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# X-ray structures and oxidative electrochemistry of phosphine sulfides and phosphine selenides ${}^{\bigstar}$

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## ABSTRACT

A variety of mono- and bisphosphine sulfides and selenides were synthesized and structurally characterized by NMR spectroscopy. In addition, the X-ray crystal structures were determined for eleven of these compounds. The percent buried volume was determined from the X-ray structures and the use of this measurement in estimating the steric bulk in phosphine sulfides and selenides was further developed. The oxidation of the mono- and bisphosphine chalcogenides was examined using cyclic voltammetry in methylene chloride and acetonitrile. The solvent had little effect on the observed trends in the potentials at which oxidation occurred. Both the mono- and bisphosphine chalcogenides display an irreversible oxidative wave. Many of the phosphine selenides also display a follow-up, irreversible reductive wave indicative of the formation of a Se–Se bond upon oxidation. However, the products for the oxidation of the phosphine sulfides occurs is more positive than the analogous phosphine selenides.

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## 1. Introduction

The one electron, iron-centered oxidation of ferrocene has been known for almost as long as ferrocene itself [1]. While many derivatives of ferrocene undergo an iron-centered oxidation, the two electron oxidation of 1,1'-bis(di-*tert*butylphosphine selenide)ferrocene (dtbpfSe<sub>2</sub>) is selenium based and yields a dicationic species in which intramolecular Se–Se bond formation has occurred (Fig. 1) [2]. While the cyclic voltammograms of the oxidation of other 1,1'-bis(phosphine selenide)ferrocene compounds are similar to that of dtbpfSe<sub>2</sub>, similar Se–Se bonded dications have not been isolated [3–6]. The oxidation of the monophosphine Se=PFc<sub>3</sub> also suggests the formation of a Se–Se bonded dimer, but the oxidation product has not been isolated [7]. Oxidation of the analogous phosphine sulfides has also been investigated, but the oxidation appears to be iron-based rather than occurring at the sulfur atoms [2–6].





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<sup>\*</sup> Dedicated to Professor T. Don Tilley whose dedication and enthusiasm as a chemist and mentor has led to significant advancements in the fields of organometallic and materials chemistry and catalysis.

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Fig. 1. Oxidation of dtbpfSe<sub>2</sub>.

The oxidation of phosphine sulfides has received significantly more attention. The reaction of  $S=P(NR_2)_3$  (R = Me or Et) with copper (II) or bromine yields the S–S bonded dications, [(R<sub>2</sub>N)<sub>3</sub>P–S–S–  $P(NR_2)_3]^{2+}$ , which were spectroscopically characterized but not structurally characterized [19–21]. The reaction of copper (II) with the monophosphine sulfide, S=PMe<sub>2</sub>Ph, and the bisphosphine sulfides, S=PMe<sub>2</sub>-Me<sub>2</sub>P=S and S=PPh<sub>2</sub>CH<sub>2</sub>Ph<sub>2</sub>P=S, was examined [21]. A S–S bonded cation was not observed, leading the authors to conclude that the S-S bonded dication would only form if the phosphine had strongly donating dialkylamino-substituents. Similarly, the reaction of copper (II) with the monophosphine sulfide S=PMe<sub>3</sub> results in the reduction of the metal to copper (I) and no S–S bonded product [22]. In addition, the reaction of  $S=PPr_2-Pr_2$ P=S with BiCl<sub>3</sub> yielded a 1:1 adduct, BiCl<sub>3</sub> (S-PPr<sub>2</sub>)<sub>2</sub>, as opposed to giving oxidative S–S bond formation [11]. The reaction of the phosphine sulfides S=PR<sub>3</sub> (R = Me, Et, <sup>i</sup>Pr or Ph) with copper (II) was proposed to yield a dicationic species in which P-P bond formation was implied, but structural or spectroscopic characterization of the dications was not reported [23]. Further studies of this reaction report <sup>1</sup>H NMR data and suggested that the dication products contained a S–S bond, [R<sub>3</sub>P–S–S–PR<sub>3</sub>]<sup>2+</sup>, but the dications were not structurally characterized [24]. Oxidation of S=PPh<sub>3</sub>, either chemically with [NO]<sup>+</sup> or electrochemically, is reported to yield [Ph<sub>3</sub>P-S-S-PPh<sub>3</sub>]<sup>2+</sup> which was characterized by <sup>1</sup>H NMR [25]. Additional electrochemical studies of phosphine sulfides have been performed, but have focused on the reduction of aryl phosphine sulfides [26,27].

To further examine these systems, the oxidative electrochemistry of a variety of mono- and bisphosphine chalcogenides was examined. For the monophosphine chalcogenides, various alkyl and aryl substituted phosphines were investigated (Table 1).

The substituents were also varied for the bisphosphine chalcogenides, as were the groups linking the two phosphorus atoms (Table 2). The oxidative electrochemistry of all of the compounds was examined by cyclic voltammetry, which was performed in methylenechloride and acetonitrile. In the course of preparing the compounds of interest, crystals of eleven compounds suitable for X-ray diffraction were prepared and the structures obtained.

Table 1	l
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Abbreviations for monophosphines (PR<sub>3</sub>).

	1 1 1 1		
R group	Abbreviation	R group	Abbreviation
Methyl	PMe <sub>3</sub>	ethyl	PEt <sub>3</sub>
iso-propyl	P <sup>i</sup> Pr <sub>3</sub>	tert-butyl	P <sup>t</sup> Bu <sub>3</sub>
phenyl	PPh <sub>3</sub>	p-C <sub>6</sub> H <sub>4</sub> F	$P(C_6H_4F)_3$
p-C <sub>6</sub> H <sub>4</sub> Cl	$P(C_6H_4Cl)_3$	1-naphthyl	$P(1-Nap)_3$
Cyclohexyl	PCy <sub>3</sub>		
<sup>i</sup> Bu <sup>i</sup> Bu	<sup>iBu</sup> SB	Me Me	MeSB
N P N Bu		N P W N Me	
N N		N	

Table 2

Abbreviations for b	isphosphines (	(R <sub>2</sub> P(brid	lge)PR <sub>2</sub> ).	•
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R group	Bridge	Abbreviation
Ph	-CH2-	dppm
Ph	-CH <sub>2</sub> CH <sub>2</sub> -	dppe
Me	-CH <sub>2</sub> CH <sub>2</sub> -	dmpe
Ph	(-CH <sub>2</sub> -) <sub>3</sub>	dppp
Ph	$(-CH_2-)_4$	dppb
Ph	(-CH <sub>2</sub> -) <sub>5</sub>	dpppent
Су	-CH <sub>2</sub> CH <sub>2</sub> -	dcpe
1S,4S-PhCHCH <sub>2</sub> CH <sub>2</sub> CHPh	-CH <sub>2</sub> CH <sub>2</sub> -	<sup>Ph</sup> ple
Ph	-CHMe-CHMe-	2,3-dppb
Ph	$\rightarrow$	dppbz
	н	
	ННН	

## 2. Experimental

## 2.1. General procedures

Standard Schlenk and glovebox techniques were employed and all reactions were performed under an atmosphere of argon. Hexanes, methylene chloride  $(CH_2Cl_2)$ , and diethyl ether  $(Et_2O)$  were purified under Ar using a Solv-tek purification system [28]. Toluene, benzene and CDCl3 were dried over molecular sieves and degassed prior to use. Acetontrile (MeCN) was distilled over CaH<sub>2</sub> prior to use. Ferrocene, decamethylferrocene, sulfur, selenium, nitrosonium hexafluorophosphate ([NO][PF<sub>6</sub>]), nitrosonium tetrafluoroborate ([NO][BF<sub>4</sub>]) and all phosphines were purchased from Strem Chemicals, Inc. The tris-4-(bromophenyl)ammoniumyl hexachloroantimonate ([N(p-C<sub>6</sub>H<sub>4</sub>Br][SbCl<sub>6</sub>]) and tetrabutylammonium hexafluorophosphate ([NBu4][PF6]) were purchased from Aldrich; [NBu<sub>4</sub>][PF<sub>6</sub>] was dried in vacuo at 100 °C prior to use. Unless otherwise noted, the sulfides and selenides were prepared according to the literature procedures [29–48]. The synthesis of  $SP(1-Nap)_3$  was a modification of the literature procedure [49]. While SeP(1-Nap)<sub>3</sub> has been reported, no experimental details were provided [50]. <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectra were obtained using a JEOL Eclipse 400 FT-NMR spectrometer. The <sup>1</sup>H spectra were referenced to internal TMS while the <sup>31</sup>P{<sup>1</sup>H} spectra were referenced to an external sample of 85% H<sub>3</sub>PO<sub>4</sub>. Mass spectrometry data was collected on a Fisons Instruments Trio 1000 instrument with the solids probe and electron ionization. Elemental analyses were performed by Quantitative Technologies, Inc.

#### 2.2. Synthesis

#### 2.2.1. SP(1-Nap)<sub>3</sub>

P(1-Nap)<sub>3</sub> (0.5124 g, 1.242 mmol) and sulfur (0.0560 g, 1.748 mmol) were heated at reflux in toluene (30 mL) for 60 h. Upon cooling, the colorless solution was filtered and the solvent was removed *in vacuo*. The resulting white solid was triturated with Et<sub>2</sub>O (3 × 5 mL) to give white SP(1-Nap)<sub>3</sub> (0.2372 g, 43% yield). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$ (ppm) 42.3 (s). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$ (ppm) 8.78 (br s, 3H), 7.95 (dd,  $J_{H-H}$  = 19.6 Hz,  $J_{H-H}$  = 3.25 Hz, 9H), 7.48–7.32 (m, 9H). *Anal.* Calc. for C<sub>30</sub>H<sub>21</sub>PS: C, 81.06%; H, 4.76%. Found: C, 80.95%; H, 4.77%.

#### 2.2.2. SeP(1-Nap)<sub>3</sub>

 $P(1-Nap)_3$  (0.5830 g, 1.413 mmol) and selenium (0.1216 g, 1.540 mmol) were heated at reflux in toluene (30 mL) for 48 h. Upon cooling, the colorless solution was filtered and the solvent was removed *in vacuo*. The resulting white solid was triturated with Et<sub>2</sub>O (3 × 5 mL) to give white SeP(1-Nap)<sub>3</sub> (0.6539 g, 94%)

yield). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$ (ppm) 26.2 (s, <sup>1</sup>*J*<sub>P-Se</sub> = 697 Hz). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$ (ppm) 8.78 (br s, 3H), 7.94 (dd, *J*<sub>H-H</sub> = 20.8 Hz, *J*<sub>H-H</sub> = 3.26 Hz, 9H), 7.47–7.33 (m, 9H). *Anal.* Calc. for C<sub>30</sub>H<sub>21</sub>PSe: C, 73.32; H, 4.31. Found: C, 73.12; H, 4.26%.

## 2.2.3. dmpeSe<sub>2</sub>

dmpe (1.0 g, 6.7 mmol) and selenium (1.1437 g, 14.48 mmol) were dissolved in toluene (20 mL) in a glovebox. The solution was removed from the glovebox and refluxed for 44 h. The solution was filtered and the solvent was removed *in vacuo* to yield a light gray solid. The solid was triturated with Et<sub>2</sub>O (3 × 5 mL) to produce light pink dmpeSe<sub>2</sub> (0.060 g, 2.9%). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$ (ppm) 21.8 (s, <sup>1</sup>*J*<sub>P-Se</sub> = 706 Hz, <sup>3</sup>*J*<sub>P-P</sub> = 60.7 Hz, <sup>4</sup>*J*<sub>P-Se</sub> = 55.5 Hz). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$ (ppm) 2.30 (m, 4H, -CH<sub>2</sub>-), 1.96 (virtual triplet, 12H, -CH<sub>3</sub>). *Anal.* Calc. for C<sub>6</sub>H<sub>16</sub>P<sub>2</sub>Se<sub>2</sub>: C, 23.39; H, 5.24. Found: C, 23.52; H, 5.60%.

## 2.2.4. dcpeS<sub>2</sub>

dcpe (0.4993 g, 1.181 mmol) and sulfur (0.0729 g, 2.27 mmol) were heated at reflux in toluene (30 mL) for 16 h. Upon cooling the colorless solution was filtered, and the solvent was removed *in vacuo*. The resulting solid was triturated with Et<sub>2</sub>O (3 × 5 mL) to give dcpeS<sub>2</sub> as a white solid (0.514 g, 90% yield). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$ (ppm) 62.4 (s). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$ (ppm) 1.84 (m, 44H, -C<sub>6</sub>H<sub>11</sub>) 1.20 (m, 4H, -CH<sub>2</sub>-). *Anal.* Calc. for C<sub>26</sub>H<sub>48</sub>P<sub>2</sub>S<sub>2</sub>: C, 64.16; H, 9.94. Found: C, 64.17; H, 9.98%.

#### 2.2.5. dcpeSe<sub>2</sub>

dcpe (0.6639 g, 1.569 mmol) and selenium (0.2510 g, 3.179 mmol) were heated at reflux in toluene (30 mL) for 16 h. Upon cooling the light yellow solution was filtered, and the solution was dried *in vacuo*. The residue was triturated with Et<sub>2</sub>O (3 × 5 mL) to give dcpeSe<sub>2</sub> as a light orange solid (0.8570 g, 94% yield). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$ (ppm) 57.6 (s, <sup>1</sup>*J*<sub>P-Se</sub> = 714 Hz, <sup>3</sup>*J*<sub>P-P</sub> = 45.0 Hz, <sup>4</sup>*J*<sub>P-Se</sub> = 17.3 Hz). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$ (ppm) 1.85 (m, 44H, -C<sub>6</sub>H<sub>11</sub>), 1.25 (m, 4H, -CH<sub>2</sub>). *Anal.* Calc. for C<sub>26</sub>H<sub>48</sub>P<sub>2</sub>Se<sub>2</sub>: C, 53.79; H, 8.33. Found: C, 54.12; H, 8.43%.

## 2.2.6. PhpleS<sub>2</sub>

<sup>Ph</sup>ple (0.0507 g, 0.100 mmol) and sulfur (0.0062 g, 0.19 mmol) were heated at reflux in toluene (10 mL) for 1.5 h. The solution was filtered and the solvent was removed *in vacuo*. The resulting solid was triturated with Et<sub>2</sub>O ( $3 \times 5$  mL) to give white <sup>Ph</sup>pleS<sub>2</sub> (0.0294 g, 54% yield). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$ (ppm) 71.0 (s). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$ (ppm) 7.34 (m, 8H, –Ph), 7.17 (m, 12H, –Ph), 3.54 (m, 2H, –CH–), 3.24 (m, 2H, –CH–), 2.35 (m, 4H, –CH<sub>2</sub>CH<sub>2</sub>–), 2.15–2.01 (m, 4H, –CH<sub>2</sub>–), 1.63 (m, 2H, –CH<sub>2</sub>–), 0.84 (m, 2H, –CH<sub>2</sub>–). *Anal.* Calc. for C<sub>34</sub>H<sub>36</sub>P<sub>2</sub>S<sub>2</sub>: C, 71.55; H, 6.36. Found: C, 71.91; H, 6.28%.

## 2.2.7. PhpleSe<sub>2</sub>

<sup>Ph</sup>ple (0.0504 g, 0.0995 mmol) and selenium (0.0191 g, 0.241 mmol) were heated at reflux in toluene (10 mL) for 1.5 h. The solution was filtered and the solvent was removed *in vacuo*. The resulting solid was triturated with Et<sub>2</sub>O (3 × 5 mL) to give pink <sup>Ph</sup>pleSe<sub>2</sub> (0.0573 g, 87% yield). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$ (ppm) 63.4 (s, <sup>1</sup>*J*<sub>P-Se</sub> = 737 Hz, <sup>3</sup>*J*<sub>P-P</sub> = 43.3 Hz, <sup>4</sup>*J*<sub>P-Se</sub> = 25.9 Hz). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$ (ppm) 7.36 (m, 8H, -Ph), 7.18 (m, 10H, -Ph), 3.76 (m, 2H, -CH-), 3.40 (m, 2H, -CH-), 2.34 (m, 4H, -CH<sub>2</sub>CH<sub>2</sub>-), 2.11 (m, 4H, -CH<sub>2</sub>-), 1.77 (m, 2H, -CH<sub>2</sub>-), 0.91 (m, 2H, -CH<sub>-</sub> *Anal*. Calc. for C<sub>34</sub>H<sub>36</sub>P<sub>2</sub>Se<sub>2</sub>: C, 61.45; H, 5.46. Found: C, 61.09; H, 5.49%.

## 2.2.8. S<sup>iBu</sup>SB

In a glovebox, <sup>iBu</sup>SB (0.50 g, 1.5 mmol) and sulfur (0.0499 g, 1.53 mmol) were dissolved in 20 mL toluene. The solution was removed from the glovebox and heated at reflux under argon for

20 h. After cooling, the dark blue solution was filtered and the solvent was removed *in vacuo*. The resulting orange solid was recrystallized from Et<sub>2</sub>O in the freezer to yield clear, colorless crystals of S<sup>iBu</sup>SB (0.1859 g, 34% yield). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$ (ppm) 80.2 (s). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$ (ppm) 2.97 (br s, 12H, bridging –CH<sub>2</sub>–), 2.80 (d,  $J_{H-H} = 2.23$  Hz, 6H, <sup>i</sup>Bu –CH<sub>2</sub>–), 2.30 (m, 3H, –CH–), 0.94 (d,  $J_{H-H} = 2.67$  Hz, 18H, –CH<sub>3</sub>). *Anal.* Calc. for C<sub>18</sub>H<sub>39</sub>N<sub>4</sub>PS: C, 57.72; H, 10.49. Found: C, 57.74; H, 10.62%.

## 2.2.9. Se<sup>iBu</sup>SB

In a glovebox, <sup>iBu</sup>SB (0.50 g, 1.5 mmol) and selenium (0.1154 g, 1.46 mmol) were dissolved in 20 mL toluene. The solution was removed from the glovebox and heated at reflux under argon for 20 h. After cooling, the yellow solution was filtered and the solvent was removed *in vacuo*. The solid was washed with Et<sub>2</sub>O (2 mL) to yield a light pink solid. The solid was recrystallized through slow evaporation at room temperature of the solvent, CH<sub>2</sub>Cl<sub>2</sub>, to yield clear colorless crystals of S<sup>iBu</sup>SB (0.0427 g, 7.7% yield). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$ (ppm) 78.2 (s, <sup>1</sup>J<sub>P-Se</sub> = 770 Hz). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$ (ppm) 2.97 (br s, 12H, bridging –CH<sub>2</sub>–), 2.80 (d, J<sub>H-H</sub> = 2.09 Hz, 6H, <sup>i</sup>Bu –CH<sub>2</sub>–), 2.30 (m, 3H, –CH–), 0.96 (d, J<sub>H-H</sub> = 2.67 Hz, 18H, –CH<sub>3</sub>). *Anal.* Calc. for C<sub>18</sub>H<sub>39</sub>N<sub>4</sub>PSe: C, 51.30; H, 9.33. Found: C, 51.32; H, 9.50%.

#### 2.2.10. 2,3-dppbS<sub>2</sub>

2,3-dppb (0.1248 g, 0.2926 mmol) and sulfur (0.0218 g, 0.680 mmol) were stirred in toluene (10 mL) for 48 h. The solution was filtered and the solvent was removed *in vacuo*. The resulting solid was rinsed with Et<sub>2</sub>O (2 × 5 mL). The solid was recrystallized twice from minimal CH<sub>2</sub>Cl<sub>2</sub> and Et<sub>2</sub>O yielding clear, colorless crystals (0.0360 g, 25% yield). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$ (ppm) 80.2. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$ (ppm) 7.77 (m, 12H, –Ph), 7.45 (m, 8H, –Ph), 3.45 (m, 2H, –CH–), 1.27 (m, 6H, –CH<sub>3</sub>). *Anal.* Calc. for C<sub>28</sub>H<sub>28</sub>P<sub>2</sub>S<sub>2</sub>: C, 68.55; H, 5.75. Found: C, 68.20; H, 5.91%.

#### 2.2.11. 2,3-dppbSe<sub>2</sub>

2,3-dppb (0.1269 g, 0.2976 mmol) and selenium (0.0476 g, 0.603 mmol) were stirred in toluene (10 mL) for 24 h. The solution was filtered and the solvent was removed *in vacuo*. The resulting solid was rinsed with Et<sub>2</sub>O (3 × 5 mL). The solid was recrystallized from minimal CH<sub>2</sub>Cl<sub>2</sub> and Et<sub>2</sub>O, filtered, and rinsed with Et<sub>2</sub>O (2 × 5 mL). The solid was dried *in vacuo* to give an initial crop of product as a white solid (0.0076 g, 4.4% yield). A second crop of product was obtained as clear, colorless crystals from the supernatant through slow evaporation of CH<sub>2</sub>Cl<sub>2</sub> (0.0292 g, 17% yield) for a 21% total yield. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$ (ppm) 48.7 (s, <sup>1</sup>J<sub>P-Se</sub> = 735 Hz, <sup>3</sup>J<sub>P-P</sub> = 62.4 Hz, <sup>4</sup>J<sub>P-Se</sub> = 59.4). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$ (ppm) 7.82 (m, 12H, -Ph), 7.45 (m, 8H, -Ph), 3.69 (m, 2H, -CH–) 1.22 (m, 6H, -CH<sub>3</sub>). *Anal.* Calc. for C<sub>28</sub>H<sub>28</sub>P<sub>2</sub>Se<sub>2</sub>: C, 57.55; H, 4.83. Found: C, 57.92; H, 4.65%.

#### 2.3. X-ray crystallography

Crystals of dppbS<sub>2</sub>, dpppentS<sub>2</sub>, dpppSe<sub>2</sub>, dppbZe<sub>2</sub>, Se<sup>Me</sup>SB, S<sup>iBu</sup>SB and Se<sup>iBu</sup>SB were obtained by vapor diffusion of Et<sub>2</sub>O into a solution of the corresponding compound in CH<sub>2</sub>Cl<sub>2</sub> (Table 3). Crystals of 2,3-dppbS<sub>2</sub> and 2,3-dppbSe<sub>2</sub> were obtained by slow evaporation of an Et<sub>2</sub>O solution of the compound (Table 3). X-ray diffraction data were collected on a Bruker-AXS Kappa APEX II CCD diffractometer with 0.71073 Å Mo K $\alpha$  radiation. All of the samples were mounted onto a glass fiber using Loctite Super Glue, and data were collected at the reported temperatures. Cell parameters were found using APEX II software and refined using saINT+ on all observed reflections [51,52]. Unit cell parameters were obtained from 60 data frames, 0.5°  $\phi$ , from three different sections of the Ewald sphere. Each data set was treated with sADABS absorption

#### Table 3

Crystal data and structure refinement for X-ray structures.

	Se <sup>Me</sup> SB	S <sup>iBu</sup> SB	S <sup>iBu</sup> SB	Phospholanose <sub>2</sub>	2,3-dppbS <sub>2</sub>	2,3-dppbSe <sub>2</sub> . ½ Et <sub>2</sub> O
Formula	C <sub>9</sub> H <sub>21</sub> N <sub>4</sub> PSe	C <sub>18</sub> H <sub>39</sub> N <sub>4</sub> PS	C <sub>18</sub> H <sub>39</sub> N <sub>4</sub> PSe	C34H36P2Se2	$C_{28}H_{28}P_2S_2$	C <sub>30</sub> H <sub>33</sub> O <sub>0.5</sub> P <sub>2</sub> Se <sub>2</sub>
Formula weight	295.23	374.56	421.46	664.49	490.56	621.42
Crystal system	monoclinic	orthorhombic	orthorhombic	orthorhombic	monoclinic	orthorhombic
Space Group	P21/c	<i>P</i> bca	Pbca	$P2_{1}2_{1}2_{1}$	P21	P212121
a (Å)	13.7323(11)	10.3069(5)	10.3220(6)	8.0824(8)	10.7257(7)	9.3190(5)
b (Å)	14.1386(12)	16.5396(8)	16.5892(10)	15.0997(15)	17.2911(11)	10.0626(6)
<i>c</i> (Å)	13.7645(11)	25.0452(13)	25.2080(14)	26.090(3)	13.6721(9)	61.061(4)
α (Å)	90	90	90	90	90	90
β (Å)	111.0600(10)	90	90	90	92.1220(10)	90
γ (Å)	90	90	90	90	90	90
V (Å <sup>3</sup> )	2493.9(4)	4269.5(4)	4316.5(4)	3184.1(5)	2533.9(3))	5725.9(6)
Ζ	2	8	8	4	4	8
D <sub>calc</sub>	1.573	1.165	1.297	1.386	1.286	1.442
Crystal size	$0.21\times0.15\times0.08$	$0.32 \times 0.22 \times 0.17$	$0.48 \times 0.22 \times 0.17$	$0.53 \times 0.10 \times 0.10$	$0.32 \times 0.25 \times 0.11$	$0.19 \times 0.12 \times 0.04$
Crystal color	colorless	colorless	colorless	colorless	colorless	colorless
T (K)	100(2)	100(2)	100(2)	296(2)	100(2)	100(2)
Radiation; λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Absorption coefficient	3.116	0.235	1.822	2.444	0.351	2.714
F(000)	1216	1648	1792	1352	1032	2520
$\theta$ Range (°)	1.59-28.59	1.63-24.71	1.62-28.87	1.56-28.66	1.49-28.82	2.00-28.89
Data collected						
h	-18 to 18	-12 to 12	-14 to 13	-10 to 10	-13 to 13	-12 to 11
k	-18 to 19	-19 to 19	-21 to 21	-19 to 19	-23 to 22	-13 to 13
1	-18 to 18	-29 to 29	-33 to 33	-34 to 33	-18 to 18	-77 to 77
Absorption correction	SADABS	SADABS	SADABS	SADABS	SADABS	SADABS
Final R indices	0.0324	0.0359	0.0294	0.0353	0.0442	0.0480
$R_1$	0.0552	0.0473	0.0498	0.0720	0.0625	0.0789
$wR_2$	0.0665	0.0887	0.0729	0.0615	0.0937	0.0679
Goodness-of-fit (GOF)	1.003	1.040	1.029	1.008	1.051	0.984

corrections based on redundant multiscan data [53]. The structure was solved by direct methods and refined by least-squares methods on  $F^2$  using the SHELXTL program package [54]. All hydrogen atoms were treated as idealized contributions. Except as noted, all non-hydrogen atoms were refined with anisotropic displacement parameters.

## 2.4. Electrochemistry

Cyclic voltammetry (CV) experiments were performed under an Ar atmosphere at room temperature  $(22 \pm 1 \circ C)$ . An analyte concentration of 1.0 mM in 10.0 ml of either CH<sub>2</sub>Cl<sub>2</sub> or MeCN was used in the experiments. The solutions were also 0.1 M in [NBu<sub>4</sub>][PF<sub>6</sub>] as the supporting electrolyte. Experiments were done with a three electrode system using a 1.5 mm glassy carbon disk working electrode, a platinum wire auxiliary electrode and an Ag/AgCl (nonaqueous) reference electrode separated from the solution by a fine glass frit. Data was collected at scan rates from 100 to 1000 mV/s in 100 mV/s intervals using a CH Instruments Model 620D potentiostat. Ferrocene or decamethylferrocene were added as an internal reference at the end of the experiments to give a solution that was 1.0 mM in the reference [55]. Bulk electrolysis using a Pt basket working electrode was carried out on a 2.5 mM solution of dppmSe<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> with 0.1 M in [NBu<sub>4</sub>][PF<sub>6</sub>] as the supporting electrolyte.

## 2.5. Chemical oxidation

Approximately 0.02 M solutions of Se<sup>Me</sup>SB, SPPh<sub>3</sub>, dpppSe<sub>2</sub>, dpppS<sub>2</sub>, dppmSe<sub>2</sub>, <sup>Ph</sup>pleSe<sub>2</sub>, 2,3-dppbSe<sub>2</sub> and 2,3-dppbS<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> were reacted with stoichiometric amounts of the chemical oxidants [NO][PF<sub>6</sub>], [NO][BF<sub>4</sub>], and [N(C<sub>6</sub>H<sub>4</sub>Br)<sub>3</sub>][SbCl<sub>6</sub>] at room temperature with stirring. The reactions were monitored by <sup>31</sup>P{<sup>1</sup>H} NMR. With the mono- and bisphosphine selenides, a red precipitate appeared immediately upon addition of the chemical oxidant.

## 3. Results and discussion

The phosphine chalcogenides were synthesized by addition of either elemental sulfur or selenium in stoichiometric quantities to the phosphine. The reactions were either stirred at room temperature or heated to reflux depending on the phosphine. The desired products were obtained in good yield and required little purification. The products display an upfield shift in the <sup>31</sup>P NMR signal as compared to the starting phosphines. The <sup>31</sup>P NMR spectra of the phosphine selenides display P–Se coupling. The <sup>1</sup>*J*<sub>P-Se</sub> values are similar to that of Se=PPh<sub>3</sub>, where the first order coupling constant is 730 Hz [56]. The <sup>31</sup>P[<sup>1</sup>H] NMR spectra of 2,3-dppbSe<sub>2</sub> and <sup>Ph</sup>pleSe<sub>2</sub> show all the possible isotopomers which allow assignment of the <sup>1</sup>*J*<sub>P-Se</sub>, <sup>3</sup>*J*<sub>P-P</sub> and <sup>4</sup>*J*<sub>P-Se</sub> coupling constants.

In the course of preparing these compounds, crystal structures of Se<sup>Me</sup>SB (Fig. 2), S<sup>iBu</sup>SB (Fig. 3), Se<sup>iBu</sup>SB (Fig. 4) were obtained through single crystal X-ray diffraction. The structure of S<sup>Me</sup>SB has been reported [57]. The structural parameters of Se<sup>Me</sup>SB are



Fig. 2. Structure of Se<sup>Me</sup>SB: structure is one of two crystallographically independent molecules in the unit cell.



Fig. 3. Structure of S<sup>iBu</sup>SB.



**Table 4**Structural data for SSB and SeSB.

	S <sup>Me</sup> SB	Se <sup>Me</sup> SB	S <sup>iBu</sup> SB	Se <sup>iBu</sup> SB
Avg. P–E (Å)	1.957ª	2.119	1.957	2.118
Avg. P–N <sub>eq</sub> (Å)	1.651 <sup>a</sup>	1.652	1.662	1.662
Avg. P–N <sub>ax</sub> (Å)	3.214 <sup>b</sup>	3.224	3.322	3.299
N <sub>ax</sub> planarity <sup>c</sup>	0.092 <sup>a</sup>	0.092	0.157	0.144

<sup>a</sup> Ref. [57].

<sup>b</sup> The P–Nax distance is typically cited as 3.250 Å [57,58] however, this value is the distance in one of the two crystallographically independent molecules in the unit cell. The value listed here is the average of the two crystallographically independent molecules.

 $^{\rm c}$  The distance the  $N_{\rm ax}$  is above the plane (closer to P) defined by the three carbon atoms to which it is bonded.

similar to those of S<sup>Me</sup>SB (Table 4). The reported P–N<sub>ax</sub> distance in S<sup>Me</sup>SB has been suggested to be evidence of a weak P–N<sub>ax</sub> interaction [57], however calculations suggest that there is not a significant amount of P–N<sub>ax</sub> bonding in this molecule [58]. Despite the previous suggestion of a limited P–N<sub>ax</sub> interaction in Se<sup>Me</sup>SB using the magnitude of the <sup>1</sup>J<sub>P-Se</sub> coupling constant [59], the similarity of the P–N<sub>ax</sub> distances in S<sup>Me</sup>SB and Se<sup>Me</sup>SB suggests that there is also not a P–N<sub>ax</sub> interaction in Se<sup>Me</sup>SB. The phosphorus-chalcogen bond

lengths in S<sup>iBu</sup>SB and Se<sup>iBu</sup>SB are the same as those found in the methyl analogues. The P–N<sub>eq</sub> lengths are slightly longer while the P–N<sub>ax</sub> lengths are substantially longer, which further suggests that like the methyl analogues, there is not a P–N<sub>ax</sub> interaction in S<sup>iBu</sup>SB or Se<sup>iBu</sup>SB.

The structures of  $dppbS_2$  (Supporting information Fig. 1),  $dpppentS_2$  (Supporting information Fig. 2),  $dpppSe_2$  (Supporting



Fig. 5. Structure of PhpleSe<sub>2</sub>.



Fig. 6. Structure of 2,3-dppbS<sub>2</sub>: structure is one of two crystallographically independent molecules in the unit cell.



Fig. 7. Structure of 2,3-dppbSe<sub>2</sub>: structure is one of two crystallographically independent molecules in the unit cell.

Table 5	
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Bisphosphine	S	References	Se	References
dppm	1.944 <sup>a</sup>	[60]	2.103	[61]
dppe	1.943	[62]	2.106	[63]
dppp			2.109 <sup>a</sup>	
dppb	1.953(1)		2.106	[64]
dpppent	1.950 <sup>a</sup>			
dmpe			2.118(1)	
dppbz			2.111 <sup>a</sup>	
2,3-dppb	1.9552 <sup>a</sup>		2.1093 <sup>a</sup>	
PhpleSe <sub>2</sub>			2.0998 <sup>a</sup>	

<sup>a</sup> Average value.

information Fig. 3), dppbzSe<sub>2</sub> (Supporting information Fig. 4), dmpeSe<sub>2</sub> (Supporting information Fig. 5), <sup>Ph</sup>pleSe<sub>2</sub> (Fig. 5), 2,3-dppbS<sub>2</sub> (Fig. 6), and 2,3-dppbSe<sub>2</sub> (Fig. 7) were also determined. Structures of several closely related bisphosphine chalcogenides have also been reported. Of particular interest are the phosphorus-chalcogen bond lengths for these related compounds (Table 5). The P=Se bond lengths are similar for the compounds linked by  $(-CH_2-)_n$ 

#### Table 6

	Calculated %V <sub>bur</sub> val	lues for phosph	ine sulfides and p	hosphine selenides. <sup>a</sup>
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(n = 1-4) groups and having phenyl substituents on the phosphorus atoms. However, the P=Se bonds are slightly longer in the cases where the phosphorus substituents are changed to methyl (dmpeSe<sub>2</sub>) or the backbone is changed to an aromatic ring (dppbzSe<sub>2</sub>).

The percent buried volume (%V<sub>bur</sub>) calculation [65] has been used as a measure of the steric bulk of phosphines in a variety of compounds [66]. Of particular interest to this study is the %V<sub>bur</sub> of phosphine sulfides and phosphine selenides. Previous %V<sub>bur</sub> calculations on phosphine sulfides and phosphine selenides focused on 1,1'-bis(phosphino)ferrocene derivatives [4]. In addition to the structures reported in this work, the %V<sub>bur</sub> was calculated for several other phosphine sulfides and phosphine selenides (Table 6). As seen with [PR<sub>3</sub>AuCl] complexes [66], there is a reasonable correlation between the  $V_{bur}$  of the phosphine sulfides and phosphine selenides with the Tolman cone angle of the free phosphine (Fig. 8). The limited data, in particular for the phosphine sulfides. prevents additional analysis. As was noted for the [PR<sub>3</sub>AuCl] complexes, the P(OPh)<sub>3</sub> does not appear to fit the trend and is therefore shown, but not included in the calculation [66]. There is a good correlation between the %V<sub>bur</sub> for the phosphine sulfides and the %V<sub>bur</sub>

$W_{bur}$ Refs. $W_{bur}$ Refs.           PMe3,         118         27.7         67         6.2         68           PE43,         132         -b         69         -b         70           PM73,         160         37.6         71.1         35.1(0.3) <sup>c</sup> 72           PBu3,         182         43.2         73         41.3         74           PCy3,         70         69.9         75         35.20.2) <sup>c</sup> 78           P(roto)3,         194         -b         88.8         79           P(m-to)3,         145         50.02) <sup>c</sup> 77         33.20.1) <sup>c</sup> 78           P(p-cyLef,F),         44.8         81         33.20.1) <sup>c</sup> 88         81           P(p-cyLef,F),         44.8         84         43.3         81         81           P(2-6-C <sub>6</sub> H <sub>3</sub> (OMe) <sub>2</sub> ) <sub>3</sub> 128         35.20(2) <sup>c</sup> 57         33.8(0.8) <sup>c</sup> His work           P(NMe2) <sub>3</sub> 32         24.23         81         80         4.7         88           M*Sg         33.0.1         52         57         33.8(0.8) <sup>c</sup> His work           Mp001         128 <th>Phosphine</th> <th>Cone angle</th> <th>-Sulfide-</th> <th></th> <th>-Selenide-</th> <th></th>	Phosphine	Cone angle	-Sulfide-		-Selenide-	
PMe311827.767]26.2(88)Ptr3132-b69]-b70135.10.3°721PBr316037.67135.10.3°721P1PBu318243.273141.3741PCy317036.9075135.20761Ph31455.00.2)°77133.20.2)°781P(n-tol)3194-b79138.8791P(m-tol)3145-b80130.0821P(p-tol)3145-b81133.0821P(p-tol)3145-b81133.0851P(26-C <sub>6</sub> H <sub>4</sub> F)312838.186136.0861P(Neb_3)312838.186136.0861P(Neb_3)312836.687133.80.85165P(OPh3)12836.16040.761mm363.3(0.1)*33.083161163ampm433.3(1.0)*33.3(1.0)*81163163ampm433.3(1.1)*12.4(2.9)*9040.5(2.6)*191dppe-3.3(0.1)*8335.1163163ampm4*-5.5This work33.4(1.0)*163dppb25.5This work31.1192dppb25.5This work32.0.5this workdppb1-3.4(1.1)*This work32.0.5*this			%V <sub>bur</sub>	Refs.	%V <sub>bur</sub>	Refs.
PErs       132 $-b$ [69] $-b$ [70]         P'Pr3       160       37.6       [71]       35.1(0.3)°       [72]         P'Bus       182       43.2       [73]       41.3       [74]         PCy3       170       36.9       [75]       35.2       [76]         Phy3       145       35.0(0.2)°       [77]       33.2(0.2)°       [78]         P(artol)3       194 $-b$ [80] $-b$ [80]         P(p-tol)3       145       34.2       [37]       33.2(0.1)°       [83]         P(p-tol)3       145       34.2       [37]       33.2(0.1)°       [83]         P(p-tol)4 $-b$ [80] $-b$ [81]       33.2(0.1)°       [83]         P(p-tol,4(Mbe)3)       128       81.1       [84]       34.1       33.2(0.1)°       [83]         P(26-CaH4(OMe)3)       128       81.1       [85]       85.5       [87]       33.8(0.8)°       this work         MSB       35.2       55.5       [60]       40.7       [61]         Mapp       33.1       [92]       33.1       [92]         dppb	PMe <sub>3</sub>	118	27.7	[67]	26.2	[68]
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	PEt <sub>3</sub>	132	_b	[69]	_b	[70]
$P^B B u_3$ 18243.27341.374 $P C y_3$ 17036.97535.276 $P (y_3)$ 14535.0(c.2)°7733.2(0.2)°78 $P (o-tol)_3$ 194-b7938.879 $P (p-tol)_3$ 194-b80-b80 $P (p-tol)_3$ 145-b80-b80 $P (p-tol)_3$ 145-b8133.0.082 $P (p-tol)_3$ 145-b8133.0.082 $P (p-tol)_3$ 12838.18636.086 $P (2-c_4H_4\Gamma)_3$ 12881.18636.086 $P (NMe_2)_3$ 12838.18636.086 $P (NMe_2)_3$ 12833.18644.788 $P (DPh)_3$ 12833.0.1°5733.8(0.8)°this work $i h v S B$ 33.3(0.1)°89116363 $q p p m^4$ 33.3(1.1°1816236.(1.0)°163 $d p p e^1$ 33.3(1.1°1816236.(1.0)°163 $d p p e^1$ 35.5This work35.564 $d p p P$ 55.5This work35.20.5°1818 $q p p P$ 35.5This work35.664 $2,3 - d p D$ 40.1(0.2)°This work37.3(1.6)°18 $q p p P$ 40.1(0.2)°This work37.3(0.5)°this work $q p p P$ 40.63h00.0000000000000000000000000000000000	P <sup>i</sup> Pr <sub>3</sub>	160	37.6	[71]	35.1(0.3) <sup>∈</sup>	[72]
$PCy_3^{-}$ 170       36.9       75       35.2       76 $Ph_3$ 145       35.0(2.) <sup>c</sup> 77       33.2(0.2) <sup>c</sup> 78 $P(\alpha-tol)_3$ 194 $-^b$ 79       38.8       79 $P(n-tol)_3$ 194 $-^b$ 79       38.8       79 $P(n-tol)_3$ 145 $-^b$ 80 $-^b$ 80 $P(p-c_4l_F)_3$ 145 $-^b$ 81       33.0       82 $P(p-c_4l_F)_3$ 34.2       37       33.2(0.1) <sup>c</sup> 83 $P(2,c-c_4l_5(OMe)_2)_3$ 44.8       84       43.3       85 $P(OHb_3)$ 128       38.1       86       37.0       47.7       88 $N^{S}S$ 35.2(0.2) <sup>c</sup> 57       33.8(0.8) <sup>c</sup> this work $dppm$ 42.6       160       47.7       18       18 $M^{S}S$ 33.0.1) <sup>c</sup> 89       110       160       100       100       100       100 $dppm^{0}$ 42.4(2.9) <sup>c</sup> 190       40.5(0.0 <sup>c</sup> ) <sup>c</sup> 91       33.6(1.0 <sup>c</sup> ) <sup>c</sup> 101 $dpppe^{thylene^{t}}$ 33.3(0.1) <sup></sup>	P <sup>t</sup> Bu <sub>3</sub>	182	43.2	[73]	41.3	[74]
PPh3       145       35.0(0.2)°       [77]       33.2(0.2)°       [78]         P(o-tol)3       194       -b       [79]       38.8       [79]         P(m-tol)3       -b       80]       -b       [80]       -b       [80]       -b       [80]       -b       [80]       -b       [81]       33.0       [82]         P(p-tol)3       145       -b       [81]       33.0       [82]       [83]       [85]       [81]       [81]       [81]       [81]       [81]       [81]       [85]       [81]       [81]       [85]       [81]       [85]       [81]       [85]       [82]       [83]       [85]       [81]       [85]       [86]	PCy <sub>3</sub>	170	36.9	[75]	35.2	[76]
$P(o-tol)_3$ 194 $-b$ [79]       38.8       [79] $P(m-tol)_5$ $-b$ 80] $-b$ 80] $-b$ 80] $P(p-tol)_3$ 145 $-b$ 81]       33.0       82] $P(p-C_6H_4F)_3$ 34.2       37]       33.2(0.1) <sup>c</sup> 83] $P(2-C_6H_4F)_3$ 44.8       84]       43.3       85] $P(O-b)_3$ 128       38.1       86]       36.0       86] $P(NMe_2)_3$ 128       38.1       86]       34.7       88] $P(NMe_2)_3$ 128       35.2(0.2) <sup>c</sup> 57]       33.8(0.8) <sup>c</sup> this work $m^{eSB}$ 35.2(0.2) <sup>c</sup> [57]       33.8(0.8) <sup>c</sup> this work         dppm       42.5       [60]       40.7       [61]         dmpm <sup>d</sup> 33.3(0.1) <sup>c</sup> 89]       [61]       [62]       36(1.0) <sup>c</sup> [63]         dppe       33.3(0.1) <sup>c</sup> 89]       33.3(1.1) <sup>c</sup> [63]       [64]       [64]       [64]         dppb       2.5       Isovark       33.3(1.1) <sup>c</sup> [64]       [64]       [64]       [64]       [64]       [64] <td< td=""><td>PPh<sub>3</sub></td><td>145</td><td>35.0(0.2)<sup>c</sup></td><td>[77]</td><td>33.2(0.2)<sup>c</sup></td><td>[78]</td></td<>	PPh <sub>3</sub>	145	35.0(0.2) <sup>c</sup>	[77]	33.2(0.2) <sup>c</sup>	[78]
$P(m-toi)_3$ $-b$ $80$ $-b$ $80$ $-b$ $80$ $P(p-t_{c}H_{r})_{3}$ $145$ $-b$ $81$ $33.0$ $82$ $P(p-t_{c}H_{r})_{3}$ $34.2$ $37$ $33.2(0.1)^{c}$ $83$ $P(2,6-t_{c}H_{3}(OMe)_{2})_{3}$ $44.8$ $84$ $43.3$ $85$ $P(OPh_{3}$ $128$ $81.1$ $86$ $36.0$ $86$ $P(NMe_{2})_{3}$ $128$ $81.1$ $86$ $36.0$ $86$ $P(NMe_{2})_{3}$ $128$ $38.1.2$ $57$ $33.8(0.8)^{c'}$ this work $m^{e}SB$ $52_{2}(0.2)^{c'}$ $57$ $33.8(0.8)^{c'}$ this work         dppm $42.6$ $44.6$ this work $42.6$ this work         dppm $33_{3}(0.1)^{c'}$ $89$ $-10^{c'}$ $33.6(1.0)^{c'}$ $63$ dmpm <sup>d</sup> $32.4(2.9)^{c'}$ $90$ $40.5(2.6)^{c'}$ $91$ $92$ $93.11.6^{c'}$ $163$ dppb2 $-10^{c'}$ $35.5$ This work $33.5(1.1)^{c'}$ this work $qppb$ $-10^{c'}$	$P(o-tol)_3$	194	_b	[79]	38.8	[79]
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$P(m-tol)_3$		_b	[80]	_b	[80]
$P[p-C_6H_4F)_3$ $34.2$ $[37]$ $33.2(0.1)^c$ $[83]$ $P(2.6-C_6H_5(OMe)_2)_3$ $44.8$ $[84]$ $43.3$ $[85]$ $P(OPb_3$ $128$ $38.1$ $[86]$ $36.0$ $[86]$ $P(NMe_2)_3$ $36.6$ $[87]$ $34.7$ $[88]$ $M^eSB$ $35.2(0.2)^c$ $[57]$ $33.8(0.8)^c$ this work $dppm$ $42.6$ this work $42.6$ this work $dppm$ $42.5$ $[60]$ $40.7$ $[91]$ $dmpm^d$ $33.3(0.1)^c$ $[89]$ $(11)^c$ $[63]$ $dmpe^c$ $36.1$ $[62]$ $33.6(1.0)^c$ $[63]$ $dppb$ $36.1$ $[62]$ $33.6(1.0)^c$ $[63]$ $dppbe$ $36.1$ $[62]$ $33.6(1.0)^c$ $[63]$ $dppb$ $35.5$ $[90]$ $40.5(2.6)^c$ $[91]$ $dppbh$ $35.5$ $[83]$ $33.(1.1)^c$ this work $31.1$ $[92]$ $43.3(1.1)^c$ $[83]$ $33.(1.0)^c$ $[83]$ $dppbh$ $35.5$ <td><math>P(p-tol)_3</math></td> <td>145</td> <td>_b</td> <td>[81]</td> <td>33.0</td> <td>[82]</td>	$P(p-tol)_3$	145	_b	[81]	33.0	[82]
$P(2,6-c_{6}H_{3}(OMe)_{2})_{3}$ 128       38.1       [84]       43.3       [85] $P(OPh)_{3}$ 128       38.1       [86]       36.0       [86] $P(Ne_{2})_{3}$ 36.6       [87]       34.7       [88] $MeSB$ 35.2(0.2) <sup>c</sup> [57]       33.8(0.8) <sup>c</sup> this work $dppm$ 44.6       this work       42.6       this work $dppm$ 42.5       [60]       40.7       [61] $dmpm^{d}$ 33.3(0.1) <sup>c</sup> [89]       100       [63] $dmpe$ 42.4(2.9) <sup>c</sup> [90]       40.5(2.6) <sup>c</sup> [91] $dppe$ 36.1       [62]       33.6(1.0) <sup>c</sup> [63] $dmpe$ 2.8.4       this work       43.3(1.1) <sup>c</sup> this work $dppbt$ 55.5       This work       33.5       [64] $2,3$ -dppb       40.1(0.2) <sup>c</sup> This work       33.5.       [64] $2,3$ -dppb       40.5       3 <sup>h</sup> 37.3       3 <sup>h</sup> $dppeff$ 40.6       10.20 <sup>c</sup> 10.60 <sup>c</sup> 3 <sup>h</sup>	$P(p-C_6H_4F)_3$		34.2	[37]	33.2(0.1) <sup>∈</sup>	[83]
P(OPh)_3       128       38.1       [86]       36.0       [87]         P(NPh_2)_3       36.6       [87]       34.7       [88]         MeSB       35.2(0.2) <sup>c</sup> [57]       33.8(0.8) <sup>c</sup> this work         iBuSB       44.6       this work       42.6       this work       42.6       this work         dppm       42.5       [60]       40.7       [61]         dmpm <sup>d</sup> 33.3(0.1) <sup>c</sup> [89]       11         dmapma <sup>e</sup> 42.4(2.9) <sup>c</sup> [90]       40.5(2.6) <sup>c</sup> [91]         dppe       36.1       [62]       33.6(1.0) <sup>c</sup> [63]         dppe       36.1       [62]       33.6(1.0) <sup>c</sup> [92]         dppe       36.1       [62]       33.6(1.0) <sup>c</sup> [93]         dppe       35.5       Is work       33.1       [92]         dppb       35.5       This work       33.5       [64]         2,3-dppb       40.1(0.2) <sup>c</sup> This work       33.5       [64]         2,3-dppb       40.4(1.4) <sup>c</sup> This work       37.3(0.5) <sup>c</sup> this work         dppf <sup>e</sup> 40.6       3 <sup>h</sup> 37.3       3 <sup>h</sup> dippf <sup>f</sup> 40.6 <td><math>P(2,6-C_6H_3(OMe)_2)_3</math></td> <td></td> <td>44.8</td> <td>[84]</td> <td>43.3</td> <td>[85]</td>	$P(2,6-C_6H_3(OMe)_2)_3$		44.8	[84]	43.3	[85]
P(NMe_2)_3 $36.6$ $87$ $34.7$ $88$ MeSB $35.2(0.2)^c$ $57$ $33.8(0.8)^c$ this work         dppm $44.6$ this work $42.6$ this work         dppm $42.5$ $60$ $40.7$ $[61]$ dmpm <sup>d</sup> $33.3(0.1)^c$ $[89]$ $meg$ $42.4(2.9)^c$ $90$ $40.5(2.6)^c$ $91$ dppe $36.1$ $[62]$ $33.6(1.0)^c$ $[63]$ dppe $36.1$ $55.5$ $57.5$ $57.5$ $57.5$ $57.5$ $57.5$ $57.5$ $57.5$	P(OPh) <sub>3</sub>	128	38.1	[86]	36.0	[86]
Mess       35.2(0.2)° $[57]$ 33.8(0.8)°       this work         iBuSB       44.6       this work       42.6       this work         dppm       42.5 $[60]$ 40.7 $[61]$ dmpm <sup>d</sup> 33.3(0.1)° $[89]$ $(1, 2, 2, 2, 2, 2, 2, 2, 2, 2, 2, 2, 2, 2,$	$P(NMe_2)_3$		36.6	[87]	34.7	[88]
$i^{Bu}SB$ 44.6this work42.6this workdppm42.5[60]40.7[61]dmpmd33.3(0.1)c[89]	<sup>Me</sup> SB		35.2(0.2) <sup>c</sup>	[57]	33.8(0.8) <sup>c</sup>	this work
dppm42.5[60]40.7[61]dmpmd33.3(0.1)°[89]-dmapma°42.4(2.9)°[90]40.5(2.6)°[91]dppe36.1[62]33.6(1.0)°[63]dmpe8.4this workdppethylene <sup>f</sup> 33.1[92]dppbz33.3(1.1)°this workPhple33.3(1.1)°this workdppb34.8(2.6)°this workdppb35.5This work35.2[64]2,3-dppb40.1(0.2)°This work37.2(0.5)°this workdpppent40.53h37.33hdippff40.53h30.3(0.2)°3hdippff41.43h40.63hdippffdippffdippffdippffdippffdippffdippffdippff <td><sup>iBu</sup>SB</td> <td></td> <td>44.6</td> <td>this work</td> <td>42.6</td> <td>this work</td>	<sup>iBu</sup> SB		44.6	this work	42.6	this work
dmpmd $33.3(0.1)^c$ $89$ dmapmac $42.4(2.9)^c$ $90$ $40.5(2.6)^c$ $91$ dppe $36.1$ $62$ $3.6(1.0)^c$ $63$ dmpe $28.4$ $33.1$ $92$ dpptlylenef $33.1$ $92$ dppb $35.5$ $37.3(1.6)^c$ this workdppb $35.5$ This work $37.2(0.5)^c$ this workdppb $40.1(0.2)^c$ This work $37.3(3.1)^c$ $64$ $2,3$ -dppb $40.1(0.2)^c$ This work $37.3(0.5)^c$ this workdppff $40.5$ $3^h$ $37.3$ $3^h$ dippff $40.5$ $3^h$ $30.2(0.2)^c$ $3^h$	dppm		42.5	[60]	40.7	[61]
dmapma <sup>e</sup> $42.4(2.9)^{c}$ $[90]$ $40.5(2.6)^{c}$ $[91]$ dppe $36.1$ $[62]$ $3.6(1.0)^{c}$ $[63]$ dmpe $28.4$ this workdppethylene <sup>f</sup> $33.1$ $[92]$ dppbz $43.3(1.1)^{c}$ this work <sup>ph</sup> ple $37.3(1.6)^{c}$ this workdppp $35.5$ This work $33.5$ $[64]$ 2,3-dppb $40.1(0.2)^{c}$ This work $37.2(0.5)^{c}$ this workdppfs $40.5$ $3^{h}$ $37.3$ $3^{h}$ dippff $40.6$ $3^{h}$ $30.6(2.5)^{c}$ $3^{h}$	dmpm <sup>d</sup>		33.3(0.1) <sup>c</sup>	[89]		
dppe $36.1$ $[62]$ $3.6(1.0)^c$ $[63]$ dmpe $28.4$ this workdppthylene <sup>f</sup> $33.1$ $[92]$ dpbz $43.3(1.1)^c$ this work $^{Ph}ple$ $7.3(1.6)^c$ this workdppp $5.5$ This work $3.5.5$ $2,3-dppb$ $40.1(0.2)^c$ This work $3.5.5$ $dppfs^f$ $40.5$ $3^h$ $37.3(2.5)^c$ this work $dppfs^f$ $40.5$ $3^h$ $37.3$ $3^h$ $dipff^f$ $40.62(2)^c$ $3^h$ $30.2(0.2)^c$ $3^h$	dmapma <sup>e</sup>		42.4(2.9) <sup>c</sup>	[90]	40.5(2.6) <sup>c</sup>	[91]
dmpe       28.4       this work         dppethylene <sup>f</sup> 33.1       [92]         dppbz       43.3(1.1) <sup>c</sup> this work         p <sup>h</sup> ple       37.3(1.6) <sup>c</sup> this work         dppp       35.5       This work       33.5         dppb       35.5       This work       35.2         dppb       35.4       40.1(0.2) <sup>c</sup> This work         dpppent       34.4(1.4) <sup>c</sup> This work       this work         dppf <sup>§</sup> 40.5       3 <sup>h</sup> 37.3       3 <sup>h</sup> dippf <sup>§</sup> 40.6       3 <sup>h</sup> 40.6       3 <sup>h</sup>	dppe		36.1	[62]	33.6(1.0) <sup>c</sup>	[63]
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	dmpe				28.4	this work
dppbz $43.3(1.1)^c$ this work         phple $37.3(1.6)^c$ this work         dppp $35.5$ This work $34.8(2.6)^c$ this work         dppb $35.5$ This work $33.5$ [64]         2,3-dppb $40.1(0.2)^c$ This work $37.2(0.5)^c$ this work         dpppent $40.5$ $3^h$ $37.3$ $3^h$ dippff $40.6$ $3^h$ $40.6$ $3^h$	dppethylene <sup>f</sup>				33.1	[92]
phple       37.3(1.6) <sup>c</sup> this work         dppp       34.8(2.6) <sup>c</sup> this work         dppb       35.5       This work       33.5       [64]         2,3-dppb       40.1(0.2) <sup>c</sup> This work       37.2(0.5) <sup>c</sup> this work         dpppent       34.4(1.4) <sup>c</sup> This work       37.3       3 <sup>h</sup> dppf <sup>g</sup> 40.5       3 <sup>h</sup> 37.3       3 <sup>h</sup> dippf <sup>g</sup> 41.4       3 <sup>h</sup> 40.6       3 <sup>h</sup>	dppbz				43.3(1.1) <sup>c</sup>	this work
dpp $34.8(2.6)^c$ this workdppb $35.5$ This work $33.5$ [64]2,3-dppb $40.1(0.2)^c$ This work $37.2(0.5)^c$ this workdpppent $34.4(1.4)^c$ This work $This work$ $This work$ dppf <sup>6</sup> $40.5$ $3^h$ $37.3$ $3^h$ dippf <sup>6</sup> $41.4$ $3^h$ $40.6$ $3^h$	<sup>Ph</sup> ple				37.3(1.6) <sup>c</sup>	this work
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2,3-dppb40.1(0.2)^cThis work $37.2(0.5)^c$ this workdpppent $34.4(1.4)^c$ This work $40.5$ $3^h$ $37.3$ $3^h$ dppf <sup>6</sup> $40.5$ $3^h$ $37.3$ $3^h$ $3^h$ dippf <sup>6</sup> $41.4$ $3^h$ $40.6$ $3^h$	dppb		35.5	This work	33.5	[64]
dpppent $34.4(1.4)^{c}$ This work       dppf <sup>g</sup> $40.5$ $3^{h}$ $37.3$ $3^{h}$ dippf <sup>f</sup> $41.4$ $3^{h}$ $40.6$ $3^{h}$ dippf <sup>f</sup> $42.4(2.2)^{c}$ $2^{h}$ $2^{h}$ $3^{h}$	2,3-dppb		40.1(0.2) <sup>c</sup>	This work	37.2(0.5) <sup>c</sup>	this work
dppf <sup>g</sup> 40.5         3 <sup>h</sup> 37.3         3 <sup>h</sup> dippf <sup>f</sup> 41.4         3 <sup>h</sup> 40.6         3 <sup>h</sup> dipf <sup>f</sup> 42.4         3 <sup>h</sup> 20.2         3 <sup>h</sup>	dpppent		34.4(1.4) <sup>c</sup>	This work		
$dippf^i$ 41.4 3 <sup>h</sup> 40.6 3 <sup>h</sup>	dppf <sup>g</sup>		40.5	3 <sup>h</sup>	37.3	3 <sup>h</sup>
	dippf <sup>i</sup>		41.4	3 <sup>h</sup>	40.6	3 <sup>h</sup>
$42.4(0.2)^{-2}$ 3" $39.2(0.2)^{-2}$ 3"	dcpf <sup>i</sup>		42.4(0.2) <sup>c</sup>	3 <sup>h</sup>	39.2(0.2) <sup>c</sup>	3 <sup>h</sup>
dmap <sup>fk</sup> 40.7 3 <sup>h</sup> 38.7 3 <sup>h</sup>	dmapf <sup>k</sup>		40.7	3 <sup>h</sup>	38.7	3 <sup>h</sup>
deapf <sup>4</sup> 43.7 3 <sup>h</sup> 41.9 3 <sup>h</sup>	deapf		43.7	3 <sup>h</sup>	41.9	3 <sup>h</sup>
<sup>s</sup> EtFT <sup>m</sup> 38.0 3 <sup>h</sup> 36.0 3 <sup>h</sup>	<sup>s</sup> EtFT <sup>m</sup>		38.0	3 <sup>h</sup>	36.0	3 <sup>h</sup>

 $^{a}$  Unless otherwise noted, references refer to the original structure; the %V<sub>bur</sub> values were calculated in this report.

<sup>b</sup> Although the structure has been published, it does not have an R-factor less than 7% [66].

<sup>c</sup> Values in parentheses are average deviations from the mean due to either crystallographically independent molecules in the unit cell or differences between the two phosphorus atoms in a bisphosphine.

<sup>d</sup> 1,1-Bis(dimethylphosphino)methane.

- <sup>e</sup> 1,1-Bis(dimethylaminophosphino)methyl amine.
- <sup>f</sup> 1,2-Bis(diphenylphosphino)ethylene.
- <sup>g</sup> 1,1'-Bis(diphenylphosphino)ferrocene.
- $^{\rm h}\,$  Reference to the calculated %V  $_{\rm bur}$
- <sup>i</sup> 1,1'-Bis(diiso-propylphosphino)ferrocene.
- <sup>j</sup> 1,1'-Bis(dicyclohexylphosphino)ferrocene.
- <sup>k</sup> 1,1'-Bis(di(dimethylamino)phosphino)ferrocene.
- <sup>1</sup> 1,1'-Bis(di(diethylamino)phosphino)ferrocene.
- <sup>m</sup> 1,1'-Bis((2S, 4S)-2,4-diethylphosphetanyl)ferrocene.



**Fig. 8.** Plot of cone angle vs.  $V_{bur}$  for phosphine sulfides (—, slope = 4.262, y-intercept = 1.238,  $R^2$  = 0.9279) and phosphine selenides (—, slope = 5.027, y-intercept = -15.027,  $R^2$  = 0.8841). The points for SP(OPh)<sub>3</sub> (•) and SeP(OPh)<sub>3</sub> (•) are shown but not included in the line.



**Fig. 9.** Plot of  $%V_{bur}$  for phosphine selenides vs.  $%V_{bur}$  for phosphine sulfides (slope = 1.008, y-intercept = 1.641,  $R^2$  = 0.9796).

for the phosphine selenides (Fig. 9). The slope indicates that the bulk of the R groups have a consistent effect on these compounds.

The oxidative electrochemistry of monophosphine sulfide and selenides was studied using cyclic voltammetry (Table 7). All of the trialkylphosphine sulfides and selenides show an irreversible oxidation wave at potentials positive of FcH<sup>0/+</sup> which can be attributed to oxidation at the chalcogen. The wave is irreversible at all of the scan rates employed in this study. In general, the oxidation occurs at more positive potentials for the phosphine sulfides, suggesting that the selenium is more electron rich than the corresponding sulfur in these systems. This supports the proposed bonding interactions in phosphine sulfides and phosphine selenides in which the lone pairs of the chalcogen are more delocalized in the case of the phosphine sulfides [93], the calculated dipole moments are higher for the phosphine selenides [94,95] and the P=E bond order is higher for the phosphine sulfides [96,97]. In addition, the nature of the phosphorous-chalcogen bonding in dppmS<sub>2</sub> and dppmSe<sub>2</sub> has been studied by examining the <sup>1</sup>H NMR shift of the methylene protons [98]. The NMR data supports a higher positive charge on the phosphorus atoms in dppmSe<sub>2</sub> compared to dppmS<sub>2</sub>, so the selenide is more anionic and oxidized at lower potentials.

In addition to the nature of the P=E (E = S or Se) bond, the solvent and the substituents on phosphorus impact the oxidative electrochemistry. Cyclic voltammetry experiments were conducted in two solvents with vastly different polarities,  $CH_2Cl_2$  ( $\varepsilon = 8.9$ ) and MeCN ( $\varepsilon = 36$ ). The differences in the conductivity of [NBu<sub>4</sub>][PF<sub>6</sub>] solutions of these solvents have been noted and can lead to significant ohmic errors [99]. In general, the phosphine selenides undergo oxidation at a more positive potential in  $CH_2Cl_2$  than in MeCN. There is no trend in the data for the phosphine sulfides. In addition, oxidation of the compounds with alkyl substituents generally occur at less positive potentials than that of the aryl compounds.

The trialkylphosphine selenides studied display a follow-up reductive feature (Fig. 10). Based on the oxidation of

1,1'-bis(di-*tert*butylphosphine selenide)ferrocene [2], this suggests that oxidation results in the formation of a dicationic dimer with a Se–Se bond. Also, a separation of 1.02 V is seen in the cyclic voltammogram of SPPh<sub>3</sub>, where the cyclic voltammetry oxidation product is supported by the results of the oxidation of SPPh<sub>3</sub> with  $[NO][BF_4]$  to form  $[Ph_3P-S-S-PPh_3]^{2+}$  [25]. The separation of the oxidative and reductive features is approximately 0.90 V in CH<sub>2</sub>Cl<sub>2</sub> for the trialkylphosphine selenides studied and triphenylphosphine selenide, supporting a structural change that occurs as a result of the oxidation of selenium. The trialkylphosphine sulfides displayed only the oxidation wave. The tri(1-naphthyl)phosphine selenide displayed the follow-up reduction only in MeCN and the halogenated triarylphosphine sulfides and selenides displayed only the oxidation wave. Attempts at isolating the oxidation products were made using chemical and bulk electrochemical oxidation. For both the phosphine sulfides and phosphine selenides the reaction mixtures gave complex <sup>31</sup>P{<sup>1</sup>H} NMR spectra indicative of multiple products. This indicates that if a dimer is formed, it is not stable at times longer than the cyclic voltammetry time scale. In addition, the chemical and bulk oxidation of the phosphine selenides also gave a red precipitate which was confirmed to be Se<sub>8</sub> by mass spectrometry. This indicates that the oxidation product undergoes cleavage of the P-Se bonds and additional reactions then occur at the phosphorus atom.

Table 7	
Electrochemical potentials $(M)$ for monophosphing sulfides an	d col

Electrochemical potentials (V) for monophosphine sulfides and se	elenides
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Compound	Methyle	ne chloride	Acetoni	Acetonitrile			
	Epox	Epred	$E_p^{ox1}$	Epox2	Epred		
S=PMe <sub>3</sub>	0.76		0.70				
Se=PMe <sub>3</sub>	0.55	-0.35	0.73		-0.67		
S=PEt <sub>3</sub>	0.74		0.68				
Se=PEt <sub>3</sub>	0.84	-0.10	0.68		-0.21		
S=P <sup>i</sup> Pr <sub>3</sub>	1.05		1.26				
Se=P <sup>i</sup> Pr <sub>3</sub>	0.80	-0.15	0.78		-0.10		
S=P <sup>t</sup> Bu <sub>3</sub>	1.10		1.13				
Se=P <sup>t</sup> Bu <sub>3</sub>	0.68	-0.13	0.73		-0.25		
S=PCy <sub>3</sub>	1.15		1.16				
Se=PCy <sub>3</sub>	0.76	-0.27	0.74		-0.13		
S <sup>Me</sup> SB	0.60		0.51				
Se <sup>Me</sup> SB	0.34	-0.55	0.32		-0.95		
S <sup>iBu</sup> SB	0.57		0.49				
Se <sup>iBu</sup> SB	0.42	-1.41	0.42				
$S = P(C_6H_4CI)_3$	1.30		1.54				
$Se = P(C_6H_4Cl)_3$	1.19		0.32				
$S = P(C_6H_4F)_3$	1.43		1.50				
$Se = P(C_6H_4F)_3$	1.17		1.08				
S=PPh <sub>3</sub>	1.43		1.13				
Se=PPh <sub>3</sub>	0.73	0.04	0.73		-0.10		
S=P(1-Nap) <sub>3</sub>	1.13		1.19				
Se=P(1-Nap) <sub>3</sub>	0.99		0.65	0.99	-0.17		



Fig. 10. Cyclic voltammogram for the oxidation of  $1.0 \text{ mM SePEt}_3$  in CH<sub>2</sub>Cl<sub>2</sub>/0.1 M [NBu<sub>4</sub>][PF<sub>6</sub>] at a glassy carbon electrode and a scan rate of 100 mV/s.

The oxidative electrochemistry of bisphosphine sulfides and bisphosphine selenides was also studied (Table 8). The effect of the chalcogen on the potential at which oxidation of the bisphosphine chalcogenides occurs is similar to that seen in the monophosphine chalcogenides; the sulfides are oxidized at more positive potentials than the selenide analogues. Unlike the monophosphine chalcogenides, there is no noticeable trend in the potentials at which oxidation occurs in CH<sub>2</sub>Cl<sub>2</sub> vs. MeCN for the bisphosphine chalcogenides. The effect of the substituents on phosphorus on the redox properties were examined by studying bis(phosphino)ethane selenides, with phenyl, cyclohexyl, and methyl substituents. The chemically irreversible oxidation and reduction features were present at similar potentials. The analogous dppe and dmpe sulfides show only an irreversible oxidation. In dppeSe<sub>2</sub>, a second oxidation at a more positive potential is seen when the cyclic voltammetry is studied in MeCN. The bisphosphine selenides dcpeSe<sub>2</sub>, 2,3-dppbSe<sub>2</sub> and <sup>Ph</sup>pleSe<sub>2</sub> show an irreversible oxidation and follow-up reduction, as anticipated. Interestingly, the analogous sulfides also show a follow-up reduction in MeCN. No significant changes in these patterns were observed by changing the scan rate.

Table 8

Electrochemical	potentials	(V)	for	bisphosphine	sulfides	and	selenides.
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Methylene chloride		Acetonitrile		
Epox	Epred	E <sub>p</sub> <sup>ox1</sup>	Epox2	Epred
0.72		0.75		
0.28	-0.38	0.29		-0.27
1.02		0.90		
0.44	-0.27	0.49	0.72	-0.72
0.84		0.74		
0.45	-0.18	0.46		-0.19
0.94		0.96		
0.54	-0.16	0.51	0.59	-0.98
0.97		0.95		
0.51	-0.03	0.53	0.62	-0.95
0.99		0.98		
0.97		0.60		-0.16
0.87		0.86		-0.22
0.51	-0.21	0.38		-0.14
0.45		0.38		
0.05		0.04	0.71	
0.98		1.08		-0.33
0.61	-0.09	0.57		-0.01
1.27		1.04		-0.19
0.65	-0.01	0.69		0.03
	Methyler           Epx           0.72           0.28           1.02           0.44           0.84           0.45           0.94           0.54           0.97           0.51           0.99           0.97           0.51           0.45           0.93           0.961           1.27           0.65	$\begin{tabular}{ c c c } \hline Methylene chloride \\ \hline \hline E_p^{ox} & E_p^{red} \\ \hline 0.72 & & & \\ 0.28 & -0.38 & & \\ 1.02 & & & \\ 0.44 & -0.27 & & \\ 0.84 & & & \\ 0.45 & -0.18 & & \\ 0.94 & & & \\ 0.54 & -0.16 & & \\ 0.97 & & & \\ 0.51 & -0.03 & & \\ 0.99 & & & \\ 0.51 & -0.03 & & \\ 0.97 & & & \\ 0.51 & -0.21 & & \\ 0.45 & & & \\ 0.05 & & & \\ 0.98 & & & \\ 0.61 & -0.09 & & \\ 1.27 & & & \\ 0.65 & -0.01 & \\ \hline \end{tabular}$	$\begin{tabular}{ c c c c } \hline Methylene chloride & Acetoni \\ \hline \hline F_p^{ox} & F_p^{red} & F_p^{ox1} \\ \hline \hline C & C & C & C & C \\ \hline 0.72 & 0.75 & 0.28 & -0.38 & 0.29 \\ \hline 1.02 & 0.90 & 0.90 & 0.90 & 0.90 & 0.90 & 0.94 & 0.96 & 0.74 & 0.46 & 0.94 & 0.96 & 0.51 & 0.94 & 0.96 & 0.51 & -0.18 & 0.65 & 0.51 & -0.03 & 0.53 & 0.99 & 0.98 & 0.97 & 0.60 & 0.87 & 0.60 & 0.87 & 0.60 & 0.87 & 0.68 & 0.51 & -0.21 & 0.38 & 0.45 & 0.38 & 0.05 & 0.04 & 0.98 & 1.08 & 0.61 & -0.09 & 0.57 & 1.27 & 1.04 & 0.65 & -0.01 & 0.69 & 0.60 & 0.69 & 0.60 & 0.69 & 0.60 & 0.69 & 0.60 & 0.69 & 0.60 & 0.69 & 0.60 & 0.69 & 0.60 & 0.69 & 0.60 & 0.69 & 0.60 & 0.69 & 0.60 & 0.69 & 0.60 & $	$\begin{tabular}{ c c c } \hline Methylene chloride & Acetonitrile \\ \hline \hline E_p^{ox} & E_p^{red} & E_p^{ox1} & E_p^{ox2} \\ \hline \hline E_p^{ox} & -0.38 & 0.29 & 0.72 & 0.49 & 0.72 & 0.49 & 0.72 & 0.84 & 0.74 & 0.72 & 0.84 & 0.74 & 0.45 & -0.18 & 0.96 & 0.96 & 0.96 & 0.96 & 0.96 & 0.51 & 0.59 & 0.97 & 0.95 & 0.61 & -0.03 & 0.53 & 0.62 & 0.99 & 0.98 & 0.97 & 0.60 & 0.87 & 0.86 & 0.51 & -0.21 & 0.38 & 0.45 & 0.38 & 0.05 & 0.04 & 0.71 & 0.98 & 1.08 & 0.61 & -0.09 & 0.57 & 1.27 & 1.04 & 0.69 & 0.69 & 0.69 & 0.66 & 0.67 & 0.66 & 0.67 & 0.66 & 0.67 & 0.66 & 0.67 & 0.66 & 0.67 & 0.66 & 0.67 & 0.66 & 0.67 & 0.66 & 0.67 & 0.66 & 0.67 & 0.66 & 0.67 & 0.66 & 0.67 & 0.66 & 0.67 & 0.66 & 0.67 & 0.66 & 0.67 & 0.66 & 0.67 & 0.66 & 0.67 & 0.66 & 0.66 & 0.67 & 0.66 & 0.66 & 0.67 & 0.66 & 0.66 & 0.66 & 0.67 & 0.66 & 0.66 & 0.67 & 0.67 & 0.66 & 0.67 & 0.66 & 0.67 & 0.67 & 0.67 & 0.66 & 0.67 & 0.67 & 0.67 & 0.67 & 0.67 & 0.67 & 0.67 & 0.67 & 0.67 & 0.67 & 0.67 & 0.67 & 0.67 & 0.67 & 0.67 & 0.67 & 0.67 & 0.67 & 0.67 &$



**Fig. 11.** Cyclic voltammogram for the oxidation of 1.0 mM dpppentSe<sub>2</sub> (red) and 1.0 mM dpppSe<sub>2</sub> (blue) in CH<sub>2</sub>Cl<sub>2</sub>/0.1 M [NBu<sub>4</sub>][PF<sub>6</sub>] at a glassy carbon electrode and a scan rate of 100 mV/s. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The effect of the length of the bridging group,  $(-CH_2-)_n (n = 1-5)$  on the oxidative electrochemistry was also examined (Fig. 11). The cyclic voltammogram of dpppentSe<sub>2</sub> displays only an irreversible wave while the cyclic voltammograms of the bis(diphenylphosphine) selenides with shorter bridging groups display a chemically irreversible oxidation with a follow-up reductive feature. The oxidation wave is attributed to selenium, and the presence of the reductive feature supports the formation and subsequent reductive cleavage of an Se–Se bridge. The potential at which oxidation occurs increases as the number of bridging carbons increase. Attempts at isolating the oxidation product from a bulk electrolysis and chemical oxidation were unsuccessful. The oxidative electrochemistry of the analogous sulfides shows only a chemically irreversible oxidation.

## 4. Conclusion

A series of mono- and bisphosphine chalcogenides have been synthesized by the addition of a chalcogen to a phosphine and characterized using NMR spectroscopy. In the course of this study, the structures of eleven compounds were determined using X-ray crystallography. The length of the phosphorus-chalcogen bond is affected by the substituents on the phosphorus atoms. For these compounds, the  $V_{bur}$  is a suitable measurement of steric bulk as indicated by the good correlation between the Tolman cone angle of the free phosphines and %V<sub>bur</sub> of the phosphine sulfides and selenides. Also, a high correlation is seen between the %V<sub>bur</sub> for the phosphine sulfides and the  $V_{bur}$  for the phosphine selenides. The oxidative electrochemistry of these compounds was also examined. In general, the phosphine selenides display an irreversible oxidation and a follow-up reductive wave, which may suggest the formation of a Se-Se bonded cationic species. In attempts to isolate the oxidation products, chemical oxidation of these compounds was examined. The reactions gave multiple products in the <sup>31</sup>P NMR spectrum and precipitated elemental selenium. Therefore, the presence of a ferrocene backbone appears to accomodate oxidative Se-Se bond formation as seen in the oxidation of 1,1'-bis(di-*tert*butylphosphine selenide)ferrocene [2]. The nature of the phosphorus-chalcogen bond interaction, in particular the bond order and the polarity, affects the potential at which oxidation occurs, as the oxidation of the phosphine selenides occurs at potentials more positive than the analogous phosphine sulfides. Cyclic voltammetry of the analogous sulfides displays only an irreversible oxidation, with the exception of 2,3-dppbS<sub>2</sub> which shows a follow-up reduction. However, chemical oxidation of 2,3-dppbS<sub>2</sub> did not yield a single oxidation product. The effect of the solvent on the potential at which oxidation occurs was studied using solvents with drastically different polarity; with the exception of the monophosphine selenides the solvent had little impact on the potential at which oxidation of these compounds occurred.

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## Appendix A. Supplementary material

CCDC 995183–995193 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2014.06.004.

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