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Electron Transfer Reactions of Bis[dicarbonyl(pentamethylcyclopentadienyl)iron] with Organic Compounds

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Abstract

$[(C_5Me_5)Fe(CO)_2]_2$ (**A**) reacts with one equivalent of tetracyanoethylene (TCNE) and tetracyanoquinodimethane (TCNQ) to give the compounds $\{2[(C_5Me_5)Fe^+(CO)_2]\cdot TCNE^{2-}\}$ (**B**) and $\{2[(C_5Me_5)Fe^+(CO)_2]\cdot TCNQ^{2-}\}$ (**D**) respectively. The reaction of **A** with two equivalents of TCNE gives the polymeric compound $[(C_5Me_5)Fe(CO)_2TCNE]_n$ (**C**) in which the $TCNE^{2-}$ anion is coordinated to the metal through nitrogen of the CN group. Electronic, IR and ESR spectra indicate that compounds **B** and **D** are formed by two one-electron steps involving the rather elusive $[(C_5Me_5)Fe(CO)_2^{\bullet}]$ radicals. The electron transfer processes are discussed on the basis of the thermodynamic redox potentials of donor **A** and of two acceptors TCNE and TCNQ.

Introduction

Complexes of transition metals containing metal–metal bonds are remarkable for the richness of their chemistry [1]. In most compounds with this type of bond the valence molecular orbitals accessible to either oxidation or reduction, are usually largely M–M in character [2]. In relatively simple compounds like $[(C_5R_5)M(CO)_2]_2$ (R = H, Me; M = Fe, Ru) the highest energy filled molecular orbital appears to be σ(M–M). Electrons can be lost from M–M bonding which are essential to the structure and thus oxidation normally leads to changes in the primary structure $[(C_5R_5)M(CO)_2]_2 \rightarrow 2[(C_5R_5)M(CO)_2^{\bullet}]$.

From these considerations and from the available results of rapid-scan cyclic voltammetry [3] it may be supposed that upon oxidation of the neutral dimer, two electrons are removed from the metal–metal bond framework giving the corresponding paramagnetic $[(C_5R_5)M(CO)_2^{\bullet}]$ species. The expected properties are the ability of these systems:

(i) to render feasible studies of stoichiometric electron transfer reactions with substrates having various redox potentials;

(ii) to behave catalytically in electron transfer processes;

(iii) to generate thermally or photochemically [4] paramagnetic species (with less than 18 electrons) having a strong reactivity, *i.e.* the 17e radical $[(C_5Me_5)Fe(CO)_2^{\bullet}]$.

The following are reported here:

(a) Single and double electron transfer reactions of $[(C_5Me_5)Fe(CO)_2]_2$ (**A**) with TCNE and TCNQ forming the $TCNE^{\bar{\bullet}}$, $TCNE^{2-}$, $TCNQ^{\bar{\bullet}}$ and $TCNQ^{2-}$ anions.

(b) The examination of ESR, electronic and IR spectra of the paramagnetic intermediates formed in the electron transfer reaction.

(c) The product distribution and related formation mechanism of $\{2[(C_5Me_5)Fe^+(CO)_2]\cdot TCNE^{2-}\}$, $[(C_5Me_5)Fe(CO)_2\cdot TCNE]_n$ and $\{2[(C_5Me_5)Fe^+(CO)_2]\cdot TCNQ^{2-}\}$ compounds.

Experimental

Chemicals

$[(C_5Me_5)Fe(CO)_2]_2$ (Strem Chemicals), TCNE, TCNQ (Aldrich) were used without further purification. Where necessary solvents were dried by standard laboratory procedures. Solutions were degassed under vacuum. All experiments were carried out under an N_2 atmosphere.

General Procedures and Measurements

Elemental analyses were performed by Alfred Bernard Mikroanalytisches Laboratorium, Elbach, F.R.G. and by the Microanalytical Laboratory, University of Padova, Italy. Infrared spectra were obtained on a Perkin-Elmer 283 B infrared spectrophotometer and a Nicolet MX-1 spectrophotometer. UV–Vis spectra were obtained with a JASCO UVIDEC-650 recording spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker 80 Spectrometer. EPR measurements were made at room temperature and 77 K on both powder and solution samples using

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a Bruker ER 200D spectrometer. Mössbauer data were obtained with a 25 mCi ^{57}Co–Rh source.

Preparation of Compounds

$\{2[(C_5Me_5)Fe^+(CO)_2]\cdot TCNE^{2-}\}$ (B)

To a solution of **A** (0.988 g, 2 mmol) in boiling acetonitrile TCNE (0.256 g, 2 mmol) in hot acetonitrile (stoichiometry 1/1) was added. The reaction mixture was stirred and refluxed for 2 h after which time the volume was reduced to 10 cm^3. Upon cooling to room temperature complex **B** was obtained. *Anal.* Calc. for $C_{30}H_{30}Fe_2N_4O_4$: C, 57.94; H, 4.86; Fe, 17.96; N, 9.06. Found: C, 58.01; H, 4.78; Fe, 17.92; N, 8.98%. *Mw*: 620.88.

$[(C_5Me_5)Fe(CO)_2TCNE]_n$ (C)

TCNE and **A** were refluxed (2:1 ratio) in hot acetonitrile for 2 h. Upon cooling the solution to room temperature complex **C** was obtained. The complex was washed with benzene and dried with a vacuum pump. *Anal.* Calc. for $C_{18}H_{15}FeN_4O_2$: C, 57.62; H, 4.03; Fe, 14.88; N, 14.9. Found C, 57.15; H, 4.01; Fe, 14.68; N, 15.02%. Recrystallization was not possible as the product is only very sparingly soluble in a wide range of solvents including toluene, ethanol, methylene chloride and acetone.

$\{2[(C_5Me_5)Fe^+(CO)_2]\cdot TCNQ^{2-}\}$ (D)

This complex was prepared in two ways.

Method 1. A solution of TCNQ (64.3 mg, 0.314 mmol) in deoxygenated acetonitrile (10 ml) was slowly added at 20 °C to a suspension of **A** (155.7 mg, 0.314 mmol) in deoxygenated acetonitrile (10 ml) (stoichiometry: 1/1). The MeCN solution became green (λ: 743, 760, 842 nm). The ESR spectra of the solution showed the hyperfine coupling ($a_N = 1.01$, $a_H = 1.45$ g) and the g value ($g = 2.003$) of the $TCNQ^{\bar{\cdot}}$ radical anion [5]. Upon heating for 2 h at 70 °C the solution became red and a dark solid was collected after solvent evaporation under vacuum. Recrystallization from chloroform–diethyl ether gave a purple solid which analysed as $\{2[(C_5Me_5)Fe^+(CO)_2]\cdot TCNQ^{2-}\}$. *Anal.* Calc. for $C_{36}H_{34}Fe_2O_4N_4$: C, 61.91; H, 4.91; Fe, 15.99; N, 8.02. *Mw*: 698.38. Found: C, 61.87; H, 4.80; Fe, 15.86; N, 7.98%. *Mw*: 697.2.

Method 2. Photolysis (λ = 420 nm, 10 min) of a diluted (10^{-4} M) green solution (obtained as indicated in Method 1) caused a sharp colour change from dark green to red. The physical properties (UV–Vis and IR spectra) of the irradiated solution indicated the formation of a product identical to the one prepared by Method 1.

Results and Discussion

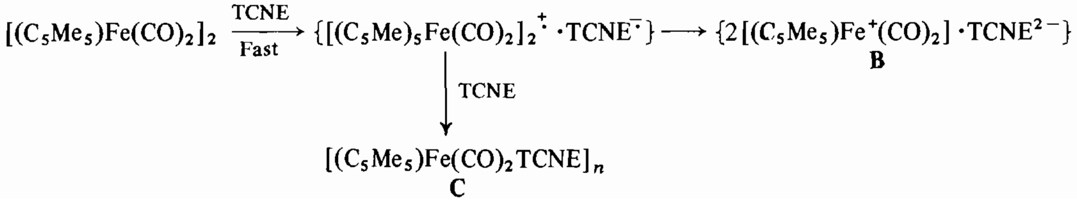
Reaction of A with TCNE

The red–purple complex **A** reacts readily in acetonitrile solution with a stoichiometric amount of TCNE under argon. The acetonitrile solution becomes green with a broad band in the visible region. The band shows closely spaced vibrational maxima at 395, 400, 410, 419, 429, 438, 460 and 470 nm [6]. Such spectra and the observed strong ESR signal of $TCNE^{\bar{\cdot}}$ radical anions is evidence for the presence of $TCNE^{\bar{\cdot}}$ in solution (eqn. (1)).

After some hours complex **B** separated in 25% yield. The IR spectrum of **B** in the CN stretching region (ν(CN) = 2160, 2098 cm^{-1}) is very similar to that reported [7] for $TCNE^{2-}$ coordinated via nitrogen to Ir in the dimeric compound $[(Ph_3P)_2(CO)Ir(NC)_2CC(CN)_2Ir(CO)(PPh_3)_2]$.

The IR spectrum of **B** exhibits CO (terminal) stretching bands [8] at 2005 and 1965 cm^{-1}. The absence of IR bands in the region of bridging CO ligands (1800–1700 cm^{-1}) indicates that the Fe–Fe bond has been oxidatively broken. Based on these results a charge transfer type structure for **B** would involve a sandwich arrangement with a $TCNE^{2-}$ layer lying between two $[(C_5Me_5)Fe^+(CO)_2]$ moieties. This implies a complete electron transfer from **A** to TCNE. The experimentally observed diamagnetism for **B** supports this conclusion. The observed $TCNE^{\bar{\cdot}}$ radical anion in the first stage of reactions indicates a radical pathway [1] probably involving the radical $[C_5Me_5)Fe(CO)_2]_2^{+\cdot}$. Fragmentation of the di-iron radical followed by electron transfer inside the solvent cage yields the diamagnetic products **B** and in the presence of an excess of TCNE the product **C**.

Nitrogen coordination as observed for **B** provides a reasonable mechanism by which a polymeric species involving a continuous chain of alternating $TCNE^{2-}$ and $[(C_5Me_5)Fe^+(CO)_2]$ groups could be formed.

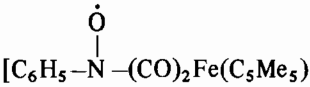


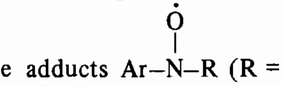
$$\begin{tikzcd}[(C_5Me_5)Fe(CO)_2]_2 \arrow[r, "TCNE", "Fast"'] & \{[(C_5Me)_5Fe(CO)_2]_2^{+\cdot}\cdot TCNE^{\bar{\cdot}}\} \arrow[r] \arrow[d, "TCNE"] & \underset{\mathbf{B}}{\{2[(C_5Me_5)Fe^+(CO)_2]\cdot TCNE^{2-}\}} \\ & \underset{\mathbf{C}}{[(C_5Me_5)Fe(CO)_2TCNE]_n} & \end{tikzcd} \qquad (1)$$

This is a possible structure for the intractable solid isolated from acetonitrile solutions containing **A** and TCNE in stoichiometry 1:2. Elemental analysis gives $[(C_5Me_5)Fe(CO)_2TCNE]_n$ as the approximate stoichiometry and the IR absorptions in the C≡N stretching region (ν(CN) = 2185, 2100 cm^{-1}) are similar to those observed [9] for $TCNE^{2-}$ coordinated through the nitrogen atoms of the CN group to the metal.

Reaction of A with TCNQ

The complex **A** reacts instantaneously in acetonitrile solution with a stoichiometric amount of TCNQ at 20 °C. The acetonitrile solution becomes green (the colour of $TCNQ^{\overline{\cdot}}$ radicals in solution). Simultaneous monitoring by ESR showed these changes to be associated with $TCNQ^{\overline{\cdot}}$ radical anions.

Photolysis (λ = 420 nm) of the green solution causes a sharp colour change from dark green to red. Monitoring the photoreaction in the ESR cavity in the presence of C_6H_5NO as spin-trap, a 34-line spectrum is obtained. This spectrum is assigned to the  $[C_6H_5{-}\overset{\overset{\dot{O}}{|}}{N}{-}(CO)_2Fe(C_5Me_5)]$ adduct for the following reasons:

(i) The hyperfine splitting constants, $a_N = 11.75$ G, $a_{o,p\mathrm{H}} = 3.2$ G, $a_{m\mathrm{H}} = 1$ G and the $g = 2.0043$ are typical of phenyl nitroxide adducts  $Ar{-}\overset{\overset{\dot{O}}{|}}{N}{-}R$ (R = $[(CO)_2M(C_5H_5)]$; M = Fe, Ru) [10]. The similarity of the coupling constants and the *g* factor to those found for spin-adducts suggests that these compounds are best regarded as nitroxide radicals with no substantial spin density in the d-orbitals.

(ii) The same ESR spectrum is obtained by photolysis of **A** in acetonitrile solutions containing C_6H_5NO but in the absence of TCNQ. The $[(C_5Me_5)Fe(CO)_2^{\cdot}]$ radicals are the observed [11] primary products in the photolytic process of *trans*-$[(C_5Me_5)Fe(CO)_2]_2$.

(iii) In control experiments with no spin-trap present irradiated (λ = 420 nm) solutions of the dimer **A** gave no ESR signals. These observations indicate a thermal 'single electron transfer' reaction through a radical cation–radical anion pair formation (eqn. (2)).

$$[(C_5Me_5)Fe(CO)_2]_2 + TCNQ \longrightarrow \{[(C_5Me_5)Fe(CO)_2]_2^{\overset{+}{\cdot}}\cdot TCNQ^{\overline{\cdot}}\} \qquad (2)$$

The normal site for oxidation in compounds containing metal–metal bonds is at the M–M bond [4]. The UV–Vis and ESR spectra indicate that the oxidation of the metal–metal bond in the dimer **A** occurs by two one-electron steps. The removal of the first electron gives the radical cation–radical anion pair $\{[(C_5Me_5)Fe(CO)_2]_2^{\overset{+}{\cdot}}\cdot TCNQ^{\overline{\cdot}}\}$. Removal of a further electron from the Fe–Fe bond in **A** is photochemically induced ($\sigma \rightarrow \sigma^*$ excitation) and gives the complete oxidative breaking of the Fe–Fe bond via $[(C_5Me_5)Fe(CO)_2^{\overset{+}{\cdot}}]$ radical formation [12]. The resulting radicals react with $TCNQ^{\overline{\cdot}}$ to form **D**. The red solid **D** analyses for $[(C_5Me_5)Fe(CO)_2]TCNQ$ and exhibits absorptions at 1990 and 2030 cm^{-1} (terminal carbonyl bands) and at 2160 and 2190 cm^{-1} (C≡N stretching vibrations [13] of $TCNQ^{2-}$).

The diamagnetism and ESR spectrum (which shows only an extremely weak signal of $TCNQ^{\overline{\cdot}}$ from trace impurities) show the absence of significant amounts of $TCNQ^{\overline{\cdot}}$ or Fe(III) salts in the solid product **D**. Mössbauer data (*IS* = 0.42 mm/s *versus* Fe, *QS* = 2.10 mm/s at 293 K) suggest that the complex **D** contains formal Fe(II) [13]. The presence of Fe(II) in **D** would require that it be formulated as a salt of $TCNQ^{2-}$, $\{2[(C_5Me_5)Fe^{+}(CO)_2]\cdot TCNQ^{2-}\}$.

The presence of C≡N stretching vibrations in **D** at 2160 and 2190 cm^{-1} is consistent with $TCNQ^{2-}$ formulation [14] where a further electron has been placed in the LUMO orbital, thereby weakening the C≡N bonds. Both in solution or in the solid state **D** is extremely sensitive to oxygen as observed for both electrogenerated [15] $TCNQ^{2-}$ and solid state [14] $Li_2TCNQ\cdot THF$. The large organometallic cation $[(C_5Me_5)Fe(CO)_2]^{+}$ is apparently unable to completely shut off the O_2 decay reaction of $TCNQ^{2-}$ leading to the α,α-dicyano-*p*-toluoylcyanide anion $[(N{\equiv}C)_2C\cdot C_6H_4{-}CO(CN)]^{-}(DCTC^{-})$ [15] as evidenced by the presence of an IR band at 1645 cm^{-1} (carbonyl) and an electronic transition at 480 nm analogous to the one observed for NaDCTC. ^{1}H NMR spectroscopy of the red complex showed the presence not only of **D** but also of two further products probably $DCTC^{-}$ derivatives of **D** which, however, could not be isolated.

Redox Potentials and Electron Transfer Reactions

The electron transfer process between **A** and the acceptors TCNE and TCNQ can be rationalized on the basis of the thermodynamic redox potentials *E* (Table I).

TABLE I. Redox Potentials *E* (V *vs.* saturated calomel electrode)

Acceptor	*E*	Donor	*E*
TCNQ[a]	+0.20	A	−1.10[c]
$TCNQ^{\overline{\cdot}}$	−0.33	A	−1.27[d]
TCNE[b]	+0.14		
$TCNE^{\overline{\cdot}}$	−0.75		

[a]Solvent: DMF with 0.1 M Bu_4NBF_4 (ref. 16). [b]Solvent: CH_3CN (ref. 17). [c]Solvent: CH_3CN with Bu_4NBF_4 (ref. 18). [d]*E vs.* Ag/Ag^{+}. Solvent: CH_3CN with Bu_4NPF_6. A = $[(C_5Me_5)Fe(CO)_2]_2$.

$[(C_5Me_5)Fe(CO)_2]_2$ ($E = -1.27$ V) is capable of reducing TCNE, $TCNE^{\cdot}$, TCNQ and $TCNQ^{\cdot -}$. From the reduction potential of **A** it is evident that the production of $TCNE^{2-}$ and $TCNQ^{2-}$ (eqns. (1) and (2)) would have a very low equilibrium constant in solution and could be driven to the right by optical excitation which efficiently cleaves the metal–metal bond. Equation (2) is representative of the chemistry; ESR spectroscopy coupled with the spin-trap technique confirm that the homolytic cleavage of the bridged Fe–Fe unit produces the 17-electron fragment $[(C_5Me_5)Fe(CO)_2^{\cdot +}]$. The reactions are driven to produce $TCNE^{2-}$ and $TCNQ^{2-}$ by the irreversible reaction of the substrate radical cation. Study of the reactivity of the 17-electron species $[(C_5Me_5)Fe(CO)_2{}^{\cdot}]$ is in progress.

References

1 A. C. Stiegman and D. R. Tyler, *Acc. Chem. Res., 17,* 61 (1984).
2 H. B. Abrahamson, M. C. Palazzotto, C. L. Reichel and M. S. Wrighton, *J. Am. Chem. Soc., 101,* 4123 (1979).
3 M. Moran, I. Chadrado and J. Losada, *Inorg. Chim. Acta, 118,* 25 (1986).
4 G. L. Geoffroy and M. S. Wrighton, 'Organometallic Photochemistry', Academic Press, New York, 1979.
5 L. R. Melby, R. J. Harder, W. R. Hutter, W. Mahler, R. E. Benson and W. E. Mochel, *J. Am. Chem. Soc., 84,* 3374 (1962).
6 O. Traverso, V. Carassiti, M. Graziani and U. Belluco, *J. Organomet. Chem., 57,* (1973) C22.
7 W. Beck, R. Schlodder and K. M. Lechler, *J. Organomet. Chem., 54,* 303 (1973).
8 (a) B. D. Moore, M. B. Sympson, M. Poliakoff and J. J. Turner, *J. Chem. Soc., Chem. Commun.,* 972 (1984). (b) A. F. Hepp, J. P. Blaha, C. Lewis and M. S. Wrighton, *Organometallics, 3,* 174 (1984).
9 W. H. Bradley, *Inorg. Chim. Acta Rev., 2,* 7 (1968).
10 A. Hudson, M. F. Lappert and B. K. Nicholson, *J. Chem. Soc., Dalton Trans.,* 551 (1977).
11 A. J. Dixon, M. A. Healy, M. Poliakoff and J. Turner, *J. Chem. Soc., Chem. Commun.,* 994 (1968).
12 J. K. Kochi, 'Organometallic Mechanism and Catalysis', Academic Press, New York, 1978.
13 N. N. Greenwood and T. C. Gibb, 'Mössbauer Spectroscopy', Chapman and Hall, London, 1971.
14 M. S. Khatkale and J. P. Devlin, *J. Chem. Phys., 70,* 1851 (1979).
15 M. R. Suchanski and R. P. Van Duyne, *J. Am. Chem. Soc., 87,* 250 (1976).
16 M. H. Desbois, P. Michaud and D. Astruc, *J. Chem. Soc., Chem. Commun.,* 450 (1985).
17 Q. B. Webster, W. Mahler and R. E. Benson, *J. Am. Chem. Soc., 84,* 3678 (1962).
18 P. Bergamini, S. Sostero and O. Traverso, unpublished results.