# Carbon−Fluorine Bond Cleavages and Organoiron Ring Transformations: Reaction of a Perfluorosulfanylvinyldiiron(I) Complex with Amines

Karine Guennou-de Cadenet, René Rumin, and François Y. Pétillon*

*UMR CNRS 6521, Laboratoire de Chimie, Electrochimie Moléculaires et Chimie Analytique, Faculté des Sciences, Université de Bretagne Occidentale, BP 809, 29285 Brest-Cedex, France*

Kenneth W. Muir*

*Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, U.K.*

*Received January 3, 2000*

The reaction of the perfluorosulfanylvinyldiiron(I) complex [{$Fe(CO)_3$}$_2${$\mu$-C(SMe)($CF_3$)-$C_\beta$($C_\alpha F_2$)}] (**1**) with secondary mono- and diamines (L = $Me_2NH$, $(CH_2)_4NH$, $HN(CH_2)_4NH$) in a 1:1 ratio in dichloromethane at room temperature led in a multistep reaction to the new monoaminocycloferrathiapentadiene compounds [{$Fe(CO)_3$}$_2${$\mu$-S(Me)C($CF_3$)CFCX}] (X = $NMe_2$ (**2**), $N(CH_2)_4$ (**3**), $N(CH_2)_4NH$ (**4**)) and [[{$Fe(CO)_3$}$_2${$\mu$-S(Me)C($CF_3$)CFC]$_2${$\mu$-$N(CH_2)_4N$}] (**5**). However, when the reaction of **1** was conducted in THF with a large excess of amine, the diaminocycloferrathiabutene complexes [{$Fe(CO)_3$}$_2${$\mu$-S(Me)C($CF_3$)C($CX_2$)}] (X = $NMe_2$ (**6**), $N(CH_2)_4$ (**7**)) and [{$Fe(CO)_3$}$_2${$\mu$-S(Me)C($CF_3$)C(CX)}] (X = $MeN(CH_2)_2NMe$ (**8**), $HN(CH_2)_2$ NH (**9**)) were formed. It is suggested that these compounds form via initial nucleophilic attack at $C_\alpha$ to give the common zwitterionic intermediate [{$Fe(CO)_3$}$_2${$\mu$-S(Me)C-($CF_3$)C($CFNX_2$)] (**C**). Thermally induced C−F bond activation is a feature of these reactions. Thermolysis of diaminocycloferrathiabutene compounds (**6**−**9**) in tetrahydrofuran gave the amidinium-substituted $\mu_{||}$-alkyne derivatives [{$Fe(CO)_3$}$_2$($\mu$-SMe){$\mu$-($CF_3$)C═C($CX_2$)}] (X = $NMe_2$ (**10**), $N(CH_2)_4$ (**11**)) and [{$Fe(CO)_3$}$_2$($\mu$-SMe){$\mu$-($CF_3$)C═C(CX)}] (X = $MeN(CH_2)_2$ NMe (**12**), $NH(CH_2)_2NH$ (**13**)), in quantitative yields via C−S bond scission. The molecular structures of **6**, **8**, and **10** have been established by X-ray diffraction studies.



## Introduction

The low reactivity typical of fluorocarbon compounds is usually ascribed to the great strength of the C−F bond.[1] Nevertheless, over the past decade many organometallic complexes have been shown to promote the functionalization and activation of C−F bonds.[2] Early examples involved drastic reaction conditions which led to low chemical yields,[3] but now several systems capable of C−F bond activation under milder conditions are known.[2] In this paper we will be concerned exclusively with the activation under mild conditions of C−F bonds in which the participating carbon atom is unsaturated.

Most earlier work has focused on the activation and cleavage of aromatic C−F bonds, and several types of reaction between aryl compounds and transition-metal complexes have been described. For example, facile intramolecular oxidative addition of the C−F bond of a perfluoroaromatic Schiff base bonded to a tungsten(0)[4] or platinum(II)[5] center has been shown to lead to fluoride compounds. It has also been demonstrated that the C−F bond in simple aromatic substrates is selectively cleaved under mild conditions, even in the presence of weaker C−H or C−X (X = Cl, Br) bonds.[6] The metal-assisted functionalization of aromatic fluorocarbon ligands has been achieved through the insertion of unsaturated organic molecules into the metal−C(aryl) bonds formed in these complexes.[7] Recently, it has been shown that the inertness of the C(aryl)−F bond in oxidative addition reactions of 16-electron osmium and rhodium complexes is not due to a thermodynamic factor but is of kinetic origin.[8] Electron transfer is another process which has been postulated to account for intermolecular aromatic C−F activation reactions by iridium(I)[9] or ruthenium(II)[10] complexes. Activation of

(1) Smart, B. E. In *The Chemistry of Functional Groups*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1983; Supplement D, Chapter 14.

(2) For reviews, see: (a) Burdeniuc, J.; Jedlicka, B.; Crabtree, R. H. *Chem. Ber. Recl.* **1997**, *97*, 3425. (b) Kiplinger, J. L.; Richmond, T. G.; Osterberg, C. E. *Chem. Rev.* **1994**, *94*, 373.

(3) Osterberg, C. E.; Richmond, T. G. In *Inorganic Fluorine Chemistry: Toward The 21st Century*; Thrasher, J. S., Strauss, S. H., Eds.; American Chemical Society: Washington, DC, 1992; Chapter 25.

(4) Richmond, T. G.; Osterberg, C. E.; Arif, A. M. *J. Am. Chem. Soc.* **1987**, *109*, 8091.

(5) Anderson, C. M.; Puddephatt, R. J.; Ferguson, G.; Lough, A. J. *J. Chem. Soc., Chem. Commun.* **1989**, 1297.

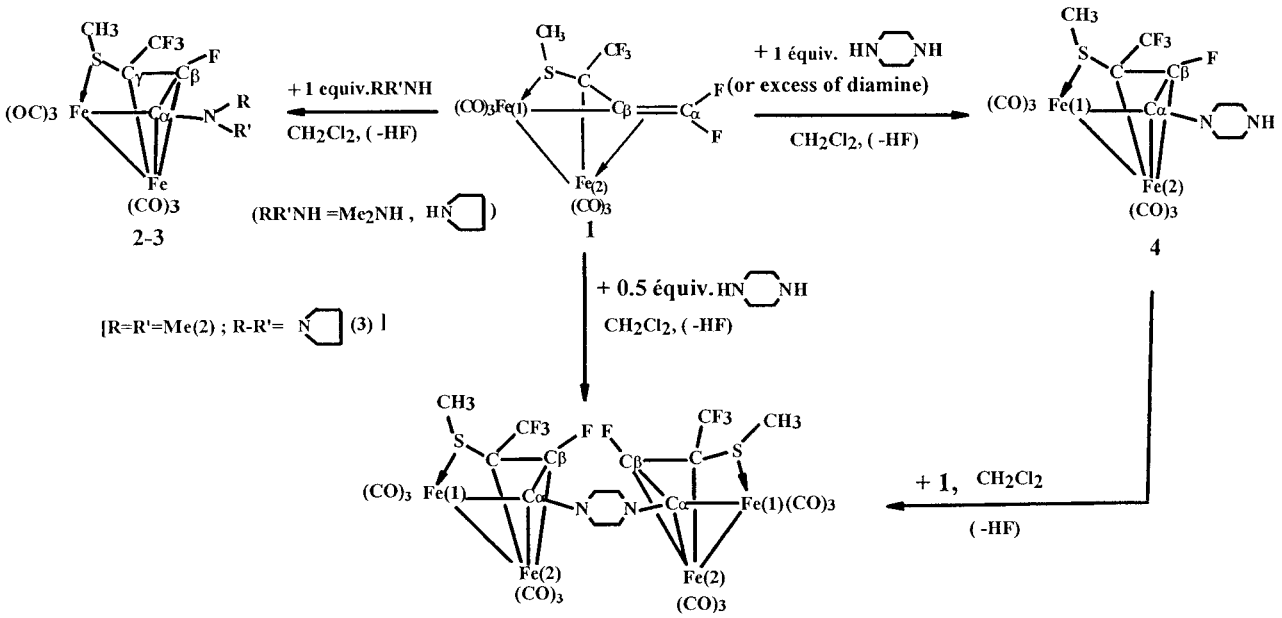
(6) (a) Anderson, C. M.; Crespo, M.; Ferguson, G.; Lough, A. J.; Puddephatt, R. J. *Organometallics* **1992**, *11*, 1177. (b) Crespo, M.; Martinez, M.; Sales, J. *J. Chem. Soc., Chem. Commun.* **1992**, 822. (c) Lopez, O.; Crespo, M.; Font-Bardia, M.; Solans, X. *Organometallics* **1997**, *16*, 1233. (d) Crespo, M.; Martinez, M.; de Pablo, E. *J. Chem. Soc., Dalton Trans.* **1997**, 1231.

(7) (a) Kiplinger, J. L.; Richmond, T. G.; Arif, A. M.; Dücker-Benfer, C.; van Eldik, R. *Organometallics* **1996**, *15*, 1545. (b) Kiplinger J. L.; King, M. A.; Fechtenkötter, A.; Arif, A. M.; Richmond, T. G. *Organometallics* **1996**, *15*, 5292.

(8) Bosque, R.; Clot, E.; Fantacci, S.; Maseras, F.; Eisenstein, O.; Perutz, R. N.; Renkema, K. B.; Caulton, K. G. *J. Am. Chem. Soc.* **1998**, *120*, 12634.

10.1021/om000003k CCC: $19.00 
Publication on Web 04/12/2000

**Scheme 1. Synthesis and Proposed Structure of Complexes 2−5**




5

aromatic C−F bonds through nucleophilic attack by transition-metal carbonyl anions on highly fluorinated aromatic compounds was well established over 30 years ago.[11] Cyclometalation reactions involving intramolecular activation of aromatic C−F bonds at a platinum(II) metal center have been reported.[12]

As is apparent from the previous discussion, activation of *aryl* C−F bonds by transition metals has been thoroughly studied. In contrast, reports of the activation of C−F bonds in coordinated fluoro*alkene* ligands are much less numerous.[2b] It is known that coordination of perfluoroalkenes alters their chemical reactivity and makes them subject to chemical attack, leading to C−F bond cleavage. The course of such a reaction depends on the nature of the coordinated ligand. For example, fluoroolefins become more reactive upon coordination and are therefore more susceptible to attack from Lewis acids, giving vinyl complexes via fluoride abstraction.[13] When tetrafluoroethylene is coordinated to the bimetallic complex $[Fe(CO)_3(\mu\text{-}SCH_3)]_2$, it can be thermally transformed into a bridging $C(F)CF_3$ carbene by cleavage of a C−F bond and fluoride migration onto the electrophilic $\beta$-carbon atom of a $\sigma-\pi$-bonded vinyl group which is present in a dinuclear intermediate.[14] The observation that the C−F bonds of ligands coordinated to mononuclear $\eta^2$-vinyl molybdenum or tungsten complexes can be cleaved at room temperature to yield metal fluoride compounds[15] led us to investigate the behavior of the reactive perfluorovinyldiiron(I) cluster $[\{Fe(CO)_3\}_2\{\mu\text{-}C(SMe)(CF_3)CCF_2\}]$ (**1**) with nucleophiles such as thiols and secondary and tertiary phosphanes.[16] We have demonstrated that coordination of the difluorovinyl ligand to the diiron residue in **1** facilitates its reaction with these nucleophiles, leading to C−F bond cleavage, organoiron ring expansion, and the production either of neutral species $[\{Fe(CO)_3\}_2\{\mu\text{-}C(SMe)(CF_3)C(X)CF\}]$ (X = SR,[16b] $PR_2$,[16b] P(F)$(OMe)_2$,[16a] P(O)$(OMe)_2$[16a]) or of ionic species $[(Ph_3P)(CO)_2Fe\{\mu\text{-}CFC(PPh_3)C(CF_3)(SMe)\}Fe(CO)_3][\{Fe(CO)_3\}_2\{\mu\text{-}C(CF_3)C(CF_3)(SMe)\}]$.[16a]

These results led us to investigate the part played by the nucleophile and by the solvent in the reactions of $[\{Fe(CO)_3\}_2\{\mu\text{-}C(SMe)(CF_3)CCF_2\}]$ (**1**). We show here that the substitution pattern in the carbon chain of the final product depends on the choice of nucleophile, with mono- and diamines giving rise to a pattern distinctly different from that obtained earlier with softer thiol or phosphane nucleophiles. The influence of excess nucleophile on the reactions of **1** and the thermal stability of the new products are also reported. A preliminary account of some of this work has been previously published.[17]

## Results and Discussion

**1. Reaction of $[\{Fe(CO)_3\}_2\{\mu\text{-}C(SMe)(CF_3)CCF_2\}]$ (1) with Stoichiometric Amounts of Secondary Amines in Dichloromethane. Formation and Characterization of Cycloferrathiapentadiene Derivatives.** As depicted in Scheme 1, the complex **1** reacted quantitatively in dichloromethane solution at room temperature with 1 equiv of $Me_2NH$ to give a red



(9) Blum, O.; Frolow, F.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1991**, 258.
(10) Whittlesey, M. K.; Perutz, R. N.; Moore, M. H. *J. Chem. Soc., Chem. Commun.* **1996**, 787.
(11) (a) King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* **1964**, *2*, 38. (b) Bruce, M. I.; Stone, F. G. A. *J. Chem. Soc. A* **1966**, 1837.
(12) Park, S.; Pontier-Johnson, M.; Roundhill, D. M. *Inorg. Chem.* **1990**, *29*, 2689.
(13) Maples, P. K.; Green, M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1973**, 2069.
(14) Bonnet, J. J.; Mathieu, R.; Poilblanc, R.; Ibers, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 7487.
(15) (a) Agh-Atabay, N. M.; Canoira, L. J.; Carlton, L.; Davidson, J. L. *J. Chem. Soc., Dalton Trans.* **1991**, 1175. (b) Carlton, L.; Davidson, J. L.; Ewing, P.; Manojlovic-Muir, Lj.; Muir, K. W. *J. Chem. Soc., Chem. Commun.* **1985**, 1474.
(16) (a) Rumin, R.; Guennou, K.; Pétillon, F. Y.; Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1997**, 1381. (b) Rumin, R.; Guennou, K.; Pichon, R.; Pétillon, F. Y.; Muir, K. W.; Yufit, D. S. *J. Organomet. Chem.* **1997**, *533*, 177.
(17) Rumin, R.; Pétillon, F. Y.; Manojlovic-Muir, Lj.; Muir, K. W.; Yufit, D. S. *J. Chem. Soc., Chem. Commun.* **1995**, 1431.

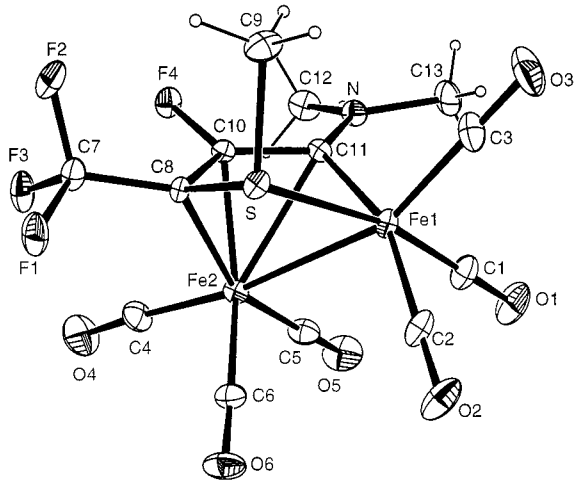



**Figure 1.** View of a molecule of complex **2**, showing 20% probability ellipsoids for non-hydrogen atoms.[19]

solution from which the red solid **2** was obtained on evaporation of the solvent. Similarly, treatment of **1** with 1 equiv of pyrrolidine gave orange crystals of **3** in 80% yield. Reaction of **1** with 1 equiv of piperazine in $CH_2Cl_2$ solution for 15 min gave **4** (~40%); the yield was improved (96%) when **1** was treated with an excess of piperazine (10 equiv). Since piperazine is a secondary diamine, it could, in principle, react with two molecules of **1** to achieve a double removal of hydrogen fluoride. Under conditions almost identical with those used for the reaction of **1** with excess piperazine, it was found that **1** with 0.5 equiv of piperazine affords the tetrairon complex **5** as the only product (98%). To dispel any doubt about the identification of **5**, a pure sample of this complex was also synthesized in 98% yield by a two-step procedure: obtaining **4** from **1** and 1 equiv of piperazine and then reacting it with a further 1 equiv of **1**. Hydrogen fluoride was evolved in all the reactions described in Scheme 1, though the amounts produced were not determined quantitatively; it was unambiguously characterized in the form of the corresponding amine fluoride when **1** was treated with 2 equiv of amine.

The complexes **2**−**5** were formulated by a combination of X-ray diffraction and spectroscopic studies. The molecular structure of **2** (see Figure 1) was reported in the preliminary communication[17] and will not therefore be described here in detail. **2** contains a puckered $FeSC_3$ cycloferrapentadiene ring with C(11)−$NMe_2$ and C(10)−F groups α and $\beta$ to the Fe(1) iron atom. The Fe(1)═C(11)−C(10)═C(8) portion of this ring may formally be regarded as a ferrabutadiene-like unit $\pi$-bonded to Fe(2).[17] The solid-state structure of **2** was shown definitively to persist in solution by multinuclear NMR spectroscopy (see Table 1 and additional resonances given in the Experimental Section). The $^{19}F$ and $^{13}C$ NMR spectra are consistent with the formation of **2** from **1** by rupture of one vinylic C−F bond, followed by a 1,2-shift of the second vinylic fluorine atom from $C_\alpha$ to $C_\beta$. The $^{13}C\{^1H\}$ NMR spectrum showed a doublet at $\delta$ 120.0 ($J_{CF} = 307$ Hz) indicative of coupling to a single fluorine nucleus; the chemical shift of this carbon atom is consistent with it being positioned $\beta$ to Fe(1) in the Fe(1)−$C_\alpha$−$C_\beta$−$C_\gamma$−($CF_3$) ring. The assignments of the remaining quaternary carbon atoms of the cycloferrapentadiene ring were completed on the basis of the observed $^{13}C-^{19}F$ coupling constants and chemical shifts. The resonances at $\delta$ 190.75 (d, $^2J_{CF} = 9$ Hz) and $\delta$ 49.3, which appeared as a split quartet due to the couplings $^2J_{C(C)F_3} = 37$ Hz and $^2J_{C(C)F} = 9$ Hz, were respectively attributed to $C_\alpha$ and $C_\gamma$. The high-field resonance for the $C_\alpha$ carbon atom differs greatly from that observed for the $C_\alpha$ carbon atom ($\delta$ 225.2) in the closely related phosphino complex [{$Fe(CO)_3$}$_2${$\mu$-$C_\alpha$(F)-$C_\beta$($PPh_2$)$C_\gamma$($CF_3$)SMe}],[16b] indicating that in **2** $C_\alpha$ possesses only a small amount of carbene-like character relative to that observed in the phosphino complex. This was confirmed by the Fe(1)−$C_\alpha$ bond length (1.998(4) Å) which is significantly longer than that in the phosphino compound (1.918(3) Å).[16b]

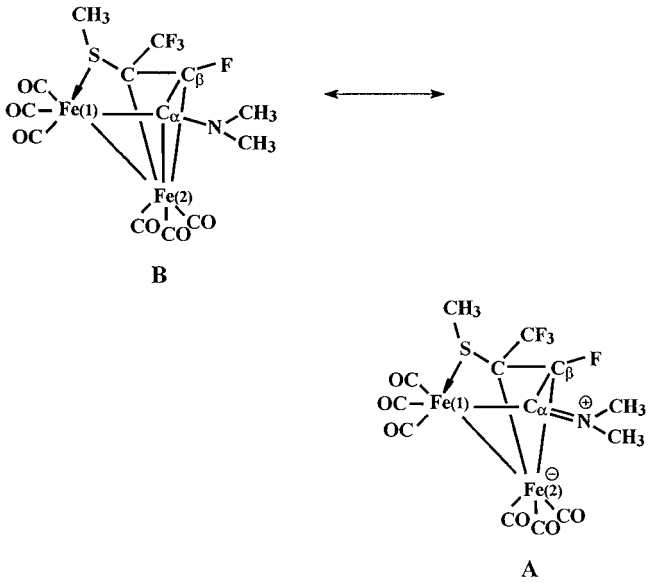
The $^{13}C\{^1H\}$ NMR spectrum of **2** at room temperature gave, in the carbonyl region, three singlets at $\delta$ 211.2, 210.7, and 205.0 and a broad resonance at $\delta$ 210.2 (Table 1), clearly indicating the presence of only terminal Fe−CO groups. By comparison with the related phosphino

**Table 1. Comparison of Selected NMR Chemical Shift Data ($\delta$)[a] for Cycloferrathiapentadiene (2−5) and Cycloferrathiabutene (6−9 and C) Derivatives**

| | $^{19}F$ | | $^{13}C\{^1H\}$ | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| compd | C*F*$_3$ | C*F* | S*C*H$_3$ | *C*$_\beta$ | *C*$_\alpha$ | *C*O(Fe(1)) | *C*O(Fe(1)) | *C*O(Fe(1)) | *C*O(Fe(2)) |
| **2** | −59.2 (d, $^4J_{FF} = 12$) | −152.65 (q, $^4J_{FF} = 12$)[c] | 34.4 (s) | 120.0 (d, $J_{CF} = 307$) | 190.75 (d, $^2J_{CF} = 9$) | 205.0 (s) | 210.7 (2) | 211.2 (s) | 210.2 (s, br) |
| **3** | −59.1 (d, $^4J_{FF} = 12$) | −154.5 (q, $^4J_{FF} = 12$) | 34.6 (s) | 120.6 (d, $J_{CF} = 307$) | 186.0 (d, $^2J_{CF} = 8$) | 205.3 (s) | 211.1 (s) | 211.5 (s)2 | 210.6 (s, br) |
| **4** | −59.0 (d, $^4J_{FF} = 12$) | −147.4 (q, $^4J_{FF} = 12$) | 34.4 (s) | 120.9 (d, $J_{CF} = 307$) | 191.7 (d, $^2J_{CF} = 10$) | 206.7 (s) | 212.0 (s) | 212.0 (s) | 211.6 (s, br) |
| **5** | −58.9 (d, $^4J_{FF} = 11$) | −146.2 (q, $^4J_{FF} = 11$) | 34.6 (s) | 122.9 (d, $J_{CF} = 310$) | 186.05 (d, $^2J_{CF} = 10.5$) | 205.65 (s) | 210.5 (s) | 210.5 (s) | 210.1 (s, br) |
| | | −147.5 (q, $^4J_{FF} = 11$) | | 123.1 (d, $J_{CF} = 308$) | 186.6 (d, $^2J_{CF} = 10$) | | | | |
| **C**[b] | −63.35 (s) | −19.05 (s) | 33.3 (s) | 73.1 (d, $^2J_{CF} = 19$) | 182.1 (d, $J_{CF} = 287.5$) | 207.7 (s) | 209.9 (s) | 212.0(s) | 215.4 (s) |
| **6a** | −64.6 (s) | | 24.05 (s) | 88.7 (s) | 185.6 (s) | | 213.6 (s) | | 214.9 (s, br) |
| **6b** | −63.1 (s) | | 31.0 (s) | 88.45 (s) | 186.5 (s) | | 213.1 (s) | | 214.9 (s, br) |
| **7a** | −64.4 (s) | | 23.8 (s) | 89.6 (s) | 177.0 (s) | | 214.5 (s) | | 215.4 (s, br) |
| **7b** | −62.85 (s) | | 31.4 (s) | 89.7 (s) | 177.3 (s) | | 213.8 (s) | | 215.4 (s, br) |
| **8a** | −64.4 (s) | | 24.5 (s) | 79.9 (s) | 177.2 (s) | | 214.2 (s) | | 216.1 (s) |
| **8b** | −62.5 (s) | | 31.7 (s) | 80.1 | 176.7 (s) | | 213.6 (s) | | 215.8 (s, br) |
| **9** | −58.9 (s) | | 34.2 (s) | 78.1 (s) | 182.1 (s) | | 213.3 (s) | | 215.4 (s) |

[a] Measured in $CDCl_3$ solution at 293 K unless stated by footnote[b], J in Hz. [b] In $CD_2Cl_2$ at 233 K. [c] From ref 19.

**Chart 1**




complex [{Fe(CO)$_3$}$_2${$\mu$-C(F)C(PPh$_2$)C(CF$_3$)SMe}],[16b] which has a five-membered FeSC$_3$ ring like that in **2**, we assigned the broad resonance to the three CO groups bonded to Fe(2) and the three singlets to the carbonyls attached to Fe(1). At low temperature (200 K), the broad resonance at $\delta$ 210.2 splits into three peaks which broadened on heating, finally collapsing at 258 K. No line-shape change involving the Fe(1) carbonyl resonances was noticed throughout the temperature range 200−373 K. The activation barrier of the observed dynamic process was estimated from the chemical shift difference ($\Delta\nu$ = 306 Hz) and the coalescence temperature (258 K).[18] The value of the energy barrier associated with site exchange is low ($\Delta G^*$ = 48.9 ± 1.0 kJ mol$^{-1}$) and is of the order expected for localized scrambling of the carbonyls on a metal atom.[19]

In the solid-state carbon C$_\alpha$ of **2** is engaged in only a very weak interaction with Fe(2) (Fe(2)−C(11) = 2.379(4) Å).[17] Moreover, as previously noted, the C$_\alpha$−N bond has some multiple character. This suggests that in the solid state **2** should have the zwitterionic structure **A** (Chart 1) resulting from nitrogen lone pair delocalization with electron redistribution along the metallacycle. However, the $^1$H NMR spectrum in CDCl$_3$ at room temperature gave, in addition to the SMe peak, a single methyl resonance at $\delta$ 3.38 which appeared as a doublet due to a small coupling to a single $^{19}$F nucleus ($^5J_{HF}$ = 2.5 Hz), providing evidence for the presence of two equivalent methyl groups bonded to the nitrogen atom. The equivalence of the two methyl groups bonded to N implies a fast rotation about the C$_\alpha$−N bond, which would be hindered if the bond in question has much multiple character. Possibly the alternative structure **B** (Chart 1) with a C−N single bond is more significant in solution. A similar effect was reported by Daran et al. for the ferracyclopentadiene compound [{Fe(CO)$_3$}$_2$-{$\mu$-C(NEt$_2$)C(Ph)C(CCPh)C(Ph)}].[20]

The analytical and spectroscopic data for **3**−**5** are given in Table 1 and in the Experimental Section. The very close similarities between the NMR spectra of **3**−**5** and that of **2** (see Table 1) strongly suggest that all four complexes contain the same FeC(N)C(F)C(CF$_3$)S(Me) cycloferrapentadiene ring $\pi$-bonded to an Fe(CO)$_3$ group. The upper parts of the mass spectra of complexes **3** and **4** were characterized by the molecular ion [M]$^+$ and the ions of the sequence [M$^+$ − $n$CO] ($n$ = 1−6); in addition, [M$^+$ − 6CO − $x$FeF$_2$] ($x$ = 1, 2) fragments arising from C−F bond scission were also obtained. Mass spectroscopy (CI) confirms the proposed structure of complex **5**; in particular, the [M + H]$^+$ signal was detected in the spectrum. In the $^{13}$C NMR spectrum of **3** the pair of pyrrolidine ring carbon atoms α to the N atom gave a single resonance at $\delta$ 26.1, while the two ring carbon atoms $\beta$ to N likewise gave a single resonance at $\delta$ 56.7, clearly indicating the presence of fast C$_\alpha$(cycloferrapentadiene)−N rotary motion as in **2**. The resonances attributed to the methylene carbon atoms in the $^{13}$C NMR spectrum and to the CF groups in the $^{19}$F NMR pattern of **5** (see Table 1) are split, indicating the absence of a mirror plane.

**2. Reaction of [{Fe(CO)$_3$}$_2${$\mu$-C(SMe)(CF$_3$)CCF$_2$}] (1) with either a Large Excess of Secondary Monoamines or Secondary and Primary Diamines in Tetrahydrofuran. Formation and Characterization of Cycloferrathiabutene Derivatives.** The reaction of **1** with a large excess of secondary monoamines was carried out in THF instead of CH$_2$Cl$_2$ to test whether C−F bond activation might be assisted by precoordination of either amine or donor solvent. The reactions were carried out at room temperature, proceeding quickly under these conditions. In a typical experiment 20 equiv of secondary monoamine, either Me$_2$NH or pyrrolidine, and 1 equiv of **1** were stirred in THF. After ca. 5 minutes the diamino complex, **6** or **7**, had formed almost quantitatively with apparent loss of two fluorine atoms (Scheme 2). These reactions require a large excess of secondary monoamine to activate the two vinylic C−F bonds of **1**. To widen the scope of this preparative route, we investigated reactions between **1** and secondary or primary diamines, since the two amine functions of these reactants could act like an excess of secondary monoamine to activate the two C−F bonds.

The reactions between 1 equiv of **1** and 2 equiv of *N*,*N*′-dimethylethylenediamine or 1 equiv of ethylenediamine were also carried out in THF. Stirring the mixtures for 5 min gave good yields of the diamino complexes **8** (97%) and **9** (80%) according to Scheme 2.

Analytical data and mass, infrared, and multinuclear ($^1$H, $^{19}$F and $^{13}$C) NMR spectroscopic data for all compounds discussed in this part are given in either Table 1 or the Experimental Section. It is immediately apparent from the examination of the selected NMR data reported in Table 1 that complexes **6**−**9** have the same basic structure. However, discussion of these results is deferred until after the molecular structures of two of these compounds have been described.

The crystals of **8** used in the diffraction study (Table 2 and Figure 2) were obtained from hexane−CH$_2$Cl$_2$ at −20 °C. **8** contains a cycloferrathiaalkene ring, defined by Fe(1), S, C(8), and C(9), which is folded across the Fe(1)···C(8) diagonal by 32.5(2)°. The Fe(2) tricarbonyl

(18) Shanan-Atidi, H.; Bar-Eli, K. H. *J. Chem. Phys.* **1970**, *74*, 961.
(19) Robin, F.; Rumin, R.; Talarmin, J.; Pétillon, F. Y.; Muir, K. W. *Organometallics* **1993**, *12*, 365.
(20) Daran, J. C.; Gilbert, E.; Gouygou, M.; Halut, S.; Heim, B.; Jeannin, Y. *J. Cluster Sci.* **1994**, *5*, 373.

**Scheme 2. Synthesis and Proposed Structure of Complexes 6−9**

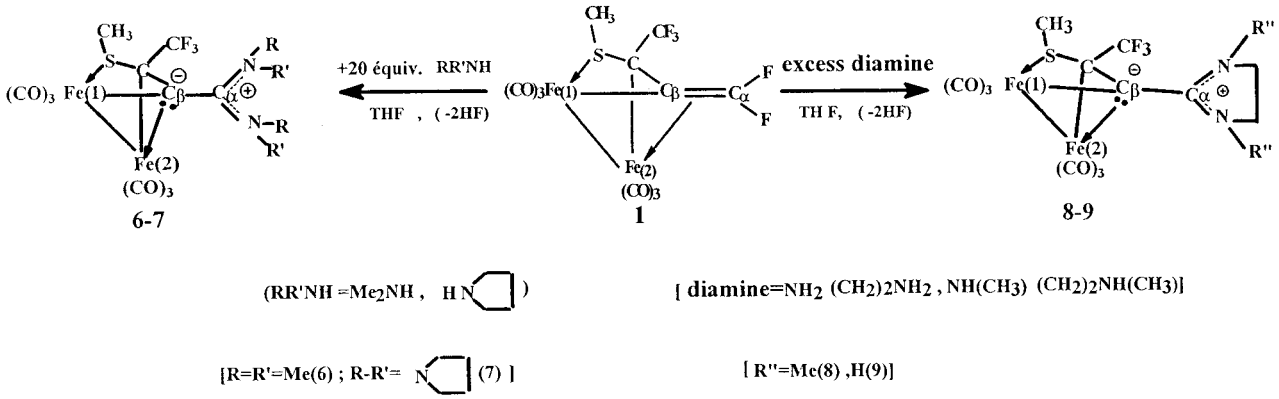



**Table 2. Selected Bond Lengths (Å) and Angles (deg) for 8**

| | | | |
|---|---|---|---|
| Fe−CO | 1.768(3)−1.801(3) | N(1)−C(13) | 1.440(4) |
| Fe(1)−C(9) | 2.026(2) | N(1)−C(12) | 1.462(3) |
| Fe(1)−S | 2.305(1) | N(2)−C(10) | 1.343(3) |
| Fe(1)−Fe(2) | 2.591(1) | N(2)−C(14) | 1.430(4) |
| Fe(2)−C(9) | 1.935(2) | N(2)−C(11) | 1.462(3) |
| Fe(2)−C(8) | 2.010(2) | C(7)−C(8) | 1.511(4) |
| S−C(15) | 1.800(3) | C(8)−C(9) | 1.464(3) |
| S−C(8) | 1.800(2) | C(9)−C(10) | 1.443(3) |
| N(1)−C(10) | 1.329(3) | C(11)−C(12) | 1.511(4) |

| | | | |
|---|---|---|---|
| C(15)−S−C(8) | 108.15(14) | C(7)−C(8)−Fe(2) | 122.97(19) |
| C(15)−S−Fe(1) | 115.70(14) | S−C(8)−Fe(2) | 112.48(12) |
| C(8)−S−Fe(1) | 77.31(8) | C(10)−C(9)−C(8) | 127.9(2) |
| C(10)−N(1)−C(13) | 128.9(2) | C(10)−C(9)−Fe(2) | 139.84(17) |
| C(10)−N(1)−C(12) | 112.3(2) | C(8)−C(9)−Fe(2) | 70.99(13) |
| C(13)−N(1)−C(12) | 118.7(2) | C(10)−C(9)−Fe(1) | 124.36(16) |
| C(10)−N(2)−C(14) | 127.2(2) | C(8)−C(9)−Fe(1) | 94.68(14) |
| C(10)−N(2)−C(11) | 111.9(2) | Fe(2)−C(9)−Fe(1) | 81.67(8) |
| C(14)−N(2)−C(11) | 119.0(2) | N(1)−C(10)−N(2) | 109.4(2) |
| C(9)−C(8)−C(7) | 124.4(2) | N(1)−C(10)−C(9) | 126.2(2) |
| C(9)−C(8)−S | 104.82(17) | N(2)−C(10)−C(9) | 124.4(2) |
| C(7)−C(8)−S | 116.20(18) | N(2)−C(11)−C(12) | 103.2(2) |
| C(9)−C(8)−Fe(2) | 65.51(12) | N(1)−C(12)−C(11) | 103.3(2) |

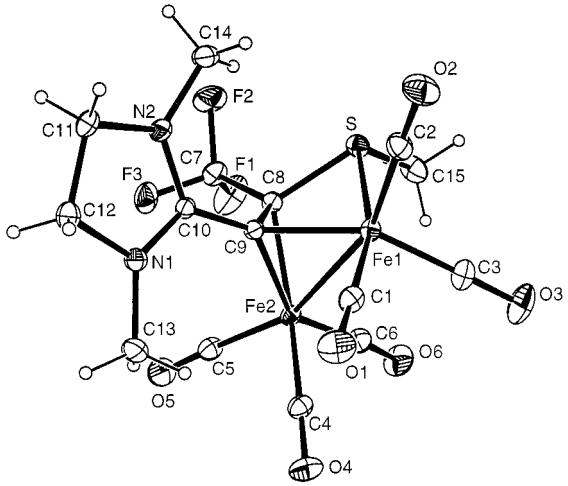



**Figure 2.** View of a molecule of complex **8**, showing 20% probability ellipsoids for non-hydrogen atoms.

unit forms a normal Fe−Fe bond (2.591(1) Å) with Fe(1) and is also $\pi$-bonded to the C(8)−C(9) double bond, being somewhat closer to C(9) (1.935(2) Å) than to C(8) (2.010(2) Å). The latter value agrees well with the Fe(1)−C(9) distance (2.026(2) Å), and both are close to the mean database values for $\sigma$-Fe−C(vinyl) (1.991 Å) or terminal Fe−C(carbene) (1.978 Å) bonds.[21] The folding of the cylcloferrathiaalkene ring increases the intramolecular Fe(2)···S distance to 3.170(1) Å. The sulfur lone pair points away from Fe(2) so that Fe(2) and C(15), the *S*-methyl carbon atom, are cis relative to the Fe(1)−S−C(8)−C(9) ring. Atom C(10) has a planar coordination and is involved in a delocalized $\pi$-system with N(1) and N(2) (C(10)−N = 1.329(3) and 1.343(3) Å), so that the atoms C(10)−C(14), N(1), and N(2) are coplanar to within 0.11 Å. The orientation of this plane, defined for example by the Fe(1)−C(9)−C(10)−N(2) torsion angle of 82.2(3)°, is unfavorable for $\pi$-overlap across C(9)−C(10). Evidently C(9)−C(10) is a single bond, despite its length (1.443(3) Å) which is short for an unconjugated $C_{sp^2}-C_{sp^2}$ bond of unit order. The multiple character of the C(10)−N bonds and the carbene-like character of C(10) may indicate a zwitterionic structure for **8**, as depicted in Scheme 2. Reaction of **1** with *N,N′*-dimethylethylenediamine thus leads to the formation of an imidazoline ring by cleavage of both C−F bonds and cyclization of the ligand onto the $C_\alpha$ carbon atom. It is known that *N,N′*-dimethylethylenediamine can be cyclized to give imidazolines by reaction with aldehydes.[22]

The structure of **8** could alternatively be described as a $\mu_2$-$\eta^1$:$\eta^2$ vinyl complex in which the C(8)−C(9) unit is $\sigma$-bonded to Fe(1) and $\pi$-bonded to Fe(2). The $\eta^2$-vinyl coordination mode, although uncommon, has been observed in mononuclear complexes of metals of group 6[15,23] and, more particularly, in binuclear iron compounds.[24] The Fe−C distances found here broadly agree with those reported by Daran et al. for $\mu_2$-$\eta^1$:$\eta^2$ vinyl complexes ($Fe^1-C_\alpha$ = 2.007(9)−2.016(3), $Fe^2-C_\alpha$ = 2.030(8)−2.068(2), $Fe^1-C_\beta$ = 1.872(3)−1.883(2) Å).[24] However, the C(8)−C(9) distance (1.464(3) Å) in **8** is long compared with values reported by Daran et al. (1.369(9)−1.391(4) Å).

Attempts to grow good-quality crystals of **6** were generally unsuccessful, but a single crystal data set, albeit of poor quality, was finally obtained. The molecular structure determined from it, though of low precision (Table 3), strongly resembles that of **8** (cf. Figures 2 and 3). Like **8**, compound **6** contains a cycloferrathiaalkene ring, defined by Fe(2), S, C(8), and C(10). Fe(2) and the two carbon atoms C(8) and C(10) are all

(21) *International Tables for Crystallography*; Kluwer Academic: Dordrecht, The Netherlands, 1992; Vol. C, Table 9.6.3.3.
(22) Harris, T. D.; Roth, G. P. *J. Org. Chem.* **1979**, *44*, 2004.
(23) (a) Kiplinger, J. L.; Richmond, T. G. *Polyhedron* **1997**, *16*, 409. (b) Feng, S. G.; Templeton, J. L. *Organometallics* **1992**, *11*, 2168.
(24) Daran, J. C.; Heim, B.; Gouygou, M.; Jeannin, Y. *J. Organomet. Chem.* **1994**, *479*, 109.

**Table 3. Selected Bond Lengths (Å) and Angles (deg) for 6**

| | | | |
|---|---|---|---|
| Fe−CO | 1.67(4)−1.78(3) | N(1)−C(14) | 1.44(4) |
| Fe(1)−C(10) | 1.91(3) | N(1)−C(15) | 1.53(4) |
| Fe(1)−C(8) | 2.05(3) | N(2)−C(11) | 1.31(3) |
| Fe(1)−Fe(2) | 2.593(6) | N(2)−C(12) | 1.36(4) |
| Fe(2)−C(10) | 1.99(3) | N(2)−C(13) | 1.50(4) |
| Fe(2)−S(1) | 2.307(9) | C(8)−C(10) | 1.49(4) |
| S(1)−C(8) | 1.79(3) | C(8)−C(9) | 1.49(4) |
| S(1)−C(7) | 1.79(4) | C(10)−C(11) | 1.49(4) |
| N(1)−C(11) | 1.31(3) | | |

| | | | |
|---|---|---|---|
| C(8)−S(1)−C(7) | 106.5(16) | C(10)−C(8)−Fe(1) | 62.9(15) |
| C(8)−S(1)−Fe(2) | 78.6(10) | C(9)−C(8)−Fe(1) | 123(2) |
| C(7)−S(1)−Fe(2) | 118.8(13) | S(1)−C(8)−Fe(1) | 110(2) |
| C(11)−N(1)−C(14) | 123(3) | C(11)−C(10)−C(8) | 124(2) |
| C(11)−N(1)−C(15) | 124(3) | C(11)−C(10)−Fe(1) | 141(2) |
| C(14)−N(1)−C(15) | 113(3) | C(8)−C(10)−Fe(1) | 73(2) |
| C(11)−N(2)−C(12) | 127(3) | C(11)−C(10)−Fe(2) | 124(2) |
| C(11)−N(2)−C(13) | 118(3) | C(8)−C(10)−Fe(2) | 97(2) |
| C(12)−N(2)−C(13) | 115(3) | Fe(1)−C(10)−Fe(2) | 84(1) |
| C(10)−C(8)−C(9) | 127(3) | N(2)−C(11)−N(1) | 114(3) |
| C(10)−C(8)−S(1) | 103(2) | N(2)−C(11)−C(10) | 125(2) |
| C(9)−C(8)−S(1) | 118(2) | N(1)−C(11)−C(10) | 121(3) |

attached to Fe(1). The Fe(1)−Fe(2) distance, 2.593(6) Å, is appropriate for an Fe−Fe single bond. Other structural results for **6** (Table 3) are consistent with delocalization of the nitrogen lone pair and subsequent electron redistribution along the carbon chain, leading to a zwitterionic structure for **6**, similar to that proposed for **8** (see above).

Having considered the crystal structures of **6** and **8**, we turn to the spectroscopic data for these compounds and their related complexes **7** and **9**. First, it is apparent that the solution structures are consistent with those observed in the solid state. However, it was shown by multinuclear NMR spectroscopy that in solution all of the complexes except for **9** are present as the two interconverting isomeric forms **a** and **b**. The **a**:**b** ratios depend little on temperature but change with solvent: in more polar solvents the relative amount of the minor isomer **b** increases (e.g. **6a**:**6b** = 2.33:1 in $CDCl_3$ and 1.56:1 in $CDCl_3 + CD_3CN$). The NMR spectra of the two isomers are very similar, differing mainly in their SMe patterns (see Table 1). For example, in the $^{13}C$ NMR spectrum of **6**, the SMe carbon signals appear for **6a** (major isomer) and **6b** (minor isomer) at $\delta$ 24.05 and 31.0, respectively. On the basis of these NMR data, it can be concluded that the two isomers only differ by the position of the methyl group relative to the cycloferrathiaalkene ring. When pure crystalline compound **6** was redissolved at low temperature (−60 °C), only the major isomer was observed. We therefore conclude that the structure of the major isomer **6a** in solution is identical with that found in the crystal, with cis *S*-methyl and Fe(1)$(CO)_3$ groups (see Figure 3), while **6b** is the trans isomer, arising from inversion of the SMe group (Chart 2). In the $^{13}C\{^1H\}$ NMR spectra of these complexes the SMe resonances at ca. $\delta$ 24.0 and 31.4 are respectively assigned to the major isomer **a** and minor isomer **b** (Table 1). Complex **9** was identified as isomer **b** by its low-field SMe $^{13}C\{^1H\}$ chemical shift value at $\delta$ 34.2.

Since the NMR spectra of these complexes are all very similar, whatever the isomeric form may be, this discussion will illustrate their main features using the data for **6** and **9**. The room-temperature $^1H$ NMR spectrum of **9** (Experimental Section) shows the presence of only

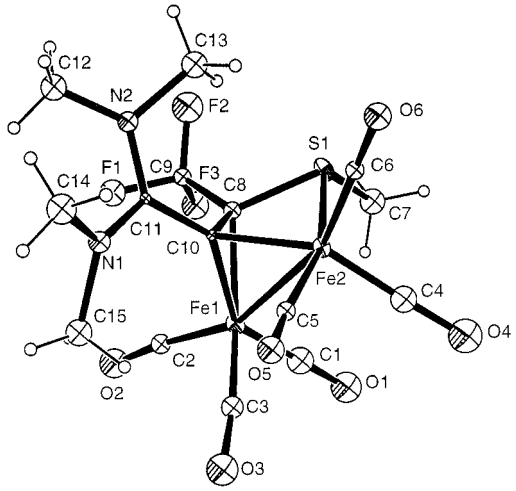
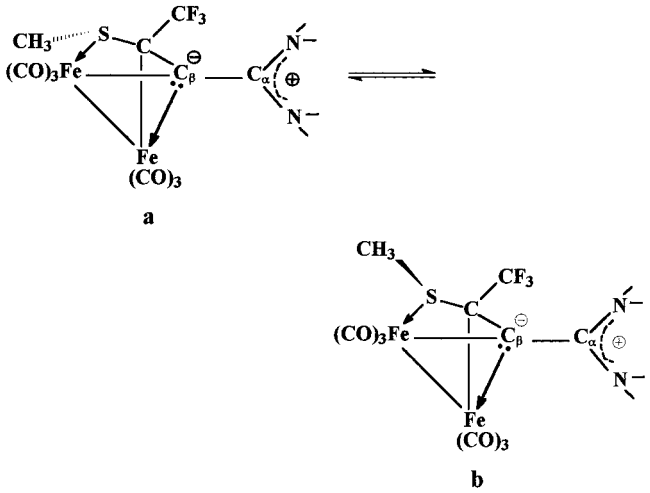



**Figure 3.** View of a molecule of complex **6**, showing 20% probability ellipsoids for non-hydrogen atoms.

**Chart 2**




one diamine ligand in the molecule. The equivalence of the two pairs of protons from the amine groups on one hand, and of the two pairs of protons from the imidazoline methylene groups on the other hand, implies that a fast $C_\alpha-C_\beta$ rotary motion takes place in this molecule. Furthermore, the equivalence of all 12 amine protons in **6** (see Experimental Section) indicates that in addition to $C_\beta-C_\alpha$ rotary motion there are also two $C_\alpha-N$ rotations in this molecule. Similar rotary motions are observed at room temperature in **7** but not in **8**, as shown by its $^{13}C\{^1H\}$ NMR spectrum, where four signals due to nonequivalent pairs of carbons from methyl and methylene groups of the 1,3-dimethylimidazoline are observed, indicating that in **8** the rotational effect was hindered by the two methyl groups. At this point, it was necessary to identify the two sets of carbon peaks observed at ca. $\delta$ 85.0 and 180.0 in the $^{13}C$ NMR spectra of complexes of the series (Table 1). This was readily accomplished via a $^1H-^{13}C$ 2D HMBC experiment, as illustrated in Figure 4 for complex **9**. It is obvious from this spectrum that methylene protons ($\delta$ 3.9) are coupled to carbon at $\delta$ 182.1, which is then attributed to $C_\alpha$ ($^3J_{C-H}$), while no proton couples with the resonance at $\delta$ 78.1, which is therefore assigned to the $C_\beta$ carbon. We have shown above that the carbenoid character of $C_\beta$ was reflected in the shortness of the Fe(2)−C(9) bond

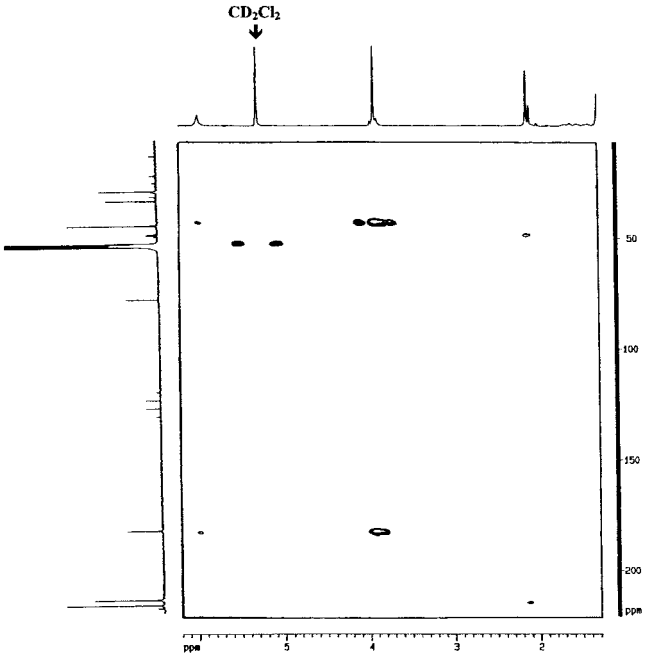


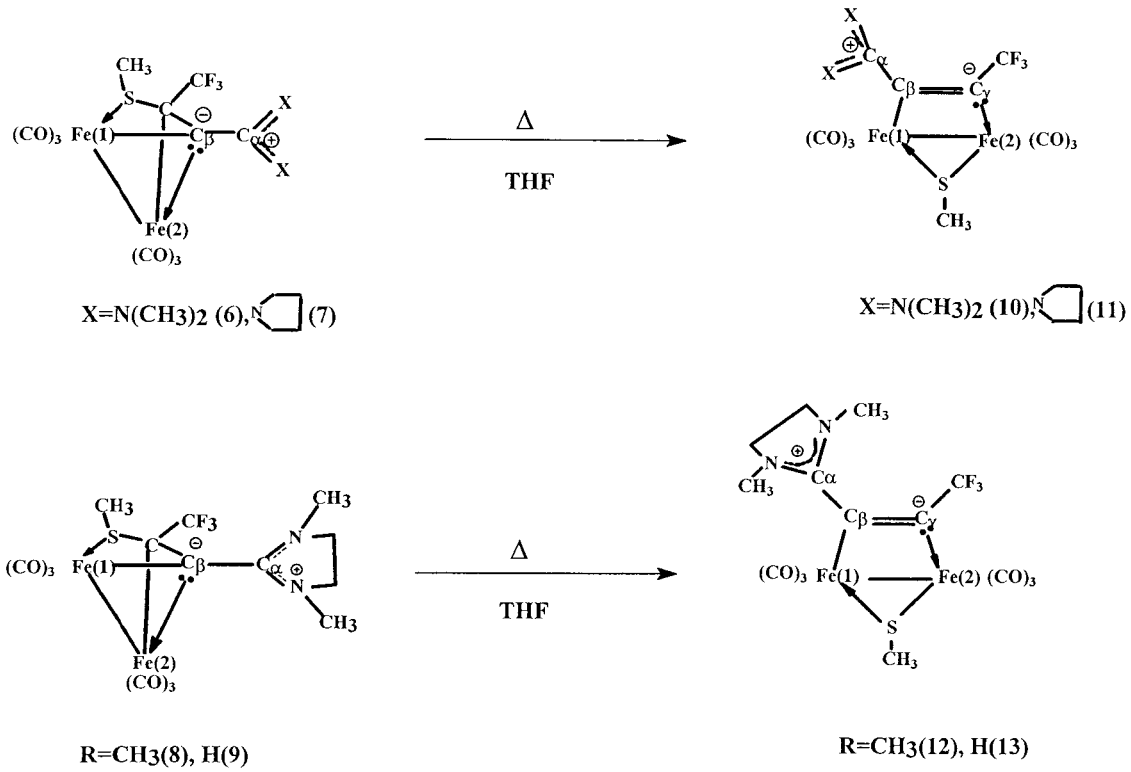

**Figure 4.** $^1H-^{13}C$ 2D HMBC spectrum of **9** (298 K, $CD_2Cl_2$).

in **8**. However, the $C_\beta$ chemical shift value ($\delta$ 78.1) exhibited by complex **9** is very high-field for a carbon atom having a typical carbene character, but this may be a consequence of the presence of a negative charge on this carbon atom. Two resonances in the carbonyl region of the $^{13}C$ NMR of **9** are observed at $\delta$ 215.4 and 213.3. The $^1H-^{13}C$ 2D HMBC spectrum of **9** (see Figure 4) displays an unusually small correlation between the carbonyl signal at $\delta$ 213.3 and the SMe proton signal at $\delta$ 2.1. This coupling ($^4J_{C-H}$) allows the signal at $\delta$ 213.3 to be assigned to Fe(1)-bound terminal carbonyls, since Fe(2)-bound terminal carbonyls would require a $^5J_{C-H}$ coupling. Interestingly, the $\nu$(CO) bands in the spectra of **6** and **9** (Experimental Section) are shifted to lower frequencies than those of the cycloferrathiapentadiene complexes **2**−**5**, reflecting greater $\pi$ backbonding to CO for cycloferrathiabutene derivatives. This is probably due to delocalization of the negative charge of the zwitterion onto the $Fe(CO)_3$ groups. The downfield shifting of the $^{13}C$−carbonyl resonances of **6**−**9** compared to those of **2**−**5** are consistent with the IR data.

**3. Thermal Isomerization of Cycloferrathiabutene Derivatives. Formation and Characterization of Amidinium-Substituted $\mu_{||}$-$\eta^1$:$\eta^1$ Complexes 10−13.** Thermolysis of cycloferrathiabutene compounds **6**−**9** in tetrahydrofuran afforded in high yields amidinium-substituted $\mu_{||}$-$\eta^1$:$\eta^1$-alkyne complexes **10**−**13**, formed via carbon−sulfur bond scission and coordination of the thiolato fragment onto the diiron framework (Scheme 3). This transformation was conveniently followed by $^1H$ NMR spectroscopy. Qualitatively, the rate of isomerization increases as the total steric bulk of the amine substituents decreases, in the order $CH_3NCH_2$-$CH_2NCH_3 \approx \{N(CH_2)_4\}_2 > \{N(CH_3)_2\}_2$. The steric bulk of the amine is related to the NCN angle in the precursor complexes (e.g., NCN = 114(3)° in **6** and 109.4(2)° in **8**). The isomerization of **7** and **8** was complete after 2 h in THF at 60 °C, while the corresponding isomerization of **6** occurred after 24 h under the same conditions.

Complexes **10**−**13** were characterized by their spectroscopic data as well as by the crystallographic study of the dimethylethylenediamine derivative **10** described below. The pattern and intensities of the peaks of the upper parts of the mass spectra of compounds **10**−**13** closely resemble those for the precursor complexes, thereby supporting the formulations in Scheme 3. The

**Scheme 3. Synthesis and Proposed Structure of Complexes 10−13**



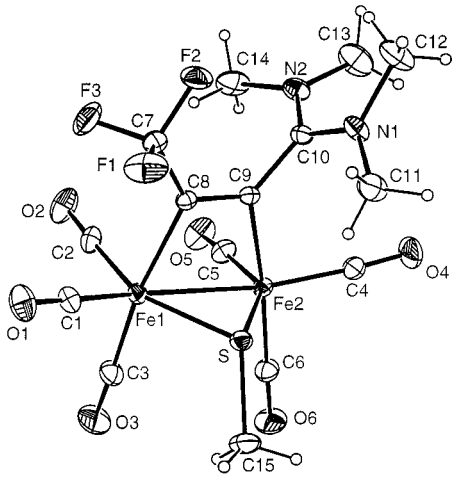



**Figure 5.** View of a molecule of complex **10**, showing 20% probability ellipsoids for non-hydrogen atoms.

**Table 4. Selected Bond Lengths (Å) and Angles (deg) for 10**

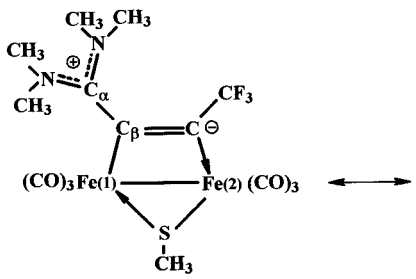
| | | | |
|---|---|---|---|
| Fe−CO | 1.774(3)−1.795(3) | N(1)−C(11) | 1.463(3) |
| Fe(1)−C(8) | 2.006(2) | N(1)−C(12) | 1.484(3) |
| Fe(1)−S | 2.2398(6) | N(2)−C(10) | 1.342(3) |
| Fe(1)−Fe(2) | 2.6136(5) | N(2)−C(13) | 1.455(4) |
| Fe(2)−C(9) | 2.040(2) | N(2)−C(14) | 1.459(4) |
| Fe(2)−S | 2.2629(7) | C(7)−C(8) | 1.483(3) |
| S−C(15) | 1.823(3) | C(8)−C(9) | 1.322(3) |
| N(1)−C(10) | 1.314(3) | C(9)−C(10) | 1.475(3) |

| | | | |
|---|---|---|---|
| C(15)−S−Fe(1) | 113.87(12) | C(9)−C(8)−C(7) | 125.1(2) |
| C(15)−S−Fe(2) | 114.42(12) | C(9)−C(8)−Fe(1) | 109.51(15) |
| Fe(1)−S−Fe(2) | 70.96(2) | C(7)−C(8)−Fe(1) | 125.4(2) |
| C(10)−N(1)−C(11) | 121.6(2) | C(8)−C(9)−C(10) | 128.7(2) |
| C(10)−N(1)−C(12) | 121.4(2) | C(8)−C(9)−Fe(2) | 107.63(14) |
| C(11)−N(1)−C(12) | 115.5(2) | C(10)−C(9)−Fe(2) | 123.7(2) |
| C(10)−N(2)−C(13) | 124.0(3) | N(1)−C(10)−N(2) | 120.8(2) |
| C(10)−N(2)−C(14) | 122.0(2) | N(1)−C(10)−C(9) | 120.8(2) |
| C(13)−N(2)−C(14) | 111.8(3) | N(2)−C(10)−C(9) | 118.3(2) |

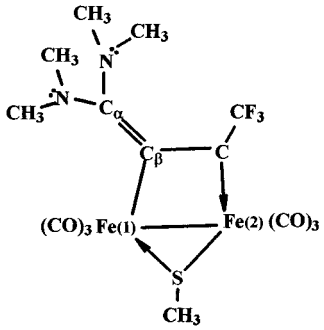
pattern of $\nu$(CO) bands differs somewhat from those for the precursors, although the frequences for **10**−**13** are as low as those of **6**−**9** and those of the related ylide−carbene complex [{Fe(CO)$_3$}$_2$(*μ*-SBu$^t$)(*μ*-Ph$_3$PC═CPh)],[25] reflecting a large $\pi$-back-bonding to CO, consistent with delocalization of the negative charge of the zwitterion onto the Fe(CO)$_3$ groups. The $^{13}$C NMR spectra of compounds **10**−**13** displayed four distinct resonances in the range 100−200 ppm; their assignment to carbon atoms of the bridging amidinium ligand is based on the nature of the $^{13}$C−$^{19}$F couplings. Two quartets at ca. $\delta$ 148.0 ($^2J_{CF} \approx 32$ Hz) and 142.5 ($^3J_{CF} \approx 8$ Hz) were found in the range expected for a parallel acetylene complex, with weak carbene-like character, and are therefore assigned to C$_\gamma$ and C$_\alpha$ carbon atoms, respectively. The low-field singlet at ca. $\delta$ 174.5 is due to the C$_\alpha$ atom; the chemical shift of the last resonance is closely similar to those observed for the C$_\alpha$-amidinium atoms of the precursors, which is consistent with the formulation. Discussion of the $^{13}$C{$^1$H} NMR data for the substituents on the nitrogen atoms of the amidinium-substituted fragment is deferred until after the molecular structure of **10** has been described (Figure 5, Table 4).

Molecules of **10** contain two iron atoms asymmetrically bridged by an amidinium-substituted parallel alkyne $\sigma$-bonded through C(8) and C(9). The C(10)−N distances (1.314(3) and 1.342(3) Å) differ slightly but suggest that C(10) is conjugated with its two NMe$_2$ substituents. The C(8)−C(9) distance of 1.322(3) Å indicates a bond order close to 2 and is similar to C−C bond lengths observed in the closely related dimetallacyclobutene complexes [{Fe(CO)$_3$}$_2$(*μ*-PPh$_2$){*μ*-C[CNMe(CH$_2$)$_2$NMe]C(C$_6$H$_5$)}][26] and [{Fe(CO)$_3$}$_2$(*μ*-PPh$_2$){*μ*-C(t-BuHNC)NHPr$^i$)C═C(CH$_3$)}].[27] These results point to a major contribution from the dipolar canonical form **10a** to the ground state of **10** (Chart 3), with the positive charge localized on nitrogen atoms and the negative charge formally on C(8) delocalized into the Fe(2)(CO)$_6$S skeleton. The zwitterionic nature of **10** may alternatively be depicted by its neutral resonance form **10b** (Chart 3), which implies a carbene-like interaction between Fe(1) and C(8) (Figure 5) and a double bond between C(9) and C(10). This canonical form can only be a very minor contributor to the overall structure. It is consistent with the slight shortening of Fe(1)−C(8) (2.006(2) Å) relative to Fe(2)−C(9) (2.040(2) Å) but not with the high-field shift of C(8) in the $^{13}$C NMR spectrum at $\delta$ 146.0 nor with the C(9)−C(10) bond length of 1.475(3) Å, both of which are best explained by a bond of unit order. The four atoms of the dimetallacyclobutene ring, Fe(1), Fe(2), C(8), and C(9), are coplanar to within 0.028 Å. The thiolato ligand asymmetrically bridges the two iron atoms (Fe(1)−S = 2.240(1), Fe(2)−S = 2.263(1) Å) and the dihedral angle between the plane defined by Fe(1), Fe(2), and S, and that of the dimetallacyclobutene ring is 91.6(1)°. The four atoms N(1), N(2), C(10), and C(9) are coplanar to within 0.008 Å. This supports our interpretation of the bonding in the amidinium ligand. The planes defined

**Chart 3**




**10a**



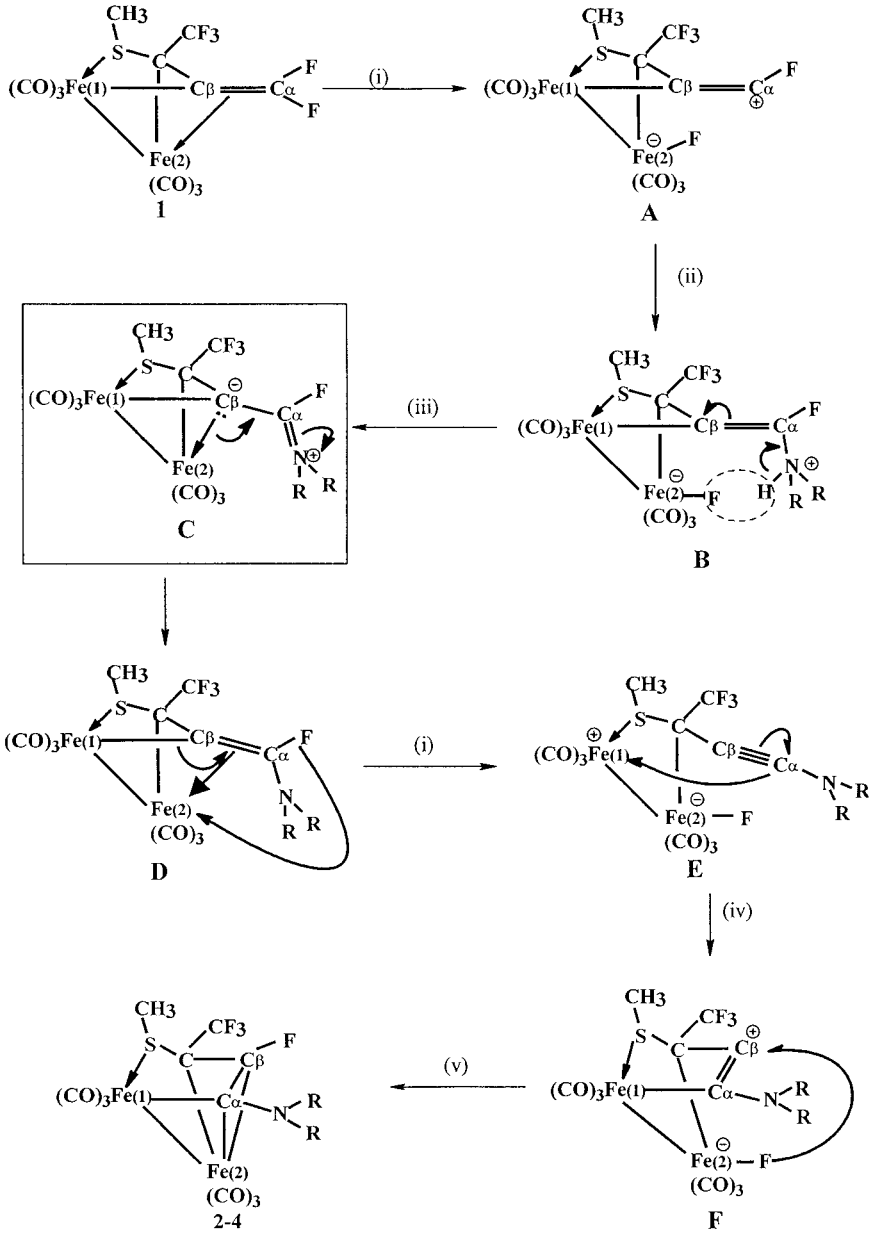

**10b**

(25) Seyferth, D.; Hoke, J. B.; Wheeler, D. R. *J. Organomet. Chem.* **1988**, *341*, 421.

(26) Carty, A. J.; Taylor, N. J.; Smith, W. F.; Lappert, M. F.; Pye, P. L. *J. Chem. Soc., Chem. Commun.* **1978**, 1017.

(27) Doherty, S.; Hogarth, G.; Waugh, M.; Scanlan, T. H.; Clegg, W.; Elsegood, M. R. J. *Organometallics* **1999**, *18*, 3178.

**Scheme 4. Possible Pathway to the Formation of Monoaminocycloferrathiapentadiene Derivatives 2−4**[a]




[a] Legend: (i) α-elimination of F; (ii) nucleophilic attack of $R_2NH$ at $C_\alpha$; (iii) −HF; (iv) internal rearrangement; (v) F migration.

by the $Fe_2C_2$ metallacyclic frame and N(1), C(10), and N(2) are nearly perpendicular (dihedral angle of 93.2°). The $NMe_2$ groups twist out of the coordination plane of C(10) to relieve the overcrowding of the C(12) and C(13) methyl groups (C(12)···C(13) = 2.888(5) Å). This may explain the lengthening of C(10)−N(2) relative to C(10)−N(1), since the twisting is greater for the N(2) amidinium group (cf. C(9)−C(10)−N(1)−C = 5.1(4) and −160.1(3)° with C(9)−C(10)−N(2)−C values of 20.2(4) and −141.6(3)°). These data reflect the inequivalence of the four *N*-methyl groups in the solid state. The two $Fe(CO)_3$ groups adopt an almost eclipsed conformation in **10**.

We have shown above that the four methyl groups bonded to nitrogen atoms in **10** are inequivalent in the solid state. At room temperature the $^{13}C\{^1H\}$ *N*-methyl pattern for this compound exhibits only two signals at $\delta$ 42.4 and 42.35, indicating the operation of exchange processes in the solution. The $^{13}C$ NMR spectrum of **10** at 235 K shows all four *N*-methyl resonances, but when the temperature is raised, the signals first broadened and then collapsed, two at 279 K and the remaining two at 284 K. Above 284 K, sharpening of the resonances occurred, leading to the limiting high-temperature spectrum at 373 K, which consists of two singlets in an integral ratio of 1:1; above 373 K, the complex underwent thermal decomposition. It is readily apparent from these results that only $C_\alpha$−N rotary motions can account for the pattern of two *N*-methyl signals obtained above 284 K; an additional $C_\alpha$−$C_\beta$ rotary motion would give rise to a *N*-methyl pattern exhibiting only one signal. The activation barriers of the observed dynamic processes are estimated from the chemical shift differences ($\Delta\nu_1$ = 151 Hz; $\Delta\nu_2$ = 126 Hz) and coalescence temperatures ($T_c(1)$ = 284 K; $T_c(2)$ = 279 K).[18] The values of the energy barrier associated with the site exchanges resulting from $C_\alpha$−N rotation are low ($\Delta G^{\ddagger}_1 = 55.7 \pm 1.0$ kJ mol$^{-1}$; $\Delta G^{\ddagger}_2 = 55.1 \pm 1.0$ kJ mol$^{-1}$) compared to

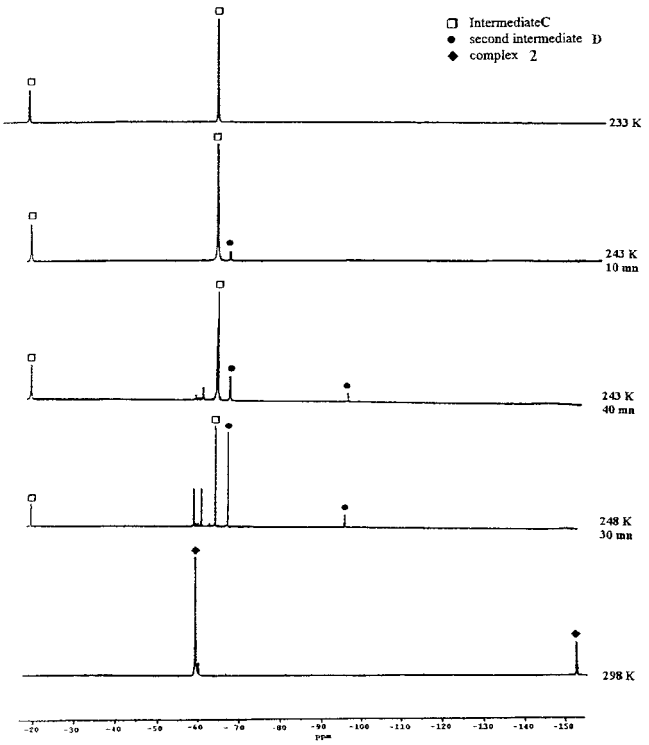
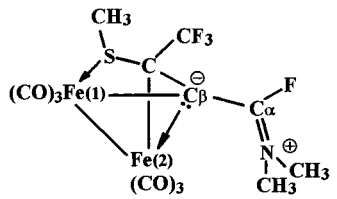



**Figure 6.** Reaction of **1** with a stoichiometric amount of dimethylamine monitored by $^{19}F$ NMR spectroscopy.

that for a $C_\alpha-C_\beta$ rotary motion, which is estimated to be higher than 81.4 kJ $mol^{-1}$.

**4. Possible Reaction Pathways for the Formation of Cycloferrathiapentadiene and Cycloferrathiabutene Complexes. a. Cycloferrathiapentadiene Complexes (2−5).** A possible mechanism of formation of cluster **2** has already been proposed.[17] However, by reinvestigating the reaction of **1** with dimethylamine to give **2**, we have been able to characterize fully an intermediate complex. Thus, the mechanistic results for the formation of **2** are updated here and extended to the other monoamino complexes **3**−**5**. At room temperature the reaction to form **2** takes only a few minutes. When the reaction was undertaken at low temperature, it was possible to detect several intermediates. In light of the NMR data, an appropriate reaction pathway for the formation of monoamino complexes is shown in Scheme 4. When the reaction of **1** with 1 equiv of dimethylamine was monitored by $^{19}F$ NMR at 233 K, only one long-lived species **C** (R = Me) (see Figure 6) could be identified. This compound is stable at 233 K and has been fully characterized by $^{19}F$ and $^{13}C$ NMR spectroscopy. The $^{19}F$ NMR spectrum of **C** consists of two singlets at $\delta$ −63.34 and −19.05 with an intensity ratio of 3:1, clearly indicating the presence of $CF_3$ and CF groups. The C−F resonance is at much lower field ($\delta$ −19.05) than either the $C_\beta F$ resonance in monoaminocycloferrathiapentadiene complexes (e.g. $\delta$ −152.65 for **2**) or the $C_\alpha F$ resonance in monophosphinocycloferrathiapentadiene compounds (e.g. $\delta$ −45.0 for the PPhH derivative). These data are indicative of great differences between the basic structures of **C** and those of the two other types of complexes mentioned above. Thus, the structure of **C** can be solved by $^{13}C\{^1H\}$ NMR spectroscopy. Indeed, with some understandable exceptions, the $^{13}C$ NMR spectra of **C** and **6**−**9** (zwitterionic

**Chart 4**



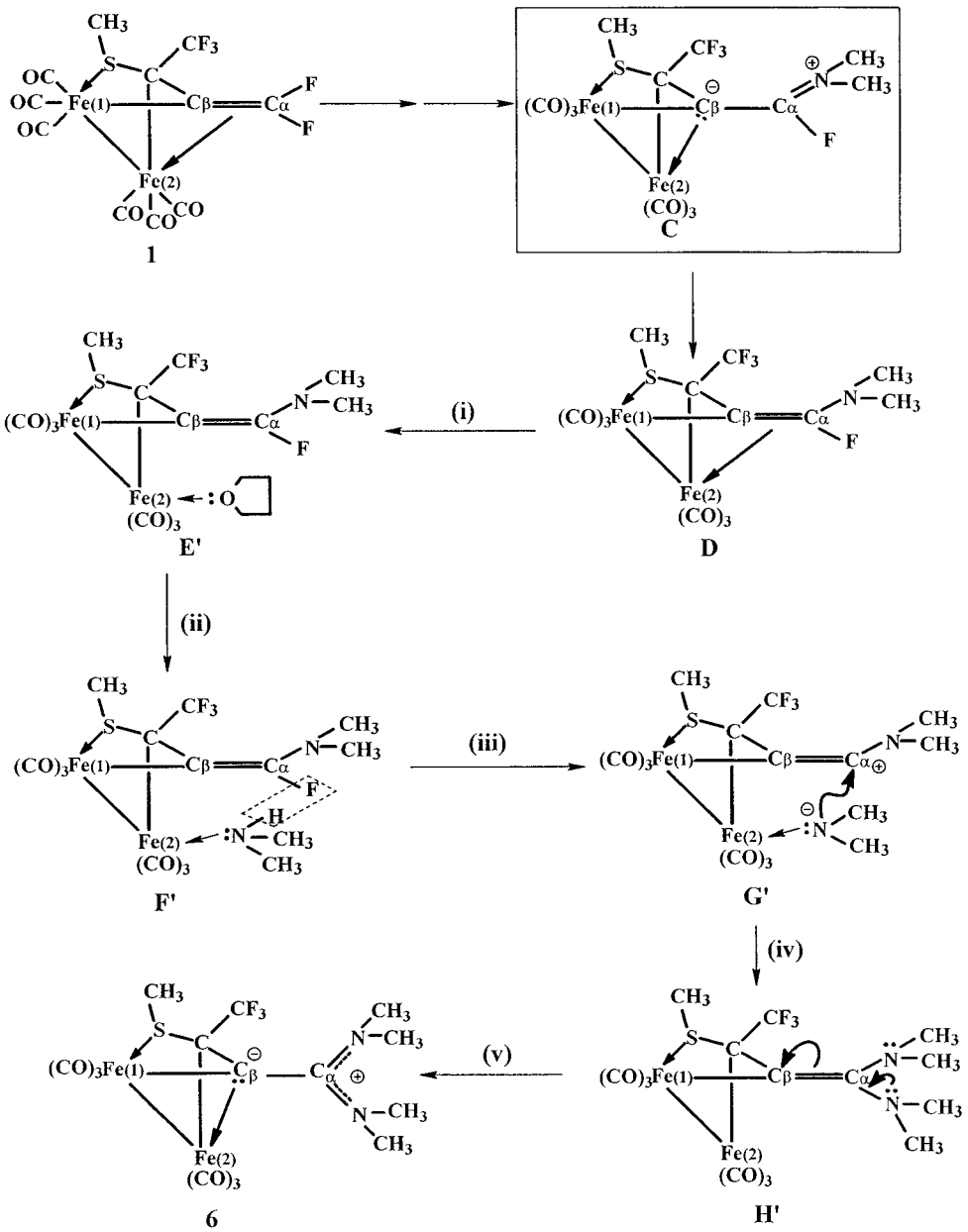

**Intermediate C**

cycloferrathiabutene complexes) are closely similar (see Table 1). This strongly suggests that **C** and **6**−**9** have a common skeletal structure, containing a four-membered Fe−S(Me)−$C(CF_3)$−C ring bonded to a second iron atom. The presence of a low-field doublet at $\delta$ 185.6 ($^1J_{CF}$ = 287.5 Hz) for $C_\alpha$ and a high-field doublet at $\delta$ 73.1 ($^2J_{CF}$ = 19 Hz) for $C_\beta$ in the $^{13}C$ NMR spectrum of **C** is consistent with the formulation depicted in Chart 4. Furthermore, at low temperature the expected inequivalence of the two *N*-methyl groups is in accord with the presence of two signals at $\delta$ 39.7 and 42.5 in the N−Me pattern.

There was no evidence for direct conversion of **1** to **C** by simple fluoride dissociation and direct nucleophilic attack onto the $CF_2$ groups. Moreover, the lack of reaction between strong nucleophiles such as sodium amide or sodium dimethylamide with dichlorodifluoroethylene, which contains the $C{=}CF_2$ group also present in **1**, renders it unlikely that **1** could undergo a similar direct reaction. This tends to strengthen support for the alternative mechanism in which a vacant coordination site on Fe(2) acts as an internal Lewis acid in the intramolecular migration of a vinyl fluoride to the metal. The resulting $FeF^-\cdots C{=}CF^+$ ion pair (**A**) is trapped by the added nucleophilic reagent to give **B** as a possible intermediate. However, the complexed amine intermediate was not detected at 233 K (see Figure 6). The lifetime of such a species might be short, which would explain why by subsequent elimination of HF it converts cleanly to the intermediate **C**. When the temperature is raised, **C** converts successively into two intermediates, **D** and **E**, before yielding the final product **2** (see Figure 6). The two intermediates were detected by $^{19}F$ NMR spectroscopy. Although they were long-lived species, they could not be unambiguously characterized. Indeed, at no time during the reaction were these two compounds present in large enough quantities to be completely characterized by $^{13}C$ NMR spectroscopy, nor could pure samples of them be obtained. However, the $^{19}F$ NMR pattern of the first intermediate, consisting of two singlets at $\delta$ −66.5 and −95.1 in an integrated intensity ratio of 3:1, is in accord with the formulation suggested for **D** in Scheme 4. This formulation for **D**, which is closely related to that of the starting compound **1**, is supported by the similarities of their $^{19}F$ NMR spectra; for instance, the fluorine pattern of **1** exhibits $CF_3$ and CF signals at $\delta$ −58.9 and −81.0, respectively.[28] The last intermediate detected on the usual $^{19}F$ NMR scale gave only one signal, which was found in the range expected for a trifluoromethyl group. Despite the paucity of data, it is likely, by analogy with the movements undergone during the first steps of the reaction, that a

(28) Rumin, R.; Pétillon, F. Y.; Manojlovic-Muir, Lj.; Muir, K. W. *Organometallics* **1990**, *9*, 944.

**Scheme 5. Possible Pathway to the Formation of Diaminocycloferrathiabutene Derivative 6[a]**




[a] Legend: (i) + THF; (ii) −THF, +$Me_2NH$; (iii) −HF; (iv) amido migration; (v) isomerization.

second α-elimination of fluoride onto Fe(2) could induce the formation of the zwitterionic complex **E**, which might correspond to the last intermediate detected by $^{19}F$ NMR spectroscopy. Concomitant internal rearrangement would give rise to the final short-lived intermediate **F**, which undergoes an internal migration of the fluoride to the *β*-carbon atom to afford product **2** cleanly. Elimination of HF drives the overall thermodynamics of the transformations involved in the reaction, and its characterization was therefore of importance. This has been qualitatively done in the form of the corresponding amine hydrofluoride, $Me_2NH{\cdot}HF$ (which was characterized by IR), by trapping the compound with $Me_2NH$.

**b. Cycloferrathiabutene Complexes (6−9).** Through the preceding sections, we have shown that the nature of products (cycloferrathiapentadiene versus cycloferrathiabutene derivatives) resulting from reaction of compound **1** with amines is critically dependent upon the conditions (particularly the mole ratio of nucleophile to compound **1** and the nature of the solvent). Reactions involving stoichiometric amounts of reagents in the poorly coordinating solvent $CH_2Cl_2$ gave only cycloferrathiapentadiene derivatives, while cycloferrathiabutene formation was favored by a large excess of amine and a solvent (THF) with greater donor ability.

At low temperature (−30 °C), when the reaction of **1** with a large excess of amine was conducted in THF, the diaminocycloferrathiabutene derivatives (**6**−**9**) were almost quantitatively formed in 5 min. Under similar conditions, when the reaction was carried out in $CH_2Cl_2$, the diaminocycloferrathiabutene compounds were formed in only 60% yield and the reaction took longer (6 h). In addition, monoaminocycloferrathiapentadiene derivatives were obtained in about 35% yield. These data clearly show that the solvent plays a major role in the mechanism of the reaction of **1** with a large excess of amine. The reaction pathway proposed in Scheme 5

to explain the formation of diaminocycloferrathiabutene products takes this into account.

Monitoring the reaction of **1** with 20 equiv of dimethylamine in THF-$d_8$ by $^{19}$F NMR at 243 K showed instantaneous formation of an intermediate which has been clearly identified as the monoamino complex **C** (Schemes 4 and 5). Thus, the reactions of **1** with either stoichiometric amounts or a large excess of amine would yield a common intermediate. Subsequent steps differentiate the two types of reactions and depend on both the solvent and the large excess of amine. As the solvent is observed to influence the reaction, it appears reasonable to consider that **C** is decomposed by the donor THF to give the intermediate **E′** via compound **D**. A large excess of $Me_2NH$ would then favor the formation of **F′** by substitution of the weak donor THF by the amine, which is a stronger donor. We have checked the correctness of the proposed reaction pathway by using $CH_2Cl_2$ instead of THF. The reaction proceeded differently: the intermediate **C** underwent conversion to the final products much more slowly and, in addition, appreciable yields of monoaminocycloferrathiapentadiene complex **2** were formed. The loss of a molecule of HF would be favored by the closeness of the hydrogen atom of the methylamine ligand and the remaining vinyl fluorine in the coordination sphere of Fe(2) in **F′**, yielding the intermediate **G′**. The latter may then be converted to the final product **6b** via the intermediate **H′** by successive internal migration of the dimethylamide group from Fe(2) to $C_\alpha$ and by bond polarization. **H′** and subsequent intermediates are short-lived species, since they have not been detected by $^{19}$F NMR spectroscopy. At −30 °C, isomer **6b** was the only complex obtained in about 5 min; **6b** is then the kinetic product of the reaction. When the temperature of the solution is raised to room temperature, **6b** isomerizes to give an equilibrium mixture of **6a** and **6b** in the ratio 2.33:1.

**5. Conclusions.** We have described the reaction of the perfluorovinyldiiron complex **1** with amines in which the C−F bonds of the coordinated ligand undergo activation. It is of interest to note how the pattern of reactivity changes with the nucleophile used in these reactions. We have previously shown that with soft nucleophiles (phosphines, thiols) **1** gives only $\beta$-adducts containing an Fe(1)−$C_\alpha$(F)−$C_\beta$(Nu)−C($CF_3$)−S(Me) ring,[16] whereas here with harder nucleophiles (amines) **1** affords uniquely α-adducts with Fe(1)−$C_\alpha$(Nu)−$C_\beta$-(F)−C($CF_3$)−S(Me) rings. The change in product distribution for the two types of nucleophiles appears to have its origin in variations in the degree of polarization of the $C_\alpha$−$C_\beta$ bond in the various precursors.[16] Furthermore, the formation of cycloferrathiapentadiene compounds **2**−**5** shows interesting ligand transformations involving C−F bond activation upon reaction of **1** with stoichiometric amounts of secondary mono- or diamines. The mechanism proposed to account for the formation of **2** and its related monoamino complexes **3**−**5** implies C−F bond cleavage and migration of a fluorine atom from $C_\alpha$ to $C_\beta$ via the second iron atom to give novel ligands. The initial steps of the reaction process are not changed when the reaction is conducted with a large excess of nucleophile in tetrahydrofuran. The cycloferrathiabutene complexes **6**−**9** are proposed to form via initial nucleophilic attack at $C_\alpha$ to give [{Fe(CO)$_3$}$_2$($\mu$-SMe){$\mu$-S(Me)C($CF_3$)C(CFNMe$_2$)}] (**C**), a zwitterionic thiaalkene-bridged intermediate similar to that characterized in the reaction of **1** with stoichiometric amounts of amine. **C** subsequently undergoes sequential solvent and amine substitution, C−F activation, and C−N bond formation to give **6**−**9**. Thermolysis in tetrahydrofuran of the cycloferrathiabutene compounds **6**−**9** affords dimetallacyclobutene complexes **10**−**13** via carbon−sulfur bond cleavage.

## Experimental Section

**General Procedures.** The reactions were performed under either argon or nitrogen using standard Schlenk techniques, 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 bimetallic complex [{Fe(CO)$_3$}$_2$($\mu$-C(SMe)($CF_3$)C$CF_2$}] (**1**) was prepared as described previously.[28] All other reagents were commercial grade and were used as obtained. Yields are with respect to the starting cluster **1** for the preparation of all the products.

Infrared spectra were recorded on a Perkin-Elmer 1430 spectrophotometer from either hexane or dichloromethane solutions. The mass spectra were measured either on a GC/MS Hewlett-Packard 5595C or on a GC/MS Ribermag R10-10 spectrometer at the Laboratoire de Biochimie, Faculté de Médecine (Brest, France). Chemical analyses were performed either by the "Centre de Microanalyses du CNRS de Lyon" or by the "Laboratoire de Spectroscospie Atomique" at the University of Brest. The NMR spectra ($^1$H, $^{13}$C, $^{19}$F), in $CDCl_3$ or $CD_2Cl_2$ solutions, were recorded on either a Bruker AC 300 or DRX 400 spectrometer and were referenced to $SiMe_4$ ($^1$H, $^{13}$C) or $CFCl_3$ ($^{19}$F). The spectroscopic data for **2** are updated here, and the new $^1$H, $^{13}$C{$^1$H}, and IR data are added. Part of the NMR data for **2**−**9** and **C** are compared in Table 1; the remaining spectral data of these complexes are reported in this section.

**Synthesis of [{Fe(CO)$_3$}$_2${$\mu$-S(Me)C($CF_3$)CFC(NMe$_2$)}] (2).** Complex **1** (235.0 mg, 0.5 mmol) was dissolved in 10 mL of $CH_2Cl_2$. After the mixture was cooled to −50 °C, dimethylamine (33 $\mu$L, 0.5 mmol) was added; then, the solution was warmed to room temperature and was stirred for 5 min. The solution was filtered through deoxygenated silica gel and the solvent removed in vacuo to leave a powdery solid. This solid was washed at −50 °C with a mixture of pentane and dichloromethane (5.5/1) to give **2** as a red powder in 98% yield (242.5 mg).

IR ($\nu$(CO), cm$^{-1}$; $C_6H_{12}$): 2070 s, 2028 s, 2000 s, 1996 s, 1982 m, 1970 m. $^1$H NMR ($CDCl_3$, room temperature; $\delta$): 3.38 (d, 6H, $^5J_{HF}$ = 2.5 Hz, N(C$H_3$)$_2$), 1.98(s, 3H, SC$H_3$). $^{13}$C{$^1$H} NMR ($CDCl_3$, room temperature; $\delta$): 126.3 (dq, $J_{CF}$ = 275 Hz, $^3J_{CF}$ = 2.5 Hz, C$F_3$), 49.3(dq, $^2J_{CF}$ = 37 Hz, $^2J'_{CF}$ = 7.0 Hz, C$CF_3$), 48.7 (s, SC$H_3$). Anal. Calcd for $C_{13}H_9F_4Fe_2NO_6S$: C, 31.5; H, 1.8; N, 2.8. Found: C, 32.0; H, 1.9;. N, 2.9.

**Synthesis of [{Fe(CO)$_3$}$_2${$\mu$-S(Me)C($CF_3$)CFCN(CH$_2$)$_4$}] (3).** A dichloromethane solution (10 mL) of pyrrolidine (14.2 mg, 0.20 mmol) and **1** (94.0 mg, 0.20 mmol) was stirred at room temperature for 5 min. After filtration through Celite and evaporation of the solvent, the residue was crystallized at −70 °C from pentane (5 mL) to give **3** as orange crystals in 80% yield (83.4 mg).

IR ($\nu$(CO), cm$^{-1}$; $CH_2Cl_2$): 2060 s, 2015 s, 1990 s, 1980 m, 1960 sh. $^1$H NMR ($CDCl_3$, room temperature; $\delta$): 3.4 (m, 4H, 2C$H_2$), 2.06 (m, 4H, 2C$H_2$), 2.02 (s, 3H, SC$H_3$). $^{13}$C{$^1$H} NMR ($CDCl_3$, room temperature; $\delta$): 130.1 (q, $J_{CF}$ = 274 Hz, C$F_3$), 56.7 (d, $^4J_{CF}$ = 6 Hz, 2$C_\alpha$H$_2$), 49.2 (dq, $^2J_{CF}$ = 42.0 Hz, $^2J'_{CF}$ = 6 Hz, C$CF_3$), 26,1 (s, 2$C_\beta$, H$_2$). Anal. Calcd for $C_{15}H_{11}F_4Fe_2NO_6S$: C, 34.7; Fe, 21.5; N, 2.8. Found: C, 34.6; Fe, 21.4; N, 2.7. Mass spectrum: $m/z$ 521 [M]$^+$, 493, 465, 437, 409, 381,

353 [$M^+ - n$CO] ($n = 1-6$), 259 [$M^+ - 6$CO $-$ $FeF_2$], 165 [$M^+ - 6$CO $- 2FeF_2$].

**Synthesis of [{Fe(CO)$_3$}$_2${$\mu$-S(Me)C(CF$_3$)CFC(N(CH$_2$)$_4$NH)}] (4).** A dichloromethane solution (5 mL) of piperazine (86.2 mg, 1 mmol) and **1** (47.0 mg, 0.10 mmol) was stirred at room temperature for 15 min. The solvent was removed, and the residue was extracted at −50 °C with ether. The solvent was then removed to leave a red residue, which was washed at −50 °C with 2 × 5 mL portions of pentane to afford **4** as an analytically pure solid in 98% yield (51.5 mg).

IR ($\nu$(CO), cm$^{-1}$; $CH_2Cl_2$): 2070 m, 2025 s, 1998 m, 1970 sh. $^1$H NMR ($CDCl_3$, room temperature; $\delta$): 3.76 (s br, 2H, C$H_2$), 3.59 (s br, 2H, C$H_2$), 3.06 (s br, 4H, 2C$H_2$), 2.03 (s, 3H, SC$H_3$). $^{13}$C{$^1$H} NMR (THF-$d_8$, room temperature; $\delta$): 127.6 (q, $J_{CF} = 273$ Hz, $CF_3$), 59.8 (d, $^4J_{CF} = 7$ Hz, $C_\alpha H_2$), 47.7 (s, $2C_\beta H_2$). Anal. Calcd for $C_{15}H_{12}F_4Fe_2N_2O_6S$: C, 36.6; H, 2.2; Fe, 20.8; N, 5.2 Found: C, 36.7; H, 2.4; Fe, 20.6; N, 5.1. Mass spectrum: *m*/*z* 536 [M]$^+$, 480, 452, 424, 396, 368 [$M^+ - n$CO] ($n = 2-6$), 274 [$M^+ - 6$CO $-$ $FeF_2$], 180 [$M^+ - 6$CO $- 2FeF_2$].

**Synthesis of [[{Fe(CO)$_3$}$_2${$\mu$-S(Me)C(CF$_3$)CFC}]$_2${N(CH$_2$)$_4$N}] (5).** A dichloromethane solution (5 mL) of piperazine (4.3 mg, 0.05 mmol) and **1** (47.0 mg, 0.10 mmol) was stirred at room temperature for 15 min. After filtration through Celite and evaporation of the solvent, the residue was washed at −50 °C with 2 × 5 mL portions of pentane to give **5** as a fine orange powder in 93% yield (45.9 mg).

Complex **5** was also prepared on stirring at room temperature for 30 min a dichloromethane solution of stoichiometric amounts of piperazine and **4**. Workup of the product as described above afforded **5** in 100% yield.

IR ($\nu$(CO), cm$^{-1}$; $CH_2Cl_2$): 2072 m, 2030 s, 2000 sh, 1980 sh. $^1$H NMR ($CDCl_3$, room temperature; $\delta$): 3.95 (m, 4H, 2C$H_2$), 3.70 (m, 4H, 2C$H_2$), 2.05 (s, 6H, 2SC$H_3$). $^{13}$C{$^1$H} NMR ($CD_2Cl_2$, room temperature; $\delta$): 126.6 (q, $J_{CF} = 271$ Hz, $CF_3$), 56.8 (d, $^4J_{CF} = 6$ Hz, 2$CH_2$), 56.4 (d, $^4J_{CF} = 6$ Hz, 2$CH_2$), 49.6 (m, $CCF_3$). Anal. Calcd for $C_{26}H_{14}F_8Fe_4N_2O_{12}S_2$: C, 31.7; H, 1.4; N, 2.8. Found: C, 31.6; H, 1.6; N, 2.9. Mass spectrum (CI): *m*/*z* 987 [MH]$^+$, 959, 931, 903, 875, 847, 819 [$MH^+ - n$CO] ($n = 1-6$).

**Synthesis of [{Fe(CO)$_3$}$_2${$\mu$-S(Me)C(CF$_3$)C(CFNMe$_2$)}] (C).** The intermediate **C** was formed almost instantaneously and quantatively in the NMR tube on mixing in $CD_2Cl_2$ solution (at −40 °C) stoichiometric amounts of **1** and dimethylamine.

$^1$H NMR ($CD_2Cl_2$, 233 K; $\delta$): 3.06 (s, 6H, N(C$H_3$)$_2$), 2.72 (s, 3H, SC$H_3$). $^{13}$C{$^1$H} NMR ($CD_2Cl_2$, 233 K; $\delta$): 125.9 (q, $J_{CF} = 276$ Hz, $CF_3$), 48.6 (m, $CCF_3$), 42.5 (s, NC$H_3$), 39.7 (s, NC$H_3$).

**Synthesis of [{Fe(CO)$_3$}$_2${$\mu$-S(Me)C(CF$_3$)C(C(NMe$_2$)$_2$)}] (6).** Complex **1** (94.0 mg, 0.20 mmol) was dissolved in 10 mL of THF and the solution was cooled to 5 °C; then, 20 equiv of $Me_2NH$ (180 mg, 265 $\mu$L) was added to the solution. After it was stirred for 5 min, the reaction mixture was filtered through deoxygenated silica gel and then the solvent was evaporated. The resulting residue was washed at −50 °C with 10 mL of a mixture (1/1) of dichloromethane and pentane. Evaporation of the solvent gave **6** as an analytically pure orange solid in 100% yield (104 mg). Complex **6** was formed as two inseparable isomers.

**Isomer 6a.** IR ($\nu$(CO), cm$^{-1}$; $C_6H_{12}$): 2040 m, 1998 s, 1965 m, 1950 sh, 1925 sh. $^1$H NMR ($CDCl_3$, room temperature; $\delta$): 3.26 (s, 12H, 2N(C$H_3$)$_2$), 2.02 (s, 3H, SC$H_3$). $^{13}$C{$^1$H} NMR ($CDCl_3$, room temperature; $\delta$): 124.05 (q, $J_{CF} = 277$ Hz, $CF_3$), 49.75 (q, $^2J_{CF} = 37$ Hz, $CCF_3$), 43.1 (s, br, N(C$H_3$)$_2$).

**Isomer 6b.** IR ($\nu$(CO), cm$^{-1}$; $C_6H_{12}$): 2040 m, 1998 s, 1965 m, 1950 sh, 1925 sh. $^1$H NMR ($CDCl_3$, room temperature; $\delta$): 3.26 (s, 12H, 2N(C$H_3$)$_2$), 2.08 (s, 3H, SC$H_3$). $^{13}$C{$^1$H} NMR ($CDCl_3$, room temperature; $\delta$): 124.7 (q, $J_{CF} = 278$ Hz, $CF_3$), 43.05 (s br, N(C$H_3$)$_2$).

Anal. Calcd for $C_{15}H_{15}F_3Fe_2N_2O_6S$: C, 34.6; N, 5.4. Found: C, 34.7; N, 5.6. Mass spectrum: *m*/*z* 520 [M]$^+$, 492, 464, 436, 408, 380, 352 [$M^+ - n$CO] ($n = 1-6$), 258 [$M^+ - 6$CO $-$ $FeF_2$].

**Synthesis of [{Fe(CO)$_3$}$_2${$\mu$-S(Me)C(CF$_3$)CC(N(CH$_2$)$_4$)$_2$}] (7).** A tetrahydrofuran solution (10 mL) of **1** (94.0 mg, 0.20 mmol) was treated at room temperature with 20 equiv of pyrrolidine (284.0 mg, 334 $\mu$L). After it was stirred for 5 min, the reaction mixture was filtered through Celite and the volatiles were removed under vacuum. The residue was then washed at −50 °C with pentane (5 mL) to give **7** as an analytically pure red solid in 93% yield (106.4 mg). Compound **7** was formed as two inseparable isomers.

**Isomer 7a.** IR ($\nu$(CO), cm$^{-1}$; $CH_2Cl_2$): 2040 m, 1992 s, 1958 sh, 1946 sh, 1906 sh. $^1$H NMR ($CDCl_3$, room temperature; $\delta$): 3.80 (m, 8H, 4C$H_2$), 2.00 (m, 8H, 4C$H_2$), 1.98 (s, 3H, SC$H_3$). $^{13}$C{$^1$H} NMR ($CDCl_3$, room temperature; $\delta$): 123.9 (q, $J_{CF} = 277$ Hz, $CF_3$), 54.0 (s br, $2C_\alpha H_2$), 49.4 (q, $^2J_{CF} = 36.5$ Hz, $CCF_3$), 25.85 (s br, $2C_\beta H_2$).

**Isomer 7b.** IR ($\nu$(CO), cm$^{-1}$; $CH_2Cl_2$): 2040 m, 1992 s, 1958 sh, 1946 sh, 1906 sh. $^1$H NMR ($CDCl_3$, room temperature; $\delta$): 3.80 (m, 8H, 4C$H_2$), 2.08 (s, 3H, SC$H_3$), 2.00 (m, 8H, 4C$H_2$). $^{13}$C{$^1$H} NMR ($CDCl_3$, room temperature; $\delta$): 124.5 (q, $J_{CF} = 276$ Hz, $CF_3$), 54.05 (s, br, $2C_\alpha H_2$), 25.6 (s, br, $2C_\beta H_2$).

Anal. Calcd for $C_{19}H_{19}F_3Fe_2N_2O_6S$: C, 39.9; N, 4.9. Found: C, 39.8; N, 5.0. Mass spectrum: *m*/*z* 572 [M]$^+$, 544, 516, 488, 460, 432, 404 [$M^+ - n$CO] ($n = 1-6$), 310 [$M^+ - 6$CO $-$ $FeF_2$].

**Synthesis of [{Fe(CO)$_3$}$_2${$\mu$-S(Me)C(CF$_3$)C(CN(CH$_3$)CH$_2$CH$_2$N(CH$_3$))}] (8).** A tetrahydrofuran solution (10 mL) of *N*,*N*′-dimethylethylenediamine (35.2 mg, 42.5 $\mu$L, 0.40 mmol) and **1** (94.0 mg, 0.20 mmol) was stirred at room temperature for 5 min. 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 **8** as an analytically pure orange solid in 97% yield (100.5 mg). Compound **8** was formed as two inseparable isomers.

**Isomer 8a.** IR ($\nu$(CO), cm$^{-1}$; $CH_2Cl_2$): 2040 m, 1997 s, 1965 sh, 1950 sh, 1918 sh. $^1$H NMR ($CDCl_3$, room temperature; $\delta$): 3.80 (s br, 4H, 2C$H_2$), 3.32 (s, 6H, 2C$H_3$), 2.02 (s, 3H, SC$H_3$). $^{13}$C{$^1$H} NMR ($CDCl_3$, room temperature; $\delta$): 124.5 (q, $J_{CF} = 277$ Hz, $CF_3$), 52.85 (q, $^2J_{CF} = 37$ Hz, $CCF_3$), 51.3 (s, $CH_2$), 49.65 (s, $CH_2$), 36.9 (s, $CH_3$), 35.6 (s, $CH_3$).

**Isomer 8b.** IR ($\nu$(CO), cm$^{-1}$; $CH_2Cl_2$): 2040 m, 1997 s, 1965 sh, 1950 sh, 1918 sh. $^1$H NMR ($CDCl_3$, room temperature; $\delta$): 3.80 (s br, 4H, 2C$H_2$), 3.45 (s, 6H, 2C$H_3$), 2.14 (s, 3H, SC$H_3$). $^{13}$C{$^1$H} NMR ($CDCl_3$, room temperature; $\delta$): 125.1 (q, $J_{CF} = 275.5$ Hz, $CF_3$), 51.05 (s, $CH_2$), 49.2 (s, $CH_2$), 47.7 (q, $^2J_{CF} = 37$ Hz, $CCF_3$), 36.8 (s, $CH_3$), 36.1 (s, $CH_3$).

Anal. Calcd for $C_{15}H_{13}F_3Fe_2N_2O_6S$: C, 34.7; N, 5.4. Found: C, 34.9; N, 5.4. Mass spectrum: *m*/*z* 518 [M]$^+$, 490, 462, 434, 406, 378, 350 [$M^+ - n$CO] ($n = 1-6$), 256 [$M^+ - 6$CO $-$ $FeF_2$].

**Synthesis of [{Fe(CO)$_3$}$_2${$\mu$-S(Me)C(CF$_3$)C(C(NHCH$_2$CH$_2$NH)}] (9).** A tetrahydrofuran solution (10 mL) of ethylenediamine (12.0 mg, 13.4 $\mu$L, 0.20 mmol) and **1** (94.0 mg, 0.20 mmol) was stirred at room temperature for 5 min. After evaporation of the solvent, the residue was chromatographed on a silica gel column. Elution with $CH_2Cl_2$−hexane (1:1) gave a red band. After evaporation of the solvent **9** was obtained as an analytically pure red solid in 80% yield (78.5 mg).

IR ($\nu$(CO), cm$^{-1}$; $CH_2Cl_2$): 2045 m, 1998 s, 1970 s, 1954 m, 1934 sh. $^1$H NMR ($CD_2Cl_2$, room temperature; $\delta$): 5.90 (s br, 2H, 2N*H*), 3.90 (s, 4H, 2C$H_2$), 2.10 (s, 3H, SC$H_3$). $^{13}$C{$^1$H} NMR ($CD_2Cl_2$, room temperature; $\delta$): 125.4 (q, $J_{CF} = 276$ Hz, $CF_3$), 49.3 (q, $^2J_{CF} = 36.5$ Hz, $CCF_3$), 45.2 (s, 2$CH_2$). Anal. Calcd for $C_{13}H_9F_3Fe_2N_2O_6S$: C, 31.9; Fe, 22.8; N, 5.7. Found: C, 32.0; Fe, 23.0; N, 5.4. Mass spectrum: *m*/*z* 490 [M]$^+$, 434, 406, 378, 350, 322 [$M^+ - n$CO] ($n = 2-6$), 228 [$M^+ - 6$CO $-$ $FeF_2$].

**Synthesis of [{Fe(CO)$_3$}$_2$($\mu$-SMe){$\mu$-C(CF$_3$)CC[N(CH$_3$)$_2$]$_2$}] (10).** Complex **6** (104.0 mg, 0.20 mmol) was dissolved in 10 mL of THF. After the residue was stirred at 50 °C for 24 h, the solvent was removed. The resulting residue was washed

**Table 5. Crystal Data and Structure Refinement Details**

| | 6 | 8 | 10 |
|---|---|---|---|
| empirical formula | $C_{15}H_{15}F_3Fe_2N_2O_6S$ | $C_{15}H_{13}F_3Fe_2N_2O_6S$ | $C_{15}H_{15}F_3Fe_2N_2O_6S$ |
| formula wt | 520.05 | 518.03 | 520.05 |
| cryst syst | monoclinic | monoclinic | monoclinic |
| space group | $P2_1/c$ | $P2_1$ | $P2_1/c$ |
| $a$, Å | 8.324(1) | 8.0830(8) | 13.7620(13) |
| $b$, Å | 14.841(3) | 15.5721(12) | 9.9905(10) |
| $c$, Å | 16.296(2) | 8.6170(5) | 15.0431(15) |
| $\beta$, deg | 93.010(7) | 116.660(6) | 93.064(4) |
| $V$, Å$^3$ | 2010.4(5) | 969.30(13) | 2065.3(4) |
| Z | 4 | 2 | 4 |
| $D_{calcd}$, Mg/m$^3$ | 1.718 | 1.775 | 1.673 |
| $\mu$, mm$^{-1}$ | 1.608 | 1.667 | 1.565 |
| $F$(000) | 1048 | 520 | 1048 |
| cryst size, mm$^3$ | 0.40 × 0.10 × 0.03 | 0.44 × 0.41 × 0.07 | 0.55 × 0.35 × 0.10 |
| $\theta$ range, deg | 2.4−22.4 | 2.6−32.9 | 2.4−30.4 |
| index ranges | $0 \le h \le 7$, $0 \le k \le 13$, $-17 \le l \le 15$ | $-12 \le h \le 10$, $\lvert k\rvert \le 21$, $-3 \le l \le 12$ | $\lvert h\rvert \le 19$, $0 \le k \le 14$, $-21 \le l \le 0$ |
| no. of rflns collected | 1929 | 6981 | 6455 |
| no. of indep rflns | 1773 ($R_{int}$ = 0.12) | 5743 ($R_{int}$ = 0.021) | 6234 ($R_{int}$ = 0.012) |
| no. of rflns with $I > 2\sigma(I)$ | 766 | 5085 | 4547 |
| abs cor | none | $\psi$-scans | $\psi$-scans |
| $T_{max}$, $T_{min}$ | | 0.718, 0.557 | 0.579, 0.377 |
| no. of data/params | 1281/132 | 5743/266 | 6230/267 |
| goodness of fit on $F^2$ | 0.869 | 1.043 | 1.010 |
| R1, wR2 ($I > 2\sigma(I)$) | 0.124, 0.31 | 0.034, 0.081 | 0.039, 0.101 |
| R1, wR2 (all data) | 0.29, 0.47 | 0.043, 0.085 | 0.062, 0.112 |
| Flack param | | 0.027(13) | |
| $\Delta\rho$ range, e Å$^{-3}$ | +1.4 to −1.1 | +0.79 to −0.34 | +0.62 to −0.44 |



at −50 °C with 10 mL of pentane. The complex **10** was obtained as an analytically pure red solid in 100% yield.

IR ($\nu$(CO), cm$^{-1}$; $C_6H_{12}$): 2050 s, 2004 s, 1970 sh, 1930 sh. $^1$H NMR ($CDCl_3$, room temperature; $\delta$): 3.03 (s, 6H, 2C$H_3$), 2.98 (s, 6H, 2C$H_3$), 2.20 (s, 3H, SC$H_3$). $^{19}$F NMR ($CDCl_3$, room temperature; $\delta$): −64.07 (s, C$F_3$). $^{13}$C{$^1$H} NMR ($CDCl_3$, room temperature; $\delta$): 213.7 (s, *C*O), 213.5 (s br, 3*C*O), 211.9 (s, *C*O), 210.4 (s, *C*O), 177.75 (s br, $C_\alpha$), 147.6 (q, $^3J_{CF}$ = 8 Hz, $C_\beta$), 146.0 (q, $^2J_{CF}$ = 31.5 Hz, $C_\gamma$CF$_3$), 122.25 (q, $J_{CF}$ = 276 Hz, *C*F$_3$), 42.4 (s, 2*C*H$_3$), 42.35 (s, 2*C*H$_3$), 24.3 (s, S*C*H$_3$). Anal. Calcd for $C_{15}H_{15}F_3Fe_2N_2O_6S$: C, 34.6; N, 5.4. Found: C, 34.8; N, 5.2. Mass spectrum: *m*/*z* 520 [M]$^+$, 492, 464, 436, 408, 380, 352 [M$^+$ − *n*CO] (*n* = 1−6), 258 [M$^+$ − 6CO − $FeF_2$].

**Synthesis of [{Fe(CO)$_3$}$_2$($\mu$-SMe){$\mu$-C(CF$_3$)CC[N(CH$_2$)$_4$]$_2$}] (11).** A tetrahydrofuran solution (10 mL) of compound **7** (114.4 mg, 0.20 mmol) was heated in a Schlenk tube to 60 °C for 2 h. After evaporation of the solvent, the residue was washed at −50 °C with 10 mL of pentane to give **11** as a red solid in 100% yield.

IR ($\nu$(CO), cm$^{-1}$; $CH_2Cl_2$): 2050 s, 2004 s, 1968 sh, 1928 sh. $^1$H NMR ($CDCl_3$, room temperature; $\delta$): 3.50 (m, 8H, 4C$H_2$), 2.22 (s, 3H, SC$H_3$), 1.94 (s br, 8H, 4C$H_2$). $^{19}$F NMR ($CDCl_3$, room temperature; $\delta$): −63.9 (s, C$F_3$). $^{13}$C{$^1$H} NMR ($CDCl_3$, room temperature; $\delta$): 214.0 (s br, 3*C*O), 213.7 (s, *C*O), 212.1 (s, *C*O), 210.2 (s, *C*O), 172.6 (s, $C_\alpha$), 147.7 (q, $^3J_{CF}$ = 8 Hz, $C_\beta$), 139.05 (q, $^2J_{CF}$ = 31.5 Hz, $C_\gamma$CF$_3$), 122.6 (q, $J_{CF}$ = 276 Hz, *C*F$_3$), 52.4 (s br, 4*C*H$_2$), 26.1 (s br, 4*C*H$_2$), 24.5 (s, S*C*H$_3$). Anal. Calcd for $C_{19}H_{19}F_3Fe_2N_2O_6S$: C, 39.9; N, 4.9. Found: C, 40.1; N, 5.0. Mass spectrum: *m*/*z* 572 [M]$^+$, 544, 516, 488, 460, 432, 404 [M$^+$ − *n*CO] (*n* = 1−6), 310 [M$^+$ − 6CO − $FeF_2$].

**Synthesis of [{Fe(CO)$_3$}$_2$($\mu$-SMe){$\mu$-C(CF$_3$)C[$\overline{\text{CN(CH}_3\text{)CH}_2\text{CH}_2\text{N(CH}_3\text{)}}$]}] (12).** In a manner similar to that above, compound **12** was formed from thermolysis of **8** as a red-orange powder in 100% yield.

IR ($\nu$(CO), cm$^{-1}$; $CH_2Cl_2$): 2050 s, 2004 s, 1965 sh, 1930 sh. $^1$H NMR ($CDCl_3$, room temperature; $\delta$): 3.70 (s br, 4H, 2 C$H_2$), 2.95 (s, 3H, NC$H_3$), 2.82 (s, 3H, NC$H_3$), 2.22 (s, 3H, SC$H_3$). $^{19}$F NMR ($CDCl_3$, room temperature; $\delta$): −63.65 (s, C$F_3$). $^{13}$C{$^1$H} NMR ($CDCl_3$, room temperature; $\delta$): 213.9 (s, *C*O), 213.1 (s br, 3*C*O), 211.6 (s, *C*O), 210.7 (s, *C*O), 172.7 (s, $C_\alpha$), 151.9 (q, $^2J_{CF}$ = 32 Hz, $C_\gamma$CF$_3$), 137.8 (q, $^3J_{CF}$ = 8 Hz, $C_\beta$), 122.7 (q, $J_{CF}$ = 276 Hz, *C*F$_3$), 49.0 (s, *C*H$_2$), 48.9 (s, *C*H$_2$), 34.1 (s, *C*H$_3$), 33.8 (s, *C*H$_3$), 24.55 (s, S*C*H$_3$). Anal. Calcd for $C_{15}H_{13}F_3Fe_2N_2O_6S$: C, 34.7; N, 5.4. Found: C, 34.9; N, 5.3. Mass spectrum: *m*/*z* 518 [M]$^+$, 462, 434, 406, 378, 350 [M$^+$ − *n*CO] (*n* = 2−6), 256 [M$^+$ − 6CO − $FeF_2$].

**Synthesis of [{Fe(CO)$_3$}$_2$($\mu$-SMe){$\mu$-C(CF$_3$)C($\overline{\text{CNH-CH}_2\text{CH}_2\text{NH}}$)}] (13).** A tetrahydrofuran solution (10 mL) of compound **9** (98 mg, 0.20 mmol) was heated in a Schlenk tube to 60 °C for 18 h. The solution was then filtered through Celite, and the solvent was evaporated. The resulting residue was washed at −50 °C with 10 mL of pentane to give **13** as a red powder in 85% yield (83.4 mg).

IR ($\nu$(CO), cm$^{-1}$; $CH_2Cl_2$): 2050 s, 2004 s, 1970 sh, 1928 sh. $^{12}$H NMR ($CDCl_3$, room temperature; $\delta$): 6.20 (s br, 2H, 2N*H*), 3.90 (s, 4H, 2C$H_2$), 2.20 (s, 3H, SC$H_3$). $^{19}$F NMR ($CDCl_3$, room temperature; $\delta$): −60.8 (s, C$F_3$). $^{13}$C{$^1$H} NMR ($CDCl_3$, room temperature; $\delta$): 213.9 (s, *C*O), 212.0 (s br, 3 *C*O), 211.2 (s, CO), 210.8 (s, *C*O), 174.9 (s, $C_\alpha$), 155.2 (q, $^2J_{CF}$ = 32 Hz, $C_\gamma$-CF$_3$), 137.1 (q, $^3J_{CF}$ = 9 Hz, $C_\beta$), 122.7 (q, $J_{CF}$ = 276 Hz, *C*F$_3$), 44.4 (s, 2 *C*H$_2$), 24.5 (s, S*C*H$_3$). Anal. Calcd for $C_{13}H_9F_3Fe_2N_2O_6S$: C, 31.9; N, 5.7. Found: C, 32.1; N, 5.8.

**Crystal Structure Determinations of 6, 8, and 10.** Pertinent data are summarized in Table 5. All measurements were made at 20 °C on an Enraf-Nonius CAD4 diffractometer fitted with a graphite monochromator using Mo K$\alpha$ radiation ($\lambda$ = 0.710 73 Å). Structures were solved by Patterson and Fourier methods. Refinements were carried out by full-matrix least squares on $F^2$ using scattering factors and dispersion corrections incorporated in SHELXL-97.[29]

For **8** and **10** $U_{ij}$ parameters were refined for all non-hydrogen atoms, hydrogen atoms rode on the atoms to which they are attached, and a single orientation parameter was refined for each methyl group. For **6**, after many attempts, a partial data set was collected from a poor-quality crystal before it decomposed. $U_{ij}$ values were refined only for Fe and S atoms

(29) Programs used: Sheldrick, G. M. SHELX97—Programs for Crystal Structure Analysis (Release 97-2); Institüt für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998. Farrugia, L. J. WinGX—A Windows Program for Crystal Structure Analysis. *J. Appl. Crystallogr.* **1999**, *32*, 837.

because of the small number of available intensities, while hydrogen atoms were not included in the calculations.

**Acknowledgment.** We thank the CNRS, the EPSRC, and the Universities of Brest and Glasgow for financial support. The Ministère de l'Enseignement Supérieur et de la Recherche is acknowledged for providing studentships (K.G.-d.C.).

**Supporting Information Available:** For **6**, **8**, and **10** tables giving details of structure determinations, non-hydrogen atomic positional parameters, all bond distances and angles, anisotropic displacement parameters, and hydrogen atomic coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000003K