



Zwitterionic diiron vinyliminium complexes: Alkylation, metalation and oxidative coupling at the S and Se functionalities

Luigi Busetto^a, Marco Dionisio^a, Fabio Marchetti^{b,1}, Rita Mazzoni^a, Mauro Salmi^a, Stefano Zacchini^a, Valerio Zanotti^{a,*}

^a Dipartimento di Chimica Fisica e Inorganica, Università di Bologna, Viale Risorgimento 4, I-40136 Bologna, Italy

^b Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Risorgimento 35, I-56126 Pisa, Italy

ARTICLE INFO

Article history:

Received 18 March 2008

Received in revised form 4 April 2008

Accepted 4 April 2008

Available online 11 April 2008

Keywords:

Vinyliminium

Zwitterionic complexes

Oxidative coupling

Alkylation

Disulfides

Diselenides

ABSTRACT

The zwitterionic vinyliminium complex $[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C(R')=C(S)C=N(Me)(Xyl)}\}\{\mu\text{-CO}\}\{\text{CO}\}\{\text{Cp}\}_2]$ (**2a**) ($\text{R}' = p\text{-Me-C}_6\text{H}_4$ (Tol), $\text{Xyl} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$) undergoes electrophilic addition at the S atom by HSO_3CF_3 , MeSO_3CF_3 , SiMe_3Cl , BrCH_2Ph , $\text{ICH}_2\text{CH=CH}_2$ affording the complexes $[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C(Tol)=C(SX)C=N(Me)(Xyl)}\}\{\mu\text{-CO}\}\{\text{CO}\}\{\text{Cp}\}_2][\text{Y}]$ ($\text{X} = \text{H}$, $\text{Y} = \text{SO}_3\text{CF}_3$, **4a**; $\text{X} = \text{Me}$, $\text{Y} = \text{SO}_3\text{CF}_3$, **4b**; $\text{X} = \text{SiMe}_3$, $\text{Y} = \text{Cl}$, **4c**; $\text{X} = \text{CH}_2\text{Ph}$, $\text{Y} = \text{Br}$, **4d**; $\text{X} = \text{CH}_2\text{CH=CH}_2$, $\text{Y} = \text{I}$, **4e**).

Compound **2a** and the corresponding vinyliminium complexes **2b** and **2c** ($\text{R}' = \text{CH}_2\text{OH}$, **2b**; $\text{R}' = \text{Me}$, **2c**) react also with etherated BF_3 leading to the formation of the corresponding S-adducts $[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C(R')=C(SBF}_3\text{)C=N(Me)(Xyl)}\}\{\mu\text{-CO}\}\{\text{CO}\}\{\text{Cp}\}_2]$ ($\text{R}' = \text{Tol}$, **5a**; $\text{R}' = \text{CH}_2\text{OH}$, **5b**; $\text{R}' = \text{Me}$, **5c**).

In analogous reactions, the zwitterionic vinyliminium complexes undergo S-metalation upon treatment with *in situ* generated $[\text{Fp}]^+[\text{SO}_3\text{CF}_3]^-$ [$\text{Fp} = \text{Fe}(\text{CO})_2(\text{Cp})$], leading to the formation of $[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C(R')=C(S-Fp)C=N(Me)(Xyl)}\}\{\mu\text{-CO}\}\{\text{CO}\}\{\text{Cp}\}_2][\text{SO}_3\text{CF}_3]$ ($\text{R}' = \text{CH}_2\text{OH}$, **6a**; $\text{R}' = \text{Me}$, **6b**; $\text{R}' = \text{Bu}^n$, **6c**).

Similarly, zwitterionic vinyliminium containing Se in the place of S also undergo Se-electrophilic addition. Thus, the complexes $[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C(R')=C(SeX)C=N(Me)(R)}\}\{\mu\text{-CO}\}\{\text{CO}\}\{\text{Cp}\}_2][\text{SO}_3\text{CF}_3]$ ($\text{R} = \text{X} = \text{Me}$, $\text{R}' = \text{Tol}$, **7a**; $\text{R} = \text{Xyl}$, $\text{R}' = \text{Me}$, $\text{X} = \text{Fp}^+$, **7b**) are obtained upon treatment of the neutral zwitterionic precursors with MeSO_3CF_3 and $[\text{Fp}][\text{SO}_3\text{CF}_3]$, respectively.

Alkylation at the S or Se atom of the bridging ligand is also accomplished by CH_2Cl_2 , used as solvent, although the reaction is slower compared to more efficient alkylating reagents. The complexes formed by this route are $[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C(R')=C(E-CH}_2\text{Cl)C=N(Me)(R)}\}\{\mu\text{-CO}\}\{\text{CO}\}\{\text{Cp}\}_2][\text{X}]$ ($\text{E} = \text{S}$, $\text{R} = \text{Xyl}$, $\text{R}' = \text{Tol}$, $\text{X} = \text{Cl}$, **8a**; $\text{E} = \text{S}$, $\text{R} = \text{Xyl}$, $\text{R}' = \text{Me}$, $\text{X} = \text{Cl}$, **8b**; $\text{E} = \text{Se}$, $\text{R} = \text{R}' = \text{Me}$, $\text{X} = \text{BPh}_4$, **8c**).

Finally, treatment of the zwitterionic vinyliminium complexes with I_2 results in the oxidative coupling with formation of S–S (disulfide) or Se–Se (diselenide) bond. The reactions, performed in the presence of NaBPh_4 afford the tetranuclear complexes $[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C(R')=C(E)C=N(Me)(R)}\}\{\mu\text{-CO}\}\{\text{CO}\}\{\text{Cp}\}_2]_2[\text{BPh}_4]_2$ ($\text{R} = \text{Xyl}$, $\text{R}' = \text{CH}_2\text{OH}$, $\text{E} = \text{S}$, **9a**; $\text{R} = \text{Xyl}$, $\text{R}' = \text{Me}$, $\text{E} = \text{S}$, **9b**; $\text{R} = \text{Xyl}$, $\text{R}' = \text{Bu}^n$, $\text{E} = \text{S}$, **9c**; $\text{R} = \text{Xyl}$, $\text{R}' = \text{Me}$, $\text{E} = \text{Se}$, **9d**; $\text{R} = \text{Me}$, $\text{R}' = \text{Bu}^n$, $\text{E} = \text{Se}$, **9e**).

The molecular structures of **4a**, **8c** and **9e** have been determined by X-ray diffraction studies.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Multisite bound organic fragments display unique reaction patterns, which allow transformations not observed in uncoordinated species or in complexes containing a single metal centre [1]. This is also the case of the bridging vinyliminium ligand, in diiron complexes of the type **1** (Scheme 1) which we have investigated in recent years [2]. The presence of an iminium functionality and the overall positive charge of the complex **1** make the bridging vinyliminium

ligand susceptible to nucleophilic addition by a variety of reagents. However, as a consequence of the bridging coordination, these nucleophilic attacks exhibit unconventional routes: instead of the usual 1,4 conjugated addition (Michael type nucleophilic addition), attacks involve iminium carbon or the adjacent C_β position [3].

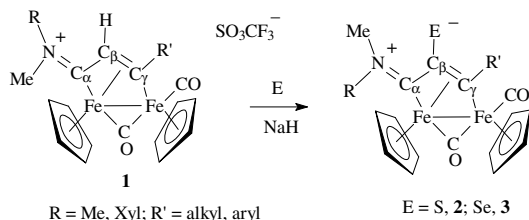
Further transformations of the vinyliminium ligand have been obtained exploiting the iminium–enamine activation and the consequent acidic character of the $\text{C}_\beta\text{-H}$ hydrogen [4]. The latter has been replaced by different functionalities [5], including group 16 heteroatoms, leading to the transformation of **1** into the thio- and seleno-complexes **2** and **3**, shown in Scheme 1 [6].

Compounds **2** and **3** evidence a zwitterionic character, with the positive charge localized on the N atom and the negative charge

* Corresponding author. Tel.: +39 0512093695.

E-mail address: valerio.zanotti@unibo.it (V. Zanotti).

¹ Fabio Marchetti, born in 1974 in Bologna, Italy.



Scheme 1.

on the S/Se atoms. It has been shown that bridging coordination largely contributes to the stabilization of the dipolar iminium thiolate/selenoate ligands in these complexes [6]. Zwitterionic organometallic complexes, although relatively uncommon, represent a topic of great interest, in that they might provide new interesting properties [7]. For example, formally charge separated species might exhibit enhanced catalytic activity due to the absence of counterion effects [8]. Furthermore, charge separation should be exploited for the construction of three-dimensional (3D) porous metal-organic frameworks [9], and for possible application as carriers for membranes [10].

Herein we report on the reactions of the zwitterionic complexes of the type **2** and **3** with electrophiles, Lewis acids and coordinatively unsaturated metal frames. More specifically, the purpose was to determine whether or not the S or Se atoms, formally bearing a negative charge, might be exploited to add electrophilic fragments, providing routes to the construction of bridging frames of increased size and complexity.

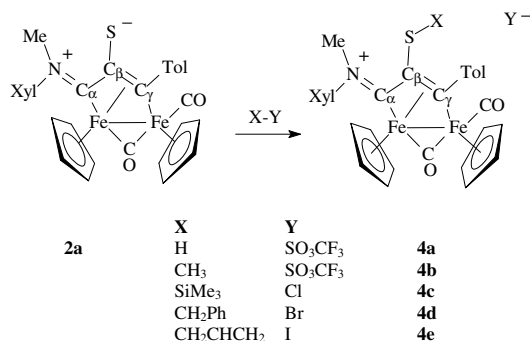
2. Results and discussion

2.1. Alkylation, protonation and metalation reactions

Complex **2a**, in CH_2Cl_2 solution, rapidly reacts with strong electrophiles, such as HSO_3CF_3 and MeSO_3CF_3 , to give the corresponding C_β -substituted vinyliminium complexes **4a–b** in about 90% yield (Scheme 2).

Analogous results have been obtained upon treatment of $[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C}_\gamma(\text{Tol})\text{=C}_\beta(\text{S})\text{C}_\alpha\text{=N}(\text{Me})(\text{Xyl})\}\{\mu\text{-CO}\}(\text{CO})(\text{Cp})_2]$ (**2a**, Tol = *p*-Me- C_6H_4 , Xyl = 2,6-Me₂- C_6H_3) with Me_3SiCl , benzylbromide (BrCH_2Ph), and allyliodide ($\text{ICH}_2\text{CH=CH}_2$), affording the complexes **4c–e**, respectively (Scheme 2).

Complexes **4a–e** have been spectroscopically characterized. In addition, the molecular structure of **4a** has been determined by X-ray diffraction studies. The ORTEP molecular diagram is reported in Fig. 1 whereas relevant bond lengths and angles are reported in Table 1. The S-attached hydrogen atom has been located unambiguously in the Fourier map and refined with restrained S–H dis-



Scheme 2.

tance; its presence is in agreement with the cationic charge of the complex as inferred from the presence of the CF_3SO_3^- anion in the unit cell. There is also a H_2O molecule but only the oxygen atom has been located. A hydrogen bond exists between the –SH group and the water molecule [$\text{S}(1)\cdots\text{O}(4)$ 2.884(16) Å]. The structure of the cationic complex **4a** resembles those previously reported for other diiron vinyliminium complexes [2]. The Cp ligands in the $[\text{Fe}_2(\mu\text{-CO})(\text{CO})(\text{Cp})_2]$ core display a relative *cis* arrangement and, as usually found in C_β -substituted vinyliminium complexes, the Me and Xyl groups with respect to the $\text{C}_\alpha\text{=N}$ double bond possess a *Z* geometry [2b]. The bonding parameters of the bridging $\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C}_\gamma(\text{Tol})\text{=C}_\beta(\text{SH})\text{C}_\alpha\text{=N}(\text{Me})(\text{Xyl})\}$ ligand of **4a** are compared in Table 2 with those of the parent zwitterionic compound **2a** and a typical C_β -substituted vinyliminium complex, i.e. *cis*- $[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C}_\gamma(\text{Me})\text{=C}_\beta(\text{Me})\text{C}_\alpha\text{=N}(\text{Me})(\text{Xyl})\}\{\mu\text{-CO}\}(\text{CO})(\text{Cp})_2]^+$ (**1**) [2b]. A comparison between the bond lengths in **4a** and **1** clearly indicates that the bridging ligand is better described as a vinyliminium (form **A**, Scheme 3). S-Protonation of **2a** to give **4a** results in the elongation of the C(14)–S(1) interaction [1.736(4) Å in **2a** vs. 1.788(10) Å in **4a**] and shortening of Fe(2)–C(14) [2.151(4) Å in **2a** vs. 2.072(14) Å in **4a**], which can be interpreted as an increase of the π -allyl ligand character with respect to the Fe(2), and is better described by the resonance form **A**. On the other hand, since the Fe(2)–C(15) bond is even shortened with respect to **2a**, a contribution of the resonance form **B** (Scheme 3), is also to be considered.

The spectroscopic properties of **4a–e** are in agreement with those of analogous cationic vinyliminium complexes [2]. The IR spectra (in CH_2Cl_2 solution) exhibit the typical $\nu\text{-CO}$ band pattern consisting of two absorptions due to terminal and bridging carbonyls (e.g. for **2a** at 1990 and 1830 cm^{-1}). These are 30–40 cm^{-1} shifted to higher frequencies compared to the parent neutral zwitterionic complexes, due to the cationic character of the complexes. The NMR spectra, in CDCl_3 or CD_3CN solution, evidence the presence of a single isomer, which maintain a *cis* configuration (*cis-trans* is referred to the mutual position of the Cp ligands) and a *Z* configuration (referred to the orientation of the Me and Xyl groups with respect to the $\text{C}_\alpha\text{=N}$ double bond), as deduced by NOE investigations carried on **4a–e**.

Major feature in the ^{13}C NMR spectra is given by the resonances of the bridging C_3 carbon skeleton: the resonances due to C_α and C_γ are in the typical regions for an aminocarbene (e.g. for **4b** at 227.8 ppm), and bridging alkylidene (e.g. for **4b** at 208.5), respectively. The C_β carbon resonance (at 64–70 ppm) is high field shifted compared to the parent compound **2a** (at 112.8 ppm). These data suggest some contribution of the resonance form **B** (Scheme 3).

Then, the reactions of the zwitterionic complexes with Lewis acids were studied. Beside **2a**, other vinyliminium complexes were considered, in order to evidence possible effects due to different nature of the substituents on the bridging frame. Indeed, the complexes $[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C}_\gamma\text{R}'\text{=C}_\beta(\text{S})\text{C}_\alpha\text{=N}(\text{Me})(\text{Xyl})\}\{\mu\text{-CO}\}(\text{CO})(\text{Cp})_2]$ ($\text{R}' = \text{CH}_2\text{OH}$, **2b**; $\text{R}' = \text{Me}$, **2c**; $\text{R}' = \text{Bu}^n$, **2d**) differ from **2a**, in that they, respectively, contain CH_2OH , CH_3 and Bu^n in the place of the Tol group on the C_γ position. In spite of these differences, **2a–c** react in the same manner with BF_3 , in etherated solution, leading to the addition of the Lewis acid at the S atom (Scheme 4).

Likewise, the addition of the Fp^+ fragment ($\text{Fp}^+ = [\text{Fe}(\text{CO})_2\text{Cp}]^+$) takes place at the sulphur atom and generates the trinuclear complexes **6a–c** (Scheme 4). The cationic Fp^+ , generated in situ upon treatment of $[\text{Fe}(\text{CO})_2(\text{Cp})]_2$ with AgSO_3CF_3 [11], has been selected among other possible electrophilic metal complexes for the reason that it is similar to the other metal fragments already present in **2**, and because it is known to coordinate sulphur containing ligands [12].

The spectroscopic properties of **5a–c** and **6a–c** resemble those of the complexes **4** above discussed. The addition of BF_3 to the bridging ligand produces a shift in the $\nu\text{-CO}$ frequencies of the

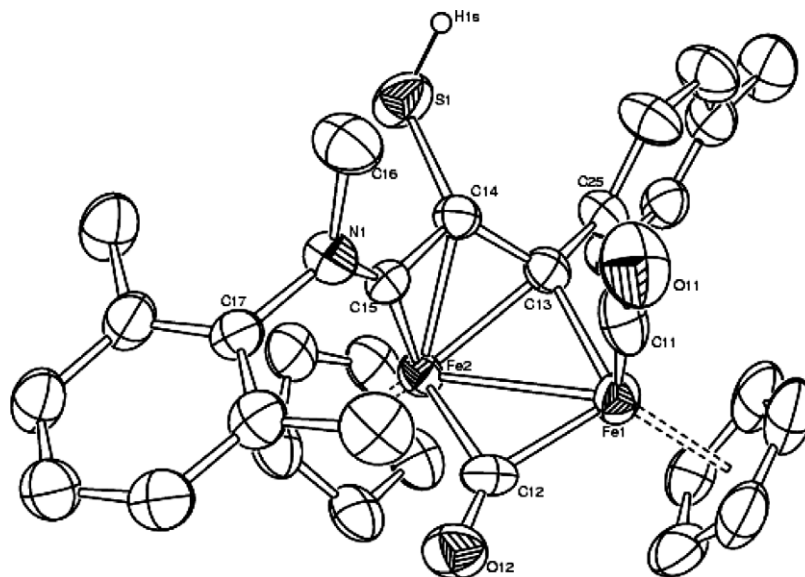


Fig. 1. Molecular structure of **4a**, with key atoms labelled. Displacement ellipsoids are at 30% probability level. All H-atoms (except H(1s)) have been omitted for clarity.

Table 1

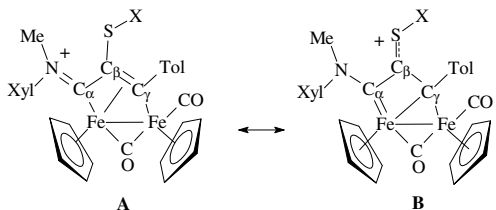
Selected bond lengths (Å) and angles (°) for $[\text{Fe}_2\{\mu\text{-}\eta^1\text{-}\eta^3\text{-C}_7\text{(Tol)}\text{=C}_\beta\text{(SH)}\text{C}_\alpha\text{=N(Me)}\text{(Xyl)}\}\{\mu\text{-CO}\}\{\text{CO}\}\{\text{Cp}_2\}\}\{\text{SO}_3\text{CF}_3\}]$ (**4a**)

Fe(1)–Fe(2)	2.571(2)	Fe(2)–C(15)	1.846(9)
Fe(1)–C(11)	1.765(13)	C(13)–C(14)	1.421(13)
Fe(1)–C(12)	1.873(11)	C(14)–C(15)	1.433(12)
Fe(2)–C(12)	1.997(10)	C(15)–N(1)	1.287(11)
Fe(1)–C(13)	1.977(10)	C(14)–S(1)	1.788(10)
Fe(2)–C(13)	2.043(9)	C(11)–O(11)	1.131(12)
Fe(2)–C(14)	2.072(9)	C(12)–O(12)	1.156(11)
Fe(1)–C(13)–C(14)	120.2(7)	C(15)–N(1)–C(17)	120.6(8)
C(13)–C(14)–C(15)	116.3(8)	C(16)–N(1)–C(17)	116.9(8)
C(14)–C(15)–N(1)	131.4(9)	C(15)–N(1)–C(16)	122.3(8)

Table 2

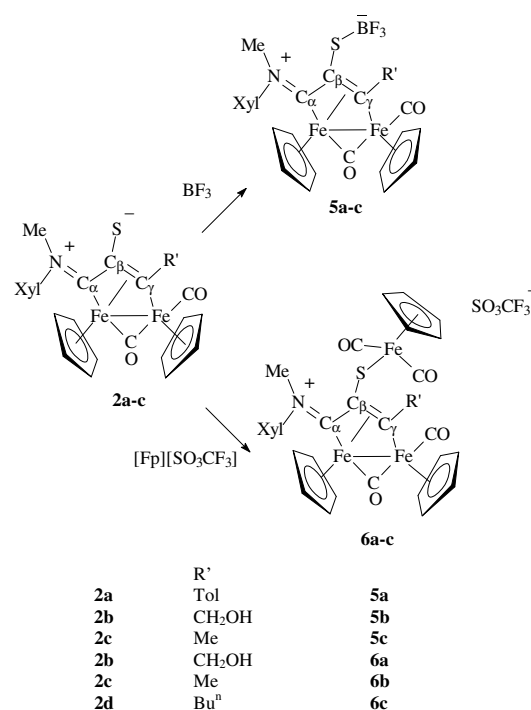
Comparison between the bonding parameters (Å) of the bridging ligands in **2a**, **4a** and $\text{cis-}[\text{Fe}_2\{\mu\text{-}\eta^1\text{-}\eta^3\text{-C}_7\text{(Me)}\text{=C}_\beta\text{(Me)}\text{C}_\alpha\text{=N(Me)}\text{(Xyl)}\}\{\mu\text{-CO}\}\{\text{CO}\}\{\text{Cp}_2\}\}]^+$ (**1**)

	2a	4a	1
Fe(1)–C(13)	1.988(4)	1.977(10)	1.955(7)
Fe(2)–C(13)	2.040(4)	2.043(9)	2.035(7)
Fe(2)–C(14)	2.151(4)	2.072(9)	2.080(7)
Fe(2)–C(15)	1.860(4)	1.846(9)	1.839(7)
C(13)–C(14)	1.430(6)	1.421(13)	1.39(1)
C(14)–C(15)	1.440(6)	1.433(12)	1.43(1)
C(15)–N(1)	1.307(5)	1.287(11)	1.314(8)
C(14)–S(1)	1.736(4)	1.788(10)	–



Scheme 3.

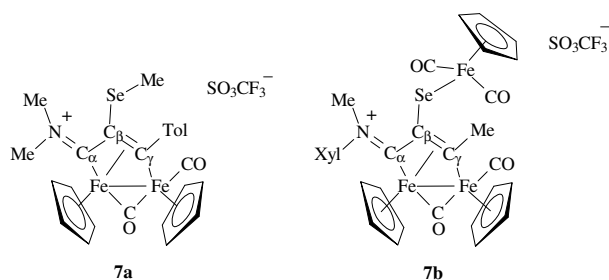
diiron moiety, of about 30 cm^{-1} , and the ^{13}C NMR spectra of **5a–c** exhibit the usual pattern for the C_α , C_β and C_γ resonances. The presence of the BF_3 unit in **5a–c** is also documented by the occurrence



Scheme 4.

of a resonance, in the ^{19}F NMR spectra, at about -152 ppm . Conversely, the addition of Fp^+ gives rise to a more complex $\nu\text{-CO}$ band pattern, derived from the absorptions attributable to the Fp moiety in addition to those of the dinuclear frame. Nevertheless, a $20\text{--}25\text{ cm}^{-1}$ shift to higher frequencies for the bridging CO well evidences the presence of the electrophilic Fp^+ fragment.

Additional studies were aimed to evidence possible effects due to the presence of selenium in the place of sulphur in the bridging ligand. Therefore, the reaction of the complex $[\text{Fe}_2\{\mu\text{-}\eta^1\text{-}\eta^3\text{-C}_7\text{(Tol)}\text{=C}_\beta\text{(Se)}\text{C}_\alpha\text{=N(Me)}_2\}\{\mu\text{-CO}\}\{\text{CO}\}\{\text{Cp}_2\}\}]$ (**3a**) with MeSO_3CF_3 was investigated. Methylation occurred at the Se atom yielding **7a** (Scheme 5) in a reaction which parallels those of the corresponding S-functionalized vinyliminium complexes **2a–c**. Likewise, the



Scheme 5.

reaction of $[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C}_\beta(\text{Me})\text{=C}_\gamma\text{N}(\text{Me})(\text{Xyl})\}(\mu\text{-CO})(\text{CO})(\text{Cp})_2]$ (**3b**) with Fp^+ leads to the formation of the trinuclear complex **7b** (Scheme 5), analogous to **6a–c**.

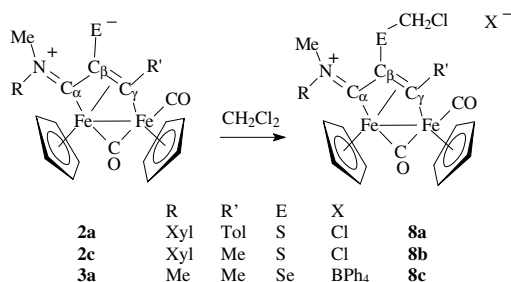
Compounds **7a–b** display spectroscopic properties similar to those of the corresponding species of type **4** and **6**, respectively (see 4).

The formation of the trinuclear complexes **6a–c** and **7b** evidences that the S or Se atom, which formally bears the negative charge in the parent zwitterionic complexes, can be exploited to coordinate unsaturated metal fragments and, consequently increase the nuclearity and the complexity of the bridging frame.

In the reactions with Fp^+ and, at a lesser extent, in the alkylation reactions reported in Scheme 2, we noticed the formation of minor amounts (less than 5–8%) of a secondary product. Further investigations suggested that these products might derive from the reactions of **2** and **3** with the solvent, which was CH_2Cl_2 in all of cases. Indeed, we found that complexes **2a**, **2c** and **3a**, upon standing in CH_2Cl_2 solution, slowly react with the solvent leading to the alkylation of the S (Se) atom (Scheme 6).

Formation of the complexes **8a–b** occurs in about 80% yield after 12 h at room temperature. Complex **8c** was isolated as BPh_4^- salts, after anion exchange in order to obtain crystals suitable for X-ray diffraction. In addition to X-ray structural determination, complexes **8a–c** were characterized by spectroscopy and elemental analysis.

The molecular structure of **8c** is displayed in Fig. 2 whereas the most relevant bond distances and angles are reported in Table 3. Moreover, the bonding parameters of the bridging ligands in **8c**, the closely related zwitterionic complex **3b** (which differs from the parent **3a** only for having a Xyl instead of a Me-group on the nitrogen) [6], the tetranuclear diselenide **9e** (which will be described in the next section) and a typical vinyliminium complex (**1**) are compared in Table 4. The cationic complex **8c** can be perfectly described as a bridging vinyliminium, as indicated by its bonding parameters. As reported above for S-protonation of **2a**, also Se-alkylation results in elongation of $\text{C}(14)\text{-Se}(1)$ [1.899(3) Å in **3b** vs. 1.949(4) Å in **8c**] which becomes an almost pure single



Scheme 6.

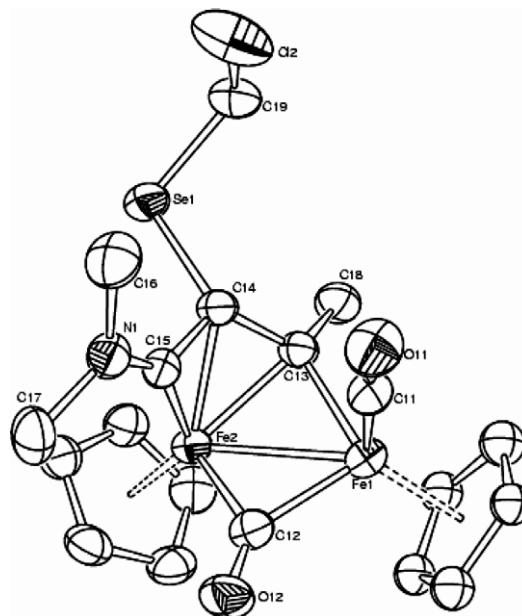


Fig. 2. Molecular structure of **8c**, with key atoms labelled. Displacement ellipsoids are at 30% probability level. All H-atoms have been omitted for clarity. Only the main image of the disordered Cp bound to Fe(1) is drawn.

Table 3

Selected bond lengths (Å) and angles ($^\circ$) for $[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C}_\beta(\text{Me})\text{=C}_\gamma\text{N}(\text{Me})\text{CH}_2\text{Cl}\}\text{-C}_\alpha\text{=N}(\text{Me})_2\}(\mu\text{-CO})(\text{CO})(\text{Cp})_2][\text{BPh}_4]$ (**8c**)

Fe(1)–Fe(2)	2.5460(8)	C(13)–C(14)	1.409(6)
Fe(1)–C(11)	1.755(5)	C(14)–C(15)	1.416(5)
Fe(1)–C(12)	1.908(5)	C(15)–N(1)	1.284(5)
Fe(2)–C(12)	1.942(5)	C(14)–Se(1)	1.949(4)
Fe(1)–C(13)	1.957(4)	Se(1)–C(19)	1.931(5)
Fe(2)–C(13)	2.020(4)	C(19)–Cl(2)	1.767(5)
Fe(2)–C(14)	2.046(4)	C(11)–O(11)	1.138(5)
Fe(2)–C(15)	1.841(4)	C(12)–O(12)	1.163(5)
Fe(1)–C(13)–C(14)	119.0(3)	C(15)–N(1)–C(17)	121.1(4)
C(13)–C(14)–C(15)	116.5(3)	C(16)–N(1)–C(17)	115.6(4)
C(14)–C(15)–N(1)	132.5(4)	C(14)–Se(1)–C(19)	99.2(2)
C(15)–N(1)–C(16)	123.3(4)	Se(1)–C(19)–Cl(2)	116.1(3)

Table 4

Comparison between the bonding parameters (Å) of the bridging ligands in **3b**, **8c**, **9e** and $\text{cis-}[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C}_\beta(\text{Me})\text{=C}_\gamma\text{N}(\text{Me})(\text{Xyl})\}(\mu\text{-CO})(\text{CO})(\text{Cp})_2\}^+(\mathbf{1})$

	3b	8c	9e	1
Fe(1)–C(13)	1.966(4)	1.957(4)	1.967(6)	1.955(7)
Fe(2)–C(13)	2.034(4)	2.020(4)	2.033(6)	2.035(7)
Fe(2)–C(14)	2.158(3)	2.046(4)	2.044(6)	2.080(7)
Fe(2)–C(15)	1.864(3)	1.841(4)	1.855(6)	1.839(7)
C(13)–C(14)	1.435(5)	1.409(6)	1.427(8)	1.39(1)
C(14)–C(15)	1.431(5)	1.416(5)	1.439(8)	1.43(1)
C(15)–N(1)	1.307(4)	1.284(5)	1.275(8)	1.314(8)
C(14)–Se(1)	1.899(3)	1.949(4)	1.952(6)	–

bond, and strengthening of the Fe(2)–C(14) interaction [2.158(3) Å in **3b** vs. 2.046(4) Å in **8c**].

Spectroscopic characterization of **8a–c** (see 4) was straightforward, in that their IR and NMR data exhibit close similarities with those of the related compounds **4b–e** and **7a**. Moreover, the addition of the CH_2Cl unit is consistent with the occurrence of two doublets (e.g. at 4.44 and 4.25 ppm for **8a**), attributable to the CH_2 protons. The chemical shift and coupling constants are similar to those observed in **4d**, which also contains diastereotopic geminal hydrogen atoms. Finally, in the cases of **8a–b**, NOE studies have

evidenced significant interaction between the resonance of one Cp and that of the N-Me group, indicating that the complexes maintain the Z configuration exhibited by their parent compounds **2a** and **2c**.

It should be remarked that CH₂Cl₂ is usually unreactive with neutral metal complexes, with relevant exceptions that mostly involve oxidative addition [13]. In general, CH₂Cl₂ is not an efficient alkylating reagent, at least compared to those reported in Scheme 2, and nucleophilic attacks on dichloromethane are uncommon [14]. In particular, chloride displacement by thiolates is rare [15], although this type of reaction might have a relevant role in the bacterial dichloromethane dehalogenase [16]. In view of these considerations, the formation of **8a–c** clearly remarks the strong nucleophilic character of the chalcogenide functionality in the zwitterionic ligand in **2** and **3**, and represent an unusual and interesting example of nucleophilic addition involving dichloromethane.

2.2. Oxidative coupling of S- and Se-functionalized vinyliminium ligands

Beside nucleophilic addition, the presence of a chalcogenide (S or Se) on the bridging ligand should be exploited to promote oxidation reactions. In particular, we have examined the reactions of zwitterionic sulfide complexes **2b–d** with iodine, in CH₃OH solution, which resulted in the formation of the bis-cationic tetranuclear complexes **9a–c** (Scheme 7). Likewise, the selenium containing complexes **3b** and [Fe₂{μ-η¹:η³-C_ν(Buⁿ)=C_β(Se)C_α=NMe₂}(μ-CO)(CO)(Cp)₂} (**3c**) react with I₂ under similar conditions affording **9d** and **9e**, respectively (Scheme 7). All these complexes have been obtained in 80–90% yield and isolated as BPh₄[−] salts, after anion exchange.

Complexes **9a–e** have been characterized by IR and NMR spectroscopy, and elemental analysis. Furthermore, the structure of **9e** has been established by X-ray studies: the ORTEP molecular diagram is shown in Fig. 3, whereas relevant bond lengths and angles are reported in Table 5. The molecule is composed by two [Fe₂{μ-η¹:η³-C(Buⁿ)=C(Se)C=N(Me)₂}(μ-CO)(CO)(Cp)₂}⁺ moieties joined by a Se–Se bond. The former has all the characteristics of cationic vinyliminium complexes and the bonding parameters parallel very well the ones previously reported for other [Fe₂{μ-η¹:η³-C(R')=C(R'')C=N(Me)(R)}(μ-CO)(CO)(Cp)₂}⁺ species [2], as well as those described in this paper for **8c** (Table 4). This is not surprising, since also the parent zwitterionic compound **3c** presented a ligand with a partial vinyliminium character. Therefore, the reaction is a selective mono-electronic oxidation of the heteroatom, which loses its negative charge and forms a homonuclear bridge, whereas the

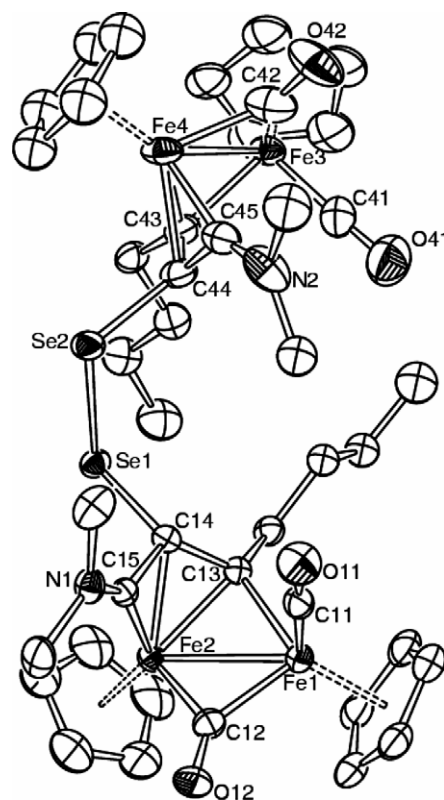
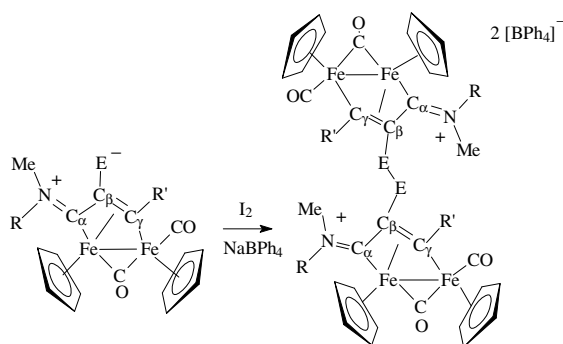


Fig. 3. Molecular structure of **9e**, with key atoms labelled. Displacement ellipsoids are at 30% probability level. All H-atoms have been omitted for clarity. Only the main images of the disordered groups are reported.

Table 5
Selected bond lengths (Å) and angles (°) for [Fe₂{μ-η¹:η³-C(Buⁿ)=C(Se)C=N(Me)₂}(μ-CO)(CO)(Cp)₂}₂[BPh₄]₂ (**9e**)

Fe(1)–Fe(2)	2.5467(14)	Fe(3)–Fe(4)	2.542(3)
Fe(1)–C(11)	1.750(8)	Fe(3)–C(41)	1.713(10)
Fe(1)–C(12)	1.892(7)	Fe(3)–C(42)	1.866(10)
Fe(2)–C(12)	1.949(7)	Fe(4)–C(42)	1.941(11)
Fe(1)–C(13)	1.967(6)	Fe(3)–C(43)	1.984(8)
Fe(2)–C(13)	2.033(6)	Fe(4)–C(43)	2.065(8)
Fe(2)–C(14)	2.044(6)	Fe(4)–C(44)	2.059(7)
Fe(2)–C(15)	1.855(6)	Fe(4)–C(45)	1.889(9)
C(11)–O(11)	1.165(8)	C(41)–O(41)	1.169(10)
C(12)–O(12)	1.185(8)	C(42)–O(42)	1.188(11)
C(13)–C(14)	1.427(8)	C(43)–C(44)	1.402(10)
C(14)–C(15)	1.439(8)	C(44)–C(45)	1.481(11)
C(15)–N(1)	1.275(8)	C(45)–N(2)	1.249(10)
C(14)–Se(1)	1.952(6)	C(44)–Se(2)	1.980(8)
Se(1)–Se(2)	2.3136(11)		
Fe(1)–C(13)–C(14)	118.8(4)	Fe(3)–C(43)–C(44)	118.7(6)
C(13)–C(14)–C(15)	116.0(5)	C(43)–C(44)–C(45)	117.2(7)
C(14)–C(15)–Fe(2)	75.7(4)	C(44)–C(45)–Fe(4)	74.2(5)
C(14)–C(15)–N(1)	136.4(6)	C(44)–C(45)–N(2)	132.8(7)
C(14)–Se(1)–Se(2)	106.85(18)	C(44)–Se(2)–Se(1)	110.0(2)



	R	R'	E	
2b	Xyl	CH ₂ OH	S	9a
2c	Xyl	Me	S	9b
2d	Xyl	Bu ⁿ	S	9c
3b	Xyl	Me	Se	9d
3c	Me	Bu ⁿ	Se	9e

Scheme 7.

positive charge remains on the vinyliminium without any major rearrangement. The C_β–Se interactions [C(14)–Se(1) 1.952(6) Å; C(44)–Se(2) 1.980(8) Å] are almost pure single bonds as in the dinuclear Se-alkylated vinyliminium **8c** [1.949(4) Å]. The Se(1)–Se(2) interaction [2.3136(11) Å] is in keeping with other organic and organometallic diselenides as well as the C(11)–Se(1)–Se(2)–C(44) torsion angle [−87.1(3)°], which indicates a skew conformation [17].

The IR and NMR data of **9a–e** are in good agreement with the presence of 2 equiv. dinuclear moieties, each containing a vinyliminium ligand. NOE studies carried on **9a–e** indicate that the *N*-substituents (Me and Xyl) adopt the *Z* configuration.

It should be remarked that, since the complexes **2** are chiral, the formation of the dimeric complexes **9** from **2**, might result in the formation of the *meso* and the *dl* forms. The XRD structure of **9e** corresponds to the *meso* isomer (with an achiral space group shown in Table 6). Moreover, different crystals have been analysed, all showing the same structure and the ¹H NMR spectra indicate the presence of a single isomeric form in solution. These data suggest that **9** consist exclusively of *meso* form.

The reaction described in Scheme 7 represents an interesting example of disulfide (diselenide) bond formation by oxidative coupling, which falls within a field of high interest for its biological and synthetic applications [18]. Indeed, oxidative coupling of thiols to disulfides is an area of active research, due to the need of providing selective reaction conditions and avoid thiols over-oxidation [19]. Disulfide bond formation in coordination and organometallic compounds mostly involve the syntheses of μ-S₂ dinuclear complexes by oxidative coupling of SH (or H₂S) ligands [20]. Examples include the formation of tetranuclear species by the oxidative coupling of the bridging hydrogen sulfido ligand in the complexes [Cp*₂MCl(μ-SH)₂MClCp*] (M = Rh, Ir, Cp* = η⁵C₅Me₅) [21]. Our findings provide an unusual example in which the S–S, and in particular Se–Se, bond formation involves a more complex ligand, resulting in an oxidative dimerization [22]. Finally, it should be remarked that the oxidative coupling is reversible, in that treatment of **9a–c** with freshly prepared solution of sodium naphthalenide in THF, at room temperature, leads to the formation of the parent complexes **2b–d** in about 70% yield.

Table 6
Crystal data and experimental details for **4a** · H₂O, **8c** and **9e** · CH₃CN

Complex	4a · H ₂ O	8c	9e · CH ₃ CN
Formula	C ₃₂ H ₃₂ F ₃ Fe ₂ NO ₅ S ₂	C ₄₃ H ₄₁ BClFe ₂ NO ₂ Se	C ₉₂ H ₉₃ B ₂ Fe ₄ N ₃ O ₄ Se ₂
Formula weight	759.41	840.69	1707.63
<i>T</i> (K)	295(2)	296(2)	293(2)
<i>λ</i> (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	8.540(4)	12.8773(9)	12.373(3)
<i>b</i> (Å)	12.444(5)	22.8722(16)	15.537(3)
<i>c</i> (Å)	16.939(7)	13.3470(10)	22.161(4)
<i>α</i> (°)	109.580(5)	90	81.87(3)
<i>β</i> (°)	97.292(5)	94.7530(10)	86.19(3)
<i>γ</i> (°)	98.813(5)	90	72.09(3)
Cell volume (Å ³)	1645.1(12)	3917.6(5)	4011.8(14)
<i>Z</i>	2	4	2
<i>D</i> _c (g cm ⁻³)	1.533	1.425	1.414
<i>μ</i> (mm ⁻¹)	1.070	1.774	1.670
<i>F</i> (000)	780	1720	1760
Crystal size (mm)	0.21 × 0.15 × 0.11	0.21 × 0.16 × 0.13	0.19 × 0.14 × 0.11
<i>θ</i> Limits (°)	1.30–25.00	1.77–27.00	0.93–25.03
Reflections collected	10687	43585	36159
Independent reflections	5684 [0.0841]	8531 [0.0595]	14177 [0.0827]
[<i>R</i> _{int}]			
Data/restraints/parameters	5684/207/419	8531/26/459	14177/506/968
Goodness-of-fit on <i>F</i> ²	0.962	1.027	1.017
<i>R</i> ₁ (<i>I</i> > 2σ(<i>I</i>))	0.0831	0.0497	0.0664
<i>wR</i> ₂ (all data)	0.2796	0.1630	0.1942
Largest difference in peak and hole (e Å ⁻³)	0.679/–0.572	0.468/–0.680	0.843/–0.622

3. Conclusions

The diiron complexes **2** and **3**, investigated in this work, contain zwitterionic bridging vinyliminium ligands, with a negative charge formally localized on the S/Se heteroatoms. These chalcogenide functionalities might, in theory, undergo three different type of reactions: (i) S (or Se) alkylation, (ii) S (or Se) metalation by unsaturated metal fragments, (iii) oxidative coupling to generate S–S (Se–Se) bonds. Each of these reactions has been successfully accomplished under very selective conditions, involving the S or Se atoms without affecting the remaining part of the complexes. The investigated reactions, and in particular the alkylation with CH₂Cl₂, reveal the remarkable nucleophilic character of the chalcogenide functionality.

The addition of the coordinatively unsaturated Fp⁺ metal fragment demonstrate that it is possible to increase the nuclearity of the complexes by coordination to S or Se, and that the zwitterionic complexes **2–3**, as a whole, might act as 'organometallic ligands'.

4. Experimental

4.1. General

All reactions were routinely carried out under a nitrogen atmosphere, using standard Schlenk techniques. Solvents were distilled immediately before use under nitrogen from appropriate drying agents. Chromatography separations were carried out on columns of deactivated alumina (4% w/w water). Glassware was oven-dried before use. Infrared spectra were recorded at 298 K on a Perkin-Elmer Spectrum 2000 FT-IR spectrophotometer and elemental analyses were performed on a ThermoQuest Flash 1112 Series EA Instrument. All NMR measurements were performed at 298 K on Mercury Plus 400 instrument. The chemical shifts were referenced to internal TMS for ¹H and ¹³C, and to external CCl₃F for ¹⁹F. The spectra were fully assigned via DEPT experiments and ¹H, ¹³C correlation through gs-HSQC and gs-HMBC experiments [23]. NOE measurements were recorded using the DPGSE-NOE sequence [24]. All the reagents were commercial products (Aldrich) of the highest purity available and used as received. [Fe₂(CO)₄(Cp)₂] was purchased from Strem and used as received. Compounds **2a–d** and **3a–c** were prepared by published methods [6].

4.2. Synthesis of [Fe₂{μ-η¹:η³-C_ν(Tol)=C_β(SX)C_α=N(Me)(Xyl)}(μ-CO)(CO)(Cp)₂][SO₃CF₃] (X = H, **4a**; X = Me, **4b**)

To a solution of **2a** (100 mg, 0.169 mmol) in CH₂Cl₂ (15 mL), was added HSO₃CF₃ (0.02 mL, 0.18 mmol). The solution was stirred for 30 min, then it was filtered on celite. Removal of the solvent gave **4a** as brown powder. Yield: 113 mg, 90%. Anal. Calc. for C₃₂H₃₀F₃Fe₂NO₅S₂: C, 51.84; H, 4.08; N, 1.89. Found: C, 51.89; H, 4.15; N, 1.93%. IR (CH₂Cl₂) ν(CO) 1990 (vs), 1830 (s), ν(CN) 1615 (m) cm⁻¹. IR (KBr) ν(SH) 2548 (m) cm⁻¹. ¹H NMR (CDCl₃) δ 7.67–7.29 (7H, Me₂C₆H₃ and MeC₆H₄); 5.01, 4.94 (s, 10H, Cp); 3.57 (s, 3H, NMe); 3.25 (s, 1H, SH); 2.59, 2.03 (s, 6H, Me₂C₆H₃); 2.49 (s, 3H, MeC₆H₄). ¹³C{¹H} NMR (CDCl₃) δ 250.9 (μ-CO); 226.8 (C_α); 210.2 (CO); 209.1 (C_ν); 149.8 (C_{ipso Tol}); 140.6 (C_{ipso Xyl}); 137.7–125.5 (C_{arom}); 92.6, 89.3 (Cp); 71.8 (C_β); 49.4 (NMe); 21.2 (MeC₆H₄); 18.0, 17.9 (Me₂C₆H₃).

Complex **4b** was obtained by a procedure analogous to that described for **4a**, by reacting **2a** (90 mg, 0.152 mmol), with MeSO₃CF₃ (0.02 mL, 0.18 mmol). The reaction mixture was dried *in vacuo* and the residue was chromatographed on alumina, with MeOH as eluent affording **4b**. Yield: 106.3 mg, 93%. Anal. Calc. for C₃₃H₃₂F₃Fe₂NO₅S₂: C, 52.47; H, 4.27; N, 1.85. Found: C, 52.58; H, 4.31; N, 1.68%. IR (CH₂Cl₂) ν(CO) 1990 (vs), 1828 (s), ν(CN) 1616 (m) cm⁻¹. ¹H NMR (CD₃CN) δ 7.70–7.30 (m, 7H, MeC₆H₄ and Me₂C₆H₃); 4.99, 4.97

(s, 10H, Cp); 3.54 (s, 3H, NMe); 2.58, 2.04 (s, 6H, Me₂C₆H₃); 2.49 (s, 3H, MeC₆H₄); 2.13 (s, 3H, SMe). ¹³C{¹H} NMR (CD₃CN) δ 252.2 (μ-CO); 227.8 (C_α); 211.1 (CO); 208.5 (C_γ); 150.9 (C_{ipso Tol}); 141.4 (C_{ipso Xyl}); 137.4–122.9 (C_{arom}); 93.7, 88.9 (Cp); 68.2 (C_β); 52.0 (NMe); 21.1 (MeC₆H₄); 19.8 (SMe); 18.4, 17.9 (Me₂C₆H₃).

4.3. Synthesis of [Fe₂{μ-η¹:η³-C₂(Tol)=C_β(SX)C_α=N(Me)(Xyl)}(μ-CO)(CO)(Cp)₂][Y] (X = SiMe₃, Y = Cl, **4c; X = CH₂Ph, Y = Br, **4d**; X = CH₂CH=CH₂, Y = I, **4e**)**

Complex **4c** was obtained by the same procedure described for **4b**, by reacting **2a** (150 mg, 0.254 mmol) with SiMe₃Cl (1.00 mL, 7.85 mmol). Yield: 124 mg, 70%. Anal. Calc. for C₃₄H₃₈ClFe₂NO₂SSi: C, 58.36; H, 5.44; N, 2.00. Found: C, 58.42; H, 5.40; N, 2.03%. IR (CH₂Cl₂) ν(CO) 1993 (vs), 1830 (s), ν(CN) 1615 (w) cm⁻¹. ¹H NMR (CDCl₃) δ 7.71–6.99 (m, 7H, MeC₆H₄ and Me₂C₆H₃); 4.67, 4.59 (s, 10H, Cp); 3.48 (s, 3H, NMe); 2.48, 1.95 (s, 6H, Me₂C₆H₃); 2.18 (s, 3H, C₆H₄Me); 0.09 (SiMe₃). ¹³C{¹H} NMR (CDCl₃) δ 248.8 (μ-CO); 226.8 (C_α); 210.2 (CO); 207.7 (C_γ); 149.0 (C_{ipso Tol}); 140.0 (C_{ipso Xyl}); 136.9–127.5 (C_{arom}); 95.4, 90.7 (Cp); 64.3 (C_β); 49.7 (NMe); 21.2 (C₆H₄Me); 18.0 (Me₂C₆H₃); 0.61 (SiMe₃).

Complexes **4d–e** were obtained by the same procedure described for **4b**, by reacting **2a** with BrCH₂Ph and ICH₂CH=CH₂, respectively.

4d (yield: 87%). Anal. Calc. for C₃₈H₃₆BrFe₂NO₂S: C, 59.87; H, 4.76; N, 1.84. Found: C, 59.92; H, 4.70; N, 1.91%. IR (CH₂Cl₂) ν(CO) 1992 (vs), 1833 (s), ν(CN) 1613 (m) cm⁻¹. ¹H NMR (CDCl₃) δ 7.97–6.84 (12H, Me₂C₆H₃, C₆H₄Me and Ph); 5.13, 5.08 (s, 10H, Cp); 4.52, 4.33 (d, ²J_{HH} = 11.71 Hz, 2H, CH₂Ph); 3.60 (s, 3H, NMe); 2.58 (s, 3H, C₆H₄Me); 2.49, 2.02 (s, 6H, Me₂C₆H₃). ¹³C{¹H} NMR (CDCl₃) δ 249.1 (μ-CO); 226.8 (C_α); 210.2 (CO); 208.4 (C_γ); 149.7 (C_{ipso Tol}); 149.1 (C_{ipso Ph}); 140.3 (C_{ipso Xyl}); 137.3–126.0 (C_{arom}) 92.2, 89.0 (Cp); 64.6 (C_β); 63.8 (CH₂Ph); 51.1 (NMe); 21.1 (C₆H₄Me); 18.0, 17.7 (Me₂C₆H₃).

4e (yield: 83%). Anal. Calc. for C₃₄H₃₄Fe₂INO₂S: C, 53.78; H, 4.51; N, 1.84. Found: C, 53.82; H, 4.60; N, 1.80%. IR (CH₂Cl₂) ν(CO) 1994 (vs), 1832 (s), ν(C₂N) 1614 (m) cm⁻¹. ¹H NMR (CDCl₃) δ 7.68–7.29 (7H, Me₂C₆H₃ and C₆H₄Me); 5.53 (m, 2H, SCH₂CH₂); 5.09, 5.05 (s, 10H, Cp); 3.85 (m, 1H, SCH₂CH); 3.61 (s, 3H, NMe); 3.17 (m, 2H, SCH₂); 2.59 (s, 3H, C₆H₄Me); 2.50, 2.04 (s, 6H, Me₂C₆H₃). ¹³C{¹H} NMR (CDCl₃) δ 249.1 (μ-CO); 226.4 (C_α); 209.9 (CO); 208.7 (C_γ); 148.9 (C_{ipso Tol}); 140.2 (C_{ipso Xyl}); 137.3–119.5 (C_{arom} and CH=CH₂); 93.1, 88.9 (Cp); 64.5 (C_β); 51.2 (NMe); 39.4 (SCH₂); 21.1 (C₆H₄Me); 17.7, 17.6 (Me₂C₆H₃).

4.4. Synthesis of [Fe₂{μ-η¹:η³-C₂(R)=C_β(SBF₃)C_α=N(Me)(Xyl)}(μ-CO)(CO)(Cp)₂] (R = Tol, **5a; R = CH₂OH, **5b**; R = Me, **5c**)**

Complex **2a** (125 mg, 0.211 mmol), in CH₂Cl₂ solution (15 mL), was treated with BF₃, in Et₂O solution (0.5 mmol). The solution, which turned immediately brown, was stirred for an additional 10 min, then was filtered on a celite pad. Removal of the solvent gave a brown powder corresponding to **5a**. Yield: 98 mg, 70%. Anal. Calc. for C₃₁H₂₉BF₃Fe₂NO₂S: C, 56.49; H, 4.43; N, 2.13. Found: C, 56.52; H, 4.36; N, 2.20%. IR (CH₂Cl₂) ν(CO) 1990 (vs), 1829 (s), ν(CN) 1608 (w) cm⁻¹. ¹H NMR (CD₃CN) δ 7.98–7.20 (m, 7H, MeC₆H₄ and Me₂C₆H₃); 5.06, 5.04 (s, 10H, Cp); 3.64 (s, 3H, NMe); 2.60, 1.96 (s, 6H, Me₂C₆H₃); 2.52 (s, 3H, MeC₆H₄). ¹³C{¹H} NMR (CD₃CN) δ 252.7 (μ-CO); 227.7 (C_α); 211.5 (CO); 206.5 (C_γ); 143.8 (C_{ipso Xyl}); 135.8–127.7 (C_{arom}); 94.7, 90.2 (Cp); 52.9 (C_β); 50.4 (NMe); 21.7 (MeC₆H₄); 19.0, 18.6 (Me₂C₆H₃). ¹⁹F NMR (CD₃CN) δ -152.2 (br, BF₃).

Complexes **5b–c** were obtained by the same procedure described for **5a**, by reacting BF₃ with **2b** and **2c**, respectively.

5b (yield: 68%). Anal. Calc. for C₂₅H₂₅BF₃Fe₂NO₃S: C, 50.13; H, 4.21; N, 2.34. Found: C, 49.99; H, 4.23; N, 2.36%. IR (CH₂Cl₂)

ν(CO) 1996 (vs), 1827 (s), ν(CN) 1609 (w) cm⁻¹. ¹H NMR (CD₃CN) δ 7.55–7.33 (m, 3H, Me₂C₆H₃); 6.79, 5.74 (dd, 2H, ²J_{HH} = 13.54 Hz, ³J_{HH} = 2.56 Hz, CH₂OH); 5.62, 5.02 (s, 10H, Cp); 3.70 (s, 3H, NMe); 2.69, 1.99 (s, 6H, Me₂C₆H₃). ¹³C{¹H} NMR (CD₃CN) δ 252.3 (μ-CO); 226.8 (C_α); 212.2 (CO); 203.9 (C_γ); 142.2 (C_{ipso Xyl}); 135.7–130.9 (C_{arom}); 93.8, 92.9 (Cp); 76.9 (CH₂); 56.5 (C_β); 51.2 (NMe); 19.4, 18.9 (Me₂C₆H₃). ¹⁹F NMR (CD₃CN) δ -152.1 (br, BF₃).

5c (yield: 74%). Anal. Calc. for C₂₅H₂₅BF₃Fe₂NO₂S: C, 51.50; H, 4.32; N, 2.40. Found: C, 51.46; H, 4.26; N, 2.45%. IR (CH₂Cl₂) ν(CO) 1991 (vs), 1825 (s), ν(C₂N) 1614 (w) cm⁻¹. ¹H NMR (CDCl₃) δ 7.45–7.25 (m, 3H, Me₂C₆H₃); 5.32, 4.65 (s, 10H, Cp); 3.96 (s, 3H, C₇Me); 3.47 (s, 3H, NMe); 2.53, 2.00 (s, 6H, Me₂C₆H₃). ¹³C{¹H} NMR (CDCl₃) δ 252.3 (μ-CO); 226.5 (C_α); 209.8 (CO); 204.0 (C_γ); 140.5 (C_{ipso Xyl}); 134.0–129.0 (C_{arom}); 91.4, 89.2 (Cp); 68.5 (C_β); 49.1 (NMe); 38.5 (C₇Me); 17.8, 17.7 (Me₂C₆H₃). ¹⁹F NMR (CDCl₃) δ -156.2 (br, BF₃).

4.5. Synthesis of [Fe₂{μ-η¹:η³-C₂(R')=C_β{S-Fe(CO)₂(Cp)₂}C_α=N(Me)(Xyl)}(μ-CO)(CO)(Cp)₂][SO₃CF₃] (R' = CH₂OH, **6a; R' = Me, **6b**; R' = Buⁿ, **6c**)**

To a solution of [Fe₂(μ-CO)₂(CO)₂(Cp)₂] (94 mg, 0.266 mmol) in CH₂Cl₂ (10 mL) was added AgSO₃CF₃ (97 mg, 0.377 mmol). The mixture was stirred for 3 h in the dark, then filtered on celite and treated with **2b** (100 mg, 0.188 mmol). The resulting solution was stirred for 1 h. Solvent removal and chromatography of the residue on alumina, using CH₃OH as eluent, gave a brown band corresponding to **6a**. Yield: 121 mg, 75%. Anal. Calc. for C₃₃H₃₀F₃Fe₃NO₈S₂: C, 46.24; H, 3.53; N, 1.63. Found: C, 46.30; H, 3.48; N, 1.56%. IR (CH₂Cl₂) ν(CO) 2034 (s), 1989 (vs), 1973 (sh), 1810 (s), ν(CN) 1610 (w) cm⁻¹. ¹H NMR (CDCl₃) δ 7.41–7.21 (m, 3H, Me₂C₆H₃); 6.20 (m, 1H, OH); 6.05, 5.80 (m, 2H, CH₂OH); 5.41, 5.34, 4.63 (s, 15H, Cp); 3.30 (s, 3H, NMe); 2.59, 2.02 (s, 6H, Me₂C₆H₃). ¹³C{¹H} NMR (CDCl₃) δ 256.0 (μ-CO); 228.3 (C_α); 217.3, 213.5, 213.4 (CO); 210.8 (C_γ); 140.9 (C_{ipso Xyl}); 134.5–128.8 (C_{arom}); 90.7, 89.1, 87.2 (Cp); 79.5 (C_β); 74.3 (CH₂OH); 48.6 (NMe); 18.0, 17.8 (Me₂C₆H₃).

Complexes **6b–c** were prepared by the same procedure described for synthesis **6a**, by reacting in situ generated [Fp][SO₃CF₃] with **2c** and **2d**, respectively.

6b (yield: 85%). Anal. Calc. for C₃₃H₃₀F₃Fe₃NO₇S₂: C, 47.11; H, 3.59; N, 1.66. Found: C, 47.04; H, 3.50; N, 1.58%. IR (CH₂Cl₂) ν(CO) 2037 (s), 1996 (vs), 1981 (sh), 1816 (s), ν(CN) 1609 (w) cm⁻¹. ¹H NMR (CDCl₃) δ 7.40–7.20 (m, 3H, Me₂C₆H₃); 5.22, 4.57 (s, 15H, Cp); 3.85 (s, 3H, C₇Me); 3.31 (s, 3H, NMe); 2.58, 1.99 (s, 6H, Me₂C₆H₃). ¹³C{¹H} NMR (CDCl₃) δ 255.2 (μ-CO); 228.9 (C_α); 213.5, 213.1 (CO); 210.5 (C_γ); 140.8 (C_{ipso Xyl}); 134.4–128.7 (C_{arom}); 91.6, 90.0, 86.9 (Cp); 77.9 (C_β); 48.9 (NMe); 40.6 (C₇Me); 17.9, 17.8 (Me₂C₆H₃).

6c (yield: 69%). Anal. Calc. for C₃₆H₃₆F₃Fe₃NO₇S₂: C, 48.95; H, 4.11; N, 1.59. Found: C, 49.02; H, 4.06; N, 1.55%. IR (CH₂Cl₂) ν(CO) 2036 (s), 1994 (vs), 1980 (sh), 1815 (s), ν(CN) 1609 (w) cm⁻¹. ¹H NMR (CDCl₃) δ 7.40–7.21 (m, 3H, Me₂C₆H₃); 5.20, 5.15, 4.64 (s, 15H, Cp); 4.74, 3.98 (m, 2H, C₇CH₂); 3.41 (s, 3H, NMe); 2.64, 1.99 (s, 6H, Me₂C₆H₃); 1.95, 1.84 (m, 4H, C₇CH₂CH₂CH₂); 1.23 (m, 3H, C₇CH₂CH₂CH₂CH₃). ¹³C{¹H} NMR (CDCl₃) δ 254.6 (μ-CO); 228.3 (C_α); 213.7, 213.5 (CO); 210.5 (C_γ); 140.3 (C_{ipso Xyl}); 134.5–128.8 (C_{arom}); 90.7, 89.8, 86.4 (Cp); 72.5 (C_β); 51.3, 36.7, 23.7, 14.5 (Buⁿ); 49.6 (NMe); 18.1, 17.8 (Me₂C₆H₃).

4.6. Synthesis of [Fe₂{μ-η¹:η³-C₂(R')=C_β(SeX)C_α=N(Me)(R)}(μ-CO)(CO)(Cp)₂][SO₃CF₃] (R = X = Me, R' = Tol, **7a; R = Xyl, R' = Me, X = Fp⁺, **7b**)**

Complex **7a** was obtained by the same procedure described for synthesis of **4b**, upon treatment of **3a** (105 mg, 0.19 mmol) with

MeSO₃CF₃ (0.022 mL, 0.20 mmol). (Yield: 122 mg, 90%). Anal. Calc. for C₂₆H₂₆F₃Fe₂NO₅Se: C, 43.85; H, 3.68; N, 1.97. Found: C, 43.92; H, 3.76; N, 2.02%. IR (CH₂Cl₂): ν(CO) 1986 (vs), 1802 (s), ν(CN) 1651 (m) cm⁻¹. ¹H NMR (CDCl₃) δ 7.58–7.09 (4H, MeC₆H₄); 5.20, 4.85 (s, 10H, Cp); 3.94, 3.22 (s, 6H, NMe); 2.39 (s, 3H, MeC₆H₄); 1.89 (s, 3H, SeMe). ¹³C{¹H} NMR (CDCl₃) δ 255.4 (μ-CO); 220.2 (C_z); 210.0 (CO); 199.6 (C_γ); 151.3 (C_{ipso Tol}); 137.3–125.5 (C_{arom}); 92.1, 88.9 (Cp); 66.3 (C_β); 47.8, 45.3 (NMe); 21.5 (MeC₆H₄); 6.5 (SeMe).

Complex **7b** was obtained by the same procedure described for synthesis of **6b**, upon treatment of **3b** (120 mg, 0.21 mmol) with *in situ* generated [Fp][SO₃CF₃] (75 mg, 0.23 mmol). (Yield: 166 mg, 88%). Anal. Calc. for C₃₃H₃₀F₃Fe₃NO₇SSe: C, 44.63; H, 3.40; N, 1.58. Found: C, 44.65; H, 3.30; N, 1.49%. IR (CH₂Cl₂): ν(CO) 2031 (s), 1993 (vs), 1982 (sh), 1815 (s), ν(CN) 1612 (w) cm⁻¹. ¹H NMR (CDCl₃) δ 7.43–7.20 (m, 3H, Me₂C₆H₃); 5.17, 4.57 (s, 15H, Cp); 3.77 (s, 3H, C_zMe); 3.24 (s, 3H, NMe); 2.61, 1.98 (s, 6H, Me₂C₆H₃). ¹³C{¹H} NMR (CDCl₃) δ 256.3 (μ-CO); 228.6 (C_z); 213.8, 213.5 (CO); 210.5 (C_γ); 140.7 (C_{ipso Xyl}); 134.4–128.9 (C_{arom}); 92.0, 90.2, 86.4 (Cp); 61.6 (C_β); 49.1 (NMe); 37.8 (C_zMe); 18.1 (Me₂C₆H₃).

4.7. Synthesis of [Fe₂{μ-η¹:η³-C_γ(R')=C_β(E-CH₂Cl)C_z=N(Me)(R)}(μ-CO)(CO)(Cp)₂][Y] [E = S, R = Xyl, R' = Tol, Y = Cl, **8a; E = S, R = Xyl, R' = Me, Y = Cl, **8b**; E = Se, R = R' = Me, Y = BPh₄, **8c**]**

Complex **2a** (90 mg, 0.152 mmol), was dissolved in CH₂Cl₂ (10 mL). The solution was stirred overnight, then it was filtered on a celite pad. Removal of the solvent gave **8a** as brown microcrystalline solid. Yield: 90 mg, 88%. Anal. Calc. for C₃₂H₃₁Cl₂Fe₂NO₂S: C, 56.83; H, 4.62; N, 2.07. Found: C, 56.88; H, 4.55; N, 1.99%. IR (CH₂Cl₂): ν(CO) 1990 (vs), 1830 (s), ν(CN) 1615 (m) cm⁻¹. ¹H NMR (CDCl₃) δ 7.63–7.21 (m, 7H, Me₂C₆H₃ and MeC₆H₄); 5.24, 5.05 (s, 10H, Cp); 4.44, 4.25 (d, ²J_{HH} = 11.3 Hz, 2H, CH₂Cl); 3.51 (s, 3H, NMe); 2.49, 1.96 (s, 6H, Me₂C₆H₃); 2.42 (s, 3H, MeC₆H₄). ¹³C{¹H} NMR (CDCl₃) δ 249.1 (μ-CO); 226.8 (C_z); 210.2 (CO); 208.0 (C_γ); 149.1 (C_{ipso Tol}); 140.2 (C_{ipso Xyl}); 137.1–126.8 (C_{arom}); 93.5, 89.2 (Cp); 64.5 (C_β); 50.9 (CH₂Cl); 48.4 (NMe); 21.0 (MeC₆H₄); 17.9, 17.6 (Me₂C₆H₃).

Complexes **8b** and **8c** were prepared by using a procedure analogous to what described for **8a**, from CH₂Cl₂ solutions of **2c** and **3a**, respectively. Anion exchange for **8c** was performed as follows: complex [Fe₂{μ-η¹:η³-C_γ(Me)C_β(Se-CH₂Cl)C_zN(Me)₂}(μ-CO)(CO)(Cp)₂][Cl] (85 mg, 0.153 mmol) was dissolved in CH₃CN (10 mL), and NaBPh₄ (157 mg, 0.459 mmol) was added. The mixture was stirred for 2 h, then it was filtered on celite. Removal of the solvent afforded **8c**. Crystals of **8c** suitable for X-ray analysis were obtained by a CH₂Cl₂ solution layered with diethyl ether, at -20 °C.

8b (yield: 86%). Anal. Calc. for C₂₆H₂₇Cl₂Fe₂NO₂S: C, 52.03; H, 4.53; N, 2.33. Found: C, 52.18; H, 4.46; N, 2.31%. IR (CH₂Cl₂): ν(CO) 1990 (vs), 1825 (s), ν(CN) 1616 (m) cm⁻¹. ¹H NMR (CDCl₃) δ 7.45–7.25 (3H, Me₂C₆H₃); 5.58, 4.86 (s, 10H, Cp); 5.39, 5.15 (d, 2H, ³J_{HH} = 11.7 Hz, CH₂); 4.26 (s, 3H, C_zMe); 3.59 (s, 3H, NMe); 2.49, 2.01 (s, 6H, Me₂C₆H₃). ¹³C{¹H} NMR (CDCl₃) δ 250.5 (μ-CO); 226.2 (C_z); 213.6 (CO); 209.7 (C_γ); 140.4 (C_{ipso Xyl}); 133.8–128.7 (C_{arom}); 92.0, 89.1 (Cp); 66.7 (C_β); 50.1 (CH₂Cl); 49.3 (NMe); 39.8 (C_zMe); 17.7, 17.4 (Me₂C₆H₃).

8c (yield: 84%). Anal. Calc. for C₄₃H₄₁ClFe₂NO₂Se: C, 61.43; H, 4.92; N, 1.67. Found: C, 61.48; H, 4.84; N, 1.59%. IR (CH₂Cl₂): ν(CO) 1997 (vs), 1817 (s), ν(CN) 1670 (m) cm⁻¹. ¹H NMR (acetone-*d*₆) δ 7.36–6.79 (m, 20H, BPh₄); 5.52, 5.15 (s, 10H, Cp); 5.30, 5.20 (d, 2H, ²J_{HH} = 10.25 Hz, CH₂Cl); 4.16 (s, 3H, C_zMe); 3.92, 3.30 (s, 6H, NMe). ¹³C{¹H} NMR (acetone-*d*₆) δ 254.2 (μ-CO); 220.9 (C_z) 209.9 (CO); 208.9 (C_γ); 164.1 (C_{ipso Ph}); 136.1, 126.0–117.6 (C_{arom}); 91.5, 88.9 (Cp); 58.3 (C_β); 48.9, 45.4 (NMe); 48.7 (CH₂Cl); 40.2 (C_zMe).

4.8. Synthesis of [Fe₂{μ-η¹:η³-C_γ(R')=C_β(E)C_z=N(Me)(R)}(μ-CO)(CO)(Cp)₂][BPh₄]₂ [R = Xyl, R' = CH₂OH, E = S, **9a; R = Xyl, R' = Me, E = S, **9b**; R = Xyl, R' = Buⁿ, E = S, **9c**; R = Xyl, R' = Me, E = Se, **9d**; R = Me, R' = Buⁿ, E = Se, **9e**]**

Complex **2b** (70 mg, 0.132 mmol), was dissolved in MeOH (10 mL), then NaBPh₄ (150 mg, 0.438 mmol) and I₂ (17 mg, 0.068 mmol) were added. The mixture, which turned immediately orange, was stirred for 60 min. Then, the solvent was removed under vacuum and the residue was filtered on a celite pad with CH₂Cl₂ (15 mL) as eluent. **9a** was obtained as a brown solid upon removal of the solvent. Yield: 101 mg, 90%. Anal. Calc. for C₉₈H₉₀B₂Fe₄N₂O₆S₂: C, 69.20; H, 5.33; N, 1.65. Found: C, 69.22; H, 5.25; N, 1.58%. IR (CH₂Cl₂): ν(CO) 2008 (vs), 1829 (s), ν(CN) 1619 (w) cm⁻¹. ¹H NMR (CD₃CN) δ 7.83–6.88 (46H, Me₂C₆H₃ and BPh₄); 6.05, 6.02 (m, 4H, ²J_{HH} = 11.1 Hz, CH₂OH); 5.63, 4.82 (s, 20H, Cp); 5.55 (m, 2H, OH); 3.88 (s, 6H, NMe); 2.61, 2.15 (s, 12H, Me₂C₆H₃). ¹³C{¹H} NMR (CD₃CN) δ 251.2 (μ-CO); 227.6 (C_z); 211.5 (CO); 210.9 (C_γ); 164.1 (C_{ipso BPh₄}); 142.3 (C_{ipso Xyl}); 136.1–131.2 (Me₂C₆H₃); 93.4, 90.3 (Cp); 74.9 (CH₂OH); 68.6 (C_β); 55.5 (NMe); 19.5, 19.3 (Me₂C₆H₃).

Complexes **9b–e** were obtained by the same procedure described for **9a**, by reacting I₂/NaBPh₄ with **2b–d** and **3b–c**, respectively. Crystals of **9e** suitable for X-ray analysis were obtained by an acetone solution, layered with diethyl ether, at room temperature.

9b (yield: 88%). Anal. Calc. for C₉₈H₉₀B₂Fe₄N₂O₄S₂: C, 70.53; H, 5.44; N, 1.68. Found: C, 70.49; H, 5.55; N, 1.62%. IR (CH₂Cl₂): ν(CO) 1996 (vs), 1833 (s), ν(CN) 1619 (w) cm⁻¹. ¹H NMR (CD₃CN) δ 7.83–6.88 (46H, Me₂C₆H₃ and BPh₄); 5.53, 4.72 (s, 20H, Cp); 4.19 (s, 6H, C_zMe); 3.74 (s, 6H, NMe); 2.54, 2.13 (s, 12H, Me₂C₆H₃). ¹³C{¹H} NMR (CD₃CN) δ 249.7 (μ-CO); 225.6 (C_z); 211.8 (CO); 210.6 (C_γ); 164.1 (C_{ipso BPh₄}); 140.7 (C_{ipso Xyl}); 137.7–117.6 (C_{arom}); 92.6, 89.0 (Cp); 64.5 (C_β); 52.9 (NMe); 39.4 (C_zMe); 17.8, 17.5 (Me₂C₆H₃).

9c (yield: 79%). Anal. Calc. for C₁₀₄H₁₀₂B₂Fe₄N₂O₄S₂: C, 71.25; H, 5.86; N, 1.60. Found: C, 71.33; H, 5.94; N, 1.51%. IR (CH₂Cl₂): ν(CO) 1989 (vs), 1835 (s), ν(CN) 1611 (w) cm⁻¹. ¹H NMR (CD₃CN) δ 7.84–6.99 (46H, Me₂C₆H₃ and BPh₄); 5.41, 4.83 (s, 20H, Cp); 3.95, 2.97 (m, 4H, C_zCH₂); 3.34 (s, 6H, NMe); 2.98 (m, 4H, C_zCH₂CH₂); 2.62, 2.07 (s, 12H, Me₂C₆H₃); 2.28 (m, 4H, C_zCH₂CH₂CH₂); 1.31 (m, 6H, C_zCH₂CH₂CH₂CH₂). ¹³C{¹H} NMR (CD₃CN) δ 249.6 (μ-CO); 225.7 (C_z); 210.8, 210.2 (CO and C_γ); 164.4 (C_{ipso BPh₄}); 140.4 (C_{ipso Xyl}); 135.2–126.8 (C_{arom}); 92.4, 89.4 (Cp); 64.8 (C_β); 50.9 (NMe); 18.2, 17.7 (Me₂C₆H₃); 52.3, 37.8, 23.7, 14.1 (Buⁿ).

9d (yield: 85%). Anal. Calc. for C₉₈H₉₀B₂Fe₄N₂O₄Se₂: C, 66.78; H, 5.15; N, 1.59. Found: C, 66.83; H, 5.19; N, 1.60%. IR (CH₂Cl₂): ν(CO) 1995 (vs), 1833 (s), ν(C_zN) 1620 (w) cm⁻¹. ¹H NMR (CD₃CN) δ 7.81–6.86 (46H, Me₂C₆H₃ and BPh₄); 5.53, 4.74 (s, 20H, Cp); 4.16 (s, 6H, C_zMe); 3.66 (s, 6H, NMe); 2.55, 2.12 (s, 12H, Me₂C₆H₃). ¹³C{¹H} NMR (CD₃CN) δ 250.1 (μ-CO); 224.7 (C_z); 210.9, 210.7 (CO and C_γ); 164.3 (C_{ipso BPh₄}); 140.6 (C_{ipso Xyl}); 136.0–117.6 (Me₂C₆H₃ and BPh₄); 92.5, 89.0 (Cp); 65.0 (C_β); 51.7 (NMe); 41.2 (C_zMe); 17.9, 17.8 (Me₂C₆H₃).

9e (yield: 75%). Anal. Calc. for C₉₀H₉₀B₂Fe₄N₂O₄Se₂: C, 64.86; H, 5.44; N, 1.68. Found: C, 64.93; H, 5.36; N, 1.60%. IR (CH₂Cl₂): ν(CO) 1994 (vs), 1819 (s), ν(C_zN) 1673 (m) cm⁻¹. ¹H NMR (CD₃CN) δ 7.30–6.86 (46H, Me₂C₆H₃ and BPh₄); 5.36, 5.10 (s, 20H, Cp); 4.21 (m, 4H, C_zCH₂); 3.83, 3.21 (s, 12H, NMe); 2.18, 1.78 (m, 8H, C_zCH₂CH₂CH₂); 1.20 (m, 6H, C_zCH₂CH₂CH₂CH₂). ¹³C{¹H} NMR (CD₃CN) δ 253.6 (μ-CO); 220.8 (C_z); 214.5 (C_γ); 210.0 (CO); 164.1 (C_{ipso BPh₄}); 136.0–117.6 (BPh₄); 91.6, 89.0 (Cp); 68.0 (C_β); 50.6, 45.4 (NMe); 53.8, 37.6, 23.6, 13.8 (Buⁿ).

4.9. X-ray crystallography for **4a** · H₂O, **8c** and **9e** · CH₃CN

Crystal data and collection details for **4a** · H₂O, **8c** and **9e** · CH₃CN are reported in Table 4. The diffraction experiments

were carried out on a Bruker Apex II diffractometer (for **4a** · **H₂O**, **8c**) and on a Bruker SMART 2000 diffractometer (for **9e** · **CH₃CN**) equipped with a CCD detector using Mo K α radiation. Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction *SADABS*) [25]. Structures were solved by direct methods and refined by full-matrix least-squares based on all data using *F²* [26]. Non-H atoms were refined anisotropically, unless otherwise stated. H-atoms were placed in calculated positions, except H(1S) in **4a** · **H₂O** which was located in the Fourier map; conversely, it has not been possible to locate the H-atoms for the water molecule. H-atoms were treated isotropically using the 1.2-fold *U_{iso}* value of the parent atom except methyl protons, which were assigned the 1.5-fold *U_{iso}* value of the parent C-atom. The Cp ligand bound to Fe(2) in **8c** is disordered. Disordered atomic positions were split and refined using one occupancy parameter per disordered group. The crystal structure of **8e** · **CH₃CN** displays some disorder, especially the moiety containing Fe(3) and Fe(4), where also the two metal atoms are split into two positions. Moreover, also the ⁿBu group bound to C(13), the two Me-groups bound to N(2) and the Cp bound to Fe(4) are disordered and have been split into two positions. For each of these disordered groups an independent occupancy parameter has been employed during refinement.

Acknowledgements

We thank the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (M.U.R.) (project: 'New strategies for the control of reactions: interactions of molecular fragments with metallic sites in unconventional species') and the University of Bologna for financial support.

Appendix A. Supplementary material

CCDC 681321, 681319, and 681320 contain the supplementary crystallographic data for **4a**, **8c**, and **9e**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.04.010.

References

- [1] (a) V. Rittleng, M.J. Chetcuti, *Chem. Rev.* 107 (2007) 797; (b) M. Cowie, *Can. J. Chem.* 83 (2005) 1043; (c) S.A.R. Knox, *J. Organomet. Chem.* 400 (1990) 255.
- [2] (a) V.G. Albano, L. Busetto, F. Marchetti, M. Monari, S. Zacchini, V. Zanotti, *Organometallics* 22 (2003) 1326; (b) V.G. Albano, L. Busetto, F. Marchetti, M. Monari, S. Zacchini, V. Zanotti, *J. Organomet. Chem.* 689 (2004) 528.
- [3] (a) L. Busetto, F. Marchetti, S. Zacchini, V. Zanotti, *Eur. J. Inorg. Chem.* (2007) 1799; (b) V.G. Albano, L. Busetto, F. Marchetti, M. Monari, S. Zacchini, V. Zanotti, *J. Organomet. Chem.* 691 (2006) 4234; (c) V.G. Albano, L. Busetto, F. Marchetti, M. Monari, S. Zacchini, V. Zanotti, *Organometallics* 23 (2004) 3348.
- [4] (a) A. Erkkilä, I. Majander, P.M. Pihko, *Chem. Rev.* 107 (2007) 5416; (b) S. Mukherjee, J.W. Yang, S. Hoffmann, B. List, *Chem. Rev.* 107 (2007) 5471.
- [5] L. Busetto, F. Marchetti, S. Zacchini, V. Zanotti, *Organometallics* 26 (2007) 3577.
- [6] L. Busetto, F. Marchetti, S. Zacchini, V. Zanotti, *Organometallics* 25 (2006) 4808.
- [7] R. Chauvin, *Eur. J. Inorg. Chem.* (2000) 577.
- [8] (a) J. Cipot, R. McDonald, M. Stradiotto, *Chem. Commun.* (2005) 4932; (b) R.J. Lundgren, M.A. Rankin, R. McDonald, G. Schatte, M. Stradiotto, *Angew. Chem., Int. Ed.* 46 (2007) 4732.
- [9] X.-W. Wang, L. Han, T.-J. Cai, Y.-Q. Zheng, J.-Z. Chen, Q. Deng, *Cryst. Growth Des.* 7 (2007) 1027.
- [10] H. Lee, D.B. Kim, S.-H. Kim, H.S. Kim, S.J. Kim, D.K. Choi, Y.S. Kang, J. Won, *Angew. Chem., Int. Ed.* 43 (2004) 3053.
- [11] (a) M. Rosenblum, A. Bucheister, T.C.T. Chang, M. Cohen, M. Marsi, S.B. Samuels, D. Scheck, N. Sofen, J.C. Watkins, *Pure Appl. Chem.* 56 (1984) 129; (b) D.L. Reger, C. Coleman, *J. Organomet. Chem.* 131 (1977) 153.
- [12] (a) L. Busetto, M. Monari, A. Palazzi, V.G. Albano, F. Demartin, *J. Chem. Soc., Dalton Trans.* (1983) 1849; (b) A. Mayr, H. Stolzenberg, W.P. Fehlhammer, *J. Organomet. Chem.* 338 (1988) 223; (c) M.E. Giuseppetti-Dery, B.E. Landrum, J.L. Shibley, A.R. Cutler, *J. Organomet. Chem.* 378 (1989) 421.
- [13] (a) see for example K.T.K. Chan, L.P. Spencer, J.D. Masuda, J.S.J. McCahill, P. Wei, D.W. Stephan, *Organometallics* 23 (2004) 381; (b) M. Oliván, K.G. Caulton, *Chem. Commun.* (1997) 1733; (c) C. Tejel, M.A. Ciriano, L.A. Oro, A. Tiripicchio, F. Uguzzoli, *Organometallics* 20 (2001) 1676.
- [14] A.W. Maverick, M.L. Ivie, F.R. Fronczek, *J. Coord. Chem.* 21 (1990) 315.
- [15] Q. Wang, A.C. Marr, A.J. Blake, C. Wilson, M. Schroeder, *Chem. Commun.* (2003) 2776.
- [16] A. Marsh, D.M. Ferguson, *Proteins* 28 (1997) 217.
- [17] (a) P.M. Dickinson, A.D. McGowan, B. Yearwood, M.J. Heeg, J.P. Oliver, *J. Organomet. Chem.* 588 (1999) 42; (b) S. Hartmann, R.F. Winter, T. Scheiring, M. Wanner, *J. Organomet. Chem.* 637–639 (2001) 240; (c) S. Kumar, S.K. Tripathi, H.B. Singh, G. Wolmershauser, *J. Organomet. Chem.* 689 (2004) 3046; (d) K.K. Bhasin, N. Singh, R. Kumar, D.G. Deepali, S.K. Metha, T.M. Klapoetke, M.-J. Crawford, *J. Organomet. Chem.* 689 (2004) 3327.
- [18] (a) E.I. Stiefel, K. Matsumoto (Eds.), *Transition Metal Sulfur Chemistry: Biological and Industrial Significance*, ACS Symposium Series No. 653; Am. Chem. Soc., Washington, DC, 1996; (b) T. Weber, R. Prins, R.A. van Santen (Eds.), *Transition Metal Sulphides: Chemistry and Catalysis*, NATO ASI Series, vol. 60, Kluwer Academic Publishers, Dordrecht, 1998; (c) E.I. Stiefel, D. Coucouvanis, W.E. Newton (Eds.), *Molybdenum Enzymes, Cofactors, and Model Systems*, ACS Symposium Series No. 535, Am. Chem. Soc., Washington, DC, 1993.
- [19] (a) A. Saxena, A. Kumar, S. Mozumdar, *J. Mol. Catal. A* 269 (2007) 35. and refs. therein; (b) F. Hosseinpoor, H. Golchoubian, *Catal. Lett.* 111 (2006) 165.
- [20] (a) C.G. Kuehn, H. Taube, *J. Am. Chem. Soc.* 98 (1976) 689; (b) R.C. Elder, M. Trkula, *Inorg. Chem.* 16 (1977) 1048; (c) J. Amarasekera, T.B. Rauchfuss, S.R. Wilson, *Inorg. Chem.* 28 (1989) 3875; (d) D. Sellmann, P. Lechner, F. Knoch, M. Moll, *J. Am. Chem. Soc.* 114 (1992) 922; (e) A. Coto, M.J. Tenorio, M.C. Puerta, P. Valerga, *Organometallics* 17 (1998) 4392.
- [21] T. Kochi, Y. Tanabe, Z. Tang, Y. Ishii, M. Hidai, *Chem. Lett.* 12 (1999) 1279.
- [22] R.Y.C. Shin, M.E. Teo, W.K. Leong, J.J. Vittal, J.H.K. Yip, L.Y. Goh, R.D. Webster, *Organometallics* 24 (2005) 1483.
- [23] W. Wilker, D. Leibfritz, R. Kerssebaum, W. Beimel, *Magn. Reson. Chem.* 31 (1993) 287.
- [24] K. Stott, J. Stonehouse, J. Keeler, T.L. Hwang, A.J. Shaka, *J. Am. Chem. Soc.* 117 (1995) 4199.
- [25] G.M. Sheldrick, *SADABS*, Program for Empirical Absorption Correction, University of Göttingen, Germany, 1996.
- [26] G.M. Sheldrick, *SHELX97*, Program for Crystal Structure Determination, University of Göttingen, Germany, 1997.