# ORGANOMETALLICS

# Redox Behavior of 2-Substituted 1,3-Benzoxaphospholes and 2,6-Substituted Benzo[1,2-*d*:4,5-*d*']bisoxaphospholes

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Supporting Information

**ABSTRACT:** The electrochemical behavior of a series of 2-substituted 1,3-benzoxaphospholes and 2,6-disubstituted benzo[1,2-*d*:4,5-*d*']bisoxaphospholes has been examined by cyclic voltammetry methods. One-electron reductions near -1.99 V vs SCE in THF (0.1 M ["Bu<sub>4</sub>N][BF<sub>4</sub>]) are observed for 2-aryl-1,3-benzoxaphospholes, with the exception of compounds where aryl = p-C<sub>6</sub>H<sub>4</sub>Br or p-C<sub>6</sub>H<sub>4</sub>Cl, which show irreversible reduction processes. 2,6-Dimesityl-benzobisoxaphosphole and 2,6-dixylyl-benzobisoxaphosphole show two reduction waves, with the first wave displaying reversibility (ca.  $E_{1/2} \approx -2.0$  V vs SCE). By contrast, 2,6-di-*tert*-butyl-benzobisoxaphosphole and 2,6-diadamantyl-benzobisoxaphosphole show single reversible reductions near -2.36 V vs SCE. DFT calculations have been conducted in order to give a greater understanding of the electronic factors influencing the electrochemical results.



## ■ INTRODUCTION

An important aspect of organophosphorus compounds having P=P and P=C  $p\pi$ - $p\pi$  bonds is that they are often more susceptible to electrochemical reduction than analogous C=C containing counterparts. This fact can be attributed to the presence of relatively low lying  $\pi^*$ -orbitals, which are characteristic of molecules possessing these types of  $p\pi - p\pi$  bonds.<sup>1</sup> Figure 1 provides an overview to compare energies of the frontier orbitals across the fundamental series of N=N, N=C, C=C, C=P, and P=P  $p\pi$ - $p\pi$  bonded systems. In addition to reduced HOMO-LUMO gaps, the relative energies of the lone pair on N or P atoms change, as does the nature of the orbital (from HOMO to HOMO-1). For phosphaalkenes the HOMO orbital is predicted to be the  $\pi$ -bond and relatively nonpolar. These facts make phosphaalkenes more analogous in behavior to olefins as compared to imines.<sup>2</sup> In this series, diphosphenes (RP=PR) should be most susceptible to electrochemical reduction due to the lowest lying  $\pi^*$ -orbitals, and this has indeed been observed. Many diphosphenes have been shown to undergo reversible oneelectron reduction to radical anions, some of which can even be isolated and can exhibit multiredox activity  $.^{3-11}$  Phosphaalkenes (RP=CR<sub>2</sub>) have somewhat higher lying LUMOs than those of diphosphenes, but still lower lying energies than for many simple olefins and can also be redox active.<sup>11-16</sup>

We recently reported on 2-substituted 1,3-benzoxaphospholes (Chart 1, left) and 2,6-disubstituted benzo[1,2-d:4,5-d']-bisoxaphospholes (Chart 1, right),<sup>17</sup> interesting heterocyclic

molecules that feature phosphaalkene units.<sup>18</sup> Unlike other P=C containing materials, these materials are highly fluorescent with emission in the blue. As part of our investigations to more deeply understand these materials and their photoelectrochemical properties, we have performed cyclic voltammetric studies of these benzoxaphospholes. These studies illuminate the relationships among electrochemical properties and optical properties.

Electrochemical studies on such heterocyclic molecules having low-coordinate phosphorus atoms without complexation by transition metals are rather limited, and no reports on the electrochemistry of 1,3-benzoxaphospholes and benzobisoxaphospholes have appeared previously. Electrochemical studies on phosphinine and biphosphinine have been reported, however.<sup>19</sup>

# RESULTS AND DISCUSSION

**Synthesis.** Compounds 1-9 (Table 1) and 11-14 (Table 2) were reported previously and prepared according to published procedures.<sup>17,18</sup> The new benzoxaphosphole 10 was synthesized by analogous methods, i.e., via a cyclocondensation reaction between mesitylimidoyl chloride and 4-isopropyl-2-phosphinophenol in THF after refluxing for two days (Scheme 1). After removal of THF under vacuum, the remaining solid was extracted into hexane

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Figure 1. Frontier molecular orbitals of some double-bonded systems.





Table 1. Reduction Potentials for 1,3-Benzoxaphospholes(V vs SCE)



and the solution treated using consecutive aqueous acid and base washes, followed by filtration through basic alumina to yield a colorless, moderately air-sensitive solid **10** in 25% yield. The <sup>31</sup>P NMR shift was determined to be  $\delta$  96.9 ppm, which is similar to other 1,3-benzoxaphospholes reported in the literature.

**Cyclic Voltammetry: Reductions.** 1,3-Benzoxaphospholes of the form 2-R-1,3-benzoxaphosphole (1-5) and 5-isopropyl-2-R-1,3-benzoxaphosphole (6-10) were studied by cyclic voltammetry under anhydrous conditions inside a nitrogen-filled drybox (Table 1). Solutions with a concentration of 0.001 M benzoxaphosphole in THF were used for reduction analyses of these compounds. A three-electrode system, with glassy carbon as the working electrode, silver wire as the quasi-reference electrode,

and platinum wire as the counter electrode, was utilized. All scans were performed with 0.1 M tetrabutylammonium tetrafluoroborate, ["Bu<sub>4</sub>N][BF<sub>4</sub>], in THF as the supporting electrolyte, with a scan rate of 0.1 V/s. Ferrocene was utilized as an internal reference because of the use of a quasi-reference electrode (silver wire) during analyses. Ferrocene (final concentration 0.001 M) was added after the initial scans of compounds. The reduction potentials were thus referenced to the ferrocene/ ferrocenium redox couple versus saturated calomel electrode ( $E_{1/2} = 0.55 \text{ V vs SCE}$ ).<sup>20</sup>

A representative cyclic voltammogram of compound 1 in the range of 1.5 to almost -2.5 V is shown in Figure 2. For each of the compounds 1-10 a reduction wave  $(E_{\rm pc})$  was recorded between -1.8 and -2.3 V. Table 1 summarizes the reduction potentials for this series of 1,3-benzoxaphospholes.

Compounds 1–3, 6, and 8–10 show reversible, one-electron reduction waves  $(E_{1/2})$  between = –1.9 and –2.2 V vs SCE. Reversibility was ascertained by scanning compound 1 at various scan rates (25 to 200 mV) and generating linear plots of scan rates versus  $\Delta E_{\rm p}$  for both ferrocene and compound 1 (see Supporting Information), confirming adherence to the Nernst equation.<sup>20</sup>

The impact of the addition of substituents on the 2-aryl ring of the nonhalogenated 2-aryl-benzoxaphospholes and the 5-isopropyl-2-aryl-benzoxaphospholes is portrayed in Figures 3 and 4, respectively. The reduction potential for 1 ( $E_{1/2} = -1.90$  V) shifts negative by 60 and 130 mV on changing to compounds 2  $(p-\text{MeC}_6\text{H}_4)$  and 3  $(p-\text{MeOC}_6\text{H}_4)$ , respectively. Similarly, the 5-isopropyl-2-aryl-benzoxaphospholes 6 (Ar =  $C_6H_5$ ), 9 (Ar =  $p-MeC_6H_4$ ), 8 (Ar =  $p-MeOC_6H_4$ ), and 10 (Ar = 2,4,6- $Me_3C_6H_2$ ) show increasing resistance to reduction. The impact of the 5-isopropyl substituent on the benzoxaphosphole ring can be assessed by looking at the pairs of compounds 1 and 6, 2 and 9, and 3 and 8, where the 2-aryl group remains constant. For these pairs, the reduction process is more difficult for the 5-isopropylsubstituted material by 30-80 mV. Very small shoulders on some the negative scans (ca. -1.8 to -2.0 V) can be descerned. The origin of these humps is uncertain at this time.

For the benzoxaphospholes possessing  $2\text{-}p\text{-}XC_6H_4$  groups, the initial reduction waves  $(E_{\rm pc})$  occur more readily. The resulting radical anions appear to be unstable under the experimental conditions, as shown in Figure 5. Varying the scan rates during the analysis of compound 4 from 25 to 200 mV did not significantly change the nature of the CV waves (see Supporting Information). It seems probable that these radical anions are prone to lose halide (either Cl or Br), and the subsequently generated radicals react with solvent, by analogy with the processes shown for other aryl halides.

The reduction potentials are similar to other phosphaalkenes with no electron-donating and electron-withdrawing substituent effects reported in the literature. For example, the phosphaalkene Mes\*P=C(H)Ph (Mes\* = 2,4,6-tri*tert*-butylphenyl) displays a reversible one-electron reduction with an  $E_{1/2} = -1.98$  V vs SCE in THF.<sup>12a</sup> In addition, the impact of remote substituents on the electrochemistry of phosphaalkenes has been amply demonstrated previously in several studies,<sup>12-15</sup> for example, the effect of electron-withdrawing groups, specifically phenyl, thiophene, and furan, on the cyclic voltammetry of phosphaalkenes.<sup>12d</sup> Analyses on diphosphathienoquinones revealed reversible oneelectron reduction at  $E_{1/2} = -1.55$  V vs Ag/Ag<sup>+</sup> for these materials having a P=C unit.<sup>14c</sup> More recently electrochemical analyses on phosphaalkenes featuring acetylenic components



Table 2. Reduction Potentials for Benzobisoxaphospholes(in V vs SCE)





Figure 2. Cyclic voltammogram of 1.

having reduction potentials ranging from  $E_{1/2} = -1.84$  V to -2.04 V vs Fc/Fc<sup>+</sup>, depending on the types of substituents, have appeared.<sup>13</sup>

By contrast to the 2-aryl-substituted 1,3-benzoxaphospholes, when 2-*tert*-butyl-1,3-benzoxaphosphole was examined by CV under the same conditions, no reduction wave was observed. This result was quite surprising and suggests that the LUMO in these materials is much higher in energy than for the 2-arylsubstituted benzoxaphospholes (*vide infra*).

The reduction of benzobisoxaphospholes, 11-14 (Table 2), was also studied by cyclic voltammetry using the same conditions as the benzoxaphospholes 1-10. The voltammograms obtained are depicted in Figure 6, with the data presented in Table 2.

Two different types of behavior are observed. Compounds 11 and 12 feature a single, reversible, one-electron reduction wave near  $E_{1/2} = -2.35$  V vs SCE, whereas compounds 13 and 14



Figure 3. Overlay of cyclic voltammograms for compounds 1, 2, and 3.

display two, one-electron reduction waves, in which the first wave occurs near  $E_{1/2} = -1.98$  V vs SCE and a second wave near  $E_{\rm pc} = -2.44$  V vs SCE. A priori, one might anticipate that if the benzoxaphospholes have one reduction wave, the benzobisoxaphospholes might have two such waves, especially since these two P=C units are firmly locked into conjugation with one another.

The electrochemistry of compounds with one or more phosphaalkene units was first reported for compounds of the form *ortho*, *para-*, and *meta-*{Mes\*P==C(H)}<sub>2</sub>C<sub>6</sub>H<sub>4</sub>.<sup>12b,c,e</sup> In one study, it was determined that two reduction waves ( $\Delta E_p = 0.083 \text{ V}$ , THF) could be seen in the voltammograms for *para-*{Mes\*P==C(H)}<sub>2</sub>C<sub>6</sub>H<sub>4</sub>.<sup>12e</sup> The extended diphosphaalkenes {Mes\*P==C(Ph)-C=C=C}<sub>2</sub>-Ar (Ar = 1,4-phenyl or 9,10-anthracenyl) clearly show two resolved reduction waves for the anthracene-bridged system ( $\Delta E_p = 0.21 \text{ V}$ , CH<sub>2</sub>Cl<sub>2</sub>), while the phenyl-bridged system in the corresponding two waves are less well resolved ( $\Delta E_p = 0.10 \text{ V}$ , CH<sub>2</sub>Cl<sub>2</sub>).<sup>13c</sup>

While a number of comparisons to acyclic phosphaalkene electrochemistry can be drawn, comparisons to similar studies involving heterocycles having P=C units are rarer. A notable example is the pair of phosphinines P1 and P2 in Chart 2.<sup>19</sup> Phosphinine P1 displays partially reversible reduction at  $E_{1/2} = -2.27$  V vs SCE (DME). The biphosphinine P2 displays multiple reductions in DMF, the first two at  $E_{1/2} = -1.85$  V and -2.42 V vs SCE. The latter process is reversible only at high scan rates (2000 V s<sup>-1</sup> and above). The electrochemistry of the benzoxaphospholes and benzobisoxaphospholes are thus not so different than that observed for these two materials.

**Cyclic Voltammetry: Oxidations.** While some phosphaalkenes display reversible reduction waves in cyclic voltammetry studies, few, if any, display reversible oxidation waves. Notable exceptions include phosphaalkenes that bear one or more N-substituents (Chart 3).<sup>2h,16</sup> In fact, the radical cation produced upon oxidation of phosphaalkene



Figure 4. Overlay of cyclic voltammograms for compounds 6, 8, 9, and 10.



Figure 5. Overlay of cyclic voltammograms for compounds 4, 5, and 7.

c (Chart 3) was sufficiently stable to allow isolation and structural characterization.<sup>16</sup> As our compounds also have heteroatom substituents (oxygen instead of nitrogen), we sought to examine some of these materials to ascertain if they might display some reversible oxidations.

Compounds 1-6 were thus examined by cyclic voltammetry for their propensity to undergo oxidation. For this purpose, the solvent was changed to dichloromethane (DCM) at concentrations of 0.001 M with 0.1 M tetrabutylammonium hexafluorophosphate, ["Bu<sub>4</sub>N][PF<sub>6</sub>], as the supporting electrolyte. A three-electrode system, with glassy carbon as the working electrode, silver wire as the quasi-reference electrode, and platinum wire as the counter electrode, was used for analysis. As above, ferrocene was utilized as an internal reference due to the use of a quasi-reference electrode (silver wire).

Cyclic voltammograms are shown in Figure 7. Table 3 summarizes the oxidation potentials for 1,3-benzoxaphospholes. Compounds 1–6 show irreversible oxidation waves near  $E_{pa} = 1.3$  V vs SCE. As with the reduction potentials, the oxidation potentials are dependent upon the specific substituent. Compared to compound 1, compounds 2 and 3 undergo more facile oxidation ( $\Delta E = 50$  and 200 mV, respectively), while compounds

**4** and **5** are more difficult to oxidize. This trend is consistent with the electron-donating or electron-withdrawing capability of the particular substituent. A comparison between **1** and **6** illustrates that there is little or no effect with the addition of the 5-isopropyl group on the oxidation potential.

Oxidation studies were also performed on benzobisoxaphospholes **12** and **13** (Figure 8 and Table 3). In general, compounds **12** and **13** displayed irreversible oxidation waves near  $E_{pa} = 1.59$  V vs SCE. The difference in oxidation potential between these two compounds is 130 mV, which is similar to changes seen in the reduction potentials. The dynamics between alkyl versus aromatic is displayed again, where **13**, having increased conjugation, results in a higher HOMO.

Irreversible electrochemical oxidation of phosphaalkenes seem to be the norm. For example, Schoeller et al. reported on the irreversible oxidation of nonaromatic-substituted phosphaalkenes in 1991.<sup>11</sup> Their oxidation potentials were determined to be between  $E_{ox} = 1.07$  and 2.94 V vs SCE in butyronitrile. Ott et al. demonstrated that acetylenic phosphaalkenes result in irreversible oxidations as well. In CH<sub>2</sub>Cl<sub>2</sub>, their results showed oxidation potentials near  $E_{ox} = 1.02$  V vs Fc/Fc<sup>+.13</sup>

Computational Studies. The electrochemical data we have obtained is mostly in accord with our expectations, with the exception that there is a rather large difference in electrochemical behavior between the aryl- and alkyl-substituted compounds. Previously we have noticed significant differences in the photoluminescence between these classes of compounds.<sup>17</sup> In order to probe these differences, the electronic structures of benzoxaphospholes and benzobisoxaphospholes were studied using DFT calculations. Kohn-Sham formalized density functional theory (DFT) was used to calculate the ground-state electronic and geometric structures with the B3LYP hybrid functional and 6-31+G<sup>\*\*</sup> basis sets (i.e., B3LYP/6-31+G<sup>\*\*</sup>) using Gaussian<sup>26</sup> and with B3LYP/6-31-G<sup>\*</sup> using SPARTAN.<sup>27</sup> The results were essentially the same for both methods, and the SPARTAN results for the key frontier orbitals of select model and real compounds are summarized in Figure 9. Several features merit comment. First, the significant impact of the p-XC<sub>6</sub>H<sub>4</sub> substituent on the LUMO of the 2-aryl benzoxaphospholes is entirely consistent with our experimental observations that show that electrondonating substituents make reduction more difficult, while electron-withdrawing substituents make the reduction more facile. The predicted impact of a 5-isopropyl substutuent on the 2-phenylbenzoxaphosphole is relatively small (Ph\* in Figure 9). The LUMOs for the 2-H- and 2-alkyl-substituted benzoxaphospholes are notably higher in energy than for the 2-aryl benzoxaphospholes. A line (red dashed) can be drawn to indicate the reductions that are reachable within our particular electrochemical window. The essential nature of the LUMO and HOMO orbitals across the series is similar and is composed of large contributions from the P=C  $\pi$ - and  $\pi$ \*-orbitals. Figure 10 portrays frontier orbitals for two examples. Importantly, the 2-aryl-substituted species show significant contributions from the 2-aryl  $\pi$ -system into the frontier orbitals and exhibit properties that indicate that the P=C unit is  $\pi$ -conjugated throughout the molecule.

The phosphorus lone pair in these (as well as for the benzobisoxaphospholes below) is predicted to be substantially below the HOMO in energy. For compound 4 the lone pair shown in Figure 11 is HOMO (-4) at -7.89 eV (vs -5.75 eV for HOMO). Another noteworthy feature of these calculations is that they are in line with our results on the optical



Figure 6. Overlaid cyclic voltammograms for compounds 11 and 12 (top) and for compounds 13 and 14 (bottom).









Figure 7. Overlay of cyclic voltammograms of 1-6.

Table 3. Oxidation Data for Benzoxaphospholes and Benzobisoxaphospholes (in V vs SCE)



	R′	R	R″	$E_{\rm pa}$
1	Н	C <sub>6</sub> H <sub>5</sub>		1.31
2	Η	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>		1.26
3	Н	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub>		1.11
4	Н	p-ClC <sub>6</sub> H <sub>4</sub>		1.35
5	Н	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub>		1.36
6	<sup>i</sup> Pr	C <sub>6</sub> H <sub>5</sub>		1.31
12			Ad	1.65
13			2,4,6-Me <sub>3</sub> C <sub>6</sub> H <sub>2</sub>	1.52



Figure 8. Overlay of cyclic voltammograms for 12 and 13.







Figure 10. Frontier molecular orbitals for benzoxaphosphole and compound 4.

spectroscopy of these materials. For the series of aryl-substituted compounds, *both* the LUMO and HOMO drop in energy, yielding a relatively constant HOMO-LUMO gap. While we have not yet performed TDDFT calculations to explore the excited states, it is interesting to note that the absorption and emission maxima vary by less that 10 nm across compounds 1-4.

The results of computations on benzobisoxaphospholes are also given in Figure 9. As there are two P=C units, there are two low-lying orbitals (LUMO and LUMO+1) that are of P=C

 $\pi^*$ -character (Figure 12). As for the calculation on benzoxaphospholes, the aryl-substituted compounds feature lower energy LUMOs than alkyl-substituted compounds. The significance of this finding is that only the LUMO, but not the LUMO(+1), falls below the proposed limit for accessibility in our electrochemical window (red dashed line). For the aryl-substituted species, both the LUMO and LUMO(+1) are below this arbitrary line, suggesting the possibility for additional reductions to be accessed by electrochemical reduction. This is a rather simple model, as it lacks computations on the radical



Figure 11. Computed HOMO(-4) for compound 4.



Figure 12. Frontier molecular orbitals for model 2,2'-diphenylbenzbisoxaphosphole.

anions, which are the actual species receiving the second electron. Nevertheless, it is consistent with experimental data.

#### CONCLUSION

A series of 1,3-benzoxaphospholes and benzobisoxaphospholes were examined by cyclic voltammetry. Many of the 2-aryl-1,3-benzoxaphospholes display reversible, one-electron reductions, with the exception of halogenated derivatives, which show irreversible reduction waves. By contrast, the 2-alkyl-1,3-benzoxaphosphole derivative did not show any reduction behavior. In the case of benzobisoxaphospholes, alkyl-substituted derivatives are harder to reduce than their aryl-substituted counterparts, which feature an additional reversible, one-electron reduction wave. Computational studies on benzoxaphospholes offer a working model to explain the number of electrochemical waves observed as well as the character of the HOMOs and LUMOs.

With this contribution, and those appearing from other groups, the opportunities for  $\pi$ -conjugated materials featuring multiply bonded phosphorus atoms has reached a very exciting stage. Polymers having conjugated P=C and P=P groups have now been realized.<sup>28,29</sup> These materials, however, face some loss of maximal  $\pi$ -conjugation, as the P=C units are often twisted out of the optimal configuration for conjugation owing to steric interactions. With careful design, one can engineer bulky ligands that favor conjugation, such as seen for a recently reported phosphasilene.<sup>30</sup> This type of

strategy, in conjunction with the use of heterocycles (such as benzoxaphospholes or phosphinines), thus offers many opportunities for maximally  $\pi$ -conjugated multiply bonded phosphorus compounds and materials.

### EXPERIMENTAL SECTION

General Procedures. Experimental procedures were performed under nitrogen either using Schlenk line techniques or in a nitrogenfilled MBraun drybox. All benzoxaphospholes were prepared according to the literature, with the exception of 5-isopropyl-2-mesityl-1,3-benzoxaphosphole (10).<sup>17,18</sup> Tetrahydrofuran, diethyl ether, and hexanes were dried by distilling over metallic sodium and benzophenone. Dichloromethane was dried over phosphorus pentoxide. NMR spectra  $(^{1}\text{H and }^{31}\text{P}{^{1}\text{H}})$  were recorded in CDCl<sub>3</sub> on a Varian INOVA AS-400 spectrometer operating at 399.7 and 161.8 Hz, respectively. <sup>31</sup>P{<sup>1</sup>H} NMR spectra were referenced to 85% H<sub>3</sub>PO. <sup>13</sup>C<sup>1</sup>H NMR spectra were recorded in CDCl<sub>3</sub> on a Varian INOVA AS-600 spectrometer operating at 150.0 Hz. High-resolution mass spectrometry was performed by the University of Michigan Mass Spectrometry facility using a VG (Micromass) 70-250-S magnetic sector spectrometer with EI technique at 70 eV. Elemental analyses were performed by Robertson Microlit Laboratories.

5-Isopropyl-2-mesityl-1,3-benzoxaphosphole (10). In a drybox, 508 mg (2.94 mmol) of 4-isopropyl-2-phosphinophenol, 726 mg (3.24 mmol) of N-(mesityl)benzimidoyl chloride, and a stir bar were added to a 100 mL round-bottom flask. To this flask was added approximately 50.0 mL of THF, and the flask was sealed and removed from the drybox. The flask was outfitted with a condenser and refluxed under nitrogen for 36 h, giving a yellow, cloudy solution. The solvent was then removed in vacuo, and the flask was taken into the drybox. The resulting solid was then extracted with hexanes, and filtration removed the insoluble material, yielding a yellow solution. This solution was removed from the drybox and washed successively with degassed solutions of 10% aqueous NaOH, 10% aqueous H<sub>2</sub>SO<sub>4</sub>, and distilled H<sub>2</sub>O. The organic solution was then dried over Na<sub>2</sub>SO<sub>4</sub> and then CaCl<sub>2</sub>. The solvent was removed in vacuo, and the flask was taken into the drybox. The solid was dissolved in hexanes, and the solution was filtered through Celite and then filtered through basic alumina. The solvent was removed in vacuo to yield 251.4 mg of a colorless solid. Yield: 25%. <sup>1</sup>H NMR: δ 7.86 (m, 1H), 7.64 (m, 1H), 7.34 (m, 1H), 6.98 (s, 2H), 3.06 (m, 1H), 2.34 (s, 3H), 2.25 (s, 6H), 1.34 (d, 6H,  ${}^{3}J_{HH} = 6.8$  Hz). <sup>31</sup>P{<sup>1</sup>H} NMR:  $\delta$  98.9 (s, 1P). <sup>13</sup>C{<sup>1</sup>H} NMR:  $\delta$  196.3 (d,  $J_{PC}$  = 53.7 Hz), 158.2 (d,  $J_{PC}$  = 3.6 Hz), 143.4 (d,  $J_{PC}$  = 9.0 Hz), 138.8, 137.5 (d,  $J_{PC}$ = 5.3 Hz, 137.0, 130.8 (d,  $J_{PC} = 13.4 \text{ Hz}$ ), 128.3, 125.8 (d,  $J_{PC} = 2.7 \text{ Hz}$ ), 125.5 (d,  $J_{PC}$  = 18.9 Hz), 113.0, 33.8, 29.5, 22, 20.8 (d,  $J_{PC}$  = 53.0 Hz). Mp: 64-70 °C. HRMS *m*/*z*: 296.1333 (calc 296.1330). Anal. Calcd for C<sub>19</sub>H<sub>21</sub>PO (296.13): C 77.06, H 7.15. Found: C 77.13, H 7.34.

**Cyclic Voltammetry for Reduction Scans.** Cyclic voltammetry experiments were performed in a nitrogen-filled MBraun drybox out-fitted with a CH Instrument workstation (CHI630C) at room temperature. Tetrabutylammonium tetrafluoroborate was recrystallized five times using ethyl acetate and ether, dried thoroughly under vacuum, and stored in the drybox. Ferrocene was purified via sublimation under vacuum and stored in the drybox. All glassware was oven-dried overnight before use. A glassy carbon working electrode was polished with 0.05  $\mu$ m alumina and thoroughly cleaned and dried before use. A silver wire was utilized as a quasi-reference electrode, and a platinum wire was the counter electrode. All spectra were referenced to SCE using ferrocene as an internal standard. Samples were analyzed without ferrocene initially and then analyzed again with ferrocene for referencing.

Typical Procedure for 1-10. In a drybox, 2.20–3.50 mg of compounds 1-10 and 329 mg of tetrabutylammonium tetrafluoroborate were dissolved in dry THF in a 10.0 mL volumetric flask to give a 0.001 M solution. The solution was loaded into an electrochemical cell with electrodes, and electrical leads were attached for analysis. After initial scanning, approximately 1.70 mg of ferrocene was added to the cell and the solution was scanned again.

Typical Procedure for **11–14**. In a drybox, 2.20–3.50 mg of compounds **11–14** and 329 mg of tetrabutylammonium tetrafluoroborate were dissolved in dry THF in a 10.0 mL volumetric flask to give a 0.001 M solution. The solution was loaded into an electrochemical cell with electrodes, and electrical leads were attached for analysis. After initial scanning, approximately 1.70 mg of ferrocene was added to the cell and the solution was scanned again.

**Cyclic Voltammetry for Oxidation Scans.** Cyclic voltammetry experiments were performed in a nitrogen-filled MBraun drybox outfitted with a CH Instrument workstation (CHI630C) at room temperature. Tetrabutylammonium hexafluorophosphate was recrystallized five times using ethyl acetate and ether, dried thoroughly under vacuum, and stored in the drybox. Ferrocene was purified via sublimation under vacuum and stored in the drybox. All glassware was oven-dried overnight before use. A glassy carbon working electrode was polished with 0.05  $\mu$ m alumina and thoroughly cleaned and dried before use. A silver wire was utilized as a quasi-reference electrode, and a platinum wire was the counter electrode. All scans were performed at a scan rate of 0.1 V/s unless otherwise stated. All spectra were referenced to SCE using ferrocene as an internal standard. Samples were analyzed without ferrocene initially and then analyzed again with ferrocene for referencing.

Typical Procedure for 1-6. In a drybox, 2.20–3.50 mg of compounds 1-6 and 387 mg of tetrabutylammonium hexafluorophosphate were dissolved in dry DCM in a 10.0 mL volumetric flask to give a 0.001 M solution. The solution was loaded into an electrochemical cell with electrodes, and electrical leads were attached for analysis. After initial scanning, approximately 1.70 mg of ferrocene was added to the cell and the solution was scanned again.

*Typical Procedure for* **12** *and* **13**. In a drybox, 2.20–3.50 mg of compounds **12** and **13** and 387 mg of tetrabutylammonium hexafluorophosphate were dissolved in dry DCM in a 10.0 mL volumetric flask to give a 0.001 M solution. The solution was loaded into an electrochemical cell with electrodes, and electrical leads were attached for analysis. After initial scanning, approximately 1.70 mg of ferrocene was added to the cell and the solution was scanned again.

**Computational Methods.** All calculations employed the Gaussian03 (Rev.D.01) software package<sup>26</sup> and were performed in parallel on Intel Pentium 4 Xeon EM64T quad-core processors. Kohn–Sham formalized density functional theory was used to calculate the ground-state electronic and geometric structures with the B3LYP hybrid functional and  $6-31+G^{**}$  basis sets (i.e., B3LYP/6-31+G<sup>\*\*</sup>).

#### ASSOCIATED CONTENT

**Supporting Information.** Scan rate vs  $\Delta E_p$  plots for ferrocence and compound 1, as well as variable scan rate voltammogram data for compound 4. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### REFERENCES

 (a) Power, P. P. Chem. Rev. 1999, 99, 3463–3503. (b) Mathey, F. Angew. Chem., Int. Ed. 2003, 42, 1578–1604. (c) Power, P. P. J. Chem. Soc., Dalton Trans. 1998, 2939–2951. (d) Galbraith, J. M.; Blank, E.; Shaik, S.; Hiberty, P. C. Chem.—Eur. J. 2000, 6, 2425–2434.

(2) (a) Dillon, K. B.; Mathey, F.; Nixon, J. F. Phosphorus: The Carbon Copy; Wiley: New York, 1998. (b) Appel, R. Pure Appl. Chem. 1987, 59, 977–82. (c) Appel, R.; Knoll, F. Adv. Inorg. Chem. 1989, 33, 259–361.
(d) Markovskii, L. N.; Romanenko, V. D. Tetrahedron 1989, 45, 6019–6090. (e) Mathey, F. Acc. Chem. Res. 1992, 25, 90–96.

(3) Culcasi, M. G.; Gronchi, G.; Escudie, J.; Couret, C.; Pujol, L.; Tordo, P. J. Am. Chem. Soc. **1986**, 108, 3130–3132.

(4) Bard, A. J.; Cowley, A. H.; Kilduff, J. E.; Leland, J. K.; Norman, N. C.; Pakulski, M.; Heath, G. A. J. Chem. Soc., Dalton Trans. 1987, 249–251.

(5) Cetinkaya, B.; Hudson, A.; Lappert, M. F.; Goldwhite, H. J. Chem. Soc., Chem. Commun. **1982**, 609–610.

(6) (a) Shah, S.; Burdette, S. C.; Swavey, S.; Urbach, F. L.; Protasiewicz, J. D. Organometallics **1997**, *16*, 3395–3400. (b) Dutan, C.; Shah, S.; Smith, R. C.; Choua, S.; Berclaz, T.; Geoffroy, M.; Protasiewicz, J. D. Inorg. Chem. **2003**, *42*, 6241–6251.

(7) Sasaki, S.; Aoki, H.; Sutoh, K.; Hakiri, S.; Tsuji, K.; Yoshifuji, M. *Helv. Chim. Acta* **2002**, *85*, 3842–3847.

(8) (a) Nagahora, N.; Sasamori, T.; Takeda, N.; Tokitoh, N. *Chem.*— *Eur. J.* **2004**, *10*, 6146–6151. (b) Sasamori, T.; Mieda, E.; Nagahora, N.; Takeda, N.; Takagi, N.; Nagase, S.; Tokitoh, N. *Chem. Lett.* **2005**, *34*, 166–167. (c) Sasamori, T.; Tsurusaki, A.; Nagahora, N.; Matsuda, K.; Kanemitsu, Y.; Watanabe, Y.; Furukawa, Y.; Tokitoh, N. *Chem. Lett.* **2006**, *35*, 1382–1383. (d) Sasamori, T.; Tsurusaki, A.; Nagahora, N.; Matsuda, K.; Kanemitsu, Y.; Watanabe, Y.; Furukawa, Y.; Tokitoh, N. *Chem. Lett.* **2006**, *35*, 1382–1383. (e) Sasamori, T.; Mieda, E.; Nagahora, N.; Sato, K.; Shiomi, D.; Takui, T.; Hosoi, Y.; Furukawa, Y.; Takagi, N.; Nagase, S.; Tokitoh, N. *J. Am. Chem. Soc.* **2006**, *128*, 12582–12588. (f) Nagahora, N.; Sasamori, T.; Watanabe, Y.; Furukawa, Y.; Tokitoh, N. *Bull. Chem. Soc. Jpn.* **2007**, *80*, 1884–1900. (g) Nagahora, N.; Sasamori, T.; Hosoi, Y.; Furukawa, Y.; Tokitoh, N. *J. Organomet. Chem.* **2008**, *693*, 625–632. (h) Sasamori, T.; Hori, A.; Kaneko, Y.; Tokitoh, N. *New J. Chem.* **2010**, *34*, 1560–1564.

(9) Moser, C.; Nieger, M.; Pietschnig, R. Organometallics 2006, 25, 2667–2672.

(10) Tsuji, K. S.; Sasaki, S.; Yoshifuji, M. Tetrahedron Lett. **1999**, 40, 3203–3206.

(11) Schoeller, W. W.; Niemann, J.; Thiele, R.; Haug, W. Chem. Ber. 1991, 124, 417–21.

(12) (a) Geoffroy, M.; Jouaiti, A.; Terron, G.; Cattani-Lorente, M.; Ellinger, Y. J. Phys. Chem. 1992, 96, 8241–8245. (b) Jouaiti, A.; Geoffroy, M.; Terron, G.; Bernardinelli, G. J. Chem. Soc., Chem. Commun. 1992, 155–156. (c) Jouaiti, A.; Geoffroy, M.; Terron, G.; Bernardinelli, G. J. Am. Chem. Soc. 1995, 117, 2251–2258. (d) Jouaiti, A.; Al Badri, A.; Geoffroy, M.; Bernardinelli, G. J. Organomet. Chem. 1997, 529, 143–149. (e) Al Badri, A.; Jouaiti, A.; Geoffroy, M. Magn. Reson. Chem. 1999, 37, 735–742. (f) Rosa, P.; Gouverd, C.; Bernardinelli, G.; Berclaz, T.; Geoffroy, M. J. Phys. Chem. A 2003, 107, 4883–4892. (g) Gouverd, C.; Brynda, M.; Berclaz, T.; Geoffroy, M. J. Organomet. Chem. 2006, 691, 72–78.

(13) (a) Oberg, E.; Schäfer, B.; Geng, X.-L.; Pettersson, J.; Hu, Q.; Kritikos, M.; Rasmussen, T.; Ott, S. J. Org. Chem. 2009, 74, 9265–9273. (b) Schäfer, B.; Öberg, E.; Kritikos, M.; Ott, S. Angew. Chem., Int. Ed. 2008, 47, 8228–8231. (c) Geng, X.-L.; Hu, Q.; Schäfer, B.; Ott, S. Org. Lett. 2010, 12, 692–695. (d) Geng, X. L.; Ott, S. Chem. Commun. 2009, 7206–7208.

(14) (a) Sasaki, S.; Murakami, F.; Yoshifuji, M. Angew. Chem., Int. Ed.
1999, 38, 340–343. (b) Murakami, F.; Sasaki, S.; Yoshifuji, M. J. Am.
Chem. Soc. 2005, 127, 8926–8927. (c) Murakami, F.; Sasaki, S.;
Yoshifuji, M. Angew. Chem., Int. Ed. 2002, 41, 2574–2576.

(15) Gudimetla, V. B.; Ma, L.; Washington, M. P.; Payton, J. L.; Cather Simpson, M.; Protasiewicz, J. D. *Eur. J. Inorg. Chem.* **2010**, 854–865.

(16) Back, O.; Celik, M. A.; Frenking, G.; Melaimi, M.; Donnadieu, B.; Bertrand, G. J. Am. Chem. Soc. **2010**, *132*, 10262–10263.

(17) Washington, M. P.; Gudimetla, V. B.; Laughlin, F. L.; Deligonul, N.; He, S.; Payton, J. L.; Simpson, M. C.; Protasiewicz, J. D. J. Am. Chem. Soc. **2010**, 4566–4567.

(18) (a) Heinicke, J.; Tzschach, A. Z. Chem. **1980**, 20, 342–343. (b) Heinicke, J.; Tzschach, A. Phosphorus Sulfur Relat. Elem. **1985**, 25, 345–356.

(19) (a) Elschenbroich, C.; Nowotny, M.; Metz, B.; Massa, W.; Graulich, J.; Biehler, K.; Sauer, W. Angew. Chem. Int., Ed. Engl. 1991, 30, 547. (b) Elschenbroich, C.; Baer, F.; Bilger, E.; Mahrwald, D.; Nowotny, M.; Metz, B. Organometallics 1993, 12, 3373–3378. (c) Le Floch, P.; Carmichael, D.; Ricard, L.; Mathey, F. Organometallics 1992, 11, 2475–2479. (d) Cataldo, L.; Choua, S.; Berclaz, T.; Geoffroy, M.; Mezailles, N.; Ricard, L.; Mathey, F.; Le Floch, P. J. Am. Chem. Soc. 2001, 123, 6654–6661. (e) Huy, N. H. T.; Donnadieu, B.; Mathey, F. Organometallics 2007, 26, 6497–6500.

(20) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*; Wiley: New York, 2001.

(21) Andrieux, C. P.; Badoz-Lambling, J.; Combellas, C.; Lacombe, D.; Saveant, J. M.; Thiebault, A.; Zann, D. J. Am. Chem. Soc. 1987, 109, 1518–1525.

(22) Hawley, M. D. In *Encyclopedia of Electrochemistry of the Elements, Organic Section*; Bard, A. J., Lund, H., Eds.; Dekker: New York, 1980; Vol. 14.

(23) Becker, J. Y. In *The Chemistry of Functional Groups, Supplement* D; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1983, pp 203–285.

(24) Sease, J. W.; Burton, F. G.; Nickol, S. L. J. Am. Chem. Soc. 1968, 90, 2595–2598.

(25) Cheng, T. C.; Headley, L.; Halasa, A. F. J. Am. Chem. Soc. 1971, 93, 1502–1503.

(26) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian 03, revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.

(27) Spartan'08, V1.2.1; Wavefunction, Inc.: Irvine, CA. Li, B.; Matsuo, T.; Hashizume, D.; Fueno, H.; Tanaka, K.; Tamao, K. J. Am. Chem. Soc. **2009**, 131, 13222–13223.

(28) (a) Wright, V. A.; Gates, D. P. Angew. Chem., Int. Ed. 2002, 41, 2389–2392. (b) Wright, V. A.; Patrick, B. O.; Schneider, C.; Gates, D. P. J. Am. Chem. Soc. 2006, 128, 8836–8844.

(29) (a) Smith, R. C.; Chen, X.; Protasiewicz, J. D. Inorg. Chem. 2003, 42, 5468–5470. (b) Smith, R. C.; Protasiewicz, J. D. J. Am. Chem. Soc. 2004, 126, 2268–2269.

(30) Li, B.; Matsuo, T.; Hashizume, D.; Fueno, H.; Tanaka, K.; Tamao, K. J. Am. Chem. Soc. **2009**, 131, 13222–13223.