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Review

Phosphetene: synthesis and reactivity

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Dedicated to Professor Maurizio Perruzini on the occasion of his 65th birthday

Abstract

Four-membered ring heterocycles are less studied than five or six-membered heterocycles. It is even more true for 4-membered P-rings and in particular their unsaturated congeners, namely phosphetenes. In this review, we report the main synthetic strategies developed to prepare such compounds. The study of their reactivity, either in organic transformations or coordination chemistry, illustrates that share both specific reactivities of unsaturated strained cycles and phosphanes making them versatile synthons for original organophosphorus derivatives.

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Keywords: Organophosphorus, dihydrophosphete, strained cycles, P-heterocycles, coordination chemistry

1. Introduction

Four-membered ring heterocycles, although being known for a long time, have been less studied than other heterocycles, such as five or six-membered rings. Most of the interest was given to the saturated cycles, such as oxetanes, azetidines, thietanes, siletanes or phosphetanes, which were viewed as more stable than their unsaturated analogues.[1,2]

Oxetanes are the most widely spread four-membered heterocycles, as they are found in numerous biologically active molecules, for example in paclitaxel (Paclitaxel (Taxol[®]), Figure 1) and docetaxel (Taxotere[®]), two anti-cancer drugs.[3] Oxetanes are strained cyclic ethers but, they are stable motifs for medicinal chemistry and reactive intermediates for synthesis. Recently, they have raised interest in the design of glycomimetic molecules, along with azetidines and thietanes (Figure 1).[4] Azetidines have been thoroughly studied. They are widely represented in a variety of biologically active molecules, like nicotianamine (Figure 1) and they have attractive properties for drug design.[5] Azetidines present a reactivity similar to aziridines and can also be used as a starting material for polymer synthesis [6] or as a synthetic precursor for other nitrogen heterocycles.[7] Thietanes (Figure 1) [8] are subunits that are also found in biological structures such as nucleosides[9,10,11]. They have been used for the development of anti-cancer drugs,[12] sweeteners,[13] thiathromboxane A₂ drugs (Figure 1),[14] and pesticides [15]. They also are useful intermediates in the preparation of sulfur-containing acyclic and heterocyclic compounds. Siletanes (silacyclobutanes) (Figure 1) are easy to handle as they are air-stable and can be purified by simple distillation.[16] They show a “strain release” Lewis acidic property, which has led to siletanes receiving more and more attention. Mukaiyama aldol reactions [17] and aldehyde allylations [18,19] don't need any external catalysts when traditional silanes are replaced with siletanes. Denmark *et al.* showed that siletanes can also serve as precursors to silanols for Hiyama-type cross-coupling reactions,[16] and the ring strain has also been exploited for insertions and ring expansions into siliranes and siletanes. [20,21]

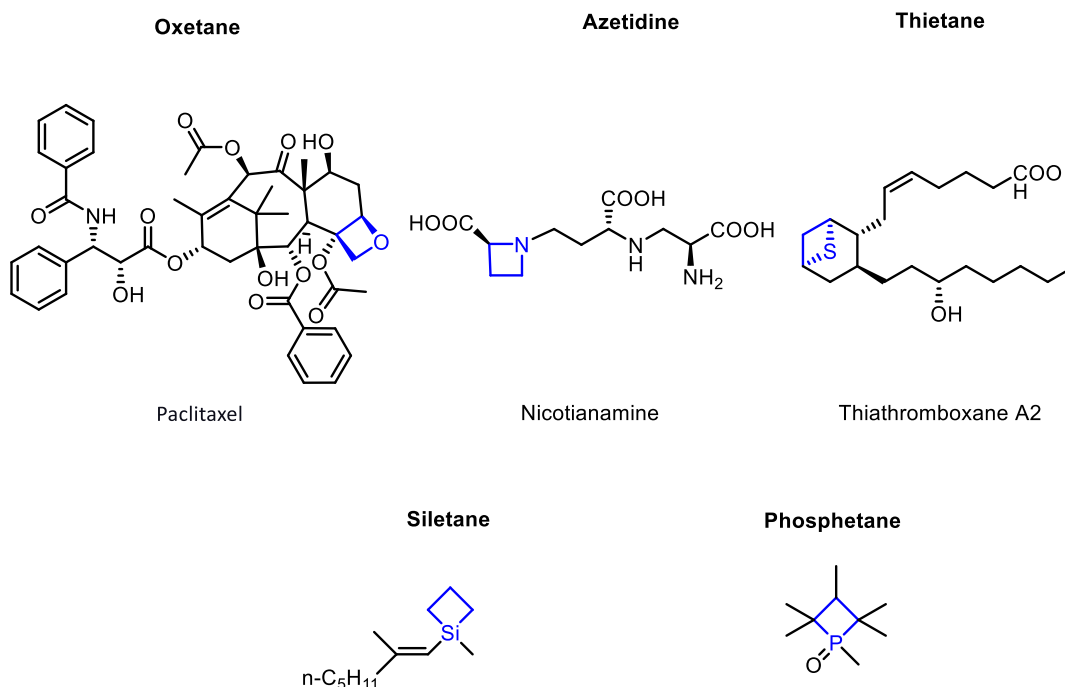


Figure 1. Examples of molecules containing hetero-four-membered rings

Phosphetanes (Figure 1) are not found in nature. They were first synthesized as a curiosity and used to investigate the acidic properties of phosphonic acids [22] and the stereochemistry of such compounds.[23,24,25] Since then, they have been widely used, for the reactivity of the strained four-membered ring and the phosphorus atom, as a ligand in coordination chemistry, as a chiral cyclic phosphine, and very recently as redox cycling organocatalysts.[26,27,28]

Despite the various interests of hetero-four-membered rings, unsaturated version of them are less studied and phosphetenes (unsaturated P-containing four-membered rings) are no exception.[29] Firstly, three kinds of unsaturated four-membered rings containing one phosphorus atom exist: Δ^1 -phosphetenes or 3,4-dihydrophosphetes, with one unsaturation involving the phosphorus atom, Δ^2 -phosphetenes or 1,2-dihydrophosphetes, where the unsaturation doesn't involve the phosphorus atom, and phosphetes,[30] with two unsaturations (Figure 2).

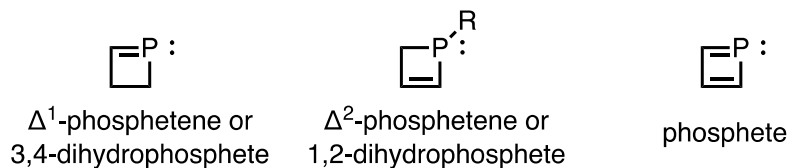


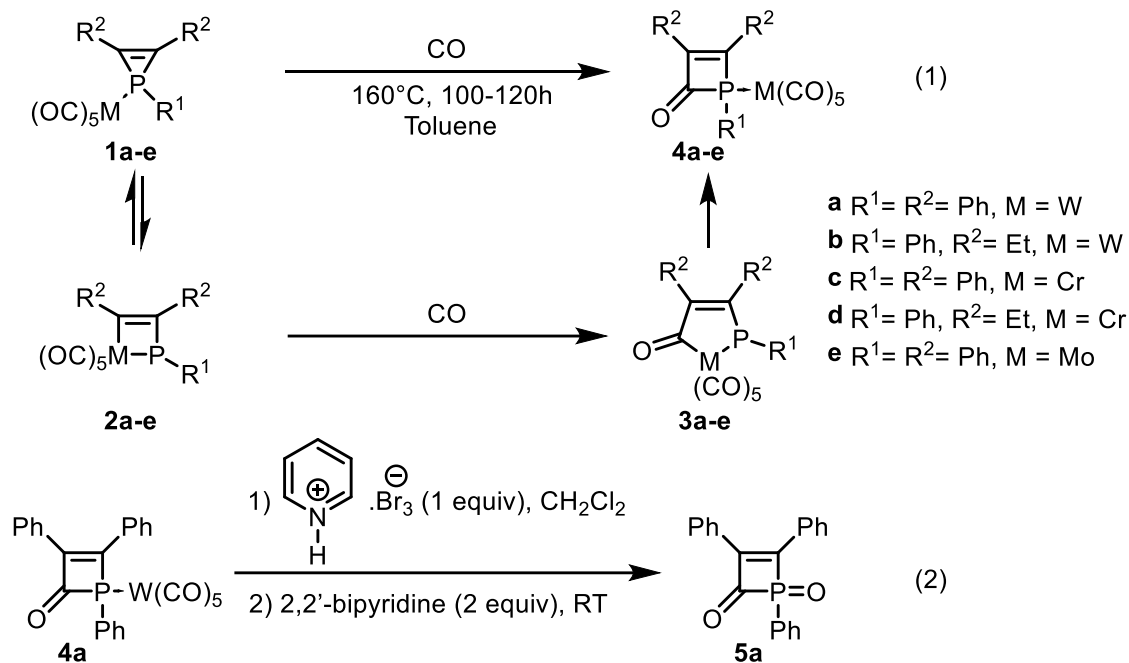
Figure 2. Unsaturated P-containing four-membered rings

The present review summarizes the phosphetene chemistry concerning their synthesis, properties and reactivities. In most of the earliest reports, phosphetes were obtained as secondary products. They were either by-products, reaction intermediates, or an unexpected product due to a particular reactivity of starting materials. However, the systematic studies carried out on these compounds showed that they are thermally and chemically stable. Furthermore, it was shown that they share both specific reactivities of strained cycles and phosphanes. This has led to the development of specific and efficient synthesis routes and their use in specific applications such as Organic Light-Emitting Diodes (OLEDs).

2. Synthesis of phosphetenes

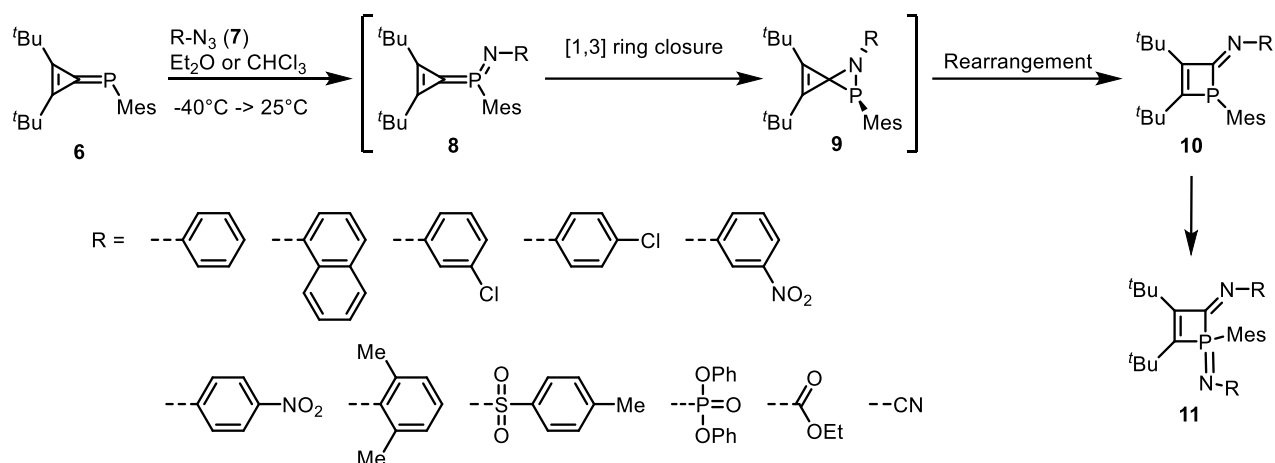
2.1. *via* ring expansion

One of the first synthesis of an unsaturated four-membered ring containing a phosphorus atom was described by Mathey *et al.* in 1985.[31] While working on the chemistry of phosphirene-chromium, -molybdenum or -tungsten pentacarbonyl complexes (Compound **1a-e**, Scheme 1), a ring expansion was observed during the thermolysis of these complexes forming unsaturated four-membered rings containing a phosphorus atom. Indeed, a CO insertion in the σ P-C bond (Scheme 1) allowed obtaining a phosphorus analogue of β -lactams **4a-e**. Then, Mathey *et al.* managed to decoordinate the ligand and thus prepare product **5a**. In presence of pyridinium tribromide, the tungsten atom is oxidized and the phosphorus-based ligand is displaced by 2,2'-bipyridine forming the σ^3, λ^3 -P-based phosphete. Unfortunately, this compound rapidly oxidizes to form compound **5a** (Equation 2). This example showed for the first time that unsaturated four-membered rings containing a phosphorus atom are stable and can be isolated.



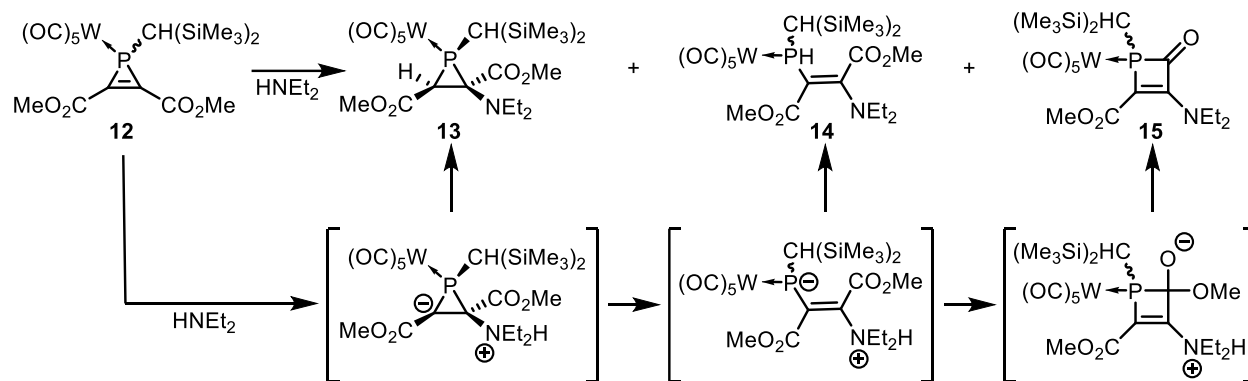
Scheme 1. First four-membered ring containing a phosphorus atom obtained from the insertion of carbon monoxide into phosphirene complexes

Later, in 1994, Regitz *et al.* described the synthesis of 1*H*-2-iminophosphetes (compound **10**, Scheme 2) by a ring expansion of phosphatriafulvenes (compound **6**, Scheme 2).[32] Compound **6** is a phosphalkene, linked to a cyclopropene, which has an increased electron density at the phosphorus atom and a lowered electron density in the cyclopropenyl moiety. The reaction of **6** with azides **7** leads to the formation of 1*H*-2-iminophosphetes **10**. *Ab initio* calculations showed that the azide react with the lone pair of the phosphorus followed by an elimination of N₂ to form an iminophosphatriafulvene (**8**). The subsequent cyclization of the iminophosphatriafulvene leads to the formation of the spiro-[2,2]azaphospholene **9**. Then, a rearrangement involving a ring expansion of the cyclopropenyl moiety results in the formation of 1*H*-2-iminophosphetes (**10**). In presence of an excess of azide, a subsequent Staudinger reaction can take place resulting in compound **11**.



Scheme 2. Synthesis of 1H-2-iminophosphetes.

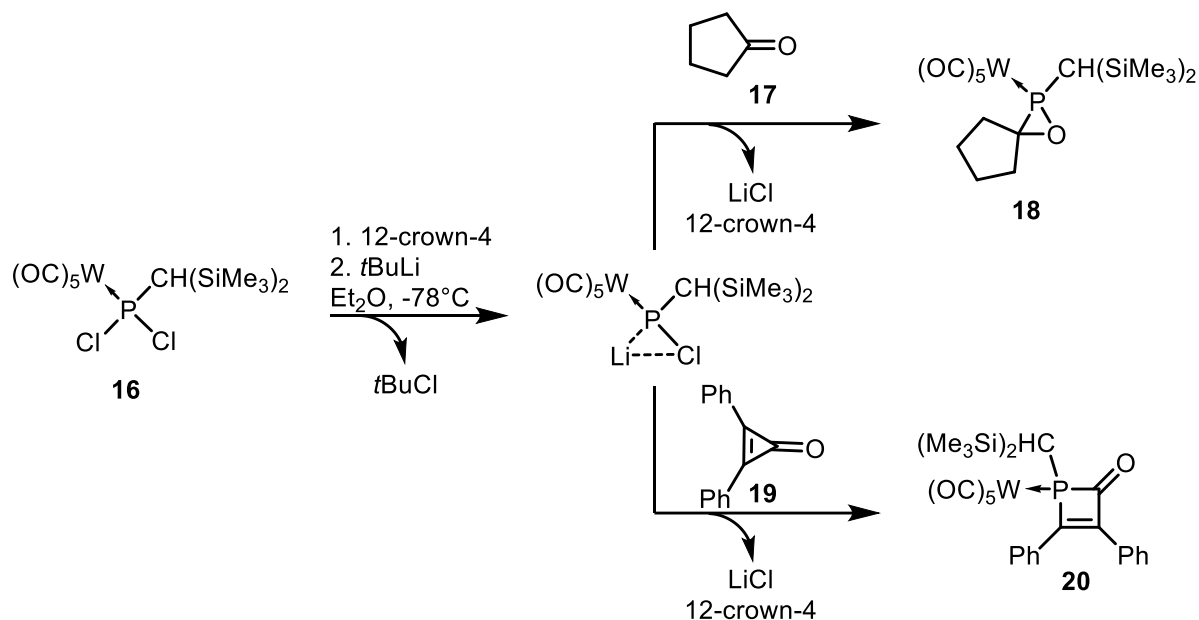
In 1999, Streubel *et al.* were looking for new routes to small- and medium-sized P-heterocycle complexes having C-methoxycarbonyl groups attached to the ring system. They thus studied the reaction of phosphirene complexes with various reactant in order to expand the phosphorous ring.[33] In particular, the reaction of the phosphirene complex **12** with diethylamine lead to the formation of three products (in a *ratio* near to 1:1:1): the 1,2-addition product **13**, the secondary vinylphosphane complex **14**, and the 1,2-dihydro-1-phosphet-2-one complex **15** (Scheme 3)



Scheme 3. Reaction of a phosphirene complex with diethylamine

In 2011, the same group was working on the synthesis of complexed spirooxaphosphiranes starting from a transient Li/Cl phosphinidenoid pentacarbonyltungsten complex, obtained from complex **16**, and cyclic ketones.[34] While the reaction with usual cyclic ketones (see cyclopentanone **17** in Scheme 4) lead to spirooxaphosphirane **18**, when 2,3-

diphenylcyclopropanone **19** was used, the authors observed the selective formation of the 1,2-dihydrophosphet-2-one complex **20** (Scheme 4)

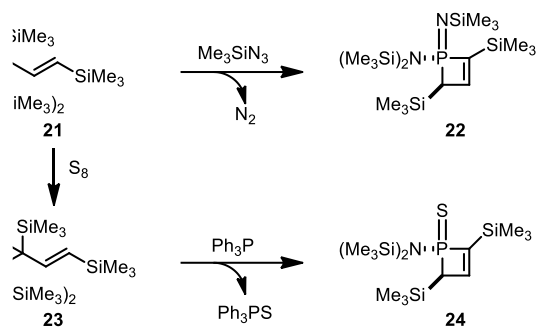


Scheme 4. Reaction of Li/Cl phosphinidenoid with cyclic ketones leading to either spirooxaphosphiranes or 1,2-dihydrophosphet-2-one complex

2.2. *via* cyclization of phosphabutadienes

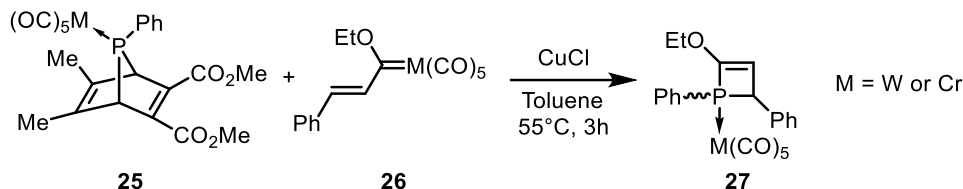
Phosphabutadienes are an important class of compounds. They are highly studied because of the analogy between the C-C and P-C bonds and of their specific reactivity.[35] For example, they can be used as dienes in Diels-Alder reactions.

In 1987, Neilson *et al.* studied oxidation reactions of 1-[bis(trimethylsilyl)amino] phosphadiene (**21** ; Scheme 5) in the presence of Me_3SiN_3 or elemental sulfur.[36,37] In the two cases, 1,2-dihydrophosphetes **22** and **24** have been obtained and their formation can be viewed as an intramolecular [2+2] cycloaddition of the C=C and P=C bonds *via* a 3-coordinate (methylene)phosphorane intermediate, $R,N-P(=E)=CRH-CH=CRH$ ($R = Me, Si$; $E = NR, S$). In the presence of Me_3SiN_3 , a ring-closed, isomeric phosphacyclobutene **22** is isolated as a distillable liquid that solidifies upon standing. In the presence of elemental sulfur, compound **23** is obtained. Then, subsequent treatment with triphenylphosphine results in a yellow solid (compound **24**). In both cases, a mixture of enantiomers is obtained.



Scheme 5. Synthesis of 1,2-dihydrophosphetes via cyclisation of phosphabutadienes.

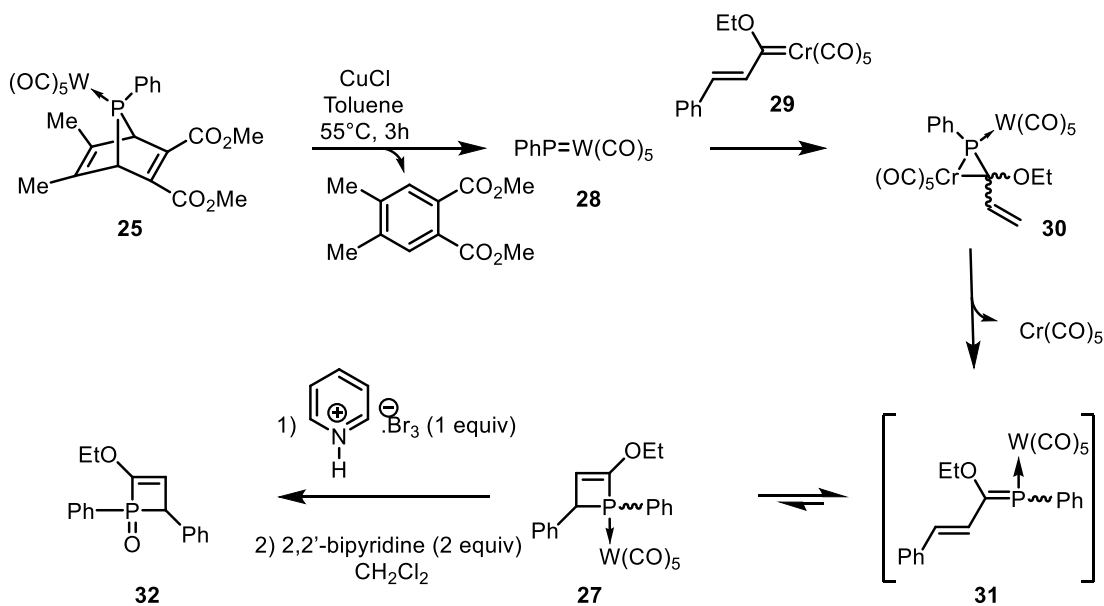
The following year, Mathey *et al.* also worked on the synthesis of 1,2-dihydrophosphete starting from *in situ* generated tungsten or chromium pentacarbonyl phosphinidene complex (Scheme 6).[38,39,40] The dihydrophosphete derivative **27** was obtained by reacting the phosphinidene precursor **25** with the carbene complex **26**.



Scheme 6. Synthesis of 1,2-dihydrophosphetes from tungsten or chromium pentacarbonyl phosphinidene complexes and carbene complex.

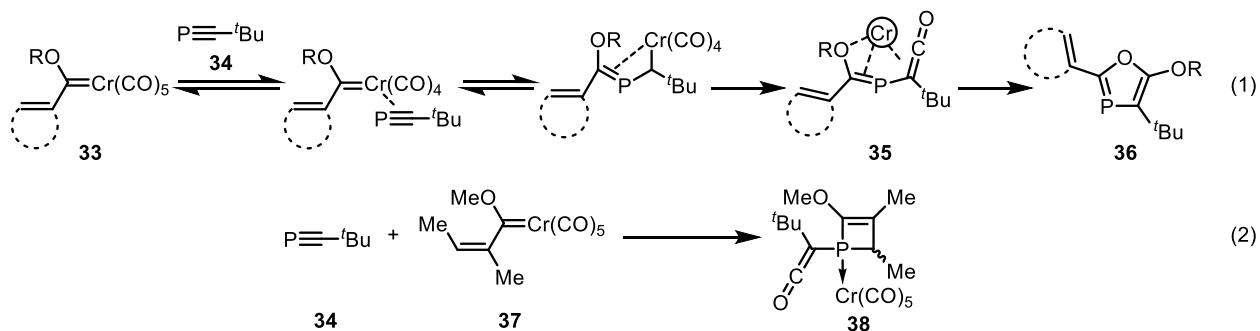
The postulated mechanism is depicted in Scheme 7. In presence of copper(I) chloride, the complex **25** decomposed into 4,5-dimethylphthalate and the corresponding phosphinidene complex **28**. Then, the phosphinidene complex **28** reacted with the carbene complex **29**. Depending on the nature of the metal pentacarbonyl (tungsten or chromium) being used in the structure of the starting materials (carbene or phosphinidene), different products can be obtained: phosphabutadienes, 1,2-diphosphetanes (saturated four-membered ring containing two adjacent phosphorus atoms) and 1,2-dihydrophosphetes. Using the tungsten pentacarbonyl complex of phosphinidenes **28** and chromium pentacarbonyl carbene complex **29**, rather than the less labile tungsten pentacarbonyl carbene complex, phosphabutadiene **31** appeared as an intermediate product and immediately electrocyclizes *via* conrotary process to give the 1,2-dihydrophosphete complexed to the tungsten pentacarbonyl fragment **27**. After purification and oxidation, 1,2-dihydrophosphete oxide (Compound **32**, Scheme 7) was isolated. The product is stable and its structure has been established by X-ray diffraction studies, showing that

the bond lengths and angles of the phosphete ring are very similar to those reported for compound **5a** (Scheme 1).[31,38]



Scheme 7. Mechanism of the cyclization of phosphabutadienes formed by the reaction between a phosphinidene and a carbene

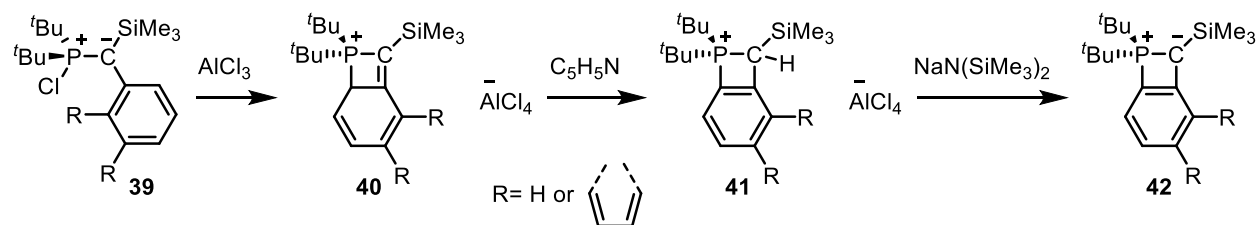
In 1989, Dötz *et al.* synthesized 1,3-oxaphospholes (compound **36**, Scheme 8, equation 1) using chromium-based carbenes **33** and phosphalkyne **34**. [41] The proposed mechanism is presented in Scheme 6 (equation 1). In the case where the alkene group carried by the carbene **33** is substituted by methyl groups in *trans* position (Compound **37**), the formation of the 1,2-dihydrophosphete **38** is promoted (equation 2, Scheme 8) during the cyclization reaction involving the intermediate **35**.



Scheme 8. 1,2-dihydrophosphete derivative obtained as a by-product from the synthesis of 1,3-oxaphospholes.

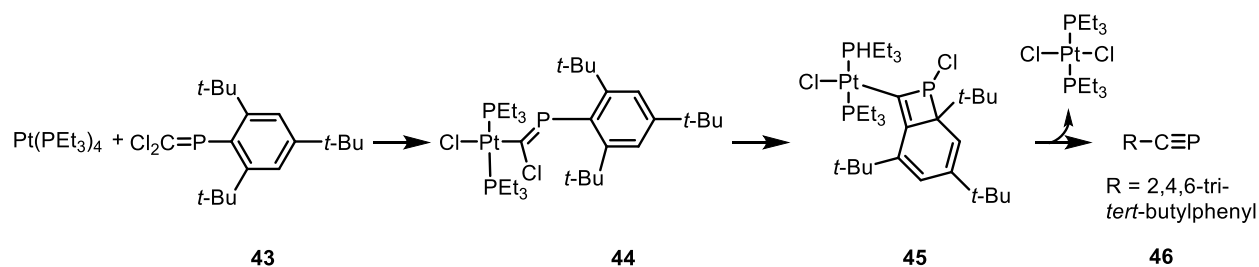
In 1993, Grützmacher *et al.* observed the formation of 1,2-dihydrophosphetium salts during their work on the polarization of multiple bonds by silylated substituents.[42]. In compound **39**

(Scheme 9), the phosphorus-carbon double bond carries a trimethylsilyl group at the carbon which increases the charge separation between the phosphorus and carbon atoms generating a strong ylide character. These halogenated ylides **39** react almost quantitatively with AlCl_3 to form a bond between the phosphorus and the benzene ring (Compound **40**, Scheme 9), which is promoted despite the loss of aromaticity of the benzene ring. The aromaticity is restored by treatment with a tertiary amine base like pyridine (compound **41**, Scheme 9). In the presence of a strong base such as sodium bis(trimethylsilyl)amide, the cyclic phosphonium salt **41** is deprotonated to give a neutral λ^5 -phosphete **42**. The latter presents a four-membered ring including a phosphorus atom with a highly polarized $\text{P}=\text{C}$ double bond fused with an aromatic ring. Additional mechanistic studies on the same family of compounds were later performed by the same group.[43]



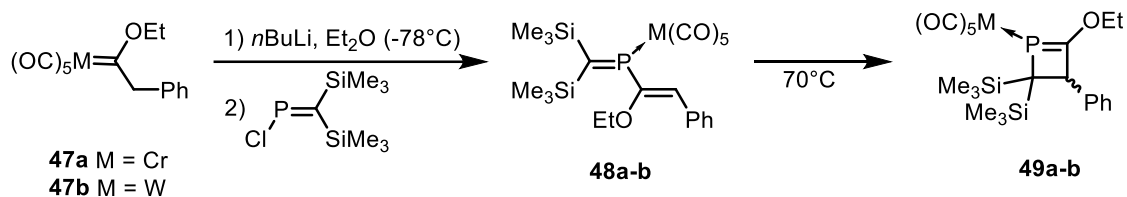
Scheme 9. Intramolecular cyclization arising from the polarization of $\text{P}=\text{C}$ bonds.

The same year, Angelici *et al.* sought to access $\text{R}-\text{C}\equiv\text{P}$ phosphalkynes, such as compound **46** (Scheme 10), from phosphalkene **43**. [44] The mechanism of this reaction has been investigated and Angelici *et al.* showed that during the course of the reaction a 1,2-dihydrophosphete (**45**) is formed. The intermediate **45**, containing a 1,2-dihydrophosphete unit, is more stable than the previous compound **44** despite the loss of aromaticity of the supermesityl group. **45** was isolated and characterized by X-ray diffraction. However, its evolution towards compound **46** occurs spontaneously in dichloromethane, and 24 hours in hexane or benzene.



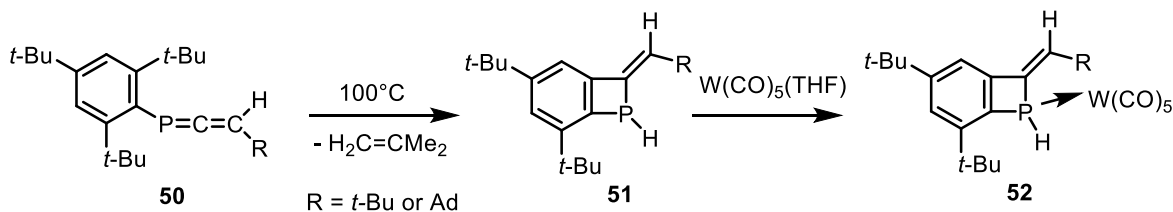
Scheme 10. Synthesis of a $\text{R}-\text{C}\equiv\text{P}$ compound using a stable 1,2-dihydrophosphete intermediate.

In 1997, Streubel *et al.* studied the stereoselective synthesis and isomerization of η^1 -2-phosphabutadiene complexes to η^1 -2,3-dihydrophosphete complexes (Scheme 11).[45] The reaction of chromium or tungsten carbene complexes **47** (Scheme 11) with [bis(trimethylsilyl)methylene]chlorophosphane leads to two phosphabutadiene metal complexes **48** which are isolated as yellow solids in moderate to good yields. These complexes (**48**) cyclize, at 70°C, to give the novel 2,3-dihydrophosphetes **49**. At the time, the 2,3-dihydrophosphete ring was only known as a subunit of 2-Dewar-phosphinines.[46]



Scheme 11. Cyclization of a 2-phosphabutadiene to obtain 3,4-dihydrophosphete.

In 2020, Uhl *et al.* studied the chemistry of phosphallenes **50** (Scheme 12).[47] They showed that phosphallenes **50** undergo a thermally induced rearrangement (toluene, 110°C) with C-H activation and isobutene elimination affording bicycles **51** in which a four-membered PC₃ heterocycle is annulated to a benzene ring. The *t*Bu group is the source of the H atom attached to phosphorus and of isobutene as a neutral leaving molecule. Compounds **51** would slowly decompose during synthesis and workup and could not be isolated in a pure form. For further characterization, Uhl *et al.* generated the compound **51** *in situ* and treated it with (OC)₅W(THF) in THF at 0 °C to yield complex **52** in about 60% yield.

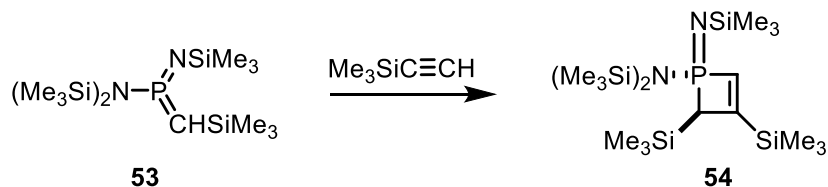


Scheme 12. 1,2-dihydrophosphetes obtained from phosphallenes

2.3. *via* [2+2] cycloaddition reactions

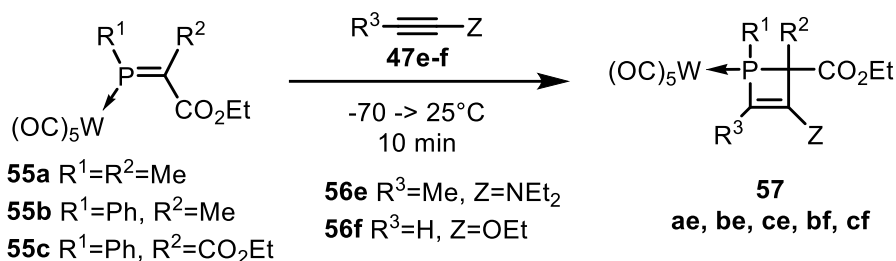
As mentioned above, Neilson *et al.* studied the formation of phosphabutadienes and their reactivity.[36] They were able to obtain 1,2-dihydrophosphetes (compounds **13** and **15**, Scheme 5) by cyclization reactions on phosphabutadienes. Furthermore, the treatment of imino(methylene)phosphorane **53** with trimethylsilylacetylene gave 1,2-dihydrophosphete **54**

(Scheme 13). This compound is a structural isomer of compound **13** in which the Me₃Si and H substituents on the C=C double bond are on opposite positions relative to **13**.



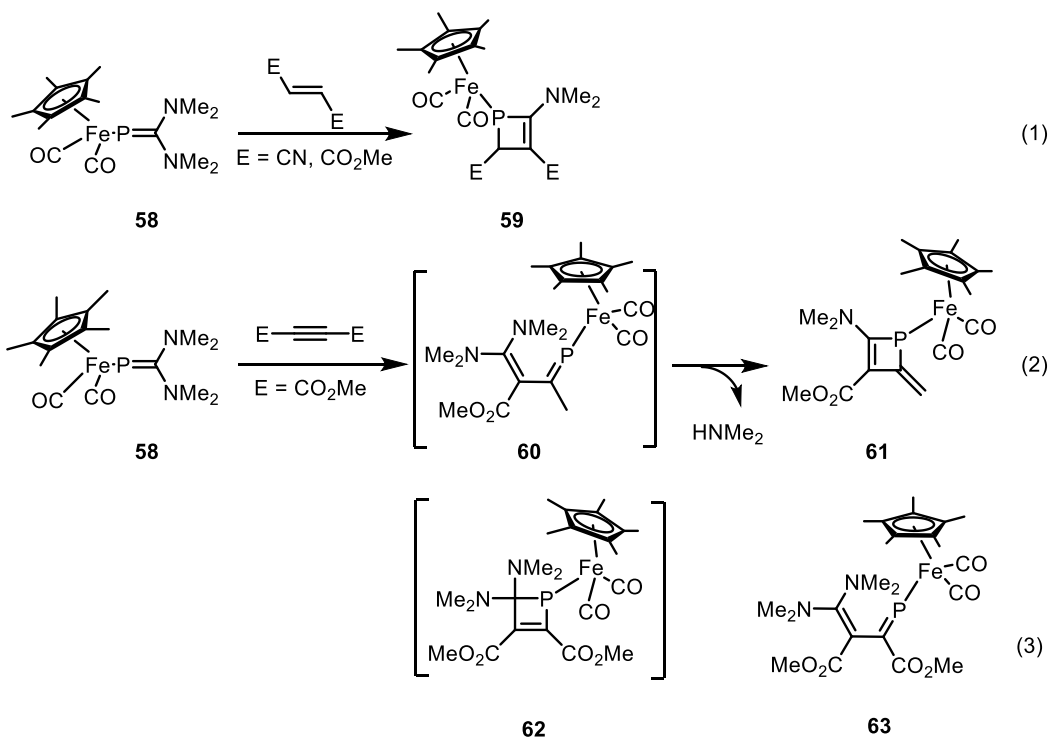
Scheme 13. 1,2-dihydrophosphetes synthesized via a [2+2] cycloaddition reaction

After studying the formation of phosphabutadienes and phosphalkenes, Mathey *et al.* investigated their reactivity. They used them in [2+2] cycloaddition reactions in the presence of electron-poor or electron-rich alkenes and alkynes.[48] For example, tungsten pentacarbonyl phosphalkene complexes, substituted on carbon atom by ethoxycarbonyl groups (Compounds **55**, Scheme 14), reacts rapidly with N,N-diethyl-1-propyn-1-amine **56e** or ethoxyacetylene **56f** to form 1,2-dihydrophosphetes **57**, resulting from [2+2] cycloaddition.



Scheme 14. 1,2-dihydrophosphetes synthesized via a [2+2] cycloaddition reaction involving phosphalkenes and alkynes

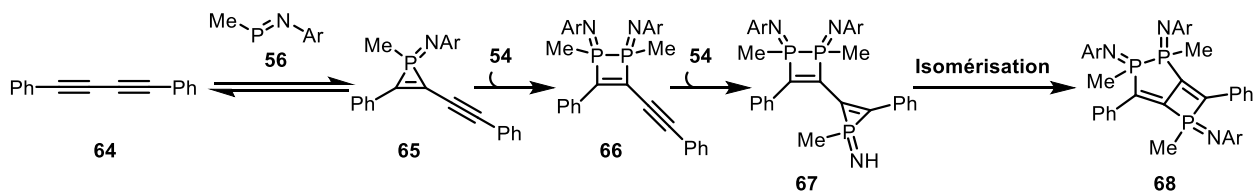
In 1994, Boese *et al.* studied the versatile reactivity of metallo-phosphalkenes since they possess, at the same time, electrophilic and nucleophilic centers.[49] The metallo-phosphalkene ($\eta^5\text{-C}_5\text{Me}_5$)(CO)₂Fe-P=C(NR₂)₂ **58** (Scheme 15) is synthesized by the reaction between ($\eta^5\text{-C}_5\text{Me}_5$)(CO)₂FeBr complex with Me₃Si-P=C(NR₂)₂. The [2+2] cycloaddition reaction involving these metallo-phosphalkenes **58** and dimethyl fumarate or fumaronitrile yields 1-metallo-1,2-dihydrophosphetes **59** (equation 1, Scheme 15). The monitoring of the reaction medium showed no trace of intermediates in the ³¹P NMR spectrum and the reaction is accompanied by spontaneous degassing indicating that the cycloaddition reaction is followed by a rapid 1,2-elimination of dimethylamine. The reaction between a metallo-phosphalkenes **58** and alkyne like methyl but-2-ynoate yielded 1,2-dihydrophosphete **61** as the final compound (equation 2, Scheme 15). However, when dimethyl but-2-yndioate is used as a reactant, 1,2-dihydrophosphete **62** is yielded transiently, no elimination occurs, and the four-membered ring opened to give a phosphabutadiene **63** (equation 3, Scheme 15).



Scheme 15. 1,2-dihydrophosphetes synthesized *via* a [2+2] cycloaddition reaction involving metallo-phosphaalkenes

2.4. *via* intramolecular rearrangement.

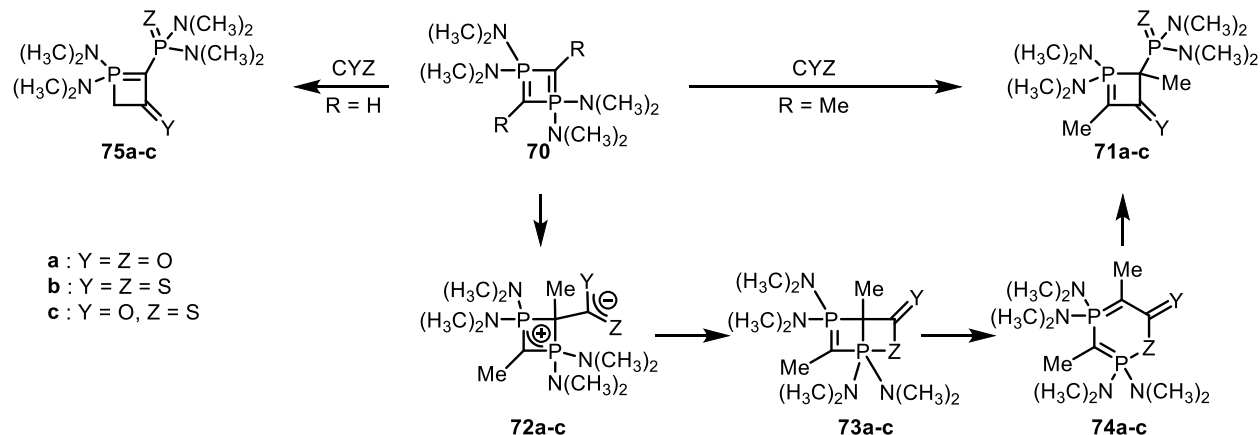
In 1994, Niecke *et al.* developed the chemistry of phosphirenes.[50] They observed that the successive addition of three iminophosphoranes (Compound **65**, Scheme 16) to diyne **64** led to the formation of compound **69** incorporating a 1,2-dihydrophosphete unit. The addition of the first equivalent of **65** to the diyne **64** allowed to obtain the phosphirene **66** which is transformed into diphosphetene **67** in the presence of a second equivalent of **65**. After the addition of the third equivalent of iminophosphorane **65** to the second triple bond, compound **68** underwent an isomerization and gave the bicycle **69** incorporating a 1,2-dihydrophosphete.



Scheme 16. Synthesis of a bicycle incorporating a 1,2-dihydrophosphetes.

One year later, Fluck *et al.* studied the reactivity of diphosphetes **70** (Scheme 17) with carbon disulfide (CS_2), carbon oxysulphide (COS) or carbon dioxide (CO_2).[51] The diphosphete is added to the carbon of the latter and this addition caused a rearrangement of the cycle to give

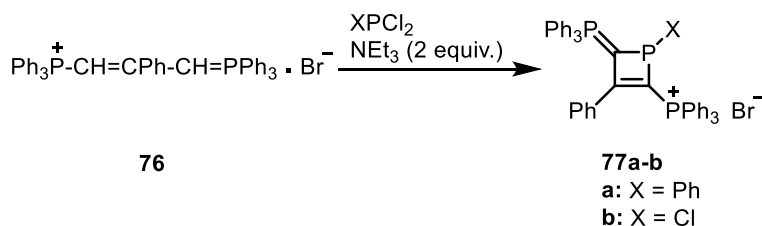
the 3,4-dihydrophosphetes **71** and **75**. If the groups carried by the diphosphete are methyl groups or hydrogen atoms, the same rearrangement takes place, except the unsaturation is not in the same position.



Scheme 17. Synthesis of 3,4-dihydrophosphetes from 1,3-diphosphetes

2.5. *via* addition reaction

In 1996, Schmidpeter *et al.* prepared 2,4-diphosponiodihydrophosphetide cations **77ab** from 1,3-diphosponiopropenide **76** and chlorophosphines (Scheme 18) [52]. This compound, having an unusual dihydrophosphetide scaffold, was only supposed to be a synthetic intermediate, although it appeared to be stable.

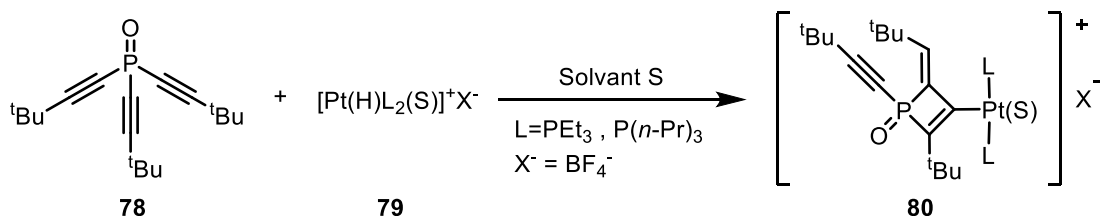


Scheme 18. Propenide to phosphetide cyclization

2.6. *via* organometallic intermediates

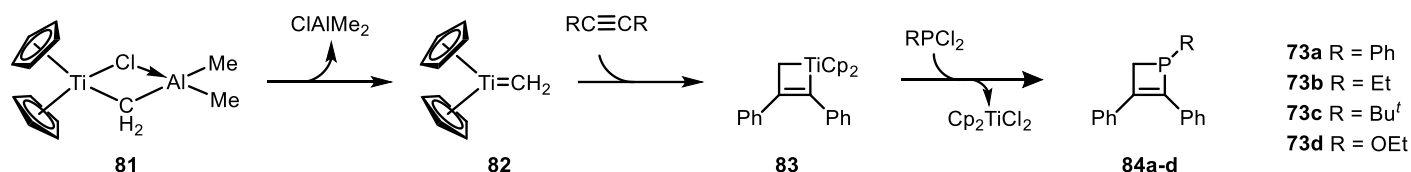
Addition of the platinum-hydride bond of [trans-Pt(H)(PEt₃)₂(THF)] **79** to the triple bond of an alkyne-substituted phosphine oxide **78** lead to an unexpected sequence of addition and insertion reactions leading to platinum complex **80** featuring 2-alkylidene-1,2-dihydro-3-phosphete-P-oxide ligand. (Scheme 19)[53] Such sequence was observed with various

platinum-hydride complexes. Preparing a phosphete « free-ligand » was envisaged as a perspective of this work.



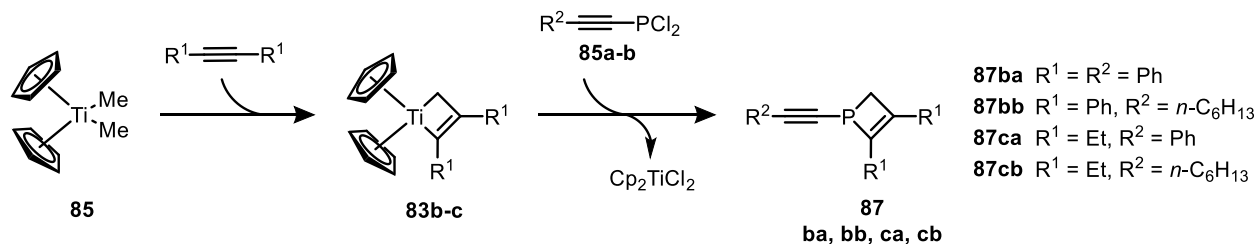
Scheme 19. 1,2-dihydrophosphetes synthesized following Pt-insertion on alkynylphosphine

Doxsee *et al.* developed one of the rare specific synthesis methods toward 1,2-dihydrophosphetes (Scheme 20). [54] This approach involved the use of titanium complexes and was inspired by the work of Tebbe on the reactivity of titanocene and in particular diphenyltitanacyclobutene **82**. [55] When **83** is treated with dichlorophenylphosphine, the dihydrophosphete **84a** is cleanly synthesized. This strategy is compatible with various exocyclic P-R groups (R = -Ph, -Et, -OEt, -^tBu, compounds **84a-d**). The σ^3, λ^3 -P derivatives are remarkably inert toward oxidation. Harlow *et al.* further showed that this methodology can be extended to heavier group 15 analogues such as arsacyclobutenes. [56]



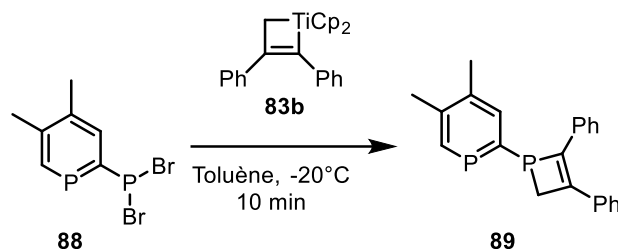
Scheme 20. Synthesis of 1,2-dihydrophosphetes from titanocyclobutene

After Petasis' observation that dimethyltitanocene Cp_2TiMe_2 **85** (Scheme 21) was as efficient as Tebbe reagent for the preparation of titanacyclobutene, [57] Mathey *et al.* used this reagent for the preparation of 1-alkynyl-1,2-dihydrophosphetes **87** (Scheme 21). [58] Compound **87** appeared as versatile intermediates for the preparation of phosphinines *via* an original 4π -cycloreversion- 6π -electrocyclization mechanism (*vide infra*).



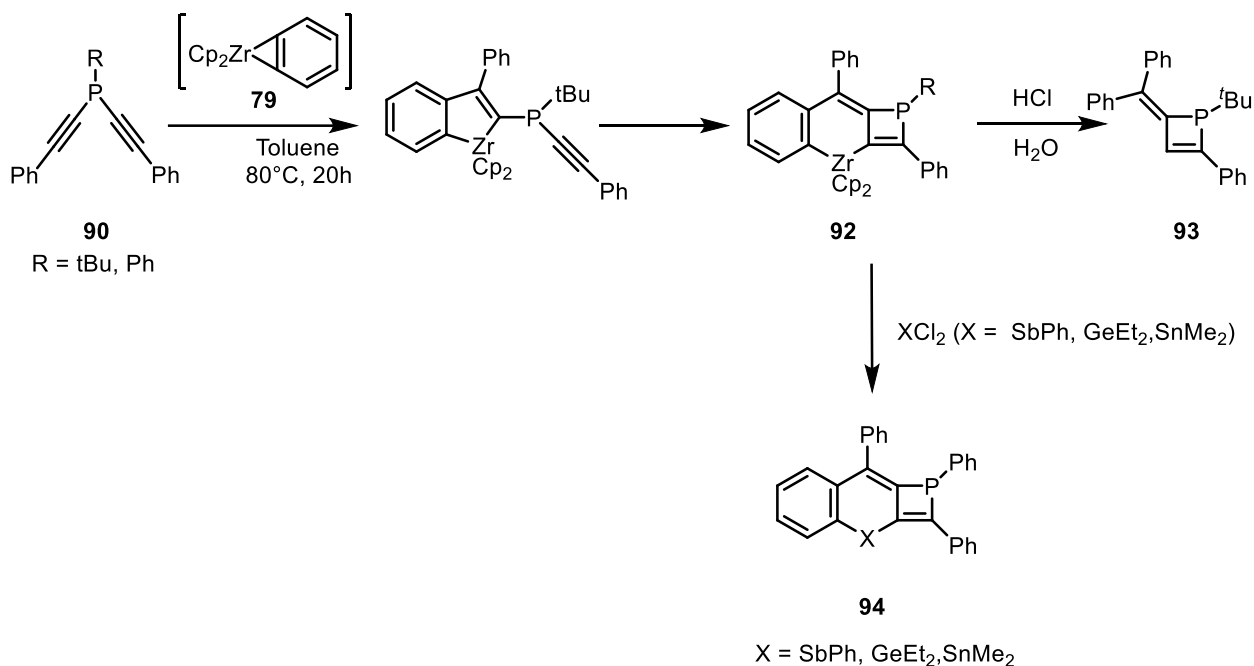
Scheme 21. Synthesis of 1,2-dihydrophosphete 88 from Cp_2TiMe_2

In 1996, Mathey *et al.* again used titanocyclobutene **83b** with 2-(dibromophosphino)-4,5-dimethylphosphinine **88** to prepare a novel bidentate ligand **89** based on phosphinine and dihydrophosphete scaffolds (Scheme 22).[59] This synthesis belongs to a more general strategy of preparation of new classes of bidentate ligands featuring unconventional P-heterocycles to further systematically investigate their coordination chemistry.



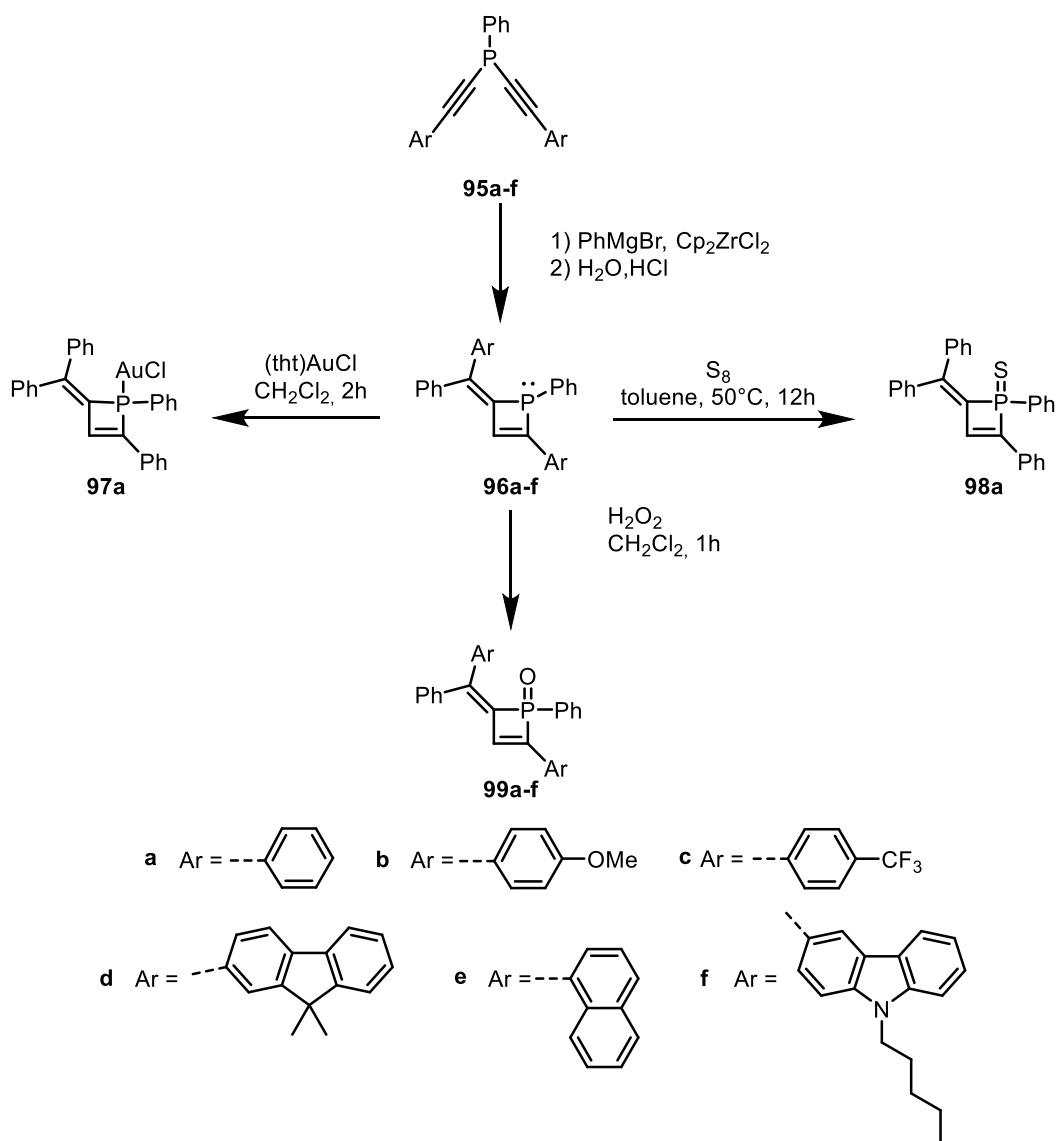
Scheme 22. Synthesis of bidentate ligands featuring dihydrophosphete scaffold

Majoral *et al.* reported a novel intramolecular coupling of a dialkynylphosphane (tBuP(C=C-Ph) **90** and zirconocene-benzyne, which provided unusual 1,2-dihydrophosphete-zirconium complexes **92** (Scheme 23).[60] This organometallic tricycle could be fully characterized including X-ray diffraction. Upon acidic treatment, **92** can be converted into π -extended dihydrophosphete **93** or, upon quenching with various chloro-derivatives of heavier main group elements (XCl₂ with X = SbPh, GeEt₂, SnMe₂), the corresponding tricycles **94** could be prepared (Scheme 23).[61] This strategy thus allows the straightforward preparation of a variety of main group elements containing polyunsaturated systems (either mono- or tricyclic heterocycles) featuring a dihydrophosphete scaffold.



Scheme 23. Synthesis of 1,2-dihydrophosphete from zirconocene

More recently, we exploited the high synthetic versatility of the latter strategy to prepare various π -extended dihydrophosphetes **96-99a-f** (Scheme 24).[62] Indeed different electron-rich and electron-poor aromatic group could be introduced on the dialkynylphosphine reactants **95a-f**, as well as different substituents on the P-atom thus allowing the first study of the optical and redox properties of these unusual π -conjugated P-heterocycles. All these compounds display blue to green emission. While the substituent on the P-atom as a negligible effect on the absorption/emission wavelengths, the introduction of electron-rich substituents on the π -backbone redshifts the absorption/emission. The bulkiness of the phosphine oxide fragment prevents solid-state aggregation and all derivatives thus retain their luminescence in the solid-state. Associated with good thermal stability and suitable redox properties, compounds **99d-f** were introduced in a multilayer OLED device displaying blue to green emission. This is to our knowledge the first example of the insertion of 4-membered P-rings into light-emitting devices.



Scheme 24. Synthesis of π -extended dihydrophosphete.

3. Reactivity of phosphetenes

Phosphetenes possess a rich reactivity linked to their chemical structure. Indeed, they display a sigma donor P-ligands and a strained 4-membered ring that can be subject to either a ring-opening or a ring-expansion. (Figure 3).

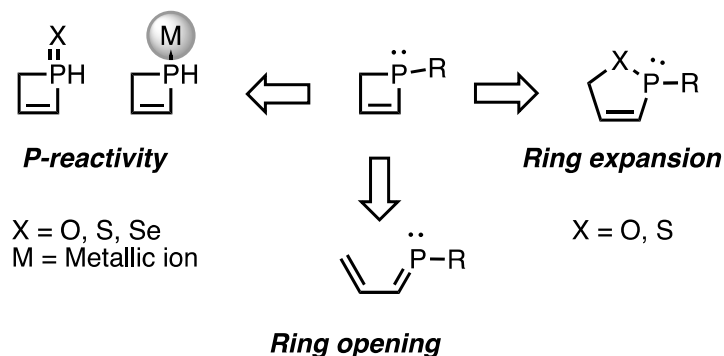


Figure 3. Schematic phosphetene reactivity

3.1. P-reactivity

The P-atom of phosphetene displays the classical reactivity of σ^3, λ^3 -phosphanes regarding oxidation, nucleophilicity (for example see **5a**, **11**, **32**, **98-99**) or coordination to metallic ions as it behaves as a classical two-electron P-donor (Figure 4). Hence, in the example previously described, numerous phosphetenes were obtained as coordination complexes (complexes of Cr, W, Fe, Au).

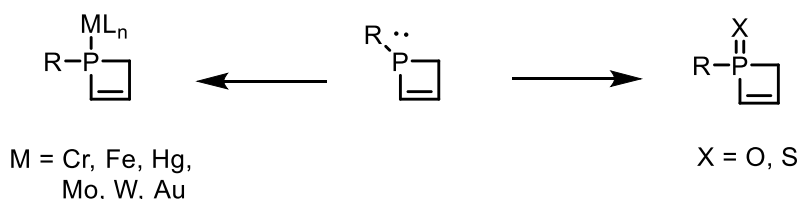
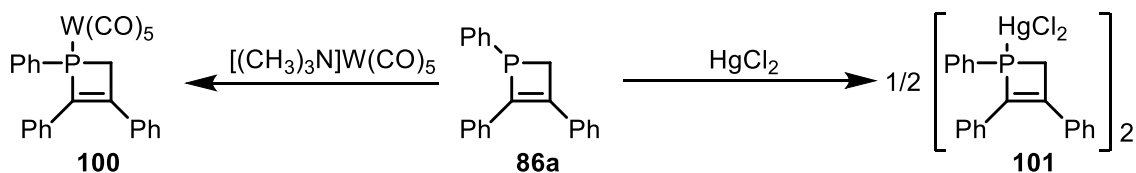


Figure 4. Chemical modification of the P-atom

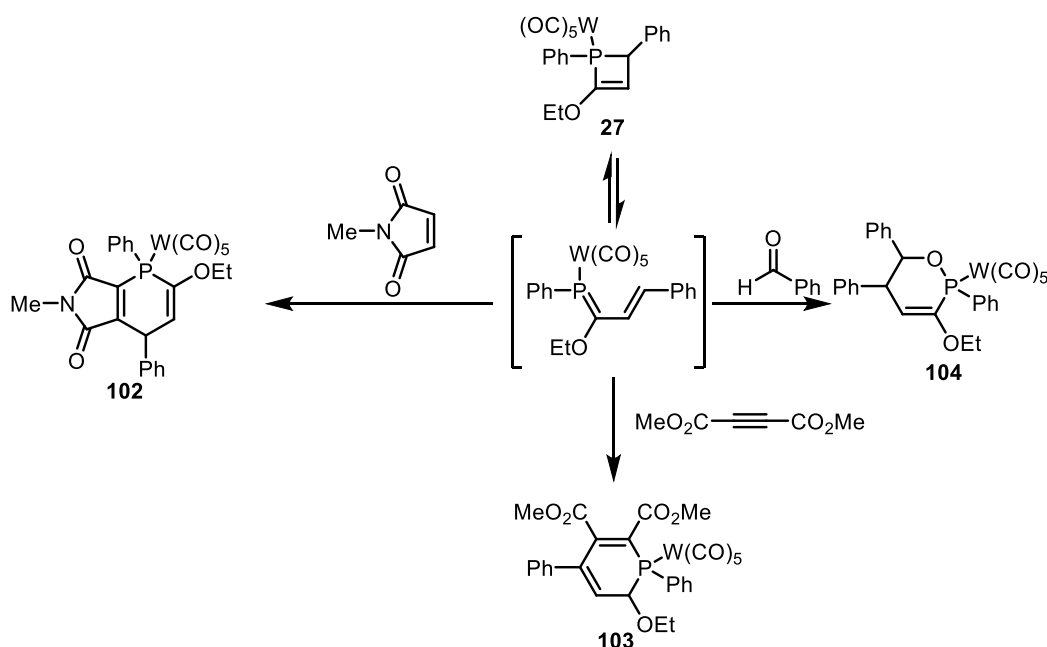
In particular, Doxsee *et al.* studied the effect of metal coordination on **84a** with W(0) (**100**) or Hg(II) (**101**) precursors (Scheme 25) on the structural properties of the phosphetene ligand, having in mind the possibility to favouring a potential ring-opening reaction.[63] Structural changes (bond lengths and angles) associated with coordination are consistent with an increased bonding contribution from the s orbital of the P-atom. The authors concluded that coordination does not lead to any significant alteration of the geometry of the 4-membered ring toward the corresponding ring-opened form (1-phosphabutadiene).



Scheme 25. Coordination chemistry of 75a.

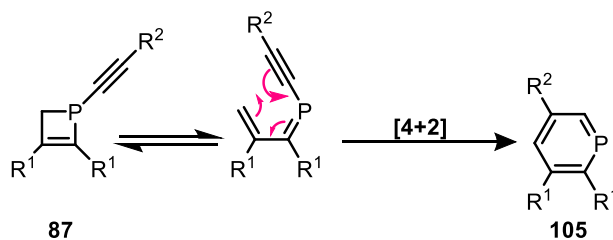
3.2. Ring-opening followed by cycloaddition

Ring-opening by retro-electrocyclisation is a classical reactivity of unsaturated 4-membered rings and usually lead to butadiene derivatives. In 1988, Mathey *et al.* exploited this analogy by using 1,2-dihydrophosphetes as masked 1-phosphabutadienes (Scheme 26).[64] When heated at high temperature, W-complex **27** reacts with dienophiles such as maleimide, dimethylacetylenedicarboxylate, or benzaldehyde, to yield the respective P-heterocycles **102-104** (Scheme 26) through [4+2] cycloaddition. Furthermore, they also showed that the substitution pattern on the P-ring alters the reactivity as no cycloaddition take place when the 1,2-dihydrophosphete is substituted by Et-groups in the 3 and 4 positions. [65]



Scheme 26. 1,2-dihydrophosphete as masked phosphabutadiene

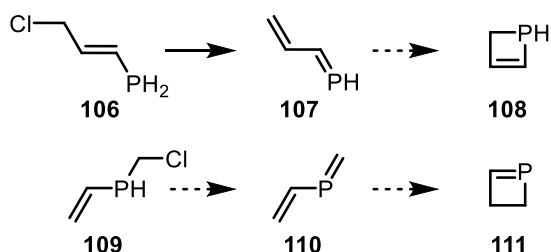
The ring opening of 1-alkynyl-1,2-dihydrophosphete **87** followed by cycloaddition was further used by these authors to prepare phosphinines **105** (Scheme 27).[58]



Scheme 27. 1,2-dihydrophosphete as a masked phosphabutadiene to prepare phosphinines

In 1992, Bachrach and Liu carried out *ab initio* calculations to model the ring opening of 1,2-dihydrophosphetes. In analogy with the ring opening of cyclobutadiene, the orbital symmetry imposes a conrotatory thermal opening. Depending on the direction of rotation of the orbitals, the opening of the 1,2-dihydrophosphete can give two isomers. Their study showed that the opening of the 1,2-dihydrophosphete is thermally neutral and that the 3,4-dihydrophosphete is slightly endothermic. [66]

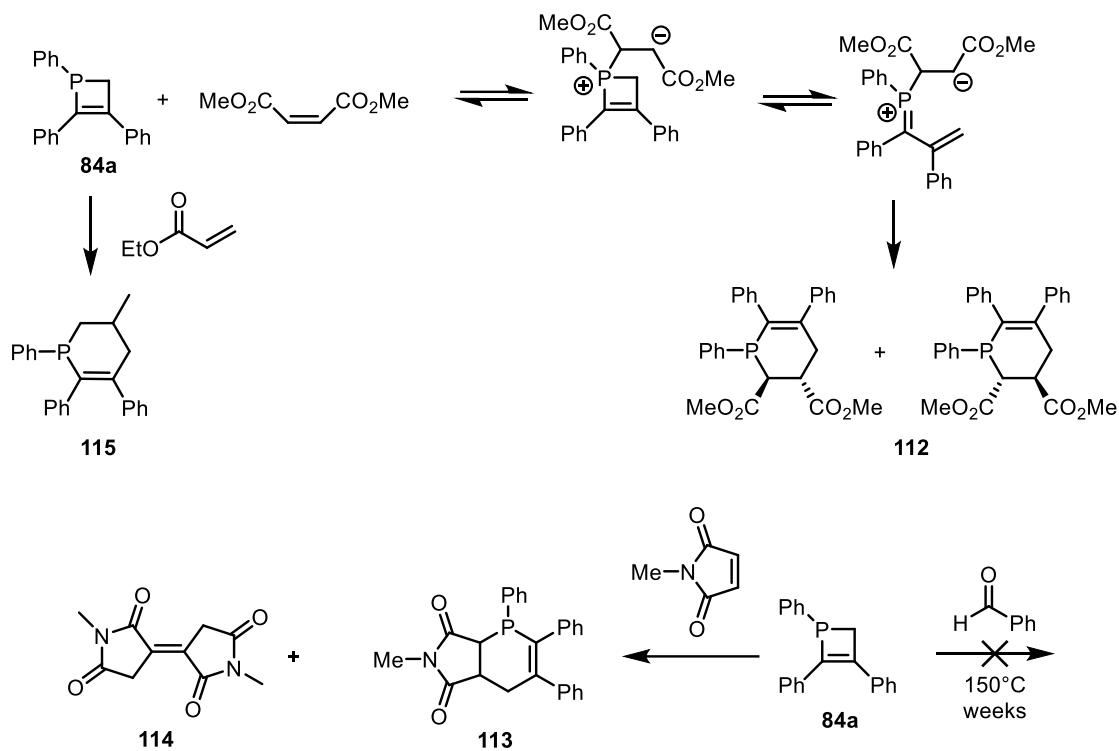
Following these studies, Denis *et al.* worked on the synthesis of phosphabutadienes and the possibility to close and form the four-membered cycle.[67] With the aim of obtaining 1,2-dihydrophosphete **108** and 3,4-dihydrophosphete **111** (Scheme 28), they synthesized products **106** and **109** and observed the transitory formation of phosphalkenes **107** and **110**. They observed the formation of derivative **107**, which could be trapped and analysed, but neither derivative **110** nor the dihydrophosphetes **108** and **111** were observed (Scheme 28). The fact that, despite the formation of phosphabutadiene **107**, no trace of the cyclized form **108** could be detected contradicts the mechanism envisaged by Bachrach and Liu.



Scheme 28. Synthesis of phosphabutadienes as intermediates to phosphetene synthesis

A similar strategy was explored by Doxsee *et al.* using a σ^3, λ^3 -P phosphetene: 3,4-triphenyl-1,2-dihydrophosphete **84a** (Scheme 29).[68,69] Contrary to Mathey's observations on tungsten coordinated 1,2-dihydrophosphetes, which undergo electrocyclic ring opening followed by [4+2] cycloaddition, the 1,3,4-triphenyl-1,2-dihydrophosphete reactivity is driven by its nucleophilicity. For example, low yields of cycloadducts are usually obtained and the reaction involved seems to be a Michael addition, as indicated by the loss of stereochemistry in the reaction of dimethyl maleate (**112**) and by the competitive formation of a phosphorus-free dimer **114** in the reaction with N-methylmaleimide (Scheme 29). This hypothesis seems to be confirmed by the reaction with ethylacrylate forming compound **115**. Such modification of reactivity with dienophiles has also been observed between coordinated and non-coordinated phospholes.[70] On this particular scaffold **84a**, Doxsee *et al.* further observed that nucleophilicity still drives the reactivity even when coordinated to metallic centers.[71] Compared to the results obtained by Mathey *et*

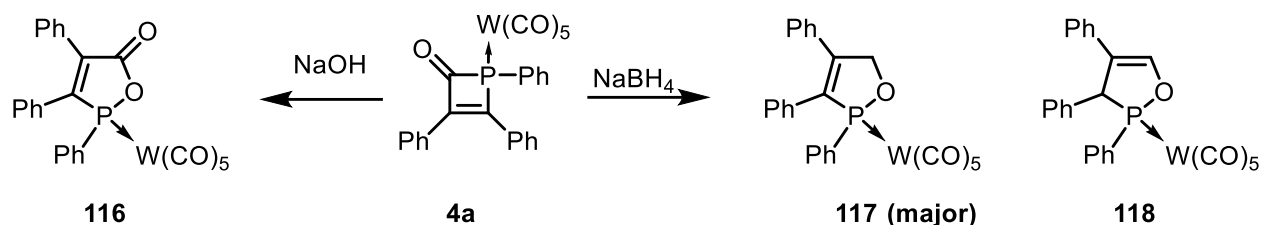
al., these results highlight the importance of the substitution pattern on the 4-membered P-ring in order to favour the ring opening.



Scheme 29. Reactivity of 1,3,4-triphenyl-1,2-dihydrophosphete with various dienophiles

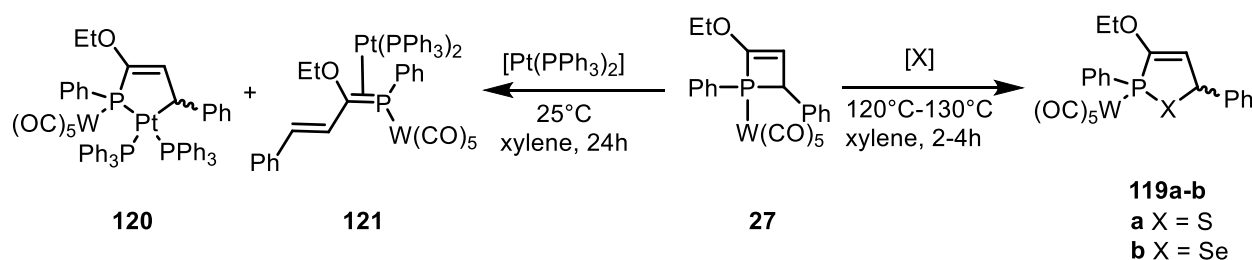
3.3. Ring expansion

The insertion of an atom in the scaffold of a 4-membered ring allows releasing of the ring strain. Such reactivity was studied by Mathey *et al.* on tungsten complexes of 2-oxo-1,2-dihydrophosphete **4a** (Scheme 30).[65] The hydrolysis in basic media of **4a** proceeds in two steps with the formation of the corresponding carboxylic acid which readily oxidizes to give 5-membered P-ring **116**. Upon reduction with NaBH₄, the alkoxide formed *in situ* further isomerizes to form two oxaphospholene complexes **117** and **118**. When the reduction is performed with LiAlH₄, the reaction stops after the reduction of the carbonyl.



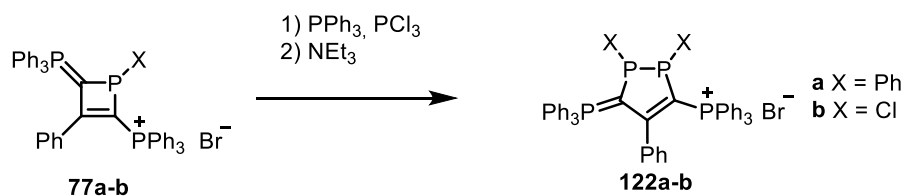
Scheme 30. Oxygen insertion into the phosphetene backbone

A chalcogen insertion (S and Se) within the P-C₂ bond (**119a-b**) was further demonstrated by the same team using W-complex **27**.^[72] (Scheme 31). The insertion of Pt into the P-C bond was further accomplished (**120**) however, the cyclic derivative is only a minor product and the main product is the phosphabutadiene **121**.



Scheme 31. Insertion of chalcogen or Pt into the framework of 18.

As previously discussed, Schmidpeter *et al.* prepared 2,4-diphosponio-dihydrophosphetide cations **77ab** (*vide supra*).^[52] Using the same strategy with one more equivalent of dichlorophosphine, triethylamine and triphenylphosphine, they observed a further ring expansion that yields 3,5-diphosponiodihydro-1,2-diphospholide cations **122ab** (Scheme 32). Such an unconventional conjugated platform allowed the author to study the conjugation within these charged P-heterocycles.



Scheme 32. Phosphetide to phospholide ring expansion

These examples show that phosphetenes display simultaneously the typical reactivity of phosphanes, and of 4-membered rings. This versatility allows a great diversification of the phosphetene family. However, the scope of these reactions remains limited by the synthetic procedure allowing for easy and straightforward preparation of phosphetenes.

4. Conclusion

The chemistry of phosphetenes has really only come to the fore following the pioneering work of Mathey *et al.* and Doxsee *et al.* In most of the earliest reports, phosphetes were obtained as secondary products. They were either by-products, reaction intermediates, or unexpected products due to a particular reactivity of the starting materials. Later, Doxsee *et al.* and Majoral *et al.* developed organometallic routes allowing a direct synthesis of the targeted phosphetenes. The chemistry of phosphetenes is still in its infancy. The systematic studies carried out on these compounds showed that they are thermally and chemically stable. Furthermore, it was shown that they share both specific reactivities of unsaturated strained cycles and phosphanes. Chemical modification on the P-atom, ring-opening or ring-expansion can be performed on these structures giving access to a large number of P-based compounds. The possibility of using phosphetenes as materials for applications in the field of OLEDs has been demonstrated. However, considering the richness and diversity of phosphorus chemistry, their true potential has not yet been fully exploited. It is very likely that new developments in this area will occur and will take full advantage of the specific properties of these organophosphorus derivatives.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

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