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Synthesis of a Trivalent *P*-Chloro-Dithienophosphole and its Reactivity with Organometallic Reagents

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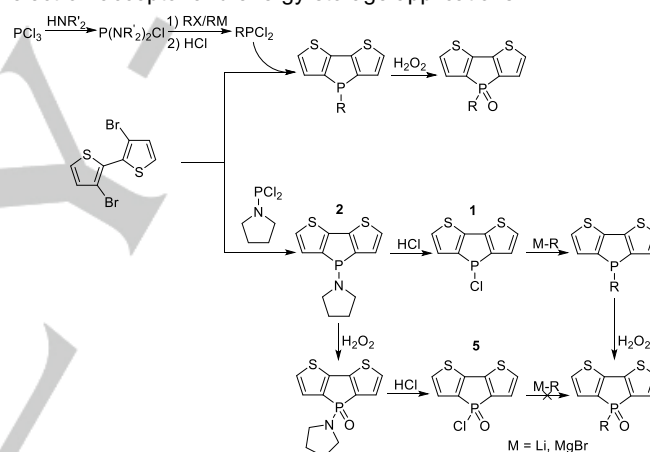
Dedicated to Koop Lammertsma and Edgar Niecke on the occasion of their 70th and 80th birthdays, respectively

Abstract: *P*-chloro-dithieno[3,2-*b*:2',3'-*d*]phosphole was synthesized and isolated from the reaction of an aminophosphole and HCl. Developed to act as a common starting material for *P*-functionalized phospholes, the compound exhibits a surprising reactivity by generating dimeric biphospholes. Despite this apparent sensitivity, when reacting with organolithium and Grignard reagents, a series of differently *P*-functionalized dithieno[3,2-*b*:2',3'-*d*]phospholes was accessible. Unexpectedly, organolithium reagents showed reduced reactivity with the chlorophosphole, limiting yields of the desired products due to the competing dimerization. Nonetheless, *P*-functionalized phospholes were isolated from reactions of the title compound with both Grignard and organolithium reagents in yields equivalent to, or higher, than by previous methods. A bithiophene-bridged bisphosphole system was also successfully synthesized without the necessity of generating a bis(dichlorophosphino) reagent. Finally, the isolated *P*-functionalized phospholes were analyzed for their photophysical properties. In general, these compounds are strong absorbers in the UV/visible range of the optical spectrum. The phospholes' emissions were consistent with several previously reported, however, with low quantum yields.

Introduction

Over the past decade, dithieno[3,2-*b*:2',3'-*d*]phospholes have developed into unique and versatile building blocks for organoelectronic materials.^{[1],[2]} One of the advantages of phospholes is the structural diversity afforded by the phosphorus center. Unlike its close relative, pyrrole, the phosphorus lone pair in phosphole does not contribute significantly to the overall conjugation of the ring system due to its strong *s* character.^[3] This makes the lone pair conveniently accessible for chemical modifications that can significantly modulate the optoelectronic as well as morphological properties of the system. At the same time, due to the weakly aromatic nature of the phosphole ring, the dithieno[3,2-*b*:2',3'-*d*]phosphole scaffold can be viewed as a phosphorus bridged bithiophene. As such, thiophene chemistry is also available for dithienophospholes.^[2]

The exocyclic R group attached via a σ bond is one of the most unique features of phospholes. In fact, the weak aromaticity of phospholes comes from the hyperconjugation of the σ orbital of the exocyclic P-R fragment with the π system of the butadiene.^[4] Consequently, the nature of the exocyclic substituent has a significant impact on the electronic properties of the phosphole. Similarly, but more importantly, the anti-bonding σ^* orbital also conjugates with the π^* orbital of the conjugated backbone; this provides a convenient handle for tuning the lowest unoccupied molecular orbital (LUMO) of phospholes. The lower LUMO levels make phospholes an attractive building block for electron-acceptor and energy-storage applications.^[4-11]



Scheme 1. Synthetic routes to *P*-functionalized dithienophospholes.

Modifying the exocyclic R-substituent has been demonstrated previously.^[2] The most common route requires the synthesis of the corresponding dichlorophosphane before formation of the phosphole ring. Each subsequent R-substituent requires the synthesis of a new chlorophosphane, and a separate ring-closing phosphole synthesis (Scheme 1, top), which limits the utility from an optoelectronic material standpoint. Nonetheless, the method has proven successful for the introduction of a varied array of R substituents, including bridged bisphospholes.^{[12],[13]} The required precursor limits the possible heteroatoms and functional groups in the substituent, and is significantly hindered by purification.^[14]

Another method for the introduction of R substituents is the direct functionalization of a *P*-halogen compound. *P*-substituted phosphanes can be easily constructed by reacting chlorophosphanes with organometallic reagents, such as Grignard and organolithium species.^[15] If the phosphole were to be constructed with a halogen substituent at the R position, it could be functionalized easily. This approach has been established by the Mathey group and generated a variety of *P*-substituted phospholes, via a *P*-cyanophosphole.^{[16],[17]} On the other hand, the reductive cleavage employed as the first step in

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this protocol proved to be incompatible with our dithienophosphole building block.

Amino protecting groups have been used in organophosphorus chemistry routinely to produce asymmetrically substituted phosphanes. Post functionalization, the amino-group can be conveniently converted to a chloro substituent by treatment with anhydrous HCl. If an amino-group were to be introduced at the exo-cyclic R position of the dithienophosphole building block, the corresponding chlorophosphole could be synthesized (Scheme 1, center).

Using this methodology, our group recently reported the *P*-chloro-dithienophosphole oxide **5** (Scheme 1, bottom).^{[18],[19]} Reactions of this compound, while generally successful with amines and alcohols, unfortunately, resulted in a ring-opening of the phosphole unit with organometallic reagents,^[19] as the phosphole oxide reacts similarly to a carbonyl with organometallic reagents.^[20] We, therefore sought the trivalent *P*-chlorophosphole derivative as a simple building block for *P*-functionalized dithienophospholes.

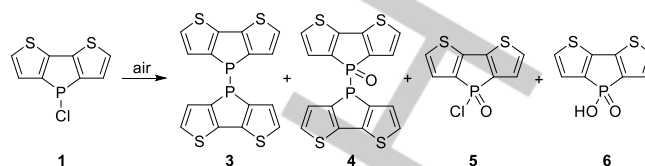
Results and Discussion

Synthesis of the trivalent chlorophosphole **1**

The first step for the generation of **1** was the synthesis of an aminophosphole. The pyrrolidinyl-substituted dithienophosphole **2** was chosen, as we recently reported that the pyrrolidinyl phosphole allows further functionalization of the phosphorus center via phosphorus chemistry, and can be synthesized in good yields.^[21] Originally, the *P*-pyrrolidinyl-dithienophosphole had been isolated as an oil that was 95% pure by NMR spectroscopy.^[21] However, with a slight modification, this precursor phosphole can be isolated as a pure solid: After the solvent removal, the concentrate was taken up in pentane and the suspension filtered through a plug of celite. The resulting solution was concentrated and chilled to 0 °C, resulting in a pure yellow solid that precipitated from solution.

At 0 °C and under an argon atmosphere, an ether solution of HCl was added to a stirring ether solution of the **2**, resulting in the rapid generation of the pyrrolidine-HCl salt. The solution was left to warm to room temperature and stirred for 5 hours, after which the salt was removed via cannula filtration. Upon concentration, the product chlorophosphole, was isolated as a yellow solid in quantitative yield. Compound **1** exhibited a single resonance, at δ 34.0 ppm by ³¹P NMR spectroscopy, which is more deshielded than (but consistent with) the related phosphole 5-chlorodibenzo[*b,d*]phosphole.^[22] The ¹H NMR spectrum exhibited only the bithiophene resonances, with no evidence of any residual pyrrolidine species. Extending the reaction time unexpectedly resulted in the formation of the recently reported biphosphole **3** (Scheme 2) as evidenced by the ³¹P NMR shift δ -37.0 ppm.^[21] While surprising at first, such dimerization is not unprecedented. In the early 1980's, the Mathey group generated 1,1'-biphosphole systems by reacting lithiophospholes with iodine, *N*-bromosuccinimide, or other similar brominating agents (Scheme 3, top).^[23] More recently, Réau et. al. showed that substituted 1,1'-biphospholes could be synthesized by generating the bromophosphole through a Fagan-Nugent reaction. By using phosphorus tribromide in the Fagan-Nugent reaction, the isolated

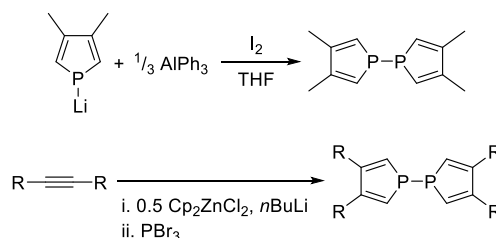
product is the 1,1'-biphosphole instead of the originally expected bromophosphole (Scheme 3, bottom).^[24] It is thus inherently plausible that the reaction conditions enable a related process in our case as well.



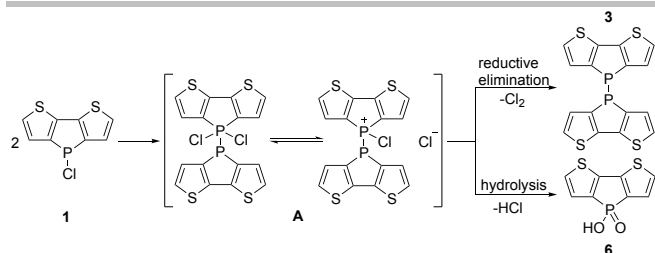
Scheme 2. Decomposition products of **1** upon exposure to air.

Notably **1** decomposes rapidly, and within as little as 15 minutes, in a sealed NMR tube. Additional resonances in the ³¹P{¹H} NMR spectrum include a resonance at δ -37 ppm, as well as a pair of doublets δ 29.7 and -48.0 ppm (*J* = 208 Hz). To determine the nature of this apparent decomposition, an ether solution of **1** was sealed at room temperature under argon with only a rubber septum and monitored by ³¹P NMR spectroscopy. After 48 hours, no trivalent chloride **1** remained in solution, instead several phosphorus resonances were present corresponding to the dithienophosphole dimer **3** (δ -37.0 ppm)^[21] the singly oxidized dithienophosphole dimer **4** (δ -50.6 ppm, d, *J*_{P-P} = 208 Hz, 35.4 ppm, d, *J*_{P-P} = 208 Hz),^[21] *P*-chloro-dithienophosphole oxide **5** (δ 17.3 ppm),^{[18],[19]} and *P*-hydroxy-dithienophosphole oxide **6** (δ 22.9 ppm),^[18] suggesting both a rapid and complex reactivity with even low levels of dioxygen and water (Scheme 2). However, none of these oxidation or hydrolysis products were consistent with the asymmetric dimer found in the sealed NMR sample. Based on the ³¹P NMR data that suggest the presence of a trivalent and a pentavalent phosphorus center that are directly linked, we propose the molecular structure **A** (Scheme 4) for this new dimer observed in the sealed NMR sample. Unfortunately, all attempts to isolate and identify the asymmetric dimer were unsuccessful, as they always resulted in the formation of dithienophosphole dimer **3** and corresponding decomposition products (primarily **4** and **6**). Moreover, addition of hydrogen peroxide to a solution containing the asymmetric dimer, results in the generation of the acid compound **6**, as indicated by the ³¹P NMR resonance at δ 22.9 ppm.

Due to the high reactivity of **1**, long term storage is thus not recommended, and the reagent should be prepared as needed and used immediately.



Scheme 3. Alternate phosphole dimerization reactions utilizing *P*-halophospholes



Scheme 4. Formation of dimer **3** and the hydrolysis product **6** via proposed intermediate dimer **A**.

To better understand the reactivity of **1**, the radical cation of the chlorophosphole (**7**) was modelled computationally. Using the Gaussian 09 software package^[25] compound **1** was optimized using DFT at the B3LYP/6-31G* level, in order to calculate the composition of the SOMO and its energy. The calculated SOMO energy can be used to predict the reactivity of trivalent phosphanes with dioxygen, and can predict the pyrophoric nature of the phosphane^[26]. A stable radical cation correlates to higher oxygen reactivity, while the SOMO subsisting of a contribution from the phosphorus lone pair is found in less reactive systems, specifically for tertiary phosphanes. The SOMO of **7**, as shown in Figure 1 has virtually no contribution from the phosphorus center and has an energy of -11.0 eV. This energy is consistent with the SOMO levels of triethyl- and trimethylphosphane, suggesting the chlorophosphole **1** will readily react with dioxygen under ambient conditions, and should be treated as pyrophoric.^[26]

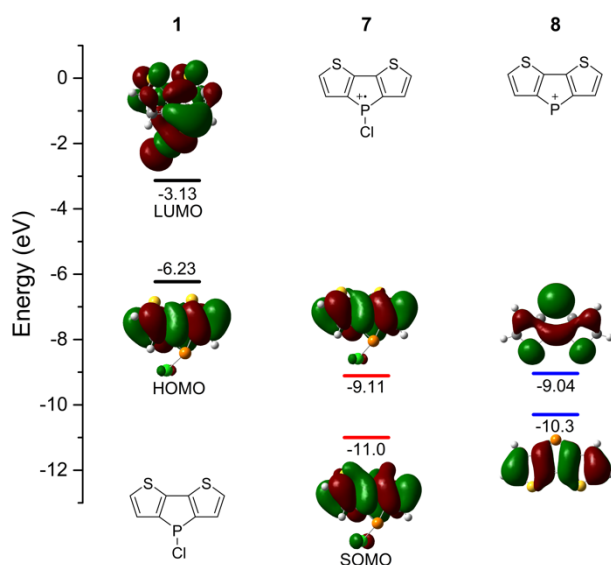


Figure 1. Calculated frontier molecular orbitals of neutral **1**, its radical cation **7**, and the phosphonium cation **8**.

Furthermore, the phosphonium cation **8**, which is another plausible intermediate, was calculated using the same parameters to compare the calculated HOMO and LUMO of **1**. The HOMO and LUMO of the phosphonium cation, as shown in Figure 1. Expectedly the HOMO consists of the bithiophene π system with an energy of -10.3 eV, while the LUMO has a significant contribution from the phosphorus p orbital. With an energy of -9.0 eV the LUMO of the phosphonium cation is 0.1 eV higher in energy than that of the LUMO of the radical cation, which

resides predominantly on the σ^* orbital. This suggests that upon dissociation of the chloride, the phospholenium **8** may react more slowly with nucleophiles when compared to a radical mechanism, as would be the case with dioxygen. This is also supported by the reduced reactivity toward nucleophiles in our *P*-functionalization reactions (*vide infra*).

P-functionalization via organometallic reagents

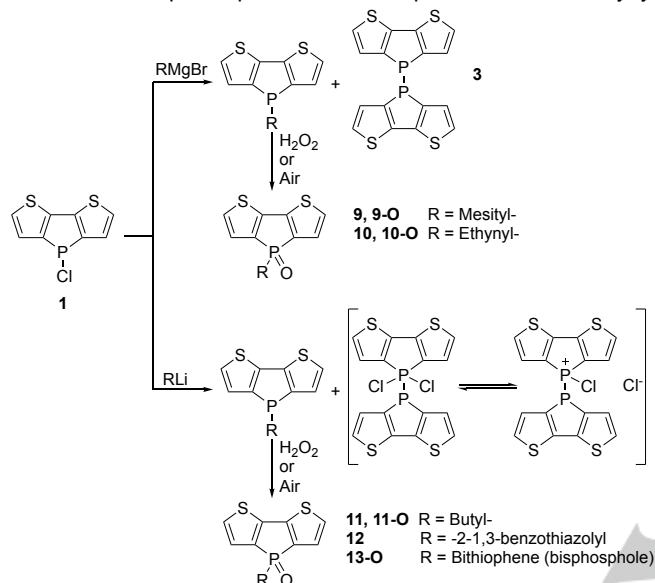
To explore the utility of the trivalent chlorophosphole as a functional building block, reactions between **1** and both Grignard and organolithium reagents were performed.

The first organometallic reagent investigated was mesitylmagnesium bromide. As an aromatic hydrocarbon, the mesityl substituted phosphole could be measured against the wide range of known aromatic hydrocarbon substituted dithienophospholes, allowing for a standard by which the utility of **1** can be compared to previous synthetic methods. The reaction between **1** and mesitylmagnesium bromide generated a yellow opaque solution after 16 hours. The solution was filtered and concentrated to yield a yellow solid. The ³¹P NMR spectrum exhibited a single peak at δ -35.2 ppm for the product, more shielded than that of the trivalent *P*-phenyl-dithienophosphole, and *P*-4'-*t*-butylphenyl-dithienophosphole at δ -21.5 and -22.5 ppm, respectively,^[27] but less shielded than *P*-pentafluorophenyl-dithienophosphole at δ -51.3 ppm.^[12] The shift is also consistent with that of *P*-mesityl functionalized *P,S*-bridged *trans*-stilbene at δ -33.4 ppm.^[28] By ¹H NMR spectroscopy, however, two compounds persisted, the *P*-mesityl-dithienophosphole, and unreacted mesitylmagnesium bromide. The residual Grignard was readily removed via filtration through celite in ether, yielding the **9** in 36% yield. This yield was not a significant improvement over that of the traditional method. While unreacted Grignard reagent was present in the crude product, the chlorophosphole **1** was completely consumed. The reason for the low yield and unreacted mesitylmagnesium bromide became clear by NMR spectroscopic analysis of the previously removed precipitate. Two phosphorus species were present in the precipitate, biphosphole **3** (Scheme 5), and corresponding monoxide **4**. The presence of these byproducts suggests that the dimerization of the chlorophosphole occurs even in the presence of an organometallic reagent as a competing reaction, which is in line with the DFT calculations (*vide supra*). Compound **9** rapidly oxidizes in solution. Samples prepared for investigation of photophysical properties would oxidize within five minutes. The phosphole oxide **9-O** could also deliberately be generated by addition of hydrogen peroxide, or by exposure of a solution to air over the course of 36 hours.

To determine if a different Grignard reagent may afford a more rapid reaction with the chlorophosphole, so as to hopefully limiting the generation of the dimeric byproducts, reaction with a second Grignard reagent was investigated. To emphasize the utility of the *P*-chlorodithienophosphole **1** as a building block, ethynylmagnesium bromide was chosen. By being able to quickly synthesize an ethynyl phosphole, subsequent functionalization via "click" chemistry could potentially be performed.^[14] Our lab has recently reported the synthesis and reactivity of *P*-ethynyl-dithienophosphole, **10**, synthesized through the traditional route utilizing an alkynyl dichlorophosphane.^[14] The reaction between the phosphane and the dilithiobithiophene to generate the phosphole, required the use of a silyl protecting group on the

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alkyne. The deprotection of the ethynyl group proved challenging, which along with the difficult isolation of the phosphole lowered the overall yield of the ethynyl functionalized phosphole. The reaction between **1** and ethynylmagnesium bromide, ultimately generated **10**, as a dark orange oil, consistent with the previously reported characterization in 60% yield, however, as with the synthesis of **9**, the yield was lower as a result of the competing reaction of the generation of **3**. Nonetheless, the product could be isolated in an improved yield over the traditional synthesis method and in fewer steps, as protection and deprotection of the ethynyl



group was not necessary.

Scheme 5. Products and dimers generated during the reaction of **1** and Grignard or organolithium reagents.

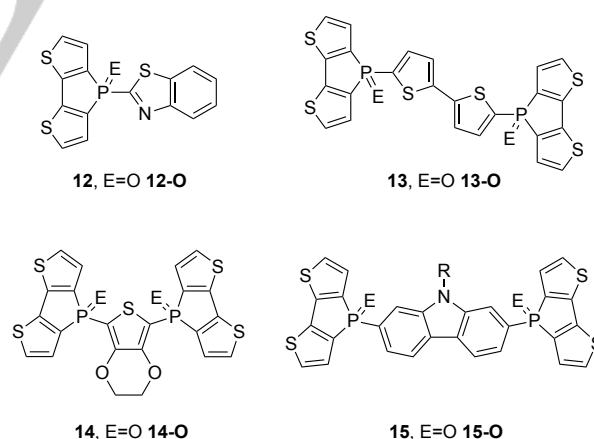
While **1** indeed successfully reacts with Grignard reagents to provide *P*-functionalized phospholes for both aryl and alkynyl reagents, the reactions also compete with the dimerization of **1** leading to overall reduced isolated yields. Considering these competing reactions, however, we surmised that the more nucleophilic carbon center of an organolithium reagent would be able to react more rapidly with **1**, thereby limiting the generation of **3** as a competing product.

We then proceeded with the investigation of the reaction between **1** and organolithium reagents, starting with *n*-butyllithium. The addition of *n*-butyllithium to an ether solution of **1** at 0 °C resulted in the rapid generation of a precipitate, however, it required 14 hours before the chlorophosphole **1** was no longer detected by ³¹P NMR spectroscopy. However, upon complete consumption of **1**, the ³¹P NMR spectra exhibited additional resonances corresponding to the above-mentioned asymmetric dimer **A** (Scheme 5). Nonetheless, the desired product **11** could be isolated in 44% yield after filtering from a pentane solution. As with the Grignard reagents, the yield was limited by the competing dimer formation. The butylated phosphole was identified by the ³¹P NMR resonance at δ -23.0 ppm. The alkyl phosphole surprisingly demonstrated no visible emission under UV light, which is in stark contrast to the *P*-aryl congeners.^[2] Moreover, the compound also exhibited an increased reactivity toward dioxygen and water in the atmosphere, which can be attributed to an increased Lewis basicity of the phosphorus center. The yield was limited by the slow, but evident reactivity between **11** and trace

water content in the dried solvent. Chlorinated solvents exhibited additional reactivity with the compound. Upon addition of hydrogen peroxide, *P*-butyl-dithienophosphole oxide **11-O** could be isolated after one hour. Unlike **11**, **11-O** exhibited visible fluorescence in both the solid and solution state. Surprisingly, after as little as 15 minutes, **11-O** also showed signs of reactivity with chlorinated solvents, as well as acetone and acetonitrile. Specifically, a chloroform solution of **11-O** exhibited several additional resonances in the ³¹P NMR spectrum, and generating a green-colored solution. A similar reaction occurred more slowly in methylene chloride, but still exhibited the generation of additional resonances during NMR spectroscopic experiments.

Theoretical Calculations

With the general utility of an organolithium protocol established, we then targeted a new set of *P*-functionalized dithienophospholes via this synthetic route. To determine suitable, and potentially value-added dithienophospholes, and to investigate the influence of the exocyclic substituent on the electronic properties of the dithienophosphole, a panel of four *P*-substituted dithienophosphole compounds were modelled computationally. DFT calculations were performed at the B3LYP/6-31G*(d) level using the Gaussian 09 software suite.^[25] The *P*-substituents, shown in Figure 2, cover a range of heterocyclic systems that may likely prove difficult to synthesize via the traditional phosphole synthesis due to the nature of the organic groups that are sensitive to the required reaction conditions. The benzothiazolyl-species bears promise for further functionalization of both the *N*- and *P*-centers, and the dimeric systems with a conjugated linker showed particular promise for desirable charge transfer properties. The calculated HOMO and LUMO energy levels for the four proposed phospholes are shown in Table S1 and, along with the frontier molecular orbitals, are



included in the Supporting Information.

Figure 2. *P*-functionalized phospholes and bisphospholes targeted as a result of theoretical computations (E = lone pair, O).

Efforts to synthesize the *P*-benzothiazole species

Lithiation of the 2-position of benzothiazole with butyllithium occurs almost immediately at -78 °C, as indicated by the color change of the solution to a bright orange.^[30] Upon addition of **1** in ether to the 2-lithio-1,3-benzothiazole solution, the color of the reaction mixture slowly changed from orange to yellow, and the solution became luminescent under UV light. When monitored by ³¹P NMR spectroscopy, however, the reaction required 18 hours

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until all chlorophosphole was consumed, as indicated by the loss of the resonance at δ 34.0 ppm. The product peak for **12** could be identified at δ -34.5 ppm, understandably further shielded than the *P*-mesityl-dithienophosphole **9**. Upon complete consumption of the starting material, however, several additional phosphorus-containing compounds were again present in the reaction mixture as a result of the self-reactivity of the starting material. After filtration of the precipitate, the crude product consisted of the benzothiazolyl-dithienophosphole product **12**, and unreacted benzothiazole, the separation of which proved inhibiting to the already low yielding reaction. Nonetheless, the crude product could be identified as a roughly 3:1 ratio of benzothiazole to the phosphole. The crude mixture of benzothiazole and **12** was taken up in chilled ether and filtered through celite. The filtrate was then slowly evaporated, affording the precipitation of the benzothiazole as a solid. The mother liquor was extracted via syringe and concentrated to yield a yellow residue that slowly solidified in < 5% yield, and in several instances still contained a mixture of **12** and 2*H*-benzothiazole.

Due to the difficulties in isolating **12**, hydrogen peroxide was added directly to the reaction mixture to afford the corresponding phosphole oxide. By ^{31}P NMR spectroscopy, however, instead of the conversion to **12-O**, only *P*-hydroxy-dithienophosphole oxide **6** could be detected.

Efforts to synthesize bisphospholes

We then sought to generate a bisphosphole utilizing **1**, as such compounds are even more challenging to synthesize using the traditional approach. The first targeted spacer was 5,5'-2,2'-bithiophene to afford **13**. 5,5'-dibromobithiophene was first lithiated using a standard protocol. Afterwards, the dilithiated species was added to an ether solution of crude chlorophosphole **1** at 0°C. The solubility of the resulting product made it difficult to isolate from the proposed dimerization byproduct **A**. Therefore, hydrogen peroxide was added directly to the crude reaction mixture, affording **13-O** in 35% yield. However, **13-O** also exhibited very poor solubility, and characterization of the compound was limited. Nonetheless, the successful isolation demonstrated that bisphosphole compounds are accessible via the reaction between **1** and an organometallic reagent, providing an alternate route to the traditional method. This method afforded slightly improved yields, as it does not require necessity to undergo two phosphole ring-closures in a single reaction.^[13]

With the successful isolation of a bithiophene bridged bisphosphole **13-O**, we surmised that an ethylenedioxythiophene (EDOT) linker would have similar reactivity, but create a more soluble, yet rigid compound with potentially improved emissive properties. The reaction with 2,5-dilithio-EDOT, prepared from the lithiation of 2,5-dibromo-EDOT, however, proved significantly less successful than that with 5,5'-dilithiobithiophene. After 48 hours, the reaction mixture consisted predominantly of the proposed asymmetric dimer **A** discussed above and **1** with virtually no *P*-functionalized phosphole **14** detected by ^{31}P NMR spectroscopy. Continuation of the reaction only resulted in the complete conversion of the starting material to a mixture of **3** and **A**.

Continuing to pursue our original target compounds, the attempt to install a carbazole linker (**15**) proved even more challenging, and the reaction with two equivalents of **1** and *N*-dodecyl-2,7-dilithiocarbazole, prepared from the *N*-dodecyl-2,7-

dibromo-carbazole was ultimately also unsuccessful. The reaction was run over 36 hours, and when monitored by ^{31}P NMR spectroscopy, slowly generated what was proposed to be the first and second addition of phosphole to the carbazole, as indicated by the shifts at δ -21.7, and -22.7 ppm respectively. The major phosphorus containing product, however, was again biphosphole **3**, consisting of over 90% of the phosphorus containing species in solution with less than five percent of the starting material reacting with the lithiocarbazole. While removal of **3** was successful by filtering a chilled ether solution of the crude product through a plug of celite, the resulting mixture consisted predominantly of unreacted carbazole. A method for separating the unreacted carbazole from the phosphole product without destruction of the phosphole **15** (or **15-O**) could unfortunately not be developed.

To our general dissatisfaction, organolithium reagents proved far less effective for the synthesis of *P*-functionalized species via the *P*-chloro-dithienophosphole **1**. Somewhat unexpectedly, the reactions occurred more slowly than those with Grignard reagents, and predominantly resulted in the occurrence of the competing dimerization of **1**. This was significantly more prevalent with more conjugated, and thereby more stable organolithium reagents, which was again supported by our DFT computational results. Attempts to mitigate the self-reactivity of the chlorophosphole **1** through variation of concentration or temperature were unsuccessful. While a dilute solution of the chlorophosphole did reduce the amount of the dimeric species formed in solution, the reaction of the chlorophosphole with the organometallic was further slowed. As compound **1** does indeed demonstrate reactivity with organometallic reagents without compromising the phosphole backbone, it is a valuable reagent for developing a variety of *P*-functionalized-dithienophospholes in principle. Without a method to inhibit the self-reactivity, however, practical use of the reagent is limited at this point.

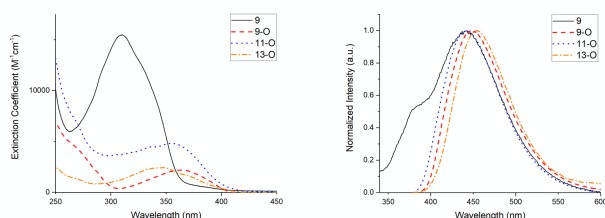
Table 1. Photophysical data of isolable *P*-functionalized phospholes in CH_2Cl_2

Compound	λ_{ex} (nm)	ϵ ($\text{M}^{-1}\text{cm}^{-1}$)	λ_{em} (nm) ^[a]	Φ_{PL}
9	309	16000	441	3% ^[b]
9-O	365	2100	453	79% ^[b]
10 ^[c]	282 329	7800 9200	423	35%
10-O ^[c]	372	5700	459	69%
11-O	339 353	4500 4800	441	45% ^[b]
13-O	349	2800	447	5% ^[c]

[a] Excited at λ_{ex} . [b] Measured as an absolute value using an integrating sphere excited at λ_{ex} . [c] Measured as a relative value against quinine sulfate excited at 365 nm. [d] Data from previous report [14].

Photophysical Properties

The absorption and emission spectra for the isolated *P*-functionalized phospholes are shown in Figure 3, and their photophysical properties are presented in Table 1 along with data previously reported for *P*-ethynyl-dithienophosphole **10**.^[14] In general, the absorbance of the generated phospholes is consistent with previously studied phospholes, such as *P*-phenyl-dithienophosphole ($\lambda_{\text{ex}} = 338 \text{ nm}$).^[27] Mesityl-dithienophosphole **9**, however, had a uniquely blue shifted absorption, which can be attributed to a different phosphorus geometry, induced by the bulky mesityl substituent, which impacts the $\sigma^*-\pi^*$ interaction.^{[4],[28],[30]} Consistent with previous dithienophospholes, the absorption maximum is red-shifted by approximately 30 nm between the trivalent and oxidized species. All species are strong absorbers with extinction coefficients ranging from 2800 to 16000 $\text{M}^{-1}\text{cm}^{-1}$. Fluorescent emissions were red-shifted in comparison to *P*-phenyl-dithienophosphole. The oxides, with the exception of **13-O** exhibited a significant increase in quantum yield with respect to the trivalent species. This is likely due to rotational/vibrational flexibility arising from the *P*-substituents,^[30] or the presence of



competing chromophores, respectively.^[31]

Figure 3. Absorption (left) and normalized emission (right) spectra of phospholes **9**, **9-O**, **11-O**, and **13-O**.

Conclusions

Dithieno[3,2-*b*:2',3'-*d*]phospholes have proven to be robust building blocks for organic electronic materials. While modification of the bithiophene backbone has been thoroughly investigated, functionalization of the exocyclic *R*-substituent has been previously hindered by the accessibility of the required dichlorophosphanes. By utilizing a chlorine-substituted dithienophosphole, functionalization of the exocyclic ring becomes possible with Grignard reagents, and moderate to good yields can be achieved. In addition, the compounds can be used for further modification via standard phosphorus chemistry avenues. Due to the high reactivity of the compound, including with dioxygen, water, and itself, compound **1** appears to have only limited utility as a universal starting material for *P*-functionalization. Reactions with organolithium reagents are slow, resulting in the generation of several, primarily dimeric products from competing reactions of the starting material. These reactions are further limited by difficult isolation of the products. Nonetheless, several new phosphole and phosphole oxides have been generated. In general, these compounds exhibit strong absorption of UV and visible light but are poor emitters with low quantum yields. Further investigation of **1**, and in particular its unexpected self-reactivity, may allow for development of a method to limit the generation of dimeric species, further enforcing its utility as a common building block for *P*-functionalized dithienophosphole species.

Experimental Section

General Considerations

Unless otherwise stated, all manipulations were performed under an argon atmosphere using standard Schlenk techniques. Solvents were dried with an MBraun Solvent Purification System. Unless stated otherwise, all starting materials were used as received. ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker DRX400, or Avance (II, III) 400 spectrometers tuned to 399.8 MHz, 100.4 MHz, and 162.0 MHz respectively. ^1H and ^{13}C NMR shifts were referenced to residual solvent protons. ^{31}P NMR chemical shifts were referenced externally to 85% H_3PO_4 . UV/Visible absorption measurements were performed on a Cary 5000 spectrophotometer. Fluorescence measurements were made with either a Jasco FP-6600 Fluorometer equipped with an IDF-513 integrating sphere, or an Edinburgh Instruments FS-5 spectrofluorometer and corresponding FS-30 integrating sphere. High resolution mass spectra were measured using a Finnigan SSQ 7000 spectrometer or a Bruker Daltonics AutoFlex III system. Elemental analysis was performed using an Elementar vario EL cube. DFT calculations were performed at the B3LYP/6-31G*(d) level using the GAUSSIAN 09 software suite.^[25]

Synthesis of 2: A flask containing a solution of 3,3'-dibromo-2,2'-bithiophene (6.33 g, 19.5 mmol) in a 2:1 ratio of ether:THF (300 mL) was stirred until all solid fully dissolved. The flask was then chilled in an ethyl acetate/liquid nitrogen bath. Upon chilling, *n*-butyllithium (1.6 M in hexanes, 25 mL, 40 mmol) was added slowly via syringe. The solution stirred for 20 minutes, after which it was removed from the bath and let warm to room temperature after which it was allowed to stir an additional 20 minutes until the solution became a dark orange color. The flask was returned to an ethyl acetate/liquid nitrogen bath and chilled again. Pyrrolidinyldichlorophosphine (3.40 g, 19.7 mmol) was then added all at once to the solution. The flask was quickly removed from the cold bath and placed in a 30 °C water bath and the solution was stirred for 16 hours. The solution was concentrated to yield a brown solid, which was washed with pentane. The pentane solution was filtered through a column of celite to yield a clear yellow solution. The solution was concentrated to yield a yellow oil that upon chilling at (freezer temperature) solidified from a brown oil. The solid was taken up in ether, and separated from any residual oil. The ether solution was concentrated to yield **2** as a yellow solid (3.62 g, 69.9%). Characterization data were consistent with those previously reported.^[21]

Synthesis of 1: A flask was charged with ether (100 mL) and **2** (0.65 g, 2.5 mmol) and the solution stirred until all solid dissolved, generating a clear yellow solution. The solution was placed in an ice bath. Upon chilling, HCl (1.3 mL, 2 M in ether) was added dropwise via syringe. Each drop resulted in the generation of an orange solid that would slowly dissolve back into solution. After complete addition, the solution was cloudy with a yellow precipitate. The flask was removed from the bath, and stirred while warming to room temperature. The solution was stirred for 5 hours, and monitored via ^{31}P NMR spectroscopy. Upon complete consumption of **2** by NMR, the reaction was filtered via cannula filter, and the filtrate concentrated to yield **1** as a yellow solid (0.56g, 97%). ^1H NMR (400 MHz, CDCl_3) δ 7.29 (dd, $J = 5.0, 2.8 \text{ Hz}$, 2H), 7.25 (d, $J = 5 \text{ Hz}$, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 146.44 (d, $J = 31.2 \text{ Hz}$), 144.55, 127.32 (d, $J = 4.8 \text{ Hz}$), 126.97 (d, $J = 22.5 \text{ Hz}$); $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3) δ 34.0. HRMS (EI+) m/z : [M]⁺ calcd 229.9181, found 229.9176.

General reaction between 1 and Grignard reagents: A flask containing an ether solution of freshly prepared **1** at approximately 0.03 M was placed in an ice water bath. To the flask was added the Grignard reagent, drop-wise via syringe. The solution was stirred vigorously and warmed to room temperature. After warming, the solution was monitored by ^{31}P NMR spectroscopy until the shift at δ 34.0 ppm, corresponding to **1** was no longer present. The solution was then filtered via cannula filter, and

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concentrated. The concentrate was taken up in chilled ether ($\sim 0^\circ\text{C}$) and filtered through a plug of celite. The filtrate was concentrated to yield the corresponding product.

Synthetic data for **9**: **1**: 0.47 g, 2.0 mmol. Mesitylmagnesium bromide: 2.1 mL, 1 M in ether. **9**: 0.22 g, 0.71 mmol, yellow solid, 35% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.25 (t, $J = 2$ Hz, 2H), 7.09 (d, $J = 5$ Hz, 2H), 6.83 (2H), 2.25 (3H), 2.12 (6H); ^{13}C $\{^1\text{H}\}$ (100 MHz, CDCl_3) 146.2 (d, $J = 29$ Hz), 146.1 (d, $J = 6$ Hz), 140.7 (d, $J = 1$ Hz), 140.6 (d, $J = 7$ Hz), 128.8 (d, $J = 5$ Hz), 126.4 (d, $J = 19$ Hz), 125.9 (d, $J = 6$ Hz), 124.6 (d, $J = 19$ Hz), 21.6 (d, $J = 18$ Hz), 21.2; ^{31}P $\{^1\text{H}\}$ (162 MHz, CDCl_3) -35.2. Anal. calc'd for $\text{C}_{17}\text{H}_{15}\text{PS}_2$: C 64.94%, H 4.81%, S 20.39%.

Synthesis of **9-O**: To a stirring solution of 0.12 g (0.40 mmol) of **9** in methylene chloride under an inert atmosphere was added 0.05 mL of 30 wt% in water hydrogen peroxide (0.4 mmol) via syringe. The solution immediately began to bubble and transition from a yellow color to orange. After 1 hour, the solution was concentrated to yield **9-O** as an orange solid, 0.13 g, 0.39 mmol, 98%. ^1H NMR (400 MHz, CDCl_3) δ 7.24 (t, $J = 3$ Hz, 2H), 7.13 (m, 2H), 6.88 (d, $J = 3$ Hz, 2H), 2.39 (s, 6H), 2.27 (s, 3H); ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 145.4 (d, $J = 23$ Hz), 143.9 (d, $J = 12$ Hz), 141.9 (d, $J = 3$ Hz), 140.8 (d, $J = 109$ Hz), 131.4 (d, $J = 12$ Hz), 128.2 (d, $J = 15$ Hz), 126.2 (d, 15 Hz), 122.3 (d, $J = 104$ Hz), 22.9 (d, $J = 5$ Hz) 21.2; ^{31}P $\{^1\text{H}\}$ NMR (162 MHz, CDCl_3) δ 18.6. Anal. calc'd for $\text{C}_{17}\text{H}_{15}\text{OPS}_2$: C 61.80%, H 4.58%, S 19.41%. Found C 62.10%, H 4.02%, S 20.13%.

Synthetic data for **10**: **1**: 0.13 g, 0.57 mmol. Ethynylmagnesium bromide: 1.0 mL, 0.5 M in THF. **10**: 0.075 g, 0.34 mmol, 60%. Characterization data were consistent with those previously reported.^[14]

General reaction between **1** and organolithium reagents: As above with Grignard reagents, with the following modification. After filtration, the precipitate was washed with chloroform, which was also filtered via cannula filter. The ether and chloroform solutions were concentrated. The resultant residues were dissolved in dichloromethane, combined, and run through a plug of celite. The filtrate was concentrated to yield the corresponding product.

Synthetic data for **11**: **1**: 0.18 g, 0.80 mmol. *n*-Butyllithium: 0.32 mL, 2.5 M in hexanes. **11**: yellow solid, 0.089 g, 44%. ^{31}P NMR (162 MHz, CDCl_3) δ -22.7. **11** immediately began to oxidize forming an orange oil. The product mixture was dissolved in methylene chloride and 0.1 mL of hydrogen peroxide (30 wt% in water, 0.8 mmol) was added. The solution bubbled vigorously and was stirred for 1 hour. The solution was concentrated to yield an orange solid that was luminescent in the solid state. The solid, however, began to react with CDCl_3 during NMR spectroscopic analysis. ^{31}P $\{^1\text{H}\}$ NMR (162 MHz, CDCl_3) δ 30.6

Synthetic data for **13-O**: **1**: 0.78 g (3.4 mmol) of **1**. The addition of the dilithiobithiophene was performed at -78°C instead of 0°C . Instead of concentration of the trivalent product, excess H_2O_2 was added to the dichloromethane solution. Oxidation was carried out overnight. The dichloromethane solution was washed with brine then dried over anhydrous MgSO_4 . The solution was concentrated, and purification was achieved by column chromatography on silica (ethyl acetate). The product was obtained as a yellow powder (0.39 g, 35% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.55 (dd, $J = 8, 4$ Hz, 1H), 7.38 – 7.30 (m, 4H), 7.24 (dd, $J = 5, 3$ Hz, 2H), 7.20 (dd, $J = 4, 2$ Hz, 1H); ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 145.66 (d, $J = 26.5$ Hz), 143.32 (d, $J = 8$ Hz), 138.39 (d, $J = 119.6$ Hz), 137.04 (d, $J = 10$ Hz), 131.62, 128.66 (d, $J = 16$ Hz), 126.19 (d, $J = 14$ Hz), 125.86 (d, $J = 15$ Hz); ^{31}P $\{^1\text{H}\}$ NMR (162 MHz, CDCl_3) δ 8.27. HRMS (EI+) m/z : [M]⁺ calcd 585.8637, found 585.8634.

Supporting Information. DFT-computational data, NMR Spectra, and Optical Spectra of individual compounds are provided in the Supporting Information

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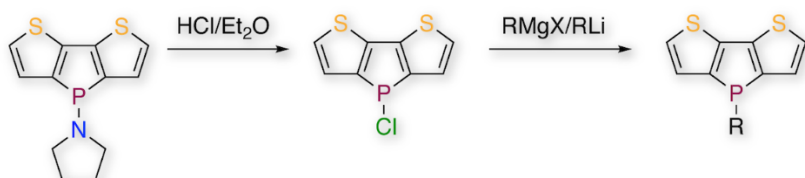
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**Phosphole Functionalization**

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Synthesis of a Trivalent *P*-Chloro-Dithienophosphole and its Reactivity with Organometallic Reagents

The synthesis of a *P*-chloro dithienophosphole is achieved from the corresponding *P*-amino precursor with HCl. The *P*-chloro species shows a surprisingly sluggish reactivity toward organometallic reagents and *P*-functionalization appears to compete with a dimerization reaction.