Coordinating properties of [M(CO)$_5$(CN)]$^-$ [M = Cr; Mo; W] ligands: formation of ion pairs or dinuclear cyanide-bridged complexes, spectroscopic and X-ray diffraction studies

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Abstract

The reaction of sodium cyanopentacarbonylmetalates Na[M(CO)$_5$(CN)] (M = Cr; Mo; W) with cationic Fe(II) complexes [Cp(CO)(L)Fe(thf)][O$_3$SCF$_3$], [L = PPh$_3$ (**1a**), CN-Benzyl (**1b**), CN-2,6-Me$_2$C$_6$H$_3$ (**1c**); CN-Bu^t (**1d**), P(OMe)$_3$ (**1e**), P(Me)$_2$Ph (**1f**)] in acetonitrile solution, yielded the metathesis products [Cp(CO)(L)Fe(NCCH$_3$)][NCM(CO)$_5$] [M = **W**, L = PPh$_3$ (**2a**), CN-Benzyl (**2b**), CN-2,6-Me$_2$C$_6$H$_3$ (**2c**); CN-Bu^t (**2d**), P(OMe)$_3$ (**2e**), P(Me)$_2$Ph (**2f**); M = **Cr**, L = (PPh$_3$) (**3a**), CN-2,6-Me$_2$C$_6$H$_3$ (**3c**); M = **Mo**, L = (PPh$_3$) (**4a**), CN-2,6-Me$_2$C$_6$H$_3$ (**4c**)]. The ionic nature of such complexes was suggested by conductivity measurements and their main structural features were determined by X-ray diffraction studies. Well-resolved signals relative to the [M(CO)$_5$(CN)] moieties could be distinguished only when ^{13}C NMR experiments were performed at low temperature (from −30 to −50 °C), as in the case of [Cp(CO)(PPh$_3$)Fe(NCCH$_3$)][NCW(CO)$_5$] (**2a**) and [Cp(CO)(Benzyl-NC)Fe(NCCH$_3$)][NCW(CO)$_5$] (**2b**). When the same reaction was carried out in dichloromethane solution, neutral cyanide-bridged dinuclear complexes [Cp(CO)(L)FeNCM(CO)$_5$] [M = **W**, L = PPh$_3$ (**5a**), CN-Benzyl (**5b**); M = **Cr**, L = (PPh$_3$) (**6a**), CN-2,6-Me$_2$C$_6$H$_3$ (**6c**), CO (**6g**); M = **Mo**, L = CN-2,6-Me$_2$C$_6$H$_3$ (**7c**), CO (**7g**)] were obtained and characterized by infrared and NMR spectroscopy. In all cases, the room temperature ^{13}C NMR measurements showed no broadening of cyano pentacarbonyl signals and, relative to tungsten complexes [Cp(CO)(PPh$_3$)FeNCW(CO)$_5$] (**5a**) and [Cp(CO)(CN-Benzyl)FeNCW(CO)$_5$] (**5b**), the presence of ^{183}W satellites of the ^{13}CN resonances ($J_{CW} \sim 95$ Hz) at room temperature confirmed the formation of stable neutral species. The main ^{13}C NMR spectroscopic properties of the latter compounds were compared to those of the linkage isomers [Cp(CO)(PPh$_3$)FeCNW(CO)$_5$] (**8a**) and [Cp(CO)(CN-Benzyl)FeCNW(CO)$_5$] (**8b**). The characterization of the isomeric couples **5a–8a** and **5b–8b** was completed by the analyses of their main IR spectroscopic properties. The crystal structures determined for **2a**, **5a**, **8a** and **8b** allowed to investigate the geometrical and electronic differences between such complexes. Finally, the study was completed by extended Hückel calculations of the charge distribution among the relevant atoms for complexes **2a**, **5a** and **8a**.
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Keywords: Saline compounds; Dinuclear complexes; Cyanide-bridges; IR and NMR spectroscopy; X-ray diffractometry; Theoretical studies

1. Introduction

It is well known that the cyanide ligand in cyano metal complexes reacts with a variety of electrophilic agents. By this method, using suitable alkylating agents, it has been possible to prepare complexes containing functionalized isocyanide ligands, M–C≡NX [X = H, R, R$_3$M′ (M′ = Si, Ge, Sn), PR$_2$] [1a–1f]. The cyanide ligand basicities have been recently determined by Angelici and co-workers [2] in a series of Cp(L)$_2$MCN complexes, (M = Ru, Fe). Typically, the reaction with electrophilic inorganic or organometallic substrates allows the synthesis of dinuclear complexes in which the cyanide ligand is end-on coordinated to two metal atoms, LnM–CN–M′Ln [3a–3k,9a–9c]. Furthermore, the

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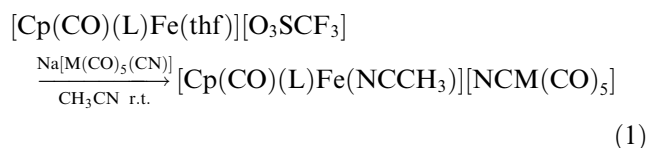*E-mail address:* palazzi@ms.fci.unibo.it (A. Palazzi).

ambidentate character of the cyanide ligand plays a key role in the synthesis of infinite chain-like complexes [4a–4f]. Over the past two decades, di- or polymetallic cyanide-bridged systems have received massive attention in connection with the peculiar properties of the cyanide bridging unit [5a–5k]. Indeed, the CN bridge ability to act as an efficient charge transfer mediator made this class of compounds potentially useful for designing optical and electronic devices based on the asymmetry of the cyanide linker [6a,6b]. Moreover, studies about the presence of magnetic exchange interaction through a bridging CN ligand have shown that transition metal cyanides might represent good candidates for molecule-based magnetic materials [7a–7e]. With the aim of exploiting the spectroscopic properties of organometallic fragments coordinated either to the nitrogen or the carbon extremity of the bridging cyanide unit, we reported a series of di- and trinuclear organometallic cyano-bridged complexes of iron [8]. Among plenty of suitable building blocks, cyanopentacarbonylmetalates such as $[M(CO)_5(CN)]^-$ (M = Cr; Mo; W) represent some of the most widely employed in the synthesis of cyanide-bridged arrays. In the first part of this paper, we report the study of their reactions with cationic Fe(II)-organometallic fragments to achieve the formation either of saline compounds $[Cp(CO)(L)Fe(NCCH_3)][NCM(CO)_5]$ or dinuclear cyano-bridged complexes $[Cp(CO)(L)FeNCM(CO)_5]$. The main spectroscopic and structural features of the obtained products are compared to those of the isomeric complexes $[Cp(CO)(L)FeCNM(CO)_5]$, in which the electronic properties of the iron atom are modulated by ligands with different σ/π bonding abilities. A series of analogous compounds has been reported by Vahrenkamp and co-workers [9a,9b,9c], who has largely contributed to the elucidation of the factors determining the extent of electronic interaction between remote metal centers in cyanide-bridged arrays of redox-active transition metal ions [10a–10d].

2. Results and discussion

2.1. Ion pairs

As an initial attempt to synthesize [LnFe–NC–M(CO)_5] type complexes, we reacted the cationic precursors $[CpFe(CO)(L)(thf)][O_3SCF_3]$, [L = PPh$_3$ (**1a**), CN-Benzyl (**1b**), CN-2,6-Me$_2$C$_6$H$_3$ (**1c**); CN-Bu^t (**1d**), P(OMe)$_3$ (**1e**), P(Me)$_2$Ph (**1f**)] with cyano-pentacarbonyl anions such as $[M(CO)_5(CN)]^-$, (M = Cr, Mo, W) in acetonitrile medium. Even though the analysis of IR spectroscopic data might suggest the formation of the expected neutral species, the NMR characterization of the product complexes allowed to establish the presence of coordinated acetonitrile ($\delta_H = 2.0$ ppm; $\delta_C = 5.2$ and

135.9 ppm; CDCl$_3$ as solvent). In addition, conductivity measurements showed values typical of uni-univalent electrolytes, suggesting the formation of ion pairs such as $[Cp(CO)(L)Fe(NCCH_3)][NCM(CO)_5]$, [M = W, L = PPh$_3$ (**2a**), CN-Benzyl (**2b**), CN-2,6-Me$_2$C$_6$H$_3$ (**2c**); CN-Bu^t (**2d**), P(OMe)$_3$ (**2e**), P(Me)$_2$Ph (**2f**); M = Cr, L = (PPh$_3$) (**3a**), CN-2,6-Me$_2$C$_6$H$_3$ (**3c**); M = Mo, L = (PPh$_3$) (**4a**), CN-2,6-Me$_2$C$_6$H$_3$ (**4c**)]

$$[Cp(CO)(L)Fe(thf)][O_3SCF_3]$$
$$\xrightarrow[\text{CH}_3\text{CN r.t.}]{\text{Na}[M(CO)_5(CN)]} [Cp(CO)(L)Fe(NCCH_3)][NCM(CO)_5]$$
(1)

The ^{13}C NMR analyses of the latter complexes showed a temperature-dependent behaviour and well-resolved patterns of the cyanopentacarbonyl anions could be observed only between −30 and −50 °C, as in the case of [Cp(CO)(PPh$_3$)Fe(NCCH$_3$)][NCW(CO)$_5$](**2a**) (Fig. 1) and [Cp(CO)(CN-Benzyl)Fe(NCCH$_3$)][NCW(CO)$_5$] (**2b**).

An analogous effect has been described by Darensbourg et al. [11] for the cyanide-bridged dinuclear compound [(PPh$_3$)$_3$CuNCW(CO)$_5$]. In that case, one of the proposed mechanisms which could account for the observed line broadening consisted in the rapid exchange reaction involving the insertion of a solvent molecule in the bridging unit. In our complexes, coordinated acetonitrile was detected at every temperature, confirming the presence of stable ion pairs in solution. In addition, the low temperature ^{13}C NMR spectra of complexes **2a** and **2b** showed shifts values (δ_CWCN ca. 140 ppm) in agreement with those of uncoordinated $[W(CO)_5(CN)]^-$ anion [12]. From a different viewpoint, the observed line broadening effect might be attributed to some carbonyl scrambling. On the other hand, it is worth noting that many mononuclear systems of type $[M(CO)_5L]$ are reported to be stereochemically rigid at room temperature, as inferred by stabilization energy considerations [13a,13b]. At the same time, carbonyl rearrangements in $[M(CO)_5L]$ (M = Cr, Mo, W) derivatives have already been documented and rate constants for *cis*-to-*trans* equilibration in $[M(CO)_4(^{13}CO)PR_3]$ (M = Cr, W) were measured, suggesting intramolecular CO ligand rearrangements [14]. Nondissociative intramolecular isomerization has also been proposed by Dombeck and Angelici [15] for the conversion of *trans*-$[W(CO)_4(^{13}CO)(CS)]$ to the corresponding *cis*-isomer. In our complexes, the cyanocarbonyl counterions $[M(CO)_5(CN)]^-$, whichever metal is employed, exhibit fluxional behavior at room temperature.

2.2. $[Cp(CO)(L)FeNCM(CO)_5]$ complexes (M = Cr, Mo, W)

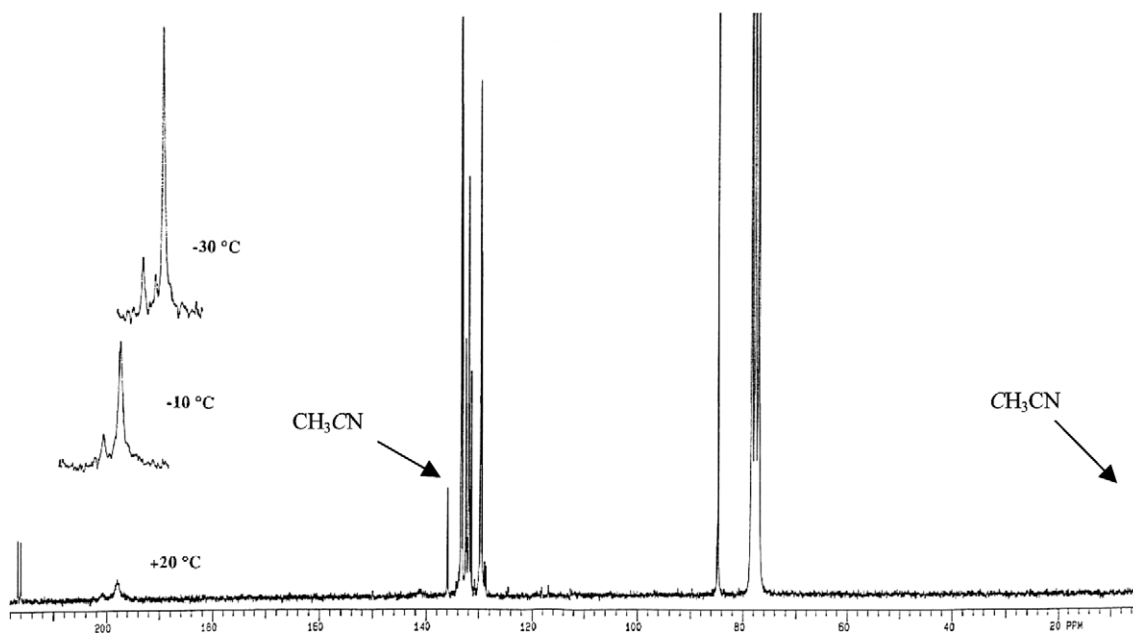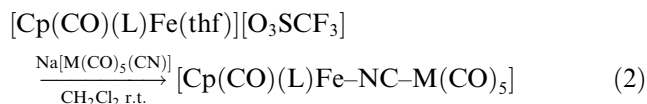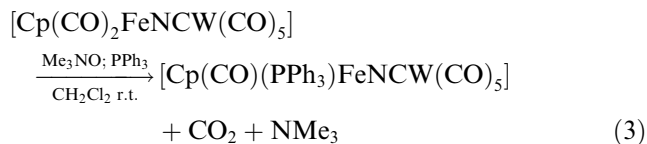The exclusive formation of saline species $[Cp(CO)(L)Fe(NCCH_3)][M(CO)_5(CN)]$ in place of

Fig. 1. Variable temperature ^{13}C NMR spectra of [Cp(CO)(PPh$_3$)Fe(NCCH$_3$)][NCW(CO)$_5$] (**2a**).

[CpFe(CO)(L)NCM(CO)$_5$] is probably due to a mass effect of acetonitrile as solvent or eluant in the purification process. Thus, in order to obtain the target dinuclear compounds, a less coordinating solvent was considered. In particular, the reaction of the cationic precursors [Cp(CO)(L)Fe(thf)][O$_3$SCF$_3$], [L = PPh$_3$ (**1a**), CN-Benzyl (**1b**), CN-2,6-Me$_2$C$_6$H$_3$ (**1c**); CO (**1g**)] with the appropriate amount of Na[M(CO)$_5$(CN)] (M = Cr, Mo, W) in dichloromethane solution afforded the expected neutral cyano-bridged dinuclear complexes [Cp(CO)(L)FeNCM(CO)$_5$] [M = W, L = PPh$_3$ (**5a**), CN-Benzyl (**5b**); M = Cr, L = (PPh$_3$) (**6a**), CN-2,6-Me$_2$C$_6$H$_3$ (**6c**), CO (**6g**); M = Mo, L = CN-2,6-Me$_2$C$_6$H$_3$ (**7c**), CO (**7g**)]

[Cp(CO)(L)Fe(thf)][O$_3$SCF$_3$]

$$\xrightarrow[\text{CH}_2\text{Cl}_2 \text{ r.t.}]{\text{Na[M(CO)}_5\text{(CN)]}} [\text{Cp(CO)(L)Fe–NC–M(CO)}_5] \qquad (2)$$

In a different approach, a dinuclear cyano bridged complex such as [Cp(CO)(PPh$_3$)FeNCW(CO)$_5$] (**5a**) could be obtained from its carbonyl precursor [Cp(CO)$_2$FeNCW(CO)$_5$] (**5g**) by the well-established procedure involving addition of triphenylphosphine in the presence of trimethylamine *N*-oxide

[Cp(CO)$_2$FeNCW(CO)$_5$]

$$\xrightarrow[\text{CH}_2\text{Cl}_2 \text{ r.t.}]{\text{Me}_3\text{NO; PPh}_3} [\text{Cp(CO)(PPh}_3\text{)FeNCW(CO)}_5]$$
$$+ \text{CO}_2 + \text{NMe}_3 \qquad (3)$$

All the neutral complexes were purified by column chromatography by using dichloromethane as eluant. Our results suggest that the basic properties of the

nitrogen lone pairs in the metallacyanide [16a,16b] are weak and favourable to coordination only in the absence of competitive bases. Further evidence of such solvent-dependent behaviour is that, when the saline compound [Cp(CO)(PPh$_3$)Fe(NCCH$_3$)][NCW(CO)$_5$] (**2a**) was refluxed in toluene for 2 h, the IR spectrum showed the carbonyl bands of the cyanide-bridged complex [Cp(CO)(PPh$_3$)FeNCW(CO)$_5$] (**5a**). The pattern of IR stretchings for the neutral cyanide-bridged compounds **5–7** is very similar to that of the corresponding saline derivatives **2–4** (Fig. 2).

The observed wavenumbers, as expected, are shifted to lower values for the iron-coordinated carbonyl and to higher wavenumber for the CN group ($\cong$30 cm^{-1}). This frequency increase has been associated with a kinematic coupling effect, i.e., a constraint of the motion of the bridging CN due to its coordination to the second metal center [17]. Actually, the factors affecting the stretching frequency of bridging cyanides are more complicated and the back-bonding from the C-bonded and the N-bonded metal atoms should also be considered. As these three factors operate in opposition but concomitantly, the magnitude and direction of the frequencies shift depend on their relative importance [18]. In light of these considerations, the increasing of the σ/π bonding ratio of the ligand L at the iron atom (L = CO, [8] CNR, PR$_3$) resulted not only in the expected decrease of the carbonyl vibration but also in a minor but significant decrease of the CN stretching wavenumber (i.e., 2136 cm^{-1} in [Cp(CO)$_2$FeNCW(CO)$_5$] [8] versus 2127 cm^{-1} in [Cp(CO)(PPh$_3$)FeNCW(CO)$_5$] (**5a**)). All the [LnFe–NC–M(CO)$_5$]-type compounds have been characterized
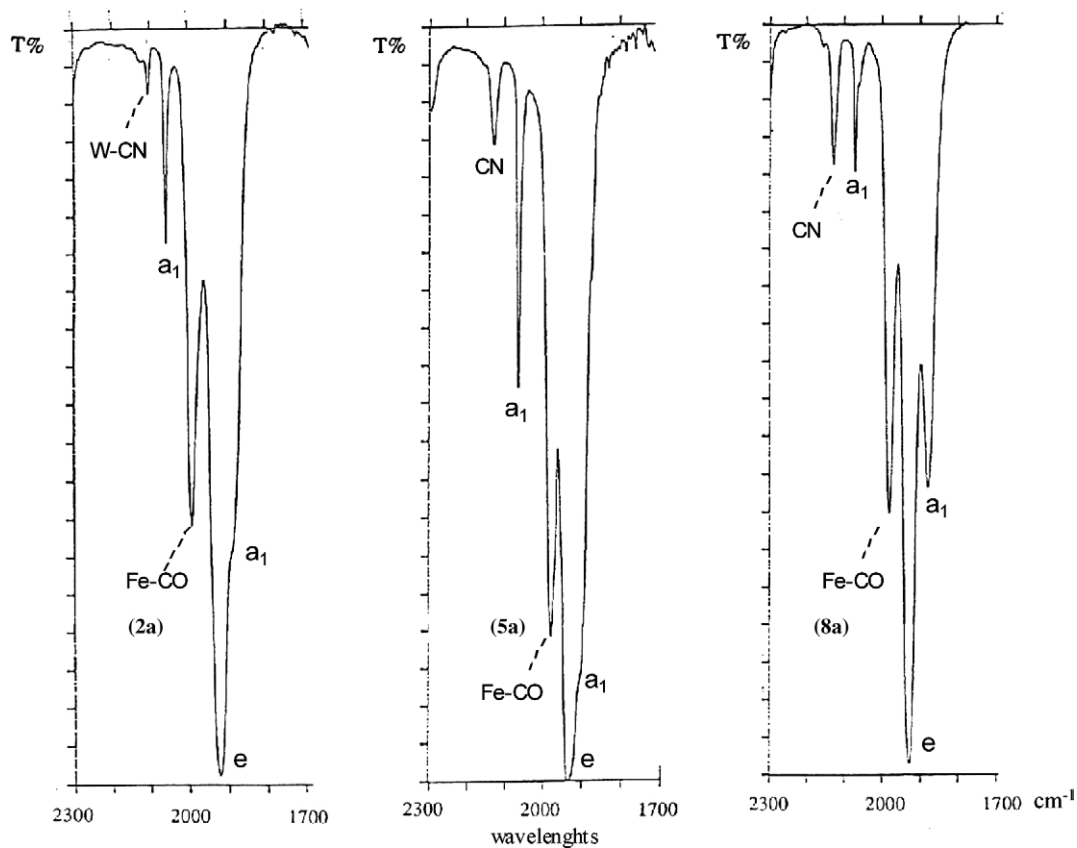
Fig. 2. IR spectra of [Cp(CO)(PPh$_3$)Fe(NCCH$_3$)][NCW(CO)$_5$] (**2a**); [Cp(CO)(PPh$_3$)FeNCW(CO)$_5$] (**5a**) and [Cp(CO)(PPh$_3$)FeCNW(CO)$_5$] (**8a**).

by spectroscopic methods (IR, ^{1}H and ^{13}C NMR) and no significant difference has been observed in the Fe moieties on going from Cr, Mo, to W derivatives. The most important feature of the ^{13}C NMR spectra of all the neutral cyano-bridged complexes **5–7** is given by the presence, at room temperature, of well-resolved resonances attributed to M(CO)$_5$CN moiety (Fig. 3), being

the anchorage of the M(CO)$_5$CN group to iron a key factor to prevent easy CO scrambling. Moreover, in [Cp(CO)(CN-Benzyl)FeNCW(CO)$_5$] (**5b**), it has been possible to distinguish the resonances of the isocyanide from the cyanide bridging ligand, showing the latter a typical pattern due to coupling with ^{183}W (see further on).
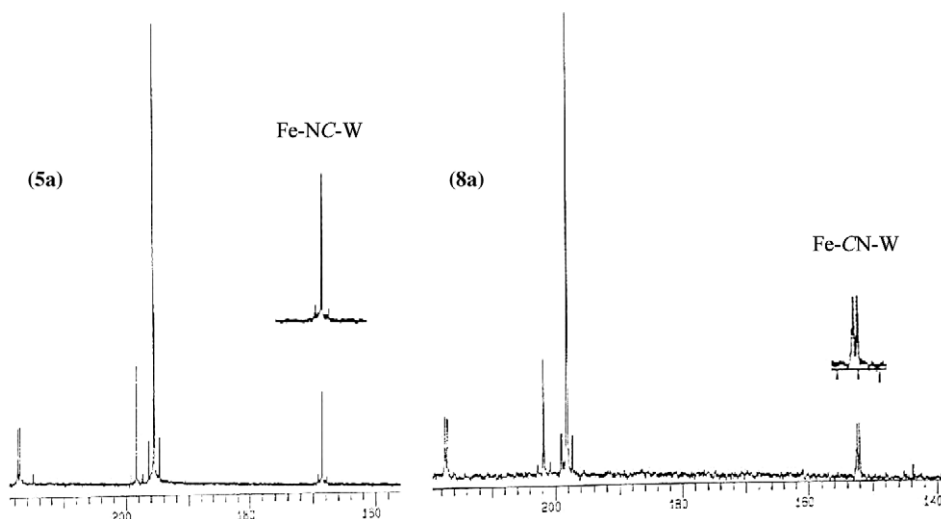

Fig. 3. Selected ^{13}C NMR signals for [Cp(CO)(PPh$_3$)Fe–NC–W(CO)$_5$] (**5a**) and [Cp(CO)(PPh$_3$)Fe–CN–W(CO)$_5$] (**8a**).

2.3. [Cp(CO)(L)FeCNM(CO)₅] complexes (M = Cr, W)

The synthesis of the isomeric compounds [Cp(CO)(L)FeCNM(CO)$_5$] [M = W, L = PPh$_3$ (**8a**), CN-Benzyl (**8b**); M = Cr, L = (PPh$_3$) (**9a**), CN-2,6-Me$_2$C$_6$H$_3$ (**9c**)], required the previous preparation of precursor complexes [Cp(CO)(L)FeCN] (L = PPh$_3$, CN-Benzyl, CN-2,6-Me$_2$C$_6$H$_3$), which were obtained by addition of the stoichiometric amount of the desired ligand L to a refluxing solution of [Cp(CO)$_2$FeCN] in toluene and in the presence of a catalytic quantity of [Fe$_2$(μ-CO)$_2$(CO)$_2$(Cp)$_2$]. Thus, the reaction of precursors [CpFe(CO)(L)CN] with a slight excess of [M(CO)$_5$(thf)] (M = Cr, W) in tetrahydrofuran solution afforded the target complexes **8a,b** and **9a,c** in acceptable yields (ca. 50%), while the synthesis of dinuclear compounds with the Mo(CO)$_5$ unit proved unsuccessful

$$[Cp(CO)(L)Fe(CN)]$$

$$\xrightarrow[\text{thf r.t.}]{[M(CO)_5\text{thf}]} [Cp(CO)(L)FeCNM(CO)_5] \qquad (4)$$
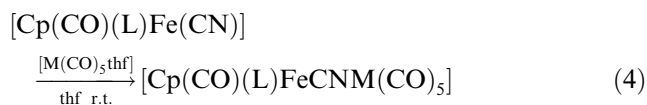
A comparison of the spectroscopic IR and NMR features of **8a,b** and **9a,c** with those of the linkage isomers **5a,b** and **6a,c**, allow the following considerations:

(i) The Δv between the two **a$_1$** absorptions of the M(CO)$_5$ fragments is always larger in [LnFeCNM(CO)$_5$] complexes **8a,b** and **9a,c**. In particular, while the **a$_1$** stretching absorption of the axial CO is always well observable for the latter compounds, it appears as a shoulder of the intense **e** absorption in the related isomers [LnFeNCM(CO)$_5$] (**5a,b**) (see Fig. 2) and **6a,c**. This feature might be explained in terms of lower π-backdonation from the N-end of the bridging cyanide [19a,19b,19c]. It follows that the presence of a well-de-fined **a$_1$** absorption, attributable to the axial carbonyl, is diagnostic of the –CNM(CO)$_5$ bonding mode. The IR evidences are in good agreement with the geometric features observed in the X-ray molecular structures of **5a** and **8a** (see next section).

(ii) Ligand substitution in the iron fragment does not appreciably influence the carbonyl stretchings in the M(CO)$_5$ moieties.

(iii) The ^{13}C NMR resonance of the bridging CN, which is increasingly shielded in the order Cr, Mo, W, in [Cp(CO)(L)Fe–NC–M(CO)$_5$] complexes, is always found at lower field (i.e., 168.6 ppm. in complex **5a**) with respect to the corresponding isomers [Cp(CO)(L)Fe–CN–M(CO)$_5$] (i.e., 152.3 ppm in **8a**). A further distinction between the Fe–NC–M and Fe–CN–M isomers is provided by the coupling of the bridging cyanide carbon with phosphine ligands ($^2J_{CP}$ ca. 30 Hz) in complexes **8a** (M = W; L = PPh$_3$) and **9a** (M = Cr; L = PPh$_3$), which allows the unambiguous assignment of the cyanide carbon bonded to iron. On the other hand, the presence of ^{183}W satellites is diagnostic of the Fe–NC–W bonding mode, as in the case of **5a** and **5b** ($^1J_{CW}$ ca. 95 Hz; see Fig. 3).

Furthermore, as we already reported for some related compounds [8], the typical broadness of the isocyanide resonance [20] in the isonitrile complexes **5b**, **8b**, (M = W; L = CN-Benzyl) and **9c** (M = Cr; L = CN-2,6-Me$_2$C$_6$H$_3$) makes this signal clearly distinguishable from the one of the bridging cyanide (Fig. 4).

(iv) The ^{13}C NMR signals of the W(CO)$_5$ groups in [Cp(CO)(PPh$_3$)Fe–NC–W(CO)$_5$] **5a** and [Cp(CO)(CN-Benzyl)Fe–NC–W(CO)$_5$] **5b** are upfield shifted with respect to those of the related isomers [Cp(CO)(L)Fe–CN–W(CO)$_5$] **8a** (L = PPh$_3$) and (L = Benzyl-NC) **8b** and exhibit (Fig. 4) a narrower separation (Δ_{CO} =
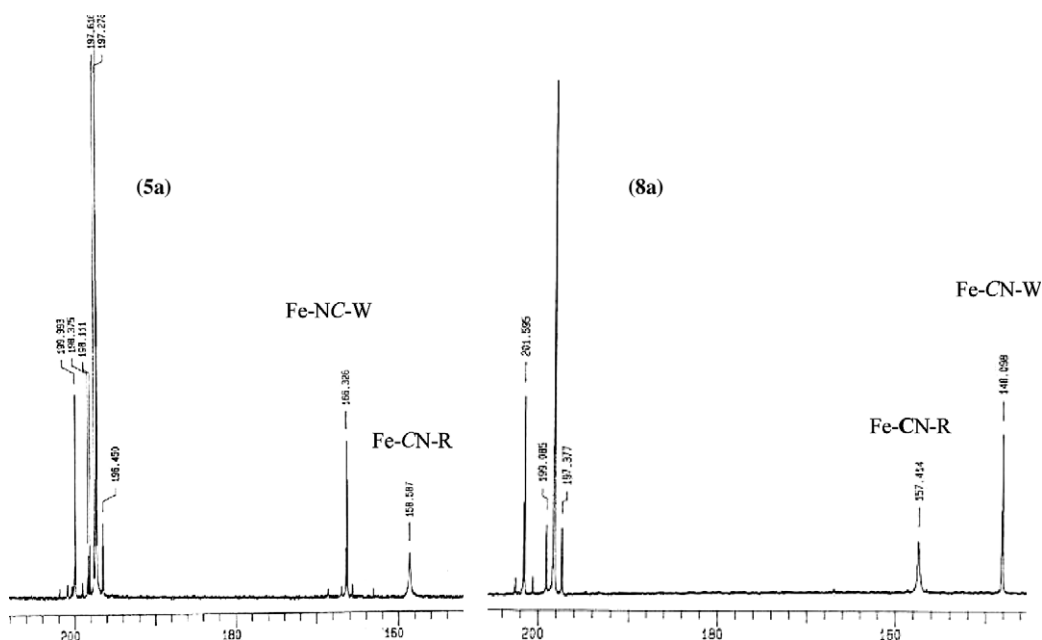

Fig. 4. Selected ^{13}C NMR signals for [Cp(CO)(CN-Benzyl)Fe–NC–W(CO)$_5$] (**5b**) and [Cp(CO)(CN-Benzyl)Fe–CN–W(CO)$_5$] (**8b**).

2.7–2.8 ppm) between the signals of axial and equatorial carbonyls (Δ_{CO} = 3.7 ppm in **8a**; 3.4 ppm in **8b**), as we previously reported in the case of L = CO [8]. This effect is even more pronounced in the [Cp(CO)(L)Fe–NC–Cr(CO)$_5$] complexes **6a** and **6c** (Δ_{CO} = 3.3 and 2.9 ppm, respectively) compared to the isomers **9a** and **9c** (Δ_{CO} = 4.5 and 4.9 ppm). These results further confirm that in M(CO)$_5$L complexes the chemical shift of the *trans*-CO moves downfield relative to those of the *cis*-carbonyls as the σ/π bonding ratio of the ligand L increases [21a,21b].

2.4. X-ray molecular structures of 2a, 5a, 8a and 8b and extended-Hückel calculations

The molecular structures of the title compounds are shown in Figs. 5 (**2a**), 6 (**5a**), 7 (**8a**) and 8 (**8b**). Relevant bond distances and angles are reported in Table 1.
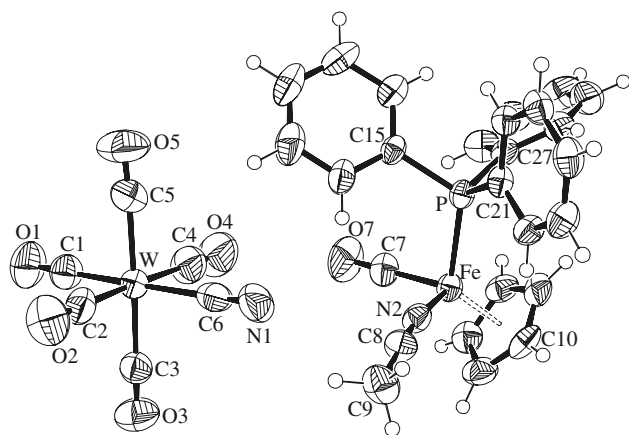

Fig. 5. Molecular structure of [Cp(CO)(PPh$_3$)Fe(NCCH$_3$)][NCW-(CO)$_5$] (**2a**) showing the atom numbering (thermal ellipsoids at 50% probability level).
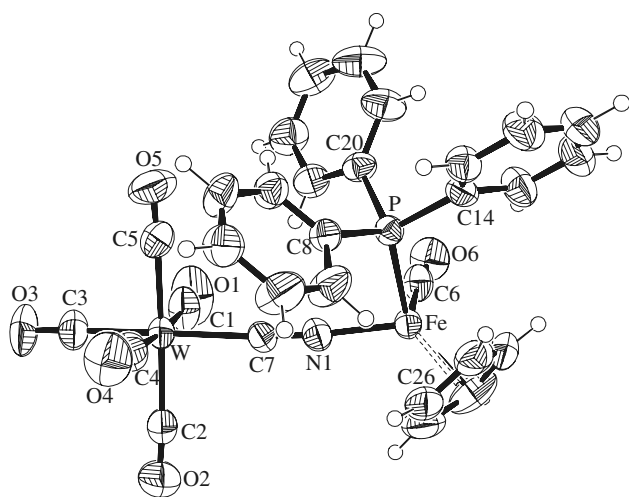
Fig. 6. Molecular structure of [Cp(CO)(PPh$_3$)FeNCW(CO)$_5$] (**5a**) showing the atom numbering (thermal ellipsoids at 50% probability level).
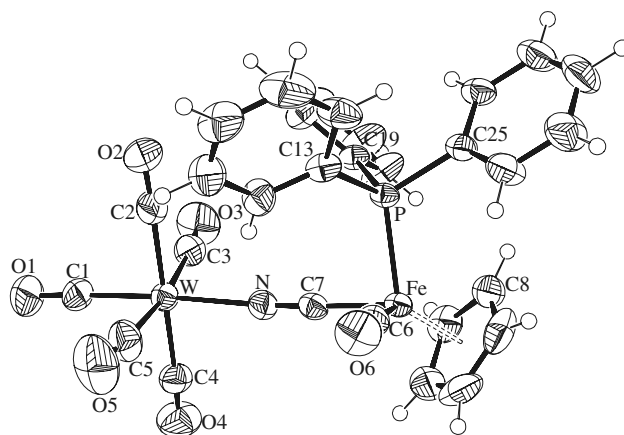
Fig. 7. Molecular structure of [Cp(CO)(PPh$_3$)FeCNW(CO)$_5$] (**8a**) showing the atom numbering (thermal ellipsoids at 50% probability level).
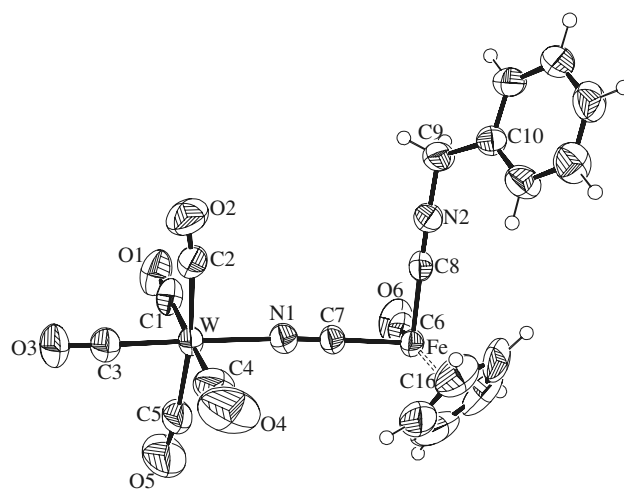
Fig. 8. Molecular structure of [Cp(CO)(CN-Benzyl)FeCNW(CO)$_5$] (**8b**) showing the atom numbering (thermal ellipsoids at 50% probability level).

The following discussion will be focused on the geometry of the linear fragment M–C≡N–M′, in an attempt to detect electronic effects connected to structural changes and to correlate metric and spectroscopic features.

2.4.1. [Cp(CO)(PPh$_3$)Fe(NCCH$_3$)][NCW(CO)$_5$] (2a)

This saline compound contains discrete ions and the anion unambiguously shows a C$_{4v}$ symmetry with the cyanide ligand well discernible from the CO groups. The ordered packing of the anion clearly means that the negative charge is significantly localized on the cyanide ligand, as indicated by the W–C distances. The W–C(cyanide) [2.198(9) Å] is 0.2 Å longer than the average W–C(carbonyl) [mean value for the equatorial groups 2.02 Å]. Such a significant difference can be attributed to the net negative charge on the cyanide group that swells

Table 1
Relevant bond parameters in compounds **2a**, **5a**, **8a** and **8b**

Complex	Fe–C$_{(CO)}$	Fe–P	Fe–C/N$_{(CN)}$	W–N/C$_{(CN)}$	C≡N	W–CO$_{trans}$	W–CO$_{cis}$(av)
Bond distances (Å)							
2a	1.763(8)	2.242(2)	1.925(7)$_{NCMe}$	2.198(9)$_C$	1.142(9)	1.981(9)	2.02(1)
5a	1.746(7)	2.234(2)	1.921(5)$_N$	2.178(6)$_C$	1.158(8)	1.983(8)	2.02(1)
8a	1.735(5)	2.218(1)	1.884(5)$_C$	2.194(5)$_N$	1.149(7)	1.964(6)	2.04(1)
8b	1.767(5)	–	1.895(4)$_{C(CNW)}$	2.194(4)$_N$	1.149(5)$_{CNW}$	1.972(5)	2.035(4)
			1.843(4)$_{C(CNBz)}$		1.144(5)$_{CNBz}$		

	W–C–N	W–N–C	Fe–C–N	Fe–N–C
Bond angles (°) in the moieties M–C≡N–M′				
5a	174.8(6)	–	–	175.5(6)
8a	–	172.8(4)	177.2(5)	–
8b	–	173.9(4)	177.8(4)	–

up its orbitals and, more than that, makes the ligand a poor π acceptor. This is consistent with the W–C(carbonyl) distance *trans* to CN [1.981(9) Å] being 0.04 Å shorter than the equatorial values, an indication of a more consistent π back-bonding for this ligand (see also Table 1 and the discussion later on). Substantially, longer W–C(cyanide) and W–N(cyanide) than W–C(CO) distances are present also in **5a**, **8a**, **8b** (see further on) and in all the reported W(CN)(CO)$_5$ fragments. In particular the [(CO)$_5$WCNW(CO)$_5$]$^-$ anion exhibits a symmetrically bridging cyanide ligand [W–C 2.184(8); W–N 2.187(7) Å] and an average W–C(carbonyl) distance 2.02 long [22]. The molecular structure of an isolated [W(CN)(CO)$_5$] anion has been recently reported [23] but, unfortunately, a comparison is not possible because CN/CO disorder is probable. The bond distances in the [Cp(CO)(PPh$_3$)Fe(NCCH$_3$)] cation will be analyzed in comparison with the corresponding values in **5a**. It is worth citing here the significant difference between the Fe–C(carbonyl) [1.763(8) Å] and Fe–N(nitrile) [1.925(7) Å] distances. It is in keeping with that just discussed for the anion, the shorter distance being found for the better acceptor carbonyl ligand. An analysis of the anion–cation contacts in the crystals allows to recognize the formation of a preferential ion pair, the one shown in Fig. 5. The nitrogen atom in the cyanide ligand, which is the most negatively charged atom in the anion (see Table 2), is oriented towards the cation and one of the closest contacts, N(1)···C(8), is 3.24 Å long.

2.4.2. [(Cp)(CO)(PPh$_3$)FeNCW(CO)$_5$] (5a)

This molecule is a condensation product of the ions in **2a** by elimination of the NCCH$_3$ ligand in the cation and

coordination of the N-end of the cyanide ligand in the anion. It is of interest to study the fine structural changes in the neutralized molecular moieties with respect to the separated ions. The Fe–C(O), 1.746(7) Å and the Fe–P, 2.234(2) Å, interactions are slightly shorter than in **2a** [1.763(8) and 2.242(2) Å, respectively].

The Fe–N(cyanide) distance [1.921(5) Å] is similar to the Fe–N(nitrile) in the cation, while the C≡N value [1.158(8) Å] is some 0.02 Å longer than in the coordinated acetonitrile [1.131(9) Å] and 0.01 Å longer than that in [W(CN)(CO)$_5$]$^-$. Therefore, one can infer that the antibonding π orbitals in the bridging CN group are more populated than in NCCH$_3$ and monodentate CN$^-$ ligands. The W–C(cyanide) distance [2.178(6) Å] is 0.02 Å shorter than in the anion, in accord with an improved tungsten-to-cyanide back-donation consequent to a lower net charge on the bridging ligand. No measurable effects are observed in the W–CO interactions. The data discussed above are consistent with the chemical evidence that the negative charge in the anion moiety is primarily localized on the cyanide ligand, while the positive charge in the cationic moiety is reasonably more centred at the iron atom (see later in this section).

2.4.3. [Cp(PPh$_3$)(CO)FeCNW(CO)$_5$] (8a) and [Cp(CO)(CN-Benzyl)FeCNW(CO)$_5$] (8b)

The molecules **8a** and **8b** are very similar and differ only in the donor properties of the PPh$_3$ and CN-Benzyl ligands. The geometric changes induced by these ligands are hardly detectable. The W–N≡C distances are found equal in the two species [W–N 2.194(5), C≡N 1.149(7) Å] and the Fe–C(cyanide) [1.884(5) and 1.895(4) Å in **8a** and **8b**, respectively] is only 0.01 Å shorter in the molecule

Table 2
Net charges (e) on atoms of interest in **2a**, **5a** and **8a** obtained by extended-Hückel calculations

Complex	W	C$_{CN}$	N$_{CN}$	C$_{cis CO}$(av)	O$_{cis CO}$(av)	C$_{trans CO}$	O$_{trans CO}$	Fe
2a	−0.07	+0.31	−0.95	+0.66	−0.69	+0.60	−0.76	+0.77
5a	−0.02	+0.07	−0.49	+0.66	−0.69	+0.60	−0.74	+0.77
8a	+0.06	+0.28	−0.73	+0.64	−0.67	+0.53	−0.78	+0.80

containing the better donor phosphine ligand that improves the iron-to-cyanide back-donation. It is of interest to compare the bond parameters of the cyanide ligand in the linkage isomers [Cp(CO)(PPh$_3$)FeCNW (CO)$_5$] (**8a**) and [Cp(CO)(PPh$_3$)FeNCW(CO)$_5$] (**5a**). The difference in the C≡N distance [1.149(7) in **8a** and 1.158(8) Å in **5a**] is not statistically significant, what one can say is that the total backbonding in the two cases is comparable and probably greater in **5a**, where the better acceptor C atom is linked to the zerovalent tungsten atom. The W–C [2.178(6) Å] and W–N [2.194(5) Å] distances show that W–N is 0.016 Å longer, in spite of the smaller atomic radius of N. The lengthening is attributable to a lower tungsten-to-nitrogen back-donation. This consideration is in keeping with the corresponding distances Fe–C [1.884(5) Å] and Fe–N [1.921(5) Å], for which an even more significant difference is observed [0.04 Å] in the same way as above. These statements are even more significant if one remember that the W–C and W–N distances have been found equal in [(CO)$_5$-WCNW(CO)$_5$]$^-$ [average 2.18 Å], as discussed above [22]. Bond values in accord with those discussed in this section have been found in the cation [Fe$_4$S$_4${NCW(CO)$_5$}$_4$]$^{2+}$, in which four WCNFe units are present [9a]. Another pair of bridging cyanide linkage isomers in a comparable bonding environment has been reported, i.e., [(CO)$_5$Cr–CN/NC–Fe(dppe)Cp] [9b].

Just one comment on the M–C≡N–M′ angles reported in Table 1. The angles involving W are moderately but systematically more bent than those involving Fe. This is proof that the W–cyanide interactions are weaker than the Fe-cyanide ones and, therefore, more sensitive to asymmetric packing forces, in accord with what was previously observed [9c].

The results of the molecular structures are usefully complemented by extended-Hückel calculations [24] of the net charges on the relevant atoms. The figures in Table 2 put on a quantitative basis the inferences based on the geometric evidence and their analysis allows the following considerations:

(i) The free anion [W(CO)$_5$(CN)]$^-$ exhibits the highest negative and the least positive charges at the N and C atoms of the cyanide ligand [−0.95 and +0.31 e, respectively], with a resulting net charge on the ligand of −0.64 e. These values, if compared with the average charges on the *cis*- and *trans*-C–O atoms (+0.66, −0.69 and +0.60, −0.76 e, respectively) quantify the charge localization in the anion and its polarity, explaining its ordered crystallization in the saline species **2a**.

(ii) When the cyanide ligand is N-coordinated to the iron atom, forming the sequence WCNFe as in **5a**, the negative charge on N promptly drops to −0.49 e. This effect is accompanied by a significant lowering of the positive charge on C [+0.07 e]. The new charge balance on the bridging ligand indicates that while the negative charge on N drops by donation to Fe, the positive

charge on C is lowered by a more significant back-donation from W.

(iii) When the cyanide ligand is N-bonded to W, forming the sequence WNCFe as in **8a**, the charge localization turns more similar to that in the free anion [N −0.73 and C +0.28 e] indicating that N of the CN$^-$ ligand is a poorer donor to the almost neutral W (net charge on the heavy metal +0.06 e) than to positively charged Fe (net charge on the metal in the range +0.7–0.8 e). In this context it is useful to remember that the same kind of calculations for the cyanide anion bridging two W(CO)$_5$ groups in the already cited [(CO)$_5$WCN(CO)$_5$]$^-$ anion showed much more balanced charge distribution with net charges 0 and −0.13 e at C and N, respectively [22].

3. Conclusions

The reaction between cyanopentacarbonylmetalates [M(CO)$_5$(CN)]$^-$ (M = Cr; Mo; W) and various cationic Fe(II) organometallic fragments can be driven to the formation either of ion pairs such as [Cp(CO)(L)Fe-(NCCH$_3$)][NCM(CO)$_5$] or neutral cyanide-bridged complexes of the type [Cp(CO)(L)FeNCM(CO)$_5$], the coordinating ability of the solvent being crucial for determining the [M(CO)$_5$(CN)]$^-$ coordination. In all the saline compounds, the ^{13}C NMR spectroscopy suggested the fluxionality of the cyanopentacarbonyl counterions, which was confirmed by low-temperature experiments on complexes [Cp(CO)(PPh$_3$)Fe(NCCH$_3$)] [NCW(CO)$_5$] (**2a**) and [Cp(CO)(CN-Benzyl)Fe(NCCH$_3$)][NCW(CO)$_5$] (**2b**). In particular, the crystal structure of **2a** revealed the presence of well-defined ion pairs, the formation of which was invoked to account for some similar line broadening effects [11]. The absence of acetonitrile, both as the reaction solvent and in the work-up procedures, allowed the recovery of cyanide-bridged complexes of the type [Cp(CO)(L)FeNCM(CO)$_5$]. All products were fully characterized by IR and NMR (^{1}H; ^{13}C) spectroscopy and their properties compared to those of the competitive ion pairs [Cp(CO)(L)Fe(NCCH$_3$)][NCM-(CO)$_5$] and of some isomeric compounds [Cp(CO)-(L)FeCNM(CO)$_5$]. This study was corroborated by the investigation of the crystal structures of complexes [Cp(CO)(PPh$_3$)Fe(NCCH$_3$)][NCW(CO)$_5$] (**2a**), [Cp(CO)-(PPh$_3$)FeNCW(CO)$_5$] (**5a**), [Cp(CO)(PPh$_3$)FeCNW-(CO)$_5$] (**8a**) and [Cp(CO)(CN-Benzyl)FeCNW(CO)$_5$] (**8b**).

4. Experimental

4.1. General

All reactions with organometallic reagents or substrates were carried out under argon using standard

Schlenk techniques. Solvents were dried and distilled under nitrogen prior to use. The prepared derivatives were characterised by elemental analysis and spectroscopic methods. IR spectra were recorded with a FT-IR spectrometer Perkin–Elmer Spectrum 2000. The routine NMR spectra (^1H, ^{13}C) were always recorded using a Varian Gemini 300 instrument (^1H, 300.1; ^{13}C, 75.5 MHz). The spectra were referenced internally to residual solvent resonance, and were recorded at 298 K for characterisation purposes. Elemental analyses were performed on a ThermoQuest Flash 1112 Series EA Instrument. The compounds [CpFe(CO)$_2$CN], Na[M(CO)$_5$(CN)], (M = Cr, Mo, W) were prepared by the literature procedures. Cationic precursors like [Cp(CO)-(L)Fe(THF)]$^+$, [L = PPh$_3$ (**1a**), CN-Benzyl (**1b**), CN-2,6-Me$_2$C$_6$H$_3$ (**1c**); CN-Bu^t (**1d**), P(OMe)$_3$ (**1e**), P(Me)$_2$Ph (**1f**), CO (**1g**)] were prepared from the corresponding iodides [25] by reaction with a stoichiometric amount of Ag(CF$_3$SO$_3$) in a THF solution (15 ml) at room temperature. Filtration through a Celite pad and subsequent evaporation to dryness afforded a mixture which was used without any further purification. All reactions were monitored by IR spectroscopy. Petroleum ether (Etp) refers to a fraction of b.p. 60–80 °C. Typically, all chromatographies were performed on alumina column (diameter:1.5 cm; height 15 cm) under Argon atmosphere and using petroleum ether-dichloromethane mixtures as eluant.

4.2. Typical procedure for the preparation of [Cp(CO)(L)Fe(NCCH$_3$)][NCW(CO)$_5$] [L = PPh$_3$ (2a); CN-Benzyl (2b); CN-2,6-Me$_2$C$_6$H$_3$ (2c); CN-Bu^t (2d); P(OMe)$_3$ (2e); P(Me)$_2$Ph (2f)]

Complexes **1a–f** (0.71 mmol), dissolved in dry acetonitrile (10 ml), was added dropwise to a stirred suspension of Na[W(CO)$_5$(CN)] (0.270 g, 0.71 mmol) in 15 ml of CH$_3$CN. The resulting dark mixture was maintained at −30 °C for 2 h, then left to warm to room temperature. Filtration through a Celite pad and evaporation to dryness afforded a crude product which was purified by alumina column chromatography. CH$_2$Cl$_2$ was first used as eluant to remove neutral impurities, after which the fractions containing the title compounds **2a–f** were obtained by eluting with CH$_3$CN. (**2a**) 0.270 g, 50%, red crystals obtained from a dichloromethane solution of pure **2a** layered with diethyl ether at −5 °C. IR (CH$_2$Cl$_2$) ν_{max} (cm^{-1}): 2102w (CN); 2057w, 1990m, 1920vs, 1895sh (CO); NMR: δ_H (CDCl$_3$) 7.2–7.7 (m, 15H, C$_6$H$_5$), 4.7 (s, 5H, C$_5$H$_5$), 2.0 (s, 3H, CH$_3$CN); δ_C (CDCl$_3$; 25 °C): 216.4 (Fe*C*O, d, $^2J_{CP}$ = 40 Hz), 135.9 (CH$_3$*C*N), 133.4 133.2 132.5, 131.6 131.9 129.8 (C$_6$H$_5$); 84.7 (C$_5$H$_5$) 5.2 (*C*H$_3$CN); δ_C (CDCl$_3$; −30 °C): 216.6 (Fe*C*O, d, $^2J_{CP}$ = 35 Hz) 201.1

(W*C*Oax), 197.7 (W*C*Oeq), 142.4 (N*C*W), 135.9 (CH$_3$*C*N), 133.5 132.2, 131.4, 130.9 129.8 (C$_6$H$_5$), 84.9 (C$_5$H$_5$), 5.3 (*C*H$_3$CN). Λ_M (10^{-3} M in CH$_3$CN, r.t.): 125 Ω^{-1} cm^2 mol^{-1}. Anal. Calc. for C$_{32}$H$_{23}$N$_2$O$_6$PFeW: C, 47.9; H, 2.87; N, 3.5. Found: C, 48.1; H, 2.85; N, 3.7%. (**2b**) 0.195 g, 41%, red oil. IR (CH$_2$Cl$_2$) ν_{max} (cm^{-1}): 2196m, 2103w (CN), 2058w, 2024m, 1921vs 1890sh (CO); NMR: δ_H (CDCl$_3$, 25 °C): 7.5–7.3 (m, 5H, C$_6$H$_5$), 4.9 (s, 5H, C$_5$H$_5$) 2.2 (s, 2H, CH$_2$-Ph), 2.0 (s, 3H, CH$_3$CN); δ_C (CDCl$_3$, r.t.), 213.5 (Fe–CO), 152.9 (*C*NBenzyl), 134.8 (CH$_3$*C*N), 132.3, 129.9, 129.6, 127.6 (C$_6$H$_5$), 83.8 (C$_5$H$_5$), 50.1 (CH$_2$), 5.4 (CH$_3$CN); δ_C (CDCl$_3$ −50 °C): 212.7 (Fe–CO), 200.5 (W*C*Oax), 197.1 (W*C*Oeq), 150.9 (*C*NBenzyl), 142.1 (N*C*W), 133.2 (CH$_3$*C*N), 131.4, 129.3, 129.0, 127.0 (C$_6$H$_5$) (C$_5$H$_5$), 49.2 (CH$_2$), 5.4 (CH$_3$CN); Λ_M (10^{-3} M in CH$_3$CN, r.t.): 115 Ω^{-1} cm^2 mol^{-1}. Anal. Calc. for C$_{22}$H$_{15}$N$_3$O$_6$FeW: C, 40.2; H, 2.28; N, 6.4. Found: C, 40.5; H, 2.31; N, 6.5%. (**2c**) 0.200 g, 42%, dark microcrystalline powder. IR (CH$_2$Cl$_2$) ν_{max} (cm^{-1}): 2157s, 2104w (CN), 2024s, 1921vs, 1890sh (CO); NMR: δ_H (CDCl$_3$): 7.3–7.1 (m, 3H, C$_6$H$_3$-2,6-(CH$_3$)$_2$), 5.2 (s, 5H, C$_5$H$_5$) 2.5 (s, 6H, C$_6$H$_3$-2,6-(C*H$_3$*)$_2$) 2.3 (s, 3H, CH$_3$CN); δ_C (CDCl$_3$); 212.3 (Fe–CO), 163.9 (*C*NC$_6$H$_3$(CH$_3$)$_2$), 134.7 (CH$_3$*C*N), 134.9, 129.4, 128.1, 127.4 (C$_6$H$_3$(CH$_3$)$_2$), 84.0 (C$_5$H$_5$), 18.5 (C$_6$H$_3$(*C*H$_3$)$_2$), 5.0 (CH$_3$CN); Λ_M (10^{-3} M in CH$_3$CN, r.t.): 115 Ω^{-1} cm^2 mol^{-1}. Anal. Calc. for C$_{23}$H$_{17}$N$_3$O$_6$FeW: C, 41.1; H, 2.53; N, 6.3. Found: C, 41.5; H, 2.55; N, 6.2%. (**2d**) 0.150 g, 33%, yellow oil. IR(CH$_2$Cl$_2$) ν_{max} (cm^{-1}): 2181m, 2104w (CN), 2056w, 2020s, 1921vs (CO); NMR: δ_H (CDCl$_3$): 5.1 (s, 5H, C$_5$H$_5$), 2.3 (s, 3H, CH$_3$CN), 1.6 (s, 9H, C(CH$_3$)$_3$); δ_C (CDCl$_3$): 213.5 (Fe-*C*O), 148.8 (*C*NBu^t), 83.7 (C$_5$H$_5$), 60.1 (*C*CH$_3$), 30.7 (C*C*H$_3$), 5.0 (CH$_3$CN); Λ_M (10^{-3} M in CH$_3$CN, r.t.): 121 Ω^{-1} cm^2 mol^{-1}. Anal. Calc. for C$_{19}$H$_{17}$N$_3$O$_6$FeW: C, 36.6, H, 2.73, N, 6.7. Found: C, 36.8; H, 2.77; N, 6.5%. (**2e**) 0.180 g, 38%, red oil. IR (CH$_2$Cl$_2$) ν_{max} (cm^{-1}): 2103w (CN), 2058w, 2004m, 1920vs, 1890sh (CO); NMR: δ_H(CDCl$_3$): 4.9 (s, 5H, C$_5$H$_5$) 3.7 (9H, d, (OC*H$_3$*)$_3$, $^3J_{HP}$ = 9 Hz) 2.3 (s, 3H, CH$_3$CN); δ_C (CDCl$_3$): 214.1 (Fe*C*O, d, $^3J_{CP}$ = 45 Hz), 135.3 (CH$_3$*C*N), 83.8 (C$_5$H$_5$), 53.7 (O*C*H$_3$, d, $^3J_{CP}$ = 5 Hz), 5.18 (*C*H$_3$CN). Λ_M (10^{-3} M in CH$_3$CN, r.t.): 116 Ω^{-1} cm^2 mol^{-1}. Anal. Calc. for C$_{17}$H$_{17}$N$_2$O$_9$PFeW: C, 30.7; H, 2.56; N, 4.2. Found: C, 30.9; H, 2.60; N, 4.4%. (**2f**) 0.238 g; 50%, red oil. IR (CH$_2$Cl$_2$) ν_{max} (cm^{-1}): 2104w, 2059w, 1986m, 1922vs, 1898sh (CO); NMR: δ_H (CDCl$_3$) 7.4–7.7 (m, 5H, C$_6$H$_5$), 4.8 (s, 5H, C$_5$H$_5$), 2.3 (s, 6H, CH$_3$), 2.0 (s, 3H, CH$_3$CN); δ_C (CDCl$_3$): 215.9 (Fe*C*O, d, $^3J_{CP}$ = 30 Hz), 134.8 (CH$_3$*C*N), 135.9, 135.3, 131.1, 129.6, 129.4, 129.3 (C$_6$H$_5$), 83.6 (C$_5$H$_5$), 16.9, (P*C*H$_3$, d, $^2J_{CP}$ = 15 Hz), 17.4 (P*C*H$_3$, d, $^2J_{CP}$ = 15 Hz), 5.4 (CH$_3$CN). Λ_M (10^{-3} M in CH$_3$CN, r.t.): 120 Ω^{-1} cm^2 mol^{-1}; Anal. Calc. for C$_{22}$H$_{19}$N$_2$O$_6$PFeW: C, 38.9; H, 2.80; N, 4.1. Found: C, 39.1; H, 2.85; N, 4.3%.

4.3. Synthesis of complexes [Cp(CO)(L)Fe(NCCH₃)] [NCM(CO)₅], [L = PPh₃, M = Cr (3a); L = CN-2,6-Me₂C₆H₃, M = Cr (3c); L = PPh₃, M = Mo, (4a); L = CN-2,6-Me₂C₆H₃, M = Mo, (4c)]

The title saline compounds were prepared in the same manner as reported for their tungsten homologues. (**3a**) 0.250 g, 60%, orange powder. IR (CH₃CN) ν_{max} (cm^{-1}): 2101w (CN), 2056m, 1985s, 1929vs, 1890sh (CO); NMR: δ_H (CDCl₃): 7.3–7.5 (m, 15H, C₆H₅) 4.7 (s, 5H, C₅H₅) 1.9 (s, 3H, CH₃CN) δ_C (CD₃CN): 221.5 (Cr*CO*ax) 217.4 (Cr*CO*eq) 215.1 (Fe*CO*, d, $^2J_{CP}$ = 23 Hz) 134.7 (CH₃CN) 132.2, 130.9 130.5 128.6 (C₆H₅), 83.7 (C₅H₅) 4.3 (*C*H₃CN); Λ_M (10^{-3} M in CH₃CN, r.t.): 118 Ω^{-1} cm^2 mol^{-1}. Anal. Calc. for C₃₂H₂₃N₂O₆PFeCr: C, 57.3, H, 3.43, N, 4.2. Found: C, 58.1; H, 3.50; N, 4.4%. (**3c**) 0.471 g, 70%, orange powder. IR (CH₃CN) ν_{max} (cm^{-1}): 2155w, 2098vw (CN), 2052m, 2026s, 1928vs (CO); NMR: δ_H (CDCl₃): 7.3–7.1 (m, 3H, C₆H₃-2,6-(CH₃)₂), 5.1 (s, 5H, C₅H₅), 2.5 (s, 6H, C₆H₃-2,6-(CH₃)₂), 2.3 (s, 3H, CH₃CN); δ_C (CD₃CN): 213.4 (Fe*CO*), 164.9 (*C*NC₆H₃(CH₃)₂), 134.9 (CH₃*C* N), 135.3, 129.5, 128.1, 127.9, (CN C₆H₃(CH₃)₂), 84.5 (C₅H₅), 17.9 (CNC₆H₃(*C*H₃)₂), 5.1 (*C*H₃CN). Anal. Calc. for C₂₃H₁₇N₃O₆FeCr: C, 51.2, H, 3.15, N, 7.8. Found: C, 51.0; H, 3.20; N, 7.5%. (**4a**) 0.322 g, 62%, orange powder. IR (CH₃CN) ν_{max} (cm^{-1}): 2102w (CN), 2060m, 1989s, 1931vs, 1890(sh) (CO); NMR: δ_H (CDCl₃): 7.5–7.2 (m, 15H, C₆H₅), 4.71 (s, 5H, C₅H₅), 2.0 (s, 3H, CH₃CN); δ_C (CD₃CN): 216.9 (Fe*CO*, d, $^2J_{CP}$ = 28 Hz), 136.2 (CH₃*C*N), 133.3, 133.1, 132.4, 131.8, 131.5, 129.3, 129.2 (C₆H₅), 84.7 (C₅H₅), 4.3 (*C* H₃CN). Anal. Calc. for C₃₂H₂₃N₂O₆FeMoP: C: 53.8, H: 3.22, N: 3.9. Found: C, 54.0; H, 3.27; N, 4.0%. (**4c**) 0.312 g, 65%, orange powder. IR (CH₃CN) ν_{max} (cm^{-1}): 2158w, 2100vw (CN), 2060m, 2025s, 1929vs (CO); NMR: δ_H (CDCl₃): 7.3–7.1 (m, 3H, C₆H₃-2,6-(CH₃)₂), 5.2 (s, 5H, C₅H₅), 2.5 (s, 6H, C₆H₃-2,6-(CH₃)₂), 2.4 (s, 3H, CH₃CN); δ_C (CD₃CN): 214.1 (Fe*CO*), 166.0 (*C*NC₆H₃(CH₃)₂), 135.6 (CH₃*C* N), 136.0, 130.1, 128.8 128.6 (CNC₆H₃(CH₃)₂), 85.1 (C₅H₅), 18.6 (CNC₆H₃(*C*H₃)₂), 5.3 (*C*H₃CN). Anal. Calc. for C₂₃H₁₇N₃O₆FeMo: C, 47.3, H, 2.91, N, 7.2. Found: C, 47.5; H, 2.95; N, 7.0%.

4.4. Cyanide-bridged complexes

4.4.1. Synthesis of [Cp(CO)(PPh₃)FeNCW(CO)₅] (5a)

Method (A): To a suspension of 0.270 g (0.71 mmol) of Na[W(CO)₅(CN)] in 20 ml of CH₂Cl₂ were slowly added 0.450 mg (0.71 mmol) of **1a** dissolved in 20 ml CH₂Cl₂. The reaction mixture was stirred at −30 °C for 1hr and then filtered through a Celite pad to eliminate NaO₃SCF₃. The solvent was evaporated under vacuum and the residue was purified by alumina filled column chromatography. Elution with a mixture of Etp/CH₂Cl₂ (2:1 v/v) gave a red-orange fraction containing **5a** (0.378

g, 70%). IR (CH₂Cl₂) ν_{max} (cm^{-1}): 2127w (CN), 2062m, 1974s, 1928vs, 1900sh (CO); NMR: δ_H (CDCl₃): 7.6–7.2 (m, 15H, C₆H₅) 4.5 (5H, s, C₅H₅); δ_C (CDCl₃): 217.3 (Fe*CO*, d, $^2J_{CP}$ = 30 Hz), 198.3 (W*CO*ax, $^1J_{CW}$ = 125 Hz), 195.5 (W*CO*eq, $^1J_{CW}$ = 128 Hz), 168.6 (NC*W*, $^2J_{CW}$ = 96 Hz), 132.9, 132.3, 132.1, 130.0, 127.9, 127.6 (C₆H₅), 83.1 (C₅H₅). Anal. Calc. for C₃₀H₂₀NO₆FePW: C, 47.3; H, 2.63; N, 1.8. Found: C, 47.4; H, 2.70; N, 1.9%. *Method (B)*: 0.030 g of Me₃NO, dissolved in 5 ml of CH₂Cl₂ were slowly added to a stirred solution of CH₂Cl₂ (20 ml) containing 0.140 g (0.27.mmol) of [Cp(CO)₂FeNCW(CO)₅] (**5g**), the preparation of which has been reported elsewhere [8], and 0.150 gr (0.57 mmol) of PPh₃. After 1 h the solvent was removed and the residue, dissolved in CH₂Cl₂, was purified by alumina filled column chromatography by eluting with a Etp/CH₂Cl₂ (3:2, v/v) mixture. Compound **5a** was obtained as the first fraction (0.270 g, 50% yield). Suitable crystals were grown by diffusion of diethyl ether into a CH₂Cl₂ solution of pure **5a** at −5 °C.

4.4.2. Synthesis of [Cp(CO)(CN-Benzyl)FeNCW-(CO)₅] (5b)

By following method A, 0.300 g (0.6 mmol) of [CpFe(CO)(CN-Benzyl)(thf)][O₃SCF₃] in 20 ml of CH₂Cl₂ were slowly added to a suspension of 0.230 gr (0.6 mmol) of Na[W(CO)₅CN] in 20 ml of the same solvent. After 30 m stirring, the reaction mixture was filtered through Celite and chromatographed on an alumina column. Elution with Etp/CH₂Cl₂ (2/1, v/v) gave a red-orange fraction containing **5b** (0.262 g, 60%). Deep orange crystals suitable for X-ray analysis were grown by slow diffusion of petroleum ether in a dichloromethane solution of pure **5b**, IR (CH₂Cl₂) ν_{max} (cm^{-1}): 2187m, 2137w (CN), 2057w, 2005s, 1929vs, 1900sh (CO); NMR: δ_H (CDCl₃): 7.4–7.2 (m, 5H, C₆H₅), 4.7 (s, 5H, C₅H₅) 2.2 (*C*H₂–C₆H₅); δ_C (CDCl₃): 215.8 (Fe*C* O), 200.0 (W*CO*ax, $^1J_{CW}$ = 125 Hz), 197.3 (W*CO*eq, $^1J_{CW}$ = 127 Hz), 166.3 (NC*W*, $^2J_{CW}$ = 96 Hz), 158.6 (*C*N-Benzyl), 132.6, 129.9, 129.4, 127.1 (C₆H₅), 83.5 (C₅H₅), 49.9 (*C*H₂–C₆H₅). Anal. Calc. for C₂₀H₁₂N₂O₆FeW: C, 39.0; H, 1.95; N, 4.5. Found: C, 39.3; H, 1.98; N, 4.7%.

4.5. Synthesis of [Cp(CO)(PPh₃)FeNCCr(CO)₅] (6a), [Cp(CO)(CN-2,6-Me₂C₆H₃)FeNCCr(CO)₅] (6c), [Cp(CO)₂FeNCCr(CO)₅] (6g); [Cp(CO)(CN-2,6-Me₂C₆H₃)FeNCMo(CO)₅] (7c) [Cp(CO)₂FeNCMo-(CO)₅] (7g)

The title compounds were prepared by following method A adopted for their tungsten analogues, starting from the cationic precursors such as [CpFe(CO)(L)(thf)] [OSO₂CF₃] (L = P(C₆H₅)₃ (**1a**); CN-2,6-Me₂C₆H₃ (**1c**); CO (**1g**)) and the appropriate cyanoanions Na[M (CO)₅(CN)] (where M = Cr, Mo). (**6a**) 0.183 g, 52%, dark

yellow microcrystalline powder. IR (CH$_2$Cl$_2$) ν_{max} (cm^{-1}): 2131w (CN), 2063w, 1976s, 1936vs; NMR: δ_H (CDCl$_3$): 7.4–7.6 (m, 15H, C$_6$$H_5$) 4.52 (C$_5$$H_5$); δ_C (CDCl$_3$): 219.7 (CrCOax), 218.7 (FeCO, d, $^2J_{CP}$ = 30 Hz), 216.4 (CrCOeq), 182.1 (NCCr), 133.7–128.4 (C$_6$H$_5$), 84.1 (C$_5$H$_5$). Anal. Calc. for C$_{30}$H$_{20}$NO$_6$CrFeP: C, 57.2; H, 3.18; N, 2.2. Found: C, 57.0; H, 3.12; N, 2.1%. (**6c**) 0.167 g, 40%, pale yellow microcrystalline powder. IR (CH$_2$Cl$_2$) ν_{max} (cm^{-1}): 2148s (CN), 2059w, 2008s, 1932vs, 1900sh (CO); NMR: δ_H (CDCl$_3$): 7.3–7.1 (m, 3H, C$_6$$H_3$-2,6-(CH$_3$)$_2$), 4.9 (C$_5$$H_5$), 2.4 (s, 6H, C$_6H_3$-2,6-(C$H_3$)$_2$); δ_C (CDCl$_3$): 220.4 (CrCOax), 217.5 (CrCOeq), 215.2 (FeCO), 182.6 (NCCr), 169.1 (CNC$_6$H$_3$(CH$_3$)$_2$), 135.4, 129.2, 128.5, 128.3 (C_6H$_3$(CH$_3$)$_2$), 83.7 (C$_5$H$_5$), 18.9 (CNC$_6$H$_3$(CH$_3$)$_2$). Anal. Calc. for C$_{21}$H$_{14}$N$_2$O$_6$CrFe: C, 50.6; H, 2.81; N, 5.6. Found: C, 50.8; H, 2.79; N, 5.9%. (**6g**) 0.229 g, 34%, orange microcrystalline powder. IR (CH$_2$Cl$_2$) ν_{max} (cm^{-1}): 2133w (CN), 2071m, 2057m, 2025m, 1935vs (CO); NMR: δ_H(CDCl$_3$): 5.1 (C$_5$$H_5$); δ_C (CDCl$_3$): 219.7 (CrCOax), 216.7 (CrCOeq), 210.8 (FeCO), 182.7 (NCCr), 86.2 (C$_5$H$_5$). Anal. Calc. for C$_{13}$H$_5$NO$_7$CrFe: C, 39.5; H, 1.27; N, 3.5. Found: C, 39.7; H, 1.28; N, 3.7%. (**7c**) 0.135 g, 71%, orange microcrystalline powder. IR (CH$_2$Cl$_2$) ν_{max} (cm^{-1}): 2149w (CN), 2064m, 2008s, 1933vs (CO); NMR: δ_H (CDCl$_3$): 7.3–7.1 (m, 3H, C$_6$$H_3$-2,6-(CH$_3$)$_2$), 4.9 (C$_5$$H_5$), 2.5 (s, 6H, C$_6H_3$-2,6-(C$H_3$)$_2$); δ_C (CD$_3$CN): 215.7 (FeCO), 209.6 (MoCOax) 205.2 (MoCOeq), 174.7 (NCMo), 134.9–127.6 (C_6H$_3$(CH$_3$)$_2$), 83.9 (C$_5$H$_5$), 17.7 (CNC$_6$H$_3$(CH$_3$)$_2$). Anal. Calc. for C$_{21}$H$_{14}$N$_2$O$_6$CrMo: C, 46.8; H, 2.60; N, 5.2. Found: C, 47.0; H, 2.64; N, 5.4%. (**7g**) 0.287 g, 68%, orange microcrystalline powder. IR (CH$_2$Cl$_2$) ν_{max} (cm^{-1}): 2132w (CN), 2072m, 2062m 2024m, 1937vs (CO); NMR: δ_H (CDCl$_3$): 5.1 (C$_5$$H_5$). δ_C (CDCl$_3$): 210.6 (FeCO), 209.4 (MoCOax), 205.1 (MoCOeq), 177.8 (NCMo), 86.2 (C$_5$H$_5$). Anal. Calc. for C$_{13}$H$_5$NO$_7$CrMo: C, 25.5; H, 1.14; N, 3.2. Found: C, 25.6; H, 1.16; N, 3.0%.

4.6. Synthesis of [Cp(CO)(L)Fe(CN)] (L = PPh$_3$; CN-Benzyl; CN-2,6-Me$_2$C$_6$H$_3$)

L = PPh$_3$: A solution of 0.820 g (4.0 mmol) of CpFe(CO)$_2$CN in 50 ml of toluene was added of a slight excess of PPh$_3$ 1.10 g (4.2 mmol) and of a catalytic amount of [CpFe(CO)(μ-CO)]$_2$. The reaction mixture was stirred at reflux for 2 h. Evaporation to dryness afforded a residue which was purified by alumina filled column chromatography. Elution with Etp/CH$_2$Cl$_2$ (3/1, v/v) gave a first fraction containing [CpFe(CO)(μ-CO)]$_2$, then the eluant was switched to pure CH$_2$Cl$_2$ and the title compound was recovered (1.40 g, 63%). IR (CH$_2$Cl$_2$) ν_{max} (cm^{-1}): 2097s (CN), 1969s (CO). The neutral precursors with L = Benzyl-NC; and L = CN-2,6-Me$_2$C$_6$H$_3$ were prepared in the same manner. Their properties are: L = CN-Benzyl (yield: 60%), IR (CH$_2$Cl$_2$) ν_{max} (cm^{-1}): 2181vs, 2105m (CN), 1989s (CO);

L = CN-2,6-Me$_2$C$_6$H$_3$ (yield: 55%), IR (CH$_2$Cl$_2$) ν_{max} (cm^{-1}): 2145s, 2105m (CN), 2000s (CO).

4.7. Synthesis of [Cp(CO)(PPh$_3$)FeCNW(CO)$_5$] (8a)

A solution of 0.500 g (1.14 mmol) of [CpFe(CO)(PPh$_3$)(CN)] in 30 ml of thf was treated with a slight excess of W(CO)$_5$(thf), and the reaction mixture was kept at room temperature, with stirring, for 24 h. Evaporation to dryness afforded a residue which was purified by alumina filled column chromatography. Excess W(CO)$_6$ was removed eluting with petroleum ether and the target product **8a** was obtained as a yellow powder (0.304 g, 35%) after elution with Etp/CH$_2$Cl$_2$ (4/1, v/v). Yellow crystal were obtained by slow diffusion of petroleum ether in a dichloromethane solution of pure **8a**. IR (CH$_2$Cl$_2$) ν_{max} (cm^{-1}): 2129w (CN), 2072w, 1980m, 1928vs, 1878m (CO); NMR: δ_H (CDCl$_3$): 7.6–7.2 (m, 15H, C$_6$$H_5$), 4.5 (C$_5$$H_5$); δ_C (CDCl$_3$): 217.3 (FeCO, d, $^2J_{CP}$ = 30 Hz), 201.9 (WCOeq), 198.2 (WCOax), 152.3 (FeCN, d, $^2J_{CP}$ = 30 Hz), 135.1 134.5, 133.6, 131.7 129.6, 129.5 (C$_6$H$_5$), 85.1 (C$_5$H$_5$). Anal. Calc. for C$_{30}$H$_{20}$NO$_6$CrFePW: C, 49.3; H, 2.63; N, 1.9. Found: C, 49.1; H, 2.65; N, 2.1%.

4.8. Synthesis of [Cp(CO)(CN-Benzyl)FeCNW(CO)$_5$] (8b)

0.210 g (0.72 mmol) of [CpFe(CO)(CNCH$_2$C$_6$H$_5$)(CN)], dissolved in 20 ml of THF, were added of a twofold excess of W(CO)$_5$(THF) and the resulting mixture was left with stirring at r.t. After 24 h, I.R. spectrum of the reaction mixture still showed a large presence of the starting reagents together with the expected bands due to compound **8b**. Further W(CO)$_5$(thf) (five equivalents), freshly prepared by irradiation of W(CO)$_6$ in THF, was added in small portions. After two days the reaction was stopped and the solvent stripped out under vacuum. The excess W(CO)$_6$ was removed by sublimation and the resulting residue was purified by alumina filled column chromatography. Elution with Etp afforded a first fraction containing W(CO)$_6$. Successive elution with CH$_2$Cl$_2$ gave a yellow fraction containing compound **8b**. A further fraction containing the starting complex [CpFe(CO)(CNCH$_2$C$_6$H$_5$)(CN)] was collected by elution with CH$_2$Cl$_2$/CH$_3$CN (1/1, v/v). Compound **8b** (0.26g, 58%) was obtained as yellow crystals by slow diffusion of petroleum ether in a dichloromethane solution of pure **8b**. IR (CH$_2$Cl$_2$) ν_{max} (cm^{-1}): 2202m, 2135w (CN), 2068w, 2011s, 1981m, 1911vs, 1872sh (CO). NMR: δ_C (CD$_3$CN): 214.5 (FeCO), 201.6 (WCOax), 198.2 (WCOeq), 157.4 (CNBenzyl), 148.1 (CNW), 132.8, 129.6, 129.1 127.0 (C$_6$H$_5$), 83.9 (C$_5$H$_5$), 49.7 (CH_2). Anal. Calc. for C$_{20}$H$_{12}$N$_2$O$_6$FeW: C, 39.2; H, 1.96; N, 4.6. Found: C, 39.1; H, 2.00; N, 4.5%.

4.9. Synthesis of [Cp(CO)(PPh₃)FeCNCr(CO)₅] (9a) and [Cp(CO)(CN-2,6-Me₂C₆H₃)FeCNCr(CO)₅] (9c)

The procedure used to prepare these compounds is the same adopted for their tungsten analogues, involving [CpFe(CO)(L)(CN)] (L = PPh₃; CN-2,6-Me₂C₆H₃) and [Cr(CO)₅(thf)] as starting materials. Their physical and spectroscopic properties are: (**9a**) 0.183 g, 52%, dark yellow microcrystalline powder. m.p. 163–165 °C (dec.). IR (CH₂Cl₂) v_{max} (cm⁻¹): 2135w (CN), 2069w, 1980s, 1937vs, 1884sh (CO). NMR: δ_H (CDCl₃): 7.6–7.4 (m, 15H, C₆H₅), 4.5 (s, 5H, C₅H₅); δ_C (CD₃CN): 219.10 (Cr*C*Oax), 217.2 (Fe*C*O, d, $^2J_{CP} = 30$ Hz), 214.6 (Cr*C*Oeq), 155.5 (Fe*C*N, d, $^2J_{CP} = 30$ Hz), 128.20–133.40 (*C₆H₅*), 84.5 (*C₅H₅*). Anal. Calc. for C₃₀H₂₀NO₆CrFeP: C, 57.2; H, 3.18; N, 2.2. Found: C, 57.4; H, 3.15; N, 2.1%.

(**9c**) 0.167 g, 40%, pale yellow microcrystalline powder, m.p.: 107–109 °C. IR (CH₂Cl₂) v_{max} (cm⁻¹): 2153m, 2138m (CN), 2067w, 2006s, 1932vs, 1879sh (CO); NMR: δ_H (CDCl₃): 7.3–7.1 (m, 3H, C₆H₃-2,6-(CH₃)₂), 4.9 (C₅H₅) 2.4 (s, 6H, C₆H₃-2,6-(C*H₃*)₂); δ_C (CD₃CN): 219.7 (Cr*C*Oax), 214.8 (Cr*C*Oeq), 214.4 (Fe*C*O), 168.5 (CN-2,6-Me₂C₆H₃), 149.6 (*C*NCr), 134.8–127.7 (*C₆H₃* (CH₃)₂), 84.05 (*C₅H₅*), 17.60 (CNC₆H₃(*C*H₃)₂). Anal. Calc. for C₂₁H₁₄O₆N₂FeCr: C, 50.6; H, 2.81; N, 5.6. Found: C, 50.8; H, 2.90; N, 5.3%.

4.9.1. X-ray crystallography and extended-Hückel calculations

Crystals of **2a**, **5a**, **8a** and **8b** suitable for structural studies were grown by slow diffusion of diethyl ether or petroleum ether into dichloromethane solutions of the pure compounds. Diffraction intensities were collected by the ω scan method at room temperature on a graphite monochromated Enraf-Nonius CAD-4 diffractometer and reduced to F_o^2 values. Structure models were obtained by direct methods and refined by full-matrix least-squares calculations. For all computations SHELXS-86 and SHELXL-93 [26] were employed. No decay correction was needed, while absorption correction was done by ψ-scan methods for all compounds. Thermal vibrations for all non-H atoms were treated anisotropically. All H atoms were found in difference Fourier maps and refined with constraints (C–H = 0.96 Å). Cyclopentadienyl rings were treated as rigid bodies. Final difference Fourier maps showed residual peaks lower than 0.7 e Å⁻³ in all the structures in the proximity of the W atom. Table 3 reports the experimental parameters of data collection and refinement for all compounds. Compounds **5a** and **8a** are strictly isomorphous. In order to check the correct location of the N and C atoms in the C≡N moiety for all compounds and especially **2a**, where it had to be discerned from the CO ligands, models were refined with inverted location of the atomic species involved. As a result, for all the wrong structural models the R factors increased significantly and the thermal ellipsoids of the mislabelled atoms became clearly unreasonable. Extended-Hückel molecular orbital calculations [24] were carried out on the experimental structures of **2a**, **5a** and **8a** using the modified Wolfberg–Helmholz formula [27]. Standard atomic parameters were used for C, O, N and H, while those for Fe and W were taken from the literature

Table 3
Crystal data and experimental details for **2a**, **5a**, **8a** and **8b**

	2a	5a	8a	8b
Formula	C₃₂H₂₃FeN₂O₆W	C₃₀H₂₀FeNO₆PW	C₃₀H₂₀FeNO₆PW	C₂₀H₁₂FeN₂O₆W
T (K)	293	293	293	293
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a (Å)	14.062(2)	10.345(2)	10.366(2)	11.084(2)
b (Å)	7.639(1)	12.087(2)	12.031(2)	15.164(3)
c (Å)	29.790(4)	12.656(2)	12.651(2)	12.857(2)
α (°)	90	89.75(2)	89.46(2)	90
β (°)	101.88(3)	106.91(3)	106.71(2)	102.58(2)
γ (°)	90	107.32(2)	108.22(3)	90
V (Å³)	3131(1)	1439(1)	1429(1)	2109(1)
Z	4	2	2	4
$F(000)$	1568	740	740	1176
λ (Mo Kα) (Å)	0.71069	0.71069	0.71069	0.71069
μ (Mo Kα) (mm⁻¹)	4.09	4.44	4.63	5.96
θ Range (°)	2–25	2–30	2–30	2–30
Octants explored	$\pm h, +k, +l$	$\pm h, \pm k, +l$	$\pm h, \pm k, +l$	$\pm h, +k, +l$
Measured reflections	5585	8723	8655	6615
Unique reflections used in the refinement	2848	4325	5831	6133
Number of refined parameters	380	361	367	269
Goodness-of-fit on F^2	1.004	1.002	1.006	1.083
R_1 (on F, $I > 2\sigma(I)$)	0.035	0.030	0.040	0.029
wR_2 (on F^2)	0.094	0.110	0.117	0.087

[28,29]. A self-consistent charge calculation was performed assuming a quadratic dependence of H_{ii} on charge.

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 230991, 230992, 230993, 230994 for compounds **2a**, **5a**, **8a** and **8b**, respectively. Copies of the data can be obtained, free of charge, from The Director CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

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