $CDCl_3$ solutions, were recorded at room temperature with a Bruker AC 300 or DRX 400 spectrometer and were referenced to $SiMe_4$ (^{1}H, ^{13}C), $CFCl_3$ (^{19}F) and H_3PO_4 (^{31}P). Part of the NMR spectroscopic data for **2**−**7** and [**f**] are compared in Table 1; the remaining spectroscopic data of these complexes are reported in this section.

Synthesis of [{$Fe(CO)_3$}$_2${μ-S(Me)C(CF_3)CC($OR)_2$}] (2): A tetrahydrofuran (10 mL) solution of **1** (94.0 mg, 0.20 mmol) was treated at room temperature with 40 equiv. of alcohol (CH_3OH: 256.0 mg, 324 μL; C_2H_5OH: 369.0 mg, 542 μL). After it had been stirred for 3 h, the reaction mixture was filtered through Celite and the volatiles were removed under vacuum. The residue was then washed at −50 °C with pentane (10 mL) to give either **2a** (with CH_3OH) as an analytical pure red solid in 98% yield (97.0 mg) or **2b** (with C_2H_5OH) as an orange solid in 99% yield (103.0 mg). **2a:** $C_{13}H_9F_3Fe_2O_8S$ (493.96): calcd. C 31.6, H 1.8; found C 31.4, H 1.8. MS: *m*/*z* = 494 $[M]^+$, 466, 438, 410, 382, 354, 326 [M − *n* CO (*n* = 1−6)]$^+$, 232 [M − 6 CO − $FeFe_2$]$^+$. IR (hexane): ṽ =2077 m, 2062 w, 2032 s, 2004 s, 1983 m [ν(CO)] cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 2.2 (s, 3 H, SCH_3), 3.7 (s, 6 H, 2OCH_3). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = 65.2 (q, $^{2}J_{C,F}$ = 38.0 Hz, CCF_3), 123.1 (q, $J_{C,F}$ = 278.0 Hz, CF_3). **2b:** $C_{15}H_{13}F_3Fe_2O_8S$ (522.01): calcd. C 34.5, H 2.5; found C 34.3, H 2.4. MS: *m*/*z* = 522 $[M]^+$, 507 $[M - CH_3]^+$, 466, 438, 410, 382, 354 [M − *n* CO (*n* = 2−6)]$^+$, 260 [M, 6 CO − FeF_2]$^+$. IR (CH_2Cl_2): ṽ = 2070 m, 1995 s, 1955 w, 1925 s [ν(CO)] cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 1.32 (t, 6 H, $^{3}J_{H,H}$ = 7.0 Hz, 2CH_3), 2.40 (s, 3 H, SCH_3), 3.98 (q, 2 H,^{3} $J_{H,H}$ = 7.0 Hz, CH_2), 4.02 (q,

$^3J_{H,H}$ = 7.0 Hz, 2 H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 14.2 (s, 2CH_2), 62.2 (q, $^2J_{C,F}$ = 38.5 Hz, CCF_3), 123.4 (q, $J_{C,F}$ = 277.5 Hz, CF_3). Similarly, a tetrahydrofuran (10 mL) solution of ethylene glycol (497.0 mg, 448 μL) and **1** (94.0 mg, 0.20 mmol) was stirred at room temperature for 5 h. After evaporation of the solvent, the residue was chromatographed on a silica gel column. Elution with hexane/CH_2Cl_2 (1:0.66) gave an orange band. After evaporation of the volatiles, **2c** was obtained as an analytical pure orange solid in 90% yield (88.5 mg). $C_{13}H_7F_3Fe_2O_8S$ (491.95): calcd. C 31.7, H 1.4; found C 31.5, H 1.3. MS: *m*/*z* = 492 $[M]^+$, 477 $[M - CH_3]^+$, 464, 436, 408, 380, 352, 324 $[M - n\ CO\ (n = 1-6)]^+$, 230 $[M - 6\ CO - FeF_2]^+$. IR (CH_2Cl_2): ν̃ =2070 m, 1995 s, 1960 w, 1928 s [ν(CO)] cm^{-1}. ^1H NMR ($CDCl_3$): δ = 2.3 (s, 3 H, SCH_3), 4.5 (s, 4 H, 2 CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 61.1 (q, $^2J_{C,F}$ = 39.0 Hz, CCF_3), 68.2 (s br, 2 CH_2), 123.5 (q, $J_{C,F}$ = 277.0 Hz, CF_3).

Synthesis of [{Fe(CO)$_3$}$_2${μ-S(Me)C(CF$_3$)C(OMe)C(NMe$_2$)}] (3a): A dichloromethane (5 mL) solution of methanol (128.0 mg, 162 μL, 0.4 mmol) and [{Fe(CO)$_3$}$_2${μ-S(Me)C(CF$_3$)C(F)C (NMe$_2$)}] (**A**: R = R′ = Me) (49.5 mg, 0.10 mmol) was stirred at 60 °C for 4 h. After evaporation of the solvent, column chromatography of the residue produced a red band of **3a** (49.7 mg, 98%) eluted with hexane/CH_2Cl_2 (1:0.2). $C_{14}H_{12}F_3Fe_2NO_7S$ (507.00): calcd. C 33.2, H 2.4, N 2.8; found C 33.3, H 2.4, N 2.7. MS: *m*/*z* = 507 $[M]^+$, 479, 451, 423, 395, 367, 339 $[M - n\ CO\ (n = 1-6)]^+$, 245 $[M - 6\ CO - FeF_2]^+$. IR (CH_2Cl_2): ν̃ =2065 m, 2025 s, 1995 s, 1966 sh [ν(CO)] cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.90 (s, 3 H, SCH_3), 3.10 [s, 6 H, N(CH_3)$_2$], 3.66 (s, 3 H, OCH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 47.1 [s, N(CH_3)$_2$], 54.0 (q, $^2J_{C,F}$ = 34.0 Hz, CCF_3), 59.9 (s, OCH_3), 126.6 (q, $J_{C,F}$ = 274.0 Hz, CF_3).

Synthesis of [{Fe(CO)$_3$}$_2${μ-S(Me)C(CF$_3$)C[OC(O)NMe$_2$]-C(NMe$_2$)}] (3b): Carbon dioxide was bubbled at −50 °C for 5 min through a dichloromethane (10 mL) solution containing 49.5 mg (0.10 mmol) of **A** (R = R′ = Me). At −50 °C, 20 equiv. (90.0 mg, 132 μL) of Me_2NH was added. The mixture was warmed to 60 °C and stirred for 1 h. After evaporation of the solvent, the residue was chromatographed on deoxygenated silica gel. Elution with CH_2Cl_2/hexane (1:0.66) afforded an orange band, which gave **3b** as orange solid (98% yield). $C_{16}H_{15}F_3Fe_2N_2O_8S$ (564.04): calcd. C 34.1, H 2.7, N 5.0; found C 34.2, H 2.7, N 5.1. MS: *m*/*z* = 536, 508, 480, 452, 424, 396 $[M - n\ CO\ (n = 1-6)]^+$. IR (hexane): ν̃ =2066 m, 2020 s, 1998 m, 1990 sh, 1965 sh, 1725 m [ν(CO)] cm^{-1}. ^1H NMR ($CDCl_3$): δ = 2.18 (s, 3 H, SCH_3), 2.96 [s, 3 H, C(O)NCH_3], 2.99 (s, 3 H, C(O)NCH_3), 3.28 [s, 6 H, N(CH_3)$_2$]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 36.15 [s, C(O)NCH$_3$], 36.8 [s, C(O)NCH$_3$)], 48.5 [s, N(CH_3)$_2$], 51.9 (q, $^2J_{C,F}$ = 35.0 Hz, CCF_3), 126.7 (q, $J_{C,F}$ = 274.0 Hz), 154.7 (s, *C*=O).

Synthesis of [{Fe(CO)$_3$}$_2${μ-S(Me)C(CF$_3$)C(SEt)C(NMe$_2$)}] (4a): Complex **A** (R = R′ = Me) (49.5 mg, 0.10 mmol) and 20 equiv. of ethanethiol were stirred in CH_2Cl_2 (5 mL) at 60 °C for 6 h. Compound **4a** was isolated as red solid (80% yield) by column chromatography on deoxygenated silica gel with hexane/dichloromethane (4:1). $C_{15}H_{14}F_3Fe_2NO_6S_2$ (537.08): calcd. C 33.5, H 2.6, N 2.6; found C 33.6, H 2.4, N 2.5. MS: *m*/*z* = 537 $[M]^+$, 509, 481, 453, 425, 397, 369 $[M - n\ CO\ (n = 1-6)]^+$. IR (CH_2Cl_2): ν̃ = 2065 s, 2022 s, 1988 sh, 1968 sh [ν(CO)] cm^{-1}. ^1H NMR ($CDCl_3$): δ =1.30 (t, $^3J_{H,H}$ = 7.5 Hz, 3 H, CH_3), 1.85 (s, 3 H, SCH_3), 2.60 (m, ABX_3, $^2J_{AB}$ = 11.5, $^3J_{H,H}$ = 7.5 Hz, CH_2), 3.00 (m, ABX_3, $^2J_{AB}$ = 11.5, $^3J_{H,H}$ = 7.5 Hz, CH_2), 3.19 [s, 6 H, N(CH_3)$_2$]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 14.05 (s, CH_2CH_3), 30.2 (s, CH_2CH_3), 48.4 [s, N(CH_3)$_2$], 59.15 (q, $^2J_{C,F}$ = 32.0 Hz, CCF_3), 126.8 (q, $J_{C,F}$ = 274.0 Hz, CF_3).

Synthesis of [{Fe(CO)$_3$}$_2${μ-S(Me)C(CF$_3$)C[SC(S)NMe$_2$]C(NMe$_2$)}] (4b): Complex **A** (R = R′ = Me) (49.5 mg, 0.10 mmol) and 1 equiv. of dimethylammonium dimethylthiocarbamate were stirred in CH_2Cl_2 (5 mL) at room temperature for 1 h. The solution was then concentrated and chromatographed on a silica gel column. Elution with hexane/$CHCl_2$ (1:0.4) removed an orange band, which gave orange crystals of **4b** (53.5 mg, 90% yield). $C_{16}H_{15}F_3Fe_2N_2\ O_6S_3$ (596.16): calcd. C 33.2, H 2.5, Fe 18.7, N 4.8; found C 33.4, H 2.5, Fe 18.8, N 4.8. MS: *m*/*z* = 596 $[M]^+$, 568, 540, 512, 484, 456, 428 $[M - n\ CO\ (n = 1-6)]^+$, 334$[M - 6\ CO - FeF_2]^+$. IR (CH_2Cl_2): ν̃ = 2064 s, 2022 s, 1998 sh, 1970 sh [ν(CO)] cm^{-1}. ^1H NMR ($CDCl_3$): δ = 2.3 (s, 3 H, SCH_3), 3.4 (s, 9 H, 3 CH_3), 3.5 (s, 3 H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 42.0 (s, C(S)NCH_3), 45.3 (s, C(S)NCH_3), 49.8 [s, N(CH_3)$_2$], 59.7 (q, $^2J_{C,F}$ = 33.0 Hz, CCF_3), 127.0 (q, $J_{C,F}$ = 274.0 Hz, CF_3), 197.3 (s, *C*=S).

Synthesis of [{Fe(CO)$_3$}$_2${μ-S(Me)C(CF$_3$)C[SCMeNPh]C(NMe$_2$)}] (4c): This compound was prepared as described for **2a**, by using **A** (R = R′ = Me) (49.5 mg, 0.10 mmol) and *N*-phenylthioacetamide (15.2 mg, 0.10 mmol) as starting materials. Red crystals: yield 56.5 mg (90%). $C_{21}H_{17}F_3Fe_2N_2O_6S_2$ (626.16): calcd. C 40.3, H 2.7, N 4.5; found C 40.5, H 2.8, N 4.6. MS: *m*/*z* = 626 $[M]^+$, 598, 570, 542, 514, 486, 458 $[M - n\ CO\ (n = 1-6)]^+$. IR (CH_2Cl_2): ν̃ = 2065 s, 2022 s, 1990 sh, 1975 sh [ν(CO)] cm^{-1}. ^1H NMR ($CDCl_3$): δ = 2.02 (s, 3 H, CH_3 or SCH_3), 2.08 (s, 3 H, CH_3 or SCH_3), 3.3 [s, 6 H, N(CH_3)$_2$], 6.6−7.25 (m, 5 H, C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 20.3 (s, CCH_3), 33.1 (s, SCH_3), 49.1 [s, N(CH_3)$_2$], 59.3 (q, $^2J_{C,F}$ = 33.5 Hz, CCF_3), 119.7 (s, 2C, C_6H_5), 123.6 (s, *p*-*C* in C_6H_5), 126.8 (q, $J_{C,F}$ = 274.0 Hz, CF_3), 129.2 (s, 2 C, C_6H_5), 149.9 (s, quaternary C in C_6H_5), 167.4 [s, *C*(NPh)].

Synthesis of [{Fe(CO)$_3$}$_2${μ-S(Me)C(CF$_3$)C[SC(S)N(CH$_2$)$_4$]-C(NMe$_2$)}] (4d): A dichloromethane solution (5 mL) of **A** (R = R′ = Me) (49.5 mg, 0.10 mmol) and pyrrolidinium pyrrolidylthiocarbamate (43.6 mg, 0.20 mmol) was stirred at 60 °C for 2 h. The reaction mixture was then filtered through deoxygenated silica gel. After evaporation of the solvent, the residue was washed at −50 °C with pentane (5 mL) to afford **4d** as an analytically pure orange solid in 95% yield (59 mg). $C_{18}H_{17}F_3Fe_2N_2O_6S_3$ (622.19): calcd. C 34.7, H 2.8, N 4.5; found C 34.7, H 2.7, N 4.6. MS: *m*/*z* = 594, 566, 538, 510, 482, 454 $[M - n\ CO\ (n = 1-6)]^+$. IR (CH_2Cl_2): ν̃ = 2064 s, 2022 s, 1995 sh, 1966 sh [ν(CO)] cm^{-1}. ^1H NMR ($CDCl_3$): δ = 2.0 (m, 2 H, $C_\beta H_2$), 2.1 (m, 2 H, $C_\beta H_2$), 2.3 (s, 3 H, SCH_3), 3.4 [s, 6 H, N(CH_3)$_2$], 3.6 (m, 2 H, $C_\alpha H_2$), 3.9 (t, 2 H, $C_\alpha H_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 24.3 (s, $C_\beta H_2$), 26.4 (s, $C_\beta H_2$), 49.8 [s, N(CH_3)$_2$], 51.1 (s, $C_\alpha H_2$), 54.9 (s, $C_\alpha H_2$), 59.7 (q, $^2J_{C,F}$ = 33.0 Hz, CCF_3), 126.8 (q, $J_{C,F}$ = 274.0 Hz, CF_3), 192.6 (s, *C*=S).

Synthesis of [{Fe(CO)$_3$}$_2${μ-S(Me)C(CF$_3$)C[SC(S)N(CH$_2$)$_4$]-C[N(CH$_2$)$_4$]}] (4e): This compound was prepared as described for **4d**, by using [{Fe(CO)$_3$}$_2${μ-S(Me)C(CF$_3$)C(F)C[N(CH$_2$)$_4$]}] [**A**: R−R′ = (CH$_2$)$_4$] (52.1 mg, 0.10 mmol) and pyrrolidinium pyrrolidylthiocarbamate (43.6 mg, 0.20 mmol) as starting materials. Orange crystals: yield 55.0 mg (85%). $C_{20}H_{19}F_3Fe_2N_2O_6S_3$ (648.23): calcd. C 37.1, H 2.9, N 4.3; found C 37.3, H 3.0, N 4.5. MS: *m*/*z*: 64 $[M]^+$, 592, 564, 536, 508, 480 $[M - n\ CO\ (n = 2-6)]^+$, 386 $[M - 6\ CO - FeF_2]^+$. IR (CH_2Cl_2): ν̃ = 2064 s, 2022 s, 1995 sh, 1966 sh [ν(CO)] cm^{-1}. ^1H NMR ($CDCl_3$): δ = 2.0 (t, 4 H, 2 $C_\beta H_2$), 2.05 (m, 4 H, 2 $C_\beta H_2$), 2.3 (s, 3 H, SCH_3), 3.7 (m, 2 H, $C_\alpha H_2$), 3.8 (t, 2 H, $C_\alpha H_2$), 3.9 (m, 4 H, 2 $C_\alpha H_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 24.3 (s, $C_\beta H_2$), 26.2 (s, 2 $C_\beta H_2$), 26.4 (s, $C_\beta H_2$), 51.0 (s, $C_\alpha H_2$), 54.8 (s, $C_\alpha H_2$), 58.2 (s, 2 $C_\alpha H_2$), 61.3 (q, $^2J_{C,F}$ = 33.0 Hz, CCF_3), 127.0 (q, $J_{C,F}$ = 274.0 Hz, CF_3), 194.9 (s, *C*=S).

Treatment of [{Fe(CO)$_3$}$_2${μ-S(Me)C(CF$_3$)C(L1)C(F)}] [D: L$_1$ = PPh$_2$, P(O)(OMe)$_2$] and [{Fe(CO)$_3$}$_2${μ-S(Me)C(CF$_3$)C(L$_2$)C(F)}]

[F: L_2 = SC(NPh)CH_3] with Nucleophiles: Dichloromethane solutions of **D** (0.10 mmol) or **F** (0.10 mmol) and an excess of nucleophile {5 equiv. of RNH_2 (R = Ph, *t*Bu), 10 equiv. of R′NH [R′ = Me_2, $(CH_2)_4$], 10 equiv. of EtSH, 40 equiv. of MeOH, 5 equiv. of PPh_3} were stirred at 60 °C for 18 h. After this time the starting materials were wholly recovered. This was checked by IR analysis.

Synthesis of [{Fe(CO)$_3$}$_2${μ-S(Me)C(CF$_3$)C(NHPh)C(NHPh)}] (5a): A dichloromethane (10 mL) solution of **1** (94.0 mg, 0.20 mmol) and 3 equiv. of aniline (55.8 mg, 54.6 μL) was stirred at room temperature for 2 h. The reaction mixture was then filtered through deoxygenated silica gel. After evaporation of the solvent, the residue was crystallized from pentane (5 mL) at −60 °C to give **5a** as orange crystals in 95% yield (111.0 mg). $C_{23}H_{15}F_3N_2O_6S$ (616.11): calcd. C 44.8, H 2.45, Fe 18.1, N 4.5; found C 44.5, H 2.4, Fe 18.3, N 4.3. MS: *m*/*z* = 616 $[M]^+$, 588, 560, 532, 504, 476, 448 $[M - n\ CO\ (n = 1-6)]^+$, 354 $[M - 6\ CO - FeF_2]^+$. IR (CH_2Cl_2): $\tilde{\nu}$ = 2070 m, 2022 s, 2002 m, 1965 sh [ν(CO)] cm^{-1}. ^1H NMR ($CDCl_3$): δ = 2.0 (s, 3 H, SC*H*$_3$), 4.6 (s, 1 H, PhN*H*), 6.9−7.4 (m, 10 H, 2 C$_6$*H*$_5$), 8.5 (s, 1 H, PhN*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 53.4 (q, $^2J_{C,F}$ = 33.0 Hz, *C*CF$_3$), 127.0 (q, $J_{C,F}$ = 273.5 Hz, *C*F$_3$), 110.0−150.0 (8 s, *C*$_6$H$_5$).

Synthesis of [{Fe(CO)$_3$}$_2${μ-S(Me)C(CF$_3$)C[NHNHC(O)OMe]C-[NHNHC(O)OMe)}] (5b): This compound was prepared as described for **5a**, by using **1** (94.0 mg, 0.20 mmol) and (methoxycarbonyl)hydrazine (72.0 mg, 0.80 mmol) as starting materials. Orange crystals: yield 112.3 mg (97%). $C_{15}H_{13}F_3Fe_2N_4O_{10}S$ (610.01): calcd. C 29.5, H 2.15, N 9.2; found C 29.8, H 2.2, N 9.1. IR (CH_2Cl_2): $\tilde{\nu}$ =2075 m, 2030 s, 1980 sh, 1950 sh, 1720 s [ν(CO)] cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.90 (s, 3 H, SC*H*$_3$), 3.78 (s, 3 H, OC*H*$_3$), 3.79 (s, 3 H, OC*H*$_3$), 4.74s (s br, 1 H, N*H*), 6.55 (s br, 1 H, N*H*), 6.85 (s br, 1 H, N*H*), 9.46 (s br, 1 H, N*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 52.5 (m, *C*CF$_3$), 53.1 (s, OC*H*$_3$), 53.3 (s, OC*H*$_3$), 127.7 (q, $J_{C,F}$ = 273.5 Hz, *C*F$_3$), 156.8 (s, *C*(O)OMe), 158.8 (s, *C*(O)OMe).

Synthesis of [{Fe(CO)$_3$}$_2${μ-S(Me)C(CF$_3$)CC(NHPh)$_2$}] ([f]): The intermediate [**f**] was formed rapidly in the NMR tube on mixing **1** (23.5 mg, 0.05 mmol) with 3 equiv. of aniline (13.9 mg, 13.6μL) in $CDCl_3$ solution (at −10 °C). The reaction was monitored by ^{19}F NMR spectroscopy. When the yield of product [**f**] reached about 50%, a $^{13}C\{^1H\}$ (and ^1H) NMR analysis was undertaken at −40 °C in order to characterise this intermediate (see Table 1).

Synthesis of 6a: A tetrahydrofuran solution (10 mL) of **1** (94.0 mg, 0.20 mmol) and 1 equiv. of 4-methyl-3-thiosemicarbazide (21 mg) was stirred at room temperature for 3 h. After evaporation of the solvent, the residue was chromatographed on a deoxygenated silica gel column. Elution with ether/CH_2Cl_2 (1:4) gave an orange band. After evaporation of the volatiles, **6a** was obtained as an analytical pure orange solid in 86% yield (89.2 mg). $C_{13}H_8F_3Fe_2N_3O_6S_2$ (535.01): calcd. C 29.2, H 1.5, N 7.85; found C 29.5, H 1.5, N 7.7. MS: *m*/*z* = 535 $[M]^+$, 520 $[M - CH_3]^+$, 507, 479, 451, 423, 395, 367 $[M - n\ CO\ (n = 1-6)]^+$, 352 $[M - 6\ CO - CH_3]^+$, 273 $[M - 6\ CO - FeF_2]^+$, 258 $[M - 6\ CO - FeF_2 - CH_3]^+$. IR ($CH_2Cl_2$): $\tilde{\nu}$ = 2055 s, 2010 s, 1994 s, 1970 sh [ν(CO)], 1650 s [ν(C=N)] cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.87 (s, 3 H, SC*H*$_3$), 3.18 (s, 3 H, C*H*$_3$), 4.67 (s, 2 H, N*H*$_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 40.9 (s, *C*H$_3$), 49.8 (q, $^2J_{C,F}$ = 37.0 Hz, *C*CF$_3$), 126.7 (q, $J_{C,F}$ = 274.0 Hz, *C*F$_3$), 159.4 (s, *C*=N).

Synthesis of 6b: This compound was prepared as described for **6a**, by using **1** (94.0 mg, 0.20 mmol) and 1 equiv. of *N*-methylthiourea (18.0 mg) as starting materials. The elution of product **6b** was performed with ether/dichloromethane (1:19) to give an orange solid in 88% yield (86.9 mg). $C_{13}H_7F_3Fe_2N_2O_6S_2$ (520.00): calcd. C 30.0, H 1.35, N 5.4; found C 30.2, H 1.4, N 5.7. MS: *m*/*z* = 520 $[M]^+$, 505 $[M - CH_3]^+$, 492, 464, 436, 408, 380, 352 $[M - n\ CO\ (n = 1-6)]^+$, 258 $[M - 6\ CO - FeF_2]^+$. IR (CH_2Cl_2): $\tilde{\nu}$ = 2075 s, 2035 s, 2005 s, 1998 sh [νCO), 1595 s [ν (C=N)] cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.90 (s, 3 H, SC*H*$_3$), 3.71 (s, 3 H, C$_α$N*H*$_3$), 7.59 (s br, 1 H, N*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 35.7 (s, C$_α$NCH$_3$), 49.1 (q, $^2J_{C,F}$ = 37.5 Hz, *C*CF$_3$), 126.5 (q, $J_{C,F}$ = 27**1.0** Hz, *C*F$_3$), 166.0 (s, *C*=N).

Synthesis of 6c: A tetrahydrofuran solution (10 mL) of **1** (94.0 mg, 0.20 mmol) and 1 equiv. of *N*,*N*′-dimethylthiourea (20.8 mg) was stirred at room temperature for 2 h. The solvent was then removed under vacuum and **6c** was extracted with CH_2Cl_2/pentane (1:9) (10 mL) and then recrystallized at −60 °C in pentane (91.3 mg, 90% yield). $C_{14}H_9F_3Fe_2N_2O_6S_2$ (534.03): calcd. C 31.5, H 1.7, N 5.2; found C 31.9, H 1.8, N 5.2. MS: *m*/*z* = 534 $[M]^+$, 519 $[M - CH_3]^+$, 506, 478, 450, 422, 394, 366 $[M - n\ CO\ (n = 1-6)]^+$, 272 $[M - 6\ CO - FeF_2]^+$. IR (CH_2Cl_2): $\tilde{\nu}$ = 2075 s, 2032 s, 2004 s, 1980 sh [ν(CO)], 1630 s [ν(C=N)] cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.88 (s, 3 H, SC*H*$_3$), 3.15 (s, 3 H, C*H*$_3$ N=C), 3.68 (s, 3 H, C*H*$_3$NC$_α$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 36.4 (s, *C*H$_3$NC$_α$), 41.4 (s, *C*H$_3$N=C), 49.5 (q, $^2J_{C,F}$ = 37.0 Hz, *C*CF$_3$), 126.7 (q, $J_{C,F}$ = 274.0 Hz, *C*F$_3$), 106.6 (s, *C*=N).

Synthesis of 7a: This compound was prepared as described for **5a**, by using **1** (94.0 mg, 0.20 mmol) and 3 equiv. of acetylhydrazine (44.4 mg) as starting materials. Red crystals: yield 93.8 mg (98%). $C_{13}H_7F_3Fe_2N_2O_7S$ (503.94): calcd. C 31.0, H 1.4, Fe 22.2, N 5.6; found C 31.1, H 1.4, Fe 21.8, N 5.5. MS: *m*/*z* = 504 $[M]^+$, 476, 448, 420, 392, 364, 336 $[M - n\ CO\ (n = 1-6)]^+$, 242 $[M - 6\ CO - FeF_2]^+$. IR (CH_2Cl_2): $\tilde{\nu}$ = 2072 m, 2022 s, 2002 m, 1950 sh [ν(CO)] cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.87 (s, 3 H, C*H*$_3$), 2.49 (s, 3 H, SC*H*$_3$), 2.86 (s, 1 H, C*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 11.3 (s, *C*H$_3$), 24.4 (s, *C*H), 44.6 (q, $^2J_{C,F}$ = 36.5 Hz, *C*CF$_3$), 128.6 (q, $J_{C,F}$ = 274.0 Hz, *C*F$_3$), 163.0 (s, O*C*CH$_3$).

Synthesis of 7b: A dichloromethane solution (5 mL) of **7a** (50.4 mg, 0.10 mmol) and 2 equiv. of PPh_2Me (40.0 mg, 37.2 μL) was stirred at 60 °C for 1 h. The reaction mixture was then filtered through Celite and the volatiles were removed under vacuum. The residue was then washed at −50 °C with pentane (5 mL) to give **7b** as a red solid in 85% yield (57.5 mg). $C_{25}H_{20}F_3Fe_2N_2O_6PS$(676.14): calcd. C 44.4, H 3.0, Fe 16.5, N 4.1; found C 44.6, H 3.0, Fe 16.1, N 4.0. IR (CH_2Cl_2): $\tilde{\nu}$ = 2030 s, 1985 s, 1960 s [ν(CO)] cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.53 (s, 3 H, C*H*$_3$), 1.97 (d, $^2J_{PH}$ = 8.0 Hz, 3 H, PC*H*$_3$), 2.49 (s, 3 H, SC*H*$_3$), 2.74 (s, 1 H, C*H*), 7.5 (m, 10 H, 2 C$_6$*H*$_5$). ^{31}P NMR ($CDCl_3$): δ = 29.12 (s, *P*Ph$_2$Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 11.2 (s, *C*H$_3$), 15.6 (d, $J_{C,P}$ = 16.0 Hz, P*C*H$_3$), 42.1 (q, $^2J_{C,F}$ = 36.5 Hz, *C*CF$_3$), 129.0 (q, $J_{C,F}$ = 274.5 Hz, *C*F$_3$), 128.4 (s, *C*$_6$H$_5$), 128.6 (d, $J_{C,P}$ = 9.0 Hz, *C*$_6$H$_5$), 129.3 (d, $J_{C,P}$ = 9.0 Hz, *C*$_6$H$_5$), 129.9 (d, $J_{C,P}$ = 10.0 Hz, *C*$_6$H$_5$), 130.8 (s, *C*$_6$H$_5$), 132.3 (d, $J_{C,P}$ = 11.0 Hz, *C*$_6$H$_5$), 134.8 (d, $J_{C,P}$ = 33.0 Hz, *C*$_6$H$_5$), 138.5 (d, $J_{C,P}$ = 41.0 Hz, *C*$_6$H$_5$), 160.6 (s, O*C*CH$_3$).

Synthesis of 7c: This compound was prepared as for **7b**, by using **7a** (50.4 mg, 0.10 mmol) and 5 equiv. of $P(OMe)_3$ (62.0 mg, 59 μL) as starting materials. The stirring was undertaken for 20 h. Red solid: yield 58.8 mg (98%). $C_{15}H_{16}F_3Fe_2N_2O_9PS$ (600.01): calcd. C 30.0, H 2.7, Fe 18.6, N 4.7; found C 29.3, H 2.6, Fe 18.1, N 4.6. MS: *m*/*z* = 600 $[M]^+$, 572, 544, 516, 488, 460 $[M - n\ CO\ (n = 1-5)]^+$. IR (CH_2Cl_2): $\tilde{\nu}$ = 2036 s, 1990 s, 1968 s [ν(CO)] cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.88 (s, 3 H, C*H*$_3$), 2.44 (s, 3 H, SC*H*$_3$), 2.72 (s, 1 H, C*H*), 3.7 [d, $^3J_{PH}$ = 10.5 Hz, 9 H, P(OC*H*$_3$)$_3$]. ^{31}P NMR ($CDCl_3$): δ = 157.73 [s, *P*(OMe)$_3$]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 11.2 (s, C*C*H$_3$), 42.9 (q, $^2J_{C,F}$ = 36.5 Hz, *C*CF$_3$), 52.25 [d, $^2J_{C,P}$ =

Table 4. Crystallographic data for **2a**, **3b**, **5a**, **5b**, **6a** and **7a**; data collected with Mo-K_α radiation (λ = 0.7073 Å) at 20 °C; structures refined by full-matrix least squares

	2a	**3b**	**5a**	**5b**	**6a**	**7a**
Empirical formula	$C_{13}H_9F_3Fe_2O_8S$	$C_{16}H_{15}F_3Fe_2N_2O_8S$	$C_{23}H_{15}F_3Fe_2N_2O_6S{\cdot}0.2CH_2Cl_2$	$C_{15}H_{13}F_3Fe_2N_4O_{10}S$	$C_{13}H_8F_3Fe_2N_3O_6S_2$	$C_{13}H_7F_3Fe_2N_2O_7S$
Formula mass	493.96	564.06	633.12	610.05	535.04	503.97
Crystal size [mm]	0.11 × 0.12 × 0.45	0.42 × 0.10 × 0.03	0.54 × 0.18 × 0.13	0.40 × 0.20 × 0.20	0.15 × 0.09 × 0.06	0.40 × 0.10 × 0.10
Crystal system	monoclinic	triclinic	triclinic	monoclinic	triclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	Pn	$P\bar{1}$	$C\bar{1}$
a [Å]	9.757(2)	9.780(1)	11.451(2)	11.754(2)	9.535(2)	13.3286(10)
b [Å]	10.518(2)	15.671(1)	12.838(3)	11.613(2)	15.019(3)	13.5509(9)
c [Å]	18.437(4)	16.097(1)	19.367(5)	18.051(4)	15.306(3)	20.5896(13)
α [°]		70.031(5)	86.79(2)		114.92(3)	90.057(6)
β [°]	102.30(3)	87.141(6)	75.83(2)	108.87(3)	94.60(3)	104.456(7)
γ [°]		75.323(6)	78.48(2		91.47(3)	90.013(7)
V [Å^3]	1848.6(7)	2241.2(3)	2704.7(10)	2331.5(8)	1977.1(7)	3601.0(4)
Z	4	4	4	4	4	8
$D_{calcd.}$ [Mg/m^3]	1.775	1.672	1.555	1.738	1.797	1.859
μ [mm^{-1}]	1.749	1.456	1.249	1.415	1.741	1.797
θ_{max} (Mo-K_α) [°]	28.3	25.0	27.4	30.4	25.0	27.0
Index ranges	$-13 \le h \le 1$	$0 \le h \le 11$	$-14 \le h \le 13$	$-16 \le h \le 16$	$-11 \le h \le 11$	$-16 \le h \le 16 - 17 \le$
	$-1 \le k \le 14$	$-18 \le k \le 18$	$0 \le k \le 15$	$-2 \le k \le 16$	$-17 \le k \le 16$	$k \le 17$
	$-24 \le l \le 24$	$-19 \le l \le 19$	$-23 \le l \le 23$	$-2 \le l \le 25$	$0 \le l \le 18$	$0 \le l \le 26$
Reflections collected	5932	9337	10408	8801	7239	8132
Reflections unique	4594	7881	9933	7963	6951	7793
R(int.)	0.018	0.046	0.036	0.058	0.050	0.016
Reflections with $I > 2\sigma(I)$	3177	4629	5196	6243	2927	6251
Data/parameters	4594/244	7881/578	9933/667	7963/632	6951/517	7793/505
GoF on F^2	0.919	0.945	0.889	1.027	0.946	0.986
$R1$ [$I > 2\sigma(I)$]	0.030	0.065	0.055	0.050	0.043	0.033
$wR2$ [$I > 2\sigma(I)$]	0.072	0.161	0.123	0.125	0.090	0.081
$R1$ (all data)	0.058	0.116	0.141	0.073	0.177	0.046
$wR2$ (all data)	0.077	0.186	0.150	0.139	0.129	0.086
Δρ(max)/Δρ(min) [e/Å^3]	0.36/−0.32	0.91/−0.76	0.51/−0.39	1.80/−0.41	0.68/−0.55	0.43/−0.45

9.0 Hz, $P(OCH_3)_3$], 128.9 (q, $J_{C,F}$ = 274.0 Hz, CF_3), 160.9 (s, CCH_3).

Synthesis of 8: A solution of **7a** (50.4 mg, 0.10 mmol) in dichloromethane (2 mL) was added to a chilled solution (−15 °C) of $(NH_4)_2Ce(NO_3)_6$ (274 mg, 0.50 mmol) in methanol (2 mL). The reaction mixture was stirred at −15 °C for 45 min and was then slowly warmed to room temperature The volatiles were removed under vacuum and the product **8** was extracted with pentane (5 mL) and then recrystallized at −80 °C. White crystals were formed and filtered off to give 19.0 mg (85%) of **8**; m.p. 44 °C. $C_7H_7F_3N_2OS$ (224.18). MS: m/z = 224 $[M]^+$, 209 $[M - CH_3]^+$, 141 $[HCC(CF_3)SMe]^+$, 83 $[NNC(CH_3)OC]^+$. ^{1}H NMR ($CDCl_3$): δ = 2.54 (s, 3 H, CH_3), 2.60 (s, 3 H, SCH_3), 7.02 (s, 1 H, CH). ^{19}F NMR ($CDCl_3$): δ = −62.5 (s, CF_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 11.1 (s, CH_3), 15.9 (q, $^4J_{C,F}$ = 3.0 Hz, SCH_3), 111.5 (q, $^3J_{C,F}$ = 7.0 Hz, CH), 121.9 (q, $J_{C,F}$ = 276.0 Hz, CF_3), 137.5 (q, $^2J_{C,F}$ = 32.0 Hz, CCF_3), 161.7 (s, $NCCH$), 163.9 (s, $NCCH_3$).

Single-Crystal X-ray Analyses of 2a, 3b, 5a, 5b, 6a and 7a: Measurements were made with a Nonius CAD4 diffractometer. Subsequent calculations were performed with the WINGX system, the structures being refined with SHELXL97.[19] Crystallographic data for **2a**, **3b**, **5a**, **5b**, **6a** and **7a** are presented in Table 4. Full details of each structure have been deposited.[20] All the structures apart from **2a** involve asymmetric units that contain two independent molecules. Differences between these molecules are insignificant and are easily accounted for by packing forces. Crystals of **3b**, **5a** and **6a** are metrically triclinic. The collection of high-angle data for **5a** had to be abandoned when the crystal decomposed. The structure has two independent sites which contain disordered CH_2Cl_2 at about 20% occupancy. The scattering of the disordered CH_2Cl_2 was included by back-transformation of the difference map using the SQUEEZE facility of the PLATON program.[19] In **6a**, the CF_3 fluorine atoms are disordered equally over two sites. The structure of **5b** has several unusual features. It appears to be a distortion from space group $P2_1/n$ in that the two independent molecules are *roughly* related by the pseudo-screw operation $-x$, $-0.28 + y$, $-z$. The Laue symmetry is undoubtedly $2/m$, although it is possible to choose a centred orthorhombic cell. Four small residual peaks of 1.8−1.0 e/Å^3 suggest a very minor disorder of the O and OMe groups attached to C(8), but attempts to derive a satisfactory model of the disorder were unsuccessful. Compound **7a** is *metrically C*-centred monoclinic, although its Laue symmetry is that of a triclinic crystal.

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[1] [1a] T. G. Richmond, *Angew. Chem. Int. Ed.* **2000**, *39*, 3241−3244. [1b] J. Burdeniuc, B. Jedlicka, R. H. Crabtree, *Chem. Ber./Recueil* **1997**, *130*, 145−154. [1c] T. Braun, L. Cronin, C. L. Higgit, J. E. McGrady, R. N. Perutz, M. Reinhold, *New J. Chem.* **2001**, *25*, 19−21. [1d] M. E. van der Boom, Y. Ben-David, D. Milstein, *J. Am. Chem. Soc.* **1999**, *121*, 6652−6656.

[2] [2a] T. H. Peterson, J. T. Golden, R. G. Bergman, *Organometallics* **1999**, *18*, 2005−2020. [2b] M. Fujiwara, J. Ichikawa, T. Okauchi, T. Minami, *Tetrahedron Lett.* **1999**, *40*, 7261−7265. [2c] J. L. Kiplinger, T. G. Richmond, C. E. Osterberg, *Chem. Rev.* **1994**, *94*, 373−431. [2d] P. J. Brothers, W. R. Roper, *Chem. Rev.* **1988**, *88*, 1293−1326.

[3] [3a] J. J. Bonnet, R. Mathieu, R. Poiblanc, J. A. Ibers, *J. Am. Chem. Soc.* **1979**, *101*, 7487−7496. [3b] L. Carlton, J. L. Davidson, P. Erwing, Lj. Manojlovic-Muir, K. W. Muir, *J. Chem. Soc., Chem. Commun.* **1985**, 1474−1476.

[4] [4a] R. Rumin, F. Y. Pétillon, Lj. Manojlovic-Muir, K. W. Muir, D. S. Yufit, *J. Chem. Soc., Chem. Commun.* **1995**, 1431−1432. [4b] R. Rumin, K. Guennou, F. Y. Pétillon, K. W. Muir, *J. Chem. Soc., Dalton Trans.* **1997**, 1381−1386. [4c] R. Rumin, K. Guennou, R. Pichon, F. Y. Pétillon, K. W. Muir, D. S. Yufit, *J. Organomet. Chem.* **1997**, *533*, 177−185. [4d] K. Guennou-de Cadenet, R. Rumin, F. Y. Pétillon, K. W. Muir, *Organometallics* **2000**, *19*, 1912−1926.

[5] R. G. Pearson, J. Songstad, *J. Am. Chem. Soc.* **1967**, *89*, 1827−1836.

[6] K. Guennou-de Cadenet, Ph. D Thesis, Université de Bretagne Occidentale, Brest, **1998**.

[7] [7a] *International Tables for Crystallography*, International Union of Crystallography, Kluwer, Dordrecht, **1992**, vol. C, p.723−791. [7b]P. E. Riley, R. E. Davis, N. T. Allison, W. M. Jones, *Inorg. Chem.* **1982**, *21*, 1321−1328.

[8] J. C. Daran, B. Heim, M. Gouygou, Y. Jeannin, *J. Organomet. Chem.* **1994**, *479*, 109−116.

[9] J. Sandström, *Dynamic NMR Spectroscopy*; Academic Press: London, New York, **1982**.

[10] R. Rumin, F. Robin-Le Guen, F. Y. Pétillon, R. Pichon, J. Talarmin, *Organometallics* **1993**, *12*, 1597−1607.

[11] S. Doherty, G. Hogarth, M. Waugh, W. Clegg, M. R. J. Elsegood, *Organometallics* **2000**, *19*, 4557−4562.

[12] K. Gruet, R. H. Crabtree, D-H. Lee, L. Liable-Sands, A. L. Rheingold, *Organometallics* **2000**, *19*, 2228−2232.

[13] W. P. Fehlhammer, T. Bliβ, W. Sperber, J. Fuchs, *Z. Naturforsch., Teil B* **1994**, *49*, 494−500.

[14] R. D. Adams, J. E. Babin, H. S. Kim, J. T. Tanner, T. A. Wolfe, *J. Am. Chem. Soc.* **1990**, *112*, 3426−3435.

[15] T. Fässler, G. Huttner, D. Günauer, S. Fielder, B. Eber, *J. Organomet. Chem.* **1990**, *381*, 409−428.

[16] M. Crutchfield, C. Dungan, J. Letcher, V. Mark, J. Van Wazer in *Topics in Phosphorus Chemistry*, Interscience Publishers, New York, **1967**, vol. 5.

[17] [17a] C. Ainsworth, *J. Am. Chem. Soc.* **1965**, *87*, 5800−5801. [17b] C. Ainsworth, R. E. Hackler, *J. Org. Chem.* **1966**, *31*, 3442−3444.

[18] R. Rumin, F. Y. Pétillon, L. Manojlovic-Muir, K. W. Muir, *Organometallics* **1990**, *9*, 944−952.

[19] SHELXS: G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467−473. G. M. Sheldrick, *SHELXL97*, University of Göttingen, Germany, **1997**. WINGX: L. J. Farrugia. *J. Appl. Crystallogr.* **1997**, *30*, 565.

[20] Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication of CCDC-168607 (**2a**), -168608 (**3b**), -168609 (**5a**), -168610 (**5b**), -168611 (**6a**) and -168612 (**7a**). Copies of the data can be obtained free of charge on applicaton to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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