Phosphaalkynes: New Building Blocks in Synthetic Chemistry[1]

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Received July 5, 1989 (Revised Manuscript Received October 27, 1989)

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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 elements were not possible. The syntheses of compounds of trivalent phosphorus with P=C double bonds such as, for example, the phosphamethine cyanine cations[3] or the phosphabenzenes[4] 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 compounds[5] 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 P_2 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 P_3N_5 (eq 2),[6] isolated in an argon matrix, and characterized by IR spectroscopy.[9] Later, the terminal η^1-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

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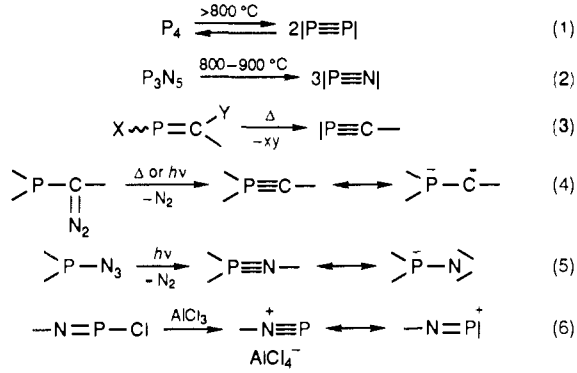
SCHEME 1



compounds are generally prepared by β-elimination reactions according to eq 3; they are stable under normal conditions when the substitutent on the carbon atom is sufficiently bulky (kinetic stabilization). Since the ligand properties of these compounds have recently been reviewed in this Journal[12] (see also ref 11), the present article is concerned mainly with the syntheses of the phosphaalkynes and their applications as building blocks in organic chemistry.

Phosphaalkynes containing $\lambda^5\sigma^3$-phosphorus atoms have now been known for a few years. They are accessible from phosphino diazo compounds under photochemical or thermal conditions according to eq 4[13,14] and react, on the one hand, at the P/C triple bond and, on the other hand, at the carbene center. Compounds of this type constitute the topic of a survey by G. Bertrand to be published in *Chemical Reviews* at about the same time as the present article and therefore will not be discussed here.

Phosphanitriles containing $\lambda^5\sigma^3$-phosphorus atoms can be generated in a similar manner by the decomposition of azidophosphanes according to eq 5.[15,16] Although these species exhibit triple-bond character, they are also able to behave as nitrenes. Finally, the first representative of a class of cationic compounds containing a P/N triple bond should be mentioned. The iminophosphenium salt with a 2,4,6-tri-*tert*-butylphenyl substituent—obtained according to eq 6—is stable, and its structure has been confirmed by an X-ray crystallographic analysis.[18,19]

All of the above-mentioned compounds are characterized by the presence of the P≡X bond. The significance of such compounds may be assessed differently by the individual preparative chemist but these evaluations will most certainly change with the course of time.

II. Short History of the Phosphaalkynes

The first indications in the literature concerning the existence of methylidynephosphane ("phosphaacetylene" (**1a** (Scheme 2))]—the parent compound of the class of trivalent but monocoordinated phosphorus compounds—appeared in 1950.[20] However, a further decade had passed before this attractive compound was unambiguously synthesized and identified experimentally.[21] Methylidynephosphane (**1a**) was formed by striking an electric arc between carbon electrodes in an atmosphere of phosphane; other products formed simultaneously were the isoelectronic acetylene and—not unexpectedly—ethylene.[21] The unusual phosphorus compound **1a** was initially identified by IR spetroscopy

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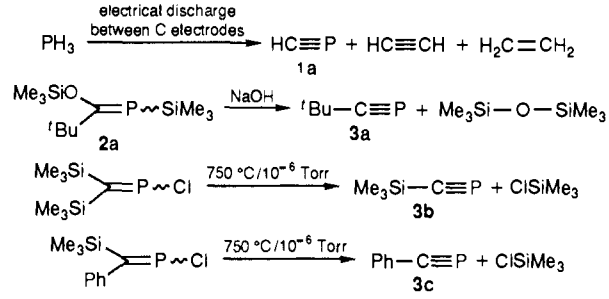


and the synthesis was later optimized.[22] It should be mentioned that in the following years more short-lived phosphaalkynes have been generated and characterized by spectroscopic methods in the groups of J. F. Nixon and H. W. Kroto (for details and references, see section III.A.1.).

With the present state of knowledge, it is hardly comprehensible that a further 20 years passed before Gier's trailblazing work[21] was followed by the synthesis of the first kinetically stabilized phosphaalkyne. (2,2-Dimethylpropylidyne)phosphane ("*tert*-butylphosphaacetylene" (**3a**)) was obtained by the sodium hydroxide catalyzed β elimination of hexamethyldisiloxane from the phosphaalkene **2a**.[23] This synthesis was later optimized and generalized with respect to the substituents.[11,24] Practically all of the pioneering experiments on the reactivity of phosphaalkynes have been performed with **3a**.[11,24]

Concomitantly with the synthesis of **3a**, the β eliminations of chlorotrimethylsilane from the respectively substituted phosphaalkenes under flash vacuum pyrolysis conditions to produce (trimethylsilyl)phosphaacetylene[25] (**3b**) and phenylphosphaacetylene[26,27] (**3c**) were realized. The latter two phosphaalkynes are, however, thermally less stable ($\tau/2$ = 50 min/20 °C[25] and 7 min/0 °C,[26,27] respectively) than **3a**, which only undergoes cyclooligomerization at temperatures of ~130 °C and higher (see below).

III. Preparations of Phosphaalkynes[11,28-30]

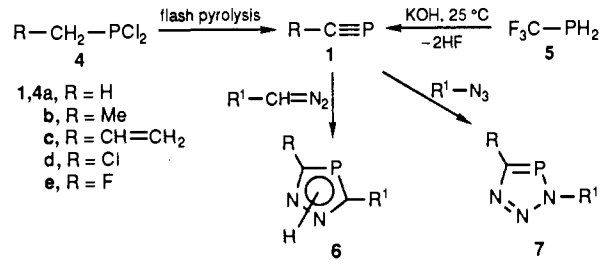
The β-elimination methodology has acquired the most significance for the construction of P/C triple bonds. The thermal elimination of HCl plays a dominating role in the generation of the short-lived phosphaalkynes whereas the sodium hydroxide catalyzed elimination of hexamethyldisiloxane is used above all for the synthesis of the kinetically stabilized members of this class of compounds. All other methods are of relatively minor importance and are used only in special cases.

A. Elimination Reactions

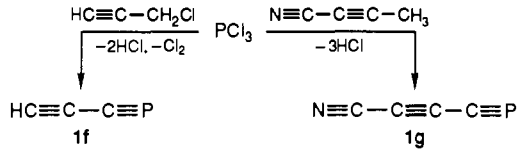
1. Of Hydrogen Halides

When the dichlorophosphane **4a** is subjected to flash vacuum pyrolysis conditions at 900–1100 °C/10^{-2}–10^{-5} Torr, a mixture of phosphaacetylene (**1a**) and HCl is formed (Scheme 3). The latter product has been separated by absorption on KOH at −78 °C,[31] on 1,3,5-tricyclohexylhexahydro-*s*-triazine at 20 °C,[32] or on KOH/K_2CO_3 at −78 °C[22] since it can otherwise participate in an undesired retro reaction. The phosphaacetylene (**1a**) can be unequivocally identified by, for

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 (→formation of 1,2,4-diazaphospholes **6**, R = H[22]) or with azides (→ formation of 1,2,3,4-triazaphospholes **7**, R = H[22]).

1-Phospha-1-propyne can be generated by an analogous method (**4b** → **1b**) in which the hydrogen chloride is either frozen out[33] 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 phosphaalkyne on a finger cooled with liquid nitrogen.[34] Like **1a**, the phosphaalkyne **1b** may also be transformed into phospholes (**6**, **7**, R = Me) by trapping reactions with diazoalkane and azide dipoles.[34]

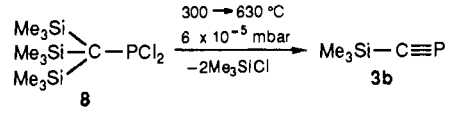
Propenylidynephosphane (**1c**)—a phosphaalkyne possessing an additional conjugated vinyl group—is also accessible from the dichlorophosphane **4c** by the thermal HCl elimination route;[35-37] however, its identification was based solely on microwave spectroscopic investigations. Chlorophosphaacetylene (**1d**) was prepared for the first time by flash vacuum pyrolysis of **4d** at 850 °C/3 × 10^{-4} mbar; PCl_3 was also formed as a byproduct.[38] The structure of **1d** was confirmed by ^{31}P NMR spectroscopy [(toluene-d_8, −70 °C): δ = +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 phosphaalkynes containing additional triple-bond units, namely, 1-phospha-1,3-butadiyne (**1f**; μ = 0.74 D)[37,44] and the hetero triyne **1g** (μ = 4.3–4.5 D),[45] respectively (Scheme 4).

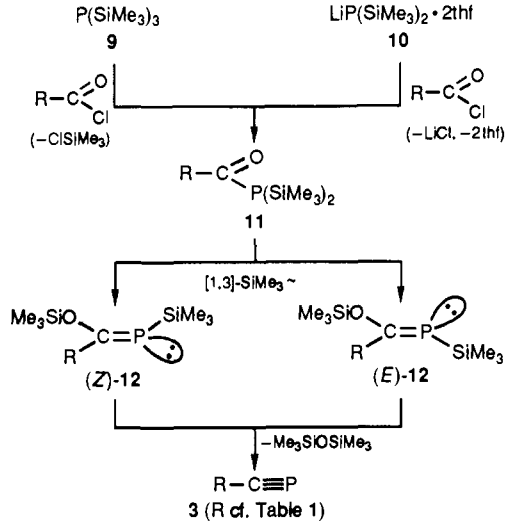
2. Of Chlorotrimethylsilane

The historical significance of the elimination of chlorotrimethylsilane in phosphaalkyne chemistry (→ **3b**,[25] →**3c**[26,27]) has already been mentioned. These reactions profit from the Si/Cl bond energy; a further advantage of this methodology is that the addition of the base, as required in eliminations of HCl, is no longer necessary.

SCHEME 5



SCHEME 6



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

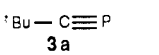
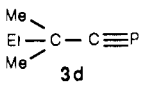
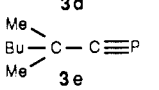
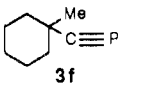
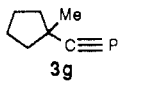
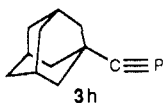
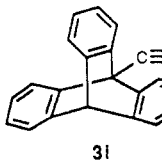
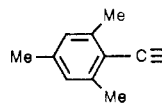
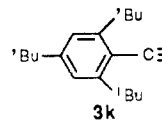
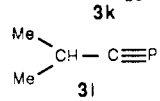
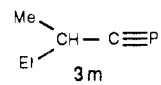
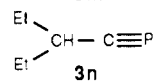
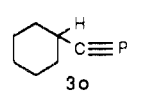
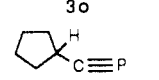
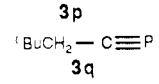
3. Of Hexamethyldisiloxane

The elimination of hexamethyldisiloxane from suitably substituted phosphaalkenes (e.g., (*E*/*Z*)-**12** → **3**) already occupies a prominent position in phosphaalkyne 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 alkyllithium 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 ^{31}P NMR spectroscopy.[52,55] However, these compounds cannot be isolated since they undergo rapid [1,3]-silyl shifts to furnish the phosphaalkenes **12** of which the *Z* isomers predominate. It is not yet known which isomer takes part in the elimination reaction to produce the phosphaalkyne **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** → **3** in solution, as originally reported,[23] but

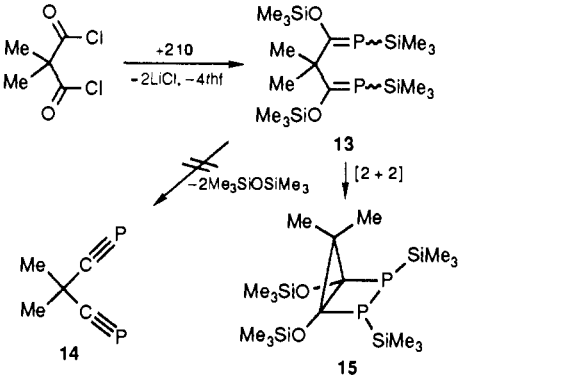
TABLE 1. Kinetically Stabilized Phosphaalkynes (3a,d-q) Prepared by Elimination of Hexamethyldisiloxane from Phosphaalkenes

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

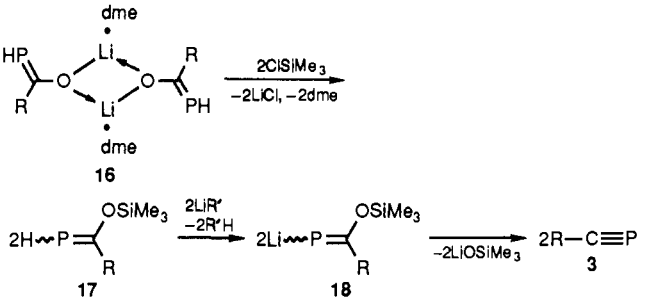
rather to work at temperatures of 120–200 °C in the absence of a solvent.[24,48,49] Using this variation, it was possible to prepare not only phosphaalkynes with tertiary carbon substituents (**3a,d–g,j**) but also those with secondary carbon substituents (see Table 1). In addition, tetrabutylammonium 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 **3i**[53] and **3k**[54] 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).

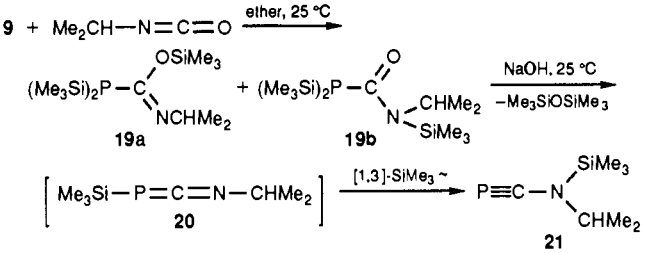
SCHEME 7



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-diphosphabicyclo[2.1.0]pentane **15**.[57]

4. *Of Lithium Trimethylsilanolate*

The elimination of lithium trimethylsilanolate from the phosphaalkenes **18** to furnish **3**[58] represents a variation of the reaction **12** → **3** which takes place under very mild conditions. Key substances in this process are the complexes **16**[59]—obtained from carboxylic acid chlorides and $LiPH_2$·dme—which are successively silylated (→**17**) and lithiated (→**18**) before the spontaneous elimination step (→**3**) can occur (Scheme 8).[58]

B. Rearrangement Reactions

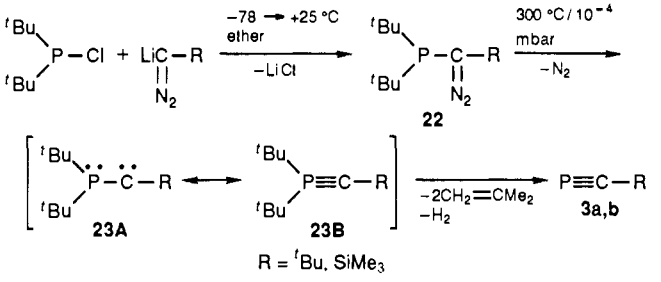
The decisive step in the preparation of a donor-substituted phosphaalkyne is the [1,3] shift of a trimethylsilyl group.[60] Reactions of this type are well-known in carbodiimide chemistry.[61] Starting materials are **9** and isopropyl isocyanate, which react to form a tautomeric mixture of **19a** and **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 ^{t}Bu-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_σ MO), eV	12.86	69	11.45	70
NMR (δ)				
^{1}H	2.90[a] ($^2J_{P,H}$ = 44.0 Hz)	22, 32	1.15[b] ($^4J_{P,H}$ = 0.9 Hz)	23
^{13}C	158.0[a] ($^1J_{P,C}$ = 56.0 Hz)	32	184.8[c] ($^1J_{P,C}$ = 38.5 Hz, $^2J_{P,C}$ = 18.2 Hz, $^3J_{P,C}$ = 6.0 Hz)	23
^{31}P	−32[a,d]	22, 32	−69.2[c,d]	23

[a] CD_2Cl_2, −80 °C. [b] Pure compound. [c] C_6D_6. [d] External H_3PO_4.

SCHEME 10



The 1-aza-3-phosphaallene **20** is presumed to be the initial product but it cannot be detected since the phosphaalkyne **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 phosphaalkynes 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 substitution[62] 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 phosphaalkynes (e.g., to 3a in 50% yield, to **3b** in 30% yield).[63] A phosphinocarbene or a λ^5-phosphaalkyne (**23A** ↔ **23B**[15]), respectively, is assumed to be the intermediate in this double-α-elimination reaction.

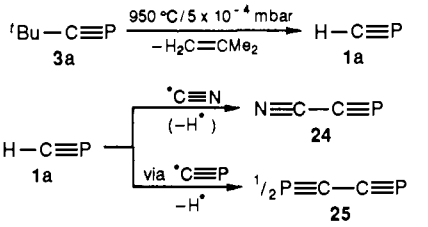
D. Transformation of Other Phosphaalkynes

Since short-lived phosphaalkynes 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 phosphaalkynes **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 phosphaalkynes.

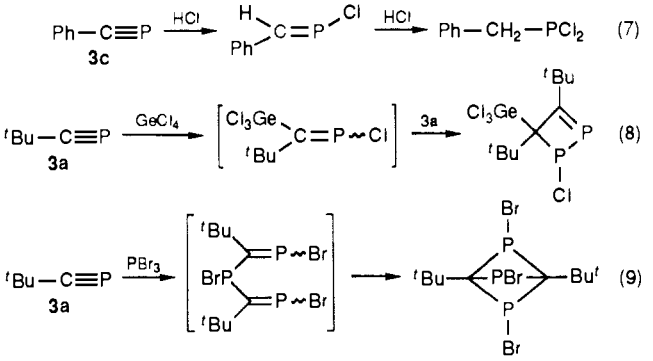
Phosphaacetylene (**1a**) is highly reactive and pyrophoric; it is best handled in dilute solutions. It can be stored for longer periods of time in toluene solution at −70 °C; on allowing the solution to warm, white phosphorus, among other products, is formed.[22] Under reduced pressure, **1a** is even 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 cyclotetramerization (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 ^{1}H, ^{13}C, and ^{31}P 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 phosphaalkynes 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 P≡C bond length of 1.516 (13) Å;[73] this is comparable with the values establishd for **1a** and **3b** by other methods (see Table 2).

For the preparative chemist, the NMR spectroscopic data of the P≡C structural unit of the phosphaalkynes are of particular interest. The ^{13}C NMR signals are observed in the region δ = 154–201 with, in some cases, a widely varying doublet splitting ($^1J_{C,P}$ = 14–56 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 δ = +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

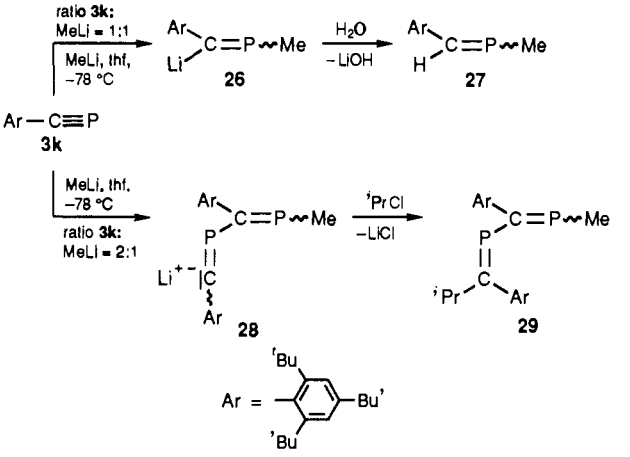
1. With Halogen Compounds

The ability of phosphaalkynes 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 phosphaalkynes.[74]

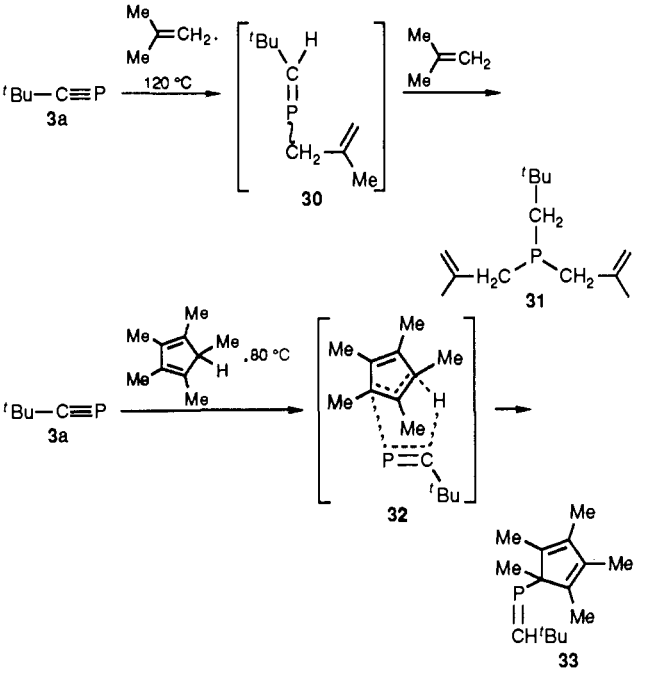
The addition of halogens to phosphaalkynes is not specific and is followed in a second step by the complete saturation and finally even in the cleavage of the P/C single bond.[50,75] Similar to halogens, boron tribromide and tin(IV) chloride undergo nonstereospecific additions to **3a** in which the 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 phosphaalkene intermediate be detected. In the case of $GeCl_4$, a subsequent [2 + 2] cycloaddition of **3a** according to (eq 8) follows,[75] wheras with PBr_3 the reaction is completed by intramolecular saturation according to (eq 9).[50,75]

2. With Organolithium Derivatives

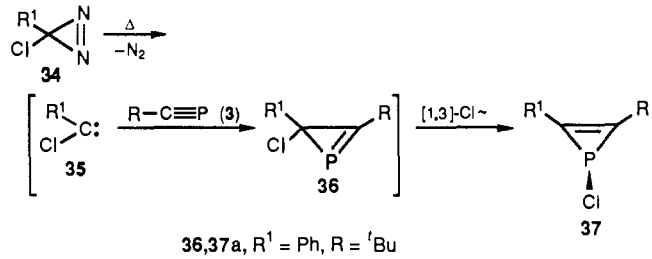
The 1,2-addition of methyllithium to the arylphosphaalkyne **3k** is dependent on the molar ratio of the reaction components and can thus be guided (Scheme 13).[73]

The lithiated phosphaalkene **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 phosphaalkene **26** is converted to **28** by reaction with excess phosphaalkyne **3k**. Subsequent alkylation with isopropyl chloride then furnishes the 1,3-diphosphadiene **29**.[73]

3. With Enophiles

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

SCHEME 15



36,37a, R^1 = Ph, R = ^{t}Bu
b, R^1 = R = ^{t}Bu
c, R^1 = PhO, R = ^{t}Bu
d, R^1 = MeO, R = ^{t}Bu
e, R^1 = Ph, R = 1-adamantyl
f, R^1 = Ph, R = C(Me$_2$)Et
g, R^1 = PhO, R = C(Me$_2$)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 phosphaalkene **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 phosphaalkene 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 phosphaalkene 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 ^{1}H 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 phosphaalkynes 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 phosphaalkyne 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

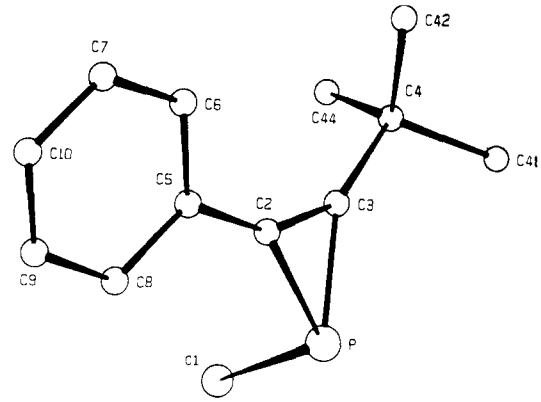
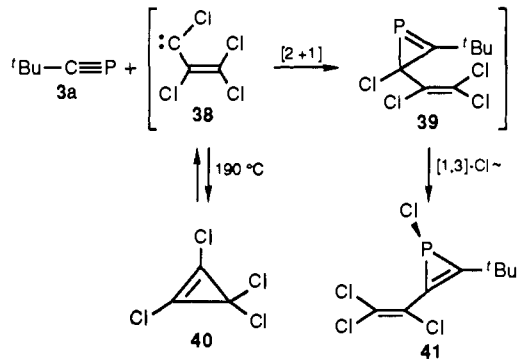


Figure 1. Crystal structure analysis of **37a** (hydrogen atoms neglected). Selected bond lengths (Å) and angles (deg): P–C2 = 1.784 (4), P–C3 = 1.784 (4), C2–3 = 1.303 (5), C1–P = 2.166 (2); C2–P–C3 = 42.9 (2), P–C2–C3 = 68.4 (2), P–C3–C2 = 68.7 (2), Cl–P–C2 = 104.2 (1), Cl–P–C3 = 103.7 (1).

SCHEME 16



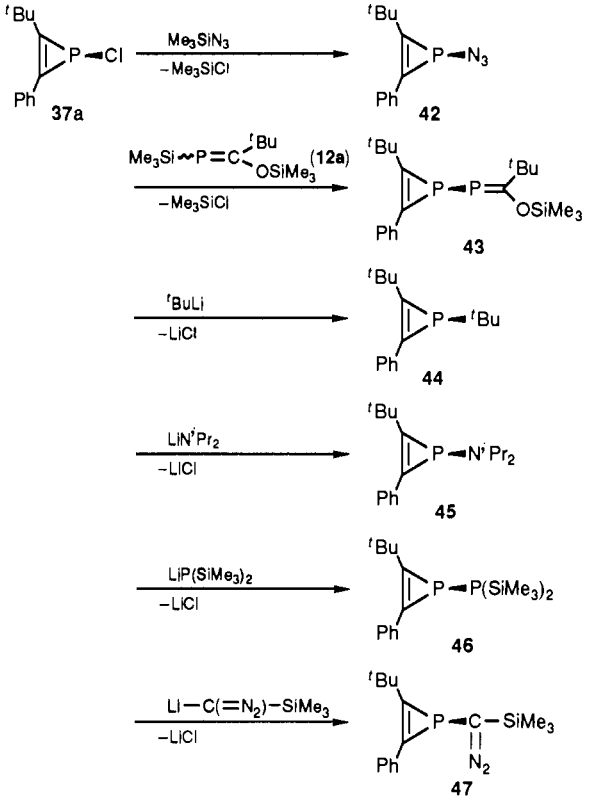
temperature is governed by the thermal stability of the respective diazirine.[79]

It is at first surprising that reactions of chloro-substituted diazirines **34** or carbenes **35** with kinetically stabilized phosphaalkynes **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.

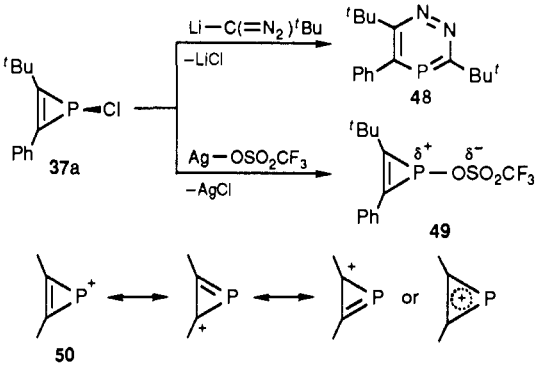
The general nature of the reaction sequence **3** + **35** → **36** → **37** is further emphasized by the reaction of **3a** with perchlorovinylcarbene (**38**). The latter substrate exists in a thermal equilibrium with tetrachlorocyclopropene (**40**)[81] and can be trapped by the phosphaalkyne (Scheme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

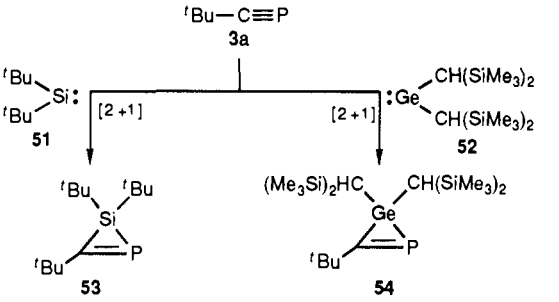
SCHEME 17



SCHEME 18



SCHEME 19



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

The above-mentioned nucleophilic exchange reactions of 1-chloro-1*H*-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 phosphaalkene **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** → **47**. The corresponding diazo compound, however, cannot now be isolated since it immediately undergoes isomerization to the phosphabenzene **48** (Scheme 18).[83] λ^3-Phosphabenzenes 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-1*H*-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 trifluoromethanesulfonate (triflate), the 1-trifloxy-1*H*-phosphirene **49** (100% yield, ^{31}P NMR: δ = −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 phosphaalkynes. However, and in contrast to the reactions of chlorocarbenes, the primary adducts containing $\lambda^3\sigma^2$-phosphorus atoms can be isolated.

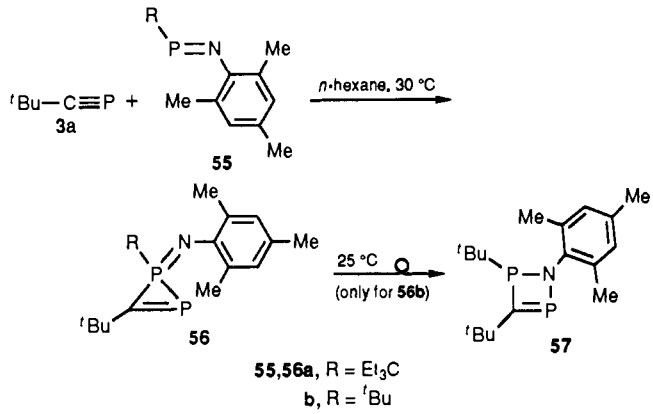
The silylene **51**, generated photochemically by cycloelimination from hexa-*tert*-butylcyclotrisilane, readily adds to **3a**, as well as to other phosphaalkynes, to furnish the phosphasilirene **53** (^{31}P NMR: δ = 274.0) (Scheme 19).[85] The structure of this three-membered-ring compound has been 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 [W(CO)$_5$·(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 phosphagermirenes **54**;[86] the P/C bond length amounts to 1.661 (11) Å.

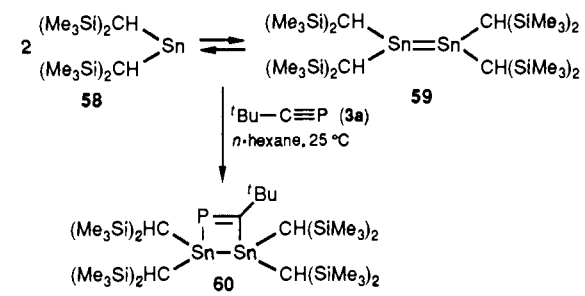
3. With Low-Coordinated Phosphorus Compounds

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 phosphaalkynes. 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: δ = 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 [$(CO)_5W$=P—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 phosphadistannacyclobutene **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

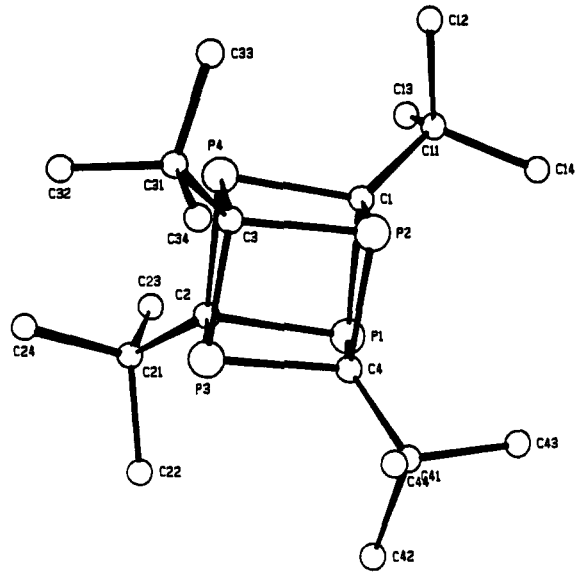
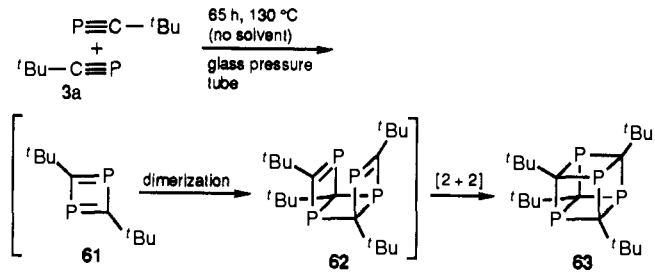


Figure 2. Crystal structure analysis of **63**. Selected bond lengths (Å) and angles (deg): P1–C1 = 1.880 (3), P1–C2 = 1.886 (3), P1–C4 = 1.877 (3), P2–C1 = 1.883 (3), P2–C3 = 1.891 (3), P2–C4 = 1.882 (4), P3–C2 = 1.881 (3), P3–C3 = 1.875 (4), P3–C4 = 1.886 (3), P4–C1 = 1.885 (3), P4–C2 = 1.876 (3), 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).

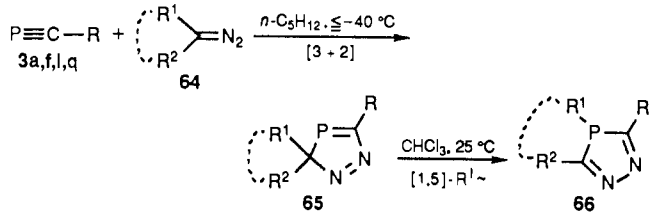
SCHEME 22



below). However, when it is heated in the absence of solvents and other reaction partners at temperatures ≥130 °C, a cyclotetramer with the confirmed structure of the tetraphosphacubane **63** is formed together with other products.[92] Previously, it was only known that cyclodimerization[93] and also cyclotrimerization[94] 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 δ = −29.07 and the low field position of the phosphorus resonance (δ = 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; $R^1 = R^2 = {}^t$Bu
b, R = ^{t}Bu; $R^1 = {}^t$Bu; R^2 = Me
c, R = ^{t}Bu; $R^1 = R^2 = {}^i$Pr
d, R = ^{t}Bu; $R^1 - - - R^2 = -CMe_2CH_2CMe_2-$
e, R = ^{t}Bu; $R^1 - - - R^2 = -CMe_2(CH_2)_2CMe_2-$
f, R = ^{t}Bu; $R^1 - - - R^2 = -CMe_2(CH_2)_3CMe_2-$
g, R = ^{t}Bu; $R^1 - - - R^2 = -CMe_2(CH_2)_4CMe_2-$
h, R = ^{t}Bu; $R^1 = R^2 = CF_3$
i, R = 1-methylcyclohexyl; $R^1 = R^2 = {}^t$Bu
j, R = ^{i}Pr; $R^1 = R^2 = {}^t$Bu
k, R = $CH_2{}^t$Bu; $R^1 = R^2 = {}^t$Bu

erage P/C bond length in the cube amounts to 1.881 Å and thus agrees well with those of the 1,3-diphosphacyclobutanes[97] (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 phosphaalkyne to furnish the λ^3-1,3-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

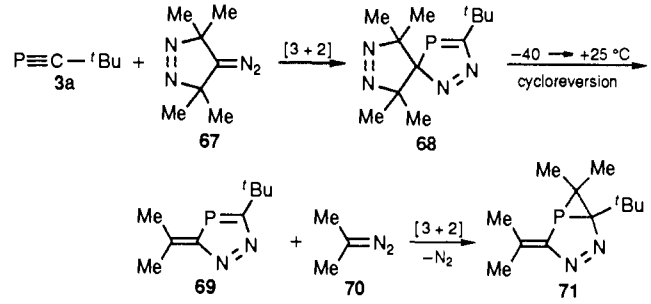
1,3-Dipolar cycloaddition reactions of diazonium and nitrilium betaines to phosphaalkynes constitute a major extension of the synthetic methodology for phospholes.[49,98,99] Previously, compounds of these types, which have played a major role in the development of the chemistry of low-coordinated phosphorus 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 regiospecifically to phosphaalkynes, the formation of regioisomeric heterocyclic products is observed in the reactions with the azomethine dipoles.

1. With Diazo Compounds

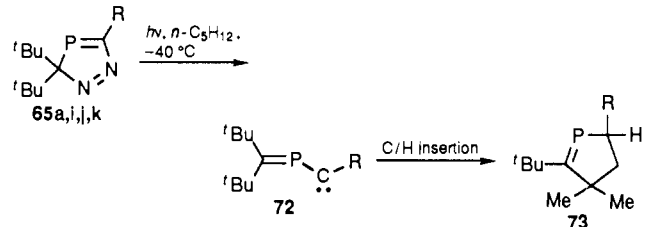
The primary products, i.e., 3*H*-1,2,4-diazaphospholes, can only be isolated from the reactions of phosphaalkynes with diazo compounds when the latter are doubly substituted with substituents that are unable to undergo sigmatropic [1,5] shifts in the product. Diazomethane, monosubstituted diazomethanes,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

(*a*) *To 3H-1,2,4-Diazaphospholes.* Diazoalkanes of the type **64** undergo regiospecific [3 + 2]-cycloaddition reactions with alkyl-substituted phosphaalkynes **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



72,73a, R = ^{t}Bu
b, R = 1-methylcyclohexyl
c, R = ^{i}Pr
d, R = $CH_2{}^t$Bu

their low-field ^{31}P NMR chemical shifts (δ = 263–204). The adducts **65d,e** cannot be isolated as a result of sigmatropic [1,5]-R^1 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]

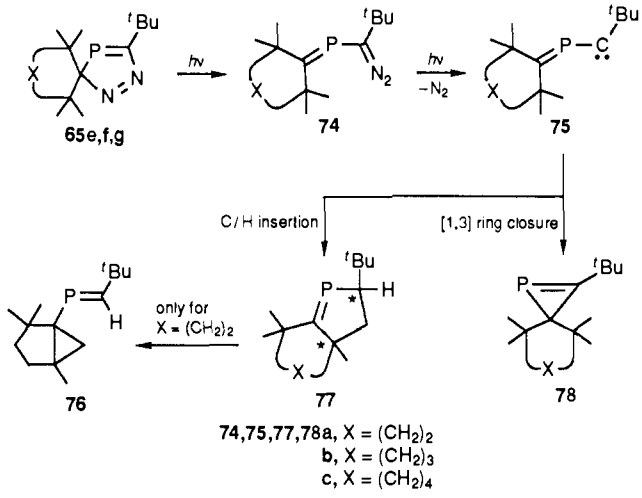
A 4*H*-1,2,4-diazaphosphole **66** (R = ^{t}Bu; $R^1 = R^2$ = Ph) is the product obtained from the reaction of diazodiphenylmethane with **3a**; the probable primary intermediate, the 3*H*-1,2,4-diazaphosphole, cannot be isolated, and the structure of the end product has been confirmed by a crystal structure 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 diazapyrazoline **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]

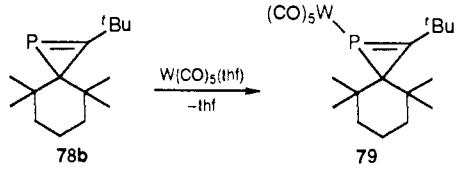
When it is assumed that **68** first undergoes [3 + 2] cycloreversion to give the isopropylidene-3*H*-1,2,4-diazaphosphole **69** and 2-diazopropane (**70**), the formation of **71** can easily be interpreted as proceeding through a [3 + 2]-cycloaddition process of the diazo dipole to the P/C double 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 $\lambda^3\sigma^2$-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-cyclopentenes **73a–d** are formed in high yields (70–85%) (Scheme 25). The products exhibit characterisitc low-field ^{31}P NMR spectroscopic resonances (δ = 250.1–262.9).[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** → **77** and **75** → **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 = $(CH_2)_2$], 1:5 [X = $(CH_2)_3$], and 1:22 [X = $(CH_2)_4$].

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 phosphavinyldiazoalkane. Since all of the 2*H*-phosphirenes obtained exhibited ^{31}P NMR signals at unexpectedly high fields [**78a**: δ = 46.8; **78b**: δ = 71.7; and **78c**: δ = 73.4; for comparison, the diastereomeric mixture of **77b** exhibits signals at δ = 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

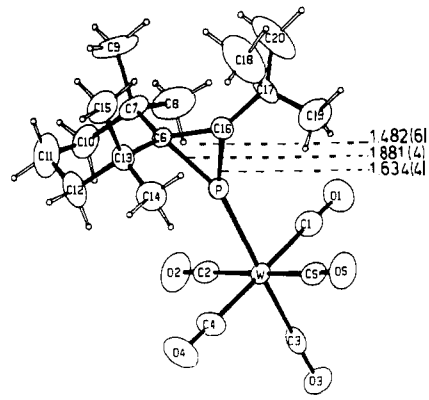
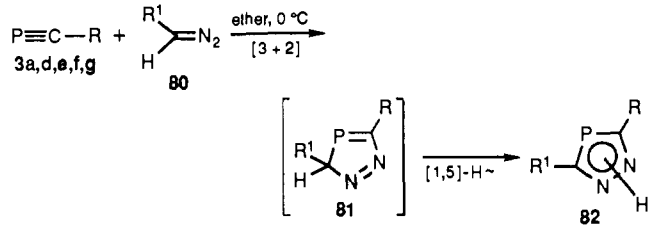


Figure 3. Crystal structure analysis of **79**. Selected bond lengths (Å) and angles (deg): P–C6 = 1.881 (4), P–C16 = 1.634 (4), C6–C16 = 1.482 (6), P–W = 2.458 (1); W–P–C6 = 157.7 (2), W–P–C16 = 153.1 (2), C6–P–C16 = 49.2 (2), P–C6–C16 = 56.7 (2), P–C16–C6 = 74.1 (3).

SCHEME 28



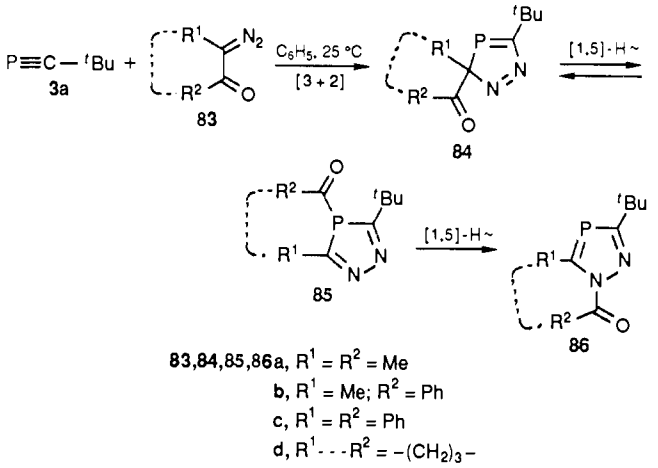
comprised exchange of the only loosely bound tetrahydrofuran ligand (Scheme 27).

The P/C double-bond length in **79** amounts to 1.634 (4) Å and is thus shorter than those of a comparable phosphasilirene complex[85] and other "end-on" coordinated complexes of open-chain phosphaalkenes.[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** (R^1 = 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**, R^1 = $SiMe_3$) to **3a**, a silyl shift completely dominates over the H shift (→**82**, R = ^{t}Bu, R^1 = H, $SiMe_3$ instead of H).[24] It is not surprising that the phosphaalkynes **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 phosphaacetylene (**1a**) with *tert*-butyl diazoacetate (**80**, R^1 = $COOBu^t$) 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



83,84,85,86a, $R^1 = R^2 = Me$
b, $R^1 = Me$; $R^2 = Ph$
c, $R^1 = R^2 = Ph$
d, $R^1 \cdots R^2 = -(CH_2)_3-$

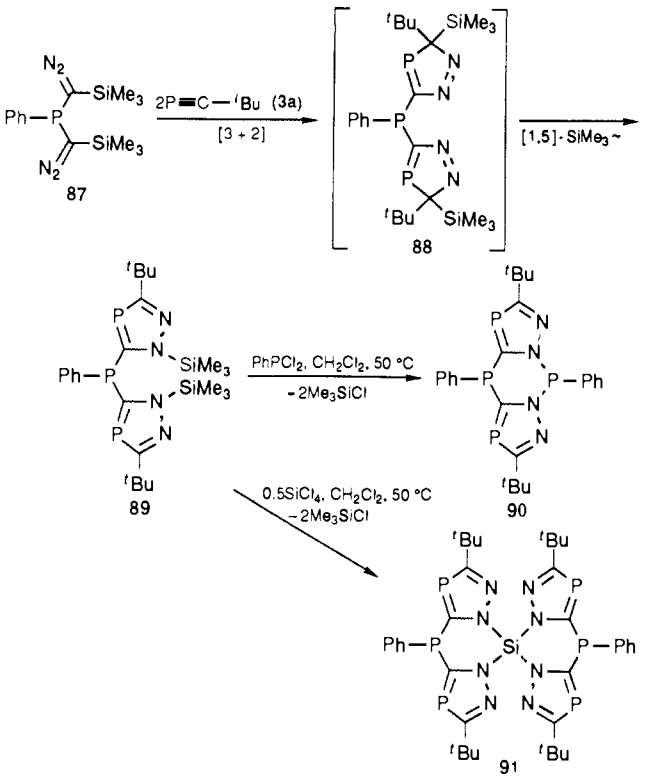
Both open-chain and cyclic α-diazo ketones such as **83a–d** react in a similar manner to the diazomethyl compounds **80** with the phosphaalkyne **3a**, the only exception being that the sigmatropic H shift is replaced by an acyl shift.[24] Again, the 3-acyl-3*H*-1,2,4-diazaphospholes **84** cannot 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 ^{31}P 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 diazoacenaphthenone react analogously (Scheme 29).[24]

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

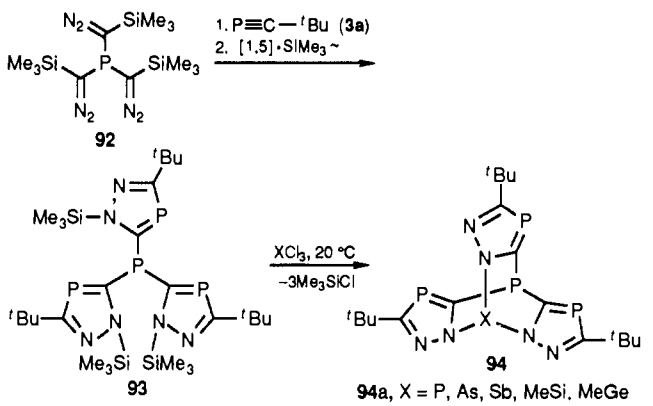
The bis(diazomethyl)phosphane **87** is readily accessible from dichlorophenylphosphane and lithiated diazo(trimethylsilyl)methane; its reaction with **3a** in a molar ratio of 1:2 gives rise to the bis(diazaphospholyl)phosphane **89** in 81% yield. In this case also, the double cycloaddition is of necessity 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 $SiCl_2$ 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



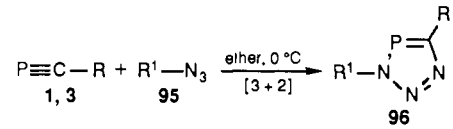
substituted bicyclic compounds **94** (Scheme 31).

2. With Azides

Azides are isoelectronic with diazo compounds and it is thus to be expected that their cycloadditions to phosphaalkynes 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 ^{31}P 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).

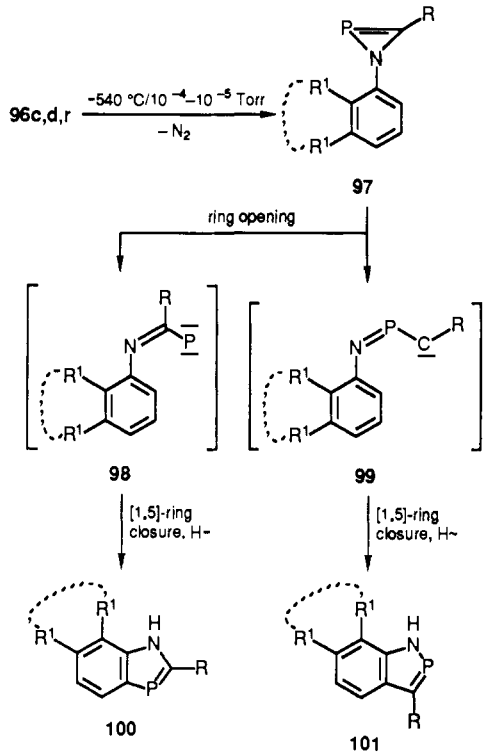
Analogous additions of methyl azide to the phosphaalkynes **3d–f,h**, and **j** are known and give rise to the

SCHEME 32



96 a, R = ^{t}Bu; R^1 = Me
b, R = R^1 = ^{t}Bu
c, R = ^{t}Bu; R^1 = Ph
d, R = ^{t}Bu; R^1 = 1-naphthyl
e, R = ^{t}Bu; R^1 = CO_2Me
f, R = ^{t}Bu; R^1 = $SiMe_3$
g, R = ^{t}Bu; R^1 = H
h, R = Me_2EtC; R^1 = Me
i, R = $Me_2{}^tBuC$; R^1 = Me
j, R = 1-methylcyclohexyl; R^1 = Me
k, R = 1-adamantyl; R^1 = Me
l, R = mesityl; R^1 = Me
m, R = ^{i}Pr; R^1 = Me
n, R = Et_2CH; R^1 = Me
o, R = cyclohexyl; R^1 = Me
p, R = $^tBuCH_2$; R^1 = Me
q, R = H; R^1 = Me
r, R = Me; R^1 = Ph

SCHEME 33



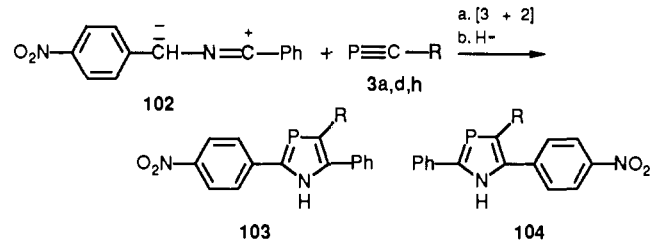
97,98,99,100,101a, R = ^{t}Bu; R^1 = H (95%; **100a**:**101a** = 1:4)[109]
b, R = ^{t}Bu; R^1---R^1 = —CH=CHCH=CH— (99%; **100b**:**101b** = 1:3)[109]
c, R = Me; R^1 = H (60%; **100c**:**101c** = 2:1)[34]

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 phosphaalkynes bearing secondary carbon substituents such as **31**, **n–q**. This is also valid for the short-lived phosphaalkynes **1a,b**, which can be frozen out and then subsequently reacted with methyl or phenyl azide to yield triazaphospholes (→**96q**,[22] **96r**[34]).

Appearances can be deceptive and it is thus not easy to eliminate nitrogen from the 3*H*-1,2,3,4-triazaphospholes **96**; this elimination occurs only under flash vacuum pyrolysis conditions. When 3-aryl-substituted 3*H*-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]

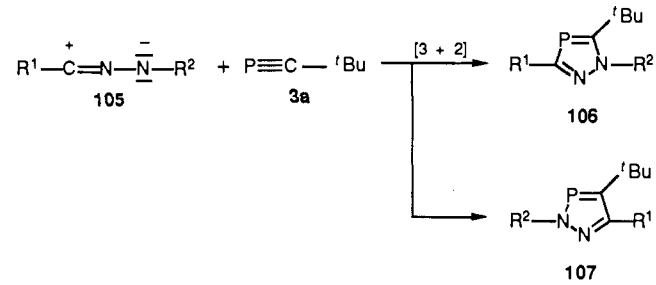
In each case, an isomeric mixture of **100** and **101** is obtained and, in some cases, the isomers could be separated. The pronounced differences in the ^{31}P NMR

SCHEME 34



103,104a, R = ^{t}Bu
b, R = Me_2EtC
c, R = 1-adamantyl

SCHEME 35



105,106,107a, R^1 = Ph; R^2 = Me
b, R^1 = Me; R^2 = Ph
c, R^1 = R^2 = Ph

chemical shifts are of decisive importance for the structural assignments of the isomers (**100a–c**: δ = 66.3–74.4; **101a–c**: δ = 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** → **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** → **100** and **99** → **101**, respectively).[34,109]

3. With Nitrilium Betaines

The nitrile ylide dipole **102** readily takes part in addition reactions with the phosphaalkynes **3a,d,h** to form 1*H*-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]

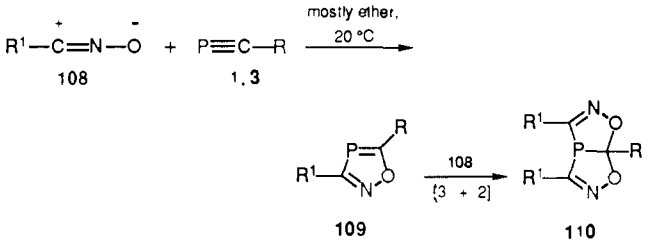
This addition is strictly regiospecific but the constitutions of the formed 1,3-azaphospholes (**103a–c** and **104a–c**) cannot be determined with certainty by NMR spectroscopy[110] (see also the synthesis of a 1*H*-1,3-azaphosphole from **3a** and an oxazolium-olate).

The nitrilium dipoles **105a** and **105b** react with **3a** to produce regioisomeric mixtures of products **106a,b** and **107a,b**; in both cases, the 1*H*-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).

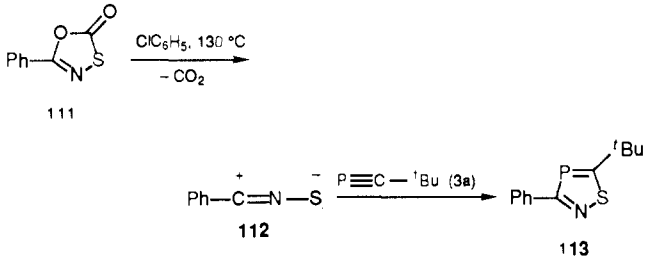
The low-field positions of the ^{31}P NMR signals of **107** (δ = 224.4 and 218.5) in comparison to those of the 1,2,4 isomers **106** (δ = 86.6–91.9) define the direction of the addition unambiguously.[111]

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

SCHEME 36



SCHEME 37



phospholes would be expected from the reactions of phosphaalkynes 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.

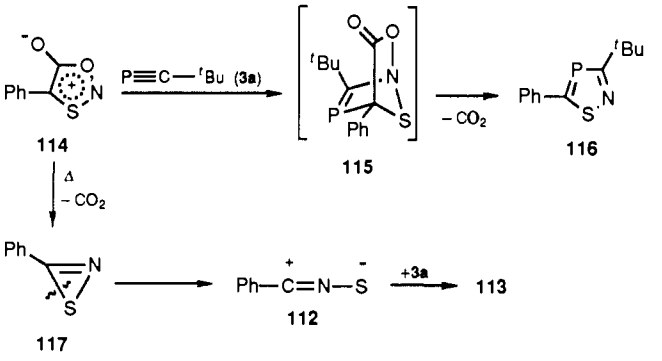
As illustrated by the wide range of 1,2,4-oxazaphospholes prepared (**110a–c**,[111] **110d,e**,[51] **110f**,[48] **110g**,[52] **10h**,[51]), the nature of the substituents on both reaction partners may be varied greatly. In the reaction of 2,2-dimethylpropanenitrile oxide (**108**, R^1 = ^{t}Bu) with **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 phosphaalkynes 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 **111**[112] (Scheme 37) (for the formation of **113** from **3a** and an oxathiazolium-olate, see below).

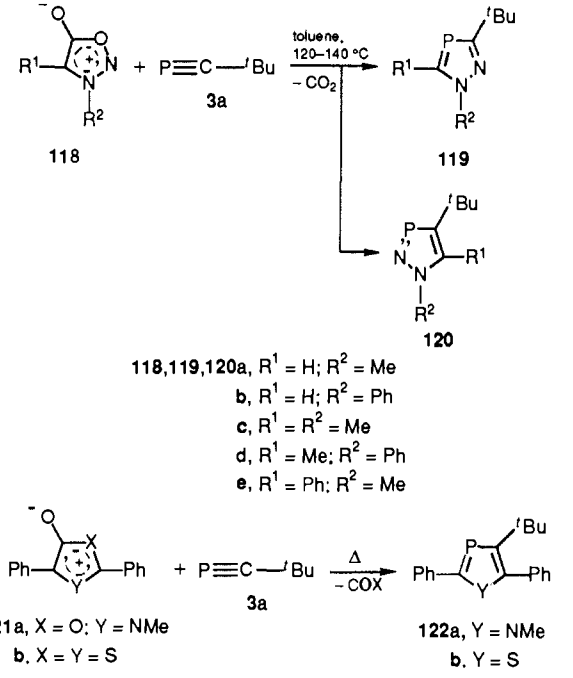
4. With Mesoionic Compounds

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

SCHEME 38



SCHEME 39



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 **114**[113] and **3a**, cannot be detected in any case. The decomposition process to give—in this case—the thiazaphosphole **116** and CO_2 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** → **117** → **112** at least provides a feasible interpretation of the experimental result.[114]

The sydnones **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 phosphaalkynes and diazo compounds. As has been shown for the case of **82a–c**, these compounds can be converted to the "syndone 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 1*H*-1,2,3-diazaphosphole **120a** is characterized by a low-field signal (δ = 229.4) (see also ref 115) whereas, in contrast, the signals for the phosphorus atoms of the 2*H*-1,2,4-diazaphospholes **119a–e** appear at considerably higher fields in the ^{31}P NMR spectra.[114]

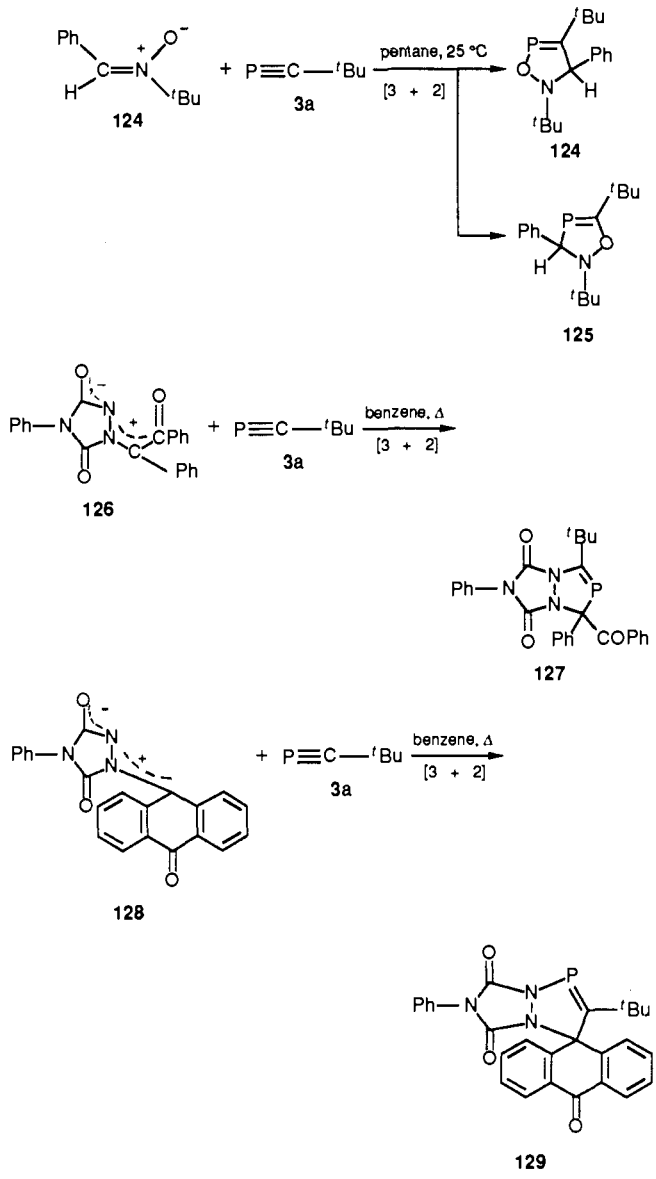
The münchnone **121a** reacts with the phosphaalkyne **3a** under moderate conditions (80 °C in benzene) to form the 1*H*-1,3-azaphosphole **122a** in 63% yield.[114] Several other routes of access to this class of compounds are also known.[116–119] The short-lived, highly reactive phosphaacetylene (**1a**) 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-thiaphospholes,[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 regiospecific or highly selective, this uniformity is not observed with nitrone 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: δ = 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: δ = 180.3),[122] which is assumed to arise from an electronically controlled cycloaddition process.

SCHEME 40



E. [4 + 2]-Cycloaddition Reactions

The particular fascination of the Diels–Alder reactions of phosphaalkynes 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 of the latter can be recognized on account of the high-field ^{31}P NMR absorptions of the two nonequivalent phosphorus atoms (δ = −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** → **131**). This reaction is not regiospecific 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** → **132**). Finally, an intramolecular [4 + 2]-cycloaddition process (**132** → **133**) gives rise to the tricyclic product.[76]

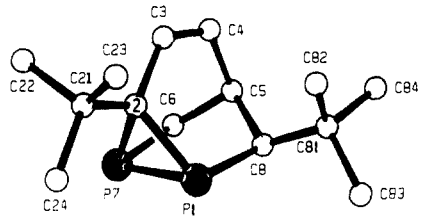
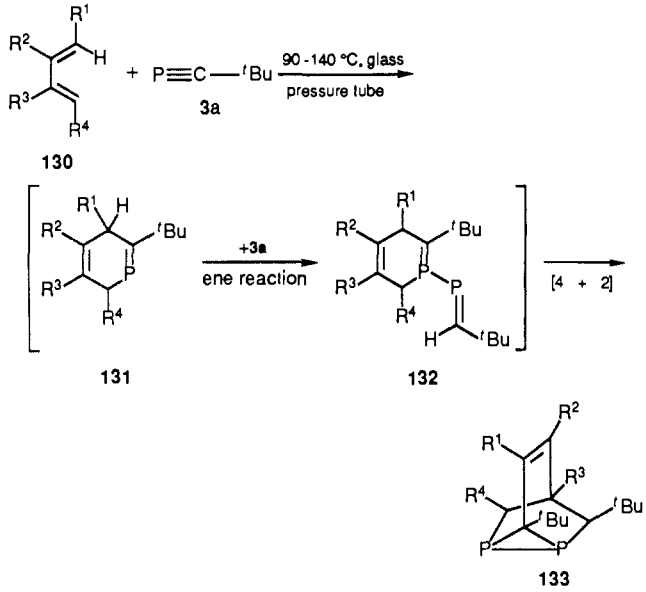


Figure 4. Crystal structure analysis of **133a**. Selected bond lengths (Å) and angles (deg) of the carbon/phosphorus skeleton: P1–P7 = 2.183 (2), P1–C2 = 1.886 (4), P1–C8 = 1.869 (4), P7–C2 = 1.888 (4), P7–C6 = 1.847 (6), C2–C3 = 1.478 (6), C3–C4 = 1.317 (6), C4–C5 = 1.492 (6), C5–C6 = 1.511 (7), C5–C8 = 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

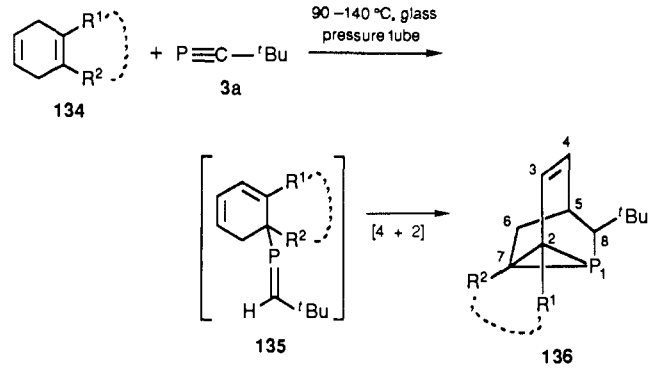


130,131,132,133a, $R^1 = R^2 = R^3 = R^4 = H$ (90%)
b, $R^1 = R^2 = R^4 = H$; $R^3 = Me$ (85%)
c, $R^1 = R^4 = H$; $R^2 = R^3 = Me$ (86%)
d, $R^1 = R^2 = R^3 = H$; $R^4 = Me$ (66%)
e, $R^1 = R^4 = Me$; $R^2 = R^3 = H$ (≤10%)
f, $R^1 = PO(OMe)_2$; $R^2 = R^4 = H$; $R^3 = Me$ (73%)
g, $R^1 = PO(OMe)_2$; $R^2 = R^4 = H$; $R^3 = {}^tBu$ (57%)
h, $R^1 = R^3 = R^4 = H$; $R^2 = PO(OMe)_2$ (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 phosphaalkene **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 ^{31}P NMR chemical shift (δ = −192.0 to −234.0) (Scheme 42).[76]

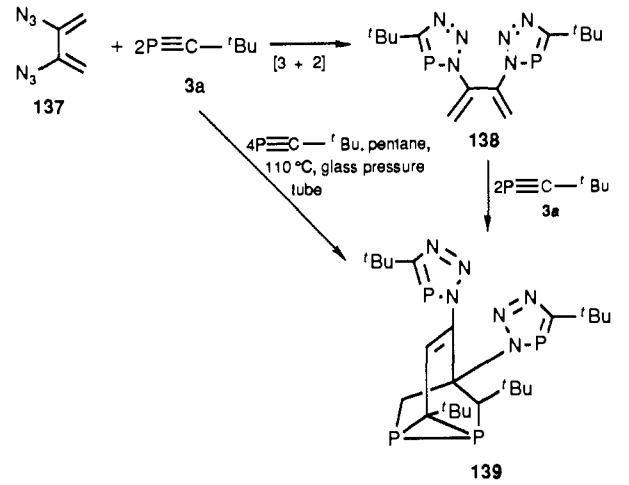
In the reactions of **134c** or **134d** with **3a** (but not in that of **134b** + **3a**), about 10% of a constitutionally isomeric tricyclic product in which the R^1–R^2 substituent now occupies the positions 4 and 5 is formed in each case in addition to the above-mentioned major products **136c** or **136d**. The ene reaction **134b** → **135b** proceeds exclusively at the substituted, electron-rich

SCHEME 42



134,135,136a, $R^1 = R^2 = H$
b, R^1---R^2 = —CH_2—CH=CH—CH_2—
c, $R^1 = R^2$ = Me
d, R^1---R^2 = —$CH_2CH_2CH_2$—

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]

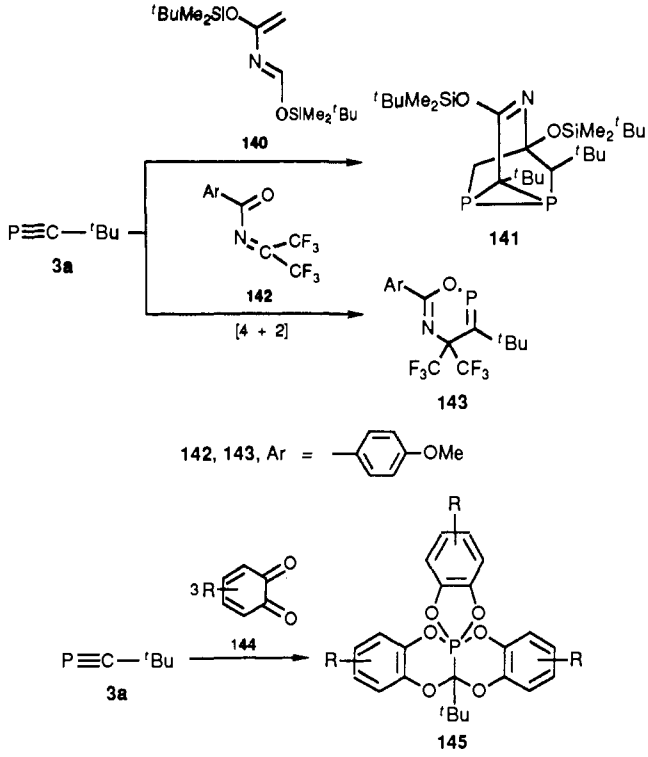
An interesting combination of a 1,3-dipolar cycloaddition, Diels–Alder reaction, and ene reaction as well as an intramolecular [4 + 2]-cycloaddition step takes place in the one-pot reaction of 2,3-diazido-1,3-butadiene (**137**) with 4 equiv of the phosphaalkyne **3a**. The product obtained is **139**, which, as exposed, exhibits four signals in the ^{31}P NMR spectrum [δ = −168, −204 (diposphirane 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 (^{31}P NMR: δ = +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: δ = −180.2, −208.2; $^{1}J_{P,P}$ = 162.7 Hz) (Scheme 44).[128]

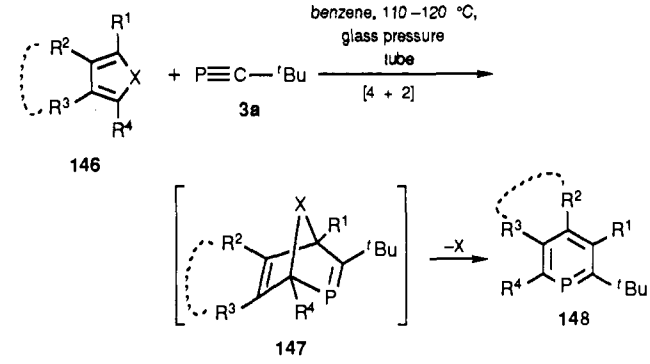
In this case also, the ene reaction must occur specifically at the phosphorus atom of the 1-aza-4-phospha-1,4-cyclohexadiene intermediate to provide the P/P bond, as is again demonstrated by the formation of a diphoshirane unit.[128] The acyl imine **142** also possesses heterodiene character, but its reaction with **3a** comes to a standstill after the Diels–Alder step (→**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 phosphaalkyne **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]

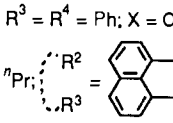
3. *With Cyclic 1,3-Dienes Possessing an "Extruding Group"*

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 phosphaalkynes 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 **148a**[131] 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 phosphabenzenes is very rapid (Scheme 45).

SCHEME 45



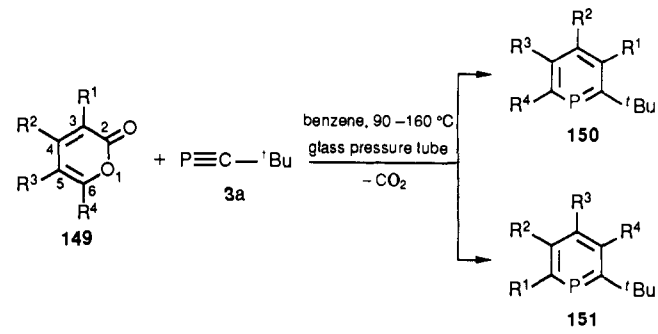
146,147,148a, $R^1 = R^2 = R^3 = R^4$ = Ph; X = CO [92%; $\delta(^{31}P)$ = 202]

b, $R^1 = R^4 = {}^n$Pr; R^2, R^3 =  ; X = CO [93%; $\delta(^{31}P)$ = 266]

c, $R^1 = R^4$ = H; $R^2 = R^3$ = Me; X = P(=S)Ph [61%; $\delta(^{31}P)$ = 187]

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]

SCHEME 46



149,150,151a, $R^1 = R^2 = R^3 = R^4$ = H [91% **150** (≡ **151**); $\delta(^{31}P)$ = 202]

b, $R^1 = R^3$ = Ph; $R^2 = R^4$ = H [48% **150**; $\delta(^{31}P)$ = 187]

c, $R^1 = R^2 = R^3$ = H; R^4 = Cl [75% **150**; $\delta(^{31}P)$ = 196]

d, $R^1 = R^3$ = H; R^2 = Cl; R^4 = Me [40% **150**; $\delta(^{31}P)$ = 190]

e, R^1 = H; $R^2 = R^4$ = Me; R^3 = CO_2Me [84% **150**; $\delta(^{31}P)$ = 188]

f, $R^1 = R^2 = R^4$ = H; R^3 = CO_2Me [27% **150**/54% **151**; $\delta(^{31}P)$ = 202/229]

g, R^1 = Br; $R^2 = R^3 = R^4$ = H [64% **151**; $\delta(^{31}P)$ = 203]

h, R^1 = CO_2Me; $R^2 = R^3 = R^4$ = H [75% **151**; $\delta(^{31}P)$ = 219]

i, $R^1 = R^2 = R^3$ = H; R^4 = Me [28% **150**; $\delta(^{31}P)$ = 197]

j, $R^1 = R^3$ = H; R^2 = $OSiMe_3$; R^4 = Me [5% **150**; $\delta(^{31}P)$ = 160]

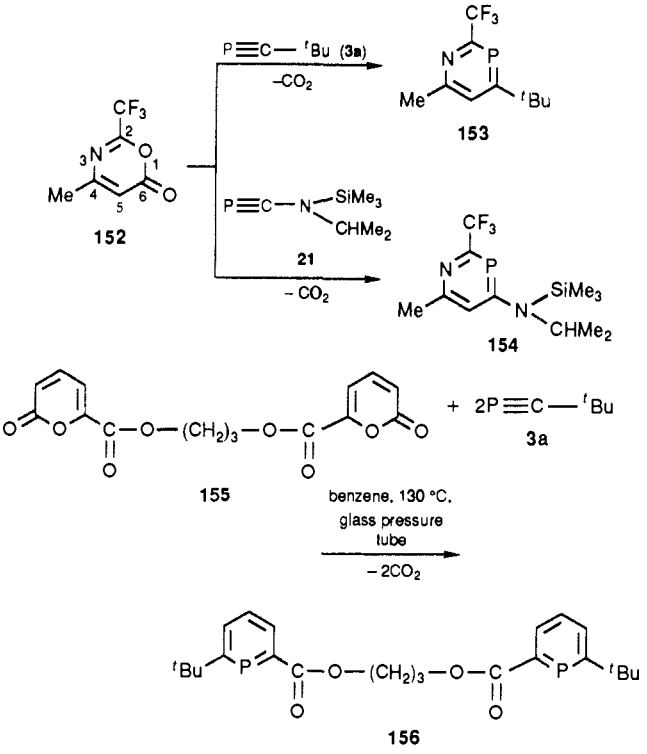
k, $R^1 = R^3$ = Me; R^2 = Me; R^4 = OMe [22% **150**; $\delta(^{31}P)$ = 119]

l, $R^1 = R^3 = R^4$ = H; R^2 = OEt [3% **150**/7% **151**; $\delta(^{31}P)$ = 156/203]

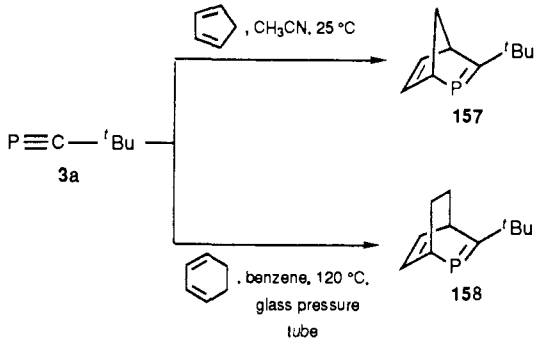
To date, the largest range of substituted λ^3-phosphabenzenes **150** and **151** has been prepared from the α-pyrones **149** and **3a** under the usual thermal conditions.[129,131] α-Pyrones bearing acceptor substituents react under milder conditions and give better yields than those bearing donor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

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

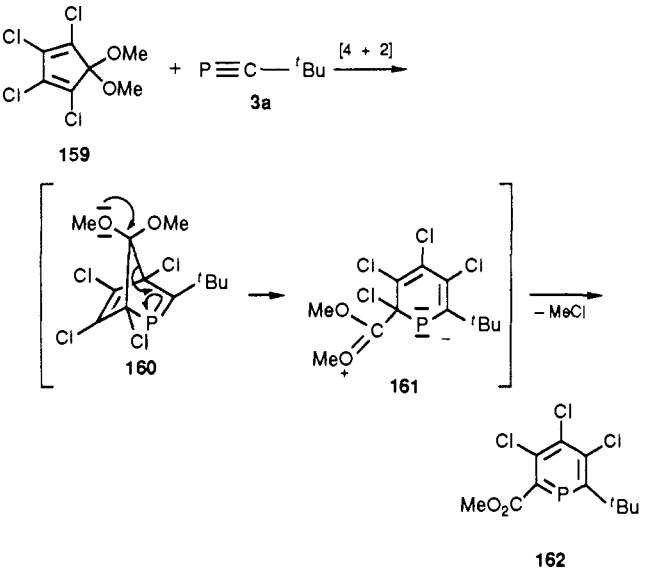
SCHEME 47



SCHEME 48



SCHEME 49



α-pyrones on the product formation (→**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., **149f** + **3a** → **150f** + **151f** (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 **150/151i–l**).[129]

The inverse electron demand of the reactions of α-pyrones with phosphaalkynes 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-azaphosphabenzenes **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

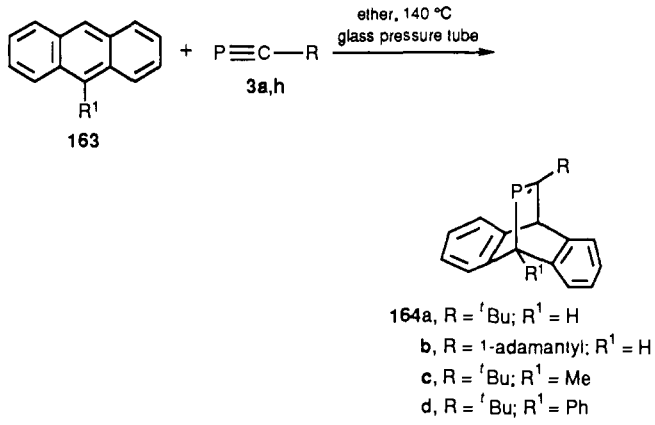
An obvious question now is whether the previously unknown bicyclic phosphaalkenes potentially accessible from the reactions of **3a** with cyclic 1,3-dienes lacking a group suitable for elimination will be stable. The initial experiments were not able to provide an answer to this problem since the addition 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 isolated[129] (see also the section on homo-Diels–Alder reactions (Scheme 48).

However, the reaction of the homologous cyclohexadiene with the same phosphaalkyne (but under 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: δ = 225.6). Cycloelimination of the ethano bridge (as ethylene) occurs only under flash vacuum pyrolysis conditions to furnish the *tert*-butyl-substituted phosphabenzene **150a** (≡**151a**).[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 phosphabenzenes. 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 (→**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 phosphabenzenes 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 phosphaalkynes **3a,h** to furnish the adducts **164a–d** (28–91% yields). These products possess low-coordinated phosphorus atoms (^{31}P NMR: δ = 230.2–246.4) 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 phosphaalkyne **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 phosphaalkynes, the highly reactive cyclobutadienes **168**, including those bearing sterically demanding substituents, take part in quantitative addition reactions with the phosphaalkynes **3a,f,h,l,q** even at low temperatures to furnish the regioisomeric Dewar 2-phosphabenzenes **169** (≥85%) and

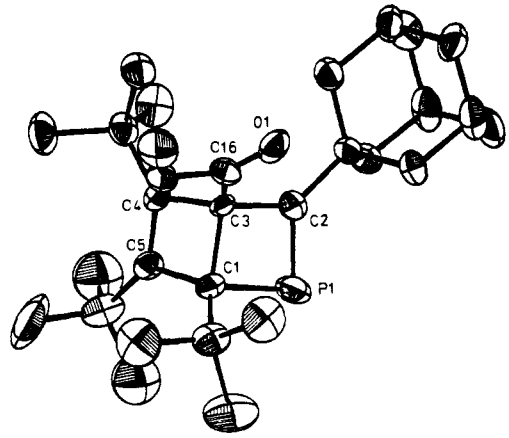
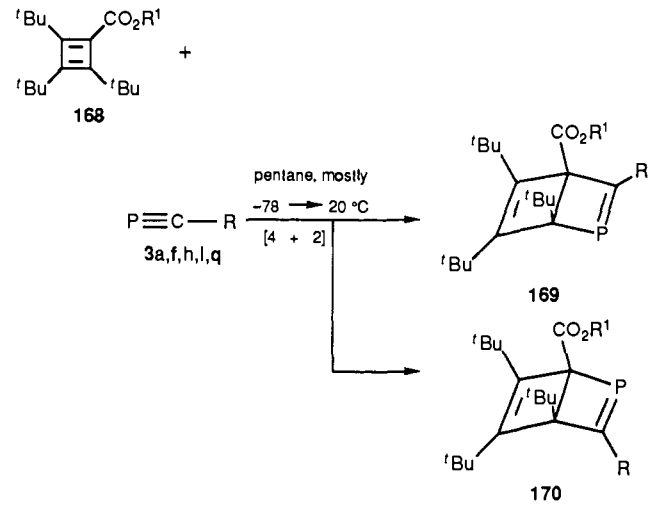


Figure 5. Crystal structure analysis of **169c**. Selected bond lengths (Å) and angles (deg): P1–C1 = 1.89 (1), P1–C2 = 1.68 (1), C1–C3 = 1.59 (1), C1–C5 = 1.53 (1), C2–C3 = 1.54 (1), C3–C4 = 1.54 (1), C4–C5 = 1.35 (1); C1–P1–C2 = 79.5 (4), P1–C1–C3 = 88.2 (5), C3–C1–C5 = 85.3 (6), P1–C2–C3 = 98.3 (6),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



169,170a, R^1 = Me; R = tBu; ratio **169**:**170** = 96:4
b, R^1 = Me; R = 1-methylcyclohexyl; ratio **169**:**170** = 98:2
c, R^1 = Me; R = 1-adamantyl; ratio **169**:**170** = 100:0
d, R^1 = Me; R = iPr; ratio **169**:**170** = 97:3
e, R^1 = Me; R = CH_2tBu; ratio **169**:**170** = 93:7
f, R^1 = R = tBu; ratio **169**:**170** = 85:15
g, R^1 = tBu; R = 1-methylcyclohexyl; ratio **169**:**170** = 85:15
h, R^1 = tBu; R = 1-adamantyl; ratio **169**:**170** = 85:15

170 (≤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** (R^1 = Me) with **3h** is even regiospecific. 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 ^{31}P NMR signals appear at lower field (δ = 312–317) than those of the isomeric products **170** (δ = 285–300).[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).

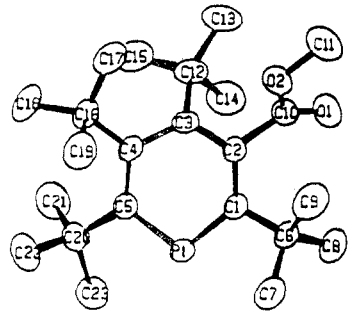
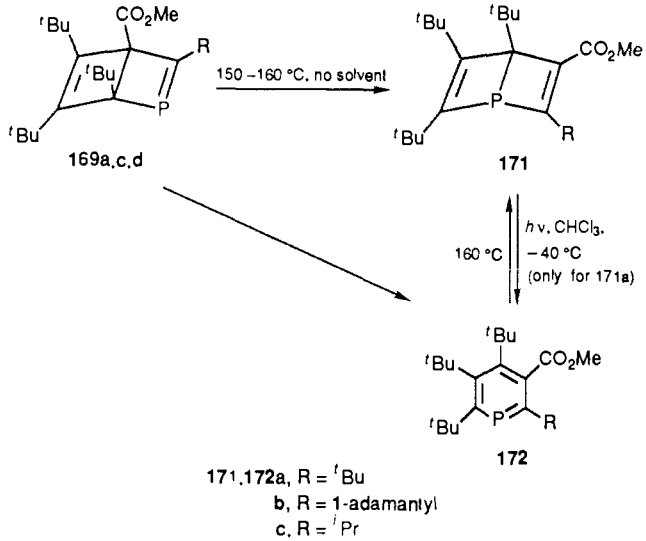


Figure 6. Crystal structure analysis of **172a**. Selected bond lengths (Å) and angles (deg): P–C1 = 1.730, C1–C2 = 1.404, C2–C3 = 1.411, C3–C4 = 1.437, C4–C5 = 1.402, C5–P = 1.758; C5–P–C1 = 105.0, P–C1–C2 = 118.4, C1–C2–C3 = 124.0, C2–C3–C4 = 120.3, C3–C4–C5 = 116.8, C4–C5–P = 119.8.

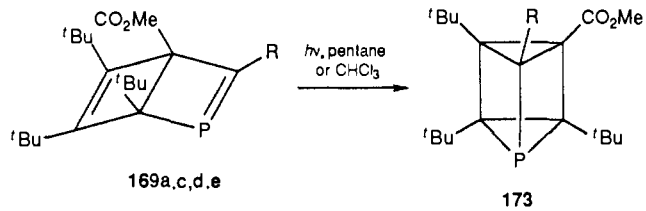
SCHEME 52



When the Dewar 2-phosphabenzenes **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-phosphabenzenes **171a–c**.[102,142–144] The isomerization process is accompanied by an enormous shift of the ^{31}P NMR signals to higher field (**169a,c,d**: δ = 312–315; **171a–c**: δ = –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 phosphabenzenes **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]

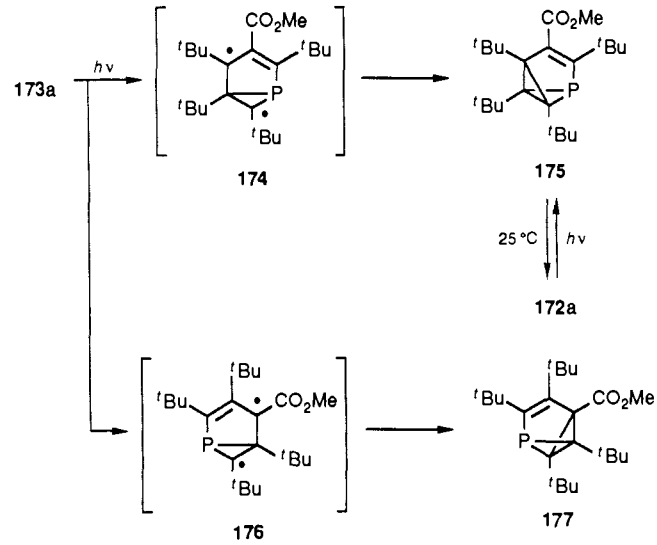
The heterocyclic six-membered ring of **172a** exists in a twisted boat form in which the C4 and C1 atoms represent the points of the bow and the stern positions, respectively. The bow and stern angles amount to 33.7 and 17.9°, the sum of the angles thus being 51.6°. The phosphabenzene **172a** therefore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

SCHEME 53



173a, R = ^{t}Bu[$\delta(^{31}P)$ – 130.2]
b, R = 1-adamantyl [$\delta(^{31}P)$ = –133.0]
c, R = ^{i}Pr [$\delta(^{31}P)$ = –128.4]
d, R = $CH_2{}^{t}$Bu [$\delta(^{31}P)$ = –101.3]

SCHEME 54



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

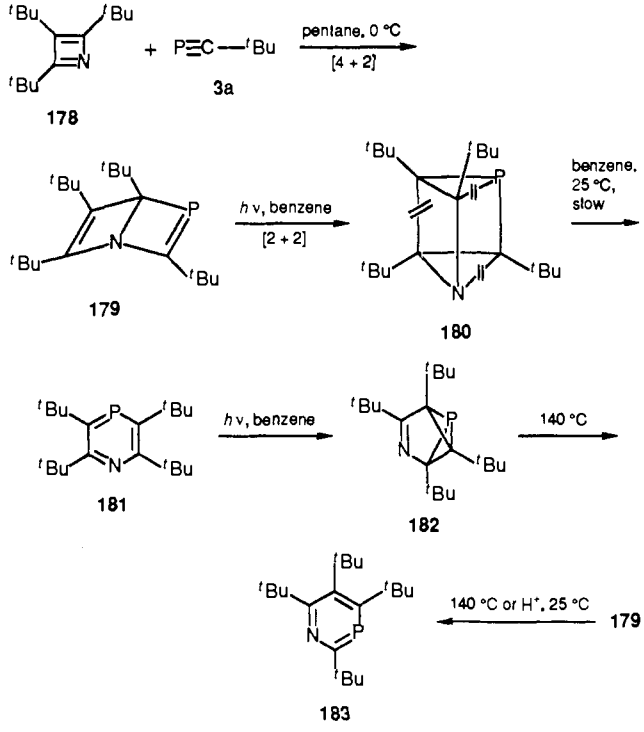
Since Dewar benzenes with sterically demanding groups can be converted photochemically into prismanes without difficulty,[140] an analogous behavior could be expected of the Dewar 2-phosphabenzenes. Indeed, the desired intramolecular [2 + 2]-cycloaddition reactions do proceed smoothly when **169a,c–e** 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 ^{31}P NMR signals (**169a,c–e**: δ = 312–315; **173a–d**: δ = –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

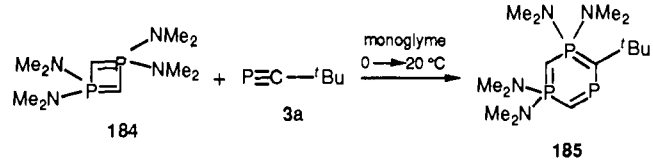


This process can be reversed (**172a** → **175**) under photochemical conditions.[142] The transformation of a phosphaprismane into the phosphabenzvalene system (**173a** → **175** + **177**) can probably best be interpreted as proceeding through the biradical intermediates **174** and **176**.[142]

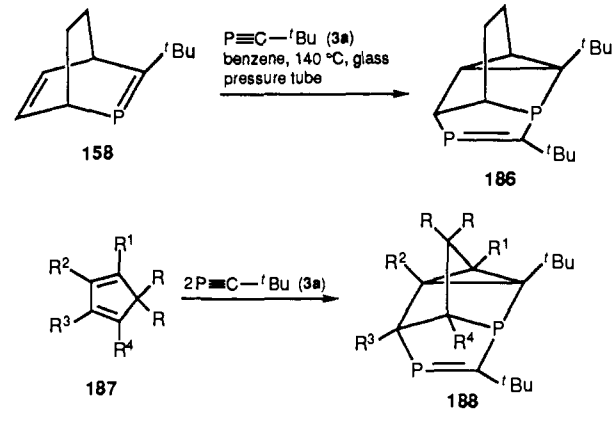
(*b*) *Azetes.* The recently prepared tri-*tert*-butylazete (**178**)[146] is also very amenable to cycloaddition reactions and represents an ideal starting material for the study of the valency isomers of pyridines bearing sterically demanding substituents by means of its reaction with acetylenes and the thermally and photochemically induced subsequent reactions of the products thus obtained.[147-150] Bi-, tri-, and tetracyclic isomers of azaphosphabenzenes[151] are also analogously accessible from the reactions of **178** with phosphaalkynes.

In contrast to the additions of phosphaalkynes to cyclobutadienes, the Diels–Alder reaction of **178** with **3a** is orientation specific and produces the Dewar 1,3-azaphosphabenzene **179** (92% yield; ^{31}P NMR: δ = 202) in a sterically controlled process (Scheme 55).[149] The phosphaalkynes **3d**[152] and **3q**[147] react analogously with **178**. The photochemical isomerization of **179** to give the tetracyclic product **180** (^{31}P 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** (^{31}P NMR: δ = 228).[152] The azaphosphabenvalene **182** (^{31}P NMR: δ = -50) is formed highly selectively in the photoreaction of **181**; the high-field ^{31}P 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 °C or under proton catalysis even at 25 °C.[148]

SCHEME 56



SCHEME 57



187,188a, R = R^1 = R^2 = R^3 = R^4 = H; 95% [$\delta(^{31}P)$ = 4.8, 322.4; $^2J_{P,P}$ = 18.0 Hz

b, R = Me; R^1 = R^4 = H; R^2 = R^3 = CO_2Me; 85% [$\delta(^{31}P)$ = 32.6, 348.6; $^2J_{P,P}$ = 16.2 Hz]

c, R = R^1 = R^3 = H; R^2 = R^4 = tBu; 66% [$\delta(^{31}P)$ = 37.3, 271.5; $^2J_{P,P}$ = 18.0 Hz]

(*c*) *1,3-λ⁵-Diphosphetes.* The diphosphete **184**—a formal head-to-tail dimer of a λ⁵-phosphaalkyne[153]—reacts with **3a** to furnish the 1,3,5-triphosphabenzene **185** (^{31}P NMR: δ = 295, 59.0, 57.5) containing both $\lambda^3\sigma^2$-phosphorus and $\lambda^5\sigma^4$-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 reactions[155] 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 phosphaalkyne **3a** to give the tetracyclic product **186** (^{31}P 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 ^{31}P 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 phosphaalkynes. 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.

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