

## Electrochemical investigations on phospho ferrocenes

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### Abstract

The redox behaviour of di-, tri-, penta- and hexaphospha ferrocene complexes and of five transition metal carbonyl complexes of the triphospha ferrocene  $[\text{Fe}(\eta^5\text{-C}_2^1\text{Bu}_2\text{P}_3(\eta^5\text{-C}_5\text{Me}_5)]$  **2** has been investigated by cyclic voltammetry. The oxidation potential of the phospho ferrocene complexes is determined by the number of electron-donating alkyl groups and phosphorus atoms, the latter showing electron-withdrawing properties. Electrochemical investigations on metal carbonyl complexes of **2** revealed an anodic shift of the oxidation potential of **2**. The data allow conclusions to be drawn about the overall  $\sigma$ -donor– $\pi$ -acceptor properties of **2**.

**Keywords:** Phosphorus; Iron; Electrochemistry; Metallocenes

### 1. Introduction

Among the numerous dynamic methods of electroanalytical chemistry which have been developed in the last decade, cyclic voltammetry has achieved great popularity and almost replaced classical polarography [1]. Several electrochemical investigations have been performed on phospho ferrocenes. Mathey and coworkers [2–4] have reported electrochemical investigations on 1,1'-diphospha ferrocenes. Scheme 1 summarises experimental oxidation potentials  $E_{\text{ox}}$  (versus the standard calomel electrode (SCE)) on three types of system [4], as well as the results of quantum mechanical calculations [5,6].  $E_{\text{ox}}$  values vs. ferrocene are shown in brackets.

Mathey and coworkers have reported that increasingly positive oxidation potentials result from the replacement of CH fragments in the cyclopentadienyl ring of ferrocene by phosphorus atoms which have greater overall electron-withdrawing properties. Phospho ferrocenes become harder to oxidize when hydrogen atoms are replaced by phenyl groups, whereas the presence of

electron-donating methyl groups on the ring carbon atoms creates an opposite effect.

Both effects partly compensate each other and determine the overall oxidation potentials, which are found to be more positive than ferrocene itself in nearly all the phospho ferrocenes studied so far. With the exception of  $[\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_4\text{H}_2\text{Me}_2\text{P})]$  shown above ( $E_{\text{ox}} = -20$  mV vs. ferrocene), all phospho ferrocenes studied have more positive  $E_{\text{ox}}$  values than ferrocene itself.

Electrochemical studies have also been performed on  $\eta^1$ -ligated transition metal carbonyl complexes of 3,3',4,4'-tetramethyl-1,1'-diphospha ferrocene  $[\text{Fe}(\eta^5\text{-C}_4\text{H}_2\text{Me}_2\text{P})_2]$  [7]. The reduction potentials of the coordination compounds  $[\text{Fe}(\eta^5\text{-C}_4\text{H}_2\text{Me}_2\text{P})_2\{\text{M}(\text{CO})_5\}_x]$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}; x = 1, 2$ ) were determined and reversible one-electron reduction of the diphospha ferrocene was observed. Furthermore, both one ( $x = 1$ ) and two ( $x = 2$ ) additional irreversible reduction steps were detected, involving the carbonyl metallate anions  $[\text{M}(\text{CO})_5]^-$ . The electrochemical oxidation of  $\{\text{Fe}(\eta^5\text{-C}_4\text{H}_2\text{Me}_2\text{P})_2[\text{M}(\text{CO})_5]_x\}$  has also been reported, and it has been established that oxidation of the iron takes place most readily, while the  $[\text{M}(\text{CO})_5]$  moieties participate in the subsequent oxidation steps [7].

Elschenbroich et al. [8] investigated the electrochemistry of diphospha benzene vanadium(0)  $[\text{V}(\eta^6\text{-C}_5\text{H}_5\text{P})_2]$

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Table 1

Oxidation and reduction potentials of the phospho ferrocene complexes 1–6 and ferrocene determined by RD and CV methods. All values in millivolts vs. SCE

Compound	Method: RD		Method: CV	
	$E_{1/2}^{\text{ox}}$	$N = I_{\text{ring}} / I_{\text{disk}}$	$E_p^{\text{ox}}$	$E_p^{\text{red}}$
ferrocene	640	0.225	670	450
1	470	0.225	510	330
2	890	0.225	830	670
3	—	—	900	—
4	—	—	1170	—
5	1030	0.157	1100	*
6	1230	0.200	1250	*

\* The determination of the peak potentials was not possible due to indistinct peak shapes.

1 is the first phospho ferrocene which shows a negative oxidation potential vs. ferrocene (–160 and –180 mV respectively). The positive inductive effect of the five methyl groups obviously overcompensates the electron-withdrawing effect of the two phosphorus atoms, and 1 is easier to oxidize than ferrocene itself. In 2 the presence of five methyl groups is not sufficient to compensate the electron-withdrawing effect of the three phosphorus atoms and the resulting oxidation potential remains positive. As expected, compound 2 is easier to oxidize than the corresponding cyclopentadienyl complex 4.

Similar conclusions can be drawn by comparison of the reduction potentials. Electron-donating alkyl groups cause a cathodic shift in the reduction potentials, while electron-withdrawing phosphorus atoms cause an anodic shift. Comparison of reduction and oxidation potentials leads to the conclusion that a phospho ferrocene, which is easy to reduce, is difficult to oxidize. The value for  $N = I_{\text{ring}} / I_{\text{disk}}$  shows a significant deviation only for 5 ( $N = 0.157$ ) compared with compounds 1, 2 and 6 and ferrocene (see Table 1). This can be explained by enhanced passivation or adsorption effects at the electrode and/or by partly irreversible processes.

Table 2

Oxidation and reduction potentials of the phospho ferrocene complexes 1–6 determined by RD and CV methods. All values in millivolts vs. ferrocene

Compound	Method: RD	Method: CV	
	$E_{1/2}^{\text{ox}}$	$E_p^{\text{ox}}$	$E_p^{\text{red}}$
1	–180	–160	–120
2	250	160	220
3	—	260	—
4	—	530	—
5	390	430	*
6	590	580	*

\* The determination of the peak potentials was not possible due to indistinct peak shapes.

Table 3

Oxidation and reduction potentials of the metal carbonyl complexes  $[\text{Fe}(\eta^5\text{-C}_2^t\text{Bu}_2\text{P}_3)(\eta^5\text{-C}_5\text{Me}_5)\text{M}_x(\text{CO})_y]$  7–11 and ferrocene determined by RD and CV methods. All values in millivolts vs. SCE

Compound	$\text{M}_x(\text{CO})_y$	Method: RD		Method: CV	
		$E_{\text{ox}}$	$N = I_{\text{ring}} / I_{\text{disk}}$	$E_{\text{ox}}$	$E_{\text{red}}$
ferrocene	—	640	0.225	670	450
7	$\text{Fe}(\text{CO})_4$	780	0.033	830	680
8	$\text{Cr}(\text{CO})_5$	830	0.222	890	650
9	$\text{Mo}(\text{CO})_5$	1010	0.211	1100	830
10	$\text{W}(\text{CO})_5$	1000	0.201	1080	850
11	$\text{Mn}(\text{CO})_2(\text{C}_5\text{H}_4\text{Me})$	580	0.203	610	460

## 2.2. Determination of oxidation potentials on transition metal carbonyl complexes of phospho ferrocenes

The electrochemical measurements on metal carbonyl complexes of the triphospha ferrocene  $[\text{Fe}(\eta^5\text{-C}_2^t\text{Bu}_2\text{P}_3)(\eta^5\text{-C}_5\text{Me}_5)]$  2 (Scheme 3) were all carried out under the same experimental conditions as described above. The results of the electrochemical investigations on the metal carbonyl complexes  $[\text{Fe}(\eta^5\text{-C}_2^t\text{Bu}_2\text{P}_3)(\eta^5\text{-C}_5\text{Me}_5)\text{M}_x(\text{CO})_y]$  7–11 are collected in Table 3.

The redox behaviour of the phospho ferrocene metal carbonyl complexes 7–11 is characterized by single electron transfer processes. This allows the conclusion that only the triphospha ferrocene moiety is involved in the electrochemical processes.

Coordination of a metal carbonyl fragment to 2 should lower the overall electron density at the iron centre, thereby rendering oxidation more difficult by comparison with 2. This behaviour is indeed observed for the  $[\text{M}(\text{CO})_5]$  complexes 8 ( $\text{M} = \text{Cr}$ ), 9 ( $\text{M} = \text{Mo}$ ) and 10 ( $\text{M} = \text{W}$ ), and for the  $[\text{Fe}(\text{CO})_4]$  complex 7 and  $[\text{Mn}(\text{CO})_2(\text{C}_5\text{H}_4\text{Me})]$  11.

The triphospha ferrocene moiety can be considered as a good  $\pi$ -acceptor and poor  $\sigma$ -donor towards metal carbonyl fragments and this is supported by bond length measurements on the  $[\text{M}(\text{CO})_5]$  adducts and  $^{95}\text{Mo}$

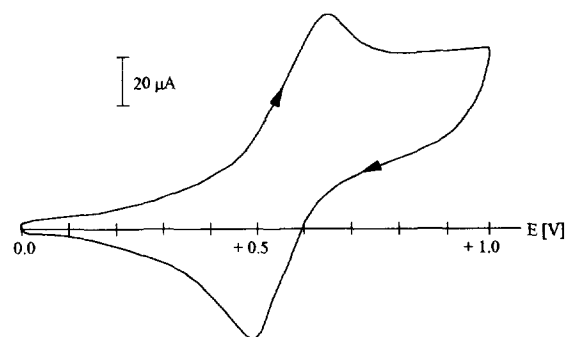


Fig. 1. Cyclic voltammogram of  $[\text{Fe}(\eta^5\text{-C}_2^t\text{Bu}_2\text{P}_3)(\eta^5\text{-C}_5\text{Me}_5)\text{Mn}(\text{CO})_2(\text{C}_5\text{H}_4\text{Me})]$  11 (6.1 mg in 10 ml of  $\text{CH}_2\text{Cl}_2$ , 0.1 mol  $[\text{TBA}][\text{BF}_4]$ , CV method, Pt electrode, scan speed  $0.2 \text{ V s}^{-1}$ , vs. SCE).

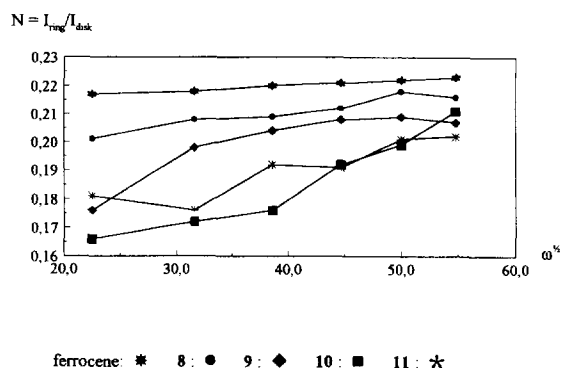


Fig. 2. Dependence of the correlation  $N = I_{\text{ring}} / I_{\text{disk}}$  on the rotation rate  $\omega$  for the metal carbonyl complexes **8–11** and for ferrocene.

chemical shift data on **9** [10]. The oxidation potential of the manganese complex **11** is found to be lower than those of the corresponding  $[M(\text{CO})_5]$  adducts (**8–10**), which is presumably due to the poorer overall  $\pi$ -acceptor ability of the manganese fragment arising from the electron-donating behaviour of the cyclopentadienyl ring.

The reduction potentials and the oxidation potentials reflect the same tendencies as described above, however the occurrence of carbonyl metallate anions could not be observed.

A typical cyclic voltammogram is presented in Fig. 1.

In the case of complete reversibility of an electron transfer process, the quotient  $N = I_{\text{ring}} / I_{\text{disk}}$  should have the value found for ferrocene ( $N = 0.225$ ). Interestingly, a significantly different value of  $N$  is found for the  $[\text{Fe}(\text{CO})_4]$  complex **7**, and strong adsorption of this compound on the electrode surface could possibly account for this effect. For some RD measurements the coefficient  $N$  also depends on the rotation rate  $\omega$ , as shown in Fig. 2. This provides further evidence for the partly irreversible nature of the electron transfer processes or secondary reactions occurring after oxidation. Reversible conditions can best be realized at high rotation rates.

### 3. Experimental details

The phospho ferrocene complexes **1**, **9**, **11** [10], **2** [11], **3**, **4** [12], **5**, **6** [13], **7**, **8** and **10** [14] were prepared as described in the literature. The cyclic voltammograms were recorded on a Pine AFRDE 5 potentiostat equipped with the modulated rotator Pine AFMSRX and disk–ring platinum electrodes as working electrodes ( $R_{\text{disk}} = 2.29$  mm,  $R_{\text{ring}} = 2.46$  mm,  $R_{2\text{ring}} = 2.69$  mm). The measurements were performed using  $10^{-3}$  molar

solutions in dichloromethane with  $[\text{TBA}][\text{BF}_4]$  as supporting electrolyte. Dichloromethane was dried over  $\text{K}_2\text{CO}_3$  and  $\text{P}_4\text{O}_{10}$  and redistilled.  $[\text{TBA}][\text{BF}_4]$  was purchased, purified by recrystallization from a 1:10 mixture of methanol and water, and dried in vacuo for 6 h at  $90^\circ\text{C}$ . Prior to the measurements, dry argon gas was bubbled through the 0.1 molar solution of  $[\text{TBA}][\text{BF}_4]$  in  $\text{CH}_2\text{Cl}_2$ .

The electrochemical investigations were carried out in an electrochemical cell with separate cathode and anode region. CV data were obtained using a platinum wire as the working electrode and the potential is referenced to the SCE. In addition, in situ potential calibration was performed after completion of each determination by recording the ferrocene peak in the same solution.

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