ADVANCES IN INORGANIC CHEMISTRY, VOL. 33

DOUBLE BONDS BETWEEN PHOSPHORUS AND CARBON

R. APPEL and F. KNOLL

Institute of Inorganic Chemistry, University of Bonn,
D-5300 Bonn 1, Federal Republic of Germany

I. Introduction and History

In addition to the periodic system of the elements, in chemistry two rules have proved particularly useful with respect to attempts to classify and systemize the variety of elements and their compounds: the octet rule and the double-bond rule.

The latter rule denies the possibility of stable $p\pi$–$p\pi$ double bonds between elements beyond the second period. Thus carbon dioxide is a volatile molecule in which the electronic stabilization of the carbon with the oxygens is reached via two π bonds. Silicon, on the contrary, prefers four single bonds to stabilize the electronic structure within silicon dioxide, forcing the oxygen atoms into tetrahedral positions. The coordination number four for silicon bonding to oxygen represents a polymeric, solid, and high-melting-temperature compound.

The double-bond rule requirement, which has proved correct with numerous natural as well as synthesized compounds, with respect to modern conceptions, is due to enlarged and diffused p orbitals of the heavier elements that do not allow sufficient overlap for the stabilization of covalent π bonds (*1, 2*). Because of this interpretation it is easily neglected that the periodic system of the elements is related to natural law; the strict interpretation of the two doctrines, which are only rules, may hinder the discovery of new classes of compounds. Fortuitous observations, however, sometimes lead to new directions of research. Examples are the investigations on noble gas compounds, in progress since 1962, and the discovery of heavy nonmetallic elements such as phosphorus, silicon, and arsenic in compounds showing real $p\pi$ multiple bonds. At the beginning of the period of rather impetuous development in the last decade in the area of compounds exhibiting PC multiple bonds was Gier's (*3*) discovery of phosphaacetylene HCP, which is stable only below $-120°$C. Due to classical considerations phosphorus was linked to the carbon via three bonds, one σ bond and two π bonds. Therewith the ability of phosphorus to establish $p\pi$ bonds was, although only at low temperatures, proved. With respect to this observation such compounds could no longer be excluded and the question was, what could be done to stabilize a multiple bond between phosphorus and carbon against the energetically privileged polymerization?

As shown in Fig. 1 there are two chances. First, the stability can be reached thermodynamically by lowering the energy of the PC double bond via mesomeric π-electron delocalization. Second, the stability can be kinetically obtained by introducing voluminous and bulky bridgehead atoms to shield the reactive center. Substituents for the latter process are *t*-butyl, mesityl, or especially tri-*t*-butylphenyl, the so-called supermesityl group.

In order to lower the energy of the PC double bond for stabilization, ring systems are rather suitable; indeed, for the first time, Dimroth and Hoffmann (*4*), with the phosphamethine cyanin cation, and later on Märkl (*5*) and Ashe (*6*), with phosphabenzene, succeeded in synthesizing such molecules as stable species.

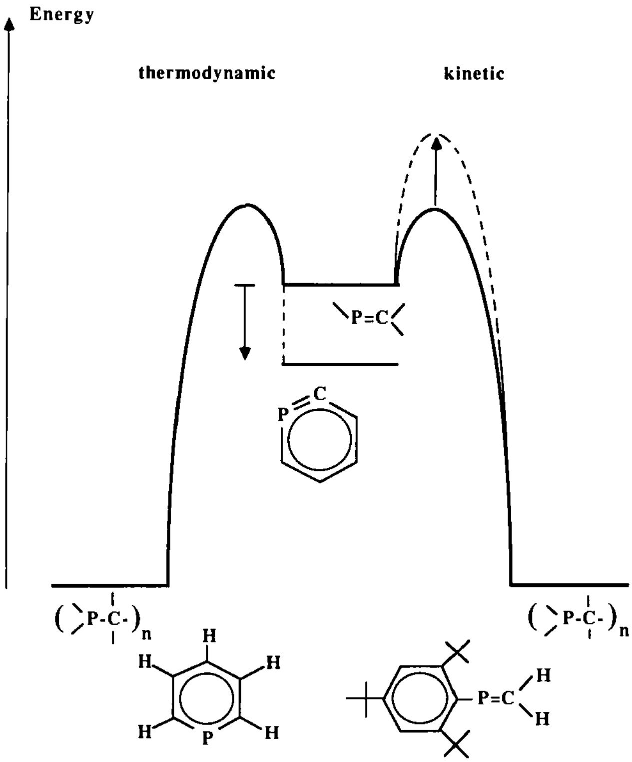
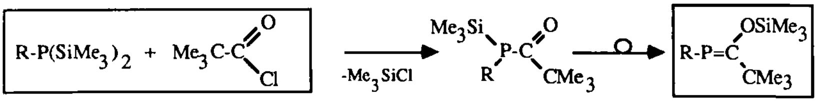


FIG. 1. Stabilization of the (−P=C<) bond.

The kinetic stabilization of the reactive PC double bond by using bulky substituents to shield the bond originates from Becker (7), who in 1976 noticed the formation of a PC double bond during the reaction of disilylphosphanes with pivaloylchloride via a silatropic movement from the phosphorus to the oxygen [Eq (1)].

 (1)

R = Me, $\underline{t}$Bu, Ph, $\underline{c}$-C_6H_{11}

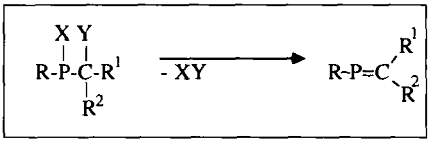
It certainly was this observation that promoted publication of a deluge of papers from numerous laboratories around the world. Due to these results we have today a complete arsenal of different synthetic methods at our disposal.

II. Formation of the PC Double Bond

Because the main routes to phosphaalkene formation have already been published in diverse review articles (*8–11*), this report can be restricted to a short survey of the general principles.

A. 1,2-ELIMINATION

In analogy to the chemistry of olefins, 1,2-elimination with suitable organyl phosphanes has proved valid. Those molecules with substituents showing inverse polarities may give thermodynamically favored leaving molecules XY [Eq. (2)]. The formation of XY is initiated thermally by bases or metals (*12–21*).

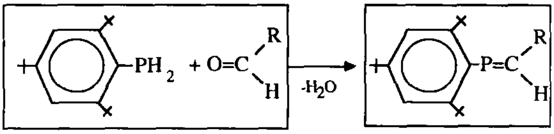


(2)

X	H	Cl	Br	I	Cl	Cl
Y	F	H	H	H	$SiMe_3$	Cl

B. CONDENSATION REACTIONS

It is possible in many cases to create PC double bonds via condensation in separations of halosilane, siloxane (*22*), or even water (*23a–c*). Likewise, formaldehyde or benzaldehyde reacts with 2,4,6-*tri-t*-butylphenylphosphane, forming the phosphaalkene, supported by dehydration agents such as P_4O_{10} or $CaO/CaCl_2$ [Eq. (3)]. This method is exceptionally favorable for synthesis of compounds that stabilize the PC double bond, with ring formation, for instance, 1,3-benzazaphospholes, 1,3-benzoxaphospholes, and 1,3-benzthiaphospholes (*24, 25*).

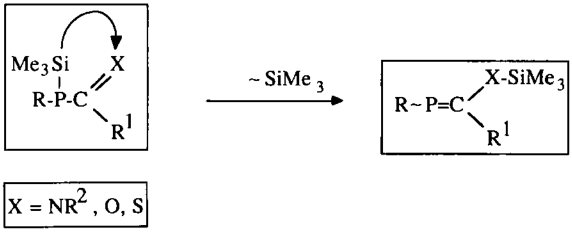


(3)

R = H, Ph

C. 1,3-TRIMETHYLSILYL MIGRATION

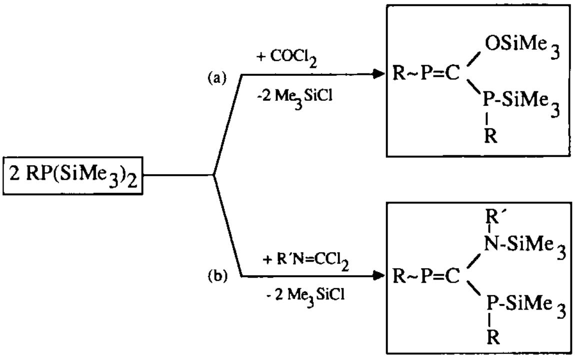
Another well-established process available for the preparation of PC double bonds is related to the easy migration of phosphorus-bonded silyl functions toward an α-positioned, doubly bonded element such as N, O, or S [Eq. (4)]. By this silatropic movement the double bond is shifted to the phosphorus atom, which is energetically favored along with the formation of a stable silicon element bond. This method of synthesis can be used in combination with the preceding condensation or addition reactions.



(4)

1. *Condensation and Silatropy*

Condensations followed by silyl migrations are achieved easily with carbon acid chlorides, imid chlorides (*7*, *26–28*), and adequate derivatives of carbonic acid such as phosgene [Eq. (5a)] and isocyanide dichlorides [Eq. (5b)] (*29–31*). After the primary condensation to the corresponding silylacylphosphane, a fast, irreversible migration of the silyl group usually takes place, forming the phosphaalkene structure.



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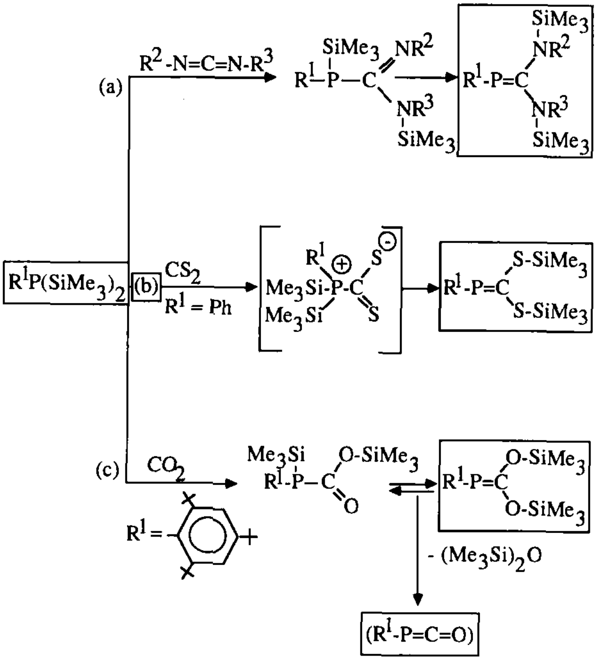
2. *Addition and Silatropy*

The silatropic process combined with the addition reaction can be realized with quite a number of compounds, including carbodiimides [Eq. (6a)], isocyanates, carbon disulfide [Eq. (6b)], or carbon dioxide [Eq. (6c)], which exhibit cumulated hetero double bonds. The first step, insertion between the P–Si bond, is followed by a silyl migration (*32–35*).



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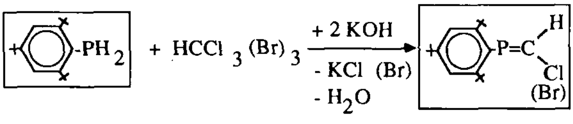
D. Carbene Addition

In certain cases the process analogous to the isonitrile synthesis for the preparation of phosphaalkenes, showing proton- and halogene-substituted C-bridged atoms, is a successful one. 2,4,6-*tri-t*-butylphenylphosphane can be transferred to the phosphaalkene using a strong alkaline solution of chloroform [Eq. (7)] or methylene chloride [Eq. (8)]. A carbene addition mechanism is involved in this reaction (*36, 37*).

The P-halogenated as well as silylated phosphaalkenes synthesized via the above-mentioned methods for the generation of the PC double



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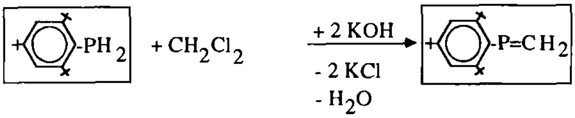
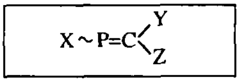


(8)

bond have proved to be valuable key substances for the preparation of numerous and novel compounds exhibiting PC double bonds. A CAS-ON-LINE literature search up to the end of 1987 for all open-chained and non-saltlike compounds is enlisted in the tables at the end of this article. The following diagram gives evidence of the types of substituents realized so far (Diagram 1).



X, Y, Z alternative
H
C-organyl/silyl
Si-alkyl
Sn-alkyl
Ge-alkyl
N-organyl/silyl
P-organyl/silyl
O-organyl/silyl
S-organyl/silyl
halogen: F, Cl, Br, I

DIAGRAM 1. Substitution pattern of the phosphaalkenes.

As a stable compound the basic HP=CH_2 is still unknown. Nevertheless there exist phosphaalkenes that are entirely hydrogen substituted either at the phosphorus or at the carbon atom. Compounds stable up to room temperature should have at least one bulky substituent on either side of the double bond, although compounds shielded by bulky substituents still demonstrate an amazingly strong reactivity.

III. Structure of and Proofs for Genuine $p\pi$ Bonds

The proofs to justify defining real $p\pi$–$p\pi$-double bonds within these compounds are found in the parameters of the chemical structure as well as in properties that show the evident affinity to the classical CC double bond, thus confirming the designation ***phosphaalkenes*** not only for formal reasons. Ocassionally the term "alkyliden(methylene)phosphanes" is used for these types of compounds.

X-Ray analysis of more than 50 different phosphaalkenes shows PC bond lengths between 161 and 171 pm. The average value is 167 pm, in contrast to the single-bond length of 185 pm. Bond lengths alone, however, do not establish compulsory evidence for the existence of a genuine double bond. Moreover, there have to be sufficiently high barriers of energy for the rotation around the PC axis and for the in-plane vibration to enable stabilized cis/trans (E/Z) isomeric compounds of differently substituted (at the carbon atom) phosphaalkenes (*38*).

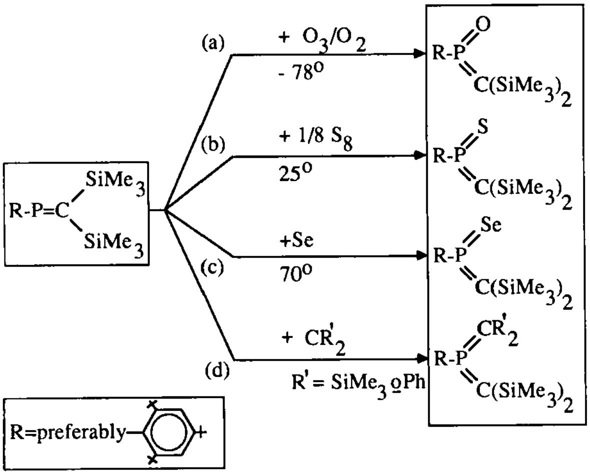
The existence of E/Z isomers has been suspected due to different ^{31}P NMR signals (*8, 19, 26*). Clear evidence of this has been provided after separation and isolation of the two 2,4,6-*tri-t*-butylphenylphenylmethylenephosphanes Ar—P=CHPh (*39–40a*). The more stable of the two isomeric compounds melts at 148°C and corresponds to the E configuration as confirmed by X-ray analysis. The Z isomer, as determined by X-ray analysis, melts at 84°C. Contrary to the other phosphaalkenes examined so far, the arrangements of these isomers are stable with respect to their configurations in solutions even at elevated temperatures. Radiation leads to an equilibrium with 40% E and 60% Z isomer. Parameters determined by X-ray analysis, such as distances and angles, as well as the ^{13}C NMR data, indicate π bonds within these phosphaalkenes. The sp^2-hybridized carbon produces characteristic shift values between 170 and 210 ppm relative to TMS. In addition the ^{31}P NMR signal of the sp^2-hybridized twofold-coordinated P atom is shifted in a typical way to the low-field side. A compilation of the ^{31}P NMR data is given in Ref. (*41*).

IV. Reactivity

The reactions of phosphaalkenes given here are restricted to those that are characteristic for the PC bond. The double bond holds two reactive centers: one is the P atom with a coordination number of two and the other is the π bond.

A. Reactions of the Phosphorus Atom

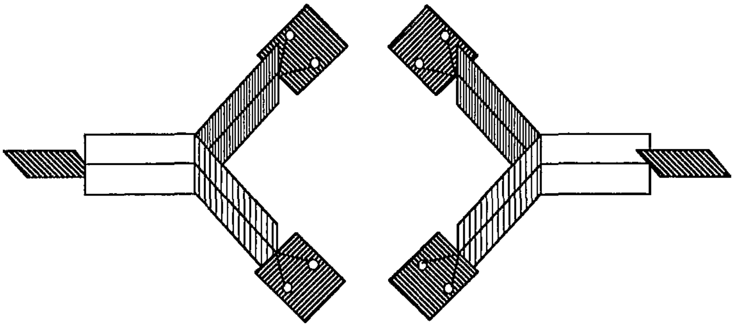
A reaction at the P atom preserving the double bond and culminating in an oxidative increase of the coordination can be realized with special phosphaalkenes using ozone, sulfur, selenium [Eq. (9a–c)] (*42–46*), or some carbenes [Eq. (9d)] (*47–49*).



(9)

Starting with 2,4,6-*tri*-*t*-butylphenyl[bis(trimethylsilyl)]methylenephosphane one gets the methyleneoxo-, methylenethiooxo-, or methyleneselenooxophosphorane as well as the *bis*(methylene)phosphoranes. According to X-ray structure determinations all molecules show a trigonal symmetry, which could be predicted on the basis of the theory of valence shell electron pair repulsion by Gillespie.

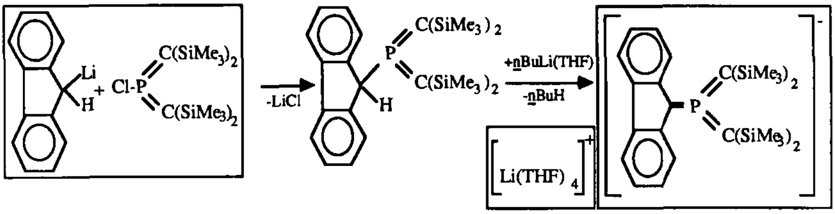
The bis(methylene)phosphoranes hold two carbon atoms doubly bonded to the same phosphorus atom. The molecule is chiral in the solid state due to the propeller-like orientation of the silyl groups as demonstrated in Fig. 2.



positive angle negative angle

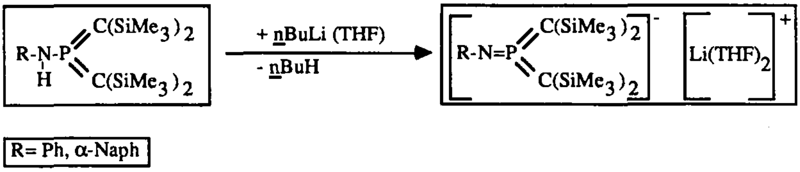
FIG. 2. σ^3, λ^5 Phosphoranes as propellanes.

Fluorenyl substituents at the phosphorus atom enable the molecule to be deprotonated with butyllithium, giving the tris(methylene) phosphate anion, now showing three double bonds between the phosphorus and carbon atoms [Eq. (10)] (*50*).



(10)

The deprotonation of amino-bis(methylene)phosphoranes leads to imino-bis(methylene) phosphate anions, which show one PN and two PC double bonds [Eq. (11)] (*50a*).



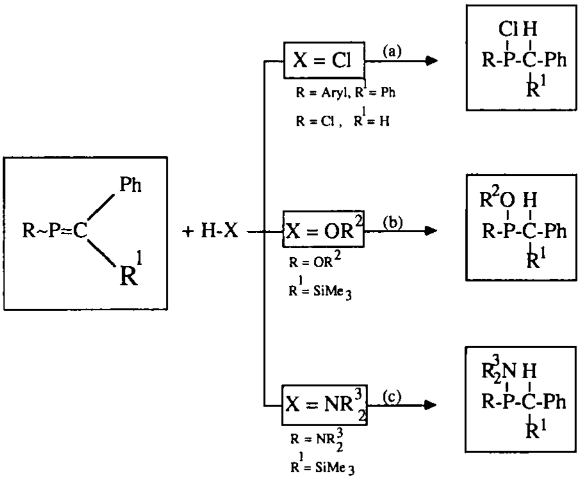
(11)

B. REACTIONS AT THE PC DOUBLE BOND

The second characteristic center of reactivity within phosphaalkenes is the $(p\text{-}p)\text{-}\pi$ bond. The reactivity is more similar to the C=C than to the corresponding C=N or P=N double bond. This is in accordance with the highest occupied molecular orbital (HOMO) energy levels of the phosphaalkenes, which frequently are π orbitals, as with olefins (*51*). The "olefinic" character is also demonstrated by the lower polarity of the P—C bond in comparison with the C—N or P—N bond.

1. *Addition of Proton-Active Reagents*

In these compounds the carbon atom is mostly negative and the phosphorus is positive polarized, thus in the case of an addition of proton-active reagents such as hydrogen halides, alcohols, or amines the proton moves to the carbon and the anionic part moves to the phosphorus atom [Eq. (12)] (*8, 14*).

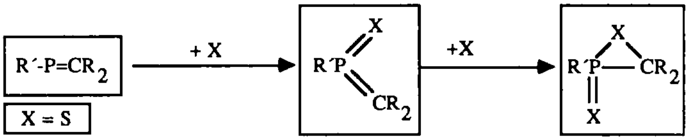


(12)

2. *Cycloadditions*

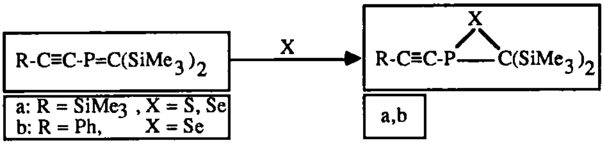
An extensive similarity between olefins and phosphaalkenes is demonstrated by quite a number of $[2 + n]$ cycloadditions.

a. [2 + 1] Cycloaddition. Reactions of phosphaalkenes with sulfur or selenium proceed predominantly via oxidation of the phosphorus atom to the corresponding methylenethio- or methyleneselenooxophosphoranes, which to some extent can be transferred to the λ^5-thiaphosphiranes with sulfur [Eq. (13)] (*44, 45*).



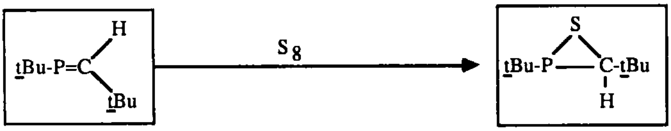
(13)

On the contrary, ethinylphosphaalkenes react with sulfur or selenium, forming 1,2-λ^3-thiaphosphirane or 1,2-λ^3-selenium phosphirane, respectively, via a [2 + 1] cycloaddition [Eq. (14)] (*52*).



(14)

These findings can be attributed to the relative energy levels of the two HOMOs (π and σ orbitals) of the double-bond system. MO calculations (*51*) yield two energetically close-lying HOMOs for the double-bond system of the three-coordinated phosphorus, while the lowest unoccupied molecular orbital (LUMO) is the π^* orbital. Whether the reaction occurs at the π system or at the free electron pair of the phosphorus atom is controlled by the relative position of the two HOMOs in relation to each other. In turn, this can be influenced by the substituents at the PC double bond. Substituents exhibiting π-donor qualities cause a higher energy level for the π orbital with respect to the σ orbital (free electron at the phosphorus atom), therewith forming a HOMO/LUMO sequence of the type π/π^* orbital similar to that of the alkenes. In consequence, the reaction takes place at the π system of the PC double bond. According to this bis(*t*-butyl)-substituted phosphaalkenes react with the chalcogens S and Se, giving the thia(seleno)-phosphiranes [Eq. (15)] (*53*).



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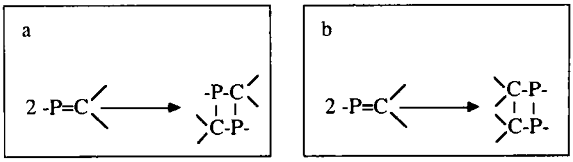


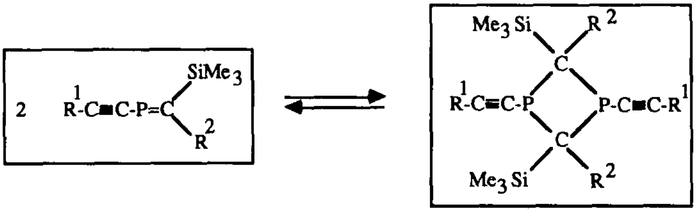
Diagram 2. Self-addition ([2 + 2] cycloaddition). (a) 1,3-Diphosphetanes. (b) 1,2-Diphosphetanes.

The two *t*-butyl groups initiate via the +M-effect (π donor) a destabilization of the π orbital with respect to the σ orbital. Probably the ethinyl group acts as a π donor, which is shown in the reaction given by Eq. (14).

b. [2 + 2] Cycloadditions. Among the 1,2-dipolar additions the self-addition of the phosphaalkenes leading to the diphosphetanes is an important type of reaction (*54–58*). Predominantly this proceeds via a head–tail combination (giving the 1,3-diphosphetanes) that is initiated by light or elevated temperatures. Dimerization of two different phosphaalkenes has likewise been observed (Diagram 2). In solution there might be a partial or complete dissociation forming monomers. In the literature one even finds mention of the trimerization of phosphaalkenes (*59, 60*). Despite the difference in polarities, bulky substituents at the phosphorus and small groups at the C atom favor the head to head or tail to tail combination, respectively (*59, 61, 62*). The mechanism of this [2 + 2] cycloaddition is still not quite clear.

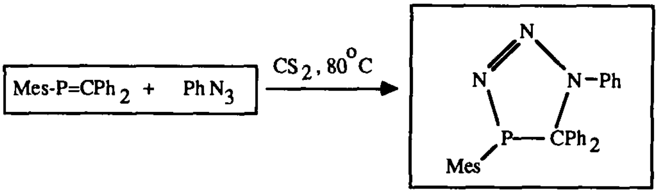
The formation of uniform diphosphetanes refers to a stereospecific reaction, which, according to the Woodward–Hoffmann rules, may proceed via a $[\pi_s^2 + \pi_a^2]$ process or, if photochemically induced, along a geometrically more favored $[\pi_s^2 + \pi_s^2]$ mode. A two-step mechanism is most probable for the formation of different diastereomeric 1,3-diphosphetanes, which is observed in the case of ethinyl phosphaalkenes. The first step determines the regioselective head-to-tail addition. According to theoretical calculations the first bond is established between positions exhibiting the greater orbital coefficient of the HOMO and the LUMO (*51*). Substituents with π-donor abilities at the phosphorus of phosphaalkenes (such as ethinyl) show the greater coefficient in the HOMO of the localized carbon atom, while the greater coefficient in the LUMO is at the phosphorus. In this case the dimerization yields the 1,3-diphosphetane [Eq. (16)] (*63*).

Alkyl substituents at the phosphorus and π-donor substituents at the carbon atom (such as O—SiMe$_3$) of the PC double bond generate


(16)

a HOMO with a greater coefficient at the phosphorus. This in turn, during a dimerization, gives first a P—P linkage, finally yielding 1,2-diphosphetanes.

c. [3 + 2] Cycloadditions. The formation of five-membered rings via addition to an open-chained, mesomerically unstabilized phosphaalkene takes place with a number of 1,3-dipolar reagents. Thus 1-mesityl-2,2-diphenyl-1-phosphaalkene reacts with phenylazide [Eq.(17)] or diphenyl diazomethane [Eq. (18)], respectively, giving 4,5-dihydro-1,2,3,4-triazaphospholes or 4,5-dihydro-1,2,3-diazaphospholes (*64*).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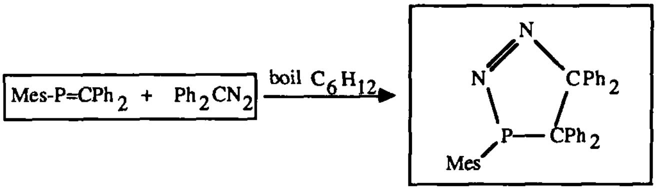
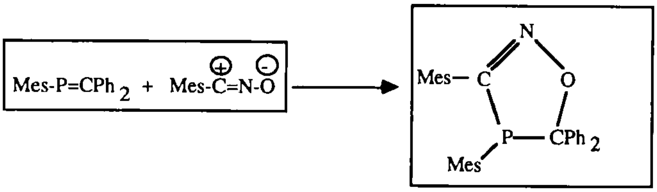
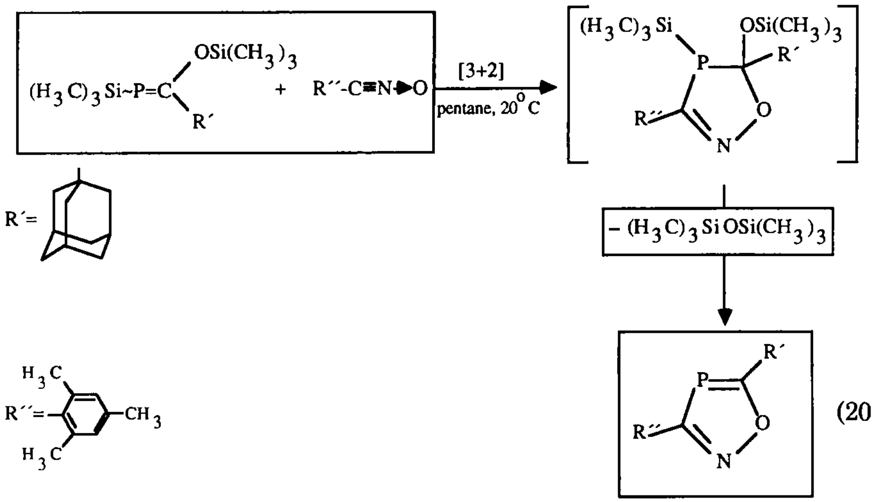

(18)

A dihydro-1,2,4-diazaphosphole is obtained by reaction of bis(trimethylsilyl)amino-trimethylsilylmethylenephosphane with *t*-Bu-CHN_2 resp. trimethylsilyl diazomethane in *n*-hexane at 0°C (*65, 66*). Correspondingly, one gets at room temperature the 4,5-dihydro-5,5-diphenyl-3,4-di(2,4,6-trimethyphenyl)-1,2,4-oxazaphosphol with mesityl nitriloxide and the phosphaalkene [Eq. (19)] (*64*).



(19)

A [3 + 2] cycloaddition of mesityl nitriloxide on 1-trimethylsilyl-2-trimethylsiloxi-2-adamantyl-1-phosphaethene gives the 1,2,4-oxaazaphosphole [Eq. (20)]. Probably the dihydro compound is formed in the

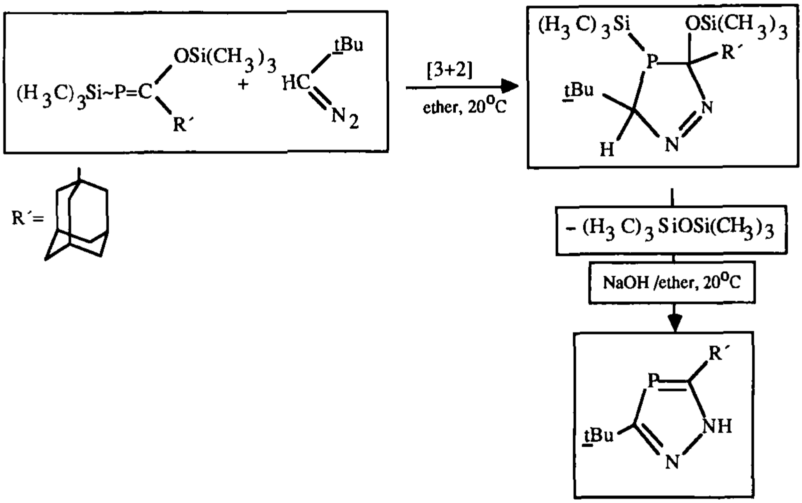


(20)

first step followed by a spontaneous cleavage of hexamethyldisiloxane, which stabilizes the aromatic oxazaphosphole (*67*).

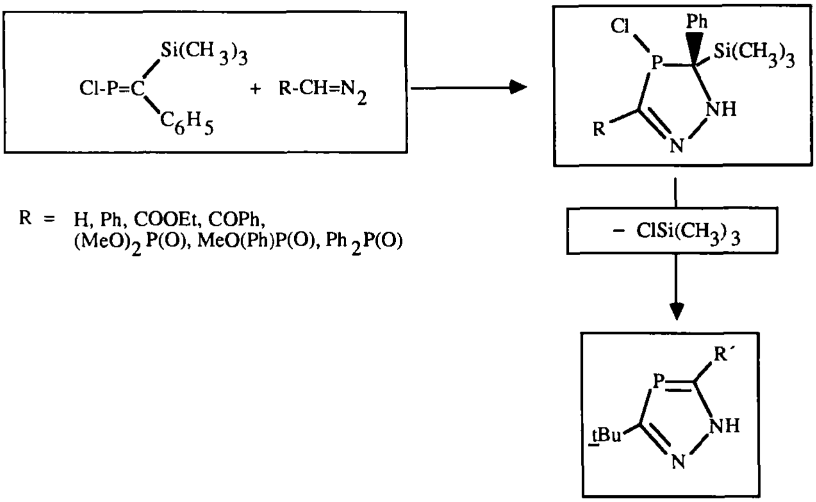
The cycloaddition of diazaalkanes with the phosphaalkene leads, contrary to the reaction with the nitriloxide, to the primary adduct, which can be isolated. The cleavage of hexamethyldisiloxane is catalyzed by sodium hydroxide and finally gives diazaphosphole [Eq. (21)] (*67*).

The distinct dipolarophilic reactivity of the phosphaalkenes can be demonstrated, among others, with the 1-chloro-2-phenyl-2-trimethylsilyl-1-phosphaethene. It reacts at once with diazoalkanes even at room temperature in a [3 + 2] cycloaddition. The expected primary products of addition aromatize, spontaneously eliminating trimethylchlorosilane, to the 1*H*-1,2,4-diazaphospholes, showing the triply



(21)

bonded phosphorus in a coordination of two [Eq. (22)]. The cycloaddition is regioselective corresponding to the polarity of the PC-double bond (*68*).



(22)

d. [4 + 2] Cycloadditions. Numerous papers have been published in recent years on [4 + 2] cycloadditions (Diels–Alder reactions) with participation of PC double bonds. Here the P=C sequence reacts mainly as the dienophile (*58, 69–74*). 2,3-Dimethylbutadiene, cyclopen-

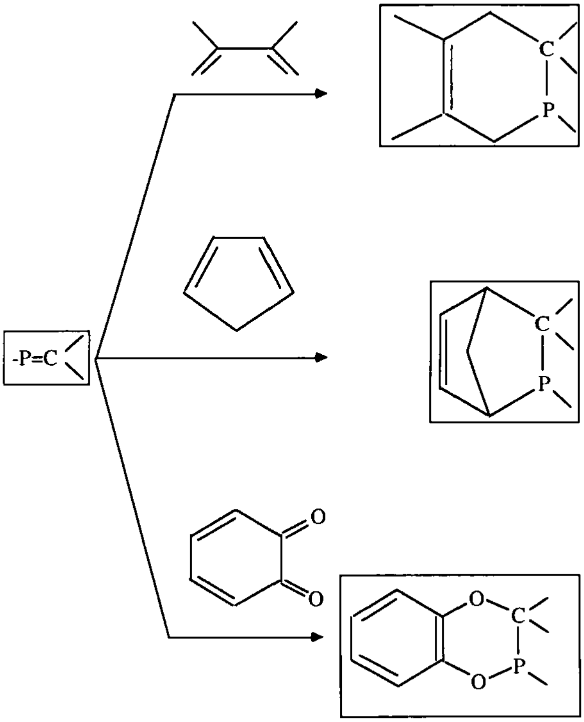


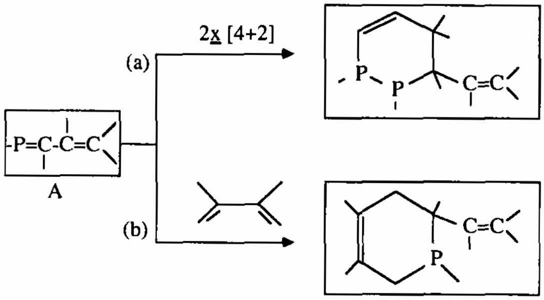
DIAGRAM 3.

tadiene, and orthoquinones are used as diene components. These [4 + 2] cycloadditions proceed generally at much lower temperatures than in analogous carba systems, indicating a drastic reduction of the energy of activation, which can be observed and calculated for other electrocyclic reactions of the PC double bond (Diagram 3).

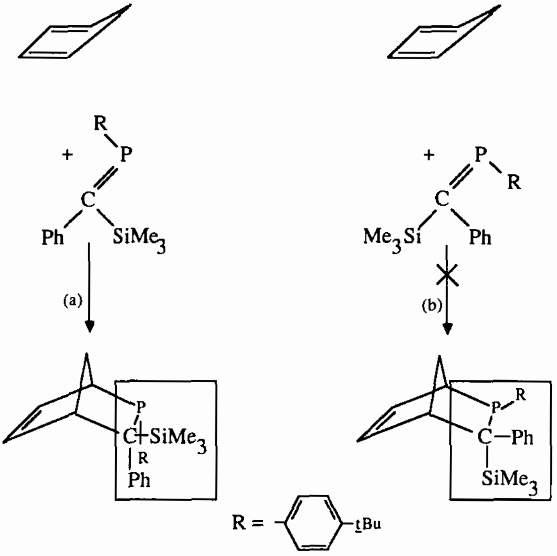
Phosphaalkenes exhibiting C═X—P═C (X = N, CR) sequences react only as dienophiles, activating the PC double bond. On the other hand, phosphaalkenes of type A are able to act as ene or as diene components [Eq. (23)] (*62, 72, 75, 76*).

The reaction of P-(4-*t*-butylphenyl)-C-phenyl-C-(trimethylsilyl)phosphaalkene with cyclopentadiene proceeds under stereochemical control [Eq. (24)]. Of the two possibilities of attack on the diene by the E-configured dienophile, only the left route is realized (*77*).

Even at −30°C one gets the homogeneous (with respect to the silyl group) exo-aligned product. This result is in agreement with the assumption of a synchronous reaction mechanism with conservation of the



(23)



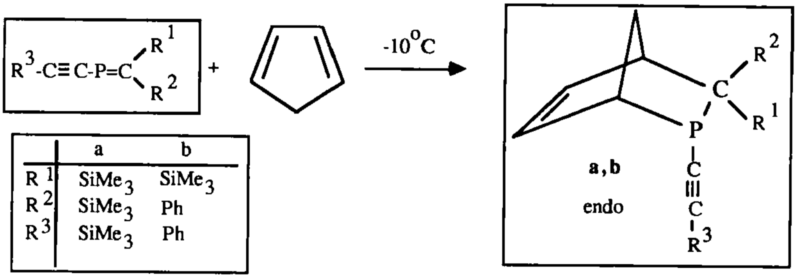
(24)

orbital symmetry, as demonstrated by the findings with ethinylphosphaalkene [Eq. (25)] (*52*).

The endoselectivity and the "cis" principles were obeyed during this Diels–Alder reaction. Not so clear were the [4 + 2] cycloadditions carried out with isomerically pure P-chlorophosphaalkene, Cl—P=CPhR (R = $SiMe_3$, $SiMe_2CH_2$—Ph, $SiPh_2CH_2Ph$), and dimethylbutadiene, which yielded both diastereomeric Diels–Alder products [Eq. (26)] (*63*).

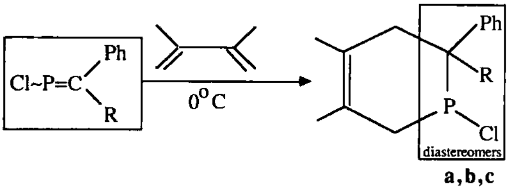
Similar results can be realized in a reaction with cyclopentadiene [Eq. (27)] where in each case (a, b, and c) four isomers can be detected by ^{31}P NMR (*63*).

A possible explanation is the isomerization of the P-chlorophosphaalkenes, as was published recently (*78*) for Me_5C_p—P=C$(SiMe_3)_2$.



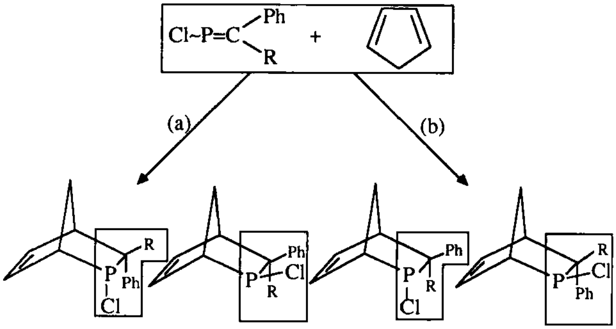
	a	b
R^1	$SiMe_3$	$SiMe_3$
R^2	$SiMe_3$	Ph
R^3	$SiMe_3$	Ph

(25)



	a	b	c
R	$SiMe_3$	$SiMe_2CH_2Ph$	$SiPh_2CH_2Ph$

(26)

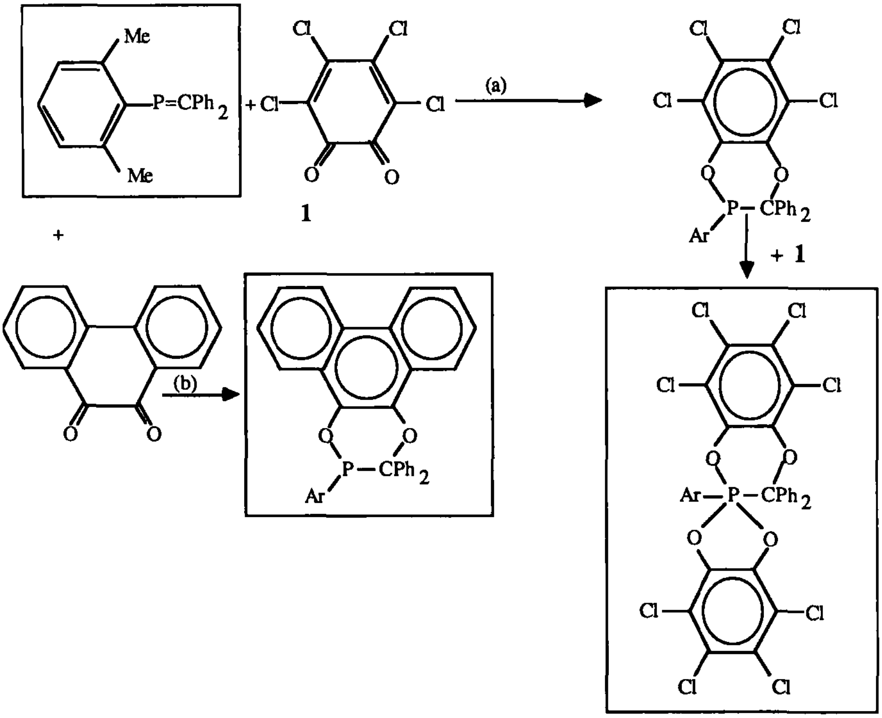


	a	b	c
R	$SiMe_3$	$SiMe_2CH_2Ph$	$SiPh_2CH_2Ph$

(27)

Since an inversion at the phosphorus atom is most unlikely at 0°C, a two step mechanism has to be taken in consideration.

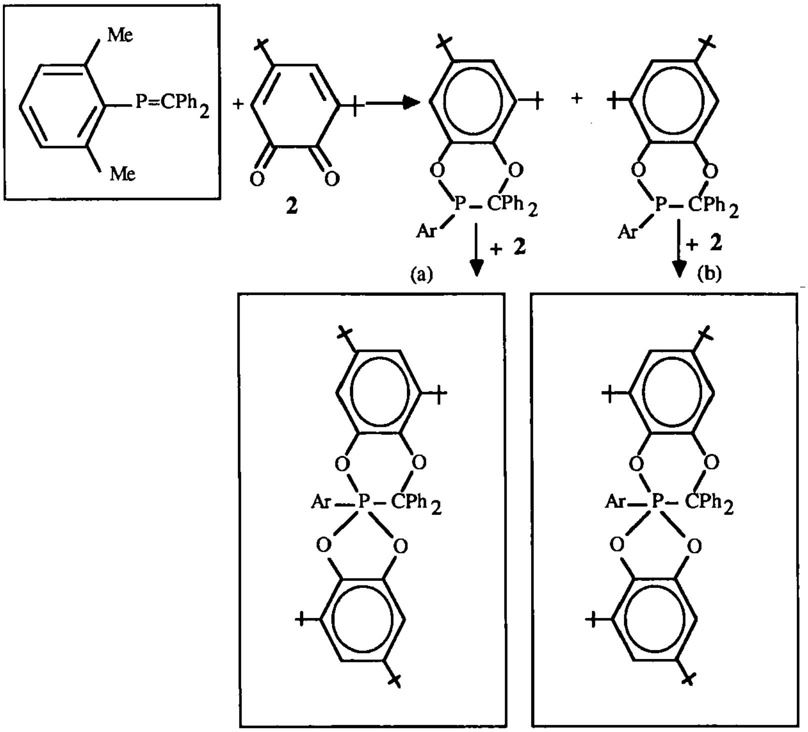
e. [4 + 2] Cycloaddition of Heterodienes. The reaction of (2,6-dimethylphenyl)diphenyl methylenephosphane with three *o*-quinones, tetrachloro-*o*-benzoquinone [Eq. (28a)], 3,5-di-*t*-butyl-*o*-benzoquinone



(28)

[Eq. (29)], and phenanthrene quinone [Eq. (28b)], leads to the [4 + 2] *Diels–Alder* adducts; the two benzoquinone adducts add a second molecule of the quinone **1** resp. **2**, forming the trioxyphosphoranes. The mechanism of this [4 + 2] cycloaddition, either symmetry allowed or stepwise, is not yet clear (*73*).

The reaction of 1-chloro-2-phenyl-2-trimethylsilylphosphaethene **1** with α-pyrones **2** yields the λ^3-phosphinines **4a–e**. With cyclopentadienones **3** the phosphinines **4f,g** are obtained [Eq. (30)]. [The reaction proceeds via the 2-phenyl-1-phosphaethine that is formed under these reaction conditions (*80*).]



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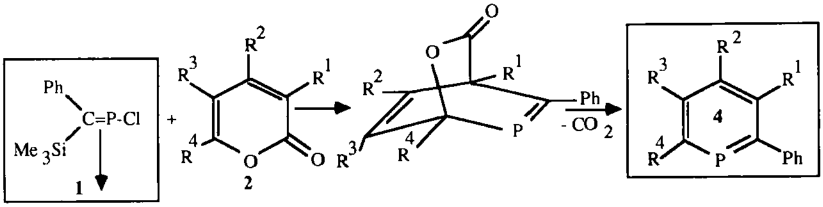
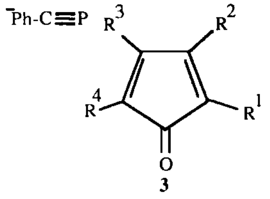
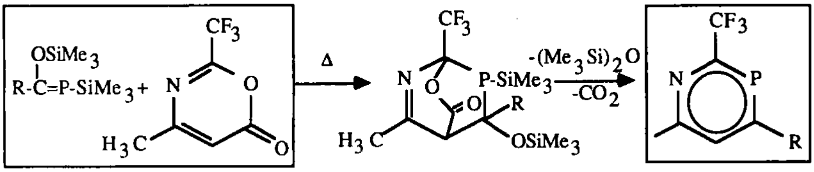




2,3,4	R^1	R^2	R^3	R^4
a	Ph	Ph	Ph	Ph
b	H	Ph	Ph	Ph
c	H	Ph	H	Ph
d	H	Ph	Ph	H
e	H	H	H	Ph
f	Et	Ph	Ph	Et
g	Me	Ph	Ph	Me

(30)

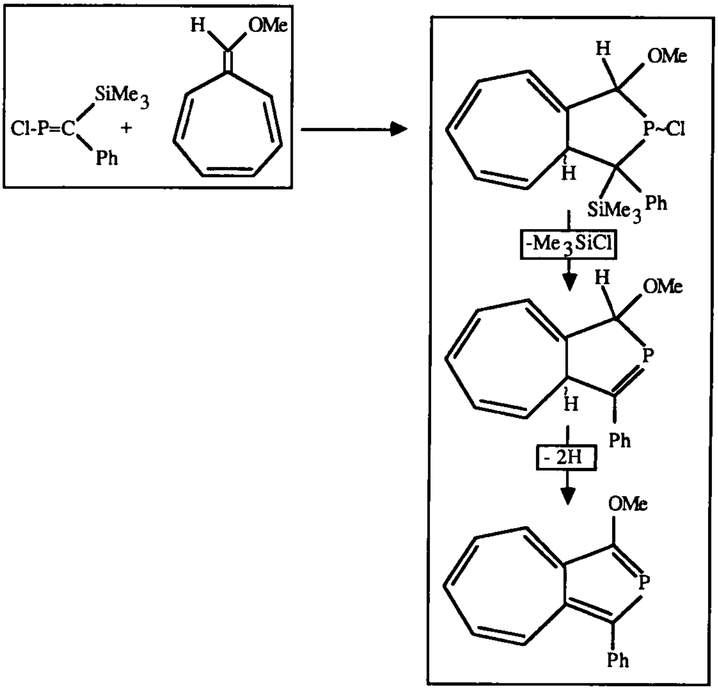
The hitherto unknown 1-aza-3-phosphabenzenes are obtained via a regiospecific *Diels–Alder* reaction with inverse electron demand of 2-trifluormethyl-4-methyl-6*H*-1,3-oxazin-6-one with phosphaalkynes (*81*) or phosphaalkenes [Eq. (31)] (*82*).



(31)

R = Ad, iPr, CH_2-tBu

f. [8 + 2] Cycloaddition. Until now there has been only one [8 + 2] cycloaddition reported. Starting with 8-methoxyheptafulven and 1-chloro-2-phenyl-2-trimethylsilylphosphoethene one gets the first 2-phosphaazulen [Eq. (32)]. There is evidence that the reaction proceeds via tetrahydroazulen or dihydroazulen as intermediates (*83*).



(32)

More information regarding cycloadditions, especially on cyclic compounds containing PC double bonds, is given in a review by Arbuzov and Dianova (*84*).

V. Compounds with Several PC or Partially CC Double Bonds

Phosphacarbapolyenes will be dealt with in this section. Here we have compounds that can be deducted from small polyenes by means of substitution of individual CH moieties with phosphorus atoms, creating PC double bonds in conjugation with another PC or CC sequence. The reactivity most impressively demonstrates the amazing affinity for pure carbon systems.

A. PHOSPHABUTADIENES

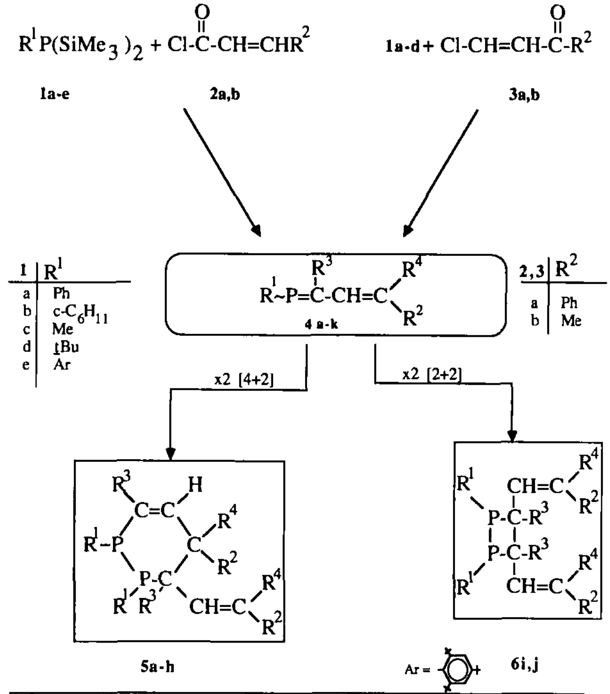
1. *Monophosphabutadienes*

Attempts to synthesize 1-phosphabuta-1,3-dienes by means of condensation of organylbis(trimethylsilyl)phosphanes **1a–c** and α,β-unsaturated acid chlorides **2a** and **2b** yielded the six-membered 1,2,3,4-tetrahydro-1,2-diphosphinines **5a–d**. Even the reaction of organylbis(trimethylsilyl)phosphanes with chlorovinylketones **3a** and **3b**, which can be considered as vinylogous acid chlorides, ended up with the corresponding substituted 1,2-diphosphinines **5e–h**. The substitution of the phosphorus-positioned organyl group by the *t*-butyl substituent in **d** initiates a completely different reaction pattern. In this case the isomerically pure 1,2-diphosphetane **6i** is formed quantitatively (Scheme 1) (*62*).

Finally, the introduction of the sterically pretentious 2,4,6-tri-*t*-butylphenyl group in **1e** made it possible to protect the PC double bond from further reactions of the diene, which was assumed to be an intermediate in all other cases presented herein (compound **4k**).

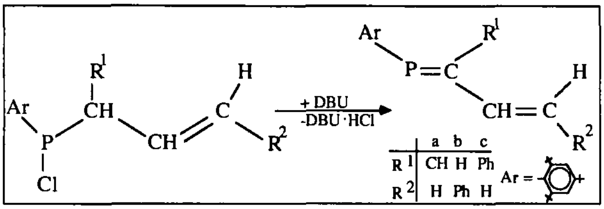
Recent investigations showed that 1-phosphabuta-1,3-dienes can be synthesized by HCl elimination of the corresponding chlorophosphanes **a–c** [Eq. (33)]. While **b** is converted completely into the 1-phosphabutadiene at room temperature within a few hours, the HCl elimination requires a semimolar surplus of DBU and a prolonged reaction time of 2 weeks (*85*).

With **c**, 6 days at 60–70°C is necessary to complete the reaction. Sulfur reacts with **b** to form the thiophosphathiirane, metal carbonyls give η^1 complexes, and with norbornadiene the Diels–Alder adduct is



4,5 6,7	a	b	c	d	e	f	g	h	i	j	k
R^1	Ph	c-C_6H_{11}	Me	Ph	Ph	c-C_6H_{11}	Me	Ph	tBu	tBu	Ar
R^2	Ph	Ph	Ph	Me	Ph	Ph	Ph	Me	Ph	Ph	Ph
R^3	$OSiMe_3$	$OSiMe_3$	$OSiMe_3$	$OSiMe_3$	H	H	H	H	$OSiMe_3$	H	$OSiMe_3$
R^4	H	H	H	H	$OSiMe_3$	$OSiMe_3$	$OSiMe_3$	$OSiMe_3$	H	$OSiMe_3$	H

SCHEME 1.



(33)

realized, in which the 1-phosphabutadiene serves as the diene component, but with dimethylbutdiene or cyclopentadiene no reaction could be observed (see Diagram 4).

The 2-phosphabuta-1,3-dienes can presently be synthesized via two different routes. A thermally stable P-bis(trimethylsilyl)amino-substi-

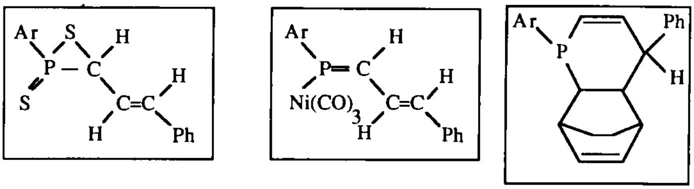
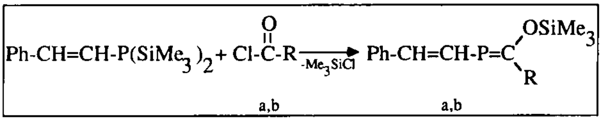


DIAGRAM 4.

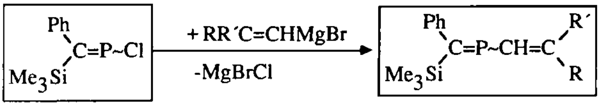
tuted 1-phosphabutadiene is also obtained by HCl elimination with DBO (*85a*). One route starts with α,β-unsaturated bis(silyl)phosphanes and addition of acid chlorides [Eq. (34)] (*62*); the other route starts



$$\underset{\mathbf{a,b}}{\text{Ph-CH=CH-P(SiMe}_3)_2 + \text{Cl-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-R}} \xrightarrow[-\text{Me}_3\text{SiCl}]{} \underset{\mathbf{a,b}}{\text{Ph-CH=CH-P=C}\begin{smallmatrix}\text{OSiMe}_3\\ \text{R}\end{smallmatrix}} \qquad (34)$$

	a	b
R	Me	*t*Bu

with P-chlorophosphane and addition of vinyl magnesium bromides [Eq. (35)]. Pairs of isomers will be generated if there are different substituents at the carbon in position 4 (*86*).



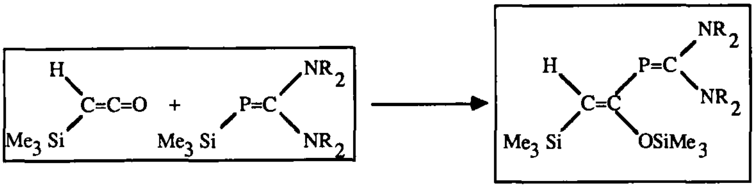
$$\begin{smallmatrix}\text{Ph}\\ \text{Me}_3\text{Si}\end{smallmatrix}\text{C=P}\sim\text{Cl} \xrightarrow[-\text{MgBrCl}]{+\text{RR}'\text{C=CHMgBr}} \begin{smallmatrix}\text{Ph}\\ \text{Me}_3\text{Si}\end{smallmatrix}\text{C=P}\sim\text{CH=C}\begin{smallmatrix}\text{R}'\\ \text{R}\end{smallmatrix} \qquad (35)$$

	R	R′
a	Me	Me
b	Me	H
c	H	H

In the reaction with cyclopentadiene, the PC double bond in **a,b** acts as the ene component (*62*). A 1-diamino-substituted 2-phospha-1,3-butadiene could be synthesized by reaction of the ketene with the phosphaalkene [Eq. (36)] (*87*).

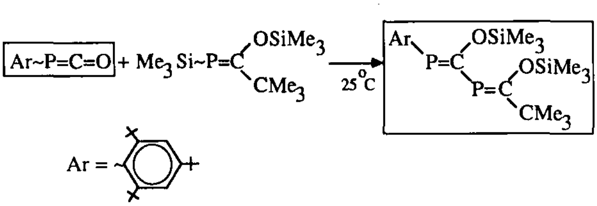
2. *Diphosphabutadienes*

a. 1,3-Diphosphabutadienes. A stable compound showing the skeleton of a 1,3-diphosphabutadiene was synthesized for the first time via



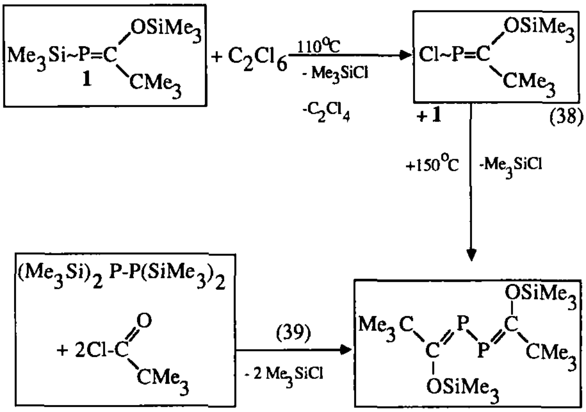
(36)

addition of trimethylsilyl-substituted phosphaalkene to the phosphaketene [Eq. (37)] (*88*).



(37)

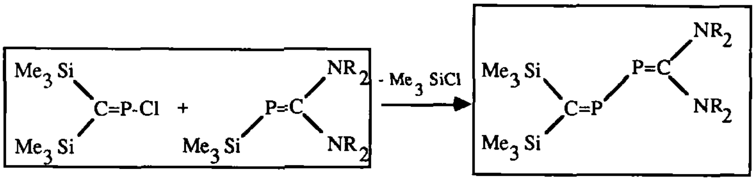
b. 2,3-Diphosphabutadienes. The 2,3-diphosphabutadienes can be created from phosphaalkene **1** with hexachloroethane [Eq. (38)] or starting with a diphosphane and adding pivaloylchloride [Eq. (39)]. The compound exhibits an s-trans configuration, very similar to the most stable arrangement of 1,3-butadienes and showing the same substitution pattern (*89*).



(38)

(39)

1,4-Bis(trimethylsiloxy)-1,4-bis(2,4,6-tri-*t*-butylphenyl)-2,3-diphosphabutadiene was prepared by reaction of 2,4,6-tri-*t*-butylbenzoyl chloride with tris(trimethylsilyl)phosphane (*90*). The synthesis of a 1-diamino-



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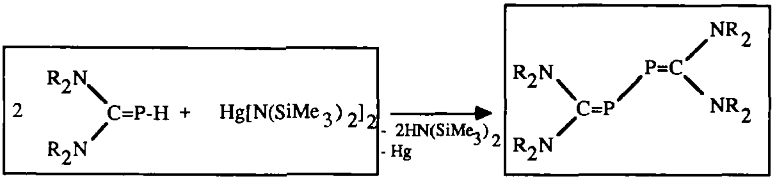


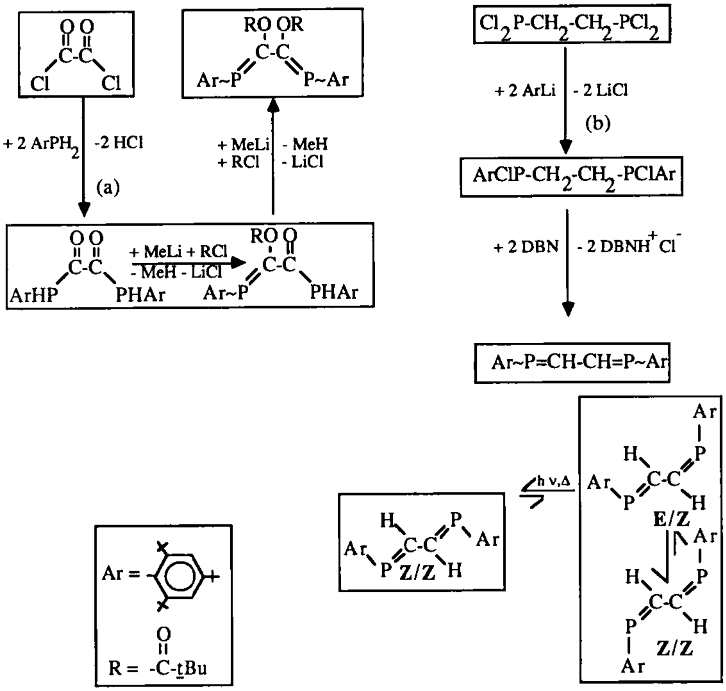
(41)

[Eq. (40)] and a 1,4-tetraamino-2,3-substituted 2,3-diphosphabuta-1,3-diene [Eq. (41)] is also reported (*91, 92*).

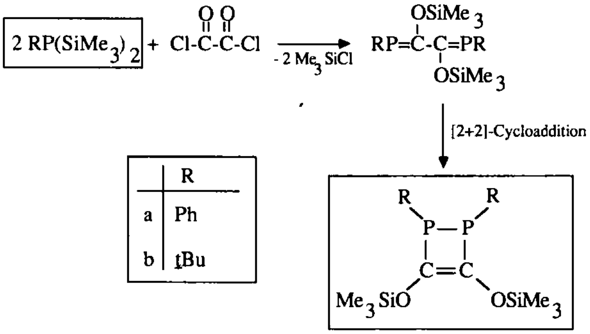
c. 1,4-Diphosphabutadienes. The successful synthesis of two compounds with the open skeleton of a 1,4-diphosphabutadiene was reported recently (Scheme 2). The oxalychloride first reacts with methyllithium, forming the lithium enolate, which is then converted into the 1,4-diphosphabutene by pivaloylchloride. Repetition of this reaction sequence at the second acylphosphide end of the molecule leads to the 1,4-diphospha-1,3-butadiene [route (a)] (*93*). The C-unsubstituted 1,4-diphospha-1,3-butadiene can be prepared by reaction of ethylenebis(dichlorophosphane) with 2,4,6-tri-*t*-butylphenyllithium in a molar ratio 1:2 at −80°C in THF [route (b)]. The compound thereby obtained can be dehydrochlorinated at −40°C with 1,5-diazabicyclo[4.3.0]none-5-ene (DBN). The diphosphabutadiene is synthesized as a mixture of the E,E and E,Z stereoisomers, which can be separated by fractional crystallization with toluene. The Z,Z isomer is exclusively formed from the E,Z isomer upon irradiation (λ = 254 nm) or warming in benzene (60°C) (*93*).

The 1,4-diphospha-1,3-butadienes are suitable as ligands for σ-coordinated complexes with transition metals. Attempts to carry out pericyclic reactions with maleinic anhydride, acetylene dicarboxylate esters, dimethylbutadiene, or cyclopentadiene failed, but Diels–Alder reactions with norbornadienes were successful (*94*). Earlier attempts to synthesize 1,4-diphosphabuta-1,3-dienes with oxalychloride and phenylbis(silyl)phosphane proceeded via ring closure [Eq. (42)] (*89*), where R = Ph (a) or *t*Bu (b).

The formation of diphosphacyclobutene is amazing only on the first view, because from carbon chemistry it is well known that butadienes



SCHEME 2.



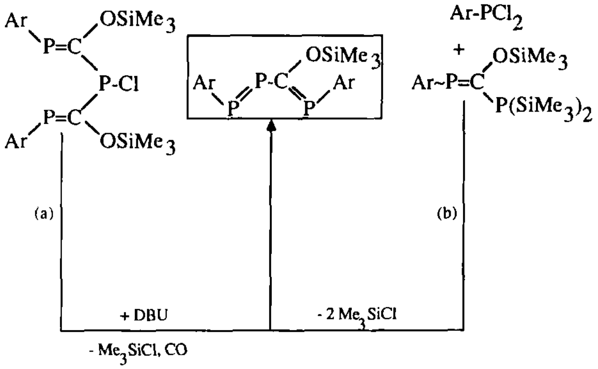
	R
a	Ph
b	tBu

(42)

can be formally transformed into cyclobutenes in electrocyclic reactions. These reactions always proceed stereospecifically controlled if they follow a synchronous process. Even here we find the obvious parallel to carbon chemistry, because according to X-ray investigations only one of the two possible stereoisomers is formed in nearly quantitative yield.

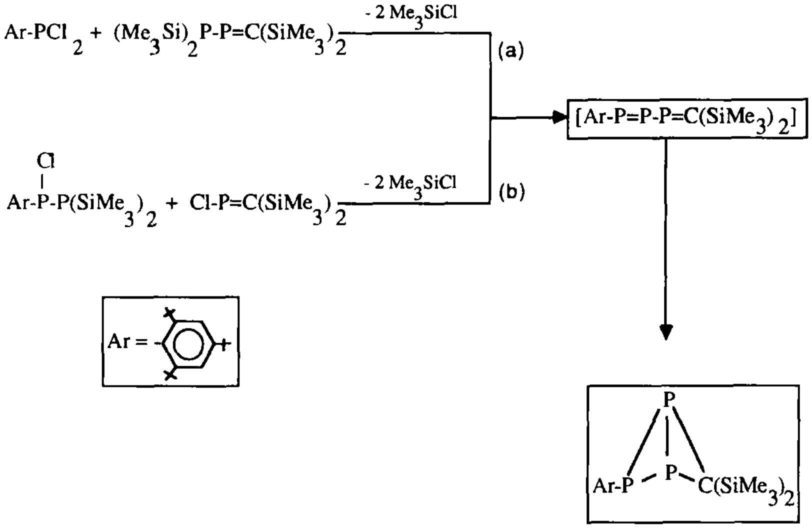
3. *Triphosphabutadienes*

Presently only the 1,2,4-triphosphabuta-1,3-diene is known. It was synthesized for the first time via a reaction making use of DBU or DBO on 1,3,5-triphosphapenta-1,4-diene [Eq. (43a)]. In a different procedure 1,3-diphosphapropene is condensed with dichlorophosphane [Eq. (43b)]. Due to the X-ray structure determination, the double bonds are positioned cis to each other (*95*).



(43)

The other 1,2,3-triphosphabuta-1,3-diene is yet not known as a stable compound. It has been suggested to be an intermediate during reactions given in Eq. (44a,b), but an intramolecular [2 + 2] cycloaddition yielded the first 1,2,3-cyclobutane (*96, 97*).

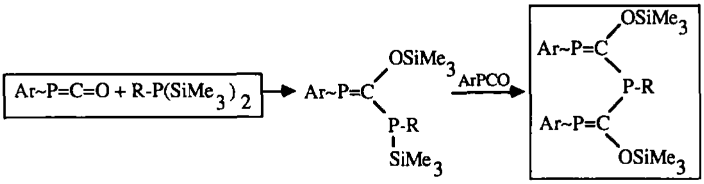


(44)

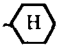
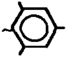
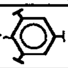
B. PHOSPHAPENTADIENES

1. 1,3,5-Triphosphapenta-1,4-dienes

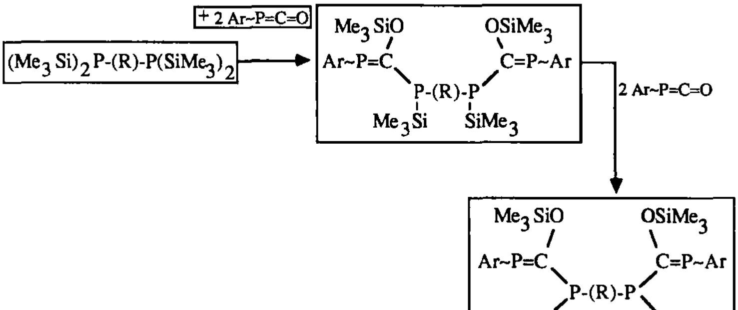
A key compound for the synthesis of substances exhibiting the molecular structure of higher phosphacarbadienes proved to be the phosphaketene, presented later on. The reaction of Ar—P=C=O on bis(trimethylsilyl)phosphanes at a ratio of 2:1 leads to the class of compounds of 1,3,5-trisphosphapenta-1,4-dienes via the intermediate 1,3-diphosphapropenes [Eq. (45)] (*98*).



(45)

	a	b	c	d	e	f	g
R	Me	$\underline{t}$Bu					C(SiMe$_3$)$_3$

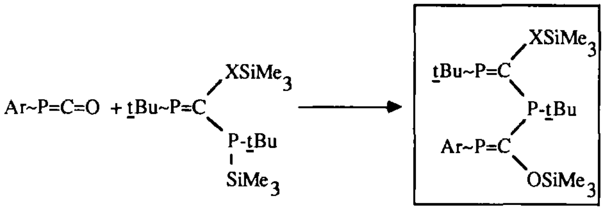
The straightforward reaction forms aryl-, alkyl-, or alkenyl-bridged bis(triphosphapentadienes) after multiple addition of phosphaketene to bis(trimethylsilyl)phosphanes, which are coupled by carbon chains [Eq. (46)].



(46)

	$\underline{h}$	$\underline{i}$	$\underline{j}$
(R)	1,4-C$_6$H$_4$	(CH$_2$)$_3$	$\underline{\text{cis}}$-CH$_2$CH=CHCH$_2$

The intermediate 1,3-diphosphapropenes can be synthesized in a separate reaction of bis(trimethylsilyl)phosphanes with phosgene or isocyanide dichlorides (*29, 99*), respectively, and can be converted to the unsymmetrically substituted pentadienes with phosphaketene [Eq. (47)].



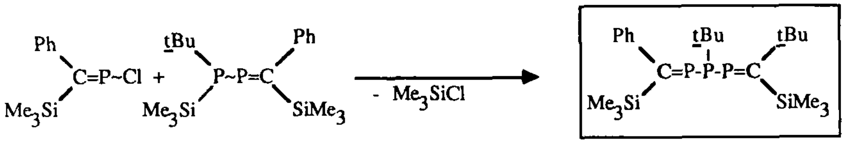
(47)

	k	l
X	O	NpC$_6$H$_4$CF$_3$

Compounds showing the 1,3-diphosphapenta-1,4-diene structure could be synthesized in a similar way by addition of 1,3-diphospha-3-silyl-prop-1-ene to diphenylketene (*98*). The following reaction, Scheme 3, gives a survey on transformations performed with 1,3,5-diphosphapenta-1,4-dienes.

2. *2,3,4-Triphosphapenta-1,4-dienes*

Efforts to synthesize compounds exhibiting the atomic sequence of a 2,3,4-triphosphapenta-1,4-diene in an experiment with *p*-chlorophenyl-(trimethylsilyl)phosphaethene and 1-*t*-butyl-2-[phenyl(trimethylsilyl)-methylene-1-(trimethylsilyl)diphosphane had only a limited success, as the compound could only be detected spectroscopically [Eq. (48)]. During the process of isolation decomposition took place (*86*).



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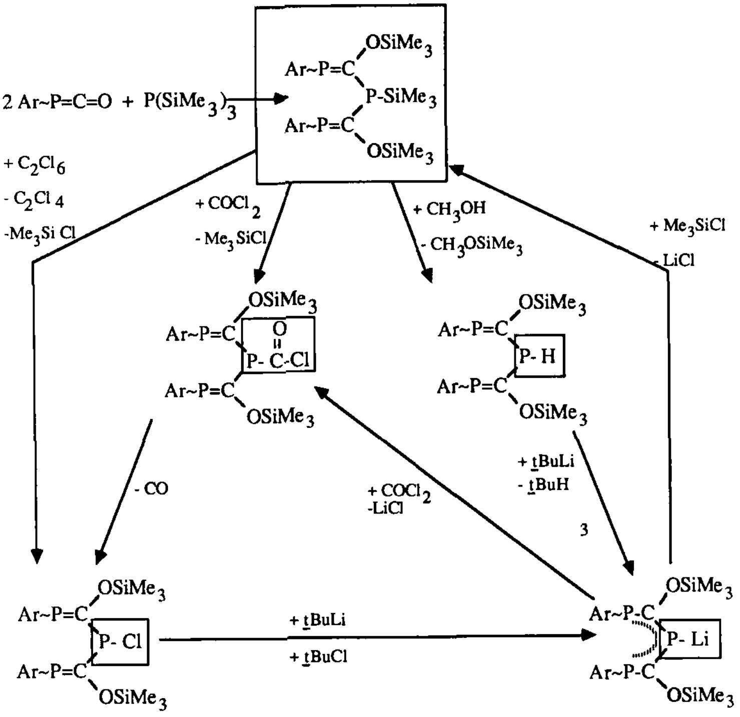
C. PHOSPHAHEXADIENES AND "PHOSPHA COPE REARRANGEMENTS"

Compounds possessing a phosphahexadiene structure are fascinating because their chemistry uncommonly analogous to pure carbon

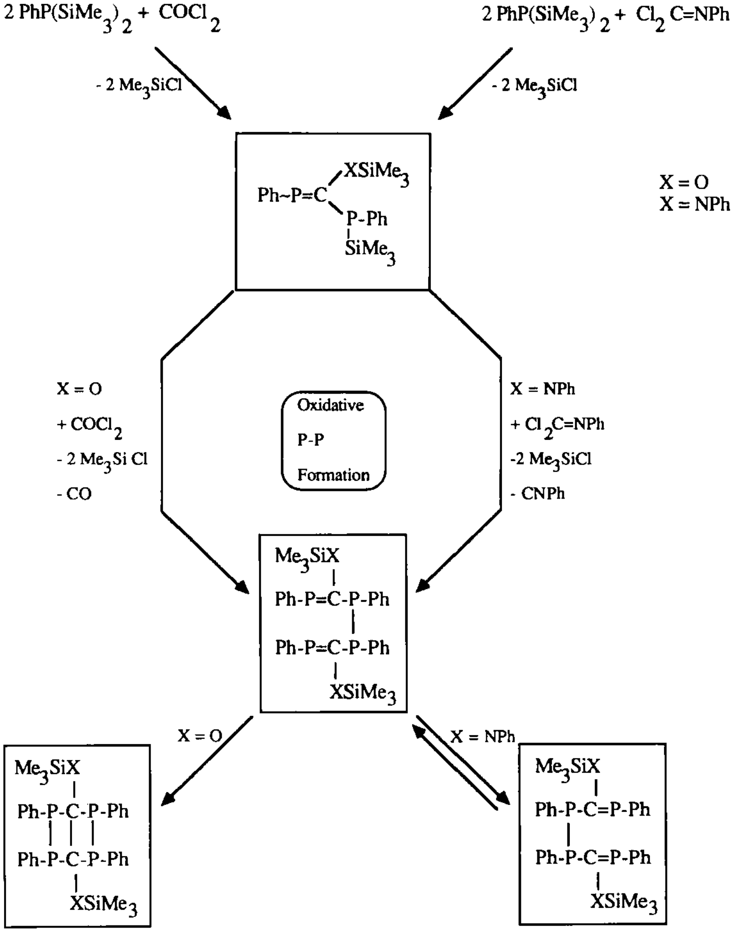


Scheme 3.

chemistry. This can be seen in a number of theoretically interesting cycloaddition and valence isomerization reactions, pointing to a stable $(2p3p)-\pi$ bond between the $3p$ orbitals of the sp^2-hybridized phosphorus and the $2p$ orbitals of the carbon atom. A combination of NMR spectroscopic, stereochemical, and kinetic results prove that the Woodward–Hoffmann rules for pericyclic reactions apply for this class of compounds.

1. 1,3,4,6-Tetraphosphahexa-1,5-dienes

This phenomenon of these molecules was first discovered through derivatives of 1,3-4,6-tetraphosphahexa-1,5-diene. These derivatives can be synthesized from organyltrimethylsilylphosphanes and phosgene or isocyanide dichlorides. Primarily 1,3-diphosphapropenes, which can be isolated, are formed and then react further with phosgene or isocyanide dichlorides, eliminating CO or isocyanide, respectively, and halosilane, and through oxidative combination of the two phos-



SCHEME 4.

phorus atoms yield 1,3,4,6-tetraphosphahexadiene. Then the reaction path divides. The siloxy-substituted compound (phosgene reaction) proceeds via a [2 + 2] cycloaddition to tetraphosphabicyclohexane. The open-chain structure of the nitrogen-substituted compound (isocyanide dichloride reaction) is retained and, surprisingly shows the interesting phenomenon of a fluctuating bond system (Scheme 4) (*29, 30, 100, 101*).

The tetraphosphahexadiene, a symmetrically different substituted diphosphane with two neighboring P atoms representing chiral centers, is yielded as a mixture of the meso and the enantiomeric racemic form. NMR spectroscopic and X-ray structure investigations done on isolated

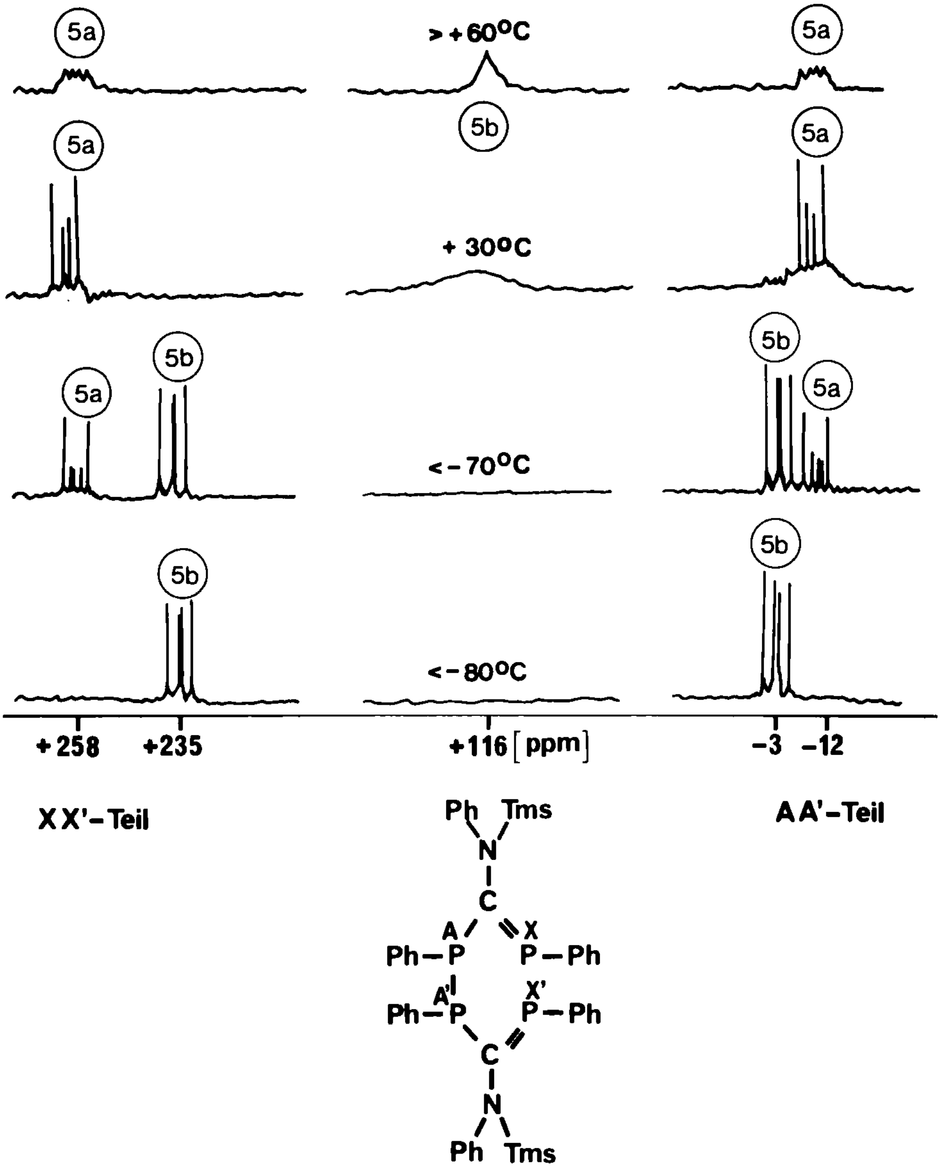

5a
> +60°C
5a
5b
5a
+ 30°C
5a
5b
5a
<-70°C
5b
5a
5b
<-80°C
5b
+258
+235
+116 [ppm]
-3
-12
XX'-Teil
AA'-Teil
Ph
Tms
N
C
A
X
Ph–P
P–Ph
A'
X'
Ph–P
P–Ph
C
N
Ph
Tms

FIG. 3.

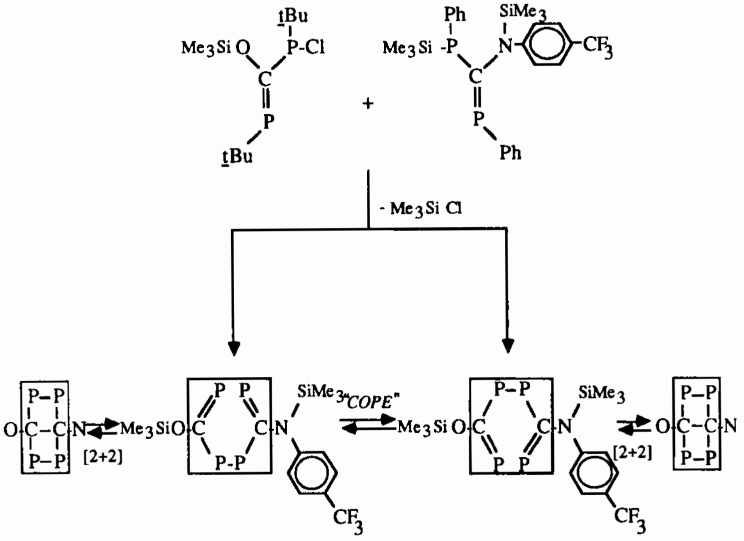
crystals have shown that the meso compound does not have fluctuating bonds in solution. The meso compound was transformed, however, into the racemic compound above $-50°C$, as monitored by ^{31}P NMR during the solution process. At $-80°C$, due to the meso compound only, the characteristic spectrum of the four-spin system (type AA′–XX′) is detected. During an increase of temperature the inner AA′–XX′ system of the racemic form appears and then collapses at room temperature into a centrosymmetric broad hump. This dynamic phenomenon can be explained by means of a fast bond exchange relative to the NMR time scale, no longer discriminating between the phosphorus atoms exhibiting coordination numbers two and three. A [3.3] sigmatropic bond shift takes place, opening the original P–P bond and simultaneously forming a new P–P bond between the two other phosphorus atoms displacing the π system. This phenomenon, first observed with a 1,5-hexadiene is named after the discoverer and is thus commonly known as the "Cope rearrangement." It is distinguished from the "phospha Cope rearrangement" by the rather high energy of activation required to promote the process (Fig. 3).

Tetraphosphahexadienes substituted with either O or N groups at the bridging C atoms show, with respect to reactivity, the ruling influence of substituents in these positions. The O-substituted compounds undergo [2 + 2] cycloadditions, whereas N-substituted compounds do not. A cross-test with a partially O-, partially N-substituted compound demonstrated both possibilities, with the bicyclos and the tetraphosphahexadiene interconnected via an equilibrium [Eq. (49)].

The cross-test results became evident via ^{19}F NMR monitoring of the decoupled peripheral CF_3 group of the molecule (*102, 103*). Another equilibrium is incorporated in this system, as detected by ^{1}H NMR of the *t*-butyl groups, proving the phospha Cope rearrangement of the hexadiene. These results were verified by X-ray structure determinations of the crystallized valence isomers. Crystals, uniform with respect to solid-state NMR and X-ray analyses, dissolved instantaneously, yielding the corresponding compound, traceable in the liquid by NMR signals.

With respect to the calculated kinetic and thermodynamic parameters one is able to make the following statement about the intercombination of the different equilibria: Valence isomerization and tetraphospha Cope rearrangement are independent equilibria exhibited by different energies of activation (Fig. 4).

The enthalpy of activation is distinctively higher for the valence isomerization than for the Cope process. This clearly shows that the bicyclo is not an intermediate during the Cope rearrangement. The stereochemical process of the Cope rearrangement, in which the



RRRR **RR** **SS** **SSSS**

(49)

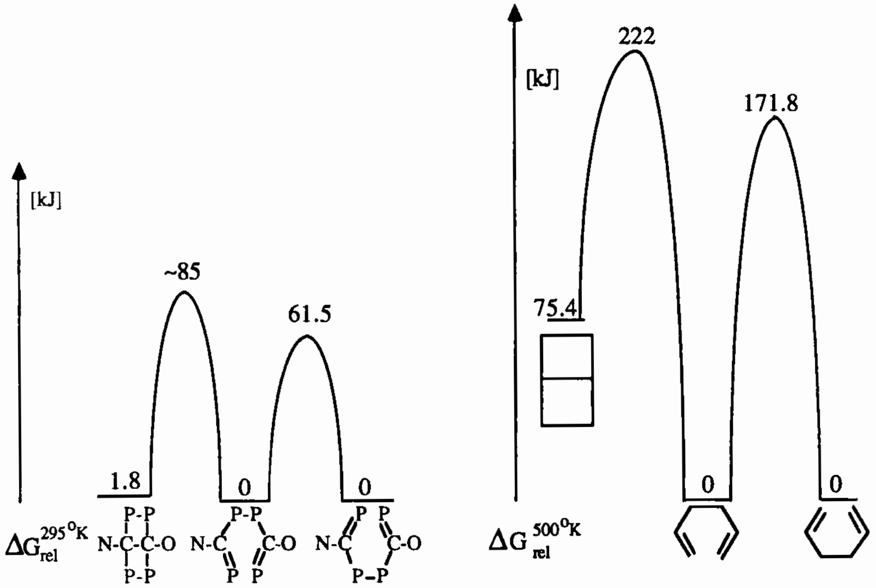
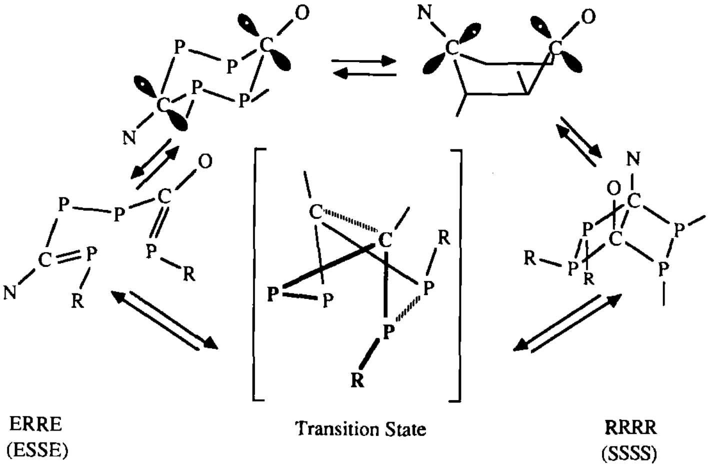


FIG. 4. Free energy of activation.



SCHEME 5.

RR-configured educt is transferred to the SS-configured product and vice versa, proceeds in agreement with the rules of maintained orbitals given by Woodward and Hoffmann, making it a coordinated pericyclic reaction. The mechanism of the valence isomerization is not yet so clear. Besides the thermally allowed $[2\pi s + 2\pi a]$ cycloaddition one also has to take into consideration a radical mechanism demanding a diyl radical (Scheme 5).

Though the stereochemistry is in agreement with the $[2\pi s + 2\pi a]$ process—the hexadiene of ERRE configuration turns into the RRRR bicyclo and correspondingly the ESSE-configured compound is transformed into the SSSS bicyclohexane—there are some points to be made for the radical mechanism, because it supports an explanation for the fact that O-substituted compounds favor the bicyclo, while N-substituted compounds form the hexadiene only. This can be deduced from a careful analysis of the X-ray structures, which shows that the substituents at the nitrogen atoms are organized in a planar sp^2 arrangement, leaving the free electron pair in the perpendicular *p* orbital (Fig. 5). If there is sufficient overlap the *p* orbital is able to communicate with the π system. The picture of the molecule clearly shows the nearly parallel orientation of the free electron pair with respect to the *p* orbitals belonging to the aromatic group within the open-chained tetraphospha hexadiene. The conjugation is verified by a shortened bond length to the first aromatic carbon atom of 139 pm and by a reduction of the outer angle, as expected from the VEPA model

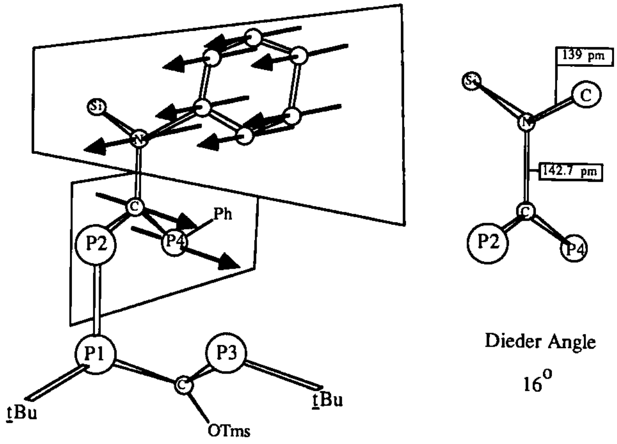


FIG. 5.

data. The picture of the bicyclo again shows the orientation of the free electron pair *p* orbital (Fig. 6).

The dieder angle is 69° with respect to the aromatic *p* orbitals, not allowing any conjugation with the aromatic ring. This is realized by a normal N–C distance of 144.5 pm and an outer angle that is 5° wider than in the previous case. But with respect to the nearly orthogonal orientation of the planes Si_2, N_1, C_A and C_1–C_2–N_1 (89°) there is an extensively parallel alignment of the free-electron *p* orbitals toward the central C–C bond. This may be interpreted as an interchange with the C atom orbitals in the sense of hyperconjugation, which, according

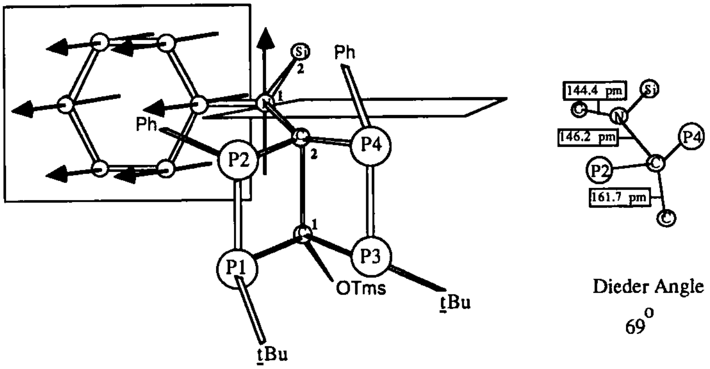


FIG. 6.

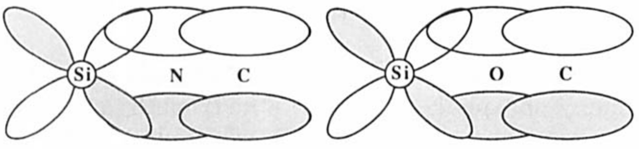


Fig. 7.

to investigations by Dewar, is important for molecules in the transition state (*104*). In the case of a homolytic C–C bond split, the *p* orbital at the nitrogen supports the stabilization of a diradical transition state because of its useful orientation. The favored stabilization can be interpreted as a multicentered π bond (three centers, three electrons) in which free *d* orbitals of the silicon take part (Fig. 7). The trimethylsiloxy group acts in a similar way, since even the oxygen tends to establish a coordinative π bond toward the silicon.

One may therefore tentatively conclude from this, in the case of a [2 + 2] cycloaddition or reversion, that a diradical transition state is most likely, if it is stabilized by substituents in the 2,5-position by means of a mesomeric interaction. Otherwise the equilibrium is shifted to the tetraphosphahexadiene. This explains the observations with respect to the reaction proceeding and hence the influence of the substituents at the two carbon atoms. If, in the case of a hindered orbital overlap between the substituents and the PC double bonds, a quasiaromatic interaction is blocked, the equilibrium is shifted to the tetraphosphahexadiene. On the other hand, if substituents in the 2,5-position are able to interact with the PC double bond, a mesomeric charge transfer into the side chain takes place, obstructing the aromatic transition state and so favoring the 1,4-cyclohexadiyl radical, which recombines to the bicyclic compound (Fig. 8). The carbon atom and its substituents

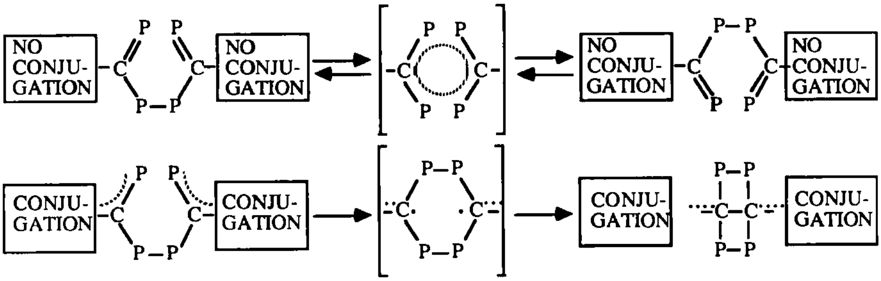
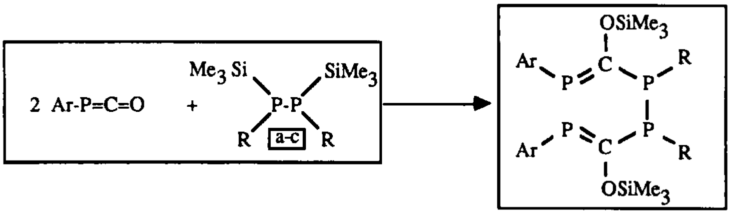


Fig. 8.

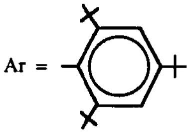
act as a shunt in keeping the electron current within or directing it out of the ring.

The reactions of the bis(trimethylsilyl)diphosphanes **a–c** with 2,4,6-tri-*t*-butylphenylphosphaketene lead to the trimethylsiloxy-substituted tetraphosphahexadienes **a–c** [Eq. (50)], which do not undergo a Cope rearrangement (*105*).



(50)

	a	b	c
R	$SiMe_3$	Ph	iPr

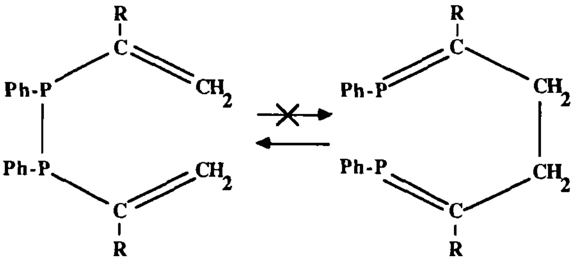


2. *3,4-Diphosphahexa-1,5-dienes*

The ability of the PC double bond within tetraphosphahexadienes to participate in pericyclic reactions initiated interest in the synthesis of additional phosphahexadienes and studies of their properties. Attempts to synthesize 1,6-diphosphahexadiene **a** via a [1,1′] Cope rearrangement out of 3,4-diphosphahexa-1,5-diene, derived from 1,2-dipotassium-1,2-diphenyl diphosphide and vinylbromide, were not successful when carried out up to the temperature of decomposition (above 120°C).

The inverted process, however, of transforming 1,6-diphosphahexa-1,5-diene **b** into 3,4-diphosphahexadiene or divinyl diphosphane proceeds under very mild conditions [Eq. (51)]. The diphosphide, prepared from succinylchloride and phenylbis(trimethylsilyl)phosphane between −70 and −80°C, rearranges after silyl migration above 0°C, forming the spectroscopically detectable 1,6-diphosphahexadiene intermediate, and finally ending up with the divinyl diphosphane via a [3.3] sigmatropic bond shift (*101*).

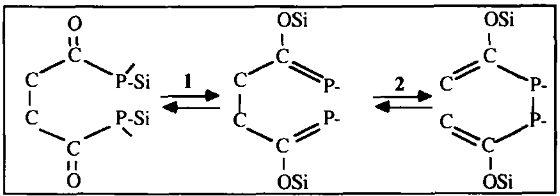
As opposed to the 1,2,4,6-tetraphosphahexadiene, the [3.3] sigmatropic displacement is not reversible, thus making it a degenerated Cope rearrangement, exhibiting different enthalpies of the educt and the product. The stereochemical analysis of the NMR-monitored reaction shows the primary product of the [3.3] sigmatropic shift to be exclusively the racemic divinylphosphane, supporting an electrocyclic reaction maintaining the symmetry of the orbitals.



(51)

	a	b
R	H	$OSiMe_3$

a. Estimation of the P=C Bond Energy. The Cope rearrangement, a reversible reaction in principle, leads to an equilibrium that is determined by the relative thermodynamic stabilities of educts and products. This is shifted to the side of the divinyl diphosphane in the case of compounds **a** and **b** in the temperature range between −80 and +80°C. The balance of energies is positive for the opening of a C−C σ and two C−C π bonds as well as for the closing of a P−P σ and two C−C π bonds. The balance of the two equilibria enables an estimation of the PC double bond. Using the second thermodynamic theorem and bond energies taken from the literature one gets the following calculation for the first equilibrium (Fig. 9):



$$0 > \Delta H^{o}_{298} = 708 + 214 + 264 - 343 - 368 - \boxed{BE_{P=C}}$$

$$0 > 475 - \boxed{BE_{P=C}}$$

for the second equilibrium respectively:

$$0 > \Delta H^{o}_{298} = \boxed{2xBE_{P=C}} + 2x331 + 331 - 2x264 - 2x620 - 214$$

$$0 > \boxed{2xBE_{P=C}} - 989$$

$$\boxed{BE_{P=C} < 494.5 \text{ kJ/mol}}$$

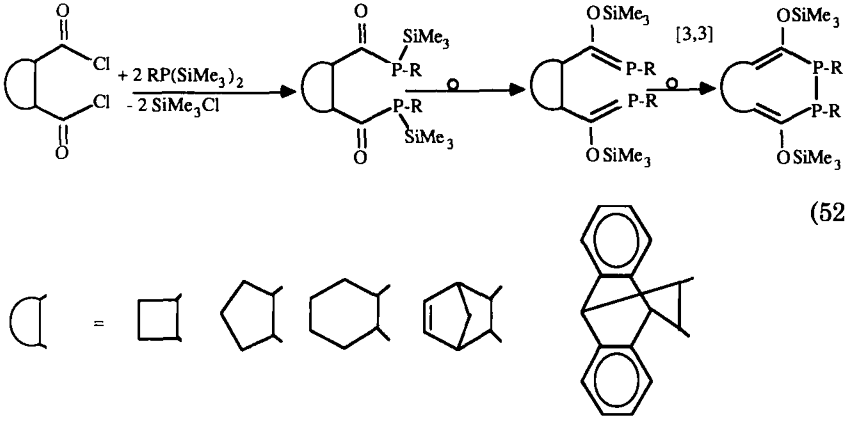
BE = bond energy

FIG. 9.

From here the energy of a λ^3-P=C double bond has to be located between 475 and 494.5 kJ/mol. The average value of 485 ± 10 kJ/mol is in good agreement with the *ab initio* calculated value of 491 kJ/mol for $HP{=}CH_2$ (*38*). Keeping in mind the drastic simplifications in using averaged bond energies and the assumption of $\Delta H^0 \gg T \times \Delta S^0$ incorporated into the calculation, the resulting value can only be used for an orientation.

b. Ring Expansion to Cyclic Diphosphanes by Cope Rearrangement. Phospha Cope rearrangements that do not degenerate have been corroborated along with analogous investigations on a number of cyclic 1,2-dicarbonic acid dichlorides.

The *trans*-1,2-dicarbonic acid dichlorides of cyclohexane, cylopentane, cyclobutane, and bicyclo[2.2.2]2,3:5,6-dibenzoocta-2,5-diene react with phenyl-, *t*-butyl-, and cyclohexylbis(trimethylsilyl)phosphanes [Eq. (52)], as determined by the spectroscopically detectable intermediates, by bond splitting, ring opening, P–P linking, and ring expansion, finally forming the cyclic diphosphanes. The starting temperature of the reaction (silyl migration) is very much dependent on the organyl substituent of the phosphane component. It is −10°C for the phenyl substituent; otherwise it is between +10°C and room temperature (*103, 106*).



(52)

R = as one chooses: phenyl, c-hexyl, t-butyl, or silyl

Because of an extremely fast valence isomerization, the 1,6-diphospha-1,5-hexadienes have not yet been isolated. The stereochemistry of the reaction is related to the dicarbonic acid dichloride precursors, which show a fixed bisequatorial orientation of the two carbonyl functions for the cycloalkane series. The same configuration is due to the preformed bond positions of the cyclic framework. Besides the similar conformation all show a trans orientation for the functional acyl groups (racemic mixture R,R + S,S). The twist angles differ slightly due to different ring tensions, but are still within the limits of a bisequatorial alignment (Fig. 10) (*107*).

The principle of maintaining the symmetry of molecular orbitals within stereoselectivity requirements during the phosphacarba valence isomerization is supported by comparison of the stereochemically important atomic centers of the educts (1,6-diphosphahexa-1,5-dienes) and products (1,2-diphosphacycloalkandiene):

1. Independently of the configuration of the phosphaalkene unit within the 1,6-diphospha-1,5-hexadiene structure the four-centered transition state (seat configuration) for the rearrangement favors an E-configured CC double bond for the 1,2-diphosphacycloalkane.
2. The configuration of the atoms, at the beginning and the end (1.1′ versus 3.3′) of the rearrangement, is unchanged.
3. The Z configuration of the educt PC double bond is transferred to a gauche orientation between the substituent at the phosphorus and the vicinal trimethylsiloxy group, as well as to a gauche conformation between the organyl groups at the phosphorus. The E configuration ends up with an anti orientation.
4. Educt, transition state, and product have an element of symmetry (C_2 axis) in common.

c. Balance of Energy. The position of the equilibrium of the basically reversible [3.3′]disphospha Cope rearrangement is determined by the relative thermodynamic stabilities of the two valence isomers. In the preceding systems it is completely shifted to the side of the cyclic diphosphanes with respect to the temperature interval between −80 to +70°C. An estimation of the enthalpy difference according to the two structures by means of disappearing and reappearing bonds resulted in $\Delta H^0 = 19$ kJ/mol (Fig. 11).

3. 1,6-Diphosphahexa-1,5-dienes by Cope Rearrangement from 3,4-Diphospha-1,5-hexadienes

Examples given in Section V,C,2 show that the 1,6-diphospha-1,5-hexadienes rearrange irreversibly at low temperatures to 3,4-diphospha-1,5-hexadienes, transforming the double-coordinated phosphorus into the preferred triple-coordinated atom. An experiment to convert 3,4-diphosphahexadiene via Cope rearrangement to 1,6-diphosphahexa-1,5-diene should thus be undertaken with the intention

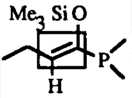
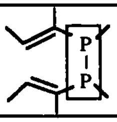
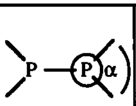
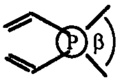
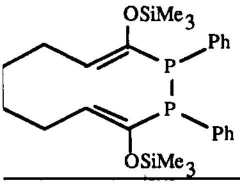
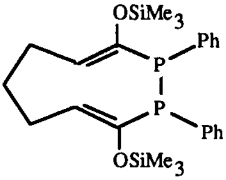
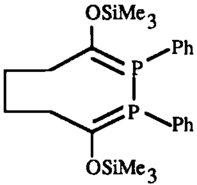
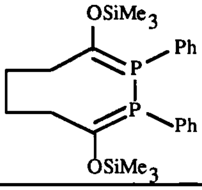
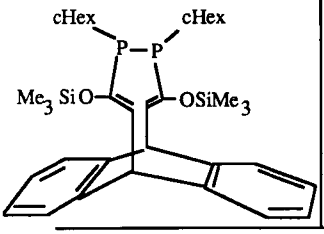
	Configuration		Torsion Angle [°]	
				
	E,E	rac.	19.2	85.3
	E,E	rac.	21.2	93.5
	E,E	rac.	23.2	89.9
	E,E	rac.	172.9	175.8
	E,E	rac.	171.1	171.5

FIG. 10. Structure criteria for the 3,3-diphospha Cope rearrangement as a sigmatropic reaction process of the 1,2-diphospha cycloalkane dienes, of which structures were determined by X-ray investigations.

Disappearing Bonds	Newly Formed Bonds
2x P=C = 2x 485	2x P-C = 2x 264
2x C-C = 2x 331	2x C=C = 2x 620
C-C = 331	P-P = 214
1963	1982

FIG. 11.

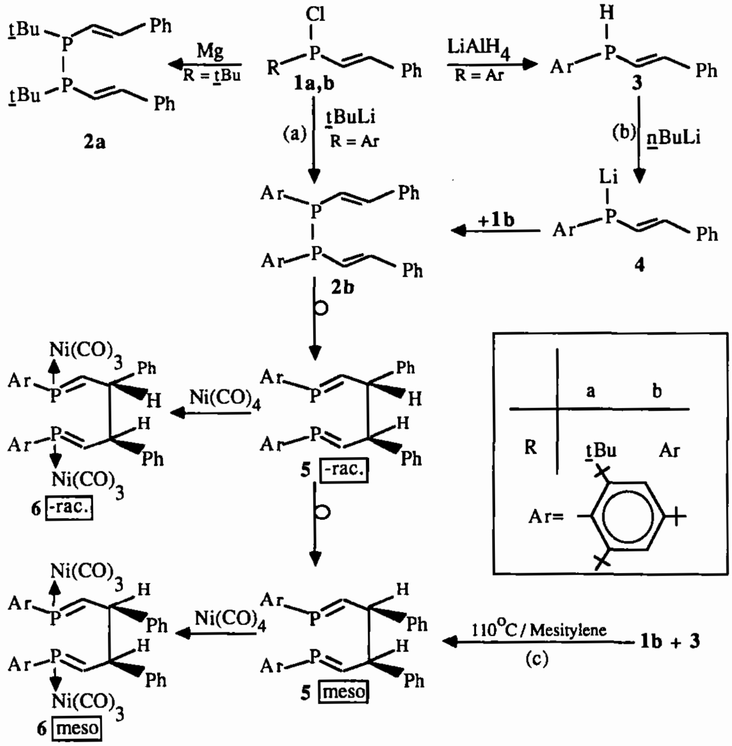
to weaken the PP bond by introducing bulky substituents. This could be tested for with *t*-butyl- and 2,4,6-tri-*t*-butylphenyl-substituted distyryldiphosphanes **2a** and **2b**. Though the weakening of the bond by means of the *t*-butyl group was not sufficient to promote the valence isomerization, the tri-*t*-butylphenyl group turned out to be a success even at room temperature. X-ray structure determinations show that **5** is a racemic mixture exhibiting an EE configuration. Racemic **5** in solution at room temperature slowly turns into the meso compound, coming off in the form of needles of low solubility (Scheme 6) (*108*).

For the transformation of **2b** into racemic **5** an ionic mechanism is most unlikely, since in nonpolar solvents the meso hexadiene **5** may also be formed following reaction path (c), ruling out detection of the intermediate racemic **5** because of thermodynamic instability. Because the previous estimation of the enthalpy difference for the 1,6- and 3,4-diphosphahexa-1,5-diene structures turned out to favor the diphosphane arrangement by 19 kJ/mol, the bulky substituent has to overcome at least this level of energy to enable the valence isomerization of **2b** into racemic **5**.

4. *Valence Isomerization of 3,4-Diphosphahexa-1,5-diine to 3,4-Bis(phosphamethylene)-1-cyclobutene*

Another example of the preceding valence isomerization via phospha Cope rearrangement, shown in Scheme 7, is the transformation of 3,4-diphospha-1,5-hexadiine to the hexatetraene followed by a [2 + 2] cycloaddition to give 3,4-bis(phosphamethylene)-1-cyclobutene (*109*).

The change from 3,4-diphospha-1,5-hexadiine to cyclobutene derivatives corresponds completely to the known synthesis of 3,4-bis(methylene)cyclobutenes from 1,5-hexadiines by thermal isomerization (*110, 111*). The transfer of the mechanistic idea developed for this

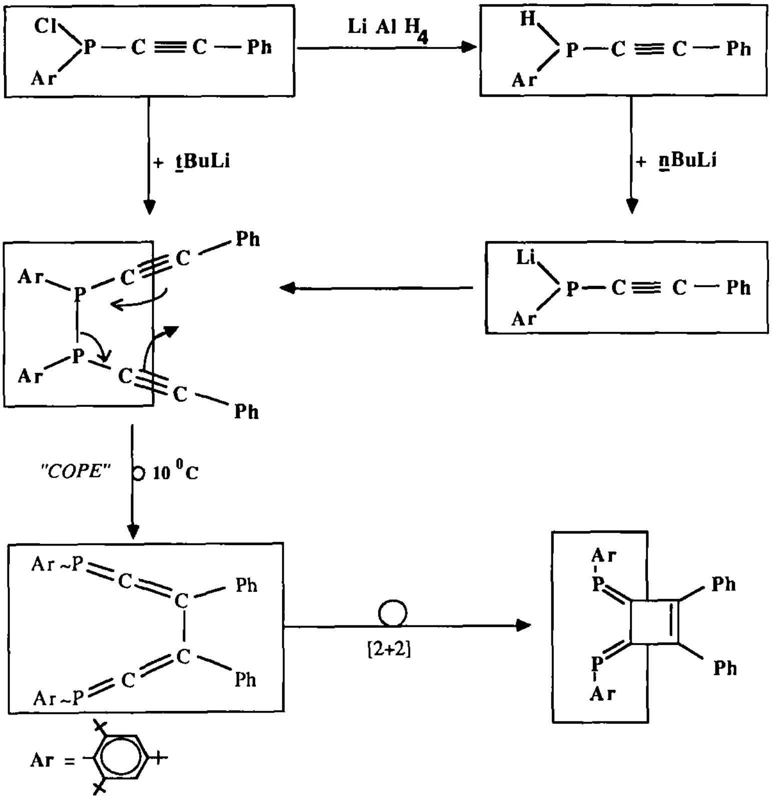


SCHEME 6.

case makes it most probable to assume a Cope rearrangement generating the 1,6-diphosphahexatetraene, which becomes the cyclobutene via an intramolecular [2 + 2] cycloaddition. While pure carbahexadiines rearrange above 350°C, the 3,4-diphospha-1,5-hexadiine turns into the cyclobutene at 10°C. The high reactivity may be due to the release of energy from the tri-*t*-butylphenyl groups weakening the PP bond, while the carbon analog compound withstands high thermal stress (>200°C), possibly due to the 2π aromatic character of this class of compounds. A X-ray structure determination shows the P atoms in the plane of the planar four-membered ring, EE configured with respect to the PC double bond.

5. *1,3-Diphosphahexa-1,5-dienes*

Compounds exhibiting the framework of a 1,3-diphosphahexa-1,5-diene can be synthesized in a reaction between chloro-1,3-phospha-



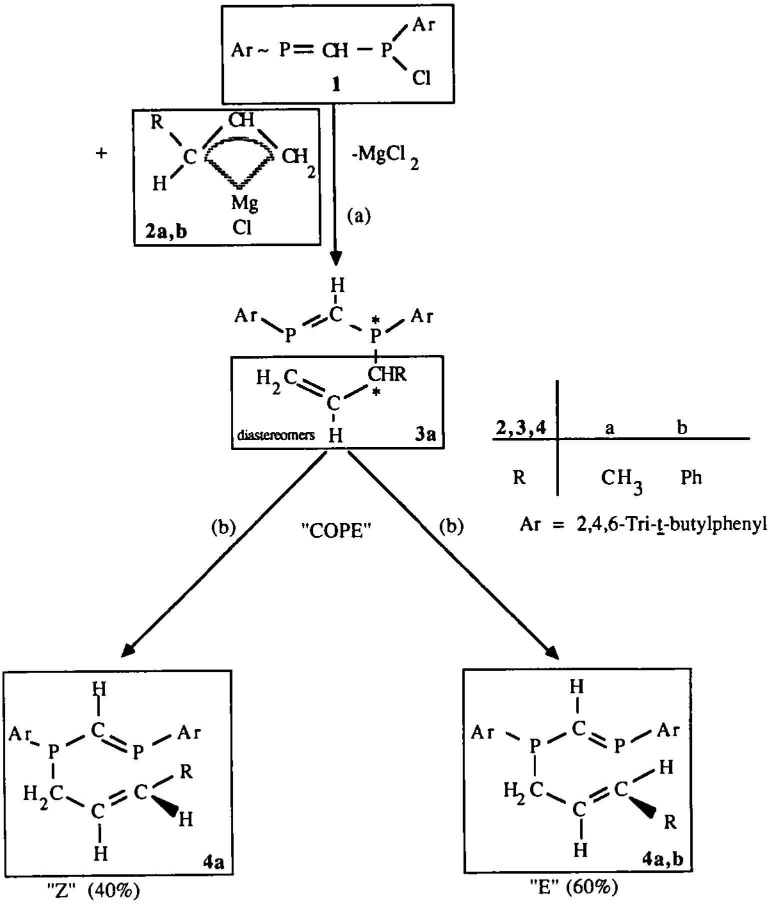
SCHEME 7. Cope rearrangement of 3,4-diphospha-1,5-hexadiine and [2 + 2] cycloaddition.

propene and crotyl or cinnamyl magnesium chloride, respectively, and are yielded as a mixture of diastereoisomers (*112*) (Scheme 8).

Inversion of configuration at the phosphane phosphorus atom of **3a** is most likely due to ^{31}P NMR spectroscopically monitored dynamic phenomena. Keeping **3a** at 60°C for 3 hours leads to an irreversible thermodynamically more stable **4aE**. The energy of activation is calculated to 80.5 kJ/mol. According to X-ray structure determinations of **3a** and **4aE** the SS stereoisomeric compound is subject to a Cope rearrangement, resulting in the EE stereoisomeric form (Scheme 9).

6. Monophosphahexadienes

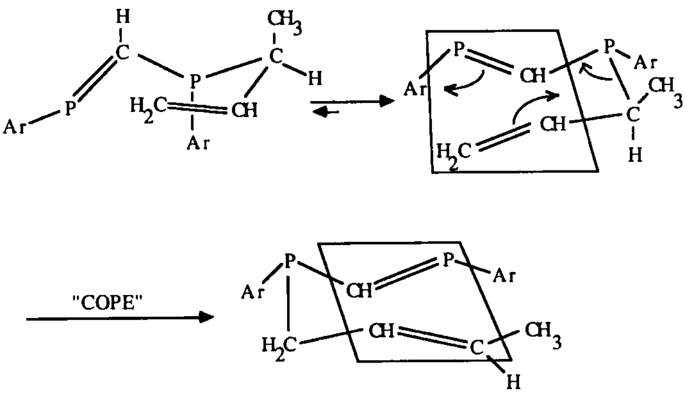
a. Rearrangement of 3-Phosphahexa-1,5-Dienes to 1-Phosphahexa-1,5-dienes. 3-Phosphahexadienes **3a–c** (Scheme 10) can be prepared



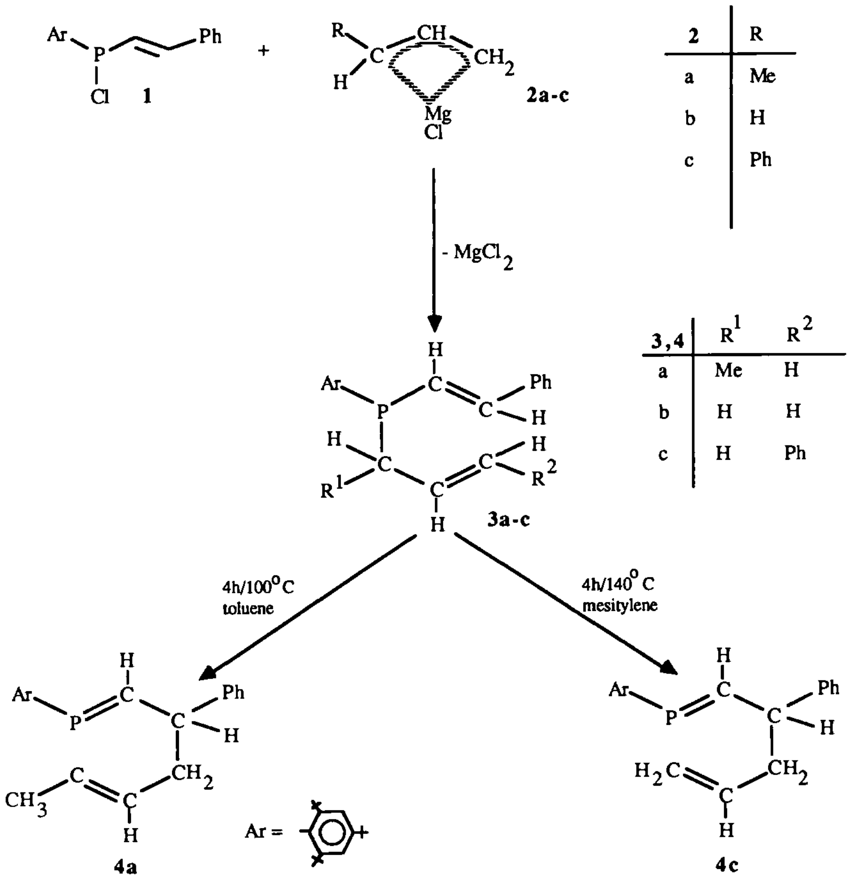
2,3,4	a	b
R	CH_3	Ph

Ar = 2,4,6-Tri-t-butylphenyl

SCHEME 8. Cope rearrangement of 1,3-diphospha-1,5-hexadienes.



SCHEME 9.



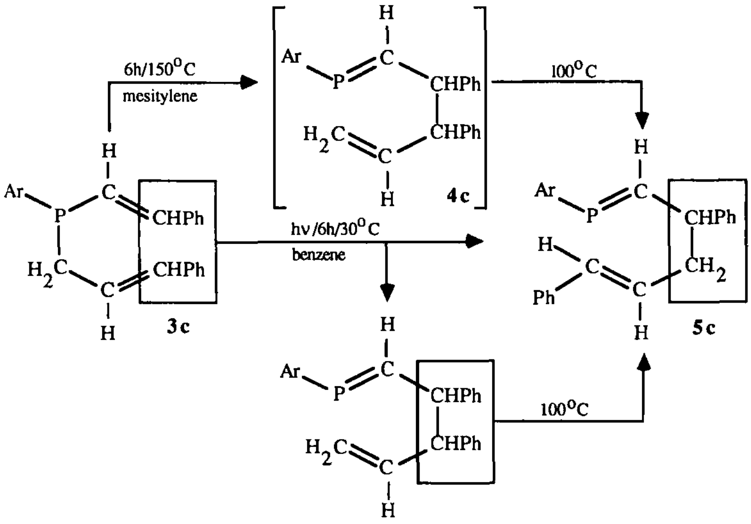
2	R
a	Me
b	H
c	Ph

3,4	R^1	R^2
a	Me	H
b	H	H
c	H	Ph

SCHEME 10.

in a reaction of styryl chlorophosphanes with crotyl, allyl, or cinnamyl magnesium chloride (*113*). The compound **3a**, exhibiting asymmetric centers at the phosphorus and the neighboring carbon atom, yields a mixture of diastereomers. Prolonged heating to 100°C causes an irreversible rearrangement to the 1-phosphahexa-1,5-diene. An analogous transformation takes place with **3b**. Due to the absence of steric influence of the α-methyl group in **3b**, a much higher temperature (4 hours, 140°C) is needed for the rearrangement.

During the valence isomerization of **3c** the phosphaalkene **5c** is formed unexpectedly and exclusively (Scheme 11). Its origin is attributed to the rearrangement of the primary product **4c** via a [3.3]



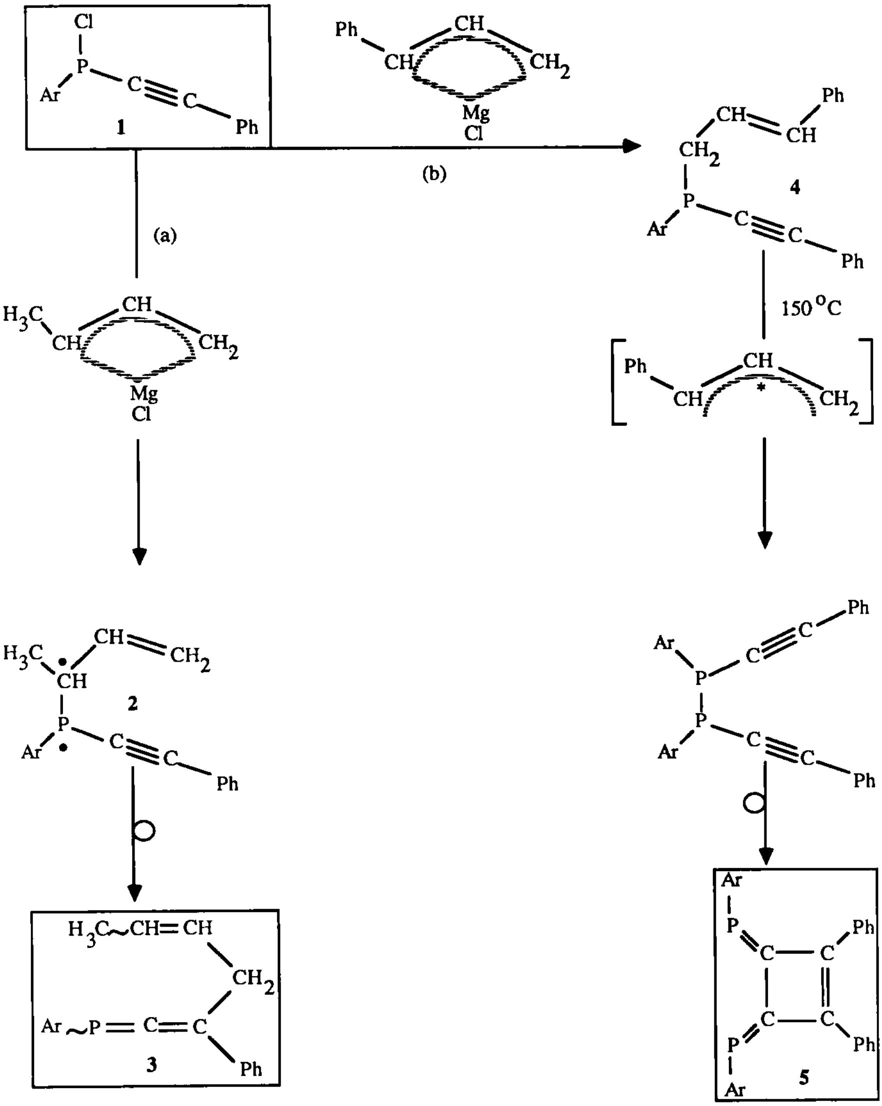
SCHEME 11.

sigmatropic shift. The spectra indicate an E-configured PC double bond. Irradiation of compound **3c** generates the diastereomeric form of **4c** as well as the product **5c**, with additional transformation.

The unhomogeneous composition of the products generated by the photochemical reaction is due to another mechanism. While the thermal isomerization of 1,5-dienes proceeds via a cyclic transition state in a synchronous sense, the photochemically induced transformation causes a reorientation of the allyl radicals generated from the educts. Warming up the reaction mixture to 100°C activates a complete transfer from **4c** to **5c**) of all isomers. This step may be explained by a radical CC bond split of the 1,2-diphenylethylene unit. Since the isomerization of the diastereomeric compound **4c** to **5c** is activated at much lower temperatures than for the Cope rearrangement (from **3c** to **4c**), it is clear that the thermal transfer exclusively forms the twofold changed product.

Valence isomerization could also be observed with the phosphapropargyl system (*113*). Monophosphahexenine **2** synthesized from chloroethinylphosphane **1** and crotyl magnesium chloride forms the E,Z isomeric mixture of 1-phosphaallene **3** during several hours at 150°C (Scheme 12).

The reaction is first order according to time-dependent spectra monitored at different temperatures. The formation of phosphaallene



SCHEME 12.

has to be interpreted by means of a Cope rearrangement via an intramolecular valence isomerization [reaction (a)].

From the reaction of chlorophosphane **1** with cinnamyl magnesium chloride the stereospecifically and uniformly E configured monophosphahexenine **4** is developed, exhibiting a phenyl group in the γ-position with respect to the phosphorus atom [reaction (b)]. Several hours at 150°C generates mainly the cyclobutene **5**. The formation of this compound under the given conditions may be understood as a radical cleavage of the cinnamyl group. The following dimerization of the remaining phosphapropargyl radicals possibly proceeds via the diphosphane intermediate (which is known to be thermolabile and is therefore not detectable) to the cyclobutene. The analogous Cope rearrangement to the phosphaallene is not observed in this case, this may be due to different reasons. (1) The phosphane **4** does not have any additional sterical hindrance from another substituent at the α-C atom, causing the PC bond to be separated, as is the case in the reaction with the crotonyl compound. (2) The vinylic phenyl group sterically hinders a possible cyclic transition state and since it is in conjugation it blocks the possible migration of the double bond.

VI. Cumulated Bond Systems with Participation of the PC Double Bond

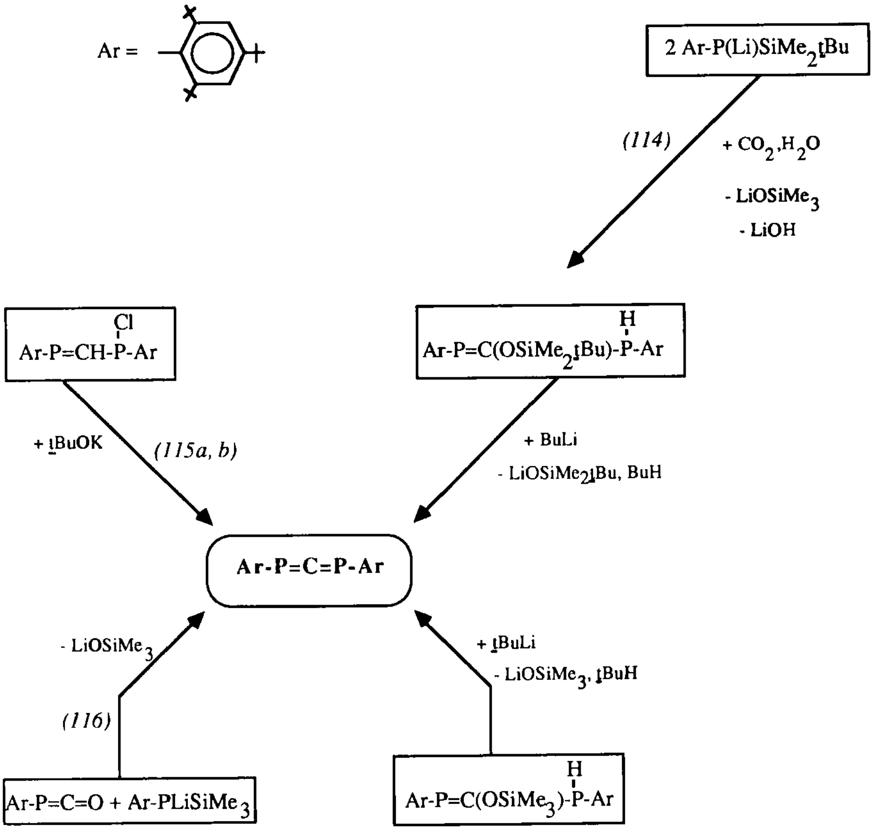
A. DIPHOSPHAALLENES

A number of heteroallenes incorporating the λ^3 phosphorus demonstrate the amazing relationship between the PC double bond and the CC double bond. Up to now compounds have been synthesized showing cumulated P=C and C=X bond systems (X = PR, NR, O, S, CR_2, $C{=}CR_2$). Only those having bulky groups such as 2,4,6-tri-*t*-butylphenyl (or in a few examples the *t*-butyl substituent), at the phosphorus could be identified and to some extent be isolated.

1. 1,3-Diphosphaallenes

The preparation of 1,3-diphosphaallenes can be attained starting with different 1,3-diphosphapropenes, which can be transferred to the carbodiphosphane via cleavage of siloxane or silanolate, or via HX abstraction (*114–116*) (Scheme 13).

During the reaction of the phosphaketene and lithium phosphide, an analogue to the well-known Peterson olefination, a lithium salt, can



SCHEME 13.

be detected by NMR and shows a characteristic lithium–phosphorus coupling (Fig. 12) (*117*).

Another way to synthesize 1,3-diphosphaallenes is via a reaction between lithium trimethylsilylphosphide and carbon disulfide at 0°C [Eq. (53)] (*118*).

$$2\ \mathrm{Ar\text{-}P(Li)SiMe_3} + \mathrm{CS_2} \longrightarrow \mathrm{Ar\text{-}P{=}C{=}P\text{-}Ar} + 2\ \mathrm{LiSSiMe_3} \qquad (53)$$

Insertion into the phosphorus silicon bond primarily generates a phosphaalkene, which splits off trimethylsilylthiolate and frees the phosphathioketene **1**. A renewed addition of the phosphide followed by a splitting off of thiolate finally yields the diphosphaallene **2** [Eq. (54)].

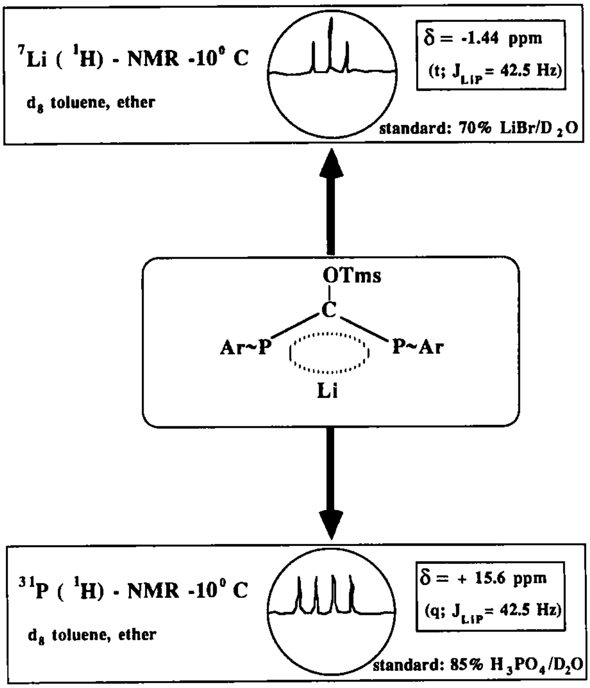
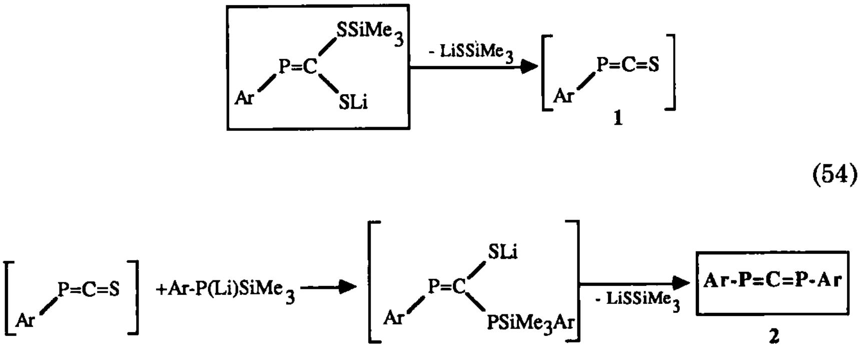


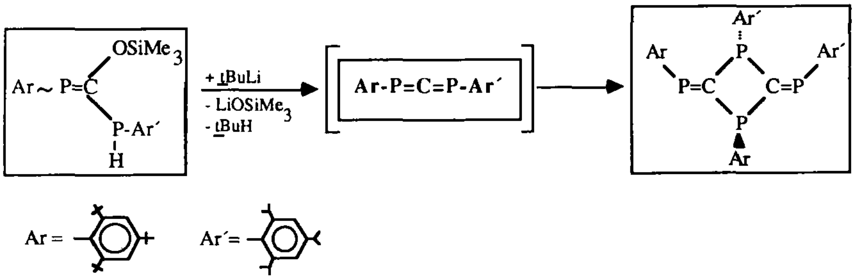
FIG. 12. Lithium salt.



(54)

Only a minor bond shortening of the PC double bond (163 pm) occurred with respect to the isolated PC double bond (167 pm), but an important stereochemical criterion, the orthogonal orientation of the aryl substituents relative to the nearly linear P—C—P axis (172.6°), can be elucidated from X-ray structure determinations. Like all allenes exhibiting an even number of double bonds, this molecule is chiral. Separation of the racemic mixture generated during the synthesis has been accomplished by using a chiral column filling (*119*).

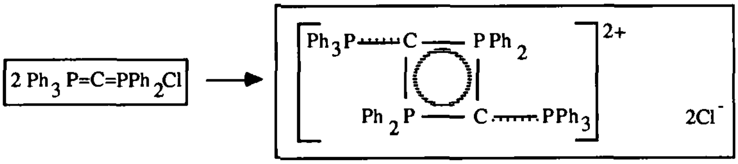
Mixed substituted diphosphaallenes are still unknown. Attempts to react the 2,4,6-tri(isopropylphenyl)phospha-substituted diphosphapropene with *t*-butyllithium according to Eq. (55) yielded the dimeric compound (*117*).



(55)

According to X-ray investigations the structure is a 1,3-diphosphetane ring, keeping two exocyclic PC double bonds and showing the aryl groups in the trans position relative to the ring. The two substituents at the PC double bonds are E configured (*117*, p. 73). The total sum of the angles is 358.3°, demonstrating a nearly planar ring structure. Attempts to obtain the known diphosphaallene **2** [Eq. (54)] or another symmetrically substituted diphosphaallene via a thermally or photochemically induced decomposition failed.

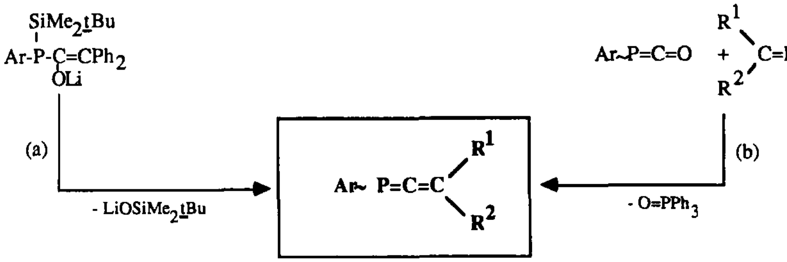
The dimerization of the diphosphallene has an interesting parallel with the carbodiphosphoranes. The chloro-substituted λ^5 phosphacumulene reacts under cycloaddition to give the diphosphacyclobutadiene dichloride [Eq. (56)] (*120a, 120b*).



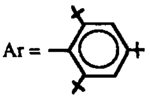
(56)

2. *1-Phosphaallenes*

The elimination of lithium silanolate is a method for the synthesis of 1,3-diphosphaallenes and can also be used for the preparation of 1-phosphaallenes (*121*) [Eq. (57a)]. Additionally, these compounds



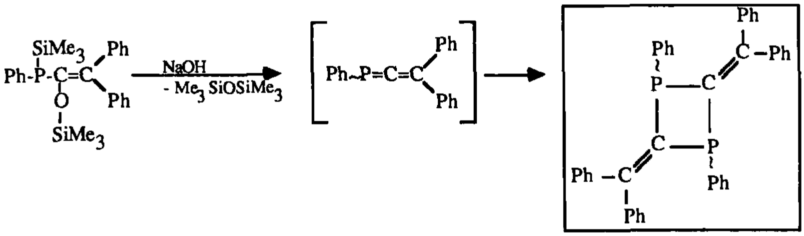
(57)



	a	b	c
R^1	Ph	Ph	CO_2Et
R^2	Ph	H	H

can be yielded from phosphaketenes and the phosphoranylylides by a Wittig reaction (*116*, *122*). [Eq. (57b)].

Efforts to generate a 1-phosphaallene with a less bulky phenyl group at the P atom via a siloxane elimination from a phosphapropene gave the diphosphetane [Eq. (58)], easily imaginable as a dimer of the

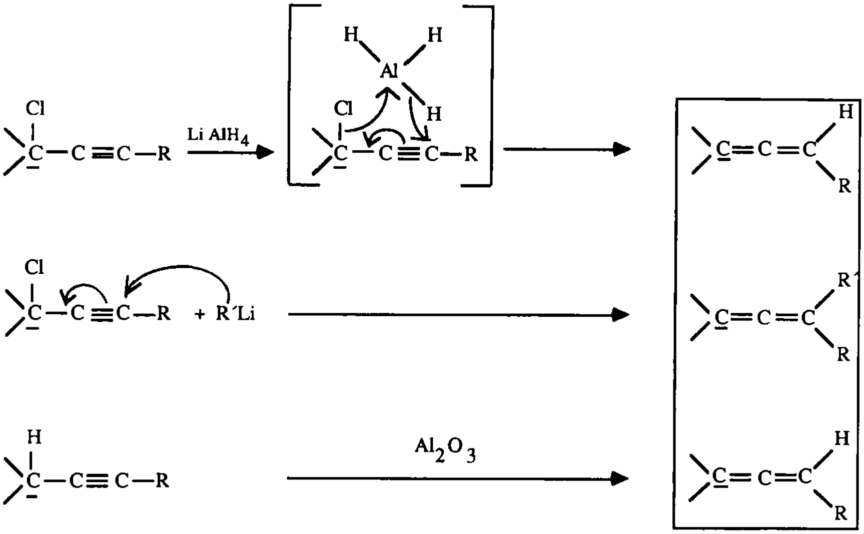


(58)

intermediate phosphaallene. The reason for this distinct tendency to dimerize is undoubtedly related to the absence of a sterically protected phosphorus atom (*122*).

The application of ideas primarily developed for pure carbon chemistry to the chemistry of organophosphorus compounds, especially sp^2-hybridized phosphorus atoms, has again advanced the route for synthesis of the 1-phosphaallenes.

It is well known that allenes can be synthesized from ethinylalkanes (*123*). Reactions (59) and (60) are of the type $S_{N'}$ substitutions, which means that incoming and leaving groups for the substitution are not restricted to one and the same carbon atom but may be separated by a distance of two CC bonds, and the reaction proceeds via a simultaneous shift of electrons. Equation (61) shows an aluminium-catalyzed 1,3-proton migration, which, with respect to the allyl reorientation, is a propargyl rearrangement. The analogous reactions [Eqs. (59)–(61)] with phosphaallenes means that the labeled C atoms have to be substituted with phosphorus.



(59)

(60)

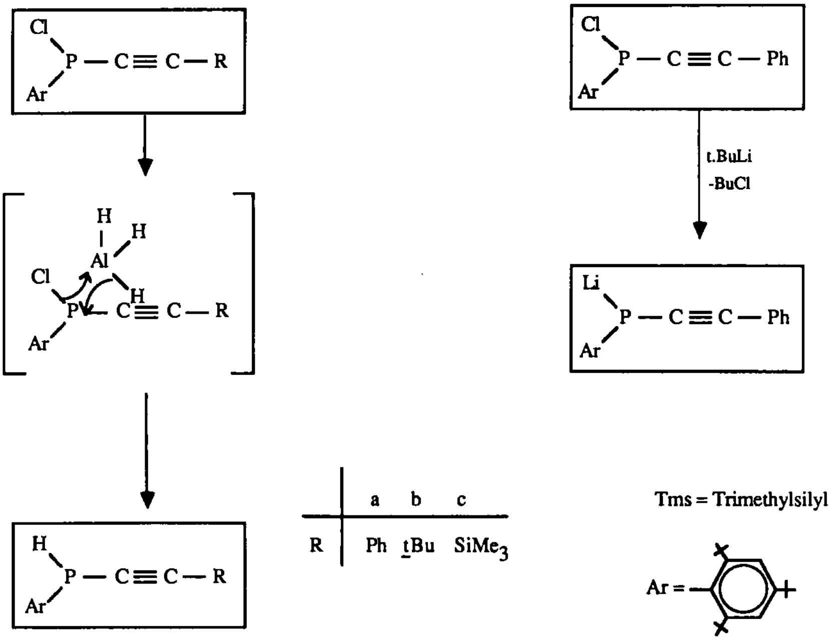
(61)

Attempts with chloroethinylphosphane failed, because the chloro group vigorously increased the electronegativity of the phosphorous atom (*124*). Instead of the phosphaallenes, phosphanes were obtained (Scheme 14).

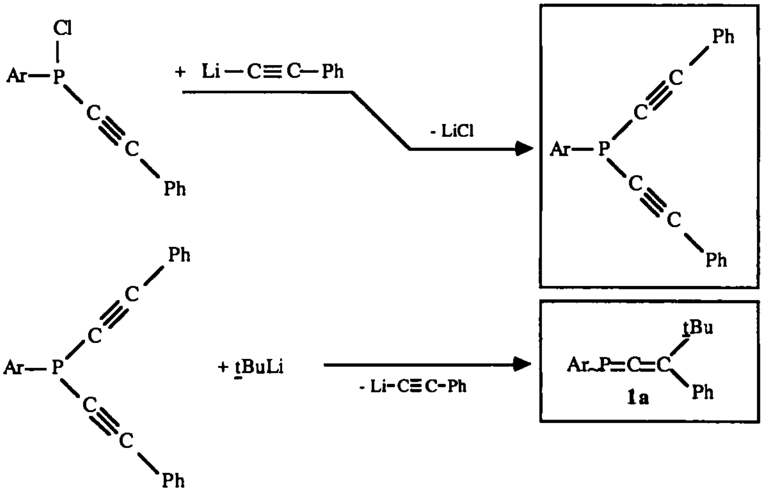
A more appropriate leaving group in comparison to Cl was the phenylethinyl substituent, as can be seen from the successful synthesis of the phosphane using *t*-butyllithium. Here the phosphaallene system is generated in good yields via a $S_{N'}$ substitution (*124*) [Eq. (62)].

1-Phosphaallenes can be synthesized in the same way as 1,3-diaryl-substituted allenes following an aluminium-catalyzed propargyl rearrangement. Using sodium hydroxide-activated aluminium oxide (*125*), the synthesis is suitable on an enlarged scale without any detectable by-products [Eq. (63)]. A similar proton migration within a coordinated phosphaalkyne was reported recently (*126*).

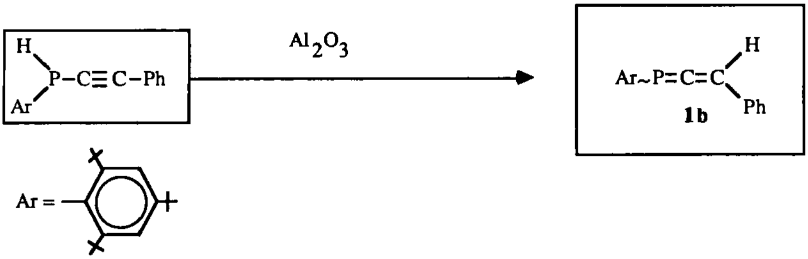
1-Phosphaallenes similar to **1a,b** [Eq. (62) and (63)] exhibiting different substituents are chiral, because the original molecule and the


Cl
P — C ≡ C — R
Ar
H
H
Al
Cl
H
P — C ≡ C — R
Ar
H
P — C ≡ C — R
Ar
Cl
P — C ≡ C — Ph
Ar
t.BuLi
-BuCl
Li
P — C ≡ C — Ph
Ar
a b c
R Ph tBu SiMe3
Tms = Trimethylsilyl
Ar =

SCHEME 14.


Cl
Ar—P
C
C
Ph
+ Li—C≡C—Ph
- LiCl
Ar—P
C
C
Ph
C
C
Ph
Ar—P
C
C
Ph
C
C
Ph
+ tBuLi
- Li-C≡C-Ph
Ar–P=C=C
tBu
Ph
1a

(62)



(63)

corresponding mirror image of it are not identical. Enantiomeric compounds of such phosphaallenes could be detected in chiral solvents by NMR. A sample of **1b** solvated in (+)-phenylethylamine shows in the ^{31}P NMR spectrum two signals centered at 75 ppm with respect to 85% H_3PO_4, separated by only 2 Hz (*124*, p. 46) (Fig. 13).

Removal of the chiral solvent and dissolving the residue in toluene gives only one single peak, showing the same shift as before. This test verifies the reversibility of the solvent effect, thus excluding any chemical reaction between the amine and the phosphaallene. As expected, the intensities of the two signals are equivalent, because the enantiomeric compounds generated in a nonstereospecific manner are formed in equal proportions. If the proton is substituted in **1b** by a *t*-butyl group as in **1a** [Eq. (62)], it becomes impossible to detect different signals. The reason for this phenomenon may be the reinforced sterical

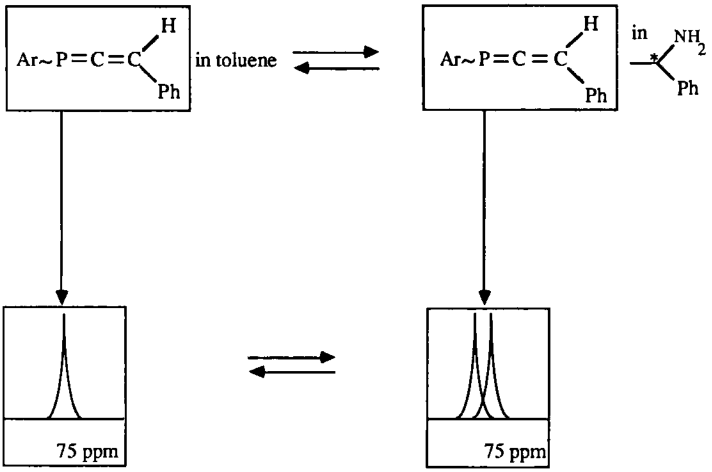


FIG. 13.

protection of the substrate, apart from the only minor alternating effects with the chiral solvent.

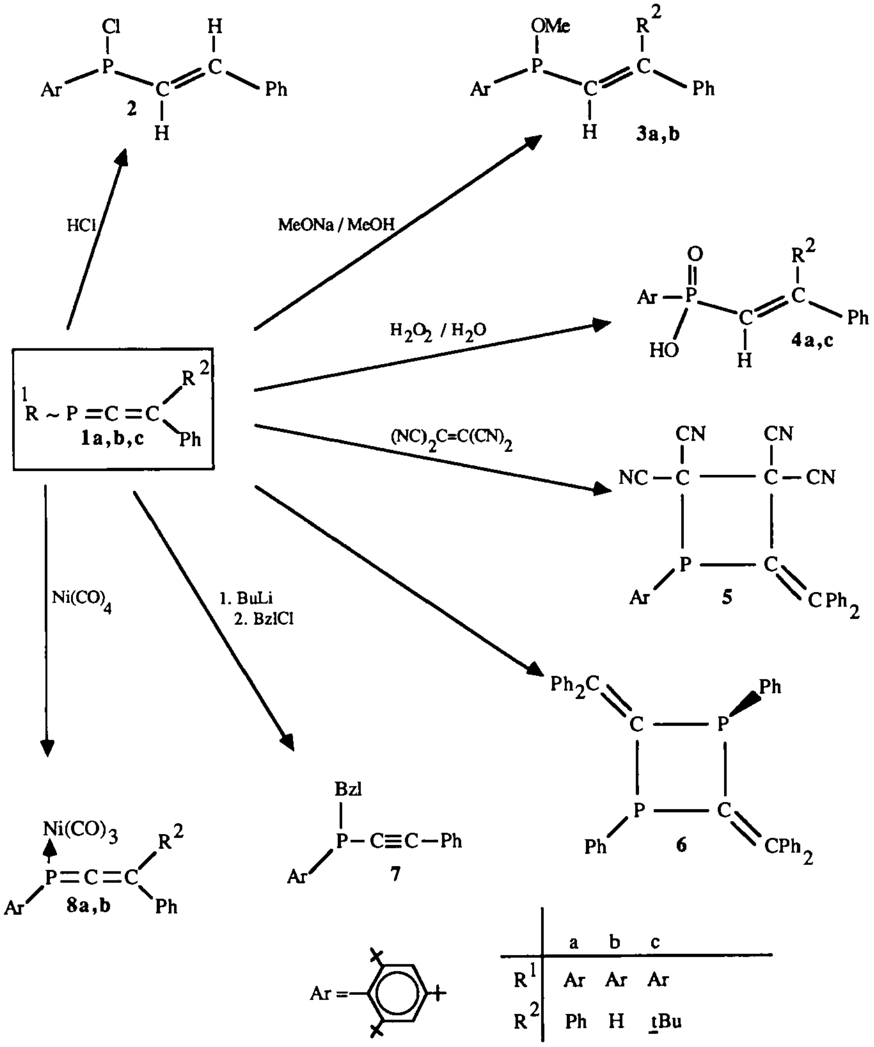
3. Reactivity of the 1-Phosphaallenes

1-Phosphaallenes exhibit three reactive centers, the PC double bond, the CC double bond, and the phosphorus atom. Here the PC double bond is significantly more reactive than the neighboring second double bond. The reactivity pattern is very similar to the phosphaalkenes, as far as the addition, cycloaddition, and coordination reactions are concerned. The cumulated CC double bond therefore has to be treated as an isolated group that is not greatly influenced by reactions at the PC π system.

Thus phosphaallenes react with HCl or methanolate, respectively, adding to the PC double bond and forming the phosphinous acid chloride or the corresponding methyl ester. In these cases the phosphorus atom acts as an electrophilic center. During the turnover of **1a,c** together with H_2O_2/H_2O the phosphorus atom again is attacked in a nucleophilic way and is oxidized to phosphinic acid **4a,c** (Scheme 15).

An *ab initio* calculation for the 1-phosphaallene $HP{=}C{=}CH_2$ and the predictions thereof are in remarkably good agreement with the findings (*127*). According to the experiments these calculations draw a parallel between $HP{=}CH_2$ and $HP{=}C{=}CH_2$. For the cumulenes such as $HP{=}C{=}O$ (*128*), $HP{=}C{=}NH$, $HP{=}C{=}PH$ (*129*), and $HN{=}C{=}CH_2$ (*127*), this relationship does not exist or at least is less marked. The π orbitals of the PC bonds within the 1-phosphaallenes and the phosphaalkenes are HOMO orbitals with only a minor difference of energy to the lower n orbitals of the phosphorus atom. Even the orbital overlap of the phosphorus with the doubly bonded carbon is of the same order for these two types of compounds. Referring to the phosphaallenes, the coefficients for the HOMO and LUMO three-center orbitals clearly show the preference of the PC in comparison to the CC bond. This explains the similarity with respect to the chemical behavior between the phosphaalkenes and the phosphaallenes (Fig. 14).

Calculations give additional information concerning the capacity of dipoles of the phosphaallenes. Accordingly, the positive end is at the phosphorus atom and the negative end sticks to the vinyl group, shifting the main point of the negative charge to the α-C atom. A protonation will therefore be privileged at this point. The addition of CH-acid reagents to 1-phosphaallenes as well as the direction of dimerization of 1-phoshaallenes was correctly predicted.



	a	b	c
R^1	Ar	Ar	Ar
R^2	Ph	H	tBu

SCHEME 15.

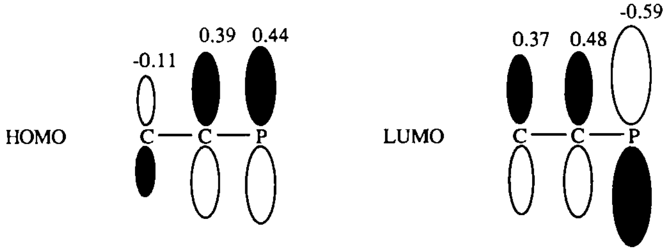
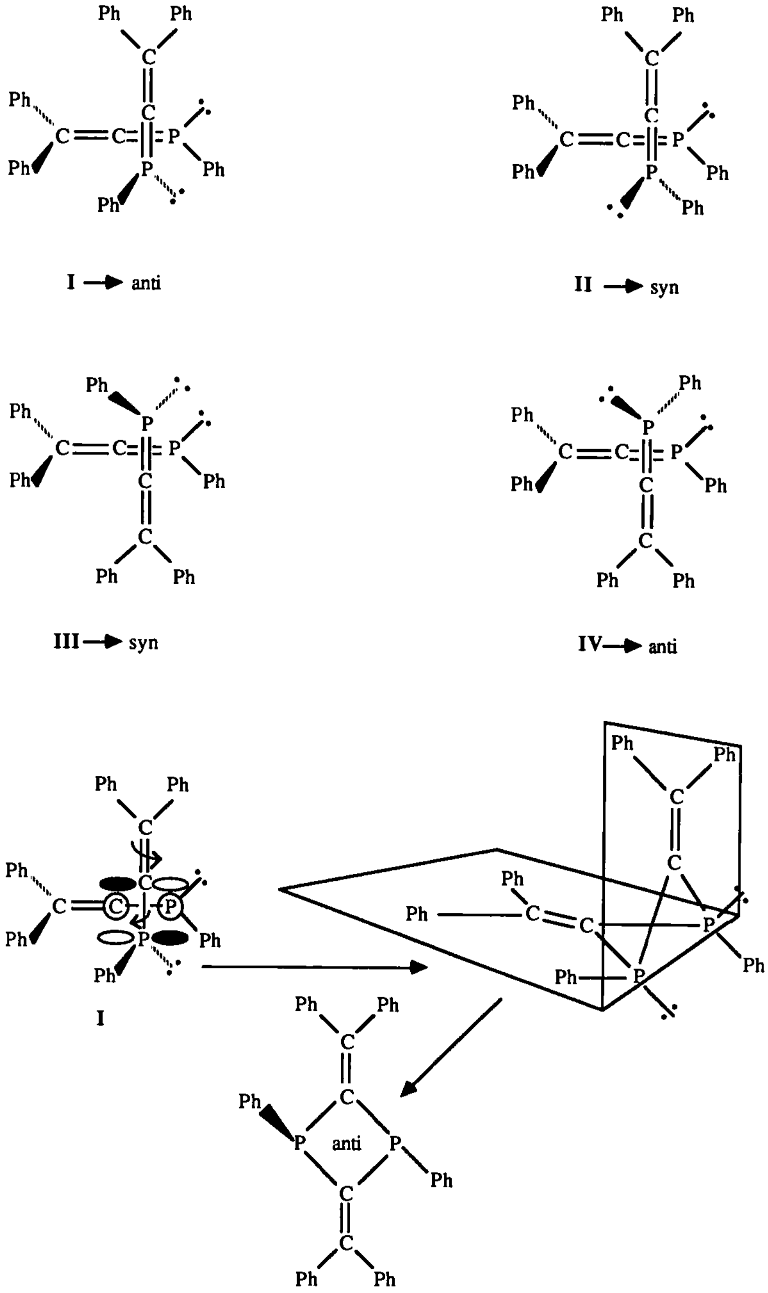


FIG. 14. HOMO and LUMO orbitals of $CH_2{=}C{=}PH$.



I → anti

II → syn

III → syn

IV → anti

FIG. 15.

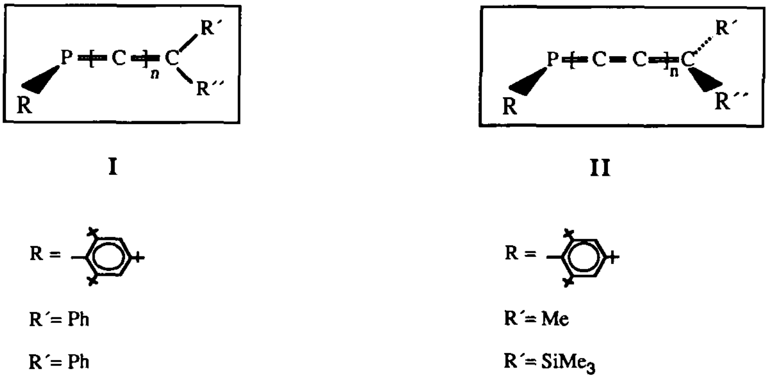
Tetracyanoethylene reacts via a [2 + 2] cycloaddition with **1a**, forming phosphetane, while **1a** reacts in a head-to-tail combination to diphosphetane (Scheme 15). NMR spectra and X-ray structure determinations show that only one of the regio- and stereospecific diastereomers is formed. The molecule exhibits a centrosymmetric geometry and a planar ring structure. The stereospecific reaction, which does not allow a possible syn orientation of the P-phenyl group, may be due to a thermally induced symmetry-allowed ($\pi^2s + \pi^2a$) process. Such a process is only possible with linear systems exhibiting a low density of substitution. Out of the four possible transition states, conformation I is most favored for sterical reasons, because the alternating effects between the phenyl groups are very low. The mutually HOMO/LUMO effect favors the experimentally found anti product due to the given mechanism (*124*, p. 34) (Fig. 15).

B. 1-PHOSPHA-1,2,3-BUTATRIENES

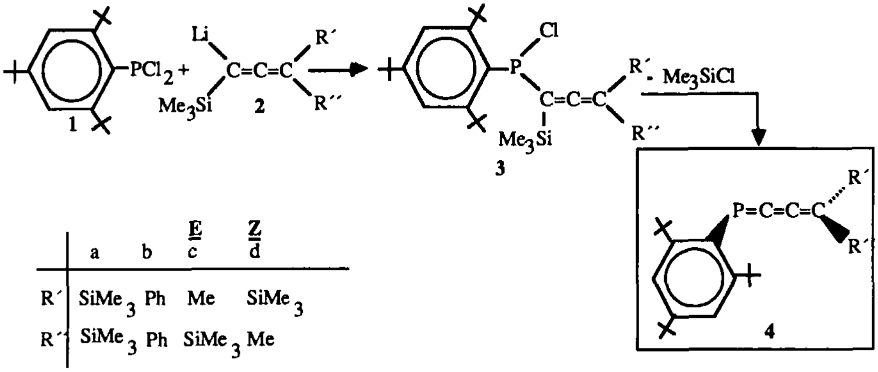
After the synthesis of some 1-phosphaallenes (type I, $n = 1$), 1-phospha-1,2,3-butatrienes (type II, $n = 1$) were synthesized recently for the first time (Scheme 16).

These can be realized in a transformation of monolithiated allenes with dichlorophosphane via the coupling products and elimination of trimethylchlorosilane [Eq. (64)] in a so-called Peterson–Wittig reaction (*130*).

The phosphabutatrienes **4** [Eq. (64)] are pale yellow oils (**4a, 4c**) that crystallize when kept cool for some time, and with ethanol form little shiny yellow sheets. NMR spectroscopic data show, in accordance



SCHEME 16.



	a	b	E c	Z d
R′	$SiMe_3$	Ph	Me	$SiMe_3$
R′′	$SiMe_3$	Ph	$SiMe_3$	Me

(64)

with the structure, significant low-field ^{31}P shifts (**4a**: $\delta = +343.3$ ppm; **4b**: $\delta = +156.7$ ppm; **4c**: $\delta = +288.6$ ppm; **4d**: $\delta = +332.3$ ppm). As expected E,Z isomers are detected by ^{1}HNMR with $R' \neq R''$, thus the compounds exhibit the E orientation of the substituent R′ with the lower shift and the greater P/H coupling. E,Z compounds can be separated using chromatography on silica gel with petroleum ether. The X-ray structure determination of **4b** verifies the rod-shaped molecule of the phosphabutatriene.

C. MONOPHOSPHACARBODIIMIDES

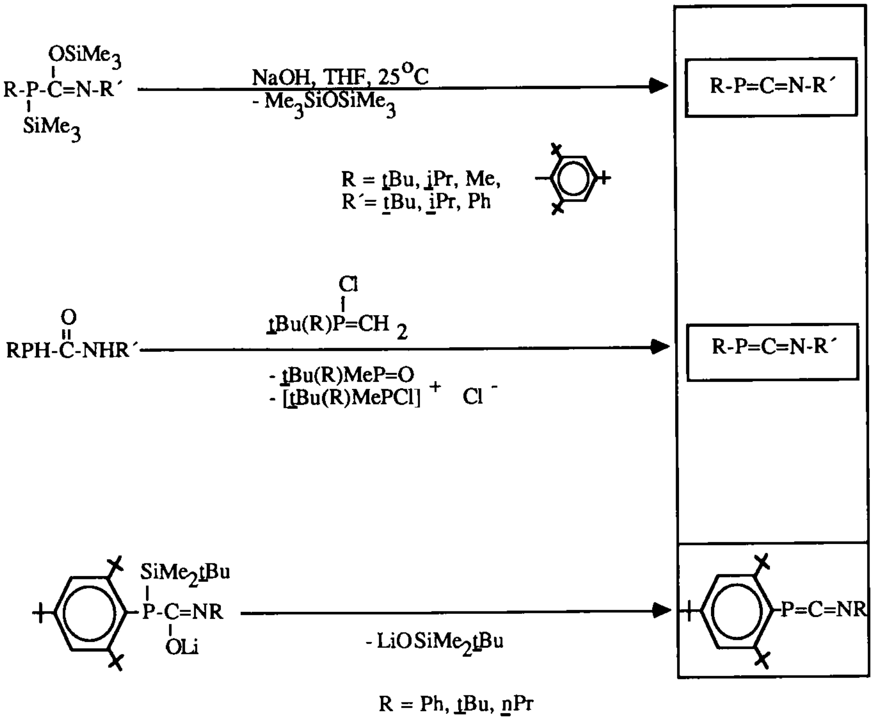
The first hints of the intermediate appearance of the 1-phospha-3-azaallenes, as one may call this class of compounds, were obtained during investigations of the system bis(trimethylsilyl)phosphane/isocyanide dichloride. Depending to the course of reaction, bis(imino)-1,3-diphosphetane or 1,3-diphosphapropene is synthesized via addition of excess silylphosphane to the primarily formed monophosphacarbodiimode or its dimerization product (*31*).

Starting materials for the preparation of compounds in this class are the phospha urea molecules, synthesized from silylphosphanes using isocyanate. These can be transformed in a catalytic siloxane separation [Eq. (65)], by dehydratization [Eq. (66)], or by silanolate elimination [Eq. (67)] to monophosphacarbodiimides (*121, 131a–132*).

Another possibility is a Wittig analog reaction as given in Eq. (68). (*133*).

Reactivity of Monophosphacarbodiimides

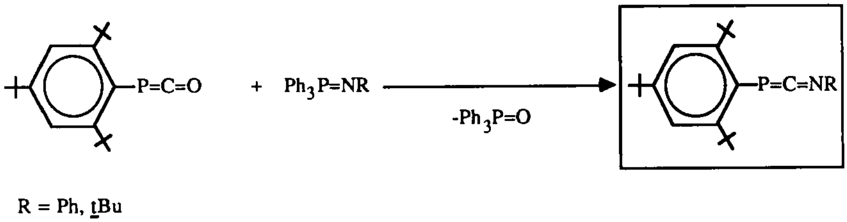
In comparison to the phosphaalkenes or phosphaketenes (RP=C=O), the significant high-field shift of the ^{31}P NMR signals of iminomethyl-



(65)

(66)

(67)



(68)

idene phosphanes (−64 to −127 ppm) as well as the ^{13}C NMR low-field shifts of the central carbon atoms (about 200 ppm) indicate an Umpolung (Fig. 16).

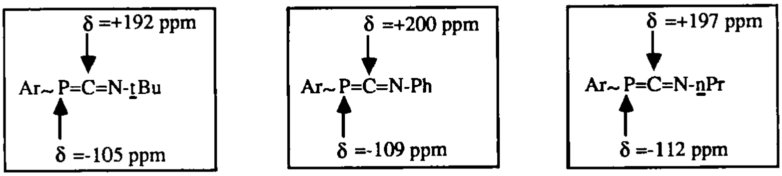
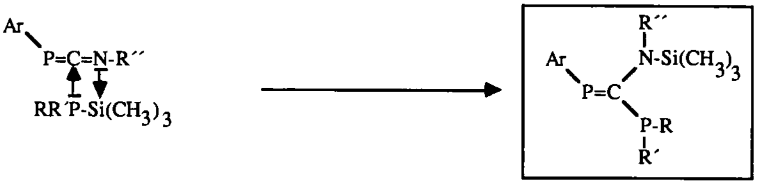
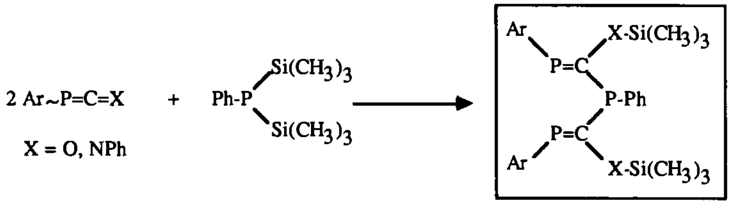


FIG. 16.

Therefore, nucleophiles attack the carbon, while the corresponding electrophile approaches the phosphorus or the nitrogen. Accordingly, silylphosphanes are added to 1,3-diphosphapropenes [Eq. (69)], triphosphapentadienes [Eq. (70)], and tetraphosphahexadienes [Eq. (71)]. All products are E-configured, indicating a stereoselective reaction (*134*).



(69)



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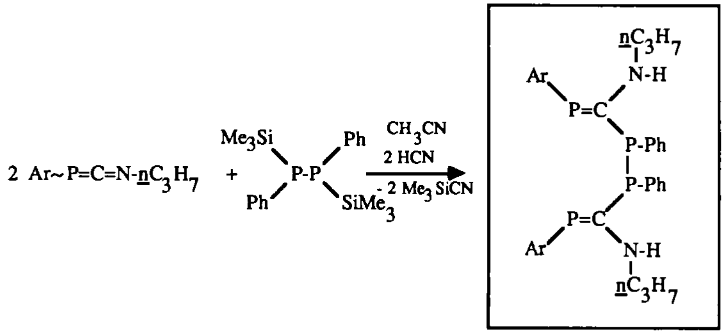
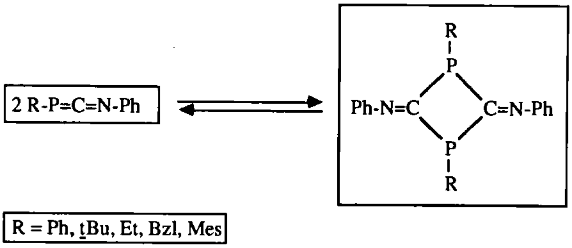


(71)

Among the cycloadditions, the addition to the PC double bond prevails. 2,4-Bisimino-1,3-diphosphetane is formed in a [2 + 2] cycloaddition of the unstable monomer 1-phospha-3-azaallene (*54*, *60*). It can be decomposed into the monomer compound in a flashlight vacuum pyrolysis (*135*). Nevertheless, this method cannot be used to produce the monomer compound on a preparative scale [Eq. (72)].

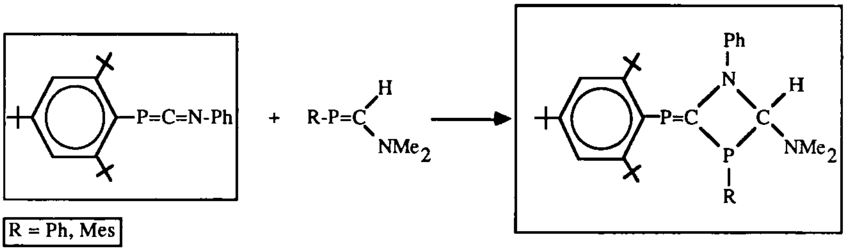
All X-ray tested 2,4-bisimino-1,3-diphosphetanes exhibit a planar four-membered ring with the P-attached substituents in a trans orientation. NMR spectroscopic investigations on solvated diphosphetanes prove, depending on the substituents, the existence of different stereo-



(72)

isomeric compounds. Isomers with sterically unfavored CN orientation of the substituents at the P atoms (A + B) (Fig. 17) can be excluded, as shown with numerous 2,4-bis(phenylimino)-1,3-diphosphetanes (*136, 137*). Addition to the PC double bond is also observed with cumulenes such as carbodiimides, isocyanates, and diphenyl ketene (*132*) (Scheme 17).

A reaction with C-amino-substituted phosphaalkenes [Eq. (73)] demonstrates a possible addition to the C=N bond (*133*).



(73)

D. PHOSPHAKETENES

Presently, only two phosphaketenes are known, which show either a *t*-butyl or a tri-*t*-butylphenyl substituent at the P atom. These can

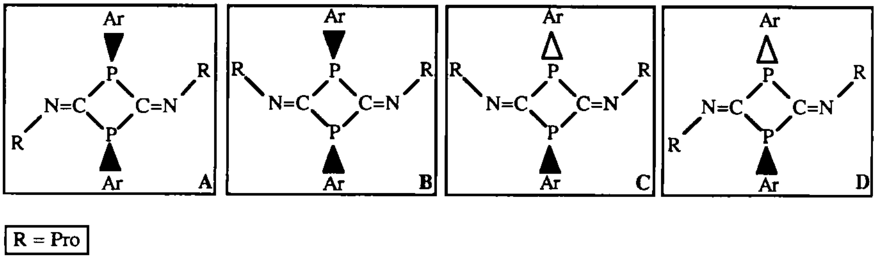
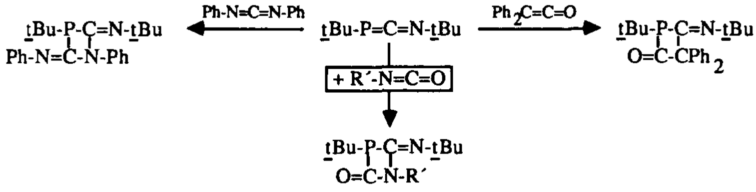


FIG. 17.

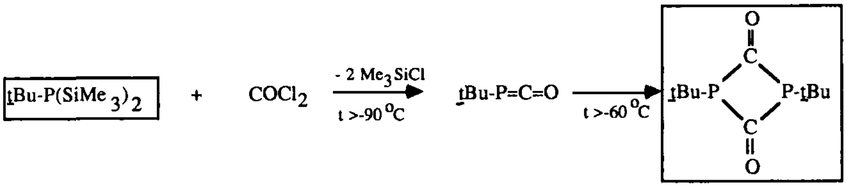


SCHEME 17.

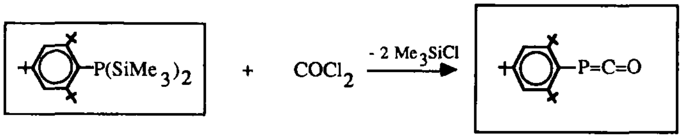
be best synthesized in a twofold trimethylchlorosilane condensation from the corresponding bis(trimethylsilyl)phosphanes and phosgene (*138, 139*).

The formation of *t*-butylphosphaketene starts shortly above −90°C, whereby the phospha analog of the carbamide acid chloride can be detected as an intermediate by ^{31}P NMR. Above −60°C its dimerization to the diphosphetandione [Eq. (74)] takes place; this molecule is only reasonably stable at room temperature in unpolar solvents such as pentane. Adding polar agents or exposure to light causes decomposition. One of the products is triphosphetanone, which was synthesized before (*102, 140*). Even the better characterized tri-*t*-butylphenyl-substituted phosphaketene shows a slow decomposition in toluene, when irradiated by a mercury lamp over a period of 24 hr, splitting off CO. Some of the ^{31}P NMR spectroscopically identified products are dihydrophosphaindole, phosphane, and diphosphene (Scheme 18). Attempts to detect the expected phosphinidene intermediate failed. The decomposition mechanism itself is still unclear (*117*, p. 24).

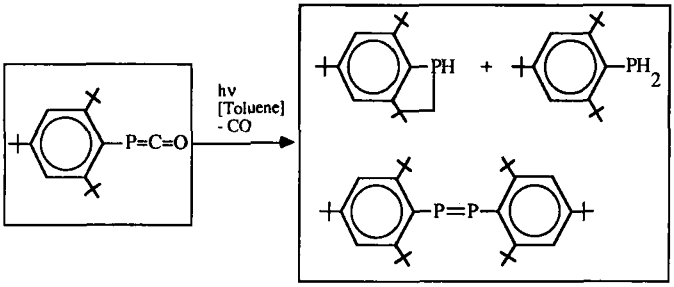
The tri-*t*-butylphenyl-substituted compound is formed at room temperature [Eq. (75)]. The compound, monitored by ^{31}P NMR within the range of room temperature and −35°C, generates, diphosphetandione



(74)

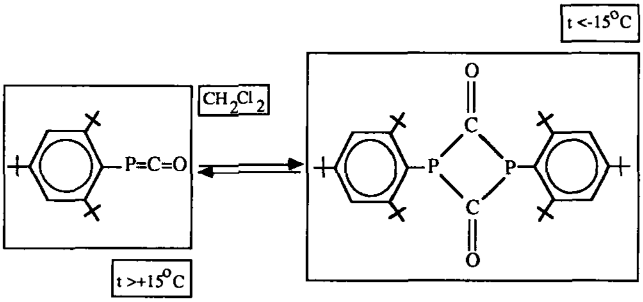


(75)



SCHEME 18.

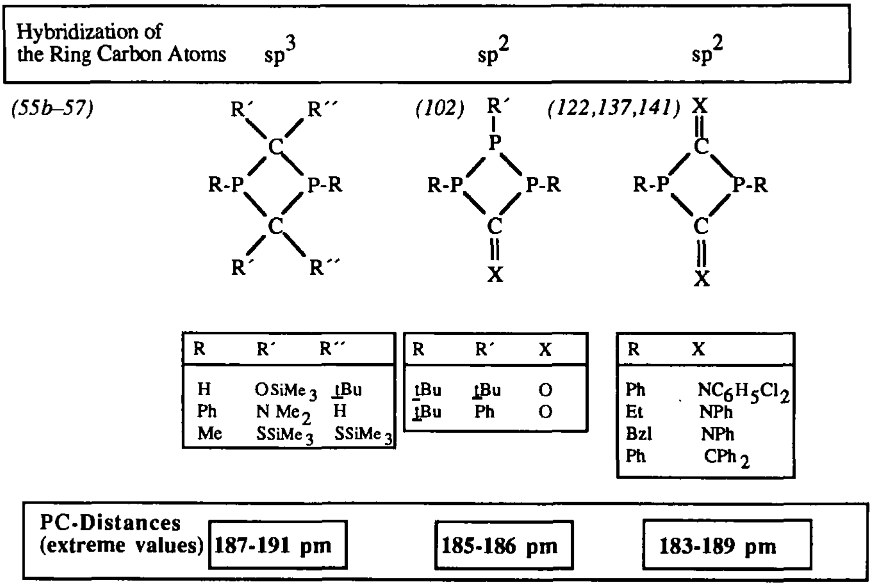
during the cooling-down process of the solvated phosphaketene, with the concentrations changing in favor of the monomeric compound upon rewarming [Eq. (76)]. Between 50 and 60°C the equilibrium is shifted completely to the left side (*117*, p. 13).



(76)

Below $-20°C$ the dimeric form crystallizes from the solution, exhibiting an orthorhombic and a monoclinic crystal form for the planar diphosphetane ring, with trans orientations of the aryl substituents. PC single bond lengths within the ring vary between 179.6 and 183.8 pm, therewith being close to the lowest values measured for endocyclic PC bonds of comparable phosphetanes (Fig. 18) [see also Refs. (*55b–57, 102, 122, 137, 141*)].

The decrease in bond lengths in $(\mathrm{Ar{-}P{=}C{=}O})_2$ may be due to the reduced covalent radius of the sp^2 ring carbon compared to the sp^3-hybridized C atom. The dimerization of the phosphaketenes extensively corresponds to analogous reactions of ketoketenes (*142, 142a*). The small difference of energies between HOMO and LUMO molecular orbitals in the case of the unsubstituted phosphaketene explains the



R	R′	R″
H	$OSiMe_3$	tBu
Ph	NMe_2	H
Me	$SSiMe_3$	$SSiMe_3$

R	R′	X
tBu	tBu	O
tBu	Ph	O

R	X
Ph	$NC_6H_5Cl_2$
Et	NPh
Bzl	NPh
Ph	CPh_2

FIG. 18. Endocyclic PC distances of some phosphetane structures.

facility of the reaction (Fig. 19). In addition, we find the outstanding orbital coefficients of the pertinent frontier orbitals localized at the phosphorus and the carbon atoms (*128, 129*).

Thus, similar to the carbaketenes (*143, 144*), one gets a head-to-tail combination and 1,3-diphosphetanones are formed. This is in agreement with the type of addition predicted for the polar electronic structures (Fig. 20), as well as orbital theory.

Reactivity of Phosphaketenes

A strong shielding of the P atom is indicated by ^{31}P NMR data on the butyl- (−180 ppm) and the tri-*t*-butylphenylphosphaketene (−207.4ppm). According to this the direction of addition of hydrochloric acid to the phosphaketenes is opposite to that of the phosphaalkenes (Scheme 19).

Due to mesomeric structures the central carbon atom is the electropositive center for a nucleophilic attack (Scheme 19a). There are two types of addition for the electrophilic component. Both possibilities can be realized, depending on the substrate YZ (Scheme 20).

These addition reactions show a close relationship to the chemistry of isocyanates, which also undergo the two types of addition. Proton-

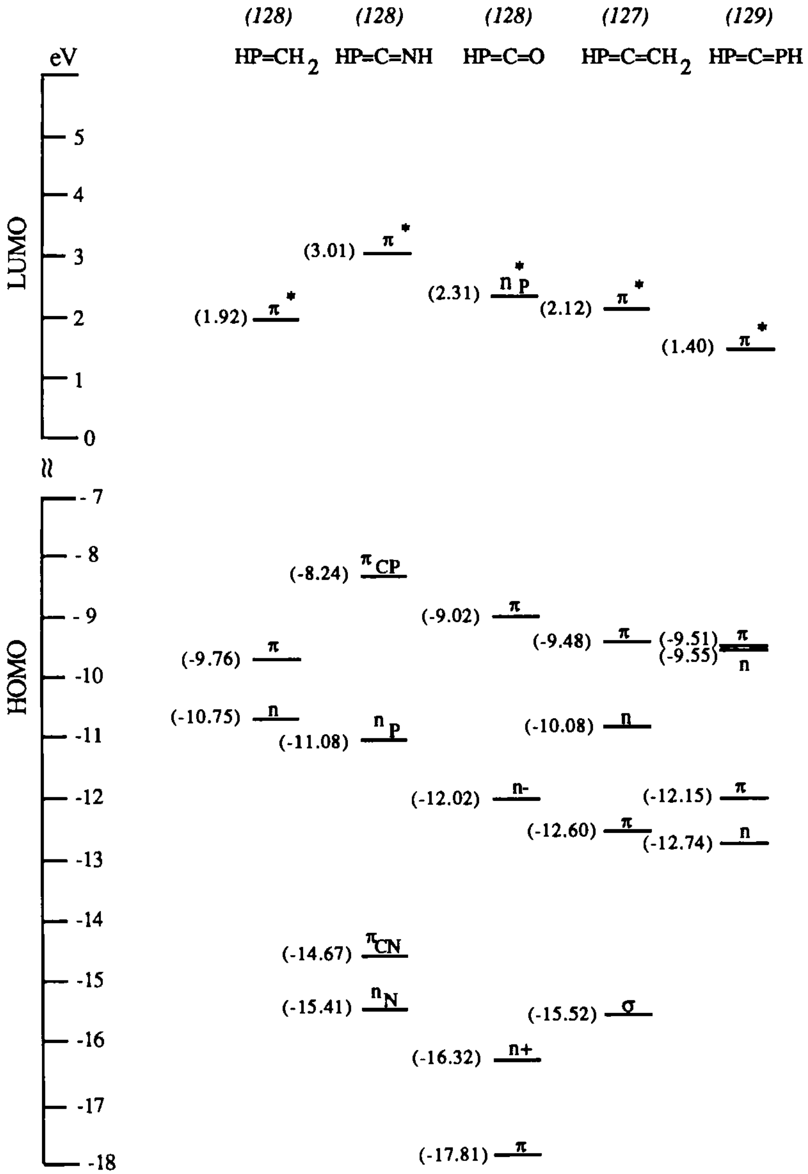


FIG. 19. Front orbitals of olefinic and cumulated phosphorus π systems.

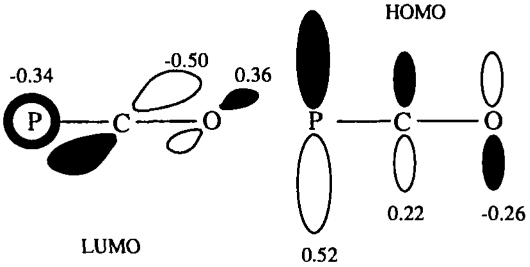
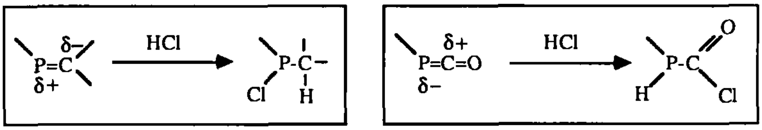
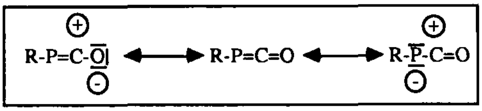


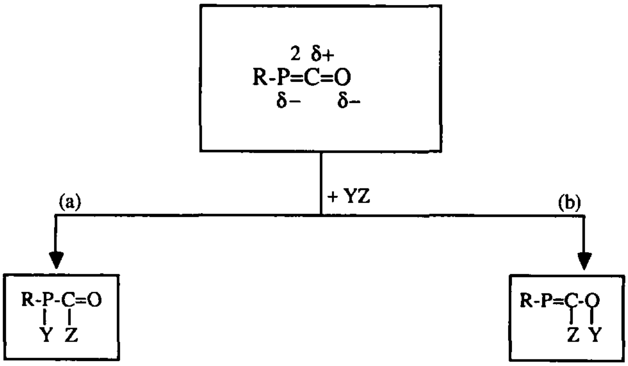
FIG. 20.



SCHEME 19.

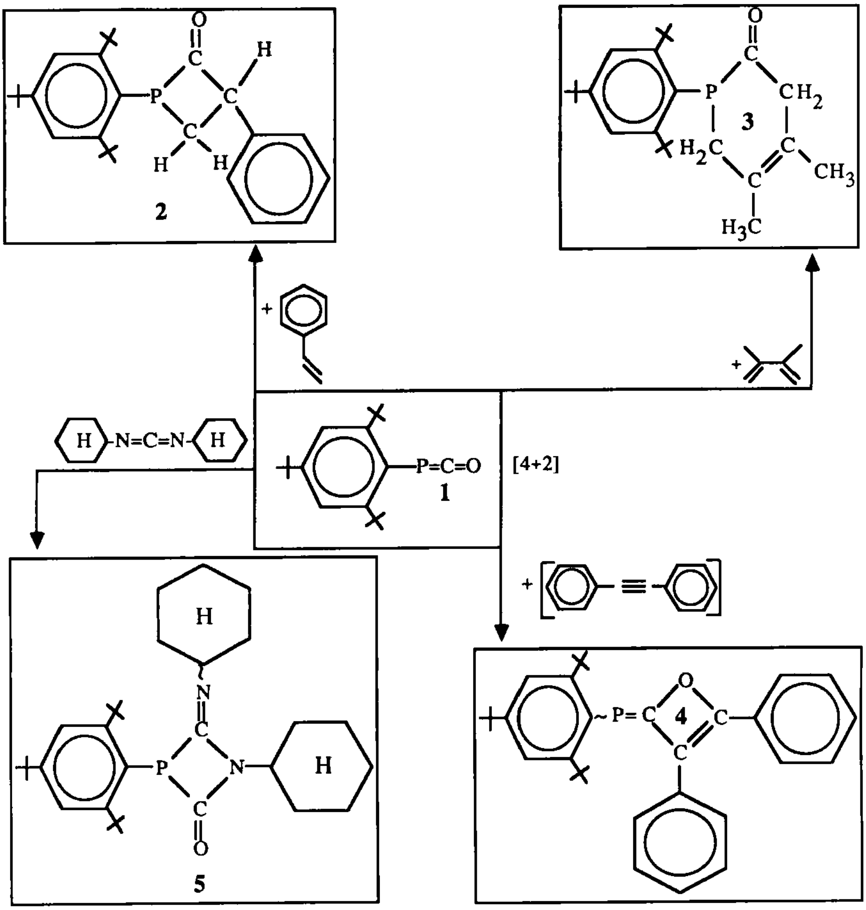


SCHEME 19a.



SCHEME 20.

active compounds such as acids, alcohols, or amines add to the PC double bond, with the proton always to the phosphorus, while the nucleophilic part moves to the carbon (a). The other type of addition to the CO double bond can be observed with silylphosphanes (b). Cyclo-



SCHEME 21.

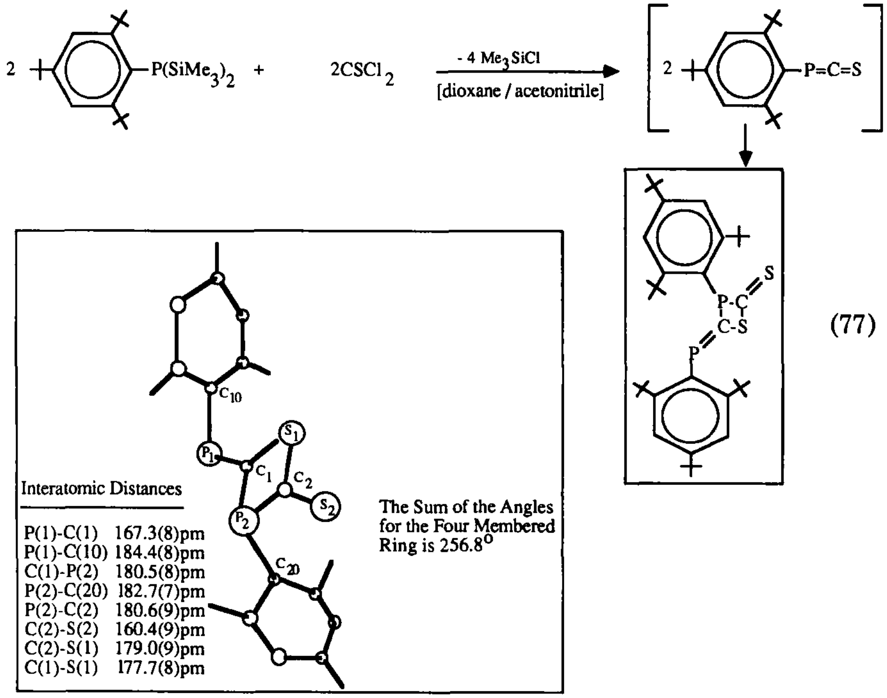
addition of the phosphaketene **1** (Scheme 21) proceeding via an addition to the PC double bond gives, with 2,3-dimethyl-1,3-butadiene, the Diels–Alder adduct **3**, and, with styrol, yields the phosphetanone **2**. Phosphaketene **1** reacts with tolan, adding to the carbonyl bond and ending up as the oxetene **4**, while, with carbodiimide, the azaphosphetidine **5** is obtained (*117*, p. 16 and 17).

E. PHOSPHATHIOKETENES

Attempts to produce phosphathioketenes analogous to the synthesis of phosphaketenes in a reaction of Ar—P$(SiMe_3)_2$ with thiophosgene did not turn out to be as simple. In addition, the yield proved to be very much dependent upon the solvent. The dark red 1-thia-3-phosphetane is formed in a polar solvent mixture such as dioxane/acetonitrile following an exothermic reaction [Eq. (77)] (*145*).

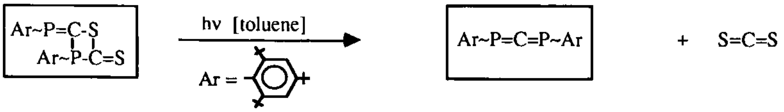
Its structure as determined by an X-ray investigation is shown in Fig 21. It may be understood as a dimer of the assumed phosphathioketene intermediate. The cycloaddition of the phosphathioketene corresponds to the behavior of unsubstituted carbaketenes (*146*) and so is different from that of the phosphaketenes described earlier, while thioketenes dimerize to 1,3-dithietanes (*147, 148*). An asymmetric retro ring cleavage can be initiated if 1-thia-3-phosphetane is irradiated by a mercury lamp generating carbon disulfide and the 1,3-diphosphaallene [Eq. (78)] (*117*, p. 33).

Irradiation of $(Ar—P{=}C{=}O)_2$ in the presence of the phosphane generates 1,3-diphosphapropene in addition to the 1,3-diphosphaallene [Eq. (79)]. A possible explanation for this is the assumption of an equi-

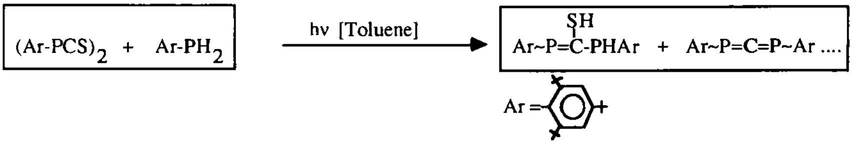


(77)

FIG. 21.



(78)

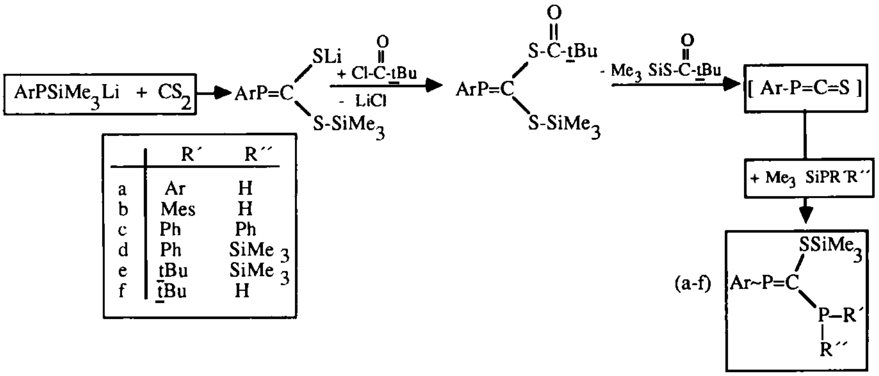


(79)

librium between the dimer phosphathioketene and its monomer, which adds to the phosphane, forming the 1,3-diphosphapropene.

Conversions in pentane proceed in an nonuniform manner at high temperatures. In addition to unidentified products exhibiting different ^{31}P NMR AX patterns, as well as the main product dichlorophosphane and another unknown substance, which exhibits a ^{31}P NMR shift of +301 ppm, one obtains a red compound, of which elemental analysis and the molecular mass point to the trimer phosphathioketene. The number of isomer compounds of this composition is limited by the ^{31}P NMR spectrum. The A_2X system, of which the X triplet is split into a double doublet if detected in solution in chloroform, indicates two acyclic PC double bonds and one phosphorus atom as a ring member (*117*). A possible explanation is given in Fig. 22. This could be in agreement with the addition of a monomer to the dimer, forming the six-membered ring compound with the proposed structure.

Another possibility to generate phosphathioketenes on a larger scale for intercept reactions starts with the lithium phosphide [Eq. (80)]. Lithium phosphide reacts with CS_2, which is inserted into the LiP bond



	R′	R″
a	Ar	H
b	Mes	H
c	Ph	Ph
d	Ph	SiMe 3
e	tBu	SiMe 3
f	tBu	H

(80)

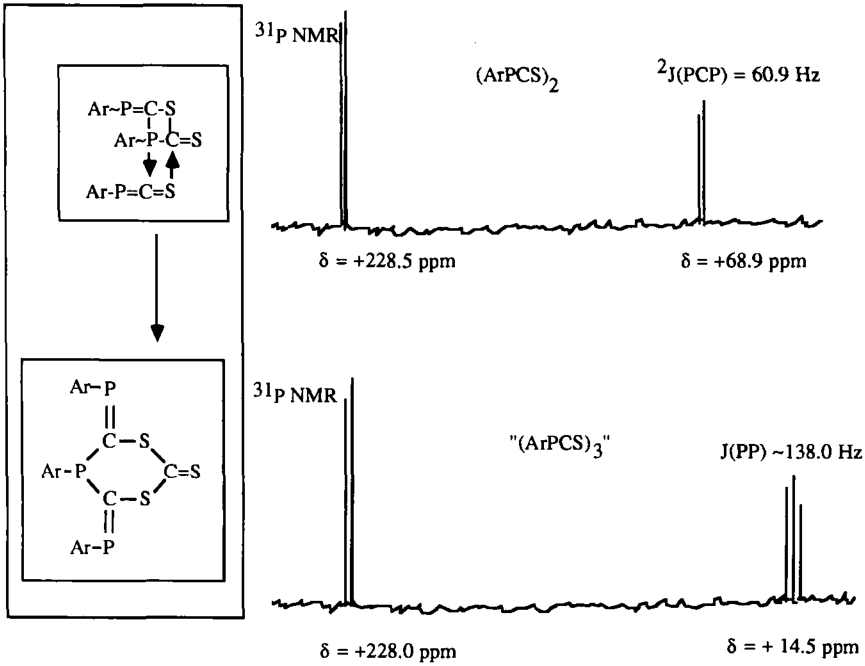
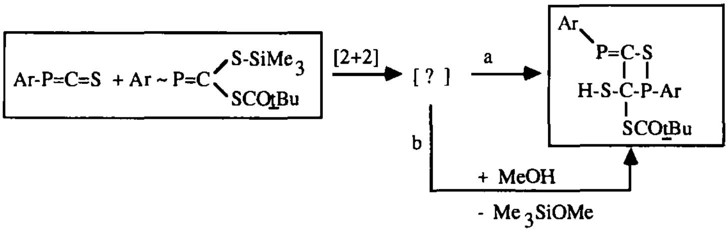


FIG. 22.

to form 2-lithium sulfido-2-(trimethylsilylmercapto)-1-phosphaethene, which can be acylated at the SLi bond by pivaloyl chloride, finally easily splitting off the thiopivalic acid O-trimethylsilyl ester and so ending up with the phosphathioketene. The intermediate existence of the very reactive phosphathioketene can be proved by the clearly characterized 1,3-diphosphapropenes formed in good yield after addition of phosphanes (*118*).

If a suitably reactive reagent for the interception is missing, a [2 + 2] cycloaddition of the phosphathioketene is observed, which takes place with the precursor and leads to the phosphathietane [Eq. (81)] (*118*, p. 30).



(81)

VII. Coordination Chemistry of Phosphaalkenes

Complexation of phosphorus-containing multiple-bond systems to transition metals has been investigated extensively in recent years. In this regard, bonding between the phosphaalkene and transition metal carbonyls can be achieved via the free electron pair of the phosphorus (η^1 coordination, type A) (*149–151*) as well as via the π system (η^2 coordination, type B) (*152–154*). The latter reaction type can be explained by two different electronic resonance structures. Type C is a combination of the two possibilities and can be occasionally observed (*155, 156*) (Fig. 23).

Complexes of type A with phosphane are determined by the σ-donor bond of the phosphorus atom. On the contrary, the $(d-d)\pi$ back donation of the phosphorus is poor, due to much lower π-acceptor ability, and the balance of electrons cannot take place within the phosphorus metal bond. With respect to ^{31}P NMR the phosphorus molecule is deshielded, exhibiting a low-field shift for the η^1-coordinated P atom of about 30–60 ppm compared to the uncoordinated phosphane phosphorus.

Phosphaalkene complexes of type A show shifts that differ less from the free phosphane phosphorus, but this time more to the higher field. Herein, the π system prevails, as can be seen from the ^{13}C NMR signal of the methylene carbon atom. The signals for it and the η^1-coordinated species are detected in the area of sp^2-hybridized C atoms.

The kind of bond with respect to type B may be interpreted analogous to the ethylene complexes as a dative π-alternating effect (Fig. 24). As opposed to type A complexes, the properties of type B complexes are determined in a characteristic way by the back donation into the unoccupied π^* molecular orbital (LUMO) of the double bond (Fig. 24). This strengthens the metal–ligand bond, as proved by a shorter interatomic distance, and weakens the double bond (occupying anti bonding molecular orbitals), as is evident by a widened PC distance. The phosphaalkene P atom has, so to speak, more of a phosphane

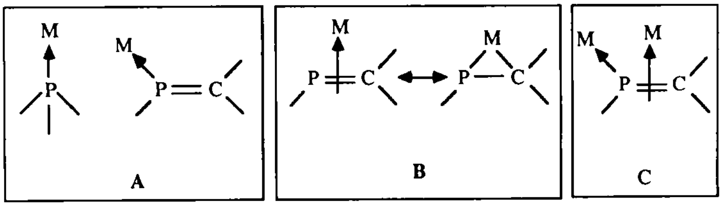


FIG. 23.

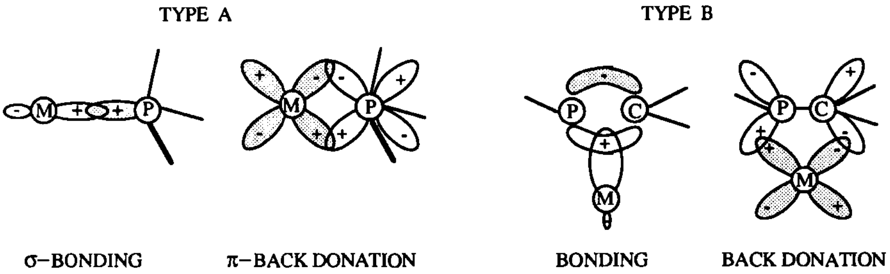


Fig. 24.

character, as indicated by the ^{31}P NMR high-field shift and by the corresponding ^{13}C NMR high-field shift of the methylene carbon atom. Due to these facts it follows that the type C of coordination should be compared with phosphane complexes. Because of the additional deshielding effect of the η^1-coordinated metal component the small low-field shift of about 30 ppm in the ^{31}P NMR spectrum compared to the free phosphane may be understood. Molecular orbital calculations (*38, 51*) for the basic phosphaalkene $HP{=}CH_2$ are in agreement with this. The highest occupied orbital is a π orbital but the difference to the lower σ orbital is only 0.8 eV. As determined by He(I) photoelectron spectra the distance becomes shorter and finally the orbitals nearly degenerate if the proton at the phosphorus is substituted by halogenes (*157*). This should leave the types of bonds in A and B in a nearly equal position with respect to energy. A preparative proof for this interesting *ab initio* calculation can be provided in the example of the platinum complex, which is η^1 in the crystalline state pure and η^2 in solution (*158, 159*) (see Diagram 5).

Out of the enormous number of coordination compounds exhibiting PC double bonds so far synthesized, some well-investigated examples are given in Fig. 25 [see also Refs. (*156, 160, 161*)]. An extended description of the various possibilities and the individual cases would be beyond the scope of this article. The interested reader should refer to the review which will be published by J. F. Nixon in *Chemical Review* (*161a*).

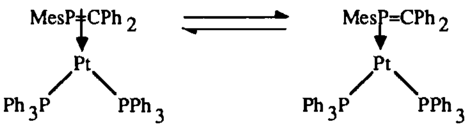
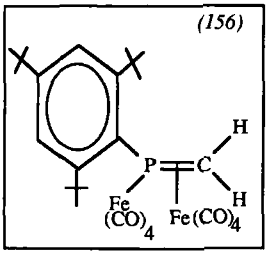
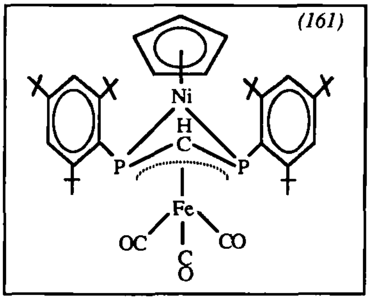


Diagram 5.


(156)


(161)

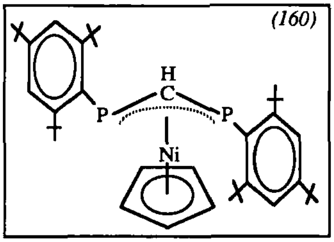

(160)

FIG. 25.

VIII. Concluding Remarks

During the introduction of this review, reference was made to the classical rule of the double bond. The theory, which in its original predictions supports the exceptional position for the elements boron, carbon, nitrogen, and oxygen, has lost its validity and needs modifications, as can be seen from the erratic increase in the numbers of compounds that contradict the rule that have been discovered within the last 12 years. These compounds are not found only as low-valent phosphorus–carbon species, but also increasingly as heteronuclear and even homonuclear molecules built up by heavier elements of the fourth to sixth main groups, such as Si, Ge, As, Sb, S, and Se.

Even though stabilization demands bulky substituents that are attached at least to one of the atoms of the double bond, the reactivity of the new and rarely seen compounds is only slightly reduced. This can be judged from the above-described behavior, such as the smooth and straightforward pericyclic reactions. Those substituents are *t*-butyl, trimethylsilyl, mesityl, adamantyl, or 2,4,6-tri-*t*-butylphenyl groups.

Thus, 7 years after we published the first survey concerning the chemistry of compounds with PC multiple bonds (*8*), the expectations, with respect to the low-valent PC compounds, of opening a new chapter of organophosphorus chemistry have been answered positively. This new area of chemistry has produced many surprises and challenges during the last 12 years and the field continues to be of great excitement and activity.

Whether the theoretically interesting results will lead to applications of the new phosphaalkenes as synthones for the class of heterocyclic compounds or, in coordination chemistry, to animate catalysis research, will be answered in the future.

IX. Compilation of Acyclic Phosphaalkenes

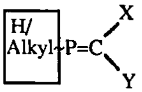
A. ABBREVIATIONS

Superscripts: *n*, normal; *i*, iso; *s*, secondary; *t*, tertiary.

Groups: Me, methyl; Et, ethyl; Pr, propyl; Bu, butyl; Ac, acetyl; Cp, cyclopentadienyl; Ph, phenyl; Bzl, benzyl; Mes, mesityl; Ar = T*t*bPh, tri-*tertiary*-butylphenyl; Ad, adamantyl; Tms, trimethylsilyl.

B. TABLES I–XI

TABLE I



H/Alkyl—P=CXY	X	Y	Reference
H	H	H	*12*
H	Me	NMe_2	*162*
H	*t*Bu	OTms	*26, 60*
H	NMe_2	NMe_2	*92, 162, 163*
H	NMe_2	NEt_2	*163*
H	NEt_2	NEt_2	*163*
H	F	F	*12, 13*
Me	H	H	*164*
Me	H	NMe_2	*55a*
Me	*t*Bu	OTms	*7, 89*
Me	Ph	OTms	*165*
Me	NPh(Tms)	NPh(Tms)	*32*
Me	OTms	OTms	*35*

(*continued*)

TABLE I (*Continued*)

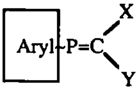
H/Alkyl—P=CXY	X	Y	Reference
Me	OTms	PMe(Tms)	*166*
Me	STms	STms	*57*
Et	Ph	Tms	*86*
Bu	Ph	Tms	*86*
*t*Bu	H	*t*Bu	*167*
*t*Bu	H	NMe_2	*55a*
*t*Bu	H	Tms	*168*
*t*Bu	Me	OTms	*169*
*t*Bu	*i*Pr	OTms	*169*
*t*Bu	*t*Bu	OTms	*7, 89*
*t*Bu	$CHPh_2$	OTms	*169*
*t*Bu	CHPh(COOMe)	OTms	*170*
*t*Bu	Ph	COOMe	*171*
*t*Bu	Ph	Tms	*172, 173*
*t*Bu	Ph	OTms	*165*
*t*Bu	CF_3	OTms	*169*
*t*Bu	NMe_2	NMe_2	*162*
*t*Bu	NMe_2	STms	*165*
*t*Bu	NPh(Tms)	NPh(Tms)	*32*
*t*Bu	NPh(Tms)	STms	*165*
*t*Bu	OTms	OTms	*35*
*t*Bu	OTms	PH(*t*Bu)	*166*
*t*Bu	OTms	PMe(*t*Bu)	*166*
*t*Bu	OTms	PBu(*t*Bu)	*166*
*t*Bu	OTms	P(C(O)Me)*t*Bu	*166*
*t*Bu	OTms	P(C(O)Ph)*t*Bu	*166*
*t*Bu	OTms	P(C(O)Cl)*t*Bu	*166*
*t*Bu	OTms	P(Tms)*t*Bu	*166*
*t*Bu	OTms	PCl*t*Bu	*166*
*t*Bu	Tms	Tms	*19, 173*
*t*Bu	S(*i*Bu)	S(*i*Bu)	*174, 175*
*t*Bu	STms	STms	*176*
C_6H_{11}	*t*Bu	OTms	*7*
C_6H_{11}	Ph	Tms	*86*
C_6H_{11}	NPh(Tms)	NPh(Tms)	*32*
Fluorenyl	Tms	Tms	*177*
Me_5C_5	Tms	Tms	*78, 178*
Ph—C÷C	Ph	Tms	*86*
Ph—C÷C	Tms	Tms	*52, 58*
Tms—C÷C	Ph	Tms	*52, 58*
Tms—C÷C	Tms	Tms	*52, 58*
Me(O)C	Me	OH	*179, 180*
Me(O)C	Me	OTms	*179*
*t*Bu(O)C	*t*Bu	OH	*180, 181*
*t*Bu(O)C	*t*Bu	OTms	*180, 181*

(*continued*)

TABLE I (*Continued*)

H/Alkyl—P=CXY	X	Y	Reference
T*t*bPh(O)C	T*t*bPh	OH	*90*
TmsPhN(O)C	NMe_2	NMe_2	*87*
F_3C	NMe_2	NMe_2	*182*
F_3C	NMe_2	F	*182*
F_3C	NEt_2	F	*182*
F_3C	OMe	F	*182*
F_3C	F	F	*182–186*
F_3C	F	PMe_2	*182*
CF_3F_2C	CF_3	F	*187*
$TmsH_2C$	*t*Bu	OTms	*188*
TmsMeHC	*t*Bu	OTms	*188*
Tms(COO*t*Bu)HC	*t*Bu	OTms	*188*
$(Tms)_2HC$	Tms	Tms	*189, 190*
$(Tms)_2HC$	Tms	$SiMe_2CH_2P[C(Tms)_2]_2$	*191*
$(Tms)_3C$	Tms	Tms	*190*
$(Ph_2P)(Tms)_2C$	Tms	Tms	*192*
$(Tms)_2PPh_2C$	Tms	Tms	*192*
$(Tms)_2P(PhC{\equiv}C)_2C$	Tms	Tms	*192*
$(Tms)_2P(Me_3SiC{\equiv}C)_2C$	Tms	Tms	*192*
$(Tms)_2ClC$	Tms	Tms	*48*

TABLE II



Aryl—P=CXY	X	Y	Reference
Ph	H	NMe_2	*55a*
Ph	Me	NMe_2	*193, 194*
Ph	*t*Bu	NPhC(O)Me	*27*
Ph	*t*Bu	NPhC(O)Ph	*27*
Ph	*t*Bu	NPhTms	*27*
Ph	*t*Bu	OTms	*7*
Ph	Ph	Ph	*55a*
Ph	Ph	NPhC(O)Me	*27*
Ph	Ph	NMeTms	*27*
Ph	Ph	$NC_6H_{11}Tms$	*27*
Ph	Ph	NPhTms	*27*
Ph	Ph	$N(2,6\text{-}Et_2C_6H_3)Tms$	*27*
Ph	Ph	$N(4\text{-}MeOC_6H_4)Tms$	*27*

(*continued*)

TABLE II (*Continued*)

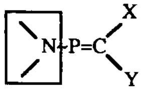
Aryl—P=CXY	X	Y	Reference
Ph	Ph	N(4-EtC$_6$H$_4$)Tms	*27*
Ph	Ph	OTms	*165*
Ph	Ph	Tms	*86*
Ph	Mes	NPhTms	*27*
Ph	4-MeOC$_6$H$_4$	NPhTms	*27*
Ph	4-ClC$_6$H$_4$	NPhTms	*27*
Ph	NMe$_2$	NMe$_2$	*195*
Ph	NPhTms	NPhTms	*32, 31*
Ph	NPhTms	N(2-FC$_6$H$_4$)Tms	*31*
Ph	NPhTms	N(2-ClC$_6$H$_4$)Tms	*31*
Ph	NPhTms	N(3-ClC$_6$H$_4$)Tms	*31*
Ph	NPhTms	N(4-ClC$_6$H$_4$)Tms	*31*
Ph	NPhTms	N(2,3-Cl$_2$C$_6$H$_3$)Tms	*31*
Ph	NPhTms	OTms	*165*
Ph	NPhTms	PPhTms	*100*
Ph	N(2-MeC$_6$H$_4$)Tms	PPhTms	*166*
Ph	N(4-MeC$_6$H$_4$)Tms	PPhTms	*166*
Ph	N(2-CF$_3$C$_6$H$_4$)Tms	PPhTms	*166*
Ph	N(4-CF$_3$C$_6$H$_4$)Tms	PPhTms	*196*
Ph	N(2-MeOC$_6$H$_4$)Tms	PPhTms	*166*
Ph	N(2-FC$_6$H$_4$)Tms	PPhTms	*166*
Ph	N(4-FC$_6$H$_4$)Tms	PPhTms	*166*
Ph	N(2-ClC$_6$H$_4$)Tms	PPhTms	*166*
Ph	N(3-ClC$_6$H$_4$)Tms	PPhTms	*166*
Ph	N(4-ClC$_6$H$_4$)Tms	PPhTms	*166*
Ph	N(2,3-Cl$_2$C$_6$H$_3$)Tms	PPhTms	*166*
Ph	N(4-BrC$_6$H$_4$)Tms	PPhTms	*166*
Ph	NC(O)PhTms	PPhTms	*197*
Ph	N(COOEt)Tms	PPhTms	*166*
Ph	OTms	OTms	*35*
Ph	OTms	PPhTms	*29*
Ph	Tms	Tms	*18, 19, 173*
Ph	STms	STms	*176*
4-MeC$_6$H$_4$	Ph	Tms	*86*
4-*t*BuC$_6$H$_4$	Ph	Tms	*77*
2,6-Me$_2$C$_6$H$_3$	Ph	Ph	*198*
Mes	H	NMe$_2$	*55a*
Mes	*t*Bu	OTms	*165*
Mes	Ph	Ph	*55a, 173, 198–200*
Mes	Ph	2-MeC$_6$H$_4$	*201*
Mes	Ph	4-MeC$_6$H$_4$	*201*
Mes	Ph	4-CNC$_6$H$_4$	*201*
Mes	Ph	4-NMe$_2$C$_6$H$_4$	*201*
Mes	Ph	4-OMeC$_6$H$_4$	*201*
Mes	Ph	4-FC$_6$H$_4$	*201*
Mes	Ph	4-BrC$_6$H$_4$	*201*
Mes	2-MeC$_6$H$_4$	2-MeC$_6$H$_4$	*201*
Mes	4-MeC$_6$H$_4$	4-MeC$_6$H$_4$	*201*

(*continued*)

TABLE II (*Continued*)

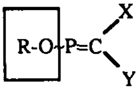
Aryl—P=CXY	X	Y	Reference
Mes	4-MeC$_6$H$_4$	4-CNC$_6$H$_4$	*201*
Mes	4-CNC$_6$H$_4$	4-CNC$_6$H$_4$	*201*
Mes	4-NMe$_2$C$_6$H$_4$	4-NMe$_2$C$_6$H$_4$	*201*
Mes	4-OMeC$_6$H$_4$	4-OMeC$_6$H$_4$	*201*
Mes	4-OMeC$_6$H$_4$	4-BrC$_6$H$_4$	*201*
Mes	4-BrC$_6$H$_4$	4-BrC$_6$H$_4$	*201*
Mes	Ph	OTms	*165*
Mes	NMe$_2$	NMe$_2$	*195*
Mes	NPhTms	STms	*165*
Mes	Tms	Tms	*173, 202, 203*
Mes	STms	STms	*176*
T*t*bPh	H	H	*36, 156, 204*
T*t*bPh	H	Ph	*23b, 39, 40a, 205*
T*t*bPh	H	NMe$_2$	*194, 206*
T*t*bPh	H	Tms	*204, 207*
T*t*bPh	H	P(H)T*t*bPh	*115b*
T*t*bPh	H	P(*t*Bu)T*t*bPh	*115b*
T*t*bPh	H	P(T*t*bPh)$_2$	*115b*
T*t*bPh	H	P(T*t*bPh)O*t*Bu	*115b*
T*t*bPh	H	P(T*t*bPh)Cl	*112, 115b, 208*
T*t*bPh	H	P(T*t*bPh)Br	*115b*
T*t*bPh	H	P(T*t*bPh)I	*115b*
T*t*bPh	H	Cl	*36*
T*t*bPh	H	Br	*36, 39, 46*
T*t*bPh	Me	NMe$_2$	*194, 206*
T*t*bPh	Me	Cl	*209*
T*t*bPh	Me	Br	*209*
T*t*bPh	Ph	OSiMe$_2$*t*Bu	*210, 211*
T*t*bPh	Ph	Tms	*39, 42, 46, 86*
T*t*bPh	C(O)P(H)T*t*bPh	OC(O)*t*Bu	*93*
T*t*bPh	N(H)COOMe	Cl	*212*
T*t*bPh	NCO	Cl	*212*
T*t*bPh	OTms	P(H)T*t*bPh	*116*
T*t*bPh	OTms	P(Tms)$_2$	*88, 95*
T*t*bPh	OSiMe$_2$*t*Bu	P(H)T*t*bPh	*114*
T*t*bPh	Tms	Tms	*39, 46, 190, 213*
T*t*bPh	Tms	Br	*46, 209*
T*t*bPh	P(H)T*t*bPh	SH	*34*
T*t*bPh	STms	STms	*34*
T*t*bPh	Cl	Cl	*209*
T*t*bPh	Cl	SnMe$_3$	*209*
T*t*bPh	Br	Br	*209*
T*t*bPh	Br	SnMe$_3$	*209*
4-Me$_2$NC$_6$H$_4$	NPhTms	NPhTms	*32*
2-Tms$_2$PC$_6$H$_4$	NPhTms	NPhTms	*214, 215*
2-Pyridyl	H	NMe$_2$	*216*
2-Pyridyl	1-Ad	OH	*216*
2-(6-Tms)pyridyl	H	NMe$_2$	*216*
2-(6-Tms)pyridyl	Me	OH	*216*
2-(6-Tms)pyridyl	1-Ad	OH	*216*

TABLE III



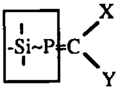
RR′N—P=CXY	X	Y	Reference
*t*Bu(H)N	Ph	Tms	*86*
*t*Bu(H)N	SMe	SMe	*175*
*t*Bu(H)N	S(*i*Bu)	S(*i*Bu)	*175*
Me$_2$N	Ph	Tms	*172*
*i*Pr$_2$N	H	Tms	*207*
*i*Pr$_2$N	Ph	Tms	*172*
*i*Pr$_2$N	N(*i*Pr)$_2$	P[N(*i*Pr)$_2$]$_2$	*217*
*i*Pr$_2$N	SMe	SMe	*175*
*i*Bu$_2$N	Ph	Tms	*86*
PhMeN	Ph	Tms	*172*
Pip	Ph	Tms	*172*
Tmp	Tms	Tms	*218*
[PhC(O)]PhN	Ph	Tms	*86*
[*s*Bu(H)N]*s*BuN	Ph	Tms	*75*
[C$_6$H$_{11}$(H)N]C$_6$H$_{11}$N	Ph	Tms	*75*
[Ph(H)N]PhN	Ph	Tms	*75*
Tms(*t*Bu)N	H	Tms	*207*
Tms(*t*Bu)N	Tms	Tms	*218–220*
Tms(*t*Bu)N	SMe	SMe	*221*
Tms(*t*Bu)N	Cl	Cl	*222*
Tms(1-Ad)N	Tms	Tms	*219, 220*
Tms(Mes)N	Tms	Tms	*220*
Tms(T*t*bPh)N	Tms	Tms	*223*
(Tms)$_2$N	H	*t*Bu	*167, 224*
(Tms)$_2$N	H	Ph	*168*
(Tms)$_2$N	H	COOMe	*168*
(Tms)$_2$N	H	Tms	*168*
(Tms)$_2$N	H	P(*t*Bu)$_2$	*168, 225*
(Tms)$_2$N	H	P[N(Tms)$_2$]$_2$	*168, 225*
(Tms)$_2$N	H	Cl E/Z	*222*
(Tms)$_2$N	H	Br E/Z	*222*
(Tms)$_2$N	Me	*t*Bu	*224*
(Tms)$_2$N	NMe$_2$	NMe$_2$	*226*
(Tms)$_2$N	Tms	Tms	*218*
(Tms)$_2$N	SMe	SMe	*175*
(Tms)$_2$N	S(*i*Bu)	S(*i*Bu)	*175*
(Tms)$_2$N	Cl	Cl	*222*
(Tms)$_2$N	Br	Br	*222*

TABLE IV



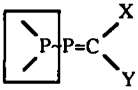
R—O—P=CXY	X	Y	Reference
MeO	Ph	Tms	*172*
*t*BuO	Ph	Tms	*172*
PhO	Ph	Tms	*172*
4-*t*BuC$_6$H$_4$O	Ph	Tms	*86*

TABLE V



RR′R″Si—P=CXY	X	Y	Reference
Tms	CH$_2$*t*Bu	OTms	*227*
Tms	*i*Pr	OTms	*227*
Tms	*t*Bu	OTms	*89, 188, 228, 229*
Tms	1-MeC$_6$H$_{10}$	OTms	*227*
Tms	1-Ad	OTms	*67*
Tms	Ph	Ph	*55a*
Tms	T*t*bPh	OTms	*90*
Tms	NMe$_2$	NMe$_2$	*163, 226*
Tms	NMe$_2$	NEt$_2$	*230*
Tms	NEt$_2$	NEt$_2$	*87, 163*
Tms	STms	STms	*231*
PhMe$_2$Si	NMe$_2$	NEt$_2$	*232*
Ph$_3$Si	NMe$_2$	NMe$_2$	*232*

TABLE VI



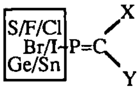
RR′P—P=CXY	X	Y	Reference
T*t*bPh(H)P	Tms	Tms	*233*
(C$_6$H$_{11}$)$_2$P	Ph	Tms	*86*
*t*Bu$_2$P	Ph	Tms	*86, 172*
*t*Bu$_2$P	NMe$_2$	NMe$_2$	*234*
*t*Bu$_2$P	NMe$_2$	NEt$_2$	*234*

(*continued*)

TABLE VI (*Continued*)

RR′P—P=CXY	X	Y	Reference
*t*Bu$_2$P	NEt$_2$	NEt$_2$	*234*
*t*Bu$_2$P	Tms	Tms	*235*
*t*Bu$_2$P	SMe	SMe	*175*
*t*Bu$_2$P	S(*i*Bu)	S(*t*Bu)	*235*
Ph$_2$P	Ph	Tms	*172, 236*
Ph$_2$P	Tms	Tms	*236*
(Tms)C$_6$H$_{11}$P	Ph	Tms	*86*
(Tms)*t*BuP	Ph	Tms	*86*
(Tms)*t*BuP	Tms	Tms	*223*
(Tms)PhP	Ph	Tms	*86*
(Tms)$_2$P	Ph	Tms	*86*
(Tms)$_2$P	STms	STms	*231*
*t*Bu$_2$(S)P	NMe$_2$	NMe$_2$	*234*

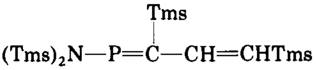
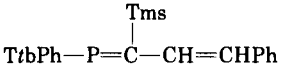
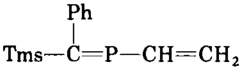
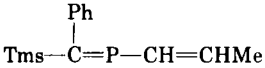
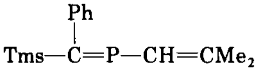
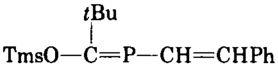
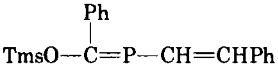
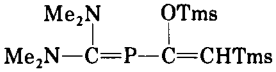
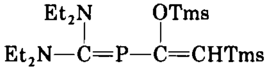
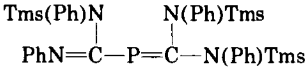
TABLE VII



S/F/Cl/Br/I/ Ge/Sn—P=CXY	X	Y	Reference
BuS	Ph	Tms	*172*
F	Tms	Tms	*237*
Cl	H	H	*12*
Cl	H	Ph	*16*
Cl	H	Tms	*18*
Cl	*t*Bu	OTms	*89*
Cl	Ph	Cl	*15*
Cl	Ph	Tms	*15*
Cl	COOEt	Tms	*238*
Cl	Tms	Tms	*205*
Cl	SMe	SMe	*17*
Cl	S(*i*Bu)	S(*i*Bu)	*175*
Br	Ph	Tms	*175*
Br	Tms	Tms	*18*
I	Ph	Tms	*18, 237*
I	Tms	Tms	*235, 237*
Ph$_3$Ge	NEt$_2$	NEt$_2$	*232*
Ph$_2$Sn	NEt$_2$	NEt$_2$	*232*

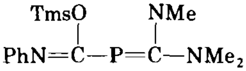
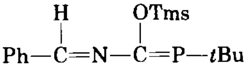
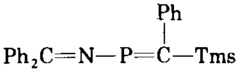
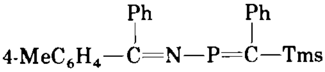
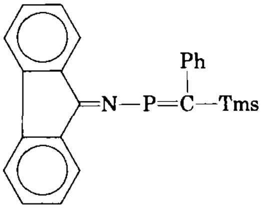
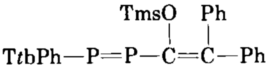
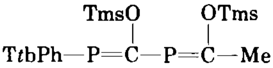
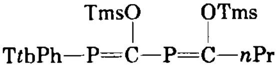
TABLE VIII

BUTADIENES

Structure	Reference
$\boxed{\sim P{=}C}C{=}C$	
 $(Tms)_2N{-}P{=}\overset{Tms}{C}{-}CH{=}CHTms$	*202*
 $TtbPh{-}P{=}\overset{Tms}{C}{-}CH{=}CHPh$	*62*
$\boxed{\sim C{=}P}C{=}C$	
 $Tms{-}\overset{Ph}{C}{=}P{-}CH{=}CH_2$	*86*
 $Tms{-}\overset{Ph}{C}{=}P{-}CH{=}CHMe$	*86*
 $Tms{-}\overset{Ph}{C}{=}P{-}CH{=}CMe_2$	*86*
 $TmsO{-}\overset{tBu}{C}{=}P{-}CH{=}CHPh$	*62*
 $TmsO{-}\overset{Ph}{C}{=}P{-}CH{=}CHPh$	*62*
 $Me_2N{-}\overset{Me_2N}{C}{=}P{-}\overset{OTms}{C}{=}CHTms$	*87*
 $Et_2N{-}\overset{Et_2N}{C}{=}P{-}\overset{OTms}{C}{=}CHTms$	*87*
$N{=}C\boxed{P{=}C}$	
 $PhN{=}\overset{Tms(Ph)N}{C}{-}P{=}\overset{N(Ph)Tms}{C}{-}N(Ph)Tms$	*239*

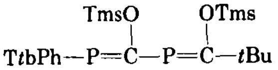
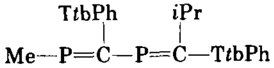
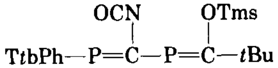
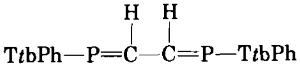
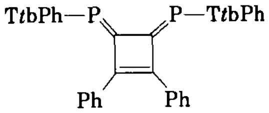
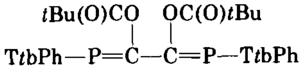
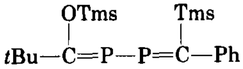
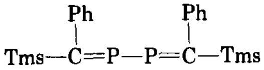
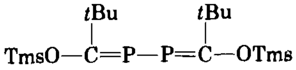
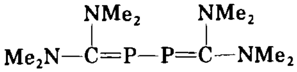
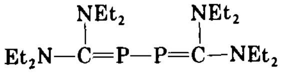
(*continued*)

TABLE VIII (*Continued*)

Structure	Reference
 $\mathrm{PhN{=}\overset{TmsO}{C}{-}P{=}\overset{NMe}{C}{-}NMe_2}$	*87*
$\mathrm{C{=}N}\,\boxed{\mathrm{C{=}P}\sim}$	
 $\mathrm{Ph{-}\overset{H}{C}{=}N{-}\overset{OTms}{C}{=}P{-}\mathit{t}Bu}$	*240*
$\mathrm{C{=}N}\,\boxed{\mathrm{P{=}C}}$	
 $\mathrm{Ph_2C{=}N{-}P{=}\overset{Ph}{C}{-}Tms}$	*69*
 $\mathrm{4\text{-}MeC_6H_4{-}\overset{Ph}{C}{=}N{-}P{=}\overset{Ph}{C}{-}Tms}$	*69*
	*69*
$\boxed{\sim\mathrm{P{=}P}}\,\mathrm{C{=}C}$	
 $\mathrm{T\mathit{t}bPh{-}P{=}P{-}\overset{TmsO}{C}{=}\overset{Ph}{C}{-}Ph}$	*241*
$\boxed{\sim\mathrm{P{=}C}}\,\mathrm{P{=}C}$	
 $\mathrm{T\mathit{t}bPh{-}P{=}\overset{TmsO}{C}{-}P{=}\overset{OTms}{C}{-}Me}$	*88*
 $\mathrm{T\mathit{t}bPh{-}P{=}\overset{TmsO}{C}{-}P{=}\overset{OTms}{C}{-}\mathit{n}Pr}$	*88*

(*continued*)

TABLE VIII (*Continued*)

Structure	Reference
 $\text{T}t\text{bPh—P=}\overset{\text{TmsO}}{\text{C}}\text{—P=}\overset{\text{OTms}}{\text{C}}\text{—}t\text{Bu}$	*88*
 $\text{Me—P=}\overset{\text{T}t\text{bPh}}{\text{C}}\text{—P=}\overset{i\text{Pr}}{\text{C}}\text{—T}t\text{bPh}$	*242*
 $\text{T}t\text{bPh—P=}\overset{\text{OCN}}{\text{C}}\text{—P=}\overset{\text{OTms}}{\text{C}}\text{—}t\text{Bu}$	*212*
~P=C C=P~	
 $\text{T}t\text{bPh—P=}\overset{\text{H}}{\text{C}}\text{—}\overset{\text{H}}{\text{C}}\text{=P—T}t\text{bPh}$	*93*
	*109*
 $\text{T}t\text{bPh—P=}\overset{t\text{Bu(O)CO}}{\text{C}}\text{—}\overset{\text{OC(O)}t\text{Bu}}{\text{C}}\text{=P—T}t\text{bPh}$	*93*
C=P-P=C	
 $t\text{Bu—}\overset{\text{OTms}}{\text{C}}\text{=P—P=}\overset{\text{Tms}}{\text{C}}\text{—Ph}$	*86*
 $\text{Tms—}\overset{\text{Ph}}{\text{C}}\text{=P—P=}\overset{\text{Ph}}{\text{C}}\text{—Tms}$	*86*
 $\text{TmsO—}\overset{t\text{Bu}}{\text{C}}\text{=P—P=}\overset{t\text{Bu}}{\text{C}}\text{—OTms}$	*89*
 $\text{Me}_2\text{N—}\overset{\text{NMe}_2}{\text{C}}\text{=P—P=}\overset{\text{NMe}_2}{\text{C}}\text{—NMe}_2$	*92*
 $\text{Et}_2\text{N—}\overset{\text{NEt}_2}{\text{C}}\text{=P—P=}\overset{\text{NEt}_2}{\text{C}}\text{—NEt}_2$	*92*

(*continued*)

TABLE VIII (*Continued*)

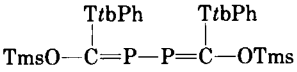
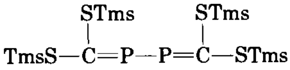
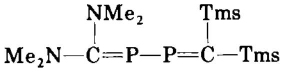
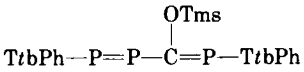
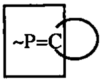
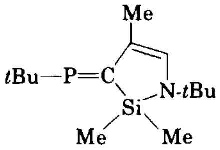
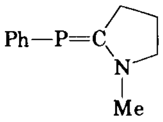
Structure	Reference
 $\text{TmsO—}\overset{\text{T}t\text{bPh}}{\text{C}}\text{=P—P=}\overset{\text{T}t\text{bPh}}{\text{C}}\text{—OTms}$	*90*
 $\text{TmsS—}\overset{\text{STms}}{\text{C}}\text{=P—P=}\overset{\text{STms}}{\text{C}}\text{—STms}$	*231*
 $\text{Me}_2\text{N—}\overset{\text{NMe}_2}{\text{C}}\text{=P—P=}\overset{\text{Tms}}{\text{C}}\text{—Tms}$	*243*
~P=P$\boxed{\text{C=P}\sim}$	
 $\text{T}t\text{bPh—P=P—}\overset{\text{OTms}}{\text{C}}\text{=P—T}t\text{bPh}$	*95*

TABLE IX

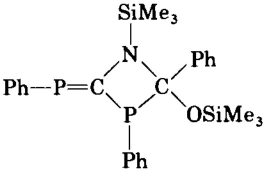
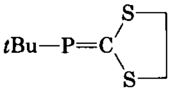
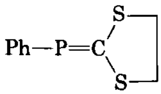
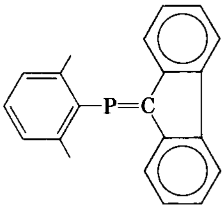
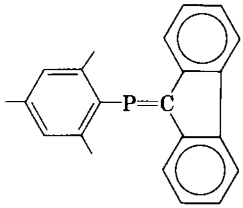
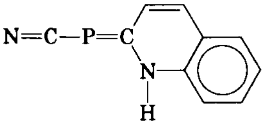
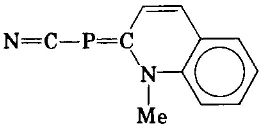
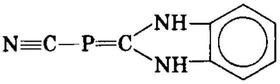
METHYLENE CARBON WITHIN A RING SYSTEM



Structure	Reference
	*244*
	*245*

(*continued*)

TABLE IX (*Continued*)

Structure	Reference
	*197*
	*214*
	*214*
	*199, 246*
	*246*
	*247*
	*248*
	*247*

(*continued*)

TABLE IX (*Continued*)

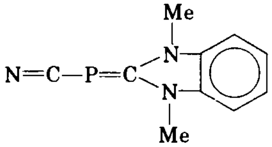
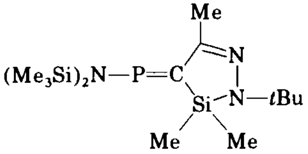
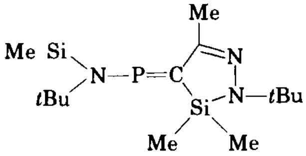
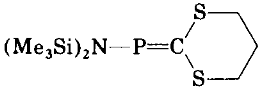
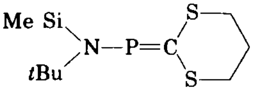
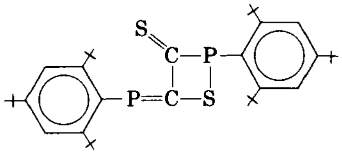
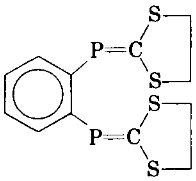
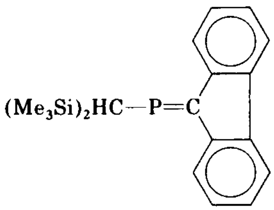
Structure	Reference
	*248*
	*249*
	*249*
	*250*
	*250*
	*145*
	*214*
	*251*

TABLE X

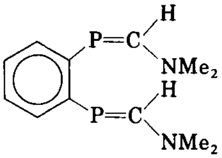
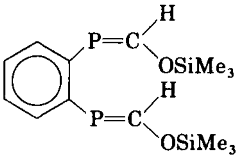
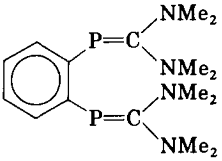
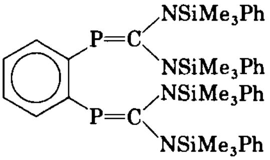
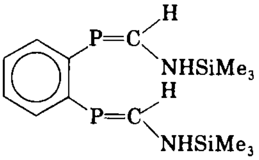
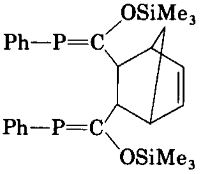
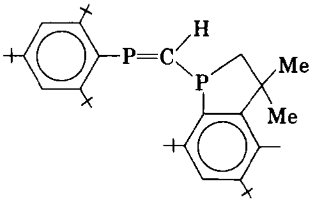
Structure	Reference
	*214*
	*214*
	*252*
	*214*
	*214*
	*253*
	*115b*

TABLE XI

CUMULENES

$$\boxed{E{=}C{=}P{\sim}X}$$

E	X	Reference
PhHC	T*t*bPh	*122*
EtO(O)HC	T*t*bPh	*122*
Ph_2C	T*t*bPh	*116, 121, 122*
$Me_3SiMeCC$	T*t*bPh	*130*
Ph_2CC	T*t*bPh	*130*
$(Me_3Si)_2CC$	T*t*bPh	*130*
*i*PrN	Me	*132*
*t*BuN	Me	*132*
PhN	Me	*132*
PhN	Et	*60, 135*
PhN	CH_2Ph	*135*
*i*PrN	*i*Pr	*132*
*t*BuN	*i*Pr	*132*
PhN	*i*Pr	*132*
*i*PrN	*t*Bu	*132*
*t*BuN	*t*Bu	*131a–132*
PhN	*t*Bu	*132, 254*
*i*PrN	Ph	*132*
*t*BuN	Ph	*132, 254*
PhN	Ph	*132, 135*
*i*PrN	Mes	*132*
*t*BuN	Mes	*132, 254*
PhN	Mes	*132, 135*
PhN	T*t*bPh	*121*
O	*t*Bu	*138*
O	T*t*bPh	*88, 105, 116, 122, 139*
PhTms(TmsO)P(λ^5)	Ph	*166*
T*t*bPhP	T*t*bPh	*114, 115a–116*
S	T*t*bPh	*34*

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