

Journal of Organometallic Chemistry 545-546 (1997) 117-123



# Synthesis and spectroscopic properties of heteropolynuclear cyano-bridged complexes

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Received 21 January 1997; received in revised form 23 May 1997

### Abstraci

The heteropolynuclear cyano-bridged complexes  $[(C_5H_5)Fe(CO)(CNMLn)(CNM'L'n)]$ ,  $\{MLn = M'L'n = (C_5H_5)Fe(CO)_2$  or  $W(CO)_5$ ;  $MLn = (C_5H_5)Fe(CO)_2$ ,  $M'L'n = W(CO)_5$ } and mixed isocyanide complexes  $[(C_5H_5)Fe(CO)(CNMLn)(CNR)]$ ,  $\{MLn = W(CO)_5, R = CPh_3$ ;  $MLn = (C_5H_5)Fe(CO)_2$ ,  $R = CH_3$ } have been obtained by metallation or alkylation of the two terminal CN ligands of  $K[(C_5H_5)Fe(CO)(CN)_2]$ . Comparison of the bonding properties of the CNMLn and CNR ligands, based upon their relevant spectroscopic data, are discussed. Furthermore, two new isomeric heterobinuclear cyano-bridged complexes of the form  $[(C_5H_5)(CO)_2FeCNW(CO)_5]$  and  $[(C_5H_5)(CO)_2FeNCW(CO)_5]$  have been synthesized and fully characterized by spectroscopic techniques. Finally the reactions with nucleophiles of the last two compounds have been also examined. © 1997 Elsevier Science S.A.

### **1. Introduction**

The ability of the cyanide group to act as an ambident bridging ligand has been fruitfully used to generate a great number of complexes having the M-CN-M' moiety [1-7]. The interest in these derivatives arises mainly from their potential ability to allow intramolecular electron transfer processes and from the different chemical and spectroscopic properties induced on the metal fragment when C- or N-bonded [8-10]. For example, electrochemical studies have shown that, in homobinuclear cyano-bridged complexes, the N-bonded metal units are easier to oxidize than C-bonded ones [11].

In order to gain understanding of the coordination properties of cyanide bridge we have synthesized organometallic complexes having two CNMLn groups linked to the same centra! iron atom of the type [CpFe(CO)(CNMLn)<sub>2</sub>] or [CpFe(CO)(CNMLn)-(CNM'Ln)], (Cp =  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>). Since carbon monoxide is a suitable ligand to ascertain the electronic properties of the metal that is coordinated to, we have directed our efforts toward the synthesis of bridging cyanide complexes containing carbonyl metal fragments.

Since the CNMLn fragment can be viewed as a

'metal isocyano ligand' [12] it might be of interest to compare their chemical and spectroscopic properties with those of common organic CNR ligands. In this context we have been stimulate to synthesize complexes of the type [CpFe(CO)(CNMLn)(CNR)], having simultaneously coordinated these ligands.

Furthermore, the different spectroscopic properties of metal fragments, C- or N-bonded to the cyano bridging group of two isomeric -CN- or -NC- cyano-bridged complexes, will be described.

### 2. Results and discussion

### 2.1. Synthesis of polynuclear cyano-bridged complexes

Compounds bearing terminal cyanide ligands can be easily alkylated to afford a wide series of isocyanide complexes [13,14]. Analogously, reactions with electrophilic metal fragments have been successfully used to synthesize  $\mu$ -CN dinuclear complexes.

We have found that  $K[CpFe(CO)(CN)_2]$  reacts with two equivalents of  $[Fp(THF)]BF_4$   $[Fp = CpFe(CO)_2]$  to form the complex  $[CpFe(CO)\{CNFe(CO)_2Cp\}_2]$   $BF_4$ complex, 1. The reaction of an equimolar amount of  $[Fp(THF)]BF_4$  affords the monoadduct  $[CpFe(CO)(CN)\{CNFe(CO)_2Cp\}]$ , 2, together with a

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small amount of 1. To overcome the difficulties in purifying 2 from 1, a more selective and cleaner synthetic route has been followed. Indeed, an easily separable mixture of 2 and [CpFe(CO)<sub>2</sub>(CN)] has been obtained by reacting compound 1 with a stoichiometric amount of (Bu<sub>4</sub>N)CN. Complex 2 reacts with [Fp(THF)]BF<sub>4</sub> to form 1 (Scheme 1).

The <sup>13</sup>C NMR spectrum of  $[CpFe(CO)(CN)-{CNFe(CO)_2Cp}]$  2, in CD<sub>3</sub>NO<sub>2</sub>, is consistent with its formulation, showing two signals attributable to the CN carbon atoms at  $\delta$ 170.2 and 166.3. The upfield CN signal is absent in the cationic complex 1, whereas its cyclopentadienyl resonances occur at  $\delta$ 86.3 and 82.6, the former being of double intensity. As for complex 2, a comparison of these spectroscopic features unambiguously assigns the CN upfield resonance to terminal cyanide and the downshifted cp signal to the N-bonded fragment.

The absorption at 2095 cm<sup>-1</sup>, attributed to terminal cyanide in 2, disappears in the IR spectrum of complex [CpFe(CO){CNFe(CO)<sub>2</sub>Cp}<sub>2</sub>]BF<sub>4</sub> 1. The  $\nu$ (CN) of the bridging cyanide occurs, as expected, at higher wavenumbers compared to that of terminal CN. The carbonyl pattern of the N-bonded Fp fragments are almost coincident in 1 and 2, whereas the absorption

related to the carbonyl coordinated to the C-bonded iron atom is largely influenced by its cationic nature and is shifted of  $15 \text{ cm}^{-1}$  to higher wavenumbers in **1**.

The terminal cyanide ligand in complex 2 reacts with an excess of Lewis acid W(CO)<sub>5</sub>(THF) yielding {CpFe(CO){CNFe(CO),Cp}{CNW(CO),}], 3; its formulation is supported by the presence in the IR spectrum of two distinct bridging cyanide vibrations at 2141 and  $2126 \text{ cm}^{-1}$ , together with the characteristic band pattern of  $W(CO)_5$  fragment. The nature of complex 3 is also ascertained from the <sup>13</sup>C NMR data, showing two distinct signals at  $\delta$ 171.4 and 156.5 attributable respectively to the carbon atom of Fe-CN-Fe and Fe-CN-W bridges. It has been possible to assign the cyclopentadienyl signals (CN-Fe-C<sub>5</sub>H<sub>5</sub>,  $\delta = 86.6$ ; NC-Fe-C<sub>5</sub>H<sub>5</sub>,  $\delta = 82.8$ ) and to distinguish carbonyl resonances of tungsten from those of iron fragment [W(CO)eq = $198.2 + {}^{183}W$  satellites (J = 135.4 Hz); W(CO)ax = 201.6; Fe(CO)<sub>2</sub> = 211.7 and Fe(CO) = 218.7] (Fig. 1).

Analogously, an excess of  $W(CO)_5(THF)$  reacts with a THF solution of  $K[CpFe(CO)(CN)_2]$  affording in a moderate yield (25%) the complex  $K[CpFe(CO)\{CNW(CO)_5\}_2]$  4, (Scheme 1).

Comparison between 1, 3 and 4 shows that replacement of the Fp moiety with the  $W(CO)_5$  fragment does





not significantly influence the chemical shift values in the  $^{13}$ C spectra, in spite of the different charge owned by the complexes.

#### 2.2. CNR and CNMLn as ligands

The complex  $[CpFe(CO){CNFe(CO)_2Cp}(CNCH_3)]^+$ 5, has been synthesized in order to compare the bonding ability of 'metal-isocyanide' ligands, CNMLn, with the ones of classical isocyanides, CNR. Two different pathways have been used (Scheme 1): a) metallation of  $[CpFe(CO)(CNCH_3)(CN)]$  with  $[CpFe(CO)_2(THF)]BF_4$ ; b) N-alkylation of  $[CpFe(CO)(CN){CNFe(CO)_2Cp}]$  2 with MeOSO<sub>2</sub>CF<sub>3</sub>.

The stretching CN vibration of the CNMe ligand in 5 appears as a medium-strong band at 2206 cm<sup>-1</sup>, whereas the CNFp band is weaker and at lower wavenumbers (2149 cm<sup>-1</sup>). The <sup>13</sup>C NMR spectrum exhibits a resonance (165.8 ppm), due to CNFp bridge, while an upfield resonance (151.4 ppm) has been attributed to the CNMe. The broadness exhibited by the latter signal, due to <sup>13</sup>C-<sup>14</sup>N spin coupling and to partial quadrupolar relaxation, is usually found in the isonitrile resonance of [CpFe(CO)(CNR)L]<sup>+</sup> complexes [15].

An interesting trend in the IR spectra is observed when varying the ligands of the Fe atom by substituting metal-iso cyanides (CNFp or CNW(CO)<sub>5</sub>) with organic iso cyanides (CNR) both in cationic  $\{[CpFe(CO)(CNFp)_2]^+1, (\nu(CO) = 1986 \text{ cm}^{-1}), [CpFe(CO)(CNFp)(CNCH_3)]^+ 5, (\nu(CO) = 2005 \text{ cm}^{-1}) \text{ and } [CpFe(CO)(CNCH_3)(CNC_2H_5)]^+ (\nu(CO) = 2019 \text{ cm}^{-1})[16]\}$  and in neutral derivatives {[CpFe(CO){CNFe(CO)<sub>2</sub>Cp}{CNW(CO)<sub>5</sub>]] **3**, ( $\nu$ (CO) = 1981 cm<sup>-1</sup>) and [CpFe(CO){CNW(CO)<sub>5</sub>}(CNCPh<sub>3</sub>)] **6**, ( $\nu$ (CO) = 2008 cm<sup>-1</sup>)}. The shift of the  $\nu$ (CO) coordinated to the central iron atom seems to indicate that the  $\sigma/\pi$  ratio of the CNFp is higher than CNR.

Compound 6 has been obtained by reacting  $[CpFe(CO)(CN)(CNCPh_3)]$  [17] with an excess of  $[W(CO)_{\varsigma}(THF)]$ .

Exploiting the ability of neutral cyanocomplexes to coordinate unsaturated metal fragments we have synthesized [Cp(CO), FeCNFe(CO), Cp]<sup>+</sup> 7, by simple reaction between FpCN and Fp<sup>+</sup>. Compound 7 has been isolated as a microcrystalline solid, but its slow decomposition in solution has precluded a reliable <sup>13</sup>C NMR characterization. The complex 7 can be viewed as formally derived from 1 by replacing one CNFp ligand with the more  $\pi$ -acid CO ligand. The  $\nu$ (CN) absorption in the IR spectrum of 7, in CH<sub>2</sub>Cl<sub>2</sub> solution, is consequently shifted to higher wavenumbers, (2166 cm<sup>-1</sup>), with respect to that of 1, [CpFe(CO){CNFe(CO)<sub>2</sub>Cp},] BF<sub>4</sub> (2136 cm<sup>-1</sup>). Likewise the  $\nu$ (CN) of compound 7, in the solid, occurs about 100 cm<sup>-1</sup> higher to the one showed by  $[Cp(dppe)FeCNFe(dppe)Cp]^+$ , (dppe =Ph, PCH, CH, PPh, [11], according with the backbonding competition exercised by carbonyl ligands. Therefore, the variations of the  $\nu(CN)$  values of the cyanide bridge are related to the nature of the two coordinated metal fragments, reflecting their  $\sigma/\pi$  bonding character as recently shown by Bignozzi et al. [18], who have examined the factors that influence the cyanide stretching frequency after bridge formation: kinematic coupling and back-bonding.

The poor  $\pi$ -acid character of the metalloisocyanide

ligand is evidenced by the trend of stretching vibration values exhibited by cyanide bridges in the sequence:



#### 2.3. Isomeric -CN- or -NC- cyanobridged complexes

Few isomeric binuclear cyano-bridged complexes have been isolated. Vahrenkamp has recently synthesized the [(CO)<sub>5</sub>CrCNFe(dppe)Cp] complex and its linkage isomer [19]. The scarcity of this class of compounds may be attributed to the lability of M-N bond. Reaction between [CpFe(CO)<sub>2</sub>(CN)] and [W(CO)<sub>5</sub>(THF)] affords the  $\mu$ -CN complex [Cp(CO)<sub>2</sub>FeCNW(CO)<sub>5</sub>], **8**, in low yield. The [W(CO)<sub>5</sub>(CN)]<sup>-</sup> anion reacts with [CpFe(CO)<sub>2</sub>(THF)]<sup>+</sup> yielding the linkage isomer [Cp(CO)<sub>2</sub>FeNCW(CO)<sub>5</sub>], **9**. [(C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>(CN)] + [W(CO)<sub>5</sub>(THF)]

$$\rightarrow [(C_5H_5)(CO)_2Fe-C \equiv N-W(CO)_5]8$$
  
[(C\_5H\_5)Fe(CO)\_2(THF)]BF<sub>4</sub> + Na[W(CO)\_5(CN)]  
$$\rightarrow NaBF_4 + [(C_5H_5)(CO)_2Fe-N \equiv C-W(CO)_5]9$$

Both 8 and 9 have been characterized by spectroscopy and microanalysis. They are stable in the solid state and no evidence of  $CN \leftrightarrow NC$  isomerization has been observed in solution.

The IR frequency values of carbonyl absorptions in the W(CO)<sub>5</sub> fragment are indicative of  $\pi$ -acidity of the ligand which this group is bound to. In particular, an increasing of stretch-stretch interaction constant of the two a<sub>1</sub> modes has been associated to the carbonyl replacement by ligands of lower  $\pi$ -bonding ability [20]. This phenomenon is well evidenced by comparing the IR spectra of the two isomeric compounds (A) and (B) [21]:



It is worth noting that all the inferences adopted to explain the IR band pattern of the  $W(CO)_5$  moieties in the nitrile (A) and isocyano-like (B) compound can be

proposed by discussing the IR spectra of 8 and 9. Analogously the absorption of the carbonyl of the W(CO)<sub>5</sub> fragment sited trans to the N-coordinated cyanide group appears to be at lower wavenumbers  $[\nu(CO) = 1881 \text{ cm}^{-1} \text{ in 8}]$  with respect to the axial carbonyl of the relative isomer  $[\nu(CO) = 1900 \text{ cm}^{-1} \text{ in 9}]$ . Furthermore, the electron withdrawing effect of W(CO)<sub>5</sub> fragment is responsible for the frequency values of bridged cyanide  $[\nu(CN) = 2152 \text{ cm}^{-1} \text{ in 8}]$ . By contrast in complex 9 the W-C backdonation influence appears to be prevalent  $[\nu(CN) = 2136 \text{ cm}^{-1}]$ .

The two isomers 8 and 9 are easily distinguishable from their  $\mu$ -CN resonances in the <sup>13</sup>C NMR spectra, which are remarkably different:  $[\delta C-W, 168.6 \text{ in } 9;$  $\delta C$ -Fe, 139.1 in 8]. The W(CO)<sub>5</sub> carbonyl pattern of the 'tungsten isocyanide isomer' 9 is upfield shifted with respect to the isomeric form 8 and exhibits a narrower separation (2.5 ppm) between the signals of the equatorial and axial carbonyls (3.4 ppm in 8), as already found in compounds (A) and (B) [21]. These results are in accord with the observation that the chemical shift of trans-CO moves downfield compared to those of the cis-carbonyls as the  $\sigma/\pi$  ratio of L increases in M(CO)<sub>5</sub>L complexes [22].

Recently the structure of  $(OC)_5WCNW(CO)_5^-$  anion [23], according with a lower backdonation from metal to carbonyl, showed for the CO group trans to the C-bonded cyanide bridge, a longer W-C, which corresponds to a shorter C-O distance.

Therefore a strict analogy exists between isocyanide  $M-C \equiv N-R$ , and the related 'metallated isocyano' complexes,  $M-C \equiv N-M'Ln$ , as well as between the nitrile  $M-N \equiv C-R$ , and metal-nitrile  $M-N \equiv C-M'Ln$  complexes.

An analysis of U.V. spectra of compounds 8 and 9 confirms these statements. Two LF bands are expected for compounds of the type W(CO)<sub>5</sub>L: an higher energy one for  ${}^{1}A_{1}-{}^{1}E$  spin allowed transition, while the lowest one corresponds to a singlet-triplet  ${}^{1}A_{1}-{}^{3}E$  spin forbidden transition [24]. Therefore the U.V. spectrum of complex 9 in acetonitrile exhibited an intense band at 359 nm ( $\epsilon \approx 3700$ ) with a shoulder at 380 nm, while in case of complex 8 these two bands occur at 383 ( $\epsilon \approx 3300$ ) and 430 nm, respectively.

These values are consistent with the hypothetical relative location of C=NFp and N=C-Fp ligands in the spectrochemical series, being isocyanides  $\pi$ -acceptor while nitriles merely  $\sigma$ -donor ligands.

We have reacted compounds 8 and 9 with piperidine  $(C_5H_{10}NH)$  to test a possible nucleophilic addition to the CN bond, as already found in related isocyanide complexes [25,26]. However the reaction proceeds with cleavage of metal-N( $\mu$ -CN) bond in both the cases. Complex 8 affords FpCN and  $[W(CO)_5(pip)]$ , whereas the piperidinium salt of  $[W(CO)_5(CN)]^-$  and the carbonyl dimer  $[Cp(CO)_2Fe]_2$  have been isolated by react-

ing complex 9. Similar results were obtained from reaction of 9 with NaBH<sub>4</sub>, that gives Na[W(CO)<sub>5</sub>CN] and [Cp(CO)<sub>2</sub>Fe]<sub>2</sub>. The only example of hydride addition to a cyano-bridged complex reported so far, involved complexes of the type [CpL<sub>2</sub>Ru( $\mu$ -CN)ML'<sub>2</sub>Cp]<sup>+</sup>, [M = Ru or Fe; L<sub>2</sub>, L'<sub>2</sub> = (PPh<sub>3</sub>)<sub>2</sub>, dppe], and led to formation of [CpL<sub>2</sub>Ru(CN)] and [CpL'<sub>2</sub>MH] [27]. An analogous mechanism can be invoked in our case: nucleophilic attack of the hydride on the carbon atom of the cyano bridge; subsequent  $\beta$ -elimination affords the W(CO)<sub>5</sub>CN<sup>-</sup> anion and FpH. The latter rapidly decomposes in solution to give the dicyclopenta-dienylcarbonyl dimer.

### 3. Experimental

### 3.1. General procedures

All manipulations were performed under an inert atmosphere of dry nitrogen or argon by using standard vacuum-line and schlenk techniques. The solvents were deoxygenated and dried prior to use. Diethyl ether, tetrahydrofurane and petroleum ether were distilled immediately prior to use from purple solutions of sodium and benzophenone; CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>CN were dried over CaH<sub>2</sub>. Unless stated otherwise, all other reagentgrade chemicals were used as received. The compounds  $[(C_{1}H_{2})Fe(CO),I]$  [28],  $[(C_{1}H_{2})Fe(CO),CN]$  [29],  $K[(C_5H_5)Fe(CO)(CN)_2][17]$  and  $Na[W(CO)_5(CN)][13]$ were prepared by literature procedures. The compound  $[(C,H_{5})Fe(CO)_{2}(THF)]BF_{4}$  has been obtained by reacting FpI with a stoichiometric amount of AgBF<sub>4</sub> in tetrahydrofurane solution. Infrared spectra were measured on a Perkin-Elmer 983 G spectrophotometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian XL 200. Cr(acac), 0.1 M was added to <sup>13</sup>C NMR samples as a shiftless relaxation agent. Electrolytic conductance measurements were carried out using a LKB 5300 B conductometer. Melting points were determined with a Büchi instrument and are uncorrected.

# 3.2. Synthesis of $[(\eta-C_5H_5)Fe(CO)](CNFe(CO)_2(\eta-C_5H_5)]_2$ ]BF<sub>4</sub> 1

A tetrahydrofurane solution  $(20 \text{ cm}^3)$  of  $K[(C_5H_5)Fe(CO)(CN)_2]$  (0.223 g, 0.93 mmol), and  $[(C_5H_5)Fe(CO)_2(THF)]BF_4$  (0.606 g, 1.8 mmol), was stirred for two hours at  $-20^{\circ}$ C. The solution was then carried out to room temperature and additionally stirred for other 4 h during which time product 1 precipitated as golden-yellow microcrystalline solid. The crystals were filtered off, washed with petroleum ether, dissolved in CH<sub>2</sub>Cl<sub>2</sub> and chromatographed on alumina column (8 × 2 cm). A red band containing some [Cp(CO)<sub>2</sub>Fe]<sub>2</sub> was first eluted with a mixture of

petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> (i:1, v/v). CH<sub>2</sub>Cl<sub>2</sub> then removed compound **1** which was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether yielding golden-yellow microcrystals of **1** (0.137 g, 23%), m.p. 154–156°C (decomp.). (Found: C 40.70; H 2.43; N 4.58. C<sub>22</sub>H<sub>15</sub>BF<sub>4</sub>Fe<sub>3</sub>N<sub>2</sub>O<sub>5</sub> requires C 41.17; H 2.36; N 4.37%). IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu_{max}$ /cm<sup>-1</sup> 2136 m (CN), 2069 vs, 2024 vs, 1986 s (CO). NMR:  $\delta_{H}$ (CD<sub>2</sub>Cl<sub>2</sub>) 5.27(10H, s, C<sub>5</sub>H<sub>5</sub>), 4.64(5H, s, C<sub>5</sub>H<sub>5</sub>);  $\delta_{C}$  (CD<sub>3</sub>CN): 217.6 (FeCO), 211.1 (Fe(CO)<sub>2</sub>), 170.2 (CN), 86.3 (C<sub>5</sub>H<sub>5</sub>), 82.6 (C<sub>5</sub>H<sub>5</sub>).  $\Lambda_{M}$ 120.6 ohm<sup>-1</sup>. cm<sup>2</sup>. mole<sup>-1</sup> (acetone, 10<sup>-3</sup> M).

# 3.3. Synthesis of $[(\eta - C_5 H_5)Fe(CO)(CN)/CNFe(CO)_2(\eta - C_5 H_5)]]$ 2

To a THF solution  $(10 \text{ cm}^3)$  of  $[(C_{5}H_{5})Fe(CO)_{2}(THF)]BF_{4}$  (0.808 g, 2.4 mmol), was added K[(C<sub>5</sub>H<sub>5</sub>)Fe(CO)(CN)<sub>2</sub>] (0.540 g, 2.4 mmol), dissolved in the same solvent (50 cm<sup>3</sup>). The solution was stirred for two hours at  $-30^{\circ}$ C and for other four hours at room temperature. After evaporation of the solvent, the residue was dissolved in CH<sub>3</sub>CN, filtered through a Celite pad and chromatographed on Florisil  $(7 \times 2 \text{ cm column})$ , with ether/CH<sub>3</sub>CN (1:1, v/v) as eluent. A red band of [Cp(CO)<sub>2</sub>Fe]<sub>2</sub> followed by a yellow one containing some [CpFe(CO)<sub>2</sub>(CN)] were eluted first. Addition of CH<sub>3</sub>CN then removed compound 2 which was recrystallized from CH<sub>3</sub>CN/ether to give 0.170 g (19%) of orange-brown microcrystals; m.p. 132-135°C (decomp.). Compound 2 is rather unstable in solution, especially in chlorinated solvents. (Found: C, 47.5; H, 2.5; N, 7.1. C<sub>15</sub>H<sub>10</sub>Fe<sub>2</sub>N<sub>2</sub>O<sub>3</sub> requires C, 47.66; H, 2.67; N, 7.41%) IR  $\nu_{max}/cm^{-1}$ (CH<sub>2</sub>Cl<sub>2</sub>) 2134 m, 2095 m (CN), 2067 s, 2022 s, 1971 s (CO). NMR  $\delta_{\rm H}$  (CD<sub>3</sub>NO<sub>2</sub>): 5.47, 4.62 (C<sub>5</sub>H<sub>5</sub>);  $\delta_{\rm C}({\rm CD}_3{\rm NO}_2)$ : 215.8 (FeCO), 207.2 (Fe(CO)<sub>2</sub>), 170.2 (CNFe), 166.3 (CN), 82.1, 78.2 (C<sub>5</sub>H<sub>5</sub>).

#### 3.4. Reaction of I with $(Bu_{\downarrow}N)CN$

Complex 1, (0.100 g, 0.16 mmol.), dissolved in 10 cm<sup>3</sup> of CH<sub>3</sub>CN was reacted at room temperature for 4 h with a stoichiometric amount of  $(Bu_4N)CN$  (0.48 g, 0.16 mmol.). The solution was filtered on Celite (2 × 2 cm), the volume reduced to ca. 2 ml and chromatographed on alumina column (7 × 2 cm) with ether/CH<sub>3</sub>CN (1:1, v/v) as eluent. A yellow band containing FpCN was first eluted. Addition of CH<sub>3</sub>CN th e n r e m o v e d c o m p l e x 2, [(C<sub>3</sub>H<sub>3</sub>)Fe(CO)(CN){CNFe(CO)<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>)}].

# 3.5. Synthesis of $[(\eta - C_5 H_5)Fe(CO)](CNFe(CO)_2(\eta - C_5 H_5))](CNW(CO)_5)]$ 3

A THF solution of complex 2, (0.160 g, 0.42 mmol), was treated with a slight excess of W(CO)<sub>5</sub>(THF),

obtained by photolysis of  $W(CO)_6$  in THF. After 20 h stirring, the solvent was evaporated under vacuum and the vellow-brown residue was dissolved in CH<sub>3</sub>CN, filtered on Celite and then chromatographed on Florisil  $(10 \times 2 \text{ cm})$ . W(CO)<sub>6</sub> was eluted first with petroleum ether followed by a band containing compound 3 by elution with CH<sub>3</sub>CN. The solvent was stripped out and the residue crystallized from CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether to give 0.70 g (24%) of pure 3, m.p. 132-136°C. (Found: C, 34.12; H, 1.43; N, 4.21. C<sub>20</sub>H<sub>10</sub>Fe<sub>2</sub>N<sub>2</sub>O<sub>8</sub>W requires C, 33.96; H, 1.40; N, 4.26%).IR  $v_{\text{max}}/\text{cm}^{-1}(\text{CH}_2\text{Cl}_2)$ : 2141 w, 2126 w (CN), 2024 m, 1981 m (Fe-CO), 2068 m, 1923 vs, 1873 m (W-CO). NMR  $\delta_{\rm H}$ (CDCl<sub>3</sub>) 5.17, 4.62 (C<sub>5</sub>H<sub>5</sub>);  $\delta_{\rm C}$ (CD<sub>3</sub>CN) 218.7 (FeCO), 211.7 (Fe(CO)<sub>2</sub>), 201.6(WCOax), 198.2 (WCOeq), 171.4 (CNFe), 156.5 (CNW), 86.6  $(C_5H_5FeNC)$ , 82.8  $(C_5H_5FeCN)$ .

# 3.6. Synthesis of $K[(\eta - C_5H_5)Fe(CO)[CNW(CO)_5]_2]$ 4

A suspension of 173 mg (0.72 mmol) of  $K[(C_5H_5)Fe(CO)(CN)_2]$  in tetrahydrofuran (10 cm<sup>3</sup>) was treated with excess (5:1) of W(CO)<sub>5</sub>(THF) for 20 h. The solvent was evaporated under vacuum, the residue dissolved in CH<sub>3</sub>CN and filtered on Celite. After evaporation of the solvent, the residue was chromatographed on Florisil  $(10 \times 2 \text{ cm})$  with petroleum ether as eluent to remove  $W(CO)_6$ . Subsequent elution with CH<sub>3</sub>CN gave a green band which was collected and concentrated to ca. 2 ml. Layering the solution with ether gave 4 as a green powder (0.126 g, 25%), m.p. 124-128°C (decomp.). (Found: C, 25.12; H, 0.68; N, 3.34.  $C_{18}H_5FeKN_2O_{11}W_2$  requires C, 24.35; H, 0.56; N, 3.16%). IR  $\nu_{max}/cm^{-1}$  (CH<sub>2</sub>Cl<sub>2</sub>): 2121 w (CN), 1979 m (Fe-CO), 2070 w 1928 vs, 1874 m (W-CO). NMR  $\delta_{\rm H}$  (CDCl<sub>3</sub>): 4.6 (C<sub>5</sub>H<sub>5</sub>).  $\delta_{\rm C}$ (CD<sub>3</sub>CN): 219.0 (FeCO), 201.8 (WCOax), 198.2 (WCOeq), 156.9 (CN), 82.8 (C<sub>5</sub>H<sub>5</sub>).  $A_{\rm M}$  105.4 ohm<sup>-1</sup> cm<sup>2</sup>. mole<sup>-1</sup>(acetone, 10<sup>-3</sup>) M)

# 3.7. Synthesis of $[(\eta - C_5 H_5)Fe(CO)](CNFe(CO)_2(\eta - C_5 H_5)](CNCH_3)]X 5$

### 3.7.1. Method a

[(C<sub>5</sub>H<sub>5</sub>)Fe(CO)(CN)(CNCH<sub>3</sub>)] (0.150 g, 0.69 mmol) [17] was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (15 cm<sup>3</sup>) and treated with stoichiometric amount of [Fp(THF)]BF<sub>4</sub> (0.232 g, 0.69 mmol). After stirring for 4 h, the solution was filtered on Celite and concentrated to ca. 3 cm<sup>3</sup>; addition of ether gave an yellow precipitate, which after washing with hexane and drying yielded complex 5 [(C<sub>5</sub>H<sub>5</sub>)Fe(CO){CNFe(CO)<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>)](CNCH<sub>3</sub>)]BF<sub>4</sub> (0.170 g, 45.5%). (Found: C, 40.72; H, 2.95; N, 5.15. C<sub>16</sub>H<sub>13</sub>BF<sub>4</sub>Fe<sub>2</sub>N<sub>2</sub>O<sub>3</sub> requires C, 40.39; H, 2.75; N, 5.05%). IR  $\nu_{max}$ /cm<sup>-1</sup>(CH<sub>2</sub>Cl<sub>2</sub>): 2206 m, 2149 w (CN), 2070 vs, 2025 vs, 2005 sh (CO). NMR  $\delta_{c}$ (CD<sub>3</sub>CN): 215.4 (FeCO), 211.2 (Fe(CO)<sub>2</sub>), 165.8 (CNFe), 151.4 br (CNCH<sub>3</sub>), 86.3 (C<sub>5</sub>H<sub>5</sub>), 83.7(C<sub>5</sub>H<sub>5</sub>), 30.3 (CH<sub>3</sub>).  $A_{\rm M}$  135 ohm<sup>-1</sup> cm<sup>2</sup> mole<sup>-1</sup> (acetone,  $10^{-3}$  M)

### 3.7.2. Method b

To a  $CH_2Cl_2$  solution (10 cm<sup>3</sup>) of compound 2,  $[(C_{3}H_{5})Fe(CO)(CN)(CNFe(CO)_{2}(C_{5}H_{5}))]$  (0.50 g, 0.13 mmol) was added an excess (0.5 mmol) of CH<sub>3</sub>OSO<sub>2</sub>CF<sub>3</sub>. After stirring for one hour at room temperature the yellow solution was evaporated under vacuum. The residue was dissolved in CH<sub>3</sub>CN and filtered on Florisil  $(2 \times 2 \text{ cm})$ . Evaporation of solvent gave a residue that crystallized from CH<sub>2</sub>Cl<sub>2</sub>/ether to  $[(C_5H_5)Fe(CO)]$ give 5  $(CNFe(CO)_2(C_5H_5))(CNCH_3)O_3SCF_3$  (0.022 g, 30%) as yellow microcrystalline powder, m.p. 139-140°C (decomp.). Found: C, 37.8; H, 2.3; N, 5.3.  $C_{17}H_{13}F_{3}Fe_{2}N_{2}O_{6}S$  requires C, 37.67; H, 2.42; N, 5.16.

# 3.8. Synthesis of $[(\eta - C_5 H_5)Fe(CO) - (CNW(CO)_5](CNCPh_3)] 6$

A THF solution (15  $cm^{3}$ ) of  $[(C_5H_5)Fe(CO)(CN)(CNCPh_3)]$  (0.150 g, 0.34 mmol) [17] was treated with W(CO)<sub>5</sub>(THF) (0.8 mmol) and stirred for 20 h. The solvent was then evaporated and the residue chromatographed on an alumina column  $(10 \times 2 \text{ cm})$  with petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> (4:1, v/v) as eluent to remove  $W(CO)_6$ . A fraction containing 6 was eluted with a mixture of petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> (1:1, v/v). Crystallization from CH<sub>2</sub>Cl<sub>2</sub>/hexane gave brown microcrystals of 6 (0.120 g, 46%); m.p. 157-160°C (decomp.). (Found: C, 50.2; H, 2.5; N, 3.7. C<sub>32</sub>H<sub>20</sub>FeN<sub>2</sub>O<sub>6</sub>W requires C, 50.03; H, 2.62; N, 3.64%). IR  $\nu_{max}/cm^{-1}(CH_2Cl_2)$ : 2164 m, 2135 w (CN), 2008 s (Fe-CO), 2070 w, 1925 vs, 1876 s (W-CO).

3.9. Synthesis of  $[(\eta - C_5 H_5)(CO)_2 FeCNFe(CO)_2(\eta - C_5 H_5)]BF_4$  7

To a THF solution (10 cm<sup>3</sup>) of FpCN (0.100 g, 0.49 mmol) was added an equimolar amount of [Fp(THF)]BF<sub>4</sub> (0.165 g, 0.49 mmol). The mixture was stirred for 48 h during which time a red-brown precipitate was formed. After filtration and washing with light petroleum ether, it was dried in vacuo to give 7 (0.090 g, 39%); m.p. 145–148°C (decomp.). The compound decomposes slowly in solution and cannot be recrystallyzed. NMR  $\delta$ H (CD<sub>3</sub>NO<sub>2</sub>) 5.26 (C<sub>5</sub>H<sub>5</sub>). IR  $\nu_{max}/cm^{-1}$  (CH<sub>2</sub>Cl<sub>2</sub>): 2166 m (CN), 2070 vs, 2028 vs (CO); (KBr): 2168 m (CN), 2062 vs, 2012 vs (CO).

# 3.10. Synthesis of $[(C_5H_5)(CO)_2 FeCNW(CO)_5]$ 8

A tetrahydrofurane solution  $(20 \text{ cm}^3)$  of FpCN (0.190 g, 0.93 mmol) was stirred for 20 h at room temperature

with two equivalents of W(CO)<sub>5</sub>(THF), previously obtained by photolysis of  $W(CO)_6$  in THF. The solvent was removed under reduced pressure and the residue, dissolved with CH<sub>2</sub>Cl<sub>2</sub>, was chromatographed on a alumina column  $(7 \times 2 \text{ cm})$  with petroleum ether as eluent After eluting  $W(CO)_6$ , a yellow-brown band was eluted with  $CH_2Cl_2$  to give the crude 8. A third yellow band contained unreacted FpCN. After evaporation of the solvent, the residual solid of the second fraction was crystallyzed from a CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether mixture at  $-20^{\circ}$ C to give a yellow-brown powder of 8, (0.079 g, 16%), m.p. 138-139°C (decomp.). (Found: C, 29.75; H, 0.98; N, 2.75. C<sub>13</sub>H<sub>5</sub>FeNO<sub>7</sub>W requires C, 29.63; H, 0.96; N, 2.66%) IR  $\nu_{max}/cm^{-1}$  (CH<sub>2</sub>Cl<sub>2</sub>): 2152 w (CN), 2073 m, 2024 m (Fe-CO), 2064 m, 1927 vs, 1881 s (W-CO). NMR  $\delta_{\rm H}$ (CDCl<sub>3</sub>): 5.19 (C<sub>5</sub>H<sub>5</sub>);  $\delta_{\rm C}({\rm CD}_2{\rm Cl}_2)$ : 210.1 (FeCO), 202.2 (WCOax), 198.8 (WCOeq), 133.1 (CN), 86.6 ( $C_5H_5$ ). UV  $\lambda_{max}/nm$ 

## 3.11. Synthesis of $[(\eta - C_5 H_5)(CO)_2 FeNCW(CO)_5]$ 9

 $(CH_3CN)$  334, 383( $\epsilon/dm^3$  mol<sup>-1</sup> cm<sup>-1</sup> 3300), 430(sh).

An equimolar amount of Na[W(CO)<sub>5</sub>(CN)] (0.491 g, 1.2 mmol) was added to an acetonitrile solution (40  $cm^3$ ) of  $[(C_5H_5)Fe(CO)_2(THF)]BF_4$  (0.450 g, 1.2 mmol), and the mixture was stirred for 4 h at  $-30^{\circ}$ C The solvent was then removed under vacuum and the residue, dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20 cm<sup>3</sup>), was filtered on Celite, concentrated to about 3 ml and applied to an alumina column (10  $\times$  2 cm). Elution with CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether (1:5, v/v) gave three fractions containing: (1)  $[Cp(CO)_2 Fe]_2$ , (2) the desidered product 9 and (3) small traces of FpCN. After evaporation of the solvent, the residue of the second fraction was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and layered with petroleum ether. On cooling to  $-20^{\circ}$ C red-orange crystals of 9 were obtained (0.330 g, 52%) m.p. 140-144°C (decomp.) (Found: C, 29.6: H, 0.93; N, 2.76. C<sub>13</sub>H<sub>5</sub>FeNO<sub>2</sub>W requires C, 29.63; H, 0.96; N, 2.66%). I.R.  $v_{max}/cm^{-1}$  (CH<sub>2</sub>Cl<sub>2</sub>): 2136 w (CN), 2061 m, 2026 m (Fe-CO), 2073 m, 1931 vs, 1900 sh (W-CO). NMR  $\delta_{\rm H}$  (CDCl<sub>3</sub>): 5.16 (C<sub>5</sub>H<sub>5</sub>);  $\delta_{\rm C}$  (CD<sub>2</sub>Cl<sub>2</sub>): 209.6 (FeCO), 198.4 (WCOax). 195.9 (WCOeq), 168.6 (CN), 85.0 (C<sub>5</sub>H<sub>5</sub>). UV  $\lambda_{max}$ /nm (CH<sub>3</sub>CN): 330, 359 ( $\epsilon$ /dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 3700), 380 (sh).

#### Acknowledgements

Financial support from MURST (Ministero dell'Università e della Ricerca Scientifica e Tecnologica), the CNR (Consiglio Nazionale delle Ricerche), and the University of Bologna (Project 'Sintesi, Modelli e Caratterizzazioni per Materiali Funzionali') is gratefully acknowledged.

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