

A Study of Mono- and 1,1'-Diphosphaferrocenes as Building Blocks for π -Conjugated Systems

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Received July 14, 2005

The synthesis of mono- and 1,1'-diphosphaferrocenes bearing thienyl or phenyl substituents at the PC α carbon is described. Monophosphaferrocenes can be obtained using a "one-pot" procedure involving the oxidative coupling of phenyl- or thienyl-capped octa-1,7-diyne with zirconocene. This route implies a Cp transfer from a Zr species to the iron centers. These novel compounds have been characterized by X-ray diffraction study, and their optical and electrochemical behaviors have been elucidated. These data revealed that the optical gaps vary with the substitution pattern and the nature of the metallocene (mono vs diphosphaferrocenes), whereas their electrochemistry is mainly controlled by the structure of the metallocene. The lowest gaps are obtained with thienyl-substituted mono- and diphosphaferrocenes. Compared to the corresponding oligomers featuring phosphole units, these phosphoferrocene-based compounds exhibit higher thermal stability and higher HOMO–LUMO separation.

Introduction

π -Conjugated systems have attracted considerable interest in the past decades due their potential applications as materials for optoelectronics such as light-emitting diodes, field effect transistors, photovoltaic cells, and lasers.¹ These materials combine the advantages of being processable with the possibility to have their optical and electronic properties tuned by exploiting the enormous versatility and scope of organic chemistry. The development of new advanced organic materials is directly linked to the ability of chemists to design and create novel structures and, subsequently, to establish structure–property relationships. A fruitful approach for the tailoring of π -conjugated systems involves the incorporation of heterocyclopentadienes into their backbones since these building blocks offer a range of electronic properties (aromaticity, electronic affinity, ionization potential, etc.) depending on the nature of the heteroatoms.^{1,2} For example, thiophene

and pyrrole are aromatic "electron-excessive" heteroarenes, whereas siloles combine diene character with high electron affinity due to a unique $\sigma^*-\pi^*$ interaction.^{2a,b} Phosphorus heterocycles have been considered only very recently as possible building blocks with the synthesis of phosphole-based oligomers **A–C** and polymers **D–F** (Figure 1).³ In contrast to pyrroles or thiophenes, the sextet of the phosphole ring is weakly delocalized, and thus phospholes possess a low aromatic character and a nucleophilic heteroatom.⁴ Insertion of this P-heterocycle within classical π -conjugated systems results in a lowering of their HOMO–LUMO gaps^{3c–e} since conjugation is enhanced for macromolecules incorporating units exhibiting low resonance energies.^{1,2} Moreover, the phosphole building block is a potential source of further structural variations by (i) changing the nature of the P substituent, (ii) chemical modifications of the nucleophilic P atom, or (iii) using this P ring as a precursor of other P heterocycles featuring a π -system such as phosphametallocenes. The two first possibilities have

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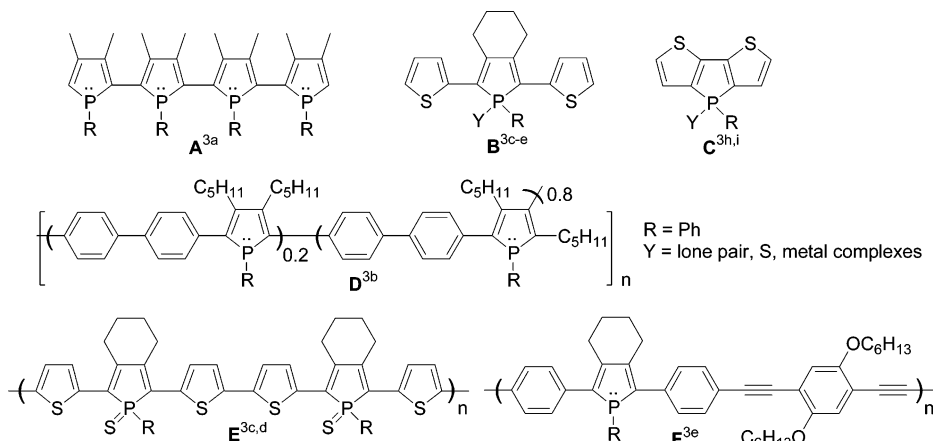


Figure 1. Representative π -conjugated systems incorporating phosphole units.

been exploited and appeared to be key issues for optoelectronic applications of phosphole-based π -conjugated systems since they allow a fine-tuning of their physical properties.^{3c-i} Until now, the last possibility has not been investigated,⁵ although the chemistry of phosphametalocenes is well-developed.⁶ The incorporation of phosphametalocenes into a π -conjugated system is of particular interest since they possess properties that are completely different from those of phospholes. First, they feature a fully delocalized (aromatic) endocyclic π -system and an sp^2 -hybridized P atom exhibiting some electrophilic character.⁶ Second, the LUMO of phosphametalocenes has an appreciable ligand character, whereas the HOMO exhibits an essentially pure metal character.^{6c} Last, the possibility to prepare mono- and 1,1'-diphosphametalocenes offers an appealing route to structural variations. In this paper, we describe the synthesis, solid-state structures, and optical and electrochemical properties of mono- and 1,1'-diphosphametalocenes, the oldest class of phosphametalocenes, bearing either phenyl or thienyl substituents at the PC α carbon atoms. The properties of these novel P-containing π -conjugated systems are compared to those of the corresponding phosphole-based derivatives.

Results and Discussion

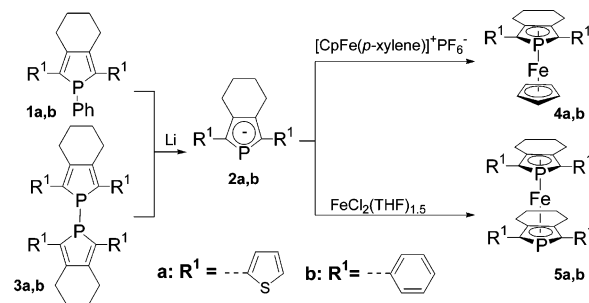
Synthesis of Phosphametalocenes **4a,b** and **5a,b**

The target mono- and 1,1'-diphosphametalocenes have been prepared via a classical two-step sequence.^{4a,b,6} The

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Scheme 1



highly moisture sensitive phospholyl anions **2a,b**, characterized by a ³¹P resonance at low field (³¹P NMR: **2a**, +91.4; **2b**, +78.0), are obtained by reductive cleavage either of the P–Ph bond of the corresponding 1-phenylphospholes **1a,b**^{3c} or of the P–P bond of 1,1'-diphospholes **3a,b**⁷ (Scheme 1). The route using **3a,b** is more convenient since it avoids the formation of phenyl-containing byproducts. The phospholyl anions **2a,b** are then converted into compounds **4a,b** and **5a,b** upon reaction with (*p*-xylene)cyclopentadienedienyliron(II) hexafluorophosphate salt and FeCl₂, respectively (Scheme 1).⁸ Mono- and 1,1'-diphosphametalocenes can be isolated as air-stable derivatives in satisfactory yields following purification by crystallization (Table 1). Note that the main byproducts formed along with the mono- and diphosphametalocenes are 1,1'-diphospholes **3a,b**.

We have recently described that 1,1'-diphospholes **3a,b** are accessible according to an expedient one-pot synthesis involving subsequent reaction of "zirconocene" and PBr₃ with thienyl- or phenyl-capped 1,7-octadiynes **6a,b**⁷ (Scheme 2). This feature prompted us to investigate the direct synthesis of **4a,b** and **5a,b** via a one-pot procedure involving five steps starting from these diynes. Octadiynes **6a,b** were thus subsequently treated with Cp₂ZrCl₂, *n*-BuLi, PBr₃, lithium, and [(*p*-xylene)-FeCp]⁺PF₆⁻ (Scheme 2). The intermediate formations of 1,1'-diphospholes **3a,b** and of the phospholyl anions **2a,b** were monitored by ³¹P NMR spectroscopy of the crude reaction mixtures after addition of PBr₃ and lithium,

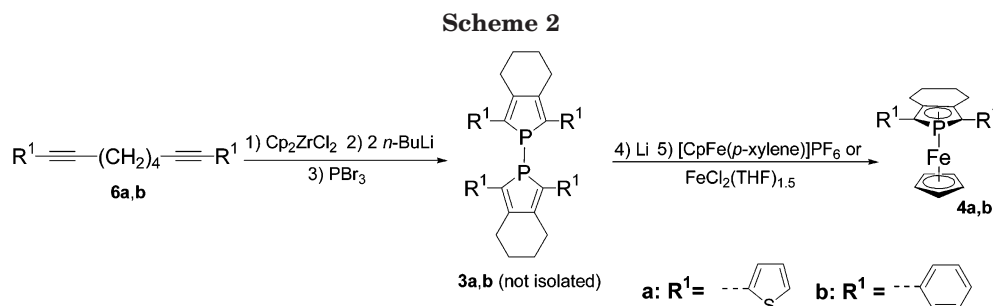
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Table 1. Yields, NMR Data,^a T_{d5} ,^b UV–Vis Data,^c and Oxidation Potentials^d for Monophosphaferrocenes **4a,b and Diphosphaferrocenes **5a,b****

	yield ^e (%)	$\delta(^{31}\text{P})$	$\delta(^{13}\text{C})$		T_{d5} (°C)	λ_{max} (nm)	ϵ (mol ⁻¹ L cm ⁻¹)	λ_{onset} (nm)	E°_{ox1} (V)	E_{pa}^f (V)
			PC α	PC β						
4a	64 (24)	-65.9	87.8 (56.2)	95.7 (4.4)	375	282 445	19 750 1400	570	0.22	1.19
4b	53 (30)	-64.2	96.8 (56.7)	95.3 (4.2)	380	274 447	17 000 450	550	0.20	
5a	67	-53.1	92.6 (54.0)	97.4 (3.7)	297	305 488	37 350 1370	640	0.13	1.18
5b	58	-53.9	99.4 (52.7)	98.8 (5.1)	355	277 492	32 350 800	620	0.14	

^a Measured in CD₂Cl₂ at 298 K. ^b Decomposition temperature estimated by thermogravimetric analysis, 5% weight loss. ^c Measured in CH₂Cl₂. ^d Referenced to the reversible potential of the ferrocene/ferrocenium couple. ^e Yields using **3a,b** (Scheme 1). In brackets, yields obtained with the “one-pot” procedure (Scheme 2). ^f Irreversible process.

**Table 2. Summary of Crystal Data and Structure Refinement for **4a**, **4b**, **5a**, and **5b****

	4a	4b	5a	5b
molecular formula	C ₂₁ H ₁₉ PS ₂ Fe	C ₂₅ H ₂₃ PFe	C ₃₂ H ₂₈ P ₂ S ₄ Fe	C ₄₀ H ₃₆ P ₂ Fe
molecular weight	422.30	410.25	658.57	634.52
<i>a</i> (Å)	7.125(5)	9.310(5)	9.256(5)	25.168(5)
<i>b</i> (Å)	13.894(5)	10.341(5)	10.504(5)	17.118(5)
<i>c</i> (Å)	18.632(5)	10.440(5)	15.503(5)	15.236(5)
α (deg)	90	85.409(5)	99.012(5)	90
β (deg)	90	84.841(5)	106.469(5)	108.563(5)
γ (deg)	90	82.864(5)	91.192(5)	90
<i>V</i> (Å ³)	1844.5(15)	990.9(9)	1424.2(11)	6223(3)
<i>Z</i>	4	2	2	8
<i>D_c</i> (g cm ⁻³)	1.521	1.375	1.536	1.355
cryst system	orthorhombic	triclinic	triclinic	monoclinic
space group	<i>Pc</i> 21 <i>n</i>	<i>P</i> 1	<i>P</i> 1	<i>C</i> 2/ <i>c</i>
temperature (K)	293(2)	293(2)	293(2)	293(2)
wavelength Mo K α (Å)	0.71069	0.71069	0.71069	0.71069
cryst size (mm)	0.14 × 0.08 × 0.06	0.4 × 0.26 × 0.22	0.30 × 0.20 × 0.10	0.25 × 0.12 × 0.1
μ (mm ⁻¹)	1.131	0.848	0.958	0.616
<i>F</i> (000)	872	428	680	2656
θ limit (deg)	2.93–27.48	2.70–30.04	2.99–27.57	2.21–27.49
index ranges <i>hkl</i>	-9 ≤ <i>h</i> ≤ 9, -17 ≤ <i>k</i> ≤ 18, -24 ≤ <i>l</i> ≤ 24	-13 ≤ <i>h</i> ≤ 13, -14 ≤ <i>k</i> ≤ 14, -14 ≤ <i>l</i> ≤ 14	-12 ≤ <i>h</i> ≤ 12, -13 ≤ <i>k</i> ≤ 13, -20 ≤ <i>l</i> ≤ 18	-32 ≤ <i>h</i> ≤ 32, -22 ≤ <i>k</i> ≤ 22, -19 ≤ <i>l</i> ≤ 19
no. of reflns collected	3998	11 021	11 371	14 037
no. of indep reflns	3998	5782	6519	7144
no. of reflns [<i>I</i> > 2 σ (<i>I</i>)]	2855	4292	4343	4543
no. of data/restraints/params	3998/19/209	5782/0/245	6519/0/357	7144/0/389
goodness-of-fit on <i>F</i> ²	1.029	1.019	1.024	1.013
final <i>R</i> indices	<i>R</i> 1 = 0.0541 w <i>R</i> 2 = 0.1307	<i>R</i> 1 = 0.0391 w <i>R</i> 2 = 0.0987	<i>R</i> 1 = 0.0614 w <i>R</i> 2 = 0.1599	<i>R</i> 1 = 0.0483 w <i>R</i> 2 = 0.1196
[<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> 1 = 0.0858 w <i>R</i> 2 = 0.1519	<i>R</i> 1 = 0.0607 w <i>R</i> 2 = 0.1105	<i>R</i> 1 = 0.1010 w <i>R</i> 2 = 0.1864	<i>R</i> 1 = 0.0892 w <i>R</i> 2 = 0.1407
<i>R</i> indices (all data)				
largest diff peak and hole (e Å ⁻³)	0.612 and -0.593	0.476 and -0.430	0.942 and -0.777	0.515 and -0.423

respectively. Although this “one-pot” procedure afforded monophosphaferrocenes **4a,b** in rather modest yields (Table 1), it is more convenient than that starting from isolated 1,1'-diphospholes **3a,b** since it is much less time-consuming. Very surprisingly, when this “one-pot” procedure is conducted with FeCl₂(THF)_{1.5}, monophosphaferrocenes **4a,b** are obtained instead of the expected diphosphaferrocenes **5a,b** (Scheme 2). The only source of the Cp ligand of monophosphaferrocenes **4a,b** is the zirconium complex used to prepare the 1,1'-diphospholes **3a,b**. Hence, the formation of monophosphaferrocenes

4a,b implies the transfer of one Cp ligand from a zirconium species to the Fe(II) center. This reaction can involve either a direct zirconium to iron transfer of a Cp ligand or a reduction of a Cp₂Zr fragment by lithium leading to CpLi, which will be the cyclopentadienyl ligand source. It is noteworthy that this Cp transfer is very efficient since the yields are very similar (ca. 30%) using [CpFe(*p*-xylene)]PF₆ or FeCl₂(THF)_{1.5} as a source of Fe(II).

Spectroscopic and Solid-State Characterizations of Phosphametalloenes **4a,b and **5a,b**.** The

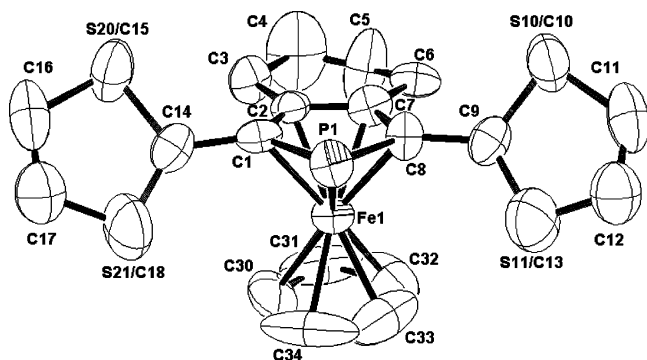


Figure 2. Molecular structure of **4a** (thermal ellipsoids 50% probability). Hydrogen atoms have been omitted for clarity.

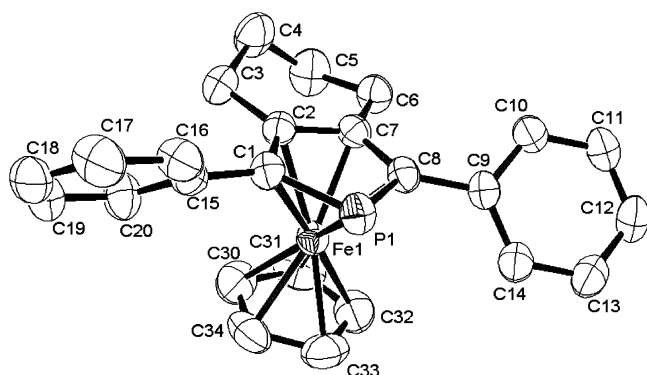


Figure 3. Molecular structure of **4b** (thermal ellipsoids 50% probability). Hydrogen atoms have been omitted for clarity.

novel mono- and diphosphaferrocenes **4a,b** and **5a,b** were characterized by NMR techniques, high-resolution mass spectrometry, and elemental analysis. Their multinuclear NMR data are comparable to those of related compounds bearing alkyl substituents.⁶ The ¹³C NMR spectrum showed two signals for the PC_α and PC_β carbon atoms with typical large J^1_{PC} and small J^2_{PC} coupling constants, respectively (Table 1). It is noteworthy that the ¹³C chemical shifts of the PC_α carbon atoms vary with the nature of the aromatic substituent; they are downfield shifted by ca. 6 ppm in the thienyl series (Table 1). Of particular importance for potential applications in the field of material science, mono- and 1,1'-diphosphaferrocenes are much more thermally stable than the corresponding phospholes **1a,b**. Derivatives **4a,b** and **5a,b** decompose above 300 °C, as estimated by thermal gravimetric analysis performed in air (Table 1), whereas the corresponding phospholes **1a** and **1b** decompose at 210 and 199 °C, respectively.^{3d}

These new phosphametalloenes have been subjected to X-ray diffraction studies (Table 2). The phospholyl and cyclopentadienyl ligands of **4a,b** are eclipsed, and their two planes are almost parallel (Figures 2 and 3). The two diphosphaferrocenes **5a** and **5b** exhibit different conformations. Tetrathienyl derivative **5a** adopts a C_{2h} conformation with the two P atoms pointing in opposite directions ($\alpha = 180^\circ$, Figure 4). Phenyl-capped derivative **5b** possesses a C_1 conformation in which the P atoms of the phospholyl units superpose with the C_β of the other P ligand ($\alpha = 127^\circ$, Figure 5). This conformation is not maintained in solution since NMR spectra show that both P atoms and phenyl substituents

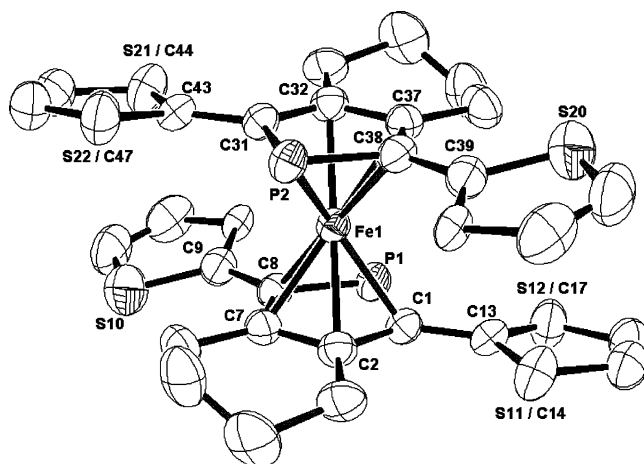


Figure 4. Molecular structure of **5a** (thermal ellipsoids 50% probability). Hydrogen atoms have been omitted for clarity.

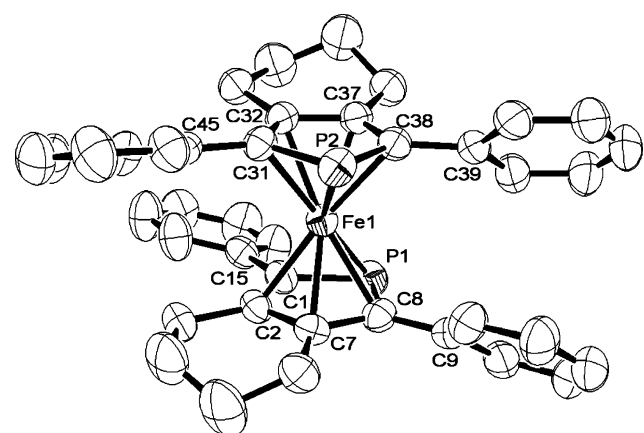


Figure 5. Molecular structure of **5b** (thermal ellipsoids 50% probability). Hydrogen atoms have been omitted for clarity.

are magnetically equivalent. These data suggest a very weak rotation barrier as supported by calculations on the parent compound FeC₅H₅P₂, showing that the energy difference between the two C_{2h} and C_1 conformers is low (ca. 6 kcal mol⁻¹),^{6e} and the observation of different conformers in the cell unit of octaethyl-diphosphaferrocene.⁶ⁿ The planarity of the diarylphospholyl moieties, a key structural factor influencing the delocalization of the π -system,^{1b} depends on the structure of the phosphametalloenes. Monophosphaferrocenes **4a** and **4b** both exhibit considerable rotational disorder in the solid state (Figures 2 and 3). The twist angles between the phospholyl ligand and the aromatic substituents are slightly higher for thienyl-capped **4a** (54.9° and 57.6°) than for phenyl-capped **4b** (43.4° and 49.1°) derivatives. In the diphosphaferrocene series, the reverse trend is observed. The two di(2-thienyl)phospholyl moieties of compound **5a** are almost planar (twist angles: 0.5–12.9°), while for phenyl-substituted derivative **5b**, the twist angles range from 17.2° to 46.8° (Figures 3 and 4). The large rotational disorder observed for derivatives **4a,b** and **5b** prevents an efficient delocalization of the π -system over the three cycles in the solid state since the orbital overlap varies approximately with the cosine of the twist angle.^{1b} Only diphosphaferrocene **5a** possesses planar π -conjugated systems as

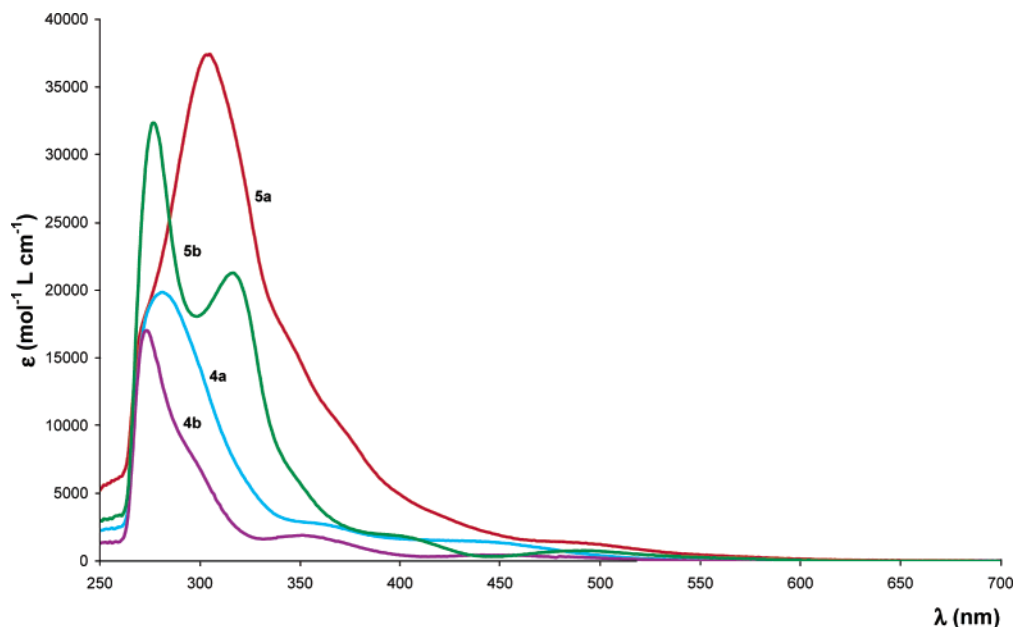


Figure 6. UV/vis spectra (250–700 nm) of monophosphaferrocenes **4a,b** and diphosphaferrocenes **5a,b** in CH₂Cl₂.

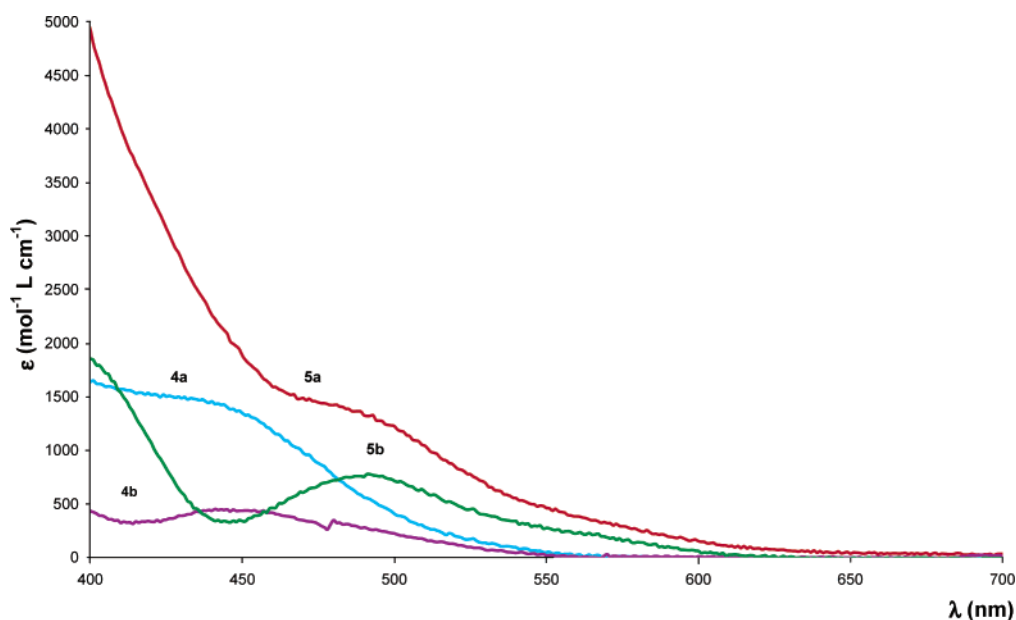


Figure 7. Visible spectra (400–700 nm) of monophosphaferrocenes **4a,b** and diphosphaferrocenes **5a,b** in CH₂Cl₂.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Monophosphaferrocenes **4a,b** and Diphosphaferrocenes **5a,b**

	4a	4b	5a	5b		5a	5b
P1–C1	1.775(8)	1.788(2)	1.783(4)	1.788(3)	P2–C31	1.782(4)	1.787(3)
C1–C2	1.414(9)	1.427(2)	1.438(6)	1.434(4)	C31–C32	1.435(6)	1.428(4)
C2–C7	1.410(6)	1.428(2)	1.424(6)	1.424(4)	C32–C37	1.431(7)	1.431(4)
C7–C8	1.426(9)	1.427(2)	1.425(6)	1.423(4)	C37–C38	1.427(6)	1.417(4)
C8–P1	1.796(7)	1.789(2)	1.781(4)	1.775(3)	C38–P2	1.785(5)	1.777(3)
C8–C9	1.461(12)	1.486(2)	1.469(6)	1.483(4)	C31–C43	1.460(6)	
C1–C13	1.505(12)		1.463(6)		C32–C45		1.488(4)
C1–C15		1.488(2)		1.493(4)	C38–C39	1.460(7)	1.483(4)
C1–P1–C8	88.77(17)	89.45(8)	90.2(2)		C31–P2–C38	90.1(2)	90.07(13)

observed for the corresponding 2,5-dithienylphosphole **1a** (twist angles: 12.5° and 16.2°).^{3d} Note that the bond distances for **5a** and **5b** are similar, excepted the interring distances, which are slightly smaller for the planar di(2-thienyl)phosphophyl moieties of **5a** than for the rotationally disordered diphenylphosphophyl unit of **5b** (Table 3).

Optical and Redox Properties of Phosphametalloenes 4a,b and 5a,b. The UV/vis and fluorescence spectra of all new phosphametalloene derivatives were recorded in CH₂Cl₂. For each compound, intense bands are observed between 350 and 450 nm (Figure 6, Table 1) along with a red-shifted broad shoulder (Figure 7). Although care must be taken in the interpretation of

these data, since the orbitals of the P ligands interact with the Fe atom,^{6e} some conclusions can be drawn. The molecular extinction coefficients of the high-energy absorptions (ϵ : 17 000–38 000 mol⁻¹ L cm⁻¹, Table 1, Figure 6) are by far superior to those of the red-shifted shoulders (ϵ : 450–1500 mol⁻¹ L cm⁻¹, Table 1, Figure 7). Furthermore, the intensity of the high-energy absorptions approximately doubles on going from monophosphaferrocene to the corresponding diphosphaferrocene (**4a** vs **5a**, **4b** vs **5b**, Table 1, Figures 6 and 7). These data strongly suggest that the bands of high energy are mainly ligand centered, whereas those of lower energy can be assigned to ligand–metal charge transfer. This hypothesis is supported by the fact that ferrocene also displays a weak absorption band at 442 nm. In light of this, two features are particularly noteworthy. First, for both series, a bathochromic shift is observed by replacing phenyl by thienyl substituents (**4a** vs **4b**; **5a** vs **5b**, Figure 6), this trend being less pronounced for the λ_{onset} (Table 1, Figure 7). A similar bathochromic shift induced by phenyl/thiophene substitutions was already observed in the phosphole series (λ_{max} : **1a**, 410 nm; **1b**, 354 nm).^{3d} Second, the spectra of 1,1'-diphosphaferrocenes are red shifted compared to those of the corresponding monophosphaferrocenes (**5a** vs **4a**; **5b** vs **4b**, Figure 6). These data suggest an interesting decrease of the HOMO–LUMO separation of the π -ligand on going from mono- to 1,1'-diphosphaferrocenes. It is noteworthy that the λ_{max} of phosphaferrrocene-based π -conjugated systems are blue shifted compared to the corresponding phosphole-based derivatives. This increase of the “optical” HOMO–LUMO gap of the π -system can be attributed to the fact that phospholyl ligands exhibit a higher aromatic character than phospholes. No fluorescence behavior was observed for mono- and 1,1'-diphosphaferrocenes in degassed THF or CH₂Cl₂ solutions. In conclusion, this study revealed interesting optical properties–relationships. Both the nature of the 2,5-substituent and the structure of the metallocene influence the absorption properties of these novel P-containing π -conjugated systems. π -Conjugated systems incorporating phosphametallocene building blocks are more thermally stable and exhibit higher gap than the corresponding systems featuring phosphole units.

The electrochemical behavior of mono- and diphosphaferrocene derivatives was investigated by cyclic voltammetry (CV). The CV at 100 mV s⁻¹ has been performed in a three-electrode cell configuration (Pt disk working electrode, Pt wire counter electrode, Ag/AgCl secondary reference electrode, internally calibrated vs the redox couple ferrocene/ferricenium: Fc/Fc⁺) with dichloromethane as solvent and tetrabutylammonium hexafluorophosphate (TBAHFP) (0.1 M) as electrolyte. A reversible oxidation is observed for **4a** (+0.20 V) and **4b** (+0.22 V) at potentials that are similar to that of monophosphaferrocene lacking in aromatic 2,5-substituents ($E^{\circ}_{1/2} = +0.18$ V vs Fc/Fc⁺).⁹ These data strongly suggest that this first oxidation process is metal centered (Fe²⁺ → Fe³⁺). For the thienyl-capped derivative **4a**, a second and irreversible oxidation process occurs at 1.19 V. This second oxidation very probably involves

the terminal thiophene rings, which are known to undergo irreversible oxidation in this potential range.^{1a} The same general trends are observed in the 1,1'-diphosphaferrocene series. Thienyl- and phenyl-substituted derivatives **5a** and **5b** undergo a first reversible oxidation at similar potentials (ca. 0.13 V, Table 1), which is assigned to an Fe²⁺ → Fe³⁺ process. Only thienyl-substituted **5a** shows a second irreversible oxidation process at a potential (1.18 V) similar to that observed for monophosphaferrocene **4a** (1.19 V). These data suggest that, as usually observed for phosphaferrrocenes,^{6e} the HOMOs of thienyl- or phenyl-substituted derivatives **4a,b** and **5a,b** have an essentially pure metal character. The oxidation of the di(2-thienyl)-phospholyl moiety of **4a** and **5a** occurs at more anodic potential compared to di(2-thienyl)phosphole **1a** ($E^{\circ} = +0.40$ V vs Fc/Fc⁺),^{3b,c} probably due to the preliminary oxidation of the Fe center. It is noteworthy that no anodic electropolymerization process was observed with compounds **4a** and **5a**.

Conclusion

We have described the synthesis of a novel series of mixed conjugated oligomers including mono- and diphosphaferrocene units and elucidated their optical and electrochemical properties. These model molecules have revealed interesting structure–property relationship. Both the nature of the 2,5-substituent (phenyl vs thienyl) and the structure of the metallocene (mono- vs 1,1'-di-) influence their optical properties, while their electrochemical behavior is mainly controlled by the structure of the metallocene. It is worth noting that the $\lambda_{\text{max}}(\pi-\pi^*)$ of 1,1'-diphosphaferrocene-based oligomers are red shifted compared to those of their monophosphaferrocene-containing analogues. As observed for structurally related phosphole-based oligomers, the lowest HOMO–LUMO π -gap is obtained with thienyl-substituted metallocenes. However, the properties of phosphaferrrocene- and phosphole-containing conjugated systems differ markedly due to the profoundly different electronic nature of these two P building blocks. These results nicely illustrate the potential of P building blocks to create structural diversity and to tune the physical properties of π -conjugated systems.¹⁰

Experimental Section

General Remarks. All experiments were performed under an atmosphere of dry argon using standard Schlenk techniques. Solvents were freshly distilled under argon from sodium/benzophenone (tetrahydrofuran, diethyl ether, toluene) or from phosphorus pentoxide (pentane, dichloromethane, acetonitrile). Triethylamine was freshly distilled under argon

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from potassium hydroxide, and PBr_3 was also freshly distilled under argon. Cp_2ZrCl_2 , Li, Na, and $n\text{-BuLi}$ were obtained from Aldrich Chemical Co. and were used as received without further purification. 1,8-Di(2-thienyl)octa-1,7-diyne,^{3d} 1,8-di(1-phenyl)octa-1,7-diyne,^{3d} 2,5-di(2-thienyl)-1-phenylphosphole,^{4d} 2,5-di(phenyl)-1-phenylphosphole,^{4d} 1,1'-di[2,5-di(2-thienyl)-phosphole],⁷ 1,1'-di[2,5-di(phenyl)phosphole],⁷ and [$p\text{-xylene}$]- $\text{FeCp}^+\text{PF}_6^-$ ¹¹ were prepared as described in the literature. $\text{FeCl}_2(\text{THF})_{1.5}$ was prepared through a reduction of FeCl_3 with aluminum in THF at -40°C . Preparative separations were performed by gravity column chromatography on basic alumina (Aldrich, Type 5016A, 150 mesh, 58 Å) in 3.5–20 cm columns. ^1H , ^{13}C , and ^{31}P NMR spectra were recorded on Bruker AM300, DPX200. ^1H and ^{13}C NMR chemical shifts were reported in parts per million (ppm) relative to Me_4Si as external standard. ^{31}P NMR downfield chemical shifts were expressed with a positive sign, in ppm, relative to external 85% H_3PO_4 . Assignment of carbon atoms is based on HMBC and HMQC experiments. High-resolution mass spectra were obtained on a Varian MAT 311 or ZabSpec TOF Micromass instrument at CRMPO, University of Rennes. Elemental analyses were performed by the CRMPO, University of Rennes. UV/vis spectra were recorded at room temperature on a UVIKON 942 spectrophotometer. Cyclic voltammetry experiments were performed with a computer-controlled EG&G PAR 273 potentiostat in a three-electrode single-compartment cell (5 mL). The platinum working electrode consisted of a platinum wire sealed in a soft glass tube with a surface of $A = 0.785\text{ mm}^2$, which was polished down to $0.5\text{ }\mu\text{m}$ with Buehler polishing paste prior to use in order to obtain reproducible surfaces. The counter electrode consisted of a platinum wire, and the reference electrode was an Ag/AgCl secondary electrode. All potentials were internally referenced to the ferrocene/ferrocenium couple.¹² For the measurements concentrations of 10^{-3} M of the electroactive species were used in freshly distilled and degassed dichloromethane (Lichrosolv, Merck) and 0.1 M tetrabutylammonium hexafluorophosphate (TBAHFP, Fluka), which was twice recrystallized from ethanol and dried under vacuum prior to use.

2,5-Di(2-thienyl)-1-monophosphaferrocene, 4a. (a) From 2,5-Di(2-thienyl)-1-phenylphosphole, 1a. Li metal in excess was added, at room temperature, to a THF solution (10 mL) of 2,5-di(2-thienyl)-1-phenylphosphole **1a** (120 mg, 0.32 mmol). The mixture was stirred vigorously at room temperature, and the formation of phospholyl anion **2a** was monitored by ^{31}P NMR spectroscopy. After 12 h, the excess of lithium was removed and 2-chloro-2-methylpropane (27 mg, 0.32 mmol) was added. The reaction mixture was stirred for 3 h, and neat [$p\text{-xylene}$] $\text{CpFe}^+\text{PF}_6^-$ (120 mg, 0.32 mmol) was added to the green solution. The reaction was monitored by ^{31}P NMR spectroscopy and, after 4 h, the volatile materials were removed in a vacuum. Compound **4a** was extracted with pentane (15 mL) and ether (15 mL). **4a** was obtained as air-stable red crystals from a saturated pentane solution at room temperature (yield: 13 mg, 0.032 mmol, 10%).

(b) From 1,1'-Diphosphole 3a. Li metal in excess was added, at room temperature, to a THF solution (25 mL) of 1,1'-di[2,5-di(2-thienyl)phosphole], **3a** (90 mg, 0.15 mmol). The mixture was stirred vigorously at room temperature, and the formation of phospholyl anion **2a** was monitored by ^{31}P NMR spectroscopy. After 4 h, neat [$p\text{-xylene}$] $\text{CpFe}^+\text{PF}_6^-$ (350 mg, 0.90 mmol) was added at room temperature to the red-green solution. The reaction was monitored by ^{31}P NMR spectroscopy, and after 3 h, the solution was filtered through basic alumina and the solvent was removed in vacuo. **4a** was obtained as air-stable red crystals from a saturated pentane solution at room temperature (yield: 81 mg, 0.19 mmol, 64%).

(c) From Dyne 6a. A solution of $n\text{-BuLi}$ in hexane (1.6 M, 1.3 mL, 2.1 mmol) was added at -78°C to a THF solution (25 mL) of 1,8-di(2-thienyl)octa-1,7-diyne (**6a**; 270 mg, 1.0 mmol) and [Cp_2ZrCl_2] (293 mg, 1.0 mmol). The reaction was warmed to room temperature and stirred for 15 h. Freshly distilled PBr_3 (271 mg, 0.1 mL, 1 mmol) was added to this solution at -78°C . The solution was allowed to warm to room temperature and stirred for 4 h. Li metal in excess was added to this solution at room temperature, and the formation of phospholyl anion **2a** was monitored by ^{31}P NMR spectroscopy. The solution was stirred for 5 h, and the excess of Li was removed. Solid [$p\text{-xylene}$] $\text{FeCp}^+\text{PF}_6^-$ (387 mg, 1.0 mmol) or solid $\text{FeCl}_2(\text{THF})_{1.5}$ (235 mg, 0.1 mmol) was added at room temperature to the solution, which was then stirred overnight. The solution was filtered through basic alumina, and the solvent was removed in vacuo. The residue was extracted with pentane, and **4a** was obtained as red crystals by crystallization from a pentane solution at room temperature [yield: 101 mg, 0.24 mmol, 24%, using [$p\text{-xylene}$] $\text{FeCp}^+\text{PF}_6^-$; 127 mg, 0.3 mmol, 30% using $\text{FeCl}_2(\text{THF})_{1.5}$]. ^1H NMR (300 MHz, CD_2Cl_2): δ 1.93 (m, 2H, $=\text{CCH}_2\text{CH}_2$), 2.21 (m, 2H, $=\text{CCH}_2\text{CH}_2$), 2.79 (m, 2H, $=\text{CCH}_2$), 3.06 (m, 2H, $=\text{CCH}_2$), 4.23 (s, 5H, CpH), 6.92 (dd, $^3J_{\text{HH}} = 3.7$ and 5.1 Hz, 2H, H₄ Thio); 6.99 (dd, $^3J_{\text{HH}} = 3.7$ Hz, $^4J_{\text{HH}} = 1.0$ Hz, 2H, H₃ Thio), 7.22 (dd, $^3J_{\text{HH}} = 5.1$ Hz, $^4J_{\text{HH}} = 1.0$ Hz, 2H, H₅ Thio). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.46 MHz, CD_2Cl_2): δ 23.2 (s, $=\text{CCH}_2\text{CH}_2$), 27.9 (s, $=\text{CCH}_2$), 75.4 (s, Cp), 87.8 (d, $J_{\text{CP}} = 56.2$ Hz, PC_α), 95.7 (d, $J_{\text{CP}} = 4.4$ Hz, $\text{PC}=\text{C}_\beta$), 124.2 (d, $J_{\text{CP}} = 2.1$ Hz, C₅ Thio), 125.7 (d, $J_{\text{CP}} = 7.3$ Hz, C₃ Thio), 126.9 (s, C₄ Thio), 143.3 (d, $J_{\text{CP}} = 20.8$ Hz, C₂ Thio). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.49 MHz, CD_2Cl_2): δ -65.9 (s). HR-MS (EI): m/z 422.0011 [M^+]; calcd for $\text{C}_{21}\text{H}_{19}\text{PS}_2\text{Fe}$ 422.0015. Anal. Calcd for $\text{C}_{21}\text{H}_{19}\text{S}_2\text{PFe}$: C, 59.72; H, 4.53. Found: C, 59.91; H, 4.59.

2,5-Di(phenyl)-1-monophosphaferrocene, 4b. Following procedure b described for the compound **4a**, the reaction of 1,1'-di[2,5-di(phenyl)phosphole] (**3b**; 40 mg, 0.07 mmol), sodium, and [$p\text{-xylene}$] $\text{FeCp}^+\text{PF}_6^-$ (150 mg, 0.40 mmol) afforded **4b** as an air-stable red solid (yield: 30 mg, 0.07 mmol, 53%). Following procedure c described for compound **4a**, reaction of $n\text{-BuLi}$ in hexane (1.6 M, 1.3 mL, 2.1 mmol), 1,8-di(phenyl)octa-1,7-diyne (**6b**; 258 mg, 1.0 mmol), [Cp_2ZrCl_2] (293 mg, 1.0 mmol), PBr_3 (271 mg, 0.1 mL, 1.0 mmol), lithium, and solid [$p\text{-xylene}$] $\text{FeCp}^+\text{PF}_6^-$ (387 mg, 1.0 mmol) or solid $\text{FeCl}_2(\text{THF})_{1.5}$ (240 mg, 1 mmol) afforded **4b** as an air-stable red solid [yield: 123 mg, 0.30 mmol, 30%, using [$p\text{-xylene}$] $\text{FeCp}^+\text{PF}_6^-$; 110 mg, 0.27 mmol, 28%, using $\text{FeCl}_2(\text{THF})_{1.5}$]. ^1H NMR (200 MHz, CD_2Cl_2): δ 1.89 (m, 2H, $=\text{CCH}_2\text{CH}_2$), 2.16 (m, 2H, $=\text{CCH}_2\text{CH}_2$), 2.72 (m, 2H, $=\text{CCH}_2$), 3.00 (m, 2H, $=\text{CCH}_2$), 4.21 (s, 5H, CpH), 7.24 (m, 6 H, $p\text{-Ph}$ and $m\text{-Ph}$), 7.42 (m, 4H, $o\text{-Ph}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.46 MHz, CD_2Cl_2): δ 23.4 (s, $=\text{CCH}_2\text{CH}_2$), 28.0 (s, $=\text{CCH}_2$), 74.8 (s, Cp), 95.3 (d, $J_{\text{CP}} = 4.2$ Hz, $\text{PC}=\text{C}_\beta$), 96.8 (d, $J_{\text{C-P}} = 56.7$ Hz, PC_α), 126.0 (s, $p\text{-Ph}$), 127.8 (s, $m\text{-Ph}$), 129.9 (d, $J_{\text{C-P}} = 7.1$ Hz, $o\text{-Ph}$), 140.0 (d, $J_{\text{C-P}} = 17.4$ Hz, $ipso\text{-Ph}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (81.02 MHz, CDCl_3): δ -64.2 (s). HR-MS (ES, CH_2Cl_2): m/z 410.0888 [M^+]; calcd for $\text{C}_{25}\text{H}_{23}\text{PFe}$ 410.0887. Anal. Calcd for $\text{C}_{25}\text{H}_{23}\text{PFe}$: C, 73.19; H, 5.65. Found: C, 73.09; H, 5.52.

1,1'-Di[2,5-di(2-thienyl)diphosphaferrocene], 5a. (a) From 2,5-Di(2-thienyl)-1-phenylphosphole, 1a. Li metal in excess was added, at room temperature, to a THF solution (10 mL) of 2,5-di(2-thienyl)-1-phenylphosphole (**1a**; 100 mg, 0.26 mmol). The mixture was stirred vigorously at room temperature, and the formation of phospholyl anion **2a** was monitored by ^{31}P NMR spectroscopy. After 12 h, the excess lithium was removed and 2-chloro-2-methylpropane (25 mg, 0.26 mmol) was added. The reaction mixture was stirred for 3 h, and solid $\text{FeCl}_2(\text{THF})_{1.5}$ (30 mg, 0.13 mmol) was added to the green solution. The reaction was monitored by ^{31}P NMR spectroscopy, and after 6 h, the volatile materials were removed in a vacuum. Compound **4a** was extracted with pentane (15 mL) and ether (15 mL). **4a** was obtained as air-

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stable red crystals from a saturated pentane solution at room temperature (yield: 13 mg, 0.02 mmol, 15%).

(b) From 1,1'-Diphosphole, 3a. Li metal in excess was added, at room temperature, to a THF solution (25 mL) of 1,1'-di[2,5-di(2-thienyl)phosphole], **3a** (85 mg, 0.14 mmol). The mixture was stirred vigorously at room temperature, and the formation of phospholyl anion **2a** was monitored by ^{31}P NMR spectroscopy. After for 4 h, solid $\text{FeCl}_2(\text{THF})_{1.5}$ (110 mg, 0.47 mmol) was added to the solution. The reaction was monitored by ^{31}P NMR, and after 3 h the solution was filtered through basic alumina. The solvent was removed in vacuo, and **5a** was obtained as air-stable red crystals by crystallization from a pentane solution at room temperature (yield: 62 mg, 0.09 mmol, 67%). ^1H NMR (300 MHz, CDCl_3): δ 1.61 (m, 4H, =CCH₂CH₂), 1.86 (m, 4H, =CCH₂CH₂), 2.40 (m, 4H, =CCH₂), 2.63 (m, 4H, =CCH₂), 6.66 (d, $^3J_{\text{HH}} = 4.0$ Hz, 4H, H₃ Thio), 6.72 (dd, $^3J_{\text{HH}} = 4.0$ and 5.1 Hz, 4H, H₄ Thio), 7.02 (d, $^3J_{\text{HH}} = 5.1$ Hz, 4H, H₅ Thio). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.47 MHz, CDCl_3): δ 22.7 (s, =CCH₂CH₂), 26.8 (s, =CCH₂), 92.6 (d, $J_{\text{CP}} = 54.0$ Hz, PC _{α}), 97.4 (d, $J_{\text{CP}} = 3.7$ Hz, PC=C _{β}), 124.1 (d, $J_{\text{CP}} = 7.0$ Hz, C₅ Thio), 125.9 (d, $J_{\text{CP}} = 11.9$ Hz, C₃ Thio), 127.3 (s, C₄ Thio), 139.5 (d, $J_{\text{CP}} = 22.1$ Hz, C₂ Thio). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.49 MHz, CDCl_3): δ -53.1 (s). HR-MS (ES, CH_2Cl_2): (m/z) 657.9908 [M^+]; calcd for C₃₂H₂₈FeP₂S₄ 657.9899. Anal. Calcd for C₃₂H₂₈P₂S₄Fe: C, 58.36; H, 4.29. Found: C, 58.26; H, 4.65.

1,1'-Di[2,5-di(phenyl)diphosphaferrocene], 5b. Following procedure b described for compound **5a**, reaction of 1,1'-di[2,5-di(phenyl)phosphole] (**3b**; 30 mg, 0.05 mmol), sodium, and solid $\text{FeCl}_2(\text{THF})_{1.5}$ (145 mg, 0.62 mmol) afforded **5b** as an air-stable red solid (yield: 20 mg, 0.03 mmol, 58%). ^1H NMR (200 MHz, CD_2Cl_2): δ 1.50 (m, 4H, =CCH₂CH₂), 1.69 (m, 4H, =CCH₂CH₂), 2.34 (m, 4H, =CCH₂), 2.88 (m, 4H, =CCH₂), 7.10 (m, 12H, *p*-Ph and *m*-Ph), 7.22 (m, 8H, *o*-Ph). ^{13}C NMR{ ^1H } (75.46 MHz, CD_2Cl_2): δ 22.7 (s, =CCH₂CH₂), 27.0 (s, =CCH₂), 98.8 (d, $J_{\text{CP}} = 5.1$ Hz, PC=C _{β}), 99.4 (d, $J_{\text{CP}} = 52.7$ Hz, PC _{α}), 126.2 (s, *p*-Ph), 127.7 (s, *m*-Ph), 130.2 (d, $J_{\text{CP}} = 12.1$ Hz, *o*-Ph), 136.4 (d, $J_{\text{CP}} = 17.2$ Hz, *ipso*-Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (81.02 MHz, CD_2Cl_2): δ -53.9 (s). HR-MS (ES, CH_2Cl_2): (m/z) 634.1647 [M^+]; calcd for C₄₀H₃₆FeP₂ 634.1642. Anal. Calcd for C₄₀H₃₆P₂Fe: C, 75.72; H, 5.72. Found: C, 75.48; H, 5.99.

X-ray Crystallographic Study. Single crystals suitable for X-ray crystal analysis were obtained by slow evaporation of 80:20 $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ solutions of **4a**, **4b**, **5a**, and **5b** at room temperature. Single-crystal data collection was performed at room temperature with a Nonius Kappa CCD diffractometer

(Center 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 data merging process was performed using the SCALEPACK program.¹³ Structure determinations were performed by direct methods with the solving program SIR97,¹⁴ which revealed all the non-hydrogen atoms. The SHELXL program¹⁵ was used to refine the structures by full-matrix least-squares 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. For compound **4a**, the thienyl moieties are disordered and were modeled with a equidistribution of the sulfur atoms and the C₃H₃ atoms of the thienyl moieties over positions 1 and 3 of the thienyl ring. For compound **5a**, half of the thienyl moieties were found disordered and were modeled as for compound **4a**. Atomic scattering factors for all atoms were taken from International Tables for X-ray Crystallography.¹⁶ Details of crystal data and structural refinements are given in Table 2. CCDC reference numbers 277996–277999 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) + 44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgment. We thank the Ministère de l'Éducation Nationale, de la Recherche et de la Technologie, the Institut Universitaire de France, the Centre National de la Recherche Scientifique, and the Deutsche Forschungsgemeinschaft for financial support (CNRS-DFG program).

OM050593S

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