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Phospholes – development and recent advances

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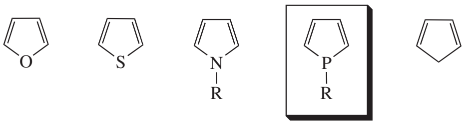
The recent advances in synthesis, bonding, reactivity and application of phospholes, five-member phosphorus cycles, are summarized.

Phospholes are the least aromatics of the family of 5-membered unsaturated heterocycles, and have properties rather different from those of their S, N, O counterparts – thiophenes, pyrroles and furans, respectively. The dienic system of phospholes displays a rich and versatile cyclopentadiene-like cycloaddition reaction and serves for the preparation of a variety of novel polycyclic phosphines, phosphinines, phosphinidenes, *etc*. At the same time, phospholes in contrast to pyrroles, furans or thiophenes undergo easily oxidation, sulfurization and quaternization reactions, form complexes with transition metals, that open new horizons for their applications.[1,2]

Although the chemistry of phospholes was well reviewed,[3–7] a fair number of publications appeared in last ten years in this field. They are devoted to synthesis, structural data and aromaticity, cycloaddition reactions, coordination chemistry and practical applications of these important P-heterocycles and need to be summarized to rationalize trends and perspectives of this class of compounds.



1. Synthesis of mono-, di- and triphospholes

Significant number of methods were developed for the synthesis of phospholes, which can be divided into two major groups. The first group includes the methods based on the ring forming reactions leading to phospholes, the second approach is based on the reactions of readily available phospholide anions with electrophiles.

1.1. Synthesis of phospholes by ring forming reactions

Several specialized methods have been developed for the ring forming synthesis of monophospholes, which can be subdivided into three major types.

From zirconacyclopentadienes. The majority of new monophospholes was created by ring closure method first introduced by Fagan and Nugent in 1988.[8] Thus, symmetrical and unsymmetrical alkynes react with zirconium cyclopentadiene (Cp) complex in the presence of butyllithium forming zirconacyclopentadiene **1**

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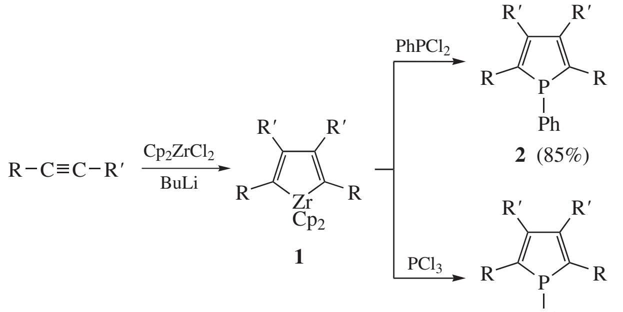
bearing the desired C-substituents. The latter reacts easily with $RPCl_2$ or PCl_3 to form monophospholes **2** or **3**, respectively.[9,10]



1

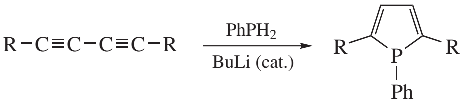
2 (85%)

3 (85%)

R = R′ = Alk, Ar
R ≠ R′ = $SiMe_3$, Bu^t, 2-pyridyl, 2-thienyl

It is now clear whether the Fagan–Nugent method represents a major advance in phosphole chemistry. The method is ideally suited to provide phospholes **2** with novel substituents (*e.g.*, silyl groups, 2-pyridyl, 2-thienyl),[11–13] which are desired in certain phosphole applications (Section 4.2).

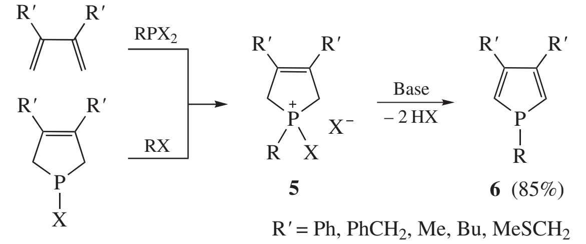
From 1,3-diynes and primary phosphines. This old and 'classical' method developed in 1970s continues to find occasional use, the latter examples include the synthesis of phospholes **4** with cyclohexyl[14] or chiral (–)-menthyl[15] groups in the 2,5-positions.



4 (50–85%)

a R = Me
b R = Ph
c R = naphthyl
d R = 4-MeC_6H_4
e R = menthyl
f R = Cy

From 1,4-cycloadducts of diene and phosphorus halide. This approach has been a standard method for phosphole synthesis since its discovery by F. Mathey in 1969. The usual P-substituents are alkyl or aryl, but it was shown that this method can be used for preparation of phospholes **6c** with (diisopropyl)amino group at phosphorus atom.[16]

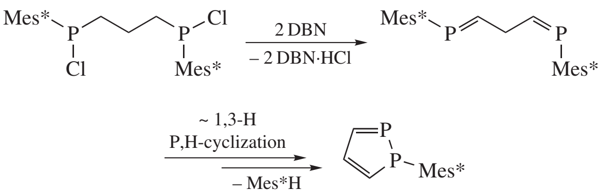


5

6 (85%)

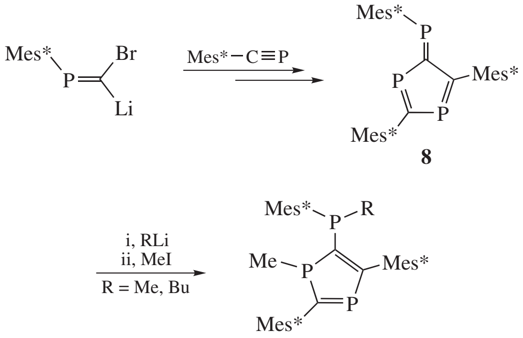
R′ = Ph, $PhCH_2$, Me, Bu, $MeSCH_2$
a R = Ph
b R = Alk
c R = NPr^i_2

Compared with the well-studied monophospholes only a small number of polyphospholes containing more than one phosphorus atom in the ring is known. Synthesis of di- and triphospholes by the ring forming reactions is based on dimerization and trimerization of phosphaalkenes and phosphaalkynes. Thus, 1-(2,4,6-tri-*tert*-butylphenyl)-1,2-diphosphole **7** was isolated from the unintentional and unexpected dehydrohalogenation of 1,3-bis-[chloro(2,4,6-tri-*tert*-butylphenyl)phosphino]propane with DBN. The reaction proceeds through the stages of the formation of two P=C bonds, 1,3-migration of a proton and subsequent P,H-cyclization.[17]



7 (31%)

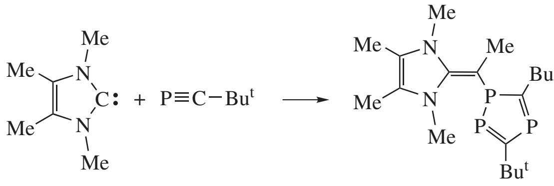
The addition of two molecules of phosphaalkyne, generated *in situ*, to phosphanylidene carbenoid Mes*–P=C(Br)Li leads to 1,3,6-triphosphafulvene **8**,[18] whose sequential processing with RLi and MeI gives 5-phosphino-1,3-diphosphole **9**.[19]



8

9 (31%)

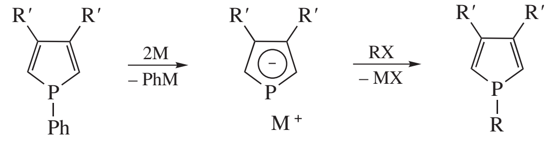
The trimerization of phosphaalkyne in the presence of stable heterocyclic carbenes is also a convenient tool for the preparation of 1,2,4-triphosphole derivatives **10**.[20,21]



10 (70%)

1.2. Synthesis of phospholes by the reaction of phospholide anions with electrophiles

Most readily available P-phenyl derivatives **6a** are useful precursors for the synthesis of new phospholes with pyridyl,[22] cyano,[23] alkoxy,[24] alkenyl[25] and alkynyl[26] substituents. The P–C bond of 1-phenylphospholes can be cleaved by reaction with Li, Na, K to form phospholide anions **11**, which are important ligands in coordination complexes (Section 3.2), as well as starting compounds for synthesis of α-[27] and β-functional[28] phospholes and β-functional phosphinines.[29] At the same time, phospholide anions **11** were used to obtain novel phospholes with P–P, P–As[30–32] and P–N[23] bonds. Also new non-racemic phospholes with chiral neomenthyl and oxazoline substituents were successfully prepared by this approach.[33] P-Halo, cyano and



6a

11

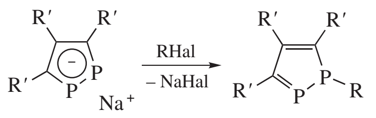
12a–g (60–95%)

X = Cl, Br
R′ = Ph, $PhCH_2$, Me

a R = CN
b R = OAlk
c R = $CH_2CH_2CH=CH_2$
d R = $CH_2C{\equiv}CPh$
e R = Fc
f R = C≡CPh
g R = Cp*

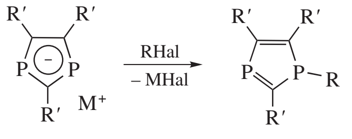
alkoxy phospholes can be also transformed into functionally-substituted ones by treatment with carbanions.[34–36]

Most of new di- and triphosphole rings have been synthesized in last decades by alkylation of the corresponding di- and triphospholide anions **13**, **15**, **17**. This simple and reproducible synthetic route allowed the chemistry of variously substituted 1,2-diphospholes **14**,[37,38] 1,3-diphospholes **16**[39,40] and 1,2,4-triphospholes **18**[41–43] to be studied in detail.



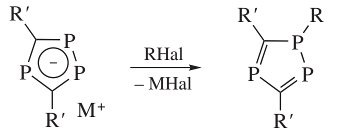
13 **14** (60–80%)

Hal = Br, I
R′ = Ph, 4-MeC$_6$H$_4$, 4-FC$_6$H$_4$, NR$_2$
a R = Me **f** R = Bu^i
b R = Et **g** R = Cy
c R = Pr **h** R = SiMe$_3$
d R = Pr^i **i** R = SnMe$_3$
e R = Bu



15 **16** (40–60%)

Hal = Cl, Br
R′ = Bu^t, CMe$_2$Et
a R = Me **d** R = PPh$_2$
b R = Pr **e** R = SnPh$_3$
c R = Bu



17 **18** (50–90%)

Hal = Cl, Br
R′ = Bu^t, Mes*, SiMe$_3$
a R = Me
b R = CH$_2$Ph
c R = CH(SiMe$_3$)$_2$
d R = SnMe$_3$

As expected, the electrophilic attack takes place exclusively at the less sterically hindered phosphorus atom. The presence of bulky substituents (Bu^t, Mes*, SiMe$_3$) promotes kinetic stabilization of the P=C bond, at the same time aromatic delocalization within the ring gives thermodynamic stabilization of the P=C bond.

Note that of all theoretically possible triphospholes only 1,3,4-triphosphole in the form of a complex with W(CO)$_5$ was obtained.[44] To the best of our knowledge there is no example of tetra- and pentaphosphole. The expected pentaphospholes are so unstable due to high reactivity of the P=P bond that they give spontaneously a mixture of polyalkylphosphanes.[45]

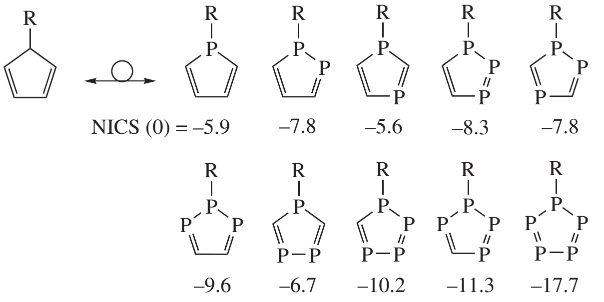
2. Structural data and aromaticity of phospholes

The question of the structure and aromaticity of phospholes is particularly important for understanding of their reactivity in the cycloaddition and complexation reactions, as well as for practical applications.[46] From the different observations it is widely accepted that monophospholes are only weakly aromatic.[47] The reason of the nonaromatic behaviour of monophosphole, however, is the nonplanarity of the tricoordinate phosphorus and as a consequence insufficient overlap between the phosphorus lone pair and the dienic π-system.

However, sterically hindered substituents at the phosphorus atom can significantly decrease its pyramidality and thus increase the aromaticity of monophosphole.[48,49] For example, according to X-ray structure, the sum of angles at the phosphorus atom is 302.7° for 1-benzylphosphole in comparison to 331.7° for 1-(2,4,6-tri-*tert*-butyl-6-methylphenyl)-3-methylphosphole.[50] As a result, the latter compound has pronounced characteristics of aromaticity and easily undergoes Friedel–Crafts acylation.[51,52]

According to calculations, the pyramidality of the phosphorus atom can also be significantly reduced by σ-donor and π-acceptor groups (BH$_2$, SiH$_3$, AlH$_2$).[53] It has been recently shown that 1-boratabenzene-(2,3,4,5-tetramethylphosphole) possessing a strong σ-donor boratabenzene group on the P-atom, proved to demonstrate some degree of planarization for the monophosphole.[54]

In polyphospholes the CH-units of phosphole are replaced by one or more P-units. It has been shown that with the gradual increase in the number of the phosphorus atoms in the ring, the inversion barrier of the tricoordinated phosphorus is decreasing[55] and consequently, aromaticity of polyphospholes is increasing.[56] Bond-length equalization, aromatic stabilization energies (ASE) and nucleus independent chemical shifts (NICS) were calculated as useful indicators of aromaticity.[57,58]



According to these calculations, all measures of aromaticity are of similar values for the planar polyphospholes and are comparable or in some cases larger than those for the other five-membered heterocycles (pyrrole, thiophene and furan).[55] However, according to other authors P$_5$R easily dimerizes by [4+2] cycloaddition reaction with a gain of energy 30 kcal mol^{-1}, which agrees well with the experimental data.[45]

According to the X-ray structure analysis of certain phospholes, aromaticity actually increases in a series of 1-monophosphole < 1,3-diphosphole < 1,2,4-triphosphole. Thus, upon going from mono- to triphospholes there is a significant increase in the phosphorus centre planarity (ΣP_{angles} = 302.7°, 320.0° and 342.3°, respectively) and the cyclic P–C-bond length becomes shorter.[6] These observations clearly demonstrate that the electronic delocalization is much stronger in triphospholes than in monophosphole rings. Moreover, in the series of 1,2-diphospholes and 1,2,4-triphospholes there are two striking examples of fully planar polyphospholes containing sterically hindered groups.[17,42] The sum of angles at the tricoordinated phosphorus atom is 351° and 359°, respectively, and these structures are not only planar, but also aromatic, in agreement with quantum-chemical calculations.

The increase in aromaticity for 1,2,4-triphospholes **18** has a significant impact on their chemical behaviour. 1,2,4-Triphospholes **18** unlike monophospholes exhibit low reactivity in cycloaddition and add only highly reactive dienophiles (Section 3.1). In addition, 1,2,4-triphospholes form η^5-complexes with M(CO)$_3$ (M = Cr, Mo, W)[59] and Ru (η^4-C$_8$H$_{12}$).[60]

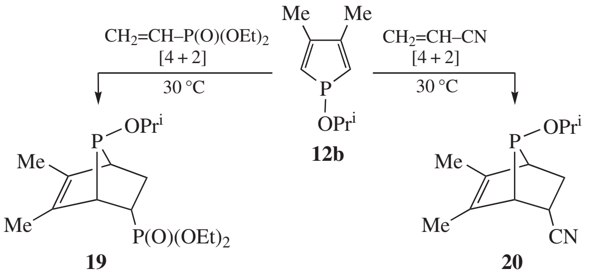
Thus, pyramidality of phosphorus atom can be reduced by (1) σ-donor and π-acceptor groups; (2) steric strain, which increases the angle on phosphorus; (3) replacing the CH-units by P-units. The obvious question is, how large the impact of aromaticity of phospholes on their chemical reactivity is. Aromatic systems are generally considered as thermodynamically stable and inert in cycloaddition reactions. However, 1,2,4-triphosphole can be rearranged at room temperature under visible light irradiation to 1,3,5-triphosphabicyclo[2.1.0]pent-2-ene.[61] For the planar systems the aromatic stabilization is just compensated by the energy factor of the planarization at phosphorus. If a nonplanar tricoordinated phosphorus can be formed as a result of a chemical reaction, the energy can be gained during the repyramidalization. Due to this counterbalancing effect a very rich chemistry can be anticipated for phospholes.

3. Chemical properties of mono-, di- and triphospholes

3.1. Cycloaddition reactions of mono-, di- and triphospholes

There are plenty of experimental data (reviews[3,5,6]) on the cycloaddition of mono-, di- and triphospholes. This is undoubtedly due to the practical importance of the resulting phosphorus polycycles with chiral bridgehead P-atom, which are regarded as bulky electron-withdrawing ligands in homogeneous catalysis (Section 4.1).

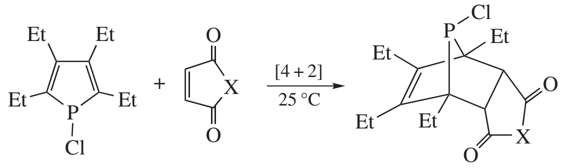
It has been stated that the diene system of monophospholes is poorly reactive due to some delocalization within the ring, which diminishes the availability of the four π-electrons.[3,62] That is why the [2+2] cycloaddition of an 1*H*-phosphole with an alkene derivative has been observed only recently under UV irradiation.[63] However, recent calculations complement previous theoretical studies on phosphole aromaticity as well as recent experimental work, which demonstrates the possibility of fine-tuning of the reactivity of 1*H*-phospholes by choosing the appropriate substituents at phosphorus.[64] So, it was recently reported that the presence of electron-acceptor substituents (cyano-, alkoxy-, halo-) at the phosphorus atom can dramatically increase the reactivity of the diene system of 1*H*-phospholes. Thus, whereas 3,4-dimethyl-1-phenylphosphole does not undergo the Diels–Alder reaction with acrylonitrile even at high temperatures, 1-isopropoxyphosphole **12b** gives exclusively the *anti*-isomers **19** and **20** with acrylonitrile or diethyl vinylphosphonate even within 1 h at 30 °C.[24]



12b

19

20



3

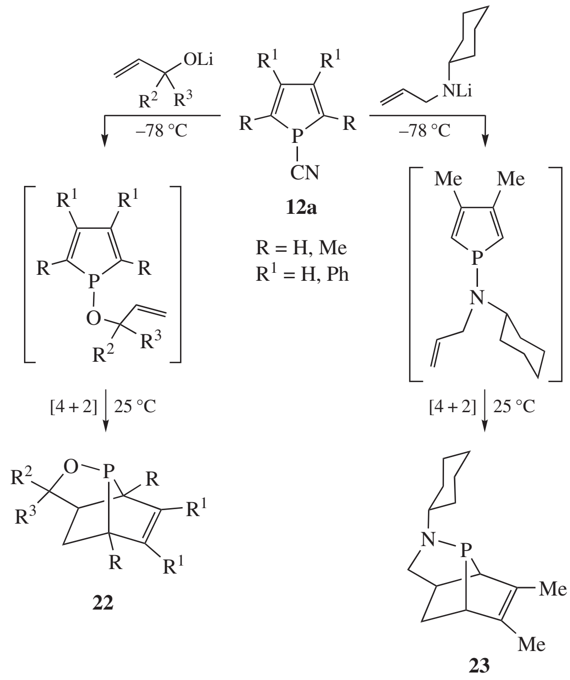
X = O, NH

21

Similarly, 1-chloro-2,3,4,5-tetraethylphosphole **3** reacts at room temperature with maleic acid derivatives to form 7-phosphanorbornenes **21** in good yields.[65] The presence of electron-withdrawing substituents (allyl-O, allyl-N) at the phosphorus atom significantly accelerates intramolecular cycloaddition at room temperature to give novel tricyclic products **22**, **23**. In the case of unactivated phosphole **12c**, such a reaction takes place at 110–160 °C.[66] Thus obtained 7-phosphanorbornenes can find application as ligands in catalysis (Section 4.1).

More interesting are 2*H*-phospholes **24** (still unknown) containing a reactive P=C bond formed as a result of a [1,5]-sigmatropic shift.[7] The 2*H*-phospholes **24** exhibit dual reactivity in cycloaddition reactions: as powerful dienes towards carbon–carbon double or triple bonds or C=O double bonds[67] and as dienophiles towards conjugated dienes. Recently dienic system of **24** was used as a prochiral motif for the asymmetric synthesis of P-chiral phosphanes.[68]

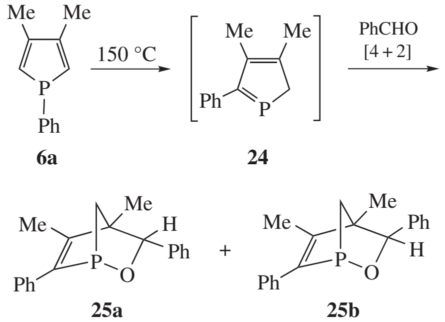
Recent studies have shown that it is possible to combine thermal stability of 1*H*-phospholes and high reactivity of 2*H*-phospholes in one molecule of 1,2-diphospholes. Thus, 1-alkyl-1,2-diphospholes **14**, as stable analogues of 2*H*-phospholes, exhibit dual reactivity in [4+2] cycloaddition with maleic acid derivatives and in [2+4] cycloaddition with 2,3-dimethyl-1,3-butadiene forming new polycyclic phosphines **26** and **27** with high stereoselectivity.



12a

22

23

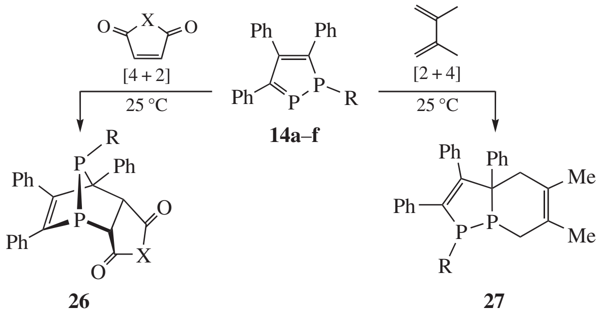


6a

24

25a

25b



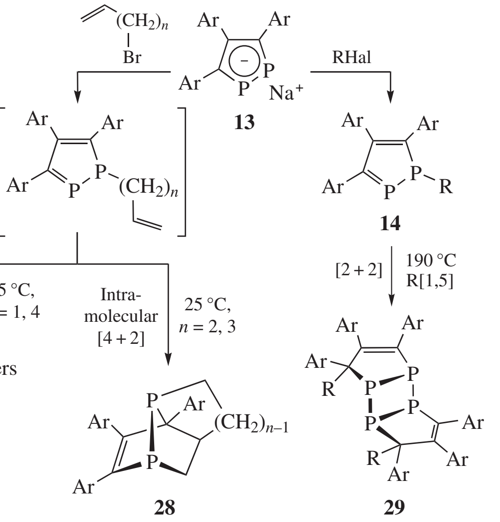
14a–f

26

27

Compared with monophospholes, 1-alkyl-1,2-diphospholes **14** are more reactive in intramolecular cycloaddition reactions. Alkylation of **13** with 4-bromo-1-butene or 5-bromo-1-pentene proceeds highly regioselectively with the formation of tricyclic cage phosphines **28** already at room temperature. They are the products of intramolecular [4+2] cycloaddition reactions.[69] All reactions proceed under mild conditions (25 °C, 6–12 h) with high regio- and stereoselectivity. In each case only one diastereomer (as the racemate) instead of the several possible ones is formed.[70]

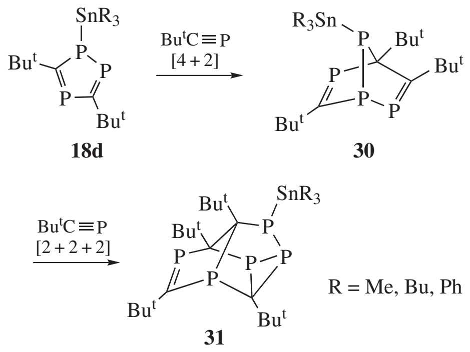
At the same time, 1-alkyl-1,2-diphospholes **14** reveal a great thermal stability as 1*H*-phospholes – dimerization of **14** was observed only upon heating up to 190 °C leading the tricyclic

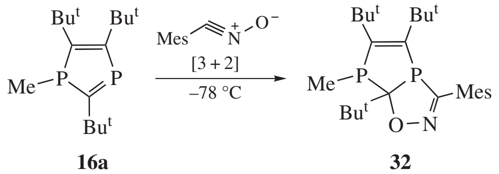


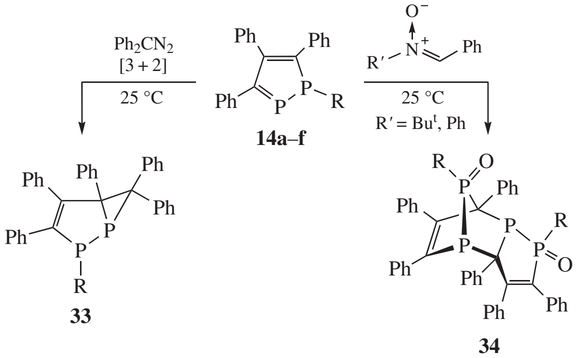
R = Me, Et, Pr, Pr^i, Bu, Bu^i, Cy
Ar = Ph, 4-MeC_6H_4, 4-FC_6H_4

product **29** of [2+2] cycloaddition reaction of 1,2-diphospholes[71] formed by R[1,5]-shift of alkyl group.[72]

Furthermore, the formation of only one diastereomer instead of 16 possible takes place in sterically controlled [4+2] cycloaddition reaction of 1,2,4-triphospholes **18d** with highly reactive *tert*-butyl cyaphide.[73] The introducing of chiral substituents [R* = (–)-*cis*-myrtanyl, (–)-*trans*-myrtanyl, 3-(born-2-en-2-yl) phenyl] to the tin atom in SnR_3[74] and the subsequent cycloaddition reaction with phosphaalkyne provides a diastereomeric mixture of cycloadducts **31**, which can be separated and hydrolysed to give enantiopure novel P–C cages.[75]





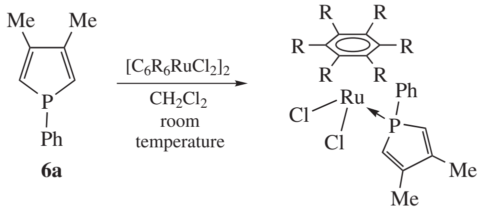


At the same time, 1,3-dipolar cycloaddition reactions of phospholes are still poorly studied in contrast to their Diels–Alder reactions.[76] Obviously, two-coordinated organophosphorus compounds can be regarded as novel dipolarophiles for construction of novel P-heterocycles with useful properties.

[3+2] Cycloaddition reaction between 1,3-diphosphole **16a** and mesitylenenitrile oxide proceeds with high regioselectivity. However, interaction of 1-alkyl-1,2-diphospholes **14** with 1,3-dipolar reagents (diphenyldiazomethane and nitrones) leads to unexpected bicyclic phosphiranes **33** and dimer of 1-alkyl-1,2-diphosphole oxides **34**.[77]

3.2. Coordination properties of phospholes

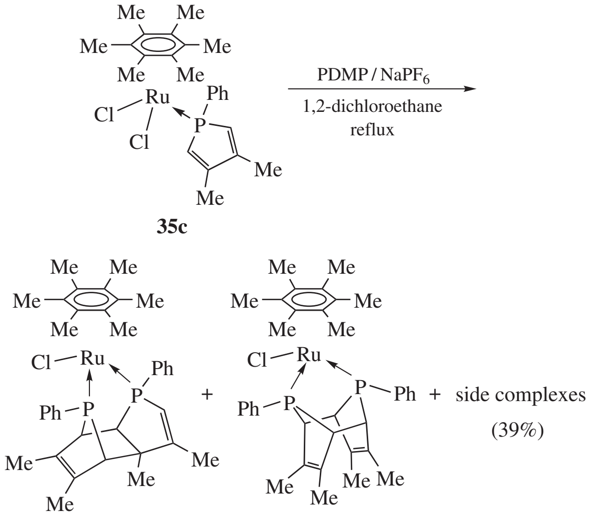
Complexes of phospholes with transition metals attract a great attention since they provide one with the opportunity to carry out a lot of chemical transformations unknown to the free phospholes. The presence of the diene system and the phosphorus lone pairs in molecules of mono- and polyphospholes predetermines their coordination properties toward transition metal and has a significant influence on the reactivity of phospholes. Coordination of the phosphorus atom to the transition metal atom reduces the delocalization within the phosphole ring and as a consequence ‘activate’ diene system of phospholes. This was exemplified by the reaction of ruthenium(II) halides with 1-phenyl-3,4-dimethylphosphole (PDMP) **6a**.[78] In products **35** the molecule of monophosphole coordinates with ruthenium atom through phosphorus lone pair, whereas the diene system remains free.

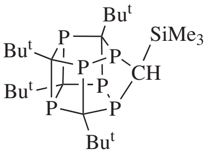


a $C_6R_6 = MeC_6H_5$
b C_6R_6 = 4-$MeC_6H_4CHMe_2$
c $C_6R_6 = C_6Me_6$
d $C_6R_6 = C_6H_6$

Refluxing of **35c** in 1,2-dichloroethane in the presence of additional equivalent of PDMP and $NaPF_6$ in molar ratio of 1 : 1.5 : 1 results in a mixture of compounds **36** and **37** as the products of intramolecular [4+2] and [4+4] cycloadditions.[79]

Moreover, formation of several novel organophosphorus cage compounds – hexaphosphapentaprismanes **38**–**40** was found as





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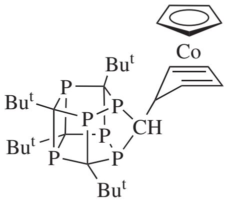

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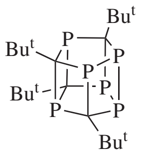
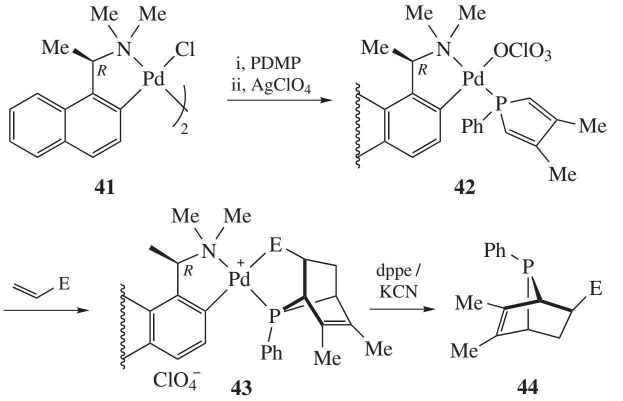


40

a result of the cycloaddition of 1,2,4-triphospholes **18** in coordination spheres of $[CrCl_3(THF)_3]$[80] or $[Co(\eta^5\text{-}C_5H_5)_2]$.[81]

The reactivity studies of monophosphole complexes were continued with the emphasis on the asymmetric Diels–Alder reactions bearing in mind increased reactivity of the diene system of monophosphole in the coordination sphere of the transition metal ion.[82] This feature provides a unique opportunity for controlling the stereochemistry of cycloaddition by incorporating an appropriate chiral auxiliary to the activating metal ion. Thus, an asymmetric Diels–Alder reaction of PDMP **6a** with various dienophiles [CH_2=CH–E, E = C(O)NMe_2,[83] C(S)OEt,[84] C(S)NMe_2,[85] $AsPPh_2$,[86] $As(C_6H_{11})_2$,[87] PPh_2,[88] 2-pyridyl,[89] DMPP[90]] in the coordination sphere of chiral complexes of palladium **41** provides enantiopure complexes **42**, **43** and the enantiopure *exo*-phosphanorbornenes **44**.

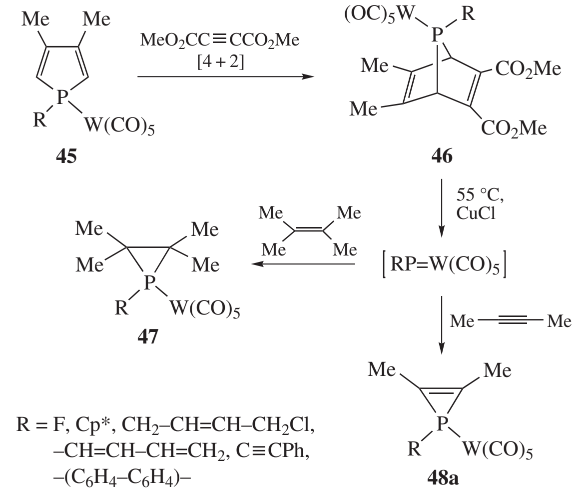


E = C(O)NMe_2, C(O)Et, C(O)OMe, C(S)OEt,
C(S)NMe_2, SPh, S(O)CH=CH_2, C_5H_4N, $AsPh_2$

Cycloaddition of chiral complex **42** with diphenylvinylphosphine sulfide or oxide gave new chiral P–P(O)- and P–P(S)-*exo*-phosphanorbornenes.[91,92] The analogue of chiral complex **42** containing Pd–Cl bond was used to obtain *endo*-phosphanorbornenes. In this case a mixture of diastereomers separable by fractional crystallization or column chromatography was formed.[93–95]

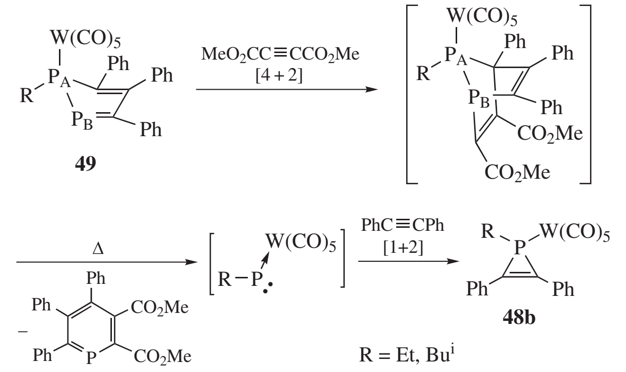
Cycloaddition of phospholes and alkynes in the coordination sphere of transition metals was efficiently used to produce phosphinidene complexes. Thermolysis of 7-phosphanorbornadienes, formed during [4+2] cycloaddition of tungsten complex of 1-phenylphosphole **45** with dimethyl acetylenedicaraboxylate (DMAD), is the common and convenient method for generation of phosphinidenes RP=$W(CO)_5$. The well known decomposition of 7-phosphanorbornadiene–pentacarbonyltungsten complex **46** catalyzed by Cu^ICl which takes place at 50–60 °C instead of 110 °C for the non-catalytic process was studied from a theoretical standpoint.[96]

Thus, 1-fluorophosphinidene,[97] 1-chloro-2-butenylphosphinidene,[98] butadienylphosphinidene,[99] 4,4-*para*-biphenyl bis(phosphinidene),[100] pentamethylcyclopentadienylphosphinidene[101] complexes were generated and trapped by alkynes, alkenes or butadienes. The first successful attempt to introduce a chiral substituent (menthyl, murtanyl, 4-isopropyloxazolinophenyl) in this chemistry was also described.[33] On using the self-condensation of alkynylphosphinidene complexes, polyphosphirene oligomer was obtained.[35]



R = F, Cp*, CH_2–CH=CH–CH_2Cl,
–CH=CH–CH=CH_2, C≡CPh,
–(C_6H_4–C_6H_4)–

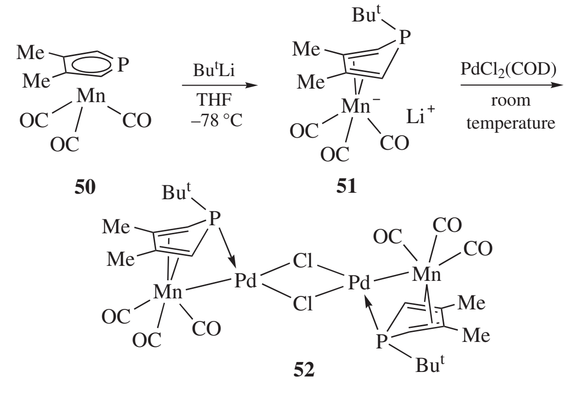
The formation of phosphinidene species was also observed in the reaction of tungsten complexes of 1-alkyl-1,2-diphospholes **49** with DMAD.[102]



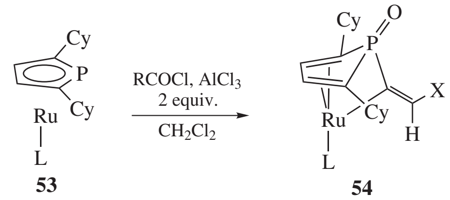
R = Et, Bu^i

The lability of the P–P bond in comparison to the P–C bond allows one to generate electrophilic phosphinidene complexes under milder conditions (50 °C) than for monophospholes (110 °C).

The unusual method for the synthesis of monophosphole complexes is based on the nucleophilic[103] or electrophilic[104] attack of organic species at transition metals complexes with aromatic monophospholide ligands. The treatment of phosphacymantrene **50** with Bu^tLi results in the monophosphole manganese complex **51** with the η^4 metal-ligand coordination mode. The distortion of aromaticity in the five-membered ring allows one to use **51** as a chelating ligand which reacts further with $PdCl_2$(COD) to form tetranuclear complex **52** with mixed coordination modes of phosphole ligand.



Furthermore, the formation of unpredictable μ-vinylidene monophosphole oxide ruthenium complexes as main products was shown on the example of electrophilic substitution in monophospha- and 1,1′-diphospharuthenocene **53**. The presence of substituents in α-positions of phospholide complexes **53** changes the reaction route and the acetyl electrophile attacks the ruthenium centre rather than phospholide ring. Further intramolecular rearrangement occurs in the μ-vinylidene complex **54**.

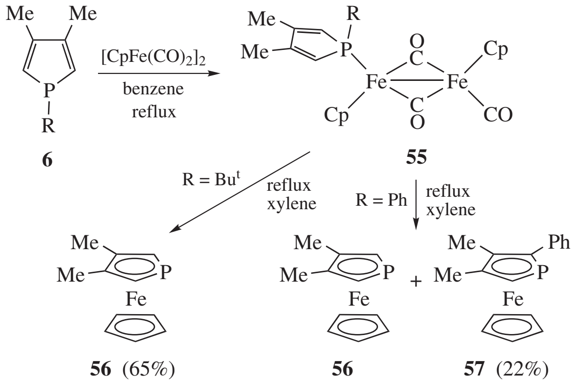


53 **54**

L = Cp*, $C_4H_2(Cy)_2P$
R = Me or Et
X = H, Me

Note that realization of η^4 coordination mode of the monophosphole moiety to metal was also observed in the reaction of 2,3,4,5-tetraethyl-1-(phenylethynyl)phosphole sulfide and $CpCo(CO)_2$.[105]

Another type of complexation of phospholes proceeds with the P–C or P–P bond cleavage that results in the phospholyl metal complexes.[106,107] Thus, refluxing 1-*tert*-butyl-3,4-dimethylphosphole in xylene at 180 °C with iron carbonyl complex **55** leads to monophosphaferrocene **56** in a yield up to 65%.[108] At the same time, thermolysis of phenyl substituted 3,4-dimethylphosphole under similar conditions gives a mixture of phosphaferrocenes **56** and **57** due to the occurrence of [1,5]-sigmatropic shift.[109,110]



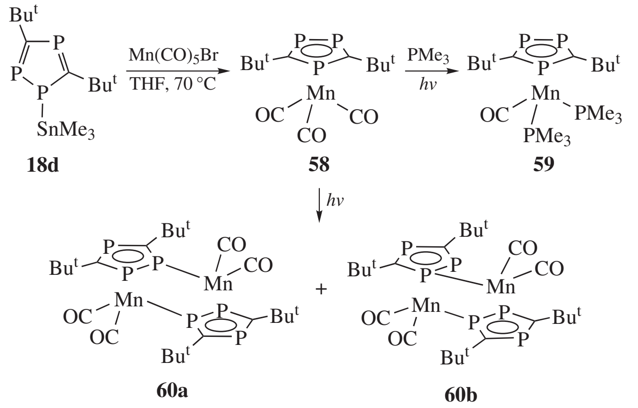
6 **55**

56 (65%) **56** **57** (22%)

The driving force of this process is the formation of aromatic system in phospholide moiety which is the donor of 6π electrons and shows η^5 coordination mode with the transition metal to afford 18-electron complexes. This kind of phospholyl complexes is of special interest due to their application as ligands in homogeneous catalysis (Section 4.1).

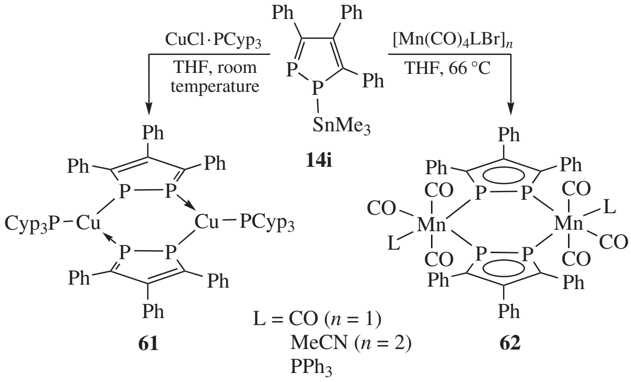
A more convenient way for the preparation of phospholyl transition metal complexes from phospholes are the reactions of tin-substituted phospholes with transition metal halides.[14] Owing to phosphorus–tin bond lability the reaction of 1-trimethylstannyl-3,5-di-*tert*-butyl-1,2,4-triphosphole **18d** with manganese halides leads to the corresponding triphospholyl complexes **58** under mild conditions.[111] The presence of lone pairs at phosphorus atoms in phospholide ring makes it possible to coordinate additional metal atoms and access bridged polynuclear complexes **60**.[112,113]

Moreover, the realization of the different metal–ligand coordination modes can take place due to the availability of several coordination centres in polyphospholide moiety.[114,115] The bridged binuclear complexes **61** and **62** with $\mu,\eta^1:\eta^1$ coordination modes were formed in the reaction of 1-trimethylstannyl-3,4,5-triphenyl-1,2-diphosphole **14** with copper(I) and manganese(I) derivatives.[116,117]



18d **58** **59**

60a **60b**



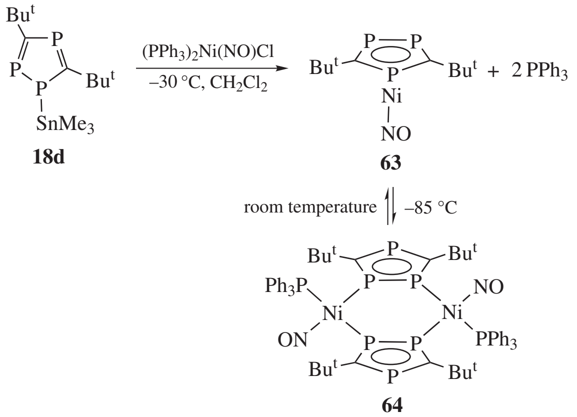
14i

61 **62**

L = CO (n = 1)
MeCN (n = 2)
PPh$_3$

Obtained binuclear 1,2-diphospholyl manganese complexes **62** exhibit magnetic properties characteristic of Mn^{II} compounds due to the intramolecular redistribution of the electronic density and can be efficiently controlled by the co-ligand substitution.[117,118]

On example of the reaction of 1,2,4-triphosphole **18d** with nickel(II) halide at room temperature, generation of the mononuclear half-sandwich nickel complex **63** was fixed. However, lowering the reaction temperature to –85 °C results in the change in coordination type and gives binuclear bridged nickel complex **64**.[119]



18d **63**

64

Thus, the coordination behaviour of phospholes is very diverse and depends not only on the number of coordination centres of phosphole or phospholyl moiety. A significant role in the formation of complexes with desired structure belongs to reaction conditions and the nature of the substituents in the phosphole.

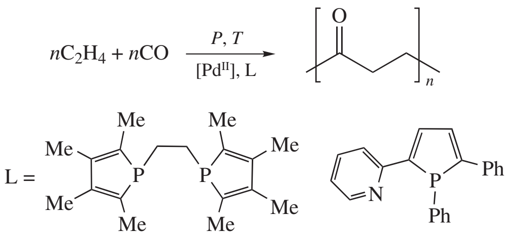
4. Applications of phospholes and their derivatives

During the last decade there has been a significant increase in testing of monophospholes for various practical applications. One of the most important properties of phospholes is the ability to form coordination complexes, which was successfully used to create catalysts of various organic reactions. New applications are also being considered, especially in the electrooptical and biological fields.

4.1. Phospholes and their derivatives as ligands in homogeneous catalysis

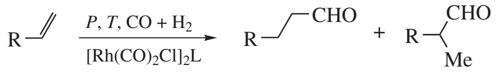
Phospholes attracted much attention as labile, π-acceptor mono- or bidentate ligands for catalysts of organic reactions. Varying substituents at the P- and C-atoms of the phosphole ring gives the opportunity of fine-tuning the electronic and steric properties of ligands for the successful implementation in catalysis.

The most studied derivatives are P,N- and P,P-bidentate ligands: pyridyl containing monophospholes and 2,2′-biphospholes (BIPHOS). Thus, high molecular polyketones (–[$COCH_2CH_2$]–, $M_r > 1\times10^5$) with narrow distribution were prepared by copolymerization of ethylene and carbon monoxide with the catalyst based on the ligand **65** in the presence of $MeSO_3H$ at 90 °C.[120] Similar results were obtained with the cationic catalysts **66**, containing P,N-ligand.[13]

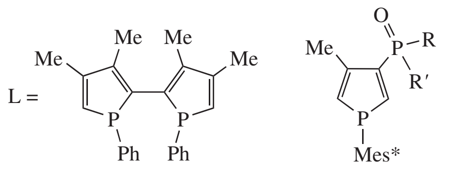


65 **66**

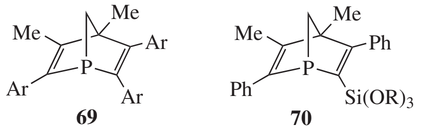
2,2′-Biphosphole **67** also showed high selectivity in Rh-catalyzed hydroformylation of styrene: the ratio of branched to linear aldehyde was 98 : 2.[121] The use of sterically hindered monophosphole **68** in the same process led to a decrease of selectivity, but the reaction proceeded at lower temperature of 40 °C.[122–125] Monophosphole cycloadduct 1-phosphanorbornadiene (NORBOS) **69**, was successfully used as highly active and selective ligand in the biphasic Rh-catalyzed hydroformylation of terminal olefins such as styrene and acrylates.[126] Smart recyclable catalyst based on the complex of $[Rh(CO)_2]L_2$ with 1-phosphanorbornadiene **70**, immobilized on the surface of silica or zirconium oxide is very active in hydrogenation and hydroformylation of internal olefins (2,3-dimethylbut-2-ene, 1-methylcyclohexene) and Knoevenagel condensation.[127,128]



R = Ph, Me, C(O)OEt



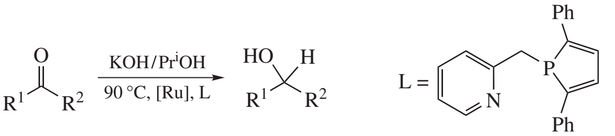
67 **68**



69 **70**

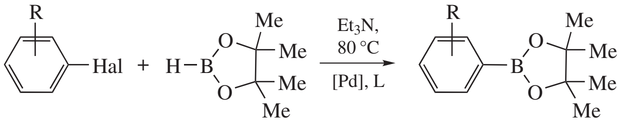
Ar = *p*-$C_6H_4SO_3Na$

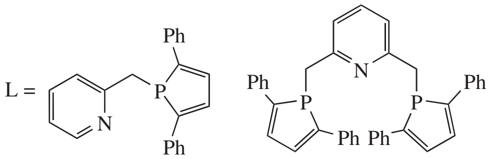
Ruthenium complex with chelate P,N-ligand **71** demonstrated high activity in transfer hydrogenation of various ketones. The number of catalytic cycles (TON) varied from 1×10^5 to 1×10^6 depending on the nature of the substituents in the substrate.[22]



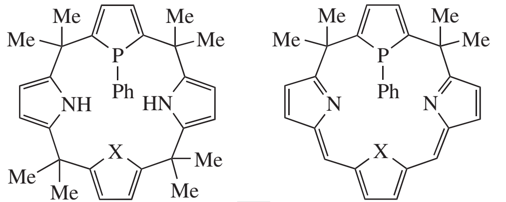
71

Above mentioned P,N-chelate **71**,[129] P,N,P-scorpionate ligands **72**[130] and 1,1′-diphosphaferrocene[131,132] form complexes with Pd^{II} or Pd^0 and exhibit a very high activity in the Suzuki–Miyaura cross-coupling. Thus, the reaction of aryl halides with pinacolborane occurs in 100% yield with a 0.001 mol% catalyst loading within 48 h at 80 °C in dioxane. Number of catalytic cycles TON = 1×10^5 is one of the best results for this cross-coupling catalytic reaction. Novel phosphole-containing hybrid macrocycles (X = O, S, N): flexible PXN_2 calixpyrroles **73**, hemilabile PXN_2 calixphyrins **74** and rigid PXN_2 porphyrins **75** were obtained to be used as ligands in various cross-coupling reactions and as novel receptors and π-spacers.[133–137]

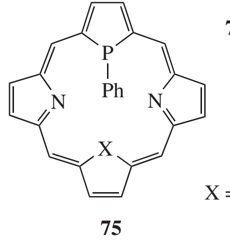




71 **72**



73 **74**

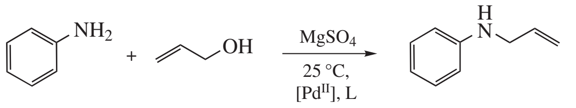


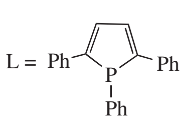
X = O, S, NH

75

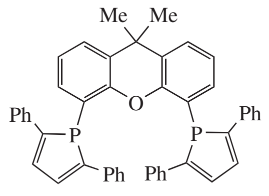
An important method of C–N bond formation – allylation of primary and secondary amines – is effectively catalyzed by Pd complexes with phospholes **4b** and **76**. Thus, allylation of aniline occurs at room temperature within several hours in 100% yield only with 1 mol% catalyst loading, that is one of the best results for this reaction.[138,139] Various allylic alcohols as well as allyl carboxylates can be applied as substrates.[140]

In addition, the complex of $NiBr_2$ with Xanthene-phosphole ligand **76** demonstrates high activity in dimerization of ethylene to afford 1-butene in 97% yield.[141] Meantime, the complex of $NiCl_2$ with 1-(2-pyridyl)phosphole **71** in the same reac-





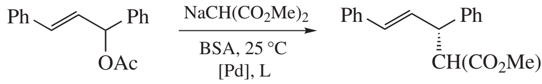
4b

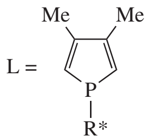


76

tion gives 1-butene only with 80% selectivity.[142] Gold(I)–1,2,5-triphenyl-1-monophosphole **4b** complex is of considerable interest as a catalyst of recently discovered cycloisomerization of enynes.[143]

However, the most striking and demanded use of phosphole complexes and their cycloadducts is asymmetric catalysis. Thus, the catalysts based on 1-monophospholes with chiral substituents R* (menthyl, myrtanyl, 4-isopropyloxazolinylphenyl, 2-methoxymethylpyrrolidine) at the phosphorus atom **77**, monophospholyl metal complexes **78** and BIPHOS with axial chirality **79** exhibit good activity and selectivity in the asymmetric allylic alkylation of 1,3-diphenylprop-2-enyl acetate. The reaction proceeds under mild conditions with the following enantiomeric yields: *ee* 89% for **77**,[33,144] *ee* 99% for **78**,[145] *ee* 80% for **79**.[146,147] Good enantioselectivity (*ee* 89%) and moderate activity in the asymmetric Heck reaction between iodobenzene and 2,3-dihydrofuran were achieved by the use of a palladium complex with chiral P,N-phosphole **81**.[129]





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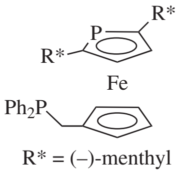

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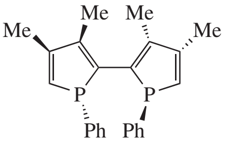

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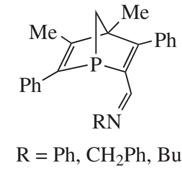

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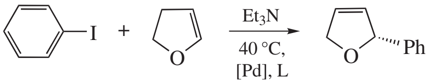

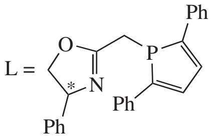

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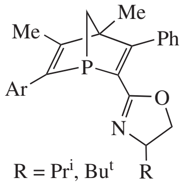

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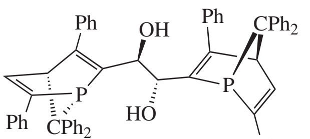
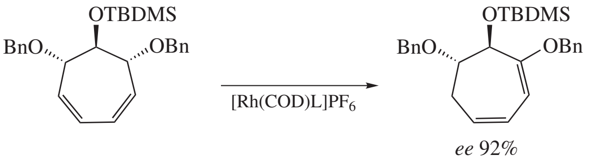
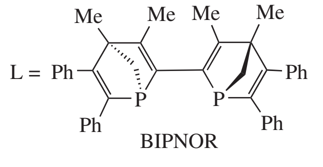


83

The most promising results were obtained with the use of catalysts based on cycloadducts of phospholes such as 1-phosphanorbornenes and 1-phosphanorbornadienes. They are regarded as structurally rigid, bulky, labile, weak σ-donor ligands. These systems are characterized by the presence of a chiral non-racemizable phosphorus atom located at the bridgehead of a bicyclic system. This is the reason why these phosphorus ligands are of industrial interest for asymmetric catalysis (high TON, heating the reaction mixture, recycling the catalyst).[148] These frame phosphines were successfully employed in various asymmetric reactions and compete with the best reported ligands in terms of both activity and enantioselectivity. Thus, enantiopure P,N-hybrid ligands **80**, **82**, **83** derived from enantiopure 1-phosphanorbornadiene-2-carboxaldehyde[149] show excellent enantioselectivity in allylic alkylation (*ee* 94%) and asymmetric Heck reactions (*ee* 94%).[150–152] A new derivative C_2-BIPNOR **83** has also demonstrated the excellent enantioselectivity in hydrogenation (*ee* 88–93%), allylic alkylation (*ee* 86%) and the Heck reactions (*ee* 96%).[153]

The cycloadduct of 1,1′-biphosphole and diphenylacetylene BIPNOR **84** exhibits similar activity as BINAP and DIOP in Rh-catalyzed hydrogenation of dehydrocarboxylic acids (*ee* 93–98%) and aryl methyl ketones (*ee* 60–81%).[154] However, the activity of Rh-BIPNOR catalysts is much higher than that of BINAP and DIOP based systems in asymmetric isomerization of cyclic diene (*ee* 92%).[155,156] At the same time, the ferrocenyl analogue of BIPNOR **85** showed a lower enantioselectivity in hydrogenation, hydroformylation and allylic alkylation reactions, *ee* in this case was 15–54%.[34]





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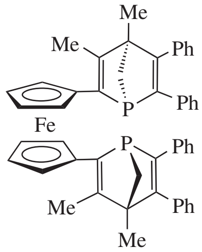
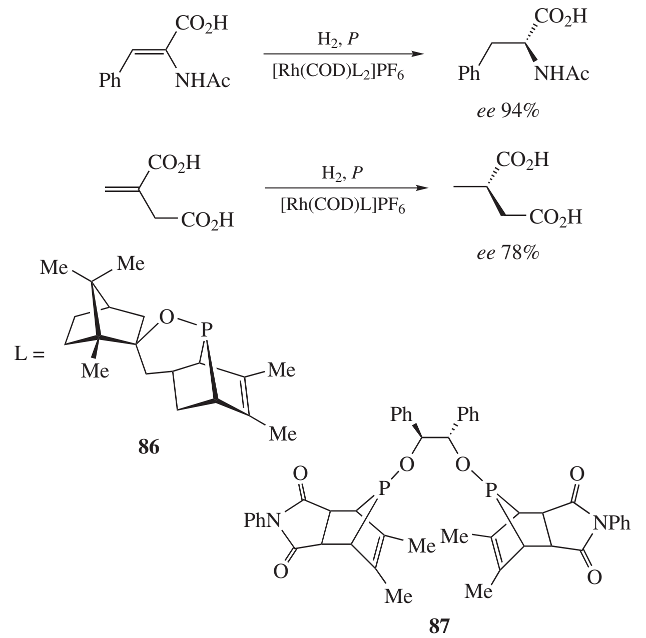


85

7-Phosphanorbornenes **86** and **87** display high activity (100% yield, the reaction time is 15–30 min) and good enantioselectivity (*ee* 41–44% for **86** and *ee* 78–94% for **87**) in the hydrogenation of functional alkenes. This type of structures is readily accessible by [4+2] cycloaddition of phospholes with dienophiles and can be easily fine-tuned. These preliminary experiments illustrate the potential of the readily available 7-phosphanorbornenes in enantioselective catalysis.[157]

4.2. Electro-optical materials based on phospholes and their derivatives

Electro-optical substances (various heterocyclopentadienes, linear π-conjugated oligomers and polymers) have extended double bond conjugation, low HOMO–LUMO energy gap and thus reveal electronic absorption and emission at relatively high wavelengths. In the last decade, numerous applications of monophos-



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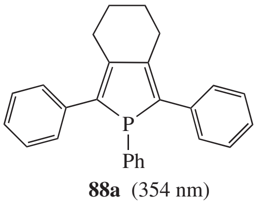
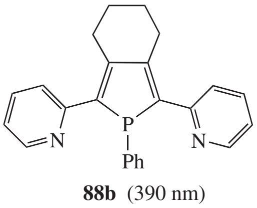
phole derivatives as electro-optical substances, in particular, light-emitting diodes (LED), photovoltaic cells and thin-film transistors, were described.[158–160] Theoretical studies of the light absorption by conjugated phospholes have been published.[161–164] Geometric and electronic features of phospholes prevent an efficient endocyclic conjugation of the electron-sextet. In fact, the delocalization within the phosphole ring arises from a hyperconjugation involving the exocyclic P–R σ-bond and the π-system of the dienic moiety.

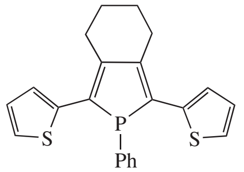
One appealing property of these P-building blocks is that they possess reactive phosphorus centres providing direct access to a range of novel π-conjugated systems. Thus, chemical modifications (oxide, sulfide, quaternary salt, metal complex) at the phosphorus atoms allow the fine-tuning of the optical and electrochemical properties of phosphole-based π-conjugated materials. Furthermore, the ability of P-centres to coordinate transition metals offers manifold opportunities to build supramolecular architectures in which the π-systems can be organized in a well-defined manner.[165] The following series demonstrates well how the absorption maximum λ_{max} (and emission maximum, respectively) changes by varying the substituents in 1-phenylphosphole.[166]



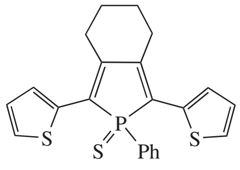
88a (354 nm)



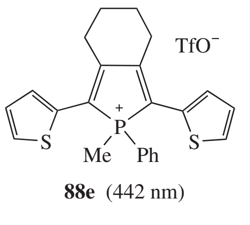
88b (390 nm)



88c (412 nm)

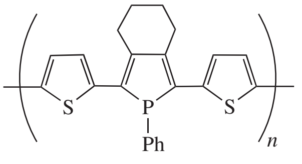


88d (432 nm)

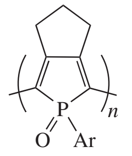


88e (442 nm)

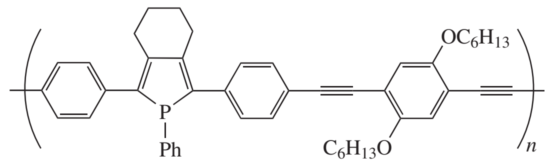
Another useful property of the phosphole-based systems **88c–e** is that they can be electrochemically oxidized forming radical cations that polymerize on the electrode to afford π-conjugated polymers **89a**. Such polymers have absorption maximum λ_{max} in the range 550–600 nm and are of potential value as novel electroconductors.[12,167–170] Another polymer **89b** with $M_r = 10200$ obtained by the Sonogashira coupling had $\lambda_{max} = 410$ nm. Compared to $\lambda_{max} = 354$ nm for the building block **88a**, it is obvious that conjugation must include acetylenic π-orbitals. The fluorescence emission spectrum had a $\lambda_{max} = 490$ nm in the blue-green region.[171] Striking example is α,α′-linked polyphosphole **90** which possesses an extremely narrow band gap ($\lambda_{max} = 655$ nm) and a high electron-accepting ability.[172]



89a (550 nm)

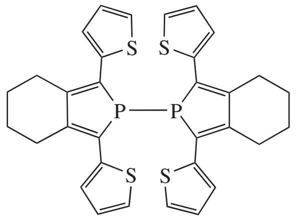


90 (655 nm)



89b (410 nm)

It has also been noted that the P–P bond, as in **91**, can act as a σ-transmitter of the conjugation and can exert an influence on the electronic spectrum.[173] Recently, the synthesis of novel phospholes with triazole **93**,[174] azulene and thiazole **94**[175] moieties in the α-position was reported. A striking application of the conjugated phospholes is their functioning in LEDs.[176,177] Indeed this represents the first use of an organophosphorus compound for this purpose. Compound **88d** was deposited as a thin film and sandwiched between a bilayer anode and cathode. The device gave yellow emission with a turn-on voltage of 2 V. The AuCl complex **92** was also used in a LED device. It is now obvious that monophosphole and its derivatives deserve serious consideration in LED technology.[178]



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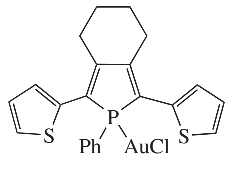

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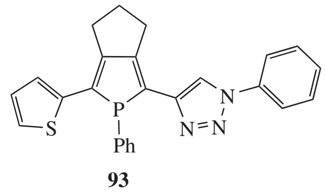

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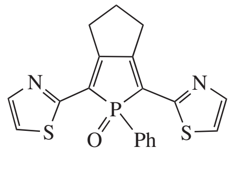

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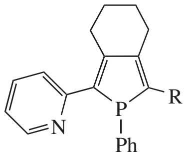
Note that due to their nonaromaticity, asymmetric 2,5-disubstituted phospholes containing electron-donor and electron-withdrawing substituents in the α-position, are regarded as promising candidates for the development of P-materials for nonlinear



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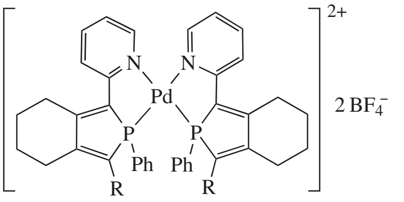

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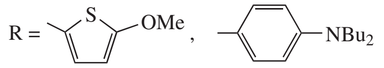

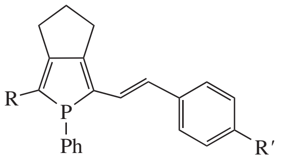

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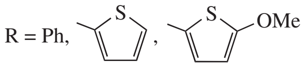
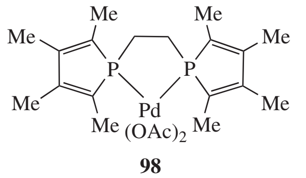


R′ = H, CF_3, Cl, CO_2Me

optics (NLO). Thus, phosphole-based NLO chromophores **95**, **97** and their metal complexes **96** demonstrate a high molecular hyperpolarizability and excellent NLO properties.[179–181]

4.3. Biological applications of phospholes and their derivatives
Recently, some pioneering works have been done in the field of biological and medical applications of P-heterocycles and their derivatives. Due to the weak aromaticity of the ring and nucleophilic properties of the phosphorus atom, monophospholes are of considerable interest for the inhibition of disulfide reductases, such as thioredoxin reductase (hTrxR) and glutathione reductase (hGR). For example, phosphole–palladium(II)[182] **98** and phosphole–gold(I) **99**[183,184] complexes are highly potent nanomolar inhibitors of hTrxR and the related human hGR. The extraordinary properties of these metallodrugs might be exploited for cell biological studies or medical applications, *e.g.* as antitumor or antiparasitic drugs.[185] A dimer of 3-methyl-1-(2,4,6-triisopropylphenyl)phosphole oxide **100** showed GI_{50} values in the micromolar region against different cell lines.[186] In addition, recently phosphole moieties have been incorporated into the side chain of alanine, tyrosine and phenylalanine **101** and **102**. These molecules are seen as valuable building blocks for the preparation of phosphole-containing polypeptides and metalloproteins for chemical, biological and medical applications.[187,188]



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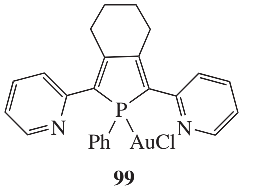

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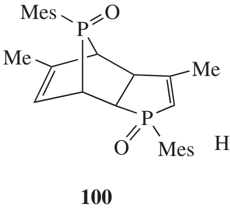

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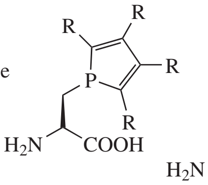

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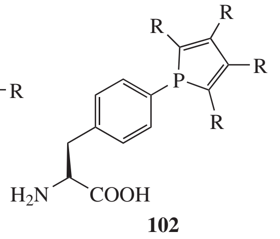

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Note that phospholes, as well as heterophospholes and annelated heterophospholes containing an additional O, S, N heteroatom are regarded as analogues of classical heterocycles and are of great fundamental and practical interest for biological and medical applications.[189] The synthesis of P–C and P–N analogues of natural heterocycles, their cycloaddition reactions and coordination chemistry open gateway to a new class of P-heterocycles, biologically active substances and drugs.[190]

Conclusion and outlook

The pioneering work on monophosphole synthesis in the 1970s spurred the development of novel higly effective phosphole-based catalysts, materials for light-emitting diodes, nonlinear optics, conductive polymers and metallodrugs in the past ten years. These intriguing, young research areas are now wide open for investigation. Structure-property relationships have still to be established for these P-heterocycles in order to fully exploit their potential for practical applications.

Although di- and triphospholes have been synthesized only recently, great work has been done in organic and coordination chemistry of these compounds. In our opinion, these P-based building blocks can offer specific properties different from monophosphole and its S, N, O counterparts both from the theoretical and practical standpoints.

Polyphospholes are stable analogues of 2*H*-phosphole and can exhibit high reactivity in cycloaddition reactions leading to novel polycyclic polyphosphorus compounds, which are promising structurally rigid, bulky, labile, weak σ-donor ligands for the use in homogeneous as well as asymmetric catalysis. Furthermore, the gradual increase in the donor P-atoms number and aromaticity in polyphospholes could be used for construction of η^1, η^2, η^4, η^5 type metal complexes and clusters, coordination polymers. For this ‘aromaticity’ reason it is also intriguing to investigate di- and triphospoles as new building blocks for organophosphorus π-conjugated systems and electro-optical substances. It is quite clear that the coordination chemistry of these P=C bond containing systems is expected to be remarkably different from that of classical C, N and other P-based ligands, including 1*H*-phospholes. This may promote widering range of catalytic applications of the polyphosphole metal complexes.

As we have seen, chemistry of phospholes opens a gateway to novel organophosphorus compounds having significant potential in coordination chemistry and homogeneous catalysis, new P-based molecular materials, biologically active substances and drugs. It is thus very likely that new developments will arise in the nearest future.

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