

## Low Valence State of Metal Chelates. I. Complexes of Iron(II) Perchlorate with 1,10-phenanthroline, 4,7-dimethyl-1,10-phenanthroline and 4,7-diphenyl-1,10-phenanthroline

S. Musumeci, E. Rizzarelli, I. Fragalà, S. Sammartano, and R.P. Bonomo

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*D. C. polarographic and cyclic voltammetric studies on the reduction of iron(II) complexes with bidentate imine ligands: 1,10-phenanthroline, 4,7-dimethyl-1,10-phenanthroline and 4,7-diphenyl-1,10-phenanthroline, have been carried out in acetonitrile solutions with 0,8 M tetraethyl ammonium perchlorate as supporting electrolyte. The iron(II) complexes gave a five-step reduction wave. The behavior of the first three steps were to be considered as successive reductions of the iron(II) in the complex. The other steps were to be ascribed to the reduction of the ligand. All three complexes led to the formation of the species  $Fe(L)_3^-$  (where L is the ligand). The effect of substituent upon the reduction mechanism was also discussed.*

### Introduction

Ligands such 1,10-phenanthroline and 2,2'-bipyridine are known to form complexes of great stability with transition metal ions in their normal valencies as well as in low valence states.<sup>1</sup> The source of the stability of these complexes is due to the  $\pi$ -bond formation between the central metal atom and the ligand molecules. A recent study upon the electronic structure of tris (1,10-phenanthroline)iron(II) complex showed that the formation of  $\pi$ -bonds causes a stabilization of 26.3 Kcal/mol.<sup>2</sup>

Continuing the studies carried out in this laboratory on the polarographic reduction of several metal complexes with 1,10-phenanthroline and 2,2'-bipyridine,<sup>3-6</sup> we investigated the reduction of substituted tris (1,10-phenanthroline)iron(II) complexes. These compounds have been extensively studied by their spectral properties. One would expect that electron donor substituents would produce a hypsochromic shift of the visible absorption bands, while electron withdrawing substituents would produce a bathochromic shift. In

iron(II) tris diimine complexes substituent effects do not follow such simple pattern.<sup>7</sup> But the absorption spectra of species in solutions do not furnish in most cases data on the complete removal of the electron from the particle,<sup>8</sup> thus we are interested in explaining the reduction mechanism in order to give a contribution to the knowledge of these compounds.

Other workers were interested in the polarographic behavior of transition metal complexes both in aqueous and aprotic solvents.<sup>9-18</sup> The use of aprotic solvents permits the complete investigation of the reduction behavior up to the discharge of the ligand itself. Acetonitrile is a good solvent for electrochemical studies, because it has a relatively high dielectric constant, a low viscosity and a lower coordinating ability than the water.<sup>19</sup> In acetonitrile the electrode processes are quite different from the behavior in water, mainly because no reduction of hydrogen ions is occurring.

The purpose of this investigation was to detect the low valence states and the effects of substituents in the complexes of iron(II) with 1,10-phenanthroline (phen), 4,7-dimethyl-1,10-phenanthroline (4,7 dmphen) and 4,7-diphenyl 1,10-phenanthroline (4,7 dpphen), using voltammetric techniques in acetonitrile solutions.

### Experimental Section

*Apparatus.* D.C. polarograms were obtained with a Methrom polarecorder E 261 and cyclic voltammograms with an Amel cathod-ray instrument type 448. The measurements were carried out in a conventional H-cell thermostated in a water-bath at  $25 \pm 0.1^\circ\text{C}$ . The d.m.e. had an m value of 0.879 mg/sec and a

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(7) P. Krumholz, *Structure and Bonding*, vol. 9, Springer-Verlag, 1971, p. 139.

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drop time of 3.2 sec. obtained by an electromagnetic hammer, when it was measured in air free water at 500 mm height of mercury reservoir, with no applied potential. An aqueous saturated (NaCl) calomel electrode served as reference electrode, connected to the cell by an agar-salt bridge with sodium chloride. The bridge was inserted in the compartment separated from the working compartment by a medium porosity sinter. In this compartment the level of acetonitrile solutions was kept lower than the one in working compartment, in order to prevent some introduction of water. Dissolved oxygen was removed from the solutions of the complex, by bubbling high purity nitrogen previously saturated with acetonitrile.

All the solutions were prepared using acetonitrile as solvent, containing 0.8 M of tetraethyl ammonium perchlorate, in order to reduce the vapour pressure of the acetonitrile and the resistance of the cell (less than 3.5 K $\Omega$ ).

**Chemicals.** Carlo Erba acetonitrile RP was purified according to the method of J.F. Cotzee<sup>20</sup> by shaking with aqueous KOH, for two days, then stirring this distillate over P<sub>2</sub>O<sub>5</sub>, for one day, and finally stirring the latter distillate over CaH<sub>2</sub> for two days; the last distillate was polarographic grade.

Technical grade tetraethyl ammonium perchlorate (C. Erba) was recrystallized twice from ethanol and dried in a vacuum oven at 60°C. Tris(1,10-phenanthroline)iron(II), tris(4,7-dimethyl-1,10-phenanthroline)iron(II) and tris(4,7-diphenyl-1,10-phenanthroline)iron(II) perchlorates were synthesized according to the procedure used by N. Sutin and B.M. Gordon.<sup>21</sup>

A slight excess of the ligand stoichiometric quantity in water-ethanol mixture was added to an aqueous solution of Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub> · 6H<sub>2</sub>O. The solutions of the complexes were evaporated to small volume and treated with a saturated solution of NaClO<sub>4</sub>. Dark red crystals that separated from the solutions were filtered, washed with water, dried in a vacuum oven at 80°C and stored over H<sub>2</sub>SO<sub>4</sub> conc. All the products obtained were identified by absorption spectra.<sup>22</sup>

## Results and Discussion

Tris(1,10-phenanthroline)iron(II) perchlorate gave a five-step reduction wave, tris(4,7-dimethyl-1,10-phenanthroline)iron(II) perchlorate a five-step reduction wave with a large maximum on the fifth step, and tris(4,7-diphenyl-1,10-phenanthroline)iron(II) perchlorate a five-step reduction wave. Half wave potentials for each step of the iron complexes are reported in Table I. Complete polarograms are shown in Figure 1A, together with polarograms of the reduction steps of the free ligands Figure 1B. For our purpose we first considered the reduction steps occurring in the range of potentials from -1 to -2 volts.

In this range the iron(II) complexes showed a three-step reduction wave. The limiting currents of

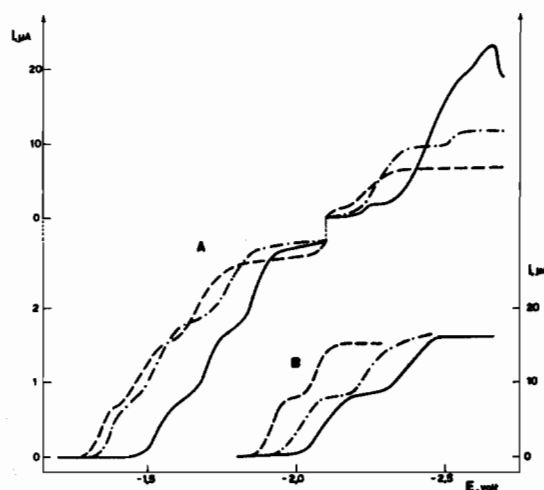
**Table I.** Half wave potentials of the reduction steps of the iron (II) complexes 0.5 mM in acetonitrile solution when 0.8 M tetraethyl ammonium perchlorate was used as supporting electrolyte.

	E <sub>1/2</sub> (V vs SCE)				
	I	II	III	IV	V
Fe(phen) <sub>3</sub> <sup>2+</sup>	-1.39	-1.55	-1.80*	-2.28	-2.54
Fe(4,7dmphen) <sub>3</sub> <sup>2+</sup>	-1.55	-1.70	-1.87	-2.10	-2.42
Fe(4,7dphen) <sub>3</sub> <sup>2+</sup>	-1.36	-1.48	-1.65	-2.06	-2.27

\* For iron (II) complex concentration less than 0.5 mM.

**Table II.** Slopes of log-plot for the first three steps of reduction of Fe(phen)<sub>3</sub><sup>2+</sup> varying the concentration of the iron complex and adding an excess of free 1,10-phenanthroline.

Concentration (mM)	Slopes (mV)		
	I	II	III
2	56	56	78
1	56	56	70
0.75	59	59	72
0.5	59	54	68
0.25	56	54	60
0.1	58	54	61
2 + phen	61	56	57
0.5 + phen	56	54	62



**Figure 1.** A) D.C. polarograms of reduction waves of 0.5 mM Fe(phen)<sub>3</sub>(ClO<sub>4</sub>)<sub>2</sub> (—), Fe(4,7dmphen)<sub>3</sub>(ClO<sub>4</sub>)<sub>2</sub> (---), Fe(4,7dphen)<sub>3</sub>(ClO<sub>4</sub>)<sub>2</sub> (· · ·) at d.m.e. in an AN solution of 0.8 M (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NClO<sub>4</sub> at 25°C. B) D.C. polarograms of reduction waves of 1.5 mM phen (— · — · —), dmphen (---), dphen (— · — · —) at d.m.e. in an AN solution of 0.8 M (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NClO<sub>4</sub> at 25°C. Potentials are referred to an aqueous SCE.

these steps were found to be proportional to the square root of the mercury pressure between 420 mm and 580 mm on the d.m.e. and to the concentration of the iron complexes in the range from 0.1 to 1 mM. Between 25 and 37°C the limiting currents of the first three steps were also proportional to the temperature, with temperature coefficients that are in agreement with theoretical values within 1-2%.<sup>23</sup> A slight variation from the theoretical value of the third step

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(21) N. Sutin and B.M. Gordon, *J. Am. Chem. Soc.*, 83, 70 (1961).

(22) A.A. Schilt, *Analytical applications of 1,10-phenanthroline and related compounds*. Pergamon Press, 1969, p. 56.

(23) L. Meites, *Polarographic Techniques*, Interscience, 1955, p. 55.

of the  $\text{Fe}(\text{phen})_3^{2+}$  will be explained later. These results indicated that the processes involved in the first three steps were to be considered diffusion controlled. The ratio of the wave heights of the first three steps of the iron complexes was 1:0.94:0.98; 1:1.08:1.12; 1:0.85:1.04 respectively for  $\text{Fe}(\text{phen})_3^{2+}$ ,  $\text{Fe}(4,7\text{dmphen})_3^{2+}$  and  $\text{Fe}(4,7\text{d\phi phen})_3^{2+}$  cations. The results of log-plot analysis for the first three steps of  $\text{Fe}(\text{phen})_3^{2+}$  are given in Table II.

While the first two species gave slopes that agreed with the theoretical value of  $59/n$  mV expected for a reversible reduction processes at  $25^\circ\text{C}$ ,<sup>24</sup> the third step gave slopes variable with concentration of the iron complex and with the addition of free 1,10-phenanthroline. One can see from values of Table II, that slopes approached the value of  $59/n$  mV, decreasing the concentration of the iron complex and adding 3 mM free 1,10-phenanthroline.

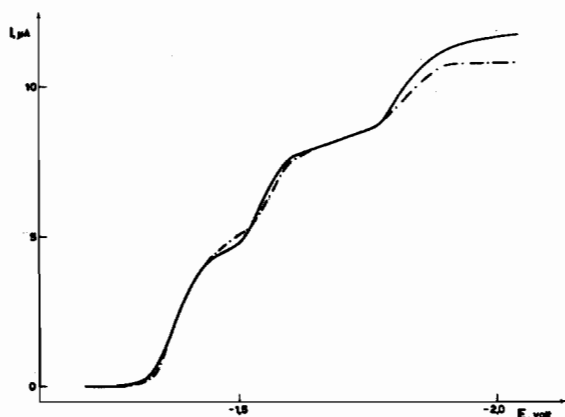


Figure 2. The effect of the addition of 1,10-phenanthroline upon the third step of reduction wave of  $\text{Fe}(\text{phen})_3(\text{ClO}_4)_2$ . The concentration of the iron complex is 2 mM and that of the free added ligand is 3 mM. As one can see the addition of the ligand influences slightly the first two steps, while the third appears deeply modified. Potentials are referred to aqueous SCE.  $\text{Fe}(\text{phen})_3(\text{ClO}_4)_2$  2 mM  $\cdots\cdots\cdots$   $\text{Fe}(\text{phen})_3(\text{ClO}_4)_2$  2 mM phen + 3 mM phen  $\text{—}$

In Figure 2 we report the first three steps of reduction at the concentration of 2 mM  $\text{Fe}(\text{phen})_3^{2+}$  before and after the addition of 3 mM 1,10-phenanthroline. As one can see from the polarogram, the addition of free 1,10-phenanthroline influences only the third step, increasing the limiting current and shifting slightly the half wave potential to more negative values.

Plots of  $-E$  versus  $\log i/i_{a-i}$  for  $\text{Fe}(4,7\text{dmphen})_3^{2+}$  and  $\text{Fe}(4,7\text{d\phi phen})_3^{2+}$  gave straight lines the slopes of which are in agreement with theoretical value of  $59/n$  mV.

To test further the reversibility of the reduction processes involved in the first part of polarograms of the iron(II) complexes, analysis was made of the way in which  $E_{1/2}$  changed with drop-time.<sup>25</sup> Half wave potentials kept constant in the range from 2.5 to 6 seconds with an experimental error not larger

than 5 mV. Only the third step of the  $\text{Fe}(\text{phen})_3^{2+}$  showed a slight difference of approximately 13 mV.

The reduction steps that appeared in the second part of the polarograms ( $E < -2$  volts vs SCE) showed a different behavior.

Their limiting currents were linearly proportional neither to the square root of mercury pressure, nor to the concentration of the iron complexes. These facts showed that the processes involved in this range of potentials were not diffusion controlled. Free ligands gave a two-step reduction wave at potentials nearly corresponding to the fourth and fifth step of the polarograms of the iron(II) complexes. This behavior is shown in Figure 1B. Half wave potentials are reported in Table III. Polarograms of iron(II) complexes containing an excess of the ligand showed that the addition of free ligand increased only the limiting currents of the steps involved in the range of potentials beyond  $-2$  volts, while the steps involved in the first part of polarograms were not affected (in this consideration we exclude the third step of  $\text{Fe}(\text{phen})_3^{2+}$ , that undergoes a certain modification, as previously described).

Table III. Half wave potentials of the reduction steps of the free ligands.

Ligand	$E_{1/2}$ (V vs SCE)	
	I	II
Phen	-1.99	-2.25
4,7dmphen	-2.09	-2.37
4,7d\phi phen	-1.89	-2.05

These results indicated that the electrode processes of the first three steps and the other two respectively in the former and in the latter range of polarograms were different in nature. In fact the first three steps involved processes that were diffusion controlled and reversible (with the exception of the third step of the  $\text{Fe}(\text{phen})_3^{2+}$  the behavior of which will be discussed later), while the other two were not diffusion controlled and were influenced by the addition of the free ligands.

Investigations using cyclic voltammetry have been carried out for testing the reversibility of the iron(II) complexes by a very precise different technique. Voltammograms were made at the same experimental conditions of D.C. polarograms and we considered only the first three steps of iron(II) complexes and left aside the precise examination of the other two. Voltammograms of  $\text{Fe}(4,7\text{dmphen})_3^{2+}$  and  $\text{Fe}(4,7\text{d\phi phen})_3^{2+}$  are reproduced in Figure 3 and 4. In Table IV and V are reported potentials for cathodic and anodic peaks, separation of peaks, ratio of cathodic and anodic peak currents, at the sweep rates used in the analysis. As one can see the separation of cathodic and anodic peaks varied from 61 to 91 mV.

The theoretical value expected for a reversible reduction process is  $57/n$  mV,<sup>25</sup> thus these processes

(24) L. Meites, *ibidem*, p. 209.

(25) A.A. Vlcek, *Progress in Inorg. Chem.*, vol. 5, Interscience, 1963, ed. by F.A. Cotton, p. 211.

(26) J.B. Headridge, *Electrochemical Techniques for Inorganic Chemists*, Academic Press, 1969, chap. V, London.

**Table IV.** Voltammetric data for reduction of  $\text{Fe}(4,7\text{dmphen})_3^{2+}$ . Potentials are referred to SCE.

	Sweep rate (mV/sec)	Epc (V)	Epa (V)	$\Delta E_p$ (mV)	$I_{pc}/I_{pa}$
first step	250	-1.573	-1.512	61	1.10
	150	-1.573	-1.511	62	1.10
	100	-1.573	-1.510	63	1.00
	60	-1.573	-1.513	60	1.00
second step	250	-1.726	-1.646	80	0.95
	150	-1.726	-1.646	80	0.91
	100	-1.726	-1.646	80	0.93
	60	-1.726	-1.647	79	1.00
third step	250	-1.887	-1.797	90	0.89
	150	-1.887	-1.796	90	0.88
	100	-1.890	-1.799	91	0.90
	60	-1.890	-1.799	91	0.90

**Table V.** Voltammetric data for reduction  $\text{Fe}(4,7\text{d}\phi\text{phen})_3^{2+}$ . Potentials are referred to SCE.

	Sweep rate (mV/sec)	Epc (V)	Epa (V)	$\Delta E_p$ (mV)	$I_{pc}/I_{pa}$
first step	250	-1.384	-1.320	64	1.10
	150	-1.384	-1.320	64	1.11
	100	-1.384	-1.320	64	1.12
	60	-1.384	-1.320	63	1.14
second step	250	-1.494	-1.430	64	0.89
	150	-1.494	-1.430	64	0.90
	100	-1.494	-1.431	63	0.89
	60	-1.495	-1.431	64	0.87
third step	250	-1.662	-1.582	80	0.75
	150	-1.662	-1.582	80	0.74
	100	-1.663	-1.584	79	0.77
	60	-1.664	-1.584	80	0.77

are to be considered one electron reductions close to the reversibility.

Evaluation of cyclic voltammograms for  $\text{Fe}(\text{phen})_3^{2+}$  solutions was complicated by a strong absorption process that appeared on the third peak, therefore it

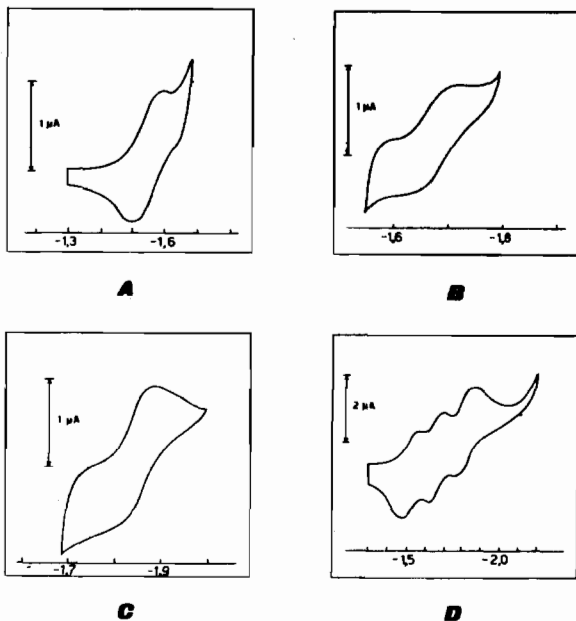


Figure 3. Cyclic voltammograms for reduction steps of  $\text{Fe}(4,7\text{dmphen})_3(\text{ClO}_4)_3$ . The sweep rate is 0,25 V/sec and potentials are referred to aqueous SCE. A) first step; B) second step; C) third step; D) the first three steps together.

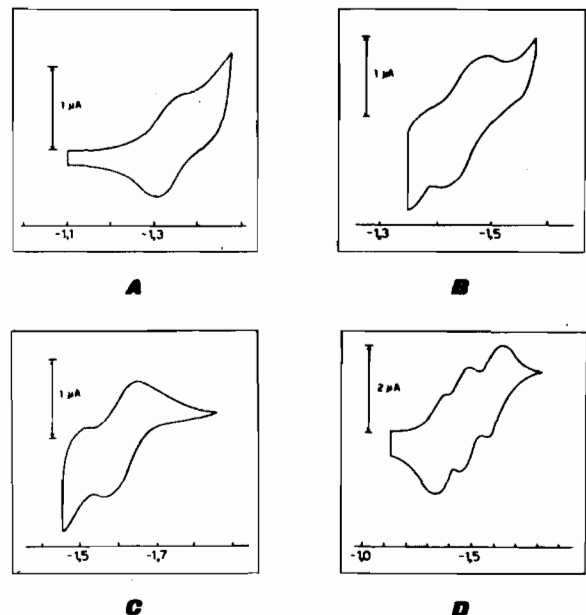


Figure 4. Cyclic voltammograms for reduction steps of  $\text{Fe}(4,7\text{d}\phi\text{phen})_3(\text{ClO}_4)_3$ . The sweep rate is 0,25 V/sec and potentials are referred to aqueous SCE. A) first step; B) second step; C) third step; D) the first three steps together.

was not possible to carry out a complete analysis. A cyclic voltammogram is shown in Figure 5.

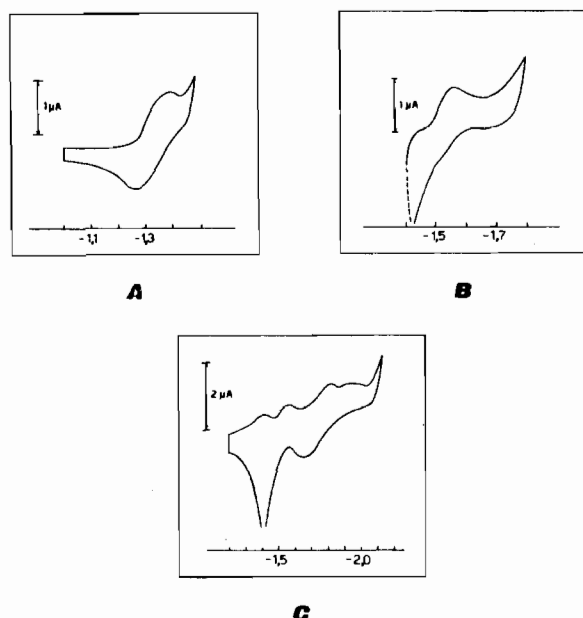
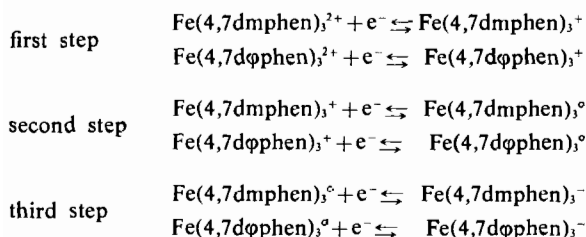


Figure 5. Cyclic voltammogram for reduction steps of  $\text{Fe}(\text{phen})_3(\text{ClO}_4)_2$ . The sweep rate is 0,25 V/sec and potentials are referred to aqueous SCE. A) first step; B) second step; C) the first three steps together.

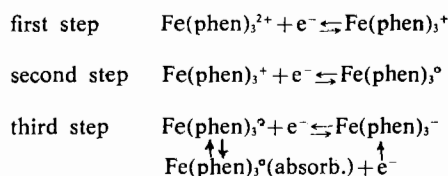
From data of D.C. polarography and cyclic voltammetry we can state that the processes involved in the reduction at d.m.e. of  $\text{Fe}(4,7\text{dmphen})_3^{2+}$  and  $\text{Fe}(4,7\text{d}\phi\text{phen})_3^{2+}$  are diffusion controlled and one electron reversible reductions (near the reversibility from cyclic voltammetry data). Thus the reaction scheme may be written as:



In the case of  $\text{Fe}(\text{phen})_3^{2+}$  from data of limiting current dependence on the height of mercury pressure, the concentration and the temperature, one can state that reduction processes are diffusion controlled, with the exception of the dependence of the limiting

current of the third step on the temperature, that showed a slight difference from the theoretical value (0,9 instead of 1-2%). From data of log-plot and on the ground of cyclic voltammograms, one can conclude that the first two steps involves one electron reversible reduction, while the third step involves one electron irreversible reduction that approaches the reversible behavior decreasing concentration and adding free ligand to the solution of the iron(II) complex. This behavior suggests the idea of an absorption process due to the species  $\text{Fe}(\text{phen})_3^0$  that complicates the reduction occurring at the potential of the third step.

Thus for the electrode processes of tris (1,10-phenanthroline) iron(II) cation we can write the following reactions:



The behavior of  $\text{Fe}(\text{phen})_3^{2+}$ ,  $\text{Fe}(4,7\text{-dmphen})_3^{2+}$  and  $\text{Fe}(4,7\text{d}\phi\text{phen})_3^{2+}$  cations can be discussed from the point of view of the influence of substitution. Substituents will affect both the  $\sigma$  and  $\pi$  bonding between the iron and the nitrogen atoms in substituted complexes.

The  $\sigma$  bonds involves electron donation from nitrogen to iron, but  $\pi$  bonding involves back-donation of electrons from the iron to the resonating ring; hence substituent effects will act in opposite directions on the two types of bonding.

The most negative half wave potentials found for  $\text{Fe}(4,7\text{dmphen})_3^{2+}$  show that strong  $\sigma$  bonds are present in this complex. All this agreed with the fact that methyl groups are electron donating groups and cause the great stability of this compound.

In the case of  $\text{Fe}(4,7\text{d}\phi\text{phen})_3^{2+}$  we found half wave potentials less negative than  $\text{Fe}(\text{phen})_3^{2+}$ .

It must be considered that phenyl groups are electron withdrawing groups and therefore they reduce the force of the  $\sigma$  bonds from the nitrogen atoms to the iron.

There is no increase of back-donation, because it is not possible to make phenyl groups coplanar with the phenanthroline nucleus, as a matter of fact there is overcrowding of the hydrogen atoms.

Thus phenyl groups are responsible for the shift to less negative potentials of  $\text{Fe}(\text{d}\phi\text{phen})_3^{2+}$  half-wave values.