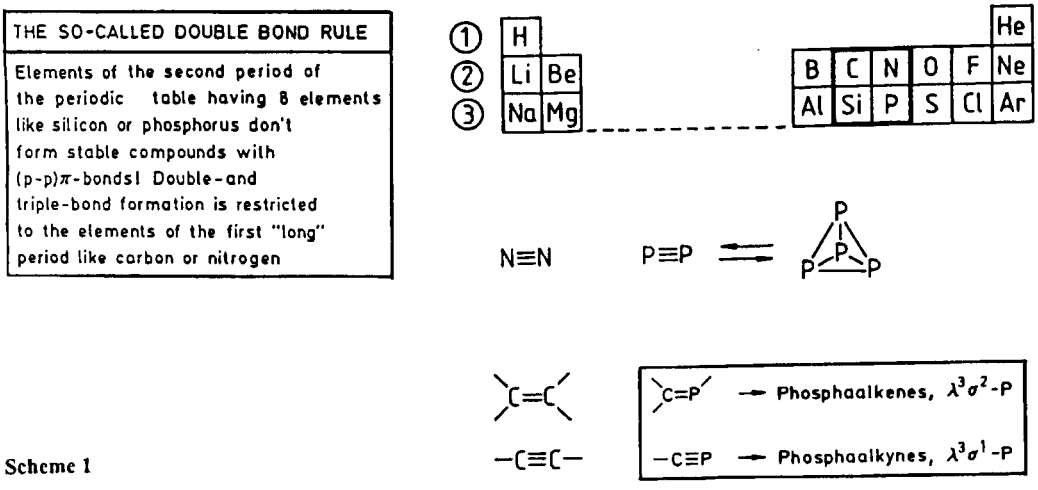
Organophosphorus Compounds. 75 [1]. Phosphaalkynes - New Building Blocks in Heterocyclic Chemistry

Manfred Regitz

Fachbereich Chemie der Universität Kaiserslautern, Erwin-Schrödinger-Strasse, D-67663 Kaiserslautern, Federal Republic of Germany

J. Heterocyclic Chem., **31**, 663 (1994).

Rules are useful: they provide a system of order and frequently facilitate surveys of the various fields of chemistry. However, they are sometimes also a barrier to further advances - as was the case, for instance, in the chemistry of compounds containing low coordinate phosphorus atoms where the so-called "double bond rule" (Scheme 1) provides a striking example. This rule, among others, prohibited the formation of C/Si and C/P multiple bonds [2] as well as those of elements of the second, eight-element period of the periodic table.



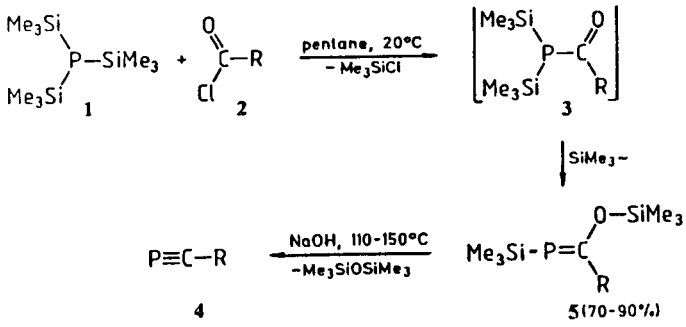
Scheme 1

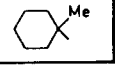
Accordingly, N_2 is a stable molecule while P_2 can only be detected in equilibrium with P_4 at higher temperatures. Further examples can also be cited in support of the rule: alkenes are stable and of unmeasurable importance in synthetic organic chemistry. However, when the CR_2 moiety in an alkene is replaced by an isoelectronic P—R fragment, the phosphaalkenes are created [3], a class of compounds containing a "forbidden" C/P double bond at a trivalent, dicoordinated phosphorus atom ($\lambda^3\sigma^2$-P) which should, according to the rule, not be stable. The same is true for the phosphaalkynes (containing $\lambda^3\sigma^1$-P), which can formally be derived from alkynes by RC/P exchange [4]. The latter compounds are the subject of the present review and their role as building blocks in synthetic, heterocyclic chemistry will be illustrated.

The parent compound of the phosphaalkynes (HC≡P; **4**, R = H) was first generated and identified by spectroscopy in 1961 [5] but did not attract any special interest. The synthesis of the first kinetically stabilized member of this class of compounds bearing a bulky substituent (**4a**) [6] met a similar fate. However, the generalization of the synthetic method [7,8,9] and the first experiments suggesting the wide range of reactivity of this class of compounds [10, 11] then initiated an explosive development.

Starting material for the synthesis of the phosphaalkynes **4** (Scheme 2) is the trisilylated phosphane **1** [12] which is converted into the title compounds by condensation with an acid chloride and successive cleavage of chlorotrimethylsilane and hexamethyldisiloxane [6,7,8,9]. From a mechanistic point of view, the reaction comprises the initial formation of the acylphosphane **3** which can, in some cases, be detected by ^{31}P nmr spectroscopy [9,13]. Compound **3** then undergoes a rapid P→O trimethylsilyl shift which results in the formation of the phosphaalkene **5**. The final β-elimination of the silyl ether group from **5** is catalyzed by NaOH. In comparison to the original preparation of **4a** [6], the following technique has proved to be more advantageous: the phosphaalkene **5** is added dropwise to a flask containing the solid base preheated to 110-150° with simultaneous removal of the phosphaalkyne **4** and the silyl ether from the reaction chamber under reduced pressure [7,8,9,14]. The phosphaalkynes are characterized by highfield signals in their ^{31}P nmr spectra (δ = -51.4 to -68.9) as well as the lowfield position of the signals for the sp-hybridized carbon atom and the carbon-phosphorus couplings in the ^{13}C nmr spectra (δ = 173.7- 185.6, $^1J_{C,P}$ = 37.2-45.5 Hz).

The reactivity of the phosphaalkyne **4a** has been inves-



R	yield [%]	$^{31}P(C_6D_6)$	$^{13}C(C_6D_6)$
*t*Bu (4a)	85	– 68.9	184.5 ($^1J_{P,C}$ = 38.6 Hz)
CH_2*t*Bu	50	– 51.4	173.7 ($^1J_{P,C}$ = 45.5 Hz)
*i*Pr	60	– 64.3	183.4 ($^1J_{P,C}$ = 41.3 Hz)
1-Ad	71	– 67.2	185.6 ($^1J_{P,C}$ = 39.5 Hz)
	76	– 57.7	184.9 ($^1J_{P,C}$ = 37.2 Hz)

Scheme 2

tigated the most thoroughly; however, practically all of the reactions of the phosphaalkyne moiety described in this article have been generalized with regard to the phosphaalkyne component [10,11].

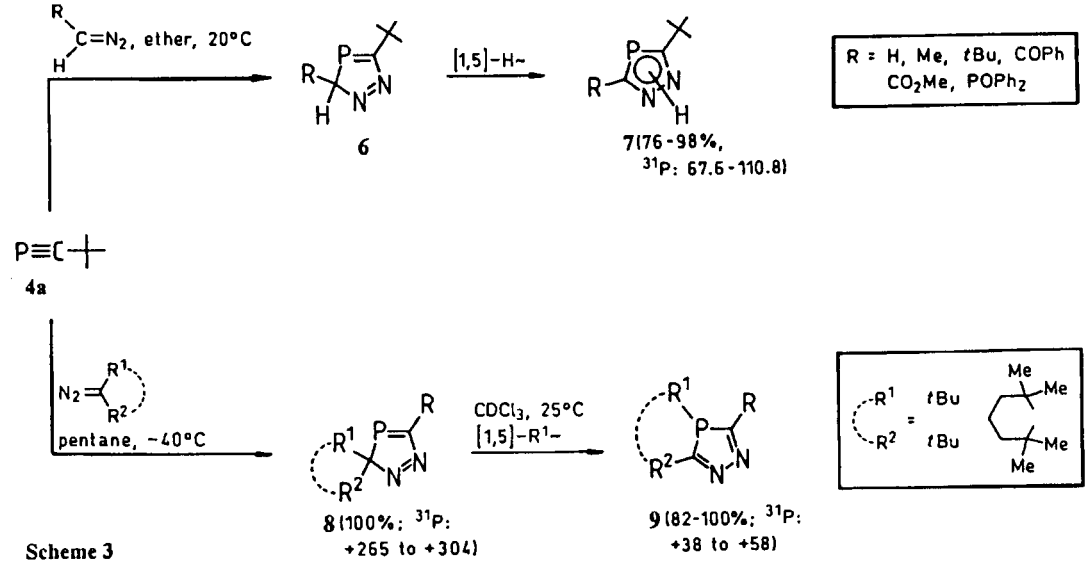
The exceptional cycloaddition potential of the phosphaalkynes **4** was first uncovered in 1,3-dipolar cycloadditions with diazo compounds [15]. Thus, reactions of **4a** with a variety of diazomethyl derivatives gave rise to the 1,2,4-diazaphospholes **7** in high selectivity [14,15]. The primary products of the cycloaddition process are the 3*H*-isomers **6** which can be detected in some cases by nmr spectroscopy. The sigmatropic [1,5]-proton shifts to furnish **7** are facilitated by the gain in aromatization energy.

The [3 + 2]-cycloaddition is orientation specific and most probably electronically controlled (and not, as one might expect at first, sterically controlled). Thus, for example, the parent phosphaacetylene (**4**, H in place of R) reacted with diazomethane to furnish also the 1,2,4-diazaphosphole **7** (H in place of R and *t*-Bu [16]) - a reaction free of any steric constraints (Scheme 3).

If the primarily formed 3*H*-1,2,4-diazaphospholes **6** are to be isolated, for example for conversion into the previously unknown 1-phosphirenes - the lowest representatives of the 1-phospha-1-cycloalkenes - by photochemical elimination of N_2, the sigmatropic H-shift must be prevented. In other words: diazo compounds with substituents that are either not able to undergo shift reactions (or are only able to do so under harsher conditions) have to be employed in place of diazomethyl compounds. In addition, the substituents should be bulky in order to effect a potential kinetic stabilization of the resultant, most certainly energy-rich, 1-phosphirenes.

In this way, the 3*H*-1,2,4-diazaphospholes **8** were obtained in quantitative yield from **4a** by reaction with di-*tert*-butyldiazomethane or 1-diazo-2,2,6,6-tetramethylcyclohexane [17,18]. The ^{31}P nmr signals at very low field provide unequivocal evidence for the cyclic heterodiene structures. Even so, if these compounds are left in deuteriochloroform solution for longer times they do undergo kinetically controlled, sigmatropic alkyl shifts to furnish the 4*H*-1,2,4-diazaphospholes **9** (possibly under H^+ catalysis) [17,18]. This undesired isomerization process can be avoided by low temperature photolysis in aprotic solvents (Scheme 4).

Hence, for example, when the cycloadduct **10** is subjected to irradiation in *n*-pentane at -40°, the first reaction step is ring-opening to the phosphavinyl-substituted diazo



Scheme 3

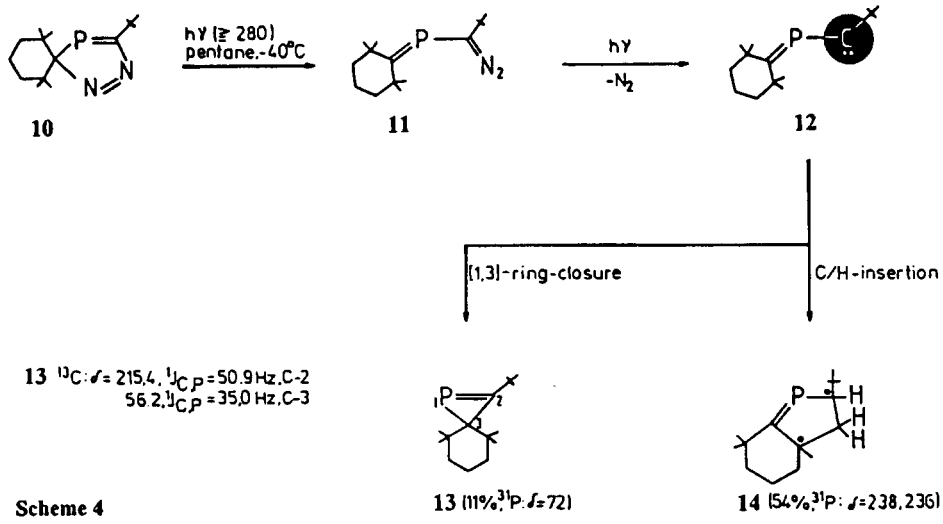
isomer **11** which, in an analogous case, was identified by its diazo valency vibration (see footnote 10 in ref [17]). The action of light is also responsible for the generation of the carbene **12**, the starting point for the decisive reaction step leading to the formation of the 1-phospha-1-cycloakenes (Scheme 4).

[1,3]-Ring closure of the carbene center with the sp^2-hybridized carbon atom produces the spirocyclic 1-phosphirene **13** while C/H insertion of the electron-deficient carbon atom into a methyl group at the 2 position gives rise to the ring-fused phosphacyclopentene **14** [17]. The reaction products obtained in a total yield of 65% and a ratio of ≈ 1:5 can be separated cleanly by bulb-to-bulb distillation with subsequent flash chromatography and then identified by nmr spectroscopy. The bicyclic compound was isolated as a mixture of diastereomers (see ^{31}P nmr data in Scheme 4) whereas the spirocyclic structure is characterized by a surprising diamagnetic shift of its ^{31}P nmr signal ($\delta = 72$); the structure was finally clarified by an X-ray crystallographic analysis of a tungsten complex (**13** itself was obtained as an oil).

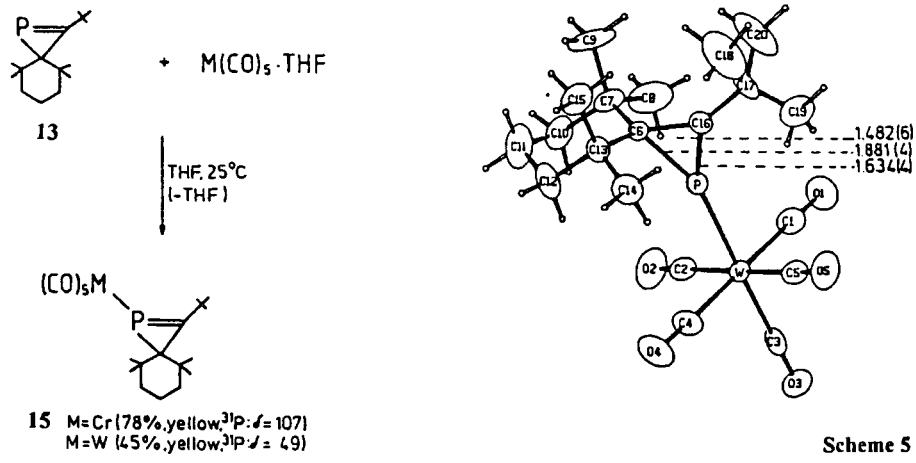
When the 1-phosphirene **13** is treated with the chromium or tungsten pentacarbonyl-tetrahydrofuran complex, the solvent is expelled by the $\lambda^3\sigma^2$-phosphorus atom and the "end-on" complex **15** is obtained [17,18] (Scheme 5).

The tungsten complex **15** (M = W) provided crystals for the structure analysis which then also fulfilled the expectations (Scheme 5). The 1-phosphirene fragment was confirmed unambiguously, the length of the P/C double bond, 1.634(4) Å, was of a size considered to be characteristic for phosphaalkenes with an open-chain structure [19]. The 2-Dewar phosphinines (**46**) discussed below with a P/C double bond incorporated in a four-membered ring exhibit comparable phosphorus-carbon bond lengths (see Scheme 13).

The next question to be answered is: can 1-phosphirenes also be obtained from the [2 + 1]-cycloaddition of carbenes to phosphaalkynes **4**? Diazo compounds obviously cannot be employed as carbene sources since, as mentioned above, they undergo rapid addition to the phos-



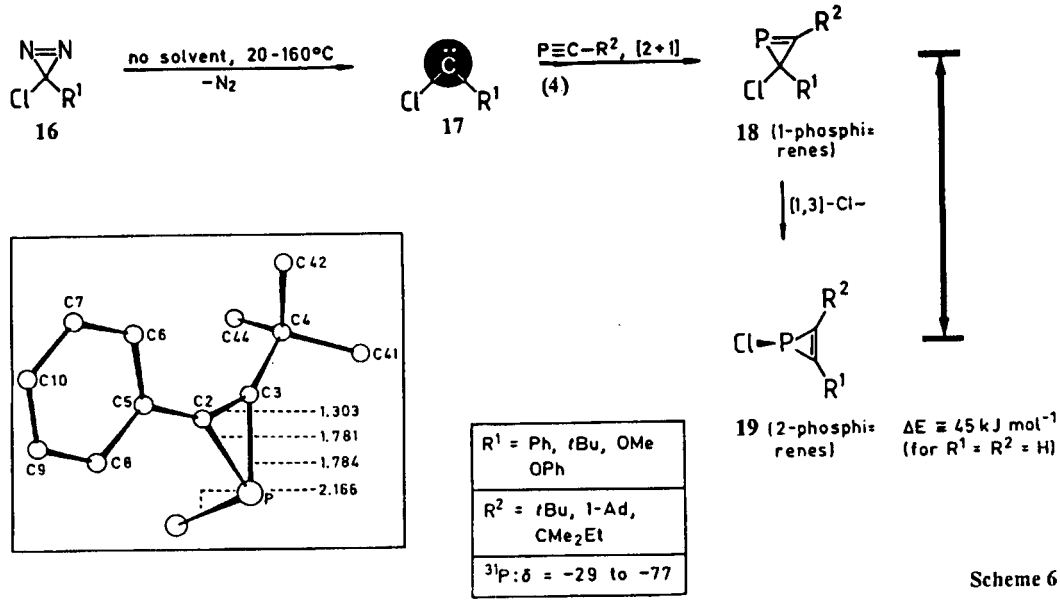
Scheme 4



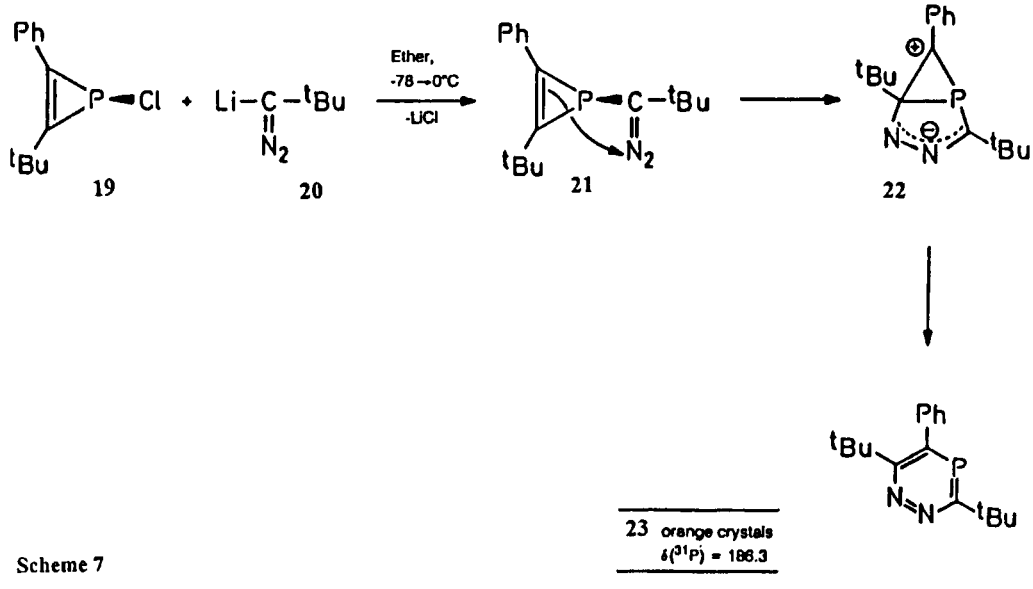
Scheme 5

phaalkynes **4** with retention of the N_2 unit to furnish 1,2,4-diazaphospholes (Scheme 3). For this reason, attention was directed to diazirines as starting materials for the generation of the carbenes. It is known that diazirines themselves do not react with phosphaalkynes **4**. The final decision in favor of the chlorodiazirines **16** was based on practical reasons; these compounds are readily accessible from amidines and hypochlorite.

Contrary to expectations, however, thermal decomposition of the diazirines between room temperature and 160°, depending on the substituent R^1, in the presence of phosphaalkynes **4** did not furnish the 1-phosphirenes **18** but rather the 2-isomers **19** (Scheme 6) [20,21]. This means that, although the energy-rich 1-phosphirenes are most certainly formed first, they have undergone rearrangement by [1,3]-Cl shifts to furnish the thermodynamically more stable 2-phosphirenes **19**. An energy difference of 45 kJ mol^{-1} in favor of the latter species has been calculated for the parent compounds (**18, 19**; $R^1 = R^2 = H$) [22]. The result of the reaction has been confirmed without doubt by an X-ray crystallographic analysis of **19**, R^1 = Ph, R^2 = *t*-Bu. The phosphorus atom in the molecule of this product has sp^3-hybridization, and the P–Cl bond length is extremely large (2.166 Å). This observation suggests that the halogen atom will be readily exchangeable on treatment with nucleophiles. The preparative utility of such



Scheme 6



Scheme 7

reactions will be illustrated by two examples.

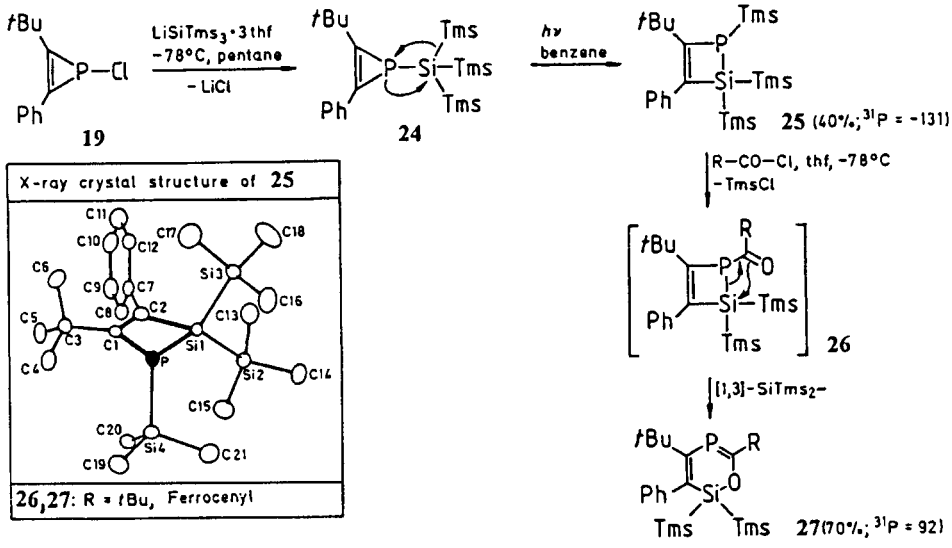
When the lithiated diazo compound **20** is allowed to react with the 2-phosphirene **19** in diethyl ether at -78°, the 1-diazoalkyl-2-phosphirene **21** can be identified as the initial intermediate by low temperature ir and nmr spectroscopy [23].

On warming to 0° an isomerization process takes place to furnish the first example of the previously unknown 1,2,4-diazaphosphinines (**23**) (Scheme 7). A convincing rationale for this transformation involves the betaine **22** as an intermediate, formed by a highly selective nucleophilic attack of the π-bond of the three-membered ring at the terminal nitrogen atom in **21** with bond formation to the *tert*-butyl-substituted carbon atom (→ **22**). The positive charge is stabilized as a benzyl cation and the negative charge by delocalization in a diazaallyl anion. Ring-opening (thermal disrotatory) and charge compensation are then responsible for the formation of **23**.

Lithium tris(trimethylsilyl)silane•3THF was used as a further nucleophile in reaction with the chlorophosphirene **19** (Scheme 8). In this case also, the nucleophilic exchange (→ **24**) takes place already at low temperature [24].

However, the dihydrophosphasilete **25** is not the final result of this strategy but rather represents the starting point for the preparation of the also previously unknown dihydrooxaphosphasilines **27** by *P*-acylation of **25** with acid chlorides under cleavage of chlorotrimethylsilane. The intermediately formed acyl(silyl)phosphanes **26** cannot be detected since they presumably undergo spontaneous P→O silyl shifts to furnish the six-membered heterocyclic compounds **27** [24]. An X-ray crystal structure analysis of one of these products (R = ferrocenyl) has since been reported [25]. Silyl group migrations of this type - as was shown in Scheme 2 - have also been employed with success in the decisive step (**3**→**5**) of the preparation of the phosphaalkynes **4**.

In this context, the scope of application of [1,3]-dipolar cycloadditions to phosphaalkynes deserves mention again. Not unexpectedly, azides - which are isoelectronic to diazo compounds - also undergo addition to phosphaalkynes **4** to give the 3*H*-1,2,3,4-triazaphospholes [15,26]. The same is true for nitrile oxides, although in this case the dipole orientation is reversed [15,27], and other nitrilium betaines [28]. Furthermore, mesoionic compounds of various types also participate in cycloaddi-

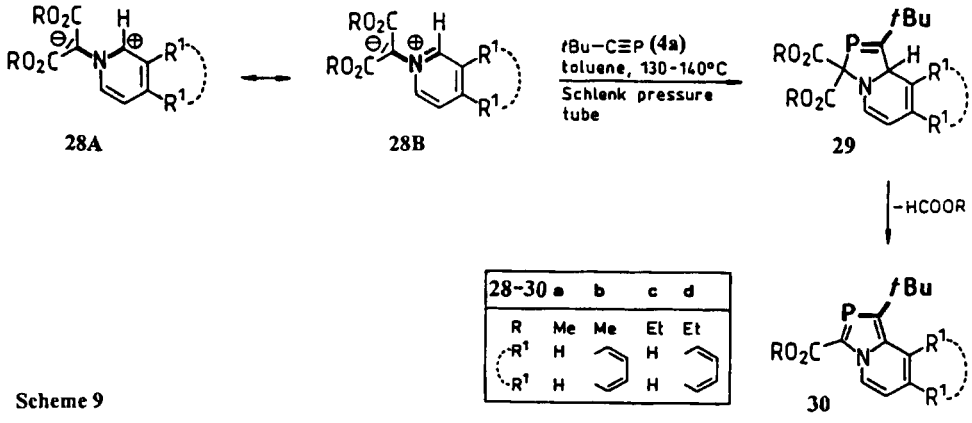


Scheme 8

When the silylated 2-phosphirene **24** is subjected to photolysis (mercury high pressure lamp, Duran 50 filter), the 1,2-dihydro-1,2-phosphasilete **25** is formed [24]. An X-ray crystallographic analysis of this new heterocyclic system confirmed the ring enlargement and the associated Si→P shift. The mechanism of this isomerization can be interpreted in terms of a diotropic reaction (as shown by the arrows in **24**).

tion/"extrusion-type" reactions with the phosphaalkynes **4** leading to heterophospholes [29]. In this article, only the examples of azomethine ylide dipoles and selenoxocarbenes (sextet dipoles) which give rise to novel classes of compounds will be mentioned (Schemes 9, 10, and 11).

Azomethine ylides (Scheme 9) in which the nitrogen atom is incorporated in a pyridinium system (**28A** ↔ **28B**) undergo addition to the phosphaalkyne **4a** albeit



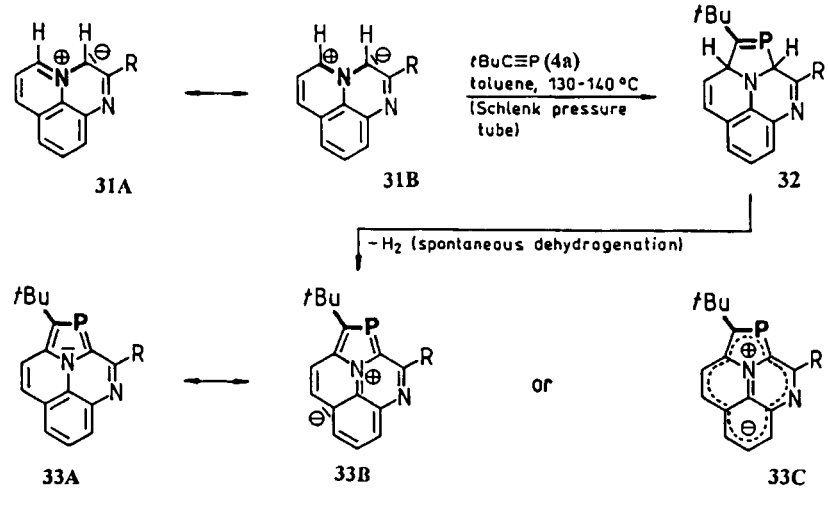
Scheme 9

only under drastic conditions to form initially the dihydrophosphaindolizines **29**; in some other cases, these species can be identified as the primary adducts [30]. Subsequent elimination of methyl or ethyl formate then gives rise to the actual phosphaindolizines **30** [30]; the scope of such cycloaddition/elimination sequences is enormous.

The reaction sequence starting from the azomethine ylides **31A** ↔ **31B** (Scheme 10) is comparable and finally enabled the preparation of the first anulene containing a $\lambda^3\sigma^2$-phosphorus atom in a "Hückel-aromatic" perimeter.

products is satisfactorily described by the mesomeric limiting formulae **33A** ↔ **33B** can be answered as follows: although the nitrogen atom does possess imonium character, the negative charge is delocalized over practically the entire 14π-electron system (according to the limiting form **33C**). In harmony with this, the ^{31}P nmr signals experience a pronounced shift to high field (δ = 108.2 and 115.9, respectively) [31].

Finally, the cycloaddition behavior of the selenoxocarbenes (**35B**) (Scheme 11), which may also be considered



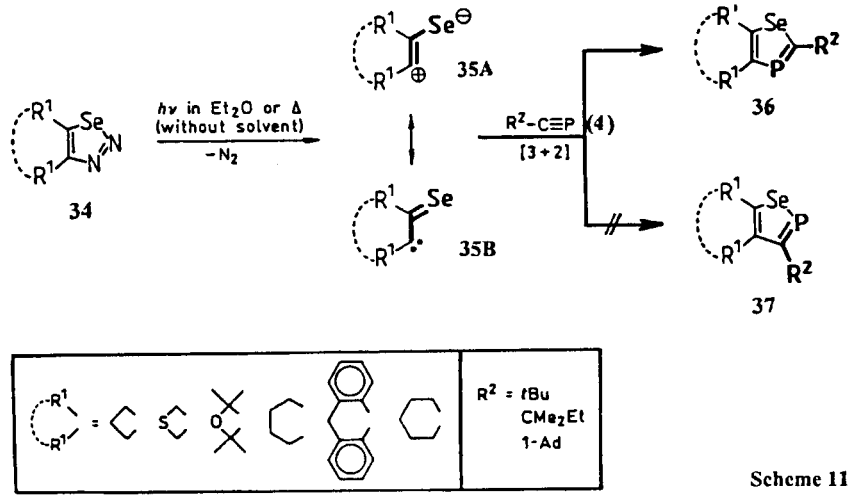
Scheme 10

31 - 33 : R = Me, Ph (yield: 40 %)

Once again, the dihydro derivative **32** is initially formed by the [3 + 2]-cycloaddition of **31** with **4a** and then experiences dehydrogenation to furnish the 14π-heteroaromatic system **33** [31] . With regard to the heteroatom substitution in the perimeter, these products should be named as azaphosphaullazines [32]. The question as to whether the electron distribution in the reaction

as sextet dipoles according to **35A**, will be discussed briefly.

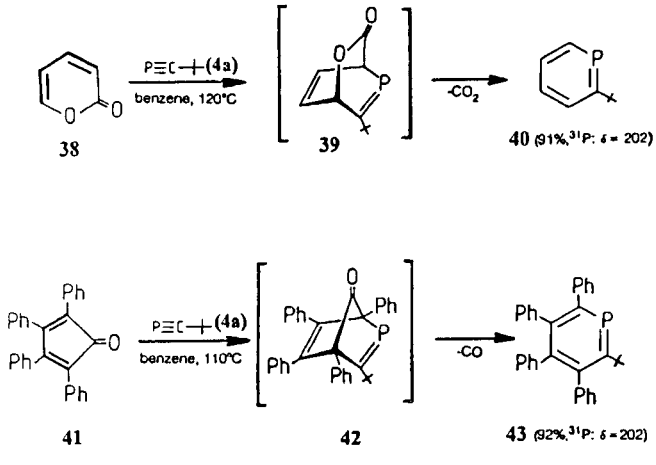
It cannot be excluded from the start that species of this type participate in the cycloaddition reaction also as 1,3-diradicals. The cycloaddition partners are generated by photolysis or thermal decomposition of the 1,2,3-selenadiazoles (**34**) giving rise to highly reactive intermediates.



Scheme 11

The 1,3-dipolar cycloaddition occurs in the presence of the phosphaalkynes **4** to yield the 1,3-selenaphospholes **36** [33]. Within the limits of detection, the nmr spectra provide no evidence for the occurrence of the opposite dipole orientation which would lead to the 1,2-heteroatom isomers **37**. Thioxocarbenes (**35A** ↔ **35B**, S in place of Se) exhibit a comparable cycloaddition behavior towards the phosphaalkynes **4** [34].

Up to now, the question of whether phosphaalkynes **4** can also be employed as dienophiles in Diels-Alder reactions has not been addressed in this survey. First reactions with α-pyrone (**38**) and tetracyclone (**41**) appeared to be promising although drastic reaction conditions were necessary (Scheme 12).

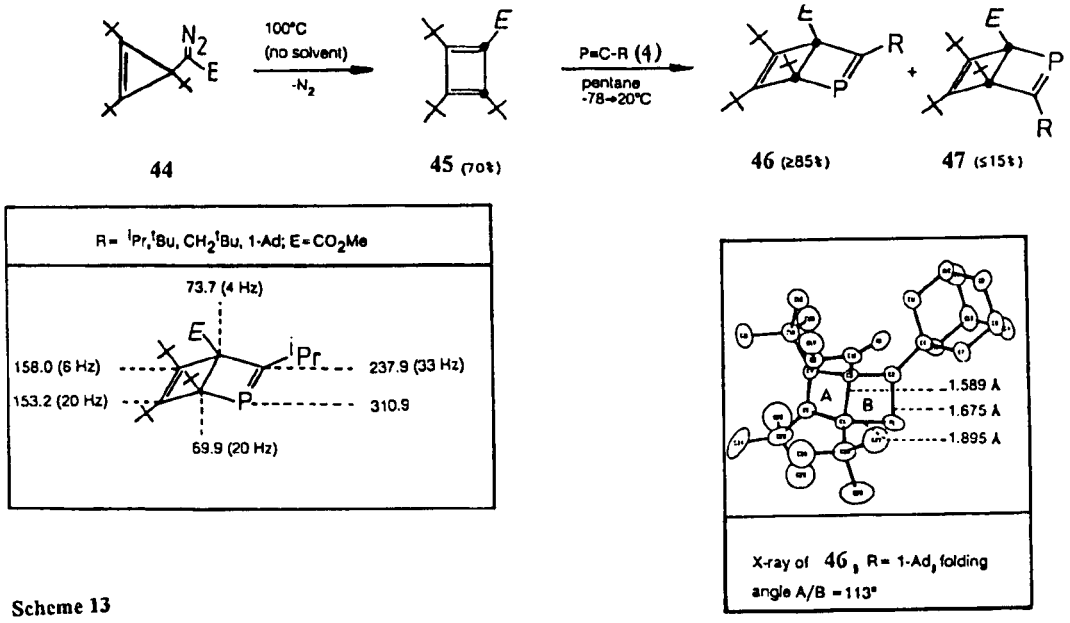


Scheme 12

As expected, in neither case can the bicyclic intermediate **39** or **42**, respectively, be isolated since they both undergo extrusion of CO_2 or CO to yield the λ^3-phosphinines **40** or **43** [35,36]. The reaction is very flexible with regard to the substitution patterns of both components and even permits the introduction of functional groups [37]. The process thus represents a competitive supplementary method to the classical conversion of pyrylium salts into λ^3-phosphinines by reaction with synthetic equivalents of PH_3 [38].

When cyclic, six- and five-membered 1,3-dienes are able to participate in Diels-Alder reactions with phosphaalkynes (see Scheme 12) then it must inevitably be assumed that 1,3-cyclobutadienes are capable of similar reactions. Further support for this hypothesis is provided by, for example, the previously reported [39] realization of [4 + 2]-cycloadditions of acetylenes to **45** to furnish Dewar benzenes, as well as the conversions of the latter to subsequent products. In other words: this concept provided the first potential access to the previously unknown Dewar λ^3-phosphinines and other classical valency isomers of λ^3-phosphinines. And, of course, this opportunity was exploited, as will be discussed below.

The kinetically stabilized cyclobutadienecarboxylate **45** can be prepared in any desired amount by the photochemical or, preferably, thermal treatment of the cyclopropenyldiazoacetate **44** and easily purified by distillation [40]. It reacts specifically at the marked 1,3-diene termini, *i.e.* in the sterically most favorable situation, with phosphaalkynes **4** to furnish mixtures of the 2-Dewar λ^3-phosphinines **46** (≥85%) and **47** (≤15%) regioselectively [41] (Scheme 13). The products **46** and **47** can be separated. The former species are the products of the sterically controlled Diels-Alder reaction while the latter species arise through electronic control. The following discussion is restricted to the main products of the reaction, the bicyclic system **46**. A complete set of ^{13}C and ^{31}P nmr data for the skeletal atoms of the adduct with **4** (R = *i*-Pr) is given in Scheme 13 to illustrate the structure elucidation. Final doubts about the existence of the previously unknown 2-Dewar λ^3-phosphinine structure were removed by an X-ray crystallographic analysis of **46** (R = 1-Ad).

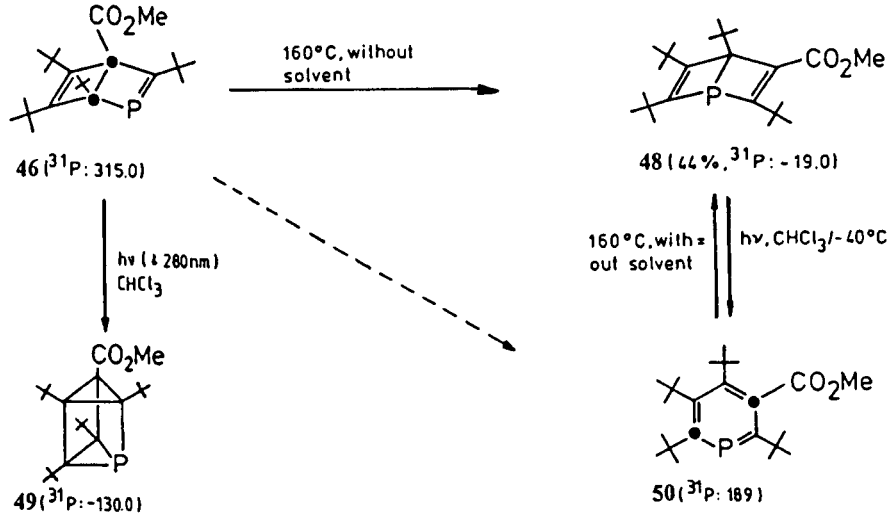


Scheme 13

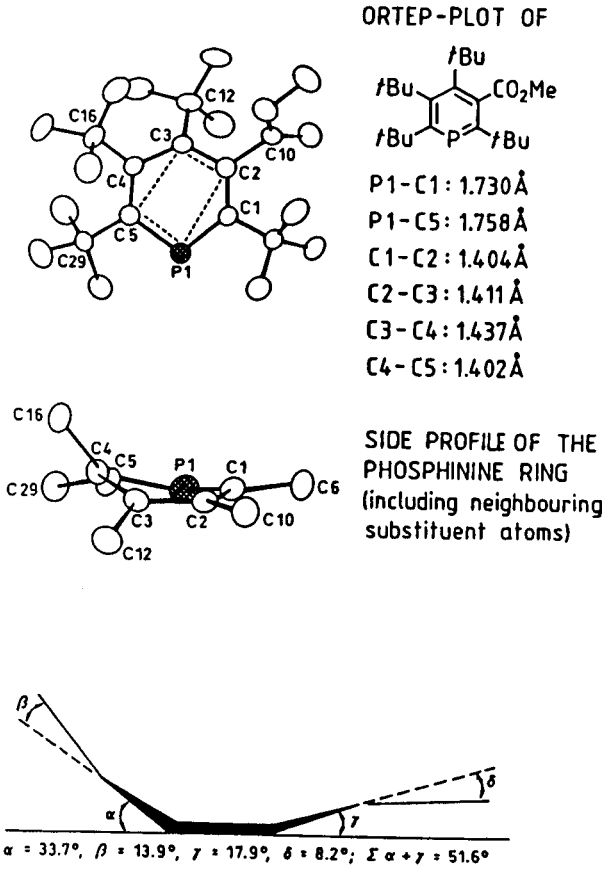
The P/C double bond length (1.675 Å) is in the expected range (compare, *e.g.*, with that of the 1-phosphirene complex **15**, M = W) [17]; the folding angle between the two four-membered rings A and B amounts to 113° [41].

The favorable, opposing orientations of the two double bonds in, for example, the bicyclic compound **46** (E = CO_2Me, R = *t*-Bu) are predestined for an intramolecular, photochemically-induced [2 + 2]-cycloaddition to the phosphaprismane **49**. And this can be realized without difficulty by irradiation of a chloroform solution of **46** [8,42]. Alone the "dramatic" highfield shift of the ^{31}P nmr signal from δ = +315.0 (**46**) to δ = -130.0 (**49**) provides irrevocable evidence for the existence of the phosphirane moiety (Scheme 14).

On the other hand, when **46** is heated in the absence of a solvent to 160°, the 2-Dewar λ^3-phosphinine/1-Dewar λ^3-phosphinine rearrangement (**46** → **48**) occurs [8,42]; this is also associated with an enormous highfield shift of the ^{31}P nmr signal (to δ = -19.0). It is easy to assume that the λ^3-phosphinine **50** is an intermediate of the isomerization reaction, *i.e.* that the mechanism of the reaction comprises electrophilic ring opening of **46** and subsequent electrocyclic ring closure of **50**. The postulated phosphinine **50** can indeed be obtained from **48** under the influence of light; thus providing experiinental evidence in support of the mechanistic considerations. And, as predicted, **50** isomerizes under authentic conditions (160°, no solvent) to **48**. To the best of our knowledge, this is a



Scheme 14



Scheme 15

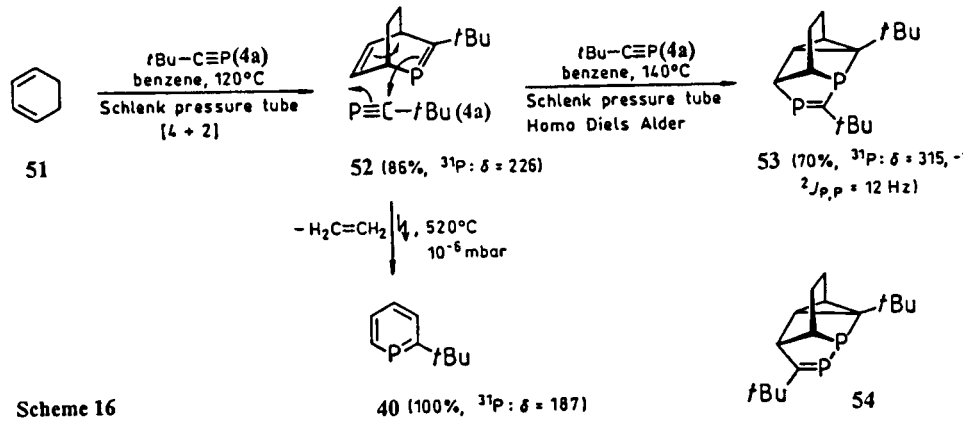
unique example of a Dewar-heteroarene apparently possessing a greater thermodynamic stability than the corresponding heteroarene itself.

The X-ray crystal structure analysis of **50** reveals possible reasons for this unusual thermal behavior of the λ^3-phosphinine (Scheme 15) [43].

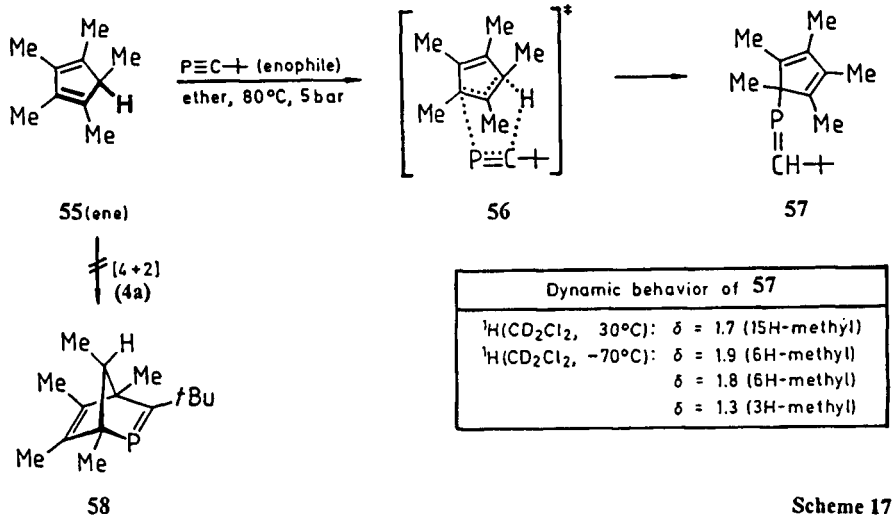
With the exception of the two P/C bonds, the C3–C4 bond (1.437 Å) is the longest in the heterocyclic system. This is due to steric hindrance between the two *tert*-butyl substituents at these atoms and also induces the twisted boat structure of the molecule. The atoms P1, C2, C3, and C5 are no longer in a plane; bow and stern of the boat (represented by the carbon atoms C1 and C4, see side profile of the molecule in Scheme 15) are noticeably inclined with $\alpha = 33.7°$ and $\gamma = 17.9°$. Furthermore, the *tert*-butyl groups at C2 and C4 are no longer in the planes defined by the atoms C3, C4, C5 and P1, C1, C2, respectively, but are rather tilted away from them ($\beta = 13.9°$, $\delta = 8.2°$) [43]. Taken together, these observations explain the thermodynamic difference between **50** and **48**.

Diels-Alder reactions with cyclohexa-1,3-diene (**51**) which, in contrast to, for example, **38** or **41**, does not possess any easily cleavable groups and **4a** provided the first access to bicyclo[2.2.2]octa-1,4-dienes containing $\lambda^3\sigma^2$-phosphorus atoms (→ **52**) (Scheme 16). The ethano bridge can only be eliminated in the form of ethylene under flash vacuum pyrolysis conditions to furnish the phosphinine **40**. Neither the feasible retroreaction nor the cleavage of acetylene can be detected [35].

The phosphabicyclic compound **52** is a hetero-1,4-diene and thus fulfills the prerequisites for a homo-Diels-Alder reaction with the phosphaalkyne **4a**. This takes place at 140° in the direction of the arrows in formula **52** to produce the diphosphatetracyclodecene **53** [44]. If the attack of *t*-Bu-C≡P were to take place at the opposite end of the heterodiene system, a phosphirane would be formed instead of the cyclopropane ring in **53**. This possibility can be discounted on the basis of the absence of a high-field ^{31}P nmr signal for a phosphorus atom in a three-membered ring. Also, another feasible alternative, **54**, with the reverse orientation of the dienophile **4a** is excluded by the ^{31}P nmr data. The coupling constant of merely 12 Hz between the two heteroatoms is unequivocally attributable to a $^2J_{P,P}$ coupling. Since both reaction steps, *i.e.* **51** → **52** and **52** → **53**, proceed under similar thermal conditions, the preparation of the bicyclic compound **53** can be carried out as a "one-pot" process from the cyclohexadiene **51** and the phosphaalkyne **4a** in a



Scheme 16

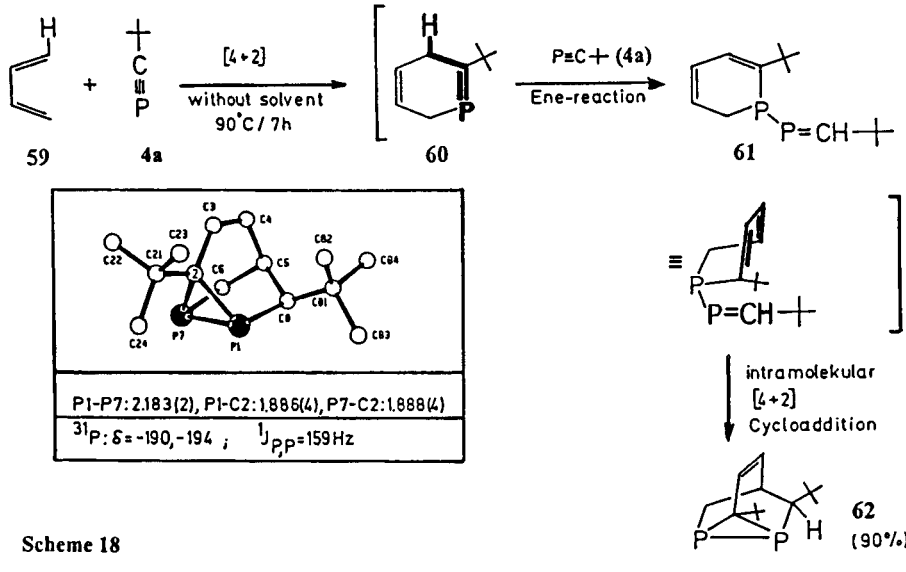


Scheme 17

molar ratio of 1:2.

Limitations of the above-described reaction sequence become apparent from the reaction of pentamethylcyclopentadiene (**55**) with the phosphaalkyne **4a** (Scheme 17). Whereas the Diels-Alder and homo-Diels-Alder reactions with less highly substituted cyclopentadienes proceed in the sense of formation of polycyclic products (see Scheme 16), not even the primary reaction (**55** + **4a** → **58**) takes place in the present case [44].

for such reactions. However, it is interesting to note that, when the ^{1}H nmr spectrum of **57** is recorded at 30°, only one signal integrating for 15 H is observed for all the methyl group protons. This observation can be rationalized by assuming that the phosphavinyl group undergoes rapid (in comparison to the nmr time scale) [1,5]-sigmatropic positional exchanges over all five ring carbon atoms. This thermally allowed process is slowed sufficiently at -70° so that three magnetically different methyl



Scheme 18

Instead, a previously unknown ene reaction occurs in which the methylated cyclopentadiene **55** acts as the ene and the phosphaalkyne **4a** plays the part of the enophile [44]. This reaction of phosphaalkynes has since been generalized [45,46]. The final product isolated is the phosphavinylcyclopentadiene **57** which is presumably formed *via* the transition state **56** of the type generally accepted

groups can be observed in a ratio of 2:2:1 (see Scheme 17) [44].

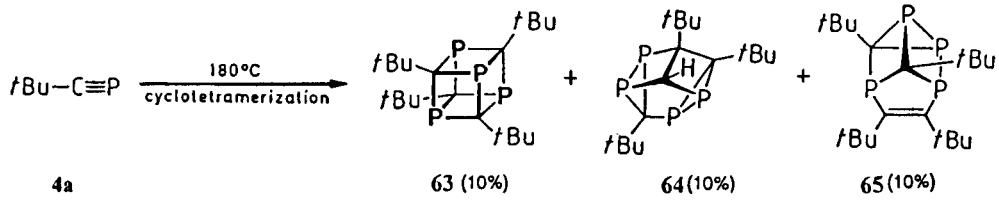
The next question to arise is whether 1,3-butadiene (**59**) can also take part in a normal Diels-Alder reaction with the phosphaalkynes. The answer is yes, although the actual [4 + 2]-cycloaddition process is in fact masked by the subsequent reactions. For example, the reaction of **59** with

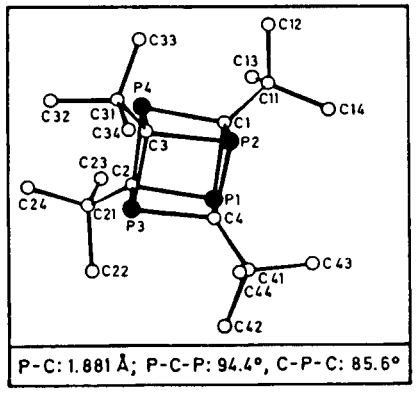
the phosphaalkyne **4a** in a molar ratio of 1,3-diene:dienophile = 1:2 gives the diphosphatricyclooctene **62** in high selectivity (Scheme 18) [47]

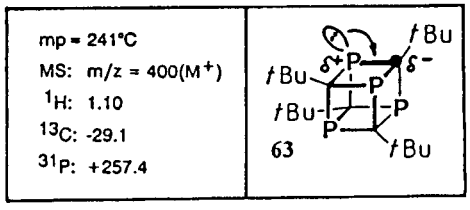
The presence of the diphosphirane ring is already apparent from the highfield positions of the ^{31}P nmr signals of the two phosphorus atoms and their $^{1}J_{P,P}$ coupling constant; the structure of the 1:2 adduct was unequivocally confirmed by X-ray crystallography [47]. Substituted 1,3-dienes and azabutadienes react analogously [47,48]. In place of the substrate pair 1,3-butadiene/phosphaalkyne, 1,4-cyclohexadienes (**60**; CR in place of P and H in place of *t*-Bu) can also be employed in the reaction to produce the corresponding monophosphatricyclooctenes [47]. This evidence convincingly supports the following reaction mechanism.

(Scheme 19) [50,51]. Thus, for example, when **4a** is heated in the absence of a solvent to 180°, three cyclotetramers can be isolated after a complex work-up procedure: these are the tetraphosphacubane **63**, the tetraphosphacuneane **64** (one *tert*-butyl group is lost *via* cleavage of isobutylene), and the tetraphosphabis(homo)prismane **65**, the products being isolated in yields of about 10% each [50,51].

Without doubt, the cubane **63** is the most interesting of these cyclotetramers and will be discussed in detail here. Like many of the compounds mentioned above, the structure of **63** was confirmed by X-ray crystallography. All P/C bond lengths in the cage are identical with 1.881 Å, but this is, of course, not the case for the bonding angles in the skeleton: the angles at phosphorus succumb and are







Scheme 19

The sequence commences with a Diels-Alder reaction (**59** + **4a** → **60**) which is followed by a chemospecific ene reaction at the phosphaallyl increment (**60** + **4a** → **61**) to form the P/P bond. An intramolecular [4 +2]-cycloaddition between the phosphaalkene and 1,3-diene moiety of **61** is finally responsible for the formation of the polycyclic system (→ **62**) [47].

The enormous cycloaddition potential of the phosphaalkynes **4** automatically poses the question of their thermal cyclooligomerization behavior which should lead to complete (or at least extensive) coordinative saturation of the phosphorus atom. Cyclodimerization [49] and cyclotrimerization [49] have been realized with the help of organometallic auxiliary reagents. However, the purely thermal reaction will be discussed first since this has opened a new dimension of phosphaalkyne cyclotetramers

reduced to 85.6° while those at carbon are widened to 94.4° [50]. A peak for the monomer **4a** is observed in the mass spectrum of **63**; **4a** is also formed by flash vacuum pyrolysis of the pentacyclic compound. In the ^{1}H, ^{13}C, and ^{31}P nmr spectra, the respective atoms give rise to only one signal each (see Scheme 19) [50]. But the real surprise is the highfield signals of the skeletal carbon atoms and the lowfield signals for the phosphorus atoms: one would expect the latter to appear about 400 ppm to higher field and the carbon atoms to have at least positive chemical shifts.

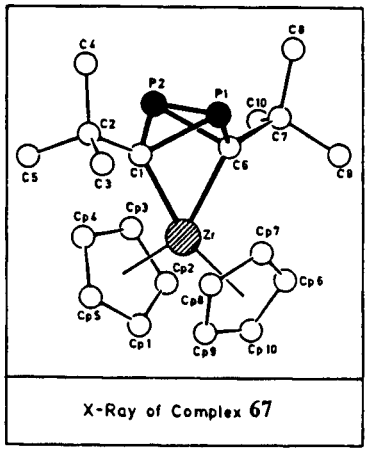
However, it is now known from photoelectron spectroscopic experiments and from MO calculations [52] that the lone electron pairs on phosphorus participate in the P/C σ-bonds of the cube *via* electron transfer. Thus, the phosphorus atoms have a formal positive charge and the

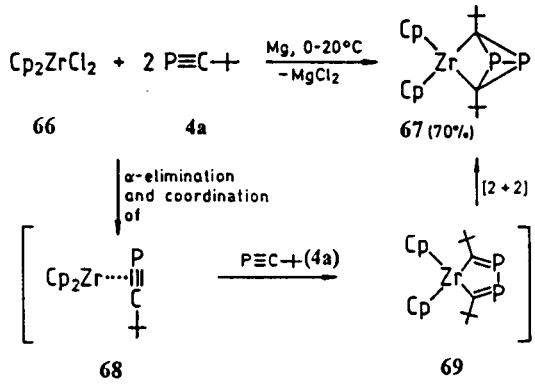
carbon atoms a formal negative charge [52] which helps to explain the unusual nmr chemical shifts of the respective nuclei. As will be mentioned below, this of course has consequences on the basicity (nucleophilicity) of the phosphorus atoms.

But first, a high-yield synthesis of **63** was needed before this concept could be examined further. This was realized by assuming that the cyclotetramerization process can be broken down into two cycloaddition steps as follows. The first step was achieved with the system biscyclopentadienylzirconium dichloride (**66**)/phosphaalkyne (**4a**)/magnesium which gave rise to the zirconium/phosphaalkyne dimer complex **67** [53] whose structure was confirmed by X-ray crystallography [53] (Scheme 20).

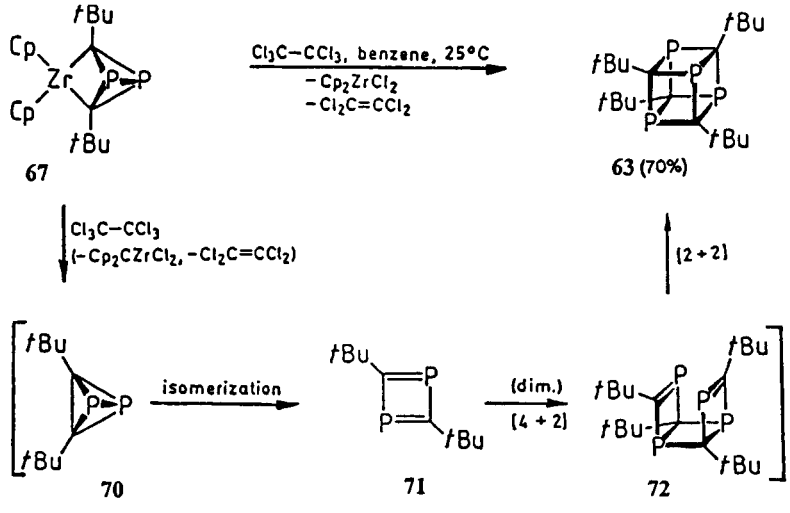
In analogy to results from acetylene chemistry, it may reasonably be assumed that "side-on" coordination of the Cp_2Zr fragment to **4a** (→ **68**) and subsequent incorporation of a second molecule of phosphaalkyne **4a** leads to the diphosphazirconacyclopentadiene **69** which then undergoes a crossed, intramolecular [2 + 2]-cycloaddition to furnish the tricyclic product **67** [53]. The problem now remained of how to remove the Cp_2Zr fragment and to induce the resultant fragment to undergo dimerization to the tetraphosphacubane **63**.

After numerous unsuccessful experiments, it was found that the mild halogenating reagent hexachloroethane had the desired effect. The tetraphosphacubane **63** was obtained in 70% yield from the reaction of the zirconium complex **67** with hexachloroethane in benzene at room





Scheme 20

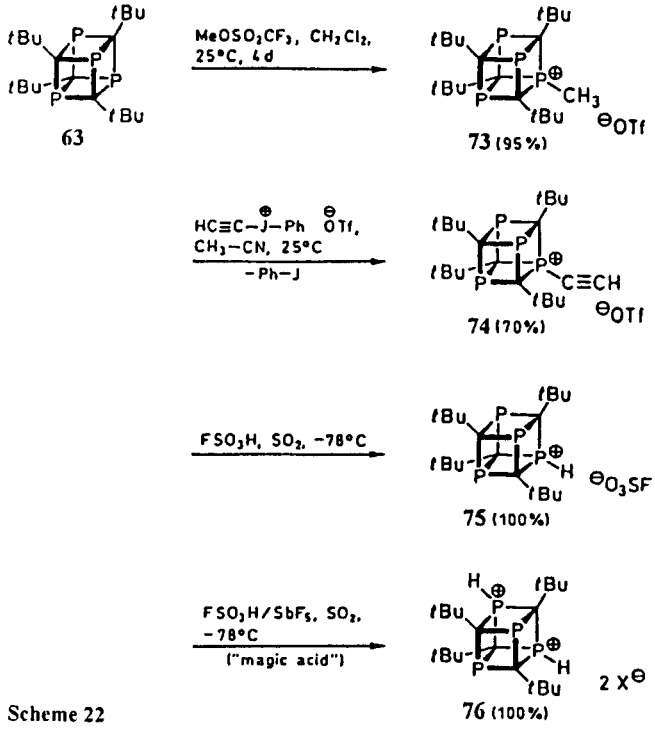


Scheme 21

temperature (Scheme 21) [54,55]. Bis(cyclopentadienyl)-zirconium dichloride and tetrachloroethene were identified as the elimination products.

Although contrary to energetic reasoning [56], the diphosphatetrahedrane **70** may be postulated as an intermediate on the way to the cubane. In any case, the 1,3-diphosphete **71** is most certainly an intermediate of the reaction [54]: dimerization of **71** in a hetero-Diels-Alder reaction (formation of the tricyclic species **72**) and subsequent, intramolecular [2 +2]-cycloaddition [54] satisfactorily explain the formation of the pentacyclic product **63**. As also shown in Scheme 21, the reaction sequence can be generalized [54,57].

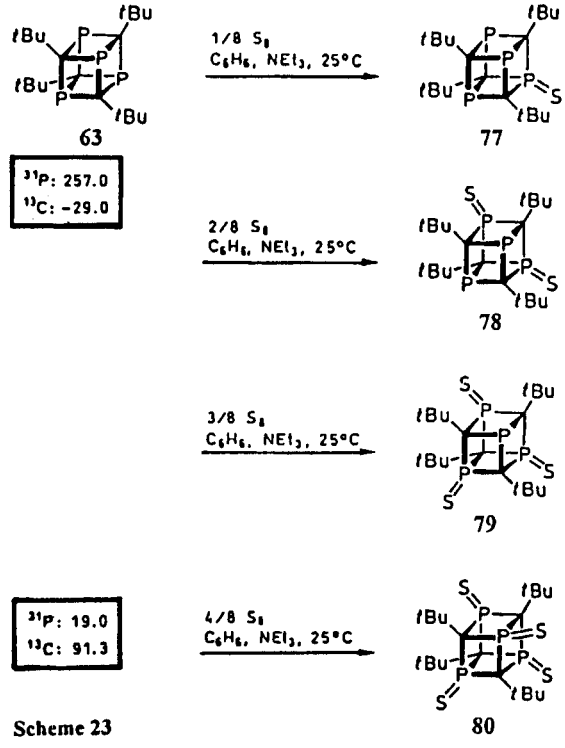
The final question as to whether the phosphorus atoms in the cubane **63** are indeed only slightly nucleophilic (or basic) can now be addressed. At least S_N1-active halides and normal acids are not able to quaternize the heteroatoms; stronger electrophiles are required (Scheme 22).



Scheme 22

Even when **63** is treated with an excess of "magic methyl" only the monophosphonium salt **73** is formed [58]. The same is true for the alkylating reagent ethynyl(phenyl)iodonium triflate (formation of **74**) [58,59]. Monoprotonation (→ **75**) results from the treatment of **63** with fluorosulfonic acid in liquid SO_2 at -78° and diprotonation (→ **76**) from its treatment with "magic acid" under otherwise identical conditions [58]. Since no cleavage of the cage occurs during the latter two reactions, it can be deduced that hydrolysis of the protonation products predominantly leads back to **63** [58].

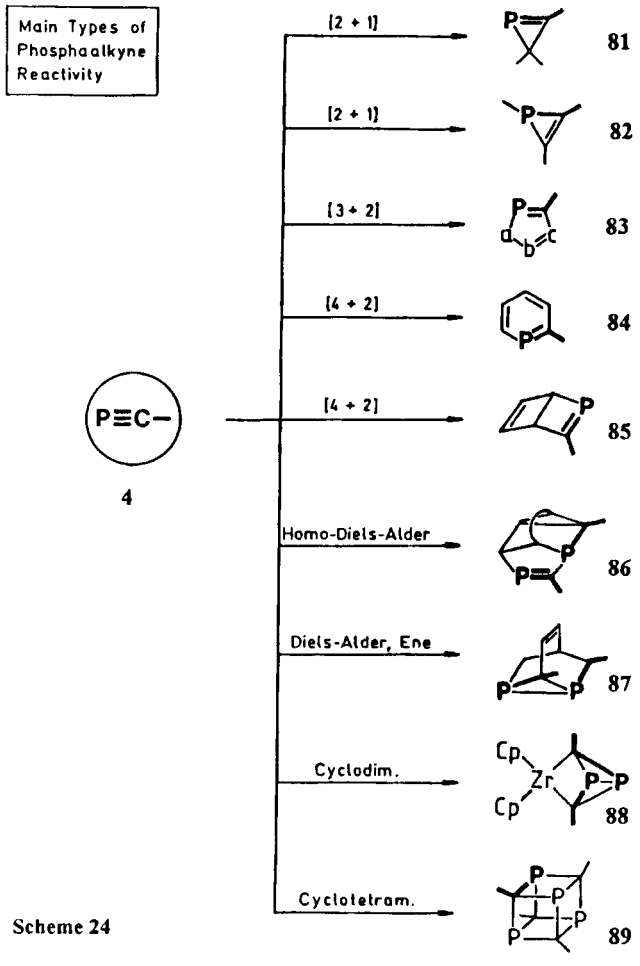
It can also be demonstrated chemically that the lone pairs on phosphorus are responsible for the unique bonding situation in the tetraphosphacubane **63**. When these are blocked by, for example, oxidative addition of sulfur, a normal situation should be created and reflected in the nmr signals of the skeletal atoms (Scheme 23). The reaction with sulfur is catalyzed by triethylamine and produces the tetraphosphacubane sulfides **77, 78, 79,** or **80** depending on the stoichiometry employed [60,61].



Scheme 23

In this context, a comparison of the ^{13}C and ^{31}P nmr data of the cage atoms of **63** and **80** provides sufficient information. The elimination of the lone pair effect in the tetraphosphacubane tetrasulfide **80** does indeed lead to the expected consequences: the phosphorus signal is diamagnetically shifted by 238 ppm and the carbon signal is paramagnetically shifted by 114 ppm (for the exact chemical shifts of **63** and **80**, see Scheme 23) [61,62].

In summary, it can be concluded that the chemical behavior of the phosphaalkynes **4** resembles that of the alkynes much more than that of the nitriles. The reactivity is determined by their endeavor to convert the $\lambda^3\sigma^1$-phosphorus atom ultimately into a $\lambda^3\sigma^3$-phosphorus atom. In the process, phosphaalkenes possessing $\lambda^3\sigma^2$-phosphorus can often be isolated (Scheme 24).



Scheme 24

When the major results are surveyed once more, it can be seen that the syntheses of the 1- and 2-phosphirenes (**81** and **82**, respectively) were one of the biggest surprises. The 1,3-dipolar cycloadditions leading to the heterophospholes (**83**) have revealed new dimensions in this field. Diels-Alder reactions with 1,3-dienes possessing an easily removable group (→ **84**) have enriched the chemistry of phosphinines. Cycloadditions to kinetically stabilized cyclobutadienes have provided the very first access to valency isomers such as **85** (and others) of the phosphinines. Finally, numerous polycyclic systems such as, for example, **86** and **87** have been prepared for the first time by reaction sequences involving Diels-Alder, homo-Diels-Alder, and ene reactions. Among the metal-assisted cyclooligomerization reactions, I consider the synthesis of the zirconatricyclic compound **88** to be the most significant. Although the tetraphosphacubane **89** can be prepared directly by thermal cyclotetramerization, its high-yield synthesis from the reaction of **88** with hexachloroethane played a major role in the investigations on the chemistry of this cage compound.

Acknowledgements.

I would like to thank my coworkers, whose names appear in the references, not only for their successful work but also for their enthusiasm in the solution of our problems and for their own creative contributions. I am also grateful to the organiser of the congress, Professor Alderweireldt, where this contribution was first presented.

Our investigations were made possible by generous financial support from the Deutsche Forschunsgemeinschaft (Graduiertenkolleg "Phosphor" among others), the Stiftung Volkswagenwerk, and the Fonds der Chemischen Industrie, as well the Regierung des Bundeslandes Rheinland-Pfalz who granted us numerous post-graduate research stipendia.

REFERENCES AND NOTES

[1] Part **74**: A. B. Kostitsyn, O. M. Nefedov, H. Heydt and M. Regitz, *Synthesis*, 163 (1993).

[2] General consideration on multiple bonds between heavy main group elements: M. Drieß, *Chemie in unserer Zeit*, **27**, 141 (1993).

[3] Summary: R. Appel, in M. Regitz O. J. Scherer eds.: Multiple Bonds and Low Coordination in Phosphorus Chemistry, Thieme Publishers, Stuttgart, New York, 1990, p 157 ff.

[4] Summary: M. Regitz, in M. Regitz and O. J. Scherer, eds.: Multiple Bonds and Low Coordination in Phosphorus Chemistry, Thieme Publishers, Stuttgart, New York, 1990, p 58 ff.

[5] T. E. Gier, *J. Am. Chem. Soc.*, **63**, 1769 (1961).

[6] G. Becker, G. Gresser and W. Uhl, *Z. Naturforsch.*, **36b**, 16 (1981).

[7] W. Rösch, U. Vogelbacher, T. Allspach and M. Regitz, *J. Organomet. Chem.*, **306**, 39 (1986).

[8] M. Regitz, W. Rösch, T. Allspach, U. Annen, K. Blatter, J. Fink, M. Hermesdorf, H. Heydt, U. Vogelbacher and O. Wagner, *Phosphorus Sulfur*, **30**, 479 (1987).

[9] T. Allspach, M. Regitz, G. Becker and W. Becker, *Synthesis*, 31 (1986).

[10] Review: M. Regitz and P. Binger, *Angew. Chem.*, **100**, 1541 (1988); *Angew. Chem., Int. Ed. Engl.*, **27**, 1484 (1988).

[11] Review: M. Regitz, *Chem. Rev.*, **90**, 191 (1990).

[12] G. Becker and W. Hölderich, *Chem. Ber.*, **108**, 2484 (1975).

[13] G. Becker, *Z. Anorg. Allg. Chem.*, **430**, 66 (1977).

[14] W. Rösch, U. Hees and M. Regitz, *Chem. Ber.*, **120**, 1645 (1987).

[15] W. Rösch and M. Regitz, *Angew. Chem.*, **96**, 898 (1984); *Angew. Chem., Int. Ed. Engl.*, **23**, 900 (1984).

[16] E. Fuchs, M. Hermesdorf, W. Schnurr, W. Rösch, H. Heydt and M. Regitz, *J. Organomet. Chem.*, **338**, 329 (1988).

[17] O. Wagner, G. Maas and M. Regitz, *Angew. Chem.*, **99**, 1328 (1987); *Angew. Chem., Int. Ed. Engl.*, **26**, 1257 (1987).

[18] M. Regitz and O. Wagner, unpublished results, Kaiserslautern, 1989.

[19] *C.f.* ref [3], p 160.

[20] O. Wagner, M. Ehle and M. Regitz, *Angew. Chem.*, **101**, 227 (1989); *Angew. Chem., Int. Ed. Engl.*, **28**, 225 (1989).

[21] O. Wagner, M. Ehle, M. Birkel, J. Hoffmann and M. Regitz, *Chem. Ber.*, **124**, 1207 (1991).

[22] M. T. Nguyen, H. Vansweevelt and L. G. Vanquichenborne, *Chem. Ber.*, **125**, 923 (1992).

[23] M. Regitz and J. Hoffmann, unpublished results, Kaiserslautern, 1989.

[24] S. Haber, R. Boese and M. Regitz, *Angew. Chem.*, **102**, 1523 (1990); *Angew. Chem., Int. Ed. Engl.*, **29**, 1436 (1990).

[25] M. Regitz and S. Haber, unpublished results, Kaiserslautern, 1991.

[26] W. Rösch, T. Facklam and M. Regitz, *Tetrahedron*, **43**, 3247 (1987).

[27] W. Rösch and M. Regitz, *Synthesis*, 689 (1987).

[28] *C. f.* ref [11], p 203.

[29] W. Rösch, H. Richter and M. Regitz, *Chem. Ber.*, **120**, 1809 (1987).

[30] U. Bergsträßer, A. Hoffmann and M. Regitz, *Tetrahedron Letters*, **33**, 1049 (1992).

[31] M. Regitz and U. Bergsträßer, unpublished results, Kaiserslautern, 1992.

[32] H. Balli and M. Zeller, *Helv. Chim. Acta*, **66**, 2135 (1983).

[33] B. Burkhart, S. Krill, Y. Okano, W. Ando, M. and Regitz, *Synlett*, 356 (1991).

[34] M. Regitz and S. Krill, unpublished results, Kaiserslautern, 1993.

[35] W. Rösch and M. Regitz, *Z. Naturforsch.*, **41b**, 931 (1986).

[36] M. Regitz and U. Annen, unpublished results, Kaiserslautern, 1988.

[37] U. Annen, M. Regitz and H. Kluge, *Chem. Ber.*, **123**, 935 (1990).

[38] Summary: G. Märkl, in M. Regitz and O. J. Scherer eds.: Multiple Bonds and Low Coordination in Phosphorus Chemistry, Thieme, Publishers, Stuttgart, New York, 1990, p 220 ff.

[39] See H. Wingert and M. Regitz, *Chem. Ber.*, **119**, 244 (1986); H. Wingert and M. Regitz, *Z. Naturforsch.*, **41b**, 1306 (1986); H. Wingert, G. Maas and M. Regitz, *Tetrahedron*, **42**, 5341 (1986); H. Wingert, H. Irngartinger, D. Kallfass and M. Regitz, *Chem. Ber.*, **120**, 825 (1987).

[40] S. Masamune, N. Nakamure, M. Suda and H. Ona, *J. Am. Chem. Soc.*, **95**, 8481 (1973); H. Wingert, H. Irngartinger, D. Kallfass and M. Regitz, *Chem. Ber.*, **120**, 825 (1987).

[41] J. Fink, W. Rösch, U.-J.Vogelbacher and M. Regitz, *Angew. Chem.*, **98**, 265 (1986); *Angew. Chem., Int. Ed. Engl.*, **25**, 280 (1986).

[42] K. Blatter, W. Rösch, U.-J. Vogelbacher, J. Fink and M. Regitz, *Angew. Chem.*, **99**, 67 (1987); *Angew. Chem., Int. Ed. Engl.*, **26**, 85 (1987).

[43] G. Maas, J. Fink, H. Wingert, K. Blatter and M. Regitz, *Chem. Ber.*, **120**, 819 (1987).

[44] U. Annen and M. Regitz, *Tetrahedron Letters*, **29**, 1681 (1988).

[45] A. Marinetti, L. Ricard, F. Mathey and M. Slany, *Tetrahedron*, **49** (1993), in press.

[46] M. Regitz and T. Mackewitz, unpublished results, Kaiserslautern, 1993.

[47] E. P. O. Fuchs, W. Rösch and M. Regitz, *Angew. Chem.*, **99**, 1058 (1987); *Angew. Chem., Int. Ed. Engl.*, **26**, 1011 (1987).

[48] M. Regitz and R. Fässler, unpublished results, Kaiserslautern, 1992.

[49] Reviews: *c. f.* ref [10] as well as J. F. Nixon, *Chem. Rev.*, **88**, 1327 (1988).

[50] T. Wettling, J. Schneider, O. Wagner, C. G. Kreiter and M. Regitz, *Angew. Chem.*, **101**, 1035 (1989); *Angew. Chem., Int. Ed. Engl.*, **28**, 1013 (1989).

[51] M. Regitz and T. Wettling, unpublished results, Kaiserslautern, 1991.

[52] R. Gleiter, K.-H. Pfeifer, M. Baudler, G. Scholz, T. Wettling and M. Regitz, *Chem. Ber.*, **123**, 757 (1990).

[53] P. Binger, B. Biedenbach, C. Krüger and M. Regitz, *Angew. Chem.*, **99**, 798 (1987); *Angew. Chem., Int. Ed. Engl.*, **26**, 764 (1987).

[54] T. Wettling, B. Geißler, R. Schneider, S. Barth, P. Binger and M. Regitz, *Angew. Chem.*, **104**, 761 (1992); *Angew. Chem., Int. Ed. Engl.*, **31**, 879 (1992).

[55] M. Regitz, T. Wettling, B. Breit, M. Birkel, B. Geißler, U. Bergsträßer, S. Barth and P. Binger, *Phosphorus, Sulfur, Silicon*, **76**, 261 (1993).

[56] In this context *c. f.* the lecture of M. Hofmann/Erlangen (working group of Professor v. Schleyer), held on July 16 in Kaiserslautern.

[57] M. Regitz and B. Geißler, unpublished results, Kaiserslautern, 1992.

[58] K. K. Laali, M. Regitz, M. Birkel, P. J. Stang and C. M. Critell, *J. Org. Chem.*, **58**, 4105 (1993).

[59] Review on iodonium salts: P. J. Stang, *Angew. Chem.*, **104**, 281 (1992); *Angew. Chem., Int. Ed. Engl.*, **31**, 274 (1992).

[60] M. Birkel, J. Schulz, U. Bergsträßer and M. Regitz, *Angew. Chem.*, **104**, 870 (1992); *Angew. Chem., Int. Ed. Engl.*, **31**, 879 (1992).

[61] M. Regitz, in D. Enders, H.-J. Gais and W. Keim, eds.: Organic Synthesis *via* Organometallics, Vieweg, Braunschweig, Wiesbaden, 1992, p 93 ff.

[62] M. Regitz and M. Birkel, unpublished results, Kaiserslautern, 1992.