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PHOSPHAALKYNES AND PHOSPHAALKENES

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CONTENTS

1. INTRODUCTION

Investigation of unstable and metastable compounds is a basis for the development of many high-priority branches of modern chemistry, among which we find the recent emergence of the chemistry of doubly and triply bonded trivalent phosphorus.[1,2] Over a comparatively short period, this field has developed from theoretical consideration of hypothetical structures and experimental studies of ephemeral or "illusive" molecules,[3] to the synthesis of stable compounds with a $p\pi$-hybridized phosphorus atom.

The first experimental evidence in favour of $(p—p)_\pi$-bonds involving trivalent phosphorus was obtained by Gier in 1961 who revealed the formation of rather unstable phospha-acetylene HCP by passing PH_3 through an electric arc between graphite electrodes.[4] The emergence of the chemistry of stable compounds of silicon and phosphorus in a low coordination state is associated with pioneer studies by Dimroth (1964),[5] Märkl (1966),[6] Melnikov and Shvetsov-Shilovskii (1967)[7] on the synthesis and the analysis of two-coordinate phosphorus derivatives with a delocalized $(C2p\text{—}P3p)_\pi$-bond. The next step was the synthesis of an acyclic two-coordinate phosphorus compound with a N—P=N group.[8,9] In 1976, Nixon *et al.* succeeded in obtaining a series of short-lived phospha-alkenes by eliminating hydrogen halides from alkyl halophosphines or (haloalkyl)phosphines.[10,11] At the same time Becker reported on the synthesis of the first stable acyclic compound with localized PC-double bond.[12] The first examples of stable phosphaalkynes were obtained five years later.[13–16] These works triggered a breakthrough in the field of unsaturated trivalent phosphorus compounds with phosphorus-element $p\pi$-bonds.

The above results appeared to be a substantiation of novel theoretical concepts developed in the mid-sixties and early seventies. They were also further reflected in three approaches to the stabilization of the $p\pi$-hybridized phosphorus state. Chronologically, the first approach is of thermodynamic origin and consists of an increase in the $(p\text{—}p)_\pi$-bond stability when this bond is included in a conjugate system. Stabilization of this type is observed in phosphamethine cyanine cations, phosphabenzenes and diazaphospholes.[17–23] The second approach aims at increasing the efficiency of overlapping the $3p$-orbital of phosphorus and $2p$-orbital of the element at the expense of generating a positive charge on the phosphorus atom.[24–27] The third and a most rewarding approach is the kinetic stabilization of the $p\pi$-bond based on spatial screening effects.[28–30] The wide use of the latter principle is a typical feature characterizing state of the art research in the field of low-coordinate phosphorus compounds.[31–34]

Phosphaalkynes (R—C≡P) and phosphaalkenes ($RP{=}CR_2$) occupy a separate place in the chemistry of the $p\pi$-hybridized phosphorus. Being the heteroanalogues of nitriles and azomethines and, thus, genetically connected with acetylenes and alkenes, these are further links in the chain coupling inorganic and organic chemistry. The present Report attempts, besides considering the common methods of synthesis and properties of compounds with (P≡C)- and (P=C)-bond, to demonstrate the specificity of $p\pi$-bonds formed with participation of the elements of the third and lower rows of the main groups of the Periodic Table on the one hand, and their common character with classical $p\pi$-systems, on the other.

The Report covers the literature dated prior to the middle of 1987. Earlier findings related to the initial stages of studies on the chemistry of phosphaalkynes and phosphaalkenes can be found in refs 35–38. Certain aspects of the problem are considered in concluding articles.[39–48] Taking into account the fact that structural and spectroscopic problems connected with PC-multiple bonds were discussed in detail elsewhere,[10,36,48b,49–51] these are not included in the present Report.

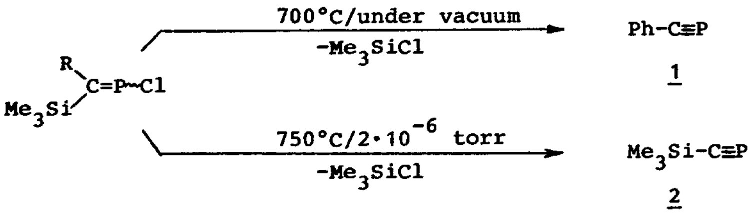
2. FORMATION OF PHOSPHORUS—CARBON $(p\text{—}p)_\pi$-MULTIPLE BONDS

2.1. 1,2-*Elimination reactions*

Like alkenes, the most significant preparative pathway for the formation of C≡P and C=P bonds includes 1,2-elimination reactions. Here, it is worthwhile to note that practically all known compounds having PC-triple bond were obtained by reactions of this type (Table 1).

Simplest phosphaalkynes are produced by vapor phase pyrolysis (700–1000°C) of organophosphines[52–58] or low-temperature dehydrohalogenation of (haloalkyl)phosphines on the surface of strong bases such as NaOH or KOH.[59,60] Owing to a high level of impurities and rather low thermal stability, the products of these reactions are normally hard to obtain in their pure state. These were characterized, particularly by Kroto, Nixon and co-workers, by microwave, photoelectron and NMR spectra. A brief account is given in refs 10, 11, 15.

Evidence on the stability of simple phosphaalkynes is rather incomplete. This is explained by



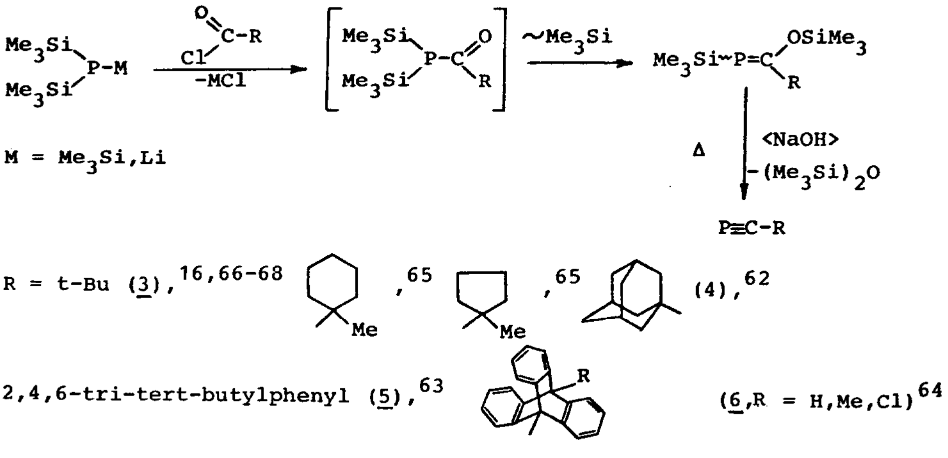
Scheme 1.

the purity of the compounds under study. Thus, phosphaethyne HCP obtained from CH_3PCl_2 flash vacuum thermolysis followed by HCl removal on solid base is characterized by a 5 min half-life period at $-10°C$,[61] whereas according to Gier,[4] this compound is polymerized at temperatures exceeding $-120°C$. Phosphapropyne $CH_3C{\equiv}P$ appears to be more stable than was reported earlier.[52] In the absence of HCl, it may be kept in solution at room temperature for three days without noticeable decomposition.[61]

Successes in phosphaalkene synthesis are associated with application of elimination reactions involving stable compounds of two-coordinate phosphorus. In 1981 Appel *et al.* established that thermally induced elimination of Me_3SiCl from the vicinal chloro- and trimethylsilyl-substituted phosphaalkenes led to phosphaalkynes in almost quantitative yield (Scheme 1). Phosphaalkyne **1** only exists at low temperatures in its monomeric form and above $-50°C$ slow decomposition takes place.[13] The silyl-substituted phosphaalkyne **2** is more stable (half-life at 20°C *ca* 50 min).[14]

Becker *et al.* suggested, from a preparative view-point, the most significant route to phosphaalkynes by NaOH-promoted elimination of hexamethyldisiloxane from phosphaalkenes $Me_3Si{-}P{=}C(OSiMe_3)R$.[16] This approach was applied successfully for the synthesis of a wide variety of stable phosphaalkynes (Scheme 2).[62–68]

Kroto and Nixon with co-workers[69] were the first to reveal that 1,2-elimination reactions may be used to form $(P{=}C)_\pi$-bonds. They found that at temperatures close to 1000°C pyrolysis of $(CH_3)_2PH$, CH_3PCl_2 and CF_3PH_2 resulted in the formation of transient species of the type $X{-}P{=}CR_2$. Later, pyrolysis techniques[70–73] or base-induced dehydrohalogenation[74–77] were used



Scheme 2.

Table 1. Phosphaalkynes, R-C≡P

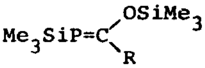
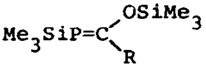
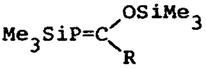
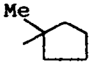
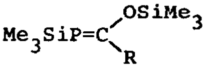
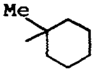
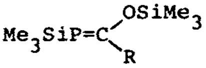
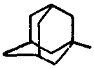
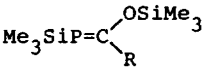
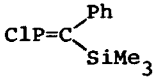
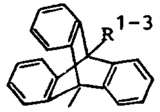
R	Method[a]	Starting Reagent	Yield (%)	Reaction Conditions	Comment	Ref.
H	A	$MePCl_2$	-	1000°C, $2\cdot10^{-5}$torr	unstable at ordinary conditions	54,55, 61
F	B	CF_3PH_2	-	20°C, 30 torr	-"-	59,60
Me	A	$MeCH_2PCl_2$	-	900°C, 0.05 torr	-"-	52,53, 61
F_3C	A	$CF_3CF_2PH_2$	-	-	-"-	58
NC	A	HCP, NCN_3	-	700°C, $5\cdot10^{-5}$ torr	-"-	54
Me_3Si	A	$ClP{=}C(SiMe_3)_2$	100	750°C, $2\cdot10^{-6}$ torr	half-life-time 50 min at 20°C	14
Me_2CH	C	 $Me_3SiP{=}C(OSiMe_3)R$	63	140-160°C, 0.75 torr, NaOH	decomposes above -30°C	65
Bu^tCH_2	C	 $Me_3SiP{=}C(OSiMe_3)R$	75	140-160°C, 0.75 torr, NaOH	-"-	65
Bu^t	C	 $Me_3SiP{=}C(OSiMe_3)R$	76	20°C,DME, NaOH	stable at 20°C, b.p. 61°C	16
	C	-"-	96	160°C, 0.45 torr, NaOH		67
	C	 $Me_3SiP{=}C(OSiMe_3)R$	66	150°C, NaOH	stable at 20°C	65
	C	 $Me_3SiP{=}C(OSiMe_3)R$	76	120°C, 11 torr, NaOH	-"-	65
	C	 $Me_3SiP{=}C(OSiMe_3)R$	83	20°C,DME, NaOH	thermally stable crystalline substance	62
	C	-"-	71	90°C, $[Bu_4N]F$		62
R^1-Tript[b]	C	R^1-TriptCOCl, $(Me_3Si)_3P$	12-18		stable at 20°C	64
R^2-Tript[b]	C	R^2-TriptCOCl, $(Me_3Si)_3P$	24-30		-"-	64
R^3-Tript[b]	C	R^3-TriptCOCl, $(Me_3Si)_3P$	15-20		-"-	64

Table 1. - Continued

R	Method[a]	Starting Reagent	Yield (%)	Reaction Conditions	Comment	Ref.
$H_2C{=}CH$	A	$H_2C{=}CH{-}CH_2PCl_2$	-	1000°C, 30-60 torr	unstable at ordinary conditions	56
$HC{\equiv}C$	A	$HC{\equiv}C{-}CH_2Cl, PCl_3$	-	1100°C, 30-60 torr	-"-	57
Ph	A	 $ClP{=}C(Ph)(SiMe_3)$	100	700°C under vacuum	half-life-time 7 min at 0°C	13,66
Ttb[c]	C	TtbCOCl, $(Me_3Si)_3P$	10-15	20°C, DME	thermally stable crystalline substance	63

[a] A - Gas phase pyrolysis, B - elimination of hydrogen halides with potassium or sodium hydroxide, C - base induced elimination of siloxane.

[b] R^{1-3}-Tript = 

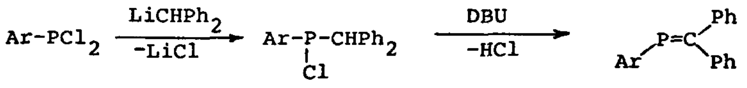
, R^1 = H, R^2 = Me, R^3 = Cl .

[c] Ttb = 2,4,6-tri-tert-butylphenyl

for generation of a large number of short-lived phosphaalkenes, some of which are listed below. The review by Kroto contains details of other unstable phosphaalkenes.[10]

$HP{=}CH_2$	$Me{-}P{=}CH_2$	$NC{-}P{=}CH_2$
Ref.69,70	Ref. 71	Ref. 72
$F{-}P{=}CH_2$	$Cl{-}P{=}CH_2$	$Br{-}P{=}CH_2$
Ref.10	Ref.69	Ref.10
$H{-}P{=}CF_2$	$F_3C{-}P{=}CF_2$	
Ref.60,69	Ref.46,73-77	

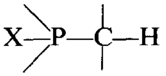
The first preparative synthesis of stable phosphaalkenes, with 1,2-elimination reaction as a key step, was achieved in 1978 by Bickelhaupt and collaborators (Scheme 3).[78-80] Steric protection of the reactive phosphorus–carbon double bond is the most important factor determining the stability of the triaryl-substituted phosphaalkenes **7** and **8**.



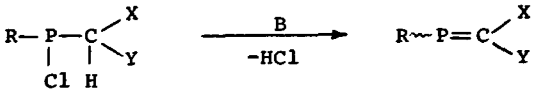
7 Ar = $2,4,6\text{-}Me_3C_6H_2$, 63%

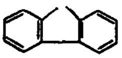
8 Ar = $2,6\text{-}Me_2C_6H_3$, 83%

Scheme 3.

Detailed analysis of 1,2-elimination reactions in the  $\mathrm{X{-}P{-}C{-}H}$ group revealed the basic requirements of the dehydrohalogenation reagent and halophosphines. Besides 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU),[81–83] phosphaalkene synthesis may involve 1,4-diazabicyclo[2.2.2]octane (DABCO),[14,84–86] lithium or sodium bis(trimethylsilyl)amides[87–94] and, in some cases, triethylamine.[84,87,90] Alkyl halophosphines used in phosphaalkene synthesis should contain a sufficiently acid α-proton and have substituents which provide kinetic or thermodynamic stabilization of the forming (P=C)-bond. Acidity decrease of the α-hydrogen atom in alkyl halophosphines R—P(Hlg)—CHXY results in nucleophilic substitution of halogen at the phosphorus atom instead of the elimination reaction. Dehydrohalogenation is also favoured by spatial shielding of the phosphorus centre.[89]

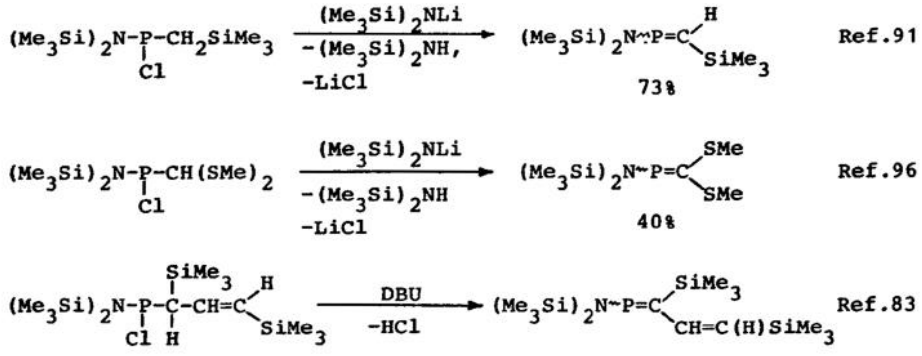
Various P-alkyl(aryl)phosphaalkenes were obtained by dehydrochlorination of chlorophosphines meeting the above requirements (Scheme 4). Similarly P-(amino)phosphaalkenes—the phosphorous analogues of enamines—were obtained from amino(chloro)phosphines (Scheme 5).



R	Ref.	X	Y	Ref.
t-Bu	87,89,92,96	Ph	Ph	80
$2,6\text{-}Me_2C_6H_3$	80,81	Me_3Si	H	89
$2,4,6\text{-}Me_3C_6H_2$	80,81,95	Me_3Si	Me_3Si	95
Ttb	82,97			81
		AlkS	AlkS	92,96
		MeOOC	MeOOC	87
		Ph	MeOOC	87
		Cl	Cl	97
		H	Ttb(Hlg)P	82

Ttb = $2,4,6\text{-}t\text{-}Bu_3C_6H_2$

Scheme 4.



Scheme 5.

Sodium bis(trimethylsilyl)amide reacts with alkyl dichlorophosphines as a nucleophile and as a dehydrohalogenating agent. The reactions proceed in the molar ratio of 1 : 2 and lead to formation of P-(amino)methylenephosphines (Scheme 6).[89,94]

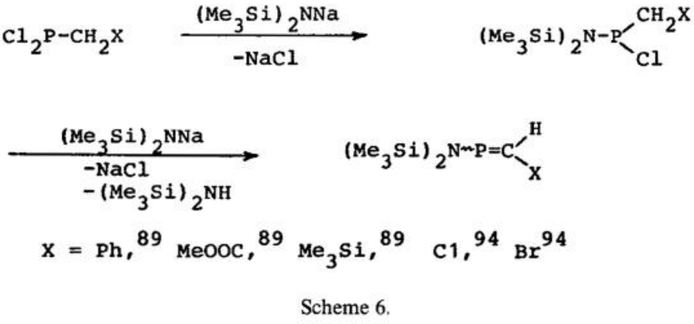
The first stage of the reaction between Hlg_2PCHlg_2 and $(Me_3Si)_2NNa$ is a nucleophilic substitution. On addition of a further mole of the base to the reaction mixture then phosphaalkenes of the type **9** have been isolated.[90,94]

The reaction of a more basic *t*-Bu(Me_3Si)NLi with dichloromethyl–dichlorophosphine (1 : 1, −70°C) gives rise to the phosphaalkene **10**.[94] Such a result is obviously connected with the fact that dehydrochlorination of the intermediate chlorophosphine is much faster than its formation. Treatment of Cl_2PCHCl_2 with triethylamine gives a 73% yield of 1,3-diphosphacyclobutane **11** which is obviously a product of the unstable phosphaalkene $ClP{=}CCl_2$ dimerization (Scheme 7).[90]

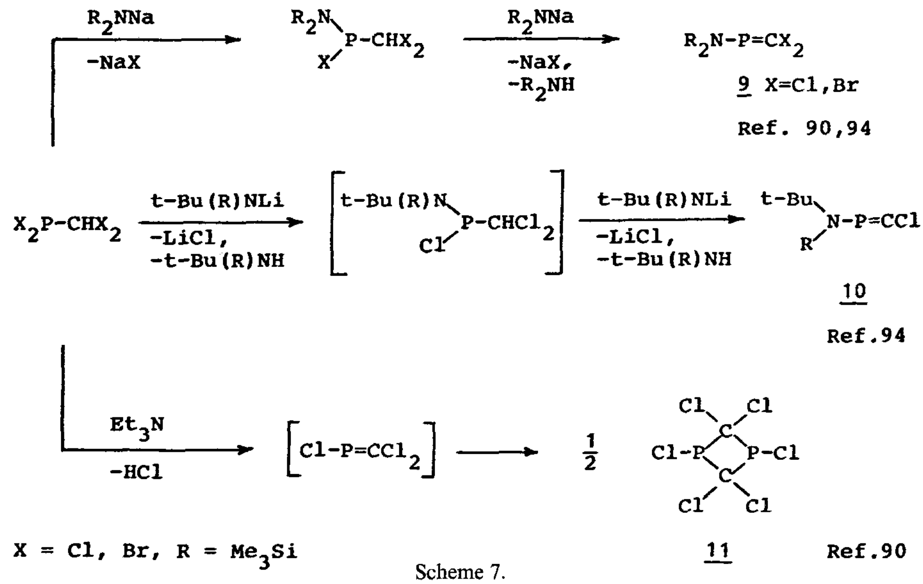
Tetrachloromethylenediphosphine reacts with two equivalents $(Me_3Si)_2NNa$ with the formation of **12** whose further interaction with the base leads to P-(amino)methylenephosphine **13**.[88] The formation of 1,3-diphosphaallene **14** in this reaction was not observed. This opportunity was also not realised in the dehydrohalogenation of the methylenediphosphine **15**. The reaction is accompanied both by nucleophile substitution and dehydrochlorination, and by 1,3-migration of tert-butyl group. As a result, the phosphaalkene **16** is formed (Scheme 8).[88,89]

Reactions of certain dihalophosphines Hlg_2PCHR_2 with DABCO or triethylamine give rise to P-halogenated methylenephosphines, $Hlg{-}P{=}CR_2$, which are valuable key compounds for the preparation of a large variety of novel phosphaalkenes (Table 2).

Dehydrohalogenation of alkyl halophosphines is also a version of a PC-double bond formation based upon 1,2-elimination reactions. The synthesis of phosphaalkenes is sometimes more

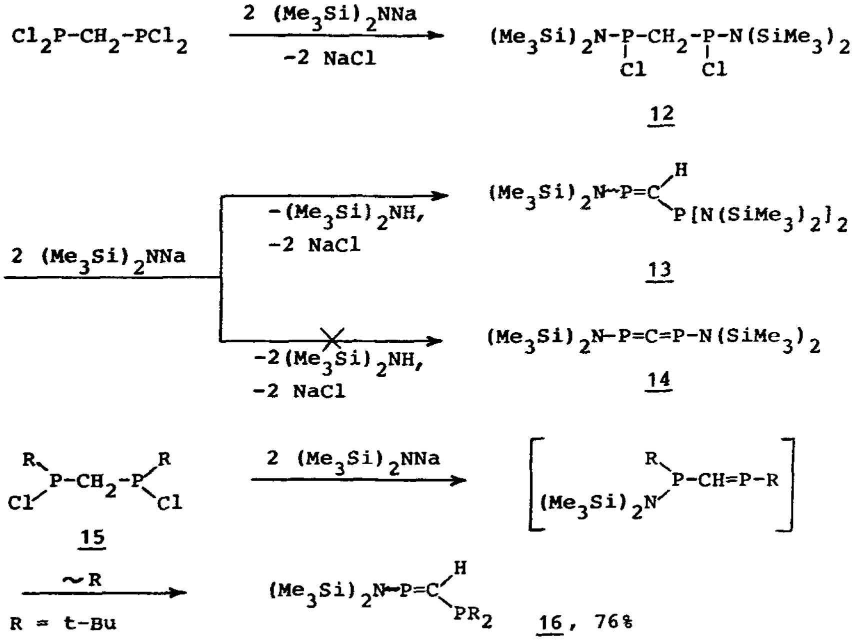


Scheme 6.

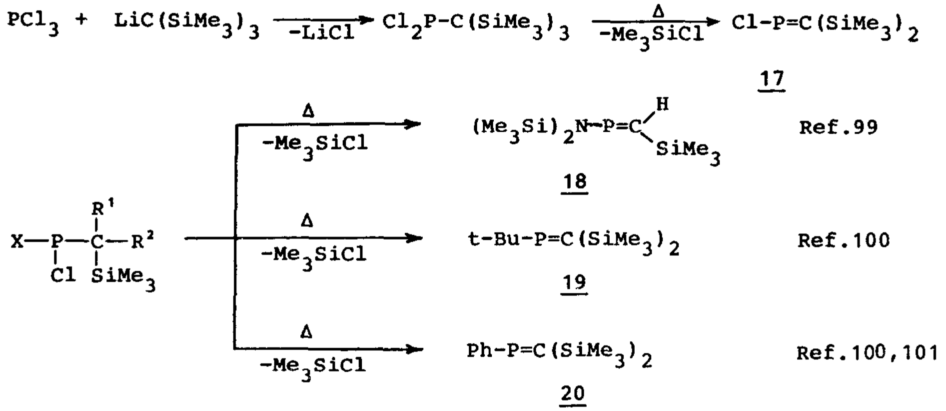


Scheme 7.

effective where the key stage is either the thermal elimination of Me_3SiCl or the base-induced elimination of siloxanes. The cleavage of Me_3SiCl or $(Me_3Si)_2O$ in the group, —P(X)—C($SiMe_3$)— (X = Cl, Me_3SiO), is activated by the energy gained from Si—Cl or Si—O bond formation and the reduction of steric hindrance at the phosphorus atom by cleavage of the bulky Me_3Si-group. The latter circumstance is essential because sterically unhindered halophosphines, containing Hlg—P—C—$SiMe_3$ group, are thermally quite stable. For instance, among the compounds $Me_3SiCH_2PCl_2$, $(Me_3Si)_2CHPCl_2$ and $(Me_3Si)_3CPCl_2$ only the last one splits off Me_3SiCl under sufficiently gentle conditions (100–120°C, 0.1 torr), giving phosphaalkene **17**.[98] Syntheses of com-



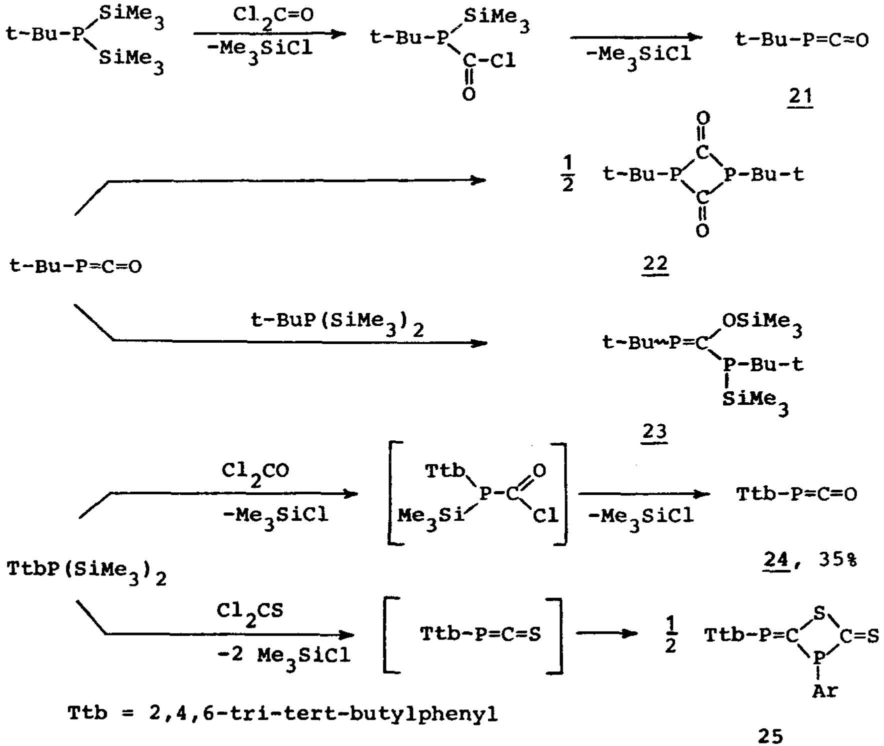
Scheme 8.



Scheme 9.

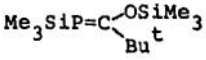
pounds **18**,[99] **19**[100] and **20**[100] may be examples of the use of chlorosilane elimination reactions to obtain P-amino- and P-organo-substituted phosphaalkenes (Scheme 9).

The interaction of *t*-BuP(SiMe$_3$)$_2$ with phosgene yields *t*-butyl phosphaketene **21** which is stable in solutions and at low temperatures. When the temperature exceeds −60°C, then it dimerizes yielding the 1,3-diphosphetane **22**. The presence of silylphosphine excess leads to the phosphaalkene **23**.[102] Shielding the phosphorus centre with the extremely bulky 2,4,6-tri-*t*-butylphenyl substituent yielded the phosphaketene **24**, which is stable at room temperature.[103] Similar reaction with thiophosgene produces **25** (Scheme 10). The very reactive Ttb—PCS could be regenerated from **25** by photolysis and trapped with nucleophiles by addition across the C=S double bond.[104]



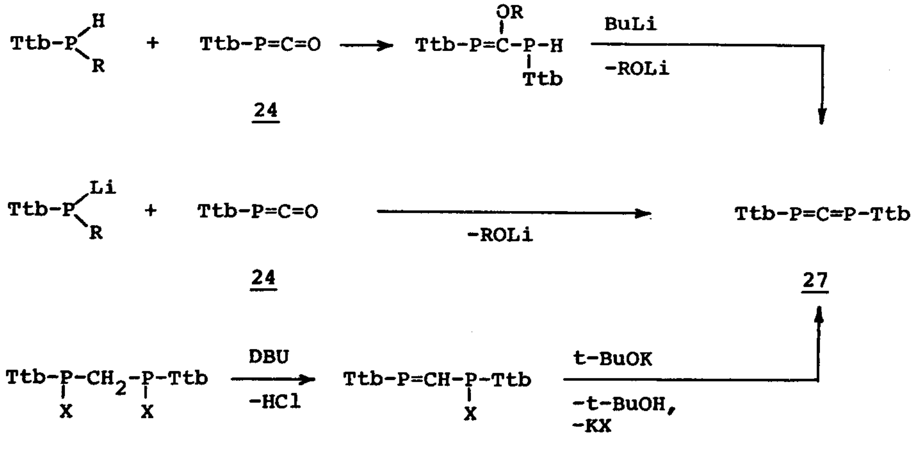
Scheme 10.

Table 2. P-(Halogeno)phosphaalkenes

Phosphaalkene	Method[a]	Phosphorus Substrate	Reagent and Preparative Conditions	Yield (%)	Comment	Ref.
$F-P=C(SiMe_3)_2$	C	$Cl-P=C(SiMe_3)_2$	AgF, ether, 0°C	40	slowly decomposes above 0°C	331
	C	$Cl-P=C(SiMe_3)_2$	$AgBF_4$, CH_2Cl_2, 20°C	38		332
$Cl-P=C(H)Ph$	A	$PhCH_2PCl_2$	DABCO, ether, 20°C	-	unstable at room temperature	84
$Cl-P=C(H)SiMe_3$	A	$Me_3SiCH_2PCl_2$	DABCO, ether, 20°C	-	-"-	85
$Cl-P=CPh_2$	A	Ph_2CHPCl_2	Et_3N, 20°C	-	-"-	84
$Cl-P=C(Ph)SiMe_3$	A	$Me_3Si(Ph)CHPCl_2$	DABCO, ether, 20°C	54	stable at room temperature	84
$Cl-P=C(SiMe_3)_2$	A	$(Me_3Si)_2CHPCl_2$	DABCO, ether, 20°C	57	-"-	85
	B	$(Me_3Si)_3CPCl_2$	200°C, 0.01 torr	74		98
$Cl-P=C(OSiMe_3)Bu^t$	C	 $Me_3SiP=C(OSiMe_3)(Bu^t)$	C_2Cl_6, toluol, 110°C	65	-"-	167
$Cl-P=C(SiMe_3)CO_2Et$	A	$EtO_2C(Me_3Si)CHPCl_2$	DABCO, ether, -78°C	-	decomposes above -40°C	86

Cl-P=C(SMe)$_2$	A	(MeS)$_2$CHPCl$_2$	Et$_3$N, ether, -10°C	90-95	stable in solution up to 0°C	96
Cl-P=C(SBu^i)$_2$	A	(Bu^{i}S)$_2$CHPCl$_2$	Et$_3$N, ether, -10°C	90-95	-"-	96
Br-P=C(Ph)SiMe$_3$	A	Me$_3$Si(Ph)CHPBr$_2$	DABCO, ether, 20°C	57	stable at room temperature	85
Br-P=C(SiMe$_3$)$_2$	C	Cl-P=C(SiMe$_3$)$_2$	Me$_3$SiBr, 20°C	50	-"-	331
	A	(Me$_3$Si)$_2$CHPBr$_2$	DABCO, ether, 20°C	63		85
I-P=C(Ph)SiMe$_3$	A	Me$_3$Si(Ph)CHPI$_2$	DABCO, ether, 20°C	-	stable at room temperature	85
I-P=C(SiMe$_3$)$_2$	C	Cl-P=C(SiMe$_3$)$_2$	Me$_3$SiI, 20°C	69	-"-	331

[a] A - Dehydrohalogenation with base, B - thermal elimination of chlorotrimethylsilane, C - substitution at the dicoordinated phosphorus atom.



Ttb = 2,4,6-tri-tert-butylphenyl, R = Me_3Si,[106] t-$BuMe_2Si$,[107,108]
X = Cl, Br [82,105]

Scheme 11.

A number of phosphaallenes have recently been prepared by 1,2-elimination reactions. Diphosphaallene **27** has been prepared independently by three groups. Appel[106] and Yoshifuji[107] used lithium silanolate elimination and Karsch[82] eliminated potassium chloride (Scheme 11).

The addition of lithium 2,4,6-tris-*t*-butylphenylphosphide to diphenylketene and subsequent 1,2-elimination results in the formation of the 1-phosphaallene **28a**.[109–111] Appel has reported an independent synthesis of **28** using the phosphaketene **24** by a variation of the Wittig reaction.[106,112] Attempts to synthesize 1-phosphaallene $PhP{=}C{=}CPh_2$ by an elimination of disiloxane from the addition product diphenylketene and disilylphenylphosphine led to the dimeric phosphaallene **29**[112] (Scheme 12).

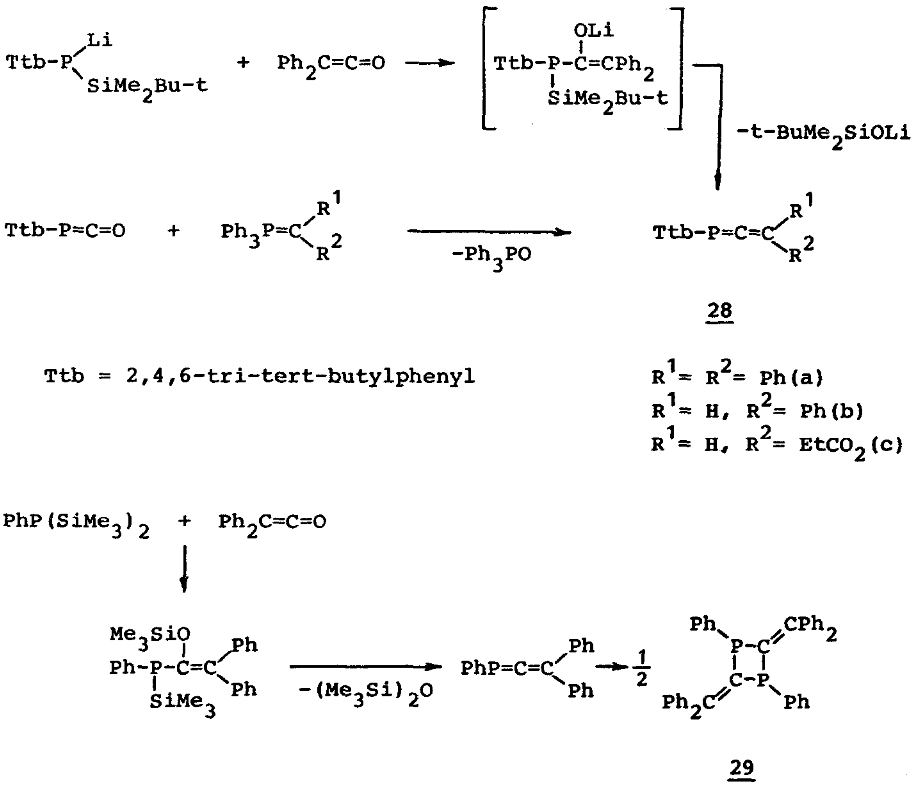
The 1,2-elimination reaction is a key stage in the synthesis of 1-phospha-1,2,3-butatrienes **30**.[113]

(Iminomethylene)phosphines were first obtained by NaOH-promoted elimination of hexamethyldisiloxane from phosphaureas **31**.[114–116] One of the most stable compounds of this type is the di-*t*-butyl-substituted iminomethylphosphine **32a**. The cleavage of hexamethyldisiloxane from phosphaurea **31d** ($R^1 = R^2 = Ph$) leads to the 1,3-diphosphetane **33**. Under conditions of flash vacuum pyrolysis (400°C, 10^{-5} torr), the latter dissociates with the formation of monomeric (iminomethyllene)phosphine **32d**, stable at −196°C but dimerizing at temperatures above −55°C.[117] Catalyzed by small amounts of solid sodium hydroxide, the adducts **31** formed from $PhCH_2P(SiMe_3)_2$ or $EtP(SiMe_3)_2$ and PhNCO, react at 20°C slowly giving hexamethyldisiloxane and oligomeric (phenyliminomethylene)phosphines.[118] In the reaction of $PhP(SiMe_3)_2$ with $ArN{=}CCl_2$, only dimeric structure products were obtained.[119] Later, the (iminomethylene) phosphine **35** was synthesized by reaction of lithium 2,4,6-tri-*t*-butylphenylphosphide **35** with PhNCO.[109]

2.2. *Condensation reactions*

Phosphaalkene synthesis by condensation is a two-stage process of which the final stage is a 1,2-elimination reaction. This results in the formation of a (P=C)-bond. These conversions are distinguished as a separate group because they cannot be realized step by step.

Condensation reactions are widely used for the synthesis of cyclic systems of two-coordinate



28

Ttb = 2,4,6-tri-tert-butylphenyl

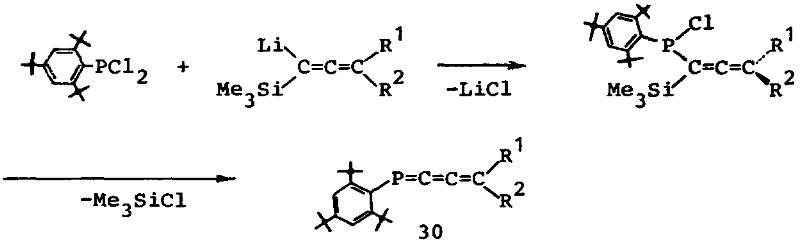
$R^1 = R^2 =$ Ph(a)
$R^1 =$ H, $R^2 =$ Ph(b)
$R^1 =$ H, $R^2 = EtCO_2$(c)

29

Scheme 12.

phosphorus. (P=C)-Bond formation in these conversions is favoured by its inclusion in a conjugated system.[120–125]

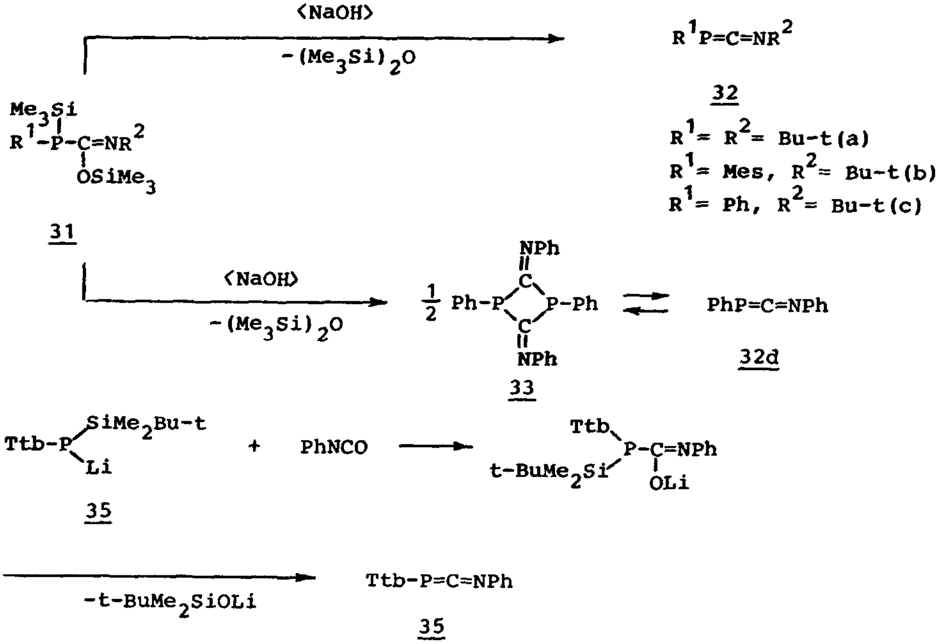
The simplest route for the synthesis of compounds with (N=C)-group is the condensation of carbonyl compounds with amines which is catalyzed by acids.[126] A similar approach may be used for compounds with a (P=C)-group in those cases where the phosphaalkene is sterically hindered and shows low reactivity. This is illustrated by phosphaalkene synthesis by the condensation of 2,4,6-



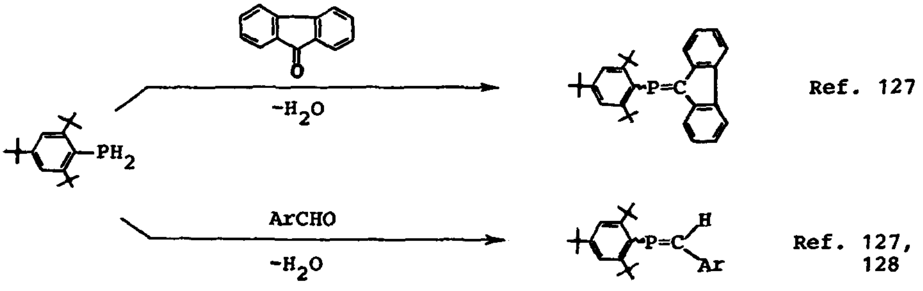
30

$R^1 = R^2 = Me_3Si$
$R^1 = R^2 =$ Ph
$R^1 =$ Me, $R^2 = Me_3Si$

Scheme 13.



Scheme 14.



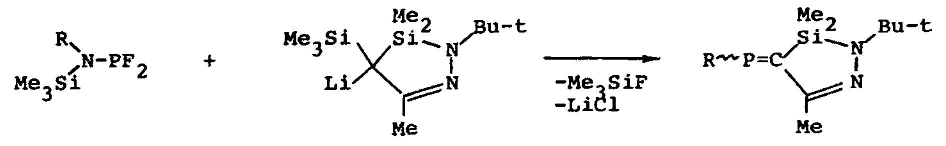
Scheme 15.

tri-*t*-butylphenylphosphine with fluorenone and aromatic aldehydes in the presence of catalyzing quantities of $BF_3 \cdot Et_2O$ or *p*-toluenesulfonic acid (Scheme 15).[127,128]

Much wider synthetic abilities are shown by the reactions of phosphines and metal phosphides with highly reactive masked carbonyl compounds. For example, amide acetals condense with arylphosphines forming C-(dialkylamino)methylenephosphines.[129,130] Alkylphosphines are inert with respect to amide acetals. However, sodium phosphides readily react with carbeniumtetrafluoroborates giving phosphaalkenes[131–134] (Scheme 16).

When dimethylformamide, *t*-butanol or benzophenone are treated with bis(trimethylsilyl)phosphines or lithium trimethylsilylphosphides, phosphaalkenes and disiloxane or Me_3SiOLi are produced by addition and subsequent elimination (Scheme 17). The formation of strong Si—O bonds must be taken to be the driving force of these reactions.

A one-pot process for the production of the phosphaalkenes **36** has been reported.[140,141]



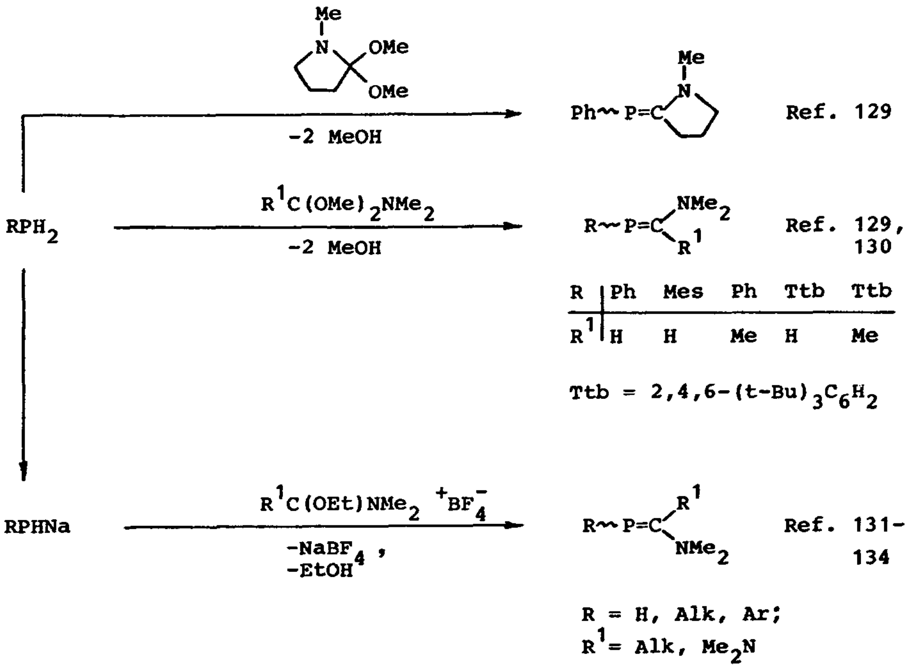
36 R=Me$_3$Si, t-Bu

High reactivity of α,α-difluoroalkylamines and high affinity of silicon for fluorine ensure adequate yields of C,C-bis(dialkylamino)methylenephosphines **37** by the reaction of silylated phosphines with bis(dialkylamino)difluoromethanes.[142,143] The method is particularly suitable for obtaining phosphaalkenes **38** with a two-coordinate phosphorus atom in a Si—P═C triad. Unlike fluorinated analogues, compounds R^1(Me$_2$N)CCl$_2$ react with (Me$_3$Si)$_3$P in 2 : 1 ratio, forming mesomerically stabilized phosphaalkenes **39** (Scheme 18).

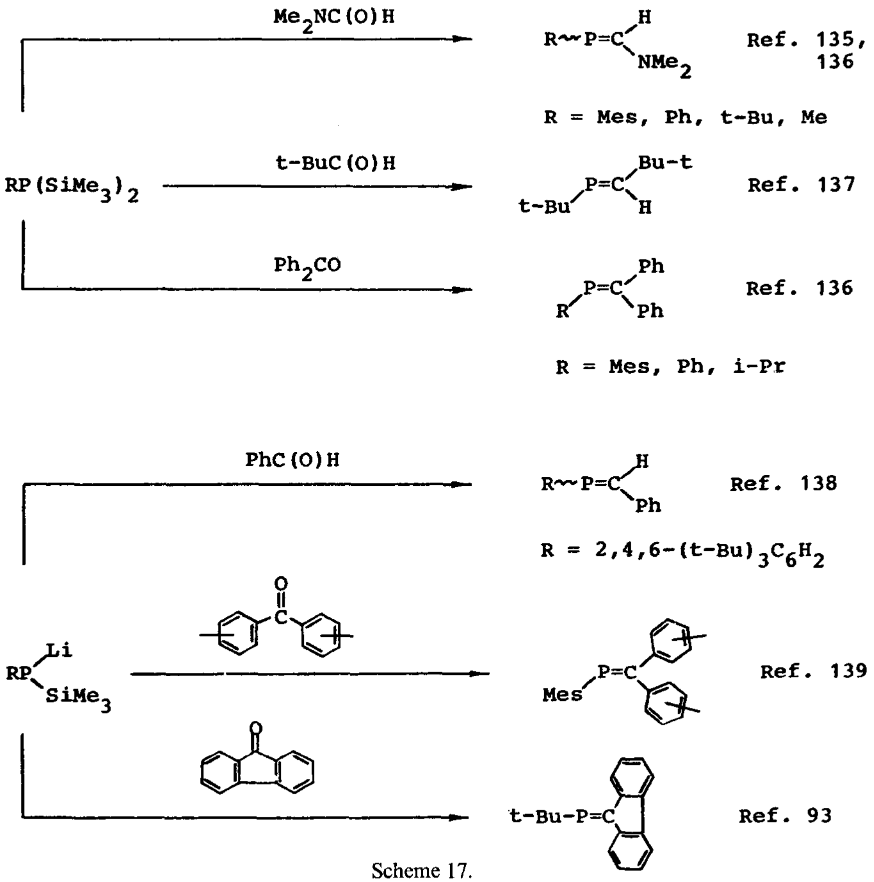
In principle, the reaction of organophosphines RPH$_2$ with polyhaloalkanes containing mobile halogen atoms could represent a general synthetic pathway to phosphaalkenes. However, at the present time there are only two examples of this approach. Thus, Appel *et al.* prepared compounds **40** and **41** by the condensation of 2,4,6-tri-*t*-butyl-phenylphosphine with chloroform and bromoform in the presence of finely divided KOH.[146,147] This route has been successfully used in obtaining the first and so far unique stable phosphaalkene **42** with an unsubstituted carbon atom[146] (Scheme 19).

Schmidpeter and Zwaschka were the first to demonstrate that phosphorus tricyanide reacts with dialkylphosphites giving the dicyanophosphide ion.[148] P(CN)$_2^-$ may be used to introduce this group by nucleophilic substitution. This reaction has been used to prepare the dicyanophosphino derivatives of heterocyclic cations and P-cyano-substituted phosphaalkenes[149] (Scheme 20).

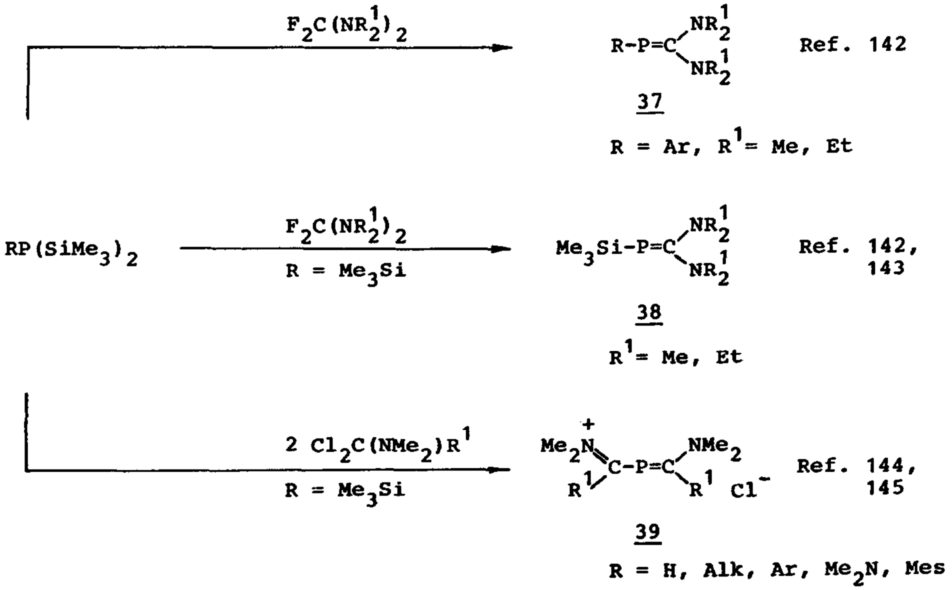
Triethylammonium and sodium dicyanophosphide anion salts are unstable. However, the sodium [18-crown-6] salt is stable in solution and in crystalline solids.[150]



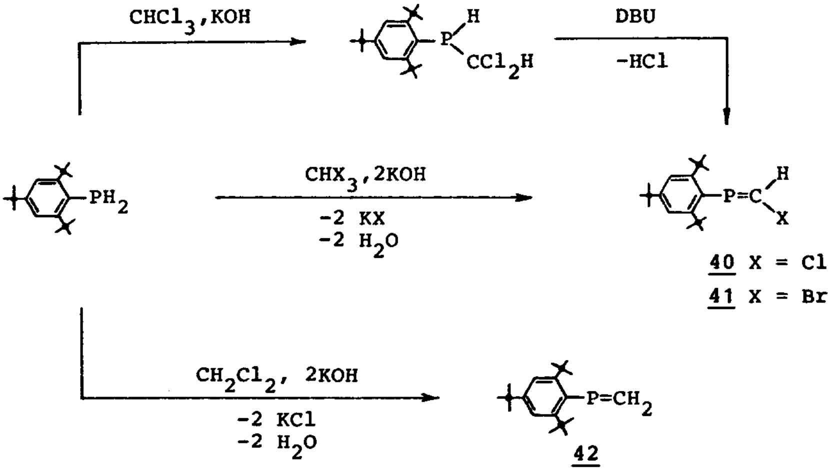
Scheme 16.



Scheme 17.



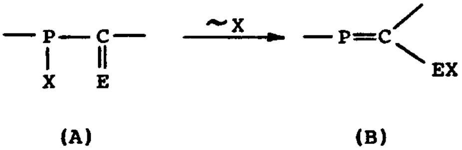
Scheme 18.



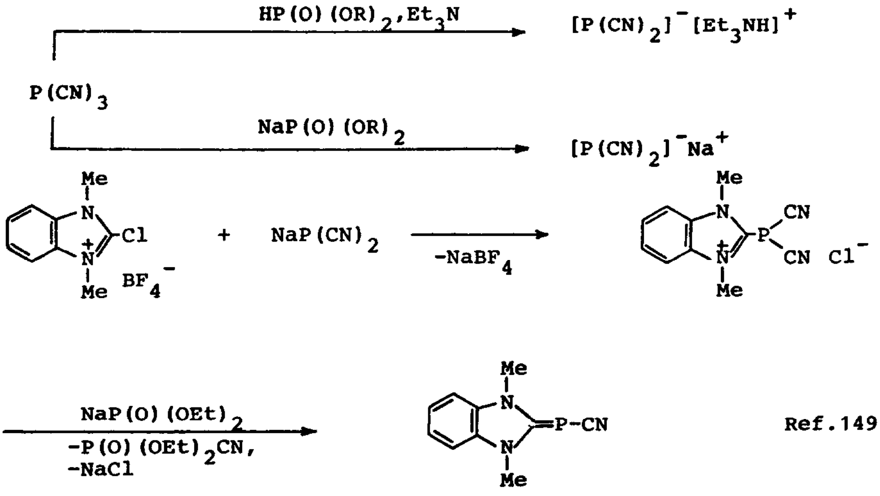
Scheme 19.

2.3. *Intramolecular reactions and rearrangements*

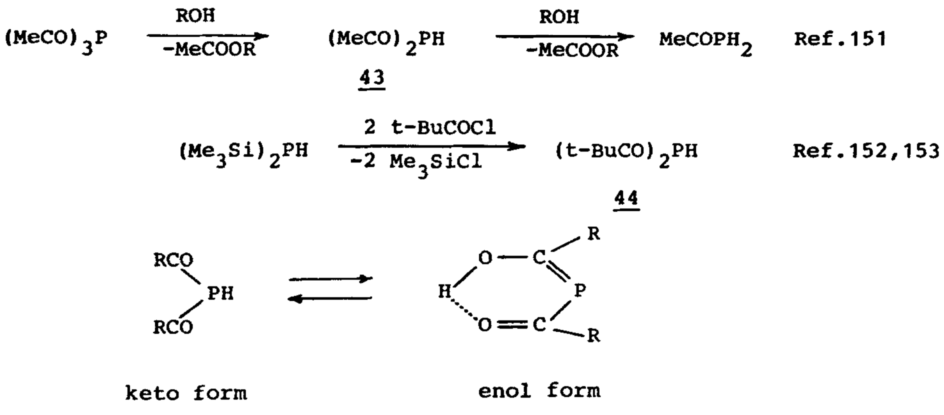
This group of methods for phosphaalkenes synthesis is based on the reactions which proceed according to the following general scheme:



It has been established that, by analogy to 1,3-diketones, diacylphosphines may exist in enolic form.[39] For example, compounds **43** and **44** in solutions exhibit a keto-enol equilibrium (Scheme 21).



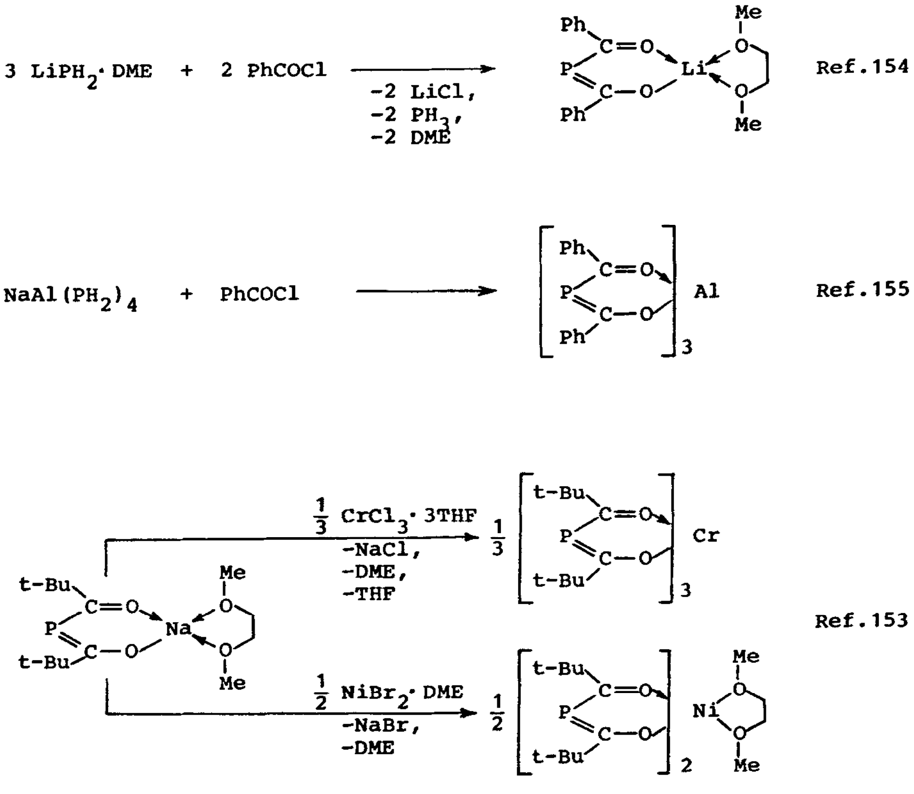
Scheme 20.



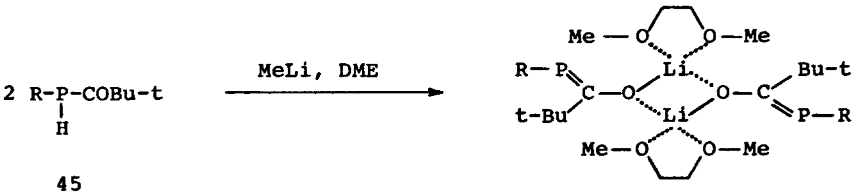
Scheme 21.

As in the case with the classical keto-enol tautomerism, the enolic form of diacylphosphines may be stabilized by chelation. Accordingly, many diacylphosphides exist as salts of the enolic forms (Scheme 22).[153–155]

Monoacylphosphines t-BuCOPH$_2$,[156] t-BuCOPHBu-t and t-BuCOPHPh[157] are characterized by a lower PH-acidity compared with diacylphosphines and usually they show no keto-enol taut-



Scheme 22.



45

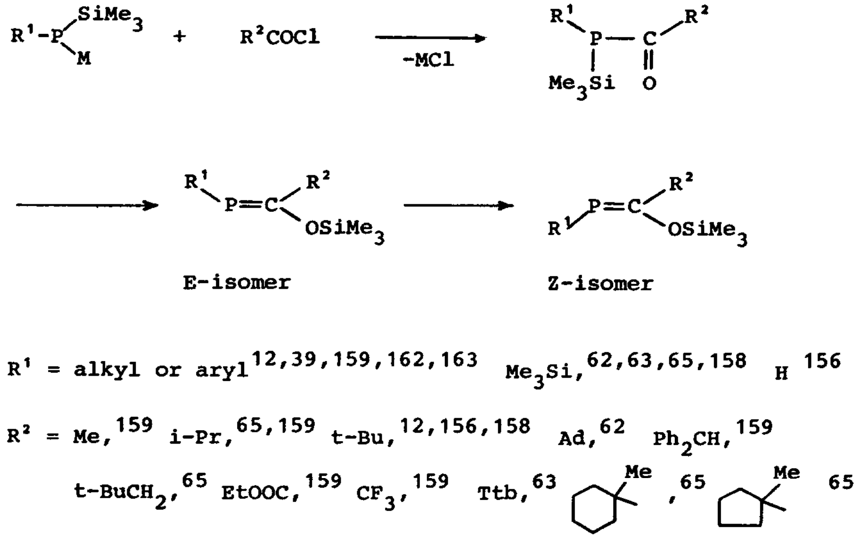
R = t-Bu, Ph

Scheme 23.

omerism. However, monoacylphosphides may exist in the form of enolates when, due to chelation effects, additional stabilization of the methylenephosphine structure occurs. This may be illustrated by reaction of acylphosphines **45** with methyllithium in 1,2-dimethoxyethane (DME).[156,157]

In the preparation of phosphaalkenes, a major role can be played by elementotropic versions of the (A) → (B) isomerization, in which the formation of a stable X—*E* bond is the driving force. These reactions include silyl group transfer from the phosphorus atom to oxygen, sulfur, or nitrogen (X = Me_3Si, *E* = O, N, S). This approach to phosphaalkenes was first realized by Becker, who in 1976 observed the formation of a PC-double bond during the reaction of bis(trimethylsilyl)phosphines with pivaloyl chloride followed by a silatropic migration from phosphorus to oxygen.[12] Later, this method was applied in the synthesis of a great number of (trimethylsilyloxy)methylenephosphines (Scheme 24). The staircase character of the reactions is supported by NMR data. In many cases the *E*-phosphaalkene is formed initially and is then converted into the thermodynamically more stable *Z*-isomer.[39,68,165]

As shown in Scheme 24 phosphaalkenes $Me_3Si—P{=}C(OSiMe_3)R$ may be obtained from



R^1 = alkyl or aryl[12,39,159,162,163] Me_3Si,[62,63,65,158] H[156]

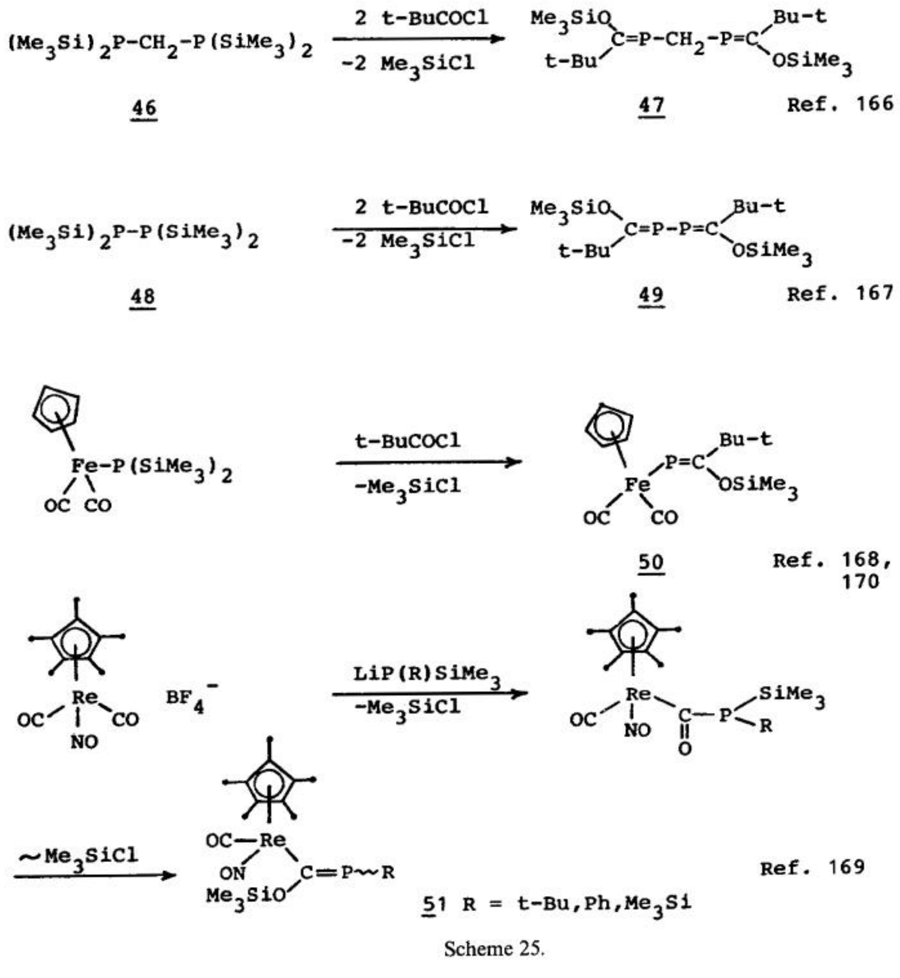
R^2 = Me,[159] i-Pr,[65,159] t-Bu,[12,156,158] Ad,[62] Ph_2CH,[159] t-$BuCH_2$,[65] EtOOC,[159] CF_3,[159] Ttb,[63] ,[65] [65]

Scheme 24.

tris(trimethylsilyl)phosphine and acyl chlorides (Table 3). These products are important intermediates for the preparation of phosphaalkenes (see Section 2.1). Silylphosphines **46** and **48** react with pivaloyl chloride in a ratio of 1 : 2, forming the phosphaalkenes **47**[166] and **49**[167] in high yield. This silylotropic route of the PC-double bond formation is also suitable for the synthesis of metallo-substituted phosphaalkenes (Scheme 25).[168–170]

1,2- and 1,4-dicarboxylic acid dichlorides react with bis(trimethylsilyl)phosphines in an unusual way. The initially formed phosphaalkenes are normally unstable and undergoing further conversions (Section 3.1.2). Imidoyl halides react with disilylphosphines in the same way as their oxygen analogues.[171] However, the reaction of $RP(Li)SiMe_3$ with $Me_2NC(S)Cl$ led to no phosphaalkene formation.[172] Phosgene[173,174] and isocyanide dichlorides[175–178] undergo double substitution easily giving the phosphaalkene **52** and **53**, respectively. Interaction of $PhP(SiMe_3)_2$ with benzoylisocyanide dichloride yields by halosilane condensation the phosphaalkene **54**, which then undergoes cyclization and P → O migration of silyl group yielding the isomeric 1,3-azaphosphetidine **55** with an exocyclic (P=C)-bond (Scheme 26).[179]

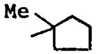
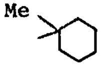
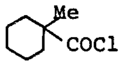
Another approach to phosphaalkenes, the key stage of which is the 1,3-migration within the $Me_3Si—P—C=X$ bond system, consists in the nucleophilic addition of silylphosphines to hetero-



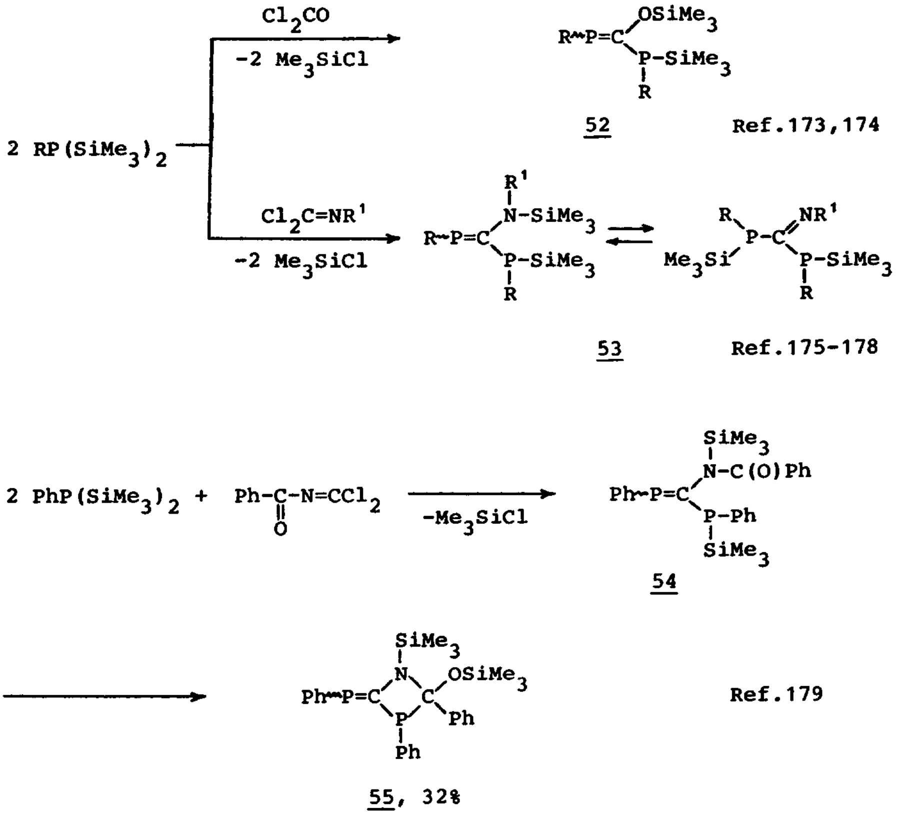
Scheme 25.

Table 3. P-(Trimethylsilyl)phosphaalkenes, 

$Me_3Si\sim P{=}C(R^1)(R^2)$

Phosphaalkene		Method[a]	Starting reagents	Preparative Conditions	Yield	Ref.
R^1	R^2				(%)	
t-Bu	Me_3SiO	A	t-BuCOCl, $(Me_3Si)_3P$	cyclopentane, 20°C	91	158
Ad[b]	Me_3SiO	A	AdCOCl, $(Me_3Si)_3P$	pentane, 20°C	67	62
		A	AdCOCl, $(Me_3Si)_2PLi$ 2THF	cyclopentane, -40°C	96	62
Ttb[c]	Me_3SiO	A	TtbCOCl, $(Me_3Si)_3P$	-	-	63
i-Pr	Me_3SiO	A	i-PrCOCl, $(Me_3Si)_3P$	pentane, 20°C	84	65
t-BuCH$_2$	Me_3SiO	A	t-BuCH$_2$COCl, $(Me_3Si)_3P$	pentane, 20°C	91	65
	Me_3SiO	A	 , $(Me_3Si)_3P$	pentane, 20°C	81	65
	Me_3SiO	A	 , $(Me_3Si)_3P$	cyclopentane/THF, -40°C	75	65
Me_2N	Me_2N	B	$(Me_2N)_2CF_2$, $(Me_3Si)_3P$	without solvent, 35°C	72	142,143
Me_2N	Et_2N	B	$Me_2N(Et_2N)CF_2$, $(Me_3Si)_3P$	without solvent, 35°C	75	142,143
Et_2N	Et_2N	B	$(Et_2N)_2CF_2$, $(Me_3Si)_3P$	without solvent, 35°C	70	142,143

[a] A - 1,3-Trimethylsilyl migration, B - condensation. [b] Ad = 1-adamantyl. [c] Ttb = 2,4,6-tri-tert-butylphenyl.



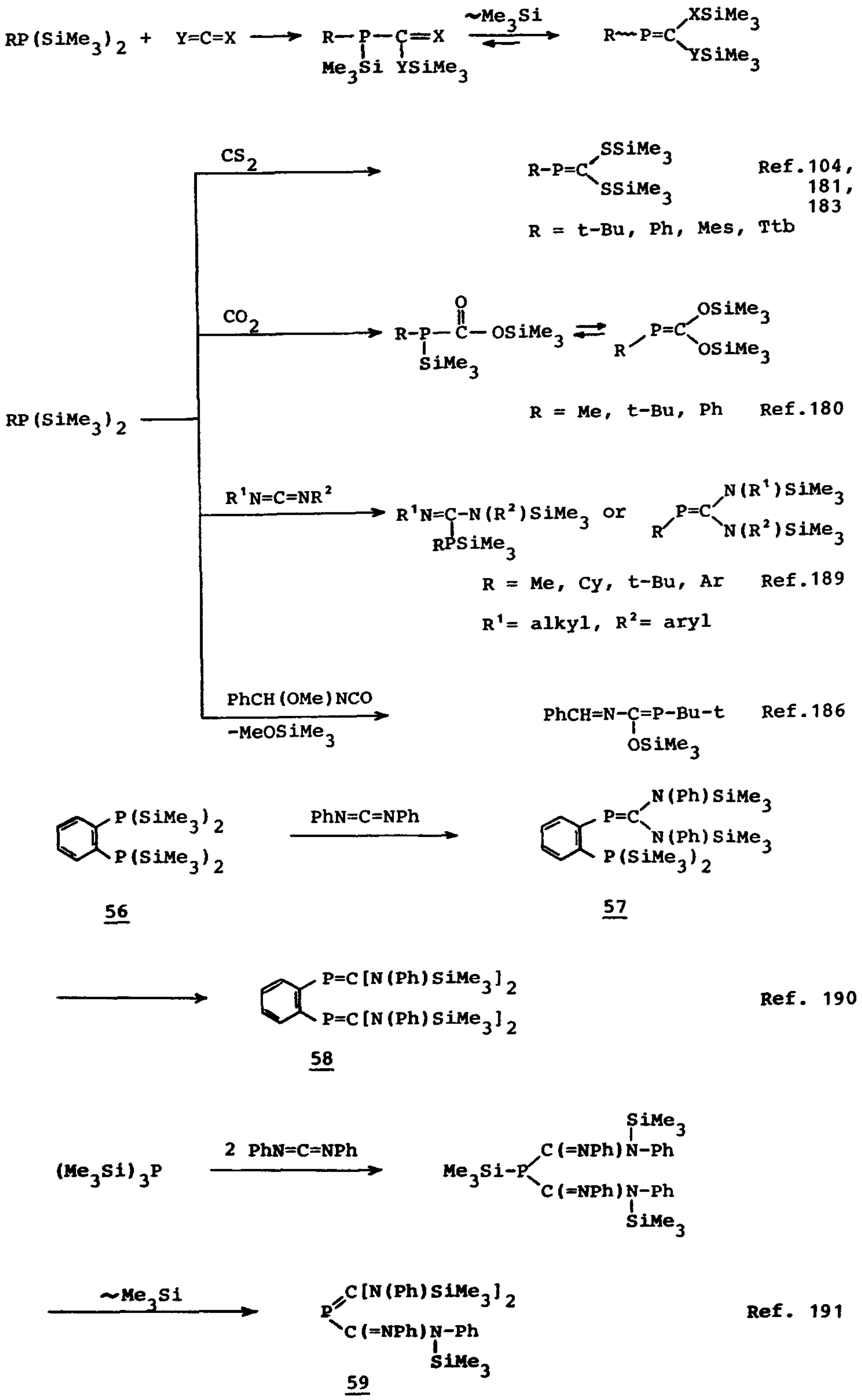
Scheme 26.

cumulenes. The method is not general. Depending upon the nature of the heterocumulene, interaction of reagents may lead either to phosphaalkenes or the reaction is terminated by the formation of addition products. Reactions of organobis(trimethylsilyl)phosphines with carbon dioxide,[180] carbon disulfide,[104,181-183] isocyanates,[184-186] isothiocyanates,[187,188] carbodiimides[189,190] and ketenes[160] have been studied in detail. Examples of the successful application of this method are shown in Scheme 27. It is of interest to note that the synthesis of phosphaalkenes **57** and **58** was achieved from phosphine **56** and diphenylcarbodiimide.[190] The treatment of $(Me_3Si)_3P$ by two moles of diphenylcarbodiimide leads to compound **59**.[191]

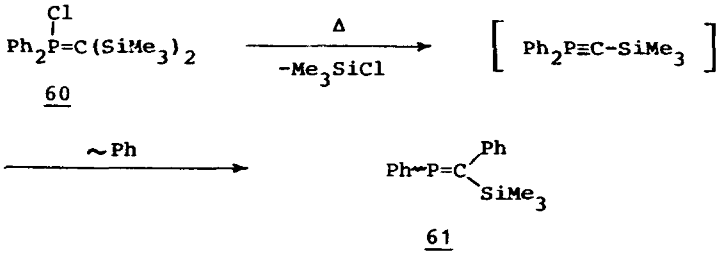
Although almost all syntheses of phosphaalkenes are based upon isomerization within the X—P—C=*E* bond system, other elementotropic conversions of this type are possible in principle. It was recently reported that acylphosphines of the $RP(BR^1_2)COR^2$ type, due to the strength of the oxygen–boron bond, are capable of isomerization into phosphaalkenes.[192]

2.4. *Miscellaneous reactions*

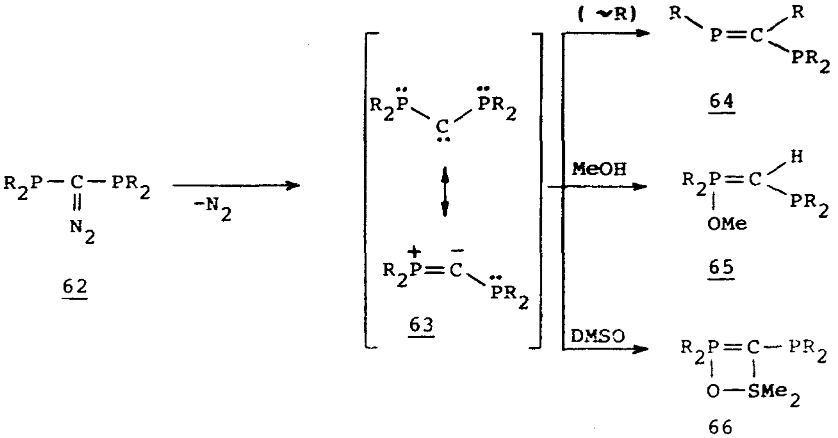
A non trivial reaction was described by Appel *et al.*[193] Thermolysis of P-chloro(methylene) phosphorane **60** at 120°C results mainly in the formation of the phosphaalkene **61**. This conversion was explained in terms of the formation of an intermediate with triply bonded pentavalent phosphorus. The general applicability of this synthesis, based upon 1,2-(P,C)-shift of an organyl substituent is restricted so far to P-aryl substituted compounds.


~Me3Si
CS2
Ref.104, 181, 183
R = t-Bu, Ph, Mes, Ttb
CO2
R = Me, t-Bu, Ph Ref.180
R¹N=C=NR²
or
R = Me, Cy, t-Bu, Ar Ref.189
R¹= alkyl, R²= aryl
PhCH(OMe)NCO
-MeOSiMe3
Ref.186
PhN=C=NPh
56
57
58
Ref. 190
2 PhN=C=NPh
~Me3Si
59
Ref. 191

Scheme 27.



Scheme 28.



Scheme 29.

Photolysis in benzene solution or attempted distillation of bis(phosphino)diazomethane **62** at 100°C led to the phosphaalkene **64** in nearly quantitative yield.[194] This rearrangement can result either from a concerted migration–nitrogen-loss mechanism or involve a phosphinocarbene intermediate **63**. In fact, the products **65** and **66** obtained by irradiation of **62** in the presence of methanol or dimethyl sulfoxide respectively, clearly demonstrate the intermediacy of a phosphinocarbene **63**.

3. PROPERTIES AND REACTIVITY OF PHOSPHAALKYNES AND PHOSPHAALKENES

Phosphaalkynes and phosphaalkenes possess the properties of classical $p\pi$-systems formed by the elements occupying the second row of the Periodic Table on the one hand, and trivalent three-coordinate phosphorus derivatives, on the other.

By the character of change in coordination number (σ) and valency (λ) of the phosphorus atom, we may define five main types of reactions with participation of PC-multiple bonds:

$\sigma^1\lambda^3 \rightarrow \sigma^2\lambda^3$, $\sigma^2\lambda^3 \rightarrow \sigma^3\lambda^3$ (reactions of cyclodimerization, cycloaddition, 1,2-addition etc.);

$\sigma^2\lambda^3 \rightarrow \sigma^3\lambda^5$ (conversion of two-coordinate phosphorus compounds into compounds of three-coordinate pentavalent phosphorus);

$\sigma^2\lambda^3 \rightarrow \sigma^2\lambda^3$ (reactions of functionalization proceeding without changes of valency and coordination number of the phosphorus atom);

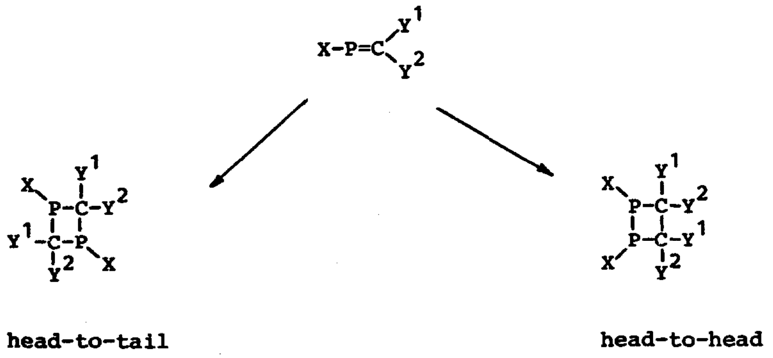
$\sigma^2\lambda^3 \rightarrow \sigma^1\lambda^3$ (reaction of 1,2-elimination).

The latter type of reaction is discussed in Section 2.1. which is concerned with the synthesis of phosphaalkynes.

3.1. *Addition to multiple PC-bonds*

3.1.1. *Self-addition.* Under certain conditions, the simple phosphaalkynes and phosphaalkenes are polymerized yielding resins. Phosphaalkenes containing a poorly stabilized P=C bond are oligomerized by [2+2]-cycloaddition. Simple olefins do not cyclodimerize.[195] The reason for the abnormal behaviour of phosphaalkenes consists in the stepwise character of their cyclodimerization reactions which presumably involve ionic or biradical intermediates.

[2+2]-Cycloaddition of phosphaalkenes may result in the formation of 1,3-diphosphetanes (head-to-tail dimerization) or 1,2-diphosphetanes (head-to-head dimerization). In most cases, phosphaalkenes undergo head-to-tail cyclodimerization.[36,39,89,196]

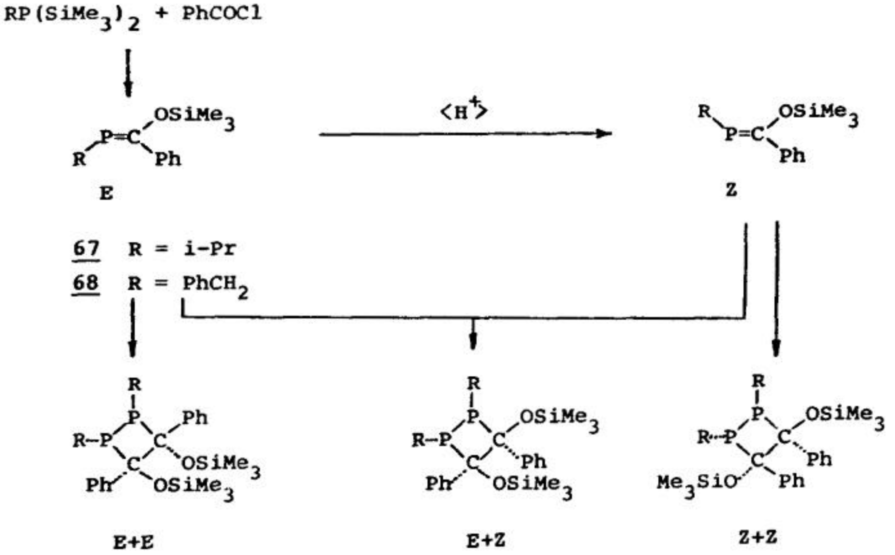


Experimental results[39,93,163,196,197] lead to the conclusion that head-to-head dimerization is typical of phosphaalkenes with bulky substituents at the phosphorus and small substituents at the carbon atoms. 1,2-Diphosphetane cycles with 'long' P—P and 'short' C—C single bonds can obviously reduce the intramolecular repulsions much better than the 1,3-diphosphetane cycle with four equal P—C bonds of intermediate length.[196]

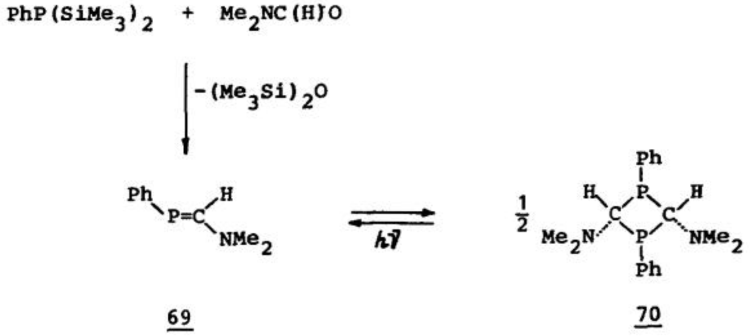
A detailed structural analysis of diphosphetanes produced by dimerization of phosphaalkenes **67** and **68** has shown that the configuration of the monomer can still be recognized in the dimer. Reaction of $PhCH_2P(SiMe_3)_2$ or i-$PrP(SiMe_3)_2$ with PhCOCl in the presence of acidic catalysts, where the *E*-phosphaalkene formed at the first step is rapidly isomerized into the *Z*-phosphaalkene. This then leads to 1,2-diphosphetane with a $(Z+Z)$-configuration. If the benzoyl chloride used is carefully freed from acidic impurities then the rearrangement of the *E*- to the *Z*-phosphaalkene is retarded and a competitive dimerization can occur. As a result one obtains a mixture of two other diphosphetanes with the $(E+E)$ and the $(E+Z)$ configurations (Scheme 30).[39]

The high thermal stability of the enolic forms of diacylphosphines and of diacylphosphides must be attributed to the existence of an extended conjugated bonding system. In C-(dialkylamino)-substituted phosphaalkenes an interaction between the free electron pair at nitrogen and the π-system of the P=C bond also contributes to the stability of these compounds.[129,131,135,171] The stabilizing action of conjugation is connected with the observed lack of a tendency to self-addition shown by phosphaalkenes $HP{=}C(NR_2)_2$ containing virtually non-shielded $p\pi$-bonds.[134,198] The same factor, at the least partially, also explains the comparatively high stability of the phosphaalkene, $HP{=}C(OSiMe_3)Bu$-t, with small steric protection.[156]

Some reactions involving phosphaalkene dimerization are reversible. In some cases, the monomerization energy barrier of diphosphetanes is not high so when in solution[136,200,201] or when



Scheme 30.



Scheme 31.

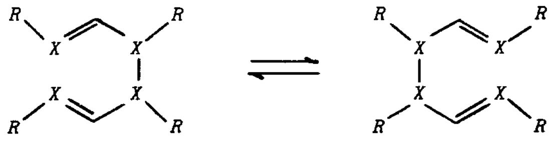
UV-irradiated,[202] then these dissociate into the monomeric phosphaalkenes. The monomerization process is significantly simplified when the P═C bond in the phosphaalkene is stabilized by conjugation effects. The **69** ⇄ **70** conversions serve as examples of monomer–dimer transitions.[136,199,202]

Appel with co-workers discovered reversible transitions between the phosphaalkene **71** and the 1,3-diphosphetane **72**.[201] Monomer–dimer interconversion was also observed in the case of the phosphaalkene **73**. The latter is stable in solutions at temperatures below 0°C whereas at room temperature it dimerizes forming the crystalline 1,3-dichlor-1,3-diphosphetane **74**. The reverse reaction occurs when the dimer is heated to 100–150°C or is UV-irradiated.[200]

Steric poorly protected (phenyliminomethylene)phosphines RP═C═NPh dimerize with the formation of 2,4-bis(phenylimino)-1,3-diphosphetanes.[117,118,119]

3.1.2. *Pericyclic reactions*. Of particular interest is the behaviour of phosphaalkynes and phosphaalkenes in reactions which are typical of classical $p\pi$-systems.

It has been established that just as hexa-1,5-dienes undergo easy [3,3]-sigmatropic rearrangements so 1,3,4,6-tetraphosphahexa-1,5-dienes also show similar valence isomerizations.[44,203,204]



X = CH (Cope rearrangement)
X = P (phospha-Cope rearrangement)

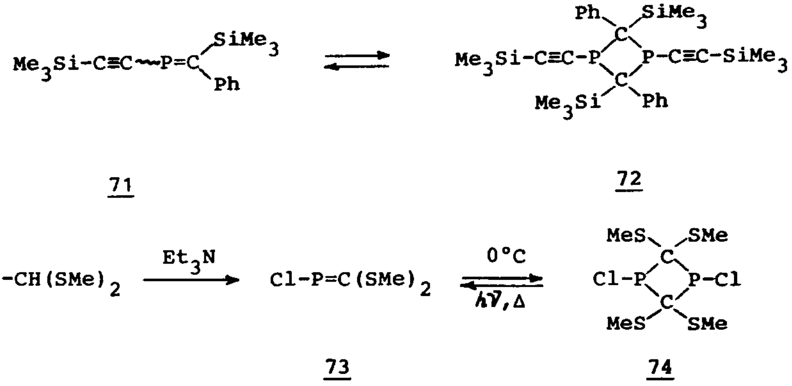
The existence of the degenerate phospha-Cope rearrangement by 1,3,4,6-tetraphospha-1,5-hexadienes was initially revealed by ^{31}P-NMR spectroscopic investigations of the compounds **75**, produced by reaction of $PhP(SiMe_3)_2$ with isocyanide dichlorides.[175,176] The O-silylated compound **76**, formed in the phosgene reaction, in contrast with **75**, shows no fluctuation of bond skeleton. This compound undergoes cyclization at the PC-double bond giving stable 2,3,5,6-tetraphosphabicyclo[2.2.0]hexane derivative **77** (Scheme 33).

The significant difference between the oxygen and nitrogen substituted compounds **75** and **76** encouraged the synthesis of the substituted compound **78** containing one oxygen and one substituted nitrogen on the bridging C-atoms. As a result there are two structures, the bicyclic and the open tetraphosphahexadiene molecules in solution linked by cycloaddition and cycloreversion equilibria.

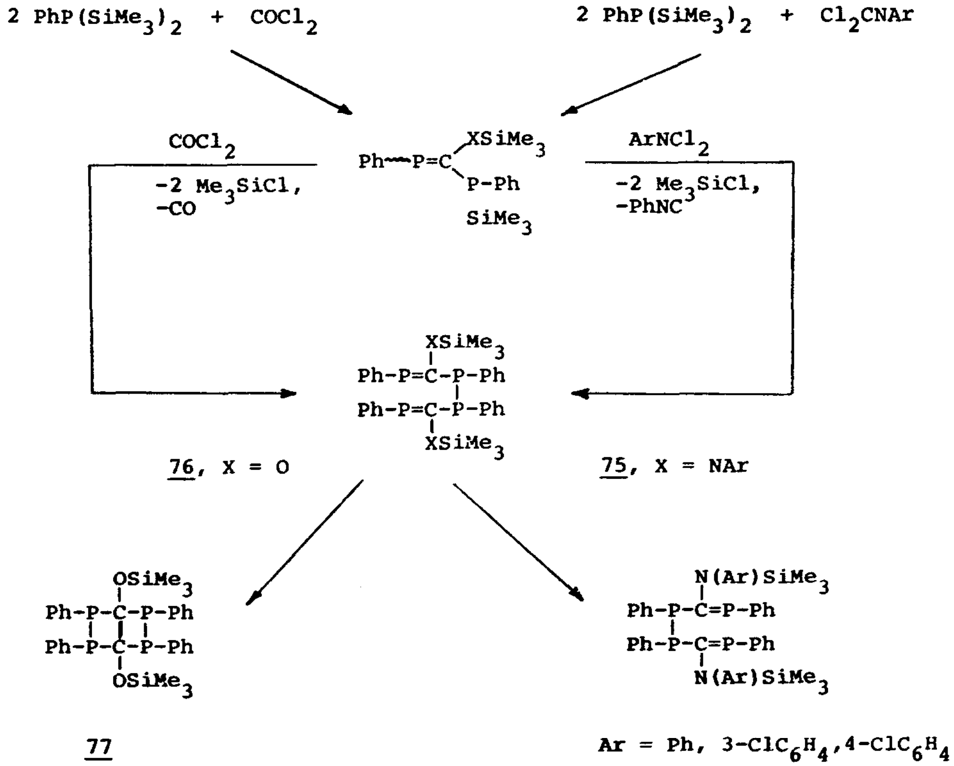
A further example of similar chemical behaviour between hexa-1,5-dienes and their phosphorus analogues is provided by the irreversible [3,3]-sigmatropic rearrangements 1,6-diphospha-1,6-dienes. It was revealed that succinyl dichloride reacting with $PhP(SiMe_3)_2$ does not give the expected **79**, but rather the product of its sigmatropic rearrangement, i.e. 1,2-diphenyl-1,2-divinyl-diphosphine **80**.[176] Other examples have been found in the reactions of cyclic 1,2-dicarboxylic acid dichlorides, which proceed by [3,3]-sigmatropic rearrangement, ring opening and formation of the cyclic diphosphines (Scheme 35).[204–206]

Diphospha-1,5-hexadienes with the phosphorus atoms in the 1,3-position can also undergo the Cope rearrangement. Conversions of this type are shown in Scheme 36. Compound **81** rearranges into phosphaalkene **82** when slightly heated.[207]

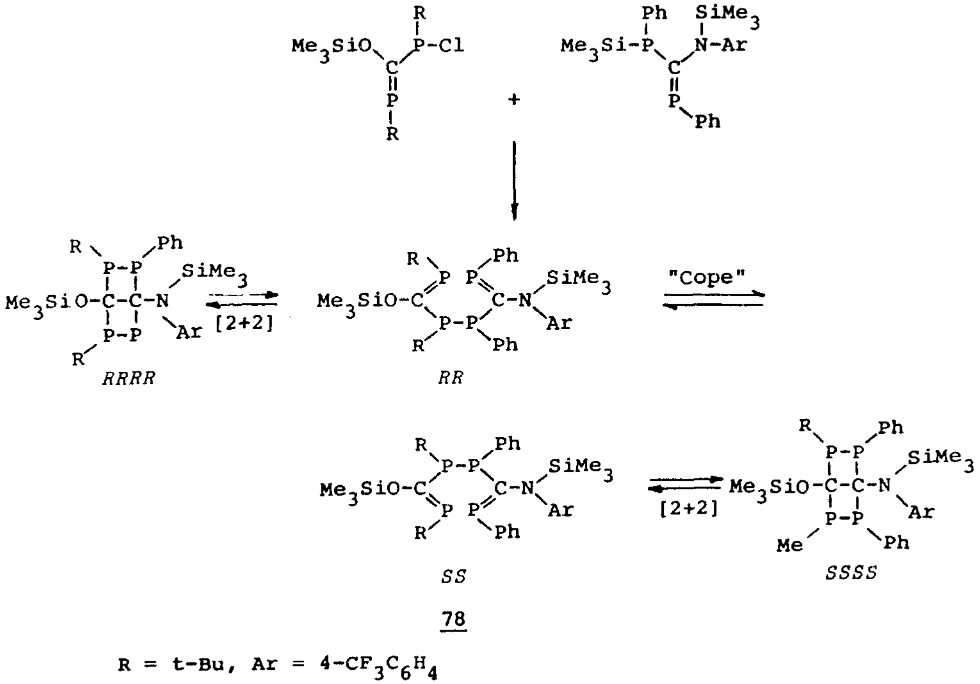
Pericyclic reactions considered earlier followed the change from the double coordinated to the more stable triple coordinated species. Evidence for an inverse Cope rearrangement in which



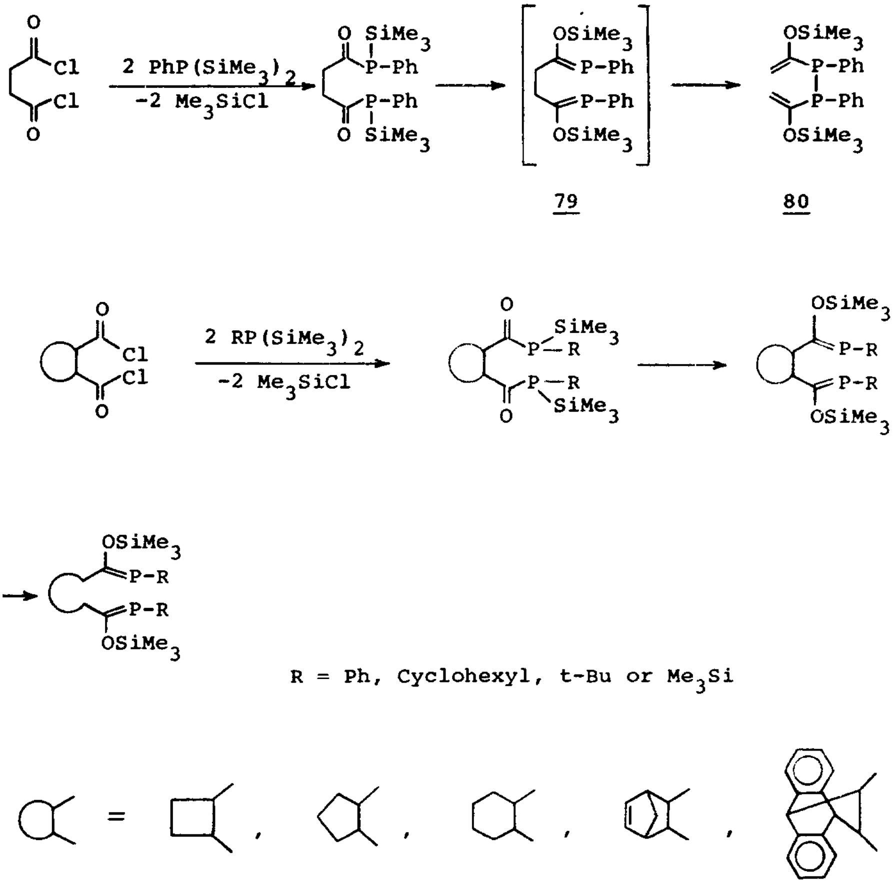
Scheme 32.



Scheme 33.



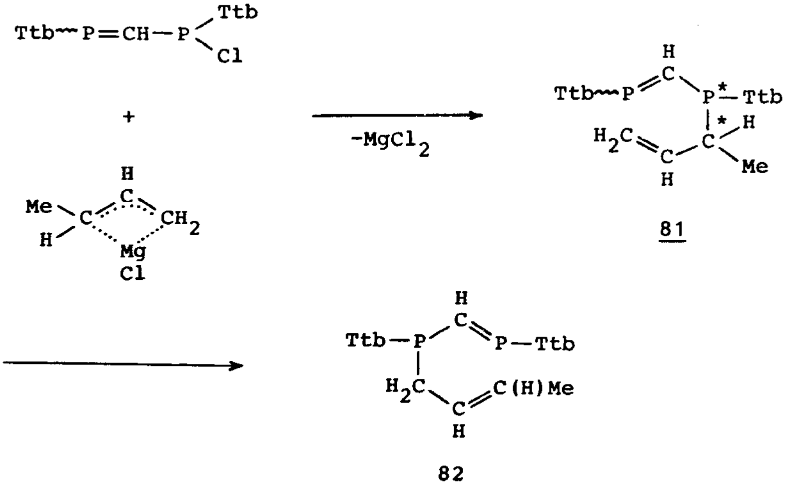
Scheme 34.



79 80

R = Ph, Cyclohexyl, t-Bu or Me$_3$Si

Scheme 35.



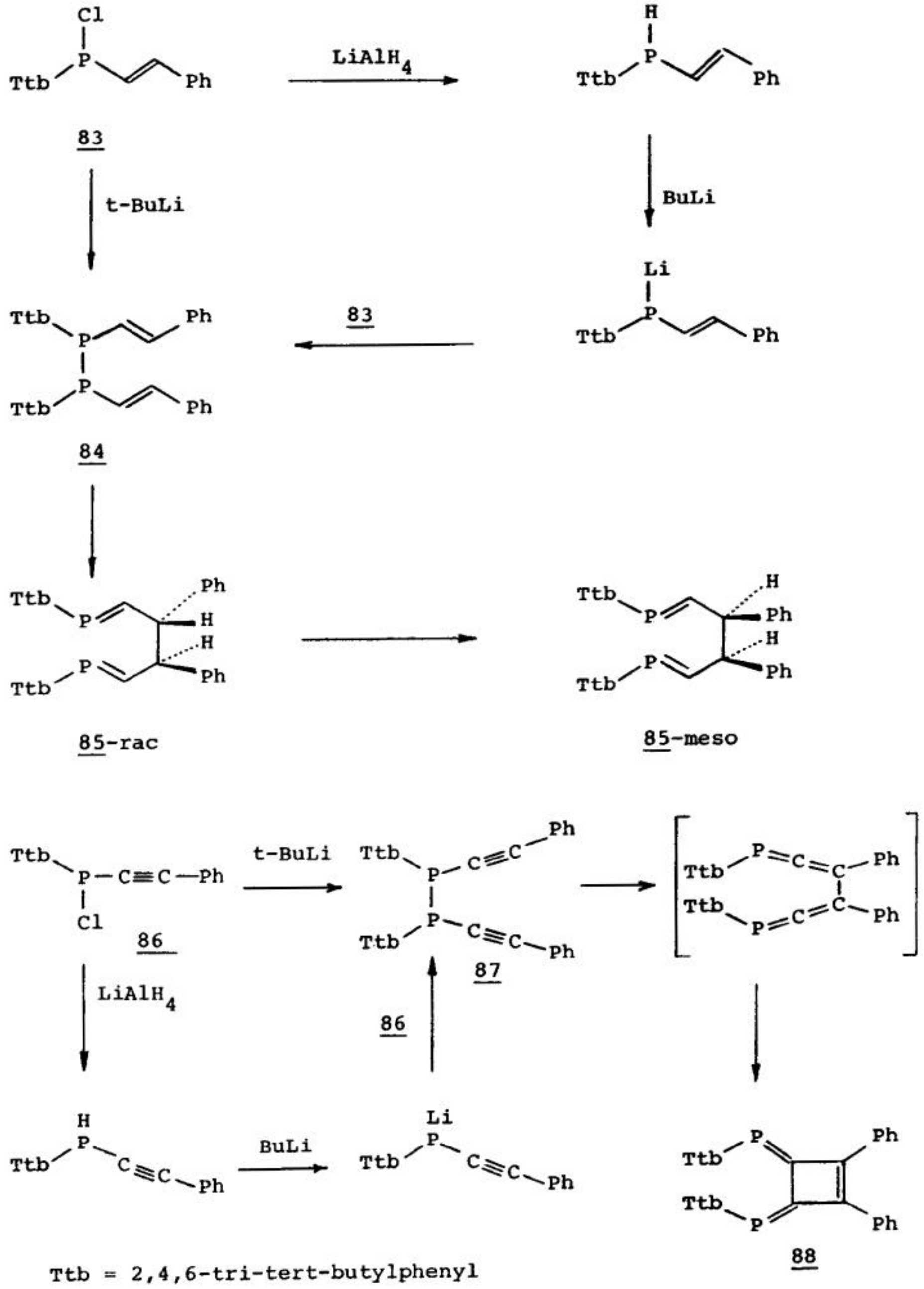
81

82

Scheme 36.

diphosphines can be transformed into phosphaalkenes was given for the first time during the synthesis of 1,2-distyryl-1,2-bis(2,4,6-tri-*t*-butylphenyl)diphosphine **84**.[208] Another example of an inverse phospha-Cope rearrangement including the valence isomerization of a diphosphine into a phosphaalkene is the thermally induced conversion of 3,4-diphospha-1,5-hexadiyne **87** into 3,4-bis(phosphamethylene)-1-cyclobutene **88** (Scheme 37).[209]

Remarkable conversions confirming the resemblance of P=C and C=C π-bonds were found in

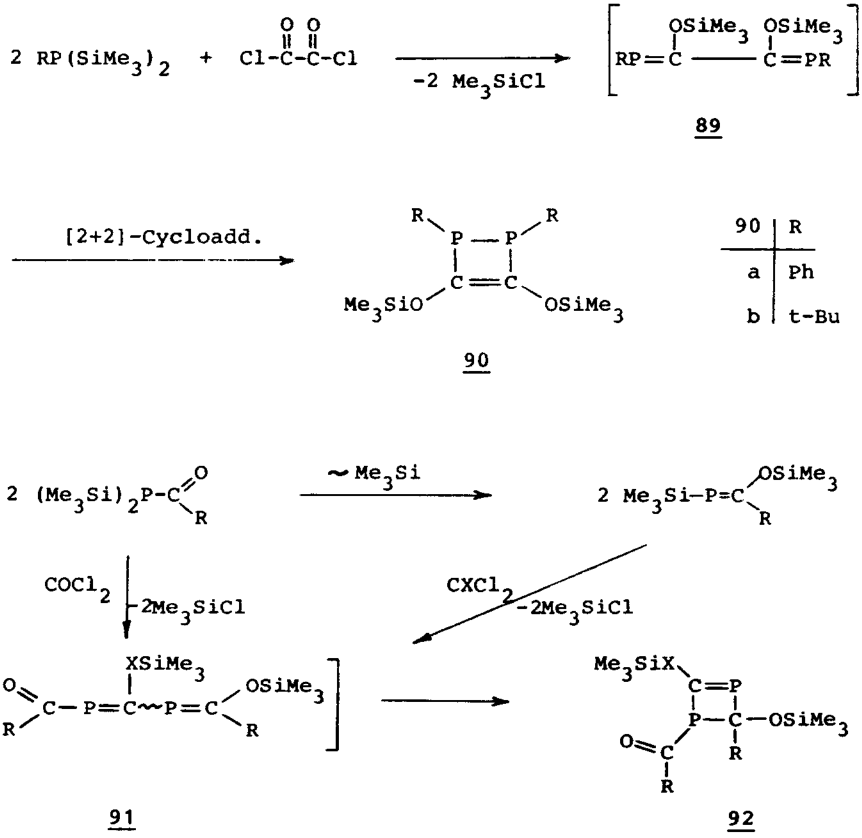


Scheme 37.

studies of compounds with the diphosphabutadiene bond system. 1,4-Diphospha-1,3-butadienes **89** generated in reactions of disilyphosphines with oxalyl dichloride are immediately isomerized into 1,2-phosphetenes **90**.[167,210] This conversion may be treated as an electrocyclic reaction similar to conversion of 1,3-butadienes into cyclobutenes. 1,3-Diphospha-1,3-butadienes **91** also undergo cyclisation with formation of the 1,3-diphosphacyclobutenes **92**, the structure of which was confirmed by X-ray methods[167] (Scheme 38).

Significant attention was paid to the study of the diene synthesis based on phosphaalkynes and phosphaalkenes.[211] The first examples of Diels–Alder reactions with the participation of PC-multiple bond were obtained by Appel and co-workers in the series of phosphaalkenes $XP{=}C(Ph)SiMe_3$.[212] Later, it was established that many one- or two-coordinate phosphorus derivatives react with conjugated dienes by [4+2]-cycloaddition.[204,213]

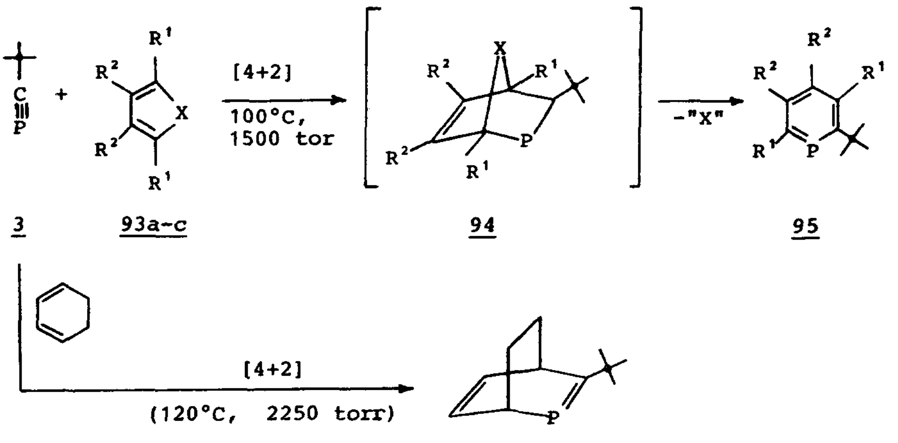
[4+2]-Cycloaddition is the first step in the reaction between 2,2-dimethylpropylidynephosphine and α-pyrones **93a**, cyclopentadienones **93b** and phosphole sulfides **93c**. Bicyclic intermediates **94** cannot be detected directly as they undergo aromatization with elimination of the X-bridge. However, the adducts obtained from the reactions of **3** with cyclohexadiene or anthracene are sufficiently stable to be isolated (Scheme 39).[214] Interaction of *t*-BuCP with acyclic 1,3-dienes



90	R
a	Ph
b	t-Bu

R = t-Bu; X = O, $2\text{-}CF_3C_6H_4N$

Scheme 38.

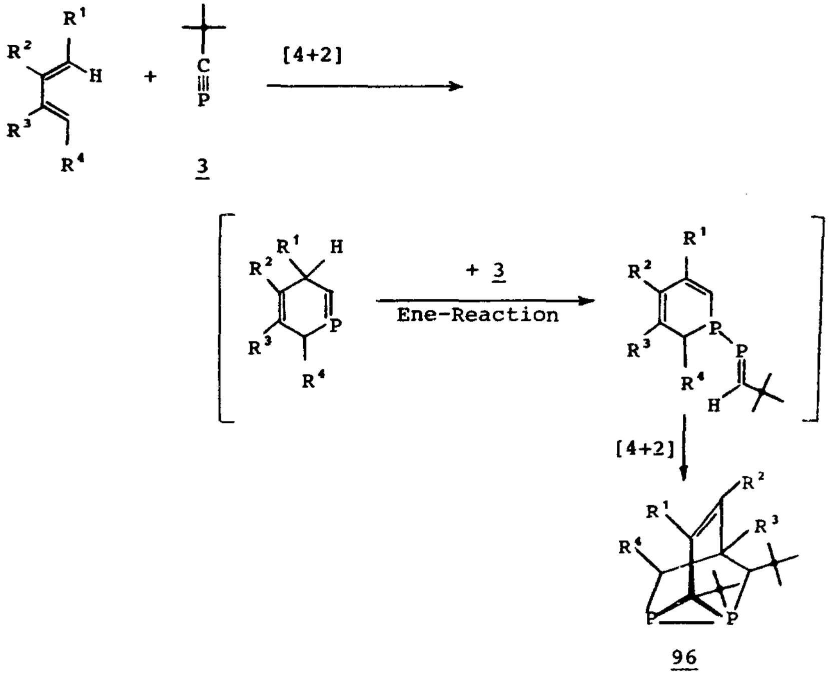


93	a	b	c
X	$-O-C(=O)-$	$-C(=O)-$	$-P(=S)Ph-$
R^1	Ph	H	H
R^2	Ph	H	Me

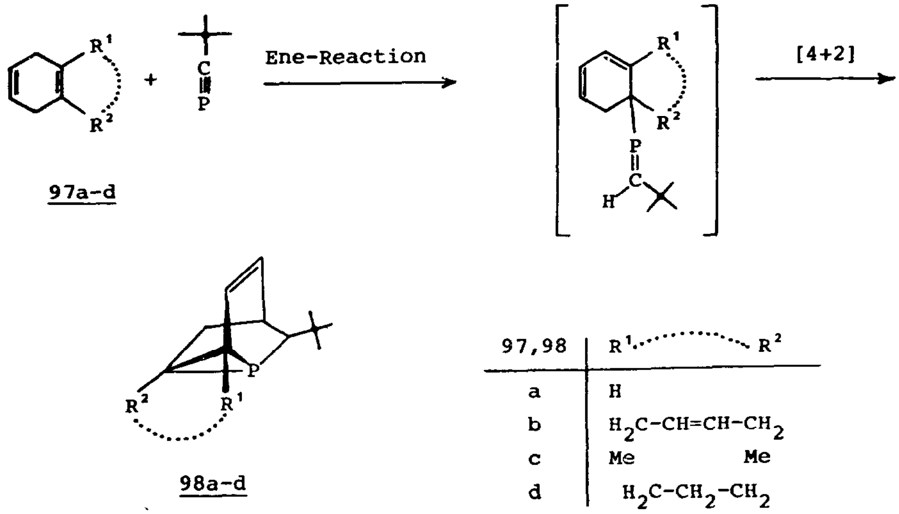
Scheme 39.

proceeds in a 2 : 1 ratio and includes an ene-reaction followed by an intramolecular [4+2]-cycloaddition. The end products were diphosphatricyclo[3.2.1.0^{2,7}]oct-3-enes **96** (Scheme 40).[215]

Reaction of *t*-BuCP with 1,4-dienes of the type **99** leads to the monophosphatricyclooctenes **98**[215] (55–80% yield).



Scheme 40.



97,98	$R^1 \cdots R^2$
a	H
b	$H_2C\text{-}CH{=}CH\text{-}CH_2$
c	Me Me
d	$H_2C\text{-}CH_2\text{-}CH_2$

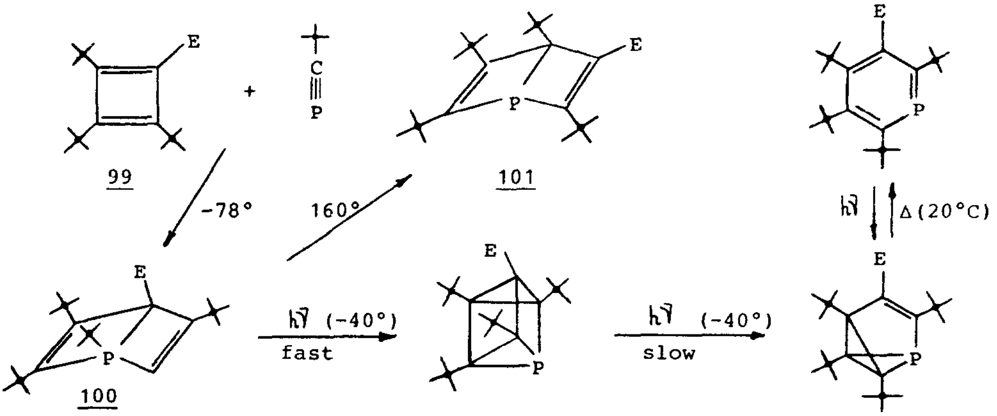
Scheme 41.

Reaction of the *t*-BuCP with cyclobutadiene **99** was used for the synthesis of the previously unknown valence isomers of phosphabenzene (Scheme 42).[216]

Behaviour of phosphaalkenes in Diels–Alder reactions has been investigated by several groups.[212,217,218] It was established that the effect of substituents in phosphaalkenes and dienes on the rate of [4+2]-cycloaddition was similar to that in the classical diene synthesis: electron-attracting groups in dienophile and electron-donating groups in the diene increase the rate of the reaction.

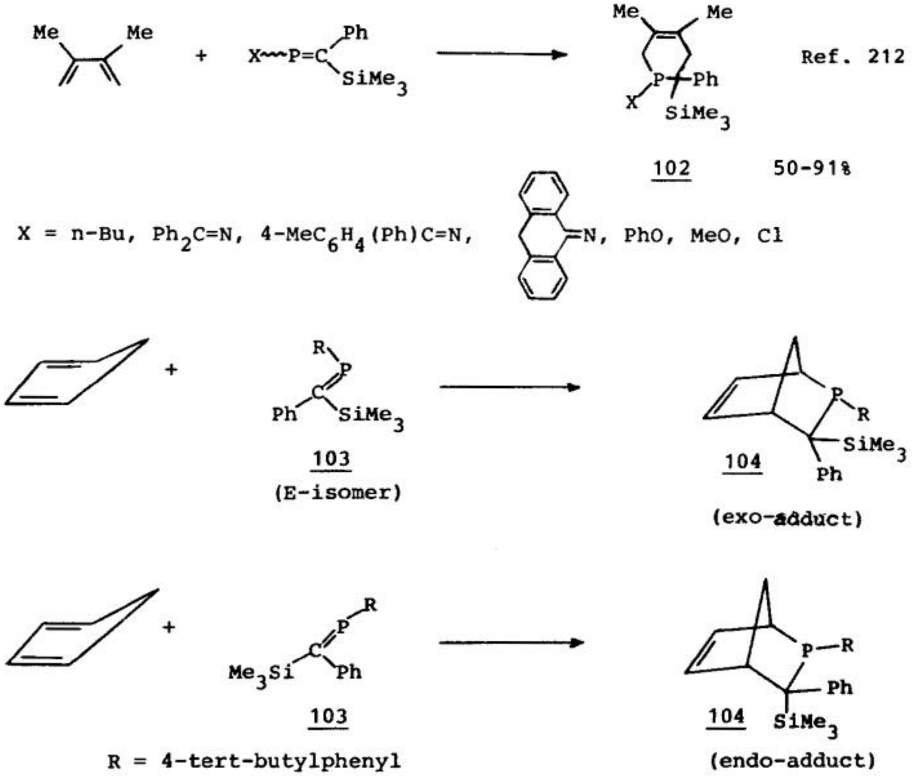
Phenyl(trimethylsilyl)methylenephosphines even at room temperature react with 2,3-dimethylbutadiene giving 1,2,5,6-tetrahydrophosphorines **102**[212] (50–91% yield).

Cyclopentadiene reacts with the *E*-isomer of *p*-*t*-butyl-phenyl(trimethylsilyl)-phenylphosphaalkene **103** giving only the exo-product, indicating a stereospecific [4+2]-cycloaddition. The cycloaddition product maintains the original configurations of the adducts. This result supports a synchronous reaction mechanism and conservation of orbital symmetry[219] (Scheme 43).



E = CO_2Me

Scheme 42.



Scheme 43.

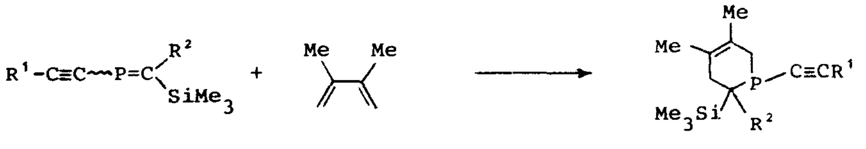
Under the very mild conditions (benzene, 20°C) phosphaalkenes Hlg—$P{=}C(SiMe_3)_2$ react with electron-rich or electron-poor 1,3-dienes.[217,218] Analogous behaviour is observed for the phosphaalkenes Cl—$P{=}C(SiMe_3)R$ (R = CO_2Et or CO_2SiMe_3), which can be generated *in situ* and trapped by the dienes. The resultant adducts are valuable substrates for the synthesis of functionalized λ^3-phosphabenzenes.[220,221]

Diels–Alder reactions of various phosphaalkenes with 2,3-dimethylbutadiene take place more easily than with azomethines or olefins. Thus, phosphaalkenes $R^1R^2C{=}N{-}P{=}C(Ph)SiMe_3$ form adducts with 2,3-dimethylbutadiene solely by reaction involving the P=C bond.[212] Relative reactivities of the P=C and the C≡C bonds are compared in the reactions of P-(ethynyl)phosphaalkenes **105**.[201,222] Reactions of these compounds with 2,3-dimethylbutadiene result in 1,2,5,6-tetrahydrophosphorines **106** (Scheme 44) (68–80% yield).

Only one example has so far been reported of the Diels–Alder reaction involving electron-rich phosphaalkenes. When boiled in benzene with the excess of 2,3-dimethylbutadiene, compound $PhP{=}C(H)NMe_2$ forms a product of [4+2]-cycloaddition (40% yield).[202]

A remarkable reaction of intramolecular [4+2]-cycloaddition was revealed when the phosphaalkene **107** reacted with N,N′-diorganylhydrazines (Scheme 45).[223] This observation is additional evidence regarding the relation between the PC-double bond and olefinic systems.

Semistable phosphaalkene $F_3C{-}P{=}CF_2$ reacts as a dienophile at temperature between −20°C and +15°C with cyclopentadiene, 1,3-cyclohexadiene, butadiene, and 2,3-dimethylbutadiene giving the corresponding Diels–Alder adducts in high yields.[224–227]



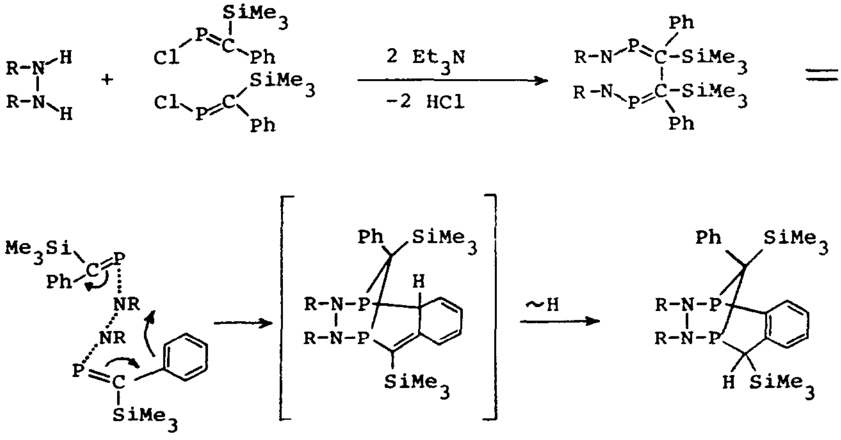
105a-d 106

105	a	b	c	d
R^1	Me_3Si	Ph	Ph	Me_3Si
R^2	Me_3Si	Ph	Me_3Si	Ph

Scheme 44.

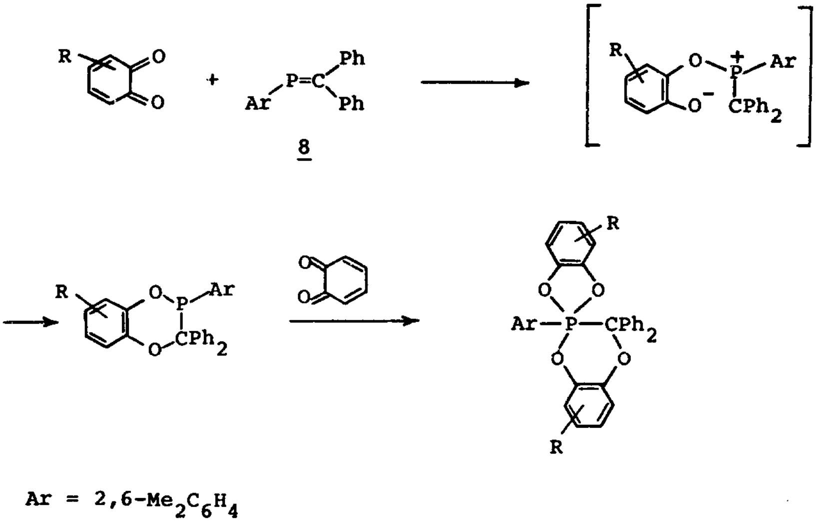
Unlike heterosubstituted phosphaalkenes, organosubstituted phosphaalkenes manifest low reactivity as dienophiles. Thus the compound $Mes{-}P{=}CPh_2$ reacts neither with electron-rich, nor with electron-poor dienes.[79] However, 2,6-dimethylphenyl(diphenylmethylene)phosphine **8** readily adds tetrachloro-*o*-benzoquinone, 3,5-di-*t*-butyl-*o*-benzoquinone and phenantrenequinone. The reaction rate decreased in this order; the more reactive quinones tended to add to the primary adduct with the formation of a phosphorane (Scheme 46).[228,229] It seems reasonable to assume that this addition is not concerted, but a multistep reaction. It is probably initiated by single electron transfer from **8** to the quinone followed by the formation of the dipolar intermediate. The phosphaalkene, $Me_3SiP{=}C(OSiMe_3)Bu$-*t*, reacts with 2,5-di-*t*-butyl-*o*-benzoquinone by a similar scheme.[230]

Preparative capacities of cycloaddition reactions involving PC-multiple bonds are not limited to [4+2]-cyclizations. Phosphaalkynes and phosphaalkenes are useful precursors for three-membered phosphorus heterocycles. Thus, starting from **3** and **4**, the first phosphasilirenes **108** have been



	a	b	c	d	e	f	g	h
R	Me	Et	n-Pr	n-Bu	i-Bu	s-Bu	$c\text{-}C_6H_{11}$	Ph

Scheme 45.

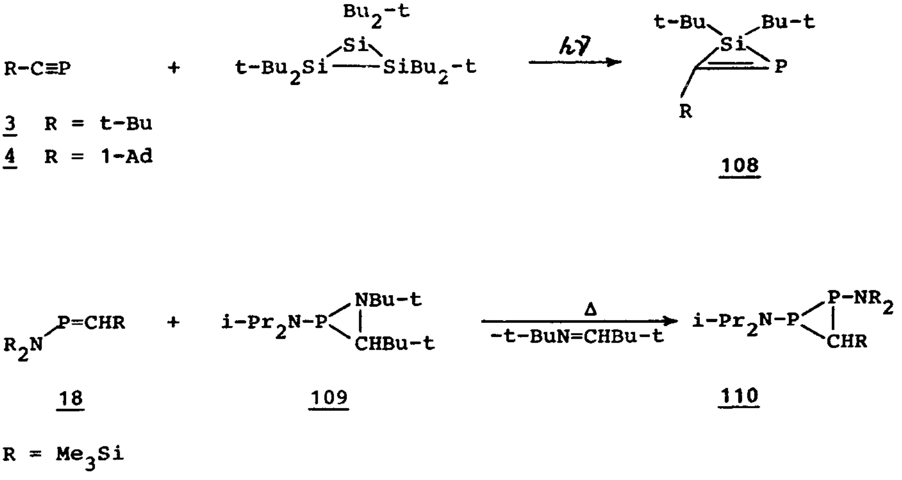


Scheme 46.

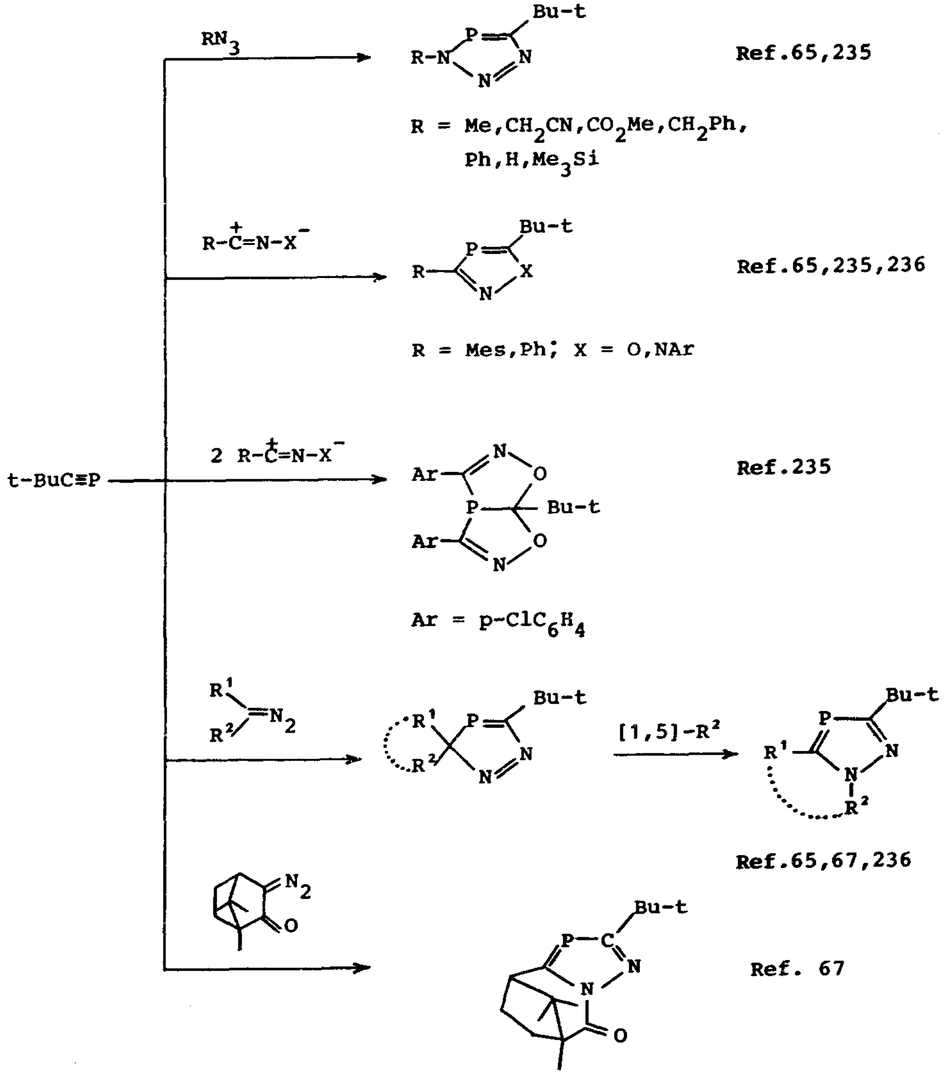
synthesized.[231] Thermolysis of the azaphosphirane **109** in the presence of **18** affords the 1,2-diphosphirane **110**.[232]

Phosphaalkynes and phosphaalkenes react easily with 1,3-dipolar compounds. Here, due to a wide structural diversity of the latter, reactions of 1,3-dipolar cycloaddition are valuable and flexible methods for the synthesis of various phosphorus-containing heterocycles. Examples of 1,3-dipolar cycloadditions with participation of *t*-BuCP are given in Scheme 48. Other syntheses of this type are discussed in the references.[62,213,233,234] Märkl *et al.* succeeded in obtaining heterocyclic systems by generating PhCP via phosphaalkene $ClP{=}C(Ph)SiMe_3$ thermolysis directly during the cycloaddition reactions (Scheme 49).[237–240]

The reactivity of the phosphaalkenes with 1,3-dipoles has been studied in many cases. Niecke,



Scheme 47.

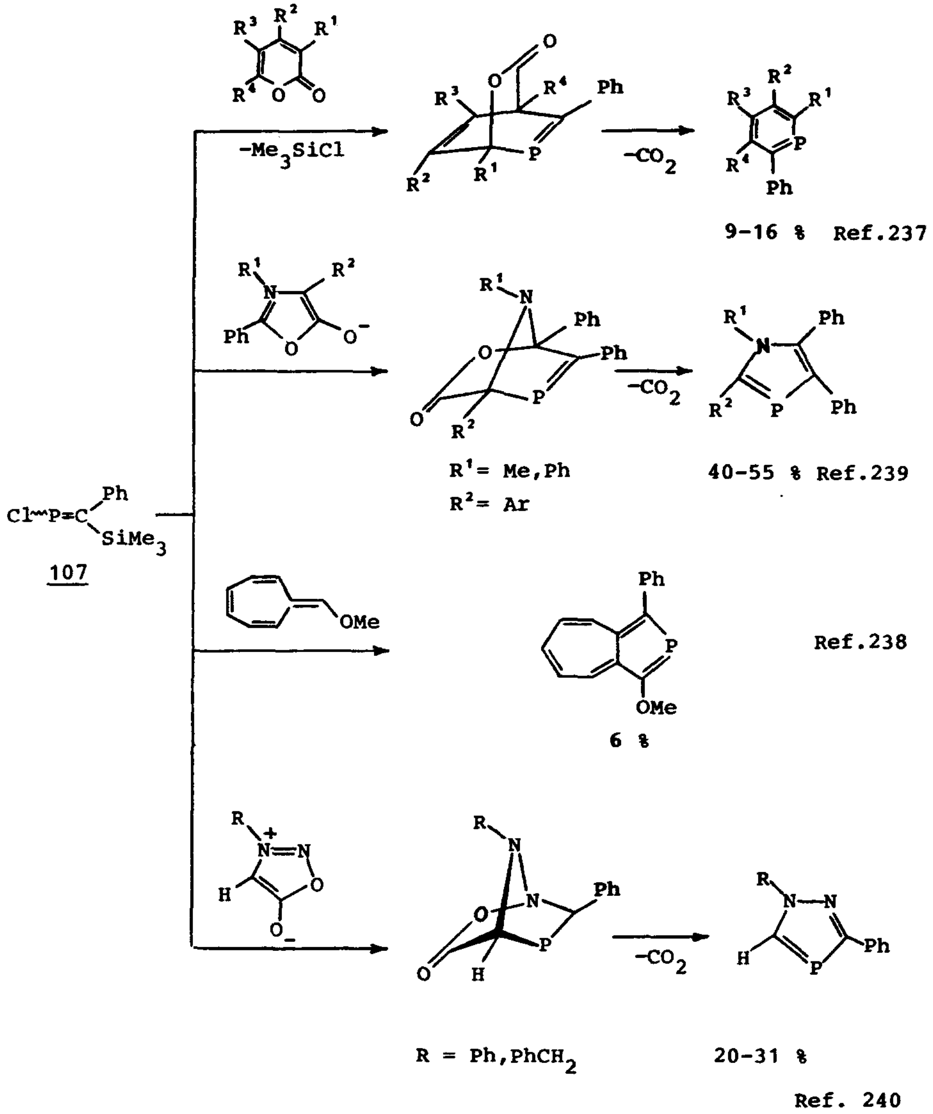


Scheme 48.

Schoeller and Wildbredt have reported the reaction of 2,2-dimethyldiazopropane with the phosphaalkene, $(Me_3Si)_2N{-}P{=}CHSiMe_3$.[99] Van der Knaap and co-workers have reported 1,3-dipolar cycloadditions of triaryl-phosphaalkenes.[241] Yeung Lam Ko and Carrié have studied the reactions of *p*-chloro-bis(trimethylsilyl)methylenephosphine with azides, diazo compounds and *p*-chlorobenzonitrile oxide.[217] The results of the cycloaddition reactions of the phosphaalkene **7** are shown in Scheme 50.[241]

Further examples of the reactivity of phosphaalkenes toward octet-stabilized 1,3-dipoles are provided by the reactions of **107** and **92** with diazo compounds and nitrile oxides. The primary products of the type **113** or **114** undergo spontaneous aromatization with elimination of chlorosilane or siloxane (Scheme 51).[242,243]

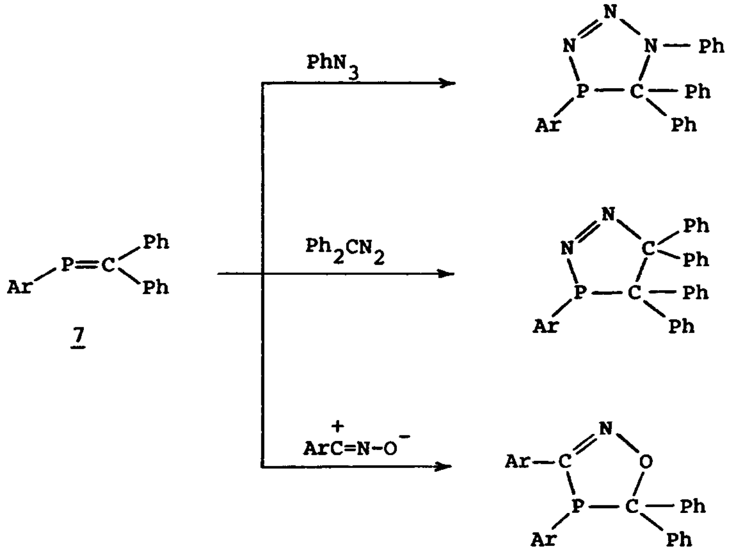
3.1.3. *Addition of polar reagents.* Phosphaalkynes and phosphaalkenes are capable of adding electrophilic and nucleophilic reagents, but due to low polarity of PC-bonds,[244–246] these reactions are not common.



Scheme 49.

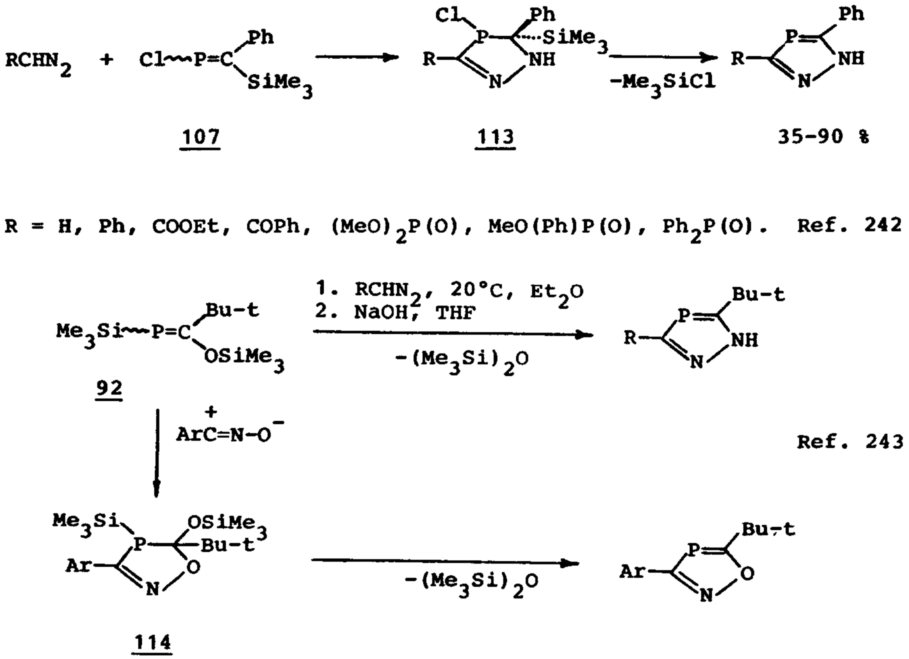
Gier,[4] Nixon[10] and Appel[13,14] have used the reaction between hydrogen chloride and phosphaalkynes in order to identify these compounds. Like hydrogen chloride, halogens add stepwise to the PC-triple bond of 2,2-dimethylpropylidynephosphine. Volatile halides of Main Group elements show a similar behaviour towards phosphaalkynes. In the reaction with germanium(IV)chloride, initially a mixture of *E*/*Z*-isomeric phosphaalkenes **115** is formed which after the addition of *t*-BuCP yields the 1,2-diphosphetene **116**. The formation of the phosphaalkenes **117** and **118** was observed with tin(IV)chloride and boron(III)bromide (Scheme 52).[247]

Much attention has been paid to reactions involving the addition of polar reagents to compounds with PC-double bonds. Descriptions have been given of how phosphaalkenes react with hydrogen halides,[78,87,92,100] alcohols,[78,88,91,92,95,248,249] amines,[94,248–251] thiols,[249] 1,3,2-benzodioxaborole,[252] and bis(trimethylsilyl)amine.[227] Organosubstituted phosphaalkenes easily add hard H-acidic



Ar = 2,4,6-trimethylphenyl

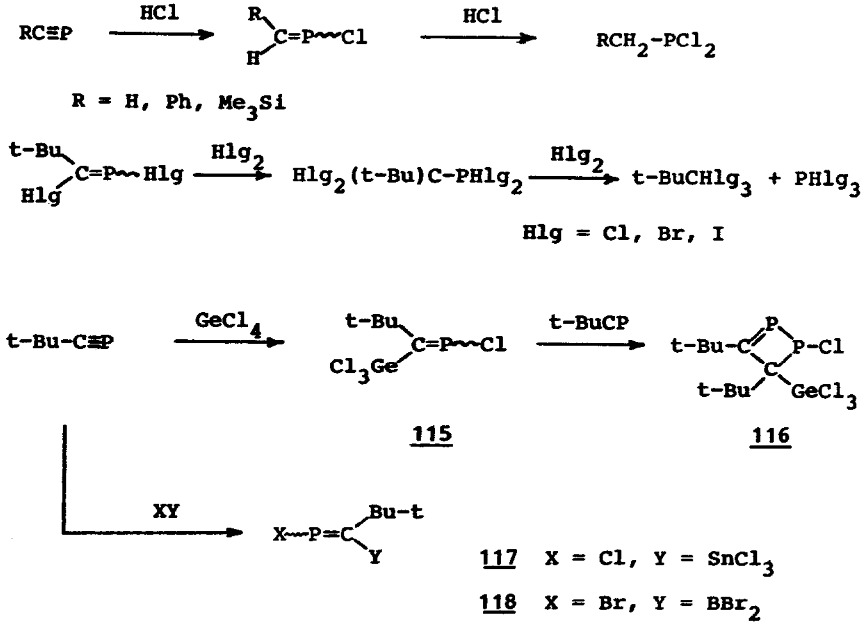
Scheme 50.



R = H, Ph, COOEt, COPh, (MeO)$_2$P(O), MeO(Ph)P(O), Ph$_2$P(O). Ref. 242

Ref. 243

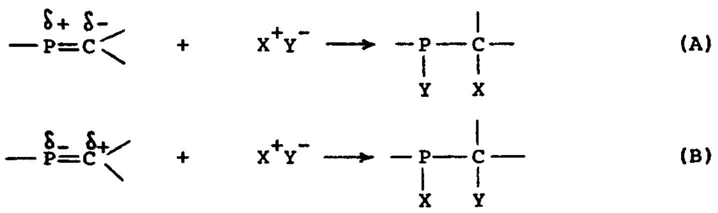
Scheme 51.



Scheme 52.

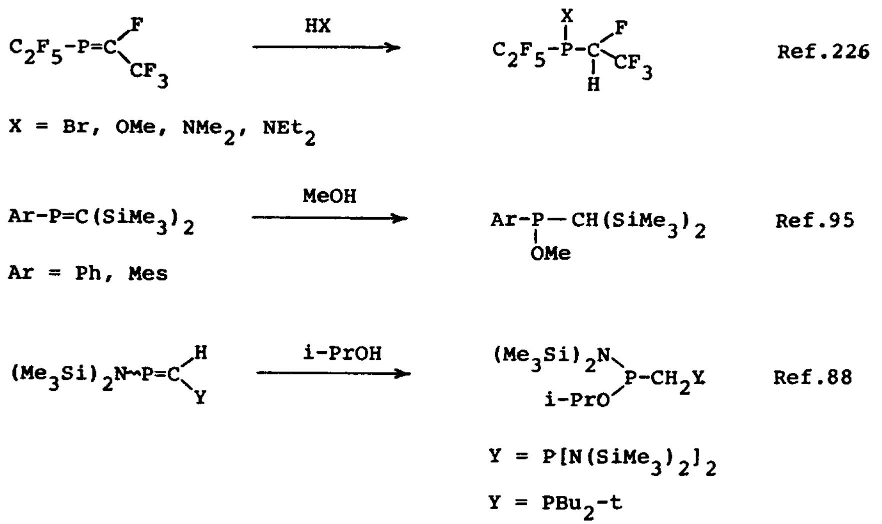
reagents, e.g. hydrogen halides. Reactions with alcohols require the use of either acidic or basic catalysts.[253] With heterosubstituted phosphaalkenes reactions of polar addition proceed with less effort. For all types of phosphaalkenes, the rate of 1,2-addition is sharply decreased with the increasing reagent volume and steric shielding of the π-bond.

The direction of addition of highly polar reagents towards P═C and N═C bonds is generally opposite. For phosphaalkenes, of the two possible directions of addition (A, B), in the overwhelming majority of cases, route (A) is realized.



The reactions shown in Scheme 53 are examples of the smooth addition of H-acidic reagents to phosphaalkenes.

Addition of proton-donor nucleophilic reagents by route (B) is typical of two-coordinate phosphorus derivatives having cumulenic systems of bonds —P═C═X (X = O, NR). For instance, phosphaketene *t*-BuP═C═O adds HCl forming acylphosphine *t*-Bu—PH—COCl.[102] Imino (methylene)phosphine *t*-BuP═C═NBu-*t* reacts with *tert*-butylamine forming *t*-BuPH—C(═NR) NHBu-*t*.[114–116] It is evident that the observed character of the addition of H-acidic reagents to phosphacumulenes is analogous to the addition of polar reagents to allenes, ketenes, isocyanates,

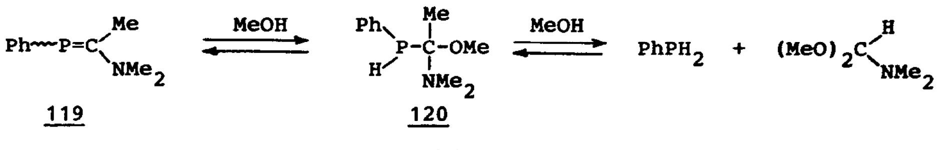


Scheme 53.

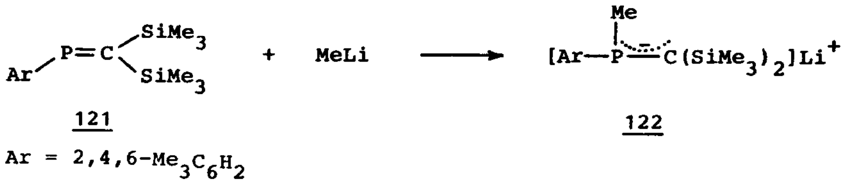
and other isoconjugate compounds containing heterocumulene systems. Apparently, it reflects the character of the compounds discussed which shows that electrophilic centre in cumulenes is found on the sp-hybridized carbon atom. In case of phosphacumulenes, it implies polarization of the $\mathrm{R}\overset{\delta_-}{-}\mathrm{P}\overset{\delta_+}{=}\mathrm{C}\overset{\delta_-}{=}\mathrm{X}$ type.

A rare instance of proton-donor reagent addition to the P═C bond was observed for the electron-rich phosphaalkene **119** (Route B).[202,254] Heating of the latter in MeOH—MeCN solution leads to the formation of the phosphine **120**, and products of the complete alcoholysis of the P—C bond.

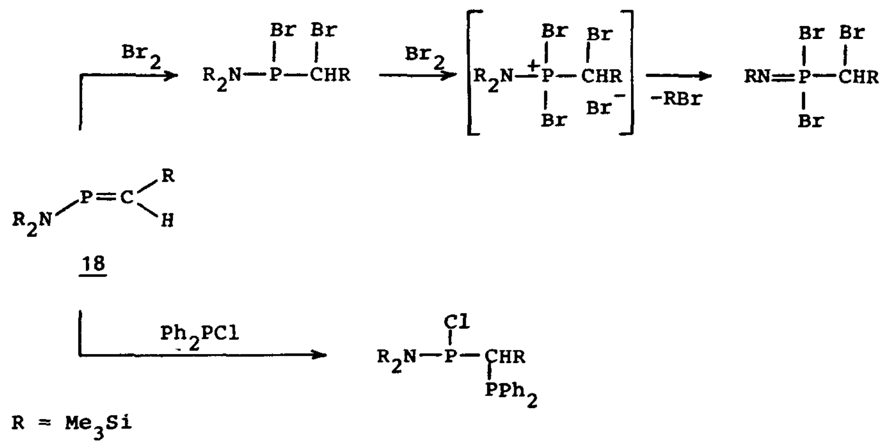
Organolithium compounds are easily added to the PC-double bond. Reaction of the phosphaalkene **121** with methyllithium in ether at −78°C leads to formation of phosphine **122** in almost quantitative yield.[95] P-Amino-substituted phosphaalkenes in similar reactions behave differently. Organolithium compounds usually cleave the P—N bond.[255] In those cases when a nucleophile is



Scheme 54.



Scheme 55.



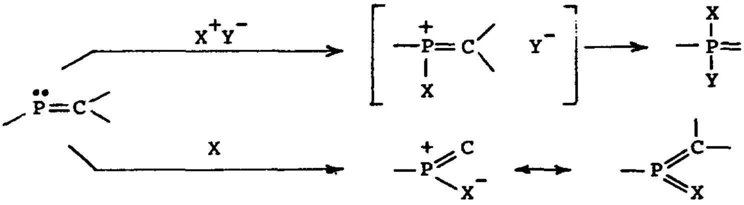
Scheme 56.

sterically hindered, the reaction leads to substitution at the two-coordinate phosphorus atom (Section 3.4).

Interaction of the phosphaalkene **18** with Br_2 proceeds through the stages of double addition of the halogen followed by elimination of a molecule of bromotrimethylsilane.[256] It is interesting that diphenylchlorophosphine is capable of adding to the phosphorus—carbon π-bond of **18** (Scheme 56).[256]

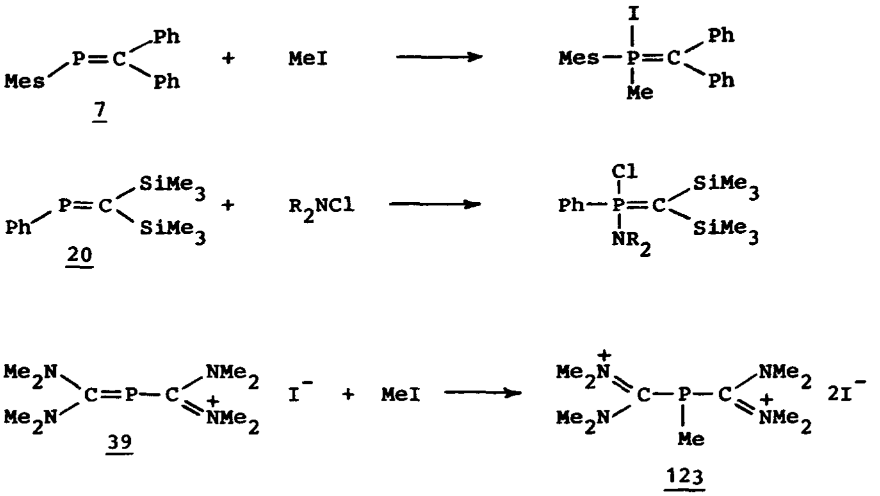
3.2. *Oxidative extension of the phosphorus atom coordination*

MO estimates suggest that phosphaalkenes have two closely set frontier orbitals, i.e. σ(P) and π-(P=C).[257–260] Consequently, there is a vast number of reactions in which phosphaalkenes exhibit 'phosphinic' character. Such reactions may be expressed by the following schemes.



A relatively high s-character of the non-bonding electron pair at the two-coordinate phosphorus atom causes phosphaalkenes to be less active in reactions of oxidative addition, than phosphines. Some examples, in which the addition of electrophilic reagents to phosphaalkenes realized by route (A), are known. Phosphaalkenes **7** and **20** are converted into the corresponding P-iodo- or P-chloro-ylides by treatment with iodomethane[261] or N-haloamines,[262] respectively. In highly acidic media the 2-phosphaallylic cation **39** is reversibly protonated at the phosphorus atom.[263] Reaction of **39** with iodomethane seems also to start with an attack on the phosphorus centre by the electrophilic agent then phosphorus rehybridization leads to phosphine **123**.[264]

Oxidative addition to phosphaalkenes proceeding by route (B) has been studied in more detail. Di-ylides of the three-coordinate pentavalent phosphorus are highly reactive compounds with a



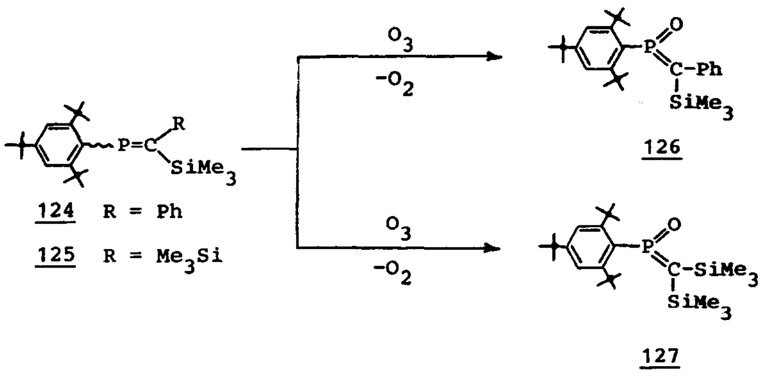
Scheme 57.

relatively narrow boundary of stability. These are not therefore always isolated as monomers. Two representatives of stable methylene(oxo)phosphoranes have been obtained. They were synthesized by oxidation of the phosphaalkenes **124** and **125** with ozone in toluene at −78°C (Scheme 58).[265,266]

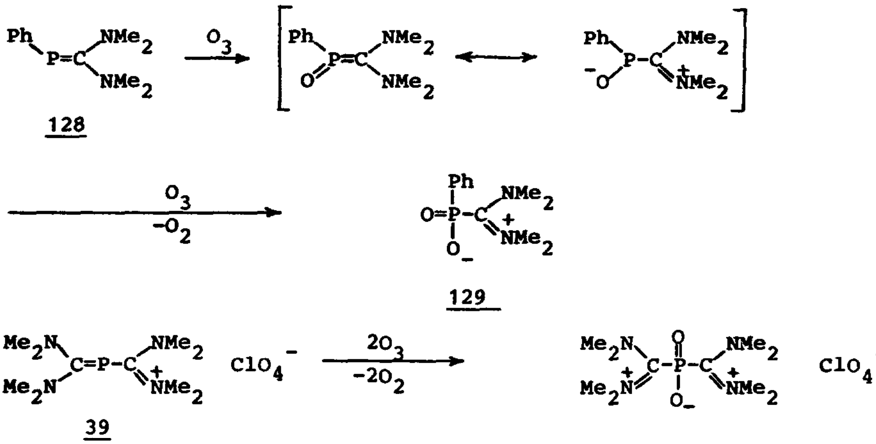
The phosphaalkene **128** is oxidized by ozone in a specific manner. The reaction produces the compound **129** which is obviously a result of a two-stage process. The phosphaalkene **39** reacts with ozone in a similar way (Scheme 59).[267]

In some cases, oxidation of phosphaalkenes by oxygen or ozone occurs with P=C bond cleavage and formation of a complex mixture of products. Such reactions may include intermediate formation of phosphinidene oxide [RP=O].[253]

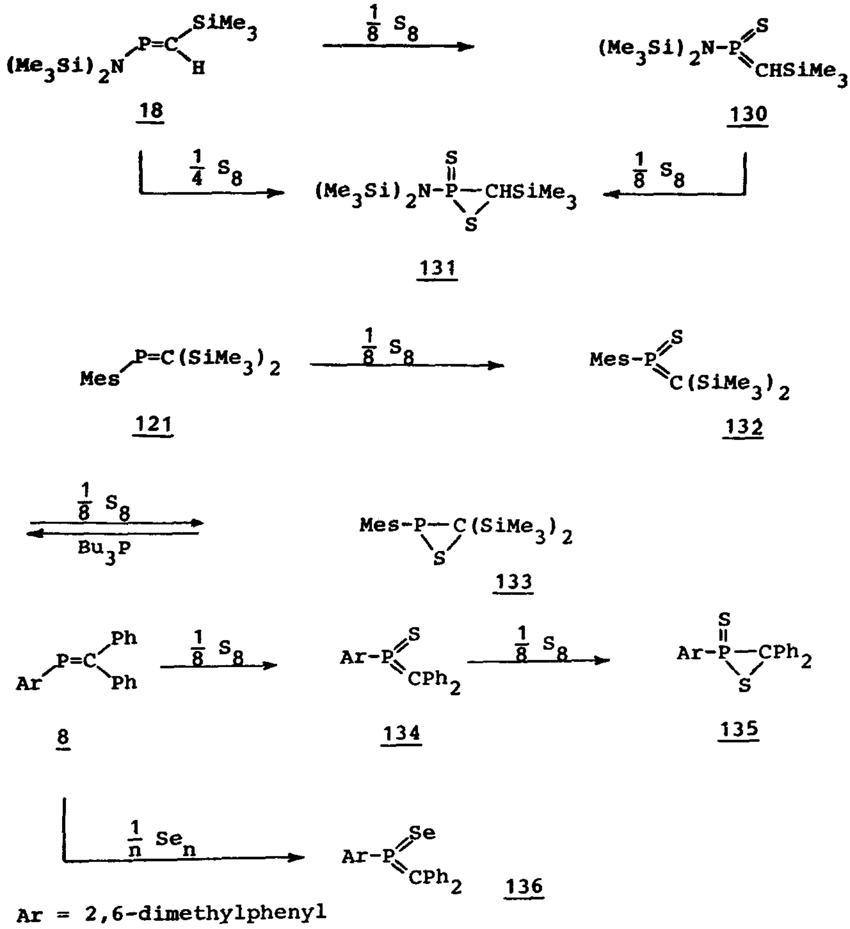
Boiling the equimolar amounts of phosphaalkene **18** and sulfur in benzene leads to methylene(thioxo)phosphorane **130** with a lower yield of the thiaphosphirane **131**.[268] Similar conversions were described for the phosphaalkene **121**. However, in this case, the rate of **132** → **133** conversion is probably higher because treatment of **121** with one equivalent of sulfur resulted in an inseparable mixture of the methylene(thioxo)phosphorane **132**, the thiaphosphirane **133**, and starting material



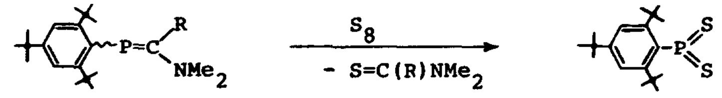
Scheme 58.



Scheme 59.



Scheme 60.



137 R = H

138 R = Me

139

Scheme 61.

121. Addition of second equivalent of sulfur results in complete conversion of the mixture into **133**. A pure sample of **132** was obtained by reaction of **133** with tributylphosphine.[250,269] The sulfurization of **8** in benzene leads to the thiaphosphirane **135**.[270] Grey selenium adds to the phosphaalkene to form the stable methylene(selenoxo)phosphorane **136**.[271]

Heating of **137** or **138** with an excess of elemental sulfur in benzene is accompanied by oxidative cleavage of the P=C bond and formation of the dithioxophosphorane **139** (Scheme 61).[130,272] Compound **139** is obtained more easily and in higher yield from 2,4,6-tri-*t*-butylphenylphosphine or its silylated derivative by treatment with sulfur or S_2Cl_2.[272–274]

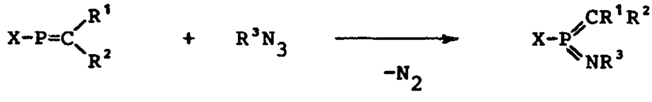
Phosphaalkene $\mathrm{Ttb{-}P{=}C(SiMe_3)_2}$ reacts with sulfur and selenium without complications forming derivatives of three-coordinate pentavalent phosphorus.[266]

Application of the Staudinger reaction on phosphaalkenes yields compounds of the type, $\mathrm{X{-}P({=}NR^1){=}CR^2_2}$. However this method is not a general one because the decreased nucleophilicity of the two-coordinate phosphorus causes many phosphaalkenes not to react easily with azides. Successful synthesis of methylene(imino)phosphoranes from phosphaalkenes was achieved in a few cases only (Scheme 62).

Interaction of 1-diazo-2,2-dimethylpropane with the phosphaalkene **18** yields the stable product of [2+3]cycloaddition. When heated in vacuum, the 1,2,4λ^3-diazaphospholidine **140** loses nitrogen, forming the λ^3-phosphirane **141** which shows no tendency to isomerize to the methylene(imino) phosphorane **142** (Scheme 63).[99] The formation of the three-membered ring **141** in the reaction of **18** would indicate that the gain in energy by cyclization exceeds that gained by resonance stabilization. Consistent with this conclusion are the MINDO/3 calculations on this system. These show the ylide form to be energetically less favorable and give a relatively high energy barrier for this valence isomerization.

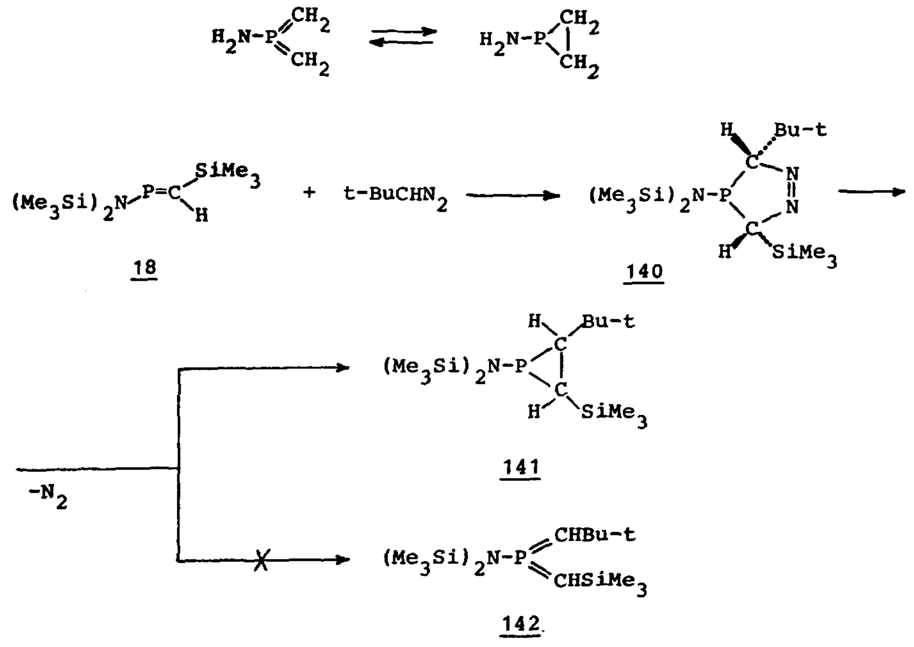
3.3. *Coordination chemistry*

3.3.1. *Phosphaalkyne transition metal complexes*. He(I) photo-electron spectroscopic studies on a variety of RC≡P molecules indicate that the HOMO in phosphaalkynes is represented by the π-



X = $(Me_3Si)_2N$, R^1 = H, R^2 = R^3 = Me_3Si	Ref. 91
X = Mes, R^1 = R^2 = R^3 = Me_3Si	Ref. 95
X = Mes, R^1 = R^2 = R^3 = Ph	Ref.241
X = 2,6-$Me_2C_6H_3$, R^1R^2C = 9-fluorenilidene, R^3 = Ph	Ref. 81

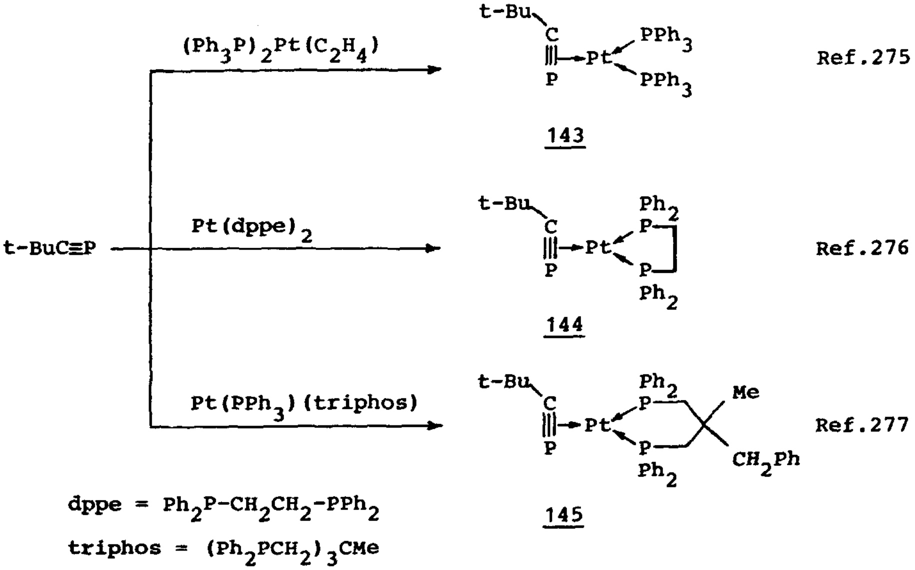
Scheme 62.



Scheme 63.

type orbital and the π(PC)—σ(P) separation is much greater than that found in analogous RC≡N systems.[257–260] This conclusion agrees with experimental results in which known transition metal complexes of phosphaalkynes are formed with participation by the (P≡C)$_\pi$-bond.

The complexes in which phosphaalkyne behaves as a two-electron donor ligand are synthesized by reactions of ligand exchange (Scheme 64).[275–277] A single crystal X-ray diffraction study of the complex **143** indicates that the phosphaalkyne ligand is bonded to platinum in a side-on fashion:



Scheme 64.

the phosphorus lone pair does not interact significantly with the metal. A remarkable feature of the structure is the considerable lengthening of the C—P bond length 1.672 Å in the coordinated *t*-BuCP compared with the typical values of 1.544 Å found for the related free ligands (FCP, MeCP and PhCP). This probably reflects the effect of back-bonding from the zerovalent platinum.

Treatment of *t*-BuCP with $[Co_2(CO)_8]$ readily affords the deep red, light- and air-sensitive liquid complex **146** in which the phosphaalkyne plays the role of a four-electron donor.[278,279] The reaction of **146** with $[W(CO)_5THF]$ results in the formation of light- and air-stable, wine-red crystals of the complex **147**. The structure of the latter is confirmed by the X-ray crystallographic analysis. Of particular interest is the establishment of the side-on coordination of the phosphaalkyne to the Co_2 system and the attachment of the $W(CO)_5$ unit by the phosphorus lone pair.[279] It should be noted that complexes of the type **146** were obtained earlier by the dechlorination of $RCCl_2PCl_2$ with $[Co_2(CO)_8]$.[280]

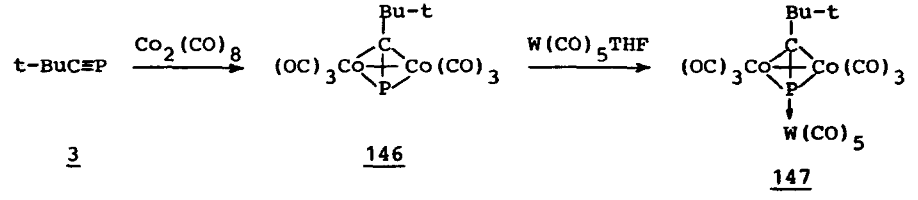
The phosphaalkyne *t*-BuCP reacts readily with $[Ni(\eta^5\text{-}C_5H_5)CO]_2$ at room temperature giving the green crystalline complex **148**. The mixed metal complex **150** was obtained as a green oil by two routes. The most efficient method (30% yield) involved heating a mixture of $[Ni(\eta^5\text{-}C_5H_5)CO]_2$ with the phosphaalkyne complex **149** at 80°C in toluene. The second approach includes the synthesis of the carbonyl complex **151** and its subsequent reaction with the phosphaalkyne. The complex **150** readily enters into further coordination with other transition metals via the phosphorus lone pair (Scheme 66).[281]

At $-60°C$, *t*-BuCP is quantitatively added to Mo≡Mo and Rh═Rh multiple bonds with the formation of the complexes **154** and **155**. These are related to the complex **149** and in all cases the phosphaalkyne behaves as a four-electron donor.[282]

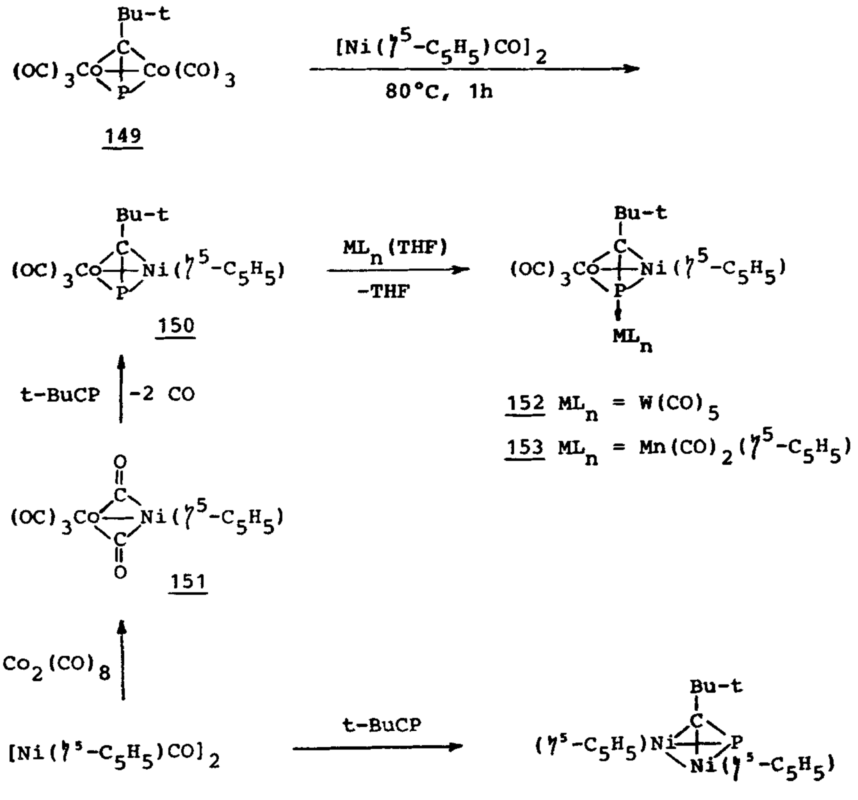
The lone pair on phosphorus in **154** is available for utilization in further bonding by transition metals. Thus, the treatment of **154** with $[Os_3(CO)_{11}(CH_3CN)]$ in THF at room temperature leads to quantitative formation of deep red dimolybdenum–triosmium complex **156**.[283] The ruthenium complex **157** was obtained by direct reaction of **154** with $[Ru_3(CO)_{12}]$ in THF in the presence of Me_3NO. An analogous approach was used in the synthesis of the platinum(II), palladium(II), and ruthenium(I) complexes of di-η^5-cyclopentadienyltetracarbonyl-μ-(3,3-dimethyl-1-phosphabutyne) dimolybdenum (Scheme 68).[284]

A new mode of coordination for a phosphaalkyne ligand has been found in the trinuclear complex **161**.[276] A single crystal X-ray diffraction study on **161** reveals that the phosphaalkyne *t*-BuCP fragment transversely bridges the Fe—Fe bond so that the phosphorus atom is coordinated to the three metal atoms of the Fe_2Pt ring. This type of bonding is similar to examples known for alkynes RC≡CR in complexes $[Ni_4(CO)_4(C_2(CF_3)_2)_3]$, $[Ni_4(CNBu\text{-}t)_4(C_2Ph_2)_3]$, and $[Fe_3(CO)_9(C_2Ph_2)]$.[285] Another example of η^2-phosphaalkyne complexes use in heterometallic cluster synthesis may serve the reaction between $[Pt(PPh_3)_2(t\text{-}BuCP)]$ and $[Pd(PPh_3)_4]$ resulting in the pentametallic complex $[Pd_2Pt_3(PPh_3)_5(t\text{-}BuCP)_3]$.[286]

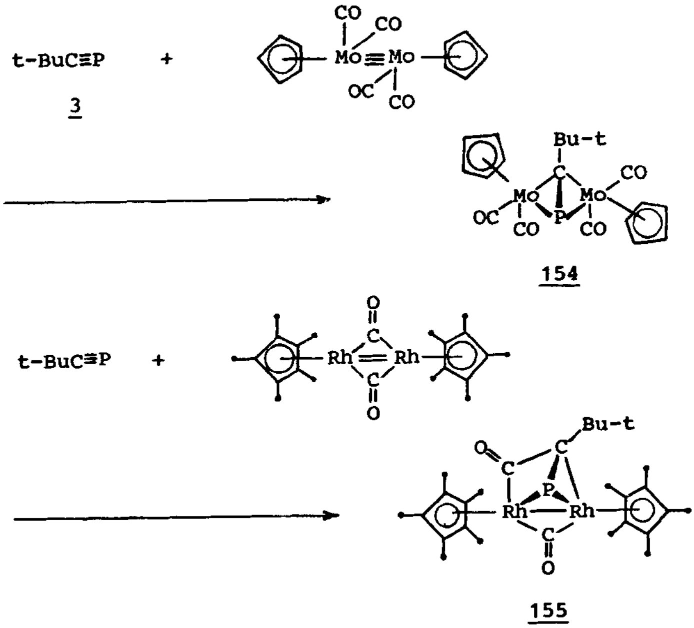
At present, the μ^3-η^2 anionic phosphaalkyne complexes are represented by compounds **162** and **163** (Scheme 70).[287] The latter are structurally related to neutral and anionic alkyne complexes



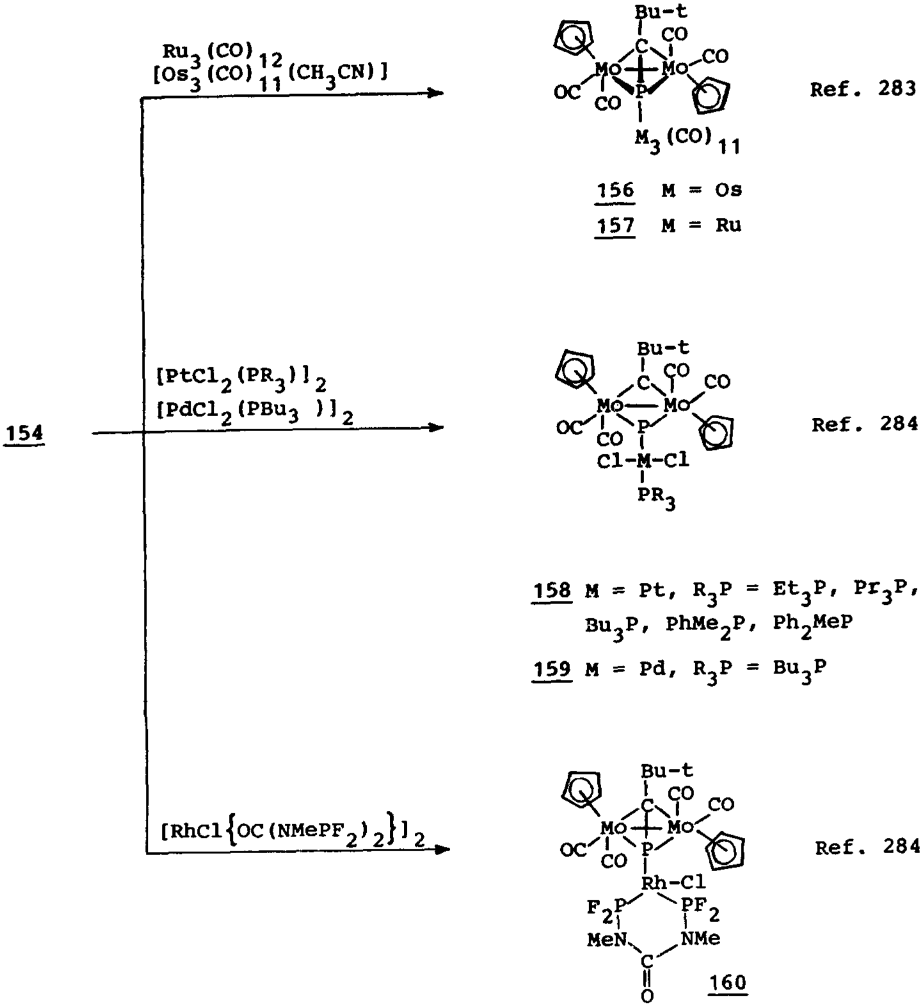
Scheme 65.



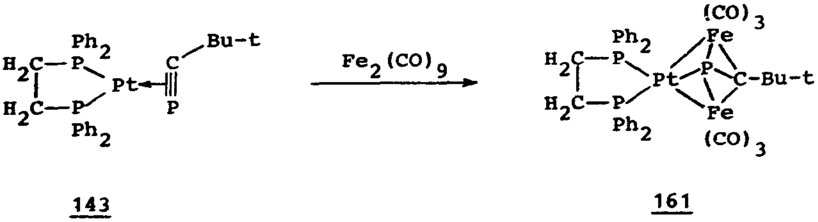
Scheme 66.



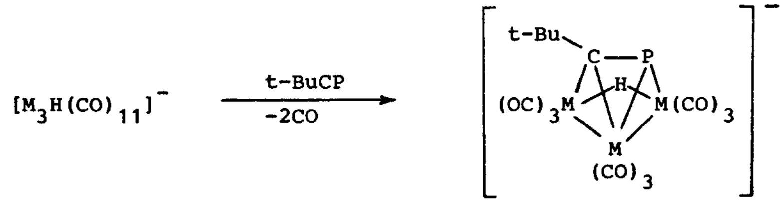
Scheme 67.



Scheme 68.



Scheme 69.



162 M = Fe (as PPh_4^+ salt)

163a M = Ru (as $(Ph_3P)_2N^+$ salt)

163b M = Ru (as Na^+ salt)

163c M = Ru (as Et_4N^+ salt)

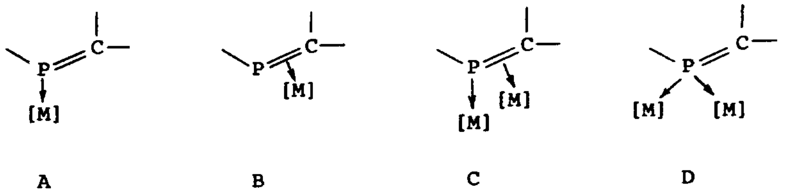
Scheme 70.

$[MNi_2(\eta^2\text{-}C_5H_5)(CO)_3(C_2Ph_2)]$ (M = Fe, Ru) and $[Fe_2Ni(\eta^3\text{-}C_3H_5)(CO)_6(C_2Ph_2)]$. It is remarkable that in spite of the enhanced basicity of the phosphorus lone pair electrons in **162** and **163** attempts to alkylate the phosphorus with MeI or $[Et_3O]^+[BF_4]^-$ were unsuccessful. This is possibly due to electron delocalization over the metal framework.

Reactions of *t*-BuCP with transition metal complexes followed by phosphaalkyne ligand oligomerization are shown in Scheme 71.

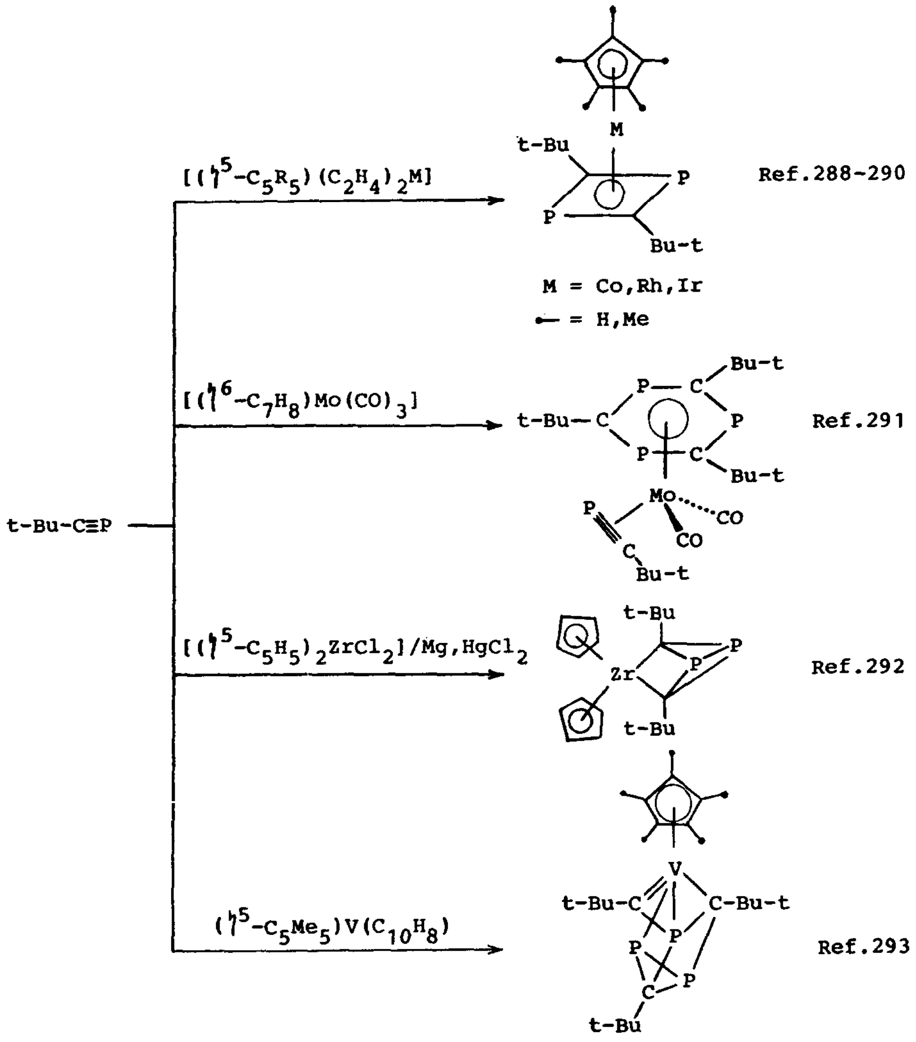
Similar to a metathesis, tungsten(VI) or molybdenum(V) chloride and *t*-BuCP react in $POCl_3$ to yield PCl_3 and di(*t*-butyl)acetylene complexes of tungsten(IV) and molybdenum(III) chloride.

3.3.2. *Phosphaalkene transition metal complexes.* Compounds with PC-double bonds can react with transition metal derivatives to form various complexes. The most significant ones are represented by A–D structures.



Because of an insignificant π(PC)–σ(P) separation, the mode of phosphaalkene coordination is largely dependent on the nature of the transition metal and the ligands attached to it. The η^1-mode of coordination of phosphaalkenes (Type A) was established for chromium(0),[138,295,296] tungsten(0),[296] rhodium(I),[296] platinum(II),[296–299] nickel(0),[300] iron(0).[146,256,266,301] The majority of η^1-phosphaalkene complexes were derived via reactions of the ligand exchange.

The chemistry of η^2-coordinated phosphaalkenes (Type B) dates back to the synthesis of the platinum complex **164**.[299] In the crystalline state, **164** possesses the structure **164a** with σ-bonded phosphaalkene. In toluene solution an η^1/η^2 equilibrium **164a** $\rightleftarrows$ **164b** has been revealed ($\Delta H = -3.9$ kcal.mol^{-1} and $\Delta S = -15$ kcal.mol^{-1}.degree^{-1}). Theoretical calculations on models confirm the greater stability of the η^2-complex.[229] The redox reaction of $(Me_3P)_2NiCl_2$ with $[(Me_3Si)_2CH]_2PNa$ gave the complex **165**, wherein phosphaalkene retains the η^2-coordination both in the crystalline and dissolved states.[302] The structure **165** has been solved by the single crystal X-ray method. The geometry at nickel is square planar, the PC-bond length of 1.773 Å is

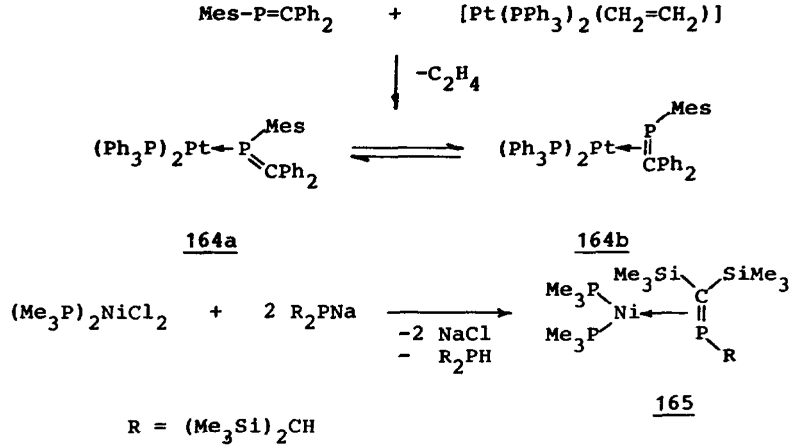


Scheme 71.

approximately midway between the P—C single bond length of 1.85 Å and the P═C bond length of 1.67 Å which has been reported for uncoordinated phosphaalkenes. It should be emphasized that a comparative elongation of the C═C-bond stemming from the η^2-coordination is also observed in alkenes (1.40–1.47 Å instead of 1.34 Å in simple olefins).[303]

The structure of phosphaalkene complexes largely depends on the nature of ligands connected with the metal. Thus, the reaction of $Ni(CO)_4$ with phosphaalkene **8** leads to the η^1-complexes **166** or **167**. Nevertheless in the zero-valent nickel complex **168**, the phosphaalkene is η^2-coordinated (Scheme 73).[300] The observed difference in the mode of Ni(0) coordination in carbonyl and 2,2′-dipyridyl complexes may be explained by the fact that CO-ligands, as strong π-acceptors, reduce the π-donor ability of the metal with respect to phosphaalkene, thus destabilizing η^2-coordination. On the contrary, 2,2′-dipyridyl, as a weak π-acceptor, contributes to the η^2-coordination of nickel.

Differing modes of coordination have been reported for complexes of platinum(0) containing the phosphaalkene **7**. In the complex **170** the phosphaalkene is η^2-bonded to the metal whereas in **169** it is η^1-coordinated (Scheme 74).[298]

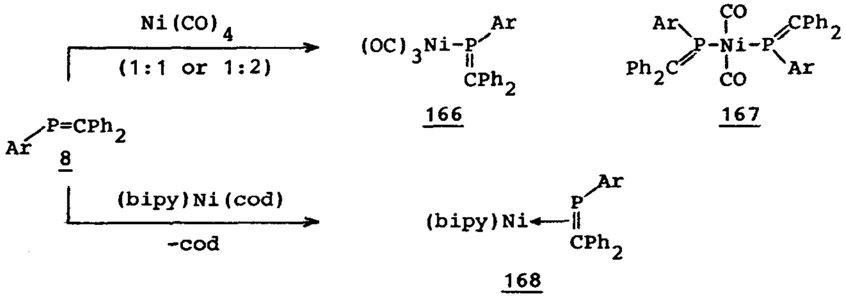


Scheme 72.

When the phosphaalkene **42** reacts with $Fe_2(CO)_9$ in a 1 : 1 ratio, it gives a mixture of the complexes **171** and **172**. The reaction of the above agents in a 1 : 2 ratio results in complex **173**, in which the phosphaalkene ligand is η^1,η^2-coordinated (Type C).[301]

The different behaviour of phosphaalkynes and phosphaalkenes with respect to transition metals is obvious in the reaction of bis-(cycloocta-1,5-diene)platinum with the mixture of the phosphaalkene, $MesP{=}CPh_2$, and the phosphaalkyne, *t*-BuCP (2 : 1). The product of this reaction is an interesting example of a complex containing at the same time the η^1-coordinated phosphaalkene and the η^2-coordinated phosphaalkyne (Scheme 76).[298]

Of particular interest are the metal-substituted phosphaalkenes of the $ML_n{\sim}P{=}CR^1R^2$ type.[304–306] At present, there are three main synthetic approaches to these compounds: (i) formation of the PC-double bond in the coordination sphere of transition metal via trimethylsilyl- or acylphosphido-complexes,[168–170,307] (ii) nucleophilic substitution of P-chlorophosphaalkenes with carbonylmetallate anions,[308–312] and (iii) rearrangement of complexes of Me_5C_5-substituted phosphaalkenes with transfer of the Me_5C_5-ligand from phosphorus to a metal centre.[313–316]

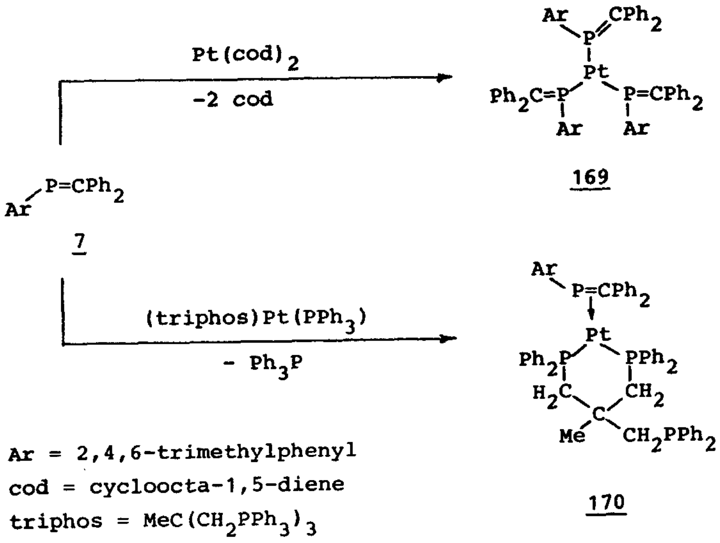


Ar = 2,6-$Me_2C_6H_3$

bipy = 2,2′-bipyridyl

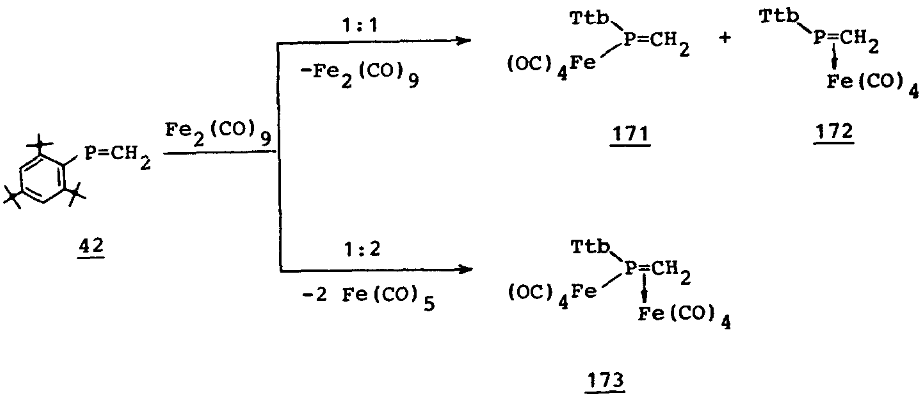
cod = cycloocta-1,5-diene

Scheme 73.

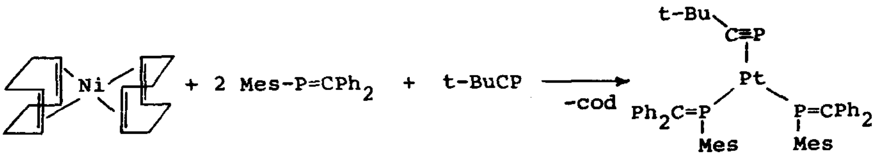


Ar = 2,4,6-trimethylphenyl
cod = cycloocta-1,5-diene
triphos = $MeC(CH_2PPh_3)_3$

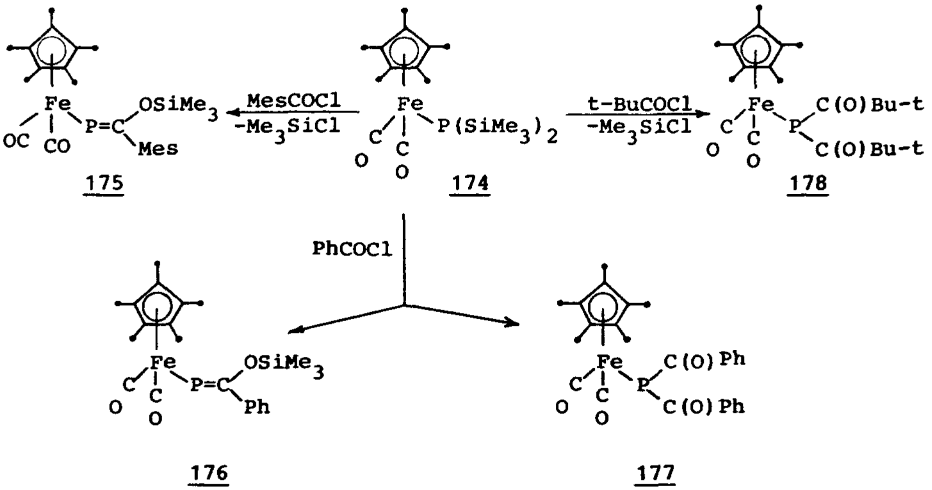
Scheme 74.



Scheme 75.



Scheme 76.



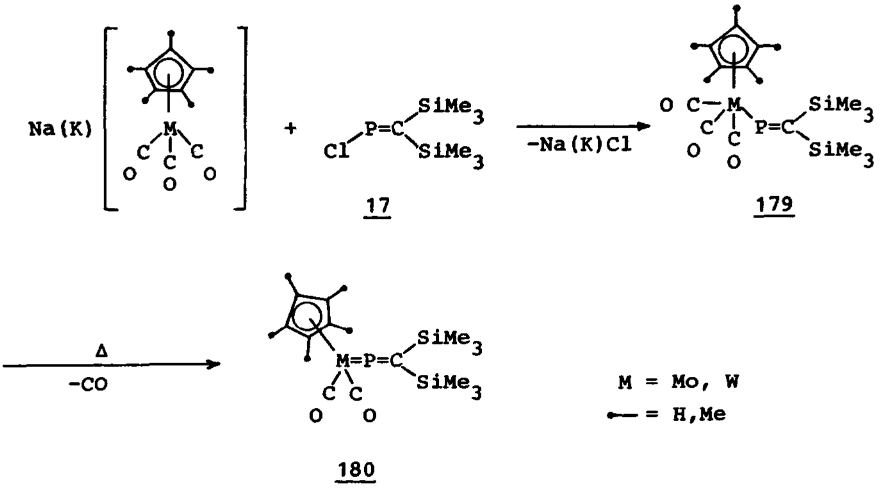
Mes = 2,4,6-trimethylphenyl

•— = Me

Scheme 77.

The synthesis of phosphaalkenyl complex, $(C_5H_5)(CO)_2Fe—P{=}C(OSiMe_3)(Bu\text{-}t)$, from $(C_5H_5)(CO)_2Fe—P(SiMe_3)_2$ and *t*-BuCOCl was discussed earlier (Scheme 25). A similar reaction took place with benzoyl chloride and mesitoyl chloride. However, complex **174**, in which the C_5H_5-ring at iron is substituted by the more bulky and more electron releasing C_5Me_5-ligand, reacts with benzoyl chloride to form a mixture of the phosphaalkenyl complex **176** and the diacylphosphido complex **177**. In case of pivaloyl chloride, the only product of the reaction is the diacylphosphido complex **178** (Scheme 77).[307] The exchange of Fe by the higher homologues Ru and Os leads to a similar reaction pattern. The tendency to form diacylphosphido complexes instead of phosphaalkenyl complexes is more pronounced with the heavier and more basic homologues.[170]

Scheme 78 illustrates the use of the procedure of heterogeneous metallation for the synthesis of



M = Mo, W

•— = H,Me

Scheme 78.

P-metallophosphaalkenes.[308,309] Treatment of **17** with sodium or potassium carbonylmetallates yields the molybdenum and tungsten substituted phosphaalkenes **179**. On heating, intramolecular substitution of one carbonyl ligand occurs with the formation of the metallophosphaallenes **180**.

Reaction of the phosphaalkene **17** with $Na_2[Fe(CO)_4]$ results in formation of the bridging phosphaalkenyl complex **181**, the structure of which was established by an X-ray study.[310] Each molecule of **181** possesses crystallographically imposed C_2 symmetry and the P_2Fe_2 core is of the 'butterfly' type. The PC-bond length for **181** (1.65 Å) corresponds to a bond order of 2.0 and falls in the range observed for η^1-coordinated and free phosphaalkenes. Two competitive reactions occur when an equimolar amount of $[Ph_4P][HFe(CO)_4]$ is added to a dichloromethane solution of the phosphaalkene **17**: elimination of tetraphenylphosphonium chloride and formation of the η^2-phosphaalkene complex **182**, and hydrogen chloride evolution with the formation of the minor product **183** (Scheme 79).[311,312]

A novel synthetic approach to complexes $ML_nP{=}CR^1R^2$ was developed by Niecke *et al.*[313–316] The key step of the method includes a transfer of a pentamethylcyclopentadienyl ligand from phosphorus to the metal, as shown in Scheme 80.

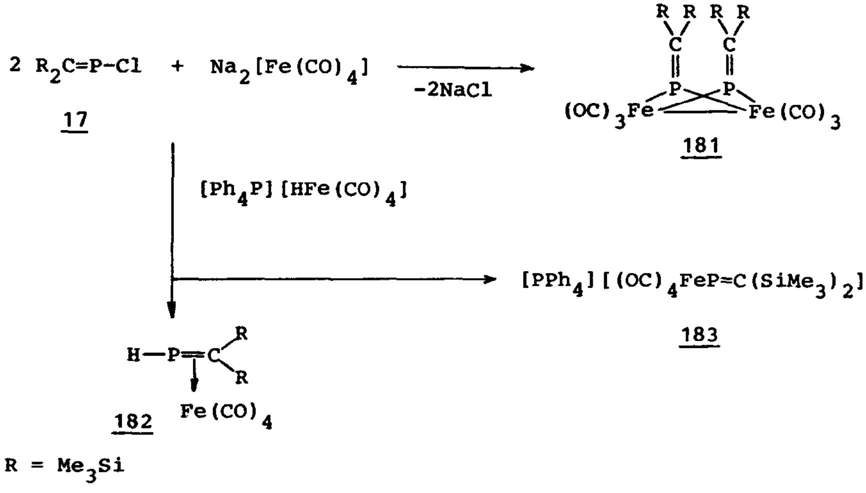
In recent years, significant attention has been paid to the study of the η^3-phosphaallyl and η^4-phosphabutadiene complexes.[317,318] In many instances such complexes may be obtained directly by reaction of phosphaalkenes with transition metal derivatives. Thus, by analogy with the classical method of synthesis of π-allyl complexes, the reactions of 1,3-diphosphapropenes **184**, **185** with organometallic compounds led to 1,3-diphosphaallyl complexes (Scheme 81).

1,3-Diphosphapropene **186** reacts with $Na[M(CO)_3(\eta^5\text{-}C_5H_5)]$ (M = Mo, W) to form s-*trans*-1,3-diphospha-4-metallobutadienes **187**. The reaction of **187** (M = W) with $Fe_2(CO)_9$ led to the η^4-phosphabutadiene complexes **188**.[322]

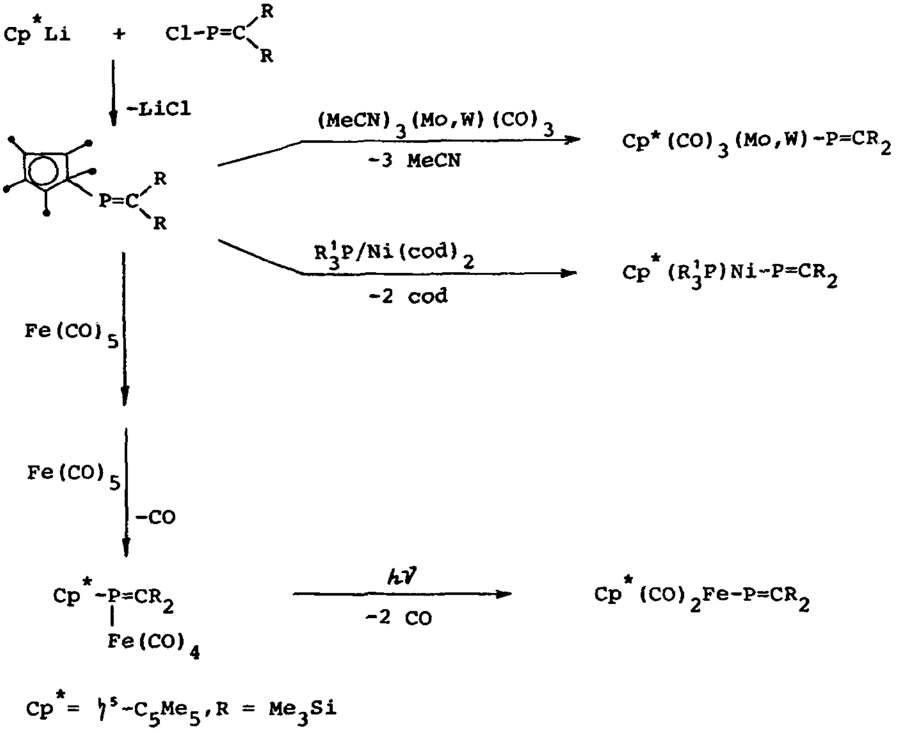
In summarizing the current situation in coordination chemistry of compounds with P≡C- and P=C-bonds, it must be emphasized that there is a great similarity between the complexes of phosphaalkynes and phosphaalkenes and the π-complexes of alkynes and alkenes. It is a significant confirmation of the close similarity between PC- and CC-multiple bonds.

3.4. *Reactions with retention of the coordination number of the phosphorus atom*

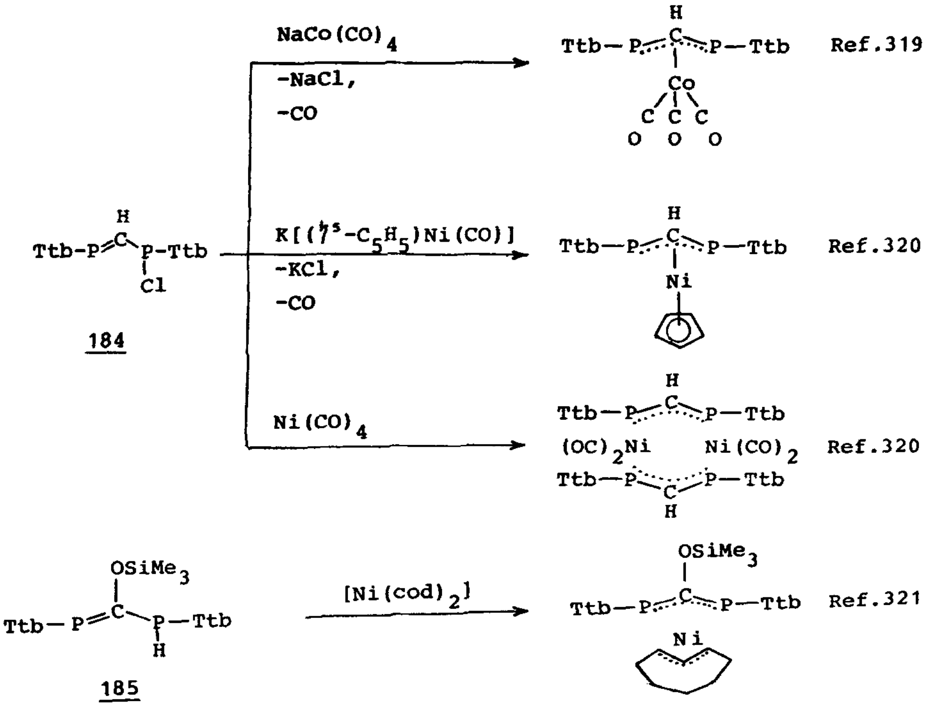
The interest in reactions of this type is explained by wide opportunities of derivatization offered by certain relatively available phosphaalkenes containing reactive bonds or substituents at two-coordinate phosphorus or methylene carbon atoms.



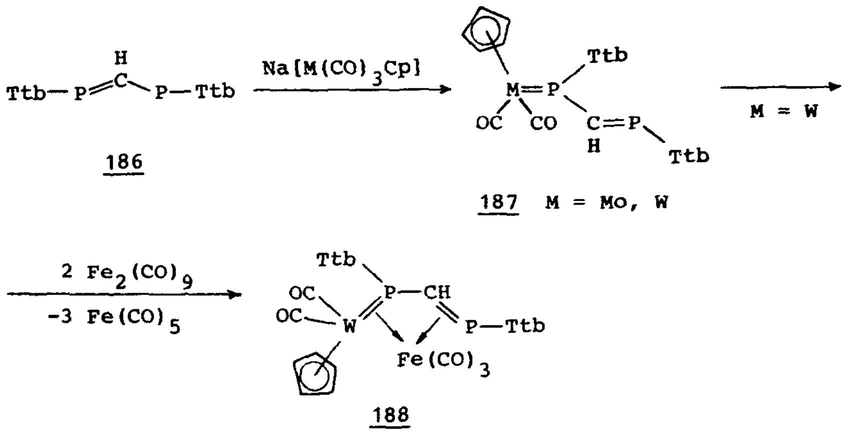
Scheme 79.



Scheme 80.



Scheme 81.

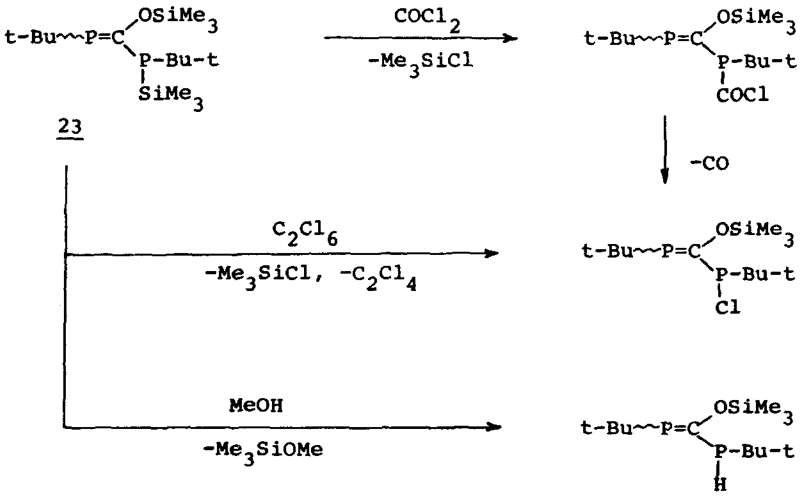


Scheme 82.

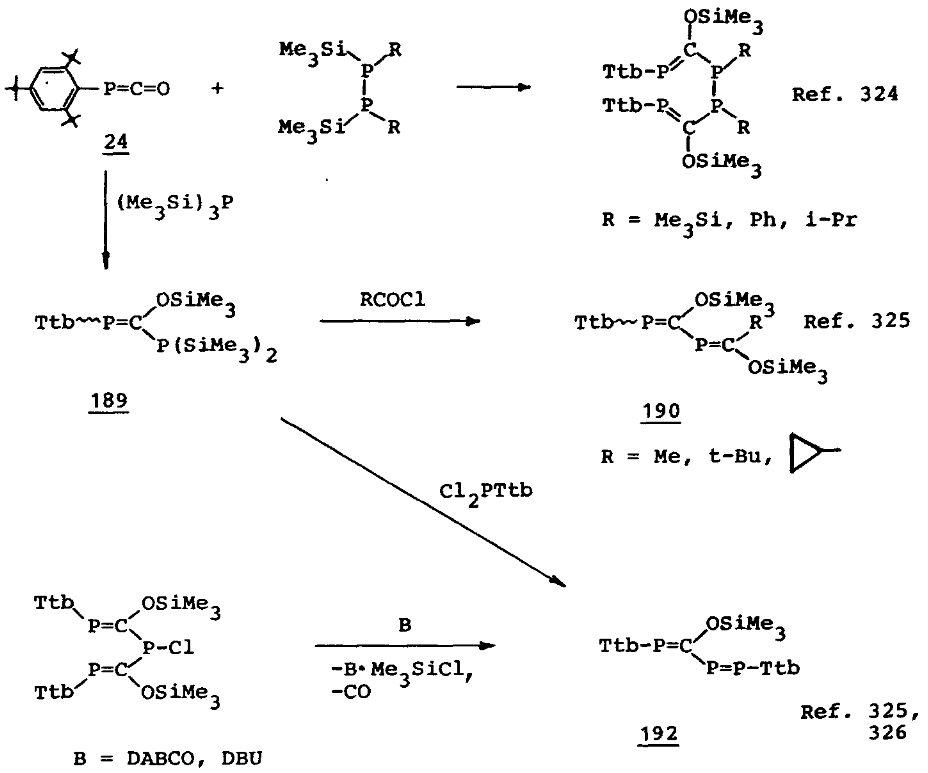
3.4.1. *Reactions at the periphery*. Phosphaalkenes of the type **23** can undergo various conversions to form a large number of products.[173,174,323] In many instances such reactions proceed with participation of the P—Si bond without the involvement of two-coordinate phosphorus as demonstrated in Scheme 83.[174]

Despite the fact that the reaction of phosphaketene **24** with silylphosphines occurs with destruction of the cumulene grouping, the PC-double bond is not involved in these conversions.[324] The reactions of the phosphaalkene **189** with carboxylic acid chlorides[325] and 2,4,6-tri-*t*-butylphenyldichlorophosphine[326] are used for the synthesis of 1,3-diphospha- and 1,2,4-triphospha-1,3-butadienes **190**, **192** (Scheme 84). The compound **192** is also formed when the phosphaalkene **191** is treated with strong bases (DABCO, DBU).[326]

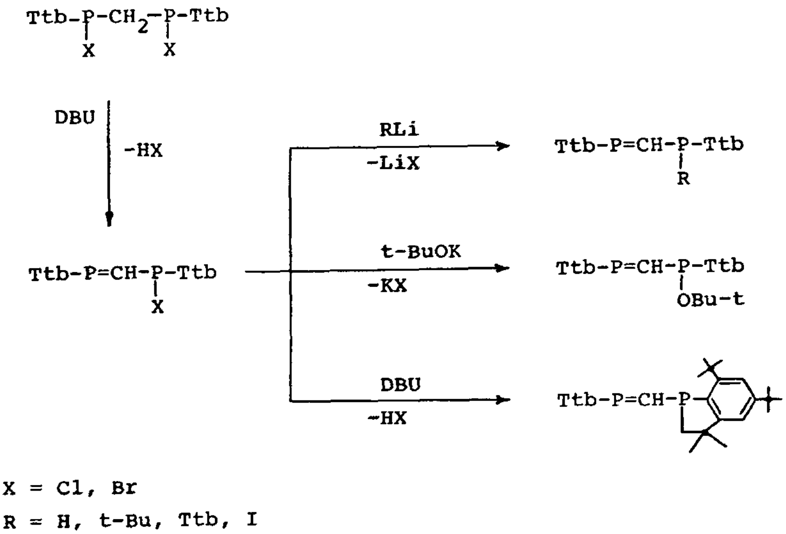
1,3-Diphosphapropenes, containing at the phosphorus atoms a bulky 2,4,6-tri-*t*-butylphenyl group are used to synthesize the various $\mathrm{P}^{\mathrm{III}}$-functionalized derivatives (Scheme 85).[82]



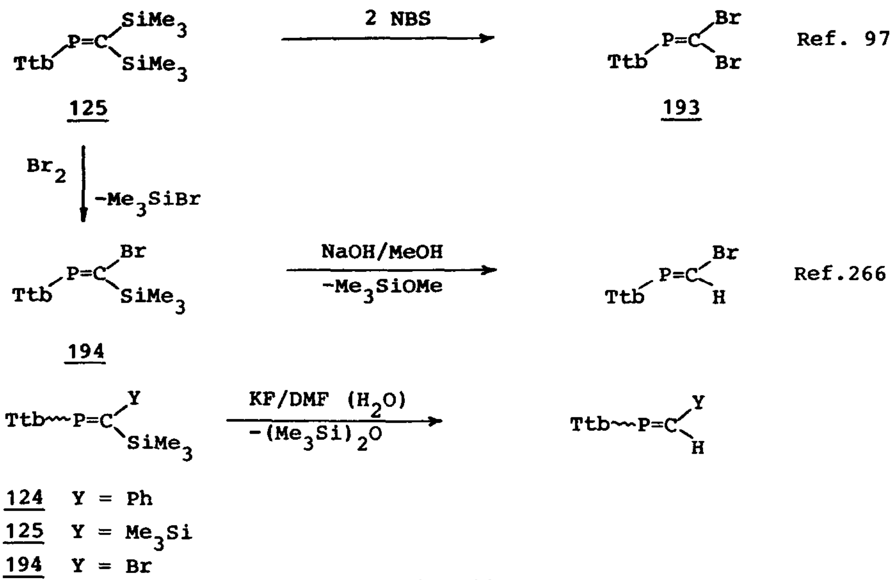
Scheme 83.



Scheme 84.



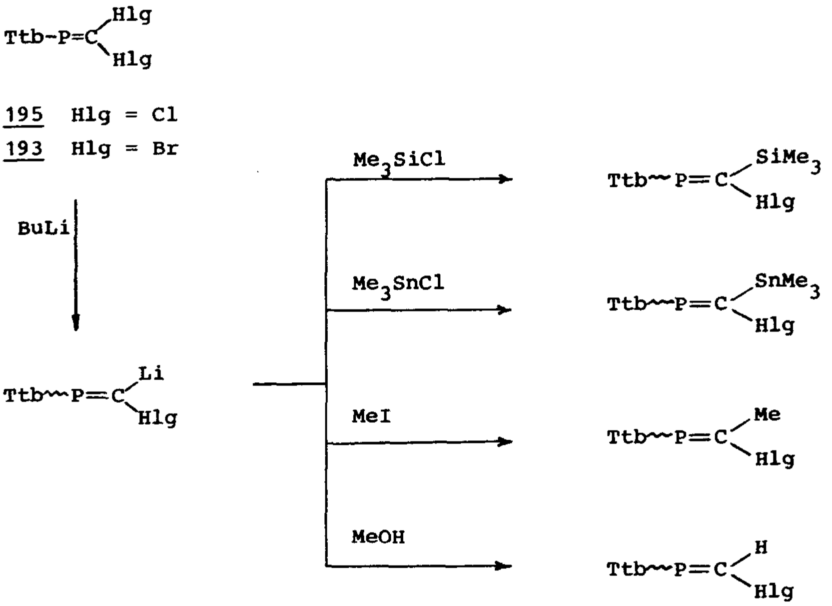
Scheme 85.



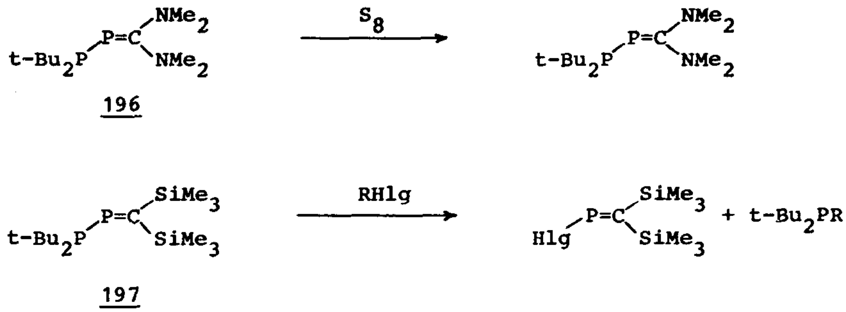
Scheme 86.

Treatment of the highly hindered phosphaalkene **125** with bromine or N-bromosuccinimide leads to the compounds **193**[97] and **194**.[266] The exchange of the silyl group by a proton in the phosphaalkenes **124**, **125**, and **194** may be achieved by heating them with KF in moist dimethylformamide.[327]

The C—Cl and C—Br bonds in 2,4,6-tri-*t*-butylphenyl-C,C-dihalophosphaalkenes **193** and **195** are selectively cleaved by butyllithium. The products are valuable substrates for the synthesis of other functionally substituted phosphaalkenes (Scheme 87).[97]



Scheme 87.



R = Me, Et, Ac
Hlg = Cl, Br, I

Scheme 88.

Phosphaalkene **196** reacts with equimolar quantity of sulfur in ether at −78°C by addition to three-coordinate phosphorus atom.[328] However, treatment of **197** with alkyl halides or acetyl chloride results in cleavage of the P—P bond.[329,330]

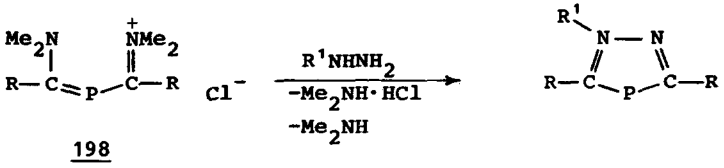
Schmidpeter and Willhalm have found that phosphaalkenes **198** undergo heterocyclization when treated with hydrazines (Scheme 89).[145]

3.4.2. *Substitution at the two-coordinate phosphorus atom and insertion into the P—Si bond.* P-(Halo)phosphaalkenes allow derivatization at the two-coordinate phosphorus. Thus, the P-fluoromethylenephosphine **199** was obtained by exchange reactions with AgF[331] or AgBF$_4$.[332] Chlorine substitution at the two-coordinate phosphorus atom in **17** by bromine and iodine with Me$_3$SiBr and Me$_3$SiI proceeds as readily as with chlorophosphines.[331] The reactions of **107** with proton donor nucleophilic reagents may illustrate the use of nucleophilic substitution for obtaining novel phosphaalkenes, such as the alkoxy-, alkylthio-, and phosphino-substituted compounds[248,333] (Scheme 90).

Similar transformations were realized for the phosphaalkenes Cl—P=C(SiMe$_3$)$_2$, and Cl—P=C(SR)$_2$. Due to their low stability, P-chloro-bis(alkylthio)methylenephosphines are obtained and used in ether at a temperature of −30°C.[96] The reaction of phosphaalkene **17** with *t*-Bu$_2$AsLi gave the P-arsino-substituted phosphaalkene.[329]

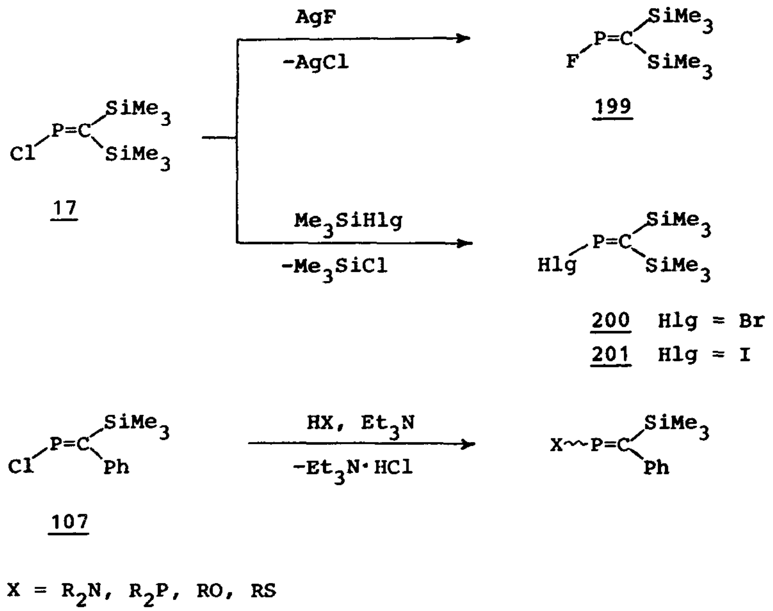
Despite the fact that organolithium and organomagnesium compounds show high nucleophilicity and add to the PC-double bond, in some cases it is possible to realize the selective substitution of chlorine in P-chlorophosphaalkenes by alkyl and aryl groups (Scheme 91).

P-Ethynylphosphaalkenes were obtained in high yield by reacting alkyne Grignard reagents RC≡CMgCl (R = Ph, Me$_3$Si) with ClP=C(SiMe$_3$)$_2$ and ClP=C(Ph)SiMe$_3$.[201] However, the reactions of the phosphaalkene **17** with organolithium reagents[202] do not stop at the stage of nucleophilic



R = H, Alk, Ar, Me$_2$N, MeS

Scheme 89.

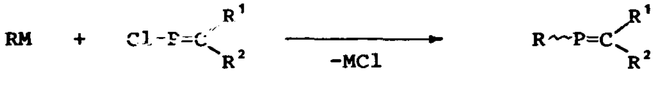


Scheme 90.

substitution but proceed through a multistage process giving 2,4-diphospha-1-butenes **203** (Scheme 92).[336]

In compounds of the type R_2N—P=CYZ, the role of pseudohalogen may be played by the R_2N group. In particular, P-bis(trimethylsilyl)amino-substituted phosphaalkenes can react with sterically hindered nucleophilic bases by nucleophilic displacement at the two-coordinate phosphorus atom without involvement of the P=C bond (Scheme 93).[337]

The second major group of reactions of P-functionalization involves either electrophilic substitution at the P-atom or insertion of unsaturated reagents into the Si—P bond in Me_3Si—P=CR^1R^2 derivatives. Acylation of the phosphaalkene **92** by pivaloylchloride (80°C, 72 h) leads to the phosphaalkene **204**. When heated, the latter loses a CO molecule and is converted into the phosphaalkene **205** (Scheme 94).[158,161]



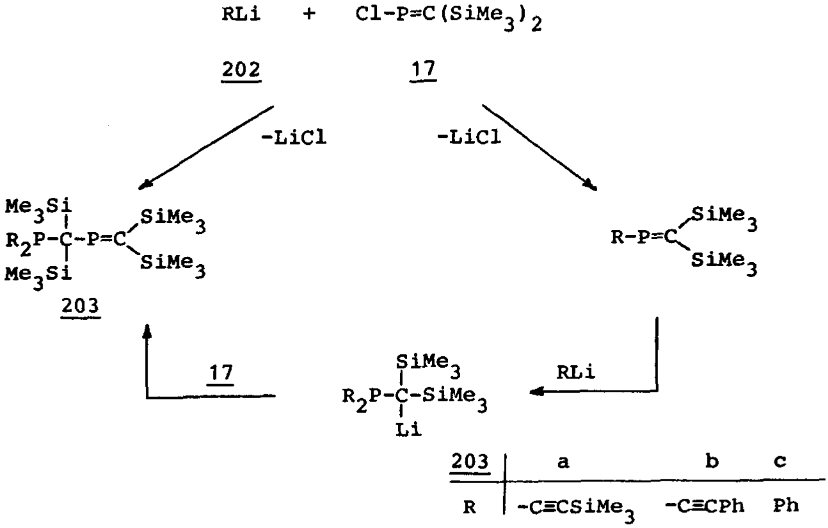
R^1= Ph, R^2= Me_3Si [219,248,333]

R^1= R^2= Me_3Si [266,303,309,334,336]

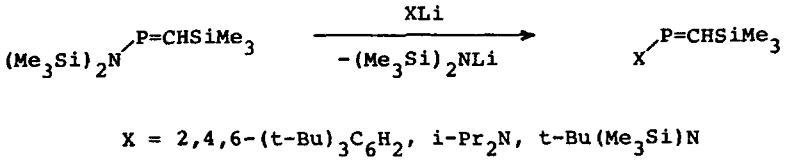
R^1= t-Bu, R^2= Me_3SiO [167]

RM = t-BuLi,[167,248] PhLi,[167] 4-t-BuC_6H_4Li,[219] FlLi (Fl = 9-fluorenyl),[334] TtbLi,[266,303] $(Me_3Si)_3$CLi,[303] $(Me_3Si)_2$CHLi,[303,335] AlkMgBr[167,333]

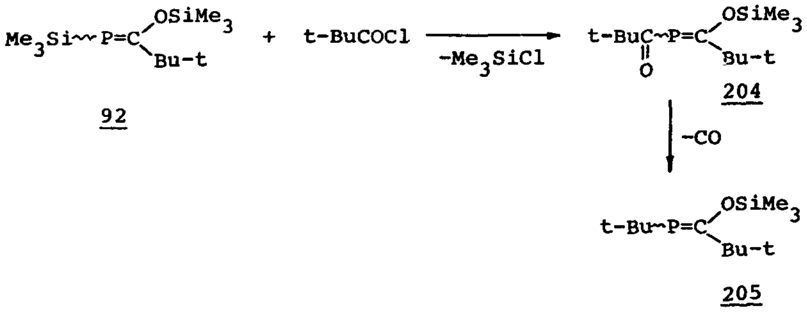
Scheme 91.



Scheme 92.



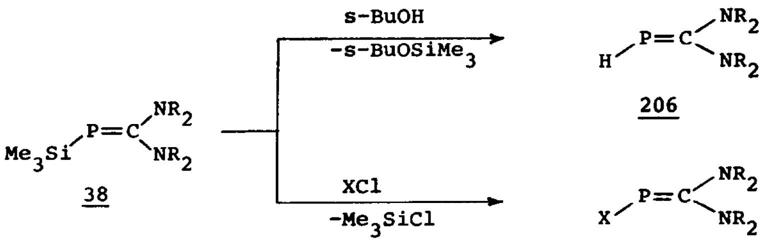
Scheme 93.



Scheme 94.

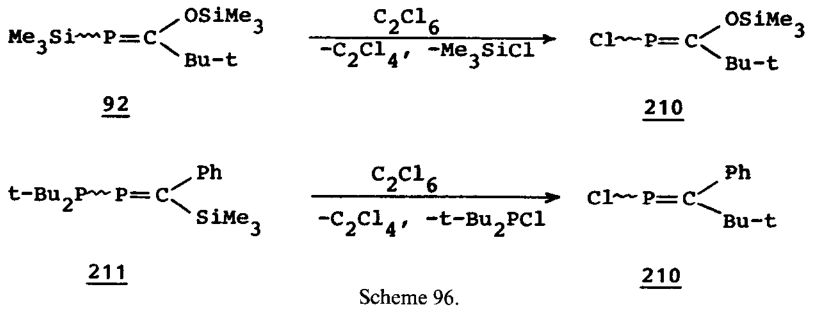
Treatment of the compound **92** with methanol (1 : 1) leads to the phosphaalkene HP=C(OSiMe$_3$)Bu-*t*.[198] The exchange of the Me$_3$Si group at the two-coordinate phosphorus atom for other functional groups is used to synthesize the phosphaalkenes **196**, **206–209**.[328,338]

Pure P-chloro-substituted phosphaalkene **210** was obtained in high yield from the reaction of **92** with hexachloroethane.[167] Compound **211** can be converted into **210** in the same way[333] (Scheme 96). The cleavage of the PP-bond and formation of I—P=C(SiMe$_3$)$_2$ occurred in the reaction of the phosphaalkene *t*-Bu$_2$P—P=C(SiMe$_3$)$_2$ with iodomethane.[329]

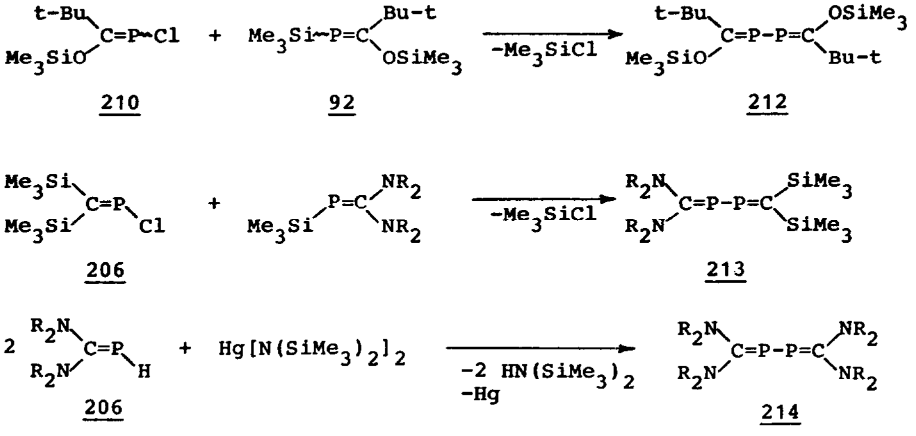


196 X = t-Bu$_2$P
207 X = Ph$_3$Si
208 X = Ph$_3$Ge
209 X = Ph$_3$Sn

Scheme 95.

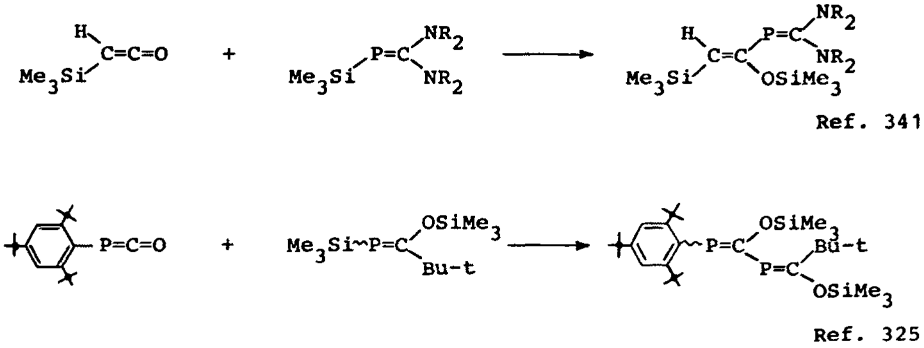


Scheme 96.



Scheme 97.

The reactions proceeding with the retention of the phosphorus atom coordination number are a valuable route to compounds with a phosphadiene system. Thus, the heating of equimolar amounts of phosphaalkenes **92** and **210** leads to 2,3-diphosphabutadiene **212**.[167] A similar approach has been used for the synthesis of 2,3-diphosphabutadienes **213**.[339] The bis(dialkylamino)methylenephosphines **206** were converted into the hitherto unknown 2,3-diphosphabutadienes **214** by their reaction with Hg[N(SiMe$_3$)]$_2$.[340]

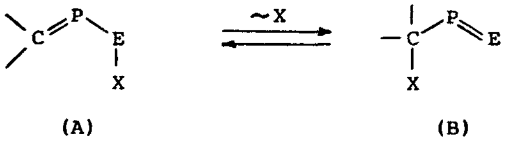


Scheme 98.

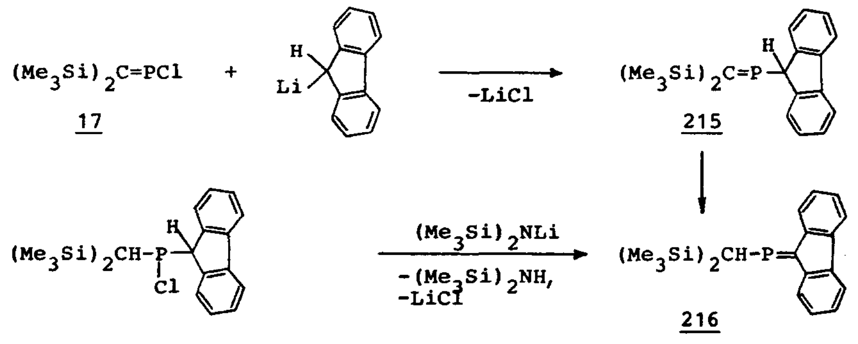
P-Silyl-substituted phosphaalkenes react with heterocumulenes by insertion into the PSi-bond giving phosphabutadienes (Scheme 98).[325,341]

3.4.3. *Structural isomerization of phosphaalkenes.* Similar to alkenes, the compounds $XP{=}CR^1R^2$ ($R^1 \neq R^2$) may exist in the form of geometrical isomers. The interconversions of *Z*- and *E*-isomers have been studied for several isomeric pairs.[36,327,342,343] Correlation of the NMR spectroscopic data with the geometry at the PC-double bond was discussed by Appel and co-workers.[36]

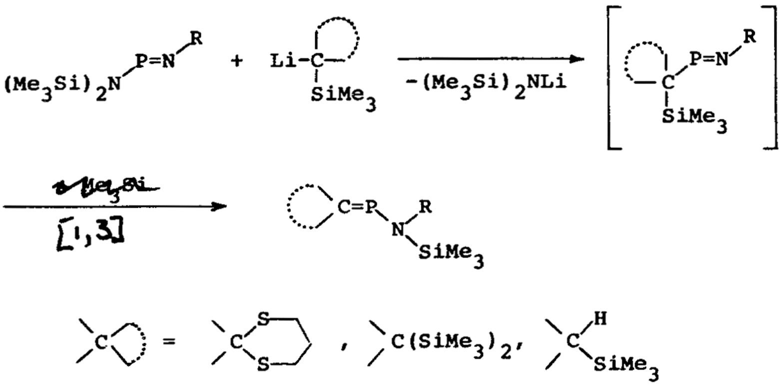
In principle, for the phosphaalkenes of the type (A) having a weak E—X bond there is a possibility of either reversible or irreversible isomerization into compounds with the P=E bond (B). A driving force for the (A) → (B) interconversion may involve the formation of an energetically favoured bond system or the reduction of intramolecular steric interactions.



The simplest example of such isomerization is a 1,3-prototropic rearrangement **215** → **216** described by Kolodyazhnyi and Kukhar (Scheme 99).[334] Phosphaalkene **215** was obtained in high yield by the reaction of **17** in the THF with fluorenyllithium. It is stable in pure state, but is readily isomerized into the phosphaalkene **216** in the presence of DBU or $(Me_3Si)_2NLi$. The rearrangement



Scheme 99.



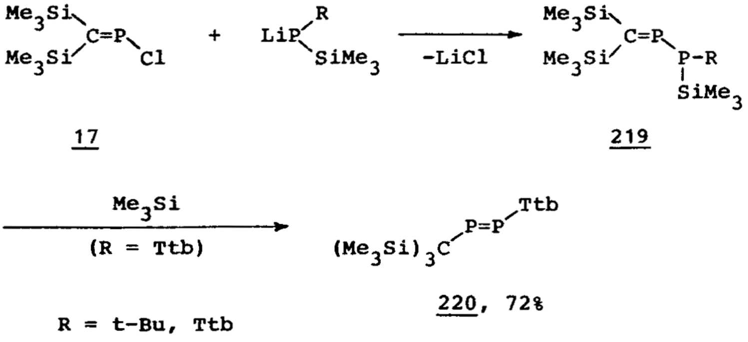
Scheme 100.

is irreversible and proceeds exclusively towards the phosphaalkene **216** which is stabilized by conjugation of the PC-double bond with the fluorene group.

Of particular interest are the isomeric conversions connecting various classes of two-coordinate phosphorus compounds. When a comparatively high stability of P=C bond in the series of other π-bonds formed by the two-coordinate phosphorus is considered then it is evident that electronic factors could make unfavourable contributions to the thermodynamics of the (A) → (B) conversion. This could assist reverse isomerization. Indeed, it was found that N,N-bis(trimethylsilyl)amino-iminophosphines react with sterically hindered C-silylated organolithium compounds forming the thermodynamically stable P-aminomethylenephosphines via nucleophilic displacement at the dicoordinated phosphorus atom with subsequent [1,3] silyl migration from carbon to nitrogen (Scheme 100).[344,345]

Rearrangement of the (A) → (B) type was realized in the series of the P-phosphino-substituted phosphaalkenes (Scheme 101).[346,347] Reaction of **17** with *t*-BuP($SiMe_3$)Li leads to the thermostable phosphaalkene **219** (R = *t*-Bu). The more sterically crowded lithium trimethylsilyl-2,4,6-tri-*t*-butylphenylphosphide reacts with **17** giving in quantitative yield the structurally rearranged product **220** (R = Ttb). In this case the rate of formation of the diphosphene is so fast that the intermediate P-phosphinomethylenephosphine could not be observed by ^{31}P NMR spectroscopy.

It is evident that these approaches may be useful for the synthesis of compounds which are not easily accessible by traditional methods.



Scheme 101.

4. CONCLUSION

Today a surprisingly wide variety of stable compounds with $P^{III}C$-multiple bonds is known. A systematic study of the chemical behaviour of alkylidyne- and alkylidene-phosphines ($RC{\equiv}P$, $RP{=}CR_2$) leads to description of these compounds as 'genuine' phosphaalkynes and phosphaalkenes having PC-multiple bond analogous to those of the alkenes and alkynes. However, the $P{\equiv}C$ and $P{=}C$ bonds are thermodynamically and kinetically less stable than the double and triple NC- and CC-bonds. Therefore, phosphaalkynes and phosphaalkenes cannot be isolated under ordinary conditions unless they are stabilized by steric factors or conjugation. In the light of the above data, it becomes clear that the Double Bond Rule, according to which compounds with $(p{-}p)_\pi$-bonds between elements of the first and those higher periods should not exist, requires updating. A more correct generalisation reads that the tendency to $(p{-}p)_\pi$-bond formation decreases in the Periodic Table from top to bottom.

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