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Electron transfer reactions of bis[dicarbonyl(pentamethylcyclopentadienyl)iron] with 2,3-dichloro-5,6-dicyanobenzoquinone

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Abstract

The thermal and photochemical reactions of $[(C_5Me_5)Fe(CO)_2]_2$ with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) yield the binuclear complex $\{[(C_5Me_5)Fe(CO)_2]_2 \cdot (DDQ)_2\}$. EPR studies using nitroso spin traps support the conclusion that the primary products are $[(C_5Me_5Fe(CO)_2]^+$ radicals. The metal-centered radical transfers an electron to DDQ acceptor to yield $\{[(C_5Me_5)Fe(CO)_2]_2 \cdot (DDQ)_2\}$ as the only Fe-containing product. Spectroscopic evidence for dimerization of $DDQ^{\overline{\cdot}}$ to form diamagnetic $[DDQ]_2^{2-}$ in the solid is discussed.

Organometallic compounds containing metal–metal bonds have a remarkably rich chemistry [1]. This chemistry is dominated by cleavage of the metal–metal bond and involves the population of an orbital which is mainly antibonding (σ^*) in character with respect to metal–metal bond. A number of qualitative observations have been reported which clearly reveal a symmetrical cleavage of the CO bridged system following electronic excitation or thermal reactions with organic compounds [2,3]. Homolytic cleavage of the Fe–Fe bond dominates the photochemistry of $[(C_5Me_5)Fe(CO)_2]_2$, but photoreactions of the dimer, carried out in media such as pyridine or THF, give rise to net heterolytic cleavage products [1]. However, it is likely that such chemistry occurs as a consequence of disproportionation reactions of the $[(C_5Me_5)Fe(CO)_2]^+$ radicals that are the primary photoproducts [1]. It is noteworthy that the 17-electron iron radicals may subsequently undergo a single electron transfer (SET) process with organic and inorganic acceptors [2].

The application of the SET concept to photogenerated metal centered radicals can lead to a variety of interesting reactions such as:

- Electron transfer processes with organic substrates having various redox potentials.
- Formation of new inorganic compounds with unusual optical and magnetic properties.

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- Synthesis of electrically-conducting salts with polymers [4] and electron-rich olefins [5] to give semiconducting materials for practical applications.
- Generation of paramagnetic species with less than 18 electrons as good candidates for C–H bond activation.

This paper is concerned with the reactions of bis[dicarbonyl(pentamethylcyclopentadienyl)iron(I)] with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ).

Experimental

Materials. All solvents for synthesis and spectroscopic studies were of spectroquality and used as supplied. $[(C_5Me_5)Fe(CO)_2]_2$ was prepared by a published procedure [6]. 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) (Aldrich) was recrystallized from chloroform prior to use. Nitrosodurene (ND), used as spin trap, was prepared as previously described [7].

General data

All manipulations of oxygen- or water-sensitive materials were conducted under N_2 in a drybox or by use of standard Schlenk or vacuum-line techniques. Elemental analysis was performed by the microanalytical laboratory, University of Ferrara.

Infrared spectra were recorded with KBr disks on a Bruker IFS88 FTIR spectrometer. Solution UV–Vis spectra were recorded on a JASCO UVIDEC-650 recording spectrometer. EPR measurements were made at room temperature and at 77 K with both powder and solution samples on a Bruker ER200 D spectrometer. The compounds were prepared by the following procedures:

Method 1. A solution of DDQ (69 mg) in deoxygenated acetonitrile (6 ml) was slowly added at 30 °C to a suspension of an equimolar amount of $[(C_5Me_5)Fe(CO)_2]_2$ (150 mg) in deoxygenated acetonitrile (6 ml). The solution became brown. The UV–Vis spectrum was recorded immediately after filtration: λ_{max}: 585, 545, 506, 455, 432 and 345 nm. The multitude of absorptions in the visible region indicates the presence of $DDQ^{\cdot-}$ radicals since an identical spectrum is observed when $DDQ^{\cdot-}$ is formed from the reaction of $[Et_4N]I$ with DDQ [7]. The absorption band at 345 nm is due to the $\sigma_b \rightarrow \sigma^*$ transition of the bridged Fe species [3].

The reaction was also monitored by EPR spectroscopy. The acetonitrile solution at room temperature and a low gain showed a single EPR line with a g factor of 2.0052. With THF/HMPA 10 : 1 as solvent the solution showed a spectrum (Fig. 1) consisting of a quintet derived from a weak hyperfine interaction of the unpaired

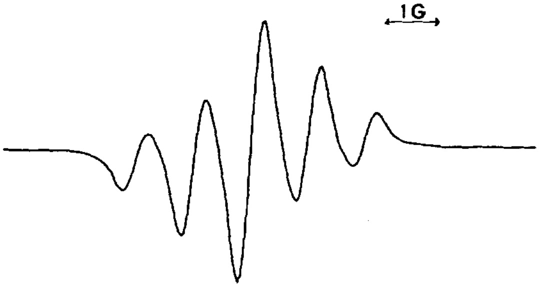

Fig. 1. EPR spectrum of $\{[(C_5Me_5)Fe(CO)_2]_2\cdot(DDQ)_2\}$ in THF/HMPA (10:1) at 293 K.

Table 1

Spectral properties of relevant compounds [a]

Compounds	UV–Vis, nm (ϵ)	IR, cm^{-1}
DDQ [b]	370 (870), 280 (123000) 270 (11500)	2250 ν(CN) 1680s, 1690s ν(CO) 1550s ν(C=C)
DDQ$^{\bar{\cdot}}$ [c]	588 (6300), 547 (5775) 508 (4350) 456 (6050), 432 (5275)	2217s ν(CN) 1635m ν(CO) 1550s ν_{ar}(C=C)
$[(C_5Me_5)Fe(CO)_2]_2$	515 (720), 410 (5775) 346 (9160)	1919s ν(CO) terminal 1743s ν(CO) bridge 1357s δ(CH)
$\{[(C_5Me_5)Fe(CO)_2]_2 \cdot (DDQ)_2\}$		2219 ν(CN) 2049s, 1999s ν(CO) terminal 1541s ν_{ar}(C=C) 1405s δ(CH)
$[(C_5Me_5)Fe(CO)_2(THF)]^+$ [d]	403(600), 347 (885)	2070s, 2005s ν(CO) terminal 1400s δ(CH)
$[(C_5Me_5)Fe(CO)_2(Py)]^+$ [e]	404 (605), 350 (890)	2070s, 2010s ν(CO) terminal 1405s δ(CH)

[a] All spectral data are for CH_3CN solutions at 298 K unless otherwise noted. [b] DDQ = 2,3-Dichloro-5,6-Dicyanobenzoquinone. [c] $[N(Et)_4]^+$ salt. [d] DDQ$^{\bar{\cdot}}$ salt in THF at 298 K. The carbonyl absorption of the coordinated tetrahydrofurane molecule occurs at ca. 1445 cm^{-1}, [e] DDQ$^-$ salt in dichloromethane–Pyridine (90/10 in Vol.) at 298 K.

electron with two equivalent ^{14}N nuclei ($\alpha_N = 0.6$ G; g = 2.00517), corresponding to the DDQ$^{\bar{\cdot}}$ radical anion [8].

The brown solution was heated for 2 h at 60 °C then filtered and the solvent removed under vacuum. The solid was taken up in $ClCH_2CH_2Cl$, leaving a large amount of an insoluble dark solid. The FT-IR spectrum of the solid (Table 1) showed absorptions attributable to $\{[(C_5Me_5)Fe(CO)_2]_2 \cdot (DDQ)_2\}$. The elemental analysis was satisfactory: Found: C, 50.75; H, 3.22; N, 5.85; Mw = 946.6. $C_{40}H_{30}Fe_2O_8N_4Cl_4$ calcd.: C, 50.66; H, 3.19; N, 5.9%; Mw = 948.22.

Method 2. A solution containing $[C_5Me_5)Fe(CO)_2]_2$ ($2 \cdot 10^{-3}$ *M*) and DDQ ($2 \cdot 10^{-3}$ *M*) was photolyzed ($\lambda = 350$ nm) for 1 h, during which the colour of solution changed from red to dark brown. Infrared spectroscopy (Table 1 and Fig. 2) revealed prominent bands at 2219 cm^{-1} ν(CN), 2049 and 1999 cm^{-1} ν(CO), 1541 cm^{-1} ν_{ar}(C=C), 1405 cm^{-1} δ(CH). No absorption at 1919 cm^{-1} due to ν(CO) of the starting bridged form of iron complex was noted. After the irradiation (1 h), the solution was filtered and the solid washed with $ClCH_2CH_2Cl$ and dried *in vacuo*. Its IR spectrum was identical with that of the material prepared by Method 1.

The outcome of other photoreactions was investigated by UV–Vis spectroscopy without isolation of the carbonyl product $\{[(C_5Me_5)Fe(CO)_2]_2 \cdot (DDQ)_2\}$. In a typical reaction an equimolar (10^{-3} *M*) mixture of $[(C_5Me_5)Fe(CO)_2]_2$ and DDQ in acetonitrile was irradiated with 350 nm light. The course of the photoreaction was monitored by periodically recording the UV–Vis spectrum. Irradiation was continued until the spectrum either showed no further changes or the initially formed products began to decompose. Primary photoproducts were identified by EPR spin trapping experiments with direct photolysis of $[(C_5Me_5)Fe(CO)_2]_2$ in the EPR cavity in the presence of ND as spin trap. The SET reaction was calibrated with a solution prepared by the *in situ* reduction of DDQ with an excess of $[Et_4N]I$ (assuming complete conversion to the anion). Analysis of the $DDQ^{\cdot-}$ band (Table 1) at 588nm ($\epsilon = 6300\ M^{-1}\ cm^{-1}$) indicated a 98.6% yield of $\{[(C_5Me_5)Fe(CO)_2]^+(DDQ)^{\cdot-}\}$ after 1 h of irradiation.

Results and discussion

The dinuclear carbonyl bridged compound $[(C_5Me_5Fe(CO)_2]_2$ reacts readily in acetonitrile with a stoichiometric amount of DDQ under nitrogen. The acetonitrile solution turns brown and the bands in the visible region of the spectrum are identical to those observed for solutions of the $DDQ^{\cdot-}$ generated electrochemically or chemically by reaction of DDQ with $[Et_4N]I$ [7]. Very revealingly the solution displays an unresolved EPR signal at $g = 2.0052$ identical with that obtained in the reaction of DDQ with $[C_{10}H_8]Na$ in the same solvent.

Upon increasing the polarity and nucleophilicity of the solvent by use of THF/HMPA (10 : 1) a good resolution of signal was obtained. The spectrum consists of a quintet with hyperfine interactions, identical with that observed for $[Et_4N]^+(DDQ)^{\cdot-}$ [8].

In an attempt to distinguish between the primary homolytic cleavage of Fe–Fe bond of $[(C_5Me_5)Fe(CO)_2]_2$ and a process involving a thermal SET reaction of photoproducts some EPR spin trapping experiments were carried out. Significantly photolysis of $[(C_5Me_5)Fe(CO)_2]_2$ in acetonitrile solution containing ND (as spin trap) but in absence of DDQ produces an EPR signal with a g factor (2.0064) and a coupling constant ($a_N = 1.735$ mT) identical with the one observed for the spin adduct formed when the $[(C_5Me_5)Fe(CO)_2]^{\dagger}$ radical interacts with nitrosodurene [9]. This result confirms previous photochemical studies that indicated homolysis to the radical $[(C_5Me_5)Fe(CO)_2]^{\dagger}$ [1,9,10]. To complement the above EPR experiments, a competition reaction between ND and DDQ with $[(C_5Me_5)Fe(CO)_2]^{\dagger}$ was performed. The photolysis of $[(C_5Me_5)Fe(CO)_2]_2$ with an equimolar mixture of ND and DDQ yields in the first stage of photoreaction only the EPR signal of the spin adduct of the metal-centered radical with ND. We regard the EPR results as consistent with formation of $[(C_5Me_5)Fe(CO)_2]^{\dagger}$ radicals as primary photoproducts (eq. 1) and transfer of an electron from these radicals to DDQ in a thermal SET reaction (eq. 2).

$$\underset{(1)}{[(C_5Me_5)Fe(CO)_2]_2} \xrightarrow{h\nu} 2[(C_5Me_5)Fe(CO)_2]^{\dagger} \tag{1}$$

$$[(C_5Me_5)Fe(CO)_2]^{\dagger} + DDQ \xrightarrow{SET} \underset{(2\ \text{solution})}{[(C_5Me_5)Fe(CO)_2]^{+}[DDQ]^{\cdot-}} \tag{2}$$

$$\underset{(2\ \text{solution})}{2[(C_5Me_5)Fe(CO)_2]^{+}[DDQ]^{\cdot-}} \rightarrow \underset{(3\ \text{solid state})}{\{[(C_5Me_5)Fe(CO)_2]_2 \cdot (DDQ)_2\}} \tag{3}$$

Compound **3** is diamagnetic, as indicated by measurements on a Faraday balance at room and liquid nitrogen temperatures. Furthermore, the EPR measurements of

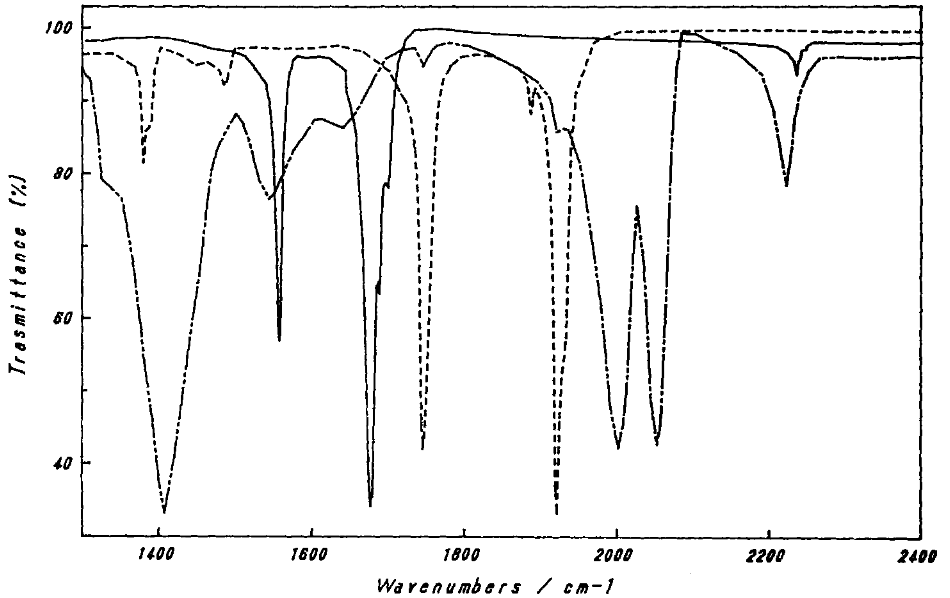

Fig. 2. Key infrared bands for $\{[(C_5Me_5)Fe(CO)_2]_2 \cdot (DDQ)_2\}$ (–··–), $[(C_5Me)Fe(CO)_2]_2$ (— — —) and DDQ (———) at 293 K in KBr pellets.

the solid shows the absence of the $DDQ^{\overline{\cdot}}$ radical. These observations indicate that in the solid state the single unpaired electron on $DDQ^{\overline{\cdot}}$ becomes paired, probably as consequence of the spontaneous dimerization of the radical $DDQ^{\overline{\cdot}}$ to $[DDQ]_2^{2-}$ [8]. The observations suggest that **3** has a stack structure involving $[DDQ]_2^{2-}$ dimers held together by $[(C_5Me_5)Fe(CO)_2]^+$ cations. There is structural information on $[DDQ]_2^{2-}$; it has been observed in the $[Et_4N]I$ and tetrathiofulvalenium salts, in which intra-dimer separations are 2.906 and 2.97 Å, respectively [11,12]. Thus dimerization of $DDQ^{\overline{\cdot}}$ can account for the diamagnetic electron configuration by enabling coordination of the dianion via the cyano groups to the 17 electron species $[(C_5Me_5)Fe(CO)_2]^+$.

Arguments in favour a dimeric structure involving nitrogen coordination are as follows:

(i) In the complex $\{[(C_5Me_5)Fe(CO)_2]_2 \cdot (DDQ)_2\}$ the IR vibration frequencies $\nu(CO)$ of the organometal fragment are shifted to higher energies, while those of DDQ $\nu(CN)$ and $\nu_{ar}(C{=}C)$ are shifted to lower energies (Table 1). The important observations here is the presence of frequencies due only to terminal CO (2049 cm^{-1}, 1999 cm^{-1}) and a broad strong band at 1405 cm^{-1} $\delta(CH)$, indicating a non-bridged iron cation $[(C_5Me_5)Fe(CO)_2]^+$ [3].

(ii) There is a shift of the absorption of the cyanide groups to lower frequency from that for free DDQ (Table 1).

(iii) The position and intensity of $\nu_{ar}(C{=}C)$ stretching at 1541 cm^{-1} is consistent with coordination through the CN groups of $[DDQ]_2^{2-}$ [11].

On the basis of these considerations and the spectroscopic results it can concluded that a charge transfer type structure for $\{[(C_5Me_5)Fe(CO)_2]_2 \cdot (DDQ)_2\}$ involves a sandwich arrangement with $[DDQ]_2^{2-}$ unit lying between two

$[(C_5Me_5)Fe(CO)_2]^+$ moieties. If there is a similar interaction between the iron species and $[DDQ]_2^{2-}$ dimer arranged in a chain similar to those observed in $[Et_4N]^+[DDQ]^{\cdot-}$ salt, the expected attractive interaction between permanent dipole moments of $DDQ^{\cdot-}$ anions may contribute to the stabilization of the dimeric structure in the complex **3** [11]. Nitrogen coordination, as described above, provides a reasonable means by which a dimeric species involving a chain of alternating $[DDQ]_2^{2-}$ and $[(C_5Me_5)Fe(CO)_2]^+$ cations could be formed. The existence of $DDQ^{\cdot-}$ radical anion in solvents of high coordinating ability and the complete dissociation of **3** giving UV–Vis detectable $[(C_5Me_5)Fe(CO)_2S]^+$ species (S = THF, pyridine) also seem plausible with this kind of structure. Thus it seems reasonable to envisage that the solvent S coordinating ability could destabilize the stacking of dimeric units $[DDQ]_2^{2-}$ in the solid to form the solvento-complex $[(C_5Me_5)Fe(CO)_2S]^+(DDQ)^{\cdot-}$.

The solvento complex $[(C_5Me_5)Fe(CO)_2S]^+$ must also be regarded as a good candidate for alkane and alkene C–H bond activation since its donor atom lability makes it a coordinatively unsaturated species [13]. Such reactions are being studied.

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