

# Single Electron Reduction of Tetracyanoquinodimethane, TCNQ, and Phenazine and Two Electron Reduction of TCNQ by Organo-iron Electron Reservoir Complexes<sup>1</sup>

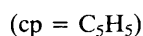
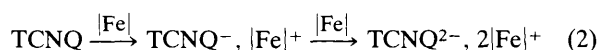
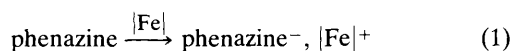
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$\text{cp}(\text{C}_6\text{Me}_6)\text{Fe}^{\text{I}}$ , (**1**), ( $\text{cp} = \text{C}_5\text{H}_5$ ) reacts with one equivalent of phenazine and tetracyanoquinodimethane, TCNQ, to give the single electron transfer salts  $\text{cp}(\text{C}_6\text{Me}_6)\text{Fe}^+, \text{phenazine}^-$ , (**2**), and  $\text{cp}(\text{C}_6\text{Me}_6)\text{Fe}^+, \text{TCNQ}^-$ , (**3**), whereas addition of TCNQ to 2 equivalents of (**1**) or  $\text{cp}(\text{Pr}^i\text{Ph})\text{Fe}^{\text{I}}$  gives the crystalline salts  $\{\text{cp}(\text{arene})\text{Fe}^+\}_2\text{TCNQ}^{2-}$ , (**4**) and (**5**);  $(\text{C}_6\text{Me}_6)_2\text{Fe}^0$ , (**7**), also reacts with one equivalent of these acceptors to give  $(\text{C}_6\text{Me}_6)_2\text{Fe}^+, \text{phenazine}^-$ , (**8**) and  $(\text{C}_6\text{Me}_6)_2\text{Fe}^+ \text{TCNQ}^-$ , (**9**).

Stoichiometric and catalytic electron transfer from organo-iron electron reservoir complexes to small substrates ( $\text{O}_2$ ,  $\text{RX}$ ,  $\text{NO}_3^-$ ,  $\text{CO}_2$ ) the radical anions of which are unstable ( $\text{O}_2^-$ ,  $\text{RX}^-$ ,  $\text{NO}_3^{2-}$ ,  $\text{CO}_2^-$ ) has proved useful for C-H<sup>2</sup> and N-H<sup>3</sup> activation ( $\text{O}_2$ ), C-C bond formation ( $\text{RX}$ ,  $\text{CO}_2$ ),<sup>4</sup> and nitrate electro-reduction.<sup>5</sup> These reductions are feasible even if the reduction potentials of the substrates ( $\text{RX}$ ,  $\text{NO}_3^-$ ,  $\text{CO}_2$ ) are more negative than the oxidation potentials of the 'electron-reservoir' complexes, since the reactions are driven to products by the irreversible reaction of the substrate radical anions.<sup>6</sup> It is also useful to understand the cage chemistry<sup>7</sup> between the oxidized iron complex and the substrate radical anions.<sup>8</sup>



In this context, we report single- and double-electron reduction of molecules forming thermodynamically and kinetically stable anions (Table 1), equations (1) and (2). On the basis of the thermodynamic redox potentials  $E$  (see Table 1),  $\text{cp}(\text{C}_6\text{Me}_6)\text{Fe}^{\text{I}}$  ( $E = -1.55 \text{ V}$ )<sup>9</sup> and  $(\text{C}_6\text{Me}_6)_2\text{Fe}^0$  ( $E = -1.37 \text{ V}$ )<sup>10</sup> are capable of reducing acridine ( $E = -1.25 \text{ V}$ ), tetracyanoquinodimethane, TCNQ ( $E = +0.20 \text{ V}$ ), and  $\text{TCNQ}^-$  ( $E = -0.33 \text{ V}$ ). Although there have been a number of conductivity studies on TCNQ and  $\text{TCNQ}^-$ ,<sup>11</sup> reports on  $\text{TCNQ}^{2-}$  are scarce.<sup>12</sup>

The green 19-electron  $d^7$  complex  $\text{cp}(\text{C}_6\text{Me}_6)\text{Fe}^{\text{I}}$ , (**1**), is readily available in crystalline form;<sup>9a</sup> it reacts instantaneously in tetrahydrofuran, THF, solution with a stoichiometric amount of phenazine in THF at 20 °C under Ar (equation 3). The THF solution becomes purple and a deep purple precipitate is formed. Recrystallization from acetonitrile at -40 °C gives a 72% yield of air sensitive crystals of a salt analysing as  $\text{cp}(\eta^6\text{-C}_6\text{Me}_6)\text{Fe}^+, \text{phenazine}^-$ , (**2**) (equation 3).<sup>†</sup>

The i.r. spectrum of (**2**) (Nujol) shows an aromatic C-N absorption at  $1315 \text{ cm}^{-1}$ , and the Mössbauer doublet (I.S.: 0.5 mm/s vs. Fe; Q.S.: 2 mm/s at 293 K) indicates the classical  $\{\text{cp}(\text{arene})\text{Fe}^{\text{II}}\}^+$  structure. The e.s.r. spectrum of (**2**) (Figure

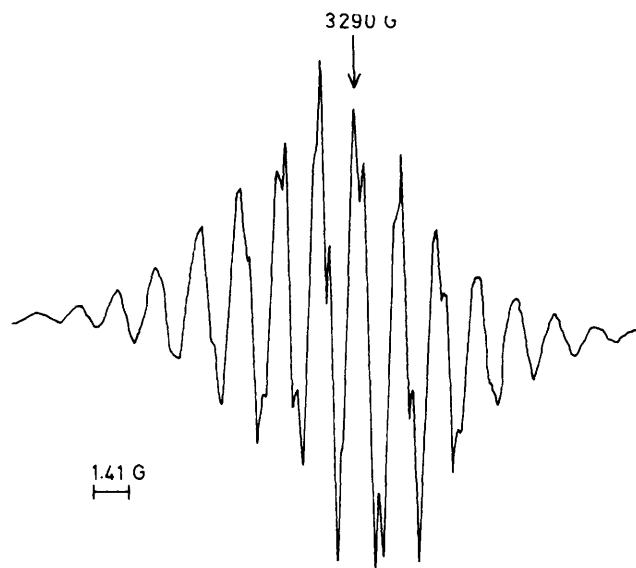


Figure 1. E.s.r. spectrum (-80 °C) of  $\text{cp}(\text{C}_6\text{Me}_6)\text{Fe}^+, \text{phenazine}^-$ , (**2**), in THF solution  $2 \times 10^{-3} \text{ M}$ .

**1**) in THF at -80 °C shows the hyperfine couplings of the phenazine radical anion. Upon contact with air, in the solid state (**2**) immediately turns yellow, the colour of  $\{\text{cp}(\text{arene})\text{Fe}^{\text{II}}\}^+$  salts, previously hidden by the intense purple colour of the counter anion in (**2**).

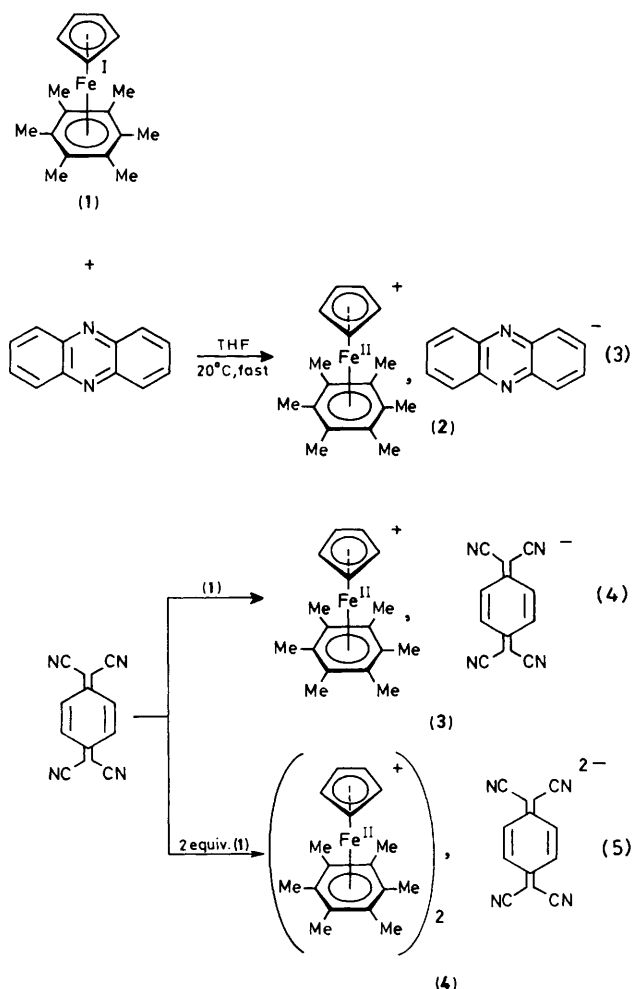
With TCNQ, the reaction of (**1**) depends on the stoichiometry (equations 4 and 5). Addition of a green THF solution of (**1**) to a THF solution of TCNQ (stoichiometry: 1/1) immediately gives a different green solution (the colour of  $\text{TCNQ}^-$  in solution) and a dark turquoise-blue solid (the usual colour of  $\text{TCNQ}^-$  salts in the solid state). Recrystallization from MeCN gives a 72% yield of crystals analysing as  $\text{cp}(\text{C}_6\text{Me}_6)\text{Fe}^+, \text{TCNQ}^-$ , (**3**).<sup>†</sup> However, on addition of a THF solution of TCNQ to a THF solution of (**1**) an immediate, sharp colour change occurs from dark green to orange when the stoichiometry  $\text{TCNQ}/(\text{1}) = 1/2$  is achieved, whereas the precipitate formed is purple (the colour of  $\text{TCNQ}^{2-}$ ).<sup>12</sup> Recrystallization from MeCN gives a 70% yield of large purple crystals analysing as  $\{\text{cp}(\text{C}_6\text{Me}_6)\text{Fe}^+\}_2, \text{TCNQ}^{2-}$ , (**4**).<sup>†</sup> A 7.78 mm long needle (0.3 mm)<sup>2</sup> of (**4**) gave no conductivity along this axis. Powders of (**3**) and (**4**) gave very low conductivity [(4-7)  $\times 10^6 \Omega \text{ mm}$ ]. Powdered samples of  $\{\text{cp}(\text{C}_6\text{Me}_6)\text{Fe}^+\}_{1+x}$ ,

<sup>†</sup> Satisfactory elemental analyses were obtained for all new compounds.

**Table 1.** Reaction product, if any, between acceptors, A, and organoiron donors, D, as a function of thermodynamic redox potentials  $E$  (V vs. saturated calomel electrode). Hg cathode; DMF, 0.1 M  $\text{Bu}_4\text{NBF}_4$  [(1) reduces  $\text{CO}_2$ ,  $\text{NO}_3^-$ , and RX, and (7) reduces RX; but  $\text{CO}_2$ ,  $\text{NO}_3^-$ , and RX are reduced irreversibly above  $-2$  V, their thermodynamic reduction potentials being unknown).

Acceptor, A	$E/V$	Donor, D		
		(1)	(6)	(7)
TCNQ	+0.20	-1.55	-1.49	-1.45
TCNQ <sup>-</sup>	-0.33	(3)		(9)
$\text{O}_2$	-0.7	(4)	(5)	
Phenazine	-1.25	$\text{cpFe}^{\text{II}}\text{C}_6\text{Me}_5\text{CH}_2$	$\text{cpFe}^{\text{II}}\text{C}_6\text{H}_5\text{CMe}_2$	$\text{C}_6\text{Me}_6\text{Fe}^{\text{II}}\text{C}_6\text{Me}_4(\text{CH}_2)_2$
2,3-Benzanthracene	-1.60	(2)		(8)
Acridine	-1.62	a	a	a
		$\text{cpFe}^{\text{II}}\text{C}_6\text{Me}_5\text{CH}_2$		a

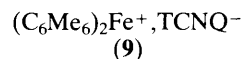
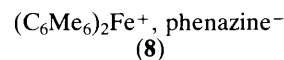
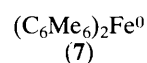
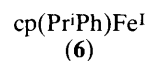
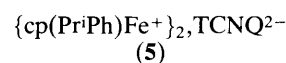
<sup>a</sup> No reaction.



$\text{TCNQ}^{(1+x)-}$  with  $0 < x < 1$  (e.g.  $x = 0.5$ ) prepared similarly gave comparable results.

In contrast to salts of  $\text{TCNQ}^-$  which were not prepared in a crystalline form until long after<sup>12</sup> they were first identified,<sup>11</sup>  $\text{TCNQ}^{2-}$  crystallizes easily, at least with iron sandwich complexes as counter cations. Indeed, even thermally unstable  $\text{Fe}^{\text{I}}$  complexes react as cleanly as (1) with  $\text{TCNQ}$ . For instance, crystals analysing as  $\{\text{cp}(\text{Pr}^{\text{i}}\text{Ph})\text{Fe}^+\}_2, \text{TCNQ}^{2-}$ , (5),<sup>†</sup> suitable for X-ray analysis were made by addition of  $\text{TCNQ}$  (1 equiv.) to

a green THF solution of  $\text{cp}(\text{Pr}^{\text{i}}\text{Ph})\text{Fe}^{\text{I}}$  (6) (2 equiv.) at  $-20^\circ\text{C}$  {the latter was prepared directly from  $[\text{cp}(\text{Pr}^{\text{i}}\text{Ph})\text{Fe}^{\text{II}}] + \text{PF}_6^-$  and  $\text{Na-Hg}$  in THF at  $-20^\circ\text{C}$ , followed by filtration}.



The readily available 20-electron complex  $(\text{C}_6\text{Me}_6)_2\text{Fe}^0$ , (7),<sup>10</sup> also gives some preliminary results. Reactions of THF solutions of (7) with equimolar amounts of phenazine and of  $\text{TCNQ}$  in THF, under Ar at  $20^\circ\text{C}$ , immediately gave respectively a purple precipitate in 68% yield, analysing as  $(\text{C}_6\text{Me}_6)_2\text{Fe}^+, \text{phenazine}^-$ , (8),<sup>†</sup> and a blue purple precipitate of  $(\text{C}_6\text{Me}_6)_2\text{Fe}^+, \text{TCNQ}^-$ , (9).<sup>†</sup> However elemental analyses for (9) were not satisfactory, probably due to the kinetic instability of the 19-electron cation in polar solvents such as  $\text{MeCN}$ .

The Mössbauer data confirm the  $d^7 \text{Fe}^{\text{I}}$  structure<sup>9,10</sup> of (8) and (9) (I.S. : 0.82 mm/s vs. Fe, Q.S. : 0.53 mm/s at 293 K)<sup>10</sup> in which both the cation and the anion are paramagnetic. The reactions of (7) with several other acceptors gave unsatisfactory Mössbauer data and elemental analyses, probably indicating further reaction between the organometallic species and the organic radicals. Compounds (1) and (7) do not react with polyaromatic species which do not contain a basic heteroatom and which have reduction potentials more negative than the oxidation potential of (1) (e.g. 2,3-benzanthracene, Table 1). However, reaction of (1) with acridine gives  $\text{cp}(\text{C}_6\text{Me}_5\text{CH}_2)\text{Fe}$  resulting from deprotonation of (1)<sup>+</sup> by the acridine radical anion in the ion pair  $\{(1)^+, \text{acridine}^-\}$ . This deprotonation drives the otherwise unfavourable electron transfer from (1) ( $E = -1.55$  V) to acridine ( $E = -1.62$  V, see Table 1).

As well as new donor-acceptor reactions and their features, these investigations give some indication of the use of electron reservoir complexes as electron transfer reagents.

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