

# Derivatives of 1,1'-bis(diphenylphosphino)ferrocene (dppf): Electrochemistry, complexation and the X-ray structures of 1,1'-bis(diphenylphosphino)osmocene (dppo) and [PdCl<sub>2</sub>(dppo)]

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## Abstract

The oxidative electrochemistry of 1,1'-bis(diphenylphosphino)osmocene (dppo) and 1,1'-bis(diphenylarsino)ferrocene (dpaf) was studied in dichloromethane with tetrabutylammonium hexafluorophosphate as the supporting electrolyte. The [MCl<sub>2</sub>(P<sup>∞</sup>P)] (M = Pd or Pt; P<sup>∞</sup>P = dppo or 1,1'-bis(diphenylphosphinoindenyl)iron) complexes were prepared, studied electrochemically and the X-ray structures of dppo and [PdCl<sub>2</sub>(dppo)] were determined.

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## 1. Introduction

A number of bidentate phosphines with metallocene backbones are known, however the most widely investigated is 1,1'-bis(diphenylphosphino)ferrocene (dppf). Most of the studies involving dppf have focused on the catalytic properties of transition metal compounds containing dppf ligands [1–5]. In addition, the oxidative electrochemistry of dppf has been reported. The oxidation of dppf is complicated by a follow-up reaction that has been proposed to be a dimerization [6]. However, upon coordinating dppf to another transition metal the dppf-based oxidation is typi-

cally reversible [6–8]. Finally, the X-ray structures of dppf and several dppf-containing complexes have been reported [9,10].

While the chemistry of dppf is the most developed of the bidentate phosphines with metallocene backbones, a variety of closely related compounds are known. These related compounds can vary from dppf in a number of different ways. First, the R-groups on the phosphorus atoms can be substituted such as in 1,1'-bis(diisopropylphosphino)ferrocene (dippf). The oxidative electrochemistry of dippf has been studied; the potential at which oxidation occurs is less positive than that of dppf due to the more electron donating alkyl groups [11]. A second series of analogues is formed by changing the iron in the metallocene backbone to one of the other members of the group to give 1,1'-bis(diphenylphosphino)ruthenocene (dppr) and 1,1'-bis(diphenylphosphino)osmocene (dppo). The oxidation of dppr is irreversible and occurs at a potential that is more positive than that of dppf [6]. A third variation, is created by changing the phosphorus atoms in dppf to another

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pnictogen such as arsenic giving 1,1'-bis(diphenylarsino)ferrocene (dpaf), which has been synthesized [12] but not examined electrochemically. A final sequence of alternatives results from changing the groups on the C<sub>5</sub> rings. For example, the oxidative electrochemistries of 1,1'-bis(diphenylphosphino)octamethylferrocene (dppomf) [13] and 1,1'-bis(diphenylphosphinoindenyl)iron (dppind)<sub>2</sub>Fe [14] have been examined, and the potentials at which oxidation of these compounds occur as well as the reversibility of the oxidation are significantly different from dppf.

Herein we report the oxidative electrochemistries of dppo and dpaf. In addition, the syntheses, NMR (<sup>31</sup>P and <sup>1</sup>H) spectra and electrochemistry of [MCl<sub>2</sub>(P<sup>⊖</sup>P)] (M = Pt, P<sup>⊖</sup>P = dppo; M = Pd or Pt, P<sup>⊖</sup>P = (dppind)<sub>2</sub>Fe) are reported. Finally, the structures of dppo and [PdCl<sub>2</sub>(dppo)] as determined by X-ray crystallography are presented.

## 2. Experimental

### 2.1. General procedures

All manipulations were carried out under argon using standard Schlenk techniques. The compounds dppo [15], [PdCl<sub>2</sub>(dppo)] [15], chlorodiphenylarsine [16], dpaf [12] and (dppind)<sub>2</sub>Fe [17] were prepared according to the literature procedures. Osmocene, arsenic trichloride, [PdCl<sub>2</sub>(MeCN)<sub>2</sub>], [PtCl<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>CN)<sub>2</sub>], ferrocene and decamethylferrocene were purchased from Strem. Tetrabutylammonium hexafluorophosphate ([NBu<sub>4</sub>]<sup>+</sup>[PF<sub>6</sub>]<sup>-</sup>), indene, chlorodiphenylphosphine, butyllithium (1.6 M in hexanes) and iron (II) chloride were purchased from Aldrich. Dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>), diethyl ether (Et<sub>2</sub>O), and hexanes were purified under Ar using a Solvtek purification system similar to one previously described [18]. NMR spectra were obtained in CDCl<sub>3</sub> using a JEOL Eclipse 400 FT-NMR. TMS (δ = 0.00 ppm) was used as an internal standard for the <sup>1</sup>H NMR acquisitions while 85% H<sub>3</sub>PO<sub>4</sub> was used as the external reference value for the <sup>31</sup>P{<sup>1</sup>H} NMR data. Elemental analyses were performed by Quantitative Technologies, Inc.

### 2.2. Electrochemistry

All experiments were performed under an atmosphere of Ar at ambient temperature (22 ± 1 °C) using 10.0 mL of a 0.1 M solution of [NBu<sub>4</sub>]<sup>+</sup>[PF<sub>6</sub>]<sup>-</sup> in CH<sub>2</sub>Cl<sub>2</sub> as the supporting electrolyte. A three electrode system was used with a glassy carbon (1.5 mm) working electrode, a platinum wire auxiliary electrode and an Ag/AgCl (non-aqueous) reference electrode separated from the solution by a fine glass frit. The analyte concentration was 1.0 mM and the cyclic voltammetric data was collected at scan rates of 100–1000 mV/s at 100 mV/s intervals using a Princeton Applied Research 263-A potentiostat. All data presented is at a scan rate of 100 mV/s. Depending on the potential at which oxidation of the analyte occurred, either ferrocene or decamethylferrocene was added at the end of the experiment to give a solution that was 1.0 mM in the standard [19].

ethylferrocene was added at the end of the experiment to give a solution that was 1.0 mM in the standard [19].

### 2.3. X-ray crystallography

Crystals of dppo and [PdCl<sub>2</sub>(dppo)] were grown by vapor diffusion of Et<sub>2</sub>O into a solution of approximately 10 mg of compound in 1.0 mL of CH<sub>2</sub>Cl<sub>2</sub>. Crystallographic data are presented in Table 3. Crystals of dppo and [PdCl<sub>2</sub>(dppo)] were mounted on a CryoLoop<sup>®</sup> with Paratone-N<sup>®</sup> oil [20] and immediately placed in a cold nitrogen stream on a Bruker SMART APEX CCD system. Data collection occurred at –173 °C for dppo and –60 °C for [PdCl<sub>2</sub>(dppo)] with Mo Kα radiation and corrected for absorption using the SADABS program [21]. The structures were solved from a Patterson difference map, developed by successive difference Fourier syntheses, and refined by full matrix least squares on all F<sup>2</sup> data. All non-hydrogen atoms were refined as being anisotropic and hydrogen atoms were placed in calculated positions with temperature factors fixed at 1.2 or 1.5 times the equivalent isotropic U of the C atoms to which they were bonded. For the structure of dppo, residual electron densities of 1.78 and 1.74 e<sup>-</sup> were found within 0.852 and 0.812 Å of Os1. In addition, the crystal was found to be twinned with a 40/60 ratio of enantiomers. For the structure of [PdCl<sub>2</sub>(dppo)], residual electron densities of 2.14, 1.91 and 1.21 e<sup>-</sup> were found within 0.952, 0.879 and 1.008 Å of Os1 and electron densities of 1.50, 1.37 and 1.21 e<sup>-</sup> were found within 0.866, 0.909 and 0.850 Å of Pd1. Both hydrogen atoms on the CH<sub>2</sub>Cl<sub>2</sub> were placed at 0.5 occupancy and allowed to reach full occupancy via the growth command.

### 2.4. Synthesis of [PtCl<sub>2</sub>(dppo)]

In separate flasks, PtCl<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>CN)<sub>2</sub> (0.146 mmol, 0.0689 g) and dppo (0.160 mmol, 0.1005 g) were dissolved in 5.0 mL of benzene. The dppo solution was transferred by cannula to the PtCl<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>CN)<sub>2</sub> solution and the reaction was stirred for 16 h during which time an off-white precipitate formed. The solution was filtered and the solid was washed with benzene and then dried *in vacuo* giving [PtCl<sub>2</sub>(dppo)] (0.0719 g, 52%) as an off-white solid. Anal. Calc. for C<sub>34</sub>H<sub>28</sub>Cl<sub>2</sub>OsP<sub>2</sub>Pt: C, 42.77; H, 2.96. Found: C, 42.40; H, 2.64%. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ (ppm) 16.5 (s, <sup>1</sup>J<sub>P-Pt</sub> = 3870 Hz). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ (ppm) 7.84 (t, 8H, J<sub>H-H</sub> = 9.3 Hz, –C<sub>6</sub>H<sub>5</sub>), 7.43 (m, 4H, C<sub>5</sub>H<sub>3</sub>), 7.35 (m, 8H, C<sub>5</sub>H<sub>3</sub>), 5.07 (s, 4H, C<sub>5</sub>H<sub>4</sub>), 4.63 (s, 4H, C<sub>5</sub>H<sub>4</sub>).

### 2.5. Synthesis of [PdCl<sub>2</sub>((dppind)<sub>2</sub>Fe)]

PdCl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub> (0.139 mmol, 0.0530 g) and (dppind)<sub>2</sub>Fe (0.138 mmol, 0.0905 g) were dissolved in 5.0 mL of CH<sub>2</sub>Cl<sub>2</sub>. The reaction was stirred for 4 h and then 10.0 mL of Et<sub>2</sub>O was added. The solution was placed in a freezer overnight during which time a yellow solid formed. The solution was filtered and the solid was washed with

ether and then dried *in vacuo* giving  $[\text{PdCl}_2((\text{dppind})_2\text{Fe})]$  (0.0513 g, 45%) as a yellow solid. Anal. Calc. for  $\text{C}_{42}\text{H}_{34}\text{Cl}_2\text{FeP}_2\text{Pd} \cdot 1/2\text{CH}_2\text{Cl}_2$ : C, 58.25; H, 4.03. Found: C, 58.05; H, 3.91%.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 36.0 (s).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.3–7.2 (m, 28H,  $-\text{C}_6\text{H}_5$  and H5–H8), 5.10 (s, 2H, H2), 3.25 (s, 2H, H1).

### 2.6. Synthesis of $[\text{PtCl}_2((\text{dppind})_2\text{Fe})]$

$\text{PtCl}_2(\text{C}_6\text{H}_5\text{CN})_2$  (0.151 mmol, 0.0767 g) and  $(\text{dppind})_2\text{Fe}$  (0.150 mmol, 0.0985 g) were dissolved in 15.0 mL of  $\text{CH}_2\text{Cl}_2$ . The reaction was stirred for 1 h and then the volume of the solution was reduced to approximately 5 mL *in vacuo*.  $\text{Et}_2\text{O}$  (10.0 mL) were added and the solution was placed in a freezer overnight during which time a yellow solid formed. The solution was filtered and the solid was washed with ether and then dried *in vacuo* giving  $[\text{PtCl}_2((\text{dppind})_2\text{Fe})]$  (0.0168 g, 12%) as a yellow solid. Anal. Calc. for  $\text{C}_{42}\text{H}_{34}\text{Cl}_2\text{FeP}_2\text{Pt} \cdot \text{CH}_2\text{Cl}_2$ : C, 51.27; H, 3.60. Found: C, 51.14; H, 3.59%.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 11.6 (s,  $^1J_{\text{P-Pt}} = 3830$  Hz).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.8–6.4 (m, 28H,  $-\text{C}_6\text{H}_5$  and H5–H8), 5.01 (s, 2H, H2), 3.14 (s, 2H, H1).

### 3. Results and discussion

The molecular structure of dppo was determined by X-ray crystallography (Fig. 1). This structure completes the series of compounds from the iron triad: dppf [9], dppr [22] and dppo. Select measurements for comparison of these three compounds are presented in Table 1. The structure of dppo is slightly different from the related dppf and dppr structures. While dppf and dppr adopt an antiperiplanar ( $\tau = 180^\circ$ ) structure, dppo adopts a structure that is intermediate to antiperiplanar and anticlinal ( $\tau = 144^\circ$ )

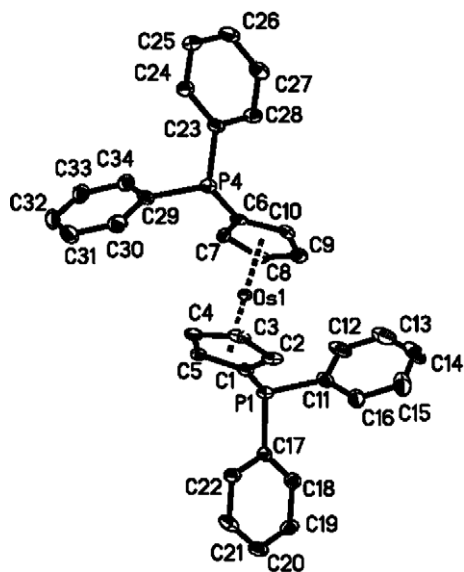


Fig. 1. Perspective view of dppo with 30% ellipsoids. H atoms are omitted for clarity.

Table 1  
Select measurements for dppf, dppr and dppo

	dppf	dppr	dppo
Reference	9	22	This work
$X_A-M-X_B$ ( $^\circ$ ) <sup>a</sup>	180.00	180.00	178.10
$\tau$ ( $^\circ$ ) <sup>b</sup>	180.00	180.00	167.93
$\theta$ ( $^\circ$ ) <sup>c</sup>	0.00	0.00	2.39
Avg. $\delta_P$ ( $\text{\AA}$ ) <sup>d</sup>	-0.066	-0.060	0.038
Avg. M–C ( $\text{\AA}$ )	2.040	2.169	2.186

<sup>a</sup> Centroid-M-Centroid.

<sup>b</sup> The torsion angle  $C_A-X_A-X_B-C_B$  where C is the carbon bonded to the P and X is the centroid.

<sup>c</sup> The dihedral angle between the two Cp rings.

<sup>d</sup> Deviation of the P atom from the Cp plane, a positive value meaning the P is closer to the Fe/Ru.

[23]. In addition, there is significant ring tilt ( $\theta$ ) in the dppo structure, while there is none in the structures of dppf and dppr. The parent metallocenes display some ring tilt;  $\theta$  equals  $0.61^\circ$ ,  $0.81^\circ$  and  $1.79^\circ$  for  $\text{Cp}_2\text{Fe}$  [24],  $\text{Cp}_2\text{Ru}$  [25] and  $\text{Cp}_2\text{Os}$  [26], respectively.

The complex  $[\text{PtCl}_2(\text{dppo})]$  was prepared in good yield using a synthesis similar to those used to prepare the dppf and dppr analogues [6,7]. The  $^{31}\text{P}$  signal for the complex is shifted downfield from that of free dppo. The structure of  $[\text{PdCl}_2(\text{dppo})]$  was also determined (Fig. 2). This structure completes the series of structures  $[\text{PdCl}_2(\text{P}^\cap\text{P})]$  ( $\text{P}^\cap\text{P} = \text{dppf}$  [27], dppr [6] or dppo) and select bond lengths and angles are presented in Table 2. The dppo ligand adopts a synclinal ( $\tau = 36^\circ$ ) [23] structure similar to the dppf [27] and dppr [6] analogues. The bite angle, P–Pd–P, for the dppo complex is significantly larger than the corresponding angle in the dppf complex and slightly larger than that found in the dppr complex. This is not surprising as the average Os–C distance in  $\text{Cp}_2\text{Os}$  [26] and dppo are longer than the average Fe–C and Ru–C distances in the iron [24,27] and ruthenium [6,25] analogues. Additional distortion of the osmocene backbone upon bonding to palladium is observed. Somewhat surprisingly, the angle  $\theta$  in

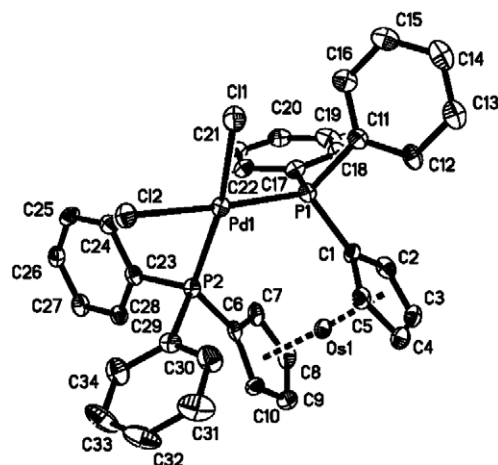


Fig. 2. Perspective view of  $[\text{PdCl}_2(\text{dppo})]$  with 30% ellipsoids. H atoms are omitted for clarity.

Table 2

Select measurements for  $[\text{PdCl}_2(\text{dppf})] \cdot \text{CH}_2\text{Cl}_2$ ,  $[\text{PdCl}_2(\text{dppr})] \cdot \text{CH}_2\text{Cl}_2$ , and  $[\text{PdCl}_2(\text{dppo})] \cdot \text{CH}_2\text{Cl}_2$

	$[\text{PdCl}_2(\text{dppf})] \cdot \text{CH}_2\text{Cl}_2$	$[\text{PdCl}_2(\text{dppr})] \cdot \text{CH}_2\text{Cl}_2$	$[\text{PdCl}_2(\text{dppo})] \cdot \text{CH}_2\text{Cl}_2$
Reference	27	6	This work
P–Pd–P (°)	97.98(4)	100.02(17)	100.82(9)
Cl–Pd–Cl (°)	89.96(4)	90.14(17)	87.62(9)
M	Fe	Ru	Os
$X_A\text{–M–}X_B$ (°) <sup>a</sup>	176.6	175.7	176.8
P–M–P (°)	61.5	62.1	61.9
$\tau$ (°) <sup>b</sup>	34.1	39.3	31.5
$\theta$ (°) <sup>c</sup>	6.2	9.2	7.8
Avg. P–Pd (Å)	2.284	2.305	2.296
Avg. Pd–Cl (Å)	2.348	2.358	2.338
P–P (Å)	3.446	3.531	3.538
Avg. $\delta_P$ (Å) <sup>d</sup>	0.048	0.088	0.038
Avg. M–C (Å)	2.035	2.168	2.170

<sup>a</sup> Centroid–M–Centroid.

<sup>b</sup> The torsion angle  $C_A\text{–}X_A\text{–}X_B\text{–}C_B$  where C is the carbon bonded to the P and X is the centroid.

<sup>c</sup> The dihedral angle between the two Cp rings.

<sup>d</sup> Deviation of the P atom from the Cp plane, a positive value meaning the P is closer to the Fe/Ru.

$[\text{PdCl}_2(\text{dppo})]$  falls directly between the  $\theta$  angles for the dppf and dppr analogues. However, the deviation of the phosphorus from the  $C_5$  plane,  $\delta_P$ , is the least positive for the dppo complex meaning that the phosphorus atoms of the ligand are not as bent in toward the osmium center as in the dppf and dppr complexes.

Only three other structures of complexes containing dppo have been reported. The average P–Pd distance for

Table 3

Crystallographic data and details of refinement of dppo and  $[\text{PdCl}_2(\text{dppo})] \cdot \text{CH}_2\text{Cl}_2$

	dppo	$[\text{PdCl}_2(\text{dppo})] \cdot \text{CH}_2\text{Cl}_2$
Formula	$\text{C}_{34}\text{H}_{28}\text{OsP}_2$	$\text{C}_{69}\text{H}_{58}\text{Cl}_6\text{Os}_2\text{P}_4\text{Pd}_2$
Formula wt.	688.70	1816.93
Crystal size (mm)	$0.15 \times 0.15 \times 0.07$	$0.15 \times 0.15 \times 0.10$
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$Cc$
$a$ (Å)	24.3141(16)	33.381(19)
$b$ (Å)	9.9594(6)	10.492(6)
$c$ (Å)	11.4820(7)	18.642(11)
$\beta$ (°)	106.9020(10)	106.606(8)
$V$ (Å <sup>3</sup> )	2660.3(3)	6257(6)
$Z$	4	4
$D_{\text{calc}}$ (g/cm <sup>3</sup> )	1.720	1.929
$F(000)$	1352	3512
$\mu$ (mm <sup>−1</sup> )	4.936	5.016
Number of reflections collected	11090	19939
Number of unique reflections	5650 ( $R_{\text{int}} = 0.0197$ )	7175 ( $R_{\text{int}} = 0.0517$ )
Number of parameters	335	375
Final $R$ indices		
$R_1$	0.0227	0.0855
$wR_2$	0.0512	0.1429
Goodness-of-fit	1.022	1.081

$[\text{PdCl}_2(\text{dppo})]$  is significantly longer than the P–Pd length in  $[(\text{C}_5\text{H}_4\text{P}(\text{O})\text{Ph}_2\text{OsC}_5\text{H}_4\text{PPh}_2)\text{PdCl}]_2(\mu\text{-Cl})_2$  (2.229 Å) [28]. This is likely due to dppo being bidentate in  $[\text{PdCl}_2(\text{dppo})]$  and monodentate in the dimeric complex. In  $[(\text{CH}_3\text{CN})\text{Pd}(\text{dppo})][\text{CF}_3\text{SO}_3]_2$  the dppo ligand is bidentate, but the average P–Pd distance is shorter (2.265 Å) than the average P–Pd distance in  $[\text{PdCl}_2(\text{dppo})]$  [15]. This is likely due to the unusual bonding in  $[(\text{CH}_3\text{CN})\text{Pd}(\text{dppo})][\text{CF}_3\text{SO}_3]_2$  in which there is a Pd–Os bond that forces the P–Pd–P angle to be 164.9° [15]. The third reported structure is  $[\text{Rh}(\text{CO})_2(\text{dppo})][\text{PF}_6]$  in which the dppo is a bidentate ligand to the Rh atom. Although the P–Rh–P angle (155.9°) is significantly larger than P–Pd–P angle in  $[\text{PdCl}_2(\text{dppo})]$ , the average P–Rh distance (2.284 Å) is similar to the average P–Pd distance in  $[\text{PdCl}_2(\text{dppo})]$  [5].

The oxidative electrochemistry of dppo was examined in  $\text{CH}_2\text{Cl}_2$ . The oxidation is irreversible and occurs at 0.35 V vs.  $\text{FcH}^{0/+}$ . This potential is more positive than that of dppf (0.24 V) but less positive than dppr (0.44 V) [6]. The same trend is seen in the potentials at which the parent metallocenes are oxidized:  $\text{Cp}_2\text{Fe}$  (0.47 V) <  $\text{Cp}_2\text{Os}$  (0.83 V) <  $\text{Cp}_2\text{Ru}$  (1.03 V) [29]. Similar to the dppr analogues [6], the oxidation of the dppo containing complexes,  $[\text{MCl}_2(\text{dppo})]$  (M = Pd or Pt), is irreversible. The potentials at which oxidation of these dppo complexes occur are approximately 0.5 V more positive than that of dppo. The 0.5 V difference between free dppo and the palladium and platinum complexes is similar to the difference between dppr and the corresponding palladium and platinum complexes [6].

Although dpaf has been known since 1971 [12,30–32], the electrochemistry of this compound has not been investigated. The potential at which oxidation of dpaf occurs is 0.14 V vs.  $\text{FcH}^{0/+}$  which is approximately 0.1 V less positive than the potential at which oxidation of dppf occurs. In the oxidation of triaryl pnictogens,  $\text{EPh}_3$  and  $\text{E}(2,4,6\text{-triisopropylphenyl})_3$  (E = P or As), the potential at which oxidation of the arsenic occurs is more positive than that of the corresponding phosphine [33]. However, oxidation of dpaf does not appear to occur at the arsenic atom. The potential at which oxidation of a disubstituted ferrocene occurs can be estimated using the Hammett parameter ( $\sigma_p$ ) for the substituent and Eq. (1), where  $E_L$  equals  $1/2E^0$  vs. NHE [34]. The reported value of  $\sigma_p$  for the  $-\text{AsPh}_2$  group is 0.09 [35], which, when referenced to  $\text{FcH}^{0/+}$ , predicts a potential of 0.14 V for the oxidation of dpaf. The less positive potential for the oxidation of dpaf is in good agreement with the  $pK_a$  values for  $p\text{-Ph}_2\text{AsC}_6\text{H}_4\text{CO}_2\text{H}$  and  $p\text{-Ph}_2\text{PC}_6\text{H}_4\text{CO}_2\text{H}$  which show that the arsine is the weaker acid, and therefore the  $-\text{AsPh}_2$  group is a better donor than the  $-\text{PPh}_2$  group [36].

$$E_L = 0.45\sigma_p + 0.36 \quad (1)$$

Unlike dppf, the oxidation of dpaf is reversible at the conditions employed in this study. The peak separation is 0.098 V and the peak current ratio ( $i_t/i_r$ ) is 0.98 (Fig. 3). Oxidation of triaryl phosphines and arsines has been shown to occur at the pnictogen atom [33]. If oxidation

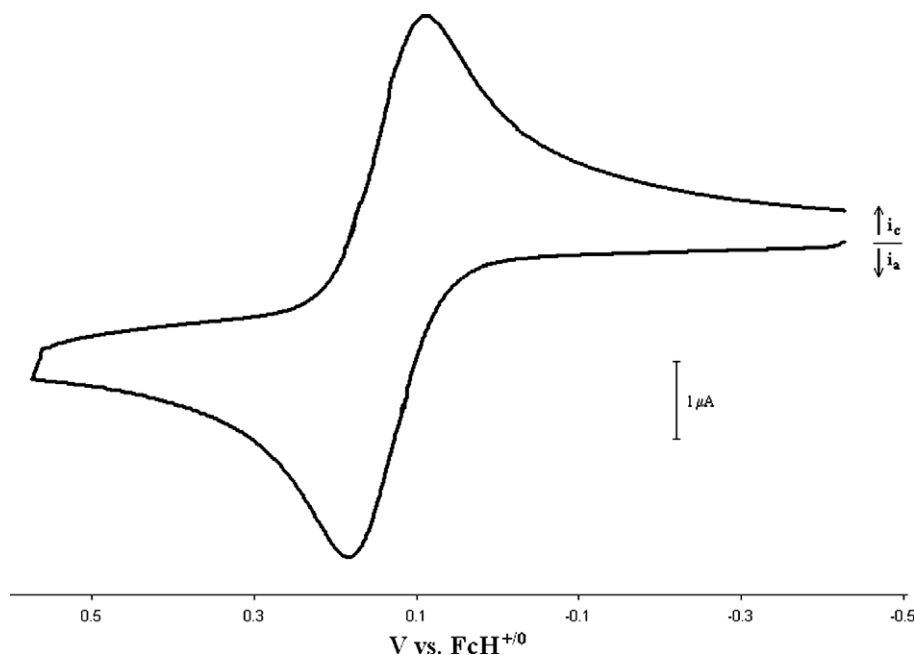


Fig. 3. Cyclic voltammetry scan of the oxidation of 1.0 mM dpaf in DCM/0.10 M Bu<sub>4</sub>NPF<sub>6</sub> at 100 mV/s.

of dpaf occurred at the arsenic, it is anticipated that the arsenic radical cation could undergo a reaction similar to that proposed for the phosphorus radical cation formed in the oxidation of dppf. While it is unclear why such a reaction does not seem to occur, it is possible that the lone pair on arsenic is tied up in  $\pi$ -bonding to the C<sub>5</sub> ring to a greater extent than the lone pair on phosphorus, and therefore, formation of an arsenic radical cation is less likely.

The oxidative electrochemistry of (dppind)<sub>2</sub>Fe was recently reported and, unlike dppf, the oxidation of (dppind)<sub>2</sub>Fe is reversible [14]. The compounds, [MCl<sub>2</sub>((dppind)<sub>2</sub>Fe)] (M = Pd or Pt), were prepared by methods similar to the dppf analogues [7]. Upon coordination, the <sup>31</sup>P signal shifts downfield. The oxidative electrochemistry for both of these compounds is reversible; the peak separation for both complexes is 0.075 V while the peak current ratios ( $i_r/i_f$ ) are 0.90 for the palladium complex and 0.99 for the platinum. The potential at which the oxidation of the complexes occurs is more positive than that of free (dppind)<sub>2</sub>Fe. Oxidation of [PdCl<sub>2</sub>((dppind)<sub>2</sub>Fe)] occurs at 0.25 V vs. FcH<sup>0/+</sup> while oxidation of the platinum analogue occurs at 0.24 V vs. FcH<sup>0/+</sup>. The difference between the potential at which oxidation of the free (dppind)<sub>2</sub>Fe occurs (-0.14 V) [14] and that of these complexes is approximately 0.35 V, which is identical to the difference between dppf and [MCl<sub>2</sub>(dppf)] (M = Pd or Pt) [6]. This similarity suggests that an equation similar to Eq. (1) may be developed for diindenyliron complexes. An analysis of the reported CV data of four diindenyliron complexes (Fig. 4) in CH<sub>2</sub>Cl<sub>2</sub> suggests the following equation (Eq. (2)).

$$E_L = 0.62\sigma_p + 0.40 \quad (2)$$

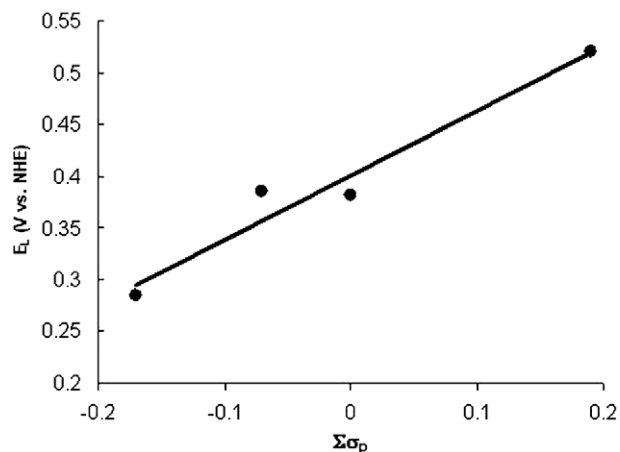


Fig. 4. Slope = 0.62, intercept = 0.40,  $R^2 = 0.96$ . The  $\sigma_p$  [35] and  $E_L$  values presented in this plot are for the compounds (1-RC<sub>9</sub>H<sub>6</sub>)<sub>2</sub>Fe where R = Me (-0.17, 0.14 V [37]), SiMe<sub>3</sub> (-0.07, 0.19 V [38]), H (0.00, 0.19 V [37]), and PPh<sub>2</sub> (0.19, 0.26 V [14]).

#### 4. Summary

The electrochemistry of dppf derivatives has been investigated. The oxidation of dpaf is reversible under the conditions used in this study. The oxidation of dppo, either free or coordinated, is irreversible, similar to the ruthenium analogue [6]. The X-ray structures of dppo and [PdCl<sub>2</sub>(dppo)] were determined, and the dppo bite angle in [PdCl<sub>2</sub>(dppo)] is not significantly larger than that of dppr. The oxidative electrochemistry of (dppind)<sub>2</sub>Fe is also reversible upon coordination.

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## Appendix A. Supplementary material

Crystallographic data (CIF files) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 605379 for dppo and CCDC No. 605378 for  $[\text{PdCl}_2(\text{dppo})] \cdot (1/2 \text{CH}_2\text{Cl}_2)$ . Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.05.012.

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