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Reactions of acetonitrile di-iron μ-aminocarbyne complexes; synthesis and structure of $[Fe_2(\mu\text{-}CNMe_2)(\mu\text{-}H)(CO)_2(Cp)_2]$

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Abstract

The complexes $[Fe_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(NCMe)(CO)(Cp)_2]SO_3CF_3$ (R = Me, **2a**; $2,6\text{-}Me_2C_6H_3$, **2b**; CH_2Ph, **2c**), easily obtained from the corresponding $[Fe_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(CO)_2(Cp)_2]SO_3CF_3$ (**1a**–**c**) precursors, react with NBu_4CN affording the cyano complexes $[Fe_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(CN)(CO)(Cp)_2]$ (**3a**–**c**) by displacement of the MeCN ligand. The analogous reaction with NBu_4Cl leads to the formation of $[Fe_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(Cl)(CO)(Cp)_2]$ (**4a**–**b**). The μ-hydride complexes $[Fe_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}H)(CO)_2(Cp)_2]$ (**5a**–**b**) have been prepared by reaction of **1a**–**b** with $NaBH_4$. The corresponding diruthenium compound $[Ru_2(\mu\text{-}CNMe_2)(\mu\text{-}H)(CO)_2(Cp)_2]$ (**6**) has been similarly obtained from $[Ru_2(\mu\text{-}CNMe_2)(\mu\text{-}CO)(NCMe)(CO)(Cp)_2]SO_3CF_3$. The X-ray molecular structure of **5a** is that expected for *cis* isomers of this family of compounds. It shows a chiral conformation of the C_5H_5 ligands and the crystals are a conglomerate of enantiomeric individuals. NMR spectra of the various compounds, which are indicative of the presence of α–β or *cis*–*trans* isomeric mixtures, are reported and discussed.

Keywords: Hydride; Acetonitrile; Carbyne complexes; Crystal structure

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1. Introduction

Recent work of our group has focused on the reactions of the dinuclear bridging aminocarbyne complexes $[M_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(CO)_2(Cp)_2]SO_3CF_3$ (M = Fe, Ru; R = Me, CH_2Ph; $Cp = \eta^5\text{-}C_5H_5$) with carbon nucleophiles, aimed at forming carbon–carbon bonds via addition at the Cp and CO ligands [1].

Continuing our studies on their chemistry [2], we have become interested in replacing a CO with acetonitrile in order to drive the nucleophilic attack at the metal. In fact, in related di-ruthenium complexes, the presence of the labile acetonitrile ligand has proved crucial for a direct involvement of the metal in oxidative additions, substitution reactions and intramolecular rearrangements thus making those complexes valuable models for Fischer–Tropsch catalytic processes [3]. Here we report on the reactions of acetonitrile-substituted μ-aminocarbyne complexes with cyanide, chloride and hydride anions.

2. Results and discussion

A carbonyl ligand in $[Fe_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(CO)_2(Cp)_2]SO_3CF_3$ (R = Me, **1a**; $2,6\text{-}Me_2C_6H_3$, **1b**; CH_2Ph, **1c**) is readily substituted by MeCN in the presence of Me_3NO, to afford $[Fe_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(NCMe)(CO)(Cp)_2]SO_3CF_3$ (R = Me, **2a**; $2,6\text{-}Me_2C_6H_3$, **2b**; CH_2Ph, **2c**), in about 95% yield. Their formulation is based on elemental microanalytical and spectroscopic data. Replacement of CO by NCMe makes the two Fe centers non-equivalent; consequently two Cp singlet signals are observed in the NMR spectra. Unlike **2a**, the NMR spectra of compound **2b**–**c** indicate the presence of two isomeric forms (e.g. for **2c** two signals for each of the unequivalent Cp are observed). Since **2b**–**c** differ from **2a** having the asymmetrically substituted μ-CN(Me)R (R = CH_2Ph, $2,6\text{-}Me_2C_6H_3$) ligand in place of the $\mu\text{-}CNMe_2$, these

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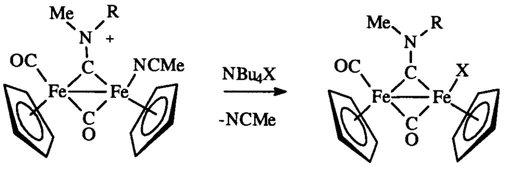
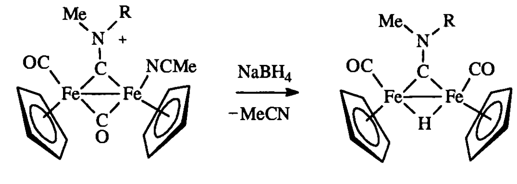
isomeric forms are presumably due to the different orientation of Me and R with respect to the non-equivalent Fe atoms (α and β isomers) rather than being assigned to a *cis* or *trans* arrangements of the Cp ligands. Isomeric α and β forms, are usually found in complexes of the type $[M_2\{\mu\text{-CN(Me)R}\}(\mu\text{-CO})(L)(CO)(Cp)_2]$ (M = Fe [1a,4], Ru [1b]). Finally it should be noted that these isomers are present in comparable amounts for **2c**, whereas one is largely predominant in **2b**.



	R
2a	Me
2b	2,6-Me$_2$C$_6$H$_3$
2c	CH$_2$Ph

	X	R
3a	CN	Me
3b	CN	2,6-Me$_2$C$_6$H$_3$
3c	CN	CH$_2$Ph
4a	Cl	Me
4b	Cl	2,6-Me$_2$C$_6$H$_3$

Scheme 1.



	R
2a	Me
2b	2,6-Me$_2$C$_6$H$_3$

	R
5a	Me
5b	2,6-Me$_2$C$_6$H$_3$

Scheme 2.

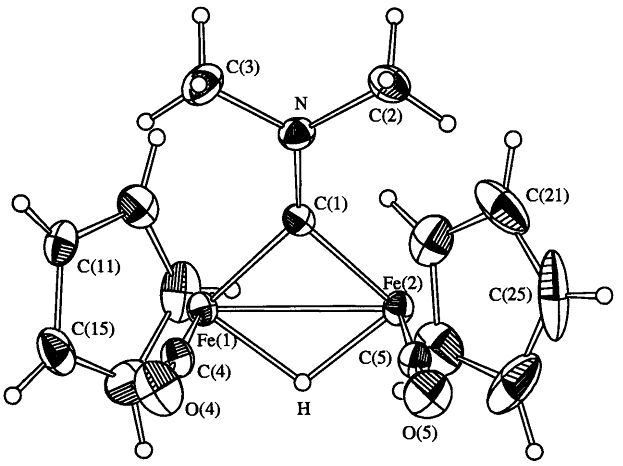


Fig. 1. ORTEP drawing of $[Fe_2(\mu\text{-CNMe}_2)(\mu\text{-H})(CO)_2(Cp)_2]$ (**5a**) (thermal ellipsoids are drawn at 30% probability). Selected bond lengths: Fe(1)–Fe(2) 2.5877(9), Fe(1)–C(1) 1.864(2), Fe(2)–C(1) 1.860(3), C(1)–N 1.312(3), N–C(2) 1.470(3), N–C(3) 1.461(4), Fe(1)–H 1.63(2), Fe(2)–H 1.59(2), Fe(1)–C(4) 1.736(3), Fe(2)–C(5) 1.730(3), C(4)–O(4) 1.152(3), C(5)–O(5) 1.157(3), Fe(1)–C(Cp$_{av}$) 2.118(3), Fe(2)–C(Cp$_{av}$) 2.113(3) Å.

By addition of NBu$_4$CN to CH$_2$Cl$_2$ solutions of **2a–c** the displacement of the coordinated acetonitrile by cyanide takes place, producing the cyano complexes $[Fe_2\{\mu\text{-CN(Me)R}\}(\mu\text{-CO})(CN)(CO)(Cp)_2]$ (**3a–c**) (Scheme 1), which have been isolated in good yields after column chromatography.

Compound **3a** has been identified by comparison of its spectroscopic data with those previously reported for the *cis* isomer [4b]. Compounds **3a–c** show an IR absorption of the ν(CN) at about 2091 cm^{-1}, moreover in the ^{13}C-NMR spectrum the characteristic downfield resonance of the μ-carbyne carbon is observed (at δ 339.0 for **3b**). As for its precursor **2c**, compound **3c** exhibits, in its ^{1}H-NMR spectrum, a double set of signals for the Cp ligands, indicating the presence of two isomers (α and β forms) occurring in comparable amounts. By contrast, **3b** shows the large predominance of one isomeric form.

The results here described are to be compared with those previously obtained in the absence of the labile CNMe ligand. Cyanide anion has been shown to add at the bridging carbyne carbon of $[Fe_2\{\mu\text{-CN(Me)R}\}(\mu\text{-CO})(CO)_2(Cp)_2]SO_3CF_3$ (R = Me, CH$_2$Ph) yielding the corresponding μ-cyanoaminocarbene complexes $[Fe_2\{\mu\text{-C(CN)N(Me)R}\}(\mu\text{-CO})(CO)_2(Cp)_2]$ [2a]. Therefore replacement of CO with NCMe has proved to be quite effective in directing the nucleophilic attack at the metal atom.

Likewise, treatment of **2a–b** with NBu$_4$Cl in dichloromethane solution results in the displacement of acetonitrile by chloride leading to the formation of the complexes $[Fe_2\{\mu\text{-CN(Me)R}\}(\mu\text{-CO})(Cl)(CO)(Cp)_2]$ (**4a–b**) (Scheme 1), in moderate yield. The ^{1}H-NMR spectrum of **4a** has been straightforward with a singlet for each of the non-equivalent Cp and Me groups (at δ 4.75, 4.65 and 4.71, 4.26, respectively). The NMR spectra of **4b** reveal the presence, in solution, of only one of the two possible α and β isomers. A major feature in its ^{13}C-NMR spectrum is the expected low field resonance, at δ 343.3, attributable to the aminocarbyne carbon.

Somewhat unexpectedly, we found that MeCN solutions of **2a–b** react with NaBH$_4$ to give the μ-hydride complexes $[Fe_2\{\mu\text{-CN(Me)R}\}(\mu\text{-H})(CO)_2(Cp)_2]$ (**5a–b**) (Scheme 2).

The structure of **5a** has been ascertained by X-ray diffraction and is shown in Fig. 1, together with some relevant bond parameters. The overall stereochemistry is that of all the *cis* isomers of this family of compounds. Although the bond distances conform to an idealized *Cs* symmetry the molecule adopts a chiral conformation in the crystal. The chirality is generated by the mutually staggered conformation of the C$_5$H$_5$ ligands generated by the optimization of the intraligand H···H contacts. The Fe–Fe distance [2.588(1) Å)] is longer than that found in similar compounds in which a bridging CO is in the place of the hydride: 2.504(1) Å in $[Fe_2(\mu\text{-}CNMe_2)(\mu\text{-}CO)(CO)\{C(O)C_4H_9\}(Cp)_2]$ [1a], 2.509(2) Å in $[Fe_2\{\mu\text{-}CN(Me)CH_2Ph\}(\mu\text{-}CO)(CO)\text{-}\{C(O)th\}(Cp)_2]$ ($th = C_4H_3S$) [5], and 2.519(1) Å in $[Fe_2\{\mu\text{-}CN(CH_2)_4CH_2\}(\mu\text{-}CO)(CO)_2(Cp)_2]$ [6]. The μ-C=NMe$_2$ ligand is symmetrically bound [μ-C–Fe 1.86_{av} Å] and its geometry does not significantly differ from that found in the species cited above, in spite of the substitution of the hydride for a carbonyl ligand. A similar bonding situation is present in $[Fe_3(\mu\text{-}H)(\mu\text{-}CNMe_2)(CO)_{10}]$ [7] in which slightly longer μ-C–Fe distances [$1.90(1)_{av}$ Å] should be attributed to the different chemical environment of the Fe atoms. The μ-H–Fe distances, on the other hand, are in very good agreement in the two species [1.61_{av} Å in both compounds].

The NMR data for compound **5a** are in complete agreement with the structure established in the solid state. A single Cp resonance (at δ 4.64) and one sharp singlet for the two N bonded Me groups (at δ 4.09) indicate the presence, in solution, of a single species **5a** and the bridging hydride resonance, at -17.75 ppm, occurs within the expected range [8]. Finally, two IR ν(CO) absorptions (at 1935 and 1891 cm^{-1}, in CH_2Cl_2 solution) show the typical strong–weak intensity pattern which accounts for the two terminal CO ligands in a mutual *cis* position.

In contrast with **5a**, two isomers are observed in the NMR spectra of **5b** (e.g. two high field μ-H signals are displayed at δ -16.72 and -17.71). Since the Fe atoms are equivalent in this molecule, α and β isomers are excluded; therefore the observed forms must be *cis–trans* isomers. Unlike **5a**, the IR ν(CO) band pattern of **5b** consists of two absorptions of comparable intensity (at 1940 and 1901 cm^{-1}), which is consistent with the presence of both *cis* and *trans* isomers.

The formation of **5a–b** presumably occurs via the terminal hydride intermediates $[Fe_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(CO)(H)(Cp)_2]$ which undergo site exchange with the bridging CO. Compared to $[Fe_2(\mu\text{-}CNMe_2)(\mu\text{-}CO)(X)(CO)(Cp)_2]$ (X = CN, **3a**; Cl, **4a**), in which the cyanide or chloride ligands steadily occupy the terminal coordination position, the rearrangement of the hydride ligand is explained by its tendency to adopt the bridging coordination whenever a more symmetric structure can be attained. Again, these results differ from those previously obtained in the absence of the labile CNMe ligand. Indeed, H$^-$ from $NaBH_4$, has been shown to add at the bridging carbyne carbon of $[Fe_2\text{-}\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(CO)_2(Cp)_2]SO_3CF_3$ (R = Me, CH_2Ph) causing a rearrangement in which the μ-CHN(Me)R ligand shifts from bridging to terminal coordination to yield the corresponding aminocarbene complexes $[Fe_2(\mu\text{-}CO)_2\{CHN(Me)R\}(CO)(Cp)_2]$ [2a].

A few other di-iron μ-hydride complexes are known. They are also generally bridged by phosphorus ligands like PPh_2 and/or $Ph_2PCH_2PPh_2$ (dppm), which strongly contribute to the stability of the dinuclear unit. Examples include $[Fe_2(\mu\text{-}PPh_2)(\mu\text{-}H)(CO)_2(Cp)_2]$ [9], $[Fe_2(\mu\text{-}PPh_2)(\mu\text{-}H)(\mu\text{-}dppm)(Cp)_2]$ [10], $[Fe_2(\mu\text{-}PPh_2)(\mu\text{-}H)\text{-}(\mu\text{-}dppm)(\mu\text{-}CO)(CO)_4]$ [11] and $[Fe_2(\mu\text{-}H)(\mu\text{-}dppm)(\mu\text{-}CO)(CO)_6]BF_4$ [12]. It is noteworthy that these complexes have been obtained by protonation at the metal or by P–H oxidative addition of the diphenylphosphine, whereas complexes **5a–b** result from hydride addition.

In contrast with related μ-hydride di-iron complexes, which readily insert acetylenes into the metal–hydride functionality [11,12], compound **5a** has been found to be unreactive toward HC≡CPh and MeOC(O)C≡CC(O)OMe. Compound **5a** is not attacked or deprotonated by buthyllithium whereas the reaction with HSO_3CF_3, in the presence of MeCN affords **1a** in about 60% yield, confirming that the bridging hydrogen in **5a** is not acidic but hydridic.

Finally we have investigated the reaction of $NaBH_4$ with the diruthenium complex $[Ru_2(\mu\text{-}CNMe_2)(\mu\text{-}CO)(NCMe)(CO)(Cp)_2]SO_3CF_3$ (**2d**), which was generated by treatment of $[Ru_2(\mu\text{-}CNMe_2)(\mu\text{-}CO)\text{-}(CO)_2(Cp)_2]SO_3CF_3$ with Me_3NO in CH_3CN. The reaction parallels that of the di-iron counterpart **2a**, leading to the formation of $[Ru_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}H)\text{-}(CO)_2(Cp)_2]$ (**6**), which has been characterized by elemental analyses, IR and NMR spectroscopy. This result was somewhat predictable on the basis of the similar behavior that diruthenium complexes $[Ru_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(CO)_2(Cp)_2]SO_3CF_3$ (R = Me, CH_2Ph) and their di-iron counterparts have shown so far [1b, 13]. However **6** differs from the analogous iron compound **5a** in its isomeric composition: the ν(CO) band pattern of the former consists of two absorptions, at 1943 and 1907 cm^{-1} of weak and strong intensity, that reveal the predominance of the *trans* isomer.

3. Experimental

3.1. General

All reactions were routinely performed under an inert atmosphere of nitrogen by using Schlenk techniques. Solvents were distilled immediately before use under nitrogen from appropriate drying agents. All the reagents were commercial products (Aldrich) of the highest purity available and used as received. $[Ru_2(CO)_4(Cp)_2]$ was from Strem and used as received. Instruments employed: IR, Perkin–Elmer Spectrum 2000; NMR, Varian Gemini 200 and 300. Unless otherwise stated NMR signals due to trace amounts of second isomeric form are italicized. The compounds $[Fe_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(CO)_2(Cp)_2]SO_3CF_3$ (R = Me,

1a; 2,6-$Me_2C_6H_3$, **1b**; CH_2Ph, **1c**) [4] and $[Ru_2(\mu\text{-}CNMe_2)(\mu\text{-}CO)(CO)_2(Cp)_2]SO_3CF_3$ [13] were prepared from the corresponding isocyanide complexes according to published methods.

*3.2. Synthesis of $[Fe_2(\mu\text{-}CNMe_2)(\mu\text{-}CO)(NCMe)(CO)(Cp)_2]SO_3CF_3$ (**2a**)*

Compound $[Fe_2(\mu\text{-}CNMe_2)(\mu\text{-}CO)(CO)_2(Cp)_2]SO_3CF_3$ (152 mg, 0.29 mmol) in MeCN (10 ml) was treated with anhydrous Me_3NO (23 mg, 0.30 mmol). Filtration on a Celite pad and removal of the solvent gave a brown residue that was crystallized from CH_2Cl_2 layered with *n*-pentane at −20°C yielding **2a** as a brown microcrystalline solid (143 mg, 96%). Anal. Found: C, 40.31; H, 3.66. $C_{18}H_{19}F_3Fe_2N_2O_5S$ requires: C, 39.73; H, 3.52%. IR (CH_2Cl_2) ν_{max} (cm^{-1}): 1984vs, 1815s (CO) and 1584m (CN). ^1H-NMR ($CDCl_3$): δ 4.98 (5 H, s, Cp), 4.86 (5 H, s, Cp), 4.66 (3 H, s, NMe), 4.31 (3 H, s, NMe) and 1.92 (3 H, s, NCMe). ^{13}C-NMR (CD_2Cl_2): δ 330.4 (μ-C), 266.2 (μ-CO), 211.2 (CO), 130.7 (MeCN), 88.7, 87.0 (Cp), 53.2 (NMe, the other NMe resonance is obscured by the solvent) and 4.4 (MeCN).

*3.3. Synthesis of $[Fe_2\{\mu\text{-}CN(Me)Me_2C_6H_3\}(\mu\text{-}CO)(NCMe)(CO)(Cp)_2]SO_3CF_3$ (**2b**) and $[Fe_2\{\mu\text{-}CN(Me)CH_2Ph\}(\mu\text{-}CO)(NCMe)(CO)(Cp)_2]SO_3CF_3$ (**2c**)*

Complexes **2b**–**c** were prepared following the same procedure described for the synthesis of **2a** by treatment of **1b** and **1c** with Me_3NO in MeCN, respectively.

2b: (92%). Anal. Found: C, 47.18; H, 3.94. $C_{25}H_{25}F_3Fe_2N_2O_5S$ requires: C, 47.34; H, 3.97%. IR (CH_2Cl_2) ν_{max} (cm^{-1}): 1988vs, 1820s (CO) and 1523m (CN). ^1H-NMR ($CDCl_3$): δ 7.42–7.02 (3 H, m, $Me_2C_6H_3$), *5.11*, 5.00 (5 H, s, Cp), 4.81 (3 H, s, NMe), 4.46, *4.32* (5 H, s, Cp), 2.69, 2.13 (6 H, s, $Me_2C_6H_3$) and 2.01 (3 H, s, NCMe). ^{13}C-NMR ($CDCl_3$): δ 338.9 (μ-C), 265.0 (μ-CO), 212.1 (CO), 148.5–128.9 (MeCN and $Me_2C_6H_3$), 88.4, 88.1 (Cp), 54.8 (NMe), 19.5, 18.1 ($Me_2C_6H_3$), and 4.8 (MeCN).

2c: (95%). Anal. Found: C, 46.44; H, 3.76. $C_{24}H_{23}F_3Fe_2N_2O_5S$ requires: C, 46.47; H, 3.74%. IR (CH_2Cl_2) ν_{max} (cm^{-1}): 1987vs and 1820s (CO) and 1566m (CN). ^1H-NMR ($CDCl_3$): δ (α isomer) 7.45–7.39 (m, C_6H_5), 6.37 (1 H, d, $J = 15$ Hz, CH_2Ph), 6.21 (1 H, d, $J = 15$ Hz, CH_2Ph), 5.04 (5 H, s, Cp), 4.81 (5 H, s, Cp), 4.13 (3 H, s, NMe), 1.83 (3 H, s, NCMe); (β-isomer) 7.45–7.39 (m, C_6H_5), 5.89 (1 H, d, $J = 15$ Hz, CH_2Ph), 5.74 (1 H, d, $J = 15$ Hz, CH_2Ph), 4.96 (5 H, s, Cp), 4.90 (5 H, s, Cp), 4.40 (3 H, s, NMe) and 1.88 (3 H, s, NCMe); α/β isomer ratio 0.8. ^{13}C-NMR ($CDCl_3$): δ 333.4 (μ-C), 266.4, *266.2* (μ-CO), 212.0, *211.5* (CO), 135.6–127.4 (MeCN and $Me_2C_6H_3$), 88.4, 88.1, *89.1*, *87.5* (Cp), 71.3, *70.9* (CH_2Ph), *51.4*, 50.5 (NMe), 19.5, 18.1 ($Me_2C_6H_3$), and *4.8*, 4.6 (MeCN); signals due to the α form are italicized.

*3.4. Synthesis of $[Fe_2(\mu\text{-}CNMe_2)(\mu\text{-}CO)(CO)(CN)(Cp)_2]$ (**3a**), $[Fe_2\{\mu\text{-}CN(Me)Me_2C_6H_3\}(\mu\text{-}CO)(CN)(CO)(Cp)_2]$ (**3b**) and $[Fe_2\{\mu\text{-}CN(Me)CH_2C_6H_5\}(\mu\text{-}CO)(CN)(CO)(Cp)_2]$ (**3c**)*

A mixture of **2a** (140 mg, 0.27 mmol) and NBu_4CN (80 mg, 0.30 mmol) was stirred in CH_2Cl_2 (10 ml) for 60 min. Removal of the solvent and chromatography of the residue on an alumina column, with 2:1 (v/v) CH_2Cl_2–petroleum ether (b.p. 40–60°C) as eluent, gave a green band which was collected. Crystallization from CH_2Cl_2 layered with *n*-pentane at −20°C yielded **3a** (86 mg, 84%) which was identified by comparison of the spectroscopic properties with those reported in the literature [4b]. Compound **3b** and **3c** were obtained from **2b** and **2c**, respectively following the same procedure above described.

3b: (76%). Anal. Found: C, 58.65; H, 4.71. $C_{23}H_{22}Fe_2N_2O_2$ requires: C, 58.76; H, 4.72%. IR (CH_2Cl_2) ν_{max} (cm^{-1}): 1982vs, 1804s (CO) and 2091m (CN). ^1H-NMR ($CDCl_3$): δ 7.33–7.28 (3 H, m, $Me_2C_6H_3$), 5.07, *4.88* (5 H, s, Cp), *4.55*, 4.46, (3 H, s, NMe), 4.20, *4.31* (5 H, s, Cp) and 2.65, *2.54*, 2.45, *2.42* (6 H, s, $Me_2C_6H_3$). ^{13}C-NMR ($CDCl_3$): δ 339.0 (μ-C), 262.7 (μ-CO), 211.8 (CO), 149.1–129.0 (CN and $Me_2C_6H_3$), 90.7, 89.3, *91.3*, *89.9* (Cp), 54.8 (NMe) and 18.7, 18.4 ($Me_2C_6H_3$).

3c: (79%). Anal. Found: C, 57.90; H, 4.44. $C_{22}H_{20}Fe_2N_2O_2$ requires: C, 57.93; H, 4.42%. IR (CH_2Cl_2) ν_{max} (cm^{-1}): 1980vs, 1806s (CO) and 2092m (CN). ^1H-NMR ($CDCl_3$): δ 7.61–7.42 (5 H, m, Ph), 6.06 (1H, d $J_{AB} = 15$ Hz, CH_2Ph), 5.61 (1H, d $J_{AB} = 15$ Hz, CH_2Ph), 4.87 (5 H, s, Cp), 4.72 (5 H, s, Cp), 3.95 (3 H, s, NMe); β isomer: 7.61–7.42 (5 H, m, Ph), 5.80 (1H, d $J_{AB} = 15$ Hz, CH_2Ph), 5.54 (1H, d $J_{AB} = 15$ Hz, CH_2Ph), 4.83 (5 H, s, Cp), 4.78 (5 H, s, Cp), 4.11 (3 H, s, NMe), α/β ratio 0.9.

*3.5. Synthesis of $[Fe_2(\mu\text{-}CNMe_2)(\mu\text{-}CO)(CO)(Cl)(Cp)_2]$ (**4a**) and $[Fe_2\{\mu\text{-}CN(Me)Me_2C_6H_3\}(\mu\text{-}CO)(Cl)(CO)(Cp)_2]$ (**4b**)*

A solution of **2a** (151 mg, 0.28 mmol) in CH_2Cl_2 (8 ml) was treated with NBu_4Cl (83 mg, 0.30 mmol). The mixture was stirred for 180 min and the solvent was then removed under reduced pressure. Chromatography of the residue on an alumina column, with 1:1 (v/v) CH_2Cl_2–petroleum ether (b.p. 40–60°C) as eluent, gave a brown band which was collected and crystallized from CH_2Cl_2–*n*-pentane mixture yielding **4a** (45 mg 41%). Anal. Found: C, 46.10; H, 4.16. $C_{15}H_{16}ClFe_2NO_2$

Table 1
Crystal data and experimental details for [$Fe_2(\mu\text{-}CNMe_2)(\mu\text{-}H)(CO)_2(Cp)_2$] (**5a**)

Formula	$C_{15}H_{17}Fe_2NO_2$
M	355.00
Temperature (K)	293(2)
Wavelength (Å)	0.71069
Crystal symmetry	Orthorhombic
Space group	$P2_12_12_1$ (no. 19)
a (Å)	8.000(2)
b (Å)	8.810(3)
c (Å)	20.531(7)
Cell volume ($Å^3$)	1447.0(8)
Z	4
D_{calc} ($Mg\ m^{-3}$)	1.630
μ(Mo–K_α) (mm^{-1})	2.003
F(000)	728
Crystal size (mm)	0.15 × 0.20 × 0.27
θ Range (°)	2.5–30
Scan mode	ω
Reflections collected	4561 ($\pm h$, $+k$, $+l$)
Unique observed reflections [$I>2\sigma(I)$]	3226
Goodness of fit on F^2	1.031
R_1 $(F)^a$, wR_2 $(F^2)^b$	0.0284, 0.0687
Absolute structure parameter	0.03(2)
Weighting scheme	$a=0.0445$, $b=0.0381$ [b]
Largest difference peak and hole (e $Å^{-3}$)	0.31 and −0.39

[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 $P=(F_o^2+2F_c^2)/3$.

requires: C, 46.26; H, 4.14%. IR (CH_2Cl_2) ν_{max} (cm^{-1}): 1980vs, 1801s (CO). ^{1}H-NMR ($CDCl_3$): δ 4.75 (5 H, s, Cp), 4.71 (3 H, s, NMe), 4.65 (5 H, s, Cp) and 4.26 (3 H, s, NMe).

Compound **4b** was obtained from **2b** and NBu_4Cl with the same procedure described for the synthesis of **4a**.

4b: (61%). Anal. Found: C, 55.27; H, 4.46. $C_{22}H_{22}ClFe_2NO_2$ requires: C, 55.10; H, 4.62%. IR (CH_2Cl_2) ν_{max} (cm^{-1}): 1980vs and 1799s (CO). ^{1}H-NMR ($CDCl_3$): δ 7.35–7.15 (3 H, m, $Me_2C_6H_3$), 4.85 (3 H, s, NMe), 4.72 (5 H, s, Cp), 4.29 (5 H, s, Cp) and 2.69, 2.13 (6 H, s, $Me_2C_6H_3$). ^{13}C-NMR ($CDCl_3$): δ 343.3 (μ-C), 269.0 (μ-CO), 213.8 (CO), 148.8–128.9 ($Me_2C_6H_3$), 87.6, 86.9 (Cp), 54.8 (NMe) and 18.7, 17.6 ($Me_2C_6H_3$).

3.6. Synthesis of [$Fe_2(\mu\text{-}CNMe_2)(\mu\text{-}H)(CO)_2(Cp)_2$] (5a) and [$Fe_2\{\mu\text{-}CN(Me)Me_2C_6H_3\}(\mu\text{-}H)(CO)_2(Cp)_2$] (5b)

Complex **2a** (160 mg, 0.31 mmol) was stirred with $NaBH_4$ (15 mg, 0.4 mmol) in MeCN (8 ml) for about 30 min. Removal of the solvent and chromatography on an alumina column, with 2:1 Et_2O–MeCN (v/v) as eluent, gave a red–orange band which was collected. Dark-brown crystals of **5a** were obtained upon slow solvent evaporation (70 mg, 64%). Anal. Found: C, 50.75; H, 4.78. $C_{15}H_{17}Fe_2NO_2$ requires: C, 50.70; H, 4.83%. IR (CH_2Cl_2) ν_{max} (cm^{-1}): 1935s and 1891w (CO). ^{1}H-NMR ($CDCl_3$): δ *4.64* (10 H, s, Cp), 4.09 (6 H, s, NMe_2) and −17.75 (1 H, s, μ-H). ^{13}C-NMR (CD_3CN): δ 338.4 (μ-$CNMe_2$), 217.2 (CO), 81.4 (Cp), and 51.1 (NMe_2).

Compound **5b** was obtained from **2b** and $NaBH_4$ following the same procedure described for the synthesis of **5a**.

5b: (69%). Anal. Found: C, 59.34; H, 5.13. $C_{22}H_{23}Fe_2NO_2$ requires: C, 59.36; H, 5.21%. IR (CH_2Cl_2) ν_{max} (cm^{-1}): 1940s and 1901s (CO). ^{1}H-NMR ($CDCl_3$): δ 7.20–6.90 (3 H, m, $Me_2C_6H_3$), 4.64, 4.61 (5 H, s, Cp), 4.10, *4.07* (5 H, s, Cp) 4.26 (3 H, s, NMe), 2.47, *2.32*, *2.27*, 2.15 (6 H, s, $Me_2C_6H_3$), and −16.72, *−17.71*, (1 H, s, μ-H); signals due to the *trans* isomer are italicized (*cis*/*trans* isomers ratio 1.4). δ_C ($CDCl_3$), *cis* isomer: 327.8 (μ-C), 218.9, 216.9 (CO), 135.1–128.0 ($Me_2C_6H_3$), 82.8, 81.4 (Cp), 53.1 (NMe) and 18.8, 18.2 ($Me_2C_6H_3$); *trans* isomer: 217.8, 217.7 (CO), 82.3, 82.0 (Cp), 18.8, 18.2 ($Me_2C_6H_3$).

3.7. Synthesis of [$Ru_2(\mu\text{-}CNMe_2)(\mu\text{-}H)(CO)_2(Cp)_2$] (6)

A solution of [$Ru_2(\mu\text{-}CNMe_2)(\mu\text{-}CO)(CO)_2(Cp)_2$]-$SO_3CF_3$ (150 mg, 0.24 mmol) in MeCN (10 ml) was treated with anhydrous Me_3NO (21 mg, 0.28 mmol). The mixture was stirred for 30 min then filtered on a Celite pad. Removal of the solvent gave a brown oily residue of [$Ru_2(\mu\text{-}CNMe_2)(\mu\text{-}CO)(CO)(NCMe)(Cp)_2$]-$SO_3CF_3$ (**2d**), showing the following spectroscopic data: IR (CH_3CN) ν_{max} (cm^{-1}): 1979vs and 1812s (CO). ^{1}H-NMR (CD_3CN): δ 5.43 (5 H, s, Cp), 5.20 (5 H, s, Cp) 3.99 (3 H, s, NMe), 3.92 (3 H, s, NMe). Compound **2d** was redissolved in NCMe and treated with $NaBH_4$ (18 mg, 0.47 mmol). The reaction mixture was allowed to stir for an additional 90 min, then filtered on alumina. Crystallization from CH_2Cl_2 layered with Et_2O at −20°C yielded **6** (61 mg, 57%). Anal. Found: C, 40.44; H, 3.86. $C_{15}H_{17}NO_2Ru_2$ requires: C, 40.44; H, 3.85%. IR (CH_2Cl_2) ν_{max} (cm^{-1}): 1943m and 1907vs (CO). ^{1}H-NMR ($CDCl_3$): δ 5.06, *5.02* (10 H, s, Cp), *3.89*, 3.86 (6 H, s, NMe_2) and −13.29, *−13.54* (1 H, s, μ-H); signals due to the *cis* isomer are italicized (*cis*/*trans* isomer ratio 0.4).

3.8. X-ray crystallographic study of 5a

Crystal data and details of the data collection for [$Fe_2(\mu\text{-}CNMe_2)(\mu\text{-}H)(CO)_2(Cp)_2$] (**5a**) are given in Table 1. 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 was necessary. The compound crystallized as a racemic conglomerate of chiral crystals in the space group $P2_12_12_1$ and the absolute configuration of the specimen under investigation was determined (absolute structure parameter 0.03(2)). The positions of the metal atoms were found by direct methods using the SHELXS-86 program [14] and all the non-hydrogen atoms located in electron density maps. As usual the C_5H_5 rings were treated as rigid groups (C–C 1.42 Å) because they do not contain information of chemical relevance and both the methyl and cyclopentadienyl hydrogen atoms were located in successive Fourier-difference maps but added in calculated positions. The hydride was located in the Fourier map and refined with isotropic thermal factor and the constraint of equal Fe–H distance. The C_5H_5 group on the right of Fig. 1 [C(21)–C(25)] is affected by a higher thermal motion while the facing methyl group [C(2)] shows some evidence of a second orientation around the N–C axis (occupation ca. 0.33) almost staggered with respect to the main image. The final refinement on F^2 proceeded by full-matrix least-squares calculations (SHELXL-93) [15] using anisotropic thermal parameters for all non-hydrogen atoms. The methyl and cyclopentadienyl hydrogen atoms were assigned isotropic thermal parameters 1.2 times U_{eq} of the pertinent carbon atoms.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 141113. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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