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The μ -sulfonium-methylidene diiron complexes [Fe₂{ μ -C(X)SMe₂}(μ -CO)(CO)₂(Cp)₂]SO₃CF₃ (X = CN, H) as precursors of μ -alkylidene complexes

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Abstract

The reactions of $[Fe_2{\mu-C(X)SMe_2}(\mu-CO)(CO)_2(Cp)_2]SO_3CF_3$ (X = CN 2a, H 2b; Cp = η -C₅H₅) with Li₂Cu(CN)R₂ (R = Me, Buⁿ, Ph, CCC₆H₄Me-4, C₄H₃S) give the neutral μ -alkylidene complexes $[Fe_2{\mu-C(X)R}(\mu-CO)(CO)_2(Cp)_2]$ (3) arising from nucleophilic attack at the bridging carbon and SMe₂ displacement. Likewise, 2a,b react with the sodium salt of dimethylmalonate, diethylmalonate, ethylacetoacetate, 2,4-pentanedione, dibenzoylmethane and benzylcyanide, resulting in the formation of the corresponding functionalized μ -alkylidene complexes $[Fe_2{\mu-C(X)R}(\mu-CO)(CO)_2(Cp)_2]$ (5–7) (X = CN, H; R = CH(COOMe)_2, CH(COOEt)_2, CH(COOMe)(COMe), CH(COMe)_2, CH(COPh)_2, CH(Ph)CN). The dichetone adducts $[Fe_2{\mu-C(X)CH(COR)_2}(\mu-CO)(CO)_2(Cp)_2]$ (X = CN, H; R = Me, Ph) undergo deacylation upon treatment with alumina, leading to the formation of the complexes $[Fe_2{\mu-C(X)CH_2(O)}_2(Cp)_2]$. Reactions of 2a,b with LiBu or PhLi result in the formation the metallacycles $[Fe_2{\mu-C(X)S(Me)CH_2}(\mu-CO)(CO)(CO)(CD)_2(Cp)_2]$ (X = CN, 4a; H 4b) which arise from the deprotonation of an SMe group and the intramolecular addition at a terminally coordinated carbonyl. Finally, a comparison of the reactivity of 2a,b with that of the μ -carbyne diiron complexes $[Fe_2(\mu-CX)(\mu-CO)(CO)_2(Cp)_2]SO_3CF_3$ (X = H, SMe, NMe₂) is presented. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

We have recently reported [1] on the carbon–carbon bond formation at the cationic diiron μ -carbyne complexes [Fe₂(μ -CX)(μ -CO)(CO)₂(Cp)₂]SO₃CF₃ (X = NMe₂, **1a**; SMe, **1b**) via addition of carbon nucleophiles, like organo-copper, -magnesium and -lithium reagents. Interestingly, these addition reactions have been shown to occur selectively at the different ligands: the bridging carbyne, the carbonyl and the C₅H₅ ring, depending on the nature of the nucleophiles and of the heteroatom adjacent to the bridging carbyne carbon [2].

Carbon-carbon bond forming reactions in dinuclear complexes are of considerable interest because of their

potential as models for related processes occurring on metal surfaces. Dirhodium [3], diruthenium [4], and diiron [5] complexes with bridging carbene ligands, have offered valuable model systems for investigating the Fisher-Tropsch polymerization reaction [6]. Therefore, we decided to extend our investigations on C-C bond formation to the diiron thiocarbene complexes $[Fe_2{\mu-C(X)SMe_2}(\mu-CO)(CO)_2(Cp)_2]SO_3CF_3$ (X = CN, 2a; H, 2b) which, like 1a,b, exhibit a considerable electrophilic character. Indeed, both 2a [7] and 2b [8] have been shown to undergo SMe₂ displacement easily by a variety of nucleophiles forming heteroatom substituted bridging alkylidene complexes. In particular, the reactions of 2a with amines [9], alcohols [10], and phosphines [11], have been described in detail. In contrast, only a few reactions of 2a,b with carbon nucleophiles, including NBu₄ⁿ CN, have been investigated [7c,8]. Herein, we report on the reactivity of 2a,b towards stabilized carbanions, and organolithium, Grig-

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Scheme 1.

nard and organocopper reagents, aimed at developing synthetic entries into disubstituted μ -CR₂ complexes via formation of a C–C bond.

2. Results

2.1. Reactions with of organocopper reagents

The reactions of 2a,b with $Li_2Cu(CN)R_2$, in the at $-40^{\circ}C$, afforded the alkylidene complexes [Fe₂{ μ -C(X)R}(μ -CO)(CO)₂(Cp)₂] (3a-g) (Scheme 1).

These complexes, which are moderately air-stable solid red crystals, have been isolated after column chromatography in 30-50% yield. Their IR spectra, in CH₂Cl₂, exhibit the expected three band pattern for the two terminal and one bridging v(CO) bands (with relative intensities strong-weak-medium) that typify the μ -alkylidene compounds [Fe₂{ μ -C(X)R}(μ -CO)(CO)₂-(Cp)₂] [7,9–11], adopting a *cis* conformation (Cp *cis* to each other). Moreover, a weak band attributable to the v(CN) is observed in the cvanoalkylidene complexes 3a-e (e.g. at 2148 cm⁻¹ for 3a). Both ¹H and ¹³C NMR spectra of 3a-c and 3f,g show one singlet for the Cp ligands according to the presence of only one of the two possible cis-isomers (e.g. for 3a at 4.99 and 91.5 ppm, respectively); presumably that with the smaller (CN or H) substituent on the carbon carbon on the more hindered Cp side of the molecule, as found in the structurally characterized µ-cyanoalkylidene complexes [7a,10,11a,12]. However, as in the case of the complex $[Fe_2\{\mu-C(H)CN\}(\mu-CO)(CO)_2(Cp)_2]$ [7c], compounds 3d,e present a small amount of the *trans* isomer, beside the more abundant cis. For example, the ¹H NMR spectrum of 3d shows, in addition to the usual Cp resonances at 4.92, two minor signals of equal intensity at 4.95 and 4.82 ppm which account for the presence of the *trans* isomer. Finally, the ¹³C NMR spectra of 3a-eshow resonances for the bridging carbene carbon at about 130-165 ppm, within the range typical for bridging alkylidene carbons. Complexes 3f,g have been identified by comparison of their spectroscopic properties with those previously reported in the literature [13].

2.2. Reactions with organolithium and Grignard reagents

In contrast with the above described reactions, treatment of **2a,b** with alkyl- or aryl-lithium led to the metallacycles **4a,b**, presumably via deprotonation of an SMe, followed by addition at the terminally coordinated CO ligand (Scheme 2). Compounds **4a,b** have been obtained as dark green crystalline solids in about 41-34% yield, from **2a** and **2b**, respectively, together with minor amounts of by-products. For example, in the case of **2a**, [Fe₂(μ -CO)₂(CO)₂(Cp)₂] (12%) and [Fe₂{ μ -C(H)CN}(μ -CO)(CO)₂(Cp)₂] (7%) were also obtained.

The IR spectra of **4a**,**b** show three v(CO) absorptions (at 1946s, 1788m, 1634m cm⁻¹ for **4a**) attributable to the terminally bonded, bridging and acyl CO groups, respectively. Moreover, a weak v(CN) band is observed at 2168 cm⁻¹ in the spectrum of **4a**. The non equivalence of the Cp ligands in **4** originates two equally intense resonances in the NMR spectra (e.g. for **4a** at 4.83, 4.66 ppm and at 90.5, 88.2 ppm in the ¹H and ¹³C NMR, respectively). The diastereotopic methylene protons in the metallacycle give rise to two doublets (J_{AB} 17 Hz).

Reactions of 2a,b with RMgCl (R = Me, CH₂Ph) unexpectedly failed to produce any identifiable product. Previously reported electrochemical investigations [14] have shown that the diiron cyanoalkylidene complexes can undergo one electron reduction to unstable 19-electron species. This suggests that other processes, based upon electron-transfer, may effectively take place.



Scheme 2.





2.3. Reactions with stabilized carbanions

Like the reactions of Scheme 1, the SMe₂ molecule in **2a,b** is readily displaced by the sodium salt of dimethylmalonate, diethylmalonate and ethylacetoacetate to afford the corresponding alkylidene complexes **5a**-**d** and **6a,b** in high yield (80-90%) (Scheme 3).

The IR spectra of 5a-d and 6a,b in CH₂Cl₂ solution, show, in addition to the usual v(CO) band pattern due to the terminal and bridging carbonyls, the absorptions attributable to the COOR and COMe groups (e.g. for **5b** at 1747 and 1725 cm⁻¹). Moreover, the cyanoalkylidene complexes 5a,b and 6a exhibit a weak v(CN) absorption (for 5b at 2160 cm^{-1}). Only one singlet signal is observed in the NMR spectra of 5a-d for the Cp ligands, indicating their equivalence and the presence, in solution, of one single cis-isomer. The two Me groups in 5a also appear as one single resonance (at 3.87 ppm in the ¹H NMR) whereas, in 5b the methylene protons of the ethyl group are diastereotopic because of their prochiral relationship, and originate two distinct multiplets (at 4.29 and 4.28 ppm).

Unlike 5a-d, that possess a plane of symmetry, compounds 6a,b are chiral molecules and two diastereotopic Cp groups are observed in their NMR spectra (e.g. for 6a at 4.92 and 4.88 ppm in the ¹H NMR). Compounds 5c,d and 6b show the characteristic downfield resonance at about 12 ppm assigned to the proton on the bridging carbon which appears as a doublet due to the coupling to the tertiary β -hydrogen.

Complexes **5d** and **6b** have been previously obtained from $[Fe_2(\mu-CH)(\mu-CO)(CO)_2(Cp)_2]^+$ by treatment with the $CH_2(COOMe)_2$ and $CH_2(COOEt)_2$, respectively, in the presence of a tertiary amine [13a].

The bridging carbene carbon resonance of type **5** and **6** complexes occurs, as expected, in the 160-116 ppm range. It is worth noting that cyanocarbene-carbon resonances (**5a**,**b**, **6a**) are about 30-40 ppm upfield shifted with respect to the methylidene analogues (**5c**,**d**, **6b**).

Treatment of 2a, b with NaCH(COR)₂ (R = Me, Ph) provided the expected alkylidene derivatives [Fe₂{ μ -C(X)CH(COR)₂}(μ -CO)(CO)₂(Cp)₂] (7a-d) in good yields (Scheme 4). As previously described by Casey [13a], 7c was deacetylated to form 8c upon chrom-





matography on alumina. Similarly, compounds **7a,b**, **7d** have been converted into **8a,b**, **8c**, respectively, upon analogous treatment (Scheme 4). As reported [13a], the deacylation reaction does not occur by using silica gel in place of alumina.

The characterization of 7 and 8 has been straightforward since their spectroscopic properties are similar to those of compounds 3 and 5 discussed above.

Reactions with carbanions stabilized by the presence of CN groups have also been investigated. Upon treatment with NaCH(CN)Ph, compounds **2a,b** afforded the expected μ -carbene complexes [Fe₂{ μ -C(X)CH(CN)Ph}-(μ -CO)(CO)₂(Cp)₂] (X = CN **9a**; H, **9b**) in 88 and 51% yields, respectively. These complexes, like **6a,b**, are chiral molecules and two diastereotopic Cp groups are observed in their NMR spectra (e.g. for **9a** at 4.92 and 4.88 ppm).

Rather surprisingly, the analogous reaction of **2b** with NaCH(CN)₂ instead of forming the expected μ -alkylidene [Fe₂{ μ -C(CN)CH(CN)₂}(μ -CO)(CO)₂(Cp)₂], gave a mixture of products which included the vinylidene complex [FpC(CN)=C(CN)₂] (Fp = Fe(CO)₂Cp) and the trinuclear cyanocarbyne [Fe₃(μ ₃-CCN)(μ -CO)₃(Cp)₃] in 12 and 31% yields, respectively. Their formation must be interpreted in terms of Fe–Fe bond cleavage in **2b** and rearrangements of the metal fragments, generating both mononuclear and trinuclear species. The latter has been identified by comparison of its spectroscopic properties with those of the same compound previously obtained by a different route [15].

3. Discussion

The reactions presented confirm our previous findings which suggested that the sulfonium-methylidene complexes 2a,b provide excellent entries into disubstituted µ-methylidene diiron complexes via SMe₂ replacement by a variety of nucleophiles [7-11]. Here the method has been used to synthesize μ -CRR' (R' = CN, H) derivatives by reactions with carbon nucleophiles such as organocopper reagents $Li_2Cu(CN)R_2$ (R = Me, Bu, Ph, C=CC₆H₅Me, C₄H₃S) and carbanions derived from methyl or ethyl malonate, ethyl acetoacetate, 2,4pentanedione, dibenzoylmethane and benzylnitrile, yielding the functionalized alkylidene complexes 5-7. Note, the compounds 3f,g, 5d, 6b and 7c have been previously obtained by nucleophilic addition at the μ -methylidyne complex [Fe₂(μ -CH)(μ -CO)(CO)₂(Cp)₂]- SO_3CF_3 [13]. However, since the latter is considerably more reactive and difficult to handle, compound 2b can be viewed as an advantageous alternative to [Fe₂(µ-CH)(μ -CO)(CO)₂(Cp)₂]SO₃CF₃, at least for the reaction with the above mentioned carbon nucleophiles. On the other hand, 2a is a remarkable source of cyanoalkylidene complexes, contributing to the emerging field of CN-based organometallic complexes [16].

Compared to the related μ -carbyne complexes [Fe₂(μ - $CX)(\mu-CO)(CO)_2(Cp)_2]SO_3CF_3$ (X = NMe₂, 1a; SMe, 1b), which have been shown to be susceptible of nucleophilic addition at the µ-carbyne as well as at the CO and Cp ligand [1,2], in compounds 2a,b the μ - $C(X)SMe_2$ (X = CN, H) moiety appears as the unique target of nucleophiles, thus favoring the C-C bond formation at the bridging carbene carbon atom with organocuprates and stabilized carbanions. However, in the reactions with organo-lithium reagents, 4a,b derivatives are formed as a consequence of a intramolecular cyclization. Thus, the goal of forming a C-C bond is achieved via nucleophilic addition of deprotonated SMe at the terminally bonded carbonyl group. Although there are examples of intramolecular cyclization involving the μ -carbene ligand in the complexes [Fe₂{ μ - $C(CN)X)(\mu-CO)(CO)_2(Cp)_2$] (X = SMe, $OCH_2CH=$ CH₂) [10,12a] this represents the first case in which cyclization includes the CO instead of producing its displacement. The cyclization appears possible because the SMe₂ and the CO groups are placed on the same side of the Fe-Fe bond [12c]. The formation of 4a,b was rather unexpected in view of the fact that SMe deprotonation has never been observed so far, in spite of the large variety of nucleophiles and bases with which 2a,b have been treated.

It should finally be noted that only Li₂Cu(CN)R₂, and, not LiR or RMgCl, appears to be able to form C-C bonds at the μ -carbene carbon of **2a,b**. Organocopper reagents have been shown to be the most efficient at forming C-C bonds at the μ -carbyne of [Fe₂(μ -CR)(μ -CO)(CO)₂(Cp)₂]⁺ (R = H, Ph) including the μ -ethylinyl complex (R = Me), in which deprotonation of the acidic hydrogens of the μ -CMe unit might compete with the nucleophilic addition [13a,17]. Likewise, Li₂Cu(CN)R₂ complexes have been shown to attack selectively the μ -carbyne carbon of [Fe₂(μ -CSMe)(μ -CO)(CO)₂(Cp)₂]SO₃CF₃ (**1b**) [2a].

4. Experimental

4.1. 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. IR spectra were recorded on a Perkin– Elmer 983-G spectrophotometer, ¹H and ¹³C NMR spectra on a Varian Gemini 300. The shiftless relaxation reagent [Cr(acac)₃] (acac = acetylacetonate) was added to solution studied by ¹³C NMR spectroscopy. 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 $[Fe_2{\mu-C(X)SMe_2}(\mu-CO)(CO)_2(Cp)_2]SO_3-CF_3$ (X = CN, **2a**; H, **2b**) were prepared as described in the literature [8,12c]. Li₂Cu(CN)R₂ species were prepared from CuCN and the appropriate organolithium reagent according to the literature [18].

4.2. Synthesis of [Fe₂{μ-C(CN)Ph}(μ-CO)(CO)₂(Cp)₂] (3a)

Compound 2a (99 mg, 0.171 mmol) in thf (10 ml) at -30° C was treated with Li₂Cu(CN)Ph₂ prepared from dry CuCN (0.018 g, 0.2 mmol) and LiPh (0.4 mmol) in thf (4 ml) at -60° C. The mixture was then warmed to 0°C, stirred for an additional hour and filtered on an alumina pad. Removal of the solvent and chromatography on an alumina column with CH₂Cl₂ as eluent gave a first red fraction containing $[Fe_2(\mu-CO)_2(CO)_2(CP)_2]$ followed by a second red fraction which was collected. Evaporation of the solvent and crystallization from CH_2Cl_2 and *n*-pentane at $-20^{\circ}C$ afforded yellow crystals of 3a (30 mg, 39%). Anal. Found: C, 57.16; H, 3.43%. C₂₁H₁₅Fe₂NO₃ requires: C, 57.19; H, 3.43%. IR $(CH_2Cl_2) v_{max}(cm^{-1})$ 2148w (CN), 2001s, 1964m and 1801m (CO). NMR: $\delta_{\rm H}$ (CDCl₃): 7.52–7.21 (5 H, m, Ph) and 4.99 (10 H, s, Cp) ppm. $\delta_{\rm C}$ (CDCl₃): 266.3 (μ-CO), 209.8 (CO), 157.4 (μ-C), 135.8 (CN); 131.2, 130.4, 128.0, 126.8 (Ph) and 91.5 (Cp) ppm.

4.3. Syntheses of $[Fe_2 {\mu-C(CN)R}(\mu-CO)(CO)_2(Cp)_2]$ $(R = Me, 3b; Bu^n, 3c; C \equiv CC_6H_4Me-4 3d; C_4H_3S, 3e)$

Complexes 3b-e were obtained following the same procedure described for the synthesis of 3a by reacting 2b with $Li_2Cu(CN)Me_2$, $Li_2Cu(CN)Bu_2^n$, $Li_2Cu(C \equiv CC_6H_4Me-4)_2$, $Li_2Cu(C_4H_3S)_2$, respectively.

3b: (42%). *Anal.* Found: C, 50.55; H, 3.49%. $C_{16}H_{13}Fe_2NO_3$ requires: C, 50.71; H, 3.46%. IR (CH₂Cl₂) v_{max} (cm⁻¹) 2150w (CN), 1993s, 1960w and 1799m (CO). NMR: δ_H (CDCl₃): 4.81 (10 H, s, Cp) and 2.71 (3 H, s, Me) ppm. δ_C (CDCl₃): 267.9 (µ-CO), 211.2 (CO), 127.3 (µ-C), 91.1 (Cp) and 45.5 (Me) ppm.

3c: (52%). *Anal.* Found: C, 54.18; H, 4.49%. $C_{19}H_{19}Fe_2NO_3$ requires: C, 54.20; H, 4.45%. IR (CH₂Cl₂) ν_{max} (cm⁻¹) 2151w (CN), 1986s, 1951w and 1800m (CO). NMR: δ_{H} (CDCl₃): 4.82 (10 H, s, Cp), 2.60 (2 H, m, CH₂CH₂CH₂CH₃), 2.01 (2 H, m, CH₂CH₂CH₂CH₃), 1.42 (2 H, m, CH₂CH₂CH₂CH₃), and 0.96 (3 H, t, CH₂CH₂CH₂CH₃) ppm. δ_{C} (CDCl₃): 267.1 (µ-CO), 210.7 (CO), 136.0 (µ-C), 134.1 (CN), 90.6 (Cp), 57.5, 37.3, 22.9, and 14.2 (Buⁿ) ppm.

3d: (47%). *Anal.* Found: C, 60.21; H, 3.63%. $C_{24}H_{17}Fe_2NO_3$ requires: C, 60.13; H, 3.58%. IR (CH₂Cl₂) ν_{max} (cm⁻¹) 2178w (C=C), 2164w (CN), 2005s, 1973m and 1805m (CO). NMR: (resonances at-

tributable to the *trans* isomer are italicized) $\delta_{\rm H}$ (CDCl₃): 7.28–7.00 (4 H, m, C₆H₄), 4.92, 4.95 4.82 (10 H, s, Cp), 2.32 and 2.27 (3 H, s, CH₃) ppm (*cis/trans* ratio = 4.1). $\delta_{\rm C}$ (CDCl₃): 265.6 (µ-CO), 209.3 (CO), 137.9 (µ-C), 130.9, 129.9, 129.5, 122.1 (*C*₆H₄Me), 107.4, 96.3 (C=C), 90.8, 92.9, 92.3 (Cp), and 22.0 (Me) ppm.

3e: (31%). *Anal.* Found: C, 51.07; H, 3.01%. $C_{19}H_{13}Fe_2NO_3S$ requires: C, 51.05; H, 2.93%. IR (CH₂Cl₂) v_{max} (cm⁻¹) 2157w (CN), 2001s, 1963m and 1803m (CO). NMR: (resonances attributable to the *trans* isomer are italicized) δ_H (CDCl₃): 7.12, 6.90, 6.77, 7.41, 7.27, 6.88 (3 H, m, C_4H_3S), 4.95, 4.92, and 4.70 (10 H, s, Cp) ppm. δ_C (CDCl₃): 265.6 (μ -CO), 210.4, 209.7 (CO), 164.3 (μ -C), 134.6 (CN), 128.4, 127.3, 125.7, 125.3, 124.8, 124.3, 116.1 (C_4H_3S), 91.6, 90.8, 92.9, 92.0 (Cp), and 22.0 (Me) ppm.

4.4. Syntheses of $[Fe_2\{\mu-C(H)R\}(\mu-CO)(CO)_2(Cp)_2]$ (*R* = *Ph*, **3***f*; *R* = *Me*, **3***g*)

Compound **2b** (182 mg, 0.33 mmol) in thf (10 ml) at -30° C was treated with Li₂Cu(CN)Ph₂ prepared from dry CuCN (0.075 g, 0.84 mmol) and LiPh (1.69 mmol) in thf (4 ml) at -60° C. The mixture was then warmed to room temperature (r.t.) and stirred for an additional 2 h. Filtration on an alumina pad and removal of the solvent gave a red residue which was chromatographed on an alumina column with CH₂Cl₂ as eluent. A first red fraction afforded [Fe₂{ μ -C(H)Ph}(μ -CO)(CO)₂-(Cp)₂] (45 mg, 33%) which was identified by comparison of its spectroscopic properties with those reported in the literature [13a]. A second red fraction obtained in about 6% yield was identified as [Fe₂{ μ -C(CN)H}(μ -CO)(CO)₂(Cp)₂] [7a].

Complex 3g, identified by comparing spectroscopic data with those reported [13b], was obtained as described for the synthesis of 3f, by reacting 2b (186 mg, 0.34 mmol) in thf (10 ml) at -10° C, with a slight excess of Li₂Cu(CN)Bu₂ⁿ (0.35 mmol). Yield: 42 mg (34%).

4.5. Reaction of 2a with BuLi

Buthyllithium (0.49 ml, 0.78 mmol, 1.6 M in hexane) was added to **2a** (0.45 g, 0.78 mmol) in thf (25 ml) at -50° C. The mixture was stirred for 1 h at -50° C and then allowed to warm to r.t. Filtration on an Celite pad and removal of the solvent gave a brown residue that was chromatographed on an alumina column with a CH₂Cl₂-hexane mixture (1:1, v/v) as eluent. A first red fraction, containing [Fe₂(μ -CO)(CO)₂(Cp)₂] (12%), was followed by a second red fraction of [Fe₂{ μ -C(CN)H}(μ -CO)(CO)₂(Cp)₂] (21 mg, 7%) [7c]. Further elution with thf gave a green band of [Fe₂{ μ -C(CN)S(Me)CH₂}(μ -CO)(CO)(CO)(CO)(CP)₂] (4a) (0.14 g,

Found: C, 41%). Anal. 48.15; H, 3.57%. $C_{17}H_{15}Fe_2O_3NS$ requires: C, 48.04; H, 3.56%. IR (CH₂Cl₂) v_{max}(cm⁻¹) 2168w (CN), 1946s, 1788ms and 1634m (CO). NMR: δ_H (CDCl₃): 4.83 (5 H, s, Cp), 4.66 (5 H, s, Cp), 2.55 (1 H, d, J_{AB} 17 Hz, CH₂SCH₃), 2.02 (1 H, d, J_{AB} 17 Hz, CH₂SCH₃) and 1.45 (3 H, s, CH₂SCH₃) ppm. δ_{C} (CD₂Cl₂): 269.4 (µ-CO), 218.9 (CH₂CO), 209.7 (CO), 117.6 (µ-C), 133.1 (CN), 90.5 (Cp), 88.2 (Cp), 40.3 and 21.2 (CH₂SCH₃) ppm. Reactions of 2a with LiPh or LiC=CPh proceeded as above described, giving the same products.

4.6. Reaction of 2b with BuLi

Compound **2b** (0.22 mg, 0.40 mmol) was treated with LiBuⁿ as described for the synthesis of **4a** yielding $[Fe_2{\mu-C(H)S(Me)CH_2}(\mu-CO)(CO)(CO)(Cp)_2]$ **(4b)** (52 mg, 34%). *Anal.* Found: C, 50.22; H, 4.29%. C₁₆H₁₆Fe₂O₃S requires: C, 50.31; H, 4.22%. IR (CH₂Cl₂) v_{max} (cm⁻¹) 1927s, 1771ms and 1667m (CO). NMR: $\delta_{\rm H}$ (CDCl₃): 10.97 (1 H, s, μ -CH), 4.77 (5 H, s, Cp), 4.53 (5 H, s, Cp), 2.53 (1 H, d, $J_{\rm AB}$ 17 Hz, CH₂SCH₃), 2.20 (1 H, d, $J_{\rm AB}$ 17 Hz, CH₂SCH₃) and 1.38 (3 H, s, CH₂SCH₃) ppm. $\delta_{\rm C}$ (CD₂Cl₂): 276.3 (μ -CO), 220.5 (CH₂CO), 216.7 (CO), 152.0 (μ -CH), 87.5 (Cp), 85.1 (Cp), 41.0 and 21.3 (CH₂SCH₃) ppm.

4.7. Synthesis of [Fe₂ {μ-C(CN)CH(COOMe)₂}(μ-CO)(CO)₂(Cp)₂] (**5***a*)

A solution of 2a (0.27 g, 0.47 mmol) in thf (15 ml) was treated with NaCH(COOMe)₂ (0.49 mmol) freshly obtained from CH₂(COOMe)₂ and NaH. The mixture was stirred for 30 min and then evaporated to dryness. Chromatography of the residue on an alumina column eluting with CH_2Cl_2 -hexane mixture (1:2; v/v) gave a red fraction of $[Fe_2\{\mu-C(CN)CH(COOMe)_2\}(\mu-CO) (CO)_2(Cp)_2$ (5a) which was crystallized from CH_2Cl_2 layered with *n*-pentane at -20° C (0.18 g, 77%). Anal. Found: C, 48.49; H, 3.59%. C₂₀H₁₇Fe₂NO₇ requires: C, 48.52; H, 3.46%. IR (CH₂Cl₂) v_{max}(cm⁻¹) 2158w (CN), 1996s, 1961w, 1805m, 1752mw and 1732mw (CO). NMR: $\delta_{\rm H}$ (CDCl₃): 4.91 (10 H, s, Cp), 3.87 (6 H, s, CH₃) and 3.73 (1 H, s, μ -CCH) ppm. δ_{C} (CDCl₃): 264.7 (µ-CO), 210.5 (CO), 169.3 (COOMe), 134.4 (CN), 116.5 (µ-C), 92.2 (Cp), 73.1 (µ-CCH), and 53.3 (Me) ppm.

4.8. Syntheses of $[Fe_2\{\mu-C(CN)CH(COOEt)_2\}(\mu-CO)-(CO)_2(Cp)_2]$ (**5***b*) and $[Fe_2\{\mu-C(CN)CH(COOEt)-(COMe)\}(\mu-CO)(CO)_2(Cp)_2]$ (**6***a*)

Complexes **5b** and **6a** were obtained following the same procedure described for the synthesis of **5a**, by reacting **2a** with equimolar amounts of sodium diethylmalonate and sodium ethylacetoacetate, respectively.

5b: (91%). *Anal.* Found: C, 50.45; H, 4.11%. $C_{22}H_{21}Fe_2NO_7$ requires: C, 50.51; H, 4.05%. IR (CH₂Cl₂) $\nu_{max}(cm^{-1})$ 2159w (CN), 1996s, 1961w, 1804m, 1747mw and 1725mw (CO). NMR: δ_H (CDCl₃): 4.87 (10 H, s, Cp), 4.29 (2 H, q, C*H*HCH₃, *J* = 7,1 Hz), 4.28 (2 H, q, C*H*HCH₃, *J* = 7.1 Hz), 3.64 (1 H, s, µ-CCH) and 1.31 (6 H, t, CH₂CH₃, *J* = 7.1 Hz) ppm. δ_C (CDCl₃): 264.9 (µ-CO), 210.5 (CO), 168.7 (COOEt), 134.3 (CN), 116.9 (µ-C), 92.1 (Cp), 73.4 (µ-CCH), 62.1 (OCH₂CH₃) and 14.8 (OCH₂CH₃) ppm.

6a: (68%). Anal. Found: C, 51.12; H, 3.89%. C₂₁H₁₉Fe₂NO₆ requires: C, 51.16; H, 3.88%. IR (CH₂Cl₂) v_{max} (cm⁻¹) 2157w (CN), 1994s, 1959w, 1804m, 1736mw and 1714mw (CO). NMR: $\delta_{\rm H}$ (CDCl₃): 4.92 (5 H, s, Cp), 4.88 (5 H, s, Cp), 4.35 (2 H, q, CH₂CH₃, J = 7.0 Hz), 3.77 (1 H, s, µ-CCH), 2.38 (3 H, s, COCH₃), and 1.38 (3 H, t, CH₂CH₃, J = 7.0 Hz) ppm. $\delta_{\rm C}$ (CDCl₃): 265.0 (µ-CO), 211.2, 210.6 (CO), 201.8 (COMe), 169.3 (COOEt), 126.2 (µ-C), 92.3, 92.1 (Cp), 81.0 (µ-CCH), 62.4 (OCH₂CH₃), 31.0 (COCH₃), and 14.9 (OCH₂CH₃) ppm.

4.9. Syntheses of $[Fe_2{\mu-C(H)CHRR'}(\mu-CO)(CO)_2(Cp)_2]$ (R = R' = COOMe, 5c; R = R' = COOEt, 5d;R = COOEt, R' = COMe, 6b)

The complexes **5c,d** and **6b** were obtained following the same procedure described for the synthesis of **5a,b** and **6a**, by reacting **2b** with NaCH(COOMe)₂, NaCH-(COOEt)₂ and NaCH(COOEt)(COMe), respectively.

5c: (65%). *Anal.* Found: C, 48.56; H, 3.89%. C₁₉H₁₈Fe₂O₇ requires: C, 48.55; H, 3.86%. IR (CH₂Cl₂) ν_{max} (cm⁻¹) 1982s, 1943w, 1785m, 1748mw and 1728mw (CO). NMR: $\delta_{\rm H}$ (CDCl₃): 11.01 (1 H, d, J = 11 Hz, μ-CH), 4.75 (10 H, s, Cp), 3.85 (6 H, s, CH₃) and 4.45 (1 H, d, J = 11 Hz, μ-CCH) ppm. $\delta_{\rm C}$ (CDCl₃): 271.0 (μ-CO), 212.1 (CO), 171.0 (COOMe), 157.9 (μ-C), 88.3 (Cp), 73.5 (μ-CCH), and 53.0 (Me) ppm.

Compounds **5d** (71%) and **6b** (78%) were identified by comparison of their spectroscopic properties with those reported in the literature [13a].

4.10. Synthesis of $[Fe_2\{\mu-C(X)CH(COR)_2\}(\mu-CO)-(CO)_2(Cp)_2]$ (X = CN, R = Me, **7a**; X = CN, R = Ph, **7b**; X = H, R = Me, **7c**; X = H, R = Ph, **7d**)

Compound **2a** (0.19 g, 0.33 mmol) and NaCH-(COMe)₂ (0.33 mmol), freshly obtained from NaH and 2,4-pentanedione, were stirred in thf (15 ml) for 2 h. The solvent was then removed and the residue chromatographed on silica-gel column with CH_2Cl_2 -hexane (1:1, v:v) mixture as eluent. A first red fraction of $[Fe_2(CO)_4(Cp)_2]$ (31 mg, 27%) was discharged. Elution with CH_2Cl_2 gave a second red fraction of $[Fe_2\{\mu$ -

C(CN)CH(COMe)₂}(μ -CO)(CO)₂(Cp)₂] (**7a**) which was recrystallized from CH₂Cl₂ layered with *n*-pentane at – 20°C. Yield: 69 mg (45%). *Anal.* Found: C, 3.79; H, 52.02%. C₂₀H₁₇Fe₂NO₅ requires: C, 51.88; H, 3.70%. IR (CH₂Cl₂) ν_{max} (cm⁻¹) 2153w (CN), 1992s, 1956w, 1805m, 1732mw and 1695mw (CO). NMR: $\delta_{\rm H}$ (CDCl₃): 4.89 (10 H, s, Cp), 4.00 (1 H, s, μ -CCH), and 2.41 (3 H, s, CH₃) ppm. $\delta_{\rm C}$ (CDCl₃): 211.0 (CO), 203.0 (*C*OMe), 131.6, 129.5 (CN and μ -C), 92.3 (Cp), 90.3 (μ -CCH), and 30.7 (CH₃) ppm.

Compound **7b** was analogously prepared from **2a** (0.22 g, 0.38 mmol) and NaH(COPh)₂ (94 mg, 38 mmol). Yield: 0.13 g (60%). *Anal.* Found: C, 61.43; H, 3.65%. C₃₀H₂₁Fe₂NO₅ requires: C, 61.36; H, 3.60%. IR (CH₂Cl₂) v_{max} (cm⁻¹) 2157w (CN), 1990s, 1953w, 1804m, 1670mw and 1673mw (CO). NMR: $\delta_{\rm H}$ (CDCl₃): 7.99–7.43 (10 H, m, Ph), 5.77 (1 H, s, μ -CCH) and 4.77 (10 H, s, Cp) ppm. $\delta_{\rm C}$ (CDCl₃): 265.0 (μ -CO), 211.0 (CO), 196.0 (COPh), 138.2–129.2 (Ph), 92.6 (Cp) and 80.5 (μ -CCH) ppm.

Compounds **7c** and **7d** were obtained as described above by reacting **2b** with equimolar amounts of NaH-(COMe)₂ and NaHC(COPh)₂, respectively.

7c: (53%). The spectroscopic properties of 7c were identical to those reported [13a].

7d: (64%). *Anal.* Found: C, 61.83; H, 3.99%. C₂₉H₂₂Fe₂O₅ requires: C, 61.96; H, 3.94%. IR (CH₂Cl₂) v_{max} (cm⁻¹) 1975s, 1935w, 1784m, 1693mw and 1657mw (CO). NMR: δ_{H} (CDCl₃): 11.36 (1 H, d, J = 12 Hz, μ -CH), 7.60–7.45 (10 H, m, Ph), 6.78 (1 H, d, J = 12 Hz, μ -CCH) and 4.66 (10 H, s, Cp) ppm. δ_{C} (CDCl₃): 272.2 (μ -CO), 212.9 (CO), 196.4 (*C*OPh), 164.6 (μ -C), 137.9–129.5 (Ph), 88.6 (Cp) and 80.5 (μ -CCH) ppm.

4.11. Syntheses of $[Fe_{\{u=C(X)\in H\}}(u=CO)(Cu)]$

 $[Fe_2\{\mu-C(X)CH_2(COR)\}(\mu-CO)(CO)_2(Cp)_2]$ (X = CN, R = Me, **8a**; X = CN, R = Ph, **8b**; X = H, R = Me, **8c**)

The complexes 8a-c were obtained following the same procedure described for the synthesis of 7a-c, using alumina in place of silica gel, for the column chromatography.

8a: (58%) *Anal.* Found: C, 3.79; H, 52.02%. $C_{18}H_{15}Fe_2NO_4$ requires: C, 51.35; H, 3.59%. IR (CH₂Cl₂) ν_{max} (cm⁻¹) 2151w (CN), 1990s, 1956w, 1801m and 1719w (CO). NMR: δ_H (CDCl₃): 4.88 (10 H, s, Cp), 3.76 (2 H, s, μ -CCH₂) and 2.19 (3 H, s, CH₃) ppm. δ_C (CDCl₃): 266.1 (μ -CO), 211.5 (CO), 205.9 (COMe), 162.0 (μ -C), 129.8 (CN), 91.7 (Cp), 68.3 (μ -CCH₂), and 30.6 (CH₃) ppm.

8b: (65%) Anal. Found: C, 3.79; H, 52.02%. $C_{23}H_{17}Fe_2NO_4$ requires: C, 57.19; H, 3.55%. IR (CH₂Cl₂) v_{max} (cm⁻¹) 2155w (CN), 1990s, 1955w, 1801m and 1689w (CO). NMR: δ_H (CDCl₃): 7.96–7.45 (5 H, Ph), 4.95 (10 H, s, Cp) and 4.35 (2 H, s, μ -CCH₂) ppm. $\delta_{\rm C}$ (CDCl₃): 266.3 (µ-CO), 211.6 (CO), 197.9 (COMe), 150.0 (µ-C), 137.6–129.3 (Ph), 128.5 (CN), 91.9 (Cp) and 63.7 (µ-CCH₂), ppm.

8c: (54%) Compound **8c** was identified by comparison of its spectroscopic data with those reported in the literature [13a].

4.12. Syntheses of $[Fe_2 {\mu-C(X)CH(Ph)(CN)}(\mu-CO)-(CO)_2(Cp)_2] (X = CN, 9a; X = H, 9b)$

To a solution of **2a** (0.19 g, 0.33 mmol) in thf (15 ml) was added NaCH(C₆H₅)(CN) (0.33 mmol) obtained from benzylcyanide and NaH. The mixture was stirred for 60 min and then evaporated to dryness. Chromatography of the residue on an alumina column with CH₂Cl₂ as eluent, gave a purple–red fraction of **9a** which was crystallized from CH₂Cl₂ layered with n-pentane at -20° C (0.14 g, 88%). *Anal.* Found: C, 57.44; H, 3.41%. C₂₃H₁₆Fe₂N₂O₃ requires: C, 57.54; H, 3.36%. IR (CH₂Cl₂) v_{max} (cm⁻¹) 2159w (CN), 1994s, 1958w and 1810m (CO). NMR: $\delta_{\rm H}$ (CDCl₃): 7.50 (5 H, m, Ph), 5.02 (5 H, s, Cp), 4.58 (5 H, s, Cp) and 4.07 (1 H, s, μ -CCH) ppm. $\delta_{\rm C}$ (CDCl₃): 262.4 (μ -CO), 211.6, 210.6 (CO), 138.1–121.5 (Ph), 133.2 (CN), 126.9 and 121.5 (μ -C and CN), 92.7, 91.7 (Cp) and 58.5 (μ -CCH) ppm.

Compound **9b** was analogously prepared from **2b** (0.27 g, 0.49 mmol) and NaCH(C₆H₅)(CN) (0.50 mmol). Yield: 0.12 g (51%). *Anal.* Found: C, 56.22; H, 3.70%. C₂₃H₁₇Fe₂N₂O₃ requires: C, 56.33; H, 3.65%. IR (CH₂Cl₂) v_{max} (cm⁻¹) 2230w (CN), 1980s, 1940w and 1792m (CO). NMR: δ_{H} (CDCl₃): 10.77 (1 H, d, *J* = 12 Hz, μ -CH), 7.68–7.45 (5 H, m, Ph), 4.91 (5 H, s, Cp), 4.46 (1 H, d, *J* = 12 Hz, μ -CCH) and 4.31 (5 H, s, Cp) ppm. δ_{C} (CDCl₃): 165.6 (μ -C), 129.8–121.8 (Ph), 98.1, 88.3 (Cp) and 58.2 (μ -CCH) ppm.

4.13. Reaction of 2a with NaCH(CN)₂

Complex 2a (0.17 g, 0.29 mmol) in thf (15 ml) at -30° C was treated with NaCH(CN)₂ (0.30 mmol) generated from NaH and malononitrile. The mixture is then allowed to warm to r.t. and stirred for further 60 min. Evaporation of the solvent and chromatography of the residue on an alumina column with CH₂Cl₂-hexane (1:2, v:v) mixture as eluent afforded a first red fraction of $[Fe_2(CO)_4(Cp)_2]$ (20%) that was discharged. Elution with CH₂Cl₂-hexane (1:1, v:v) gave a brown fraction of $[Fe_3(\mu-CO)_3(\mu_3-CCN)(Cp)_3]$ (31%) which was identified by comparison with the reported spectroscopic data [15]. Further elution with CH₂Cl₂ gave a yellow fraction of $[Fe(CO)_2 \{C(CN)=C(CN)_2\}(Cp)]$ (12%). Anal. Found: C, 51.66; H, 1.88%. C₁₂H₅FeN₃O₂ requires: C, 51.65; H, 1.81%. IR (CH₂Cl₂) $v_{max}(cm^{-1})$ 2225w (CN), 2057s and 2015s (CO). Mass spectrum: m/z 279 (M^+ , 1), 251 (M^+ – CO, 2), 223 (M^+ – 2CO, 4), 147 (CpFeCN⁺, 100%).

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