The Synthesis and (Spectro)electrochemical Behavior of 2,5-Diferrocenyl-1-phenyl- 1*H*-phosphole

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Abstract: 2,5-Diferrocenyl-1-phenyl-1*H*-phosphole (**3**) has successfully been prepared by a cyclization reaction of phenylphosphine with 1,4-diferrocenylbutadiyne. Subsequent reaction with elemental sulfur and selenium, respectively, leads to the formation of the appropriate phosphole sulfide (**4**) or selenide (**5**). Molecules **4** and **5** have structurally been characterized by single crystal X-ray diffraction. Despite the tetrahedral environment at the phosphorus atom, the

C_4P ring itself is planar and coplanar to the cyclopentadienyl rings of the ferrocenyl termini. Electrochemical measurements revealed that the two ferrocenyl groups could be oxidized at discrete potentials, with separation of the individual redox waves of 280 mV (**3**), 240 mV (**4**) and 235 mV (**5**), respectively. These values agree with other examples of heterocyclic-bridged diferrocenyl compounds such as diferrocenyl thiophene (260 mV) and diferrocenyl furan (290 mV). Compounds [**3**]⁺, [**4**]⁺ and [**5**]⁺ exhibit IVCT absorptions of weak to moderate strength which conforms well to the predictions of the Hush two-state model for weakly coupled mixed-valence systems. These conclusions are supported by DFT and TD-DFT results, which satisfactorily model the observed structural and spectroscopic parameters. The computational work assists in assigning the various low energy (LF, IVCT) electronic transitions and also highlights the key role of the unsaturated *cis*-diene-like C_4H_2 building block of the heterocycle in promoting the $\text{Fc} \rightarrow \text{Fc}^+$ electron-transfer transition.

Introduction

Compounds with two redox-active transition metal fragments connected *via* a π -conjugated spacer unit are of considerable interest as they can be regarded as model compounds for molecular wires.^{1–14} In the last years huge efforts in the development of molecules in which the two redox-active metal centers exhibit a pronounced electronic communication across the spacer unit have been made. During the course of these investigations, a wide variety of π -conjugated spacers have been explored including systems based on all-carbon chains, vinylogous moieties, aromatic hydrocarbons, metallacycles or heteroatom-containing groups.^{15–24} An equally wide variety of metal fragments have been used as redox active termini, including half-sandwich, 5- and 6-coordinate metal centers, metallocenyl groups, bimetallic complexes and clusters, with the

degree of electronic interaction between them in the mixed-valence state assessed by drawing on electrochemical and spectroscopic (UV-Vis/NIR, IR, EPR) data, often supported by quantum chemical calculations.^{2,11,12,25} Whilst it is well-known that the electronic structure of such linear arrays, and hence the ‘intermetallic communication’ or coupling in the mixed-valence state, depends on the nature of both the metal termini and the spacer unit, predicting these *a priori* is not always a simple task.

Within recent studies of our research group it could be demonstrated on the example of di-, tri- and tetra-ferrocenyl heterocycles (thiophenes, furans and pyrroles)^{22,24} and metallacycles featuring a Cp^*_2M ($\text{M} = \text{Ti}, \text{Zr}$)^{17,18} moiety that the electronic characteristics (conjugation and electron balance) greatly influence the intermetallic communication between the mixed valent termini. In continuation of this work we herein present the synthesis and characterization of diferrocenyl phosphole as well as its chalcogenides. While neglected for decades, phospholes have gained increasing levels of interest during the last years.^{26–31} Its successful application in metal-containing organic light-emitting devices (OLEDs) accelerated the research on this topic furthermore.^{32,33} The phosphole ring shows a degree of aromaticity depending on the substituents in 1-, 2- and 5-position, as bulky substituents force the phosphorus to adopt a planar environment. However, blocking the phosphorus lone pair by coordination or oxidation reactions, for example, prevents the extended conjugation around the ring system and removes the aromaticity. Hence, the phosphole motif may offer a tool to fine-tune the electronic nature of the π -conjugated connector unit and hence the electronic effects that may be transmitted across it. This potential electronic flexibility prompted us to study the mixed-valence behavior of diferrocenyl phospholes as a function of the chemical nature of the phosphorus atom.

Results and discussion

Synthesis and characterization. 2,5-Diferrocenyl-1-phenyl-1*H*-phosphole (**3**) was synthesized by cyclization of phenylphosphine with diferrocenylbutadiyne according to a reaction procedure firstly described by Märkl and Potthast.³⁴ Phenylphosphine (**1**) was reacted with 0.8 eq. of *n*-butyllithium and the resulting solution was added slowly to 1,4-diferrocenylbutadiyne (**2**) giving 2,5-diferrocenyl-1-phenyl-1*H*-phosphole (**3**) (Scheme 1). Treatment of **3** with elemental sulfur or selenium resulted in the formation of the corresponding phosphole chalcogenides **4** and **5** (Scheme 1).

Scheme 1. Synthesis of phospholes 3 – 5.^a

^a (i) benzene/thf (1:1, v/v), 0 °C, 1 h; (ii) thf, 25 °C, 12 h, Fc = **Fe**(η^5 -C₅H₅)(η^5 -C₅H₄).

Compounds **3** – **5** are stable towards air and moisture both in the solid state and in solution. They have been characterized by elemental analysis, IR and NMR (^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{31}\text{P}\{^1\text{H}\}$) spectroscopy and ESI-TOF mass spectrometry. The electrochemical and spectroelectrochemical behavior was investigated by cyclic voltammetry (CV), square wave voltammetry (SWV) as well as *in situ* UV-Vis /NIR and IR spectroelectrochemistry.

For the ^1H NMR spectra of all three diferrocenyl phospholes **3** – **5** one singlet for the C_5H_5 rings and four multiplets for the C_5H_4 protons of the ferrocenyl substituents appear as the α - and

β -protons are diastereotopic, which is due to the prochiral nature of the phosphorus atom. The signals of the CH phosphole protons appear almost at the same chemical shift (**3**: 6.87 ppm; **4**: 6.87 ppm; **5**: 6.90 ppm) as doublets with $^3J_{\text{PH}} = 11.4$ Hz (**3**), $^3J_{\text{PH}} = 36.5$ Hz (**4**) and $^3J_{\text{PH}} = 35.9$ Hz (**5**). The respective carbon atoms in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of these species are observed at ca. 130.5 ppm, which indicates that the electronic character of the carbons (and attached protons) in 3- and 4-position of the heterocycle remain unchanged upon oxidation of the phosphorus atom, while the J_{PH} coupling constants change upon oxidation ($J_{\text{P(III)H}} < J_{\text{P(V)H}}$). The signals of the *meta*- and *para*-protons of the phenyl group in **3** appear as an unresolved multiplet at 7.4 ppm (Experimental Section). For the respective *ortho*-protons a multiplet at 7.6 ppm could be observed. In contrast, the *ortho*-protons in **4** and **5** appear as doublet-of-doublets-of-doublets at 8.02 ppm (**4**) and 8.04 ppm (**5**) with $^4J_{\text{HH}} = 1.6$ Hz, $^3J_{\text{HH}} = 7.9$ Hz and $^3J_{\text{HP}} = 14.0$ Hz for **4** and $^4J_{\text{HH}} = 1.7$ Hz, $^3J_{\text{HH}} = 7.8$ Hz and $^3J_{\text{HP}} = 14.3$ Hz for **5**. After oxidation of P(III) in **3** to P(V) in **4** and **5** the signals of the ferrocenyl and phenyl protons in **4** and **5** are shifted to lower field. In the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of phosphole **3** a singlet at 5.1 ppm is characteristic. After oxidation with sulfur and selenium, respectively, a shift to lower field (46.6 ppm (**4**), 33.2 ppm (**5**)) occurred.

For selenide **5** the characteristic selenium satellites with a $^1J_{^{31}\text{P}^{77}\text{Se}}$ coupling constant of 745 Hz could be found. Typically, the $^1J_{^{31}\text{P}^{77}\text{Se}}$ values allow a quantification of the donor abilities of phosphines PR_3 .^{35–38} An electron-withdrawing group results in increased values for the coupling constants indicating an increased *s* character for the phosphorus orbital involved in the phosphorus-selenium bond. $^{31}\text{P}\{^1\text{H}\}$ NMR data and $^1J_{^{31}\text{P}^{77}\text{Se}}$ coupling constants for several seleno phosphines are summarized in Table 1. A comparison with other P(III) species showed that phosphole **3** can be characterized as a weak donor.^{36–38}

Table 1. ^{31}P NMR chemical shifts and ^{31}P - ^{77}Se coupling constants for **5** and several phosphine-selenides.

Compd.	δ (ppm)	$^1J(^{31}\text{P}-^{77}\text{Se})$ (Hz)
5	33.2	745
Se=PPh_3 ³⁵	35.9	732
$\text{Se=P(4-Cl-C}_6\text{H}_4)_3$ ³⁹	2.21	753
$\text{Se=P(2,4,6-(MeO)}_3\text{-C}_6\text{H}_2)_3$ ³⁵	-16.8	703
$\text{Se=P(4-NMe}_2\text{-C}_6\text{H}_4)_3$ ⁴⁰	41.6	683

The molecular structures of **4** and **5** in the solid state have been determined by single crystal X-ray diffraction analysis. Suitable crystals were obtained by diffusion of *n*-hexane into a dichloromethane solution of either **4** or **5** at ambient temperature. The ORTEP diagrams with selected bond lengths, bond angles and torsion angles are shown in Figures 1 and 2.

Compounds **4** and **5** both crystallize in the orthorhombic space group $P2_12_12_1$. The ferrocenyl groups are antiparallel oriented and are almost coplanar to the heterocyclic core (torsion of the plane of the C_5H_4 unit to the plane of the phosphole core: **4**: $-4.4(18)^\circ$ for Fe1, $3.0(19)^\circ$ for Fe2; **5**: $3.3(12)^\circ$ for Fe1, $-1.7(11)^\circ$ for Fe2). The conformation of the cyclopentadienyl ligands in individual ferrocenyl units is almost eclipsed (**4**: $-8.73(81)^\circ$ for Fe1, $5.33(75)^\circ$ for Fe2; **5**: $2.79(53)^\circ$ for Fe1, $-4.00(47)^\circ$ for Fe2). The P1-C1-C2-C3-C4 arrangement is planar (**4**: rms deviation $0.0025 \text{ \AA}$, highest deviation from planarity observed for P1 with $-0.0302(158) \text{ \AA}$; **5**: rms deviation $0.0078 \text{ \AA}$, highest deviation from planarity observed for P1 with $0.0280(101) \text{ \AA}$). The phosphorus atom possesses, as expected, a tetrahedral environment (Figure 1). The

structural features found in phosphole chalcogenides **4** and **5** resemble those typically found in other examples of this family of molecules.^{41,42}

Figure 1. ORTEP diagram (50% probability level) of the molecular structure of **4** with the atom-numbering scheme. All hydrogen atoms have been omitted for clarity. Selected bond distances (Å), angles (deg), and torsion angles (deg): D1 – Fe1 1.6417(15), D2 – Fe1 1.6542(15), D3 – Fe2 1.6487(16), D4 – Fe2 1.6504(16), P1 – C1 1.815(12), C1 – C2 1.363(15), C2 – C3 1.450(14), C3 – C4 1.337(14), C4 – P1 1.851(10), C1 – C5 1.431(15), C4 – C15 1.411(15), P1 – C25 1.834(11), P1 – S1 1.951(4), C2 – C1 – P1 106.6(8), C1 – P1 – C4 93.8(5), C3 – C4 – P1 105.6(8), C2 – C1 – C5 128.0(11), C3 – C4 – C15 130.2(9), D1 – Fe1 – D2 177.88(11), D3 – Fe2 – D4 179.78(12), C1 – P1 – C25 104.1(5), C25 – P1 – C4 106.2(5), C1 – P1 – S1 116.9(4), C25 – P1 – S1 114.7(4), C4 – P1 – S1 118.4(4), C3 – C4 – C15 – C16 3.0(19), C2 – C1 – C5 – C9 -4.4(18), C2 – C3 – C4 – P1 1.5(11), P1 – C1 – C2 – C3 -0.5(12), C5 – D1 – D2 – C10 - 8.73(81), C15 – D3 – D4 – C20 5.33(75) (D = denotes the centroids of C₅H₄ or C₅H₅).

Figure 2. ORTEP diagram (50% probability level) of the molecular structure of **5** with the atom-numbering scheme. All hydrogen atoms have been omitted for clarity. Selected bond distances (Å), angles (deg), and torsion angles (deg): D1 – Fe1 1.6420(10), D2 – Fe1 1.6496(10), D3 – Fe2 1.6406(10), D4 – Fe2 1.6411(10), P1 – C1 1.827(7), C1 – C2 1.349(9), C2 – C3 1.443(9), C3 – C4 1.358(9), C4 – P1 1.819(8), C1 – C5 1.415(10), C4 – C15 1.439(10), P1 – C25 1.807(7), P1 – Se1 2.1047(15), C2 – C1 – P1 106.4(6), C4 – P1 – C1 93.8(4), C3 – C4 – P1 106.3(6), C2 – C1 – C5 128.2(7), C3 – C4 – C15 127.8(7), D1 – Fe1 – D2 177.45(8), D3 – Fe2 – D4 179.97(10), C25 – P1 – C1 104.5(3), C25 – P1 – C4 106.8(3), C1 – P1 – Se1 116.3(2), C25 – P1 – Se1 115.0(2), C4 – P1 – Se1 117.8(2), C3 – C4 – C15 – C16 -1.7(11), C2 – C1 – C5 – C9 3.3(12), C2 – C3 – C4 – P1 -2.5(7), P1 – C1 – C2 – C3 -0.6(8), C5 – D1 – D2 – C10 2.79(53), C15 – D3 – D4 – C20 -4.00(47) (D = denotes the centroids of C₅H₄ or C₅H₅).

Electrochemistry and Spectroelectrochemistry. The redox properties of heterocycles **3** – **5** were investigated by cyclic voltammetry, square wave voltammetry and spectroelectrochemistry (UV-Vis/NIR, IR). As supporting electrolyte a dry dichloromethane solution containing

0.1 mol·L⁻¹ of [NⁿBu₄][B(C₆F₅)₄] or [NⁿBu₄][PF₆] was used, allowing effects of ion-pairing on the stability of the redox products to be assessed in a qualitative fashion.^{43–45} The cyclic voltammetry measurements were performed at 20 °C at a scan rate of 100 mV·s⁻¹. All potentials are referenced to the FcH/FcH⁺ redox couple.⁴⁶ The data of the cyclic voltammetry experiments are summarized in Table 2. The voltammograms of **3** – **5** measured in the presence of [NⁿBu₄][B(C₆F₅)₄] are shown in Figure 3 and the ones measured using [NⁿBu₄][PF₆] as supporting electrolyte are depicted in Figure SI1.

Figure 3. Left: Cyclic voltammograms of **3** – **5**; scan rate: 100 mV·s⁻¹. Right: Square wave voltammograms of **3** – **5** in dichloromethane solutions (1.0 mmol·L⁻¹) at 20 °C, supporting electrolyte 0.1 mol·L⁻¹ [NⁿBu₄][B(C₆F₅)₄], working electrode: glassy carbon electrode (surface area 0.031 cm²).

The ferrocenyl groups of compounds **3** – **5** could be oxidized separately showing two reversible redox events in each electrolyte system with differences between cathodic peak

potential and the anodic peak potential (ΔE_p) falling between 68 and 80 mV (Table 2), and peak currents proportional to $\nu^{1/2}$ being observed confirming the essentially reversible character of these ferrocenyl-based oxidation events. The electron-withdrawing character of the P(V) center in **4** and **5** leads to a shift of the $E_1^{\circ'}$ values to more positive potentials relative to the P(III) species **3**. The more electron-rich P(III) center also leads to an enhanced thermodynamic stability of the mono-oxidized complex $[\mathbf{3}]^+$ evidenced by the greater comproportionation constant (K_C) (Table 2). Due to the higher ion-pairing capability (spherical diameter $[\text{PF}_6]^-$, 3.3 Å; $[\text{B}(\text{C}_6\text{F}_5)_4]^-$, 10 Å), the use of dichloromethane and $[\text{N}^n\text{Bu}_4][\text{PF}_6]$ as solvent/supporting electrolyte results in a lower resolution and hence the redox splitting ($\Delta E^{\circ'}$) decreases (Table 2).⁴⁷ The difference between $\Delta E^{\circ'}_{[\text{PF}_6]^-}$ to $\Delta E^{\circ'}_{[\text{B}(\text{C}_6\text{F}_5)_4]^-}$ of about 75 – 100 mV mostly reflects the electrostatic contribution to the stability of mixed-valent monocationic molecules $[\mathbf{3}]^+ - [\mathbf{5}]^+$. A comparison of phospholes **3** – **5** with analogous bis(ferrocenes) featuring thiophene-, furan- and pyrrole-derived bridges, reveal similar trends in the first oxidation potential, $E_1^{\circ'}$, and $\Delta E^{\circ'}$ under identical conditions, with the more readily oxidized complexes bearing the more electron donating heteroatoms giving rise to the larger $\Delta E^{\circ'}$ values and hence larger K_C . For example, $\Delta E^{\circ'}$ for **3** – **5** and other 2,5-diferrocenyl substituted heterocycles fall in the sequence NPh (450 mV) > NMe (410 mV) > O (290 mV) $\approx$ **3** (280 mV) > S (260 mV) > **4** (240 mV) = **5** (235 mV).²² The significant $\Delta E^{\circ'}$ values indicate considerable stability of the monocations with respect to disproportionation to the neutral and dicationic forms. Assuming that the oxidation processes are ferrocene-based, which seems eminently reasonable given the chemical composition, and given the robustness of the ferrocene / ferrocenium redox states, the formally mixed-valence monocations $[\mathbf{3}]^+ - [\mathbf{5}]^+$ were viewed likely to be sufficiently stable to permit spectroscopic

observation using spectroelectrochemical methods and further characterization to address the underlying electronic structures and influence of the bridging ligand on the electronic properties.

Table 2. Cyclic voltammetry data of complexes **3 – **5**.**

Compd.	$E_1^{o'}$ in mV (ΔE_p in mV)	$E_2^{o'}$ in mV (ΔE_p in mV)	$\Delta E^{o'}$ in mV	$K_C / 10^4$
3 , [N ⁿ Bu ₄][PF ₆]	-135 (76)	50 (62)	185	0.14
4 , [N ⁿ Bu ₄][PF ₆]	-65 (76)	100 (76)	165	0.05
5 , [N ⁿ Bu ₄][PF ₆]	-60 (80)	100 (78)	160	0.05
3 , [N ⁿ Bu ₄][B(C ₆ F ₅) ₄]	-110 (72)	170 (80)	280	5.4
4 , [N ⁿ Bu ₄][B(C ₆ F ₅) ₄]	-15 (68)	225 (74)	240	1.1
5 , [N ⁿ Bu ₄][B(C ₆ F ₅) ₄]	-15 (74)	220 (80)	235	0.9

Potentials vs FcH/FcH⁺, scan rate 100 mV·s⁻¹ at glassy carbon electrode of 1.0 mmol·L⁻¹ solutions of **3** – **5** in dry dichloromethane; 0.1 mol·L⁻¹ [NⁿBu₄][B(C₆F₅)₄] or [NⁿBu₄][PF₆] as supporting electrolyte at 20 °C.

The UV-Vis/NIR spectroelectrochemical measurements of dichloromethane solutions containing **3** – **5** (2.0 mmol·L⁻¹) and [NⁿBu₄][B(C₆F₅)₄] (0.1 mol·L⁻¹) as supporting electrolyte were performed in an OTTLE (OTTLE = Optically Transparent Thin-Layer Electrochemical) cell.⁴⁸ The compounds were oxidized by stepwise increments in the applied potential (step width: 25 mV, 50 mV or 100 mV). During the measurements, oxidation of the neutral compounds to mixed-valence monocationic [**3**]⁺, [**4**]⁺ and [**5**]⁺, and finally to the dicationic species [**3**]²⁺ – [**5**]²⁺ could be observed. To proof the reversibility after full oxidation, each compound was reduced and the resulted UV-Vis/NIR spectra are identical with the starting compound. The UV-Vis/NIR spectra of phospholes **3** – **5** measured in dichloromethane are depicted in Figures 4 (**3**), SI2 (**4**)

and SI3 (**5**) and the spectra measured in acetonitrile are shown in Figures SI4 (**3**), SI5 (**4**) and SI6 (**5**). Phospholes **3** – **5** show, as expected, no absorptions in the NIR region (1000 – 3000 nm). Upon oxidation of these molecules mixed-valence [**3**]⁺ – [**5**]⁺ are formed, resulting in the appearance of a broad band enveloping between 1500 nm and 2500 nm (Figures 4 and SI2). A further potential increase above 500 mV vs Ag/AgCl leads to the disappearance of these absorptions, a behavior typically observed for intervalence charge transfer (IVCT) excitations. The observed spectra can be deconvoluted into three Gaussian-shaped bands, which are assumed to represent the IVCT transition, a LF (ligand field) transition associated with the ferrocenium moiety and a third band simulating the edge to the higher energy absorptions. The sum of these three Gaussian functions allows an almost exact overlay with the experimental spectra. Therefore, the intensity ϵ_{max} , the full-width-at-half-height $\Delta\nu_{1/2}$ and the ν_{max} values associated with the IVCT component could be determined.

Table 3. NIR data of the IVCT absorptions of phospholes [3]⁺ – [5]⁺.^a

Solvent	Compd.	$\nu_{\max}$ (cm ⁻¹) ($\epsilon_{\max}$ (L·mol ⁻¹ ·cm ⁻¹))	$\Delta\nu_{1/2}$ (cm ⁻¹)	($\Delta\nu_{1/2}$) _{theo} ^b (cm ⁻¹)
dichloromethane	[3] ⁺	5000 (1750)	3050	3400
	[4] ⁺	4900 (1300)	4200	3360
	[5] ⁺	4850 (1100)	4200	3350
acetonitrile	[3] ⁺	6500 (1600)	3200	3870
	[4] ⁺	6900 ^c	3100	3990
	[5] ⁺	6900 ^c	3400	3990

^a In dry dichloromethane or acetonitrile containing 0.1 mol·L⁻¹ of [NⁿBu₄][B(C₆F₅)₄] as supporting electrolyte at 20 °C. ^b Values calculated as ($\Delta\nu_{1/2}$)_{theo} = (2310· $\nu_{\max}$)^{1/2} according to the Hush relationships for weakly coupled systems.⁴⁹ ^c Due to the lack of solubility of compounds **4** and **5** in acetonitrile the extinction coefficients were not determined.

The data derived from deconvoluted IVCT absorption bands from [3]⁺ – [5]⁺ are summarized in Table 3, although the assignment and interpretation of absorption profiles taken from deconvolution should always be treated with caution as the underlying band-shapes are sensitive to the degree of coupling. To help confirm the IVCT assignment, the spectroelectrochemical UV-Vis/NIR experiments were also carried out in acetonitrile as a solvent, as the IVCT band of a class II compound should display solvatochromic behavior.^{3,13,50} Changing the polarity of the solvent from $P = 3.1$ (dichloromethane) to $P = 5.8$ (acetonitrile) resulted in a hypsochromic shift of 1500 cm⁻¹ (**3**⁺), 2000 cm⁻¹ (**4**⁺, **5**⁺) (Table 3).⁵¹ This solvatochromic behavior is entirely consistent with the IVCT assignment.

Analysis of the IVCT absorption allows classification of **3** as a moderately coupled class II system within the scheme proposed by Robin and Day.⁵ A comparison of the IVCT absorption of

phosphole **3** ($\epsilon_{\text{max}} = 1750 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$, $\Delta\nu_{1/2} = 3050 \text{ cm}^{-1}$) with analogous 2,5-diferrocenyl substituted heterocycles shows that regarding to the extinction it can be placed between 2,5-diferrocenyl furan ($\epsilon_{\text{max}} = 1496 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$) and 2,5-diferrocenyl-1-methyl-1*H*-pyrrole ($\epsilon_{\text{max}} = 3145 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$).²² Nevertheless, the full-width-at-half-height of the IVCT band in **3** exceeds those found in all other molecules of the thus mentioned series indicating a weaker interaction. Please note that the Hush two state model is only valid in the weak class II regime while stronger coupling includes partly delocalization and therefore a more narrow bandwidth is observed.^{49,52} Brunschwig, Creutz and Sutin stated that the quotient between the observed bandwidth and the theoretical bandwidth according to Hush can be taken as a measure for the strength of this coupling.⁵⁰ Nevertheless solvent broadening as observed for [**4**]⁺ and [**5**]⁺ in dichloromethane (Table 3) also contributes to the bandwidth and therefore hinders the direct comparability. A good comparison to other diferrocenyl heterocycles is complicated because phosphole **3** possesses a somewhat different geometry at the ^oC₄P backbone, as in contrast to other heterocycles the phosphorus lone pair only to some extend involves in the delocalization of the ^oC₄E ring.^{53,54} Thus the phosphole behaves similar to a *cis*-diene system rather than an aromatic five membered heterocycle. The IVCT absorptions of sulfide **4** and selenide **5** show smaller intensities (**4**: $1300 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$; **5**: $1100 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$) (Table 3). This indicates that the occupation of the lone pair slightly decreases the interaction among the ^oC₄P ring and characterizes those two molecules as weak class II compounds. In generally, the characteristics of the IVCT absorptions resemble those found for 1,4-diferrocenylbutadiene ($\nu_{\text{max}} = 5290 \text{ cm}^{-1}$, $\epsilon_{\text{max}} = 2280 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$, $\Delta\nu_{1/2} = 3900 \text{ cm}^{-1}$).⁵⁵ One may conclude that the C₄ backbone mainly promotes the electron transfer between the ferrocenyl termini.

Figure 4. Left: UV-Vis/NIR spectra of **3** at 20 °C in dichloromethane (2.0 mmol·L⁻¹) at rising potentials (bottom: -200 to 560 mV; top: 560 to 800 mV vs Ag/AgCl); supporting electrolyte [NⁿBu₄][B(C₆F₅)₄]. Right: Deconvolution of the NIR absorptions of [3]⁺ using three Gaussian shaped bands determined by spectroelectrochemistry in an OTTLE cell.

Computational studies

To help characterize the redox products and better understand the nature of the electronic transitions, electronic structure calculations were carried out. The computational systems are designated [3']ⁿ⁺, [4']ⁿ⁺ and [5']ⁿ⁺ (n = 0, 1, 2) to distinguish them from the experimental complexes. All geometry optimizations and TD-DFT calculations were undertaken using the B3LYP functional and 3-21G* basis set combination. In the case of the dications, the triplet states were found to be considerably more stable than the analogous singlet states (ΔE_{T-S} : -134.27 kJ/mol [3']²⁺; -81.21 kJ/mol [4']²⁺; -76.74 kJ/mol [5']²⁺) and the latter are not considered further. Selected bond lengths (Å) and angles (°) (Table SI1), orbital energy and composition

(Table SI2), calculated and spectroelectrochemically observed IR data (Table 4) and TD-DFT results (Table SI3) are tabulated in the supporting information.

The optimized geometries are in excellent agreement with the available experimentally determined structures of **4** and **5**, with individual bond lengths being over-estimated by less than 0.03 Å. Within the neutral members of the series, **3'**, **4'** and **5'**, oxidation of the PPh center from P(III) to P(V) leads to a modest increase in the localization of the double bonds in the heterocyclic ring and a small contraction of the Fc-C₄H₂ bond lengths, probably due to increased electrostatic attraction. However, these variations are small and in all cases the phosphole ring system presents a clear alternation in bond lengths consistent with a description in terms of a cyclic diene. This description is entirely consistent with the distribution and nodal properties of the HOMOs, which are derived from the *cis*-butadiene-like π -system of the C₄H₂ fragment mixed with the ferrocenyl moieties, with vanishingly small contributions from the phosphorus atom and its substituents (Figure SI9, Table SI2).

Scheme 2. Numbering scheme for the calculation of phospholes 3 – 5.

The optimized structures of the radical cations [**3'**]⁺, [**4'**]⁺ and [**5'**]⁺ reflect the depopulation of the parent HOMO, with a subtle (≤ 0.03 Å) contraction of the Fc-C₄H₂ and C(3)-C(4) bond

lengths and concomitant elongation in the C(3)-C(4) bond (Table SI2, Scheme 2). Interestingly, whilst the C(1)-C(2) and C(5)-C(6) bond lengths are arguably different in $[3']^+$ (C(1)-C(2) 1.4315; C(5)-C(6) 1.4199 Å), and there is little difference in the C(2)-P and C(5)-P bond lengths (1.8337, 1.8255) the opposite is true of the P(V) complexes $[4']^+$ and $[5']^+$ (Table SI2). However, whilst only small structural distortions in the phosphole ring fragment hint at a localized electronic structure, plots of the critical frontier molecular orbitals (Figure 5, Table SI2) and the spin density distributions (Figure 6) are more compelling. Again, the phosphorus group makes little if any contribution to the electronic description, and each of $[3']^+$, $[4']^+$ and $[5']^+$ can be accurately described in terms of a localized oxidation on the ferrocenyl moiety *anti* to the phosphole phenyl ring.

Figure 5. Plots of the β -LUMO (top) and β -HOMO (bottom) of $[3']^+$ (isosurface ± 0.04 ($e \text{ bohr}^{-3}$) $^{1/2}$).

Figure 6. A plot of the spin density for the cation radical $[3']^+$ (isosurface ± 0.04 ($e \text{ bohr}^{-3}$) $^{1/2}$).

The triplet dications $[3']^{2+}$, $[4']^{2+}$ and $[5']^{2+}$ are also well described in terms of ferrocene-based oxidation processes, and interestingly the structural parameters of the phosphole ring are almost indistinguishable from those of the parent neutral analogues. The β -LUMO and β -LUMO+1 are each largely localized on a ferrocenyl moiety, with the β -LUMO+1 in $[4']^{2+}$ and $[5']^{2+}$ also containing a small contribution from the C_4H_2 fragment (Figure SI10).

IR spectroscopy and calculated molecular vibrational frequencies provide a useful link between experimentally observable and calculated parameters, allowing the accuracy of the optimized geometries to be assessed. IR spectroelectrochemical methods were employed to obtain experimental IR data, with measurements carried out on solutions of **3** – **5** in dichloromethane ($10 \text{ mmol}\cdot\text{L}^{-1}$) containing $0.1 \text{ mol}\cdot\text{L}^{-1}$ $[N^m\text{Bu}_4][\text{PF}_6]$ as supporting electrolyte in an OTTLE cell with CaF_2 windows (Figures 7, SI7 and SI8). The IR spectra of the neutral complexes **3**, **4** and **5** are each characterized by a weak band near 1590 cm^{-1} , which is replicated by calculated frequencies between $1550 - 1600 \text{ cm}^{-1}$ for the computational models **3'**, **4'** and **5'** (Table 4). Analysis of the atomic displacements confirms this feature to be an asymmetric $\nu(\text{C}=\text{C}-\text{C}=\text{C})$ stretch associated with the *cis*-butadiene fragment of the phosphole moiety.

The cation radicals $[3]^+$, $[4]^+$ and $[5]^+$ generated by one-electron oxidation in the spectroelectrochemical cell display new vibrational band envelopes between 1400 - 1500 cm^{-1} . In addition, a degree of decomposition of $[3]^+$ is also evident by appearance of a new feature near 1700 cm^{-1} in the spectrum that is not sensitive to further changes in redox state (vide infra). The lower frequency feature ($[3]^+$ 1407; $[4]^+$ 1421; $[5]^+$ 1419 cm^{-1}) can be assigned to the butadiene-like $\nu(\text{C}=\text{C}-\text{C}=\text{C})$ stretch ($[3']^+$ 1363; $[4']^+$ 1378; $[5']^+$ 1376, 1374 cm^{-1}). The shift of this band to lower frequency in the cation radicals when compared with the neutral species is consistent with the structure of the HOMO ($3'$, $4'$ and $5'$) and β -LUMO ($[3']^+$, $[4']^+$ and $[5']^+$). The calculations also reveal a relatively strong $\nu(\text{C}-\text{C})$ stretch for the $\text{Fc}^+-\text{C}_4\text{H}_2$ moiety ($[3']^+$ 1421; $[4']^+$ 1423; $[5']^+$ 1423 cm^{-1}) and a weaker $\nu(\text{C}-\text{C})$ stretch for the $\text{Fc}-\text{C}_4\text{H}_2$ fragment ($[3']^+$ 1398; $[4']^+$ 1404; $[5']^+$ 1402 cm^{-1}). These calculated bands are consistent with the observed features at 1471, 1413 ($[3]^+$); 1486, 1434 ($[4]^+$) and 1481, 1434 cm^{-1} ($[5]^+$).

The IR spectra of the dications $[3]^{2+}$, $[4]^{2+}$ and $[5]^{2+}$ are characterized by a complicated series of bands between 1415 and 1556 cm^{-1} . These complicated band patterns are consistent with the calculated vibrational frequencies (Table 4); the strongest IR active modes have similar $\nu(\text{C}=\text{C}-\text{C}=\text{C})$ and $\nu(\text{C}-\text{C})$ ($\text{Fc}^+-\text{C}_4\text{H}_2$) character as noted for the monocations, admixed with additional aromatic $\nu(\text{CC})$ modes from both the ferrocenium moieties and the phosphole phenyl ring.

Figure 7. IR spectra of **4** at 20 °C in dichloromethane (10 mmol·L⁻¹) at rising potentials (left: -200 to 600 mV (**4** → [**4**]⁺); right: 600 to 1300 mV ([**4**]⁺ → [**4**]²⁺) vs Ag/AgCl); supporting electrolyte [NⁿBu₄][PF₆].

TD-DFT calculations can provide a very useful link between the calculated electronic structure and experimentally observable electronic absorption spectra. Whilst pure DFT functionals perform poorly for excitations with considerable charge transfer character, hybrid functionals with increasingly sophisticated treatments of direct exchange can result in much better match, especially when calculations are augmented by a suitable solvent model. In the present case, TD-DFT calculations with even the relatively simple B3LYP functional and small basis set (3-21G*) performed surprisingly well. The UV-Vis/NIR spectra of **3**, **4** and **5** feature two absorption bands near 500 and 400 nm (20000 and 25000 cm⁻¹). TD-DFT calculations with **3'** contain two excitations with significant oscillator strength at 18975 cm⁻¹, which has largely ferrocene-based LF character admixed with ferrocene to C₄H₂ charge transfer character, and 25445 cm⁻¹, which has more clearly defined Fc→C₄H₂ character. For each of **4'** and **5'** TD-DFT calculations reveal

two excitations of similar energy and character that are likely responsible for the lower energy absorption band observed in the experimental spectra (**4'** 17921, 18050 cm⁻¹; **5'** 17986, 18166 cm⁻¹) and a higher energy transition with Fc→C₄H₂ character (**4'** 23255 cm⁻¹; **5'** 23584 cm⁻¹). TD-DFT calculations with the cation radicals [**3'**]⁺, [**4'**]⁺ and [**5'**]⁺ reveal two low energy (NIR) excitations arising from the β-HOMO→β-LUMO transition (*i.e.*, IVCT character, Figure 5, Table SI3) and a lower lying filled ferrocenium orbital (β-HOMO-11 ([**3'**]⁺ or β-HOMO-12 [**4'**]⁺ and [**5'**]⁺) to the β-LUMO and hence offering more intraligand ferrocenium character. It is noteworthy that the calculated oscillator strength of the transition with IVCT character for [**3'**]⁺ is higher, when compared with [**4'**]⁺ and [**5'**]⁺, consistent with the trends in absorptivity observed in the experimental spectra (Table SI3), which may be taken as an indication of increased electronic interaction in the non-oxidized phosphole. Although the relative energies of the IVCT and ferrocenium-based LF transitions in the model cation radicals [**3'**]⁺, [**4'**]⁺ and [**5'**]⁺ are reversed relative to experiment, the results support the general conclusions drawn from initial inspection of the UV-Vis/NIR spectroelectrochemical results. The TD-DFT calculations of [**3'**]⁺, [**4'**]⁺ and [**5'**]⁺ also contain two higher energy excitations near 11000 and 12000 cm⁻¹, with FcC₄H₂→Fc⁺ and Fc→C₄H₂Fc⁺ charge transfer character, which together account for the absorption features observed in the experimental spectra of the radical cations between 1000 - 650 nm (10000 - 15380 cm⁻¹). In the case of the triplet dications test calculations with [**3'**]²⁺ confirm the absence of transitions with any oscillator strength below 16500 cm⁻¹. The most significant excitation is calculated at 19493 cm⁻¹ with considerable C₄H₂→Fc⁺ character, consistent with the intense absorption feature near 500 nm in the experimental spectra.

Table 4. Selected calculated (and observed) IR active $\nu(\text{C}=\text{C})$ vibrations (cm^{-1}) for $[\mathbf{3}]^{n+}$, $[\mathbf{4}]^{n+}$ and $[\mathbf{5}]^{n+}$ ($n = 0, 1, 2$).^a

	n = 0	n = 1	n = 2
$[\mathbf{3}]^{n+}$ ($[\mathbf{3}]^{n+}$)	1595w (-) ^b	1421s (1471m) 1398m (1413m) 1363s (1407m)	1505m (1556w) 1430m (1455w) 1403s (1415w)
$[\mathbf{4}]^{n+}$ ($[\mathbf{4}]^{n+}$)	1548m (1587w)	1423s (1486m) 1404 m (1434m) 1378s (1421m)	1543m (-) ^b 1455m (1434w) 1409s (1419w)
$[\mathbf{5}]^{n+}$ ($[\mathbf{5}]^{n+}$)	1546m (1585w)	1423s (1481m) 1402m (1434m) 1376m (1419m) 1374m (-) ^b	1541m (-) ^b 1452m (1463w) 1409s (1434w) 1390s (1417)

^a Correction factor of 0.95 applied to all calculated frequencies. ^b Signal-noise-ratio too low.

Conclusion

2,5-Diferrocenyl-1-phenyl-1*H*-phosphole (**3**) and its chalcogenides **4** (P=S) and **5** (P=Se) have been successfully prepared by a cyclization reaction of phenylphosphine with 1,4-diferrocenylbutadiyne and subsequent reaction with sulfur and selenium, respectively. NMR spectroscopic studies revealed a tetrahedral environment at phosphorus in **3** – **5**. Therefore, the interaction of the phosphorus' lone pair with the dienic π system is hindered. Oxidation to P(V) with sulfur or selenium blocks any involvement in the delocalization of the C₄ backbone. Nevertheless, the electronic character at the carbon atoms in 3- and 4-position seems to remain unchanged. Molecules **4** and **5** have been structurally characterized by single crystal X-ray diffraction

showing that they exhibit, as expected, a planar geometry of the heterocyclic core. The ferrocenyl groups are antiparallel oriented and are almost coplanar to the ${}^{\text{c}}\text{C}_4\text{P}$ setup. Electrochemical measurements revealed that the two ferrocenyl groups in **3** – **5** undergo two sequential one-electron oxidation processes, with a significant separation of the two waves (280 mV (**3**), 240 mV (**4**) and 235 mV (**5**)) due to a combination of environmental and inherent electronic effects. As observed in spectroelectrochemical investigations, all three compounds **3** – **5** exhibit IVCT absorptions of weak to moderate strength. Upon oxidation of phosphorus the intensity of the IVCT absorption decreases from $\epsilon_{\text{max}} = 1750 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ (**3**) to $\epsilon_{\text{max}} = 1300 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ (**4**) and $\epsilon_{\text{max}} = 1100 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ (**5**), while the band broadens ($\Delta\nu_{1/2} = 3050 \text{ cm}^{-1}$ (**3**), $\Delta\nu_{1/2} = 4200 \text{ cm}^{-1}$ (**4**, **5**)). This indicates that the occupation of the lone pair slightly decreases the interaction among the ${}^{\text{c}}\text{C}_4\text{P}$ ring. However the electronic characteristics of this series of molecules resemble those of a *cis*-diene structure more than those of an aromatic system and the changes upon oxidation of the phosphorus are therefore small. DFT and TD-DFT calculation in combination with *in situ* IR spectroscopy support the general interpretation of the electrochemical- and *in situ* UV-Vis/NIR data, allocating the main contribution of the electron transfer to the C_4H_2 part of the bridging unit.

Experimental Section

General data. All reactions were carried out under an argon or nitrogen atmosphere using standard Schlenk techniques. Tetrahydrofuran and benzene were purified by distillation from sodium/benzophenone ketyl; dichloromethane was purified by distillation from calcium hydride. For column chromatography silica was used with a particle size of 40 – 60 μm (230 – 400 mesh (ASTM), Fa. Macherey-Nagel).

Instruments. FT IR spectra were recorded with a Nicolet IR 200 spectrometer (Fa. Thermo). NMR spectra were recorded with a Bruker Avance III 500 spectrometer (500.3 MHz for ^1H , 125.7 MHz for $^{13}\text{C}\{^1\text{H}\}$ and 202.5 MHz for $^{31}\text{P}\{^1\text{H}\}$ spectra). Chemical shifts are reported in δ (parts per million) downfield from tetramethylsilane with the solvent as reference signal (^1H NMR: CHCl_3 , $\delta = 7.26$; $^{13}\text{C}\{^1\text{H}\}$ NMR: CDCl_3 , $\delta = 77.16$; CD_2Cl_2 , $\delta = 53.8$; $^{31}\text{P}\{^1\text{H}\}$ NMR: standard external rel. 85% H_3PO_4 , $\delta = 0.0$; $\text{P}(\text{OMe})_3$, $\delta = 139.0$, respectively). The melting points were determined using a Gallenkamp MFB 595 010 M melting point apparatus. Elemental analyses were measured with a Thermo FlashAE 1112 instrument. High-resolution mass spectra were recorded on a Bruker Daltonik micrOTOF-QII spectrometer.

Electrochemistry. Electrochemical measurements on $1.0 \text{ mmol}\cdot\text{L}^{-1}$ solutions of compounds **3** - **5** in dichloromethane were performed in a dried, argon purged cell at 20°C with a Radiometer Voltalab PGZ 100 electrochemical workstation interfaced with a personal computer. $0.1 \text{ mol}\cdot\text{L}^{-1}$ $[\text{N}^n\text{Bu}_4][\text{B}(\text{C}_6\text{F}_5)_4]$ or $[\text{N}^n\text{Bu}_4][\text{PF}_6]$ were used as supporting electrolyte. For the measurements a three electrode cell containing a Pt auxiliary electrode, a glassy carbon working electrode (surface area 0.031 cm^2) and an Ag/Ag^+ ($0.01 \text{ mmol}\cdot\text{L}^{-1}$ $[\text{AgNO}_3]$) reference electrode fixed on a Luggin capillary was used. The working electrode was pretreated by polishing on a Buehler microcloth first with 1 micron and then $\frac{1}{4}$ micron diamond paste. The reference electrode was constructed from a silver wire inserted in a $0.01 \text{ mmol}\cdot\text{L}^{-1}$ $[\text{AgNO}_3]$ and $0.1 \text{ mol}\cdot\text{L}^{-1}$ $[\text{N}^n\text{Bu}_4][\text{B}(\text{C}_6\text{F}_5)_4]$ or $[\text{N}^n\text{Bu}_4][\text{PF}_6]$ acetonitrile solution in a Luggin capillary with a vycor tip. This Luggin capillary was inserted in a second Luggin capillary containing a $0.1 \text{ mol}\cdot\text{L}^{-1}$ $[\text{N}^n\text{Bu}_4][\text{B}(\text{C}_6\text{F}_5)_4]$ or $[\text{N}^n\text{Bu}_4][\text{PF}_6]$ dichloromethane solution and a vycor tip. Experiments under the same conditions showed that all reduction and oxidation potentials were reproducible within 5 mV. Experimental potentials were referenced against an Ag/Ag^+ reference

electrode but the presented results are referenced against ferrocene as an internal standard as required by IUPAC.⁴⁶ To achieve this, each experiment was repeated in the presence of 1 mmol·L⁻¹ decamethylferrocene (Fc*). Data were processed on a Microsoft Excel worksheet to set the formal reduction potentials of the FcH/FcH⁺ couple to 0.0 V. Under our conditions the Fc*/Fc*⁺ couple was at -619 mV vs FcH/FcH⁺, $\Delta E_p = 60$ mV, while the FcH/FcH⁺ couple itself was at 220 mV vs Ag/Ag⁺, $\Delta E_p = 61$ mV.⁵⁶

Spectroelectrochemistry. Spectroelectrochemical UV-Vis/NIR measurements of 2.0 mmol·L⁻¹ solutions of **3** – **5** in dry dichloromethane containing 0.1 mol·L⁻¹ of [NⁿBu₄][B(C₆F₅)₄] as the supporting electrolyte were performed in an OTTLE (OTTLE = Optically Transparent Thin-Layer Electrochemical)⁴⁸ cell with a Varian Cary 5000 spectrophotometer at 20 °C. Spectroelectrochemical IR measurements of 10 mmol·L⁻¹ solutions of **3** – **5** in dry dichloromethane containing 0.1 mol·L⁻¹ [NⁿBu₄][PF₆] as supporting electrolyte were performed in an OTTLE cell with CaF₂ windows. The values obtained by deconvolution could be reproduced within $\varepsilon_{\max}$: 100 L·mol⁻¹·cm⁻¹; $\nu_{\max}$ 50 cm⁻¹; $\Delta\nu_{1/2}$ 50 cm⁻¹.

Single Crystal X-ray Diffraction Analysis. Suitable single crystals of **4** and **5** for X-ray diffraction analysis were obtained by diffusion of *n*-hexane into a dichloromethane solution containing **4** or **5** at ambient temperature. Data were collected with an Oxford Gemini S diffractometer at 100 K with graphite monochromated Cu K_α radiation ($\lambda = 1.54184$ Å) (**4**) or Mo K_α radiation ($\lambda = 0.71073$ Å) (**5**). The structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2 .^{57,58} All non-hydrogen atoms were refined anisotropically, and a riding model was employed in the treatment of the hydrogen atom positions.

Reagents. All starting materials were obtained from commercial suppliers and used without further purification. Phenylphosphine⁵⁹ and 1,4-diferrocenylbutadiyne⁶⁰ were prepared according to published procedures.

Synthesis of 2,5-Diferrocenyl-1-phenyl-1*H*-phosphole (3). To 0.25 g (2.3 mmol) of **1** in 30 mL of a tetrahydrofuran/benzene mixture of ratio 1:1 (v:v) at 0 °C, 0.7 mL (1.8 mmol) of *n*-butyllithium were added drop wise. The resulting yellow solution was stirred for 10 min at 0 °C and was then added drop wisely to a solution of 0.95 g (2.3 mmol) of 1,4-diferrocenylbutadiyne (**2**) in 20 mL of tetrahydrofuran. The deep red solution was stirred overnight at ambient temperature and then all volatiles were removed in vacuum. The remaining solid was purified under argon by column chromatography (column size: 4 × 20 cm) on silica using a mixture of *n*-hexane/dichloromethane 5:1 (v:v) as eluent to give **3** as a red solid. Yield 0.61 mg (1.2 mmol, 52 % based on **1**.) Anal. Calcd. for C₃₀H₂₅Fe₂P (528.04 g/mol): C, 68.22; H, 4.77. Found: C, 68.15; H, 4.73. Mp.: 207 °C. IR data (KBr, ν/cm^{-1}): 3086 m, 3037 m, 2954 m, 2920 w, 2847 w, 1714 w, 1635 w, 1562 m, 1477 m, 1433 m, 1408 m. ¹H NMR (CDCl₃, δ): 3.92 (s, 10H, C₅H₅), 4.17 (m, 2H, C₅H₄), 4.18 (m, 2H, C₅H₄), 4.25 (m, 2H, C₅H₄), 4.39 (m, 2H, C₅H₄), 6.87 (d, ³*J*_{HP} = 11.4 Hz, 2H, C₄H₂P), 7.38 - 7.40 (m, 3H, H^m, H^p/C₆H₅), 7.58 – 7.62 (m, 2H, H^o/C₆H₅). ¹³C{¹H} NMR (CDCl₃, δ): 65.83 (d, *J*_{CP} = 3.9 Hz, C₅H₄), 67.18 (d, *J*_{CP} = 6.8 Hz, C₅H₄), 68.64 (d, *J*_{CP} = 12.0 Hz, C₅H₄), 69.84 (s, C₅H₅), 82.39 (d, ²*J*_{CP} = 20.0 Hz, Cⁱ/C₅H₄), 128.92 (d, *J*_{CP} = 8.7 Hz, C₆H₅), 130.07 (d, ²*J*_{CP} = 1.7 Hz, CH/C₄H₂P), 130.57 (d, *J*_{CP} = 9.3 Hz, C₆H₅), 133.05 (d, *J*_{CP} = 11.7 Hz, Cⁱ/C₆H₅), 134.98 (d, ⁴*J*_{CP} = 21.1 Hz, C^o/C₆H₅), 147.96 (d, *J*_{CP} = 1.5 Hz, Cⁱ/C₄H₂P). ³¹P{¹H} NMR (CDCl₃, δ): 5.10 (s). HRMS (ESI-TOF) [*m/z*]: calcd for C₃₀H₂₅Fe₂P: 528.0388, found: 528.0384 [M]⁺.

Synthesis of 2,5-Diferrocenyl-1-phenyl-1*H*-phosphole sulfide (4). To 0.10 g (0.19 mmol) of **3** in dichloromethane (20 mL) 0.07 g (0.27 mmol) of elemental sulfur was added in a single portion. The deep purple solution was stirred overnight at ambient temperature. All volatiles were removed in vacuum and the remaining solid was purified by column chromatography (column size: 3 × 15 cm) on silica using a mixture of *n*-hexane/dichloromethane of ratio 3:1 (v:v). Compound **4** was obtained as a purple solid. Yield 0.097 mg (0.17 mmol, 89 % based on **3**.) Anal. Calcd. for C₃₀H₂₅Fe₂PS·0.5CH₂Cl₂ (601.99 g/mol): C, 60.78; H, 4.35. Found: C, 60.57; H, 4.33. Mp.: 248 °C. IR data (KBr, ν/cm⁻¹): 3081 w, 3039 w, 2960 m, 2923 m, 2853 w, 1727 w, 1646 w, 1585 m, 1464 m, 1433 m, 1405 m. ¹H NMR (CDCl₃, δ): 3.98 (s, 10H, C₅H₅), 4.27 (m, 2H, C₅H₄), 4.29 (m, 2H, C₅H₄), 4.47 (m, 2H, C₅H₄), 4.62 (m, 2H, C₅H₄), 5.30 (s, CH₂Cl₂), 6.87 (d, ³J_{HP} = 36.5 Hz, 2H, C₄H₂P), 7.48 – 7.52 (m, 3H, H^m, H^p/C₆H₅), 8.02 (ddd, ³J_{HH} = 7.9 Hz, ⁴J_{HH} = 1.6 Hz, ³J_{HP} = 14.0 Hz, 2H, H^o/C₆H₅). ¹³C{¹H} NMR (CD₂Cl₂, δ): 53.52 (s, CH₂Cl₂), 66.45 (d, J_{CP} = 6.3 Hz, C₅H₄), 67.53 (d, J_{CP} = 5.8 Hz, C₅H₄), 69.84 (d, J_{CP} = 12.5 Hz, C₅H₄), 70.58 (s, C₅H₅), 77.65 (d, ²J_{CP} = 22.5 Hz, Cⁱ/C₅H₄), 129.26 (d, J_{CP} = 12.4 Hz, C₆H₅), 129.68 (d, ¹J_{CP} = 12.8 Hz, Cⁱ/C₆H₅), 130.61 (d, ²J_{CP} = 24.1 Hz, CH/C₄H₂P), 130.95 (d, ²J_{CP} = 11.6 Hz, C^o/C₆H₅), 132.46 (d, J_{CP} = 3.4 Hz, C₆H₅), 140.49 (d, ¹J_{CP} = 81.3 Hz, Cⁱ/C₄H₂P). ³¹P{¹H} NMR (CDCl₃, δ): 46.61 (s). HRMS (ESI-TOF) [*m/z*]: calcd for C₃₀H₂₅Fe₂PS: 560.0109, found: 560.0111 [M]⁺.

Crystal Data for **4**: C₃₀H₂₅Fe₂PS, M = 560.23 g·mol⁻¹, orthorhombic, *P*2₁2₁2₁, λ = 1.54184 Å, *a* = 7.5138(6) Å, *b* = 16.1833(17) Å, *c* = 19.6680(19) Å, *V* = 2391.6(4) Å³, *Z* = 4, ρ_{calcd} = 1.556 mgm⁻³, μ = 11.300 mm⁻¹, *T* = 100(2) K, Θ range = 3.54-62.48°, reflections collected: 4528, independent: 3235 (*R*_{int} = 0.0616), *R*₁ = 0.0871, *wR*₂ = 0.2106 [*I* > 2σ(*I*)], absolute structure parameter: 0.001(12).

Synthesis of 2,5-Diferrocenyl-1-phenyl-1*H*-phosphole selenide (5). Using the procedure described above, 0.11 g (0.21 mmol) of **3** were reacted with 0.02 g (0.25 mmol) of selenium to give **5** as purple solid. Yield 0.109 mg (0.18 mmol, 86 % based on **3**.) Anal. Calcd. for C₃₀H₂₅Fe₂PSe (607.96 g/mol): C, 59.35; H, 4.15. Found: C, 59.15; H, 4.49. Mp.: 263 °C. IR data (KBr, ν/cm⁻¹): 3074 w, 3048 w, 2958 m, 2923 m, 2853 w, 1738 m, 1653 w, 1582 m, 1461 m, 1433 m, 1407 m. ¹H NMR (CDCl₃, δ): 3.97 (s, 10H, C₅H₅), 4.27 (m, 2H, C₅H₄), 4.29 (m, 2H, C₅H₄), 4.53 (m, 2H, C₅H₄), 4.63 (m, 2H, C₅H₄), 6.90 (d, ³J_{HP} = 35.9 Hz, 2H, C₄H₂P), 7.47 - 7.52 (m, 3H, H^m, H^p/C₆H₅), 8.04 (ddd, ³J_{HH} = 7.8 Hz, ⁴J_{HH} = 1.7 Hz, ³J_{HP} = 14.3 Hz, 2H, H^o/C₆H₅). ¹³C{¹H} NMR (CD₂Cl₂, δ): 66.80 (d, J_{CP} = 6.2 Hz, C₅H₄), 67.42 (d, J_{CP} = 6.0 Hz, C₅H₄), 69.81 (d, J_{CP} = 9.3 Hz, C₅H₄), 70.67 (s, C₅H₅), 77.71 (d, ²J_{CP} = 16.3 Hz, Cⁱ/C₅H₄), 129.29 (d, J_{CP} = 12.5 Hz, C₆H₅), 129.51 (d, ¹J_{CP} = 12.7 Hz, Cⁱ/C₆H₅), 130.54 (d, ²J_{CP} = 22.5 Hz, CH/C₄H₂P), 131.64 (d, ²J_{CP} = 11.9 Hz, C^o/C₆H₅), 132.59 (d, J_{CP} = 3.1 Hz, C₆H₅), 141.57 (d, ¹J_{CP} = 74.4 Hz, Cⁱ/C₄H₂P). ³¹P{¹H} NMR (CDCl₃, δ): 33.21 (¹J_{31P77Se} = 745 Hz). HRMS (ESI-TOF) [*m/z*]: calcd for C₃₀H₂₅Fe₂PSe: 607.9556, found: 607.9562 [*M*]⁺.

Crystal Data for **5**: C₃₀H₂₅Fe₂PSe, *M* = 607.13 g·mol⁻¹, orthorhombic, *P*2₁2₁2₁, λ = 0.71073 Å, *a* = 7.5250(3) Å, *b* = 16.0764(13) Å, *c* = 19.8209(11) Å, *V* = 2397.8(3) Å³, *Z* = 4, ρ_{calcd} = 1.682 mgm⁻³, μ = 2.813 mm⁻¹, *T* = 100(2) K, Θ range = 2.90-25.25°, reflections collected: 9898, independent: 4283 (*R*_{int} = 0.0880), *R*₁ = 0.0578, *wR*₂ = 0.0839 [*I* > 2σ(*I*)], absolute structure parameter: -0.017(16).

Supporting Information Available: Figures giving further (spectro)electrochemical spectra, computational data and CIF files giving crystallographic data for **4** and **5**. This material is

available free of charge via the Internet at <http://pubs.acs.org>. Crystallographic data of **4** and **5** are also available from the Cambridge Crystallographic Database as file nos. CCDC 928309 (**4**) and 928310 (**5**).

Acknowledgement. We are grateful to the Fonds der Chemischen Industrie (FCI) and the Deutsche Forschungsgemeinschaft (DFG) for generous financial support.

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The Synthesis and (Spectro)electrochemical Behavior of 2,5-Diferrocenyl-1-phenyl- 1*H*-phosphole

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The synthesis of 2,5-diferrocenyl-1-phenyl-1*H*-phosphole and its sulfide and selenide analogue is presented. The chalcogenides have been structurally characterized by single crystal X-ray structure diffraction. Electrochemical measurements revealed a separate oxidation for each ferrocenyl group present. As observed in spectroelectrochemical investigations, the phospholes exhibit weak to moderate IVCT absorptions. All compounds can be classified as weak to moderate coupled class II systems according to Robin and Day.