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New Aspects in Phosphorus Chemistry V

Volume Editor: Jean-Pierre Majoral

With contributions by
M. Alajarín · S. Constant · R. De Jaeger · P. W. Dyer · D. P. Gates
M. Gleria · M. Hissler · J. Lacour · P. Llamas-Lorente
C. López-Leonardo · S. Marque · R. Reau · P. Tordo

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Preface

In volumes 220, 223, 229, and 232 several experts reported on the recent progress of phosphorus chemistry in many fields. This chemistry is so rich, so diversified, that a new volume appeared to be necessary in order to cover some other aspects of such a topic and to point out the key role played by this element.

Indeed contributions of this issue can be classified into three different groups: i) new developments of "old themes" with different approaches and ideas (Chaps. 1 and 6), ii) state of the art for two topics of general interest (Chaps. 2 and 3), and iii) emerging fields of research (Chaps. 4 and 5).

The high diversity of hexacoordinated phosphorus compounds and their use as versatile reagents are fully illustrated in Chap. 1 by S. Constant and J. Lacour. A large number of new structures are reported with applications in different fields such as classical organic chemistry, bioorganic chemistry, electrochemistry and photochemistry, thus affording a general overview of the new trends in hexacoordinated phosphorus chemistry.

Studies on the formation and reactivity of phosphorus-centered radicals continue to be a versatile source of mechanistic information and reactions in synthetic chemistry. The recent literature devoted to the chemical reactivity of these derivatives is surveyed by S. Marque and P. Tordo in Chap. 2. Various new persistent or stable phosphorus-centered radicals have been described and find applications, for example, as paramagnetic probes.

The design and the rich chemistry of phosphinous amides are described in Chap. 3 by M. Alajarin, C Lopez-Leonardo, and P. Llamas-Lorente. Important applications of these derivatives as metals ligands in the area of catalysis are also emphasized.

In Chap. 4, D. P. Gates reports elegant examples of similarities that can be found between the chemistry of carbon and that of phosphorus in low coordination numbers. The analogy between P=C and C=C bonds can be extended to polymer chemistry. Recent advances in the addition polymerization of phospha-alkenes and the synthesis and properties of π-conjugated poly (p- phenylene phosphaalkene)s are described.

Chapter 5, written by M. Hissler, P. W. Dyer, and R. Reau, concerns an area of important expansion, i.e., the synthesis and properties of π-conjugated oligomers and polymers containing phosphorus moieties. The possibility of using such systems as materials for applications in different fields (nonlinear optics, organic light emitting diodes, or conductive polymers) is demonstrated.

Polyphosphazenes have been known for a long time. However their synthesis and properties continue to attract interest because of the broad range of applications of these polymers in different fields ranging from biology to new materials. The contribution of M. Gleria and R. de Jaeger reports the variety of synthetic procedures based on the ring-opening polymerization of monomers such as $(NPCl_2)_3$ and $(NPCl_2)_n$ followed by the nucleophilic replacement of the reactive chlorines with selected nucleophiles and on polycondensation reaction processes of new monomers and of phosphoranimines. The use of polyphosphazenes as fluoroelastomers, flame retardants and self-extinguishing macromolecules, polymeric ionic conductors, biomaterials, and photosensitive polymeric compounds is outlined.

This volume, as well as the four precedent volumes, describes only in part the huge number of original papers on phosphorus-related topics. Some further volumes will be necessary in the future to cover all aspects of this chemistry in perpetual rebirth.

The constructive cooperation of all the co-authors and of Springer, Heidelberg, is gratefully acknowledged.

Jean-Pierre Majoral Toulouse, November 2004

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New Trends in Hexacoordinated Phosphorus Chemistry

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Abstract Phosphorus derivatives with six substituents at the immediate periphery of the heteroatom are quite common, more than usually imagined, and this review presents some of the novel structures that have been reported in the last 5–10 years. Many derivatives of varied charge and geometry have been synthesized in studies devoted to phosphorus reactivity. A large number of compounds have also been prepared for applications in fields as varied as: (i) classical organic chemistry, (ii) stereoselective synthesis and analysis, (iii) bioorganic chemistry, (iv) electrochemistry, and (v) photochemistry. Selected examples of applied transformations, industrial and academic, have been selected to present a general overview of the new trends in P(VI) chemistry.

Keywords 6-Coordinate · Hypervalent · Octahedral · Chirality · Electrochemistry · Photochemistry

Abbreviations

BINOL	[1,1′]Binaphthalenyl-2,2′-diol
BINPHAT	Bis(tetrachlorobenzenediolato)mono([1,1′]binaphthalenyl-2,2′-diolato)-phosphate(v)
o-Chloranil	3,4,5,6-Tetrachloro-[1,2]benzoquinone
HYPHAT	Bis(tetrachlorobenzenediolato)mono(1,2-diarylethanediolato)phosphate(v)
LiHMDS	Lithium 1,1,1,3,3,3-hexamethyl-disilazane
TARPHAT	Bis(tetrachlorobenzenediolato)mono(dialkyl 2,3-di(hydroxybutanediolato)-phosphate(v)
TRISPHAT	Tris(tetrachlorobenzenediolato)phosphate(v)

1
Introduction

“Modern” hexacoordinated phosphorus chemistry essentially started in 1963 when Allcock and coworkers studied the reaction of phosphonitrilic chlorides with pyrocatechol and isolated the unexpected tris(benzenediolato)phosphate anion **1** (Fig. 1) which sees a central octahedral phosphorus bound to six oxygen atoms [1–4]. Since this discovery, and now for more than 40 years, chemists interested in organic, inorganic, physical, and applied chemistry have generated compounds based on hexacoordinated phosphorus and studied these many derivatives for a variety of applications. Earlier work was reviewed in 1972 by Hellwinkel [5] and more recent articles are those of Cavell [6] and Holmes [7, 8]. Several manuscripts or book chapters have also been written on the topic giving a good – yet slightly outdated – overview of the field [9–12].

The purpose of this chapter will be to describe the structures that have been reported over the last few (5–10) years and detail the synthetic protocols used or developed to make them. The compounds have been classified according to their charge in three categories: anionic, neutral, and cationic. Care has been taken to demonstrate the importance of the relationship between penta- [P(V)]

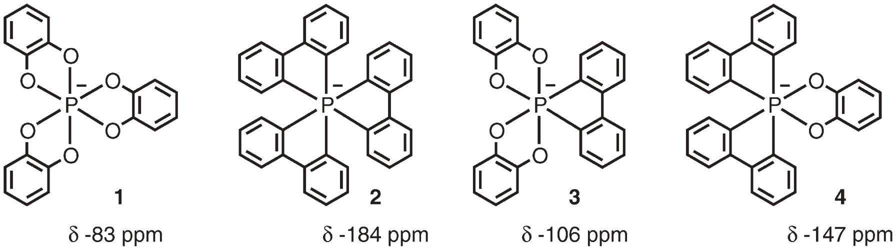


Fig. 1 Selection of “historical” hexacoordinated phosphate anions

and hexacoordinated [P(VI)] phosphorus as the later compounds can be often viewed as Lewis salts arising from a donor group interacting with a 5-coordinate phosphorus. Many of the compounds are chiral and efforts to obtain these derivatives in enantiomerically and/or diastereomerically pure forms has been noted. Then, in the second part, some of the recent uses of P(VI) adducts are detailed as the structural scaffold and reactivity of (pseudo-)octahedral phosphorus allows applications in fields as varied as: (i) classical organic chemistry, (ii) stereoselective synthesis and analysis, (iii) bioorganic chemistry, (iv) electrochemistry, and (v) photochemistry.

2
New Hexacoordinated Phosphorus Derivatives

2.1
Preamble

Hexacoordinated phosphorus centers are formally "hypervalent" and the nature of the bonding (sp^3d^2) in such phosphorus compounds has been debated in the literature, in particular with regards to the involvement of d orbitals [13]. These compounds can be designated as σ^6, λ^6 in which σ corresponds to the coordination number and λ to the total number of bonds; this last parameter thus representing the valence of phosphorus. In general, hexacoordinated phosphorus adopts (i) an octahedral geometry (*Oh*) with six identical substituents positioned at same distance and at a 90° angle from each other or (ii) a pseudo-octahedral arrangement (*D4h*) with ligands in two axial and four equatorial positions, respectively. The main criterion for establishing the presence of P(VI) is the observance of lower frequency shifts in ^{31}P NMR relative to analogous P(V). When known, ^{31}P NMR chemical shifts (δ in ppm, usually negative) have been specified.

Chemical assemblies around hexacoordinated phosphorus atoms can be anionic, neutral or cationic depending upon the nature of the ligands. This is described in the following paragraphs.

2.2
Anionic P(VI) Derivatives

2.2.1
Introduction

The flagship of anionic P(VI) chemistry is of course the hexafluorophosphate anion PF_6^-, which is routinely used in all fields of chemistry as a "non-coordinating" counter-ion [14]. In his pioneering work of the 1970s Hellwinkel prepared several anionic phosphates, among which are compounds **1** to **4** (Fig. 1), by combining around an octahedral P atom (i) three benzenediolato ligands (e.g., **1**) [15, 16], (ii) three identical bidentate biphenylidene ligands (e.g., **2**) [17–24] and (iii) combinations of the two types of chelating moieties (e.g., **3** and **4**) [15]. Since then, the field has evolved towards the formation of more complex and/or more stable derivatives.

Figures 2, 3, 5, and 6 show anionic compounds **5** to **22** and **25** to **30**, which have been described in the literature since 1997. In these adducts, as in examples **1** to **4**, the P(VI) derivatives have carbon or oxygen atoms in the immediate proximity of the central (pseudo-)octahedral atom. This is probably due to the accessibility of the ligand precursors, the ease of their manipulation and, more importantly, to the sheer strength of the resulting P–C and P–O bonds. They all present tris(bidendate) structures in which the three chelating rings can be identical (Fig. 2 and most of Fig. 6) or of two different types (Fig. 3). The ligands can be monooxo (Fig. 6) or dioxo (Fig. 2 and Fig. 3). These differences in composition have, of course, consequences for the making of the derivatives,

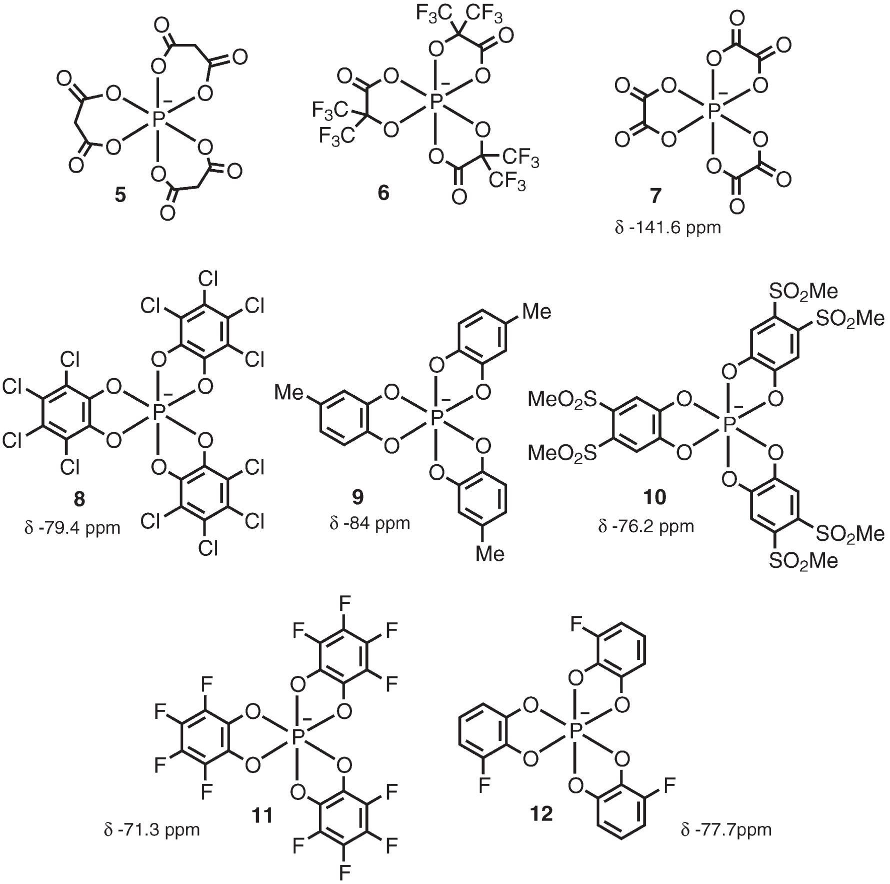


Fig. 2 Recently published anionic P(VI) derivatives of "P(aa)$_3$" type

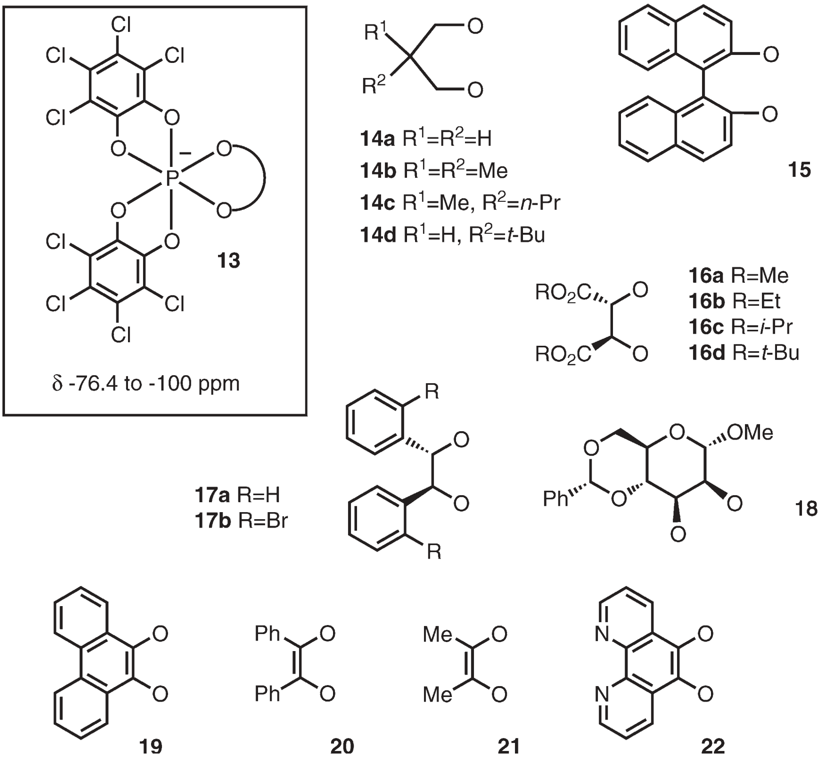


Fig. 3 Recently published anionic P(VI) derivatives of "P(aa)$_2$(bb)" type

as different synthetic strategies need to be used for their preparation in high yields and analytically pure form. These are detailed in the next section.

2.2.2
Synthesis

Most of the anionic compounds that have been reported contain six oxygen atoms at the periphery of the pseudo-octahedral phosphorus. Two different strategies have been used for the preparation of the moieties depending upon the homogeneous (three times the same chelate) or heterogeneous (two different types) distribution of the bidentate ligands.

When the three ligands are the same, procedures similar to the ones developed by Hellwinkel [16, 17], Koenig [25–28] and coworkers can be utilized – that is the one-time addition of three equivalents of bidentate ligands to PCl_5 to afford the hexacoordinated phosphate anions. Ligands as varied as malonic acid, 3,3,3-trifluoro-2-hydroxy-2-trifluoromethyl-propionic acid or oxalic acid have been used to form **5**, **6**, and **7**, respectively [29]. Aromatic 1,2-diols are also particularly good ligands as tetrachloropyrocatechol [30, 31], 4-methylpyrocatechol [32], 4,5-bis(methanesulfonyl)catechols [33],tetrafluorocatechol [34] and 3-fluoropyrocatechol [35] afford phosphates **8** (known as TRISPHAT), **9**, **10**, **11**, and **12**, respectively. The process can be easily driven to completion by the addition of a base to the medium (aliphatic amines, lithium salts, etc.). This last step is not always necessary as the phosphate anion is sometimes isolable as its Brønstedt acid, as in the case of **7** [29, 36].

However, for the making of anionic phosphates containing different dioxo ligands around the phosphorus, as exemplified by the general structure **13** in Fig. 3, this synthetic protocol is not adapted as it leads to a random distribution of ligands around the phosphorus and to the usually unwanted formation of complex mixtures of products.

For instance, if 1 equivalent of three different bidentate symmetrical ligands are added to 1 equivalent of PCl_5 and 1 equivalent of a base, then a "library" of 10 compounds is likely to be generated. This is represented in Fig. 4, considering the theoretical case of three different ligands (aa), (bb) and (cc) (1:1:1 ratio) which react simultaneously with PCl_5 and subsequent derivatives. A statistical 1:1:1:3:3:3:3:3:3:6 repartition among 10 possible products is expected; the desired compound [P(aa)(bb)(cc)] being synthesized with a maximum 22% (6/27) theoretical yield.

To overcome this problem and obtain desired [$P(aa)_2(bb)$] or [P(aa)(bb)(cc)] type products in high yields and to the exclusion of all others, it is necessary to consider a synthetic route that allows the sequential introduction of each of the three ligands in three different and orthogonal chemical steps. This is done by treating PX_3 derivatives (X=halogens, NR_2, OR_f) with diols to form monocyclic adducts, which are in turn oxidized to bicyclic spirophosphoranes using

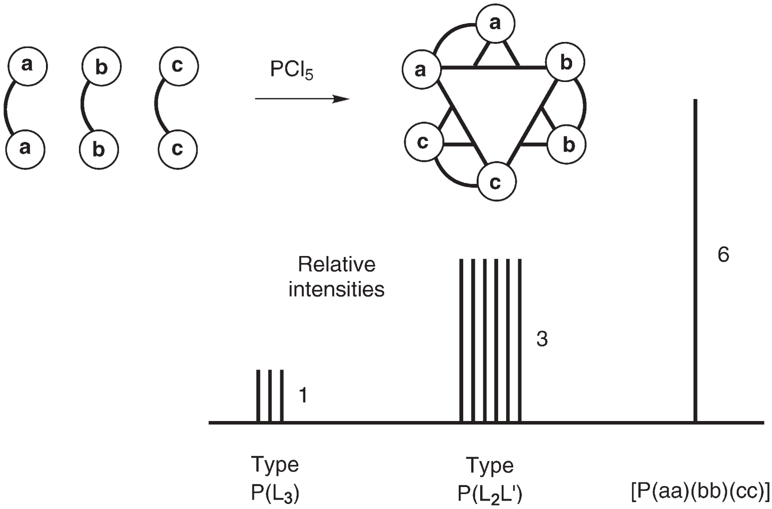
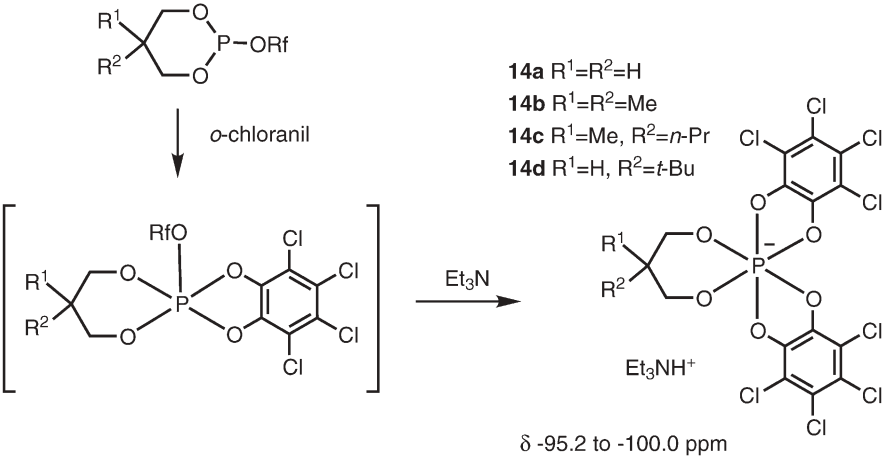


Fig. 4 Statistical distribution among possible hexacoordinated phosphates from the reaction of three different ligands (aa, bb and cc, 1:1:1 ratio) and PCl_5. L, L′=(aa), or (bb), or (cc)

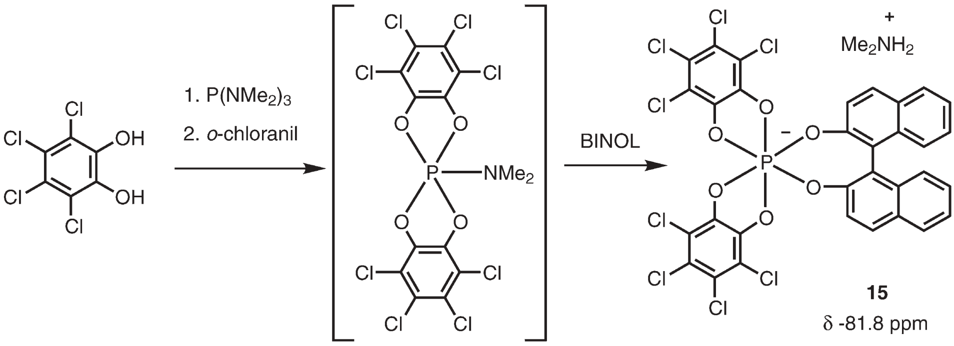
α-diketones or *ortho*-quinones as oxidants, and *o*-chloranil in particular. To carry out the final chelation step, it is sufficient to add a third diol ligand (ligand cc). After nucleophilic displacement of the last substituent X, chelation occurs, usually in the presence of a base, to form the final ring. If substituent X is itself a base – such as an amino group – then the two protons delivered by the last diol are directly scavenged in solution.

This type of process was performed in 2000 by Skowronska and coworkers when studying the formation of hexacoordinated phosphates of type **14** containing 1,3,2-dioxaphosphorinane rings [37]. The starting phosphorinane is substituted by a perfluorinated alcohol and subsequent treatment with *o*-chloranil and addition of tetrachlorocatechol and Et_3N afforded the desired triethylammonium phosphate salts **14** (Scheme 1). Careful monitoring in ^{31}P NMR of the reaction medium after the addition of the oxidant allowed the researchers to detect many intermediates shedding light on reaction pathways.



Scheme 1 Synthesis of hexacoordinated phosphates **14** containing 1,3,2-dioxaphosphorinane rings

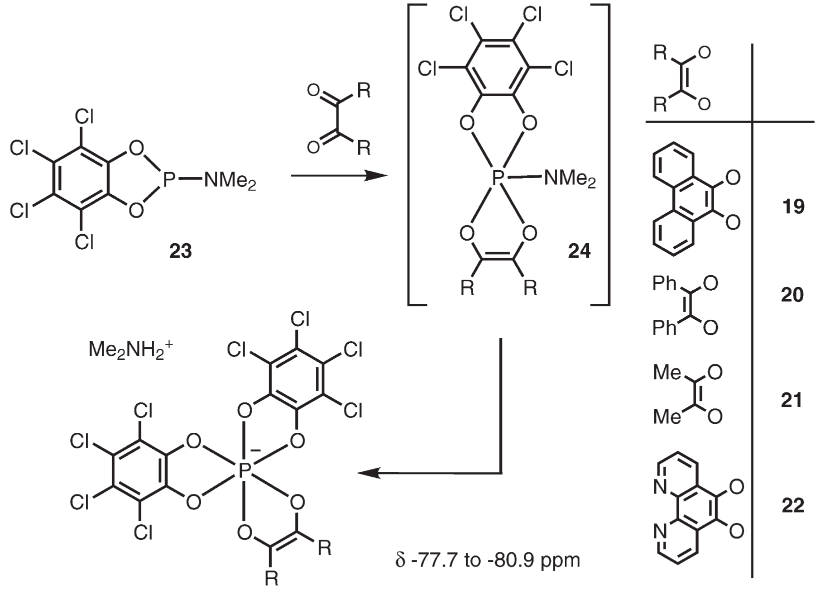
In 2000, Lacour and coworkers reported a similar one-pot three-step protocol to afford phosphate anion **15**, known as BINPHAT, containing a BINOL moiety along with two tetrachlorocatecholate ligands [38]. Starting from tris-(dimethylamino)phosphine, subsequent additions of tetrachlorocatechol, *o*-chloranil and BINOL affords anion **15** in good yield and chemical purity (Scheme 2). This procedure was extended to aliphatic 1,2-diols such as tartrate esters, hydrobenzoins and mannose derivatives to afford the corresponding anions in modest to good yields (61–86%): **16a–16d** TARPHAT (R=Me, Et, *i*-Pr, *t*-Bu) [39], **17a–17b** HYPHAT (R=H, Br) [40] and **18**, respectively [41] (Fig. 3). In all these examples, the chiral ligands were introduced in the last step in place of the BINOL moiety.



Scheme 2 Synthesis of BINPHAT anion **15** containing a BINOL ligand

Following a similar protocol, novel hexacoordinated phosphate anions **19** to **22** bearing two different dioxo ligands could be simply prepared as their dimethylammonium salts from the reaction of tetrachlorocatechol derived phosphoramidite **23** with a variety of symmetrical diones other than *o*-chloranil (α-diketones or *ortho*-quinones) and subsequent addition of tetrachlorocatechol to the corresponding phosphorane **24** (Scheme 3) [42].

Finally, two more anionic phosphate anions with six oxygen substituents at phosphorus (Fig. 5) were isolated by serendipity. Compound **25** [43] was isolated from the reaction of naphthalene-2,3-diol and phosphonitrilic chloride in



Scheme 3 Possible synthetic route to anionic P(VI) derivatives of "P(aa)$_2$(bb)" type

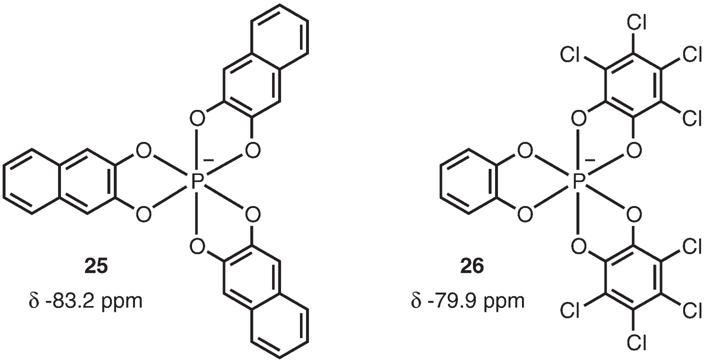


Fig. 5 Anionic hexacoordinated phosphates **25** and **26**

a process analogous to the one observed by Allcock [1]. Compound **26** was isolated as a decomposition product from the oxidation with *o*-chloranil of a bis(4,5-benzo-1,3-dioxy-2-phospholano)dichloromethane [44].

Other anionic phosphates **27a–27e**, **28**, **29**, and **30** (Fig. 6), which contain both P–C and P–O bonds, have been reported since 1997. In these cases, as shown by Akiba, Kawashima and Holmes, the synthetic strategy is slightly different as P–C bonds usually need to be formed prior to P–O ones.

The formation of **27a–27e**, **28**, and **29** makes use of a chemistry developed by Akiba and coworkers in the 1990s for the synthesis and applications of cyclic 10-P-5 phosphoranes made of two Martin ligands. Methyl, benzyl and phenylth-

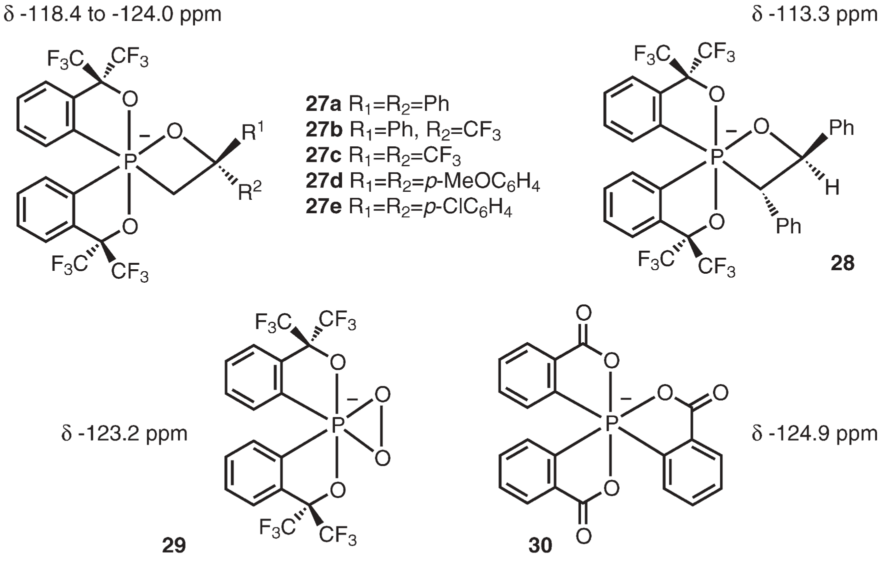
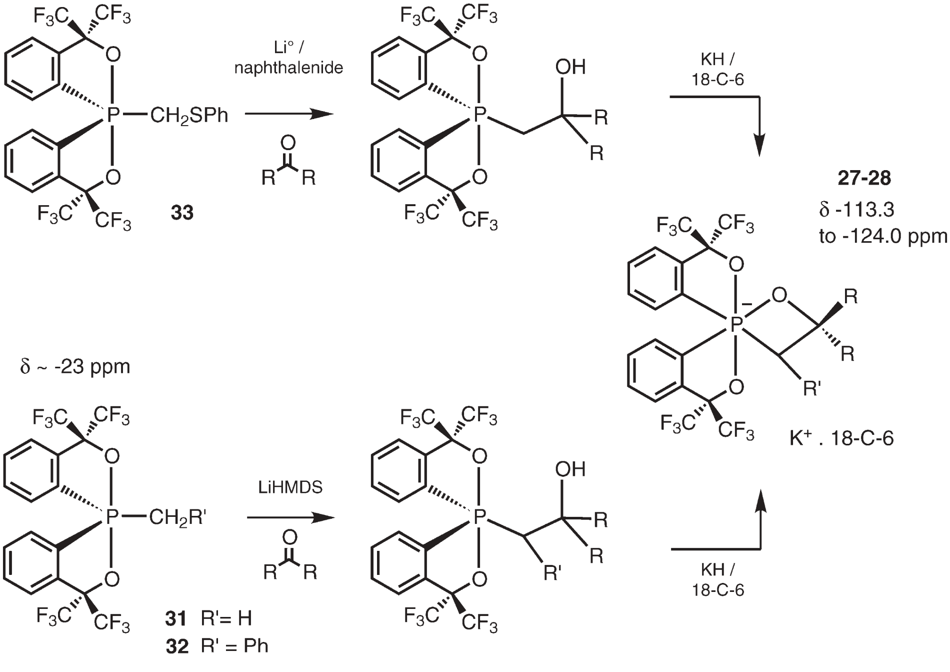


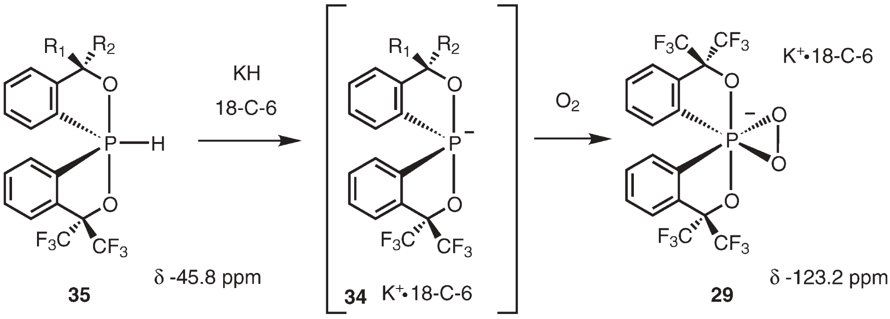
Fig. 6 Isolated anionic hexacoordinated phosphates containing both P–C and P–O bonds

iomethyl phosphoranes, **31**, **32**, and **33**, respectively (Scheme 4), were prepared and studied in the context of P(VI) chemistry. In the case of **33**, reduction of the carbon–sulfur bond in the presence of lithium naphthalenide generated a carbanion, which was reacted with ketones to form the corresponding P(V) β-hydroxyalkylphosphoranes [45]. Similarly, treatment of **31** and **32** with *n*-butyllithium, and quenching with aldehydes and ketones yielded analogous β-hydroxyphosphoranes [46, 47]. Then, reactions of the isolated P(V) alcohols with a combination of KH and 18-crown-6 afforded the hexacoordinated 2-oxaphosphetanides **27a**–**27e** and **28** in moderate yields (39–49%). It is interesting to note that the lithium salts of the β-hydroxyalkylphosphorane precursors do not undergo cyclization reactions to form P(VI) oxaphosphetanides. These compounds are quite kinetically stable and only the more reactive "naked" potassium salts can form stable hexacoordinated phosphates.



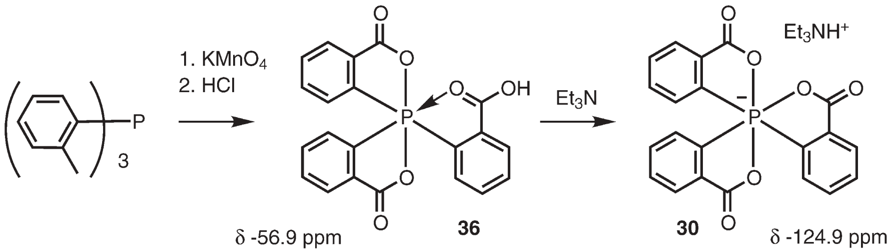
Scheme 4 Synthesis of anionic oxaphosphetanides 27–28

Akiba and coworkers reported a new type of anionic hexacoordinated phosphorus derivative exemplified by compound **29** bearing a stable three-membered dioxaphosphirane ring [48]. Phosphoranide **34**, generated from P-H phosphorane **35** with KH in the presence of 18-crown-6, was exposed to dioxygen to give crystalline **29** (50%). Phosphate **29** was found to be quite stable as a solid to ordinary room light as well as to the air at ambient temperature for several months (Scheme 5).



Scheme 5 Synthesis of hexacoordinated phosphate **29** containing a dioxaphosphirane ring

Finally, in the case of **30** made by Holmes and coworkers, the starting material was tris(*o*-tolyl)phosphine, which was treated sequentially with potassium permanganate and HCl to generate phosphorane **36**, which was then treated with triethylamine to yield the desired phosphate **30** in 64% yield as its Et_3NH^+ salt [49, 50] (Scheme 6).



Scheme 6 Synthesis of hexacoordinated phosphate **30**

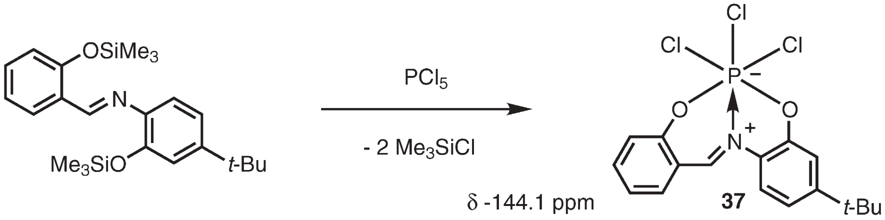
2.3
Neutral P(VI) Derivatives

As previously mentioned, the interaction between Lewis acidic 5-coordinate phosphorus centers and a Lewis base donor atom is a simple route to a 6-coordinate phosphorus centers and, if the donor atom is neutral (usually a nitrogen, sulfur or oxygen atom), then the appearance of a positive charge on that atom upon coordination upsets the negative character of the pseudo-octahedral phosphorus and yields a compound with a global charge neutrality. This field of phosphorus chemistry was extensively reviewed, most recently by Cavell and Holmes [6–8], and only novel structures since 1996 are detailed. A different approach to the generation of neutral P(VI) adducts consists in the generation of dinuclear zwitterionic $\lambda^4P^{(+)}\lambda^6P^{(-)}$ species. This chemistry will also be presented.

2.3.1
Via P–N Interaction

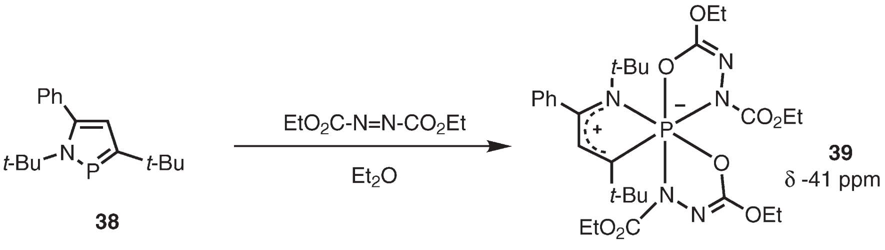
As mentioned, stabilization of neutral hexacoordinated phosphorus via nitrogen donation is possible and this topic has been widely studied in the past few years. As P–N bonds are weaker and longer than those of P–C and P–O, chemists have essentially relied on chelation to enforce their formation. Most structures involve five- and six-membered chelating rings and the compounds that have been reported are described in Schemes 7, 8, and 9 and Figs. 7 and 8.

In 1996, Cavell described the synthesis of neutral P(VI) compound **37** containing a divalent tridentate diphenol imine ligand and three chlorine atoms by the reaction of a bis silylated Schiff base with PCl_5 to give **37** after elimination of two equivalents of Me_3SiCl (Scheme 7) [51].



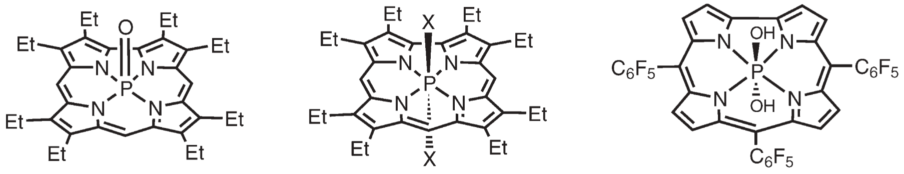
Scheme 7 Synthesis of neutral P(VI) derivative **37**

Regitz has shown that the reaction of azaphosphole **38** with two equivalents of DEAD furnishes the zwitterionic 2:1 adduct **39** (Scheme 8) [52]. The extreme low frequency shift of the ^{31}P NMR signal by more than 220 ppm in comparison to that of the azaphosphole confirms the formation of a betaine possessing a hexacoordinated phosphorus atom.



Scheme 8 Synthesis of neutral P(VI) betaine **39**

Octaethyl and tris(pentafluorophenyl) corroles, known as oec and tpfc, respectively, are also efficient for the stabilization of P(VI) phosphorus [53, 54]. The electron-rich oec reacts with PCl_3 to form (oec)P=O **40** that can be further derived into dihydrido **41a**, dimethyl **41b** and diphenyl **41c** compounds by reduction with $LiAlH_4$ and reactions with methyl and phenyl Grignard reagents,



40 δ -99.4 ppm

41a X = H

41b X = Me

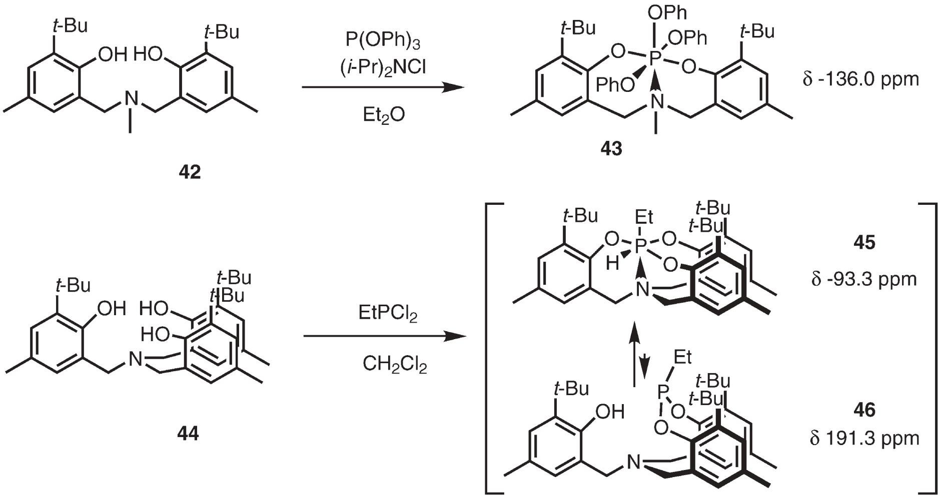
41c X = Ph

41d δ -215.9 to -252.5 ppm

Fig. 7 Corrole-derived neutral P(VI) derivatives **41**

respectively. On the other hand, electron-poor tpfc does not react with PCl_3 but with $POCl_3$ to directly form the bis(hydroxo) coordinated adduct **41d**.

Most of the work published before 1996 by Holmes and coworkers has concentrated on rigid cyclic systems that exhibited little flexibility, thus strongly fixing the coordination geometry around the phosphorus. By way of contrast, the group of Amherst has recently utilized more flexible ring systems containing a nitrogen donor group, which allows different kinds of geometries and ring conformations. Treatment of nitrogen-containing diphenol **42** with $P(OPh)_3$, in the presence of *N*-chlorodiisopropylamine, resulted in an oxidative addition to give a pentaoxyphosphorane with a definite P–N coordination (**43**, Scheme 9) [55]. Interestingly, reaction of analogous nitrogen-containing triphenol **44** with $EtPCl_2$ leads to the formation of a hexacoordinated phosphorane-phosphatrane system **45**; a species that exists in solution in equilibrium with its phosphonite form **46**. This is the first example of a direct conversion of 3-coordinate to 6-coordinate phosphorus [56].



42

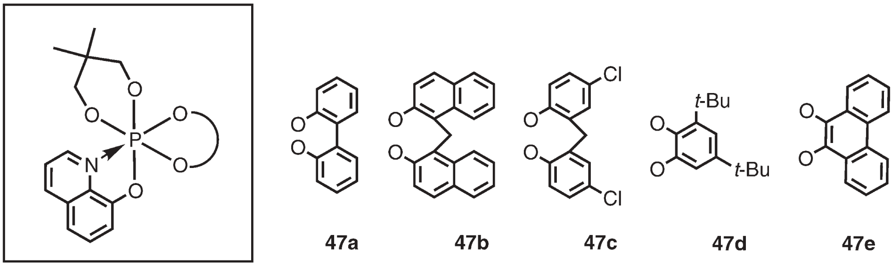
43 δ -136.0 ppm

44

45 δ -93.3 ppm

46 δ 191.3 ppm

Scheme 9 Synthesis of adducts **43** and **45** and equilibrium between P(V) **45** and P(III) **46**



47a **47b** **47c** **47d** **47e**

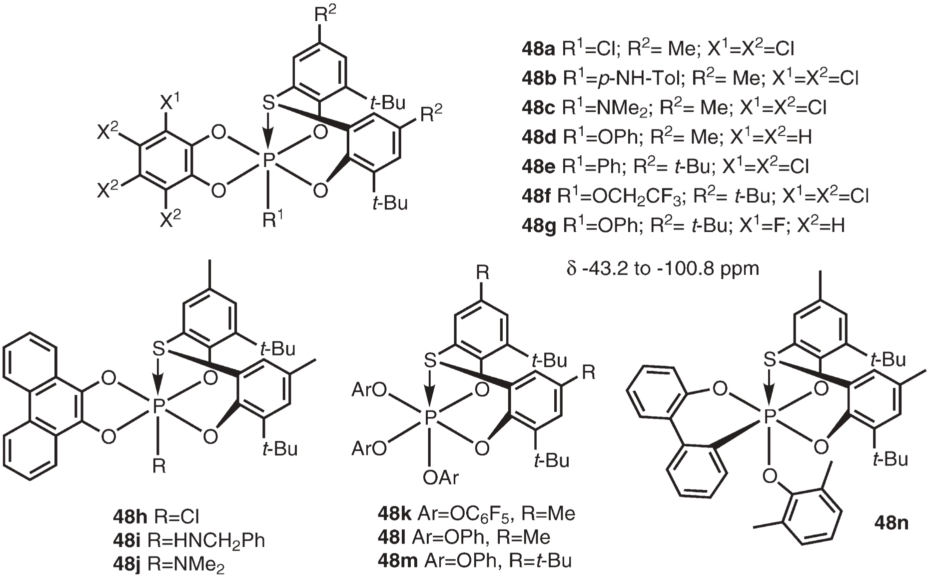
δ -100.0 to -127.1 ppm

Fig. 8 Some tricyclic neutral hexacoordinated phosphorus derivatives with P–N donations

Finally, new tricyclic hexacoordinated phosphoranes with internal P–N coordination were synthesized by Swamy and coworkers by oxidative addition of cyclic phosphite precursors with quinones or with a combination of diols and (i-Pr)$_2$NCl [57, 58]. Various ring sizes from five to eight membered were obtained showing the generality of the approach. A selection of compounds (**47a**–**47e**) is presented in Fig. 8.

2.3.2
Via P–S or P–O–S Interactions

Since 1996, Holmes and coworkers have investigated further the formation of hexacoordinated phosphorus derivatives by virtue of sulfur donation [59–64].



48a R^1=Cl; R^2= Me; X^1=X^2=Cl
48b R^1=p-NH-Tol; R^2= Me; X^1=X^2=Cl
48c R^1=NMe$_2$; R^2= Me; X^1=X^2=Cl
48d R^1=OPh; R^2= Me; X^1=X^2=H
48e R^1=Ph; R^2= t-Bu; X^1=X^2=Cl
48f R^1=OCH$_2$CF$_3$; R^2= t-Bu; X^1=X^2=Cl
48g R^1=OPh; R^2= t-Bu; X^1=F; X^2=H

δ -43.2 to -100.8 ppm

48h R=Cl
48i R=HNCH$_2$Ph
48j R=NMe$_2$

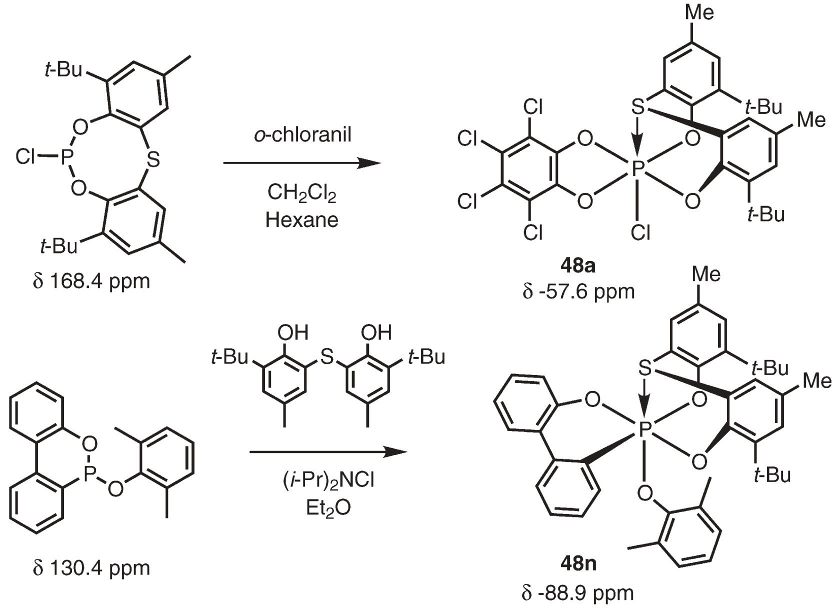
48k Ar=OC$_6$F$_5$, R=Me
48l Ar=OPh, R=Me
48m Ar=OPh, R=t-Bu

48n

Fig. 9 Tricyclic neutral hexacoordinated phosphorus derivatives (**48a**–**48n**) with P–S donation

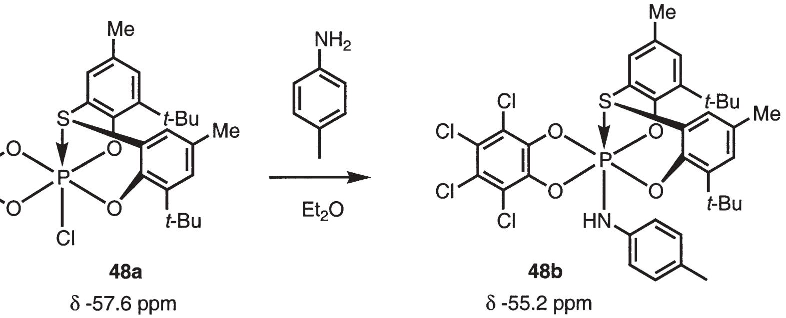
Series of pentaoxyphosphoranes containing a sulfur atom as part of a tricyclic ring have been characterized (**48a–48n**). They are reported in Fig. 9.

X-ray crystallographic analyses of the structures show that the P–S bond distance vary over one-half of an Angstrom (2.36–2.88 Å). The derivatives were generated using procedures similar to those utilized to form pentaoxyphosphoranes with P–N bonds, that is (i) the oxidation of sulfur containing cyclic chlorophosphines with a quinone or (ii) treatment of phosphites with the sulfur-containing diol in presence of *N*-chlorodiisopropylamine. Two typical examples of these synthetic protocols are shown in Scheme 10.



Scheme 10 Principal synthetic routes to compounds **48**

The stability of the resulting P(VI) is emphasized by displacement coordinate experiment as shown in Scheme 11 [59].



Scheme 11

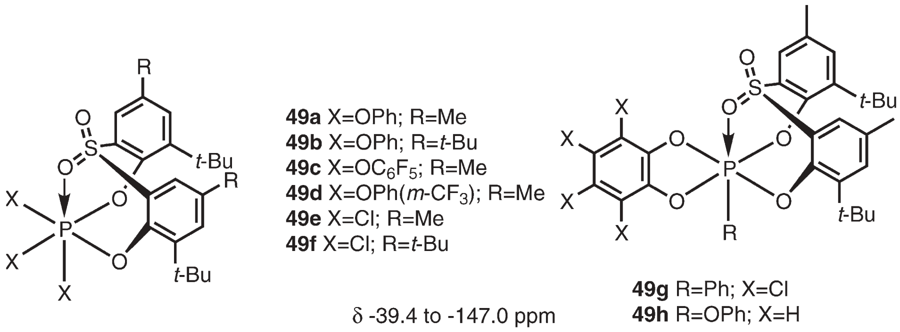


Fig. 10 Tricyclic neutral hexacoordinated phosphorus derivatives with P–O donations

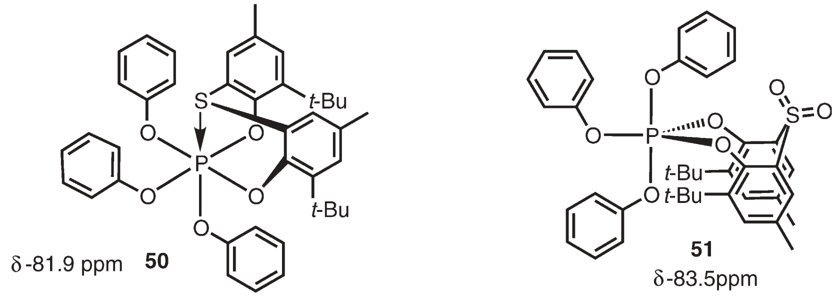


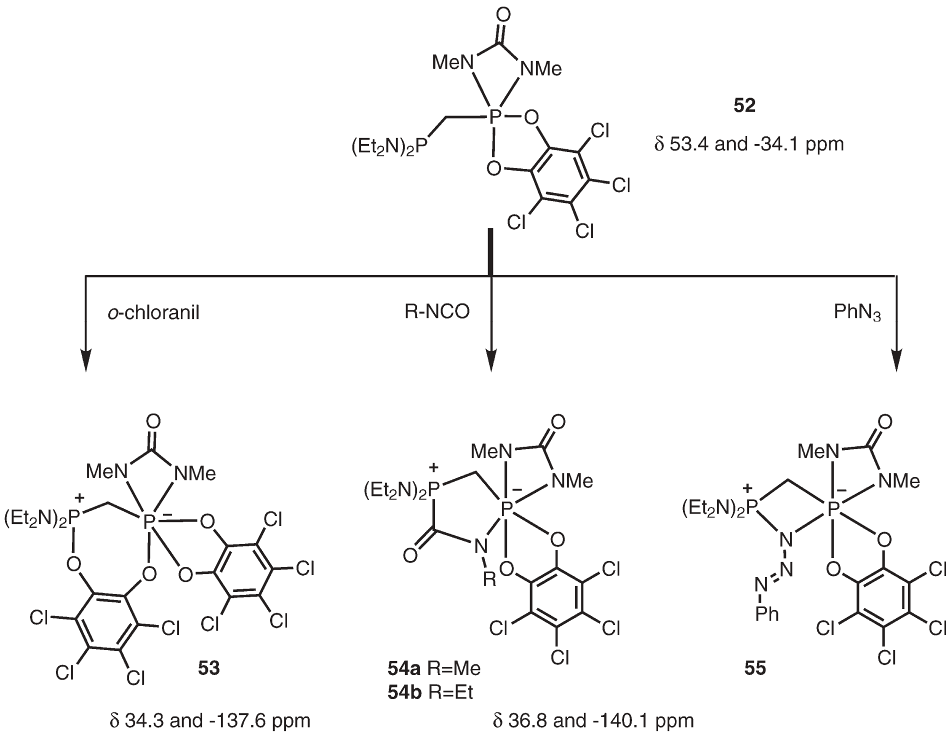
Fig. 11 Neutral hexacoordinated phosphorus derivatives **50** and **51**

If the sulfur atom is oxidized to a sulfonyl moiety, then oxygen donation occurs to the phosphorus as observed in compounds **49a–49h** (Fig. 10) [61, 64–66]. In most examples, the existence of an equilibrium between penta- and hexacoordinated phosphorus was demonstrated in solution. Introduction of electron withdrawing substituents on the ligands around the phosphorus increase its Lewis acidity and consequently enhance the proportion of P(VI) over P(V).

Furthermore, it was determined that sulfur is a stronger coordinating atom than the oxygen of a sulfonyl group. This was established by noting that sulfur coordinates to give phosphorus when the sulfonyl usually does not. This is the case for compounds **50** and **51** (Fig. 11) [64].

2.3.3
Zwitterionic $\lambda^4P^{(+)},\lambda^6P^{(-)}$ Compounds

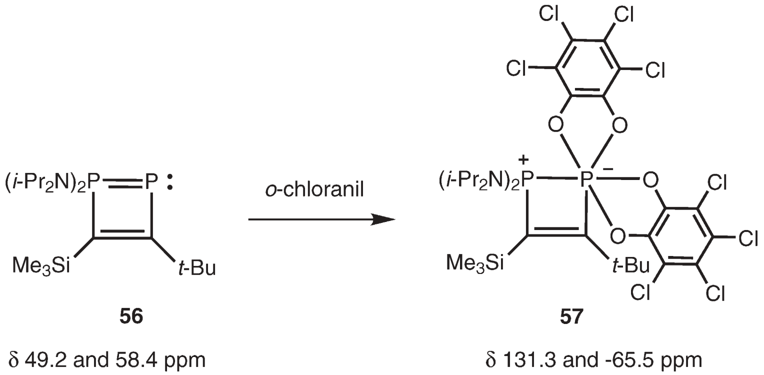
Zwitterionic heterocyclic compounds with two phosphorus atoms of opposite charge and different coordination were a rarity 10 years ago. This field has emerged recently with the reports of a variety of new structures as shown in Schemes 12, 13, and 14. Schevchenko and Schmutzler described a compound of this type in 1993, formed by reaction of methylenephosphinophosphorane **52**, containing a diethylaminophosphine linked to a spirophosphorane via a methylene group, with *o*-chloranil to form the zwitterionic adduct **53** (Scheme 12) [67]. Later, Schevchenko extended the protocol to the reaction of **52** with isocyanates to give 5-membered heterocycles **54a** and **54b** (R=Me and Et, respectively) [68]. In 1999, he and Grützmacher further demonstrated the reactivity of **52** with azides [69]. The organic azide moiety undergoes a Staudinger reaction with the P(III) atom and the distal nitrogen then takes a bridging position between the two phosphorus atoms to give **55**.



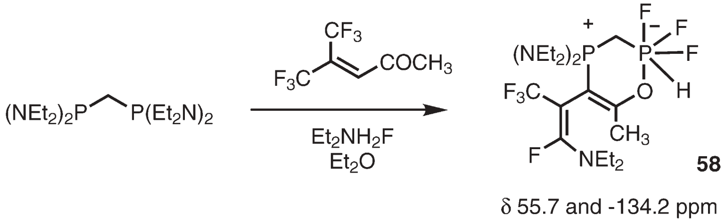
Scheme 12 Synthesis of zwitterionic $\lambda^4P^{(+)},\lambda^6P^{(-)}$ compounds 53, 54 and 55

Studying the reactivity of $1\sigma^4,2\sigma^2$-diphosphete **56** with *o*-chloranil, Bertrand and coworkers reported the synthesis of zwitterionic **57** in which the two phosphorus atoms are directly linked by a σ bond (Scheme 13). Structural details of **57** were further obtained through a X-ray crystallographic analysis [70].

Finally, Schevchenko and Roschenthaler reported a new type of zwitterionic $\lambda^4P^{(+)},\lambda^6P^{(-)}$ compound through the reaction of a methylenediphosphine with an electron-poor enone giving rise to **58** in the presence of a small amount of Et_2NH_2F [71].



Scheme 13 Synthesis of zwitterionic $\lambda^4P^{(+)},\lambda^6P^{(-)}$ compound **57**

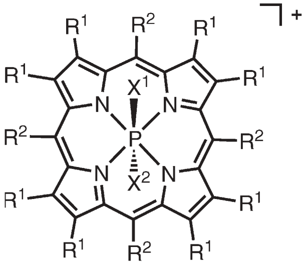


Scheme 14 Synthesis of zwitterionic $\lambda^4P^{(+)},\lambda^6P^{(-)}$ compound **58**

2.4
Cationic P(VI) Derivatives

Four types of cationic hexacoordinated phosphorus compounds have been recently reported and their structures are shown in Figs. 12, 13, and 14 and Scheme 15. In the last 10 years, a large number of substituted porphyrins (**59**) have been described with hexacoordinated phosphorus atoms in the center of the tetracoordinate ligands (Fig. 12) [72–97]. As for the neutral octaethyl corroles, most of these compounds can be prepared by the reaction of the hemes with phosphorus(III) precursors such as PCl_3 or $RPCl_2$. The mechanism of the oxidation of the phosphorus(III) to the phosphorus(v) porphyrin is not clear. Peripheral tuning of properties can be achieved through the synthesis of variously substituted porphyrins. Furthermore, due to the high chemical stability of the porphyrinatophosphorus derivatives, "axial" substitutions of labile substituents (e.g., Cl, OH) are conveniently realized and proceed in moderate to good yield. This brings a nice structural diversity, as shown in Fig. 12.

Hexacoordinated phosphorus compounds derived from phthalocyanines have been similarly prepared. Hanack investigated the reaction of metal-free phthalocyanines with $POBr_3$ or $POCl_3$ in presence of pyridine [98]. The corresponding dihydroxyphosphorus phthalocyanine hydroxides **60** were characterized.



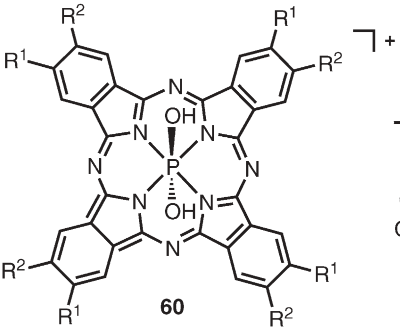
59

δ -159.5 to -229.2 ppm

R^1	R^2	X^1	X^2
Et	H	Me	OMe
Et	H	Et	O*i*Pr
Et	H	Et	O*Sec*Bu
Et	H	Et	NEt_2
Et	H	Et	NHBu
Et	H	Ph	OMe
Et	H	Ph	OEt
Et	H	Ph	O*n*Pr
Et	H	Ph	O*i*Pr
Et	H	Me	Cl
Et	H	Et	Cl
Et	H	Ph	Cl
Et	H	Me	OH
Et	H	Et	OH
Et	H	Ph	OH
Et	H	Me	F
Et	H	Et	F
Et	H	Ph	F
Et	Ph	Me	OH
Et	Ph	Me	Me
Et	Ph	Me	F
Et	H	Me	OOH
Et	H	Et	OOH
Et	H	Ph	OOH
H	Tol	OH	Tol
H	Tol	OAr	OAr
H	(*p*-CO_2H)Ph	OC_2H_4OH	OC_2H_4OH
H	Ph	OPyrene	OPyrene
H	Ph	OC_2H_4SH	OC_2H_4SH

Fig. 12 List of some recent cationic phosphorus porphyrins of type **59**

δ -166 ppm



60

R^1	R^2
H	H
H	*t*-Bu
C_3H_7	C_3H_7
C_5H_{11}	C_5H_{11}

Fig. 13 List of some recent cationic phosphorus phthalocyanines of type **60**

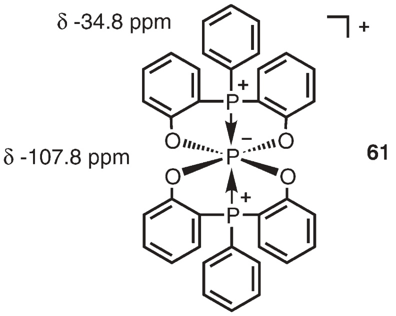
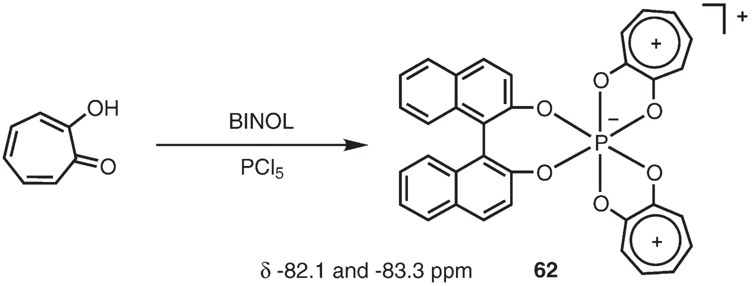


Fig. 14 Cationic P(VI) compound **61** with two axial P^{III}–P^{V} bonds

Many types of phosphorus–phosphorus bonds are known, but it is rare to find such bonds in hexacoordinated phosphorus compounds (with the exception of 57). Cavell reported in 1998 the reaction of PCl_5 with phenylbis(*o*-(trimethylsiloxy)phenyl)phosphane, yielding the corresponding bischelate **61** in decent yield (52%) [99]. The octahedral nature of the central phosphorus atom was unambiguously determined by X-ray structural analysis. Two "short" axial P^{III}–P^{V} bonds (2.202 Å) lie perpendicular to the pseudo-octahedral equatorial plane.

Finally, Lacour and coworkers reported the synthesis of hexacoordinated phosphorus cation **62** [100]. Tropolone, BINOL and PCl_5 react in CH_2Cl_2 at reflux to generate in one step a novel hexacoordinated phosphorus cation.



Scheme 15 One-step synthesis of BINOL-containing P(VI) cation **62**

2.5
Chirality and Isomerism

2.5.1
Preamble

Chirality is an important part of today's chemistry and, in this respect, the pseudo-octahedral geometry of hexacoordinated phosphorus derivatives is interesting as it suffices to coordinate to the central atom three identical sym-

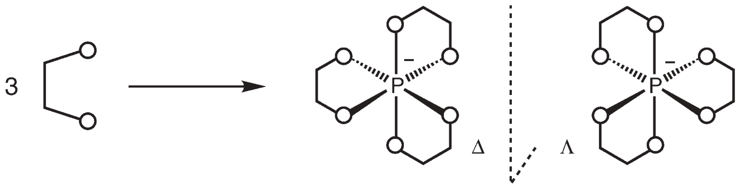


Fig. 15 Enantiomeric Δ and Λ hexacoordinated phosphates of "P(aa)$_3$" type

metric bidentate ligands to form chiral D_3-symmetric helical molecules of type P(aa)$_3$ [101]. Such compounds exist either as Λ (*M*) or Δ (P) enantiomers of left- and right-handed propeller shape, respectively (Fig. 15) [102]. Many of the compounds described in Sect. 2.2 belong to this group of molecules (e.g., **5**, **7** and **11**). To the exception of a few (see below in Sect. 2.5.2), they have been reported only in racemic form (1:1 mixture of enantiomers).

Coordination to the central P atom of two different types of symmetrical bidentate ligands leads to structures of type P(aa)$_2$(bb), which are this time C_2-symmetric as detailed in Fig. 16. The same chiral descriptors Λ and Δ apply to these compounds. Derivatives like **3**, **4**, **14–17** and **19–22** fit this description and have only been reported in racemic form so far. If the ligand bb is itself chiral, then diastereomers are generated. This will be described in the next section.

The presence of substituents on the bidentate ligands often degenerate their local C_2-symmetry and, as a consequence, further isomerism occurs. This results in trisbidentate derivatives of type P(ab)$_3$ in the presence of facial or meridional isomers, as depicted in Fig. 17 [102]. Usually, the meridional isomer is preferred over the facial and a statistical 3:1 ratio is observed. Compounds **6**, **9**, **12** and **30**

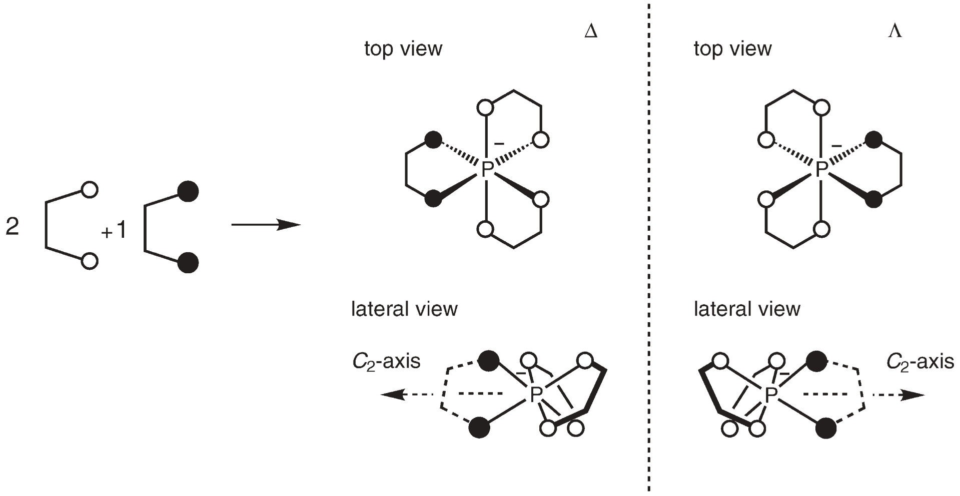


Fig. 16 Enantiomeric Δ and Λ hexacoordinated phosphates of "P(aa)$_2$(bb)" type

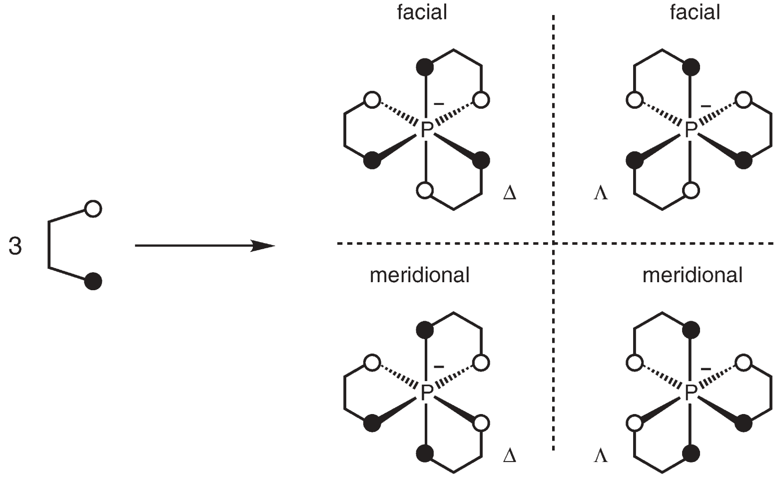
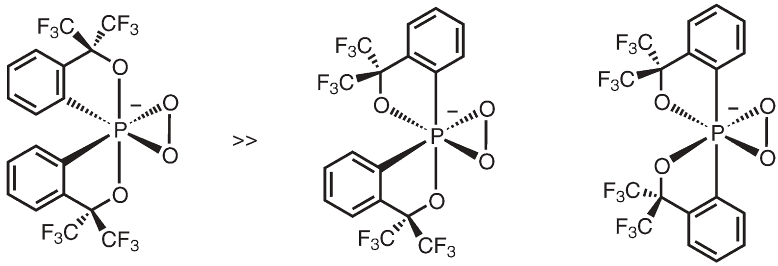


Fig. 17 Enantiomeric (Δ, Λ) and diastereomeric (meridional, facial) hexacoordinated phosphates of "$P(ab)_3$" type

belong to this group. To our knowledge, the question of their stereochemical integrity has not been studied. For **30**, Holmes and coworkers only report the formation of the meridional isomer (isolated after a crystallization). No mention was made of the presence of the facial derivative.

Finally, the lower symmetry of compounds **27** and **28**, of type $P(ab)_2(cd)$, and **29**, of type $P(ab)_2(cc)$, could have lead to the formation of many (racemic) diastereomers. Interestingly, this is not the case as the configuration of the 10-P-5 phosphorane precursors is translated integrally to the P(VI) derivatives, as shown by Akiba and Kawashima [45–48]. Further manifestation of this phenomenon will be described in Sect. 3.1. A particularly striking example is the exclusive formation of **29** over **29′** and **29″** (Fig. 18) [48].



29 **29'** **29"**

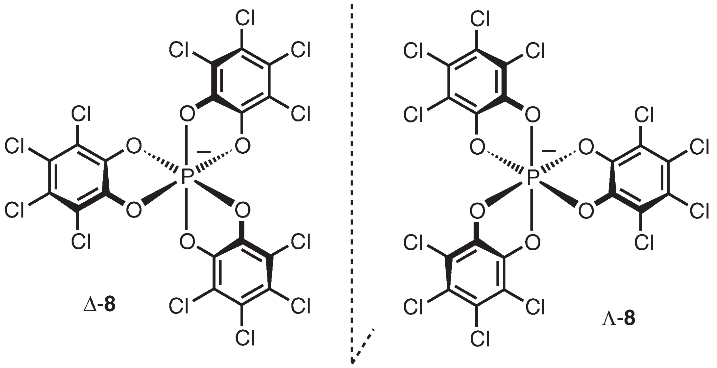
Fig. 18 Diastereomeric phosphates **29**, **29′** and **29″**

2.5.2
Enantiopure (Diastereomerically Enriched) Phosphates

Most of the phosphorus compounds described in the previous sections are chiral *and* racemic. Attempting their resolution – that is a physical separation of the enantiomers – was obviously attractive and this was realized as early as 1965 by Hellwinkel, who obtained both optical antipodes of **2** [18]. A patent on the synthesis and possible applications of enantiopure phosphate **2** was even filed at the time [103].

Tris(benzenediolato)phosphate anion **1**, of particular interest for its simple preparation from pyrocatechol, PCl_5 and an amine, is unfortunately configurationally labile in solution as an ammonium salt. Mechanistic studies by Koenig and coworkers have shown that the racemization of **1** is acid-catalyzed and proposed an intramolecular one-ended dissociation mechanism to explain it [25–28]. In 1997, Lacour and coworkers demonstrated that the introduction of electron-withdrawing chlorine atoms on the aromatic nuclei of the catecholate ligands increases the configurational (and chemical) stability of the resulting tris(tetrachlorobenzenediolato)phosphate(V) derivative (Fig. 19). This D_3-symmetric TRISPHAT anion **8** can be resolved by an association with a chiral ammonium cation [31]. The Λ enantiomer is isolated as the tri-*n*-butylammonium salt, $[Bu_3NH][\Lambda\text{–}\mathbf{8}]$, which is soluble in pure $CDCl_3$ and CD_2Cl_2. The Δ-enantiomer is prepared as the cinchonidinium derivative, which is only soluble in polar solvent mixtures (>7.5% DMSO in $CDCl_3$). Interestingly, pseudo-enantiomeric cinchoninium cation is essentially inefficient for the resolution of the hexacoordinated phosphate [104].

The stereoselective synthesis of hexacoordinated phosphate anions was also reported by the same group. A general one-pot process was developed for the preparation of C_2-symmetric anions **15**, **16** and **17** containing enantiopure BINOL, hydrobenzoin, and tartrate-derived ligands respectively [38–40]; C_1-symmetric anion **18** being prepared similarly in two steps from methyl-α-


Δ-**8**

Λ-**8**

Fig. 19 Δ and Λ enantiomers of TRISPHAT anion **8**

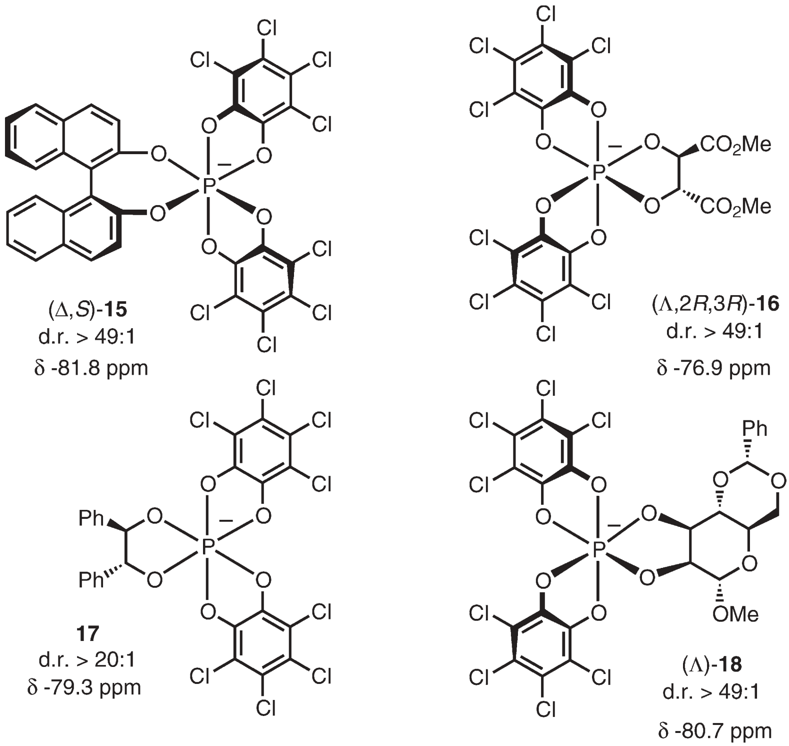
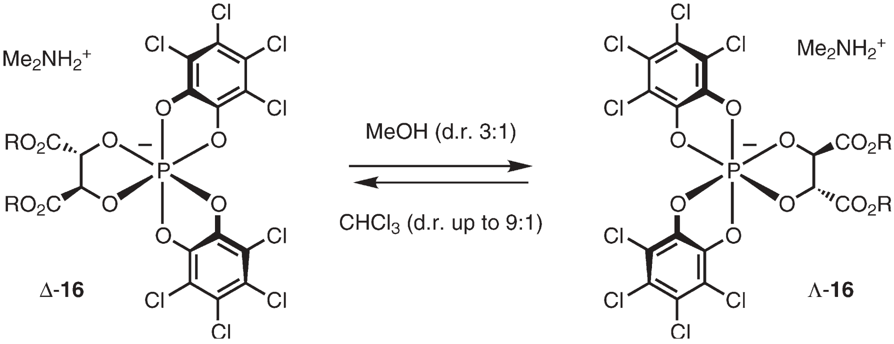


Fig. 20 Diastereomeric purity and relative configuration of enantiopure chiral phosphate anions **15** to **18** isolated after initial precipitation

D-mannopyranoside [41]. All these anions were isolated as their dimethylammonium salts in good yields and chemical purity. The presence of the stereogenic centers of the chiral ligands induces the formation of diastereomers. In essentially all cases, the initial salts are obtained in high diastereomeric purity. Figure 20 shows the diastereomeric ratios and, when known, the relative configuration of the major isolated compounds.

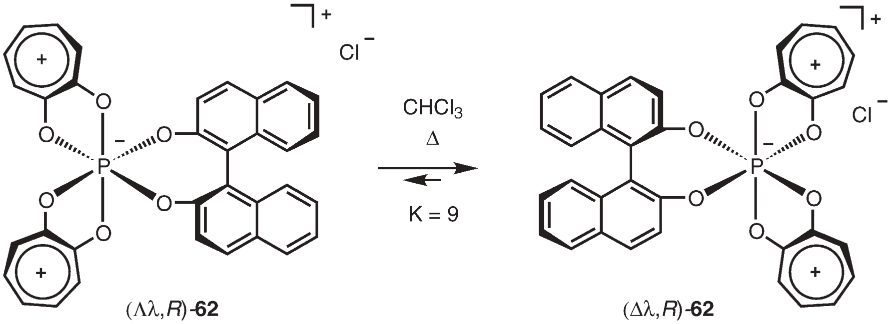
However, upon dissolution, an epimerization of the anions can occur in the presence of acidic counter-ions. This is particularly true for **16a–16d** [39]. The nature of the solvent (MeOH, $CHCl_3$) plays a crucial role on the kinetics of epimerization and the position of the resulting equilibrium. For anions made with a (2*R*, 3*R*) tartaric backbone, a Λ configuration is always preferred in MeOH; the selectivity, obtained after a slow equilibration, being independent of the nature of the ester alkyl chain (diastereomeric ratio (d.r.) 3:1). However, in chloroform, the Δ diastereomer is rapidly obtained and the selectivity is best if the ester side chain is sterically demanding (d.r. 2:1 to 9:1 from **16a** to **16d**) (Scheme 16).

For the BINPHAT anion **15**, of enantiomeric (Δ,*S*) or (Λ,*R*) configuration, no such epimerization occurs. However, due to the strain of the 7-membered ring,



Scheme 16 Solvent-induced (controlled) epimerization of TARPHAT anions **16**

a decomposition of the hexacoordinated phosphate anion can happen if the $Me_2NH_2^+$ cation is not rapidly exchanged in solution for a non-acidic counterion. Finally, if two strongly electron-withdrawing ligands, such as tropyliumdiolato moieties, are introduced along with BINOL around the P atom then the two diastereomers can be observed, isolated and fully characterized [100]. It was shown, using BINOL ligand of same *R* configuration, that the thermodynamic isomer of the cationic derivative **62** has a relative Δ configuration different from the Λ one of BINPHAT anion **15**. This might indicate that the selectivity in favor of the diastereomer (Λ,*R*)-**15** comes from a kinetic rather than a thermodynamic control (Scheme 17).



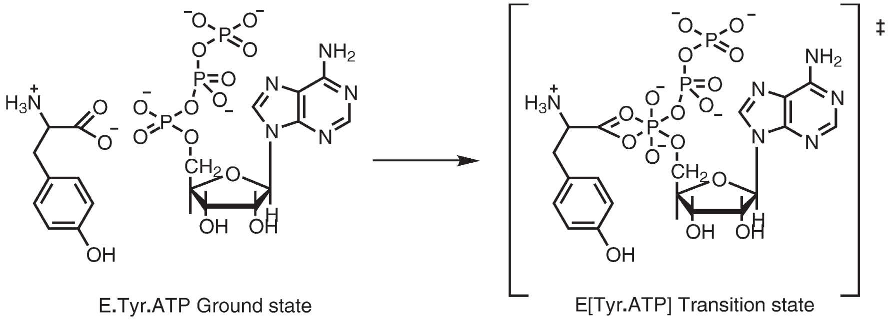
Scheme 17 Temperature-induced epimerization of chiral cationic phosphate **62**

3
Applied P(VI) Chemistry

The previous section focused on the structure of novel P(VI) derivatives that have appeared in the literature in recent years. Many of the articles describing these molecules essentially detailed the making and the characterization of the compounds. However, quite a few reports have dealt more with applications of the derivatives than their characterization since P(VI) compounds find useful roles in fields as varied as: (i) bioorganic chemistry, (ii) classical organic chemistry, (iii) photochemistry, (iv) electrochemistry, and (v) stereoselective synthesis and analysis. A rather broad selection of very diverse applications is therefore presented in the following part.

3.1
P(VI) Derivatives in Bioorganic Studies

Modeling the active site for phosphoryl transfer enzymes represents an important and challenging task for biochemists. Most studies have outlined mechanisms of nucleophilic attack at pseudo-tetrahedral phosphate centers that proceed by in-line displacement reactions. However, due to (i) better understanding of P(V) chemistry, (ii) better understanding of the P(V)⇆P(VI) equilibrium, and (iii) the building of experimental evidence that P(VI) adducts are easily formed, refined mechanistic models taking into account the possible role of high valent phosphorus have been proposed [8, 49, 50]. If the role of P(V) is unambiguously recognized, P(VI) could also intervene. Holmes has recently proposed that a carboxylate group can play a role in the activation of tyrosine in tyrosyl-tRNA synthetase leading to the formation of a P(VI) adduct in the transition state (Scheme 18).



Scheme 18 Possible carboxylate group participation in the activation of tyrosine in tyrosyl-tRNA synthetase

Much effort has also been directed toward mimicking electron transfer on natural photosynthetic systems. Recently, the group of Harada has been able to prepare monoclonal antibodies against metallo porphyrins and show that the biological edifice can control photoinduced electron transfer from the porphyrin to organic acceptor molecules in solution. As it was important to design a biomolecule able to accommodate not only the metalloporphyrin unit but also organic substrates, Harada recently used a hexacoordinated phosphorus

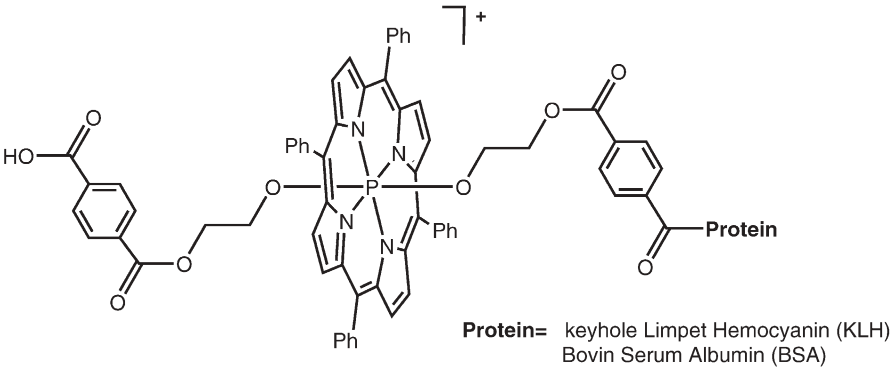
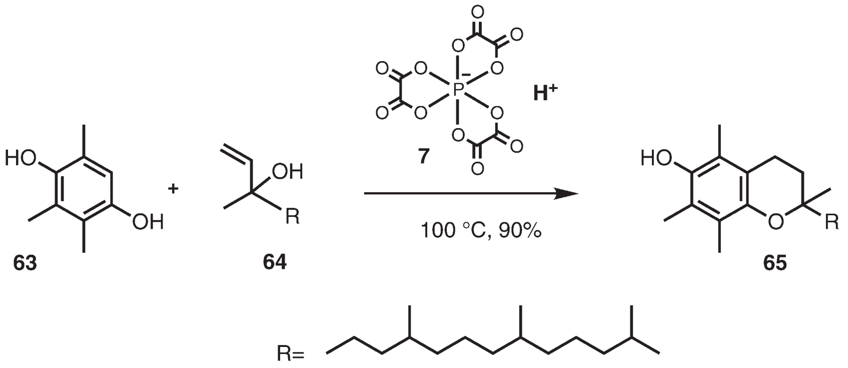


Fig. 21 Cationic P(VI) hapten for biomimetic photosynthetic studies

porphyrin as a hapten because of its ability to form water-stable derivatives with specific ligands attached at the axial positions of the central P atom [90]. The resulting antibodies recognized not only the porphyrin moiety but also the axial ligands. High selectivity, strong coordination and facile electron transfer from the porphyrin to acceptor molecules were then displayed by the bio-assembly. The hapten used is described in Fig. 21.

3.2
P(VI) Derivatives in Organic Chemistry

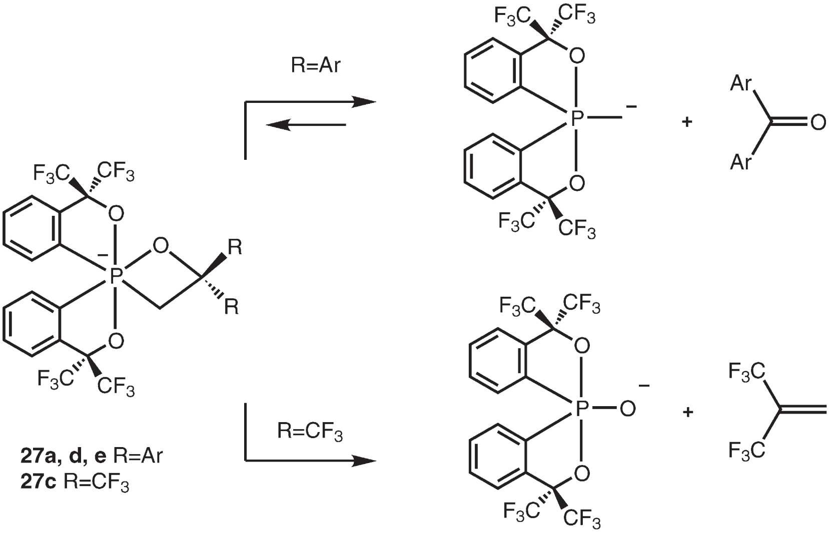
The strong Brønstedt acid nature of some hexacoordinated phosphorus derivatives, $[7^-,H^+]\cdot(Et_2O)_4$ in particular, was recently used within the context of an industrial application [36]. The conjugated acid of tris(oxalato)phosphate anion **7** was found to effectively catalyze the ring-forming reaction of trimethylhydroquinone **63** with isophytol **64** to give (*all rac*)-α-tocopherol **65** (ethylenecarbonate/heptane 1:1, 100 °C, 90%, Scheme 19). This process is particularly



Scheme 19 Tocopherol (**65**) synthesis mediated by the conjugate acid of anion **7**

efficient as it evolves a small amount of catalyst (0.5 mol% or less) and affords low quantities of by-products. Other advantages are the easy and cheap preparation of **7**, and the absence of heavy metals and sulfur- and fluorine-containing compounds in the process.

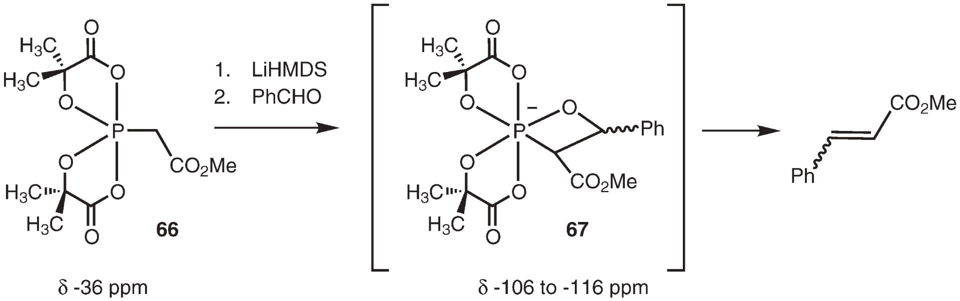
Kawashima [45] and Akiba [46, 47] have reported a possible use of 1,2- oxaphosphetanides **27–28** to generate olefins via a higher-order Horner–Wadsworth–Emmons process. Upon heating at 80–100 °C, derivative **27c** undergoes a cycloreversion reaction to afford the corresponding olefin and a hydroxyphosphorane. However, this process is strongly substrate-dependent as compounds **27a**, **27d** and **27e** react at the same temperature to "form again" benzophenones and methylphosphorane **31**, respectively (Scheme 20).



Scheme 20 Temperature-induced reactions of oxaphospheranides **27–28**

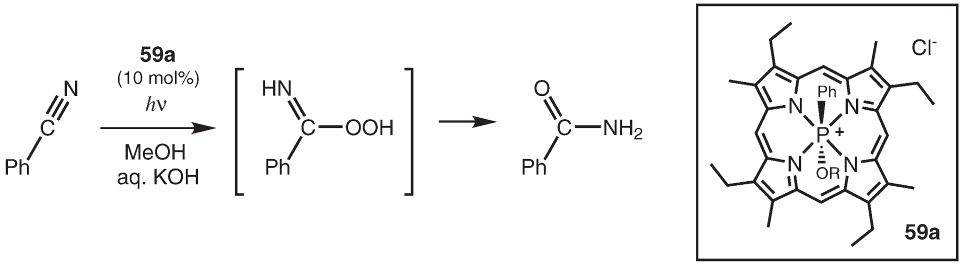
Evans Jr. and coworkers reported a similar olefination reaction employing spirooxyphosphoranes of type **66**. Upon treatment with a strong base (LiHMDS) and subsequent addition of benzaldehyde, the reaction proceeded to form anionic P(VI) intermediates (**67**, δ −106 to −116 ppm) that decomposed at room temperature to form the corresponding olefins and spiropentaoxyphosphoranes [105]. The stereoselectivity (*E*:*Z* ratio) of the double bond-forming reaction depended upon the conditions; evidence indicated the possibility of kinetic or thermodynamic control (Scheme 21).

Finally, phosphorus porphyrins, such as some of those detailed in Sect. 2.3.1 have attracted attention in organic chemistry for their unique photochemical properties. Aida reported that basic aqueous solutions of benzonitrile in the presence of **59a** undergo under irradiation (λ>420 nm) a clean transformation



Scheme 21 Higher order Horner–Wadsworth–Emmons olefination via hexacoordinated intermediates **67**

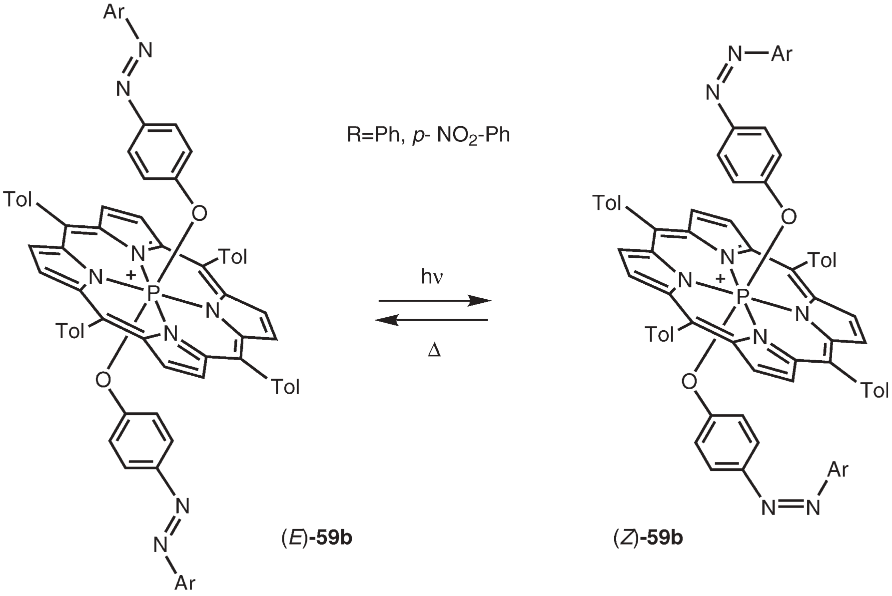
to benzamide [80]. Most probably, **59a** upon photoexcitation in the presence of OH^- is reduced to the corresponding anion radical, which then undergoes electron-transfer to existing O_2 to generate O_2^- (or HO_2^- in the presence of water); this latter reagent being responsible for the observed reactivity. Obviously, this application of **59a** could have been part of the next paragraph on photochemical applications and it constitutes a good introduction to the next topic (Scheme 22).



Scheme 22 Hydration of benzonitrile catalyzed by cationic porphyrin **59a**

3.3
Photochemical and Photophysical Properties of P(VI) Derivatives

As just mentioned, phosphorus porphyrins have unique photochemical properties. Their photophysics is also interesting. Emitter-quencher assemblies based on porphyrin building blocks have attracted attention due to their potential to serve as models in photosynthetic research (see [90] for an example) or for the development of photoswitches that could be used for the fabrication of molecular electronic/optical devices. In this context, Maiya and coworkers constructed a P(VI) porphyrin system **59b** with two "switchable" azobenzene groups positioned in the "apical" positions of the pseudo-octahedral phosphorus atom [92]. Photoswitch ability (luminescence on/off) was demonstrated as a result of the *E* to *Z* isomerization-induced modulation of the intramolecular photo-induced electron transfer between the axial azobenzene subunits and the basal porphyrin scaffold (Scheme 23).



Scheme 23 Photoswitch ability (luminescence on/off) of **59b** as a result of the *E* to *Z* isomerization-induced modulation

The ease of introduction of axial substituents on phosphorus porphyrins was also used by Shimidzu and coworkers to link a large number of porphyrin arrays with molecular conducting tetrathiophene wires (Fig. 22) [76, 77]. The P(VI) porphyrin unit tending to be an electron acceptor acts as a photo-induced hole generator. The tetrathiophene tending to be an electron donor is able to transfer the positive hole just as molecular electric wire. The conductivity of this donor-acceptor polymer was shown to be strongly enhanced by photoirradiation, indicating that the formation and transfer occur efficiently along the polymeric chain. This also suggests the possibility of effective photoswitching.

Rao reported measurement of third-order optical non-linearity in the nanosecond and picosecond domains for phosphorus tetratolyl porphyrins bearing two hydroxyl groups in apical position [89]. Strong nonlinear absorption was found at both 532 nm and 600 nm. The high value of nonlinearity for nanosecond pulses is attributed to higher exited singlet and triplet states. Time resolved studies indicate an ultra-fast temporal evolution of the nonlinearity in this compound.

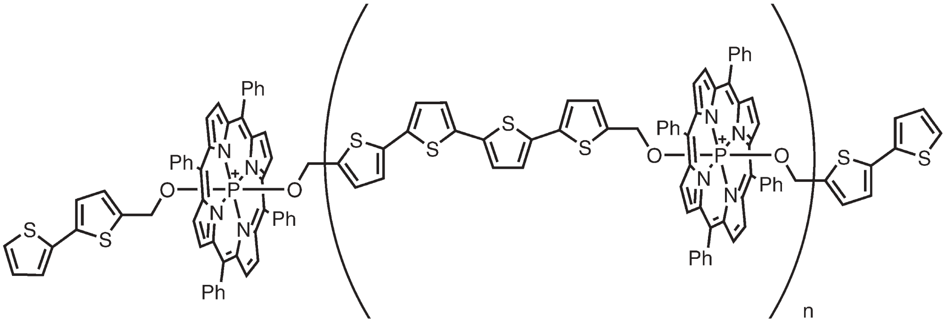


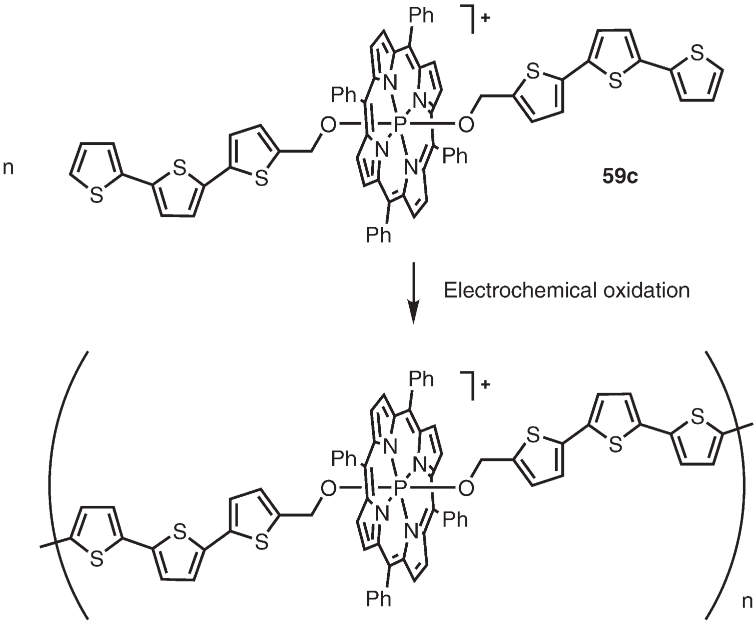
Fig. 22 Phosphorus porphyrin arrays with molecular conducting tetrathiophene wires

3.4
Electrochemical Applications of P(VI) Derivatives

Numerous investigators have attempted to develop inexpensive, nontoxic, highly soluble and thermally, chemically and electrochemically stable lithium salts to replace the common but problematic $LiPF_6$ in so-called lithium batteries. In this context, lithium tris[benzenediolato]phosphate or [Li,**1**] was synthesized and utilized as Li battery electrolytes for Li/V_2O_5 cells [106]. The specific conductivity (3.89 mS cm^{-1}) in an ethylene carbonate-tetrahydrofuran binary mixture was somewhat low. It can be explained by the high viscosity of the large anion. In spite of the low conductivity, a rather high cutoff potential of 3.7 V vs Li/Li^+ was measured. For the lithium salt of tris(oxalato)phosphate anion or [Li,**7**] much higher specific conductivity (7.0–9.7 mS cm^{-1}) was measured in a variety of solvent conditions and the cutoff potential was found to be higher (~4.0 V) [29]. Later, Nanbu investigated the thermal stability and electrolytic properties of tris[4-methyl-1,2-benzenediolato]phosphate or [Li,**9**] [32]. The specific conductivity of the salt itself is rather modest (2.3 mS cm^{-1}) but the equimolecular mixture of [Li,**9**] and [Li,PF_6] showed – not too surprisingly – an improvement in conductivity (5.3 mS cm^{-1}). However, more importantly, the cyclic efficiencies in the electrolyte solutions containing a mixture of [Li,**9**] and $LiPF_6$ were much better than those in $LiPF_6$ only. Finally, Nanbu, Eberwei and coworkers reported the electrochemical study of [Li,**11**] and [Li,**12**] [34, 35]. These two salts presented the very high cutoff potentials vs. Li^+/Li with values of 3.95 and 4.3 V, respectively.

Akiba investigated the electrochemical behavior of a variety of phosphorus octaethylporphyrin derivatives; all compounds showing a single reversible oxidation wave [91]. The absolute difference in potential between the first ring-centered oxidation and reduction varies from 2.19 to 2.36 V in dichloromethane. These values are within the range of the HOMO-LUMO gap observed for most metalloporphyrins.

The synthesis of thin films of organic conducting polymers on a nanometer scale is one of the challenges of nanotechnology. Electrochemical poly-



Scheme 24 Electrochemical Polymerization of "wheel-and-axle" type phosphorus porphyrins

merization is a well-established method for preparation of such films as their thickness can be controlled by limiting the charge passed during the polymerization. Tanaka [81] and Shimidzu [72, 76] and coworkers reported the construction of ultra-thin films by deposition on gold crystals or on electrodes of oxidatively polymerized "wheel-and-axle" type phosphorus porphyrins (**59c**)/oligothienyl units. A selected example of the chemical process is described above (Scheme 24).

3.5
Stereoselective Applications of Enantiopure Anionic P(VI) Derivatives

Many chemical reactions and processes involve cationic reagents, intermediates or products. Cations can be sometimes *prochiral* or *chiral* and most applications that involve these moieties lead to racemic molecular or supramolecular assemblies. To afford instead non-*racemic* or enantiopure products, and benefit from possible new applications, an asymmetric ion pairing with chiral anions can be considered – the counterions behaving as asymmetric auxiliaries, ligands or reagents [107]. Recently, the chemistry of P(VI) phosphate anions has been rejuvenated for exactly this purpose [108, 109]. Applications of anions like **8** and **15** as NMR chiral shift reagents, as resolving agents for organic and inorganic cations and as chiral auxiliaries in stereoselective processes have been reported and some of them are detailed below.

3.5.1
NMR Determination of Enantiomeric Purity

As already mentioned, chiral cations are involved in many areas of chemistry and, unfortunately, only few simple methods are available to determine their optical purity with precision. In the last decades, NMR has evolved as one of the methods of choice for the measurement of the enantiomeric purity of chiral species [110, 111]. Anionic substances have an advantage over neutral reagents to behave as NMR chiral shift agents for chiral cations. They can form diastereomeric contact pairs directly and the short-range interactions that result can lead to clear differences in the NMR spectra of the diastereomeric salts.

An overall efficiency of TRISPHAT **8** and BINPHAT **15** anions as NMR chiral shift agents for chiral cations has been demonstrated over the last few years. Additions of ammonium salts of the Δ or Λ enantiomers of **8** and **15** to solutions of racemic or enantioenriched chiral cationic substrates have generally led to efficient NMR enantiodifferentiations [112–121]. Well-separated signals are usually observed on the spectra of the diastereomeric salts generated in situ.

Sometimes, a direct ion-pairing of the chiral cations and anions **8** or **15** is necessary to maximize the NMR separation of the signals [115, 116]. Cationic species as different as quaternary ammonium, phosphonium, [4]heterohelicenium, thiiranium ions, (η^6-arene)manganese, ruthenium tris(diimine) have been analyzed with success (Fig. 23).

TRISPHAT anion **8** seems to be more particularly efficient with cationic metallo-organic and organometallic substrates. BINPHAT **15** has often-superior chiral shift properties than **8** when associated with organic cations such as ammonium cation **68** (Fig. 24). In all these examples, solvent polarity influences the quality of the separation since ion association is crucial. Solvent or solvent mixtures of low polarity are preferred for these experiments.

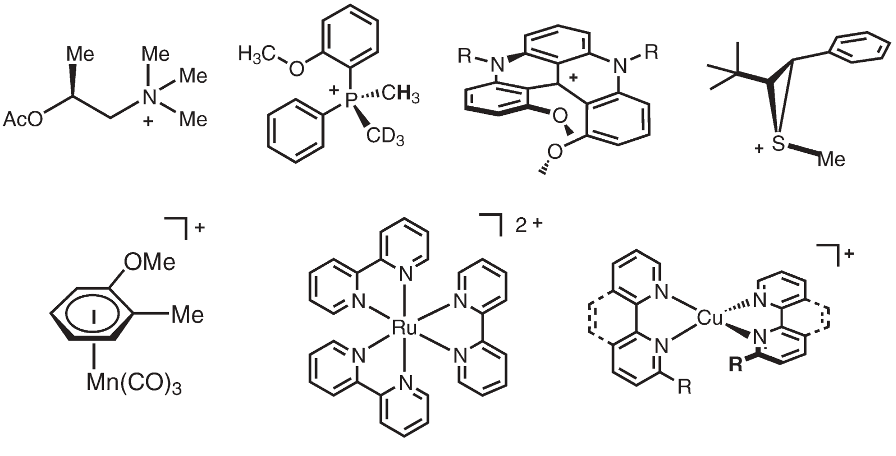


Fig. 23 Selected examples of chiral cations analyzed successfully with anions **8** or **15**

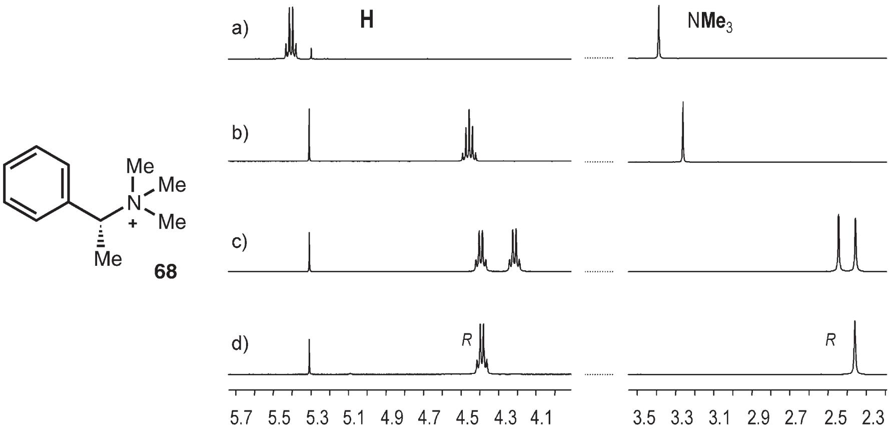


Fig. 24 ^{1}H NMR spectra (400 MHz, $CDCl_3$, parts) of *a)* [*rac*-**68**][I], *b)* [*rac*-**68**][Δ-**8**], *c)* [*rac*-**68**] [Δ,*S*)-**15**] and *d)* [*R*-**68**][(Δ,*S*)-**15**]

Recently, Lacour, Sauvage and coworkers were able to show that the association of chiral $[CuL_2]^+$ complexes (L=2-R-phen, 6-R-bpy and 2-iminopyridine) with TRISPHAT **8** leads to an NMR enantiodifferentiation, which allows the determination of the kinetics of racemization of the complexes (bpy=2,2′-bipyridine; phen=1,10-phenanthroline) [119]. This type of application has recently been reported in conjunction with chiral sandwich-shaped trinuclear silver(I) complexes [122]. Several reports, independent from Lacour's group, have confirmed the efficiency of these chiral shift agents [123–127]. Finally, TRISPHAT can be used to determine the enantiomeric purity of (η^6-arene)chromium complexes. These results broaden the field of application of **8** to chiral neutral, and not just cationic, species [114, 128, 129].

3.5.2
Resolution of Chiral Cations

Many chemical reactions and processes yield cationic racemic products, and either a resolution or a stereoselective synthesis must be envisaged to obtain the chiral cations in an enantioenriched or enantiopure form. Resolution has been strongly studied [130] and selected representative examples of such processes mediated by chiral P(VI) anions are presented.

Preparative chromatographic resolution procedures have overall freed chemists from the constraint of dependency on crystallization. They are most often performed with covalent diastereomer mixtures but ionic salts can also be separated. Recently, it was found that the lipophilicity of TRISPHAT anion **8** profoundly modifies the chromatographic properties of the cations associated with it and the resulting ion pairs are usually poorly retained on polar chromatographic phases (SiO_2, Al_2O_3) [131]. Using enantiopure TRISPHAT anion,

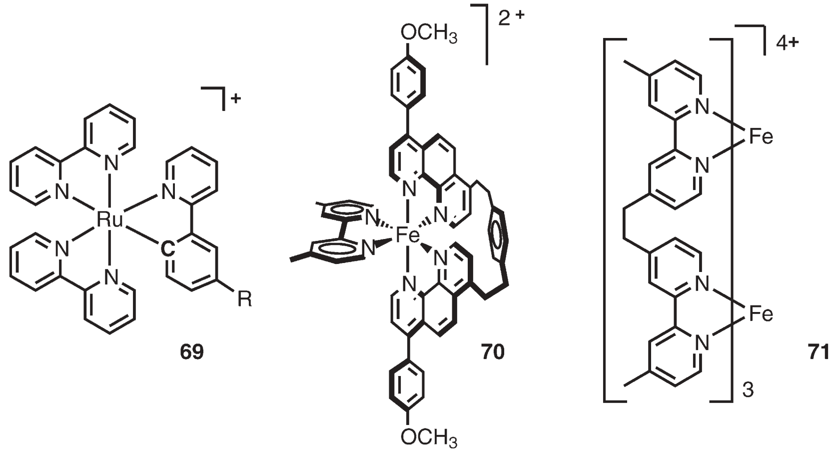


Fig. 25 Chiral cationic coordination complexes **69**, **70** and **71**

accessible from [cinchonidinium][Δ-**8**] or [Bu_3NH][Λ-**8**] salts, the chromatographic resolution of chiral cations is feasible, as the diastereomeric ion pairs often possess rather different retardation factors. For instance, $[Ru(bpy)_3]^{2+}$ and $[Ru(Me_2bpy)_3]^{2+}$ (Me_2bpy: 4,4′-dimethyl-2,2′-bipyridine) complexes were separated into diastereomeric homochiral [Δ-RuL_3]$[Δ\text{-}\mathbf{8}]_2$ and heterochiral [Λ-RuL_3]$[Δ\text{-}\mathbf{8}]_2$ salts by column chromatography over silica gel (eluent CH_2Cl_2) [132]. Rather large differences in retardation factors were observed (ΔR_f 0.10–0.23). The resolution can also be performed on preparative thin-layer chromatographic (TLC) plates. The protocol was extended to monocationic cyclometallated ruthenium complexes **69** and to a configurationally stable mononuclear iron(II) complex **70** (Fig. 25) [116, 133].

The lipophilicity of the TRISPHAT anion **8** also confers to its salts an affinity for organic solvents and, once dissolved, the ion pairs do not partition in aqueous layers. This rather uncommon property was used by Lacour's group to develop a simple and practical resolution procedure of chiral cationic coordination complexes by asymmetric extraction [134, 135]. Selectivity ratios as high as 35:1 were measured for the enantiomers of ruthenium(II) trisdiimine complexes, demonstrating without ambiguity the efficiency of the resolution procedure [134].

An extension of this protocol was further developed for a diiron(II) triple helicate and afforded in separated phases the *P* or *M* enantiomers of the $[Fe_2L_3]^{4+}$ helix **71** (Fig. 25) [135].

3.5.3
Stereoselective Chemistry Induced by Chiral Anions

Chiral compounds are sometimes configurationally stable as solids and configurationally labile in solution. When optically active samples of these derivatives are solubilized, a racemization occurs due to the free interconversion of the enantiomers in solution. To obtain these compounds in one predominant configuration over time, a possible strategy is to add stereogenic elements to their backbone; intramolecular diastereoselective interactions happen and favour one of equilibrating diastereomers [136, 137]. If the chiral compounds are charged, an alternative strategy to control their configuration is to consider their asymmetric ion pairing with chiral counter-ions [138]; intermolecular – rather than intramolecular – diastereoselective interactions then control the stereoselectivity (Pfeiffer effect) [139, 140].

Unfortunately, in most of the previous examples, the extent of the asymmetry-induction was determined by chiroptical measurements (ORD, CD) that gave qualitative and not quantitative information. The NMR chiral shift efficiency of TRISPHAT **8** and other hexacoordinated phosphate anions was therefore considered as an excellent analytical tool to provide accurate measurement of the induced selectivity by NMR spectroscopy.

Configurationally labile cations, as varied as [Fe(Me$_2$bpy)$_3$]$^{2+}$ **72** (Fig. 26), [Fe(phen)$_3$]$^{2+}$ and [Co(Me$_2$bpy)$_3$]$^{2+}$ complexes, dicobalt(II) triple helicates, di-

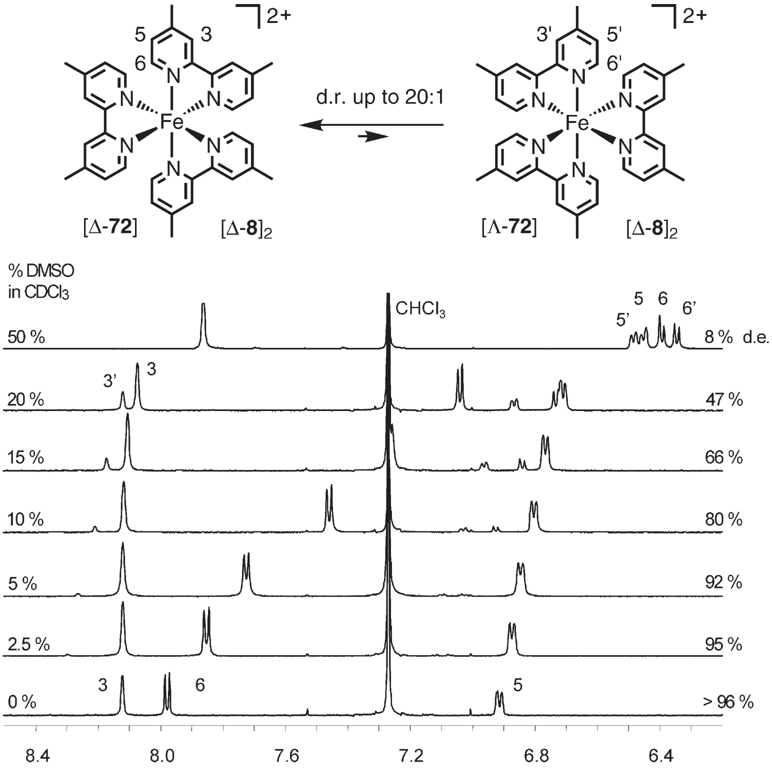
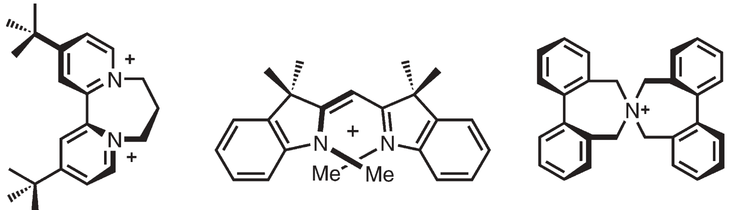


Fig. 26 ^{1}H NMR spectra (parts) of equilibrating salts [Δ-**72**]Δ-**8**]$_2$ and [Λ-**72**][Δ-**8**]$_2$ in [D$_6$]DMSO/CDCl$_3$ and resulting diastereoselectivity



73 **74** **75**

Fig. 27 Chiral configurationally labile cations **73**, **74** and **75**

quat **73**, monomethine dye **74** and quaternary ammonium **75**, were paired with enantiopure anions **8** and/or **15** [38, 41, 141–144]. In all cases, an enantiodifferentiation of the interconverting enantiomers of the chiral cations was observed in ^{1}H NMR spectroscopy. In most cases, the analyses could be performed at room temperature, as the interconversion was slow on the NMR time scale, e.g., **72** (Fig. 26).

For cations **74**–**75** (Fig. 27), low temperature NMR experiments were necessary to reveal stereodynamical behaviors and allow the observation of split signals for the enantiomers [38, 144]. Stereoselective recognition between the chiral cations and anions was observed in essentially all cases as integration of the split signals revealed the preferential occurrence of one diastereomeric salt over the other.

Diastereomeric ratios as high as 20:1 can be observed for some of the substrates, e.g., salt [72][Δ-**8**] [41, 141]. The selectivity strongly depends upon the polarity of the solvent medium. An increase in the diastereoselectivity is usually observed upon the decrease of solvent polarity. This is interpreted as the result of closer interactions between the ions. In most cases, induced CD spectra could also be measured allowing the determination of the preferred configuration of the chiral cations.

4
Conclusion

In this review, we hope that we have been able to show the high diversity of P(VI) chemistry in the nature of its derivatives as well as in their subsequent applications. Our feeling is that P(VI) chemistry has strongly matured over the last 5–10 years. However, there is still much ground to be covered and, no doubt, new and more selective P(VI) chemistry will be prepared to achieve new structures and develop more efficient solutions to desired goals.

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Reactivity of Phosphorus Centered Radicals

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Abstract The recent literature devoted to the chemical reactivity of the main families of phosphorus centered radicals is surveyed. Various tin-free radical chain reactions involving L_2P-H or $L_2P(O)$-H compounds as hydrogen donors and the corresponding phosphinyl ($L_2P^\bullet$) or phosphonyl [$L_2P(O)^\bullet$] radicals as chain carriers have been developed. The photo-Arbuzov rearrangement of arylalkylphosphites has been intensively investigated and applied to the preparation of biologically active phosphonates. Single electron transfer reactions involving phosphoniumyl radicals have been applied to the dediazoniation of arenediazonium salts and to the oxidation of trivalent phosphorus compounds. The versatile chemistry of phosphoranyl radicals has been illustrated through various original reactions like the synthesis of phosphonates via free radical Arbuzov reactions and radical chain desulfurizations. New persistent or stable phosphorus centered radicals have been characterized. Different reports have shown that the properties of an organic free radical can be dramatically changed when a phosphorus group is in the vicinity of the radical center.

Keywords Phosphinyl · Phosphonyl · Phosphoniumyl · Phosphoranyl · Persistent phosphorus centered radicals

Abbreviations

ACN	Acetonitrile
AIBN	Azobisisobutyronitrile
a_N	EPR nitrogen hyperfine coupling constant
a_P	EPR phosphorus hyperfine coupling constant
BPO	Benzylperoxide
DCA	9,10-Dicyanoanthracene
DCN	1,4-Dicyanonaphtalene
DEPMPO	2-Diethoxyphosphoryl-2-methyl-3,4-dihydro-2*H*-pyrrole-1-oxide
DMPO	2,2-Dimethyl-3,4-dihydro-2*H*-pyrrole-1-oxide
EPHP	Ethylpiperidinyl hypophosphorus acid
EPR	Electron paramagnetic resonance
HIV	Human immunodeficiency virus
ISC	Inter-system crossing
Mes	2,4,6-Trimethylphenyl
Mes*	2,4,6-Tri*t*-butylphenyl
Ms	Mesyl group
NMP	Nitroxide-mediated radical polymerization
Nu	Nucleophile
Ph	Phenyl
P_m	Polymer chain of m units
R_f	Perfluoroalkyl
RT	Room temperature
S	Singlet state
SET	Single electron transfer
SG1	*N*-*tert*-Butyl-*N*-(1-diethylphosphono-2,2dimethylpropyl)nitroxide
SOMO	Single occupied molecular orbital
T	Triplet state
TBDMS	*tert*-Butyldimethylsilyl
TBP	Trigonal bipyramidal
TEMPO	2,2,6,6-Tetramethyl-1-piperidinyloxy radical
TMS	Trimethylsilyl group
Tol	Tolyl group

1
Introduction

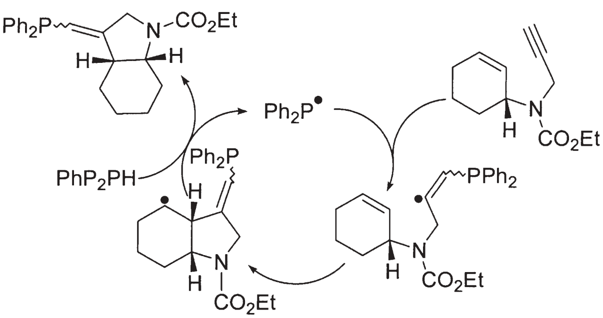
This chapter surveys the literature published from 1995 to 2003, concerning the reactivity and the chemical applications of the four main families of phosphorus centered radicals, i.e., phosphinyl ($L_2P^\bullet$), phosphonyl ($L_2P^\bullet{=}O$), phosphoniumyl ($L_3P^{\bullet+}$) and related charged species, and phosphoranyl ($L_4P^\bullet$) radicals. Due to their specificity, a section is devoted to the generation and properties of persistent and stable phosphorus centered radicals.

2
Phosphinyl Radicals, $L_2P^\bullet$

Although their chemistry is less developed than that of phosphonyl, phosphoniumyl or phosphoranyl radicals, many structural studies have been devoted to phosphinyl radicals [1]. Like their nitrogen analogs, phosphinyl radicals are π-type radicals (Fig. 1) and because of the very small s character of their SOMO, the magnitude of their phosphorus hyperfine coupling constants a_P is below 15 mT [1].

Due to their weak P–H bonds (≈370 kJ mol^{-1}) [2] and the high rate constants for the transfer of the P–H hydrogen [3] (k=1.5 10^7 L mol^{-1}s^{-1} for Ph_2PH and k=5.0 10^5 L mol^{-1}s^{-1} for (c-hexyl)$_2$PH), diaryl and dialkyl phosphines present a high interest as H-donors. Since the corresponding phosphinyl radicals are good chain carriers [4, 5], diaryl and dialkyl phosphines can be added to olefinic or acetylenic compounds through radical chain reactions. Simpkins et al. [6] used

Fig. 1 Structure of phosphinyl radicals



Scheme 1 5-*exo* Cyclization initiated by phosphinyl radical addition onto an alkyne

the H-donor capability of diarylphosphines and the rapid addition of the corresponding phosphinyl radical onto unsaturated center to trigger 5-*exo* cyclizations, which afforded good yields (60%) of phosphinated bicyclo compounds (Scheme 1).

3
Phosphonyl Radicals, $L_2P^{\bullet}=O$

3.1
Reactivity

The characteristics of a large number of phosphonyl radicals $[L_2P(O)]^{\bullet}$ have been extensively listed over the last three decades [1]. Phosphonyl radicals are σ radicals [7] (Fig. 2) and due to the significant s-character of their SOMO they exhibit phosphorus hyperfine coupling constants a_P ranging from 30 mT to 70 mT [1].

The reactivity of electrochemically generated phosphonyl radicals has been recently reviewed by Kargin and Budnikova [8] and will not be considered here. The reactivity of phosphonyl radicals is mainly accounted for by the three processes [9] shown in Scheme 2: radical addition (1), atom transfer (2 and 3), and electron transfer (4).

The substitution of a functional group for a hydrogen atom is a very important transformation in synthetic organic chemistry. Barton et al. [10] developed various radical chain defunctionalization reactions using dialkylphosphonates

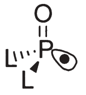
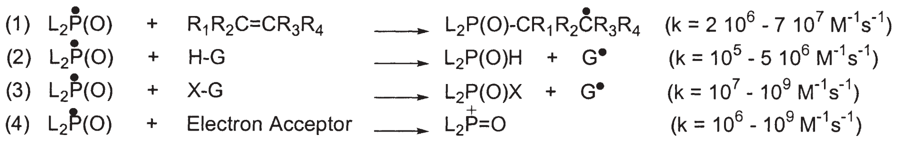


Fig. 2 Structure of phosphonyl radicals



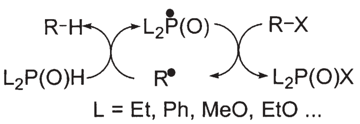
$$\text{(1)}\quad L_2\overset{\bullet}{P}(O) + R_1R_2C{=}CR_3R_4 \longrightarrow L_2P(O)\text{-}CR_1R_2\overset{\bullet}{C}R_3R_4 \quad (k = 2\ 10^6 - 7\ 10^7\ M^{-1}s^{-1})$$

$$\text{(2)}\quad L_2\overset{\bullet}{P}(O) + H\text{-}G \longrightarrow L_2P(O)H + G^{\bullet} \quad (k = 10^5 - 5\ 10^6\ M^{-1}s^{-1})$$

$$\text{(3)}\quad L_2\overset{\bullet}{P}(O) + X\text{-}G \longrightarrow L_2P(O)X + G^{\bullet} \quad (k = 10^7 - 10^9\ M^{-1}s^{-1})$$

$$\text{(4)}\quad L_2\overset{\bullet}{P}(O) + \text{Electron Acceptor} \longrightarrow L_2\overset{+}{P}{=}O \quad (k = 10^6 - 10^9\ M^{-1}s^{-1})$$

Scheme 2 Reactivity of phosphonyl radicals



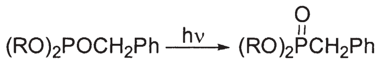
Scheme 3 Radical chain reaction involving phosphonyl radicals

($R_2P(O)H$) and phosphonates ($RO_2P(O)H$) as hydrogen atom donors and the corresponding phosphonyl radicals as chain carriers (Scheme 3).

The reactivity shown in Scheme 3 results from the low bond dissociation energy (BDE) of the P–H bond [11] (k=1.2 10^5 $M^{-1}s^{-1}$ for the H-transfer from $RO_2P(O)H$ to a primary C-centered radical) and the fast halogen-atom transfer from a C-halogen bond to a phosphonyl radical [9, 12] (k=4 10^5 $M^{-1}s^{-1}$ for *t*-Bu-Br and k=8.3 10^8 $M^{-1}s^{-1}$ for Cl_3C-Br). Piettre et al. [13] pointed out that these chain reactions were even more efficient when dialkylthiophosphites and the corresponding dialkylphosphinothioyl radicals were involved.

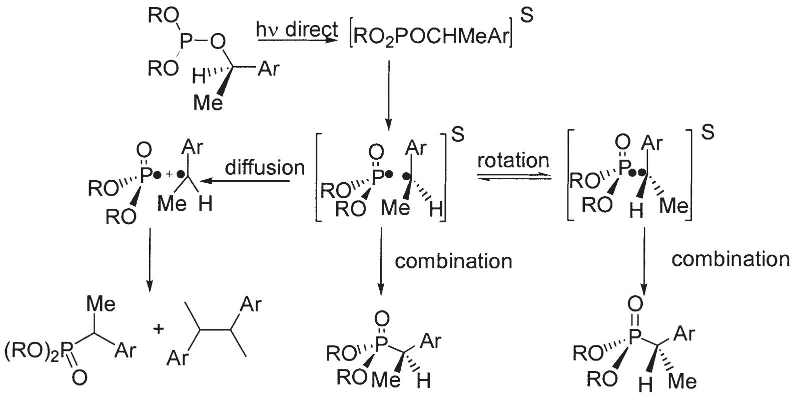
Addition of phosphonyl radicals onto alkenes or alkynes has been known since the sixties [14]. Nevertheless, because of the interest in organic synthesis and in the initiation of free radical polymerizations [15], the modes of generation of phosphonyl radicals [16] and their addition rate constants onto alkenes [9, 12, 17] has continued to be intensively studied over the last decade. Narasaka et al. [18] and Romakhin et al. [19] showed that phosphonyl radicals, generated either in the presence of manganese salts or anodically, add to alkenes with good yields.

Bentrude et al. [20] reported the first photo-Arbuzov rearrangement of arylethylphosphites (Scheme 4). The direct photolysis of arylethylphosphites



$$(RO)_2POCH_2Ph \xrightarrow{h\nu} (RO)_2\overset{O}{\overset{\|}{P}}CH_2Ph$$

Scheme 4 Photo-Arbuzov rearrangement of arylethylphosphites

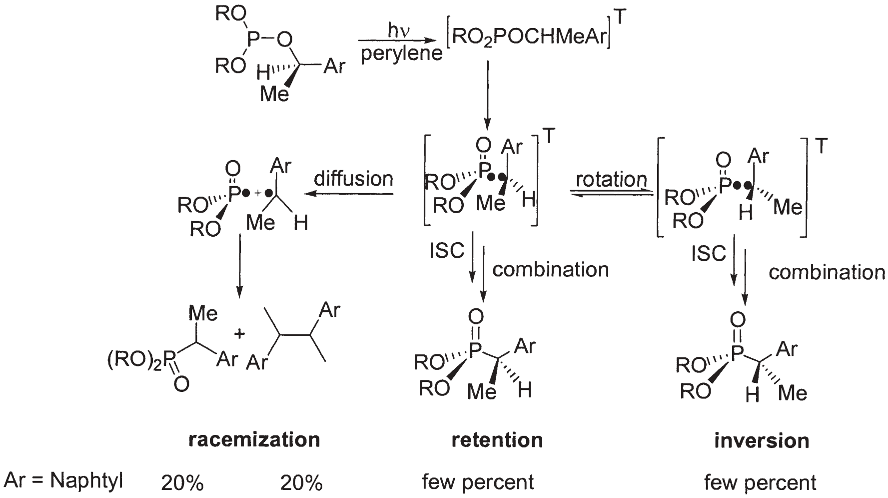


	racemization	retention	inversion
Ar = Ph	few percent	60%	10%
Ar = Naphtyl	few percent	56%	4%

Scheme 5 Photo-Arbuzov rearrangement of arylethylphosphites via a short-lived singlet proximate radical pair mechanism. Reprinted with permission from [22]. Copyright 2001 American Chemical Society

generates a short-lived singlet proximate radical pair of benzylic and phosphonyl radicals in the solvation cage [16a, 21, 22]. Then, high degree of recombination in the solvation cage affords the Arbuzov products [21, 22] (Scheme 5). The change in the configuration of the benzylic carbon strongly depends on the structure of the radicals involved in the radical pair [22].

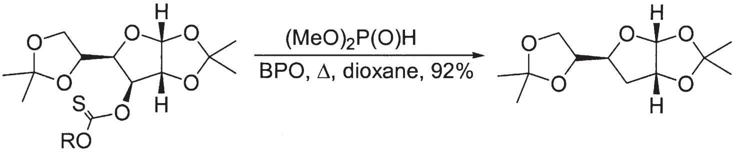
Different results were observed when a triplet-state photosensitizer (such as perylene) was used to generate long-lived triplet proximate radical pairs in the solvation cage. Because of the long-lived triplet state, radicals escape from the solvation cage and the typical reactivity of free radicals is observed, i.e., high amounts of aryldimer and complete stereorandomization when chiral phosphites were used (Scheme 6) [22]. The small amounts of compounds with retention or inversion of configuration result from the slow triplet to singlet inter-system crossing (ISC) [22].



Scheme 6 Photo-Arbuzov rearrangement of arylethylphosphites via a long-lived triplet proximate radical pair mechanism. Reprinted with permission from [22]. Copyright 2001 American Chemical Society

3.2 Applications

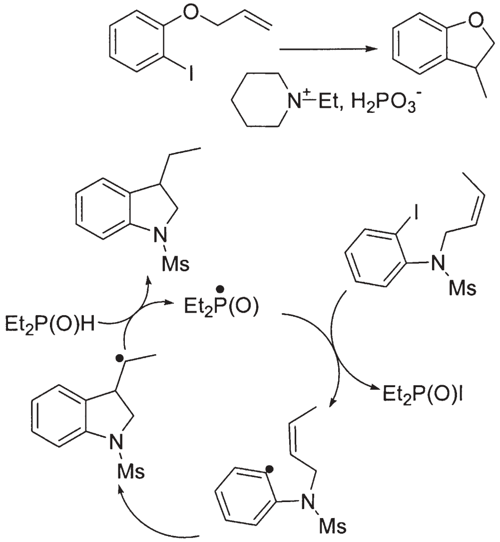
The versatility, predictability and functional-group tolerance of free radical methodology has led to the gradual emergence of homolytic reactions in the armory of synthetic chemistry. Tin hydrides have been successfully employed in radical chemistry for the last 40 years; however, there are drawbacks associated with tin-based chemistry. Organotin residues are notoriously difficult to remove from desired end products, and this, coupled with the fact that many organotin compounds are neurotoxins, makes techniques using tin inappropriate for syntheses of drugs, medicines and other formulations intended for human consumption [23]. Therefore, to overcome these problems [23], it is of the highest interest for radical chemists to develop new tin-free reducing agents and radical chain carriers [24]. The versatility of phosphorus compounds as tin hydride substitutes has been reviewed by Parsons [4] and Studer [5], and only a few typical examples are mentioned hereafter. Barton et al. [10] developed the use of $R_2P(O)H$ compounds as reducing agents and their corresponding $R_2P(O)^{\bullet}$ radicals as chain carriers in the Barton–McCombie deoxygenation reactions (Scheme 7).



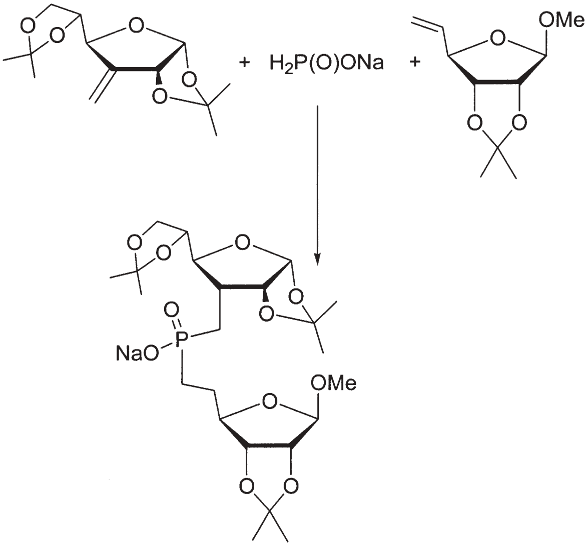
Scheme 7 Barton–McCombie deoxygenation reaction in the presence of $(MeO)_2P(O)H$

Murphy et al. showed that EPHP [25] and $L_2P(O)H$ [26] can also be used in radical C–C bond forming reactions (Scheme 8). Recently, Piettre et al. [27] used the sodium salt of hypophosphorous acid as H-donor and the subsequent phosphonyl radical as phosphonylating agent for the preparation of 3-furanosyl-6′-furanosylphosphinate (Scheme 9).

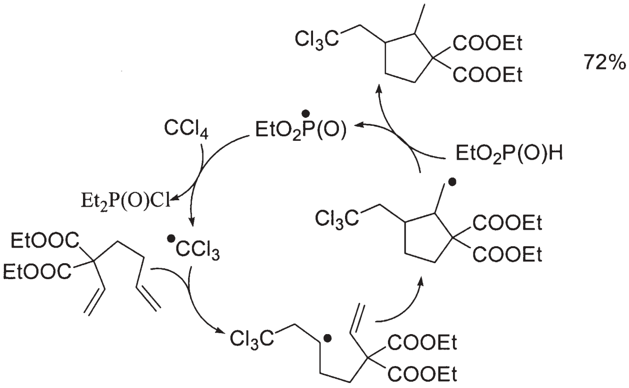
Good yields in conjunctive reductive/addition/cyclization reactions carried out with $(RO)_2P(O)H$ compounds were obtained by Parson et al. [28] (Scheme 10).



Scheme 8 C–C Bond forming reactions involving the use of $L_2P(O)H$ reagents



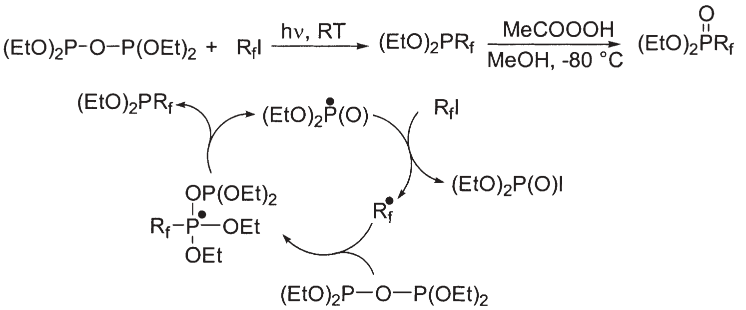
Scheme 9 Tandem sequential radical process using the sodium salt of hypophosphorous acid. Reprinted with permission from [27]. Copyright 2002 American Chemical Society



Scheme 10 Reductive cyclization involving phosphonyl radicals. Reprinted with permission from [28a]. Copyright 2001 Pergamon Press

Fluorinated phosphonates exhibit interesting properties as enzyme inhibitors, chelating agents or as fuel cell electrolytes [29]; however, only few methods of preparation for these compounds are available. Burton et al. [30] developed several methods to prepare fluorinated phosphates which involve phosphonyl, and likely phosphoranyl radicals as chain carriers (Scheme 11).

Because of their fast addition onto alkenes, phosphonyl radicals have found wide use as initiating radicals in photo-polymerizations. Several groups [31]



Scheme 11 Preparation of fluorinated phosphonates involving phosphonyl and phosphoranyl radicals as chain carriers

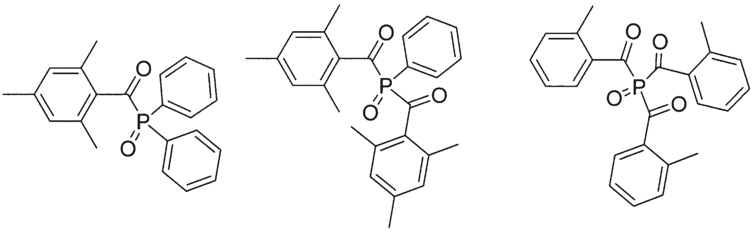
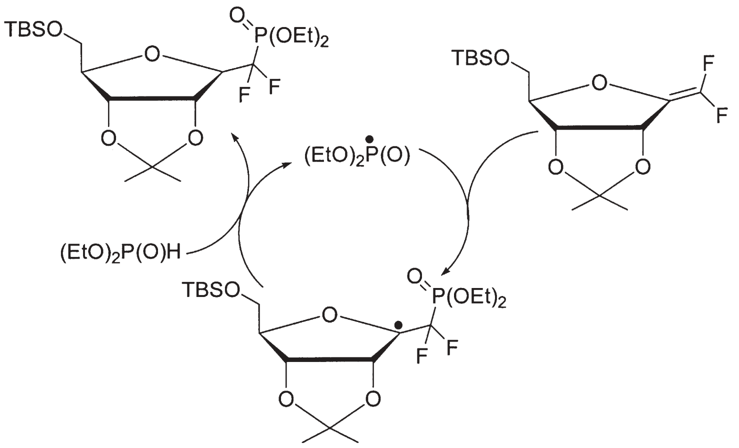


Fig. 3 Photo-initiators releasing phosphonyl radicals for photo-initiated free radical polymerizations

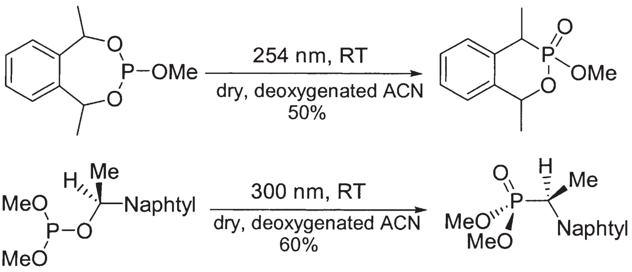
developed various precursors (typical examples are given in Fig. 3) and the P-centered radicals resulting from their photolytic decomposition were studied intensively [9, 12, 17]. The preparation of cross-linked biodegradable *poly*-ester-*poly*-(propylene fumarates) [32], the preparation of polymers for transdermal curing, and stereolithography [33] are typical applications of these photo-initiated free radical polymerizations. Diethylphosphonyl radical has been used to initiate the radical telomerization of vinylidene fluoride [34].

Phosphonyl radicals have been used to functionalize the (60)-, (70)- and (76)-fullerenes [35]. Radical phosphonylation (Scheme 12) of alkenes has been developed by Motherwell et al. [36] for the preparation of fluorophosphonylated analogs of riboses that exhibit high potential biological activity [37].

The photo-Arbuzov rearrangement of allyl-, benzyl- and naphtylmethyl-phosphites (Scheme 13), first developed by Bentrude et al. [20], found applications in the preparation of phosphonates (70–90%) [38]. Arylphosphonates have been shown to act as protein tyrosine kinase inhibitors [39] or non-hydrolyzable analogs of phosphorylated tyrosine residues [40].



Scheme 12 Radical phosphonylation of difluoromethylencarbohydrates



Scheme 13 Photo-Arbuzov rearrangement of arylphosphites

4
Phosphoniumyl Radicals, $L_3P^{\bullet+}$

The electrochemical generation and reactivity of phosphoniumyl and related charged radicals have been recently reviewed by Kargin and Bunikova [8]. In 1995, Yasui reviewed the reactivity of trivalent phosphorus compounds in single electron transfer (SET) processes [41] and, in 1990, the EPR features and reactivity of phosphoniumyl radicals were reviewed by Tordo [42].

The structures of phosphoniumyl and related charged radicals have been extensively listed over the last three decades [1]. Phosphoniumyl radicals are σ

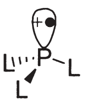
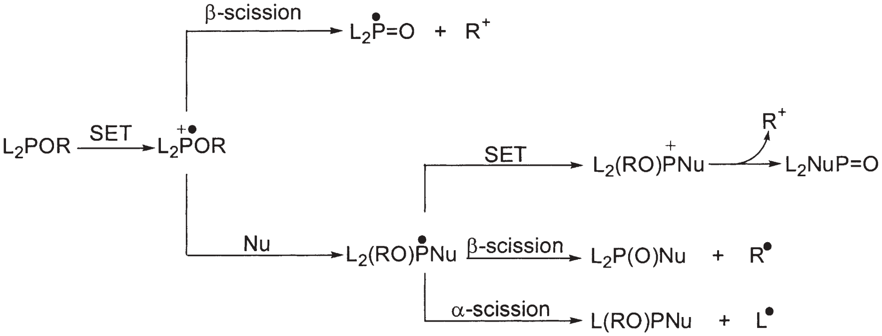


Fig. 4 Structure of phosphoniumyl radicals

radicals (Fig. 4) with phosphorus hyperfine coupling constants a_P in the range 20 to 80 mT [1].

4.1
Reactivity

The β-scission of a phosphoniumyl radical yields a cation and a phosphonyl radical, while its reaction with a nucleophile generates a phosphoranyl radical which can undergo SET reactions and α- or β-fragmentations (Scheme 14).



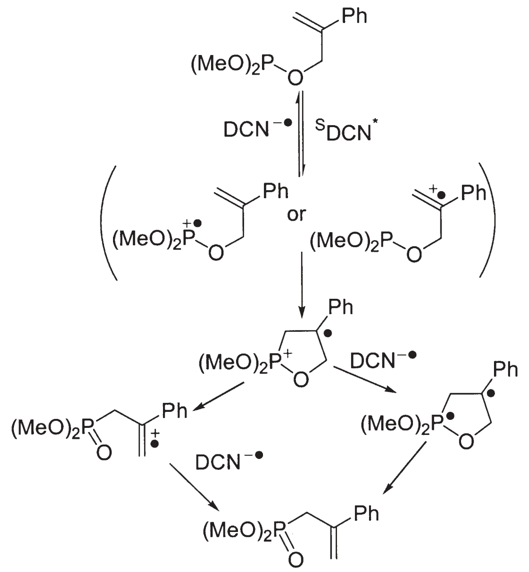
Scheme 14 Reactivity of phosphoniumyl radicals

4.1.1
Phosphoniumyl Radicals in Single Electron Transfer

Under irradiation, in the presence of sensitizers like 9,10-dicyanoanthracene (DCA) or 1,4-dicyanonaphtalene (DCN), phenylallylphosphites are able to rearrange to yield the corresponding phosphonates [43]. First, a radical cation (vinyl radical cation or phosphoniumyl radical) is generated by SET to the excited single state of DCA or DCN. Then, a nucleophilic or a radical attack of the phosphorus atom onto the vinyl moiety provides a 1,3-distonic radical cation. The rearrangement of the distonic radical cation to yield a phosphonate could proceed either through the formation of a diradical which undergoes β-fragmentations or through the homolytic cleavage of the C–O bond to provide the phosphonate moiety and a vinyl radical cation, the latter being reduced by SET (Scheme 15).

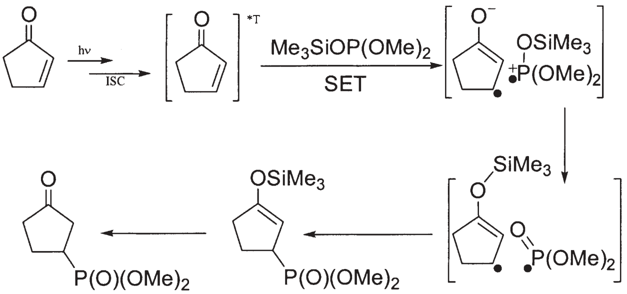
Recent results of Bentrude et al. [44] suggest that a vinyl radical cation is first generated, and that the 1,3-distonic radical cation is reduced to a diradical involving a phosphoranyl radical moiety. However, because the phosphite and styryl moieties of phenylallylphosphites exhibit very close oxidation potentials [45], the presence of a phosphoniumyl radical cannot be totally ruled out.

Bentrude et al. [46] developed the 1,4-conjugate addition of silylphosphites to cyclic enones induced by photochemical SET. They showed that high yields



Scheme 15 SET induced photorearrangement of phenylallylphosphites. Reprinted with permission from [43]. Copyright 2000 American Chemical Society

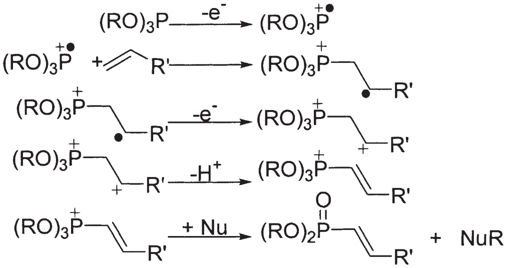
of phosphonylated cyclic ketones can be obtained in very mild conditions (6 h at RT) while in the absence of photo-excitation the reaction requires much more drastic conditions (12 h at 180 °C) [47]. Under irradiation, conjugated ketones are readily excited to a triplet state [48] and in the presence of $Me_3SiOP(OMe)_2$, a SET occurs to generate a radical ion pair. The decomposition of the ensuing phosphoniumyl radical generates the trimethylsilyl cation and a phosphonyl radical, which recombine with the enone radical anion to yield (78–92%) the 4-phosphonylated ketones (Scheme 16).



Scheme 16 1,4-Addition of phosphonyl radical to enones triggered by a SET

4.1.2
Addition of Phosphoniumyl Radicals onto Alkenes

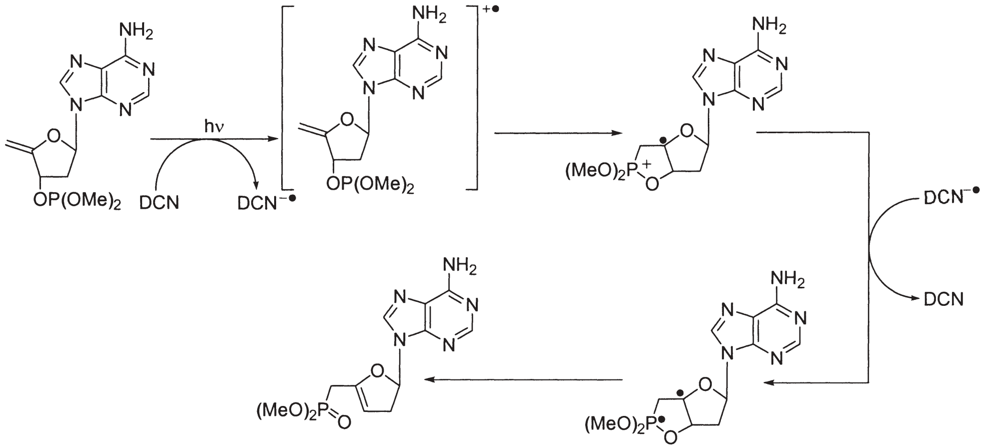
Romakhin et al. [49] showed that anodically generated phosphoniumyl radicals can add onto alkenes to yield phosphonylated alkenes through an anodic oxidation/addition/anodic oxidation/elimination/nucleophilic attack sequence (Scheme 17).



Scheme 17 Oxidative addition of phosphoniumyl radicals onto alkenes

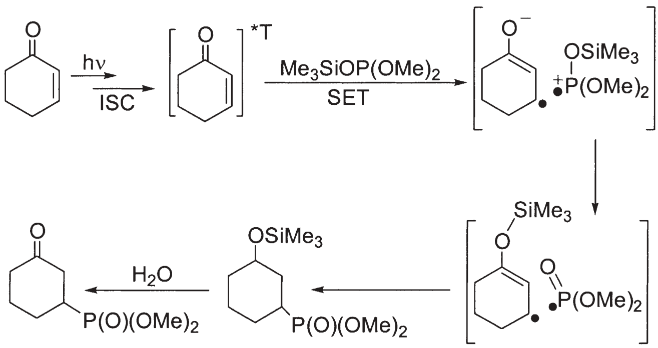
4.2
Applications

The SET-induced rearrangement of phenylallylphosphites developed by Bentrude et al. [43, 44] was used for the synthesis of new nucleotides bearing phosphonate moieties (Scheme 18) [40, 50, 51], which are active against HIV [52] and act as adenosine deaminase inhibitors [53].



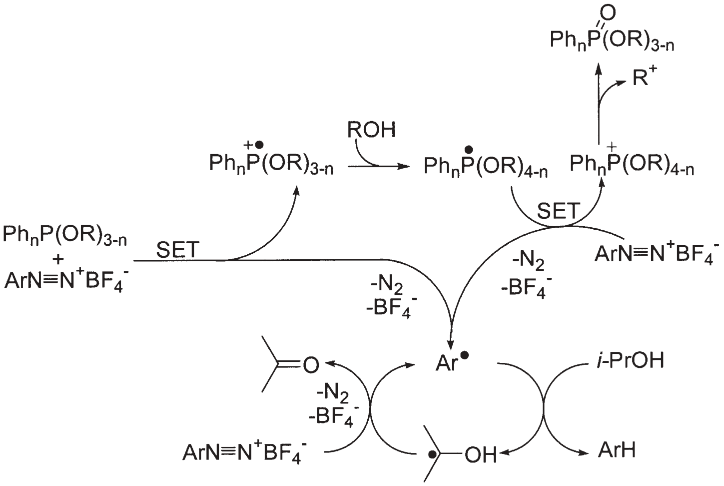
Scheme 18 Preparation of nucleotide-based phosphonates via SET-induced rearrangement of allylphosphites

Properly substituted phosphonates, which serve as key intermediates for the synthesis of biologically active compounds [39, 54], have been prepared via the photo-induced 1,4-addition of phosphites onto Michael ketones (Scheme 19).



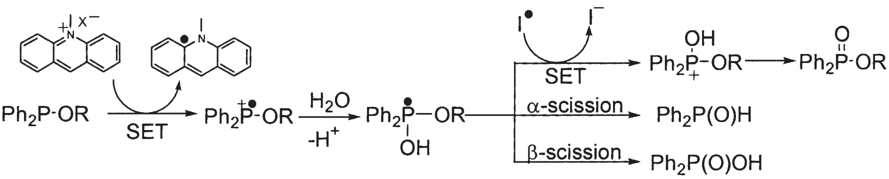
Scheme 19 1,4-Addition of phosphite onto Michael ketones via photoinduced SET

SET reactions involving phosphoniumyl radicals have been developed by Yasui et al. [41, 55], particularly for the dediazoniation of arenediazonium salts [56] (Scheme 20) and for the oxidation of trivalent phosphorus compounds [41, 57] (Scheme 21).

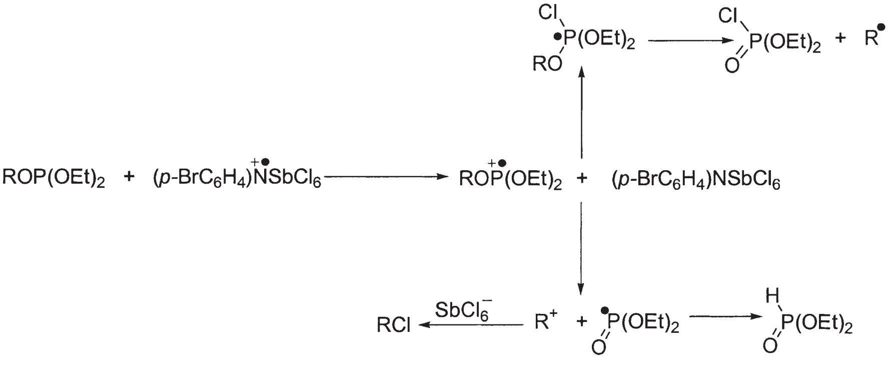


Scheme 20 Dediazoniation of arenediazonium salts via SET

Recently, Lee [58] showed that phosphoniumyl radicals generated via SET can be used to generate carbocations (Scheme 22).



Scheme 21 Oxidation of diarylphosphites via SET



Scheme 22 Carbocations resulting from the SET generation of phosphoniumyl radicals. Reprinted with permission from [58]. Copyright 2000 Korean Chemical Society

5
Phosphoranyl Radicals, $L_4P^•$

The various structures [59], EPR parameters [1] and reactivity [59] of phosphoranyl radicals have been extensively reviewed over the last three decades. This section presents only the main trends, and the last developments concerning these species.

5.1
Structures

It is commonly accepted that, depending on the substituents bonded to the phosphorus atom, phosphoranyl radicals adopt either a trigonal bipyramidal (TBP-e) structure (Fig. 5a), with the odd electron in a phantom equatorial site, or a tetragonal (σ^*) structure (Fig. 5b) [59b, 59c, 1]. The TBP-e structure with the highest spin density in equatorial position is the most frequent structure for $L_4P^•$. However, calculations [60] and a few experimental results [1c] suggested the existence of TBP-a structures (Fig. 5c), a conclusion that has been violently controverted [61]. TBP-e and σ^* structures have been clearly identified by EPR spectroscopy and their EPR spectra are characterized by very large phosphorus hyperfine coupling constants (0.6 T to more than 1.0 T for some TBP-e structures [1]). It is noteworthy that for phosphoranyl radicals bearing

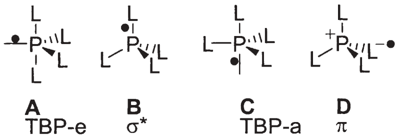


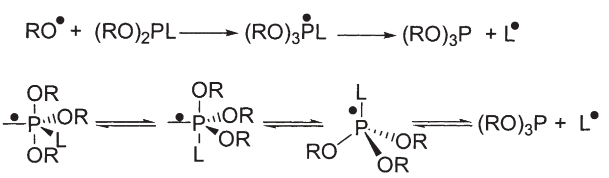
Fig. 5 Structures of phosphoranyl radicals

a vinyl or an aryl ligand the odd electron is localized in the π system of the unsaturated ligand (Fig. 5d). Nevertheless, the main decay routes for these radicals are analogous to those of phosphoranyl radicals with a TBP-e structure [62].

5.2
Reactivity

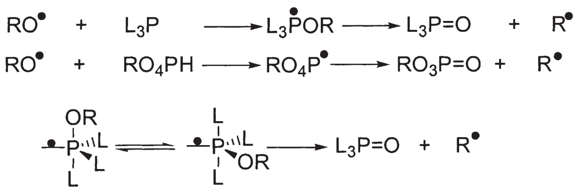
5.2.1
Displacement (α-scission) and Free Radical Arbuzov (β-scission) Reactions

The displacement of a ligand L from the phosphorus atom of a phosphoranyl radical can easily occur via α-scission of the L–P bond (Scheme 23). The fragmentation is a regiospecific process, i.e., the leaving group must be apical (Scheme 23) and it occurs via an intermediate σ* structure (Fig. 5).



Scheme 23 α-Scission of phosphoranyl radicals

Three- and pentacoordinate organic phosphorus compounds can be oxidized through a free radical Arbuzov reaction, i.e., formation and β-scission of a phosphoranyl radical (Scheme 24). The β-scission is regioselective; homolysis occurs on a ligand located in an equatorial site. Both α- and β-scissions are strongly dependent on the strength (bond dissociation energy) of the cleaved

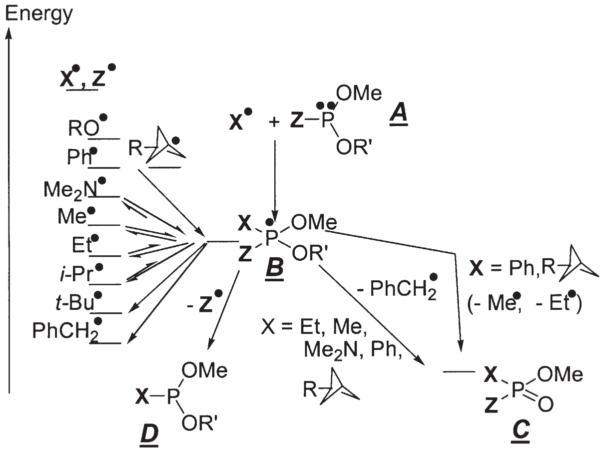


Scheme 24 β-Scission of phosphoranyl radicals

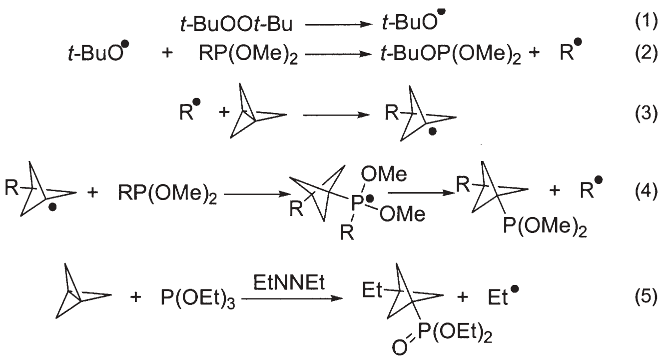
bond and on the polarity and steric effects of the phosphorus ligands. Detailed studies of α- and β-scission of phosphoranyl radicals are available in the reviews of Bentrude [59a–c] and Roberts [59d]. Other possible reactions of phosphoranyl radicals have also been listed in these reviews [59a–d].

The trapping of alkyl, alkoxyl and alkylthiyl radicals by trivalent phosphorus compounds, followed by either α-scission or β-scission of the ensuing phosphoranyl radical, is a powerful tool for preparation of new trivalent or pentavalent phosphorus compounds [59]. However, the products of these reactions strongly depend on the BDE of the bonds, which are either formed or cleaved. For example, the addition of phenyl radicals on a three-coordinate phosphorus molecule occurs irreversibly, while that of dimethylaminyl ($Me_2N^\bullet$) or methyl radicals is reversible, the amount of subsequent β-scission (formation of compound *C*) depending on the nature of Z and R′ (Scheme 25). For tertiary alkyl radicals and stabilized alkyl radicals no addition is observed (Scheme 25) [63].

The strained hydrocarbon [1,1,1] propellane is of special interest because of the thermodynamic and kinetic ease of addition of free radicals ($R^\bullet$) to it. The resulting R-substituted [1.1.1]pent-1-yl radicals (Eq. 3, Scheme 26) have attracted attention because of their highly pyramidal structure and consequent potentially increased reactivity. R-substituted [1.1.1]pent-1-yl radicals have a propensity to bond to three-coordinate phosphorus that is greater than that of a primary alkyl radical and similar to that of phenyl radicals. They can add irreversibly to phosphines or alkylphosphinites to afford new alkylphosphonites or alkylphosphonates via radical chain processes (Scheme 26) [63]. The high propensity of a R-substituted [1.1.1]pent-1-yl radical to react with three-coordinate phosphorus molecules reflects its highly pyramidal structure, which is accompanied by the increased s-character of its SOMO orbital and the strength of the P–C bond in the intermediate phosphoranyl radical.

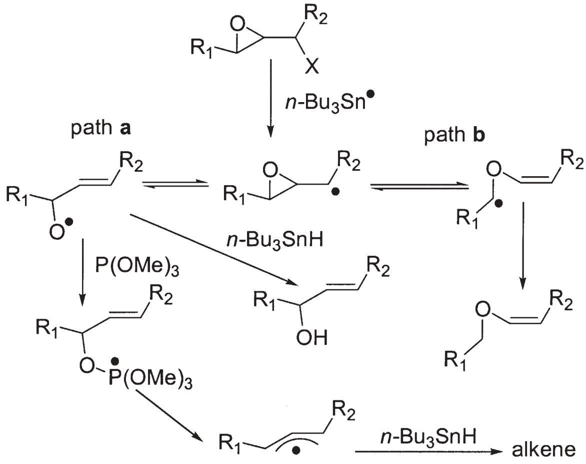


Scheme 25 Influence of the nature of ligands on the α- and β-scission of phosphoranyl radicals. Reprinted with permission from [63]. Copyright 1997 American Chemical Society



Scheme 26 Reaction of R-substituted [1,1,1]pent-1-yl radical with three-coordinate phosphorus compounds. Reprinted with permission from [63]. Copyright 1997 American Chemical Society

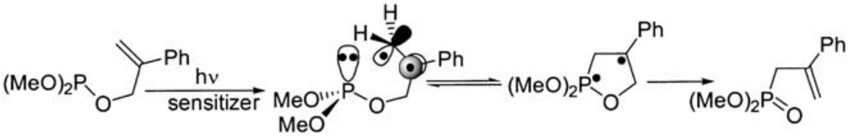
Alkoxy (RO$^•$) radicals react at near diffusion controlled rates with trialkyl phosphites to give phosphoranyl radicals [ROP(OR′)$_3$]$^•$ that typically undergo very fast β-scission to generate alkyl radicals (R$^•$) and phosphates [OP(OR′)$_3$]. In a mechanistic study, trimethyl phosphite, P(OMe)$_3$, has been used as an efficient and selective trap in oxiranylcarbinyl radical systems formed from haloepoxides under thermal AIBN/*n*-Bu$_3$SnH conditions at about 80 °C (Scheme 27) [64]. The formation of alkenes resulting from the capture of allyloxy radicals by P(OMe)$_3$ fulfils a prior prediction that, under conditions close to kinetic control, products of C–O cleavage (path a, Scheme 27), not just those of C–C cleavage (path b, Scheme 27) may result.



Scheme 27 Trimethyl phosphite as alkoxyl radical scavenger to characterize C–O vs C–C fragmentation for oxyranylcarbinyl radicals. Reprinted with permission from [64]. Copyright 2003 American Chemical Society

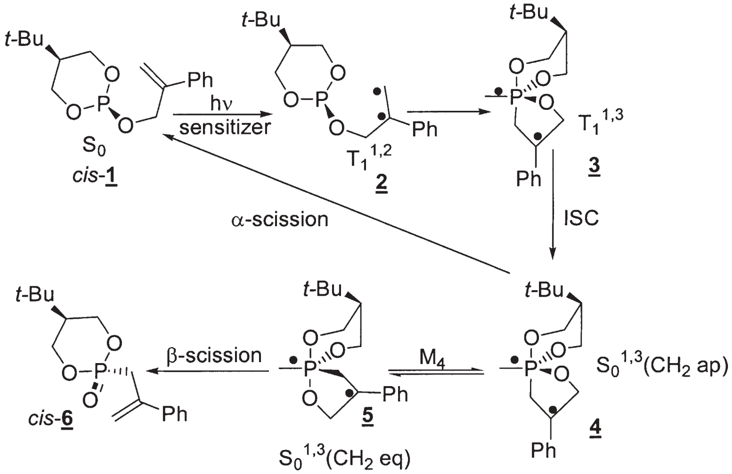
5.2.2
Triplet-Sensitized Photorearrangement

During the last decade, Bentrude et al. [65] has shown that the triplet-sensitized photorearrangement of allylphosphites and analogs (Scheme 28) is a powerful method for preparation of alkylphosphonates from phosphites. Moderate to high yields were observed when triphenylene was used as photosensitizer [66, 67].



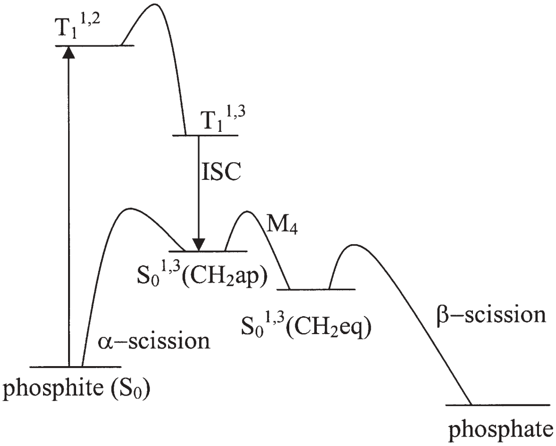
Scheme 28 Triplet-sensitized photorearrangement of allylphosphites. Reprinted with permission from [67]. Copyright 2000 American Chemical Society

Stereo studies involving spirophosphoranyl biradicals showed that the rearrangement occurs with almost complete retention of configuration at phosphorus (Scheme 29) [66, 67].



Scheme 29 Intermediates involved in the triplet-sensitized photorearrangement of allylphosphites. Reprinted with permission from [67]. Copyright 2000 American Chemical Society

Scheme 30 represents the energy diagram for the photorearrangement shown in Scheme 29. Quenching of the triplet state of the sensitizer by the *cis* allyl phosphate, *cis*-**1**, generates the triplet state, $T_1^{1,2}$, of the 1,2-biradical **2**. The 1,2-biradical is trapped by the phosphorus atom to afford the triplet state, $T_1^{1,3}$, of the spirophosphoranyl 1,3-biradical **3**. Then, inter-system crossing generates the



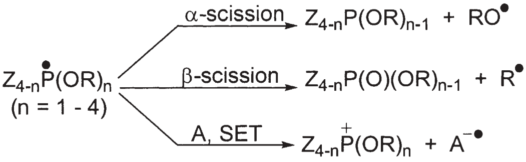
Scheme 30 Energy diagram of the triplet-sensitized rearrangement of allylphosphites. Reprinted with permission from [67]. Copyright 2001 American Chemical Society

more stable $S_0^{1,3}$ singlet state, **4**, which may either fragment via α-scission to regenerate the starting material or undergo pseudorotation (M_4 mode) to bring the CH_2 group to an equatorial position, **5**, before to fragment to the final *cis*-phosphonate, *cis*-**6** (Scheme 29) [66, 67].

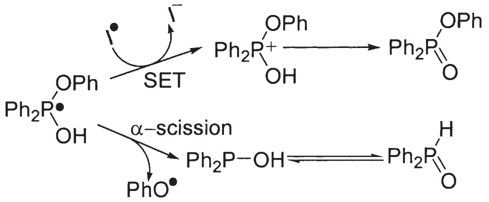
5.2.3
Single Electron Transfer Processes

In the course of the 1990s, Yasui et al. [41b, 68] showed that, depending on the ligands attached to the phosphorus atom, phosphoranyl radicals may decay via three main processes: α-scission, β-scission and SET (Scheme 31). For example, in the presence of 10-methylacridinium iodide, phosphoranyl radicals generated from phenyl diphenylphosphinite decayed mainly via α-scission (Scheme 32) whereas phosphoranyl radicals generated from *iso*-propyl diphenylphosphinite decayed only via a SET process (Scheme 33). The reactivity of the phosphoniumyl/phosphoranyl radical tandem has already been discussed in Sect. 3.

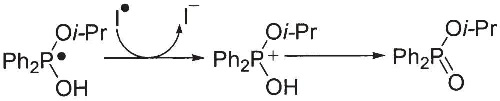
Kampmeier [69] reported that, under irradiation at 313 nm, di-*p*-tolyliodonium hexafluorophosphate reacts rapidly with triphenylphosphine in acetone-



Scheme 31 Decay of phosphoranyl radicals via α-scission, β-scission and SET. Reprinted with permission from [68]. Copyright 1994 Wiley Interscience

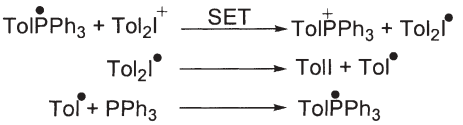


Scheme 32 Decay reactions of $[Ph_2P(OH)OPh]^{\bullet}$. Reprinted with permission from [68]. Copyright 1994 Wiley Interscience



Scheme 33 SET decay of $[Ph_2P(OH)O\textit{i}\text{-}Pr]^{\bullet}$. Reprinted with permission from [68]. Copyright 1994 Wiley Interscience

d_6 or acetonitrile-d_3 to give *p*-tolyltriphenylphosphonium salt and 4-iodotoluene (Scheme 34). All the experimental observations agree with a radical chain reaction involving tolyl and phosphoranyl radical intermediates.



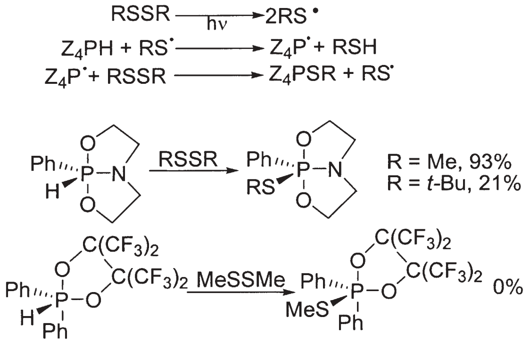
Scheme 34 SET process for tetraaryl phosphoranyl radicals. Reprinted with permission from [69]. Copyright 1993 American Chemical Society

5.2.4
Second Order Homolytic Substitution, S_H2

During the last two decades, Bentrude et al. [70] has shown that phosphoranyl radicals exhibiting very slow α- and β-fragmentations react with alkyl disulfides via S_H2 homolytic substitution (Scheme 35) [70b]. The reactivity of phosphoranyl radicals in these S_H2 reactions depends strongly on the substituents attached to the phosphorus atom and on the structure of the disulfides [70c].

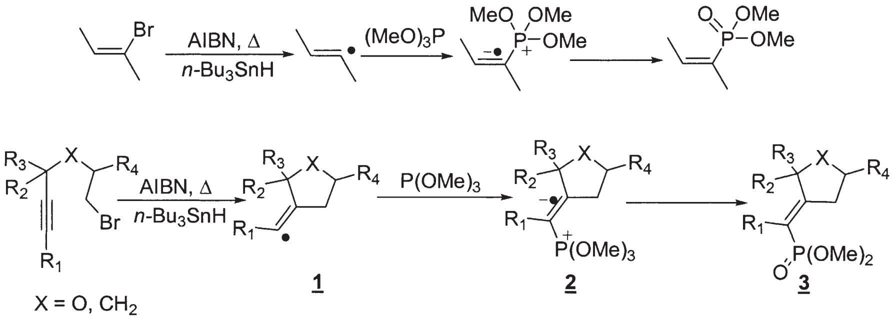
5.3
Applications

The free radical Arbuzov reaction has been developed for the preparation of vinyl- and arylphosphonates in good to excellent yields. Oligonucleotides, suitably modified in the vicinity of the phosphorus backbone to impart nuclease



Scheme 35 S_H2 reactions of phosphoranyl radicals with alkyl disulfides

resistance, are the key molecules in the antisense approach to antiviral and antitumor therapy [51, 71]. The free radical Arbuzov reaction has been used to prepare phosphonate oligonucleotide precursors. For example [72], the rapid 5-*exo* digonal cyclization of 5-hexynyl and 3-oxa-5-hexynyl free radicals generates vinyl radical intermediates, **1** (Scheme 36), which are readily trapped by $P(OMe)_3$. β-Scission of the resulting phosphoranyl radicals, **2**, yields the targeted vinylphosphonates, **3**, which are precursors of deoxy ribonucleoside-based phosphonates (*vide infra*) [62, 72, 73].



Scheme 36 Preparation of vinylphosphonates via free radical Arbuzov reaction

The reactivity of phosphites described in Scheme 27 has been applied to various oxiranes to afford the expected alkenes in low (15%) to excellent (95%) yields (Fig. 6) [64].

Roberts et al. [74] took advantage of the rapid and selective β-scissions of phosphoranyl radicals, to develop a radical chain desulfurization affording new substituted α-alkyl acrylates in good to moderate yields (Scheme 37).

Various phosphines are valuable ligands for metal centers involved in catalytic and noncatalytic organometallic chemistry. Unfortunately, phosphines are readily oxidized to phosphine oxides and to prevent their oxidation they

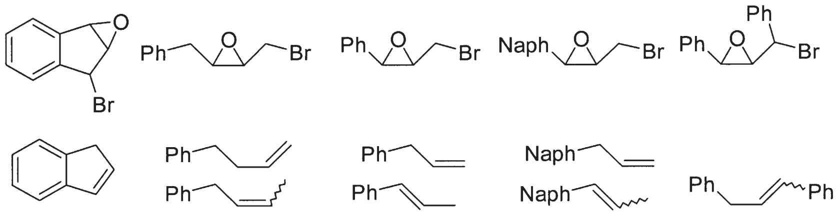
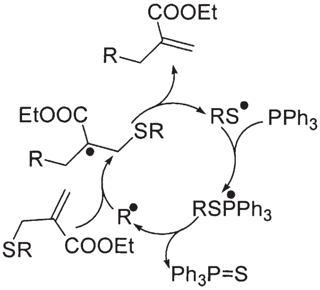
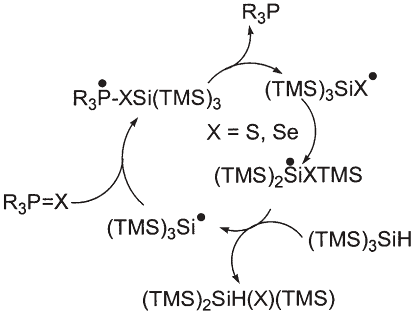


Fig. 6 Alkenes issued from the reduction of oxiranes in the presence of trialkylphosphites

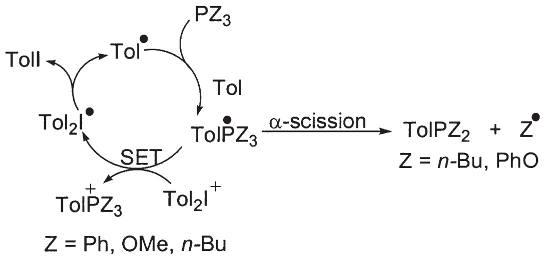


Scheme 37 Radical chain desulfurization involving phosphoranyl radicals as chain carriers. Reprinted with permission from [74]. Copyright 1998 Pergamon Press

must be stored in unreactive forms [75] such as phosphine sulfides ($R_3P{=}S$) or selenides ($R_3P{=}Se$). Then, an easy and friendly method for removal of the sulfur or the selenide atom is needed. Taking advantage of the fast addition of silyl radicals to a P=S or P=Se bond and the fast and selective α-scission of the $^{\bullet}$P–S or $^{\bullet}$P–Se bond of a phosphoranyl radical, Chatgilialoglu et al. [76] showed that phosphine sulfides and phosphine selenides, in the presence of tris(trimethylsilyl)silane, are reduced to the corresponding phosphines with high yields (Scheme 38).



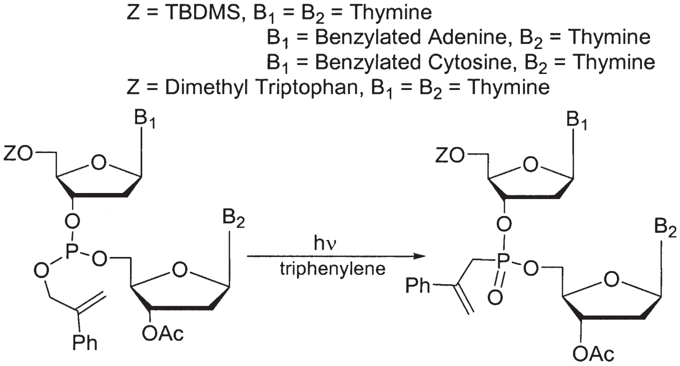
Scheme 38 Radical chain desulfurization or deselidization of phosphine sulfides or selenides to afford phosphines



Scheme 39 SET reaction involving phosphoranyl radicals. Reprinted with permission from [69]. Copyright 1993 American Chemical Society

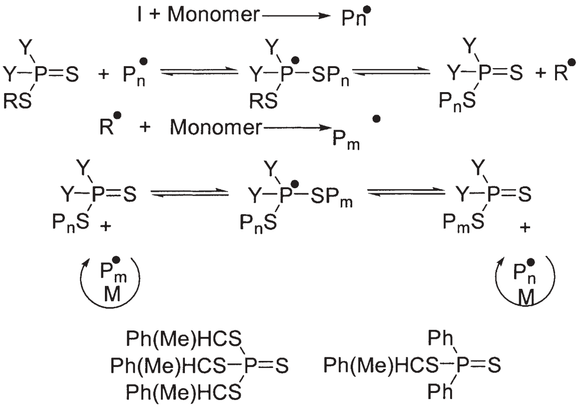
As already mentioned, the reduction of di-*p*-tolyliodonium salt into *p*-tolyliodide in the presence of triphenylphosphine (Scheme 39) [69] involves a SET, the intermediate phosphoranyl radical behaving as one electron-reductant.

The triplet-sensitized photorearrangement of allylphosphites [65– 67] offers a rapid and efficient access (60–70% yields) to oligonucleotides, which are key molecules in the antisense approach to antiviral and antitumor therapy (Scheme 40) [39, 40, 73].



Scheme 40 Triplet-sensitized photorearrangement of allylphosphites applied to the preparation of dinucleosides

Phosphoranyl radicals can be involved [77] in RAFT processes [78] (reversible addition fragmentation transfer) used to control free radical polymerizations [79]. We have shown [77] that tetrathiophosphoric acid esters are able to afford controlled/living polymerizations when they are used as RAFT agents. This result can be explained by addition of polymer radicals to the P=S bond followed by the selective β-fragmentation of the ensuing phosphoranyl radicals to release the polymer chain and to regenerate the RAFT agent (Scheme 41).



Scheme 41 Phosphoranyl radicals as intermediates in RAFT polymerizations

6
Persistent and Stable Phosphorus Centered Radicals

Since the discovery of the first persistent radical by Gomberg [80], the preparation of persistent and stable organic radicals has been a stimulating challenge for chemists [81]. Hereafter, P-centered radicals are classified as persistent or stable according to the definition given by Ingold and Griller [81]. Persistent and stable P-centered radicals have been recently reviewed by Power [82] and Geoffroy [83], therefore, only some typical examples will be discussed. It must be noted that although the characterization of various persistent and/or stable P-centered radicals can be considered as an outstanding result, their chemistry is not developed and many of them are still considered to be chemical curiosities.

6.1
Structures

Recently, Rankin et al. [84] obtained the X-ray structure of the stable pnictinyl radical and observed a very unusual conformational arrangement, i.e., a *syn-syn* arrangement of the H–C–P–C–H bond sequence (Fig. 7).

The first *p*-phosphaquinone radical anion (Fig. 8), another example of stable phosphinyl, was prepared by Yoshifuji et al. in 1998 [85].

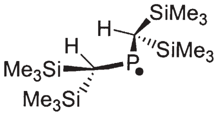


Fig. 7 Preferred conformation of the stable pnictinyl radical

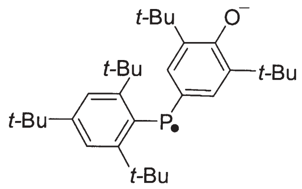
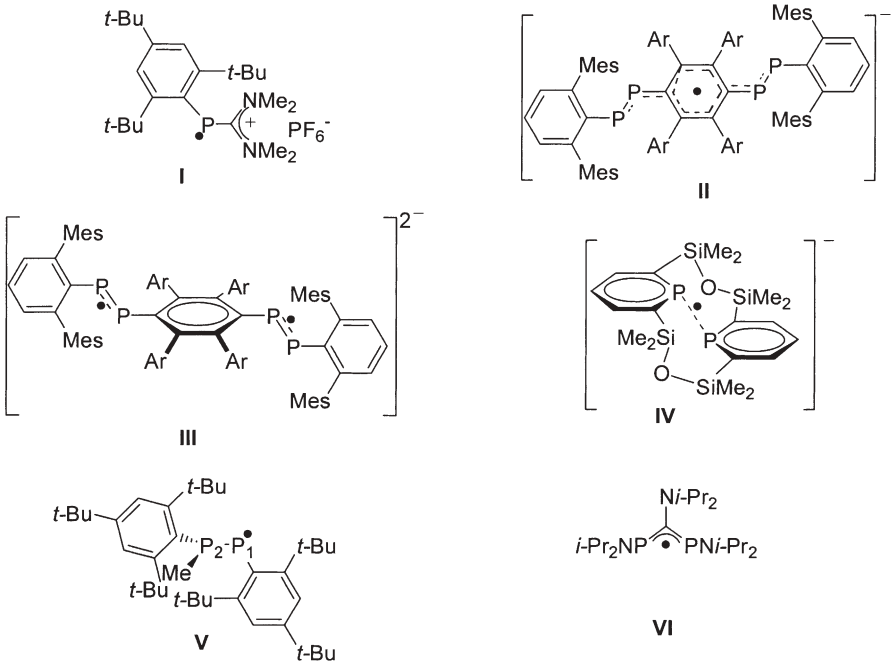


Fig. 8 Structure of *p*-phosphaquinone radical anion

Other recently discovered π or σ stable or persistent P-centered radicals are shown in Fig. 9. Chemical or electrochemical oxidation of Mes*P=C$(NMe_2)_2$ results in the immediate formation of a deep violet solution of radical cation **I** (Fig. 9) [86]. The violet solid **I** can be kept for a few weeks in a glove box or for a few days in solution under nitrogen atmosphere.

The persistent radical anion **II** was obtained by chemical or electrochemical reduction of the parent neutral compound. The EPR spectrum of **II** is composed of a triplet of triplet (a_P(2P)=3.50 mT and a_P(2P)=0.89 mT) characteristic of a planar conjugated structure (Fig. 9) [87]. Amazingly, the dianion **III** was found to be paramagnetic exhibiting an EPR spectrum composed of a distorted dou-



Mes = 2,4,6-trimethylphenyl
Ar = *p*-*t*Butylphenyl

Fig. 9 Structures of new persistent and/or stable P-centered radicals blet of doublet (a_P(1P) 6.17=mT and a_P(1P)=2.78 mT) [87]. The authors interpreted the EPR spectrum of **III** assuming that each diphosphene moiety bears an unpaired electron (occupying the P=P π* orbital) and is independent of the other CPPC group (Fig. 9). The dianion **III** has a non-planar geometry, the middle ring adopts an orientation that "insulates" the spins from one another. The redox-induced geometrical changes for **III** are analogous to the behavior of a so-called molecular switch [87].

Radical **IV** can be considered as a unique phosphorus radical species. Reduction of the parent macrocycle with sodium naphtalenide in THF at room temperature gave a purple solution. The EPR spectrum displayed a signal in a 1:2:1 pattern, with a_P(2P)=0.38 mT. DFT calculations on radical **IV** models indicated a P–P distance of 2.763 Å (P···P is3.256 Å in the crystal structure of the parent compound and the average value of a single P–P bond is 2.2 Å). According to the authors, the small coupling constant arises from the facts that the principal values of the hyperfine tensor are of opposite sign and that the σ P•P one electron bond results from overlap of two 3p orbitals [88].

Radical **V** represents the first phosphorus analog of hydrazyl radical [89] (Fig. 9), obtained by the chemical reduction of $[\mathrm{Mes^*MeP{=}PMes^*}]^+\mathrm{O_3SCF_3^-}$ using tetrakis(dimethylamino)ethylene as electron donor. The isotropic coupling constants (a_{P1}=13.92 mT and a_{P2}=8.92 mT) indicate a larger spin density on P1 than on P2, which retains a significant degree of pyramidalization. It is noteworthy that, due to stronger interaction between nitrogen 2p orbitals, for hydrazyl radicals the unpaired electron is almost equally delocalized over the two planar nitrogen centers [89].

Bertrand et al. [90] isolated red crystals of radical **VI**, which were stable under inert atmosphere. The EPR signal of a THF solution of **VI** displayed a five-line pattern with an intensity ratio 1:3:4:3:1 due to coupling to two equivalent phosphorus (a_P=0.94 mT) and one nitrogen (a_N=0.99 mT) nucleus.

Phosphoranyl radicals were observed by EPR at the end of the sixties [91]. For a long time, phosphoranyl radicals, particularly the alicyclic ones [59], were considered as elusive species. However, recently, Marque et al. [92] observed the first strongly persistent ($t_{1/2}$=45 min at RT) alicyclic phosphoranyl radicals (Fig. 10) when they irradiated bis(trialkylsilyl)peroxides in the presence of tris(trialkylsilyl)phosphites. The increased lifetime of the ensuing phosphoranyl radicals is a consequence of the presence of four bulky R_3SiO groups around the phosphorus. The bulkiness of the substituents hampers the dimerization and the S_H2 reaction of phosphoranyl radicals with the peroxide initiator. Furthermore, the high strength of the P–O and O–Si bonds results in slow α- and β-scissions [93].

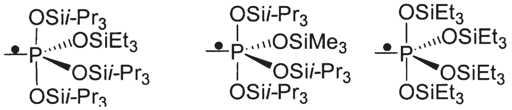
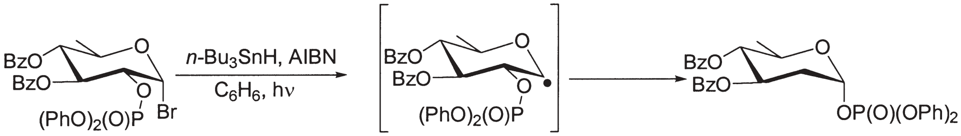


Fig. 10 Structure of persistent phosphoranyl radicals

7
Miscellaneous

The results reported in the previous sections illustrate the importance and versatility of P-centered radicals in organic chemistry. In this last section we would like to mention various reports that show that the presence of a phosphorus substituent close to a radical center can dramatically influence its properties.

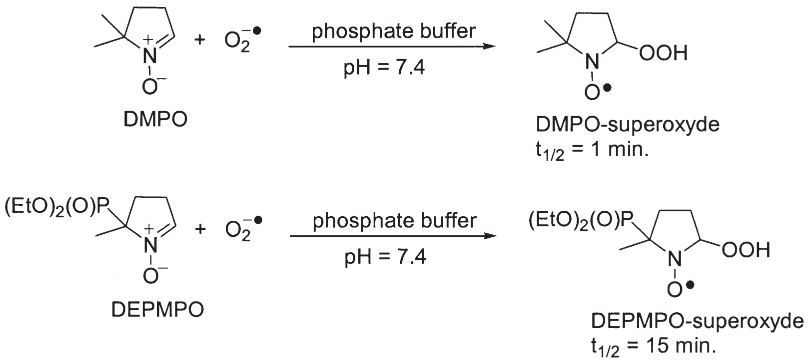
The β-(phosphatoxy)alkyl radical migration was first described, independently, by Crich et al. and Giese et al. [94]; an example of this rearrangement is shown in Scheme 42 [95]. A huge amount of work has been reported concerning the applications and the mechanism of this rearrangement [95, 96]. Very strong evidence has emerged that the whole range of chemistry observed is due to a radical ionic fragmentation, the differences being due to the extent of portioning between contact ion pairs (CIP), solvent-separated ion pairs (SSIP), and diffusively free radical ions and ions [97].



Scheme 42 Example of β-(phosphatoxy)-alkyl rearrangement

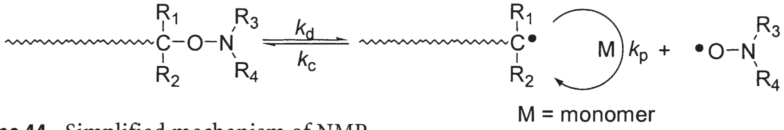
Spin trapping coupled with EPR allows the visualization of transient free radical populations by reacting short-lived radicals with a spin trap to produce persistent spin adduct radicals [98]. The technique has been widely used in the field of biological sciences, particularly to characterize oxygen-centered radicals ($O_2^{\bullet-}$, HOO$^\bullet$, HO$^\bullet$) involved in oxidative stress [99]. For a long time DMPO (2,2-dimethyl-3,4-dihydro-2*H*-pyrrole-1-oxide) has been the most widely used spin trap for superoxide ($O_2^{\bullet-}$), one of the most important transient radical in free radical biology. However, the half life of the DMPO superoxide spin adduct is short (close to 1 min) and in many instances its EPR detection is rather tedious. Tordo et al. [100] showed that the trapping of superoxide is much easier when 2-diethoxyphosphoryl-2-methyl-3,4-dihydro-2*H*-pyrrole-1-oxide (DEPMPO, Scheme 43) is used as spin trap, the half life of the DEPMPO-superoxide spin adduct being close to 15 min. Although the influence of the phosphoryl group is not yet completely understood, preliminary results clearly show that it favors conformations of the spin adduct stabilized by anomeric interactions involving the nitroxyl π system and the C–OOH bond. DEPMPO has also been shown to be more convenient than DMPO for the spin trapping of other oxygen- and sulfur-centered free radicals.

The development of controlled/living radical polymerization processes, yielding polymers with narrow polydispersities and a high percentage of liv-

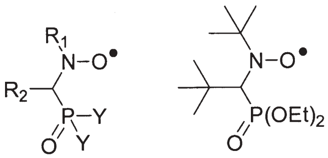


Scheme 43 Spin trapping of superoxide with DMPO and DEPMPO

ing chains is a major achievement of the last decade of research in the polymer field [101]. Nitroxide-mediated radical polymerization (NMP) is illustrated in Scheme 44 When the persistent radical effect [102] is established, the excess of free nitroxide prevents the self-termination of polymer radicals, which grow through successive deactivation–dissociation cycles whereby they are alternatively transformed into dormant alkoxyamines and activated into active polymer radicals by thermal homolysis. Hence, a majority of dormant living chains can grow until the monomer is depleted, resulting in a polymer with large living character and small polydispersity index. A complete kinetic modeling of NMP has been carried out, and the kinetic conditions required for a successful process have been established. [103] These studiesand various experimental results have emphasized the importance of the equilibrium constant $K=k_d/k_c$. For the polymerization of a monomer M, the K value depends on the structure of the nitroxide used to control the polymerization. For example, only the radical polymerization of styrenic monomers can be partially controlled with 2,2,6,6-tetramethyl-1-piperidinyloxy radical (TEMPO). To overcome the TEMPO limitations, other types of nitroxides were tailored. Tordo et al. [104] prepared stable acyclic β-phosphonylated nitroxides (Fig. 11) and showed that for the NMP of a given monomer, the optimal K value can be approached by adjusting the size and the electronegativity of the phosphonyl group $Y_2P{=}O$ (Y=R, RO, Ph, PhO...). Nowadays, the [*N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2dimethylpropyl)nitroxide], named SG1 (Fig. 11), is the most efficient nitroxide to control the radical polymerization of various styrenic and acrylic monomers [105].



Scheme 44 Simplified mechanism of NMP



SG1

Fig. 11 Acyclic β-phosphonylated nitroxides

8
Conclusion

Studies on the formation and reactivity of P-centered radicals continue to be a versatile source of mechanistic information and reactions of interest in synthetic chemistry. Various new persistent or stable P-centered radicals have been described and could find applications as paramagnetic probes. The possibility of influencing the properties of organic free radicals bearing an appropriately located phosphorus group should find interesting applications.

Acknowledgements The authors thank the University of Provence for its support.

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The Chemistry of Phosphinous Amides (Aminophosphanes): Old Reagents with New Applications

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Abstract This chapter is devoted to phosphinous amides, a particular class of tervalent aminophosphanes. First, attention is focused on their stability and synthetic procedures. Reports dealing with their prototropic equilibrium and main group chemistry are also considered. Last but not least the really important applications of these species as metal ligands in the field of catalysis are reviewed, including asymmetric variants.

Keywords Phosphinous amides · Aminophosphanes · Phosphanamines · Catalysis

Abbreviations

AMMP	Aminophosphane phosphinite
BARF	Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate
CAS	Chemical Abstracts Service
Cp	Cyclopentadienyl
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
DIPEA	Diisopropylethylamine
DMAP	4-Dimethylaminopyridine
NMR	Nuclear magnetic resonance
PNP	*N*,*N*-Bis(diphenylphosphino)-2,6-diaminopyridine
TEA	Triethylamine

1
Introduction, Scope and Time Frame

Tervalent organophosphorus compounds containing one single P-N bond with the valency of each atom saturated by protons or carbons (but no other heteroatoms) have been known since their discovery by Michaelis more than one century ago [1] and named indistinctly as aminophosphanes, phosphanamines, phosphazanes, or phosphinous amides. This last chemical nomenclature is the one used by the Chemical Abstracts Service (CAS) for indexing these compounds and is also the one that best delimits the scope of this review: those species derived from the parent $H_2P\text{-}NH_2$ (phosphinous amide in CAS nomenclature) by partial or total substitution of protons by hydrocarbon radicals (Table 1).

Between all the classes of substituted phosphinous amides summarized in Table 1, those with the P atom totally substituted are more stable than others with H–P bonds, as in many other classes of organophosphorus compounds. Between those, the trisubstituted or fully substituted (typed in boldface) are by far the most stable and the main actors of the chemistry described in the following pages.

Also covered by this review are those compounds bearing two or three phosphane units at the same N atom, that is those derived from $(H_2P)_2NH$ (*N*-phosphino phosphinous amide in CAS nomenclature) and from $(H_2P)_3N$, *N*,*N*-bis(phosphino) phosphinous amide, *but not* those bearing more than one amino

Table 1 Phosphinous amides

Parent Compound	Monosubstituted	Disubstituted	Trisubstituted	Tetrasubstituted
$H_2P\text{-}NH_2$	$R^1P(H)\text{-}NH_2$ $H_2P\text{-}N(H)R^2$	$R^1R^2P\text{-}NH_2$ $H_2P\text{-}NR^1R^2$ $R^1P(H)\text{-}N(H)R^2$	$\mathbf{R^1R^2P\text{-}N(H)R^3}$ $R^1P(H)\text{-}NR^2R^3$	$\mathbf{R^1R^2P\text{-}NR^3R^4}$

group at the same P atom, i.e., derived from $HP(NH_2)_2$, phosphonous diamide, or $P(NH_2)_3$, phosphorous triamide, which have been left out of the following discussion in order to keep this review within reasonable space limits.

This chapter will also deal with compounds containing two or three phosphinous amide units, which, for simplicity, will be named here as bis(aminophosphanes) or tris(aminophosphanes) *but not* with phosphinous amides containing other additional organophosphorus functionalities as, for instance, the so-called aminophosphine phosphinites (AMMP), which have been the subject of increasing attention in the literature dealing with catalytic asymmetric transformations and have been treated in other reviews [2, 3].

This chapter will not cover compounds containing heteroatoms linked to the P and/or N atom of the P–N unit, with the notorious exception of those with N–Si bonds (*N*-silyl phosphinous amides) due to its particular relevance in terms of chemical reactivity.

To the best of our knowledge, the chemistry of phosphinous amides has not been reviewed before. This is why this account, whilst not comprehensive due to space limitations, is intended to serve as a summary of the most representative details of the chemistry of these species and also as an introduction to their use in catalysis. For these reasons, the time frame is not restricted to the last few years (although focused on them) but occasionally dates back as far as necessary. We will present first a short overview of the main reactions used for preparing phosphinous amides and second the more relevant characteristics of their chemical behavior. Special attention will be devoted to the most recent developments of these compounds as ligands in transition metal complexes with catalytic applications. Although we have tried to be thorough, most probably we have omitted some works that merit citation due to the difficulty in coping with the strong dissemination of the pertinent literature. We apologize in advance to any authors who find their work in this area neglected in this account.

Other recently published treatises and reviews on organophosphorus chemistry that partially deal with phosphinous amides include those dedicated to the preparation and properties of tervalent phosphorus acid derivatives [4], inorganic backbone phosphanes [5], new chiral phosphorus ligands for enantioselective hydrogenation [6, 7], the asymmetric synthesis of organophosphorus compounds [8], bidentate organophosphorus ligands [9] and to bis(diphenylphosphino)amine and related ligands [10].

2
Stability and Properties

The stability of phosphinous amides depends, to a large extent, on the substituents at phosphorus and nitrogen. Normally, tetrasubstituted and *N*,*P*,*P*-trisubstituted phosphinous amides are stable and well-known compounds. The parent compound H_2PNH_2 is a volatile compound that is formed on hydrolysis of a solid state solution mixture of magnesium phosphide and magnesium nitride [11]. It has been proposed that H_2PNH_2 is presumably formed by photolysis of NH_3+PH_3 mixtures, and that this compound decomposes to a reddish polymer $(PN)_x$ that is partially responsible of the coloration of Jupiter's atmosphere [12].

P-Unsubstituted phosphinous amides H_2PNR_2 are practically unknown, with the notorious exceptions of $H_2PN(SiMe_3)_2$ [13] and $H_2PN(CF_3)_2$ [14, 15]. PH-Phosphinous amides are also rare, although some examples of $RP(H)NH_2$, RP(H)NHPh and $RP(H)NEt_2$ have been prepared with their phosphorus atom coordinated to a $W(CO)_5$ fragment, and were, in this form, stable towards air oxidation [16]. In free state, they decompose via α-elimination of HNR_2 to phosphinidenes RP and their secondary products [17]. The two silyl substituents on nitrogen make $RP(H)N(SiMe_3)_2$ stable [18].

All attempts to prepare $(CH_3)_2PNH_2$ have met with failure [19, 20] but $(CF_3)_2PNH_2$ [14], Ph_2PNH_2 [21] and ${}^t Bu_2PNH_2$ [22] are moderately stable. Although bis(phosphino)amines have occasionally been claimed to exist in two isomeric forms, $R^1N(PR^2{}_2)_2$ and $R^2{}_2P\text{-}P(=NR^1)R^2{}_2$ [23, 24], they have been widely used as normal tervalent organophosphorus compounds.

N,*N*-Bis(phosphino) phosphinous amides $N(PR_2)_3$, commonly called triphosphinoamines, are still virtually unknown, with the exceptional reported existence of $N(PF_2)_3$ and $N[P(CH_3)_2]_3$ [15, 19, 20]. The usual synthetic approaches to $N(PPh_2)_3$ give instead the isomeric $Ph_2P\text{-}P(Ph_2)\text{=}N\text{-}PPh_2$ [25].

The P–N bond in phosphinous amides is essentially a single bond, so the lone pairs on N and P are available for electrophilic reagents and for donor bonding towards metal atoms. Proton addition to the N atom of H_2PNH_2 has been calculated to loosen the P–N bond, whereas protonation at P renders this bond stronger than in the parent molecule [26]. NH-Phosphinous amides are practically not associated by intermolecular hydrogen bonds [27].

Hindered rotation around the P–N bond has been observed at low temperature in tetrasubstituted phosphorus amides [28]. For $Ph_2PN(SiMe_3)_2$, two different Me_3Si groups are observed below –65 °C, the calculated activation energy for P–N rotation being 10.2 Kcal mol^{-1} [29]. Chiral phosphinous amides with stereogenic phosphorus atoms have been prepared [30, 31].

3
Synthesis

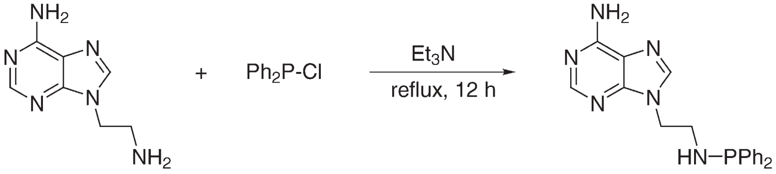
Among the routes for preparing phosphinous amides, the most frequently used method is the aminolysis of halophosphanes, most usually chlorophosphanes [32–34], because a number of such halophosphanes are easily accessible from commercial sources. These reactions usually provide the target species, i.e., trisubstituted compounds **1** in Scheme 1, in high yield. The HCl liberated from the reaction forms a salt with an organic base (either excess of the starting amine or externally added as, for example TEA or DBU, sometimes in the presence of DMAP) which is insoluble in the reaction solvent, typically diethyl ether

1

Scheme 1 Base: R^3-NH_2 or R_3N

or tetrahydrofuran, and therefore leads to facile separation and purification of the desired products. Care needs to be taken to exclude water from the reaction medium to prevent the hydrolysis of the phosphinous amides.

The reaction temperature varies between –40 and 110 °C, depending on the reactivity of both counterparts, amine and chlorophosphane. As usual, aliphatic amino groups react faster than aromatic and heteroaromatic ones due to their greater nucleophilic strength. These differences in reactivity allow chemoselective phosphinous amide formation, as that represented in Scheme 2 where the P–N bond is formed exclusively at the aliphatic NH_2 group of **2** but not at the heteroaromatic NH_2, whose lone pair is extensively delocalized in the electron-withdrawing purine ring [35].



2

Scheme 2

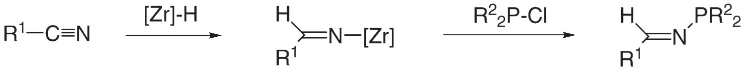
The generalized application of the aminolysis of halophosphanes has been the method of choice for the preparation of a wide variety of chiral phosphinous amides by starting from enantioenriched primary amines [36]. The aminolysis reaction occurs efficiently even when the halophosphane is placed in the coordination sphere of a metal, as in the palladium and platinum complexes of the type *cis*-$M(Ph_2PCl_2)_2Cl$ (M=Pd, Pt) [37, 38].

Not only N–H bonds from amines can participate in the aminolysis reaction, but also less nucleophilic urea, thiourea and biuret NH units can react with halophosphanes in an effective manner, forming the corresponding phosphinous amides with additional functionalities at the nitrogen atom [39–44].

N-Unsubstituted imines have been similarly converted into *N*-alkylidene phosphinous amides, as **3**, in reactions run in the presence of triethylamine [45] (Scheme 3).

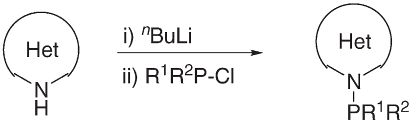
Scheme 3 **3**

An elegant preparation of similar compounds, **4**, has been recently reported by Majoral [46]. The hydrozirconation of nitriles with Schwartz's reagent $[Cp_2Zr(H)Cl]_n$ (abbreviated as [Zr]-H in Scheme 4) leads efficiently to the corresponding *N*-zirconaimine, which when reacted with chlorophosphanes gave **4** by an exchange reaction, along with the loss of the metal fragment $[Cp_2ZrCl_2]$.



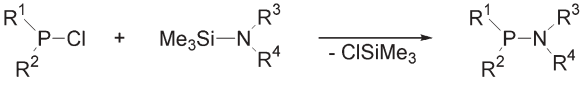
Scheme 4 **4**

In the aminolysis processes for preparing phosphinous amides it is possible to replace the organic base by *n*-BuLi, Na or K, which leads to the initial deprotonation of the amine and formation of an amide anion. This anion can be subsequently reacted with the halophosphane for forming the new P–N bond [47–51]. This methodology has been particularly successful for preparing phosphinous amides with the nitrogen atom forming part of an heteroaromatic ring [52–57] (Scheme 5).



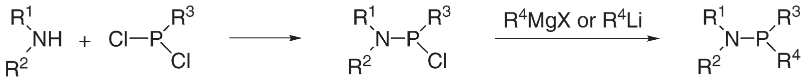
Scheme 5

An alternative method for preparing phosphinous amides makes a profit on the high affinity between silicon and halogen atoms. This is the driving force of the reactions between halophosphanes and *N*-(trimethylsilyl)anilines, *N*-(trimethylsilyl)amides or *N*-(trimethylsilyl)ureas and thioureas, as represented in the Scheme 6. In these processes the desired P–N bond and an halosilane are simultaneously formed [53, 58–60].



Scheme 6 R^3 = Ar, RCO, R_2NCO

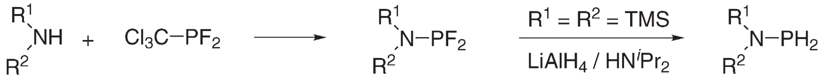
A slightly different approach to phosphinous amides is represented in Scheme 7. It consists of the sequential substitution of the two halogen atoms of a dihalophosphane first by an amine and then by an alkyl group, by using an organometallic reagent in this last step. The method is especially well suited for synthesizing tetrasubstituted phosphinous amides with two different groups at



Scheme 7 R^3 = Cl, alkyl

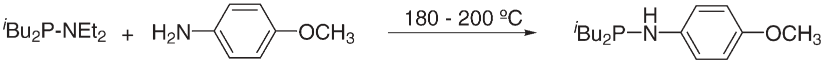
the phosphorus [20, 61–64]. A number of the required dihalophosphanes are commercially available.

Species **5** (Scheme 8), commonly known as dialkylaminodifluorophosphines, are readily synthesized via the selective cleavage of the phosphorus–carbon bond of difluoro(trichloromethylphosphane) by the action of secondary amines [65, 66]. Compounds **5** show selective F/H exchange with LiAlH$_4$/HN(^{i}Pr)$_2$ to give the respective PH$_2$ (*P*-unsubstituted) phosphinous amides [13].



Scheme 8 **5**

The amino interchange reaction is another method commonly used for preparing phosphinous amides [67] (Scheme 9). The low boiling points of dimethylamine and diethylamine allow their displacement from *N*,*N*-dimethyl and *N*,*N*-diethyl phosphinous amides, respectively, by other less volatile amines, leading to new members of the same class. High reaction temperatures are nevertheless required.



Scheme 9

4
Prototropic Equilibrium

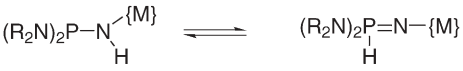
Phosphinous amides bearing protons at the nitrogen atom, that here we will call NH phosphinous amides, such as **6**, may be involved in prototropic equilibria with their PH phosphazene forms **7** [18, 68–70] (Scheme 10). This kind of prototropic equilibria, paralleling that between phosphinous acids R$_2$P-OH and phosphane oxides R$_2$P(O)H [4], have been evidenced in some particular

Scheme 10 **6** **7**

cases by means of spectroscopic methods, mainly NMR [71, 72]. Ab initio calculations have shown the tervalent phosphinous amide $H_2P\text{-}NH_2$ to be nearly 30 Kcal mol^{-1} more stable than the tautomeric tetracoordinate form, phosphazene $H_3P{=}NH$ [50, 70].

The position of the phosphorus–nitrogen diad tautomeric equilibrium **6** to **7** depends on the nature of the solvent and the substituents at the phosphorus and nitrogen atoms, shifting towards the tautomeric form possessing the least mobile protons. It has been postulated that the presence of an electron-withdrawing group, whether on the N or P atom, decreases the basicity of such atom and thus the proton migrates to the one that has become the more basic center of the molecule [69, 73–75]. As far as the solvent is concerned, Kolodiazhnyi and coworkers reported that going right in the following solvent sequence: chloroform – methylene chloride – benzene – diethyl ether, the tautomeric equilibrium is gradually shifted towards the NH phosphinous amide form [72].

This prototropic equilibrium has been also studied in substrates bearing metals linked to the nitrogen atom in the form of Cp_2MCl or $CpMCl_2$ groups [76–78], and the influence of different ligands at the metal center on the resulting equilibrium between the kinetically favored NH phosphinous amide and the thermodynamically stable tautomeric PH phosphazene form has been discussed (Scheme 11).



{M} = group 4 metal fragment

Scheme 11 R = ^{i}Pr, Cy

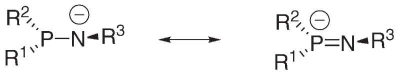
The equilibrium position corresponds well with the Lewis acidity of the metal center. By increasing the electrophilicity of the metal fragment the equilibrium concentration of the PH form increases [79]. Some computational studies unambiguously confirm the experimental results [78].

5
General Chemistry

5.1
The Phosphinous Amide Anions

Phosphinous amides of general structure $R^1R^2PNHR^3$ are easily converted to their respective anions by metals or bases. For instance, they can be easily deprotonated by alkyllithium reagents to give the $[R^1R^2PNR^3]$ anions (**8-A** or **8-B**, illustrated in Scheme 12).

The phosphorus atom in both resonance forms is in the P(III) oxidation state. Resonance form **8-A** has a formal negative charge on the nitrogen atom,

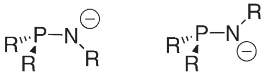


Scheme 12

whereas in resonance form **8-B** the negative charge is located on the phosphorus atom. Form **8-A** is expected to predominate if the greater electronegativity of the nitrogen atom is the dominant factor; however, form **8-B**, in which phosphorus has expanded its octet, results in additional stabilization due to resonance delocalization of the charge and N–P multiple bonding [50].

Although anions of type **8-A** have been known for many years, almost as long as their parent phosphinous amides, detailed studies on these species have attracted less attention. In 1982, Cowley presented spectroscopic and synthetic evidences indicating that an anion similar to type **8-B** was preferred over type **8-A** [80, 81]. The first known X-ray structure of one of such anions was not reported until 1992 [82]. The specific anion, $[PhNPPh_2]^-$, with lithium as the countercation, exhibits a dimeric structure and also contains diethyl ether, and is best described as $[PhN(Li)PPh_2(OC_2H_5)]_2$. Because there are both N-Li and P-Li interactions in the solid state, this anion was viewed as a resonance hybrid phosphinous amide-iminophosphide (**8-A**-**8-B**) ion. Since then, several papers have been published describing the structure of some related anions and dianions in which the lithium ion is not always associated exclusively with the nitrogen [50, 74, 83, 84]. In all the examples where a P–Li interaction is observed in the solid state, this interaction could not be ascertained in solution by using ^{31}P or ^{7}Li NMR spectroscopy.

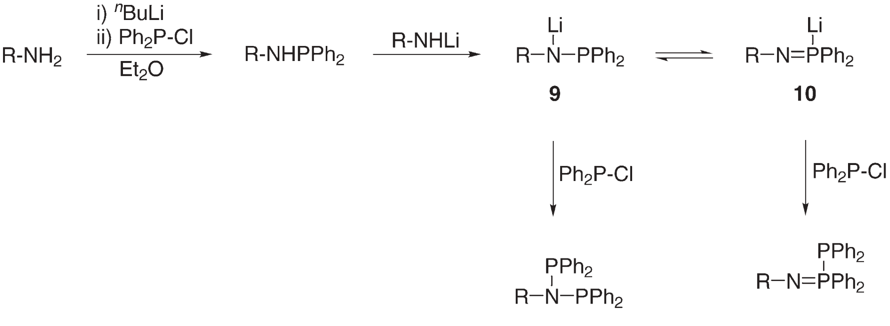
Complexation of these anions with other metals gives interesting heterometallic complexes in which both the N- and P-centers are involved in coordination to the metal [47, 85, 86]. In addition to the experimental work, ab initio calculations have been carried out that focus on the short N–P bond to delineate the location and/or distribution of the negative charge [87]. These theoretical investigations suggest that the most simple alkyl/aryl derivatives are best described as phosphinous amide anions with the negative charge essentially located on nitrogen, and that there is enough hyperconjugative bonding to enforce two ground-state conformations for **8-A**, *cis* and *trans* (Scheme 13).



Scheme 13

The experimental barrier for interconversion of the *cis* and *trans* isomers of $[PhNPPh_2]^-$ is 8 kcal mol^{-1}, and the barriers of other derivatives have been calculated to be in the range 7–32 kcal mol^{-1}, where the larger barriers are associated with the presence of substituents on the nitrogen that are moderately electron-withdrawing [50, 87].

These phosphinous amide anions are presumably responsible for the formation of the by-products *N*-phosphino phosphinous amides **11** and monophosphazenes derived from diphosphanes **12** in the sequential treatment of primary amines with *n*-BuLi and chlorophosphanes for preparing NH phosphinous amides [75, 88] (Scheme 14). Compounds **11** and **12** are presumably derived from anions **9** and **10**, respectively, generated by deprotonation of the newly formed phosphinous amide with the lithiated amine R^1NHLi. In solution, **9** can establish a metallotropic equilibrium with **10**.



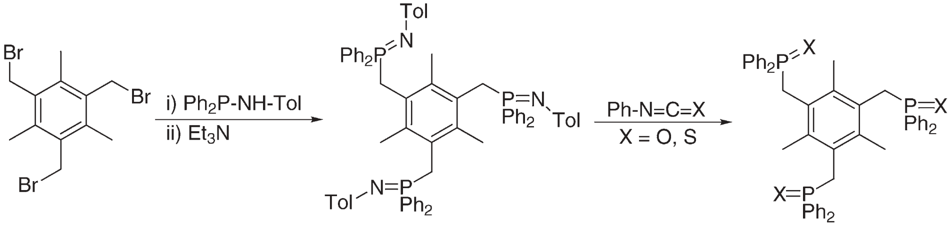
Scheme 14

5.2
Reactions at Phosphorus or Nitrogen

Phosphinous amides behave as normal phosphanes in many of their reactions occurring at the phosphorus atom. The presence of the lone pair on the adjacent nitrogen atom has been shown to increase the nucleophilicity of the phosphorus although in an extent not comparable to the α effect seen in N–N and N–O nucleophiles [89]. It has been argued that repulsive interaction between the N and P lone pairs may raise the energy of the latter, thus rendering it more basic and nucleophilic [90], whereas dπ-pπ interactions are of minor relevance in this respect. The effect is relatively small, and phosphinous amides are not classified among the typical α-nucleophiles. Besides nucleophilic reagents, phosphinous amides are also electrophilic at phosphorus, as the nitrogenated part can be displaced by strong nucleophiles, as will be shown below.

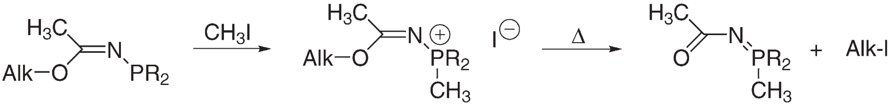
Oxidation occurs when exposed to air, with hydrogen peroxide [30], dialkyl peroxides [18] or manganese dioxide [32, 91] to produce the corresponding oxide, that is, the phosphinic amides $R^1R^2P(O)NR^3R^4$. Reactions with sulfur [30, 92] or selenium [93] yield the respective thio- or selenoanalogs. Similarly, the Staudinger imination reaction of phosphinous amides with organic azides produces the expected imines $R^1R^2P(=NR^5)NR^3R^4$ [67, 94], the P(V) phosphaanalogs of the amidines. When R^3=H, these compounds can be deprotonated by the action of sodium and the resulting salts further alkylated at the nitrogen [94].

Phosphinous amides are regioselectively alkylated at phosphorus, and the resulting aminophosphonium salts are generally stable [20, 61]. With phosphinous amides bearing protons attached to the nitrogen atom, the NH-aminophosphonium salts can be easily deprotonated by organic bases such as TEA, DIPEA and DBU, to yield the corresponding phosphazenes (iminophosphoranes, phosphane imines) [92, 95–97]. The full sequence constitutes a novel entry, via P–C bond formation, to this widely utilized class of P(V) derivatives, from which the P=O and P=S analogs can be readily prepared by aza-Wittig type reactions [98–101]. The method has been applied to the preparation of polyfunctional organophosphorus compounds, such as the tris(iminophosphorane) **13**, trioxide **14** (X=O), and trisulfide **14** (X=S), starting from reactive organic polyhalides [95] (Scheme 15).



Scheme 15 **13** **14**

In this context, the treatment of the *N*-phosphinyl iminoethers **15** with methyl iodide furnish the *P*-methyl phosphonium iodides, which by heating experience an *O*-dealkylation, reminiscent of the Arbuzov reaction, for yielding the *N*-acylphosphazenes **16** [45] (Scheme 16).

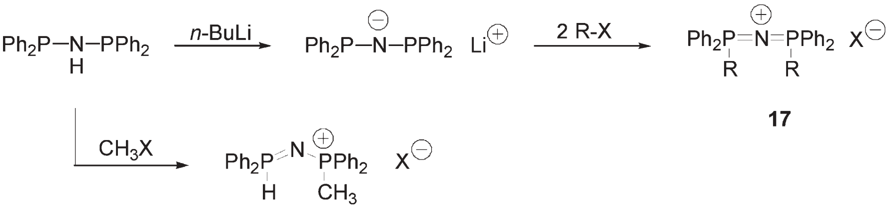


15 **16**

Scheme 16

A number of NH phosphinous amides have been *P*-alkylated by previous conversion to their corresponding anions [59, 74]. A particular case of double alkylation takes place with the anion derived from the *N*-phosphino phosphinous amide $NH(PPh_2)_2$ yielding the diphosphonium salt **17** [102] (Scheme 17). When neutral, its methylation is reported to give the P–H phosphazene-phosphonium salt **18** [103].

NH-Phosphinous amides are also alkylated at phosphorus by electrophilic olefins, such as acrylonitrile and acrylamide, with concomitant formation of a

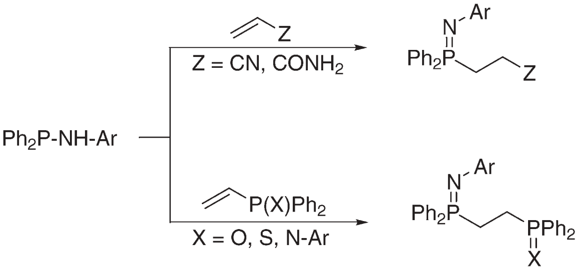


17

Scheme 17

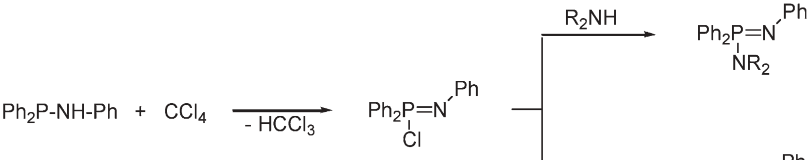
18

phosphazene unit [104] (Scheme 18). Similar P–H additions to the activated C=C double bond of *P*-vinyl phosphane oxides, sulfides and imines have been recently been carried out by our research group [105]. We have also used other types of electrophilic olefins and acetylenes in related processes, and the results will be reported in due course.



Scheme 18

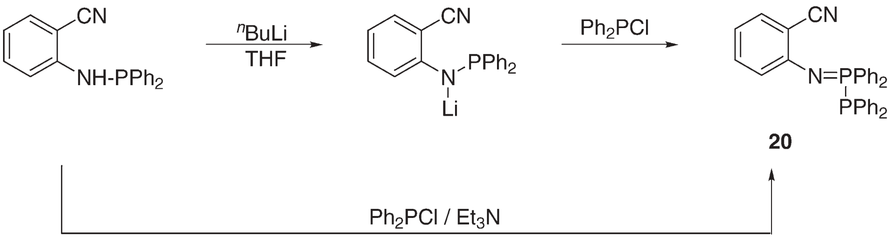
Other reactions that resulted in the formation of P=N double bonds are those of NH phosphinous amides with tetrahalomethanes [106–108]. The reaction products, *P*-halophosphazenes **19**, may be further elaborated by substituting the halogen atom with amines or Grignard reagents (Scheme 19).



19

Scheme 19

Occasionally, attempts at introducing a new PR_2 group on the nitrogen atom of an NH phosphinous amide, with the aim of preparing *N*,*N*-bis(phosphino) phosphinous amides, result in the generation of monophosphazenes derived from diphosphanes, as seen in the preparation of **20** which occurs by P–P bond formation [74] (Scheme 20). The authors of this work claimed that the electron-



20

Scheme 20

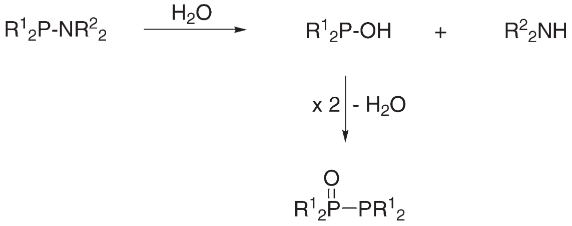
withdrawing cyano group may determine that the tautomeric phosphazene $R^1_2P(H){=}NR^2$ dominates in the reaction with Ph_2PCl.

Tetrasubstituted phosphinous amides of the type R_2NPPh_2 have been successfully arylated at phosphorus by the action of bromobenzene, in a process catalyzed by $NiBr_2$, to give the aminophosphonium bromides $[R_2NPPh_3]^+\ Br^-$ [109]. Other representative members of this class form phosphane–borane complexes [62], are aminated at phosphorus by chloramine to yield bis(amino)phosphonium salts [110] and have been claimed to be protonated at phosphorus by ethereal tetrafluoroboric acid, as determined by NMR analysis [111].

NH-Phosphinous amides can be metallated at nitrogen, via their corresponding anions [78, 112, 113] as well as borylated [114] and silylated [22, 115, 116]. In this last case, the isomeric *P*-silylphosphazenes are also occasionally obtained.

5.3
Reactions that Fragment the P–N Bond

The hydrolysis of phosphinous amides leading to their constituents, amine and phosphinous acid, is an easy process that is usually followed by the self-condensation of the acid to yield the diphosphane monoxides **21** [117, 118] (Scheme 21).



Scheme 21

21

The P–N bond also breaks when the phosphinous amides react with gaseous HCl, producing the expected amine hydrochloride and the corresponding chlorophosphane [14] (Scheme 22).

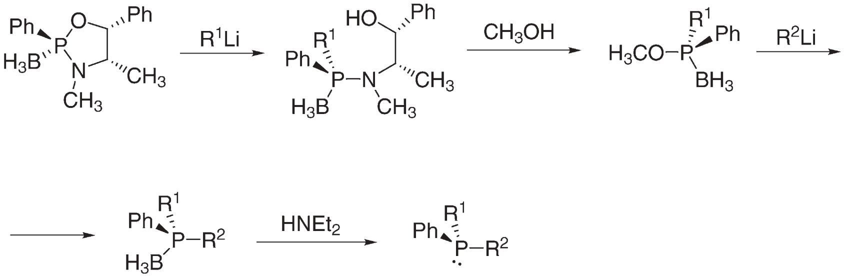
$$Ph_2P\text{-}NEt_2 \xrightarrow{HCl\ (g)} Ph_2P\text{-}Cl \quad + \quad Et_2NH \cdot HCl$$

Scheme 22

Aqueous HCl solutions hydrolyze the P–N bond to give the amine hydrochloride and R_2P-OH, which then disproportionates and is oxidized to diphenylphosphinic acid. A "free" phosphinous amide anion, with the countercation complexed by a crown ether, has been shown to be hydrolyzed and oxidized to the corresponding phosphinite with unusual ease [119]. Formic acid in toluene can be utilized for converting *P*,*P*-disubstituted phosphinous amides into their respective phosphane oxides [30].

The course of the reaction of phosphinous amides with carboxylic acid chlorides is dependent on the characteristics of the *N*-residue. Thus with *N*-aryl compounds this reaction gives chlorophosphanes and carboxamides. With *N*-alkyl analogs the primary reaction products have not been identified but they hydrolyzed to carboxaldehydes [120].

In a similar way to the aminolysis of the P–N bond mentioned above (Scheme 9), alcoholysis of phosphinous amides leads to the alkyl esters of the respective phosphinous acids [30, 121]. This reaction occurs with inversion of the absolute configuration of the phosphorus atom, and has been used in a synthetic sequence leading to optically active tertiary phosphanes **22** [122] (Scheme 23).

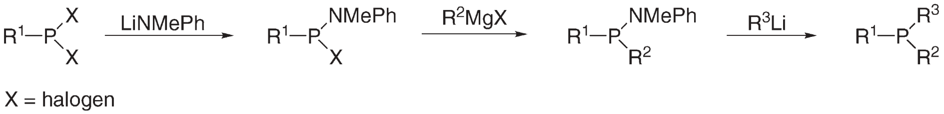


Scheme 23

22

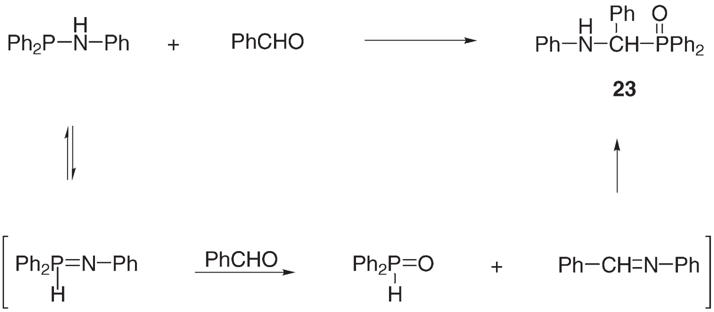
Only in a particular case can the R_2N group of *N*,*N*-disubstituted phosphinous amides be nucleophilically displaced by the action of organometallic reagents at phosphorus, as recently reported [123]. Whereas NEt_2 or N^iPr_2 remained unaltered by Grignard reagents and alkyllithiums, the NMePh group could be displaced by RLi reagents. This fact has been used in a sequential synthesis of chiral tertiary phosphanes that is based on the selective displacement at phosphorus of a Cl in the presence of a NMePh residue and further displacement of this last by RLi (Scheme 24).

The results of the reaction of carbonyl compounds, aldehydes and ketones, with NH phosphinous amides can be interpreted as occurring on the PH phos-



Scheme 24

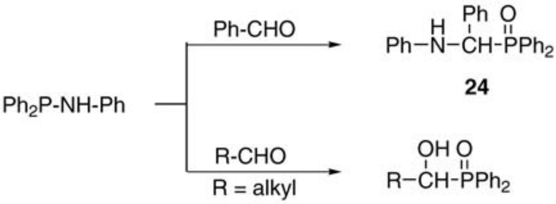
phazene tautomeric form, via aza-Wittig processes. Thus, as early as 1966 benzaldehyde was reported to react with *N*,*P*,*P*-triphenyl phosphinous amide to give α-diphenylphosphinyl-*N*-benzylaniline **23** [124] (Scheme 25). The reaction products result from the addition of diphenylphosphane oxide to the C=N bond of the imine resulting from the initial aza-Wittig process.



23

Scheme 25

More recently, Balakrishna et al. disclosed that the reaction of similar substrates with formaldehyde occurs with insertion of a methylene group between phosphorus and nitrogen to give $PhNHCH_2P(O)Ph_2$ [125]. This is simply a new example of the same type of reaction. Following this communication, the reaction was studied in more depth by the same research group using different aldehydes. They showed that whereas benzaldehyde and formaldehyde behave as above yielding **24**, other aliphatic aldehydes give instead α-hydroxyalkyl phosphane oxides **25** [118] (Scheme 26).



24

25

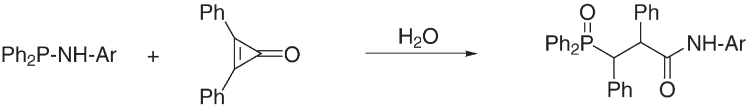
Scheme 26

Cyclohexanone reacts similarly to give the corresponding imine and $Ph_2P(O)PPh_2$ [124].

In contrast to the results above, the reaction of α-ketocarboxylic esters follows a different course giving **26**, the product of P–H addition of the tautomeric PH phosphazene form to the keto C=O double bond [126] (Scheme 27).

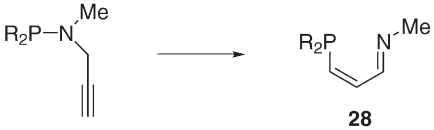
Scheme 27 R = CH_3, Ph, EtO_2C **26**

We have investigated the reaction of NH phosphinous amides with diphenylcyclopropanone. The products were unequivocally identified as the corresponding β-phosphinyl carboxamides **27** resulting from the hydrolysis of a presumed heterocyclic intermediate (Scheme 28) These results await publication.



Scheme 28 **27** (*syn* + *anti*)

Finally, the *N*-propargyl-*P*,*P*-dialkyl or diaryl phosphinous amides rearrange at room temperature to the *P*-(4-azabutadienyl)phosphanes **28** [127] (Scheme 29). Interestingly, this rearrangement did not occur in other structurally similar P–N functionalities (R=OEt, O^iPr, NEt_2).



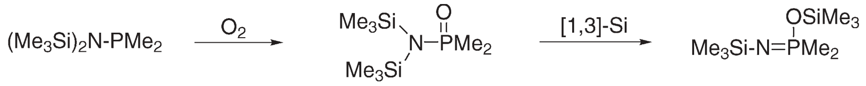
28

Scheme 29 R = Et, Ph

6
N-Silyl Phosphinous Amides

The *N*-silyl phosphinous amides present some particularities in their reactivity that make these compounds worth commenting on separately. They are stable and can be easily prepared in the usual way by reaction of *N*-silyl substituted primary amines or hexamethyldisilazane with halophosphanes [48, 49, 128, 129] or by *N*-silylation of the appropriate phosphinous amides [72, 107]. The reductive Ph–P bond cleavage in *N*-silyl phosphazenes $Ph_3P{=}NSiMe_3$ by the action of sodium is a peculiar example of preparing $Ph_2PNHSiMe_3$ [130].

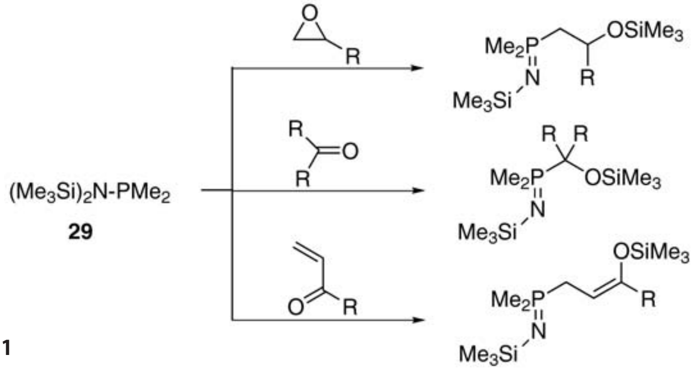
It is well known that trialkylsilyl groups are prone to migrate via different types of molecular rearrangements [131]. This behavior serves to explain some of the most important reactions of *N*-(trialkylsilyl)phosphinous amides, always in connection with their nucleophilicity at phosphorus. Thus, oxidation of *N*,*N*-bis(trimethylsilyl)-*P*,*P*-dimethylphosphinous amide **29** does not end at the primary oxidation product **30** but instead this step is followed by a subsequent [1,3]-Si shift from nitrogen to oxygen yielding **31** [48, 132, 133] (Scheme 30).



29 **30** **31**

Scheme 30

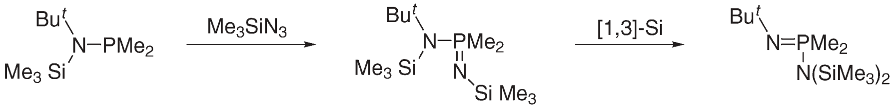
The oxophilicity of silicon is also the driving force that allows the reaction of the same silylated reagent **29** with oxiranes [134], aldehydes and ketones [135, 136], and enones [136] for yielding functionalized *N*-silylphosphazenes (Scheme 31).



Scheme 31

The reactivity of *N*-silyl phosphinous amides versus some of the functional groups in the scheme above has no precedent in nonsilylated analogs.

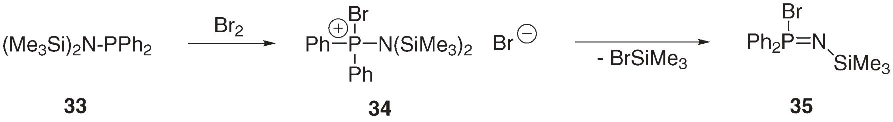
An interesting [1,3]-Si shift from nitrogen to nitrogen has been observed in the Staudinger imination reaction of *N*-*tert*-butyl-*N*-trimethylsilyl-*P*,*P*-dimethyl phosphinous amide **32** with trimethylsilylazide [137]. The steric bulk provided by the *tert*-butyl group seems to determine the direction of the silyl shift (Scheme 32).



32

Scheme 32

Apart from silyl shifts, other reactions that are also characteristic of this class of compounds or their derivatives are due to the easy formation of halogen–silicon bonds. Phosphonium salt **34**, resulting from the addition of bromine to **33**, undergoes spontaneous desilylation by the action of the bromide anion to give the *P*-bromophosphazene **35** [138, 139] (Scheme 33).



Scheme 33

The stable *P*-unsubstituted phosphinous amide $H_2PN(SiMe_3)_2$ has been shown to suffer the nucleophilic displacement of the disilazane moiety by the action of thiols R-SH giving the phosphinous thioesters R-S-PH_2 [13]. For the sake of brevity we shall not comment on other relevant reactions of *N*-silyl phosphinous amides, such as the anionic *P*-silylation [115] and *P*-alkylation [22], the consecutive dialkylation of PH derivatives [18] and the fluorodesilylation of *P*-fluoro-*N*-silyl derivatives [140].

7

Organic Reactions Catalyzed by Metal Complexes Bearing Phosphinous Amide Ligands

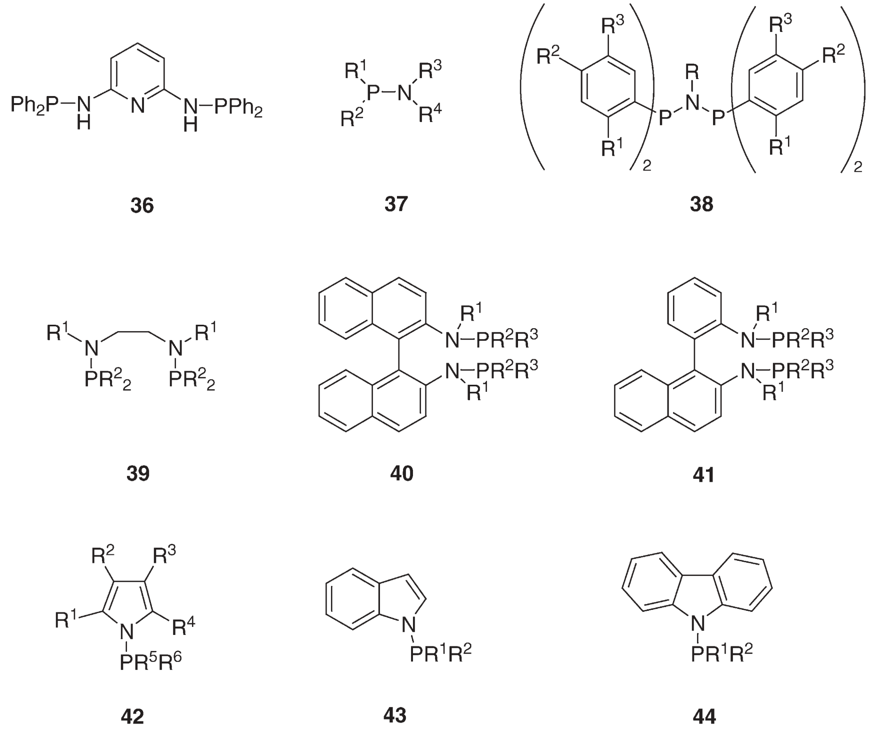
Almost neglected for long time, phosphinous amides are now being widely used as ligands in the preparation of metallic complexes and this utilization is characterized by a spectacular growth in the last ten years, especially by the numerous contributions, among others, of Woollins and coworkers [141–145]. As the volume of published work in this theme is really huge, we will focus here on those complexes bearing phosphinous amide ligands that have advanced into the field of catalysis of important organic transformations. The pioneering works in this area of Fiorini and coworkers in the late seventies should be specially recognized [146–150].

Following the general trend of this account, monodentate phosphinous amide ligands and bidentate *N*-phosphino phosphinous amides or bis(aminophosphanes) are included in the following discussion, but not other bidentate ligands bearing additional, different phosphorus functionalities, as for instance phosphinous amide-phosphane bidentate ligands.

The complexes are presented here under the heading of the organic reaction they catalyze.

7.1
Alkene Hydrogenation, Hydroformylation and Polymerization

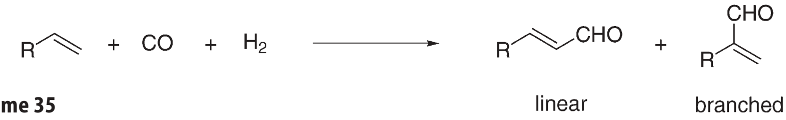
The ligand *N*,*N*-bis(diphenylphosphino)-2,6-diaminopyridine (PNP, **36** in Scheme 34) has been used in the preparation of complexes of type [M(PNP)-Cl]Cl·L (M=Ni, L=H_2O; M=Pd, L=EtOH, M=Pt) and *mer*-[M(NPN)$(CO)_3$]·2THF (M=Cr, Mo, W), which have been used as catalysts in the hydrogenation of styrene to ethylbenzene. The relative activity in the homogeneous catalytic reaction decreases in the series of the [M(PNP)Cl]Cl·L complexes on going from M(II)=Ni to Pd and then to Pt [151].



Scheme 34

The catalytic hydroformylation of alkenes has been extensively studied. The selective formation of linear versus branched aldehydes is of capital relevance, and this selectivity is influenced by many factors such as the configuration of the ligands in the metallic catalysts, i.e., its bite angle, flexibility, and electronic properties [152, 153]. A series of phosphinous amide ligands have been developed for influencing the direction of approach of the substrate to the active catalyst and, therefore, on the selectivity of the reaction. The use of Rh(I) catalysts bearing the ligands in Scheme 34, that is the phosphinous amides **37** (R^1,

R^2=Ph; R^3=R^4=alkyl, aryl), **38** (R=Et; R^1=R^2=R^3=H) the bis(aminophosphanes) **39** R^1=Me, CH_2Ph, Tos; R^2=^{i}Pr, Ph), **40** (R^1=H; R^2=R^3=Ph) and **41** (R^1=H; R^2=R^3=Ph), or the heterocyclic monodentate ligands **42** (R^1=H, $COCH_3$, R^2=R^3=R^4=H, R^5=R^6=Ph), **43** (R^1=R^2=Ph) and **44** (R^1=R^2=Ph) achieved a high degree of regioselectivity in favor of the formation of linear versus branched aldehyde [142, 154–157] (Scheme 35).

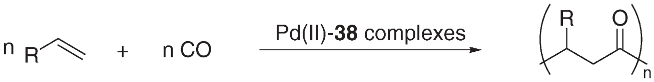


Scheme 35

In most cases the conversion degrees and the yields in aldehydes are good (86–95%) and the regioselectivity goes from 1.2:1 to 31.1:1, depending on the ligand used.

Wass and coworkers have reported several applications of catalysts based on nickel(II) complexes of bulky *N*-phosphino phosphinous amides **38**. In fact, the ligands bearing *ortho*-methoxy-substituted aryl groups (**38**, R^1=OCH_3 in Scheme 34), along with a chromium source and an alkyl aluminoxane activator, are extremely active and selective ethylene trimerization catalysts [158]. Analysis of the products in the hydroformylation of 1-hexene by GCMS reveals good selectivity, typically >85%, the main by-products being C_{10} olefins. The steric bulk provided by the *ortho*-substituents on ligand **38** plays a critical role in establishing the catalytic performance. Specifically, the potential for the *ortho*-methoxy groups to act as pendant donors and to increase the coordinative saturation of the chromium center is an important factor.

Nickel(II) complexes of ligands **38** (R=H, Me; R^1=H, Me, Et, ^{i}Pr, CH_3O; R^2=H, CH_3O; R^3=H, F, CH_3O) are highly active catalysts for ethylene polymerization [86, 159], whereas palladium(II) complexes possess catalytic properties in the copolymerization of CO and alkenes [160] (Scheme 36).



Scheme 36

7.2
Suzuki–Miyaura Reaction

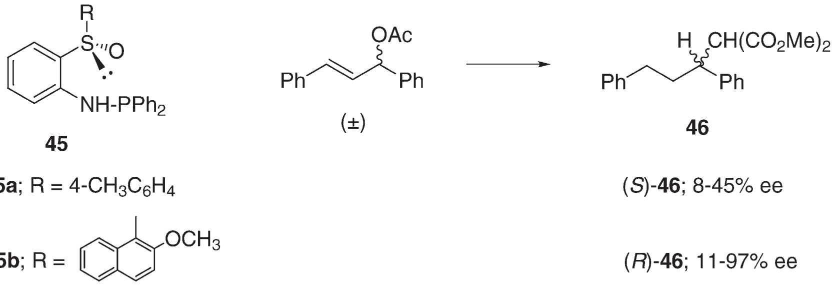
It is well known that the use of electron-rich phosphanes as ligands accelerate the key oxidative addition step of the Suzuki–Miyaura reaction [161]. In that sense, phosphinous amides are good candidates for testing as efficient ligands for this cross-coupling reaction: the amino groups are strongly electron-donating making the phosphanes stronger σ-donor ligands and so facilitating the easy oxidation of the transition metal. Thus, aminophosphanes **37** (R^1=R^2=Ph, cyclohexyl,^{i}Pr, *tert*-butyl; R^3=R^4=^{i}Pr, Me_3Si, 2-pyridyl, 2-pyrimidyl, pyrazinyl, 2-quinolinyl; R^3-R^4=$(CH_2)_5$, $(CH_2)_2O(CH_2)_2$; R^3=Me, R^2=$Me_2NCH_2CH_2$) have been used in the preparation of Pd(II)-**37** catalytic complexes and tested in several Suzuki couplings (Scheme 37). The biphenyl products are obtained in 76–99% yields [162–164].

$$Ar^1\text{-}Br \quad + \quad Ar^2\text{-}B(OH)_2 \xrightarrow{\text{Pd(II)-}\mathbf{37}\text{ complexes}} Ar^1\text{-}Ar^2$$

Scheme 37

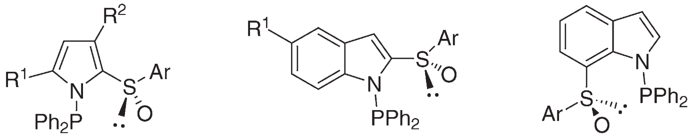
7.3
Asymmetric Allylic Alkylations

Chiral phosphinous amides have been found to act as catalysts in enantioselective allylic alkylation. Horoi has reported that the palladium-catalyzed reaction of (±)-1,3-diphenyl-2-propenyl acetate with the sodium enolate of dimethyl malonate in the presence of $[PdCl(\pi\text{-allyl})]_2$ and the chiral ligands **45** gave **46** in 51–94% yields and up to 97% ee (Scheme 38). It is notorious that when the reaction is carried out with the chiral phosphinous amide (*S*)-**45a**, the product is also of (*S*) configuration, whereas by using (*R*)-**45b** the enantiomeric (*R*) product is obtained [165].



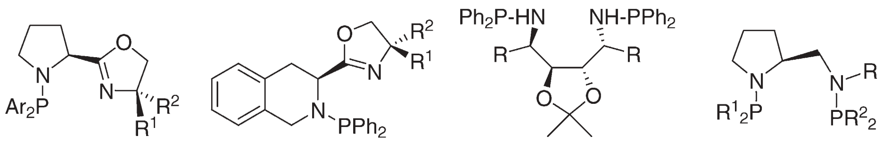
Scheme 38

Phosphinous amides **47–49** (Scheme 39), closely related to those in the scheme above but with a new scaffold supporting the sulfur and phosphorus functionalities, have been recently reported to catalyze the same reaction [166].



Scheme 39 **47** **48** **49**

Phosphinous amides, based on proline and tetrahydroisoquinoline carboxylic acid, bearing a second donor center (**50**, Ar=Ph; R^1=H, CH_3,^{i}Pr, Ph; R^2=H, CH_3,^{i}Pr, Ph and **51**, R^1=H,^{i}Pr; R^2=H,^{i}Pr) (Scheme 40) have been developed for use in allylic alkylation and amination of substituted propenyl acetates, yielding the corresponding products in 87–98% (5–94% ee) and 29–97% (14–93% ee) respectively [55, 167]. With bidentate ligands of type **38** where R=(*S*)-PhMeCH, and with the bis(aminophosphanes) **52** (R=Ph) similar allylic alkylations have been also tested [168, 169].



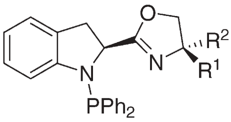
50 **51** **52** **53**

Scheme 40

The efficiency of a catalytic system based on the bis(aminophosphane) **53** in the asymmetric alkylation of 3-acetoxycyclohexene with dimethyl malonate has been tested [170]. Concerning the enantioselectivity of this reaction, the ee values are generally quite low and the best result for this ligand is only 31% ee.

7.4
Asymmetric 1,4-Addition to Enones

A series of chiral phosphinous amides bearing pendant oxazoline rings (**50**, R^1=H,^{i}Pr; R^2=H,^{i}Pr, **51**, R^1=H,^{i}Pr; R^2=H,^{i}Pr and **54**, R^1=H,^{i}Pr; R^2=H,^{i}Pr in Scheme 41) have been used as ligands in the copper-catalyzed 1,4-addition of diethylzinc to enones. Two model substrates have been investigated, the cyclic 2-cyclohexenone and the acyclic *trans*-chalcone. The addition products are obtained quantitatively in up to 67% ee [171].



Scheme 41 **54**

7.5
Asymmetric Hydrogenation of C=C and C=O Bonds

In the area of the asymmetric hydrogenation of C=C double bonds, the reduction of unfunctionalized olefins has been scarcely explored, in comparison with the extensively explored asymmetric reduction of functionalized alkenes containing heteroatoms. Gilbertson and coworkers have developed a series of iridium catalysts with enantio-enriched phosphinous amide ligands **50** based on proline (Scheme 42). The catalytic family resulted from variation of the substituents at the oxazoline ring and at the phosphorus atom, and by combining with several counterions [57].

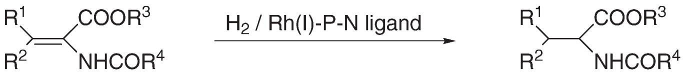
50

Ar = Ph, o-Tol, 2-ethylphenyl, 2,3-dimethylphenyl, 2,4-dimethylphenyl
R^1 = ^{i}Pr, ^{t}Bu
R^2 = H
X = PF_6, BARF

Scheme 42

The asymmetric hydrogenation of various methylstilbenes led to the corresponding 1-methyl-1,2-diarylethanes with enantioselectivities ranging from 83:17 to 97:3. The use of catalysts prepared with ligands **50** was extended to the asymmetric hydrogenation of a number of styrene derivatives, proving that, in general, the reduction of trisubstituted double bonds proceeds with fair to good enantioselectivity.

In recent years, the catalytic asymmetric hydrogenation of α-acylamino acrylic or cinnamic acid derivatives has been widely investigated as a method for preparing chiral α-amino acids, and considerable efforts have been devoted for developing new chiral ligands and complexes to this end. In this context, simple chiral phosphinous amides as well as chiral bis(aminophosphanes) have found notorious applications as ligands in Rh(I) complexes, which have been used in the asymmetric hydrogenation of α-acylamino acrylic acid derivatives (Scheme 43).

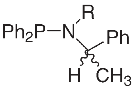
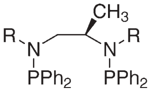
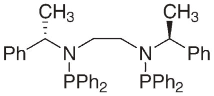
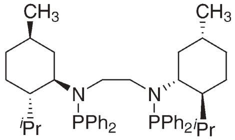
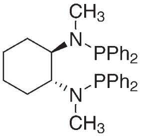
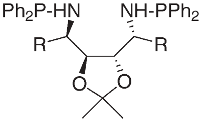
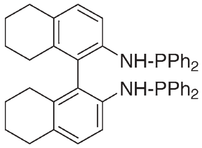
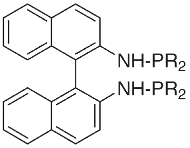


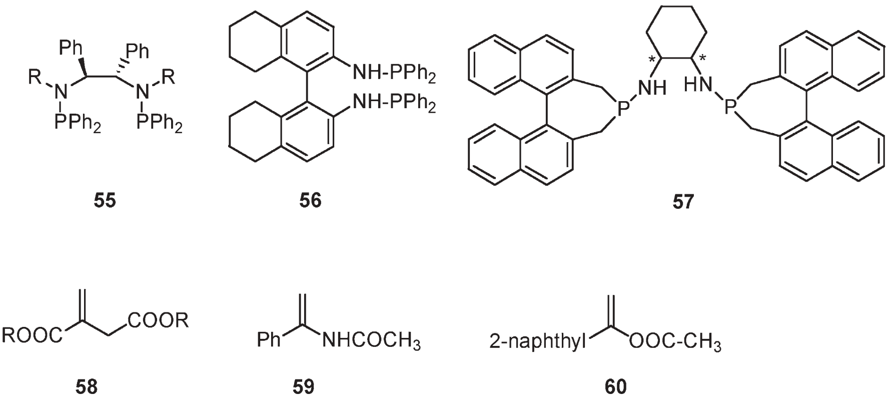
Scheme 43

In Table 2 we have summarized the optical yields obtained by using the different enantio-enriched ligands investigated in this reaction, and the respective literature citations.

Bidentate chiral bis(aminophosphanes) such as **55–57** (Scheme 44) have been used for the Rh(I)-catalyzed asymmetric hydrogenation of itaconic acid

Table 2 Enantioselective hydrogenation of α-acylamino acrylic acid derivatives

Ligand	cc (%)	Reference
 (*R*) or (*S*)	<3	[172]
	6–74	[173, 174]
	9–83	[175]
	70–93	[147]
	41–94	[173, 174, 176–179]
	77–99	[180]
 (*R*) or (*S*)	90–99	[181]
 (*R*) or (*S*) R = Ph, cyclohexyl, 3,5-dimethylphenyl	77–99	[181–184]



Scheme 44

derivatives **58**, the enamide **59** and the enol acetate **60**. Good to excellent enantioselectivities were obtained (up to 99.5% ee) [150, 185, 186].

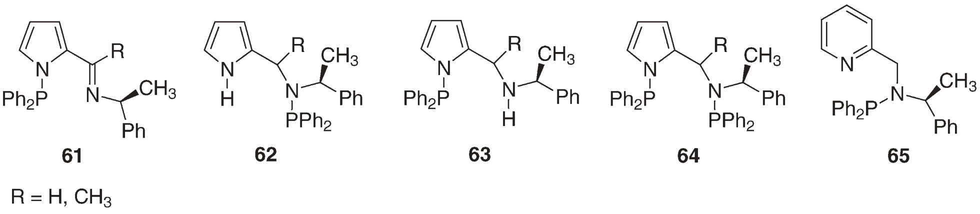
The use of C_2 symmetric bis(aminophosphanes) such as **39** (R^1=(*S*)-(–)Ph-CH(CH_3); R^2=Ph) and not symmetrically substituted bis(aminophosphanes) such as **52** (R^1=cyclopentyl, cyclohexyl, Ph; R^2=cyclopentyl, cyclohexyl, Ph) as ligands in asymmetric hydrogenation reactions of activated ketones has resulted in the preparation of the corresponding optically active alcohols in 17–80% ee [148, 187]. Complexes bearing the bis(aminophosphane) ligands **52** have been used for the asymmetric reduction of dihydro-4,4-dimethyl-2,3-furandione and of *N*-benzylbenzoylformamide. They can be modulated for obtaining alternatively both enantiomers of the product, just by replacing a phenyl by a cycloalkyl group at the phosphorus atoms of the ligand.

7.6
Asymmetric Hydroboration

Despite the extensive applications of phosphinous amides as chiral ligands in Rh(I) complexes with catalytic activity, there is still playground available for expanding its usefulness to other relevant organic transformations. One of these reactions is the catalytic hydroboration of alkenes, where the attempts made to date with this kind of ligands have not been specially successful in terms of optical yield. Bis(aminophosphanes) **52** (R=Ph, 2-MeC_6H_4, 2-MeOC_6H_4; R^1=R^2 cyclohexyl, Ph) have been used in the asymmetric catalyzed hydroboration of norbornene by catecholborane, giving *exo*-norborneol as the major product in all the reaction conditions investigated, although with moderate enantioselectivities (12–77% ee). On the other hand, hydroboration of styrene, 3-methyl-2-cyclohexen-1-one and isophorone, and further transformation of the resulting alkylboranes into the corresponding alcohols, have been achieved in moderate chemical yields (57–64%), and poor enantiomeric excesses (8–42%) [188].

7.7
Asymmetric Hydrosilylation

Finally, the participation of the *N*,*P*-bidentated phosphinous amides **61–65** (Scheme 45) as chiral ligands in the catalytic enantioselective hydrosilylation of acetophenone with diphenylsilane is worth mentioning, despite low ee (2–20%) [52].



Scheme 45

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Expanding the Analogy Between P=C and C=C Bonds to Polymer Science

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Abstract Many similarities between the chemistry of carbon and phosphorus in low coordination numbers (i.e., CN=1 or 2) have been established. In particular, the parallel between the molecular chemistry of the P=C bond in phosphaalkenes and the C=C bond in olefins has attracted considerable attention. An emerging area in this field involves expanding the analogy between P=C and C=C bonds to polymer science. This review provides a background to this new area by describing the relevant synthetic methods for P=C bond formation and known phosphorus–carbon analogies in molecular chemistry. Recent advances in the addition polymerization of phosphaalkenes and the synthesis and properties of π-conjugated poly(*p*-phenylenephosphaalkene)s will be described.

Keywords Phosphorus · Phosphaalkenes · Addition polymerization · Conjugated polymers · Inorganic polymers

1
Introduction

Given the fact that phosphorus is in Group 15 while carbon is in Group 14, one might predict that the structures, bonding and reactivity of their respective compounds would be quite different. In many respects this is the case. However, a remarkable parallel chemistry has built up around the fact that, in low-coordination numbers, phosphorus strongly resembles carbon. In many ways, low-coordinate phosphorus behaves more like its diagonal relative than its vertical congener, nitrogen. This has led to phosphorus being called "the carbon copy" and the establishment of a burgeoning field of chemistry at the interface between organic and inorganic chemistry (for comprehensive reviews see [1, 2]).

This review will outline a new area of research that has, until recently, been unexplored in low-coordinate phosphorus chemistry. Researchers are beginning to extend the established analogy between P=C and C=C bonds to macromolecular science. The motivation for these investigations is the prevalence of C=C bonds in polymer chemistry, both as monomers for addition polymerization and as functional units in π-conjugated polymers. Furthermore, the incorporation of phosphorus into the polymer backbone may lead to materials with interesting properties and possible specialty applications. This article will review recent developments and provide the author's perspective on combining the areas of multiple bonding in phosphorus chemistry with inorganic polymer synthesis.

2
The Phosphorus–Carbon Analogy

As an illustration of the phosphorus–carbon analogy, consider the result of replacing a carbon fragment (CR_2) by a phosphorus moiety (PR) in each of the common low-coordinate organic compounds (**1C**–**4C**) shown in Fig. 1. For example, the replacement of a single carbon in an alkene (**1C**) results in a phosphaalkene (**1P**). Similarly, the phosphaalkynes (**2P**) are isolobal relatives of the alkynes (**2C**), and terminal phosphinidene complexes (**3P**) can be related to the

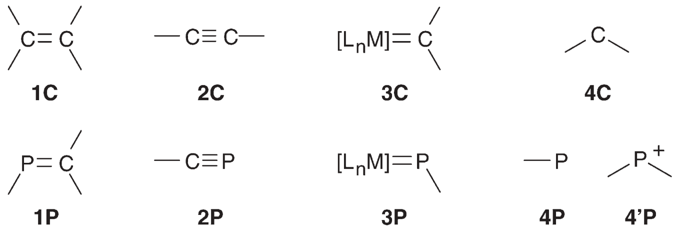
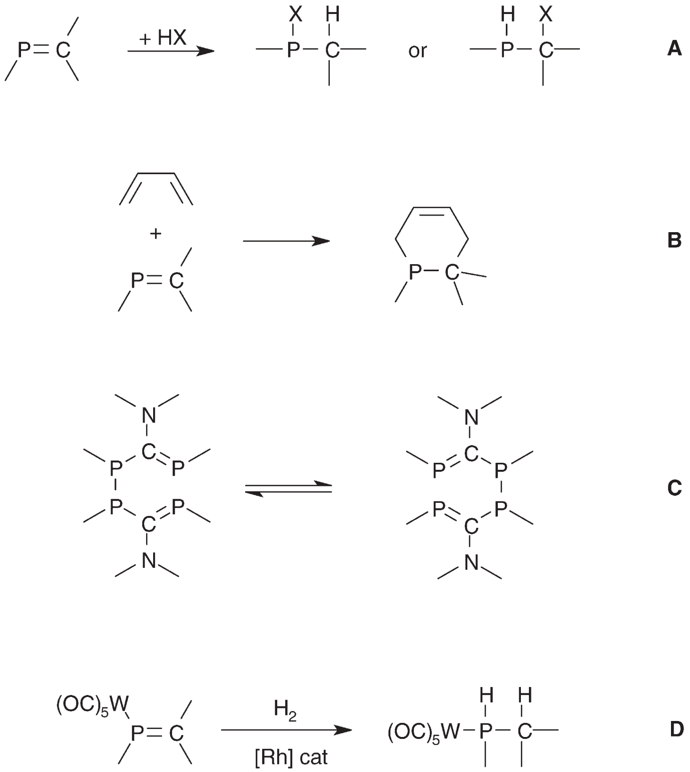


Fig. 1 Most common low coordinate bonding environments for carbon and phosphorus

metal carbenes (**3C**). In the case of free carbenes (**4C**), there are two possible phosphorus analogs, the free phosphinidenes (**4P**) and the phosphenium ions (**4′P**). With the exception of olefins and alkynes, many of the simple compounds depicted in Fig. 1 were not known as isolable species until the later part of the last century. For example, isolable carbenes have only been reported recently [3, 4], yet their impact on chemistry has been immense; from challenging our ideas of structure and bonding to their applications as ligands in catalysis (for reviews see [5–7]). The development of the various classes of low-coordinate phosphorus compounds depicted in Fig. 1 is fascinating and the reader is urged to consult the many excellent reviews outlining this vast area. Reference[8] has detailed chapters on **1P–4′P** . For selected reviews on phosphaalkenes and phosphaalkynes see [9–14]. Reviews dealing specifically with phosphaalkenes are cited elsewhere in this review. For recent reviews on phosphinidines and metal- phosphinidines see [15–18]. For reviews on phosphenium ions see [19–21].

This review deals specifically with the parallels between P=C and C=C bonds [1, 2, 22]. The analogy between phosphaalkenes (**1P**) and olefins (**1C**), as shown in Fig. 1, manifests itself not only in their structure and bonding, but also in the synthetic methods used for their preparation (see Sect. 3) and their reactivity. Many of the parallels in the reactivity of P=C and C=C bonds can be explained, in part, by the similar electronegativities of the elements (C 2.5 vs P 2.2) and their electron accepting and releasing abilities. In addition, the results of calculations and photoelectron spectroscopy have revealed that the π-bond in phosphaethylene is the HOMO (–10.3 eV) while the phosphorus lone pair is slightly lower in energy (–10.7 eV) [23]. This suggests that, like ethylene, most reactions of phosphaethylene will occur at the π-bond, although the close spacing of the orbitals also makes reaction at the phosphorus lone pair possible.

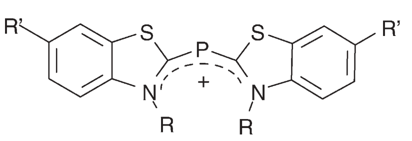
It is not within the scope of this review to exhaustively discuss the novel reactivity of phosphaalkenes. Here, just a few striking examples from molecular chemistry will be chosen to highlight the phosphorus–carbon analogy. For more details regarding the fascinating reactivity of phosphaalkenes, the reader is urged to consult the numerous reviews from which the following examples are taken [1, 2, 22, 24–32]. Firstly, simple reactions of olefins such as the 1,2-addition of polar molecules (i.e., HX) across the C=C bond are also observed with phosphaalkenes (**A**). Depending upon the substituents, the P=C bond can either be normally polarized $P(\delta^+)$-$C(\delta^-)$ or inversely polarized $P(\delta^-)$-$C(\delta^+)$ [24] towards addition. There is also a remarkable [n+2]-cycloaddition chemistry for phosphaalkenes. A well known example would be the phosphorus analog of the Diels–Alder reaction (**B**). This method represents a powerful route to new types of heterocycles. There are also phosphorus analogs of the Cope rearrangement (**C**). Even catalytic hydrogenations using rhodium phosphine catalysts are known for P=C bonds, however, the lone-pair at phosphorus must first be protected through coordination to tungsten (**D**). Like olefins, η^2 complexes of phosphaalkenes to transition metals are observed although η^1 complexation



through phosphorus is the most common coordination mode. There are even phosphorus analogs of π-allyl complexes and phospha-ferrocenes. Numerous parallels have also been observed in the methods used to prepare P=C bonds, and this is the subject of the next section.

3
Phosphaalkenes: Background and Synthesis

A brief history of (3p-2p)π bonds between phosphorus and carbon followed by an introduction to the methods of phosphaalkene synthesis that are pertinent to this review will be provided. The earliest stable compound exhibiting (3p-2p)π bonding between phosphorus and carbon was the phosphamethine cyanine cation (**1**) [33]. An isolable substituted phosphabenzene (**2**) appeared just two years later [34]. The parent phosphabenzene (**3**) was later reported in 1971 [35]. These were remarkable achievements and, collectively, they played an important role in the downfall of the long held "double bond rule". The electronic delocalization of the phosphorus–carbon multiple bond in **1**–**3**, which gives rise to their stability, unfortunately prevented a thorough study of the chemistry and reactivity of the P=C bond.



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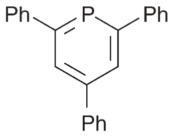

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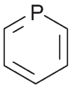
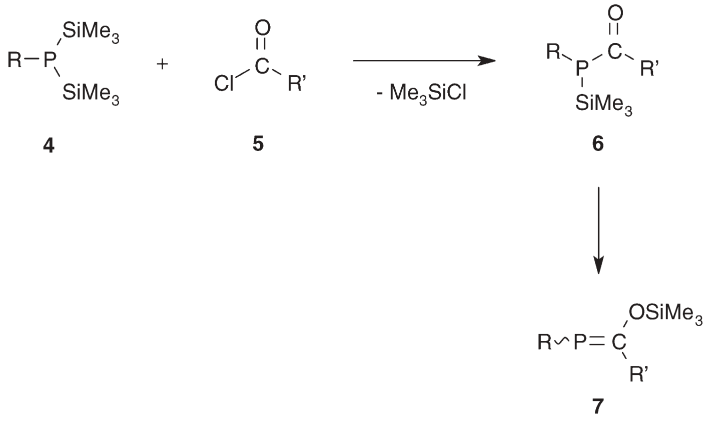
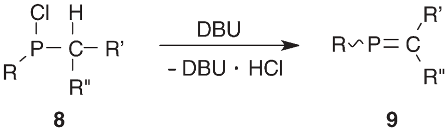


3

It wasn't until 1976, when G. Becker reported the first stable and isolable acyclic compounds featuring localized π-bonding between carbon and phosphorus (**7**: R=Me, ^{t}Bu, Cy, Ph; R′=^{t}Bu) [36], that detailed investigations of the chemistry of the P=C bond could be undertaken. This elegant reaction involves condensing a bis(trimethylsilyl)phosphine (**4**) with an acid chloride (**5**) to give an intermediate acylphosphine (**6**), which rearranges to the phosphaalkene (**7**), often isolated as a mixture of *E*- and *Z*- isomers. This 1,3-silatropic rearrangement is analogous to the keto-enol tautomerization observed in organic chemistry. However, in this case the phosphaalkene tautomer **7** (enol) is formed quantitatively because of the relative weakness of the P–Si bond in the acylphosphine **6** relative to the strong Si–O bond in **7**. From a preparative standpoint, this method is probably the most convenient and versatile route to phosphaalkenes with minimal steric protection [37–43]. The rearrangement reaction can also be exploited to prepare phosphaalkenes with α-positioned nitrogen or sulfur atoms.

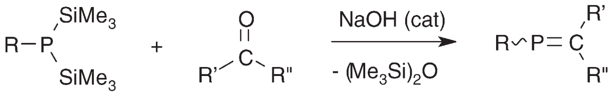


The first phosphaalkenes without heteroatom substituents (**9**, R=2,4,6-$Me_3C_6H_2$, 2,6-$Me_2C_6H_3$; R′=R″=Ph) were reported by Bickelhaupt and coworkers in 1978 [44]. The synthesis involved the base-induced dehydrohalogenation of **8**, and the P=C bond was stabilized by the sterically bulky substituents at phosphorus and carbon. A key observation, as it relates to this review, was that the attempted synthesis of phosphaalkenes bearing the 2-methylphenyl or phenyl group at phosphorus using the same strategy gave an uncharacterized product which was called "polymeric" material [44, 45].



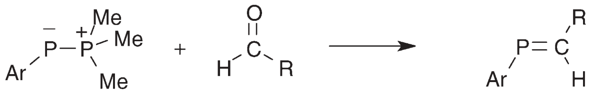
8 **9**

Another method that has been used to prepare phosphaalkenes is the phospha-Peterson reaction, a phosphorus analog of the Peterson olefination [46–49]. In this reaction a lithium silylphosphide is treated with an aldehyde or ketone to yield the phosphaalkene (**9**). Analogous reactions can be conducted with bis(trimethylsilyl)phosphines (**10**) and ketones (**11**) using a catalytic quantity of anhydrous base (i.e., NaOH, KOH) [50]. Generally, the reactions proceed cleanly and in high yield. Sufficiently bulky substituents must be employed to stabilize the P=C bond and prevent rapid dimerization to 1,3-diphosphetaines.



10 **11** **9**

The phosphorus analog of the Wittig reaction is another interesting route to phosphaalkenes [51]. This reaction involves treating a phosphoranylidenephosphine **12** (the "phospha-Wittig" reagent) with an aldehyde **13** and yields the corresponding phosphaalkene (*E*-**14**) in high yield. Initial work involved coordinating the phospha-Wittig reagent to transition metals [52]. Recently, it was discovered that reducing $ArPCl_2$ with Zn dust in the presence of excess PMe_3 affords free phospha-Wittig reagents (**12**) provided bulky *ortho*-substituted aryl groups (i.e., 2,6-dimesitylphenyl or Mes*=2,4,6-tri-*tert*-butylphenyl) are used [53]. Treatment of **12** with aldehyde generally affords the phosphaalkene with *E*-stereochemistry. This is a very convenient method of preparing phosphaalkenes with bulky substituents.



12 **13** *E*-**14**

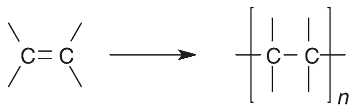
Numerous other reactions can be used to access phosphaalkenes. For example, treating the primary phosphine Mes*PH_2 with CH_2Cl_2 in the presence of KOH gives Mes*P=CH_2 [54]. In addition, interesting reactions of tantalum- or zirconium-phosphinidenes with aldehydes have afforded phosphaalkenes [55, 56]. The 1,3-hydrogen rearrangement of secondary vinylphosphines to phosphaalkenes has also been used to prepare phosphaalkenes [57, 58].

4

Addition Polymerization of P=C Bonds

The addition polymerization of olefins (**E**) is perhaps the most common method of polymer synthesis, and is an industrially important reaction for the C=C bond. Despite widespread interest in developing stable multiply bonded systems containing inorganic elements [59], addition polymerization has been limited primarily to C=C, and in some cases C=O, bonds. The possible extension of addition polymerization to other multiple bonds would provide access to novel macromolecules containing inorganic elements. The incorporation of inorganic elements into the backbone of linear macromolecules has attracted considerable attention due to the prospect of finding materials with novel properties and, therefore, possible specialty applications [60, 61]. However, the main barrier to the widespread development of inorganic polymers has been the lack of suitable methods for their preparation. In this regard, condensation and ring-opening polymerization methods have attracted the most attention and are viable routes to a variety of inorganic macromolecules. In contrast, addition polymerization has often been dismissed as a method to prepare inorganic polymers due to the lack of suitable multiply bonded monomers. Given the numerous examples discussed in Sects. 2 and 3, where the molecular chemistry of phosphaalkenes appears to copy that of olefins, it might be possible to extend addition polymerization to P=C bonds (**F**).

This section will provide details of recent efforts to polymerize phosphaalkenes. It will begin with an introduction to the factors that must be considered when attempting to polymerize P=C bonds. In addition, a historical context will be provided since, perhaps ironically, it was so-called polymerization reactions that plagued early efforts to prepare compounds possessing heavier element multiple bonds. Finally, it will close with the first successful polymerization of a P=C bond to give poly(methylenephosphine)s.



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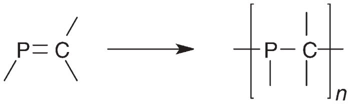


F

4.1

Enthalpy Considerations

The addition polymerization of carbon–carbon double bonds is driven by the thermodynamic favorability of forming two σ bonds in the polymer from a $\sigma+\pi$ bond in the monomer. A simple calculation based upon theoretically determined bond enthalpies for ethylene ($E_{\sigma+\pi}$=660 kJ mol^{-1}; E_{σ}=370 kJ mol^{-1} [62]) gives an enthalpy of polymerization (ΔH_p^o) of –80 kJ mol^{-1}. For phosphaethylene, a similar rough calculation based upon calculated bond dissociation energies ($E_{\sigma+\pi}$=482 kJ mol^{-1}; E_{σ}=276 kJ mol^{-1} [62]) gives a $\Delta H_p^o$of –70 kJ mol^{-1}. These calculations suggest that, at least on the basis of enthalpy considerations, it should be possible to polymerize P=C bonds. By extension, except for simple diatomics of the first row (i.e., N_2, O_2, etc.), it should be possible to prepare polymers from numerous multiple bonds of the p-block elements since most are thermodynamically unstable with respect to polymerization.

The exact enthalpy of polymerization for a particular monomer will depend on the steric and electronic effects imposed by the substituents attached to the E=E′ double bond. For olefins, resonance stabilization of the double bond and increased strain in the polymer due to substituent interactions are the most important factors governing ΔH_p^o. For example, propylene has a calculated $\Delta H_p^o$of –94.0 kJ mol^{-1}, whereas the polymerization of the bulkier 2-methylpropene is less exothermic (–78.2 kJ mol^{-1}) [63]. Due to resonance effects, the experimentally determined ΔH_p^o of styrene (–72.8 kJ mol^{-1}) is less exothermic than that for propylene, while that for bulkier α-methylstyrene is even less favorable (–33.5 kJ mol^{-1}) [63]. In general, bulky 1,2-disubstituted olefins (i.e., PhHC=CHPh) are either very difficult or impossible to polymerize.

Similar considerations must be made when choosing the appropriate monomers for polymerization studies of phosphaalkenes. The substituents on the P=C bond should be large enough to kinetically stabilize the starting material, but not large enough to make polymerization endothermic. The polymerization reaction must be exothermic since most addition polymerization reactions carry a large negative ΔS_p^o (i.e., –103.8 J K^{-1} mol^{-1} for styrene) [63].

4.2
"Polymerization" in Early Attempts to Isolate Compounds with Heavier Element Multiple Bonds?

"Polymerization" has often been mentioned as an undesired consequence in many early efforts to isolate heavier element analogs of common organic functionalities. A famous example is from Kipping's work, from which it was shown that "silicone" was in fact a polymer $[R_2SiO]_n$ and not the simple ketone analog "$R_2Si{=}O$" initially postulated [64]. Although $R_2Si{=}O$ is still unknown as a stable compound [65, 66], and does not factor into the formation of polysiloxanes by condensation, the common name for the polymer (silicone) has stuck. The lack of success in early attempts to prepare heavy element (p-p)π bonds led to their inclusion in Dasent's 1965 monograph entitled *Non-Existent Compounds*. This book alluded to polymerization as a common fate in failed attempts to prepare heavy element multiple bonds [67]. Experimental and theoretical studies of the instability of E=E′ bonds also led to the "classical double bond rule", which stated that elements of principle quantum number greater than two should not be able to form (p-p)π bonds with themselves or with other elements [68, 69].

In phosphorus chemistry, the association of multiple bonds with "polymerization" goes back to the proposed structure of "phosphobenzene" (PhP=PPh) isolated in 1877 by Köhler and Michaelis. This compound was later shown to be the cyclic oligomeric $(PhP)_n$ (n=5 or 6) [70]. Another example comes from Gier's breakthrough 1961 paper reporting the synthesis of HC≡P, the phosphorus analog of hydrogen cyanide [71]. Interestingly, he mentioned that "The monomer polymerizes slowly at –130 ° and more rapidly at –78 ° to a black solid" which analyzed as $(HCP)_x$ and was pyrophoric. Spontaneous polymerization of kinetically unstable phosphaalkynes has subsequently been mentioned numerous times [72–75]; however, the "polymers" have received little or no characterization. Recently, a deliberate attempt to polymerize PhC≡P showed that low molecular weight products (MS up to 1200 g mol^{-1}), primarily composed of saturated P–C rather than P=C bonds, were formed [76]. It is well-known that the kinetically stabilized phosphaalkyne $^tBuC{\equiv}P$ will undergo multiple cycloaddition reactions forming the fascinating tetraphosphacubane $(^tBuCP)_4$ [77] and more recently a hexamer [78]. Theoretical studies have provided evidence that open chain alternatives may be thermodynamically more stable [79]. Clearly, the possibility of polymerizing phosphaalkynes to high polymers is very exciting. Of particular interest is the linear polymer $(RC{=}P)_n$, which would be the phosphorus analog of poly(acetylene) and would likely possess exciting properties.

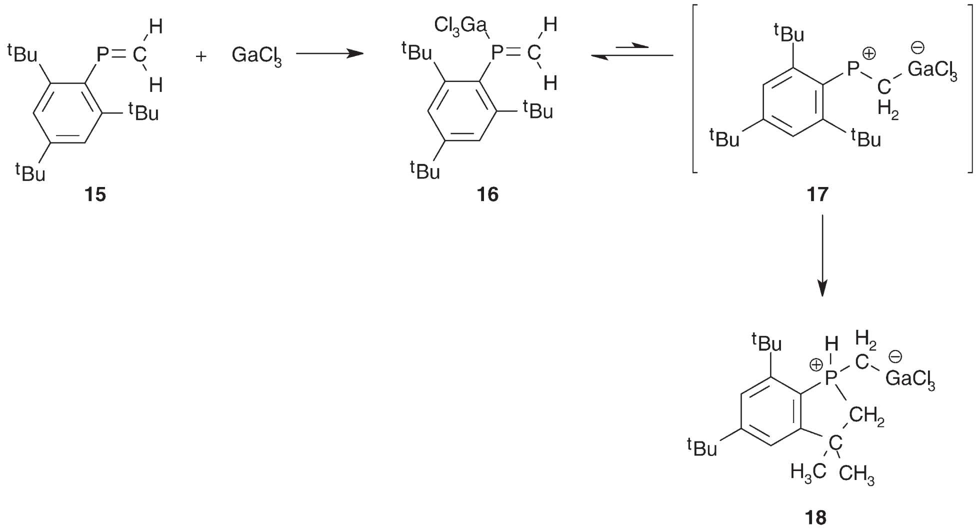
"Polymerization" has also been mentioned or alluded to in the preparation of kinetically unstable transient phosphaalkenes [27]. In their landmark paper on the first detection of unstable phosphaalkenes, including $HP{=}CH_2$, Hopkinson, Kroto, Nixon, and Simmons reported short half lives (1–2 min) for these species [80]. In later studies on the preparation of $HP{=}CH_2$, it was mentioned that the compound was not stable at 77 K in the solid state and forms a polymer of low solubility [81]. The generation of the transient phosphaalkenes $RP{=}C(H)CH_3$ (R=H, Me, Ph) by the base-induced rearrangement of $RP(H)CH{=}CH_2$, reportedly led to a "slow polymerization ... in the absence of chemical trapping agents" (R=H) [82]. The other phosphaalkenes (R=Me, Ph) were also unstable with "self-condensation" being the major decomposition pathway, however, the product(s) were not characterized. Similarly, in the thermal decomposition of phosphabicyclooctadienes ("masked phosphaalkenes"), in situ generated phosphaalkenes ($PhC{=}CH_2$ and $MeP{=}CH_2$) underwent "intermolecular reactions to give product mixtures ... consistent with tertiary phosphines as would arise from head-to-head or head-to-tail reactions" [83].

A common theme in the speculated "polymerization" reactions discussed in this section is that the "polymers" were generally uncharacterized or were composed of small cyclic oligomers. No evidence for high molecular weight polymers from low-coordinate phosphorus compounds was obtained. Of course, multiple bond formation, not polymerization, was the focus of these studies.

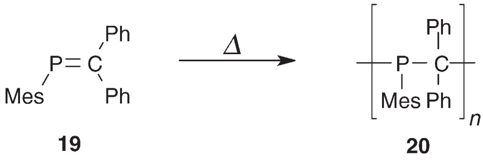
4.3
Poly(methylenephosphine)s

The problem with using the unstable species discussed in Section 4.2 as monomers for addition polymerization is that they are not like ethylene. They are not kinetically stable. It is the kinetic stability of olefins that makes them so useful as monomeric precursors to high molecular weight macromolecules. To mimic olefins, kinetically stable phosphaalkenes would be chosen as monomers. However, this is a balancing act, since for C=C bonds it is known that too much kinetic stability (i.e., employing very large substituents) leads to monomers that will not polymerize. Therefore, when my group began to investigate this area in 1999, we tried to copy carbon and study the reactions of potential polymerization initiators with kinetically stable phosphaalkenes possessing minimal steric protection.

Initial investigations were focused on phosphaalkene **15** containing the bulky supermesityl group, which is easily prepared from the reaction of Mes*PH_2 (Mes*=2,4,6-tri-*tert*-butylphenyl) and CH_2Cl_2 in the presence of KOH [54]. Compound **15** was chosen as a possible monomer for polymerization studies because large substituents would only be found on every second atom in the polymer. The stoichiometric reaction of **15** and $GaCl_3$, a potential cationic initiator, resulted in intramolecular C–H activation of the o-^{t}Bu group to afford coordinated ylid **18,** which was characterized crystallographically [84]. The adduct **16** was detected as an intermediate in the low temperature ^{31}P NMR spectrum of the reaction mixture. Evidence for the involvement of a transient phosphenium species **17**, the anticipated propagating species in a cationic polymerization, was obtained from labeling studies in analogous reactions with DOTf. To date, high molecular weight polymers have not been obtained from **15**.



In a separate study, a stable phosphaalkene **19** that was less likely to undergo intramolecular C–H activation was studied [85]. This monomer can be prepared using based induced dehydrochlorination [44] or following a phospha-Peterson route [50, 86]. If the monomer **19** is vacuum distilled to purify, in addition to the distilled product, a gummy material that solidifies upon cooling is obtained as a residue [85]. From this residue poly(methylenephosphine) **20** can be separated, which has a molecular weight (M_n) of 11,500 g mol^{-1} (PDI=1.25) by GPC (vs. polystyrene). The NMR spectra of **20** were consistent with a regioregular polymer resulting from head-to-tail enchainment. Polymer **20** is the first to contain a backbone of alternating phosphorus and carbon atoms. The polymer is stable in water-containing solutions however, solutions of the polymer are slowly oxidized under air atmosphere.



The presence of a phosphine in the main chain of polymer **20** provides numerous possibilities for chemical functionalization. Indeed, air- and moisture-stable poly(methylenephosphine oxide) **21** can be obtained on oxidation with air, or more conveniently, using H_2O_2 [85]. Reaction of **20** with elemental sulfur affords the phosphine sulfide polymer **22** and the phosphine-borane polymer **23** can be obtained after treating **20** with BH_3·THF (Fig. 2). It is also possible to functionalize the phosphine centers in **20** using several other well-established reactions of molecular phosphines [87]. In each reaction, there is no evidence for degradation of the polymer and the GPC molecular weights determined are virtually the same as those for **20**. Laser-light scattering results on **22** suggest that the GPC molecular weights (vs. polystyrene) underestimate the true molecular weight by roughly a factor of two [85]. Remarkably, the phosphine oxide poly-

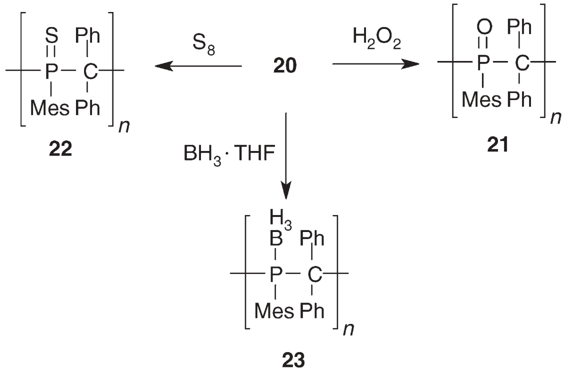
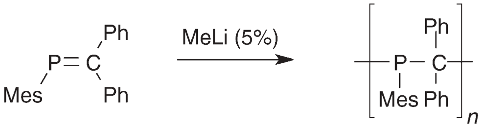


Fig. 2 Film of the poly(methylenephosphine oxide) **21**

mer **21** is quite thermally stable and shows no weight loss until 320 °C when analyzed using TGA.

The monomer **19** can also be polymerized using analogous methods of initiation to those employed in organic polymer science. Radical initiators afford regioirregular polymers, whereas anionic initiators add selectively to the phosphorus atom of the P=C bond and thus yield a regioregular polymer [85]. The product of the initial addition of MeLi across the P=C bond, Mes(Me)P-CPh_2Li, was identified spectroscopically. The polymers obtained from anionic initiation are spectroscopically identical to those obtained from the thermolysis. Reasonable molecular weights (ca. 5000–10,000 g mol^{-1}) are obtained when methyllithium is used as an initiator.



19 **20**

To a polymer chemist, it is perhaps surprising that a multiple bond containing three rather large substituents can be polymerized. In olefin chemistry, similar highly substituted olefins would not polymerize on the basis of the kinetic and thermodynamic factors discussed in Section 4.1. Using cyclodimerization as a model, the calculated enthalpies for substituted olefins suggest that the dimerization of Mes(H)C=C(H)Mes is slightly endothermic (+21 kJ mol^{-1}), whilst that for $Mes_2C=CMes_2$ is a whopping +2191 kJ mol^{-1} [88]. Therefore, why is phosphaalkene **19** polymerizable while olefins bearing similar substituents are not? One possible explanation is that the increased size of phosphorus with respect to carbon (P, r_{cov}=1.10 Å; C, r_{cov}=0.77 Å [89]) reduces steric interactions in the polymer. For comparison, high molecular weight peraryl polysilanes $[Ar_2Si]_n$ (Si, r_{cov}=1.18 Å) are common while the analogous peraryl polymethylenes $[Ar_2C]_n$ are unknown [90]. In addition to size, in poly(methylenephosphine)s the phosphorus atom only possesses one side-group rather than two in a polyolefin. This may leave room for phosphorus to accommodate larger substituents than are possible in analogous olefin polymers where there are two substituents at each carbon. Of course, theoretical studies of the energy parameters in the polymerization of **1** will need to be performed to either confirm or refute these hypotheses.

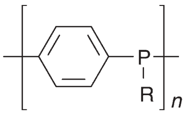
5
π-Conjugated Polymers Containing P=C Bonds

Polymers with π-conjugated backbones are an important class of materials that have captured the imagination of the scientific community due to their remarkable properties and exciting applications [91–95]. While most of the work on π-conjugated polymers has focused on all-carbon systems, there has been considerable interest in incorporating heteroatoms into the π-conjugated backbone (i.e., polythiophene, polypyrrole, polyaniline) to tune their properties.

5.1
Survey of π-Conjugated Phosphorus Polymers

In the past few years, there have been an increasing number of reports of π-conjugated polymers that incorporate phosphorus atoms into the main chain. For example, phosphorus analogs of polyaniline have been prepared. Low molecular weight poly(*p*-phenylenephosphine)s **24** can be prepared using a palladium-catalyzed condensation polymerization of 1,4-diiodobenzene and primary phosphines, while *p*-bromophenyl-substituted secondary phosphines afford higher molecular weight polymers [96, 97]. There has also been considerable interest in the development of poly(ferrocenylphosphine)s **25,** however, their possible π-conjugation has not been thoroughly investigated [98, 99]. It is also worth mentioning that novel emissive poly(vinylene arsine)s **26** have recently been prepared [100, 101], although, at present their phosphorus analogs are unknown.

To date, most of the research on π-conjugated phosphorus polymers has focused on incorporating phosphole units into the polymer backbone, by analogy with polypyrrole. For example, Tilley and coworkers have isolated the luminescent phosphole polymer **27** (R=$^nC_5H_{11}$) as an isomeric mixture after the skeletal replacement of a Cp_2Zr moiety by PhP in a pre-polymer that was prepared using a novel zirconocene diyne-coupling strategy [102]. Low optical band gap hybrid polyphosphole-polythiophene polymers **28** have been prepared by Réau and coworkers using electropolymerization [103, 104]. Recently,



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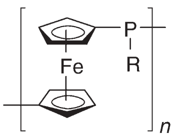

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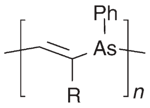

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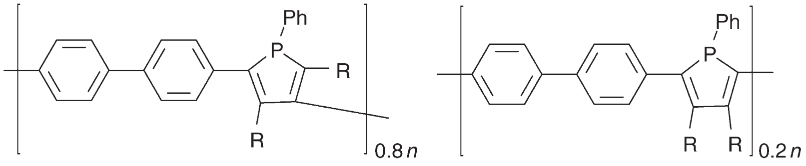

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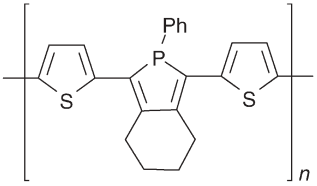

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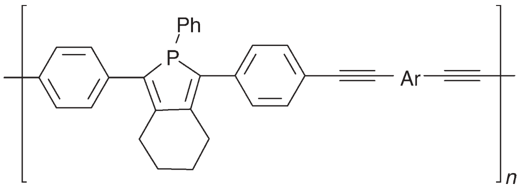
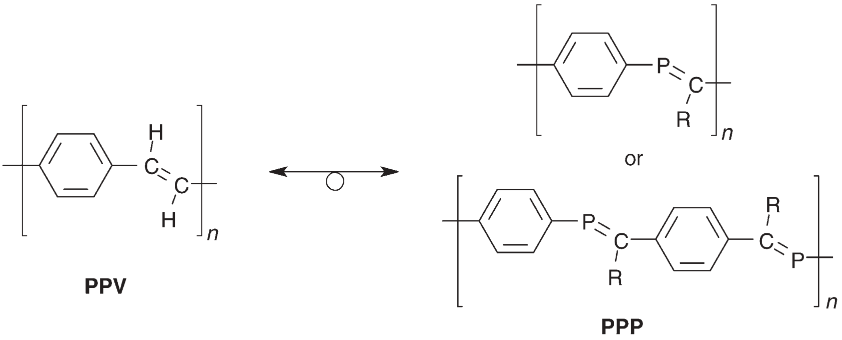


29

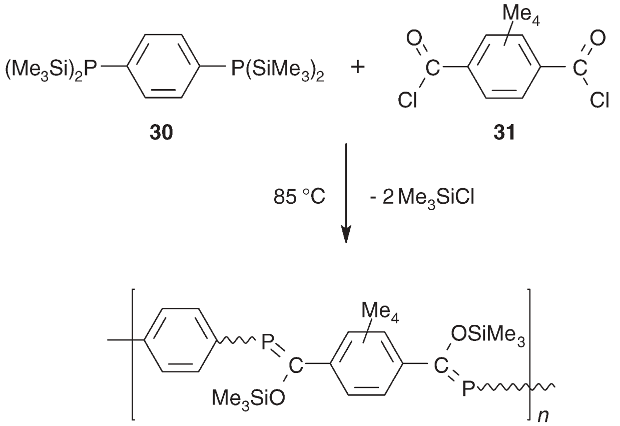
an exciting application for phosphole oligomers was reported with the development of the first phosphorus-based LEDs [105]. Chujo's group have recently reported the synthesis of the phosphole polymers **29** using the Heck–Sonogashira reaction [106]. An excellent recent review is available on π-conjugated molecular and polymeric systems containing Group 14 and 15 elements, in particular phospholes and siloles [107].

5.2
Poly(*p*-phenylenephosphaalkene)s

One of the most important π-conjugated organic polymers is poly(*p*-phenylenevinylene) **PPV**, which consists of a backbone of alternating phenylene and vinylene moieties [91–95]. Due to the isolobal relationship between P=C and C=C bonds, the possible replacement of the vinylene groups in **PPV** with phosphaalkene units might give a poly(*p*-phenylenephosphaalkene) **PPP** that possesses interesting electronic properties. The key challenge to making **PPP**s is to find suitable methods to assemble the alternating phenylene and phosphaalkene units into a linear polymeric structure. A step growth polymerization would require monomers of high purity and reactions that proceed with high conversions (>99%) to give reasonable molecular weights of **PPP**. Despite these possible problems, there have recently been several reports of the synthesis and characterization of **PPP**s.

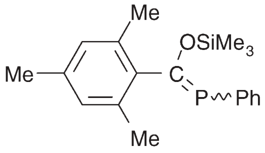


In 2002, the first example of a poly(*p*-phenylenephosphaalkene) **32** was prepared in our laboratory using condensation followed by 1,3-silatropic rearrangement to assemble the P=C bond [108]. The silylated diphosphinobenzene **30** was simply heated for ca. 1 day at 85 °C in the melt with diacid chloride **31**. The new π-conjugated PPV analog was soluble in polar organic solvents and the molecular weight was determined using end group analysis (M_n=2900–10,500 g mol^{-1}). This modest molecular weight corresponds to a degree of polymerization of 5–21. Heating for longer periods yields insoluble polymers, presumably arising from higher molecular weights or partial crosslinking.



32

UV-vis spectra of samples of **32** exhibit broad absorbances (λ_{max}=328–338 nm) that presumably result from a π-π* transition. For comparison, model mono- and bis-phosphaalkenes **33** and **34** were also prepared and their UV-vis spectra show broad absorbances at 310 and 314 nm, respectively. As expected, the polymer **32** is red-shifted with respect to these small molecule models. The red-shift is moderate (ca. 20 nm) when compared with the red shift observed with that for *trans*-PPV versus *trans*-stilbene (ca. 130 nm). More striking is the



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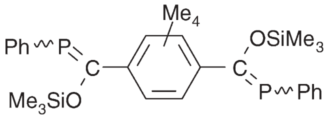

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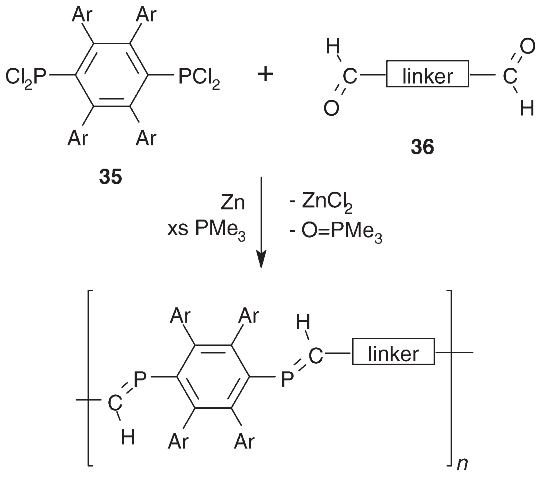
Fig. 3 THF solutions of monophosphaalkene (*left*) and poly(*p*-phenylenephosphaalkene) (*right*) at similar concentration

yellow color of polymer **32** compared to the colorless monophosphaalkene **33** (Fig. 3).

Recently, a second report by Protasiewicz and coworkers outlined an alternate synthesis of poly(*p*-phenylenephosphaalkene)s [109]. This approach used the phospha-Wittig route to assemble the P=C bonds. Insoluble PPPs **37** were obtained when with the bulky diphosphine **35** (Ar=4-^{t}BuC_6H_4) was treated with various dialdehydes **36** (linker=1,4-phenylene, 2,5-thienyl, 1,1′-ferrocenyl) in the presence of Zn and PMe_3. Using a *n*-hexyloxy-substituted 1,4-phenylene linker in the aldehyde afforded a soluble orange polymer **38**. The molecular weight (M_n) of **38** was estimated at 6500 g mol^{-1} using end group analysis. This corresponds to a degree of polymerization of 6.

Interestingly, the absorbance band maximum for the polymer **38** (λ_{max}= 445 nm), was identical to the model compound **39**. This suggests that the presence of the bulky 2,3,5,6-tetraaryl-substituted phenylene spacer might partially disrupt the π-conjugation. X-ray crystallographic data for the model compound **39** seems to support a moderate degree of π-conjugation [110]. For a fully conjugated system the phenylene and P=C bonds should be coplanar. In the solid-state structure of **39** the central phenylene unit is twisted by 71° out of the plane of the P=C moiety while the outer phenyl groups are only twisted by 22°.



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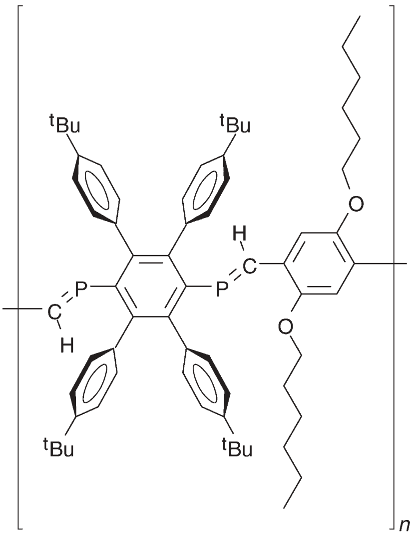
Remarkably, the polymer **38** showed fluorescent properties with an emission maxima at 545 nm and an efficiency of approximately 8% of that for *E*-stilbene [109]. This is the first time fluorescence has been reported for a **PPP**.



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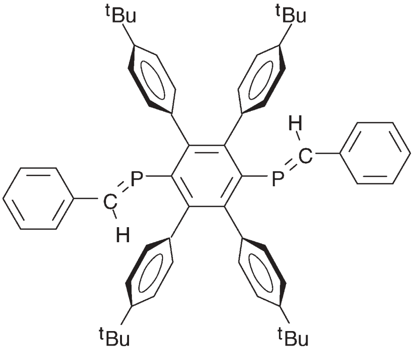

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As a final note, during the final stages of preparing this review the first example of a "diphosphene-PPV" was reported [111]. This exciting new polymer contains P=P bonds spaced by *p*-phenylenevinylene units in the main chain, has a degree of polymerization of approximately 6, and shows emissive properties.

6
Conclusion and Outlook

This review has shown that the analogy between P=C and C=C bonds can indeed be extended to polymer chemistry. Two of the most common uses for C=C bonds in polymer science have successfully been applied to P=C bonds. In particular, the addition polymerization of phosphaalkenes affords functional poly(methylenephosphine)s; the first examples of macromolecules with alternating phosphorus and carbon atoms. The chemical functionality of the phosphine center may lead to applications in areas such as polymer-supported catalysis. In addition, the first π-conjugated phosphorus analogs of poly(*p*-phenylenevinylene) have been prepared. Comparison of the electronic properties of the polymers with molecular model compounds is consistent with some degree of π-conjugation in the polymer backbone.

This new area of chemistry is still at a very early stage of development with most of the breakthroughs occurring in the last couple of years. The future holds promise for more exciting developments in the use of P=C bonds in polymer science and it is very possible that applications may be found for these new types of materials. In addition, an exciting prospect for the future is the further expansion of these methodologies, which are so common for C=C bonds, to other phosphorus-containing multiple bonds and other p-block elements.

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The Rise of Organophosphorus Derivatives in π-Conjugated Materials Chemistry

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Abstract This chapter concerns the synthesis and properties of π-conjugated oligomers and polymers containing phosphorus moieties, an area of increasing interest since the early 1990s. Emphasis is placed on the versatility engendered by the incorporation of phosphorus, especially with regard to tuning the photophysical and electronic characteristics of the new materials. This review also describes the first applications of these P-based materials in optoelectronics (nonlinear optics, organic light emitting diodes, *etc.*).

Keywords π-Conjugated systems · Phosphorus · Phosphaalkenes · Phospholes · Optoelectronics

Abbreviations

Alq$_3$	Aluminium tris(2-hydroxyquinolate)
β	Quadratic hyperpolarisability
DCJTB	4-(Dicyanomethylene)-2-tert-butyl-6 (1,1,7,7-tetramethyljulolidyl-9-enyl)-4H-pyran
DR1	Disperse red 1
Eg	HOMO-LUMO gap
EL	Electroluminescence
ITO	Indium-tin-oxide
NLO	Nonlinear optic
α-NPD	*N*′-Diphenyl-*N*, *N*′-bis(α-naphthyl)-1,1′-biphenyl-4,4′-diamine
OLED	Organic light emitting diode
PDI	Polydispersity index
PPV	*para*-Phenylene-vinylene
T_g	Glass transition temperature

1
Introduction

In the last decade, π-conjugated oligomers and polymers based on a backbone of sp^2-bonded carbon atoms have attracted huge interest owing to their potential application in electronic devices (e.g. light-emitting diodes, thin film transistors, photovoltaïc cells, laser dyes, NLO materials, etc.) [1]. These conjugated organic materials combine the advantages of being lightweight with ease of processing and offer the potential to have their optical and electronic properties tuned by exploiting the enormous versatility and scope of organic chemistry. Significantly, oligomers are not only model compounds used for elucidating the properties of the corresponding polymers, but can also themselves be used as advanced materials for devices (e.g. OLEDs, field effect transistors, etc.) [1].

The simplest organic π-conjugated polymer, polyacetylene (**A**) (Fig. 1) can exhibit conductivities in the metallic regime upon doping [2]. Following this seminal discovery in the 1970s, there has been intense research into the preparation of new linear-conjugated frameworks of increased robustness and enhanced performance. Aromatic building blocks have been widely used due both to their high stability and ease of substitution, allowing chemical engineering on the molecular scale. A prominent class of organic material of this type are

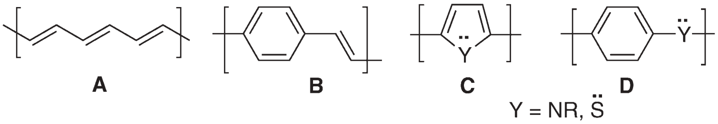


Fig. 1 Structure of classical organic π-conjugated systems

the poly(*p*-phenylenevinylene)s (**B**) (PPVs), which are probably nowadays the most studied π-conjugated systems [1]. The discovery in 1990 that PPVs are electroluminescent was a milestone in the field of molecular materials, with modified PPVs now being used commercially for the manufacture of OLEDs [3].

A related, but equally fruitful strategy for the preparation of new opto-electronic materials, involves the incorporation of heteroatoms into the backbone of conjugated polymers, with two general approaches being possible. The first involves the use of aromatic heterocyclopentadiene subunits, such as pyrrole or thiophene. Oligomers and polymers (**C**) (Fig. 1) are two important classes of conjugated systems offering a combination of novel electronic properties, excellent stabilities and structural diversity. Thiophene-based derivatives (**C**) are among the most widely investigated π-conjugated systems and have been used in numerous applications (e.g. electrical conductors, sensors, NLO materials, etc.) [1].

The second strategy is to replace the vinylene bridges of PPV (**B**) by a heteroatom possessing a lone pair that can participate in the π-conjugation [4]. Representative examples of this class of derivative (**D**) (Fig. 1) are the polyanilines and poly(*p*-phenylenesulfide) [1a,b].

Clearly, the development of new advanced organic materials is directly related to the ability of chemists to design and create novel structures and, subsequently, to establish structure–property relationships, with a view to further honing the desired attributes of the materials. It is now well recognised that the optical and electronic properties of macromolecules (**A**)–(**D**) vary significantly with both the magnitude of their HOMO-LUMO gaps and the electron density associated with their carbon backbones [1e–h, 5]. The most commonly used approach for tuning these two parameters consists of introducing pendent substituents with specific electronic and/or steric properties. However, derivatives (**C**) and (**D**) offer another unique tuning mode, which arises due to the presence of heteroatomic moieties in the main polymer backbone. This opens up the possibility of incorporating heteroatoms with different properties (such as electronegativity, polarisability, size of atoms and orbitals, energies of s and p valence orbitals, hybridisation, etc.), which allows materials engineering to be undertaken at the molecular level. Nitrogen and sulphur have been used extensively for such purposes. In marked contrast, phosphorus has received little attention until very recently. This is rather surprising, since organophosphorus derivatives offer a variety of structures and exhibit a versatile reactivity [6, 7].

This account will summarise results in the development of π-conjugated materials incorporating phosphorus moieties with emphasis on the conceptual design and specific properties that result directly from the presence of the P-atom. Polyphosphazenes, which are the most familiar synthetic polymers incorporating phosphorus [8], will not be included in this review since they do not display the type of π-conjugation as sought in systems (**A**)–(**D**).

2
Macromolecules Containing Phosphaalkene Moieties

The properties and reactivity of low-coordinate carbon and phosphorus species are very similar in many regards [6]. The P=C unit is almost apolar, and its conjugative properties are comparable to those of the C=C bond [6, 9]. Thus, using this diagonal analogy, the simplest π-conjugated system incorporating phosphorus that can be envisaged would be poly(phosphaalkyne) (**F**) (Fig. 2), the P-containing analogue of polyacetylene. Indeed, it has been established that phosphaalkynes (**E**) that lack sterically demanding R substituants (e.g. those bearing merely R=H, Ph) can undergo thermally induced polymerisation reactions [6, 7]. However, the resulting macromolecules feature mainly saturated trivalent P-fragments with only some phosphaalkene moieties [10]. In contrast, thermolysis of the more hindered *t*-BuC≡P affords a mixture of tetraphosphacubane and other cage compounds [6, 11a]. Alternatively, in the presence of metal complexes, several types of oligomer can be formed including 1,3,5-triphosphabenzene, tricyclic derivatives or cage compounds [6, 11b,c].

Kinetically stabilised 1,3-diphosphabutadienes are known [7, 12], but the formation of oligomers or polymers (**F**) (Fig. 2) is probably hampered by the quite low thermodynamic stability of the P=C π-bond (43 kcal mol^{-1} versus 65 kcal mol^{-1} for ethylene). Hence, by once again invoking the carbon-phosphorus analogy [6], incorporation of an aromatic aryl group into the backbone of the polymers appeared as a clear strategy for increasing the stability of these π-conjugated systems. Indeed, the first π-conjugated macromolecule containing phosphaalkene moieties was the PPV-analogue (**3**) (Scheme 1) [13]. This compound was prepared by thermolysis of bifunctional derivatives (**1**) and (**2**), a process involving thermodynamically favourable [1,3]-silatropic rearrangements of an intermediate acylphosphine to phosphaalkene moieties [7]. According to NMR measurements, macromolecule (**3**) is a mixture of *Z* and *E* isomers, with the degree of polymerisation varying from 5 to 21. Remarkably, thermogravimetric analysis revealed that this polymer is stable up to 190 °C under an atmosphere of dry helium [13].

The family of P=C-containing polymers was considerably broadened following the introduction of a highly efficient synthetic strategy based on intermediate "di-phosphaWittig" reagents [14]. Polymers (**6a–d**) featuring different linkers were readily obtained from aryl-substituted derivative (**5**) (Scheme 1) [15]. The soluble macromolecule (**6d**) contains an average of 12 phosphaalkene moieties per chain (n=6) in an *E*-configuration. Remarkably, although (**6d**) decomposes slowly in solution, it is stable under air for a week in the solid state [15].

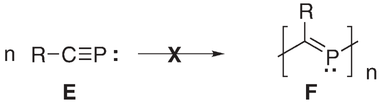
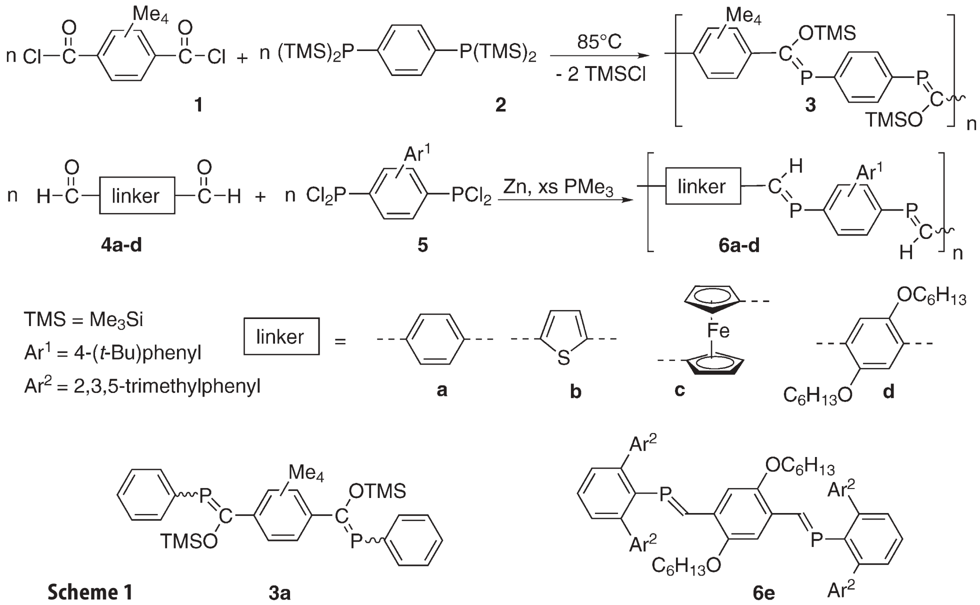


Fig. 2 Structure of poly(phosphaalkene)



Scheme 1

Derivatives (**3**) and (**6d**) (Scheme 1) exhibit broad absorption bands with values of λ_{max} of 328–338 nm and 445 nm, respectively. In both cases, these bands extend into the visible region with high optical end absorption, λ_{onset} ca. 400 nm for (**3**) and ca. 540 nm for (**6d**), revealing rather low optical HOMO-LUMO separations. These low energy transitions are not observed for model diphosphaalkenes (**3a**) and (**6e**) (Scheme 1) featuring the same substitution pattern [13, 15]. Together, these data are clearly in favour of extended π-conjugation involving the phosphaalkene moieties in oligomers (**3**) and (**6d**). Notably, (**6d**) showed fluorescence with broad emission centred around 530 nm [15]. However, the fluorescence intensity is weak compared to that of the corresponding all-carbon analogues.

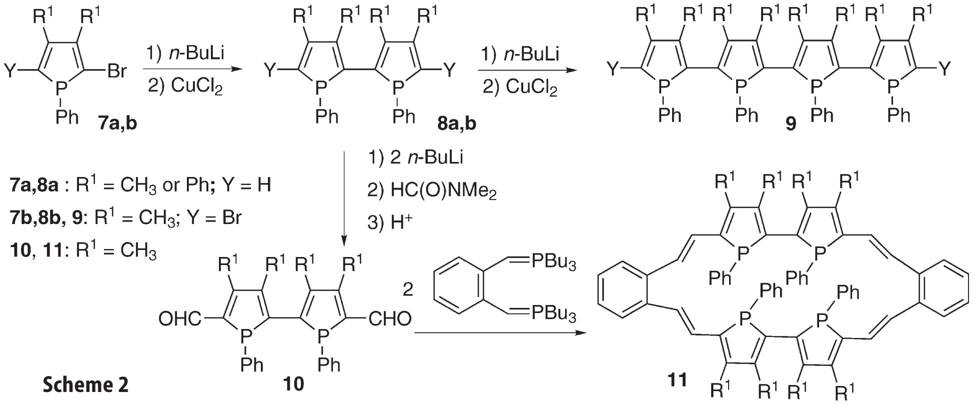
These preliminary results show that oligomers incorporating phosphaalkene moieties are readily available by different routes and suggest that the P=C units exhibit efficient conjugative ability. Although structure/property relationships have still to be established, it is clear that macromolecules of increased stability, higher degree of polymerisation and controlled chain length are exciting targets.

3
Macromolecules Containing Phosphole Rings

The extraordinary impact of thiophene and pyrrole derivatives for the engineering of π-conjugated materials, naturally led to the consideration of phospholes as potential building blocks. However, phosphole exhibits electronic properties that are markedly different from those of the highly aromatic thiophene and pyrrole rings [16]. The tricoordinate phosphorus atom of phosphole possesses a pyramidal geometry, with a lone pair having pronounced s-character. These geometric and electronic features prevent an efficient endocyclic conjugation of the electron-sextet. In fact, delocalisation within the phosphole ring arises from a hyperconjugation involving the exocyclic P-R σ-bond and the π-system of the dienic moiety [17]. The consequence, which was confirmed by experimental and theoretical studies [16], is that phosphole exhibits low aromatic character. This property, which sets phosphole apart from thiophene and pyrrole, may be of great interest for the tailoring of π-conjugated materials since conjugation is enhanced for macromolecules built from monomer units exhibiting low resonance energies [1h, 5a]. This phenomena is nicely illustrated by theoretical work that showed that the energy gaps *E*g of oligo(phosphole)s are significantly lower than those of the corresponding oligo(pyrrole)s (ΔEg=0.9–1.6 eV) or oligo(thiophene)s (ΔEg=0.5–0.8 eV) [5a, 18a].

3.1
Oligo(phosphole)s and Derivatives

Phospholes can readily be prepared on a large scale and are known with a vast range of substituants [6, 16b,c]. However, the synthesis of oligo(phosphole)s analogous to (**C**) (Fig. 1) is a real synthetic challenge since the low aromatic character of phosphole prevents the functionalisation of the P-Cα,α′ carbon atoms via electrophilic substitution and inhibits their preparation using electropolymerisation. As a consequence, no poly(phosphole)s have yet been reported, although bi- and tetra-phospholes have been prepared by stepwise routes (Scheme 2).



Scheme 2

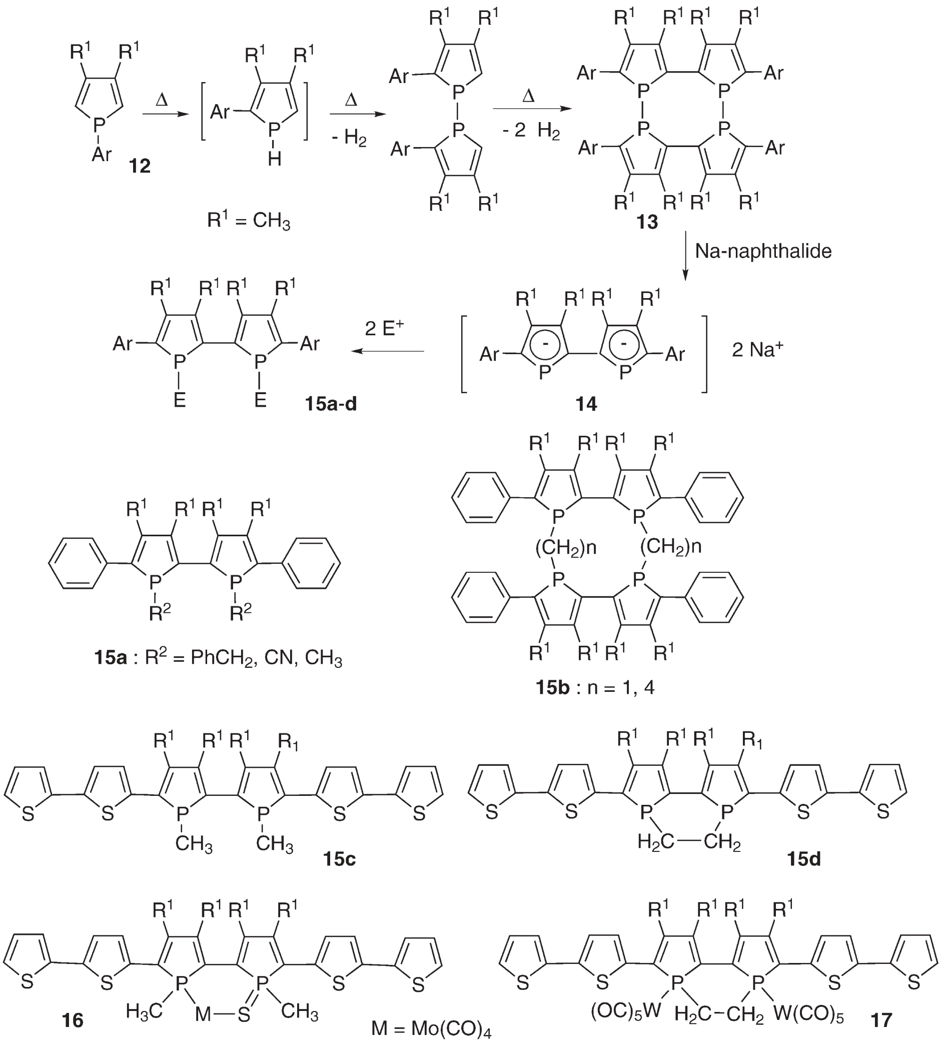
The discovery that the oxidative coupling of 2-lithiophosphole, obtained from (**7a**), led to biphosphole (**8a**) (Scheme 2) was a breakthrough [19], opening the way to oligo(phosphole)s. This very efficient methodology has been applied to the preparation of the quater(phosphole) (**9**), the longest oligo(phosphole) known to date, using bromo-capped biphosphole (**8b**) (Scheme 2) [20]. Di- and tetra-(phosphole)s are generally obtained as mixtures of diastereoisomers, due to the presence of stereogenic P-centres.

X-ray diffraction studies of (**8a**) (R^1=CH_3) and (**9**) revealed that these derivatives suffer from rotational disorder. The dihedral angle between the two phosphole rings in (**8a**) is about 46.6° [21], while in (**9**) the twist angle between the two inner rings is 25.1°, and that between the outer pair is 49.7° [20]. These distortions should preclude these oligo(phosphole)s from possessing extended π-conjugated systems. However, the twists are probably due to packing effects in the solid state since the colour of these compounds varies from pale yellow (**8a,b**) to deep orange (**9**), suggesting rather high λ_{max} values and, consequently, low optical HOMO-LUMO gaps. The red shift observed on going from (**8a,b**) to (**9**) hints that, in line with theoretical studies [5a, 18], the energy gap of oligo(phosphole)s seems to decrease with increasing chain length.

Bromo-capped biphosphole (**8b**) is also the precursor of cyclic derivatives, as illustrated by the synthesis of the fully unsaturated macrocycle (**11**), via a Wittig reaction involving the 5,5′-bis(carboxaldehyde) (**10**) (Scheme 2) [22]. An X-ray diffraction study revealed that macrocycle (**11**) is distorted, with an *all-trans*-disposition of the four P-phenyl substituants.

Other conjugated systems featuring biphosphole cores have also been prepared by an elegant and efficient method, which starts from the readily available 1-arylphospholes (**12**) (Scheme 3) [23]. Thermolysis of (**12**) yields the cyclic tetramer (**13**) via a series of concerted [1,5]-sigmatropic shifts of Ar, H and P, together with two dehydrogenation steps (Scheme 3). The reductive cleavage of the P-P bonds of (**13**) gives the 2,2′-biphospholide dianions (**14**), which act as bidentate nucleophiles towards a wide variety of electrophiles, allowing for the preparation of oligomers (**15a-d**) [23, 24]. Note that 2,2′-biphospholes lacking from substituent at the 5,5′-postions are also accessible via the dehydrohalogenation of the corresponding 1,1′-di(halogenophospholium) salts.

The versatility of this latter synthetic approach is underlined by the diversity of substituents that can be included on the P-ring (e.g. phenyl, dithienyl) and the secondary structures possible (namely linear or cyclic). Furthermore, the reactivity of the P-atom of the phosphole ring is retained in these compounds (**15a–d**), affording ready access to derivatives including those bearing transition metal fragments (**16**) and (**17**) [24]. Complexes (**16**) and (**17**) were obtained as single diastereoisomers and were studied by X-ray diffraction [24]. In both compounds, the bithienyl moieties are almost coplanar, the angles between the phosphole and the thiophene rings being rather small (15.2°–24.3°), while the phosphole-phosphole interplane twist angles are somewhat larger: 66.26±0.14° for (**16**) and 55.6±0.3° for (**17**). The lengths of the C–C links between the rings (1.42–1.47 Å) are in the range expected for Csp^2–Csp^2 single bonds. These data suggest a certain degree of delocalisation of the π-system over the six heterole rings, in spite of the rather large twist angles. This assumption is supported by an electrochemical study performed on the bis(thioxophosphole)



Scheme 3

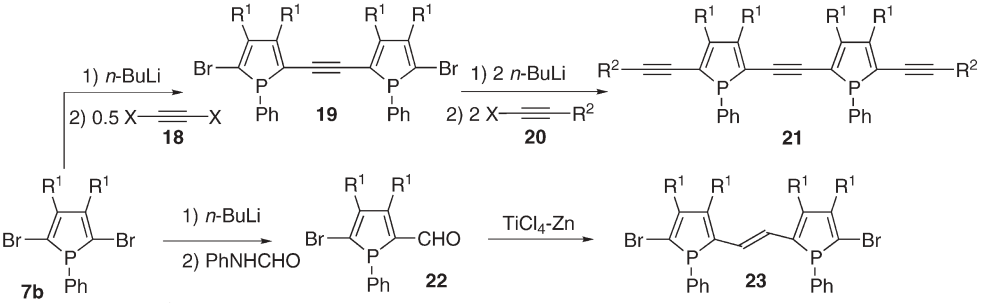
derivatives of (**15a**) and (**15c**), which revealed that the anion-radicals and dianions exhibit relatively good stabilities and that the nature of the 2,5-biphosphole substituents (phenyl versus bithienyl) has a profound influence on the electrochemical behaviour of these species [23c].

In conclusion, a variety of linear or cyclic oligo(phospholes)s and their derivatives are accessible via a set of efficient synthetic strategies. The potential of these compounds as advanced π-conjugated systems is broadened by the presence of reactive trivalent P-centres, which allow a range of additional chemical modifications to be achieved. However, elucidation of structure–property relationships for these derivatives is still needed.

3.2
Co-Oligomers and Derivatives

3.2.1
Phospholes Linked by All-Carbon Bridges

Macromolecules in which aromatic building blocks are linked by ethenyl or ethynyl bridges (e.g. PPV, oligo(thienylenevinylene)s [1h, 25], poly(*para*-phenyleneethynylene)s [26], etc.) are versatile molecular wires that have found numerous applications in the field of OLEDs, NLOs, sensors, polarisers for liquid crystal displays, etc. Surprisingly though, very few derivatives incorporating phosphole rings linked by a double or a triple bond have been reported to date. Initially, access to oligo(phospholyleneethynylene)s was hampered since 2,5-dibromophosphole (**7b**) (Scheme 4) and its iodo-bromo analogue were found not to undergo Stille-type couplings with 1-stannyl-alkynes [27]. Again, a route to the target co-oligomers was made possible using 2-lithiophospholes. Treating the intermediate 2-lithio-5-bromophosphole with (*tert*-butylsulfonylacetylene **18**) (Scheme 4) gave rise to derivative (**19**) that can be converted into (**21**) using the same synthetic strategy employing trimethylsilyl-protected alkyne (**20**) (Scheme 4). The modest yields of these reaction sequences (typically around 30%) precludes using this approach to prepare polymers starting from (**18**) and (**19**).



$R^1 = CH_3$ (**7b, 19, 21, 22, 23**) or Ph (**7b, 22, 23**)

18 : X = t-$BuSO_2$; **20** : $R^2 = SiMe_3$, X = p-$CH_3C_6H_4SO_2$

Scheme 4

Only the simplest oligo(phospholylenevinylidene), i.e. two phosphole rings linked by an ethenyl bridge, is known to date. The aldehyde (**22**) (Scheme 4), readily obtained from the corresponding 2-lithiophospholes, undergo McMurry coupling to afford the *E*-derivatives (**23**) in high yields [19b]. The efficiency of this synthetic route from (**7b**) to (**23**) underlines the robustness of the phosphole ring!

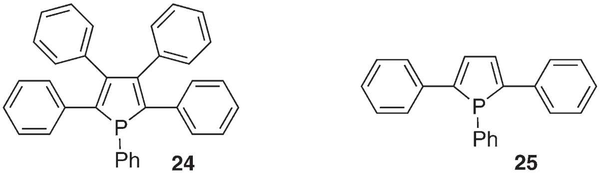
Notably, derivatives (**19**), (**21**) and (**23**) are all orange in colour, suggestive of the presence of an extended π-conjugated system [19b, 27]. This is supported by an X-ray diffraction study of 2,5-di-(phenylethynyl)phosphole, which revealed that the C–C linkages between the P-ring and the C≡C moieties are rather short, 1.423(3)–1.416(3) Å [27].

Thus, compounds (**19**), (**21**) and (**23**) are potential building blocks for the preparation of longer oligomers or polymers since they possess reactive termini. However, further progress towards longer oligomers or polymers is currently hampered by the low efficiency of coupling reactions involving phosphole rings.

3.2.2
Alternating Phosphole–Heterole Structures

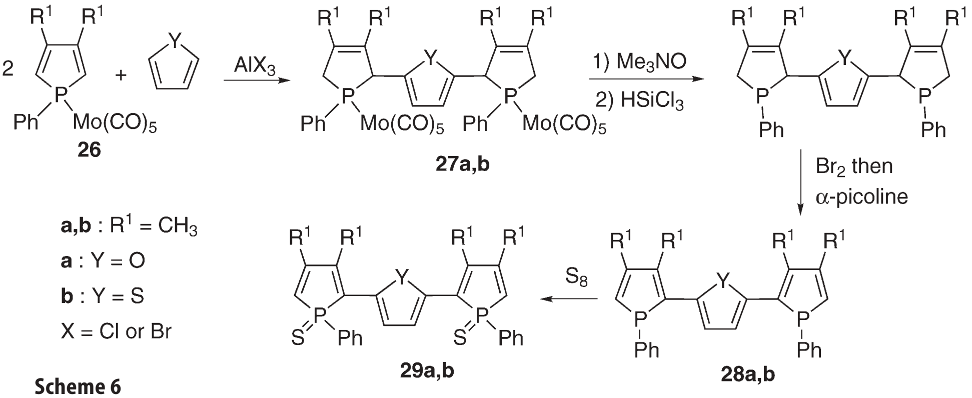
Amazingly, the 2,5-diphenylphospholes (**24**) and (**25**) (Scheme 5), which were the first phospholes to be prepared in the early sixties [28], exhibit extended π-conjugated systems. Both derivatives show absorption in the visible region, λ_{max} 358 nm for (**24**) and 374 nm for (**25**), and Stoke's shifts varying from 100 nm for (**24**) to 120 nm for (**25**) [29]. Furthermore, X-ray analysis of compound (**25**) revealed that the three rings are almost coplanar [30]. However, this important structural observation was not considered at that time. Consequently, the interest in the use of phospholes as building blocks for the construction of π-conjugated systems only dates from the 1990s.

Scheme 5



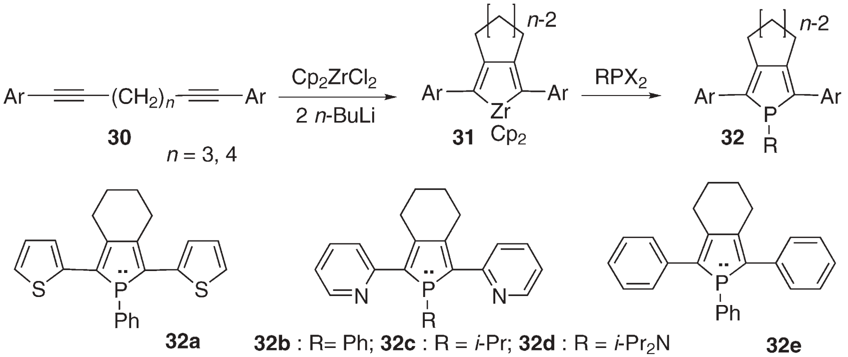
In 1991, Mathey et al. prepared a series of 2,5-(diphosphole)-thiophene and -furan oligomers (**28a,b**), and the corresponding thiooxo-derivatives (**29a,b**) (Scheme 6) [31]. The key step in their synthesis is an electrophilic substitution performed on the protected phosphole (**26**). Adducts (**27a,b**) [31] were then transformed into the σ^3,λ^3-phospholes (**28a,b**) through a classical deprotection–bromination–dehydrohalogenation sequence [32]. No UV-vis or electrochemical data are reported for these co-oligomers, however, the colour of the crystalline derivatives (**28a**) (orange) and (**28b**) (bright yellow), suggest relatively high values of λ_{max}. Note that an X-ray diffraction study of (**28b**) showed that one phosphole ring is coplanar with the central furan unit, while the second P-heterocycle is twisted (dihedral angle, 40.1±0.1°). The two inter-ring C–C bond distances, 1.452(4) and 1.461(6) Å, lie between those observed for C–C single and double bonds, a feature that is in favour of a certain degree of delocalisation [31].

The first systematic evaluation of the optical and electrochemical properties of phosphole-based co-oligomers, and subsequent optimisation of their struc-



Scheme 6

ture for optoelectronic applications, was undertaken with 2,5-di(heteroaryl)-phospholes (**32**) (Scheme 7). These compounds are not accessible by electrophilic substitution on protected phosphole (**26**) (Scheme 6), since this reaction gives rise to 2,4-dithienylphospholene [31]. However, they are readily prepared via a general organometallic route known as the Fagan–Nugent method [33].



Scheme 7

The key to obtaining the desired 2,5-substitution pattern is to perform the metal-mediated oxidative coupling of diynes (**30**) possessing a $(CH_2)_3$ or a $(CH_2)_4$ spacer (Scheme 7) [34, 35, 36, 37]. The zirconacyclopentadienes (**31**) are extremely air- and moisture-sensitive derivatives that react with dihalogenophosphines to give the corresponding phospholes (**32a–e**) in medium to good yields (Scheme 7). This route is highly flexible since it not only allows electron-deficient and electron-rich rings to be introduced in the 2,5-positions, but also permits the nature of the P-substituent to be varied. This is a crucial point in order to be able to fully elucidate the structure/property relationships for these new types of phosphole-based co-oligomers.

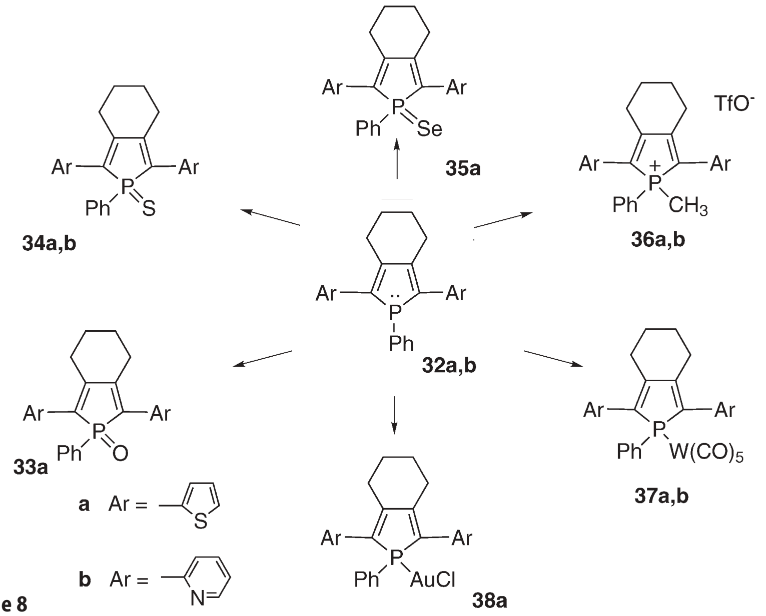
At the outset, it is interesting to note that the stability of derivatives (**32**) is directly related to the nature of the P-substituent. 1-Phenylphospholes are easily purified, air-stable solids, while the 1-alkyl- (**32c**) and 1-amino-phospholes (**32d**) (Scheme 7) are extremely air- and moisture-sensitive compounds. According to X-ray diffraction studies, the three heterocycles of σ^3,λ^3-phospholes (**32a**) [35] and (**32b**) [34] are almost coplanar, with the phosphorus atoms being strongly pyramidalised. For both compounds, the lengths of the C–C linkages between the rings are in the range expected for Csp^2–Csp^2 single bonds. These solid state data suggest a delocalisation of the π-system over the three heterocycles.

In solution, phospholes (**32a–e**) present broad absorptions in the visible region attributed to π-π* transitions [36]. The values of λ_{max} and the optical end absorption λ_{onset}, depend dramatically upon the nature of the 2,5-substituents of the phosphole ring [34, 35, 36]. An important red-shift was recorded on replacing the phenyl groups of (**32e**) either by 2-pyridyl (λ_{max}=36 nm) or 2-thienyl rings (λ_{max}=58 nm) [36]. These data suggest that the HOMO-LUMO gap gradually decreases in the series (**32e**)/(**32b**)/(**32a**), a feature that was confirmed by high-level theoretical calculations. The origin of these bathochromic shifts was initially interpreted in terms of intramolecular charge transfer that favours the delocalisation of the π-system [36]. The observation that the highest value of λ_{max}, i.e. the lowest HOMO-LUMO gap, was recorded for 2,5-dithienylphosphole (**32a**) was attributed to the fact that phospholes possess low-lying LUMO levels (high electron affinity), favouring charge-transfer from the electron-rich thienyl substituents. A recent study proposed that the more pronounced π-conjugation in (**32a**) was due to a better interaction between the HOMO of phosphole with the HOMO of thiophene, compared to that with pyridine [18e].

The optical data and theoretical studies show that the lowest HOMO-LUMO gap is achieved for (**32a**), structurally based on an alternating arrangement of thiophene and phosphole rings. The value of λ_{max} recorded for (**32a**) (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 very close to that of the 2,5-dithienyl-derivative based on a non-aromatic silole unit (420 nm) [38]. These results clearly establish that phospholes are excellent building blocks for the construction of π-conjugated co-oligomers exhibiting low HOMO-LUMO gaps.

Not only the absorption behaviour, but also all the physical properties of derivatives (**32**) are related to the nature of the 2,5-substitution pattern. For example, a blue-green emission is observed for di(2-pyridyl)phosphole (**32b**) whereas the emission of di(2-thienyl)phosphole (**32a**) is red-shifted ($\Delta\lambda_{em}$= 35 nm) [36]. Likewise, cyclic voltammetry (CV) revealed that derivative (**32a**), featuring electron-rich thienyl substituents, is more easily oxidised than compound (**32b**), which possesses electron-deficient pyridyl substituents [36].

In contrast to other heterocyclopentadienes (e.g. siloles and pyrroles), phospholes possess a reactive heteroatom. This feature allows direct access to a range



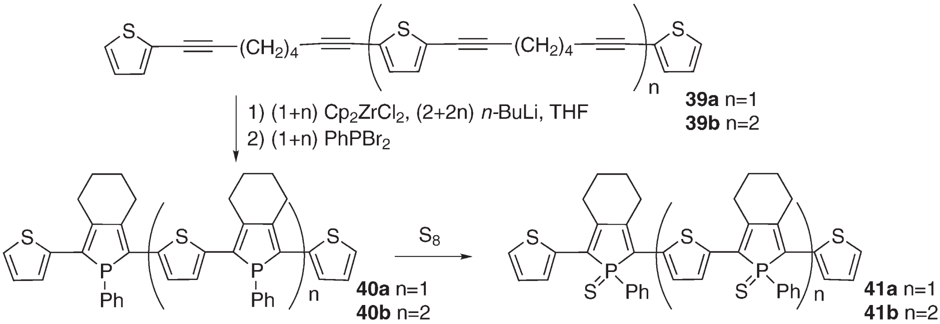
Scheme 8

of new π-conjugated systems (**33**)–(**38**) from single P-containing chromophores (**32a,b**), without the need for additional multi-step syntheses (Scheme 8). Significantly, these chemical modifications of the nucleophilic P-centres have a profound impact on the properties of the phosphole oligomers as a whole. Exploitation of this unique way of tailoring π-conjugated systems has led to the optimisation of the properties of thiophene-phosphole co-oligomers, which have subsequently been used as materials for OLEDs. Upon sublimation, phosphole (**32a**) decomposed while the more thermally stable thioxo-derivative (**34a**) formed homogeneous thin films on an indium-tin-oxide semi-transparent anode (ITO), allowing a simple layer OLED to be prepared [39]. This device exhibited yellow emission for a relatively low turn-on voltage of 2 V. The comparatively low maximum brightness (3613 cd m^{-2}) and electroluminescence (EL) quantum yields (0.16%) can be increased by nearly one order of magnitude using a more advanced device, in which the organic layer consisting of (**34a**) was sandwiched between hole- and electron-transporting layers (α-NPD and Alq_3, respectively). Upon doping the layer with the red-emitting dopant (DCJTB), the EL efficiency is further enhanced up to 1.83% with a maximum brightness of ca. 37,000 cd m^{-2} [39]. These results constitute the first examples of OLEDs based on π-organophosphorus materials.

In an extension to this work, the ligand behaviour of (**32a**) can be utilised in an innovative approach whereby metal complexes are investigated as materials for OLEDs. The Au(I) complex (**38a**) is thermally stable enough to give homogeneous thin films upon sublimation in high vacuum. The corresponding single layer device exhibited an EL emission covering the 480–800 nm domain

[39]; the low energy emissions are very probably due to aurophilic interactions in the solid state [40]. This work nicely illustrates the contribution of P-chemistry to the tuning of the optical properties of phosphole-based 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 [1e,h, 41]. Considering the interest in thiophene-phosphole (Th-Phos) derivatives as smart materials, the synthesis of yet longer, but still well-defined oligomers, has been investigated [42]. The Fagan–Nugent method allows for the preparation of oligomers (**40a,b**) (Scheme 9), in moderate yields, from the corresponding bis- and tris-diynes (**39a,b**). Compounds (**40a,b**), as well as their thiooxo-derivatives (**41a,b**), are obtained as air stable powders. They exist as a mixture of diastereoisomers due to the presence of stereogenic P-centres.

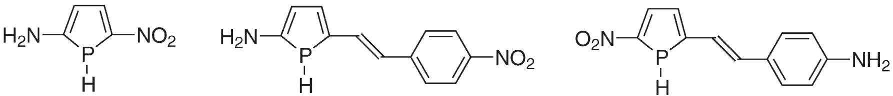


Scheme 9

The UV-vis spectra of Th-(Phos-Th)$_2$ (**40a**) revealed a λ_{max} (490 nm) considerably higher than that recorded for quinquethiophenes (ca. 418 nm) [43]. Thus, as observed for the model molecule (**32a**), replacing a thiophene subunit by a phosphole ring induces an important decrease in the optical HOMO-LUMO gap. It is also noteworthy that oxidation of the P-atoms of (**40a**) induces a bathochromic shift in the value of λ_{max} [42]. A similar trend has been observed with the shorter oligomers (**32a**), hence it seems a general feature that oligo(α,α′-thiophene-phosphole)s incorporating σ^4-P rings have smaller HOMO-LUMO gaps relative to those based on σ^3-P rings. The absorption maxima (λ_{max}), as well as the longest wavelength absorption (λ_{onset}) regularly shift to lower energy as the extent of the π-conjugated path increases [42]. Chain extension also leads to a decrease in their oxidation potentials and an increase of their reduction potentials. These data clearly showed a lowering of the HOMO-LUMO gap upon increasing the chain length of the α,α′-(thiophene-phosphole) oligomers. It is thus likely that the saturation of the effective conjugation has not been reached with oligomer (**41b**) containing seven rings. This result, along with the good stability and solubility of Th-(Phos-Th)$_{2,3}$, should encourage the search for new pathways to longer oligomers with alternating thiophene and phosphole subunits.

3.2.3
Miscellaneous Structures

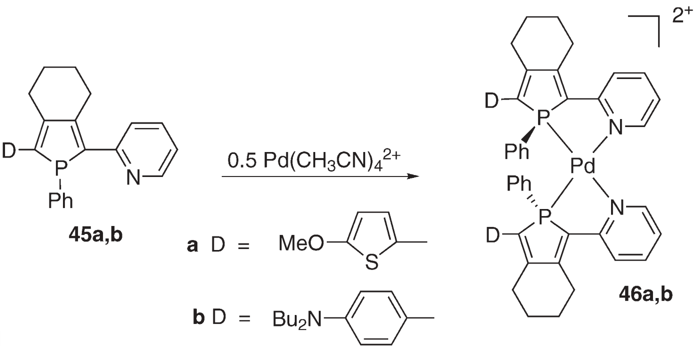
The fact that phospholes can act as ligands toward transition metals has considerably expanded the potential of phosphole-based derivatives for further development as OLEDs. The situation is very similar in the field of NLO materials. The archetypical NLO-phores can be represented as *D*-(π-bridge)-*A*, where *D* and *A* are donor and acceptor groups, respectively [44]. Theoretical studies have suggested that phospholes can act as efficient (π-bridges) for the engineering of NLO-phores [16f, 5b]. The NLO response of donor/acceptor-substituted phosphole (**42**) (Scheme 10) (β_x=6.17×10^{-30} e.s.u.) was computed to be significantly greater than that of related derivatives featuring a pyrrole (β_x=5.59×10^{-30} e.s.u.), a thiophene (β_x=5.49×10^{-30} e.s.u.) or a cyclopentadiene (β_x=6.04×10^{-30} e.s.u.) central ring [5b]. This trend was attributed to the low aromatic character of phosphole compared to that of either the pyrrole or thiophene rings. However, the electronic density (i.e. the excess/deficiency of electrons) associated with the π-bridge has also been shown to play a crucial role. According to theoretical calculations, chromophores (**43**) and (**44**) (Scheme 10) having stilbene-like bridges in which one phenyl is replaced by a phosphole ring, also exhibit good NLO responses [5b]. As expected from the quite high electronic density found on the α-P carbon atoms [5b], the highest NLO activity is observed for derivative (**44**) having a donor NH_2 substituent on the phosphole ring.



42 **43** **44**

Scheme 10

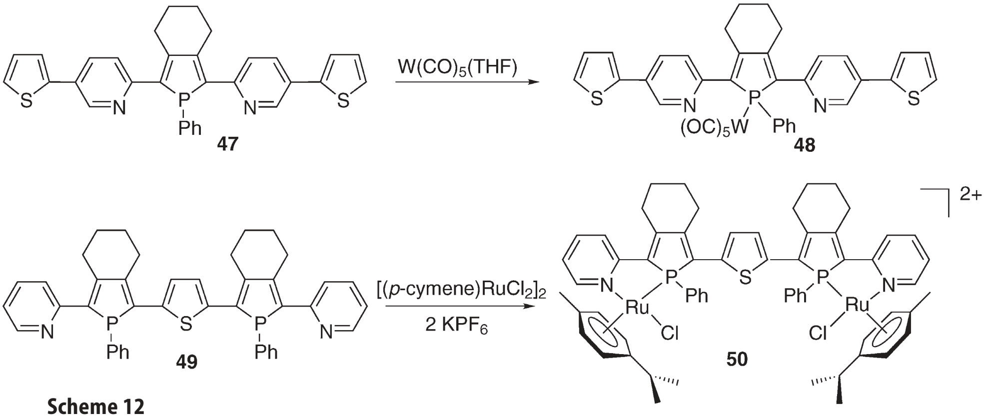
Phospholes (**45a**) and (**45b**) (Scheme 11), which bear an electron-deficient pyridine group and a classical electron-donor group at the 2- and 5-positions, respectively, exhibit moderate NLO activities ($\beta_{1.9\ \mu m,}$ ca. 30×10^{-30} e.s.u.) compared to classical chromophores such as DR1 ($\beta_{0,}$ 50×10^{-30} e.s.u.) [45]. These low values are consistent with the weak acceptor character of the pyridine group. However, the potential of dipoles (**45a**) and (**45b**) in NLO is considerably increased by their P,N-chelate behaviour towards d^8 metal centres such as Pd(II) [37, 46]. 2-(2-Pyridyl)phospholes (**45a,b**) react with $[Pd(CH_3CN)_4][BF_4]_2$ to afford the corresponding complexes (**46a,b**) (Scheme 11). In accordance with the *trans-influence* [47], heteroditopic P,N-dipoles (**45a,b**) undergo a stereoselective coordination leading to a close parallel alignment of the dipoles on the square-planar d^8 palladium template. Thus, the *trans-influence* can overcome the natural anti-parallel alignment tendency of dipolar chromophores at the molecular level. Furthermore, complexes (**46a,b**) exhibit high NLO activities ($\beta_{1.9\ \mu m}$, ca. 170–180×10^{-30} e.s.u), which are much higher than the sum of the



Scheme 11

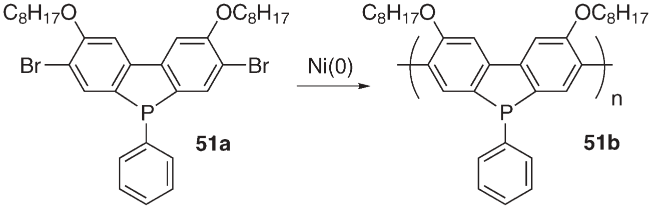
contributions of the two sub-chromophores (**45a,b**) [45]. The augmentation of the NLO activity upon coordination is probably due to the onset of ligand-to-metal-to-ligand charge transfer that contributes coherently to the second harmonic generation.

Other types of π-conjugated systems incorporating pyridylphosphole moieties have been prepared with a view to establishing structure–property relationships (derivative (**47**), Scheme 12) or to study the photophysical properties of dinuclear transition metal complexes containing bridging π-conjugated ligands (derivative (**49**), Scheme 12). As expected, derivative (**47**) exhibits a value of λ_{max} that has been red-shifted compared to the simple di(2-pyridyl)-phosphole (**32b**) ($\Delta\lambda_{max}$=37 nm). An X-ray diffraction study of the corresponding complex (**48**) showed that the five heterocycles are almost coplanar with twist angles ranging from 1.8(16)° to 18.3(17)° [35]. Dinuclear transition metal complexes (**50**), containing bridging π-conjugated ligands based on two terminal 2-pyridylphosphole moieties bridged by a thiophene ring, are readily obtained from (**49**) (Scheme 12) [48]. Coordination of chromophore (**49**) to ruthenium centres has been shown to have only a marginal influence on the π-π* transition of the extended conjugated system [48].



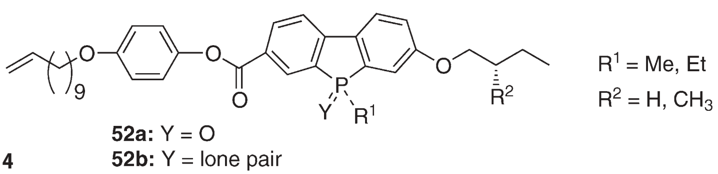
Scheme 12

Dibenzophosphole was the first phosphole to be prepared [49], and the related fused dithienophosphole derivative (**54**) (Scheme 15) is also known [50]. It is important to note that these benzo-annulated derivatives do not exhibit the typical electronic properties and reactivity pattern of phospholes, since the dienic system is engaged in the delocalised benzene or thiophene sextet [6b, 16]. Dibenzophospholes have only very recently been used as building blocks for the preparation of π-conjugated systems (**51b**) (Scheme 13) relevant to OLED applications [51]. This polymer (**51b**), prepared by Ni-catalysed coupling of derivative (**51a**) (Scheme 13), is obtained with a high polydispersity (M_n=5×10^2, M_w=6.2×10^3). Interestingly, this macromolecule is photoluminescent in the solid state with a λ_{em} of 516 nm [51].



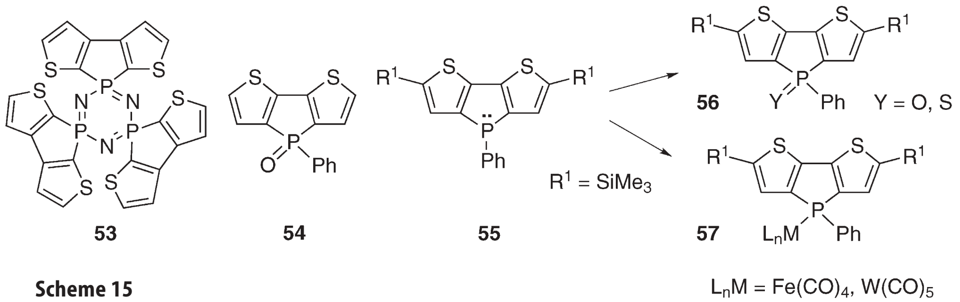
Scheme 13

P-chiral dibenzophosphole oxide (**52a**) (Scheme 14) shows liquid crystalline behaviour [52], a property that is of interest in the area of electro-optical displays [53]. Chiral resolution of (**52a**) was achieved by column chromatographic separation of the diastereoisomers obtained following coordination of the σ^3-benzophosphole (**52b**) to chiral cyclometallated palladium(II) complexes [52]. Notably, the presence of a stereogenic P-centre is sufficient to generate a chiral cholesteric phase.



Scheme 14

Two types of symmetric fused dithienophospholes exist, which differ according to the position of the S atoms as illustrated by compounds (**53**) [54] and (**54**) [50] (Scheme 15). The σ^3,λ^3-dithieno[3,2-*b*:2′,3′-*d*]phosphole (**55**) has recently been considered as a potential subunit for the construction of π-conjugated materials [55] (Scheme 15). Exploitation of the reactivity of the nucleophilic P-atom of (**55**) allows access to derivatives (**56**) and complexes (**57**) (Scheme 15). The absorption and emission behaviour of these species varies with the nature of the P-moieties. Upon oxidation of the P-centre of (**55**), bathochromic shifts of λ_{max} and λ_{em} were observed: λ_{max} 344 nm for (**55**) and ca. 373 nm for (**56**), and λ_{em} 422 nm for (**55**) and ca. 460 nm for (**56**) [55]. These results nicely illustrate

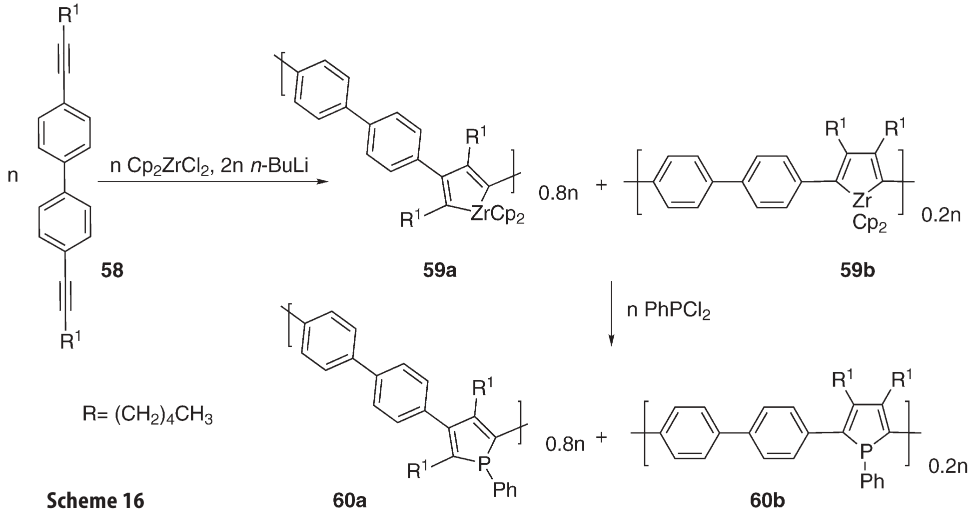


Scheme 15

how the tuning of the optical properties of these chromophores can be achieved via modifications at phosphorus.

3.3
Copolymers

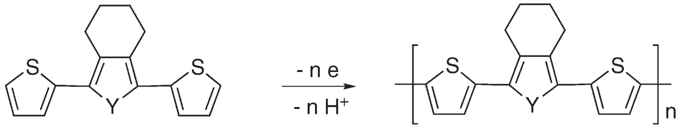
Although, to date, no homo-polymers based on phosphole are known, three types of copolymer incorporating phosphole rings have been prepared. The first type, (**60a,b**) (Scheme 16), has been described by Don Tilley and co-workers [56]. These macromolecules were obtained as an 80/20 isomeric mixture of 2,4- and 2,5-connected phospholes by zirconocene-coupling of rigid diynes (**58**), affording intermediate complexes (**59a,b**) (Scheme 16) [56]. The biphenylphospholyl polymers were isolated as air stable, soluble powders exhibiting rather high molecular weights (M_w=16,000, M_n=6200) according to GPC analysis. Although multinuclear NMR spectroscopy and elemental analysis support the proposed structures, the presence of a small number of diene units cannot be ruled out [56]. The polymer mixture (**60a,b**) exhibits an absorption maxima



Scheme 16

in its UV-vis spectrum at 308 nm with a λ_{onset} of 400 nm. These values are consistent with a relatively high band gap, probably due to a preponderance of cross-conjugated segments [56]. Polymers (**60a**,**b**) exhibit interesting photoluminescence properties with emissions in the bluish-green region associated with large Stokes shifts of 162 nm.

A second type of phosphole-containing π-conjugated copolymer was obtained by electropolymerisation of thienyl-capped monomers [35, 36], which involves the generation and coupling of radical cations [57]. The major coupling process should induce α,α′-linkages, but the formation of some 2,4-linkages that disrupt the conjugation can also take place. Insoluble and electro-active materials (**61**) (Scheme 17) were obtained on the working Pt electrode with 2,5-(dithienyl)phosphole monomers featuring σ^3,λ^3-, σ^4,λ^4- and σ^4,λ^5-P moieties (Scheme 17) [35, 36]. Polymers (**61**) were amenable to p- and n-doping processes with good reversibility. Absorption spectra of the de-doped polymers showed that the values of λ_{onset} were considerably red-shifted compared with those observed for the corresponding monomers (**32a**)–(**36a**) (Scheme 17, Table 1) [36]. These data suggest that the electro-active materials formed on the electrode possess rather long conjugation pathways. A remarkable feature is that the electrochemical (doping range) and optical properties (λ_{max}, λ_{onset}) of these materials obtained by electropolymerisation depend on the nature of the phosphorus moiety (Scheme 17, Table 1), exactly as was observed for the P-containing monomers (**32a**)–(**36a**).



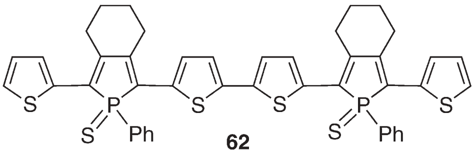
32a-36a **61**

Scheme 17

Table 1

	Y	λ_{max}	λ_{onset}		λ_{max}	λ_{onset}
32a	PPh	434	500	poly(**32a**)	463–567	724
33a	P(O)Ph	432	496	poly(**33a**)	568	780
34a	P(S)Ph	423	503	poly(**34a**)	529	754
36a	P⁺MePh	442	528	poly(**36a**)	627	905

It is difficult to establish the degree of polymerisation of materials (**61**) due to their insolubility, which prevents GPC analysis and standard spectroscopic studies. The important bathochromic shift of the λ_{onset} observed in the series: (**34a**) (496 nm)/(**62**) (600 nm) (Scheme 18)/poly(**34a**) (754 nm), suggests that (**61**) are oligomers. Note that electropolymerisation of monomers (**40a**) and



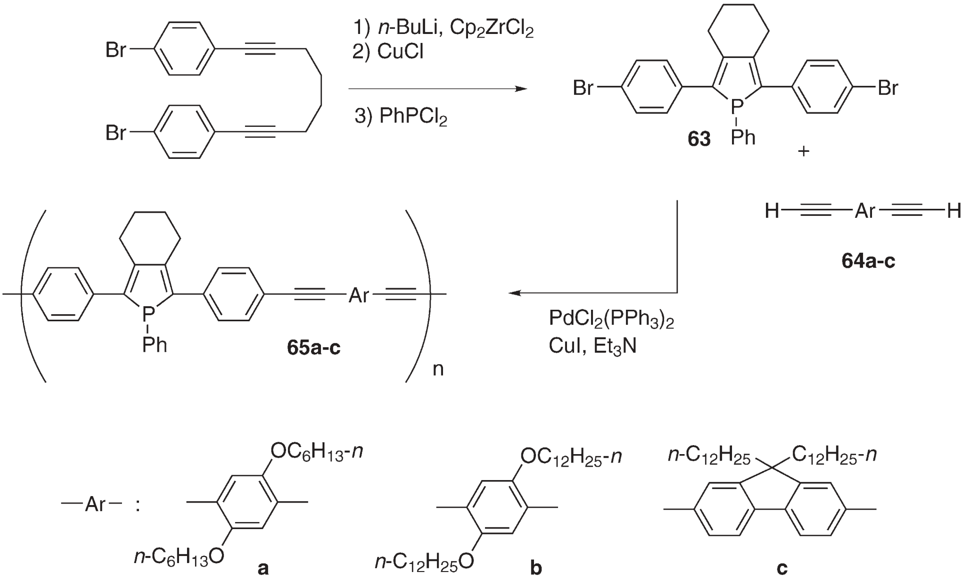
62

Scheme 18

(**41a**) (Scheme 9) also leads to electro-active materials presenting almost reversible p-doping behaviour [42].

The first well-defined π-conjugated polymer having a phosphole ring in a repeating unit was obtained by Chujo et al., using the Heck-Sonogashira coupling of (**63**) with the co-monomers (**64a–c**) (Scheme 19) [58]. Note that the preparation of 2,5-(diaryl)-phosphole of type (**63**) according to the Cu-modified Fagan–Nugent method (Scheme 19) was recently patented [59]. Macromolecules featuring free σ^3,λ^3-P centres (**65a–c**) are isolated in moderate to low yields as soluble powders. They are air-stable in the solid state and their degree of polymerisation ranges from 15, for (**65a**), to 7 for (**65c**). The UV-vis absorptions of (**65a–c**) are red-shifted in comparison to that of 2,5-diphenylphosphole (**32e**) (Scheme 7), indicating an effective extension of the π-conjugation. The emission properties of these macromolecules can be tuned by varying the nature of the co-monomer, green and blue emission are observed with polymers (**65a,b**) and (**65c**), respectively [58].

Polymers incorporating phosphole subunits are still very rare. However, the pioneering work described in this section shows that such macromolecules are



Scheme 19

accessible via diverse synthetic routes, and that they exhibit quite good stability as well as valuable optical and electrochemical properties.

4
Macromolecules Containing Phosphine Moieties

Over the last decade, poly(*p*-phenylenevinylene)s and related materials have found a place amongst the most industrially significant materials for the preparation of OLED-type devices [1, 60]. Since replacing carbon moieties by heteroelements as constituents of the primary polymer backbone has proved an excellent means of tuning the materials' opto-electronic properties, it is unsurprising that phosphorus-containing analogues of PPV and related macromolecules have been prepared and investigated.

4.1
Poly(*p*-Phenylenephosphine)s

Redox active polyanilines (**D′**) (Fig. 3), in which the heteroatom participates in π-conjugation by virtue of its lone pair, are amongst the oldest and best known photochromic materials, often prepared by galvostatic polymerisation of aqueous HCl solutions of anilines [61]. More recently, polymer (**D′**) has been prepared via metal-mediated C–N bond formation from aryl-halides or -triflates with amines, affording N-substituted polyanilines [62] and oligoanilines [63]. Despite the prevalence of such polymers containing nitrogen, the corresponding poly(*para*-phenylenephosphine)s (**D″**) that possess main chain σ^3,λ^3-phosphorus centres have appeared only recently.

By analogy with modern routes for the preparation of well-defined polyanilines (**D′**), palladium-catalysed cross coupling of 1,4-diiodobenzene and primary aryl- and alkyl-phosphines affords the comparatively short chain polymers (**66a–c**) (M_n=1000–4000) (Scheme 20), that can be oxidised either by atmospheric

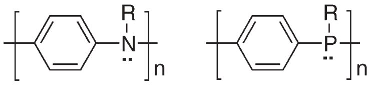
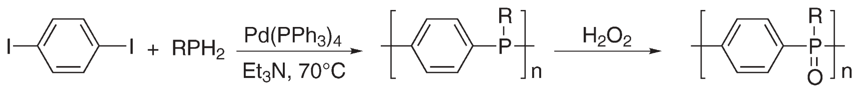

D' **D"**

Fig. 3 Structure of polyanilines and poly(*para*-phenylenephosphine)s



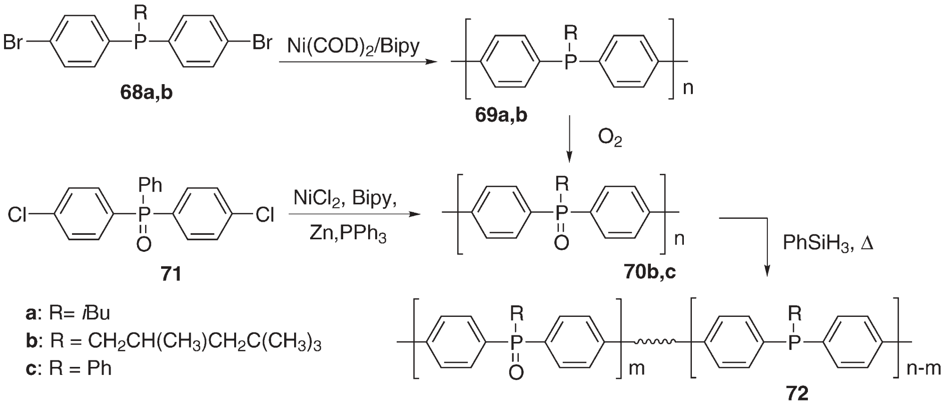
66a-c **67a-c**

Scheme 20

a : R = $CH_2CH(CH_3)_2$ (n = 10)
b : R = Ph (n = 7)
c : R = $CH_2CH(CH_3)CH_2C(CH_3)_3$ (n = 14)

oxygen or by H_2O_2 to afford derivatives (**67a–c**) [64]. Soluble materials (**66a–c**) are formed with narrow polydispersities (PDI=1.3–1.5) and are amenable to characterisation by GPC and multinuclear NMR spectroscopy. The UV-vis spectra of polymers (**66a–c**) show absorption values attributed to π-π* transitions with λ_{max} ranging between 276 and 291 nm [64]. These rather low values are probably due to the fact that the P-atoms of these polymers retain a tetrahedral geometry that prevents efficient conjugation of the phosphorus lone pair with the aryl groups. However, the bathochromic shift observed on going from triphenylphosphine (λ_{max}=263 nm) to 1,4-diphenylphosphinobenzene (λ_{max}=275 nm) and then to (**66b**) (λ_{max}=291 nm) is supportive of the presence of some extended π-delocalisation for the latter. Contrastingly, the oxidised materials (**67a–c**) exhibit a number of new absorption bands and all display a shift in λ_{onset} from 520 (unoxidised) to 800 nm (oxidised).

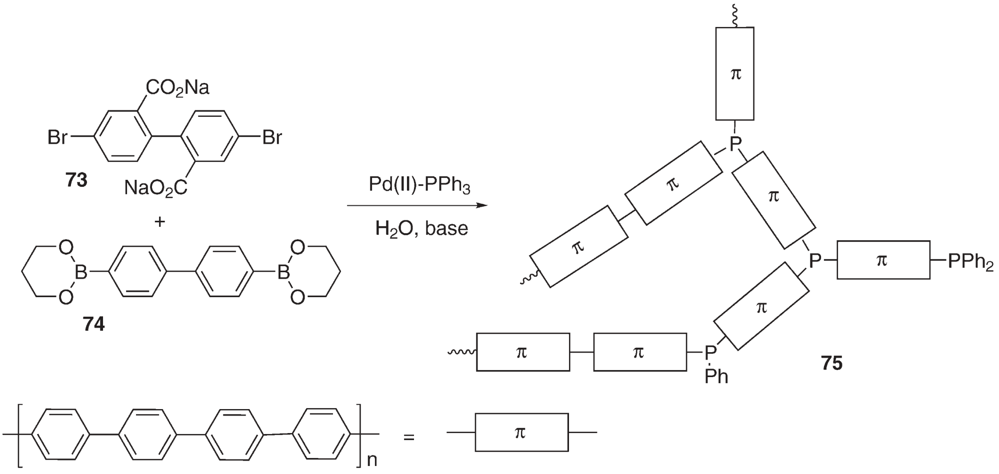
Since metal-catalysed C–C bond-forming reactions are extremely well-established and reliable, an alternative route to polymers (**D″**) has been investigated starting with the bis(*p*-bromophenyl)phosphines (**68a,b**) (Scheme 21) [65]. Disappointingly, though, this approach was also found to be inappropriate for the formation of high molecular weight polymers. A dark red insoluble solid was isolated from the Ni-catalysed coupling reaction of (**68a**), which was believed to be (**69a**). However, homo-coupling of phosphine (**68b**) afforded a low molecular weight (M_n=1000), pale yellow material (**69b**), which could be oxidised to afford (**70b**). The colour of (**69b**) is indicative of limited π-conjugation.



Scheme 21

Although of limited success, this Ni-catalysed coupling strategy builds on a previous report of the successful, direct synthesis of poly(4,4′-diphenylphenylphosphine oxide) (**70c**) from bis(*p*-chlorophenyl)-phenylphosphine oxide (**71**) (Scheme 21) [66]. The white soluble material (**70c**) (λ_{max}~280 nm) was found to have a single phosphorus environment by ^{31}P NMR spectroscopy, a comparatively high molecular weight (M_n=15,300) together with a low molecular weight distribution (PDI=1.6), and to exhibit a high T_g (365 °C) with considerable thermal stability (<5% weight loss at 550 °C). Reduction of (**70c**) was achieved by reaction with phenylsilane, to give a poorly soluble, intensely brown-red-coloured material (**72**). Surprisingly, however, despite the intense coloration, only a small red-shift was observed relative to (**71**) ($\Delta\lambda_{max}$~20 nm), which has been attributed to a possible partial re-oxidation at phosphorus.

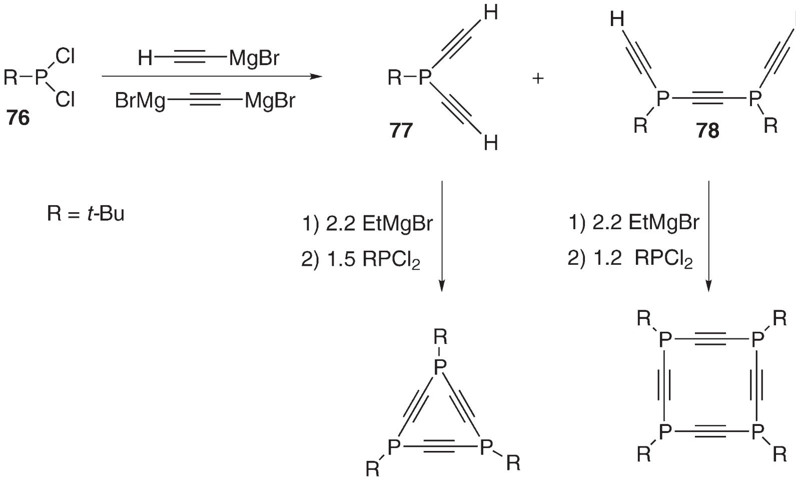
An example of branched (*p*-phenylene)s (**75**) incorporating phosphorus moieties (Scheme 22) was obtained adventitiously during attempts to synthesise soluble linear (*p*-phenylenes) using Pd-catalysed Suzuki couplings [67a]. Thus, reaction of derivatives (**73**) and (**74**) in the presence of a palladium-tri-(*o*-tolyl)phosphine catalyst system, led to the formation of linear poly(*p*-phenylene)s of high molecular weight [67a]. In contrast, on replacing tri(*o*-tolyl)-phosphine by triphenylphosphine, aryl-aryl interchange took place with the $ArPd(PPh_3)_2I$ complexes [67b] leading to the formation of branched polymer (**75**) (Scheme 22). It should be noted that although the concentration of the phosphine 'defects' is very low, they have a significant impact on the properties (e.g. molecular weight, viscosity, etc.) of the polymers. A related exchange between phenyl groups of triphenylphosphine and iodophthalocyanines in the coordination sphere of Pd(II), leading to mono-, bis- and tris-(phthalocyanine)aryl phosphonium salts, has recently been reported [68].



Scheme 22

4.2
Phosphine-Ethynyl Co-Oligomers

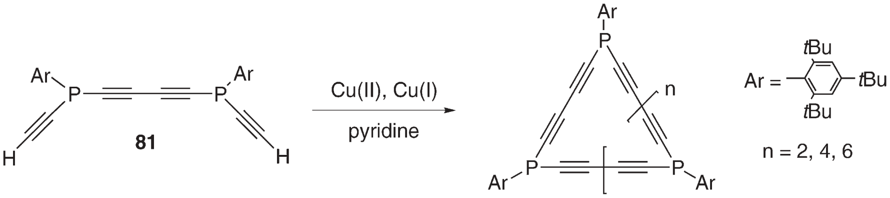
Replacement of the *para*-substituted phenyl unit of alternating phosphine-arylene polymers by an ethynyl group, gives rise to a new family of π-conjugated materials. Indeed, compounds (**77**) and (**78**) were prepared in 53% and 3% isolated yields, respectively, through reaction of dihalophosphine (**76**) with an excess of ethynylmagnesium bromide (Scheme 23) [69]. These derivatives were subsequently transformed into triphospha[3]pericyclyne (**79**) and tetraphospha[4]pericyclyne (**80**) via a double deprotonation, followed by addition of 1.5 equivalents of dihalophosphine (**76**). Notably, derivatives (**79**) and (**80**) exhibit strong absorption bands in their UV-vis spectra that extend out to nearly 300 nm, showing that these heterocycles display cyclic electronic interactions [69].



79 **80**

Scheme 23

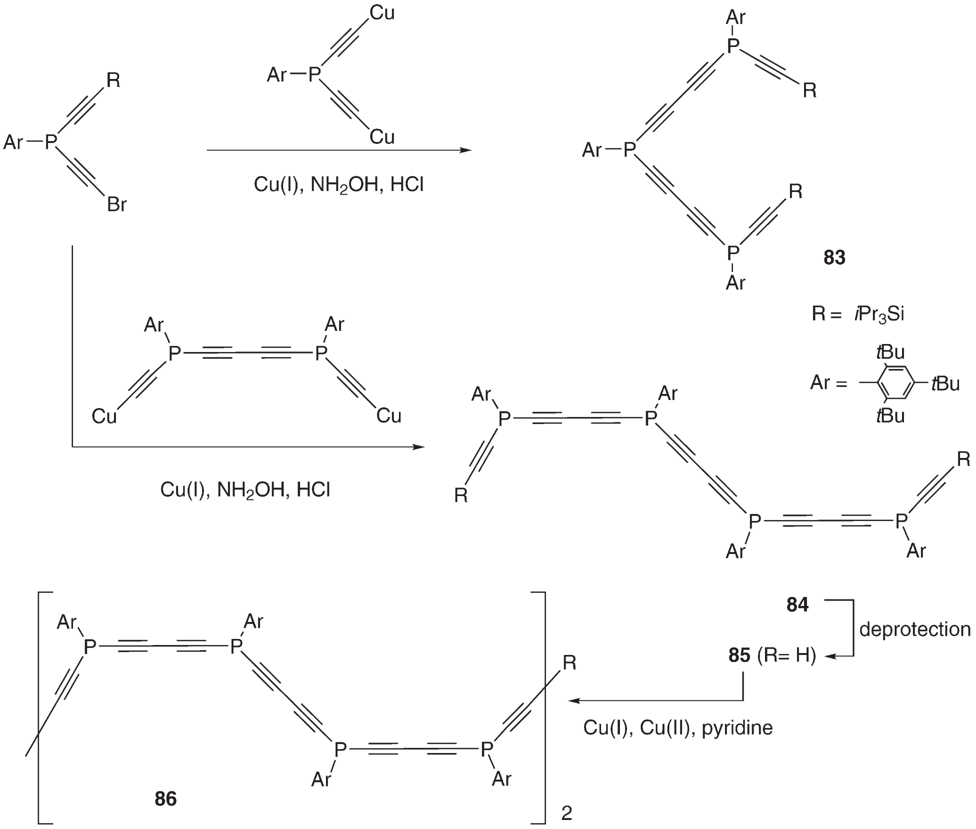
In a related strategy, ethynylphosphines (**81**) have been prepared with a view to synthesising polyphosphacyclopolyyne materials such as (**82**) (Scheme 24) [70]. Interaction between the phosphorus lone pairs and the organic π-systems is supported by the fact that the phosphorus atoms of mono- and di-silyl-capped analogues of bis(arylphosphine) derivative (**81**) exhibit an unusually low inversion barrier (65 kJ mol^{-1} versus 130–140 kJ mol^{-1} for classical alkyl- or aryl-phosphines). Indeed, the rings (**82**) exhibit values of λ_{max} at ca. 300 nm, consistent with this assumption.



82

Scheme 24

In a further extension to this approach, longer chain oligomers (**83**)–(**86**) have been prepared via two different methodologies, either a Cadiot–Chodkiewicz coupling involving bis(copper) salts, or an Eglinton coupling of terminal alkyne moieties (Scheme 25) [70]. Each of the oligomers (**83**)–(**85**) presents a number of bands in their UV-vis spectra in the range λ_{max}=308–210 nm, consistent with a degree of extended π-conjugation. Notably, however, the insolubility of the higher molecular weight, yellow-coloured oligomer (**86**) precluded UV-vis analysis.



Scheme 25

It is noteworthy that photoluminescent poly(vinylene-arsine)s have also been prepared by radical copolymerisation of phenylacetylene and an arsenic atomic biradical equivalent [71].

4.3
Phosphine-Ferrocene Co-Oligomers

Ferrocene has been extensively used as a building block to prepare organometallic polymers and heteroatom-bridged poly(metallocenes)(**G′**)–(**G‴**)(Fig. 4).

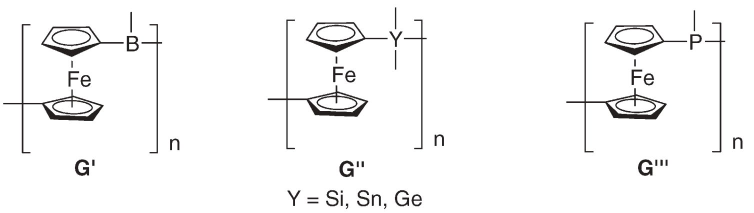
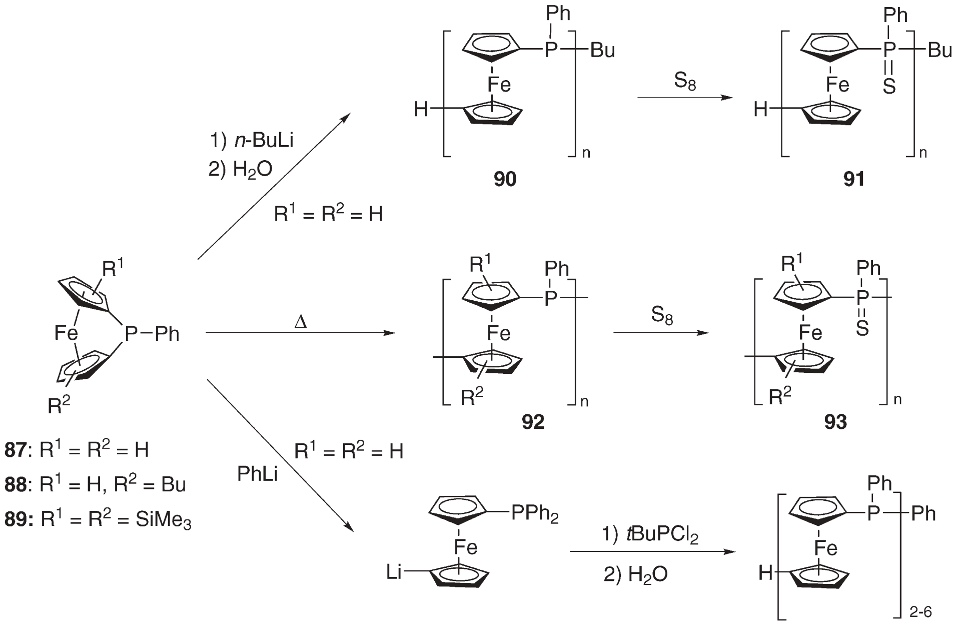


Fig. 4 Heteroatom-bridged poly(metallocenes)

These derivatives have been the focus of numerous investigations since the nature of the bridging atom has key implications for the properties of the polymers [72]. Although, not π-conjugated materials in the true sense, the phosphorus-containing materials (**G‴**) show a range of properties that offer significant promise for the future. In particular, the ring-opening polymerisation (ROP) of the strained [1]-ferrocenophane monomers (**87**)–(**89**) allows the various polymers (**90**)–(**95**) to be prepared with high molecular weights and narrow polydispersities (Scheme 26) [73]. In line with the living nature of this process, block copolymers with either poly(dimethylsiloxane) or poly(ferrocenylsilane) segments have also been isolated.



Scheme 26

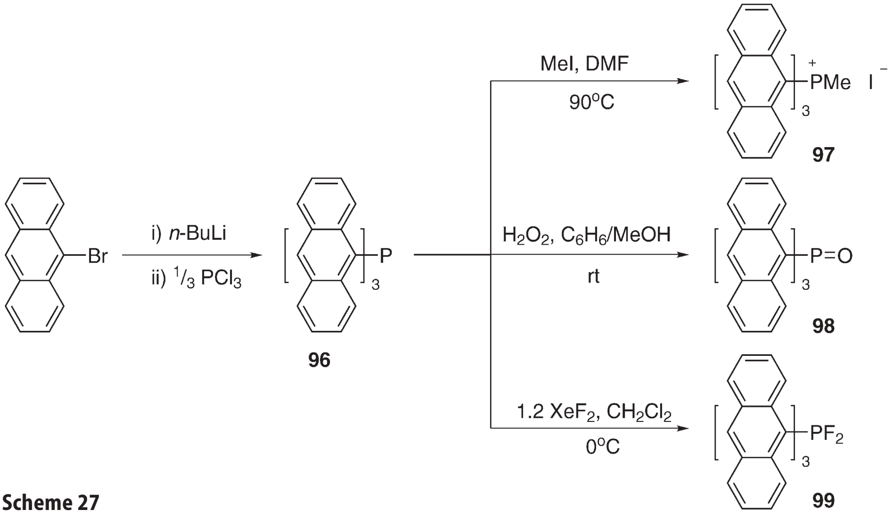
94

95

5
Phosphorus Bearing Extended π-Conjugated Substituents

Conceptually and synthetically more straightforward molecules can be prepared through incorporation of chromophores onto simple phosphine moieties. The phosphorus fragment can be used either to influence or to organise the π-conjugated systems. This section will focus only on derivatives tailored in order to exhibit specific properties related to applications in NLO, opto-electronics or as sensors.

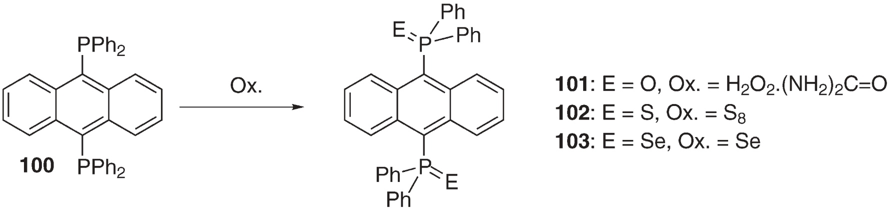
In a series of remarkable papers, K. Tamao and S. Yamaguchi have shown that the physical properties of triarylboranes and triarylsilanes can be modified using structural changes induced by increasing coordination numbers [74]. In the same way, the tuning of the photophysical properties of PAr_3 systems (**96–99**) (Scheme 27) according to the coordination number of the P-atom has been achieved [75].



Scheme 27

UV-vis spectroscopic analysis revealed that the σ^3,λ^3-phosphine (**96**) 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, probably due to extended π-conjugation through the P-lone pair [76]. The UV-vis spectra of derivatives (**97**)–(**99**) are blue-shifted ($\Delta\lambda_{onset}$, ca. 40–80 nm). This bathochromic shift can be ascribed to the inductive effects of the phosphorus moieties or to a through-space interaction between the anthracene substituents [75]. Moreover, it has been established that the fluorescence properties of these partially conjugated molecules are highly dependent upon the coordination number of the central P-atom. The σ^3,λ^3-phosphine (**96**) has almost no fluorescence as a result of quenching by the P-lone pair. The σ^4,λ^4- (**97**) and σ^4,λ^5- (**98**) derivatives show weak fluorescence with relatively large Stokes shifts, again presumably as a result of through-space interactions between the anthracene substituents. In sharp contrast, the penta-coordinate σ^5,λ^5-compound (**99**) shows an intense fluorescence with a small Stokes shift; the quantum yield is ~30–100 times greater than those of either (**97**) or (**98**), comparable to that of anthracene itself. This latter phenomenon is thought to result from the equatorial disposition of the three anthracenyl moieties, an arrangement evident from ^{31}P NMR spectroscopy.

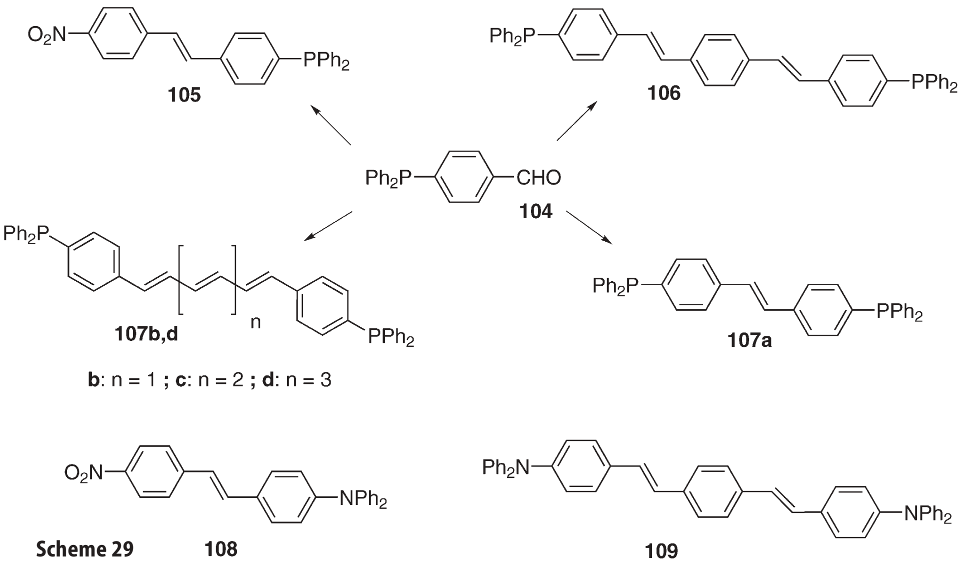
More recently, the fluorescence properties of related 9,10-diphospha-anthracenes (**100–103**) (Scheme 28) have been investigated [77], since previous studies have shown that the analogous N- and Si-disubstituted species exhibitphotoluminescence [78], electroluminescence, and are potential materials for light-emitting electroluminescent devices [79]. Starting from the known phosphine 9,10-$(Ph_2P)_2C_{14}H_{18}$ (**100**) [80], the bis(chalcogenide) derivatives (**101**)–(**103**) have been isolated in high yields (Scheme 28).



Scheme 28

In solution, only compound (**101**) exhibits a detectable emission (λ_{em}~ 450 nm). Contrastingly, in the solid state, derivative (**102**) shows very intense fluorescence at λ_{em}=508 nm, (**101**) displays a weak, broad emission at λ_{em}= 482 nm, while (**103**) shows no emission at all [77]. However, it was established that the presence of near stoechiometric quantities of toluene are necessary to observe fluorescence of (**102**) in the solid state. Indeed, the asymmetric unit of (**102**), established crystallographically, contains one toluene molecule that interacts via its *ortho*-hydrogen atoms with the central ring of the anthracene. The emission is thus due to this solid state T-shaped excimer. Hence, (**102**) can act as a potential toluene chemosensor [77]. It is noteworthy that this T-shaped orientation is not possible with derivatives (**101**) and (**103**), nicely illustrating the possible impact of P-chemistry for tuning the properties of π-conjugated systems in the solid state.

Diphenylphosphino groups have also been investigated as auxiliary donor groups for the tailoring of potential second- and third-order NLO-phores. Their syntheses used the versatile starting material *p*-diphenylphosphanyl-benzaldehyde (**104**) (Scheme 29) and a set of classical synthetic transformations (e.g. Wittig reactions, McMurry couplings) [81]. Dipole (**105**) exhibited a blue-shifted value of λ_{max}, relative to that of its N-analogue (**108**). This property may be of interest in terms of a trade-off between transparency and NLO activity,



Scheme 29

which are important parameters for the engineering of valuable second order NLO-phores [44]. Again, these results highlight the ease of tuning of the opto-electronic properties of heteroatom-containing polymers.

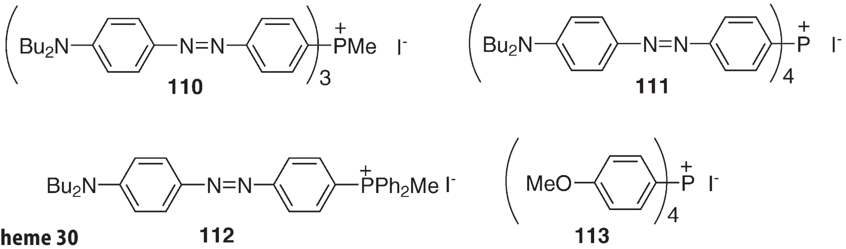
Two series of centrosymmetric diphenylphosphino-capped chromophores (**106**) and (**107a–d**) (Scheme 29) have been synthesised with a view to preparing materials with potential third order NLO properties [81]. Comparison of the UV-vis data of compounds (**106**) and (**109**) confirms that replacing N by P induces a blue-shift in the value of λ_{max} [81]. The systematic increase in the number of conjugated C–C double bonds in the series of polyenes (**107a–d**) (Scheme 29) led to a pronounced red-shift in the values of λ_{max}: 341 nm for (**107b**) and 418 nm for (**107d**), as expected. Notably, these UV-vis data are significantly blue-shifted from the values obtained for the analogous series of bis(diphenylaminodiphenyl)polyenes, which span the range λ_{max} 389 (n=1) to 449 nm (n=3) [81].

The opto-electronic properties of branched structures have been an area of some interest for a number of years, especially as NLO and light-emitting materials [82]. In particular, the use of π-conjugated dendrimers (mono-disperse macromolecules [83]) has flourished for a number of reasons:

1. The possibility of their bearing multichromophores (arranged either symmetrically or asymmetrically about the core)
2. Their ability to achieve a high chromophore density (for example, it is possible to introduce three conjugated chains about a single N-atom core in contrast to the two more normally possible with a linear macromolecule) [84]
3. The prospect of investigating the ternary structure of these materials as a consequence of their potentially 3D nature [85]

Indeed, conjugated dendrimers built from an N-containing core exhibit impressive energy transfer efficiencies as well as very strong electronic interactions of the participating chromophore building blocks, a result of planarisation at nitrogen facilitating good orbital overlap between the different chromophores [86].

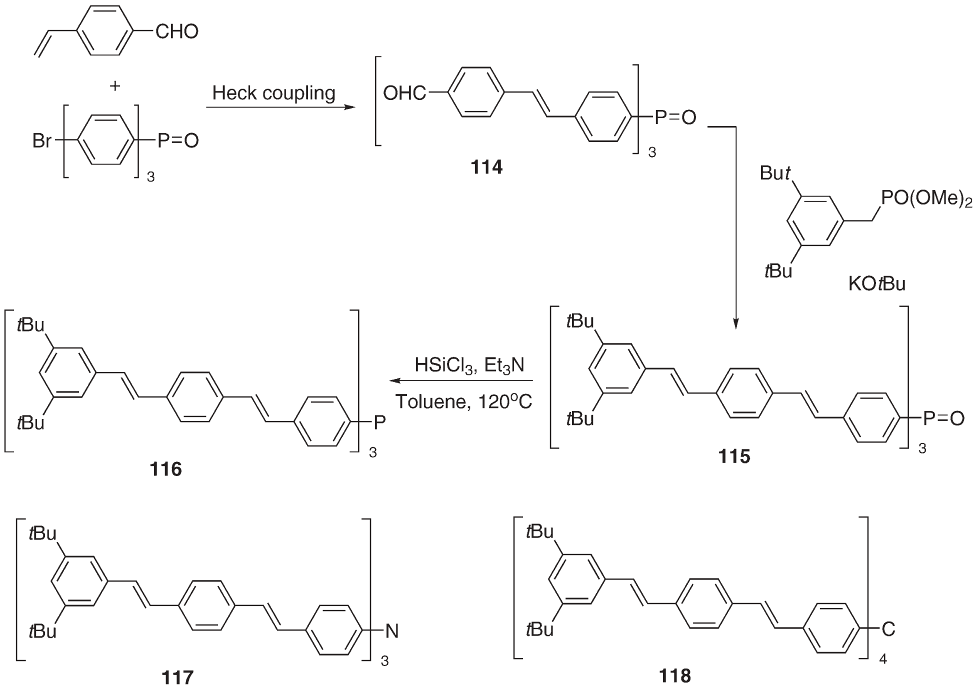
More recently, efforts have been made to prepare P-containing dendritic core branched structures bearing π-conjugated substituents. The 3-D chromophores (**110**) and (**111**) with a C_3 and D_2 (approximate T) symmetry (Scheme 30), respectively, have been prepared according to classical routes [87]. The UV-vis data suggest that the subchromophores in (**110**) and (**111**) are almost electronically independent. Derivative (**110**) has a small dipole moment, and can be viewed as an almost purely octupolar system, like (**111**). Compared to their tin analogues, the phosphorus derivatives (**110**) and (**111**) have higher β values due to the more efficient phosphonium acceptor [87]. Furthermore, the NLO activity of octupolar compound (**111**) is almost three times larger than that of the dipolar subchromophore (**112**) with almost no cost in terms of transparency. The related octupolar phosphonium salt (**113**) (Scheme 30) was investigated with the aim of obtaining NLO-active crystals that remain transparent across all, or nearly all, the visible region [88]. Structural analysis of (**113**) revealed a weakly distorted ionic structure of the NaCl-type. The tetrahedral phosphonium ion retains an almost pure octahedral symmetry in the solid state. The crystal is transparent throughout the visible region and exhibits a moderate NLO activity [88]. These two examples nicely illustrate the potential of phosphorus derivatives for the engineering of octupolar derivatives.



Scheme 30

More recently, P-cored derivative (**116**) was prepared from a straightforward combination of a Heck coupling, to afford an intermediate functionalised stilbene phosphine oxide (**114**), a Horner–Wittig reaction yielding the phosphine oxide (**115**), and finally trichlorosilane reduction (Scheme 31) [89]. Using similar strategies, both the valence isoelectronic N- (**117**) and C- (**118**) cored dendrimers have been prepared (Scheme 31).

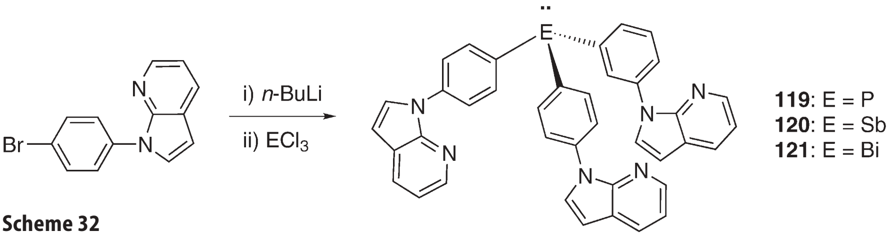
The geometry of the central core P-atom of (**116**) was found to be pyramidal, as might be expected for a (p-substituted triphenyl)-σ^3,λ^3-phosphine, while that for the N-based systems was trigonal planar (in agreement with the pla-



Scheme 31

nar structure of NPh_3 [90]). An examination of the UV-vis spectra of derivatives (**116**)–(**118**) revealed that the value of λ_{max} for the P-containing species (376 nm) is red-shifted relative to that for the C-cored species (λ_{max}=325 nm), but blue-shifted with respect to the N-based analogues (**117**) (λ_{max}=430 nm). This effect has been rationalised in terms of mesomeric effects. For the planar-cored compound (**117**) an efficient overlap of the N-lone pair with the adjacent carbon p-orbital gives rise to efficient conjugation with the oligo-PPV chains, whereas for the larger pyramidal phosphorus (**116**), the P-lone pair to Cp-orbital overlap will be significantly less efficient. Further studies to examine the fluorescence behaviour of the three compounds (**116**)–(**118**), found that the geometry, structural arrangement of dipoles about the core, and extent of electronic delocalisation, all have a direct impact on this property [89]. This conclusion was confirmed by a study on related tris(4-styrylphenyl)phosphine derivatives [91].

A similar investigation has probed the photophysical behaviour of some related "dendrimer-like" σ^3,λ^3-pnictogens (**119**)–(**121**) bearing potentially conjugating side chains (Scheme 32) [92]. These molecules are related to 1,3,5-tris(*N*-7-azaindolyl)benzene and 4,4-bis(*N*-7-azaindolyl)benzene that have shown considerable promise as bright blue-emitting OLEDs [93]. Each of the three group 15-based compounds has been shown to adopt a similar pyramidal geometry, with a propeller-like, approximate C_3 symmetry, characterised in



Scheme 32

the solid state by X-ray crystallography; the C–E–C bond angles decrease down the series, as expected.

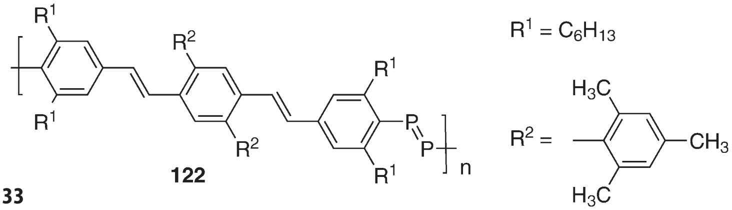
Luminescence studies revealed that compounds (**119**)–(**121**) displayed broad emission bands at 298 K, with λ_{max} ranging from 387 nm to 371 nm for the P to Bi derivatives, respectively [92]. On cooling to 77 K, compound (**119**) displays both a fluorescent band (λ_{max}=372 nm) and a phosphorescent band (λ_{max}=488 nm, lifetime 38(6) ms). For the heavier congeners only an enhanced phosphorescent band could be observed at 77 K (λ_{max}=483 nm (**120**), lifetime 3.44(4) ms; λ_{max}=478 nm (**121**), lifetime 0.577(8) ms), consistent with efficient interstate mixing of the singlet and triplet states. The attenuation in phosphorescent decay lifetimes down the series corresponds with the increasing heavy-atom effect. These luminescence data have been probed using ab initio calculations for compounds (**119**) and (**120**), which revealed that although both have HOMOs involving π-orbitals localised on the side chains, for (**105**) the HOMO is dominated by the P-lone pair. Significantly, however, the HOMO-LUMO gap is comparable for both compounds, suggesting that the observed luminescence is due to π-π* transitions with some lone pair contribution from the central atom, E. The low phosphorescent emission intensities and long decay lifetimes in the solid-state makes compounds (**119**)–(**120**) poor candidates for OLED emitter components. However, this investigation does, once again, highlight that incorporation of main group elements into conjugated systems can have a profound influence on photophysical properties.

6
Conclusions

The chemistry of π-conjugated systems incorporating P-moieties has really only come to the fore following the pioneering work started in 1990 on phosphole-based oligomers, and that on related phosphine-ethynyl co-oligomers. The last five years have seen an extraordinary expansion in this new area with the synthesis of novel derivatives exhibiting a plethora of different structures. However, the chemistry of π-conjugated systems incorporating P-units remains in its infancy. Structure–property relationships have still to be established in order to fully exploit the potential of P-moieties in the construction of conjugated frameworks. Furthermore, new methodologies are needed to prepare oligomers and polymers of defined structure and length. Nevertheless, it has already been clearly established that organophosphorus derivatives offer specific advantages in comparison with their widely used sulphur or nitrogen analogues. Three are particularly noteworthy: First, phospholes appear to be excellent building blocks for the tailoring of low band gap materials due to the low aromatic character of this P-ring. Second, the possibility of chemically modifying λ^3-P centres gives a unique way to tune the physical properties of P-containing π-conjugated systems. This facet is of particular importance for the tailoring of organophosphorus materials for applications in optoelectronics. Lastly, the coordination ability of λ^3-P centres toward transition metals offers manifold opportunities to build supramolecular architectures in which the π-systems can be organised in a defined manner.

The possibility of using organophosphorus π-conjugated systems as materials for applications in the field of nonlinear optics, organic light emitting diodes or conductive polymers has been demonstrated. However, considering the richness and diversity of phosphorus chemistry, their true potential has not yet been fully exploited. It is very likely that new developments will occur in this area in the near future, which exploits the specific properties of organophosphorus derivatives to the full.

Note Added in Proof This is nicely illustrated by the landmark publication of Protasiewicz et al. [94] who describe derivative (**122**), the first conjugated polymers featuring phosphorus–phosphorus multiple bonds (Scheme 33). The diphosphene-PPV (**122**) exhibits an extended π-conjugated system as shown by the optical HOMO-LUMO gap that is close to that of related PPV [94].



Scheme 33

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Polyphosphazenes: A Review

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Abstract In this paper the synthesis, properties and applications of poly(organophosphazenes) have been highlighted. Five different classes of macromolecules have been described, i.e. phosphazene fluoroelastomers, aryloxy-substituted polymeric flame-retardants, alkoxy-substituted phosphazene electric conductors, biomaterials and photo-inert and/or photo-active phosphazene derivatives. Perspectives of future developments in this field are briefly discussed.

1
Introduction

It is now a common feeling that our world cannot survive as it is without plastics [1]. Starting from 1930, when the macromolecular concept started to gain acceptance in the scientific community [2], the advances in polymer science have been so striking that plastics have invaded almost every aspect of modern human life, both as daily materials and as sophisticated substrates able to cover high-tech applications [3]. A very easy and simple way to check this assertion is to visit the "The Macrogalleria" web site (1st floor) [4] where an extensive exemplification of the most common and important plastic applications in different fields is provided in a really immediate and impressive way.

From a historical point of view, organic macromolecules were developed first [5], and the reasons for this are basically twofold. On one side the ease of the preparation of these materials in a controlled and reproducible way [1] and the outstanding properties of the resulting organic polymers [6–8]; on the other side the availability of oil on the market and the big effort put by oil companies into the production of a large variety of different monomers at very low prices [9].

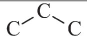
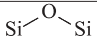
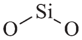
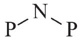
After 50 years of almost uncontested domination of the plastics market by organic polymeric materials, however, some important drawbacks of these substrates are becoming evident [10]. These problems mainly concern their poor flexibility at very low temperature, limited stability at high temperature (especially in oxygenated environments), high tendency to swell in the presence of organic solvents, scarce biomedical compatibility, lack of thermal and/or electric conductivity, and low resistance to fire and to UV and high energy radiations (X- and γ-rays, electron beams, etc.) [11].

During the last three decades the consideration of inorganic [10, 12–16] and organometallic [17–20] polymers in an effort to overcome these problems and to expand the utilization of plastics to situations where organic materials fail has become more and more important; this is marked by the astonishingly high number of publications appearing in this area.

The reasons for the success of inorganic and organometallic macromolecules over the corresponding organic materials stand on the structure–property relationships existing in these polymers.

As reported in Table 1, inorganic polymers (e.g. polysiloxanes and polyphosphazenes) usually posses wider angles and longer bonds among skeletal atoms

Table 1 A few general features of both organic and inorganic polymers

Polymers	Angles (Degrees)	Bond Length (Å)	Percentage of Ionic Character (%)	Bond Dissociation Energy (Kcal/mole)
Polyethylene	 109.3	C-C 1.54[10]	--	82.6[21]
Polysiloxanes	 143[19]  110[19]	Si-O 1.63[21,22]	40-50[21,22]	110.0[21]
Poly(phosphazenes)	 119°[10]  130°-160[10]	P-N 1.55-1.60[10]	--	above 70[23]

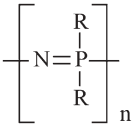
than do organic macromolecules, the inorganic linkage also showing a considerable ionic character.

The structural characteristics of inorganic macromolecules bring about important consequences as far as their chemico-physical features are concerned [9], compared to the corresponding properties of organic polymers. Inorganic plastics, in fact, form very good elastomers at low temperatures (due to an enhanced skeletal flexibility and depressed values of T_g). They are much more stable towards homolytic chain scission and high temperature oxidation and behave as flame- and fire-resistant substrates due to the elevated content of inorganic elements. In some cases, furthermore, they show very good biological compatibility, water solubility, and radiation resistance due to the presence of stronger bonds and transparency to very short wavelength radiation.

At present the situation in the field of inorganic polymeric materials is dominated by polysiloxanes (silicones) [14, 24–27], whose utilization as low temperature elastomers, thermally stable fluids, biomaterials etc., is definitely well established.

There are, however, other classes of inorganic and organometallic polymers that deserve consideration due to their considerable scientific and applicative relevance, such as polysilanes [28–31], polycarbosilanes [32, 33], polysilazanes [33], polyborazines [34, 35], polythiazenes [36], and, as an example, polymetallocenylsilanes [37].

Among these polymers, poly(organophosphazenes), POPs, occupy a special position [38].



$$\left[-N{=}\overset{R}{\underset{R}{P}}- \right]_n$$

Although the preparation of the starting material for synthesizing these macromolecules dates back to 1834 [39], their synthesis and characterization was described by H. R. Allcock only in the middle of the 1960s [40–43]. Since then, they have experienced an explosive development [10, 12, 13, 15]. Almost every industrialized country in the world (USA, Europe, India, East Asia, etc.) has put years of effort into investigating and developing these materials, preparing an elevated number of macromolecules of different structures and properties, with a great deal of potential in a wide range of industrial and technological fields.

Now polyphosphazenes seem to be ready to move from the level of a mere scientific curiosity to the rank of industrially and commercially important macromolecules [10, 12, 13, 15].

In this article we highlight some fundamentals concerning phosphazene macromolecules, together with the most significant achievements that have appeared in literature during the last 10 years. For previous important information on these substrates adequate literature will be provided.

2

Synthesis of Poly(organophosphazenes)

2.1

Preliminary Synthetic Considerations

The synthesis of poly(organophosphazenes), POPs, is a research area that has involved a lot of effort in the past by many scientists active in the phosphazene domain. There are several important reasons for this, basically related to the high cost of the starting products [44] used to prepare POPs, to difficulties in carefully controlling the reactions involved in the preparative processes [38] and to the need for accurately predicting both molecular weight and molecular weight distribution of the POPs produced [38, 45].

Decreasing the cost of production of POPs is a major problem, to make them competitive with other less expensive or almost inexpensive organic macromolecules. For this reason, different synthetic approaches have been taken into consideration, implying the use of different monomers (such as hexachlorocyclophosphazene) [13], low molecular weight starting reagents (PCl_5, NH_4Cl, $(NH_4)_2SO_4$, etc.) [46–52], short linear phosphazene oligomers [53, 54], and variable types of chlorinated or substituted phosphoranimines [10, 55, 56] and phosphoranes [38, 57].

At the same time, ring-opening-polymerization (ROP) processes, which dominated the phosphazene field for decades [38], tend now to be substituted by polycondensation reactions. These seem to be more feasible and reproducible, easier to carry out, and able to guarantee predictable MWs and MW distributions for these materials [10].

Finally, substituted phosphoranimines seem to be able to avoid substitutional processes carried out on highly reactive polymeric phosphazene intermediates (e.g. polydichlorophosphazene), whose completeness is mandatory for the stability and constancy of properties of the final POPs [38].

In this section we will provide an almost exhaustive view of the synthetic strategies used to prepare POPs.

2.2
Synthesis of Poly(organophosphazenes)

In general terms, the synthesis of poly(organophosphazenes) can be obtained by using three main strategies, as reported in Fig. 1. These approaches imply:

I. Preparation of poly(dichlorophosphazene), $(NPCl_2)_n$, a polymeric intermediate from which the great majority of POPs have been prepared by nucleophilic substitution of the highly reactive chlorine atoms with carefully selected organic substituents
II. Use of polycondensation processes of substituted phosphoranimines to obtain already substituted poly(organophosphazenes)
III. Utilization of ROP processes of completely or partially substituted cyclophosphazenes to obtain POPs having predictable chemical structures

All these processes will be illustrated in some detail.

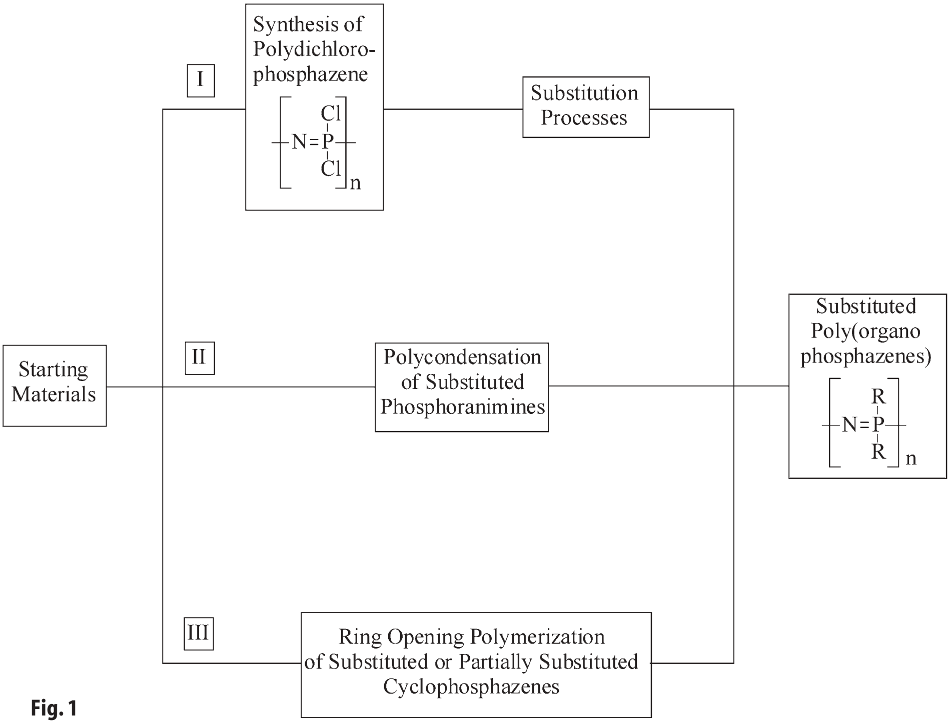
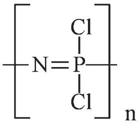


Fig. 1

2.3
Process I: Synthesis of Poly(organophosphazenes) Through Polydichlorophosphazene and Nucleophilic Substitution of its Chlorines with Nucleophiles

2.3.1
Part 1 – Synthesis of Polydichlorophosphazene

Polydichlorophosphazene is commonly considered as the "key polymer" from which almost all poly(organophosphazenes) are generated [38].



$$\left[-N=\overset{Cl}{\underset{Cl}{P}}- \right]_n$$

The synthesis of this material is one of the major processes in phosphazene chemistry, as proved by the unbelievably high number of papers and patents that have appeared since the beginning of the phosphazene history [10, 58].

A list of different authors that have been involved in designing new preparative strategies for obtaining this polymer under controlled conditions is given in Table 2.

Table 2 Synthesis of polydichlorophosphazene by different methods

Year	Author(s)	References
1897	N.S. Stokes	59
1939	O. Schmitz-Dumont	60
1949	B.R. Dishon	61
1951	F.Patat	62–65
1959	T.R. Manley	66
	J.O. Konecny	67, 68
1960	D. Chakrabartty	69
	N.L. Paddock	70, 71
1961	M.W. Spindler	72
	R.A Shaw	73
1962	V. Caglioti	74, 75
	F.G.R. Gimblet	76
1963	J.R. Soulen	77
	M. Kajiwara	78–82
1965	F.L. Chui	83
	H.R. Allcock	13, 40–42, 84–89
1966	P. Porta	90
1967	J.R. MacCallum	91, 92
1968	R.O. Colcluogh	93

Table 2 (continued)

Year	Author(s)	References
1970	R.W. Jenkins	94
	G. Allen	95
1971	V.V. Kireev	96–104
1972	J. Emsley	105
1977	K.A. Reynard	106–108
1978	A.F. Halasa	109, 110
	D.L. Snyder	111, 112
	R.L. Dieck	113–116
1979	T.A. Antkowiak	117
	J. Retuert	118, 119
	V.V. Korshak	120–123
1980	–	124–126
	J. Behnke	127, 128
	T. Kinoshita	129, 130
	D.P. Sinclair	131
	Y. Osada	132–135
	J.W. Fieldhouse	136–139
	E.D. Hornbaker – H.M. Li	46, 47, 53, 54, 140–147
1982	E. Devadoss	148–150
	H.G. Horn	151
	S. Besecke	152
	R. De Jaeger	38, 57, 153–180
1983	–	181
	M.S. Sennett – R.E. Singler – M.K. Potts	58, 182–188
1984	M. Gleria	189–191
1985	D.F. Graves	192
1986	B. Chu	193, 194
1987	A.J. Klein	195
	C.C. Kirkpatrick	196
	S.S. Krishnamurthy	197
1988	I. Maruyama	198, 199
	M.V. Milashvili	200
1989	W.L. Hergenrother	201
	J.H. Magill	202–207
	M. Kouril	208, 209
1990	V.T. Stannett	210
1991	C.H. Kolich	211
1993	Y.S. Sohn	212, 213
1994	F. Okada	214
1995	H.R. Allcock – I. Manner	215–243
1998	C.W. Allen	48–50
	C.H. Chen	244
2003	G.A. Carriedo	51, 52

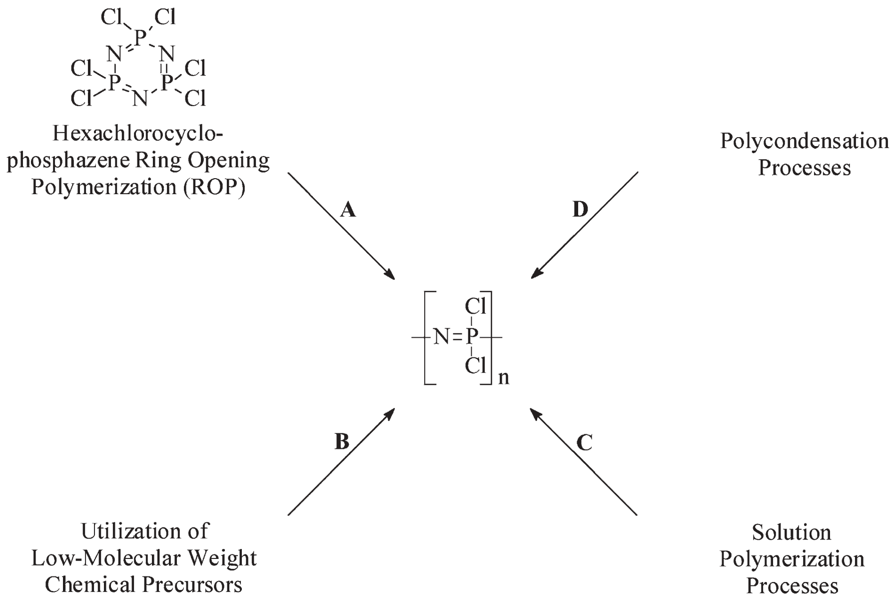


Fig. 2

As can be seen, this list encompass authors starting from the end of 1800, up to the beginning of this century. For the preparation of $(NPCl_2)_n$ they used at least four different methods (Fig. 2), which will be described in some detail in the paragraphs below.

2.3.1.1
Ring-Opening Polymerization Process of Hexachlorocyclophosphazene

This ROP of hexachlorocyclophosphazene to polydichlorophosphazene is very relevant in phosphazene chemistry as it has been used in almost every laboratory in the world for the preparation of poly(organophosphazenes) starting from the middle of the 1960s up to recent times [38]. H. R. Allcock discovered in 1965 [40–42] that $(NPCl_2)_3$ can open its inorganic ring thermally, under strictly controlled experimental conditions (250 °C, vacuum of 10^{-2} torr, and reaction time of 8–12 h), to form polydichlorophosphazene in a reasonable yield, but in a rather slow and irreproducible way [38]. Moreover, the final polymer obtained shows a very variable MW and MW distribution, with a strong tendency to produce crosslinked materials [45].

Attempts at controlling the experimental parameters governing this reaction led many scientists active in the phosphazene field to:

1. Consider alternative polymerization processes in solid state, inducing the polymerization reaction of $N_3P_3Cl_6$ thermally [40–42], photochemically [61, 67, 68], γ-radiolytically [66, 210], using X-rays [74, 75, 90] or electron irra-

diation [72], under plasma conditions [132, 135, 195, 208, 209], or in the ionization chamber of a mass spectrometer [189–191]. In many cases, a variety of catalysts having a very variable chemical structure have been used [38] to promote the ROP process.

2. Move from solid to solution conditions [68, 80, 89, 108, 118, 119, 131, 138, 182–184, 186, 187, 202, 205–207, 245], mostly using chloroarylated solvents (e.g. *o*-dichlorobenezene [80, 245] or 1,2,4-trichlorobenzene [182–188, 202, 205–207]) and Lewis acids [58, 182–188] or sulphonated chemical compounds [131, 202, 205–207] as catalysts to improve reaction efficiency.

Most of these methods have been widely reviewed in previous literature [38] and will not be commented on further in this article.

2.3.1.2
Utilization of Low Molecular Weight Chemical Precursors

The use of low molecular weight phosphorus compounds (e.g. PCl_3 or PCl_5) in combination with variable types of ammonium salts [NH_4Cl or $(NH_4)_2SO_4$], under suitable experimental conditions, leads to the preparation of linear chlorinated phosphazenes of different molecular weight and molecular weight distribution, according to one-pot syntheses or two-step processes. This approach to the synthesis of polydichlorophosphazene is described in Fig. 3.

Hornbaker and Li [46, 47, 53, 54, 136–147] used this approach to prepare $[Cl\text{-}(PCl_2{=}N)_nPCl_3]^+PtCl_6^-$ of relatively low molecular weight by using a two-step process based on the preliminary reaction of PCl_3, Cl_2, HCl and NH_3 in monochlorobenzene at 100–140 °C to produce linear phosphazene oligomers (having the chemical structure reported above and n=2–9) followed by a successive reaction with NH_4Cl at 130–150 °C to enhance the final polymerization degree of the material to 300–900.

More interesting, especially from the applicative point of view, is the approach proposed by C.W. Allen in 1998 [48–50], based on the utilization of a one-pot two-step reaction of ammonium sulfate with phosphorus pentachloride, to produce dichlorophosphynoyliminotrichlorophosphorane (vide infra) at 165 °C followed by polycondensation of this monomer to polydichlorophosphazene by heating at 225 °C. The great advantage of this process is the possibility of producing the polymer starting from very simple and inexpensive compounds in just one step, using a procedure that does not imply the use of organic solvents.

The most recent approach to the synthesis of polydichlorophosphazene starting from low molecular weight phosphorus precursors was proposed by Carriedo in 2002 [51, 52], who reacted PCl_5 in combination with NH_4Cl in 1,2,4-trichlorobenzene at reflux temperature in the presence of $CaSO_4{\cdot}2H_2O$ and sulfamic acid, HSO_3NH_2. A total yield of 31% (vs PCl_5) in high molecular weight (10^6 Dalton) $(NPCl_2)_n$ could be obtained. However, a few technical problems reported by the authors concerning this synthetic approach presently limit the preparation of polydichlorophosphazene to laboratory scale level.

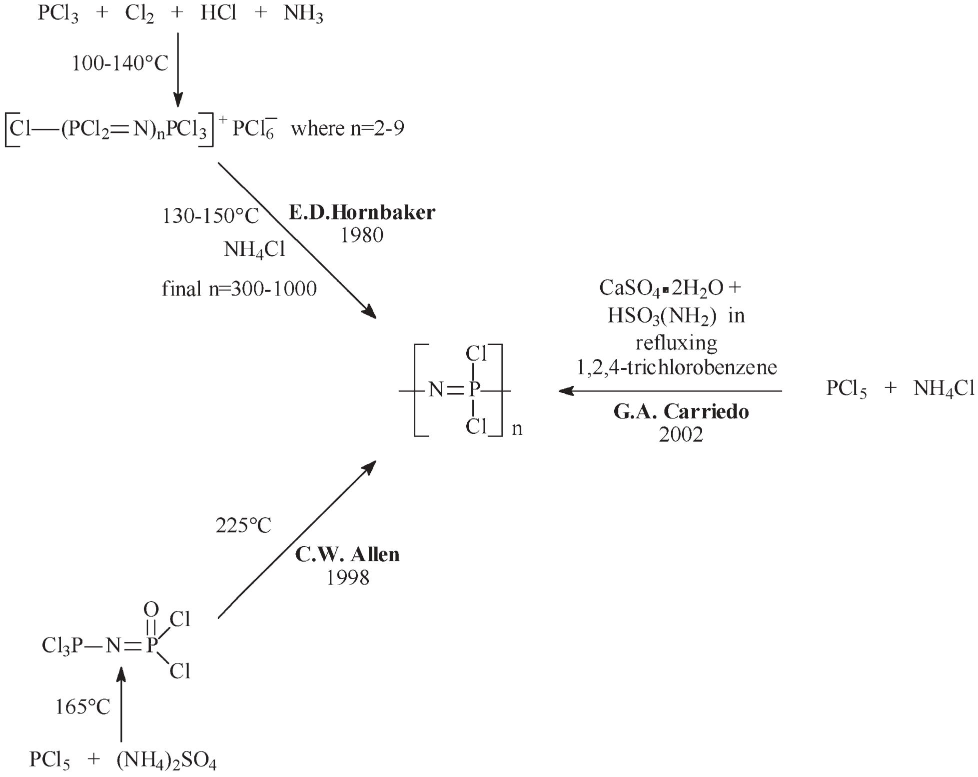


Fig. 3

2.3.1.3
Solution Polymerization Processes

The solution polymerization process for hexachlorocyclophosphazene to polydichlorophosphazene is an interesting and attractive alternative to the classic bulk thermal polymerization reaction of this trimer.

Several authors have attempted to accomplish this process, experimenting with different solvents and variable experimental conditions. The most significant experiments are reported in Fig. 4 for the solution polymerization of $(NPCl_2)_3$ using different solvents.

In general terms, the conclusions that can be drawn from these experiments are that solution polymerization processes have some basic advantages with respect to the corresponding molten state analogous reactions: the reaction speed in solution is usually reduced to half or one third of the original value in solid state [89] and appears therefore to be much more controllable, while the polymer viscosity is usually decreased. They show, however, some important drawbacks consisting mostly in the low molecular weight of the polymers prepared [89], in a strong influence in the type of polymer formed [118] (linear or cross-

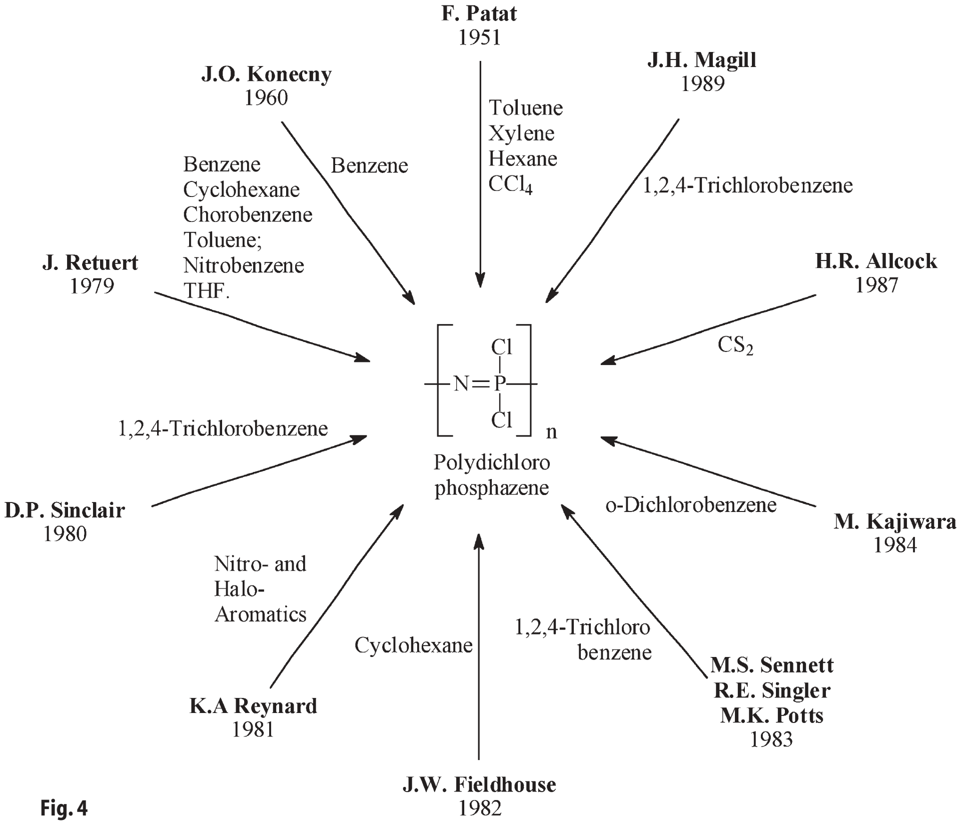


Fig. 4

linked) and, mostly, in the pronounced reactivity of the P–Cl bond of hexachlorocyclophosphazene with some of the solvent (typically protic solvents) exploited for the polymerization process [118, 119].

2.3.1.4
Polycondensation Reaction

The discovery that new types of monomers, as alternatives to hexachlorocyclophosphazene, can be used to prepare polydichlorophosphazene is due to R. De Jaeger in the early eighties [57, 153, 172, 174–176, 178–180, 246–252] who first reported the thermally induced polymerization process of dichlorophosphynoyliminotrichlorophosphorane $Cl_3P=N\text{-}P(O)Cl_2$ at 270–300 °C to form $(NPCl_2)_n$ with delivery of $POCl_3$ as by-product. This process was immediately brought to pilot plant scale by Ph. Potin at Atochem [57, 155, 158, 161–168, 170–180, 248, 250–261]. According to this procedure, the molecular weight of the final polymer obtained could be better regulated than in the ROP process of $(NPCl_2)$, and the molecular weight distribution limited to around 2 [166, 168, 178], while the effect of water on the polydichlorophosphazene reticulation could be controlled [155, 171, 175, 179].

Following the same line I. Manners and H. R. Allcock [215, 216, 218, 219, 241] reported, in the middle of the nineties, an analogous polycondensation process using a different monomer (i.e. trichloro(trimethylsilyl)phosphoranimine, $Cl_3P{=}NSiMe_3$) at room temperature, both in the solid state and in solution (e.g. dichloromethane), activated by traces of PCl_5. This led to the preparation of polydichlorophosphazene accompanied by the concurrent formation of chlorotrimethylsilane, a low molecular weight by-product delivered during the process. These polycondensation processes are summarized in Fig. 5.

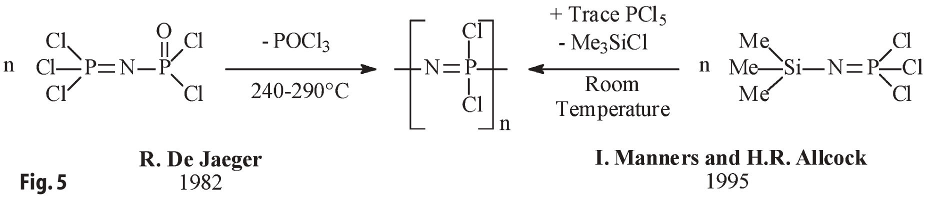


Fig. 5

As the synthetic approach to polydichlorophosphazene put forward by R. De Jaeger has been already described in several recent review articles [10, 38, 57, 172], in this paper we will illustrate only the polycondensation approach proposed by I. Manners and H. R. Allcock, together with the consequences of this reaction on the preparation of *chain* phosphazene copolymers (block copolymers) [220, 223, 224, 232–234, 240], and star polymers [222].

The experimental conditions for this reaction are as follows: carefully purified trichloro(trimethylsilyl)phosphoranimine, both in solid state or in solution (anhydrous dichloromethane or toluene) is treated with PCl_5 in a well defined monomer/initiator ratio in a temperature range between −10 °C and 35 °C for variable periods of time. The lower the initiator concentration, the smaller the number of initiated chains and the higher the final molecular weight of $(NPCl_2)_n$ obtained. Furthermore, the higher the reaction temperature, the slower the time needed for the reaction to occur. Finally, the molecular weight of the polydichlorophosphazene prepared by condensation polymerization processes in solid state appears to be lower and have a broader molecular weight distribution

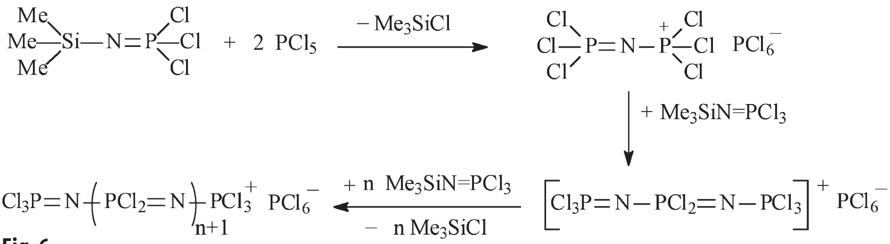


Fig. 6

than the same process carried out in solution. The reaction mechanism proposed for this process is shown in Fig. 6.

This reaction mechanism is able to account for several characteristics shown by this reaction. First of all the existence of a terminal group (e.g. $-PCl_3^+$) that remains reactive after completing the consumption of the phosphoranimine classifies this reaction in the category of the living polymerization processes. This fact has important consequences that can be summarized below:

a. The living head is able to add more of the same monomer, increasing the molecular weight of the final material in a way that depends on the feeding conditions.
b. It can also initiate different monomers, i.e. partially or completely substituted phosphoranimine monomers, providing the way to produce phosphazene block copolymers of well defined structure. Interesting materials synthesized in this way have the structure reported in Fig. 7.

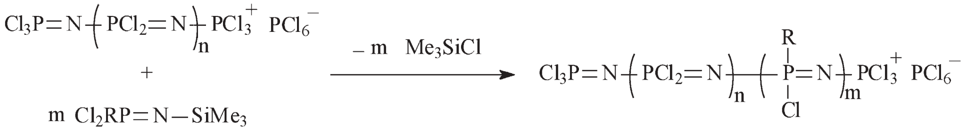


Fig. 7

c. Star polymers can be prepared if multifunctional cores are used that contain 3 or more phosphoranimine units, like Fig. 8.

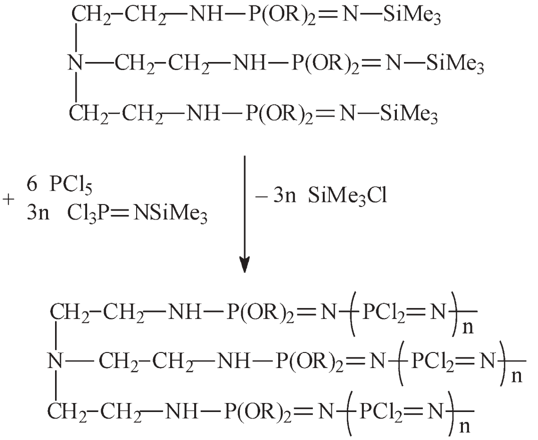


Fig. 8

The fact that this polycondensation process takes place at room temperature, with careful control of both molecular weight and molecular weight distribution of the final polymers or copolymers produced are definitive advantages over the corresponding ROP reaction of $(NPCl_2)_3$ in molten state.

2.3.1
Part 2 – Substitution reaction of the chlorines

Regardless of the way in which polydichlorophosphazene is prepared (vide supra), this polymer should be handled almost immediately because of the extreme reactivity of the chlorine atoms attached to the phosphorus of the polyphosphazene chain toward nucleophilic groups and water.

This argument has been reviewed in many articles in the past and the corresponding problems in reaching the highest substitution level of the P–Cl bonds in the polydichlorophosphazene deeply analysed [38]; therefore, it will not be considered in detail here. What is important to stress in the present paper is that the replacement of these chlorine atoms with variable types of nucleophiles provides many different classes of hydrolytically stable phosphazene materials, as reported in Fig. 9.

Up to now, nine classes of different polyphosphazenes are known and characterized: substituted with aliphatic alcohols [40, 41, 262–281] or phenols [41, 95, 277, 282–297], with aliphatic [42, 298–300] or aromatic [301–304] amino groups, with di-functional spiro hydroxy (e.g. dihydroxybiphenyl [305] or di hydroxy-

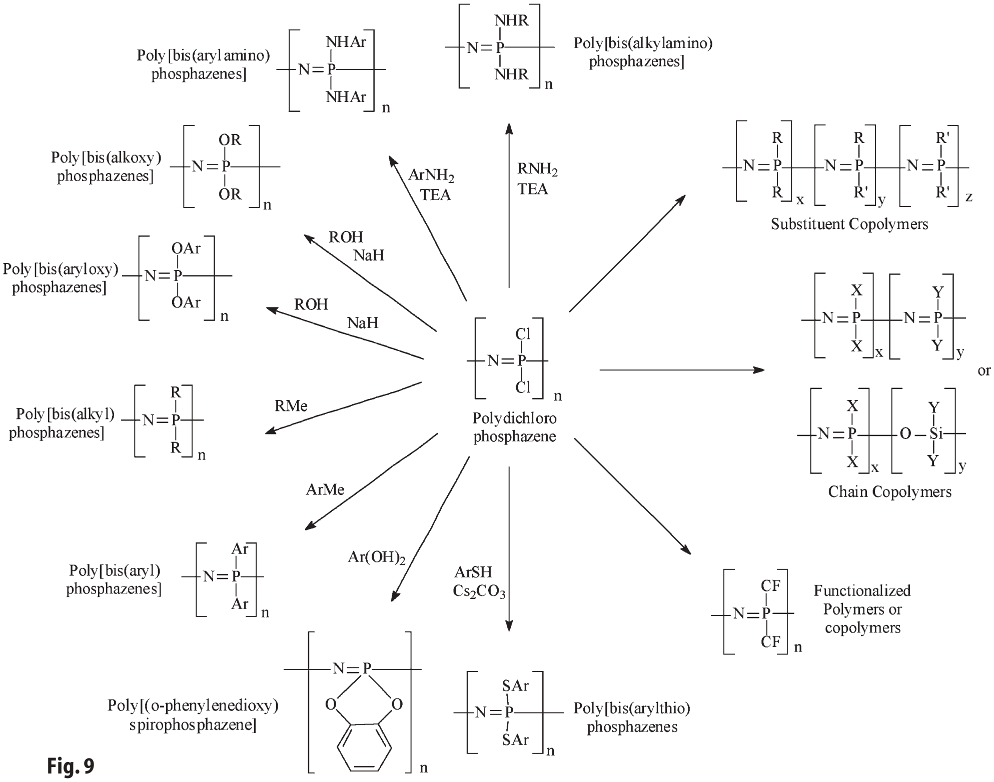


Fig. 9

binaphthyl [306–308] derivatives), or thiolic groups [292, 309, 310], and with aliphatic and aromatic residues directly attached to the polyphosphazene skeleton through P–C bonds [311–313].

In the same scheme, moreover, it is evident that, besides phosphazene homopolymers, the substitution of the chlorines with two (or more) different substituents leads to the preparation of *substituent* phosphazene copolymers [263] containing different homosubstituted and heterosubstituted monomeric units. Moreover, the cationic polymerization of phosphoranimines [215–217] produces polymers with living reactive ends (vide supra) from which the preparation of *chain* phosphazene copolymers (block copolymers) [220, 223, 225, 229, 232–235, 239, 240] formed by different polymeric backbones linked together in a unique macromolecule could be obtained.

2.4
Process II: Synthesis of Poly(organophosphazenes) Through the Polymerization of Substituted Phosphoranimines

In spite of the fact that the preparation of polydichlorophosphazene nowadays can be reached in many different ways and with great efficiency (vide supra), the substitution of the chlorine atoms of this polymer to form stable poly(organophosphazenes) is still a source of problems as it can be seldom driven to completeness and a very small amount of unreacted chlorines is always present in the final phosphazene material [38]. The complete elimination of these chlorines is mandatory if the modification of the phosphazene materials over time has to be successfully prevented.

In this context, phosphoranimine compounds (both homosubstituted with an unique group or bearing two different groups at the phosphorus) play a fundamental role because their polymerization under different experimental conditions eventually leads to fully substituted polyphosphazenes with no residual chlorines on the phosphazene skeleton. The general scheme of the phosphoranimine polymerization processes is reported in Fig. 10.

As can be seen, the first example of phosphoranimine polymerization process was proposed by E. P. Flindt and H. Rose [314] in 1977 for tris(trifluoroethoxy)-*N*-(trimethylsilyl)phosphoranimine, which could be polymerized to poly[bis(trifluoroethoxy)phosphazene] (MW 4000–10,000) by simple heating at 200 °C.

A few year later (1980) R. H. Neilson and P. Wisian-Neilson started their long term research project on the preparation of alky, aryl, and alkyl/aryl phosphazene polymers and copolymers [55, 56, 315–334] prepared in the same way by thermal polymerization of a variety of phosphoranimine derivatives [55, 329, 335, 336] to the corresponding phosphazene macromolecules. The polymers obtained by long heating (several days) at high temperatures (160–220 °C) showed relatively low (about 50,000) molecular weight.

At the beginning of the nineties K. Matyjaszewsky [337–353] re-investigated this field and discovered that phosphoranimine polymerization processes could be induced in an anionic fashion by the action of tetrabutylammonium-

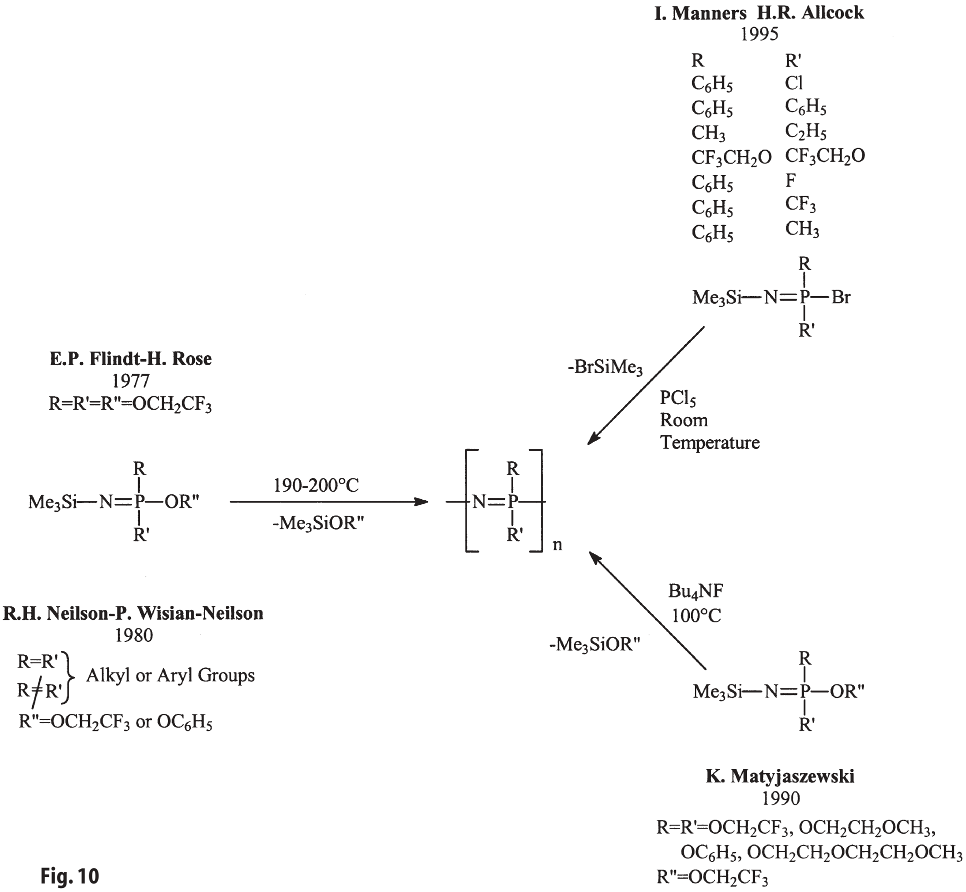


Fig. 10

fluoride [337–343, 345, 348, 350–352] or *N*-methyl-imidazole [339, 345, 354] initiators under considerably milder experimental conditions (90–100 °C), and for considerably shorter reaction times (a few hours). Both phosphazene homopolymers [337–341, 343, 345, 352] and random [342, 348, 351, 352] and block [348, 350–352, 354] copolymers could be prepared according to this method, which made the synthesis of phosphazene *chain* copolymers accessible for the first time.

Finally, in 1995, the room temperature polymerization approach put forward by I. Manners and H. R. Allcock [217, 221, 227] allowed the cationic polymerization of variably substituted phosphoranimines, according to Fig. 10. The substituents exploited for the polyphosphazenes synthesized are also reported in the same scheme.

2.5
Process III: Preparation of Polyphosphazenes by Ring Opening Polymerization Processes of Substituted or Partially Substituted Cyclophosphazenes

The problem of the thermally induced polymerization reaction of partially or completely substituted cyclophosphazenes has been considered in the past by several authors [355–357], and more recently by H. R. Allcock [358]. This is because of the ease of synthesizing these substrates, the possibility of preparing structurally regulated poly(organophosphazenes), and the lack of any additional nucleophilic substitution processes on the poly(organophosphazenes) obtained by the ROP process of fully saturated trimers.

Following these investigations, however, it emerged quite clearly that the reduction in the number of chlorine atoms on the cyclophosphazenes, and the corresponding increase in the number of organic side groups, dramatically changes the polymerization behaviour of the phosphazene cycles. This is possibly due to the fact that in substituted cyclophosphazenes, the original P–Cl bonds of hexachlorocyclophosphazene (responsible for the ionic nature of the ROP process of this trimer) are replaced by pure covalent P–C bonds, which usually break in an homolytic fashion.

When the ROP process is attempted on partially or completely substituted cyclophosphazenes in molten state several phenomena can take place:

1. A true polymerization reaction
2. A ring-expansion reaction to tetramers, pentamers, etc.
3. The decomposition reaction of the cyclophosphazene phosphorus substituents
4. No reaction at all

The occurrence of one of these situations rather than another depends on the chemical nature of the cyclophosphazene exploited and on the experimental conditions selected for the polymerization process. These facts are illustrated in Table 3.

In general terms it appears that:

a. The higher the number of organic groups inserted in the cyclophosphazene, the lower is the probability of the polymerization process and the higher is the possibility that a ring-expansion reaction takes place on the trimer
b. The higher the bulkiness of the substituent organic groups on the trimer, the higher the probability of ring-expansion polymerization processes
c. The presence of non-geminal substituent groups on the trimer favours polymerization processes, while geminal substitution can favour side reactions
d. Substituent groups on the cyclophosphazene that show strained structure or ring distorsion favour polymerization processes
e. Cyclophosphazenes that are not able to polymerize thermally for any reason may open their cycle and form polymer chains during thermal treatments in the presence of variable amount of $N_3P_3Cl_6$

Table 3 Influence of experimental parameters on the reactivity of partially or completely substituted cyclophosphazenes during a ROP process

Favoured Reaction	Number of small dimension substituents on the trimers	Bulkiness of the substituent groups on the trimers	Non-Geminal substituents	Ring-Strained Groups	Co-polymerization Reaction in the presence of $(NPCl_2)_3$	Presence of Catalyzing Species
A)Ring Opening Polymerization						
	↓	↓	↑	↑	↑	↑
B)Ring Expansion Reaction						

f. Hexa-substituted cyclophosphazenes can polymerize under particular conditions to the corresponding fully substituted polyphosphazenes, even if this event is rather unusual
g. Thermal and/or chemical instability of the cyclophosphazene side substituents usually prevent both polymerization and ring-expansion processes from taking place, favouring the onset of decomposition phenomena
h. The presence of chlorine instead of fluorine atoms in the cyclophosphazene usually depress the polymerization temperature of the cyclophosphazene

The following substituent groups for the cyclophosphazenes have been studies in great detail: alkyl [357, 359–363], aryl [362, 364, 365], trifluoroethoxy [88, 362, 366–368], phenoxy [369], organosilicon [362, 370–375], carboranyl [376–378], ruthenocenyl and/or ferrocenyl groups, the latter being linked to the cyclophosphazene ring with a single bond [379, 380] or in a transanular fashion [379–382] (see Fig 11).

To conclude this synthetic section, it appears very clear that the experimental approaches for preparation of POPs are very numerous and give accessibility to phosphazene polymers and copolymers with different structures and properties. Moreover, it has been recently estimated [10, 383] that the total number of polyphosphazenes reported up to now in the literature is about 700, and that these materials can find potential practical application as flame- and fire-resistant polymers [44, 283, 384–388] and additives [389, 390]; thermally stable macromolecules [391]; chemically inert compounds [392]; low temper-

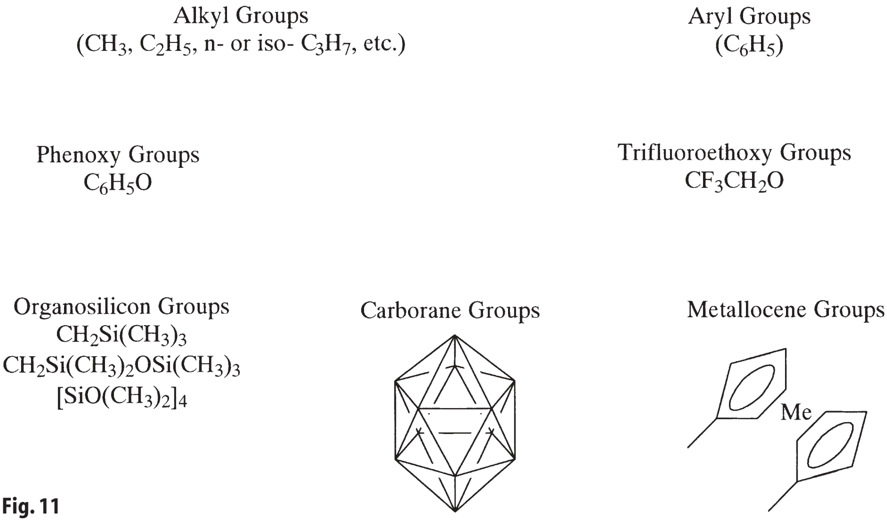


Fig. 11

ature elastomers [393–399]; biomaterials [400–407]; and as photosensitive and photostable substrates [408–413]. In addition they can be used as materials for nonlinear optics [414–422]; liquid crystals [423–429]; membranes [430, 431]; microelectronic technologies [304, 432–435]; organometallic and coordination chemistry [436–440]; electric conductivity [441, 442]; preparation of hybrids [443] (sometimes using the sol-gel approach [444–446]); polymer blends [447]; piezoelectricity [448, 449] and electrochromism [450]. In this respect, poly(organophosphazenes) can be considered as one of the most important classes of macromolecules ever invented by human mind.

3
Polyphosphazene Properties

Understanding the properties of poly(organophosphazenes) is a fascinating and relatively simple problem, and the analysis of the structure–property relationships of these compounds is a powerful tool for solving this problem.

In fact, considering the basic structure of these materials (vide supra), it can be immediately realized that the basic features of poly(organophosphazenes) are the result of two main contributions. The first one is fixed and is basically related to the intrinsic properties of the -P=N- inorganic backbone, while the second is variable and mostly connected to the chemical and physical characteristics of the phosphorus substituent groups. Skeletal properties in phosphazene macromolecules intrinsically due to the polymer chain are briefly summarized below.

3.1
Skeletal Features

Chain Flexibility

Chain flexibility of the POP skeleton is very high and the corresponding torsional barriers for these macromolecules are estimated to be well below 1 kcal/bond/repeat [451].

As described in several review articles [409, 452–454] and books [10, 13, 15], this is basically due to the inherent features of the d_π-p_π bond in phosphazenes, which allows the permanent overlapping of the $2p_z$ orbital of the skeletal nitrogens with any one of the 3p orbitals of the phosphorus atoms [455]. Such a high chain flexibility generated very low glass transition temperatures in these polymers, which can reach values of about –100 °C when suitable flexible substituent groups (e.g. *n*-butanol) are present on the skeletal phosphorus [274].

Thermal Stability

The phosphazene backbone has a particularly high resistance to thermal treatment and to homolytic scission of the -P=N- bonds, possibly due to the combination of the high strength of the phosphazene bond and its remarkable ionic character [456]. As a consequence, the onset of thermal decomposition phenomena (as detected, for instance, by TGA) are observed at considerably high temperatures for poly[bis(trifluoroethoxy)phosphazene], $[NP(OCH_2CF_3)_2]_n$ [391, 399, 457], for phosphazene copolymers substituted with fluorinated alcohols of different length [391, 399, 457], for polyspirophosphazenes substituted with 2,2′-dihydroxybiphenyl groups [458], and for poly(alkyl/aryl)-phosphazenes [332].

Fire and Flame Resistance, and Self-Extinguishing Properties

A major feature of the polyphosphazene skeleton is its ability to resist fire and combustion due to the inorganic elements constitutive of its structure [44, 387, 388, 459, 460]. Moreover, the action of skeletal nitrogen and phosphorus atoms can be enhanced by inserting additional inorganic elements (F, Cl, Br, J, B, metals, etc.) in the substituent groups [459, 460].

The intrinsic limiting oxygen index (LOI) for certain POPs could be about 60 when the phosphazene chemical structure is based almost exclusively on inorganic elements, decreasing considerably when the organic component in the chemical structure of the side substituents is enhanced [459, 460]. Additional features which may be of potential practical interest in polyphosphazenes are that these polymers can export their inherent fire stability to other macromolecules, for instance by blending processes, thus acting as outstanding flame-retardant additives for commercial organic macromolecules [44, 389, 390, 461–463].

Biomedical Features

Phosphazene polymers can act as biomaterials in several different ways [401, 402, 407]. What is important in the consideration of skeletal properties is that the -P=N- backbone can be considered as an extremely stable substrate when fluorinated alcohols [399, 457] or phenoxy [172] substituents are used in the substitution process of the chlorine atoms of $(NPCl_2)_n$, but it becomes highly hydrolytically unstable when simple amino acid [464] or imidazole [405–407] derivatives are attached to the phosphorus. In this case, an extraordinary demolition reaction of the polymer chain takes place under mild hydrolytic conditions transforming skeletal nitrogen and phosphorus into ammonium salts and phosphates, respectively [405–407, 464]. This opens wide perspectives in biomedical sciences for the utilization of these materials, for instance, as drug delivery systems [213, 401, 405, 406, 464] and bioerodible substrates [403, 404].

Spectral Transparence to UV and Visible Radiation

Due to the special nature of the -P=N- bond present in the phosphazene polymer chain no delocalization of the π electron is allowed in these materials, their resonance being limited within the three P-N-P atomic system [409]. This fact introduces important chemical characteristics to the phosphazene skeleton, i.e. lack of the classic organic double bond reactivity (e.g. halogen or hydracid addition reactions); the impossibility of light- or heat-induced *cis-trans* isomerization reactions on the phosphazene "double bond", and the absence of electric- or thermal-skeletal conductivity. For the same reason, moreover, the phosphazene backbone is completely transparent to visible and deep UV radiation up to 220–230 nm [408–411, 413]. From a spectroscopic and a photochemical point of view these facts account for the fact that any absorption at wavelengths below these values has to be attributed to σ-σ^* transition of the -P=N- skeletal bond [465], while for absorptions at wavelengths longer than 230 nm the spectroscopic features of the substituent groups attached to the phosphorus atoms of the -P=N- inorganic chain have to be invoked [409–411]. This observation, in combination with the great synthetic versatility of polyphosphazenes described above, makes these macromolecules ideal candidates for the preparation of photo-inert or photosensitive materials tailored for particular applications [413].

Two Geminal Substituent Groups Attached at the Skeletal Phosphorus Atoms

The synthetic versatility based on the nucleophilic substitution of the chlorine atoms of $(NPCl_2)_n$ described in Fig. 9 gives the possibility of preparing phosphazene homopolymers bearing nine different classes of possible substituents. Moreover, it is also possible to use two (or more than two) nucleophiles to replace the chlorines of an unique $(NPCl_2)_n$ macromolecule, also using these groups in different relative percentages. In this way, phosphazene s*ubstituent* copolymers [263] are accessible that bear in their chemical structure hetero-substituted -P=N- units (see Fig. 9).

The presence of monomeric units bearing mixed substituents is an important contribution to the disruption of the regular structure of phosphazene homopolymers [274, 409]. From this originates the lack of crystallinity in phosphazene *substituent* copolymers with respect to the corresponding homopolymers, together with the formation of amorphous materials and the onset of elastomeric properties [274, 409]. The larger the structural difference between the substituent groups at the phosphorus, the higher the efficiency of this phenomenon [466]. Furthermore, it has been evaluated, on the basis of simple molecular models, that the distance between two substituent groups geminally substituted to the same phosphorus of the polymer skeleton is about 2.5–3 Å [412]. This distance is sufficiently short to allow the onset of intramolecular interactions between the two phosphorus substituents. These facts open the possibility of forming intramolecular excimers [467–473], of inducing energy [410, 474, 475] or electron transfer [410, 476] processes, and of obtaining hydrogen abstraction phenomena [296, 477] in suitably designed phosphazene macromolecules. Eventually, substituting different groups on the same polyphosphazene skeleton may induce modifications in solvent solubility [478, 479], chemical reactivity [296, 480], and in other very important chemico-physical properties of these materials.

3.2
Substituent characteristics

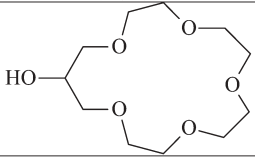
In contrast, considering the characteristics of the substituent groups currently used in the chlorine replacements of polydichlorophosphazene, it can be immediately realized that they can be very variable depending on the chemical structure of the nucleophile selected for these reactions. A list of the preferred chemical compounds usually exploited for the phosphazene substitutional processes is reported in Table 4.

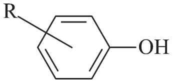
Table 4 shows that the substrates usually involved in the reaction with polydichlorophosphazene belong to the categories of aliphatic or aromatic compounds containing in their own chemical structure free -OH and/or -NH_2 functionalities, which can be easily found on the market in great abundance and at cheap prices.

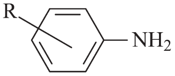
These circumstances being so and given:

1. The large number of possible substituents available for the substitution processes of the chlorine atoms on polydichlorophosphazene [38]
2. The possibility of substituting two or more different groups on the same polyphosphazene skeleton [263], even in different relative percentages, to form phosphazene *substituent* copolymers [399, 457]
3. The possibility, through living cationic polymerization processes, to produce linear *chain* phosphazene copolymers [486]
4. The great ease of polyphosphazene functionalization processes [38]

Table 4 Usual substituent groups in phosphazenes

Type of Substituent	Formula	References
Alcohols		
Aliphatic	$H(CH_2)_x$-OH where x = 1, 2, 3,……12	274,481
Fluorinated	$Z(CF_2)_x$-CH_2OH Z = H or F x = 1, 2, 3, 4,….	399,457
Monomethylated Ethylene Glycols	CH_3-$(OCH_2CH_2)_x$-OH x = 1, 2, 3, …….	273,481
Hydroxylated Crown Ethers		482-484

Phenols		
Phenol and Variably Ring-Substituted Phenols	 where R may be: H, CH_3, C_2H_5, C_7H_9 iso or n; etc. C_6H_5, $C_{10}H_8$ α or β, etc. O-R or CO-Ar; F, Cl, Br, J; CN; CHO, COOR, COOH; OCH_3; OC_2H_5; OC_3H_7, etc.; OH; CF_3 o-dihydroxybiphenyl or binaphthyl $N_2C_6H_5$ 4-Hydroxy-azobenzene	485

Amines		
Aliphatic	$H(CH_2)_x$-NH_2 where x = 1, 2, 3,……12	299
Aromatic	 where R may be: H, CH_3, C_2H_5, C_7H_9 iso or n; etc. C_6H_5, $C_{10}H_8$ α or β, etc.	301

it can be concluded that the number of phosphazene macromolecules accessible in this way is almost infinite, and that the range of properties and potential applications covered by these substrates is extremely large.

3.3
Polymer properties

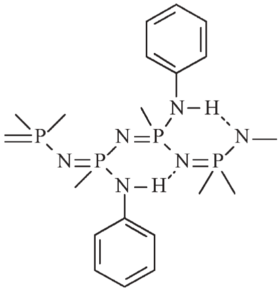
This statement can be proved very easily by considering four different types of general POP properties and their variability as a function of the side substituents on the polymer skeleton, i.e. glass transition temperature (T_g), morphology, solvent solubility and limiting oxygen index (LOI). The values of these parameters are reported in Tables 5–8.

Considering first Table 5, it can be seen that T_g values for the reported poly(organophosphazenes) spanned from very low (–105 °C in the case of poly[bis(*n*-butoxy)phosphazene]) up to very high (+220 °C for poly[tris(2,2′-dioxy-1,1′-binaphthyl)phosphazene]), covering almost all the intermediate temperatures between these two limits. Low T_gs are indicative of very high torsional freedom of the polyphosphazene chain, which is manifested clearly when flexible substituents of reduced bulkiness are used in the substitution

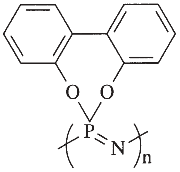
Table 5 Glass transition temperature values for selected poly(organophosphazenes)

Polymer	T_g	References
$[NP(OCH_2CH_2CH_2CH_3)_2]_n$	–105	274
$(NPF_2)_n$	–96	452
$[NP(OCH_2CH_3)_2]_n$	–84	274
$[NP(OCH_3)_2]_n$	–76	40
$[NP(OCH_2CF_3)_2]_n$	–66	274
$(NPCl_2)_n$	–63	452
$\{NP[O(CH_2)_3C_6H_5]_2\}_n$	–47	274
$\{NP[OCH_2(CF_2)_6CF_3]_2\}_n$	–40	487
$[NP(OC_6H_4\text{-p-}n\text{-}C_3H_7)_2]_n$	–34	283
$[NP(OC_6H_4\text{-p-}C_2H_5)_2]_n$	–19	283
$[NP(OC_6H_4\text{-p-}sec\text{-}C_4H_9)_2]_n$	–16	283
$[NP(OC_6H_5)_2]_n$	–8	274
$[NP(OC_6H_4\text{-p-}iso\text{-}C_3H_7)_2]_n$	–0.10	283
$[NP(OC_6H_4\text{-p-}CH_3)_2]_n$	+2	283
$[NP(OC_6H_4\text{-p-}CH_2C_6H_5)_2]_n$	+13,8	488
$[NP(NHCH_3)_2]_n$	+14	452
$[NP(OC_6H_4\text{-p-}SCH_3)_2]_n$	+37	489
$[NP(OC_6H_4\text{-p-}COC_6H_5)_2]_n$	+50	490
$\{NP[OC_6H_4\text{-p-}N(CH_3)_2]_2\}_n$	+60	489
$[NP(OC_6H_4\text{-p-}OH)_2]_n$	+80	491
$[NP(NHC_6H_4\text{-m-}F)2]n$	+80	301
$[NP(NHC_6H_5)_2]_n$	+91	452
$[NP(O_2C_{12}H_8)]_n$	+160	305, 307
$[NP(O_2C_{13}H_8Cl_2)]_n$	+220	306

process of polydichlorophosphazene (e.g. short chain aliphatic alcohols, fluorinated alcohols, etc.). As soon as more rigid substituents are inserted in the phosphazene chain (e.g. one aromatic ring), T_gs start to increase significantly, passing from −34 °C for poly[bis(4-*n*-propylphenoxy)phosphazene] up to +2 °C for poly[bis(4-methylphenoxy)phosphazene]. T_g values are further enhanced as soon as the number of aromatic ring in the phenoxy substituents along the skeleton increases to 2, increasing from +13.8 °C for poly[bis(4-benzylphenoxy)phosphazene] up to +50 °C for poly[bis(4-benzoylphenoxy)phosphazene]. This is the result of the increased rigidity of the substituent inserted in the polymer chain, and may also be manifested with substituents of different nature, such as 4-*N*,*N*′-dimethylamino-phenoxy groups, reported by Haddon [489]. Moving from alkoxyde or aryloxide substituents in polyphosphazenes to aliphatic or aromatic amino derivatives, T_g values are further increased (from +14 °C for poly[bis(methylamino)phosphazene] to +91 °C for poly[bis(anilino)-phosphazene]), basically because of the contribution of two factors: the increased rigidity of the amino substituents passing from aliphatic to aromatic primary amines, and the onset of intramolecular hydrogen bonding [301, 492]. These lead to the formation of the chain structures (see Formula below) that introduce a strong decrease in the skeletal flexibility of the phosphazene polymer backbone and induce a corresponding increase in the T_g of the resulting materials.



Additional lack of chain flexibility is introduced in the polyphosphazene skeleton when polyspirophosphazenes are considered. These materials are obtained by reacting 2,2′-di-hydroxy biphenyl or 1,1′-binaphthyl derivatives with polydichlorophosphazene [305], leading to the formation of polymers having the structure shown in Formula below.



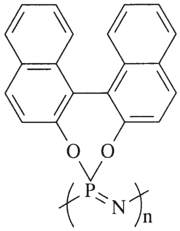


Table 6 Solubility of selected poly(organophosphazenes)

Polymer	Solvent	References
$[NP(OCH_3)_2]_n$	Methanol, o-Dichlorobenzene	493
$[NP(OCH_2CF_3)_2]_n$	Tetrahydrofuran, Acetone, Freon	494
$[NP(OC_6H_5)_2]_n$	Tetrahydrofuran, Dioxane, Benzene, Toluene, Xylene, Dichloromethane, Chloroform	282
$[NP(OC_6H_4\text{-}C_2H_5)_2]_n$	Tetrahydrofuran, Dioxane, Benzene, Toluene, Xylene, Dichloromethane, Chloroform	297
$[NP(OCH_2CH_2OCH_2CH_2OCH_3)_2]_n$	Water	273
$[NP(OGlucosyl)_2]_n$	Water	495
$[NP(OCH_2CH(OH)CH_2OH)_2]_n$	Water	496
$[NP(OC_6H_4\text{-m-}SO_3H)_2]_n$	Water	497,498
$[NP(NHCH_3)_2]_n$	Water	84
$[NP(NHC_2H_5)_2]_n$	Soluble in aqueous acid	499
$[NP(OC_6H_4COOH)_2]_n$	Soluble in aqueous base	499
$[NP(OC_6H_4OH)_2]_n$	Soluble in aqueous base	295

In this case chain mobility is strongly inhibited by the rigid structure of the side phosphorus substituents and the resulting T_gs are exceedingly high for the usual standard of phosphazene macromolecules.

Moving now to solubility parameters, Table 6 reports the solubility of a variety of polyphosphazenes according to the nature of the phosphorus substituent groups present in these macromolecules. As can be seen, inserting nucleophiles with marked hydrophobic character in the phosphazene skeleton (e.g. methoxy-, thrifluoroethoxy-, phenoxy-, etc. substituents), makes the resulting macromolecules predominantly soluble in organic solvents. As soon as the polarity of the side substituents increases (like in methylamino-, polyethyleneoxide- of glucosyl- derivatives) water solubility become accessible. The same holds true when sulfonic acid groups are introduced in aromatic aryloxy-substituted polyphosphazenes, while for polyphosphazenes containing free hydroxylic, carboxylic groups or ethylamine substituents, the solubility is promoted by using alkaline or acid solutions, respectively.

Similarly, Table 7 shows the morphology characteristics of selected polyphosphazenes.

Morphological features for POPs can range from low-temperature elastomers (when aliphatic alkoxy substituents of different length are attached to the polyphosphazene skeleton), to crystalline, film- and fibre-forming materials

Table 7 Morphology of selected poly(organophosphazenes)

Polymer	Morphology	References
$[NP(OCH_3)_2]_n$	Amorphous Polymer Low-Temperature Elastomer	499
$[NP(OC_2H_5)_2]_n$	Elastomer	499
$[NP(OC_3H_7)_2]_n$	Elastomer	499
$[NP(OCH_2CH_2OCH_2CH_2OCH_3)_2]_n$	Elastomer	499
$[NP(OC_4H_9)_2]_n$	Elastomer	499
$[NP(OCH_2CF_3)_2]_n$	Microcrystalline, film- and fiber- forming Polymer	500
$[NP(OC_6H_5)_2]_n$	Microcrystalline, film-forming Polymer	500
$[NP(OC_6H_4COOEt)_2]_n$	Microcrystalline, Film-Forming, Thermoplastic	499
$[NP(OC_6H_5\text{-p-}C_6H_5)_2]_n$	Microcrystalline Thermoplastic	499
$[NP(NHCH_3)_2]_n$	Flexible and Thermoplastic Polymer	499
$[NP(NHC_6H_5)_2]_n$	Glass Amorphous Polymer	499

(for trifluoroethoxy or phenoxy polymers), to microcrystalline thermoplastic materials in the case of poly[bis(4-ethylbenzoatephenoxy)phosphazene], and eventually to amorphous glassy materials when aromatic amines (e.g. aniline) are attached to the polyphosphazene chain.

If we consider the LOI values reported in Table 8, it can be clearly seen that the flame resistance of polyphosphazenes is very high and can reach values above 60 when halogenated phenoxy groups (e.g. 4-bromophenoxy) are attached to the polymer chain. However, enhancement of the carbon content in the materials (i.e. by increasing the percentage of organic substituents in the chain) induces a concurrent decrease in the flame resistance of POPs, which can be depressed to 23.4 in the case of poly[bis(4-*iso*propylphenoxy)phosphazene].

Two additional observations are also possible looking at the LOI numbers reported in the Table:

1. Almost every intermediate value between the above mentioned limits can be obtained just by selecting the appropriate substituent to support on the phosphazene skeleton
2. Even the lowest value of LOI reported in Table 8 for the 4-*iso*-propylphenoxy-substituted POP is still considerably higher than those of the most common organic polymers (17.4 for polyethylene, 17.8 for polystyrene and 18.3 for ABS rubber [283])

Table 8 Limiting oxygen index (LOI) for selected poly(organophosphazenes)

Polymers	LOI	References
$\left[NP\left(OC_6H_4-iso-C_3H_7\right)_2\right]_n$	23.4	283
$\left[NP\left(OC_6H_4-n-C_4H_9\right)_2\right]_n$	23.7	283
$\left[NP\left(OC_6H_4-sec-C_3H_7\right)_2\right]_n$	23.9	283
$\left[NP\left(OC_6H_4-4-C_2H_5\right)_2\right]_n$	25	283
$\left[\left(NP-OC_6H_4-tert-C_4H_9\right)_2\right]_n$	25.2	283
$\left[NP\left(OC_6H_4-4-OCH_3\right)_2\right]_n$	25.5	283
$\left[NP\left(OC_6H_4-n-C_3H_7\right)_2\right]_n$	25.5	283
$\left[NP\left(OC_6H_4-4-CH_3\right)_2\right]_n$	26.4-27	283,284
$\left[NP\left(OCH_3\right)_2\right]_n$	26.5	460
$\left[NP\left(OC_6H_4-3-CH_3\right)_2\right]_n$	28	284,452
$\left[NP\left(OC_6H_5\right)_2\right]_n$	33-33.8	283,284,452,460
$\left[NP\left(OC_6H_4-3-Cl\right)_2\right]_n$	41	284
$\left[NP\left(OC_6H_4-4-Cl\right)_2\right]_n$	43-44	284,452
$\left[NP\left(OCH_2CF_3\right)_2\right]_n$	48	452
$\left[NP\left(OC_6H_4-4-Br\right)_2\right]_n$	65	284

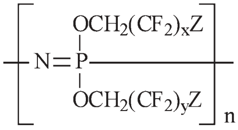
The general conclusion is that the phosphazene macromolecules synthesized and characterized up to now show a large range of properties and that they can potentially be exploited in many different applicative domains.

Of course, not all the phosphazene polymers that have been synthesized are equally important. Many of them, in fact, have a mere academic or speculative interest, and will not be described in this article. A few other classes of POPs, however, do occupy an important place in phosphazene history, and have been seriously considered for industrial development and commercialization. These polymers are basically those in which *the properties of the inorganic -P=N- skeleton overlap to the highest extent those of the phosphorus side substituents.* In the successive sections of this article we will describe in some detail the most important classes of polyphosphazenes that fulfil this condition.

4
Polyphosphazenes Substituted with Fluorinated Alcohols

Fluorinated polyphosphazene materials are very important substrates that were synthesized and developed at the end of sixties [41, 263] both by academic and industrial laboratories. Several industries and government agencies showed an extraordinary interest until the middle of the eighties because of their outstanding mechanical properties [396, 398, 491, 501], low temperature elastomericity [393, 394, 502–507], chemical inertness [41, 392] and reactivity [482, 483, 508–512], water [41] (contact angle value for PTFEP films at about 100 [513]) and oil [502–506] repellency, surface functionability [514–516], flame retardancy [452, 460] and self-extinguishibility [501], thermal stability [391, 517–519], and relative resistance to UV [520], γ-radiation [41, 521] and oxidative processes [522, 523]. These materials were also found to be useful for the preparation of membranes [430, 431, 524–527], fuel hoses and gaskets [528, 529], seals and o-rings [530, 531], channel sealants [532], coatings on fabrics [533, 534], and biomaterials [535–539]. Furthermore, they are presently the object of a renewed interest because of the ease of introducing fluorinated residues in partially substituted phosphazene macromolecules during *substituent* and/or *chain* copolymerization processes (see, as examples references [312, 540]). The whole topic has been reviewed recently [399, 457].

The general structure of polyphosphazenes substituted with fluorinated alcohols is described by the Formula below while the basic structure–property relationships for these substrates are collected in Table 9.



$$\left[N = \underset{OCH_2(CF_2)_yZ}{\overset{OCH_2(CF_2)_xZ}{P}} \right]_n$$

where "x" or "y" may be 1, 2, 3, ……, and Z = H or F

Table 9 General characteristics of fluorinated phosphazene polymers and copolymers

Skeletal properties	Substituent properties	Polymer properties
Chain flexibility	Small dimensions and/ or chain mobility	Low T_g materials
Chain flexibility	One substituent	x=y, Z=F Crystalline materials
Chain flexibility. Two different substituents at the P	Two substituents of different length	x=1, y≠1, Z=F Amorphous elastomers
Presence of P and N	Presence of F	Self-extinguishing materials. Potential flame retardant additives
Presence of P and N	Presence of F	Thermally stable polymers
Presence of P and N at the highest oxidation state	Presence of F. Low tendency to oxidation of the fluorinated substituents	Chemically resistant polymers. Low surface energy. Biocompatibility. Polymers for airspace applications
Presence of P and N	Presence of fluorinated alkoxy groups	Chemical reactivity and properties modification

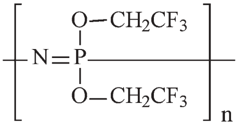
As reported in Table 5 and in other recent publications [399, 491], polymers with very low T_g are expected when the inherent skeletal flexibility of polyphosphazenes is coupled with fluorinated alcohols of low dimensions and/or of high chain mobility. In fact, the T_g values for POPs substituted with fluorinated alcohols vary between –50 °C and –90 °C, confirming the extreme chain mobility of these polymers and the existence in them of very low torsional energy barriers.

As far as the morphology of these materials is concerned, we can distinguish at least two different cases depending on the type of fluorinated alcohol(s) attached to the phosphorus atoms of the polyphosphazene skeleton:

1. x=y=1, 2, 3,...., and Z=H or F
2. x≠y, with x=1 and y=2, 3, 4, and Z=H or F

In the first case only one type of fluorinated alcohol is exploited in the substitution reaction of the reactive chlorines present in polydichlorophosphazene to form polyphosphazene homopolymers. Possible fluorinated substituents explored are: CF_3CH_2O [41], $H(CF_2)_2CH_2O$ [541, 542], $CF_3CF_2CH_2O$ [541], $CF_3CHFCF_2CH_2O$ [543], $CF_3(CF_2)_2CH_2O$ [541, 542, 544, 545], $CF_3O(CF_2)_2CH_2O$ [542], $HCF_2(CF_2)_3CH_2O$ [542], $CF_3(CF_2)_3CH_2O$ [542], $CF_3(CF_2)_5CH_2O$ [542], $HCF_2(CF_2)_5CH_2O$ [542] and $CF_3(CF_2)_6CH_2O$ [95, 487, 542, 545]. Although for some of these materials only marginal studies have been carried out in the determination of their morphology, the general conclusion [546] is that most of them are semi-crystalline materials, possibly because of the similarity of the phosphorus substituents attached to the polyphosphazene skeleton that facilitate chain packing and crystallization processes.

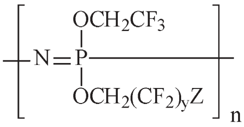
The most known and investigated substrate of this class is poly[bis(trifluoroethoxy)phosphazene], PTFEP, a polymer formally derived by the general formula above by putting x=y=1 and Z=F. The general structure of this compound is shown below.



$$\left[-N{=}\overset{O-CH_2CF_3}{\underset{O-CH_2CF_3}{P}}- \right]_n$$

This polymer is important in the polyphosphazene field, both because it was the first macromolecule of this class early synthesized by H. R. Allcock in 1965 [40, 41] and also because of its extremely interesting properties and applicability [399, 457, 547]. This is a semi-crystalline material [399], with a T_g of −66 °C [392], a T(1) at about 78–80 °C (variable with the thermal heating), and a melting temperature of 242 °C [399]. It is soluble in most common organic solvents (THF, acetone, methylethylketone), but insoluble in alcohols, hydrocarbons, and water. It is able to form transparent tough films [541] and to be drawn in fibres [548]. From a morphological point of view it behaves in a rather complex way [424, 452, 549], passing reversibly from the original spherulitic structure (3D, α-orthorombic) below T(1), as obtained by solvent casting [550], to a more extended mesomorphic arrangement (2D-hexagonal) above T(1) [551], to melt eventually at 242 °C. Cooling below T_m reforms the 2D-hexagonal morphology, while additional cooling below T(1) results in the formation of a new needle-shaped and brittle microcrystalline phase with a 3D-γ-orthorombic arrangement. The whole morphological behaviour of PTFEP is described exhaustively [547].

When x=1 and y=2, 3, 4, ... and Z=H or F, a new class of polyphosphazene substrates is obtained, which derive from the simultaneous substitution of two different fluorinated alcohols of different lengths on the same polydichlorophosphazene macromolecule. The general structure of the substrates is reported below.



$$\left[-N{=}\overset{OCH_2CF_3}{\underset{OCH_2(CF_2)_yZ}{P}}- \right]_n$$

where "y" may be 2, 3, 4,……, and Z = H or F

The presence in these copolymers of hetero-substituted monomeric units randomly dispersed along the phosphazene skeleton brings about the extreme difficulty of the polymeric chains to be packed in regular structures. They lose, therefore, the original stereo-regularity of the parent phosphazene homopolymers (microcrystalline materials), and show only amorphous structures, with sharp decrease in the values of the T_g (collapsed up to about –90 °C) and with the onset of remarkable elastomeric properties [399, 409, 457].

S. H. Rose in 1968 [263, 265] first described the reaction of polydichlorophosphazene with trifluoroethoxy groups coupled with a second fluorinated alkoxy residue of longer chain. During the successive twenty years they were deeply investigated by Horizon Inc. [263, 265, 502–506, 518, 544, 552–554], AMMRC [396, 452, 555–557], NASA [517, 522, 523], The Firestone Tire and Rubber [393, 519, 528, 530, 533, 558, 559], and Ethyl Co. [507, 560, 561] for the applications described above (vide supra).

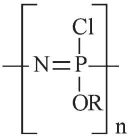
A new series of properties are expected for polyphosphazenes when the percentage of inorganic elements inherently present in the -P=N- skeleton is artificially enhanced by introducing fluorinated alcohols as side phosphorus substituents. This facilitates their application in different fields.

The first phenomenon observed is the improved resistance of these materials to combustion, in a way that they may be classified as intrinsically self-extinguishing substrates. For instance, the LOI value for PTFEP is reported to be 48 [452], which is much higher than reported for classical organic plastics [283], while phosphazene fluoroelastomers have been considered as fire-retardant materials since the very beginning of their preparation and utilization [562]. Similarly to aryloxy- and arylamino- substituted POPs [389, 390] (vide infra), it may be expected that the flame-resistance properties of phosphazene fluoroelastomers could be successively exported to stabilize organic macromolecules when blended with these materials.

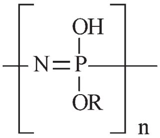
An additional consequence of the heavy presence of fluorinated substituents in phosphazene fluoroelastomers is their remarkable thermal stability, strictly correlated to the high inertness of the C–F bonds present in the side fluoroalkoxy substituents. The thermal behaviour of PTFEP, for example, has been investigated by a variety of scientists [391, 563–567] under different experimental conditions. From these investigations it seems that the processes undergone by the polymer under thermal treatment are basically depolymerization reactions forming low molecular weight cyclic oligomers (basically trimers and tetramers $[NP(OCH_2CF_3)_2]_{3,4}$ [564]), accompanied by random scission phenomena that take place at weak points statistically distributed along the polyphosphazene skeleton [565, 566].

Similarly to PTFEP, phosphazene fluoroelastomers proved to be rather stable to thermal treatments up to 175 °C [560, 561], while for temperatures above this value degradation phenomena start to be relevant.

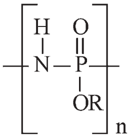
Also for these substrates, chain scission is believed to start from weak sites having the structure shown in Formula below [391], which possibly derived from the incompleteness of the chlorine atom substitutional processes in the



$\left[-N=\overset{\displaystyle Cl}{\underset{\displaystyle OR}{P}}-\right]_n$



$\left[-N=\overset{\displaystyle OH}{\underset{\displaystyle OR}{P}}-\right]_n$



$\left[-\overset{\displaystyle H}{N}-\overset{\displaystyle O}{\underset{\displaystyle OR}{\overset{\|}{P}}}-\right]_n$

parent polydichlorophosphazene with fluorinated nucleophiles, and are thought to be able to induce polymer chain scission and degradation with severe decrease in the molecular weight of the materials. These reactive units seem to be the major factor in the determination of the successive thermal history of phosphazene fluoroelastomers.

From literature data it clearly appears that three strategies are of importance in enhancing the thermal stability of these materials:

1. The possibility of reducing the number of weak points randomly distributed along the polyphosphazene skeleton by using different types of transition metal complexes as polymer stabilizing species [568–575], according to the general stabilization mechanism reported below using Zn/hydroxyquinolate complex as an additive [568, 570] (Fig 12)

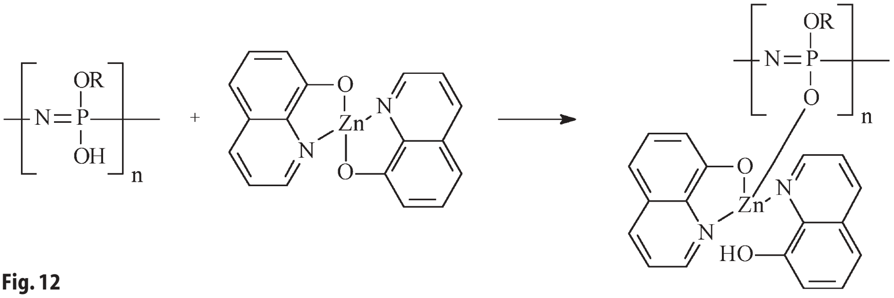
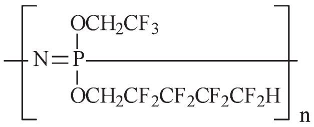


Fig. 12

2. The presence of an appropriate compounding [560, 561], which is generally obtained by reinforcing polymers with clay, carbon black, silica, etc.
3. The possibility of reticulating the materials by carefully introducing additional substituent groups in the polymer during the synthetic process (1–2% or less), prone to undergo selected reactions (e.g. allylic double bonds [576–579]), and/or by addition of appropriate external additives (e.g. sulfur [578] or hydroperoxides [531, 576–578, 580]) to these polymers

The mixed substituent polyphosphazene shown in Formula below is an example [391]. In the typical formulation:

Polyphosphazene	100 parts
Coated silica	30 parts
Magnesium oxide	6 parts
Antioxidants	2 parts
Peroxide	1 part



$$\left[-N=\overset{OCH_2CF_3}{\underset{OCH_2CF_2CF_2CF_2CF_2H}{P}}- \right]_n$$

it shows a service life of about 1000 h at 150 °C, which decreases to 300 h at 175 °C and falls to 120 h when the polymer is thermally treated at 200 °C.

The presence of fluorinated alcohol substituents in polyphosphazenes has relevant implications also as far as the chemical stability and reactivity of these substrates is concerned.

In fact, fluorinated polyphosphazenes are usually considered to be extremely stable towards chemical agents and aggressives due to the presence of C–F bonds in the side phosphorus substituents. PTFEP, for instance, appears to be completely insensitive to several, most common, solvents (aliphatic and aromatic hydrocarbons, alcohols and water), to acids (e.g. acetic acid), and to bases (e.g. pyridine and concentrated NaOH solutions), although some decomposition could be observed in triethylamine and in concentrated H_2SO_4 [41]. Phosphazene fluoroelastomers, moreover, are known to be completely insoluble in aromatic solvents [533] and petroleum-resistant materials [502–506, 552].

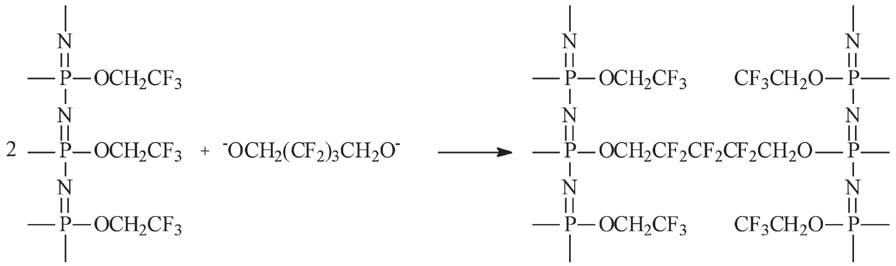


Fig. 13

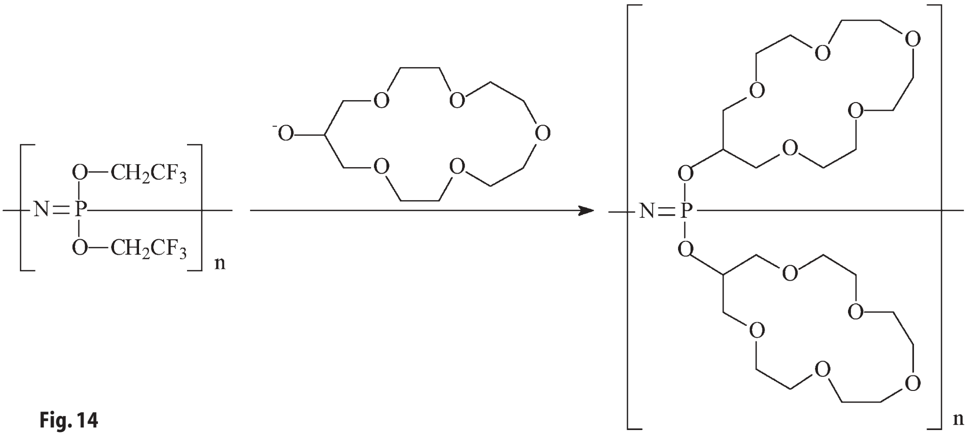


Fig. 14

The same fluoroalkoxy substituents, however, are able to enhance substitutional reactivity of fluorinated polyphosphazenes by originating methatetical exchange reactions on polymers in the presence of new nucleophiles and under appropriate experimental conditions. Thus, a series of exchange reactions at phosphorus atoms bearing the trifluoroethoxy substituents in PTFEP have been described by H. R. Allcock [508] (Fig. 13), Cowie [482, 483] (Fig. 14), and Ferrar [509] (Fig. 15), while surface modification of PTFEP films were reported by Allcock [514, 515] (Fig. 16 or 17) and by Lora [516] (Fig. 18).

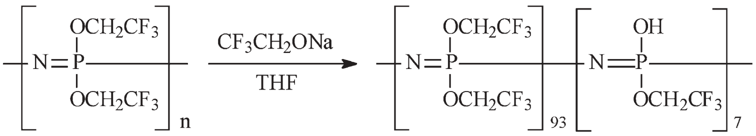


Fig. 15

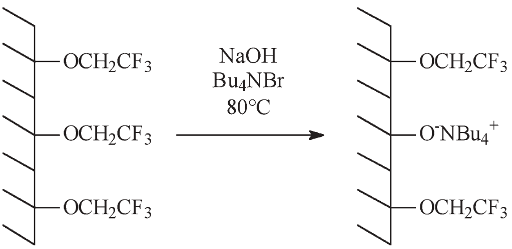


Fig. 16

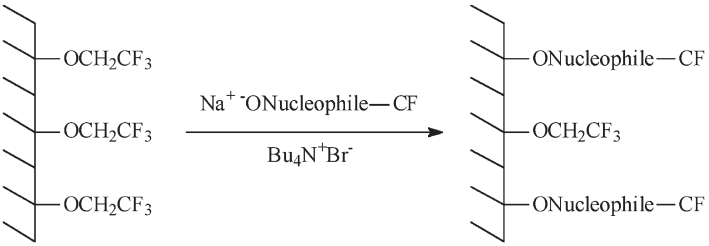


Fig. 17

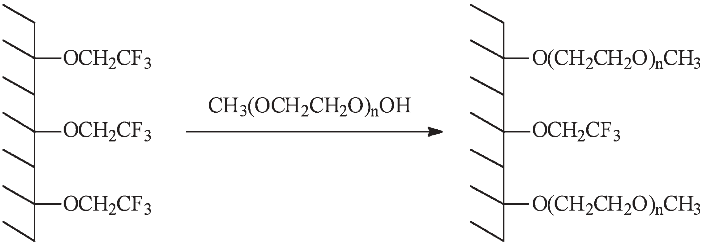


Fig. 18

These reactions allowed a light crosslinking reaction of PTFEP to occur (providing an alternative way to prepare phosphazene fluoroelastomers [508]); permitted the introduction of free hydroxyl groups in fluorinated polyphosphazenes and the successive preparation of hybrid materials through the sol-gel approach [512, 581]; led to the synthesis of new electric conducting polymers [482, 483]; and offered the possibility of deeply modifying both adhesion properties and hydrophilicity of the PTFEP films [514–516].

In conclusion, polyphosphazenes containing fluoroalkoxy groups as side phosphorus substituents constitute one of the most relevant class of macromolecules of this family and have attracted remarkable interest in the past because of their outstanding properties and wide range of applicability, especially in low and high temperature domains, and have received renewed interest in more recent times [399, 457].

5
Aryloxy-Substituted Polyphosphazenes

Fire retardancy is an often occurring theme in phosphazene chemistry and numerous reviews have focused on this subject over the years [10, 44, 387, 393, 396, 582]. In this article we will treat only aspects related to the flame-retardant properties of aryloxyphosphazene copolymers, which are the subject of the greatest number of applications.

Polyphosphazenes are intrinsically fire-resistant materials because of the presence of phosphorus and nitrogen in the polymeric chain. A low flammability is thus one of the most important properties of polyphosphazenes, particularly of the polyaryloxyphosphazenes **I**, in which R may be H, halogens, and alkyl or alkoxy groups.

$$[N{=}P(OC_6H_4R)_2]_n \qquad \textbf{I}$$

These polymers are self-extinguishing in air with LOI between 24 and 65 (see Table 8). Their thermal stabilities (300–400 °C) are typical of organic polymers, but the char yields are higher (~30%), and a low heat release capacity is observed [582].

The development relative to the flame-retardant properties of polyphosphazenes has been principally centred around the aryloxyphosphazenes copolymers **II**.

$$[N{=}P(OC_6H_4R)_x(OC_6H_4R')_{2-x}]_n \qquad \textbf{II}$$

Small amounts of reactive sites, e.g. *o*-allylphenoxy, eugenol groups (0.1–5 mole%) are generally incorporated in these copolymers to assist crosslinking reactions, which can be attained by using peroxides, sulfur or radiation [578, 583].

Table 10 Glass transition temperatures and limiting oxygen index values for selected aryloxyphosphazenes copolymers [284, 584, 585]

$[N{=}P(OC_6H_4R)_x(OC_6H_4R')_{2\text{-}x}]_n$

x	R	R′	T_g	LOI
1	H	*p*-CH_3		27
	H	*p*-C_2H_5	−18	28, 27
	H	*p*-OCH_3	+0.74	25
	H	*p-iso*-C_3H_7		25.8
	H	*p*-O-*n*-C_4H_9	−11.2	23.7
	H	*p-sec*-C_4H_9	−8.1	25.9
	H	*p-tert*-C_4H_9	+22	26
	m-CH_3	*p*-CH_3		27
	p-C_2H_5	*p*-O-*n*-C_4H_9	−16.9	24.8
	p-OCH_3	*p*-CH_3	+5.9	25.3
	p-OCH_3	*p*-C_2H_5	−3.76	24
	p-OCH_3	*p-iso*-C_3H_7	+3	26
	p-OCH_3	*p-tert*-C_4H_9	+24.1	25
	p-OCH_3	*p*-O-*n*-C_4H_9	−5.03	24
	p-OCH_3	*p*-C_9H_{19}	2.23	25
	p-O-*n*-C_4H_9	*p*-iso-C_3H_7	−9.47	23.9
0.5	*p*-OCH_3	H		25.8
0.4	p-OCH_3	H		28.7

The properties and applications are very variable according to the nature and the ratio of the substituents, the crosslinking reaction and the formulation; but one always finds a good fire resistance resulting in a high oxygen index, a low smoke and low toxicity/corrosivity of off-gases. Some LOI values and T_g for the unfilled copolymers are reported in Table 10. The corresponding polymers ranged from rigid-like materials to elastomers with T_g between −18 and +24 °C.

Among these copolymers, the two structures **III** and **IV** are of particular interest. They have been commercially available for a limited period of time from the Ethyl Corporation and Atochem Societies under the trademarks EYPEL A and ORGAFLEX A, respectively. Polymer **III** is more elastomeric (T_g=−18 °C [10]) than polymer **IV** (T_g=−5 °C [584]).

$$[N{=}P(OC_6H_5)(OC_6H_4\text{-}p\text{-}C_2H_5)]_n \qquad \textbf{III}$$

$$[N{=}P(OC_6H_4\text{-}p\text{-}OCH_3)(OC_6H_4\text{-}p\text{-sec-}C_4H_9)]_n \qquad \textbf{IV}$$

After formulation with a flame retardant filler such as alumina trihydrate $Al_2O_3{\cdot}3H_2O$, hydrated silica or calcium carbonate, a peroxide curing agent and a chemical blowing agent such as azobis formamide, these polymers can be used to form materials with an excellent combination of physical, mechanical and flame-retardant properties for the following end uses: thermal and acoustic insulation foams [586, 587], cushioning foams [384], electric cable insulation and jacketing [588, 589], and fire resistance in a wide range of areas from floor covering to coatings for electronic devices [590]. Oxygen indicies of 28–48 were obtained.

As an example, a foam prepared from **III**, alumina trihydrate as a filler, benzoyl peroxide as a curing agent, and azobis formamide as a blowing agent, leads to a material with an oxygen index of 48, a long-term stability to at least 150 °C, and a smoke density about one fifth that of a commercial foam [284].

Aryloxyphosphazene copolymers can also confer fireproof properties to flammable materials when blended. Dieck [591] have used the copolymers **III**, and **IV** containing small amounts of reactive unsaturated groups to prepare blends with compatible organic polymers crosslinkable by the same mechanism which crosslinks the polyphosphazene, e.g. ethylene-propylene and butadiene-acrylonitrile copolymers, poly(vinyl chloride), unsaturated urethane rubber. These blends were used to prepare foams exhibiting excellent fire retardance and producing low smoke levels or no smoke when heated in an open flame. Oxygen index values of 27–56 were obtained.

Flexible foams with oxygen index values of 40–53 were also prepared by the same authors from blends of copolymer **IV** and a silicone elastomer, (a phenyl vinyl polydimethylsiloxane) [592].

We can finally note the preparation of blends from an elastomeric and an non-elastomeric copolymers **II** (x=1) [585]. These blends can be used to prepare films, fibres or coatings, and foams that exhibit excellent fire resistance and produce low smoke levels.

6
Polyphosphazenes as Ionic Conductors

The classical example of a solid organic polymer electrolyte and the first one found is the poly(ethylene oxide) (PEO)/salt system [593]. It has been studied extensively as an ionically conducting material and the PEO/lithium salt complexes are considered as reference polymer electrolytes. However, their ambient temperature ionic conductivity is poor, on the order of 10^{-8} S cm^{-1}, due to the presence of crystalline domains in the polymer which, by restricting polymer chain motions, inhibit the transport of ions. Consequently, they must be heated above about 80 °C to obtain isotropic molten polymers and a significant increase in ionic conductivity.

In these complexes, the cations coordinate with the oxygen atoms of the backbone and, under the influence of an electrical potential, they are transferred from an oxygen atom to another through the amorphous region of the polymer assisted by the segmental motion of the polymer backbone.

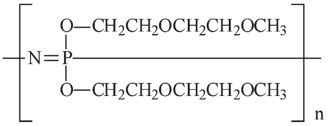
Table 11 Structure and properties of phosphazene-based ionic conductors

Skeletal properties	Substituent properties	Polymer properties
Flexibility	Low dimensions or great flexibility of the substituents	Low-temperature elastomers $-60\ ^\circ C < T_g < -100\ ^\circ C$ Amorphous
Insulating skeleton	Able to coordinate metals	Ionic conductivity

Therefore, an ideal polymer electrolyte must be flexible (associated with a low T_g), completely amorphous, and must have a high number of cation-coordination sites to assist in the process of salt solvatation and ion pair separation (see Table 11). A review on this subject has been recently published by Inoue [594].

6.1
Polymer Electrolytes Based on Poly[bis(methoxyethoxyethoxy)phosphazene]

The first polyorganophosphazene to be studied as polymer electrolyte was poly-[bis(methoxyethoxyethoxy)phosphazene] (MEEP), **V**, synthesized by Allcock [272] in 1984.

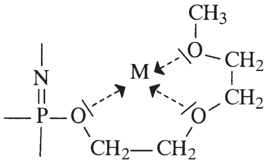


$$\left[-N=\overset{\displaystyle O-CH_2CH_2OCH_2CH_2OCH_3}{\underset{\displaystyle O-CH_2CH_2OCH_2CH_2OCH_3}{P}}- \right]_n$$

V

This polymer, which is characterized by a very low T_g(−84 °C) and an absence of crystallinity, forms complexes with a large variety of salts, e.g. MSO_3CF_3 (M=Li, Na, Ag), $Sr(SO_3CF_3)_2$, $LiBF_4$, $LiCF_3COO$, LiSCN and $LiClO_4$ [595].

It is believed that in these systems the cations coordinate with the oxygen atoms of the methoxyethoxyethoxy side groups as indicated in Formula below, thus facilitating ion-pair separation.



Lithium triflate was the most used salt and the temperature dependence of the electrical conductivity of a series of $(LiSO_3CF_3)_x$/MEEP complexes with a ratio metal cation/MEEP repeat unit $0.125 \le x \le 0.25$ was studied. It was shown that the conductivity and T_g increase with x, whereas a higher T_g lowers the conductivity. Consequently the conductivity passes through a maximum, which was found for x=0.167 [272].

Therefore, the temperature dependence of the conductivity of complexes $(LiX)_{0.167}$/MEEP (X=CF_3COO, SCN, SO_3CF_3, BF_4) were also compared. The highest conductivity was obtained with BF_4, and the activation energies for ion transport were found to be similar, suggesting that the mechanism for ion motion is independent on the salt. The lithium transport number, which varies from 0.3 to 0.6, depending on the complexed salt, does not change with concentration.

Similarly, the temperature dependence of the conductivity of (triflate salts)$_{0.25}$/MEEP complexes (the cations being Sr, Na, Li, Ag) has been studied. It was shown that the conductivity increases in the order Sr<Na≈Li<Ag.

The conductivity of the LiX/MEEP complexes, which is in the range of 2.7×10^{-5} S cm^{-1} for X=SO_3CF_3,increases to 5×10^{-5} and 6×10^{-5} S cm^{-1} for X=AsF_6 and CLO_4, respectively [10].

Complexes of MEEP with alkali-metal polyiodide salts MEEP$_x$,MI$_n$ (M=Li, Na, x=2–16, n=1–9) were also prepared by reaction of the complexes MEEP$_x$,MI with I_2 vapour. Complexes with higher iodine content show high conductivity, for example 4×10^{-3} S cm^{-1} at 30 °C for MEEP,NaI$_{15}$. The variation of the conductivity of the MEEP$_x$,NaI$_n$ complexes as a function of salt concentration is characterized by the absence of a maximum, indicating that the conduction mechanism is less reliant on the segmental motion than in the other MEEP/salt complexes. This mechanism is thought to involve an iodide transfer between polyanions [596].

The conductivity of the $LiSO_3CF_3$/MEEP complexes, although higher than those of the lithium salts/PEO complexes (3 orders of magnitude higher), are still inadequate for practical devices. This was the reason for the attempt at increasing these values by synthesizing a series of poly(organophosphazene)s with longer linear ethyleneoxy [597], mixtures of linear alkoxy and methoxyethoxyethoxy [278] or branched ethyleneoxy [597] side chains. The maximum ionic conductivity obtained for all these $LiSO_3CF_3$/polymer systems are reported in Tables 12–14.

In the case of linear oligoethyleneoxy side groups (Table 12), the maximum conductivity increases with the length of the side group from 2.6×10^{-5} S cm^{-1} for x=1 to 4.8×10^{-5} S cm^{-1} for x=6. After x=6, the conductivity decreases probably on account of the formation of microcrystallites.

A Raman vibrational spectroscopy study of a series of complexes $[N{=}P(O(CH_2CH_2O)_xCH_3)_2]_n/LiSO_3CF_3$ (x=1, 2, 5) with oxygen/lithium concentration ratios of 10/1 and 40/1 (oxygen atoms from the side chains) was undertaken by Frech [598]. By using the analysis of the δ_s (CF_3) mode in the triflate anion, it was shown that for x=1, 2, 5 at the 40/1 concentration the percentage of free ions increases with the length of the side chain (2–24%) and the ion-pairs predominate (98–71%). For the same complexes at the 10/1 concentration there are no free ions observed and the triple ions $[Li_2Tf]^+$ predominate (~95%).

Table 12 Maximum conductivity of the $[N{=}P(O(CH_2CH_2O)_xCH_3)_2]_n/LiSO_3CF_3$ systems at 25 °C

$[N{=}P(OR)_2]_n$/lithium triflate systems $[R{=}(CH_2CH_2O)_xCH_3]$						
x	1	2	3	4	6	8
Conductivity ($\sigma \times 10^5$ S cm^{-1})	2.6	2.7	3.2	3.7	4.8	4.5

The mechanism of ion transport in the MEEP/metal salt complexes has been modelled on the PEO transport mechanism, that is to say in terms of jumps of the metal ion between the ether oxygen nuclei of the side groups, the nitrogen atoms of the backbone being not involved in the coordination [599].

However, a recent study of the lithium ion complexation with ^{15}N-labelled polyphosphazenes, including ^{15}N-MEEP, was performed by Luther [600]. The data obtained for the MEEP/$LiSO_3CF_3$ system by NMR, IR and Raman spectroscopies do not support that assumption, and show that the coordination of the lithium ion also occurs with the nitrogen nuclei.

The introduction in the polymer of non-coordinative $\text{-O-}(CH_2)_x\text{-}CH_3$ side chains (Table 13) leads to a decrease of the conductivity from 1.29×10^{-5} for x=2 to 1.9×10^{-6} S cm^{-1} for x=9, which shows that a great number of donor sites is primordial for the ion transport [278].

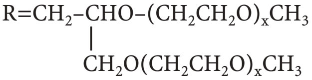
The conductivity obtained for the polymers bearing branched side chains (Table 14) are similar to those obtained with the linear oligoethyleneoxy ana-

Table 13 Maximum conductivity of the $[N{=}P(O(CH_2CH_2O)_2CH_3)(O(CH_2)_xCH_3)]_n/LiSO_3CF_3$ systems at 25 °C

$[NP(OR_1)(OR_2)]_n$/lithium triflate systems*; $R_1{=}(CH_2CH_2O)_2CH_3$; $R_2{=}(CH_2)_xCH_3$								
x	2	3	4	5	6	7	8	9
Conductivity ($\sigma \times 10^5$ S cm^{-1})	1.29	1.06	0.91	0.72	0.54	0.37	0.21	0.19

* In these polymers, the ratios of the different side groups determined by ^1H NMR spectroscopy are approximately 1

Table 14 Maximum conductivity of the polyphosphazenes with branched ethyleneoxy sidechains/lithium triflate systems at 25 °C

$[N{=}P(OR)_2]_n$/lithium triflate systems;  $R{=}CH_2{-}CH(O{-}(CH_2CH_2O)_xCH_3)(CH_2O(CH_2CH_2O)_xCH_3)$				
x	0	1	2	3
Conductivity ($\sigma \times 10^5$ S cm^{-1})	0.16	1.2	3.7	3.9

logues. However, they have the advantage of a higher dimensional stability, since they can be cast as thin films whereas MEEP is a viscous gum.

Polyphosphazenes bearing crown ethers (12-crown-4, 15-crown-5 and 18-crown-6) as single or as mixed substituents with trifluoroethoxy or methoxyethoxyethoxy groups were synthesized by Cowie [601, 602] and Allcock [484] and their conductivity studied because it was shown that the incorporation of crown ether molecules into a polymer electrolyte could increase their ionic conductivity. In these macromolecules, the crown ether units were linked to the backbone through oxymethylene spacer groups.

The conductivity of the single-substituent polymer complexed with lithium triflate or lithium perchlorate is not measurable ($<10^{-8}$ S cm^{-1}). The conductivity of the co-substituted polyphosphazenes with methoxyethoxyethoxy groups in the ratio methoxyethoxyethoxy/crown ethers 3/1 complexed with $LiClO_4$ are 6×10^{-6}, 1.2×10^{-5} and 1.1×10^{-5} S cm^{-1} for 12-crown-4, 15-crown-5 and 18-crown-6, respectively [10]. (The highest conductivity found for the co-substituted polyphosphazenes with trifluoroethoxy groups and 12-crown-4 with a six methylene spacer, complexed with $LiBF_4$, is 10^{-5} S cm^{-1} at room temperature).

The ionic conductivity of the MEEP/metal salt systems was improved by adding α-Al_2O_3 particles into the complexes. Chen-Yang [603] obtained a conductivity $\sigma=9.7\times10^{-5}$ S cm^{-1} for the composite polymer complex MEEP/$LiClO_4$/2.5 wt% Al_2O_3. The cation transport number was in this case 0.77.

To improve the dimensional stability of the oligoethyleneoxy phosphazene/metal salt complexes, some attempts have been reported which concern the chemical modification of the parent polymers, their chemical or radiation cross-linking, or the use of blends.

An example of this approach concerns the incorporation in the polymer of aryloxy groups. The two structures **VI** and **VII** have been synthesized both containing the same 50/50 molar ratio of aryloxy and oligoethyleneoxy groups.

$[N{=}P(OC_6H_5)(O(CH_2CH_2O)_xCH_3)]_n$

VI (x = 2, 3, 7.3)

$[N{=}P(OC_6H_4\,p\text{-}O(CH_2CH_2O)_xCH_3)_2]_n$

VII (x = 2, 3, 7.3)

The gum-like co-substituted polymers **VI** have lower T_g than polymers **VII**, which form excellent films. The highest ionic conductivity at 25 °C reported for the **VI** and **VII**/$LiN(SO_2CF_3)_2$ complexes are 3.5×10^{-5} and 2.4×10^{-5} S cm^{-1} for **VI** (x=7.3) and **VII** (x=7.3) complexed with 0.328 and 0.5 mol salt/polymer repeat unit, respectively [604].

Gel electrolytes were also prepared by Allcock [605] from co-substituted polyphosphazenes with various ratios of methoxyethoxyethoxy and trifluoroethoxy side groups, lithium triflate and propylene carbonate. These gel electrolyte systems have a better mechanical stability than MEEP. The highest ionic conductivity obtained was 7.7×10^{-4} S cm^{-1} at 25 °C for a gel containing 37.5% of polymer with 80% and 20% of methoxyethoxyethoxy and trifluoroethoxy side groups, respectively, 12.5% of lithium triflate and 50% of propylene carbonate.

A chemical cross-linking of MEEP was obtained by Shriver [606] by using polyethylene glycol (PEG) dialkoxide, which also forms polymer salt complexes. The cross-linked polymers were prepared by substituting a part (1 and 10 mole%) of the methoxyethoxyethoxy ethanol by PEG in the synthesis of MEEP. Contrary to the MEEP, the amorphous polymers obtained do not flow and are stable even at 140 °C. The maximum ionic conductivity at 30 °C, obtained after complexation with $LiSO_3CF_3$, are 4.1×10^{-5} S cm^{-1} for MEEP/PEG 1% complexed with 6.4 wt% salt and 3×10^{-5} S cm^{-1} for MEEP/PEG 10% complexed with 8.9 wt% salt. These values are comparable with those obtained with the parent linear polyphosphazenes.

The dimensional stability of MEEP/$LiSO_3CF_3$ complexes were also improved without loss of conductivity by irradiation with γ-rays [607, 608], or by UV irradiation, with or without photo-initiator [609].

MEEP/$(LiX)_n$ electrolytes, which can be processed into thin films without physical treatment or addition of a second polymer, have been obtained by Abraham [610]by dissolving MEEP and $LiAlCl_4$ in acetonitrile. The complexes MEEP/$(LiAlCl_4)_{0.13}$ and MEEP/$(LiCLO_4)_{0.25}$ have almost the same conductivity at 25 °C, 1.2×10^{-5} and 1.7×10^{-5} S cm^{-1}, respectively.

Dimensionally stable MEEP-based polymer electrolytes were also obtained by the same authors forming composites with poly(ethylene oxide) PEO, poly(propylene oxide) PPO, poly(ethylene glycol diacrylate) PEGDA and poly(vinylpyrrolidinone) PVP. Several complexes MEEP/PEGDA-$(LiX)_n$, MEEP/PVP-$(LiX)_n$ ($X=BF_4$, ClO_4) and MEEP/PEO-$(LiX)_n$, MEEP/PPO-$(LiX)_n$ [$X=BF_4$, ClO_4, AsF_6, SO_3CF_3, $AlCl_4$, $N(SO_2CF_3)_2$] have been studied [611].

The maximum conductivity at 25 °C, 6.7×10^{-5} S cm^{-1}, was obtained for the complex MEEP/PEO-$[LiN(SO_2CF_3)_2]_n$ containing 55 wt% of MEEP, 45 wt% of PEO and a 0.13 Li/O mole ratio. A similar conductivity 6.5×10^{-5} S cm^{-1} was obtained for the complexes MEEP/$[LiN(SO_2CF_3)_2]$.

The study of the MEEP/PEO-$(LiX)_n$ and MEEP/PPO-$(LiX)_n$ complexes, ($X=BF_4$, ClO_4) by ^7Li NMR spectroscopy, DSC and X-ray diffraction showed that they were multiphase with amorphous MEEP and crystalline PEO phases. Strong cation–anion association effects were also observed [612].

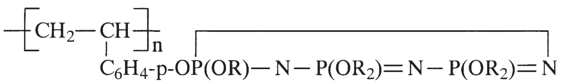
The sol-gel technique was also used to prepare solid electrolytes containing MEEP, triethoxysilane (TEOS) and lithium triflate. Homogeneous, transparent and mechanically stable materials have been obtained by Guglielmi [611] from a partially hydroxylated MEEP and TEOS, which after doping with $LiSO_3CF_3$ exhibited a conductivity in the range 3×10^{-6} S cm^{-1} at 60 °C.

Similar materials were synthesized by Kim [613] from MEEP and TEOS. The highest conductivity 4.6×10^{-5} S cm^{-1} at room temperature was obtained for 10 wt% of TEOS and 15 wt% of $LiSO_3CF_3$. The conductivity decreases with increasing of the amount of TEOS, contrary to the T_g, which is not significantly affected. Phase separation between MEEP and TEOS seems to be responsible for this behaviour.

6.2
Phosphazene Electrolytes with Alternative Structures

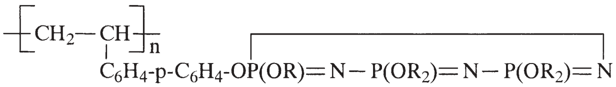
Other research has been performed with the objective of determining how changes in the structure of the polymer affect the solid ionic conductivity. Some examples are given below.

The polystyrene derivatives with pendant oligo(oxyethylene)cyclotriphosphazenes **VIII** and **IX** were synthesized by Inoue [614, 615] and the ionic conductivity of their complexes with $LiClO_4$ investigated. The maximum ionic conductivity obtained for these complexes are reported in Table 15.



$$-\!\left[CH_2-\underset{C_6H_4\text{-}p\text{-}OP(OR)-N-P(OR_2)=N-P(OR_2)=N}{\underset{|}{CH}}\right]_n\!-$$

VIII



$$-\!\left[CH_2-\underset{C_6H_4\text{-}p\text{-}C_6H_4\text{-}OP(OR)=N-P(OR_2)=N-P(OR_2)=N}{\underset{|}{CH}}\right]_n\!-$$

IX

$R = CH_3\text{-}(OCH_2CH_2)_x\text{-}$ $x = 2, 3$

The authors explain these high conductivities by an ion transport through a conducting phase consisting of a number of oxyethylene chains. Being obtained from polystyrene derivatives, these values also indicate that the flexibility of the backbone is not essential to achieve a high conductivity.

The ionic conductivity of complexes of the polymer **VIII** n=3 with potassium, sodium and cesium thiocyanates were also determined. The conductivity of the polymer complexed with CsSCN is in the order of 10^{-4} S cm^{-1} at 30 °C, and 10^{-3} S cm^{-1} at 90 °C [616].

Polymers with $-CH_2O(CH_2CH_2O)_n-$ spacers (n=1, 2) between the polystyrene backbone and the pendant penta(methoxyethoxyethoxy)cyclotriphosphazene

Table 15 Maximum conductivity of the polystyrene derivatives **VIII**, **IX**/$LiClO_4$ systems

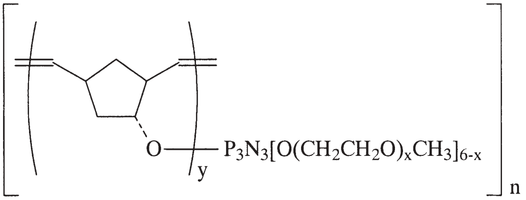
Polymers **VIII**, **IX**/$LiClO_4$ systems			
n		2	3
Conductivity ($\sigma \times 10^5$ S cm^{-1})	Polymer **VIII**	1.8 (30 °C) 25.7 (100 °C)	1.8 (30 °C) 37.8 (100 °C)
	Polymer **IX**	12 (90 °C)	11 (60 °C)

were also synthesized. A maximum conductivity close to 10^{-4} S cm^{-1} at 50 °C was obtained for n=2 [617].

Complexes $LiClO_4$/crown ethers (18-crown-6 and 12-crown-4) and $LiClO_4$/azacrown (1,4,8,11-tetra(2-methoxyethyl)-1,4,8,11-tetraazacyclotetradecane) were added to the polymer **VIII** (n=3) [618]. All these additives improve the conductivity of the complex **VIII**/$LiClO_4$, the azacrown still being more effective. The highest conductivity (12.6×10^{-5} S cm^{-1} at 30 °C, 96.2×10^{-5} S cm^{-1} at 90 °C) was obtained for the system **VIII**/$LiClO_4$/azacrown with a ratio Li/O=0.05.

Based on the behaviour of the glass transition temperature of the **VIII**/$LiClO_4$/additives systems, it was suggested that the Li^+ ions interact preferentially with the CH_3-$(OCH_2CH_2)_3$- chains in the first case (crown ethers), and with azacrown in the second. This result also suggests that in case of azacrown, the anions are mainly responsible for conduction.

The polynorbornenes **X** bearing cyclotriphosphazenes with -$O(CH_2CH_2O)_x$-CH_3 (x=1, 2, 3, 7.2) side groups have been prepared via ring opening metathesis polymerization (ROMP) and complexed with $LiSO_3CF_3$ and $LiN(SO_2CF_3)_2$ (10–60% molar ratios) by Allcock [619, 620].



X x = 1, 2, 3; y = 1; x = 7.2, y = 1-2

The mechanical properties of **X** depend partly on the length of the oligoethyleneoxy groups. The polymers are solid for x=1, highly viscous gums for x=3 and elastomers for x=7.2. The maximum conductivity of these complexes at 30 °C are reported in Table 16. Gel electrolytes have also been obtained by adding propylene carbonate (PC) (10–50 wt%) to these polynorbornene de-

Table 16 Maximum conductivity of polynorbornenes bearing cyclotriphosphazenes/lithium salt systems at 30 °C

Conductivity of polymers **X**/metal salt systems ($\sigma\times10^5$ S cm^{-1})			
x	y	**X**/$LiSO_3CF_3$	**X**/$LiN(SO_2CF_3)_2$
1	1	Not detectable	Not detectable
1	2	0.5	2.2
1	3	0.9	2.1
1–2	7.2	3.8	4.9

rivatives. The conductivity of the **X**/$LiSO_3CF_3$/PC and **X**/$LiN(SO_2CF_3)_2$/PC systems are two orders of magnitude higher than the solvent-free complexes. At 30 °C, the maximum conductivity is 1.9×10^{-3} S cm^{-1} for 50 wt% of PC and $LiN(SO_2CF_3)_2$, and 1.2×10^{-3} S cm^{-1} for 50 wt% of PC and $LiSO_3CF_3$.

Multi-armed polymers with a cyclotriphosphazene core **XI** and **XII** have been synthesized from the reaction of polyethylene glycol monomethyl ethers with acid chlorides of hexakis(3,5-dicarboxyphenoxy) and hexakis(4-carboxyphenoxy) cyclotriphosphazenes. Their complexes with $LiClO_4$ were investigated, and their maximum conductivities are reported in Table 17 [621].

$$N_3P_3[OC_6H_4\text{-}p\text{-}C(=O)O(CH_2CH_2O)_nCH_3]_6 \qquad n = 11.8$$

XI

$$N_3P_3[OC_6H_3\text{-}m,p\text{-}(C(=O)O(CH_2CH_2O)_nCH_3)_2]_6 \qquad n = 3,\ 7.2,\ 11.8$$

XII

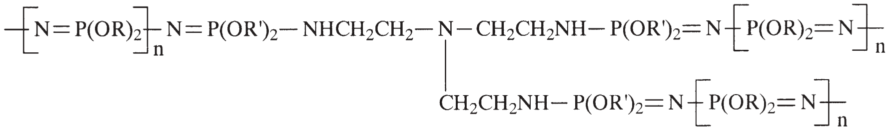
In the systems with polystyrene derivatives **VIII, IX** and multi-armed cyclotriphosphazenes **XI, XII** the conductivity seems to be dependent on the relative concentrations of inter- and intra-molecular complexes (Table 17).

Three other MEEP-type polyphosphazenes were synthesized by Allcock [622]. Polymers **XIII** and **XIV** were prepared via the cationic "living" polymerization of phosphoranimines, and polymers **XV** by ring opening polymerization.

$$-\!\left[N{=}P(OR)_2\right]_n\!-N{=}P(OR')_2-NHCH_2CH_2NH-P(OR')_2{=}N-\!\left[P(OR)_2{=}N\right]_n\!-$$

XIII

n = 540



$$-\!\left[N{=}P(OR)_2\right]_n\!-N{=}P(OR')_2-NHCH_2CH_2-N(CH_2CH_2NH-P(OR')_2{=}N-\!\left[P(OR)_2{=}N\right]_n\!-)-CH_2CH_2NH-P(OR')_2{=}N-\!\left[P(OR)_2{=}N\right]_n\!-$$

XIV

n = 20, 60, 180

$R = CH_3(OCH_2CH_2)_2\text{-}$ $\qquad R' = CF_3CH_2\text{-}$

$[N{=}P(OR)_2]_n$ $\qquad R = N_3P_3(OR')_5(O\text{-}CH_2\text{-}CH_2)_3\text{-}$ $\qquad R' = CH_3\text{-}(O\text{-}CH_2\text{-}CH_2)_2\text{-}$ **XV**

Table 17 Maximum conductivity of multiarmed cyclotriphosphazene/$LiClO_4$ systems

$[N{=}P(OR)_2]_n/LiClO_4$ systems				
$R{=}4\text{-}CH_3\text{-}(OCH_2CH_2)_n\text{-}OC(O)C_6H_4$-**XI**		$R{=}3,5\text{-}(CH_3\text{-}(OCH_2CH_2)_n\text{-}OC(O))_2C_6H_3$-**XII**		
n	11.8	3	7.2	11.8
Conductivity ($\sigma \times 10^5$ S cm^{-1})	1.7 (30 °C) 26 (90 °C)	0.4 (30 °C) 10.0 (90 °C)	1.8 (30 °C) 29.1 (90 °C)	4.0 (30 °C) 60.1 (90 °C)

Table 18 Maximum conductivity of the polymers **XIII-XV**/lithium triflate systems at 25 °C

Polymer	**XIII**	**XIV**	**XV**
Conductivity ($\sigma \times 10^5$ S cm^{-1})	2.38	3.70 (n=60) 2.70 (n=180)	4.3

The variations of the conductivity of the corresponding complexes with salt concentration with lithium triflate were similar to those of MEEP, with a passage through a maximum when this concentration increased. The maximum conductivities of these complexes are reported Table 18.

The maximum ionic conductivities of the complexes **XV**/$LiAsF_6$ and **XV**/$LiClO_4$ at the same temperature are 5×10^{-5} and 6×10^{-5} S cm^{-1}, respectively [10]. **XV** is completely amorphous from –100 to +100 °C. Its T_g is –74 °C in the absence of salt. Its dimensional stability is considerably higher than that of the linear MEEP with a similar molecular weight, and it forms free-standing films.

Poly[bis(amino)phosphazenes] **XVI** and a series of polyphosphazenes bearing Methoxy-ethoxyethoxy and alkylamine side groups **XVII** have been synthesized and complexed with $LiClO_4$ by Chen-Yang [623, 624].

$$\left[N{=}P[NH(CH_2)_xCH_3]_2\right]_n \quad x = 4,5$$

XVI

$$\left[N{=}P[O(CH_2CH_2O)_2CH_3]_x[NH(CH_2)_mCH_3]_y\right]_n$$

m = 2, x = y = 1; x = 0.8, y = 1.2
m = 3, x = y = 1; x = 0.8, y = 1.2
m = 4, x = 0.8, y = 1.2; x = 0.6, y = 1.4
m = 5, x = y = 1; x = 0.4, y = 1.6

XVII

The maximum conductivities of **XVI** /$LiClO_4$ complexes at 30 °C are 1.5×10^{-7} (x=4) and 2.2×10^{-8} S cm^{-1} (x=5) for a molar ratio $LiClO_4$/PN=0.2. The FTIR and

NMR spectra of these polymer electrolytes indicate an interaction of the side chain nitrogen with the lithium ions. The co-substituted polymers **XVII** have a T_g between –50 and –65 °C and form amorphous polymer electrolytes with $LiClO_4$ which give free-standing films with a good dimensional stability. It was shown that the conductivity increases with the percentage of $-O(CH_2CH_2O)_2CH_3$ side groups. The highest conductivity at 30 °C, 2.2×10^{-5} S cm^{-1}, was obtained for m=4, x=0.8, y=1.2 and a ratio $LiClO_4$/PN=0.25.

Based on the synthesis of polyphosphazenes and of diblock copolyphosphazenes by the living cationic polymerization of phosphoranimines [237, 241], the triblock poly(phosphazene-ethylene oxide) copolymer **XVIII** was synthesized by Allcock [223].

$$-\!\!\left[(RO)_2P{=}N\right]_m\!\!-P(OR)_2HN-(CH_2CH_2O)_n-CH_2CH_2NH(RO)_2P-\!\!\left[N{=}P(OR)_2\right]_m\!\!-$$

$$R = CH_2CF_3$$

XVIII

XVIII shows in DSC a melting transition at 38 °C for the PEG segment. The conductivity at room temperature of the complexes of **XVIII** with $LiSO_3CF_3$ (5–10 wt%) are between 8×10^{-6} and 2×10^{-5} S cm^{-1}.

Polyphosphazenes sulfonates **XIX** with the anion covalently attached to the polymer are a new class of cation conductors that have been synthesized by Shriver [625]. They were obtained by reaction of $NaOC_2H_4SO_3Na$ with an excess of polydichlorophosphazene in the presence of 15-crown-5, followed by the reaction of the partially substituted product with the sodium salt of poly(ethylene glycol methyl ether). The conductivity at 80 °C of the polymer with x=1.8, m=7.22 is 1.7×10^{-6} S cm^{-1}. This low conductivity can be attributed to an extensive ion pair formation between the sodium and sulfonate ions.

$$[N{=}P(O(CH_2CH_2O)_mCH_3)_x(OCH_2CH_2SO_3)_{2-x}]_n$$

XIX

In conclusion, polymer electrolytes based on phosphazene backbone and containing ether side chains are, after complexation with alkali metal salts, among the highest ionically solvent-free polymer salt complexes, with conductivities in the order of 10^{-5}–10^{-4} S cm^{-1}. However, these conductivities are still below the value of 10^{-3} S cm^{-1}, which is considered to be the minimum for practical applications. Therefore the design of new polyphosphazenes electrolytes with a higher conductivity and also a higher dimensional stability still remains a challenge for future researchers.

7
Polyphosphazene Biomaterials

As already stressed in the Introduction to this article, the use of organic plastics as biomaterials is expected to evolve in a natural way towards the utilization of increasingly higher quantities of inorganic polymers, because of the limitations inherently present in the first class of materials which seem to be absent or reduced in the second type of macromolecules.

In this section we will describe the general principles that determined the biological applications of polyphosphazenes in different domains, putting an effort into establishing their specific utilization on the basis of structure–property relationships. This argument has been covered by several different review articles in the past [400–406, 626] and has been recently highlighted by H. R. Allcock [627] and E. Schacht [407].

Polyphosphazenes can be considered as "biomaterials" in several different ways, depending on the type of utilization one can predict for these substrates. In this regard, we will consider three different topics concerning water-soluble POPs and their hydrogels, bioerodible POPs for drug delivery systems and for tissue engineering, and the surface implications of POP films.

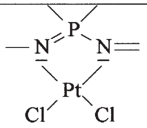
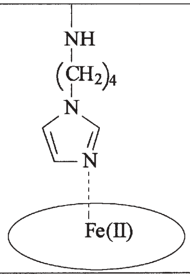
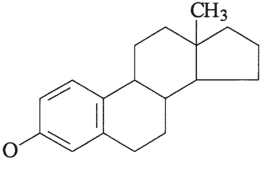
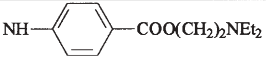
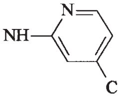
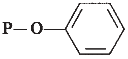
As already reported in Table 6, the solubility of phosphazene polymers is strongly influenced by the nature of the substituent groups attached at the phosphorus atoms along the -P=N- skeleton. Water-solubility, for instance, can be induced in polyphosphazenes by using strongly polar substituents (e.g. methylamine [84], glucosyl [495], glyceryl [496], polyoxyethylene monomethylether [273] or sulfonic acid [497, 498] derivatives), or may be promoted by acids or bases when basic (amino substituents like ethylamine [499]) or acid (e.g. aryloxy carboxylate [499] or aryloxy hydroxylate [295]) substituents are exploited.

Water-soluble polyphosphazenes have been extensively investigated because of their potential use for vehiculating molecules of therapeutic relevance in human bodies. Early papers by H. R. Allcock in this area dealt with phosphazenes *substituent* copolymers containing methylamino groups as water-solubilizing agents in a percentage ranging between 80 and 90% of the available sites in the phosphazene backbone, while the remaining P–Cl reactive groups were replaced by suitable bioactive molecules, as reported in Table 19.

Thus polyphosphazenes bearing $PtCl_2$ anticancer agents were reported in 1976 [628–630]; in 1979 water-soluble polyphosphazenes containing pendent imidazolyl groups were described that were able to complex Fe(II) and Fe(III) porphyrins in the attempt to produce synthetic analogues of myoglobins and hemoglobins [631, 632]; polymers functionalized with steroid moieties were reported in 1980 [633], and some local anaesthetics water-solubility were synthesized in 1982 [634, 635, 638].

Table 19 also describes polyphosphazenes bearing oligopeptide side chains (Gly-Pro-Gly and Gly-Val-Ala tripeptides) [636], potentially useful for tissue engineering, and polymers bearing *N*-acetylglycine substituents [637]. The

Table 19 Water soluble polyphosphazenes

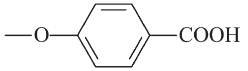
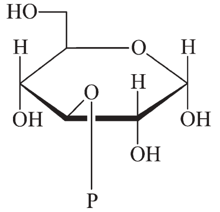
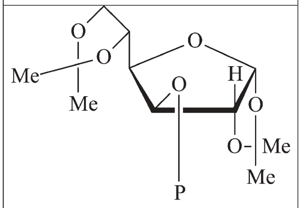
Skeletal Properties	1st Substituent	2nd Substituent	Final Polymer
Two Substituent Groups Attached to the Same Phosphazene Skeleton	-NHCH$_3$		Anticancer Platinum Complexes[628-630]
			Heme and Iron Porphyrins[631,632]
			Steroids[633],
		 	Local Anhestetics[634,635]
	 P-OCH$_2$CF$_3$	O—$\boxed{\text{Spacer}}$—Gly-Pro-Gly O—$\boxed{\text{Spacer}}$—Gly-Val-Ala	Oligopeptides side Chains[636]
	P-OCH$_2$CH$_2$OCH$_3$	P-NHCOCH$_2$NHCOCH$_3$	Polymers Carrying Bioactive Agents[637]

antibacterial or antifungal activity of water-soluble polyphosphazenes has been investigated [639].

More recently, some water-soluble polyphosphazenes have been used to prepare hydrogels by controlled reticulation under a variety of conditions, in the attempt at using them in tissue engineering or in the preparation of biological systems containing trapped drugs or biologically active molecules (e.g. enzymes, human cells, etc.). The release of these species under controlled experimental conditions was the main aim of these investigations. The resulting polyphosphazene hydrogels are reported in Table 20.

Poly[bis(methylamino)phosphazene], for instance, has been radiation crosslinked [640] for the preparation of phosphazene-based membranes. MEEP, a

Table 20 Polyphospazene hydrogels

Skeletal Properties	Phosphazene Substituent	Polymer Properties
Skeletal Flexibility.	$-NHCH_3$	Membranes[640]
	$-OCH_2CH_2OCH_2CH_2OCH_3$	Dimensionally stable[480,606-611,641,642] Drug Delivery Systems[643,644]
Skeletal Flexibility. Two Substituent Groups Attached to the Same Phosphazene Skeleton	 $-OCH_2CH_2OCH_2CH_2OCH_3$	pH Responsive Hydrogels[645]
	 $-OCH_2CH_2OCH_2CH_2OCH_3$ or $NHCH_3$	Hydrogels[646]
	 $-OCH_2CH_2OCH_2CH_2OCH_3$ or $NHCH_3$	

polymer originally prepared as a solid state polymeric electrolyte [272, 273] (vide supra), could be crosslinked under a variety of conditions [480, 606–611, 641, 642] to form highly hydrophilic, dimensionally stable, materials. Additional polyphosphazene matrices having polyethyleneoxides monomethylether residues with longer chains or branched structures as phosphorus substituents have been also prepared and investigated [647, 648]. These hydrogels were tested first for the diffusion release of dyes [643], and later it was demonstrated that they possess a lower critical solution temperature (LCST), whose value in some cases is very close to human body temperature [644]. This fact allows the polymers to contract and precipitate when heated at a temperature above LCST, while being soluble when cooled below this temperature. As a consequence, potential applications in drug release or retention as a function of temperature could be predicted for these materials. Finally, enzyme immobilization in polyphosphazene hydrogels was achieved by Allcock [649], who succeeded in trapping amidohydrolase in MEEP matrices crosslinked by ^{60}Co γ-irradiation. The interesting aspect of these hydrogels was that the trapped enzyme retained a high activity (80% of the original value) even after substrate irradiation.

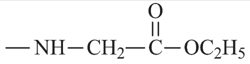
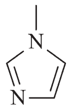
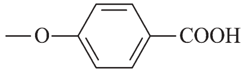
Poly[(4-carboxylatophenoxy)(methoxyethoxyethoxy)phosphazene] copolymers of variable compositions were synthesized by Allcock [645] in 1996. These polymers were found to be soluble in alkaline solutions. When crosslinked (by γ-rays or by addition of $CaCl_2$ to the polymer solution) the resulting hydrogels were found able to contract or expand as a function of the pH of the solution and their utilization as pH-responsive materials for drug delivery systems could be envisaged.

Additional polyphosphazene hydrogels deal with polymers in which glucosyl side groups are co-substituted with trifluoroethoxy, phenoxy, methylamino or methoxyethoxyethoxy moieties [646].

A different approach to polyphosphazene-based drug delivery systems deals with hydrolytically unstable phosphazene substrates, able to degrade in a controlled way under physiological conditions in human body. A list of these bioerodible substrates is reported in Table 21.

As reported elsewhere in this article, the polyphosphazene skeleton usually proved to be highly inert to chemical aggressives. Starting from the end of seventies [464, 650] there was a series of papers in which it was clearly

Table 21 Polyphosphazene-based bioerodible materials

Skeletal Characteristics	Substituents	Polymer Features
Skeletal Biocompatibility. Two Substituent Groups Attached to the Same Phosphazene Skeleton. Hydrolytical Instability	 $-\mathrm{NH}-\mathrm{CH_2}-\overset{\displaystyle O}{\overset{\|}{\mathrm{C}}}-\mathrm{OC_2H_5}$ Glycine or Lower Alkyl Aminoacid Esters[464,650-653]	Hydrolytically Unstable Polymers. Bioerodible Materials. Drug Delivery Systems. Tissue Engineering
	 Imidazole[654-657]	
Skeletal Biocompatibility. Hydrolytical Instability	Glycolic Esters or Lactic Esters[658]	Hydrolytically Unstable Polymers. Bioerodible Materials
	Glyceryl[496]	Hydrolysis in 720 hs at 37°C
	Glucosyl[495,646]	Very poor Hydrolytic Instability
Skeletal Biocompatibility		Microincapsulation Processes[401,403,404,659-663]. Immunoadjuvant Polymer[403,664-670]

indicated that the presence on polyphosphazene substrates of simple aminoacids esters [464, 650–653], imidazole [654–657], or glycolic or lactic acid esters [658] is able to induce hydrolytic instability [627] in the -P=N- skeletal units.

The observed degradation of the macromolecules transforms the P and N atoms of POPs into phosphates and ammonia, respectively, i.e. into species that are biocompatible and can be metabolized and excreted when present in moderate concentration [627]. The entity of the described degradation phenomena seems to depend not only on the nature of the phosphorus substituents (amino acids, imidazole, etc.) but also on the relative percentage of possible co-substituent groups on the polyphosphazenes, their bulkiness and their hydrophilicity. The crucial step in this process seems to be correlated with the possibility of hydrolytically generating skeletal units of the structure shown in Fig. 19, which rapidly convert into phosphazane intermediates [671] able to induce the degradation of the polymer chain [464, 652, 672]. Other chemical groups like glyceryl [496] or glucosyl [495, 646] appear to be much less effective in inducing the hydrolytic instability of POPs.

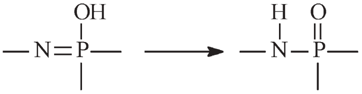


Fig. 19

These discoveries generated a lot of effort over the successive 25 years in the preparation of especially designed drug delivery systems for the controlled release of radioactive progesterone [654], colchicine [656], naproxen [657, 673, 674], mitomycin C [675–677], inulin [678], trimethoprin [657], succinylsulfathiazole [657], ethacrynic acid [653], and steroids [633], regardless of whether these drugs are physically trapped in polyphosphazene matrices, or chemically bonded to the polymer skeleton.

Concurrent with these investigations, polyphosphazene matrices, functionalized with aminoacid esters or with imidazole groups, became of importance because of their tissue engineering aspects in bone regeneration [655, 656, 679], treatment of periodontal diseases [657], and nerve reconstruction problems [680–682] in which the remarkable biocompatibility of POP matrices was coupled with their tuneable biodegradability.

The last important topic concerning the use of POP bioerodible materials deals with poly[bis(4-carboxylatophenoxy)phosphazene], PCPP [683–687]. This polymer is very important not only for the preparation of bone or tooth regeneration composites [688], but also as a micro-encapsulant of drugs [401, 659, 660], vaccines [403, 404, 661, 662], and proteins [663] under very mild experimental conditions due to the possibility of crosslinking it by the action of $CaCl_2$ solutions, according to the scheme in Fig. 20. The reticulation reaction could be reversed very easily by treating the phosphazene gel with NaCl physiological solutions, thus inducing the release of the trapped species.

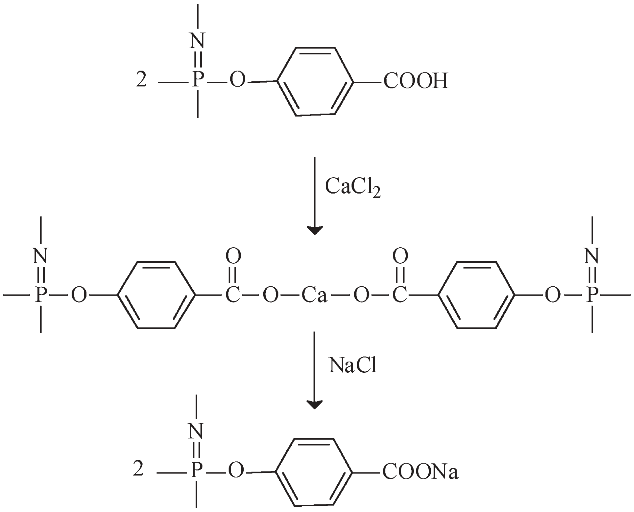


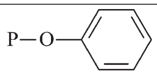
Fig. 20

The same polymer was later shown to possess striking immunoadjuvant features [403, 664–670], i.e. to be able to enhance the immunologic response of the body to the stimulus of an antigen.

The third topic in polyphosphazene biomaterials that will be described in this article concerns surface implications. One of the major problems in the utilization of polyphosphazenes in solid state is their exploitation in the construction of implantable devices, for which good physical properties, minimum biological response, and good resistance to fungal or bacterial colonization may be required.

For these goals several POPs with inert surface characteristics have been considered in the past, as reported in Table 22. As can be seen, the polyphosphazenes involved in this research are mostly substituted with phenoxy or with fluoroalkoxy groups, which are substituents able to impart hydrophobic characteristics to the surface films of these materials. Thus polyphosphazenes substituted with fluoroalkoxy, ring-substituted aryloxy or arylamino groups were first tested by Wade for intramuscular implantation in rats [689]. Penton explored the possibility of using fluoroelastomers containing trifluoroethoxy and superior fluorinated alcohols for mammalian implantation [538]. Reichert investigated the influence of molecular motion (both skeletal and side chain) on the thrombogenesis [537], while Gettleman invented a new crosslinked (by the action of di- or tri- acrylates) composite for elastomeric denture liners [539, 690–696]. Fluoroelastomer utilization for lined denture was also proposed by May [535], while Joung used crosslinked fluoroelastomers for catheter coatings [536, 580]. An additional application of elastic polyphosphazenes deals with cardiovascular problems. In this context, the elasticity of the exploited materials could be obtained by exploiting flexible side phosphorus substituents in a random distribution along the -P=N- backbone and by light crosslinking of the

Table 22 Surface implications in polyphosphazenes: surface inertness

Skeletal Properties	Substituent Properties	Final Polymer Features
Chain Flexibility. Presence of P and N	 P—O— $P\text{-}OCH_2CF_3$	Inert Polymers, with Excellent Mechanical Properties, and Low Surface Energy Suitable for Implantation Purposes[689]
Chain Flexibility. Presence of P and N. Two Substituents on the Same Phosphazene Skeleton	$P\text{-}OCH_2CF_3$ $P\text{-}O\text{-}CH_2(CF_2)_xCF_2H$	Mammalian Implantation[538]
		Effect of Chain and Substituent Mobility on Thrombogenesis[537]
		Soft Denture lines[535,539,690-696]
	Fluorinated Alcohols	Catheter Coatings[536,580]
	Random Distributed Substituents. Flexible Substituents. Light Crosslinking $P\text{-}OCH_2CF_3$ $P\text{-}O\text{-}CH_2(CF_2)_xCF_2H$ $P\text{-}OCH_2CF_3$ PCH_2SiMe_3 $P\text{-}OC_6H_5$ $P\text{-}OC_6H_5\text{-}p\text{-}C_2H_5$	Hydrophobic or Hydrophilic Polymers with Excellent Mechanical Properties and Flexibility, Tunable Surface Energy for Cardiovascular Applications. Blood Compatibility[697]

polymeric substrates. All these arguments, including blood compatibility, have been recently reviewed [697].

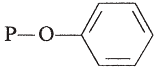
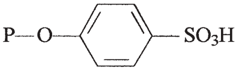
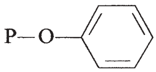
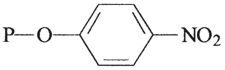
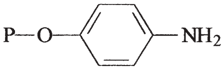
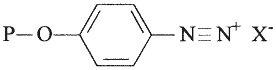
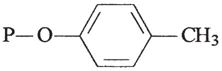
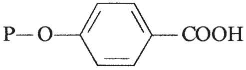
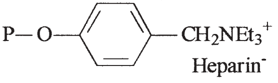
The modification of the surface properties of polyphosphazene films could be achieved in several different ways, and the most important types of modifications carried out over the years are reported in Table 23.

The first example deals with poly[bis(trifluoroethoxy)phosphazene], PTFEP, film, whose surface is intrinsically hydrophobic but can be converted to hydrophilic by the action of NaOH in dioxane at 80 °C in the presence of tetrabutylammonium bromide [514, 515], or by metathetical exchange of trifluoroethoxy moieties with variable types of alkoxides groups [482, 483, 515] (vide supra).

The surface of aryloxy-substituted polyphosphazenes can be modified by a variety of chemical reactions, such as:

a. Sulfonation to enhance surface hydrophilicity of aryloxy-substituted POPs, and to provide the possibility of forming surface hydrogels [698]; nitration to insert -NO_2 chemical groups on the surface of poly[bis(phenoxy)phosphazene] films; these functions were successively exploited for a number of reactions such as reduction to -NH_2 to achieve the surface linkage of proteins and enzymes [699], and diazotization of the amino groups for the surface insertion of cathecolamine units through coupling processes at the diazo groups [700].

Table 23 Surface implications in polyphosphazenes: surface modification by chemical reactions

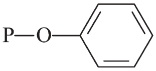
Phosphazene Substituent Groups	Substituent Modification Reactions	Features of the Resulting Polymer Film Surfaces
P-OCH_2CF_3	P-OH or P-O^- NBu_4^+	Hydrophilic Surfaces with Enhanced Biocompatibility and Adhesion Properties[482,483,514,515]
		Surface Hydrophilicity and Surface Hydrogels[698]
	  	Protein and Enzymes Surface Linkage[699]. Surface Insertion of Cathecolamines[700]
		Hydrophilic Surfaces Suitable for Additional Functionalization Reactions[701]
		Antithrombogenic Surfaces[290,702].

b. Surface oxidation of methyl groups in poly[bis(4-methylphenoxy)phosphazene] to form carboxylate moieties [701] and their successive utilization for additional functionalization reactions; the same polymer was also studied for the surface insertion of the blood anticoagulent Heparin to prepare polyphosphazene films with anti-thrombogenic properties through the preventive modification of the methyl groups with *N*-bromo-succinimide (NBS) [290, 702].

Polyphosphazene films could also be modified very easily by grafting organic polymers onto the surface using chemical, photochemical or γ-radiolytic processes. In almost all cases these studies led to the increase in the surface hydrophilicity and biocompatibility of the phosphazene films without depressing their bulk features.

According to examples reported in Table 24 the surface hydrophilicity of PTFEP films could be considerably enhanced by methatetically exchanging trifluoroethoxy moieties with polyethyleneoxide groups in a chemical way [516] (vide supra). The use of γ-rays led Allcock to graft MEEP onto the film surface of several outstanding organic macromolecules, significantly decreasing their surface hydrophobicity [703]. Using the same technique, Lora succeeded in the preparation of phenoxy- and/or trifluoroethoxy-substituted POPs with grafted

Table 24 Surface implications in polyphosphazenes: surface modification by grafting reactions

Starting Polymers	Grafted Polymers	Resulting Materials
$P-O-CH_2CF_3$	$CH_3(OCH_2CH_2)_nOH$[516] ($M_w = 5000$)	Hydrophilic Surfaces
Polypropylene Poly(vinyl chloride) Poly(ethylene Terephthalate) Polycarbonate(bisphenol-A) Poly(methyl methacrylate)	Poly[bis(methoxyethoxyethoxy) phosphazene] MEEP[703]	Hydrophilic Surfaces
 or $P-O-CH_2CF_3$	Poly(vinyl pyrrolidone)[704,705]; poly(N,N-dimethylacryl amide)[706]	Hydrophilic Surfaces
$P-O-CH_2CF_3$	Dimethylaminoethyl Methacrylate. Successive Surface Functionalization with Heparin[707]	Antithrombogenic
$P-O-CH_2CF_3$	Poly(N,N-dimethyl Acrylamide)[513]	Hydrophilic surfaces

poly(vinyl pyrrolidone) [704, 705], poly(*N*,*N*-dimethylacrylamide) [706] and poly(*N*,*N*-dimethylaminoethyl methacrylate) [707]. This last polymer was further manipulated to bind heparin antithrombogenic units [707].

Finally, surface properties of PTFEP were modified photochemically by light-induced grafting of poly(*N*,*N*,-dimethylacryl amide) onto the film surface of this material to achieve a remarkable enhancement of its hydrophilicity [513].

As a conclusion of this section we would like to stress once again the strategic importance of POPs as biological substrates that appear to be one of the most probable “break-throughs” for a wide-range industrial and commercial utilization of poly(organophosphazenes).

8
Photo-active and Photo-inert Polyphosphazenes

The behaviour of phosphazene polymers upon irradiation with UV-vis light has been the object of several review articles during the last 20 years [408–413, 708] and for this reason it will be not treated in detail in this paper. The short summary of the topic presented here deals with the consideration that the photochemical behaviour of POPs originates in the combination of the transparency of the skeleton of these materials (up to well inside in the UV range of the spectrum [409, 413, 453, 709]) with the great synthetic versatility of polyphosphazenes [15], which allows the insertion of many different chromophoric species.

The general structure of the polyphosphazenes investigated can be described by Formula below in which only one type of substituent has been attached to the polyphosphazene chain.

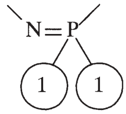


Table 25 describes the features of the -P=N- skeleton of POPs, and the spectroscopic and photochemical properties of the substituent groups, whose addition determines the final characteristics of the resulting polymers. As can be seen, the first series of polyphosphazenes considered for photochemical studies contained substituent groups (e.g. trifluoroethoxy, ethoxy and phenoxy [520]) that showed absorptions at very short wavelengths (240–280 nm), comparable with the UV limit of the skeletal transparency. These materials proved to be considerably inert to UV irradiation, giving rise only to crosslinking phenomena when irradiated in solid state using light of 254 nm [520].

When compounds with more complicated chemical structures were taken into consideration as possible polyphosphazene substituents, the polymers started to show spectroscopic absorptions at wavelengths longer than 240–280 nm. As a consequence, significant photochemical activity started to be observed for POPs, intimately correlated to the photochemical features of these groups.

Thus, phosphazene polymers substituted with 4-tolylamino [710, 711] or β-naphthoxy [711] substituents showed photo-activity originating from the first excited singlet state of these chromophores, while for phosphazene substituents containing free carbonylic groups in their chemical structure (e.g. poly[bis(4-benzoylphenoxy)phosphazene] [475, 712]) the photochemical activity was found to derive from the first excited triplet state of these substituents. In both cases, skeleton demolition and degradation of the polymers were observed upon irradiation of air-saturated solutions of the materials, while photoreticulation took place in the absence of molecular oxygen or in solid state [409–411, 413]. For arylamino-substituted polyphosphazenes, moreover, a remarkable solvent effect was observed when carrying out photolysis in solvents of increasingly high electron affinity (e.g. CH_2Cl_2, $CHCl_3$ and CCl_4) [302]. Similar results have been found during irradiation of poly(methyl/phenyl)phosphazene, as reported a few years later by Hoyle [413, 713, 714].

Substituent groups on a polyphosphazene chain containing mobile hydrogen atoms (4-isopropylphenol [715, 716], 4-benzylphenol [293, 718], etc.) showed a completely different photochemical reactivity both in solution and in solid state under accelerated conditions, based mostly on the light-induced oxidation of these groups and radical formation reactions.

Table 25 Photochemical properties of selected poly(organophosphazenes)

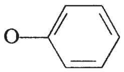
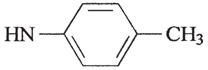
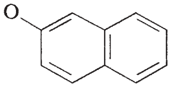
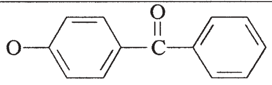
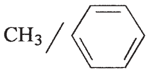
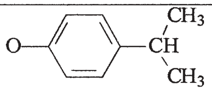
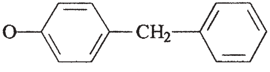
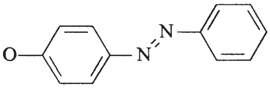
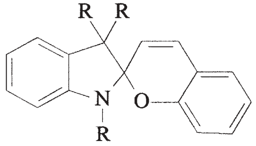
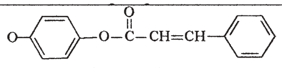
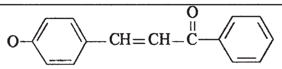
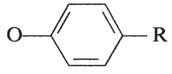
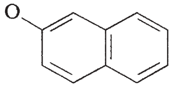
Skeletal Properties	Type of Substituent	Substituent Properties	Final Polymer Properties
Spectral Transparence Starting from 230 nm	OCH_2CF_3 Trifluoroethoxy,  Phenoxy or OCH_2CH_3 Ethoxy	Spectral Transparence in the UV range	Inertness upon Long Wavelength Irradiation; Photocrosslinking Phenomena in Solid State[520]
Spectral Transparence Starting from 230 nm	 4-Toluidino  β-Naphthoxy	Substituent Photoactive from the First Excited Singlet State	Polymers Photochemically Active from the First Excited Singlet State of the Phosphorus Substituents[302,710,711]
Spectral Transparence Starting from 230 nm	 4-Benzoylphenoxy	Substituent Active from the First Excited Triplet State	Polymers Photochemically Active from the First Excited Triplet State of the Phosphorus Substituent[712]
Spectral Transparence Starting from 230 nm	 Methyl/Phenyl	Spectral Transparence in the UV range	Polymers Photochemically Active from the First Excited Singlet State of the Phosphorus Substituents[413,713,714]
Spectral Transparence Starting from 230 nm	 4-Isopropylphenoxy	Photooxidable Groups; Presence of Labile Tertiary Hydrogen Atoms	Photooxydation and Photoreticulation Processes[715,716]; Surface Film Modification[717]
Spectral Transparence Starting from 230 nm	 4-Benzylphenoxy	Photooxidable Groups: Presence of Labile Secondary Hydrogen Atoms	Photooxidation and Photoreticulation Processes[293,718]
Spectral Transparence Starting from 230 nm	 4-Hydroxy-Azobenzene	Presence of a Thermally and Photochemically Isomerizable Azo Group	Trans-Cis Photoisomerization Photochromism[719]
Spectral Transparence Starting from 230 nm	 Spiropyran	Light-Induced Ring-Opening Reactions	Photochromism[720]

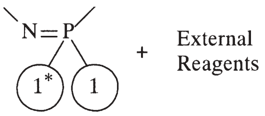
Table 25 (continued)

Spectral Transparence Starting from 230 nm	 4-Hydroxy Cinnamates	Photoreactive Groups	Photocrosslinking. Negative Photoresists[721-723]
Spectral Transparence Starting from 230 nm	 4-Hydroxy Chalcones	Photoreactive Groups	Photocrosslinking. Negative Photoresists[722-724]
Spectral Transparence Starting from 230 nm	 Phenoxy and 4-Alkylphenoxy  β-Naphthoxy	Planar Chemical Structure with Conjugated π Electrons	Intra- and Inter-Molecular Excimers Formation[468-470,473,725]

When the substituent groups in the polyphosphazenes were azobenzene [719] or spiropyran [720] derivatives, photochromic polymers were obtained, showing reversible light-induced *trans-cis* isomerization or merocyanine formation, respectively. Only photocrosslinking processes by [2+2] photo-addition reactions to cyclobutane rings could be observed when the substituent groups on the phosphazene backbone were 4-hydroxycinnamates [721–723] or 4-hydroxychalcones [722–724].

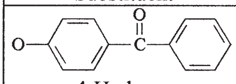
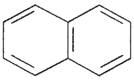
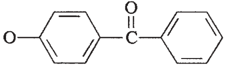
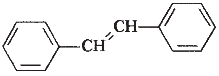
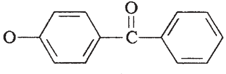
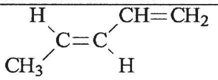
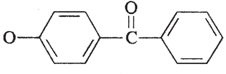
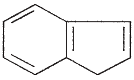
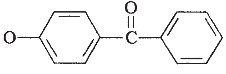
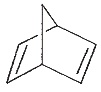
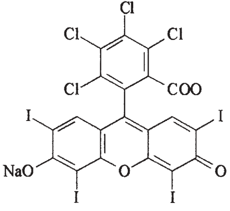
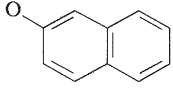
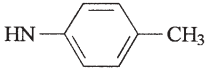
It can also be mentioned that polyphosphazenes substituted with aromatic groups, such as phenols or naphthols, can form inter- and intra- molecular excimers by coupling reaction of the planar aromatic rings of the substituents under illumination [467–471, 473, 725]. These species disappear as soon as the light is switched off.

Another class of photochemically relevant polyphosphazenes is formed by macromolecules having chromophores able to absorb light in a selective way and to transfer it to external species, thus inducing different reactions by energy transfer processes. In some cases electron transfer processes are also involved. These situations are described by Formula below and the corresponding polymers and external reagents are reported in Table 26.



Thus, the photo-activity of poly[bis(4-benzoylphenoxy)phosphazene] under illumination could be finely tuned by irradiating the polymer in the presence of variable amount of naphthalene, a typical triplet state energy quencher [474]. The same polymer could be used as polymeric photosensitizer to induce the

Table 26 Energy- and electron- transfer processes involving excited polyphosphazenechromophores

Phosphazene Substituent	External Reagents	Type of Interaction	Resulting Reactions
 4-Hydroxy Benzophenone	 Naphthalene	Energy Transfer	Photostabilization by Quenching of the Benzophenone Photoactivity[474]
 4-Hydroxy Benzophenone	 *Trans*-Stilbene	Energy Transfer	Trans-Cis Photoisomerization Process[490]
 4-Hydroxy Benzophenone	 *Trans*-Piperylene	Energy Transfer	Trans-Cis Photoisomerization Process[490]
 4-Hydroxy Benzophenone	 Indene	Energy Transfer	Cyclodimerization Reactions[490]
 4-Hydroxy Benzophenone	 Norbornadiene	Energy Transfer	Valence Isomerization to Quadriciclane[490]
 Rose Bengal	O_2 Molecular Oxygen	Energy Transfer	Singlet Oxygen Generation[726]
 β-Naphthoxy	Trinitrofluorenone	Electron Transfer Processes	Photoconductivity[291,727,728]
 4-Toluidino	Trinitrofluorenone	Electron Transfer Processes	Photoconductivity[291,727,728]

light-sensitized *trans-cis* isomerization of stilbene and piperylene, the cyclodimerization reaction of indene and the valence isomerization of norbornadiene to quadricyclane [490], while a phosphazene macromolecule functionalized with Rose Bengal residues [726] was found to be able to photosensitize the formation of singlet oxygen. All these types of processes occurred by energy-transfer reactions. When electron-transfer processes were involved, charge-transfer complexes were always formed among the polyphosphazene substituents (β-naphthoxy and/or 4-toluidine) and trinitrofluorenone as a dopant, and remarkable photoconductivity phenomena were observed [291, 727, 728].

Similarly, energy-transfer processes, together with electron transfer and hydrogen abstraction reactions could be induced in poly(organophosphazenes) in an intramolecular way by preparing POPs geminally substituted at the same phosphorus with two different substituent groups.

The general structure of these materials is shown in Formula below while the corresponding structures and processes are described in Table 27.

In these processes poly[bis(4-benzoylphenoxy)phosphazene] has mostly been used as photosensitive substrate because of the triplet state reactivity

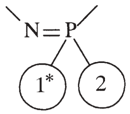
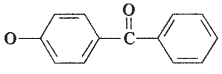
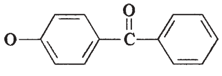
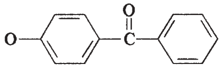
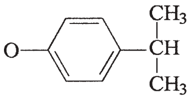
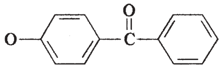
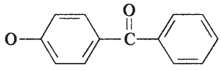
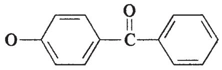
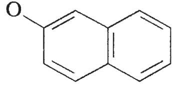
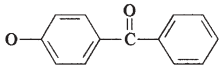
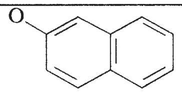
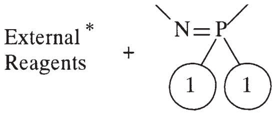


Table 27 Light-induced intramolecular processes for phosphazene copolymers

Substituent 1	Substituent 2	Type of Interaction	Processes
 4-Hydroxy Benzophenone	 4-Hydroxy Benzophenone	Hydrogen Abstraction Processes	Photocrosslinking[475,712]
 4-Hydroxy Benzophenone	 4-Isopropylphenol	Hydrogen Abstraction Processes	Photocrosslinking[296]
 4-Hydroxy Benzophenone	$O-CH_2CH_2OCH_2CH_2OCH_3$ Methoxyethoxyethoxy	Hydrogen Abstraction Processes	Photocrossslinking[480]
 4-Hydroxy Benzophenone	 3-N,N'-Dimethylamino Phenoxy	Electron Abstraction, Followed by Proton Migration	Photocrosslinking[476,729]
 4-Hydroxy Benzophenone	 β-Naphthoxy	Energy Transfer Processes	Self-Stabilized Polymers[475]
 4-Hydroxy Benzophenone	 β-Naphthoxy	Energy Transfer Processes	Triplet State Intramolecular Excimers[471]

of the excited benzophenone moiety present in its chemical structure [712]. The actual process taking place during illumination of these substrates depends strictly on the nature of the second substituent groups that is geminally attached to the same phosphorus of the phosphazene backbone. In fact, intramolecular hydrogen abstraction processes could be observed when the second phosphazene substituent was benzophenone [475, 712], 4-isopropylphenol [296] or methoxyethoxyethanol [480] followed by extremely efficient crosslinking phenomena of the polymer substrates and complete insolubilization of the materials in a very short time. The same result could be obtained when the couple benzophenone/3-*N*,*N'*-dimethylphenol [476, 729] are geminally supported on the same phosphorus atoms along the polymer chain, in this case by a light-induced electron-transfer reaction followed by a proton migration process.

In the frame of photochemical research, phosphazene polymers have also been exploited in combination with external reagents able to selectively absorb impinging light and induce reactivity on these materials. The general reaction scheme is shown below.

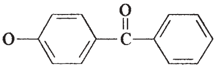
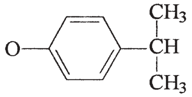
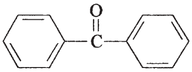
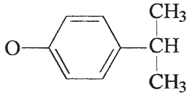
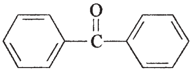
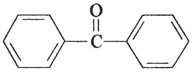
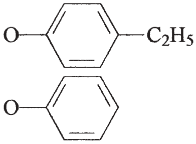
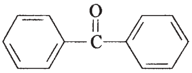
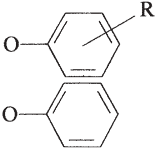


All the materials involved in this research are described in Table 28.

Poly[bis(4-benzoylphenoxy)phosphazene] could be used as polymeric photosensitizer to induce the photocrosslinking of poly[bis(4-isopropylphenoxy)-phosphazene] by means of the recombination of phosphazene macroradicals produced by hydrogen abstraction processes on the side isopropylphenoxy substituents [716]. Similarly, free benzophenone chromophores were used to photoreticulate poly[4-isopropylphenoxy)phosphazene] [715, 716] or poly[bis-(methoxyethoxyethoxy)phosphazene] [641, 642]; this last material with the aim of introducing dimensional stability in polymeric films of this polymer and to use them as solid state electrolytes for secondary batteries. In the same vein, Pintauro reported the light-induced reticulation processes of phosphazene copolymers co-substituted by phenol and 4-ethylphenol [730], and by phenol and variable 3- or 4- alkylated aryloxy groups to produce polymeric crosslinked films suitable for exploitation in membrane technology [731].

In conclusion, all these types of light-induced reactions involving polyphosphazenes readily account for the great importance assumed by this topic in the phosphazene domain and for the remarkable application potentials of especially designed phosphazene materials.

Table 28 Hydrogen abstraction reactions in phosphazene polymers and copolymers photosensitized by external reagents

External Reagents	Polyphosphazene Substituent	Type of Process	Final Polymer Properties
 4-Hydroxy Benzophenone	 4-Isopropylphenol	Hydrogen Abstraction Processes	Photocrosslinking[716]
 Benzophenone	 4-Isopropylphenol	Hydrogen Abstraction Processes	Photocrosslinking[715,716]
 Benzophenone	$O-CH_2CH_2OCH_2CH_2OCH_3$ Methoxy-ethoxy-ethanol	Hydrogen Abstraction Processes	Photocrosslinking[641,642]
 Benzophenone	 4-Ethylphenoxy/phenoxy Copolymers	Hydrogen Abstraction Processes	Photocrosslinking[730]
 Benzophenone	 where R stands for: 3-CH_3; 4-CH_3; 3-C_2H_5; 4-C_2H_4; 3-iso-C_3H_7; 4-iso-C_3H_7	Hydrogen Abstraction Processes	Photocrosslinking[731]

9
Conclusion

In this paper the scientific and technologic relevance of poly(organophosphazenes) are accounted for on the basis of the synthetic versatility of these materials and of their structure–property relationships.

A variety of synthetic procedures have been described based on the ring-opening polymerization processes of $(NPCl_2)_3$ to $(NPCl_2)_n$ followed by the nucleophilic replacement of the reactive chlorines with carefully selected nucleophiles, and on polycondensation reaction processes of new monomers and of substituted phosphoranimines.

Furthermore, polyphosphazene features are interpreted as the resultant combination of two basic contributions: one coming from the properties inherently due to the polyphosphazene inorganic backbone (-P=N-), the other being due to the characteristics possessed by the exploited nucleophilic substituents.

On this basis, five classes of different polyphosphazenes are considered as outstanding examples of this type of macromolecules, in which skeletal and substituent features overlap to the highest extent. The reported materials are elastomers, flame retardants and self-extinguishing macromolecules, polymeric ionic conductors, biomaterials, and photosensitive polymeric compounds; all of them based on the polyphosphazene structure.

A few considerations about future developments and applications of the described polyphosphazenes are also discussed.

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