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Diels–Alder reactions involving >C=P– functionality

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1. Introduction and scope of the review

Professor Otto Diels[1] and his student Kurt Alder[2] while disclosing their landmark discovery first time in 1928[3] made the prophetic announcement: "Thus it appears to us that the possibility of synthesis of

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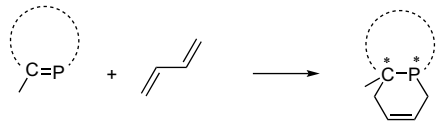
complex compounds related to or identical with natural products such as terpenes, sesquiterpenes, perhaps even alkaloids has been moved to the near prospect." In the initial stages, the most significant contribution realizing the dream of Diels and Alder was perhaps made by R.B. Woodward who used the Diels–Alder (DA) reaction in elegantly planned syntheses of a number of naturally occurring complex molecules such as cortisone, cholesterol, reserpine, etc.[4] on the one hand and rationalized the observed regio- and stereoselectivities in the reactions by proposing Woodward–Hoffmann orbital symmetry rules[5] for pericyclic reactions on the other hand.

Over the past 80 years, applications of the DA reaction in achieving the desired goals in synthetic organic chemistry have conferred a sort of cardinal status on it. The extension of the DA reaction to the organophosphorus compounds incorporating >C=P– and –C≡P functionalities is a rather new development. The first example of the DA reaction with the participation of the PC double bond of a diazaphosphole as dienophile was reported by Arbuzov and co-workers[6,7] in 1979. Almost at the same time, Bickelhaupt and co-workers[8] showed that acyclic phosphaalkenes could react as dienophiles. Subsequent work carried out in the research group of Appel[9] established several interesting features associated with the DA reactions of phosphaalkenes, such as inversion of phosphorus in the cycloadduct, kinetic preference for the *endo* adduct with cyclopentadiene and the configuration of phosphaalkene being maintained during the cycloaddition. Mathey and co-workers showed that 1*H*-phospholes underwent a 1,5-H shift followed by dimerization through a DA reaction.[10] The first DA reaction involving the –C=C–C=P– moiety of phosphinine as diene was reported by Märkl and co-worker,[11] while Mathey and co-worker showed that phosphinine could react as dienophile as well, reaction taking place at the >C=P– functionality.[12]

The diagonal relationship between the elements in the Periodic Table is well documented, but its existence in the carbon–phosphorus pair has been realized only lately.[13] The heterophospholes have been termed as a postscript chapter of the heterocyclic chemistry, due to their close resemblance with the related non-phosphorus analogues.[14] Nevertheless, there exists much difference in the strengths of the P=C and C=C bonds, the former being only 60–70% as strong as the latter.[15–17] As a result of the weakness of the P=C functionality, its participation in the pericyclic reactions, including DA reactions as shown later, is found to be rather more facile than that of the >C=C< moiety.[9,18]

During the last three decades, a variety of organophosphorus compounds incorporating the >C=P– functionality, acyclic as well as cyclic, aromatic as well as non-aromatic, has become accessible. Besides phosphaalkenes,[9,18] heterophospholes[19] including anellated azaphospholes[20] and phosphinines[21] are other such examples. In an appropriately substituted phosphaalkene, heterophosphole or phosphinine, both the phosphorus and the carbon atoms of the >C=P– moiety are prochiral and DA reaction with it leads to the generation of two stereogenic centres in one step (Scheme 1).



Scheme 1.

The results, however, indicate that the reactions normally proceed with complete diastereoselectivity and regioselectivity, evincing the possibility of making the chiral phosphines available.

With the advancement of computational facilities, in recent years theoretical studies have been extended, though in a limited manner, to the investigation of the electronic structure of the organophosphorus compounds and mechanisms of their reactions.[22] The DA reactions of phosphaethene,[23] phosphaethyne,[24] phosphabutadiene,[25] azaphospholes[26] and phosphinines[27] have been investigated theoretically.

Different aspects of the DA reactions of non-phosphorus compounds have been reviewed frequently,[28] but no comprehensive review has so far appeared exclusively on the DA reactions of organophosphorus compounds having a >C=P– functionality. The reviews dealing with the chemistry of phosphaalkenes, heterophospholes and phosphinines include, though in a limited manner, the DA reactions of the respective classes of these compounds. Thus, the DA reactions of phosphaalkenes with 1,3-dienes and heterodienes up to 1987 are included in an earlier review.[9c] The reviews on heterophospholes[19] and anellated azaphospholes[20] briefly mention the [2+4] cycloadditions on the >C=P– functionality of these systems up to the year 2001. A general review on cycloaddition reactions of heterophospholes includes their DA reactions, as well, published up to December 2003.[29] Phosphinines have not been used much as dienophiles; only two reactions are reported up to 1987, which are included in a review.[21a] However, some interesting DA reactions are given by phosphinines in which they participate as 1,3-phosphabutadienes and afford phosphabarrelene derivatives. These reactions are briefly described in recent reviews.[30] A review on phospholes dealing mainly with their coordination chemistry includes the DA reaction of 2*H*-phosphole, formed as a result of a 1,5-H shift in 1*H*-phosphole.[31]

In the present review, it is aimed to compile an up-to-date account (July, 2008) of the DA reactions of the >C=P– functionality present in phosphaalkenes, phosphadienes, heterophospholes, 2*H*-phospholes and phosphinines in a systematic manner. In many cases, a DA reaction has been used for trapping the transiently generated species such as phosphaalkenes having a >C=P– functionality; such examples are also included.[32] As regards phosphadienes, both types of their reactions, namely the reactions on the CP double bond as well as those in which they participate as the diene, will be included. A DA reaction of phosphaketene is also described. Only those DA reactions of phospholes are included, which involve the >C=P– moiety, as a component of diene or as dienophile. Similarly, the DA reactions of phosphinines in which they react as phosphadienes, as well as those involving the >C=P– bond as dienophile, will find a place in this review. A few examples of the DA reactions reported on the –P=P– functionality are also included. In many cases, the DA cycloadducts have been converted subsequently into other useful products, particularly the metal complexes. In order to enhance the utility of this overview, wherever appropriate, such further reactions of the cycloadducts will also be shown. As mentioned earlier, in recent years theoretical studies have been carried out to explain the reactivities (vis-a-vis the analogous all-carbon systems) of the compounds having a >C=P– functionality. These results will be included, wherever necessary, for explaining the observed course of the reaction. We hope that these discussions will highlight the potential of this synthetic method as an important tool to obtain a large variety of organophosphorus heterocycles or subsequent products thereof and inspire the reader to explore further the syntheses not undertaken so far.

2. Electronic structure of >C=P– functionality and energetics of its DA reaction

As mentioned earlier, a close analogy exists between the chemistries of the >C=P– and >C=C< functionalities. However, the P=C bond (45 kcal mol^{-1} in HP=CH_2) is much weaker than the C=C bond (65 kcal mol^{-1} for CH_2=CH_2).[33] Furthermore, the more electropositive character of phosphorus makes the π^* orbital of the P=C bond of lower energy as compared to that of the C=C moiety. As a consequence, phosphaalkene and phosphorus-heterocycles incorporating a >C=P– functionality undergo the DA reaction much more readily than the analogous all-carbon systems. Molecular

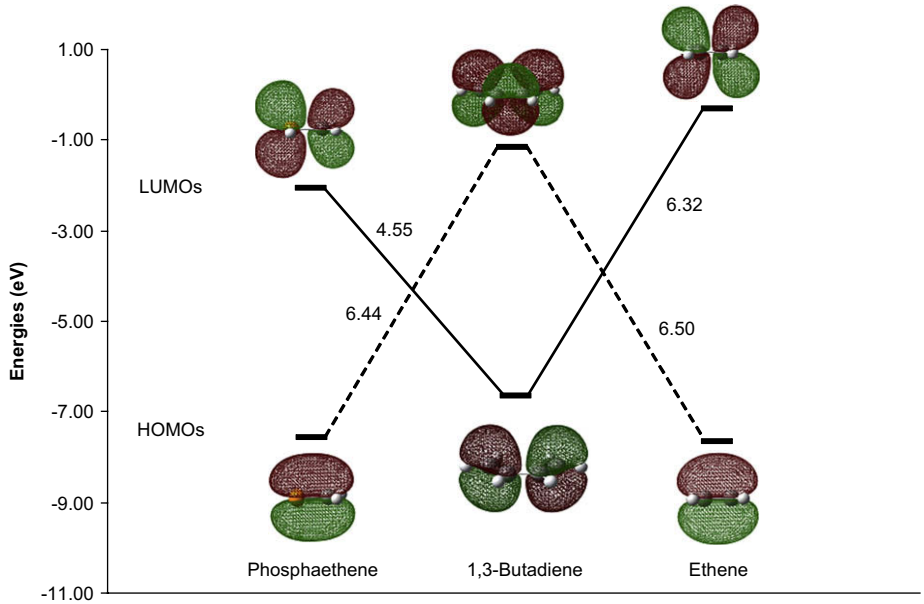


Figure 1. Frontier molecular orbitals of phosphaethene, 1,3-butadiene and ethene at B3LYP/6-311+G**.[23a]

orbital calculations of phosphaethene at the HF/STO-3G,[34] as well as DFT (B3LYP/6-311+G**)[23a] level, reveal HOMO as the π orbital. The FMOs (B3LYP/6-311+G**) of phosphaethene, 1,3-butadiene and ethene are given in Figure 1.[23a] It may be noted that the $HOMO_{diene}$–$LUMO_{phosphaethene}$ gap (4.55 eV) is much smaller than that between $HOMO_{diene}$–$LUMO_{ethene}$ (6.32 eV). Accordingly, on the basis of FMO theory, the DA reaction of phosphaethene is expected to be much faster with a lower activation barrier than that of ethene (Fig. 2). In fact, the DA reaction of phosphaethene, generated in situ, with 2,3-dimethylbutadiene occurs under much milder conditions[35] than that of ethene. A more or less similar pattern prevails for the DA reactions of other classes of organophosphorus compounds having a >C=P– group, except that the feasibility and conditions of the reaction may change, depending on the environment of the >C=P– moiety. For example, the activation barrier for the DA reaction of azaphospholes and phosphinines, wherein the >C=P– moiety is integrated with the aromatic sextet, is raised and more vigorous conditions become necessary, but still these reactions proceed at a much lower temperature than those (if at all) of the analogous all-carbon systems (see later).

3. Diels–Alder reactions of phosphaalkenes

A review on phosphaalkenes includes a detailed description of their DA reactions reported up to 1989.[9c] An earlier review covers these reactions up to the middle of 1987.[18]

The P=C functionality of phosphaalkenes participates mainly as the dienophile and DA reactions of differently substituted phosphaalkenes, stable as well as unstable (generated in situ), have been carried out successfully with 1,3-dienes and heterodienes. Electronic

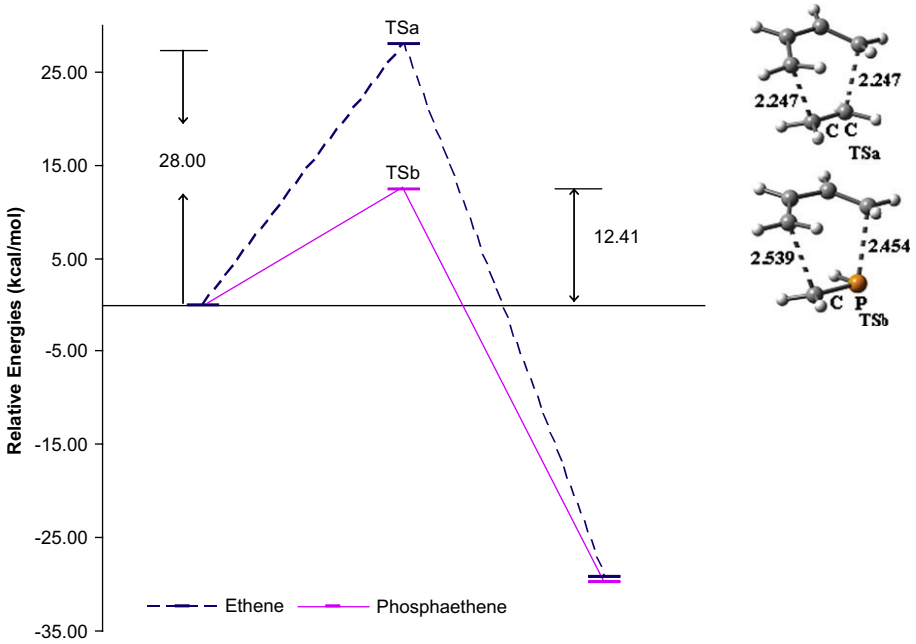
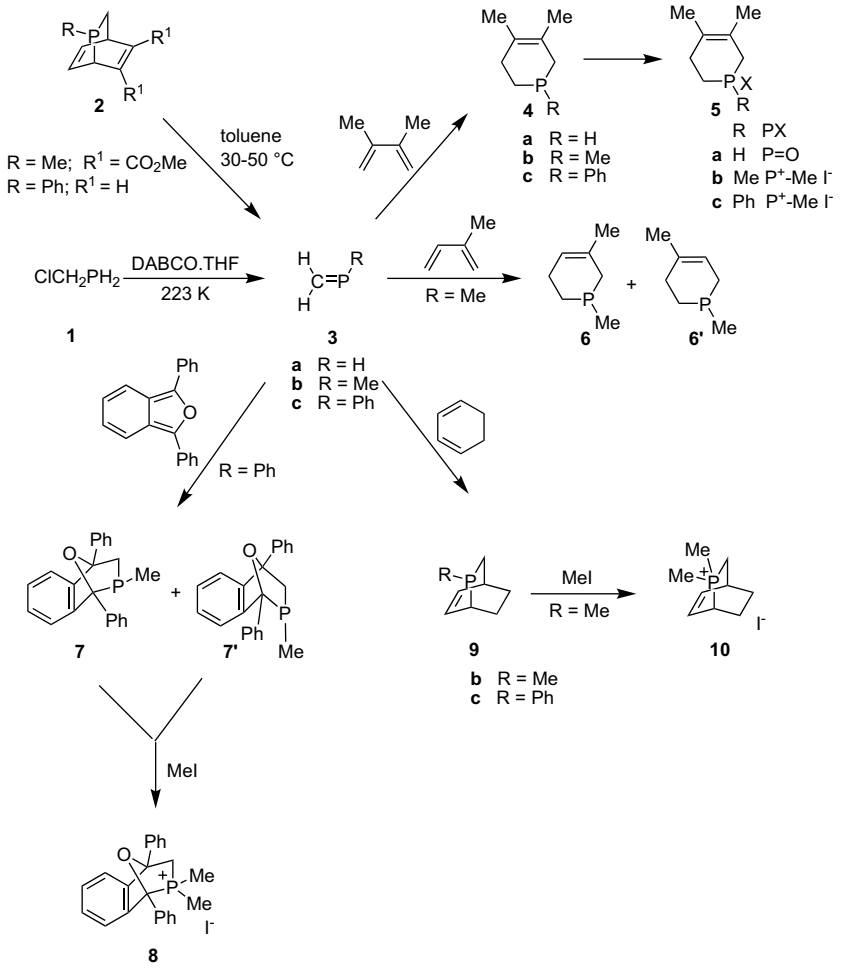


Figure 2. Relative energies at B3LYP/6-311+G**+ZPE (B3LYP/6-31G*) for the DA reaction of ethene or phosphaethene with 1,3-butadiene.[23a]



Scheme 2.

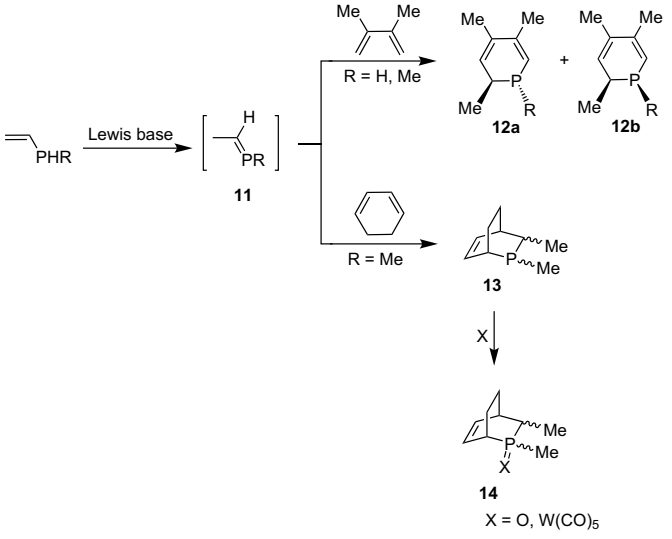
and steric factors play a prominent role in determining the reactivity of a particular phosphaalkene. The reactions proceed normally with high diastereoselectivity, the *endo*-stereoisomer being preferred. Besides, wherever applicable, regioselectivity is also observed.

3.1. With 1,3-dienes

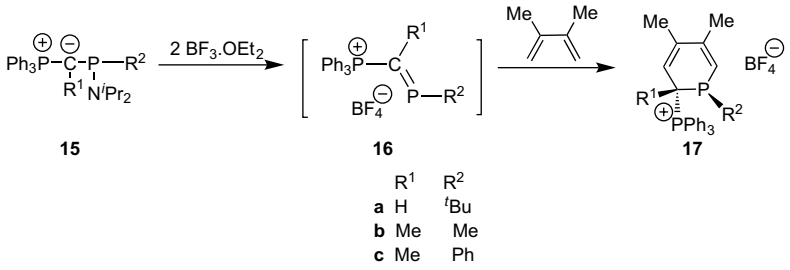
The parent phosphaalkene, namely phosphaethene (**3a**), generated in situ, was trapped with 2,3-dimethylbutadiene to give tetrahydrophosphinine (**4a**), the latter being subsequently oxidized to **5a**.[35] Likewise, *P*-methyl- and *P*-phenylphosphaethenes (**3b** and **3c**) were also produced in situ by thermally induced extrusion of the phosphorus-containing bridge from appropriately substituted 2-phosphabicyclo[2.2.2]octa-5,7-dienes (**2**)[36] and trapped with a variety of 1,3-dienes[37] in toluene (Scheme 2). The reaction with isoprene occurs regioselectively, regioisomers **6** and **6′** being formed in a 2:1 ratio. The DA reaction of **3b** with 1,3-diphenylisobenzofuran yielded both the *exo* (**7**) and *endo* (**7′**) isomers. Both on reaction with methyl iodide changed into the same quaternary salt **8**. As revealed by ^{31}P NMR, DA reaction of **3b** occurred with 2-methylfuran also, forming two isomers in a 4:1 ratio, although the products or their methyl iodides could not be isolated, due to insufficient stability. The DA reaction with cyclohexadiene gave only one isomer **9**, thought to have the *syn* geometry (vide infra).

In another approach, phosphapropenes (**11**), generated transiently from base-catalyzed rearrangement of vinylphosphines, were trapped with 1,3-dienes to give [2+4] cycloadducts **12**, **13** in highly diastereoselective manner (**12**, R=Me, ca. 97:3 molar ratio), although the configuration of the major isomer could not be assigned (Scheme 3)[38,39] The cycloadducts (**13**) obtained with 1,3-cyclohexadiene were oxidized with air and also converted into tungstenpentacarbonyl complexes (**14**) (Scheme 3).[32,38,39]

2-Phosphonio-substituted phosphaethenes **16** were generated in situ from the action of a Lewis acid on the corresponding



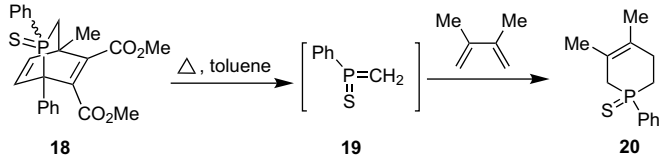
Scheme 3.



Scheme 4.

phosphonium ylide **15** and trapped with an excess of 2,3-dimethylbutadiene to give the [2+4] cycloadducts **17** in a completely diastereoselective mode, giving only one diastereomer in each case. This observation supports a concerted mechanism (Scheme 4).[40] In the DA reaction of **16** (R^1=Me, R^2=Ph), the ylide **16** (R^1=Me, R^2=N^{i}Pr$_2$) was formed as the side product. The phosphaalkenes **16** (R^1/R^2=H/N^{i}Pr$_2$; Me/N^{i}Pr$_2$) produced in this manner did not react with 2,3-dimethylbutadiene.

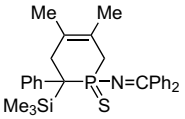
P-Phenylphosphaethene sulfide (**19**) was generated transiently from **18** and trapped with 2,3-dimethylbutadiene to yield tetrahydrophosphinine sulfide derivative **20** (Scheme 5).[41]



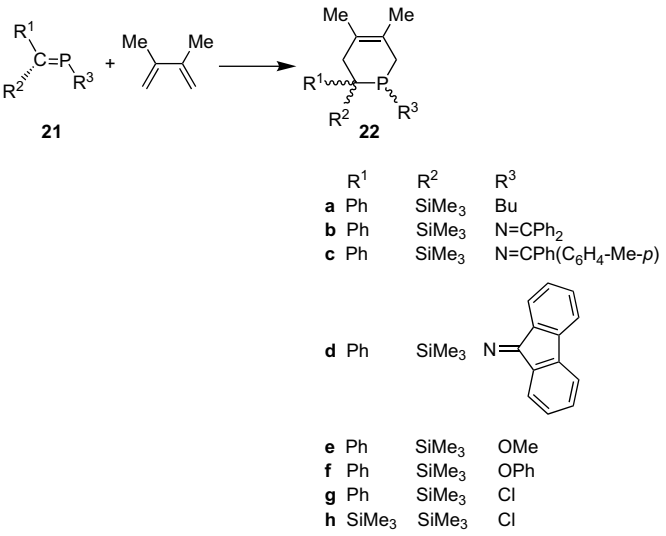
Scheme 5.

As mentioned earlier, electronic and steric factors affect the reactivity of a substituted phosphaalkene. While phosphaalkenes having bulky substituents such as 2,4,6-^{t}Bu$_3$-C$_6$H$_2$– and 2,4,6-Me$_3$C$_6$H$_2$– at phosphorus fail to undergo [2+4] cycloaddition,[42] electron-acceptor substituents in phosphaalkenes and electron-donor substituents in 1,3-dienes help the successful occurrence of the DA reaction.[9b,c] The DA reactions of differently substituted phosphaalkenes (**21**) with 2,3-dimethylbutadiene occur with high diastereoselectivity.[43–45] On heating, the kinetically preferred products change into thermodynamically more stable isomers. For **22** (R^1/R^2=SiMe$_3$/Ph; R^3=OMe, OPh), this change could also be achieved by treating the product with a solution of methanol or phenol, respectively.[43] That the interconversion of the diastereoisomer results due to inversion at the σ^3-phosphorus is confirmed by the fact that this change does not occur in the case of **23** having phosphorus oxidized with sulfur (Scheme 6). The structures of both diastereoisomers of tetrahydrophosphinine sulfide **23** were confirmed by X-ray crystallographic investigations.[43]

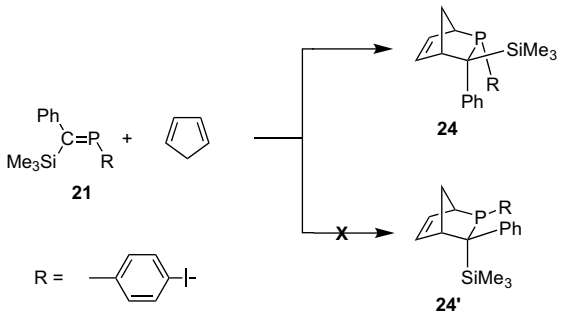
Likewise, high diastereoselectivity was observed in the DA reaction of **21** ($R^1/R^2/R^3$=NMe$_2$/H/Ph) with 2,3-dimethylbutadiene; the major isomer (δ ^{31}P=−46.0 ppm) was separated and converted into its *P*-sulfide (δ ^{31}P=31 ppm). A small amount of the [2+2] cycloadduct was also formed.[46,47]



The reaction of **21** ($R^1/R^2/R^3$=Ph/SiMe$_3$/C$_6$H$_4$-^{t}Bu-*p*) with cyclopentadiene occurred with complete stereoselectivity and isomer **24**, having the trimethylsilyl group in the *exo*-position, was the only product formed (Scheme 7). The structure of **24** was confirmed by an X-ray crystallographic determination.[48]



Scheme 6.

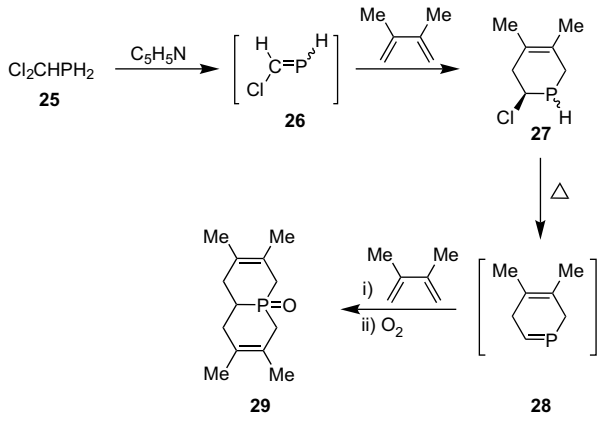


Scheme 7.

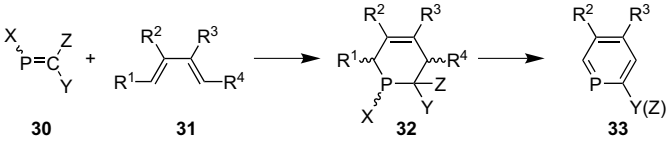
The DA reactions of *C*-chloro- and *P*-halophosphaethenes, often generated in situ by the dehydrochlorination of polychloromethylphosphines, have been employed for the preparation of phosphinines. The initially formed [2+4] cycloadducts are aromatized either by thermal 1,2-elimination or by chemical transformation.[21] The functionalized phosphinines have also been obtained in a similar manner.

C-Chlorophosphaethene (**26**) was generated transiently from the monodehydrochlorination of (dichloromethyl)phosphine (**25**) in the presence of a weak base like pyridine and trapped with 2,3-dimethylbutadiene at room temperature. ^{31}P NMR spectroscopy indicated the formation of two diastereoisomers of **27**. On heating the solution, **27** lost HCl to produce the transient dihydrophosphinine **28**, which afforded **29** through a subsequent [2+4] cycloaddition with 2,3-dimethylbutadiene followed by oxidation (Scheme 8).[49,50]

Likewise, DA reactions of differently substituted *P*-halophosphaethenes (**30**), generated transiently in situ or pre-synthesized in a stable form, have been carried out successfully with a variety of dienes (**31**) (Scheme 9). In the presence of appropriate



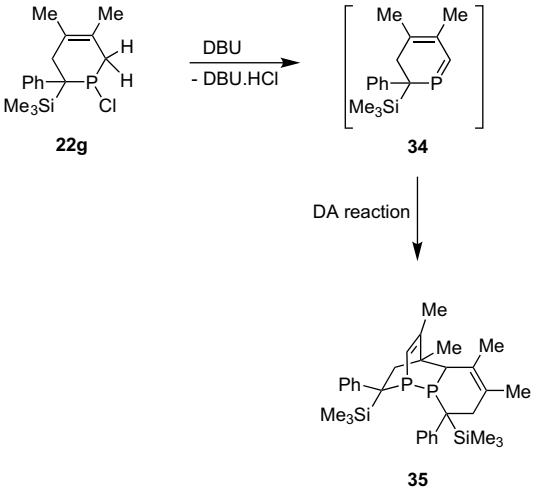
Scheme 8.



Scheme 9.

substituent groups, the initially formed [2+4] cycloadducts **32** change into phosphinine derivatives **33**.[43,51–61] Hydrogen halide and Me_3SiCl are usually lost during this conversion. Sometimes, a tandem DA reaction occurs.

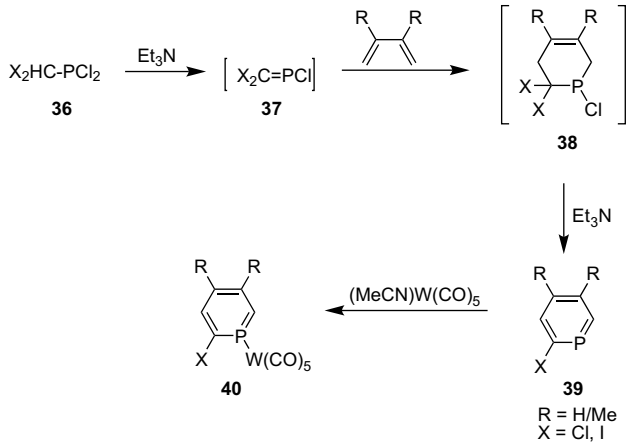
The DA cycloadduct **22g** ($R^1/R^2/R^3$=Ph/$SiMe_3$/Cl), obtained from the reaction of **21** with 2,3-dimethylbutadiene, on heating, did not split off Me_3SiCl, but, on treating with DBU, lost HCl to give **35** as the final product (Scheme 10). The latter resulted from the



Scheme 10.

dimerization of **34** in the DA reaction mode in which it (**34**) acted as dienophile as well as diene. Formation of the proposed intermediate **34** was established by NMR spectroscopy, as well as by trapping with various dienes and dienophiles. The structure of **35** was confirmed by an X-ray crystallographic investigation.[43]

Trichlorophosphaethene (**37**, X=Cl) and 1-chloro-2,2-diiodophosphaethene (**37**, X=I), generated transiently in situ, on reaction with 1,3-dienes followed by dehydrohalogenation afforded 2-chloro-[51,52] and 2-iodophosphinines,[53–55] respectively (Scheme 11). Starting from (dibromomethyl)dibromophosphine, 2-bromophosphinine was prepared in similar manner.[52] 2-Chlorophosphinine (**39**, R=H; X=Cl)[51,52] and 2-iodophosphinines (**39**, R=H, Me; X=I)[53–55] were subsequently converted into tungstenpentacarbonyl complexes **40**.



Scheme 11.

2-Iodophosphinines (**39**, R=H, Me; X=I), as such, could not be lithiated, but their $W(CO)_5$ complexes **40** showed iodo-lithium exchange with ^{n}BuLi to give **41**.[55] In contrast, no chloro-lithium exchange was observed in the reaction of the 2-chlorophosphinine.$W(CO)_5$ complex with BuNHLi, instead, attack occurred at phosphorus to generate the anion **42** (Scheme 12).[52] On using LDA, **43** was formed, which could be methylated to give **44**.[52] By X-ray crystal structural determination and theoretical calculations for **40** (R=H, X=Cl), it was shown that a 2-chloro substituent enhanced electronic delocalization (and, hence, stability) of the phosphinine ring, thereby making the substitution of chlorine less favourable.[52]

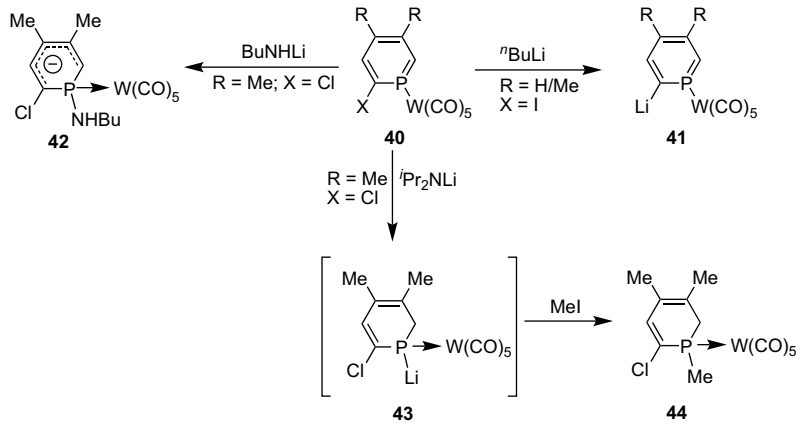
2-Iodophosphinine (**39**, R=Me, X=I) on heating with $Cr(CO)_6$ afforded n^1P-$Cr(CO)_5$ complex **45** only in low yield (12%). Several other organometallic derivatives (**46**–**49**) as well as a diphosphinine were prepared from 2-iodophosphinine or its *P*-$W(CO)_5$ complex at low temperature (Scheme 13).[55]

The methodology described above was subsequently extended to the synthesis of several interesting anellated phosphinines. Thus, the reactions of trichlorophosphaethene (**50**), generated in situ from dichloro(dichloromethyl)phosphine, with 1-vinylnaphthalene (**51**, taken in excess) and with 1-(1-methylethenyl)cyclohexene (**54**) afforded the anellated phosphinines **53** and **56**, respectively (Scheme 14).[56] On using excess of the dienes (**51** and **54**), formation of the [2+2] cycloadduct,[57] as monitored by ^{31}P NMR, could be avoided completely. However, polymerization of **50** and **51** lowered the yield of the cycloadduct **53**. The phosphinine **56** was subsequently converted into its tungstenpentacarbonyl complex **57**.

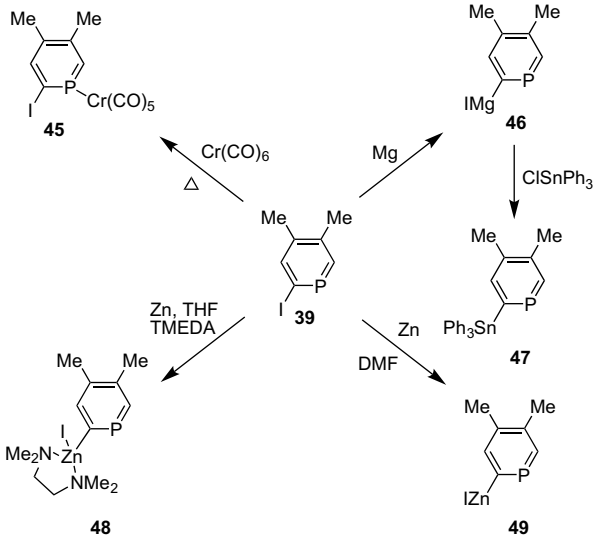
The DA reaction of **50** with 1-(1-trimethylsiloxyethenyl)cyclohexene (**58**), however, proceeded in an unexpected manner: the initially formed [2+4] cycloadduct **59** lost only 1 equiv of HCl to generate **60**. The latter behaved in a similar manner to **34** (Scheme 10) and reacted with one more equivalent of **58** on the >C=P– moiety with complete regioselectivity to yield **61** as the final product (Scheme 15).

The structure of **61** was established in several ways, particularly by carrying out another tandem DA reaction commencing with **64**, the pentacarbonyltungsten complex of **50**,[56] when **67**, the pentacarbonyltungsten complex of **61**, was obtained (Scheme 16). The observed sequence of reactions and regioselectivity were rationalized theoretically on the basis of MNDO/PM3 calculations.[56]

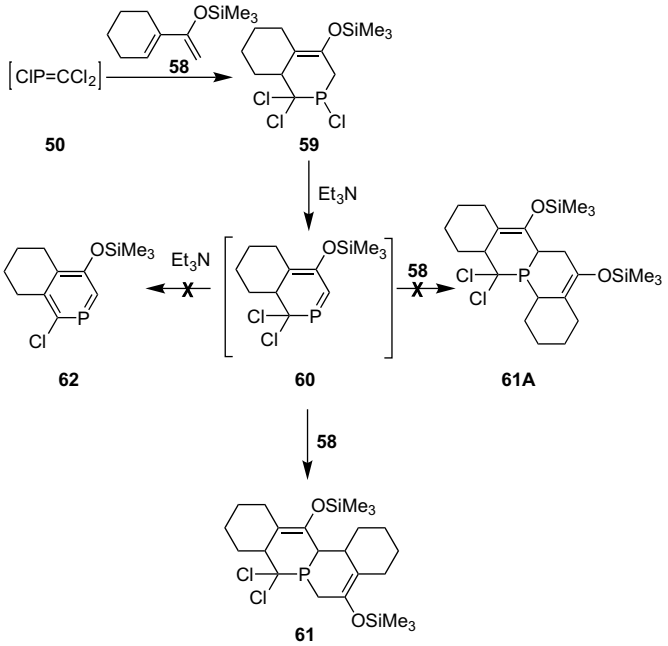
In fact, tungstenpentacarbonyl-stabilized *P*-chlorophosphaethene (**69**) was first generated from **68** transiently and used as a dienophile in the DA reactions to obtain **71** and **72** by Mathey and co-worker (Scheme 17).[58] However, PhP=$W(CO)_5$, generated in situ, reacted as phosphinidene and gave cheletropic cycloadditions with alkenes and 1,3-dienes under similar conditions.[59]



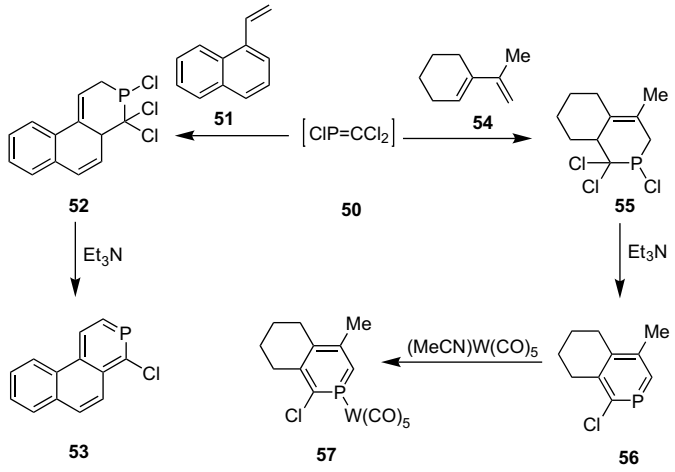
Scheme 12.



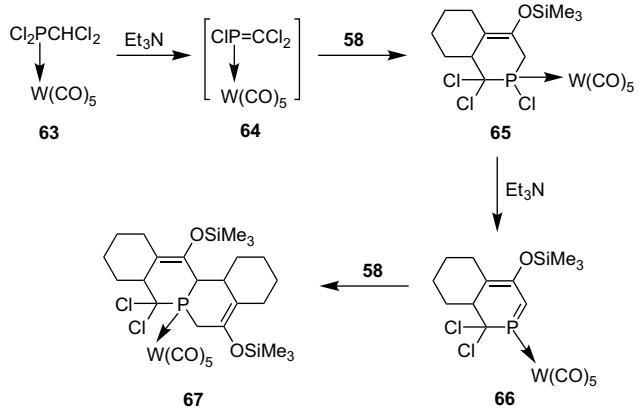
Scheme 13.



Scheme 15.



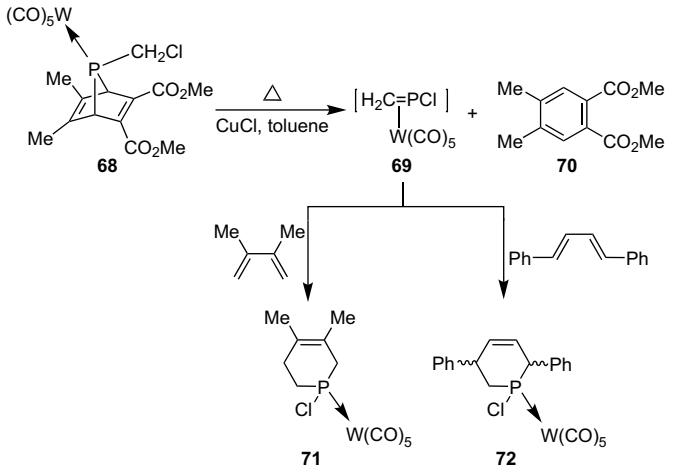
Scheme 14.



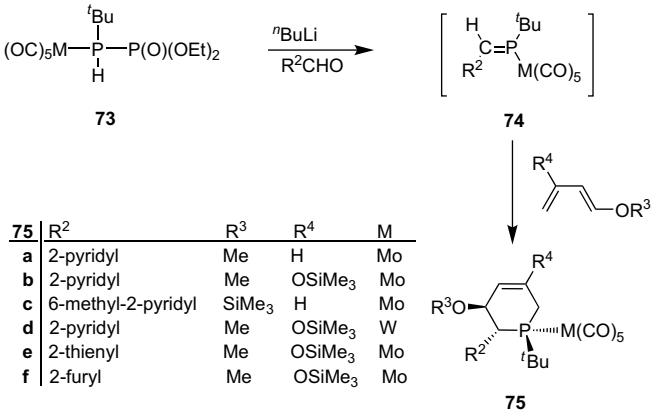
Scheme 16.

Subsequently, a simple 'Phospha-Wittig' reaction was developed to produce phosphaalkene complexes $[R^1R^2C{=}PR]M(CO)_5$ (M=Mo, W) (**74**) and 1-phosphabutadiene complexes (see later).[60–62] The phosphaalkene complexes, generated in situ, were reacted with 2,3-dimethylbutadiene and also with a variety of electron-rich dienes to give the DA cycloadducts **75** in a highly diastereoselective and regioselective manner, a single isomer being obtained as the final product in each case (Scheme 18).[61,62]

Some chemical reactions of the cycloadducts, such as with HCl, MeONa/NaOH, S_8, and desilylation followed by aromatization, have also been reported.[62]



Scheme 17.



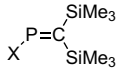
75	R^2	R^3	R^4	M
a	2-pyridyl	Me	H	Mo
b	2-pyridyl	Me	$OSiMe_3$	Mo
c	6-methyl-2-pyridyl	$SiMe_3$	H	Mo
d	2-pyridyl	Me	$OSiMe_3$	W
e	2-thienyl	Me	$OSiMe_3$	Mo
f	2-furyl	Me	$OSiMe_3$	Mo

Scheme 18.

The synthetic strategy employing a 'Phospha-Wittig' reaction was subsequently extended to the generation of prochiral L-menthyl-phosphaalkene complexes in situ and trapping them with cyclopentadiene leading to **77** as the final products (Scheme 19). A molecular model revealed, as confirmed by an X-ray crystal structure analysis, that only the *si* face of the phosphaalkene was free for the incoming diene and, consequently, [2+4] cycloaddition proceeded with full diastereoselectivity. In each case, only one isomer was formed, according to the ^{31}P NMR spectroscopic analysis of the reaction mixture. The decomplexation of the molybdenum complex **81** was carried out by heating with diphos and an optically pure 2-L-menthyl-2-phospha-5-norbornene derivative **82** could be obtained.[63]

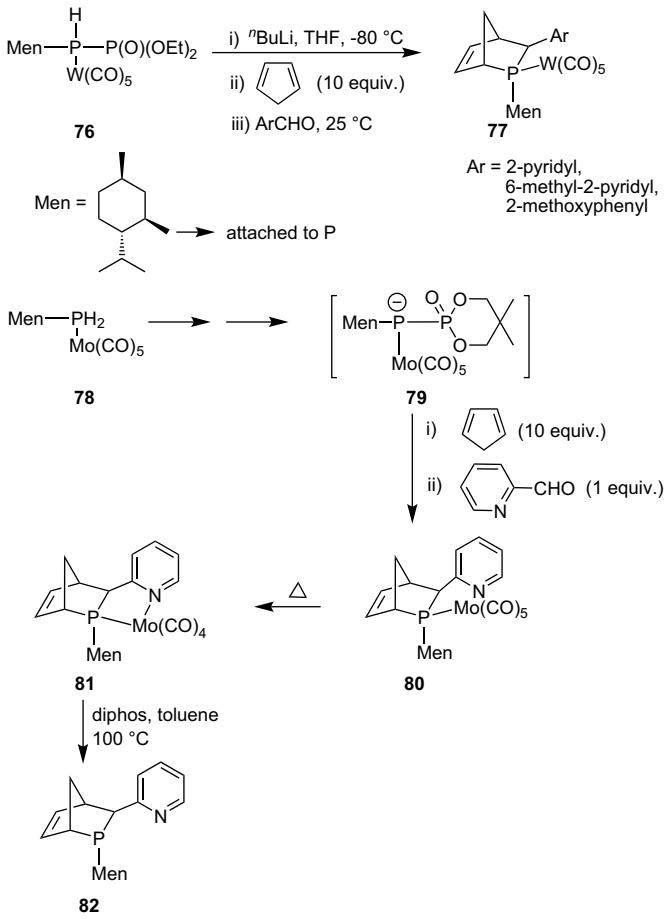
In a process complementary to Mathey's strategy described above, uncomplexed phosphaalkenes were produced from the reaction of the 'Phospha-Wittig' reagent [$(N_3N)Ta{=}PR$] with aldehydes.[64] *P*-Phenyl-*C*-ferrocenylphosphaalkene **83**, generated in this manner, was trapped with a 20-fold excess of cyclopentadiene, leading to an equimolar mixture of two diastereomers (Scheme 20). One diastereomer was isolated in a pure form and characterized as **84**.[64a]

P-Halo-2,2-bis(trimethylsilyl)phosphaethenes (**85**) constitute another class of phosphaalkenes that have been used in the DA reactions.[65–68]

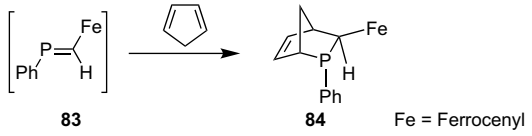


85

X = Cl, Br, I



Scheme 19.

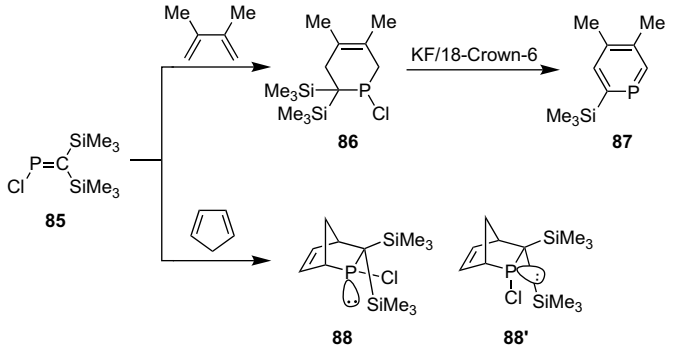


Scheme 20.

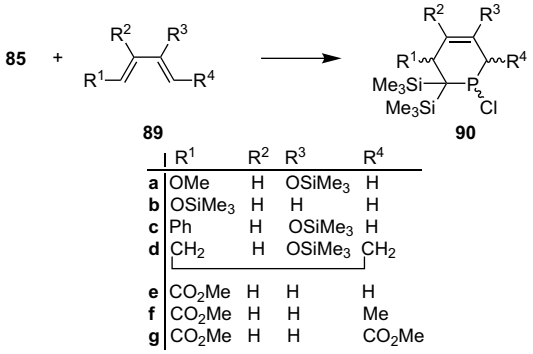
The reaction of **85** (X=Cl) with 2,3-dimethylbutadiene yielded **86**[65,68] and the latter, on treating with KF/18-Crown-6, changed into the phosphinine **87**, as indicated by ^{31}P NMR (δ ^{31}P=215 ppm).[65] The reaction with cyclopentadiene, however, leads to the formation of two diastereoisomers **88** and **88′** in a 9:1 ratio (δ ^{31}P=144, 148 ppm) (Scheme 21).[65,68]

The DA reaction of **85** (X=Cl) was subsequently extended to differently substituted 1,3-dienes **89** including Danishefsky's diene **89a**,[69] leading to [2+4] cycloadducts **90** (Scheme 22).[66–68,70] As determined by spectral studies, the reactions are completely regioselective, but the diastereoselectivity ranges from 60 to 100%. No attempt was made to separate the isomers. In some cases, the initially formed cycloadducts changed rapidly to the phosphinines, whereas, in other examples, chemical transformation was necessary. The complete regioselectivity was rationalized on the basis of second-order perturbation (CNDO/2) theory.[67]

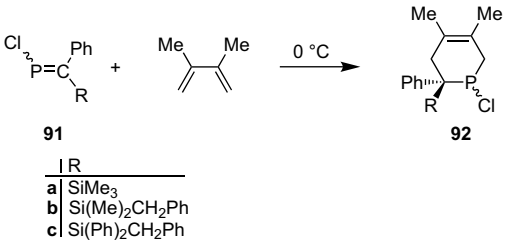
P-Chloro-(2,2-disubstituted)phosphaethenes of the type Cl–P=CR^1R^2 can exist in two geometrical isomeric forms. On reacting the isomerically pure phosphaalkenes **91** with 2,3-dimethylbutadiene, both diastereoisomers of **92** were produced (Scheme 23).[9c]



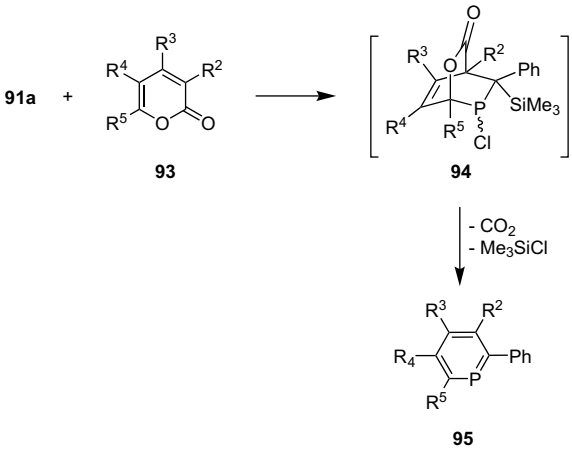
Scheme 21.



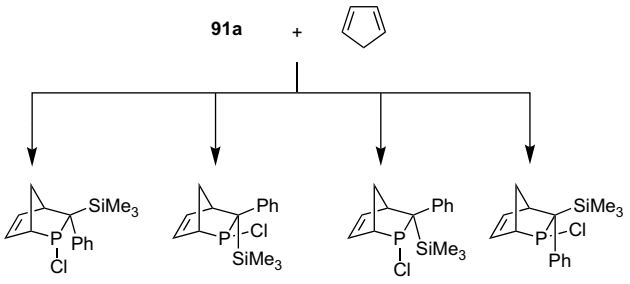
Scheme 22.



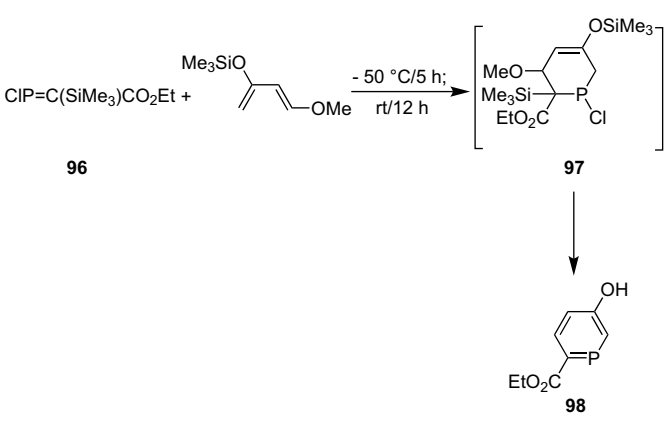
Scheme 23.



Scheme 24.



Scheme 25.



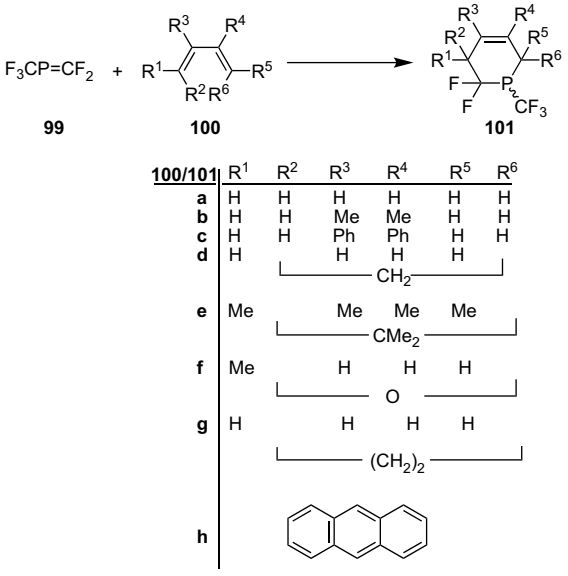
Scheme 26.

The reaction of **91a** with α-pyrones (**93**) in the presence of KF/18-Crown-6 afforded the substituted phosphinines **95** via [2+4] cycloaddition followed by loss of CO_2 (Scheme 24). Substituted cyclopentadienones could also be used in place of α-pyrone.[71] An alternative mechanism involving the initial conversion of **91a** into the phosphaalkyne followed by [2+4] cycloaddition with α-pyrone was considered to be more plausible.[71]

The reaction with cyclopentadiene yielded four products in each case, as detected by ^{31}P NMR (Scheme 25). These results indicate that the reaction possibly follows a stepwise diradical mechanism.[9c]

A transient *P*-chlorophosphaalkene **96** bearing an ethoxycarbonyl group at the carbon was generated in situ and trapped with Danishefsky's diene to give the phosphinine **98** (Scheme 26).[72]

Interesting chemistry of perfluoro- and polyfluorophosphaalkenes, including their [2+4] cycloadditions, has been developed, which has been reviewed recently.[73] These phosphaalkenes can be conveniently prepared in advance or generated in situ by 1,2-elimination of Me_3SnF from trimethyltin precursors, $Me_3SnP(RF)R'F$ or $Me_3SnP(RF)R$.[74–85] In an effective 'one-pot procedure', a stannylphosphine such as $Me_3SnP(CF_3)_2$, $Me_3SnP(C_2F_5)_2$ or $Me_3SnP(CF_3)C_2F_5$ was allowed to react with appropriate 1,3-dienes used in a 5- to 10-fold excess, at 50–70 °C, when [2+4] cycloaddition occurred more quickly than the self-addition of the phosphaalkene and the DA cycloadducts were formed in almost quantitative yields.[78–85] The reactions occur with high stereoselectivity (80–100%). The DA reactions of $F_3CP{=}CF_2$ accomplished in this manner are shown in Scheme 27 as an example.[81–83] The acyclic dienes yield two isomers in each case, which interconvert, due to inversion at three-coordinate phosphorus. In the reaction with isoprene, two regioisomers are formed in a 1:2 ratio. The reaction with cyclic dienes leads generally to two diastereomers, with the diastereoselectivity being 80–100%. The formation of four isomers was detected in the reaction with 2-methylfuran. Different isomers were defined on the basis of ^{19}F and ^{31}P NMR measurements.

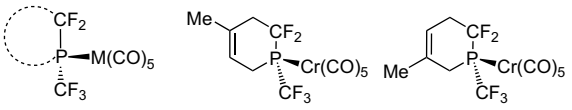


Scheme 27.

On pyrolysis of **101b**,**d**,**g**, **99** was produced as the result of a retro-Diene reaction. However, under these conditions, **101g** gave, in addition to **99**, the phosphetane **102**.[86]

102

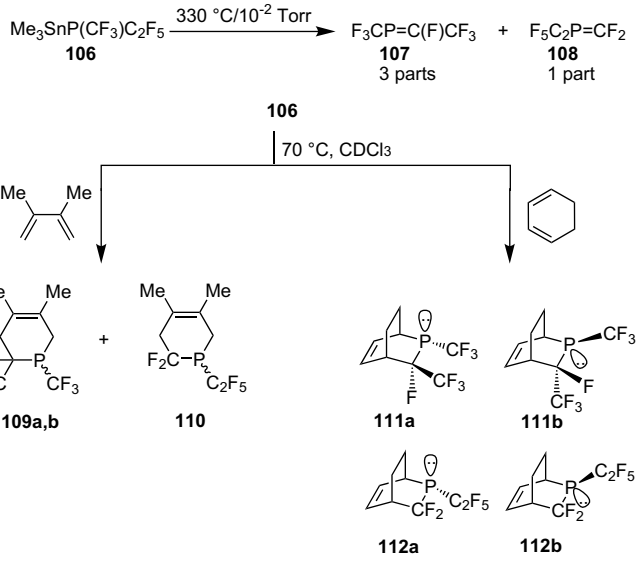
Furthermore, the cycloadducts **101b**–**g** and also those formed from the DA reactions of **99** with isoprene and 9,10-dimethylanthracene were converted into $M(CO)_5$ (M=Cr, W) complexes (**103**) from the reaction of the respective cycloadduct with photochemically produced $M(CO)_5$·THF. The NMR spectra and X-ray crystal structure determinations show that the reaction of **99** with cyclopentadiene yields an *endo* isomer.[87] The mixture of regioisomers obtained from the DA reaction of **99** with isoprene was converted into $M(CO)_5$ (M=Cr, W) complexes in a similar manner. The complexes **104** and **105** could be separated and their X-ray crystal structures were determined. Thermolysis of **104** afforded the corresponding uncomplexed cycloadduct in the pure state.[88]



103 **104** **105**

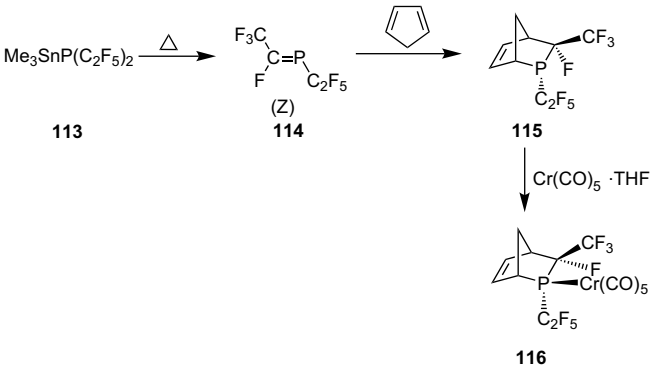
The vapour-phase pyrolysis of $Me_3SnP(CF_3)C_2F_5$ (**106**) yields a mixture of two isomeric perfluorophosphaalkenes **107** and **108** in a 3:1 molar ratio, which are effective dienophiles. In a one-pot procedure, similar to that described above, the reaction of **106** with 2,3-dimethylbutadiene or 1,3-cyclohexadiene, taken in excess, afforded mixtures of the respective DA cycloadducts, the structures of which were assigned on the basis of NMR studies (Scheme 28).[80] As before, the reactions are highly stereoselective.

On the other hand, thermal elimination of Me_3SnF from $Me_3SnP(C_2F_5)_2$ (**113**) afforded only $F_5C_2P{=}C(F)CF_3$ (**114**), the DA reactions of which were carried out successfully with 1,3-butadiene, 2,3-dimethylbutadiene, cyclopentadiene, 1,3-cyclohexadiene, isoprene and 2-methylfuran, these occurring by a concerted mechanism and giving the DA adducts in 80% yields.[78] Furthermore, the cycloadduct **115** obtained from the reaction with cyclopentadiene was converted into the $Cr(CO)_5$ complex **116**, the structure of which was determined by an X-ray crystallographic investigation. From these studies, it could be concluded that, on thermolysis, **113** yielded



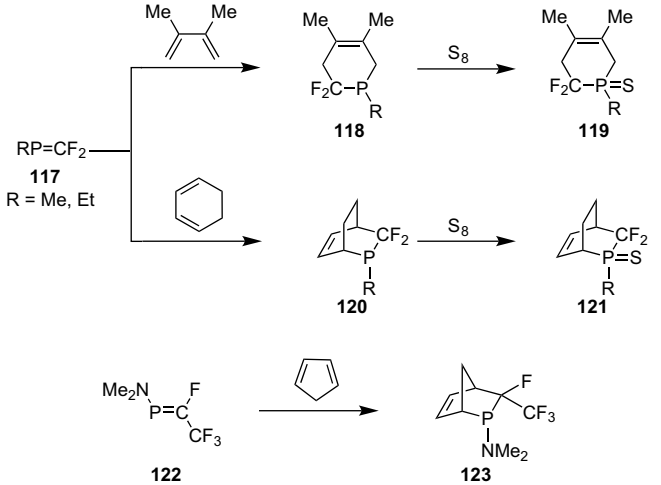
Scheme 28.

only one of the two possible isomers of $F_5C_2P{=}C(F)CF_3$, which reacted with cyclopentadiene with complete diastereoselectivity, producing only one isomer (Scheme 29).[89]



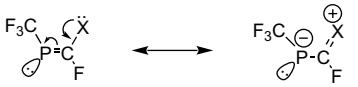
Scheme 29.

P-Alkyldifluorophosphaethenes (**117**)[84] and *P*-(dimethylamino)-polyfluorophosphaethenes ($Me_2NP{=}CF_2$ and **122**)[85] were generated from the thermal decomposition of $Me_3SnPRCF_3$, $Me_3SnP(CF_3)NMe_2$ and $Me_3SnP(C_2F_5)NMe_2$, respectively, and **117** and **122** were trapped with 1,3-dienes. The cycloadducts obtained from **117** were subsequently oxidized with sulfur (Scheme 30).[84]

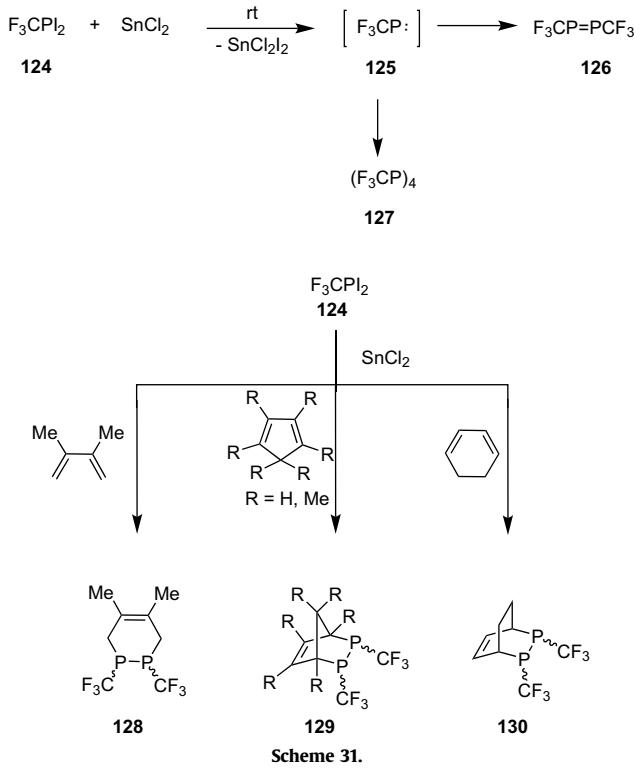


Scheme 30.

In contrast to the high dienophilic reactivity of $F_3CP{=}C(F)CF_3$, $F_3CP{=}CF_2$ and even $Me_2NP{=}C(F)CF_3$, phosphaalkenes of the type $F_3CP{=}C(F)X$ (X=OR, NR_2) and $F_3CP{=}C(NR_2)_2$ fail to undergo a DA reaction,[73,80] which can be attributed to the π-donor effect of the substituent group, as shown below.



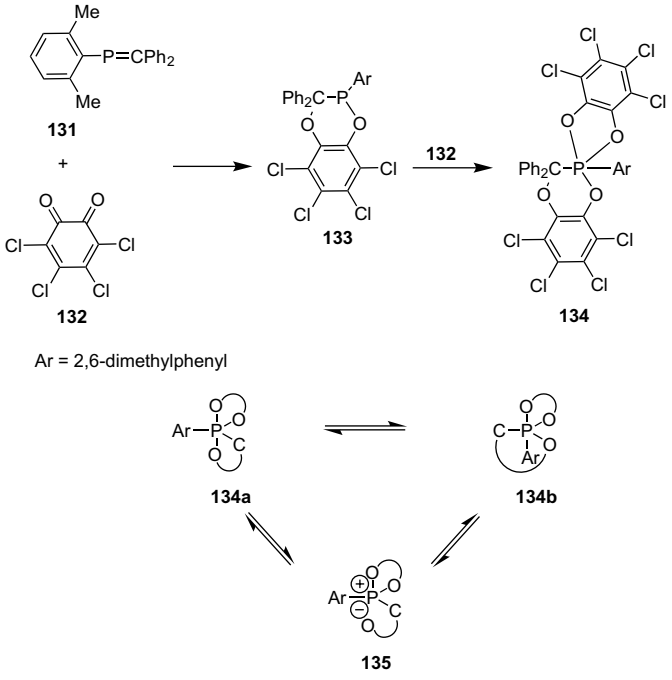
In another modification of the synthetic methodology described above, using a one-pot procedure, trifluoromethyldiiodophosphine (**124**) was treated with an equimolar amount of tin dichloride and a 1- to 10-fold excess of 1,3-diene at room temperature, leading to the [2+4] cycloadducts (**128**–**130**) in 50–100% yields. As regards the mechanism of the reaction, the initially formed trifluoromethylphosphinidene (**125**) changed rapidly into the diphosphene intermediate (**126**). The generation of **125** is confirmed by the formation of the cyclic tetraphosphane $(F_3CP)_4$ (**127**) as the only side product. The cycloreversion of **130** in the presence of 2,3-dimethylbutadiene at 70 °C gave **128** quantitatively and cyclohexadiene (Scheme 31).[90]



Scheme 31.

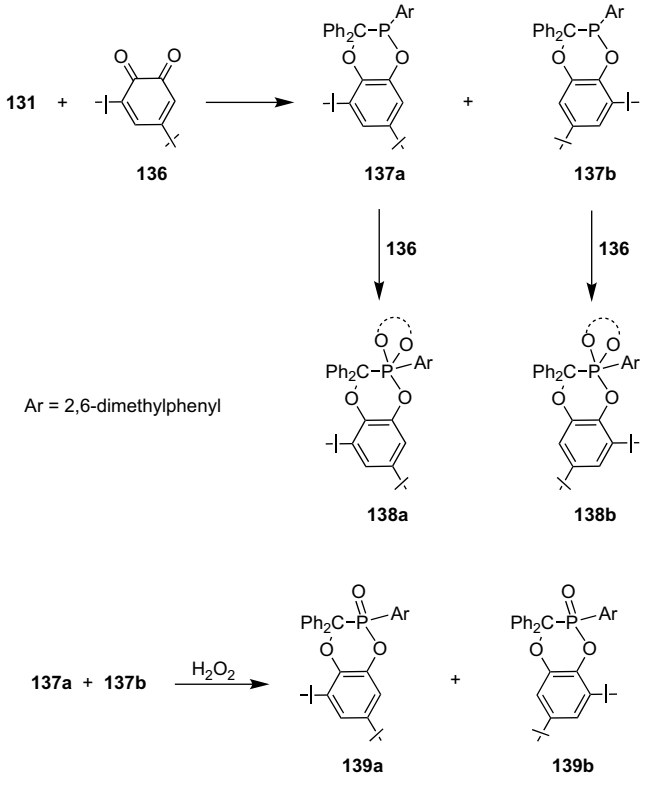
3.2. With heterodienes

The DA reactions of 1-(2,6-dimethylphenyl)-2,2-diphenylphosphaethene (**131**) with three orthoquinones, namely tetrachloro-*o*-benzoquinone (**132**), 3,5-di-*tert*-butyl-*o*-benzoquinone (**136**) and 9,10-phenanthrenequinone, have been reported, which occur in a reverse-electron-demand mode. On reacting **131** with 1 equiv of **132**, a 1:1 adduct **133** (68%) and a 1:2 adduct **134** (23%) were produced, as detected by ^{31}P NMR. On using 2 equiv of **132**, only **134** could be detected. As revealed by ^{31}P NMR, **134** exists as a mixture of two stereoisomers, which was rationalized by proposing a rapid equilibrium between two trigonal bipyramids as a result of pseudorotation (Scheme 32).[91] An alternative pathway involving a zwitterionic intermediate **135**, however, could not be ruled out.



Scheme 32.

The DA reaction of **131** with **136** occurred comparatively less readily, but regioselectively, to give **137a** and **137b** in a 4:1 ratio. As indicated by ^{31}P NMR, in this case also a small amount of the 1:2 adducts (6%, **138a**, **138b**) was formed. The 1:1 adducts were oxidized with aqueous H_2O_2 in acetone to give **139a**,**b** (Scheme 33).[91,92]

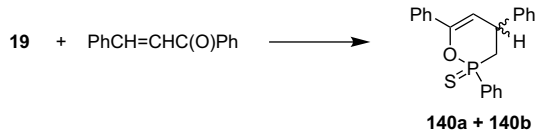


Scheme 33.

The DA reaction of **131** with 9,10-phenanthrenequinone could be completed on heating and led to 1:1 adducts only. Oxidation with H_2O_2 afforded the *P*-oxidized product.[91,92]

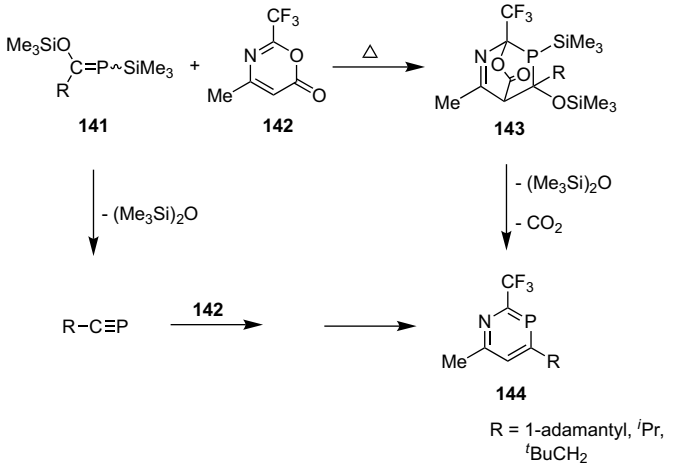
The mechanism of the above reactions, concerted or stepwise, could not be established conclusively.[91,92]

The DA reaction of *P*-phenylphosphaethene sulfide (**19**), generated in situ, with benzylideneacetophenone led to tetrahydro-1,2-oxaphosphinine (**140**) as a mixture of two diastereoisomers (**140a** and **140b**) (δ ^{31}P=82.57, 80.70 ppm). The more abundant isomer (**140b**) was separated and characterized as having *cis* (Ph)C–H and P–Ph bonds (Scheme 34).[41]



Scheme 34.

The DA reaction of **141** with 2-trifluoromethyl-4-methyl-6*H*-1,3-oxazine-6-one (**142**) afforded 1,3-azaphosphinine derivatives (**144**) regioselectively via **143** (Scheme 35).[9c] The possibility of an alternative mechanism involving the initial formation of phosphaalkyne followed by [2+4] cycloaddition cannot be ruled out.



Scheme 35.

4. Diels–Alder reactions of phosphabutadienes and phosphabutenynes

1-Phosphabutadienes (–P=C–C=C<) and 2-phosphabutadienes (>C=P–C=C<) differ in their behaviour in the DA reactions remarkably: while the unstabilized 1-phosphabutadienes (unmasked or without bulky substituent groups) dimerize in a [4+2] or [2+2] mode, 2-phosphabutadienes undergo DA reactions in which the PC double bond participates as an activated dienophile.

Theoretical studies of the DA reactions of phosphabutadienes support these results. The activation energy for the DA reaction of ethene with 1-phospha-1,3-butadiene is less than 20 kcal mol^{-1}, whereas for its reaction with 2-phospha-1,3-butadiene it is 28 kcal mol^{-1}. Moreover, these reactions are strongly exothermic.[25]

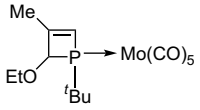
1-Phosphabutadienes **148** generated from the reaction of organylbis(trimethylsilyl)phosphanes **145a–e** with α,β-unsaturated acyl chlorides **146a**,**b** or with β-chlorovinyl ketones **147a**,**b** afforded 1,2,3,4-tetrahydro-1,2-diphosphinines **149a–h** by dimerization in the [4+2] cycloaddition mode in which **148** exhibited ambident reactivity, acting as diene as well as dienophile (Scheme 36). On the contrary, **148i**,**j** having bulky substituent groups (**i**,**j**: $R^1/R^2/R^3/R^4$=^{t}Bu/Ph/OSiMe$_3$/H; ^{t}Bu/Ph/H/OSiMe$_3$) yielded [2+2] cycloadducts through dimerization across the CP double bond. The DA reactions occurred with complete regioselectivity. Of the eight possible diastereomers in each case, only three could be detected, which changed into each other, due to ring folding and inversion at phosphorus. The cycloadducts **149a**,**b**,**e**,**f** on oxidation with sulfur gave disulfides **150a**,**b**,**e**,**f**.[93]

Similarly, 1-phosphabutadienes **152**, generated by thermolysis of the corresponding diallylphosphines **151**, dimerize on warming in a [4+2] cycloaddition mode to give **153** (Scheme 37).[94]

In a methodology analogous to that described earlier for the generation of phosphaalkenes, metal carbonyl-complexed 1-phosphadienes have been generated in situ.[60,62,95,96]

1,2-Dihydrophosphete-*P*-W(CO)$_5$ **154**[97] is in equilibrium with 1-phosphabutadiene-*P*-W(CO)$_5$ **155** at ~100 °C. The latter has been trapped with various dienophiles giving [4+2] cycloadducts **156**–**158** (Scheme 38).[96] The high reactivity of **155** is revealed by its reaction even with benzaldehyde. The reactions are stereoselective, except with DMAD, when the formation of two isomers is detected.

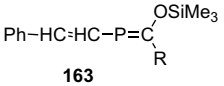
Likewise, molybdenum pentacarbonyl-complexed 1,2-dihydrophosphete **159** was prepared and used as precursor of 1-phosphabutadiene-*P*-M(CO)$_5$ for the DA reactions with *N*-phenylmaleimide and differently substituted alkynes. The reaction with maleimide occurred at room temperature, but the reactions with alkynes and also with benzoquinone and naphthoquinone required heating. The reaction with unsymmetrical alkynes occurred with complete regioselectivity. Benzoquinone reacted at the carbonyl function, whereas the reaction with naphthoquinone involved either the carbon–carbon double bond or the carbonyl moiety. Decomplexation of the cycloadducts followed by heating afforded the phosphinine derivatives.[62]



On the other hand, *P*-W(CO)$_5$-complexed 1-phosphabutadiene **161**, generated from the condensation of 'Phospha-Wittig' reagent **160** with dimethylacrolein in the presence of 2,3-dimethylbutadiene, undergoes [2+4] cycloaddition on the CP double bond, just like an ordinary phosphaalkene (Scheme 39).[60] Only one isomer of the cycloadduct **162** was obtained, thereby indicating the formation of only one isomeric 1-phosphabutadiene.

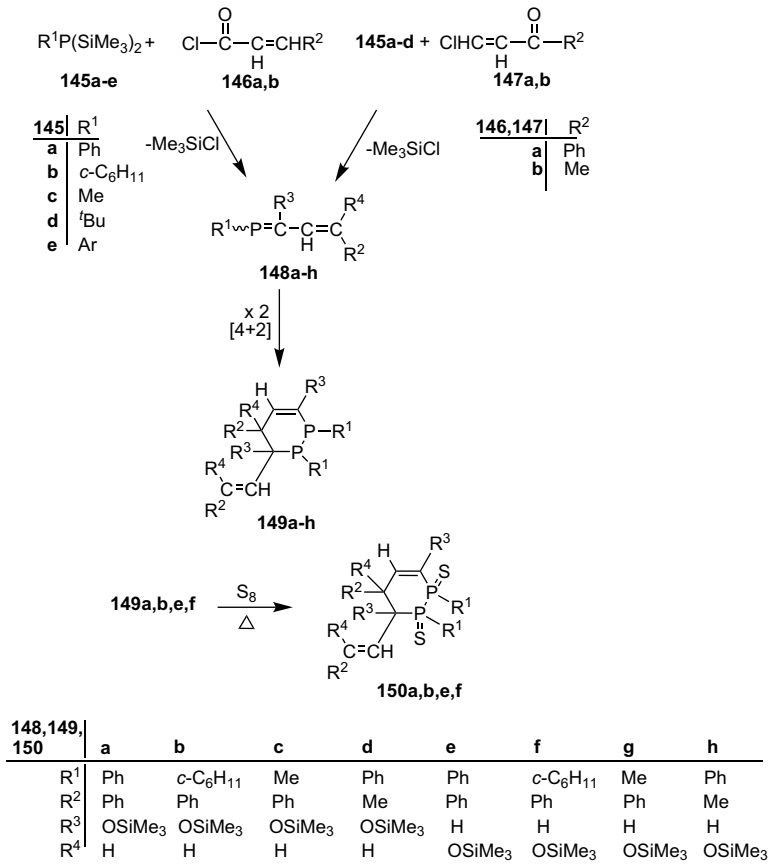
The 1-phosphabutadiene generated from the condensation of **160** with citral shows a similar behaviour.[60]

2-Phosphabutadienes **163** obtained as stable compounds reacted with cyclopentadiene as dienophile on the PC double bond.[93]



Diazadiphosphahexadienes **166**, however, could not be isolated and underwent an intramolecular DA reaction with the participation of two PC double bonds, leading to the tricyclic compounds **168** (Scheme 40).[98]

2-Phosphabutenynes **169** obtained as stable compounds react with 2,3-dimethylbutadiene to give [2+4] cycloadducts. In the case of **170b**,**d**, the formation of two diastereomers was detected, but the isomer having a downfield ^{31}P NMR chemical shift slowly changed into the isomer with a highfield ^{31}P NMR peak. This change was attributed to the result of inversion at phosphorus. The



148,149, 150	a	b	c	d	e	f	g	h
R^1	Ph	c-C_6H_{11}	Me	Ph	Ph	c-C_6H_{11}	Me	Ph
R^2	Ph	Ph	Ph	Me	Ph	Ph	Ph	Me
R^3	$OSiMe_3$	$OSiMe_3$	$OSiMe_3$	$OSiMe_3$	H	H	H	H
R^4	H	H	H	H	$OSiMe_3$	$OSiMe_3$	$OSiMe_3$	$OSiMe_3$

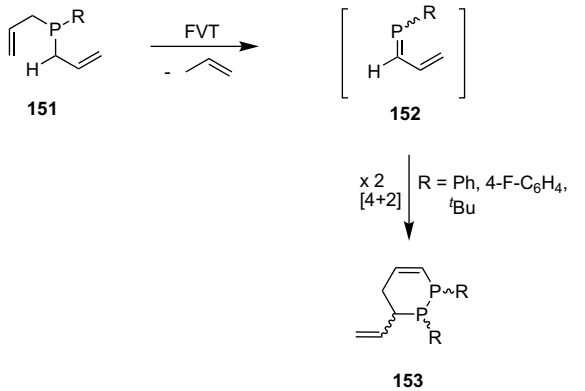
Scheme 36.

cycloadducts **170a–d** were oxidized with sulfur to give **171a–d**. The compound **170a** was oxidized with selenium also (Scheme 41).[99,100]

The reaction of **169a** with cyclopentadiene at low temperature formed the kinetically preferred *endo* [2+4] cycloadduct **172**, which, at room temperature, slowly changed into the thermodynamically more stable *exo*-product **173** (Scheme 42). It was established that the conversion of *endo*- into *exo*- occurred through retro-DA reaction.[100]

5. Diels–Alder reaction of phosphaketene

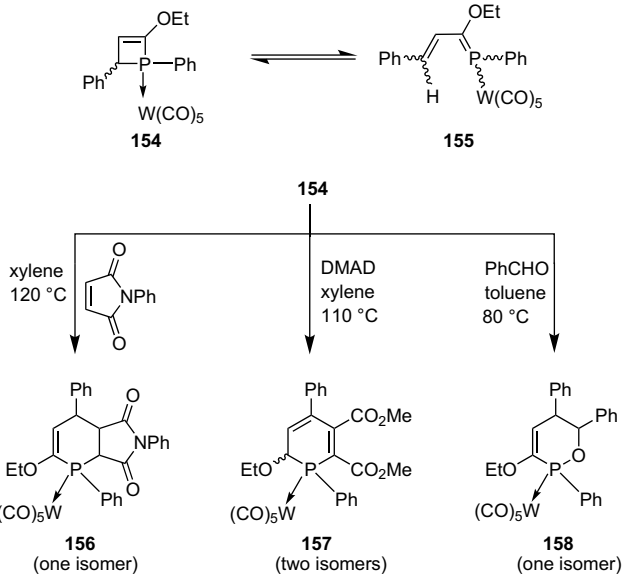
Diels–Alder reaction of phosphaketene **174** with 2,3-dimethylbutadiene has been reported to occur across the PC double bond leading to **175** (Scheme 43).[9c]



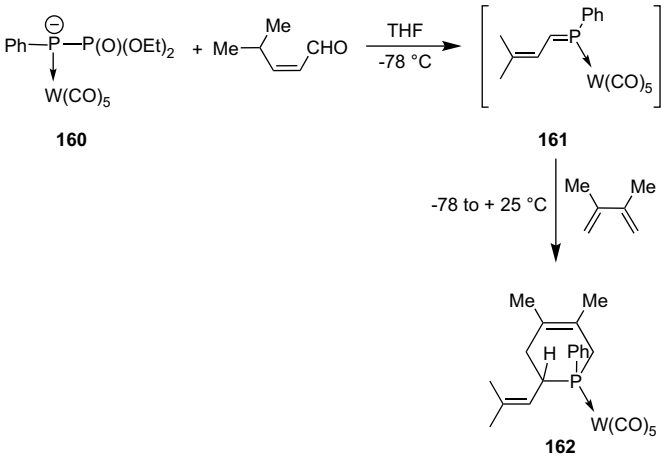
Scheme 37.

6. Diels–Alder reactions of phospholes

In the context of DA reactions of λ^3-phospholes,[101] Mathey and co-workers made an unexpected observation: 1-phenylphosphole **176** on reacting with tolane at 170 °C yielded 3,4-dimethyl-2,5,6-triphenyl-1-phosphanorbornadiene **177** quantitatively (Scheme 44).[10] The structure of **177** was established unambiguously by an X-ray crystallographic investigation. The reaction of the *P*-sulfide of

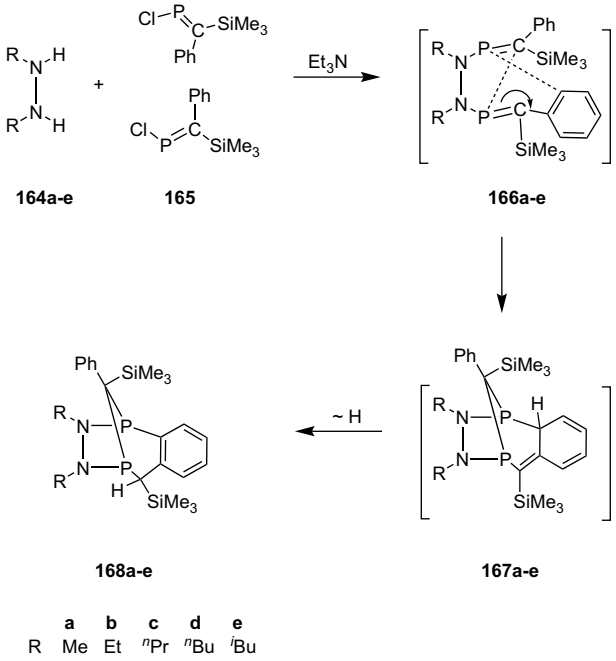


Scheme 38.



160 **161** **162**

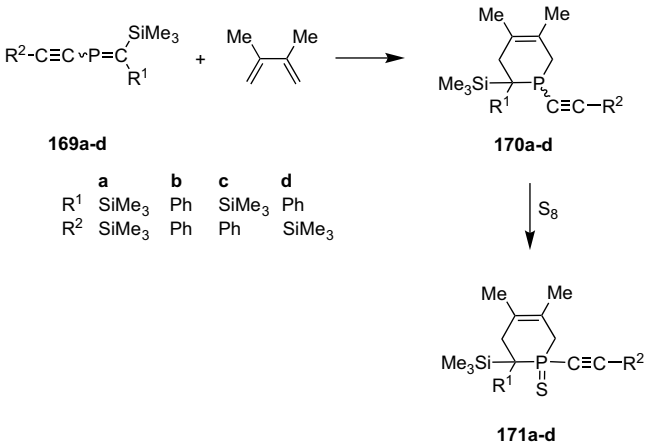
Scheme 39.



164a-e **165** **166a-e** **167a-e** **168a-e**

	a	b	c	d	e
R	Me	Et	^{n}Pr	^{n}Bu	^{i}Bu

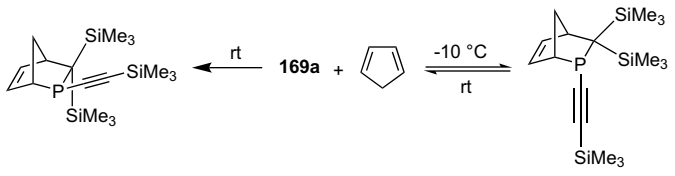
Scheme 40.



169a-d **170a-d** **171a-d**

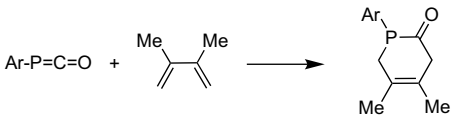
	a	b	c	d
R^1	$SiMe_3$	Ph	$SiMe_3$	Ph
R^2	$SiMe_3$	Ph	Ph	$SiMe_3$

Scheme 41.



173 **169a** **172**

Scheme 42.

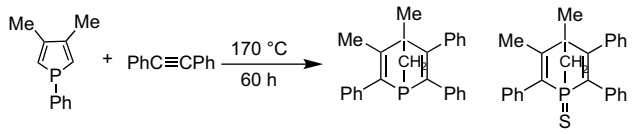


174 **175**

Ar = 2,4,6-^{t}Bu$_3$C$_6$H$_2$

Scheme 43.

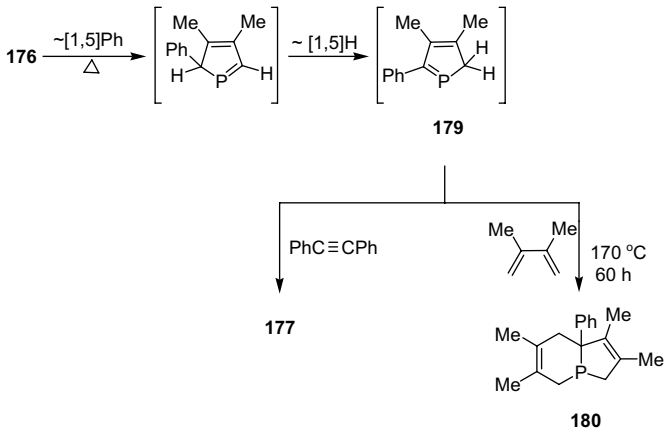
176 with tolane afforded **178**, which could also be obtained from the oxidation of **177** with sulfur, ruling out the possibility of involvement of phosphorus lone pair in the initial attack of tolane.



176 **177** (100%) **178**

Scheme 44.

The results could be rationalized by proposing a [1,5] sigmatropic shift in **176** to generate the 2*H*-phosphole **179** transiently, which reacted as diene with tolane to give **177**. The proposed mechanism was confirmed by trapping **179** with 2,3-dimethylbutadiene to give **180** (Scheme 45).[10]

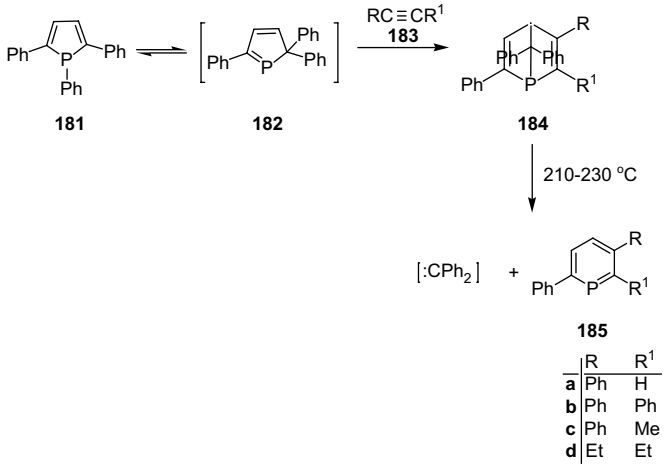


176 **179** **177** **180**

Scheme 45.

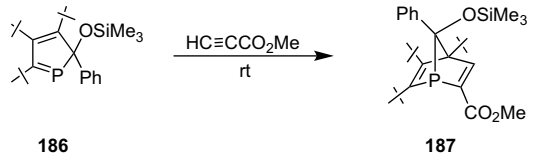
It was subsequently found that a [1,5] shift in λ^3-phospholes was a general phenomenon and even 1,2-disubstituted phospholes **181** underwent this sigmatropic rearrangement to generate 2*H*-phosphole derivative **182**, which could be trapped with various

alkyne dienophiles. The resulting products **184** at high temperature split off the bridgehead moiety to produce phosphinines **185** (Scheme 46). The reactions of **182** with **183a,c** are found to be regioselective, the isomer having a smaller group on the carbon adjacent to phosphorus being preferred.[102,103] Furthermore, **181** did not react with **183** (R=R^1=Me$_3$Si), possibly due to steric hindrance, and with benzonitrile. In both cases, a small quantity of biphospholyl was recovered.



Scheme 46.

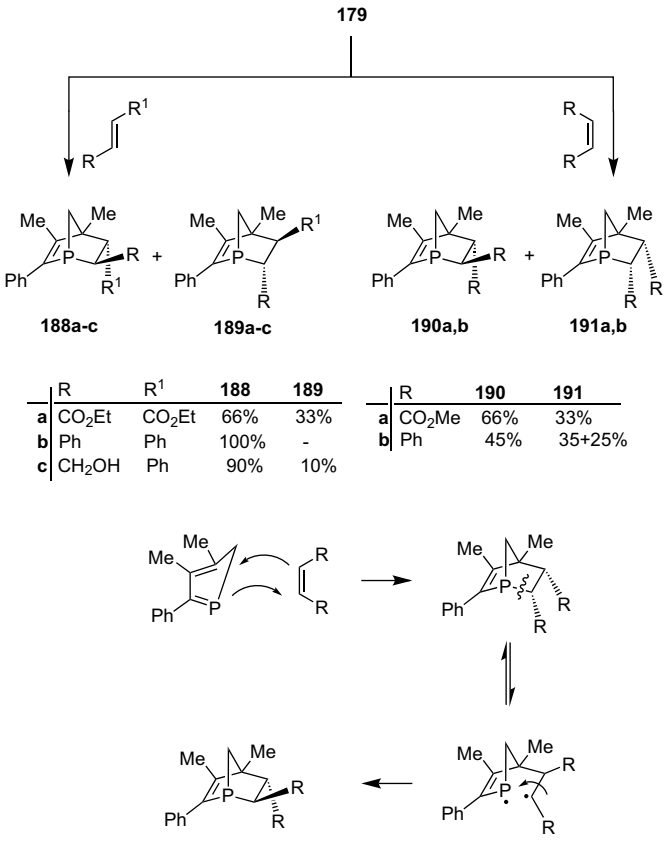
Likewise, a stable 2*H*-phosphole **186**, prepared from cyclopropenylium bromide, underwent a [4+2] cycloaddition with methyl acetylenecarboxylate with total stereo- and regioselectivities to give **187** (Scheme 47).[104]



Scheme 47.

The DA reactions of 2*H*-phosphole **179**, generated in situ from the thermal isomerization of 1*H*-phosphole, with disubstituted alkenes occur again with high stereo- and regioselectivities to give cycloadducts **188**–**191**. Symmetrical (*E*)-alkenes afforded α-*exo*, β-*endo* cycloadducts preferentially or even exclusively. The (*Z*)-alkenes, however, reacted nonstereoselectively. These results could be rationalized on the basis of a concerted cycloaddition. However, the cycloadduct formed from the addition of the (*Z*)-alkene undergoes a reversible cleavage (probably homolytic) of the P–C bond, allowing isomerization (Scheme 48). The cycloadducts were oxidized with H_2O_2 or sulfur.[105] In the reaction with poor dienophilic alkenes (e.g., stilbene), the dimer of 2*H*-phosphole may be the side product (see later). Furthermore, at lower temperatures, when no 2*H*-phosphole is present, the alkene, especially the activated alkene, may react with 1*H*-phosphole to form 7-phosphanorbornadiene.[101] The structure of the compound obtained from oxidation of **188a** with H_2O_2 was confirmed by an X-ray crystallographic investigation.[105]

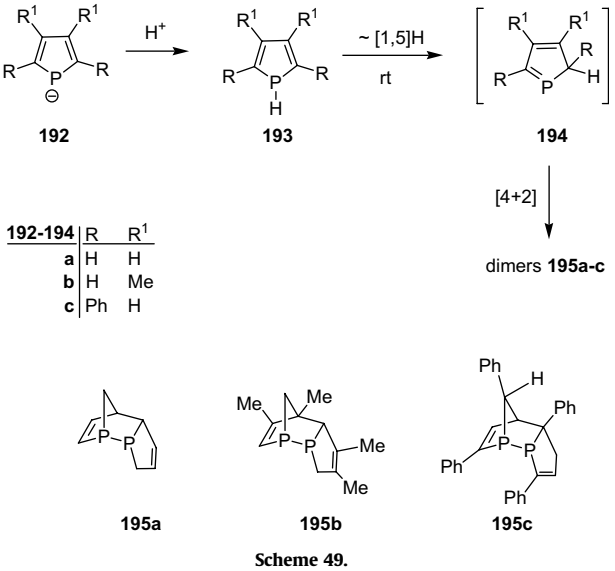
1*H*-Phospholes **193**, generated from protonation of phospholyl anions **192**, rearrange spontaneously to the 2*H*-phospholes **194** through a [1,5] H shift. The 2*H*-phospholes so formed are unstable and dimerize instantaneously in a [4+2] cycloaddition mode, exhibiting ambident reactivity, reacting as diene as well as dienophile to give **195**. Dimerization occurs with complete stereo- and



Scheme 48.

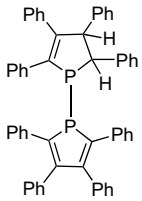
regioselectivities, the *endo* product having a P–P bond, that is formed exclusively (Scheme 49).[10,106–108]

The structure of **195b** was confirmed by an X-ray crystallographic analysis.[107] The 2*H*-phosphole generated from **192** (R=R^1=Ph), however, on dimerization gave **196**, instead of the [4+2] cycloadduct. Actually, isomerization of **193** (R=R^1=Ph) to the corresponding **194** is sluggish, even at room temperature, and the initially formed **194** combines with **193**, addition of the P–H



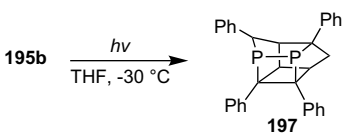
Scheme 49.

bond of the latter taking place onto the P=C bond of the former to yield **196**.[108]



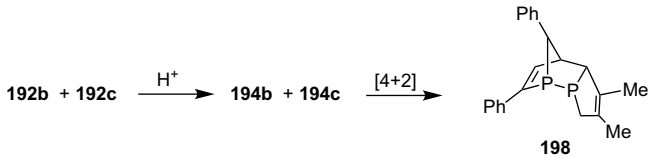
196

On heating **195b** at ~100 °C, it changed into the *exo* isomer. A similar behaviour is exhibited by **195c** on heating in boiling toluene. Furthermore, **195c** on being irradiated under UV light undergoes an intramolecular [2+2] cycloaddition to give the cage compound **197** (Scheme 50).[108]



Scheme 50.

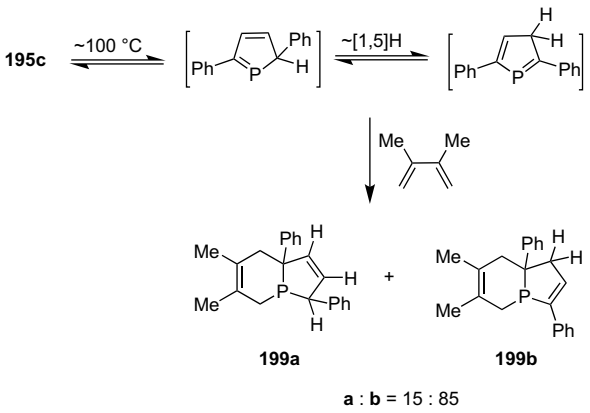
On the contrary, the *exo* isomer formed on boiling **195c** in toluene remains unaffected under these conditions. These results indicate that the dimerization of 2*H*-phospholes occurs by a concerted mechanism, just like the dimerization of cyclopentadiene.[109] Furthermore, thermal isomerization of the *endo* to the *exo* isomer implies that, at around 100 °C, these dimers are in equilibrium with the corresponding monomers. The reaction of **195a** with sulfur leads to oxidation of only phosphorus at the junction, indicating that the nucleophilicity of the phosphorus at the bridgehead is much lower. On hydrolyzing a 1:1 mixture of the two phospholyl anions **192b** and **192c**, the mixed DA cycloadduct **198**, resulting from the addition of **194c** as diene with **194b** as dienophile, was obtained as the major product (Scheme 51).[108] It is obvious that the formation of **198** is governed mainly by steric factors. However, in the case when the two dimers are similarly hindered, electronic factors determine the course of the reaction.[108]



Scheme 51.

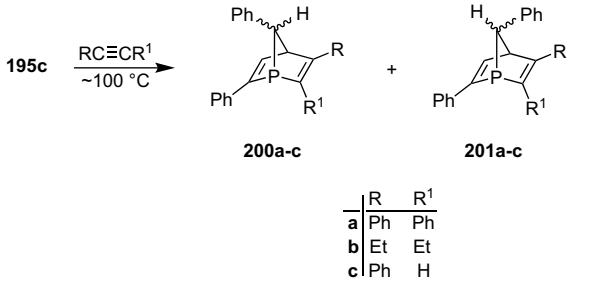
It has been found that 2*H*-phospholes are regenerated on heating their dimers. The 2*H*-phospholes so produced can act as dienophiles, reacting with 1,3-dienes on the CP double bond, or as conjugated dienes in the presence of alkynes, affording the DA cycloadducts in both cases. This behaviour has been studied for **195c** (Scheme 52)[108] and also for **195b**.[107]

In a similar manner to the results described above, 2*H*-phospholes, generated from sigmatropic rearrangement of 1-(2,4,6-trialkylphenyl)phospholes at 150 °C, reacted with tolane to yield [4+2] cycloadducts **202** or dimerized to **203**. On heating **203a** at 150 °C in the presence of tolane, dedimerization followed by a DA reaction gave **202a**. However, dedimerization of **203a** at 0 °C under



199a **199b**

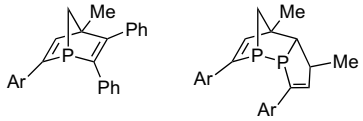
a : **b** = 15 : 85



	R	R^1
a	Ph	Ph
b	Et	Et
c	Ph	H

Scheme 52.

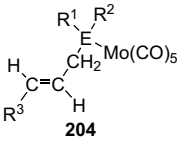
oxidative conditions led to the phosphole oxide dimer without the involvement of 2*H*-phosphole.[110]



202a,b **203a**

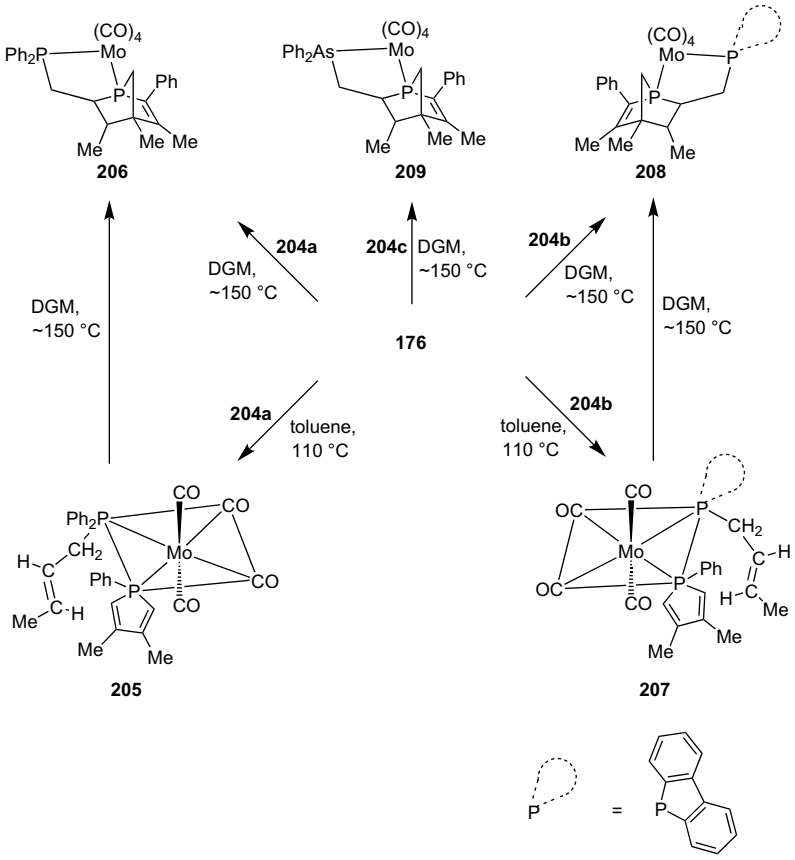
a Ar = 2,4,6-tri*iso*propylphenyl
b Ar = 2,4-di-*tert*-butyl-6-methylphenyl

In another interesting extension of the chemistry of 2*H*-phospholes, the reaction of 3,4-dimethyl-1-phenylphosphole (**176**) was carried out with *trans*-crotylphosphino and -arsino $Mo(CO)_5$ complexes and the analogous allyl tertiary phosphine complexes (**204**), wherein intramolecular DA cycloaddition occurred within the coordination sphere of the transition metal, leading to a new class of conformationally rigid bidentate ligands incorporating the 1-phosphinonorbornene bicyclic ring system. By carrying out the reaction at a lower temperature, it has been shown that the first step involves the stereoselective formation of the cis mixed ligand complexes **205** and **207**, which undergo a [1,5] sigmatropic shift followed by an intramolecular DA reaction between the 2*H*-phosphole and alkene moieties to afford **206** and **208**, respectively, which can be obtained directly by heating **176** with **204a** or **204b** at ~150 °C. The arsine complex **204c** gave **209** under these conditions (Scheme 53).[111]



204

	E	R^1	R^2	R^3
a	P	Ph	Ph	Me
b	dibenzophosphino			Me
c	As	Ph	Ph	Me
d	P	Ph	Ph	H
e	dibenzophosphino			H



Scheme 53.

Allyl tertiary phosphine complexes **204d**,**e** reacted with **176** under similar conditions to give the corresponding 2*H*-phosphole [4+2] cycloadducts in high yields. The structures of all the products were confirmed by X-ray crystallographic analyses.[111]

Dimerization of 2*H*-phospholes has been investigated theoretically at the ab initio[112] and DFT[113] levels. In complete agreement with the experimental studies, the results at the DFT level reveal that dimerization leading to P–P bonded products involves quite low activation barriers, of the order of 3–5 kcal mol^{-1} only, which may be attributed to the breaking of two weak P=C bonds during the course of the reaction. Furthermore, cycloaddition of a 2*H*-phosphole across the C=C bond of another 2*H*-phosphole ring involves an activation barrier, about 7–13 kcal mol^{-1} higher than the reaction across the C=P bond, which explains the observed regioselectivity. The formation of the *endo* isomer is rationalized by the fact that the *endo* transition state is more stable than the *exo* transition state by about 2 kcal mol^{-1}.[113]

The DA reactions of 2*H*-phosphole with 1,3-butadiene, in which butadiene acts as a dienophile, have been investigated theoretically.[114] Ab initio studies show that the DA reaction between phosphaketene and 2*H*-phosphole is kinetically favoured over the [2+2] cycloaddition by 6.2 kcal mol^{-1}. This is in contrast to the reaction between ketene and cyclopentadiene, wherein the [2+2] cycloaddition is kinetically favoured over the DA reaction by 12 kcal mol^{-1}.[115]

7. Diels–Alder reactions of heterophospholes

The >C=P– functionality in heterophospholes undergoes DA reactions normally as a dienophile, leading to [2+4] cycloadducts. In some cases, however, the –C=C–C=P– moiety of the heterophosphole ring reacts as diene with alkynes or phosphaalkynes to give [4+2] cycloadducts. If the >C=P– moiety is not sufficiently activated, the DA reaction is carried out in the presence of an oxidizing agent such as sulfur, selenium or even oxygen. In such cases, oxidation of phosphorus either precedes cycloaddition, thereby enhancing the dienophilic reactivity of the CP double bond, or follows cycloaddition to push a reversible reaction in the forward direction. Sometimes, a DA reaction of heterophospholes is followed by a tandem DA reaction.

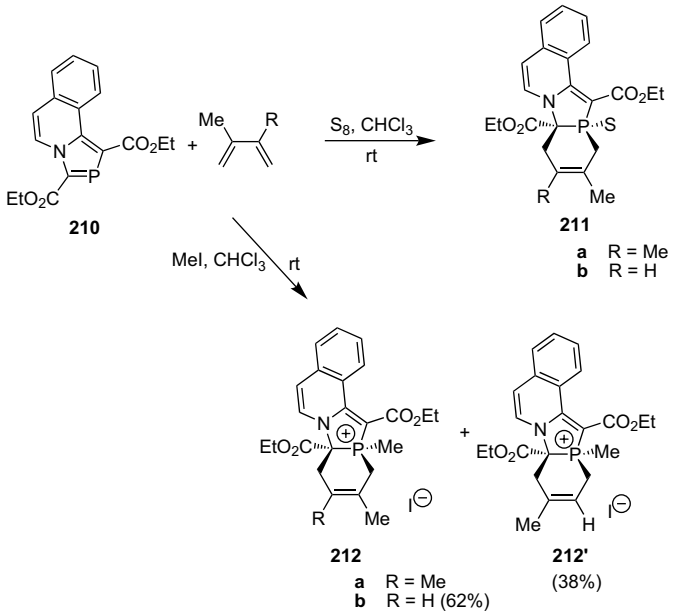
An earlier review on 'cycloadditions on λ^3,σ^2-phosphorus multiple bonds' includes DA reactions of heterophospholes.[116] The reviews on heterophospholes[19] and anellated azaphospholes[20] mention these reactions briefly. A general review on 'cycloaddition reactions of heterophospholes' includes DA reactions published up to December 2003.[29]

DA reactions of heterophospholes are reviewed here under two subheadings, namely [2+4] cycloadditions involving >C=P– as dienophile and [4+2] cycloadditions in which the phosphadiene component of the heterophosphole ring reacts as diene.

7.1. [2+4] Cycloadditions

1,3-Bis(ethoxycarbonyl)-1,3-azaphospholo[5,1-*a*]isoquinoline (**210**) reacted with 2,3-dimethylbutadiene in the presence of sulfur or methyl iodide to give [2+4] cycloadducts **211** and **212**, respectively.[117,118] The reaction with isoprene in the presence of sulfur occurred with full diastereo- and regioselectivities, but, in the presence of methyl iodide, the regioselectivity was lowered and two regioisomers **212b** (62%) and **212′** (38%) were formed (Scheme 54). The structure of **211b** was confirmed by X-ray crystallographic studies. The reaction of **210** with 2,3-dimethylbutadiene alone was found to be sluggish at room temperature and could be completed

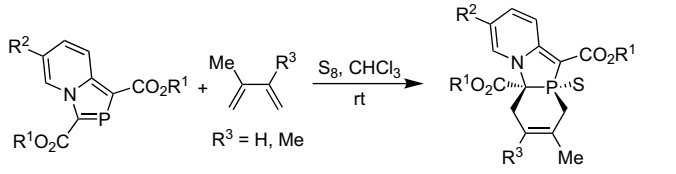
(δ ^{31}P=14.1 ppm) only on refluxing in chloroform for 4 days. This indicates that the role of sulfur or methyl iodide is to push a reversible reaction in the forward direction by oxidizing the σ^3-P atom of the initially formed cycloadduct.[118]



Scheme 54.

The DA reactions of **210** with 2,3-dimethylbutadiene and isoprene in the presence of sulfur could be accomplished under microwave irradiation in much shorter times (10–22 min) without affecting the yields and regioselectivity.[119]

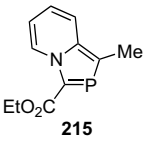
The pyridinium analogues of **210**, namely 1,3-bis(ethoxycarbonyl)-1,3-azaphospholo[1,5-*a*]pyridines **213**, prepared from disproportionation followed by 1,5-electrocyclization of the pyridinium dichlorophosphinomethylides,[120,121] behave similarly and undergo DA reactions with 2,3-dimethylbutadiene and with isoprene in the presence of sulfur with complete diastereo- and regioselectivities to afford **214** (Scheme 55). In the absence of sulfur, the reaction is slow, but is completed at room temperature.[122] The reaction of **213** (R^1=R^2=Et) with 2,3-dimethylbutadiene in the presence of methyl iodide yielded the expected [2+4] cycloadduct methylated on phosphorus.[118]



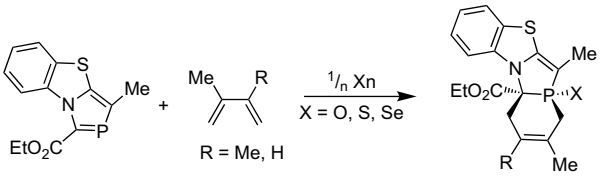
	R^1	R^2	R^3
a	Et	H	Me
b	Et	H	H
c	Me	Me	Me
d	Me	Me	H
e	Et	Me	Me
f	Et	Me	H

Scheme 55.

The observed regioselectivity in the above case has been rationalized theoretically.[122] In contrast to **213**, 3-ethoxycarbonyl-1-methyl-1,3-azaphospholo[1,5-*a*]pyridine (**215**), obtainable through a [4+1] cyclocondensation method,[123] did not react with 2,3-dimethylbutadiene or isoprene, even on refluxing in toluene in the presence of sulfur. This unusual substituent effect (in spite of CO_2Et being bonded directly to the dienophilic moiety) has been investigated theoretically, wherein NBO interactions reveal that the bridgehead nitrogen acting as an electron-donor reduces the dienophilic activity of **215** remarkably, but, in **213**, this electron-donating effect of nitrogen is compensated by the second CO_2Et group, making it amenable to undergo a DA reaction. The calculated global electrophilicity power values (ω) corroborate this trend.[124] The difference in the dienophilic reactivities of **213** and **215** was rationalized also on the basis of FMO energies calculated by a semi-empirical PM3 method.[117]



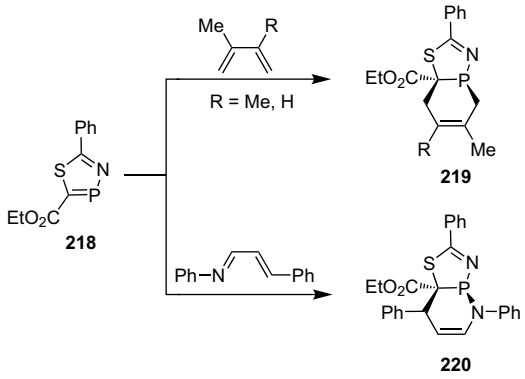
The dienophilic reactivity of 1,3-azaphospholo[5,1-*b*]benzothiazole **216**, prepared through a [4+1] cyclocondensation method,[125] lies between those of **210** and **213** and its DA reactions with 1,3-dienes occurred only in the presence of oxygen, sulfur or selenium to yield **217**. The reaction with isoprene proceeded with total regioselectivity to give **217d**,**e** (Scheme 56).[126]



	R	X
a	Me	O
b	Me	S
c	Me	Se
d	H	S
e	H	Se

Scheme 56.

A similar pattern of reactivity was shown by 1,3,4-thiazaphosphole **218**,[127] which gave DA reactions with 1,3-dienes and 1,4-diphenyl-1-azabutadiene with complete diastereo- and regioselectivities (Scheme 57).[19b]



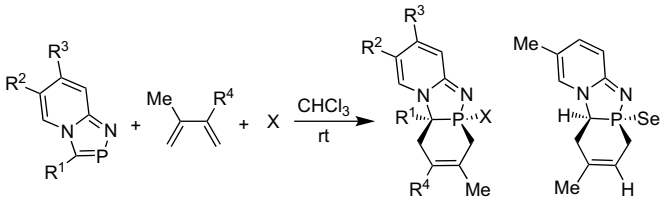
Scheme 57.

The DA reactions of a number of diazaphospholes have been accomplished successfully in our research group. These compounds

exhibit enhanced dienophilic reactivity and undergo DA reactions without the aid of an oxidizing agent. Nevertheless, the reactions are usually carried out in the presence of sulfur or selenium, to avoid oxidation of the cycloadducts during workup.

[1,4,2]Diazaphospholo[4,5-*a*]pyridines **221**[128,129] reacted with 2,3-dimethylbutadiene and with isoprene in the presence of sulfur or selenium at room temperature to give DA cycloadducts diastereo- and regioselectively.

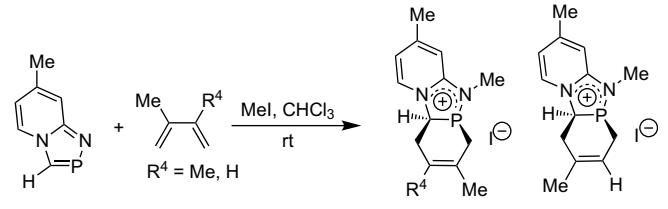
The reaction of **221b** (R^1, R^3=H, R^2=Me) with isoprene in the presence of selenium yielded **222g** and **222g′** in an approximate 4:1 ratio (as determined by ^{31}P NMR) (Scheme 58).[130]



222	R^1	R^2	R^3	R^4	X
a	H	H	H	Me	S
b	H	Me	H	Me	S
c	H	H	Me	Me	S
d	H	H	Me	Me	Se
e	CO_2Et	H	H	Me	S
f	CO_2Et	H	H	Me	Se
g	H	Me	H	H	Se

Scheme 58.

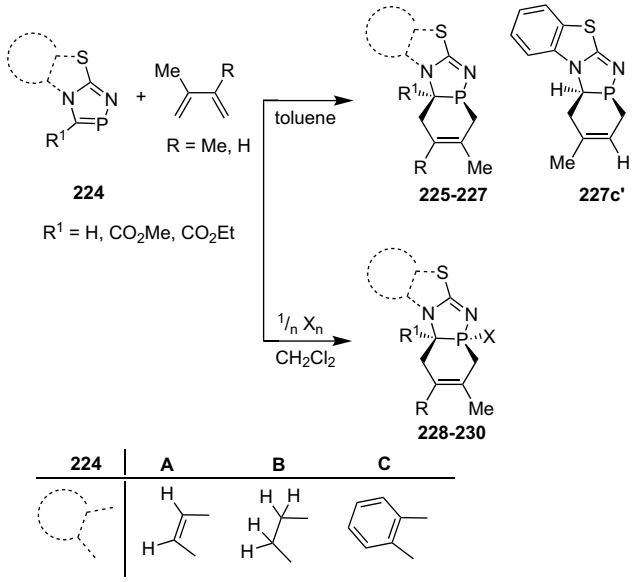
The reaction of **221b** with 2,3-dimethylbutadiene alone was very slow at room temperature and could be completed only after refluxing in chloroform for 24 days (δ ^{31}P=66.0 ppm). Furthermore, the reaction of **221c** with 2,3-dimethylbutadiene and methyl iodide under these conditions afforded **223** (R^4=Me), methylation occurring at the σ^2,λ^3-nitrogen atom of the cycloadduct. Likewise, the reaction with isoprene under these conditions yielded σ^2,λ^3-nitrogen methylated cycloadducts, but, in this case, both the regioisomers **223** (R^4=H) and **223′** were produced, the former being formed predominantly (70%) (Scheme 59).[130]



Scheme 59.

In view of the reported non-reactivity of **221** (R^1=R^2=R^3=H) with methyl iodide,[131] it can be concluded that methylation occurs after the [2+4] cycloadduct is formed and the +M effect of the junction nitrogen makes σ^2,λ^3-N more nucleophilic than σ^3-P. The observed regioselectivity in the above case has been explained on the basis of DFT calculations.[130]

A similar behaviour is shown by thiazolo[3,2-*d*][1,4,2]-diazaphospholes and their 5,6-dihydro and benzo derivatives (**224**). These compounds, obtainable through a [4+1] cyclocondensation method,[132] reacted with 2,3-dimethylbutadiene and with isoprene to give [2+4] cycloadducts diastereo- and regioselectively. On carrying out the reaction in the presence of sulfur or selenium, the corresponding oxidized products **228–230** were obtained. The reactions with isoprene occurred with complete regioselectivity, except in the case of **224C** (R^1=H), when two regioisomers **227c** and **227c′** were formed in a 2:1 ratio, as indicated by ^{31}P NMR of the reaction mixture (Scheme 60).[126]



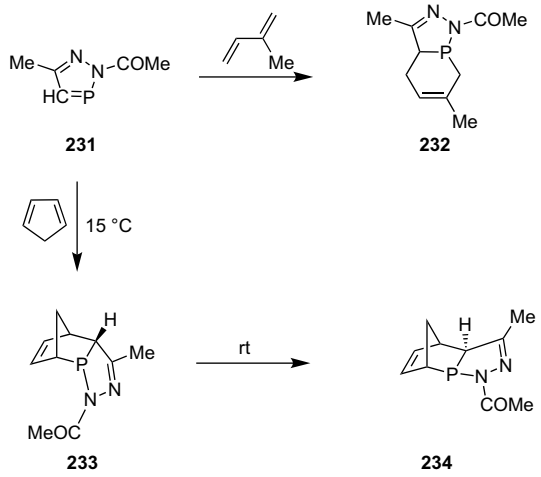
	R^1	R	X		R^1	R	X
	225a	CO_2Me	Me	-	**228a**	CO_2Me	Me	S
	225b	CO_2Et	Me	-	**228b**	CO_2Et	Me	S
	225c	CO_2Me	H	-	**228c**	CO_2Me	H	S
	225d	CO_2Et	H	-	**228d**	CO_2Et	H	S
	226a	CO_2Me	Me	-	**229a**	CO_2Me	Me	S
	226b	CO_2Et	Me	-	**229b**	CO_2Et	Me	S
	226c	CO_2Me	H	-	**229c**	CO_2Me	H	S
	226d	CO_2Et	H	-	**229d**	CO_2Et	H	S
					229e	CO_2Et	Me	Se
	227a	CO_2Et	Me	-	**230a**	CO_2Et	Me	S
	227b	CO_2Et	H	-	**230b**	CO_2Et	H	S
	227c	H	H	-	**230c**	CO_2Et	Me	Se
					230d	CO_2Et	H	Se

Scheme 60.

DFT level (B3LYP/6-311++G**//B3LYP/6-311G**) investigations of the DA reactions of **224A**,[26a] 1,3-azaphospholo[5,1-*b*]thiazole[26a] and **224B**[26b] with 1,3-butadiene and with isoprene reveal that these reactions occur by a concerted mechanism. The aromatic nature of the corresponding transition structures has been confirmed by their NICS values.[22b] The ratios of the *endo*/*exo* stereoisomers as well as those of the *meta*/*para* regioisomers were calculated according to the reported method,[133] and the values so obtained agreed well with the experimental results.

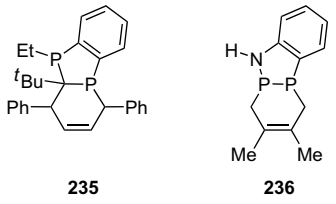
The DA reactions of 2-acetyl-[1,2,3]diazaphosphole (**231**) with isoprene[134] and with cyclopentadiene[135] occurred with complete regio- and stereoselectivities to form **232** and **234**, respectively (Scheme 61). The *endo*-product **233** formed at low temperature (15 °C), on keeping in solution at room temperature, changed to the

thermodynamically more stable *exo*-product **234** in 3 days through cycloreversion.[135]

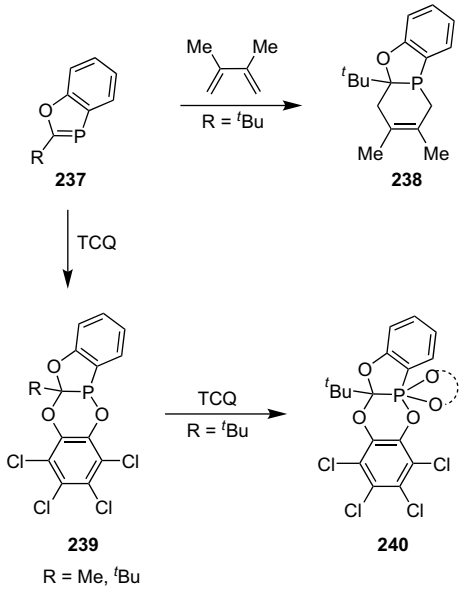


Scheme 61.

2-*tert*-Butyl-1-ethyl-1,3-benzodiphosphole[136,137] and 1*H*-1,2,3-benzazadiphosphole[138] have been reported to form [2+4] cycloadducts with 1,4-diphenylbutadiene and 2,3-dimethylbutadiene to give **235** and **236**, respectively.



1,3-Benzoxaphospholes (**237**) reacted with 2,3-dimethylbutadiene on prolonged heating and with tetrachloro-*o*-benzoquinone (TCQ) at room temperature, leading to the [2+4] cycloadducts **238** and **239**, respectively (Scheme 62).[139] The structure of **239** (R=Me) was confirmed by an X-ray crystallographic analysis.[140]



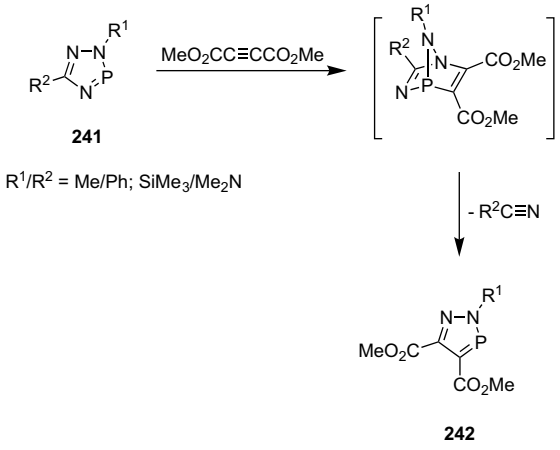
Scheme 62.

Furthermore, **239** on reacting with more TCQ gave **240** resulting from cheletropic 1,1-addition on phosphorus.[139]

7.2. [4+2] Cycloadditions

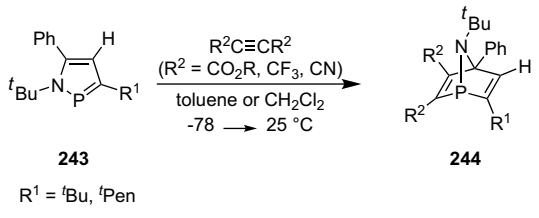
It has been found that the hetero-1,3-diene system present in heterophospholes having a heteroatom (N, O, S, Se) adjacent to the two-coordinate phosphorus combines with an electron-deficient dienophile such as an alkene, acetylene or phosphaacetylene to form a [4+2] cycloadduct. The cycloaddition with acetylene derivatives is usually followed by cycloreversion accompanied by the loss of a nitrile or similar molecule, leading to a new heterophosphole. On the other hand, the [4+2] cycloadduct formed with phosphaacetylenes has been found to subsequently undergo a homo Diels–Alder reaction by reacting with more phosphaacetylene to yield interesting cage compounds.

Schmidpeter and co-worker first reported the participation of [1,2,4,3]triazaphosphole **241** as 1,3-heterodiene in its reaction with DMAD, leading to [1,2,3]diazaphosphole **242** (Scheme 63). Monoalkyl esters of acetylenedicarboxylic acid formed both regioisomers.[141]



Scheme 63.

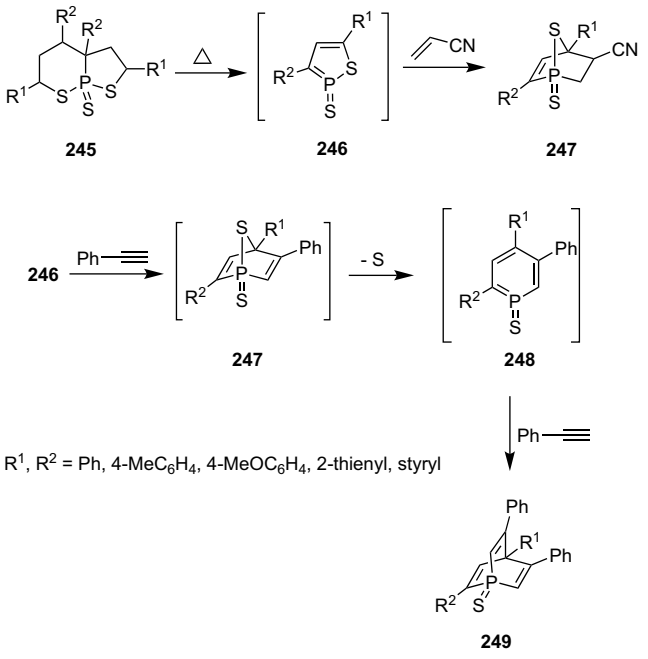
[1,3,2]Diazaphosphole-4,5-dicarbonitrile showed a similar behaviour and reacted with electron-deficient acetylene derivatives to afford 1*H*-1,2-azaphosphole-5-carbonitriles through [4+2] cycloaddition/reversion.[142] In contrast to this observation, 1*H*-1,2-azaphospholes (**243**) formed stable [4+2] cycloadducts (**244**) with electron-deficient acetylenes (Scheme 64).[143] The structure of **244** (R^1=^{t}Bu, R^2=CF_3) was confirmed by an X-ray crystallographic analysis.[143]



Scheme 64.

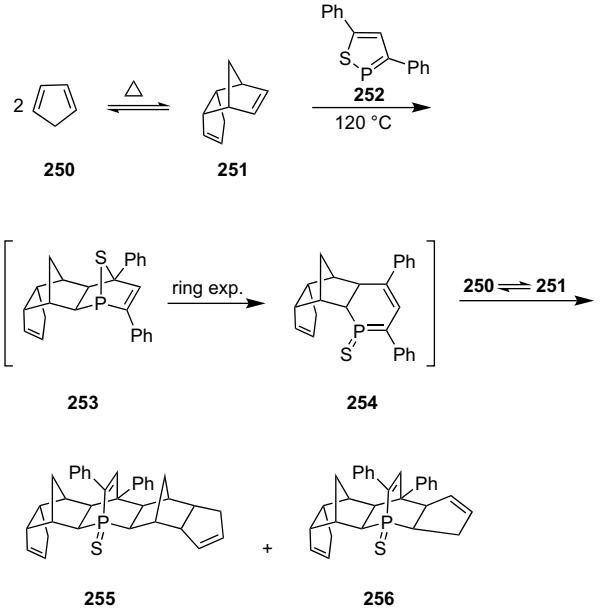
Likewise, 1,2-thiaphosphole-2-sulfides (**246**), generated in situ from the thermolysis of **245** in the absence of a phosphine,[144] yielded [4+2] cycloadducts with a variety of dienophiles such as acrylonitrile, norbornene, norbornadiene, phenylacetylene and DMAD.[145,146] In many cases, tandem DA reactions occur, or the

initially formed DA cycloadduct undergoes secondary reactions such as ring expansion or Michael addition.[147] DA reactions of **246** with acrylonitrile[145] and with phenylacetylene[146] occurring with complete regioselectivity to afford **247** and **249**, respectively, are shown in Scheme 65.



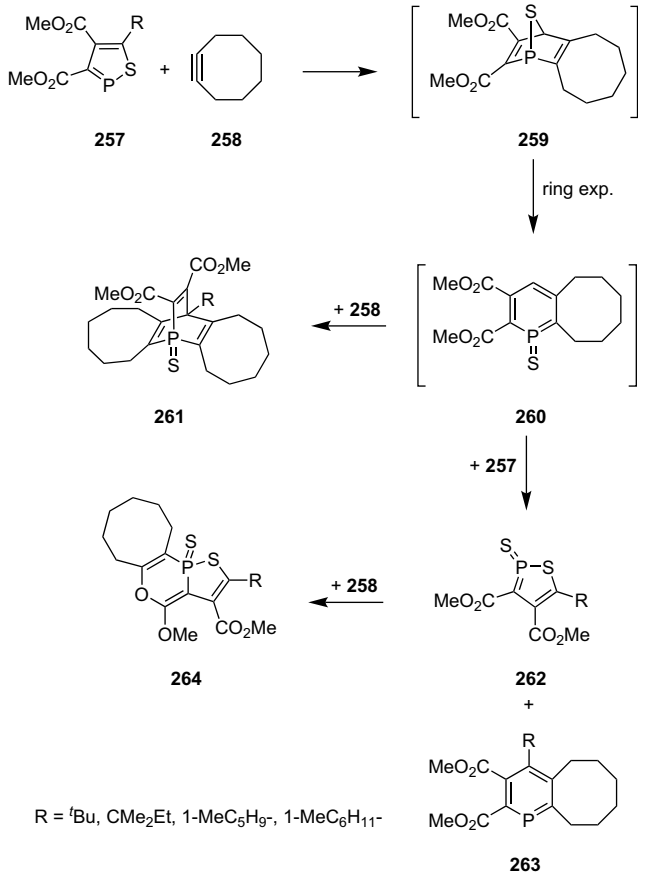
Scheme 65.

Similarly, interesting tandem DA reactions of 1,2-thiaphospholes acting as heterodienes, have been reported with cyclopentadiene[148] and with cyclooctyne.[149] No reaction was observed between 3,5-diphenyl-1,2-thiaphosphole (**252**) and cyclopentadiene at 20–80 °C, but, at 120 °C in a sealed tube, **252** combined with dicyclopentadiene to form a [4+2] cycloadduct (**253**). The latter after ring expansion reacted either with dicyclopentadiene or cyclopentadiene to produce **255** and **256**, respectively (Scheme 66). The structure of **255** was confirmed by X-ray crystallographic studies.[148]



Scheme 66.

The reaction of 1,2-thiaphosphole **257** (R=^{t}Bu) with a 2-fold excess of cyclooctyne led to the polycyclic compounds **261** and **264** through successive [4+2] cycloaddition, cycloexpansion and then again [4+2] cycloaddition (Scheme 67). It is interesting to note that, in the [4+2] cycloaddition of **262** with **258**, the carbonyl moiety of an ester group is also involved. The reaction of other derivatives **257** (R=CMe$_2$Et, 1-methylcyclopentyl, 1-methylcyclohexyl) under similar conditions generated mainly the corresponding compounds **264**, with **261** being formed in much smaller quantities, which, however, could not be isolated in pure form. The formation of **263** was detected by ^{31}P NMR.[149]

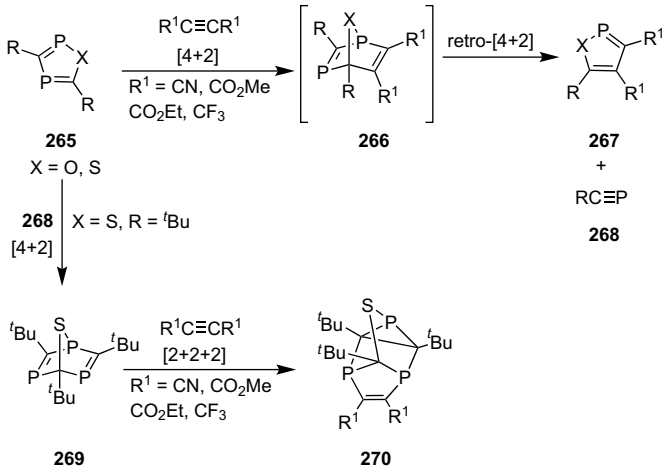


Scheme 67.

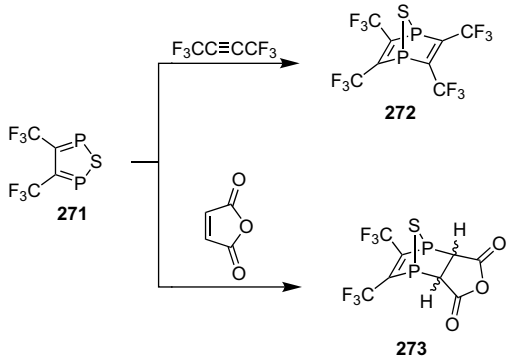
[1,2,4]Thiadiphospholes, [1,2,4]oxadiphospholes and even [1,2,4]selenadiphospholes have been found to participate in the DA reaction as heterodienes. The [4+2] cycloaddition of **265** with acetylene derivatives was followed by cycloreversion accompanied by the loss of phosphaacetylene (**268**), leading to 1,2-thiaphosphole **267** (X=S) or 1,2-oxaphosphole **267** (X=O) (Scheme 68).[150,151] In the reaction of [1,2,4]thiadiphosphole (**265**, X=S; R=^{t}Bu), a side product **270** was also formed, resulting from [2+4] cycloaddition of phosphaacetylene (**268**), liberated in the reaction, with **265** (X=S), followed by a homo DA reaction of **269** with the acetylene derivative.[150]

Unlike [1,2,4]thiadiphospholes, 3,4-bis(trifluoromethyl)-[1,2,5]-thiadiphosphole (**271**) afforded stable [4+2] cycloadducts **272** and **273** with bis(trifluoromethyl)acetylene and with maleic anhydride, respectively (Scheme 69).[152]

The complete regioselective [4+2] cycloaddition of [1,2,4]oxadiphospholes **265** (X=O),[151] [1,2,4]thiadiphospholes **265** (X=S)[150,153] and [1,2,4]selenadiphospholes **265** (X=Se)[154,155] with phosphaacetylenes **274** is followed by a homo DA reaction with a second molecule of **274**, leading to hetero-tetraphospha cage

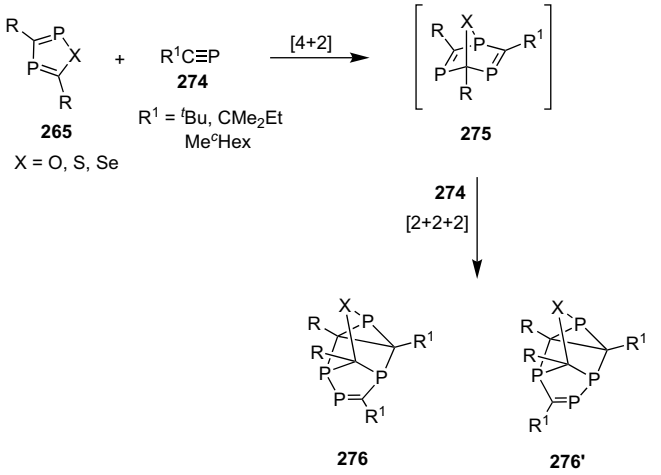


Scheme 68.



Scheme 69.

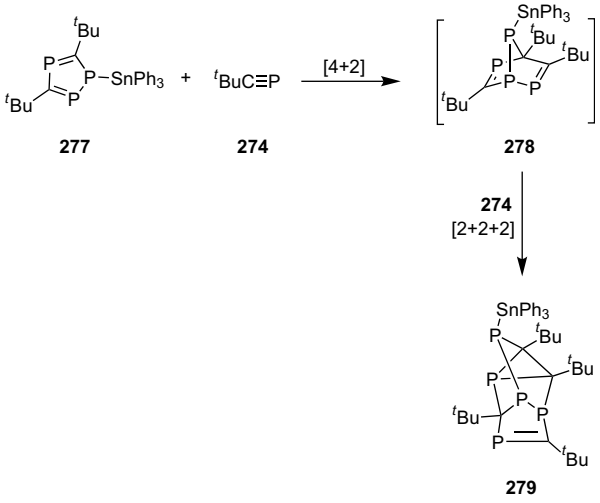
compounds **276** (Scheme 70). The homo DA reaction of the intermediate bicyclodienes **275** produced by [1,2,4]thiadiphospholes (**265**, X=S)[150,153] with phosphaacetylenes occurs fully regioselectively, but, in the case of [1,2,4]selenadiphospholes (**265**, X=Se)[154,155] and [1,2,4]oxadiphospholes (**265**, X=O),[151] the other regioisomers **276′** are also formed.



Scheme 70.

The structures of the final products obtained from [1,2,4]thiadiphospholes[150,153] and [1,2,4]selenadiphospholes[154] have been confirmed by X-ray crystallographic analyses. It was not possible to detect the intermediates **275** by ^{31}P NMR, but a structurally related molecule, [1,3,5]triphospha-Dewar-benzene, was found to undergo a similar homo DA reaction with acetylene.[156]

Likewise, 1-triphenylstannyl-[1,2,4]triphosphole **277** gave **279** through [4+2] cycloaddition followed by [2+2+2] cycloaddition with *tert*-butylphosphaacetylene (Scheme 71). Both cycloadditions occurred with complete regioselectivity.[157]



Scheme 71.

The structure of **279** was confirmed by X-ray crystallographic studies.[157]

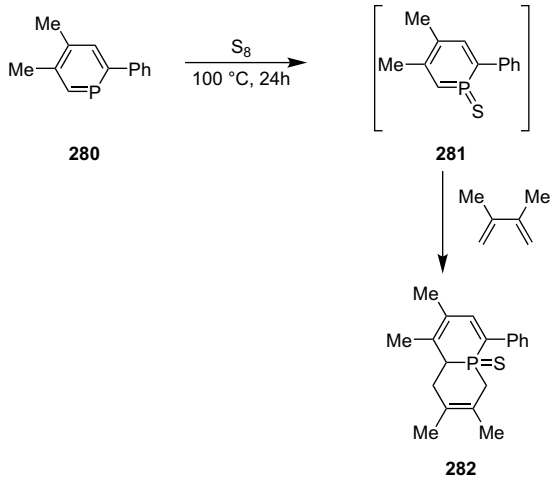
8. Diels–Alder reactions of phosphinines

Like heterophospholes, phosphinines (or more appropriately called λ^3-phosphinines)[30b] also exhibit ambident reactivity in the DA reactions: depending upon the nature of the reagent, these compounds can participate in the reaction as dienophiles via >C=P– bonds ([2+4] cycloaddition) or as 1-phosphadienes via P=C–C=C systems ([4+2] cycloadditions). However, in contrast to heterophospholes, the >C=P– functionality of phosphinine appears to be a weaker dienophile and does not undergo a DA reaction unless activated by oxidation (with sulfur or selenium) or complexation of phosphorus. Similarly, the 1-phosphadiene system of phosphinine reacts only with highly electron-deficient dienophiles, such as bis(trifluoromethyl)acetylene, dicyanoacetylene or benzyne, or must be activated by oxidation of phosphorus or its complexation to metal carbonyl moiety. An earlier review[158] included a few DA reactions of phosphinines reported up to 1971. The general review on 'cycloaddition on σ^2,λ^3-phosphorus multiple bonds'[116] and the reviews[21a,30] dealing with the chemistry of phosphinines also include these reactions, although in a limited manner.

8.1. [2+4] Cycloadditions

Mathey for the first time reported the reaction of the CP double bond of 4,5-dimethyl-2-phenylphosphinine (**280**) as dienophile with 2,3-dimethylbutadiene in the presence of sulfur to give **282**.[159,160] The reaction involved initial sulfurization of phosphorus to generate the intermediate **281** (δ ^{31}P=145.7 ppm), which subsequently underwent [2+4] cycloaddition on the CP double bond (Scheme 72).

Recently, we investigated the concerted and diradical stepwise mechanisms of the DA reactions of phosphinines with 1,3-butadiene and with DMAD theoretically at the DFT level (B3LYP/6-311++G**//B3LYP/6-31G**). The results confirm that the role of sulfur is to oxidize phosphorus to generate a phosphinine

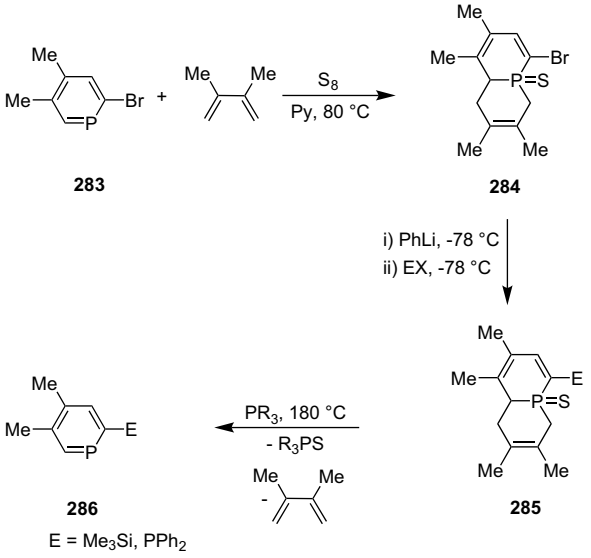


Scheme 72.

sulfide intermediate, which subsequently undergoes a DA reaction by a concerted mechanism.[161]

The cycloadduct **282** could be subsequently converted into 3,4-dimethylphosphinine through successive sulfur/oxygen exchange, [4+2] cycloaddition with DMAD, oxygen/sulfur exchange and, finally, reductive cycloreversion.[160]

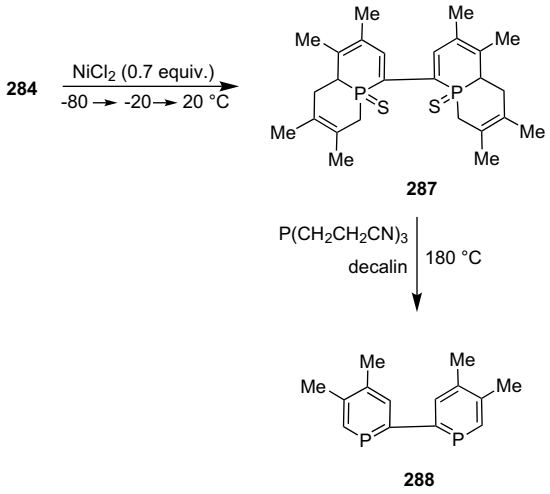
Several 2-functional phosphinines (**286**) were obtained through [2+4] cycloaddition of 2-bromophosphinine (**283**)[51,52] with 2,3-dimethylbutadiene in the presence of sulfur, followed by successive Br/Li exchange, reaction with an appropriate electrophilic reagent and, finally, reductive cycloreversion (Scheme 73).[162]



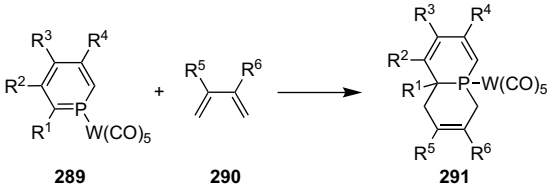
Scheme 73.

2,2′-Biphosphinine (**288**) could be obtained through coupling of **284** in the presence of $NiCl_2$ followed by reductive cycloreversion (Scheme 74).[163]

In another approach, the dienophilic as well as dienic activities of phosphinine are enhanced by complexation to a metal carbonyl. Thus, phosphinine *P*-W(CO)$_5$ (**289**, R^1=Ph, R^2=H, R^3=R^4=Me) afforded a [2+4] cycloadduct with 2,3-dimethylbutadiene.[12] Likewise, [2+4] cycloadducts were obtained from the DA reactions of **289** (R^1=R^3=H, R^2=R^4=Ph) with various 1,3-dienes. The reactions with isoprene and 2-trimethylsiloxy-1,3-butadiene occurred regioselectively and, in the latter case, only one regioisomer **291** (R^1=R^3=R^5=H, R^2=R^4=Ph, R^6=$OSiMe_3$) was formed (Scheme 75).[164]



Scheme 74.

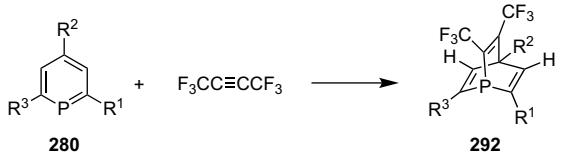


	R^5	R^6
a	Me	Me
b	H	Me
c	$OSiMe_3$	$OSiMe_3$
d	H	$OSiMe_3$

Scheme 75.

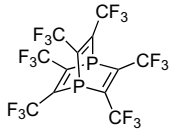
8.2. [4+2] Cycloadditions

Märkl and co-worker for the first time reported the DA reaction in which phosphinines **280** participated as dienes and reacted with bis(trifluoromethyl)acetylene to afford the [4+2] cycloadducts, 1-phosphabarrelenes **292** (Scheme 76).[11] Subsequently, the [4+2] cycloaddition of the parent phosphinine **280** (R^1=R^2=R^3=H) with bis(trifluoromethyl)acetylene was also reported.[165]



	R^1	R^2	R^3
a	Ph	Ph	Ph
b	^{t}Bu	Me	^{t}Bu
c	Me	Ph	Me

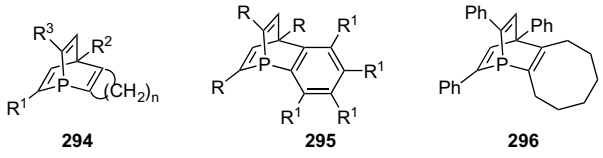
Scheme 76.



In fact, an earlier report[166] of the formation of 1,4-diphosphabarrelene (**293**) from the reaction of bis(trifluoromethyl)acetylene

with red phosphorus could also be rationalized as resulting from the DA reaction of the initially formed 1,4-diphosphinine with bis(trifluoromethyl)acetylene.

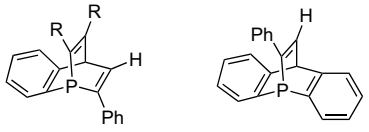
Subsequently, highly strained cycloalkynes, dehydrobenzenes and tetrachloro- dehydrobenzene were found to be sufficiently reactive dienophiles to give **294**,[21a] **295a**[167] and **295b**[167] DA cycloadducts, respectively, with 2,4,6-trisubstituted phosphinines. A similar result was observed in the reaction of **280** (R^1=R^2=R^3=Ph) with cyclooctyne, when **296** was obtained.[168]



294 **295** **296**

a R^1 = H, R = ^{t}Bu/Ph
b R^1 = Cl, R = ^{t}Bu/Ph

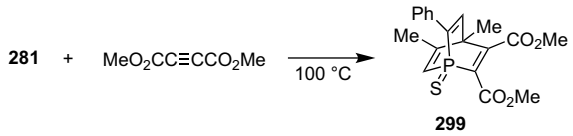
This work was subsequently extended to 2-phenyl-1-phosphanaphthalene that reacted with alkynes (R–C≡C–R; R=CF_3, Ph; R,R=–$(CH_2)_6$–) and benzyne to afford benzophosphabarrelenes **297** and dibenzophosphabarrelene **298**, respectively.[169] However, 2-phosphanaphthalene on reacting with bis(trifluoromethyl)acetylene gave rise only to 2,3-bis(trifluoromethyl)naphthalene, instead of the corresponding 2-phosphabarrelene.[170]



297 **298**

R = CF_3, Ph
R,R = -$(CH_2)_6$-

As mentioned earlier, the reactivity of phosphinine as diene could be increased by sulfurization or complexation of phosphorus. Phosphinine *P*-sulfide **281**, formed as an intermediate, reacted with DMAD to give the [4+2] cycloadduct **299** (Scheme 77).[159]



281 + $MeO_2CC{\equiv}CCO_2Me$ → (100 °C) → **299**

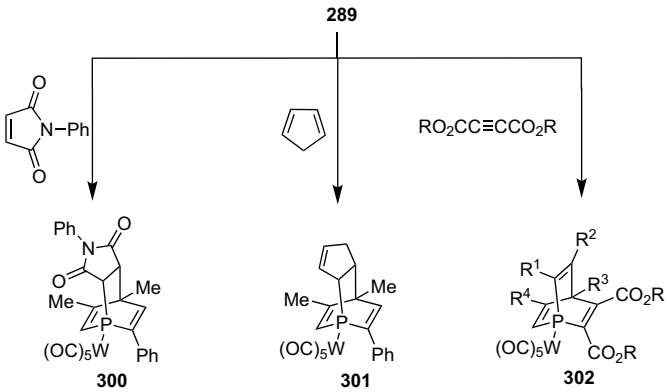
Scheme 77.

Phosphinine *P*-$W(CO)_5$ complex **289** (R^1=Ph, R^2=H, R^3=R^4=Me[12] and R^1=R^3=H, R^2=R^4=Ph[164]) afforded [4+2] cycloadducts (**300**–**302**) with a variety of dienophiles, such as DMAD,[12] *N*-phenylmaleimide,[12] cyclopentadiene[12] and DEAD[164] (Scheme 78).

Likewise, 1-methylphosphininium tetrachlorogallate **303** exhibits enhanced reactivity and forms a [4+2] cycloadduct (**304**) with 4-octyne (Scheme 79).[171] The enhanced reactivity of **303** and facile formation of **304** were rationalized on the basis of DFT calculations.[171]

It is interesting to note that even the exocyclic diphenylphosphine sulfide moiety in **305** enhances the dienic activity of the phosphinine nucleus, which undergoes [4+2] cycloaddition with alkynes to give **306** (Scheme 80).[172]

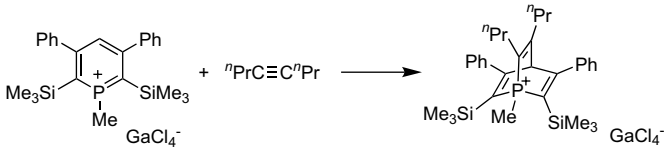
1-Phosphabarrelenes **306a** and **306c** act as tridentate and bidentate ligands, respectively, in their reaction with [Pd(COD)Cl_2]. Furthermore, DFT calculations (B3LYP/6-311+G**) reveal that the formation of 1-phosphabarrelene is thermodynamically favoured when dimethyl acetylenedicarboxylate is used as the alkyne.[172]



289 → **300**, **301**, **302**

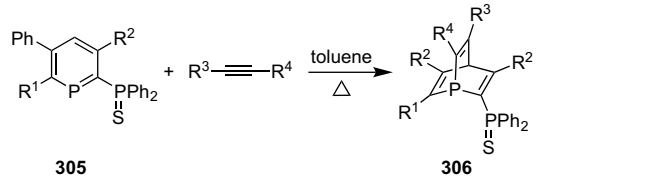
302	R	R^1	R^2	R^3	R^4
a[11]	Me	Ph	H	Me	Me
b[164]	Et	H	Ph	H	Ph

Scheme 78.



303 + ^{n}PrC≡C^{n}Pr → **304**

Scheme 79.

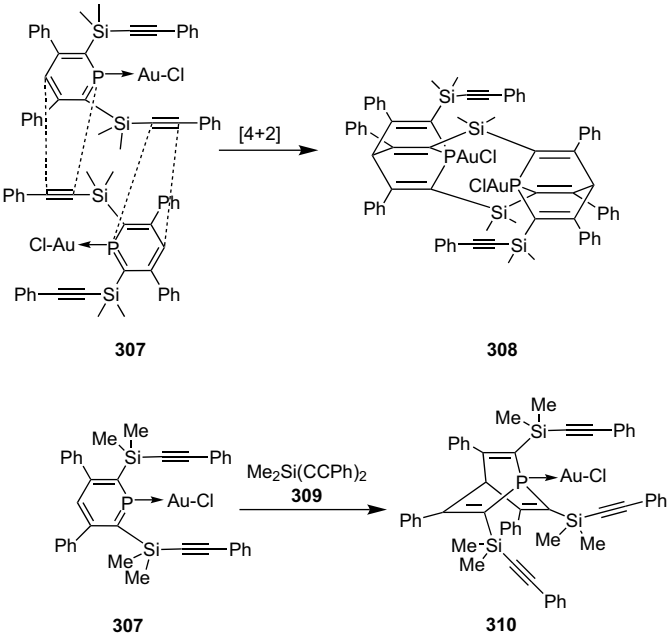


305 + R^3–≡–R^4 (toluene, △) → **306**

a, R^1 = Ph; R^2 = Me
b, R^1 = PPh_2(S); R^2 = Ph

a, R^1 = PPh_2(S); R^2 = R^3 = R^4 = Ph
b, R^1 = PPh_2(S); R^2 = Ph; R^3 = R^4 = CO_2Me
c, R^1 = Ph; R^2 = Me; R^3 = R^4 = CO_2Me

Scheme 80.



307 → [4+2] → **308**

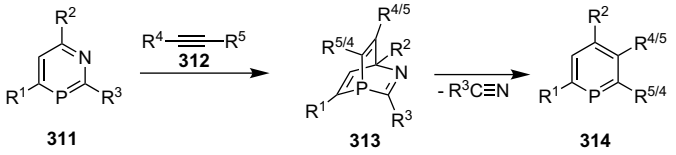
307 + $Me_2Si(CCPh)_2$ (**309**) → **310**

Scheme 81.

An interesting dimerization of an AuCl complex of bis(trimethylsilyl)phosphinine (**307**) involving a double [4+2] cycloaddition between one alkynyl group of each phosphinine complex and the other phosphinine subunit has been reported (Scheme 81).[173] Interestingly, the transformation occurred only during crystal formation and an attempt to replicate the reaction in solution failed. However, the proposed hypothesis could be confirmed by accomplishing the [4+2] cycloaddition of **307** with **309** in a concentrated solution (mimicking crystal formation conditions) successfully (Scheme 81).[173]

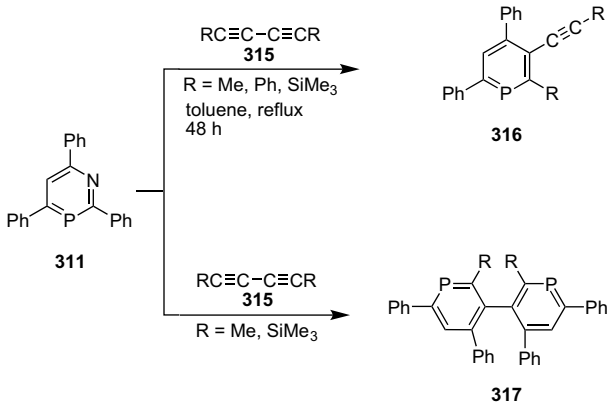
The structures of **308** and **310** were established by X-ray crystallographic analysis.[173]

The reactivities of phosphinine, its *P*-sulfide and *P*-Me cation as dienes in the DA reactions with acetylene have been rationalized by DFT calculations.[27b] The theoretical results confirm that the reactivity of phosphinine sulfide lies between those of phosphinine and the phosphininium cation and may provide sulfurized 1-phosphabarrelene upon mild heating, in conformity with the earlier results,[159a,b] whereas the phosphininium cation yields phosphabarrelene with electron-rich alkynes at room temperature.[171]

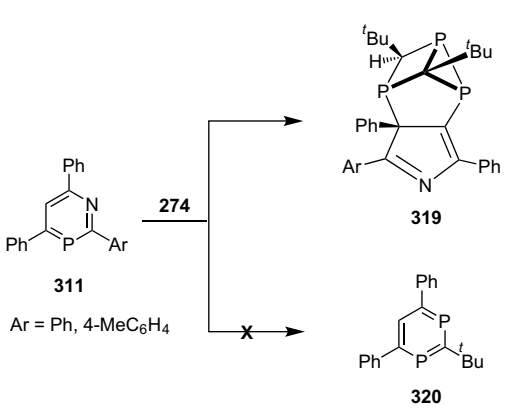


312	a	b	c	d	e	f	g	h	i
R^4	CO_2Me	H	H	Ph	Ph	H	Me	Ph	H
R^5	CO_2Me	CO_2Me	Ph	CO_2Et	COMe	PPh_2	PPh_2	PPh_2	$SiMe_2$

Scheme 82.



Scheme 83.



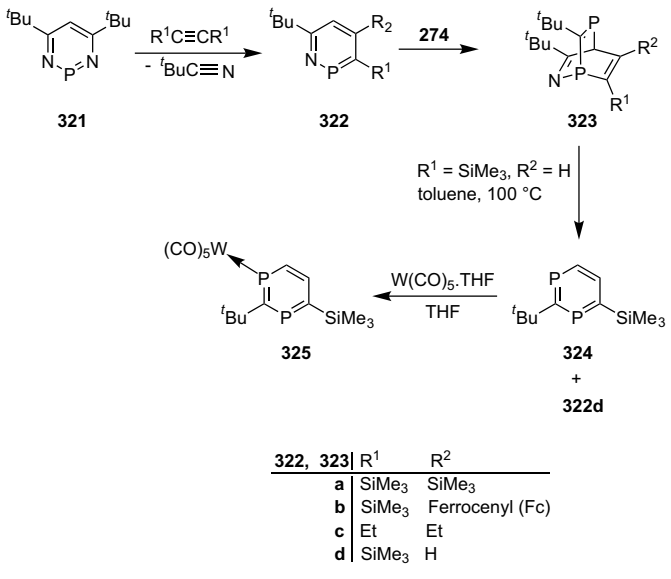
Scheme 84.

9. Diels–Alder reactions of azaphosphinines

The presence of additional nitrogen(s) in the phosphinine ring enhances its reactivity as a diene in the DA reactions. Thus, while phosphinines undergo [4+2] cycloaddition with highly electron-deficient alkynes, such as bis(trifluoromethyl)acetylene, 1,3-aza- and 1,3,5-diazaphosphinines react with a variety of alkynes to furnish azaphosphabarrelenes. The latter are thermally unstable under the reaction conditions and decompose by [4+2] cycloreversion accompanied by loss of a nitrile molecule to furnish phosphinines or 1,3-azaphosphinines, respectively. A similar behaviour is exhibited by 1,3,2-diazaphosphinines. A recent review[174] dealing with the chemistry of phosphinines having additional nitrogen(s) and/or phosphorus atoms in the ring includes DA reactions also of these compounds.

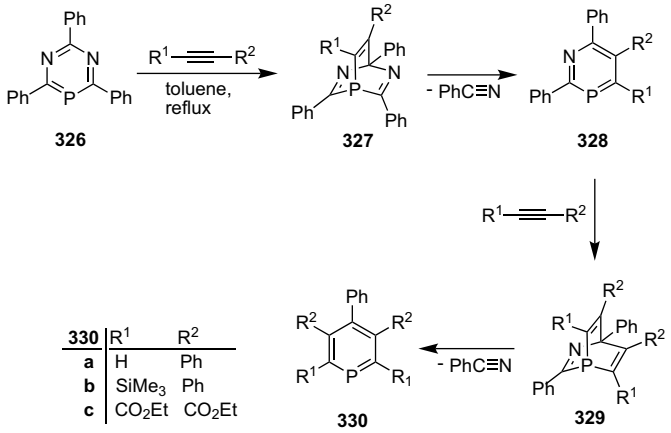
9.1. [4+2] Cycloadditions of 1,3-azaphosphinines

2,4,6-Triaryl-1,3-azaphosphinines (**311**) on reacting with differently substituted alkynes **312** afforded the phosphinines **314** through [4+2] cycloaddition followed by cycloreversion and loss of a nitrile molecule (Scheme 82).[175] The reactions with unsymmetrical



322, 323	R^1	R^2
a	$SiMe_3$	$SiMe_3$
b	$SiMe_3$	Ferrocenyl (Fc)
c	Et	Et
d	$SiMe_3$	H

Scheme 85.



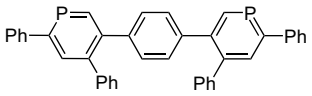
330	R^1	R^2
a	H	Ph
b	$SiMe_3$	Ph
c	CO_2Et	CO_2Et

Scheme 86.

alkynes occurred with high regioselectivity. The DA reactions with phosphino- and trimethylsilyl-substituted alkynes required higher temperatures and longer reaction times, giving poor yields of the products. However, under high pressure, both the temperature and reaction times could be reduced and the yields improved.

The reaction of **311** (R^1=R^2=R^3=Ph) with 1,3-butadiyne derivatives **315** in refluxing toluene yielded **316** involving regioselective [4+2] cycloaddition on one CC triple bond only. However, on carrying out the reaction of **311** with **315** (R=Me, $SiMe_3$) under high pressure (7–8 kbar) in toluene, 3,3′-biphosphinine **317** was obtained through complete regioselective [4+2] cycloadditions on both CC triple bonds (Scheme 83).[175c]

On using 1,4-diethynylbenzene in place of **315**, **318** was obtained. Similarly, 1,3- and 1,2-diethynylbenzenes, and also 4,4′- and 2,2′-diethynyldiphenyls, were additionally used as dienophiles successfully.[175c]



318

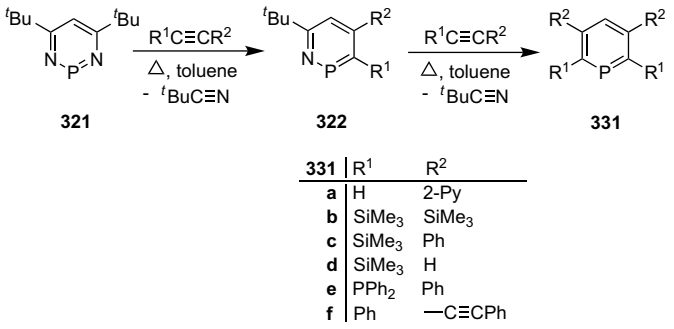
The reaction of **311** (R^1=R^2=Ph, R^3=Ph, 4-MeC_6H_4) with 2-*tert*-butyl-1-phosphaethyne (**274**), however, proceeded in an unexpected manner and furnished **319** (Scheme 84).[176] A plausible mechanism for the formation of **319** has been proposed. The structure of **319** (Ar=Ph) has been confirmed by an X-ray crystallographic investigation.[176]

9.2. [4+2] Cycloadditions of 1,2-azaphosphinines

1,2-Azaphosphinines **322**, generated in situ from 1,3,2-diazaphosphinines **321**, reacted with **274** regioselectively, leading to the [4+2] cycloadducts, azadiphosphabarrelenes **323**, stable at room temperature. Thermolysis of **323a–c** under reflux in toluene reproduced **322a–c** through cycloreversion, but **323d**, under these conditions, gave **324** also, besides **322d**, which was identified unambiguously by analysis of its $W(CO)_5$ complex **325** (Scheme 85).[177]

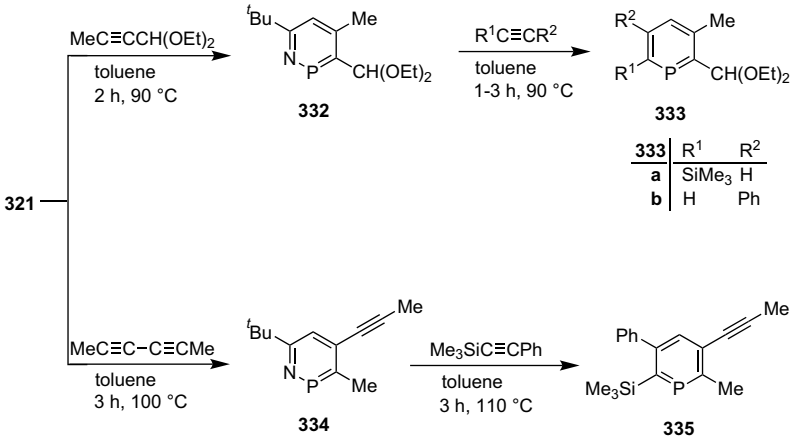
9.3. [4+2] Cycloadditions of diazaphosphinines

Märkl and co-worker for the first time reported the synthesis and [4+2] cycloadditions of 1,3,5-diazaphosphinines (**326**),[178] the



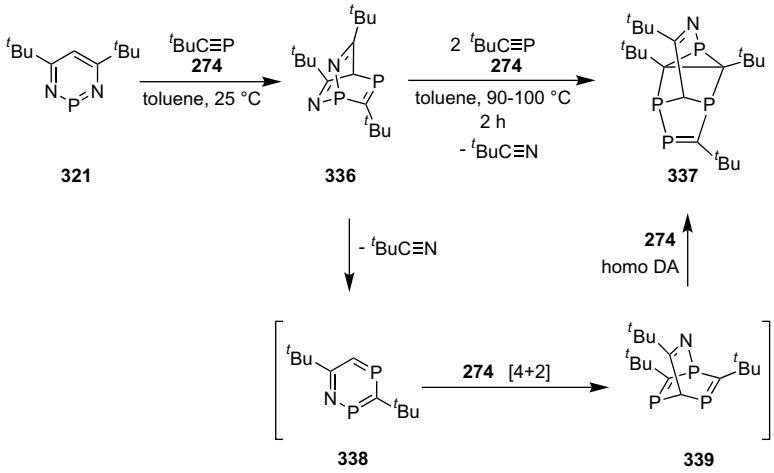
331	R^1	R^2
a	H	2-Py
b	$SiMe_3$	$SiMe_3$
c	$SiMe_3$	Ph
d	$SiMe_3$	H
e	PPh_2	Ph
f	Ph	—C≡CPh

Scheme 87.



333	R^1	R^2
a	$SiMe_3$	H
b	H	Ph

Scheme 88.



Scheme 89.

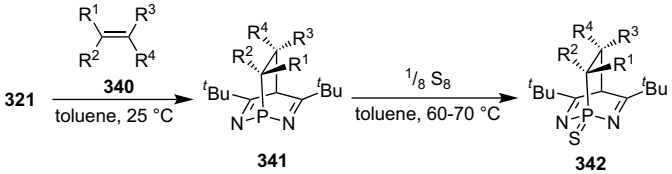
reactivity of which resembled that of 1,3-azaphosphinine. These compounds, on refluxing in toluene with various alkynes, undergo 'Domino' reactions, leading to pentasubstituted phosphinines (**330**) through successive [4+2] cycloaddition, cycloreversion, [4+2] cycloaddition and again cycloreversion (Scheme 86).[178] The reaction with unsymmetrical alkynes occurred with complete regioselectivity. The diaza- and azaphosphabarrelenes **327** and **329**, respectively, are unstable under the reaction conditions.

In recent years, interesting chemistry has been developed starting with the DA reactions of 1,3,2-diazaphosphinines.[177,179–186] Like 1,3,5-diazaphosphinines, 1,3,2-diazaphosphinines (**321**) also undergo [4+2] cycloaddition, but, on carrying out the reaction under controlled conditions, the intermediate 1,2-azaphosphinines (**322**; see Section 9.2) could be isolated in these cases. On heating **322** at a higher temperature with a second equivalent of alkyne, tetrasubstituted phosphinines **331** were obtained.[179] Almost in all cases, the reaction occurred with complete regioselectivity and only one regioisomer was formed (Scheme 87).

Furthermore, following the above methodology, it has been possible to use different alkynes in the two steps, making a variety of phosphinines, e.g., **333** and **335**, available. The method is illustrated in Scheme 88.[180]

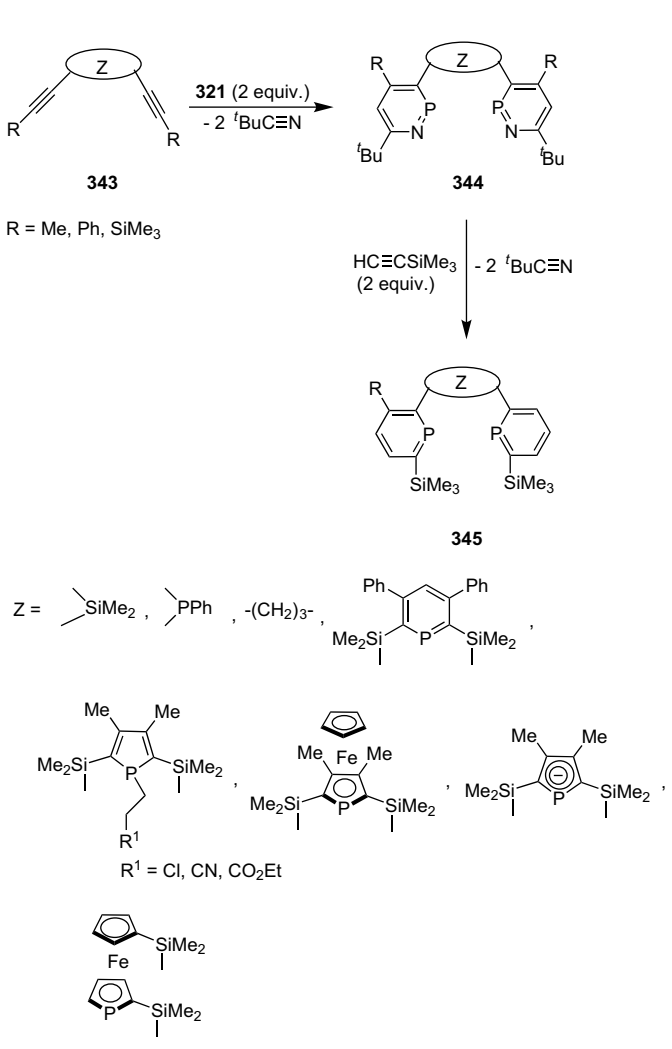
The reaction of 1,3,2-diazaphosphinine **321** has been investigated with phosphaethyne **274** also.[177] In contrast to the reaction with alkynes, diazadiphosphabarrelene **336** formed in the first step in this case could be isolated. Thermolysis of **336** in the presence of a 3-fold excess of **274** gave **337**. Formation of the latter could be rationalized on the basis of [4+2] cycloreversion of **336** to generate the intermediate, 1,2,4-azadiphosphinine **338**, followed by its [4+2] cycloaddition with **274** to produce azatriphosphabarrelene **339**. The last step in the sequence is a homo DA reaction between the two P=C double bonds in **339** and a second equivalent of **274**, leading to **337** (Scheme 89). It may be noted that all [4+2] cycloadditions occur with complete regioselectivity, which is in accordance with the polarities of **321** and the intermediate species. The structure of **337** was confirmed by an X-ray crystallographic investigation of its tungstenpentacarbonyl complex.[177]

1,3,2-Diazaphosphinine **321** undergoes [4+2] cycloaddition with activated alkenes (**340**) also, leading to stable diazaphosphabarrelenes (**341**) (Scheme 90). However, the latter could not be

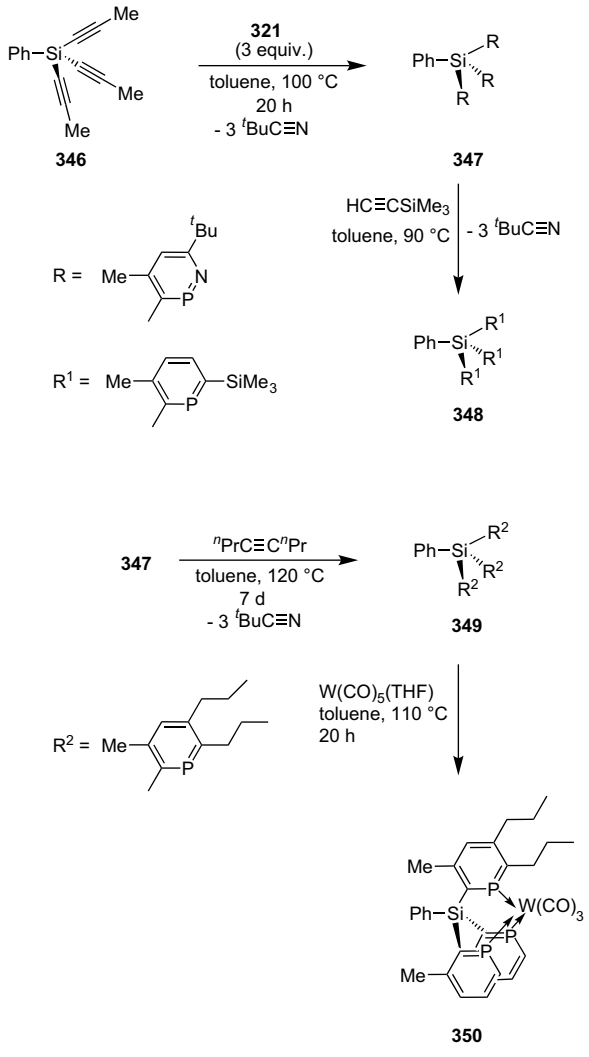


340	R^1	R^2	R^3	R^4
a	CO_2Me	H	H	CO_2Me
b	CO_2Et	H	H	H
c	CN	H	H	H

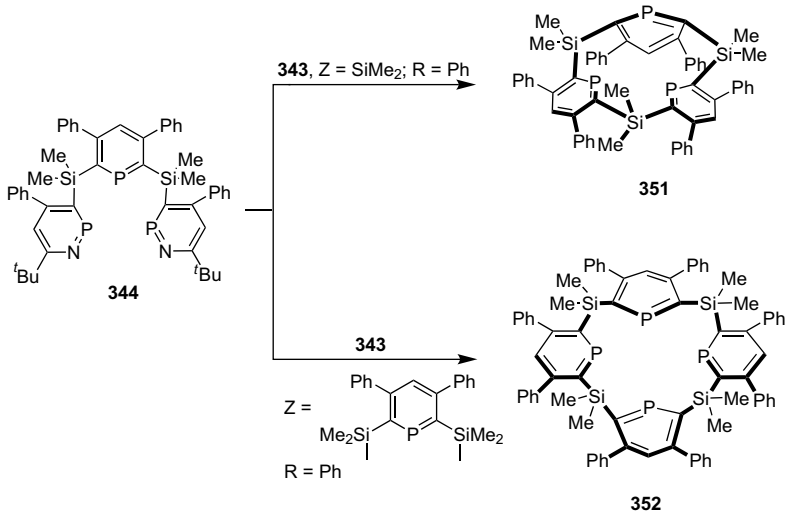
Scheme 90.



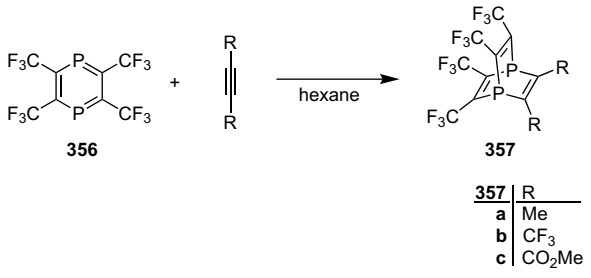
Scheme 91.



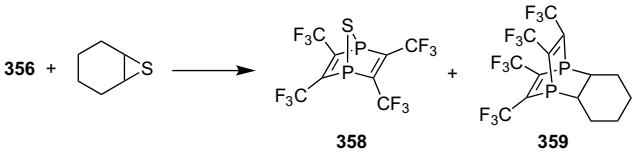
Scheme 92.



Scheme 93.



Scheme 94.



Scheme 95.

purified, due to their sensitivity to oxygen, and were therefore sulfurized prior to purification. The structure of **342** (R^1=CN, R^2=R^3=R^4=H) was confirmed by an X-ray crystallographic analysis.[181] The reaction with **340b** and **340c** gave two regioisomers in each case in a ratio 9:1 and 5:1, respectively.

Based on a [4+2] cycloaddition/cycloreversion strategy involving successive reactions between 1,3,2-diazaphosphinine and appropriately substituted alkynes or bis(phenylethynyl)silane (**343**), a new approach has been devised for the synthesis of phosphinine-based, as well as mixed phosphinine-phospholebased, polydentate ligands **345** (Scheme 91). This methodology has made a variety of ligands available.[180,182–186]

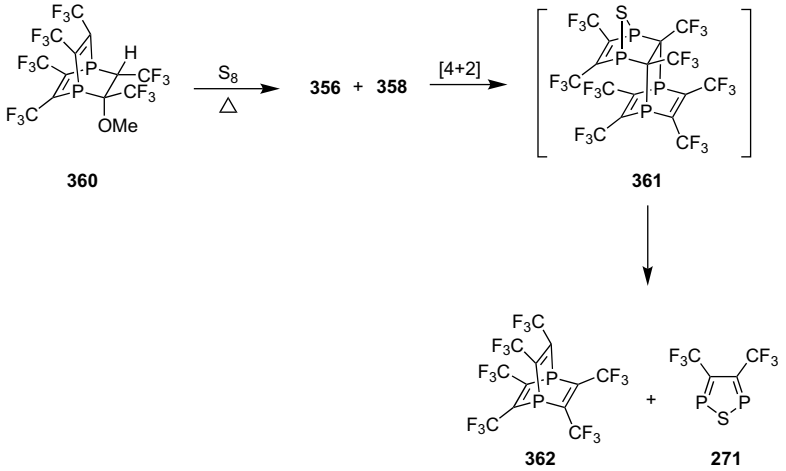
Starting with tris(propynyl)phenylsilane (**346**), the above strategy provided the interesting tripodal ligands **347**, **348** and **349** (Scheme 92). The structure of **349** was confirmed by an X-ray crystal structure investigation of its $W(CO)_5$ complex **350**.[183]

The methodology described above has been used for the synthesis of silacalix[*n*]phosphinines **351** (*n*=3) and **352** (*n*=4) (Scheme 93).[182]

The structures of silacalix[3]phosphinine **351**, silacalix[4]phosphinine **352** and several other products were confirmed by X-ray crystallographic investigations.[182]

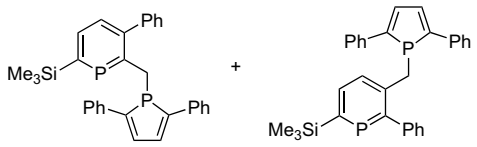
Likewise, mixed phosphinine-thienyl and -furyl silacalix[4]-phosphinines have been prepared.[182]

1-Phospholyl-substituted phosphinines (**353**+**353′**) and the *P*-sulfides (**354** and **355**) have also been obtained through [4+2]

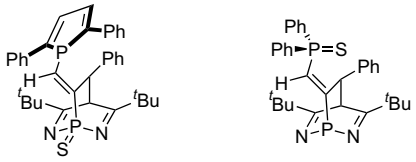


Scheme 96.

cycloaddition/cycloreversion of **321**. Formation of the *P*-sulfide involved a 1,3-H shift from the methylene carbon to the bridge of the barrelene moiety, leading to an exocyclic double bond.[181]



353 **353'**



354 **355**

The [4+2] cycloadditions of 1,3,2- and 1,3,5-diazaphosphinines with acetylenes have been studied theoretically at the DFT level (B3LYP/6-31G*). The lower activation energy barrier for the DA reaction of 1,3,2-diazaphosphinine is in conformity with its comparatively higher reactivity. Nevertheless, steric effects are also expected to determine the ultimate reactivities of the two systems as dienes.[27a]

10. Diels–Alder reactions of diphosphinines

1,4-Diphosphinine **356**, when trapped with alkynes, gave 1,4-diphosphabarrelenes **357** through [4+2] cycloaddition (Scheme 94).[187]

The reaction of **356** with cyclohexene thioxide yielded **358** and **359**, the latter being formed through [4+2] cycloaddition of **356** with cyclohexene, generated in situ (Scheme 95).[152]

Furthermore, on thermolysing **360**, a precursor of **356**, with 0.5 molar equivalent of sulfur, **362** and **271** were obtained. The formation of **362** can be rationalized by cycloreversion of the initially formed DA cycloadduct **361** (Scheme 96).[152]

11. Concluding remarks

During the last three decades, the chemistry of the DA reactions involving the >C=P– functionality, as a dienophile or as a part of a phosphadiene, has progressed in an amazing manner. After realization of the close analogy between carbon and phosphorus atoms and the weakness of the CP double bond, as compared to the CC double bond, it is expected that many more systems of phosphorus-heterocycles having a >C=P– functionality will be investigated for their DA reactions. The synthetic approach based on multiple [4+2] cycloaddition/cycloreversion steps, leading to interesting multidentate ligands, is a spectacular development in recent years and is expected to keep this topic still a frontline area, not only in organophosphorus chemistry, but also in coordination chemistry. Furthermore, the use of phosphaalkynes as dienophiles, leading to interesting polyphospha cage compounds, is hitherto limited to only a few systems and has the potential of being extended to other phosphorus-heterocycles. It is hoped that the present report will be able to stimulate further work in these areas.

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