# Heteropolymetallic complexes of 1,1'-bis(diphenylphosphino)ferrocene (dppf)

# VII *. Redox behaviour of dppf

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## Abstract

The electrochemical oxidation of 1,1'-bis(diphenylphosphino)ferrocene (dppf) at a platinum electrode in 1,2-dichloroethane has been studied by cyclic voltammetry, controlled potential electrolysis, and $^{31}P$ NMR spectroscopy. The compound undergoes a ferrocene-based reversible oxidation, which is followed by a fast chemical reaction, involving the phosphorus substituent on the cyclopentadienyl rings, to give dppfO, dppfO$_2$, dppfH$^+$ and dppfH$_2^{2+}$. Kinetic data suggest that the reaction involves a reversible intramolecular electron transfer between the ferrocene core and the electron-rich substituents to give a phosphinium radical ion, which undergoes a second order rate-determining dimerization or a reaction with the parent compound to give a ferrocenylphosphine dimer cation radical, the ultimate fate of which is the formation of protonated and oxygenated dppf derivatives by nucleophilic attack by water present in the reaction medium. Evidence for the formation of the transient monomeric phosphinium radical was obtained by trapping it with 1,1'-diphenylethylene to give phosphorus-bonded monoalkene adducts of dppf.

## Introduction

As part of our continuing investigations of the coordination chemistry of 1,1'-bis(diphenylphosphino)ferrocene (dppf) [1], we found that Pt$^{II}$- and Pd$^{II}$-dppf complexes exhibit an uncomplicated reversible electron transfer pattern involving the ferrocenyl moiety [1a,c]. Cyclovoltammetric tests, carried out in dichloromethane (DCM) and in 1,2-dichloroethane (DCE), revealed that the metal-coordinated ligand undergoes a simple one-electron transfer with potential values considerably more anodic than that displayed by the uncoordinated ligand ($E° = 0.183$ V vs. [FeCp$_2$]$^+$/FeCp$_2$) [1e]. In keeping with the simple electrochemi-
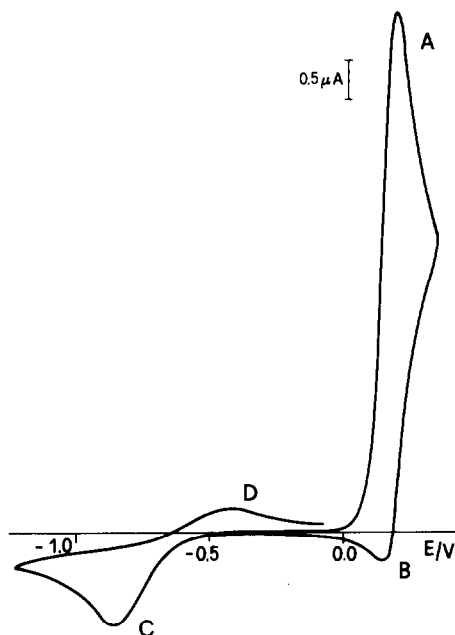
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* For Part VI see ref. 1g.

Fig. 1. Cyclic voltammogram for oxidation of 10.0 m$M$ dppf in DCE in 0.2 $M$ TBAP at 25 °C (scan rate 0.2 V s$^{-1}$).

cal and chemical character of the anodic process, we found that the stable species [(dppf)PtCl$_2$]BF$_4$ could be obtained by oxidation of (dppf)PtCl$_2$ with NOBF$_4$ in DCM [1a,e]. Similar ferrocene-based reversible electrochemical and chemical oxidations have been reported for rhenium ferrocenyl-derived phosphine complexes [2].

In striking contrast with this behaviour, reminiscent of that well known for FeCp$_2$, the redox pattern for free dppf is much more complicated under identical experimental conditions. Thus the ligand is found to undergo an essentially reversible one-electron oxidation followed by a fast chemical reaction (EC mechanism) [1e]. We report here on an extensive investigation aimed at identifying the chemical process following the electrochemical oxidation of the ferrocenyl core in dppf.

## Results

A representative cyclic voltammogram (CV) of dppf is depicted in Fig. 1.

A single one-electron reversible anodic peak, A, is exhibited at +0.21 V. During the cathodic scan, in addition to reversibly coupled peak B, a peak, C, attributable to the chemical evolution of the primary oxidation product is clearly apparent at −0.85 V, with which a broad peak, D, is associated in the corresponding reverse scan. Reduction peak C and oxidation peak D have been identified as due to the reduction of dppfH$^+$ and to the oxidation of dihydrogen in the presence of dppf as shown in eq. 1.

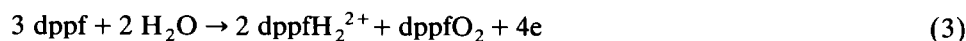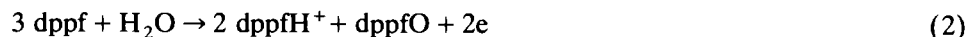$$dppfH^+ + e \rightleftarrows dppf + 1/2\ H_2 \qquad (1)$$

The identification is based on independent experiments on DCE solutions of pure dppfH$^+$ (see Experimental) and of dppf with molecular hydrogen.

Controlled potential electrolyses carried out at potentials of peak A in 50% acetonitrile (AN)/DCE, 0.15 $M$ NaClO$_4$, at 25°C confirm that protons, which are trapped by dppf, are released in the anodic process. Subsequent electrochemical reductions indicate a ratio very close to 1:1 between the H$^+$ moles formed and the charge passed in the oxidation step with regeneration of approximately 0.66 mol of the initial species. Exhaustive electrochemical oxidations result in the removal of about 1.33 electrons/dppf to yield ca. 0.66 mol of dppfH$_2$$^{2+}$ (see Experimental).

The $^{31}$P NMR spectra of the anolytes reveal the presence of dppfO associated with dppfH$^+$ or dppfO$_2$ associated with dppfH$_2$$^{2+}$ (depending on the number of removed electrons), as shown by comparison with those given by solutions of authentic samples.

The electrochemical results may be accounted for in terms of the overall main reactions shown in eqs. 2 and 3:

$$3 \text{ dppf} + H_2O \rightarrow 2 \text{ dppfH}^+ + \text{dppfO} + 2e \tag{2}$$

$$3 \text{ dppf} + 2 H_2O \rightarrow 2 \text{ dppfH}_2{}^{2+} + \text{dppfO}_2 + 4e \tag{3}$$

Apparently, the water content of nominally anhydrous AN/DCE solutions is large enough to allow reactions 2 and 3 to take place. We find that: (i) dppfH$^+$ can be electrochemically converted to dppfH$_2$$^{2+}$, in that voltammograms of dppfH$^+$ in AN/DCE solutions exhibit kinetic oxidation waves at potentials very close to those observed in voltammograms of dppf. This kinetic character is attributed to the moderately fast equilibrium:

$$2 \text{ dppfH}^+ \rightleftarrows \text{dppf} + \text{dppfH}_2{}^{2+} \tag{4}$$

involving the formation of dppf prior to oxidation; (ii) dppfO displays a CV pattern quite similar to that of dppf showing a redox couple centred at a potential only about one hundred millivolts more positive ($E° = 0.295$ V, as a mean value $(E_p^a + E_p^c)/2$), with even more incomplete chemical reversibility [3*]. Hence, process 3 probably takes place via reactions 2, 4 and 5:

$$\text{dppfO} + H_2O + \text{dppf} \rightarrow \text{dppfO}_2 + \text{dppfH}_2{}^{2+} + 2e \tag{5}$$
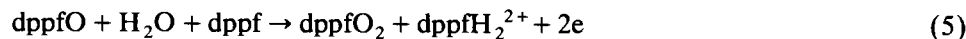
as sequential steps. Evidence for the occurrence of reactions 2 and 5 is provided by the course of the electrochemical oxidation of dppf in water-containing AN/DCE solvent mixtures in the presence of pyridine as proton scavenger. Under these conditions, the two-electron oxidation to produces dppfO as major product (see Experimental), while the exhaustive electrolysis involves the removal of four electrons/dppf to give the clean formation of dppfO$_2$. In this connection, it is noteworthy that the oxidation pattern exhibited by dppf is reminiscent of that previously observed for triphenylphosphine [4].

These observations, coupled with the above-mentioned absence of any chemical complication associated with metal-coordinated or oxygen-bonded dppf, lead to the conclusion that the primary oxidation product of dppf, i.e. 1,1'-bis(diphenyl-phosphino)ferrocenium cation, behaves just like a phosphinium radical ion [4,5],

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* Reference number with asterisk indicates a note in the list of references.
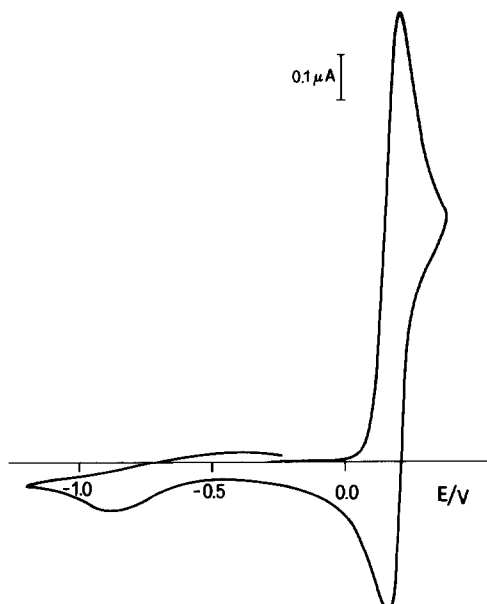
Fig. 2. Same as Fig. 1 with 1.5 m$M$ dppf.

the ultimate fate of which is the well-known conversion into phosphine oxide by nucleophilic attack of water present in the reaction medium.

To achieve the driest possible conditions, bulk oxidative electrolysis experiments were carried out with the cell put inside a controlled atmosphere dry-box in carefully dried AN/DCE, 0.15 $M$ NaClO$_4$, solvent mixture. Under these rigorous conditions one electron/dppf is required and dppfO$_2$ is obtained as the major product (mass spectral monitoring involving comparison with authentic samples). It is thus evident that perchlorate ion is the source of the oxygen atoms of dppfO$_2$, and that the atom transfer is relevant to the rapid decay of the ferrocenyl cation.

In order to clarify the mechanism of decay of the transiently formed 1,1'-bis(di-phenylphosphino)ferrocenium ion, we carried out a kinetic investigation of the chemical reaction associated with the electron transfer step. This study involved examination of the effect of scan rate and depolarizer concentration on the ratio of cathodic to anodic peak currents under conditions in which the anodic step maintains the features of an one-electron diffusion-controlled process. This was confirmed both by the constancy of the $i_a V^{-1/2}$ value in the explored range of scan rates, $V$, and/or that of the $it^{1/2}$ value in the relevant time span, as shown by preliminary chronoamperometric tests.

*Kinetic investigations*

Figure 2 shows a CV of dppf recorded under conditions identical with those specified in Fig. 1 except for the substrate concentration. Inspection of the cathodic portion of the figures reveals that the chemical reaction is much more prominent at higher concentrations, suggesting that the chemical step has a kinetic order > 1. The data were, in fact, found to fit satisfactorily the theory developed for an electrochemically-initiated homogeneous dimerization reaction [6] (see

Table 1

Determination of the second-order rate constant, $k_2$ (dm$^3$ mol$^{-1}$ s$^{-1}$)$^a$, for the dimerization of electrogenerated 1,1'-bis(diphenylphosphino)ferrocenium from the ratio of cathodic to anodic peak currents, $i_c/i_a$, according to ref. 6 ($\rho = 0$; $\alpha\tau = 4.0$). Conditions: DCE 0.2 $M$ TBAP at 0°C, $E_\lambda - E° = 95$ mV

| Scan rate (mV s$^{-1}$) | [dppf] = $1.5 \times 10^{-3}$ $M$ | | | [dppf] = $5.4 \times 10^{-3}$ $M$ | | | [dppf] = $9.5 \times 10^{-3}$ $M$ | | |
|---|---|---|---|---|---|---|---|---|---|
| | $i_c/i_a$ | $k_2C°\tau$ | $10^{-2}k_2$ | $i_c/i_a$ | $k_2C°\tau$ | $10^{-2}k_2$ | $i_c/i_a$ | $k_2C°\tau$ | $10^{-2}k_2$ |
| 15 | 0.60 | 2.10 | 2.2 | – | – | – | – | – | – |
| 25 | 0.69 | 1.14 | 2.0 | 0.51 | 4.10 | 2.0 | – | – | – |
| 50 | 0.78 | 0.62 | 2.2 | 0.59 | 2.25 | 2.2 | 0.51 | 4.10 | 2.3 |
| 100 | 0.87 | 0.30 | 2.1 | 0.68 | 1.20 | 2.3 | 0.61 | 2.00 | 2.2 |
| 200 | 0.93 | 0.14 | 2.0 | 0.78 | 0.62 | 2.4 | 0.70 | 1.05 | 2.3 |
| 400 | – | – | – | 0.88 | 0.27 | 2.1 | 0.82 | 0.45 | 2.0 |

$^a$ Average value: $2.2 \pm 0.2 \times 10^2$ dm$^3$ mol$^{-1}$ s$^{-1}$.

Table 1). Moreover, additions of water over the whole range of miscibility with DCE, did not change the CV profile.

The effective constancy, within a standard deviation of $\pm 10\%$, of the values obtained in three independent determinations of the rate constant, $k_2$, corroborates the proposed mechanism.

The activation parameters, estimated with a least-squares fitting of the rate constant values at three temperatures, in the $-20$ to $+20$°C range, are $\Delta H^{\#} = 19$ kJ mol$^{-1}$ and $\Delta S^{\#} = -130$ J K$^{-1}$ mol$^{-1}$, both subject to a standard error of $\pm 10\%$.

## Discussion

The results, namely the products of bulk electrolysis, the kinetic data and activation parameters, can be accounted for in terms of the cation radical–substrate coupling (RSC) mechanism depicted in Scheme 1.
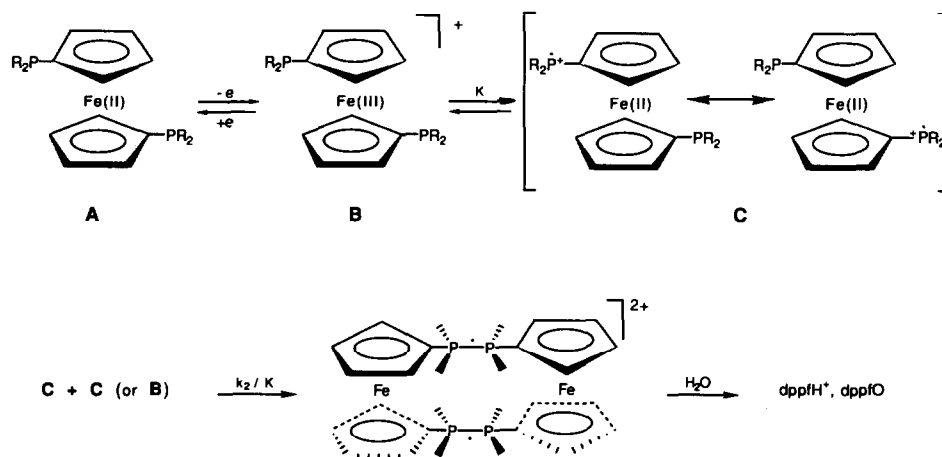


Scheme 1

It is assumed that the conversion from ferrocenium-phosphine **B** into the ferrocene-phosphinium ion **C** is rapid and reversible. The mechanism is supported by the following observations and considerations: (i) phosphine dimer radical cations, $(R_3P-PR_3)^+$, are known [7] to be produced by fast reaction of initially formed phosphinium radical cations, $R_3P^+$ (produced by electrochemical oxidation of $R_3P$ compounds in solution) with a further phosphine molecule. These dimeric products, characterized by ESR spectroscopy, were found to be fairly long-lived at low temperature (ca. $-80\,°C$) only in 'water free solvents'. In addition, they were found to exhibit no tendency to dissociate into $R_3P^+$ and $R_3P$; (ii) higher concentrations of **B** are generated close to the electrode surface, so that the **C-B** and **C-C** couplings appear to be favoured in comparison with the **C-A** one in the rate-determining step; (iii) the large and negative activation entropy is consistent with rate-determining association; (iv) the relatively low activation enthalpy for the overall process is not unreasonable for radical–substrate coupling reactions, especially when pre-rate-determining equilibria are involved [8].

Compelling evidence for the proposed mechanism, particularly in respect of the formation of fugitive **C** species, is provided by the course of the reaction between the one-electron oxidation product of dppf and olefins. It has been previously reported that electrogenerated phosphine monomer cation radicals, $R_3P^+$, can be instantaneously trapped by 3,3-dimethyl-2-t-butylbut-1-ene to give long-lived carbon centred di-t-butylalkyl radicals with a $\beta$-phosphonium substituent, ${}^tBu_2\dot{C}CH_2\overset{+}{P}R_3$ [7]. In contrast, the dimer radical cations, $(R_3P-PR_3)^+$, were found to be unable to add directly to the alkene. Under conditions in which the voltammetric profile of dppf appears to posses the features of an uncomplicated one-electron oxidation process, i.e., low temperature, fast scan rate, and low depolarizer concentration, the profile is strongly affected by addition of 1,1'-diphenylethylene; addition of increasing amounts of alkene leads to a concomitant decrease in the reversibly coupled cathodic peak, so that the signal completely disappears when a large excess of olefin is present (Fig. 3). Control experiments reveal that 1,1'-diphenylethylene has no effect on the voltammetric pattern of ferrocene.

Exhaustive bulk electrolysis of dppf in the presence of an excess of diphenylethylene requires one electron per dppf and gives a mixture of phosphorus bonded monoalkene adducts, isolated as the $BPh_4^-$ salts. This is not surprising since the initial reaction between the phosphinium radical cation and the alkene is likely to produce an unstable carbon-centred radical intermediate, so that the overall reaction is expected to be complex and to give more than one product. Although the identities of these species remain to be definitely established, the ${}^{31}P$ NMR and mass spectral (FAB) data show that they are phosphorus-bonded alkene adducts of dppf. Thus, the ${}^{31}P\{{}^1H\}$ NMR spectrum shows two main sets of resonances in the range typical of phosphonium salts ($\delta$ 25.7 – 16.4 ppm) [9] and uncoordinated dppf ligand ($\delta$ $-19.1$ to $-19.7$ ppm) [1e], respectively. In addition, the relative peak areas of the two sets of signals are in a ratio of ca. 1 : 1. The ${}^1H$ NMR spectrum is complex, and consistent with the association of one diphenylethylene skeleton with a dppf moiety in a tetraphenylborate salt. Moreover, under FAB conditions the mass spectrum of these salts contains a dominant molecular ion ($m/z$ 733) consistent with the addition of the ferrocenyl phosphinium radical ion to the double bond of the diphenylethylene.
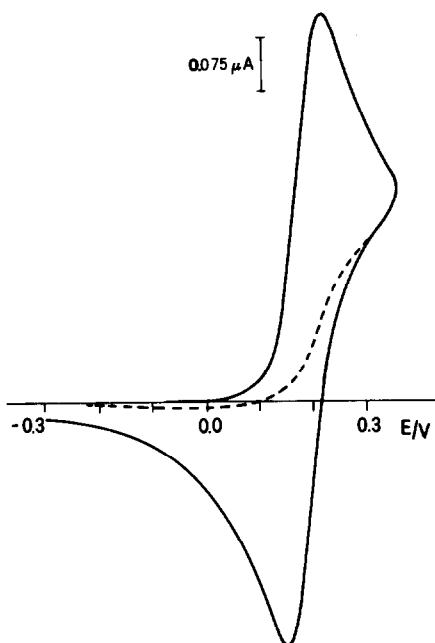
Fig. 3. Cyclic voltammogram (0.2 V s$^{-1}$) for oxidation of 1.5 m$M$ dppf in DCE 0.2 $M$ TBAP at $-30\,^\circ$C in the absence (full line) and in the presence (broken line) of 0.1 $M$ 1,1'-diphenylethylene.

In conclusion, we have shown that a facile and reversible electron transfer process takes place between the ferrocene core and the electron-rich substituent on the cyclopentadienyl rings. Consequently, the removal of one electron from one diphenylphosphine moiety is achieved at far less positive potentials than those usually required to oxidize phosphorus(III) compounds [5].

## Experimental

### Chemicals and reagents

Reagent-grade acetonitrile (AN) and 1,2-dichloroethane (DCE) were purified by refluxing over CaH$_2$; the solvents were stored over CaH$_2$ and carefully distilled under nitrogen before use. Tetrabutylammonium perchlorate (TBAP) was recrystallized twice from ethyl acetate and dried in vacuo at 60 $^\circ$C. NaClO$_4$ was dried by heating in vacuo immediately prior to use. 1,1'-Bis(diphenylphosphine)ferrocene (dppf) was purchased from Strem and recrystallized from CH$_2$Cl$_2$/CH$_3$OH.

The tetrafluoroborate of diprotonated dppf, [dppfH$_2$](BF$_4$)$_2$, was prepared by adding a slight excess of 85% tetrafluoroboric acid–diethyl ether complex dropwise to a stirred suspension of the bisphosphine in acetonitrile. The solution was concentrated under vacuum, and Et$_2$O/pentane was added, to produce an orange oil which was separated and washed with Et$_2$O. Attempts to crystallize the oil failed, and it was dried under vacuum to give an orange waxy solid. $^{31}$P NMR in CDCl$_3$ at $-65\,^\circ$C: $\delta$ 4.0, doublet with $^1J$(PH) = 530 Hz.

The tetrafluoroborate of the monoprotonated bisphosphine, [dppfH]BF$_4$, was prepared by mixing solutions in CHCl$_3$ of dppf and [dppfH$_2$](BF$_4$)$_2$, in 1:1 ratio.

The product was isolated as yellow-orange microcrystals by addition of $Et_2O$ and overnight cooling at $-20°C$. $^{31}P$ NMR data in $CDCl_3$ at $-65°C$: $\delta$ 4.9, doublet with $^1J(PH) = 530$ Hz, and $\delta$ $-20.5$, singlet. Both phosphonium tetrafluoroborates retained small amounts of $Et_2O$ of crystallization (ca. 0.2 mol per mol of iron) as shown by $^1H$ NMR spectroscopy.

The bisphosphine dioxide, $dppfO_2$, was made as described by Slinkard and Meek (reaction of dppf with $H_2O_2$ in toluene) [10*]. Orange crystals were obtained by recrystallization from $CHCl_3/CH_3CN$. $^{31}P\{^1H\}$ NMR data in $CDCl_3$ at $27°C$: $\delta$ 28.4 ppm.

Attempts to prepare dppfO similarly by reaction of an excess of dppf with $H_2O_2$ failed (the $^{31}P$ NMR spectrum of the reaction mixture demonstrated that it contained $dppfO_2$ as the major product and only minor amounts of the desired compound). The bisphosphine monoxide was therefore synthesized, in high yields, by an electrochemical procedure making use of reaction 2. Thus, a slurry of dppf (0.60 g, 1.08 mmol) in 50% AN/DCE (50 ml), 0.15 $M$ in $NaClO_4$, ca 0.2 $M$ in $H_2O$ and ca 0.2 $M$ in pyridine as proton scavenger, was electrolyzed at 0.22 V [11] vs. $Ag/0.1$ $M$ $AgClO_4$ acetonitrile electrode in a two-compartment cell on a platinum gauze electrode and a mercury pool counter-electrode. After removal of 2 mol of electrons per mol of dppf, the resulting homogeneous solution was exhaustively electrolyzed at $-1.2$ V by simply inverting the polarity of the electrodes in order to reduce the protonated pyridine previously formed during the oxidation step. The spent catholyte was then evaporated to dryness under reduced pressure, the residue was extracted with 20 ml of $CH_2Cl_2$, and the extract filtered. The orange filtrate was concentrated in vacuo to give an oil. Addition of MeOH (25 ml) afforded a yellow precipitate of unchanged dppf (15%), which was filtered off. The filtrate was concentrated under vacuum to 10 ml and allowed to stand overnight at $-30°C$ to deposit orange-yellow crystals of the product (0.3 g). The mother liquor, containing residual dppfO and some $dppfO_2$, was chromatographed on silica gel with 5% EtOH in $CHCl_3$ as eluent to give an additional 0.1 g of dppfO. Total yield: 0.4 g (66%). Its identity was checked by mass spectrometry and $^{31}P$ NMR spectroscopy. $^{31}P\{^1H\}$ NMR in $CDCl_3$ at $27°C$: one to one singlets at $\delta$ 28.5 and $-17.4$. Both mono- and di-oxide species are air stable when solid but decompose slowly in solution, particularly in the sunlight.

All the products gave satisfactory elemental analyses. All other chemicals were of reagent-grade quality and were used without further purification. High-purity argon, further purified from oxygen by passage over reduced copper at $450°C$, was used in the electrochemical experiments. Syntheses and manipulation of solutions were performed under nitrogen by standard Schlenk-line techniques.

*Apparatus and procedure*

Cyclic voltammetry measurements were performed with an Amel 551 potentiostat modulated by an Amel 566 function generator, and the recording device was a Hewlett–Packard 7090 A measurement plotting system. Experiments were carried out in deoxygenated DCE solutions with 0.2 $M$ TBAP as the supporting electrolyte, using a conventional three-electrode liquid jacketed cell. The working electrode was a planar platinum microelectrode (ca. 0.3 $mm^2$) surrounded by a platinum spiral counter electrode. The potential of the working electrode was determined by use of a Luggin capillary-reference electrode compartment whose

position was made adjustable by mounting it on a syringe barrel. Compensation for $iR$ drop was achieved by positive feedback.

Bulk electrolyses were performed with an Amel 552 potentiostat linked to an Amel 731 digital integrator in 50% v/v AN/DCE, 0.15 $M$ NaClO$_4$, solutions. The working electrode was platinum gauze (ca. 100 cm$^2$) and the counter electrode was an external mercury pool, the connection being made through an appropriate salt bridge. In all cases a silver/0.1 $M$ silver perchlorate electrode in AN, separated from the test solution by either 0.2 $M$ TBAP in DCE or 0.15 $M$ NaClO$_4$ in AN solution sandwiched between two fritted disks, was used as the reference electrode. Ferrocene was added at the end of each experiment as an internal reference. All potentials are referred to the ferrocenium/ferrocene couple.

$^1$H and $^{31}$P NMR spectra were recorded on a JEOL 90 Q spectrometer equipped with a variable temperature apparatus and were referenced to internal SiMe$_4$ and external H$_3$PO$_4$ (85% w/w), respectively.

## Acknowledgments

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3 Under identical conditions, dppfO$_2$ undergoes a ferrocene-based reversible uncomplicated one-electron oxidation centred at $E°$ = 0.43 V.

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11 As the formal redox potentials, $E°$, of dppf and dppfO differ by only ca 0.1 V (see Results), the critical choice of the working potential value was optimized to give satisfactory current densities and to minimize the production of dppfO$_2$ by competitive oxidation of electrogenerated dppfO.