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Carbon–carbon bond formation in the reactions of diiron μ-carbyne complexes with 2-thienyllithium, synthesis and structural characterization

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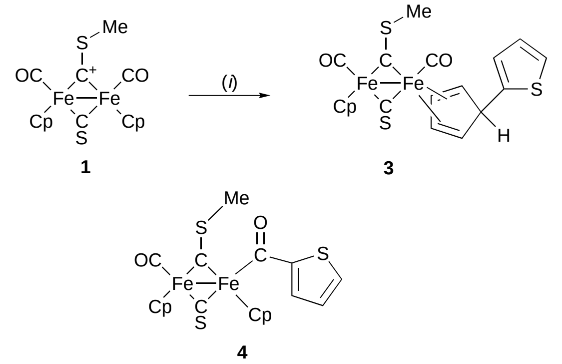
The reactions of 2-thienyllithium (Lith) with a variety of carbyne complexes result in C–C bond formation at different sites of the molecules. The thiocarbyne *cis*-$[\mathrm{Fe_2(\mu\text{-}CSMe)(\mu\text{-}CS)(CO)_2(Cp)_2}]^+$ **1** (Cp = η-C_5H_5) underwent Cp addition forming $[\mathrm{Fe_2(\mu\text{-}CSMe)(\mu\text{-}CS)(CO)_2(Cp)(\eta^4\text{-}C_5H_5th)}]$ **3** and trace amounts of $[\mathrm{Fe_2(\mu\text{-}CSMe)(\mu\text{-}CS)\{C(O)th\}(CO)(Cp)_2}]$ **4**. By contrast all the aminocarbynes $[\mathrm{Fe_2(\mu\text{-}CNRR')(\mu\text{-}CO)(CO)_2(Cp)_2}]^+$ (R = R′ = Me **2a**; R = Me, R′ = $PhCH_2$ **2b**) and $[\mathrm{Ru_2(\mu\text{-}CNMe_2)(\mu\text{-}CO)(CO)_2(Cp)_2}]^+$ **6** gave the corresponding acyl derivatives $[\mathrm{M_2(\mu\text{-}CNRR')(\mu\text{-}CO)(CO)\{C(O)th\}(Cp)_2}]$ (M = Fe **5a** and **5b**; R = R′ = Me, M = Ru **7**). When R ≠ R′, the NMR spectra of these neutral species show the presence of two isomers α and β arising from hindered rotation around the μ-C=N bond. The relevance of these reactions is discussed in terms of selective C–C bond formation in comparison with analogous carbon nucleophile addition at $[\mathrm{Fe_2(\mu\text{-}CSMe)(\mu\text{-}CO)(CO)_2(Cp)_2}]^+$. The crystal structures of **3** and $[\mathrm{Fe_2\{\mu\text{-}CN(Me)CH_2Ph\}(\mu\text{-}CO)(CO)\{C(O)th\}(Cp)_2}]$ **5b** are reported and discussed. The conformation of the Fe_2C_2 diamond is shown to depend on the nature of the bridging ligands. Simple models of electronic structure are outlined on the basis of the geometric evidence.

For some time now, we have been involved in studying the reactivity toward nucleophiles of cationic dinuclear thio- and amino-carbyne derivatives of iron and ruthenium. As representative examples we can cite the works on complexes of the type $[\mathrm{Fe_2(\mu\text{-}CR)(\mu\text{-}CO)(CO)_2(Cp)_2}]^+$ (R = SMe or NR_2, Cp = η-C_5H_5), especially their reactions with cyanide and hydride ions.[1]

More recently we have extended our research to the reactions with carbanions and found that carbon–carbon bonds are formed at different sites of the aforementioned derivatives depending on the nature of the carbon nucleophile.[2] In particular the reaction of $[\mathrm{Fe_2(\mu\text{-}CSMe)(\mu\text{-}CO)(CO)_2(Cp)_2}]^+$ with 2-thienyllithium (Lith) has been shown to form a mixture of thiocarbyne $[\mathrm{Fe_2(\mu\text{-}CSMe)(\mu\text{-}CO)(CO)_2(Cp)(C_5H_5th)}]$ and thiocarbene $[\mathrm{Fe\overline{Fe\{\mu\text{-}C(S}Me)C(O)th\}(\mu\text{-}CO)(CO)(Cp)_2}]$ containing thienyl functionalized ligands.[2b] Since the C–C bond formation[3] and the thienyl activation studies[4] on multicenter metal complexes are relevant in heterogeneously catalyzed processes, we have focused our attention on analogous reactions with different dinuclear carbyne complexes. Here we report on the reactions of $[\mathrm{Fe_2(\mu\text{-}CSMe)(\mu\text{-}CS)(CO)_2(Cp)_2}]^+$ **1** and $[\mathrm{M_2(\mu\text{-}CNRR')(\mu\text{-}CO)(CO)_2(Cp)_2}]^+$ (R = R′ = Me, R = Me, R′ = CH_2Ph, M = Fe **2** or R = R′ = Me, M = Ru **6**) with Lith together with the molecular structures of the derivatives $[\mathrm{Fe_2(\mu\text{-}CSMe)(\mu\text{-}CS)(CO)_2(Cp)(\eta^4\text{-}C_5H_5th)}]$ **3** and $[\mathrm{Fe_2\{\mu\text{-}CN(Me)CH_2Ph\}(\mu\text{-}CO)(CO)\{C(O)th\}(Cp)_2}]$ **5b**.

Results and Discussion

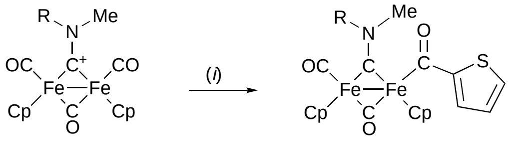
We have reported that the complex $[\mathrm{Fe_2(\mu\text{-}CSMe)(\mu\text{-}CO)(CO)_2(Cp)_2}]^+$ reacts with Lith to form the derivatives $[\mathrm{Fe_2(\mu\text{-}CSMe)(\mu\text{-}CO)(CO)_2(Cp)(\eta^4\text{-}C_5H_5th)}]$ and $[\mathrm{Fe_2\{\mu\text{-}C(SMe)C(O)th\}(\mu\text{-}CO)(CO)(Cp)_2}]$ resulting from carbanion addition at the Cp and CO ligands, respectively. The same reaction, carried out on the thiocarbyne analogue *cis*-$[\mathrm{Fe_2(\mu\text{-}CSMe)(\mu\text{-}CS)(CO)_2(Cp)_2}]^+$ **1**[5] (Scheme 1) under identical experimental conditions (thf solvent, at −70 °C), has been found to generate a mixture of products which, after separation by column chromatography gives the air stable red $[\mathrm{Fe_2(\mu\text{-}CSMe)(\mu\text{-}CS)(CO)_2(Cp)(\eta^4\text{-}C_5H_5th)}]$ **3** (60% yield) and a trace amount of a fairly unstable green derivative $[\mathrm{Fe_2(\mu\text{-}CSMe)(\mu\text{-}CS)\{C(O)th\}(CO)(Cp)_2}]$ **4**.



Scheme 1 (*i*) Tetrahydrofuran (thf), Lith, −70 °C

The instability and extensive decomposition during chromatographic purification of **4** has prevented a full spectroscopic characterization. Nevertheless, its nature has been established by IR spectroscopy which shows a ν(CO) band pattern consistent with a terminal (1982 cm^{-1}) and an acyl (1566 cm^{-1}) carbonyl group and with the presence of the ν(CS) bridging thiocarbonyl ligand (1139 cm^{-1}).[6] The position of the terminal ν(CO) confirms our attribution and rules out the other possible structure $[\mathrm{Fe\overline{Fe\{\mu\text{-}C(S}Me)C(O)th\}(\mu\text{-}CS)(CO)(Cp)_2}]$ which, according to our previous observations, should display the carbonyl absorption at lower wavenumber because of the S-co-ordination to iron.[6] Furthermore, the ν(C=O) absorption is directly comparable with that of $[\mathrm{Fe(CO)_2\{C(O)th\}(Cp)}]$ (1570 cm^{-1}) which represents the only reported complex containing the $C(O)SC_4H_3$ group σ bonded to an iron atom.[7]

The spectroscopic properties of the main product **3** are



R = Me **2a,** CH_2Ph **2b** R = Me **5a,** CH_2Ph **5b**

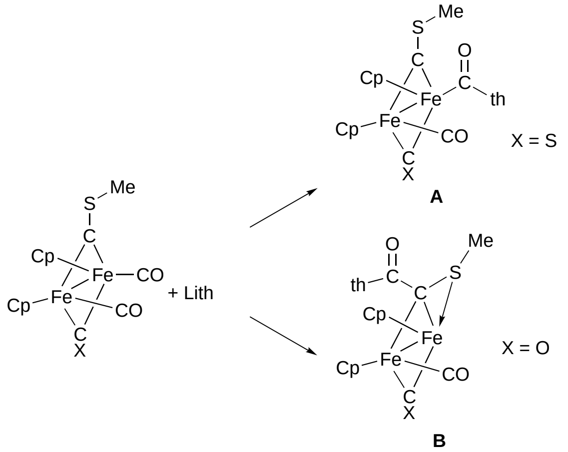
Scheme 2 (*i*) Lith, thf, −70 °C

similar to those of the corresponding carbonyl complex $[Fe_2(\mu\text{-}CSMe)(\mu\text{-}CO)(CO)_2(Cp)(\eta^4\text{-}C_5H_5th)]$.[2b] The IR spectrum shows a ν(CO) band pattern consistent with two *cis*-CO (1993vs, 1963s cm^{-1}) suggesting that, as previously reported for reactions involving complex **1,** the *cis* stereogeometry is retained[5b] in the reaction reported in Scheme 1. The crystal structural study (see later) indicates that the 2-thienyl addition at the Cp ring occurs at the *exo* position, in agreement with the absence in the IR spectrum of the $C\text{–}H_{exo}$ band at about 2750 cm^{-1}. The lack of this absorption has previously been used as a criterion for assigning the side of the nucleophilic addition at the Cp in the absence of crystal structural characterizations.[8] The ^1H NMR spectrum shows in addition to the Cp and Me protons at δ 4.86 and 3.10 respectively, eight multiplet signals due to the diastereotopic protons of the $\eta^4\text{-}C_5H_5C_4H_3S$ at δ 7.03, 6.86, 6.68 (C_4H_3S); 5.14, 4.58, 4.38, 4.12, and 3.91 (C_5H_5). This ligand is easily released under electronic impact, as indicated by the presence of the signal at *m*/*z* 148 ($Cpth^+$) which appears as the base peak in the mass spectrum of complex **3.** As a characteristic feature, the ^{13}C NMR spectrum of **3** shows the μ-CS resonance at δ 376.9 in the range expected for a bridging thiocarbonyl carbon ligand.[9]

If the reaction in Scheme 1 is carried out at higher temperature (−20 °C) the same products in lower yields are generated; no intramolecular rearrangements leading to complexes arising from carbyne–carbonyl coupling or hydrogen migration from Cp to μ-C have been observed.

The reaction of the aminocarbyne complexes $[Fe_2(\mu\text{-}CNRR')(\mu\text{-}CO)(CO)_2(Cp)_2]^+$ (R = R′ = Me **2a**; R = Me, R′ = CH_2Ph **2b**) with 2-thienyllithium, in thf at −70 °C, rapidly forms the green, moderately air stable acyl $[Fe_2(\mu\text{-}CNRR')(\mu\text{-}CO)(CO)\{C(O)th\}(Cp)_2]$ **5a** and **5b** complexes resulting from Lith addition at the carbonyl group (Scheme 2). Chromatographic purification has not provided evidence for the formation, even in trace amounts, of complexes of the type $[Fe_2(\mu\text{-}CNRR')(\mu\text{-}CO)(CO)_2(\eta^4\text{-}C_5H_5th)(Cp)]$ arising from Cp addition. Noteworthy, we have recently found that these latter derivatives are obtained from the reaction of **2** with LiR (R = Me, Bu or Ph).[10]

The spectroscopic characterization of **5a** and **5b** is straightforward. As a common feature the IR spectra exhibit one terminal, one bridging and one acyl carbonyl absorption (*e.g.* for **5a** 1963, 1771 and 1573 cm^{-1}, respectively) and a ν(C=N) band in the range 1555–1525 cm^{-1}. The ^1H and ^{13}C NMR spectra reveal the non-equivalence of the N-bonded methyl groups in **5a** (δ 4.32, 4.16 and 51.0, 49.3, respectively) because of restricted rotation around the C=N bond. This hindrance is responsible for the existence of two isomers of **5b,** α and β, arising from a different orientation of the N-substituents Me and CH_2Ph with respect to the non-equivalent iron atoms.[9,10] The two isomeric forms are revealed by doubling of the resonances in the NMR spectra of **5b**. For example the ^1H and ^{13}C NMR spectra show two methyl resonances (δ 4.09, 4.04 and 51.3, 48.6, respectively) with intensity ratio 1 : 1.5. However, because of a fortuitous coincidence, the resonance at δ 335.3 of the bridging aminocarbyne carbon appears as a single signal. Variable-temperature ^1H NMR experiments (30–80 °C) in toluene show the same isomeric ratio between the two forms. Attempts to separate the α from the β isomer of **5b** have failed and the crystallization gives a mixture of isomers. One of the two, **5b**, probably the most abundant crystalline form, has been characterized by an X-ray study (see later).



Scheme 3

The reaction of the diruthenium complex $[Ru_2(\mu\text{-}CNMe_2)(\mu\text{-}CO)(CO)_2(Cp)_2]^+$ **6** with 2-thienyllithium at −50 °C in thf has also been investigated. As in the case of the diiron analogues, selective addition of the carbanion at the terminal CO group has been found. The resulting complex $[Ru_2(\mu\text{-}CNMe_2)(\mu\text{-}CO)(CO)\{C(O)th\}(Cp)_2]$ **7**, after separation by chromatography, shows spectroscopic properties directly comparable to those of complex **5a**. The transformation of the CO into the $C(O)C_4H_3S$ ligand is shown by the ν(CO) of the acyl group at 1567 cm^{-1} and by the presence of three multiplets (δ 7.82, 7.25, 7.05) associated to the three thienyl ring protons in the ^1H NMR spectrum. Moreover, because of CO addition the ruthenium atoms in **7** become non-equivalent chiral centres (δ 5.24 and 5.17, Cp ring protons) and the two N-bonded Me groups diastereotopic (δ 4.00 and 3.89).

Irradiation of **5a**, **5b** or **7** in thf solvent does not afford decarbonylated products as found for the mononuclear acyl complex $[Fe(CO)_2\{C(O)th\}(Cp)]$ which, under photochemical conditions has previously been reported to form the σ-thienyl derivative $[Fe(CO)_2(th)(Cp)]$.[7] In agreement, the dinuclear acetonitrile derivatives $[Fe_2(\mu\text{-}CSMe)(\mu\text{-}CX)(CO)(NCMe)(Cp)_2]^+$ (X = O or S) do not form the thienyl-substituted complexes on reaction with an excess of the carbanion.

The reactions between Lith and the dinuclear carbyne derivatives result in the formation of a C–C bond *via* addition at the CO (**2a**, **2b** and **6**) or both at the C_5H_5 ring and terminal carbonyl group (complex **1**). As previously found, neither addition at the μ-C nor displacement of CO has been observed. Therefore the product distribution seems to be determined by the nature of the complex; in particular the addition at the CO in the aminocarbyne case confirms the tendency shown by other stabilized carbanions (*e.g.* LiCCR) to form acyl complexes.[2b,10]

The reactivity of the μ-CS complex **1** has to be related to that of the analogous μ-CO thiocarbyne $[Fe_2(\mu\text{-}CSMe)(\mu\text{-}CO)(CO)_2(Cp)_2]^+$ which gives 2-thienyl addition at both the CO and Cp ligands. However, in the latter case, the reaction does not stop at the acyl complex but proceeds ultimately to form the complex $[FeFe\{\mu\text{-}C(SMe)C(O)th\}(\mu\text{-}CO)(CO)(Cp)_2]$ **8** *via* carbyne–carbonyl migratory coupling and S-co-ordination to one Fe atom.[1a,2b] It is noteworthy that the crystal structure of **8**[2b] has revealed that the migrated C(O)th group is placed opposite to the remaining terminal CO, despite the *cis* arrangement of the CO ligands in the precursor. Therefore the inability of $[Fe_2(\mu\text{-}CSMe)(\mu\text{-}CS)\{C(O)th\}(CO)(Cp)_2]$ **4** (type **A** in Scheme 3) to rearrange to $[FeFe\{\mu\text{-}C(SMe)C(O)th\}(\mu\text{-}CS)(CO)(Cp)_2]$, may be ascribed to the demonstrated higher stability of the Fe_2C_2 diamond in the μ-CS complexes[5b,6] which prevents rearrangement to a more favourable geometry *via* the bridge-opening mechanism that must be invoked in the formation of **8** from $[Fe_2(\mu\text{-}CSMe)(\mu\text{-}CO)(CO)_2(Cp)_2]^+$ in the μ-CO case.

Table 1 Selected bond lengths (Å) and angles (°) for [Fe_2(μ-CSMe)(μ-CS)$(CO)_2$(Cp)(η^4-C_5H_5th)] **3**

Fe(1)–Fe(2)	2.5077(7)	Fe(1)–C(13)	2.062(3)
Fe(1)–C(9)	1.874(2)	Fe(1)–C(14)	2.151(2)
Fe(2)–C(9)	1.938(2)	C(11)–C(12)	1.401(3)
Fe(1)–C(7)	1.804(2)	C(12)–C(13)	1.429(4)
Fe(2)–C(7)	1.889(2)	C(13)–C(14)	1.390(4)
S(9)–C(9)	1.605(2)	C(14)–C(15)	1.510(3)
S(7)–C(7)	1.667(2)	C(11)–C(15)	1.513(3)
S(7)–C(8)	1.804(4)	C(15)–C(16)	1.517(3)
Fe(2)–C(1)	1.758(3)	S(16)–C(16)	1.710(3)
O(1)–C(1)	1.140(3)	S(16)–C(19)	1.695(3)
Fe(1)–C(10)	1.785(3)	C(16)–C(17)	1.422(4)
O(10)–C(10)	1.137(3)	C(17)–C(18)	1.437(4)
Fe(1)–C(11)	2.160(2)	C(18)–C(19)	1.337(5)
Fe(1)–C(12)	2.063(2)	Fe(2)–C (Cp_{ave})	2.118(2)
S(7)–C(7)–Fe(2)	125.4(1)	S(9)–C(9)–Fe(2)	136.6(1)
S(7)–C(7)–Fe(1)	149.0(1)	C(10)–Fe(1)–C(7)	101.5(1)
C(7)–C(7)–C(8)	106.7(1)	O(1)–C(1)–Fe(2)	176.0(2)
C(1)–Fe(2)–C(7)	86.4(1)	O(10)–C(10)–Fe(1)	177.1(3)
S(9)–C(9)–Fe(1)	140.9(1)	C(17)–C(16)–S(16)	111.3(2)
C(17)–C(16)–C(15)	126.3(2)	C(19)–C(18)–C(17)	114.7(3)
C(15)–C(16)–S(16)	122.4(2)	C(16)–C(17)–C(18)	109.1(2)
C(19)–S(16)–C(16)	92.7(2)	C(18)–C(19)–S(16)	112.2(3)

Table 2 Bond lengths (Å) and angles (°) for [Fe_2{μ-CN(Me)CH_2Ph}(μ-CO)(CO){C(O)th}$(Cp)_2$] **5b**

Fe(1)–Fe(2)	2.509(2)	C(2)–O(2)	1.149(2)
Fe(1)–C(3)	1.845(4)	Fe(1)–C(20)	1.964(4)
Fe(2)–C(3)	1.879(4)	C(20)–O(20)	1.228(4)
C(3)–N	1.303(5)	C(20)–C(21)	1.490(5)
N–C(4)	1.468(5)	C(21)–S	1.723(4)
N–C(11)	1.488(5)	C(24)–S	1.692(5)
C(11)–C(12)	1.515(5)	C(21)–C(22)	1.381(5)
Fe(1)–C(1)	1.846(4)	C(22)–C(23)	1.392(6)
Fe(2)–C(1)	2.007(4)	C(23)–C(24)	1.335(7)
C(1)–O(1)	1.176(4)	Fe(1)–C (Cp_{ave})	2.147(2)
Fe(2)–C(2)	1.745(4)	Fe(2)–C (Cp_{ave})	2.123(2)
N–C(3)–Fe(2)	135.9(3)	C(3)–Fe(1)–C(20)	87.9(2)
N–C(3)–Fe(1)	139.4(3)	O(20–C(20)–Fe(1)	124.4(3)
C(3)–N–C(4)	122.2(3)	C(21)–C(20)–Fe(1)	120.8(3)
C(3)–N–C(11)	123.1(4)	C(20)–C(21)–S	117.2(3)
C(4)–N–C(11)	114.8(3)	C(22)–C(21)–C(20)	133.0(4)
N–C(11)–C(12)	112.3(4)	C(24)–S–C(21)	91.9(2)
O(1)–C(1)–Fe(1)	146.2(3)	C(22)–C(21)–S	109.8(3)
O(1)–C(1)–Fe(2)	132.5(3)	C(21)–C(22)–C(23)	112.5(4)
C(2)–Fe(2)–C(3)	90.8(2)	C(24)–C(23)–C(22)	113.4(5)
O(2)–C(2)–Fe(2)	176.0(4)	C(23)–C(24)–S	112.3(4)

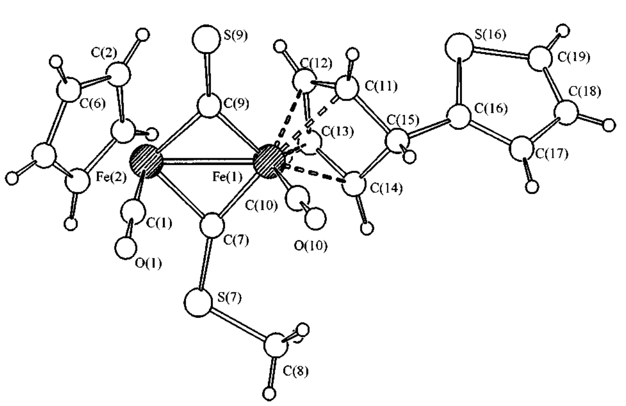


Fig. 1 Molecular structure of [Fe_2(μ-CSMe)(μ-CS)$(CO)_2$(Cp)(η^4-C_5H_5th)] **3**

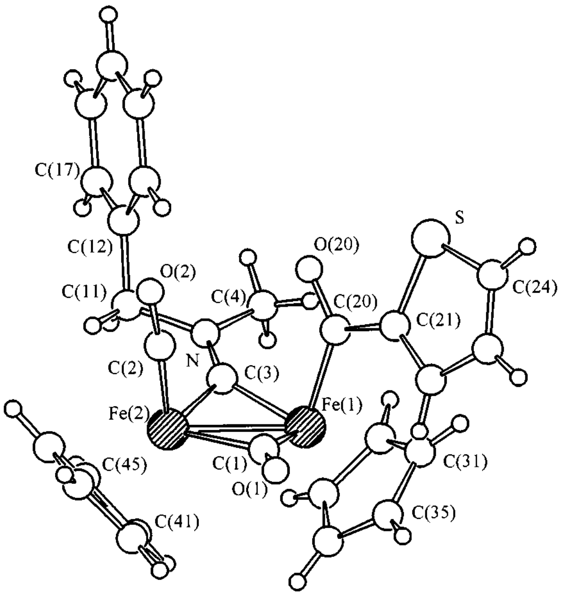


Fig. 2 Molecular structure of [Fe_2{μ-CN(Me)CH_2Ph}(μ-CO)(CO){C(O)th}$(Cp)_2$] **5b**

Molecular structures of [Fe_2(μ-CSMe)(μ-CS)$(CO)_2$(Cp)(η^4-C_5H_5th)] 3 and [Fe_2{μ-CN(Me)CH_2Ph}(μ-CO)(CO){C(O)th}$(Cp)_2$] 5b

The structures of complexes **3** and **5b** are shown in Figs. 1 and 2, respectively and relevant bond lengths and angles are reported in Tables 1 and 2. They share some common features; primarily they retain the overall *cis* geometry of the parent cations. As a consequence of the nucleophilic attack at a η-C_5H_5 ligand in **3** and a terminal CO in **5b** the two halves of the molecules are no longer related by mirror symmetry and become chiral. As the attack takes place at either ligand of equivalent pairs racemic mixtures result. The bridging ligands are bent away from the cyclopentadienyl rings and the dihedral angles around the Fe–Fe hinge are 16.8(2) in **3** and 24.3(1)° in **5b**. The flatter conformation of **3** is to be attributed to the different nature of the bridging ligands. In fact the corresponding angle is 23.9(3)° in [Fe_2(μ-CNC_5H_{10})(μ-CO)$(CO)_2$$(Cp)_2$]$^+$[11] and 16.6° in [$Fe_2$(μ-CS)$_2$$(CO)_2$$(Cp)_2$],[12] the closest terms of comparison for **5b** and **3**, respectively. The phenomenon is an effect of the highest π μ-C–Fe bond order in the thio derivatives which exhibit a lower bond order for the μ-C–S interactions. The Fe–Fe bond [2.508(1) in **3** and 2.509(2) Å in **5b**] on the contrary is totally unaffected by the different nature of the bridging ligands and the asymmetries in electronic structures.

A relevant effect of the thienyl anion attack on the η-C_5H_5 ring in **3** is a partial saturation of the ligand which rearranges to the four-electron donor η^4-C_5H_5th. As a consequence the pertinent iron atom [Fe(1)] remains apparently one electron short if one electron is ideally transferred to the μ-CSMe group, the formally positive ligand in the parent cation **1**. The electron deficiency is now relieved by the neutral three-electron donor μ-CSMe carbyne ligand which donates two electrons to Fe(1) and one electron to Fe(2). Actually the mechanism of electron saturation of Fe(1) is more complex than that outlined above; it takes place only in part through the bridging methylthiocarbyne ligand [C(7)–Fe(1) 1.804(2), C(7)–Fe(2) 1.889(2) Å]. The thiocarbonyl ligand contributes as well, as shown by a significant bond asymmetry [C(9)–Fe(1) 1.874(2), C(9)–Fe(2) 1.938(2) Å]. Even the terminal carbonyl ligands exhibit a slight non-equivalence that can be explained by a weaker back donation from Fe(1) [Fe(1)–C(10) 1.785(3), Fe(2)–C(1) 1.758(3) Å]. This last observation corroborates the attribution of an electron deficiency to Fe(1).

One should note that, although the thiocarbyne sulfur [S(7)] is electronically saturated, the μ-C(7)–S(7) distance [1.667(2) Å] has significant double-bond character, as confirmed by a comparison with the lengths of the genuine double bond in the thiocarbonyl ligand [C(9)–S(9) 1.605(2) Å] and the single bond of S(7)–C (methyl) [S(7)–C(8) 1.804(4) Å]. The S(7)–C(7) π bond can be described as a donation from the sulfur to the carbyne carbon, compensating for the thre-electron donation of this atom.

In conclusion an extensive electron delocalization from the sulfur to the iron atoms takes place. It is noteworthy that, in spite of the neutral nature of this molecule, the electron delocalization is substantially equivalent to that in cationic species containing the μ-C–SR unit, such as $[Fe_2(\mu\text{-}CSMe)\{\mu\text{-}CNC(O)SMe\}(CO)_2(Cp)_2]^{+}$[5b] and $[Fe_2(\mu\text{-}CSEt)(\mu\text{-}CO)(CO)_2(Cp)_2]^{+}$.[13]

The electron bookkeeping in **5b** can be done in two alternative ways, *i.e.*: (*a*) the acyl ligand is considered a one-electron donor and the bridging aminocarbyne a three-electron donor that contributes an electron pair to the electron short Fe(1) atom, (*b*) the acyl group is considered as a two-electron anionic ligand, also considering its mechanism of formation, and the bridging ligand as a two-electron donor iminium cation, as in the parent cation $[Fe_2\{\mu\text{-}CN(Me)CH_2Ph\}(\mu\text{-}CO)(CO)_2(Cp)_2]^{+}$ **2b**. We lean in favour of the latter model on the basis of the following structural evidence. (*i*) The μ-C–Fe distances in the $\mu\text{-}CN(Me)CH_2Ph$ ligand are only slightly asymmetric [C(3)–Fe(1) 1.845(4), C(3)–Fe(2) 1.879(4) Å] and do not justify substantially different modes of bonding on the two sides of the bridge. In fact in the molecule $[(OC)_4Fe(\mu\text{-}CNEt_2)Fe(NO)(CO)_2]$[14] in which an uneven three-electron donation is required from the bridging ligand in order to balance the electron counts of the iron atoms, the μ-C–Fe distances are more asymmetric [1.87(1), 1.95(1) Å], the shorter distance being that from the electron deficient metal atom. (*ii*) The distance C(3)–N [1.303(5) Å] has the same double-bond character observed in various cationic derivatives in which the positive charge is formally located at the nitrogen atom, *e.g.* $[Fe_2(\mu\text{-}CNC_5H_{10})(\mu\text{-}CO)(CO)_2(Cp)_2]^{+}$ 1.280(8),[11] $[Fe_2(\mu\text{-}CNMe_2)(\mu\text{-}CO)(CO)(CNMe)(Cp)_2]^{+}$ 1.303(7),[15] $[Fe_2(\mu\text{-}CNMe_2)_2(CO)_2(\eta\text{-}C_5H_4Me)_2]^{2+}$ 1.289(7), 1.301(6),[15] $[Fe_2(\mu\text{-}CNMe_2)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_4Me)_2]^{+}$ 1.30(3).[16] (*iii*) The acyl anion ligand $C(O)C_4H_3S^{-}$, acting as a better donor than CO, accumulates negative charge on Fe(1) that in turn is dissipated by a stronger back donation to the bridging carbonyl, as indicated by a pronounced bonding asymmetry [C(1)–Fe(1) 1.846(4), C(1)–Fe(2) 2.007(4) Å]. In the above discussion the molecule is considered a sort of zwitterion with the negative pole at the acyl ligand and the positive pole at the iminium ligand; in reality the charge separation is neutralised through a modulation of the σ–π interactions.

Experimental

All the reactions were routinely carried out under nitrogen using standard Schlenk techniques. Solvents were distilled immediately before use under nitrogen from appropriate drying agents. Glassware was oven-dried before use. Infrared spectra were recorded on a Perkin-Elmer 983-G spectrophotometer, ^{1}H and ^{13}C NMR spectra on a Varian Gemini 200. The shiftless relaxation reagent $[Cr(acac)_3]$ (acac = acetylacetonate) was added to solutions studied by ^{13}C NMR spectroscopy. Elemental analyses were by Pascher Microanalytical Laboratory (Remagen Germany). All the reagents were commercial products (Aldrich) of the highest purity available and used as received. The compounds $[M_2(CO)_4(Cp)_2]$ (M = Fe or Ru) were from Strem. Compound $[Fe_2(\mu\text{-}CSMe)(\mu\text{-}CS)(CO)_2(Cp)_2]SO_3CF_3$ [**1**]SO_3CF_3 was synthesized according to published methods;[5a,b] $[Fe_2(\mu\text{-}CNMe_2)(\mu\text{-}CO)(CO)_2(Cp)_2]SO_3CF_3$ [**2a**]SO_3CF_3, $[Fe_2\{\mu\text{-}CN(Me)CH_2Ph\}(\mu\text{-}CO)(CO)_2(Cp)_2]SO_3CF_3$ [**2b**]SO_3CF_3 and $[Ru_2(\mu\text{-}CNMe_2)(\mu\text{-}CO)(CO)_2(Cp)_2]SO_3CF_3$ [**6**]SO_3CF_3 were prepared from the corresponding isocyanide complexes.[17]

Syntheses

Reaction of $[Fe_2(\mu\text{-}CSMe)(\mu\text{-}CS)(CO)(Cp)_2]^{+}$ 1 with 2-thienyllithium to give compounds 3 and 4. To a stirred solution of $[Fe_2(\mu\text{-}CSMe)(\mu\text{-}CS)(CO)_2(Cp)_2]SO_3CF_3$ (0.20 g, 0.36 mmol) in thf (15 cm^3) at −70 °C was added Lith (0.50 cm^3 of a solution 1.0 M in Et_2O). The solution was filtered on an alumina pad and the solvent was removed under reduced pressure. The residue was chromatographed on an alumina column, with CH_2Cl_2–light petroleum (b.p. 40–70 °C) (1 : 2, v/v) as eluent, to give first an orange band, which afforded dark crystals of $[Fe_2(\mu\text{-}CSMe)(\mu\text{-}CS)(CO)_2(Cp)(\eta^4\text{-}C_5H_5th)]$ **3** (0.10 g, 60%) (Found: C, 47.0; H, 3.3. $C_{19}H_{16}Fe_2O_2S_3$ requires C, 47.1; H, 3.3%); ν_{max}/cm^{-1} (CH_2Cl_2) 1993vs, 1963s (CO) and 1132m (CS); $\delta_H(CDCl_3)$ 7.03 (1 H, d, C_4H_3S), 6.86 (1 H, dd, C_4H_3S), 6.68 (1 H, d, C_4H_3S), 4.86 (5 H, s, Cp), 5.14, 4.58, 4.38, 4.12, 3.91 (5 H, ms, $C_5\mathit{H}_5$th) and 3.10 (3 H, s, Me); $\delta_C(CD_2Cl_2)$ 376.9 (μ-CS), 220.3, 211.1 (CO), 153.2, 127.1, 123.4, 122.4 (th), 90.0 (Cp), 33.5 (SMe). Mass spectrum: *m*/*z* 456 (M^{+} − CO, 6), 427 (M^{+} − 2CO, 10), 148 ($C_5H_5th^{+}$, 100%).

Further elution gave a green fraction containing a small amount of a product identified as $[Fe_2(\mu\text{-}CSMe)(\mu\text{-}CS)\{C(O)th\}(CO)(Cp)_2]$ **4** on the basis of its IR spectrum: ν_{max}/cm^{-1} 1982vs, 1566s (CO) and 1139m (CS).

$[Fe_2(\mu\text{-}CNMe_2)(\mu\text{-}CO)(CO)\{C(O)C_4H_3S\}(Cp)_2]$ 5a. To a stirred solution of $[Fe_2(\mu\text{-}CNMe_2)(\mu\text{-}CO)(CO)_2(Cp)_2]SO_3CF_3$ [**2a**]SO_3CF_3 (0.24 g, 0.45 mmol) in thf (15 cm^3) at −70 °C was added Lith (0.50 cm^3 of a solution 1.0 M in Et_2O). The mixture, which immediately turned dark green, was warmed to room temperature. Removal of the solvent and chromatography on an alumina column, with CH_2Cl_2 as eluent, gave a green band, which afforded dark green crystals of **5a** (78 mg, 37%) (Found: C, 51.5; H, 4.1. $C_{20}H_{19}Fe_2NO_3S$ requires C, 51.6; H, 4.1%); ν_{max}/cm^{-1} (CH_2Cl_2) 1963vs, 1771s, 1573 (CO) and 1554mw (C=N); $\delta_H(CDCl_3)$ 8.10 [1 H, dd, *J*(HH) = 3.7 and 1.1, C_4H_3S], 7.18 [1 H, dd, *J*(HH) = 5.0 and 1.1, C_4H_3S], 7.06 [1 H, dd, *J*(HH) = 5.0 and 3.7 Hz, C_4H_3S], 4.77 (5 H, s, Cp), 4.73 (5 H, s, Cp), 4.32 (3 H, s, NMe) and 4.16 (3 H, s, NMe); $\delta_C(CD_2Cl_2)$ 330.0 (μ-*C*NMe$_2$), 267.0 (μ-CO), 253.6 (COth), 211.3 (CO), 153.1, 129.6, 125.0, 124.9 (th), 86.9, 85.2 (Cp), 51.0 and 49.3 (NMe).

$[Fe_2\{\mu\text{-}CN(Me)CH_2Ph\}(\mu\text{-}CO)(CO)\{C(O)C_4H_3S\}(Cp)_2]$ 5b. Compound **5b** was prepared as described above by treating $[Fe_2\{\mu\text{-}CN(Me)CH_2Ph\}(\mu\text{-}CO)(CO)_2(Cp)_2]SO_3CF_3$ [**2b**]SO_3CF_3 (0.28 g, 0.46 mmol) with a slight excess of Lith (0.50 mmol). Yield 0.21 g, 84% (Found: C, 57.5; H, 4.3. $C_{26}H_{23}Fe_2NO_3S$ requires C, 57.7; H, 4.3%); ν_{max}/cm^{-1} (CH_2Cl_2) 1965vs, 1775s, 1563 (CO) and 1526mw (C=N); $\delta_H(CDCl_3)$ 7.70–7.44 (5 H, m, Ph), 8.05, 7.20, 7.06 (3 H, m, C_4H_3S), 6.19, 5.57 [d, *J*(AB) = 16, C*H*$_2$Ph, β isomer], *5.83*, *5.76* [d, *J*(AB) = 15 Hz, C*H*$_2$Ph, *α isomer*], *4.91*, *4.82*, 4.87, 4.74 (10 H, s, Cp, *α isomer* and β isomer), 4.73 (5 H, s, Cp), *4.09*, 4.04 (3 H, s, NMe, *α isomer* and β isomer); $\delta_C(CD_2Cl_2)$ (α and β isomers) 335.3 (μ-*C*NMe$_2$), 268.0, 260.0 (μ-CO), 255.4, 255.1 (*C*Oth), 213.6, 213.3 (CO), 156.2, 137.7, 136.7, 131.6, 131.5 (th), 137.7–127.1 (Ph) 89.1, 88.9, 87.4, 87.3 (Cp), 71.29, 69.31 (*C*H$_2$Ph), 51.3, 48.6 (NMe).

$[Ru_2(\mu\text{-}CNMe_2)(\mu\text{-}CO)(CO)\{C(O)C_4H_3S\}(Cp)_2]$ 7. This compound was prepared as described for the analogous iron complex **5a** by treating $[Ru_2(\mu\text{-}CNMe_2)(\mu\text{-}CO)(CO)_2(Cp)_2]SO_3CF_3$ [**6**]SO_3CF_3 (70 mg, 0.11 mmol) with a slight excess of Lith (0.12 mmol). Yield (23 mg, 37%) (Found: C, 43.2; H, 3.5. $C_{20}H_{19}NO_3Ru_2S$ requires C, 43.2; H, 3.4%); ν_{max}/cm^{-1} (CH_2Cl_2) 1963vs, 1782s, 1567 (CO) and 1530mw (C=N); $\delta_H(CDCl_3)$ 7.82 [1 H, dd, *J*(HH) = 3.8 and 1.1, C_4H_3S], 7.25 [1 H, dd, *J*(HH) = 5.0 and 1.1, C_4H_3S], 7.05 [1 H, dd, *J*(HH) = 5.0 and 3.8 Hz, C_4H_3S], 5.24 (5 H, s, Cp), 5.17 (5 H, s, Cp), 4.00 (3 H, s, NMe) and 3.89 (3 H, s, NMe).

Table 3 Crystal data and experimental details for [Fe_2(μ-CSMe)(μ-CS)$(CO)_2$(Cp)(η^4-C_5H_5th)] **3** and [Fe_2{μ-CN(Me)CH_2Ph}(μ-CO)(CO){C(O)th}$(Cp)_2$] **5b**

	3	**5b**
Formula	$C_{19}H_{16}Fe_2O_2S_3$	$C_{26}H_{23}Fe_2NO_3S$
M	484.20	541.21
T/K	293(2)	293(2)
λ/Å	0.710 69	0.710 69
Crystal symmetry	Orthorhombic	Monoclinic
Space group	*Pbca* (no. 61)	$P2_1/c$ (no. 14)
a/Å	10.764(2)	10.655(2)
b/Å	14.666(7)	13.415(8)
c/Å	25.175(8)	16.770(4)
β/°	90	100.55(2)
U/Å^3	3974(2)	2356(2)
Z	8	4
D_c/Mg m^{-3}	1.618	1.526
μ(Mo-K_α)/mm^{-1}	1.785	1.348
F(000)	1968	1112
Crystal size/mm	0.27 × 0.32 × 0.37	0.15 × 0.20 × 0.25
θ Limits/°	2.5–30	2.5–27
Scan mode	ω	ω
Absorption correction	Empirical *via* ψ scans	Empirical *via* ψ scans
Maximum, minimum transmission factors	0.988, 0.697	0.999, 0.783
Reflections collected	11 274 ($\pm h$, $+k$, $+l$)	5387 ($+h$, $+k$, $\pm l$)
Unique observed reflections [$F_o > 4\sigma(F_o)$], parameters (R_{int})	5769, 250 (0.020)	5098, 269 (0.034)
Goodness of fit on F^2	1.080	1.130
$R1$ (F),[a] $wR2$ (F^2)[b]	0.0344, 0.0906	0.0368, 0.0796
Weighting scheme *a*, *b*	0.0551, 1.3699[b]	0.0435, 0.0889[b]
Largest difference peak, hole/e Å^{-3}	0.561, −0.489	0.372, −0.349

[a] $R1 = \Sigma||F_o| - |F_c|/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$.

Crystallography

Crystal data and details of the data collection for complexes **3** and **5b** are given in Table 3. The diffraction experiments were carried out at room temperature on a fully automated Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo-Kα radiation. The unit-cell parameters were determined by a least-squares fitting procedure using 25 reflections. Data were corrected for Lorentz and polarization effects. No decay correction was necessary. An empirical absorption correction was applied by using the azimuthal scan method.[18]

[Fe_2(μ-CSMe)(μ-CS)$(CO)_2$(Cp)(η^4-C_5H_5th)] 3. The positions of the metal atoms were found by direct methods using the SHELXS 86 program[19] and all the non-hydrogen atoms located from Fourier-difference syntheses. One of the C_5H_5 rings was treated as a rigid group (C–C 1.42 Å) and its hydrogen atoms were included at calculated positions (C–H 0.93 Å). The Cp ring co-ordinated η^4 and bearing the C_4H_3S group was refined without constraints. The hydrogen atoms of the η^4-co-ordinated C_5H_5 ring, the thienyl ring and the methyl group were located from Fourier-difference maps and their positional parameters were allowed to refine. The final refinement on F^2 proceeded by full-matrix least-squares calculations (SHELXL 93)[20] using anisotropic thermal parameters for all the non-hydrogen atoms. The cyclopentadienyl, thienyl and methyl H atoms were assigned an isotropic thermal parameter 1.2 times U_{eq} of the carbon atoms to which they were attached.

[Fe_2{μ-CN(Me)CH_2Ph}(μ-CO)(CO){C(O)C_4H_3S}$(Cp)_2$] 5b. The structure was solved by direct methods using the SHELXS 86 program[19] and all the non-hydrogen atoms were located from Fourier-difference maps. The cyclopentadienyl rings were treated as rigid groups and their hydrogen atoms were included in calculated positions and treated using a riding model constraint with fixed isotropic displacement parameters as for **3**. The hydrogen atoms of the thienyl ring and of the methyl and the phenyl groups were located in the Fourier-difference map but calculated positions were used. The final refinement on F^2 (SHELXL 93)[20] proceeded by full-matrix least-squares calculations, thermal motion being treated anisotropically for all non-hydrogen atoms. The cyclopentadienyl, thienyl and methyl H atoms were assigned isotropic thermal parameters 1.2 times those of the attached atoms and were constrained to ride on the attached atoms.

CCDC reference number 186/757.

Acknowledgements

We thank the Consiglio Nazionale delle Ricerche, Ministero dell'Universita'e della Ricerca Scientifica e Tecnologica and the University of Bologna (projects 'Sintesi Modelli e Caratterizzazione per Materiali Funzionali' and 'Molecole ed Aggregati Molecolari Intelligenti') for financial support.

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Received 22*nd July* 1997; *Paper* 7/05245F