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# Reduction Behavior of Anisyl-substituted P-Ferrocenyl Phospholes

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P-Ferrocenylphospholes with differing substituents in  $\alpha$ -position have been synthesized and their identity and purity was confirmed using multinuclear NMR spectroscopy, MS, elemental analysis and single crystal X-ray diffraction. Furthermore, the redox properties have been explored with electrochemical measurements. Transferring the reduction to a preparative scale using lithium leads to reductive P–C bond cleavage

furnishing the corresponding phospholide which has been transformed to P-*tert*-butyl substituted phosphole. In addition to phospholide formation reductive demethoxylation with transformation of the anisyl substituent to its phenyl analog was observed. For comparison analogous reactions have been explored for the respective P-phenylphospholes which show a different reactivity.

## Introduction

Ferrocenylphosphanes are attractive ligands for transition metal complexes used for catalysis purposes.<sup>[1]</sup> One of the most popular bisphosphanylferrocene ligands is dppf (1,1'-bis-(diphenyl-phosphanyl)ferrocene) which was first described by Sollot *et al.* in 1965.<sup>[2]</sup> It served as a starting point for exploring its rich coordination chemistry,<sup>[3]</sup> which recently has been amended by that of more bulky dppf analogs.<sup>[4]</sup> Special characteristics of such compounds arise from their electronic properties as well as the redox activity of the ferrocene unit. Already 40 years ago, intervalence charge transfer processes have been observed in binuclear ferrocene derivatives and also electronic interactions of the iron atom in ferrocene containing ligands with the central atom in different complexes have been reported.<sup>[5]</sup> However, 1-ferrocenylphospholes are only rarely described. Mathey *et al.* discussed some synthetic approaches towards 1-ferrocenylphospholes, where the ferrocenyl unit is introduced post-synthetically to a precursor phosphole with a phosphorus halogen bond. On the contrary, Lang *et al.* prepared such compounds starting from ferrocenylphosphane according to the procedure by Märkl *et al.*, also with ferrocenyl groups in 2- and 5-position.<sup>[6]</sup> Based on previous observations that electron transfer between P(III) centers and adjacent cationic ferrocenium units may occur,<sup>[7]</sup> we set out exploring

the redox properties of 1-ferrocenylphospholes in comparison with their phenyl substituted counterparts.

## Results and Discussion

The Fagan-Nugent as well as the Sato-Urabe methods for synthesizing phospholes have been employed in the past successfully for 1-ferrocenylphospholes but limited the substitution pattern in the phosphole's  $\beta$ -position.<sup>[8]</sup> By contrast the lithiophosphanation of 1,3-diyne has recently been shown to give access to phospholes with more versatile variation of the substitution pattern at the phosphorus heterocycle.<sup>[9]</sup> Based on this approach we wanted to explore the synthesis of 1-ferrocenylphospholes to further investigate their general reactivity and redox properties in particular.

Targeted preparation of phospholes with an asymmetric  $\alpha$ -substitution pattern is only rarely described, so far. Mislow *et al.* prepared some  $\alpha$ -asymmetric 1-phenylphospholes using the Märkl method but also asymmetric phosphindole and dibenzophosphole derivatives.<sup>[10]</sup> Tobrman *et al.* discovered a method for the postsynthetic introduction of an asymmetric  $\alpha$ -substitution pattern to the phosphole starting from an  $\alpha$ -unsubstituted compound and with this could prepare a high variety of asymmetrically pentasubstituted phospholes.<sup>[11]</sup> We presented asymmetric 1-phenylphospholes with phenyl-thienyl, phenyl-naphthyl and thienyl-naphthyl substituents in  $\alpha$ -position so far.<sup>[9b,d]</sup> However,  $\alpha$ -asymmetric 1-ferrocenylphospholes have not been reported yet. Therefore, we have chosen a system with one phenyl and one anisyl substituent in the phosphole's  $\alpha$ -positions for our investigations. To this end we reacted ferrocenylphosphane with butyllithium and subsequently added 1-anisyl-4-phenylbuta-1,3-diyne to receive the asymmetrically  $\alpha$ -substituted 1-ferrocenylphosphole **2a** (scheme 1).

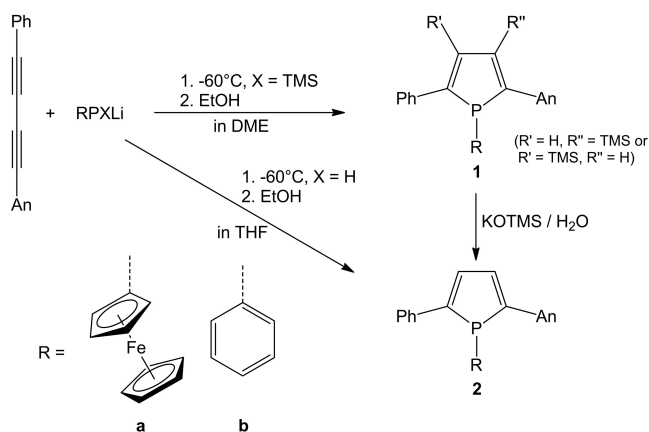
A silyl group can be introduced in  $\beta$ -position by initial treatment of the lithiumphosphanide with TMSCl and subsequent further lithiation followed by diyne addition providing phosphole **1a**. Desilylation is possible in a next step using KOTMS (potassium trimethylsilanolate) in DMSO resulting again

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**Scheme 1.** Synthesis of phospholes **1 a–b** and **2 a–b**. (An = anisyl, Ph = phenyl, Et = ethyl, KOTMS = potassium trimethylsilylanolate, TMS = trimethylsilyl).

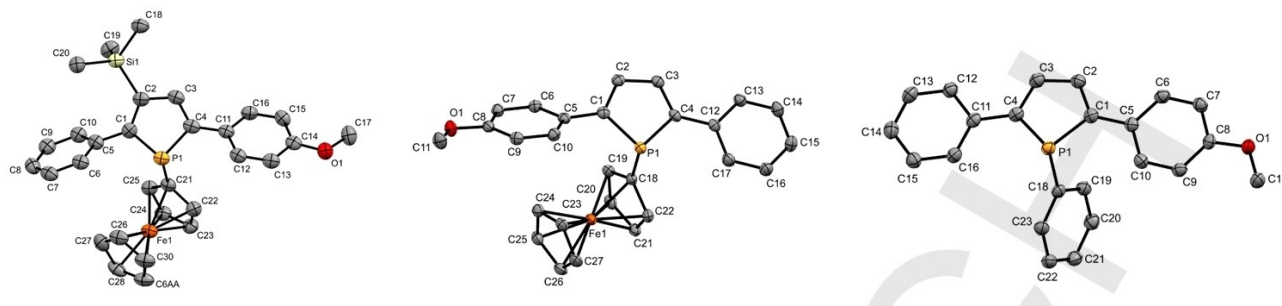
in **2a**.<sup>[12]</sup> Analogous syntheses have been reported earlier for related symmetric and asymmetric 1-phenylphospholes.<sup>[9a–c]</sup> The corresponding 2-anisyl-1,5-diphenylphospholes **1b** and **2b** were successfully synthesized in a similar fashion like **1a** and **2a**, starting from phenylphosphane instead of ferrocenylphosphane.

Due to the asymmetric substitution pattern in  $\alpha$ -position the phosphorus atom is a center of chirality but since its pyramidal inversion barrier is reduced due to aromatic stabilization of the planar transition state by the phosphole ring the enantiomers undergo a constant inversion. However, from the  $\beta$ -silyl-phospholes **1** two isomers can be distinguished depending on the TMS groups position. In case of the 1-ferrocenylphosphole **1a** the ratio of the isomers is nearly 1:1. A separation was not possible. In the  $^{31}\text{P}$ -NMR spectra two signals, one for each isomer, occur at 12.5 and 13.0 ppm, the  $^{29}\text{Si}$ -NMR spectrum provides resonances at  $-8.0$  and  $-8.1$  ppm with a  $^3J_{\text{PSi}}$  coupling constant of 4 Hz each. The  $^1\text{H}$ -NMR spectrum nicely shows a signal with doublet splitting in the aromatic region at 7.17 ppm for one isomer and 7.08 ppm for the other isomer which can be assigned to the  $\beta$ -proton with a  $^3J_{\text{PH}}$  coupling of 10.3 Hz. Mass spectrometry and elemental analysis confirm the formation of **1a**. Removal of the silyl group causes a high-field shift of the phosphorus signal resonating at  $-5.7$  ppm for phosphole **2a**. This time the two  $\beta$ -protons show

signals split into doublets of doublets in the  $^1\text{H}$ -NMR spectra at 7.11 and 7.02 ppm with  $^3J_{\text{PH}}$  coupling of 10.2 Hz and  $^3J_{\text{HH}}$  coupling of 3.2 Hz. Again, mass spectrometry and elemental analysis prove successful synthesis.

For both 1-ferrocenylphospholes **1a** and **2a** single crystals were obtained and analyzed by X-ray diffraction measurements. The molecular structures are depicted in figure 1 together with the structure of 1-phenylphosphole **2b**. In both molecules the phosphole ring is planar while the phosphorus atom possesses a pyramidal conformation (sum of angles:  $300.1(2)^\circ$  (**1a**),  $292.7(2)^\circ$  (**2a**)). For the  $\beta$ -TMS-phosphole **1a** only one of the two isomers crystallized which is the one with the silyl group vicinal to the phenyl ring in  $\alpha$ -position. The sterically demanding TMS group leads to a twisting of the phenyl ring ( $50.8(2)^\circ$ ) with respect to the phosphole plane. Such behavior has already been observed earlier for similar  $\beta$ -TMS phospholes.<sup>[9c]</sup> The twisting of the anisyl ring ( $32.5(2)^\circ$ ) can be explained by an off-center parallel  $\pi$ -stacking with anisyl rings of neighboring molecules in the crystal lattice. The bond length between the silicon and the phosphole's  $\beta$ -carbon atom amounts to 1.895(5) Å which is comparable to similar compounds. In the  $\beta$ -unsubstituted compound **2a** the phenyl ring is nearly coplanar to the phosphole ring ( $4.32(5)^\circ$ ) while the twist angle of the anisyl ring is significantly higher ( $45.49(5)^\circ$ ). However, the asymmetric unit contains two molecules which only differ in the relative orientation of the  $\alpha$ -substituents. In the second molecule the twisting of phenyl and anisyl ring is inverted compared to the depicted molecule. From the solid-state packing  $\pi$ -stacking as reason for the twisting of one ring from the phosphole ring plane is improbable. More likely are steric interactions with the ferrocene substituent, which always points in the direction of the twisted ring.

When comparing the two 1-ferrocenylphospholes **1a** and **2a** with their phenyl substituted analogues **1b** and **2b** the first significant difference is the color. While 1-ferrocenylphospholes are orange compounds and non-fluorescent, the 1-phenylphospholes are bright yellow and show strong fluorescence under UV-light. The  $\pi$ -donating phenyl and anisyl rings interact with the dienic unit of the phosphole ring resulting in luminescence. By contrast, ferrocene is prone to luminescence quenching, despite few examples of luminescent phosphanyl ferrocenes.<sup>[13]</sup> In terms of  $^{31}\text{P}$ -NMR-spectroscopy the phenyl substituted phospholes **1b** and **2b** show a low-field shift (**1b**:

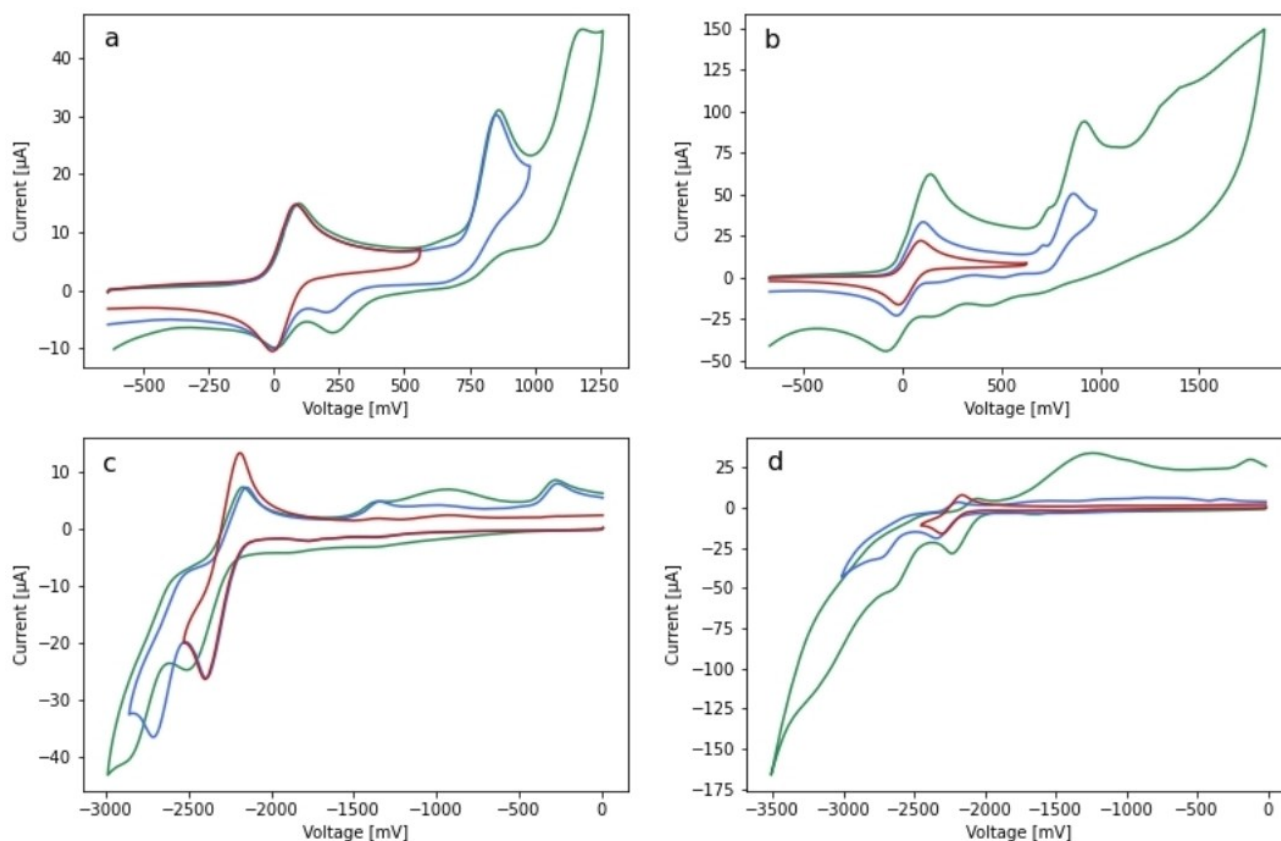


**Figure 1.** ORTEP plots of the molecular structure of **1a** and **2a–b** in the solid state with ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

21.8 ppm/22.6 ppm, **2b**: 1.8 ppm) compared to their ferrocenyl counterparts. The same trend applies to the  $^{29}\text{Si}$ -NMR shifts of both  $\beta$ -TMS substituted isomers **1b** (-7.7 ppm/-7.9 ppm), which also occur in a ratio near 1:1. The  $^3J_{\text{P}_{\text{Si}}}$  coupling constant is the same with 4 Hz. The configuration of the phosphorus atom in **2b** is also pyramidal (sum of angles: 301.9(3)°).

The redox properties of ferrocene are available for investigation with electrochemical methods. Ferrocene is known to be oxidized reversibly at comparably low potentials (e.g., +0.31 V half wave potential versus SCE in 90% ethanol).<sup>[14]</sup> While for P(V)-substituted ferrocenes the redox activity is limited to the ferrocene site which has been employed in flow-cell battery systems,<sup>[15]</sup> for P(III)-substituted ferrocenylphosphanes oxidation of the phosphorus atom needs to be considered as well. In order to receive information about the redox behavior of our 1-ferrocenylphospholes we performed CV-measurements of **1a** and **2a**. For both compounds the oxidation of the ferrocene substituent is detectable as a quasi-reversible process (figure 2 a and b, red curve). Variable scan rate investigations of this redox process showed increasing peak separation and half wave potentials with increasing scan rate, proving the quasi-reversible character (see Figure S7 in the SI).<sup>[16]</sup> The half wave potential is similar for both phospholes with  $E_{1/2} = 38$  mV (measured in DCM and referenced to the Fc/Fc<sup>+</sup> couple). When applying higher positive potentials to the

sample (blue and green curve), the quasi-reversible oxidation of ferrocene is unchanged in terms of the half wave potential. Especially for **2a** the maximum or rather minimum current and corresponding voltages differ slightly which probably is due to local fluctuations of concentration or convection in the sample. Both 1-ferrocenylphospholes **1a** and **2a** show two further oxidation processes at  $E_{\text{pa}} = 852$  mV and  $E_{\text{pa}} = 1182$  mV (**1a**) and  $E_{\text{pa}} = 865$  mV and  $E_{\text{pa}} = \sim 1470$  mV (**2a**), which from looks of the cyclovoltammograms seem to be irreversible. Possible oxidation sites in the molecules would be the phosphorus atom and the dienic system. Small peaks in the cathodic branch of the blue and green curves between 0 and 500 mV indicate reductive processes which probably belong to fragmentation products since they only occur when going to higher oxidizing voltages. The similar oxidation behavior of **1a** and **2a** indicate that the presence or absence of the silyl group does not have a significant influence here. A possible reduction site in the molecule is again the dienic system which should undergo a reversible reduction. Other reduction processes would involve a fragmentation of the molecule, for example the cleavage of the ferrocenyl substituent or the methoxy group. For both molecules **1a** and **2a** one quasi-reversible reduction was observed (figure 2 c and d, red curve) with half wave potentials of  $E_{1/2} = -2294$  mV (**1a**) and  $E_{1/2} = -2223$  mV (**2a**). Applying even more cathodic potentials reveals a second reduction process in both

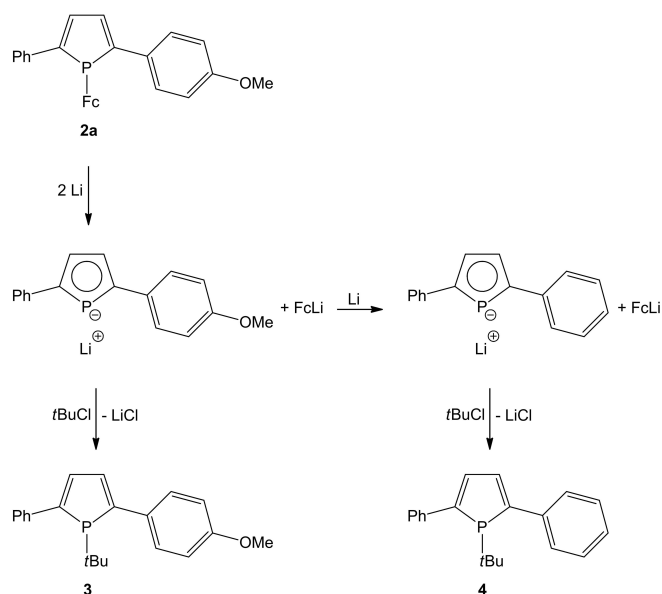


**Figure 2.** Cyclovoltammograms of 1-ferrocenylphospholes **1a** (a and c) and **2a** (b and d). Oxidative curves (a and b) are measured in DMC and reductive curves (c and d) are measured in THF. Referencing was done using Decamethylferrocene. As conducting salt tetrabutylammonium hexafluorophosphate was used with a concentration of 0.1 mol/l. The feed rate was 250 mV/s. Shown is always the first scan of different measurements starting from 0 V then going anodically (oxidation processes) or cathodically (reduction processes) and back.

compounds ( $E_{pc} = -2714$  mV (**1a**) and  $E_{pc} = \sim -2772$  mV (**2a**)) but furthermore leads to fragmentation of the molecule. This interpretation is supported by new peaks in the anodic branch between  $-1500$  and  $0$  mV which do not occur at lower return voltages. These experimental results fit to the theoretical assumption, that the dienic system is reduced reversibly while on further reduction the molecules encounter fragmentation. The latter is further corroborated by mass spectrometric analysis of the solution after bulk electrolysis at negative potentials, indicating fragments with loss of the ferrocenyl group as will be discussed later (*v. i.*).

The peak potentials of the second oxidation and the first reduction process of both, **1a** and **2a**, are in a comparable range as for literature-known related 1-phenylphosphole derivatives.<sup>[17]</sup> Réau *et al.* showed that the electronic nature of the phosphole substituents strongly influences the redox potentials. Electron rich substituents decrease the oxidation potential while electron poor substituents increase it.<sup>[17b]</sup> The oxidation potentials of the investigated compounds ( $+0,85$  V (**1a**) and  $+0,86$  V (**2a**)) are higher than for related  $\alpha$ -symmetric 1,2,5-triphenylphospholes (e.g. 4,5,6,7-tetrahydro-1,2,3-triphenyl-2*H*-isosphindole:  $+0,69$  V<sup>[17b]</sup>) although the methoxy group should further enhance the electron density with its +M-effect. However, differences in the substitution pattern at 1- and 3,4-position as well as varying measurement parameters like scan rate make an accurate comparison difficult. One might speculate that the second oxidation step could involve oxidation of the lone pair at phosphorus giving rise to a mesomerically stabilized radical, related to the findings by Boéré *et al.* on reversible oxidation of tertiary phosphanes.<sup>[18]</sup> So far, electrochemical data neither of  $\alpha$ -unsymmetric phospholes nor 1-ferrocenylphospholes are reported. Interestingly, the silyl group seems not to be involved in the reduction processes.

After examining the redox behavior of 1-ferrocenylphospholes via CV-experiments in a next step the reactivity towards a chemical reducing agent is considered. With the asymmetric 1-ferrocenylphosphole **2a** we performed a phospholide reaction, which is a common method used for P-substituent exchange.<sup>[19]</sup> An elemental alkali metal, lithium in our case, cleaves the P–C bond providing ferrocenyllithium and a phospholide anion. In this species the phosphorus is reduced, and its negative charge is delocalized in the phosphole ring which thus is highly aromatic. The change in aromaticity can be seen in the <sup>31</sup>P-NMR spectrum which shows a significant low-field shift of the signal towards 70–80 ppm. The ferrocenyllithium should be quenched in a next step using one equivalent of *tert*-butylchloride which would enable selective introduction of an organic residue to the phosphorus atom by using an organohalide. However, instead of quenching the ferrocenyllithium the *tert*-butylchloride immediately reacted with the phospholide anion forming 1-*tert*-butylphospholes and lithium-chloride (scheme 2). This unexpected reaction behavior is not observed when starting from the 1-phenylphosphole **2b**. In this case the *tert*-butylchloride as intended quenches the phenyllithium whereas the phospholide remains unchanged even with a large excess (4 eq.) of *tert*-butylchloride. We were wondering whether the presence of the resulting ferrocene could foster



**Scheme 2.** Phospholide reaction of phosphole **2a** resulting in the *tert*-butylphospholes **3** and **4**. (tBu = *tert*-butyl, Fc = ferrocenyl, Ph = phenyl)

formation of the 1-*tert*-butylphosphole, but addition of 1 eq. of ferrocene to the phospholide derived from 1-phenylphosphole **2b** prior to adding *tert*-butylchloride made no difference and the phospholide anion remained unchanged. Nevertheless, we speculate that intermolecular interactions might play a role in the different reactivity behaviors. Since organolithium compounds are known to form clusters with themselves or with donor molecules, like for example the  $FcLi_2$ -TMEDA (*N,N,N',N'*-tetramethyl-ethylenediamine) adduct,<sup>[20]</sup> also in our case in situ generated ferrocenyllithium or phenyllithium could interact with the phospholide anion. Comparable phospholyl lithium clusters are known and the interaction of a lithium cation with a negatively charged phospholide ring in an  $\eta^5$ -fashion has been demonstrated via SCXRD.<sup>[21]</sup> In consequence, different cluster motifs of the phospholide anion with either the ferrocenyllithium or the phenyllithium may entail different reactivity towards *tert*-butylchloride we assume without further proof.

Regardless, of the underlying mechanism the protocol provides a novel access strategy towards 1-*tert*-butylphospholes. So far related compounds were usually synthesized via treatment of a 1-substituted phosphole with *tert*-butyllithium or alternatively starting from a *tert*-butyl substituted primary phosphane.<sup>[22]</sup>

During the reduction with lithium, which was carried out in THF, we could also observe another interesting reaction behavior. Besides the phosphorus atom, the carbon atom of the anisyl ring, to which the methoxy group is bonded, can be reduced as well such that the methoxy group is cleaved off. This reduction is slower than the phospholide formation. In consequence depending on the reaction time, we either observed a mixture of the asymmetric 2-anisyl-5-phenylphosphole **3** and the symmetric 2,5-diphenylphosphole **4** (1 hour) or only the symmetric species **4** (24 hours). The corresponding

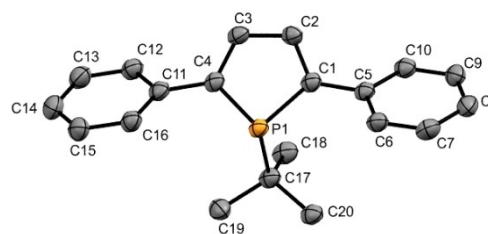
phospholides have not been isolated but could be detected with  $^{31}\text{P}$ -NMR spectroscopy in situ. In deuterated THF solution the 2-anisyl-5-phenylphospholide resonates at 77.2 ppm and slowly converts to the 2,5-diphenylphospholide resonating at 82.1 ppm.

The phenomenon of ether cleavage by alkali metals is already well known and extensively studied.<sup>[23]</sup> However, the detailed mechanism and the aspect of competing dealkylation and dealkoxylation, especially in alkyl aryl ethers is still not fully understood. Maercker performed systematic studies in this field mainly focusing on anisole and could identify structural motifs of alkyl/aryl residues including steric aspects and the solvent as influencing factors of the regioselectivity. The alkali metal does not seem to have a major impact.<sup>[23b]</sup> Interestingly, treatment of anisole with elemental lithium in THF leads to 94% dealkylation while in our case only dealkoxylation was observed. Seemingly, the phosphole based substituent in *para*-position with respect to the methoxy group on the anisyl ring conducts the reaction towards preferred aryl oxygen cleavage. The above cited study also concluded that an increasing aromatic system of the aryl substituent facilitates dealkoxylation. In our case, the aromaticity of the phospholide anion might well be the decisive factor for the observed regioselectivity.

The specific role of the metal can be further elucidated by comparison with electrochemical investigations. To this end we reduced 1-ferrocenylphosphole **2a** electrochemically via bulk electrolysis ( $E_c = -2.9\text{ V}$  for 80 min) and subsequently recorded mass spectra of the solution (see Figures S8 and S9 in the SI). In the negative APCI we were able to observe the phospholide together with its mono- and di-oxygenated counterparts. In the positive APCI both, the starting 1-ferrocenylphosphole as well as a fragment without the ferrocene substituent can be detected. Despite the limitation of an excess of conduction salt in the mixture and brief exposure to aerobic conditions, these results indicate, that the cleavage of the phosphorus bonded substituent can also be achieved electrochemically. By contrast, we could not observe any fragments providing evidence for the electrochemical cleavage of the methoxy group. Therefore, we speculate that for the ether cleavage the presence of lithium in the reaction mixture might be essential.

The  $^{31}\text{P}$ -NMR chemical shift values of both 1-*tert*-butylphospholes **3** and **4** differ only slightly (27.0 ppm (**3**), 27.6 ppm (**4**)) since the presence or absence of the distant methoxy group does not significantly influence the phosphorus atom. However, proton and carbon NMR show distinct differences in number and splitting pattern of the signals due to the gained symmetry in phosphole **4** compared to the asymmetric compound **3**. Looking again at the  $^1\text{H}$ -NMR signals of the  $\beta$ -protons, two different signals with a doublet of doublet splitting occur for phosphole **3** (7.07 ppm, 7.00 ppm) while in phosphole **4** only one doublet signal is visible (7.08 ppm) since the  $\beta$ -protons are now equivalent and only couple to the phosphorus atom.

The symmetric 1-*tert*-butyl-2,5-diphenylphosphole **4** was also investigated via X-ray diffraction analysis (figure 3). Both phenyl rings are nearly coplanar (twist angle:  $1.4(1)^\circ$ ) but are tilted with respect to the phosphole ring by  $36.9(1)^\circ$ . However, intermolecularly two neighboring molecules are aligned in a



**Figure 3.** ORTEP plot of the molecular structure of **4** in the solid state with ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

way that always the phosphole plane of one molecule is nearly coplanar to the phenyl ring plane of the other molecule and vice versa. The conformation of the phosphorus atom is pyramidal with a sum of angles of  $301.2(4)^\circ$ .

## Conclusion

In summary, we successfully synthesized 1-ferrocenylphospholes **1a** and **2a** using the procedure earlier developed by us. The corresponding 1-phenylphospholes **1b** and **2b** could be obtained analogously. The 1-ferrocenylphospholes were characterized and compared with their phenyl substituted counterparts. Compounds **1a** and **2a** were furthermore investigated with respect to their redox properties via CV-measurements. In both compounds the quasi-reversible oxidation of ferrocene is observable and two more oxidation processes as well as two reduction processes, from which one is quasi reversible, were detected. When applying high negative voltages, fragmentation is observable for which characteristic fragments have been identified with mass spectrometry. Moreover, ferrocenyl substituted phosphole **2a** was converted to the corresponding phospholide via reduction with lithium, during which cleavage of the methoxy group was observed. In this case the dealkoxylation is favored compared to demethylation, presumably owing to mesomeric interaction of the side group with the aromatic phospholide system. The cleavage of the methoxy group is a slow process compared to the phospholide formation. Addition of *tert*-butylchloride results in the formation of the 1-*tert*-butylphospholes **3** and **4**. Remarkably, 1-phenylphosphole **2b** does not react in a similar fashion and no reaction of the corresponding phospholide with *tert*-butylchloride is observed. These findings suggest a significant difference of the ferrocene substituent compared with its phenyl counterpart in terms of reactivity impacting the course of reaction.

## Experimental Section

Ferrocenyl- and phenylphosphane as well as the 1-anisyl-4-phenylbuta-1,3-diyne have been prepared according to literature known procedures.<sup>[24]</sup> All reactions have been carried out under argon atmosphere and exclusion from air and moisture. The used solvents were dried over a NaK-alloy.  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR measurements were performed using a Varian 400 MHz spectrometer and for  $^{29}\text{Si}$ - and

<sup>31</sup>P-NMR measurements a 500 MHz spectrometer. Chemical shifts are referenced to Me<sub>4</sub>Si (<sup>1</sup>H, <sup>13</sup>C, <sup>29</sup>Si) and phosphoric acid 85 % (<sup>31</sup>P). As internal standard in <sup>1</sup>H- and <sup>13</sup>C-NMR spectra the solvent signal of DCM was used (5.32 ppm for <sup>1</sup>H-NMR, 54.0 ppm for <sup>13</sup>C-NMR). The APCI-mass spectra have been recorded on the time-of-flight mass spectrometer micrOTOF (Bruker Daltonics, Bremen, D) and elemental analysis has been performed using a HEKAtech Euro EA CHNS elemental analyzer. Crystal structure analysis has been performed using a Stoe Stadi Vari diffractometer with Dectris Pilatus 200 K detector. Direct methods were used to solve the measurements and refined by “least-square” cycles (SHELXL-2017).<sup>[25]</sup> All non-hydrogen atoms were anisotropically refined without restriction. The evaluation of the data sets, as well as the graphical preparation of the structures was carried out using Olex2<sup>[26]</sup> and Mercury.<sup>[27]</sup> Details of the structure determinations and refinement are summarized in Table S1–S2. The CCDC depositions 2250173–2250176 contain the supplementary crystallographic data for this paper, which can be obtained free of charge via emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre at 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033. All CV-measurements, including the bulk electrolysis, have been performed under argon atmosphere with a WaveDriver 20 Bipotentiostat Pine Research and have been analysed with the software AfterMath. As electrodes a platinum working electrode, a silver counter electrode and a pseudo reference electrode have been used. As feed rate for the CV-measurements 250 mV/s has been chosen. Oxidation experiments have been performed in dry DCM as solvent and reduction experiments in dry THF. As conduction salt [Bu<sub>4</sub>N][PF<sub>6</sub>] has been added in a concentration of 0.1 mol/l. For all measurements decamethylferrocene has been used as standard and they have been referenced to the Fc/Fc<sup>+</sup> couple with the solvent dependent potentials according to Lay *et al.*<sup>[28]</sup> The bulk electrolysis has been performed in a 0.1 M [Bu<sub>4</sub>N][PF<sub>6</sub>] solution in THF. A negative potential of –2.9 V has been applied for 80 min.

### General Procedure for Phospholes 1

In a 250 mL Schlenk flask 0.66 g ferrocenylphosphane (3 mmol) or rather 0.33 g phenylphosphane (3 mmol) were dissolved in 60 mL anhydrous DME and cooled down to –60 °C. 1.2 mL of a 2.5 M *n*-BuLi solution in *n*-hexane (1 equiv.) were added and the mixture was stirred for 1 h. After successive addition of 0.38 mL TMSCl (1 equiv.) and 1.2 mL *n*BuLi (1 equiv.) the solution was again stirred for 1 h. 0.697 g of 1-anisyl-4-phenylbuta-1,3-diyne (1 equiv.) were dissolved in 20 mL anhydrous DME and added dropwise to the reaction mixture. After 2 h the reaction mixture was warmed up to room temperature and quenched with EtOH. Under vacuum the solvent was evaporated and the product was purified by column chromatography with a silica gel column and an eluent mixture of pentane and DCM (10:1).

### Phosphole 1 a

The desired phosphole **1 a** was obtained as orange oil with a yield of 0.976 g (1.87 mmol, 62.4%). <sup>1</sup>H-NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 7.61 (d, *J* = 7.8 Hz, 2 H, CH), 7.54 (d, *J* = 8.2 Hz, 2 H, CH), 7.49–7.34 (m, 9 H, CH), 7.29–7.25 (m, 1 H, CH), 7.17 (d, <sup>3</sup>*J*<sub>PH</sub> = 10.3 Hz, 1 H, CH<sub>β-position</sub>), 7.08 (d, <sup>3</sup>*J*<sub>PH</sub> = 10.3 Hz, 1 H, CH<sub>β-position</sub>), 6.97 (d, *J* = 8.6 Hz, 2 H, CH), 6.93 (d, *J* = 8.7 Hz, 2 H, CH), 4.07–3.83 (m, 18 H, CH<sub>CP</sub>), 3.81 (s, 3 H, OCH<sub>3</sub>), 0.12 (s, 9 H, Si(CH<sub>3</sub>)<sub>3</sub>), 0.10 (s, 9 H, Si(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (100.57 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 162.7 (d, *J* = 5 Hz, C<sub>q</sub>), 161.2 (d, *J* = 4 Hz, C<sub>q</sub>), 159.8 (d, *J* = 1 Hz, C<sub>q</sub>), 159.6 (s, C<sub>q</sub>), 151.9 (d, *J* = 1 Hz, C<sub>q</sub>), 151.4 (d, *J* = 2 Hz, C<sub>q</sub>), 148.4 (d, *J* = 5 Hz, C<sub>q</sub>), 147.1 (d, *J* = 5 Hz, C<sub>q</sub>), 141.0 (d, *J* = 20 Hz, C<sub>q</sub>), 138.5 (d, *J* = 17 Hz, C<sub>q</sub>), 137.3 (d, *J* = 13 Hz, CH),

135.4 (d, *J* = 13 Hz, CH), 133.0 (d, *J* = 20 Hz, C<sub>q</sub>), 131.1 (d, *J* = 8 Hz, CH), 130.8 (d, *J* = 18 Hz, C<sub>q</sub>), 130.1 (d, *J* = 8 Hz, CH), 129.2 (s, CH), 128.8 (d, *J* = 9 Hz, CH), 128.5 (s, CH), 127.8 (d, *J* = 9 Hz, CH), 127.6 (s, CH), 127.3 (s, CH), 114.6 (s, CH), 113.9 (s, CH), 73.4 (d, *J* = 10 Hz, Fc), 70.8 (d, *J* = 11 Hz, Cp), 70.0 (m, CH<sub>CP</sub>), 69.5 (s, CH<sub>CP</sub>), 55.9 (s, OCH<sub>3</sub>), 0.7 (d, <sup>4</sup>*J*<sub>PC</sub> = 1 Hz, Si(CH<sub>3</sub>)<sub>3</sub>), 0.7 (d, <sup>4</sup>*J*<sub>PC</sub> = 1 Hz, Si(CH<sub>3</sub>)<sub>3</sub>). <sup>29</sup>Si{<sup>1</sup>H}-NMR (99.28 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = –8.0 (d, <sup>3</sup>*J*<sub>PSi</sub> = 4 Hz), –8.1 (d, <sup>3</sup>*J*<sub>PSi</sub> = 4 Hz). <sup>31</sup>P {<sup>1</sup>H}-NMR (202.30 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 12.5 (s), 13.0 (s). Elemental analysis (%): calculated: C 68.97, H 5.98, found: C 69.25, H 6.15. HRMS (APCI) *m/z*: 523.1304 [M + H]<sup>+</sup>, calculated: 523.1309.

### Phosphole 1 b

The desired phosphole **1 b** was obtained as yellow oil with a yield of 0.557 g (1.34 mmol, 45%). <sup>1</sup>H-NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 7.71 (d, *J* = 8.0 Hz, 2 H, CH), 7.64 (d, *J* = 8.1 Hz, 2 H, CH), 7.59 (d, <sup>3</sup>*J*<sub>PH</sub> = 10.7 Hz, 1 H, CH<sub>β-position</sub>), 7.49 (d, <sup>3</sup>*J*<sub>PH</sub> = 10.9 Hz, 1 H, CH<sub>β-position</sub>), 7.44–7.24 (m, 20 H, CH), 6.96–6.93 (m, 4 H, CH), 3.83 (s, 3 H, OCH<sub>3</sub>), 0.32 (s, 9 H, Si(CH<sub>3</sub>)<sub>3</sub>), 0.29 (s, 9 H, Si(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (100.57 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 164.2 (d, *J* = 5 Hz, C<sub>q</sub>), 162.8 (d, *J* = 5 Hz, C<sub>q</sub>), 159.8 (s, C<sub>q</sub>), 159.7 (s, C<sub>q</sub>), 150.6 (d, *J* = 3 Hz, C<sub>q</sub>), 150.2 (d, *J* = 3 Hz, C<sub>q</sub>), 148.4 (d, *J* = 5 Hz, C<sub>q</sub>), 147.3 (d, *J* = 5 Hz, C<sub>q</sub>), 139.7 (d, *J* = 20 Hz, C<sub>q</sub>), 138.6 (d, *J* = 13 Hz, CH), 137.5 (d, *J* = 17 Hz, C<sub>q</sub>), 136.7 (d, *J* = 13 Hz, CH), 134.3 (d, *J* = 19 Hz, CH), 132.0 (s, C<sub>q</sub>), 131.9 (s, C<sub>q</sub>), 131.8 (s, C<sub>q</sub>), 130.8 (d, *J* = 8 Hz, CH), 130.2 (s, C<sub>q</sub>), 130.0 (s, CH), 129.8 (d, *J* = 8 Hz, CH), 129.3 (d, *J* = 6 Hz, CH), 129.2 (s, CH), 128.4 (s, CH), 128.2 (d, *J* = 9 Hz, CH), 127.6 (s, CH), 127.5 (s, CH), 127.2 (d, *J* = 9 Hz, CH), 114.8 (s, CH), 114.5 (s, CH), 113.9 (s, CH), 55.8 (s, OCH<sub>3</sub>), 55.7 (s, OCH<sub>3</sub>), 0.9 (d, <sup>4</sup>*J*<sub>PC</sub> = 1 Hz, Si(CH<sub>3</sub>)<sub>3</sub>), 0.8 (d, <sup>4</sup>*J*<sub>PC</sub> = 1 Hz, Si(CH<sub>3</sub>)<sub>3</sub>). <sup>29</sup>Si{<sup>1</sup>H}-NMR (99.28 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = –7.7 (d, <sup>3</sup>*J*<sub>PSi</sub> = 4 Hz), –7.9 (d, <sup>3</sup>*J*<sub>PSi</sub> = 4 Hz). <sup>31</sup>P {<sup>1</sup>H}-NMR (202.30 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 21.8 (s), 22.6 (s). Elemental analysis (%): calculated: C 75.33, H 6.57, found: C 75.65, H 6.93. HRMS (APCI) *m/z*: 415.1642 [M + H]<sup>+</sup>, calculated: 415.1647.

### General Procedure for Phospholes 2

**Direct synthesis:** In a 100 mL Schlenk flask 0.22 g ferrocenylphosphane (1 mmol) or rather 0.11 g phenylphosphane (1 mmol) were dissolved in 20 mL anhydrous THF and cooled down to –60 °C. 0.44 mL of a 2.5 M *n*-BuLi solution in *n*-hexane (1 equiv.) were added and the mixture was stirred for 1 h. 0.232 g of 1-anisyl-4-phenylbuta-1,3-diyne (1 equiv.) were dissolved in 10 mL anhydrous THF and added dropwise to the reaction mixture. After 1 h the reaction mixture was warmed up to room temperature and quenched with EtOH. Under vacuum the solvent was evaporated and the product was purified by column chromatography with a silica gel column and an eluent mixture of pentane and DCM (10:1).

**Desilylation of 1:** 0.523 g of phosphole **1 a** (1 mmol) or rather 0.415 g of phosphole **1 b** (1 mmol) and 2.57 mg KOTMS (0.02 equiv.) were put into a 100 mL Schlenk tube and dissolved in 5 mL anhydrous DMSO. Three drops of degassed water were added to the stirring mixture. After 1.5 h again 2.57 mg KOTMS (0.02 equiv.) were added to the solution. The reaction was stopped after another 1.5 h, the solvent was evaporated under vacuum and the product was purified by column chromatography with a silica gel column and an eluent mixture of pentane and DCM (10:1).

### Phosphole 2 a

Phosphole **2 a** was obtained as orange solid with a yield of 0.215 g (0.48 mmol, 50.5% (desilylation procedure)). <sup>1</sup>H-NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 7.66 (d, *J* = 8.1 Hz, 2 H, CH), 7.59 (d, *J* = 7.6 Hz, 2 H, CH), 7.42 (d, *J* = 7.7 Hz, 2 H, CH), 7.32–7.28 (m, 1 H, CH), 7.11 (dd, <sup>3</sup>*J*<sub>PH</sub> =

10.2 Hz,  $^3J_{\text{HH}}=3.2$  Hz, 1 H,  $\text{CH}_{\beta\text{-position}}$ ), 7.02 (dd,  $^3J_{\text{PH}}=10.2$  Hz,  $^3J_{\text{HH}}=3.2$  Hz, 1 H,  $\text{CH}_{\beta\text{-position}}$ ), 6.96 (d,  $J=8.7$  Hz, 2 H, CH), 4.08–3.89 (m, 9 H,  $\text{CH}_{\text{CP}}$ ), 3.84 (s, 3 H,  $\text{OCH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$ -NMR (100.57 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta=159.8$  (s,  $\text{C}_q$ ), 152.9 (d,  $J=2$  Hz,  $\text{C}_q$ ), 151.6 (s,  $\text{C}_q$ ), 138.5 (d,  $J=17$  Hz,  $\text{C}_q$ ), 132.9 (d,  $J=9$  Hz, CH), 130.9 (d,  $J=17$  Hz,  $\text{C}_q$ ), 130.7 (d,  $J=8$  Hz, CH), 129.2 (s, CH), 128.9 (d,  $J=9$  Hz, CH), 127.8 (d,  $J=10$  Hz, CH), 127.6 (s, CH), 114.7 (s, CH), 74.0 (d,  $J=10$  Hz, Cp), 70.9 (m, Cp), 70.0 (d,  $J=5$  Hz,  $\text{CH}_{\text{CP}}$ ), 69.5 (s,  $\text{CH}_{\text{CP}}$ ), 55.9 (s,  $\text{OCH}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$ -NMR (202.30 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta=-5.7$  (s). Elemental analysis (%): calculated: C 72.02, H 5.15, found: C 72.20, H 5.42. HRMS (APCI)  $m/z$ : 451.0909  $[\text{M}+\text{H}]^+$ , calculated: 451.0914.

### Phosphole 2b

Phosphole **2b** was obtained as yellow solid with a yield of 0.189 g (0.55 mmol, 55%) (desilylation procedure).  $^1\text{H}$ -NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta=7.55$  (d,  $J=8.1$  Hz, 2 H, CH), 7.50 (d,  $J=7.8$  Hz, 2 H, CH), 7.42 (t,  $J=7.7$  Hz, 2 H, CH), 7.33–7.16 (m, 8 H, CH), 6.83 (d,  $J=8.7$  Hz, 2 H, CH), 3.77 (s, 3 H,  $\text{OCH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$ -NMR (100.57 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta=159.8$  (s,  $\text{C}_q$ ), 152.1 (s,  $\text{C}_q$ ), 150.1 (s,  $\text{C}_q$ ), 137.0 (d,  $J=17$  Hz,  $\text{C}_q$ ), 134.4 (d,  $J=20$  Hz, CH), 133.0 (d,  $J=9$  Hz, CH), 131.8 (d,  $J=8$  Hz,  $\text{C}_q$ ), 131.0 (d,  $J=9$  Hz, CH), 130.3 (d,  $J=2$  Hz, CH), 129.6 (d,  $J=17$  Hz,  $\text{C}_q$ ), 129.4 (d,  $J=9$  Hz, CH), 129.2 (s, CH), 128.0 (d,  $J=10$  Hz, CH), 127.6 (s, CH), 126.7 (d,  $J=10$  Hz, CH), 114.7 (s, CH), 55.8 (s,  $\text{OCH}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$ -NMR (202.30 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta=1.8$  (s). Elemental analysis (%): calculated: C 80.69, H 5.59, found: C 80.65, H 5.94. HRMS (APCI)  $m/z$ : 343.1246  $[\text{M}+\text{H}]^+$ , calculated: 343.1252.

### Synthesis of Phospholes 3 and 4

In a 100 mL Schlenk tube 0.135 g of phosphole **2a** (0.3 mmol) were dissolved in 5 mL anhydrous THF. 4.16 mg of elemental lithium (2 equiv.) were added and the mixture was stirred for 1 h. Successively, 0.033 mL  $t\text{BuCl}$  (1 equiv.) and 0.026 mL bromoform (1 equiv.) were added to the reaction mixture. Under vacuum the solvent was evaporated. Phospholes **3** and **4** could be separated and purified via column chromatography with a silica gel column and an eluent mixture of pentane and DCM (10:1).

### Phosphole 3

Phosphole **3** was obtained as colorless solid.  $^1\text{H}$ -NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta=7.53$  (d,  $J=7.8$  Hz, 2 H, CH), 7.46 (d,  $J=8.5$  Hz, 2 H, CH), 7.35 (t,  $J=7.6$  Hz, 2 H, CH), 7.26–7.23 (m, 1 H, CH), 7.07 (dd,  $^3J_{\text{PH}}=9.0$  Hz,  $^3J_{\text{HH}}=3.1$  Hz, 1 H,  $\text{CH}_{\beta\text{-position}}$ ), 7.00 (dd,  $^3J_{\text{PH}}=9.0$  Hz,  $^3J_{\text{HH}}=3.1$  Hz, 1 H,  $\text{CH}_{\beta\text{-position}}$ ), 6.91 (d,  $J=8.7$  Hz, 2 H, CH), 3.82 (s, 3 H,  $\text{OCH}_3$ ), 0.86 (d,  $^3J_{\text{PH}}=13.0$  Hz, 9 H,  $(\text{CH}_3)_3$ ).  $^{13}\text{C}\{^1\text{H}\}$ -NMR (100.57 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta=159.6$  (s,  $\text{C}_q$ ), 151.0 (d,  $J=8$  Hz,  $\text{C}_q$ ), 150.0 (d,  $J=7$  Hz,  $\text{C}_q$ ), 140.0 (d,  $J=17$  Hz,  $\text{C}_q$ ), 134.4 (d,  $J=6$  Hz, CH), 132.7 (d,  $J=6$  Hz, CH), 132.5 (d,  $J=17$  Hz,  $\text{C}_q$ ), 129.5 (d,  $J=8$  Hz, CH), 129.0 (s, CH), 128.3 (d,  $J=8$  Hz, CH), 127.2 (s, CH), 114.5 (s, CH), 55.8 (s,  $\text{OCH}_3$ ), 34.7 (d,  $J=11$  Hz,  $\text{C}_q$ ), 28.8 (d,  $J=11$  Hz,  $(\text{CH}_3)_3$ ).  $^{31}\text{P}\{^1\text{H}\}$ -NMR (202.30 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta=27.0$  (s). HRMS (APCI)  $m/z$ : 323.1559  $[\text{M}+\text{H}]^+$ , calculated: 323.1565.

### Phosphole 4

Phosphole **4** was obtained as yellow solid.  $^1\text{H}$ -NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta=7.54$  (d,  $J=7.9$  Hz, 4 H, CH), 7.36 (t,  $J=7.6$  Hz, 4 H, CH), 7.28–7.24 (m, 2 H, CH), 7.08 (d,  $^3J_{\text{PH}}=9.0$  Hz, 2 H,  $\text{CH}_{\beta\text{-position}}$ ), 0.86 (d,  $^3J_{\text{PH}}=13.1$  Hz, 9 H,  $(\text{CH}_3)_3$ ).  $^{13}\text{C}\{^1\text{H}\}$ -NMR (100.57 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta=151.3$  (d,  $J=8$  Hz,  $\text{C}_q$ ), 139.9 (d,  $J=17$  Hz,  $\text{C}_q$ ), 134.2 (d,  $J=6$  Hz, CH), 129.0 (s, CH), 128.5 (d,  $J=8$  Hz, CH), 127.4 (s, CH), 34.8 (d,  $J=11$  Hz,

$\text{C}_q$ ), 28.9 (d,  $J=11$  Hz,  $(\text{CH}_3)_3$ ).  $^{31}\text{P}\{^1\text{H}\}$ -NMR (202.30 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta=27.6$  (s). HRMS (APCI)  $m/z$ : 293.1454  $[\text{M}+\text{H}]^+$ , calculated: 293.1459.

### X-ray Crystallography

Deposition Number(s) 2250176 (for **1a**), 2250174 (for **2a**), 2250173 (for **2b**), 2250175 (for **4**) contain(s) the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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### Conflict of Interests

The authors declare no conflict of interest.

### Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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