

Phosphaalkynes: New Building Blocks in Synthetic Chemistry¹

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I. P≡X Bonds

Supposedly established rules have sometimes hindered the development of whole fields of chemistry; however, once breaches have been made in the generally accepted conceptions, completely novel and unexpected developments may follow rapidly. This was also valid for the so-called double-bond rule,² which stated that (p-p)π multiple bonds between, for example, phosphorus and elements of the first period possessing eight

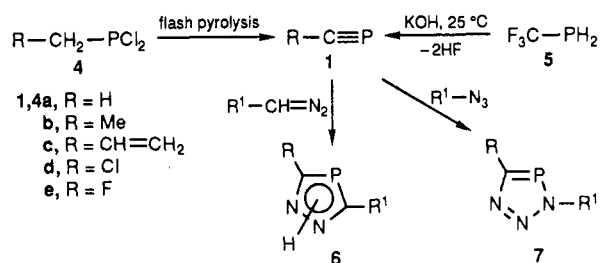


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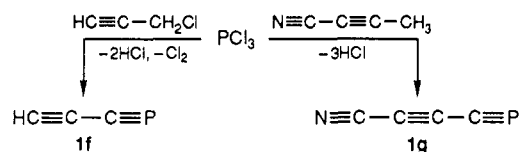
elements were not possible. The syntheses of compounds of trivalent phosphorus with P=C double bonds such as, for example, the phosphamethine cyanine cations³ or the phosphabenzene⁴ have made a major contribution to the discrediting of this rule. At present, a slowing down or end of the continuing brisk development in the field of low-coordinated phosphorus compounds⁵ cannot be foreseen, and further surprising results may be expected in the near future.

A whole range of species containing P≡X triple bonds is now known. For example, at higher temperatures, white phosphorus is in equilibrium with the P≡P unit (eq 1 (Scheme 1)); the proportion of the latter can be as much as 50%.^{6,7} Such P₂ fragments may also be found as four-, six-, and eight-electron donors in transition-metal complexes.⁸ Phosphorus(III) nitride (P≡N) is also a short-lived species; it was generated thermally from P₃N₅ (eq 2),⁶ isolated in an argon matrix, and characterized by IR spectroscopy.⁹ Later, the terminal η¹-P coordination and bridged μ-P coordination of this ligand were also realized.¹⁰ In contrast to the [P≡P] and [P≡N] moieties, a wide variety of the isoelectronic phosphaalkynes can be isolated.¹¹ These

SCHEME 3



SCHEME 4



example, NMR spectroscopy.^{22,32} It can also, however, be trapped by means of 1,3-dipolar cycloaddition reactions with diazomethyl compounds (\rightarrow formation of 1,2,4-diazaphospholes **6**, R = H²²) or with azides (\rightarrow formation of 1,2,3,4-triazaphospholes **7**, R = H²²).

1-Phospha-1-propyne can be generated by an analogous method (**4b** \rightarrow **1b**) in which the hydrogen chloride is either frozen out³³ or neutralized by a base.^{32,34} When **1b** is required for synthetic purposes, it is advantageous to blow triethylamine into the reaction mixture, to filter off the triethylammonium chloride on a transverse glass frit, and then to condense the phosphalkyne on a finger cooled with liquid nitrogen.³⁴ Like **1a**, the phosphalkyne **1b** may also be transformed into phospholes (**6**, **7**, R = Me) by trapping reactions with diazoalkane and azide dipoles.³⁴

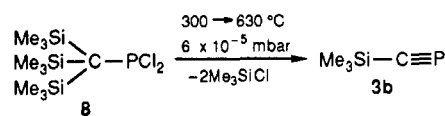
Propenylidynephosphane (**1c**)—a phosphalkyne possessing an additional conjugated vinyl group—is also accessible from the dichlorophosphane **4c** by the thermal HCl elimination route;^{35–37} however, its identification was based solely on microwave spectroscopic investigations. Chlorophosphaacetylene (**1d**) was prepared for the first time by flash vacuum pyrolysis of **4d** at 850 °C/ 3×10^{-4} mbar; PCl₃ was also formed as a byproduct.³⁸ The structure of **1d** was confirmed by ³¹P NMR spectroscopy [(toluene-*d*₈, -70 °C): $\delta = +3.4$] and the formation of cycloadducts of the type **6** by reaction with diazoacetates.³⁸ Fluorophosphaacetylene (**1e**) represents an exception in that the elimination of HF from (trifluoromethyl)phosphane (**5**) takes place at room temperature in the presence of solid potassium hydroxide.^{39,40} The product **1e** was identified by photoelectron,³⁹ IR,^{41,42} and microwave spectroscopy.⁴³

Cocondensation reactions of phosphorus trichloride with propargyl chloride or 1-propyne-1-carbonitrile under flash vacuum pyrolysis conditions proceed with intermolecular elimination of HCl and thus render possible the generation of short-lived phosphalkynes containing additional triple-bond units, namely, 1-phospha-1,3-butadiyne (**1f**; $\mu = 0.74$ D)^{37,44} and the hetero triyne **1g** ($\mu = 4.3$ – 4.5 D),⁴⁵ respectively (Scheme 4).

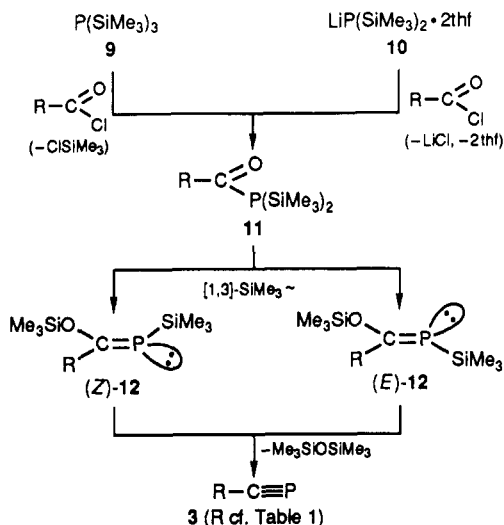
2. Of Chlorotrimethylsilane

The historical significance of the elimination of chlorotrimethylsilane in phosphalkyne chemistry (\rightarrow **3b**,²⁵ \rightarrow **3c**^{26,27}) has already been mentioned. These reactions profit from the Si/Cl bond energy; a further

SCHEME 5



SCHEME 6



advantage of this methodology is that the addition of the base, as required in eliminations of HCl, is no longer necessary.

A twofold elimination of chlorotrimethylsilane from dichloro[tris(trimethylsilyl)methyl]phosphane (**8**) opens up a direct access to **3b**.³⁸ The highly probable phosphalkene intermediate could not be detected (Scheme 5).


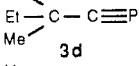
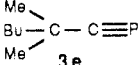
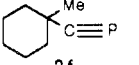
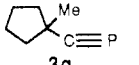
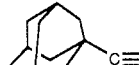
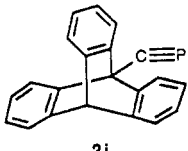
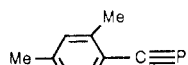
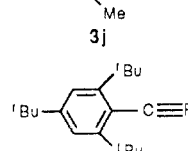
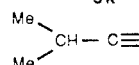
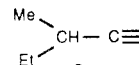
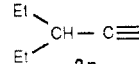
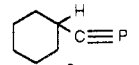
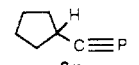
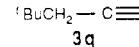
3. Of Hexamethyldisiloxane

The elimination of hexamethyldisiloxane from suitably substituted phosphalkenes (e.g., (*E/Z*)-**12** \rightarrow **3**) already occupies a prominent position in phosphalkyne synthesis even though the systematic exploitation of this method has only just begun.^{23,24} The starting material for this process is tris(trimethylsilyl)phosphane (**9** (Scheme 6)), which, in turn, is readily accessible from white phosphorus, sodium/potassium alloy, and chlorotrimethylsilane under observation of suitable safety precautions.⁴⁶ Treatment of **9** with alkylolithium reagents gives rise to the lithium phosphide **10**, which is, as to be expected, considerably more reactive than the phosphane.⁴⁷ The generalization of this synthetic route^{48,49} followed the principles originally reported for the generalization of the preparation of **3a**.^{23,50}

The reactions of **9** or **10** with carboxylic acid chlorides give rise to the acylphosphanes **11**, which, in some individual cases, can be detected by ³¹P NMR spectroscopy.^{52,55} However, these compounds cannot be isolated since they undergo rapid [1,3]-silyl shifts to furnish the phosphalkenes **12** of which the *Z* isomers predominate. It is not yet known which isomer takes part in the elimination reaction to produce the phosphalkyne **3** more readily. In some cases the thermal conditions of the elimination are so drastic that it is highly probable that an *E/Z* isomerization step—also catalyzed by NaOH—may precede the cleavage of hexamethyldisiloxane.

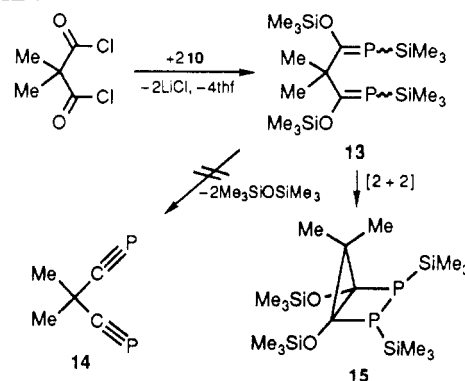
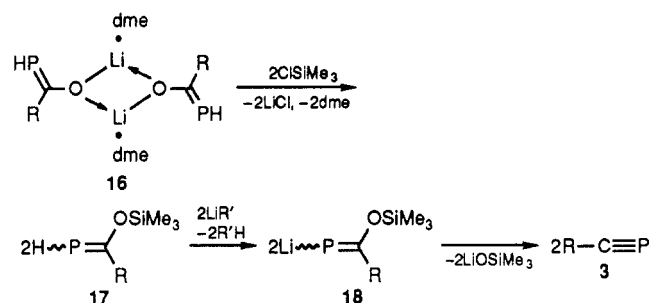
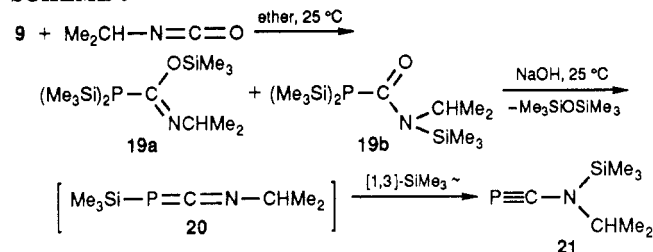
It has been found advantageous not to perform the reaction **12** \rightarrow **3** in solution, as originally reported,²³ but

TABLE 1. Kinetically Stabilized Phosphaalkynes (3a,d-q) Prepared by Elimination of Hexamethyldisiloxane from Phosphaalkenes

phosphaalkyne	yield, %	^{31}P	ref
 3a	76, 96	-69.2	23, 24
 3d	96	-62.0	49, 51
 3e	83	-57.7	51
 3f	76	-57.0	48
 3g	66	-66.0	48
 3h	83	-66.9	52
 3i	12-18	-17.5	53
 3j	43	+2.5	51
 3k	10-15	+34.4	54
 3l	63	-64.3	48
 3m	41	-59.3	51
 3n	49	-53.9	51
 3o	28	-60.9	51
 3p	29	-62.9	51
 3q	75	-51.4	48

rather to work at temperatures of 120–200 °C in the absence of a solvent.^{24,48,49} Using this variation, it was possible to prepare not only phosphaalkynes with tertiary carbon substituents (3a,d–g,j) but also those with secondary carbon substituents (see Table 1). In addition, tetrabutylammonium fluoride on silica gel (12h → 3h)⁵² and diiron nonacarbonyl ((*E/Z*-12a → 3a)⁵⁰ are also able to bring about the elimination reactions; in the cases of 3i⁵³ and 3k⁵⁴ no auxiliary reagents are necessary.

One of the limits of this synthetic methodology is apparent when attempts are made to prepare the bis(phosphaalkyne) 14 by this route (Scheme 7).

SCHEME 7**SCHEME 8****SCHEME 9**

The bis(phosphaalkene) 13 is, without doubt, formed in the reaction of dimethylmalonic acid dichloride with 10; however, instead of undergoing the desired elimination to produce 14, it rather rearranges via an intramolecular [2 + 2]-cycloaddition reaction to furnish the 2,3-diphospha-bicyclo[2.1.0]pentane 15.⁵⁷

4. Of Lithium Trimethylsilylanolate

The elimination of lithium trimethylsilylanolate from the phosphaalkenes 18 to furnish 3⁵⁸ represents a variation of the reaction 12 → 3 which takes place under very mild conditions. Key substances in this process are the complexes 16⁵⁹—obtained from carboxylic acid chlorides and LiPH₂·dme—which are successively silylated (→17) and lithiated (→18) before the spontaneous elimination step (→3) can occur (Scheme 8).⁵⁸

B. Rearrangement Reactions

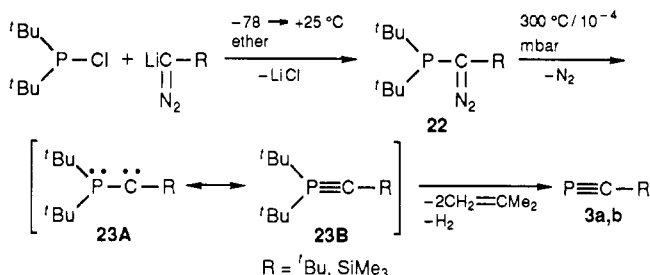
The decisive step in the preparation of a donor-substituted phosphaalkyne is the [1,3] shift of a trimethylsilyl group.⁶⁰ Reactions of this type are well-known in carbodiimide chemistry.⁶¹ Starting materials are 9 and isopropyl isocyanate, which react to form a tautomeric mixture of 19a and 19b. The latter mixture can be subjected to the NaOH-catalyzed elimination of hexamethyldisiloxane (Scheme 9).

TABLE 2. Selected Physical Properties of H—C≡P (1a) and ^tBu—C≡P (3a)

property	H—C≡P (1a)	ref	^t Bu—C≡P (3a)	ref
P≡C bond length, Å	1.5421 (5)	67	1.536 (2)	68, 68a
first ionization potential (π MO), eV	10.79	69	9.70	70
second ionization potential (n _r MO), eV	12.86	69	11.45	70
NMR (δ)				
¹ H	2.90 ^a (² J _{P,H} = 44.0 Hz)	22, 32	1.15 ^b (⁴ J _{P,H} = 0.9 Hz)	23
¹³ C	158.0 ^a (¹ J _{P,C} = 56.0 Hz)	32	184.8 ^c (¹ J _{P,C} = 38.5 Hz, ² J _{P,C} = 18.2 Hz, ³ J _{P,C} = 6.0 Hz)	23
³¹ P	-32 ^{a,d}	22, 32	-69.2 ^{c,d}	23

^a CD₂Cl₂, -80 °C. ^b Pure compound. ^c C₆D₆. ^d External H₃PO₄.

SCHEME 10



The 1-aza-3-phosphaallene **20** is presumed to be the initial product but it cannot be detected since the phosphaaalkyne **21** (56% yield),⁶⁰ resulting from a silyl group shift, is probably more stable thermodynamically.

C. Flash Vacuum Pyrolysis of Phosphino Diazo Compounds

A further novel method for the synthesis of phosphaaalkynes is based on the presence of substituents capable of undergoing elimination on neighboring phosphorus and carbon atoms. This prerequisite is found, for example, in the di-*tert*-butyl-substituted phosphino diazo compounds **22** (Scheme 10), which are accessible by the electrophilic diazoalkane substitution⁶² of lithiated diazo compounds with di-*tert*-butylchlorophosphane.⁶³

Under relatively mild flash vacuum pyrolysis conditions, the phosphino diazo compounds **22** can be converted into phosphaaalkynes (e.g., to **3a** in 50% yield, to **3b** in 30% yield).⁶³ A phosphinocarbene or a λ⁵-phosphaalkyne (**23A** ↔ **23B**¹⁵), respectively, is assumed to be the intermediate in this double-α-elimination reaction.

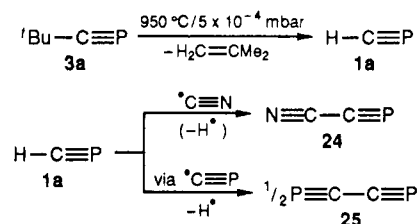
D. Transformation of Other Phosphaalkynes

Since short-lived phosphaaalkynes can be generated by flash pyrolysis (4 → 1), it is not surprising that **3a** can be converted to **1a** by cleavage of isobutylene in the same way (Scheme 11).²²

Even though this reaction is not complicated by the simultaneous evolution of hydrogen chloride, as is the case in the transformation **4a** → **1a**, the synthetic expenditure required for **3a** and the low yield of **1a** (approximately 10%)²² negate any possible advantages in comparison to the generation of **1a** from dichloromethylphosphane.

The hydrogen atom of the parent compound **1a** can be substituted by a cyano group in a radical process (**1a** → **24**). The required cyano radical is generated from cyanazide in a pyrolysis oven into which **1a** is passed simultaneously.³¹ An interesting observation should be

SCHEME 11



mentioned in this context: the formation of 1,4-diphospha-1,3-diyne (**25**) as a byproduct of the flash vacuum pyrolysis of **4a**. This diyne can be trapped as a diazaphosphole of the type **6** by reaction with a diazoacetate.³⁸ The formation of **25** is explained as follows: HC≡P is partially cleaved radically, and the [•]C≡P radicals thus generated dimerize when the reaction mixture is allowed to warm up.

IV. Some Selected Physical Properties of Phosphaalkynes

The two phosphaaalkynes **1a** and **3a** have been thoroughly investigated with regard to their general thermal behavior and spectroscopic properties. At the same time, they serve as typical representatives of the short-lived and kinetically stabilized phosphaaalkynes.

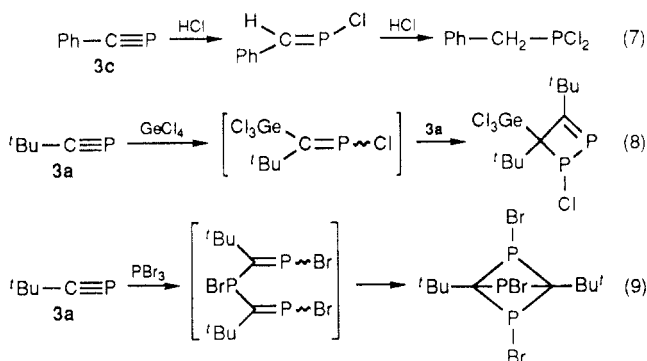
Phosphaacetylene (**1a**) is highly reactive and pyrophoric; it is best handled in dilute solutions. It can be stored for longer periods of time in toluene solution at -70 °C; on allowing the solution to warm, white phosphorus, among other products, is formed.²² Under reduced pressure, **1a** is even capable of existence at room temperature;⁶⁴ its occurrence in interstellar space has been confirmed.^{65,66}

In contrast, *tert*-butylphosphaacetylene (**3a**) is a stable liquid boiling at 61 °C.²³ At temperatures in excess of 130 °C, **3a** undergoes slow cyclo-tetramerization (see below); however, it is also able to take part in reactions with dienophiles at even higher temperatures. In comparison to **1a**, the sensitivity of **3a** toward oxygen is considerably reduced.

Some selected physical data for **1a** and **3a** such as bond lengths, first and second ionization potentials, and ¹H, ¹³C, and ³¹P NMR spectroscopic resonances are summarized in Table 2. As expected, these data show some graduated but no principal differences.

The ionization potentials of **1a** and **3a** are lower than those of the corresponding nitriles;⁷¹ this property is also reflected in the much more pronounced ligand behavior of the phosphaaalkynes in comparison with that of their nitrogen analogues.^{11,12} The C≡P stretching frequency of **3a** is 1533 cm⁻¹,²³ that of **1a** was given as 1278 cm⁻¹.²¹ The latter result will probably have to be corrected in favor of a higher value (**1b**, 1559 cm⁻¹).⁷² A recently

SCHEME 12



performed crystal structure analysis of **3k** gave a $\text{P}\equiv\text{C}$ bond length of 1.516 (13) Å;⁷³ this is comparable with the values established for **1a** and **3b** by other methods (see Table 2).

For the preparative chemist, the NMR spectroscopic data of the $\text{P}\equiv\text{C}$ structural unit of the phosphalkynes are of particular interest. The ^{13}C NMR signals are observed in the region $\delta = 154\text{--}201$ with, in some cases, a widely varying doublet splitting ($^1J_{\text{C,P}} = 14\text{--}56$ Hz). The ^{31}P NMR resonances are to be found in the high-field region (negative δ values). The presence of silyl and aryl substituents give rise to pronounced paramagnetic shifts of the signals; thus **3b** exhibits a ^{31}P NMR chemical shift of $\delta = +96$ ²⁵ (for further individual examples, see Table 1).

V. Reactions of Phosphaalkynes

Naturally, the reactivity of the P/C triple bond is molded by its addition behavior. For synthetic purposes, the most interesting feature is the clean conversion of a $\lambda^3\sigma^1$ -phosphorus atom into a $\lambda^3\sigma^2$ -phosphorus atom which can frequently be realized and which, above all, is achieved in [2 + 1]-, [3 + 2]-, and [4 + 2]-cycloaddition processes. These reactions have opened up completely new aspects in the chemistry of cyclic phosphorus compounds containing P/C double bonds. In contrast, the synthetic exploitation of 1,2-addition reactions has only just started.

A. 1,2-Addition Reactions

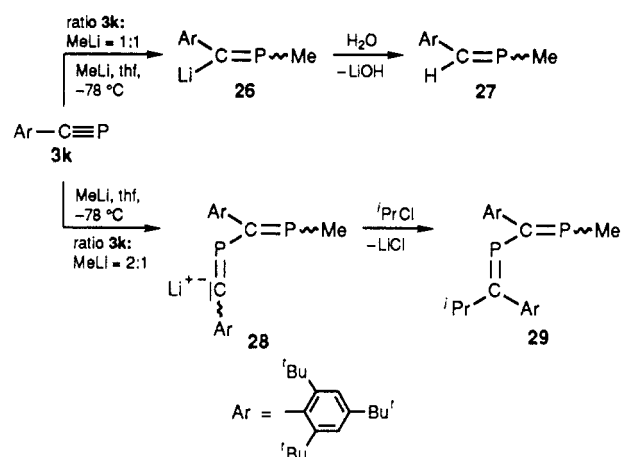
1. With Halogen Compounds

The ability of phosphalkynes to undergo addition to hydrogen chloride accompanied the discovery of the compounds themselves. In the cases of **1a**,²¹ **1b**,³³ **3b**,²⁵ and **3c**,²⁶ addition of HCl leads finally to complete saturation of the P/C triple bonds. In the case of **3c**, an initial cis addition of HCl is assumed to be followed by a further addition of HCl in the same orientation (eq 7 (Scheme 12)).²⁶ The specific orientation is followed without exception and reflects the charge distribution in the phosphalkynes.⁷⁴

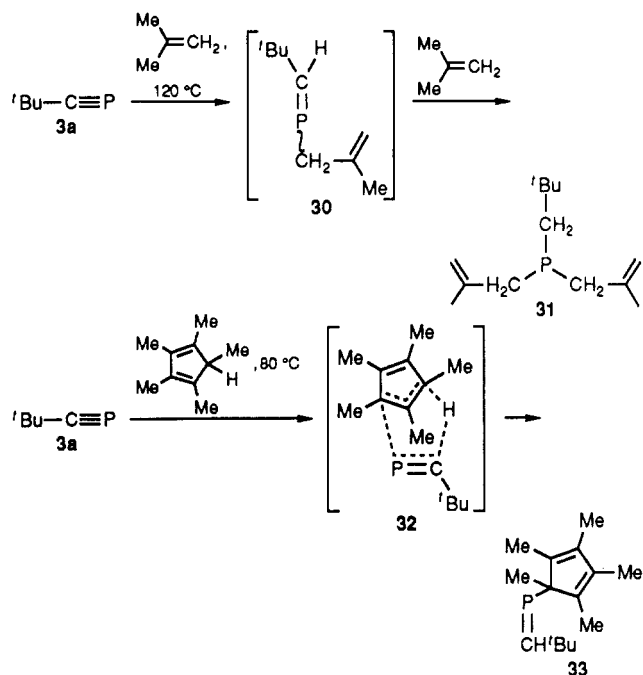
The addition of halogens to phosphalkynes is not specific and is followed in a second step by the complete saturation and finally even in the cleavage of the P/C single bond.^{50,75} Similar to halogens, boron tribromide and tin(IV) chloride undergo nonstereospecific additions to **3a** in which the metal moieties are always bonded to the carbon atom.⁷⁵

Germanium tetrachloride and phosphorus tribromide also take part in 1,2-additions to **3a**, albeit in differing

SCHEME 13



SCHEME 14



molar ratios.^{50,75} In neither reaction can the phosphalkene intermediate be detected. In the case of GeCl_4 , a subsequent [2 + 2] cycloaddition of **3a** according to (eq 8) follows,⁷⁵ whereas with PBr_3 the reaction is completed by intramolecular saturation according to (eq 9).^{50,75}

2. With Organolithium Derivatives

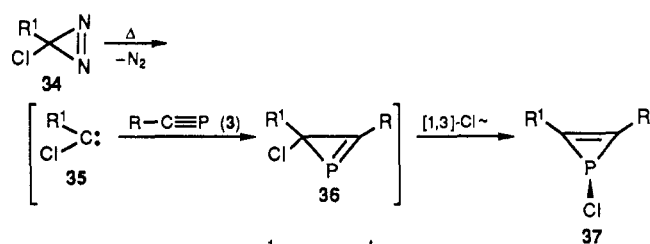
The 1,2-addition of methyllithium to the aryl phosphalkyne **3k** is dependent on the molar ratio of the reaction components and can thus be guided (Scheme 13).⁷³

The lithiated phosphalkene **26** is the initial product of the 1:1 reaction with the expected orientation of the reaction partners and can be hydrolyzed to form **27**.⁷³ In the 2:1 reaction, the primarily formed phosphalkene **26** is converted to **28** by reaction with excess phosphalkyne **3k**. Subsequent alkylation with isopropyl chloride then furnishes the 1,3-diphosphadiene **29**.⁷³

3. With Enophiles

Ene reactions of phosphalkynes require a remarkable thermal activation. Thus, reaction of isobutylene

SCHEME 15



- 36,37a, R¹ = Ph, R = ^tBu
 b, R¹ = R = ^tBu
 c, R¹ = PhO, R = ^tBu
 d, R¹ = MeO, R = ^tBu
 e, R¹ = Ph, R = 1-adamantyl
 f, R¹ = Ph, R = C(Me₂)Et
 g, R¹ = PhO, R = C(Me₂)Et

with **3a** at 120 °C gives rise to the phosphane **31** (Scheme 14).⁷⁶ The formation of **31** is most easily explained when it is assumed that the ene reaction of **3a** to give **30** is followed by a further ene reaction of the phosphalkene **30** with another molecule of isobutylene to produce the final product **31**.⁷⁶ The analogous reaction of **3a** with 2,2-dimethyl-2-butene, which is sterically more demanding than isobutylene, at 130 °C stops at the phosphalkene intermediate corresponding to **30**.⁷⁶

Cyclopentadiene and some of its substituted derivatives, but not, however, pentamethylcyclopentadiene, take part in smooth Diels–Alder reactions (see below) with **3a**. Pentamethylcyclopentadiene is more electron rich in comparison to the other derivatives and, at the same time, is more sterically handicapped so that an ene reaction takes place instead of the cycloaddition process.⁷⁷ On the basis of the accepted mechanistic considerations for ene reactions, the transition state **32** should be responsible for the formation of the (phosphavinyl)cyclopentadiene **33**. The phosphalkene moiety of **33** exhibits dynamic behavior at room temperature; the [1,5]-sigmatropic reaction can be frozen out and the activation energy barrier determined as 46 kJ·mol⁻¹ by ¹H NMR spectroscopy.⁷⁷ The principles of this phenomenon were previously known from cyclopentadiene chemistry.⁷⁸

B. [2 + 1]-Cycloaddition Reactions

The [2 + 1]-cycloaddition reactions of electron-deficient species represent a universal access into the chemistry of three-membered ring systems containing P=C increments; some of the products thus obtained are also capable of undergoing subsequent rearrangement reactions.

1. With Carbenes

Carbenes are often generated photochemically or thermally from diazo compounds, which, of course, prohibits the use of this methodology for reactions with phosphalkynes since the latter compounds themselves take part in rapid 1,3-dipolar cycloaddition reactions with diazoalkanes to form 1,2,4-diazaphospholes. For this reason, cycloisomers of the diazo compounds, i.e., the diazirines, were chosen as carbene precursors. In general, the phosphalkyne is used in excess as both reactant and solvent and the reactions are carried out at between 25 and 150 °C. The choice of the reaction

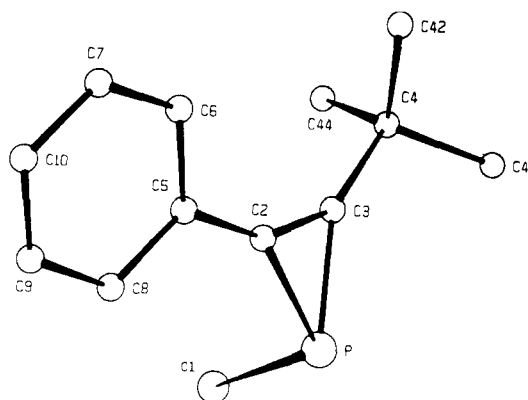
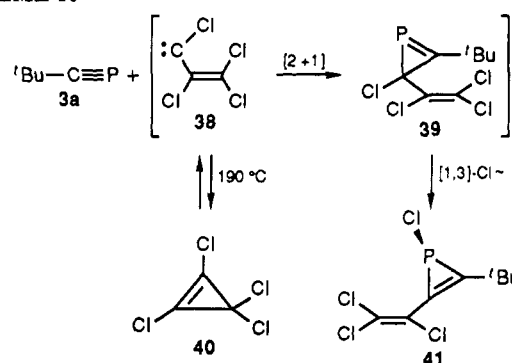


Figure 1. Crystal structure analysis of **37a** (hydrogen atoms neglected). Selected bond lengths (Å) and angles (deg): P–C2 = 1.784 (4), P–C3 = 1.784 (4), C2–C3 = 1.303 (5), C1–P = 2.166 (2); C2–P–C3 = 42.9 (2), P–C2–C3 = 68.4 (2), P–C3–C2 = 68.7 (2), Cl–P–C2 = 104.2 (1), Cl–P–C3 = 103.7 (1).

SCHEME 16



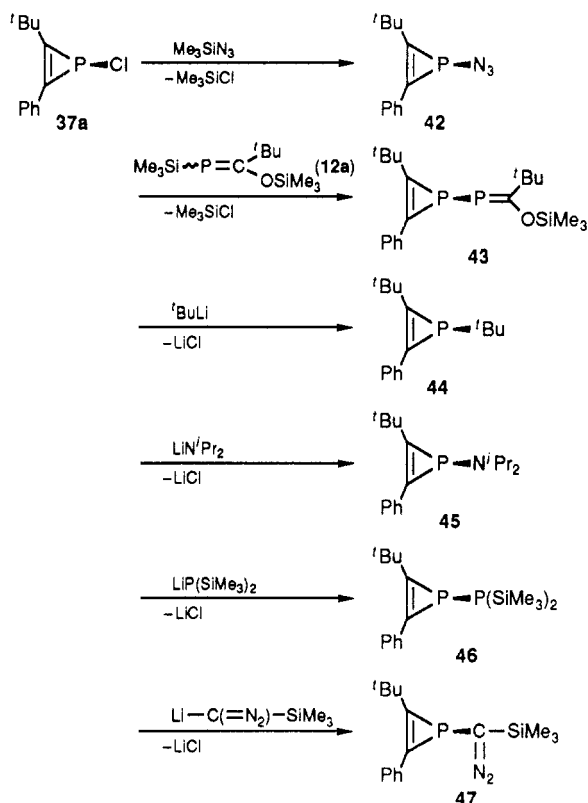
temperature is governed by the thermal stability of the respective diazirine.⁷⁹

It is at first surprising that reactions of chloro-substituted diazirines **34** or carbenes **35** with kinetically stabilized phosphalkynes **3** do not give rise to the 2*H*-phosphirenes **36** but rather to their 1*H*-isomers **37** (26–63% yields) (Scheme 15). The primarily formed adducts must, therefore, have rearranged by means of [1,3]-chlorine shifts.⁷⁹ From a thermodynamic point of view, the 1-chloro-1*H*-phosphirenes are apparently more stable than the corresponding 2*H* isomers. Compounds of the type **37** formally represent antiaromatic systems (four π electrons) but, since the environment at the phosphorus atom is not planar, the antiaromatic destabilization is lacking. A crystal structure analysis of **37a** showing an angle of 105° at chlorine is in agreement with the above state of affairs.⁸⁰ The P/Cl bond is relatively long [2.166 (2) Å] and this is certainly in part responsible for the readily achieved nucleophilic substitution of the chlorine (see below and also Figure 1). This feature provides the actual synthetic value of the reaction.

The general nature of the reaction sequence **3** + **35** → **36** → **37** is further emphasized by the reaction of **3a** with perchlorovinylcarbene (**38**). The latter substrate exists in a thermal equilibrium with tetrachlorocyclopropene (**40**)⁸¹ and can be trapped by the phosphalkyne (Scheme 16).⁸²

In this case also, the 2*H*-phosphirene **39** cannot be detected since it undergoes isomerization via a chlorine shift to furnish the 1*H*-phosphirene **41**.⁸² All 1-chloro-1*H*-phosphirenes are sensitive toward hydrolysis reactions in which the corresponding 1-hydroxy-1*H*-

SCHEME 17



phosphirene is formed in the first step. Depending on the pH value of the reaction mixture, the 1-hydroxy-1H-phosphirene can undergo ring opening to furnish the corresponding phosphonic acid or condensation to yield the bis(1H-phosphirenyl) ether.⁸⁰

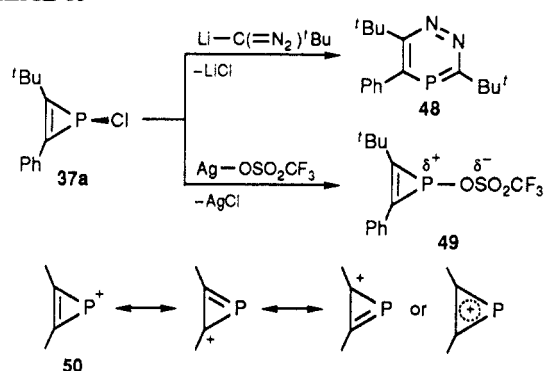
The above-mentioned nucleophilic exchange reactions of 1-chloro-1H-phosphirenes can be achieved in two ways. Starting from 37a as a model compound, the chlorine atom can be substituted by reaction with a silylated nucleophile such as trimethylsilyl azide or also with the silylated phosphalkene 12a to furnish 42 or 43, respectively.⁷⁹ These reactions even take place at room temperature and, of course, profit from the Si/Cl bond energy (Scheme 17).

In the second method, 37a is allowed to react with *tert*-butyllithium or the lithium derivatives of diisopropylamine, bis(trimethylsilyl)phosphane, and diazo(trimethylsilyl)methane in aprotic solvents. The reactions occur in the thawing cold trap and compounds 44–47 are formed very selectively. The subsequent chemistry of these compounds is fascinating and will be illustrated by two examples.

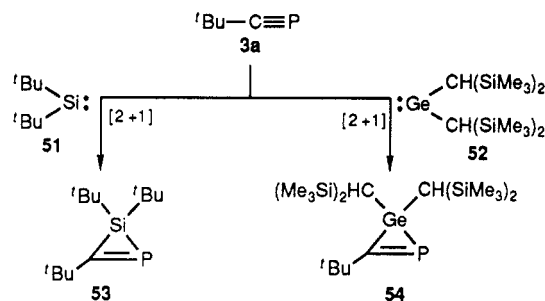
When 37a is allowed to react with lithiated 1-diazo-2,2-dimethylpropane, an initial nucleophilic substitution takes place according to $37a \rightarrow 47$. The corresponding diazo compound, however, cannot now be isolated since it immediately undergoes isomerization to the phosphabenzene 48 (Scheme 18).⁸³ λ^3 -Phosphabenzene with two further heteroatoms in the ring were previously unknown. The reaction bears a strong resemblance to the (diazomethyl)cyclopropene/pyridazine rearrangements.⁸⁴

1-Chloro-1H-phosphirenes 37 should serve as suitable substrates for the generation of phosphirenylium cations of the type 50. Hückel aromatic compounds with this structure have not yet been mentioned in the literature. When 37a is allowed to react with silver tri-

SCHEME 18



SCHEME 19



fluoromethanesulfonate (triflate), the 1-triflyloxy-1H-phosphirene 49 (100% yield, ^{31}P NMR: $\delta = -9$) is obtained. It is difficult to believe that a triflate group has taken part in a nucleophile substitution. Rather, the result is indicative of the intermediate occurrence of the phosphirenylium cation being responsible for the product formation.⁸⁰ Also, the fact that 49 can be used in electrophilic aromatic substitutions provides further evidence for the existence of species of the type 50.⁸⁰

2. With Silylenes and Germylenes

Silylenes and germylenes—which are similar to carbenes in their reactivities—undergo analogous addition reactions with phosphalkynes. However, and in contrast to the reactions of chlorocarbenes, the primary adducts containing $\lambda^3\sigma^2$ -phosphorus atoms can be isolated.

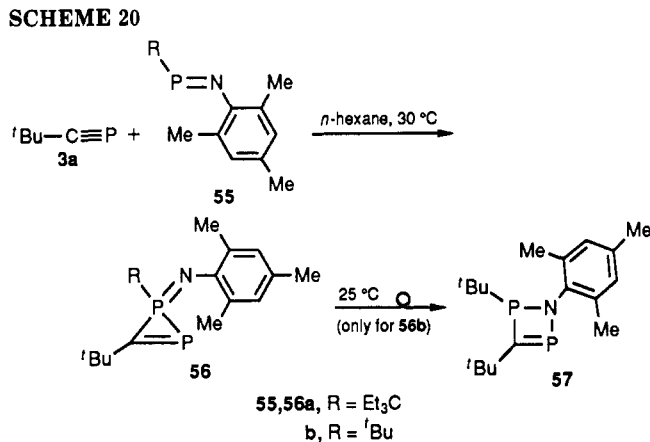
The silylene 51, generated photochemically by cycloelimination from hexa-*tert*-butylcyclotrisilane, readily adds to 3a, as well as to other phosphalkynes, to furnish the phosphasilirene 53 (^{31}P NMR: $\delta = 274.0$) (Scheme 19).⁸⁵ The structure of this three-membered-ring compound has been confirmed by an X-ray diffraction analysis of its end-on coordinated complex with tungsten pentacarbonyl. The required complex was prepared from 53 (with a 1-adamantyl group in place of the *tert*-butyl group) and $[\text{W}(\text{CO})_5\cdot(\text{THF})]$.⁸⁵ The P/C double-bond length was found to be 1.686 Å.

The [2 + 1] cycloaddition of the germylene 52 onto 3a yields the first representative of the so far unknown phosphagermyrenes 54;⁸⁶ the P/C bond length amounts to 1.661 (11) Å.

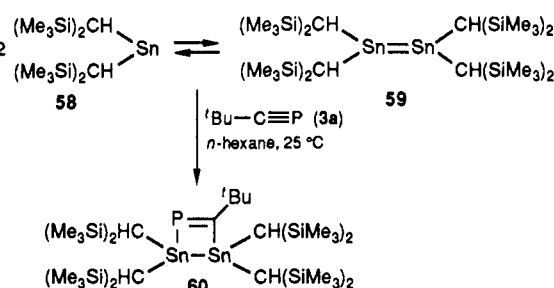
3. With Low-Coordinated Phosphorus Compounds

Iminophosphanes—compounds containing $\lambda^3\sigma^2$ -phosphorus atoms—do not take part in [2 + 2] cycloadditions, as could perhaps be expected in principle, but rather undergo [2 + 1] cycloadditions with phosphalkynes. Thus, the reactions of 3a with 55a,b give

SCHEME 20



SCHEME 21



rise to the dark red diphosphirenes **56a,b** already at -30°C (^{31}P NMR: $\delta = 351.0$ and 349.4 , respectively, for the coordinatively unsaturated phosphorus atoms) (Scheme 20).⁸⁷

Whereas compound **56a** is stable in solution at room temperature, under the same conditions compound **56b** undergoes ring expansion to form the 1,2,4-azadiphosphetine **57**, which is presumably more stable from an energetic point of view than the three-membered-ring isomer.⁸⁷ There are also some indications that the tungsten pentacarbonyl complex of phenylphosphinidene $[(\text{CO})_5\text{W}=\text{P}-\text{Ph}]$ ⁸⁸ takes part in a $[2 + 1]$ -cycloaddition reaction with **3a** as well.⁸⁹

C. $[2 + 2]$ -Cycloaddition Reactions

In contrast to the $[2 + 1]$ -, $[3 + 2]$ -, and $[4 + 2]$ -cycloaddition reactions of phosphaalkynes, the significance of $[2 + 2]$ -cycloaddition processes of these substrates to date has been extremely modest. With the exception of the Diels-Alder reactions of **3** with cyclobutadienes and azacyclobutadienes, which, although they can, in principle, be considered as $[2 + 2]$ cycloadditions, will be discussed later, to date only one example of this reaction type has been reported and even this has not yet been confirmed unequivocally.

Thus, when the stannylidene **58** is allowed to react with **3a** under moderate conditions, the phosphadi-stannacyclobutene **60** is formed. The structure of the product has been unambiguously elucidated [P/C bond length: $1.697(11)$ Å] (Scheme 21).⁹⁰

A $[2 + 2]$ -cycloaddition reaction between **3a** and the distannene **59**, which is in equilibrium with the monomer **58**, is assumed to be responsible for the formation of **60**.⁹¹

The phosphaalkyne **3a** is justifiably considered as being thermally stable; it can be distilled without difficulty and can be made to react with suitable cycloaddition reagents at temperatures up to 180°C (see

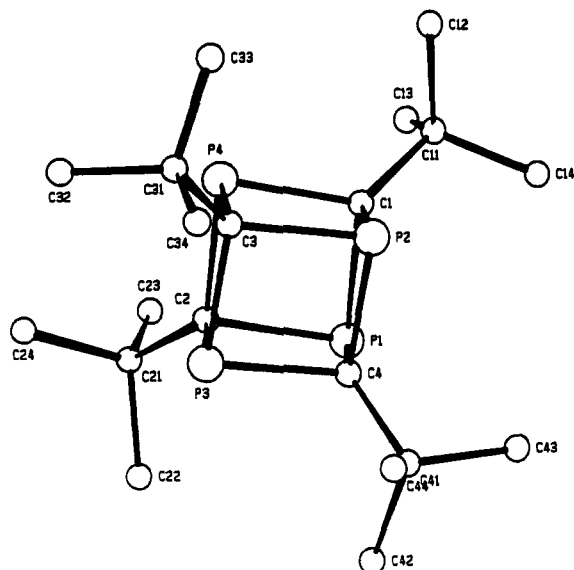
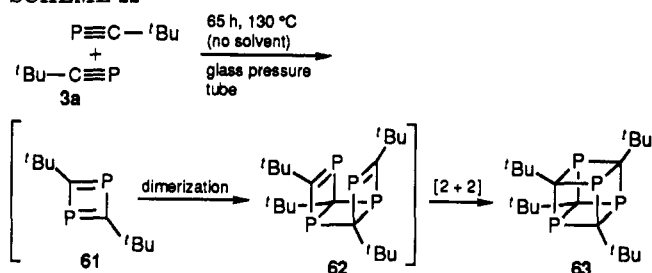


Figure 2. Crystal structure analysis of **63**. Selected bond lengths (Å) and angles (deg): P1-C1 = 1.880 (3), P1-C2 = 1.886 (3), P1-C4 = 1.877 (3), P2-C1 = 1.883 (3), P2-C3 = 1.891 (3), P2-C4 = 1.882 (4), P3-C2 = 1.881 (3), P3-C3 = 1.875 (4), P3-C4 = 1.886 (3), P4-C1 = 1.885 (3), P4-C2 = 1.876 (3), P4-C3 = 1.875 (4); C1-P1-C2 = 85.4 (1), C1-P1-C4 = 85.7 (1), C2-P1-C4 = 85.6 (1), C1-P2-C3 = 85.5 (2), C1-P2-C4 = 85.5 (1), C3-P2-C4 = 85.7 (2), C2-P3-C3 = 85.0 (2), C2-P3-C4 = 85.5 (1), C3-P3-C4 = 86.1 (2), C1-P4-C2 = 85.6 (1), C1-P4-C3 = 85.9 (1), C2-P4-C3 = 85.2 (2), P1-C1-P2 = 94.2 (2), P1-C1-P4 = 94.3 (2), P2-C1-P4 = 94.1 (1), P1-C2-P3 = 94.2 (2), P1-C2-P4 = 94.3 (2), P3-C2-P4 = 94.7 (1), P2-C3-P3 = 93.9 (2), P2-C3-P4 = 94.2 (2), P3-C3-P4 = 94.9 (2), P1-C4-P2 = 94.3 (2), P1-C4-P3 = 94.4 (2), P2-C4-P3 = 93.9 (2).

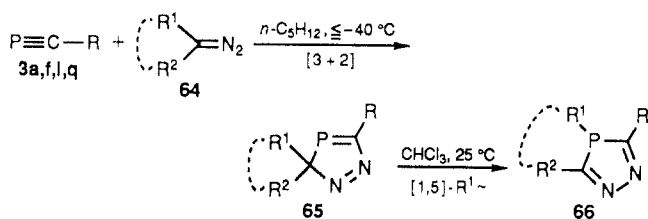
SCHEME 22



below). However, when it is heated in the absence of solvents and other reaction partners at temperatures $\geq 130^\circ\text{C}$, a cyclotetramer with the confirmed structure of the tetraphosphacubane **63** is formed together with other products.⁹² Previously, it was only known that cyclodimerization⁹³ and also cyclotrimerization⁹⁴ could be realized in the coordination sphere of metals; this continues to be valid for cyclooligomerizations of higher orders (Scheme 22).⁹⁵

The pentacyclic structure of the tetramer **63** can be deduced from its NMR spectra; hence, the skeletal carbon atoms as well as the central carbon atoms of the *tert*-butyl groups each constitute the A parts of AX_3Y spin systems which are split by coupling with three magnetically equivalent and one further nonequivalent phosphorus atom. The ^{13}C NMR signal observed for the cage carbon atoms at $\delta = -29.07$ and the low field position of the phosphorus resonance ($\delta = 257.4$) are indicative of a considerable displacement of the electron density from phosphorus to carbon.⁹² In comparison to the unsubstituted cubane (internal angle 90°),⁹⁶ the C-P-C angles in **63** are smaller (85.6°) and consequently the P-C-P angles are larger (94.4°). The av-

SCHEME 23



- 65,66a, R = *t*Bu; R¹ = R² = *t*Bu
 b, R = *t*Bu; R¹ = *t*Bu; R² = Me
 c, R = *t*Bu; R¹ = R² = *i*Pr
 d, R = *t*Bu; R¹ - - R² = -CMe₂CH₂CMe₂-
 e, R = *t*Bu; R¹ - - R² = -CMe₂(CH₂)₂CMe₂-
 f, R = *t*Bu; R¹ - - R² = -CMe₂(CH₂)₃CMe₂-
 g, R = *t*Bu; R¹ - - R² = -CMe₂(CH₂)₄CMe₂-
 h, R = *t*Bu; R¹ = R² = CF₃
 i, R = 1-methylcyclohexyl; R¹ = R² = *t*Bu
 j, R = *i*Pr; R¹ = R² = *t*Bu
 k, R = CH₂*t*Bu; R¹ = R² = *t*Bu

erage P/C bond length in the cube amounts to 1.881 Å and thus agrees well with those of the 1,3-diphosphacyclobutanes⁹⁷ (see Figure 2).

A plausible interpretation of the cyclotetramerization of **3a** to **63** is not possible without the assumption of an initial head-to-tail dimerization of the phosphalkyne to furnish the λ³-1,3-diphosphete **61**. The actual dimerization in the sense of a Diels-Alder reaction gives rise to the tricyclic product **62** and the P=C moieties of **62** provide the still absent bonds of the cubane by way of an intramolecular [2 + 2]-cycloaddition process.⁹²

D. [3 + 2]-Cycloaddition Reactions

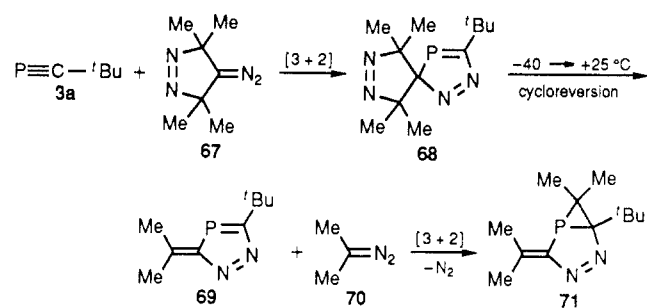
1,3-Dipolar cycloaddition reactions of diazonium and nitrilium betaines to phosphalkynes constitute a major extension of the synthetic methodology for phospholes.^{49,98,99} Previously, compounds of these types, which have played a major role in the development of the chemistry of low-coordinated phosphorus compounds, were generally synthesized by means of condensation reactions.^{100,101} Azomethine dipoles as well undergo ready addition to the P/C triple bond; however, in contrast to the diazonium and nitrilium betaines, which, with a few exceptions, add regioselectively to phosphalkynes, the formation of regioisomeric heterocyclic products is observed in the reactions with the azomethine dipoles.

1. With Diazo Compounds

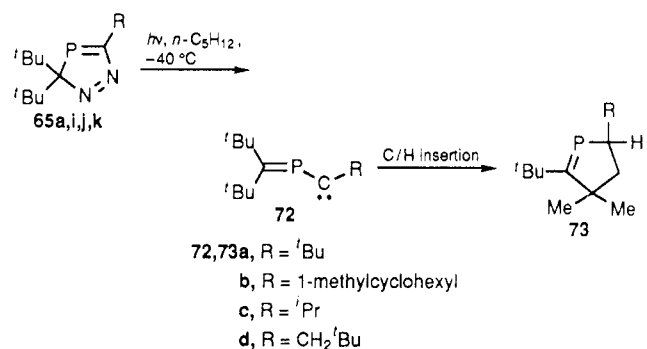
The primary products, i.e., 3*H*-1,2,4-diazaphospholes, can only be isolated from the reactions of phosphalkynes with diazo compounds when the latter are doubly substituted with substituents that are unable to undergo sigmatropic [1,5] shifts in the product. Diazo-methane, monosubstituted diazomethanes, and also diazocarbonyl compounds, on the other hand, give rise to 2*H*-1,2,4-diazaphospholes after proton or acyl group shifts.

(a) *To 3H-1,2,4-Diazaphospholes.* Diazoalkanes of the type **64** undergo regioselective [3 + 2]-cycloaddition reactions with alkyl-substituted phosphalkynes **3** even at -40 °C to produce 3*H*-1,2,4-diazaphospholes **65** (92–100% yields).^{49,80,102,103} These products possess 1,3-heterodiene character and this is also reflected in

SCHEME 24



SCHEME 25



their low-field ³¹P NMR chemical shifts (δ = 263–204). The adducts **65d,e** cannot be isolated as a result of sigmatropic [1,5]-R¹ group shifts which end at phosphorus (→**66d,e**) and not, as could be expected, at nitrogen.⁸⁰ Analogous isomerizations of **65a-c,f-k** (→**66a-c,f-k**) take place on storage in chloroform solution at room temperature; these reactions are assumed to be catalyzed by protons (Scheme 23).^{80,103}

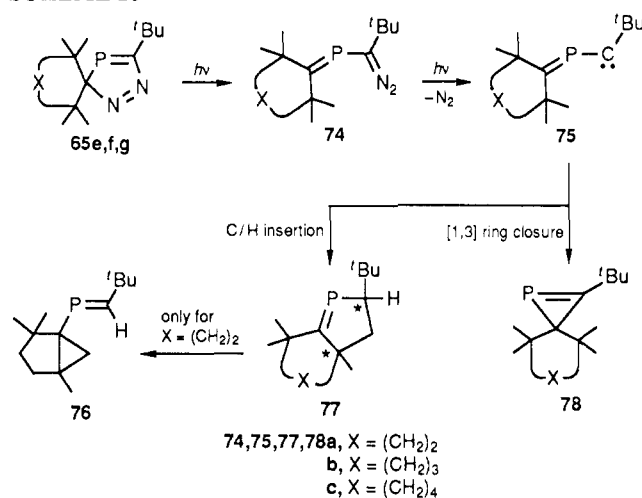
A 4*H*-1,2,4-diazaphosphole **66** (R = *t*Bu; R¹ = R² = Ph) is the product obtained from the reaction of diazodiphenylmethane with **3a**; the probable primary intermediate, the 3*H*-1,2,4-diazaphosphole, cannot be isolated, and the structure of the end product has been confirmed by a crystal structure analysis.¹⁰⁴ The 4*H*-1,2,4-diazaphospholes **66a,i-k**, which all possess *tert*-butyl substituents at phosphorus, undergo quantitative cleavage of isobutylene and subsequent H shifts to furnish 2*H*-1,2,4-diazaphospholes when subjected to thermal stress.^{80,102}

The 3*H*-1,2,4-diazaphosphole **68** is most certainly the initial product from the reaction of **3a** with the diazopyrazoline **67**; however, it presumably undergoes a sigmatropic rearrangement to give the corresponding 4*H* isomer. When the latter is allowed to warm from -40 to +20 °C, nitrogen is evolved and the heterobicyclic product **71** is formed (Scheme 24).⁸⁰

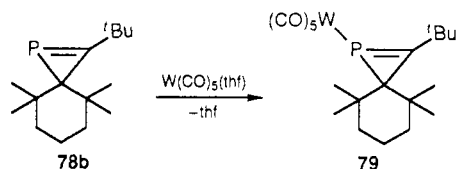
When it is assumed that **68** first undergoes [3 + 2] cycloreversion to give the isopropylidene-3*H*-1,2,4-diazaphosphole **69** and 2-diazopropane (**70**), the formation of **71** can easily be interpreted as proceeding through a [3 + 2]-cycloaddition process of the diazo dipole to the P/C double bond of **69** with subsequent elimination of nitrogen.⁸⁰

The isolation of the 3*H*-1,2,4-diazaphospholes was of particular interest since its photochemical decomposition could provide a potential entry into the chemistry of the previously unknown 2*H*-phosphirenes which contain λ³σ²-phosphorus atoms and represent P analogues of the cyclopropenes. An analogous synthetic route to the latter compounds is known.¹⁰⁵

SCHEME 26



SCHEME 27



When the heterocyclic compounds **65a,i-k** are excited photochemically, the 1-phospha-1-cyclopentenenes **73a-d** are formed in high yields (70–85%) (Scheme 25). The products exhibit characteristic low-field ³¹P NMR spectroscopic resonances ($\delta = 250.1\text{--}262.9$).^{80,102} Informally, the formation of these products can be explained by way of the phosphavinylcarbene intermediates **72a-d**. Apparently, the C/H insertion of the carbene center into a methyl group of the *tert*-butyl substituent leading to **73** is so rapid that the actual and hoped for [1,3]-ring closure to give the 2*H*-phosphirene cannot come into operation. The situation in the spirocyclic 3*H*-1,2,4-diazaphospholes **65e-g** is more suitable for phosphirene formation since the methyl group required for the insertion is held further away from the carbene center by the bridging ring elements so that this separation may indirectly favor the ring-closure reaction (Scheme 26).

Thus, the expectations are at least partly fulfilled: when the spirocyclic compounds **65e-g** are irradiated in pentane at -40°C , the carbene reactions $75 \rightarrow 77$ and $75 \rightarrow 78$ compete with each other although the C/H insertion reaction always dominates. After photolysis of **65e**, the isomerization product **76** is isolated in place of the expected condensed phosphabicyclo[3.3.0]octene **77a**.^{80,103} The product ratios of insertion versus [1,3]-ring closure amount to 1:4 [X = (CH₂)₂], 1:5 [X = (CH₂)₃], and 1:22 [X = (CH₂)₄].

The isolation and IR spectroscopic characterization of **74b**¹⁰³ have convincingly demonstrated that this reaction sequence does indeed commence with a ring opening to furnish a phosphavinyl diazoalkane. Since all of the 2*H*-phosphirenes obtained exhibited ³¹P NMR signals at unexpectedly high fields [**78a**: $\delta = 46.8$; **78b**: $\delta = 71.7$; and **78c**: $\delta = 73.4$; for comparison, the diastereomeric mixture of **77b** exhibits signals at $\delta = 238.5$ and 236.3], a crystal structure analysis of the tungsten pentacarbonyl complex **79** was performed (see also Figure 3).¹⁰³ The complex was prepared by the reaction of the 2*H*-phosphirene **78b** with W(CO)₅(THF) and

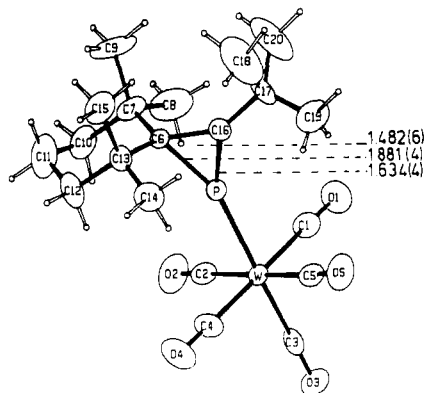
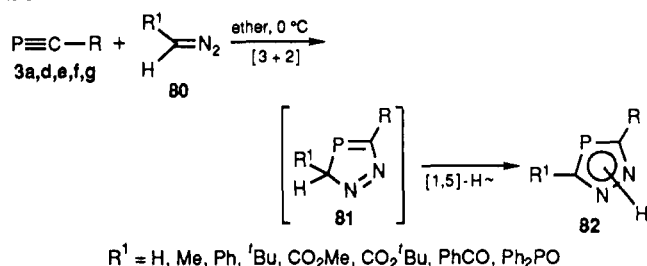


Figure 3. Crystal structure analysis of **79**. Selected bond lengths (Å) and angles (deg): P-C6 = 1.881 (4), P-C16 = 1.634 (4), C6-C16 = 1.482 (6), P-W = 2.458 (1); W-P-C6 = 157.7 (2), W-P-C16 = 153.1 (2), C6-P-C16 = 49.2 (2), P-C6-C16 = 56.7 (2), P-C16-C6 = 74.1 (3).

SCHEME 28



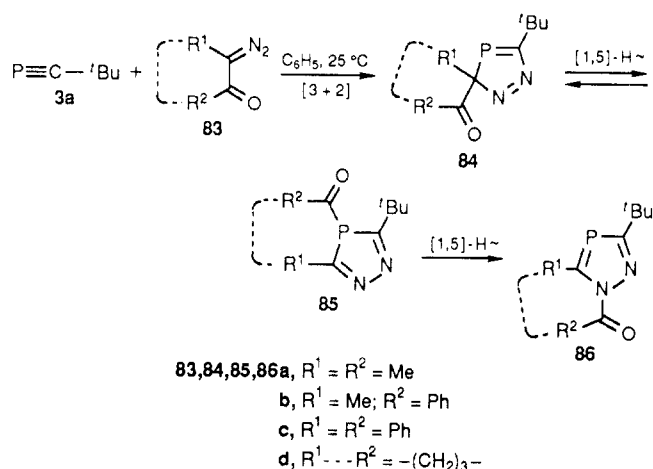
comprised exchange of the only loosely bound tetrahydrofuran ligand (Scheme 27).

The P/C double-bond length in **79** amounts to 1.634 (4) Å and is thus shorter than those of a comparable phosphasilirene complex⁸⁵ and other "end-on" coordinated complexes of open-chain phosphalkenes.^{106,107}

(b) *To 2H-1,2,4-Diazaphospholes.* Diazo compounds of the structural type **80** such as diazomethane, diazoethane, diazophenylmethane, 1-diazo-2,2-dimethylpropane, methyl and *tert*-butyl diazoacetates, 1-diazo-2-phenylethanone ("ω-diazoacetophenone"), and diazo(diphenylphosphoryl)methane all undergo addition to **3a**—for which the complete range of addition partners has been investigated—in the usual orientation to produce 2*H*-1,2,4-diazaphospholes of the type **82**.^{24,49,98,99} Only in the case of the reaction of **3a** with **80** (R¹ = COOMe) was it possible to detect the intermediate corresponding to **81** by NMR spectroscopy. In all other cases, the sigmatropic H shifts accompanied by the gain of aromatization energy were too rapid to permit the detection of the 3*H*-1,2,4-diazaphospholes (Scheme 28).

In the analogous cycloaddition of diazo(trimethylsilyl)methane (**80**, R¹ = SiMe₃) to **3a**, a silyl shift completely dominates over the H shift ($\rightarrow 82$, R = *t*Bu, R¹ = H, SiMe₃ instead of H).²⁴ It is not surprising that the phosphalkynes **3d,e**,⁵¹ **3f,g**,⁴⁸ and **3h**⁵² with similar, sterically demanding substituents also react with diazomethane in the above-mentioned manner. This is also valid for the short-lived species **1b**, which undergoes addition in the same orientation to other diazomethyl compounds as well.³⁴ Up to the present, the reaction of phosphacetylene (**1a**) with *tert*-butyl diazoacetate (**80**, R¹ = COOBu^t) is the only reported example of a diazoalkane addition to a P/C triple bond that does not proceed in an orientation-specific manner.²²

SCHEME 29



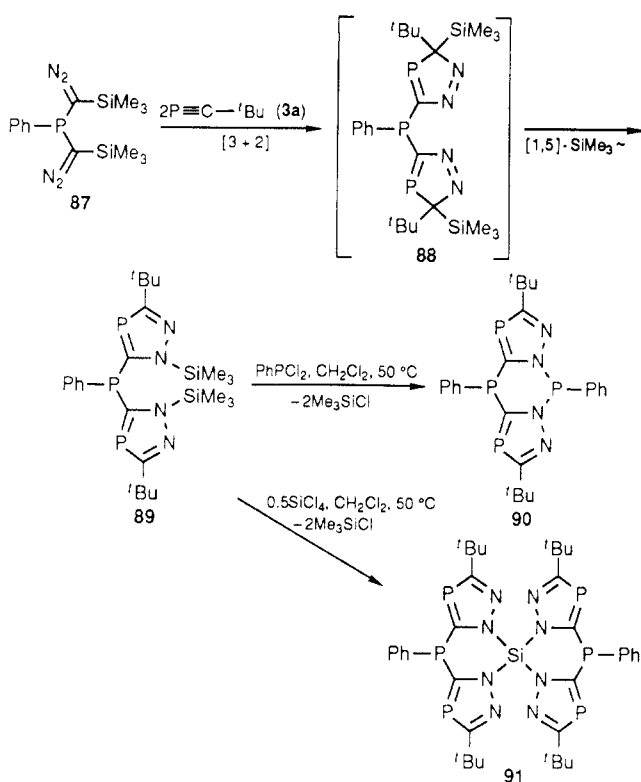
Both open-chain and cyclic α -diazo ketones such as **83a-d** react in a similar manner to the diazomethyl compounds **80** with the phosphalkyne **3a**, the only exception being that the sigmatropic H shift is replaced by an acyl shift.²⁴ Again, the 3-acyl-3*H*-1,2,4-diazaphospholes **84** cannot be detected or isolated since they rapidly rearrange to the corresponding 2-acyl-2*H* isomers **86**. In contrast to the reaction sequence **3** + **80** → **81** → **82**, it can be shown in the present case by ³¹P NMR spectroscopy that the sigmatropic [1,5]-acyl shift initially proceeds to phosphorus (**84** → **85**) and then ends at nitrogen (**85** → **86**).²⁴ The syntheses of "condensed" diazaphospholes (e.g., **86d**) are worthy of particular note since they open up new perspectives and can be generalized. Diazocamphor and diazoacacenaphthenone react analogously (Scheme 29).²⁴

The [3 + 2] cycloaddition of diazo compounds to phosphalkynes with subsequent substituent shifts can be extended into a promising and versatile synthesis of polycyclic systems containing numerous heteroatoms. Starting materials are the phosphalkyne **3a** and the bis- or tris(diazo) compounds **87** and **92** (Scheme 30).¹⁰⁸

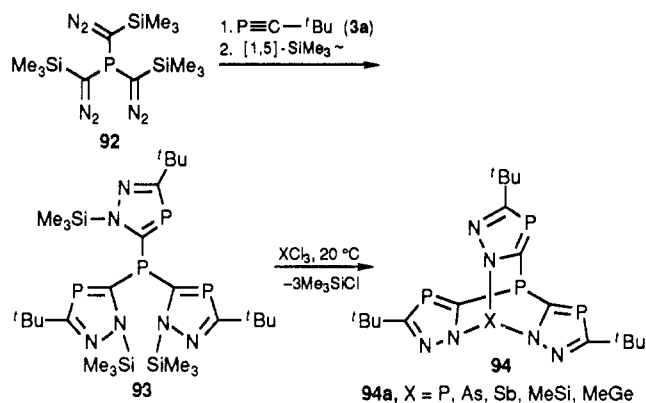
The bis(diazomethyl)phosphane **87** is readily accessible from dichlorophenylphosphane and lithiated diazo(trimethylsilyl)methane; its reaction with **3a** in a molar ratio of 1:2 gives rise to the bis(diazaphospholyl)phosphane **89** in 81% yield. In this case also, the double cycloaddition is of necessity followed by a spontaneous sigmatropic substituent shift (**88** → **89**).¹⁰⁸ The silyl groups now bonded to nitrogen can easily be condensed with the chlorides of various elements. Thus, condensation reactions of **89** with dichlorophenylphosphane give rise to the polycyclic product **90** (76%) and with tetrachlorosilane (0.5 equiv) to the spirocyclic silicon compound **91** (58%). In the latter reaction, it was demonstrated that the spiro coupling was preceded initially by cleavage of two molecules of chlorotrimethylsilane and incorporation of an SiCl₂ moiety.¹⁰⁸

The tris(diazomethyl)phosphane **92**—also accessible through electrophilic diazoalkane substitution—reacts analogously to **87** with 3 equiv of **3a** to furnish the tris(diazaphospholyl)phosphane **93** in 73% yield.¹⁰⁸ Product **93** also reacts with the chlorides of elements such as phosphorus(III), arsenic(III), and antimony(III) as well as with methyltrichlorosilane and -germane at room temperature via cleavage of three molecules of chlorotrimethylsilane to produce the multiply hetero-

SCHEME 30



SCHEME 31



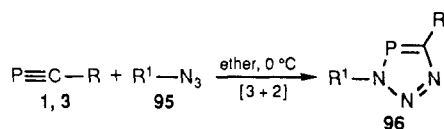
substituted bicyclic compounds **94** (Scheme 31).

2. With Azides

Azides are isoelectronic with diazo compounds and it is thus to be expected that their cycloadditions to phosphalkynes proceed with the same orientations as the diazo compounds. Nonspecific reaction courses are as yet unknown, and 3*H*-1,2,3,4-triazaphospholes have become accessible for the first time by means of this route.^{98,99} Thus, the reactions of **3a** with azides **95** bearing widely differing substituents gave rise to the triazaphospholes **96a-e**.¹⁰⁹ Only in the cases of the reactions of **3a** with trimethylsilyl azide and hydrazoic acid were substituent shifts from the 3-position (**96f,g**) to the central nitrogen atom observed.¹⁰⁹ In comparison to the 2*H*-1,2,4-diazaphospholes **82**, the ³¹P NMR chemical shifts of **96a-g** exhibit a pronounced displacement to low field (δ = ca. 170), and this is attributed to the direct bonding between nitrogen and phosphorus (Scheme 32).

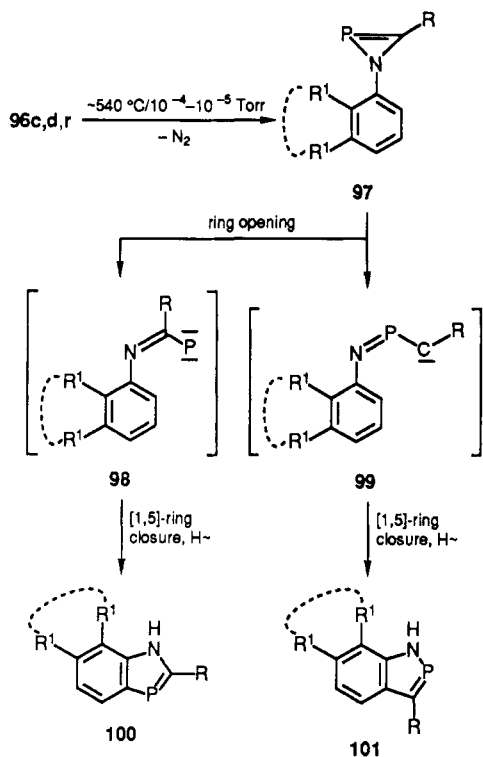
Analogous additions of methyl azide to the phosphalkynes **3d-f,h**, and **j** are known and give rise to the

SCHEME 32



- 96 a, R = ^tBu; R¹ = Me
 b, R = R¹ = ^tBu
 c, R = ^tBu; R¹ = Ph
 d, R = ^tBu; R¹ = 1-naphthyl
 e, R = ^tBu; R¹ = CO₂Me
 f, R = ^tBu; R¹ = SiMe₃
 g, R = ^tBu; R¹ = H
 h, R = Me₂EtC; R¹ = Me
 i, R = Me₂^tBuC; R¹ = Me
 j, R = 1-methylcyclohexyl; R¹ = Me
 k, R = 1-adamantyl; R¹ = Me
 l, R = mesityl; R¹ = Me
 m, R = ⁱPr; R¹ = Me
 n, R = Et₂CH; R¹ = Me
 o, R = cyclohexyl; R¹ = Me
 p, R = ^tBuCH₂; R¹ = Me
 q, R = H; R¹ = Me
 r, R = Me; R¹ = Ph

SCHEME 33



97,98,99,100,101a, R = ^tBu; R¹ = H (95%; 100a:101a = 1:4)¹⁰⁹

b, R = ^tBu; R¹ = ---CH=CHCH=CH---
 (99%; 100b:101b = 1:3)¹⁰⁹

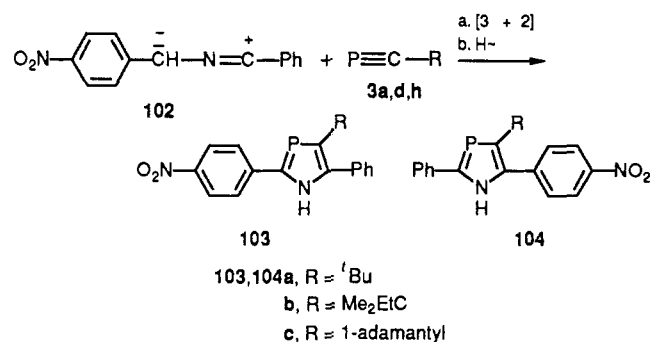
c, R = Me; R¹ = H (60%; 100c:101c = 2:1)³⁴

1,2,3,4-triazaphospholes **96h-j**,⁵¹ **96k**,⁵² and **96l**.⁵¹ The methyl azide adducts such as **96m**,⁴⁸ **96n,o**,⁵¹ and **96p**¹⁸ are highly suitable for the chemical characterization of phosphalkynes bearing secondary carbon substituents such as **31**, **n-q**. This is also valid for the short-lived phosphalkynes **1a,b**, which can be frozen out and then subsequently reacted with methyl or phenyl azide to yield triazaphospholes (\rightarrow **96q**,²² **96r**³⁴).

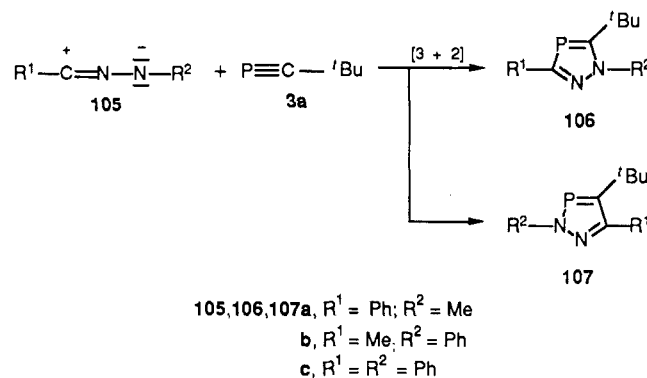
Appearances can be deceptive and it is thus not easy to eliminate nitrogen from the 3H-1,2,3,4-triazaphospholes **96**; this elimination occurs only under flash vacuum pyrolysis conditions. When 3-aryl-substituted 3H-1,2,3,4-triazaphospholes such as **96c,d,r** are subjected to such conditions, the substituents are to be found in the products as the benzo or naphtho parts of the annelated azaphospholes.^{34,109}

In each case, an isomeric mixture of **100** and **101** is obtained and, in some cases, the isomers could be separated. The pronounced differences in the ³¹P NMR

SCHEME 34



SCHEME 35



chemical shifts are of decisive importance for the structural assignments of the isomers (**100a-c**: $\delta = 66.3-74.4$; **101a-c**: $\delta = 180.1-210.2$) (Scheme 33).^{34,109}

The formation of these products can be explained convincingly by the assumption of an azaphosphirene intermediate (**96** \rightarrow **97**). Thermally induced ring opening of **97** gives rise to the phosphinidenes **98** on the one hand and to the carbenes **99** on the other hand. Both species are electron deficient and highly reactive; they both undergo [1,5]-cyclization with subsequent H shift to furnish the final products (**98** \rightarrow **100** and **99** \rightarrow **101**, respectively).^{34,109}

3. With Nitrilium Betaines

The nitrile ylide dipole **102** readily takes part in addition reactions with the phosphalkynes **3a,d,h** to form 1H-1,3-azaphospholes in 85-91% yields. Thus, the actual cycloaddition process must also be followed by an H shift which, in turn, brings about aromatization (**103/104**) (Scheme 34).¹¹⁰

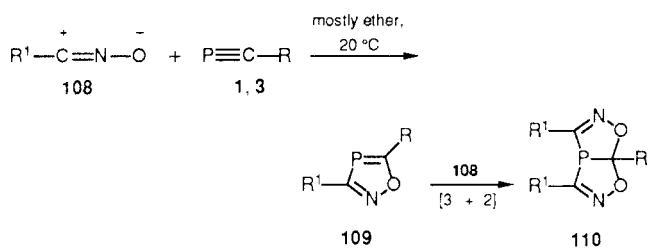
This addition is strictly regiospecific but the constitutions of the formed 1,3-azaphospholes (**103a-c** and **104a-c**) cannot be determined with certainty by NMR spectroscopy¹¹⁰ (see also the synthesis of a 1H-1,3-azaphosphole from **3a** and an oxazolium-olate).

The nitrilium dipoles **105a** and **105b** react with **3a** to produce regioisomeric mixtures of products **106a,b** and **107a,b**; in both cases, the 1H-1,2,4-diazaphosphole **106** is the major product (molar ratio 98:2). The reaction of **105c** with **3a** gives exclusively the product **106c** (Scheme 35).

The low-field positions of the ³¹P NMR signals of **107** ($\delta = 224.4$ and 218.5) in comparison to those of the 1,2,4 isomers **106** ($\delta = 86.6-91.9$) define the direction of the addition unambiguously.¹¹¹

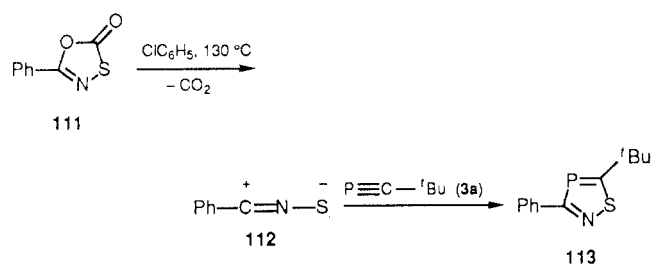
As a consequence of the well-known affinity of phosphorus for oxygen, the formation of 1,2,5-oxaza-

SCHEME 36



- 109,110a, R = *t*Bu; R¹ = Ph
 b, R = *t*Bu; R¹ = mesityl
 c, R = R¹ = *t*Bu
 d, R = Me₂EtC; R¹ = Ph
 e, R = Me₂*t*BuC; R¹ = Ph
 f, R = 1-methylcyclohexyl; R¹ = Ph
 g, R = 1-adamantyl; R¹ = mesityl
 h, R = mesityl; R¹ = Ph
 i, R = H; R¹ = Ph
 j, R = Me; R¹ = Ph
 k, R = Me; R¹ = mesityl

SCHEME 37



phospholes would be expected from the reactions of phosphalkynes with nitrile oxides. However, just the opposite result is obtained experimentally: 1,2,4-oxazaphospholes are in fact obtained.^{98,111} The steric requirements of the cycloaddition partners are more favored by this reversed dipole orientation.

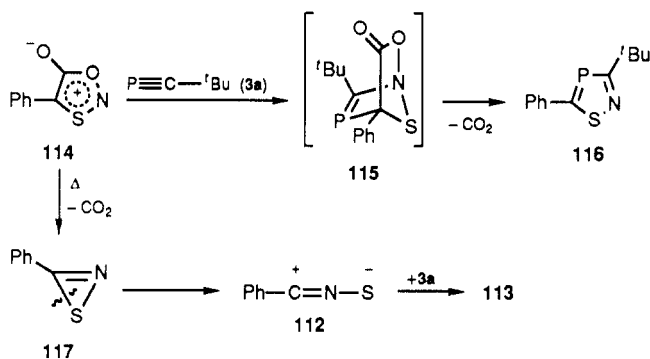
As illustrated by the wide range of 1,2,4-oxazaphospholes prepared (110a-c,¹¹¹ 110d,e,⁵¹ 110f,⁴⁸ 110g,⁵² 10h,⁵¹), the nature of the substituents on both reaction partners may be varied greatly. In the reaction of 2,2-dimethylpropanenitrile oxide (108, R¹ = *t*Bu) with 3a, the 2:1 adduct 110c is formed in addition to the already mentioned product 109c.¹¹¹ In light of the extreme steric hindrance, it is very surprising that this reaction can take place at all. It is also interesting to note that the direction of addition is the same in each step. A corresponding heterocyclic product has also been obtained from the reaction of 3a with 4-chlorobenzonitrile oxide.⁹⁹ The short-lived phosphalkynes do not react homogeneously with nitrile oxides. Whereas the reaction of 1b with 2,4,6-trimethylbenzonitrile oxide gives rise to the 1:1 adduct 109k,³⁴ the reactions of 1a and 1b with benzonitrile oxide take place in a 1:2 molar ratio to yield the adducts 110i and 110j (Scheme 36).

The above-mentioned regiochemistry is retained in the 1,3-dipolar cycloaddition of benzonitrile sulfide (112) to 3a, as is indicated by the formation of the 1,2,4-thiazaphosphole 113 in 82% yield.¹¹¹ The dipole 112 was generated by the thermally induced elimination of carbon dioxide from 111¹¹² (Scheme 37) (for the formation of 113 from 3a and an oxathiazolium-olate, see below).

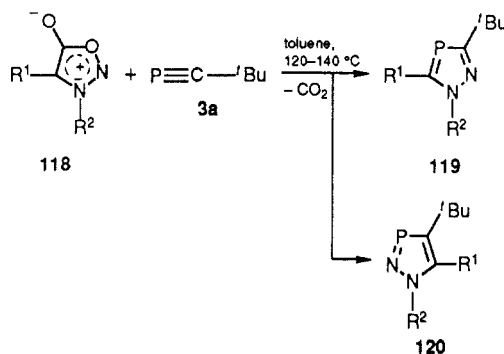
4. With Mesoionic Compounds

Mesoionic compounds are considerably less reactive toward phosphalkynes than the diazonium and nitrilium betaines discussed above. In some cases, it is

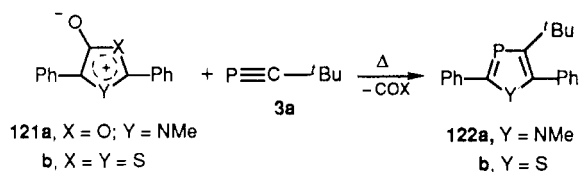
SCHEME 38



SCHEME 39



- 118,119,120a, R¹ = H; R² = Me
 b, R¹ = H; R² = Ph
 c, R¹ = R² = Me
 d, R¹ = Me; R² = Ph
 e, R¹ = Ph; R² = Me



even necessary to heat the reaction partners to 140 °C in a pressure vessel in order to bring about the reaction. Heterobicyclic intermediates, like 115 formed in the reaction of 114¹¹³ and 3a, cannot be detected in any case. The decomposition process to give—in this case—the thiazaphosphole 116 and CO₂ is apparently much more rapid than the formation of the potential bicyclic product (Scheme 38).¹¹⁴

A byproduct of this reaction is the isomeric thiazaphosphole 113 (3% yield) mentioned above as a product from the addition of 3a to the nitrile sulfide.¹¹⁴ In the present reaction, 113 may have been formed in the same way, with the dipole 112 being generated from the mesoionic compound 114. The reaction sequence 114 \rightarrow 117 \rightarrow 112 at least provides a feasible interpretation of the experimental result.¹¹⁴

The sydnone 118a-c react very selectively with 3a under pressure conditions to yield the 2*H*-1,2,4-diazaphospholes 119a-e (67–96%).¹¹⁴ Compounds with the same ring skeleton are also obtained from reactions between phosphalkynes and diazo compounds. As has been shown for the case of 82a-c, these compounds can be converted to the “sydnone products” 119a,c,e via lithiation and subsequent methylation with methyl iodide (Scheme 39).

Only in the case of the reaction of 118a with 3a was a regioisomeric mixture of products 119a and 120a

(ratio 87:13) formed. On attempts to separate this mixture by HPLC, the product **120a** decomposed. The constitutions were assigned unambiguously with the help of ^{31}P NMR spectroscopy: the phosphorus atom of the *1H*-1,2,3-diazaphosphole **120a** is characterized by a low-field signal ($\delta = 229.4$) (see also ref 115) whereas, in contrast, the signals for the phosphorus atoms of the *2H*-1,2,4-diazaphospholes **119a–e** appear at considerably higher fields in the ^{31}P NMR spectra.¹¹⁴

The münchnone **121a** reacts with the phosphalkyne **3a** under moderate conditions (80 °C in benzene) to form the *1H*-1,3-azaphosphole **122a** in 63% yield.¹¹⁴ Several other routes of access to this class of compounds are also known.^{116–119} The short-lived, highly reactive phosphoacetylene (**1a**) even reacts in the same way with **121a** in a thawing cold trap.²² Finally, the reaction of **121b** with **3a** (130 °C in toluene) opens a new access to the chemistry of the previously unknown 1,3-thia-phospholes,¹²⁰ in the present case **122b** (91% yield).¹¹⁴

5. With Azomethinium Dipoles

Whereas the [3 + 2]-cycloaddition processes of 1,3-dipoles to the P/C triple bond discussed above are mainly regioselective or highly selective, this uniformity is not observed with nitron and azomethinium dipoles. The dihydrooxazaphospholes **124** and **125** in a ratio of 2:1 are the products of the reaction of **3a** with **123** and can be separated by chromatographic workup.¹⁰² Compound **125** is thermally unstable and decomposes during attempts to separate the isomeric mixture by bulb-to-bulb distillation. The characterizable product of the decomposition is benzaldehyde *N*-*tert*-butylimine while the fate of the complementary fragment is still unknown (Scheme 40).¹⁰²

Preliminary experiments with azomethine imine dipoles such as **126**¹²¹ and **128**¹²¹ suggest that they are able to react with **3a** under both steric and electronic control. Hence, the combination **3a** + **126** gives rise to **127** (100% yield; ^{31}P NMR: $\delta = 138.8$)—the product of steric control—exclusively.¹²² In contrast, the reaction of **3a** with **128** furnishes the spirocyclic dihydro-1,2,3-diazaphosphole **129** (60% yield; ^{31}P NMR: $\delta = 180.3$),¹²² which is assumed to arise from an electronically controlled cycloaddition process.

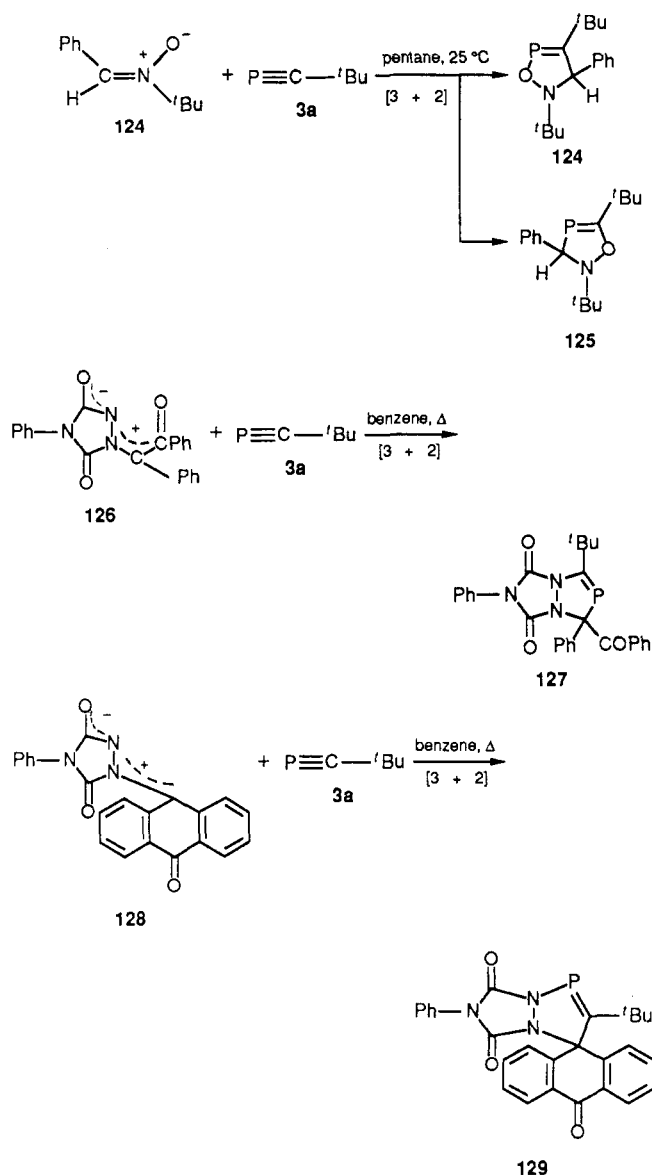
E. [4 + 2]-Cycloaddition Reactions

The particular fascination of the Diels–Alder reactions of phosphalkynes is the possibility for the specific transformation of $\lambda^3\sigma^1$ -phosphorus atoms into $\lambda^3\sigma^2$ -phosphorus atoms, in other words, the first method for the construction of 1-phospha-1-cycloalkenes. Of course, surprising and unexpected subsequent reactions may also arise. In general, [4 + 2]-cycloaddition reactions with 1,3-dienes require an extremely high thermal activation; the reactions with antiaromatic compounds, however, provide the only known exception to this rule.

1. With 1,3-Butadienes

Thermal reactions of the 1,3-butadienes **130a–h** with **3a** only give rise to satisfactory yields of the corresponding adducts when the diene and dienophile are employed in a molar ratio of 1:2 (**130e** is an exception). The reaction sequence is surprising and the products obtained are the tricyclooctenes **133a–h**, characterized by the presence of a diphosphirane moiety. The ring

SCHEME 40



of the latter can be recognized on account of the high-field ^{31}P NMR absorptions of the two nonequivalent phosphorus atoms ($\delta = -164.1$ to -210.6) and their mutual coupling of about 150 Hz.^{76,123,124} In addition, the structure of the tricyclic product **133a** was confirmed by a crystal structure analysis; the P/P bond length was found to be 2.183 (2) Å (see also Figure 4).¹²⁵ When unsymmetrically substituted butadienes such as **130b** or **130d** are used in the reaction, product mixtures in which **133b** or **133d** are the major products (ratios 60:40 or 90:10, respectively) are obtained. The minor products have the same basic skeleton, but with the order of the substituents R^1 to R^4 being reversed (Scheme 41).

It must be assumed that the 1:2 molar reaction sequence commences with a Diels–Alder reaction (**130** + **3a** \rightarrow **131**). This reaction is not regioselective in every case and is thus responsible for the formation of isomers in the reactions of **130b** and **130d** mentioned above. The next step is a chemospecific ene reaction with the second molecule of **3a** in which the P/P bond is constructed (**131** \rightarrow **132**). Finally, an intramolecular [4 + 2]-cycloaddition process (**132** \rightarrow **133**) gives rise to the tricyclic product.⁷⁶

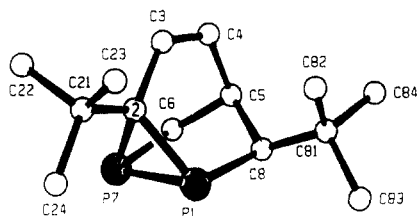
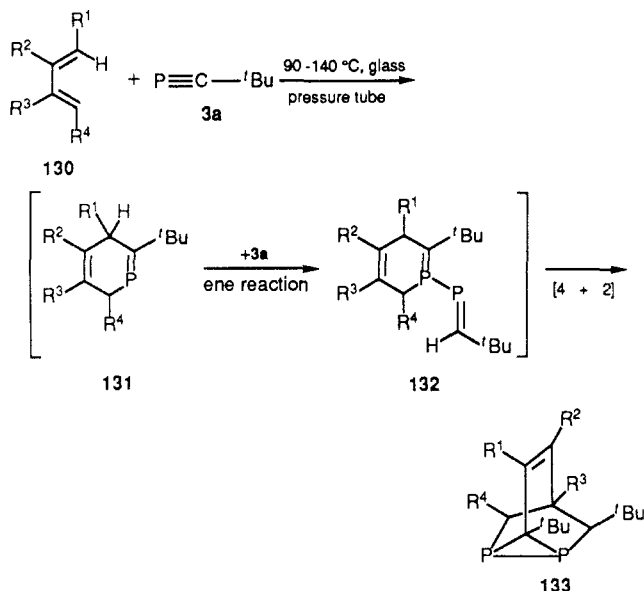


Figure 4. Crystal structure analysis of **133a**. Selected bond lengths (Å) and angles (deg) of the carbon/phosphorus skeleton: P1-P7 = 2.183 (2), P1-C2 = 1.886 (4), P1-C8 = 1.869 (4), P7-C2 = 1.888 (4), P7-C6 = 1.847 (6), C2-C3 = 1.478 (6), C3-C4 = 1.317 (6), C4-C5 = 1.492 (6), C5-C6 = 1.511 (7), C5-C8 = 1.553 (6); P7-P1-C2 = 54.7 (1), P7-P1-C8 = 94.8 (1), C2-P1-C8 = 100.9 (2), P1-P7-C2 = 54.6 (1), P1-P7-C6 = 93.8 (2), C2-P7-C6 = 98.6 (2), P1-C2-P7 = 70.7 (2), P1-C2-C3 = 116.3 (3), P7-C2-C3 = 114.7 (3), C2-C3-C4 = 123.3 (4), C3-C4-C5 = 118.3 (4), C4-C5-C6 = 108.5 (4), C4-C5-C8 = 111.2 (3), C6-C5-C8 = 107.1 (4), P7-C6-C5 = 111.5 (3), P1-C8-C5 = 108.2 (3).

SCHEME 41

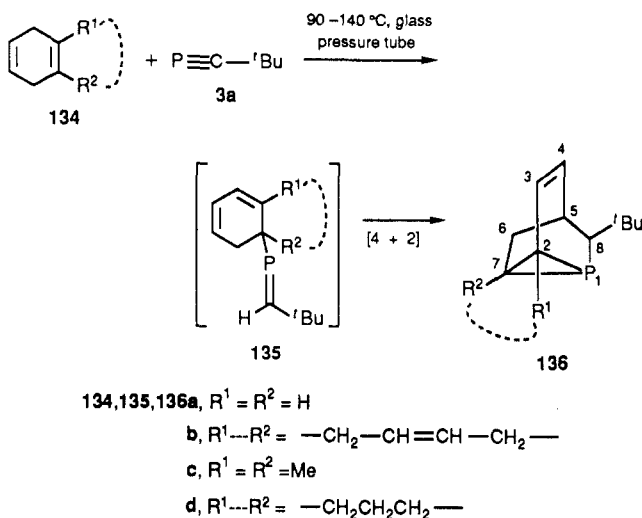


- 130, 131, 132, 133a**, R¹ = R² = R³ = R⁴ = H (90%)
b, R¹ = R² = R⁴ = H; R³ = Me (85%)
c, R¹ = R⁴ = H; R² = R³ = Me (86%)
d, R¹ = R² = R³ = H; R⁴ = Me (66%)
e, R¹ = R⁴ = Me; R² = R³ = H (≤10%)
f, R¹ = PO(OMe)₂; R² = R⁴ = H; R³ = Me (73%)
g, R¹ = PO(OMe)₂; R² = R⁴ = H; R³ = *t*Bu (57%)
h, R¹ = R³ = R⁴ = H; R² = PO(OMe)₂ (53%)

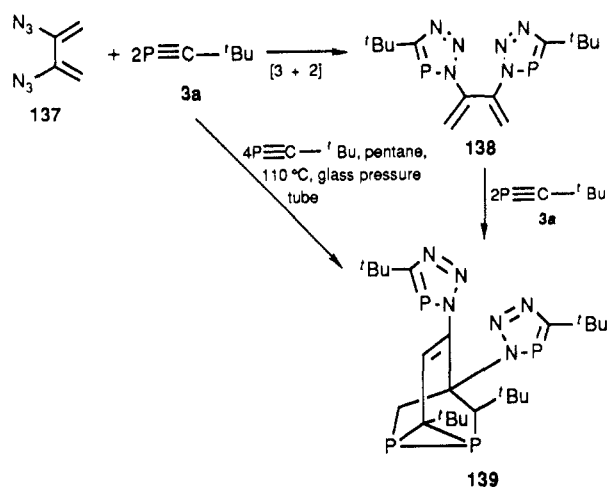
Indirect support for a reaction course of the above type is provided by the observation that the 1,4-cyclohexadienes **134a-d** react analogously with only 1 equiv of **3a** to furnish the monophosphatricyclooctenes **136a-d**.⁷⁶ It is easy to suppose that the phosphalkene **135**, initially formed by the ene reaction but not isolable, undergoes a rapid intramolecular cycloaddition to produce **136**. The trivalent, tricoordinated phosphorus atom in the three-membered-ring unit again exhibits the expected high-field ³¹P NMR chemical shift ($\delta = -192.0$ to -234.0) (Scheme 42).⁷⁶

In the reactions of **134c** or **134d** with **3a** (but not in that of **134b** + **3a**), about 10% of a constitutionally isomeric tricyclic product in which the R¹-R² substituent now occupies the positions 4 and 5 is formed in each case in addition to the above-mentioned major products **136c** or **136d**. The ene reaction **134b** → **135b** proceeds exclusively at the substituted, electron-rich

SCHEME 42



SCHEME 43



C/C double bond of the ene whereas those of **134c** and **134d** proceed with high selectivities. It is known from the literature that cyclohexa-1,4-diene (**134a**) reacts with dimethyl acetylenedicarboxylate to produce a tricyclic compound corresponding to **136**.^{126,127}

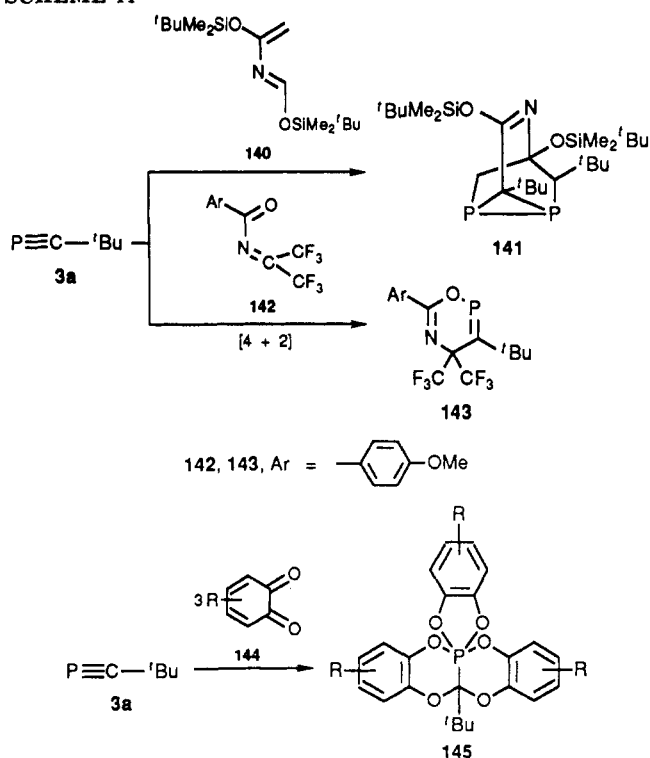
An interesting combination of a 1,3-dipolar cycloaddition, Diels-Alder reaction, and ene reaction as well as an intramolecular [4+2]-cycloaddition step takes place in the one-pot reaction of 2,3-diazido-1,3-butadiene (**137**) with 4 equiv of the phosphalkyne **3a**. The product obtained is **139**, which, as exposed, exhibits four signals in the ³¹P NMR spectrum [$\delta = -168, -204$ (diphosphirane ring); $+182, +187$ (triazaphosphole rings)] (Scheme 43).¹²⁴

The reaction sequence most certainly starts with a double [3+2] cycloaddition of **137** to **3a** yielding **138**. This product is also formed when the substrates are allowed to react in diethyl ether at 0 °C (³¹P NMR: $\delta = +176$). Thus, it is not surprising that **138** subsequently reacts with a further 2 equiv of **3a** under the conditions of the one-pot reaction (pentane, 110 °C) to furnish the tricyclic product **139**.¹²⁴ The ene reaction step presumably required the thermal activation.

2. With 1,3-Heterodienes

A further extension of the above-described synthesis of tricyclic compounds is provided by the fact that aza-1,3-butadienes such as **140** also react with **3a** via the

SCHEME 44



sequence Diels–Alder reaction, ene reaction, and subsequent intramolecular [4 + 2]-cycloaddition step (120 °C, glass pressure vessel) to produce, in this example, 141 (^{31}P NMR: $\delta = -180.2, -208.2$; $^1J_{\text{P,P}} = 162.7$ Hz) (Scheme 44).¹²⁸

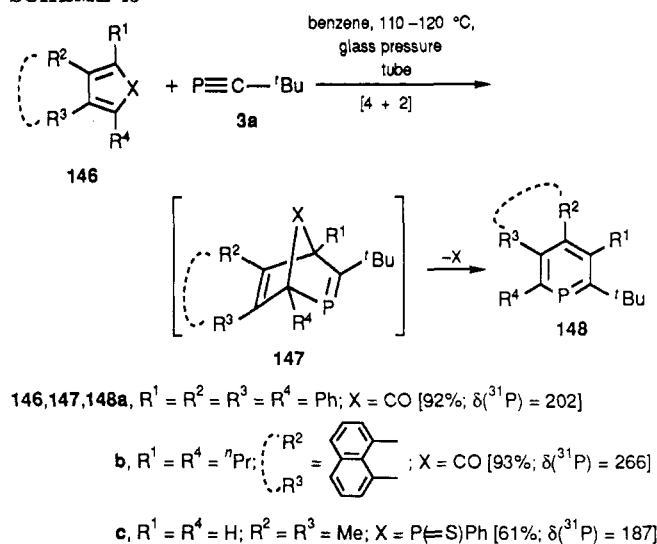
In this case also, the ene reaction must occur specifically at the phosphorus atom of the 1-aza-4-phospho-1,4-cyclohexadiene intermediate to provide the P/P bond, as is again demonstrated by the formation of a diphosphirane unit.¹²⁸ The acyl imine 142 also possesses heterodiene character, but its reaction with 3a comes to a standstill after the Diels–Alder step ($\rightarrow 143$). In contrast to the other examples, the constitutional prerequisites for the subsequent ene reaction are lacking in this case.¹²⁹

The quinones 144 react with the phosphoalkyne 3a in a molar ratio of 3:1 to furnish 145. Although no conclusive results concerning the sequence of the individual cycloaddition steps are available, it may safely be assumed that the [4 + 1] process is preceded by the hetero-Diels–Alder reaction.¹²⁹

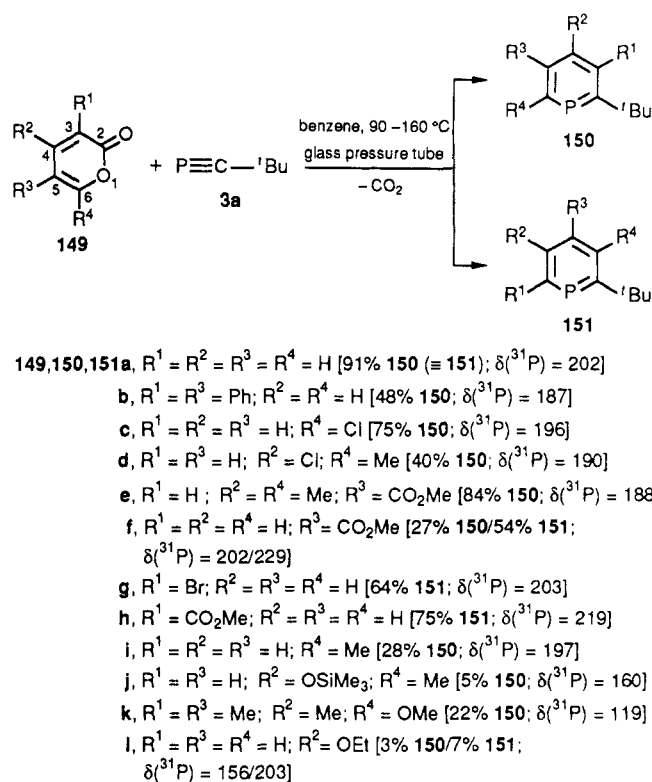
3. With Cyclic 1,3-Dienes Possessing an "Extruding Group"

The conventional syntheses of λ^3 -phosphabenzenes involve condensation of pyrylium salts with PH_3 (or its synthetic equivalents).¹³⁰ The Diels–Alder reactions of phosphoalkynes with cyclic 1,3-dienes in which the chain ends are joined by an easily removable group (e.g., 146 and 149)⁴⁹ thus constitute an enrichment of the synthetic methodology. However, these reactions usually also require exceptionally high temperatures. Hence, the reactions of 3a with the cyclopentadienones 146a,b give rise to the completely substituted phosphabenzene 148a¹³¹ and 148b.¹²⁹ Neither in the above reactions nor in similar cases could bicyclic intermediates such as 147 be detected since their extrusion behavior to yield "X" (CO in this case) and the phos-

SCHEME 45



SCHEME 46



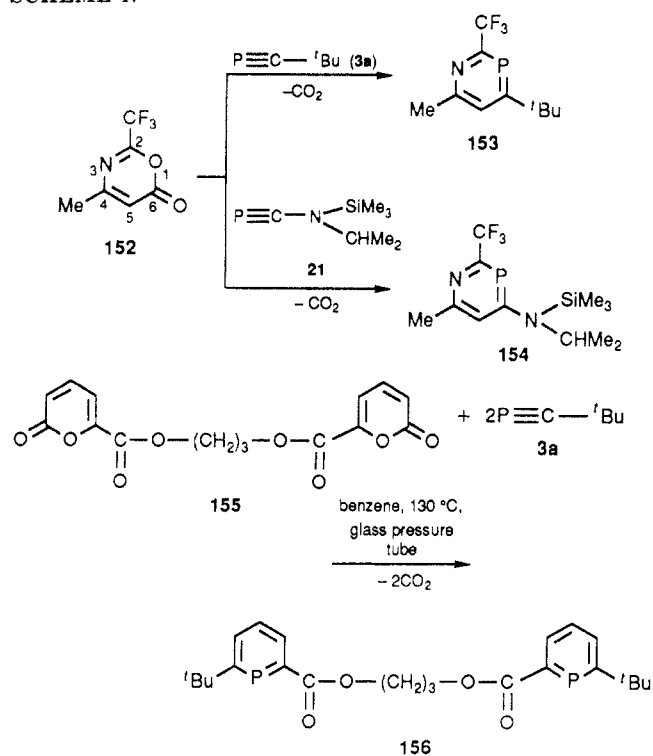
phabenzene is very rapid (Scheme 45).

Even phosphole sulfides such as 146c can serve as cycloaddition partners for 3a, as is demonstrated by the formation of the phosphabenzene 148c.¹³¹ In this case, the short-lived species phenylthioxophosphane [PhP(=S)] containing a $\lambda^3\sigma^2$ -phosphorus atom is cleaved from the bicyclic intermediate. The existence of the molecule PhP(=S) has been confirmed by various trapping reactions.¹³²

To date, the largest range of substituted λ^3 -phosphabenzenes 150 and 151 has been prepared from the α -pyrones 149 and 3a under the usual thermal conditions.^{129,131} α -Pyrones bearing acceptor substituents react under milder conditions and give better yields than those bearing donor substituents (Scheme 46).

From the variations of the substituents, the steric influence of groups in the 3- and 6-positions of the

SCHEME 47



α -pyrones on the product formation ($\rightarrow 150$ or 151) can be recognized easily. In the absence of substituents in these positions, both directions of addition take place in competing reactions [e.g., $149\text{f} + 3\text{a} \rightarrow 150\text{f} + 151\text{f}$ (ratio 1:2)].¹²⁹ The actual cycloaddition step thus apparently has an inverse electron demand; i.e., acceptor-substituted α -pyrones react more readily with 3a than do those with donor substituents. Hence, the yields of phosphabenzenes obtained from α -pyrones with substitution patterns of this type are rather modest (see $150/151\text{i}-1$).¹²⁹

The inverse electron demand of the reactions of α -pyrones with phosphalkynes is also apparent in the reactions of 2-(trifluoromethyl)-4-methyl-6*H*-1,3-oxazin-6-one (152) with 3a and 21 . After elimination of CO_2 , the 1,3-azaphosphabenzene 153 ¹³⁴ and 154 ⁶⁰ are obtained as products (Scheme 47).

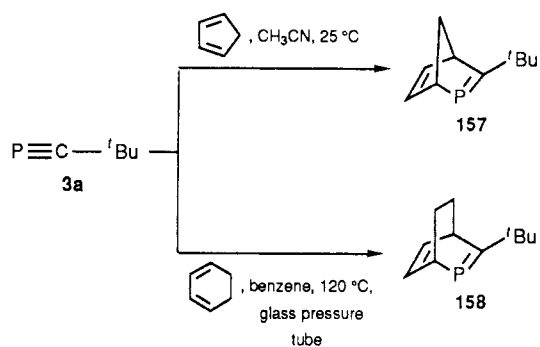
The wide scope of application of the λ^3 -phosphabenzene synthesis involving a primary Diels–Alder step is also reflected in the preparations of chain-linked heteroaromatic products. Thus, the reaction of 155 with 3a in a molar ratio of 1:2 and under the usual drastic conditions gives rise to the bis(phosphabenzene) 156 .¹²⁹

4. With Cyclopentadienes and Cyclohexadienes

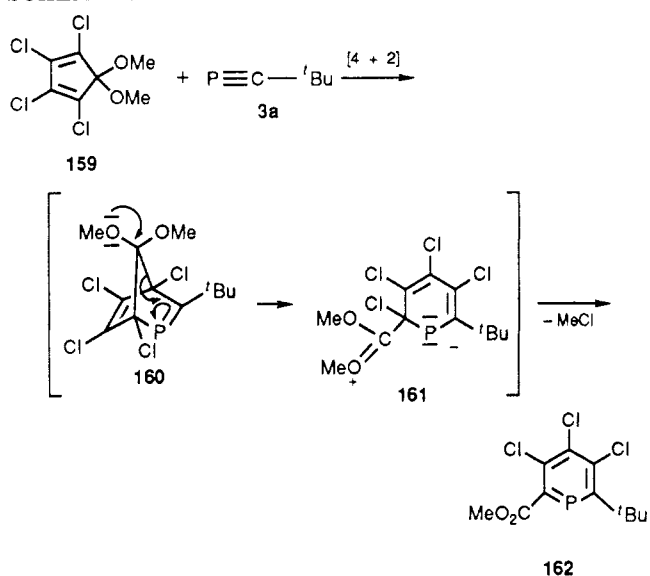
An obvious question now is whether the previously unknown bicyclic phosphalkenes potentially accessible from the reactions of 3a with cyclic 1,3-dienes lacking a group suitable for elimination will be stable. The initial experiments were not able to provide an answer to this problem since the addition of 3a to cyclopentadiene under normal conditions produced the bicyclo[2.2.1]heptadiene 157 . This product was characterized spectroscopically in solution but could not be isolated¹²⁹ (see also the section on homo-Diels–Alder reactions (Scheme 48)).

However, the reaction of the homologous cyclohexadiene with the same phosphalkyne (but under

SCHEME 48



SCHEME 49

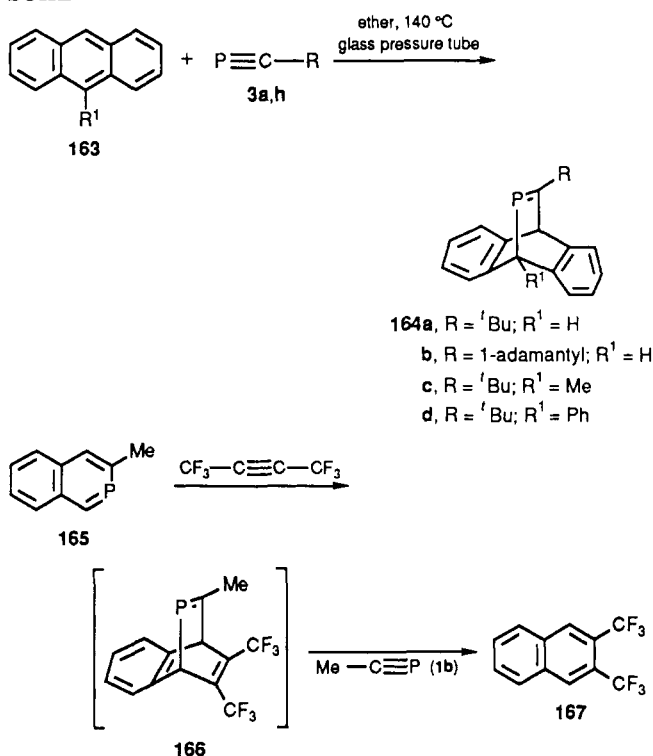


much more drastic thermal conditions) opened up new perspectives. The 2-phosphabicyclo[2.2.2]octa-2,5-diene 158 is stable and can be distilled (^{31}P NMR: $\delta = 225.6$). Cycloelimination of the ethano bridge (as ethylene) occurs only under flash vacuum pyrolysis conditions to furnish the *tert*-butyl-substituted phosphabenzene 150a ($\equiv 151\text{a}$).¹³¹ The corresponding bicyclic product obtained from 3h and cyclohexa-1,3-diene underwent the respective cycloreversion under considerably milder conditions.¹²⁹

The reaction of 1,2,3,4-tetrachloro-5,5-dimethylcyclopentadiene (159) with 3a provides a completely new entry into the chemistry of highly functionalized phosphabenzene. The expected product was not the functionalized phosphabicyclo[2.2.1]heptadiene 160 , but instead the λ^3 -phosphabenzene 162 was obtained in 80% yield.¹³⁵ A comparable conversion of the same cyclopentadiene into a benzene derivative on reaction with dimethyl acetylenedicarboxylate (with the elimination of MeCl) had been reported previously (Scheme 49).¹³⁶

It may safely be assumed that the unusual reaction course starts at the stage of the adduct 160 : rearrangements as shown in Scheme 49 lead from the bicyclic to the monocyclic system ($\rightarrow 161$) and finally to the heteroaromatic product 162 by elimination of chloromethane.¹³⁵ The feasible formation of isomers via opening of the 1-bridge between the ketal group and the P-substituted carbon atom has not yet been observed.¹³⁵ This synthesis of phosphabenzene can, in principle, be generalized, provided that the indispen-

SCHEME 50



sable constitutional requirements are maintained.¹³⁵

The 1,3-diene reactivity of anthracenes **163** is known so it is not surprising that they also react with the phosphalkynes **3a,h** to furnish the adducts **164a-d** (28–91% yields). These products possess low-coordinated phosphorus atoms (³¹P NMR: $\delta = 230.2\text{--}246.4$) and thus complement the known range of phosphabarellenes; previously, only representatives of this class of compounds containing $\lambda^3\sigma^3$ -phosphorus atoms had been reported (Scheme 50).¹³⁸

Attempts to prepare phosphabarellenes containing $\lambda^3\sigma^2$ -phosphorus atoms by the reverse route were unsuccessful since the reaction of the 2-phosphanaphthalene with hexafluoro-2-butyne gave rise only to 2,3-bis(trifluoromethyl)naphthalene (**167**) and the phosphalkyne **1b**.¹³⁹ Presumably, the intermediately formed phosphabarellene **166** was not able to survive the drastic reaction conditions employed (250 °C in the gas phase or up to 150 °C in solution).¹³⁹

5. With Antiaromatic Compounds

Reactions of cyclobutadienes with acetylenes give rise to Dewar benzenes which can be subjected to further photochemically and thermally induced isomerization processes.¹⁴⁰ Thus, the reaction partners cyclobutadiene/phosphaalkyne or azacyclobutadiene/phosphaalkyne offer the promise of a potential access to the valency isomers of phosphabenzenes and azaphosphabenzenes, respectively. In contrast to the parent heteroaromatic compounds, their classic valency isomers were not previously accessible by other routes.

(a) *Cyclobutadienes*. In contrast to the above-discussed Diels–Alder reactions of phosphalkynes, the highly reactive cyclobutadienes **168**, including those bearing sterically demanding substituents, take part in quantitative addition reactions with the phosphalkynes **3a,f,h,l,q** even at low temperatures to furnish the regioisomeric Dewar 2-phosphabenzenes **169** ($\geq 85\%$) and

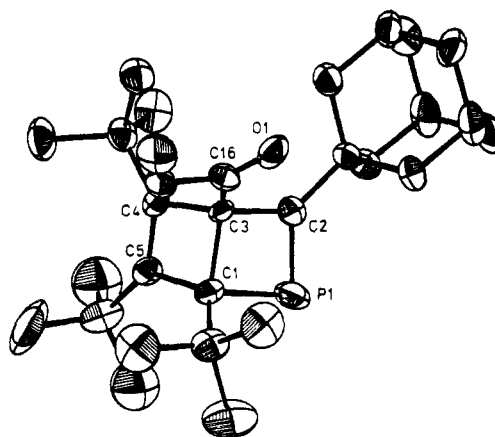
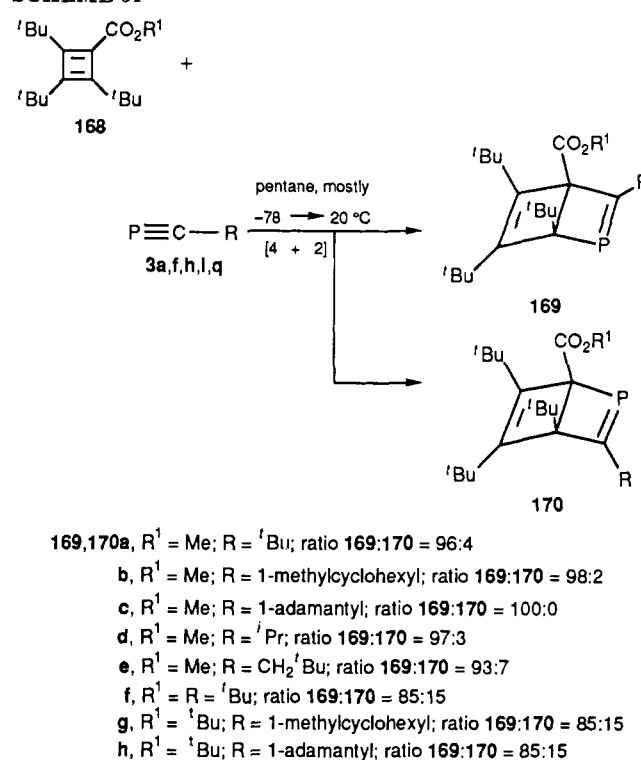


Figure 5. Crystal structure analysis of **169c**. Selected bond lengths (Å) and angles (deg): P1–C1 = 1.89 (1), P1–C2 = 1.68 (1), C1–C3 = 1.59 (1), C1–C5 = 1.53 (1), C2–C3 = 1.54 (1), C3–C4 = 1.54 (1), C4–C5 = 1.35 (1); C1–P1–C2 = 79.5 (4), P1–C1–C3 = 88.2 (5), C3–C1–C5 = 85.3 (6), P1–C2–C3 = 98.3 (6), C1–C3–C2 = 93.9 (6), C1–C3–C4 = 85.8 (6), C3–C4–C5 = 93.9 (6), C1–C5–C4 = 95.0 (7).

SCHEME 51



170 ($\leq 15\%$). For steric reasons, the 1,3-diene system of **168** bearing the two terminal *tert*-butyl groups is not attacked.¹⁴¹ It is understandable that the methyl esters of **168** exhibit a higher selectivity than the corresponding *tert*-butyl esters; the reaction of **168** (R¹ = Me) with **3h** is even regioselective. Thus, ultimately, steric control of the reaction is the dominant process (Scheme 51).¹⁴¹

The main products **169a,b, d–h** are obtained free of the other isomers by means of fractional crystallization. The ³¹P NMR signals appear at lower field ($\delta = 312\text{--}317$) than those of the isomeric products **170** ($\delta = 285\text{--}300$).¹⁴¹ A crystal structure analysis performed on **169c** gave a P/C double-bond length of 1.68 (1) Å; the folding angle of the two four-membered rings amounted to 114° (see also Figure 5).

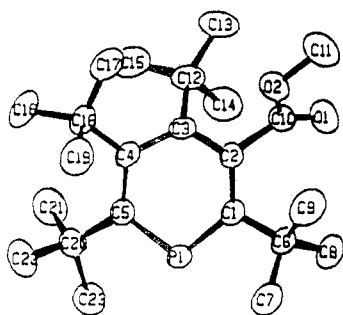
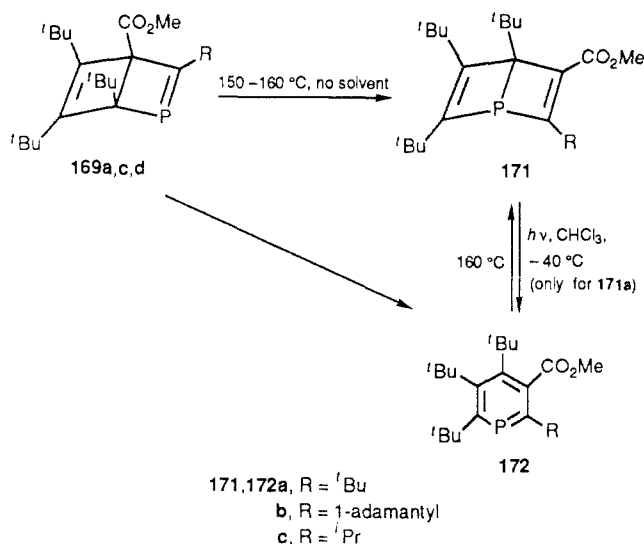


Figure 6. Crystal structure analysis of **172a**. Selected bond lengths (Å) and angles (deg): P-C1 = 1.730, C1-C2 = 1.404, C2-C3 = 1.411, C3-C4 = 1.437, C4-C5 = 1.402, C5-P = 1.758; C5-P-C1 = 105.0, P-C1-C2 = 118.4, C1-C2-C3 = 124.0, C2-C3-C4 = 120.3, C3-C4-C5 = 116.8, C4-C5-P = 119.8.

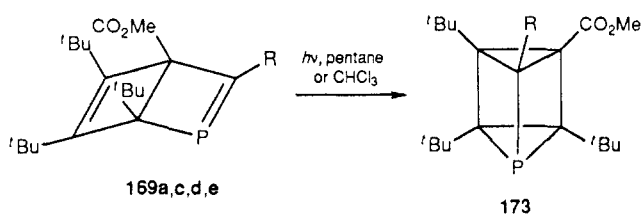
SCHEME 52



When the Dewar 2-phosphabenzene **169a,c,d** are heated at 150–160 °C in the absence of a solvent, they undergo isomerization to the also previously unknown Dewar 1-phosphabenzene **171a-c**.^{102,142–144} The isomerization process is accompanied by an enormous shift of the ³¹P NMR signals to higher field (**169a,c,d**: $\delta = 312\text{--}315$; **171a-c**: $\delta = -19$ to -25). The driving force for these isomerizations is assumed to be principally the increase in the coordination number at phosphorus. From a mechanistic point of view, it is reasonable to postulate the occurrence of the phosphabenzene **172a-c** as intermediates and there is a valid argument in support of this hypothesis. When compound **171a** is irradiated, the bridge is cleaved to form the heteroaromatic compound **172a**. Product **172a** itself undergoes the retroisomerization to **171a** when subjected to authentic thermolysis conditions (160 °C).¹⁴² The Dewar heteroaromatic compound **171a** is thus apparently thermodynamically more stable than the heteroaromatic compound itself; this unexpected stability is presumably the result of the steric effects that have been revealed by a crystal structure analysis of **172a** (see also Figure 6) (Scheme 52).¹⁴⁵

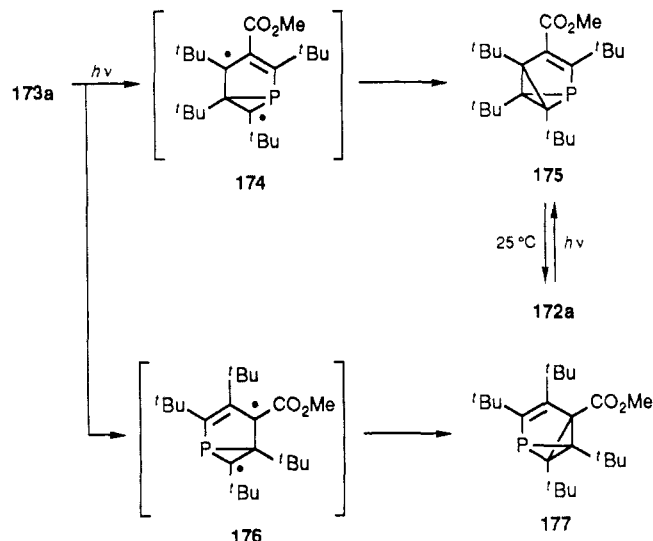
The heterocyclic six-membered ring of **172a** exists in a twisted boat form in which the C4 and C1 atoms represent the points of the bow and the stern positions, respectively. The bow and stern angles amount to 33.7 and 17.9°, the sum of the angles thus being 51.6°. The phosphabenzene **172a** therefore represents the most

SCHEME 53



173a, R = *t*Bu [$\delta(^{31}\text{P}) = -130.2$]
b, R = 1-adamantyl [$\delta(^{31}\text{P}) = -133.0$]
c, R = *i*Pr [$\delta(^{31}\text{P}) = -128.4$]
d, R = CH₂*t*Bu [$\delta(^{31}\text{P}) = -101.3$]

SCHEME 54



highly deformed, nonannulated and nonbridged 6 π system known to date. The aromatic stabilization naturally is deleteriously affected by this conformational situation.¹⁴⁵

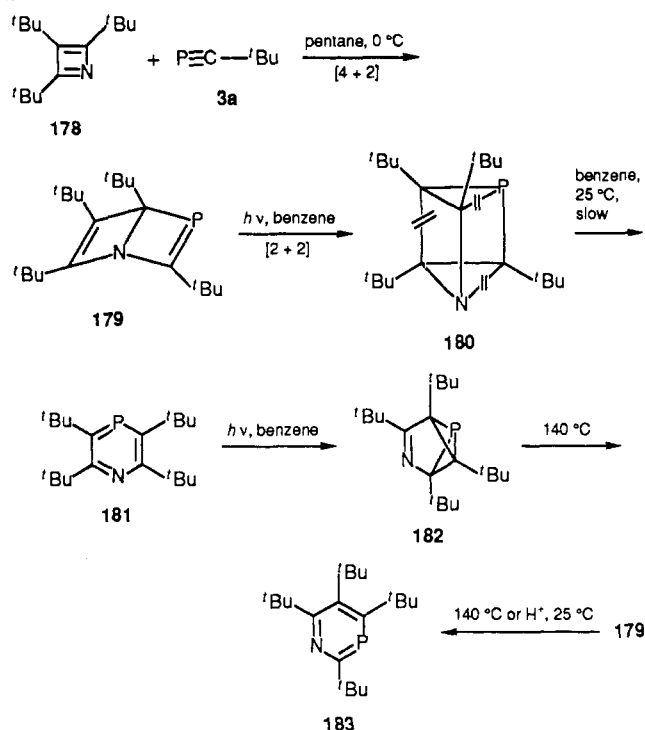
Since Dewar benzenes with sterically demanding groups can be converted photochemically into prismanes without difficulty,¹⁴⁰ an analogous behavior could be expected of the Dewar 2-phosphabenzene. Indeed, the desired intramolecular [2 + 2]-cycloaddition reactions do proceed smoothly when **169a,c-e** are irradiated for short periods of time [**173a** (40%),¹⁴² **173b** (59%),¹⁴³ **173c** (63%),¹⁰² **173d** (70%)¹⁴⁴ (Scheme 53).

Once again, the conversion of $\lambda^3\sigma^2$ -phosphorus atoms into $\lambda^3\sigma^3$ -phosphorus atoms and the incorporation of the latter into phosphirane ring systems are reflected in a dramatic diamagnetic shift of the ³¹P NMR signals (**169a,c-e**: $\delta = 312\text{--}315$; **173a-d**: $\delta = -101$ to -133).

The yields of phosphaprismanes **173** are only satisfactory when the photolysis reactions of compounds **169** are stopped after the appropriate times; otherwise the products of light-induced subsequent reactions dominate. These reactions have been investigated in detail for the example of compound **173a** (Scheme 54).¹⁴²

Thus, long-duration photolysis of **169a**, and also of **173a**, results in the formation of the also previously unknown isomeric phosphabenzvalenes **175** and **177**. Only the latter product is stable at room temperature and can be isolated without difficulty.¹⁴² In contrast, the isomer **175** undergoes quantitative "aromatization" even at 25 °C to furnish the phosphabenzene **172a**.

SCHEME 55

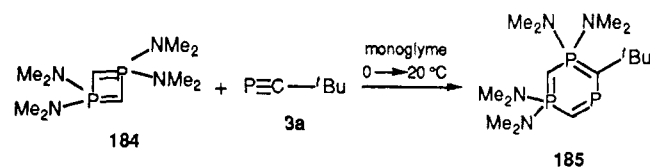


This process can be reversed (172a → 175) under photochemical conditions.¹⁴² The transformation of a phosphaprismane into the phosphabenzvalene system (173a → 175 + 177) can probably best be interpreted as proceeding through the biradical intermediates 174 and 176.¹⁴²

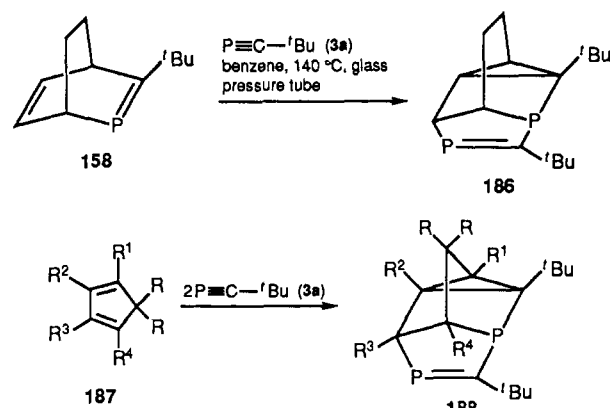
(b) *Azetes*. The recently prepared tri-*tert*-butylazete (178)¹⁴⁶ is also very amenable to cycloaddition reactions and represents an ideal starting material for the study of the valency isomers of pyridines bearing sterically demanding substituents by means of its reaction with acetylenes and the thermally and photochemically induced subsequent reactions of the products thus obtained.¹⁴⁷⁻¹⁵⁰ Bi-, tri-, and tetracyclic isomers of azaphosphabenzene¹⁵¹ are also analogously accessible from the reactions of 178 with phosphoalkynes.

In contrast to the additions of phosphoalkynes to cyclobutadienes, the Diels-Alder reaction of 178 with 3a is orientation specific and produces the Dewar 1,3-azaphosphabenzene 179 (92% yield; ³¹P NMR: δ = 202) in a sterically controlled process (Scheme 55).¹⁴⁹ The phosphoalkynes 3d¹⁵² and 3q¹⁴⁷ react analogously with 178. The photochemical isomerization of 179 to give the tetracyclic product 180 (³¹P NMR: δ = -111) proceeds smoothly even though the azaphosphaprismane itself is not very stable thermally.¹⁵² Three of the bonds in compound 180 (see Scheme 55) are broken already at room temperature to give rise to the 1,4-azaphosphabenzene 181 (³¹P NMR: δ = 228).¹⁵² The azaphosphabenzvalene 182 (³¹P NMR: δ = -50) is formed highly selectively in the photoreaction of 181; the high-field ³¹P NMR chemical shift of 182 indicates that the phosphorus atom is incorporated in a three-membered ring.¹⁵² The expected retroisomerization of 182 to 1,4-azaphosphabenzene did not occur on heating. Instead, the 1,3-azaphosphabenzene 183 was formed at 140 °C.¹⁵² The structural confirmation of 183 was also based on the independent isomerization process 179 → 183, which takes place under thermal conditions at 140

SCHEME 56



SCHEME 57



- 187, 188a, R = R¹ = R² = R³ = R⁴ = H; 95% [δ(³¹P) = 4.8, 322.4; ²J_{P,P} = 18.0 Hz
 b, R = Me; R¹ = R⁴ = H; R² = R³ = CO₂Me; 85% [δ(³¹P) = 32.6, 348.6; ²J_{P,P} = 16.2 Hz]
 c, R = R¹ = R³ = H; R² = R⁴ = ^tBu; 66% [δ(³¹P) = 37.3, 271.5; ²J_{P,P} = 18.0 Hz]

°C or under proton catalysis even at 25 °C.¹⁴⁸

(c) *1,3-λ⁵-Diphosphetes*. The diphosphete 184—a formal head-to-tail dimer of a λ⁵-phosphaalkyne¹⁵³—reacts with 3a to furnish the 1,3,5-triphosphabenzene 185 (³¹P NMR: δ = 295, 59.0, 57.5) containing both λ³σ²-phosphorus and λ⁵σ⁴-phosphorus atoms in modest yield (Scheme 56).¹⁵⁴

In this case, however, it was not possible to demonstrate the occurrence of a Dewar intermediate as was possible in the analogous reactions of 168 and 178.¹⁵⁴

F. Homo-Diels-Alder Reactions

Homo-Diels-Alder reactions¹⁵⁵ are scarce in comparison to the enormous number of Diels-Alder reactions known. However, just the homo-Diels-Alder reaction opens up new perspectives for the synthesis of polycyclic systems in the chemistry of low-coordinated phosphorus compounds. The first example reported was the reaction of the 2-phosphabicyclo[2.2.2]octa-2,5-diene 158 with the phosphoalkyne 3a to give the tetracyclic product 186 (³¹P NMR: δ = -16.8, +314.8; ²J_{P,P} = 12.6 Hz).⁷⁷ The di- and tricoordinated phosphorus atoms exhibit the expected large differences in their ³¹P NMR chemical shift values; the only small P,P coupling serves to rule out the possibility of a reversed orientation of 3a in the cycloaddition process (Scheme 57).

Since, as mentioned above, the Diels-Alder adduct 157 from cyclopentadiene and 3a is not very stable while, on the other hand, it does fulfill the prerequisites for a homo-Diels-Alder reaction, both reaction steps were performed in a one-pot procedure. Hence, reaction of 187a with 2 mol of 3a gave the tetracyclononene 188a directly.⁷⁷ Substituted cyclopentadienes reacted analogously (e.g., 187b,c + 23a → 188b,c).¹²⁹

VI. Acknowledgments

The major portion of the results reviewed here were carried out by my research group in Kaiserslautern and I would like to thank all of my co-workers whose results have been mentioned in this survey for their conscientious and constructive contributions to the chemistry of phosphalkynes. In addition, we are very grateful to the Deutsche Forschungsgemeinschaft, the Volkswagenstiftung, the Fonds der Chemischen Industrie, and the Government of the State of Rheinland-Pfalz for generous financial support of our work.

VII. References

- (1) Unusually Coordinated Phosphorus Compounds. 41. Part 40: Schnurr, W.; Regitz, M. *Tetrahedron Lett.* **1989**, *30*, 3951.
- (2) Pitzer, K. S. *J. Am. Chem. Soc.* **1948**, *70*, 2140. Mulliken, R. S. *J. Am. Chem. Soc.* **1950**, *72*, 4493.
- (3) Dimroth, K.; Hoffmann, P. *Angew. Chem.* **1964**, *76*, 433; *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 384.
- (4) Märkl, G. *Angew. Chem.* **1966**, *78*, 907; *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 846.
- (5) Regitz, M.; Scherer, O. J. *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Thieme: Stuttgart, in press.
- (6) Corbridge, D. E. C. *The Structural Chemistry of Phosphorus*; Elsevier: New York, 1974.
- (7) Photoelectron spectroscopic studies: Bock, H.; Müller, H. *Inorg. Chem.* **1984**, *23*, 4365.
- (8) Review: Scherer, O. J. *Comments Inorg. Chem.* **1987**, *6*, 1. See also: Scherer, O. J.; Sitzmann, H.; Wolmershäuser, G. *J. Organomet. Chem.* **1984**, *268*, C9. Scherer, O. J.; Sitzmann, H.; Wolmershäuser, G. *Angew. Chem.* **1984**, *96*, 979; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 968. Schäfer, H.; Binder, D.; Fenske, D. *Angew. Chem.* **1985**, *97*, 523; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 522. Vizi-Orosz, A.; Palyi, G.; Markó, L.; Boese, R.; Schmid, G. *J. Organomet. Chem.* **1985**, *288*, 179.
- (9) Atkins, R. M.; Timms, P. L. *Spectrochim. Acta* **1977**, *33A*, 853.
- (10) Atkins, R. M.; Timms, P. L. *Inorg. Nucl. Chem. Lett.* **1978**, *14*, 113.
- (11) Review: Regitz, M.; Binger, P. *Angew. Chem.* **1988**, *100*, 1541; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1484.
- (12) Nixon, J. F. *Chem. Rev.* **1988**, *88*, 1327.
- (13) Baceiredo, A.; Bertrand, G.; Sicard, G. *J. Am. Chem. Soc.* **1985**, *107*, 4781.
- (14) Keller, H.; Maas, G.; Regitz, M. *Tetrahedron Lett.* **1986**, *27*, 1903.
- (15) Bertrand, G. *Chem. Rev.*, in press.
- (16) Sicard, G.; Baceiredo, A.; Bertrand, G.; Majoral, J.-P. *Angew. Chem.* **1984**, *96*, 450; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 459.
- (17) Majoral, J.-P.; Bertrand, G.; Baceiredo, A.; Mavarez, E. O. *Phosphorus Sulfur* **1986**, *27*, 75.
- (18) Niecke, E.; Nieger, M.; Reichert, F. *Angew. Chem.* **1988**, *100*, 1781; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1715.
- (19) Niecke, E.; Nieger, M.; Reichert, F.; Schoeller, W. W. *Angew. Chem.* **1988**, *100*, 1779; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1713.
- (20) Albers, H. *Angew. Chem.* **1950**, *62*, 451.
- (21) Gier, T. E. *J. Am. Chem. Soc.* **1961**, *83*, 1769.
- (22) Fuchs, E. P. O.; Hermesdorf, M.; Schnurr, W.; Rösch, W.; Heydt, H.; Regitz, M. *J. Organomet. Chem.* **1987**, *338*, 329.
- (23) Becker, G.; Gresser, G.; Uhl, W. *Z. Naturforsch., B* **1981**, *36*, 16.
- (24) Rösch, W.; Hees, U.; Regitz, M. *Chem. Ber.* **1987**, *120*, 1645.
- (25) Appel, R.; Westerhaus, A. *Tetrahedron Lett.* **1981**, *22*, 2159.
- (26) Appel, R.; Maier, G.; Reisenauer, H.-P.; Westerhaus, A. *Angew. Chem.* **1981**, *93*, 215; *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 197.
- (27) Burckett-St. Laurent, J. C. T. R.; Kroto, H. W.; Nixon, J. F.; Ohno, K. *J. Mol. Spectrosc.* **1982**, *92*, 158.
- (28) Review: Appel, R.; Knoll, F.; Ruppert, I. *Angew. Chem.* **1981**, *93*, 771; *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 731.
- (29) Review: Regitz, M. In *Houben-Weyl: Methoden der Organischen Chemie E1*; Thieme: Stuttgart, 1982; p 28.
- (30) Review: Becker, G.; Becker, W.; Mundt, O. *Phosphorus Sulfur* **1983**, *14*, 267.
- (31) Cooper, T. A.; Kroto, H. W.; Nixon, J. F.; Ohashi, O. *J. Chem. Soc., Chem. Commun.* **1980**, 333.
- (32) Pellerin, B.; Denis, J. M.; Perrocheau, J.; Carrié, R. *Tetrahedron Lett.* **1986**, *27*, 723.
- (33) Hopkinson, M. J.; Kroto, H. W.; Nixon, J. F.; Simmons, N. P. C. *Chem. Phys. Lett.* **1976**, *42*, 460.
- (34) Hermesdorf, M.; Birkel, M.; Heydt, H.; Regitz, M. *Phosphorus Sulfur* **1989**, *46*, 31.
- (35) Westwood, N. P. C.; Kroto, H. W.; Nixon, J. F.; Simmons, N. P. C. *J. Chem. Soc., Dalton Trans.* **1979**, 1405.
- (36) Ohno, K.; Kroto, H. W.; Nixon, J. F. *J. Mol. Spectrosc.* **1981**, *90*, 507.
- (37) Burckett-St. Laurent, J. C. T. R.; Cooper, T. A.; Kroto, H. W.; Nixon, J. F.; Ohashi, O.; Ohno, K. *J. Mol. Struct.* **1982**, *79*, 215.
- (38) Regitz, M.; Hermesdorf, M., unpublished results, Kaiserslautern, 1989.
- (39) Kroto, H. W.; Nixon, J. F.; Simmons, N. P. C.; Westwood, N. P. C. *J. Am. Chem. Soc.* **1978**, *100*, 446.
- (40) Esthiag-Hosseini, H.; Kroto, H. W.; Nixon, J. F. *J. Chem. Soc., Chem. Commun.* **1979**, 653.
- (41) Ohno, K.; Matsuura, H.; Kroto, H. W.; Murata, H. *Chem. Lett.* **1982**, 981.
- (42) Ohno, K.; Matsuura, H.; McNaughton, D.; Kroto, H. W. *J. Mol. Spectrosc.* **1985**, *111*, 415.
- (43) Kroto, H. W.; Nixon, J. F.; Simmons, N. P. C. *J. Mol. Spectrosc.* **1980**, *82*, 185.
- (44) Kroto, H. W.; Nixon, J. F.; Ohno, K. *J. Mol. Spectrosc.* **1981**, *90*, 512.
- (45) Durrant, M. C.; Kroto, H. W.; McNaughton, D.; Nixon, J. F. *J. Mol. Spectrosc.* **1985**, *109*, 8.
- (46) Becker, G.; Hölderich, W. *Chem. Ber.* **1975**, *108*, 2484.
- (47) Fritz, G.; Hölderich, W. *Z. Anorg. Allg. Chem.* **1976**, *422*, 104.
- (48) Rösch, W.; Vogelbacher, U.; Allspach, T.; Regitz, M. *J. Organomet. Chem.* **1986**, *306*, 39.
- (49) Regitz, M.; Rösch, W.; Allspach, T.; Annen, U.; Blatter, K.; Fink, J.; Hermesdorf, M.; Heydt, H.; Vogelbacher, U.; Wagner, O. *Phosphorus Sulfur* **1987**, *30*, 479.
- (50) Becker, G.; Becker, W.; Knebl, R.; Schmidt, H.; Weber, U.; Westerhausen, M. *Nova Acta Leopoldina (Neue Folge)* **1985**, *59*, 55.
- (51) Regitz, M.; Allspach, T., unpublished results, Kaiserslautern, 1986.
- (52) Allspach, T.; Regitz, M.; Becker, G.; Becker, W. *Synthesis* **1986**, 31.
- (53) Märkl, G.; Sejpka, H. *Tetrahedron Lett.* **1985**, *26*, 5507.
- (54) Märkl, G.; Sejpka, H. *Tetrahedron Lett.* **1986**, *27*, 171.
- (55) Becker, G. *Z. Anorg. Allg. Chem.* **1977**, *430*, 66.
- (56) Barron, A. R.; Cowley, A. H.; Hall, S. W. *J. Chem. Soc., Chem. Commun.* **1987**, 980.
- (57) Regitz, M.; Allspach, T. *Chem. Ber.* **1987**, *120*, 1269.
- (58) Cf. ref 50, where it is cited as Becker, G.; Westerhausen, M., unpublished.
- (59) Schäfer, H.; Fritz, G.; Hölderich, W. *Z. Anorg. Allg. Chem.* **1977**, *428*, 222.
- (60) Appel, R.; Poppe, M. *Angew. Chem.* **1989**, *101*, 70; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 53.
- (61) Ruppert, I. *Tetrahedron Lett.* **1977**, *18*, 1987.
- (62) Regitz, M.; Maas, G. *Diazo Compounds—Properties and Synthesis*; Academic Press: Orlando, FL, 1986; p 436.
- (63) Regitz, M.; Facklam, T., unpublished results, Kaiserslautern, 1989; cf. ref 11.
- (64) Lehmann, K. K.; Ross, S. C.; Lohr, L. L. *J. Chem. Phys.* **1985**, *82*, 4460.
- (65) Lellouch, E.; Destombes, J. L. *Astron. Astrophys.* **1985**, *152*, 405.
- (66) Klaye, J. A.; Strobel, D. F. *Icarus* **1984**, *59*, 314.
- (67) Tyler, J. K. *J. Chem. Phys.* **1964**, *40*, 1170.
- (68) Oberhammer, H.; Becker, G.; Gresser, G. *J. Mol. Struct.* **1981**, *75*, 283. The P/C bond length in 3k is 1.516 (13) Å (X-ray structure analysis): Arif, A. M.; Barron, A. R.; Cowley, A. H.; Hall, S. W. *J. Chem. Soc., Chem. Commun.* **1988**, 171.
- (69) Frost, D. C.; Lee, S. T.; McDowell, C. A. *Chem. Phys. Lett.* **1973**, *23*, 47.
- (70) Solouki, B.; Bock, H.; Appel, R.; Westerhaus, A.; Becker, G.; Uhl, G. *Chem. Ber.* **1982**, *115*, 3747.
- (71) Burckett-St. Laurent, J. C. T. R.; King, M. A.; Kroto, H. W.; Nixon, J. F.; Suffolk, R. J. *J. Chem. Soc., Dalton Trans.* **1983**, 755.
- (72) Ohno, K.; Yamamoto, Y.; Matsuura, H.; Murata, H. *Chem. Lett.* **1984**, 413.
- (73) Arit, A. M.; Barron, A. R.; Cowley, A. H.; Hall, S. W. *J. Chem. Soc., Chem. Commun.* **1988**, 171.
- (74) Robert, J. B.; Marsmann, H.; Absar, J.; van Wazer, J. R. *J. Am. Chem. Soc.* **1971**, *93*, 3320.
- (75) Becker, G.; Becker, W.; Knebel, R.; Schmidt, H.; Mildnerbrand, M.; Westerhausen, M. *Phosphorus Sulfur* **1987**, *30*, 349.
- (76) Fuchs, E. P. O.; Rösch, W.; Regitz, M. *Angew. Chem.* **1987**, *99*, 1058; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1011.
- (77) Annen, U.; Regitz, M. *Tetrahedron Lett.* **1988**, *29*, 1681.
- (78) Gudat, D.; Niecke, E.; Krebs, B.; Dorfmann, M. *Chimia* **1985**, *39*, 277.
- (79) Wagner, O.; Ehle, M.; Regitz, M. *Angew. Chem.* **1989**, *101*, 227; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 225.

- (80) Regitz, M.; Wagner, O., unpublished results, Kaiserslautern, 1989.
- (81) Weber, W.; de Meijere, A. *Angew. Chem.* 1980, 92, 135; *Angew. Chem., Int. Ed. Engl.* 1980, 19, 138.
- (82) Regitz, M.; Wettling, T., unpublished results, Kaiserslautern, 1989.
- (83) Regitz, M.; Hoffmann, J.; Wagner, O., unpublished results, Kaiserslautern, 1989.
- (84) Heydt, A.; Heydt, H.; Weber, B.; Regitz, M. *Chem. Ber.* 1982, 115, 2965.
- (85) Schäfer, A.; Weidenbruch, M.; Saak, W.; Pohl, S. *Angew. Chem.* 1987, 99, 806; *Angew. Chem., Int. Ed. Engl.* 1987, 26, 766.
- (86) Cowley, A. H.; Hall, S. W.; Nunn, C. M.; Power, J. M. *J. Chem. Soc., Chem. Commun.* 1988, 753.
- (87) Niecke, E.; Barion, D. *Tetrahedron Lett.* 1989, 30, 459.
- (88) Review: Mathey, F. *Angew. Chem.* 1987, 99, 285; *Angew. Chem., Int. Ed. Engl.* 1987, 26, 275.
- (89) Regitz, M.; Kraft, U.; Zurmühlen, F., unpublished results, Kaiserslautern, 1989.
- (90) Cowley, A. H.; Hall, S. W.; Nunn, C. M.; Power, J. M. *Angew. Chem.* 1988, 100, 874; *Angew. Chem., Int. Ed. Engl.* 1988, 27, 838.
- (91) Davidson, P. J.; Harris, D. H.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* 1976, 2268. Goldberg, D. E.; Hitchcock, P. B.; Lappert, M. F.; Thomas, K. M.; Fjeldberg, T.; Haland, H.; Schilling, B. E. R. *J. Chem. Soc., Dalton Trans.* 1986, 2385. Zilm, K. W.; Lawless, G. A.; Merrill, R. M.; Millar, J. M.; Webb, G. G. *J. Am. Chem. Soc.* 1987, 109, 7236.
- (92) Wettling, T.; Schneider, J.; Wagner, O.; Kreiter, C. G.; Regitz, M. *Angew. Chem.* 1989, 101, 1035; *Angew. Chem., Int. Ed. Engl.* 1989, 28, 1013. PE spectra, calculation of net charges for P and C, cf.: Gleiter, R.; Pfeifer, K.-H.; Baudler, M.; Scholz, G.; Wettling, T.; Regitz, M. *Chem. Ber.*, in press.
- (93) Hitchcock, P. B.; Maah, M. J.; Nixon, J. F. *J. Chem. Soc., Chem. Commun.* 1986, 737. Binger, P.; Milczarek, R.; Mynott, R.; Regitz, M.; Rösch, W. *Angew. Chem.* 1986, 98, 645; *Angew. Chem., Int. Ed. Engl.* 1986, 25, 644. Binger, P.; Milczarek, R.; Mynott, R.; Tsai, Y. H.; Raabe, E.; Krüger, C.; Regitz, M. *Chem. Ber.* 1988, 121, 637. Binger, P.; Biedenbach, B.; Krüger, C.; Regitz, M. *Angew. Chem.* 1987, 99, 798; *Angew. Chem., Int. Ed. Engl.* 1987, 26, 764.
- (94) Barron, A. R.; Cowley, A. H. *Angew. Chem.* 1987, 99, 956; *Angew. Chem., Int. Ed. Engl.* 1987, 26, 907. Milczarek, R.; Rüsseler, W.; Binger, P.; Jonas, K.; Angermund, J.; Krüger, C.; Regitz, M. *Angew. Chem.* 1987, 99, 957; *Angew. Chem., Int. Ed. Engl.* 1987, 26, 907.
- (95) Hu, D.; Schäufele, H.; Pritzkow, H.; Zenneck, U. *Angew. Chem.* 1989, 101, 929; *Angew. Chem., Int. Ed. Engl.* 1989, 28, 900.
- (96) Fleischer, E. B. *J. Am. Chem. Soc.* 1964, 86, 3889. Eaton, P.; Cole, T. *J. Am. Chem. Soc.* 1964, 86, 3157.
- (97) Becker, G.; Massa, W.; Mundt, O.; Schmidt, R. *Z. Anorg. Allg. Chem.* 1982, 485, 23. Appel, R.; Casser, C.; Knoch, F. *Chem. Ber.* 1984, 117, 2693.
- (98) Rösch, W.; Regitz, M. *Angew. Chem.* 1984, 96, 898; *Angew. Chem., Int. Ed. Engl.* 1984, 23, 900.
- (99) Yeng Lam Ko, Y. Y. C.; Carrié, R.; Münch, A.; Becker, G. *J. Chem. Soc., Chem. Commun.* 1984, 1634.
- (100) Review: Schmidpeter, A.; Karaghiosoff, *Nachr. Chem. Tech. Lab.* 1985, 33, 793.
- (101) Kerschel, S.; Wrackmeyer, B.; Wilhalm, A.; Schmidpeter, A. *J. Organomet. Chem.* 1987, 319, 49 and preceding papers of the same series.
- (102) Regitz, M.; Rösch, W., unpublished results, Kaiserslautern, 1986.
- (103) Wagner, O.; Maas, G.; Regitz, M. *Angew. Chem.* 1987, 99, 1328; *Angew. Chem., Int. Ed. Engl.* 1987, 26, 1257.
- (104) Cowley, A. H.; Hall, S. W.; Jones, R. A.; Numm, C. M. *J. Chem. Soc., Chem. Commun.* 1988, 867.
- (105) Regitz, M.; Heydt, H. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley: New York, 1984; Vol. 1, p 393.
- (106) Klebach, T. C.; Lourens, R.; Bickelhaupt, F.; Stam, C. H.; van Herk, A. *J. Organomet. Chem.* 1981, 210, 211.
- (107) Appel, R.; Casser, C.; Immenkeppel, M.; Knoch, F. *Angew. Chem.* 1984, 96, 905; *Angew. Chem., Int. Ed. Engl.* 1984, 23, 895.
- (108) Keller, H.; Regitz, M. *Tetrahedron Lett.* 1988, 29, 925.
- (109) Rösch, W.; Facklam, T.; Regitz, M. *Tetrahedron* 1987, 43, 3247.
- (110) Regitz, M.; Burkhart, B., unpublished results, Kaiserslautern, 1987.
- (111) Rösch, W.; Regitz, M. *Synthesis* 1987, 689.
- (112) Franz, J. E.; Black, L. L. *Tetrahedron Lett.* 1970, 1381.
- (113) Gotthardt, H.; Huisgen, R. *Chem. Ber.* 1968, 101, 1059.
- (114) Rösch, W.; Richter, H.; Regitz, M. *Chem. Ber.* 1987, 120, 1809.
- (115) Weinmaier, H. J.; Brumhuber, G.; Schmidpeter, A. *Chem. Ber.* 1980, 113, 2278.
- (116) Issleib, K.; Vollmer, R. *Z. Anorg. Allg. Chem.* 1981, 481, 22.
- (117) Heinicke, H.; Tzschach, A. *Tetrahedron Lett.* 1982, 23, 3643.
- (118) Heinicke, H. *Tetrahedron Lett.* 1986, 27, 5699.
- (119) Märkl, G.; Dorfmeister, G. *Tetrahedron Lett.* 1986, 27, 441.
- (120) Issleib, K.; Vollmer, R. *Tetrahedron Lett.* 1980, 21, 3483.
- (121) Bethäuser, W.; Regitz, M.; Theis, W. *Tetrahedron Lett.* 1981, 22, 2535. Theis, W.; Bethäuser, W.; Regitz, M. *Chem. Ber.* 1985, 118, 28.
- (122) Regitz, M.; Burkhart, B., unpublished results, Kaiserslautern, 1989.
- (123) Regitz, M.; Heydt, H.; Kamel, N., unpublished results, Kaiserslautern, 1988.
- (124) Regitz, M.; Fuchs, E. P. O.; Bergsträsser, U., unpublished results, Kaiserslautern, 1988.
- (125) Regitz, M.; Michels, G.; Fuchs, E. P. O., unpublished results, Kaiserslautern, 1987.
- (126) Wollweber, M. *Diels-Alder-Reaktion*; Thieme: Stuttgart, 1972; p 139.
- (127) Alder, K.; Brochhagen, F.; Kaiser, C.; Roth, W. *Liebigs Ann. Chem.* 1955, 593, 1. Huebner, C. F.; Donoghue, E.; Dorfman, L.; Stuber, F. A.; Daniel, N.; Wenkert, E. *Tetrahedron Lett.* 1966, 1185.
- (128) Regitz, M.; Fässler, R., unpublished results, Kaiserslautern, 1989.
- (129) Regitz, M.; Annen, U., unpublished results, Kaiserslautern, 1988.
- (130) Review: Märkl, G. In *Houben-Weyl: Methoden der Organischen Chemie E1*; Thieme: Stuttgart, 1982; p 72.
- (131) Rösch, W.; Regitz, M. *Z. Naturforsch., B* 1986, 41, 931.
- (132) Hussong, R.; Heydt, H.; Regitz, M. *Phosphorus Sulfur* 1985, 25, 201. *Z. Naturforsch., B* 1986, 41, 915.
- (133) Hussong, R.; Heydt, H.; Maas, G.; Regitz, M. *Chem. Ber.* 1987, 120, 1263.
- (134) Appel, R.; Grosse-Bley, M.; Souady, H.; Steglich, W. *Phosphorus Sulfur* 1987, 30, 757.
- (135) Annen, U.; Regitz, M.; Kluge, H. *Chem. Ber.*, in press.
- (136) Lemal, D. M.; Gosselink, E. P.; McGregor, S. D. *J. Am. Chem. Soc.* 1966, 88, 582.
- (137) Annen, U.; Regitz, M. *Tetrahedron Lett.* 1987, 28, 5141.
- (138) Märkl, G.; Lieb, F. *Angew. Chem.* 1968, 80, 702; *Angew. Chem., Int. Ed. Engl.* 1968, 7, 733. Ashe, A. J.; Gordon, M. D. *J. Am. Chem. Soc.* 1972, 94, 7596. Märkl, G.; Heier, K. H. *Tetrahedron Lett.* 1974, 4369. Märkl, G.; Lieb, F.; Martin, C. *Tetrahedron Lett.* 1971, 1249.
- (139) Klebach, T. C.; Turkenburg, L. A. M.; Bickelhaupt, F. *Tetrahedron Lett.* 1978, 1099.
- (140) Wingert, H.; Regitz, M. *Chem. Ber.* 1986, 119, 244. Maier, G.; Bauer, J.; Huber-Patz, U.; Jahn, R.; Kallfass, D.; Rodewald, H.; Irngartinger, H. *Chem. Ber.* 1986, 119, 1111. Wingert, H.; Regitz, M. *Z. Naturforsch., B* 1986, 41, 1306. Wingert, H.; Maas, G.; Regitz, M. *Tetrahedron* 1986, 42, 5341.
- (141) Fink, J.; Rösch, W.; Vogelbacher, U.-J.; Regitz, M. *Angew. Chem.* 1986, 98, 265; *Angew. Chem., Int. Ed. Engl.* 1986, 25, 280.
- (142) Blatter, K.; Rösch, W.; Vogelbacher, U.-J.; Fink, J.; Regitz, M. *Angew. Chem.* 1987, 99, 67; *Angew. Chem., Int. Ed. Engl.* 1987, 26, 85.
- (143) Regitz, M.; Schneider, J., unpublished results, Kaiserslautern, 1987.
- (144) Regitz, M.; Blatter, K., unpublished results, Kaiserslautern, 1987.
- (145) Maas, G.; Fink, J.; Wingert, H.; Blatter, K.; Regitz, M. *Chem. Ber.* 1987, 120, 819.
- (146) Vogelbacher, U.-J.; Regitz, M.; Mynott, R. *Angew. Chem.* 1986, 98, 835; *Angew. Chem., Int. Ed. Engl.* 1986, 25, 842.
- (147) Regitz, M.; Vogelbacher, U.-J., unpublished results, Kaiserslautern, 1986.
- (148) Regitz, M.; Hees, U., unpublished results, Kaiserslautern, 1988.
- (149) Vogelbacher, U.-J.; Ledermann, M.; Schach, T.; Michels, G.; Hees, U.; Regitz, M. *Angew. Chem.* 1988, 100, 304; *Angew. Chem., Int. Ed. Engl.* 1988, 27, 272.
- (150) Hees, U.; Vogelbacher, U.-J.; Michels, G.; Regitz, M. *Tetrahedron* 1989, 45, 3115.
- (151) Synthesis of 1,3-azaphosphabenzene: Märkl, G.; Dorfmeister, G. *Tetrahedron Lett.* 1987, 28, 1093.
- (152) Regitz, M.; Haber, S., unpublished results, Kaiserslautern, 1988.
- (153) Svara, J.; Fluck, E.; Riffel, H. *Z. Naturforsch., B* 1985, 40, 1258.
- (154) Fluck, E.; Becker, G.; Neumüller, B.; Knebl, R.; Heckmann, G.; Riffel, H. *Angew. Chem.* 1986, 98, 1018; *Angew. Chem., Int. Ed. Engl.* 1986, 25, 1002.
- (155) Review: Wollweber, M. In *Houben-Weyl: Methoden der Organischen Chemie V/1c*; Thieme: Stuttgart, 1970; p 1125.