Anodic Electrochemistry of Ferrocenylphosphine and Ruthenocenylphosphine Chalcogenide Complexes and Lewis Acid Adducts

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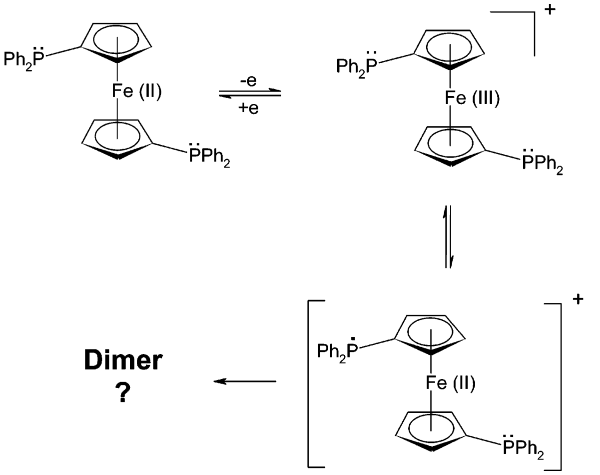
The anodic electrochemistry of a series of bidentate phosphine chalcogenides and bidentate phosphine Lewis acid adducts, both with a metallocene backbone, was examined in dichloromethane containing $[NBu_4][PF_6]$. Oxidation of the ferrocene compounds dppfE_2 and dippfE_2 ($E = O, S, BH_3, CH_3^+$) was reversible on the cyclic voltammetric (CV) time scale, while the oxidation of the dpprE_2 compounds ($E = O, S, BH_3$) was irreversible; however, the oxidation of dppfSe_2, dippfSe_2, and dpprSe_2 displayed an irreversible wave and the reduction of a follow-up product.

Introduction

1,1′-Bis(diphenylphosphino)ferrocene (dppf) has received considerable attention in recent years, particularly as a ligand in a variety of catalytic applications.[1,2] The main interest in dppf stems from the bite angle of the chelate phosphine and the redox-active ferrocene backbone.[2] Numerous studies have investigated the oxidative electrochemistry of dppf, which, unlike that of ferrocene, is complicated by a follow-up reaction that has been proposed to be dimerization.[3] The dimerization of dppf$^+$ has been attributed to the presence of the lone pair of electrons on each phosphorus atom, which can undergo an intramolecular electron transfer with the Fe(III) center, forming a phosphorus radical capable of undergoing a dimerization reaction (Scheme 1).[4] To prevent these reactions, it is necessary to occupy the lone pair of electrons on each phosphorus atom. Numerous studies have been performed in which dppf is bound to a metal center, and in many cases, the oxidation of these complexes is reversible.[3−5]

In addition to dppf, there are a variety of other bidentate phosphines with metallocene backbones that have been examined. The oxidative electrochemistry of 1,1′-bis(diisopropylphosphino)ferrocene (dippf) is similar to that of dppf; the oxidation of dippf is complicated by a follow-up reaction, but upon coordination, the dippf oxidation is frequently reversible.[6] A second chelate phosphine in this series that has been examined is 1,1′-bis(diphenylphosphino)ruthenocene (dppr). Unlike the iron-centered dppf and dippf, the oxidative electrochemistry of dppr and all of the compounds containing a dppr ligand that have been examined is irreversible.[3] While dippf likely undergoes a dimerization after oxidation, it is unclear what happens in the case of dppr. Dimerization of dppr$^+$ through phosphorus cannot be excluded; however, coordination of dppr to a metal would be anticipated to prevent this type of dimerization. Another type of dimerization could occur through the ruthenium

Scheme 1. Electrochemical Dimerization of dppf



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(4) Pilloni, G.; Longato, B.; Corain, B. *J. Organomet. Chem.* **1991**, *420*, 57.

(5) There are numerous examples in the literature. Examples include: (a) Sun, Y.; Chan, H.-S.; Dixneuf, P. H.; Xie, Z. *Organometallics* **2004**, *23*, 5864. (b) Ohs, A. C.; Rheingold, A. L.; Shaw, M. J.; Nataro, C. *Organometallics* **2004**, *23*, 4655. (c) O'Connor, A. R.; Nataro, C.; Rheingold, A. L. *J. Organomet. Chem.* **2003**, *679*, 72. (d) Longato, B.; Coppo, R.; Pilloni, G.; Corvaja, C.; Toffoletti, A.; Bandoli, G. *J. Organomet. Chem.* **2001**, *637−639*, 710. (e) Choi, N.-S.; Lee, S. W. *J. Organomet. Chem.* **2001**, *627*, 226.

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centers of two dppr$^+$, as seen in ruthenocene.[7] However, the use of supporting electrolytes with noncoordinating anions prevents this type of dimerization[7,8] but does not give a reversible oxidation in the case of dppr.[3] Additional reactions are also possible; thus, it appears that there is a combination of factors in the oxidation of dppr that lead to the instability of the complex upon oxidation.

To further explore the oxidative electrochemistry of dppf, dippf, and dppr, a series of compounds in which the lone pair of the phosphorus atoms is bonded to nonmetallic elements was examined. The first class of compounds contain two P(V) atoms with chalcogenide atoms bonded to each phosphorus. Although a number of these compounds have been prepared, only dppfO$_2$ has been studied electrochemically.[4] Those studies have shown dppfO$_2$ to undergo a reversible single-electron oxidation, indicating that the occupation of the lone pair of electrons on each phosphorus atom prevents dimerization. The second class of compounds is prepared by reacting Lewis acids with the phosphorus lone pair. The compounds formed by the reaction of chalcogenides and Lewis acids with bidentate phosphines having metallocene backbones will provide a better understanding of the oxidative electrochemistry of bidentate phosphines containing metallocene backbones.

Experimental Section

General Procedures. All reactions were carried out using standard Schlenk techniques under argon. The compounds dppfE$_2$[9] and dippfE$_2$[10] (E = O, S, Se), dppfO,[11] dppf(BH$_3$)$_2$,[12] and dppr[13] were prepared according to literature methods. Ferrocene, decamethylferrocene, dppf, and dippf were supplied by Strem Chemicals, Inc. BH$_3$·thf (1 M in THF) and [Me$_3$O][BF$_4$] were purchased from Aldrich. Dichloromethane (CH$_2$Cl$_2$) and hexanes were dried over CaH$_2$ and distilled under nitrogen. Ether and THF were dried over potassium benzophenone ketyl and distilled under nitrogen. HPLC grade dichloromethane used for electrochemistry was dried over CaH$_2$ and distilled under argon. ^{31}P{^{1}H} and ^{1}H NMR spectra were recorded using a JEOL Eclipse 400 FT-NMR spectrometer. Elemental analysis was performed by Quantitative Technologies, Inc.

^{1}H NMR of dppfO$_2$. Although this compound had been previously prepared, the ^{1}H NMR spectrum was not reported.[4] ^{1}H NMR (CDCl$_3$): δ (ppm) 7.57 (m, 20 H, *Ph*), 4.70 (s, 4 H, ($C_5H_4(O_\alpha)$), 4.25 (s, 4 H, ($C_5H_4(O_\beta)$).

Preparation of dppfOS. dppfO (0.0681 g, 0.119 mmol) was dissolved in CH$_2$Cl$_2$ (2 mL) at room temperature under argon. Sulfur (0.0044 g, 0.137 mmol) was then added, and the mixture was refluxed for 20 h with stirring. The solvent was reduced to half volume under vacuum, and 10 mL of hexanes were added. The solution was cooled to 0 °C for approximately 30 min, and a precipitate formed. The solution was removed and the solid dried under vacuum, giving 0.0406 g (56%) of dppfOS as a brown powder. Anal. Calcd for $C_{34}H_{28}FeOP_2S\cdot{}^1/_3CH_2Cl_2$: C, 65.38; H, 4.38. Found: C, 65.02; H, 4.63. ^{1}H NMR (CDCl$_3$): δ (ppm) 7.52 (m, 20 H, *Ph*), 4.72 (br s, 2 H, $C_5H_4(O_\alpha)$), 4.61 (br s, 2 H, $C_5H_4(S_\alpha)$), 4.31 (br s, 2 H, $C_5H_4(S_\beta)$), 4.19 (br s, 2 H, $C_5H_4(O_\beta)$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ (ppm) 41.01 (s, P=S), 27.98 (s, P=O).

Preparation of dppfOSe. dppfO (0.0642 g, 0.101 mmol) was dissolved in CH$_2$Cl$_2$ (2 mL) at room temperature under argon. Selenium (0.0089 g, 0.113 mmol) was added, and the mixture was refluxed for 20 h with stirring. The solvent was reduced to half volume under vacuum, and 5 mL of MeOH were added to the remaining solution. The solution was cooled to 0 °C for approximately 30 min, resulting in the formation of crystals. The solvent was decanted, and the remaining crystals were dried under vacuum, giving 0.0115 g (16%) of dppfOSe as red-brown crystals. Anal. Calcd for $C_{34}H_{28}FeOP_2Se$: C, 62.89; H, 4.35. Found: C, 63.22; H, 4.55. ^{1}H NMR (CDCl$_3$): δ (ppm) 7.41 (m, 20 H, *Ph*), 4.76 (br s, 2 H, $C_5H_4(Se_\alpha)$), 4.62 (br s, 2 H, $C_5H_4(O_\alpha)$), 4.34 (br s, 2 H, $C_5H_4(Se_\beta)$), 4.20 (br s, 2 H, $C_5H_4(O_\beta)$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ (ppm) 31.55 (s, J_{PSe} = 371 Hz, P=Se), 28.10 (s, P=O).

Preparation of dpprO$_2$. dppr (0.0497 g, 0.083 mmol) was dissolved in THF (5 mL) at room temperature. The mixture was cooled to 0 °C, and 0.020 mL (0.59 mmol) of H$_2$O$_2$ (30%) were added. The mixture was warmed to room temperature for approximately 30 min, filtered, and the solvent was removed under vacuum, leaving 0.0153 g (29%) of dpprO$_2$ as a gray solid. Anal. Calcd for $C_{34}H_{28}O_2P_2Ru\cdot{}^1/_2THF$: C, 64.76; H, 4.83. Found: C, 64.38; H, 5.02. ^{1}H NMR (CDCl$_3$): δ (ppm) 7.35 (m, 20 H, *Ph*), 4.80 (br s, 4 H, $C_5H_4(O_\alpha)$), 4.59 (br s, 4 H, $C_5H_4(O_\beta)$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ (ppm) 27.57 (s).

Preparation of dpprS$_2$. dppr (0.0508 g, 0.085 mmol) was dissolved in CHCl$_3$ (5 mL) at room temperature. Sulfur (0.0052 g, 0.162 mmol) was then added, and the mixture was refluxed for 20 h with stirring. The solution was filtered and the solvent was removed under vacuum, leaving 0.0253 g (47%) of dpprS$_2$ as a beige solid. Anal. Calcd for $C_{34}H_{28}P_2RuS_2\cdot{}^1/_3CHCl_3$: C, 58.62; H, 4.06. Found: C, 58.28; H, 4.06. ^{1}H NMR (CDCl$_3$): δ (ppm) 7.62 (m, 8 H, *Ph*), 7.35 (m, 12 H, *Ph*), 4.81 (br s, 4 H, $C_5H_4(S_\alpha)$), 4.62 (br s, 4 H, $C_5H_4(S_\alpha)$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ (ppm) 40.56 (s).

Preparation of dpprSe$_2$. dppr (0.0501 g, 0.083 mmol) was dissolved in CHCl$_3$ (5 mL) at room temperature. Selenium (0.0135 g, 0.171 mmol) was then added, and the mixture was refluxed for 20 h with stirring. The solution was filtered and the solvent was removed under vacuum, leaving 0.0328 g (52%) of dpprSe$_2$ as a gray solid. Anal. Calcd for $C_{34}H_{28}P_2RuS_2\cdot{}^1/_2CHCl_3$: C, 50.71; H, 3.52. Found: C, 50.80; H, 3.53. ^{1}H NMR (CDCl$_3$): δ (ppm) 7.62 (m, 8 H, *Ph*), 7.36 (m, 12 H, *Ph*), 4.86 (br s, 4 H, $C_5H_4(Se_\alpha)$), 4.64 (br s, 4 H, $C_5H_4(Se_\alpha)$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ (ppm) 31.36 (s, J_{P-Se} = 369 Hz).

Preparation of dippf(BH$_3$)$_2$. dippf (0.0508 g, 0.121 mmol) was dissolved in THF (5 mL), and then 0.25 mL (0.25 mmol) of BH$_3$·thf was added. The mixture was stirred at room temperature for 1 h. The solvent was removed under vacuum, and the residue was washed with ether (10 mL), giving 0.0496 g (92%) of dippf(BH$_3$)$_2$ as an orange solid. Anal. Calcd for $C_{22}H_{42}B_2FeP_2\cdot Et_2O$: C, 60.04; H, 10.08. Found: C, 60.07; H, 10.26. ^{1}H NMR (CDCl$_3$): δ (ppm) 4.69 (br s, 4 H, $C_5H_4(B_\alpha)$), 4.39 (br s, 4 H, $C_5H_4(B_\beta)$), 2.14 (m, 4 H, C*H*), 1.63 (m, 30 H, C*H$_3$* and B*H$_3$*). ^{31}P{^{1}H} NMR (CDCl$_3$): δ (ppm) 32.73 (br s).

Preparation of dppr(BH$_3$)$_2$. The preparation of this compound was carried out as per the synthesis of dippf(BH$_3$)$_2$, except 0.0511 g (0.085 mmol) of dppr and 0.20 mL (0.2 mmol) of BH$_3$·thf were used. This gave 0.0509 g (95%) of dppr(BH$_3$)$_2$ as a beige solid. Anal. Calcd for $C_{34}H_{34}B_2P_2Ru$: C, 65.10; H, 5.46. Found: C, 64.80; H, 5.76. ^{1}H NMR (CDCl$_3$): δ (ppm) 7.41

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(m, 20 H, *Ph*), 4.75 (br s, 4 H, $C_5H_4(B_\alpha)$), 4.59 (br s, 4 H, $C_5H_4(B_\beta)$), 1.35 (br s, 6H, BH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 16.53 (s).

Preparation of $[dppf(CH_3)_2][BF_4]_2$. dppf (0.0511 g, 0.092 mmol) was dissolved in hexanes (5 mL), and then $[(CH_3)_3O][BF_4]$ (0.0274 g, 0.185 mmol) was added. The mixture was stirred for 1 h at room temperature. The solvent was removed under vacuum, and the solid was washed with 5 mL of ether. The solution was filtered, and the solid was dried under vacuum, giving 0.054 g (71%) of $[dppf(CH_3)_2][BF_4]_2$ as an orange solid. Anal. Calcd for $C_{36}H_{34}B_2F_8FeP_2$: C, 57.04; H, 4.52. Found: C, 57.05; H, 4.55. ^1H NMR ($CDCl_3$): δ (ppm) 7.67 (m, 20 H, *Ph*), 4.87 (br s, 4 H, $C_5H_4(C_\alpha)$), 4.67 (br s, 4 H, $C_5H_4(C_\beta)$), 2.69 (d, $J = 13.2$ Hz, 6 H, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 22.77 (s).

Preparation of $[dppr(CH_3)_2][BF_4]_2$. The preparation of this compound was carried out as per the synthesis of $[dppf(CH_3)_2][BF_4]_2$, except 0.0524 g (0.087 mmol) of dppr and 0.0266 g (0.18 mmol) of $[(CH_3)_3O][BF_4]$ were used. This gave 0.0193 g (35%) of $[dppr(CH_3)_2][BF_4]_2$ as a yellow solid. Anal. Calcd for $C_{36}H_{34}B_2F_8P_2Ru$: C, 53.83; H, 4.27. Found: C, 54.14; H, 4.00. ^1H NMR ($CDCl_3$): δ (ppm) 7.64 (m, 20 H, *Ph*), 5.03 (br s, 4 H, $C_5H_4(C_\alpha)$), 4.96 (br s, 4 H, $C_5H_4(C_\beta)$), 2.67 (d, $J = 13.2$ Hz, 6 H, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 22.13 (s).

Preparation of $[dippf(CH_3)_2][BF_4]_2$. dippf (0.0481 g, 0.115 mmol) was dissolved in THF (5 mL), and then $[(CH_3)_3O][BF_4]$ (0.0344 g, 0.233 mmol) was added. The mixture was stirred for 1 h at room temperature. The solvent was removed, and 5 mL of ether was added. The solution was filtered, and the remaining solid was dried under vacuum, giving 0.042 g (81%) of $[dippf(CH_3)_2][BF_4]_2$ as an orange powder. Anal. Calcd for $C_{24}H_{42}B_2F_8FeP_2\cdot{}^3/_4Et_2O$: C, 47.86; H, 7.36. Found: C, 47.83; H, 7.15. ^1H NMR ($CDCl_3$): δ (ppm) 5.10 (m, 8 H, (C_5H_4), 2.16 (m, 4 H, CH), 1.33 (m, 24 H, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 43.08 (s).

Electrochemical Procedures. Standard electrochemical techniques were employed, and all scans were performed under an argon atmosphere. The supporting electrolyte was 0.1 M $[Bu_4N][PF_6]$. Glassy carbon was used as the working electrode, and Pt was used as the counter electrode. The glassy-carbon electrode was polished with two different diamond pastes, 1.0 μm and 0.25 μm, and rinsed with CH_2Cl_2 prior to use. The experimental reference electrode was Ag/AgCl, separated from the solution by a frit, and either ferrocene or decamethylferrocene were used as an internal standard. The potential was referenced to the NHE by adding 0.66 V.[14] Electrochemical experiments were conducted at ambient temperature (22 ± 1 °C) using a PAR Model 263A potentiostat/galvanostat, and voltammograms were recorded using PowerSuite software. Cyclic voltammograms were performed at scan rates of 50 mV/s and in increments of 100 mV/s from 100 to 1000 mV/s. The formal oxidation potentials and the difference between the formal potentials of each compound and the corresponding phosphine (ΔE) are presented in Table 1.

Table 1. Formal Potentials (V vs $Fc^{0/+}$) for Chalcogenides and Lewis Acid Adducts of 1,1′-Diphosphinometallocenes and Potential Difference (ΔE in V vs Corresponding Phosphine) from the Starting Phosphine[a]

	dppf		dippf		dppr	
	E°	ΔE	E°	ΔE	E°	ΔE
O_2	0.45	0.22	0.37	0.32	0.81^b	0.37
OS	0.48	0.25				
OSe	$0.45,^b$ 0.19^c	0.22				
S_2	0.48	0.25	0.38	0.33	0.51^b	0.07
Se_2	$0.32,^b$ -0.14^c	0.09	$0.21,^b$ -0.24^c	0.16	$0.32,^b$ -0.16^c	0.12
$(BH_3)_2$	0.49	0.26	0.39	0.34	0.91^b	0.47
$[(CH_3)_2]^{2+}$	0.99	0.76	0.96	0.91		

[a] A scan rate of 100 mV/s was used for all data. [b] Irreversible wave. [c] Potential for the follow-up cathodic wave.

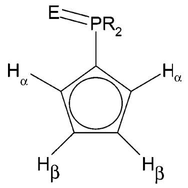

Figure 1. Proton labeling scheme.

Results and Discussion

Synthesis. The dppr chalcogenide compounds were prepared using methods similar to those used in preparing the dppf analogues.[9] The compounds were prepared in reasonable yield and characterized by NMR. Numerous attempts were made to prepare the ditellurides of dppf, dippf, and dppr, but none were successful.

Reaction of dppfO with sulfur or selenium yields the new mixed chalcogenide products dppfOS and dppfOSe. The $^{31}P\{^1H\}$ NMR spectrum shows two singlets for each product, each having a peak at approximately 28 ppm. This is very similar to the peak in $dppfO_2$; therefore, it is attributed to the P=O. The peaks further downfield have chemical shifts similar to those of the corresponding $dppfE_2$ (E = S, Se), and in the case of dppfOSe, coupling to ^{77}Se is observed. The $^{31}P-^{77}Se$ coupling is significantly less than that for $dppfSe_2$[9c] but is in the typical range for other P=Se compounds.[10] The ^1H NMR spectra show the C_5H_4 protons to be represented by four broad signals, which are assigned as $C_5H_4(E_{\alpha/\beta})$, where α/β represents the position with respect to the chalcogenide (Figure 1). The assignments of the C_5H_4 protons in the mixed-chalcogenide compounds were based upon comparison to the parent $dppfE_2$ compounds. For dppfOS, the $C_5H_4(O_\alpha)$ protons were assigned to the peak furthest downfield. The chemical shifts of the protons in the positions α/β to the $P(S)Ph_2$ group are similar to the shifts for the $C_5H_4(S_\beta)$ protons (4.64 ppm) and the $C_5H_4(S_\alpha)$ protons (4.29 ppm) of $dppfS_2$. The final peak in the C_5H_4 region is assigned as the $C_5H_4(O_\beta)$ protons. A similar technique was employed for the assignment of the protons in the dppfOSe spectrum. Since it was difficult to determine the assignments of Se_α and O_α using just ^1H NMR, $^1H-^1H$ COSY was employed. The resulting spectrum allowed for the assignment of the Se_α protons and the O_α protons.

Reactions of dppf, dippf, and dppr with $BH_3\cdot thf$ and $[(CH_3)_3O][BF_4]$ yielded Lewis acid adducts of the starting phosphines, as determined by NMR spectroscopy. The synthesis and spectroscopic data for $dppf(BH_3)_2$ have been reported.[12] The dppr and dippf analogues were prepared in a similar manner. The ^{31}P signal for the BH_3 adducts shifts upfield by approximately 30 ppm as compared to that for the phosphines; this is similar to the difference in shift for PPh_3 and $H_3B\cdot PPh_3$.[15] The preparation of $dppf(CH_3)_2{}^{2+}$ from dppf and CH_3I has been reported, but the characterization was limited to IR and elemental analysis.[9b] Complications in the

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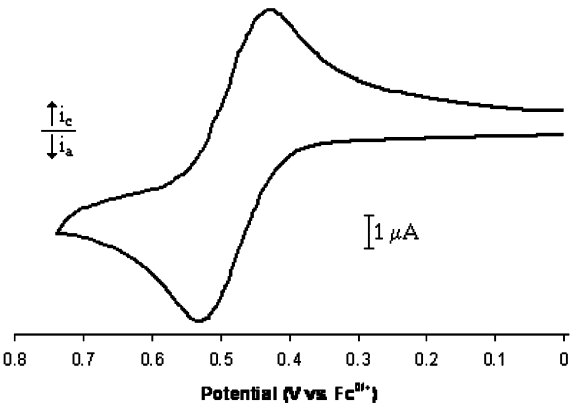

Figure 2. Cyclic voltammetry scan of the oxidation of 1.0 mM dppfS$_2$ in CH$_2$Cl$_2$/0.10 M Bu$_4$NPF$_6$ at 100 mV/s.

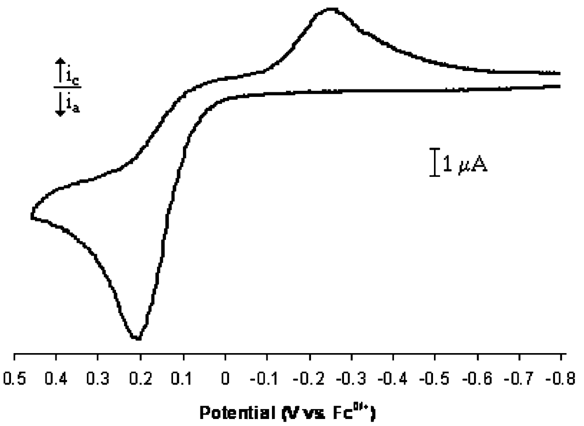

Figure 3. Cyclic voltammetry scan of the oxidation of 1.0 mM dippfSe$_2$ in CH$_2$Cl$_2$/0.10 M Bu$_4$NPF$_6$ at 100 mV/s.

oxidation of H$_3$C$-$PPh$_2$Fc$^+$I$^-$ were attributed to the iodide; therefore, a less reactive anion was desired.[16] The reaction between the phosphines and [(CH$_3$)$_3$O][BF$_4$] gives the desired diphosphonium tetrafluoroborate salts in reasonable yield. Similar to the BH$_3$ adducts and the phosphine oxides, the ^{31}P chemical shift for the CH$_3$$^+$ adducts is approximately 30 ppm downfield of the phosphine.

Electrochemistry of Chalcogenides. The oxidative electrochemistry of dppfO$_2$ has been examined in dichloroethane with tetrabutylammonium perchlorate as the supporting electrolyte; the reversible wave occurs 0.21 V positive of dppf.[4] Similar results were obtained for the oxidation of dppfO$_2$ and dippfO$_2$ in CH$_2$Cl$_2$ (Table 1). While the oxidation of dppf and dippf yields a product that is unstable with respect to dimerization, dppfO$_2$$^+$ and dippfO$_2$$^+$ are stable on the time scales used in this study. The dimerization of dppf$^+$ and dippf$^+$ is proposed to occur through the nonbonding electrons on a phosphorus atom (Scheme 1). In dppfO$_2$ and dippfO$_2$, the phosphorus atoms are not able to participate in the dimerization mechanism; therefore, the dimerization is not possible and the oxidation is reversible. Geiger has recently examined the oxidative electrochemistry of the related phosphine PFc$_2$Ph and phosphine oxide O=PFc$_2$Ph.[17] Similar to the dppf system, the oxidation of PFc$_2$Ph is complicated by a follow-up reaction, while the oxidation of O=PFc$_2$Ph is not.

Like the iron systems, the oxidation of dpprO$_2$ occurs approximately 0.4 V more positive than dppr; however, unlike the iron compounds, the oxidation is irreversible at all scan rates. This is not surprising as the parent, dppr, exhibits an irreversible oxidation under similar conditions. The irreversibility of the dpprO$_2$ suggests that the decomposition of dppr$^+$ does not have to involve the nonbonding electrons on phosphorus, but it does not preclude their involvement.

The oxidative electrochemistry of the phosphine sulfide compounds is analogous to that of the phosphine oxides; the oxidation of the compounds with the iron center, dppfS$_2$ (Figure 2) and dippfS$_2$, is reversible, while the oxidation of the ruthenium-centered dpprS$_2$ is irreversible. For the iron compounds, the potential at which the oxidation occurs for the sulfide is similar to that for the analogous oxide compounds and is approximately 0.3 V more positive than for the phosphine. The potential at which dpprS$_2$ oxidation occurs is significantly closer to dppr than to dpprO$_2$. As all of the waves for the dppr-based oxidations are irreversible, the $E_{1/2}$ values cannot be accurately determined;[18] thus, no conclusions can be drawn from the dppr data.

The oxidative electrochemistry of the diselenide complexes in this study was similar; there was an irreversible oxidation wave and a cathodic wave due to a follow-up product (Figure 3). For all three diselenide compounds, the cathodic wave is approximately 0.5 V less positive than the irreversible oxidation wave, suggesting that the follow-up products are similar. The oxidative electrochemistry of PFc$_3$ and Se=PFc$_3$ has been examined and, although slightly more complicated due to the three iron centers, there is an irreversible oxidation with a follow-up cathodic wave that is less positive by 0.5 V.[17] The follow-up product is proposed to result from a reaction that occurs following an intramolecular electron transfer from the Se to the iron(III) center.[17] However, this explanation is based upon the faulty premise that selenium is more electronegative than phosphorus. The polarizability of P=E bonds increases on going from E = O to E = Se.[20] DFT calculations suggest that the π-bond order in E=PMe$_3$ decreases going down the chalcogenides.[21] While an intramolecular electron transfer may play a role in the reactivity of the oxidized selenides, the weaker P=Se bond could greatly influence the reactivity. This difference has been noted in the reactivity of E=PR$_3$ compounds; selenium is readily transferred between different phosphines at room temperature, while the transfer of sulfur requires elevated temperatures.[22]

The oxidative electrochemistry of the mixed oxide−chalcogenide species, dppfOS and dppfOSe, showed features of both parent dichalcogenide compounds. The oxidation of dppfOS is reversible, similar to dppfO$_2$ and

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dppfS$_2$, while the potential at which oxidation occurs is identical with that of dppfS$_2$, although not substantially different from the potential at which dppfO$_2$ occurs. The potential at which the oxidation of dppfOSe occurs is the same as for dppfO$_2$. However, a cathodic follow-up product is seen, just as in the oxidation of dppfSe$_2$. It seems that the chalcogenide does play a slight role in the oxidation potential of the iron center, but the presence of even one phosphine selenide provides a route of decomposition for the oxidation product.

Electrochemistry of Lewis Acid Adducts. The addition of a Lewis acid to phosphinometallocenes has been shown to affect the electrochemistry. For example, there is an irreversible wave in the oxidation of PPh$_2$-Fc, but in the BH$_3$ adduct there is a reversible wave.[16] The oxidation of the BH$_3$ adducts of dppf, dippf, and dppr give results similar to those for the oxides; the dppf and dippf adducts display one reversible oxidation wave, while the dppr adduct has an irreversible oxidation. The potentials at which oxidation occurs for the borane adducts are more positive than those of the starting phosphines and are similar to the oxidation potentials for the chalcogenide compounds. This is similar to the trend found for the oxidation potential of H$_3$B·PPh$_2$Fc, which is 0.2 V more positive than that of PPh$_2$Fc.[16]

The electrochemistry of a second type of Lewis acid adduct was also examined. In this type, the phosphorus atoms were alkylated, yielding diphosphonium compounds. As with all of the previous iron compounds, when there is not a lone pair of electrons on either phosphorus atom, the oxidation of the compound is reversible. The potential at which the oxidation occurs for dppf(CH$_3$)$_2^{2+}$ and dippf(CH$_3$)$_2^{2+}$ is significantly more positive than that of the phosphines, and this is likely attributable to the +2 charges of the compounds that are a result of the addition of two CH$_3^+$ groups. This is similar to the case for H$_3$C−PPh$_2$Fc$^+$I$^-$, which has a reversible oxidation that is approximately 0.45 V more positive than that of PPh$_2$Fc.[16] While this difference is significantly less than what is observed for the dppf and dippf compounds, it is not surprising, since the dppf and dippf compounds are dications, while the PPh$_2$Fc adduct is a monocation. No wave is observed for the oxidation of dppr(CH$_3$)$_2^{2+}$; it is presumed to be outside of the solvent window.

For Lewis acid adducts of the iron compounds, the Lewis acid occupies the lone pair on phosphorus, and this prevents the oxidized species from displaying any reactivity on the cyclic voltammetric time scale. This compliments what is seen for the oxides, sulfides, and many metal complexes with dppf or dippf ligands. The irreversible nature of the oxidative electrochemistry of dppr and compounds containing dppr remains unexplained. Thus far, we can conclude that the supporting electrolyte does not appear to influence the reversibility of the oxidation. In addition, the availability of the phosphorus lone pair does not seem to be essential for the decomposition of the oxidation product. Additional studies will be required to explain this phenomenon.

Electrochemical Parametrization. The electrochemical parameter, E_L, for various C$_5$H$_4$R ligands can be estimated from the $^1/_2E°$ vs NHE values for 1,1′-disubstituted ferrocene compounds, Fe(C$_5$H$_4$R)$_2$.[14] A plot of E_L versus the Hammett substituent constant, σ_p, gives an excellent correlation.[14] To ensure that this correlation is applicable to 1,1′-diphosphinoferrocenes, a plot of E_L versus σ_p was constructed for compounds in which both the E_L and σ_p values are known. The slope and intercept obtained for the 1,1′-diphosphinoferrocenes are in excellent agreement with the data for the Fe(C$_5$H$_4$R)$_2$ compounds.[14] From this relationship, the σ_p for any substituent can be estimated from the E$_L$ value using eq 1.[14] The σ_p values for all of the substituents in

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

this study are presented in Table 2, including those estimated using this method. For the asymmetric compounds dppfOS and dppfOSe, the $E°$ value versus the NHE can be estimated by summing the individual E_L values. For dppfOS the $E°$ value is 1.14 V, and the estimate from the E_L values of −PO(Ph)$_2$ and −PS(Ph)$_2$ is 1.12 V. Similarly, the $E°$ value for dppfOSe is 1.11 V and the estimate is 1.04 V.

Table 2. E_L and σ_p Values for Various Phosphine Substituents

substituent	E_L	σ_p
C$_5$H$_4$PPh$_2$	0.45[a]	0.19[c]
C$_5$H$_4$PO(Ph)$_2$	0.55	0.53[c]
C$_5$H$_4$PS(Ph)$_2$	0.57	0.47[c]
C$_5$H$_4$PSe(Ph)$_2$	0.49	0.58[d]
C$_5$H$_4$PPh$_2$BH$_3$	0.57	0.62[d]
C$_5$H$_4$PPh$_2$Me$^+$	0.83	1.18[c]
C$_5$H$_4$P(*i*Pr)$_2$	0.36[b]	0.06[c]
C$_5$H$_4$PO(*i*Pr)$_2$	0.51	0.41[c]
C$_5$H$_4$PS(*i*Pr)$_2$	0.52	0.59[d]
C$_5$H$_4$PSe(*i*Pr)$_2$	0.43	0.55[d]
C$_5$H$_4$P(*i*Pr)$_2$BH$_3$	0.53	0.60[d]
C$_5$H$_4$P(*i*Pr)$_2$CH$_3^+$	0.81	0.72[d]

[a] Reference 3. [b] Reference 6. [c] Reference 19. [d] Calculated using eq 1.

Conclusion

The lone pair of electrons on the phosphorus atoms of dppf and dippf is involved in a side reaction, likely dimerization, following oxidation of the compounds. When the lone pairs of electrons are occupied with oxygen, sulfur or a Lewis acid, the follow-up reaction of the oxidation product can be avoided. However, occupying the lone pair on phosphorus with selenium gives rise to a different follow-up reaction upon oxidation. The decomposition of dppr$^+$ does not appear to involve the lone electron pairs of the phosphorus atoms, as the occupation of the electrons with chalcogenides and Lewis acids does not lead to reversibility of the oxidation. In addition, there is an excellent correlation between the potential at which oxidation occurs for 1,1′-bisphosphinoferrocenes and the Hammett parameters for the phosphine groups.

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