

Synthesis and spectroscopic properties of heteropolynuclear cyano-bridged complexes

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Abstract

The heteropolynuclear cyano-bridged complexes $[(C_5H_5)Fe(CO)(CNMLn)(CNM'L'n)]$, $\{MLn = M'L'n = (C_5H_5)Fe(CO)_2 \text{ or } W(CO)_5; MLn = (C_5H_5)Fe(CO)_2, M'L'n = W(CO)_5\}$ 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 central iron atom of the type $[CpFe(CO)(CNMLn)_2]$ or $[CpFe(CO)(CNMLn)(CNM'L'n)]$, ($Cp = \eta^5-C_5H_5$). 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 isocyanide 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 stimulated 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 $[\text{CpFe}(\text{CO})_2(\text{CN})]$ has been obtained by reacting compound **1** with a stoichiometric amount of $(\text{Bu}_4\text{N})\text{CN}$. Complex **2** reacts with $[\text{Fp}(\text{THF})]\text{BF}_4$ to form **1** (Scheme 1).

The ^{13}C NMR spectrum of $[\text{CpFe}(\text{CO})(\text{CN})\{\text{CNFe}(\text{CO})_2\text{Cp}\}]$ **2**, in CD_3NO_2 , 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^{-1} , attributed to terminal cyanide in **2**, disappears in the IR spectrum of complex $[\text{CpFe}(\text{CO})\{\text{CNFe}(\text{CO})_2\text{Cp}\}_2]\text{BF}_4$ **1**. The $\nu(\text{CN})$ 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 cm^{-1} to higher wavenumbers in **1**.

The terminal cyanide ligand in complex **2** reacts with an excess of Lewis acid $\text{W}(\text{CO})_5(\text{THF})$ yielding $[\text{CpFe}(\text{CO})\{\text{CNFe}(\text{CO})_2\text{Cp}\}\{\text{CNW}(\text{CO})_5\}]$, **3**; its formulation is supported by the presence in the IR spectrum of two distinct bridging cyanide vibrations at 2141 and 2126 cm^{-1} , together with the characteristic band pattern of $\text{W}(\text{CO})_5$ fragment. The nature of complex **3** is also ascertained from the ^{13}C NMR data, showing two distinct signals at $\delta 171.4$ and 156.5 attributable respectively to the carbon atom of $\text{Fe}-\text{CN}-\text{Fe}$ and $\text{Fe}-\text{CN}-\text{W}$ bridges. It has been possible to assign the cyclopentadienyl signals ($\text{CN}-\text{Fe}-\text{C}_5\text{H}_5$, $\delta = 86.6$; $\text{NC}-\text{Fe}-\text{C}_5\text{H}_5$, $\delta = 82.8$) and to distinguish carbonyl resonances of tungsten from those of iron fragment [$\text{W}(\text{CO})_{\text{eq}} = 198.2 + ^{183}\text{W}$ satellites ($J = 135.4\text{ Hz}$); $\text{W}(\text{CO})_{\text{ax}} = 201.6$; $\text{Fe}(\text{CO})_2 = 211.7$ and $\text{Fe}(\text{CO}) = 218.7$] (Fig. 1).

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

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

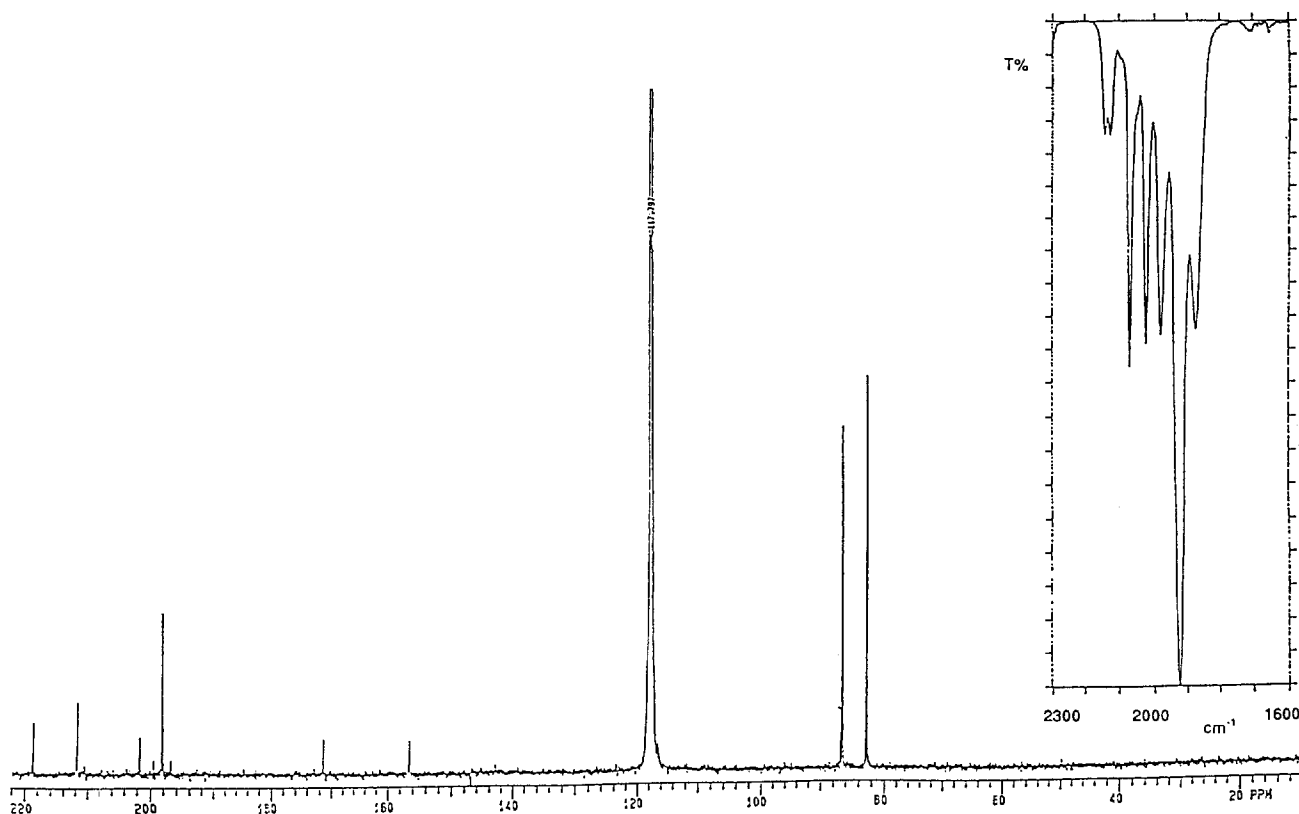
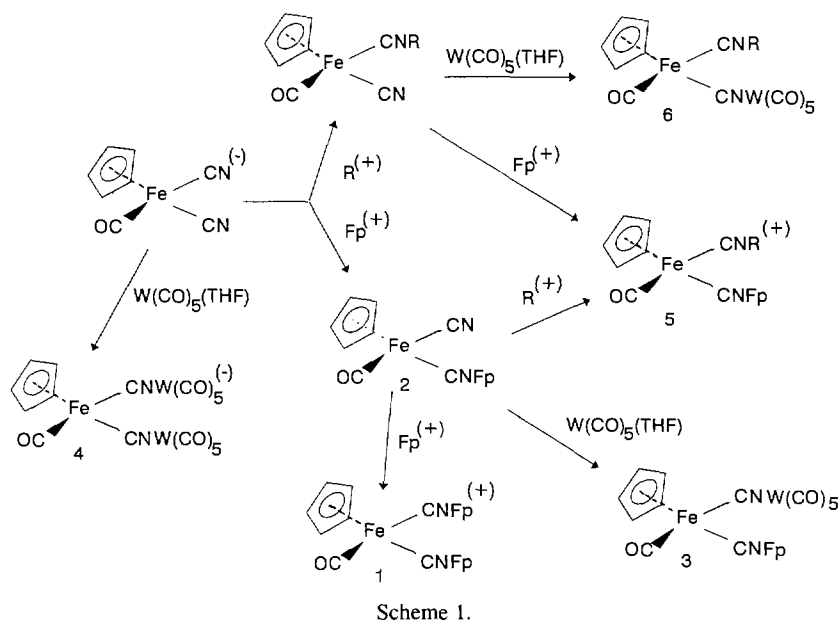


Fig. 1. IR(CH_2Cl_2) and ^{13}C NMR (CD_3CN) spectra of compound $[\text{CpFe}(\text{CO})\{\text{CNFe}(\text{CO})_2\text{Cp}\}\{\text{CNW}(\text{CO})_5\}]$, **3**.



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 $[\text{CpFe}(\text{CO})\{\text{CNFe}(\text{CO})_2\text{Cp}\}(\text{CNCH}_3)]^+$ **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 $[\text{CpFe}(\text{CO})(\text{CNCH}_3)(\text{CN})]$ with $[\text{CpFe}(\text{CO})_2(\text{THF})]\text{BF}_4$; b) N-alkylation of $[\text{CpFe}(\text{CO})(\text{CN})\{\text{CNFe}(\text{CO})_2\text{Cp}\}]$ **2** with $\text{MeOSO}_2\text{CF}_3$.

The stretching CN vibration of the CNMe ligand in **5** appears as a medium–strong band at 2206 cm^{-1} , whereas the CNFp band is weaker and at lower wavenumbers (2149 cm^{-1}). The ^{13}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 ^{13}C – ^{14}N spin coupling and to partial quadrupolar relaxation, is usually found in the isonitrile resonance of $[\text{CpFe}(\text{CO})(\text{CNR})\text{L}]^+$ complexes [15].

An interesting trend in the IR spectra is observed when varying the ligands of the Fe atom by substituting metal-isocyanides (CNFp or $\text{CNW}(\text{CO})_5$) with organic isocyanides (CNR) both in cationic $\{[\text{CpFe}(\text{CO})(\text{CNFp})_2]^+$ **1**, ($\nu(\text{CO}) = 1986\text{ cm}^{-1}$), $[\text{CpFe}(\text{CO})(\text{CNFp})(\text{CNCH}_3)]^+$ **5**, ($\nu(\text{CO}) = 2005\text{ cm}^{-1}$) and $[\text{CpFe}(\text{CO})(\text{CNCH}_3)(\text{CNC}_2\text{H}_5)]^+$ ($\nu(\text{CO}) = 2019\text{ cm}^{-1}$)[16] and in neutral derivatives

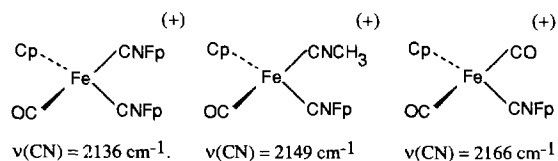
$\{[\text{CpFe}(\text{CO})\{\text{CNFe}(\text{CO})_2\text{Cp}\}\{\text{CNW}(\text{CO})_5\}]\}$ **3**, ($\nu(\text{CO}) = 1981\text{ cm}^{-1}$) and $[\text{CpFe}(\text{CO})\{\text{CNW}(\text{CO})_5\}(\text{CNCPh}_3)]$ **6**, ($\nu(\text{CO}) = 2008\text{ cm}^{-1}$). The shift of the $\nu(\text{CO})$ coordinated to the central iron atom seems to indicate that the σ/π ratio of the CNFp is higher than CNR.

Compound **6** has been obtained by reacting $[\text{CpFe}(\text{CO})(\text{CN})(\text{CNCPh}_3)]$ [17] with an excess of $[\text{W}(\text{CO})_5(\text{THF})]$.

Exploiting the ability of neutral cyanocomplexes to coordinate unsaturated metal fragments we have synthesized $[\text{Cp}(\text{CO})_2\text{FeCNFe}(\text{CO})_2\text{Cp}]^+$ **7**, by simple reaction between FpCN and Fp^+ . Compound **7** has been isolated as a microcrystalline solid, but its slow decomposition in solution has precluded a reliable ^{13}C NMR characterization. The complex **7** can be viewed as formally derived from **1** by replacing one CNFp ligand with the more π -acid CO ligand. The $\nu(\text{CN})$ absorption in the IR spectrum of **7**, in CH_2Cl_2 solution, is consequently shifted to higher wavenumbers, (2166 cm^{-1}), with respect to that of **1**, $[\text{CpFe}(\text{CO})\{\text{CNFe}(\text{CO})_2\text{Cp}\}_2]\text{BF}_4$ (2136 cm^{-1}). Likewise the $\nu(\text{CN})$ of compound **7**, in the solid, occurs about 100 cm^{-1} higher to the one showed by $[\text{Cp}(\text{dppe})\text{FeCNFe}(\text{dppe})\text{Cp}]^+$, (dppe = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) [11], according with the backbonding competition exercised by carbonyl ligands. Therefore, the variations of the $\nu(\text{CN})$ values of the cyanide bridge are related to the nature of the two coordinated metal fragments, reflecting their σ/π 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.

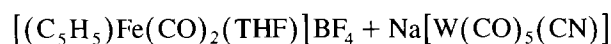
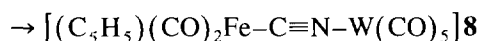
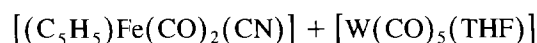
The poor π -acid character of the metalloisocyanide

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



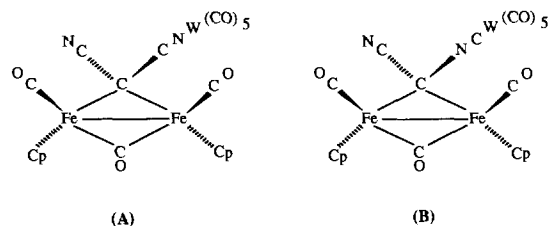
2.3. Isomeric –CN– or –NC– cyanobridged complexes

Few isomeric binuclear cyano-bridged complexes have been isolated. Vahrenkamp has recently synthesized the $[(\text{CO})_5\text{CrCNFe}(\text{dppe})\text{Cp}]$ 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 $[\text{CpFe}(\text{CO})_2(\text{CN})]$ and $[\text{W}(\text{CO})_5(\text{THF})]$ affords the $\mu\text{-CN}$ complex $[\text{Cp}(\text{CO})_2\text{FeCNW}(\text{CO})_5]$, **8**, in low yield. The $[\text{W}(\text{CO})_5(\text{CN})]^-$ anion reacts with $[\text{CpFe}(\text{CO})_2(\text{THF})]^+$ yielding the linkage isomer $[\text{Cp}(\text{CO})_2\text{FeNCW}(\text{CO})_5]$, **9**.



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

The IR frequency values of carbonyl absorptions in the $\text{W}(\text{CO})_5$ fragment are indicative of π -acidity of the ligand which this group is bound to. In particular, an increasing of stretch–stretch interaction constant of the two a_1 modes has been associated to the carbonyl replacement by ligands of lower π -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 $\text{W}(\text{CO})_5$ moieties in the nitrile (A) and isocyanide-like (B) compound can be

proposed by discussing the IR spectra of **8** and **9**. Analogously the absorption of the carbonyl of the $\text{W}(\text{CO})_5$ fragment sited trans to the N-coordinated cyanide group appears to be at lower wavenumbers [$\nu(\text{CO}) = 1881 \text{ cm}^{-1}$ in **8**] with respect to the axial carbonyl of the relative isomer [$\nu(\text{CO}) = 1900 \text{ cm}^{-1}$ in **9**]. Furthermore, the electron withdrawing effect of $\text{W}(\text{CO})_5$ fragment is responsible for the frequency values of bridged cyanide [$\nu(\text{CN}) = 2152 \text{ cm}^{-1}$ in **8**]. By contrast in complex **9** the W–C backdonation influence appears to be prevalent [$\nu(\text{CN}) = 2136 \text{ cm}^{-1}$].

The two isomers **8** and **9** are easily distinguishable from their $\mu\text{-CN}$ resonances in the ^{13}C NMR spectra, which are remarkably different: [$\delta\text{C}-\text{W}$, 168.6 in **9**; $\delta\text{C}-\text{Fe}$, 139.1 in **8**]. The $\text{W}(\text{CO})_5$ 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 σ/π ratio of L increases in $\text{M}(\text{CO})_5\text{L}$ complexes [22].

Recently the structure of $(\text{OC})_5\text{WCNW}(\text{CO})_5^-$ 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 $\text{M}-\text{C}\equiv\text{N}-\text{R}$, and the related ‘metallated isocyano’ complexes, $\text{M}-\text{C}\equiv\text{N}-\text{M}'\text{Ln}$, as well as between the nitrile $\text{M}-\text{N}\equiv\text{C}-\text{R}$, and metal–nitrile $\text{M}-\text{N}\equiv\text{C}-\text{M}'\text{Ln}$ 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 $\text{W}(\text{CO})_5\text{L}$: an higher energy one for $^1\text{A}_1 \rightarrow ^1\text{E}$ spin allowed transition, while the lowest one corresponds to a singlet–triplet $^1\text{A}_1 \rightarrow ^3\text{E}$ 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 $\text{C}\equiv\text{NFp}$ and $\text{N}\equiv\text{C}-\text{Fp}$ ligands in the spectrochemical series, being isocyanides π -acceptor while nitriles merely σ -donor ligands.

We have reacted compounds **8** and **9** with piperidine ($\text{C}_5\text{H}_{10}\text{NH}$) 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($\mu\text{-CN}$) bond in both the cases. Complex **8** affords FpCN and $[\text{W}(\text{CO})_5(\text{pip})]$, whereas the piperidinium salt of $[\text{W}(\text{CO})_5(\text{CN})]^-$ and the carbonyl dimer $[\text{Cp}(\text{CO})_2\text{Fe}]_2$ have been isolated by react-

ing complex **9**. Similar results were obtained from reaction of **9** with NaBH₄, that gives Na[W(CO)₅CN] and [Cp(CO)₂Fe]₂. The only example of hydride addition to a cyano-bridged complex reported so far, involved complexes of the type [CpL₂Ru(μ-CN)ML'₂Cp]⁺, [M = Ru or Fe; L₂, L'₂ = (PPh₃)₂, dppe], and led to formation of [CpL₂Ru(CN)] and [CpL'₂MH] [27]. An analogous mechanism can be invoked in our case: nucleophilic attack of the hydride on the carbon atom of the cyano bridge; subsequent β-elimination affords the W(CO)₅CN⁻ anion and FpH. The latter rapidly decomposes in solution to give the dicyclopentadienylcarbonyl 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; CH₂Cl₂ and CH₃CN were dried over CaH₂. Unless stated otherwise, all other reagent-grade chemicals were used as received. The compounds [(C₅H₅)Fe(CO)₂I] [28], [(C₅H₅)Fe(CO)₂CN] [29], K[(C₅H₅)Fe(CO)(CN)₂] [17] and Na[W(CO)₅(CN)] [13] were prepared by literature procedures. The compound [(C₅H₅)Fe(CO)₂(THF)]BF₄ has been obtained by reacting FpI with a stoichiometric amount of AgBF₄ in tetrahydrofurane solution. Infrared spectra were measured on a Perkin-Elmer 983 G spectrophotometer. ¹H and ¹³C NMR spectra were recorded on a Varian XL 200. Cr(acac)₃ 0.1 M was added to ¹³C 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 [(η-C₅H₅)Fe(CO)]{CNFe(CO)₂(η-C₅H₅)₂}BF₄ **1**

A tetrahydrofurane solution (20 cm³) of K[(C₅H₅)Fe(CO)(CN)₂] (0.223 g, 0.93 mmol), and [(C₅H₅)Fe(CO)₂(THF)]BF₄ (0.606 g, 1.8 mmol), was stirred for two hours at -20°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 CH₂Cl₂ and chromatographed on alumina column (8 × 2 cm). A red band containing some [Cp(CO)₂Fe]₂ was first eluted with a mixture of

petroleum ether/CH₂Cl₂ (1:1, v/v). CH₂Cl₂ then removed compound **1** which was recrystallized from CH₂Cl₂/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. C₂₂H₁₅BF₄Fe₃N₂O₅ requires C 41.17; H 2.36; N 4.37%). IR (CH₂Cl₂): ν_{max}/cm⁻¹ 2136 m (CN), 2069 vs, 2024 vs, 1986 s (CO). NMR: δ_H(CD₂Cl₂) 5.27(10H, s, C₅H₅), 4.64(5H, s, C₅H₅); δ_C(CD₃CN): 217.6 (FeCO), 211.1 (Fe(CO)₂), 170.2 (CN), 86.3 (C₅H₅), 82.6 (C₅H₅). Λ_M 120.6 ohm⁻¹. cm². mole⁻¹ (acetone, 10⁻³ M).

3.3. Synthesis of [(η-C₅H₅)Fe(CO)(CN)]{CNFe(CO)₂(η-C₅H₅)₂}

To a THF solution (10 cm³) of [(C₅H₅)Fe(CO)₂(THF)]BF₄ (0.808 g, 2.4 mmol), was added K[(C₅H₅)Fe(CO)(CN)₂] (0.540 g, 2.4 mmol), dissolved in the same solvent (50 cm³). The solution was stirred for two hours at -30°C and for other four hours at room temperature. After evaporation of the solvent, the residue was dissolved in CH₃CN, filtered through a Celite pad and chromatographed on Florisil (7 × 2 cm column), with ether/CH₃CN (1:1, v/v) as eluent. A red band of [Cp(CO)₂Fe]₂ followed by a yellow one containing some [CpFe(CO)₂(CN)] were eluted first. Addition of CH₃CN then removed compound **2** which was recrystallized from CH₃CN/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. C₁₅H₁₀Fe₂N₂O₃ requires C, 47.66; H, 2.67; N, 7.41%) IR ν_{max}/cm⁻¹ (CH₂Cl₂) 2134 m, 2095 m (CN), 2067 s, 2022 s, 1971 s (CO). NMR δ_H(CD₃NO₂): 5.47, 4.62 (C₅H₅); δ_C(CD₃NO₂): 215.8 (FeCO), 207.2 (Fe(CO)₂), 170.2 (CNFe), 166.3 (CN), 82.1, 78.2 (C₅H₅).

3.4. Reaction of **1** with (Bu₄N)CN

Complex **1**, (0.100 g, 0.16 mmol), dissolved in 10 cm³ of CH₃CN was reacted at room temperature for 4 h with a stoichiometric amount of (Bu₄N)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/CH₃CN (1:1, v/v) as eluent. A yellow band containing FpCN was first eluted. Addition of CH₃CN then removed complex **2**, [(C₅H₅)Fe(CO)(CN)]{CNFe(CO)₂(C₅H₅)₂}.

3.5. Synthesis of [(η-C₅H₅)Fe(CO)]{CNFe(CO)₂(η-C₅H₅)₂}[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)₅(THF),

obtained by photolysis of $W(CO)_6$ in THF. After 20 h stirring, the solvent was evaporated under vacuum and the yellow-brown residue was dissolved in CH_3CN , filtered on Celite and then chromatographed on Florisil (10×2 cm). $W(CO)_6$ was eluted first with petroleum ether followed by a band containing compound **3** by elution with CH_3CN . The solvent was stripped out and the residue crystallized from CH_2Cl_2 /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. $C_{20}H_{10}Fe_2N_2O_8W$ requires C, 33.96; H, 1.40; N, 4.26%). IR ν_{max}/cm^{-1} (CH_2Cl_2): 2141 w, 2126 w (CN), 2024 m, 1981 m (Fe–CO), 2068 m, 1923 vs, 1873 m (W–CO). NMR δ_H ($CDCl_3$) 5.17, 4.62 (C_5H_5); δ_C (CD_3CN) 218.7 (FeCO), 211.7 ($Fe(CO)_2$), 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^3) was treated with excess (5:1) of $W(CO)_5$ (THF) for 20 h. The solvent was evaporated under vacuum, the residue dissolved in CH_3CN and filtered on Celite. After evaporation of the solvent, the residue was chromatographed on Florisil (10×2 cm) with petroleum ether as eluent to remove $W(CO)_6$. Subsequent elution with CH_3CN 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 ν_{max}/cm^{-1} (CH_2Cl_2): 2121 w (CN), 1979 m (Fe–CO), 2070 w 1928 vs, 1874 m (W–CO). NMR δ_H ($CDCl_3$): 4.6 (C_5H_5). δ_C (CD_3CN): 219.0 (FeCO), 201.8 (WCOax), 198.2 (WCOeq), 156.9 (CN), 82.8 (C_5H_5). A_M 105.4 $\text{ohm}^{-1}\text{ cm}^2\text{ mole}^{-1}$ (acetone, 10^{-3} M)

3.7. Synthesis of $[(\eta-C_5H_5)Fe(CO)\{CNFe(CO)_2(\eta-C_5H_5)\}(CNCH_3)]X$ **5**

3.7.1. Method a

$[(C_5H_5)Fe(CO)(CN)(CNCH_3)]$ (0.150 g, 0.69 mmol) [17] was dissolved in CH_2Cl_2 (15 cm^3) and treated with stoichiometric amount of $[Fp(THF)]BF_4$ (0.232 g, 0.69 mmol). After stirring for 4 h, the solution was filtered on Celite and concentrated to ca. 3 cm^3 ; addition of ether gave a yellow precipitate, which after washing with hexane and drying yielded complex **5** $[(C_5H_5)Fe(CO)\{CNFe(CO)_2(C_5H_5)\}(CNCH_3)]BF_4$ (0.170 g, 45.5%). (Found: C, 40.72; H, 2.95; N, 5.15. $C_{16}H_{13}BF_4Fe_2N_2O_3$ requires C, 40.39; H, 2.75; N, 5.05%). IR ν_{max}/cm^{-1} (CH_2Cl_2): 2206 m, 2149 w (CN), 2070 vs, 2025 vs, 2005 sh (CO). NMR δ_C (CD_3CN): 215.4 (FeCO), 211.2 ($Fe(CO)_2$), 165.8

(CNFe), 151.4 br ($CNCH_3$), 86.3 (C_5H_5), 83.7 (C_5H_5), 30.3 (CH_3). A_M 135 $\text{ohm}^{-1}\text{ cm}^2\text{ mole}^{-1}$ (acetone, 10^{-3} M)

3.7.2. Method b

To a CH_2Cl_2 solution (10 cm^3) of compound **2**, $[(C_5H_5)Fe(CO)(CN)\{CNFe(CO)_2(C_5H_5)\}]$ (0.50 g, 0.13 mmol) was added an excess (0.5 mmol) of $CH_3OSO_2CF_3$. After stirring for one hour at room temperature the yellow solution was evaporated under vacuum. The residue was dissolved in CH_3CN and filtered on Florisil (2×2 cm). Evaporation of solvent gave a residue that crystallized from CH_2Cl_2 /ether to give **5** $[(C_5H_5)Fe(CO)\{CNFe(CO)_2(C_5H_5)\}(CNCH_3)]O_3SCF_3$ (0.022 g, 30%) as yellow microcrystalline powder, m.p. 139–140°C (decomp.). Found: C, 37.8; H, 2.3; N, 5.3. $C_{17}H_{13}F_3Fe_2N_2O_6S$ requires C, 37.67; H, 2.42; N, 5.16.

3.8. Synthesis of $[(\eta-C_5H_5)Fe(CO)\{CNW(CO)_5\}(CNCPh_3)]$ **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 $W(CO)_5$ (THF) (0.8 mmol) and stirred for 20 h. The solvent was then evaporated and the residue chromatographed on an alumina column (10×2 cm) with petroleum ether/ CH_2Cl_2 (4:1, v/v) as eluent to remove $W(CO)_6$. A fraction containing **6** was eluted with a mixture of petroleum ether/ CH_2Cl_2 (1:1, v/v). Crystallization from CH_2Cl_2 /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. $C_{32}H_{20}FeN_2O_6W$ requires C, 50.03; H, 2.62; N, 3.64%). IR ν_{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 $[(\eta-C_5H_5)(CO)_2FeCNFe(CO)_2(\eta-C_5H_5)]BF_4$ **7**

To a THF solution (10 cm^3) of $FpCN$ (0.100 g, 0.49 mmol) was added an equimolar amount of $[Fp(THF)]BF_4$ (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 recrystallized. NMR δ_H (CD_3NO_2) 5.26 (C_5H_5). IR ν_{max}/cm^{-1} (CH_2Cl_2): 2166 m (CN), 2070 vs, 2028 vs (CO); (KBr): 2168 m (CN), 2062 vs, 2012 vs (CO).

3.10. Synthesis of $[(C_5H_5)(CO)_2FeCNW(CO)_5]$ **8**

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

with two equivalents of $W(CO)_5(THF)$, previously obtained by photolysis of $W(CO)_6$ in THF. The solvent was removed under reduced pressure and the residue, dissolved with CH_2Cl_2 , was chromatographed on a alumina column (7×2 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 crystallized from a CH_2Cl_2 /petroleum ether mixture at $-20^\circ C$ to give a yellow-brown powder of **8**, (0.079 g, 16%), m.p. $138-139^\circ C$ (decomp.). (Found: C, 29.75; H, 0.98; N, 2.75. $C_{13}H_5FeNO_7W$ requires C, 29.63; H, 0.96; N, 2.66%) IR ν_{max}/cm^{-1} (CH_2Cl_2): 2152 w (CN), 2073 m, 2024 m (Fe–CO), 2064 m, 1927 vs, 1881 s (W–CO). NMR $\delta_H(CDCl_3)$: 5.19 (C_5H_5); $\delta_C(CD_2Cl_2)$: 210.1 (FeCO), 202.2 (WCOax), 198.8 (WCOeq), 133.1 (CN), 86.6 (C_5H_5). UV λ_{max}/nm (CH_3CN) 334, 383 ($\epsilon/dm^3 mol^{-1} cm^{-1}$ 3300), 430(sh).

3.11. Synthesis of $[(\eta-C_5H_5)(CO)_2FeNCW(CO)_5] \mathbf{9}$

An equimolar amount of $Na[W(CO)_5(CN)]$ (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_2Cl_2 ($20 cm^3$), was filtered on Celite, concentrated to about 3 ml and applied to an alumina column (10×2 cm). Elution with CH_2Cl_2 /petroleum ether (1:5, v/v) gave three fractions containing: (1) $[Cp(CO)_2Fe]_2$, (2) the desired product **9** and (3) small traces of $FpCN$. After evaporation of the solvent, the residue of the second fraction was dissolved in CH_2Cl_2 and layered with petroleum ether. On cooling to $-20^\circ C$ red-orange crystals of **9** were obtained (0.330 g, 52%) m.p. $140-144^\circ C$ (decomp.) (Found: C, 29.6; H, 0.93; N, 2.76. $C_{13}H_5FeNO_7W$ requires C, 29.63; H, 0.96; N, 2.66%). I.R. ν_{max}/cm^{-1} (CH_2Cl_2): 2136 w (CN), 2061 m, 2026 m (Fe–CO), 2073 m, 1931 vs, 1900 sh (W–CO). NMR $\delta_H(CDCl_3)$: 5.16 (C_5H_5); $\delta_C(CD_2Cl_2)$: 209.6 (FeCO), 198.4 (WCOax), 195.9 (WCOeq), 168.6 (CN), 85.0 (C_5H_5). UV λ_{max}/nm (CH_3CN): 330, 359 ($\epsilon/dm^3 mol^{-1} cm^{-1}$ 3700), 380 (sh).

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