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ELECTROCHEMISTRY OF COORDINATION COMPOUNDS

XVI *. NEW MIXED 1,2-BIS(DIPHENYLPHOSPHINO)ETHANE-ACETONITRILE OR -CARBON MONOXIDE IRON(II), IRON(I) AND IRON(0) COMPLEXES

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Summary

The new iron compound, *trans*-[Fe(DPE)$_2$(MeCN)$_2$] (ClO$_4$)$_2$ (DPE= PPh$_2$CH$_2$CH$_2$PPh$_2$), has been prepared and investigated electrochemically. In acetonitrile the complex shows two reduction steps, consistent with the formation of the stable iron(I) species, [Fe(DPE)$_2$(MeCN)]$^+$ and the rather labile π-bonded acetonitrile adduct, Fe(DPE)$_2$(π-MeCN), respectively. Acetonitrile substitution by carbon monoxide leads to formation of the carbonylated species, which have been characterized, and examined by electrochemical techniques. A significant feature is that *trans*-[Fe(CO)$_2$(DPE)$_2$]$^{2+}$, unlike *trans*-[Fe(DPE)$_2$(MeCN)$_2$]$^{2+}$, takes up two electrons in a single process, the unstable d^7 intermediate undergoing a fast disproportionation. A tentative interpretation of this behaviour is suggested.

Introduction

In previous papers of this series we reported on the electrochemical reduction of cationic transition metal complexes of the cobalt [1,2] and nickel [3] triads with DPE (DPE = 1,2-bis(diphenylphosphino)ethane) as ligand. The electrochemical method proved in many cases superior to the chemical one for the preparation of complexes of the above elements in unusual oxidation states as well as a very useful tool for investigating the reactitivity of these species towards carbon monoxide [4,5].

With the purpose of extending such investigations to the iron triad we pre-

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* For part XV see ref. 19.

pared the new complex, *trans*-[Fe(DPE)$_2$(MeCN)$_2$](ClO$_4$)$_2$, no iron diphosphine cationic derivative having yet been reported. A detailed study of the electrochemical behaviour of this complex, with emphasis on the properties of the reduced species, both in the presence and in the absence of carbon monoxide, has been made and the results are presented below.

Results and discussion

Acetonitrile derivatives

At 25°C the cyclic voltammetric pattern of *trans*-[Fe(DPE)$_2$(MeCN)$_2$]$^{2+}$ in acetonitrile consists of a single, one-electron, reversible oxidation process (E^0 = 1.06 V) (Fig. 1a) and of two subsequent, one-electron, reduction processes (peaks A and C in Fig. 1b). As one can see, while the second reduction step corresponds to an uncomplicated reversible transfer (E^0 = —1.78 V), the first one (E_p = —1.36 V), still reversible in shape, displays on the reverse scan a coupled oxidation peak, B, only at —0.76 V.

Exhaustive controlled potential electrolysis carried out at potentials anodic to the oxidation peak requires nine equivalents of electrons per mol of complex, and yields a yellow acid solution containing the metal in the (III) valence state and diphosphine oxide as ligand. These results indicate that the primary oxidation product, viz. [Fe(DPE)$_2$(MeCN)$_2$]$^{3+}$, is rather labile towards loss of the phosphorus ligands, which, being more easily oxidizable than the depolarizer, are converted to oxide in the presence of the water present in the medium [6].

Potentiostatic reduction at potentials on peak A, while requiring one equivalent of electrons per mol of depolarizer, produces a dark brown solution,

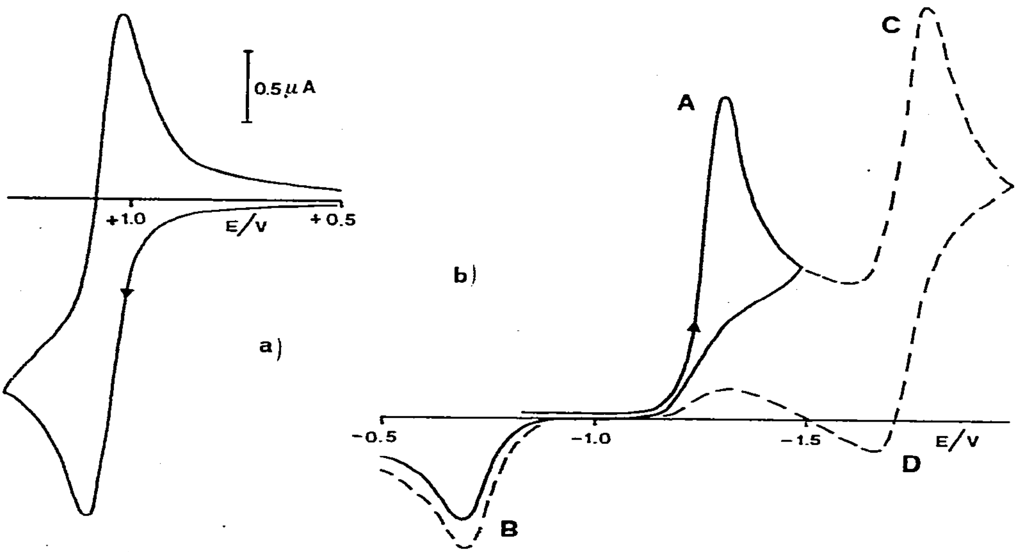


Fig. 1. Cyclic voltammograms for (a) the oxidation and (b) the reduction of *trans*-[Fe(DPE)$_2$(MeCN)$_2$]$^{2+}$ in acetonitrile (2.0 × 10^{-3} *M*, 0.1 *M* TEAP as supporting electrolyte) at a platinum electrode. Scan rate 200 mV s^{-1}, temperature 25°C.

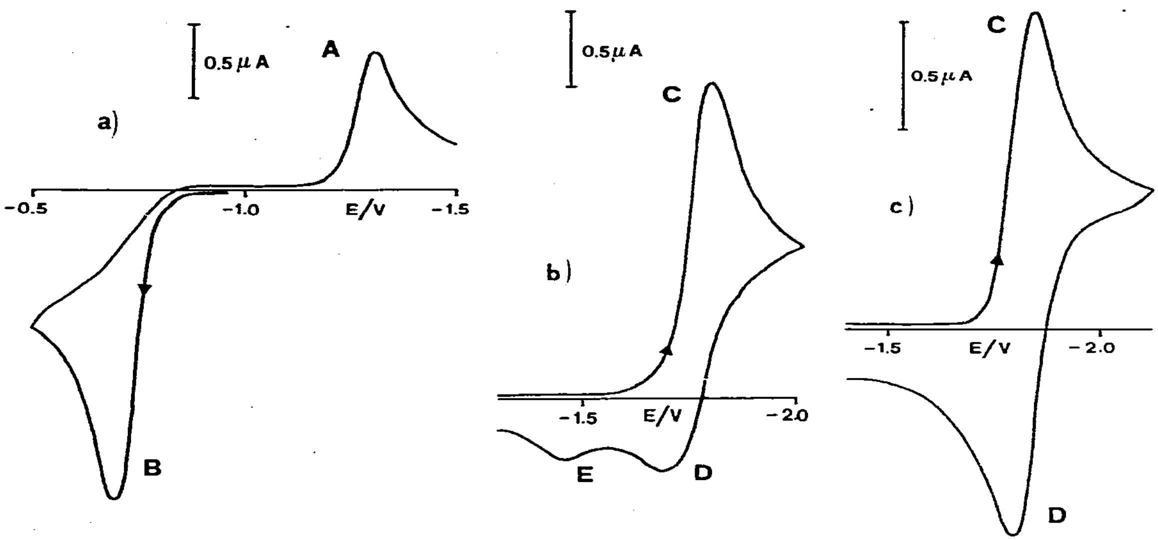


Fig. 2. Cyclic voltammograms for (a) the oxidation and (b), (c) the reduction of $[Fe(DPE)_2(MeCN)]^+$ in acetonitrile (2.0×10^{-3} *M*, 0.1 *M* TEAP). Scan rate 200 mV s^{-1}, temperature (a), (b) 25°C, (c) —30°C.

which is time-stable but exceedingly air sensitive; its voltammogram shows, in addition to the expected cathodic peak C, the fully developed one-electron, reversibly shaped, anodic peak B, regenerating peak A on the reverse sweep (Fig. 2a). It follows that the overall reduction-oxidation process is chemically reversible, charge transfers A and B being both followed by a fast irreversible chemical reaction. The brown crystalline solid isolated from the reduced solution (see below) is paramagnetic, with a magnetic moment value corresponding to the presence of one unpaired electron. Its IR spectrum shows a sharp peak at 2235 cm^{-1} attributable to a coordinated acetonitrile C≡N stretching mode. In acetonitrile the compound behaves as a 1/1 electrolyte and in the electronic spectrum shows two absorption bands at 615 nm (ϵ = 200) and 420 nm (ϵ = 4200). Elemental analysis indicates the formulation $[Fe(DPE)_2(MeCN)](ClO_4)$.

As far as the second reduction process is concerned, the anodic portion of the cyclic voltammogram, not well resolved when the iron(II) species is the depolarizer (see Fig. 1b, peak D), is now split into two peaks (Fig. 2b), i.e. a new peak, E, in addition to the reversibly coupled peak, D, appears at —1.46 V. Its position and height are strongly dependent on scan rate and temperature: on increasing scan rate it moves towards more anodic potentials, while its height decreases and the cycle approaches more and more the reversible shape; at —30°C the cycle is quite reversible (Fig. 2c). Controlled potential electrolysis at 25°C requires one equivalent of electrons per mol of $[Fe(DPE)_2(MeCN)]^+$ and produces a pale yellow solution with a large amount of brown precipitate. Elemental analysis of the filtered product fits the formula $Fe(DPE)_2$, a species known to exist in the tautomeric form $HFe(C_6H_4PPhCH_2CH_2PPh_2)(DPE)$ [7], to be benzene soluble and to show a ν(Fe—H) band in the IR spectrum. The compound we obtained is, in contrast, almost insoluble in every organic solvent and its IR spectrum, though showing an intense band at 730 cm^{-1} attributable

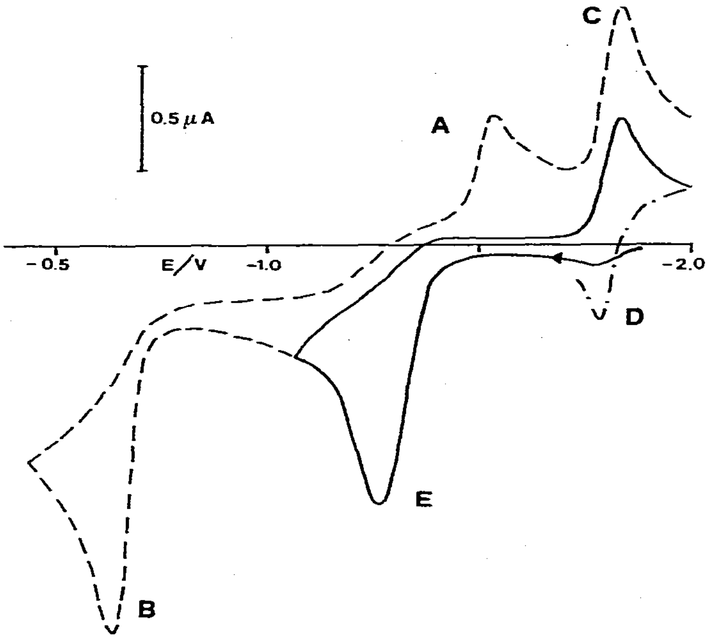
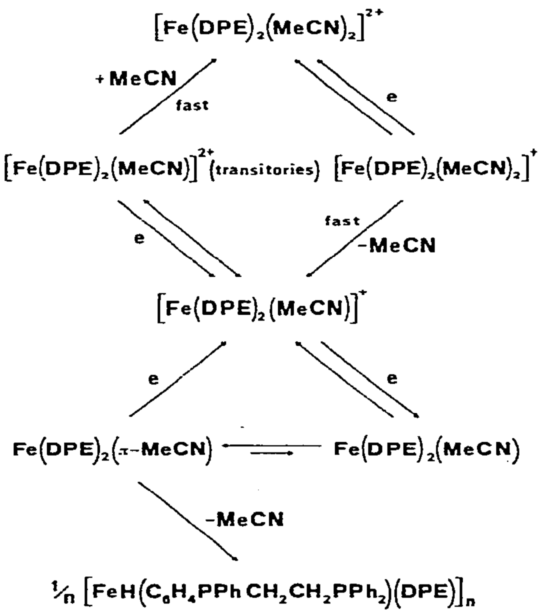


Fig. 3. Same as Fig. 1 after completion of a two-electron reduction at —30° C.

to the presence of an *ortho*-disubstituted benzene [7], does not show any absorption band assignable to an Fe—H stretching mode; its hydridic character is indicated, however, by the well known reaction with carbon tetrachloride. This discrepancy can be reconciled by assuming that the solid possesses a polynuclear structure; in fact, a binuclear structure has been established for an analogous ruthenium diphosphine complex [8]. At low temperature (—30° C) the electrolysis produces a red solution (λ_{max} 400 and 550 nm) showing the cyclic voltammetric profile of Fig. 3: besides a small amount (~10%) of the primary reduction product, $Fe(DPE)_2(MeCN)$, (peak D), a new iron(0) species (peak E), still oxidizable, though irreversibly, to $[Fe(DPE)_2(MeCN)]^+$ (peaks B and C), is present. As the ratio of peak D to peak E is time independent, an equilibrium between the two iron(0) species must have been established. The solution, which is unreactive towards hydrogen and ethylene, reacts very quickly with one equivalent of carbon monoxide, affording the known $Fe(CO)(DPE)_2$ [9]. On standing at low temperature, deep red crystals precipitate from the reduced solution with simultaneous discharge of the colour and flattening of the voltammogram. The product, filtered off and dried under vacuum at low temperature, shows in the IR spectrum a fugitive intense band at 1760 cm^{-1}: if the temperature is allowed to rise the red solid loses acetonitrile, and is converted into polymeric *ortho*-metalated hydride described above. As far as the absorption at 1760 cm^{-1} is concerned, it could be tentatively assigned either to ν(Fe—H) of the hydrido *ortho*-metalated diphosphine species, $HFe(C_6H_4PPhCH_2CH_2PPh_2)(DPE)(MeCN)$, analogous to the recently reformulated ruthenium complex, $HRu(C_6H_4PPh_2)(PPh_3)_2(MeCN)$ [10], or to ν(C=N) of an acetonitrile molecule π-bonded to iron(0); the π-bonding ability of acetonitrile has been recently ascertained in zero-valent cobalt complexes [11]. The former possibility seems very unlikely, since the IR frequency is quite low when compared with literature data, and furthermore the complex is oxidizable at a potential far more negative than that for the ruthenium hydride ($\Delta E_{\frac{1}{2}} \sim 1$ V). On the other hand we obtained evidence for the transient intermediate, hydride precursor, $Ru(PPh_3)_3(MeCN)$ [10], in the form of symmetrical oxidation-reduction peaks at a potential value very close to that of the iron(0)/iron(I) redox couple. Consequently, although the identity of the reduction product has not been definitely established, its formulation as $Fe(DPE)_2(\pi\text{-}MeCN)$ seems reasonable. The facile $\sigma \rightarrow \pi$ rearrangement of the coordinated acetonitrile is consistent with the zero-valent state of iron and accounts also for the strong increase in the activation energy for the oxidation process.

The results are summarized in Scheme 1.



SCHEME 1. Reduction-oxidation mechanism of *trans*-[$Fe(DPE)_2(MeCN)_2$]$^{2+}$ in acetonitrile.

Carbon monoxide derivatives

Carbon monoxide at 25°C and 1 atm, though unreactive towards [$Fe(DPE)_2(MeCN)_2$]$^{2+}$, produces a change in the electrochemical pattern of the complex in that the first reduction wave is higher, the total two-electron limiting current being unchanged. Cyclic voltammetric and chronoamperometric experiments demonstrate the ECE character of the process [12—14], which leads to the final $Fe(CO)(DPE)_2$, as shown by the identity of the redox couple exhibited in a multicycle scan at $E^0 = -1.11$ V with that of an authentic sample of the carbonylated complex prepared according to the literature [9]. Hence the reaction sequence is as shown in eqs. 1—3, where the species formed in the chemical reaction interposed between the two charge transfers is more readily reduced than the original compound. The pseudo-first order rate constant value for the

$$[\mathrm{Fe(DPE)_2(MeCN)_2}]^{2+} \xrightarrow[-\mathrm{MeCN}]{+e} [\mathrm{Fe(DPE)_2(MeCN)}]^{+} \qquad (1)$$

$$[\mathrm{Fe(DPE)_2(MeCN)}]^{+} \xrightarrow[-\mathrm{MeCN}]{+\mathrm{CO}} [\mathrm{Fe(CO)(DPE)_2}]^{+} \qquad (2)$$

$$[\mathrm{Fe(CO)(DPE)_2}]^{+} \underset{-e}{\overset{+e}{\rightleftharpoons}} \mathrm{Fe(CO)(DPE)_2}\ (E^0 = -1.11\ \mathrm{V}) \qquad (3)$$

chemical step (2) is found to be 0.33 s^{-1} (25° C, CO satd. soln.).

Exhaustive electrolysis under 1 atm pressure of CO, whatever the voltage, requires two equivalents of electrons per mol of complex, but the final light yellow solution does not show the cyclic voltammetric pattern, i.e. one reversible redox couple at $E^0 = -1.11$ V, and the IR spectrum (ν(CO) = 1810 cm^{-1}) of $Fe(CO)(DPE)_2$: three IR bands are shown at 1984, 1910 and 1891 cm^{-1} indicating the product to be the species $Fe(CO)_3(DPE)$ [15,16]. It follows that during the electrolysis carbon monoxide has replaced one DPE ligand also. On cooling to —30° C most of the released DPE is precipitated. Under such conditions (—30° C, 1 atm CO and DPE satd. soln.) the reduced solution exhibits the cyclic voltammetric profile drawn in Fig. 4, where peak A corresponds to a reversible, one-electron, oxidation process ($E^0 = -0.215$ V), the ratio of cathodic (B) to anodic (A) peak currents being, however, less than unity. Two additional cathodic responses, D and E, are observed on the reverse sweep, the first being reversibly coupled with peak C ($E^0 = -0.61$ V).

Controlled potential coulometry beyond the potential of peak A requires two equivalents of electrons per mol of depolarizer, with the fugutive appearance of a green colour and dissolution of the precipitated DPE. The cyclic voltammetry on the spent light yellow anolyte shows a single, two-electron, reduction process at $E_p = -0.86$ V, easily recognizable as peak E shown above (see Fig. 4). The most striking feature is the appearance in the anodic portion of the cyclic voltammogram of peaks C and A, the first peak increasing at the expense of the

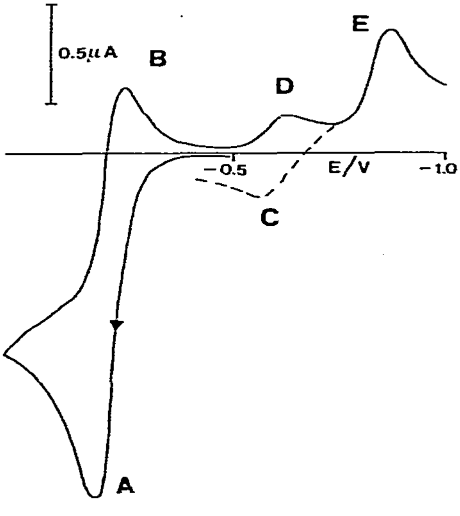


Fig. 4. Cyclic voltammogram for the oxidation of $Fe(CO)_3(DPE)$ (2.0 × 10^{-3} M) in 0.1 M TEAP acetonitrile solution saturated with CO and DPE at —30° C. Scan rate 200 mV s^{-1}.

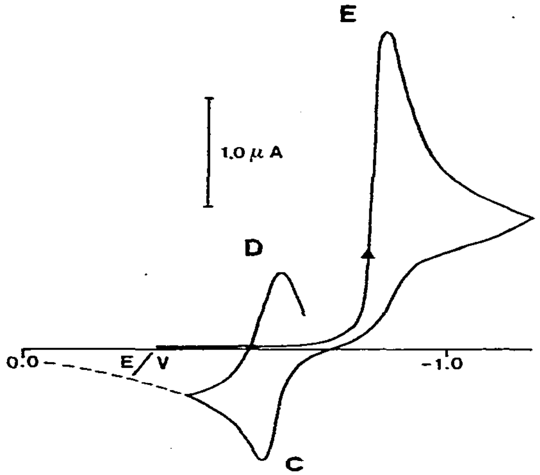


Fig. 5. Cyclic voltammogram for the reduction of *trans*-$[Fe(CO)_2(DPE)_2]^{2+}$ (2.0×10^{-3} *M*) in acetonitrile, 0.1 *M* TEAP solution at −30°C. Scan rate 200 mV s^{-1}.

second on bubbling argon through the solution, till only peak C is displayed (Fig. 5). The orange product isolated from the oxidized solution (see below) has been formulated on the basis of elemental analysis, infrared spectrum and conductivity measurements, as *trans*-$[Fe(CO)_2(DPE)_2](ClO_4)_2$, i.e. the previously unreported iron representative of the *trans*-$[M(CO)_2(DPE)_2]^{2+}$ series [17]. From these result it appears that: (i) $Fe(CO)_3(DPE)$, A, is oxidized to $[Fe(CO)_3(DPE)]^+$, B; (ii) under our experimental conditions $[Fe(CO)_3(DPE)]^+$ undergoes a chemical reaction to give an unstable intermediate, D, which is very likely to promote the transfer of a further electron leading to the final $[Fe(CO)_2(DPE)_2]^{2+}$, E; (iii) the two-electron reduction of $[Fe(CO)_2(DPE)_2]^{2+}$ regenerates $Fe(CO)_3(DPE)$ via the iron(0) species C, which is stable in the absence of CO and oxidizable in a one-electron reversible step to D. As a result of the identification of this new iron(0) derivative we were able to elucidate the reaction sequence undergone by $[Fe(CO)_3(DPE)]^+$.

Controlled potential electrolysis of $[Fe(CO)_2(DPE)_2]^{2+}$ at low temperature and under argon confirms the consumption of two equivalents of electrons per mol of complex, and leads to a yellow solution whose IR spectrum shows two intense bands at 1887 and 1827 cm^{-1}. The strong similarity to the spectrum of the known $Fe(CO)_2(PPh_3)_3$ ($\nu(CO)$ = 1882 and 1823 cm^{-1} in CS_2 [18]) suggests the formulation $Fe(CO)_2(DPE)_2^*$ for the reduction product, the label indicating that one DPE acts as monodentate ligand. As intermediate D is now formulated as $[Fe(CO)_2(DPE)_2^*]^+$ the occurrence of reaction 4 can be proposed. The instability of the complex $[Fe(CO)_2(DPE)_2^*]^+$ is confirmed by the electrochemical oxidation of $Fe(CO)_2(DPE)_2^*$: two electrons are transferrred and $[Fe(CO)_2(DPE)_2]^{2+}$ is formed. If only one electron is quickly allowed to pass, the green yellow solution of $[Fe(CO)_2(DPE)_2^*]^+$ quickly fades with the formation of $Fe(CO)_2(DPE)_2^*$ and $[Fe(CO)_2(DPE)_2]^{2+}$ in 1/1 ratio, indicating that the d^7 species

$$[Fe(CO)_3(DPE)]^+ + DPE \rightarrow [Fe(CO)_2(DPE)_2^*]^+ + CO \qquad (4)$$

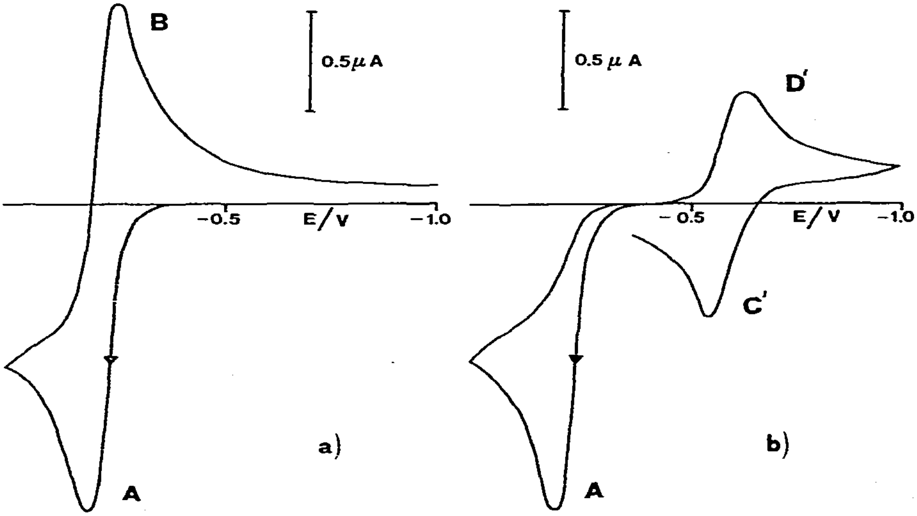


Fig. 6. (a) Cyclic voltammogram for the oxidation of $Fe(CO)_3(DPE)$ (2.0×10^{-3} *M*) in acetonitrile, 0.1 *M* TEAP, at —30°C under argon. Scan rate 200 mV s^{-1}. (b) Same as (a) after addition of one equivalent of PPh_2Me.

decays by a disproportionation pathway.

Since both $[Fe(CO)_3(DPE)]^+$ [16] and $[Fe(CO)(DPE)_2]^+$ (see below) are stable enough to be isolated, the anomalous behaviour of $[Fe(CO)_2(DPE)_2^*]^+$ could be tentatively attributed to the presence of one free phosphorus group capable of chelating. In fact, the uncomplicated voltammetric profile of $Fe(CO)_3(DPE)$ at —30°C under argon and in the absence of DPE (see Fig. 6a) upon adding one equivalent of PPh_2Me, changes into that shown in Fig. 6b. The most significant features are the disappearance of peak B and the appearance of redox couple D'/C' closely resembling ($E^0 = -0.59$ V) the D/C couple; no additional cathodic peak is observed. As one can see, the ligand PPh_2Me also quickly replaces a carbonyl group in $[Fe(CO)_3(DPE)]^+$ (see eq. 4), the resulting species being in this case stable, at least on the cyclic voltammetric time scale.

Potentiostatic oxidation of $Fe(CO)_3(DPE)$ at low temperature in the presence of an equivalent amount of PPh_2Me confirms that a single electron per molecule of complex is transferred. The IR spectrum of the stable deep-green anolyte shows two strong carbonyl bands at 1996 and 1940 cm^{-1}, i.e. at frequencies approximately 100 cm^{-1} higher than those observed in $Fe(CO)_2(DPE)_2^*$ or $Fe(CO)_2(PPh_3)_3$. The occurrence of similar shifts in going from the d^8 to the d^7 configuration in phosphine-iron tricarbonyls [16] as well as in the monocarbonylated couple $Fe(CO)(DPE)_2/[Fe(CO)(DPE)_2]^+$ (see below) strongly suggests that the electrolysis product is $[Fe(CO)_2(DPE)(PPh_2Me)]^+$. Addition to the oxidized solution of an excess of PPh_2Me has no effect; in contrast, addition of one equivalent of DPE immediately results in the formation of $Fe(CO)_2(DPE)_2^*$ and $[Fe(CO)_2(DPE)_2]^{2+}$ in 1/1 ratio, providing additional evidence that bidentate ligand species specifically promote disproportionation.

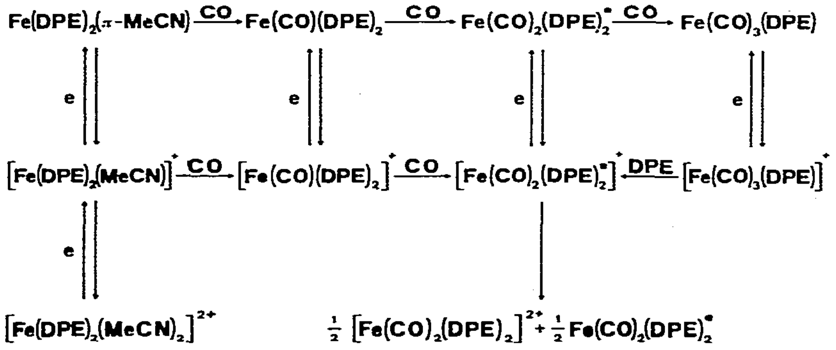
In the light of our previous findings on the decay of pentacoordinated d^7 rhodium and iridium derivatives, where an intermediate involving an increase in the coordination number was found to be responsible for the disproportionation reaction to occur [19], the unique instability among the d^7 iron complexes here described of $[Fe(CO)_2)(DPE)_2^*]^+$, in which it is reasonable to presume that the accompanying extra phosphorus group is to some degree coordinated, could be accounted for by steps 5 and 6, where step 5, lying far to the left,

$$[Fe(CO)_2(DPE)_2^*]^+ \rightleftharpoons [Fe(CO)_2(DPE)_2]^+ \tag{5}$$

$$[Fe(CO)_2(DPE)_2]^+ + [Fe(CO)_2(DPE)_2^*]^+ \rightarrow [Fe(CO)_2(DPE)_2]^{2+} + Fe(CO)_2(DPE)_2^* \tag{6}$$

indicates a change of coordination number from five to six, and step 6 implies that $[Fe(CO)_2(DPE)_2]^+$ is oxidizable at a potential more negative than the reduction potential of $[Fe(CO)_2(DPE)_2^*]^+$ ($E^0 = -0.61$ V). The two-electron reduction of $[Fe(CO)_2(DPE)_2]^{2+}$ to $Fe(CO)_2(DPE)_2^*$ has, in fact, been found to proceed by an ECE mechanism [12,13], the chemical reaction coupled between the two reversible charge transfers being reasonably recognizable in the rapid dissociation of one phosphorus ligand from the primary reduction product, viz. $[Fe(CO)_2(DPE)_2]^+$. Finally, it is noteworthy that both the d^7 complexes we prepared, $[Fe(DPE)_2(MeCN)]^+$ and $[Fe(CO)(DPE)_2]^+$, while quite stable under an inert atmosphere, immediately disproportionate upon addition of carbon monoxide into the final products, $Fe(CO)_3(DPE)$ and $[Fe(CO)_2(DPE)_2]^{2+}$.

The results are summarized in Scheme 2.



SCHEME 2. Reduction-oxidation mechanism of *trans*-$[Fe(DPE)_2(MeCN)_2]^{2+}$ in acetonitrile under CO.

This investigation shows conclusively that a good number of iron complexes of low and/or unusual valence state can be readily prepared by simply adding and/or removing a controlled number of electrons from the depolarizer at the electrode, without any of the chemical disadvantages involved in the use of most redox reagents. In addition, electrochemical techniques have proved capable of giving much information about the intermediates in the redox processes, allowing a more detailed study of the reduction-oxidation mechanisms to be made.

Experimental

Chemicals and reagents

The previously unreported *trans*-[Fe(DPE)$_2$(MeCN)$_2$](ClO$_4$)$_2$ was directly synthesized from Fe(ClO$_4$)$_2$ · 6 H$_2$O and DPE in acetonitrile. Thus a solution of iron perchlorate (0.36 g, 1.0 mmol) in acetonitrile (15 ml) was added to a stirred solution of DPE (0.85 g, 2.1 mmol) in benzene (15 ml) at room temperature under nitrogen. The resulting deep red solution was warmed for about 2 h at 65°C during which time a small discharge of the colour was observed (*CARE!* Perchlorate). The cooled solution was evaporated under reduced pressure to small volume and dichloromethane (30 ml) was added to the residue to give a pink solid. Crystallization of this material from acetonitrile/dichloromethane gave the product as red crystals, which were dried in vacuo. Anal.: Found: C, 59.0; H, 4.8; N, 2.5; P, 12.0. $C_{56}H_{54}Cl_2FeN_2O_8P_4$ calcd.: C, 59.4; H, 4.8; N, 2.5; P, 11.0%. The product is diamagnetic, behaves as a 2 : 1 electrolyte in acetonitrile, and in the electronic spectrum shows absorption bands at 385 nm (ϵ 210) and 505 nm (ϵ 192). The IR spectrum in the solid state shows a sharp absorption at 2265 cm^{-1} assignable to ν(CN). The increase in the frequency compared to that of free acetonitrile (ν(CN) 2247) indicates donor bonding through the nitrogen lone pair [20]. The exhibition of a single nitrile stretching band and the formation of the previously reported *trans*-Fe(SCN)$_2$-(DPE)$_2$ [21] in the reaction with NH$_4$SCN in acetonitrile strongly support the *trans* configuration for the complex. The solid is stable in air and very soluble in acetonitrile, but it is decomposed by other polar solvents.

The preparation of 1,2-bis(diphenylphosphino)ethane (DPE), and the purification of acetonitrile and tetraethylammonium perchlorate (TEAP) have been described previously [4]. All the chemicals employed were of reagent grade quality (C. Erba and Fluka). All solutions contained 0.1 *M* TEAP as supporting electrolyte. Argon, 99.999%, rendered oxygen-free by passage over reduced copper at 450°C, and 99.995% carbon monoxide were used.

Apparatus and procedure

All experiments were carried out in a H-shaped, liquid jacketed cell. A silver/ 0.1 *M* silver perchlorate electrode in acetonitrile separated from the test solution by 0.1 *M* TEAP solution in acetonitrile sandwiched between two fritted disks was used as reference electrode. In the voltammetric measurements the working electrode was a planar platinum microelectrode (area 0.3 mm^2) with renewal of the diffusion layer [22], the renewal time being fixed at 2.0 s. An Amel (Milan, Italy) model 471 multipolarograph was employed for voltammetric and cyclic voltammetric measurements. Cyclic voltammetric data refer to a scan rate of 200 mV s^{-1}. The compensation of ohmic drop was achieved by positive feed-back. Controlled potential electrolyses were carried out with an Amel model 552 potentiostat and the associated coulometer was an Amel model 721 analog integrator. The working electrode was a platinum gauze (approximate area 100 cm^2) and the counter electrode was external, the connection being made through an appropriate salt bridge.

Electronic spectra were recorded on a Perkin—Elmer model 575 spectrometer, IR spectra on a Perkin—Elmer 457 grating spectrometer. IR spectra of solids were measured with KBr discs; solution spectra were measured with compensation in 1 mm CaF_2 liquid cells. NMR spectroscopic determinations of the paramagnetic susceptibility were obtained using a Varian T 60 spectrometer. Molar conductivities were determined in mmolar acetonitrile solutions at 25° C.

Electrochemical preparations

trans-Bis[1,2-bis(diphenylphosphino)ethane]bis(acetonitrile)iron(II)perchlorate, $[Fe(DPE)_2(MeCN)_2](ClO_4)_2$. As an alternative to the chemical method described above, solutions of $[Fe(DPE)_2(MeCN)_2]^{2+}$ especially suitable for subsequent electrochemical preparations of iron(I) or iron(0) species can easily be generated in the electrochemical cell by anodic dissolution at room temperature with 100% current efficiency of a metallic iron foil in 50% v/v acetonitrile/toluene containing 0.1 *M* TEAP in the presence of the required amount of DPE (one mole of ligand per mol of electrons to be transferred). The electrolyzed solution is heated for about 2 h at 65° C, and after this time show a chemical and electrochemical pattern identical with that of a chemically prepared sample.

A similar preparation using Et_4NPF_6 instead of Et_4NClO_4 gives $[Fe(DPE)_2(MeCN)_2](PF_6)_2$.

Bis[1,2-bis(diphenylphosphino)ethane]acetonitrileiron(I) perchlorate, $[Fe(DPE)_2(MeCN)](ClO_4)$. A solution of $[Fe(DPE)_2(MeCN)_2](ClO_4)_2$ (1.0 g, 0.88 mmol) in 50 ml of acetonitrile containing 0.1 *M* $NaClO_4$ is electrolyzed under carefully deoxygenated argon at —1.5 V vs. Ag/0.1 *M* Ag^+ acetonitrile electrode in a two-compartment cell with a platinum gauze electrode. After completion of the electrolysis the dark brown solution is evaporated under reduced pressure almost to dryness (*CARE!* Perchlorate) and the residue dissolved in 20 ml of 1,2-dimethoxyethane. After a short time brown crystals separate, and these are filtered off, washed with a small volume of cold dimethoxyethane, and dried under vacuum. It should be remembered that this compound, besides being very reactive towards air even in the solid state, is particularly explosive. Anal.: Found: C, 65.6; H, 5.2; N, 1.3; P, 11.0. $C_{54}H_{51}ClFeNO_4P_4$ calcd.: C, 65.3; H, 5.1; N, 1.4; P, 12.5%. $\nu(CN) = 2235\ cm^{-1}$. $\mu = 2.6$ BM. Molar conductance: $133\ \Omega^{-1}\ cm^2\ mol^{-1}$.

Bis[1,2-bis(diphenylphosphino)ethane](π-acetonitrile)iron(0), $Fe(DPE)_2(\pi\text{-}MeCN)$. A suspension of $[Fe(DPE)_2(MeCN)_2](ClO_4)_2$ (1.0 g, 0.88 mmol) in 50 ml of acetonitrile at —30° C in the presence of 0.1 *M* TEAP as supporting electrolyte is electrolyzed at —2.1 V (other conditions as in the preceding preparation). At the end of the electrolysis the red solution is stirred until a red precipitate is formed. This is filtered off and dried, the temperature being kept low. Because of its thermal lability satisfactory elemental analysis data could not obtained. $\nu(CN) = 1760\ cm^{-1}$.

Carbonylbis[1,2-bis(diphenylphosphino)ethane]iron(0), $Fe(CO)(DPE)_2$. This was prepared analogously by addition of one equivalent of carbon monoxide to the solution of $Fe(DPE)_2(\pi\text{-}MeCN)$ (see above). The orange precipitate is filtered off, washed with cooled acetonitrile and dried under vacuum. Anal.: Found: C, 72.5; H, 5.3; P, 15.0. $C_{53}H_{48}FeOP_4$ calcd.: C, 72.3; H, 5.4; P, 14.1%. $\nu(CO) = 1810\ cm^{-1}$.

trans-Dicarbonylbis[1,2-bis(diphenylphosphino)ethane]iron(II) perchlorate,

$[Fe(CO)_2(DPE)_2](ClO_4)_2$. This is prepared by reduction at —1.5 V of $[Fe(DPE)_2(MeCN)_2](ClO_4)_2$ (1.0 g, 0.88 mmol) in 0.1 *M* $NaClO_4$ acetonitrile solution (50 ml) under carbon monoxide followed by oxidation at 0.0 V of the resulting light yellow solution. After addition of excess $NaClO_4$ (~6 g), the solution is cooled to —30°C and the orange precipitate which forms is filtered off, washed with ethanol, and dried under vacuum. Anal.: Found: C, 58.9; H, 4.4; P, 10.7. $C_{54}H_{48}Cl_2FeO_{10}P_4$ calcd.: C, 58.6; H, 4.3; P, 11.2%. $\nu(CO) = 1992$ cm^{-1}. Molar conductance: 272 Ω^{-1} cm^2 mol^{-1}.

Carbonylbis[1,2-bis(diphenylphosphino)ethane]iron(I) tetraphenylborate, $[Fe(CO)(DPE)_2](BPh_4)$. A suspension of $Fe(CO)(DPE)_2$ (1.0 g, 1.13 mmol) in 50 ml of acetonitrile/benzene (50% v/v) containing 0.1 *M* $NaClO_4$ is electrolyzed at —0.9 V on a platinum gauze electrode. At the end of the electrolysis the deep green solution is evaporated under reduced pressure to a small volume. After addition of $NaBPh_4$ (0.4 g, 1.2 mmol in 25 ml of methanol) the mixture is vigorously stirred for 1 h and the green precipitate is filtered off, washed with methanol, and dried under vacuum. Anal.: Found: C, 77.3; H, 5.6; P, 10.9. $C_{77}H_{68}BFeOP_4$ calcd.: C, 77.0; H, 5.7; P, 10.3%. $\nu(CO) = 1889$ cm^{-1}. $\mu =$ 1.85 BM. Molar conductance: 82 Ω^{-1} cm^2 mol^{-1}.

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