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3,4-Dithiaphosphole and 3,3',4,4'-Tetrathia-1,1'-Biphosphole π -Conjugated Systems: S Makes the Impact

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Abstract: Conjugated systems based on phospholes and 1,1'-biphospholes bearing 3,4-ethylenedithia bridges have been prepared using the Fagan-Nugent route. The mechanism of this organometallic route leading to intermediate zirconacyclopentadienes has been investigated by using theoretical calculations. This study revealed that the oxidative coupling leading to zirconacyclopentadienes is favored over oxidative addition within the S–C \equiv C bond both thermodynamically and kinetically. The impact of the presence of the S atoms on the optical and electrochemical behavior of the phospholes and 1,1'-biphospholes has been systematically evaluated both experimentally and theoretically. A comparison with their "all-carbon" analogues is provided. Of particular interest, this comparative study revealed that the introduction of S atoms has an impact on the electronic properties of phosphole-based conjugated systems. A decrease of the HOMO–LUMO separation and a stabilization of the LUMO level were observed. These general trends are also observed with 1,1'-biphospholes exhibiting σ - π conjugation. The P atom of the 3,4-ethylenedithiaphospholes can be selectively oxidized by S₈ or O₂. These P modifications result in a lowering of the HOMO–LUMO separation

Keywords: conjugation • density functional calculations • electropolymerization • phospholes • polymerization • thiophenes as well as an increase of the reduction and oxidation potentials. The S atoms of the 3,4-ethylenedithia bridge of the 2,5-phosphole have been oxidized using *m*-chloroperoxybenzoic acid. The resulting 3,4-ethylenesulfoxide oxophosphole was characterized by an Xray diffraction study. Experimental and theoretical studies show that this novel chemical manipulation results in an increase of the HOMO-LUMO separation and an important decrease of the LUMO level. The electropolymerization of 2-thienyl-capped 3,4-ethylenedithiathioxophosphole and 1,1'-biphosphole is reported. The impact of the S substituents on the polymer properties is discussed.

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Introduction

The demand for new organic π -conjugated materials with improved electrical and optical properties for plastic electronic applications necessitates extensive experimental molecular engineering and theoretical investigations of the underlying structure-property relationships.^[1] The two main strategies to diversify the properties and to expand the function of linear π -conjugated systems A (Scheme 1) involve 1) the modification of the conjugated framework composition, including the synthesis of mixed derivatives, and 2) the attachment of lateral substituents R^1 and R^2 with specific electronic or steric demands.^[1,2] Heterocyclopentadienes (A: X,Y = NR, S, SiR₂, PR(E), and so forth; Scheme 1) have been extensively used for modifying the conjugated framework composition since they exhibit electronic properties related to the nature of the heteroatom.^[1-3] Heteroles including second-row elements like silicon^[4] or phosphorus^[4a,5]

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Scheme 1. Structure of linear π -systems **A** and P building blocks used for molecular engineering.

play a specific role in this molecular engineering due to their low-lying exocyclic P–R or Si–R σ^* orbitals that can effectively overlap with the π system. This results in a lowenergy LUMO and consequently, a high electron affinity (suitable for n-type conductivity).^[6] Furthermore, a reduced HOMO-LUMO separation of π -conjugated system A is observed since these heteroles (silole and phosphole) exhibit a low level of aromaticity,^[4,6] which results in a better electronic interaction of their endocyclic π electrons with other aromatic subunits at the 2,5-positions. For example, thiophene-silole oligomers A (Scheme 1) exhibit different physical properties (improved π conjugation, lower lying LUMO level, etc.) than the corresponding oligo(thiophene)s, making these mixed systems of interest for applications such as the development of sensors, solar cells, or optimized materials for organic light-emitting diodes.^[7]

The phosphole ring **B** (Scheme 1), which is the most recently investigated heterole for the molecular engineering of linear π systems **A** (Scheme 1), possesses two further advantages: 1) the possibility to readily tune the electronic property of phosphole-based π -conjugated systems by chemical modifications of the reactive P atoms, and 2) the increased effectiveness of the hyperconjugative interaction in 1,1'-biphosphole moieties C (Scheme 1) leading to further reduction of the HOMO-LUMO gaps.^[8] These specific properties have been fully exploited by several groups for the optimization of phosphole-based π -conjugated materials exhibiting (electro)fluorescence, sensor, or electron-transporting properties.^[9] Note that this general approach can also be performed using fused-ring systems (for example, dibenzophospholes **D** or dithienophospholes **E**, Scheme 1),^[10] although these compounds are better described as whole delocalized entities and not as phosphole derivatives.

The second main strategy to diversify the properties of linear π -conjugated systems (i.e., the attachment of lateral

substituents R¹ and R² with specific electronic or steric demands, Scheme 1) has not been fully investigated with phosphole building blocks. In fact, all the phosphole moieties **B** that have been used to date for the tailoring of π systems **A** (Scheme 1) feature alkyl groups at their 3- and 4-positions, except one example concerning per-aryl derivatives.^[8a] This is mainly due to synthetic reasons since these 3,4-dialkylphosphole synthons are easily accessible using the two well-established methods depicted in Scheme 2.^[5a-c,11-13]



Scheme 2. Synthetic routes to the two families of mixed π -systems incorporating phosphole moieties.

Therefore we have investigated the synthesis of unprecedented phosphole derivatives bearing Group 16 heteroelement substituents at their 3,4-positions with the aim of tuning the electronic properties of P-based conjugated systems. This type of substituent was selected by considering the vast literature on thiophene-containing π -conjugated systems. Indeed, thiophene derivatives bearing Group 16 heteroelement substituents (alkoxy, thioalkoxy, or selenoalkoxy) at their 3,4-positions have been extensively used for the development of advanced materials since they exhibit improved properties relative to their parent analogue.^[14] Furthermore, such a substitution pattern will suppress possible thermally induced phosphole-phospholene isomerization, a process that can be a drawback for the development of these P building blocks since it modifies the extended π conjugated pathway (Scheme 3).^[6d]



 R^1 = 2-thienyl, phenyl, 2- or 4- pyridyl Scheme 3. σ^4 -Phosphole– σ^4 -phospholene isomerization.

In this paper, we describe the synthesis of the first phospholes **B** and 1,1'-biphospholes **C** (Scheme 1) bearing an SR function at their 3- and 4-positions. The choice of S- rather than O-substituents was made following a theoretical study, reported in this paper, revealing that 3,4-dithiaphospholes exhibit appealing electronic properties (stabilized LUMO

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level, low HOMO-LUMO gap). The synthetic route towards these novel phosphole derivatives containing SR functions is based on the organometallic approach described in Scheme 2 (route (2)). To the best of our knowledge, the oxidative coupling of S-functionalized divnes upon reaction with low-valent zirconium, affording intermediate metallacyclopentadienes G (Scheme 2), is unprecedented. This reaction, which extends the scope of this widely used organometallic route towards heteroles, has been investigated by theoretical calculations since S-functionalized triple bonds can potentially give oxidative addition reactions upon reaction with zirconocene. The impact of the two S-substituents at the 3,4-position on the electronic properties of the phosphole ring and phosphole-based π -conjugated systems has been elucidated following combined experimental and theoretical studies. Of particular interest, it will be shown that the presence of these S-substituents impacts the electropolymerization ability of thienyl-capped phosphole monomers, and allows for a subtle tailoring of the phosphole electronic properties following chemical S-oxidation.

Results and Discussion

Preliminary theoretical study: To evaluate the effect of the Group 16 substituents at the 3,4-positions on the HOMO-LUMO gap of the phosphole ring, model calculations have been performed. For comparison purposes, thiophene was selected as a prototype heterocyclopentadiene. The Kohn-Sham (KS)^[15] HOMO-1, HOMO, and LUMO for phosphole and thiophene are shown in Figure 1, and the energies of these KS orbitals upon replacing the H atoms at the 3,4-positions by alkyl/alkoxy/thioalkoxy-fused six-membered rings are given in Figure 2.

The introduction of Group 16 substituents at the 3,4-posi-

tions has a similar effect on the orbital energies of both phosphole and thiophene rings (Figure 2). As expected, the occupied orbitals are destabilized upon replacing H or alkyl by Group 16 substituents. Note that the HOMO of the S-substituted phosphole (-5.69 eV)and thiophene (-5.67 eV) derivatives have similar energy (Figure 2). The unoccupied orbital energies behave in a different way. The C- and O-substitutions result in a gradual destabilization of the LUMO energies compared to the parent heteroles (Figure 2), a behavior that is in accordance with the general expectation. In contrast, the S-substituted heteroles exhibit a stabilized LUMO



Figure 1. LUMO, HOMO, and HOMO-1 orbitals of phosphole (left) and thiophene (right) at the B3LYP/6-31G*//B3LYP/6-31+G* level.

with energies that are lower than those of the parent rings (Figure 2). It is remarkable that the effect of the S-substituents is similar for thiophene and phosphole rings that have very different electronic properties since the S-heterole is a highly aromatic system while its P-analogue is almost nonaromatic. This behavior is rather surprising, since an interaction between the sulfur lone pair and the unoccupied ring π orbital should result in the destabilization of the LUMO energy for both S- and P-heteroles. However, this behavior has already been reported for thiophene with theoretical calculations showing that bis-3,4-ethylenedisulfanylthiophene (EDTT) possesses a lower LUMO level than bis-3,4ethylenedioxythiophene (EDOT).^[14f] Note that, in accordance with these theoretical results, the reduction potential of an EDTT-containing oligomer was reported to be lower than that of its EDOT-containing analogue.^[14k] The understanding of this phenomenon is not straightforward and can



Figure 2. LUMO, HOMO, and HOMO-1 Kohn–Sham orbital energies and HOMO–LUMO gaps (in eV) at the B3LYP/6-31G*//B3LYP/6-31+G* level of theory.

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find its origin in different reasons. For example, theoretical calculations have shown that the d orbital involvement in the LUMO is somewhat increased in the case of the sulfur derivatives,^[16] with respect to their oxygen analogues and it can contribute to the stabilization of the LUMO. Moreover the investigation of the photodissociation dynamics of phenol and thiophenol revealed mixing between the $\pi\pi^*$ and $\pi\sigma^*$ states in the case of the sulfur derivative only, which also explained a stabilization of the LUMO level.^[17] Likewise, in the photodissociation dynamics of 2-methyl-3furanethiol, the $(n/\pi)\sigma^*$ excited state played a significant role.^[18] In conclusion, this theoretical study brings to light the special behavior of the second-row S-substituents and justifies that its introduction at the 3,4-position of the phosphole ring is worth studying to tune the electronic properties of this P building block. Another key point revealed by the theoretical calculations is that the introduction of an S-substituent at the 3,4-position of heteroles significantly reduces their HOMO-LUMO gap (Figure 3). This appealing property is nicely illustrated by time-dependent (TD)-DFT calculations clearly showing that the UV-visible spectrum of 3,4ethylenedithiaphosphole is redshifted relative to that of its "all-carbon" analogue ($\Delta \lambda_{max} = 34 \text{ nm}$; the excitation wavelengths and oscillator strengths are given in the Supporting Information, together with simulated spectra). Very interest-

ingly, this effect is also observed and even amplified for the corresponding thiooxophosphole series (Figure 3, see the Supporting Information for simulated spectra $\Delta \lambda_{\text{max}} = 92 \text{ nm}$). In fact, the HOMO-LUMO separation of the 3,4-ethylenedithiathioxophosphole is very low due an important decrease of its LUMO level (Figure 3). This theoretical study highlights the impact of S-substituents on the electronic behavior of the phosphole ring and motivated our synthetic efforts towards unknown 3,4-ethylenedithiaphosphole derivatives.

Synthesis of 3,4-ethylenedithiaphosphole derivatives: Our synthetic approach towards the target 3,4-ethylenedithiaphosphole derivatives was to use the Fagan-Nugent route described in Scheme 2 (route (2)) starting with the 1,2-bis-(ethynylthio)ethanes 2 a,b (Scheme 4). Note that this choice raises a chemoselectivity issue since the intermediate low-valent zirconocene species

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Figure 3. HOMO-LUMO separations of phospholes with and without S atoms at their 3,4-positions.

(Negishi reagent)^[13] can potentially react 1) with the triple bonds (oxidative coupling leading to the zirconacyclopentadiene **G**, Scheme 2), or 2) with the C_{sp} -S bond of **2a,b** (oxidative addition leading to $-C \equiv C - (ZrCp_2)$ -S- derivatives; Cp = cyclopentadienyl), a process that is well exemplified with vinyl sulfides (Scheme 5).^[19]

The thienyl- or phenyl-capped 1,2-bis(ethynylthio)ethanes $2a,b^{[20]}$ were obtained in medium yields (ca. 30–50%) by



Scheme 4. Synthesis of 3,4-ethylenedithiaphosphole and 3,3',4,4'-tetrathia-1,1'-biphosphole derivatives 4a,b and 5a,b. Structure of reference phospholes I and J.^[81]

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Scheme 5. Oxidative addition of intermediate low-valent zirconocene species into an $C_{\rm sp2}{-}{\rm S}$ bond.

means of a synthetic method described by Gleiter et al.^[21] involving the nucleophilic attack of lithium acetylides on the 1,2-bis(thiocyanato)ethane **1** (Scheme 4). The treatment of **2a,b** with "zirconocene", followed by addition of PhPBr₂ or PBr₃, gave rise to the target 1-phenylphospholes **4a,b** and 1,1'-biphospholes **5a,b**, respectively (Scheme 4). Note that, in the course of formation of 1,1'-biphospholes **5a,b**, intermediate 1-bromophospholes were observed (³¹P NMR: δ = +49.4 (R=2-thienyl), +46.1 ppm (R=Ph)). After filtration of the solution over basic alumina to remove Zr-containing species, the phospholes **4a,b** and 1,1'-biphospholes **5a,b** were isolated as air-stable solids in 45–60% yields (Table 1). The insertion of the sulfur substituents in the exocyclic bridge induces a shielding of the PC_{β} and PC_{α} signals by approximately $\delta = 12$ and 2 ppm in compounds **4a** and **4b**, respectively, relative to the reference molecules **I** and **J** that bear a carbocycle bridge (Scheme 4).^[81] Phosphole **4b** bearing phenyl substituents was characterized by an X-ray diffraction study (Figure 4, Table 2). The angles and bond lengths of the P ring are classical and compare well with



Figure 4. Molecular structure of phosphole **4b** in the solid state. Hydrogen atoms have been omitted for clarity.

Table 1. ${}^{31}P{}^{1}H$ NMR spectroscopic, optical, and electrochemical data for 3,4-S-substituted phosphole and 1,1'-biphosphole derivatives.

	$\delta^{[a]}$ [ppm]	Yield [%]	$\lambda_{\rm max}/\lambda_{\rm onset}^{[b]}$ [nm]	$\log \varepsilon$	$\lambda_{\mathrm{em}}^{\mathrm{[b]}} [\mathrm{nm}] / \Phi^{\mathrm{[c]}} [\%]$	$E_{\mathrm{pa}}^{\mathrm{[d]}}\left[\mathrm{V} ight]$	$E_{\rm pc}^{\rm [d]} \left[{ m V} ight]$
4a	+9.9	60	437/502	3.68	536/1.0	+0.39	-2.28
4b	+10.2	50	385/445	3.90	493/1.8	+0.60	-2.47
5a	+5.0	45	403-480/600	3.96-3.48	-	+0.30	-1.57
5b	+7.2	53	376-441/496	4.30-3.82	-	$+0.54^{[e]}$	-1.81
6a	+47.3	95	471/542	3.93	612/<1	+0.63	$-1.87^{[e]}$
6b	+47.7	95	413/477	3.35	559/<1	+0.97	-2.04
7b	+34.1	95	419/489	3.56	557/<1	+0.94	$-1.94^{[e]}$
8b	+39.1	85	390/450	3.85	537/<1	-	$-1.14^{[e]}$
I ^[81]	+12.7	75	412/468	3.93	501/5	+0.40	-
$J^{[81]}$	+13.6	40	354/430	4.20	466/14.3	+0.69	-2.88
S ^[8j]	-0.5	60	360-391-448/560	4.11-4.08-3.81	-	+0.24	-2.10
T ^[8j]	-13.6	40	329-390/460	4.22-3.81	-	+0.57	-2.24
$U^{[81]}$	+52.6	93	432/496	3.98	548/4.6	+0.70	$-1.94^{[e]}$
$\mathbf{V}^{[9h]}$	+55.3	87	380/440	4.13	516/<1	+1.09	-2.14

[a] From ³¹P(¹H) NMR spectroscopy in CDCl₃. [b] Measured in CH₂Cl₂. [c] Fluorescence quantum yields determined using fluorescein as standard, ± 15 %. [d] All potentials were obtained during cyclic voltammetric investigations in 0.2 M Bu₄NPF₆ in CH₂Cl₂. Platinum electrode diameter: 1 mm; sweep rate: 200 mV s⁻¹. All reported potentials are referenced to the reversible formal potential of the ferrocene/ferrocenium couple. [e] Reversible processes, E_{ox}° and E_{red}° values provided.

pyramidal character ($\Sigma P_{ang} =$ 294.7°) and the endocyclic P-C bond lengths (1.808(2) -1.816(2) Å, Table 3) approach that of a P-C single bond (1.84 Å). Note that the twist angles between the phosphole ring and the aromatic substituents are rather low (38.58(6)°, 40.95(0)°), thus allowing a π conjugated pathway involving the phosphole ring and its 2,5aryl substituents. The S atoms are in the plane of the sp²-C atoms forming this extended π conjugated system (S-C3-C2-S dihedral angle, -4.87°, Figure 4). The S-C(phosphole) distances (1.766 (2) Å, Table 2)

those observed for other phos-

phole derivatives.[8a,k,l] For ex-

ample, the P atom has a strong

The newly prepared P-compounds **4a,b** and **5a,b** were characterized by high-resolution mass spectrometry and elemental analysis, and their multinuclear NMR spectra support the proposed structures. Their ³¹P{¹H} NMR spectra display a singlet at classical chemical shifts for 1-phenylphosphole derivatives (**4a**, $\delta = +9.9$ ppm; **4b**, $\delta =$ +10.2 ppm) and 1,1'-biphospholes (**5a**, $\delta = +5.0$ ppm; **5b**, $\delta = +7.2$ ppm).^[5,8a,j,I] Their ¹³C NMR spectra recorded at room temperature are very simple, thereby indicating symmetric structures and/or a rapid rotation around the P–P bond for 1,1'-biphospholes. The ¹³C{¹H} data of the carbon skeleton of **5a,b** and those of the corresponding phospholes **4a,b** are very similar, except the PC_a signals that are shielded by approximately $\delta = 3-5$ ppm in **4a,b** relative to **5a,b**. are shorter than a simple C–S bond (1.81 Å) and compare to those encountered in arylsulfide (1.75 Å) for which an S– $C(sp^2)$ electronic interaction takes place.^[22] These X-ray data suggest that the sulfur atoms at the 3,4-positions interact with the π -conjugated pathway formed by the phosphole ring and its 2,5-substituents.

To the best of our knowledge, it is the first time that the metal-promoted coupling of alkynes with low-valent zirconium complexes leading to metallacyclopentadiene intermediates has been applied to sulfide substrates (Scheme 4). At first glance, the success of this synthetic approach is quite surprising since it is well known that low-valent "zirconocene" inserts into the alkenyl–sulfur bond of vinyl sulfides, sulfoxides, and sulfone alkene substrates (Scheme 5).^[19]

Table 2. Crystal data and structure refinement for 3b, 4a, and 6b.

	4b	6a	8b
molecular formula	$C_{24}H_{19}PS_2$	$C_{41}H_{32}P_2Cl_2S_{10}$	$C_{24}H_{19}O_5PS_2$
M _r	402.88	978.11	482.48
T [K]	100(2)	100(2)	120(2)
crystal system	monoclinic	monoclinic	monoclinic
space group	P21/c	P2/n	P21/c
a [Å]	9.6734(4)	10.118(1)	9.321(1)
b [Å]	9.8046(5)	8.566(2)	18.804(1)
c [Å]	20.6158(10)	25.171(1)	12.915(1)
a [°]	90	90	90
β [°]	97.879(2)	98.202(1)	107.632
γ [°]	90	90	90
V [Å ³]	1936.82(16)	2159.3(5)	2157.3(3)
Ζ	4	2	4
$ ho_{ m calcd} [m g cm^{-3}]$	1.380	1.504	1.486
$\lambda (Mo_{K\alpha}) [Å]$	0.71073	0.71073	0.71069
crystal size [mm]	$0.2 \times 0.1 \times 0.03$	$0.2 \times 0.1 \times 0.05$	$0.3 \times 0.19 \times 0.12$
$\mu [{ m mm}^{-1}]$	0.364	0.740	0.357
F(000)	840	1004	1000
θ limit [°]	1.99-26.48	2.89-27.48	3.15-27.50
index ranges hkl	$-12 \le h \le 11$	$-13 \le h \le 13$	$-12 \le h \le 12$
	$-11 \le k \le 11$	$-11 \le k \le 11$	$-24 \leq k \leq 24$
	$-25 \leq l \leq 25$	$-32 \le l \le 32$	$-15 \le l \le 16$
reflns collected	12892	8695	35 4 34
independent reflns	3929	4923	4924
reflections $(I > 2\sigma(I))$	3463	3654	3934
data/restraints/params	3929/0/244	4923/0/251	4924/0/289
GOF on F^2	1.185	1.061	0.548
final R indices	R1 = 0.0395	R1 = 0.0548	R1 = 0.0309
$(I > 2\sigma(I))$	wR2 = 0.1112	wR2 = 0.1453	wR2 = 0.0855
R indices	R1 = 0.0484	R1 = 0.0760	R1 = 0.0459
(all data)	wR2 = 0.1292	wR2 = 0.1598	wR2 = 0.1025
largest diff. peak/hole [eÅ ⁻³]	0.410/-0.524	0.475/-0.519	0.504/-0.363

Table 3. Selected bond lengths [Å] and angles [°] for compounds 4b, 6a, and 8b.



[a] Y, Z=lone pair, X=CH₂=CH₂. [b] X=S, Y=S, Z=lone pair. [c] Y, Z=O, X=CH₂=CH₂.

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Since this synthetic result is an important and novel extension of the Fagan–Nugent route, we decided to investigate the mechanism of this reaction by theoretical calculations. One key question was to elucidate whether the observed chemoselectivity leading to intermediate metallacyclopentadienes **3a**,**b** is driven only by the presence of the organic linker between the two triple bonds of **2a**,**b** (Scheme 4; entropy factor).

Several groups have already investigated the Cp_2Zr -mediated coupling reaction of two acetylene molecules theoretically.^[23] The intimate mechanism and kinetics of the elemental steps are substrate dependent. However, in accordance with experimental data, these theoretical studies clearly point to stepwise activation of the two alkynes by the Cp_2Zr fragment (Scheme 6). The first alkyne is strongly bonded to



Scheme 6. Oxidative coupling leading to zirconacyclopentadiene complex **M** illustrated here with acetylene.

the metal center (K: Zr-C, ca. 2.18 Å). In contrast, the interaction of the second alkyne with the Zr center is weak (L: metal-C > 3.5 Å, Scheme 6). The oxidative coupling leading to zirconacyclopentadiene M (Scheme 6) takes place through a nonsymmetrical transition state. It is noteworthy that, in some cases, the bis(alkyne)complex L is neither an intermediate nor a transition state on the reaction pathway. The major differences between the previously investigated alkynes and those presented in this theoretical study are the fact that 1) the two $-C \equiv C$ - moieties belong to the same molecule (the entropy factor will be affected), and 2) the two -C \equiv C- moieties are linked to π -donor S atoms that are potentially a ligand for the low-valent Zr center, and that will influence the alkyne electronic property. The mechanism of the reaction depicted in Scheme 4 was studied with the model substrate CH_3 - $C \equiv C$ -S- $(CH_2)_2$ -S- $C \equiv C$ - CH_3 (N; the difference between the real system and this one is only the nature of the terminal groups). For this divne, a conformation analysis was performed with the MM1 force field and the different isomers located were further optimized using the combination of the B3LYP functional and the ccpVDZ basis set. Eleven different rotamers have been found on the potential-energy surface (see the Supporting Information) being close in energy to each other $(2-5 \text{ kcal mol}^{-1})$. These data suggest that in the case of the different intermediate Zr complexes bearing this ligand, several rotamers with similar energy can also exist.

The geometry and total energy of the zirconium complexes were calculated using the B3LYP and BP86 functionals and the cc-pVDZ basis set with pseudopotentials for Zr. Since both the solvent and—besides the alkene—the poten-

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tial other ligands of the starting Cp₂Zr are THF molecules, it is important to gain insights into the magnitude of the solvent effects. Therefore, single-point energies were determined using the polarizable continuum model (PCM) and THF as solvent, which resulted in changes between -4.2and +4.8 kcalmol⁻¹ with respect to the gas-phase values (Figure 5). However, the overall description of the elemental steps of the reactions (vide infra) is not influenced by the solvent model used.



Figure 5. Energy profile of the competitive reactions: oxidative addition (left) and formation of zirconacyclopentadiene complex **R** (right) and relative energies (in kcalmol⁻¹) are compared with the η^2 -complex **O** (in the middle in frame) at different levels of theory. For all the levels of theory the cc-pVDZ(-PP) basis set was used. [a] Neither an intermediate nor transition state was found using BP86/cc-pVDZ(-PP).

The first investigated step is the reaction of $[Cp_2Zr(H_2C=CH_2)(thf)]$ with substrate **N**. The energy of the reaction depicted in Scheme 7 leading to the key intermediate **O** at the



Scheme 7. Coordination of model diyne N to the zirconocene fragment.

B3LYP/cc-pVDZ(-PP)(THF) level is 2.5 kcal mol⁻¹. However, because of the formation of ethylene, the Gibbs free energy of the reaction is negative ($-12.8 \text{ kcal. mol}^{-1}$), and it is reasonable to assume that the formation of the zirconacy-clopentadiene ring will take place through this intermediate **O**. The complexation on the C=C triple bond of **N** for the formation of an **O**-type η^2 complex is remarkably favored over the complexation of the S atom (the latter is 45 kcal mol⁻¹ higher in energy than the former). Indeed, the presence of the S atoms does not change the nature of the

first elemental step of the classic mechanism depicted in Scheme 6.

Starting from complex **O**, two reaction pathways can be envisaged. The first one is the oxidative coupling leading to the zirconacyclopentadiene complex **R** (Figure 5, right). The second one is the oxidative addition of the zirconocene into the -S-C(\equiv C)- bond (Figure 5, left). Although the oxidative addition has a rather low barrier (nearly 20 kcal mol⁻¹), indicating that this is a plausible reaction pathway (in accord-

ance with the results of Marek et al.^[19]), the comparison of the energy profile of these two pathways (B3LYP/cc-pVDZ-(-PP) level) clearly show that the oxidative coupling of diynes leading to zirconacyclopentadiene R is favored over the oxidative addition both from thermodynamic and kinetic points of view (Figure 5). Therefore, these theoretical data fit with the experimental results and rationalize the selective formation of phosphole derivatives 4a,b/ 5a,b using 1,2-bis(ethynylthio)ethanes 2a,b (Scheme 4). At B3LYP/cc-pVDZ(-PP) the level, the optimization runs allowed us to locate an intermediate P and a transition state **Q** leading to the zirconacyclopentadiene ring R (see Figure 5, right). The profile of

the reaction is in good accordance with the former studies on alkyne coupling reactions with zirconocene (Scheme 6). Along the pathway leading to zirconacyclopentadiene \mathbf{R} , no structure exhibiting a Zr-S interaction is observed. No transition states could be determined between the (**O**-type) η^2 complex and intermediate P on the very flat potentialenergy surface. The activation barrier to the zirconacyclopentadiene R is very small at the B3LYP/cc-pVDZ(-PP) level. Moreover, at the BP86/cc-pVDZ(-PP) level, neither an intermediate (P) nor transition state (Q) was found. Relaxed optimization scans also support the barrier-free mechanism at this level (see the Supporting Information), which is in good agreement with some previous studies.^[23] In conclusion, this theoretical study revealed that the oxidative coupling of a substrate of type N with zirconocene follows a classic mechanism in spite of its peculiar structure.

Physical properties of 3,4-ethylenedithiaphosphole and 3,3',4,4'-tetrathia-1,1'-biphosphole derivatives: Compounds 4a,b (Scheme 4) display intense absorption bands in the visible part of the absorption spectra (Figure 6) that are assigned to π - π * transitions (vide infra). As generally observed in phosphole-based conjugated systems,^[8] the spectrum of the 2-thienyl-capped derivative 4a (λ_{max} =434 nm,



Figure 6. Absorption and emission spectra of 4a (dashed line) and 4b (solid line) in CH₂Cl₂.

 $\lambda_{\text{onset}} = 502 \text{ nm}$) is shifted to lower frequencies relative to that of its phenyl-substituted analogue 4b $(\lambda_{\rm max}=385 \text{ nm},$ $\lambda_{\text{onset}} = 445 \text{ nm};$ Table 1, Figure 6). It is worth noting that the absorption maximum (λ_{max}) and the optical end absorption (λ_{onset}) of derivatives 4a,b (Table 1) are redshifted relative to those of related phospholes I and J featuring no sulfur atoms in the carbocyclic bridge (Scheme 4)^[81] (4 a/I, $\Delta \lambda_{max} = 22 \text{ nm}, \Delta \lambda_{onset} = 34 \text{ nm};$ **4b/J**, $\Delta \lambda_{max} = 31 \text{ nm}$, $\Delta \lambda_{onset} =$ 15 nm, Table 1). The cyclic voltammetry (CV) performed at 200 mV s^{-1} revealed that the derivatives with or without sulfur in the carbocycle bridge exhibit



Figure 7. Absorption spectra of 5a (dashed line), 5b (solid line), and reference compounds S (dotted line) and T (dashed-dotted line) in CH₂Cl₂.

similar oxidation potentials, but that derivatives **4a,b** are more easily reduced than reference compounds **I** and **J** (Scheme 4, Table 1) revealing a stabilization of the LUMO level. Note that the redox processes observed for **4a,b** are irreversible. Therefore, both the UV-visible and electrochemical data show a decrease of the HOMO–LUMO separation of phosphole-based conjugated systems upon introducing an S substituent at the 3,4-positions of the P ring ($I \rightarrow 4a, J \rightarrow$ **4b**, Scheme 4).

The two phospholes **4a,b** are also photoluminescent and emit in the visible region ($\lambda_{em.}$: **4a**, 536 nm; **4b**, 493 nm). Note that the Stokes shifts are relatively important (ca. 4385–5690 cm⁻¹, Figure 6), which suggests a large rearrangement of these molecules upon photoexcitation. The quantum yields of **4a,b** are notably lower than those of derivatives I and J (Table 1). derivatives **5a,b**. These data confirm that the P–P skeleton is a powerful σ scaffold to establish through-bond electronic interaction between π chromophores.^[8a,j]

P-derivatives exhibiting $\sigma-\pi$ conjugation are still rare^[8a,j,11] and it was thus of interest to elucidate whether the presence of the S-substituents has an impact on this intriguing mode of conjugation. It is noteworthy that the λ_{max} of the 3,4-ethylenedithia-1,1'-biphospholes, including the low-energy transitions, are redshifted relative to those of their "all-carbon" analogues (Figure 7: **5a/S**; **5b/T**). This effect is more pronounced for the phenyl-substituted derivatives but is also effective in the thienyl series. Indeed, these optical data show that the extent of the $\sigma-\pi$ conjugation is notably affected by the presence of the S-substituents on the phosphole ring. It is very likely that the stabilization of the phosphole LUMO upon introduction of the S atoms shown by the theoretical calculation (Figure 2) plays a key role in

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ethylenedithia-1,1'-bi-The (Scheme 4) phospholes 5a,b display absorption spectra several absorption showing with one redshifted bands shoulder $(\lambda_{onset}: 5a,$ broad 600 nm; 5b, 496 nm; Figure 7). The fact that 1) these lowenergy bands are considerably redshifted relative to the absorption of the corresponding 1-phenylphospholes 4a.b (Figure 6), and that 2) the shape of the spectra of **5a**,**b** are very similar to those of the corresponding reference derivatives $S,T^{[8j]}$ (Figure 7), clearly show that $\sigma - \pi$ conjugation is effective in the newly prepared this behavior since the main contribution to the σ - π conjugation involves the interaction of σPP and σ^*PP with the LUMO of the P ring. This assumption is nicely supported by electrochemical the data (Table 1) showing that the Ssubstituted derivatives 5a,b are more easily reduced than the reference molecules S and T (5 a/S, $\Delta E_{\rm pc} = 53 \, {\rm mV};$ 5b/T, $\Delta E_{\rm pc} = 43$ mV), whereas the oxidation processes happen at the same potential (Table 1). Therefore, as observed in the 1-phenylphosphole series, there is a considerable stabilization of the LUMO of 1,1'-biphospholes upon introduction of the S atoms within the carbocycles fused to the P rings. These results show that the introduction of sulfur substituents at phosphole 3,4-positions has a considerable impact on the electronic properties of these Pcontaining π -conjugated systems.

Tuning the electronic property of 3,4-ethylenedithiaphospholes by P and S chemical modifica-

tions: Tuning the electronic properties of phosphole-containing π -conjugated systems by chemical modification of their P atom is an appealing property that we first demonstrated in 1999,^[80] and which was then used by many other groups.^[8,10] In this regard, derivatives **4a**,**b** behave as classic phospholes and their P center can be chemoselectively oxidized using elemental sulfur or dioxygen giving rise to compounds 6a,b and 7b, respectively (Scheme 8). These phospholes were isolated in high yields (95%) as air-stable derivatives (Table 1) and their multinuclear data, as well as their high-resolution mass spectra and elemental analysis, support the proposed structures. Derivative 6a was also characterized by an X-ray diffraction study (Figure 8, Table 2). This solid-state structure is of particular interest since the σ^4 -P atom of the P ring exhibits a partial positive charge, due to the presence of the highly polarized P=S bond (Scheme 8). Therefore, a push-pull effect can potentially take place within the ring due the presence of the exocyclic π -donor S atoms (Scheme 8). These two S atoms of 6a are in the plane of the planar phosphole ring and it is noteworthy that the $S-C_{sn^2}$ bond lengths are slightly shorter than those observed for the σ^3 -phosphole derivative **4b** in which no push-pull effect can take place (Table 3). However, the metric data of the P ring of **6a** compare well with those of σ^3 -derivative



Scheme 8. Chemical derivatization of phospholes **4a**,**b** and mesomeric forms of thiooxo- and oxo-phospholes **6a**,**b** and **7b**.



Figure 8. Molecular structures of phospholes **6a** and **8b** in the solid state. Hydrogen atoms have been omitted for clarity.

4b; neither lengthening of the C1–C2 and C3–C4 distances nor shortening of the P–C1 and P–C4 separations are recorded (Table 3). Indeed, these solid-state data do not speak for the presence of a push–pull system within the P ring of **6a**.

One 2-thienyl substituent of **6a** lies in the plane of the phosphole ring (dihedral angle, 1.6°) whereas the second one exhibits a twist angle of 37.9° (Figure 8). It is noteworthy that two S atoms (i.e., one of the thiophene ring and one of the exocyclic 3,4-ethylenedithia bridge) point towards each other. The fact that the distance between these two S centers (3.04 Å) is markedly smaller than the sum of the

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van der Waals radii (3.7 Å) prompted us to perform a calculation on **6a** to elucidate whether any S···S interaction takes place. Note that this type of interaction, although being rather weak, is an invaluable tool for the design of π -conjugated oligothiophene materials.^[14] Three rotamers **6a'–6a''**



Figure 9. The three optimized rotamers of 6a. View of 6a''' showing the critical points between the S atoms.

could be optimized for **6a** (Figure 9). The details of these optimized geometries and their total energies are given in the Supporting Information. The short distances between the S centers pointing in the same direction are reproduced in the optimized structures **6a**" and **6a**"' (calculated values: 3.117-3.176 Å). By the topological analysis of the B3LYP/6-31+G* electron density, critical points were found between the S atoms for both isomers **6a**" and **6a**"'' (see Figure 9 for conformer **6a**"''). However, the electron density is quite small in these points revealing that the S---S interaction is rather weak. Accordingly, conformers **6a**" and **6a**"'' do not possess extra stabilization and the energy difference between the three conformers is $1-2 \text{ kcal mol}^{-1}$ only.

As usually observed for phosphole-based π -conjugated systems, the oxidation of the P center of **4a**,**b** results in a bathochromic shift of the UV-visible λ_{max} and λ_{onset} as well as an increase of the oxidation and reduction potentials (Table 1: **4a/6a**, **4b/6b**, and **4b/7b**). It is worth noting that the absorption maximum (λ_{max}) and the optical end absorption (λ_{onset}) of derivatives **6a**,**b** (Table 1) are redshifted compared to those of related thioxophospholes **U** and **V** featuring no sulfur atoms in the exocyclic bridge (Scheme 8)^[81,9h] (**6a/U**: $\Delta\lambda_{max} = 39$ nm, $\Delta\lambda_{onset} = 46$ nm; **6b/V**: $\Delta\lambda_{max} = 33$ nm, $\Delta\lambda_{onset} = 37$ nm, Table 1). These experimental data can be nicely reproduced by TD-DFT calculations given in the Supporting Information. The redox properties are also affected by the presence of the S atoms: compounds **6a**,**b** are slightly easier to oxidize and to reduce than reference molecules **U**/ **V**. Therefore, the general trends expected following the analysis of the impact of the S-substituent on the phosphole building blocks (Figures 2 and 3) have been confirmed both by experimental and theoretical results obtained with two different series of π -conjugated systems.

The presence of a reactive heteroatomic center is the most important attribute of phosphole-based conjugated systems for chemical engineering aiming at varying their electronic property. Quite surprisingly, although heteroles featuring 3,4-ethylenedithia bridges have been extensively used for the tailoring of conjugated systems, the presence of potentially reactive S atoms has been fairly exploited to tune their electronic property.^[24] We have therefore investigated this approach with phenyl-capped thioxophosphole 6b and oxophosphole **7b** using *m*-chloroperoxybenzoic acid (mCPBA) at room temperature (Scheme 8). The reaction performed with oxophosphole 7b will be discussed first. The isolated product 8b is an air-stable orange powder that was purified by column chromatography (85% yield). Its ³¹P NMR spectroscopic chemical shift is similar to that of its precursor 7b (Table 1). The presence of a P ring is also supported by the observation in the ¹³C NMR spectrum of two doublets corresponding to the $P{-}C_{\alpha}$ and $P{-}C_{\beta}$ carbon atoms with classic P-C coupling constants. The HRMS and elemental analysis indicate that both S atoms were fully oxidized. The proposed disulfone structure of **8b** (Scheme 8) was confirmed by an X-ray diffraction study performed on single crystals (Figure 8, Tables 2 and 3). Under the same reaction conditions (mCPBA, RT), thioxophosphole 6b is also transformed into oxophosphole 8b in 85% yield. This result was not expected, since we are not aware of this type of reactivity in phosphole chemistry; nevertheless it can be understood by considering the high stability of the P=O moiety.

The analysis of the solid state of 8b reveals certain bond localization within the P ring (Table 3), but the presence of the strongly withdrawing sulfonic groups does not induce other special structural features. In contrast, the electronic property of the π -conjugated systems are affected by the -S- \rightarrow -S(O₂)- transformation. Compared to its precursor **7b**, the absorption maximum of compound 8b is blueshifted (Figure 10, Table 1, $\Delta \lambda_{max} = 22 \text{ nm}$) and its reduction potential increased by 0.8 V (Table 1). In other words, the oxidation of the 3,4-S atoms results in an increase of the HOMO-LUMO separation and of the electron affinity (lowering of the LUMO level). To get more insight into this tuning property, theoretical calculations have been performed. The isolated phosphole building block as a model compound was firstly investigated. The $-S \rightarrow -S(O_2)$ - transformation results in a decrease of both the HOMO and LUMO energy level of the phosphole ring, accompanied by a large increase of the HOMO-LUMO separation (Figure 11). As expected, and in line with the experimental results, the presence of the electron-withdrawing groups induces a notable decrease of the LUMO level. The blueshift of the λ_{max} is also nicely reproduced by the TD-DFT calculations (see Figure S3 in the Supporting Information). Indeed, these experimental and

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Figure 10. Electronic spectra of compounds 6a (solid line), 6b (dotted line), 7b (dashed line), and 8b (dashed-dotted line) in CH₂Cl₂.



Figure 11. HOMO–LUMO separations of thiooxophospholes illustrating the impact of having the sulfur moiety at their 3,4-positions.

theoretical studies show that the oxidation of the S atoms of a 3,4-ethylenedithia P-heterole bridge is a powerful means to tune the electronic property of the five-membered ring and especially to enhance its electron affinity.

Electropolymerization of 3,4-ethylenedithiathiooxophosphole and -1,1'-biphosphole derivatives 6a and 5a: One of the most versatile routes towards π -conjugated polymers involves the electropolymerization of thienyl-capped monomers by means of an oxidation process involving the coupling of radical cations.^[25] This method has been successfully applied for the preparation of hybrid phosphole–thiophene polymers having phosphole^[8d,I] or 1,1'-biphosphole^[8j] subunits. As observed for their corresponding molecular di(2thienyl)-capped P precursors, the optical and electrochemical properties of these phosphole-modified poly(thiophene)s depend both on the nature of the P building block (phosphole/1,1'-biphosphole) and on the chemical modification of the P centers $(\sigma^3,\lambda^3-P/\sigma^4,\lambda^4-P/\sigma^4,\lambda^5-P)$. By considering the impact of the 3,4-ethylenedithia bridge on the electronic properties of di(2-thienyl)phosphole and -1,1'-biphosphole, it was of interest to elucidate whether the same trends will be observed for the corresponding electro-generated polymers. The 2-thienyl-substituted σ^3,λ^3 - and σ^4,λ^5 -phospholes **4a** and **6a**, as well as the σ^3,λ^3 -biphosphole **5a** (Scheme 9)



Scheme 9. Synthesis of poly(6a) and poly(5a) by means of electrooxidation.

were selected for this study.

The electropolymerization experiments were conducted using solutions of the mixed phosphole-thiophenes 4a-6a in CH_2Cl_2 (1 mm) with Bu_4NPF_6 (0.2 m) as the supporting electrolyte. When using the σ^3 , λ^3 -phosphole **4a**, application of repetitive potential scans between 0 and 1 V did not result in polymer formation. Under the same conditions, its "allcarbon" analogue I (Scheme 4) also could not be polymerized. This similar behavior can be rationalized by the fact that the remote S atoms do not increase the formation and/ or the stability of the radical cation (which is mainly localized on the terminal thienyl rings). In contrast, repetitive potential scans applied to the solutions of monomers 6a and 5a in CH₂Cl₂ (between 0 to 0.83 V and 0.89 V, respectively) resulted in a new anodic process well below the onset of the oxidation of the monomers (Figure 12a, b). The fact that the intensity of this new redox system regularly increased is consistent with insoluble electroactive material deposition on the working Pt electrode. The two dark blue films formed are insoluble in all common solvents (CH₂Cl₂, THF, DMF, acetone, acetonitrile, MeOH). It is important to recall that under the same reaction conditions, the "all-carbon" σ^4 , λ^5 thioxophosphole U (Scheme 8) and σ^3 , λ^3 -biphosphole S (Figure 7) also undergo oxidative polymerization.^[81] The electrochemical responses of poly(5a) and poly(6a)(Scheme 9, Figure 12) were studied by CV, recorded in monomer-free electrolytic medium. The cyclic voltammograms of these materials show anodic waves that are stable and reversible upon cycling (five recurrent sweeps between -0.5and +0.8 V; Figure 12c, d). The threshold potential oxidation of poly(5a) (-0.2 V) is less anodic than that of poly(6a)(+0.1 V), which shows that the nature of the P building block has an impact on the electronic properties of the

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Figure 12. Multiple-scan voltammogram of 10^{-2} M solutions of derivatives a) **5a** and b) **6a** in 0.2 M Bu₄NPF₆ in CH₂Cl₂ (scan rate, 200 mV s⁻¹). Cyclic voltammogramm of electropolymerized c) poly(**5a**) and d) poly(**6a**) recorded in 0.2 M Bu₄NPF₆ in CH₂Cl₂ (scan rate, 200 mV s⁻¹). Working electrode: platinum disk (d=1 mm). Potentials referred to the ferrocene/ferrocenium couple.

phosphole-thiophene copolymer. Poly(**S**), the "all-carbon" analogue of poly(**5a**), is oxidized at a slightly more positive threshold (-0.35 V). Interestingly, poly(**5a**) undergoes a reduction process at -1.63 V that is not observed for poly(**S**) up to -2.7 V (Table 4). Therefore, as observed for the corresponding 1,1'-biphosphole monomers, the presence of the S

Table 4. Polymerization potential of monomers 5a-6a and reference compounds S and U. The p-doping and n-doping potential ranges and photophysical data of the corresponding dedoped polymers are also given.^[a]

	$E_{\text{electopol}}^{[b]}$ [V]	p doping ^[c] [V]	n doping ^[c] [V]	$\lambda_{\max}^{[e]}$ [nm]	$\lambda_{\text{onset}}^{[e]}$ [nm]
poly(5a)	0.89	$-0.20 \rightarrow +0.76$	$-1.63^{[d]}$	611	800
poly(6a)	0.83	$+0.11 \rightarrow +0.73$	$-1.35^{[d]}$	600	760
poly(S)	0.80	$-0.35 \rightarrow +0.32$	-	594	730
poly(U)	1.15	$+0.30 \rightarrow +0.65$	$-1.80 \! ightarrow \!-2.42$	529	750

[a] All potentials were obtained during cyclic voltammetric investigations of solutions of monomers in CH_2Cl_2 (1 mM) with Bu_4NPF_6 (0.2 M) or in CH_2Cl_2 free of monomer with Bu_4NPF_6 (0.2 M) for the polymer response. Platinum electrode diameter: 1 mm; sweep rate: 200 mv s⁻¹. [b] Potential at the electropolymerization takes place. [c] Potential range at which the p- and n-doping processes are reversible. Potentials were referred to the ferrocene/ferrocenium couple. [d] Threshold reduction potential of the irreversible process. [e] ± 5 nm.

atoms has an influence on the electron affinity of the 1,1'-biphosphole-based films. The influence of the S atoms within the bridge is more important for poly(6a) (Scheme 9). Firstly, poly(6a) possesses a lower threshold potential than that of its "all-carbon" analogue poly(U) (Table 4)^[81] and the shape of the anodic wave of poly(6a) (Figure 12) clearly shows that its p-doping stability is higher than that of poly(U).^[81] Secondly, the reduction of poly(6a) takes place at a less negative potential than poly(U) (Table 4). Therefore, the most important modification of the electronic property of a mixed polymer based on thienyl and phosphole or 1,1'-biphosphole moieties upon introduction of the S atoms within the bridge is the lowering of the LUMO level. The electropolymerization of 6a and 5a can also be conducted on indium-tin oxide (ITO) by recurrent CV, allowing the UV-visible spectrum of the insoluble poly(6a) and poly(5a) to be recorded. The UV-visible spectra of dedoped poly(6a)and poly(5a) are considerably redshifted relative to those of their respective monomers (Figure 13). The spectra exhibit a large band with an unresolved maximum (poly(5a): λ_{max} = 611 nm; poly(6a): $\lambda_{max} = 600$ nm) and a high value of λ_{onset} (poly(**5a**): $\lambda_{\text{onset}} = 800 \text{ nm}; \text{ poly($ **6a** $): } \lambda_{\text{onset}} = 760 \text{ nm})$ (Figure 13). These wavelengths (λ_{max} and λ_{onset}) are slightly redshifted relative to the analogous "all-carbon" polymers

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Figure 13. Electronic absorption measurements in CH₂Cl₂ for derivatives **5a** (dashed line) and **6a** (solid line) and on ITO modified by poly(**5a**) (dashed line) and poly(**6a**) (solid line) dedoped at -0.4 V. Deposits were prepared by anodic oxidation of 10^{-2} M solutions of **5a**, **6a** in 0.2 M Bu₄NPF₆ in CH₂Cl₂.

(Table 4), which indicates that the S-substituents of the Pmoieties induce a lowering of the gap of these electroactive materials.

Conclusion

In this paper, we have described the use of the Fagan-Nugent route for the synthesis of the first phosphole and 1,1'-biphosphole derivatives bearing S-substituents at their 3,4-positions. The theoretical study of the mechanism of this organometallic method showed that 1,2-bis(ethynylthio)ethane substrates follow the classic mechanism proposed for nonfunctional alkynes. The presence of the S atoms has a large impact on the electronic properties of the P rings, which allows small π -conjugated systems with low HOMO-LUMO separation and a stabilized LUMO level to be prepared. The 3,4-ethylenedithiaphosphole derivatives possess two reactive nucleophilic heterotaoms, that is, the σ^3 , λ^3 -P and the σ^2 , λ^2 -S centers, that can be successively oxidized. These chemioselective modifications result in a stepwise tuning of both the optical and the electrochemical properties of phosphole-based conjugated systems. Therefore, the incorporation of 3,4-ethylenedithiaphosphole within π -conjugated systems endowed these materials with multiaddressable ability. Lastly, polymers incorporating 3,4-ethylenedithiaphosphole and -1,1'-biphosphole units can be readily prepared by electropolymerization. These results show that these multifunctional P,S building blocks are valuable synthons for the molecular engineering of π -conjugated molecular or polymeric conjugated systems, and extend the family of organophosphorus-based materials.^[26]

Experimental Section

X-ray crystallography studies: Single crystals suitable for X-ray crystal analysis were obtained by slow diffusion of vapors of pentane into a solution of 4b, 6a, or 8b in dichloromethane. Single-crystal data collection was performed at 100 K with an APEX II Bruker-AXS (Centre de Diffractométrie, Université de Rennes 1, France) with Mo_{K α} radiation ($\lambda = 0.71073$ Å). Reflections were indexed, Lorentz-polarization-corrected, and integrated by the DENZO program of the KappaCCD software package. The datamerging process was performed using the SCALEPACK program.[27] Structure determinations were performed by direct methods with the solving program SIR97,^[28] which revealed all the non-hydrogen atoms. The SHELXL program^[29] was used to refine the structures by full-matrix least-squares methods based on F^2 . All

non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealized positions and refined with isotropic displacement parameters. In the case of derivative **6b**, one of the two thienyl moieties was found disordered over two superimposed orientations. This disorder was treated for the thienyl ring with a partition of these two orientations. For each of these orientations, the relative population was refined.

Atomic scattering factors for all atoms were taken from International Tables for X-ray Crystallography.^[30] Details of crystal data and structural refinements are given in Table 1. CCDC-777639 (**4b**), -777640 (**6a**), and -777641 (**8b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computations: All the density functional calculations were carried out using the Gaussian 03 code.^[31] This level of the theory has provided satisfactory results for phosphole-thiophene oligomers before.^[4c, h, 5d, 7] The geometries were fully optimized, and vibrational analysis was performed on the optimized structures to check whether the stationary point located is a minimum of the potential-energy hypersurface or a first-order saddle point (in the case of transition states). At the saddle points intrinsic reaction coordinate (IRC) calculations were performed to locate the minima connected by the transition structure. For the phosphole and thiophene derivatives the B3LYP/6-31+G* level of theory was used; the molecular orbitals were calculated at the B3LYP/6-31G* and HF/6-31G* levels. The vertical excitation energies were calculated on the optimized structures using the time-dependent (TD) density functional method applying the B3LYP functional and the 6-31G* basis set. The zirconocene complexes were calculated using the B3LYP and BP86 functionals and the cc-pVDZ basis set; for zirconium the cc-pVDZ basis with pseudopotentials.^[32] The solvent effect of THF was modeled with the PCM.^[33] For the visualization of the structures, the Molden program^[34] was used.

Syntheses and characterization: All experiments were performed under an atmosphere of dry argon using standard Schlenk techniques. Column chromatography was performed in air, unless stated otherwise. Solvents were freshly distilled under argon from sodium/benzophenone (THF, diethyl ether) or from phosphorus pentoxide (pentane, dichloromethane). [(Cp)₂ZrCl₂] was obtained from Alfa Aesar Chem. Co. *n*BuLi, PBr₃, and S₈ were obtained from Acros Chem. Co. Ammonium chloride, magnesium sulfate, 3-chloroperoxybenzoic acid (77 % max) and elemental sulfur were obtained from Aldrich Chem. Co. All compounds were used as received without further purification. PPhBr₂,^[S5] ethynylthiophene,^[36a,b] ethynylbenzene,^[36a,c] and 1,2-biscyanoethane^[21] (1) were prepared as described in the literature. Preparative separations were performed by grav-

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ity column chromatography on basic alumina (Aldrich, Type 5016A, 150 mesh, 58 Å) or silica gel (Merck Geduran 60, 0.063–0.200 mm) in 3.5–20 cm columns. ¹H, ¹³C, and ³¹P NMR spectra were recorded on Bruker AM300 or DPX200 instruments. ¹H and ¹³C NMR spectroscopic chemical shifts were reported in parts per million (ppm) relative to Si(CH₃)₄ as external standard. ³¹P NMR spectroscopic downfield chemical shifts were expressed with a positive sign, in ppm, relative to external 85 % H₃PO₄. Assignment of proton atoms is based on COSY experiments. Assignment of carbon atoms is based on HMBC, HMQC, and DEPT-135 experiments. High-resolution mass spectra were obtained on a Varian MAT 311, Waters Q-TOF 2, or ZabSpec TOF Micromass instrument at CRMPO, University of Rennes 1. Elemental analyses were performed by the CRMPO, University of Rennes 1.

Determination of optical data: UV-visible spectra were recorded at room temperature on a UVIKON 942 spectrophotometer and luminescence spectra were recorded in freshly distilled solvents at room temperature with a PTI spectrofluorometer (PTI-814 PDS, MD 5020, LPS 220B) using a xenon lamp. Quantum yields were calculated relative to fluorescein (Φ =0.90 in 0.1 N NaOH).^[37]

Cyclic voltammetry: The electrochemical studies were carried out under argon using an Eco Chemie Autolab PGSTAT 30 potentiostat for cyclic voltammetry with the three-electrode configuration: the working electrode was a platinum disk or ITO, the reference electrode a saturated calomel electrode, and the counter electrode a platinum wire. All potentials were internally referenced to the ferrocene/ferrocenium couple. For the measurements, concentrations of 10^{-3} M of the electroactive species were used in freshly distilled and degassed dichloromethane (Lichrosolv, Merck) and 0.2 m tetrabutylammonium hexafluorophosphate (TBAHFP, Fluka), which was twice recrystallized from ethanol and dried under vacuum prior to use.

Compound 2a: A solution of BuLi in hexanes (2.5 M, 3.5 mL, 8.7 mmol) was added dropwise at -78°C to a solution of 2-ethynylthiophene (0.941 g, 8.7 mmol) in THF (40 mL). The heterogeneous red mixture was stirred for 1 h. Then, a solution of 1,2-bis(thiocyano)ethane (0.63 g, 4.4 mmol) in THF (10 mL) was added to this reaction mixture at -20 °C. After stirring overnight at room temperature, the red solution was washed 3 times with an aqueous saturated ammonium chloride solution (30 mL). After extraction, the organic layer was dried over magnesium sulfate. All volatile materials were removed under vacuum, and the product was purified by silica gel chromatography (n-heptane/ethyl acetate, 9:1, v/v $R_{\rm f}$ =0.5). The product was obtained as a brown solid (0.373 g, 28%). ¹H NMR (200 MHz, C_6D_6): $\delta = 2.72$ (s, 4H; CH₂), 6.56 (dd, ${}^{3}J(H,H) = 3.6 \text{ Hz}, {}^{3}J(H,H) = 5.1 \text{ Hz}, 2 \text{ H}; H_{4\text{thienyl}}, 6.71 \text{ (dd, } {}^{3}J(H,H) = 5.1 \text{ Hz}, 2 \text{ H}; H_{4\text{thienyl}}, 5.71 \text{ (dd, } {}^{3}J(H,H) = 5.1 \text{ Hz}, 5.1 \text{$ 5.1 Hz, ${}^{4}J(H,H) = 1.1$ Hz, 2H; $H_{5\text{thienyl}}$), 7.10 ppm (dd, ${}^{3}J(H,H) = 3.6$ Hz, ${}^{4}J(H,H) = 1.1 \text{ Hz}, 2 \text{ H}; H_{3\text{thienyl}}); {}^{13}C{}^{1}H} \text{ NMR} (75.46 \text{ MHz}, \text{ CDCl}_{3}): \delta =$ 35.2 (s; CH_2), 82.2 (s; $C \equiv C$), 87.0 (s; $C \equiv C$), 123.1 (s; C_{thienvl}), 127.0 (s; CH_{thienyl}), 128.2 (s;CH_{thienyl}), 133.4 ppm (s; CH_{thienyl}); HRMS (EI): m/z calcd for C₁₂H₆S₄: 277.93524; found: 277.9347 [M-CH₂CH₂]⁺; calcd for C₁₄H₁₀S₄: 305.9665; found: 306.0 [M]⁺; elemental analysis calcd (%) for $C_{14}H_{10}S_4$ (306.492): C 54.86, H 3.29, S 41.85; found: C 54.96, H 3.40, S 40.56.

Compound 2b: A solution of BuLi in hexanes (2.5 M, 2.5 mL, 6.3 mmol) was added dropwise at -78 °C to a solution of ethynylbenzene (0.64 g, 6.3 mmol) in THF (30 mL). The heterogeneous red mixture was stirred for 1 h. Then, a solution of 1,2-bis-thiocyanoethane (0.45 g, 3.1 mmol) in THF (10 mL) was added to this reaction mixture at -20°C. After stirring overnight at room temperature, the red solution was washed 3 times with an aqueous saturated ammonium chloride solution (3×30 mL). After extraction, the organic layer was dried over magnesium sulfate. All volatile materials were removed under vacuum, and the product was purified on silica gel chromatography (n-heptane/ethyl acetate, 95:5, v/v $R_{\rm f}$ =0.5). The product was obtained as a yellow solid (0.91 g, 58%). ¹H NMR (300 MHz, C_6D_6): $\delta = 3.22$ (s, 4H; CH_2), 7.31 (m, 6H; $H_{meta, para phenyl}$), 7.42 ppm (m, 4H; $H_{ortho phenyl}$); ¹³C{¹H} NMR (75.46 MHz, CDCl₃): $\delta =$ 35.1 (s; CH₂), 77.9 (s; C=C), 94.3 (s; C=C), 123.1 (s; C_{phenyl}), 128.4 (s; CH_{phenvl}), 131.6 ppm (s; CH_{phenvl}); HRMS (EI): m/z calcd for C₁₈H₁₄S₂: 294.05369; found: 294.0518 [M]+; elemental analysis calcd (%) for

$C_{18}H_{14}S_2$ (294.439): C 73.43, H 4.79, S 21.78; found: C 73.67, H 5.17, S 21.40.

Compound 4a: At -78°C, a solution of BuLi in hexane (2.5 M, 0.85 mL; 2.1 mmol) was added dropwise to a solution of [Cp₂ZrCl₂] (0.30 mg, 1 mmol) and 1,2-bis(thiophen-2-ylethynylthio)ethane (2a; 0.31 mg, 1 mmol) in THF (20 mL). The solution was warmed to room temperature and stirred for 12 h. To this deep red solution was added, at -78°C, freshly distilled PhPBr₂ (230 µL, 1.1 mmol). The solution was allowed to warm to room temperature and stirred for an additional 12 h. Then, the solution was filtered on basic alumina (THF, $R_{\rm f}$ =0.8). All the volatile materials were removed under vacuum. Compound 4a was washed several times with pentane and diethyl ether and isolated as a dark red solid (0.25 g, 60 %). ¹H NMR (300 MHz, C₆D₆): $\delta = 2.44$ (m, 2H; CH₂), 2.59 (m, 2H; CH₂), 6.74 (ddd, ${}^{3}J(H,H) = 5.1$ Hz, ${}^{3}J(H,H) = 3.6$ Hz, ${}^{5}J(P,H) =$ 1.2 Hz, 2H; $H_{4\text{thienyl}}$), 6.89 (m, 5H; $H_{meta,para \text{ phenyl}}$, $H_{5\text{thienyl}}$), 7.51 (d, ${}^{3}J(H,H) = 3.6 \text{ Hz}, 2 \text{ H}; H_{3\text{thienyl}}, 7.61 \text{ ppm} (ddd, {}^{3}J(H,H) = 7.7 \text{ Hz},$ ${}^{3}J(H,H) = 3.6 \text{ Hz}, {}^{5}J(P,H) = 10.4 \text{ Hz}, 2 \text{ H}; H_{ortho \text{ phenyl}}); {}^{13}C \text{ NMR} (75 \text{ MHz}, 10.4 \text{ Hz})$ CD₂Cl₂): $\delta = 28.4$ (s; CH₂), 125.8 (d, J(P,C) = 2.4 Hz; C₅H_{thienyl}), 126.5 (d, $J(P,C) = 10.3 \text{ Hz}; C_3H_{\text{thienyl}}), 127.3 \text{ (s; } C_4H_{\text{thienyl}}), 128.8 \text{ (d, } J(P,C) = 8.6 \text{ Hz};$ $C_{meta}H_{phenyl}$), 130.2 (d, J(P,C) = 1.5 Hz; $C_{para}H_{phenyl}$), 132.1 7.2 Hz; PC=C), 132.8 (d, J(P,C) = 16.4 Hz; Ci), 133.4 (d, J(P,C) = 2.9 Hz; PC=C), 133.6 (d, J(P,C) = 20.7 Hz; $C_{ortho}H_{phenyl}$), 137.9 ppm (d, J(P,C) =22.3 Hz; C_2); ³¹P{¹H} NMR (CD₂Cl₂, 121.5 MHz): $\delta = 9.9$ ppm (s); HRMS (EI): m/z calcd for C₂₀H₁₅PS₄: 413.97943; found: 413.9790 [M]⁺; elemental analysis calcd (%) for C₂₀H₁₅PS₄ (414.572): C 57.94, H 3.65, S 30.94; found: C 58.28, H 4.05; S 30.79.

Compound 4b : At -78 °C, a solution of BuLi in hexane (2.5 M, 1.12 mL; 2.8 mmol) was added dropwise to a solution of [Cp2ZrCl2] (0.39 mg, 1.3 mmol) and 1,2-bis(phenylethynylthio)ethane (2b) (0.39 mg, 1.3 mmol) in THF (30 mL). The solution was warmed to room temperature and stirred for 12 h. Freshly distilled PhPBr₂ (300 µL, 1.5 mmol) was added to this red solution at -78°C. The solution was allowed to warm to room temperature and stirred for an additional 24 h. Then, the solution was filtered on basic alumina (THF, $R_{\rm f}$ =0.8). All the volatile materials were removed under vacuum. Compound 4b was washed several times with pentane and diethyl ether and isolated as a yellow solid (0.26 g, 50%). ¹H NMR (300 MHz, CD₂Cl₂): $\delta = 3.11$ (m, 2H; CH₂), 3.31 (m, 2H; CH₂), 7.12–7.30 (m, 7H; $H_{ortho,meta,para phenyl}$, $H_{4phenyl}$), 7.37 (pseudo-t, J(H,H) =7.3 Hz, J(H,H) = 7.8 Hz, 4H; $H_{3phenyl}$), 7.54 ppm (d, J(H,H) = 7.3 Hz, 4H; $H_{2\text{phenyl}}$); ¹³C NMR (75 MHz, CD₂Cl₂): $\delta = 28.5$ (s; CH₂), 127.0 (d, $J(P,C) = 0.7 \text{ Hz}; C_4H_{phenyl}), 128.3 \text{ (s; } C_3H_{phenyl}), 128.5 \text{ (d, } J(P,C) = 8.2 \text{ Hz};$ $C_{meta}H_{phenyl}$), 129.0 (d, J(P,C) = 9.5 Hz; C_2H_{phenyl}), 129.6 (d, J(P,C) = 1.5 Hz; $_{tra}H_{phenyl}$), 131.4 (d, J(P,C) = 15.6 Hz; $C_{ipsophenyl}$), 132.4 (d, J(P,C) = 15.6 Hz; $C_{ipsophenyl}$, $C_{ipsophenyl}$), 132.4 (d, J(P,C) = 15.6 Hz; $C_{ipsophenyl}$, $C_$ C_{n} 10.2 Hz; PC=C), 133.4 (d, J(P,C) = 19.7 Hz; $C_{ortho}H_{phenyl}$), 135.6 (d, $J(P,C) = 17.2 \text{ Hz}; C_{1\text{phenyl}}, 142.9 \text{ ppm} (d, J(P,C) = 1.8 \text{ Hz}; PC=C); {}^{31}P{}^{1}H$ NMR (CD₂Cl₂, 121.5 MHz): $\delta = 10.2$ ppm (s); HRMS (EI): m/z calcd for $C_{24}H_{19}PS_2$: 402.06658; found: 402.0651 [M]⁺; elemental analysis calcd (%) for C₂₄H₁₉PS₂ (402.519): C 71.62, H 4.76, S 15.93; found: C 71.26, H 4.65, S 15.99.

Compound 5a: A solution of BuLi in hexanes (2.5 M, 0.52 mL; 1.2 mmol) was added dropwise at -78°C to a solution of [Cp₂ZrCl₂] (0.182 g, 0.62 mmol) and 1,2-bis(thienyl-2-ylethynylthio)ethane (2a) (0.181 g, 0.6 mmol) in THF (20 mL). After being stirred overnight, the solution turned deep red and neat PBr₃ (0.12 mL, 1.2 mmol) was added at -78 °C. The solution was stirred for 3 d at room temperature and turned light red. The solution was then filtered on basic alumina (THF, $R_f = 0.8$) and all volatile materials were removed under vacuum. The precipitate was washed several times with pentane and diethyl ether. Compound 5a was isolated as a red solid (0.09 g, 45%). ¹H NMR (300 MHz, CD₂Cl₂): $\delta =$ 3.08 (m, 8H; CH₂), 7.13 (dd, ${}^{3}J(H,H) = 3.6$ Hz, ${}^{4}J(H,H) = 0.9$ Hz, 4H; $H_{3\text{thienyl}}$), 7.16 (dd, ${}^{3}J(\text{H},\text{H}) = 3.6 \text{ Hz}$, ${}^{3}J(\text{H},\text{H}) = 5.1 \text{ Hz}$, 4H; $H_{4\text{thienyl}}$), 7.43 ppm (dd, ${}^{4}J(H,H) = 0.9$ Hz, ${}^{3}J(H,H) = 5.1$ Hz, 4H; H_{5thienyl}); ${}^{13}C{}^{1}H$ NMR (75.46 MHz, CD_2Cl_2): $\delta = 27.7$ (s, CH_2) 125.7 (s, $CH_{thienyl}$), 126.9 (tlike, J(P,C)=5.6, 5.5 Hz; CH_{thienyl}), 127.1 (s, CH_{thienyl}), 130.7 (brs; PC=C), 134.6 (brs; PC=C), 137.6 ppm (t-like, J(P,C) = 12.0, 12.0 Hz; C_{thienyl} ; ${}^{31}P{}^{1}H$ NMR (CD₂Cl₂, 121.5 MHz): $\delta = 5.0$ ppm (s); HRMS (ES, positive mode): m/z calcd for C₂₈H₂₀P₂S₈Na: 696.87037; found: 696.8704 [M+Na]⁺;

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Compound 5b: A solution of BuLi in hexanes (2.5 M, 0.52 mL; 1.2 mmol) was added dropwise at -78 °C to a solution of $[Cp_2ZrCl_2]$ (0.182 g, and 1,2-bis(phenylethynylthio)ethane (2b) (0.184 g, 0.62 mmol) 0.62 mmol) in THF (20 mL). After being stirred overnight, the solution turned deep red and neat PBr₃ (0.12 mL, 1.20 mmol) was added at -78°C. The solution was stirred for 3 d at room temperature and turned light red. The solution was then filtered on basic alumina (THF, $R_f = 0.8$) and all volatile materials were removed under vacuum. The precipitate was washed several times with pentane and diethyl ether. Compound 5b was isolated as an orange solid (0.10 g, 53%). ¹H NMR (300 MHz, CD₂Cl₂): δ = 2.85 (m, 4H; CH₂), 3.00 (m, 4H; CH₂), 7.32 (m, 8H; H_{phenyl}), 7.38 (m, 4H; $H_{4phenyl}$), 7.47 ppm (m, 8H; H_{phenyl}); ¹³C{¹H} NMR (75.46 MHz, CD_2Cl_2): $\delta = 27.9$ (s; CH_2), 127.0 (s; CH_{phenyl}), 128.1 (s; CH_{phenyl}), 129.3 (t-like, J(P,C)=4.8 Hz; CH_{phenyl}), 132.0 (t-like, J(P,C)= 4.5, 4.2 Hz; PC=C), 135.3 (t-like, J(P,C)=9.0, 9.2 Hz; C_{phenyl}), 137.6 ppm (d, $J(P,C) = 6.0 \text{ Hz}; PC = C); {}^{31}P{}^{1}H} \text{ NMR} (CD_2Cl_2, 121.5 \text{ MHz}): \delta =$ 7.2 ppm (s); HRMS (ES, positive mode): m/z calcd for $C_{36}H_{28}P_2S_4Na$: 673.04468; found: 673.0452 [M+Na]+; elemental analysis calcd (%) for C36H28P2S8 (650.826): C 66.44, H 4.34, S 19.71; found: C 66.23, H 4.00, S 19.82.

Compound 6a: An excess amount of elemental sulfur was added to a solution of phosphole 4a (0.50 g, 1.2 mmol) in THF (10 mL) at room temperature. The reaction mixture was stirred for 1 d, filtered, and the solvent was removed under vacuum. After purification on silica gel (heptane/CH₂Cl₂, 60:40, v/v, $R_{\rm f}$ =0.7), **6a** was obtained as an air-stable orange solid (0.51 g, 95%). ¹H NMR (300 MHz, CDCl₃): $\delta = 3.46$ (s, 4H; CH₂), 6.99 (dd, ${}^{3}J(H,H) = 5.1 \text{ Hz}$, ${}^{3}J(H,H) = 3.9 \text{ Hz}$, 2H; $H_{4\text{thienyl}}$), 7.36 (d, $^{3}J(H,H) = 5.1 \text{ Hz}, 2 \text{ H}; H_{3\text{thienvl}}), 7.48 \text{ (m, 5H; } H_{meta, para phenyl}, H_{5\text{thienvl}}),$ 7.93 ppm (ddd, ${}^{3}J(H,H) = 7.5$ Hz, ${}^{4}J(H,H) = 1.0$ Hz, J(P,H) = 9.0 Hz, 2H; $H_{ortho phenyl}$); ¹³C{¹H} NMR (75.46 MHz, CD₂Cl₂): $\delta = 27.9$ (s; CH₂), 124.7 (d, J(P,C) = 83.9 Hz; PC=C), 126.9 (s; CH_{thienyl}), 127.3 (s; CH_{thienyl}), 128.4 (d, J(P,H)=6.0 Hz; CH_{thienyl}), 129.1 (d, J(P,C)=77.9 Hz; C_{ipso phenyl}), 129.2 (d, J(P,C)=12.8 Hz; CH_{meta phenyl}), 130.8 (d, J(P,C)=12.1 Hz; CH_{ortho phenyl}), 132.2 (d, J(P,C) = 3.2 Hz; $CH_{para \text{ phenyl}}$), 133.7 (d, J(P,C) = 14.7 Hz; C_{thienyl}), 135.2 ppm (d, $J(P,C) = 24.7 \text{ Hz}; C_{\beta}$); ³¹P{¹H} NMR (CD₂Cl₂, 121.5 MHz): $\delta = +47.3 \text{ ppm}$ (s); HRMS (EI): m/z calcd for $C_{20}H_{15}PS_5$: 445.9515; found: 445.9491 [M]+; elemental analysis calcd (%) for C₂₀H₁₅PS₅ (446.636): C 53.78, H 3.39, S 35.90; found: C 53.89, H 3.25, S 35.95.

Compound 6b: An excess amount of elemental sulfur was added to a solution of phosphole 4b (0.50 g, 1.24 mmol) in THF (10 mL) at room temperature. The reaction mixture was stirred for 1 d, filtered, and the solvent was removed under vacuum. After purification on silica gel (heptane/CH₂Cl₂, 60:40, v/v, $R_f = 0.7$), **6b** was obtained as an air-stable yellow powder (0.51 g, 95%). ¹H NMR (300 MHz, CD₂Cl₂): $\delta = 3.31$ (s, 4H; CH₂), 7.31–7.50 (m, 13H; $H_{meta, para phenyl}$, $H_{2,3,4phenyl}$), 7.86 ppm (ddd, ${}^{3}J(H,H) = 7.5 \text{ Hz}, {}^{4}J(H,H) = 1.8 \text{ Hz}, J(P,H) = 15.0 \text{ Hz}, 2 \text{ H}; H_{ortho \text{ phenyl}};$ ¹³C{¹H} NMR (75.46 MHz, CD₂Cl₂): $\delta = 27.8$ (s; CH₂), 128.0 (d, J(P,C) =77.6 Hz; PC=C), 128.3 (s; CH_{phenyl}), 128.8 (s; CH_{para phenyl}), 128.9 (s; CH_{phenyl}), 129.0 (s; CH_{phenyl}), 130.7 (d, J(P,C)=80.8 Hz; C_{ipso phenyl}), 130.8 (d, J(P,C)=11.7 Hz; CH_{meta phenyl}), 131.7 (d, J(P,C)=9.9 Hz; C_{phenyl}), 132.0 $(d, J(P,C) = 9.7 \text{ Hz}; CH_{ortho phenyl}), 138.7 \text{ ppm} (d, J(P,C) = 26.9 \text{ Hz}; PC=C);$ ³¹P{¹H} NMR (CD₂Cl₂, 121.5 MHz): $\delta = +47.7$ ppm (s); HRMS (EI): m/zcalcd for C₂₄H₁₉PS₃: 434.03865; found: 434.0370 [M]⁺; elemental analysis calcd (%) for C24H19PS3 (434.58): C 66.33, H 4.41, S 22.13; found: C 66.08, H 4.34, S 21.98.

Compound 7b: A solution of phosphole **4b** (0.030 g, 0.07 mmol) in THF (5 mL) was stirred for 5 d in air and all volatile materials were removed under vacuum. The precipitate was dissolved in ethyl acetate and compound **7b** was precipitated by adding pentane. Compound **7b** was obtained as an air-stable yellow-orange powder (0.29 g, 95%).¹H NMR (200 MHz, CD₂Cl₂): δ =3.32 (m, 4H; CH₂), 7.29–7.58 (m, 9H; *H_{meta,para}* phenyl. *H*_{3,4phenyl}), 7.56 (dd, ³*J*(H,H)=6.9 Hz, ⁴*J*(H,H)=1.2 Hz, 4H; H₂ phenyl), 7.69 ppm (ddd, ³*J*(H,H)=7.7 Hz, ⁴*J*(H,H)=1.5 Hz, *J*(P,H)=12.8 Hz, 2H; *H_{ortho phenyl}*); ¹³Cl¹H] NMR (75.46 MHz, CD₂Cl₂): δ =27.7 (s; CH₂), 128.0 (d, *J*(P,C)=84.6 Hz; PC=C), 128.1 (d, *J*(P,C)=0.8 Hz; CH_{phenyl}), 128.5 (s; CH_{phenyl}), 128.6 (d, *J*(P,C)=5.5 Hz; CH_{phenyl}), 128.9 (d, *J*(P,C)=12.4 Hz;

CH_{meta} phenyl), 129.5 (d, J(P,C) = 99.3 Hz; C_{ipso} phenyl), 130.7 (d, J(P,C) = 10.5 Hz; CH_{ortho} phenyl), 132.0 (d, J(P,C) = 2.9 Hz; CH_{para} phenyl), 132.1 (d, J(P,C) = 9.2 Hz; C_{phenyl}), 139.2 ppm (d, J(P,C) = 30.6 Hz; PC=C); ³¹P[¹H] NMR (CD₂Cl₂, 81.0 MHz): $\delta = 34.1 \text{ ppm}$ (s); HRMS (ES, positive mode): m/z calcd for $C_{24}H_{19}OPS_2Na$: 441.0513; found: 441.0517 $[M+Na]^+$; elemental analysis calcd (%) for $C_{24}H_{19}OPS_2$ (418.518): C 68.88, H 4.58, S 15.32; found: C 68.75, H 4.20, S 14.98.

Compound 8b: A solution of 3-chloroperoxybenzoic acid (77% max, 6 equiv, 0.094 g, 0.44 mmol) in CH₂Cl₂ (5 mL) was added dropwise to a solution of phosphole 6b (0.032 g, 0.074 mmol) in CH₂Cl₂ (5 mL) at room temperature. The reaction mixture was stirred for 2 h, then treated with a saturated solution of NaHCO3 (2 mL) to remove the benzoic acids and was allowed to stir for another 2 h. The mixture was then extracted with dichloromethane (3×5 mL), dried over MgSO4, and solvents were removed to give an orange solid. The crude solid was subjected to chromatography on silica gel (MeOH/CH₂Cl₂, 0.2:99.8, v/v, $R_f = 0.60$). Compound 8b was obtained as an air-stable yellow-orange powder (0.030 g, 85%).¹H NMR (200 MHz, CD₂Cl₂): $\delta = 4.00$ (m, 4H; CH₂), 7.38–7.78 (m, 12 H; H_{phenyl}), 7.64 (dd, ${}^{3}J(H,H) = 7.3 \text{ Hz}$, ${}^{4}J(H,H) = 1.8 \text{ Hz}$, 1 H; H_{para} phenyl), 7.73 ppm (ddd, ${}^{3}J(H,H) = 8.4 \text{ Hz}$, ${}^{4}J(H,H) = 1.4 \text{ Hz}$, J(P,H) = 1.4 Hz, $J(P,H) = 1.4 \text{$ 12.7 Hz, 2H; $H_{ortho\ phenyl}$); ¹³C{¹H} NMR (75.46 MHz, CD₂Cl₂): δ = 48.7 (s, CH_2), 122.8 (d, $J(\dot{P}, \dot{C}) = 98.1 \text{ Hz}$; PC=C), 127.8 (s; CH_{phenyl}), 128.0 (d, $J(P,C) = 6.8 \text{ Hz}; CH_{phenyl}$, 128.3 (d, $J(P,C) = 4.9 \text{ Hz}; CH_{phenyl}$), 129.0 (d, $J(P,C) = 12.7 \text{ Hz}; CH_{meta phenyl}), 129.9 (d, J(P,C) = 10.6 \text{ Hz}; CH_{ortho phenyl}),$ 130.0 (d, J(P,C)=1.3 Hz; C_{phenyl}), 133.2 (d, J(P,C)=2.8 Hz; CH_{para phenyl}), 140.2 (d, J(P,C) = 27.0 Hz; PC=C), 144.7 ppm (d, J(P,C) = 79.9 Hz; C_{ipsc} _{phenyl}); ³¹P{¹H} NMR (CD₂Cl₂, 81.0 MHz): $\delta = 39.1$ ppm (s); HRMS (ES, positive mode): m/z calcd for C₂₄H₂₀O₅PS₂: 483.0490; found: 483.0484 $[M+H]^+$; elemental analysis calcd (%) for C₂₄H₁₉O₅PS₂ (482.516): C 59.74, H 3.97, S 13.29; found: C 59.85, H 4.10, S 12.96.

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