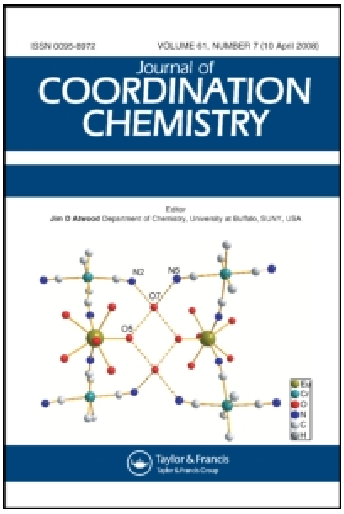

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SYNTHESIS AND ELECTROCHEMICAL PROPERTIES OF CYCLOPENTADIENYLIRON(II) COMPLEXES WITH BIS(DIPHENYLPHOSPHINO)AMINE AS LIGAND

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SYNTHESIS AND ELECTROCHEMICAL PROPERTIES OF CYCLOPENTADIENYLIRON(II) COMPLEXES WITH BIS(DIPHENYLPHOSPHINO)AMINE AS LIGAND

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The synthesis and properties of new cationic iron(II) complexes of general formula $[(\eta^5\text{-}C_5H_5)FeL(\eta^2\text{-dppa})]A$ $[A = I^-, L = CO(1); A = BF_4, L = CO(2)\ CH_3CN(4), \eta^1\text{-dppa}(5);$ $\text{dppa} = NH(PPh_2)_2]$ are described. The carbonyl complex $[(\eta^5\text{-}C_5H_5)Fe(CO)(\eta^2\text{-dppa})]BF_4$ is deprotonated to give the neutral complex $[(\eta^5\text{-}C_5H_5)Fe(CO)\{\eta^2\text{-}(PPh_2)_2N\}](3)$. All complexes have been characterized by elemental analysis and IR and NMR spectroscopies. Cyclic voltammetry of complexes **1**–**5** shows a diverse redox chemistry in acetonitrile solution. While the reduction of **1** and **2** leads to the formation of a dinuclear Fe(I) complex, **4** and **5** form mononuclear species of Fe(I); oxidation of metal centers of **1** and **2** is not observed and in complexes **3** and **4** the metal centers are oxidized at potentials < 1. Complex **5** in acetonitrile solution is transformed into complex **4**.

Keywords: Iron(II) complexes; Bis(diphenylphosphine)amine complexes; Electrochemistry; Cyclopentadienyliron(II) complexes

INTRODUCTION

The chemistry of the bis(diphenylphosphine)amine [dppa, $NH(PPh_2)_2$] has developed rapidly in recent years due to its versatile coordination properties.

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In a similar fashion to the widely employed ligand bis(diphenylphosphino)methane (dppm), dppa can bind to metal atoms in a number of ways: monodentate, chelating, bridging or tridentate bridging in its anionic form [1–9]. Crystallographic and theoretical studies on chelated complexes of bis(diphenylphosphino)amine ligands and their derivatives suggest that they should possess more ring-strain energy than those of the corresponding dppm complexes, due to the small-bite angle of the chelate ligand that compresses the P—N—P bond angle to 100° [10, 11]. However, some recent studies on coordination complexes of platinum(II) with the ligands dppa and dppma [$NMe(PPh_2)_2$], show that the mono and bis-chelate complexes have a higher stability than the dppm analogues, probably due to a more favorable metal-ligand interaction [1]. Moreover, the greater acidity of the NH proton of coordinated dppa compared with the CH_2 protons of dppm, may facilitate functionalization reactions that normally require drastic conditions for dppm. Thus, the N-derivatization of the coordinated dppa ligand in the mixed triangular cluster [$MoPd_2ClCp(\mu-CO)_2(\mu-dppa)_2$] affords the corresponding dppma derivative [12].

Cyclopentadienyliron(II) complexes of the type [$(\eta^5\text{-}C_5H_5)Fe(dppm)L$] PF_6 (L = CH_3CN, CO) were synthesized by photolytic reaction of the arene compound [$(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}MeC_6H_5)$]$PF_6$ with dppm in acetonitrile and further reactión with carbon monoxide [13]. A similar dppa carbonyl complex [$(\eta^5\text{-}C_5H_5)Fe(dppa)CO$] Cl and its ligand deprotonation reaction has been recently described [14].

Continuing our interest in the coordinating behavior of short-bite bidentate ligands [15–20], the present paper describes the synthesis, characterization and redox properties of the cationic iron(II) complexes [$(\eta^5\text{-}C_5H_5)Fe(L)(\eta^2\text{-}dppa)$]$^+$(where L = CO, CH_3CN, η^1-dppa) and the neutral complex [$(\eta^5\text{-}C_5H_5)Fe(CO)\{\eta^2\text{-}(PPh_2)_2N\}$].

EXPERIMENTAL

All reactions were carried out under purified nitrogen by using Schlenk-tube techniques. Solvents were dried, distilled, and stored under a nitrogen atmosphere. [$(\eta^5\text{-}C_5H_5)Fe(CO)_2I$] was purchased from a commercial source and the ligand $NH(Ph_2P)_2$ was prepared according to a literature method [21]. Elemental analyses (C, H, N) were made with a Fisons EA 1108 microanalyzer. FTIR spectra were recorded on a Bruker Vector-22 spectrophotometer using KBr pellets. The NMR spectra were recorded on a Bruker AC-200P spectrometer and the chemical shifts are reported in ppm relative to $SiMe_4$ (^1H) and 85% H_3PO_4 (positive shifts downfield) in D_2O (^{31}P) as internal and external standards, respectively. Electronic spectra were recorded on a Shimadzu UV-3101PC spectrophotometer.

Photolyses were performed with a medium-pressure mercury lamp (500 W) in a concentric quartz thermostated cell. Electrochemical experiments were recorded in acetonitrile solution under an argon atmosphere, at room temperature (20°C). Solutions were 3 mM in complex and 0.1 M in tetraethylammonium perchlorate (TEAP) as supporting electrolyte. The working and auxiliary electrodes were platinum, the reference electrode was silver/silver chloride modified for non-aqueous solvents and adjusted to 0.00 *vs.* sce. Cyclic Voltammetry (CV) and Bulk Electrolysis (BE) measurements were performed with a Voltammetric Analyser, CV-50W Version 2.3, Bioanalytical System Inc.

Preparation of Complexes

$[(\eta^5\text{-}C_5H_5)Fe(CO)\{\eta^2\text{-}(PPh_2)_2NH\}]I$ (1)

A solution of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2I]$ (355 mg; 1.17 mmol) and dppa (450; 1.17 mmol) in dry toluene (30 mL) was boiled under reflux for 1.5 h. The yellow solid formed was filtered off and washed with cold toluene and diethylether. The complex was dissolved in the minimal amount of dichloromethane, chromatographed by Kieselgel 60 and eluted with acetone. The solution was vacuum-concentrated and the complex precipitated adding diethyl ether. Yield 700 mg (90%). Anal. Calcd. for $C_{30}H_{26}FeINOP_2$ (%): C, 54.4; H, 4.0; N, 2.1. Found: C, 53.8; H, 4.3; N, 2.3. ^1H NMR ($CDCl_3$): δ 4.6 (t, 5H, $^3J_{PH} = 1.5$ Hz, C_5H_5), 7.7–7.9 (m, 20H, Ph) and 9.1 (t, 1H, $^2J_{PH} = 6.3$ Hz, NH) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 87.6 (s) ppm. IR(KBr): ν(NH) 3424, ν(CO) 1968 and $\nu_{sym}(P_2N)$ 837 cm^{-1}.

$[(\eta^5\text{-}C_5H_5)Fe(CO)\{\eta^2\text{-}(PPh_2)_2NH\}]BF_4$ (2)

A mixture of complex **1** (350 mg; 0.53 mmol) and silver tetrafluoroborate (103 mg; 0.53 mmol), in acetone (20 mL), was stirred for 1 h at room temperature, in the absence of light. The precipitated silver iodide formed was removed by filtration through Kieselghur and the solution evaporated to dryness. The solid residue was dissolved in the minimal amount of dichloromethane, chromatographed by Kieselgel 60 and eluted with a mixture of acetone-dichloromethane (1:1). The solution was concentrated to a small volume and yellow crystals were obtained by careful addition of diethyl ether. Yield 270 mg (82%). Anal. Calcd. for $C_{30}H_{26}$ BF_4FeNOP_2

(%): C, 58.0; H, 4.2; N, 2.3. Found: C, 57.6; H, 4.2; N, 2.3. ^{1}H NMR {CD_3CN}: δ 4.8 (t, 5H, $^3J_{PH} = 1.6$ Hz, C_5H_5), 7.5–7.7 (m, 20H, Ph) and 6.9 (s, br, 1H, NH) ppm. $^{31}P\{^1H\}$ NMR {CD_3CN}: δ 90.0 (s) ppm. IR(KBr): ν(NH) 3263, ν(CO) 1971 and $\nu(BF_4)$ 1080 cm^{-1}.

$[(\eta^5\text{-}C_5H_5)Fe(CO)\{\eta^2\text{-}(PPh_2)_2N\}]$ (3)

This complex was prepared by modification of a reported method [19]. A stoichiometric amount of sodium hydride (3 mg, dispersion in mineral oil, 80% w/w, 0.1 mmol) was added to a solution of complex **2** (62 mg; 0.1 mmol) in tetrahydrofuran. The mixture was stirred for 30 min and then vacuum evaporated to dryness. The solid residue was dissolved in diethyl ether (10 mL), filtered through Kieselghur, and the slow solvent evaporation gave an orange solid. Yield 50 mg (94%). Anal. Calcd. for $C_{30}H_{25}FeNOP_2$ (%): C, 67.5; H, 4.7; N, 2.6. Found: C, 66.7; H, 4.6; N, 2.6. ^{1}H NMR {$CDCl_3$}: δ 4.3 (t, 5H, $^3J_{PH} = 1.4$ Hz, C_5H_5) and 7.4–7.8 (m, 20H, Ph) ppm. $^{31}P\{^1H\}$ NMR {$CDCl_3$}: δ 46.3 (s) ppm. IR(KBr): ν(CO) 1937 and $\nu_{sym}(P_2N)$ 913 cm^{-1}.

$[(\eta^5\text{-}C_5H_5)Fe(CH_3CN)\{\eta^2\text{-}(PPh_2)_2NH\}]BF_4$ (4)

A solution of complex **2** (500 mg; 0.8 mmol) in acetonitrile (50 mL) was UV-irradiated at room temperature for 3 h in a quartz cell. During this time the initially yellow solution changed to red-wine. The solution was evaporated to dryness and the solid residue dissolved in minimal dichloromethane. The mixture was chromatographed by Kieselgel 60 and eluted with a mixture of acetone-dichloromethane (1:1). The red solution obtained was concentrated to a small volume and the complex precipitated by addition of diethyl ether. The red solid was filtered off, washed with diethyl ether and dried under vacuum. Yield 480 mg (95%). Anal. Calcd. for $C_{31}H_{29}BF_4FeN_2P_2$ (%): C, 58,7; H, 4.6; N, 4.4. Found: C, 58.8; H, 4.7; N, 4.5. ^{1}H NMR {CD_3CN}: δ ca. 1.9 (masked by solvent, 3H, CH_3), 4.29 (t, 5H, $^2J_{PH} = 1.7$ Hz, C_5H_5), 6.52 (t, 1H, $^2J_{PH} = 8.2$ Hz, NH) and 7.4–7.7 (m, 20H, Ph) ppm. $^{31}P\{^1H\}$ NMR {CD_3CN}: δ 100.52 (s) ppm. IR(KBr): ν(NH) 3278, ν(CN) 2273, $\nu_{sym}(P_2N)$ 801 and $\nu(BF_4)$ 1080, 551 cm^{-1}.

$[(\eta^5\text{-}C_5H_5)Fe(\eta^2\text{-}(PPh_2)_2NH)\{\eta^1\text{-}(PPh_2)_2NH\}]BF_4$ (5)

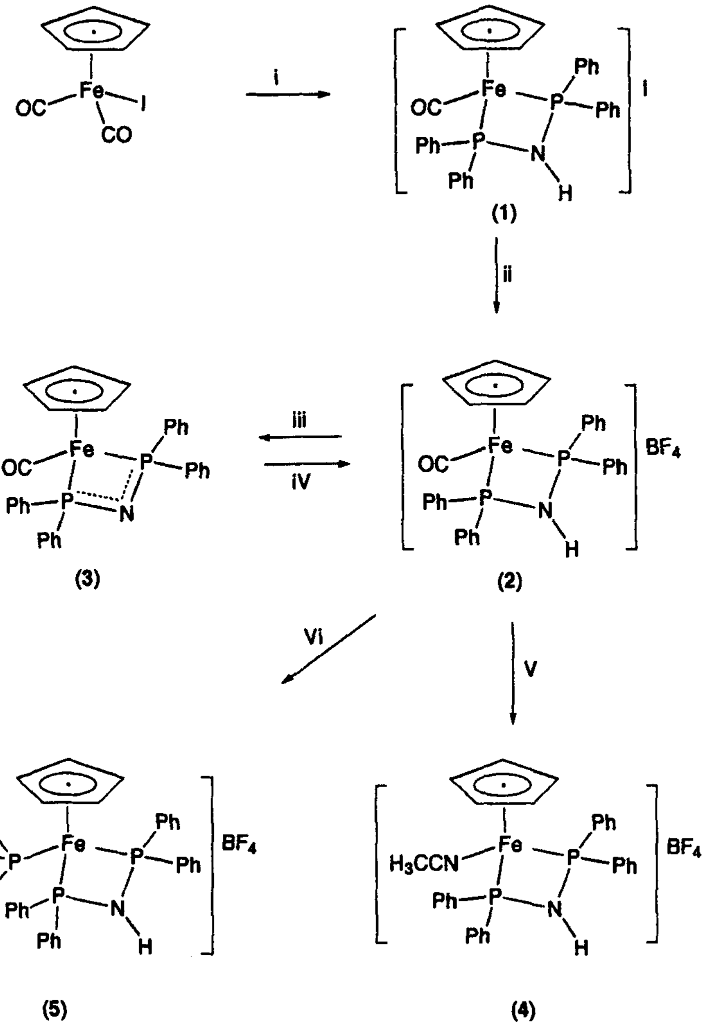
A solution of complex **2** (150 mg; 0.24 mmol) and dppa (115 mg; 0.30 mmol) in acetone (20 mL) was UV-irradiated at room temperature for 1 h. During this time the solution color changes from yellow to red-wine. The resulting solution was evaporated to dryness, the solid was extracted with the minimum amount of dichloromethane and chromatographed on Kieselgel 60. The excess of dppa was eluted with dichloromethane and the complex with dichloromethane-acetone(1:1). The addition of n-hexane caused precipitation of the complex. Yield 170 mg (72%). Anal. Calcd. for $C_{53}H_{47}BF_4FeN_2P_4.CH_2Cl_2$ (%): C, 61.0; H, 4.6; N, 2.6. Found: C, 61.7; H, 4.9; N, 2.7. ^1H NMR {$CDCl_3$}: δ 4.2 (m, 5H, C_5H_5) and 7.0–8.0 (m, 40H, Ph). $^{31}P\{^1H\}$ NMR {$CDCl_3$}: δ 22.4 [d, 2P, $^2J_{PP} = 40.5$ Hz, η^1-dppa(free P)], 85.5 (d,1P, $^2J_{PP} = 61.3$ Hz, η^2-dppa) and 111.3 [dt, 1P, η^1-dppa(P-Ru)] ppm. IR(KBr): ν(NH) 3317, $\nu_{sym}(P_2N)$ 875 and $\nu(BF_4)$ 1083, 544 cm^{-1}.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Complexes

The synthetic routes to the complexes are summarized in Scheme 1. Reaction of the neutral complex $[(\eta^5\text{-}C_5H_5)Fe(CO)_2I]$ with the ligand bis(diphenylphosphino)amine (dppa) at reflux temperature in toluene solution affords a yellow solid characterized as the cationic compound $[(\eta^5\text{-}C_5H_5)Fe(CO)\{\eta^2\text{-}(PPh_2)_2NH\}]I$ (**1**), which in turn reacts with $AgBF_4$ in acetone solution to yield the complex $[(\eta^5\text{-}C_5H_5)Fe(CO)\{\eta^2\text{-}(PPh_2)_2NH\}]BF_4$ (**2**). These complexes were isolated as stable microcrystalline solids and characterized by elemental analysis and IR and NMR spectra. In both cases their IR spectra show a strong band in the carbonyl region assigned to ν(CO) together with the characteristic ν(NH) and $\nu_{asym}(P_2N)$ absorption bands of coordinate dppa ligand (see Experimental).

The ^1H NMR spectrum of complex **1** in $CDCl_3$ shows two triplet resonances at δ 4.6 ($^3J_{PH} = 1.5$ Hz) and 9.1 ($^2J_{PH} = 6.3$ Hz) assigned to C_5H_5-ring and NH protons, respectively, together with a multiplet signal at δ 7.7–7.9 ppm corresponding to the phenyl rings. Its $^{31}P\{^1H\}$ NMR spectrum exhibits a singlet resonance at δ 87.6 ppm assigned to the equivalent phosphorus atoms of the dppa ligand. The ^1H NMR spectra of complex **2** were recorded in deuterated acetonitrile, due to poor solubility in $CDCl_3$, showing a very broad singlet at δ 6.94 assigned of the NH proton, a triplet at δ 4.8 ($^3J_{PH} = 1.57$ Hz) for the C_5H_5 ring and a multiplet in the range δ 7.5–7.7 ppm for phenyl rings. The $^{31}P\{^1H\}$ NMR spectrum in CD_3CN shows the expected singlet resonance at δ 90.0 ppm assigned to equivalent phosphorus atoms.



SCHEME 1 i) dppa; ii) $AgBF_4$; iii) NaH; iv) HBF_4/diethyl ether; v) CH_3CN(hv); vi) dppa(hv).

Complex 2 reacts with sodium hydride in dry tetrahydrofuran by deprotonation of the coordinated dppa ligand affording the previously described neutral complex [η^5-C_5H_5)Fe(CO){η^2-$(PPh_2)_2N$}] (3) [22]. The removal of the aminic proton was confirmed by the absence of the broad absorption band at 3263 cm^{-1}, corresponding to ν(NH) in the IR spectrum of the starting complex. Moreover, deprotonation of the bidentate ligand caused an increase in the electron density on the metal that should increase the extent of the Fe—C back-bonding and therefore, the CO stretching frequency should be shifted to a lower value [$\Delta\nu(CO) = 31\,cm^{-1}$]. As expected, in the $^{31}P\{^1H\}$ NMR spectrum the singlet resonance of the equivalent phosphorus atoms is displaced to higher field δ 46.3 ppm. Complex **3** is easily protonated by addition of HBF_4 as a diethylether solution, regenerating quantitatively starting complex **2**.

The UV-irradiation of an acetonitrile solution of complex **2** at room temperature displaced the carbonyl ligand with the solvent. The ligand exchange was followed by monitoring the reaction by IR spectroscopy. The initial yellow solution turned gradually to red-wine, and after 3 h the $\nu(CO)$ of the starting complex disappeared. The evaporation of the solvent leads to the cationic complex $[(\eta^5\text{-}C_5H_5)Fe(CH_3CN)\{\eta^2\text{-}(PPh_2)_2NH\}]BF_4$ (**4**). Its solid state IR spectrum shows a strong band at $2273\,cm^{-1}$ assigned to $\nu(CN)$. The $^{31}P\{^1H\}$ NMR spectrum in CD_3CN shows the expected singlet resonance at δ 100.52 ppm assigned to equivalent phosphorus atoms. The ^1H NMR spectrum in CD_3CN shows two triplet resonances at δ 4.29 ($^3J_{PH} = 1.7$ Hz) and 6.52 ($^2J_{PH} = 8.2$ Hz) ppm assigned to C_5H_5 and NH protons, respectively. The expected triplet resonance of the CH_3CN protons is masked by the solvent signal. However, the ^1H NMR spectrum recorded in acetone-d_6 solution shows a triplet resonance at δ 1.7 ($^5J_{PH} = 1.0$ Hz) assigned to coordinated CH_3CN protons. In this case the signal of the NH proton is not observed, possibly due to an exchange with deuterium of the solvent.

On the other hand treatment of complex **2** with dppa in acetone solution under UV-irradiation at room temperature affords a mononuclear cationic complex that contains a dangling monodentate dppa ligand $[(\eta^5\text{-}C_5H_5)Fe\{\eta^1\text{-}(PPh_2)_2NH\}\{\eta^2\text{-}(PPh_2)_2NH\}]BF_4$ (**5**). The $^{31}P\{^1H\}$ NMR spectrum in $CDCl_3$ is in agreement with the proposed formulation showing two doublets and a doublet of triplets signals at δ 22.4, 85.5 and 111.3 ppm ($^2J_{PP} = 40.5$ and 61.3 Hz), assigned to free P (η^1-dppa), P-Ru (η^2-dppa) and P-Ru (η^1-dppa), respectively.

Redox Behavior of the Complexes

Complexes **1**–**5** exhibit an interesting and different redox chemistry in acetonitrile solution. The electrochemical behavior of complexes **1** and **2** is very similar, except that in the cyclic voltammogram of complex **1** the redox pair at 0.30/0.08 V *vs.* sce is observed, corresponding to the oxidation of free I^- to I_2. The cyclic voltammogram of complex **2** is characterized by a *quasi*-reversible metal-localized reduction at −1.44 V (Fig. 1A, peak a, scan rate 100 mV/s). The wave current, corresponding to a reoxidation of the metal center, varies substantially with the concentration of the complex and the

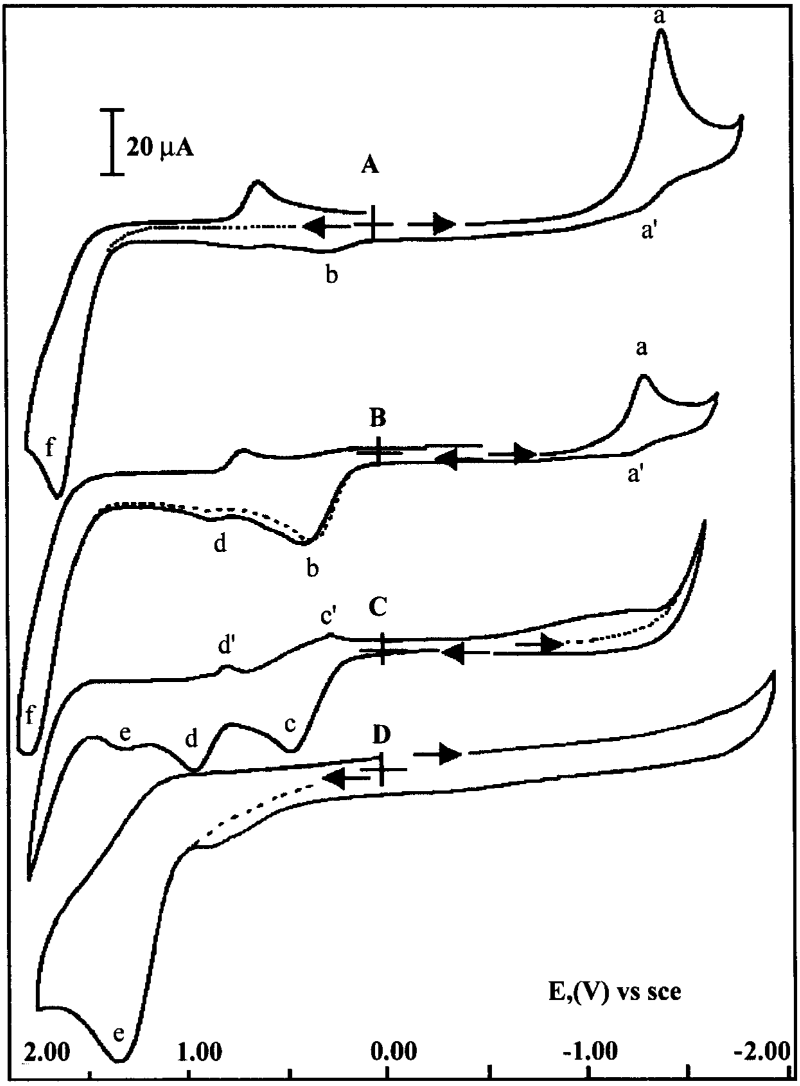


FIGURE 1 Cyclic voltammograms of 3 mM solutions in acetonitrile. Supporting electrolyte: TEAP 0,1 M. V = 100 mV/s. **A**: complex **2**; **B**: solution obtained after controlled potential electrolysis at −1.64 V *vs.* sce of complex **2** (charge equivalents = 0.5 per mol of complex). **C**: solution obtained after controlled potential electrolysis at −1.64 V *vs.* sce (charge equivalents = 1.0 per mol of complex). **D**: dppa solution.

scan rate of the cyclic voltammetry (Fig. 1A, peak a′, −1.30 V). It is important to note that the i_{pa}/i_{pc} ratio increases by increasing the scan rate from 10 to 500 mV/s, but this ratio is never equal to 1. This behavior can be explained by a chemical reaction of the reduced 17e intermediate obtaining a new species which is oxidized at a more positive potential. The cyclic voltammogram towards negative potential, at 200 mV/s or higher scan rates, shows in the reverse scan two anodic peaks at 0.38 and 1.07 V.

Potential controlled electrolysis at − 1.64 V (E_{peak} = s; − 1.44 V) produces a novel species after 0.5 equivalents of charge are transferred. Its cyclic voltammogram shows an oxidation peak at 0.38 V (Fig. 1B, peak b). After exhaustive reduction at the same potential (0.5 equiv of charge are additionally consumed), the anodic peak is shifted to a more positive value with the same current intensity (Fig. 1C, 0.47 V, peak c) and an emerging new peak at 1.07 V was observed (peak d). Consequently, the quasi-reversible reduction peak at − 1.44 V (Fig. 1A, peaks a and a′) is associated with the two oxidation peaks of the same current intensity at 0.47 and 1.07 V (Fig. 1C, peaks d and e), where the generated complexes are reduced at 0.27 and 0.80 V respectively (peaks c′ and d′). In summary, these results suggest that the electroreduction product reacts chemically affording a dinuclear complex which undergoes two consecutive electrochemical reactions (electrochemical-chemical-electrochemical mechanism). The proposed mechanism is supported by the fact that 0.5 equivalent of charge per mol of complex are consumed in each step. In addition, in the cyclic voltammogram of the latter product, a small anodic peak at 1.35 V (Fig. 1C, peak e) characteristic of the oxidation of free dppa ligand was observed. Figure 1D shows the cyclic voltammogram of dppa in acetonitrile. The electrochemical and chemical reactions are summarized in Scheme 2.

In the dinuclear Fe(I) compound, the oxidation potential separation (peaks c and d) of the two metal centers is 0.60 V ($\Delta E_{1/2} = 0.57$ V). According to the classification of Robin and Day it corresponds to a mixed-valent complex of class II [23, 24]. The considerable peak separation of the redox processes (0.57 V) indicates a strong interaction between the two metal centers, supporting the conclusion that the complex possesses a metal-metal bond and the two CO groups are bridging between the two metal

$$[\mathrm{CpFe^{II}(CO)(dppa)}]^{+} + e^{-} \underset{-1.30\,\mathrm{V}}{\overset{-1.44\,\mathrm{V}}{\rightleftharpoons}} [\mathrm{CpFe^{I}(CO)(dppa)}] \quad \text{(peaks a and a')}$$

$$2[\mathrm{CpFe^{I}(CO)(dppa)}] \longrightarrow [\mathrm{CpFe^{I}(\mu\text{-}dppa)(\mu\text{-}CO)_2Fe^{I}Cp}] + \mathrm{dppa} \quad \text{(chemical reaction)}$$

SCHEME 2 Cp = η^5-C_5H_5.

atoms. This electrochemical behavior is similar to that exhibited by the related complex $[CpFe(CO)(dppm)]PF_6$ [13].

The partial oxidation of the dinuclear complex at 0.47 V (peak c) leads to a mixed-valence complex Fe(I)-Fe(II) and the subsequent oxidation at 1.07 V (peak d) produces a Fe(II) compound. The electrochemical reactions are included in Scheme 3.

The electrochemical behavior of the neutral complex **3** is very different to that shown by complex **2**. Whereas complex **2** is easily reduced but difficult to oxidize, complex **3** is reduced at more negative potentials (−1.84 V, Fig. 2A, peak g) but is easily oxidized at 0.90 V (Fig. 2A, peak h). In our working conditions the reverse anodic reaction is not observed. The controlled potential electrolysis at −1.94 V ($E_{peak} = -1.84$ V) leads to a compound which is oxidized in one step after one equivalent of charge is consumed. Figure 2B shows the cyclic voltammogram of the electrolysis product (peak i, − 0.02 V), which indicates either that the reduction product is not a dinuclear complex or the Fe-Fe interaction is very weak and the two metal centers are oxidized at the same or at a very close potential.

The great difference in electronic properties between the CO and MeCN ligands is reflected in the cyclic volatmmograms. Complex **4** is reduced at more negative potentials than complex **2** (−1.66 V, Fig. 2C, peak j). The exhaustive reduction produces a compound that is oxidized in one step and consumes one equivalent of charge (0.16 V, Fig. 2D, peak k). In the oxidation zone it is possible to observe a reversible oxidation peak at 0.66/0.62 V (peaks 1 and 1′), corresponding to oxidation of Fe(II) to Fe(III). The current ratio i_{pc}/i_{pa} is = 1, showing the stability of the formed complex. However, it is difficult to oxidize due to formation of an insoluble compound which is adsorbed in the platinum mesh electrode during the controlled potential electroysis. Furthermore, the cyclic voltammetry shows the adsorption of Fe(III) complex in the platinum disc electrode after each cycle (Fig. 2E).

$$[Fe^{I},Fe^{I}] \underset{0.27\,V}{\overset{0.47\,V}{\rightleftharpoons}} [Fe^{I},Fe^{II}] + e^{-} \quad \text{(peaks c and c'; } E_{1/2} = 0.37\text{ V)}$$

$$[Fe^{I},Fe^{II}] \underset{0.80\,V}{\overset{1.07\,V}{\rightleftharpoons}} [Fe^{II},Fe^{II}] + e^{-} \quad \text{(peaks d and d'; } E_{1/2} = 0.94\text{ V)}$$

SCHEME 3

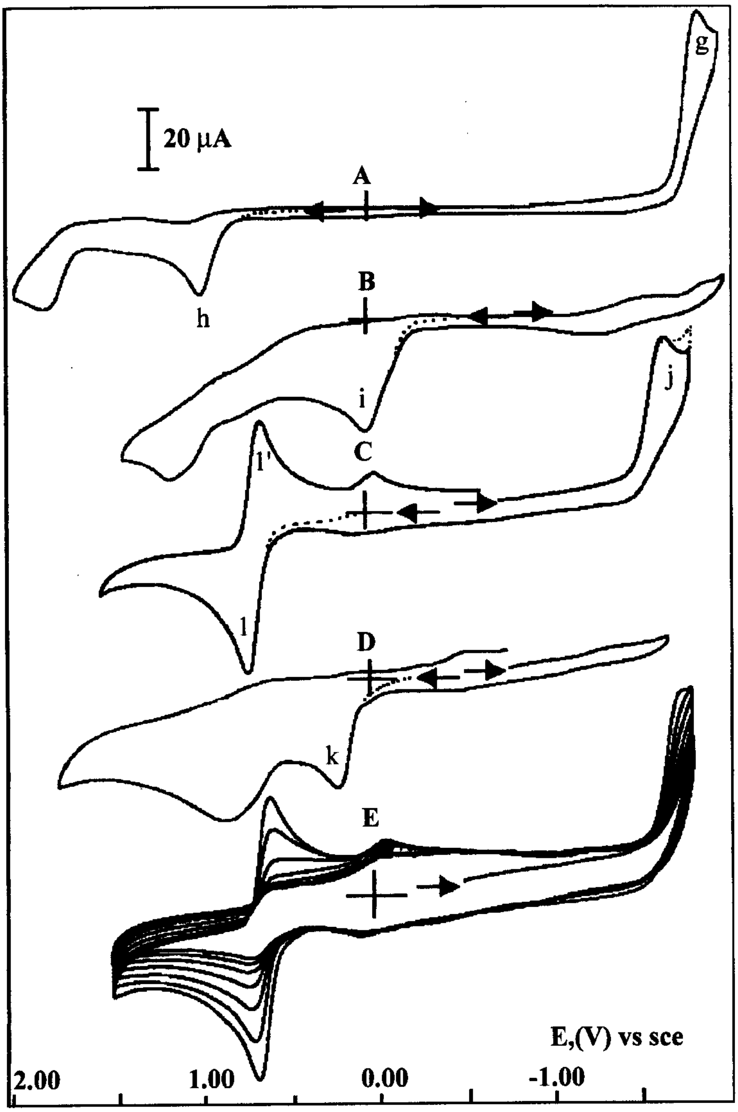


FIGURE 2 Cyclic voltammograms of 3 mM solutions in acetonitrile. Supporting electrolyte: TEAP 0,1 M. V = 100 mV/s. **A**: complex **3**. **B**: solution obtained after controlled potential electrolysis at −1.94 V *vs*. sce of complex **3** (charge equivalents = 1.0 per mol of complex). **C**: complex **4**. **D**: solution obtained after controlled potential electrolysis at −1.84 V *vs*. sce of complex **4** (charge equivalents = 1.0 per mol of complex). **E**: complex **4** n-cycles.

Finally, an acetonitrile solution of complex **5** shows an identical cyclic voltammogram to that shown by complex **4**, indicating that the monodentate dppa ligand is displaced by the solvent.

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