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Acetonitrile activation in di-iron μ-carbyne complexes: synthesis and structure of the cyanomethyl complex $[Fe_2(\mu\text{-}CNMe_2)(\mu\text{-}CO)(CO)(CH_2CN)(Cp)_2]$

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Abstract

Reactions of $[Fe_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(CO)(NCMe)(Cp)_2]SO_3CF_3$ (R = Me, **2a**; CH_2Ph, **2b**; 2,6-$Me_2C_6H_3$ **2c**) with $LiBu^n$ afford the corresponding cyanomethyl complexes $[Fe_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(CO)(CH_2CN)(Cp)_2]$ (**3a**–**c**), presumably via deprotonation and rearrangement of the coordinated acetonitrile. Likewise, the benzylnitrile complex $[Fe_2\{\mu\text{-}CN(Me)(2,6\text{-}Me_2C_6H_3)\}(\mu\text{-}CO)(CO)(NCCH_2Ph)(Cp)_2]SO_3CF_3$ yields $[Fe_2\{\mu\text{-}CN(Me)(2,6\text{-}Me_2C_6H_3)\}(\mu\text{-}CO)(CO)(CH(CN)Ph)(Cp)_2]$ (**3d**). The X-ray molecular structure of **3a** has shown the expected stereogeometry and significant asymmetry of the bridging ligands. Deprotonation and rearrangement of the coordinated MeCN are not observed in the thiocarbyne complex $[Fe_2(\mu\text{-}CSMe)(\mu\text{-}CO)(CO)(NCMe)(Cp)_2]SO_3CF_3$ (**5**) in spite of the similarities with **2a**–**c**. However, compound **5** readily reacts with $Li_2Cu(CN)R_2$ (R = Me, Ph) to form the thiocarbene complexes $[Fe\overline{Fe\{\mu\text{-}C(R)}Sme\}(\mu\text{-}CO)(CO)(Cp)_2]$ (**6a**–**b**), with displacement of the acetonitrile ligand. © 2002 Published by Elsevier Science B.V.

Keywords: Acetonitrile; Carbyne complexes; Thiocarbene complexes; Crystal structures; Dinuclear

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1. Introduction

Metal coordinated nitriles are generally considered substitution labile ligands. Therefore, nitrile-containing complexes have been often considered equivalent for the coordinatively unsaturated species, thus providing convenient precursors in organometallic syntheses and catalysis [1]. Examples include the diruthenium complexes $[Ru_2(\mu\text{-}CH_2)_n(CO)_{3-n}(NCMe)(Cp)_2]$ ($n = 1, 2$), in which the presence of acetonitrile has been proven crucial in order to induce C–C coupling reactions of the alkylidene ligand with unsaturated hydrocarbons and diazoalkanes [2]. We have recently shown that replacement of CO by MeCN in the diiron μ-aminocarbyne complexes $[Fe_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(CO)_2(Cp)_2]SO_3CF_3$ (R = Me, **1a**; CH_2Ph, **1b**; 2,6-$Me_2C_6H_3$, **1c**) results in a significant change in the reactivity pattern towards nucleophiles [3]. Addition of cyanide or hydride anions is known to occur at the carbyne carbon of **1a**–**c**, affording the alkylidene compounds $[Fe_2\{\mu\text{-}C(CN)N(Me)R\}(\mu\text{-}CO)(CO)_2(Cp)_2]$ and $[Fe_2(\mu\text{-}CO)_2\{C(H)N(Me)R\}(CO)(Cp)_2]$, respectively [4]. By contrast, the corresponding acetonitrile complexes $[Fe_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(CO)(NCMe)(Cp)_2]SO_3CF_3$ (**2a**–**c**) react with H^- and CN^- leading to the displacement of MeCN with formation of $[Fe_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}H)(CO)_2(Cp)_2]$ and $[Fe_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(CO)(CN)(Cp)_2]$, respectively [3]. Likewise, it has been shown that acetonitrile can be easily replaced by phosphines in the complexes $[Fe_2\{\mu\text{-}CNMe_2\}_2(CO)(NCMe)(Cp)_2](SO_3CF_3)_2$ [5].

In spite of their lability, coordinated nitriles can themselves undergo nucleophilic addition [6]. Here we report on the reactions of type **2** complexes towards carbon nucleophiles, which are also strong bases. Our results indicate that, in these conditions, nitrile ligands, activated by metal coordination, undergo deprotona-

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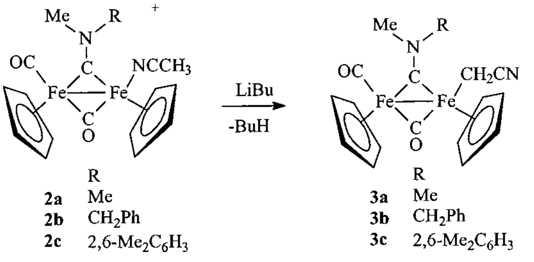
tion and an unusual rearrangement to cyanomethyl complexes.

2. Results and discussion

The reactions of compounds **2a–c**, in thf at −10 °C, with butyl-lithium afford the corresponding cyanomethyl complexes $[Fe_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(CO)(CH_2CN)(Cp)_2]$ (**3a–c**) (Scheme 1), which have been isolated in good yields after column chromatography.



Scheme 1.

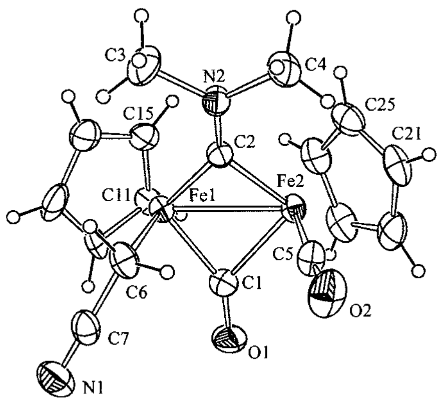


Fig. 1. ORTEP drawing of $[Fe_2(\mu\text{-}CNMe_2)(\mu\text{-}CO)(CO)(CH_2CN)(Cp)_2]$ (**3a**) (thermal ellipsoids are drawn at 30% probability).

Table 1
Selected bond lengths (Å) and angles (°) for $[Fe_2\ (\mu\text{-}CNMe_2)(\mu\text{-}CO)(CO)(CH_2CN)(Cp)_2]$ (**3a**)

Bond lengths			
Fe(1)–Fe(2)	2.502(1)	C(2)–N(2)	1.299(3)
Fe(1)–C(1)	1.852(3)	N(2)–C(3)	1.456(5)
Fe(2)–C(1)	2.003(3)	N(2)–C(4)	1.463(4)
Fe(1)–C(2)	1.843(2)	Fe(1)–C(6)	2.068(3)
Fe(2)–C(2)	1.886(3)	C(6)–C(7)	1.425(5)
C(7)–N(1)	1.142(5)	C(1)–O(1)	1.160(4)
C(5)–O(2)	1.147(4)	Fe(2)–C(5)	1.749(3)
Fe(2)–C(Cp)(av)	2.12	Fe(1)–C(Cp) [a](av)	2.10
Bond angles			
Fe(1)–C(1)–N(2)	140.2(2)	N(1)–C(7)–C(6)	176.4(4)
Fe(2)–C(2)–N(2)	135.4(2)	C(3)–N(2)–C(4)	114.0(3)
Fe(1)–C(1)–O(1)	145.7(3)	C(2)–N(2)–C(3)	122.9(3)
Fe(2)–C(1)–O(1)	133.3(3)	C(2)–N(2)–C(4)	123.1(3)

[a] Main image (see Section 3).

The structure of **3a**, ascertained by an X-ray diffraction experiment, is shown in Fig. 1 and relevant bond lengths and angles are reported in Table 1. The general stereogeometry is that expected and elements of interest are the asymmetries of the bonding interactions around the non-equivalent iron centers. The Fe_2C_2 diamond is characterized by a short Fe–Fe interaction [2.502(1) Å] and a significant bending around the Fe–Fe diagonal [28.4(2)°]. The cyanomethyl ligand, acting as a pure σ donor, generates a higher electronic saturation at Fe(1) than Fe(2), to which a terminal CO ligand is bound. The charge accumulation is spread through an increased back-donation to the accepting orbitals on μ-CO and $\mu\text{-}CNMe_2$ ligands. In fact, both ligands exhibit asymmetric bonding mode with shorter distance from the electron richer Fe(1) than Fe(2). In addition the asymmetry is more pronounced for the better π-acceptor μ-CO than $\mu\text{-}CNMe_2$ [Fe(1)–C(O) 1.852(3), Fe(2)–C(O) 2.003(3) against $Fe(1)–C(NMe_2)$ 1.843(2) and $Fe(2)–C(NMe_2)$ 1.886(3) Å]. These features are strictly equivalent to those already reported and discussed in the stereochemically similar molecules containing terminally bonded acyl ligands: $[Fe_2\{\mu\text{-}CN(Me)(CH_2Ph)\}(\mu\text{-}CO)(CO)\{C(O)th\}(Cp)_2]$ ($th = C_4H_3S$) [7] and $[Fe_2(\mu\text{-}CNMe_2)(\mu\text{-}CO)(CO)\{C(O)Bu^n\}(Cp)_2]$ [8]. For a more complete comparison we can cite the slight asymmetry found for the bridging ligands in the cation $[Fe_2(\mu\text{-}CNMe_2)(\mu\text{-}CO)(CO)(CNCH_3)(Cp)_2]^+$ [9a] and the symmetric geometries of the species $[Fe_2(\mu\text{-}CNMe_2)_2(CO)_2(C_5H_4Me)_2]^{2+}$ [9a] and $[Fe_2(\mu\text{-}CNMe_2)(\mu\text{-}H)(CO)_2(Cp)_2]$ [3].

Concerning the Fe–C(alkyl) distance [2.068(3) Å], it is expectedly far longer than the Fe–C(carbonyl) one [1.749(3) Å] but substantially in line with the sum of the covalent radii of Fe [1.25 Å, taken from the actual Fe–Fe distance] and C(sp^3) [0.77 Å].with the sum of the covalent radii of Fe [1.25 Å, taken from the actual Fe–Fe distance] and C(sp^3) [0.77 Å].

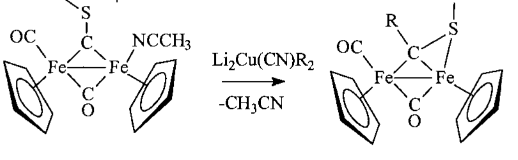
The IR spectra of **3a–c**, in CH_2Cl_2 solution, exhibit one terminal and one bridging carbonyl absorption (e.g. at 1955 and 1787 cm^{-1} for **3a**) and a ν(CN) band at about 2191 cm^{-1}. The ^1H- and ^{13}C-NMR spectra show two signals of the same intensity for the non-equivalent Cp groups of **3a** (at 4.76, 4.64 and 88.9 87.1 ppm, respectively). Likewise, each of the N-bonded methyl groups gives rise to a singlet resonance. The two hydrogens of the CH_2CN group are also non-equivalent and originate two upfield-shifted doublets (at −0.59 and −1.85 ppm). The NMR spectra of **3b–c**, which contain the asymmetrically substituted μ-CN(Me)R ($R = CH_2Ph$, $2,6\text{-}Me_2C_6H_3$), indicate the presence of two isomers in solution. These isomeric forms, which are usually found in complexes of the type $[M_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(CO)(L)(Cp)_2]$ (M = Fe, Ru) and indicated as α and β isomers [3,8–10], are due to the different orientation of R and Me with respect to the non equivalent Fe atoms. The major features, in the ^{13}C NMR spectrum of **3a**–**c**, are the characteristic low field signal of the bridging carbyne carbon (at 333 ppm for **3a**) and the upfield shifted resonance of the metal bonded cyanomethyl carbon (at −23 ppm for **3a**). In order to ascertain whether the above described reaction could be extended to other coordinated nitriles containing acidic α-hydrogens, the benzylnitrile derivative $[Fe_2\{\mu\text{-}CN(Me)(2,6\text{-}Me_2C_6H_3)\}(\mu\text{-}CO)(CO)(NCCH_2Ph)(Cp)_2]SO_3CF_3$ (**2d**) was prepared and treated with BuLi. As expected, the reaction afforded $[Fe_2\{\mu\text{-}CN(Me)(2,6\text{-}Me_2C_6H_3)\}(\mu\text{-}CO)(CO)\{CH(Ph)CN)\}(Cp)_2]$ (**3d**), which was isolated in about 68% yield. The characterization of **3d** has been straightforward since its spectroscopic properties resemble those of **3c** and indicate the presence of one single isomeric form. Complexes **3a**–**d** have also been obtained upon treatment of **2a**–**d** with NaH, although in lower yield. Other bases like NaOH, NEt_3 have been used in place of RLi but failed to accomplish the transformation described in Scheme 1. Finally we have investigated the reactions of **2c** with organo-copper reagents of the type $Li_2Cu(CN)R_2$ (R = Me, Ph), which are weaker bases compared with organo-lithium reagents but have been proven very effective in making C–C bonds at dinuclear μ-carbyne complexes [8,10,11]. Compound **2c** readily reacts with $Li_2Cu(CN)R_2$ in THF solution (at −10 °C), affording several products which we were unable to identify, except for $[Fe_2\{\mu\text{-}CN(Me)(2,6\text{-}Me_2C_6H_3)\}(\mu\text{-}CO)(CO)(CN)(Cp)_2]$ [3], and trace amounts of **3c**.

The formation of compounds **3a**–**c** presumably occurs via deprotonation of the coordinated acetonitrile followed by an unusual rearrangement to cyanomethyl derivative probably because the carbon atom results more basic than nitrogen. Proton abstraction from acetonitrile, as well as from $NCCH_2Ph$, is not surprising, in view of the acidic character of the α-C–H, enhanced by metal coordination, and of the strong basicity of organolithium reagents. For example low-valent hydrido ruthenium phosphine complexes have been found to act as effective catalysts for the condensation of nitriles with carbonyl compounds, by α-C–H activation [12]. In very few cases, removal of a proton from coordinated MeCN is followed by intramolecular rearrangement. Examples include $[Mo_2Cp_2(\mu\text{-}SMe)_3(MeCN)_2]BF_4$ in which deprotonation of one MeCN initiates its intramolecular condensation with the second acetonitrile ligand yielding $[Mo_2Cp_2(\mu\text{-}SMe)_3\{\mu\text{-}N{=}C(CH_3)CH_2CN\}]$ [13], and the heterodinuclear $[RhOs(CO)_3(NCMe)(\mu\text{-}H)(dppm)_2]^{2+}$, which has been reported to react with LiC≡CPh affording the acetylide complex $[RhOs(C{\equiv}CH)(CO)_3(dppm)_2]$ and the cyanomethyl complex $[RhOs(CH_2CN)(CO)_3(dppm)_2]$ [14]. The latter reaction strongly resembles the one we have found, since a cyanomethyl group resulted from the deprotonation of a coordinated acetonitrile ligand.

Although the intramolecular mechanism depicted above seems reasonable, one cannot exclude the possibility that the reaction occurs by release of acetonitrile from **2a**–**c**, deprotonation of the acetonitrile solvent, followed by attack of the resulting acetonitrilide. However, this seems to be ruled out by the fact that MeCN release from **2a**–**c** is a relatively slow process. The rate of acetonitrile exchange was qualitatively evaluated by observing the decrease in intensity of ^1H NMR signal of the bound MeCN (at 1.95 ppm) and a corresponding increase of the free MeCN immediately after preparation of a CD_3CN solution of **2a**, at room temperature. Under these conditions, CH_3CN–CD_3CN exchange requires about 50 min to be completed. In another experiment **3a** was prepared by treatment of **2a** with BuLi in a THF solution containing a tenfold amount of $CH_3^{*}CN$ (^{13}C carbon enriched, 99%). Compound **3a**, which was obtained after usual workup did not show any significant increase of intensity in the resonance of the iron bonded methyl carbon, suggesting that the overall mechanism is intramolecular.

In view of the fact that the bridging thiocarbyne complex $[Fe_2(\mu\text{-}CSMe)(\mu\text{-}CO)(CO)_2(Cp)_2]SO_3CF_3$ (**4**) and the aminocarbyne complexes $[Fe_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(CO)_2(Cp)_2]SO_3CF_3$ (**1**) have exhibited a comparable reactivity with respect to carbon nucleophiles [11], we decided to synthesize the acetonitrile derivative of **4** and investigate its reactions with organo-lithium reagents. The synthesis of $[Fe_2(\mu\text{-}CSMe)(\mu\text{-}CO)(CO)(NCMe)(Cp)_2]SO_3CF_3$ (**5**) parallels that of **2a**–**c**; in both cases replacement of CO with MeCN is promoted by Me_3NO. Like **3a**–**c**, compound **5** shows in its ^1H-NMR spectra that exchange between coordinated NCMe and CD_3CN solvent requires several minutes to be completed. Nevertheless the reaction with BuLi has failed to produce the expected cyanomethyl complex $[Fe_2(\mu\text{-}CSMe)(\mu\text{-}CO)(CO)(CH_2CN)(Cp)_2]$, generating extensive decomposition of **5**.

By contrast, treatment of **5** with $Li_2Cu(CN)R_2$ results in a regiospecific nucleophilic addition leading to the formation of $[Fe\overline{Fe\{\mu\text{-}C(R)S}Me\}(\mu\text{-}CO)(CO)(Cp)_2]$ (R = Me, **6a**; Ph, **6b**) (Scheme 2). Compounds **6** have been purified by column chromatography, and iden-



5

6a, R = Me; **6b**, R = Ph

Scheme 2.

tified by comparison of their spectroscopic properties with those published [11].

These results are to be compared with those reported for the corresponding reactions of [Fe$_2$(μ-CSMe)(μ-CO)(CO)$_2$(Cp)$_2$]SO$_3$CF$_3$ **4** with Li$_2$Cu(CN)Me$_2$, which afforded a mixture of [Fe$_2$(μ-C=CH$_2$)(μ-CO)(CO)$_2$-(Cp)$_2$], [Fe$_2${μ-C(SMe)Me}(μ-CO)(CO)$_2$(Cp)$_2$], and [FeFe{μ-C(Me)SMe}(μ-CO)(CO)(Cp)$_2$] (**6a**), the latter being formed in about 12% yield [11]. In a similar manner, **6b** has been previously obtained, as minor product, from **4** and Li$_2$Cu(CN)Ph$_2$ [11]. Therefore, the presence of the acetonitrile ligand in **5** makes the addition of organo-copper more selective, favoring exclusively the formation of the bridging thiocarbene complexes **6a**–**b**, with the sulfur atom coordinated to one of the Fe atoms, which is a rather common coordination mode for thio- and dithioalkylidene ligands in dinuclear complexes [15].

A plausible pathway for the formation of **6a**–**b** consists of a nucleophilic addition at the bridging carbyne carbon, followed by intramolecular displacement of the NCMe ligand by the S atom of the SMe group. However, an alternative mechanism based on an initial displacement of acetonitrile by the carbon nucleophile, followed by migration of the alkyl ligand to the bridging carbyne carbon, should not be ruled out, in view of the fact that analogous rearrangements have already been observed [11,15c].

3. Experimental

3.1. General

All reactions were carried out routinely 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 300. Unless otherwise stated, NMR signals due to trace amounts of second isomeric form are italicized. All the reagents were commercial products (Aldrich) of the highest purity available and used as received. [Fe$_2$(CO)$_4$(Cp)$_2$] was from Strem and used as received. Compounds [Fe$_2${μ-CN(Me)R}(μ-CO)(CO)(CH$_3$CN)(Cp)$_2$]SO$_3$CF$_3$ (R = Me **2a** R = CH$_2$Ph **2b**, Me$_2$C$_6$H$_3$ **2c**) [3,9] and [Fe$_2$(μ-CSMe)(μ-CO)(CO)$_2$(Cp)$_2$]SO$_3$CF$_3$ (**4**) [16] were prepared as described in the literature.

3.2. Synthesis of [Fe$_2${μ-CN(Me)2,6-Me$_2$C$_6$H$_3$}-(μ-CO)(CO)(NCCH$_2$Ph)(Cp)$_2$]SO$_3$CF$_3$ (2d)

Compound [Fe$_2${μ-CN(Me)(2,6-Me$_2$C$_6$H$_3$)}(μ-CO)-(CO)$_2$(Cp)$_2$]SO$_3$CF$_3$ (**1c**) (250 mg, 0.40 mmol) and benzylnitrile (70 mg, 0.60 mmol) in THF (10 ml) were treated with anhydrous Me$_3$NO (30 mg, 0.40 mmol) and the mixture was stirred for 60 min. Filtration on a Celite pad and removal of the solvent gave a brown residue that was washed with petroleum ether (b.p. 40–60 °C) and crystallized from CH$_2$Cl$_2$ layered with *n*-pentane at −20 °C yielding **2d** as a brown microcrystalline solid (255 mg, 90%). Anal. Found: C, 52.66; H, 4.16%. C$_{31}$H$_{29}$F$_3$Fe$_2$N$_2$O$_5$S: C, 52.41; H, 4.12%. IR (CH$_2$Cl$_2$) ν_{max}(cm^{-1}) 1988vs and 1821s (CO). NMR: δ_H (CDCl$_3$): 7.39–6.90 (8H, m C$_6$H$_5$ and C$_6$H$_3$), 5.11, 5.02 (5H, s, Cp), 4.43, 4.33 (5H, s, Cp), 4.71, 4.45 (3H, s, NMe), 3.91 (1H, d, C*H*$_2$Ph, J_{AB} = 18 Hz), 3.68 (1H, d, C*H*$_2$Ph, J_{AB} = 18 Hz), 2.67, 2.65, 1.85 and 1.76 (6H, s, Me$_2$C$_6$H$_3$). δ_C (CDCl$_3$): 339.3, (μ-C); 265.3 (μ-CO); 212.1, (CO); 148.9–128.7 (C$_6$H$_5$ and Me$_2$C$_6$H$_3$); 89.6, 89.5, 88.3, 87.4 (Cp); 55.6, 54.6 (NMe); 26.1, 24.1 (CH$_2$Ph); 19.3 and 17.5 (Me$_2$C$_6$H$_3$).

3.3. Synthesis of [Fe$_2$ (μ-CNMe$_2$)(μ-CO)(CO)(CH$_2$CN)(Cp)$_2$] (3a)

Compound **2a** (207 mg, 0.38 mmol) in THF (15 ml) was stirred with BuLi (0.40 mmol) for 30 min. Removal of the solvent and chromatography on an alumina column with CH$_2$Cl$_2$ as eluent gave a green fraction, which afforded dark-green crystals of **3a** (85 mg, 57%). Anal. Found: C, 51.68; H, 4.70%. C$_{17}$H$_{18}$Fe$_2$N$_2$O$_2$ requires: C, 51.81; H, 4.61%. IR (CH$_2$Cl$_2$) ν_{max}(cm^{-1}) 2191w (CN), 1955vs and 1787s (CO). NMR: δ_H (CDCl$_3$): 4.76 (5H, s, Cp), 4.64 (5H, s, Cp), 4.33 (s, 3H, NMe), 4.08 (s, 3H, NMe), −0.59 (1H, d, J_{AB} = 14 Hz, CH$_2$CN) and −1.85 (1H, d, J_{AB} = 14 Hz, CH$_2$CN). δ_C(CDCl$_3$): 332.7 (μ-C), 268.0 (μ-CO), 215.6 (CO), 131.8 (CN), 88.9, 87.1 (Cp), 53.4, 50.8 (NMe) and −22.9 (CH$_2$CN).

3.4. Synthesis of [Fe$_2$ {μ-CN(Me)CH$_2$Ph}(μ-CO)(CO)-(CH$_2$CN)(Cp)$_2$] (3b), [Fe$_2${μ-CN(Me)(2,6-Me$_2$C$_6$H$_3$)}-(μ-CO)(CO)(CH$_2$CN)(Cp)$_2$] (3c) and [Fe$_2${μ-CN-(Me)(2,6-Me$_2$C$_6$H$_3$)}(μ-CO)(CO){CH(Ph)CN}(Cp)$_2$] (3d)

Complexes **3b**–**d** were obtained from **2b**–**d**, respectively, following the same procedure described for the synthesis of **3a**.

3b: (64%). Anal. Found: C, 58.61; H, 4.73%. C$_{23}$H$_{22}$Fe$_2$N$_2$O$_2$: C, 58.76; H, 4.72%. IR (CH$_2$Cl$_2$) ν_{max}(cm^{-1}) 2191w (CN), 1955vs and 1788s (CO). NMR, α and β isomers in about 1:1 ratio: δ_H (CDCl$_3$): 7.47 (m, 5H, Ph), 6.36, 5.73, 5.50, 5.42 (2H, d, J = 16 Hz, CH$_2$Ph), 4.79, 4.70, 4.67, 4.57 (10H, s, Cp), 4.11, 3.89 (3H, s, NMe), and −0.57, −0.61, −1.64, −1.65 (2H, d, C*H*$_2$CN). δ_C(CDCl$_3$): 336.2

(μ-C), 267.5 (μ-CO), 215.4 (CO), 136.6–127.4 (Ph and CN), 89.2, 89.0, 87.1 (Cp), 70.9, 68.5 (CH_2Ph), 50.9, 48.0 (NMe) and −21.7 (CH_2CN).

3c: (52%). Anal. Found: C, 59.61; H, 4.97%. $C_{24}H_{24}Fe_2N_2O_2$: C, 59.53; H, 5.00%. IR (CH_2Cl_2) $\nu_{max}(cm^{-1})$ 2192w (CN), 1954vs and 1786s (CO). NMR: δ_H ($CDCl_3$): 7.43–6.90 (m, 3H, Ph), 4.78, 4.75 (5H, s, Cp), 4.63, 4.53 (3H, s, NMe), 4.32, 4.19 (5H, s, Cp), 2.67, 2.14 (6H, s $Me_2C_6H_5$), −0.31 (1H, d, $J_{AB} = 14$ Hz, CH_2CN), and −1.64 (1H, d, $J_{AB} = 14$ Hz, CH_2CN). δ_C($CDCl_3$): 338.8 (μ-C), 267.9 (μ-CO), 215.8 (CO), 134.1–128.9 ($C_6H_3Me_2$ and CN) 89.4, 87.1 (Cp), 51.8 (NMe), 19.2, 18.2 ($C_6H_3Me_2$) and −22.5 (*C*H_2CN) ppm.

3d: (68%). Anal. Found: C, 64.35; H, 5.05%. $C_{30}H_{28}Fe_2N_2O_2$: C, 64.31; H, 5.04%. IR (CH_2Cl_2) $\nu_{max}(cm^{-1})$ 2186w (CN), 1951vs and 1787s (CO). NMR: δ_H ($CDCl_3$): 7.30–7.04 (3H, m, Ph), 4.84 (3H, s, NMe), 4.53 (5H, s, Cp), 4.30 (5H, s, Cp), 2.65, 2.26 (6H, s $Me_2C_6H_5$), and −0.37 (1H, s, C*H*(Ph)CN). δ_C($CDCl_3$): 337.9 (μ-C), 267.4 (μ-CO), 217.1 (CO), 146.9–124.4 (C_6H_5 and $Me_2C_6H_3$), 89.9, 87.9 (Cp), 52.9 (NMe), 19.3, 18.4 ($Me_2C_6H_3$) and 1.7 (*C*H(Ph)CN).

*3.5. Synthesis of [Fe₂(μ-CSMe)(μ-CO)(CO)(NCMe)(Cp)₂] SO₃CF₃ (**5**)*

A solution of [Fe_2{μ-CSMe}(μ-CO)$(CO)_2(Cp)_2$] SO_3CF_3 (**4**) (180 mg, 0.34 mmol) in MeCN (15 ml) was treated with anhydrous Me_3NO (26 mg, 0.35 mmol) and the mixture was stirred for 60 min. Filtration on a Celite pad and removal of the solvent gave a brown residue that was washed with petroleum ether (b.p. 40–60 °C) and crystallized from CH_2Cl_2 layered with n-pentane at −20 °C yielding brown crystals of **5** (151 mg, 81%). The solid contained small amounts of the di-acetonitrile complex [Fe_2{μ-CSMe}(μ-CO)$(NCMe)_2$-$(Cp)_2$]SO_3CF_3 (8%, estimated from ^{1}H-NMR signal integration). IR (CH_2Cl_2) $\nu_{max}(cm^{-1})$ 1805s (CO). NMR: δ_H ($CDCl_3$): 4.73 (10H, s, Cp), 3.86 (3H, s, SMe) and 1.95 (6H, s, NCMe) ppm. δ_C(CD_2Cl_2): 423.6 (μ-CSMe), 271.6 (μ-CO), 131.1 (MeCN), 87.7 (Cp), 34.9 (SMe) and 4.4 (MeCN). Pure samples of **5**, which gave satisfactory elemental analysis, were obtained by repeated crystallization. Anal. Found: C, 37.15; H, 3.02%. $C_{17}H_{16}F_3Fe_2NO_5S_2$: C, 37.32; H, 2.95%. IR (CH_2Cl_2) ν_{max} (cm^{-1}) 2005vs and 1834s (CO). NMR: δ_H ($CDCl_3$): 5.12 (5H, s, Cp), 5.05 (5H, s, Cp), 3.77 (3H, s, br, SMe) and 1.95 (3H, s, NCMe) ppm. δ_C(CD_2Cl_2): 447.0 (μ-CSMe), 260.2 (μ-CO), 209.8 (CO), 132.0 (Me*C*N), 90.1 (Cp), 89.5 (Cp), 36.5 (SMe) and 4.6 (MeCN).

*3.6. Synthesis of [FeFe{μ-C(Me)SMe)(μ-CO)(CO)(Cp)₂] (**6a**) and [FeFe{μ-C(Ph)SMe)(μ-CO)(CO)(Cp)₂] (**6b**)*

A solution of $Li_2Cu(CN)Me_2$ prepared from dry CuCN (45 mg, 0.5 mmol) and LiMe (1.0 mmol) in THF (8 ml) at −60 °C was added to a solution of **5** (257 mg, 0.47 mmol) in THF (10 ml) at −60 °C. The mixture was warmed to room temperature, stirred for an additional 30 min, and filtered on an alumina pad. Evaporation of the solvent and chromatography of the residue on an alumina column with 1:1 CH_2Cl_2-petroleum ether (b.p. 40–60 °C) as eluent, gave a brownish-green fraction. Crystallization from CH_2Cl_2 layered with n-pentane yielded **6a** (89 mg, 51%). Anal. Found: C, 48.44; H, 4.62%. $C_{15}H_{16}Fe_2O_2S$: C, 48.42; H, 4.33%. IR (CH_2Cl_2) ν_{max} (cm^{-1}) 1935vs and 1757s (CO). NMR: δ_H ($CDCl_3$): 4.58 (5 H, s, Cp), 4.44 (5 H, s, Cp), 4.03 (3H, s, Me) and 1.53 (3 H, s, SMe) ppm. δ_C($CDCl_3$): 276.5 (μ-CO), 217.6 (CO), 185.5 (μ-C) 85.9, 83.2 (Cp), 35.9 and 23.9 (CH_3).

6b was prepared as described for **6a**, by reacting **5** (190 mg, 0.35 mmol) with $Li_2Cu(CN)Ph_2$ (0.35 mmol). Yield 91 mg, 60%. Complex **6b** was identified by comparison of its spectroscopic properties with those reported in the literature [11].

Table 2
Crystal data and diffraction experimental details for [Fe_2(μ-$CNMe_2$)(μ-CO)(CO)(CH_2CN)$(Cp)_2$] (**3a**)

Empirical formula	$C_{17}H_{18}Fe_2F_4N_2O_2$
M	394.03
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal symmetry	Monoclinic
Space group	*C c* (No. 9)
a (Å)	16.779(3)
b (Å)	7.470(2)
c (Å)	14.509(1)
α (°)	90
β (°)	114.18(3)
γ (°)	90
V, Cell volume (Å³)	1659.0(5)
Z	4
D_{calc} (mg m^{-3})	1.578
μ(Mo–K_α) (mm^{-1})	1.758
F(000)	808
Crystal size (mm)	0.13 × 0.15 × 0.20
θ limits (°)	2.5–30
Reflections collected	4827(±*h*, +*k*, ±*l*)
Unique observed reflections [$F_o > 4\sigma(F_o)$]	2418 [$R_{int} = 0.04$]
Goodness of fit on F^2	1.06
Absolute structure parameter	0.09(2)
R_1 (*F*) [a], wR_2 (F^2) [b]	0.0239, 0.0522
Weighting scheme	$a = 0.0222$, $b = 0.000$
Largest difference peak and hole, (e Å^{-3})	0.34 and −0.29

[a] $R_1 = \Sigma||F_o| - |F_c|/\Sigma|F_o|$.

[b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$.

3.7. X-ray crystallographic study of **3a**

Crystal data and details of the data collection for complex [$Fe_2(\mu\text{-}CNMe_2)(\mu\text{-}CO)(CO)(CH_2CN)(Cp)_2$] (**3a**) are given in Table 2. The diffraction experiments were carried out at room temperature on a fully automated Enraf–Nonius CAD-4 diffractometer using graphite-monochromated Mo–K_α 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 and no absorption correction were applied. The positions of the metal atoms were found by direct methods using the SHELXS-86 program [17] and all the non-hydrogen atoms located from difference Fourier syntheses. Two fold orientational disorder of one of the Cp ligands [bound to Fe(1)] around the metal-ring axis was detected and the site occupation factors were refined for this ligand, yielding the values 0.54 and 0.46, respectively. The hydrogen atoms of the methyl and methylene groups were located from successive Fourier-difference maps but were added in calculated positions. The final refinement on F^2 proceeded by full-matrix least-squares calculations (SHELXL-97) [18] using anisotropic thermal parameters for all the non-hydrogen atoms. The cyclopentadienyl the methyl and the methylene H atoms were assigned an isotropic thermal parameter 1.2, 1.3 and 1.5 times U_{eq} of the carbon atoms to which they were attached.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 174241 for **3a**. Copies of this information can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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