

Redox chemistry and substitution reactions of the μ -cyanoalkylidene complexes $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C}(\text{CN})(\text{X})\}]^{n+}$ ($n = 0$, $\text{X} = \text{CN}$, H , Me , SMe , OMe , OEt , OPh , $\text{OCH}_2\text{CH}=\text{CH}_2$, PEt_2 , or NC_5H_{10} ; $n = 1$, $\text{X} = \text{PMe}_2\text{Ph}$)

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Abstract

Electrochemistry of the μ -cyanoalkylidene complexes $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C}(\text{CN})(\text{X})\}]^{n+}$ ($n = 0$, $\text{X} = \text{CN}$, H , Me , SMe , OMe , OEt , OPh , $\text{OCH}_2\text{CH}=\text{CH}_2$, PEt_2 , piperidinyl; $n = 1$, $\text{X} = \text{PMe}_2\text{Ph}$) in nonaqueous solutions shows a one-electron reduction to the corresponding paramagnetic monoanions, which have been characterized by EPR spectroscopy. The presence of the positive charge in $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C}(\text{CN})(\text{PMe}_2\text{Ph})\}]^+$ makes the one-electron addition significantly easier than to the neutral complexes. None of the 19-electron anions are fully stable and all undergo slow decomposition reactions, the rates of which are a function of the X substituent. Access to the radical anion intermediates $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C}(\text{CN})(\text{X})\}]^-$ does not trigger Electron Transfer Chain catalytic substitution reactions of CO by phosphines, but allows these reactions to be successfully carried out by different methods, such as chemical reduction, CO photolysis and use of Me_3NO . The CO -substituted derivatives $[\text{Fe}_2(\text{cp})_2(\text{CO})(\text{PMe}_2\text{Ph})(\mu\text{-CO})\{\mu\text{-C}(\text{CN})(\text{X})\}]$ ($\text{X} = \text{CN}$, H , SMe) and $[\text{Fe}_2(\text{cp})_2(\mu\text{-CO})(\mu\text{-dppm})\{\mu\text{-C}(\text{CN})(\text{X})\}]$ ($\text{X} = \text{H}$, CN ; $\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$) were obtained. The one-electron reduction of the monophosphine-substituted complexes is fully irreversible and occurs at potentials 0.3–0.4 V more negative than those of the corresponding precursors. The different methods for promoting CO displacement in the μ -alkylidene complexes have been compared; the photolytic method affords the highest yields.

Keywords: Redox reactions; Substitution reactions; Iron; μ -Cyanoalkylidene complexes; Electrochemistry; EPR

1. Introduction

We have recently shown that the alkylidene complex $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C}(\text{CN})(\text{SMe}_2)\}]\text{SO}_3\text{CF}_3$ [1] is an excellent precursor to μ -cyanoalkylidene complexes of the type $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C}(\text{CN})(\text{X})\}]$ ($\text{X} = \text{OR}$ [2], NRR' [3], PRR' [4]) via simple SMe_2 substitution by the appropriate nucleophile. Since heteroatom-substituted μ -alkylidene complexes are still poorly explored compounds [5], we planned to study the chemistry of the complexes $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C}(\text{CN})(\text{X})\}]$ ($\text{X} = \text{SR}$, OR , NRR' , PRR'). Recent investigations on their reactions with Lewis acids have shown that the reactivity is markedly affected by the nature of

the heteroatom [6]. Electrophilic attack occurs at the X heteroatom when $\text{X} = \text{PRR}'$ or SR , whereas it results in $\mu\text{C-CN}$ bond cleavage when $\text{X} = \text{NRR}'$.

We now wish to report the redox behaviour of the μ -cyanoalkylidene complexes $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C}(\text{CN})(\text{X})\}]^{n+}$ shown in Scheme 1.

The redox chemistry of binuclear μ -carbon-functionalized transition metal complexes has been hardly investigated so far [7]. Our results indicate that, in general, one-electron reduction affords transient radical anions having enough stability to be characterized by spectroscopic (EPR, IR) techniques. In no case was the radical stable enough for isolation. The substitution reactions of CO with phosphines in the radical anion complexes $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C}(\text{CN})(\text{X})\}]^-$ ($\text{X} = \text{CN}$, H , SMe) were studied and compared with other

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The EPR features of $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C}(\text{CN})\text{H}\}]^-$ (**2a**) are very similar to those discussed for **4a**. The following gss parameters are consistent with a metal-centred axial structure:

$$g_{\parallel} = 1.901 \pm 0.003; g_{\perp} = 2.001 \pm 0.003$$

$$\langle g \rangle = 1.968 \pm 0.003$$

The room-temperature spectrum gives a singlet with a g_{iso} value of 1.967 ± 0.003 and $\Delta H_{\text{iso}} = 13 \pm 3$ G. No hpf coupling to any protons of the peripheral ligands is observed. Thus, as for **4a**, we have evidence that the exhaustive reduction process of **2** places the electron on the LUMO level, which apparently possesses a mainly M_2 -fragment character [7b].

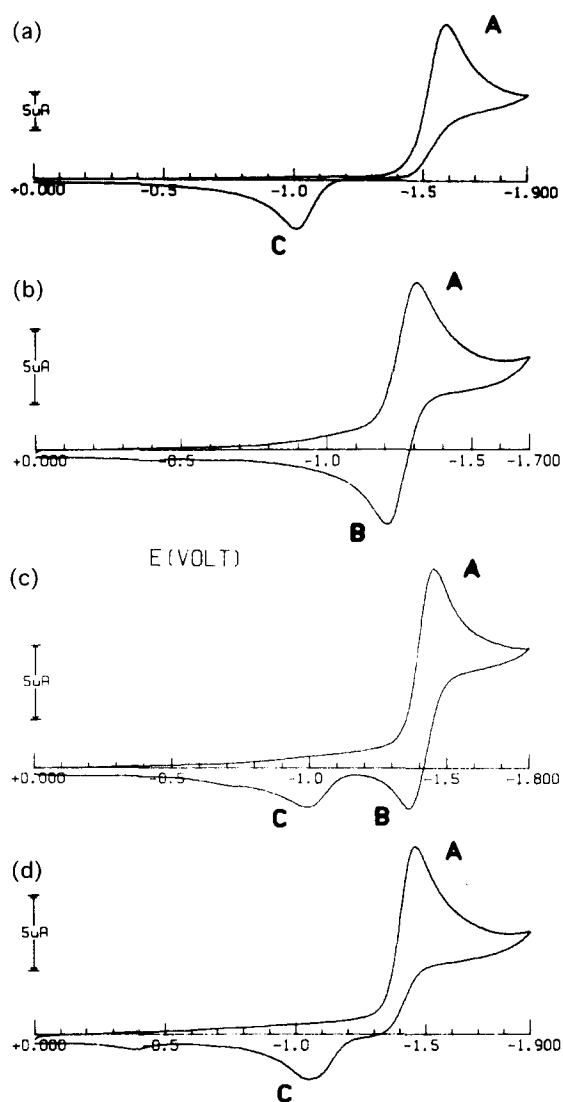


Fig. 1. Cyclic voltammograms recorded at ambient temperature on deaerated THF solutions containing $[\text{NBu}_4][\text{ClO}_4]$ (0.2 mol dm^{-3}) and: (a) $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})_2]$ ($1.7 \times 10^{-3} \text{ mol dm}^{-3}$); (b) **4** ($1.6 \times 10^{-3} \text{ mol dm}^{-3}$); (c) **5** ($1.7 \times 10^{-3} \text{ mol dm}^{-3}$); (d) **10** ($1.6 \times 10^{-3} \text{ mol dm}^{-3}$). Platinum working electrode. Scan rate 0.05 V s^{-1} .



Fig. 2. X-band EPR spectra recorded at (a) 100 K and (b) 300 K on a THF solution of **4** after its first-stage electroreduction (about 0.5 electron per molecule) at 253 K.

Interestingly, the parallel region of the axial pattern displays a second, less intense high field signal, the intensity of which is 30% of the former ($g_{\parallel} = 1.901 \pm 0.003$; $g_{\perp} = 1.894 \pm 0.003$). These spectral features can be reasonably explained by assuming the presence in solution of two isomeric forms of the monoanion (Y and Y'), the geometry of which depends on the position of the cyclopentadienyl *trans* or *cis* with respect to the Fe–Fe bond. Significantly, the nature of the X substituent of the $\mu\text{-C}(\text{CN})$ moiety does not affect the actual EPR lineshape, suggesting at most a minor interaction of the unpaired electron with either the N or H nucleus.

Chemical reduction of **1**, **2** and **4** in THF at 0°C by sodium naphthalene affords the same emerald-green solutions obtained by electrochemical reduction. All attempts to isolate the radical anions in solids failed. Evaporation of the solvent gave residues containing decomposition products together with the neutral starting complexes, probably arising from O_2 reoxidation of the radical anions. The IR spectra of **1a**, **2a** and **4a** in THF exhibit $\nu(\text{CO})$ absorptions at lower wavenumbers compared with those of the precursors **1**, **2** and **4** (eg, for **4a**: $\nu(\text{CO})$ 1933s, 1894w, 1765m, $\nu(\text{CN})$ 2141 cm^{-1} vs. 1997s, 1962w, 1804m and 2160w cm^{-1} of **4**). The presence of two terminal and one bridging $\nu(\text{CO})$ bands suggests that the molecular frame of the radical anions is similar to those of the precursors.

The tendency of the monoanion of **5**, **5a** to fragment in the short time scale of the cyclic voltammetry is clear not only from the appearance of the far reoxidation peak C in Fig. 1(c), but also from the relevant peak-current ratio $i_{p(B)}/i_{p(A)}$ of 0.7. Nevertheless, the fact that this decomposition reaction is rather slow is evident from the fact that it is sufficient to increase the scan rate to 0.2 V s^{-1} to obtain a peak-current ratio of 1. Controlled potential coulometry ($E_w = -1.5 \text{ V}$) shows the consumption of 1.7 electrons per molecule.

Further confirmation that **5a** decomposes at a relatively higher rate than the previously cited monoanions is given by the EPR spectra (Fig. 3), which refer to **5a** electrogenerated at -20°C .

The liquid-nitrogen temperature spectrum (Fig. 3(a)) is now rather complex in that it displays two different groups of anisotropic signals, a more intense set with a typical axial adsorption pattern attributable to the monoanion **5a**, and a minor, low field set, with orthorhombic symmetry, probably due to a metal-containing decomposition product ($g_i > g_e$).

In liquid solution both the anisotropic absorptions change to the relevant isotropic peaks (Fig. 3(b)) with

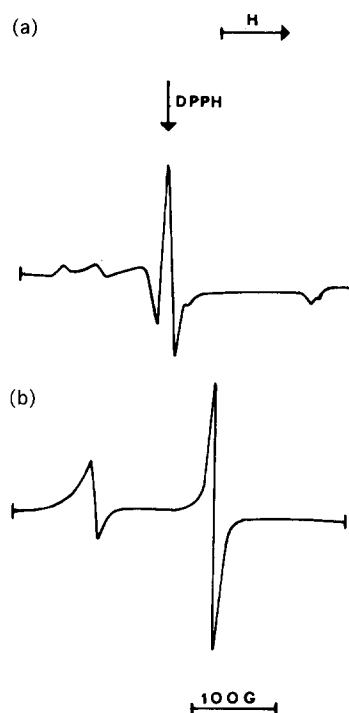


Fig. 3. X-band EPR spectrum, recorded at (a) 100 K and (b) 300 K on a THF solution of **5** after its first-stage electroreduction (about 0.5 electrons per molecule) at 253 K.

Table 1

Formal electrode potentials for the one-electron reduction of the μ -cyanoalkylidene complexes $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C}(\text{CN})(\text{X})\}]^{n+}$, and related species

Complex	E° (V vs. SCE)	ΔE_p^a (mV)	Solvent	Ref.
$[\text{Fe}_2(\text{cp})_2(\text{CO})_2(\mu\text{-CO})_2]$	$-1.57^{a,b,c}$	—	THF	^d
	-1.64^b	—	CH_2Cl_2	[7c]
1	-0.94	88	THF	^d
	-1.02	84	MeCN	^d
2	-1.31	112	THF	^d
	-1.39	86	MeCN	^d
3	-1.37	80	THF	^d
	-1.44	98	MeCN	^d
4	-1.26	100	THF	^d
	-1.32	80	MeCN	^d
5	-1.41	90	THF	^d
	-1.46	86	MeCN	^d
6	-1.42	94	THF	^d
	-1.47	90	MeCN	^d
7	-1.20	110	THF	^d
	-1.24	74	MeCN	^d
8	-1.40	94 ^e	THF	^d
	-1.44	80 ^e	MeCN	^d
9	-1.26	96	THF	^d
	-1.32	80	MeCN	^d
10	-1.41	116 ^e	THF	^d
	-1.51^b	—	MeCN	^d
11	-0.79	66	MeCN	^d
$[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\text{-}(\mu\text{-CSMe})]^+$	-0.82	75 ^f	MeCN	[7b]
$[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\text{-}(\mu\text{-C}=\text{CH}_2)]$	-1.69	80 ^e	CH_2Cl_2	[7c]

^a Measured at 0.02 V s^{-1} ; ^b peak-potential value for irreversible processes; ^c two-electron process; ^d present work; ^e measured at 0.2 V s^{-1} ; ^f measured at 0.3 V s^{-1} .

EPR parameters corresponding to the averaged low-temperature ones:

$$g_{\parallel} = 1.902 \pm 0.003; g_{\perp} = 1.998 \pm 0.003$$

$$\langle g \rangle = 1.966 \pm 0.003$$

$$g_{\text{iso}} = 1.955 \pm 0.003$$

$$g_1 = 2.106 \pm 0.003; g_m = 2.048 \pm 0.003;$$

$$g_h = 2.005 \pm 0.003$$

$$\langle g \rangle = \frac{1}{3}(g_1 + g_m + g_h) = 2.053 \pm 0.003$$

$$g_{\text{iso}} = 2.044 \pm 0.003$$

These data confirm the stability of the molecular structure of **5a** in the overall temperature range, the axial features closely recalling those previously discussed for $\text{X} = \text{SMe}$ or H . In this case, the g_{\parallel} region exhibits the two isomeric signals Y and Y' in a 2:1 molar ratio.

Complexes **3**, **6**, **8** and **9** behave like **5**. Controlled potential coulometries indicate a consumption of 1.6–1.8 electrons per molecule, suggesting a rather high decomposition rate of the relevant monoanions to produce further electroreducible fragmentation products.

As far as the redox behaviour of complex **10** is concerned, its monoanion **10a** is the most transient species among the derivatives discussed here. Fig. 1(d), which has been recorded at ambient temperature, is self-explanatory. Only at the highest scan rate of 2 V s^{-1} , is the chemical reaction destroying **10a** almost

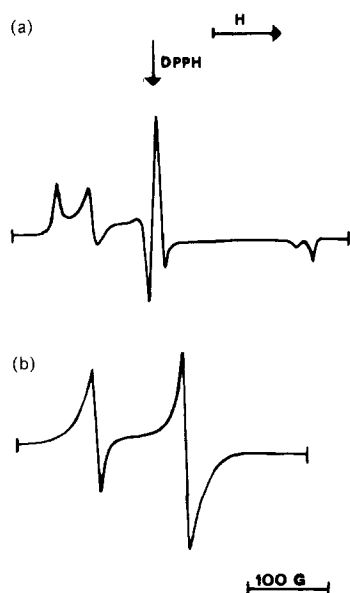


Fig. 4. EPR spectra recorded at (a) 100 K and (b) 300 K after partial reduction (about 0.3 electrons per molecule) of a THF solution of **10** at 253 K.

prevented. In contrast, at -20°C , a scan rate of 0.02 V s^{-1} is sufficient to prevent such a decomposition process on the cyclic voltammetric timescale. Nevertheless, exhaustive electroreduction at -20°C ($E_w = -1.8\text{ V}$, vs. $\text{Ag}|\text{AgCl}$) slowly consumes 2.2 electrons per molecule.

The temperature-dependent EPR lineshape analysis once again confirms the paramagnetic nature of the short-lived monoanion **10a**, even if the presence of the $S = 1/2$ metal-centred decomposition product is more and more evident, as the liquid-nitrogen temperature spectrum shown in Fig. 4(a) indicates.

The relevant parameters are:

$$g_{\parallel} = 1.893 \pm 0.003; g_{\perp} = 1.998 \pm 0.003$$

$$\langle g \rangle = 1.963 \pm 0.003$$

$$g_{\text{iso}} = 1.975 \pm 0.003$$

$$g_1 = 2.072 \pm 0.003; g_m = 2.046 \pm 0.003;$$

$$g_h = 2.000 \pm 0.003$$

$$\langle g \rangle = 2.040 \pm 0.003$$

$$g_{\text{iso}} = 2.042 \pm 0.003$$

In this case, the axial pattern exhibits a 1:3 (Y:Y') isomeric composition. All the derivatives suggest the presence of the Y, Y' isomers in different molar ratios, except for that of SMe. The slightly broad glass linewidth for **4a** may obscure the minor signal of the isomer.

The formal electrode potentials summarized in Table 1 indicate the electronic effects exerted by the different substituents on the μ -cyanoalkylidene diiron moiety. Within the neutral complexes, the electron-withdrawing

ability follows the order: $\text{CN} \gg \text{OPh} > \text{SMe} \approx \text{PEt}_2 > \text{H} > \text{Me} > \text{Oallyl} > \text{OMe} \approx \text{piperidinyl} > \text{OEt}$. The more kinetically stable monoanions generally derive from those complexes possessing the more withdrawing substituents. The positive charge in the monocation **11** makes the one-electron addition significantly easier than the neutral cyanoalkylidene complexes. This is also the case for the thiocarbonyl cation $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})(\mu\text{-CSMe})]^+$ [**7b**].

2.2. Substitution reactions of $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C}(\text{CN})(\text{X})\}]$ ($\text{X} = \text{CN}$, **1**; H , **2**; SMe , **4**) with phosphines

The above results have shown the possibility of obtaining relatively stable radical anions for some of the complexes **1–11**. This suggests a possible route to the CO displacement, because 19-electron species are known to be more labile [16]. Further support for this idea comes from the observation that the related diiron radical complex $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})(\mu\text{-CSMe})]^\cdot$, obtained by chemical or electrochemical reduction of the thiocarbonyl $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})(\mu\text{-CSMe})]^+$, exhibits enhanced lability of the CO groups which makes it a catalyst for substitution of CO groups by phosphines through an electron-transfer chain (ETC) mechanism [7b].

We have also tried [17a] to see whether ETC catalytic reactions might afford the phosphine-substituted products for complex **4**. Addition of PPh_3 or PMe_2Ph to an acetonitrile solution of the complex does not give rise to new cathodic waves with respect to that shown in Fig. 1(b). In addition, controlled potential coulometry ($E_w = -1.4\text{ V}$) consumes about 1.4 electrons per molecule, just as in the absence of phosphine. Cyclic voltammetry on the resulting solutions shows an irreversible reduction process at: $E_p = -1.63\text{ V}$ in the presence of PPh_3 and $E_p = -1.56\text{ V}$ in the presence of PMe_2Ph . As discussed below, the irreversible peak at -1.56 V is coincident with that exhibited by an authentic sample of $[\text{Fe}_2(\text{cp})_2(\text{CO})(\text{PMe}_2\text{Ph})(\mu\text{-CO})\{\mu\text{-C}(\text{CN})(\text{SMe})\}]$. These data rule out an ETC mechanism [17b], but also show that a redox-induced substitution reaction can be successful.

Chemical generation of the species **1a**, **2a** and **4a** in the presence of a large excess of PMe_2Ph results in the formation of the CO-substituted products $[\text{Fe}_2(\text{cp})_2(\text{CO})(\text{PMe}_2\text{Ph})(\mu\text{-CO})\{\mu\text{-C}(\text{CN})(\text{X})\}]$ ($\text{X} = \text{CN}$, **12**; H , **13**; SMe , **14**) in low yield ($< 10\%$). These complexes have been isolated by column chromatography and characterized by spectroscopy.

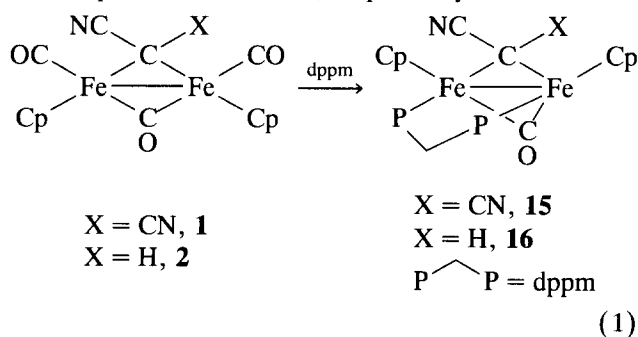
An alternative approach to the synthesis of PR_3 -substituted derivatives involves photoinduced CO cleavage. Photolytic methods have been used to promote CO substitution of $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})_2]$ by phosphines and phosphites [18]. Photogenerated $[\text{Fe}_2(\text{cp})_2(\mu\text{-CO})_3]$ has been spectroscopically characterized [19] and the

mechanism of the photoreactions of $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})_2]$ with phosphines has been investigated [20]. In contrast, little is known concerning photoinduced CO loss in bridging-alkylidene complexes of the type $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})(\mu\text{-CRR}')]]$. However, recent studies [21a] of the photochemistry of $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})(\mu\text{-C}(\text{Me})(\text{H}))]$ have shown that the effect of the μ -alkylidene is to prevent metal–metal bond cleavage [22], thus favouring the CO-loss pathway. A number of phosphine-substituted derivatives $[\text{Fe}_2(\text{CO})(\text{PR}_3)(\text{cp})_2(\mu\text{-CO})(\mu\text{-C}(\text{Me})(\text{H}))]$ have been conveniently prepared by this route [21].

Photolytically-promoted CO substitution should be more limited in heteroatom-substituted μ -alkylidene complexes because of possible competition with intramolecular CO displacement. Upon irradiation, the complexes $[\text{Fe}_2(\text{cp})_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-C}(\text{CN})(\text{SR}))]$ ($\text{R} = \text{Me}, \text{Et}$) undergo intramolecular CO substitution by the sulphur ligand affording $[\text{Fe}_2(\text{cp})_2(\text{CO})(\mu\text{-CO})(\mu\text{-C}(\text{CN})(\text{SR}))]$ [23]. In order to test this possibility, we investigated the photolysis of **4** in the presence of an equimolar amount of PMe_2Ph , and found that one CO group is replaced by the phosphine, affording $[\text{Fe}_2(\text{cp})_2(\text{CO})(\text{PMe}_2\text{Ph})(\mu\text{-CO})(\mu\text{-C}(\text{CN})(\text{SMe}))]$, **14**, in good yield (75%) and no intramolecular CO displacement is observed. Compound **14** was identified by comparison of its spectroscopic properties with those in the literature [23].

The synthesis of **14** via the anion **4a** affords significantly lower yields compared with the photolytic method (10% vs. 75%), but other methods of promoting CO substitution by phosphine should be taken in consideration. Therefore, we also investigated the reactions of **1** and **4** with PMe_2Ph in the presence of Me_3NO . The reactions afforded the substituted derivatives **12** and **14**, respectively, in 45–65% yield, comparable to photolytic yields.

Finally, we investigated substitution reactions with chelating diphosphines such as dppm ($\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$) and found that the complexes $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})(\mu\text{-C}(\text{CN})(\text{X}))]$ ($\text{X} = \text{CN}, \text{1}; \text{H}, \text{2}$) react under photolytic conditions to form CO-substituted products **15** and **16**, respectively



The complexes **15** and **16**, which are moderately air-stable in the solid state, have been characterized by

IR and NMR spectroscopy. Their IR spectra show one bridging $\nu(\text{CO})$ absorption and at 1727 cm^{-1} for **15** in agreement with the band observed at 1688 cm^{-1} in the related complex $[\text{Fe}_2(\text{cp})_2(\mu\text{-CO})(\mu\text{-dppm})(\mu\text{-CH}_2)]$ [24]. Single cp resonances are observed in both the ^1H and ^{13}C NMR spectra of complex **15** (at δ 4.45 and δ 89.3, respectively) indicating the equivalence of the two cp ligands and the presence of a single isomer, in spite of the fact that solutions of the precursor **1** are known to contain an equilibrium mixture of the *cis* and *trans* isomers [25]. The formation of a single isomer is the obvious consequence of the chelating dppm which forces the cp to adopt the *cis* configuration. In the case of $[\text{Fe}_2(\text{cp})_2(\mu\text{-CO})(\mu\text{-dppm})(\mu\text{-C}(\text{CN})(\text{H}))]$ **16**, two isomers would be expected, depending on the orientation of the CN group relative to the cp or dppm. However, even in this case a single cp resonance is observed in the ^1H NMR spectrum (at δ 4.47).

Finally it is worth mentioning that the synthesis of compounds **15** and **16** is accompanied by the formation of small amounts of the monosubstituted derivatives $[\text{Fe}_2(\text{cp})_2(\text{CO})(\text{dppm})(\mu\text{-CO})(\mu\text{-C}(\text{CN})_2)]$ and $[\text{Fe}_2(\text{cp})_2(\text{CO})(\text{dppm})(\mu\text{-CO})(\mu\text{-C}(\text{CN})(\text{H}))]$, respectively, which have been characterized by IR spectroscopy. These complexes exhibit two $\nu(\text{CO})$ absorptions, for $[\text{Fe}_2(\text{cp})_2(\text{CO})(\text{dppm})(\mu\text{-CO})(\mu\text{-C}(\text{CN})_2)]$ at 1969 cm^{-1} and 1779 cm^{-1} , attributable to terminal and bridging CO, respectively.

2.3. Electrochemistry of complexes **12** and **14**

Fig. 5 shows the cyclic voltammogram of complex **14** in acetonitrile solution.

The substitution of one terminal CO group by an electron-donating phosphine not only makes the reduction step significantly more difficult, but also irreversible.

Table 2 summarizes the redox potentials of complexes **12** and **14** and their precursors.

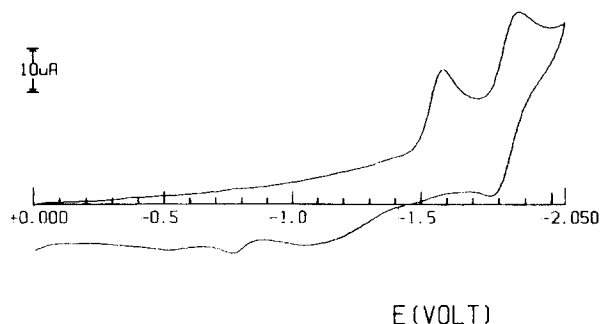


Fig. 5. Cyclic voltammogram recorded at ambient temperature on deaerated MeCN solution containing $[\text{NEt}_4](\text{ClO}_4)$ (0.2 mol dm^{-3}) and **14** ($1.4 \times 10^{-3} \text{ mol dm}^{-3}$). Platinum working electrode. Scan rate 0.5 V s^{-1} .

3. Experimental details

3.1. Materials and apparatus

All the reactions were routinely carried out under dinitrogen by standard Schlenk techniques. Solvents were distilled under nitrogen immediately before use from appropriate drying agents. Instruments employed: IR, Perkin Elmer 983-G; NMR, Varian Gemini 200. Elemental analyses were by Pascher Microanalytical Laboratory (Remagen, Germany). The complexes **1**, **2** [25], **3** [3], **4** [23], **5**, **6**, **7**, **8** [2], **9** [4a], **10** [6] and **11** [4b] were prepared according to published methods. Materials and apparatus for electrochemistry and coupled EPR measurements have been described elsewhere [26]. Unless otherwise specified, all potential values refer to the Saturated Calomel Electrode (SCE).

3.2. Synthesis of the complexes

3.2.1. Preparation of $[\text{Fe}_2(\text{cp})_2(\text{CO})_2(\mu\text{-CO})\{\mu\text{-C}(\text{CN})(\text{X})\}]^-$ ($\text{X} = \text{CN}$, **1a**; H , **2a**; SMe , **4a**) by chemical reduction

A THF solution of sodium naphthalene (NaNp) (1.0 ml; ca. 0.25 mol dm^{-3}) was added dropwise to a stirred solution of **1** (83 mg, 0.213 mmol) under Ar at 0°C . The reaction mixture, which turned emerald green, showed the following IR absorptions (THF): $\nu(\text{CO})$ 1946s, 1914w, 1773m; $\nu(\text{CN})$ 2149w cm^{-1} . A THF solution of **1a** at room temperature, turned reddish brown over a period of 1 h yielding **1** as the main product.

The species **2a** and **4a** were prepared analogously:

2a IR (THF): $\nu(\text{CO})$ 1934s, 1896w, 1765m; $\nu(\text{CN})$ 2140w cm^{-1} ;

4a IR (THF): $\nu(\text{CO})$ 1933s, 1894w, 1765m; $\nu(\text{CN})$ 2141w cm^{-1} .

Table 2

Comparison between the electrode potentials for the one-electron reduction of the μ -cyanoalkylidene complexes $[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C}(\text{CN})(\text{X})\}]^-$ and their phosphine-substituted complexes $[\text{Fe}_2(\text{CO})(\text{PMe}_2\text{Ph})(\text{cp})_2(\mu\text{-CO})\{\mu\text{-C}(\text{CN})(\text{X})\}]^-$ in MeCN

Complex	$E^{0'}$ (V vs. SCE)	Ref.
1	−1.02	^a
12	−1.32 ^b	^a
4	−1.32	^a
14	−1.56 ^b	^a
$[\text{Fe}_2(\text{CO})_2(\text{cp})_2(\mu\text{-CO})(\mu\text{-CSMe})]^+$	−0.78	[7b]
$[\text{Fe}_2(\text{CO})(\text{PMe}_2\text{Ph})(\text{cp})_2(\mu\text{-CO})(\mu\text{-CSMe})]^+$	−1.14	[7b]

^a Present work; ^b peak potential value measured at 0.2 V s^{-1} .

3.2.2. Synthesis of $[\text{Fe}_2(\text{cp})_2(\text{CO})(\text{PMe}_2\text{Ph})(\mu\text{-CO})\{\mu\text{-C}(\text{CN})_2\}]$, **12**

(a) To a mixture of **1** (83 mg, 0.21 mmol) and PMe_2Ph (0.17 g, 1.277 mmol) in THF (20 ml) at 0°C , NaNp was added (0.7 ml, 0.3 mol dm^{-3} in THF). The solution was allowed to warm to room temperature and stirred for 90 min. Then the solvent was removed under vacuum and the greenish-brown residue was washed with hexane, redissolved in CH_2Cl_2 and chromatographed on an alumina column, eluting with CH_2Cl_2 –petroleum ether (bp. $40\text{--}70^\circ\text{C}$) (1:1, v:v). A first red fraction contained some unreacted **1** (8 mg). A second brown fraction was collected, evaporated to dryness and the residue crystallized from CH_2Cl_2 layered with n-pentane at -20°C yielding **12** (12%). Anal. Calc. for $\text{C}_{23}\text{H}_{21}\text{Fe}_2\text{N}_2\text{O}_2\text{P}$: C, 55.2; H, 4.2. Found: C, 55.41; H, 4.18%. IR (CH_2Cl_2): $\nu(\text{CO})$ 1970s, 1778m; $\nu(\text{CN})$ 2172w cm^{-1} . ^1H NMR (CDCl_3): δ 7.81–7.43 (m, 5 H, Ph), 4.96 (s, 5 H, cp), 4.39 (d, $J_{\text{PH}} = 1.7 \text{ Hz}$, 5 H, cp), 1.54 (d, $J_{\text{PH}} = 9.4 \text{ Hz}$, 3 H, Me), 1.14 (d, $J_{\text{PH}} = 9.4 \text{ Hz}$, 3 H, Me).

(b) Compound **1** (79 mg, 0.20 mmol) in CH_2Cl_2 (20 ml) was treated with PMe_2Ph (42 mg, 0.30 mmol) in the presence of anhydrous Me_3NO (0.20 mmol). The mixture was stirred for 2 h at room temperature and then evaporated to dryness. The residue was worked up as described above affording **12** in 65% yield.

3.2.3. Synthesis of $[\text{Fe}_2(\text{cp})_2(\text{CO})(\text{PMe}_2\text{Ph})(\mu\text{-CO})\{\mu\text{-C}(\text{CN})(\text{H})\}]$, **13**

(a) Complex **13** was obtained by a procedure similar to that described for the synthesis of **12**, by reaction of **2** (94 mg, 0.26 mmol) with PMe_2Ph (0.21 g, 1.55 mmol) and NaNp (0.26 mmol). Yield 1%. Anal. Calc. for $\text{C}_{22}\text{H}_{22}\text{Fe}_2\text{NO}_2\text{P}$: C, 55.6; H, 4.7. Found: C, 55.41; H, 4.18%. IR (CH_2Cl_2): $\nu(\text{CO})$ 1943s, 1760m; $\nu(\text{CN})$ 2144w cm^{-1} . ^1H NMR (CDCl_3): δ 7.82–7.46 (m, 5 H, Ph), 4.90 (s, 5 H, cp), 4.35 (d, $J_{\text{PH}} = 1.5 \text{ Hz}$, 5 H, cp), 1.25 (d, $J_{\text{PH}} = 9.1 \text{ Hz}$, 3 H, Me), 1.00 (d, $J_{\text{PH}} = 9.1 \text{ Hz}$, 3 H, Me).

(b) A mixture of **2** (60 mg, 0.16 mmol), PMe_2Ph (0.25 mmol) and anhydrous Me_3NO (0.16 mmol) was stirred in CH_2Cl_2 (20 ml) at room temperature for 6 d. The mixture was then treated as described for the synthesis of **12** yielding **13** (7%).

3.2.4. Synthesis of $[\text{Fe}_2(\text{cp})_2(\text{CO})(\text{PMe}_2\text{Ph})(\mu\text{-CO})\{\mu\text{-C}(\text{CN})(\text{SMe})\}]$, **14**

(a) Complex **14** was obtained by a procedure similar to that described for the synthesis of **12**, by reaction of **4** (0.15 g, 0.36 mmol) with PMe_2Ph (0.30 g, 2.16 mmol) and NaNp (0.36 mmol). Yield 9%. Compound **14** was identified by comparison of its spectroscopic properties with those reported in the literature [23].

(b) A mixture of **4** (83 mg, 0.20 mmol), PMe_2Ph (41 mg, 0.30 mmol) and anhydrous Me_3NO (0.20 mmol)

was stirred in CH_2Cl_2 (20 ml) at room temperature for 2 d. The mixture was then treated as described for the synthesis of **12** yielding **14** (45%).

(c) To a solution of **4** (0.27 g, 0.65 mmol) in MeCN (150 ml) was added PMe_2Ph (97 mg, 0.70 mmol) and the solution was irradiated under dinitrogen with a low-pressure UV lamp for 30 min. The solvent was then removed under vacuum and the residue chromatographed on an alumina column eluting with a CH_2Cl_2 –hexane (1:1, v:v). A brown fraction was collected and evaporated to dryness, affording **14** as brown microcrystalline solid (75% yield).

3.2.5 Synthesis of $[\text{Fe}_2(\text{cp})_2(\mu\text{-CO})(\mu\text{-dppm})\{\mu\text{-C}(\text{CN})_2\}]$, **15**

To a solution of **1** (80 mg, 0.21 mmol) in toluene (20 ml) was added dppm (0.14 g, 0.36 mmol) and the mixture was photolysed, in a quartz tube under a stream of dinitrogen, for 90 min. Then the solvent was removed under vacuum, and the residue, redissolved in CH_2Cl_2 , was chromatographed on an alumina column (10 × 2 cm). Elution with CH_2Cl_2 first gave a green fraction containing some monosubstituted derivative $[\text{Fe}_2(\text{cp})_2(\text{CO})(\text{dppm})(\mu\text{-CO})\{\mu\text{-C}(\text{CN})_2\}]$ (16 mg, 10%). Anal. Calcd. for $\text{C}_{40}\text{H}_{32}\text{Fe}_2\text{N}_2\text{O}_2\text{P}_2$: C, 64.4; H, 4.3. Found: C, 65.1; H, 4.4%. IR (CH_2Cl_2): $\nu(\text{CO})$ 1969 s, 1779s; $\nu(\text{CN})$ 2172 mw cm^{-1} . ^1H NMR (CDCl_3): δ 8.1–6.8 (m, 20 H, Ph), 4.94 (s, 5 H, cp), 4.26 (s, br, 5 H, cp), 2.28 (m, 2 H, CH_2). A second red fraction was collected and evaporated to dryness under reduced pressure, and the residue crystallized from CH_2Cl_2 –hexane to yield 98 mg (65%) of complex **15**. Anal. Calc. for $\text{C}_{39}\text{H}_{32}\text{Fe}_2\text{N}_2\text{OP}_2$: C, 65.2; H, 4.4. Found: C, 66.0; H, 4.9%. IR (CH_2Cl_2): $\nu(\text{CO})$ 1727s; $\nu(\text{CN})$ 2165m cm^{-1} . ^1H NMR (CDCl_3): δ 7.4–7.6 (m, 20 H, Ph), 4.45 (s, br, 10 H, cp), 1.50 (s, br, 2 H, CH_2). ^{13}C NMR (CD_2Cl_2): δ 288.6 ($\mu\text{-CO}$, t, $J_{\text{PC}} = 16$ Hz), [141.6 ($J_{\text{PC}} = 26$ Hz), 135.2 ($J_{\text{PC}} = 5$ Hz), 132.0 ($J_{\text{PC}} = 4$ Hz), 129.4 ($J_{\text{PC}} = 5$ Hz), Ph], 133.5 ($\mu\text{-C}$, $J_{\text{PC}} = 20$ Hz), 131.3, 130.4 (CN), 89.3 (Cp), 23.8 (CH_2 , t, $J_{\text{PC}} = 17$ Hz).

3.2.6 Synthesis of $[\text{Fe}_2(\text{cp})_2(\mu\text{-CO})(\mu\text{-dppm})\{\mu\text{-C}(\text{CN})(\text{H})\}]$, **16**

Complex **16** was obtained following the procedure described for the synthesis of compound **15** starting from **2** (80 mg, 0.22 mmol). Chromatography of the reaction products first gave a red fraction containing some unreacted **2** (12 mg). A second green fraction contained the monosubstituted product $[\text{Fe}_2(\text{cp})_2(\text{CO})(\text{dppm})(\mu\text{-CO})\{\mu\text{-C}(\text{CN})(\text{H})\}]$, (9%). IR (CH_2Cl_2): $\nu(\text{CO})$ 1939s, 1760s; $\nu(\text{CN})$ 2145mw cm^{-1} . Finally, the third reddish-brown fraction yielded 79 mg (52%) of complex **16**. Anal. Calc. for $\text{C}_{38}\text{H}_{33}\text{Fe}_2\text{NOP}_2$: C, 68.5; H, 4.8. Found: C, 69.1; H, 5.0%. IR (CH_2Cl_2): $\nu(\text{CO})$ 1702s; $\nu(\text{CN})$ 2139mw cm^{-1} . ^1H NMR (CDCl_3): δ

7.4–6.9 (m, 20 H, Ph), 4.47 (s, 10 H, cp), 3.91 (m, 1 H, $\mu\text{-CHCN}$), 1.60 (m, 2 H, CH_2).

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