Journal of Organometallic Chemistry, 415 (1991) 395–405
Elsevier Sequoia S.A., Lausanne
JOM 22006

Reactions of $[Fe_2\{\mu\text{-}C(CN)SMe_2\}(\mu\text{-}CO)(CO)_2(Cp)_2]$-$SO_3CF_3$ ($Cp = \eta\text{-}C_5H_5$) with alcohols

Luigi Busetto *, Maria Cristina Cassani, Valerio Zanotti
Dipartimento di Chimica Fisica ed Inorganica dell' Università, Viale Risorgimento 4, 40136 Bologna (Italy)

Vincenzo G. Albano * and Dario Braga
Dipartimento di Chimica "G. Ciamician", Via Selmi 2, 40126 Bologna (Italy)

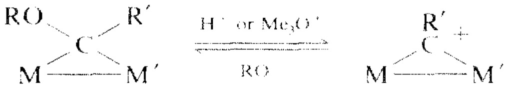
(Received April 5th, 1991)

Abstract

The reactions of $[Fe_2\{\mu\text{-}C(CN)SMe_2\}(\mu\text{-}CO)(CO)_2(Cp)_2]SO_3CF_3$ (**1**) ($Cp = \eta\text{-}C_5H_5$) with alcohols and alkoxides have been investigated. Nucleophilic attack of the oxygen atom on the μ-C carbon with displacement of the Me_2S molecule was observed in all cases. The resulting μ-cyanoalkoxycarbene derivatives $[Fe_2\{\mu\text{-}C(CN)OR\}(\mu\text{-}CO)(CO)_2(Cp)_2]$ (R = Me, **2a**; Et, **2b**; ^iPr, **2c**; CH_2Ph, **2d**; $CH_2CH{=}CH_2$, **2e**; $CH_2CH_2NMe_2$, **2f**; CH_2CH_2OH, **2g**; C_6H_5, **3a**; C_6H_4-*o*-NO_2, **3b**) have been characterized spectroscopically. The complex $[Fe_2\{\mu\text{-}C(CN)OCH_2CH{=}CH_2\}(\mu\text{-}CO)(CO)_2(Cp)_2]$ (**2e**) undergoes a photolytically-promoted intramolecular CO substitution by the olefinic termination to give $[FeFe\{\mu\text{-}C(CN)OCH_2CH{=}CH_2\}(\mu\text{-}CO)(CO)(Cp)_2]$ (**5**), which was be subjected to an X-ray diffraction study. Some structural features were as expected, in particular the location of Cp in a *cis* disposition with respect to the CN group. The molecule is asymmetric as a consequence of the coordination of the allyl in the place of a terminal CO group; the configurations of the four chiral centres are discussed.

Introduction

The limited success of the Fischer method in the synthesis of μ-carbene containing cluster complexes [1] could account for the scarcity of dinuclear μ-alkoxycarbenes reported up to now. However, several routes to this type of derivative are known. Stone and co-workers have described a general synthetic method involving attack of zerovalent metal complexes (Pd, Pt) on mononuclear alkoxycarbene complexes [2]. Similarly $[Fe_2\{\mu\text{-}C(OMe)H\}(\mu\text{-}CO)(CO)_2(Cp)_2]$ was obtained by reaction of $[Fe\{C(OMe)H\}(CO)_2(Cp)]^+$ with $[Fe(CO)_2(Cp)]^-$ [3]. The addition of RO^- to cationic dinuclear μ-alkylidyne, which might provide a simple route to μ-alkoxycarbenes [4], has been mainly applied to reverse the formation of μ-alkylidyne complexes [2] (eq. 1). Furthermore, in some cases, these latter derivatives react with RO^- (R = Me, Et) to form complexes containing a μ-carboalkoxycarbene group [μ-C(COOR)R′] [5].



(1)

We recently described the synthesis of the cationic μ-cyanocarbene complex $[Fe_2\{\mu\text{-}C(CN)SMe_2\}(\mu\text{-}CO)(CO)_2(Cp)_2]SO_3CF_3$ (**1**) and also demonstrated that the Me_2S molecule in **1** can be readily replaced by a variety of nucleophiles to give new neutral μ-cyanocarbene diiron complexes [6]. We describe below the reactions of **1** with a variety of alcohols ROH (R = Me, Et, ^iPr, CH_2Ph, $CH_2CH{=}CH_2$, $CH_2CH_2NMe_2$, CH_2CH_2OH) and alkoxides RO^- (R = Ph, o-$NO_2C_6H_5$), which give bridging cyanoalkoxycarbene complexes. The crystal structure of $[FeFe\{\mu\text{-}C(CN)OCH_2CH{=}CH_2\}(\mu\text{-}CO)(CO)(Cp)_2]$ (**5**), obtained by photolysis of $[Fe_2\{\mu\text{-}C(CN)OCH_2CH{=}CH_2\}(\mu\text{-}CO)(CO)_2(Cp)_2]$ (**2e**), is also described. Finally the reaction of **1** with CH_3COO^- is described and discussed.

Results and discussion

The reactions of **1** with alcohols result in rapid formation of complexes of type **2** (eq. 2).

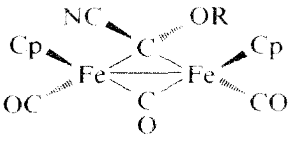
(2)

(**1**) (**2a–g**)

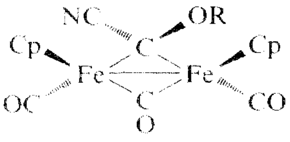
(R = Me, **2a**; Et, **2b**; ^iPr, **2c**; CH_2Ph, **2d**; $CH_2CH{=}CH_2$, **2e**; $CH_2CH_2NMe_2$, **2f**; CH_2CH_2OH, **2g**)

The reactions probably proceed via the unstable oxonium intermediates $[Fe_2\{\mu\text{-}C(CN)HOR\}(\mu\text{-}CO)(CO)_2(Cp)_2]^+$, which generate the neutral cyanoalkoxycarbenes **2a–g**. These derivatives are red crystalline solids stable under N_2 and soluble in acetonitrile, acetone, and chlorinated solvents.

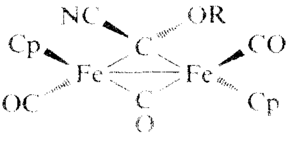
Complexes **2a–g** could be expected to exist as three possible stereoisomers.



(*cis*-**A**)



(*cis*-**B**)



(*trans*)

The IR spectra of **2a–g** (Table 1) in polar and non-polar solvents display, in addition to a weak ν(CN) band, a strong–weak–medium ν(CO) band pattern (e.g. 2007s, 1970w, 1798m cm^{-1} in CH_2Cl_2 for **2a**), consistent with a *cis* configuration [7] (Cp ligands *cis* to each other). The ^1H NMR data for **2a–g** (Table 2) also indicate the presence of only a single *cis* isomer, since the protons of the Cp ligands

Table 1

IR data for the μ-carbene complexes [a]

Compound	ν(CN) (cm^{-1})	ν(CO) (cm^{-1})
$[Fe_2\{\mu\text{-}C(CN)SMe_2\}(\mu\text{-}CO)(CO)_2(Cp)_2]SO_3CF_3$ (**1**)	2175w [b]	2013s, 1982w, 1834m [b]
$[Fe_2\{\mu\text{-}C(CN)OMe\}(\mu\text{-}CO)(CO)_2(Cp)_2]$ (**2a**)	2163w	2007s, 1971w, 1800m
$[Fe_2\{\mu\text{-}C(CN)OEt\}(\mu\text{-}CO)(CO)_2(Cp)_2]$ (**2b**)	2162w	2007s, 1970w, 1798m
$[Fe_2\{\mu\text{-}C(CN)OiPr\}(\mu\text{-}CO)(CO)_2(Cp)_2]$ (**2c**)	2161w	2005s, 1968w, 1796m
$[Fe_2\{\mu\text{-}C(CN)OCH_2Ph\}(\mu\text{-}CO)(CO)_2(Cp)_2]$ (**2d**)	2164w	2007s, 1971w, 1801m
$[Fe_2\{\mu\text{-}C(CN)OCH_2CH{=}CH_2\}(\mu\text{-}CO)(CO)_2(Cp)_2]$ (**2e**)	2164w	2007s, 1971w, 1800m
$[Fe_2\{\mu\text{-}C(CN)OCH_2CH_2NMe_2\}(\mu\text{-}CO)(CO)_2(Cp)_2]$ (**2f**)	2165w	2007s, 1971w, 1801m
$[Fe_2\{\mu\text{-}C(CN)OCH_2CH_2OH\}(\mu\text{-}CO)(CO)_2(Cp)_2]$ (**2g**)	2164w	2006s, 1971w, 1801m
$[Fe_2\{\mu\text{-}C(CN)OPh\}(\mu\text{-}CO)(CO)_2(Cp)_2]$ (**3a**)	2164w	2013s, 1979w, 1806m
$[Fe_2\{\mu\text{-}C(CN)OC_6H_5o\text{-}NO_2\}(\mu\text{-}CO)(CO)_2(Cp)_2]$ (**3b**)	2169w	2016s, 1981w, 1809m
$[Fe_2\{\mu\text{-}C(CN)OCOMe\}(\mu\text{-}CO)(CO)_2(Cp)_2]$ (**4**)	2175w	2011s, 1976w, 1809m, 1738m
$[Fe\overline{Fe\{\mu\text{-}C(CN)OCH_2CH}{=}CH_2\}(\mu\text{-}CO)(CO)(Cp)_2]$ (**5**)	2178w	1958s, 1787m

[a] Spectra obtained in CH_2Cl_2 solution. [b] In CH_3CN.

appear as a singlet. Likewise the ^{13}C NMR spectra show only one large Cp signal. Considerations based upon hindrance by the μ-C substituents and the analogy between **2a–g** and the closely related compounds $[Fe_2\{\mu\text{-}C(CN)X\}(\mu\text{-}CO)(CO)_2(Cp)_2]$ ($X = SCH_3$ [8], $N(CH_3)COSCH_3$ [9]), for which a *cis*-**A** geometry was found by an X-ray study, suggest that **2a–g** also adopt the *cis*-**A** geometry, in which the OR group is opposite to the more hindered Cp ligands. However the ^1H and ^{13}C NMR spectra of complexes **2a–g** in the Cp region reveal the presence of small amounts of the *trans* isomer and indicate the absence of the *cis*-**B**. For example, in the case of **2b**, the ^1H NMR spectrum (in CD_2Cl_2) shows, in addition to the resonance at 4.80 from the *cis* isomer, equally intense signals at 4.88 and 5.08 ppm attributed to the *trans* isomer (*cis/trans* ratio approximately 10/1). Likewise, in the ^{13}C NMR spectrum equally intense Cp resonances, attributed to the *trans* isomer, are observed at 92.2 and 91.9 ppm. The predominance of the *cis* isomer with the bulkier μ-C substituent on the side of the terminal CO groups is consistent with the results obtained for related diiron μ-carbene complexes [10].

Despite the spectroscopically-indicated *cis* nature of **1** [11], the observed mixture of isomers for the **2a–g** derivatives, can be accounted for in terms of the well known Adams–Cotton [12] mechanism of *cis–trans* isomerization in dinuclear metal systems with bridging ligands, including μ-carbene complexes [13].

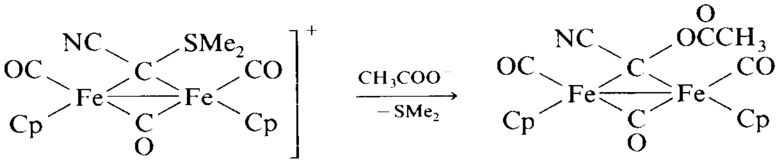
The reactions of **1** in acetonitrile with phenol or *o*-nitrophenol are very slow, probably because of the lower basicity of phenols, while reactions with NaOPh or $NaOC_6H_5$-*o*-NO_2 immediately afford the corresponding $[Fe_2\{\mu\text{-}C(CN)OR\}(\mu\text{-}CO)(CO)_2(Cp)_2]$ (R = Ph, **3a**; *o*-$NO_2C_6H_5$, **3b**) derivatives in 60–75% yield. The spectroscopic properties of complexes **3a**, **b** are as expected (Tables 1 and 2). Shifts of the ν(CO) and ν(CN) frequencies to higher wavenumbers compared with those for compounds **2a–g** (e.g. 2169, 2016, 1981, 1809 of **3b** vs. 2163, 2007, 1971, 1800 of **2a** in CH_2Cl_2) reflect the decreased electron donor properties of the phenols.

The reaction of **1** with $HOCH_2CH_2NMe_2$ was carried out in order to compare the reactivity of an alcohol with that of a tertiary amine. We had previously found that treatment of **1** with an excess of tertiary amines, such as NMe_3 or DABCO

	$^{13}C\{^1H\}$ (δ)
2a	268.3 (μ-CO); 210.8 (CO); 129.1 (CN); 176.8 (μ-C); 90.9 (Cp); 61.8 (
2b	268.9 (μ-CO); 210.9 (CO); 129.3 (CN); 175.1 (μ-C); 90.8 (Cp); 70.8 (
2c	
2d	
2e	268.2 (μ-CO); 210.6 (CO); 129.2 (CN); 174.5 (μ-C); 134.8 ($CH{=}CH_2$); 117.4 ($CH{=}CH_2$); 90.8 (Cp); 75.5 (OCH_2)
2f	
2g	
3a	
3b	
4	
5	

(DABCO = 1,4-diazabicyclo[2.2.2]octane) gave the cationic adducts $[Fe_2\{\mu\text{-}C(CN)NR_3\}(\mu\text{-}CO)(CO)_2(Cp)_2]^+$ [14]. In spite of the higher basicity of the amino group, $HOCH_2CH_2NMe_2$ reacts with **1** to yield exclusively the alkoxycarbene derivative **2f** (eq. 2); this indicates that the ammonium derivatives $[Fe_2\{\mu\text{-}C(CN)NR_3\}(\mu\text{-}CO)(CO)_2(Cp)_2]^+$ are less stable than the neutral cyanoalkoxy complexes.

The versatility of the sulphonium salt **1** in reactions with oxygen donor nucleophiles is also evident in the reaction with sodium acetate, which affords the red air-stable **4** in 69% yield (eq. 3).



(1) (4) (3)

To the best of our knowledge, complex **4** and $[Fe_2\{\mu\text{-}C(H)OCOCH_3\}(CO)_8]$ [9b] are the only examples of dinuclear μ-acetoxycarbenes so far described. The IR spectrum of **4** (Table 1) shows $\nu(CO)$ bands at 2011s, 1976m, 1809m, and 1738m cm^{-1} (in CH_2Cl_2) consistent with a *cis* configuration, the last band is attributed to the acetoxy group. In addition a weak band at 2175 cm^{-1} $\nu(CN)$ is observed. The ^1H NMR spectrum of **4** in CD_2Cl_2 (Table 2) also supports the *cis* configuration, since it shows only singlets at 4.88 (Cp) and 1.96 ppm (Me).

We had previously described the intramolecular CO substitution that occurs in photolysis of $[Fe_2\{\mu\text{-}C(CN)SMe\}(\mu\text{-}CO)(CO)_2(Cp)_2]$, to give $[FeFe\{\mu\text{-}C(CN)SMe\}(\mu\text{-}CO)(CO)(Cp)_2]$ in which the bridging ligand is η^2-C-S coordinated [8]. In an analogous reaction the complex $[W_2\{\mu\text{-}C(H)CH{=}CMe_2\}(CO)_{10}]$ generates the double bridged derivative $[WW\{\mu\text{-}C(H)CH{=}CMe_2\}(CO)_9]$ by intramolecular replacement of a CO ligand by the C–C double bond [15].

Despite the existence of η^2-C-O coordinated μ-alkoxy carbene complexes [1a,b], we found that photolysis of **2e** in THF results in intramolecular replacement of a CO ligand by the double bond of the allylic moiety to give the μ-carbene complex $[FeFe\{(\mu\text{-}C(CN)(OCH_2CH{=}CH_2)\}(\mu\text{-}CO)(CO)(Cp)]$ (**5**). The nature of complex **5** was unambiguously determined by an X-ray structural study.

The molecular geometry is depicted in Fig. 1 and some relevant bond parameters are listed in Table 3. Most features of the molecule are the same as for other members of the family, [8,9], i.e. the iron atoms are formally four coordinate, there is a *cis* configuration of the Cp groups, there are two bridging ligands, a CO ligand and a disubstituted carbene unit, stabilizing the Fe–Fe interaction [2.535(1) Å]. Peculiar to the present species is the alkoxy substituent at the carbene atom [C(3)] and the coordination of the olefinic termination of this substituent to Fe(1), replacing a terminal CO ligand. The ligand substitution results in an asymmetric molecule in which as many as four chiral centres [Fe(1), Fe(2), C(3) and C(5)] and a chiral ring [Fe(1)–C(3)–O(3)–C(4)–C(5)] are formed. The crystal contains the racemic mixture but, in order to define the diastereoisomer the configurations of the stereogenic atoms have been assigned on the basis of Fig. 1. An analysis of the molecular stereogeometry shows that the formation of this diastereoisomer out the

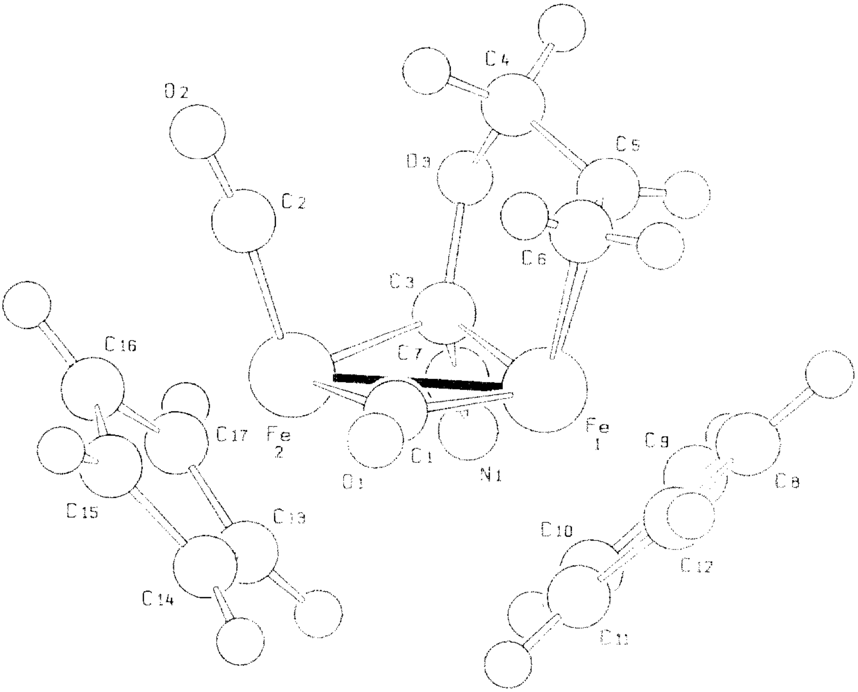


Fig. 1. View of the asymmetric molecule $[\mathrm{Fe}\overline{\mathrm{Fe}\{\mu\text{-}\mathrm{C(CN)OCH_2CH{=}CH_2}}\}(\mu\text{-}\mathrm{CO})(\mathrm{CO})_2(\mathrm{Cp})_2]$ (**5**). The crystal contains the racemic mixture of the diastereoisomer defined by the following configurations of the chiral atoms (the Fe–Fe bond is ignored): Fe(1)*R*, Fe(2)*S*, C(3)*R*, C(5)*R*.

many possible isomers is determined by the following factors: (i) The configuration adopted by the bridging carbene atom [C(3)] is that minimizing the molecular crowding, with the less hindering substituent [CN] placed *syn* to the bulky Cp ligands. (ii) The coordinated enantioface of the alkene fragment and the ring conformation are mutually correlated in order to optimize the non-bonded interactions and the strength of coordination. (The Fe(1)–C(5,6) distances are almost equal

Table 3

Relevant bond distances and angles for $[\mathrm{Fe}\overline{\mathrm{Fe}\{\mu\text{-}\mathrm{C(CN)OCH_2CH{=}CH_2}}\}(\mu\text{-}\mathrm{CO})(\mathrm{CO})(\mathrm{Cp})_2]$ (**5**)

Fe(1)–Fe(2)	2.535(1)	O(3)–C(4)	1.438(9)
Fe(1)–C(1)	1.906(7)	C(4)–C(5)	1.51(1)
Fe(2)–C(1)	1.907(7)	C(5)–C(6)	1.36(1)
C(1)–O(1)	1.185(8)	Fe(1)–C(5)	2.118(8)
Fe(2)–C(2)	1.750(9)	Fe(1)–C(6)	2.113(8)
C(2)–O(2)	1.12(1)	C(3)–C(7)	1.463(9)
Fe(1)–C(3)	1.974(7)	C(7)–N(1)	1.138(9)
Fe(2)–C(3)	1.976(7)	Fe(1)–C(Cp)	2.12(1)(av.)
C(3)–O(3)	1.423(9)	Fe(2)–C(Cp)	2.11(1)(av.)
C(3)–C(7)–N(1)	179.3(8)	O(3)–C(4)–C(5)	109.7(4)
O(3)–C(3)–C(7)	101.8(6)	C(4)–C(5)–C(6)	123.1(2)
C(3)–O(3)–C(4)	110.3(5)		

[average 2.115(8) A], and the angles in the ring are all normal.) (iii) Coordination of the opposite enantioface to Fe(1) or the same enantioface to Fe(2) would result in short contacts between the ring hydrogens and the terminal CO ligand. (iv) Coordination to Fe(2) accompanied by inversion of the coordinated enantioface affords the enantiomer and accounts for the formation of the racemic mixture.

The geometry of the /,-C(CN)(OR) fragment indicates that 0(3) does not participate in rr-interactions with the carbene atom, since the oxygen atom exhibits tetrahedral hybridization of its orbitals [C(3)-O(3)-C(4) 110.3(5)°] and there is no significant difference between O(3)-C(3)(carbene) and 0(3) C(4)(alkyl) distances [1.423(9), 1.438(9) A, respectively].

The spectroscopic properties of 5 are as expected. The IR spectrum, in CH2C12 solution, in the v(CO) region, is similar to that of [FeFe{/x-C(CN)SCH3)}(/*-CO)(CO)(Cp)2] [8] (1958s, 1787 cm-a for 5 vs. 1959s, 1783m cm-1), showing a single absorption for the terminal CO ligand at lower wavenumbers than that for the parent compound 2e. Owing to their non-equivalence, the Cp resonances of 5 show two separate singlets in the 1H and ~3C NMR (Table 2). The chelate ring in 5 also makes the OCH 2 protons chemically non equivalent. As a consequence two corresponding sets of signals, at 8 4.06 and 2.04, are observed in the 1H NMR spectrum.

Experimental

All reactions were carried out under nitrogen by standard Schlenk techniques. Solvents were distilled under nitrogen from appropriate drying agents immediately before use: CH3CN and CH2C12 from Call 2, tetrahydrofuran from sodium benzophenone ketyl, n-pentane and hexanes from sodium wire. Infrared spectra were recorded on a Perkin Elmer 983-G spectrometer. 1H and 13C{1H} NMR spectra were recorded on a Varian Gemini 200 spectrometer with SiMe4 as internal standard. Melting points were determined with a Btichi instrument and are uncorrected. Elemental analyses were determined by Pascher Microanalytical Laboratorium (Bonn Germany). The compound [Fe2{~-C(CN)SMe 2}(/,-CO)(CO)2-(Cp)2]SO3C~ (1) was prepared as previously described [6].

Synthesis of [Fe2{ I-C(CN)OMe) (I*-CO)(CO)_,(Cp):] (2a)*

To a stirred solution of [Fez{/,t-C(CN)SMe2}(/I-CO)(CO)z(Cp)2]SO3CF3 (1) (0.30 g, 0.52 mmol) in CH3CN (10 ml) was added an excess of CH3OH (4 ml). The mixture was immediately passed through an alumina column (10 x 3 cm) with CHzC12 as eluent. The red solution obtained was evaporated to dryness under vacuum and the residue recrystallized from CH2C12 layered with n-pentane at -20 °C to give red crystals of 2a. Yield 0.19 g (93%). M.p. 174-175 °C (dec.) Anal. Found: C, 48.8; H, 3.4. C16H13Fe204N calc.: C, 48.65; H, 3.32%.

Synthesis of [Fe2{tx-C(CN)OR }(tx-CO)(CO)2(Cp):] (R = Et, 2b; 'Pr 2c; CH:Ph, 2d," CH_,CH=CH2, 2e," CH2CH2NMe 2, 2f, CH:CH:OH, 2g)

These complexes were obtained by the procedure described for the synthesis of 2a.

2b. Yield 90%. M.p. 163-165°C (dec.) Anal. Found: C, 49.6; H, 3.5. C17H15Fe204N calc.: C, 49.92; H, 3.70%.

2c. Yield 75%. M.p. 144–146 °C (dec.) Anal. Found: C, 51.2; H, 4.09. $C_{18}H_{17}Fe_2O_4N$ calc.: C, 51.10; H, 4.05%.

2d. Yield 40%. M.p. 129–131 °C (dec.) Anal. Found: C, 56.1; H, 3.7. $C_{22}H_{17}Fe_2O_4N$ calc.: C, 56.09; H, 3.64%.

2e. Yield 74%. M.p. 124–126 °C (dec.) Anal. Found: C, 51.8; H, 3.5. $C_{18}H_{15}Fe_2O_4N$ calc.: C, 51.35; H, 3.59%.

2f. Yield 43%. M.p. 114–116 °C (dec.) Anal. Found: C, 49.8; H, 4.4. $C_{19}H_{20}Fe_2O_4N_2$ calc.: C, 50.48; H, 4.46%.

2g. Yield 40%. M.p. 161–163 °C (dec.) Anal. Found: C, 47.4; H, 3.5. $C_{17}H_{15}Fe_2O_5N$ calc.: C, 48.04; H, 3.5%.

*Synthesis of [Fe₂{μ-C(CN)OPh}(μ-CO)(CO)₂(Cp)₂] (**3a**)*

To a stirred solution of $[Fe_2\{\mu\text{-}C(CN)SMe_2\}(\mu\text{-}CO)(CO)_2(Cp)_2]SO_3CF_3$ (**1**) (0.26 g, 0.45 mmol) in CH_3CN (10 ml) was added NaOPh (freshly prepared from HOPh and NaH) (0.06 g, 0.50 mmol). After 5 min the mixture was passed through an alumina column (5 × 3 cm) with CH_2Cl_2 as eluent. The red solution obtained was evaporated to dryness under vacuum and the residue crystallized from CH_2Cl_2

Table 4

Crystal data and details of measurements for **5**

Formula	$C_{17}H_{15}Fe_2NO_3$
M_r	393
Crystal size (mm)	0.12 × 0.10 × 0.10
System	monoclinic
Space group	$C2/c$
a (Å)	24.89(3)
b (Å)	9.485(4)
c (Å)	14.552(6)
β (°)	118.65(5)
U (Å^3)	3014.8
Z	8
$F(000)$	1600
D_{calcd} (g cm^{-3})	1.73
λ(Mo-K_α) (Å)	0.71069
μ(Mo-K_α) (cm^{-1})	18.5
θ-range (°)	2.5–25
ω-scan width (°)	1.5
Requested counting $\sigma(I)/I$	0.02
Prescan rate (deg min^{-1})	5
Prescan acceptance $\sigma(I)/I$	0.5
Maximum scan time (s)	120
Range of reflections measured (h_{min} h_{max}, k_{min} k_{max}, l_{min} l_{max})	−29 29, 0 11, 0 17
Measured reflections	2183
Unique observed reflections used in the refinement [$I_o > 2\sigma(I_o)$]	1770
No. of refined parameters	189
R, R_w [a], S	0.064, 0.070, 0.40
K, g [a]	0.4, 0.0001

[a] $R_w = \Sigma[(|F_o| - |F_c|)w^{1/2}]/\Sigma|F_o|w^{1/2})$, where $w = k/[\sigma(F) + |g|F^2]$.

layered with n-pentane at −20°C. Yield 60%. M.p. 158–160°C (dec.). Anal. Found: C, 55.1; H, 3.4. $C_{21}H_{15}Fe_2O_4N$ calc.: C, 55.18; H, 3.31%.

Synthesis of $[Fe_2\{\mu\text{-}C(CN)OC_6H_5\text{-o-}NO_2\}(\mu\text{-}CO)(CO)_2(Cp)_2]$ ***(3b)***

Compound **3b** was obtained by the procedure described for **3a**. Yield 76%. M.p. 160–162°C (dec.). Anal. Found: C, 50.4; H, 2.8. $C_{21}H_{14}Fe_2O_6N_2$ calc.: C, 50.24; H, 2.81%.

Synthesis of $[Fe_2\{\mu\text{-}C(CN)OCOCH_3\}(\mu\text{-}CO)(CO)_2(Cp)_2]$ ***(4)***

A solution of $[Fe_2\{\mu\text{-}C(CN)SMe_2\}(\mu\text{-}CO)(CO)_2(Cp)_2]SO_3CF_3$ (**1**) (0.24 g, 0.42 mmol) in CH_3CN (10 ml) was stirred with $NaOCOCH_3$ (0.20 g, 2.44 mmol) for 60 min. After filtration through Celite, the red solution was evaporated to dryness under vacuum. The residue was dissolved in CH_2Cl_2, and the solution layered with n-pentane and set aside at −20°C to give crystals. Yield 0.12 g (69%). M.p. 135–137°C (dec.). Anal. Found: C, 48.3; H, 3.02. $C_{17}H_{13}Fe_2O_5N$ calc.: C, 48.27; H, 3.10%.

Synthesis of $[\overline{FeFe\{\mu\text{-}C(CN)OCH_2CH{=}CH_2}\}(\mu\text{-}CO)(CO)(Cp)_2]$ ***(5)***

A THF solution (30 ml) of **2e** (0.12 g, 0.28 mmol) was irradiated under nitrogen for 30 min with light from a 500 watt low pressure ultraviolet lamp. The resulting brown solution was evaporated under vacuum and the residue chromatographed on an alumina column (3 × 10 cm) with a CH_2Cl_2–hexane mixture (2 : 1) as eluent. The first fraction contained some unchanged $[Fe_2\{\mu\text{-}C(CN)(OCH_2CHCH_2\}(\mu\text{-}$

Table 5

Fractional atomic coordinates for 5

Atom	*x*	*y*	*z*
Fe(1)	0.14024(4)	0.36960(10)	0.07979(8)
Fe(2)	0.12099(4)	0.11307(10)	0.02453(7)
C(1)	0.1949(3)	0.2178(8)	0.0995(5)
O(1)	0.2483(2)	0.1989(6)	0.1357(5)
C(2)	0.1362(4)	0.0186(10)	0.1377(6)
O(2)	0.1496(4)	−0.0545(9)	0.2054(6)
C(3)	0.0651(3)	0.2558(7)	0.0310(5)
O(3)	0.0373(2)	0.2424(7)	0.0962(4)
C(4)	0.0818(3)	0.2648(9)	0.2040(6)
C(5)	0.1255(3)	0.3795(9)	0.2114(6)
C(6)	0.1860(3)	0.3561(9)	0.2449(6)
C(7)	0.0127(3)	0.2941(8)	−0.0695(6)
N(1)	−0.0278(3)	0.3252(9)	−0.1475(6)
C(8)	0.1493(3)	0.5901(6)	0.0891(4)
C(9)	0.0946(3)	0.5535(6)	−0.0029(4)
C(10)	0.1109(3)	0.4722(6)	−0.0677(4)
C(11)	0.1756(3)	0.4586(6)	−0.0159(4)
C(12)	0.1993(3)	0.5314(6)	0.0810(4)
C(13)	0.0882(3)	0.1212(5)	−0.1409(4)
C(14)	0.1501(3)	0.0760(5)	−0.0893(4)
C(15)	0.1536(3)	−0.0495(5)	−0.0334(4)
C(16)	0.0938(3)	−0.0818(5)	−0.0505(4)
C(17)	0.0534(3)	0.0237(5)	−0.1169(4)

CO)(CO)$_2$(Cp)$_2$]. The second reddish-brown fraction was evaporated to dryness under vacuum and the residue was recrystallized from CH_2Cl_2/n-pentane mixture at −20 °C to give crystals of [FeFe{μ-C(CN)OCH$_2$CH=CH$_2$}(μ-CO)(CO)(Cp)$_2$]. Yield 43% (0.05 g). M.p. 135–137 °C (dec.). Anal. Found: C, 52.0; H, 3.7. $C_{17}H_{15}Fe_2O_3N$ calc.: C, 51.95; H, 3.85%.

Data collection and structure determination of **5**

Crystal data and details of measurements for **5** are listed in Table 4. Intensity data were collected at room temperature on an Enraf–Nonius CAD4 diffractometer. Direct methods allowed location of the Fe-atoms and the remaining atoms were located by difference Fourier synthesis. Absorption correction was carried out by the Walker and Stuart method [16] after a complete structural model had been obtained and all atoms refined isotropically. All atoms except the H-atoms of the Cp ligands were placed in calculated positions (C–H 1.08 Å) and refined "riding" on their corresponding C-atoms. Those of the OCH$_2$CH=CH$_2$ group were located directly from the Fourier maps and kept in their observed position by treating the CH$_2$ and CH=CH$_2$ fragments as rigid bodies. Two values of isotropic thermal parameters were refined for the Cp and allyl H-atoms (final values 0.04 and 0.03 Å, respectively). Residual peaks were < 1 e Å^{-3} and located close to the metal atoms. For all calculations the SHELX76 [17] package of crystallographic programs was used. Fractional atomic coordinates are listed in Table 5. Lists of H-atom coordinates, thermal parameters, and structure factors are available from the authors.

Acknowledgements

We thank the C.N.R. and Ministero della Università e Ricerca Scientifica (M.U.R.S.T.) for financial support.

References

1 (a) E.O. Fischer, T.L. Lindner, H. Fischer, B.G. Huttner, P. Friedrich and F.R. Kreissl, Z. Naturforsch. B, 32 (1977) 648; (b) E.O. Fischer, E. Winkler, G. Huttner and D. Regler, Angew. Chem., Int. Ed. Engl., 11 (1972) 238; (c) G. Huttner and D. Regler, Chem. Ber., 105 (1972) 2726.
2 (a) T.W. Ashworth, J.A.K. Howard, M. Laguna and F.G.A. Stone, J. Chem. Soc. Dalton Trans., (1980) 1593; (b) M. Berry, J.A.K. Howard and F.G.A. Stone, ibid., (1980) 1601; (c) J.A.K. Howard, K.A. Mead, J.R. Moss, R. Navarro, F.G.A. Stone and P. Woodward, ibid., (1981) 743.
3 S.C. Kao, P.P.Y. Lu and R. Pettit, Organometallics, 1 (1982) 911
4 C.P. Casey and P.J. Fagan, J. Am. Chem. Soc., 104 (1982) 7360.
5 (a) J.A.K. Howard, J.C. Jeffery, M. Laguna, R. Navarro and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1981) 751; (b) C.E. Sumner, J.A. Collier and R. Pettit, Organometallics, 1 (1982) 1350.
6 U. Shubert (Ed.), Advances in Metal Carbene Chemistry, Kluwer Academic Publishers, 1989, p. 141.
7 A.R. Manning, J. Chem. Soc. (A), (1968) 1319.
8 L. Busetto, S. Bordoni, V. Zanotti, V.G. Albano and D. Braga, Gazz. Chim. Ital., 118 (1988) 667.
9 L. Busetto, L. Carlucci, V. Zanotti, V.G. Albano and D. Braga, J. Chem. Soc. Dalton Trans., (1990) 243.
10 N.C. Schroeder, R. Funchness, R.A. Jacobson and R.J. Angelici, Organometallics, 8 (1989) 521.
11 V.G. Albano, S. Bordoni, D. Braga, L. Busetto and V. Zanotti, Collected Abstracts of the Twelfth European Crystallographic Meeting, Moscow, 1989, p. 191.
12 R.D. Adams and F. Cotton, J. Am. Chem. Soc., 95 (1973) 6589.
13 (a) A.F. Dyke, S.A.R. Knox, M.J. Morris and P.J. Naish, J. Chem. Soc., Dalton Trans., (1983) 1417; (b) B.P. Gracey, S.A.R. Knox, K.A. Macpherson and A.G. Orpern, ibid., (1985) 1935.

14 V.G. Albano, S. Bordoni, D. Braga, L. Busetto, A. Palazzi and V. Zanotti, Angew. Chem., submitted.
15 (a) J. Levisalles, H. Rudler, Y. Jeannin and F. Dahan, J. Organomet. Chem., 188 (1980) 193; (b) A. Parlier, F. Rose, M. Rudler and H. Rudler, ibid., 235 (1982) C13.
16 A.F. Wells, Structural Inorganic Chemistry, Oxford Science Publications, Oxford, 5th ed., 1984, ch. 26, p. 1156.
17 G.M. Sheldrick, SHELX76 system of computer programs, University of Cambridge, 1976.