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Electrochemical behaviour of tropone diiron pentacarbonyl complexes, $Fe_2(CO)_5[(RC_2R)_3CO]$ (R = Me, Et, n-Pr). Formation of a carbon–carbon bond upon reduction

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Abstract

We herein describe the electrochemical behaviour of some tropone diiron pentacarbonyl complexes $Fe_2(CO)_5[(RC_2R)_3CO]$ (R = Et, Me, n-Pr). All these compounds exhibit a cyclic voltammetric (CV) response consisting of an electrochemically and chemically reversible one-electron reduction process at moderate cathodic potentials and a totally irreversible further reduction at c. −2 V versus SCE. At room temperature (in the long electrolysis time scale) the electrogenerated monoanion $Fe_2(CO)_5[(RC_2R)_3CO]^-$ smoothly but completely decomposes to $Fe(CO)_3[(RC_2R)_3CO]$. In this process the organic chain rearranges, and a new C–C bond is formed.

Introduction

Complexes of general formula $Fe_2(CO)_5[(RC_2R)_3CO]$ (Fig. 1) in which three acetylenic molecules oligomerize with CO insertion to form a σ/π bonded cycloheptatrienone (tropone) diradical, can be easily obtained by reaction of iron carbonyls with excess of alkynes [1]. Detailed structural descriptions have been reported for two of them, namely $Fe_2(CO)_5[(RC_2H)_3CO]$ (R = Ph [2a]; t-Bu [2b]), where the organic chain acts as an overall 8e donor. We have been interested in organometallic electrochemistry [3], in particular in evaluating the factors responsible for the stability of the electrogenerated ions. In binary metal carbonyl complexes, the HOMO and LUMO are generally metal–metal bonding and antibonding in character, respectively. Thus the anodic oxidation or the cathodic reductions of such complexes cause quick and irreversible decomposition. The coordination of large organic moieties should be able to clasp the metal atoms together and then to stabilize the electrogenerated ionic species [3]. In this context, tropone diiron complexes might represent good candidates since the cycloheptatrienone diradical interacts with the metallic moiety in a multicentered σ/π fashion [2].

Results and discussion

Syntheses

Since the title complexes are binuclear, we allowed $Fe_2(CO)_9$ to react with a four-fold excess of appropriate alkyne (3-hexyne, 2-butyne and 4-octyne, respectively) at room temperature. This procedure afforded binuclear complexes only, namely the tropone $Fe_2(CO)_5[(RC_2R)_3CO]$ (R = Et (**1**) 25%; Me (**2**) 10%; n-Pr (**3**) 10% yield), the ferrole $Fe_2(CO)_6[(RC_2R)_2]$ [1], and the flyover-bridge $Fe_2(CO)_6[(RC_2R)_2CO]$ [1] derivatives.

NMR investigations

We have investigated the spectroscopic properties of $Fe_2(CO)_5[(EtC_2Et)_3CO]$ (**1**) with several NMR techniques in order to be able to assign all the resonances in the spectrum [4]. The 1D proton spectrum at high magnetic field (9.4 T) shows quite a complicated pattern in the region 3.62–0.75 ppm due to the presence of six different ethyl groups. The proximity of the signals ruled out any possibility of assignment by using selective

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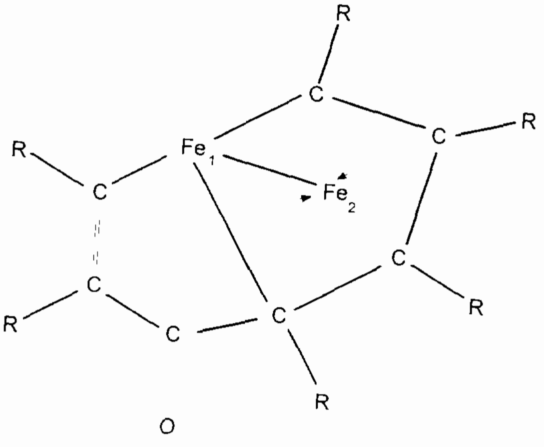

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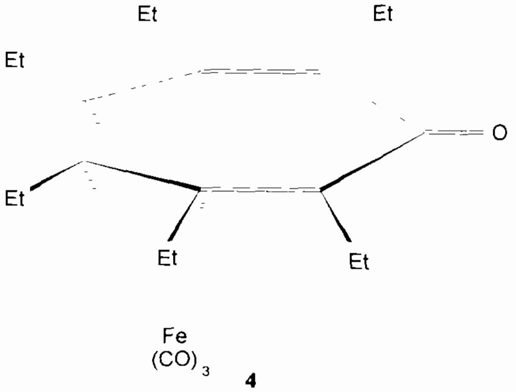

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Fig. 1. Sketch of the structures of $Fe_2(CO)_5[(RC_2R)_3CO]$ compounds (R = Et (**1**), Me(**2**), n-Pr (**3**). Carbonyl ligands are omitted for clarity; Fe_1 stands for $Fe(CO)_3$, Fe_2 stands for $Fe(CO)_2$ moieties. Sketch of the structure of $Fe(CO)_3[(RC_2R)_3CO]$ (**4**)

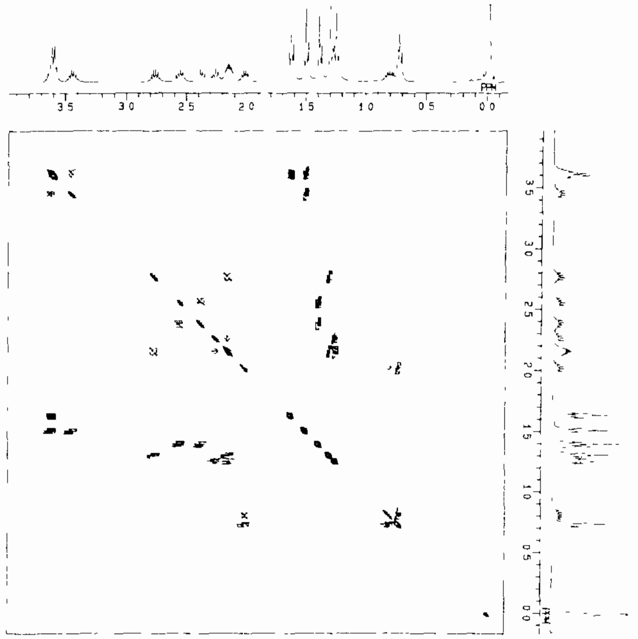

Fig. 2 Contour plot of the homonuclear (^1H–^1H) correlation spectrum (COSY) of **1** recorded at 40 °C in $CDCl_3$. The one-dimensional proton spectra are shown along both directions.

TABLE 1. Chemical shifts and assignment of proton NMR resonances in **1** and **2**

1	H_A	H_B	CH_3	2	H
Et_1	3.62	3.44	1.49	Me_1	3.15
Et_2	2.75	2.15	1.29	Me_2	3.12
Et_3	2.55	2.38	1.38	Me_3	2.17
Et_4	2.23	2.14	1.24	Me_4	2.07
Et_5	3.63	3.63	1.61	Me_5	1.68
Et_6	2.00	0.81	0.72	Me_6	0.84

decoupling techniques. A 2D COSY spectrum (Fig. 2) allowed us to assign the connectivities of five different ABX_3 and one A_2X_3 pattern (Table 1). The A_2X_3 system can be likely assigned to the ethyl group linked to the unique sp^3 hybridized carbon atom of the tropone chain (Et_5 resonance in Table 1). All ^{13}C NMR signals except two have been assigned for the organic chain on the basis of their chemical shifts and peak multiplicities under off resonance ^1H decoupling (Table 2). The presence of eight resonances in the downfield region (213–200 ppm) required further investigation for complete assignment. On performing the reaction using a ^{13}CO enriched sample of $Fe_2(CO)_9$, we can easily assign the five carbonyl resonances and the ketonic one with respect to the other two signals (attributed to the σ/π bonded acetylenic carbon atoms) simply on the basis of intensity comparison. An interesting result was achieved by direct, heterogeneous enrichment of **1** in the presence of gaseous CO in a sealed ampoule (0.5 atm., *c.* 90% ^{13}C-enriched). After 4 days of stirring at 50 °C, the ^{13}C spectrum of **1** shows selective exchange of free ^{13}CO with the carbonyl groups responsible for the resonances at 201.6 and 210.7 ppm. Larger reaction times allows the labelled ligand to distribute equally in all the available sites (five) except the ketone CO, therefore such a resonance has been unambiguously identified. Based on the assumption that localized scrambling of the carbonyl ligands is presumably faster than the delocalized exchange between those bonded to different metal atoms, we can assign the two resonances at 210.7 and 201.6 ppm at the carbonyls bonded to the Fe_2 atom (Fig. 1). To the best of our knowledge, this represents one of the few cases reported in the literature [5] in which specific intermolecular exchange of coordinated CO with gaseous ^{13}CO occurs well before the isotopic enrichment being distributed statistically by intramolecular scrambling. Derivative **2** shows similar NMR features (Tables 1 and 2).

Electrochemical behaviour

Figure 3 shows the cyclic voltammetric CV) response of an acetonitrile solution of **1** at a hanging mercury

TABLE 2 Chemical shifts and assignment of carbon NMR resonances in **1** and **2**

	C_{ac}	C=O	C_{ac}	$Fe(CO)_3$	$Fe(CO)_2$	CH_2	CH_3
1	213.31	206.15	117.35	211.81	210.71	42.88	18.75
	212.64		103.77	210.88	201.57	39.10	16.51
			85.17	209.61		32.68	15.90
			66.82			28.75	15.85
						26.39	12.33
						25.94	12.24
2	206.6	201.1	212.2	211.7	209.4		33.6
	203.6		95.3	211.1	200.2		30.8
			82.6	208.3			24.7
			58.2				24.7
							19.7
							17.2

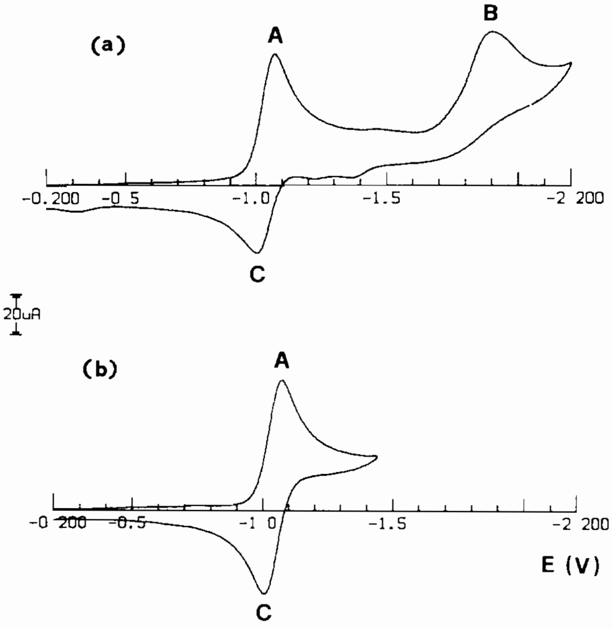

Fig. 3. Cyclic voltammetric (CV) response of an acetonitrile solution of **1** (1.9×10^{-3} M) containing $[Bu_4N][PF_6]$ supporting electrolyte at an Hg electrode, room temperature, scan rate 0.2 mV s^{-1}.

drop electrode (HMDE). Two distinct cathodic processes (A and B) are present, only the first one displaying a directly associated reoxidation peak (C). A similar feature was briefly reported by Dessy and Pohl in dimethoxyethane [6]. Controlled potential coulometry carried out at an Hg pool working macroelectrode in correspondence with the first cathodic process ($E_w = -1.20$ V) indicates the consumption of 1 mol of electrons/mol of **1**. CV tests performed during the electrolysis showed that extensive decomposition has occurred in the longer electrolysis time scale. Indeed, **1** could be obtained from the reduction/reoxidation cycle at room temperature only in *c.* 30% yield. This recovery increases as the temperature of electrolysis decreases, being almost quantitative at −20 °C. Concerning the peak system A/C (Fig. 3(b)), the analysis of the CV response with scan rates (v) varying from 0.02 to 2.00 V s^{-1} shows that: (i) the current function $i_p(A)/v^{1/2}$ remains practically constant; (ii) the peak current ratio $i_p(C)/i_p(A)$ is constantly equal to 1 indicating that the $\mathbf{1}/\mathbf{1}^-$ redox change is chemically reversible (persistence of the monoanion $\mathbf{1}^-$ in CV time scale); (iii) the peak to peak separation, $\Delta E_p = E_p(C) - E_p(A)$, is constantly equal to 60 mV, indicating that the $\mathbf{1}/\mathbf{1}^-$ redox process in Nernstian (fast electron transfer process) and likely does not involve important geometrical reorganizations. The polarographic responses of an acetonitrile solution of **1** at a dropping mercury electrode (DME) confirm the CV results. Two well-defined reduction steps at $E_{1/2}(0/1-) = -1.03$ V and $E_{1/2}(1-/2-) = -1.88$ V versus SCE are observed: the first reduction wave corresponds to an electrochemically reversible one-electron process (E versus log $(i_d - i)/i$ linear and slope 58 mV) while the second one behaves as totally irreversible: E versus log $(i_d - i)/i$ slopes 167 mV. All these data are diagnostic [7] for a simple electrochemically and chemically reversible 1e reduction, at least in the short CV time scale, followed by the totally irreversible reduction of monoanion at −1.90 V versus SCE. The same electrochemical behaviour was observed in acetone and THF solutions. Upon changing the electrode material from Hg to Pt a slightly lower electrode transfer rate was detected. The higher electrochemical reversibility at the Hg with respect to the Pt electrode is quite common in organometallic electrochemistry and has been sometimes attributed to mercury stabilized intermediates formed at the electrode surface [8]. At the Pt electrode, a very broad anodic peak is also observed (E_p *c.* 1.2 V versus SCE). The height of such oxidation peak, when compared with those of the two reduction peaks, suggests a multi-electron transfer process. The severe fouling of the Pt electrode prevents any detailed study of such oxidation process.

The voltammetric picture now described is qualitatively common to all other diiron complexes, and their most relevant electrochemical parameters in the abovesaid non-aqueous solvents are reported in Table 3. The reduction potentials are modulated by the electronic properties of the tropone substituents, R, as expected [3].

In order to obtain further information on the decomposition of the radical anion **1**$^-$, we performed an exhaustive electrolysis of an acetonitrile solution of **1** at −20 °C and then froze the sample in liquid nitrogen. The resulting EPR spectrum in CH_3CN glassy solution is reported in Fig. 4(a) and (b). The first derivative lineshape (Fig. 4(a)) is nearly isotropic, while the second derivative spectrum (Fig. 4(b)) displays a poorly resolved axial symmetry. The spectral features, which point out the unpaired spin density being metal in character [9], can be interpreted in terms of an $S=1/2$ spin Hamiltonian. The relevant EPR parameters are $g_{\parallel}=2.035$; $g_{\perp}=2.017$; $<g>_{calc}=1/3(g_{\parallel}+g_{\perp})=2.023\pm0.005$; ΔH (first derivative) $=32\pm2$ G. The increase of the temperature induces marked changes in the EPR spectrum indicating the partial decomposition of the $\{Fe_2(CO)_5[(RC_2R)_3CO]\}^-$ radical. At room temperature (Fig. 4(c)) the original resonance of **1**$^-$ (at $g_{iso}=2.019\pm0.005$, $\Delta H=3\pm2$ G) is accompanied by small signals due to new paramagnetic species, produced by the fragmentation of **1**$^-$.

TABLE 3. Redox potentials (V vs. SCE) for the diiron complexes $[Fe_2(CO)_5(RC_2R')_3CO]$ in different solvents at an Hg electrode

Compounds	Solvent	$E^{0\prime}(0/1-)$[a]	$E_p(1-/2-)$[b]
1	MeCN	−1.04	−1.90
1	acetone	−0.85	−1.91
1	THF	−0.91	−1.95
2	MeCN	−0.98	−1.85
3	MeCN	−1.09	−2.19

[a] Evaluated as $[E_p(A)+E_p(C)]/2$. [b] Measured at 0.2 V s^{-1}.

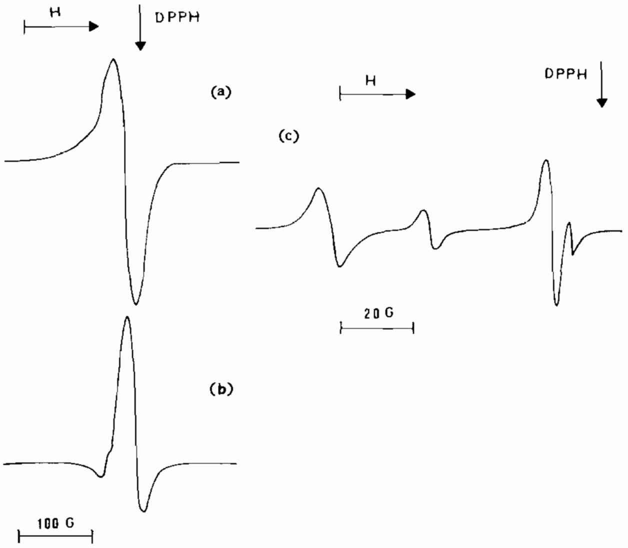

Fig. 4. X-band EPR spectrum of an acetonitrile solution of **1** exhaustively electrolyzed at −1.2 V: (a) first derivative spectrum, and (b) second derivative spectrum at −150 °C (glassy solution); (c) first derivative spectrum at room temperature.

The solution recovered after 1e exhaustive electrolysis at room temperature was dried at reduced pressure, the residue extracted with hot toluene and filtered on a silica column in order to remove the supporting electrolyte. From the eluate a yellow compound was isolated (*c.* 70% yield) and identified as the mononuclear $Fe(CO)_3[(EtC_2Et)_3CO]$ (**4**) derivative by means of IR and ^1H NMR spectroscopy, and MS spectrometry [10].

The CV response of an acetonitrile solution of an authentic sample of $Fe(CO)_3[(EtC_2Et)_3CO]$ (**4**) at an Hg electrode (Fig. 5) shows a chemically irreversible 1e reduction process at $E_p(D)=-1.58$ V. In other words, **4** is electroinactive at the working potential of 1e exhaustive electrolysis (i.e. −1.20 V).

These data suggest that **1**$^-$ is indefinitely stable only at low temperature. At room temperature, complete cleavage of the Fe–Fe bond occurs and the monoanion **1**$^-$ rearranges to $Fe(CO)_3[(EtC_2Et)_3CO]$, forming a new C–C bond in the organic chain, and loses an '$Fe(CO)_2{}^-$' fragment, probably in a highly solvated form. Precedent for the electrogeneration of highly unsaturated iron carbonyl anions can be found in the literature [11]. The breaking of the iron–iron bond agrees with the EPR results and the metal–metal antibonding character of the LUMO, forecast by theoretical calculations [12]. Interestingly enough, the thermal transformation of $Fe_2(CO)_5[(RC_2R)_3CO]$ compounds derived from disubstituted acetylenes ($R\neq H$) to $Fe(CO)_3[(RC_2R)_3CO]$ complexes has not been observed in boiling benzene [1]. In the actual case, the simple 1e reduction produces the tropone complex $Fe(CO)_3[(EtC_2Et)_3CO]$ almost quantitatively in one-pot sequence. From such a mononuclear complex, free

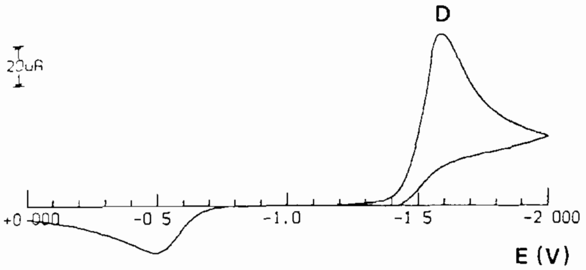

Fig 5 Cyclic voltammetric (CV) response of an acetonitrile solution of **4** (1.8×10^{-3} M) containing $[NBu_4][BF_4]$ (0.1 M) at an Hg electrode; scan rate 200 mV s^{-1}, room temperature

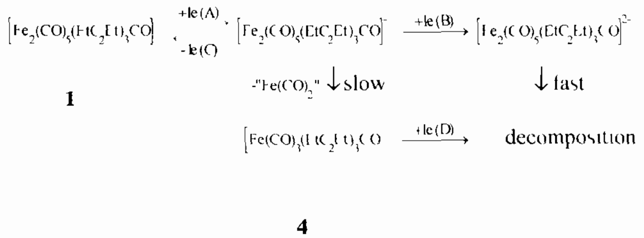

Fig. 6 Proposed mechanism for the electrochemical behaviour of **1** and **4**.

hexaethyl-tropone can be easily obtained by mild oxidation with trimethylamine-oxide [13].

On the contrary, the electrolysis of $Fe_2(CO)_5$-$[(EtC_2Et)_3CO]$ (**1**) at a working potential corresponding to the second reduction step ($E_w = -2.0$ V) caused complete decomposition even at −20 °C. Indeed, $Fe(CO)_3[(EtC_2Et)_3CO]$ (**4**), as soon as it is formed from $\mathbf{1}^-$, irreversibly decomposes at this working potential in agreement with its CV response previously described.

On the basis of the experimental results, we propose the electrochemical mechanism depicted in Fig. 6. This electrochemical pathway resemble those found for iron [14] and cobalt [15] flyover-bridge complexes.

Experimental

The title compounds **1**–**3** were synthesized by reacting a slurry of $Fe_2(CO)_9$ in anhydrous n-hexane with a four-fold excess of appropriate alkyne (3-hexyne, 2-butyne and 4-octyne, respectively) overnight. The dark brown solution was filtered and chromatographed on a silica column, using eluent mixtures of n-hexane/dichloromethane with increasing amount of the second solvent (from 1 to 10% vol./vol.). Their purity was checked by IR and ^{1}H NMR spectroscopy and MS spectrometry [1, 8]. Electron impact ionization (EI) mass spectra were recorded on a Kratos MS902 instrument with a direct inlet system and an ionizing energy of 70 eV. 1D and 2D NMR spectra were recorded at +40 °C on a Jeol EX 400 spectrometer operating at 400.0 and 100.4 MHz for ^{1}H and ^{13}C nuclei, respectively. Proton–proton correlation spectra were recorded by using the COSY-90 pulse sequence [16] with appropriate phase cycling. The free induction decays were acquired over 1024 data points and 2000 Hz for each of the 512 values of evolution time t_1. The raw data were zero filled and a sine-bell window function was applied prior to double Fourier transformation. The EPR spectra were recorded on a Bruker 200 D-SCR instrument operating at 9.78 GHz (X-band) and equipped with a variable-temperature ER 411 VT unit.

Electrochemical measurements were performed on both PAR 273 and BAS 100A electrochemical analysers A standard three-electrode cell was designed to allow the tip of the reference electrode to closely approach the working electrode. Positive feedback *iR* compensation was applied routinely. Since some *iR* drop distortion is present in the non-aqueous solvents, the peak-to-peak separation, ΔE_p, as a function of the CV scan rates, is compared to that of the $[\text{ferrocene}]^{0/1+}$ couple assumed to be 60 mV. Therefore, the statement Nernstian indicates a redox process as reversible as the oxidation of ferrocene is [17]. All measurements were carried out under Ar in anhydrous deoxygenated solvents; solutions were 1×10^{-3} M with respect to the compounds under study and 1×10^{-1} M with respect to the supporting electrolyte, $[Bu_4N][PF_6]$. The temperature of the solution was kept constant within 1 °C, by circulation of thermostatted water–ethanol mixture through the double wall of the cell. The reference electrode was a AgCl-coated silver wire dipped in a 0.1 M solution of $[Bu_4N][PF_6]$ in the relevant solvent (THF, CH_2Cl_2, CH_3COCH_3), and separated from the cell solution by a Vycor frit. At the end of each experiment, the potential of ferrocene couple was measured versus the pseudo-reference electrode and then versus an aqueous SCE, to which all data are referred. Under the actual experimental conditions the ferrocene/ferrocenium couple is located at +0.38 in MeCN, +0.54 in THF and +0.46 V versus SCE in CH_3COCH_3.

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