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Journal of Organometallic Chemistry 659 (2002) 15–21

Journal of Organo metallic Chemistry

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Dithiocarbamate derivatives of μ-thiocarbyne complexes: synthesis and X-ray molecular structure of $[Fe_2(\mu\text{-}CS)(\mu\text{-}CSMe)(\mu\text{-}S_2CNMe_2)Cp_2]$

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Received 20 May 2002; received in revised form 18 June 2002; accepted 18 June 2002

Abstract

Reaction of $[Fe_2(\mu\text{-}CS)(\mu\text{-}CSMe)Cp_2(CO)_2]^+$ (**1**) with sodium *N*,*N*-dimethyldithiocarbamate [Me$_2$dtc]Na affords a mixture of the dithiocarbene $[Fe\overline{Fe(\mu\text{-}CS)\{\mu\text{-}C(SMe)S}C(S)NMe_2\}Cp(CO)]$ (**2**) and the thiocarbyne $[Fe_2(\mu\text{-}CS)(\mu\text{-}CSMe)(\mu\text{-}S_2CNMe_2)Cp_2]$ (**3**). Complex **2** is quantitatively converted into **3** by photochemical irradiation. The X-ray molecular structure of **3** demonstrates the presence of three bridging ligands and exhibits the shortest Fe–Fe interaction found in similar systems [2.453(1) Å]. Complex **3** can also be obtained by reacting $[Me_2dtc]^-$ with the di-solvento thiocarbyne $[Fe_2(\mu\text{-}CS)(\mu\text{-}CSMe)(NCMe)_2Cp_2]^+$ (**1a**). By contrast no stable addition product has been isolated in analogous reactions involving the thiocarbyne $[Fe_2(\mu\text{-}CO)(\mu\text{-}CSMe)Cp_2(CO)_2]^+$ (**1b**). The $[Me_2dtc]^-$ nucleophilic addition at the μ-C to form $[Fe_2(\mu\text{-}CO)\{\mu\text{-}C(CN)SC(S)NMe_2\}Cp_2(CO)_2]$ (**4a**) is obtained starting from $[Fe_2(\mu\text{-}CO)\{\mu\text{-}C(CN)(SMe_2)\}Cp_2(CO)_2]SO_3CF_3$ (**1d**). Photochemical reaction of the cyanocarbene **4a** causes intramolecular ring closure affording $[Fe\overline{Fe(\mu\text{-}CO)\{\mu\text{-}C(CN)S}C(S)NMe_2\}Cp_2(CO)]$ (**5a**). © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Dithiocarbamate; Thiocarbyne; Dithiocarbene; Bridging; Dinuclear; Iron

1. Introduction

Dithiocarbamates are the subject of current research due to their potential applications and interesting coordination behaviour. They easily form chelate rings with virtually all transition elements affording a plethora of monomeric complexes [1,2]. However, binuclear species, containing these bidentate ligands symmetrically bridging two metal centres, are relatively rare [2]. To our knowledge few examples of discrete molecules have so far been reported: $[Ru_2(Et_2dtc)_5]BF_4$ [3], binuclear diauracycles as $[Au_2(\mu\text{-}R_2dtc)dppm]\text{-}BH_3CN$ [4] (dppm = $PPh_2CH_2PPh_2$, R = Et, Me, CH_2Ph) $[Au_2\{(\mu\text{-}CH_2)_2PPh_2\}(\mu\text{-}R_2dtc)]$ and $[Au_2(\mu\text{-}R_2dtc)_2]$ [5], and, more recently, the $[Rh_2(CO)_2(NBD)(RR'dtc)_2]$ (R = Me, R′ = Ph) [6] (NBD = norbornadiene).

During our investigations on the chemistry of diiron-thiocarbyne complexes of the type $[Fe_2(\mu\text{-}CX)(\mu\text{-}CSMe)Cp_2(CO)_2]OSO_2CF_3$ [X = S (**1a**); O (**1b**)], 7a[7b,7c] we have observed that substitution of the bridging carbonyl by a thiocarbonyl ligand confers different reactivity trends, likely arising from the higher $Fe_2\text{–}(\mu\text{-}CS)$ bond order, compared with $Fe_2\text{–}(\mu\text{-}CO)$ [8]. This property is here evidenced by the ability, shown by [Me$_2$dtc] anion, to differently react and/or coordinate the dimetal–carbyne complexes of type **1**. In fact when X = S we have succeeded in isolating the air stable complex $[Fe_2(\mu\text{-}CS)(\mu\text{-}CSMe)(\mu\text{-}S_2CNMe_2)Cp_2]$ (**3**), via the unstable species $[Fe\overline{Fe(\mu\text{-}CS)[\mu\text{-}C(SMe)SC(S})$

Abbreviations: dppm, $Ph_2P(CH_2)PPh_2$; $[Me_2dtc]^- = [Me_2NCS_2]^-$, dithiocarbamate; NBD, norbornadiene or bicyclo[2.2.1]hepta-2,5octene; ^{i}Pr, isopropyl.

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PII: S0022-328X(02)01652-2

$\mathrm{NMe_2(Cp)(CO)}]$ (**2**), whereas, in the case of the carbonyl analogues (X = O), the reaction with $[\mathrm{Me_2dtc}]^-$ results in a progressive degradation to the thiocarbonyl species $[\mathrm{Fe_2(\mu\text{-}CO)(\mu\text{-}CS)Cp_2(CO)_2}]$. The X-ray molecular structure of **3** provides a further report of a two-metal-centres symmetrical bridging dithiocarbamate complex [3–5].

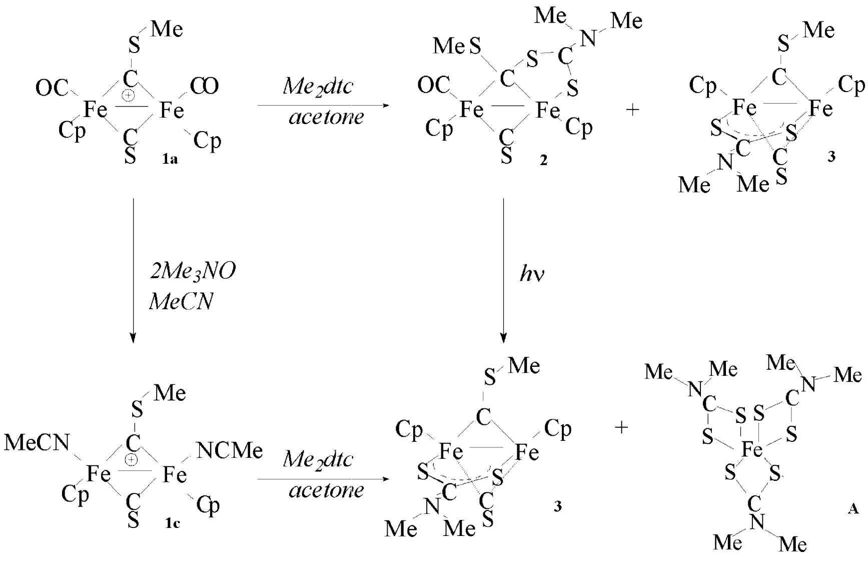
2. Results and discussion

2.1. Reactions of μ-carbyne complexes with dithiocarbamate

When an equimolar amount of sodium dimethyldithiocarbamate is added at room temperature to a bright green solution of the cationic derivative *cis*-$[\mathrm{Fe_2(CO)_2Cp_2(\mu\text{-}CS)(\mu\text{-}CSMe)}]^+$ (**1a**) in acetone, a brown cloudy mixture is rapidly formed. Chromatography on alumina column yields two main products (Scheme 1). The solvent-freed second fraction shows only a single sharp IR carbonyl absorption at 1956 $\mathrm{cm^{-1}}$ and the ν(CN) stretching band at 1506 $\mathrm{cm^{-1}}$, suggesting its formulation as $[\mathrm{Fe}\overline{\mathrm{Fe}(\mu\text{-}\mathrm{CS})\{\mu\text{-}\mathrm{C(SMe)S}}\,\mathrm{C(S)NMe_2}\}\mathrm{Cp_2(CO)}]$ (**2**). The observation, in the NMR spectra, of signals corresponding to nonequivalent Cp ligands together with the bridging μ-C dithiocarbene and thiocarbonyl carbons, at 170.6 and 393.4 ppm, respectively, agrees with the proposed structure. Moreover, the ^{1}H-NMR chemical shift at 2.98 ppm attributable to the SMe substituent, rules out the possible structure $[\mathrm{Fe}\overline{\mathrm{Fe}(\mu\text{-}\mathrm{CS})\{\mu\text{-}\mathrm{C(S}}\mathrm{Me)SC(S)N\text{-}Me_2}\}\mathrm{Cp_2(CO)}]$, which would exhibit a more upshifted signal, as already found for compounds in which the S-atom of the thioalkoxy group is metal coordinated [7c,8]. Finally, the diasterotopicity of the N–Me groups is evidenced by distinct ^{13}C signals (at 47.6 and 43.4 ppm), while a broad resonance at 3.1 ppm is observed in the ^{1}H-NMR. The first eluted fraction has been identified as $[\mathrm{Fe_2(\mu\text{-}CS)(\mu\text{-}CSMe)(\mu\text{-}S_2CNMe_2)Cp_2}]$, (**3**) (10% yield), in which both the CO ligands of **1a** have been substituted by the bidentate dithiocarbamate ligand. An exiguous third purple fraction, containing traces of the known $\mathrm{Fe(Me_2dtc)_3}$ (less than 3%), has been characterised by literature data comparison [9]. Further experiments, run at low temperatures with prolonged reaction times give similar products distribution.

The reaction depicted in Scheme 1 presumably takes place by nucleophilic addition of $[\mathrm{Me_2dtc}]^-$ to the electrophilic bridging carbon atom μ-CSMe. Then, the supposed dithiocarbene intermediate evolves with formation of the σ Fe–S bond, affording complex **2**. Nevertheless, the latter is still a rather unstable species and, on standing for a few hours in dichloromethane solution, partially turns into the thiocarbyne derivative $[\mathrm{Fe_2(\mu\text{-}CS)(\mu\text{-}CSMe)(\mu\text{-}S_2CNMe_2)Cp_2}]$ (**3**). The latter exhibits IR bands attributed to the μ-CS bridging group (1116 $\mathrm{cm^{-1}}$) and CN stretching (1492 $\mathrm{cm^{-1}}$) but no CO absorption. Single ^{1}H-NMR resonances both for cyclopentadienyl (δ 4.77) and N–Me groups (δ 3.2) and the presence, as peculiar spectroscopic feature, of signals at δ 3.52 (^{1}H-NMR) and 408 (^{13}C-NMR) relative to μ-CSMe moiety, point to a symmetrically bridging dithiocarbamate coordination, as shown by the X-ray diffraction structural study (see later).

The unusual **2** to **3** transformation, which quantitatively occurs under photochemical conditions (Scheme 1), is likely driven by the formation of a strong iron–iron interaction, due to the simultaneous presence of three bridging ligands, and by the favourable entropic



Scheme 1.

balance of the CO elimination. In addition, it should be pointed out that an analogous thiocarbene-thiocarbyne rearrangement with C–S bond breaking and migration of the thioalkoxy group, has already been observed for [Fe_2(μ-CO){μ-C(SMe)SPh}$Cp_2(CO)_2$], which affords the carbonyl-substituted derivative [Fe_2(μ-CO){μ-C(SMe)}Cp_2(CO)(SPh)] in refluxing CH_2Cl_2 [10].

It is worth noting that the ^{13}C-NMR set of signals of the neutral μ-carbyne **3** are only slightly upfield shifted with respect to the cationic precursor **1a**, in line with what reported for similar compounds [10]. This observation supports the idea that a certain charge separation persists in **3**, according to the ylide resonance formula (Fig. 1). An analysis of the bond distances agrees with this consideration (see later).

Complex **3** has also been prepared from the solvento complex [Fe_2(μ-CS)(μ-CSMe)$Cp_2(NCMe)_2$]$^+$ (**1c**). This novel acetonitrile derivative has been obtained as brown powder by replacing both the CO groups of **1a** in MeCN solvent in the presence of Me_3NO (Scheme 1). Single ^{13}C-NMR resonances at δ 87.3 (Cp) and 126.3 (NCMe) for terminal ligands suggest the retention of *cis* stereogeometry, while the dinuclear structure is confirmed by the observation of both the bridging thiocarbonyl (δ 388.3) and thiocarbyne μ-C (δ 413.3) signals. Addition of a slight excess of dithiocarbamate to an acetone solution of the solvento complex (**1c**) promptly affords the [Fe_2(μ-CS)(μ-CSMe)(μ-S_2CNMe_2)Cp_2] (**3**) in 59% yield (Scheme 1) together with the formation of the known Fe(Me_2dtc)$_3$ (30%), which has been separated by column chromatography.

The observation that the thiocarbyne complex [Fe_2(μ-CO)(μ-CSMe)Cp_2 $(CO)_2$]OSO_2CF_3 (**1b**) undergoes addition to μ-CSR by a variety of nucleophiles including SR^- [10–12] to give the corresponding thiocarbene derivatives, has prompted us to extend the reactivity investigation to dithiocarbamates. In this case, however, we have been unable to isolate stable addition products. In fact, the reaction of **1b** with [Me_2dtc]$^-$ even at 0 °C leads to the formation of the mononuclear [Fe(η_2-S_2CNMe_2)Cp(CO)] [13] together with the thiocarbonyl dimeric complex [Fe_2(μ-CO)(μ-CS)$Cp_2(CO)_2$] [14]. Our inability to isolate addition products of $^-$[SC(S)NMe_2] to μ-C probably arises from the ease with which these species undergo decomposition, via C–SR bond rupture, facilitated by the presence of the μ-CO instead of the more stabilising μ-CS group.

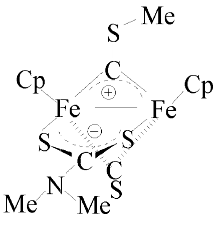
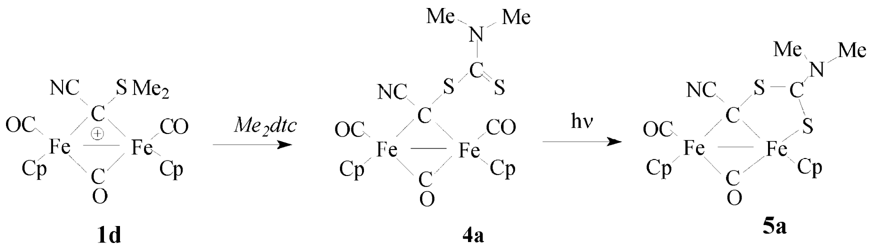


Fig. 1. Ylidic resonance form of [Fe_2(μ-CS)(μ-CSMe)(μ-S_2CNMe_2)$(Cp)_2$].

In line with our previous findings, testifying the general approach of the bridging carbene diiron complexes bearing heteroatom substituent [15], we have obtained [Fe_2(μ-CO){μ-C(CN)SC(S)NRR′}$Cp_2(CO)_2$] [R = R′ = Me (**4a**); R = H, R′ = ^{i}Pr (**4b**)] by reacting the dithiocarbamate anion with the pseudo–cyanocarbyne complex [Fe_2(μ-CO){μ-C(CN)(SMe_2)}Cp_2-$(CO)_2$]OSO_2CF_3 (**1d**), as a result of SMe_2 displacement. The broad ^{1}H-NMR signal attributed to the N–Me groups, due to hindered rotation around the CN bond, becomes a single sharp singlet as the temperature raises to 46 °C. The *cis* stereogeometry of **4** (νCO 2011vs, 1982m) is confirmed by a single cyclopentadienyl resonance (δ 4.7 in the case of **4b**). The stability of these species further confirms that the electron withdrawing effect of the cyano group [15] results in a neat stabilisation of the thiocarbene derivatives. Therefore, it has been necessary UV irradiation of type **4** complexes to promote S–Fe bond formation and to obtain [FeFe(μ-CO){μ-C(CN)SC(S)NRR′}Cp_2(CO)] [R = R′ = Me (**5a**); R = H, R′ = ^{i}Pr (**5b**)]. The IR stretching of the remaining carbonyl ligand in type **5** complexes sensibly moves to lower wavenumbers [1957 cm^{-1} for **5b**]. The intramolecular cyclization gives rise to distinct ^{1}H-NMR signals (δ 3.2 and 3.1) for the N–Me diasteroisomeric groups arising from the hindered rotation around the dithiocarbamate CN bond. Sulphur coordination, enhancing the electron density onto the metal skeleton, is responsible for the marked upfield shift of the ^{13}C-NMR carbene resonance from δ 128.8 (in **4a**) to 105.7 ppm (in **5a**) (Scheme 2).

2.2. The X-ray molecular structure of [Fe_2(μ-CS)(μ-CSMe){μ-S_2CNMe_2}Cp_2] (3)

An ORTEP drawing of **3** is shown in Fig. 2 and relevant bond parameters are reported in Table 1. The molecule contains a diiron unit coordinated by the C_5H_5 ligands in the expected *cis* configuration and three bridging ligands. The thiocarbonyl and thiomethoxy groups are positioned almost opposite to each other (dihedral angle 15.08°) and the dithiocarbamate, acting as bidentate, is almost orthogonal to the other bridging ligands. The latter ligand occupies the sites of the terminal CO groups in the precursor cation **1**. The Fe–Fe distance [2.453(1) Å] is quite short in comparison with the numerous experimental values reported for this family of compounds. The actual value falls at the lower limit of the following trend: [Fe_2(μ-CO)$_2$(CO)$_2$(Cp)$_2$] 2.531(2) [16a], [Fe_2(μ-CO)(μ-CSEt)(CO)$_2$(Cp)$_2$)]$^+$ 2.510(2) [16b], [Fe_2(μ-CS)(μ-CSMe)(CO)$_2$(Cp)(η^4-C_5H_5th)] 2.508(1) 8b, [Fe_2(μ-CO)(μ-CS)(CO)$_2$(Cp)$_2$] 2.505 (3) [16c], [Fe_2(μ-CS)$_2$(CO)$_2$(Cp)$_2$] 2.482(1) Å



Scheme 2.

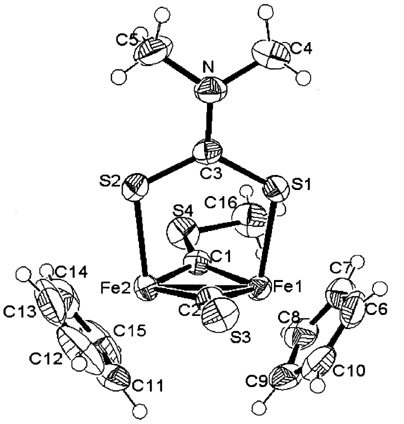


Fig. 2. Molecular structure of **3** showing the atomic numbering (thermal ellipsoids at 50% probability level).

Table 1
Relevant bond distances (Å) and angles (°) for $[Fe_2(\mu\text{-}CS)(\mu\text{-}CSMe)\{\mu\text{-}S_2CNMe_2\}(Cp)_2]$ (**3**)

Bond lengths			
Fe(1)–Fe(2)	2.453(1)	S(1)–C(3)	1.716(3)
Fe(1)–C(1)	1.806(3)	S(2)–C(3)	1.712(3)
Fe(1)–C(2)	1.881(3)	S(3)–C(2)	1.616(3)
Fe(1)–S(1)	2.259(1)	S(4)–C(1)	1.676(3)
Fe(2)–C(1)	1.813(3)	S(4)–C(16)	1.811(4)
Fe(2)–C(2)	1.865(3)	N–C(3)	1.340(4)
Fe(2)–S(2)	2.265(1)	N–C(4)	1.454(5)
Fe(1)–C(Cp)	2.14(1) av	N–C(5)	1.455(5)
Fe(2)–C(Cp)	2.12(2) av		
Bond angles			
C(1)–Fe(1)–C(2)	95.2(1)	S(2)–Fe(2)–Fe(1)	97.85(3)
C(1)–Fe(1)–S(1)	89.5(1)	C(3)–S(1)–Fe(1)	111.5(1)
C(2)–Fe(1)–S(1)	88.3(1)	C(3)–S(2)–Fe(2)	110.4(1)
S(1)–Fe(1)–Fe(2)	96.58(3)	S(4)–C(1)–Fe(1)	143.2(2)
C(1)–Fe(2)–C(2)	95.5(1)	S(4)–C(1)–Fe(2)	131.4(2)
C(1)–Fe(2)–S(2)	90.3(1)	Fe(1)–C(1)–Fe(2)	85.4 (1)
C(2)–Fe(2)–S(2)	89.1(1)	S(3)–C(2)–Fe(1)	138.0(2)
S(3)–C(2)–Fe(2)	140.2(2)	S(1)–C(3)–S(2)	123.6(2)
Fe(1)–C(2)–Fe(2)	81.8(1)	C(3)–N–C(4)	122.1(3)
N–C(3)–S(1)	117.8(2)	C(3)–N–C(5)	122.4(3)
N–C(3)–S(2)	118.5(2)	C(4)–N–C(5)	115.4(3)

[16d]. As one can infer from the figures above, μ-CS replacing μ-CO has a shortening effect on the Fe–Fe interaction. Substitution of the bidentate dithiocarbamate for two terminal COs produces a further strenghtening of the Fe–Fe interaction, very probably because of the different balance of σ and π components of the bonds for the two ligands. This effect, although small, is significant also because the S···S bite distance in the dithiocarbamate [3.02 Å] would better fit a longer metal–metal bond. A database search [17] of the metal–metal distances spanned by bridging dithiocarbamate ligands confirms that the present Fe–Fe interaction is the shortest ever found.

It is noteworthy the presence in this molecule of four types of sulphur–carbon bonds ranging from the multiple bond of the bridging thiocarbonyl [S(3)–C(2) 1.616(3) Å] to the pure single bond [S(4)–C(16)(methyl) 1.811(4) Å]. The former is a pure double bond because an analysis of the $R_2C{=}S$ distances found in thioketones reveals values in the range 1.61–1.64 Å. The S(4)–C(1) bond in the thiocarbyne ligand [1.676(3) Å], being closer to the distance in the thiocarbonyl than the S–C(alkyl), indicates substantial multiple bond explainable in terms of donation from a sulphur lone pair to the empty p-orbital of the formally positive C(1) carbon. This π interaction significantly extends to the iron atoms, as shown by the shorter Fe–C(1)(carbyne) average distance [1.809(3) Å] in comparison to Fe–C(2)(thiocarbonyl) [1.873(4) Å].

The dimethyldithiocarbamate ligand exhibits a regular geometry with significant multiple bond character of the S–C [average 1.714(3) Å] and C–N [1.340(4) Å] interactions, as one can infer from a comparison with the genuine single bonds S(4)–C(16)(methyl) [1.811(4) Å] and N–C(4,5)(methyl) [1.454(5) Å]. These distances are well within the range of values reported in the copious structural reports of the dithiocarbamate ligands in a variety of bonding modes.

3. Experimental

3.1. General methods

Standard inert-atmosphere techniques have been used in the execution of the experiments. The solvents methylene chloride (CaH_2), tetrahydrofuran (Na–benzophenone), and petroleum ether 40–70 °C were distilled immediately before use under nitrogen from the appropriate drying agents. Complex **1a** was prepared as previously reported [7,14]. $[Me_2NCS_2]Na$ was obtained from commercial sources and dried under vacuum for 2 h at 100 °C. Instruments employed: IR, FT Perkin–Elmer Spectrum 2000, NMR Varian Gemini 200 MHz. Spectra were registered at room temperature (r.t.), solvent peaks were used as internal reference, the chemical shifts are reported in δ (ppm) relative to TMS.

3.2. Reaction with $[Fe_2(\mu\text{-}CS)(\mu\text{-}CSMe)Cp_2(CO)_2]$ *(2)*

To a solution of *cis*-**1a** (0.230 g, 0.418 mmol) in acetone (10 ml) an equimolar amount of $[Me_2dtc]Na\cdot 2H_2O$ (0.076 g,0.42 mmol) was added. The initially bright green solution in 15 min changed into deep brown. The solvent was removed under reduced pressure, the residue extracted and chromatographed on an alumina column (8 × 2 cm) with a mixture of methylenechloride and petroleum ether (40–70 °C) (2:1 = v:v). A minor brown–yellow fraction (20 mg, 10% yield of **3**) and a second deep orange one (**2**) were collected and dried under vacuum. Traces of the known $Fe_3(Me_2dtc)_3$ (**A**) were obtained from the third purple band collected. Crystallisation from methylene chloride–petroleum ether at −20 °C gave brown needles of **2** (0.072 g, 0.15 mmol 35% yield). Melting point (m.p.) 162–165 °C. Elemental Analysis: C, 41.4(42.3); H, 3.9(4.5); S, 25.9(25.6)%. IR (in CH_2Cl_2): 1956s (CO), 1506m, 1391m (NCS), 1112s (CS); (in KBr): 1956vs (CO), 1503m, 1385m, 1003w (NCS), 1107s (CS), 1051m (CSMe). ^1H-NMR ($CDCl_3$) δ (ppm): 2.98(s, 3H CSMe), 4.89, 4.69 (s, 10H, Cp), 3.10 (br, 6H, NMe_2); $^{13}C\{^1H\}$ ($CDCl_3$): 393.4 (μ-CS), 214.7 (CO), 92.3, 90.9 (Cp), 170.6 (μ-C), 35.8 (SMe), 205.6 (*C*N), 47.6, 43.4 (NMe_2).

3.3. Preparation of $[Fe_2(\mu\text{-}CS)(\mu\text{-}CSMe)\{\mu\text{-}S_2CNMe_2\}Cp_2]$ *(3)*

To a stirring solution of **1a** (200 mg, 0.364 mmol) in acetonitrile (20 ml) were added two equivalents of Me_3NO (55 mg, 0.73 mmol). The initially deep green solution immediately changed to brown–yellow. After 15 min, when IR detection revealed loss of both the carbonyl groups, the solvent was removed under reduced pressure. The residue was then extracted with CH_2Cl_2 and immediate filtration on celite pad was necessary to prevent considerable decomposition.

Washing with Et_2O (2 × 5 ml) gave a brown–yellow powder (189 mg, 0.327 mmol, 90% yield) of **1c**. IR (CH_2Cl_2): 1031 (*s*, CSMe); $^{13}C\{^1H\}$ ($CDCl_3$): 388.3 (μ-CS), 87.3 (Cp), 413.3 (μ-C), 40.7 (SMe), 126.3 (CNMe). A slight excess of a solution of $Me_2NCS_2Na\cdot 2H_2O$ (107 mg, 0.6 mmol) in acetone (5 ml) was added to $[Fe_2(\mu\text{-}CS)(\mu\text{-}CSMe)Cp_2(NCMe)_2]OSO_2CF_3$ (**1c**) (0.52 mmol 300 mg) dissolved in the same solvent and stirred at r.t. for 30 min, until the reaction mixture turned from yellow to brown. The solvent-freed residue was then chromatographed on alumina column (8 × 2 cm) eluting with CH_2Cl_2–petroleum ether (30–40 °C) (2:1 = v:v). Two fractions, showing no carbonyl bands in their IR spectrum, were collected. The first brown band, gave by crystallisation from CH_2Cl_2–hexane at low temperature −20 °C (102 mg 0.218 mmol, 59% yield) of **3**. M.p. (dec.) 188–192 °C. Elemental Analysis: C, 41.3(41.8); H, 4.1 (4.3); S, 27.7(27.9)%. IR (CH_2Cl_2 in cm^{-1}): 1116s (CS), 1491m, 1374s (CN); (KBr): 1118 (CS), 1058m (CSMe), 1492m, 1370m, 1004s (NCS). ^1H-NMR ($CDCl_3$, δ in ppm): 3.52 (s, 3H, CSMe), 4.77(s, 10H, Cp), 3.19 (s, 6H, NMe_2). $^{13}C\{^1H\}$ (CD_2Cl_2): 393.7 (μ-CS), 408.0 (μ-CSMe), 201.9 (CN), 91.8 (Cp), 47.6 (NMe_2), 31.3 (SMe). Crystallisation of the second purple band yielded 46 mg (0.111 mmol, 30%yield) of the known $Fe(S_2CNMe_2)_3$ (**A**).

3.4. Preparation of $Fe_2(\mu\text{-}CO)\{\mu\text{-}C(CN)(SC(S)NRR')\}(Cp)_2(CO)_2]$ *[R, R′ = Me (**4a**); R = ^{i}Pr, R′ = H (**4b**)]*

$[Fe_2(\mu\text{-}CO)\{\mu\text{-}C(CN)(SMe_2)\}Cp_2(CO)_2]SO_3CF_3$ (**1d**) (80 mg, 0.135 mmol) dissolved in acetonitrile (5 ml) were stirred at r.t. with a slight excess of $Na[Me_2NCS_2]\cdot 2H_2O$ (40 mg). The reaction was monitored by IR spectroscopy. After 30 min the solvent was extracted under reduced pressure and the residue filtered on alumina pad by using dichloromethane as eluant. Crystallisation from CH_2Cl_2–petroleum ether gave 72 mg of bright red crystals (0.128 mmol, 95%) of **4a**, m.p. (dec.) 141–144 °C. IR (CH_2Cl_2 cm^{-1}): 2163w (CN), 2005vs, 1972m, 1807s (CO), 1495 (CNR_2 in KBr). ^1H-NMR ($CDCl_3$, δ in ppm): 5.05 (s, 10H, Cp), 3.55, 3.30 (d, br, 6H, NMe_2). $^{13}C\{^1H\}$ (CD_2Cl_2): 262.6 (μ-CO), 209.1 (CO), 200.0 (CS_2), 128.8 (CN), 91.8 (Cp), 47.6 (NMe_2); **4b**, m.p. 143–144 °C. IR (CH_2Cl_2 cm^{-1}): 2011vs, 1982m (CO), 1815s (μ-CO), 2158w (CN), 1492 (CNR_2 in KBr). ^1H-NMR ($CDCl_3$, δ in ppm): 6.9 (s, br, 1H, NH), 4.6 (m, 1H, CH), 4.7 (s, 10H, Cp), 1.2 (m, br, 6H, NMe_2).

3.5. Preparation of $[Fe\overline{Fe(\mu\text{-}CO\{[\mu\text{-}C(CN)SC(S}) NRR')\}Cp_2(CO)]$ *[R, R′ = Me (**5a**); R = ^{i}Pr, R′ = H (**5b**)]*

THF solutions (5 ml) of **5a**,**b** (100 mg, 0.18 mmol for **5a**) were irradiated under UV lamp following the reaction trend by IR spectroscopy. After 20 min the solvent was evaporated and the residue, dissolved in dichloromethane and chromatographed on alumina column (8 × 2 cm.) using CH_2Cl_2–petroleum ether (1:2 = v:v) as eluant. The first brown fraction collected was recognised as the known $[Fe(\mu\text{-}S_2CNMe_2)Cp(CO)]$ (IR *v* 1940 CO); the second brown fraction was collected and crystallised at low temperature (−20 °C) giving 53

Table 2
Crystal data and details of structure refinement for complex **3**

Empirical formula	$C_{16}H_{19}Fe_2NS_4$
Formula weight	465.26
Temperature (K)	293
Wavelength (Å)	0.71069
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions (Å)	
a	8.674(2)
b	16.827(3)
c	12.638(3)
β (°)	93.12(3)
Volume (Å^3)	1841.9
Z	4
$F(000)$	952
Crystal size (mm)	0.25 × 0.13 × 0.32
Max θ for data collection (°)	25
Number of reflections collected	3392
Number of observed independent reflections	3222
Number of parameters	322
Goodness-of-fit on F^2	1.03
Final R indices [$I > 2\sigma(I)$]	0.0335 (R) 0.089 (wR^2)
Largest difference peak and hole (e Å^{-3})	0.26, −0.15

mg (0.10 mmol, 51% yield). Complex **5a**, IR (CH_2Cl_2 in cm^{-1}): 1955 (CO), 1776 (μ-CO), 2163 (CN), 1526 (CN in KBr). ^{1}H-NMR ($CDCl_3$ in cm^{-1}, δ in ppm): 4.7, 4.5 (s, 10H, Cp), 3.1, 3.2 (s, br, 6H NMe_2).^{13}C{^{1}H} 273.3 (μ-CO), 213.3 (CO), 207.8 (CS_2), 134.4 (CN), 105.7 (μ-C), 89.1, 87.0 (Cp), 75.2, 75.6 (NMe_2). Complex **5b**, IR (CH_2Cl_2 in cm^{-1}): 1957 (CO), 1777(μ-CO), 1528 (CN in KBr). ^{1}H-NMR ($CDCl_3$, δ in ppm): 6.7 (s, br, 1H, NH), 4.7 4.6 (Cp), 3.6 (m, br, 1H, CH), 1.1 (m, br, 6H, NMe_2).

3.6. X-ray crystallography

Crystals of **3** suitable for the X-ray single crystal diffraction studies were grown from CH_2Cl_2–hexane at low temperature (−20 °C). Diffraction intensities were collected at r.t. on an Enraf–Nonius CAD-4 diffractometer using graphite monochromated Mo–K_α radiation. Data were collected using ω scanning mode and corrected for absorption empirically. Crystal data and details of structure refinement are reported in Table 2. Structure was solved by direct methods and refined on F^2 by full-matrix least-squares calculations using the SHELXTL/PC package 17b. Thermal vibrations were treated anisotropically for all non-H atoms; cyclopentadiene rings were refined as rigid groups [C–C 1.42 Å]. H atoms were located in the final difference Fourier maps and refined riding on their corresponding carbon atoms [C–H 0.96 Å for CH_3 and 0.93 Å for C_5H_5]. Refinement converged at a final $R = 0.0335$. Molecular graphics were prepared using ORTEP3 for WINDOWS NT [17c].

4. Supplementary material

Crystallographic data (excluding structure factors) for the reported structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 168588. Copies of data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336093; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We acknowledge the University of Bologna and MIUR for financial support.

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