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BoPhoz Ligands: Anodic Electrochemistry and Complexes[†]

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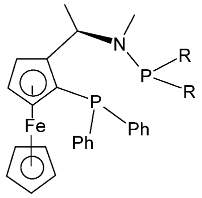
The oxidative electrochemistries of two chiral metallocene phosphine-aminophosphine (BoPhoz) ligands, R-Methyl BoPhoz ((*R*)-*N*-diphenylphosphino-*N*-methyl-[(*S*)-2-(diphenylphosphino)ferrocenyl]ethylamine) and R-Pcyco BoPhoz ((*R*)-*N*-dicyclohexylphosphino-*N*-methyl-[(*S*)-2-(diphenylphosphino)ferrocenyl]ethylamine)), were examined in methylene chloride. In addition the platinum(II) and palladium(II) complexes with a general formula [MCl_2(P−P)] (M = Pd or Pt; P−P = R-Methyl BoPhoz or R-Pcyco BoPhoz) were prepared and characterized by NMR and cyclic voltammetry; the X-ray structures of the palladium complexes are reported.

Introduction

Asymmetric catalysis has become a growing field of study as the demand for more enantiomerically pure compounds grows. The major demand for these types of compounds is in the pharmaceutical industry because of the specificity needed for effective drugs.[1] Asymmetric catalysis requires that a chiral catalyst be used in order to transfer the chirality from the catalyst to the substrate. An effective asymmetric catalyst will produce a chiral product in good yield with high enantiomeric purity of the desired enantiomer.[2] In addition to the enantiomeric selectivity, the catalysts must also be low cost, require a low ratio of catalyst to substrate, and have a fast turnover rate to be considered for industrial purposes.[3]

One class of asymmetric catalysts that has received significant attention in recent years is compounds containing chiral metallocene ligands, in particular, ferrocenylphosphines.[3] The chiral ferrocenylphosphine ligands typically have two different types of chirality. The first type is central chirality in which there is a chiral center located somewhere in the molecule.[4] This chiral group, typically a $-C^*R^1R^2R^3$ group, can have various types of functional groups that change the electronic and/or steric properties of the ligand. It is thought that this chiral center on the ligand is what interacts with the reactants in a catalytic reaction and leads to the formation of the desired chiral product.[3] The second type of chirality exhibited by chiral ferrocenylphosphine ligands is planar chirality.[4] Planar chirality is a consequence of the asymmetric structure of the ferrocene backbone. One example of this class of ligands is the series of BoPhoz ligands, (R)-Methyl BoPhoz (**1**) and (R)-Pcyco BoPhoz (**2**) (Figure 1).



R = Ph (**1**) or Cy (**2**)

Figure 1. BoPhoz.

The BoPhoz ligands have a phosphine-aminophosphine structure, which is the unique feature of this class of ligand.[5] Although only developed recently, BoPhoz ligands have been investigated in a number of catalytic applications. The primary use of BoPhoz reported in the literature has been as a ligand in rhodium-catalyzed asymmetric hydrogenation reactions.[5,6] In general, the catalysts with BoPhoz ligands perform very well, giving high enantioselectivity of the desired product. For example, in the rhodium-catalyzed asymmetric hydrogenation of methyl 2-acetamidocinnamate, BoPhoz gave the highest ee and a vastly superior turnover rate as

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[†] Dedicated to Professor Christopher W. Allen of the University of Vermont in recognition of his career and contributions to chemistry.

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Table 1. Crystal Data and Structure Analysis Results

	1PdCl$_2$		**2PdCl$_2$**	
formula	$C_{37}H_{35}Cl_2FeNP_2Pd$		$C_{37}H_{47}Cl_2FeNP_2Pd$	
fw	788.75		800.85	
temp	208(2) K		208(2) K	
wavelength	0.71073 Å		0.71073 Å	
cryst syst	orthorhombic		orthorhombic	
space group	$P2_12_12_1$		$P2_12_12_1$	
unit cell dimens	$a = 12.6296(10)$ Å	$\alpha = 90°$	$a = 8.3478(8)$ Å	$\alpha = 90°$
	$b = 14.8567(11)$ Å	$\beta = 90°$	$b = 19.0037(19)$ Å	$\beta = 90°$
	$c = 19.8143(14)$ Å	$\gamma = 90°$	$c = 22.389(2)$ Å	$\gamma = 90°$
volume	3717.8(5) Å^3		3551.9(6) Å^3	
Z	4		4	
density (calcd)	1.409 Mg/m^3		1.498 Mg/m^3	
abs coeff	1.129 mm^{-1}		1.183 mm^{-1}	
$F(000)$	1600		1648	
cryst size	$0.30 \times 0.20 \times 0.20$ mm^3		$0.30 \times 0.30 \times 0.20$ mm^3	
θ range for data collection	1.71 to 28.22°		2.11 to 28.20°	
index ranges	$-15 \le h \le 16, -19 \le k \le 19, -24 \le l \le 26$		$-11 \le h \le 10, -24 \le k \le 23, -29 \le l \le 29$	
no. of reflns collected	28 161		27 978	
indep reflns	8699 [R(int) = 0.0339]		8316 [R(int) = 0.0297]	
completeness to θ =	28.22° 97.3%		28.20° 97.3%	
abs corr	none		none	
max. and min. transmn	0.8057 and 0.7282		0.7979 and 0.7180	
refinement method	full-matrix least-squares on F^2		full-matrix least-squares on F^2	
no. of data/restraints/params	8699/0/397		8316/0/397	
goodness-of-fit on F^2	1.045		1.103	
final R indices [$I > 2\sigma(I)$]	R1 = 0.0320, wR2 = 0.0814		R1 = 0.0257, wR2 = 0.0624	
R indices (all data)	R1 = 0.0346, wR2 = 0.0825		R1 = 0.0275, wR2 = 0.0631	
absolute structure param	−0.003(17)		−0.007(12)	
largest diff peak and hole	0.722 and −0.359 e Å^{-3}		0.783 and −0.400 e Å^{-3}	

compared to JOSIPHOS, methyl DUPHOS, DIPAMP, and CHIRAPHOS.[6d] There has also been one report of palladium complexes of BoPhoz. In that study, the rate of oxidative addition of PhI to **1**Pd(*trans*-stilbene) was faster than that of the methyl DUPHOS and JOSIPHOS analogues.[7]

While complexes of BoPhoz have proven to be effective in a number of applications, very little work has been done with these ligands in terms of investigating the electronic and steric nature of the ligands. This work reports the anodic electrochemistry of **1** and **2**. The Pd(II) and Pt(II) dichloride complexes of **1** and **2** were prepared and characterized by NMR. In addition, the anodic electrochemistries of the Pd and Pt complexes were studied by cyclic voltammetry. The X-ray crystal structures of both Pd complexes were determined; these are the first reported structures of complexes with BoPhoz ligands.[7]

Experimental Section

General Procedures. Standard Schlenk techniques under an argon atmosphere were used in the preparative reactions. Dichloromethane (DCM), diethyl ether (Et_2O), and hexanes were purified under Ar using a Solv-tek purification system similar to one previously described.[8] Acetonitrile (MeCN) was distilled over CaH_2 under Ar prior to use. NMR spectra were obtained in $CDCl_3$ using a JEOL Eclipse 400 FT-NMR. TMS ($\delta = 0.00$ ppm) was used as an internal standard for the ^{1}H NMR acquisitions. An external standard, 85% H_3PO_4, was used as the reference value for the $^{31}P\{^1H\}$ NMR data. Elemental analyses were performed by Quantitative Technologies, Inc.

Ferrocene and decamethylferrocene were purchased from Strem. Ferrocene was purified by sublimation prior to use. Tetrabutylammonium hexaflurophosphate ($[NBu_4]^+[PF_6]^-$), 2,3-dichloro-5,6-dicyanoquinone (DDQ), bis(benzonitrile)dichloropalladium(II), and *cis*-bis(acetonitrile)dichloroplatinum(II) were purchased from Aldrich, and the $[NBu_4]^+[PF_6]^-$ was dried in vacuo prior to use. $Li[B(C_6F_5)_4]\cdot(OEt_2)_{2.5}$ was purchased from Boulder Scientific Co. The literature procedure was followed to metathesize $Li[B(C_6F_5)_4]$ to tetrabutylammonium tetrakis(pentafluorophenyl)borate ($[NBu_4]^+[B(C_6F_5)_4]^-$).[9]

Electrochemistry. All of the experiments were performed at ambient temperature (22 ± 1 °C) under an Ar atmosphere using 10.0 mL of a 0.1 M solution of $[NBu_4]^+[PF_6]^-$ in DCM as the supporting electrolyte. The electrochemistry of **1** was also examined in a solution containing 0.05 M $[NBu_4]^+[B(C_6F_5)_4]^-$ as the supporting electrolyte instead of $[NBu_4]^+[PF_6]^-$. The working electrode was a 1.5 mm glassy carbon electrode with a platinum wire as the auxiliary electrode and an Ag/AgCl (nonaqueous) reference electrode separated from the solution by a fine glass frit. The analyte concentration was 1.0 mM, and the cyclic votammetric data were collected using a Princeton Applied Research 263-A potentiostat at scan rates of 100−1000 mV/s at 100 mV/s intervals. Depending on the potential at which oxidation of the analyte occurred, either ferrocene or decamethylferrocene was added at the end of the experiment to give a solution that was 1.0 mM in the standard.[10]

X-ray Crystallography. Crystallographic data are collected in Table 1. For both structures the space group was unambiguously assigned from systematic absences in the diffraction data. The structures were solved by direct methods. All nonhydrogen atoms were refined with anisotropic thermal parameters, and all hydrogen atoms were treated as idealized contributions. For **1PdCl$_2$**, highly disordered solvent molecules were treated by SQUEEZE (A. Spek, Platon Crystallography

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Library), which renders them as diffuse, atom-unidentified contributions. In a total void space of 522 Å^3, 117 electrons were located in the unit cell. Contributions from the chemically unidentified solvent molecules are not included in the computation of intensive properties.

Synthesis of 1PdCl$_2$. Compound **1** (0.0934 mmol, 0.0618 g) and $(C_6H_5CH_2CN)_2PdCl_2$ (0.0934 mmol, 0.0358 g) were dissolved in 5.0 mL of DCM and stirred overnight. Et_2O (15.0 mL) was added, and the solution was placed in a freezer for 72 h. An additional 5.0 mL of Et_2O was added, and a light yellow precipitate formed. The solution was filtered, and the precipitate was determined to be unreacted **1**. The filtrate was stripped of solvent, leaving the orange-red solid, **1PdCl$_2$** (0.0637 g, 86%). Crystals were grown by dissolving **1PdCl$_2$** in minimal DCM and then allowing Et_2O to slowly diffuse into the solution in a freezer. Compound **1PdCl$_2$** has been prepared previously, by a slightly different method; spectroscopic data were in good agreement with the literature.[7]

Synthesis of 2PdCl$_2$. Compound **2** (0.0350 mmol, 0.0218 g) and $(C_6H_5CH_2CN)_2PdCl_2$ (0.0350 mmol, 0.0135 g) were dissolved in 5.0 mL of DCM and stirred for 72 h. Et_2O (20.0 mL) was added, and the solution was placed in a freezer for 48 h. An additional 5.0 mL of Et_2O was added, and this formed a fine, light yellow precipitate. The solution was filtered, and the precipitate was determined to be unreacted **2**. The filtrate was stripped of solvent, leaving the yellow-brown solid **2PdCl$_2$** (0.0224 g, 80%). Crystals were grown by dissolving **2PdCl$_2$** in minimal DCM and then allowing Et_2O to diffuse into the solution in a freezer. Anal. Calcd for $C_{37}H_{47}Cl_2FeNP_2Pd$: C, 55.49; H, 5.91; N, 1.75. Found: C, 55.35; H, 6.02; N, 1.50. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 10.1 (d, $^2J_{P-P} = 20.8$ Hz), 104.5 (d, $^2J_{P-P} = 20.8$ Hz). ^1H NMR ($CDCl_3$): δ (ppm) 7.8−7.3 (m, 10H, $-C_6H_5$), 5.48 (br, s, 1 H, C_5H_3), 4.36 (br, s, 1H, C_5H_3), 4.21 (m, 1H, C*H*Me), 3.88 (s, 5H, Cp), 3.85 (br, s, 1H, C_5H_3), 2.31 (d, $^3J_{H-P} = 5.16$ Hz, 3H, N-CH_3), 1.73 (d, $^3J_{H-H} = 6.6$ Hz, 3H, C-CH_3) 1.5−0.9 (m, 22H, $-C_6H_{11}$).

Synthesis of 1PtCl$_2$. Compound **1** (0.102 mmol, 0.0622 g) and $(CH_3CN)_2PtCl_2$ (0.103 mmol, 0.0358 g) were dissolved in 5.0 mL of DCM and stirred for 72 h. Et_2O (25.0 mL) was added, and the solution was placed in a freezer for 72 h. A precipitate was noted, and the solution was filtered and dried in vacuo, leaving an orange-brown solid, **1PtCl$_2$** (0.0626 g, 70%). Anal. Calcd for $C_{37}H_{35}Cl_2FeNP_2Pt$: C, 50.64; H, 4.02; N, 1.60. Found: C, 50.59; H, 4.42; N, 1.40. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ (ppm) −0.19 (d, $^2J_{P-P} = 12.1$ Hz, $^1J_{P-Pt} = 3950$ Hz), 60.0 (d, $^2J_{P-P} = 12.1$ Hz, $^1J_{P-Pt} = 3950$ Hz). ^1H NMR ($CDCl_3$): δ (ppm) 8.0−6.8 (m, 20H, $-C_6H_5$), 4.54 (br, s, 1 H, C_5H_3), 4.31 (br, s, 1H, C_5H_3), 4.21 (m, 1H, C*H*Me), 4.07 (s, 5H, Cp), 3.56 (br, s, 1H, C_5H_3), 2.10 (d, $^3J_{H-P} = 9.10$ Hz, 3H, N-CH_3), 1.31 (br, s, 3H, C-CH_3).

Synthesis of 2PtCl$_2$. Compound **2** (0.0380 mmol, 0.0287 g) and $(CH_3CN)_2PtCl_2$ (0.0382 mmol, 0.0133 g) were dissolved in 5.0 mL of DCM and stirred for 72 h. Et_2O (25.0 mL) was added, and the solution was placed in a freezer for 72 h. The solution was filtered and dried in vacuo, leaving an orange-brown oil. The oil was redissolved in 0.5 mL of DCM and then layered with 5 mL of Et_2O and returned to the freezer for 3 days. A precipitate formed, and the solution was then filtered. Excess solvent was removed by blowing Ar over the flask for 15 min. This left an orange-brown solid, which was determined to be **2PtCl$_2$** (0.0215 g, 64%). Anal. Calcd for $C_{37}H_{47}Cl_2FeNP_2Pt\cdot 0.5\ Et_2O$: C, 50.55; H, 5.66; N, 1.51. Found: C, 50.45; H, 5.51; N, 1.36. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ (ppm) −4.99 (d, $^2J_{P-P} = 10.4$ Hz, $^1J_{P-Pt} = 3880$ Hz), 72.5 (d, $^2J_{P-P} = 10.4$ Hz, $^1J_{P-Pt} = 3880$ Hz). ^1H NMR ($CDCl_3$): δ (ppm) 7.7−7.3 (m, 10H, $-C_6H_5$), 5.29 (br, s, 1 H, C_5H_3), 4.56 (br, s, 1H, C_5H_3), 4.30 (m, 1H, C*H*Me), 3.90 (s, 5H, Cp), 3.76 (br, s, 1H, C_5H_3), 2.33 (d, $^3J_{H-P} = 5.10$ Hz, 3H, N-CH_3), 1.73 (d, $^3J_{H-H} = 6.7$ Hz, 3H, C-CH_3) 1.5−0.9 (m, 22H, $-C_6H_{11}$).

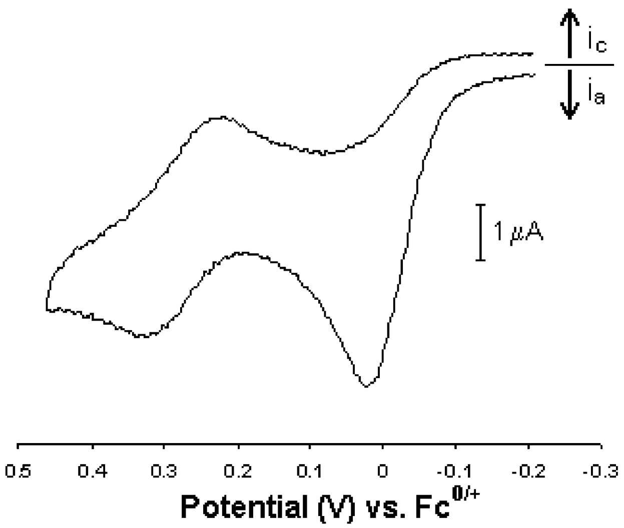

Figure 2. Cyclic voltammetry scan of the oxidation of 1.0 mM **1** in DCM/0.10 M Bu_4NPF_6 at 100 mV/s.

Table 2. Electrochemistry of BoPhoz Ligands and Complexes at 100 mV/s

compound	E_p (V vs Fc$^{0/+}$)	$E_{1/2}$ (V vs Fc$^{0/+}$)	ΔE
1	−0.02	0.19	
1PdCl$_2$		0.35	0.16
1PtCl$_2$		0.35	0.16
2	0.02	0.25	
2PdCl$_2$		0.33	0.08
2PtCl$_2$		0.31	0.06

Chemical Oxidation of 1. Compound **1** (0.0195 mmol, 0.0119 g) was dissolved in 5.0 mL of acetonitrile. In a separate flask DDQ (0.0176 mmol, 0.0040 g) was dissolved in 5.0 mL of acetonitrile. The DDQ solution was added to the solution containing **1**, and the combined solution immediately turned from light yellow to dark red-brown. The reaction was stirred for 15 min, and then the solvent was reduced in volume to approximately 2.0 mL. Et_2O (25.0 mL) was added, and the solution was placed in the freezer for 3 days. A black solid precipitated, the solvent was decanted, and the precipitate was then dried in vacuo. This gave a black solid that has not been fully characterized. $^{31}P\{^1H\}$ NMR (MeCN): δ (ppm) −22.0 (s), 119.1 (s).

Results and Discussion

The oxidative electrochemistries of compounds **1** and **2** were investigated by cyclic voltammetry. Compounds **1** and **2** exhibit similar electrochemistry; there is one irreversible oxidation and one reversible wave at a more positive potential (Figure 2). The potentials at which oxidation of **2** occur are slightly more positive than those of **1** (Table 2) most likely due to the more electron donating cyclohexyl groups in **2**.[11] The electrochemistry of **1** was also examined using $[NBu_4]^+[BC_6F_5]^-$ as the supporting electrolyte. This electrolyte is known to stabilize highly reactive species;[9,10,12] however, there was no significant difference in the cyclic voltammagram of **1**. It was anticipated that there would only be one ferrocene-based oxidation wave for **1** and **2**. In an attempt to determine the nature of the two observed waves, the chemical oxidation of **1** was examined. DDQ in acetonitrile was chosen as the chemical oxidant, as it has a potential between the two waves of **1**.[13] The

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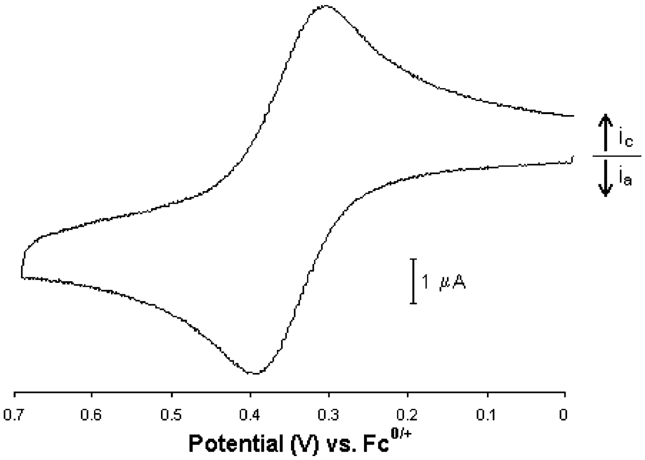

Figure 3. Cyclic voltammetry scan of the oxidation of 1.0 mM **$1PdCl_2$** in DCM/0.10 M Bu_4NPF_6 at 100 mV/s.

reaction was monitored by $^{31}P\{^1H\}$ NMR; in comparing the oxidized species, **1^+**, with **1**, the peak at 60 ppm in **1** was shifted approximately 60 ppm downfield. However, the peak at −24 ppm remained essentially unchanged. The peak at −24 ppm in **1** can be assigned as the $-PPh_2$ group bound directly to the Cp ring due to similarity to the peak for 1,1-bis(diphenylphosphino)ferrocene (dppf).[14] In addition, there is a peak at −24 ppm in the ^{31}P spectrum of **2**. The peak further downfield must therefore be due to the phosphorus bonded to the nitrogen. The large shift upon chemical oxidation suggests that the phosphorus is oxidized and reacts with DDQ to give a diamagnetic species; however the product of this reaction has yet to be structurally characterized.

The $PdCl_2$ and $PtCl_2$ complexes of **1** and **2** were prepared by reacting the phosphines with the appropriate dichlorobisnitrile metal species. The products were characterized by NMR, and in general, the ^{31}P signals of the complexes were shifted downfield as compared to the free phosphines. In all of the compounds, phosphorus−phosphorus coupling was seen, suggesting that both phosphorus atoms were bonded to the Pd(II) or Pt(II). For the $PtCl_2$ complexes, ^{195}Pt satellites were observed, indicating that both phosphorus atoms of **1** and **2** are bonded directly to the Pt.

The oxidative electrochemistry of the free ligands and the chemical oxidation of **1** suggest that upon complexation of **1** and **2**, there would no longer be an irreversible oxidation attributable to the amino-phosphine, as the amino-phosphine would be involved in bonding to a metal center. This difference in reversibility of oxidation upon coordination has been noted in other ferrocenylphosphines such as dppf.[14] For each complex of **1** and **2** only one reversible oxidative wave was observed (Figure 3). Upon coordination to Pd or Pt, the potentials at which oxidation of **1** or **2** occurs are shifted to more positive potentials. This is recorded in Table 2 as ΔE, which is the difference between the complex and the reversible wave in the free phosphine. This positive shift upon coordination has been noted in complexes of other ferrocenylphosphines such as dppf.[14] In general the complexes had a potential around 0.33 V (Table 2). The potential at which oxidation of complexes of **2** occurred was slightly less positive than the analogous complexes of **1** due to the more electron donating cyclohexyl groups in **2**.[11]

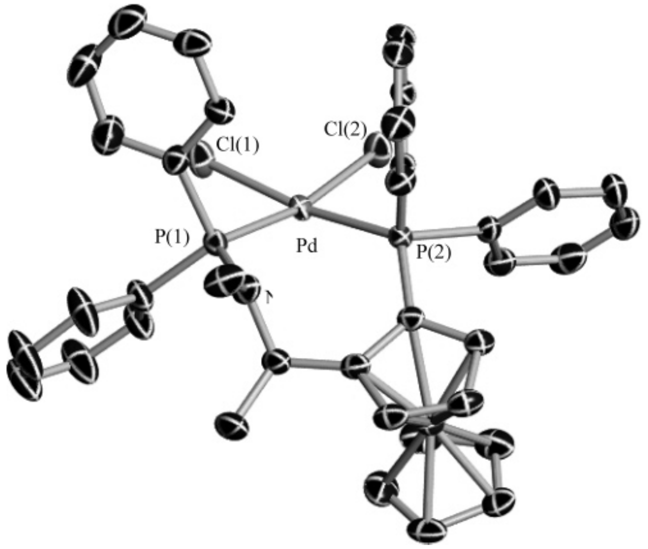

Figure 4. ORTEP diagram of **$1PdCl_2$**.

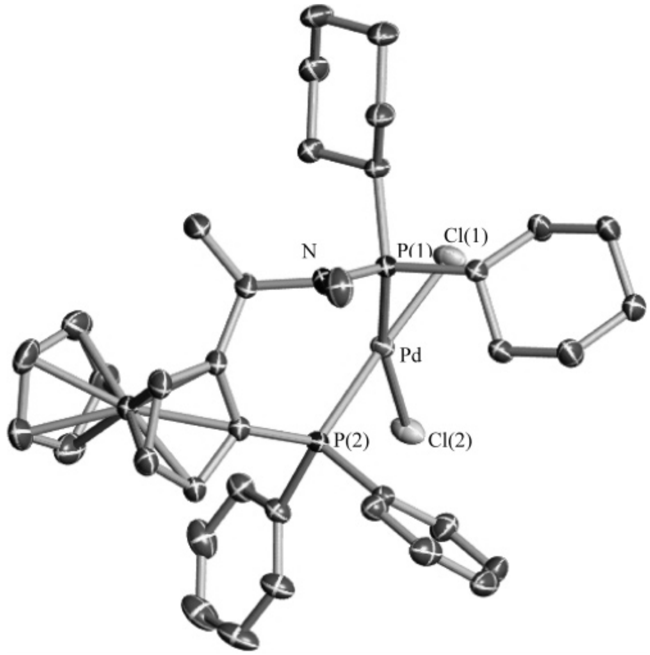

Figure 5. ORTEP diagram of **$2PdCl_2$**.

The structures of complexes **$1PdCl_2$** and **$2PdCl_2$** were determined by X-ray crystallography (Figures 4 and 5). These are the first reported structures containing a BoPhoz ligand. Select bond lengths and angles are presented in Table 3. In general, the bond lengths were similar in both complexes; however, the P−Pd−P bond angle and P_1−Pd bond length in **$2PdCl_2$** are significantly larger than the corresponding measurements in **$1PdCl_2$**. The Pd(II) center was anticipated to be square planar in both **$1PdCl_2$** and **$2PdCl_2$**; however significant distortions were noted. In both **$1PdCl_2$** and **$2PdCl_2$**, the Pd is puckered out of the P−P−Cl−Cl plane by 0.2 Å. However, there is significant twisting about the Pd in **$2PdCl_2$**, and a plane that passes through the center of both phosphorus atoms and both chlorine atoms cannot be defined. The difference in the P−Pd−P angles, the

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Table 3. Selected Bond Lengths (deg) and Distances (Å) for $1PdCl_2$ and $2PdCl_2$

Bond Lengths

	$1PdCl_2$	$2PdCl_2$		$1PdCl_2$	$2PdCl_2$
Pd–P_1	2.2512(8)	2.2795(6)	Pd–P_2	2.2968(7)	2.2914(6)
Pd–Cl_1	2.3473(8)	2.3334(7)	Pd–Cl_2	2.3485(8)	2.3585(6)
P–N	1.660(3)	1.672(2)			

Bond Angles

	$1PdCl_2$	$2PdCl_2$		$1PdCl_2$	$2PdCl_2$
P–Pd–P	96.83(6)	99.03(2)	Cl–Pd–Cl	88.23(3)	87.31(2)
P_1–Pd–Cl_1	83.78(3)	87.02(2)	P_2–Pd–Cl_2	89.79(3)	86.64(2)
N planarity	0.2 Å above	in plane	Pd planarity	0.2 Å above	
			Me–N–C–Me	46.0(3)	58.2(2)

P_1–Pd bond lengths, and the distortion around the Pd centers is likely attributed to the bulky cyclohexyl groups in **2**.[15]

Another difference is that the nitrogen atom in **$2PdCl_2$** is trigonal planar, while the nitrogen in **$1PdCl_2$** displays a shallow pyramidal geometry. Aminophosphines typically display either shallow pyramidal or trigonal planar geometry.[16] The sum of the angles about the nitrogen atom in **$1PdCl_2$** is 356.1°, while the corresponding value in **$2PdCl_2$** is 359.9°. The sum of the angles about the nitrogen in the closely related dichloro({*N*-[2-(diphenylphosphino-κ*P*)benzyl]benzylamino}diphenylphosphine-κ*P*)palladium(II) (**3**) is 355.4°, and the geometry at the nitrogen is pyramidal.[17] It is unclear why the sum of the angles about the nitrogen in **$1PdCl_2$** and **3** are similar and yet significantly smaller than the sum in **$2PdCl_2$**. Larger bond angles at nitrogen have been proposed to be due to minimization of steric repulsion of the substituents on nitrogen.[16] The larger cyclohexyl groups in **$2PdCl_2$** as compared to the phenyl groups in **$1PdCl_2$**,and **3** may contribute to this difference.

A final notable difference in the structures of **$1PdCl_2$** and **$2PdCl_2$** is the bite angle (P–Pd–P) of the phosphine. The bite angle of **1** is approximately 0.5° larger than that of the ligand in **3**, and yet 2.2° smaller than that of **2**. The larger bite angle may be due to the proximity of the cyclohexyl groups to the Pd center in **$2PdCl_2$**. However, the bite angle in dichloro-((1*R*)-1-(bis-(3,5-bis(trifluoromethyl)phenyl)phosphino)-2-((1*R*)-1-(dicyclohexylphosphino)ethyl)ferrocene-*P*,*P′*)palladium, a JOSIPHOS palladium complex in which a $-PCy_2$ group is bound to the chiral center, is approximately 0.8° less than that in **$1PdCl_2$**.[18] The larger bite angle of **2** may impact the reactivity of **$2PdCl_2$**. The rate of oxidative addition of PhI to Pd(diphosphine)(stilbene) complexes is faster with diphosphines that have large bite angles.[7] It would be useful to study the rate of oxidative addition to Pd(stilbene) complexes of **1** and **2**.

Conclusion

The oxidation of the amino-phosphine in two BoPhoz ligands is irreversible, and the potential at which oxidation occurs is not significantly effected by the groups on the amino-phosphine. There is also a reversible ferrocene-based oxidation for compounds **1** and **2**. Upon coordination to a metal, the irreversible oxidation of the amino-phosphine is no longer possible and the ferrocene-based oxidation is shifted to slightly more positive potentials. Coordination of **1** and **2** to a Pd(II) center results in the formation of a distorted square planar geometry at the palladium center. There are a number of significant differences in the structures of **$1PdCl_2$** and **$2PdCl_2$**, most likely due to the increased steric requirements of the cyclohexyl groups in **2**.

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Supporting Information Available: CIF files for the structures of **$1PdCl_2$** and **$2PdCl_2$**. This information is available free of charge via the Internet at http://acs.org.

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