ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 593–594 (2000) 335–341

Journal of Organo metallic Chemistry

New metallapyrrole complexes from $[M_2(\mu\text{-}CNMe_2)(\mu\text{-}CO)(CO)_2(Cp)_2]SO_3CF_3$ (M = Fe, Ru) and acetonitrile anions; structure of $[(Cp)(CO)FeC(NMe_2)N(H)C(Me)C(CN)]$

Luigi Busetto [a,*], Chiara Camiletti [a], Valerio Zanotti [a], Vincenzo G. Albano [b], Piera Sabatino [b]

[a] *Dipartimento di Chimica Fisica ed Inorganica, V.le Risorgimento 4, I-40138 Bologna, Italy*
[b] *Dipartimento di Chimica 'G. Ciamician', Via Selmi 2, I-40126 Bologna, Italy*

Received 17 June 1999; accepted 30 September 1999

Dedicated to Professor Fausto Calderazzo on the occasion of his 70th birthday in recognition of his outstanding contribution to chemistry.

Abstract

The reaction of $[M_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(CO)_2(Cp)_2]SO_3CF_3$ (M = Fe, R = Me, **1a**; M = Fe, R = CH_2Ph **1b**, M = Ru, R = CH_2Ph, **1c**) with a mixture of KH and acetonitrile affords $[(Cp)(CO)MC\{NMe(R)\}N(H)C(Me)C(CN)]$ (**2a**–**c**). The X-ray structure of **2a** (M = Fe, R = Me) shows the formation of a pyrrole-like metallaring FeC(2)NC(4)C(5). The double bond character of the C(4)–C(5) interaction [1.309(7)] suggests the enammine nature of the N(H)C(Me)C(CN) fragment which originates from condensation of two acetonitrile molecules. A mechanism for the formation of **2a**–**c** is proposed in light of the ^{13}C-NMR and IR evidence. Complex **2a** can be methylated at the N-end of the hexocyclic CN group, forming a cationic metallacyclo complex containing the $CC{\equiv}N^+{-}Me$ nitrilium moiety. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Metallapyrrole; Enammine nature; Acetonitrile

---

1. Introduction

Nitriles show a very rich coordination chemistry. In addition to being considered substitution labile, nitrile ligands can be converted into other organic functionalities by a number of processes such as insertion, reduction, coupling or electrophilic attack [1]. In several cases nitriles, and in particular acetonitrile, have been involved in the formation of metallacycles. Examples include nitrogen-containing pentatomic metallacycles (metallapyrroles) of Ir [2], Ta [3], W [4], Ti [5] and Zr [6]. In all of these metallarings the N atom, that is originated from the nitrile, is bonded to the metal atom.

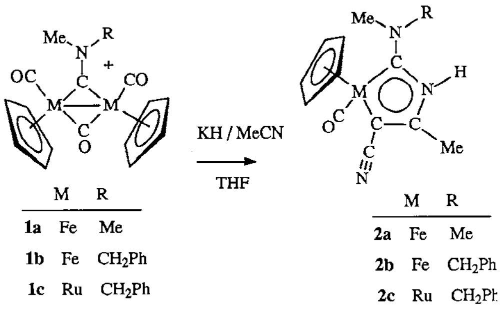
We now report an unprecedented reaction in which the metal–metal bond in the dinuclear complexes $[M_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(CO)_2(Cp)_2]SO_3CF_3$ (M = Fe, R = Me, **1a**; M = Fe, R = CH_2Ph **1b**, M = Ru, R = CH_2Ph, **1c**) is cleaved and novel metallapyrrole species $[(Cp)(CO)MC[NMe(R)]N(H)C(Me)C(CN)]$ (**2a**–**c**), involving two acetonitrile molecules, are formed. At a difference with the above mentioned metallacycles, which can be described as 1,2-metallapyrroles because of the ring atoms sequence MNCCC, the complexes here presented can be defined as 1,3-metallapyrroles corresponding to the sequence MCNCC. To our knowledge only one 1,3-metallapyrrole ring has been so far reported [7].

The present results are part of our studies on the reactivity of the dinuclear μ-carbyne complexes (**1a**–**c**) towards carbon nucleophiles [8], aimed at forming carbon–carbon bonds by attack at coordinated ligands, which also include very recent investigations on the reactions of the acetonitrile complex $[Fe_2(\mu\text{-}CNMe_2)(\mu\text{-}CO)(CO)(NCMe)(Cp)_2]SO_3CF_3$ [9].

---

[*] Corresponding author.

PII: S0022-328X(99)00579-3



Scheme 1.

2. Results and discussion

Addition of a mixture of acetonitrile and KH to a solution of $[Fe_2(\mu\text{-}CNMe_2)(\mu\text{-}CO)(CO)_2(Cp)_2]SO_3CF_3$ in thf at −40°C, results in a gradual color change from red to green and then to brownish yellow. Work up of the reaction mixture and chromatography on an alumina column yields [(Cp)(CO)FeC(NMe_2)N(H)C(Me)C(CN)] (**2a**) (63%), (Scheme 1) together with smaller amounts of $[Fe_2(CO)_4Cp_2]$.

Compound **2a**, which has been isolated as yellow crystalline solid, is moderately air stable in chlorinated solvents. In analogous reactions, the complexes [(Cp)(CO)MC{N(Me)CH_2Ph}N(H)C(Me)C(CN)] (M = Fe, **2b**; Ru, **2c**) have been obtained from $[M_2\{\mu\text{-}CN(Me)CH_2Ph\}(\mu\text{-}CO)(CO)_2(Cp)_2]SO_3CF_3$ (M = Fe, **1b**; Ru, **1c**).

The structure of **2a** has been ascertained by X-ray diffraction and is shown in Fig. 1. The bond parameters are listed in Table 1. The molecule consists of a formally four coordinate iron atom incorporated in a planar five atom ring FeC(2)N(2)C(4)C(5). The cycle carbon atoms bonded to the metal [C(2) and C(5)] are not equivalent and, as a consequence, the iron atom is a chiral center. C(2) is best defined as the two electron donor atom of a diaminocarbene ligand [C(2)–Fe 1.937(5), C(2)–N(2) 1.356(6), C(2)–N(3) 1.334(7) Å], while C(5) can be looked at as a two electron donor belonging to an enamine anion [C(5)–Fe 1.967(5), C(5)=C(4) 1.309(7) Å]. This description of the metallaring is in accord with the observed bond distances and with the attainment of the effective atomic number for the formally divalent iron center. Although multiple bond character is more pronounced in the N(2)–C(2)–N(3) and C(4)–C(5) regions, also the N(2)–C(4) interaction [1.413(6) Å] is shorter than expected for a single bond, as can be inferred from the N(3)–C(methyl) interactions [1.466av Å]. Therefore, a description of **2a** as metallapyrrole appears appropriate (Fig. 2) although it would also be considered as an enamine complex, in view of the marked double bond character of the C(4)–C(5) interaction. Similar metallapyrrole rings have been reported and structurally characterized in the molecules [$(CO)_4$MnC(=N-*p*-tolyl)C{=CH(C_6H_4-*p*-X)}N(*p*-tolyl)CNHY] (X = Cl, OMe; Y = *p*-tolyl, C_6H_{11}) which have been prepared by isocyanide insertion reactions in mangane-

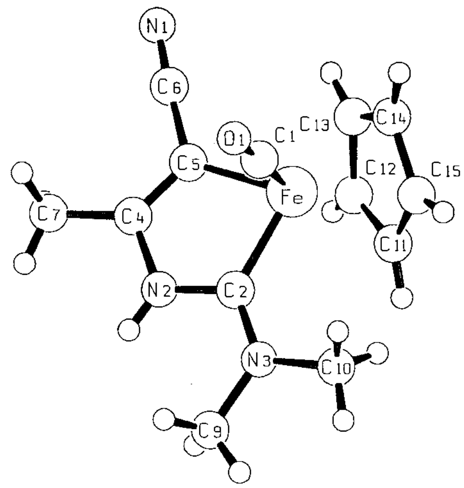


Fig. 1. Perspective view of the molecule [(Cp)(CO)FeC(NMe_2)N(H)C(Me)C(CN)] **2a**.

Table 1
Bond lengths (Å) and angles (°) for **2a**

Fe–C(1)	1.732(8)	C(1)–Fe–C(2)	89.8(3)
Fe–C(2)	1.937(5)	C(1)–Fe–C(5)	88.6(3)
Fe–C(5)	1.967(5)	C(2)–Fe–C(5)	80.0(2)
C(1)–O(1)	1.125(8)	O(1)–C(1)–Fe	176.5(6)
C(2)–N(3)	1.334(7)	N(3)–C(2)–N(2)	114.4(5)
C(2)–N(2)	1.356(6)	N(3)–C(2)–Fe	130.9(4)
N(2)–C(4)	1.413(6)	N(2)–C(2)–Fe	114.8(4)
C(4)–C(5)	1.309(7)	C(2)–N(2)–C(4)	115.1(4)
C(4)–C(7)	1.481(7)	C(5)–C(4)–N(2)	113.4(5)
C(5)–C(6)	1.424(8)	C(5)–C(4)–C(7)	131.0(5)
C(6)–N(1)	1.133(7)	N(2)–C(4)–C7	115.6(5)
N(3)–C(9)	1.457(8)	C(4)–C(5)–C(6)	118.8(5)
N(3)–C(10)	1.476(8)	C(4)–C(5)–Fe	116.6(4)
Fe–C_{Cp}(av.)	2.11(1)	C(6)–C(5)–Fe	124.6(4)
		N(1)–C(6)–C(5)	176.8(7)
		C(2)–N(3)–C(9)	124.3(5)
		C(2)–N(3)–C(10)	121.0(5)
		C(9)–N(3)–C(10)	114.5(5)

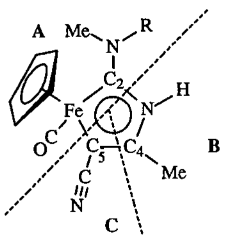


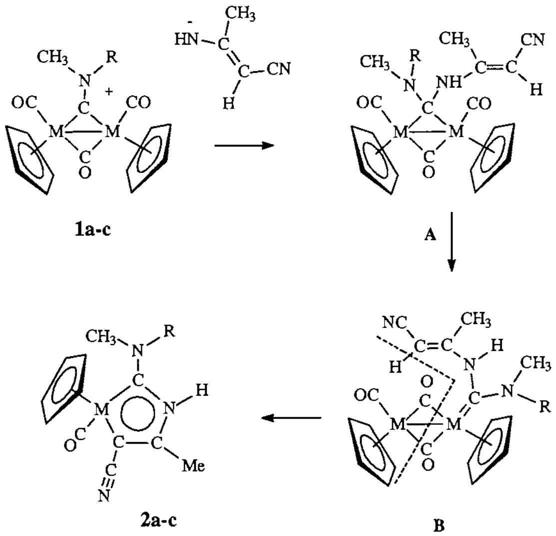
Fig. 2. C numbering scheme and the fragments A, B, C that formally originate **2a**–**b**.

se(I) alkyl and iminoacyl complexes [7]. The diaminocarbene fragment C[N(*p*-tolyl)]NHY in these molecules has a geometry strictly comparable to that in the present compound and also the Mn–C(ring) distances reproduce the trend observed for the Fe–C(ring) interactions.

Compounds **2a**–**c** exhibit in their IR spectra, in CH_2Cl_2 solution, a ν(CO) and a ν(CN) absorptions (e.g. for **2a** at 1925 and 2157 cm^{-1}) and one ν(C=N) band at 1532 cm^{-1} which is clearly indicative of the double bond character of the C(2)–N (hexocylclic) interaction. Finally a ν(NH) band is observed (for **2a** at 3260 cm^{-1} in KBr).

The ^1H- and ^{13}C-NMR spectra of **2a** are consistent with a delocalized metallapyrrole structure suggested by the X-ray diffraction data. Each of the two non-equivalent N-bonded methyl groups appears as a distinct singlet resonance (at 3.39 and 3.05 ppm) because of the restricted rotation around the C(2)–N bond. The N–H originates a broad resonance at 7.25 ppm. Other singlet signals observed at 4.51 and 2.20 ppm are due to the Cp and to the methyl group bonded to C(4). In the ^{13}C-NMR spectrum the Cp (84.1 ppm), NMe_2 (48.5 and 38.2 ppm) and the hexocyclic Me (18.0 ppm) resonances are easily identified. The CO and CN groups give rise to signals at 219.4 and 128.0 ppm, whereas more difficult appears the attribution of the remaining three resonances due to the C(2), C(4) and C(5) ring carbons. Among these, the signal at 229.1 ppm, well within the range of aminocarbene carbons, has been assigned to the C(2) (see Fig. 2).

An unambiguous attribution of the carbon resonances at 153.5 and 100.5 ppm was obtained by using acetonitrile containing the CN group enriched in ^{13}C isotope. Treatment of $[Fe_2(\mu\text{-}CNMe_2)(\mu\text{-}CO)(CO)_2(Cp)_2]SO_3CF_3$ with a mixture of KH and acetonitrile containing 10% of ^{13}C enriched $CH_3^{*}CN$, afforded **2a** and the corresponding ^{13}C-NMR spectrum showed increased intensities for the resonances at 153.5 and 128.0 ppm. Since the latter has been assigned to the hexocyclic CN group, the former has to be attributed to the C(4) carbon adjacent to the endocyclic N atom. Obviously the signal at 100.5 is due to the iron bonded C(5) carbon. This experiment also clearly indicates that two condensed acetonitrile units (fragments **B** and **C** of Fig. 2) are involved in the metallacycle formation, providing some suggestion about the reaction mechanism (see later).

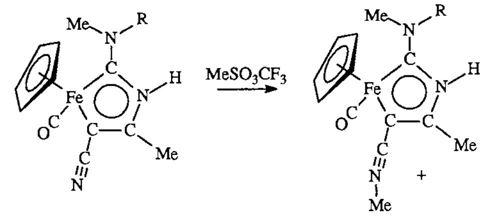


Scheme 2.

The NMR spectra of **2b**, although very similar to those of **2a**, reveal the presence of a minor amount of an isomeric form. For example two Cp signals are observed at 4.54 and 4.61 ppm in about 4:1 ratio. Since in **2b**, the two substituents of the hexoycyclic N atom are different, and rotation around C(2)–N(hexocyclic) of the diaminocarbene group is hindered, the two isomeric forms arise from the two possible orientations of the methyl and benzyl groups with respect to the chiral Fe center. The more abundant isomer is presumably that with the bulkier benzyl substituent far from the Cp ligand.

The formation of **2a**–**c** from $[M_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(CO)_2(Cp)_2]SO_3CF_3$ is rather unexpected since it requires the breaking of the dimetallic frame, which has been proved particularly robust under a variety of reaction conditions [8,10,11]. Although the reaction mechanism remains unknown, a plausible hypothesis about the specific steps leading to the formation of **2a**–**c** can be traced out (Scheme 2). It is likely that treatment of CH_3CN with KH results in the formation of a diacetonitrile anion, since the condensation of acetonitrile, under basic conditions, is a known organic reaction [12]. The diacetonitrile anion exists as an equilibrium between the imine and enamine tautomeric forms with predominance of the latter because of the presence of the CN electron withdrawing group in the alkenammine β-carbon [6,13]. The enamine form is presumably responsible for a nucleophilic attack at the bridging carbyne carbon of $[M_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(CO)_2(Cp)_2]^+$ leading to the μ-diaminocarbene complex **A**, which undergoes ligand site exchange between the diaminocarbene and the carbonyl, to yield the type **B** intermediate (Scheme 2). This rearrangement is a well described process in the diiron complexes $[Fe_2\{\mu\text{-}C(H)N(Me)R\}(\mu\text{-}CO)(CO)_2(Cp)_2]$ and $[Fe_2\{\mu\text{-}CN(CH_2)_2N\}(\mu\text{-}CO)(CO)_2(Cp)_2]$ [10], and allows the aminocarbene ligands to occupy a less hindered terminal coordination position.

Support to the above assumptions comes from the observed presence of the green and orange intermediate species in the reactions leading to **2a**–**b** and **2c**, respectively. They show two IR ν(CO) absorptions (e.g. for **2c** at 1944s and 1720s cm^{-1}, in CH_2Cl_2) in accord with a



R = Me, **2a**; CH$_2$Ph, **2b**

R = Me, **3a**; CH$_2$Ph, **3b**

Scheme 3.

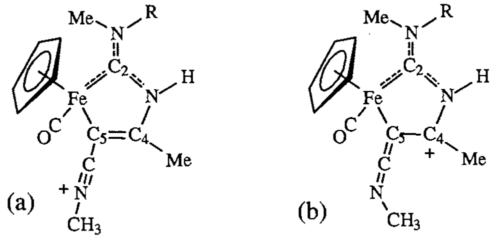


Fig. 3. Nitrilium (a) and ketenimine (b) canonic formulae for **3**.

type **B** formulation. The IR band pattern is in fact very similar to that observed for $[Fe_2(\mu\text{-}CO)_2\{C(H)NMe_2\}(CO)(Cp)_2]$ (at 1933s, 1735s cm^{-1}) [10]. Attempts to isolate and clearly identify these intermediates have failed because they rapidly convert to the final products, in particular if exposed to air and under chromatographic conditions. Furthermore in the ruthenium case the ^{1}H-NMR signals of the intermediate leading to **2c** are in agreement with a type **B** nature since two couples of resonances for the Cp ligands (at 5.17, 4.92 and 5.16, 4.99) suggest that two main isomeric forms of a dinuclear compound with non equivalent metal centers are present in solution.

Finally, the formation of monomeric species **2a**–**c** from **B** requires cleavage of the metal–metal bond and ring closure with formal release of an hydrogen atom and a $M(CO)_2Cp$ fragment. This picture is consistent with the formation of $[Fe_2(CO)_4(Cp)_2]$, isolated among the reaction products in about 1:2 ratio with respect to **2a**–**b**, and with the observation that oxidation, by exposition to air, accelerates the conversion of the intermediate to the final products. An alternative mechanism involving a KH reduction of the dinuclear species is also possible since we have shown that sodium naphtalenide acts as one electron reductant of diiron aminocarbyne complexes [14]. However, this hypothesis has been ruled out by the observation that the reaction of **1a** with Na–Hg in a mixture of THF–MeCN does not afford the metallacyclo derivative **2a**.

Complexes **2a**–**b** react with the strong alkylating reagent $CH_3SO_3CF_3$ in CH_2Cl_2 solution resulting in the formation of $[(Cp)(CO)FeC\{N(Me)R\}N(H)C(Me)C(CNMe)]SO_3CF_3$ (R = Me, **3a**; CH$_2$Ph, **3b**) (Scheme 3).

Methylation occurs at the nitrogen atom of the hexocyclic CN group, as indicated by the remarkable shift of the corresponding ν(CN) absorption in the IR spectrum (e.g. 2157 vs. 2235 cm^{-1} in **2a** and **3a**, respectively). This frequency is to be compared to that found in $[Fe_2\{\mu\text{-}C(CH_3)CNCMe_3\}(\mu\text{-}CO)(CO)_2(Cp)_2]^+$ (at 2232 cm^{-1}), in which the $\mu\text{-}C\text{–}C{\equiv}N^+\text{–}CMe_3$ moiety has been described as the nitrilium group [15]. In that case, however, structural analysis has revealed a slight deviation from linearity for the $\mu C\text{–}CN^+\text{–}CR_3$ suggesting significant contribution of the ketenimine resonance structure. Likewise, compound **3a**–**b** are better described by the resonance structures shown in Fig. 3.

The NMR spectra of **3a** show singlet resonances for the C_5H_5 ring (at 4.54 ppm) and for the three N-bonded methyl groups (at 3.78, 3.45 and 3.36 ppm), the lower field signal being attributed to the C≡N bonded methyl. The remaining Me group, substituent at C(4), gives a resonance at 2.50 ppm. Finally the N–H resonance is observed at 9.97 ppm. According to the canonic formulae a and b of Fig. 3, the largest influence due to the CN methylation are expected to be observed in the ^{13}C-NMR spectra on C(5) and C(4), with C(2) only slightly affected. In agreement with these predictions, the signals which appear more shifted compared with those of the precursor **2a** are those corresponding to C(5) (at 76.5 vs. 98.0 ppm of **2a**) and to C(4) (at 177.6 vs. 153.53 ppm of **2a**), whereas the resonance due to C(2) remains almost unchanged (229.7 vs. 229.1 ppm of **2a**).

3. Experimental

3.1. General

All reactions were routinely carried out under argon 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. The shiftless relaxation reagent [Cr(acac)$_3$] (acac = acetylacetonate) was added to solutions studied by ^{13}C-NMR spectroscopy. All reagents were commercial products (Aldrich) of the highest purity available and used as received. Compounds $[Fe_2(\mu\text{-}CNMe_2)(\mu\text{-}CO)(CO)_2(Cp)_2]SO_3CF_3$ [16] and $[M_2\{\mu\text{-}CN(Me)CH_2Ph)(\mu\text{-}CO)(CO)_2(Cp)_2]SO_3CF_3$ (M = Fe [17], Ru [18]) were synthesized according to published methods.

3.2. *Synthesis of* $[(Cp)(CO)FeC(NMe_2)N(H)C(Me)C(CN)]$ *(**2a**)*

Potassium hydride (0.40 g, 10 mmol, as 35 wt% dispersion in mineral oil) was added to CH_3CN (10 ml) under stirring. A portion of the suspension thus formed (2 ml) was transferred by cannula into a solution of $[Fe_2(\mu\text{-}CNMe_2)(\mu\text{-}CO)(CO)_2(Cp)_2]SO_3CF_3$ (0.20 g, 0.38 mmol) in thf (20 ml) at −40°C. The mixture, which immediately turned brownish–green, was allowed to warm to room temperature and stirred for an additional 30 min. Solvent removal and filtration on an alumina pad with CH_2Cl_2 as eluent, gave a brown solution which was evaporated to dryness. Chromatography of the residue on an alumina column, with CH_2Cl_2:petroleum ether (b.p. 40–70°C) 1:1 (v/v), gave a first red fraction of $[Fe_2(CO)_4Cp_2]$ (35 mg, 0.10 mmol) that was discharged. A second yellow band of **2a** was collected and crystallized from CH_2Cl_2 layered *n*-pentane, affording suitable crystals for X-ray diffraction. Yield (68 mg, 63%). Anal. Found: C, 54.26; H, 5.19; N, 14.45%. $C_{13}H_{15}FeN_3O$ requires: C, 54.76; H, 5.30; N, 14.74%. IR (CH_2Cl_2) ν_{max} (cm^{-1}) 2157s (CN), 1925vs (CO) and 1532 ms (C=N). NMR: δ_H ($CDCl_3$): 7.25 (1 H, s, NH), 4.51 (5 H, s, Cp), 3.39, (3 H, s NMe), 3.05 (3 H, s NMe) and 2.20 (3 H, s, CMe) ppm. δ_C ($CDCl_3$): 229.1 (*C*NMe$_2$), 219.4 (CO), 153.5 (*C*Me), 128.0 (CN), 100.5 (*C*CN), 84.1 (Cp), 48.5, 38.1 (NMe) and 18.0 (C*Me*) ppm. MS *m*/*e*: 285 (M^+), 257 (–CO, base peak), 242 (–CO,–Me).

In an attempt to isolate the green intermediate species, the reaction mixture, after 10 min of stirring was directly chromatographed on an alumina column with CH_2Cl_2:Petroleum ether (b.p. 40–70°C) 1:1 (v/v) as eluent. A first green fraction, which exhibited IR absorptions at 1952s and 1784s cm^{-1}, was collected. It rapidly turned brownish–yellow upon contact with air, affording **2a** and $[Fe_2(CO)_4Cp_2]$.

*3.3. Synthesis of [(Cp)(CO)MC{N(Me)CH$_2$Ph}N(H)C(Me)C(CN)] (M = Fe, **2b**; Ru, **2c**)*

Compounds **2b** and **2c** were obtained following the same procedure described for the synthesis of **2a**, starting from $[Fe_2\{\mu\text{-}CN(Me)CH_2Ph\}(\mu\text{-}CO)(CO)_2(Cp)_2]SO_3CF_3$ and $[Ru_2\{\mu\text{-}CN(Me)CH_2Ph\}(\mu\text{-}CO)(CO)_2(Cp)_2]SO_3CF_3$, respectively.

2b: Yield 45%. Anal. Found: C, 63.22; H, 5.32; N, 1.61%. $C_{19}H_{19}FeN_3O$ requires: C, 63.17; H, 5.30; N, 11.64%. IR (CH_2Cl_2) ν_{max} (cm^{-1}) 2158s (CN), 1928vs (CO) and 1512 ms (C=N). NMR: δ_H ($CDCl_3$): 7.41–7.23 (6 H, m, Ph + NH), 5.15 (1 H, d, $J = 15$ Hz, C*H*$_2$Ph), 4.96 (1 H, d, $J = 15$ Hz, C*H*$_2$Ph), 4.54, *4.61* (5 H, s, Cp), *3.52*, 2.97, (3 H, s NMe), and 2.30, *2.11* (3 H, s, CMe) ppm; signals due to the presence of minor amounts of an isomeric form are italicized (isomers ratio 4:1). δ_C ($CDCl_3$): 230.3 (*C*N(Me)Bz), 219.0 (CO), 153.5 (*C*Me), 137.3–126.8 (Ph and CN), 102.1 (*C*CN), 84.4, *84.2* (Cp), 64.6, *66.2* (CH$_2$Ph), 36.0 (NMe) and 18.1, *15.9* (C*Me*) ppm.

A green intermediate species was detected, in crude reaction mixture, by IR: (CH_2Cl_2) ν_{max} (cm^{-1}) 1943s and 1719s (CO).

2c: Yield 40%. Anal. Found: C, 56.19; H, 4.89; N, 10.31%. $C_{19}H_{19}RuN_3O$ requires: C, 56.14; H, 4.71; N, 10.34%. IR (CH_2Cl_2) ν_{max} (cm^{-1}) 2162s (CN), 1932vs (CO) and 1518 ms (C=N). NMR: δ_H ($CDCl_3$): 7.55–7.21 (6 H, m, Ph + NH), 5.23 (2 H, m, C*H*$_2$Ph), 4.96 (5 H, s, Cp), 3.01, (3 H, s NMe), and 2.30 (3 H, s, CMe) ppm. δ_C ($CDCl_3$): 217.3 (*C*N(Me)Bz), 201.7 (CO), 152.6 (*C*Me), 136.9–127.4 (Ph) 126.6 (CN), 98.0 (*C*CN), 86.2 (Cp), 65.9 (CH$_2$Ph), 34.8 (NMe) and 17.8 (C*Me*) ppm.

In an attempt to isolate the orange intermediate species, the reaction mixture, after 10 min of stirring was directly chromatographed on an alumina column with CH_2Cl_2:petroleum ether (b.p. 40–70°C) 1:1 (v/v) as eluent. A first orange fraction, which exhibited IR absorptions at 1944 and 1720 cm^{-1}, was collected. It rapidly turned to **2c** upon exposition to air.

*3.4. Synthesis of [(Cp)(CO)FeC{N(Me)R}N(H)C(Me)C(CNMe)]SO$_3$CF$_3$ (R = Me, **3a**; CH$_2$Ph, **3b**)*

A solution of **2a** (0.11 g, 0.38 mmol) in CH_2Cl_2 (10 ml) was treated with $MeSO_3CF_3$ (44 µl, 0.40 mmol). The mixture was stirred for 8 h, then the volatile material was removed and the residue was washed with Et_2O and redissolved in CH_2Cl_2. Filtration on an celite pad and crystallization from CH_2Cl_2–Et_2O mixture yielded **3a** as an orange microcrystalline solid (0.15 g, 87%). Anal. Found: C, 39.88; H, 4.27%. $C_{15}H_{18}F_3FeN_3O_4S$ requires: C, 40.10; H, 4.13%. IR (CH_2Cl_2) ν_{max} (cm^{-1}) 2235m (CN), 1945vs (CO) and 1544 ms (C=N). NMR: δ_H ($CDCl_3$): 9.97 (1 H, s, NH), 4.54 (5 H, s, Cp), 3.78 (3 H, s C≡N*Me*), 3.45 (3 H, s NMe$_2$), 3.36 (3 H, s NMe$_2$) and 2.50 (3 H, s, CMe) ppm. δ_C ($CDCl_3$): 229.7 (*C*NMe$_2$), 218.0 (CO), 177.6 (*C*Me), 121.5 (*C*NMe), 83.6 (Cp), 76.5 (*C*CNMe), 49.2, 40.8 (NMe), 32.0 (CN*Me*), and 20.9 (C*Me*) ppm.

Compound **3b** was analogously obtained starting from **2b** (0.12 g, 0.33 mmol). Yield (0.15 g, 85%). Anal. Found: C, 48.45; H, 4.19%. $C_{21}H_{22}F_3FeN_3O_4S$ requires: C, 48.01; H, 4.22%. IR (CH_2Cl_2) ν_{max} (cm^{-1}) 2238m (CN), 1944vs (CO) and 1523 ms (C=N). NMR: δ_H ($CDCl_3$): 9.96 (1 H, s, NH), 7.38–7.19 (5 H, m, Ph), 5.07 (1 H, d, $J = 14.5$ Hz, C*H*$_2$Ph), 4.86 (1 H, d, $J = 14.5$ Hz, C*H*$_2$Ph), 4.76 (5 H, s, Cp), 3.78 (3 H, s C≡N*Me*), 3.16 (3 H, s NMe), and 2.51 (3 H, s, CMe) ppm. δ_C ($CDCl_3$): 230.8 (*C*NMeBz), 218.0 (CO), 177.5 (*C*Me), 135.6–127.5 (Ph), 122 (*C*NMe), 83.6 (Cp), 76.5 (*C*CNMe), 65.1 (*C*H$_2$Ph), 38.4 (N*Me*Bz), 32.0 (CN*Me*) and 21.0 (C*Me*) ppm.

3.5. X-ray crystallography

Diffraction intensities of **2a** were collected at room temperature by the $\omega-2\theta$ scan method on an Enraf-Nonius CAD-4 diffractometer and reduced to F_o^2 values. The structure was solved by direct methods and refined by full matrix least-squares calculations. For all computations the SHELXS86 [19] and SHELXL93 [20] packages of crystallographic programs were used. Thermal vibrations were treated anisotropically for all non-H atoms. Due to the low ratio observations/number of parameters refined, the cyclopentadienyl ligand was treated as a rigid body with fixed C–C and C–H bond distances (1.42 and 0.93 Å, respectively) and C–C–C angles (108°). The hydrogen atoms bound to the N atom and to the methyl groups were experimentally located in difference Fourier maps, while the remaining hydrogen atoms were positioned geometrically and all refined with adequate constraints (C–H 0.96 and N–H 0.86 Å). Their temperature factors were constrained to be 1.5 times those of their parent atoms for the methyl groups and 1.2 times those of their parent atoms for the cyclopentadienyl ring. Final difference Fourier maps showed a residual peak lower than 0.8 e $Å^{-3}$ in the proximity of the iron atom. Crystal data and details of measurements are reported in Table 2, atomic coordinates in Table 3.

Table 2
Crystal data and details of measurements for **2a**

Formula	$C_{13}H_{15}FeN_3O$
Molecular weight	285.13
Temperature (K)	293
System	Monoclinic
Space group	$I2/a$ (no. 15)
a (Å)	13.718(4)
b (Å)	12.124(3)
c (Å)	16.539(5)
β (°)	104.10(3)
V (Å^3)	2668(1)
Z	8
F(000)	1184
λ(Mo–K$_\alpha$) (Å)	0.71069
μ(Mo–K$_\alpha$) (mm^{-1})	1.122
ϑ-range (°)	2.5–25
Octants explored	$\pm h$, $+k$, $+l$
Measured reflections	4388
Unique reflections	2342
Unique reflections [$I_0>2\sigma(I_0)$]	1298
No. of refined parameters	155
Goodness-of-fit on F^2	1.003
R_1 (on F, $I>2\sigma(I)$)	0.052

Table 3
Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for **2a**

	x	y	z	U_{eq} [a]
Fe	0.47151(6)	0.23382(6)	0.34267(6)	0.0489(3).
O(1)	0.4528(5)	0.3051(4)	0.1750(4)	0.095(2)
C(1)	0.4593(5)	0.2738(5)	0.2402(5)	0.061(2)
C(2)	0.6152(4)	0.2576(4)	0.3651(4)	0.047(1)
N(1)	0.3225(4)	0.5064(5)	0.3748(4)	0.083(2)
N(2)	0.6453(3)	0.3621(3)	0.3878(3)	0.050(1)
N(3)	0.6899(4)	0.1885(4)	0.3622(4)	0.066(2)
C(4)	0.5670(4)	0.4366(4)	0.3910(4)	0.045(1)
C(5)	0.4780(4)	0.3906(4)	0.3741(4)	0.047(1)
C(6)	0.3927(4)	0.4576(5)	0.3743(4)	0.059(2)
C(7)	0.5985(5)	0.5521(4)	0.4119(4)	0.061(2)
C(9)	0.7960(5)	0.2181(6)	0.3853(6)	0.093(3)
C(10)	0.6690(6)	0.0769(5)	0.3265(6)	0.098(3)
C(11)	0.4806(3)	0.0875(4)	0.4141(4)	0.080(2)
C(12)	0.4339(4)	0.1726(4)	0.4502(3)	0.076(2)
C(13)	0.3453(4)	0.2052(3)	0.3908(4)	0.079(2)
C(14)	0.3372(3)	0.1402(4)	0.3181(3)	0.077(2)
C(15)	0.4208(4)	0.0675(3)	0.3324(3)	0.075(2)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

4. Supplementary material

Complete listings of bond lengths and angles, anisotropic parameters, hydrogen atomic coordinates, observed and calculated structure factors have been deposited at the Cambridge Crystallographic Data Center as supplementary material (CCDC 133127).

Acknowledgements

We thank the Ministero dell'Universita' e della Ricerca Scientifica e Tecnologica (M.U.R.S.T.) Programmi di Ricerca Scientifica di Rilevante Interesse Nazionale, Cofinanziamento 1998–1999 and the University of Bologna ('Funds for Selected Research Topics') for financial support.

References

[1] R.A. Michelin, M. Mozzon, R. Bertani, Coord. Chem. Rev. 147 (1996) 299.
[2] Y. Alvarado, P.J. Daff, P.J. Pérez, M.L. Poveda, R. Sanchez-Delgado, E. Carmona, Organometallics 15 (1996) 2192.
[3] J.R. Strickler, D.E. Wigley, Organometallics 9 (1990) 1665.
[4] P. Legzdins, S.A. Lumb, Organometallics 16 (1997) 1825.
[5] S.A. Cohen, J.E. Bercaw, Organometallics 4 (1985) 1006.
[6] G. Erker, R. Pfaff, Organometallics 12 (1993) 1921.
[7] P.L. Motz, J.J. Alexander, D.M. Ho, Organometallics 8 (1989) 2589.
[8] (a) V.G. Albano, L. Busetto, C. Camiletti, C. Castellari, M. Monari, V. Zanotti, J. Chem. Soc. Dalton Trans. (1997) 4671. (b) V.G. Albano, L. Busetto, C. Camiletti, M. Monari, V. Zanotti, J. Organomet. Chem. 563 (1998) 153.
[9] Manuscript submitted for publication.
[10] V. Zanotti, S. Bordoni, L. Busetto, L. Carlucci, A. Palazzi, R. Serra, V.G. Albano, M. Monari, F. Prestopino, F. Laschi, P. Zanello, Organometallics 14 (1995) 5232.

[11] K. Boss, C. Dowling, A.R. Manning, J. Organomet. Chem. 509 (1996) 197.
[12] (a) C. Kruger, J. Organomet. Chem. 9 (1967) 125 and refs. therein. (b) J. March, in: Advanced Organic Chemistry, fourth edition, Wiley-Interscience, New York, 1992, p. 963.
[13] G. Erker, D. Kowalski, R. Noe, C. Krüger, M. Nolte, Tetrahedron Lett. 35 (1994) 6665.
[14] L. Busetto, V. Zanotti, V.G. Albano, M. Monari, C. Castellari, Gazz. Chim. Ital. 123 (1993) 703.
[15] C.P. Casey, M. Croker, G.P. Niccolai, P.J. Fagan, M.S. Konings, J. Am. Chem. Soc. 110 (1988) 6070.
[16] G. Cox, C. Dowling, A.R. Manning, P. McArdle, D. Cunningham, J. Organomet. Chem. 438 (1992) 143.
[17] L. Busetto, V. Zanotti, V.G. Albano, M. Monari, C. Castellari, Gazz. Chim. Ital. 123 (1993) 703.
[18] (a) J.A.S. Howell, A.J. Rowan, J. Chem. Soc. Dalton Trans. (1980) 502. (b) L. Busetto, L. Carlucci, V. Zanotti, V.G. Albano, M. Monari, J. Organomet. Chem. 447 (1993) 271.
[19] G.M. Sheldrick, SHELXS86, Program for crystal structure solution, University of Gottingen, Germany, 1986.
[20] G.M. Sheldrick, SHELXL93, Program for crystal structure refinement, University of Gottingen, Germany, 1993.