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Recent developments in the chemistry of three-coordinate pentavalent phosphorus compounds ($\sigma^3\lambda^5$-phosphoranes)

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Contents

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Abstract

Three-coordinate pentavalent phosphorus compounds can no longer be considered as 'exotic' species in phosphorus chemistry. Since their discovery in 1974 hundreds of stable $\sigma^3\lambda^5$-phosphoranes have been synthesized and thoroughly investigated. Early work concentrated on preparation, stability and structure of various structural types of monomeric X–P(=Y)=Z compounds. More recently the chemistry of functionalized $\sigma^3\lambda^5$-phosphoranes has been investigated, resulting both in valuable new reactions and synthetically useful, highly reactive polyfunctional $\sigma^3\lambda^5$-P reagents.

Keywords: Three-coordinate pentavalent phosphorus compounds; Phosphoranes

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1. Introduction

Two decades ago Niecke and Flick [1] and Scherer and Kuhn [2] discovered that the reaction of aminoiminophosphanes, $Tms_2N–P=NTms$ (Tms = trimethylsilyl) with $TmsN_3$ led to the stable compound $Tms_2N–P(=NTms)_2$. Since then, the chemistry of three-coordinate phosphorus(V) derivatives has been a fashionable area of research and several reviews covering different aspects of the subject have been published [3–16]. Their usefulness, however, is somewhat limited owing to the fact that a great number of the synthetically interesting reactions were developed after their publication. In the present report emphasis will be put upon rapid and continuing recent developments in the field of synthesis and reactions of the above compounds. Although for the sake of completeness all major achievements on the chemistry of $\sigma^3\lambda^5$-phosphoranes since the synthesis of the first stable compound are tabulated here, no attempt has been made to discuss the literature which was documented by the earlier reviews. For a more thorough treatment of materials published prior to 1989 readers are referred to the monographs in Refs. [8–16], of which the latter is the most recent and wide ranging of the reviews available over the whole field of low-coordinate phosphorus compounds.

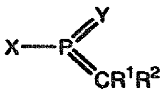
The survey covers all types of isolable compound having a formal structure X–P(=Y)=Z, whatever the nature of atoms bonded to the three-coordinate pentavalent phosphorus. However, the compounds of the general formula $X–P(ML_n)=Y$, (M = metal, L = ligand), which can be regarded as containing a formal PM double bond, are excluded from the scope of this article. Since the comprehensive review on the chemistry of transient metaphosphates, metaphosphonates and related $\sigma^3\lambda^5$-oxophosphoranes was recently published [17] (for leading references see also Ref. [18]) these species will not be discussed here. It is also beyond the scope of this survey to discuss bonding and spectroscopic properties of $\sigma^3\lambda^5$-phosphoranes, inasmuch as very authoritative reviews on the topics are available [15,16].

In addition to the above, the following abbreviations are used, beside the well-known abbreviations: Ar* (2,4,6-tri-*tert*-butyl-phenyl), DBU (1,8-diazabicyclo [5.4.0]undec-7-ene), Cp (cyclopentadienyl), Cp* (pentamethylcyclopentadienyl), Cy (cyclohexyl), Me (methyl), Mes (mesityl), Tmp (2,2,6,6-tetramethylpiperidino).

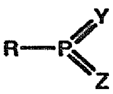
Literature coverage for this review extends up to the middle of 1995.

2. Methods of preparation

All so far known stable $\sigma^3\lambda^5$-phosphoranes may conveniently be assigned to one of three classes: three-coordinate phosphorus(V) derivatives containing the P=C multiple bond ($\sigma^3\lambda^5$-methylenephosphoranes) **A**, metaphosphonates (*P*-alkyl- or *P*-aryl-$\sigma^3\lambda^5$-phosphoranes) **B** and metaphosphoric (phosphenic) acid derivatives **C**.



A



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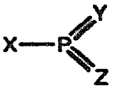


C

R = Alk, Ar ; X, Y, Z = heteroatom groups

A great variety of procedures for the preparation of the above compounds has been described in literature. These can be classified according to a key stage of the synthesis, as depicted in Table 1. However, since not all the reaction mechanisms are clear, in the following discussion the preparative methods will be mainly treated in terms of phosphorus substrates and not in terms of reaction mechanisms.

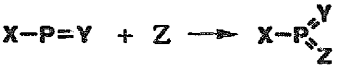
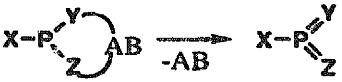
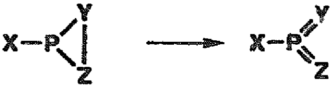
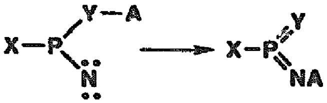
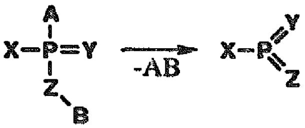
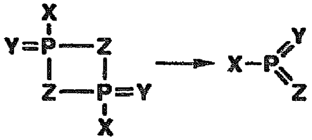
Only kinetically stabilized $\sigma^3\lambda^5$-phosphoranes exist at room temperature. Therefore, the major synthetic approaches to the title compounds involve the use of sterically bulky substituents such as Tms, ^{t}Bu, Tmp, Ar* or Mes. Compilations presented in Section 4 survey the known stable $\sigma^3\lambda^5$-phosphoranes reported to date together with selected NMR data.

2.1. *Syntheses based on two-coordinate phosphorus(III) compounds*

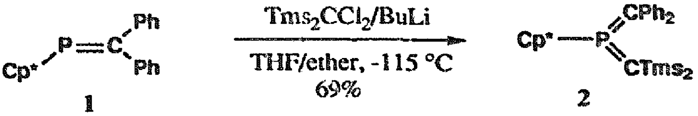
The preparation of X–P(=Y)=Z compounds by 1,1-oxidative addition reactions to dicoordinated phosphorus(III) compounds, X–P=Y, is currently the method of choice in the synthesis of many types of $\sigma^3\lambda^5$-P derivative.

A great number of bis(methylene)phosphoranes, reported in the early literature [9], were prepared by the low temperature reaction of methylenephosphines with silylated carbenoids in situ generated from Tms_2CCl_2 and butyllithium. This synthesis, first reported by Appel et al. [19], has recently been the subject of more detailed

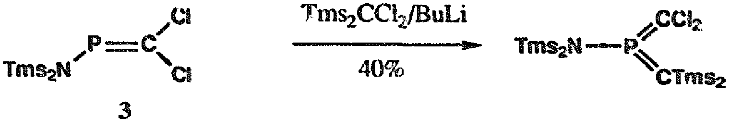
Table 1
Methods of preparation of $\sigma^3\lambda^5$-phosphoranes

Method	Description	General equation
From two-coordinate trivalent phosphorus compounds		
I	Oxidation of two-coordinate phosphorus(III) precursors via transfer of a methylene, an imino group or chalcogen	
From three-coordinate trivalent phosphorus compounds		
II	Oxidation of acyclic phosphorous(III) derivatives	
III	Thermal or photochemical fragmentation of cyclic phosphorus(III) derivatives	
IV	Thermal ring-opening of cyclic systems	
V	Intramolecular rearrangement of phosphinonitrenes	
From four-coordinate pentavalent phosphorus(V) compounds		
VI	1,2-Elimination reactions of four-coordinate phosphorus(V) compounds	
VII	Thermally induced [2+2]-cycloreversion of 1,3,2λ^5,4λ^5-diazadiphosphetidines	
From three-coordinate phosphorus(V) compounds		
VIII	Ligand exchange reactions	
IX	Reactions at the periphery	

investigation [20]. Although the method was found to be particularly effective for the preparation of bis(methylene)phosphoranes starting from the methylenephosphines, X–P=C(Tms)R (R=Tms, Ph or H), it is nor restricted by the silyl-substituted substrates. Thus, the diphenylmethylenephosphorane **2** has been prepared in 69% yield via the reaction of the diphenylmethylenephosphine **1** with $Tms_2C(Cl)Li$ (Eq. (1)). Similarly, the methylenephosphine **3** was converted in the corresponding phosphorane in yield of 40% (Eq. (2)) [20].

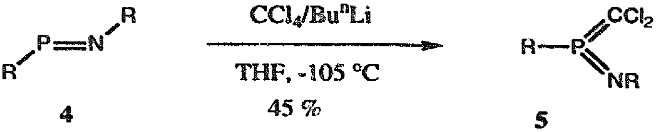


(1)



(2)

Methylene(imino)phosphoranes, X–P(=$CTms_2$)=NR, are normally synthesized by the procedure involving the treatment of a λ^3-iminophosphine with $Tms_2C(Li)Cl$ [21]. More recently, it was shown that the low temperature reaction of iminophosphine **4** bearing 2,4,6-tri-t-butylphenyl substituents with trichloromethyllithium provides a synthetically useful route to the dichloromethylene(imino)-phosphorane **5** (Eq. (3)) [22].



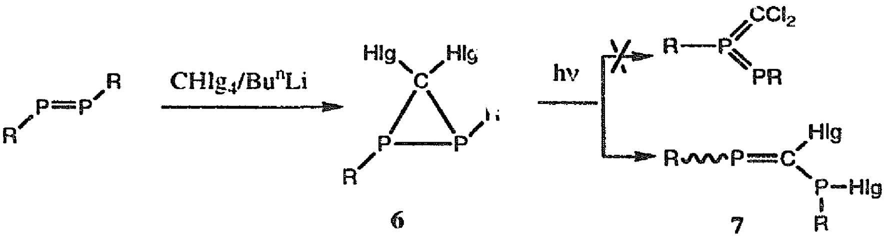
(3)

R = 2,4,6-$Bu^t_3C_6H_2$

In contrast to the iminophosphine **4**, the diphosphenes RP=PR (R=Ar*, Tms_3C) undergo [2+1]-cycloaddition reactions with halogenated carbenoids leading to three-membered heterocycles **6** [23–27]. The structure of the 3,3-dichlorodiphosphirane obtained by reaction of Ar*P=PAr* with the dichlorocarbene generated in situ by the action of butyllithium on tetrachloromethane was confirmed by X-ray diffraction [28]. The photolysis of **6** leads to the functionalized *cis*- and *trans*-1,3-diphosphapropenes **7** as major products via the diphosphiranyl and the diphosphapropenyl radical intermediates (Eq. (4)) [28].

The application of the same strategy to phosphaallenes, and diphosphaallenes invariably led to the three-membered cyclic products [29–31]. A formal [2+1]-cycloaddition was also encountered in the reactions of the cyclopentadienyl-substituted diphosphenes and diazoalkanes [32].

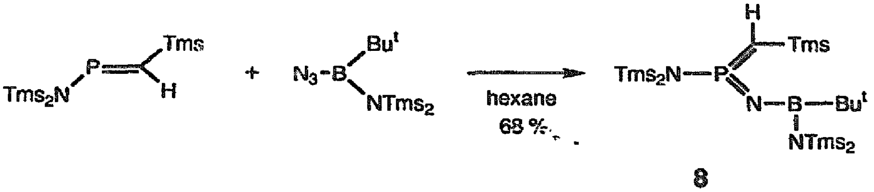
A frequently employed method for preparing stable methylene(imino)phosphoranes consists of the oxidation of phosphaalkene precursors with organic azides [10]. Neilson and coworkers have successfully used this procedure to prepare boryl-functionalized methylene(imino)phosphorane **8** in 68% yield (Eq. (5)) [33]. Oxidation of the 1-phosphadiene **9** with $TmsN_3$ would lead to the compound **10**;



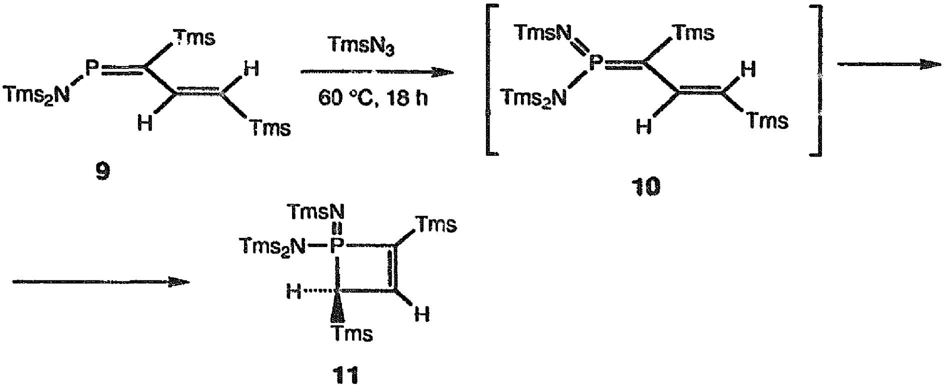
(4)

R = 2,4,6-t-Bu$_3$C$_6$H$_2$, Tms$_3$C
Hlg = Cl, Br

however, under the reaction conditions employed (heating a neat mixture of the diene and azide at 60 °C) the oxidation is accompanied by ring-closure to yield the phosphacyclobutene **11** (Eq. (6)) [34].



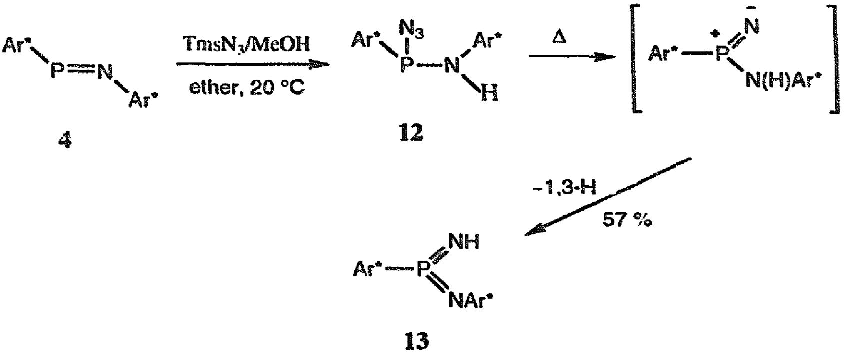
(5)



(6)

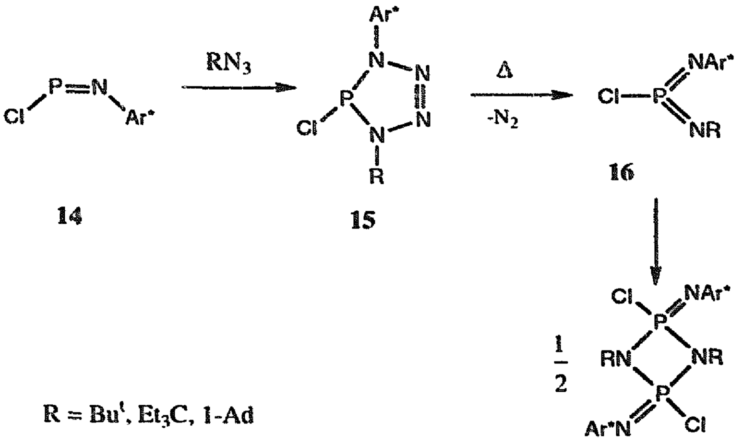
A number of bis(imino)phosphoranes, X–P(=NR^1)=NR^2, have been prepared by interaction of the λ^3-iminophosphanes with organic azides [11]. As a further development of the method, the synthesis of the first NH-functionalized three-coordinate phosphorus(V) derivative has been achieved by reaction of the iminophosphane **4** with TmsN$_3$ in the presence of one equivalent of methanol. The reaction proceeds via 1,2-addition of HN$_3$ to the PN double bond to give the azidophosphine **12**, which decomposes above 40 °C with the elimination of nitrogen. The initially formed phosphinonitrene intermediate is stabilized by a 1,3-H shift to form the bis(imino)phosphorane **13** (Eq. (7)) [35].

An entirely different reaction mechanism than that which operates in the above



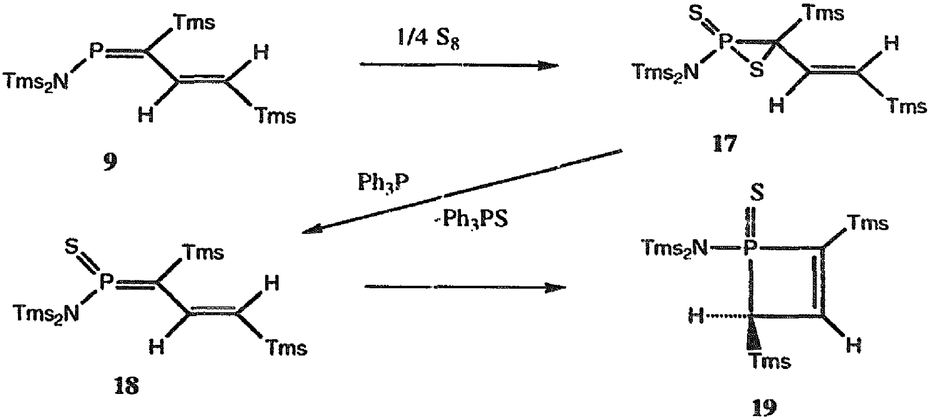
(7)

example was established for the formation of *P*-chlorobis(imino)phosphoranes from chloro(imino)phosphane **14** and alkyl azides. In this case, iminophosphane **14** reacts with azides to give 4,5-dihydro-1*H*-tetrazaphospholes **15** which undergo loss of nitrogen to furnish bis(imino)phosphoranes **16**. As a consequence of the modest bulk of the chlorine atom, the latter dimerize readily at ambient temperature to give the diazadiphosphetidines (Eq. (8)) [36].



(8)

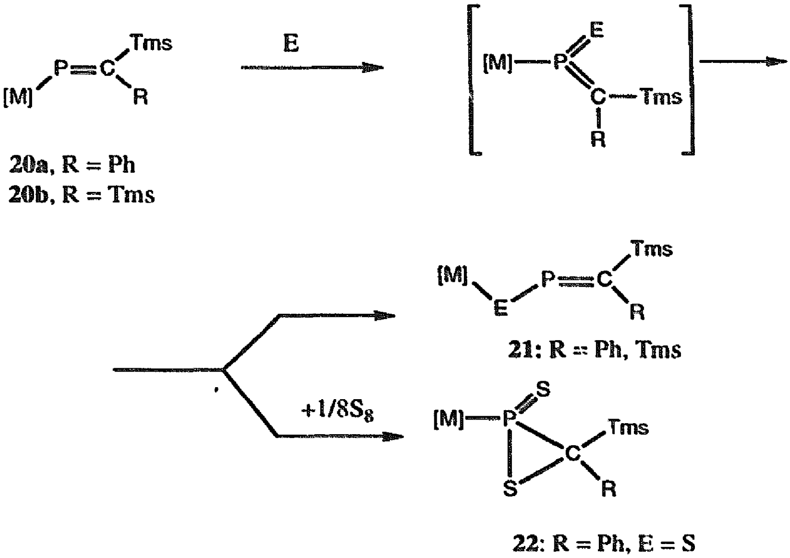
Various types of low-coordinate phosphorus compound more or less easily undergo oxidation reactions with chalcogens to give the corresponding $\sigma^3\lambda^5$-oxo(thioxo-, selenoxo)phosphoranes or the products of their subsequent transformations [10,12,13]. Section 4.3 and Section 4.5Section 4.6Section 4.7 give an overview on the available data of isolable compounds X–P(=O,S,Se)=Y. Recent studies demonstrate that although the method is quite general, it is not without some serious difficulties and limitations. Firstly, the formation of three-membered cyclic products instead of desired $\sigma^3\lambda^5$-phosphoranes is often a competitive low activation energy process. Secondly, since the compounds X–P(=O,S,Se)=Y can act as an ene-component in cycloaddition reactions, they are able to undergo further transformations such as a perchalcogenation and a self-cycloaddition. For example, the oxidation of phosphadiene **9** with elemental sulfur produces the disulfide **17** instead of the expected three-coordinate thioxophosphorane. When the reaction of **17** with Ph_3P in benzene solution was monitored by NMR spectroscopy, the formation of short-lived intermediate **18** was evident (^{31}P NMR: 171.9; ^{13}C NMR: 120.3 (P=C, $^{1}J_{PC}=79.2$ Hz)). Upon solvent removal and distillation, however, the isomeric phosphacyclobutene **19** was isolated (Eq. (9)) [34].



(9)

In the chalcogen oxidation reaction shown in Eq. (10), the initially formed three-coordinate thioxophosphoranes are stabilized via insertion of a chalcogen into an M–P bond to form methylenephosphanylthio- or methylenephosphanylseleno-metal complexes **21**; when methylenephosphanyl complex **20a** was treated with an excess of sulfur the formation of disulfurated derivative **22** has been observed [37].

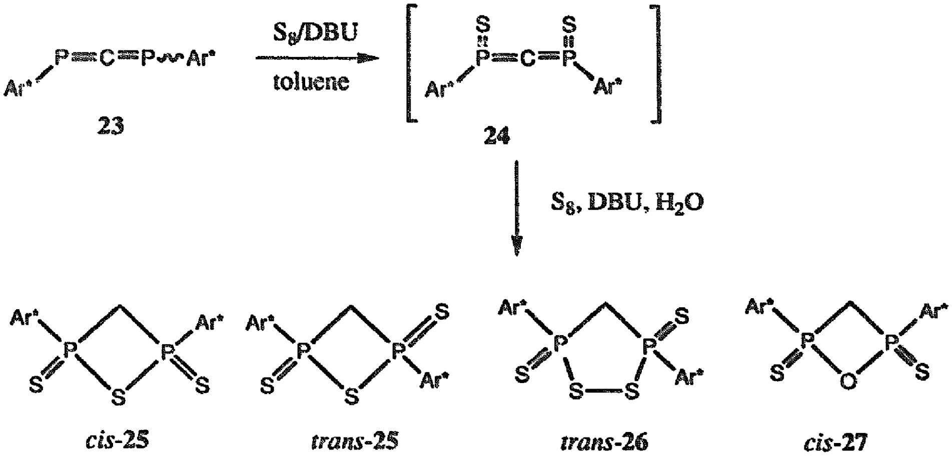
While sulfurization of 1,3-diphosphaallene **23** did not proceed at room temperature



(10)

[M] = $Cp(CO)_3W$, E = S, Se

in toluene, in the presence of DBU and water this compound reacts with elemental sulfur to give the 1,2,4-thiadiphosphetane *cis*-**25** (36% yield) as a major product, together with its trans-isomer (3%), the 1,2,3,5-dithiadiphospholane **26** (12%), and the oxadiphosphetane **27** (13%). An explanation for this result invoked the transient appearance of the highly reactive intermediate, such as **24**, which underwent reactions with water or S_8/DBU to form the above products (Eq. (11)) [38–40].



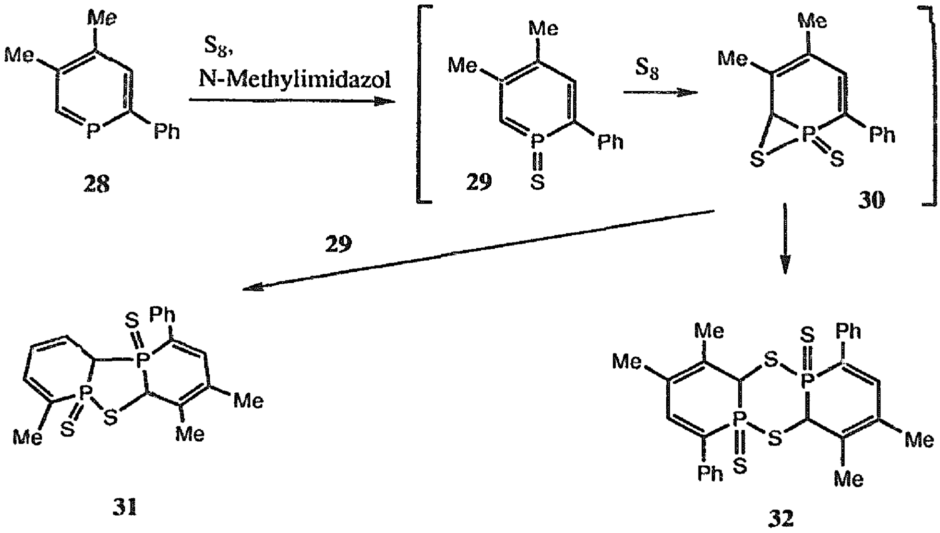
(11)

The reaction of 4,5-dimethyl-2-phenylphosphinine **28** with sulfur in the presence of *N*-methylimidazole as a catalyst first yields a P-sulfide **29** ($\delta\ ^{31}P = 147.5$) in which the aromaticity of the ring appears to have been lost. This monosulfide further reacts with sulfur to give a diphosphinine trisulfide **31** and a diphosphinine tetrasulfide **32**. An additional confirmation of the intermediacy of **29** comes from the trapping reactions with ethanol, 2,3-dimethylbutadiene and dimethyl acetylenedicarboxylate (Eq. (12)) [41].

By analogy to the synthesis of methylene(chalcogeno)phosphoranes, imino(chalcogeno)phosphoranes, may be obtained from λ^3-iminophosphines, X–P=NR, by oxidation reactions. As with other types of $\sigma^3\lambda^5$-phosphoranes, steric protection of the inherently reactive phosphorus–element double bonds is the most important factor determining the stability of the X–P(=O,S,Se)=NR species. Thus, the synthesis of an isolable imino(oxo)phosphorane has been achieved by oxidation of the iminophosphane **4** stabilized by the very bulky tri-t-butylphenyl groups. Treatment of **4** with an ozone–oxygen mixture afforded the compound **33** in 87% yield (Eq. (13)) [35].

A series of stable *N*-(2,4,6-tri-t-butylphenyl)iminophosphoranes **35a–c** has been prepared by the oxidation of λ^3-iminophosphines **34a–c** with sulfur and selenium (Eq. (14)). Methylene(thioxo- or selenoxo)phosphoranes **35d** easily undergo a self-cycloaddition at a P=S(Se) double bond to form oligomeric products **36** [42].
R = Ph (**a**), Mes (**b**), 2,4,6-^{i}Pr$_3$C$_6$H$_2$ (**c**), ^{t}Bu (**d**)

The conjugation effect was shown to be also effective in stabilizing imino(thioxo- or selenoxo)phosphoranes. Thus, the compounds **38**, which are representatives of



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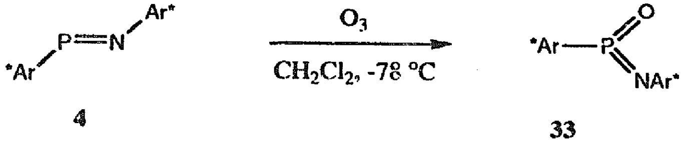
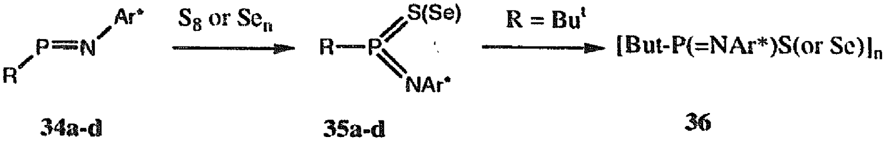


(13)



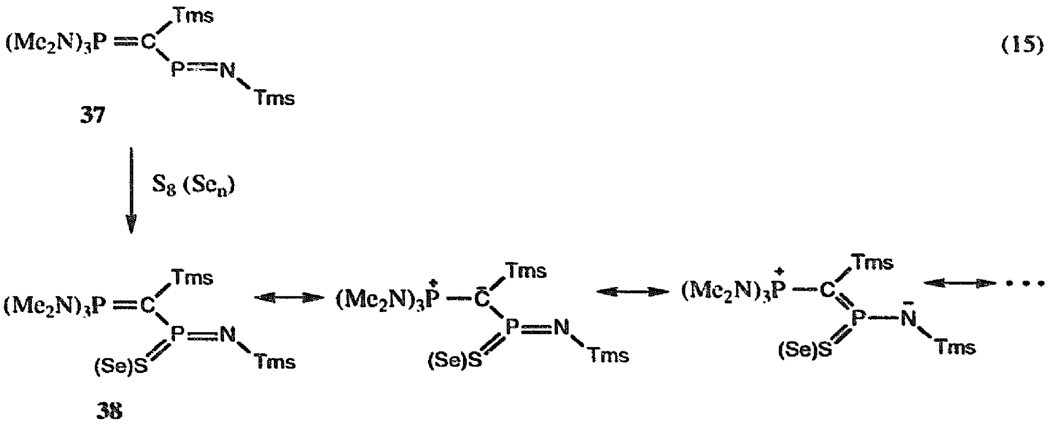
(14)

R = Ph (a), Mes (b), 2,4,6-$Pr^i_3C_6H_2$ (c), Bu^t (d)

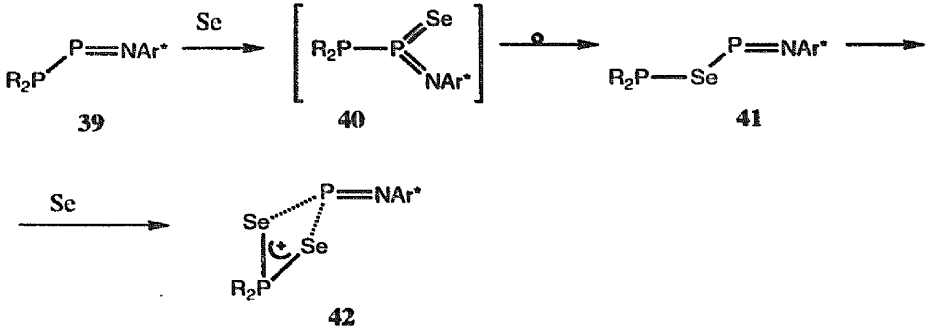
the rare type of resonance-stabilized $\sigma^3\lambda^5$-P derivatives, are accessible as monomers by the reaction of the imino(phosphoranylidenemethyl)phosphane **37** with elemental sulfur and selenium (Eq. (15)) [43].

The reaction of equimolar amounts of the iminophosphane **39** and selenium led to product of selenium insertion into the P–P bond — the iminophosphine **41**. A selenophosphorane **40** was suggested as a possible intermediate in this transformation. Further addition of selenium led to a red, crystalline 1 : 1 'adduct' of **41** and Se having the structure of the donor-stabilized iminophosphenium ion **42** (Eq. (16)) [44].

Azaphospholes are typically inert to chalcogen oxidation. The reactions were shown to proceed only if a protic reagent as a third component is added simultaneously [45]. However, it has recently been found that in hot pyridine a slow direct



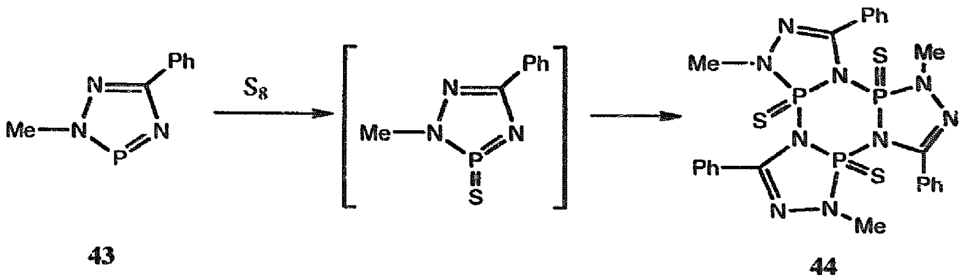
(15)



(16)

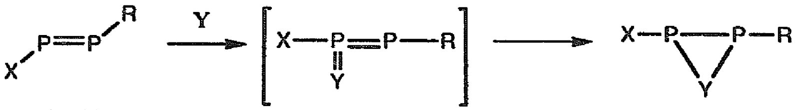
$R = Bu^t$

sulfuration of the triazaphosphole **43** can be achieved. It leads to a trimeric product **44** with a central cyclotriphosphazane-trisulfide ring. Azaphosphole sulfide containing a $\sigma^3\lambda^5$-P atom appears to be an intermediate in this transformation (Eq. (17)) [46,47].



(17)

Although several phosphinylidene(thioxo)phosphoranes, X-P(=S)=PR, have been prepared via direct reaction of the corresponding diphosphenes, XP=PR, with sulfur, in general, for heavier congeners of bis(methylene)phosphoranes, X–P(=Y)=Z (Y, Z=P, As, Sb, Ge or Si) closed-ring phosphirane structures are more favored than bis-ylenephosphorane ones [15,48]. Consequently, in many cases when diphosphenes and their heavier analogues are utilized as substrates in oxidation reactions, the cyclic σ^3-phosphiranes are the sole products. Escudie et al. have recently shown that reactions of the germaphosphene Ar*P=GeMes$_2$ with S$_8$ or Se$_n$ in benzene solution afford exclusively the germathia- and germaselena-phosphiranes [49]. In a similar fashion, some unsymmetrically substituted diphosphenes such as **45**–**48** react with sulfur or selenium to afford the corresponding diphosphiranes (Eq. (18)). Phosphinylidene(chalcogeno)-phosphoranes have been suggested as intermediates in the reactions, but they have not been detected directly.



45-48

(18)

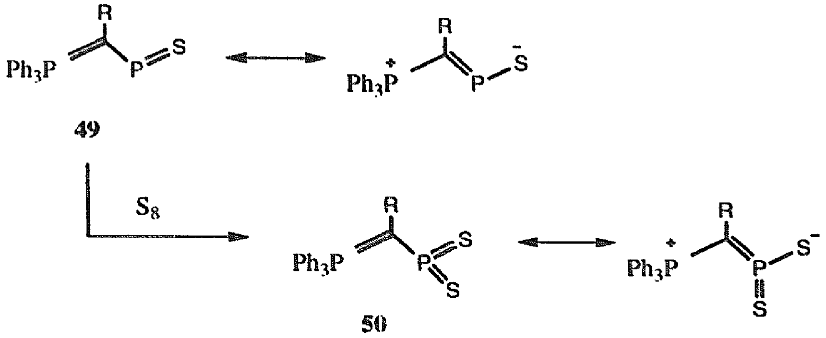
45: R = 2,4,6-Bu$^t_3$C$_6$H$_2$, X = N-methyl-N-(9-fluorenyl)amino, Y = S [42]

46: R = 2,6-(CF$_3$)$_2$C$_6$H$_3$, X = (c-C$_6$H$_{11}$)$_2$N, Y = S [43]

47: R = 2,4,6-Bu$^t_3$C$_6$H$_2$, X = (c-C$_6$H$_{11}$)$_2$N, Y = S [43]

48: R = X = 2,4,6-(CF$_3$)$_3$C$_6$H$_2$, Y = Se [44]

The ylide-substituted dithioxophosphoranes **50** have been prepared by the oxidation of thioxophosphines **49** derived from Ph$_3$P=C(R)PCl$_2$ and sodium sulfide [53]. The generality of this approach is restricted by the fact that the compounds **49** are so far the only known type of stable thioxophosphines. That the compounds **49** and **50** are monomeric and stable at room temperature seems a consequence of their polar nature, as reflected by two canonical formulae:



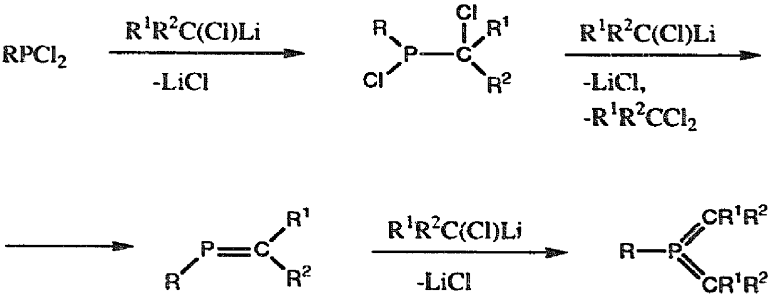
(19)

R = Me, Et, Ph

2.2. Syntheses based on three-coordinate phosphorus(III) compounds

2.2.1. Oxidation of acyclic derivatives

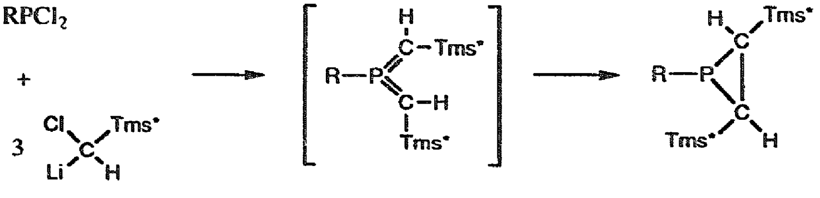
There are several useful syntheses of the $\sigma^3\lambda^5$-phosphoranes based on the reactions of dichlorophosphines and organophosphines with carbenoids or chalcogens and their derivatives. In principle, intermediate two-coordinate phosphorus compounds can take part in these transformations, but generally they are not detected by spectroscopic means. Thus, it was suggested that synthesis of bis (methylene)phosphoranes from dichlorophosphanes and lithium methanides is a three-step process, as shown in Eq. (20). In the third step the lithium methanide acts as carbene precursor which oxidizes the methylenephosphane to the bis(methylene)phosphorane [9].



(20)

R = Alk, Ar, RO, RS

Besides lithium bis(trimethylsilyl)chloromethane which was widely used in earlier work, the carbenoid ^{t}BuMe$_2$Si(H)CClLi was recently studied in the reactions with ^{t}BuPCl$_2$ and PhPCl$_2$. Interaction of these products leads to the bis(methylene)phosphoranes **51** which rearrange at low temperatures to yield the phosphiranes **52** [54].



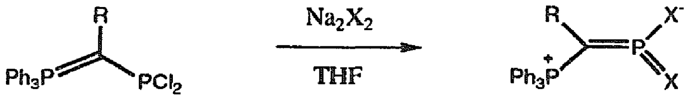
(21)

51 **52**

Tms* = Bu^{t}Me$_2$Si,

R = Bu^t, Ph

The ylide-substituted dithioxophosphoranes **50** described in Section 2.1 are also accessible by direct reaction of dichloro[organo(triphenylphosphonio)methanidyl]-phosphanes **53** with sodium sulfide in THF (Eq. (22)) [53]. The diselenoxophosphoranes **54** have been prepared analogously from **53** and Na$_2$Se [55,56].



(22)

53

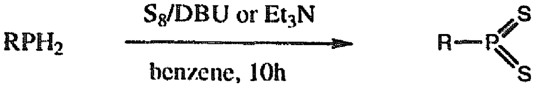
50, X = S
54, X = Se

R = Me, Et, Ph, m-MeC_6H_4

The very first synthesis of a stable aryldithioxophosphorane was accomplished in 1983 using the reaction of Ar^*PH_2 or its disilylated derivative with elemental sulfur or S_2Cl_2 [14]. Later, the same approach was successfully applied to the synthesis of 2,4-di-t-butyl-6-methyldithioxophosphorane [57,58] and 2,4,6-tri-trifluoromethylphenyldithioxophosphorane [59]. The dithioxophosphorane Ar^*PS_2 has also been found as one of the reaction products of the photolysis of $Ar^*P(SMe)_2$ and $Ar^*P(N_3)_2$ [60]; however, this route is not of practical importance.

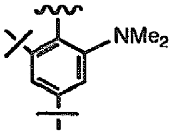
Recently, Yoshifuji and coworkers have successfully employed some novel stabilizing groups having an electron-donating part within their moieties, such as 2,4-di-t-butyl-6-(dimethylamino)phenyl (Mx group) [61], 2,4-di-t-butyl-6-(dimethylaminomethyl)phenyl (Mamx group) [62], 2,4-di-t-butyl-6-[1,1-dimethyl-2-(dimethylamino)ethyl]phenyl [63] and 2,4-di-t-butyl-6-[1-(dimethylamino)-1-methylethyl]phenyl (Maar group) [63]. Using these substituents, dithioxophosphoranes **55–58** were prepared as stable compounds. In these compounds the phosphorus–chalcogen bonds are stabilized by both steric protection of the *ortho*-t-butyl group and intramolecular coordination of the amino group of the substituents at the ortho position.

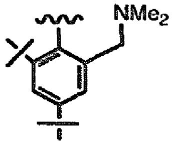
Similarly, diselenoxophosphoranes with the above groups and 2,4-di-t-butyl-



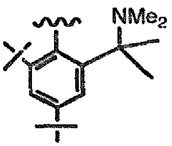
(23)

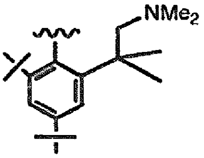
55-58

R = Mx:


(**55**), Mamx:


(**56**),

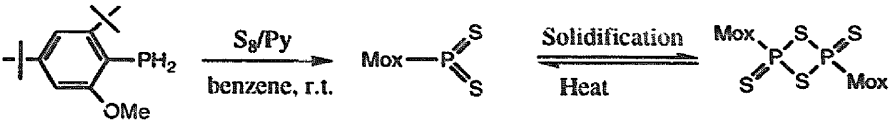


(**57**), Maar:


(**58**)

6-(1-piperidino)phenyl substituent (Pix) were prepared and the structure of the latter compound was confirmed by X-ray analysis [64].

2,6-Di-t-butyl-6-methoxyphenyldithioxophosphorane **59** was found to be stable for several days in non-polar solvents, whereas in the solid state it gave dimeric product of the Lawesson reagent type. The dimer **60** returned to its monomer **59** on heating (Eq. (24)) [65].

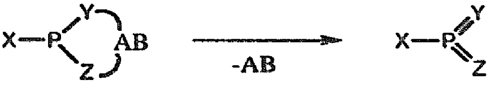


59 **60**

(24)

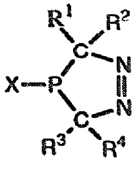
2.2.2. *Thermal or photochemical fragmentation of cyclic derivatives*

Still another possible route to $\sigma^3\lambda^5$-phosphoranes involves thermally or photochemically induced fragmentation of cyclic phosphorus(III) derivatives. Broadly speaking, all compounds of the general formula **61** which are able to split off an energetically favorable molecule AB can be regarded as potential candidates for this synthesis. In practice, dihydroazaphospholes **62–64** are the most suitable precursors for preparing stable three-coordinate phosphorus(V) derivatives [8–11,20].



61

(25)



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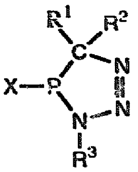
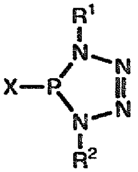


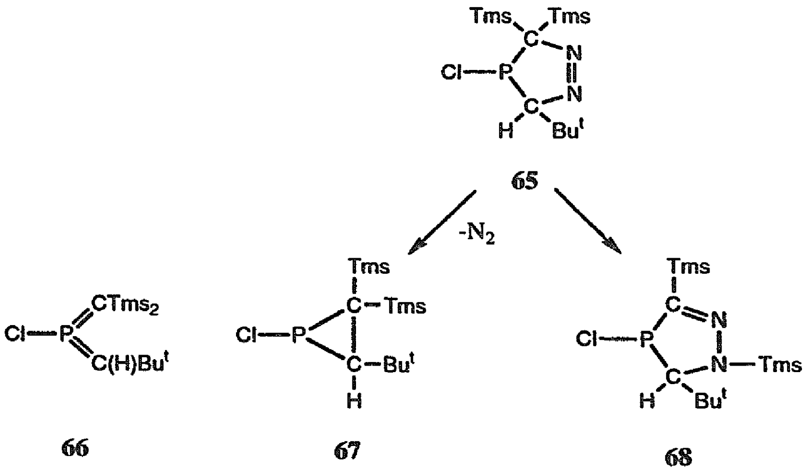
63



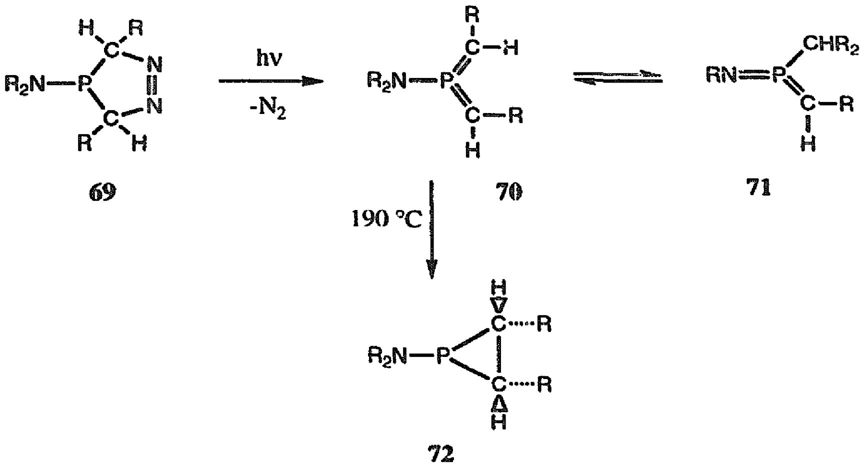
64

Although the method was found to be successful for a variety of compounds X-P(=Y)=Z (Y, Z=CR^{1}R^2 or NR), it is far from straightforward. Thus, in spite of the fact that elimination of nitrogen from the compound **65** already takes place even at 25 °C, no bis(methylene)phosphorane **66** could be isolated or spectroscopy detected. The main reaction products were found to be the compounds **67** and **68** [66].

Diazaphosphole **69** was found to produce the bis(methylene)phosphorane **70** via photochemically induced elimination of nitrogen. During the vacuum distillation the latter partially isomerizes into the methylene(imino)phosphorane **71**. Prolonged heating of **70** at 190 °C affords λ^3-phosphirane **72** (Eq. (27)) [67].



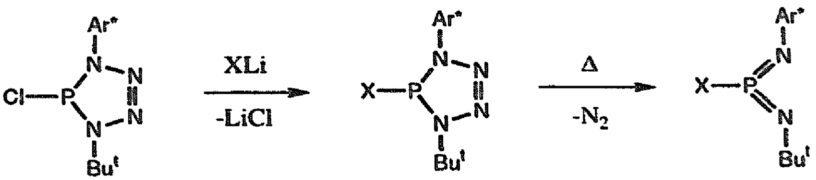
(26)



(27)

As a further development of the method, the synthesis of P-functionalized bis(imino)phosphoranes has been achieved as shown in Eq. (28). By treating the 4,5-dihydro-1*H*-tetrazaphosphole **15** with the C-, N-, O- and S-nucleophiles, the compounds **73** are obtained which, by elimination of nitrogen, form the bis(imino)-phosphoranes **74** in yields of 35–61%. The same procedure was employed for synthesis of the phosphorane derivative **75** (Eq. (29)) [36].

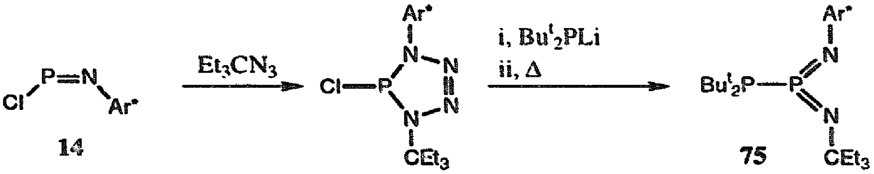
Cadogan and coworkers were the first to report the generation of aryldioxophosphoranes in the gas phase by flash vacuum pyrolysis (FVP) of 2-aryl-1,3,2-dioxaphospholanes [14]. Recently it was shown that flow pyrolysis of 2,6-bis(trifluoromethyl)phenyl-1,3,2-dioxaphospholanes **76** led to the product **78**. The formation of the latter is consistent with intermediate generation of the compound **77** followed by insertion into a C–F bond (Eq. (30)). This reaction provides a further example of the extreme electrophilicity of the aryldioxophosphoranes [68].



15 **73** **74**

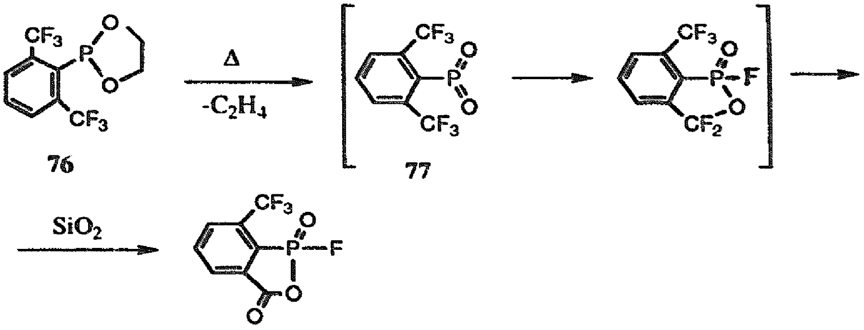
(28)

X = Bu^n, C_5Me_5, Ar*NH, Ar*O, Bu^{t}S



14 **75**

(29)



76 **77**

78

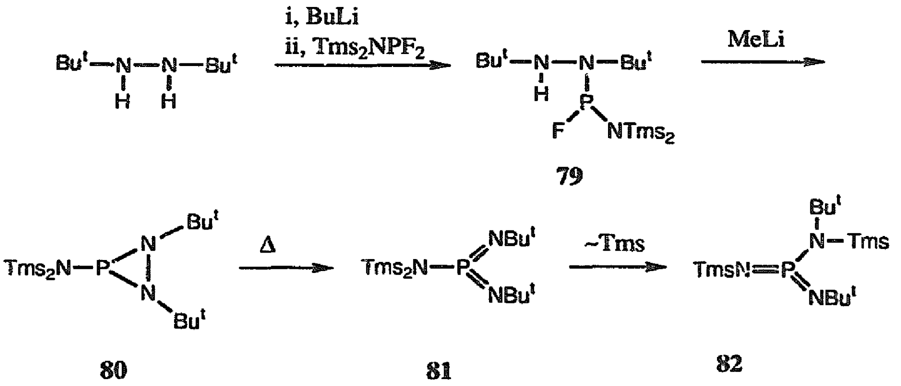
(30)

2.2.3. *Thermal ring-opening of cyclic systems*

Niecke et al. were the first to report the preparation of bis(imino)phosphoranes by this approach [69]. When hydrazinophosphine **79** is treated with methyllithium, the cyclization reaction to give 1,2,3-diazaphosphiridine **80** occurs readily. Thermolysis of the latter in toluene at 100 °C produces the compound **81** which is further converted into the isomeric product **82** (Eq. (31)). Diisopropylamino-substituted hydrazinophosphane ^{t}BuN(H)N(^{t}Bu)P(F)N^{i}Pr2 showed a similar behavior, but the corresponding bis(imino)phosphorane was not stable and underwent [2+2]-cycloaddition to give the 1,3,2,4-diazadiphosphetidine [69].

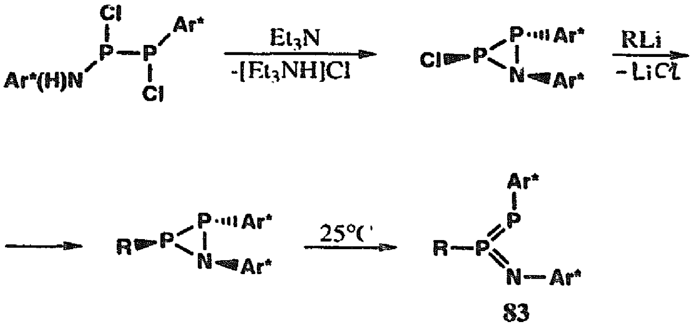
Electrocyclic ring opening of a diazaphosphiridine precursor has also been proposed as the crucial step in the reaction of 2,4,6-tri-t-butylphenylphosphane with diethyl diazodicarboxylate, but such a proposal has not received definite support [70].

Recently, the valence isomerization of azadiphosphiridines has been utilized to prepare stable imino(phosphinidene)phosphoranes [71]. Nucleophilic displacement



(31)

of the halide in *P*-chloro-azadiphosphiridine gives the corresponding P-alkylated derivatives which rearrange thermally into the compounds **83** (Eq. (32)).

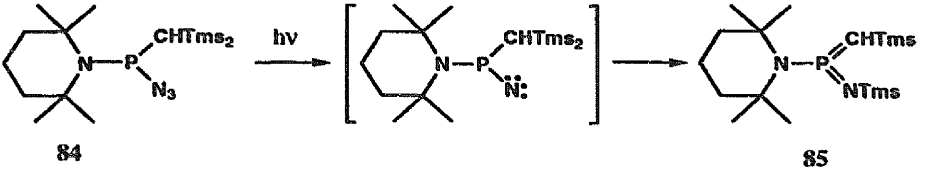


(32)

R=Me, Buⁿ, Buᵗ

2.2.4. *Intramolecular rearrangement of phosphinonitrenes and related reactions*

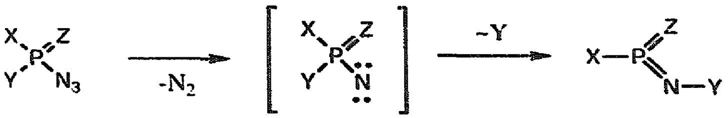
Böske et al. have reported this type of reaction for the first time [72]. The thermal or photochemical decomposition of trivalent phosphorus azide **84** affords the methylene(imino)phosphorane **85** in almost quantitative yield. Evidence for the transient formation of a phosphinonitrene was obtained by trapping experiments with chlorotrimethylsilane (Eq. (33)).



(33)

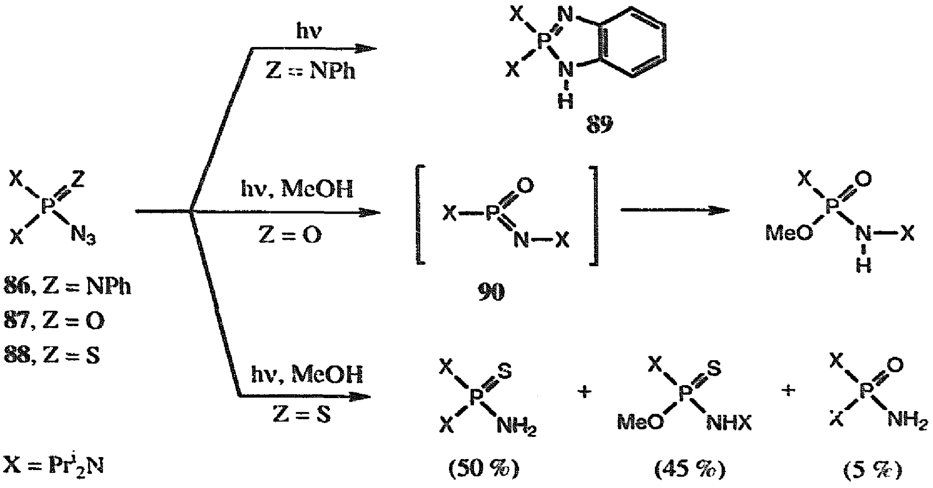
In another, already discussed, example (Eq. (7)), the reaction of iminophosphine Ar*P=NAr* with HN_3 in the presence of MeOH involves a phosphononitrene intermediate which isomerizes in the same manner to furnish bis(imino)phosphorane **13** [35].

The Curtius-type rearrangement of pentavalent phosphorus azides should produce the $\sigma^3\lambda^5$-phosphoranes provided that a suitable substituent capable of migration (Y) is present at the phosphorus atom:



(34)

However, efforts so far to synthesize stable three-coordinate phosphorus(V) derivatives by this route have met with little success. Thus, the photolysis of azide **86** does not afford the expected bis(imino)phosphorane, but gives the five-membered heterocyclic product **89**, probably via C–H insertion of nitrene at the ortho position of the phenyl substituent. The formation of imino(oxo)phosphorane **90** during the photolysis of azide **87** was demonstrated by in situ trapping with methanol, but no monomeric $\sigma^3\lambda^5$-phosphoranes could be isolated. In the case of azide **88**, both Curtius- and nitrene-type reactions occur, but again evidence for the transient formation of imino(thioxo)phosphorane comes from its trapping with methanol (Eq. (35)) [72].

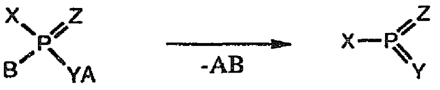


(35)

2.3. *Syntheses based on four-coordinate phosphorus(V) compounds*

2.3.1. *1,2-Elimination reaction*

This synthetic pathway for the formation of $\sigma^3\lambda^5$-phosphoranes is outlined in Eq. (36). If the substrate **91** has suitable ligands (B, YA; A = electrophilic group, B = nucleophilic group) attached to phosphorus, a base-induced elimination of a protic compound (e.g. AB = HCl) or thermally induced elimination of a stable organoelement molecule (e.g. AB = LiCl, TmsCl) represents a realistic method for generating three-coordinate phosphorus(V) derivatives.

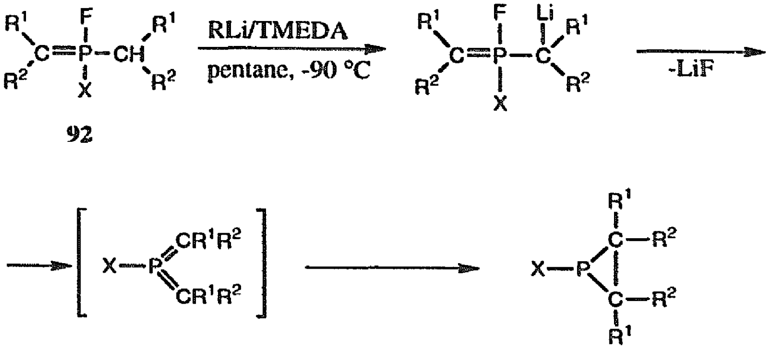


(36)

91

However, it should be noted that, just as steric factors control the formation of two-coordinate phosphorus compounds by elimination reactions, they are also responsible for the syntheses of $\sigma^3\lambda^5$-P derivatives via 1,2-elimination. Simple $\sigma^3\lambda^5$-phosphoranes, even if they are formed according to Eq. (36), usually undergo further transformations without permitting their isolation. Thus, although few dehydrochlorination reactions leading to the generation of the compounds X–P(=O/S)=CHPh from easily accessible benzylphosphonyl- or benzylthiophosphonyl-derivatives X–P(=O/S)(Cl)CH_2Ph have been reported [3,4,73,74], none of these products could be isolated or characterized by means of spectroscopic techniques. Evidence for their transient formation comes from trapping reactions with nucleophilic reagents.

The crucial influence of the nature of the substituents was further demonstrated in the reaction of *P*-fluoroylides **92** with bases. When **92** are allowed to react with alkyllithium or lithium bis(trimethylsilyl)amide in the presence of TMEDA at −90 °C, the intermediarily generated lithium derivatives undergo elimination of LiF to give the phosphiranes **93** instead of the expected bis(methylene)phosphoranes [75].



92

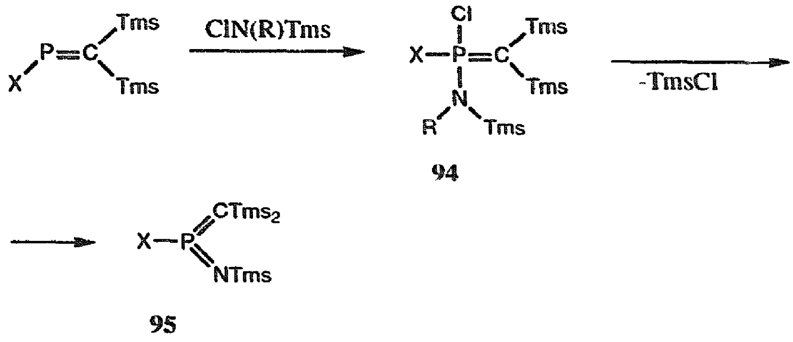
(37)

93

$R^1 = R^2 = Me$ (a), $R^1 = H$, $R^2 = Ph$ (b);

X=Pr^i, Ph CH_2, Et_2N.

The successful synthesis of stable $\sigma^3\lambda^5$-phosphoranes via 1,2-elimination reactions has been realized in the case of sterically hindered four-coordinate phosphorus substrates. In many cases the latter can be prepared from two-coordinate phosphorus compounds (see Section 2.1. For example, the treatment of bis(trimethylsilyl)methylene-phosphines with *N*-chloro-*N*-trimethylsilylamines affords sterically overcrowded ylides **94** which easily split off chlorotrimethylsilane to give the compounds **95** in 45–70% yield [76]. The transformation is analogous to the synthesis of bis(imino)-phosphoranes from λ^3-iminophosphines and *N*-haloamines; the last method has been discussed in some detail in the previous reviews [7,11] and need therefore only be mentioned here.



94

95

(38)

X = Ph, Et$_2$N,  N;

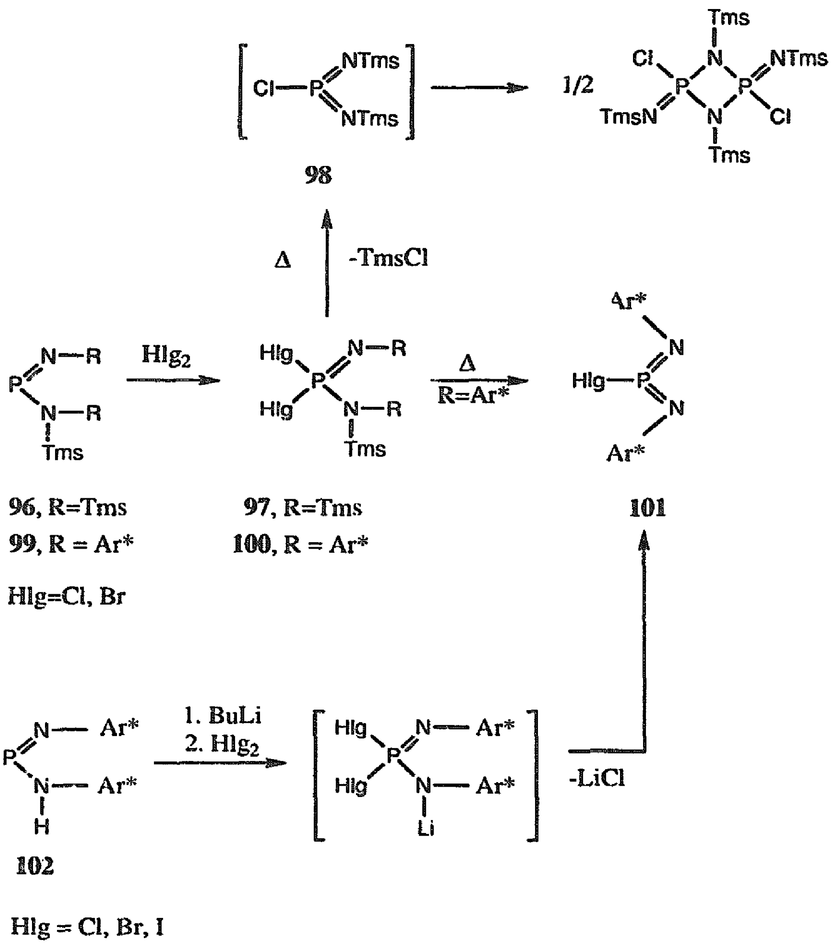
R = Bu^t, Tms

The synthesis of *P*-halobis(imino)phosphoranes, Hlg–P(=NR)$_2$, requires the presence of very bulky substituents attached to the nitrogen atoms. Early attempts to prepare *P*-chlorobis(trimethylsilyl)phosphorane **98** from the corresponding dichloro(amido)imidophosphate **97** failed since Me$_3$Si groups turned out to be unable to stabilize the elimination product against subsequent dimerization [77]. More recent studies have shown that in contrast to fully silylated derivatives, *N*,*N'*-bis(2,4,6-tri-t-butyl-phenyl)-substituted dihalo(amido)imidophosphates **100** are decomposed on being heated to 110 °C with the formation of the monomeric compounds **101** [78]. Later on, it was discovered that the most simple route to the compounds **101** involves a one-pot synthesis from the readily available aminoiminophosphine **102**. Lithiation of **102** with butyllithium and subsequent reaction with halogen provides the compounds **101** in almost quantitative yield [79].

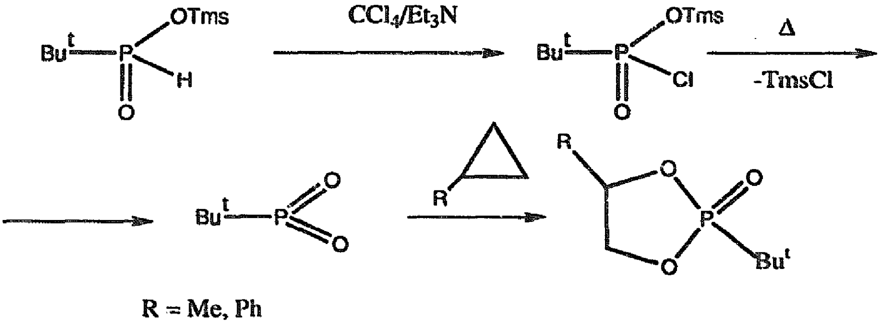
The scope of 1,2-elimination processes has been recently extended to the generation of t-butyldioxophosphorane, ^{t}BuPO$_2$, from ^{t}BuP(O)(OTms)Cl [80]. The reaction occurs in xylene solution at 100–120 °C. The transient production of ^{t}BuPO$_2$ has been supported by chemical trapping with epoxides (Eq. (40)).

2.3.2. Thermally induced [2+2]-cycloreversion of 1,3,2λ^5,4λ^5- diazadiphosphetidines and related compounds

In general, the transformation of dimeric or oligomeric, σ-bonded species [–P(X)(=Y)–Z–]$_n$ into the corresponding monomeric compounds, X–P(=Y)=Z,

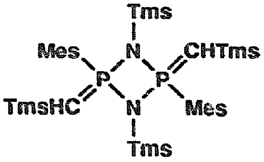


(39)

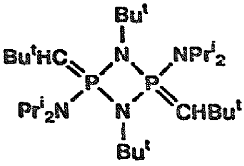


(40)

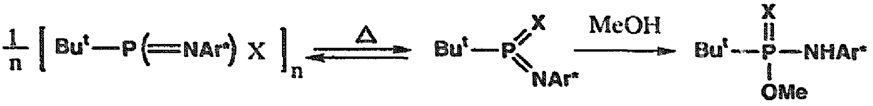
should be energetically unfavorable due to the high energy of a four-electron three-center π-system (YPZ). However, if P–Z σ-bond strength is relatively weak or the cyclic compound is of a high ring strain, the equilibrium between dimeric and monomeric forms can exist at increased temperatures. Examples are the compounds **103** [81] and **104** [82] which dissociate at temperature above 100 °C to form the monomeric $\sigma^3\lambda^5$-phosphoranes. The ability of the air- and moisture-stable dimers or oligomers to dissociate into monomers at higher temperatures renders them suitable for the preparative application as masked forms of the compounds X–P(=Y)=Z. For example, the products formed by the reaction of ^{t}Bu–P=Ar* with sulfur and selenium are oligomers **36** which in aprotic solvents at 110 °C dissociate into monomeric $\sigma^3\lambda^5$-phosphoranes **35d**. The reactions between **36** and protic reagents such as methanol take place very slowly. However, at higher temperatures (greater than 80 °C) methanol adds readily across the P=N double bond of **35d** to form, respectively, phosphonothioates or phosphonoselenoates **105** [42].



103



104

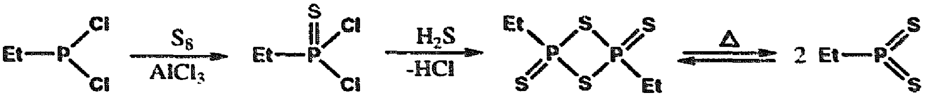


(41)

36 **35d** **105**

X = S or Se

The gas-phase pyrolysis of readily accessible dimer **106** at 970 K is the method of choice for generating ethyldithioxophosphorane **107**. The latter was characterized by its photoelectron spectrum [83].



(42)

106 **107**

4-Methoxyphenyldithioxophosphorane, ArPS$_2$, has been suggested as an intermediate in the thionation reactions of 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide, [ArP(S)S]$_2$, known as Lawesson's reagent (LR), but it has not been detected directly [84]. Very recently, it was shown that the 2,4-di-t-butyl-6-methoxyphenyldithioxo-phosphorane **59** in dilute solution was stable for several days, whereas in the solid state or on concentration it gave dimeric product of the LR type, **60**. The dimer returns to its monomer on heating and, similar to LR, reacts with benzophenone to form thiobenzophenone in 63% yield (Eq. (24)) [65].

Table 2
Reactions of $\sigma^3\lambda^5$-phosphoranes with protic compounds

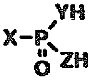
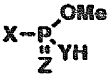
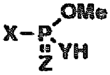
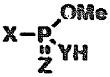
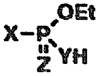
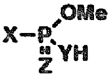
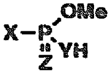
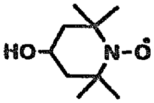
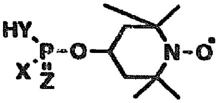
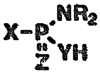
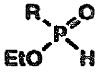
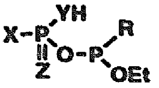
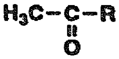
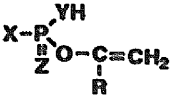
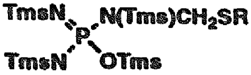
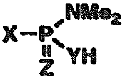
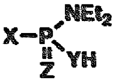
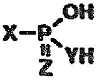
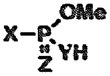
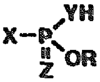
X–P(=Y)=Z			Reagent	Product	Ref.
X	Y	Z			
Mes	Ph_2C	PhN	H_2O		[85]
Mes	Tms(H)C	TmsN	MeOH		[86]
Tms_2N	Tms(H)C	TmsN	MeOH		[87]
Ar*	Tms(H)C	O	MeOH		[88]
2,6-$Me_2C_6H_3$	Ph_2C	Se	EtOH		[89]
Mes	Bu^{t}N	Ar*N	MeOH		[89]
Mes	TmsN	Ar*N	MeOH		[89]
Tms_2N	TmsN	TmsN	H_2O	$(TmsNH)_3PO$	[90]
Tms_2N	TmsN	TmsN			[91]
Tms_2N	TmsN	TmsN	R_2NH (R = Et, ^{i}Pr)		[92]
Tms_2N	TmsN	TmsN	 (R = Ph, EtO)		[93]
Tms_2N	TmsN	TmsN	$H_3C-\underset{O}{\underset{\|}{C}}-R$ (R = Me, Ph)		[94]
Tms_2N	TmsN	TmsN	$H_3C-\underset{O}{\underset{\|}{S}}-R$ (R = Me, Ph)		[94]
^{t}Bu(Tms)N	^{t}BuN	^{t}BuN	Me_2NH		[92]

Table 2 (*continued*)

X–P(=Y)=Z			Reagent	Product	Ref.
X	Y	Z			
	^{t}BuN	^{t}BuN	Et_2NH		[92]
Ar*	^{t}BuN	O	H_2O		[95]
Ar*	^{t}BuN	O, S or Se	MeOH		[95]
^{t}Bu(Tms)N	^{t}BuN	S	H_2O		[96]
Ar*	S	S	ROH		[97]

3. Reactivity of $\sigma^3\lambda^5$-phosphoranes

3.1. Polar additions

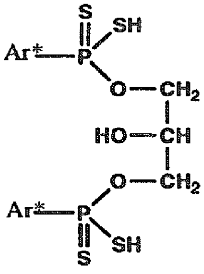
This section includes reactions of $\sigma^3\lambda^5$-phosphoranes with different types of reagent, such as proton-active nucleophiles, organometallic compounds, and Lewis acids, which can formally be classified as polar additions. The general features of all these reactions consists in increasing the coordination number of the phosphorus atom from three to four. Only in a relatively few cases have the mechanisms of these reactions been fully established.

3.1.1. Reactions with proton donor nucleophiles

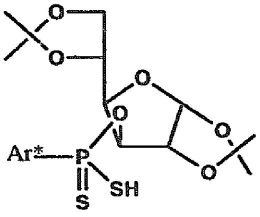
With few exceptions $\sigma^3\lambda^5$-phosphoranes, X–P(=Y)=Z, undergo a rapid and straightforward reaction with protic compounds (HA) with insertion into the HA bond and formation of four-coordinate P(V) derivatives. The anionic part of the HA reagent always adds to the P-atom, while the proton adds to the Y(Z)-atom (Table 2).

Recent examples demonstrating the utility of the process for the synthesis of phosphorylated carbohydrates was reported by Navech et al. [97]. The reaction of dithioxophosphorane Ar^*PS_2 with glycerol in a 2 : 1 molar ratio affords the compound **108**. By using the sugars with partially protected hydroxy groups, monophosphorylated D-glucose and galactopyranose derivatives **109** and **110** have been prepared.

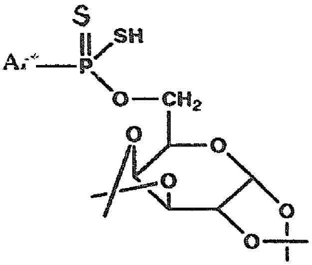
In contrast to alcohols, amines react with Ar^*PS_2 to give cyclic products via a



108

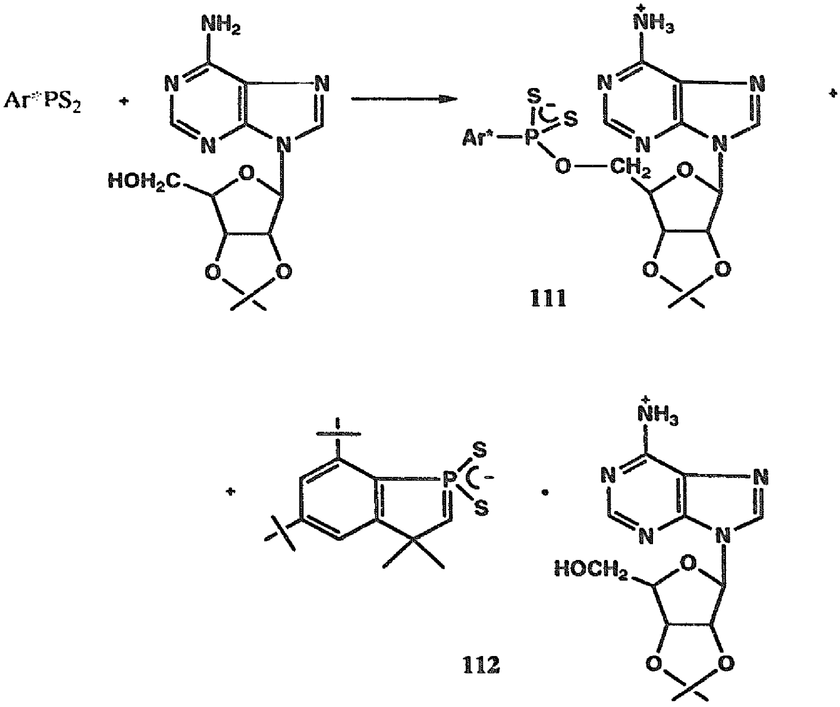


109



110

C–H insertion of o-^{t}Bu group into a P=S bond [97,98]. The reaction of Ar^*PS_2 with an equimolar amount of isopropylidene-2′,3′-adenosine leads to a mixture of the compounds **111** and **112** (Eq. (43)).



111

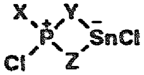
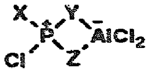
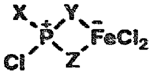
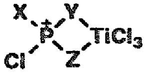
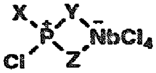
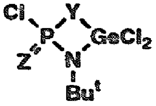
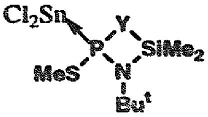
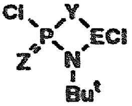
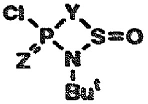
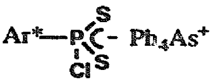
112

(43)

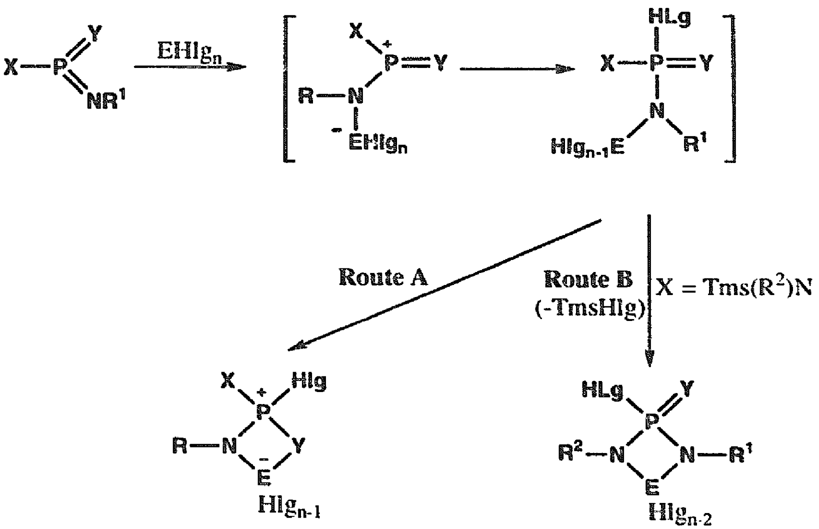
3.1.2. Metallation reactions

Addition of Lewis acidic element halides, $EHlg_n$, to the $\sigma^3\lambda^5$-phosphoranes generally follows a mechanism which involves coordination of the reagent at one of the terminal positions of the multiple bond, shift of a halide to the phosphorus atom and concomitant ring closure (Eq. (44)). The reaction gives either a betaine-like

Table 3
Reactions of $\sigma^3\lambda^5$-phosphoranes with the Group 12–15 element halides

X–P(=Y)=Z			Reagent	Product	Ref.
X	Y	Z			
Tms_2N	Tms(H)C	TmsN	$PhPCl_2$		[99]
Tms_2N	TmsN	TmsN	$SnCl_2$		[100]
Tms_2N	TmsN	TmsN	$AlCl_3$		[100]
Tms_2N	TmsN	TmsN	$FeCl_3$		[49]
Tms_2N	TmsN	TmsN	$TiCl_4$		[100]
Tms_2N	TmsN	TmsN	$NbCl_5$		[100]
$TmsCH_2$	TmsN	TmsN	TmsCl	 $X-\overset{Cl}{\underset{ZTms}{P}}=Y$	[99]
^{t}Bu(Tms)N	^{t}BuN	S	$GeCl_4$		[101]
^{t}Bu(Tms)N	^{t}BuN	S	$SnCl_4$		[101]
^{t}Bu(Tms)N	^{t}BuN	S	ECl_3 (E=P, As)		[101]
^{t}Bu(Tms)N	^{t}BuN	S	$SOCl_2$		[101]
Ar*	S	S	$Ph_4As^+Cl^-$		[98]

heterocycle (route A) or a compound with the neutral PN_2E skeleton (route B). A listing of many of these reactions is given in Table 3.

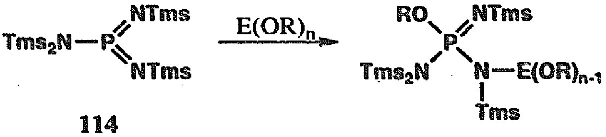


(44)

In addition to a series of metal halides ($AlCl_3$, $FeCl_3$, $ZrCl_4$, $NbCl_5$, Me_2AuCl), route A is observed for the reaction of **113** with $Ti(OR)_4$ (Eq. (45)) [102]. Interaction between **113** and $Ti(O^iPr)_4$ readily proceeds at 20 °C; the analogous reaction with $Ti(O^tBu)_4$ requires more vigorous conditions (70 °C, 70–80 h). Alkoxy-derivatives of boron, silicon and carbon react with **114** forming only the 1,2-addition product to one of the double bonds (Eq. (46)) [103].

113

(45)



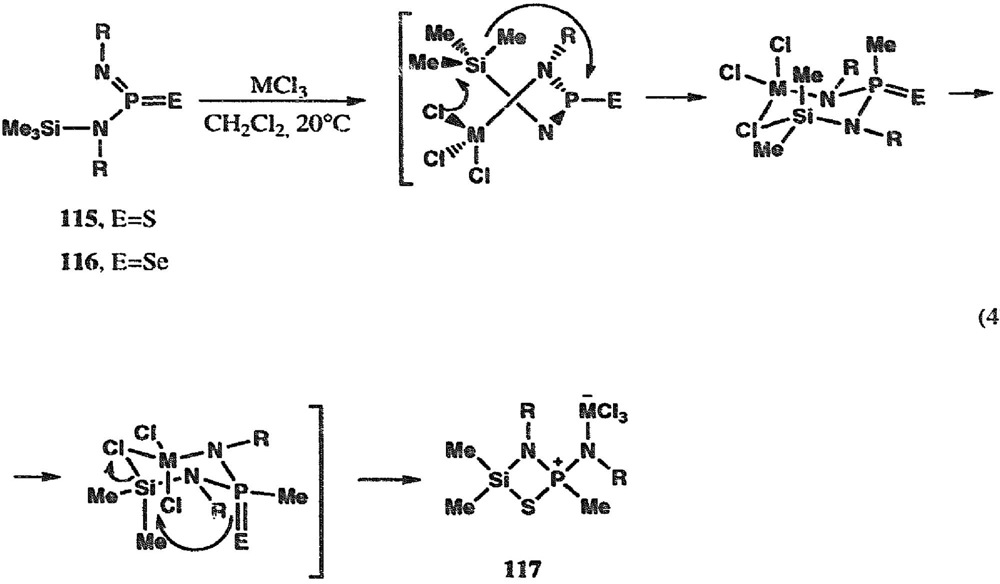
114

(46)

$E(OR)_n = B(OMe)_3, Si(OEt)_4, CH(OEt)_3$

Chalcogeno(imino)phosphoranes **115**, **116** were shown to react with Lewis acids ($AlCl_3$, $GaCl_3$) in a rather unusual manner (Eq. (47)) [104–106]. The expected zwitter-ionic adduct is generated initially, and the reaction then proceeds through a

1,3-methyl migration from the silicon center to the phosphorus center, and the formation of a silicon–chalcogen bond. The cyclic products do not incorporate the activating reagent; therefore, conceptually the process can be viewed as an isomerization of the imino-bound complexes of **115** and **116**. The generality of the cyclization reaction was demonstrated by formation of the same heterocyclic framework from an alternative starting material, $[(Tms_2N)_2]_2P(S)Cl$. In addition, a similar cyclization process was observed for the imino(thioxo)phosphorane **115** in the presence of CF_3SO_3H.



115, E=S

116, E=Se

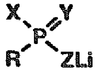
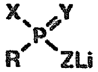
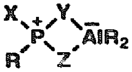
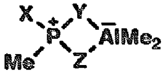
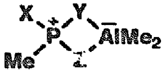
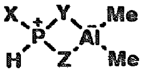
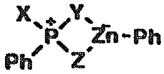
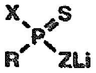
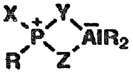
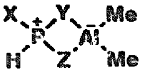
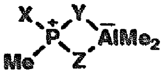
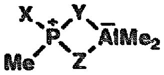
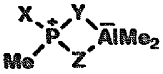
(47)

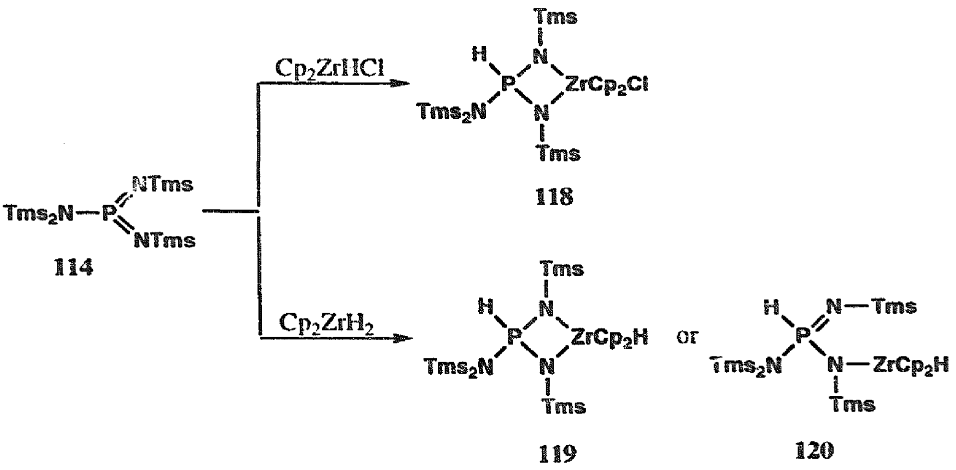
117

R=Bu^t, M=Al, Ga

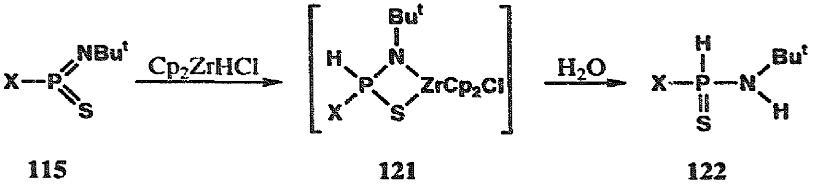
The ability to interact readily with organometallics is one of the most significant properties of $\sigma^3\lambda^5$-phosphoranes, and permits a unique and facile entry into various heterometallated compound (Table 4). The scope of these reactions has recently been extended on hydro- and carbozirconation of bis(imino)phosphorane **114** [111]. The latter reacts with Cp_2ZrHCl in THF at −20 °C to afford the four-membered zirconadiazaphosphetidine **118**. Hydrozirconation of **114** was also performed with Cp_2ZrH_2 in THF. Although the experimental values did not allow the authors to choose between a cyclic structure **119** or the corresponding linear form **120**, the polarity of the remaining P=N double bond strongly suggested cyclization and formation of the expected four-membered ring as usually observed (Eq. (48)). When Cp_2ZrHCl was added to the imino(thioxo)phosphorane **115** the main reaction product was identified as the phosphine sulfide **122**. Formation of the latter might be explained by hydrolysis of the very unstable four-membered ring **121** (Eq. (49)) [111].

Table 4
Reactions of $\sigma^3\lambda^5$-phosphoranes with organometallic compounds

X–P(=Y)=Z			Reagent	Product	Ref.
X	Y	Z			
Tms$_2$N	TmsN	TmsN	RLi (R = Me, Ph)		[107]
^{t}Bu(Tms)N	^{t}BuN	^{t}BuN	RLi (R = Me, Ph)		[107]
Tms$_2$N	TmsN	TmsN	Al$_2$R$_6$ (R = Me, Ph)		[108]
^{t}Bu(Tms)N	TmsN	TmsN	Al$_2$Me$_6$		[108]
Tmp	TmsN	TmsN	Al$_2$Me$_6$		[108]
Tms$_2$N	TmsN	TmsN	Me$_2$AlCl		[108]
Tms$_2$N	TmsN	TmsN	Me$_2$AlH		[108]
Tms$_2$N	TmsN	TmsN	Ph$_2$Zn		[109]
Tms$_2$N	TmsN	TmsN	(C$_3$H$_5$)$_2$M (M = Ni, Pd)		[110]
Tms$_2$N	^{t}BuN	S	RLi (R = Me, Ph)		[107]
Tms$_2$N	^{t}BuN	S	Al$_2$R$_6$ (R = Me, Ph)		[108]
Tms$_2$N	^{t}BuN	S	Me$_2$AlH		[108]
^{t}Bu(Tms)N	^{t}BuN	S	Al$_2$Me$_6$		[108]
Tms$_2$N	^{t}BuN	Se	Al$_2$Me$_6$		[108]
^{t}Bu(Tms)N	^{t}BuN	Se	Al$_2$Me$_6$		[108]



(48)



(49)

X=Bu^t(Tms)N

3.2. Cycloaddition reactions

Since the three-center four-electron π-system in the compounds X–P(=Y)=Z is highly reactive and $\sigma^3\lambda^5$-P atom exhibits a marked tendency in increasing its coordination number, $\sigma^3\lambda^5$-phosphoranes feature considerable cycloaddition potential. Phosphiranes with $\sigma^4\lambda^5$-phosphorus atoms, 1-phosphacyclobutenes and 1,3-diphosphetanes, four- and five-membered phosphorus cycles with widely differing additional heteroatoms, as well as phosphorus heterocycles with larger ring systems, constitute the wide range of target molecules which have now become accessible via the cycloaddition reactions of $\sigma^3\lambda^5$-phosphoranes (Table 5).

In recent times, the wide scope of application of the $\sigma^3\lambda^5$-phosphoranes in cycloaddition reactions has been demonstrated by the photochemical reaction of the azidophosphine (^{i}Pr2N)$_2$PN$_3$ with the bis(imino)phosphoranes [122]. Photolysis of the azide at 12 °C in hexane in the presence of stoichiometric amounts of **123** afforded the first stable 1,2-dihydro-1,3,2λ^5,4λ^5-diazadiphosphete **124** (Eq. (50)). When fully silylated bis(imino)phosphorane **114** was used as trapping agent, the reaction afforded transient diazadiphosphete which undergoes 1,3-silyl group shift to furnish the 'inner salt' **125** (Eq. (51)).

1,2,4,3-Thiadiazaphosphetidines of the type **130** were first prepared by Kulbach

Table 5
Cycloaddition reactions of $\sigma^3\lambda^5$-phosphoranes

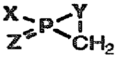
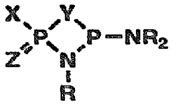
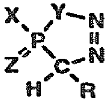
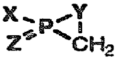
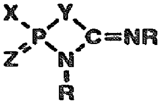
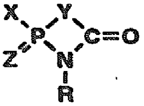
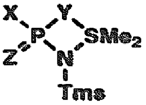
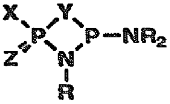
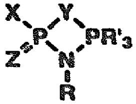
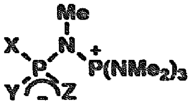
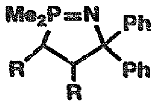
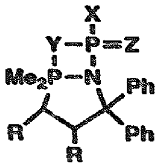
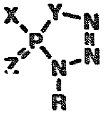
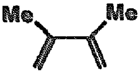
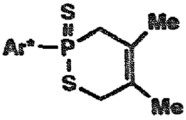
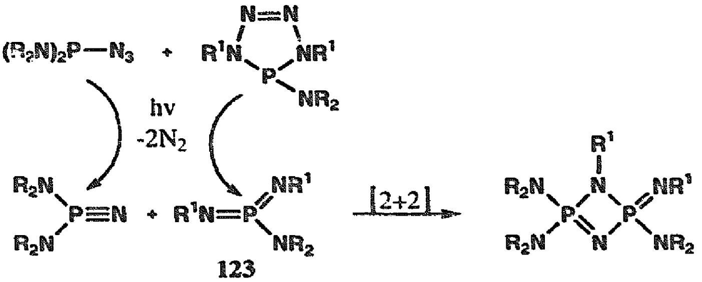
X–P(=Y)=Z			Reagent	Product	Ref.
X	Y	Z			
Tms_2N	Me_2C	TmsN	CH_2N_2		[112]
Tms_2N	Tms(H)C	TmsN	TmsC≡CH		[34]
Tms_2N	Me(H)C	TmsN	R_2N–P=NR (R=Tms)		[112]
Tms_2N	Tms(H)C	S	$RCHN_2$		[113]
Tms_2N	TmsN	TmsN	CH_2N_2		[112]
Tms_2N	TmsN	TmsN	RNCNR		[114]
Tms_2N	TmsN	TmsN	RNCO		[114]
Tms_2N	TmsN	TmsN	Tms–N=SMe_2		[114]
Tms_2N	TmsN	TmsN	R_2N–P=NR (R=Tms)		[115]
Tms_2N	TmsN	TmsN	RN=PR'_3 (R'=Alk, Ar)		[116]
Tms_2N	TmsN	TmsN	MeN=$P(NMe_2)_3$		[117]
Tms_2N	TmsN	TmsN	 (R=MeO_2C)		[118]

Table 5 (*continued*)

X–P(=Y)=Z			Reagent	Product	Ref.
X	Y	Z			
Tms_2N	TmsN	TmsN	RN_3		[119]
Ar*	S	S			[120,121]

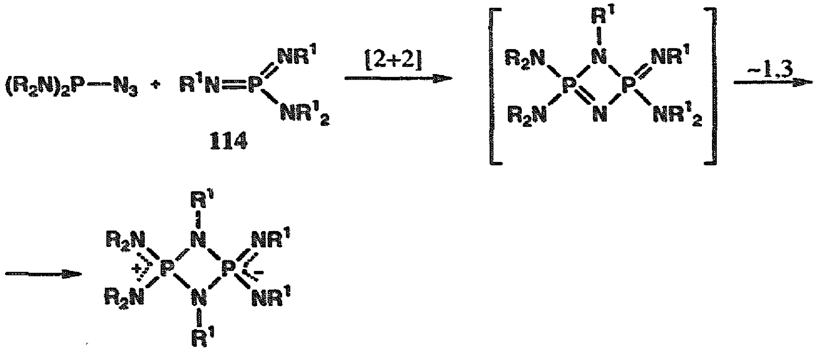


123

124

$R = Pr^i, R^1 = Bu^t$

(50)



114

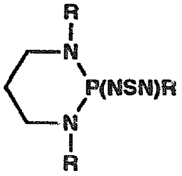
125

$R = Pr^i, R^1 = Tms$

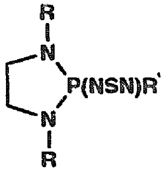
(51)

and Scherer [123] from the reaction of the imino(thioxo)phosphorane **115** with *N*,*N'*-di-*tert*-butylsulfurdiimide. Although the analogous products are obtained with aminophosphinyl-substituted sulfur diimide **126**, the reactions between **115** and the three other sulfur diimides **127–129** take a completely different course, and [2+2]-

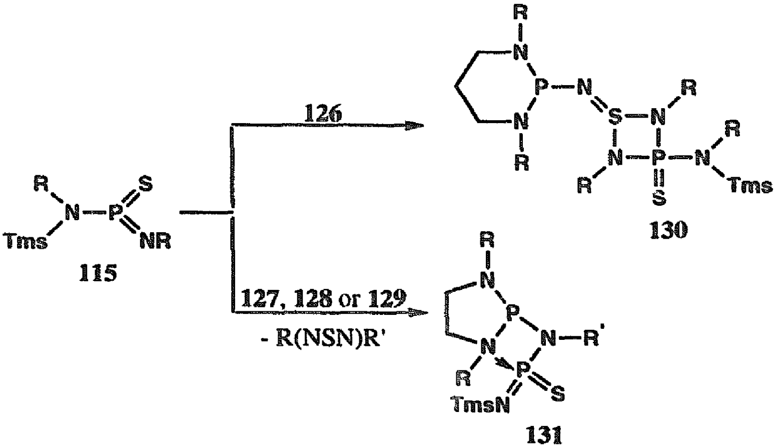
cycloaddition was not observed at all. The surprising result is shown in Eq. (52). Presumably, intramolecularly donor-stabilized imino(thioxo)phosphoranes **131** are formed as a result of exchange between imino groups at phosphorus and sulfur, followed by 1,3-shifts of Me_3Si and phosphinyl groups and final N→P coordinative stabilization. The reasons for the different behavior of **127–129** compared with **126** have not been clarified.



126



127, R' = Bu^t
128, R ' = Tms
129, R' = $P[N(Bu^t)CH_2]_2$



(52)

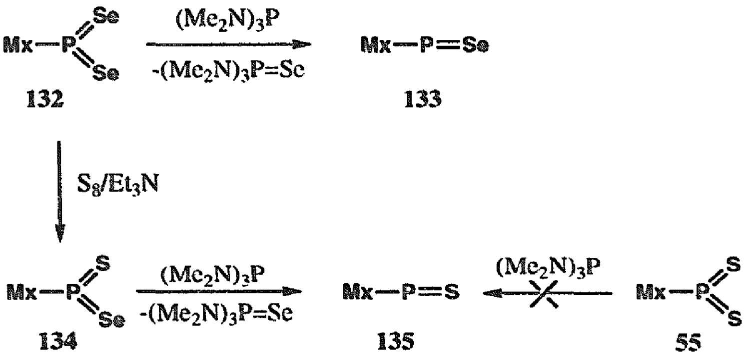
(53)

R = Bu^t

3.3. *Ylide transfer reactions*

On the basis of ab initio calculations it was predicted that the monoylene formation of $H_3P{=}X$ from $H{-}P({=}X)_2$ by corresponding group transfer reactions to PH_3 is endothermic in the case that X is more electronegative than phosphorus (O, S, NH). For the reaction $[H{-}P({=}SiH_2)_2 + PH_3]$ the calculations predict a positive energy balance, $\Delta E(SCF) = -13.7$ kcal mol^{-1} [124].

In a very elegant paper [125] Yoshifuji et al. have demonstrated the application of ylide transfer reaction of the diselenoxophosphorane **132** for the synthesis of the first thermally stable phosphinoselenoylidene **133**. An attempt to desulfurize dithioxophosphorane **55** with $(Me_2N)_3P$ was unsuccessful, indicating that **55** resists ylide transfer in contrast to the case of deselenation of **132**. Later, the phosphinothioylidene **135** was prepared by reacting the selenothioxophosphorane **134** with the same phosphine (Eq. (53)) [61].



(54)

Mx = 2,4-Bu^t_2-6-(Me_2N)C_6H_2

3.4. *Reactions at peripheral substituents*

According to a method first devised by Appel [9], Niecke and coworkers succeeded in the preparation of a great number of differently substituted bis(methylene)phosphoranes by nucleophilic substitution from bis[bis(trimethylsilyl)methylene] chlorophosphorane **136** (Eq. (54)) [20].

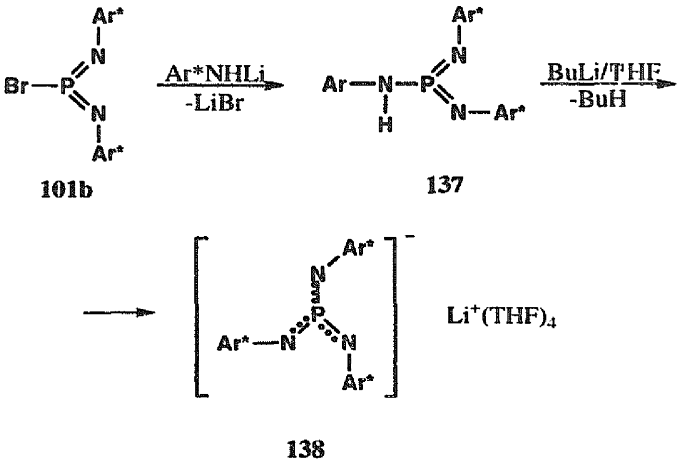
136

(55)

R	Me	Et	Pr^i	Bu^i	Ph	Et_2N	Ar*NH	Cy_2P	Ar*(H)P	Pr^iO	Pr^iS	PhS
M	R_2Al	R_2Al	MgCl	R_2Al	Li	Li	Li	Li	Li	Li	Li	Li

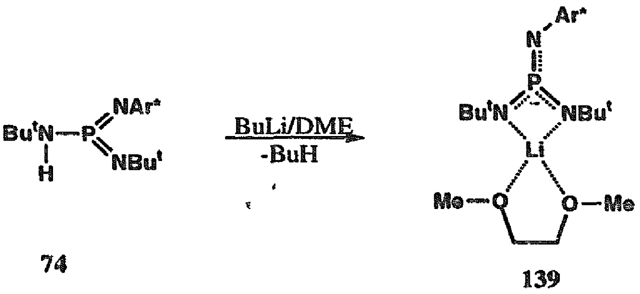
The P-halogenated bis(imino)phosphoranes, Hlg–P(=NAr*)$_2$, have also proved to be key substances for the preparation of novel P-functionalized derivatives [78]. A highly intriguing aspect of these reactions is that they permit a unique and facile entry into monomeric tris(imino)*meta*-phosphates [126]. Thus, bis(imino)phosphorane **137**, readily available from **101b** via Br/NHAr* exchange, undergoes a rapid metallation with BuLi in THF to produce salt **138**, which exists as 'separated ions'

(Eq. (55)). Metallation of the bis(imino)phosphorane **74** with *n*-butyllithium in 1,2-dimethoxyethane leads to the lithium complex **139** (Eq. (56)).



101b **137** **138**

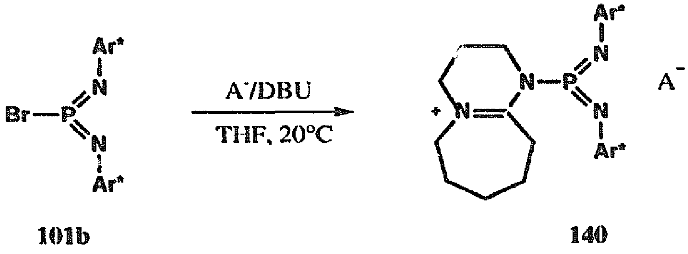
(56)



74 **139**

(57)

Bis(imino)halophosphoranes do not react with highly ionic salts such as $LiBPh_4$ containing weakly coordinating anions. However, interaction of **101b** with $LiBPh_4$ or KPF_6 in the presence of a stoichiometric amount of 1,8-diazabicyclo[5.4.0]undec-7-ene gives the corresponding onio-substituted bis(imino)phosphoranes **140** (Eq. (57)) [127].

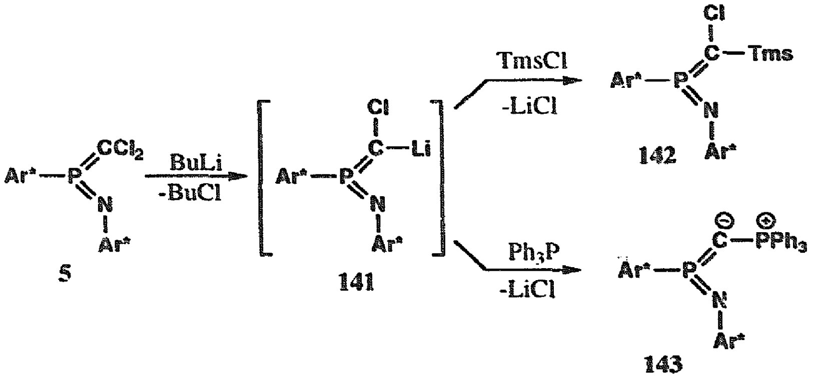


101b **140**

(58)

A = BPh_4 or PF_6

A first synthesis of an iminophosphoranylidene carbenoid from imino(dichloromethylene)phosphorane **5** has recently been reported [22]. In this reaction the C–Cl bond is selectively cleaved on treatment with butyllithium in THF at −105 °C. The intermediate **141** can be trapped as the thermally stable C-silylated imino(methylene)-phosphorane **142** by the subsequent addition of ClTms or as the 'phosphine adduct' **143** by the treatment with Ph_3P (Eq. (58)).



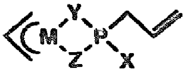
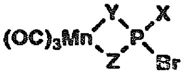
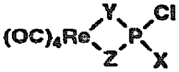
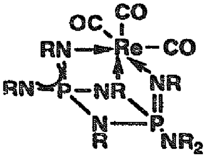
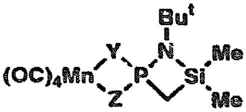
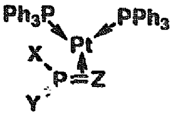
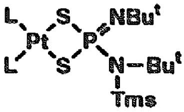
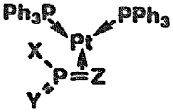
(59)

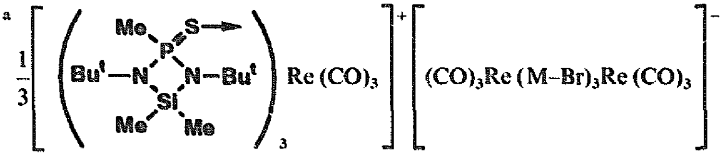
3.5. Ligand properties

Most of the reactions of $\sigma^3\lambda^5$-phosphoranes with transition metal derivatives described in the literature involve complexation which is accompanied by modification of a free ligand. End-on coordination of $\sigma^3\lambda^5$-iminophosphoranes by the nonbonding electron pair on the doubly bonded nitrogen atom seems to be the first step of these transformations; the subsequent migration of a ligand from metal to phosphorus atom or even deeper structural reorganization of a complex lead to a final product (Table 6). There are several important exceptions, however. Thus, reactions of imino(chalcogeno)phosphoranes with $(Ph_3P)_2Pt(C_2H_4)$ gave the complexes exhibiting η^2-coordination of the unchanged $\sigma^3\lambda^5$-phosphorane ligand via the PS double bond [132].

Recent synthesis of the first metallobis(methylene)phosphoranes opens up completely new perspectives [134]. Reaction of the potassium metalate **144** with the chlorobis(methylene)phosphorane **136** led to substitution of chlorine without affecting the P=C bonds and formation of **145**, as the main product (36–49% yield) (Eq. (59)). Heating of the metallobis(methylene)phosphorane **145** results in isomerization to yield the phospholene complexes **146** (42%) and **147** (8%) (Eq. (60)). The formation of **146** and **147** can formally be regarded as a cycloaddition reaction of the allyl ligand in **145** with one of the P=C double bonds of the $\sigma^3\lambda^5$-phosphorane fragment. It was proposed that the reaction proceeded via an initial nucleophilic attack of the allylic ligand at the P(V)-center, which was followed by a metal-induced 1,3-hydrogen shift from the C_3 fragment to the second methylene carbon atom. A subsequent ring closure reaction leads to the phospholene complexes. The major isomer **146** can alternatively be obtained in 82% yield at ambient temperatures by adding a small amount of PBu_3 to the metallobis(methylene)phosphorane

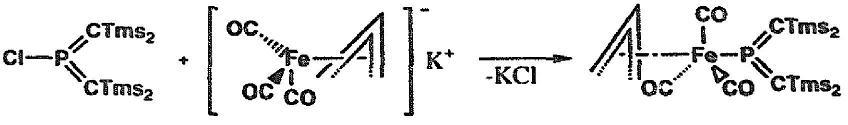
Table 6
Reactions of $\sigma^3\lambda^5$-phosphoranes with transition metal compounds

X–P(=Y)=Z			Reagent	Product	Ref.
X	Y	Z			
Tms_2N	TmsN	TmsN	 (M = Ni, Pd)		[110]
Tms_2N	TmsN	TmsN	$Mn(CO)_5Br$		[128]
Tms_2N	TmsN	TmsN	$Re(CO)_5Cl$		[129]
Tms_2N	TmsN	TmsN	$[Re(CO)_3(THF)Br]_2$	 (R = Tms)	[130]
^{t}Bu(Tms)N	^{t}BuN	S	$Mn(CO)_5Cl$		[6]
^{t}Bu(Tms)N	^{t}BuN	S	$Re(CO)_5Br$	—[a]	[131]
^{t}Bu(Tms)N	^{t}BuN	S	$(Ph_3P)_2Pt(C_2H_4)$		[132]
^{t}Bu(Tms)N	^{t}BuN	S	$PtL_3L = [^{t}Bu(Tms)N\text{–}P{=}N^{t}Bu]$		[133]
^{t}Bu(Tms)N	^{t}BuN	Se	$(Ph_3P)_2Pt(C_2H_4)$		[132]

[a] 

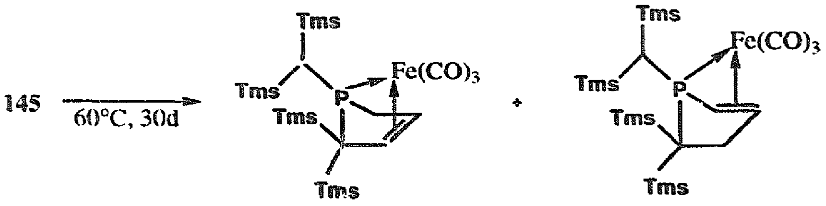
$\frac{1}{3}\left[\left(\ldots\right)_3 Re(CO)_3\right]^+\left[(CO)_3Re(M\text{–}Br)_3Re(CO)_3\right]^-$

145 [135]. A similar reactivity could be achieved in the reaction of the chlorobis(methylene)phosphorane with triisobutylaluminum at elevated temperature, which furnished two isomeric products. The formation of the major product, the butylbis(methylene)phosphorane **148**, results from the substitution of the chlorine atom in **136**. Additionally, the 1*H*-λ^5-(methylene)phospholane **149** could be obtained in 18% yield (Eq. (61)) [135].



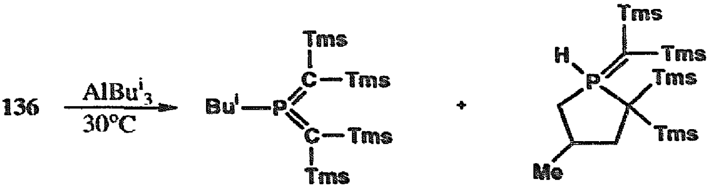
136 **144** **145**

(60)



146 **147**

(61)



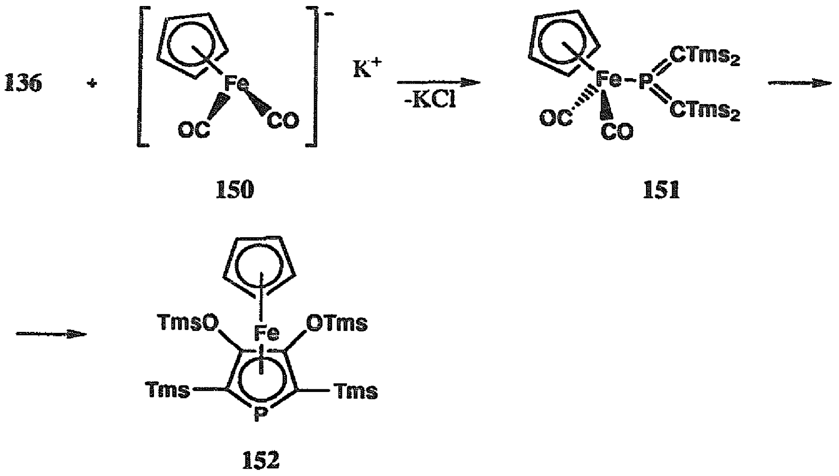
148 **149**

(62)

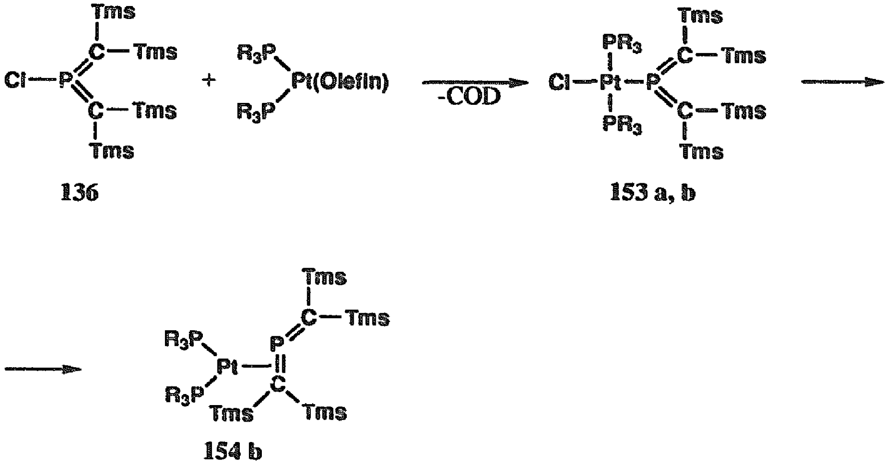
By varying the reaction conditions, Metternich and Niecke have also succeeded in synthesizing the metallobis(methylene)phosphorane **151** and its rearrangement product, the phosphaferrocene **152**, from **136** and potassium metalate **150**. Both isomers were separated by column chromatography and isolated as pure compounds. The isomerization can be regarded as a coupling of the phosphorane fragment with the two carbonyl groups of the Fe fragment (Eq. (62)) [134].

Replacement of the olefin ligand in $(R_3P)_2M$(olefin) (M=Pt, Ni) by the bis(methylene)phosphorane **136** (Eqs. (64) and (65))leads to the complexes **154b** and **155** in which 2-phosphonioallene ligand is η^2-coordinated to the metal fragment. The reactions proceed via a metallobis(methylene) phosphorane intermediate, which could be isolated in the case of the platinum complex **153a**.

The structure of 2-phosphonioallene complexes has been elucidated by NMR spectroscopy and a single-crystal X-ray study of **155a** [136].

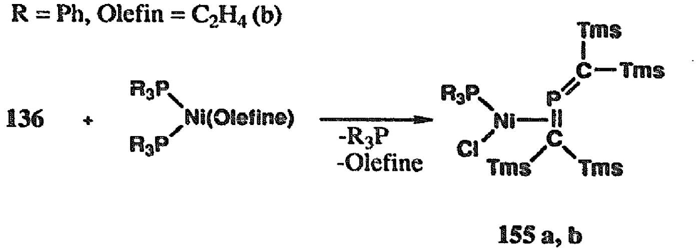


(63)



(64)

R = Et, Olefin = COD (a)
R = Ph, Olefin = C_2H_4 (b)

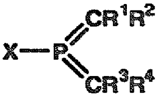


(65)

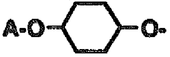
R = Et (a), Bu (b)

4. Compilations of stable $\sigma^3\lambda^5$-phosphoranes

4.1. *Bis(methylene)phosphoranes* [a]



X	R^1	R^2	R^3	^{31}P NMR (δ_P, ppm)	X-ray	Ref.
H	Tms	Tms	Tms	33.1		[137]
Me	Tms	Tms	Tms	170.3		[20]
Et	Tms	Tms	Tms	191.5		[20]
^iPr	Tms	Tms	Tms	201.3		[20]
^iBu	Tms	Tms	Tms	182.6		[20]
^sBu	Tms	Tms	Tms	198.0	+	[138,139]
^tBu	Tms	Tms	H	215.7		[20]
^tBu	H	^tBu	Tms	170.9		[20]
^tBu	Ph	Ph	Tms	167.0		[19]
^tBu	Ph	Tms	Tms	188.0		[19]
^tBu	Tms	Tms	Tms	204.5		[138,19]
C_6H_{11}	Tms	Tms	Tms	198		[140]
Ph_2CH	Tms	Tms	Tms	179.1	+	[139]
(Propenyl)	Tms	Tms	Tms	177.9		[20]
Ph–CH=CH	Tms	Tms	Tms	165.8		[138]
Ph–C≡C	Tms	Tms	Tms	109.8		[138,139]
$Tms_2CH–P=C(Tms)-SiMe_2CH_2$	Tms	Tms	Tms	177.1	+	[139]
Cp*	H	Tms	H	173.0		[20]
Cp*	Tms	Tms	H	187.9		[20]
Cp*	Ph	Ph	Tms	141.9		[20]
Cp*	Tms	Tms	Tms	175.0		[20]
Ph[b]	H	$Me_2(^tBu)Si$	H[b]	113.1		[20]
Ph	Ph	Ph	Tms	133.0		[19]
Ph	Tms	Tms	Tms	174.1		[19]
Mes	Ph	Ph	Tms	120.0		[19]
$2-MeOC_6H_4$	Tms	Tms	Tms	161.0		[138]
9-Fluorenyl	Tms	Tms	Tms	171.5	+	[139,141]
Me_2N	Tms	Tms	Tms	167	+	[140,139]
Et_2N	Tms	Tms	H	167.6		[20]
Et_2N	Tms	Tms	Ph	154.4		[20]
Et_2N	Ph	Ph	Tms	144.2		[20]
Et_2N	Tms	Tms	Tms	167.0		[20]
Et_2N	Tms	Cl	Tms	153.3		[20]
$^iPr_2N$	H	Tms	H	157.4		[20]

$^{i}Pr_2N$	Tms	Tms	H	158.6		[20]
Tmp	H	Tmp	H	155.2		[20]
PhNH	Tms	Tms	Tms	145		[109]
Ar*NH	Tms	Tms	Tms	158.2		[20]
2-Napthylamino	Tms	Tms	Tms	146		[142]
Tms_2N	H	Tms	H	161.3		[67]
Tms_2N	Tms	Tms	Cl	119.3		[20]
MeO	Tms	Tms	Tms	174.0		[138]
^{i}PrO	Tms	Tms	Tms	167.8		[138]
^{t}BuO	Tms	Tms	Tms	156.5		[138]
PhO	Tms	Tms	Tms	162.3		[138]
$H_3C(CH_2)_4S$	Tms	Tms	Tms	168.8		[138]
^{i}PrS	Tms	Tms	Tms	164.8		[138]
PhS	Tms	Tms	Tms	161.0	+	[138,139]
Cy_2P	Tms	Tms	Tms	182.1		[20]
Ar*PH	Tms	Tms	Tms	191.0		[20]
Cl	Tms	Tms	Tms	136.8	+	[138,139]
Br	Tms	Tms	Tms	122.5		[138]
I	Tms	Tms	Tms	102.9		[138]
$(Et_3P)_2Pt(Cl)$	Tms	Tms	Tms	202.2		[20]
$Cp(CO)_2Fe$	Tms	Tms	Tms	347.1		[134]
$C_3H_5(CO)_3Fe$	Tms	Tms	Tms	331.8		[134]
$A–N(CH_2CH_2)_2N$	Tms	Tms	Tms^{c}	168	+	[143]
$A–NH(CH_2)_2N$	Tms	Tms	Tms^{c}	158		[143]
$A–N(Tms)CH_2CH_2N(Tms)$	Tms	Tms	Tms^{c}	164		[143]
	Tms	Tms	Tms^{c}	167		[143]
	Tms	Tms	Tms^{c}	165		[143]
	Tms	Tms	Tms^{c}	170		[143]

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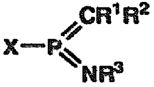
[a] R^4 = Tms unless otherwise specified; [b] $R^4 = Me_2{}^{t}BuSi$; [c] $A = (Tms_2C=)_2P$.

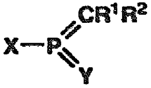
4.2. Methylene(imino)phosphoranes



X	R^1	R^2	R^3	^{31}P NMR (δ_P, ppm)	X-ray	Ref.
^{t}Bu	Tms	Tms	Ar*	164.5	+	[144]
Tms_2CH	H	Tms	Tms	145.3;129.0		[67]

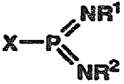
Ph	Tms	Tms	Ar*	130.2	+	[144]
2,6-Me$_2$C$_6$H$_3$	9-Fluorenylidene		Ph	17.6		[145]
Mes	Ph	Ph	Ph	18.8		[85]
Mes	Tms	Tms	Ar*	101.5	+	[144]
Mes	Tms	Tms	Tms	120.0		[146]
Ar*	H	Tetrahydrofuran-2-yl	Ar*	75.0		[22]
Ar*	Cl	Tms	Ar*	86.2	+	[22]
Ar*	Cl	Cl	Ar*	70.1		[22]
^{i}Pr$_2$N	H	^{t}Bu	^{t}Bu	77.2		[82]
Tmp	H	Tms	Tms	100.6		[147]
Tmp	Tms	Tms	Tms	85.2		[21]
^{t}Bu(Tms)N	Me	Me	Tms	86.8		[112]
Tms$_2$N	H	Tms	^{t}Bu	56.3		[35]
Tms$_2$N	H	Me	Tms	98.1;105.5		[112]
Tms$_2$N	H	^{t}Bu	Tms	81.5		[112]
Tms$_2$N	H	Tms	Tms	102.6		[148]
Tms$_2$N	Me	Me	Tms	86.4		[112]
Tms$_2$N	Me	Et	Tms	83.9;83.6		[112]
Tms$_2$N	Me	^{i}Pr	Tms	83.1;82.2		[112]
Tms$_2$N	Me	^{t}Bu	Tms	75.4		[112]
Tms$_2$N	Tms	Tms	Tms	90.5		[21]
^{t}Bu(Tms)N	Tms	Tms	^{t}Bu	84.8		[21]

4.3. *Methylene(oxo-, thioxo- or selenoxo)phosphoranes*



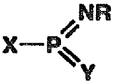
X	Y	R^1	R^2	^{31}P NMR (δ_P, ppm)	X-ray	Ref.
Ar*	O	Ph	Tms	153.7	+	[88]
Ar*	O	Tms	Tms	161.6		[149]
2,6-Me$_2$C$_6$H$_3$	S	Ph	Ph	140.5		[150]
Mes	S	Tms	Tms	190.9	+	[148,151]
Ar*	S	Tms	Tms	204.6		[149]
Tms$_2$N	S	H	Tms	185.4		[152]
2,6-Me$_2$C$_6$H$_3$	Se	Ph	Ph	125.7		[153]
Ar*	Se	Tms	Tms	195.2		[149]
Tms$_2$N	Se	H	Tms	172.4		[152]

4.4. Bis(imino)phosphoranes



X	R^1	R^2	^{31}P NMR (δ_P, ppm)	X-ray	Ref.
^{n}Bu	^{t}Bu	Ar*	62.6		[36]
Tms$_2$CH	Tms	Tms	83.4		[119]
C$_5$Me$_5$	^{t}Bu	Ar*	59.9		[36]
Mes	^{t}Bu	Ar*	47.7		[89]
Mes	Tms	Ar*	66.1	+	[89]
Ar*	EtOOC	EtOOC	104		[70]
Ar*	H	Ar*	45.8	+	[78]
^{t}BuNH	^{t}Bu	Ar*	39.5		[126]
Ar*NH	^{t}Bu	Ar*	34.3		[36]
Ar*NH	Ar*	Ar*	22.1		[126]
^{i}Pr$_2$N	^{t}Bu	^{t}Bu	50.5		[119]
(CH$_2$)$_5$N	^{t}Bu	Tms	52.0		[154]
(CH$_2$)$_5$N	Tms	Tms	47.2		[154]
^{t}Bu(Tms)N	^{t}Bu	Tms	53.1		[119]
^{t}Bu(Tms)N	^{t}Bu	^{t}Bu	35.2		[154]
Tms$_2$N	Me	Tms	46.7		[119]
Tms$_2$N	^{t}Bu	^{t}Bu	52.6		[119]
Tms$_2$N	^{t}Bu	Tms	51.5		[119,154]
Tms$_2$N	Tms	Tms	52.0	+	[119,154]
^{t}BuS	^{t}Bu	Ar*	27.4		[36]
^{t}Bu2P	Et$_3$C	Ar*	59.1	+	[36]
Ph$_2$P	Ad	Ar*	57.7		[155]
Cl	Ar*	Ar*	−18.5		[78]
Br	Ar*	Ar*	−30.2		[78]
I	Ar*	Ar*	−42.9	+	[78]

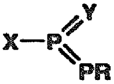
4.5. Imino(oxo-, thioxo- or selenoxo)phosphoranes



X	Y	R	^{31}P NMR (δ_P, ppm)	X-ray	Ref.
Ar*	O	^{t}Bu	93.5		[95]
Ar*	O	Ar*	34.2	+	[35]
Ph	S	Ar*	158		[42]

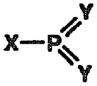
Mes	S	Ar*	162		[42]
2,4,6-^{i}Pr$_3$C$_6$H$_2$	S	Ar*	163		[42]
Ar*	S	^{t}Bu	162.4		[95]
(Me$_2$N)$_3$P=C(Tms)	S	Tms	171.2		[43]
^{t}Bu(Tms)N	S	^{t}Bu	136		[156]
Tms$_2$N	S	^{t}Bu	135		[157]
[CH$_2$(N^{t}Bu)]$_2$P(^{t}Bu)N	S	Tms	61.0	+	[158]
Ph	Se	Ar*	161		[42]
Mes	Se	Ar*	156		[42]
Ar*	Se	^{t}Bu	154.8		[95]
(Me$_2$N)$_3$P=C(Tms)	Se	Tms	159.1		[43]
^{t}Bu(Tms)N	Se	^{t}Bu	118.7		[159]
Tms$_2$N	Se	^{t}Bu	120		[157]

4.6. *Imino(oxo-, thioxo)phosphinidenephosphoranes*



X	Y	R	^{31}P NMR		X-ray	Ref.
			(δ_P, ppm)	$^1J_{PPb}$ (Hz)		
Me	NAr*	Ar*	60.4 176.5	741.9		[71]
^{n}Bu	NAr*	Ar*	66.4 186.6	762.1		[71]
^{t}Bu	NAr*	Ar*	67.2 205.9	819.5	+	[71]
Ar*	O	Ar*	69.8	683.6		[160]
Ar*	S	Ar*	247.8 255.8	629.9	+	[161]
2-Me-4,6-(^{t}Bu)$_2$C$_6$H$_2$	S	Ar*	249.1 239.3	625		[161]
Mes	S	Ar*	241.9 226.7	604.3		[161]
Ar*	S	Ar*H · Cr(CO)$_3$	254.1 247.7	666.5		[161]

4.7. Dioxo-, dithioxo-, or diselenoxophosphoranes



X	Y	^{31}P NMR (δ_P, ppm)	X-ray	Ref.
Ar*	O	13[a]		[162]
2,6-^{t}Bu$_2$–4-MeC$_6$H$_2$	S	285.2		[58]
Ar*	S	295.3	+	[121,163,164]
2,6-(CF$_3$)$_2$C$_6$H$_3$	S			
2,4-^{t}Bu$_2$–6-(Me$_2$N)C$_6$H$_2$	S	170.6		[125]
2,4-^{t}Bu$_2$–6-RC$_6$H$_2$ (R=CH$_2$NMe$_2$)	S	149.6	+	[62,63]
2,4-^{t}Bu$_2$–4-R–C$_6$H$_2$ (R=CMe$_2$NMe$_2$)	S	150.5		[63]
2,4-^{t}Bu$_2$–4-RC$_6$H$_2$ (R=CMe$_2$CH$_2$NMe$_2$)	S	135.7	+	[63]
2,4-^{t}Bu$_2$–6-(MeO)C$_6$H$_2$	S	280.1		[65]
Ph$_3$P=C(Et)	S	—		[55]
Ph$_3$P=C(Ph)	S	—	+	[55]
Ar*	Se	273.0		[165]
2,4-^{t}Bu$_2$–6-(Me$_2$N)C$_6$H$_2$	Se	149.6		[64]
2,4-^{t}Bu$_2$–6-R–C$_6$H$_2$ (R=piperidino)	Se	147.7	+	[64]
2,4-^{t}Bu$_2$–6-RC$_6$H$_2$ (R=CH$_2$NMe$_2$)	Se	123.6		[64]
2,4-^{t}Bu$_2$–6-RC$_6$H$_2$ (R=CMe$_2$CH$_2$NMe$_2$)	Se	108.7		[64]

[a] The chemical shift is highly questionable.

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