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C–H Activation in Diiron Bridging Vinyliminium Ligands: Reaction with CS_2 to Form New Zwitterionic Complexes Acting as Organometallic Ligands

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The reactions of vinyliminium complexes $[Fe_2\{\mu\text{-}\eta^1:\eta^3\text{-}C(R')=C(H)C=N(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (R = Xyl, R′ = Me, **1a**; R = Xyl, R′ = Tol, **1b**; R = Xyl, R′ = COOMe, **1c**; R = Me, R′ = Me, **1d**; R = Me, R′ = *n*Bu, **1e**; R = *p*-$MeOC_6H_4$, R′ = Me, **1f**; Tol = 4-C_6H_4Me, Xyl = 2,6-$Me_2C_6H_3$) with CS_2 and NaH resulted in the replacement of CH hydrogen (in the bridging frame) with CS_2 to give the corresponding dithiocarboxylate-vinyliminium complexes $[Fe_2\{\mu\text{-}\eta^1:\eta^3\text{-}C(R')=C(CS_2)C=N(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (**2a**–**2f**). Analogously, **1a** and **1d** reacted with NaH and SCNPh to afford the complexes $[Fe_2\{\mu\text{-}\eta^1:\eta^3\text{-}C(R')=C\{C(NPh)S\}C=N(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (R = Xyl, R′ = Me, **3a**; R = Me, R′ = Me, **3b**), respectively. Complex **2b** was methylated at the dithiocarboxylate group upon treatment with $CH_3SO_3CF_3$ to yield $[Fe_2\{\mu\text{-}\eta^1:\eta^3\text{-}C(R')=C(CS_2Me)C=N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (**4a**). Likewise, the zwitterionic complexes **2d**–**f** underwent addition of the metal fragment $[Fe(CO)_2Cp]^+$ at the dithiocarboxylate group to yield the corresponding triiron complexes $[Fe_2\{\mu\text{-}\eta^1:\eta^3\text{-}C(R')=C(CS_2Fp)C=N(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ [R = R′ = Me, **4b**; R = Me, R′ = *n*Bu, **4c**; R = *p*-$MeOC_6H_4$, R′ = Me, **4d**; Fp = $Fe(CO)_2Cp$]. In a related reaction with $[Pd(CH_3CN)_2Cl_2]$, **2a** binded to Pd through the dithiocarboxylate group as chelating ligand to afford the complex $[PdCl_2\{\kappa^2\text{-}(S,S)\text{-}\mathbf{2a}\}]$ (**5**). The X-ray structures of **2b**, **3a** and **4d** have been determined.

Introduction

Organic molecules acting as bridging ligands are expected to exhibit reaction patterns different to those observed when the same species are uncoordinated or are bound to a single metal centre.[1] An example is offered by the chemistry of the bridging vinyliminium diiron complexes **I** (Scheme 1).[2] Indeed, bridging vinyliminium ligands undergo nucleophilic addition at the iminium carbon or the adjacent α-carbon position[3] instead of the 1,4-conjugated addition normally observed in α,β-unsaturated iminium species.[4] Another unique feature of μ-vinyliminium ligands is the activation of α-C–H (C^2–H in Scheme 1), which does not occur in uncoordinated conjugated iminium species.[5] The deprotonation of μ-vinyliminium ligands has been exploited to introduce a variety of substituents and functionalities into the bridging frame, as shown in Scheme 1. The carbon atoms in the bridging chain have been numbered as shown in Scheme 1 to make clearer the discussions presented hereafter.

We previously suggested that the deprotonated intermediate is better described by two limiting formulae (**II** and **III**) in which the C^2 carbon can assume carbanionic or carbenoid character, respectively.[5] The double nature of the intermediate has been exploited to generate new single and double bonds. Examples of both possibilities are shown in Scheme 1: reactions with aryl isocyanides (CNR)[6] or diazoacetates[7] lead to bis-alkylidene complexes (**V** and **VII**, respectively) bearing a double bond at C^2. On the other hand, intermediates can be oxidized by treatment with S_8[8] or PhSSPh[9] to afford vinyliminium complexes (**VI** and **IV**, respectively) with a C^2–S single bond.

In the light of these results and with the aim of finding new possibilities for forming C–C bonds at the bridging frame, we have extended our investigations to C–H activation in the presence of heteroallenes (CS_2, CSNR). In fact, simple triatomic molecules are considered with growing interest as potential building blocks for the construction of more complex molecular architectures.[10] Moreover, CS_2 and other heteroallenes are known to be reactive towards diiron complexes under appropriate conditions, leading to the fragmentation and incorporation of the heteroallenes in the metal–ligand framework. Examples include the reactions with $[Fe_2(CO)_9]$,[11] $[Fe_2(\mu\text{-}RCCNEt_2)(CO)_7]$,[12] $[Fe_2(\mu\text{-}CO)(\mu\text{-}dppm)(CO)_6]$,[13] $[Fe_2(\mu\text{-}SR)_3Cp_2]$,[14] $[Fe_2(\mu\text{-}SR)(\mu\text{-}CO)(CO)_6]^-$ and related species,[15] which provide effective routes for the transformation of these small molecules.

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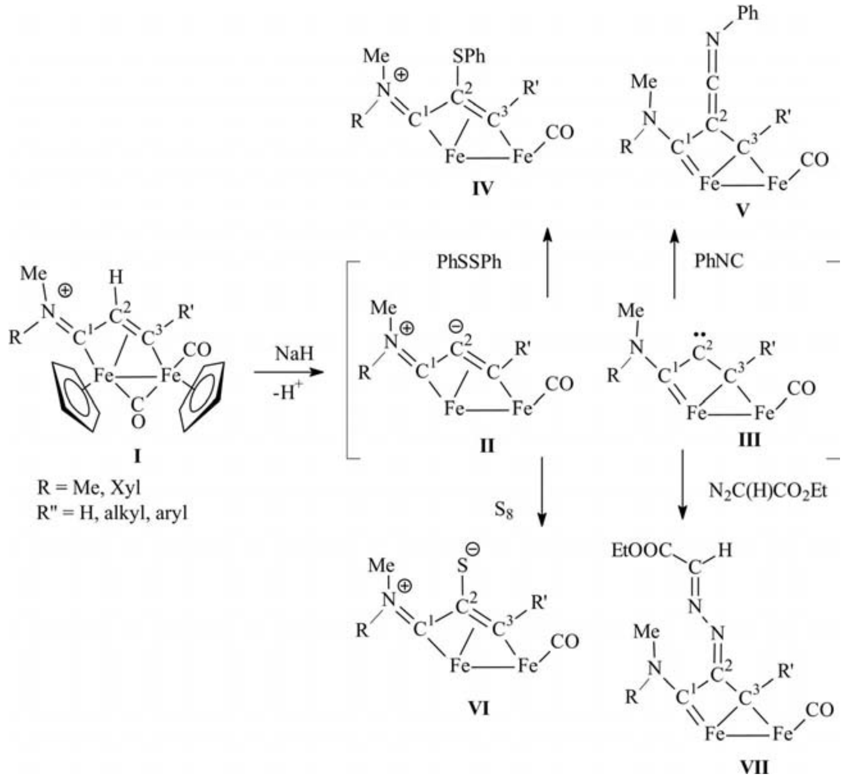
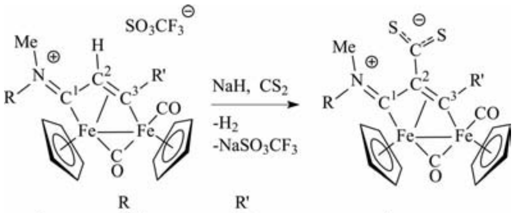


Scheme 1.

Results and Discussion

Reactions of Vinyliminium Complexes with Heteroallenes (CS_2 and SNCPh)

Treatment of vinyliminium complexes **1a**–**f** with NaH in the presence of an excess of CS_2 resulted in the formation of the corresponding zwitterionic complexes $[Fe_2\{\mu\text{-}\eta^1:\eta^3\text{-}C(R')=C(CS_2)C=N(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (**2a**–**f**) in 70–90% yields (Scheme 2).



	R	R'	
1a	Xyl	Me	**2a**
1b	Xyl	Tol	**2b**
1c	Xyl	CO_2Me	**2c**
1d	Me	Me	**2d**
1e	Me	*n*Bu	**2e**
1f	*p*-MeO-C_6H_4	Me	**2f**

Scheme 2.

Compounds **2a**–**f** were purified by chromatography and characterized by spectroscopy and elemental analysis. Moreover, the molecular structure of **2b** was determined by X-ray diffraction studies: the ORTEP molecular diagram is shown in Figure 1 and selected bond lengths and angles are reported in Table 1. The molecule comprises a *cis*-$Fe_2(\mu\text{-}CO)(CO)(Cp)_2$ core coordinated to a $\mu\text{-}\eta^1:\eta^3\text{-}C(R')=C(CS_2)C=N(Me)(R)$ ligand. The latter possesses zwitterionic character being composed of a bridging cationic vinyliminium ligand with an anionic dithiocarboxylate substituent (CS_2^-) at the C^2 position. In agreement with this, all the bonding parameters of the bridging ligand perfectly parallel those previously reported for cationic vinyliminium complexes;[16] the ligand adopts a *Z* configuration with respect to the C(15)–N(1) bond (corresponding to C^1–N in Scheme 2). Moreover, the C(14)–C(16) interaction [1.522(4) Å] (corresponding to C^2–CS_2 in Scheme 2) is typi-

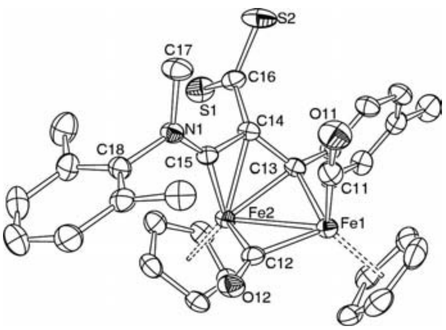


Figure 1. Molecular structure of $[Fe_2\{\mu\text{-}\eta^1:\eta^3\text{-}C(Tol)=C(CS_2)\text{-}C=N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (**2b**) with key atoms labelled (all hydrogen have been omitted for clarity). Thermal ellipsoids are drawn at the 30% probability level.

cal of a single C–C bond and confirms the complete charge separation within the bridging ligand in the presence of the anionic CS_2^- group. The C(16) atom displays perfect sp^2 hybridisation [sum of angles 359.9(4)°] and the C(16)–S(1) and C(16)–S(2) interactions are identical within experimental error [1.660(4) and 1.666(4) Å, respectively], which indicates the delocalization of the negative charge over the three atoms; the C–S bond lengths agree perfectly with those reported for other free dithiocarboxylate groups.[17]

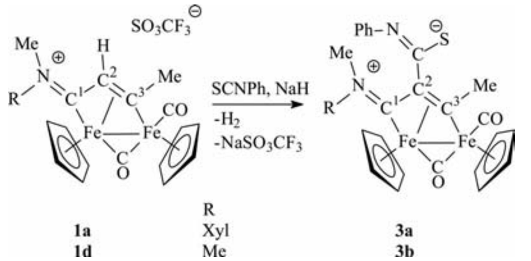
Table 1. Selected bond lengths [Å] and angles [°] for **2b**.

Fe(1)–Fe(2)	2.5546(9)	C(11)–O(11)	1.147(4)
Fe(1)–C(11)	1.757(4)	C(12)–O(12)	1.179(4)
Fe(1)–C(12)	1.889(3)	C(13)–C(14)	1.417(4)
Fe(2)–C(12)	1.946(3)	C(14)–C(15)	1.438(4)
Fe(1)–C(13)	1.969(3)	C(15)–N(1)	1.293(4)
Fe(2)–C(13)	2.038(3)	C(14)–C(16)	1.522(4)
Fe(2)–C(14)	2.119(3)	C(16)–S(1)	1.660(4)
Fe(2)–C(15)	1.862(3)	C(16)–S(2)	1.666(4)
Fe(1)–C(13)–Fe(2)	79.20(11)	C(15)–N(1)–C(17)	120.6(3)
Fe(1)–C(13)–C(14)	122.2(2)	C(17)–N(1)–C(18)	114.6(3)
C(13)–C(14)–C(15)	114.9(3)	C(14)–C(16)–S(1)	119.9(3)
C(14)–C(15)–N(1)	133.5(3)	C(14)–C(16)–S(2)	112.6(2)
C(15)–N(1)–C(17)	124.8(3)	S(1)–C(16)–S(2)	127.4(2)

The IR spectra (in CH_2Cl_2 solution) show the usual pattern exhibited by cationic disubstituted diiron vinyliminium complexes: two νCO bands arise from terminal and bridging carbonyls (e.g., for **2a** at 1984 and 1806 cm^{-1}, respectively), whereas a medium intensity absorption at around 1610 cm^{-1} accounts for the iminium group. In addition, absorptions associated with the dithiocarboxylate group were found at around 1090 cm^{-1}.

The vinyliminium complexes **2**, except for **2d** and **2e**, display two non-equivalent N substituents. Therefore they can exist in two isomeric forms (*Z* and *E* isomers) due to the orientation that the substituents can assume with respect to the C=N bond. In general, vinyliminium complexes in which the C^2–H hydrogen has been replaced by other atoms or groups assume the *Z* configuration.[8,9] This is also the case for complexes **2**: ^1H NMR spectra and NOE investigations indicate that **2a**–**c** in solution adopt the *Z* configuration, which was also found in the solid of **2b**. Compound **2f** is an exception in that it consists as an isomeric mixture (*Z* and *E*, in about a 5:1 ratio). The most significant features in the ^{13}C NMR spectra of **2a**–**f** include the resonance due to the CS_2 fragment, which falls in the range reported for dithiocarboxylate carbons (e.g., at δ = 244.4 ppm for **2a**),[3] and the resonances attributable to C^1, C^2 and C^3 (e.g., for **2a** at 225.9, 87.3 and 198.6 ppm, respectively), which are consistent with the values typical of vinyliminium ligands.[16]

Studies have been extended to other heteroallenes. Unfortunately, CO_2 proved to be unreactive: solutions of the vinyliminium complexes under CO_2 upon treatment with NaH failed to produce complexes analogous to **2**. Conversely, reactions with SCNPh under the same conditions used for the reaction with CS_2 afforded in good yields the complexes **3a**,**b**, which are analogous to **2a**–**f** (Scheme 3).



Scheme 3.

Complexes **3a**,**b** were characterized by IR and NMR spectroscopy and elemental analysis. Furthermore, the X-ray structure of **3a** was determined: the ORTEP molecular diagram is shown in Figure 2 and selected bond lengths and angles are reported in Table 2.

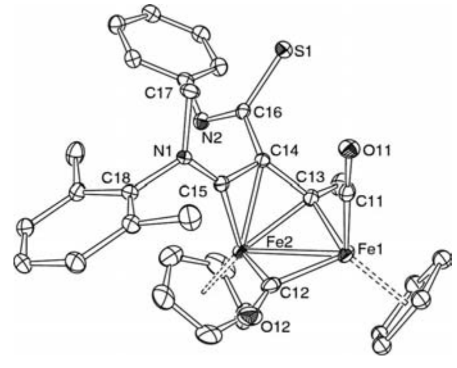


Figure 2. Molecular structure of **3a** with key atoms labelled (all hydrogen have been omitted for clarity). Thermal ellipsoids are drawn at the 30% probability level. Only the main image of the disordered Cp bound to Fe(1) is drawn.

Table 2. Selected bond lengths [Å] and angles [°] for **3a**.

Fe(1)–Fe(2)	2.5565(8)	C(11)–O(11)	1.147(4)
Fe(1)–C(11)	1.762(4)	C(12)–O(12)	1.180(5)
Fe(1)–C(12)	1.897(4)	C(13)–C(14)	1.431(5)
Fe(2)–C(12)	1.941(4)	C(14)–C(15)	1.421(5)
Fe(1)–C(13)	1.959(4)	C(15)–N(1)	1.308(4)
Fe(2)–C(13)	2.026(4)	C(14)–C(16)	1.512(5)
Fe(2)–C(14)	2.095(3)	C(16)–S(1)	1.722(4)
Fe(2)–C(15)	1.848(3)	C(16)–S(2)	1.287(5)
Fe(1)–C(13)–Fe(2)	79.81(14)	C(15)–N(1)–C(17)	120.2(3)
Fe(1)–C(13)–C(14)	120.4(3)	C(17)–N(1)–C(18)	116.4(3)
C(13)–C(14)–C(15)	115.5(3)	C(14)–C(16)–S(1)	111.4(2)
C(14)–C(15)–N(1)	132.9(3)	C(14)–C(16)–S(2)	117.5(3)
C(15)–N(1)–C(17)	123.3(3)	S(1)–C(16)–S(2)	131.1(3)

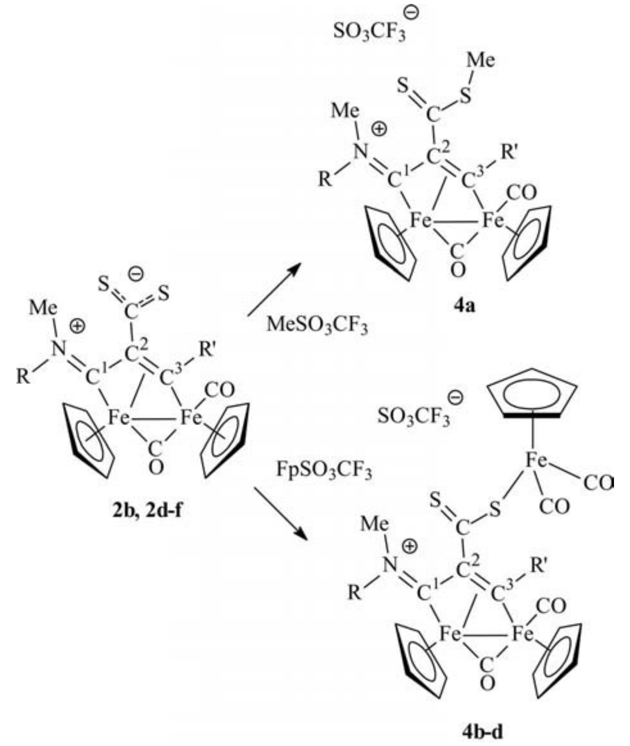
The molecular structure of **3a** is very similar to that of **2b** except for the presence of a C(NPh)S^- group in place of CS_2^-. Also in this case, the molecule displays zwitterionic character and can be described as a cationic vinyliminium complex that possesses a *Z* configuration and bears an anionic C(NPh)S^- substituent. Charge separation is almost complete with the C(14)–C(16) interaction [corresponding to C^2–C(NPh)S in Scheme 3] having a length of 1.512(5) Å, which is characteristic of a single bond. Compared with the C(NPh)S^- group, the C(16)–N(2) interaction with 1.287(5) Å is basically a double bond whereas C(16)–S(1) with 1.722(4) Å is a single bond. Thus, the negative charge is almost completely localised on the sulfur atom and thus the group is better described as an iminothiolate rather than thioamidyl.

The spectroscopic data for **3a**,**b** are similar to those discussed for **2a**–**f**. The IR spectra (in CH_2Cl_2 solution) exhibit two νCO absorptions arising from terminal and bridging carbonyls (e.g., for **3b** at 1984 and 1793 cm^{-1}, respectively). ^1H NMR spectra exhibit one single set of resonances and NOE investigations indicate that **3a** adopts the same *Z* configuration as found in the solid state. The ^{13}C NMR spectroscopic data include resonances attributable to the C^1 carbon (e.g., for **3b** at $\delta = 225.6$ ppm) and to the carbon of the SCNPh function (at about $\delta = 150$ ppm).

The reactions shown in Schemes 2 and 3 deserve further comment. First, the overall result equates to the replacement of the α-C–H hydrogen with CS_2 or PhNCS. Thus, the reactions provide a further interesting approach to the functionalization of the bridging vinyliminium at the C^2 position (α-functionalization) that takes advantage of the electrophilic character of heteroallenes. Secondly, the complexes formed are zwitterionic species. The peculiar character of complexes **2** and **3** results from the fact that both charges are formally located on the bridging ligand: the positive charge on the iminium moiety and the negative charge on the CS_2 or PhNCS group. This is unusual as zwitterionic complexes generally display a positive or negative charge on the metal centre.[18] A further atypical aspect is the way in which the heteroallenes have been incorporated into the bridging frame. Indeed, CS_2 and SCNPh frequently react with metal complexes undergoing insertion reactions into metal–heteroatom bonds. Examples are numerous and include insertion into M–O and M–N,[19] M–S,[20] M–H,[21] M–C[22] and M–M bonds in early-late heterodinuclear transition-metal complexes and bonds.[23] The reactions of CS_2 and SNCPh with M=N (double bond)[24] and M=C (metal–carbene interaction)[25] have also been reported. In all cases, the new ligands generated by insertion and rearrangement of XCS (X = S, NPh) are invariably coordinated to the metal centre through S (or N) atoms, more frequently as S,S- or S,N-chelating ligands. Conversely, the incorporation of CS_2 and SCNPh into the bridging vinyliminium ligand takes place without any coordination of the anionic function (CS_2^-, $PhNCS^-$) to iron. For example, in **2a**–**f** the bridging zwitterionic ligand is bound through the C atoms of the bridging chain and not through the S atoms of the dithiocarboxylate. As a consequence, the bridging ligands in **2** and **3** maintain the potential provided by these non-coordinated functions, as illustrated in the next section.

Addition of Metal Fragments and Electrophilic Species to the Zwitterionic Thiocarboxylate-Vinyliminium Complexes

Complexes **2** and **3** exhibit charge separation on the bridging frame and thus feature sites potentially able to bind a metal cation. In particular, complexes **2** are similar to the zwitterionic complexes **VI** (Scheme 1) in that they show negatively charged S functions. Because complexes **VI** have been demonstrated to act as "organometallic ligands"[26] and to promote the 1,3-dipolar cycloaddition of alkynes to the bridging frame,[27] similar behaviour can be reasonably expected for complexes **2**. To establish whether dithiocarboxylate vinyliminium ligands are really able to bind metal fragments or undergo electrophilic addition, the reactions of complexes **2b** and **2d**–**f** with $[Fe(CO)_2Cp][SO_3CF_3]$ ($FpSO_3CF_3$) and with a methylating agent ($MeSO_3CF_3$) were investigated (Scheme 4).



	R	R'	
2b	Xyl	Tol	**4a**
2d	Me	Me	**4b**
2e	Me	*n*Bu	**4c**
2f	*p*-MeO-C_6H_4	Me	**4d**

Scheme 4.

The cationic complex $[Fe(CO)_2Cp]^+$ (Fp^+) was used as an organometallic electrophile because of its known capacity to bind sulfur ligands. For example, it is known that the metallodithiocarboxylate $[Fe(CO)_2(Cp)(CS_2)]^-$ reacts with Fp^+ to form $[Fe(CO)_2(Cp)C(S)SFe(CO)_2Cp]$.[28]

The vinyliminium complexes **4a**–**d** were characterized by spectroscopy. In addition, the X-ray structure of **4d** was determined: the ORTEP molecular diagram is shown in Figure 3 (both the *Z* and *E* isomers are represented) and selected bond lengths and angles are reported in Table 3. The molecular structure of **4d** can be thought to derive from that of **2b** (from which it differs by one substituent at the iminium nitrogen and for the substituent at C^3) upon coordination of the $Fe(CO)_2Cp$ group at S(1). The bridging ligand coordinated to $Fe_2(\mu\text{-}CO)(CO)(Cp)_2$ maintains the character of a μ-η^1:η^3-vinyliminium and, thus, all the bonding parameters resemble those reported for similar species in this paper and in previous publications.[16] Both the *Z* and *E* isomers, with respect to the configuration at the iminium nitrogen, are present within the crystal in a 0.59:0.41 ratio due to disorder in the orientation of the substituents of the N(Me)(*p*-MeOC$_6$H$_4$) group. Also, the parent compound **2f** is present in solution as a mixture of the two isomers and this is probably due to the fact that the *p*-MeOC$_6$H$_4$ group is less sterically demanding than Xyl.

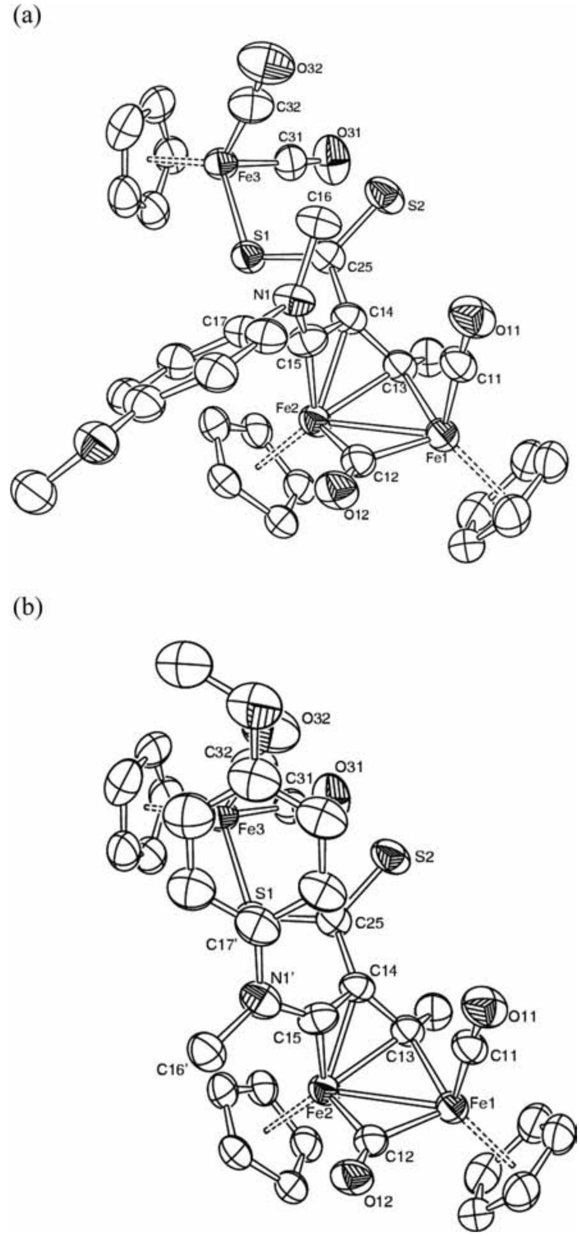


Figure 3. Molecular structure of **4d** with key atoms labelled (all hydrogen have been omitted for clarity). Thermal ellipsoids are drawn at the 30% probability level. Only the main image of the disordered Cp bound to Fe(2) is drawn. (a) *Z* isomer and (b) *E* isomer.

Table 3. Selected bond lengths [Å] and angles [°] for **4d**.

Fe(1)–Fe(2)	2.5442(13)	C(11)–O(11)	1.135(8)
Fe(1)–C(11)	1.754(8)	C(12)–O(12)	1.158(7)
Fe(1)–C(12)	1.877(7)	C(13)–C(14)	1.423(9)
Fe(2)–C(12)	1.969(6)	C(14)–C(15)	1.418(9)
Fe(1)–C(13)	1.979(6)	C(15)–N(1)	1.357(10)
Fe(2)–C(13)	2.026(6)	C(15)–N(1′)	1.372(13)
Fe(2)–C(14)	2.071(6)	C(14)–C(25)	1.506(8)
Fe(2)–C(15)	1.826(7)	C(25)–S(1)	1.676(7)
Fe(3)–S(1)	2.2376(18)	C(25)–S(2)	1.661(6)
Fe(3)–C(31)	1.752(8)	C(31)–O(31)	1.135(9)
Fe(3)–C(32)	1.793(11)	C(32)–O(32)	1.110(10)
Fe(1)–C(13)–Fe(2)	78.9(2)	C(15′)–N(1′)–C(16′)	126.4(13)
Fe(1)–C(13)–C(14)	119.6(4)	C(15′)–N(1′)–C(17′)	117.6(10)
C(13)–C(14)–C(15)	114.9(5)	C(16′)–N(1′)–C(17′)	114.5(13)
C(14)–C(15)–N(1)	124.8(7)	C(14)–C(25)–S(1)	115.8(4)
C(14)–C(15)–N(1′)	137.2(8)	C(14)–C(25)–S(2)	115.9(5)
C(15)–N(1)–C(16)	126.9(9)	S(1)–C(25)–S(2)	128.0(4)
C(15)–N(1)–C(17)	117.1(7)	C(25)–S(1)–Fe(3)	113.5(2)
C(16)–N(1)–C(17)	115.8(8)	C(31)–Fe(3)–C(32)	95.2(4)

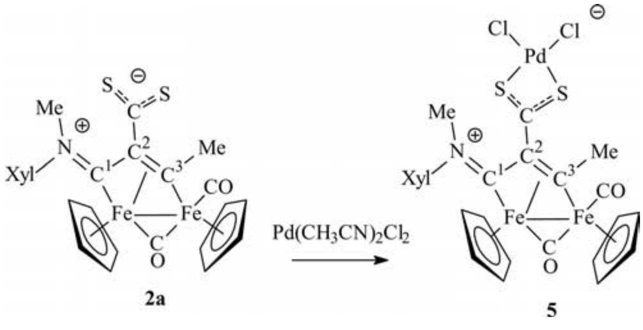
The Fe(3) atom adopts the well-known piano-stool coordination and is σ-bound to S(1) [Fe(3)–S(1) 2.2376(18) Å]. As a consequence, C(25)–S(1) is slightly elongated compared with C(25)–S(2) [1.676(7) and 1.661(6) Å, respectively]. C(25) shows almost pure sp^2 hybridisation [sum of angles 359.7(6)°], still indicating some delocalization within the dithiocarboxylate group, whereas C(14)–C(25) [1.506(8) Å] is an almost pure single bond, which confirms the lack of conjugation between the two moieties of the molecule.

The IR and NMR spectroscopic data for **4a**–**d** resemble those of the corresponding parent vinyliminium, which is consistent with structural evidence showing that electrophilic addition at the dithiocarboxylate does not significantly modify the coordination mode of the bridging vinyliminium ligand. Compared with the parent compounds, slight shifts in the νCO frequencies and in the NMR resonances are observed as a consequence of the fact that **4a**–**d** are cationic species, whereas their precursors are neutral compounds. The NMR spectra and NOE of **4a** and **4d** indicate the predominance of the *Z* isomer in solution.

The reaction with Fp$^+$ evidences the potential of the vinyliminium complexes as monodentate ligands, but the dithiocarboxylate function can also act as a chelating ligand. This was investigated by treating **2a** with [PdCl$_2$(CH$_3$CN)$_2$] in which the weakly coordinated acetonitrile ligands provide the equivalent of two adjacent vacant coordination sites. The results indicate that the zwitterionic vinyliminium complexes also act as chelating ligands through the dithiocarboxylate group to afford the trinuclear product [PdCl$_2${κ^2-(*S*,*S*)-**1a**}] (**5**) in about 90% yield (Scheme 5).

Complex **5** was characterized by spectroscopy and elemental analysis. The NMR spectra in acetone solution show only one set of resonances, which indicates the presence of a single isomer in solution. The coordination of Pd^{II} does not modify significantly the structure of the C$_3$ bridging ligand, which exhibits ^{13}C NMR resonances in the usual range (δ = 225.0, 85.6 and 200.6 ppm for C^1, C^2 and C^3, respectively) and similar to the values noted for the parent complex **2a**.

Complexes **4** and **5** display some distinct and interesting features. They can be classified as dithiocarboxylate metal complexes, which are far less common than dithiocarbam-



Scheme 5.

ate or xanthate complexes.[29] This is mainly the consequence of the relative difficulty of synthesizing dithiocarboxylate ligands. Another interesting aspect of **4** and **5** is the zwitterionic nature of the ligand, already outlined, which further restricts the number of dithiocarboxylate metal complexes that can be compared. Indeed, known zwitterionic dithiocarboxylate ligands include species such as imidazolium-dithiocarboxylates,[30] diethylaminocarbenium-dithiocarboxylates[31] and pyridinium-dithioacetate.[32] In particular, comparison with imidazolium-dithiocarboxylates is appropriate because of the fact that these zwitterionic ligands are formed by the addition of N-heterocyclic carbenes (NHC) to CS_2 in a way that resembles the formation of complexes **2**.[30a] In spite of these similarities, the nature of our zwitterionic dithiocarboxylate ligands remains distinctive in that they contain a diiron frame and thus they can be regarded as "organometallic ligands".[33]

Conclusions

Activation of the α-C–H hydrogen in diiron vinyliminium complexes can be exploited to promote the addition of electrophilic heteroallenes (CS_2, SCNPh). The reaction involves the replacement of the C–H hydrogen with CS_2 or SCNPh functionalities to yield unprecedented zwitterionic vinyliminium complexes. Complexes obtained by CS_2 addition exhibit a dithiocarboxylate group that can be used to bind metal fragments in both monodentate and chelating modes, the latter leading to complexes featuring unprecedented examples of organometallic zwitterionic dithiocarboxylate ligands.

Experimental Section

General: All reactions were routinely carried out under nitrogen using standard Schlenk techniques. Solvents were distilled immediately before use under nitrogen from appropriate drying agents. Chromatographic 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 with a Perkin–Elmer Spectrum 2000 FT-IR spectrophotometer and elemental analyses were performed with a ThermoQuest Flash 1112 Series EA Instrument. ESI-MS spectra were recorded with a Waters Micromass ZQ 4000 spectrometer with samples dissolved in CH_3CN. All NMR measurements were performed with a Mercury Plus 400 instrument. The ^1H and ^{13}C NMR chemical shifts are referenced to internal TMS. The spectra were fully assigned through DEPT experiments and $^1H,^{13}C$ correlation through gs-HSQC and gs-HMBC experiments. All NMR spectra were recorded at 298 K. NMR signals due to a second isomeric form (when it was possible to detect and/or resolve them) are italicized. NOE measurements were recorded by using the DPFGSE-NOE sequence. All the reagents were commercial products (Aldrich) of the highest purity available and used as received. Compounds **1a**, **1b**, **1d**,[16a] **1c**, **1e**[16b] and **1f**[7] were prepared according to literature methods.

Synthesis of [Fe_2{μ-η^1:η^3-C^3(R′)=C^2(CS_2)C^1=N(Me)(R)}(μ-CO)(CO)($Cp)_2$] (R = Xyl, R′ = Me, 2a; R = Xyl, R′ = Tol, 2b; R = Xyl, R′ = COOMe, 2c; R = Me, R′ = Me, 2d; R = Me, R′ = *n*Bu, 2e; R = *p*-MeOC_6H_4, R′ = Me, 2f): A THF solution (15 mL) of complex **1a** (100 mg, 0.158 mmol) was treated with CS_2 (0.20 mL, 3.32 mmol) and then with NaH (38 mg, 1.58 mmol). The mixture was stirred for 20 min and then it was filtered through alumina. Solvent removal and chromatography of the residue on alumina using THF as eluent afforded a dark-green band corresponding to **2a**, which was obtained as a green-brown solid upon solvent removal; yield 71 mg, 80%. IR (CH_2Cl_2): ṽ = 1984 (vs, CO), 1806 (s), 1606 (m, νCN) cm^{-1}. IR (KBr pellets): ṽ = 1094 (w, SCS) cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 7.38–7.17 (m, 3 H, $Me_2C_6H_3$), 5.13, *4.79* (s, 10 H, Cp), 3.90 (s, 3 H, C^3Me), 3.56 (s, 3 H, NMe), 2.63, 1.95 (s, 6 H, $Me_2C_6H_3$) ppm. ^{13}C NMR (CD_2Cl_2): δ = 257.6 (μ-CO), 244.4 (CS_2), 225.9 (C^1), 210.5 (CO), 198.6 (C^3), 142.4 ($C_{ipso\text{-}Xyl}$), 135.4, 134.2, 129.1, 128.9, 129.8 (C_{arom}), 90.4, 88.6 (Cp), 87.3 (C^2), 47.3 (NMe), 38.8 (C^3Me), 18.4, 18.2 ($Me_2C_6H_3$) ppm. MS (ES$^+$): *m*/z = 559. $C_{26}H_{25}Fe_2NO_2S_2$ (559.30): calcd. C 55.83, H 4.51, N 2.50; found C 55.87, H 4.44, N 2.46.

Compounds **2b**–**f** were prepared by following the same procedure as described for **2a** by reacting **1b** (120 mg), **1c** (100 mg), **1d** (95 mg), **1e** (110 mg) and **1f** (100 mg), respectively, with CS_2 and NaH. Crystals of **2b** suitable for X-ray analysis were collected from a CH_2Cl_2 solution layered with petroleum ether at –20 °C.

2b: Yield 95 mg, 79%. IR (CH_2Cl_2): ṽ = 1986 (vs, CO), 1806 (s), 1604 (m, νCN) cm^{-1}. IR (KBr pellets): ṽ = 1090 (w, SCS) cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 7.76–7.18 (m, 7 H, C_6H_4Me and $Me_2C_6H_3$), 4.95, *4.72* (s, 10 H, Cp), 3.71 (s, 3 H, NMe), 2.58, 1.99 (s, 6 H, $Me_2C_6H_3$), 2.40 (s, 3 H, C_6H_4Me) ppm. ^{13}C NMR (CD_2Cl_2): δ = 258.0 (μ-CO), 240.0 (CS_2), 225.0 (C^1), 211.3 (CO), 196.8 (C^3), 151.2 ($C_{ipso\text{-}Tol}$), 143.1 ($C_{ipso\text{-}Xyl}$), 136.3–125.8 (C_{arom}), 92.1, 89.2 (Cp), 87.4 (C^2), 48.4 (NMe), 21.3 (MeC_6H_4), 18.7, 18.6 ($Me_2C_6H_3$) ppm. $C_{32}H_{29}Fe_2NO_2S_2$ (635.40): calcd. C 60.49, H 4.60, N 2.20; found C 60.48, H 4.60, N 2.15.

2c: Yield 71 mg, 80%. IR (CH_2Cl_2): ṽ = 1994 (vs, CO), 1816 (s), 1711 (m), 1607 (m, νCN) cm^{-1}. IR (KBr pellets): ṽ = 1088 (w, SCS) cm^{-1}. ^1H NMR (CD_3CN): δ = 7.41–7.07 (m, 3 H, $Me_2C_6H_3$), 5.06, 4.84 (s, 10 H, Cp), 3.80 (s, 3 H, CO_2Me), 3.44 (s, 3 H, NMe), 2.53, 2.00 (s, 6 H, $Me_2C_6H_3$) ppm. ^{13}C NMR (CD_3CN): δ = 258.0 (μ-CO), 241.0 (CS_2), 225.3 (C^1), 210.6 (CO), 198.9 (C^3), 178.7, 176.3 (*C*OOMe and C^3), 135.5–128.5 ($C_{arom-Xyl}$), 91.8 (C^2), 91.4, 90.2 (Cp), 51.9 (COO*Me*), 47.8 (NMe), 18.0, 17.9 ($Me_2C_6H_3$) ppm. $C_{27}H_{25}Fe_2NO_4S_2$ (603.31): calcd. C 53.75, H 4.18, N 2.32; found C 53.81, H 4.15, N 2.37.

2d: Yield 60 mg, 73%. IR (CH_2Cl_2): ṽ = 1984 (vs, CO), 1797 (s), 1664 (w, νCN) cm^{-1}. IR (KBr pellets): ṽ = 1092 (w, SCS) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 5.10, 5.06 (s, 10 H, Cp), 3.92 (s, 3 H, C^3Me), 3.80, 3.31 (s, 6 H, NMe) ppm. ^{13}C NMR ($CDCl_3$): δ = 261.0 (μ-CO), 244.9 (CS_2), 225.5 (C^1), 209.2 (CO), 196.5 (C^3), 89.8, 88.8 (Cp), 87.8 (C^2), 45.9, 45.5 (NMe), 39.6 (C^3Me) ppm.

$C_{19}H_{19}Fe_2NO_2S_2$ (469.18): calcd. C 48.64, H 4.08, N 2.99; found C 48.68, H 4.06, N 2.93.

2e: Yield 72 mg, 75%. IR (CH_2Cl_2): ṽ = 1988 (vs, νCO), 1794 (s), 1662 (w, νCN) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 5.16, 5.12 (s, 10 H, Cp), 4.25, 3.85 (m, 2 H, C^3CH_2), 3.81, 3.35 (s, 6 H, NMe), 3.03, 1.63, 1.07 (m, 7 H, $C^3CH_2CH_2CH_2CH_3$) ppm. ^{13}C NMR ($CDCl_3$): δ = 261.1 (μ-CO), 243.3 (CS_2), 224.1 (C^1), 209.3 (CO), 201.9 (C^3), 89.3, 88.8 (Cp), 84.7 (C^2), 52.0, 36.9, 23.8 14.3 (*n*Bu), 45.6, 45.5 (NMe) ppm. $C_{22}H_{25}Fe_2NO_2S_2$ (511.26): calcd. C 51.68, H 4.93, N 2.74; found C 51.74, H 4.88, N 2.82.

2f: Yield 68 mg, 77%. IR (CH_2Cl_2): ṽ = 1983 (vs, CO), 1805 (s), 1623 (m, νCN) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = *7.46*, 7.42, *7.17*, 7.10 (d, $^3J_{HH}$ = 8.42 Hz, 2 H, C_6H_4), 5.16, 4.84, *4.72*, *4.67* (s, 10 H, Cp), 3.97, *3.90* (s, 3 H, C^3Me), 3.94 (s, 3 H, OMe), *3.70*, 3.56 (s, 3 H, NMe) ppm; *Z*/*E* ratio 5:1. ^{13}C NMR ($CDCl_3$): δ = 258.3 (μ-CO), 245.1 (CS_2), 227.8 (C^1), 209.5, *209.2* (CO), 197.4, *195.2* (C^3), 159.6, *138.1*, 137.0, 126.0, *125.4*, *114.5*, 114.1 (C_6H_4OMe), 89.9, *89.4*, *89.3*, 89.0 (Cp), 88.2 (C^2), 55.4 (OMe), 49.0, *47.6* (NMe), 39.6, *38.5* (C^3*Me*) ppm. $C_{25}H_{23}Fe_2NO_3S_2$ (561.28): calcd. C 53.50, H 4.13, N 2.50; found C 53.46, H 4.18, N 2.44.

Synthesis of [Fe_2{μ-η^1:η^3-C^3(R′)=C^2{C(NPh)S}C^1=N(Me)(R)}(μ-CO)(CO)$(Cp)_2$] (R = Xyl, R′ = Me, 3a; R = Me, R′ = Me, 3b): A THF solution of complex **1a** (120 mg, 0.190 mmol) was treated with SCNPh (1.15 mmol) and then with NaH (46 mg, 1.92 mmol). The mixture was stirred for 40 min, filtered through a pad of alumina and then evaporated under reduced pressure. Chromatography of the residue on alumina using a 1:1 (v/v) mixture of THF and MeOH as eluent afforded a brown band. The product **3a** was obtained as a brown powder upon removal of the solvent; yield 82 mg, 70%. Crystals of **3a** suitable for X-ray diffraction were obtained by layering a CH_2Cl_2 solution with petroleum ether at –20 °C. IR (CH_2Cl_2): ṽ = 1984 (vs, CO), 1793 (s), 1524 (m, νCN) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 7.62–6.87 (m, 8 H, Me_2C_6*H_3* and Ph), 5.06, 4.71 (s, 10 H, Cp), 4.04 (s, 3 H, C^3Me), 3.73 (s, 3 H, NMe), 2.61, 2.00 (C_6H_3*Me_2*) ppm. ^{13}C NMR ($CDCl_3$): δ = 256.0 (μ-CO), 217.0 (C^1), 212.9 (CO), 203.1 (C^3), 154.0 (SCN), 142.3 ($C_{ipso\text{-Xyl}}$), 139.2 ($C_{ipso\text{-Ph}}$), 128.7–123.8 (C_{arom}), 90.4, 88.1 (Cp), 76.3 (C^2), 49.5 (NMe), 39.6 (C^3*Me*), 18.3, 18.2 (*Me_2*C_6H_3) ppm. $C_{32}H_{30}Fe_2N_2O_2S$ (618.35): calcd. C 62.16, H 4.89, N 4.53; found C 62.27, H 4.82, N 4.45.

Compound **3b** was prepared by following the same procedure as described for **3a** by reacting complex **1d** (130 mg) with SCNPh and NaH.

3b: Yield 91 mg, 72%. IR (CH_2Cl_2): ṽ = 1984 (vs, CO), 1793 (s), 1605 (m, νCN) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 8.06–7.22 (m, 5 H, Ph), 5.14, 5.00 (s, 10 H, Cp), 4.05 (s, 3 H, C^3Me), 3.76, 3.18 (s, 6 H, NMe_2) ppm. ^{13}C NMR ($CDCl_3$): δ = 268.8 (μ-CO), 225.6 (C^1), 208.3 (CO), 194.3 (C^3), 152.6 (SCN), 139.2 ($C_{ipso\text{-Ph}}$), 128.7–123.8 (C_{arom}), 90.8, 88.4 (Cp), 72.0 (C^2), 48.5, 45.6 (NMe), 40.4 (C^3*Me*) ppm. $C_{25}H_{24}Fe_2N_2O_2S$ (528.23): calcd. C 56.84, H 4.58, N 5.30; found C 56.45, H 4.58, N 5.28.

Synthesis of [Fe_2{μ-η^1:η^3-C^3(R′)=C^2(CS_2Me)C^1=N(Me)(Xyl)}(μ-CO)(CO)$(Cp)_2$][SO_3CF_3] (4a): Complex **2b** (120 mg, 0.189 mol) was dissolved in CH_2Cl_2 (15 mL) and treated with $CF_3SO_3CH_3$ (0.03 mL, 0.27 mmol). The solution was stirred for 15 min and then it was filtered through an alumina column. Elution with MeOH afforded a brown band corresponding to **4a**; yield 122 mg, 90%. IR (CH_2Cl_2): ṽ = 1997 (vs, CO), 1829 (s), 1604 (m, νCN) cm^{-1}. IR (KBr pellets): ṽ = 1183 (w, SCS) cm^{-1}. ^{1}H NMR (CD_3CN): δ = 7.65–7.38 (m, 7 H, C_6*H_4*Me and Me_2C_6*H_3*), 5.32, 5.21 (s, 10 H, Cp), 3.53 (s, 3 H, NMe), 2.69, 2.13 (s, 6 H, *Me_2*C_6H_3), 2.66 (s, 3 H, C_6H_4*Me*), 2.54 (s, 3 H, SMe) ppm. ^{13}C NMR (CD_3CN): δ = 251.5 (μ-CO), 227.6 (CS_2), 223.1 (C^1), 211.5 (CO), 204.0 (C^3), 150.2 ($C_{ipso\text{-Tol}}$), 142.8 ($C_{ipso\text{-Xyl}}$), 137.5–126.8 (C_{arom}), 93.8 (C^2), 95.1, 90.6 (Cp), 50.8 (NMe), 23.2 (*Me*C_6H_4), 21.5 (SMe), 19.2, 19.0 (*Me_2*C_6H_3) ppm. $C_{34}H_{32}F_3Fe_2NO_5S_3$ (799.50): calcd. C 51.08, H 4.03, N 1.75; found C 51.13, H 4.08, N 1.69.

Synthesis of [Fe_2{μ-η^1:η^3-C^3(R′)=C^2(CS_2Fp)C^1=N(Me)(R)}(μ-CO)(CO)$(Cp)_2$][SO_3CF_3] (Fp = [Fe(CO_2Cp)]$^+$; R = R′ = Me, 4b; R = Me, R′ = *n*Bu, 4c; R = *p*-MeOC_6H_4, R′ = Me, 4d): Complex [$Fe_2(Cp)_2(CO)_4$] (75 mg, 0.212 mmol) was dissolved in CH_2Cl_2 (10 mL) and treated with $AgSO_3CF_3$ (131 mg, 0.510 mmol). The mixture was stirred for 3 h and then it was filtered through a pad of Celite. The resulting solution was added to a stirred solution of **2d** (90 mg, 0.192 mmol) in CH_2Cl_2 (15 mL) and the stirring was maintained for 1 h. Then, the mixture was filtered through an alumina column. Elution with MeOH gave a red band corresponding to **4b**; yield 124 mg, 81%. IR (CH_2Cl_2): ṽ = 2047 (s, νCO), 2004 (vs), 1989 (vs), 1810 (s), 1661 (m, νCN) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 5.27, 5.14 (s, 15 H, Cp), 3.71 (s, 3 H, C^3Me), 3.80, 2.94 (s, 6 H, NMe) ppm. ^{13}C NMR ($CDCl_3$): δ = 256.6 (μ-CO), 238.5 (CS_2), 222.4 (C^1), 209.9, 209.1 (CO), 199.0 (C^3), 90.7, 89.1, 85.9 (Cp), 84.4 (C^2), 46.1, 45.7 (NMe), 39.8 (C^3*Me*) ppm. $C_{27}H_{24}F_3Fe_3NO_7S_3$ (795.21): calcd. C 40.78, H 3.04, N 1.76; found C 40.73, H 3.12, N 1.69.

Complexes **4c** and **4d** were prepared by following the same procedure as described for **4b** by reacting [Fp][SO_3CF_3] with **2e** (100 mg) and **2f** (115 mg), respectively. Crystals of **4d** suitable for X-ray diffraction studies were obtained by layering a CH_2Cl_2 solution with diethyl ether at –20 °C.

4c: Yield 139 mg, 85%. IR (CH_2Cl_2): ṽ = 2047 (s, CO), 2001 (vs), 1993 (vs), 1819 (s), 1662 (m, νCN) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 5.24, 5.15, 5.14 (s, 15 H, Cp), 4.29, 4.00 (m, 2 H, C^3CH_2), 3.83, 3.01 (s, 6 H, NMe), 2.43, 1.95 (m, 2 H, C^3CH_2*CH_2*), 1.82 (m, 2 H, $C^3CH_2CH_2$*CH_2*), 0.98 (m, 3 H, $C^3CH_2CH_2CH_2$*CH_3*) ppm. ^{13}C NMR ($CDCl_3$): δ = 256.8 (μ-CO), 236.8 (CS_2), 220.9 (C^1), 209.7, 209.0 (CO), 204.3 (C^3), 90.1, 89.0, 85.9 (Cp), 84.5 (C^2), 46.1, 46.0 (NMe), 51.5, 33.3, 23.4, 14.2 (*n*Bu) ppm. $C_{30}H_{30}F_3Fe_3NO_7S_3$ (837.29): calcd. C 43.03, H 3.61, N 1.67; found C 43.12, H 3.55, N 1.62.

4d: Yield 140 mg, 77%. IR (CH_2Cl_2): ṽ = 2047 (s, CO), 2004 (vs), 1988 (vs), 1818 (s), 1621 (m, νCN) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 7.29, 7.07 (m, 2 H, C_6*H_4*), 5.24, 5.18, 4.85 (s, 15 H, Cp), 3.85 (s, 3 H, OMe), 3.76 (s, 3 H, C^3Me), 3.19 (s, 3 H, NMe) ppm. ^{13}C NMR ($CDCl_3$): δ = 254.3 (μ-CO), 238.6 (CS_2), 225.1 (C^1), 210.0, 209.9, 209.4 (CO), 200.4 (C^3), 160.0–114.5 (C_{arom}), 90.9, 89.5, 85.9 (Cp), 85.0 (C^2), 55.6 (OMe), 49.2 (NMe), 40.1 (C^3*Me*) ppm. $C_{33}H_{28}F_3Fe_3NO_8S_3$ (887.31): calcd. C 44.67, H 3.18, N 1.58; found C 44.74, H 3.12, N 1.50.

Synthesis of [$PdCl_2${κ^2-(*S*,*S*)-2a}] (5): A solution of **2a** (250 mg, 0.45 mmol) in CH_2Cl_2 (15 mL) was added dropwise to a solution of [$PdCl_2(CH_3CN)_2$] (117 mg, 0.45 mmol) in CH_2Cl_2 (15 mL). The colour of the reaction mixture gradually turned from green to dark red. The resulting solution was stirred at room temperature for 2 h and then the solvent was evaporated in vacuo. The resulting solid was washed three times with diethyl ether and then dried under reduced pressure; yield 310 mg, 93%. IR (CH_2Cl_2): ṽ = 1998 (vs, CO), 1818 (s) cm^{-1}. IR (KBr pellets): ṽ = 997 (w, νSCS) cm^{-1}. ^{1}H NMR ([D_6]acetone): δ = 7.48–6.98 (m, 3 H, Me_2C_6*H_3*), 5.35, 4.86 (s, 10 H, Cp), 4.12 (s, 3 H, C^3Me), 3.55 (s, 3 H, NMe), 2.38, 1.86 (s, 6 H, *Me_2*C_6H_3) ppm. ^{13}C NMR ([D_6]acetone): δ = 256.4 (μ-CO), 241.3 (CS_2), 225.0 (C^1), 209.3 (CO), 200.6 (C^3), 143.1 (*ipso*-$Me_2C_6H_3$), 136.0, 134.9, 129.5, 129.1, 125.9 (Me_2*C_6*H_3), 92.1, 89.9

Table 4. Crystal data and experimental details for **2b**·$1.5CH_2Cl_2$, **3a**·$1.5CH_2Cl_2$ and **4d**·$0.59C_4H_{10}O$.

Complex	**2b**·$1.5CH_2Cl_2$	**3a**·$1.5CH_2Cl_2$	**4d**·$0.59C_4H_{10}O$
Formula	$C_{33.5}H_{32}Cl_3Fe_2NO_2S_2$	$C_{33.5}H_{33}Cl_3Fe_2N_2O_2S$	$C_{35.36}H_{33.91}F_3Fe_3NO_{8.59}S_3$
M_r	762.77	745.73	931.09
T [K]	293(2)	100(2)	296(2)
λ [Å]	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$	$C2/c$	$P\bar{1}$
a [Å]	12.691(3)	34.362(3)	11.4407(17)
b [Å]	14.202(3)	12.3801(11)	12.3454(18)
c [Å]	20.032(4)	16.7948(15)	15.505(2)
α [°]	90	90	73.900(2)
β [°]	104.16(3)	109.5390(10)	75.126(2)
γ [°]	90	90	85.702(2)
Cell volume [Å^3]	3501.0(12)	6733.1(10)	2033.6(5)
Z	4	8	2
$D_{calcd.}$ [g cm^{-3}]	1.447	1.471	1.521
μ [mm^{-1}]	1.207	1.195	1.273
F(000)	1564	3064	950
Crystal size [mm]	0.25 × 0.21 × 0.14	0.24 × 0.21 × 0.15	0.21 × 0.16 × 0.12
θ range [°]	1.73–26.37	1.76–25.55	1.41–26.00
Reflections collected	34318	32928	21168
Independent reflections	7155 (R_{int} = 0.0595)	6289 (R_{int} = 0.0201)	7925 (R_{int} = 0.0387)
Data/restraints/parameters	7155/24/408	6289/187/404	7925/547/623
Goodness on fit on F^2	1.017	1.093	1.007
R_1 [$I > 2\sigma(I)$]	0.0460	0.0557	0.0692
wR_2 (all data)	0.1400	0.1395	0.2371
Largest diff. peak and hole [eÅ^{-3}]	0.479/–0.540	1.996/–0.866	0.702/–0.779

(Cp), 85.6 (C^2), 49.8 (NMe), 40.1 ($C^{\gamma}Me$), 20.1, 18.7 ($Me_2C_6H_3$) ppm. $C_{26}H_{25}Cl_2Fe_2NO_2PdS_2$ (736.63): calcd. C 42.39, H 3.42, N 1.90; found C 42.31, H 3.52, N 1.84.

X-ray Crystallography: Crystal data and collection details for **2b**·$1.5CH_2Cl_2$, **3a**·$1.5CH_2Cl_2$ and **4d**·$0.59C_4H_{10}O$ are reported in Table 4. The diffraction experiments were performed with a Bruker SMART 2000 diffractometer (for **2b**·$1.5CH_2Cl_2$) and a Bruker Apex II diffractometer (for **3a**·$1.5CH_2Cl_2$, and **4d**·$0.59C_4H_{10}O$) equipped with a CCD detector using Mo-K_{α} radiation. Data were corrected for Lorentzian polarization and absorption effects (empirical absorption correction SADABS).[34] Structures were solved by direct methods and refined by full-matrix least-squares based on all data using F^2.[35] All non-hydrogen atoms were refined with anisotropic displacement parameters unless otherwise stated. Hydrogen atoms were placed in calculated positions and were treated isotropically using the 1.2-fold U_{iso} value of the parent atom except for methyl protons, which were assigned the 1.5-fold U_{iso} value of the parent carbon atoms.

2b·$1.5CH_2Cl_2$: One and a half molecules of CH_2Cl_2 are present in the asymmetric unit and the latter is disordered. Disordered atomic positions were split and refined isotropically using one occupancy parameter per disordered group.

3a·$1.5CH_2Cl_2$: One and a half molecules of CH_2Cl_2 are present in the asymmetric unit and the latter is disordered as well as the Cp bound to Fe(1). Disordered atomic positions were split and refined isotropically using one occupancy parameter per disordered group.

4d·$0.59C_4H_{10}O$: Both the Z and the E isomers are present within the crystal in a disordered fashion with all the atoms overlapping except for the N(Me)(p-C_6H_4OMe) groups which have different orientations. Moreover, one molecule of diethyl ether is co-crystallised with the Z isomer, whereas there is no place for it when the E isomer is present. Thus, the two images of the N(Me)(p-$MeOC_6H_4$) group for the two isomers were refined independently with the sum of their occupancy factors restrained to unity, including the diethyl ether molecule together with the Z isomer. After convergence, the refinement resulted in the following composition for the crystal: 59% (Z)-**4d** $C_4H_{10}O$ and 41% (E)-**4d**. Minor disorder is present on the Cp ligand bound to Fe(2); this has been split onto two positions and refined using one occupancy parameter per disordered group.

CCDC-798725 (for **2b**), -798727 (for **3a**) and -798726 (for **4d**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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