

## Electrochemistry of 1,1'-Bis(2,4-dialkylphosphetanyl)ferrocene and 1,1'-Bis(2,5-dialkylphospholanyl)ferrocene Ligands: Free Phosphines, Metal Complexes, and Chalcogenides

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The oxidative electrochemistries of a series of chiral bisphosphinoferrocene ligands, 1,1'-bis(2,4-dialkylphosphetanyl)ferrocene (FerroTANE) and 1,1'-bis(2,5-dialkylphospholanyl)ferrocene (FerroLANE), were examined. The reversibility of the oxidation is sensitive to the steric bulk of the alkyl groups. New transition metal compounds and phosphine chalcogenides of these ligands were prepared and characterized. X-ray crystal structures of 10 of these compounds are reported. The percent buried volume ( $\%V_{\text{bur}}$ ) is a recently developed measurement based on crystallographic data that examines the steric bulk of N-heterocyclic carbene and phosphine ligands. The  $\%V_{\text{bur}}$  for the FerroTANE and FerroLANE structures with methyl or ethyl substituents suggests these ligands are similar in steric properties to 1,1'-bis(diphenylphosphino)ferrocene (dppf). In addition the  $\%V_{\text{bur}}$  has been found to correlate well with the Tolman cone angle for phosphine chalcogenides. The oxidative electrochemistries of the transition metal complexes occur at more positive potentials than the free ligands. While a similar positive shift is seen for the oxidative electrochemistries of the phosphine chalcogenides, the oxidation of the phosphine selenides does not occur at the iron center, but rather oxidation occurs at the selenium atoms.

### Introduction

Although there are many different types of ferrocenylphosphines, the most common are the 1,1'-bidentate phosphines such as 1,1'-bis(diphenylphosphino)ferrocene (dppf). Since

the initial synthesis of dppf<sup>1</sup> the use of 1,1'-bis(phosphino)ferrocene ligands has seen continuous growth.<sup>2</sup> While dppf and its simple derivatives can be very useful in catalytic applications, chiral derivatives are of interest as they can be used as ligands in asymmetric catalysis. One type of chiral ferrocenylphosphines has the phosphorus atoms as part of a ring and chiral carbons adjacent to the phosphorus atoms. In particular, ligands in which the phosphorus is part of a 4-membered ring (1,1'-bis(2,4-dialkylphosphetanyl)ferrocene or FerroTANE) or 5-membered ring (1,1'-bis(2,5-dialkylphospholanyl)ferrocene or FerroLANE) have been examined (Table 1).

Of these two groups of ligands, FerroTANE ligands have received more attention. The majority of studies in which FerroTANE ligands are employed are catalytic asymmetric hydrogenations. The efficacy of FerroTANE ligands in these hydrogenations is somewhat variable; the FerroTANE ligands give catalysts that are either superior,<sup>3</sup> similar,<sup>4</sup>

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Table 1. Structure and Names of FerroTANE and FerroLANE Ligands

	name	<i>n</i>	chirality	R
	<sup>R</sup> EtFT	1	<i>R,R</i>	Et
	<sup>S</sup> EtFT	1	<i>S,S</i>	Et
	<sup>R</sup> MeFL	2	<i>R,R</i>	Me
	<sup>S</sup> MeFL	2	<i>S,S</i>	Me
	<sup>R</sup> EtFL	2	<i>R,R</i>	Et
	<sup>S</sup> EtFL	2	<i>S,S</i>	Et
	<sup>R</sup> <i>i</i> -PrFL	2	<i>R,R</i>	<i>i</i> -Pr
	<sup>S</sup> <i>i</i> -PrFL	2	<i>S,S</i>	<i>i</i> -Pr

or inferior<sup>5</sup> (in terms of % conversion and/or %ee) to catalysts with other bidentate phosphines. Two studies have compared FerroTANE ligands with different R groups and found that the %ee of the product varies with the R group on the FerroTANE ligand, but not in a discernible pattern.<sup>6,7</sup> In addition to the asymmetric hydrogenation catalysis, FerroTANE ligands have been employed in catalysts for ring-opening polymerization,<sup>8</sup> cross-coupling,<sup>9</sup> phosphination,<sup>10</sup> benzylic nucleophilic substitution,<sup>11</sup> annulations,<sup>12</sup> cycloisomerizations,<sup>13</sup> alkylations<sup>14</sup> and arylations.<sup>15</sup>

Relatively few studies have employed FerroLANE ligands. In the rhodium catalyzed asymmetric hydrogenation of methyl acetoacetate, <sup>R</sup>EtFL gave a higher %ee than <sup>S</sup>MeFL which in turn gave a higher %ee than 1,3-bis(diethylphospholano)propane.<sup>16</sup> <sup>S</sup>PhFL was superior to the methyl, ethyl and *iso*-propyl analogues in terms of reaction times, conversion and %ee in the rhodium catalyzed asymmetric hydrogenation of  $\alpha$ -C-substituted cinnamic acid salts.<sup>17</sup> Finally, <sup>S</sup>PhFL was found to be the poorest (in terms of conversion and %ee) phospholane ligand for the rhodium catalyzed hydroformylation of styrene, allyl cyanide, and vinyl acetate because of the larger bite angle of <sup>S</sup>PhFL as compared to the other ligands examined.<sup>18</sup>

Comparisons of FerroTANE and FerroLANE ligands in catalytic systems have been limited. A series of FerroLANE (<sup>R</sup>MeFL, <sup>R</sup>EtFL and <sup>S</sup>*i*-PrFL) and FerroTANE (<sup>R</sup>MeFT,

<sup>R</sup>EtFT, <sup>S</sup>*i*-PrFT and <sup>S</sup>*t*-BuFT) ligands was screened for the rhodium catalyzed asymmetric hydrogenation of 2-methylenesuccinamic acid.<sup>19</sup> For a given R group the %ee was higher for the FerroTANE ligands. In the oxidative addition of phenyl iodide to [(diphos)Pd(*trans*-stilbene)], the reaction was very fast when the diphos ligand was <sup>S</sup>MeFL or <sup>S</sup>EtFT.<sup>20</sup> <sup>R</sup>*i*-PrFL, <sup>R</sup>*t*-BuFT and <sup>R</sup>MeFT were among the poorest ligands examined in terms of %conversion and %ee for the rhodium catalyzed asymmetric hydroformylation of styrene, allyl cyanide and vinyl acetate.<sup>21</sup> In rhodium catalyzed asymmetric hydrogenations, the results with FerroTANE and FerroLANE ligands were generally good in terms of % ee.<sup>22</sup> Finally, in a palladium catalyzed asymmetric phosphination <sup>S</sup>MeFL was a slightly better ligand than <sup>S</sup>EtFT, although both ligands were poor in terms of %ee.<sup>23</sup>

Previous studies in this laboratory have focused on the electrochemistry and reactivity of 1,1'-bis(phosphino)ferrocenes<sup>24</sup> and chiral phosphinoferrocenes.<sup>25</sup> In this study we combine those two interests and examine the oxidative electrochemistry of a FerroTANE and FerroLANE ligands. In addition to the free ligands, [MCl<sub>2</sub>(P<sup>R</sup>P)] (M = Pd or Pt) complexes were prepared. The anodic electrochemistry of the palladium and platinum compounds as well as two commercially available [Rh(1,5-cyclooctadiene)(P<sup>R</sup>P)][BF<sub>4</sub>] compounds was examined. Finally, the phosphine sulfides and phosphine selenides of the FerroTANE and FerroLANE ligands were synthesized, and the oxidative electrochemistry was studied.

## Experimental Section

**General Procedures.** All reactions were carried out using standard Schlenk techniques under an atmosphere of argon. The compounds (-)-1,1-bis((2*S*,4*S*)-2,4-diethylphosphotano)ferrocene (<sup>S</sup>EtFT), <sup>R</sup>EtFT and [Rh(1,5-cyclooctadiene)(<sup>S</sup>EtFT)][BF<sub>4</sub>] were purchased from Strem Chemicals, Inc. and used without further purification. FcH (Fc = ferrocenyl) was purchased from Strem Chemicals, Inc. and sublimed prior to use. The compounds *cis*-bis(acetonitrile)dichloroplatinum(II), bis(acetonitrile)dichlororhodium(II), 1,1'-bis((2*S*,5*S*)-2,5-dimethylphospholano)ferrocene (<sup>S</sup>MeFL), the related FerroLANE ligands (<sup>R</sup>MeFL, <sup>S</sup>EtFL, <sup>R</sup>EtFL, <sup>S</sup>*i*-PrFL and <sup>R</sup>*i*-PrFL), Fc\* (Fc\* = bis(pentamethylcyclopentdienyl)iron) and [Rh(1,5-cyclooctadiene)-(<sup>R</sup>EtFL)][BF<sub>4</sub>] were purchased from Aldrich Chemical Co., Inc.

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**Table 2.** Data for  $[\text{MCl}_2(\text{P}^{\text{O}}\text{P})]$  ( $\text{M} = \text{Pd}$  or  $\text{Pt}$ ) and  $[\text{Rh}(\text{COD})(\text{P}^{\text{O}}\text{P})][\text{BF}_4]$  ( $\text{COD} = 1,5\text{-cyclooctadiene}$ ) Compounds

compound	$^{31}\text{P}$ NMR	$^1J_{\text{P-M}}$	% yield	elemental analysis				color
				calculated		found		
				%C	%H	%C	%H	
$[\text{PdCl}_2(\text{R}^{\text{S}}\text{MeFL})]$	56.6 (s)		56	44.66	5.45	44.45	5.80	red
$[\text{PdCl}_2(\text{S}^{\text{S}}\text{EtFL})]$	52.5 (s)		55	48.21	6.23	48.42	6.30	orange
$[\text{PdCl}_2(\text{R}^{\text{S}}\text{EtFL})]$	52.5 (s)		58	48.21	6.23	48.38	6.08	orange
$[\text{PdCl}_2(\text{S}^{\text{S}}\text{-i-PrFL})]$	44.7 (s)		53	51.20	6.87	51.45	6.64	orange
$[\text{PdCl}_2(\text{R}^{\text{S}}\text{-i-PrFL})]$	44.7 (s)		41	51.20	6.87	51.13	7.07	orange
$[\text{PdCl}_2(\text{R}^{\text{S}}\text{EtFT})]$	57.1 (s)		52	46.52	5.86	46.70	5.58	orange
$[\text{PtCl}_2(\text{S}^{\text{S}}\text{MeFL})]$	31.1 (s)	3700	44	38.84	4.74	38.81	4.42	yellow
$[\text{PtCl}_2(\text{R}^{\text{S}}\text{MeFL})]$	31.1 (s)	3700	46	38.84	4.74	38.90	4.45	yellow
$[\text{PtCl}_2(\text{S}^{\text{S}}\text{EtFL})]$	27.6 (s)	3710	51	42.41	5.48	42.39	5.60	yellow
$[\text{PtCl}_2(\text{R}^{\text{S}}\text{EtFL})]$	27.6 (s)	3700	52	42.41	5.48	42.28	5.18	yellow
$[\text{PtCl}_2(\text{S}^{\text{S}}\text{-i-PrFL})]$	20.6 (s)	3700	57	45.47	6.11	45.24	6.30	yellow-orange
$[\text{PtCl}_2(\text{R}^{\text{S}}\text{-i-PrFL})]$	20.6 (s)	3700	83	45.47	6.11	45.55	6.08	yellow-orange
$[\text{PtCl}_2(\text{S}^{\text{S}}\text{EtFT})]$	30.4 (s)	3460	55	40.69	5.12	40.30	5.04	yellow
$[\text{PtCl}_2(\text{R}^{\text{S}}\text{EtFT})]$	30.5 (s)	3470	58	40.69	5.12	40.31	4.95	yellow
$[\text{Rh}(\text{COD})(\text{S}^{\text{S}}\text{EtFT})][\text{BF}_4]$	51.4 (d)	145.6						
$[\text{Rh}(\text{COD})(\text{R}^{\text{S}}\text{EtFL})][\text{BF}_4]$	29.9 (d)	145.6						

**Table 3.** Data for  $\text{P}^{\text{O}}\text{PE}_2$  ( $\text{E} = \text{S}$  or  $\text{Se}$ ) Compounds

compound	$^{31}\text{P}$ NMR	$^1J_{\text{P-Se}}$	% yield	elemental analysis				color
				calculated		found		
				%C	%H	%C	%H	
$^{\text{S}}\text{MeFLS}_2$	68.5 (s)		92	55.23	6.74	54.97	7.11	yellow-brown
$^{\text{R}}\text{MeFLS}_2$	68.5 (s)		72	55.23	6.74	55.05	7.11	yellow-brown
$^{\text{S}}\text{EtFLS}_2$	65.8 (s)		73	58.42	7.54	58.16	7.68	yellow-brown
$^{\text{R}}\text{EtFLS}_2$	65.8 (s)		77	58.42	7.54	58.21	7.76	yellow-brown
$^{\text{S}}\text{-i-PrFLS}_2$	62.3 (s)		91	61.01	8.19	60.68	8.50	yellow
$^{\text{R}}\text{-i-PrFLS}_2$	62.3 (s)		92	61.01	8.19	60.93	8.17	yellow
$^{\text{S}}\text{EtFTS}_2$	62.0 (s)		95	56.92	7.17	56.73	7.34	orange
$^{\text{R}}\text{EtFTS}_2$	62.0 (s)		80	56.92	7.17	56.59	7.52	orange
$^{\text{S}}\text{MeFLSe}_2$	57.5 (s)	738	85	46.18	5.64	45.92	5.29	yellow-brown
$^{\text{R}}\text{MeFLSe}_2$	57.5 (s)	735	73	46.18	5.64	45.86	5.66	yellow-brown
$^{\text{S}}\text{EtFLSe}_2$	53.9 (s)	732	83	49.70	6.42	49.92	6.33	yellow-brown
$^{\text{R}}\text{EtFLSe}_2$	53.9 (s)	725	82	49.70	6.42	49.76	6.64	yellow-brown
$^{\text{S}}\text{-i-PrFLSe}_2$	48.5 (s)	728	97	52.65	7.07	52.70	6.91	yellow
$^{\text{R}}\text{-i-PrFLSe}_2$	48.5 (s)	728	98	52.65	7.07	52.49	7.09	yellow
$^{\text{S}}\text{EtFTSe}_2$	51.4 (s)	749	92	48.02	6.05	47.95	6.05	orange
$^{\text{R}}\text{EtFTSe}_2$	51.4 (s)	749	83	48.02	6.05	48.30	5.83	orange

and used without additional purification. The compounds  $[\text{PdCl}_2(\text{S}^{\text{S}}\text{MeFL})]$  and  $[\text{PdCl}_2(\text{S}^{\text{S}}\text{EtFT})]$  were prepared according to the literature procedure.<sup>20</sup> Dichloromethane ( $\text{CH}_2\text{Cl}_2$ ), diethyl ether ( $\text{Et}_2\text{O}$ ) and hexanes were purified under Ar using a Solv-Tek purification system.<sup>26</sup> Chloroform, 1,2-dichloroethane, and di-*iso*-propyl ether were degassed and purged with Ar prior to use. The  $^{31}\text{P}\{^1\text{H}\}$  and  $^1\text{H}$  NMR spectra were recorded using a JEOL Eclipse 400 FT-NMR spectrometer. An external reference of 85%  $\text{H}_3\text{PO}_4$  was used for the  $^{31}\text{P}\{^1\text{H}\}$  spectra, and TMS was used as an internal reference for the  $^1\text{H}$  NMR. Elemental analyses were performed by Quantitative Technologies, Inc. Mass spectrometry was performed using a Trio 1000 Mass Spectrometer.

**Preparation of Palladium and Platinum Complexes.** Approximately 50 mg of the desired phosphine and one molar equivalent of either  $\text{PdCl}_2(\text{CH}_3\text{CN})_2$  or  $\text{PtCl}_2(\text{CH}_3\text{CN})_2$  were dissolved in  $\text{CH}_2\text{Cl}_2$  (20 mL) and stirred for 1 h. The volume of the solvent was then reduced to approximately 5 mL, and hexanes (20 mL) were added. The solution was then placed in the freezer for 20 h. The solution was filtered, and the remaining solid was washed with  $\text{Et}_2\text{O}$  ( $2 \times 5$  mL) and dried to give the product. The color, % yield, elemental analysis, and  $^{31}\text{P}$  NMR data for these

compounds are presented in Table 2.  $^1\text{H}$  NMR data for these compounds are reported in the Supporting Information.

**Preparation of Sulfides and Selenides.** Approximately 50 mg of the desired phosphine and 2 mol equiv of either sulfur or selenium were added to chloroform (10 mL), and the solution refluxed for 2 h. The solution was stirred an additional 2 h at room temperature and was then filtered. The residue was washed with chloroform (5 mL) and then solvent was removed from the solution. The resulting solid was washed with  $\text{Et}_2\text{O}$  ( $2 \times 10$  mL). The solid was recrystallized from a mixture (2:1 v/v) of hexanes and  $\text{CH}_2\text{Cl}_2$ . The resulting solid was collected, washed with  $\text{Et}_2\text{O}$  ( $2 \times 10$  mL), and dried under vacuum. The color, % yield, elemental analysis and  $^{31}\text{P}$  NMR data for these compounds are presented in Table 3.  $^1\text{H}$  NMR data for these compounds are reported in the Supporting Information.

**Electrochemical Procedures.** Cyclic voltammetric and bulk electrolysis experiments were conducted at ambient temperature ( $22 \pm 1$  °C). Cyclic voltammetric experiments were conducted using a PAR Model 263A potentiostat/galvanostat. All scans were performed using 0.1 M tetrabutylammonium hexafluorophosphate ( $[\text{NBu}_4][\text{PF}_6]$ ) as the supporting electrolyte and  $\text{CH}_2\text{Cl}_2$  as the solvent under an argon atmosphere. The concentration of the analyte was 1.0 mM. The working electrode was glassy carbon (1.5 mm disk) which was polished with two diamond pastes, first 1.0  $\mu\text{m}$  and then 0.25  $\mu\text{m}$ , and rinsed with

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Table 4. Crystal Data and Structure Refinement for X-ray Structures

	[PtCl <sub>2</sub> ( <sup>S</sup> MeFL)]	[PtCl <sub>2</sub> ( <sup>R</sup> EtFT)]	[PtCl <sub>2</sub> ( <sup>R</sup> <i>i</i> -PrFL)]	<sup>S</sup> EtFTS <sub>2</sub>	<sup>R</sup> MeFLSe <sub>2</sub>	<sup>S</sup> EtFTSe <sub>2</sub>
formula	C <sub>22</sub> H <sub>32</sub> Cl <sub>2</sub> FeP <sub>2</sub> Pt	C <sub>24</sub> H <sub>36</sub> Cl <sub>2</sub> FeP <sub>2</sub> Pt	C <sub>60</sub> H <sub>96</sub> Cl <sub>4</sub> Fe <sub>2</sub> P <sub>4</sub> Pt <sub>2</sub>	C <sub>12</sub> H <sub>18</sub> Fe <sub>0.5</sub> N <sub>2</sub> PS <sub>2</sub>	C <sub>22</sub> H <sub>32</sub> FeP <sub>2</sub> Se <sub>2</sub>	C <sub>12</sub> H <sub>18</sub> Fe <sub>0.5</sub> N <sub>2</sub> PSe <sub>2</sub>
FW	680.26	708.31	1584.93	253.22	572.19	300.12
crystal system	orthorhombic	orthorhombic	monoclinic	tetragonal	monoclinic	tetragonal
space group	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub>	<i>P</i> 4 <sub>3</sub> 2 <sub>1</sub> 2	<i>P</i> 2 <sub>1</sub>	<i>P</i> 4 <sub>3</sub> 2 <sub>1</sub> 2
<i>a</i> (Å)	10.4455(14)	11.2156(14)	10.6457(15)	7.7105(9)	7.7251(10)	7.8190(3)
<i>b</i> (Å)	13.0522(15)	13.7145(17)	16.942(2)	7.7105(9)	12.5474(16)	7.8190(3)
<i>c</i> (Å)	17.448(2)	16.728(2)	17.134(2)	41.386(5)	12.3730(16)	41.6262(18)
α (deg)	90	90	90	90	90	90
β (deg)	90	90	91.259(4)	90	103.315(4)	90
γ (deg)	90	90	90	90	90	90
<i>V</i> (Å <sup>3</sup> )	2378.8(5)	2573.1(5)	3089.4(7)	2460.5(5)	1167.1(3)	2544.89(18)
<i>Z</i>	4	4	2	8	2	8
<i>D</i> <sub>calc</sub>	1.899	1.828	1.704	1.367	1.628	1.567
crystal size	0.08 × 0.20 × 0.20	0.17 × 0.21 × 0.21	0.15 × 0.12 × 0.07	0.20 × 0.15 × 0.15	0.21 × 0.20 × 0.05	0.17 × 0.16 × 0.10
crystal color	yellow	yellow	yellow	orange	yellow	orange
temperature (K)	140(2)	135(2)	135(2)	135(2)	140(2)	100(2)
absorption coefficient	6.850	6.337	5.288	0.922	3.908	3.588
<i>F</i> (000)	1328	1392	1584	1072	576	1216
θ range (deg)	1.95–33.42	1.92–33.30	1.19–33.26	1.97–33.29	2.34–33.21	1.96–33.17
data collected						
<i>h</i>	–10 to 16	–14 to 17	–13 to 16	–10 to 10	–11 to 11	–12 to 11
<i>k</i>	–10 to 20	–21 to 11	–26 to 26	–11 to 11	–19 to 19	–6 to 11
<i>l</i>	–20 to 26	–21 to 25	–26 to 22	–63 to 63	–18 to 19	–55 to 64
absorption correction	SADABS	SADABS	SADABS	SADABS	SADABS	SADABS
final <i>R</i> indices	0.0256	0.0189	0.0361	0.0298	0.0262	0.0323
<i>R</i> <sub>1</sub>	0.0296	0.0205	0.0447	0.0329	0.0326	0.0442
<i>wR</i> <sub>2</sub>	0.0509	0.0412	0.0682	0.0755	0.0532	0.0667
goodness-of-fit	1.043	1.027	1.013	1.069	1.036	1.022

CH<sub>2</sub>Cl<sub>2</sub> prior to use. The reference electrode was Ag/AgCl which was separated by a fine frit from the solution. The counter electrode was a platinum wire. Fc\* was used as an internal reference for the experiments with the FerroTANE and FerroLANE ligands. FcH (Fc = ferrocenyl) was used as an internal reference for the metal complexes, phosphine sulfides and phosphine selenides. Data was recorded using PowerSuite Software, and background subtraction was performed for all experiments. Scans were performed at rates of 50 mV/s, and from 100 to 1000 mV/s in 100 mV/s increments.

Bulk electrolysis experiments were performed under argon using a CH Instruments Model 630B electrochemical analyzer. The working and auxiliary electrodes were platinum mesh baskets in compartments separated by a fine glass frit. The Ag/AgCl reference electrode was in the same compartment as the working electrode, and was also separated by a fine glass frit. A 1.5 mm glassy carbon electrode was used to obtain cyclic voltammograms before and after the bulk electrolysis experiments. The supporting electrolyte was 0.1 M [NBu<sub>4</sub>][PF<sub>6</sub>], and the solvent was CH<sub>2</sub>Cl<sub>2</sub>. The concentration of the analyte was 5.0 mM.

**Crystal Structures.** Crystals were obtained by vapor diffusion of di-*iso*-propyl ether into a solution of the desired compound in 1,2-dichloroethane at room temperature. Crystals were mounted using NVH immersion oil onto a nylon fiber and cooled to the data collection temperature. Data were collected on a Bruker-AXS Kappa APEX II CCD diffractometer with 0.71073 Å Mo-*K*<sub>α</sub> radiation (Table 4). Unit cell parameters were obtained from 90 data frames, 0.3° Φ, from three different sections of the Ewald sphere. The systematic absences in the diffraction data were consistent with the chiral space groups assigned. The data sets were treated with SADABS absorption corrections based on redundant multiscan data (Sheldrick, G. Bruker-AXS, 2001). The molecules were located on a general position with the following exceptions: [PtCl<sub>2</sub>(<sup>R</sup>*i*-PrFL)] in which the asymmetric unit contained two independent molecules each located on a general position and <sup>S</sup>EtFTS<sub>2</sub> and <sup>S</sup>EtFTSe<sub>2</sub> in which the molecules were located on a special position. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions.

## Results and Discussion

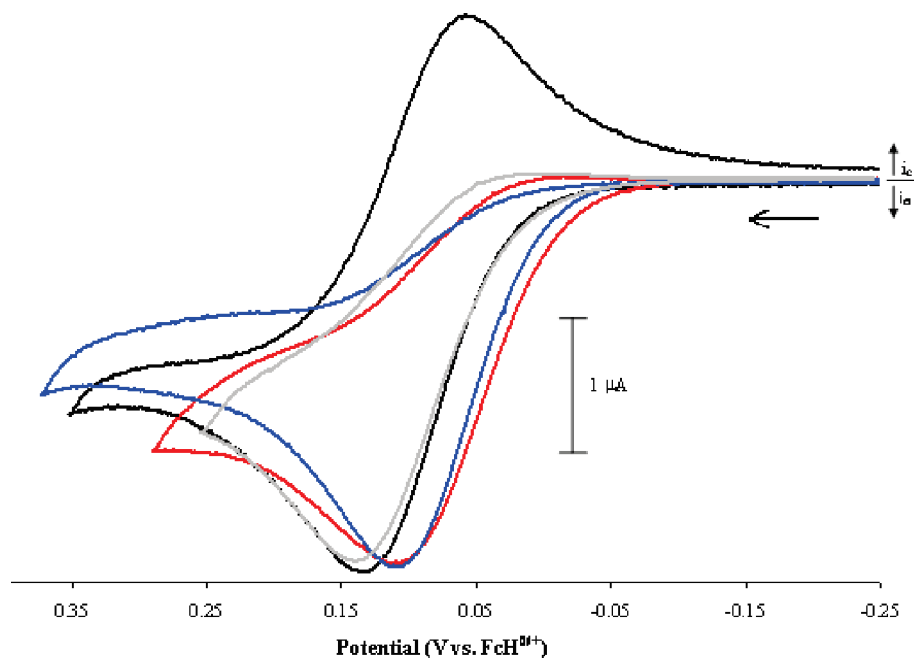
The oxidation of the free FerroTANE and FerroLANE ligands was investigated electrochemically (Figure 1). The potential at which oxidation occurs for all of these ligands is similar to that of the closely related 1,1'-bis(di-*iso*-propylphosphino)ferrocene (dippf) (0.05 V. vs FcH<sup>0/+</sup>)<sup>22b</sup> (Table 5). The redox potentials for the FerroTANE and FerroLANE ligands were not dependent on the ring size (*n* = 1 or 2), the chirality or the R groups. However, in the case of the FerroLANE ligands, the reversibility of the oxidation was influenced by the R groups as only the *i*-PrFL compounds displayed reversible oxidations. Since the potential at which oxidation of these compounds occurs is similar, it would seem that this is not an electronic effect. The steric bulk of the *i*-Pr groups must stabilize the oxidation product at least on the CV time scale. The anodic electrochemistry of the related ligands, 1,1'-bis(di-*ortho*-*iso*-propyl-phenylphosphino)ferrocene,<sup>27</sup> 1,1'-bis(pentafluorophenylphosphino)ferrocene,<sup>27</sup> and 1,1'-bis(di-*tert*-butylphosphino)ferrocene (dtbpf),<sup>24c</sup> is reversible because of the bulk of the groups on phosphorus.

The Lever parameter (*E*<sub>L</sub>) relates electrochemical data to a variety of other parameters. For 1,1'-disubstituted ferrocenes *E*<sub>L</sub>, defined as 1/2 *E*<sup>o</sup> (vs NHE), correlates with the Hammett parameter, σ<sub>p</sub>, of the group at the 1 and 1' positions.<sup>28</sup> Using eq 1 σ<sub>p</sub> can be estimated for the groups of the FerroTANE and FerroLANE ligands (Table 5).

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

(27) Gusev, O. V.; Peterleitner, M. G.; Kal'sin, A. M.; Vologdin, N. V. *Russ. J. Electrochem.* **2003**, *39*, 1293.

(28) (a) Lu, S.; Strelets, V. V.; Ryan, M. F.; Pietro, W. J.; Lever, A. B. P. *Inorg. Chem.* **1996**, *35*, 1013; From this reference, Fc = 0.66 V vs NHE. (b) Lever, A. B. P. In *Comprehensive Coordination Chemistry*, 2nd ed.; McCleverty, J. A., Meyer, T. J., Eds.; Elsevier Science: New York, 2004, Vol. 2, p 251.



**Figure 1.** CVs for the oxidation of 1.0 mM <sup>R</sup>MeFL (blue line), <sup>R</sup>EtFL (red line), <sup>S</sup>*i*-PrFL (black line), and <sup>R</sup>EtFT (gray line) 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.

**Table 5.** Electrochemistry of FerroLANE and FerroTANE Ligands in a 0.1 M [NBu<sub>4</sub>][PF<sub>6</sub>] Solution of CH<sub>2</sub>Cl<sub>2</sub>

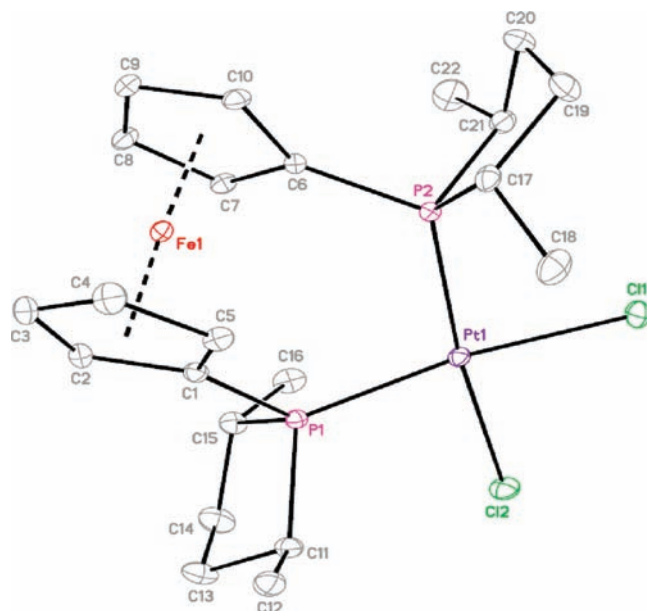
compound	<i>E</i> <sup>o</sup>	<i>i</i> <sub>r</sub> / <i>i</i> <sub>f</sub>	Δ <i>E</i> <sub>p</sub> (mV)	σ <sub>p</sub>
<sup>R</sup> MeFL	0.11			0.05
<sup>S</sup> MeFL	0.11			0.05
<sup>R</sup> EtFL	0.11			0.05
<sup>S</sup> EtFL	0.12			0.06
<sup>R</sup> <i>i</i> -PrFL	0.10	0.96	86	0.03
<sup>S</sup> <i>i</i> -PrFL	0.10	0.96	76	0.04
<sup>R</sup> EtFT	0.14			0.08
<sup>S</sup> EtFT	0.13			0.07

Although most of the ligands display irreversible oxidations, the similarity to the fully reversible *i*-Pr ligands suggests that the estimates are reasonable.

Coordination of FerroTANE and FerroLANE ligands to MCl<sub>2</sub> fragments (M = Pd or Pt) was accomplished in high yield by the reaction of the free phosphine with the appropriate bis(acetonitrile)metal dichloride. The phosphorus signal for the EtFL ligands was upfield of the signal for the EtFT ligands. In addition, the <sup>1</sup>J<sub>P-Pt</sub> coupling constants for the EtFL ligands are approximately 240 Hz greater than the analogous EtFT ligands. However, the <sup>1</sup>J<sub>P-Rh</sub> coupling constants in the [Rh(1,5-cyclooctadiene)(P<sup>R</sup>P)]<sup>+</sup> are identical.

To further examine these compounds the X-ray structures of several of the platinum compounds in this study were determined. For the MeFL (Figure 2) and EtFT (Figure 3) ligands the structures of both the R and S stereoisomers were determined.

While the EtFT are not significantly different, the MeFL structures do display significant, albeit small, differences. In addition, the structure of the <sup>R</sup>*i*-PrFL analogue was also determined (Figure 4). For the FerroLANE ligands the R group does not seem to significantly impact the structural parameters, in particular the P–Pt bond length and the bite angle of the ligand (Table 6). However, the bite angle of the ligand is smaller and the Pt–P bond length is shorter for the FerroTANE ligand

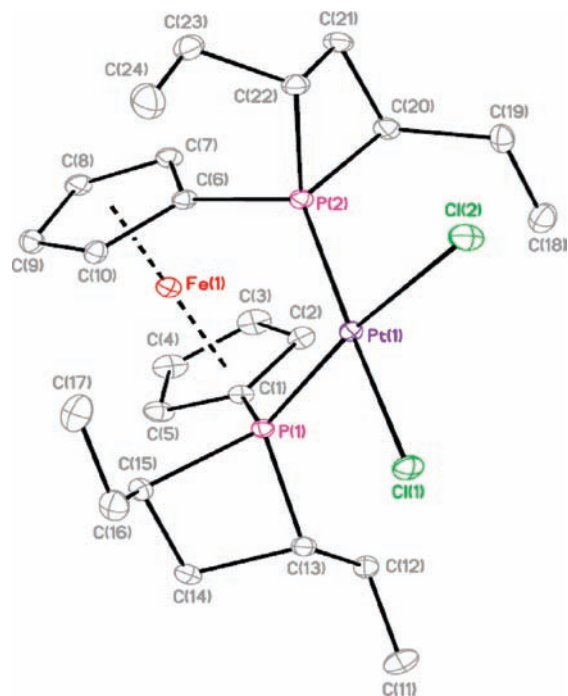


**Figure 2.** Perspective view of [PtCl<sub>2</sub>(<sup>S</sup>MeFL)] with 30% ellipsoids. H atoms are omitted for clarity.

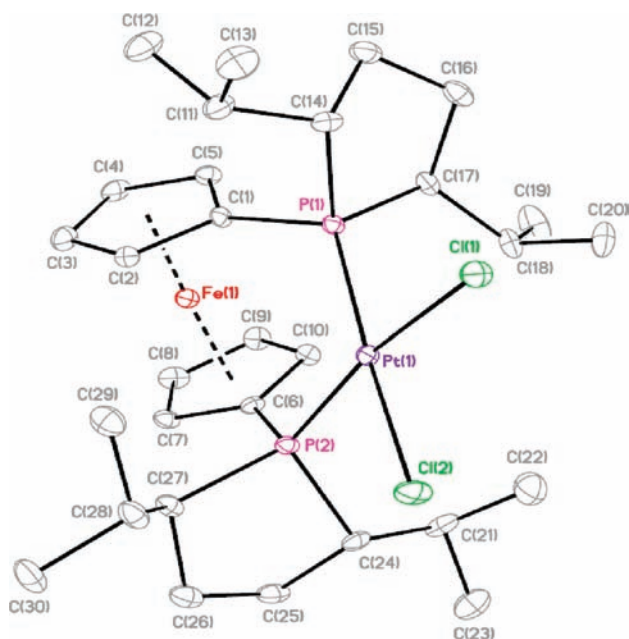
as compared to the FerroTANE ligands. Several studies have seen a correlation<sup>29</sup> between the P–Pt bond length and the <sup>1</sup>J<sub>P-Pt</sub> coupling constant in platinum phosphine compounds while others report no such correlation.<sup>30</sup> In examining the reported [PtCl<sub>2</sub>(bis(phosphino)metallocene)] structures, it is

(29) (a) Mather, G. G.; Pidcock, A.; Rapsey, G. J. N. *J. Chem. Soc., Dalton Trans.* **1973**, 2095. (b) Blau, R. J.; Espenson, J. H. *Inorg. Chem.* **1986**, *25*, 878. (c) Heuer, L.; Jones, P. G.; Schomburg, D.; Schmutzler, R. *Phosphorus, Sulfur Silicon Relat. Elem.* **1990**, *49/50*, 421.

(30) (a) Arnold, D. P.; Bennett, M. A. *Inorg. Chem.* **1984**, *23*, 2117. (b) Manojlović-Muir, L.; Muir, K. W.; Solomon, T. *J. Organomet. Chem.* **1977**, *142*, 265. (c) Hitchcock, P. B.; Jacobson, B.; Pidcock, A. *J. Chem. Soc., Dalton Trans.* **1977**, 2038. (d) Béni, Z.; Ros, R.; Tassan, A.; Scopelliti, R.; Roulet, R. *Inorg. Chim. Acta* **2005**, *358*, 497.



**Figure 3.** Perspective view of  $[\text{PtCl}_2(\text{R}^i\text{-EtFT})]$  with 30% ellipsoids. H atoms are omitted for clarity.



**Figure 4.** Perspective view of  $[\text{PtCl}_2(\text{R}^i\text{-PrFL})]$  with 30% ellipsoids. H atoms are omitted for clarity.

evident that there is no correlation between  $^1J_{\text{P-Pt}}$  coupling constants and P–Pt bond lengths for these compounds.

The structures of the palladium analogues that have been determined exhibit a similar difference between the ligands. The Pd–P distances in  $[\text{PdCl}_2(\text{S}^i\text{MeFL})]$  and  $[\text{PdCl}_2(\text{S}^i\text{EtFT})]$  have been reported, and the P–Pd distances are the same, 2.2734(7) and 2.2726(5) Å, respectively.<sup>20</sup> However, the bite angles for the ligands are quite different, 100.16(2)° for  $[\text{PdCl}_2(\text{S}^i\text{MeFL})]$  and 98.799(17)° for  $[\text{PdCl}_2(\text{S}^i\text{EtFT})]$ . There is not a significant difference between the reported  $[\text{PdCl}_2(\text{S}^i\text{MeFL})]$  structure and that of the enantiomer,  $[\text{PdCl}_2(\text{R}^i\text{MeFL})]$ .

**Table 6.** Select Bond Lengths (Å) and Angles (deg) for  $[\text{PtCl}_2(\text{P}^i\text{P})]$  Compounds

	$[\text{PtCl}_2(\text{S}^i\text{MeFL})]$	$[\text{PtCl}_2(\text{R}^i\text{EtFT})]$	$[\text{PtCl}_2(\text{R}^i\text{-PrFL})]$
P–M (avg.)	2.2469	2.2494	2.2582
M–Cl (avg.)	2.3546	2.3618	2.3579
Fe–C (avg.)	2.030	2.039	2.040
P–M–P	100.66(3)	99.54(2)	100.71 <sup>a</sup>
Cl–M–Cl	86.41(3)	85.44(2)	85.31 <sup>a</sup>
P–M–Cl <sub>centroid</sub> (avg.)	86.64	87.59	86.83
X <sub>A</sub> –Fe–X <sub>B</sub>	176.70	176.80	176.20 <sup>a</sup>
P–Fe–P	62.52	63.14	62.28 <sup>a</sup>
$\tau^b$	44.97	47.87	43.12 <sup>a</sup>
$\theta^c$	7.85	7.56	8.26 <sup>a</sup>
P–P	3.459	3.435	3.478 <sup>a</sup>
$\delta_{\text{P}}$ (avg.) <sup>d</sup>	0.076	0.192	0.066
twist angle <sup>e</sup>	6.34	5.10	2.44 <sup>a</sup>

<sup>a</sup> Average of the two independent molecules in the unit cell. <sup>b</sup> The torsion angle  $\text{C}_A\text{--X}_A\text{--X}_B\text{--C}_B$  where C is the carbon atom bonded to phosphorus and X is the centroid. <sup>c</sup> The dihedral angle between the two  $\text{C}_5$  rings. <sup>d</sup> Deviation of the P atom from the  $\text{C}_5$  plane; a positive value means the P is closer to the Fe. <sup>e</sup> The angle between the plane defined by the Pt and Cl atoms and the plane defined by the Pt and P atoms.

The percent buried volume ( $\%V_{\text{bur}}$ ) has been presented as a method to measure the steric bulk of N-heterocyclic carbene ligands, similar to the Tolman cone angle used for phosphines.<sup>31</sup> Recently, this calculation has been successfully applied to phosphines, mono- and bisphosphine gold chloride complexes and  $[\text{PdCl}_2(\text{P}^i\text{P})]$  compounds.<sup>32</sup> The  $\%V_{\text{bur}}$  values for the structures in this report have been calculated and are reported with other Pd and Pt dichloride complexes with bisphosphinometalocene ligands (Table 7). For a given ligand the  $\%V_{\text{bur}}$  is generally slightly larger for Pt than for Pd. The  $\%V_{\text{bur}}$  for  $\text{R}^i\text{-PrFL}$  is significantly larger than that of  $\text{R}^i\text{MeFL}$  and  $\text{R}^i\text{EtFT}$ . This is in good agreement with the proposed differences in the electrochemistry of the free phosphines. With the exception of the *i*-PrFL ligands, the FerroTANE and FerroLANE ligands have percent buried volumes slightly less than dpfp.

The oxidative electrochemistry of the FerroTANE and FerroLANE ligands simplified upon coordination to Pd, Pt, or Rh. All of the transition metal compounds displayed reversible oxidations regardless of the reversibility of the starting phosphine. Reversibility of the oxidation upon coordination to palladium or platinum has been noted for other 1,1'-bis(phosphino)ferrocene ligands.<sup>24</sup> The potentials at which oxidation occurred were approximately 0.4 V more positive than the free phosphines (Table 8) which has also been observed for related ligands.<sup>24</sup> There is a good correlation between the potential at which oxidation of the free phosphine occurs and the potential at which oxidation of the coordinated phosphine occurs (Figure 5). For comparison, the only other series of bidentate ferrocenyl ligands with two L (neutral,  $2e^-$ ) donor groups studied electrochemically are 1,1'-bis(thio)ferrocene ligands, and they do not display a similar correlation. In addition, a reversible reduction wave was observed for the rhodium complexes at  $-2.15$  V vs  $\text{FcH}^{0/+}$  for  $[\text{Rh}(1,5\text{-cyclooctadiene})(\text{R}^i\text{EtFL})]^+$  and  $-2.22$  V vs  $\text{FcH}^{0/+}$  for  $[\text{Rh}(1,5\text{-cyclooctadiene})(\text{R}^i\text{EtFL})]^+$ .

Reaction of the FerroTANE and FerroLANE ligands with either sulfur or selenium gave the corresponding phosphine chalcogenides in good yields. The phosphine selenides all exhibited <sup>77</sup>Se satellites. In contrast to the aforementioned

(31) (a) Poater, A.; Cosenza, B.; Correa, A.; Giudice, S.; Ragone, F.; Scarano, V.; Cavallo, L. *Eur. J. Inorg. Chem.* **2009**, 1759. (b) <http://www.molnac.unisa.it/OMtools/sambvca.php>.

(32) Clavier, H.; Nolan, S. P. *Chem. Commun.* **2010**, 46, 841.

**Table 7.** Percent Buried Volume (%  $V_{\text{bur}}$ ) for  $[\text{MCl}_2(\text{P}^{\text{O}}\text{P})]$  ( $\text{M} = \text{Pd}$  or  $\text{Pt}$ ;  $\text{P}^{\text{O}}\text{P}$  = Bidentate Phosphine) Complexes

phosphine	[PdCl <sub>2</sub> (dppf)]		[PtCl <sub>2</sub> (P <sup>O</sup> P)]	
	% $V_{\text{bur}}$	ref.	% $V_{\text{bur}}$	ref.
dppf	55.5	32	55.8	33 <sup>a</sup>
dippf	56.5	32	57.0	24b <sup>a</sup>
dppr <sup>b</sup>	54.7	32	55.3	34 <sup>a</sup>
d5Me2furpf <sup>c</sup>	53.7	35 <sup>a</sup>	53.7	36 <sup>a</sup>
<sup>S</sup> MeFL	53.1	32	53.8	This work
<sup>R</sup> MeFL	53.2	This work	53.4	This work
<sup>S</sup> EtFT	54.4	20 <sup>a</sup>	54.9	This work
<sup>R</sup> EtFT			54.9	This work
<sup>R</sup> <i>i</i> -PrFL			61.5	This work
dfmpf <sup>d</sup>			53.1	37 <sup>a</sup>
dfepf <sup>e</sup>			64.3	37 <sup>a</sup>
dmapf <sup>f</sup>			56.9	38 <sup>a</sup>
dppm	47.0	32	48.5	39 <sup>a</sup>
dppe	51.4	32	52.2	40 <sup>a</sup>
dppp	52.2	32	52.8	41 <sup>a</sup>
dppb	53.8	32	53.8	42 <sup>a</sup>
dpppent <sup>g</sup>			56.7	43 <sup>a</sup>
dcpe <sup>h</sup>	53.9	32	53.8	44 <sup>a</sup>
depe <sup>i</sup>			49.7	45 <sup>a</sup>
dtbpe <sup>j</sup>			56.9	46 <sup>a</sup>
(=CHPPH <sub>2</sub> ) <sub>2</sub>	49.3	32	49.1	47 <sup>a</sup>
1,8-dpmn <sup>k</sup>	54.5	32	54.9	48 <sup>a</sup>
TRANSphos <sup>l</sup>	59.8	32	61.2	49 <sup>a</sup>
dppb <sup>m</sup>	54.6	32	54.6	50 <sup>a</sup>
BINAP <sup>n</sup>	55.6	32	55.2	51 <sup>a</sup>
Duphos-Me <sup>o</sup>	48.0	32	48.0	52 <sup>a</sup>

<sup>a</sup> Reference is to the original structure; the %  $V_{\text{bur}}$  was calculated in this work. <sup>b</sup> dppr = 1,1'-bis(diphenylphosphino)ruthenocene. <sup>c</sup> d5Me2furpf = 1,1'-bis(di-2-methyl-5-furylphosphino)ferrocene. <sup>d</sup> dfmpf = 1,1'-bis(ditrifluoromethylphosphino)ferrocene. <sup>e</sup> dfepf = 1,1'-bis(dipentafluoroethylphosphino)ferrocene. <sup>f</sup> dmapf = 1,1'-bis(di(dimethylamino)phosphino)ferrocene. <sup>g</sup> dpppent = 1,5-bis(diphenylphosphino)pentane. <sup>h</sup> dcpe = 1,2-bis(dicyclohexylphosphino)ethane. <sup>i</sup> depe = 1,2-bis(diethylphosphino)ethane. <sup>j</sup> dtbpe = 1,2-bis(di-*tert*-butylphosphino)ethane. <sup>k</sup> 1,8-dpmn = 1,8-bis((diphenylphosphino)methyl)naphthalene. <sup>l</sup> TRANSphos = 2,11-bis((diphenylphosphino)methyl)benzo[*c*]phenanthrene. <sup>m</sup> dppb = 2,2'-bis(diphenylphosphino)biphenyl. <sup>n</sup> BINAP = 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl. <sup>o</sup> Duphos-Me = 1,2-bis(2,5-dimethylphospholano)benzene.

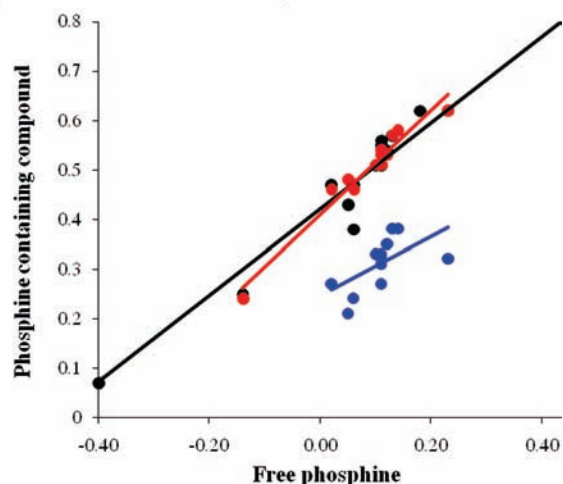
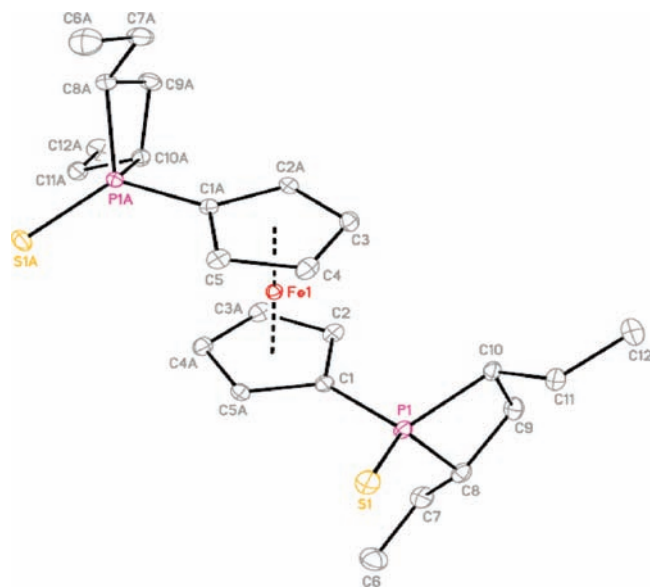
**Table 8.** Formal Potentials (V vs  $\text{FcH}^{0/+}$ ) and Potential Differences  $\Delta E$  (defined as  $E^{\circ}_{\text{cmpd}} - E^{\circ}_{\text{phosphine}}$ ) for Transition Metal Compounds Containing FERROLANE or FERROTANE Ligands<sup>b</sup>

Phosphine	[PdCl <sub>2</sub> (P <sup>O</sup> P)]		[PtCl <sub>2</sub> (P <sup>O</sup> P)]		[Rh(1,5-cyclooctadiene)-(P <sup>O</sup> P)][BF <sub>4</sub> ]	
	$E^{\circ}$	$\Delta E$	$E^{\circ}$	$\Delta E$	$E^{\circ}$	$\Delta E$
<sup>R</sup> MeFL	0.55	0.44	0.53	0.42		
<sup>S</sup> MeFL	0.55	0.44	0.54	0.43		
<sup>R</sup> EtFL	0.56	0.45	0.53	0.42	0.50	0.39
<sup>S</sup> EtFL	0.54	0.42	0.53	0.41		
<sup>R</sup> <i>i</i> -PrFL	0.51	0.41	0.51	0.41		
<sup>S</sup> <i>i</i> -PrFL	0.51	0.41	0.51	0.41		
<sup>R</sup> EtFT	0.58	0.44	0.58	0.44		
<sup>S</sup> EtFT	0.57	0.44	0.57	0.43	0.54	0.41

<sup>a</sup> Determined from the midpoint of  $E_{\text{p}}^{\text{ox}}$  and  $E_{\text{p}}^{\text{red}}$ . <sup>b</sup> All data reported at a scan rate of 100 mV/s.

platinum compounds, the <sup>1</sup>J<sub>P-Se</sub> coupling constants of the FERROTANE selenides were larger than those of the FERROLANE selenides.

The structures of <sup>S</sup>EtFTS<sub>2</sub> (Figure 6), <sup>R</sup>MeFLSe<sub>2</sub> (Figure 7), <sup>S</sup>EtFTS<sub>2</sub> (Figure 8), and <sup>R</sup>EtFTSe<sub>2</sub> were determined. The *R* and *S* stereoisomers of EtFTS<sub>2</sub> displayed very slight differences, in particular the average P–Se bond lengths are longer in <sup>S</sup>EtFTS<sub>2</sub>.

**Figure 5.** Potential (V vs  $\text{FcH}^{0/+}$  in  $\text{CH}_2\text{Cl}_2$ ) for oxidation of (1,1'-bis(phosphino)ferrocene) $\text{X}_n$  compounds vs free phosphine (black solid circles,  $\text{X} = \text{PdCl}_2$ ,  $n = 1$ ,  $y = 0.8735x + 0.4221$ ,  $R^2 = 0.93$ ; red solid circles,  $\text{X} = \text{PtCl}_2$ ,  $n = 1$ ,  $y = 1.056x + 0.4107$ ,  $R^2 = 0.96$ ; blue solid circles,  $\text{X} = \text{S}$ ,  $n = 2$ ,  $y = 0.5893x + 0.3501$ ,  $R^2 = 0.89$ ).**Figure 6.** Perspective view of <sup>S</sup>EtFTS<sub>2</sub> with 30% ellipsoids. H atoms are omitted for clarity.

With the exception of the P–S and P–Se distances, there was little difference in the structures (Table 9). The bond lengths and angles were similar to other structures reported of bis(phosphine chalcogenide)ferrocenes.<sup>24c,38–42</sup> To determine if the %  $V_{\text{bur}}$  calculation was applicable to phosphine sulfides and phosphine selenides, the calculation was performed on various  $\text{R}_3\text{P}=\text{E}$  compounds for which the structures of both the sulfide and the selenide had been reported. The calculations were performed as previously described.<sup>31</sup>

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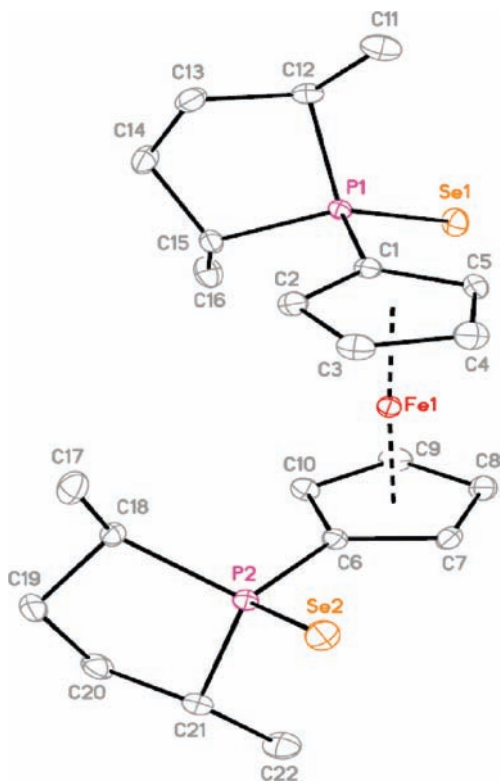
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However, the distance from the center of the sphere for the sulfides was set at 2.0 Å while the distance for the selenides was set at 2.1 Å.<sup>57</sup> There was a good correlation between the % $V_{\text{bur}}$  and the Tolman cone angle suggesting that % $V_{\text{bur}}$  is applicable to phosphine sulfides and phosphine selenides. In general, the % $V_{\text{bur}}$  decreases as the size of the chalcogenide increases. The % $V_{\text{bur}}$  values for the reported structures of bis(phosphinesulfide)ferrocene and bis(phosphineselenide)-



**Figure 7.** Perspective view of  $^R\text{MeFLSe}_2$  with 30% ellipsoids. H atoms are omitted for clarity.

ferrocene compounds have been calculated (Table 10). The percent buried volumes of the FerroTANE and FerroLANE sulfides and selenides are slightly less than those of the dpfp analogues.

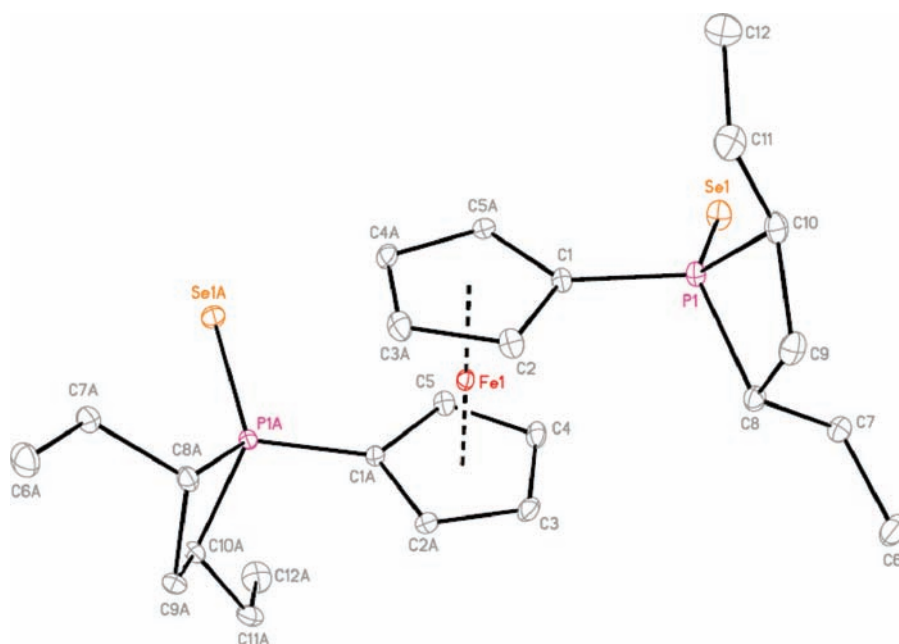
The oxidative electrochemistry of the phosphine sulfides displayed a reversible, one-electron oxidation approximately 0.3 V positive of the free phosphine (Table 11). The  $\sigma_p$  values for the phosphine sulfide substituents were calculated using eq 1. There is a correlation between the potentials at which the free phosphine and the phosphine sulfide undergo oxidation (Figure 5).

The oxidative electrochemistry of the phosphine selenides was more complicated (Figure 9). On the basis of a previous study,<sup>24c</sup> the wave at approximately 0.3 V versus  $\text{FcH}^{0/+}$  is likely attributable to oxidation of the two selenium atoms resulting in a dication in which intramolecular Se–Se bond formation has occurred. Bulk electrolysis confirmed that the initial oxidation is two-electron. There is poor correlation between the potentials at which oxidation of the phosphine selenides and the free phosphines occur since the site of oxidation is different. The selenium based oxidation also means eq 1 cannot be used to estimate the  $\sigma_p$  value for the phosphine selenide substituents.

**Table 9.** Select Bond Lengths (Å) and Angles (deg) for  $\text{P}^{\text{E}}\text{PE}_2$  (E = S or Se) Compounds

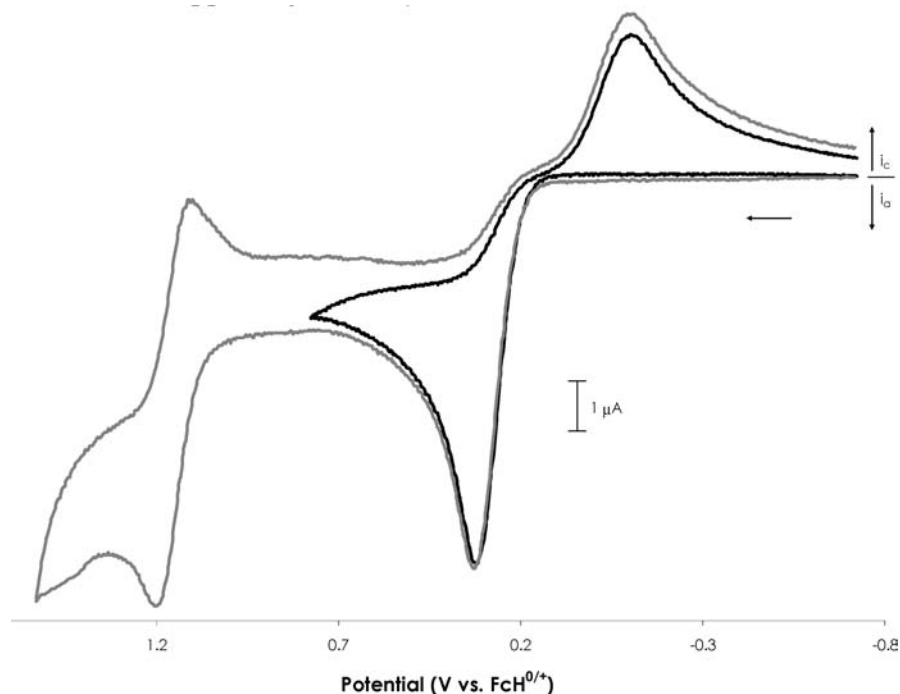
	$^R\text{MeFLSe}_2$	$^S\text{EtFTS}_2$	$^S\text{EtFTSe}_2$
P–E (avg.)	2.1066	1.9429(6)	2.0978(6)
Fe–C (avg.)	2.047	2.045	2.055
$X_A\text{–Fe–}X_B$	176.46	177.99	178.17
P–Fe–P	138.70	165.15	166.47
$\tau^a$	128.12	165.47	166.34
$\theta^b$	2.86	2.83	2.23
$\delta_P$ (avg.) <sup>c</sup>	–0.048	–0.035	0.049

<sup>a</sup>The torsion angle  $C_A\text{–}X_A\text{–}X_B\text{–}C_B$  where C is the carbon atom bonded to phosphorus and X is the centroid. <sup>b</sup>The dihedral angle between the two  $C_5$  rings. <sup>c</sup>Deviation of the P atom from the  $C_5$  plane; a positive value means the P is closer to the Fe.



**Figure 8.** Perspective view of  $^S\text{EtFTSe}_2$  with 30% ellipsoids. H atoms are omitted for clarity.





**Figure 9.** CV scan of the oxidation of 1.0 mM  $R_i$ -PrFLSe<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> with 0.1 M [NBu<sub>4</sub>][PF<sub>6</sub>] as the supporting electrolyte.

**Table 10.** Average Percent Buried Volume (% $V_{bur}$ ) for P<sup>0</sup>PE<sub>2</sub> (E = S or Se; P<sup>0</sup>P = Bisphosphinoferrocene) Compounds<sup>a</sup>

phosphine	sulfide		selenide	
	% $V_{bur}$	ref.	% $V_{bur}$	ref.
dppf	40.5	53	37.3	54
dippf	41.4	55	40.6	55
dtbpf			42.6	24c
dmapf <sup>b</sup>	40.7	38	38.7	38
deapf <sup>c</sup>	43.7	38	41.9	38
dppSdtbpSef <sup>d</sup>	43.4	56	42.4	56
dppSedtbpSf <sup>e</sup>	45.9	56	39.3	56
<sup>R</sup> MeFL			36.0	this work
<sup>S</sup> EtFT	38.0	this work	36.0	this work
<sup>R</sup> EtFT			36.2	this work

<sup>a</sup> References are to the original structures, all % $V_{bur}$  calculations were performed in this study. <sup>b</sup> dmapf = 1,1'-bis(di(dimethylamino)phosphino)ferrocene. <sup>c</sup> deapf = 1,1'-bis(di(diethylamino)phosphino)ferrocene. <sup>d</sup> dppSdtbpSef = 1-(diphenylphosphinesulfide)-1'-(di-*tert*-butylphosphineselenide)ferrocene. <sup>e</sup> dppSedtbpSf = 1-(diphenylphosphineselenide)-1'-(di-*tert*-butylphosphinesulfide)ferrocene.

**Table 11.** Formal Potentials (V vs FcH<sup>0/+</sup>),<sup>a</sup> Potential Differences  $\Delta E$  (Defined As  $E_{compd}^{\circ} - E_{phosphine}^{\circ}$ ) and Hammett Parameters ( $\sigma_p$ ) for Chalcogenides of FerroLANE or FerroTANE Ligands<sup>b</sup>

phosphine	sulfide			selenide			$E^{\circ}$
	$E^{\circ}$	$\Delta E$	$\sigma_p$	$E_p^{ox}$	$\Delta E$	$E_p^{red}$	
<sup>R</sup> MeFL	0.42	0.31	0.39	0.31	0.20	-0.04	1.12 <sup>c</sup>
<sup>S</sup> MeFL	0.42	0.31	0.39	0.33	0.22	-0.06	1.14 <sup>c</sup>
<sup>R</sup> EtFL	0.42	0.31	0.39	0.32	0.21	-0.08	1.08
<sup>S</sup> EtFL	0.42	0.30	0.39	0.35	0.23	-0.10	1.08
<sup>R</sup> <i>i</i> -PrFL	0.42	0.32	0.39	0.33	0.23	-0.10	1.16
<sup>S</sup> <i>i</i> -PrFL	0.41	0.31	0.38	0.33	0.23	-0.07	1.16
<sup>R</sup> EtFT	0.44	0.30	0.42	0.38	0.24	0.02	1.09 <sup>c</sup>
<sup>S</sup> EtFT	0.43	0.30	0.41	0.38	0.25	0.02	1.10 <sup>c</sup>

<sup>a</sup> Determined from the midpoint of  $E_p^{ox}$  and  $E_p^{red}$ . <sup>b</sup> All data reported at a scan rate of 100 mV/s. <sup>c</sup> The  $E_p^{ox}$  for the irreversible oxidation.

The proposed Se–Se bonded dication could not be isolated. Attempts a chemical oxidation with either [NO][BF<sub>4</sub>] or [N(*p*-C<sub>6</sub>H<sub>4</sub>Br)]SbCl<sub>6</sub> produced a red precipitate that was confirmed to be Se<sub>8</sub> by mass spectrometry. The resulting solution was examined by <sup>19</sup>F and <sup>31</sup>P NMR. In addition to the septet for PF<sub>6</sub><sup>-</sup>, the <sup>19</sup>F NMR spectrum showed a peak at -83.3 ppm (d, <sup>1</sup>J<sub>F-P</sub> = 980 Hz) while the <sup>31</sup>P NMR spectrum had peaks at 83.0 ppm (s) and -19.4 ppm (t, <sup>1</sup>J<sub>F-P</sub> = 980 Hz). The -83.3 (d) in the <sup>19</sup>F spectrum and -19.4 (t) in the <sup>31</sup>P spectrum can be attributed to PO<sub>2</sub>F<sub>2</sub><sup>-</sup> which results from

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the hydrolysis of  $\text{PF}_6^-$ .<sup>58</sup> The presence of trace water also accounts for the formation of elemental selenium. Oxidation of methylphenyl-*n*-propylphosphine selenide by hydrogen peroxide yield red selenium and a phosphine oxide.<sup>59</sup> While the peak at 83.0 ppm in the  $^{31}\text{P}$  could not be unambiguously assigned, formation of a phosphine oxide seems likely.

### Summary

The oxidative electrochemistries of eight bis(phosphino)-ferrocene ligands with chiral phosphine substituents were examined. The potentials at which oxidation of FerroTANE and FerroLANE ligands occur are similar and are not affected by varying the alkyl substituents on the chiral carbons. However, the reversibility of the oxidation is dependent on the steric bulk of the alkyl substituents. The electrochemical data permitted the Hammett parameters for the different phosphine substituents to be calculated.

Palladium and platinum dichloride complexes of FerroTANE and FerroLANE ligands were prepared. Several X-ray crystal structures were reported. Analysis of the percent buried volume ( $\%V_{\text{bur}}$ ) of the FerroTANE and FerroLANE ligands suggest that with Me and Et substituents, they are similar to other bis(phosphino)ferrocene ligands. The potential at which oxidation of the iron center of these ligands occurs is shifted approximately 0.4 V more positive upon coordination to palladium and platinum. In addition, the oxidation is reversible regardless of the substituents on the chiral carbon.

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Reaction of the FerroTANE and FerroLANE ligands with elemental sulfur or selenium yields the corresponding phosphine chalcogenide. X-ray crystal structures of several phosphine chalcogenides were determined. Analysis of the  $\%V_{\text{bur}}$  of phosphine chalcogenide shows a good correlation with the Tolman cone angle. This suggests that  $\%V_{\text{bur}}$  is useful for analyzing these structures. In general, the  $\%V_{\text{bur}}$  of phosphine sulfides is slightly larger than that of the analogous selenides. The oxidative electrochemistry of the phosphine sulfides displays a single reversible wave approximately 0.3 V more positive than the free phosphine. The Hammett parameters of the phosphine sulfide groups were calculated. Oxidation of the phosphine selenides is more complicated, displaying two waves. The first is presumed to be a two-electron wave that yields a Se–Se bonded dication. The second wave is likely due to oxidation of the iron center yielding a trication.

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**Supporting Information Available:** CIF files for the structures of  $[\text{PtCl}_2(\text{SMeFL})]$ ,  $[\text{PtCl}_2(\text{REtFT})]$ ,  $[\text{PtCl}_2(\text{Si-PrFL})]$ ,  $^{\text{SEtF}}\text{TS}_2$ ,  $^{\text{RMeFL}}\text{Se}_2$ , and  $^{\text{SEtFT}}\text{Se}_2$ , additional experimental detail and cif files for the structures of  $[\text{PtCl}_2(\text{RMeFL})]$ ,  $[\text{PtCl}_2(\text{SEtFT})]$ ,  $[\text{PdCl}_2(\text{RMeFL})]$ , and  $^{\text{REtFT}}\text{Se}_2$ ,  $^1\text{H}$  NMR data, cyclic voltammograms for  $[\text{PtCl}_2(\text{Si-PrFL})]$  and  $^{\text{Ri-PrFL}}\text{S}_2$ , correlation of  $\%V_{\text{bur}}$  and Tolman cone angle for phosphine chalcogenides, correlation of electrochemical data for ligands with a ferrocene backbone and correlation between P–Pt distance and  $^1J_{\text{P-Pt}}$  coupling constant for platinum compounds with 1,1'-bis-(phosphino)metallocene ligands. This material is available free of charge via the Internet at <http://pubs.acs.org>.