Organophosphorus π-Conjugated Materials

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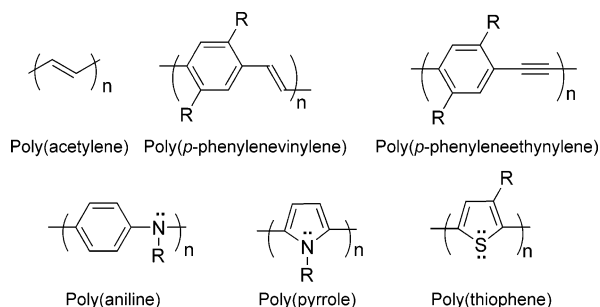
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1. Introduction

Organic π-conjugated polymers and oligomers (Chart 1) are intriguing compounds that have been intensively studied for almost 30 years by now.[1−3] The interest in these systems is primarily based on the fact that some conjugated polymers exhibit metal-like conductivities upon doping and that a broad variety of corresponding oligomers shows semiconducting properties.[1−3] These organic materials therefore have great potential for applications in electronic devices such as organic or polymer-based light-emitting diodes (OLEDs/PLEDs),[4] photovoltaic cells,[5] field-effect transistors (FET),[6] electrochromic or smart windows, photoresists, nonlinear optical (NLO) devices, or polymeric sensors.[1−7] Their organic nature allows for the fabrication of flexible, lightweight materials

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Chart 1. Structure of Organic Conjugated π-Systems Illustrating the Most Commonly Used Building Blocks

Poly(acetylene) Poly(*p*-phenylenevinylene) Poly(*p*-phenyleneethynylene)

Poly(aniline) Poly(pyrrole) Poly(thiophene)

that can be processed very conveniently, particularly for low-power, low-cost applications.[4a,5k] This is nicely illustrated by their utility in the fabrication of high-performance OLEDs that are employed as devices for flat-panel displays in a host of commercial products (e.g. cell phones, digital cameras, etc.).[4] It is well established that the performances of these organic materials are mainly determined by their chemical structure and also by their supramolecular organization in the solid state.[2−4,5k] A great deal of attention has therefore been focused on efficiently tuning the optoelectronic structure of the organic π-conjugated materials to modify and to control their electronic nature (band gap, HOMO and LUMO levels, effective conjugation length, etc.) in such a way that it suits the desired function (electroluminescence, high charge mobility, etc.).[2,8] One of the major strategies to achieve this goal is the grafting of bulky or functional side-chain substituents on the conjugated backbone (R; Chart 1). These R groups influence the optical and electronic properties of the materials via steric (planarity of the conjugated systems, supramolecular organization, etc.) and electronic (withdrawing or donating) effects. Another powerful strategy to influencing and tailoring the physical properties of organic materials via synthetic methodologies is to vary the chemical composition of the conjugated backbone chain in order to modify the nature of the conjugated segment itself (topology).[2,8] A plethora of conjugated systems have already been described as organic chemistry provides an almost infinite pool of synthetic approaches toward structural variations. However, it is striking that only a limited number of basic building blocks are commonly used to perform this engineering at the molecular level.[2b] The most widely used synthons include "all carbon moieties" such as olefins, acetylenes, and aromatic rings (benzene, naphthalene, fluorene, etc.), and aromatic heterocyclopentadienes, mainly thiophene and pyrrole (Chart 1).[1−8]

The introduction of novel building blocks is clearly a basis for further tailoring these π-conjugated oligomers and polymers. The challenge is not just simply to prepare new

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Régis Réau received his Ph.D. in 1988 under the supervision of Denis Neibecker at the Laboratoire de Chimie de Coordination (Toulouse, France). In 1989, he spent a postdoctoral year with Wolfgang Keim in Aachen (Germany) as an Alexander von Humboldt fellow. During these years, he was involved in the synthesis of transition metal-based homogeneous catalysts for hydroformylation (Toulouse) and asymmetric C–C coupling reactions (Aachen). In 1990, he joined the group of Guy Bertrand at the Laboratoire de Chimie de Coordination (Toulouse, France). There he worked on the synthesis of antiaromatic heterocycles, of 1,3-dipoles, and of super-Lewis acids. In 1997, he was appointed Professor at the University of Rennes 1 (France). In 2001, he became a junior-member of the Institut Universitaire de France. His current main research interests are the design of conjugated materials based on organophosphorus building blocks and the supramolecular assembly of chromophores using coordination chemistry.

series of conjugated materials, but to introduce synthons that exhibit properties that the already well-established building blocks do not possess, to obtain innovative molecular architectures or unique electronic properties. This approach is nicely illustrated by the use of organosilicon building blocks (e.g. silole, silanes, etc.) that exhibit unique types of conjugation ($\sigma-\pi$ hyperconjugation), leading to materials with unprecedented electronic properties.[9] Another important, recent approach toward novel building blocks for π-conju-

Chart 2. P-Based Building Blocks Used for the Construction of π-Conjugated Systems

| Arylphosphane | Phosphole | Phosphalkene | Diphosphene |
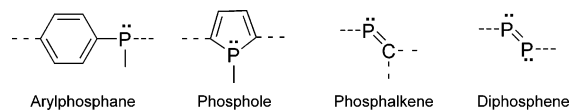
gated materials involves the incorporation of metal centers that introduce the electronic properties possessed by transition metals to the organic materials.[10] It was not until very recently that researchers have begun to explore the suitability of organophosphorus building blocks (Chart 2) for the tailoring of π-conjugated systems. This situation is very surprising considering that the chemistry of these P-containing moieties had been well developed for more than 25 years and that they exhibit properties that are markedly different from those of their N-analogues.[11–13] This review now covers the developments in the field of π-conjugated materials based on organophosphorus compounds that represent a valuable addition to the pool of building blocks for molecular electronics since the 1990s. The purpose of this review is to present a current overview of the various classes of π-conjugated oligomers and polymers incorporating P-moieties (Chart 2) and to illustrate the conceptual design and specific properties that directly result from the presence of the P-atom. For each building block depicted in Chart 2, two relevant points will be discussed in detail. The first one is their "conjugation ability" compared to those of their N- or C-analogues, and the second one is the possibility to create structural diversity using the versatile reactivity of the P-centers. It will be shown that the use of trivalent phosphorus centers is particularly appealing, as their ability to react with oxidizing agents, their Lewis basicity, and their potential for coordination to transition metals offer a broad variety for tuning the electronic properties of phosphorus-based materials by synthetically facile modifications. These are not possible in this simplicity with the commonly used building blocks shown in Chart 1. In this context, it should be mentioned that the chemistry of organophosphorus π-conjugated materials is still in its infancy compared to that of the established organic relatives. However, several successful approaches have already indicated that the incorporation of P-containing building blocks can lead to materials with unique properties. This review will therefore mainly focus on materials (oligomers, polymers, supramolecular assemblies, etc.) that have been investigated with an application in organic electronics in mind. In addition, conjugated derivatives incorporating P-moieties that show promising properties or indicate high potential for optoelectronic applications have also been included. In our opinion, the inclusion of these compounds is important as they—with many challenges remaining—might stimulate other researchers to develop novel P-containing π-conjugated systems.

2. π-Conjugated Systems Based on Arylphosphanes

The incorporation of reactive heteroatoms into the conjugated chain is a very intriguing strategy to diversify the properties and expand the functions of π-conjugated polymers.[2] This approach has been intensively investigated with Lewis-acidic boron groups that can, for example, integrate sensor properties within these materials, as they are able to bind anions or nucleophiles.[14] In the case of group 15 elements, the heteroatom can potentially participate in

π-conjugation by virtue of its lone pair. The prototype of these modified conjugated systems is polyaniline (Chart 1), which is among the oldest and best known π-conjugated materials.[1] Arylamino groups have also been widely used as building blocks for the tailoring of NLO-phores[15] and molecules acting as hole-transporting materials in multilayer OLEDs.[4,7] Already in 1981, Cabelli, Cowley, and Dewar compared the conjugation abilities of several aryl-phosphane and arylene-bisphosphanes with those of their nitrogen congeners.[16a] Their study, based on ultraviolet photoelectron spectroscopy (UPE), indicated that a certain degree of communication exists between the two phosphorus centers in 1,4-H_2P$-C_6H_4-$PH_2.[16a] For those reasons, it was tempting to prepare P-analogues of these different types of N-based π-conjugated systems, although the conjugation abilities of these two heteroatoms are markedly different. It is well-known that the π-donor ability of nitrogen is superior to that of phosphorus.[16] This difference is not due to their inherent π-donor capabilities (they are indeed comparable for N and P),[16b] but to the fact that the inversion barrier of amines (ca. 2$-$5 kcal·mol^{-1}) is quite low compared to that of phosphanes (ca. 30$-$35 kcal·mol^{-1}). As a result, nitrogen can easily achieve an optimum planar configuration (sp^2-hybridization), favoring the interaction of its lone pair with neighboring carbon p-orbitals, whereas, in the case of phosphorus, this planar geometry is more difficult to realize.[16b] However, it should not be concluded that phosphorus moieties are unable to act as π-donors, since it has been shown that phosphino groups can indeed efficiently stabilize electron deficient centers such as carbocations or carbenes.[16] Therefore, the investigation of phosphane-containing materials is of particular interest, as very different electronic properties could be expected for N- and P-based conjugated systems. This section is divided into two parts: the first one concerning the synthesis of P-modified polyanilines and the second one being devoted to the use of arylphosphane moieties to construct chromophores with specific fluorescence and NLO properties.

2.1. π-Conjugated Polymers Incorporating Arylphosphane Moieties

The synthesis of P-analogues of polyaniline has only recently been investigated due to the lack of efficient synthetic methods leading to well-defined polymers. To the best of our knowledge, the first characterized conjugated polymer containing arylphosphane moieties was obtained serendipitously by Novak and co-workers during attempts to synthesize soluble linear (p-phenylenes) by Pd-catalyzed Suzuki coupling reactions (Scheme 1).[17a] The formation of the branched polymer **1** arises from a side-reaction involving an interchange between phosphorus-bound aryl moieties and a palladium-bound aryl group of the intermediate Pd(Ar)-(I)(PPh$_3$)$_2$ complexes.[17b] According to ^{31}P NMR spectroscopy, the polymeric material **1** isolated after purification contained phosphane oxide moieties.[17a] It should be noted that although the concentration of the phosphane "defects" is very low, they have a significant impact on the properties (e.g. molecular weight, viscosity, etc.) of **1**.

The first poly(para-phenylenephosphane)s **3a**$-$**c** with a well-defined structure have been prepared by the palladium-catalyzed polycondensation of 1,4-iodobenzene with primary phosphanes **2a**$-$**c**, as reported by Lucht et al. (Scheme 2).[18a] This synthetic route represents an extension of the Buchwald$-$Hartwig methodology[19a$-$c] of metal-mediated C$-$N
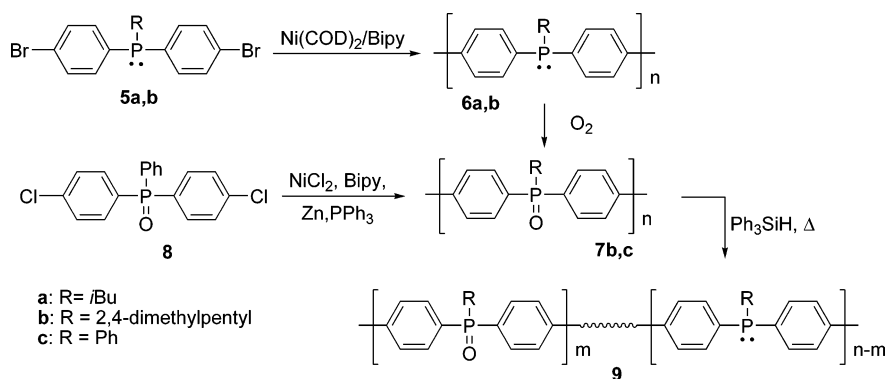
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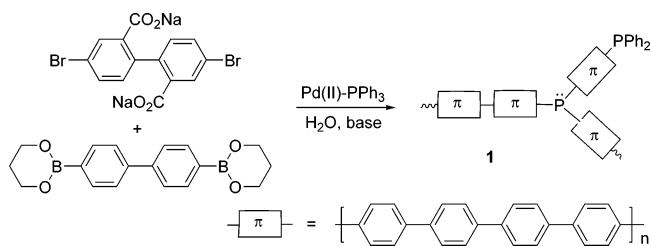
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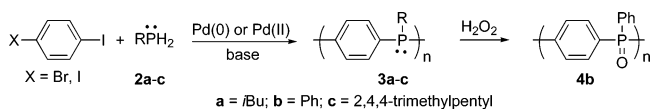
|	R	M_n	PDI	$\lambda_{max(\pi-\pi^*)}$
3a	i-Butyl	1700	1.3	278
3b	2,4,4-Trimethylpentyl	3100	1.5	276
3c	Phenyl	1300	1.4	291

bond formation from aryl-halides or -triflates with amines to phosphorus chemistry.[19d,e] Polymers **3a**$-$**c** are soluble in common organic solvents (THF, toluene, CHCl$_3$, etc.), allowing for a comprehensive analysis by gel permeation chromatography (GPC) and multinuclear NMR spectroscopy. The ^{31}P NMR spectra contain only one resonance in a chemical shift range typical for σ^3-P(III) moieties. The average number of repeating units (degree of polymerization, DP) estimated by GPC vs polystyrene standards varies from DP = 7 (**3b**) to DP = 14 (**3c**) with narrow polydispersities (PDI = 1.3$-$1.5; Scheme 2). Higher molecular weight polymers (M_n = 14 000) can be obtained via cross-condensation using 1-bromo-4-iodobenzene and alkylphosphane **2c** but to the detriment of the molecular weight distribution (PDI = 2.1).[18b] The UV$-$vis spectra of polymers **3a**$-$**c** show one absorption attributed to $\pi-\pi^*$ transitions with values of λ_{max} ranging from 276 to 291 nm (Scheme 2). The bathochromic shift observed in the series triphenylphosphane (λ_{max} = 263 nm)/1,4-bis(diphenylphosphino)benzene (λ_{max} = 275 nm)/**3c** (λ_{max} = 291 nm) suggests the presence of some extended π-delocalization involving the P-lone pair in poly(para-phenylenephosphane)s. However, polymers **3a**$-$**c** possess rather high band gap values, which is probably due to the pyramidal geometry of the P-atoms that prevents efficient conjugation of the phosphorus lone pair with the aryl groups. As observed for poly(N-arylaniline)s, oxidation of **3b** with FeCl$_3$ in the absence of oxygen affords a paramagnetic polymer.[18a] This oxidized polymer shows UV$-$vis absorptions that are considerably red-shifted, indicating the presence of an extended conjugation path involving the lone pair of the P-atoms. Remarkably, the P-atoms embedded in the backbone of polymers **3a**$-$**c** are still reactive. Polymer **3b** is readily oxidized by hydrogen peroxide, giving rise to novel derivative **4b**, which exhibited blue-shifted $\pi-\pi^*$ absorption bands.[18a]

The related biphenyl-phosphinidene polymers **6a,b** (Scheme 3) were prepared using Ni-catalyzed C$-$C-coupling reactions with the bis(p-bromophenyl)phosphanes **5a,b**.[18b] This approach was found to be inappropriate for the formation of high molecular weight polymers. Polymer **6a** is a dark red insoluble solid while derivative **6b**, bearing solubilizing groups (Scheme 3), is a pale yellow material with a low molecular weight (M_n = 1000). This material can be oxidized
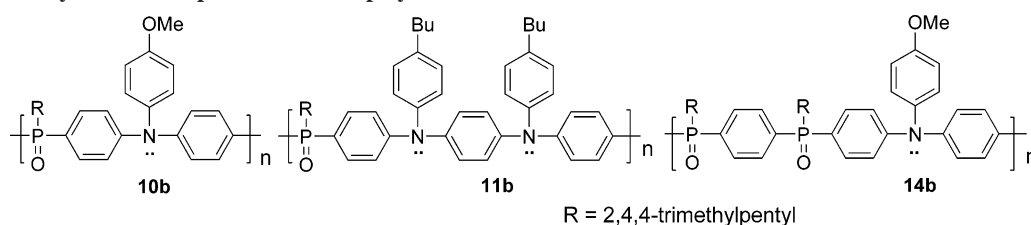
Scheme 3

Scheme 4
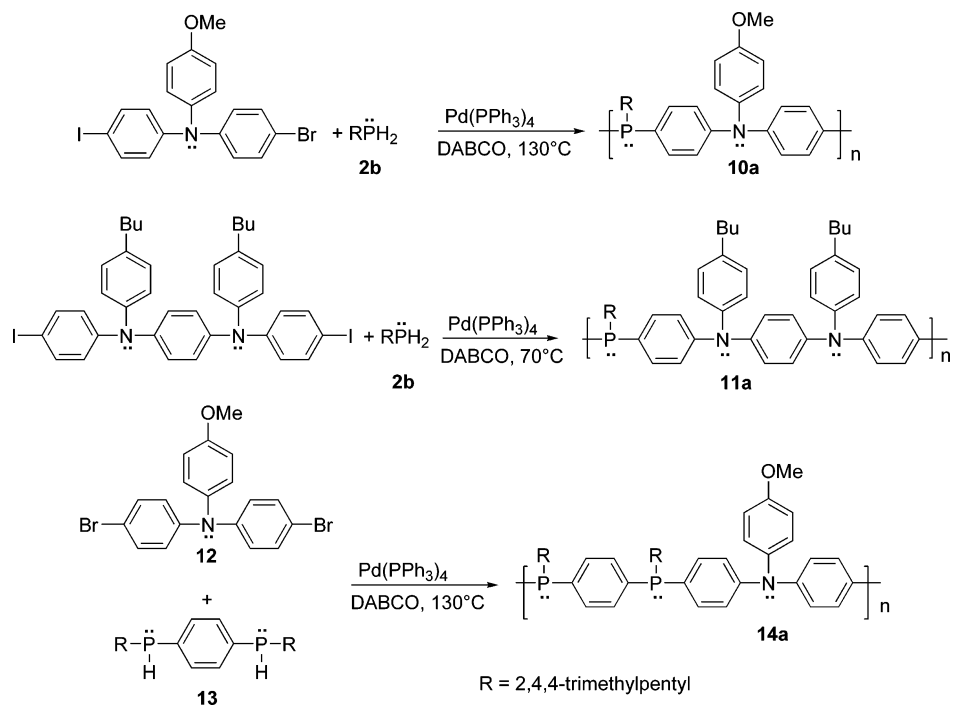
to afford **7b**, possessing a similar framework compared to that of **7c**, which was obtained by Ni-catalyzed reductive coupling of bis(p-chlorophenyl)phenylphosphane oxide **8** (Scheme 3).[20] The soluble material **7c** has a comparatively high molecular weight (M_n = 15 300) with a low molecular weight distribution (PDI = 1.6). It exhibits a high glass transition temperature (T_g) of 365 °C with considerable thermal stability (<5% weight loss at 550 °C). Its very low absorption maximum ($\lambda_{max} \sim$ 280 nm) shows that the presence of phosphane oxide units prevents extended conjugation within the polymer backbone. Partial reduction of the phosphane oxide moieties of **7c** can be achieved with phenylsilane, to give a poorly soluble, intensely reddish brown-colored material **9** (Scheme 3).[20] Surprisingly, despite the intense coloration, only a small red shift relative to **7c** ($\Delta\lambda_{max} \sim$ 20 nm) was observed, probably due to a partial reoxidation at phosphorus.

Since the lone pair of the σ^3-P(III) centers only shows limited interactions with the aryl moieties in the poly(para-phenylenephosphane)s **3a–c** (Scheme 2), alternating poly-(p-phenylenephosphane)–polyaniline polymers have been investigated by Jin and Lucht to further probe the conjugation ability of phosphino groups.[18c] Copolymers **10a**, **11a**, and **14a** (Scheme 4) with different backbone compositions have

been prepared via palladium-catalyzed P–C bond formation involving primary phosphanes and halogen-capped aryl-amines. The THF-soluble part (about $^1/_3$ to $^1/_2$ of the materials) consists of oligomers with low molecular weight (**10a**: M_w = 3000, PDI = 1.5; **11a**: M_w = 5000, PDI = 1.6). The remaining insoluble fractions are assumed to have the same structure, as they have similar IR spectra to those of the soluble fractions, but much higher molecular weights. Copolymer **14a**, possessing a P:N ratio of 2 and a DP of 16 (M_w = 11 000, PDI = 1.9), was obtained via the same approach using the bifunctional synthons **12** and **13** (Scheme 4). The higher molecular weight of **14a** is simply due to its greater proportion of solubilizing 2,4,4-trimethylpentyl substituents. Importantly, it is very likely that the molecular weights, which are determined with reference to polystyrene standards, are underestimated. These polymers have been fully characterized by multinuclear NMR spectroscopy; their ^{31}P NMR spectra support the presence of σ^3-P(III) centers. Hence, this synthetic methodology using Pd-catalyzed P–C bond formation appears to be an efficient route to poly-anilines bearing σ^3-P(III) moieties in their conjugated main chain.

As observed for the poly(para-phenylenephosphane)s **3a–c** (Scheme 2), the σ^3-P(III) centers of these mixed

Chart 3. Mixed Polyaniline/Phosphane Oxide Copolymers

R = 2,4,4-trimethylpentyl

Table 1. Cyclic Voltammetry Data^a for Copolymers 10a, 11a, and 14a (Scheme 4) and for the Corresponding Oxides 10b, 11b, and 14b (Chart 3)

	10a	11a	14a	10b	11b	14b
E_{ox1}	0.09	0.15	0.50	0.36	0.67	0.63
E_{ox2}	0.83	0.45	0.79	0.73		
E_{ox3}		0.83				

^{a} Ag/AgCl reference electrode in CH_2Cl_2.

copolymers **10a**, **11a**, and **14a** are reactive. They can be quantitatively transformed into the corresponding phosphane oxide copolymers **10b**, **11b**, and **14b** (Chart 3) using hydrogen peroxide.[18c] The molecular weights of these σ^4-P(V) derivatives, as estimated by GPC, are about half of those observed for the corresponding σ^3-derivatives, a fact that is assigned to a significant alteration in their conformation upon P-oxidation.

Cyclic voltammetry of poly(p-phenylenephosphane)−polyaniline copolymers **10a**, **11a**, and **14a** (Scheme 4) provided evidence for multiple oxidations and revealed that the N-atoms are oxidized at lower potentials than the trivalent phosphorus atoms.[18c] Comparison of these data with those observed for model compounds shows a weak electronic delocalization via the P-centers for copolymers **11a** and **14a**. In contrast, the fact that the first oxidation potential observed for **10a** is lower (Table 1) is consistent with a rather strong electronic communication between the N-moieties through the connecting P-centers.[18c] The participation of the P-lone pair in the π-delocalization along the backbone in **10a** is further supported by the large shift in oxidation potentials observed upon its conversion to **10b**, bearing phosphorus(V) centers (Chart 3) that do not possess unshared electrons (Table 1). The equivalence of the oxidation potentials for the other oxidized polymers **11b** and **14b** (Table 1) suggests the presence of electronically isolated triarylamine fragments in these P(V)-derivatives. In other words, conversion of P(III) phosphane centers to P(V) phosphane oxides switches off electronic delocalization through the P-moieties. UV−vis−NIR studies of these compounds are consistent with these general conclusions. The UV−vis absorption spectra of neutral polymers **10a**, **11a**, and **14a** are similar, and upon oxidation with NO^+, the appearance of low-energy absorptions is observed. Comparison with model compounds and related phosphane oxide derivatives supports rather strong electronic communication between the two nitrogen centers through the phosphorus moieties in **10a** and is consistent

with a loss of electronic delocalization through phosphorus upon P(III) → P(V) conversion.[18c]

Well-defined polymers **16** featuring vinylenephosphane oxides as repeating units have been prepared via metal-catalyzed hydrophosphorylation using the bifunctional monomer **15** (Scheme 5).[21] These materials can be purified by preparative GPC and exhibit quite high molecular weights (M_n = 21 400−71 900) with low PDIs (1.21−1.54). They exhibit high thermal stability, but due to the presence of phosphane oxide moieties, they appear not to be conjugated, as indicated by their white color.

2.2. Chromophores and NLO-phores Based on Arylphosphanes

Arylphosphanes constitute one of the most widely investigated families of P-derivatives due to their use as ligands in homogeneous catalysis.[22] Hence, the aim of this section is not to give a comprehensive account of all derivatives that have been synthesized, but to illustrate how phosphorus fragments can be used either to tailor or to organize π-conjugated systems based on aryl groups, with a special emphasis upon fluorescence and NLO properties.

Aryl-based chromophores can easily be grafted onto phosphane halides via simple nucleophilic substitutions, as illustrated by Yamaguchi and Tamao in the synthesis of compound **17** (Scheme 6).[23a] This readily available σ^3-phosphane exhibits a broad absorption band at ∼390 nm due to the π−π* transitions associated with the anthracene moieties, together with a band at 437 nm assigned to extended π-conjugation through the P-lone pair.[23a] This compound was prepared to investigate the changes in physical properties induced by increasing coordination number at the P-center, as studied previously with triaryl-boranes and triarylsilanes.[14d,23b−c] Therefore, phosphane **17** was transformed into derivatives **18**−**20** (Scheme 6) using well-established P-chemical modifications with good yields (78%−98%).[23a]

The σ^4-derivatives **18** and **19** both possess a tetrahedral geometry, while the σ^5-phosphorane **20** exhibits a trigonal-bipyramidal geometry with the three anthracenyl moieties adopting the equatorial positions. The fluorescence properties of these anthracene-based chromophores are highly dependent on the coordination number of the central P-atom. The σ^3-phosphine **17** exhibits almost no fluorescence as a result of quenching by the P-lone pair.[23a] The σ^4-derivatives **18** and **19** show weak fluorescence with relatively large Stokes
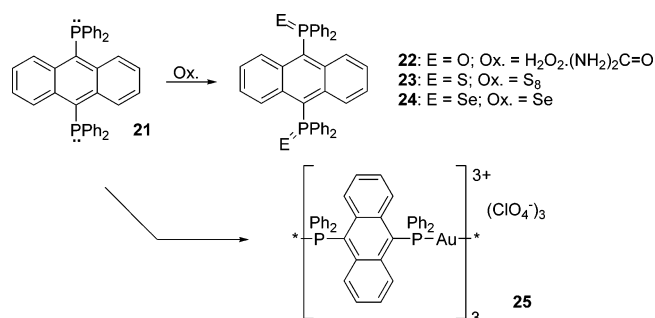
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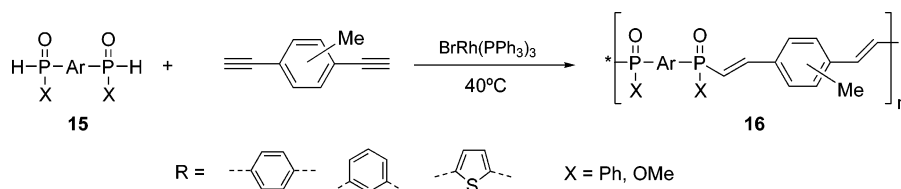
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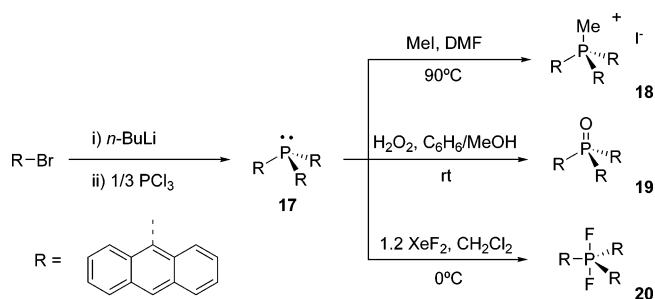
Scheme 7

shifts, presumably resulting from through-space interactions between the anthracene substituents. In sharp contrast, the pentacoordinate compound **20** shows intense fluorescence; its quantum yield ($\phi = 0.28$) is ~30−100 times greater than those of σ^4-phosphines **18** and **19** and comparable to that of anthracene itself. This latter phenomenon is thought to result from the equatorial disposition of the three anthracenyl moieties around the P-atom. Hence, the fluorescence of the anthracene moieties is switched off either by the presence of the P-lone pair or by their pyramidal arrangement around a P-atom. These results give a clear-cut example of property-control in conjugated systems through exploitation of P-chemistry.[23a]

The fluorescence properties of related 9,10-diphospha-anthracenes **21**−**24** (Scheme 7) have been investigated,[24a] as previous studies have shown that the analogous N- and Si-disubstituted species are potentially suitable materials for light-emitting electroluminescent devices.[24b−e] Starting from the known phosphane 9,10-$(Ph_2P)_2C_{14}H_{18}$ **21**,[24f] the bis-(chalcogenide) derivatives **22**−**24** have been isolated in high yields (Scheme 7).[24a] In solution, only compound **22** exhibits a detectable emission ($\lambda_{em} \approx 450$ nm). In contrast, derivative **23** shows very intense fluorescence at $\lambda_{em} = 508$ nm in the solid state, while **22** only displays a weak emission at $\lambda_{em} = 482$ nm. The derivative **24**, on the other hand, is fluorescent neither in solution nor in the solid state. Intriguingly, the presence of near stoichiometric quantities of toluene is necessary to observe fluorescence of **23** in the solid state. Indeed, an X-ray diffraction study revealed that the asymmetric unit of **23** contains one toluene molecule that interacts via its *ortho*-hydrogen atoms with the central ring of the anthracene. The emission of **23** in the solid state can therefore be attributed to this T-shaped excimer. Hence, **23** can act as a potential toluene chemosensor.[24a] It is noteworthy that this T-shaped orientation is not possible with derivatives **22** and **24**, nicely illustrating the possible impact of P-chemistry for tuning the properties of π-conjugated systems in the solid state. A luminescent gold ring **25** has been prepared via coordination-directed self-assembly of derivative **21** and $(Me_2S)AuCl$.[24f]

To further investigate the optical excitations in multichromophore architectures having a dendritic core,[25a] branched structures **29**−**31** (Scheme 8), bearing similar chromophores but different core units (C, N, P), have been studied by Goodson et al.[25b] The target P-derivative **29** was prepared from **26** in a straightforward combination of a Heck coupling, to afford an intermediate functionalized stilbene phosphane oxide **27**, a Horner−Wittig reaction yielding the phosphane oxide **28**, and finally trichlorosilane reduction to afford **29** (Scheme 8).

It is assumed that the N-based system **30** is trigonal planar (in analogy to NPh_3[25c] and as confirmed by theoretical calculations[25d]) and that the geometry of the central core P-atom of **29** is more pyramidal than the C-derivative **31** (C−P−C angles < C−C−C angles), in accordance with the reluctance of phosphorus to form sp-hybrid orbitals.[12c] Examination of the UV−vis spectral data reveals that the value of λ_{max} for the P-containing species **29** (376 nm) is blue-shifted with respect to that of the N-based analogue **30** ($\lambda_{max} = 430$ nm) but is red-shifted relative to that for the C-cored compound **31** ($\lambda_{max} = 325$ nm).[25b] The difference between N- and P-based structures has been rationalized in terms of mesomeric effects. For the planar-cored compound **30**, an efficient overlap of the N-lone pair with the adjacent carbon p-orbital gives rise to efficient conjugation with the chromophore substituents. For P-derivative **29**, this overlap with the P-lone pair is significantly less efficient due to the pyramidal geometry of the phosphorus atom. However, the red shift observed between the C-cored compound **31** and the P-derivative **29** indicates that the P-lone pair does interact with the chromophore moieties, as established on polymers containing phosphino moieties by Lucht et al.[18] Further studies to examine their fluorescence behavior revealed that an incoherent hopping type of energy transfer dynamics dominates in both the P- and C-derivatives **29** and **31**, respectively.[25b] By contrast, a coherent mechanism is suggested for **30**. These data clearly show that both (*i*) the structural arrangement of chromophores about the central single atom core and (*ii*) the extent of electronic delocalization through the heteroatom have a direct impact on energy transfer in branched conjugated structures.[25a,b] These results show that replacing an N-atom by a P-atom induces a significant alteration in the compound's optical properties due to the differences in the preferred geometries and electronic characteristics of the two heteroatoms.

Furthermore, one key advantage of the presence of a reactive P-atom is the potential access to a whole series of derivatives, including transition metal complexes, with a variety of geometries, oxidation states, and coordination numbers. Generation of this structural diversity using a single P-precursor is illustrated with tris(4-styrylphenyl)phosphane **32** (Scheme 9).[26a,b] As observed for related anthracene-substituted derivatives **17**−**20** (Scheme 6), the fluorescence behavior of the styrylphenyl phosphorus compounds **32**−**36** varies significantly depending on the coordination number and oxidation state of the P-center. Once again, the presence of a P-lone pair in **32** is responsible for fluorescence quenching and the hypervalent species **35** is the most efficient fluorophore in this series. The fact that these trends are recorded with two different families of chromophores (anthracene and styrylphenyl) suggests that they are governed by the P-atom and that they could be generalized to any type of chromophore. Note that an investigation of the photophysical behavior of a structurally related phosphane bearing

Scheme 8
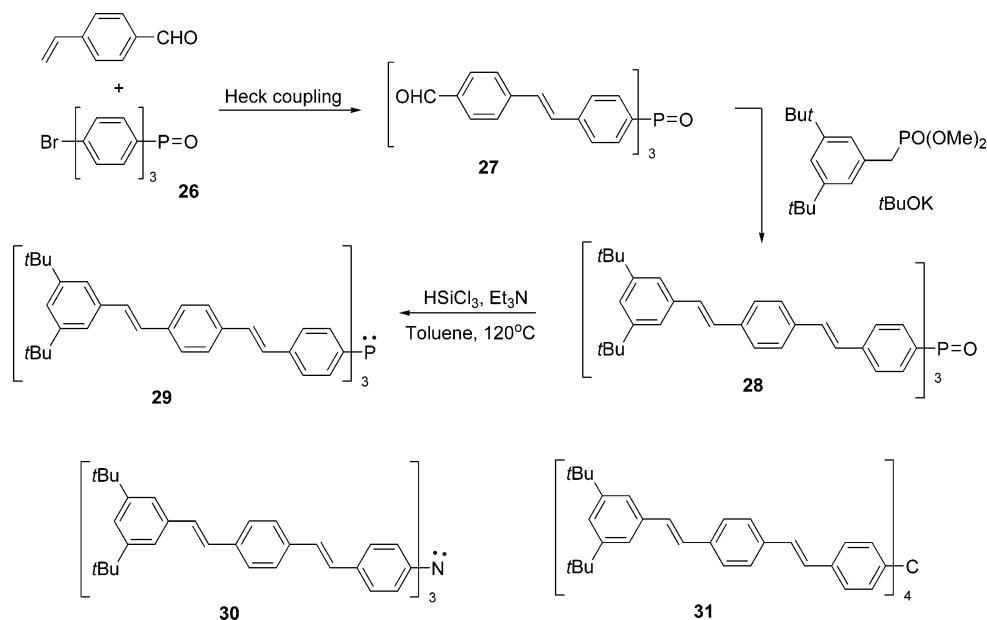
Scheme 9
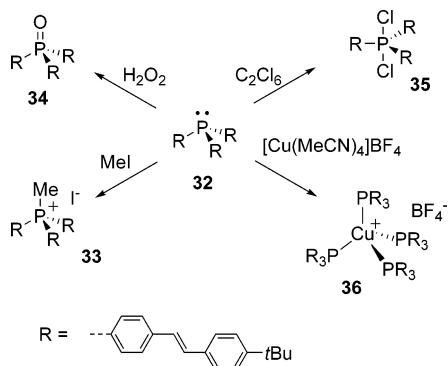
p-(N-7-azaindolyl)phenyl substituents has shown that this P-compound displays both a fluorescence band ($\lambda_{max} = 372$ nm) and a phosphorescence band ($\lambda_{max} = 488$ nm, lifetime 38(6) ms) at 77 K.[27]

The fact that triphenylphosphane oxides bearing donor dimethylamino groups exhibit an intramolecular charge transfer (ICT) character[28a] has been exploited to prepare potential fluorescent molecular sensors for alkaline cations. The design of compound **38** (Scheme 10) is also based on the coordination ability of the phosphane oxide moiety toward cations and the high fluorescent quantum yield of polyphenylacetylene moieties.[28b] This compound is prepared in ca. 30% yield from **37** according to the route described by Leray, Michelet, and co-workers (Scheme 10). As observed for the structurally related styryl-substituted phosphane oxides described above, there is only an extremely weak interaction (if any) between the chromophores in the ground state for **38**. As expected, phosphane oxide **38** is strongly fluorescent ($\phi = 0.71-0.89$) and the large Stokes shift along with the unresolved vibronic structure of the fluorescence spectrum suggests the formation of an intramolecular charge transition.

Diphenylphosphino groups have also been investigated as auxiliary donor groups for the tailoring of potential second- and third-order NLO-phores. Extensive efforts have been directed toward the design of chromophores exhibiting large second-order NLO responses.[15] Traditionally, such chro-

mophores are non-centrosymmetric dipolar molecules containing donor and acceptor end groups connected through a π-backbone. As the amino unit is one of the most widely used donor groups, phosphino moieties have also been considered as auxiliary donor groups in dipolar NLO-phores. The syntheses of P–NLO-phores **40–42** use the versatile starting material p-(diphenylphosphanyl)benzaldehyde **39** (Scheme 11) and a set of classical synthetic transformations (e.g. Wittig reaction or McMurry coupling).[29] Having in mind that the π-donating ability of a phosphino group is much lower than that of amino units, it is not surprising that the observed value of λ_{max} for the diphenylphosphino-based dipole **40** is blue-shifted relative to that of its N-analogue **43** (Scheme 11). This blue shift could be of interest in terms of transparency/NLO activity tradeoff, which is an important parameter for the engineering of valuable second-order NLO-phores.[15] The two series of centrosymmetric diphenylphosphino-capped chromophores **41** and **42a–d** (Scheme 11) have been synthesized by Madrigal and Spangler with a view to preparing materials with potential third-order NLO properties.[29] Comparison of the UV–vis data of compounds **41** and **44** confirms the general trend that replacing N by P induces a blue shift in the value of λ_{max}. As expected, systematically increasing the number of conjugated C–C double bonds in the series of polyenes **43a–d** (Scheme 11) led to a pronounced red shift in the values of λ_{max} (**42b**: 341 nm; **42d**: 418 nm).

Another example is the push–pull alkene **45a** (Chart 4), bearing a three coordinate boron moiety as a π-acceptor, described by Marder et al.[29b–d] The molecular hyperpolarizability (measured in solution by electric-field-induced second-harmonic generation) of **45a** is four times lower than that of the amino-based derivative **45b** (Chart 4). No second-harmonic generation (SHG) signal was observed in the solid state with derivative **45b**, probably due to a centrosymmetric arrangement of this dipole.[29b,c] In contrast, compound **45a** crystallizes in a non-centrosymmetric space group and did exhibit SHG in the solid state. The intensity of this SHG signal is approximately equal to that of urea (which is the reference standard).
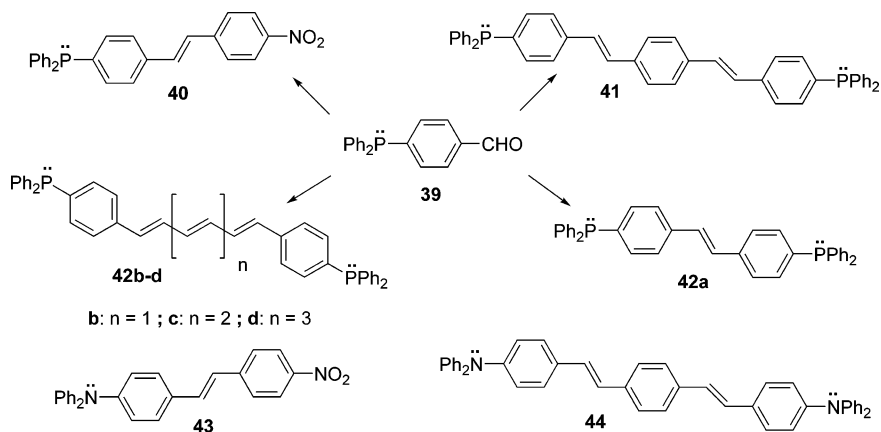
Scheme 10
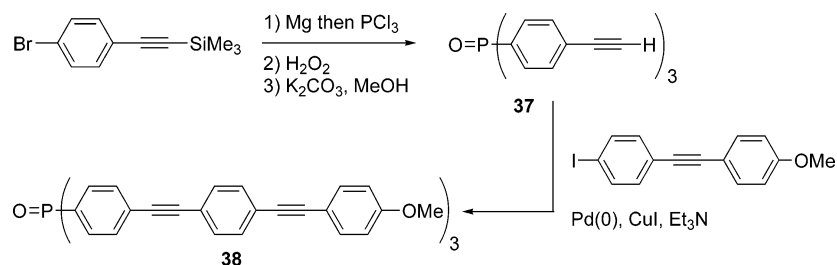
Scheme 11

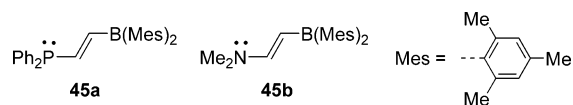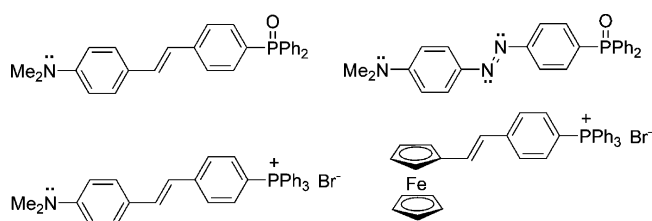**Chart 4. Push−Pull Alkenes Bearing Phosphino and Boryl Groups**

Chart 5. Dipolar NLO-phores Bearing Electron-Withdrawing Phosphane Oxide or Phosphonium Moieties

Not surprisingly, either phosphane oxide or phosphonium moieties have been used as electron-acceptor substituents for the tailoring of dipolar NLO-phores.[30] Selected examples illustrating this approach are presented in Chart 5. Phosphane oxides are weaker electron acceptors than other substituents traditionally used for the tailoring of NLO-phores (for example the nitro group), but they exhibit significantly better optical transparency in the visible and near-UV spectral regions. This is an important characteristic for certain applications of second-order NLO materials such as frequency doubling of diode lasers to the near-UV.

The search for efficient NLO-phores also includes the design of octupolar derivatives since the concept of such nonlinearities was proposed in the early 1990s on the basis of group theoretical and quantum mechanical studies.[15d] Basically, purely octupolar symmetries can be derived from a cubic structure either by projection along a C_3 axis, giving rise to the D_{3h} symmetries, or by fusion of one type of charge in the center, leading to the D_{3h}, D_3, T_d, or D_{2d} symmetries. The advantages associated with this alternative class of NLO-

phores include an improved nonlinearity/transparency tradeoff and a more facile non-centrosymmetric arrangement in the solid state due to the absence of dipolar moments. To this end, the 3-D chromophores **46** and **47** with C_3 and D_2 (approximate T) symmetry, respectively (Scheme 12), have been prepared by Lambert et al. according to classical synthetic routes.[31a] Note that, in these compounds, the cationic P-centers act as acceptor groups and bear electron-donating substituents that have been widely used for the tailoring of NLO-phores.[15]

The UV−vis data suggest that the subchromophores in **46** and **47** are almost electronically independent. Derivative **46** has a small dipole moment and can be considered as an almost purely octupolar system. The NLO activity of the octupolar compound **46** is about three times larger than that of the dipolar subchromophore **48** (Scheme 12), with almost no cost in terms of transparency. This result illustrates the superiority of the octupolar approach compared to the dipolar one. It should be mentioned that, compared to their tin analogues, the phosphorus derivatives **46** and **47** have higher β values due to the more efficient acceptor ability of the phosphonium moiety.[31a] The related octupolar phosphonium salt **49** (Scheme 12), bearing simple 4-methoxyphenyl groups, was investigated by Nicoud, Masse, and co-workers with the aim of obtaining NLO-active crystals that remain transparent across all, or nearly all, the visible region.[31b] Structural analysis of **49** revealed a weakly distorted ionic structure of the NaCl-type. The tetrahedral phosphonium ion retains almost pure octupolar symmetry in the solid state. The crystal is indeed transparent throughout the visible region and exhibits moderate NLO behavior, probably due to the weak intramolecular charge transfer from the 4-methoxyphenyl groups to the cationic P-atom.

Structurally related P-branched multichromophores have also been designed for potential application in materials for OLED fabrication. The efficiency of OLEDs can be considerably improved by sandwiching the emissive material
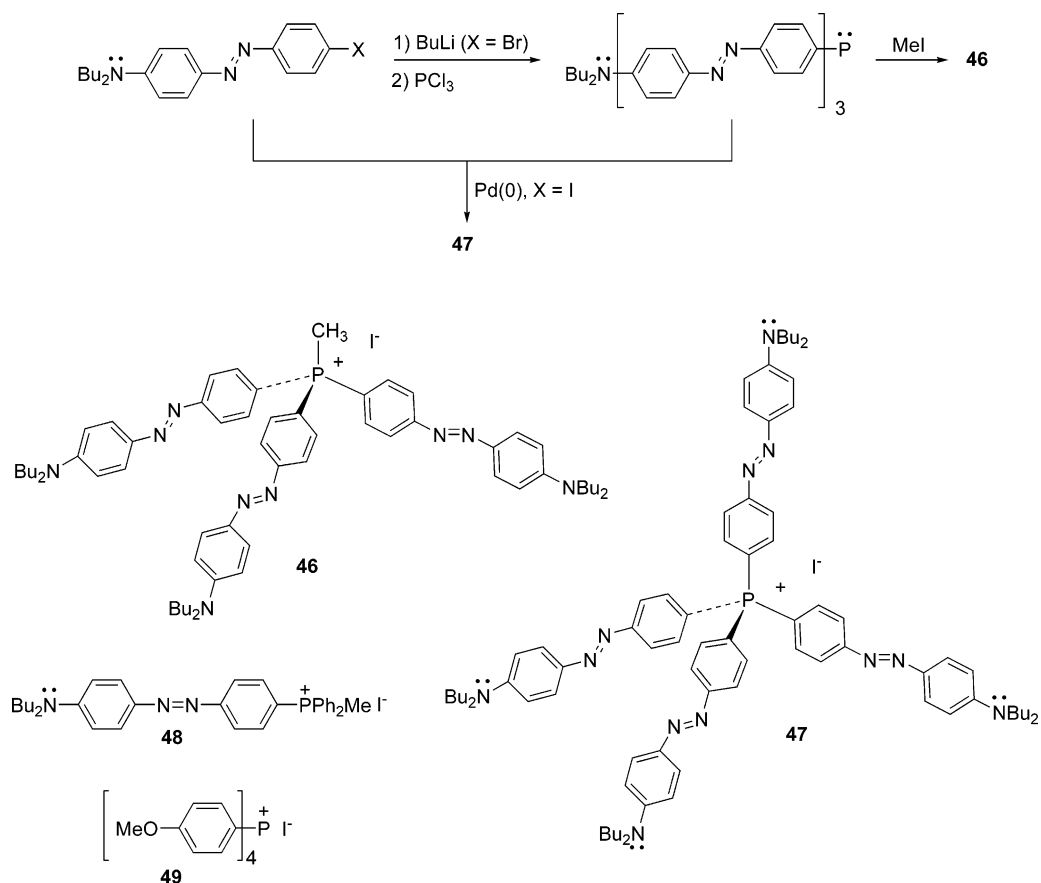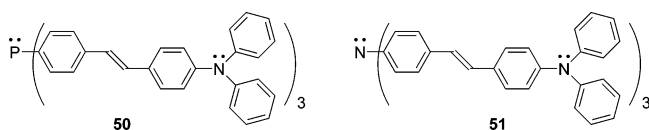
Scheme 12

Chart 6. Structure of Branched P- and N-Derivatives Used as Hole-Transporting Materials in OLEDs

between two discrete layers for hole and electron transport.[5,8] In this field, tertiary amines bearing aromatic substituents such as N,N'-diphenyl-N,N'-bis(1-naphthyl)(1,1'-biphenyl-4,4"diamine) (NDP) have been widely used as hole-transporting layer (HTL) materials. On the basis that the replacement of N for P will affect the stability of the cationic species (polaron and bipolaron), due to their different electronic properties, the use of tris(diphenylaminostilbenyl)-phosphane (**50**; Chart 6) as an HTL material was investigated by Spangler et al.[32] Not surprisingly, the values of λ_{max} for **50**, in solution and as a thin film, are both blue-shifted compared to those of its N-analogue **51** (Chart 6). Notably, substitution of P for N results in an increase of the thermal stability and of the glass transition temperatures (T_g). This improvement of thermal properties is of particular interest since high T_g and thermal stability are needed to withstand the inevitable Joule heating encountered during OLED operation, especially at high electric field and current densities. OLEDs having an ITO/**50**/Alq$_3$/Mg:Ag/Ag [ITO = indium tin oxide, Alq$_3$ = tris(quinolinato)aluminum] composition exhibit an EL efficiency of 0.13% for a voltage of 11.8 V at a constant drive current of 13 mA·cm^{-2}.[32] This EL efficiency is higher than that obtained using the corresponding N-derivative **50** (0.09%) as an HTL material, but it is still rather low compared to those of devices utilizing NDP.

It should be noted that the triphenylphosphane core has also been used by Sutter et al. as a template for associating radical moieties with the aim to prepare magnetic materials (Scheme 13).[33] The σ^3-derivative **54** coordinates to metal centers (Pd(II), Ru(II), Au(I), Mo(0), etc.) via the P-atom, affording stable complexes, and can hence be considered a spin-labeled phosphane.[33a–d] The magnetic studies and DFT calculations performed on polyradical species **55a** and **55b** (Scheme 13) did not provide evidence for intramolecular exchange interactions between the radical units.[34c]

In conclusion, conjugated derivatives based on arylphosphino units are relatively easily prepared using either nucleophilic substitution with phosphane halides or chemical modifications of the phenyl moieties of arylphosphanes. In most cases, the lone pair of the P-atoms is only marginally involved in the π-conjugation with the aryl substituents due to the pyramidal geometry of this heteroatom. Therefore, phosphorus centers have mainly been used to organize chromophores in a predictable way and to tune the optical and electronic properties of these compounds via chemical modification at phosphorus. However, this status quo can evolve in the near future through a judicious tailoring of the P-functional groups. In the introduction to this section, we recalled that the apparently inferior donor ability of phosphorus compared to nitrogen is not due to its inherent π-donor capability but to its reluctance in achieving the optimum planar configuration.[15a] One of the simplest ways to decrease the inversion barrier at phosphorus, and thus to fully exploit its π-donor capability, is to use bulky substituents.[34a] This "trick" has recently been used, for example, to stabilize carbene centers.[34b] In the field of conjugated systems, the impact of this approach is illustrated
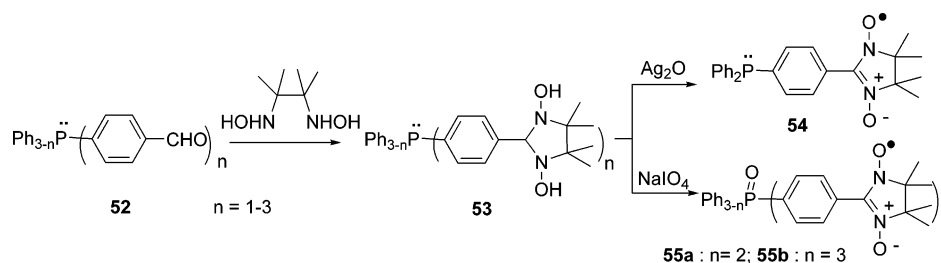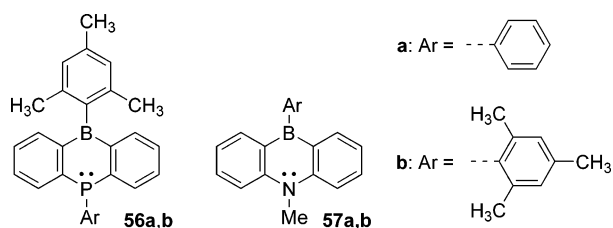
Scheme 13

Chart 7. Structure of Dibenzo-phosphaborines and -azaborines

by the dibenzophosphaborines **56a,b** featuring P-substituents with increasing steric demand, as reported by Kawashima et al. (Chart 7). The UV−vis spectra of these derivatives show absorption maxima in the near-ultraviolet region at 368 nm for **56a** and 393 nm for **56b**.[35] Theoretical calculations have shown that the electronic excitation of dibenzophosphaborines is derived from intramolecular charge transfer (ICT) from the phosphorus to the boron atom. The large red shift of the absorption observed between **56a** and **56b** was rationalized by the presence of the bulky 2,4,6-trimethylphenyl substituent, which induces a planarization of the P-atom in **56b** and hence a more efficient ICT. It is noteworthy that (*i*) this effect is not encountered with their N-analogues **57a,b** and that (*ii*) the λ_{max} of **56b** is only slightly inferior to that of **57b** (408 nm), indicating that the π-donor ability of "planarized" phosphorus can reach that of nitrogen. This example nicely illustrates that the presence of P-centers offers additional ways of tuning the photophysical properties of conjugated systems in comparison with the cases of their N-analogues.

3. Heteroaryl-, Ethenyl- and Ethynyl-phosphanes

3.1. Thiophene- and Bipyridine-Based Materials

One of the most popular heterole building blocks used to construct π-conjugated organophosphorus materials is the thiophene moiety (Chart 8).[36−41] Genuine thiophene-based systems have long been successfully established in molecular electronics,[3] and these units were also expected to benefit the properties of the corresponding P-containing materials. The major focus of the related research is the ability of phosphorus to coordinate transition metals.[13,36−38] This allows for the linkage of the desirable features of the organic π-conjugated unit (e.g. (semi)conductivity, luminescence, flexibility) with some electronically interesting functional properties of metal complexes (e.g. optical, magnetic).[36−38] Almost all publications regarding thienyl-phosphane π-conjugated derivatives therefore deal with corresponding transition metal complexes.[36−39] Only two very recent reports are dedicated to the 'free ligand'-systems and their optoelectronic properties.[40]

Although some of these compounds have been known for more than 30 years, mostly as ligands for transition metal

**Chart 8. Thiophene-Based Phosphanes**
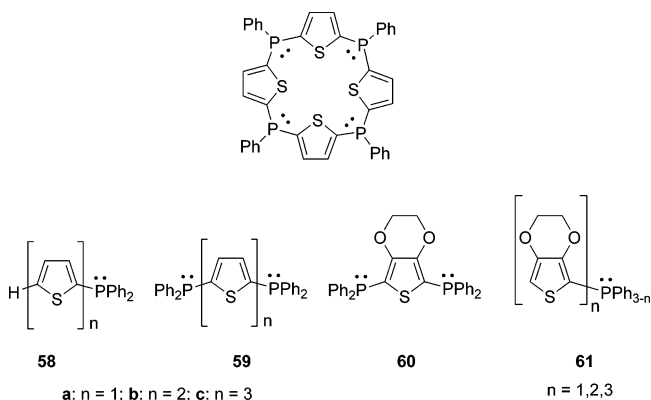
complexes, Stott and Wolf first reported the spectroscopic features of some phosphane-substituted oligothiophenes **58** and **59** only in 2004 (Chart 8).[40a] This work was triggered by the fact that the related amino-substituted oligothiophenes show very intriguing optoelectronic properties due to the interaction of the amino groups with the π-system of the thiophene units.[42] As observed with aryl moieties (vide supra), it is not possible to transpose the features of the N-containing systems to their phosphino analogues. Here, the influence of the phosphino group diminishes with the length of the oligo(thienyl) group. In monothienylphosphanes with one (**58a**) or two (**59a**) phosphane substituents, some sort of interaction of the phosphorus lone pair with the π-system is present, as supported by a large Stokes shift in the optical spectra [$\Delta\lambda = 136$ (**58a**); 196 (**59a**) nm] that is attributed to the planarization of the excited state. However, the interaction decreases significantly with increasing chain length ($n = 1 \rightarrow 3$), as determined by DFT calculations at the B3LYP/6-31G* level.[40a] This trend is also supported by the drastically reduced Stokes shifts observed upon chain lengthening [$n = 2$: $\Delta\lambda = 158$ (**58b**), 117 (**59b**) nm; $n = 3$: $\Delta\lambda = 78$ (**58c**), 75 (**59c**) nm]. The monothienyl systems **60** and **61**, based on the 3,4-ethylenedioxythiophene (EDOT) moiety, on the other hand, already do not show any perturbation of the EDOT group by the phosphane and vice versa, which is also in sharp contrast to the corresponding alkoxy- or alkylthio-functionalized EDOT systems, as reported by Hicks et al.[40b]

As mentioned before, publications based on phosphino-thiophenes mainly target organic−inorganic hybrid-systems to implement electronic properties provided by transition metal fragments within the organic materials. Although some structurally interesting complexes as well as supramolecular assemblies **62−69** (Chart 9) can be obtained by reaction of suitable 2-phosphino- or 2,2′-diphosphinothiophenes, no optical spectroscopic data have been reported for most of the systems.[38,39a] Wolf et al. reported the gold complexes **67** and **68** (Chart 9), the latter of which shows aurophilic

Chart 9. Phosphino-thiophene Complexes and Supramolecular Assemblies
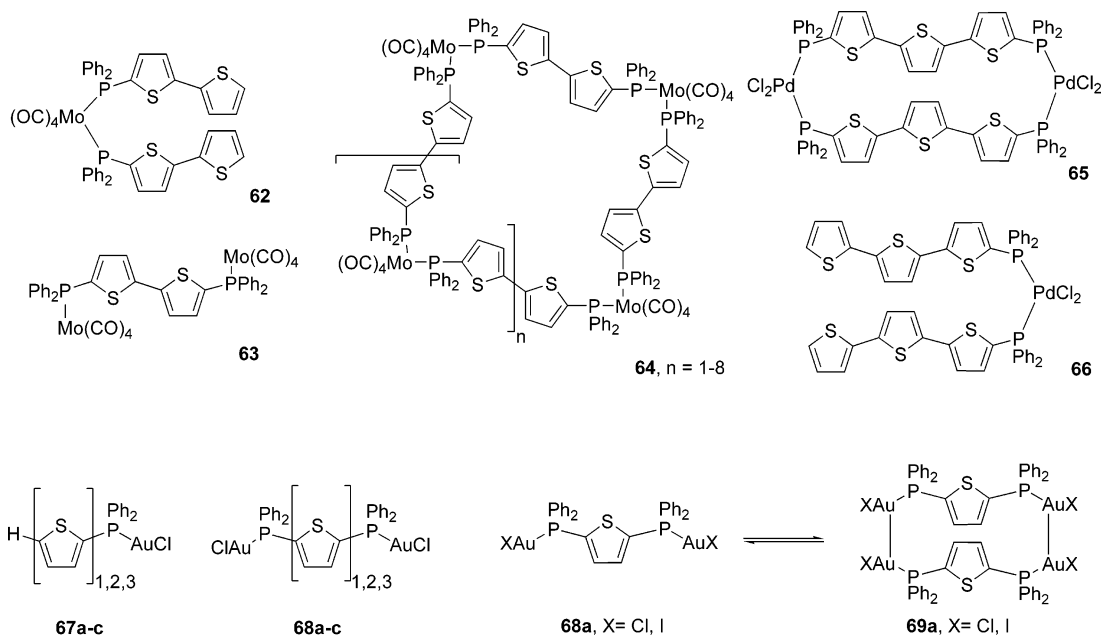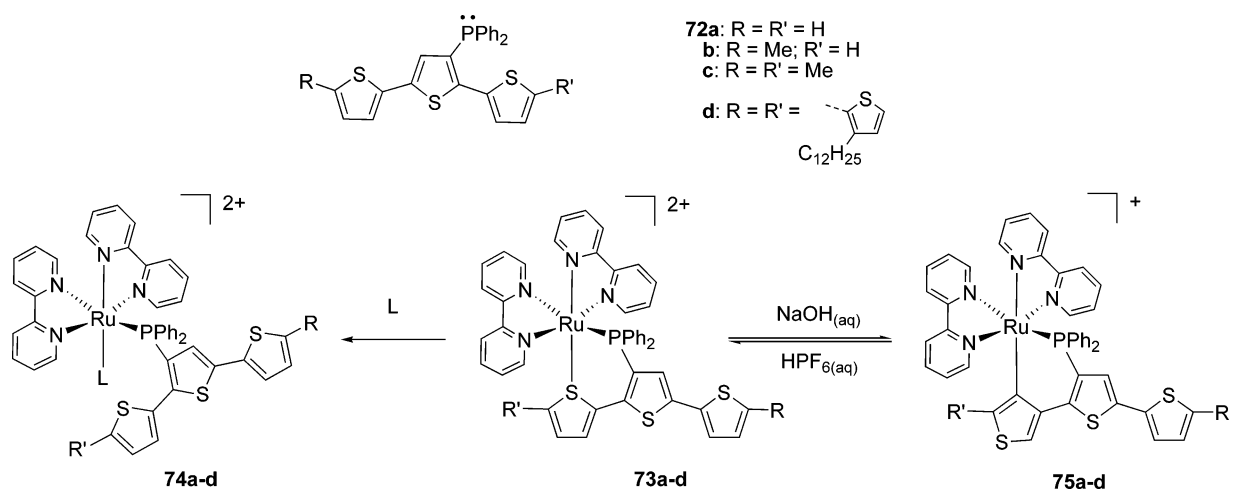

Scheme 14
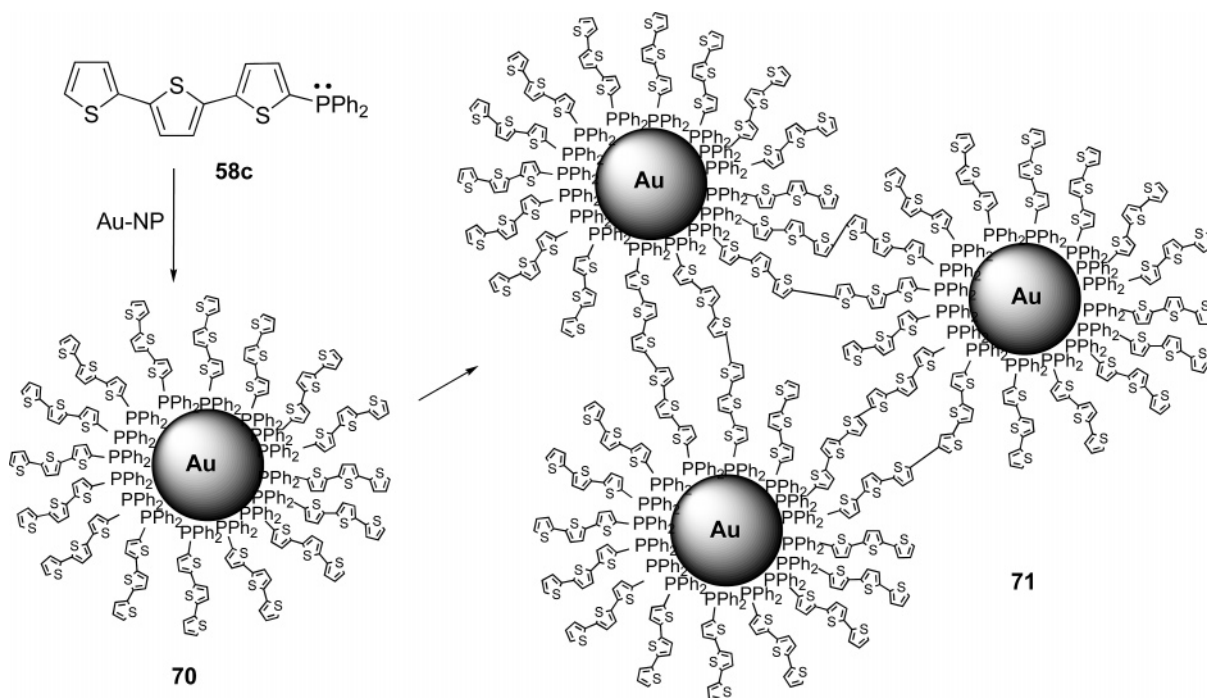
interactions in the solid state as well as in solution.[39b] A monomer−dimer equilibrium **68a−69a** in solution can be observed by fluorescence spectroscopy via an emission arising from the Au−Au interactions. The transitions observed for complexes **67** and **68** can be assigned to either pure intra-ligand $\pi-\pi^*$ or inter-metal ($d^{10}-d^{10}$) transitions, suggesting that the complexation by gold does not influence the optoelectronic properties of the π-conjugated material.

In a related project, however, Wolf and co-workers reported 2-phosphinoterthienyl **58c** capped gold nanoparticles (diameter ca. 1.7 nm) **70** (Scheme 14).[39c] The three-dimensional network of nanoparticles **71**, obtained by electrodimerization of the pendant terthienyl groups, shows a significant degree of electronic interaction between the gold

nanoparticles that is superior relative to the case of unlinked particles. Optimized electronic features in this three-dimensional network, such as increased conjugation, conductivities, as well as plasmon coupling, have been observed (Scheme 14). The fact that the π-conjugated linker affords higher conductivities than a saturated analogue accounts for an extended degree of π-conjugation throughout the phosphorus centers in this case. The electro-optical properties of the linked nanoparticles, on the other hand, have not been reported to date.

In a variation of their thiophene-approach to π-conjugated organophosphorus materials, the Wolf group has also established 3-phosphino-oligothiophenes **72** (Scheme 15) and corresponding transition metal complexes based on Ru(II) and Pd(II).[39d−h] The P-containing terthiophene ligands show
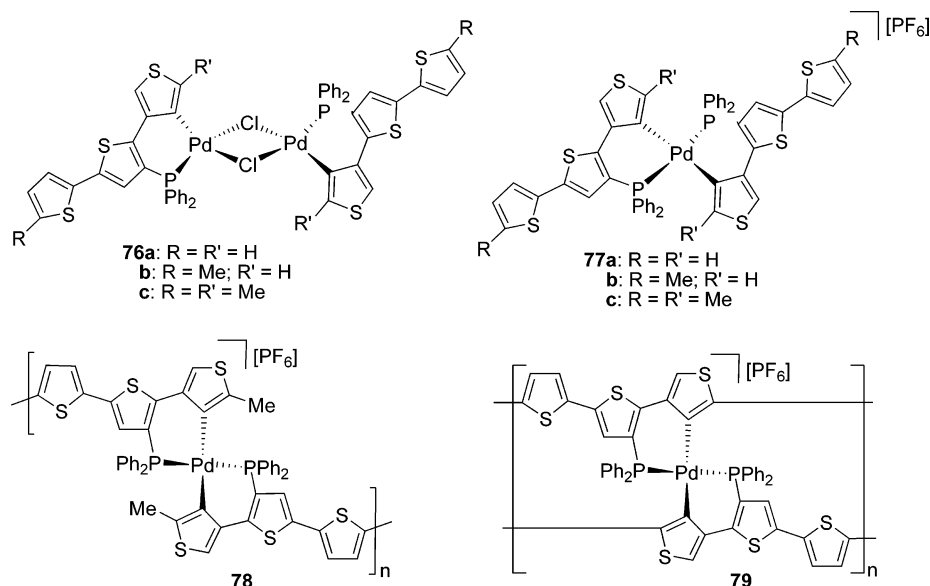
Scheme 15

chelating behavior in the Ru-complexes **73** (Scheme 15) as the terminal thiophene units exhibit some weakly coordinating character. This coordinative bond can be easily cleaved by addition of ligands [e.g. isonitriles, CO, bis(phosphanes)] to afford complexes of type **74** (Scheme 15).[39d−f] The chelated Ru-complexes **73** show red-shifted values for absorption compared to those of the free ligands **72** as well as native terthiophenes. This bathochromic shift is basically attributed to two factors: (*i*) electron donation from the metal to the terthienyl group and (*ii*) a more rigid backbone in the coordinated oligomer. The latter is due to the reduced rotational disorder along the backbone, as commonly established for organic π-conjugated materials, and is further supported by the blue shift of the absorption in the nonchelate complexes **74** (Scheme 15). The phosphorus functional groups therefore do not have a direct influence on the optoelectronic properties of the materials themselves; they rather operate as a mediator in the corresponding complexes to stabilize desirable conformations and thus optimize the electronic properties indirectly.

An interesting feature is observed when the Ru-complexes **73** are treated with a strong base (NaOH).[39g,h] Deprotonation occurs at one of the terminal thiophene moieties and induces a structural change in the coordinating mode of the ter-

thiophene by generating a metal−carbon bond, giving complexes **75** (Scheme 15). This process is reversible; addition of HPF$_6$ to **75** results in the regeneration of the S-coordinated starting complexes **73**. This switch in coordination modes is accompanied by significant changes of the $\pi−\pi^*$ and MLCT transitions, apparent in a significant red shift of both absorption wavelengths (ca. 35 nm for $\pi−\pi^*$ and ca. 60 nm for MLCT) in the P,C-coordinated complexes **75**. The complexation of the oligothienyl groups to the Ru-center quenches the thienyl-based fluorescence to some extent due to thermal population of a low-lying, metal-centered nonemissive energy level. The oxidation potentials of the materials are significantly different depending on the coordination mode, with the P,S-coordinated complexes **73** showing a large increase in the oxidation potential ($E_{1/2ox} \approx$ 1.2−1.5 V; vs SCE). In the P,C-coordinated mode, on the other hand, the oxidation potentials are even lower than those of the free ligands (**75**: $E_{1/2ox} \approx 0.5$ V; cf. free ligands $E_{1/2ox} \approx 0.8−1.4$ V; vs SCE).

In contrast to their Ru-congeners, Pd-complexes based on 3-phosphino-oligothiophenes (**76** and **77**; Chart 10) exist almost exclusively in the P,C-coordination mode. Their optical and electronic properties are similar to those of the Ru-complexes **75**.[39g,h] Cross-linked networks of these materi-

Chart 10. Pd-Complexes of 3-Phosphino-oligothiophenes and Corresponding Polymers

Scheme 16

80 a: R = H; **b**: R = [structure]

81a,b

82a,b

Scheme 17

85 a: $M_6 = M'_6 = Rh_6(CO)_{14}$; **b**: $M_6 = M'_6 = Ru_6C(CO)_{15}$
c: $M_6 = Ru_6C(CO)_{15}$; $M'_6 = Rh_6(CO)_{14}$

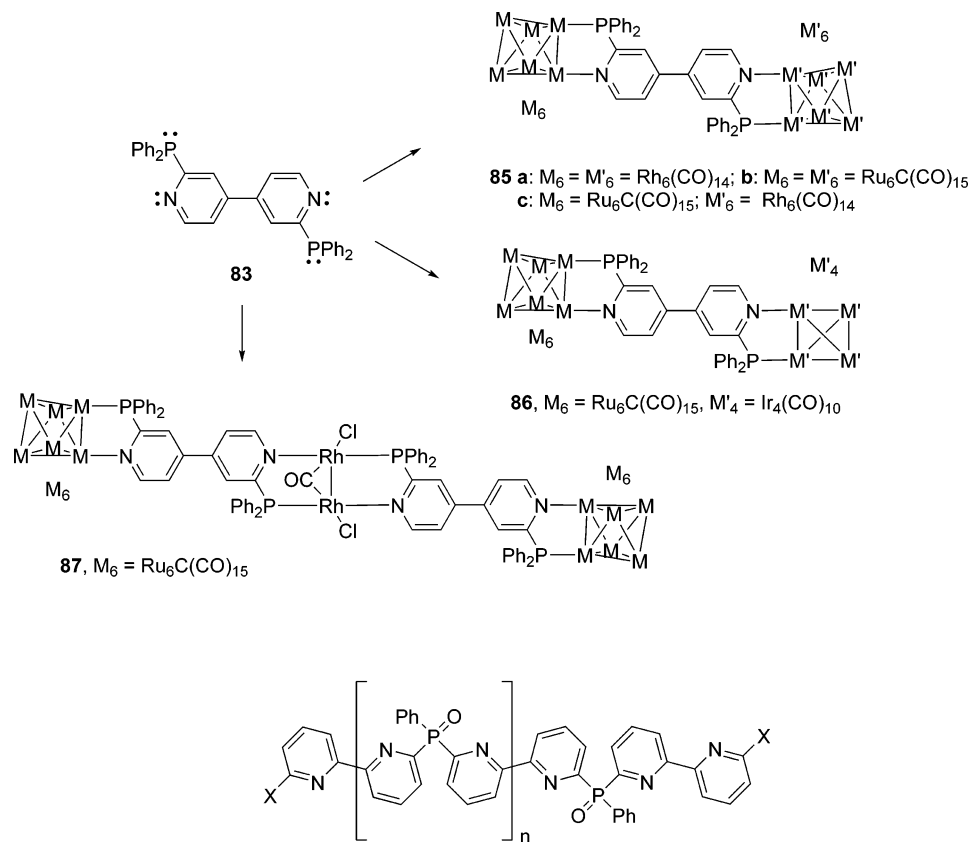**86**, $M_6 = Ru_6C(CO)_{15}$, $M'_4 = Ir_4(CO)_{10}$

87, $M_6 = Ru_6C(CO)_{15}$

84, n = 1 - 4, X = Br, COOEt, COOH
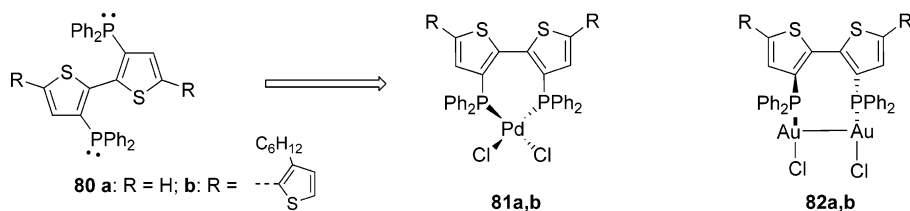
als with different possible conduction pathways are obtained by electropolymerization involving the thienyl groups (Chart 10). Depending on the substitution pattern of the terminal thiophene unit employed, conjugation can occur either via the metal centers only (**78**) or via the metal as well as along the π-conjugated backbone (**79**), as supported by UV−vis spectroscopy.[39h]

These results again emphasize the indirect influence of the phosphorus center on the electronic properties by fixating the metal center in close proximity to the π-conjugated framework. Introduction of a second phosphino group, as in 3,3′-bithiophene **80a** or 3,3′-quarterthiophene **80b**, gives rise to P,P-chelate complexes **81** and **82** based on Au(I) and Pd(II) centers (Scheme 16).[39i] These complexes also exhibit an increased degree of conjugation due to the structural fixation of the π-conjugated backbone. This suggests that the electronic behavior of polythiophenes could be drastically improved by the presence of a large number of such pendant chelate complexes within the material.

With a similar focus, phosphino-functionalized bipyridines **83** and **84** were considered by two different groups as potential building blocks for molecular materials in 2005 (Scheme 17).[43,44] In both cases, the π-conjugated framework

is also used as a mediator rather than being an inherently active part of the system, but the potentially expected material properties appear intriguing. Pakkanen and Tunik report on 2,2′-bis(diphenylphosphino)-4,4′-bipyridine (**83**) and its utility as a linker for some transition metal clusters (Rh, Ru, Ir) to afford oligomeric systems **85**−**87** (Scheme 17).[43] Although their paper only focuses on the synthesis and structure, these systems seem closely related to the terthienyl-capped nanoparticles reported by Wolf. According to the outlook, "detailed investigations of the properties of these complexes are underway".[43] Ziessel and Charbonniere describe phosphino-bridged-2,2′-bipyridine oligomer chains **84** for a potential application as a photoactive capping layer in lanthanide-based nanocrystals as well as a building block in the synthesis of poly(p-phenylene-vinylene) quantum dot composite materials.[44] Optical spectroscopic data have not been reported for both bipyridine systems yet.

3.2. Ferrocene-Based Materials and Ethenyl-/Ethynyl-bis(phosphanes)

Ferrocene-based organophosphorus materials have also been the focus of several investigations, owing to the redox-

Scheme 18

E = S, [M], BH$_3$, BCl$_3$, Me$^+$

E' = Me$^+$ or BCl$_3$

[M] = Mn(C$_5$H$_4$Me)(CO)$_2$,
      Mn(C$_5$H$_5$)(CO)$_2$, W(CO)$_5$
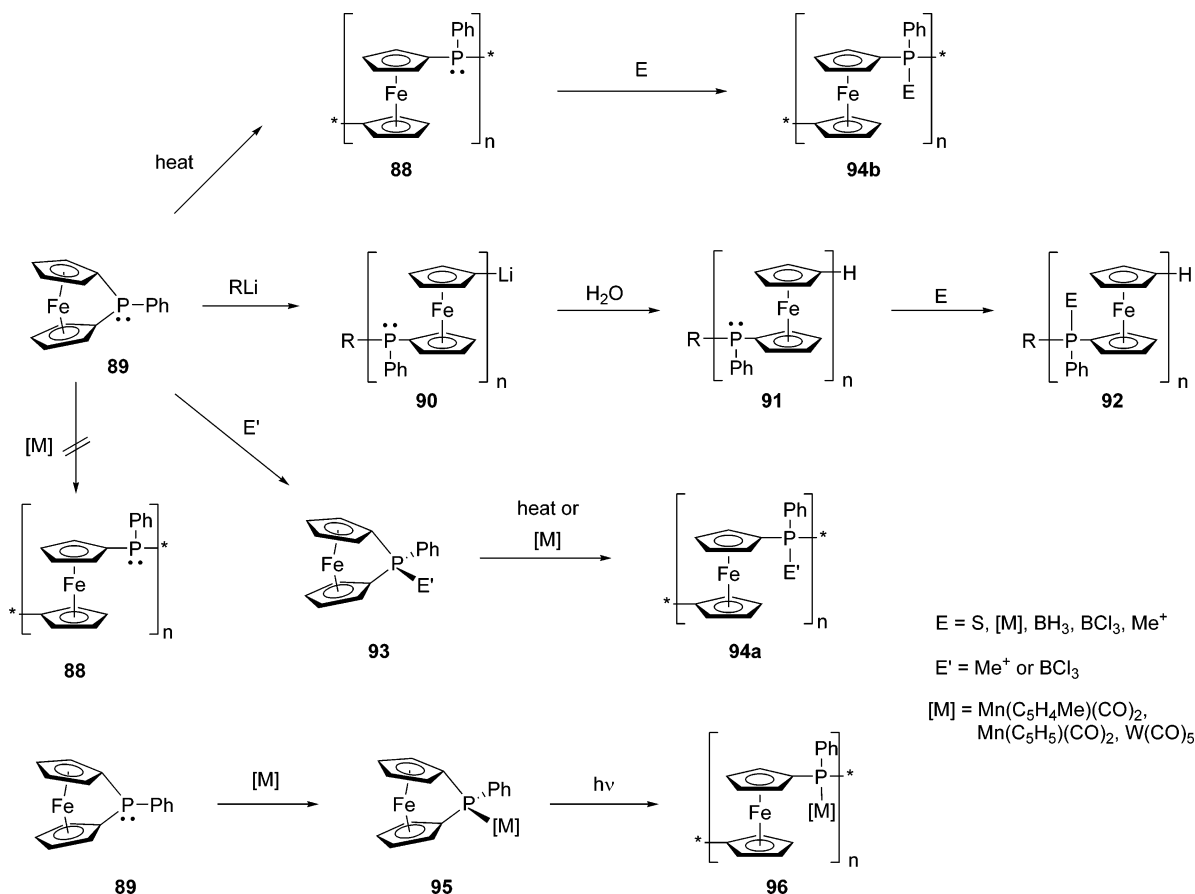
active nature of the central iron atom.[45−48] Phosphorus-bridged ferrocene polymers such as **88** (Scheme 18) were first reported by Seyferth and co-workers in 1982.[45] Their research was directed toward a potential access to electronically tunable, polymer-supported catalysts; the ability of phosphorus to coordinate to transition metals was a major focus here as well. Starting from ring-strained phospha[1]-ferrocenophanes **89**, mixtures of oligomers and short polymers are obtained via ring-opening polymerizations (ROPs) induced by phenyllithium (Scheme 18, R = Ph).

However, it was not until 10 years later that Manners' group started to investigate these organophosphorus polymers and their properties systematically to access materials with high molecular weight and well-defined structures.[46−48] Several polymerization methods toward these systems have been established over the years (Scheme 18). Whereas thermal as well as anionic ROPs (R = Bu) easily afford high molecular weight polymers **88** and **91**, respectively,[46a−c] the transition metal-catalyzed ROP causes difficulties due to the poisoning of the employed catalysts via coordination to the phosphorus centers.[46d,e] This complication can be circumvented by using tetracoordinate phosphorus centers as in the methylphosphonium-ferrocenophane **93** (E' = Me$^+$).[46d] This monomer can be polymerized thermally as well as transition metal catalyzed to afford a highly polar polymer **94a** (E' = Me$^+$, Scheme 18). In a variation of this approach, the trichloroborane-capped phospha[1]ferrocenophane **93** (E' = BCl$_3$) also gives a corresponding polymer **94a** (E' = BCl$_3$) by transition metal-catalyzed ROP, however in low yields.[46e]

Miyoshi and co-workers reported the photolytic ROP of phosphorus-bridged [1]ferrocenophane-complexes **95** in 2000

(Scheme 18).[47] The investigations have shown that, after complexation of the phosphorus center to a transition metal fragment ([M] = Mn(C$_5$H$_4$Me)(CO)$_2$, Mn(C$_5$H$_5$)(CO)$_2$, W(CO)$_5$), these complexes can undergo ROP upon irradiation with UV-light to give high molecular weight polymers **96**. The polymerization only takes place with the coordinated ferrocenophanes; the "free ligand system" **89** does not show any polymerization behavior under these conditions. Remarkably, the electronic properties of the phosphorus-bridged ferrocene polymer have already been reported in the early 1990s by Manners and co-workers, indicating that the polymer **97** (Scheme 19) exhibits two distinct oxidation processes ($E_{1/2}$ = −0.04, 0.15 mV; vs FcH/FcH$^+$), supporting electronic communication between the iron centers of the polymer. The first oxidation process leads to an alternating Fe^{II}−Fe^{III} pattern (**98**) throughout the polymer; then in a second step all the iron centers are completely oxidized (**99**) (Scheme 19). The proximity of the Fe^{III} center in **98** significantly increases the oxidation potential of the remaining Fe^{II} centers.[48a] Whether the bridging heteroatom−here phosphorus−plays an essential role in this communication has not been completely clarified to date.

However, it has been established that the materials properties of the polymers **88** and **91** can easily be effected upon chemical modification of the phosphorus centers (E = Me, S, AuCl, PdCl$_2$, Fe(CO)$_4$, BH$_3$, BCl$_3$; see Scheme 18).[46−48] Within the scope of their comprehensive studies toward the polymerization behavior of phosphorus-bridged [1]ferrocenophanes, Manners et al. also performed post-polymerization modifications to access similar polymers as obtained by ROP of already functionalized monomers for comparison.[46c−e,48b] It has been shown in this context that
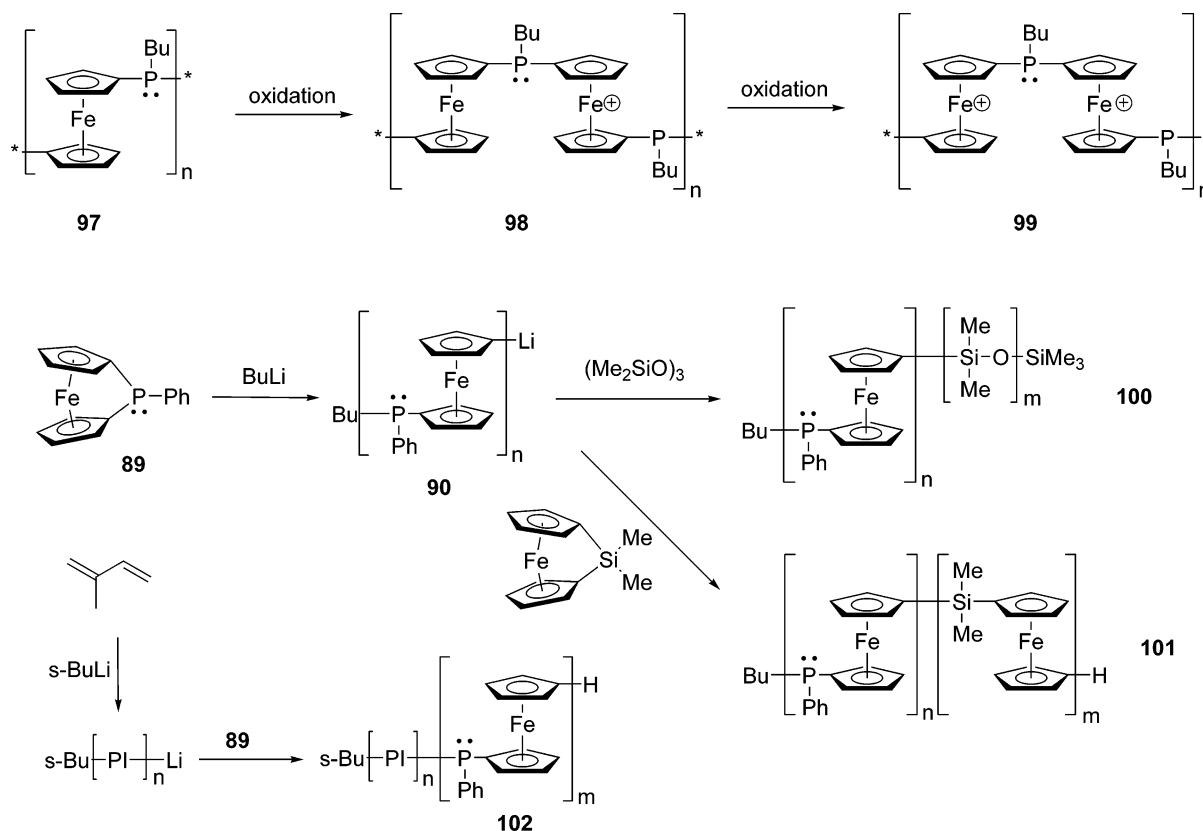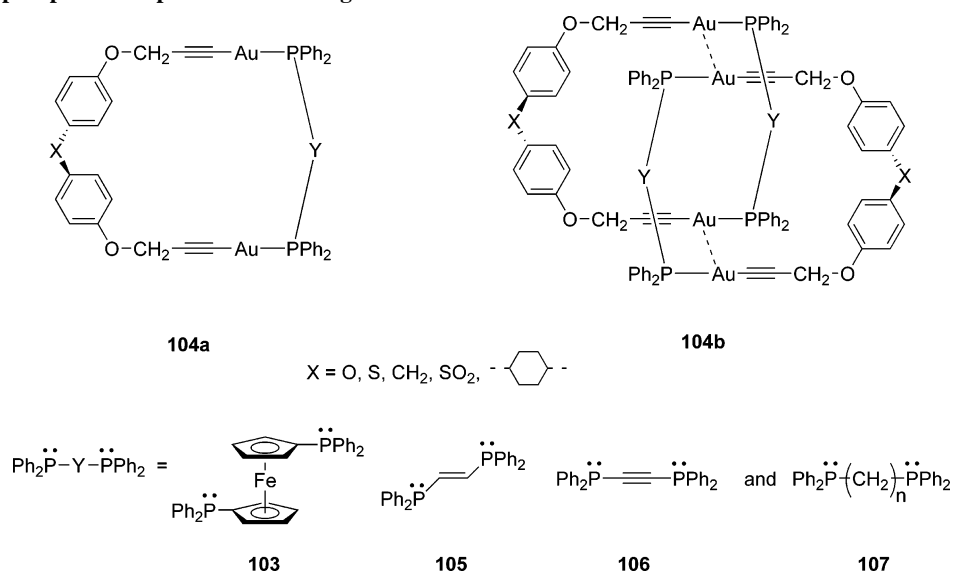
Scheme 19

Chart 11. Organophosphorus Supramolecular Rings and Catenanes

X = O, S, CH₂, SO₂, -⟨ ⟩-

these chemical modifications can influence solubility and flexibility as well as the optical and electronic properties of the polymers significantly. To further tune the materials properties of phosphorus-bridged ferrocene polymers, several block copolymers have been obtained via living anionic ROP of the ferrocenophane monomers and subsequent treatment with suitable siloxanes (→**100**, Scheme 19), sila[1]ferrocenophane (→**101**), or isoprene (→**102**).[46c,48b] The isoprene-based copolymers **102** (PI = polyisoprene) form nanoscopic micelles in suitable solvents, and the shape of these aggregates depends on the functionalization of the phosphorus centers.[48b]

Bis(diphenylphosphino)ferrocene **103**, a somewhat related building block, which is known as a valuable chelating ligand

in catalysis (dppf), was used by Puddephatt and co-workers for the self-assembly of organometallic gold-based rings and catenanes **104a,b** (Chart 11).[49] As in the majority of applications presented in this chapter, the role of the phosphino groups in these materials is simply to act as a 2-electron donor toward transition metals, however, to afford materials that exhibit interesting properties. Supramolecular systems have been the focus of several research groups owing to their potential for application in nanoscale devices. Particularly, macrocycles containing metal acetylide linkages have shown promise in the construction of electronic and optical devices or as luminescent chemical sensors.[50] With the same emphasis, Puddephatt et al. established a broad variety of bis(phosphanes) **103**, **105**−**107** as spacer groups

Scheme 20

109

RT, CHCl$_3$
3d
- 2 KCl

108a

108b

CHCl$_3$, CH$_2$Cl$_2$, MeCN
(1:1:1), RT, 4 weeks

110

Scheme 21

111

113

40°C
CH$_2$Cl$_2$

R = Cl, Me

112

114

115

tpy = terpyridine

116

117
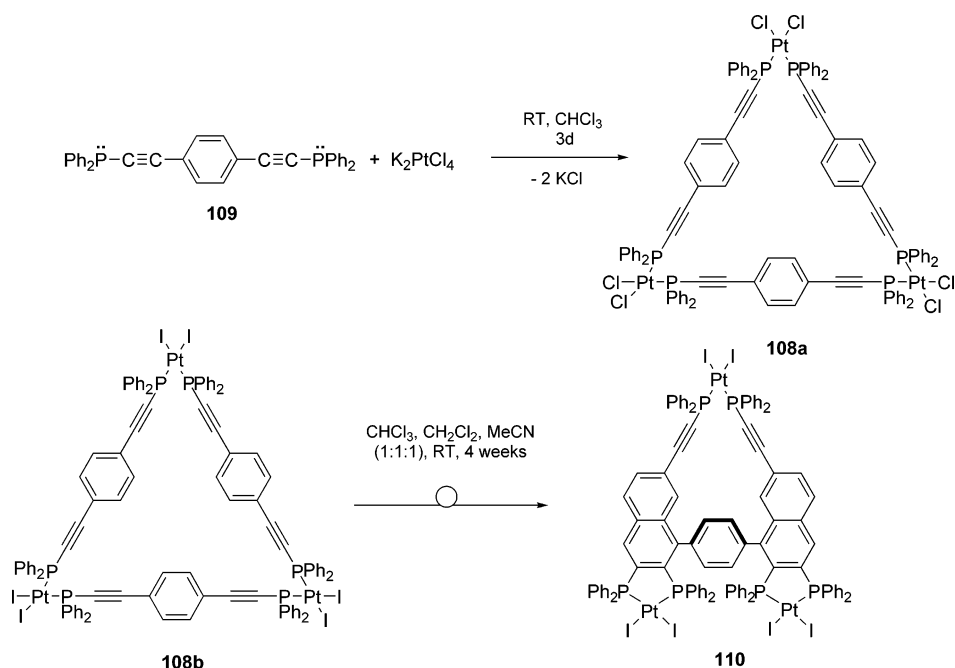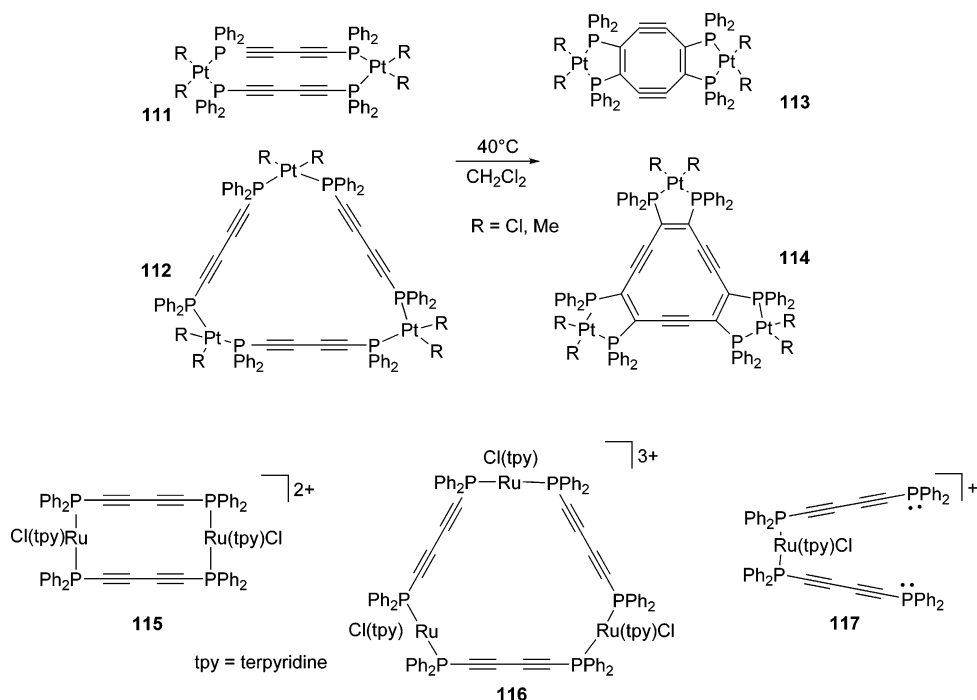
"Y", with several of them to be classified as π-conjugated organophosphorus derivatives.[49,51] The nature of this spacer group in combination of the so-called "hinge-group" (X) (Chart 11) is essential for the formation of different supramolecular assemblies. Short and sterically demanding spacer groups such as the π-conjugated ethenyl (**105**), ethynyl (**106**), or 1,1′-ferrocenylene (**103**) moieties form macrocycles of type **104a**, whereas longer, nonconjugated spacer groups (**107**) favor [2]catenanes such as **104b**.

Phosphino-acetylenes, originally implemented as rigid ligands in transition metal complexes,[52,53] were anticipated by several groups to benefit the electronic or optical properties of corresponding organometallic supramolecular assemblies.[54,55] In an extension to the observations with

molecular phosphino-acetylene complexes made by Carty and co-workers in 1979,[52] Manners et al. were able to generate unusual supramolecular 33-membered triangles **108** with the bis(phosphinoethynyl)phenylene spacer **109** in quantitative yield (Scheme 20).[54] In coherence with the molecular system,[52] the close proximity of two acetylene groups induces a [2+2+2] cycloaddition to afford bis-(phosphino)naphthalene moieties (**110**), when the bridging metal fragment is −PtI$_2$−.

Similar observations, with the related butadiynyl-bis-phosphane, were reported by Carty in 2005 (Scheme 21).[55] The synthesis of these macrocycles, however, is not as clean, affording mixtures of cyclic dimer **111** and trimer **112** (85/15) that show [4+4] or [4+4+4] cycloaddition behavior,

Scheme 22

118

X = OTf, NO₃, BF₄
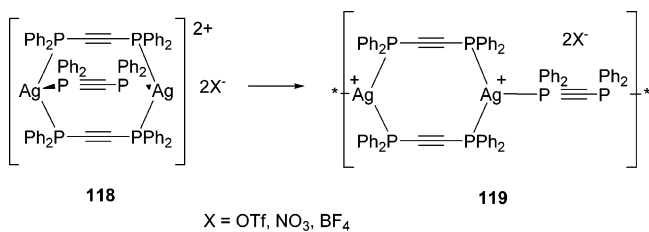
respectively, for the PtCl₂-bridged rings.[55] Due to the nature of the spacer unit, the resulting phosphino-functionalized ring systems **113** and **114** exhibit alternating double- and triple-bond units.

A few years earlier, Hong and Xu used the butadiynyl-bisphosphane spacer to generate the corresponding Ru-bridged macrocycles and chains **115**−**117** (Scheme 21).[56] The random nature of the synthesis produces several products that can be separated by column chromatography. Remarkably, the systems show interesting photoluminescence and redox features that depend on the nature of the ring. In the cyclic systems **115** and **116**, a chromophore summation effect [intense transitions at 300 nm (LC) and 800 nm (MLCT)] is found, leading to stronger luminescence than that in the open-chain system **117** due to the presence of multiple Ru-centers. An efficient electronic communication is observed between the two Ru(II) centers of **115**; however, the cyclic trimer **116** exhibits electronic properties that resemble those of

the open-chain dimer **117** with similar electrochemical behavior.

A polymeric material with bis(diphenylphosphino)acetylene linkers was reported by James and co-workers.[57] The ring-opening polymerization (ROP) of strained silver bis-(diphenylphosphino)acetylene cage molecules **118** gives the corresponding coordination polymers **119** (Scheme 22). Although the resulting materials were insoluble in common solvents, characterization by single-crystal X-ray diffraction was possible.

In summary, the observations presented in this section indicate that further careful study of the different supramolecular geometries and metal fragments employed seems promising to access intriguing materials with unique features.

3.3. Phosphino-acetylenes

Covalently conjugated derivatives possessing ethynyl-phosphane units have mostly been prepared as building blocks for the synthesis of phosphapericyclynes and poly-phosphacyclopolyynes.[58,59] The routes used to prepare these compounds were taken from the synthetic pool of classic transformations associated with the alkyne and halogeno-phosphane functions. Thus, treatment of dichlorophosphane **120** with an excess of ethynylmagnesium bromide affords a mixture of compounds **121** and **122** isolated in 53% and 3% yield, respectively (Scheme 23).[58] Double deprotonation of

Scheme 23
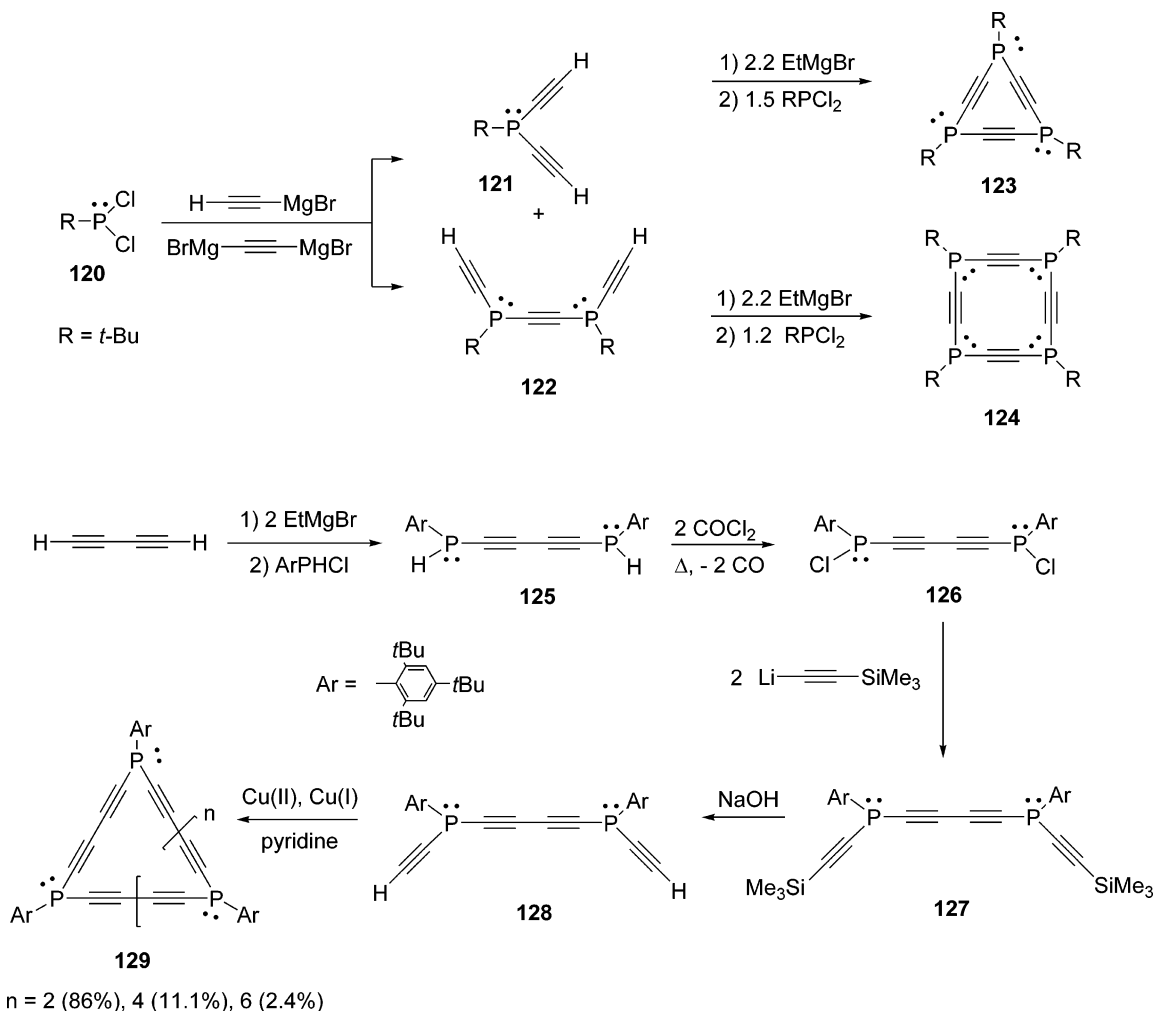
Scheme 24
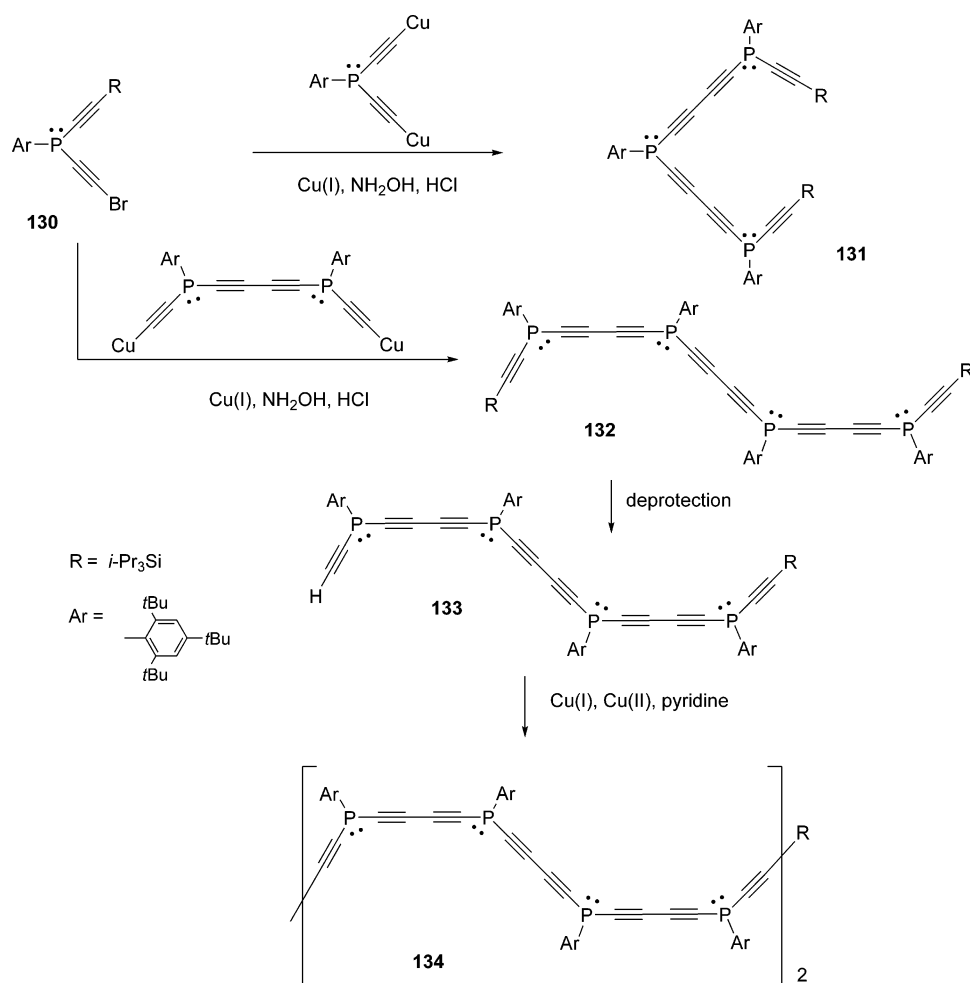
Scheme 25
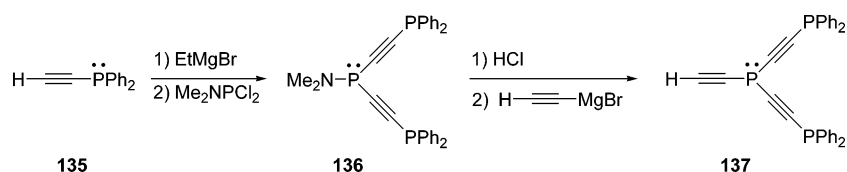
derivatives **121** and **122** followed by addition of 1.5 equiv of the dichlorophosphane **120** affords triphospha[3]pericyclyne **123** and tetraphospha[4]pericyclyne **124**. The UV−vis spectra of these cyclic derivatives show strong absorption bands that extend out to nearly 300 nm, revealing that these P-heterocycles exhibit rather strong cyclic electronic interactions.[58]

A variety of linear ethynylphosphanes **125**−**129** (Scheme 23) and **131**−**134** (Scheme 24) have been targeted by Märkl et al. as synthons for the preparation of polyphosphacyclopolyynes such as **129** (Scheme 23).[59] The ethynylphosphane **127** is obtained in a classic multistep reaction sequence exploiting the electrophilic character of halogenophosphanes. The key steps of this synthetic procedure to form cyclic (**129**) or linear (**131**−**134**) oligomers are either Eglinton coupling of terminal alkyne moieties (Scheme 23) or Cadiot−Chodkiewicz coupling involving bis-copper salts (Scheme 24). Derivatives **129** (Scheme 23) are obtained as a mixture of di-, tri-, and tetramers due to the random nature of this method. One unfortunate drawback in terms of analysis is that the corresponding ring systems are also obtained as a mixture of isomers due to the presence of several pyramidal

phosphorus centers. However, it is important to note that these Cu-mediated C−C bond-coupling reactions are compatible with the presence of these σ^3-P moieties; coordination of the phosphorus centers to the employed copper-catalyst is not observed. An interaction between the phosphorus lone pairs and the ethynyl units is supported by two facts: (*i*) derivative **127** (Scheme 23) possesses an unusually low inversion barrier (15.5 kcal mol^{-1} vs 35 kcal mol^{-1} for classical phosphanes), indicating a stabilization of the transient P-planar geometry and (*ii*) the absorption maxima (λ_{max} ca. 300 nm) recorded for the heterocycles **129** (Scheme 23) and linear oligomers **131**−**134** (Scheme 24) ($\lambda_{max} = 210-308$ nm) are consistent with an extended, increased degree of π-conjugation. The insolubility of the yellow, high molecular weight oligomer **134**, on the other hand, prevented UV−vis analysis. An application of phosphino-acetylenes in dendrimers was attempted by Majoral and co-workers, but the low-yielding preparation of dendron **137** from the tris(phosphane) **136** (Scheme 25) precluded its use as a building block for higher generation dendrimers.[60]

The results, however, indicate that although the development of this type of conjugated phosphorus system is

Scheme 26

Chart 12. Reactivity of Pyrroles and Phospholes toward Electrophiles
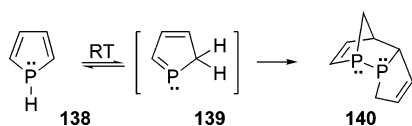
hindered by the lack of efficient syntheses that allow for gram scale preparations thus far, several routes to phosphane-ethynyl-based cyclic or linear oligomers are available.
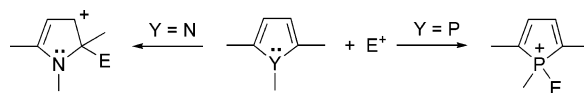
4. π-Conjugated Systems Based on Phospholes

Among the P-building blocks that have been used for the synthesis of π-conjugated systems (Chart 2), phosphole units have been the most thoroughly investigated to date. A variety of linear and cyclic oligomers as well as polymeric derivatives incorporating phospholes have been synthesized. The optical and electrochemical properties of several series have been elucidated, allowing reliable structure/property relationships to be established. Moreover, this P-building block has also been used for the tailoring of NLO-phores, conductive polymers, and emissive materials for OLEDs. It is important to recall that the first phospholes were described in the 1950s and that synthetic routes combining high yields and diversity of substitution patterns were only established in the late 1960s.[11,61] Thus, the chemistry of phospholes is quite recent compared to that of other heteroles, such as pyrrole and thiophene, that were discovered during the 19th century. Today, however, the chemistry of phospholes (synthesis, reactivity, coordination behavior, etc.) has reached a mature state, allowing its use as a building block for the engineering of π-conjugated materials to be envisaged.

4.1. Electronic Properties of Phospholes

One of the major issues toward understanding the properties of the phosphole ring is to determine its degree of aromaticity. This problem has been the subject of numerous experimental and theoretical studies. Their conclusions, based on energetic, structural, and magnetic criteria, are that the aromaticity of phosphole is very low.[11,12a,62] For example, the calculated aromatic stabilization energy (ASE) and nucleus-independent chemical shift (NICS) values are 7.0 kcal·mol^{-1} and -5.3 for phosphole, while being 25.5 kcal·mol^{-1} and -15.1 for pyrrole, respectively.[62] This is illustrated by the fact that the parent phosphole **138** (Scheme 26) was only characterized by NMR spectroscopy at -100 °C.[63a] At room temperature, it isomerizes via a [1,5]-sigmatropic shift to the 2H-phosphole **139**, which rapidly dimerizes to afford the *endo* derivative **140** (Scheme 26).[63] This weak aromatic character is a consequence of two intrinsic properties of phospholes: (*i*) the tricoordinate P-atom adopts a pyramidal geometry, and (*ii*) its lone pair exhibits a high degree of s-character. These two features prevent an efficient interaction of the P-lone pair and the endocyclic π-system. Remarkably, the aromatic character of the phosphole ring results from hyperconjugation involving the exocyclic P—R σ-bond and the π-system of the dienic moiety.[64] This hyperconjugation is possible since the P-atom adopts a tetrahedral geometry and the exocyclic P—R bonds are relatively weak, a situation that is reminiscent of that of siloles.[65] 1-Alkyl- and 1-arylphospholes show the same aromaticity as the parent phosphole. However, the aromaticity of phospholes can be strongly influenced by the nature of the ring substituents, especially those linked to the P-atom. Calculations have shown that phospholes with a planar P-atom would be more aromatic than pyrrole. This stabilization is not sufficient to overcome the high planarization barrier of the P-atom (35 kcal·mol^{-1}), but it is responsible for the reduced P-inversion barrier in phosphole (ca. 16 kcal·mol^{-1} versus 36 kcal·mol^{-1} for phospholanes).[66] Indeed, flattening the tricoordinate phosphorus atom using bulky substituents such as tri-*tert*-butylphenyl allows one to obtain unique phospholes exhibiting a Bird aromaticity index approaching that of pyrrole and showing the reactivity pattern of aromatic derivatives (i.e. electrophilic substitution).[67] In marked contrast, the cyclic delocalization is almost suppressed when the P-atom bears strongly electronegative substituents, due to a decreased effectiveness of hyperconjugation.[64b] For example, P-alkoxyphospholes exhibit a vanishing cyclic delocalization and readily undergo [4+2]-cycloadditions.[64c,f] These results show that the electronic properties of the phosphole ring can be fine-tuned by varying the P-substituent.

Finally, two other electronic properties of the phosphole ring that are of interest for the design of π-conjugated systems have to be pointed out. The first one is the rather high electronic affinity of this P-ring. Calculations at the HF/6−61+G*//B3LYP/6-31+G* level of theory have shown that the LUMO level of the parent phosphole ring (1.50 eV) is about 0.2 eV lower in energy than that of cyclopentadiene and close to that of silole (1.39 eV).[68] This property is most likely due to an interaction between the endocyclic dienic π*-orbital and the low-lying σ*(P—R)-orbital, similar to that observed for silole.[65] The second one is that the P-α carbon atoms bear a significant negative charge, higher than that calculated for pyrrole.[69] This feature is particularly important for the engineering of linear polymeric systems, as the linkages between the subunits involve these carbon centers.

These electronic properties (low aromatic character, σ−π hyperconjugation), which set phosphole apart from pyrrole and thiophene, have very important consequences. First, phosphole does not undergo electrophilic substitution, but it does possess a reactive heteroatom. As a result, an electrophile will not attack the heteroatom C-α carbon atom, as observed with pyrrole, but the P-atom instead (Chart 12). Hence, this P-containing ring has its own chemistry (synthetic routes, methods of functionalization, etc.) that cannot be predicted by simply extrapolating that of its aromatic S- and N-analogues.[61] Note that the ease of functionalization of the P-atom offers a unique way of creating structural diversity, including the preparation of transition metal complexes, from a single precursor.

Second, phospholes make appealing building blocks for the tailoring of conjugated systems, as it is well established that conjugation will be enhanced in macromolecules built from monomer units that exhibit low resonance energies due to the competition between intra-ring delocalization (aromaticity) and inter-ring delocalization (backbone π-conjugation).[2] This phenomenon is nicely illustrated by theoretical studies (DFT and TD-DFT) that have shown that the energy HOMO−LUMO gaps of oligo(phosphole)s (Phos)$_n$ are

Table 2. Calculated Energy Gap (eV) for Oligo(pyrrole)s (Py)$_n$, Oligo(thiophene)s (Thio)$_n$, and Oligo(phosphole)s (Phos)$_n$

	$n = 1$	$n = 2$	$n = 3$	$n = 4$
(Py)$_n$	5.83	4.75	4.24	3.65
(Thio)$_n$	5.99	4.13	3.49	3.06
(Phos)$_n$	5.16	3.57	2.85	2.44

significantly lower than those of the corresponding oligo-(pyrrole)s (Py)$_n$ or oligo(thiophene)s (Thio)$_n$ (Table 2).[70]

Theoretical studies have also suggested that phospholes can be useful building blocks for the engineering of dipolar chromophores with nonlinear optical (NLO) properties.[69] The NLO response of push−pull phosphole **141** (Chart 13) ($\beta_x = 6.17 \times 10^{-30}$ esu) is significantly greater than those of corresponding dipoles featuring a pyrrole ($\beta_x = 5.59 \times 10^{-30}$ esu) or a thiophene ($\beta_x = 5.49 \times 10^{-30}$ esu) central ring. The fact that the π-electrons of phosphole are easily polarizable due to the low aromatic character of this P-heterole contributes to this phenomenon. The electronic density of the π-bridge also plays a crucial role. As expected from the quite high electronic density found on the α-P carbon atoms of phosphole, dipole **142**, with a donor NH$_2$ substituent, exhibits a higher NLO activity than **143**, showing that the electron-rich P-ring acts as an auxiliary donor.[69a]

Last, if the chemistry of siloles was taken as a source of inspiration,[65] the σ−π hyperconjugation associated with the phosphole ring should allow for the synthesis of multidimensional systems exhibiting σ−π conjugation (so-called "through bond" delocalization[71]). It will be demonstrated that all these features of phosphole (presence of a reactive heteroatom, low aromatic character, σ−π conjugation), which pyrrole and thiophene cannot offer, have been fully exploited in recent years for the tailoring of conjugated oligomers and polymers.

4.2. Oligo(phosphole)s and Derivatives

The preparation of α,α′-oligo(phosphole)s is a significant synthetic challenge, since most of the classic and powerful methods employed for the preparation of thiophenes and pyrroles do not apply for phospholes. For example, Paal−Knorr condensation, direct *ortho*-lithiation, halogenation with *N*-bromosuccinimide or I$_2$/Hg^{2+}, Vilsmeier−Haack formylation, etc. are not operative in phosphole chemistry.[11] Likewise, no chemical or electrochemical oxidative polymerization of phospholes has yet been achieved.

Mathey achieved a breakthrough in this field in the 1990s with the discovery of several synthetic routes to linear bi- and quarterphospholes starting from 1-phenyl-3,4-dimethylphosphole **144** (Scheme 27), a synthon that is readily accessible in multigram quantities.[72] The best and most general route to phospholes is the dehydrohalogenation of

the corresponding 1-halogenophospholium salts.[11] This method is broad in its scope and has been extended to the synthesis of α,α′-biphospholes. The Ni(II)-promoted reductive dimerization of phosphole **144**, followed by decomplexation, affords the di-2-phospholene **145** (Scheme 27).[73a,b] Successive P-bromination and dehydrohalogenation give rise to the target 2,2′-biphosphole **146**, which is stable enough to be purified by column chromatography.[73c] The compound is obtained as a mixture of diastereoisomers, as it possesses two chirogenic P-centers. They are in rapid equilibrium at room temperature due to the low inversion barrier at phosphorus (ca. 16−17 kcal·mol^{-1}) resulting from the aromatic character of the planar transition state.[73c−e] One of the diastereomers was characterized by an X-ray diffraction study.[73e]

The discovery of a second route to biphospholes, based on intermediate 2-lithiophospholes, was a landmark in this area. This method provided the first direct means of functionalization of the phosphole ring and opened the way to metal-catalyzed coupling reactions.[74a] A quantitative bromine−lithium exchange transforms the 2-bromophospholes **147** into their highly reactive 2-lithio analogues **148** (Scheme 28). These 2-lithiophospholes undergo oxidative coupling leading to biphosphole **149** upon addition of copper(II) chloride (Scheme 28).[74] This very efficient bromine−lithium exchange methodology has also been applied to the 2,5-dibromophosphole **150** (Scheme 28) for the preparation of bromo-capped biphosphole **151** and quarterphosphole **152**. The latter is obtained in good yields (**150** → **152**, 55%) as mixtures of diastereoisomers.[75]

This synthetic methodology seems very attractive for the construction of longer α,α′-oligo(phosphole)s, as iterative coupling involving bromo-capped derivatives **151** and **152** can be envisaged. However, **152** is still the longest oligo-(phosphole) known to date, presumably due to the quite limited access to the starting bromo precursors **147** and **150** (Scheme 29),[74] which are not accessible via direct bromination of the phosphole ring.

It is noteworthy that the P-atoms of these oligo(phosphole)s retain the versatile reactivity observed with monophospholes.[11] In particular, derivative **149** can be used as a synthon for the synthesis of novel biphospholes via a two-step sequence involving the generation of the phospholyl anion **153** obtained by reductive cleavage of both exocyclic P−Ph bonds with lithium (Scheme 30). The dianion **153** can then act as a nucleophilic reagent, leading, for example, to the P-cyano biphosphole **154** (Scheme 30).[73d] The P-atoms of **149** can also be oxidized, affording oxo- and thiooxo-biphosphole **155a** and **155b** (Scheme 30), respectively, as a mixture of diastereoisomers which were separated by crystallization or column chromatography and structurally characterized.[73d,e] Biphosphole **149** exhibits a rich coordination

Chart 13. Push−Pull NLO-phores Based on Phosphole Rings Theoretically Investigated

Scheme 27

Scheme 28

147-151: R = Me, Ph
152 : R = Me

Scheme 29

R = **a**: Me, **b**: Ph
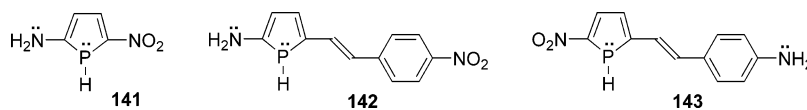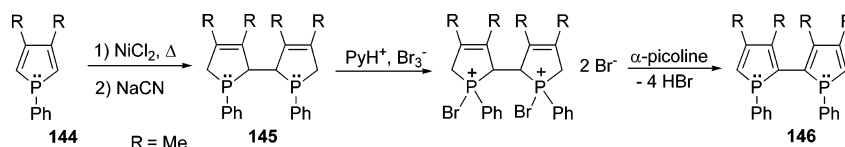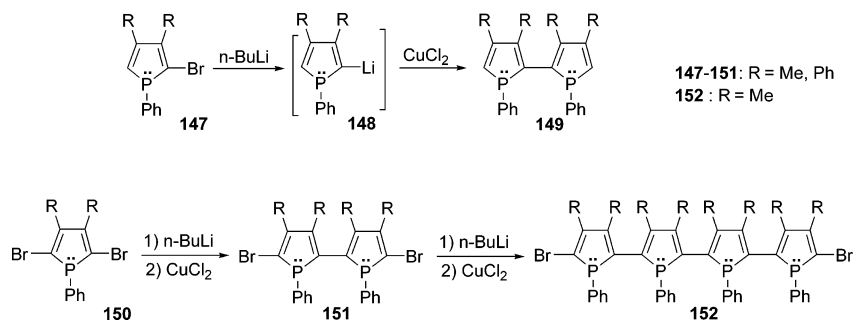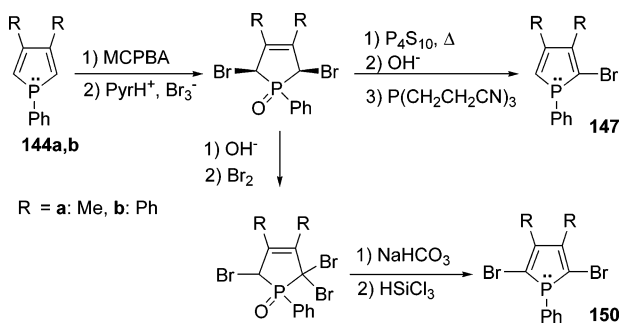
chemistry, which allows for the preparation of a variety of neutral and cationic transition metal complexes (Scheme 30).[73c−e] These complexes have been used as precursors for homogeneous catalysts.[76]

The optical and electrochemical properties of the linear oligophospholes have not been elucidated, precluding the interesting comparison with related oligopyrroles. However, biphospholes **149** and **154** (Scheme 30) and quarterphosphole **152** (Scheme 28) have been characterized by X-ray diffraction studies, giving some insight into the properties of these systems. The four phosphorus atoms of quarterphosphole **152** are mutually *syn*-disposed,[75] despite the *anti*-conformation having been predicted to be more stable.[70b,c] It is likely that the barrier between these conformers is low, as the phosphorus atoms of biphosphole **149**[73e] have an *anti*-conformation, whereas those of **154**[73d] have a *syn*-conformation. In all cases, the phosphorus atoms o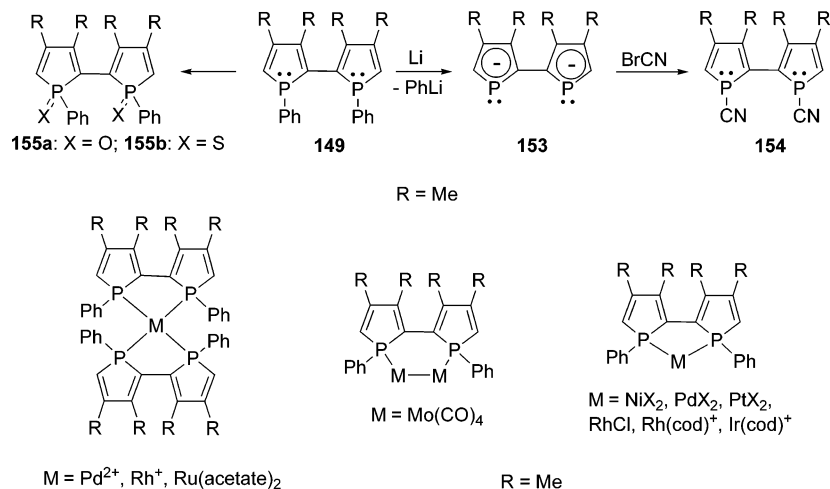f linear oligophospholes adopt a pyramidal geometry and the endocyclic P−C bond distances are consistent with single bonds. Altogether, these geometric data show that, as observed for monophospholes,

the P-lone pair is not conjugated with the endocyclic diene framework. Furthermore, the solid-state studies also revealed that the α,α′-phosphole units are not coplanar. The dihedral angle between the two phosphole rings in **149** and **154** is about 46°,[73d,e] while in quaterphosphole **152** the twist angle between the two inner rings is 25.1° and that between the outer pair is 49.7°.[75] These rotational distortions should preclude these oligo(phosphole)s from possessing extended π-conjugated systems. However, these twists are probably due to packing effects in the solid state, as the color of these compounds varies from pale yellow (**149**, **154**) to deep orange (**152**), suggesting rather high λ_{max} values and, consequently, the presence of a delocalized π-system in **152**. This is supported by the fact that the inter-ring carbon−carbon bond distances in quaterphosphole **152** [1.43(1)−1.45(8) Å] are shorter than a simple C−C bond length. Note that the observed red shift between derivatives **149** and **154** versus **152** hints that, in line with theoretical studies,[70] the energy gap of oligo(phosphole)s decreases with increasing chain length.

It can be concluded that the linear oligophosphole family is somewhat limited to di- and tetramers to date, although longer derivatives could potentially be accessible via the efficient synthetic routes developed by Mathey. The synthesis of other oligophospholes as well as the elucidation of their photophysical and electrochemical properties is still needed in order to establish reliable structure/property relationships.

Mathey et al. have also prepared a series of phenyl- and bithienyl-capped biphospholes that are very attractive derivatives due to the potential diversity of structures that are available (e.g. linear, cyclic, etc.) and the presence of electroactive thienyl termini. The synthetic routes to these compounds illustrate some of the specific methods that can

Scheme 30

155a: X = O; **155b**: X = S

149

153

154

R = Me

M = Pd^{2+}, Rh$^+$, Ru(acetate)$_2$

M = Mo(CO)$_4$

M = NiX$_2$, PdX$_2$, PtX$_2$, RhCl, Rh(cod)$^+$, Ir(cod)$^+$

R = Me
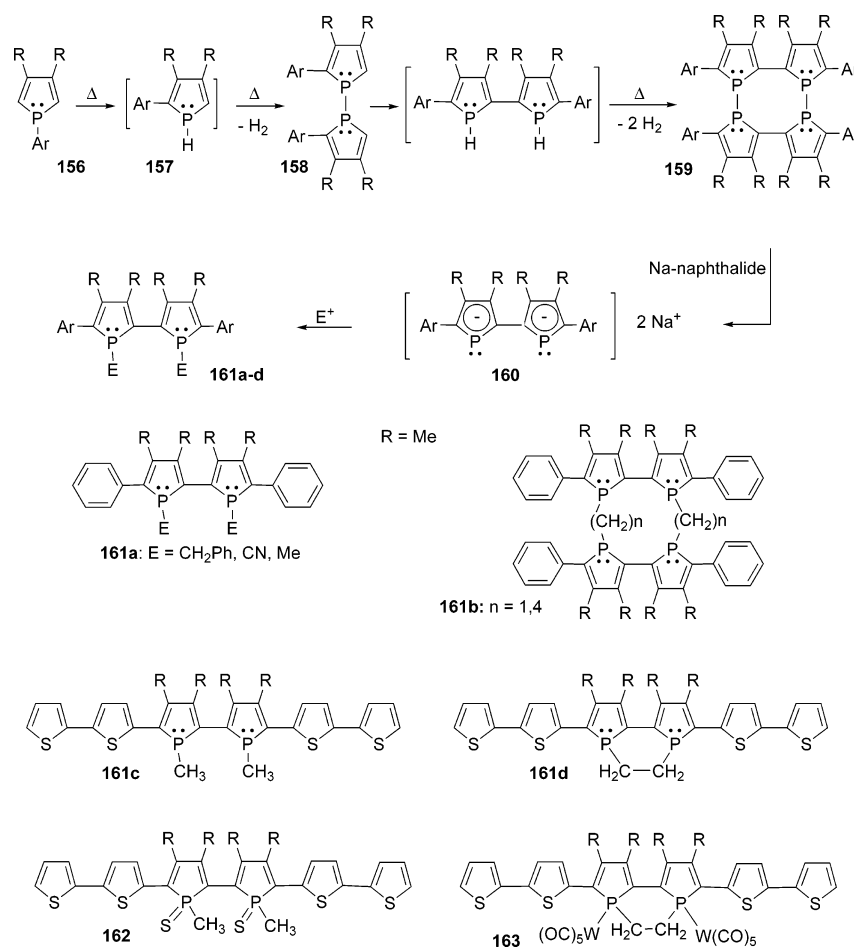
Scheme 31

Scheme 32

be used to prepare phosphole derivatives. The first one is an elegant and efficient method which starts from the readily available 1-arylphospholes **156** (Scheme 31). Prolonged thermolysis of phospholes **156** yields the cyclic tetramers **159** via the transient P−H phospholes **157** and the 1,1′-biphospholes **158** (Scheme 31).[77] The mechanism of this process involves a series of concerted [1,5]-sigmatropic shifts of Ar, H, and P plus two dehydrogenation steps (Scheme 31).[63d] The reductive cleavage of the P−P bonds of **159** gives the 2,2′-biphospholide dianions **160**. These compounds act as bidentate nucleophiles toward a wide variety of electrophiles to afford linear and cyclic derivatives **161a−d**, featuring α,α′-biphosphole moieties.[77] Bithienyl-capped derivatives **161c,d** are sensitive toward oxidation and were isolated as sulfur or tungsten pentacarbonyl adducts **162** and **163**, respectively (Scheme 31). These complexes were obtained as single diastereomers and studied by X-ray diffraction.[77d] In both compounds, the bithienyl moieties are al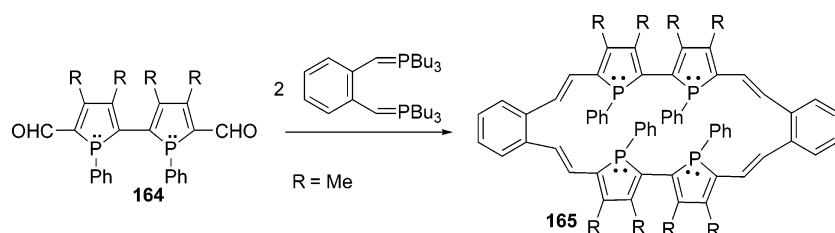most coplanar, with the angles between the phosphole and the thiophene rings being rather small (15.2°−24.3°), while the phosphole−phosphole interplane twist angles are some-

what larger [**162**, 66.26 ± 0.14°; **163**, 55.6 ± 0.3°]. The lengths of the C−C links between the rings (1.42−1.47 Å) are in the range expected for $C_{sp^2}-C_{sp^2}$ single bonds. These data suggest a certain degree of delocalization of the π-system over the six heterole rings, despite the rather large twist angles. This assumption is supported by an electrochemical study performed on the bis(thioxophosphole) derivatives of **161a** and **162**, which revealed that the anion-radicals and dianions exhibit relatively good stabilities and that the nature of the 2,5-biphosphole substituents (phenyl vs bithienyl) has a profound influence on the electrochemical behavior of these species.[77e] Note that the reduced species **162**[•−] and **162**[2−] are relatively stable on the cyclic voltammetry (200 mV·s^{−1}) time scale, suggesting the existence of extended delocalization in these compounds.[77e]

Conjugated cyclic oligomers based on α,α′-biphospholes are also available via Wittig reactions involving the 5,5′-bis(carboxaldehyde) **164** (Scheme 32).[78] An X-ray diffraction study of **165** revealed that the four P-phenyl groups have an *all-trans*-disposition and that this fully unsaturated macrocycle is distorted.[78] The cavity of the 24-membered hetero-

Chart 14. 1,1′-Biphospholes: Structures and Synthetic Routes

166 **167** **168** **169**
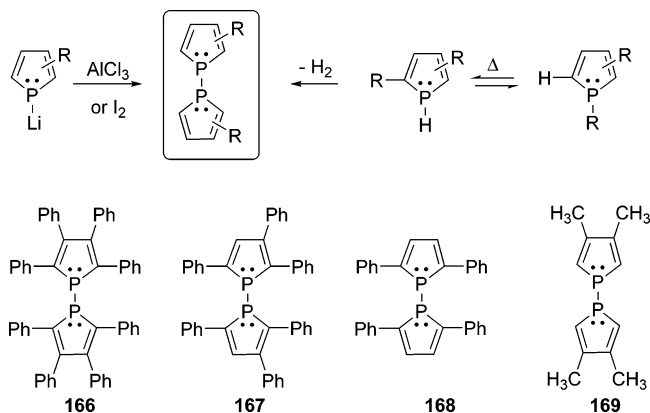
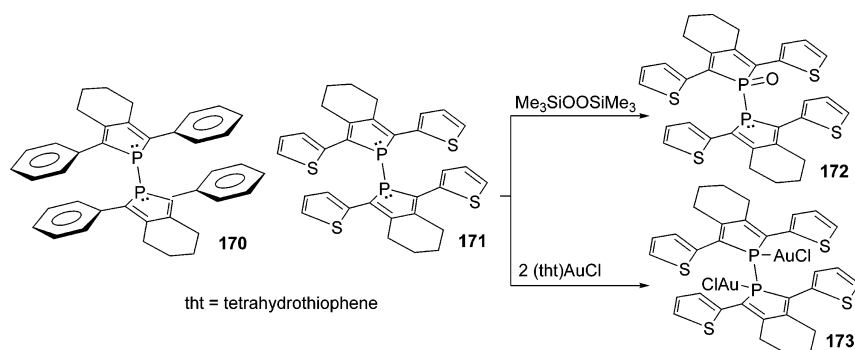cycle **165** is rather large with a diagonal distance between two P-atoms of almost 6.1 Å.

The α,α′-oligo(phosphole)s described in the previous section possess classical conjugated systems based on alternating double and single C–C bonds. The use of phospholes as building blocks allows for the variation in the topology of the conjugation pathway employing 1,1′-biphosphole subunits (Chart 14). These derivatives date back to the early days of phosphole chemistry, with the first member of the family having been prepared in 1979 by Abel and Towers (compound **166**, Chart 14)[79a] and with the three other examples, **167–169**, appearing in the early 1980s.[79b–d] The most common synthetic routes to 1,1′-biphospholes involve either the oxidative coupling of readily available phospholyl anions[79d] or the thermolysis of phospholes (Chart 14). This last route, which implies the formation of transient P–H phospholes, via 1,5-shifts of R and H, followed by loss of H$_2$, has already been detailed for the synthesis of derivative **159** (Scheme 31). An X-ray diffraction study performed on derivative **166** revealed that the P-atoms of 1,1′-biphospholes retain a pyramidal shape, as observed for the corresponding monomeric phospholes.[79e]

1,1′-Biphospholes have been mainly used as building blocks for the synthesis of other P-containing species, including mono- and diphosphaferrocenes.[80] Their electronic properties were recently investigated[81] with the aim of trying to observe any interaction between the π-systems via the P–P linkage resulting from the σ–π hyperconjugation occurring within the phosphole ring. The fact that π-chromophores can effectively be conjugated via σ-skeletons,[71] especially those exhibiting high polarizability and low σ–σ* energy gaps, was recognized by Hoffmann et al. in the late 1960s.[71a,b] This unusual conjugation pathway results in electronic properties that are starting to be exploited in

materials science. For example, in oligo(1,1′-siloles), an effective interaction (σ*–π* conjugation) occurs between the Si–Si bridges and the butadienic moieties,[83a,b] making these macromolecules very attractive chemical sensors for aromatic substrates[83c,d,g] and highly efficient electron-transporting materials for light-emitting-diode materials.[83e,f]

With a view to further exploitation of this unusual σ–π hyperconjugation involving heavy elements, the phenyl- and thienyl-substituted 1,1′-biphospholes **170** and **171** (Scheme 33), respectively, have been prepared from the corresponding monomeric phospholyl anion as air-stable powders.[81] For both compounds, theoretical calculations and UV–vis data clearly support a through-bond electronic interaction between the two 2,5-diarylphospholyl moieties via the P–P bridge. Notably, the LUMO is the antibonding combination and the LUMO+1 is the bonding combination, a behavior that is characteristic for through-bond coupling of two π-systems over an odd number of σ-bonds.[71a,b] One important consequence of this σ–π conjugation is the stabilization of the LUMO, resulting in a decrease of the HOMO–LUMO gap for compounds **170** and **171** compared to that for the corresponding 2,5-diarylphospholes.[81] It is interesting to note that the P-atoms of 1,1′-biphospholes **170** and **171** are reactive, allowing further chemical modification of the nature of the P–P bridge. For example, derivatives **172** and **173** are readily obtained using classical reactions that exploit the nucleophilic behavior of the σ³,λ³-P centers of **171** (Scheme 33). These chemical modifications have a significant impact on the optical properties of the assemblies. For example, oxidation of one P-center or complexation of both P-atoms with gold(I) results in bathochromic shifts of the band onset compared to the case of 1,1′-biphosphole **171**.[81]

A series of remarkable related macrocycles featuring both α,α′- and 1,1′-biphosphole cores has been described by Mathey et al. (Scheme 34). The synthesis of derivatives **159** has been depicted in Scheme 31.[77c] An X-ray diffraction study revealed that the P-atoms of this compound are located *trans* with respect to the linking C–C bond.[77c] However, macrocycle **159** is likely to be flexible, since the P-atoms in the corresponding Mo(CO)$_5$ complex **174** adopt mutually *cis* positions (Scheme 34).[77a] As observed in the linear α,α′-biphosphole series (vide supra), the two P-rings of the α,α′-biphosphole moieties of **159** are not coplanar (twist angle, 44.2°).[77b] The UV–vis data of this unique type of macrocycle have not been reported, but its red color suggests a low optical HOMO–LUMO separation due to σ–π conjugation. Significantly, derivative **159** can be used as a precursor to other macrocycles featuring the 1,1′-biphosphole moiety. For example, the reductive cleavage of one P–P bond with sodium gives the dianion **175** (Scheme 34).[77c] Derivative **175**
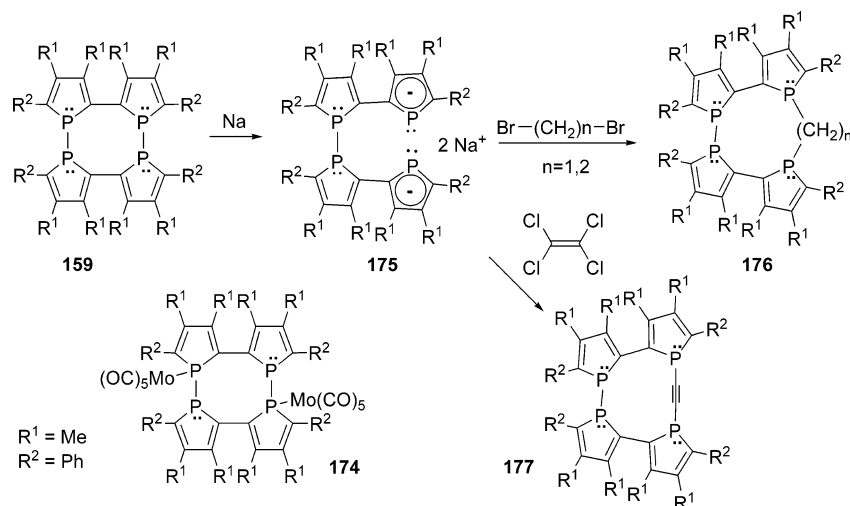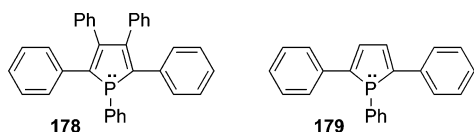
Scheme 33

tht = tetrahydrothiophene

170   **171**

Me$_3$SiOOSiMe$_3$

172

2 (tht)AuCl

173

Scheme 34

159 → **175** → **176**

174
R^1 = Me
R^2 = Ph

177

Chart 15. 2,5-Diarylphospholes

178   **179**

is a versatile nucleophile that reacts with dihalogenoalkanes and tetrachloroethylene to give the novel macrocycles **176** and **177**, respectively.[77c] Compound **177** was characterized by an X-ray diffraction study which revealed that this quite rigid 10-membered macrocyclic compound exhibits some strain, as shown by the nonlinearity of the P−C≡C−P unit [P−C−C, 170.2(8)° and 173.5(6)°].[77c]

The above-mentioned examples illustrate the diversity of structures offered through the use of α,α′- and 1,1′-biphosphole building blocks. Importantly, it has been shown that 1,1′-biphosphole units exhibit σ−π conjugation, a type of electronic interaction that is still relatively rare.

4.3. Mixed Oligomers

Amazingly, the first phospholes to be prepared in the early 1960s were the 2,5-diphenylphospholes **178** and **179** (Chart 15), which exhibit extended π-conjugated systems.[84] Both derivatives show absorptions in the visible region (λ_{max}: **178**, 358 nm; **179**, 374 nm) and Stokes shifts varying from 100 nm for **178** to 120 nm for **179**.[85a] Furthermore, an X-ray crystal structure analysis of compound **179** revealed that the phosphole ring and the 2,5-phenyl substituents are almost coplanar.[85b] However, this important structural observation, suggesting the presence of an extended delocalized π-system involving the dienic part of the phosphole ring and the two phenyl substituents, was not considered at that time. Consequently, the interest in the use of phospholes as building blocks for the construction of π-conjugated derivatives only dates from the 1990s.

In 1991, Mathey et al. prepared the first series of mixed oligomers based on phospholes and other (hetero)aromatics that are composed of 2,5-di(2-phosphole)thiophene or -furan derivatives **182a,b** (Scheme 35).[86a] The key step in their synthesis is an electrophilic substitution in which the protected phosphole **180** acts as an electrophile toward electron-rich thiophene or furan rings,[86b] leading to the 3-phospholene adducts **181a,b** (Scheme 35). These compounds can be transformed into the corresponding σ^3,λ^3-

phosphole derivatives **182a,b** through a multistep deprotection−reduction−bromination−dehydrohalogenation sequence (Scheme 35). Note that oligomer **182b**, incorporating the furan ring, was not isolated but was directly transformed into its thioxo derivative **183b**. The molecules featuring thioxophosphole moieties absorb in the visible region (**183a**, orange; **183b**, bright yellow), suggesting relatively high values of λ_{max}; however, no UV−vis data are available. An X-ray diffraction study performed on thioxo-derivative **183b** showed that only one phosphole ring is coplanar with the central furan unit (twist angle, 3.3° ± 0.1° and 40.1 ± 0.1°).[86a] The two inter-ring C−C bond distances [1.452(4) Å and 1.461(6) Å] lie between those observed for C−C single and double bonds, a feature that is in favor of a certain degree of delocalization.

The first systematic investigation of phosphole-containing π-conjugated systems, including model molecules as well as conductive polymers and materials suitable for OLED applications, was undertaken with 2,5-di(heteroaryl)phospholes by Réau and co-workers. These derivatives are not accessible by the electrophilic substitution route described above for the preparation of **182a,b**, since the second condensation step gives rise to 2,4-dithienylpholene **184** (Scheme 35).[86a] In fact, 2,5-di(heteroaryl)phospholes are readily accessible via a widely applicable organometallic route, known as the "Fagan−Nugent method", that can be used to prepare a large range of metalloles including phospholes, arsoles, stiboles, stannoles, germoles, etc.[87] The key to obtaining the desired 2,5-substitution pattern is to perform the metal-mediated oxidative coupling of diynes **185** possessing a (CH$_2$)$_3$ or a (CH$_2$)$_4$ spacer (Scheme 36).[64d,68,88] These diynes, including unsymmetrical variants, can be readily prepared using Sonogashira coupling.[64d,68,88] The zirconacyclopentadiene intermediates **186** are extremely air- and moisture-sensitive derivatives that react with dihalogenophosphanes to give the corresponding phospholes **187a−k** in medium to good yields (Scheme 36). This route is highly flexible, as it not only allows electron-deficient and electron-rich rings to be introduced in the 2,5-positions, but it also permits one to vary the nature of the P-substituent. This structural diversity is a crucial issue for the development of phospholes as materials' building blocks, since (*i*) it enables one to fully elucidate the structure/property relationships, and (*ii*) their thermal stability as well as their ease of handling and manipulation depend greatly on the nature of

Scheme 35

R = Me ; **a** : Y = O ; **b** : Y = S ; X = Cl or Br
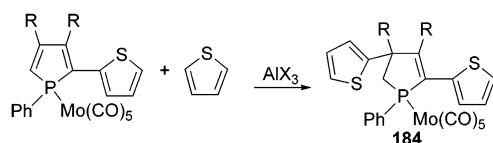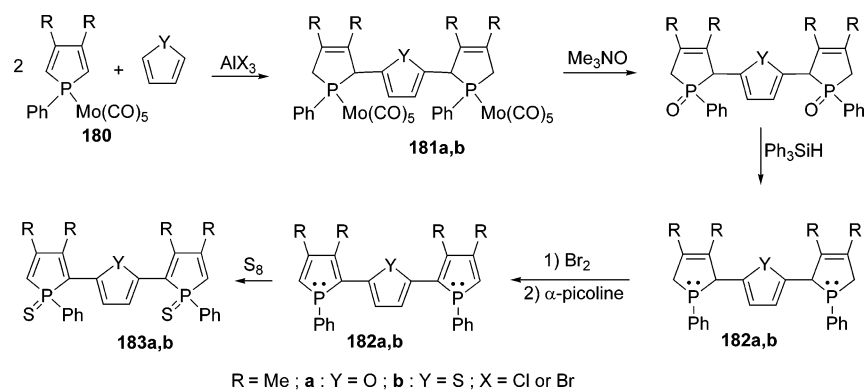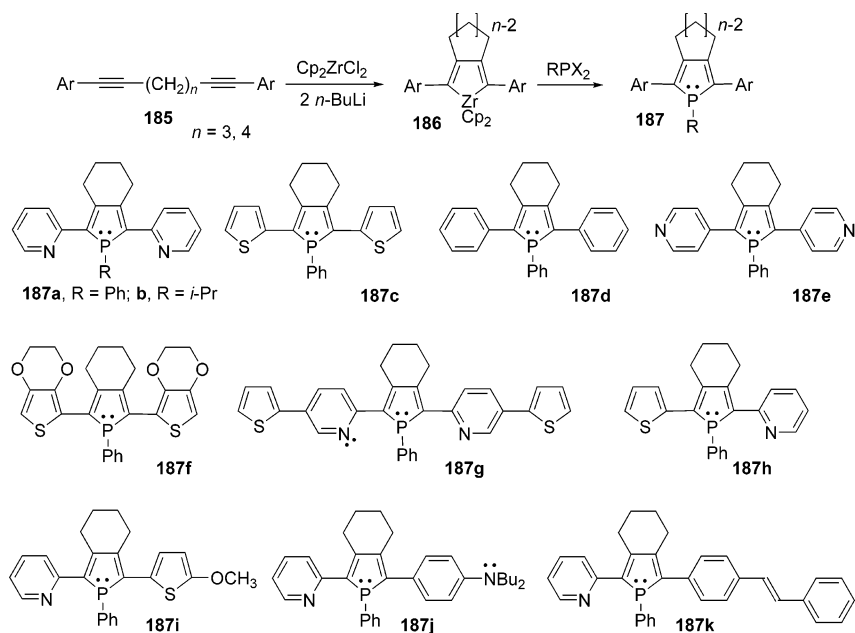
Scheme 36

the P-substituent. For example, the parent phosphole **138** can be observed only at −100 °C (Scheme 26),[63a] whereas phospholes bearing phenyl, cyclohexyl, cyano, or alkoxy substituents at phosphorus are stable at room temperature.[61] Furthermore, 2,5-substituted P-phenylphospholes are usually not air- and moisture-sensitive and can be purified by standard methods.[68] In contrast, the corresponding P-amino and P-halogeno phospholes are readily hydrolyzed and have to be handled under inert atmosphere.

The σ^3,λ^3-phospholes **187a**[88a] and **187c**,[68,88b] bearing electron-deficient and electron-rich substituents, respectively, were characterized by X-ray diffraction studies. Despite the different nature of the two 2,5-substituents (electronic disparity, shape, etc.), these compounds share some important structural features in the solid state. The twist angles between two adjacent rings are rather small [**187a**, 7.0° and 25.6°; **187c**, 12.5° and 16.7°], and the phosphorus atoms are strongly pyramidalized, as indicated by the sum of the CPC angles [**187a**, 299.3°; **187c**, 299.3°]. The lengths of the C−C linkages between the rings [1.436(6)−1.467(8) Å] are in the

range expected for $C_{sp^2}-C_{sp^2}$ single bonds. Altogether, these metric data suggest a delocalization of the π-system over the three heterocycles. The presence of an extended π-conjugated system in phospholes **187a−k** was also confirmed by the observation of an absorption maximum in the visible region. The energy of these absorptions, which are attributed to π−π* transitions,[68,82] depends dramatically on the nature of both the P- and 2,5-substituents. A red shift of the λ_{max}-values for P-aryl phospholes is observed relative to those of the corresponding P-alkyl analogues (Table 3, **187a** vs **187b**). An important bathochromic shift was recorded upon replacing the phenyl groups either by 2-pyridyl ($\lambda_{max} = 36$ nm) or 2-thienyl rings ($\lambda_{max} = 58$ nm) (Table 3).[68] Collectively, these data suggest that the HOMO−LUMO gap gradually decreases in the series **187d/187a/187c**, a feature that was confirmed by high-level theoretical calculations.[68] This variation was initially attributed to the fact that phospholes possess low-lying LUMO levels (high electron affinity) that favor intramolecular charge-transfer processes from the electron-rich thienyl substituents.[68] A more recent theoretical

Table 3. Physical Properties of Representative Di(heteroaryl)phospholes and Derivatives

	λ_{max}[a] (nm)	λ_{onset}[a] (nm)	$\log \epsilon$	λ_{em}[a] (nm)	ϕ_f[b]	E_{pa}[c] (V)	E_{pc}[c] (V)
187a	390	448	4.02	463	1.1×10^{-2}	+0.83	−2.45
187b	371	430	4.10	458		+0.79	−2.67
187c	412	468	3.93	501	5.0×10^{-2}	+0.40	
187d	354	430	4.20	466	14.3×10^{-2}	+0.69	−2.88
187k	395		4.36	497	15.2×10^{-2}	+1.04	−1.95
189c	432	496	3.98	548	4.6×10^{-2}	+0.68	−1.95
190c	442	528	3.92	593	0.8×10^{-2}	+0.92	−1.66
191c	408	475	4.04	506	1.3×10^{-2}	+0.70	−2.20
192c	428	500	4.10	544	12.9×10^{-2}	+0.82	−1.75

[a] In THF. [b] Relative to quinine sulfate or fluorescin ±15%. [c] In CH$_2$Cl$_2$, referenced to ferrocene/ferrocenium half cell.

study has proposed that the more pronounced π-conjugation in **187c** is due to the better interaction between the HOMO of the phosphole and the HOMO of the thiophene, compared to that with pyridine.[89a] The optical data and theoretical studies show that the lowest HOMO−LUMO gap is achieved for **187c**, structurally based on an alternating arrangement of thiophene and phosphole rings. It is interesting to note that the value of λ_{max} recorded for **187c** (412 nm) is considerably more red-shifted than those of related 2,5-dithienyl-substituted pyrrole (322 nm), furan (366 nm), or thiophene (355 nm) and that the value is very close to that of the 2,5-dithienyl derivative based on a nonaromatic silole unit (420 nm).[90] These observations recommend phospholes as valuable building blocks for the construction of co-oligomers exhibiting low HOMO−LUMO separations. This appealing property is due to the weak aromaticity of the phosphole ring that favors an exocyclic delocalization of the dienic π-electrons.

Varying the nature of the 2,5-substituents is also an effective way of tuning the emission and electrochemical behavior of phosphole-based extended π-electron systems. A blue-green emission is observed for diphenyl- and di(2-pyridyl)phospholes **187d** and **187a** (463−466 nm), whereas the emission of di(2-thienyl)phosphole **187c** is red-shifted ($\Delta\lambda_{em} = 35$ nm). The quantum yields also depend on the 2,5-substitution pattern, with the most efficient fluorophore being the σ^3-phosphole **187k** ($\phi_f = 15.2\%$). This value is remarkable, as chromophores featuring σ^3-P centers usually exhibit almost no fluorescence as a result of quenching by the P lone pair (vide infra). This result illustrates the unique properties of phospholes compared to "regular" phosphanes. Cyclic voltammetry (CV) performed at 200 mV·s^{-1} revealed that the redox processes observed for all the σ^3-phospholes are irreversible and that their redox properties are related to the electronic properties of the phosphole substituents (Table 3). For example, derivative **187d** featuring electron-rich thienyl substituents is more easily oxidized than compound **187a**, which possesses electron-deficient pyridyl substituents (Table 3).[68]

One of the appealing properties of phosphole rings is the versatile reactivity of the endocyclic heteroatom that allows creating structural diversity in these types of systems. This feature offers a direct access to a broad range of new π-conjugated systems from single P-containing chromophores, without the need for additional multistep syntheses, as illustrated with dipyridyl- and dithienylphospholes **187a** and **187c** (Scheme 37).[68,91d] It is noteworthy that for both series the bis(heteroaryl)phosphole moiety remains almost planar in the coordination sphere of W(CO)$_5$ and

Scheme 37
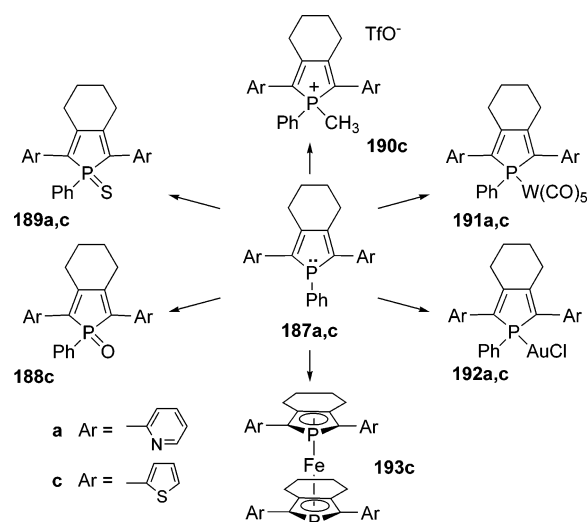
AuCl and that the bond lengths and angles are unchanged upon coordination.[68,91] However, the ring orientation depends on the substitution pattern of the σ^4-thioxophospholes. For example, the crystal structures of derivatives **194−196** (Chart 16) show that the diarylphospholyl moieties do not have a coplanar conformation. The twist angles between the phosphole ring and the aromatic substituents are similar for 2,5-diphenylphosphole **194** (50.3° and 50.5°) and 2-phenylstil-benylphosphole **195** (44.6° and 47.2°), but they are much smaller for 2-biphenyl-5-phenylphosphole **196** (35.9° and 36.3°). The smaller ring twist observed for derivative **196** should favor the delocalization of the π-system, since the orbital overlap varies approximately with the cosine of the twist angle. This is supported by the fact that the inter-ring phosphole-phenyl distances are slightly smaller for derivative **196** [1.470(3)−1.473(3) Å] than for the highly twisted compounds **194** [1.479(2)−1.480(2) Å] and **195** [1.479(2)−1.481(2) Å]. Note that the two di(2-thienyl)phospholyl moieties of diphosphaferrocene **193c** are almost planar (twist angles: 0.5°−12.9°).[91d]

The chemical modifications of the nucleophilic P-center (Scheme 37) have a profound impact on the optical and electrochemical properties of the phosphole oligomers as a whole. For example, upon modification of the σ^3-phosphole **187c** toward the neutral σ^4-derivative **189c** and the σ^4-phospholium salt **190c**, a red shift in their emission spectra, together with an increase and decrease of their oxidation and reduction potentials, respectively, is observed (Table 3). These trends can be rationalized on the basis that within this series the electronic deficiency of the P-atom is gradually augmented.[89b,c] It is also noteworthy that the quantum yield of the gold complex **192c** is higher than that of the corresponding phosphole **187c** or its thioxo derivative **189c** (Table 3), illustrating that the nature of the P-modification has a considerable impact on the optical properties of these fluorophores.[91b] The fact that chemical modifications of the phosphorus atoms allow for a fine-tuning of the optical and electrochemical properties of phosphole-based π-conjugated systems is very promising for OLED development, since it would allow (i) the emission color of the devices to be varied and (ii) a good match to be achieved between the LUMO and HOMO levels and the work functions of the electrodes. Another appealing consequence of the P-modification is that the quantum yields for σ^4-thioxophospholes are higher in the solid state than in dilute solution.[91b] This rather unusual

Chart 16. Thioxophospholes Used as Materials for OLEDs

Scheme 38

a : n = 1; **b** : n= 2
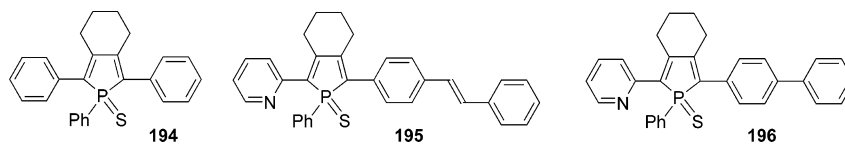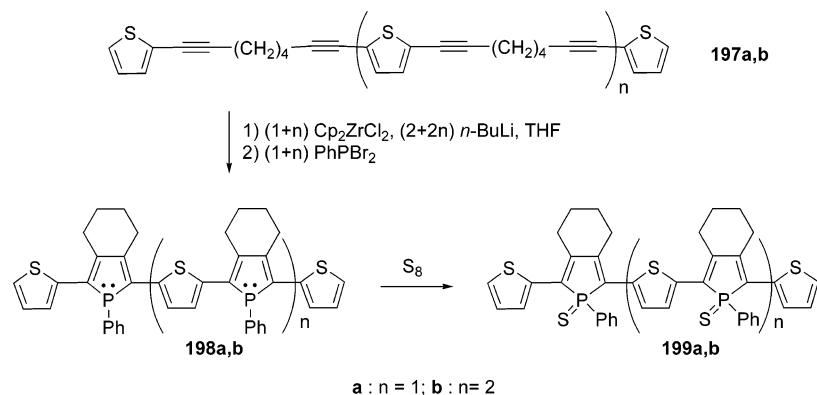
behavior[92] is probably due to the steric protection provided by the substituents (Ph, S) of the tetrahedral P atom, which preclude a close cofacial organization of these P chromophores in the solid state. This hypothesis is also supported by the fact that the UV−vis and fluorescence spectra of σ^4-thioxophospholes in solution and in thin films are very similar; no red-shifted emission revealing excimer or aggregate formation is observed. In marked contrast, the solution and thin-film emission spectra of the gold complexes (i.e. **192c**, Scheme 38, and its 2,5-diphenyl analogue) are different. Two broad emission bands are observed for the thin films: one at a wavelength similar to that of the solution spectrum, and a second, which is considerably red-shifted. These low-energy luminescence bands observed in the thin films most likely arise from the formation of aggregates. These results revealed that the nature of the P-moiety affects the bulk molecular environment and hence the photophysical behavior of these chromophores in the solid state; thioxophosphole derivatives are isolated luminophores whereas gold(I) phosphole complexes form aggregates leading to broad emission spectra from both monomer and aggregate states. This dichotomy shows that the presence of reactive phosphorus atoms allows for a unique molecular design to efficiently vary and to control the electronic structures of π-conjugated materials. Exploitation of this method of tailoring π-conjugated systems, which is simply not possible in this variety with pyrrole and thiophene units, has led to the optimization of the properties of thiophene-phosphole co-oligomers for use as materials suitable for OLED fabrication.

Single-layer OLEDs have been prepared through sublimation of phosphole-based conjugated systems onto semitransparent indium−tin-oxide (ITO) anodes. Derivatives that are thermally stable enough to be deposed by sublimation are the σ^3-phosphole **187k** (Scheme 37), the thioxo-derivatives **189c** (Scheme 37), **194−196** (Chart 16), the gold complex **192c** (Scheme 37), and its 2,5-diphenyl analogue.[91a,b] Not surprisingly, the performances of each device are significantly different depending on the phosphole material employed. The OLED device using **187k** displays greenish electroluminescence (EL) (λ_{max}^{EL} = 510 nm) for a turn-on voltage of 6.0 V. The maximum brightness attains 1000 cd·m^{-2}, but the EL quantum yield is low (ϕ = 0.08). With

relatively low turn-on voltages (2.0−3.6 V), devices employing the thioxo-derivatives **189c** and **194−196** emit green to yellow light (λ_{max}^{EL} = 524−557 nm). In all cases, the EL spectra of these devices match those of the solid-state photoluminescence (PL) spectra of the phospholes, showing that the source of the EL emission band is from the P-derivative. The highest maximum brightness (B_{max} = 3613 cd·m^{-2}) and external EL quantum efficiency (EEQE = 0.16) are obtained with the thienyl-capped phosphole **189c**. To further improve device characteristics, multilayered devices in which the phosphole layer is sandwiched between a hole-transport layer (α-NPD) and an electron-transport layer (Alq$_3$) were prepared.[91a,b] The turn-on voltages required to drive these multilayer devices are lower than or comparable to those of the corresponding single-layer OLEDs. The external EL quantum efficiency (EELQ) and brightness of the multilayer devices are dramatically superior to those of their single-layer counterparts. For example, with **189c** the maximum brightness is enhanced by 1 order of magnitude (3613 vs 37830 cd·m^{-2}) and the maximum EELQ is quintupled (0.16 vs 0.80). Another effective way to further improve OLED performance, and also to tune their color, is to dope highly fluorescent dyes as guests into an emissive host matrix. 2,5-(2-Dithienyl)thioxophosphole (**189c**) was thus evaluated as the host material for (2-(1,1-dimethylethyl)-6-(2-(2,3,6,7-tetrahydro-1,1,7,7-tetramethyl-1H,5H-benzo(ij)-quinolizin-9-yl)ethenyl)-4H-pyran-4-ylidene) propanedinitrile (DCJTB), one of the best red-emitting dopants for OLEDs.[5d] Upon doping with DCJTB, the turn-on voltage and maximal brightness remain similar, but the EL efficiency increases from 0.74% to 1.83% photon/electron and the luminous efficiency increases from 0.83 to 1.12 lm·W^{-1}.[91a,b] Furthermore, the external EL quantum efficiency of this device is unaffected by the driving current density in the range of 0−90 mA·cm^{-2}. This behavior is very promising, as the efficiency of the conventional DCJTB-doped Alq$_3$ devices usually decays rapidly upon increasing the driving current due to the quenching effects of the charged excited states of Alq$_3$ on red dopants.[5,93] Thus, 2,5-di(2-thienyl)thioxophosphole (**189c**) appears to be an attractive host material for DCJTB, as it solves the problem of luminescence quenching at high drive current. Similarly, phosphole gold complexes were subjected to electroluminescence studies using also the

Table 4. Preparation and Physical Properties of Oligo(α,α′-thiophene-thioxophosphole)s

	yield (%)	$\lambda_{max}{}^a$ (nm)	$\lambda_{onset}{}^a$ (nm)	log ε	$\lambda_{em}{}^a$	$E_{pa}{}^b$ (V)
189c (n = 0)	93	432	496	3.98	548	+0.68
199a (n = 1)	78	508	590	4.26	615	+0.45
199b (n = 2)	32	550	665	4.42		

[a] In THF. *[b]* In CH_2Cl_2, referenced to ferrocene/ferrocenium half cell.

single-layer and the multilayer structures. As observed for thin-film PL, their EL spectra also show two broad emission bands. The EL spectrum of the single-layer device using complex **192c** (Scheme 37) uniformly covers a broad spectral range of 500−800 nm due to the well balanced dual monomer and aggregate emissions. Overall, these results show that π-conjugated oligomers containing σ^3- or σ^4-phosphole moieties, including gold complexes, can be employed as multifunctional materials in single-layer OLEDs. They are a basis for the further development of P materials for optoelectronic applications, as they show that there is no inherent impossibility in using organophosphorus moieties to construct functional materials.

The evolution of optical and electrochemical properties with increasing chain length is one of the central principles used in the understanding of the characteristics of novel π-conjugated systems.[2] Hence, this evolution has been investigated for α,α′-thiophene-phosphole (Thio-Phos) oligomers. To this end, the well-defined oligomers **198a,b** were prepared using the Fagan−Nugent method from the corresponding bis- and tris-diynes **197a,b** (Scheme 38).[94] Derivatives **198a,b**, as well as their thioxo-derivatives **199a,b**, exist as a mixture of diastereomers due to the presence of stereogenic P-centers. They are air stable and soluble in common organic solvents (e.g. THF, CH_2Cl_2). Significantly, however, the yields of the various oligomers decrease dramatically with increasing chain length (Table 4), precluding the preparation of longer chain derivatives. With respect to their electronic properties, the longest wavelength absorptions, emission bands, and oxidation potentials all gradually shift to lower energies with increasing chain length (Table 4). This reflects the expected decrease in the HOMO−LUMO gap upon increasing the chain length of the α,α′-(thiophene-phosphole) oligomers. It is thus likely that the effective conjugation path length is much longer than 7 units for oligomers of these types. Notably, the λ_{max}-value for Thio-(Phos-Thio)₂ **198a** (490 nm) is considerably red-shifted compared to that of quinquethiophene (ca. 418 nm), again showing that replacing a thiophene subunit by a phosphole ring induces an important decrease in the optical HOMO−LUMO gap. It is also noteworthy that oligo(α,α′-thiophene-phosphole)s **199a,b** incorporating σ^4-thioxophospholes have smaller HOMO−LUMO gaps relative to their precursors **198a,b** based on σ^3-phospholes. A similar trend has been observed with the shorter oligomers;[68] the smaller HOMO−LUMO gaps of oligo(α,α′-thiophene-phosphole)s incorporating σ^4-P rings relative to those based on σ^3-P rings are therefore most likely a general feature for these systems.

As previously highlighted for oligophospholes, an important property of phospholes is their ability to form transition metal complexes. Indeed, the coordination of π-chromophores to transition metals is a powerful way to modify their characteristics and to engender novel properties. Two remarkable examples of this methodology are the use of cyclometalated (phenylpyridinato)Ir(II) complexes (highly
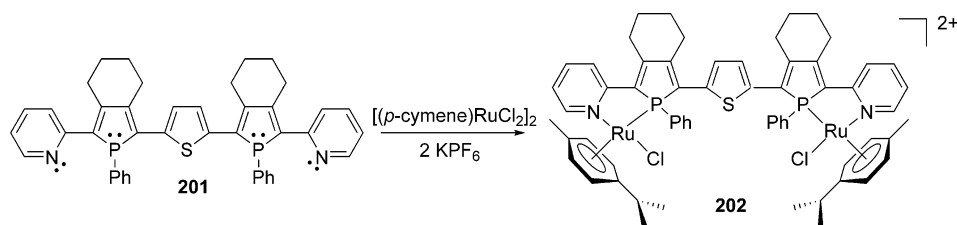
Scheme 39
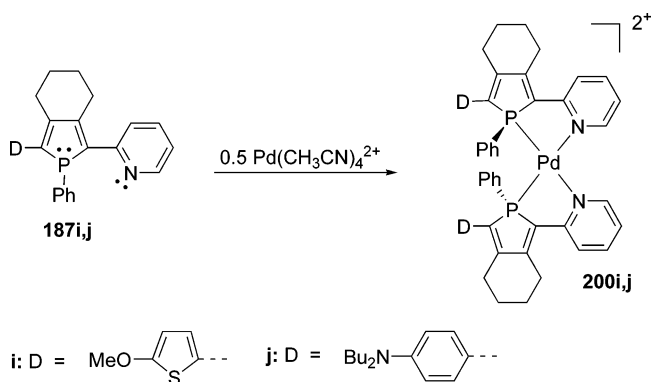
efficient phosphorescent dopants for OLEDs due to the strong spin−orbit coupling caused by the heavy metal ion)[95] and homoleptic (aminostyrylbipyridine)Ru(II) complexes (powerful octupolar NLO-phores due to the octahedral geometry of the metal center).[15a,96] Phosphole-complexes have been investigated within this context via two approaches: the P-ring either can be a part of a conjugated system or can be used as an assembling ligand. According to the first approach, 2-pyridylphosphole derivatives have been investigated due to their 1,4-chelating behavior toward transition metals.[88c,d,97] One key property of these ligands is their heteroditopic nature. They possess two coordination centers with different stereoelectronic properties which, in accordance with Pearson's antisymbiotic effect,[98] can control the orientation of a second chelating ligand in the coordination sphere of a square-planar d^8-metal center.[88d] This property has been exploited in order to control the in-plane parallel arrangement of 1D-dipolar chromophores.[88e] Phospholes **187i,j** (Scheme 39) bearing an electron-deficient pyridine group and a classical electron-donor at the 2- and 5-positions, respectively, have a typical "D-(π-bridge)-A" dipolar topology. They exhibit only moderate NLO activities ($\beta_{1.9\mu m} \approx 30 \times 10^{-30}$ esu) due to the weak acceptor character of the pyridine group. However, the potential of these dipoles in NLO is considerably increased by their P,N-chelate behavior. In accordance with the antisymbiotic effect, they undergo stereoselective coordination leading to a close parallel alignment of the dipoles on the square-planar d^8-Pd(II) template. Thus, the trans-effect can overcome the natural antiparallel alignment tendency of 1D-dipolar chromophores at the molecular level. The non-centrosymmetric complexes **200i,j** exhibit fairly high NLO activities ($\beta_{1.9\mu m} \sim (170-180) \times 10^{-30}$ esu), something that is probably due to the onset of ligand-to-metal-to-ligand charge transfer (LMLCT), which contributes coherently to the second-harmonic generation.[88e]

Derivative **201**, featuring two pyridylphosphole moieties bridged by a thiophene ring (Scheme 40), has been prepared with a view to study the photophysical properties of diruthenium complex **202**, containing bridging π-conjugated ligands.[88d] Derivative **201** exhibits a λ_{max} value (480 nm) at a much longer wavelength than the corresponding 2-(2-pyridyl)-5-(thienyl)phosphole **187h** (Scheme 36) (396 nm). Coordination of chromophore **201** to ruthenium centers has been shown to have only a marginal influence on the π−π* transition of the extended conjugated system.[88d]

Bis(2-pyridyl)phospholes **187a,c** are versatile dinucleating ligands which can effectively stabilize dinuclear metal complexes (Scheme 41).[99] In these complexes, the 2,5-bis-

Scheme 40

Scheme 41
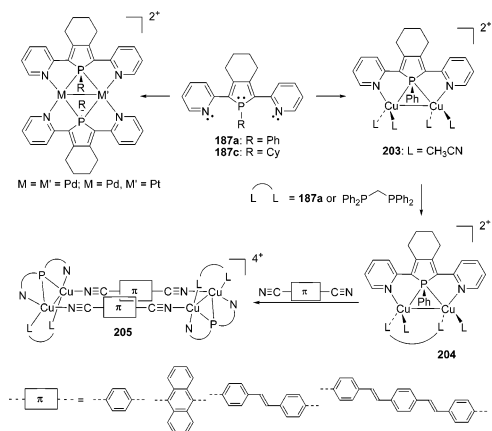
(2-pyridyl)phospholes **187a,c** act as 6-electron μ-1κN:1,2κP: 2κN donors and the P-atoms adopt a very rare[100] symmetrically bridging coordination mode. Two acetonitrile ligands of Cu(I)-dimer **203** can be displaced by another equivalent of **187a** or of diphenylphosphinomethane, leading to complexes **204** (Scheme 41). These molecular clips react with a variety of ditopic aromatic ligands to give rise to the metallo-[2,2]paracyclophanes **205**, which have been characterized by X-ray diffraction study. In all cases, the four Cu-atoms lie in the same plane, defining a rectangle, and due to the short Cu—Cu distances in the dimer clips (2.562—2.745 Å), the π-ligands participate in face-to-face π-interactions (phenyl centroid—centroid distances: 3.4—3.5 Å).

The last type of mixed oligomers incorporating phosphole rings are ethenyl- and ethynyl-based derivatives. Oligomers and polymers consisting of alternating aromatic building blocks and either ethenyl or ethynyl units (e.g. PPV, oligo(thienylenevinylene)s,[101a−c] poly(*para*-phenylene-ethynylene)s,[9e,101d−f] etc.) have found numerous applications in the fields of OLEDs, OFETs, solar cells, nonlinear optics, sensors, polarizers for liquid crystal displays, etc. Furthermore, the controlled synthesis of aromatic-ethynyl chains is driven by the need for molecular wires for the construction of a variety of nanoarchitectures.[101,102] Surprisingly, very few derivatives incorporating phosphole rings linked by a double or a triple bond have been reported to date. Once again, this is mainly due to the fact that the synthetic routes, especially metal-catalyzed C—C coupling reactions involving aromatic building blocks, are not efficient with phospholes. For example, neither 2-bromo-5-iodophosphole (**206**) nor its dibromo analogue **150** undergoes Stille-type coupling reactions with 1-stannyl-alkynes, while the Sonogashira coupling of **206** with phenylacetylene afforded derivative **207** in only 10% yield (Scheme 42).[103a]

The key to the synthesis of such target ethynyl- and ethenyl-phosphole derivatives is the mono- and dilithiation of 2,5-dibromophosphole **150**. The intermediate 2-lithio-5-bromophosphole reacts with arylsulfonylacetylene **208a**

(Scheme 42) to give derivative **207**, which can be converted into the α,α′-di(acetylenic)phosphole **208** according to a similar general strategy.[103a] Although the yields of these reaction sequences are rather modest (typically around 30%), this synthetic approach also allows the stepwise preparation of derivative **211** from **150** by employing trimethylsilyl-protected alkyne **208b** (Scheme 42).[103a] Disappointingly, the modest yields of this overall methodology preclude its use for the preparation of longer oligomers or polymers starting from **150** or **210**. X-ray diffraction analysis of the model compound **209** revealed that the C—C linkages between the P-heterocycle and the C≡C moieties are rather short [1.423(3)−1.416(3) Å].[103a] These data suggest that the endocyclic dienic π-system of the phosphole unit is efficiently conjugated with the two acetylenic substituents. The P-atom adopts a pyramidal geometry, and the P—C bond distances are typical for P—C single bonds [1.815(2)− 1.821(2) Å]. Hence, as observed for 2,5-diheteroarylphospholes, the lone pair of the P-atom does not interact with the π-system.

To date, only the simplest member of the oligo(phospholylenevinylidene) family, i.e. two phosphole rings linked by a ethenyl bridge, is known.[103b] This compound can be obtained in high yield, as the *E* isomer, by a McMurry coupling involving aldehyde **212** (Scheme 42). Note that the use of Ti-salts is compatible with the presence of σ^3-P centers. However, no photophysical data of the orange mixed phosphole-ethenyl derivative **213** have been reported. Note that 1,2-bis(phosphacymantrenyl) alkenes have also been prepared using McMurry coupling.[103c]

In conclusion, synthetic strategies are available for the synthesis of low molecular weight, well-defined mixed oligomers incorporating phosphole moieties. Comparison with related derivatives containing thiophene or pyrrole rings has shown that the introduction of the P-heterocycle furnishes these systems with unique properties (e.g. low aromaticity, reactive heteroatom, σ−π hyperconjugation, etc.) and a considerable scope for creating structural diversity. Significantly, the mixed phosphole-based oligomers described in this section are more than simple model molecules, as some of these compounds have already been used as active layers in OLED devices. These results prove that there are no inherent difficulties associated with the development of phosphole-based conjugated materials that possess optoelectronic functions. Furthermore, they clearly demonstrate that exploiting the reactivity of the P-center of phosphole-derived oligomers could provide a powerful tool for both optimizing and developing optoelectronic materials for the future.
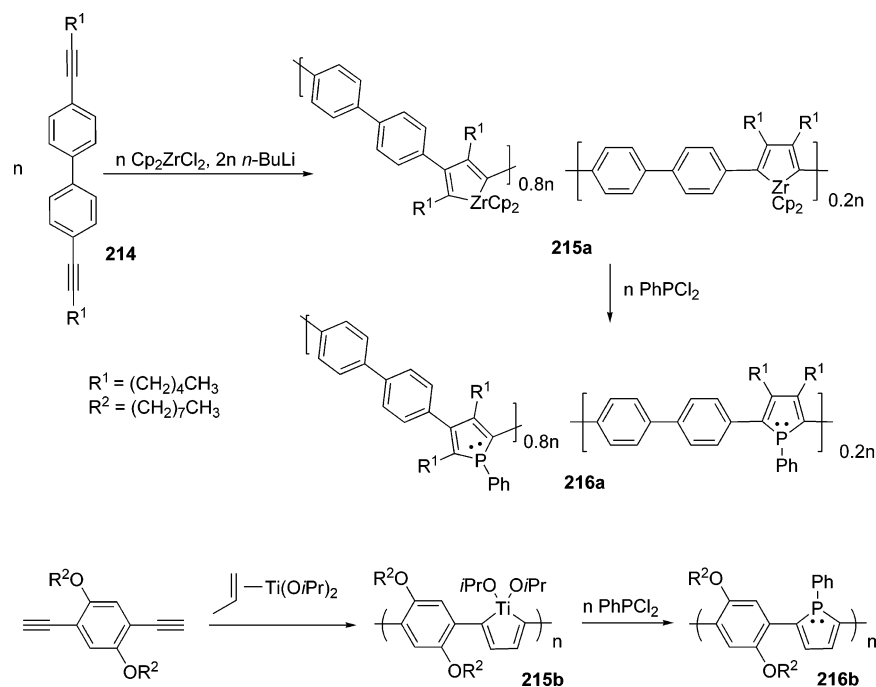
4.4. Mixed Polymers

To date, no homopolymers based on the phosphole motif are known. In contrast, three types of phosphole-containing copolymers have been reported. The first to be prepared was the biphenyl-phosphole derivative **216a** obtained by Tilley

Scheme 42

R^1 = Me
R^2 = p-CH$_3$C$_6$H$_4$ or t-Bu
R^3 = Me$_3$Si

Scheme 43
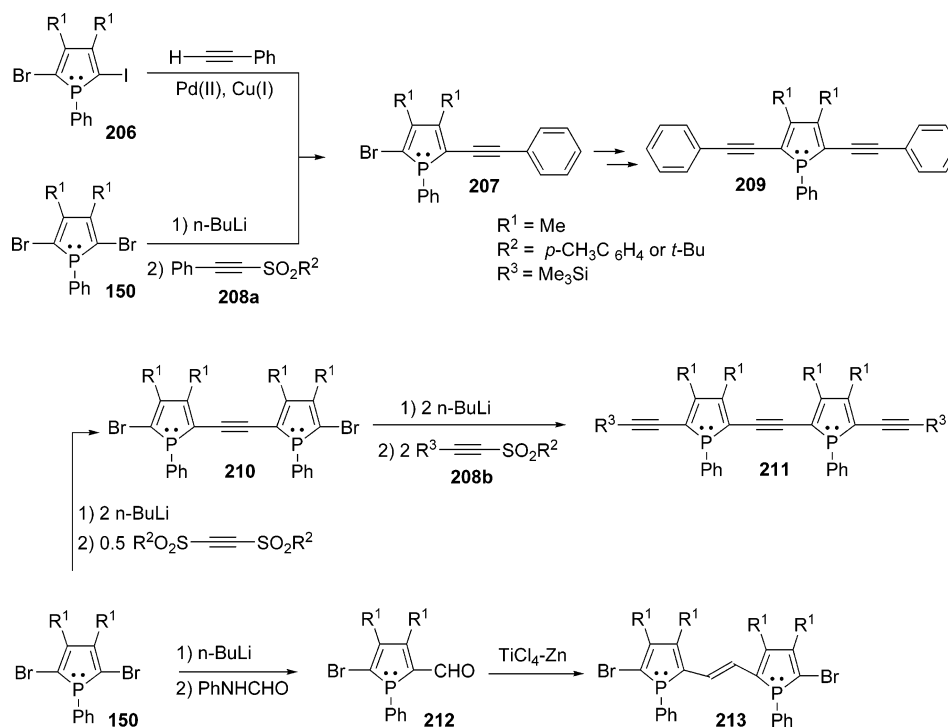
R^1 = (CH$_2$)$_4$CH$_3$
R^2 = (CH$_2$)$_7$CH$_3$

and co-workers using the Fagan–Nugent methodology (Scheme 43).[104a] Its synthesis involved the oxidative coupling of rigid diynes **214** with zirconocene, which proceeded in a nonregioselective way affording an 80:20 isomeric mixture of 2,4- and 2,5-connected metallacycles, respectively, in the polymer backbone of **215a** (Scheme 43). The reactive zirconacyclopentadiene moieties can subsequently be converted to the desired phospholes, by adding dihalogenophosphine (Scheme 43), or to a range of other structures including dienes and benzene rings.[104] The biphenyl-phosphole co-polymer **216a** is isolated as an air-stable and soluble powder exhibiting a rather high molecular weight (M_w = 16 000; M_n = 6200) according to GPC analysis. Although multi-

nuclear NMR spectroscopy and elemental analysis support the proposed structure, the presence of a small number of diene defects is very likely. Polymer **216a** exhibits a maximum absorption in its UV–vis spectrum at 308 nm with a λ_{onset} value of 400 nm. These figures are consistent with a relatively high optical band gap, a feature probably due to a preponderance of cross-conjugated segments.[104a] Interestingly, macromolecule **216a** shows photoluminescence; it emits in the bluish-green region of the spectrum (470 nm) with a quantum yield of 9.2×10^{-2}.

Phosphole-aryl polymer **216b** with a regioregular back-bone (2,5-linkages) was recently prepared by Tomita et al. using the titanacyclopentadiene-containing precursor **215b**

Chart 17. Thienyl Capped Monomers Used in Electropolymerization

188c: Y = O; **189c**: Y = S   **190c**   **199a**
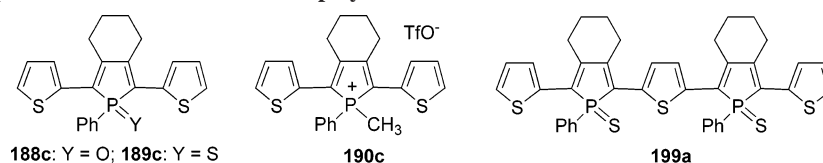
Table 5. Optimum Electropolymerization Potentials of Monomers 188c, 189c, and 190c (Chart 17), p-Doping and n-Doping Potential Ranges (V), and Photophysical Data for the Corresponding Dedoped and Doped Polymers

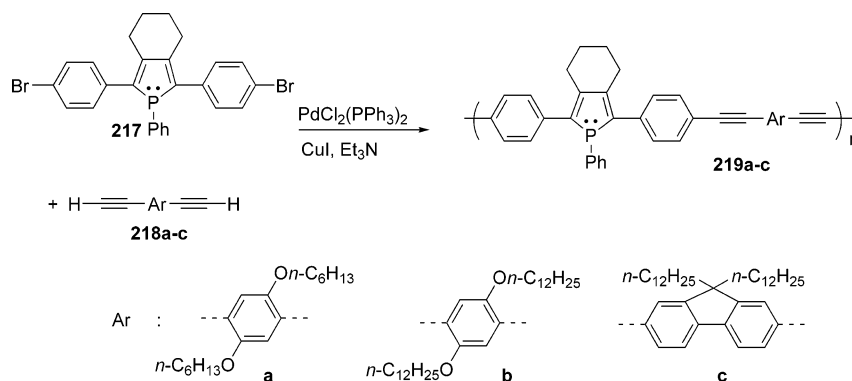|	$\lambda_{max}/\lambda_{onset}$	$E_{pol}{}^a$		p-doping^a	n-doping^a	λ_{max}	λ_{onset}
188c	434/500	1.10	poly(**188c**)	0.25 → 0.60	−1.40 → −1.92	568	780
189c	432/496	1.15	poly(**189c**)	0.30 → 0.65	−1.80 → −2.42	529	750
190c	442/528	1.20	poly(**190c**)	0.40 → 0.70	−0.60	627	905

^{a} Potentials referred to ferrocene/ferrocenium.

Scheme 44

(Scheme 43).[104c] Polymer **216b** shows a λ_{max} at about 500 nm and an emission at 600 nm. The relatively high value for λ_{max} supports the π-conjugated character of phosphole-containing polymer **216b**.

The best developed route to phosphole-containing polymers to date is the electropolymerization of thienyl-capped monomers, a process which involves the generation and coupling of radical cations.[1] Although this methodology is of great general interest for the preparation of electroactive materials based upon thiophene or pyrrole monomers, it suffers from some significant drawbacks. The electrochemically prepared polymers are often insoluble, especially with monomers lacking solubilizing substituents, preventing comprehensive analysis by NMR or GPC.[1] The phosphole-containing monomers that have proven to date to be the most successful ones for electropolymerization processes are depicted in Chart 17. σ^3,λ^3-Phosphole monomers (i.e. **170**, Scheme 33 and **187c**, Scheme 36) have also been subjected to electropolymerization. However, in the case of **170**, the process is not efficient, probably due to side reactions involving the nucleophilic P-atoms and the corresponding intermediate radical cations. Furthermore, it is likely that the P-atoms of the "as-synthesized" films obtained are protonated, at least partially, as the electropolymerization process generates protons.[68] It is noteworthy that no anodic electropolymerization process was observed with thienyl-capped 1,1'-diphosphaferrocene **193c** (Scheme 37) due to the fact that, as usually observed for phosphaferrocenes,[80e,105] the HOMO of this compound has an essentially pure metal character.

2,5-(Dithienyl)-σ^4-phosphole monomers **188c**, **189c**, **190c**, and **199a** (Chart 17) readily afford insoluble, electroactive materials.[68,88b,94] The optimum polymerization potential E_{pol}, obtained by chronoamperometric investigations, depends on

the nature of the P-moiety (Table 5). It is difficult to establish the degree of polymerization and the microstructure of these materials due to their insolubility, which prevents GPC analysis and standard spectroscopic studies. The polymers prepared with neutral phospholes **188c** and **189c** exhibit p- and n-doping characteristics with fairly good reversibilities (>70%). Cationic poly(**190c**) also exhibits a reversible p-doping, but its electroactivity dramatically decreased upon reduction. It is noteworthy that these doping processes appear at lower potentials than those of the corresponding monomers, suggesting that the electroactive materials possess much longer conjugation pathways and smaller band gaps than the monomers. This is confirmed by the fact that the values of λ_{onset} for the dedoped polymers were considerably red-shifted compared with those observed for the corresponding monomers (Table 5).[68] A remarkable feature is that the electrochemical (doping range) and optical properties (λ_{max}, λ_{onset}) of these materials obtained by electropolymerization depend on the nature of the phosphorus moiety (Table 5). The electropolymerization of monomer **199a** (Chart 17) also leads to an electroactive material possessing good reversible p-doping behavior.[94] The doping range (0.22/0.62 V) and λ_{max} of poly(**199a**) are comparable to those of poly(**189c**), as expected from their similar structures.

The first well-defined, π-conjugated polymer featuring phosphole rings was obtained by Chujo et al. using the Heck−Sonogashira coupling of bromo-capped 2,5-(diphenyl)phosphole **217** with the diynes **218a−c** (Scheme 44).[106a] Note that the preparation of 2,5-(diaryl)phospholes of type **217** according to the Cu-modified Fagan−Nugent method was recently patented.[106b] Macromolecules **219a−c**, featuring free σ^3-phosphole moieties, are isolated in moderate to low yields as soluble powders, with low degrees
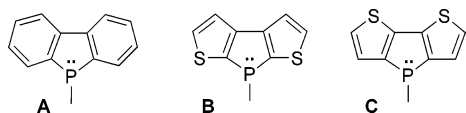
Chart 18. Dibenzo- and Dithieno-phosphole Moieties

Table 6. Photophysical Data for Benzophosphole Derivatives

	$\lambda_{max}{}^a$ (nm)	log ϵ	$\lambda_{em}{}^a$ (nm)	$\phi_f{}^a$ (%)	$Ep_{1/2}{}^b$ (eV)
220b	332	2.9	366	4.2	−1.93
220c	330	2.9	366	0.2	−1.92
220d	333	3.0	366	13.4	−1.80[c]

[a] Measured in CH_2Cl_2, fluorescence quantum yield relative to quinine sulfate. [b] In CH_2Cl_2, referenced to SCE. [c] Ep_c.

of polymerization, ranging from 7 for **219c** to 15 for **219a**. The UV−vis absorptions of **219a−c** are slightly red-shifted in comparison to that of 2,5-diphenylphosphole, indicating the effective expansion of the π-conjugated system. The emission properties of these macromolecules depend on the nature of the comonomer. Green and blue emissions are observed for **219a,b** and **219c**, respectively.[106a] However, the quantum yields in chloroform solution are rather modest (9−14%).
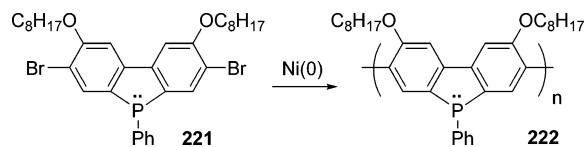
In summary, for the most part, polymers incorporating phosphole units are still rare. However, the work described above demonstrates that they are accessible by a number of diverse synthetic routes including organometallic coupling or electropolymerization processes. The general property/structure relationships established using well-defined small oligomers have been shown to be valid for the corresponding polymeric materials.

4.5. Dibenzo- and Dithienophosphole Derivatives

Dibenzophospholes **A** and dithienophospholes **B** and **C** (Chart 18) do not display the typical electronic properties and reactivity patterns of phospholes, since the dienic system is incorporated in the delocalized benzene or thiophene sextet.[61,66a,107a] In fact, these building blocks have to be regarded as nonflexible diarylphosphanes or as P-bridged diphenyl or dithienyl moieties.

Dibenzophosphole **A** was in fact the first type of phosphole to be prepared.[107c] However, it is only very recently that the photophysical and electrochemical properties have been studied and that dibenzophospholes have been used as a building block for the preparation of π-conjugated systems. In contrast to persubstituted σ^3,λ^3-diarylphospholes that are air-stable derivatives (vide supra), σ^3,λ^3-dibenzophosphole **220a** gives the corresponding oxide **220b** (Table 6) upon exposure to air in the solid state. Its oxygen sensitivity precludes **220a** from being used as a material for optoelectronic applications. Cyclic voltammetry (CV) revealed reduction processes occurring at similar potentials for the three compounds **220b−d** (Table 6).[91b] The reduction processes are reversible for compounds **220b** and **220c** and irreversible for the gold complex **220d**. No oxidation peak was observed under these experimental conditions. The UV−vis spectra of dibenzophospholes **220b−220d** are very similar; they

Scheme 45

Chart 19. P-Chiral σ^3-Dibenzophosphole Derivatives

223a: Y = lone pair
223b: Y = O
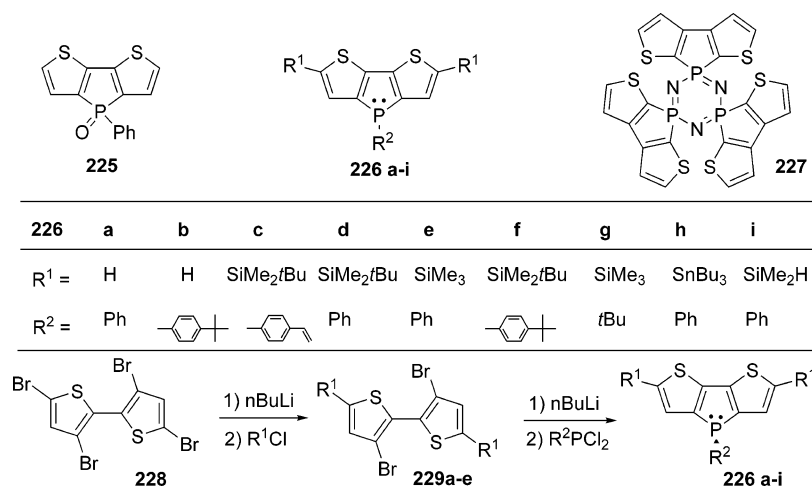
R^1 = CH_3, C_2H_5
R^2 = H, CH_3
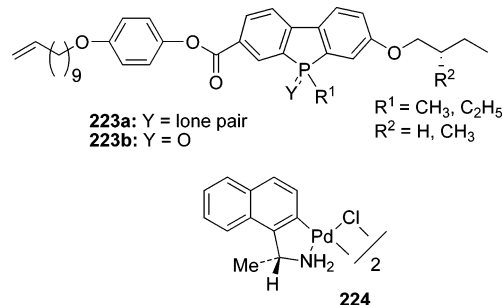
show weak absorptions around 330 nm (Table 6). These absorptions in the UV region reveal that these derivatives possess large optical HOMO−LUMO gaps, as observed for structurally related fluorenes.[108] This feature is in accordance with the view that dibenzophospholes have to be considered as P-bridged biphenyl derivatives. The three dibenzophosphole derivatives **220b−220d** are photoluminescent and emit in the UV region of the optical spectrum at similar wavelengths (Table 6). The quantum yields depend on the nature of the P-modification, with the gold(I)-complex **220d** exhibiting the highest value in solution (Table 6). In marked contrast, in the solid-state, only photoluminescence (PL) from the oxodibenzophosphole **220b** can be detected (λ_{em} = 370 nm). Attempts to use **220b** as a material for OLEDs in different device configurations failed.[91b]

Polymer **222**, based on the σ^3-dibenzophosphole moiety, was obtained with a rather high polydispersity ($M_n = 5 \times 10^2$; $M_w = 6.2 \times 10^3$; PDI = 12.4) by Ni-catalyzed homocoupling of derivative **221** (Scheme 45).[109] The presence of σ^3-P centers, which are potential donor sites for the Ni-catalyst, does not hamper the C−C bond formation. Macromolecule **222** shows photoluminescence in the solid state (λ_{em} = 516 nm), a property of potential interest for the development of OLEDs.[109]

Resolution of chiral σ^3-benzophosphole **223a** (Chart 19) was achieved by column chromatographic separation of the diastereomers obtained following its coordination to the chiral cyclometalated palladium(II) complex **224**.[110a,b] The corresponding P-chiral dibenzophosphole oxide **223b** (Chart 19) shows liquid crystalline behavior. Notably, the presence of a stereogenic P-center is sufficient to generate a chiral cholesteric phase.[110c]

The exploration of phosphole-containing bithiophene systems is of interest due to their rigidified, planar structure, which inherently affords smaller HOMO−LUMO gaps for the materials relative to, for example, simple polythiophenes, where twisting from planarity can easily disrupt conjugation.[111,112] Although the first phosphorus-bridged bithiophene **225** (Scheme 46) was published by Lampin and Mathey in 1974,[113] trivalent phosphorus species **226** were only reported in 2003 by Baumgartner.[114] In 2004, Cristau and co-workers published a cyclophosphazene featuring isomeric dithieno-[2,3-*b*:3′,2′-*d*]phosphole moieties **227** (Scheme 46), but no photophysical properties were reported.[115]

Scheme 46

226	a	b	c	d	e	f	g	h	i
R^1 =	H	H	SiMe$_2$tBu	SiMe$_2$tBu	SiMe$_3$	SiMe$_2$tBu	SiMe$_3$	SnBu$_3$	SiMe$_2$H
R^2 =	Ph	⟨⟩	⟨⟩	Ph	Ph	⟨⟩	tBu	Ph	Ph

A variety of dithieno[3,2-*b*:2′,3′-*d*]phospholes **226a−i** are accessible in a two-step reaction starting from 3,3′-5,5′-tetrabromo-2,2′-dithiophene **228** (Scheme 46).[116a−c] The first step involves the functionalization of the thiophene rings. The central phosphole ring is subsequently generated by reaction of the functionalized bithiophenes with a variety of dichlorophosphanes.

An X-ray single-crystal structure determination of the planar dithienophosphole **226a** revealed a high degree of π-conjugation for the anellated ring system, with significantly elongated C−C double bonds and shortened C−C single bonds.[116a] The endocyclic P−C bonds are only slightly shorter than the respective exocyclic P−C bonds, indicating that the strongly pyramidal phosphorus center is not an integral part of the π-system. The favorable properties of dithienophospholes **226a−i** are supported by their small optical band gaps of ∼3.0−3.2 eV, as estimated from the onsets of their UV-absorptions,[116d] and very intense blue emissions at 405−425 nm with exceptionally high PL quantum yield efficiencies (ϕ_{PL} = 0.56−0.90; see Table 7). DFT calculations at the B3LYP/6-31G* level provide frontier orbitals for the parent dithienophosphole (**226j**; R^1 = R^2 = H) that are similar to the orbitals of cyclopenta[1,2-*b*:3,4-*b*′]dithiophene.[116b] The HOMO is an antibonding combination of the thiophene-HOMOs, and at the phosphole ring, it exhibits a large similarity to the parent phosphole-HOMO. The LUMO is a bonding combination of the thiophene-LUMOs, with some contribution from the σ_{PH}*-MO, similar to the phosphole-LUMO at the central five-membered ring. Both orbitals are well delocalized over the entire molecule, describing the dithieno[3,2-*b*:2′,3′-*d*]phosphole as an entity. While the HOMO has a nodal plane through the phosphorus atom and its substituent, the LUMO has some contribution of the σ*(P−R^2) orbital. These results indicate that the LUMO is mainly affected by chemical modifications carried out at the phosphorus center to further reduce the band gap of the materials.

The nucleophilic phosphorus atom of **226a−i** can react with oxidizing agents, Lewis acids, or a variety of transition metal complexes based on Au, Fe, Pd, Pt, Rh, and W, allowing for efficiently tuning the electronic properties of the dithienophosphole materials (see Table 7) by synthetically facile modifications to afford **230−240** (Scheme 47).[116b,c,e] The functionalization with a gold(I) moiety (**236e**), for example, has been found to significantly affect the absorption properties of the strongly blue luminescent dithienophosphole
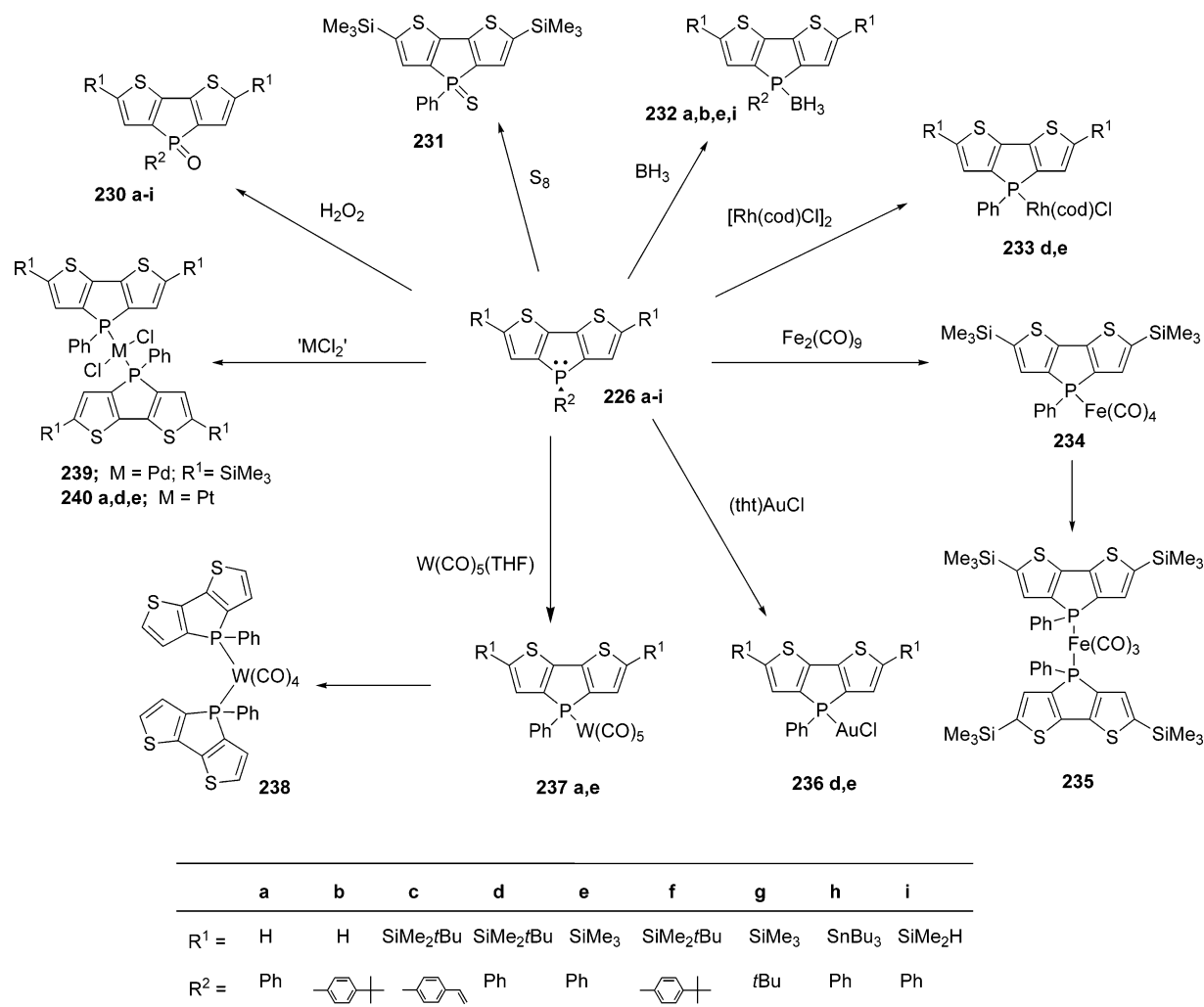
Table 7. Optoelectronic Features of Selected Dithienophospholes

compd	$\lambda_{abs}{}^a$ (nm)	$\lambda_{em}{}^b$ (nm)	$\phi_{PL}{}^c$	ref
226a	338	415	0.78	116a
226c	352	422	0.69	116a
226d	364	422	0.79	116b
226e	344	422	0.60	116b
226h	357	427	0.69	116b
226i	366	420	0.81	116c
230a	366	453	0.57	116a
230c	379	461	0.58	116a
230h	379	463	0.69	116b
230i	383	457	0.58	116c
231	374	460	0.56	116b
232a	346	424	0.69	116a
232e	355	432	0.55	116b
232i	376	447	0.63	116c
233d	396	461	0.66	116e
236d	311, 406	445	-:-	116e
236e	290, 375	445	0.56	116e
239	384	470	0.61	116b
241	398	452	0.53	116f
242	415	485	0.55	116f
243	352	424	0.74	116a
244 (E = O)	374	458	0.57	116a
245	378	460	0.56	116c
246	353, 393	459	0.57	116c
247	456, 502	555	-:-	116b

^{a} λ_{max} for excitation in CH$_2$Cl$_2$. ^{b} λ_{max} for emission in CH$_2$Cl$_2$. ^{c} Photoluminescence quantum yield (±10%), relative to quinine sulfate (0.1 M in H$_2$SO$_4$ solution); excitation at 365 nm.

236d (R^1 = tBuMe$_2$Si), resulting in two very distinct, narrow absorption processes at λ_{abs} = 311 nm (n(Au) → π*) and 406 nm (π → π*).[116e] Noteworthy is the fact that, in all the above-described functionalizations, the electron affinity of the phosphorus center is significantly increased, leading to low-lying LUMO levels. This is further supported by the wavelength maxima for absorption and emission, that are red-shifted upon complexation or oxidation, respectively ($\Delta\lambda_{abs}$ = 10−40 nm; $\Delta\lambda_{em}$ = 10−50 nm), as well as the reduced optical band gaps of ∼2.8−3.1 eV.[116d] In addition to that, a functionalization of the thiophene unit, for example, via silyl groups (**226a → 226e**), allows further tuning of the luminescence properties of the system with slight red-shifted absorptions and emissions ($\Delta\lambda_{max}$ ∼ 5−10 nm). The electronic properties can be fine-tuned by variation of the substituents at the phosphorus and silicon centers. Via this approach, the maximum wavelength for excitation (λ_{abs}) can be controlled to adjust the Stokes shift of the material selectively. The wavelength for emission (λ_{em}) remains

Scheme 47

|	a	b	c	d	e	f	g	h	i
R^1 =	H	H	$SiMe_2tBu$	$SiMe_2tBu$	$SiMe_3$	$SiMe_2tBu$	$SiMe_3$	$SnBu_3$	$SiMe_2H$
R^2 =	Ph			Ph	Ph		tBu	Ph	Ph

Scheme 48
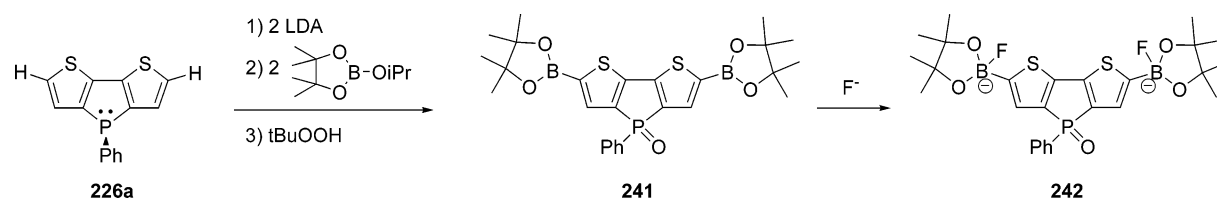
unaffected in that case (Table 7). Very importantly, the optoelectronic features of the dithienophospholes have also been predicted by means of time-dependent DFT (TD-DFT) calculations on the B3LYP/6-31G* level with an excellent match, allowing for a streamlined design for future materials.[116b]

Boryl-functionalized systems such as **241**, that are potentially suitable for cross-coupling reactions, can be obtained by treatment of the unsubstituted dithienophosphole **226a** with lithium diisopropylamide and subsequent reaction with a boronic ester (Scheme 48).[116f] Although cross-coupling reactions have not been reported to date for these compounds, it has been found that the dithienophosphole oxide **241**, in particular, represents a very sensitive and selective sensory material for the fluoride ion. The fluoride-triggered response manifests itself in a new emission at $\lambda_{em} = 485$ nm for **242** (cf.: 452 nm for **241**), shifting from blue to bluish-green, that can be noticed with the naked eye. This shift in the fluorescence emission can also be detected down to the

micromolar scale; other halides do not effect any fluorescence changes.[116f]

Polymeric systems employing the dithieno[3,2-*b*:2′,3′-*d*]-phosphole moiety have been accessed via several different approaches so far (Scheme 49).[116a−c] The first strategy involves a side chain functionalization of polystyrene with pendant dithienophospholes leading to strongly blue fluorescing polymers **243** and **244**.[116a] Copolymers with varying ratios of styrene/dithienophosphole are readily formed in a stable free radical protocol with styryl-functionalized dithienophosphole monomer **226c**, leading to high molecular weight materials **243** ($R^1 = SiMe_2tBu$; $M_n = 80\,000-150\,000$ g/mol; PDI = 1.8−2.5). The polymers exhibit optical properties that match the values for the corresponding monomer **226c** perfectly; they show maximum wavelengths for absorption at $\lambda_{abs} = 352$ nm and emission at $\lambda_{em} = 422$ nm with a very high PL quantum yield efficiency ($\phi_{PL} = 0.75$). The same is true for the reactivity of the polymers; the phosphorus center can be functionalized in complete
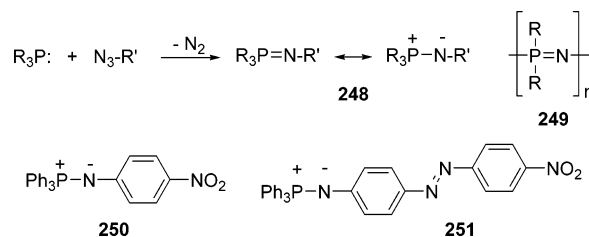
Scheme 49

Scheme 50
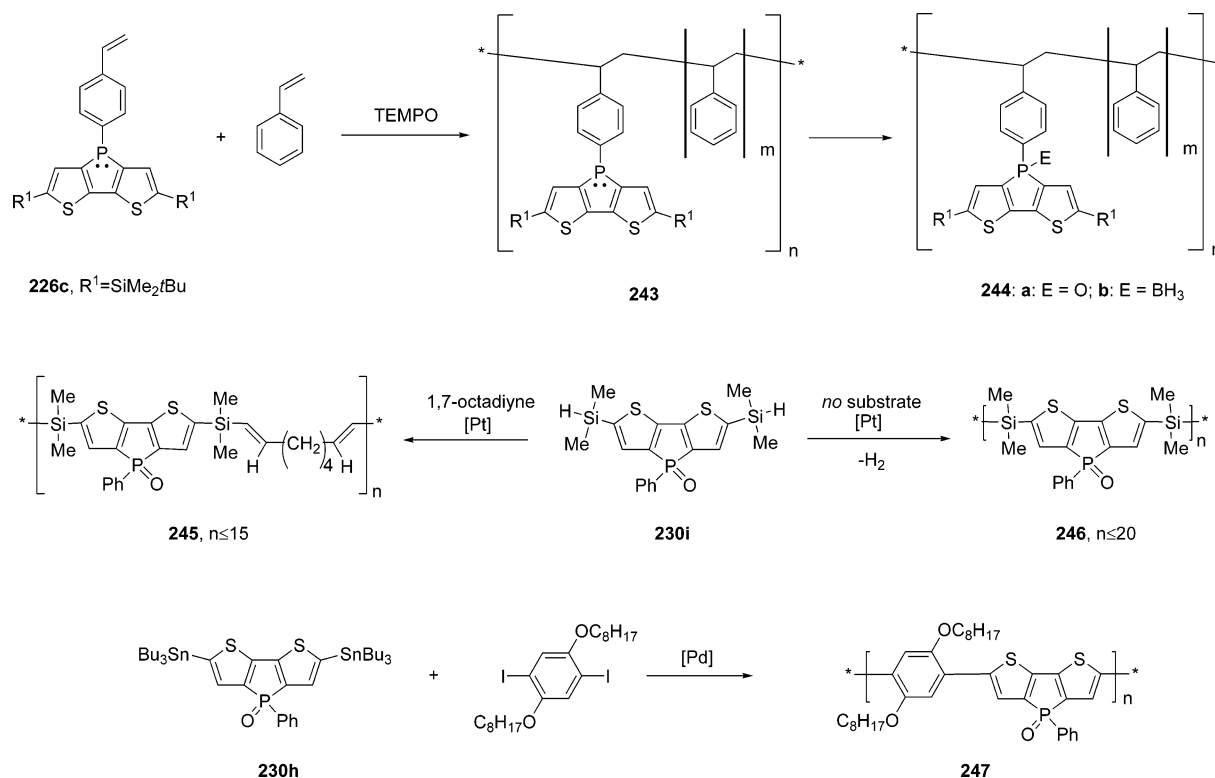
analogy to the monomers/model compounds, leading to polymers **244**, exhibiting similar optical properties to those of the corresponding monomers.[116d]

The Si−H functional groups of the corresponding dithienophospholes (e.g. **230i**) can be used to access polymeric systems via two different reaction pathways (Scheme 49).[116c] The treatment of a mixture of the Si−H-functionalized dithienophosphole **230i** and 1,7-octadiyne affords polymer **245** ($n \le 15$) via Pt-catalyzed hydrosilation, whereas, in the absence of the alkyne, a dehydrogenative homocoupling of the dithienophosphole moiety affords the disilanylene-bridged polymer **246** ($n \le 20$). The latter is the first example of a quantitative dehydrocoupling of *tert*-silanes. The optical properties of both polymers are similar with respect to emission (λ_{em} = 460 and 459 nm) and relate to those of the monomeric dithienophosphole oxides **230a−i**. The varying substitution pattern at the silicon centers, however, induces some altered absorption properties for the two polymers (**245**: λ_{abs} = 378 nm; **246**: λ_{abs} = 353 (sh), 393 nm). The presence of a second, strong transition for the Si−Si-linked polymer **246** supports an electronic interaction of this bridge with the dithienophosphole moiety. In a variation of the approach to generate dithieno[3,2-*b*:2′,3′-*d*]phosphole-based polymers, materials with an exclusively π-conjugated backbone are of particular interest, as the resulting oligomers/polymers might be expected to exhibit semiconducting properties that would open up even greater possibilities for potential applications in organic electronics. A synthetic protocol via Stille coupling, starting from a suitable tin-functionalized dithienophosphole oxide **230h**, provides polymer **247** with strongly red-shifted absorption and emission maxima ($\Delta\lambda_{abs}$ = 120 nm; $\Delta\lambda_{em}$ = 110 nm) (Scheme 49).[116b] However, the reduced solubility of the material has prevented a comprehensive study of its properties so far.

The various series of conjugated polymeric systems based on dithienophospholes that have been prepared are promising candidates for optoelectronic applications since their optical properties can be easily varied in a variety of different ways (chemical modifications of the P center, variation of the thienyl and P-substituents, etc.). Furthermore, their potential scope for a range of applications is broadened by the possibility of incorporating these conjugated derivatives into polymeric systems either as constituents of the main polymer backbone or as side-chains.

5. π-Conjugated Materials with Phosphorus Multiple Bonds

5.1. Iminophosphorane-Based Materials

Iminophosphoranes (phosphazenes) **248**, compounds with the general structure $R_3P=N−R'$, are ylides possessing a highly polarized P=N bond. They are easily prepared by the so-called Staudinger reaction, which involves treating a tertiary phosphane with an organic azide (Scheme 50).[117] Corresponding poly(phosphazenes) **249** are a well-established class of inorganic materials that has been studied for over 40 years.[118] They show a variety of useful features (e.g. flame-retardancy, etc.); however, there is no evidence for properties in terms of organophosphorus π-conjugated materials. Poly(phosphazenes) are also referred to as "inorganic rubber" and will therefore not be considered further for this review.

Chart 20. π-Conjugated Bis(iminophosphorane)s
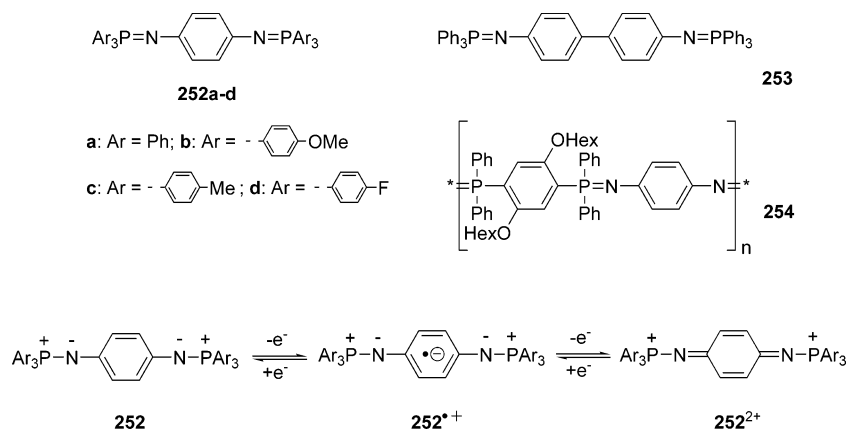
However, with regard to optimizing push−pull NLO materials, mono(phosphazenes) have been investigated as a new class of electron donors.[119] The $\mu\beta$ product values of the iminophosphoranes **250** and **251** (Scheme 50) are 310 $\times 10^{-48}$ esu and 1100×10^{-48} esu, respectively. These values are superior to that for p-nitroaniline (118×10^{-48} esu), as expected from the significant donor ability of the imino-phosphorane moiety, but they are still modest compared to those of other efficient NLO-phores.[120]

Lucht and co-workers have investigated the electron-donating properties of such iminophosphorane moieties in π-conjugated materials in detail to better understand the nature of the P=N-bond in these systems as well as the degree of overlap with adjacent π-systems.[121,122] Their strong donor character has put the conjugated bis(iminophospho-ranes) in the focus of organic electronics, as they might be utilized as efficient hole transport materials. Monomeric (**252**, **253**) as well as polymeric materials **254** (Chart 20) are accessible by the Staudinger protocol using appropriate diazido precursors and triarylphosphanes, respectively, to afford the materials in good to high yields. Investigation of the electronic properties by cyclic voltammetry of the monomeric bis(iminophosphorane) **252a** revealed the high electron-donating character with two reversible single-electron oxidations at 0.043 and 0.547 V (vs SCE). This supports the formation of stable radical cationic and di-cationic species. The low oxidation potential of **252a** indicates a better electron donor capability than tetrathia-fulvalene (TTF). Chemical oxidation by addition of 7,7,8,8-tetracyano-p-quinodimethane (TCNQ) is readily achieved, yielding a reflective black powder in the solid state or a green solution in CHCl3, respectively, due to the formation of [**252a**•+][TCNQ•−], as confirmed by UV−vis spectroscopy (TCNQ•−, 650−900 nm; **252a**•+, 450−620 nm).

DFT calculations on the B3LYP/6-31G* level revealed that the stepwise, single-electron oxidation of the bis-(iminophosphoranes) **252** occurs primarily from the N lone pairs and the *ipso*-carbon atom π-orbitals.[122] Upon further oxidation to the dicationic species **252**²⁺, the quinonediimine structure develops (Chart 20). The calculations indicate little change on the charge on the phosphorus moieties (**252** → **252**²⁺), suggesting that the P=N bonds in these materials are highly polarized with an almost complete charge separa-tion. The presence of the phosphonium groups, however, allows for a π-back-bonding from N into the σ*-orbitals of the PAr3 group to stabilize the central π-conjugated unit and support a potential utility as a hole transport material in organic devices. These observations also explain why the

electronic structure of the materials can efficiently be tuned by variation of the P-aryl substituents. Electron-withdrawing substituents reduce the donor properties of the P=N-units, whereas electron-donating substituents, such as (methoxy)-phenyl (**252b**), significantly stabilize the positive charge on the P-atoms, resulting in even further lowered oxidation potentials (−0.05 and 0.40 V, vs SCE).

## 5.2. Phosphaalkene- and Diphosphene-Based Polymers and Oligomers

Although organophosphorus compounds have been known for more than a century, it was not until the late 1970s that molecular phosphaorganic chemistry experienced a boom due to the discovery of stable low-coordinate species of phos-phorus, including two- (**D**) and three-coordinate (**E**) P(V) and one- (**F**, **G**) and two-coordinate (**H**) P(III) moieties (Chart 21).[123] The chemistry of trivalent low-coordinate phosphorus compounds, in particular, was found to resemble that observed for the corresponding carbon analogues, recently awarding phosphorus the designation: "Phosphorus— the Carbon Copy".[11] This analogy is based upon the fact that phosphorus and carbon exhibit very similar electron acceptor and electron donor abilities, allowing phosphorus compounds to be utilized instead of genuine carbon spe-cies.[11,13] Many of the parallels that exist between C=C (**I**) and P=C (**H**, E = CR2) bonds are due to the similar electronegativities of the two elements (C, 2.5; P, 2.2) and to the fact that, in surprisingly pronounced contrast to the cases of imines, the HOMO of phosphaethylene is the π-bond and not the heteroatom lone pair.[123] As a result, the P=C unit is almost nonpolar and its conjugative properties are comparable to those of the C=C bond.[11,13,123,124] Hence, the chemistry of low-coordinate phosphorus, resembling that of the diagonal relative carbon, has opened a fascinating perspective for the design and synthesis of a large variety of novel compounds.[11b]

In this context, one of the simplest π-conjugated systems incorporating phosphorus that can be imagined would be poly(phosphaalkyne) **255**, the phosphorus analogue of poly-acetylene **256** (Chart 21). Notably, it has been found that phosphaalkynes **257**, lacking sterically demanding R sub-stituents (e.g. R = Ph), can undergo thermally induced polymerization reactions.[11a,b,123] The unsubstituted phos-phaacetylene (HC≡P), as described by Gier already in 1961, was even found "to polymerize slowly at −130 °C and more rapidly at −78 °C to a black solid".[125] However, the resulting "phosphaalkyne" macromolecules feature mainly saturated

Chart 21. Low-Coordinate Phosphorus-Containing Building Blocks
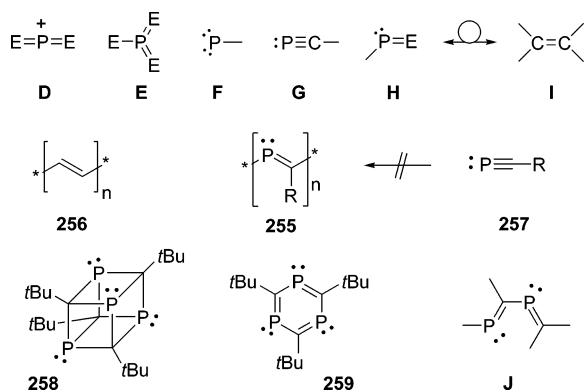
trivalent P-fragments with only some phosphaalkene moieties.[124] In contrast, thermolysis of the more hindered tBuC≡P affords a mixture of a tetraphosphacubane **258** (Chart 21) and other cage compounds.[11a,b,123,126] Alternatively, in the presence of metal complexes, several types of oligomers can be formed, including 1,3,5-triphosphabenzene **259** (Chart 21), tricyclic derivatives, or cage compounds.[11a,b,123,127]

Kinetically stabilized 1,3-diphosphabutadienes **J** are also known,[123,128a] but the formation of oligomers or polymers **255** (Chart 21) is probably hampered by the quite low thermodynamic stability of the P=C π-bond (43 kcal·mol⁻¹ vs 65 kcal·mol⁻¹ for ethylene); for example, HP=CH₂ has a short half-life of 1–2 min and is unstable in the solid state at 77 K.[128] For that reason, incorporation of an aromatic aryl group into the backbone of the polymers appeared as an obvious strategy for increasing the thermodynamic stability of these π-conjugated systems. Furthermore, some steric protection would be provided by the aryl group's substituents, potentially overcoming the kinetic instability of the P=C-moieties. Following this rationale, the first π-conjugated macromolecule containing phosphaalkene subunits was the PPV analogue **260** reported by Wright and Gates in 2002 (Scheme 51).[129a] This compound was prepared by thermolysis of the bifunctional derivatives **261** and **262**, according to a protocol established by Becker for monomeric phosphaalkenes in 1976.[130] It involves a thermodynamically favorable [1,3]-silatropic rearrangement of intermediate acylphosphanes to phosphaalkene moieties (Scheme 51, inset). Polymer **260** is soluble in polar organic solvents and, according to NMR measurements, is obtained as a mixture of Z and E isomers.
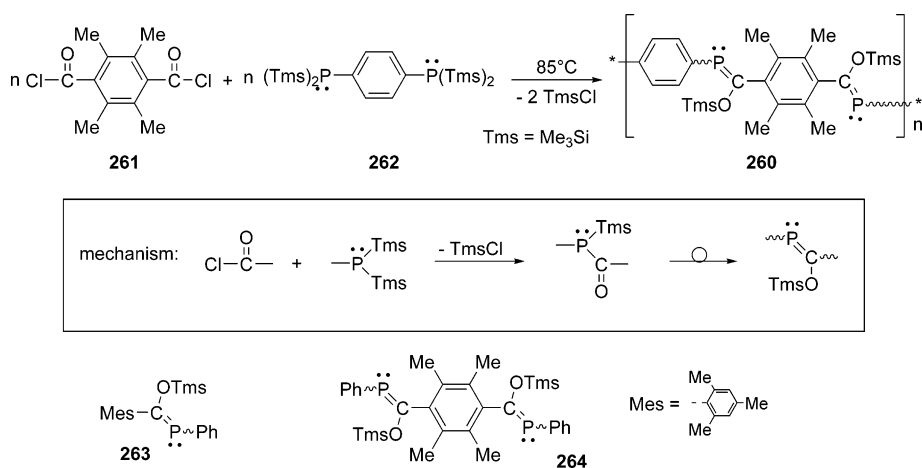
The molecular weights are rather modest, in the range of M_n = 2900–10 500 g/mol (DP = 5–21), as determined by end group analysis. Remarkably, thermogravimetric analysis revealed that this polymer is stable up to 190 °C under an atmosphere of dry helium.[129a]

To verify the molecular structure as well as the electronic properties of the polymer **260**, the corresponding model compounds **263** and **264** (Scheme 51) have also been investigated for comparison.[129a] UV–vis spectroscopy of the models **263** and **264** and the polymer **260**, respectively, indicates a red shift and a broadening of the absorption of the polymer that is consistent with an increased degree of π-conjugation upon chain lengthening (λ_{max}: **263**, 310 nm; **264**, 314 nm; **260**, 328–338 nm). However, this red shift is less pronounced than the one observed for native poly-(phenylenevinylene)s (PPV) ($\Delta\lambda_{max}$ = 120–130 nm), which the authors attribute to conformational nonplanarity in the main chain of **260**, due to the bulky C₆Me₄ groups.[129a] More recently, the same group reported the addition polymerization of phosphaalkene to yield nonconjugated polymers that also exhibit interesting materials properties.[129b,c] However, these materials do not show any π-conjugation and will therefore not be considered in detail. A full paper reporting the scope of the synthesis as well as the properties of π-conjugated PPV-analogue phosphaalkenes was published by Gates et al. after this review was submitted.[129d]

Although several examples of π-conjugated bis(phosphaalkenes) had been known for quite some time, without being the focus of organic electronics,[131] the family of P=C-containing polymers and oligomers was considerably broadened by Protasiewicz and co-workers in 2000.[132] Following the introduction of a highly efficient synthetic strategy based on intermediate "phospha-Wittig" reagents **265** (Scheme 52),[133] obtained by reacting the transient phosphinidene **267** with PMe₃, polymers **268a–d** featuring different π-linkers were readily obtained by reacting dialdehydes **269a–d** with the bulky bis(dichlorophosphane) **270** (Scheme 52).[132a,b] Macromolecules **268a–c** are insoluble materials, but polymer **268d** is soluble and could thus be investigated comprehensively. The polymer exhibits an average 12 phosphaalkene moieties per chain (n = 6), all in the E-configuration, and the molecular weight was estimated to be M_n = 6500 g/mol. Remarkably, although **268d** decomposes slowly in solution, it is stable under air for 1 week in the solid state.[132b] The polymer **268d** exhibits a broad absorption band at λ_{max} = 445 nm that presumably arises from a π–π* transition. This absorption band is significantly shifted from the one observed
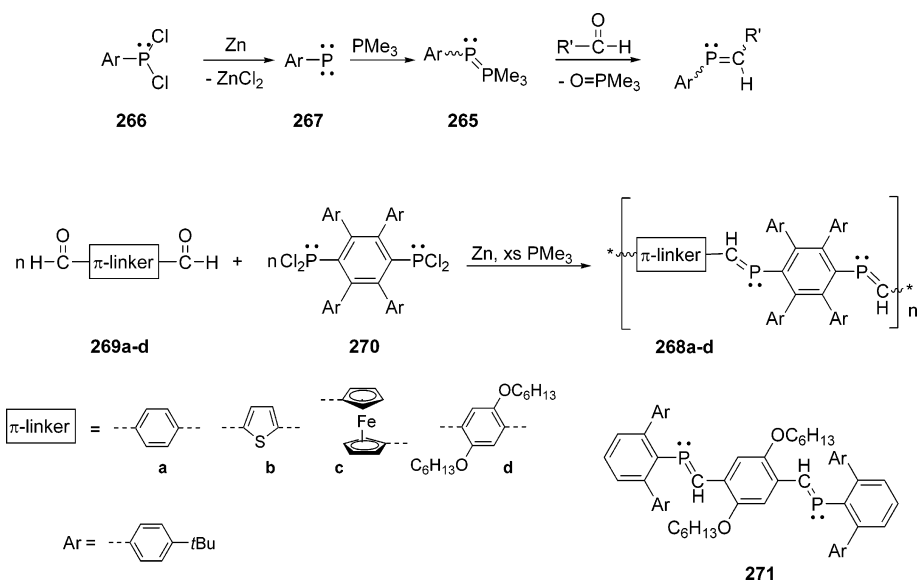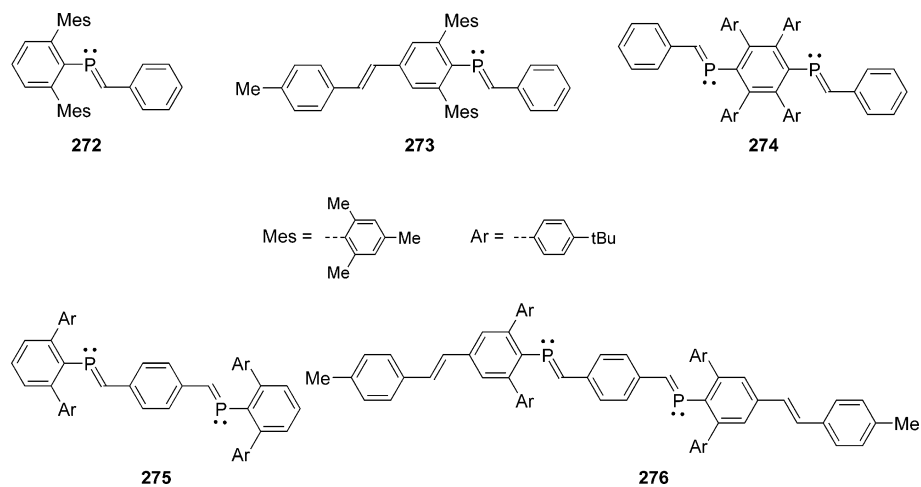
Scheme 51

Scheme 52

**Chart 22. Phosphaalkene-Based Oligo(phenylenevinylene)s (PC−OPV)**

Table 8. Absorption Data (CHCl₃) of Oligomers 272−276 and 282−285 in Comparison to Native Organic Materials[132e]

C=C	317 nm	354 nm	384 nm	385 nm
P=C	**272**: 334 nm	**273**: 341 nm		
		274: 349 nm		
		275: 411 nm		**276**: 417 nm
P=P	**282**: 372 nm	**283**: 398 nm	**284**: 407 nm	**285**: 422 nm

for **260** (λ_{max} = 328−338 nm) but exactly matches the value of the corresponding model diphosphaalkene **271** (λ_{max} = 445 nm, Scheme 52).[132b] Although the UV spectrum of polymer **260** is red-shifted by about 20 nm compared to that of **262** (Scheme 51), it should be mentioned that the bands arising from both polymeric derivatives extend into the visible region with values of the optical end absorption (λ_{onset}: **262**, ~400 nm; **268d**, ~540 nm) which are red-shifted compared to those of the model compounds **262** and **271**. These data suggest that the P=C functions are certainly involved in the π-conjugation, but the data also reveal rather limited effective conjugation path lengths for derivatives **260** and **268d**. This feature could be due to nonplanarity caused by the presence of the bulky aryl units. This is supported by

the X-ray diffraction analysis of compound **274** (Chart 22), showing HCP-phenylene dihedral angles of 71° and 22°, respectively.[132b]

The dramatic impact of such sterically induced noncoplanarity is also clearly reflected by the different values of λ_{max} obtained for compounds **274** and **275** ($\Delta\lambda_{max}$ = 57 nm, Chart 22), which possess the same geometric conjugation path length.[132a] However, the red shift observed upon comparing systems with a similar positioning of the sterically demanding units and increasing conjugation path length (**272** → **276**) strongly supports the participation of phosphaalkene moieties within the conjugated chain (Table 8). Note that polymer **268d** is fluorescent with a broad emission centered around 530 nm,[132b] but the fluorescence intensity is weak

Chart 23. π-Conjugated Diphosphenes

277
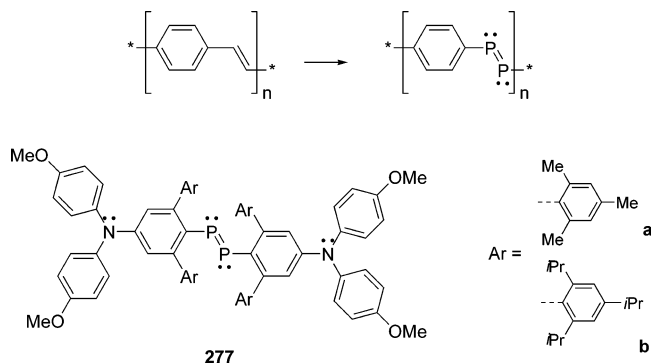
compared to those from its corresponding all-carbon analogues.

Replacement of both vinylic carbon atoms in PPV formally leads to diphosphene-based materials (Chart 23). However, the isolation of conjugated systems featuring P=P units is challenging, since this very reactive moiety needs significantly more steric protection than its phosphaalkene relative.[123,132a] Prior to the work specifically targeting organic electronics, two relevant compounds **277a,b** (Chart 23) have been pioneered by Yoshifuji and co-workers.[134] They display impressive red-shifted absorption spectra [λ_{max}: 460 ($\pi-\pi^*$) and 530 nm (n–π^*)].

Protasiewicz et al. employed the sterically demanding 2,5-dimesitylphenyl substituent in the "second-generation" π-conjugated linker **278** (Scheme 53) in 2004.[132c] The bulky, bidentate fragment with solubilizing alkyloxy groups incorporated was, however, initially used to stabilize P=C units in soluble polymers **279** that were prepared in 76–85% yields via the phospha-Wittig strategy (Scheme 53). As in all materials obtained by this route, the phosphaalkenes adopt an E-configuration, exclusively. Although the degree of polymerization is modest ($M_n = 5000-7300$) with polydispersities varying from 1.9 to 2.3, the polymers display 18–26 "phenylene-vinylene" repeat units. It is commonly established for native OPV materials that some (opto)-electronic properties level off around 10 repeat units, and a similar trend might be expected for the P-analogues such as

279. These derivatives show reasonable thermal stability in the absence of air or water. For example, polymers **279a–b** are unaffected by heating at 140 °C for 6 h under an inert atmosphere.[132c]

Following the successful isolation of stable phosphaalkene-containing polymers **279**, the use of the same substituent for the preparation of a related polymer featuring P=P moieties was attempted. It is known that diphosphenes **280** can be prepared by dimerization of transient phosphinidenes **267** generated by photolysis of phospha-Wittig reagents **265** (Scheme 53, inset).[132d] Photolysis at room temperature or thermolysis (neat, 250 °C, 2 min) of the bifunctional compound **278** does indeed result in the formation of polymer **281** in near quantitative yield (Scheme 53).[132c] This soluble material was characterized by NMR spectroscopy and GPC analysis, which revealed a molecular weight of $M_n = 5900$ potentially sufficient for materials applications (vide supra). In contrast to the polymers **279a–c**, featuring P=C units, the diphosphene-based derivative **281** is not fluorescent, which the authors attribute to fluorescence quenching by interaction with phosphorus lone pairs.[132c] The UV–vis spectrum of **281** shows a $\pi-\pi^*$ transition at $\lambda_{max} = 435$ nm accompanied by an n–π^* transition that is red-shifted to $\lambda_{max} = 481$ nm. The $\lambda_{\pi-\pi^*}$ value for **281** is in the range observed for **279a–c** (416–435 nm) and only slightly blue-shifted compared to that for poly(phenylenevinylene-alt-2,5-dihexyl-oxyphenylenevinylene) with $\lambda_{\pi-\pi^*} = 459$ nm.[135] These data indicate that diphosphene units do support conjugation across extended systems. This assumption is corroborated by the observed red shift within the series of oligomeric compounds **282–285** of increasing chain length (Chart 24) that is also coherent with the phosphaalkene-oligomer series **272–276** (Table 8).[132e]

In a more recent example, Pietschnig and co-workers[136a] as well as Tokitoh et al.[136b] have reported independently the ferrocenylene-bridged bis(diphosphenes) **286** (Chart 24). Incorporation of a ferrocene unit within the π-conjugated system was expected to provide additional electronic (redox) properties that should allow control over the electronic and magnetic properties of the materials. Indeed, UV–vis spectroscopy indicated electronic interactions of the P=P
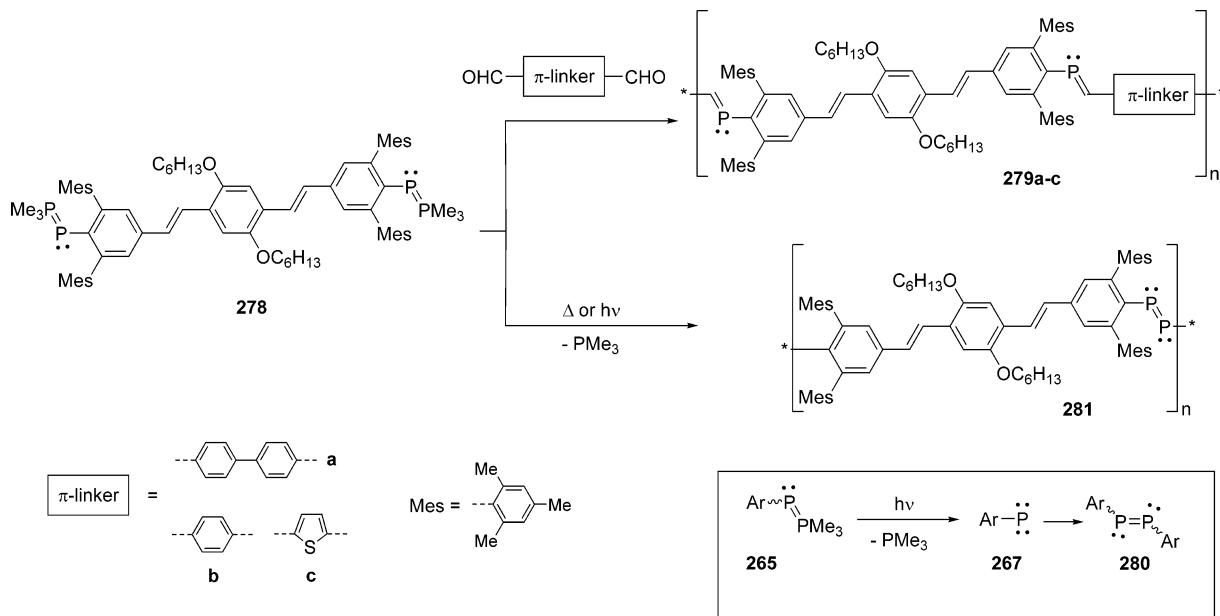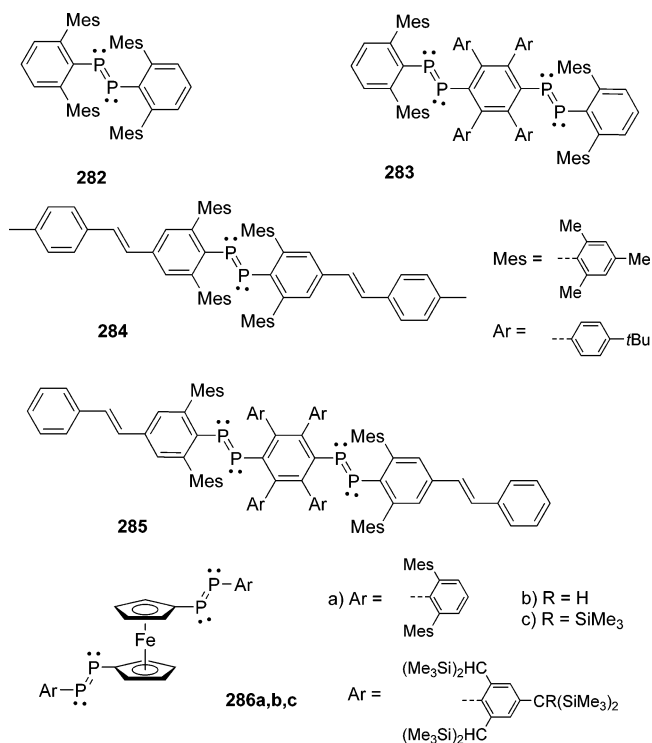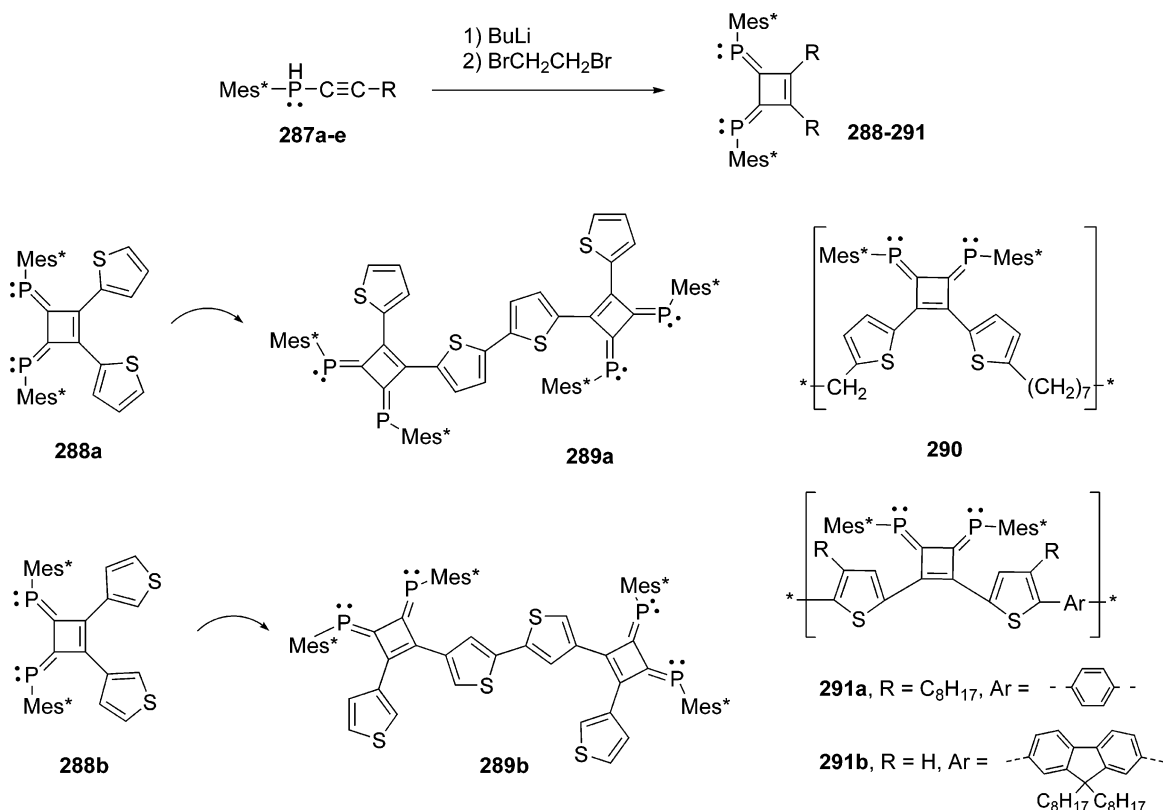
Scheme 53

**Chart 24. Diphosphene-Based Oligo(arylenevinylene)s**

chemical analyses for **286b,c** furthermore indicated the relation of these systems to the aryl-bridged systems **283** and **285**, reported by Protasiewicz.[136b]

In summary, these studies show that oligomers incorporating phosphaalkene or diphosphene moieties are readily available by a variety of different routes and prove that the P=C and P=P units are capable of supporting conjugation across extended π-systems. Although structure/property relationships have still to be established, it is clear that macromolecules with higher molecular weights and less sterically demanding substituents are valuable research targets.

A variation of the phosphaalkene approach to π-conjugated systems has been reported by Yoshifuji et al. with the bis-(phosphinidene)cyclobutene-based materials **288−291** that bear phosphaalkene moieties as π-conjugated side-chain functionalization (Scheme 54).[137] The materials are generally accessible by treatment of secondary phosphino-acetylenes **287** with BuLi and dibromoethane (Scheme 54). Depending on the nature of the exocyclic substituents, oligomeric, as well as polymeric, systems are accessible, although in fairly low yields (5−38%). In the case of the fully-π-conjugated materials **289** and **291**, a red shift for the π−π* transitions ($\Delta\lambda_{max} = 100-320$ nm; vs monomeric model compounds **288**) can be observed by UV−vis spectroscopy, indicating conjugation across these extended systems.

units with the ferrocene system that are evident in a metal-to-ligand charge transfer (MLCT, n(Fe) → π*) at $\lambda_{n-\pi^*} = 542$ (**286a**) and 545 nm (**286b**). The electron-donating capacity of the ferrocene unit was further corroborated by a DFT study at the B3LYP/LAN2DZ level.[136a] X-ray crystallography studies on **286b,c** suggested a conjugative interaction between the P=P groups and the adjacent Cp-rings due to a coplanar arrangement of theses moieties.[136b] Electro-

6. Fulvene-, Fulvalene-, and Quinone-Based Materials

Several groups have investigated organophosphorus materials that belong to the family of fulvenes or fulvalenes, respectively, and are therefore worthy of note. Tetrathiafulvalene (TTF, Chart 25) is the most prominent representative of this class of compounds with respect to organic

Scheme 54

Chart 25. Tetrathiafulvene (TTF) and Phosphorus Analogues

292: R = Me, Et, Ph   **293**
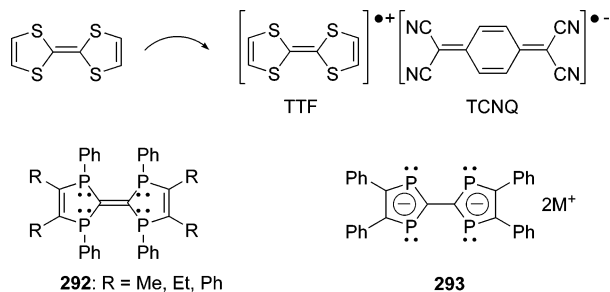
electronics. This building block allows access to so-called "synthetic metals" due to its exceptionally strong electronic donating properties in charge-transfer (CT) complexes, particularly with TCNQ (Chart 25).[138] To extend the palette of suitable TTF-like materials, Mathey and co-workers reported the related tetraphospha-analogues **292** and **293** in 1988 and 1992, respectively.[139a,b] Unfortunately, the neutral species **292** are not suitable for electronic applications, as the pyramidal nature of the phosphorus centers prevents the targeted π-stacking in the solid state,[139a] which is an essential requirement for the performance of these materials. The dianion **293**, on the other hand, is completely planar, and the bond lengths suggest some degree of π-conjugation; electronic properties, however, have not been reported.[139b]

More recently, Yoshifuji et al. have investigated a series of phosphaorganic fulvene derivatives.[140] The deep red colored 1,3,6-triphosphafulvene system **294** (Scheme 55) is accessible by reaction of the dibromophosphaalkene **295** with *tert*-butyl lithium via the carbenoid **296**.[140a] Derivative **294** can formally be regarded as a trimer of phosphanylidene carbene **297**, but the mechanism for its formation probably involves the generation of phosphaalkyne **298**. The results of an X-ray diffraction study of the tungsten pentacarbonyl

complex **299** showed that the triphosphafulvene framework is planar, as expected.[140a] Derivative **294** undergoes a reversible one-electron reduction at −0.68 V (vs Ag/Ag+).[140b] The related 1,4-diphosphafulvene **300** is accessible by several different routes (Scheme 55).[140c,d,141] Using the same carbenoid intermediate **296**, treatment with benzaldehyde or benzyl bromide, respectively, and a base (*t*BuLi or *t*BuOK) affords the fulvene **300**, along with some minor byproducts. The mechanism most likely involves the phosphaallene **302**, which dimerizes in a [3+2]-fashion to yield **300a**.[140c] In a more general approach, 1,4-diphosphafulvenes can also be obtained from suitably substituted phosphino-acetylenes **303** by a mechanism involving the phosphaallene-anion **304** (Scheme 55).[140d] All 1,4-diphosphafulvene derivatives show reversible oxidation peaks, and the tendency within the potentials [**300b** (−0.05 V) < **300c** (0.01 V) < **300a** (0.02 V) < **300d** (0.03 V) < **300e** (0.20 V); vs Ag/Ag+] indicates that electron-donating substituents lower the oxidation potential, as expected.[140d] The low values indicate a potential application in CT-complexes, which has been supported by the reaction of **300b** with TCNQ in THF resulting in a deep green solution of the corresponding [**300b**•+][TCNQ•−] complex. The electronic nature of this complex was confirmed by an IR-spectroscopic study showing values at 2185 and 2121 cm−1 (cf. neutral TCNQ: 2225 cm−1) and UV−vis spectroscopy with transitions at 853, 830, 770, and 750 nm that are typical for the radical anion of TCNQ.[140d] In 2004, Le Floch and co-workers established a route to these systems via intermediate zirconocene complexes **305** to afford a variety of sterically encumbered 1,4-diphosphafulvenes **306** (Chart 26).[141]

A final class of compounds that deserve mention are the phosphaorganic quinones **307**−**309** (Chart 26) that have been reported by Märkl and Yoshifuji.[142,143] Although the diphosphathienoquinone **309b** gives a stable radical anion upon reduction ($E_{1/2} = -1.5$ V, reversible; vs Ag/Ag+),[143b] the
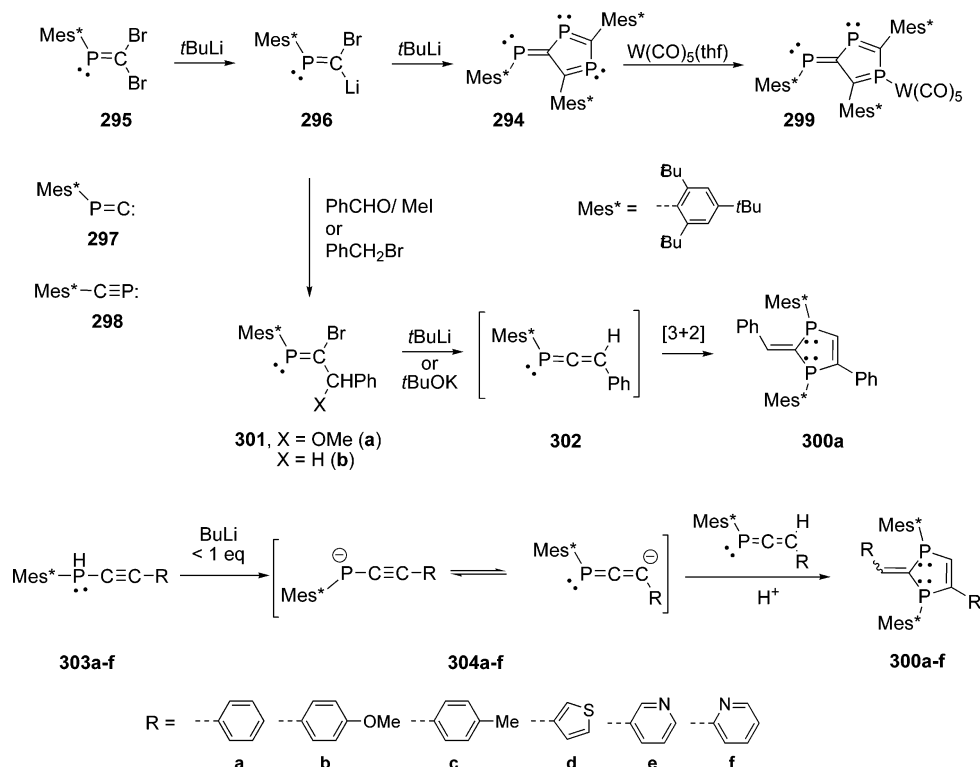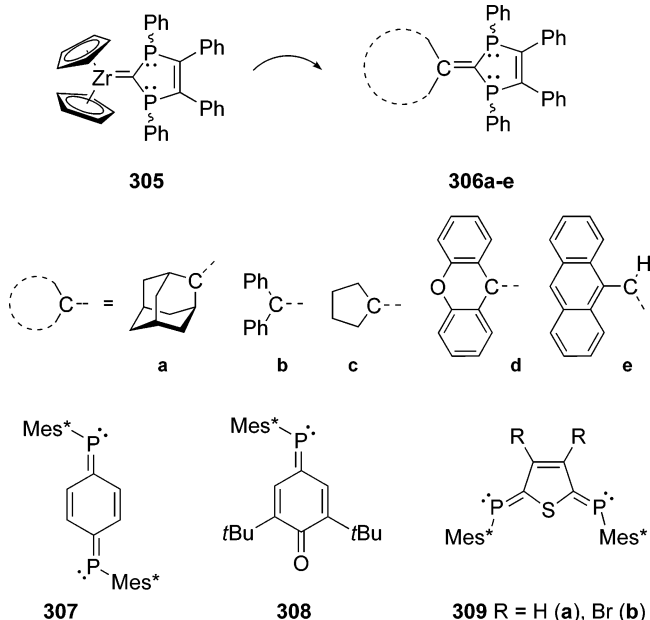
Scheme 55

Chart 26. Diphosphafulvenes and Phosphaorganic Quinones

305   **306a-e**

a   **b**   **c**   **d**   **e**

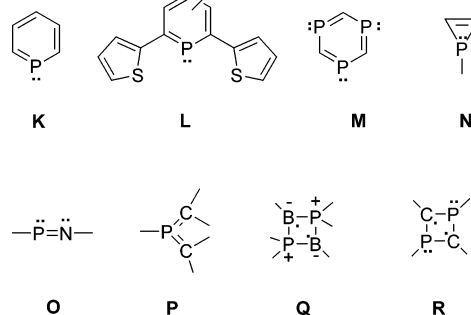**307**   **308**   **309** R = H (**a**), Br (**b**)

general stability of these compounds is limited and extensive application for these materials appears challenging.

7. Conclusion

The pioneering work on phosphole-based oligomers and phosphane-ethynyl co-oligomers in the 1990s has jump-started the development of new organophosphorus π-conjugated systems. The past five years, in particular, have seen a considerable expansion of this intriguing, young research area with the synthesis of a plethora of novel P-based π-conjugated derivatives and the elucidation of their optical and electrochemical properties. However, structure/property relationships have still to be established for many phosphorus-containing moieties in order to fully exploit their potential for the construction of conjugated frameworks. Furthermore, new methodologies are needed to prepare oligomers as well as polymers of defined structure and length. This goal should therefore motivate further fundamental research in phosphorus chemistry with the aim to discover new synthetic approaches to well-defined macromolecules.

In our opinion, the research presented within the context of this review has clearly established that organophosphorus building blocks can offer specific properties that their widely used sulfur or nitrogen analogues do not possess. In turn, P-containing conjugated systems are not superior to other classes of conjugated systems, but they are simply different. Of particular interest, the possibility of chemically modifying the P-centers provides a unique opportunity to create structural diversity and to efficiently tune the physical properties of these phosphorus-based π-conjugated systems. This facet is of particular importance for the tailoring of organophosphorus materials for optoelectronic applications. Furthermore, the ability of P-centers to coordinate to transition metals offers manifold opportunities to build supramolecular architectures in which the π-systems can be organized in a well-defined manner. Moreover, organophosphorus π-conjugated systems have already successfully been established as materials for applications in the fields of nonlinear optics, organic light emitting diodes, or conductive polymers.[144] In turn, there is no inherent limitation associated

Chart 27. Potential P-Building Blocks for the Tailoring of Novel π-Conjugated Systems

K   **L**   **M**   **N**

O   **P**   **Q**   **R**

with the use of conjugated phosphorus-containing materials for these important and appealing applications.

However, the chemistry of π-conjugated systems incorporating P-units still remains in its infancy, as illustrated by the fact that the most recent review[2b] devoted to the synthesis and properties of conjugated molecular rods does not even mention organophosphorus building blocks! Considering the richness and diversity of phosphorus chemistry, its true potential has not yet been fully recognized. For example, phosphinines **K**,[11a,123] that already exist as 2,5-dithienyl-substituted derivatives **L**,[11a,145a] triphosphabenzenes **M**,[11a,123] phosphirenes **N**,[11a] iminophosphanes **O**,[123] bis(methylene)-phosphoranes **P**,[123] and diradical species **Q**[145b−d] and **R**[145e−i] (Chart 27), are appealing building blocks for the synthesis of novel conjugated systems. It is thus very likely that new developments will occur in the near future that take full advantage of the specific properties of organophosphorus derivatives.

8. Acknowledgments

9. References

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