ELSEVIER

Coordination Chemistry Reviews 227 (2002) 175–192

COORDINATION
CHEMISTRY REVIEWS

www.elsevier.com/locate/ccr

Chemistry of λ^3-2*H*-azaphosphirene metal complexes

Rainer Streubel *

Institut für Anorganische und Analytische Chemie der TU Braunschweig Postfach 3329, D-38023 Braunschweig, Germany

Received 5 September 2001; accepted 9 November 2001

Contents

Abstract 176
1. Introduction 176
2. Synthesis of λ^3-2*H*-azaphosphirene metal complexes 176
    2.1 Synthesis via rearrangement of metal carbene complexes 176
    2.2 Synthesis via [2+1] cycloaddition of carbonitriles and electrophilic terminal phosphanediyl metal complexes 179
3. Physical properties of λ^3-2*H*-azaphosphirene metal complexes 179
    3.1 NMR, IR and UV spectroscopy 179
    3.2 Mass spectrometry 180
    3.3 Single-crystal X-ray structures 181
    3.4 Ab-initio calculations of CH_2NP isomers and λ^3-2*H*-azaphosphirene metal complexes 181
4. Reactions of λ^3-2*H*-azaphosphirene metal complexes 182
    4.1 Reactions with retention of the ring 182
        4.1.1 Reactions with organometallic nucleophiles 182
        4.1.2 Reactions with various electrophiles 182
    4.2 Ring expansion reactions with cleavage of one bond of the ring 182
        4.2.1 Ring expansion with selective P–C bond-cleavage 183
        4.2.2 Ring-expansion with selective P–N bond-cleavage 184
    4.3 Reactions with cleavage of two bonds of the ring 184
        4.3.1 Thermal generation of electrophilic terminal phosphanediyl metal complexes 185
        4.3.2 Rearrangement of electrophilic terminal phosphanediyl metal complexes 186
5. Synthetic potential of λ^3-2*H*-azaphosphirene metal complexes in phosphorus heterocyclic chemistry 186
    5.1 Synthesis of three-membered phosphorus heterocycles 186
        5.1.1 λ^3-1*H*-Phosphirene metal complexes 186
        5.1.2 λ^3-1*H*-Diphosphirene metal complexes 187
        5.1.3 λ^3-Phosphirane metal complexes 187
        5.1.4 λ^3-Azaphosphiridine metal complexes 187
        5.1.5 λ^3-Oxaphosphirane metal complexes 188
    5.2 Synthesis of five-membered phosphorus heterocycles 188
        5.2.1 λ^3-2H-1,2-Azaphosphole metal complexes 189
        5.2.2 λ^3-2*H*-1,3,2-Diazaphosphole metal complexes 189
        5.2.3 λ^3-2H-1,4,2-Diazaphosphole metal complexes 189
        5.2.4 λ^3-2*H*-1,2,3-Azadiphosphole metal complexes 189
        5.2.5 λ^3-Δ^4-1,2-Azaphospholene metal complexes 190
        5.2.6 λ^3-Δ^3-1,3,2-Oxazaphospholene metal complexes 190
        5.2.7 λ^3-Δ^2-1,3,4-Oxazaphospholene metal complexes 190
        5.2.8 λ^3-Δ^3-1,3,5-Oxazaphospholene metal complexes 190
Acknowledgements 191
References 191

---

* Fax: +49-531-391-5387.
E-mail address: r.streubel@tu-bs.de (R. Streubel).

PII: S0010-8545(02)00013-9

Abstract

In this review, important aspects of λ^3-2*H*-azaphosphirene metal complexes are discussed in relation to synthesis, physical properties and synthetic applications; ab-initio calculations on relative energies of CH_2NP isomers and of λ^3-2*H*-azaphosphirene metal complexes (Cr, Mo, W) are also presented. Currently, there are three routes to this unsaturated three-membered ring system, which are discussed in detail: two of them use a rearrangement of metal carbene complexes, whereas the other relies on [2+1] cycloaddition reactions of electrophilic terminal phosphanediyl complexes and carbonitriles. The structural data show characteristics of a very strained heterocyclic ring system, which partially helps to understand the reactivity of this heterocycle complex in solution. The synthetic potential of λ^3-2*H*-azaphosphirene metal complexes is illustrated by selected examples, which demonstrate their ability to serve, under very mild conditions as precursor for various new building blocks, i.e. nitrilium phosphanylide complexes, electrophilic terminal phosphanediyl complexes and phosphavinyl–nitrene complexes. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Azadiphospholes; Azaphosphirenes; Diazaphospholes; Heterophospholenes; Nitrilium phosphanylide complexes; Phosphanediyl complexes; Phosphavinyl–nitrene complexes

---

1. Introduction

Since the discovery of the parent phosphirane in the gas phase by Wagner [1] in 1963, derivatives of phosphiranes **I** and related saturated three-membered λ^3-P-heterocycles, such as **II**–**VI** were synthesized, which incorporate a second or a third row element in the ring and have sterically demanding substituents at the ring atoms (Scheme 1). Although stable derivatives of oxaphosphiranes **III** are still unknown [2]—most probably, due to their tendency to undergo valence isomerization [3] to give reactive methylene(oxo)-σ^3,λ^5-phosphoranes [2]—, synthesis of oxaphosphirane metal complexes [4,5] was achieved recently. Investigations in the field of such and related three-membered λ^3-P-heterocycles, including synthesis, structure, reactivity and bonding situation, have been discussed in several reviews; [6–10] related unsaturated three-membered P-heterocycles have been also reviewed (see next paragraph). Recently, the rational synthesis [11–15] and employment [16] of polycyclic phosphorus carbon cage compounds in catalysis, having a phosphirane as important structural motive, gave some fresh stimulus to this field.

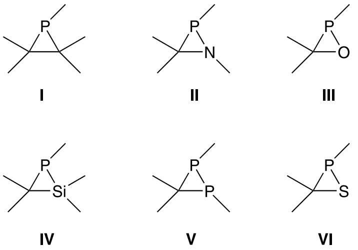
In 1982, Mathey et al. synthesized the first stable λ^3-1*H*-phosphirene [17] **VII**, the first example of an unsaturated three-membered λ^3-P-heterocycle; its chemistry has experienced an extensive development since then [18–24]. It is remarkable that λ^3-2*H*-phosphirenes [20–24] **VIII** are hardly accessible, which is quite contrary to the situation found for 1*H*-azirenes **IX** and 2*H*-azirenes **X** (Scheme 2) [25–29]; only derivatives of the latter are stable and have been investigated in detail. Compared with phosphirenes and azirenes the knowledge about azaphosphirenes **XI**–**XIII** is very scarce and derivatives of λ^3-2*H*-azaphosphirenes **XI** [30] and λ^3-1*H*-azaphosphirenes **XII** [31] have been claimed exclusively as reactive intermediates. So far, only metal complexes of λ^3-2*H*-azaphosphirenes **XI** are known [32], which, meanwhile, have found various applications in heterocyclic chemistry.

The aim of this review is to highlight important aspects concerning synthesis, physical properties and synthetic applications of λ^3-2*H*-azaphosphirene metal complexes.

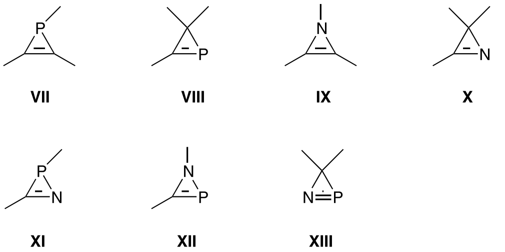
2. Synthesis of λ^3-2*H*-azaphosphirene metal complexes

2.1. Synthesis via rearrangement of metal carbene complexes

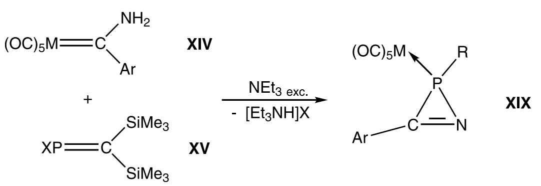
Based on the use of metal carbene complexes, two routes are currently known, providing access to λ^3-2*H*-azaphosphirene *P*-metal complexes **XIX**, which were first synthesized by Streubel et al. in 1994 [33]. The first published route uses a triethylamine induced condensation-rearrangement cascade starting from aminocarbene



Scheme 1. Saturated λ^3-P-heterocycles with ubiquitous organic substituents.



Scheme 2. Unsaturated λ^3-P-heterocycles with ubiquitous organic substituents.



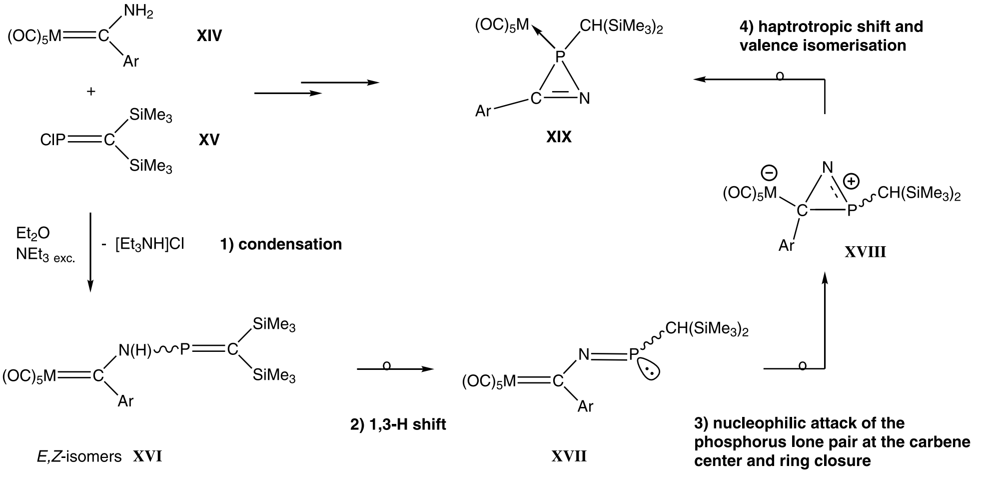
Scheme 3. Synthesis of λ^3-2H-azaphosphirene metal complexes using metal carbene complexes and P-halogeno methylenephosphanes

metal complexes **XIV** and [bis(trimethylsilyl)methylene]halogenophosphanes [33–35] **XV** (R = CH(SiMe$_3$)$_2$, X = Cl, Br) (Scheme 3); the yields are generally good (50–85%).

Other tertiary amine bases, such as DBU or DBO have been examined as well, but were found to be not so efficient as triethylamine [36]. Using a combination of **XIV** and **XV** this method gave access to a variety of 2-bis(trimethylsilyl)methyl-λ^3-2H-azaphosphirene pentacarbonyltungsten complexes having *para* [37] or *ortho* [38] mono-substituted, 2,4-, [39] 2,6- [39] or 3,5-trifluoromethyl-disubstituted, [39] 2,4,6-methyl- and 2,4,6-isopropyl-substituted phenyl groups [40] bonded to the C-3 carbon atom. At the same time, 3-heteroarene-substituted derivatives having a 2-furanyl, 2-thienyl or 2-*N*-methyl-pyrryl group bonded to the three-membered ring became also accessible [41]. 3-Methyl- and 3-*n*-butyl-substituted λ^3-2H-azaphosphirene tungsten complexes were synthesized and unambiguously identified by ^{31}P-NMR spectroscopy ($\delta = -117.2$, ^1J(W,P) = 295.5 Hz; $\delta = -121.4$, ^1J(W,P) = 291.2 Hz) [42]. Due to decomposition of these derivatives during column chromatography attempts to isolate them failed. The synthesis of the related 3-*tert*-butyl-λ^3-2H-azaphosphirene tungsten complex failed, but for a different reason. Instead of the expected product, the formation of an unidentified product with an unusual small value of the phosphorus-tungsten coupling constant of 198.4 Hz was observed by ^{31}P-NMR spectroscopy at $\delta = -111.6$ ppm [42]; this probably points to the formation of a complex of an acyclic isomer of the nitrilium phorphanylide-type.

This route also led to 3-phenyl-λ^3-2H-azaphosphirene pentacarbonyl–chromium and molybdenum complexes, which were obtained by column chromatography in lower yields [43]. It was also demonstrated that this method allows the synthesis of 3-aryl-λ^3-2H-azaphosphirene metal complexes having other co-ligands than CO in a *cis*-position of the metal coordination sphere such as triphenylphosphane or (−) (*R*) methyl(phenyl)-*n*-propylphosphane [44]. Investigations on the reaction mechanism provided strong evidence that the rearrangement cascade proceeds entirely intramolecularly [38,40,44] and *cis*-stereospecifically [44]. Due to the very small diastereomeric excess (ca. 5%) it was concluded that the metal center does not participate in the P–C bond-forming step [44]. If the reaction was carried out at ambient temperature [44], the rearrangement cascade seemed to have four reaction steps and three types of reactive intermediates **XVI**–**XVIII** as shown in Scheme 4.

Based on these findings, the following reaction course was proposed. The first reaction step is a base-induced condensation (1), thus leading to *E,Z*-isomers of the intermediate **XVI** having a N–P bond [45]. Then a 1,3-hydrogen shift leads to the formation of the 2-aza-1-phospha-4-metallabutadiene-type system **XVII** [40], which was trapped with the employed aminocarbene metal complexes **XIV** at low temperatures [42,43] and/or higher concentrations to yield dinuclear *N,N′*-λ^3-P-bridged carbene metal complexes [40,44] **XXIII** (see also below and Fig. 1). Furthermore, first ^{31}P-NMR spectroscopic evidence for the intermediacy of a derivative of type **XVII** was obtained recently [40]. An intramolecular nucleophilic attack of the phosphorus lone pair at the carbene center was suggested to explain the ring formation (step 3), thus excluding a direct participation of the metal center [40,44]. Subsequently,



Scheme 4. Proposed reaction course for the formation of λ^3-2H-azaphosphirene metal complexes.

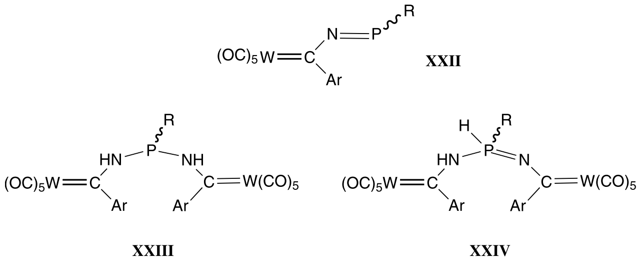


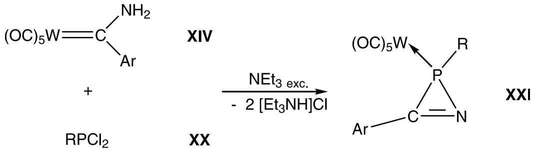
Fig. 1. Intermediates (**XXII** and **XXIII**) and side products (**XXIV**) in λ^3-2*H*-azaphosphirene metal complex synthesis.

the zwitterionic intermediate **XVIII** undergoes a combined haptotropic rearrangement and valence isomerization to give the 3-aryl-λ^3-2*H*-azaphosphirene metal complexes **XIX** as final products (step 4).

The other route to λ^3-2*H*-azaphosphirene metal complexes relies on a combination of metal carbene complexes **XIV** and organodichlorophosphanes **XX** in methylenechloride as solvent and triethylamine as base. This offers mainly access to 3-phenyl-λ^3-2*H*-azaphosphirene tungsten complexes **XXI**, which have various bulky substituents at phosphorus such as pentamethylcyclopentadienyl [46], triphenylmethyl and 2,4,6-triisopropylphenyl [42] (Scheme 5). Generally, such λ^3-2*H*-azaphosphirene tungsten complexes were obtained in considerably lower yields (20–30%) as compared with bis(trimethylsilyl)methyl-substituted derivatives synthesized according to the route shown in Scheme 3.

Most studies on the reaction course of this route were carried out employing dichloro(pentamethylcyclopentadienyl)phosphane and *para*-phenyl-substituted amino(aryl)-carbene tungsten complexes [34,46]. As already mentioned, the yields of 3-phenyl-2-pentamethylcyclopentadienyl-λ^3-2*H*-azaphosphirene tungsten complexes were only moderate (15–30%). The 3-phenyl-2-pentamethylcyclopentadienyl-λ^3-2*H*-azaphosphirene molybdenum complex ($\delta = -86.7$, ${}^1J(\mathrm{Mo,P}) = 158.0$ Hz) was obtained in comparable yield, whereas the related chromium complex was only detected by ^{31}P-NMR spectroscopy ($\delta = -59.8$) and could not be isolated [42].

There are two main reasons for the low yields in such cases. At first and predominantly, formation of dinuclear *N,N′*-λ^3-P-bridged carbene tungsten complexes **XXIII** seems to be preferred (Fig. 1) [46]. Such dinuclear metal carbene complexes might result from two-fold condensation reactions or, alternatively, from 1,2-addition reactions of the amino(aryl)carbene metal complexes to the P–N π-system of the 2-aza-1-phospha-4-tungstabutadienes **XXII**. Although dinuclear *N,N′*-λ^3-P-bridged carbene tungsten complexes **XXIII** are quite stable towards triethylamine, a subsequent elimination of amino(aryl)carbene metal complexes was achieved [44,46]. The detailed mechanism of this elimination is still uncertain, but dinuclear *N,N′*-σ^4,λ^5-P-bridged carbene tungsten complexes **XXIV** having a PH-function do not seem to play a role as intermediates (Fig. 1) (see also below) [42], although related 1,1-eliminations at σ^4,λ^5-P-centers have been described [47].



Scheme 5. Synthesis of λ^3-2*H*-azaphosphirene metal complexes using metal carbene complexes and dichloro(organo)phosphanes.

The second reason is a rather general one. It is the reaction of λ^3-2*H*-azaphosphirene tungsten complexes with triethylammoniumchloride, which gives the corresponding chloro(organo)phosphane tungsten complexes, the corresponding nitriles and triethylamine as reaction products [37,46]. Therefore, the achievable yields depend on the varying reaction rates of the formation and this subsequent reaction of λ^3-2*H*-azaphosphirene metal complexes. The latter reaction rate is much faster in methylenechloride than in diethyl ether. Accordingly, the yields are lower if the reaction conditions of the second route have to be used. Furthermore, the nature of the substituent at the phosphorus center of the employed organodichlorophosphane seems to be crucial. Under standard conditions, dichlorophosphanes with sterically less demanding substituents such as methyl and phenyl reacted with an amino(phenyl)carbene tungsten complex preferentially to multi-nuclear carbene complexes having RP as bridging units, instead of giving λ^3-2*H*-azaphosphirene tungsten complexes [36]. Dichloro(organo)phosphanes with sterically very demanding substituents such as the 2,4,6-*tert*-butyl-phenyl group gave exclusively dinuclear *N,N′*-σ^4,λ^5-P-bridged carbene tungsten complexes of type **XXIV** having a PH-function (isomer 1: δ ${}^{31}\mathrm{P} = 14.2$, ${}^1J(\mathrm{P,H}) = 593.5$ Hz and isomer 2: δ ${}^{31}\mathrm{P} = 6.5$, ${}^1J(\mathrm{P,H}) = 587.8$ Hz) [42]. It is remarkable that elimination did not occur under the reaction conditions.

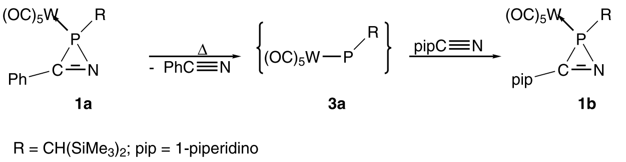
In conclusion, the reaction courses of the two routes (depicted in Schemes 3 and 5) and the ratio of the products depend on: (1) the temperature, (2) concentration, (3) solvent polarity, (4) the nature of the substituent at the carbene center and (5) of the substituent at the phosphorus center. A lowering of the temperature and raising of the concentration [44] led to increasing amounts of derivatives of type **XXIII**, a result that do not depend significantly from the nature of the metal center, as assumed earlier. Solvents with high polarity led to shorter reaction times, as compared with diethyl ether, but enhanced also the reaction rate of the subsequent ring cleavage. Aminocarbene metal complexes **XIV** having good π-donor substituents and/or sterically demanding groups reacted much slower with **XIV** or **XX** to give λ^3-2*H*-azaphosphirene metal complexes **XIX** or **XXI**. The reaction time of *ortho*-methoxy and *ortho*-dimethylamino-substituted amino(phenyl)carbene tungsten complexes was significantly enhanced compared with the related *para*-substituted derivatives; this effect was rationalized by assuming a stabilizing interaction between the oxygen and nitrogen centers of these donor groups with the phosphorus center in the 2-aza-1-phospha-4-tungsta-butadienes [38]. As described above, the nature of the substituent at the phosphorus center is especially crucial if dichloro(organo)phosphanes are employed. The great common advantage of both routes is that the rearrangement cascade(s) also proceeds at low temperatures, which enables the synthesis of thermally unstable derivatives under very mild conditions.

2.2. Synthesis via [2+1] cycloaddition of carbonitriles and electrophilic terminal phosphanediyl metal complexes

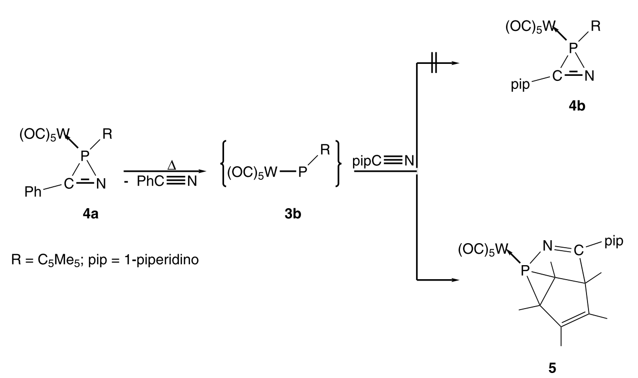
In 1998, Streubel et al. reported a novel access to λ^3-2*H*-azaphosphirene metal complexes. Thermal ring cleavage of the 3-phenyl-λ^3-2*H*-azaphosphirene tungsten complex **1a** in toluene in the presence of 1-piperidinocarbonitrile furnished the 3-(1-piperidino)-λ^3-2*H*-azaphosphirene tungsten complex **1b** [48]. At that time, it was proposed that the product formation occurred by a [2+1] cycloaddition reaction of the carbonitrile and the electrophilic terminal phosphanediyl complex [$(OC)_5WPCH(SiMe_3)_2$] (**2a**) (Scheme 6) [48]. Very recently, it was shown that 1,5-dimethyl-2-cyano-pyrrole also preferentially reacted with phosphanediyl complex **2a** to the corresponding λ^3-2*H*-azaphosphirene tungsten complex [49].

It was remarkable that the phosphanediyl complex [$(OC)_5WPC_5Me_5$] (**2b**), generated thermally from complex **4a**, did not furnish the 3-(1-piperidino)-λ^3-2*H*-azaphosphirene tungsten complex **4b** with 1-piperidinocarbonitrile [14]. Polycyclic C,P,N-carbon cage compound **5** was obtained instead (Scheme 7) (see also Section 5.2.2) [14].

A different approach to λ^3-2*H*-azaphosphirene complexes using the thermal decomposition of 7-phosphanorbornadiene complexes at 120 °C [50] for the generation of terminal phosphanediyl complexes and subsequent reaction with 1-piperidinocarbonitrile failed [51]. Possibly, the first spectroscopic evidence for a *P*-phenyl-substituted λ^3-2*H*-azaphosphirene tungsten complex was obtained by ^{31}P-NMR spectroscopy ($\delta = -47.9$ ppm) if 1-piperidinocarbonitrile was used as solvent [51]. It was remarkable that, although *P*-phenyl- or *P*-methyl-substituted nitrilium phosphanylide complexes were transiently formed, intermolecular [3+2]-cycloaddition reactions to 2*H*-1,3,2- and 2*H*-1,4,2-diazaphosphole complexes occurred preferentially (see also Sections 5.2.2 and 5.2.3) [51]. Further attempts to gain access to λ^3-2*H*-azaphosphirene complexes via thermal decomposition of 7-phosphanorbornadiene complexes at 65–70 °C using Cu(I)Cl as catalyst and 1-piperidinocarbonitrile as trapping reagent were not successful [51].



Scheme 6. Synthesis of λ^3-2*H*-azaphosphirene metal complexes via [2+1] cycloaddition reaction.



Scheme 7. Formation of the polycyclic C,P,N-carbon cage compound **5** instead of the λ^3-2*H*-azaphosphirene metal complex **6**.

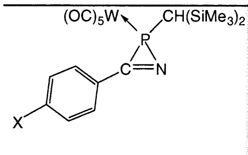
It should be pointed out that this route seems to be especially useful for 3-donor atom-substituted λ^3-2*H*-azaphosphirene metal complexes, which cannot be obtained by using the other routes—because of the simple fact that the needed metal carbene complexes, e.g. {[amino(1-piperidino)carbene]pentacarbonyltungsten(0)} (and related derivatives), are unknown.

3. Physical properties of λ^3-2*H*-azaphosphirene metal complexes

3.1. NMR, IR and UV spectroscopy

From the NMR spectroscopic data of λ^3-2*H*-azaphosphirene metal complexes (solely obtained from solutions), the phosphorus and carbon resonances are the most significant and they, together with the phosphorus–tungsten coupling constants, clearly reflect the electronic influence of substituents at the carbon atom of the three-membered ring. For example, *para*-substituted phenyl derivatives exhibit a very good correlation of δ ^{31}P values with the Hammett σ^{p}-constants, which is almost linear (Table 1) [37]. This could be useful for extrapolations of ^{31}P-NMR chemical shift values of unknown λ^3-2*H*-azaphosphirene tungsten complexes.

Table 1
Selected NMR spectroscopic data ($CDCl_3$, 25 °C) of λ^3-2*H*-azaphosphirene tungsten complexes and Hammett σ^p-constants

		δ ^{31}P [ppm]	$^1J_{W,P}$ [Hz]	δ ^{13}C [ppm]	σ^p
X = CF_3	**1c**	- 102.0	297.5	193.1	0.54
Br	**1d**	- 105.2	296.8	192.2	0.23
Cl	**1e**	- 105.4	296.1	192.0	0.23
H	**1a**	- 108.8	294.7	192.3	0.00
F[*]	**1f**	- 109.1	295.6	190.8	0.06
Me	**1g**	- 111.2	293.1	191.4	-0.17
OMe	**1h**	- 115.1	292.5	190.2	-0.27
NMe_2	**1i**	- 117.6	291.5	187.8	-0.83

Interestingly, the NMR parameters of the carbon and nitrogen atoms of the three-membered ring of the 2*H*-azaphosphirene metal complexes **1a**, **6** and **7** [43] vary very little with respect to metal exchange (Table 2).

This is not the case with the phosphorus resonances, which differ significantly on going from chromium to the tungsten complex. This is a common feature of coordinated tervalent phosphorus compounds [52]. ^{183}W chemical shifts were also determined for a series of λ^3-2*H*-azaphosphirene tungsten complexes and were observed in a small range from 3250 to 3256 ppm [41], which is common for complexes of the general type $[(R_3P)W(CO)_5]$ [52]. A very special NMR spectroscopic feature was detected in the case of *P*-pentamethylcyclopentadienyl-substituted λ^3-2*H*-azaphosphirene metal complexes. For example, complex **4a** showed a proton resonance for the C1-methyl group of the pentamethylcyclopentadienyl group at unexpected high-field ($\delta = 0.64$ ppm). This shielding was assumed to be caused by the π-system of the λ^3-2*H*-azaphosphirene ring [46].

Structurally important IR spectroscopic features of λ^3-2*H*-azaphosphirene tungsten complexes are 5 strong absorption bands between 2075 and 1910 cm^{-1}, which correspond to ν(CO) bond stretching modes and whereby absorptions between 2075 and 2070 can be assigned to the A_1^1 mode. Bands of medium intensities between 1620 and 1590 are also remarkable, which were attributed to the ν(C=N) bond stretching [37,42,43].

UV–vis spectra of the complexes **1a**, **6** and **7** showed λ_{max} values from 200 to 350 nm (Table 3) [43]. λ_{max} values of 200 and 240 nm were attributed to π–π*-electron transitions related to the phenyl groups. Bands appearing as shoulders with λ_{max} values of 330 (**6**) and 350 nm (**7**), with significantly lower log ε values, were tentatively assigned to π–π*-electron transitions of the C–N double bonds. It was noted that some metal carbonyl complexes also show charge-transfer transitions in the range of 300–350 nm [53].

A comparison of the values obtained for **1a**, **6** and **7** with those of a mixture of related 3-phenyl-1*H*-thiazirene and benzonitrile sulfide (bands with λ_{max} values of 335, 324, 295 and 240 nm) is interesting [54]. The interpretation of the UV–vis spectra of this mixture remained somewhat unsatisfactory because the bands of benzonitrile sulfide had been assigned unambigously, but those of 3-phenyl-1*H*-thiazirene had not [54].

3.2. Mass spectrometry

EI-MS experiments (electron impact, 70 eV) have shown that λ^3-2*H*-azaphosphirene metal complexes predominantly undergo ring cleavage subsequent to the ionization process under EI conditions to yield the radical cations of $[(OC)_5MPCH(SiMe_3)_2]$ (M = Cr, Mo,

Table 2
Selected NMR spectroscopic data ($CDCl_3$, 25 °C) of λ^3-2*H*-azaphosphirene metal complexes

Complex	Metal	δ ^{13}C	δ ^{15}N	δ ^{31}P	$^{(1+2)}J(P,C)$	$^{(1+2)}J(P,N)$
6	Cr	193.3	−55.3	−54.3	1.7	38.3
7	Mo	192.1	−56.3	−84.5	3.4	36.7
1a	W	192.4	−53.2	−111.0	1.7	36.9

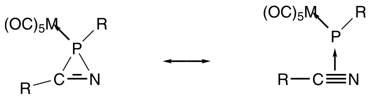
Table 3
Selected data of UV–vis spectra of λ^3-2*H*-azaphosphirene metal complexes **1a**, **6** and **7**

Complex	Metal	λ_{max} (log ε)	λ_{max} (log ε)	λ_{max} (log ε)	λ_{max} (log ε)
6	Cr	–	208 (4.637)	240 (4.599)	–
7	Mo	198 (4.625)	206 (4.610)	240 (4.697)	330 (3.394)
1a	W	198 (4.655)	216 (4.657)	254 (4.590)	350 (3.544)

W) or [$(OC)_5MPC_5Me_5$] (M = Mo, W), which then showed loss of CO [37,42,43]. Therefore, the molecule radical cations of λ^3-2*H*-azaphosphirene metal complexes have very often low intensities (< 10%). Under CI (chemical ionization, isobutane or NH_3) or FAB (fast atom bombardment, Xe) conditions the molecule radical cations showed values well beyond 30% [42]. It is also remarkable that for complexes **1a**, **6** and **7** the formation of ammonia clusters of the radical cations was detected under CI conditions if NH_3 was used [42].

3.3. *Single-crystal X-ray structures*

Molecular structures of the λ^3-2*H*-azaphosphirene metal complexes **1a, 6** and **7** were determined by single-crystal X-ray crystallography, whereby the dimensions of the tungsten complex **1a** [37] and the isostructural complexes **6** and **7** [43] differed mainly in their metal-phosphorus bond distances [**6**: 2.3125(6), **7**: 2.4772(12) and **1a**: 2.470(2) Å]. As a consequence of this, the distance between the metal atom and the geometrical center of the C–N double bond also varied (**6**: 3.542, **7**: 3.670 and **1a**: 3.659 Å). There is one especially remarkable feature of the three-membered ring, that is the similarity of the endocyclic P–C and P–N bond lengths, i.e. **1a**: 1.759(5) and 1.795(4) Å. This is even more obvious, if the structural data of **1a** are compared with those of a related azaphosphiridine tungsten complex [5] in which the bond lengths of the saturated three-membered P–C–N ring were determined to P–C 1.835(4) and P–N 1.728(3) Å (C–N 1.478(5) Å). This result seems to underline that the bonding situation of the heterocyclic ligand of 2*H*-azaphosphirene pentacarbonylmetal complexes should be described as a resonance hybrid of a three-membered ring system with a covalent bonding (**XIX**) (and a π-electron donor–acceptor complex of carbonitrile and the phosphorus atom of the terminal phosphanediyl complex unit (**XXV**) (Fig. 2) [43].



XIX **XXV**

Fig. 2. Alternative bonding descriptions of λ^3-2*H*-azaphosphirene metal complexes.

There is one common structural motive of 3-aryl- and 3-hetaryl-substituted λ^3-2*H*-azaphosphirene metal complexes, that is a coplanar arrangement of the two ring moieties, thus enabling an effective pπ–pπ-electron interaction, which can be deduced from the combination of short distances between the atoms that interconnect the different ring moieties and the elongated C–N double bonds of the λ^3-2*H*-azaphosphirene ring; the latter were observed in the range from 1.265 to 1.313 Å [41].In the case of 2-bis(trimethylsilyl)methyl-substituted derivatives this substituent is always oriented in the same manner with respect to the pentacarbonyl metal fragment, meaning that the C–H group is pointing towards the metal center, whereas the trimethylsilyl groups are pointing away. In the case of 3-*ortho*-aryl-substituted λ^3-2*H*-azaphosphirene tungsten complexes a conformational isomerism exists. A priori, the *ortho*-substituent can be on the phosphorus side (pseudo *s-cis* with respect to the interconnecting C–C bond) or on the nitrogen side of the 2*H*-azaphosphirene ring (pseudo *s-trans*) [55]. Due to steric repulsion between the *ortho*-substituent, on one hand, and the pentacarbonyltungsten fragment and the bis(trimethylsilyl)methyl group, on the other hand, the pseudo *s-cis* conformer should be disfavored. Nevertheless, the first example of such an isomer was detected very recently [38]; but more examples will be necessary to understand the conformation determining factors.

3.4. *Ab-initio calculations of CH_2NP isomers and λ^3-2H-azaphosphirene metal complexes*

Apart from a long-standing special experimental [56] and theoretical [57–59] interest of several research teams in mono-phosphacarbodiimides HN=C=PH, the theoretical knowledge about CH_2NP isomers is scarce. Very recently, Schoeller et al. carried out calculations on acyclic and cyclic CH_2NP isomers [60], whereby the relative energies of these isomers are of special interest (Table 4, Diagram 1).

Interestingly, λ^3-2*H*-azaphosphirene has the lowest energy of all cyclic CH_2NP isomers on various high levels of theory. Important structural parameters of the ring are P–N 1.905, P–C 1.787 and C–N 1.279 (Å); the endocyclic angles are C–P–N 39.1, P–N–C 67.4 and N–C–P 71.5 (°) (B3LYP/6-31g(d)+ZPE) [60]. It is also noteworthy that nitrilium phosphanylide HCNPH is

Table 4
Relative energy differences of CH_2NP isomers (kcal mol^{-1})

Isomer	DFT+ZPE[a]	MP2+ZPE[b]	CCSD(t)[c]
$CPNH_2$	67.1	48.6	57.5
Cyc-$CPNH_2$	46.1	48.6	37.2
Cyc-CP(H)NH	27.4	33.2	25.6
Cyc-C(H)PNH	22.1	21.3	17.9
HCNPH	5.8	11.0	10.3
Cyc-$C(H_2)PN$	5.6	−1.2	1.0
Cyc-C(H)P(H)N	0.0	0.0	0.0
$CNPH_2$	−10.4	−8.2	−11.1
H_2NCP	−11.4	−13.4	−14.6
HNCPH	−12.6	−7.7	−10.4
H_2PCN	−26.7	−29.6	−26.4

[a] B3LYP/6-31g(d)+zero-point vibrational energy correction.
[b] MP2(fc)/6-31g(d)+zero-point vibrational energy correction.
[c] CCSD(t)/aug-cc-pVTZ//MP2(fc)/6-31g(d).

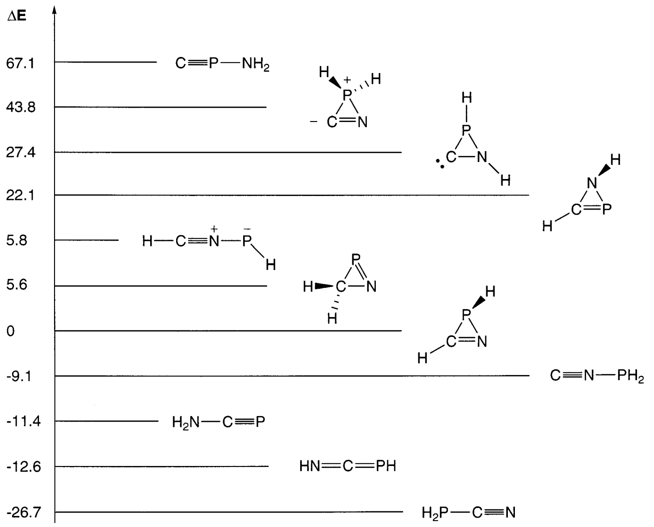


Diagram 1. Relative energies of CH_2NP isomers (kcal/mol).

Table 5
Selected structural parameters of λ^3-2*H*-azaphosphirene metal complexes (bond lengths (Å) and bond angles (°)) and energies (kcal/mol) for the complexation

Metal	P–M	P–N	P–C	C–N	ΔE
Cr	2.358	1.848	1.787	1.279	−25.1
Mo	2.509	1.853	1.789	1.278	−26.1
W	2.496	1.849	1.787	1.279	−30.1

[a] B3LYP/6-31g(d)+zero-point vibrational energy correction.

only 5.8 kcal mol^{-1} and λ^3-3*H*-azaphosphirene H_2CNP, possessing an N–P double bond, only 5.6 kcal mol^{-1} higher in energy than λ^3-2*H*-azaphosphirene. The energy for the complexation of λ^3-2*H*-azaphosphirene depends on the metal complex fragment and amounts to 25–30 kcal mol^{-1} (Table 5). Selected structural parameters of the chromium, molybdenum and tungsten complexes are given in Table 5.

These structural data are in good agreement with the experimental values obtained for the metal complexes **1a**, **6** and **7** (cf. Section 3.3), whereby some deviations might arise from substituent effects.

4. Reactions of λ^3-2*H*-azaphosphirene metal complexes

4.1. Reactions with retention of the ring

4.1.1. Reactions with organometallic nucleophiles

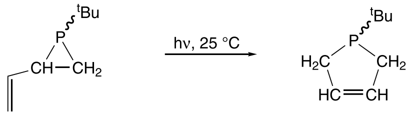
So far, exclusively preliminary investigations on the reactivity of the λ^3-2*H*-azaphosphirene tungsten complex **1a** towards organometallic nucleophiles and electrophiles were carried out, but the outcome was surprisingly general: all generated or obtained products revealed a remarkable thermal instability in solution [61]. In diethyl ether nucleophiles such as methyllithium showed addition to *cis* and *trans* carbonyl ligands of **1a** at low temperature, thus forming the corresponding tungstates. Remarkable was that even at ambient temperature, reactions of phenyllithium with **1a** were very slow, thus showing steric hindrance of the reaction by the bulky bis(trimethylsily)methyl substituent [61]. Subsequent addition of triethyloxonium tetrafluoroborate yielded 1:1 mixtures of *cis*/*trans* (ethoxy(methyl)carbene)-λ^3-2*H*-azaphosphirene tungsten complexes (*cis*: δ $^{31}P = -103.1$, $^1J(P,W) = 292.8$ Hz); *trans:* δ $^{31}P = -112.2$, $^1J(P,W) = 295.9$ Hz); only the trans isomer was isolated in moderate yields (20–25%) [61]. It is remarkable that especially the *cis*-(ethoxy(methyl)carbene)-λ^3-2*H*-azaphosphirene tungsten complex decomposed rapidly in solution, but the products could not be identified, so far.

4.1.2. Reactions with various electrophiles

Reactions of complex **1a** with organic and inorganic electrophiles were performed in diethyl ether or dichloromethane solutions. Whereas methyliodide showed no reaction with **1a**, triethyloxonium tetrafluoroborate and trimethylsilyl trifluoromethyl sulfonic acid reacted at low temperatures via ethylation and silylation of the nitrogen center of the λ^3-2*H*-azaphosphirene ring, but the initially formed products decomposed on warming up [61]. An organometallic electrophile such as the in situ generated [pentacarbonyl(tetrahydrofurane)-tungsten(0)] showed a clean reaction to afford a dinuclear κN-,κP-coordinated λ^3-2*H*-azaphosphirene complex [33]. At ambient temperature, this dinuclear complex dissociated rapidly (1–2 h) and irreversibly in solution, thus displaying a very weak coordination of the nitrogen center to the pentacarbonyltungsten fragment [33]. Metal halides such as aluminum-trichloride reacted also with **1a** at low temperatures, thus giving a short-living product (δ $^{31}P = -65$ ppm), which also decomposed on warming. The currently investigated quest is: Is it the corresponding Lewis acid/Lewis base adduct, having an aluminum-nitrogen bond, or is it the oxidized λ^3-2*H*-azaphosphirene tungsten complex [61]?

4.2. Ring expansion reactions with cleavage of one bond of the ring

Due to their fairly strong bond enthalpies (P–C 264 kJ mol^{-1} and P–N 300 kJ mol^{-1}) P–C and P–N bonds are, in general, remarkably stable. Examples of insertion

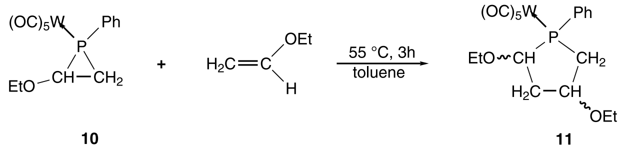


8 **9**

Scheme 8. P–C bond-selective ring expansion reaction via intramolecular rearrangement.

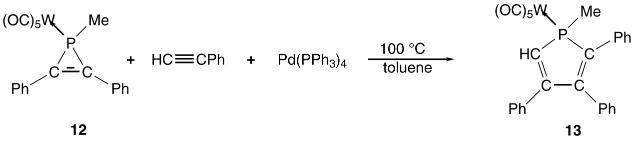
reactions into P–C and/or P–N bonds of three-membered P-heterocycles are rare and, most often, intramolecular rearrangements are involved. One early example was described by Richter et al., i.e. the thermal (150 °C) or photochemical (25 °C) rearrangement of vinyl-substituted phosphirane **8** into the Δ^3-phospholene **9** (Scheme 8) [62].

When it comes to selective insertions of homo- and/or heteronuclear π-bond systems of main group elements into P–C and/or P–N bonds, then the knowledge is even more scarce and, most often, the three-membered phosphorus heterocycles are involved at one stage or another. Related to the vinyl-phosphirane Δ^3-phospholene-rearrangement of Richter is the reaction of the activated phosphirane complex **10** with an enolether to furnish complex **11** (Scheme 9) [63].



Scheme 9. Example of a phosphirane complex ring enlargement.

Other examples, which use catalytically active transition metal complexes to promote insertion reactions into three-membered rings, were also provided by Mathey et al. e.g. the reaction of 1*H*-phosphirene complex **12** with an alkyne derivative to yield 1*H*-phosphole complex **13** in the presence of a palladium complex (Scheme 10) [64].

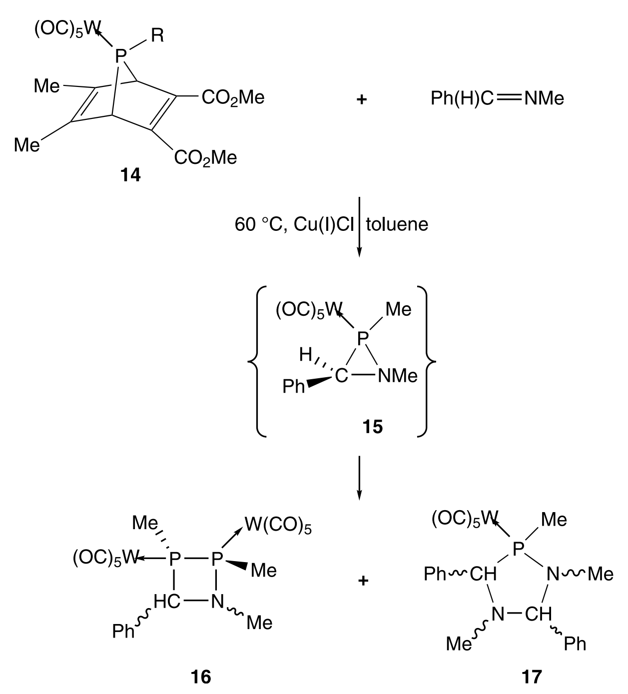


Scheme 10. Example of a 1*H*-phosphirene complex ring enlargement using $Pd(PPh_3)_4$ as catalyst.

Recently, Mathey et al. reported the reaction of 7-phosphanorbornadiene complex **14** with an imine derivative to give, presumably via the intermediate azaphosphiridine complex **15**, the 1,2,3-azadiphosphetidine complex **16** and the 1,3,4-diazaphospholane complex **17** (Scheme 11) [65]. In this case it is still not clear if it is an insertion of the imine into the P–C or the P–N bond of the three-membered ring is intermediate.

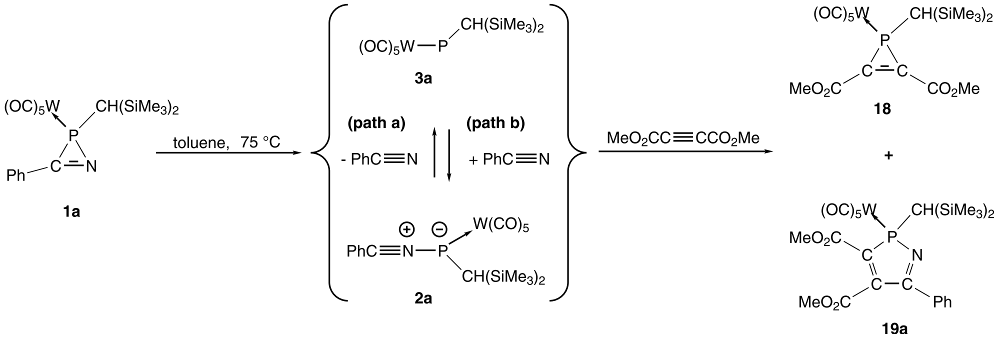
4.2.1. Ring expansion with selective P–C bond-cleavage

There is only one clear-cut example of this type of reaction: the thermally induced ring opening of λ^3-2*H*-azaphosphirene complex **1a** in toluene at 75 °C in the presence of dimethyl acetylenedicarboxylate (DMAD) and formation of the λ^3-2*H*-1,2-azaphosphole complex **19a**, which was obtained as a minor product [5]. For the formation of the major product, the 1*H*-phosphirene complex **18**, a [2+1] cycloaddition of DMAD with the terminal phosphanediyl complex **3a** was suggested (Scheme 12) [66]. Investigations on the reaction mechanism showed that adding benzonitrile to the reaction mixture significantly increased the amount of the λ^3-2*H*-1,2-azaphosphole complex **19a** (see also Section 5.2.1). Therefore, it was concluded that another reactive intermediate must be involved, which can be generated through reacting the terminal phosphanediyl complex with benzonitrile in a terminal [1+1] addition (path b in Scheme 12), thus giving the nitrilium phosphanylide complex **2a** [5].



Scheme 11. Proposed reaction course for the formation of metal complexes **16** and **17**.

The same study also revealed that adding *para*-substituted benzonitrile derivatives furnished the corresponding λ^3-2*H*-1,2-azaphosphole complexes and that their amounts significantly depended on the electronic effects of the para substituent, whereby electron-donating groups such as methoxy favored and electron-withdrawing groups such as trifuoromethyl disfavored the formation of the λ^3-2*H*-1,2-azaphosphole complexes [5]. These observations created the idea of achieving transylidation reactions of nitrilium phosphanylide complexes by simply adding differently substituted carbonitriles with better π-donor substituents to the reaction solution (see Section 5.2.1) [69]. Although, in the area of nitrile sulfides, a related observation was made earlier, it had had no important synthetic impact [68,69]. Quite the contrary happened in nitrilium phosphanylide complex chemistry; after noticing this finding, so-called three-component reactions, employing a λ^3-



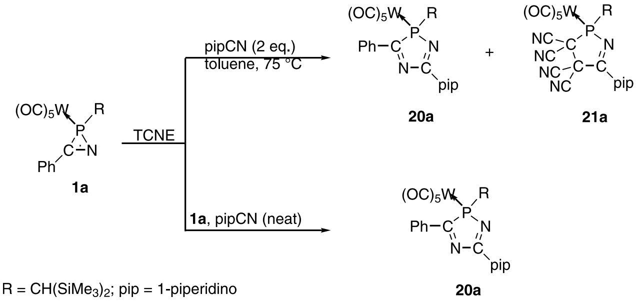
Scheme 12. Trapping reactions of reactive intermediates **2a** and **3a** with DMAD.

2*H*-azaphosphirene complex, a nitrile and a trapping reagent, were developed rapidly (see Section 5.2).

4.2.2. Ring-expansion with selective P–N bond-cleavage

Recently, the first reaction of this type was reported by Streubel et al. in 2000. They observed the curious formation of complex **20a**, which was an unexpected regioisomer of a 2*H*-1,4,2-diazaphosphole complex, during a thermal three-component reaction of λ^3-2*H*-azaphosphirene complex **1a**, 1-piperidinocarbonitrile and tetracyanoethylene in toluene (Scheme 13) [70]. Although the envisaged Δ^4-1,2-azaphospholene complex **21a** was obtained in reasonable yields, they repeated the reaction at ambient temperature and were surprised to realize that the 2*H*-1,4,2-diazaphosphole complex **20a** was formed again, being now the sole product; the reaction rate increased significantly if the reaction was carried out in neat 1-piperidinocarbonitrile. A further surprise was the result that only 0.2 equivalents of TCNE were needed to achieve the quantitative conversion of the λ^3-2*H*-azaphosphirene complex **1a** into the 2*H*-1,4,2-diazaphosphole complex **20a** [70]. This methodology was extended to other nitrile derivatives and also to the chromium and molybdenum λ^3-2*H*-azaphosphirene complexes **6** and **7** (see Section 5.2.3) [70].

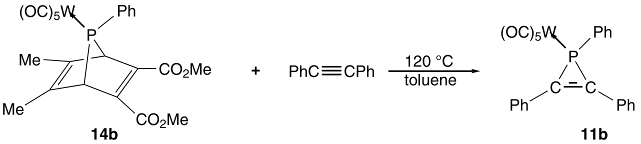
During investigations of the reaction mechanism it was observed that elemental sulfur and iodine were also good catalysts for this bond-selective ring expansion [71]. Furthermore, metal salts such as Cu(II)Cl or ferrocenium hexafluorophosphate are also capable to catalyze selectively this nitrile insertion into the P–N bond [71]. Although, the overall reaction mechanism is still unclear, all these reactions have some aspects in common: all catalytically active compounds are typical oxidants and/or in the case of the ferrocenium salt typical one-electron oxidants [72]. One can assume that in all cases, except for the latter, the primary reaction step is the formation of the Lewis-acid/Lewis-base adduct. If the interaction between the Lewis-acidic centers of the catalyst and the nitrogen center of the λ^3-2*H*-azaphosphirene ring is weak, e.g. TCNE or iodine, only a charge-transfer complex might result or if it becomes stronger, e.g. Cu(II)Cl, then electron transfer takes place giving Cu(I)Cl and a λ^3-2*H*-azaphosphirene complex radical cation, which then is transformed into the final product. In the case of the ferrocenium hexafluorophosphate-catalyzed reactions, there is still the unanswered question of the nature of the hexafluorophosphate counterion. Recently, the first results were obtained, which provided first evidence for the existence of a persistent phosphorus-containing radical cation, which was detected as part of a reaction residue. This, a blewish solid with an unknown composition, displayed two ESR resonances (solid state ESR measurements), but no ^{31}P-NMR resonance. Furthermore, upon reacting this residue with tetrakis(dimethylamino)ethylene the formation of a 2*H*-1,4,2-diazaphosphole complex, ferrocene and the tetrakis(dimethylamino)ethylene radical cation was observed [73]. Despite the fact, that many problems concerning the reaction mechanism are still unsolved, this novel synthetic methodology is very valuable because it makes use of an important new building block under very mild conditions, i.e. phosphavinyl–nitrene metal complexes; this will be shown in Section 5.2



Scheme 13. P–C bond-selective ring expansion reaction of a λ^3-2*H*-azaphosphirene metal complex.

4.3. Reactions with cleavage of two bonds of the ring

The quest for terminal phosphanediyl metal complexes is over was resumé and title of a review written by A. Cowley in 1997 [74]. Although it is true that most of the major experimental problems have been solved, the



Scheme 14. First example of a trapping reaction of an electrophilic terminal phosphanediyl complex.

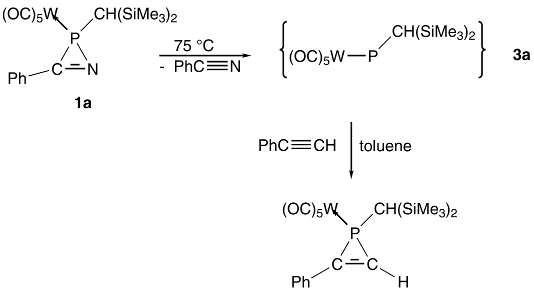
challenge to observe spectrocopically and/or to isolate a electrophilic terminal phosphanediyl metal complexes having a metal(0) center, i.e. [M(CO)$_5$], has remained. One step in this direction was done quite recently by Carty et al. with the isolation of metal(II) complexes such as [Cp*(CO)$_3$W(PN*i*Pr$_2$)][AlCl$_4$] [75]. Regarding the employment of electrophilic terminal phosphanediyl metal complexes in Organic Synthesis [76,77] the story started with a report of Mathey et al. on the thermal decomposition of 7-phosphanorbornadiene complex **14b** at 120 °C in toluene in the presence of diphenylacetylene to give the 1*H*-phosphirene complex **11b** (Scheme 14) [17]. This reaction can also be catalyzed by Cu(I)Cl at 65 °C, but then it has to be carried out in the dark.

A very important finding was that the intermediately formed electrophilic terminal phosphanediyl tungsten complex **3c** reacted in a singlet carbene-type fashion, e.g. with *trans*-stilbene to the two diastereomeric phosphirane complexes **22a** and **22b** (Scheme 15) [63]. This experimental result and its interpretation as a frontier orbital-controlled [2+1] cycloaddition reaction was also supported later on by theoretical investigations on a high level of theory, showing a singlet ground state for electrophilic terminal phosphanediyl metal complexes of the general type [(CO)$_5$M(PR)] [78–82].

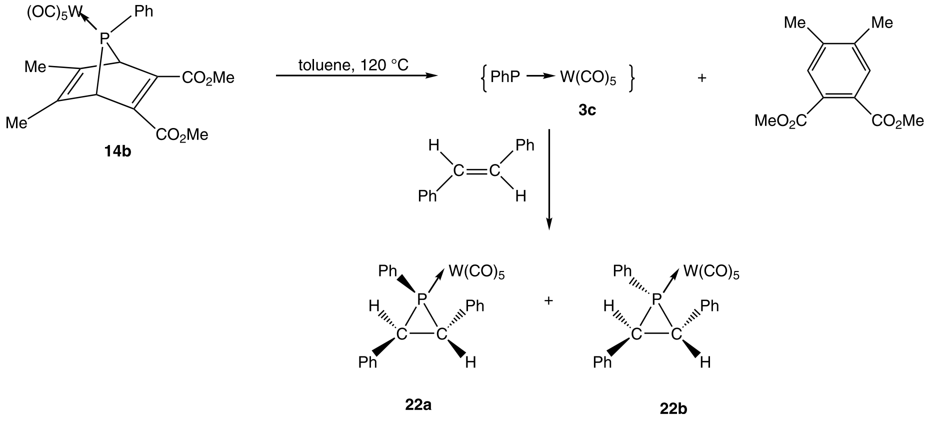
The approach of Mathey et al. to such reactive intermediates is advantageous with regard to the great variety of 7-phosphanorbornadiene complex derivatives accessible, but they do not provide access to terminal phosphanediyl complexes with bulky substituents at the phosphorus atom, meaning that they cannot provide kinetic stabilization of the final [2+1] cycloaddition product. Regarding the synthesis of strained three-membered heterocyclic phosphorus compounds with two or three heteroatoms, this method could be disadvantageous, because it needs elevated temperatures or Cu(I)Cl as catalyst; both could subsequently induce ring opening, thus destroying the target molecule.

4.3.1. Thermal generation of electrophilic terminal phosphanediyl metal complexes

The first example of a thermally induced ring cleavage of a λ^3-2*H*-azaphosphirene tungsten complex **1a** was reported in 1994, using phenylacetylene as the trapping reagent. The resulting 1*H*-phosphirene complex **23a** was obtained in good yields (Scheme 16) [33]; the carbonitrile also formed was detected via IR spectroscopy. Kinetic measurements of the thermolysis of complex **1a** in toluene showed that the reaction is first order in the concentration of λ^3-2*H*-azaphosphirene tungsten complex **1a** and of phenylacetylene, at least, for the period of ca. 30 min [83] the deviation occurring after this period was, most probably, caused by the constant increase of the benzonitrile concentration. Initially, it was assumed that the terminal phosphanediyl complex [(OC)$_5$WPCH(SiMe$_3$)$_2$] (**3a**) was formed at 75 °C as highly reactive intermediate via cleavage of the P–C and P–N ring bonds in a concerted process. But later on, it



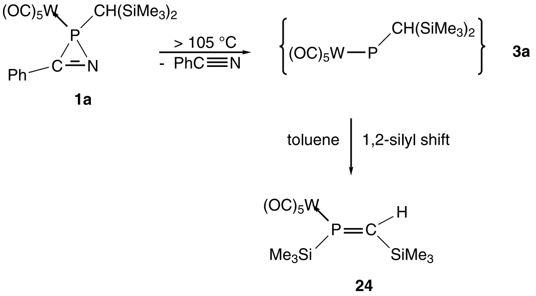
Scheme 16. First example of a trapping reaction of an electrophilic terminal phosphanediyl complex generated from a λ^3-2*H*-azaphosphirene metal complex.



Scheme 15. Example of a singlet carbene-type reaction of electrophilic terminal phosphanediyl complex.

was recognized that this is actually a two-step process starting with the cleavage of the P–C ring bond, thus furnishing the thermally labile nitrilium phosphanylide complex **2a** as the first reactive intermediate.

The ability to cleave the λ^3-2*H*-azaphosphirene ring of complexes **1a**, **6** and **7** at 75 °C (or even below) or at 65 °C in the case of the *P*-pentamethylcyclopentadienyl-substituted derivative **4a** was found to be very useful for the synthesis of other thermally labile ring systems and will be discussed in Section 5.1.

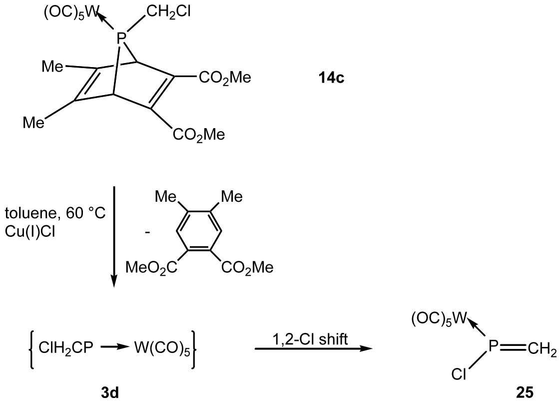


Scheme 17. Formation of a *P*-trimethylsilyl methylenephosphane complex via rearrangement of a transiently formed electrophilic terminal phosphanediyl complex.

4.3.2. *Rearrangement of electrophilic terminal phosphanediyl metal complexes*

There was one interesting observation about bulky-substituted electrophilic terminal phosphanediyl metal complexes such as **3a** and **3b** that was and still is puzzling, that is that they do not dimerize (or even trimerize) in the absence of trapping reagents, as complex **3c** [84] does! This statement, concerning complexes **3a** and **3b**, does not represent a contradiction to the formerly reported dimerization of [(OC)$_5$MoPCH(SiMe$_3$)$_2$] in the case of the thermolysis of molybdenum complex **7** [83]. This reaction seems to be a special 'molybdenum-case', meaning that the formation of the observed dimer followed a different reaction pathway. Although, the reactive intermediates [(OC)$_5$WPCH(SiMe$_3$)$_2$] (**3a**) and [(OC)$_5$WPC$_5$Me$_5$] (**3b**) were not detected by spectroscopic means, the fate of complex **3a** at even higher temperatures > 105 °C was determined recently—it rearranged to the isomeric *P*-trimethylsilyl phosphaalkene complex **24** (Scheme 17) [85]; the configuration of complex **24** was tentatively assigned.

This was a completely unexpected outcome because it most probably represents, at least in Organophosphorus Chemistry, an unprecedented intramolecular 1,2-trimethylsilyl-shift from a electronegative to a more electropositive element. Therefore, it was termed *inverse silatropy*. There is only one example in the literature of a 1,2-chlorine shift of transiently formed electrophilic terminal phosphanediyl complex [(OC)$_5$WPCH$_2$Cl] (**3d**) (generated from complex **14c**) to the *P*-chloro phosphaalkene complex **25** (Scheme 18); it has to be noted here that this rearrangement was promoted by Cu(I)Cl [86].



Scheme 18. Formation of a *P*-chloro methylenephosphane complex via rearrangement of a transiently formed electrophilic terminal phosphanediyl complex.

5. Synthetic potential of λ^3-2*H*-azaphosphirene metal complexes in phosphorus heterocyclic chemistry

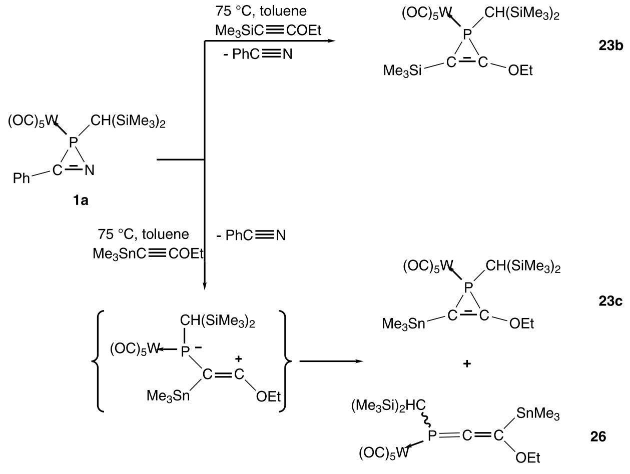
The aim of this chapter is to show the synthetic potential of λ^3-2*H*-azaphosphirene metal complexes in phosphorus heterocyclic chemistry using selected examples, and therefore, the intention is not to cover all derivatives synthesized so far. At least one derivative of each of the presented heterocycles was structurally characterized by single-crystal X-ray analysis. Furthermore, in the following chapters, few mechanistic discussions will be presented, which are beyond that of Sections 4.2.1 and 4.3.1.

5.1. *Synthesis of three-membered phosphorus heterocycles*

5.1.1. *λ^3-1H-Phosphirene metal complexes*

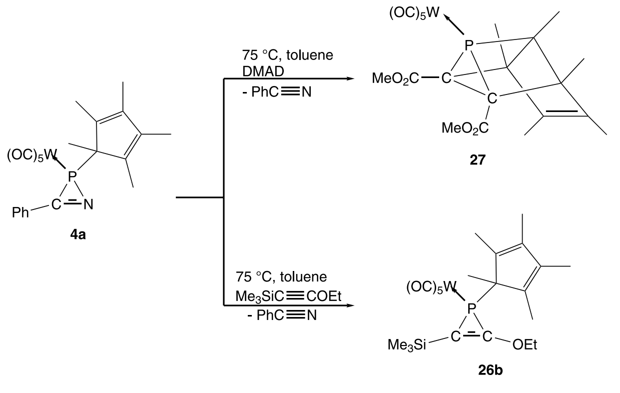
As already described for complex **1a** in Section 4.3.1, thermally induced ring cleavage of λ^3-2*H*-azaphosphirene metal complexes **1a, 6** and **7** in the presence of alkynes provide facile access to a wide variety of 1*H*-phosphirene complexes at 75 °C in toluene [85]. Most often, the easily accessible complex **1a** was used [66,87,88] e.g. with bifunctional alkynes to furnish 1*H*-phosphirene complexes **23b** and **23c**; the latter was formed together with the phosphaallene complex **26**, thus providing some evidence for a zwitterionic intermediate in the first reaction step (Scheme 19) [89,90].

The chemistry of 1*H*-phosphirene complexes such as **23a** was investigated, later on, e.g. with respect to 1,2



Scheme 19. Thermal ring cleavage of λ^3-2*H*-azaphosphirene metal complex **1a** in the presence of alkynes.

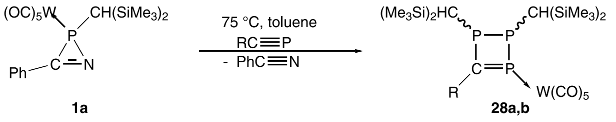
addition and [4+2] cycloaddition reactions [91]. Recently, a very interesting difference between complex **1a** and **4a** was observed concerning the synthesis of 1*H*-phosphirene complexes. In contrast to 1*H*-phosphirene complex **23a**, which is stable under these conditions, complex **26a** was only transiently formed; the final product was the phosphorus–carbon cage complex **27** (Scheme 20) [13] Furthermore, it was shown that the intramolecular Diels–Alder reaction did not occur if a electronically different alkyne was employed as trapping reagent; in this case the reaction stopped at the stage of the 1*H*-phosphirene complex **26b** (Scheme 20) [92].



Scheme 20. Thermal ring cleavage of λ^3-2*H*-azaphosphirene metal complex **4a** in the presence of alkynes.

5.1.2. λ^3-1*H*-Diphosphirene metal complexes

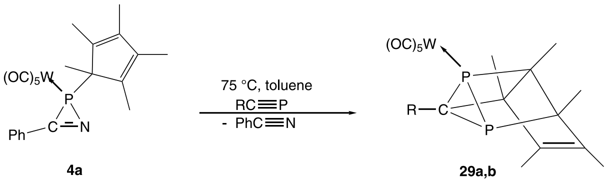
Attempts to synthesize new λ^3-1*H*-diphosphirene complexes were only partially successful because of the known thermal instability of *C*-alkyl-substituted derivatives. Therefore, the reactions of λ^3-2*H*-azaphosphirene complex **1a** with *tert*-butyl and 1-adamantyl methylidynephosphane in toluene exclusively furnished the ring expanded products, the 1,2-dihydro-1,2,3-triphosphete complexes **28a** [93] and **28b** [92] (Scheme 21).



28a: R = ^{t}Bu; **28b**: R = 1-ad

Scheme 21. Thermal ring cleavage of λ^3-2*H*-azaphosphirene metal complex **1a** in the presence of phosphaalkynes.

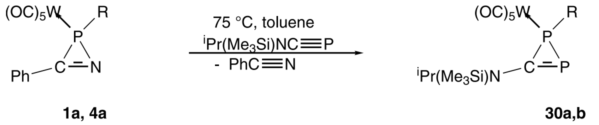
If complex **4a** was employed together with the methylidynephosphanes under the same reaction conditions then phosphorus–carbon cage complexes **29a** and **29b** were obtained as final products (Scheme 22) [94].



29a: R = ^{t}Bu; **29b**: R = 1-ad

Scheme 22. Thermal ring cleavage of λ^3-2*H*-azaphosphirene metal complex **4a** in the presence of alkynes.

With isopropyl(trimethylsilyl)amino methylidynephosphane both λ^3-2*H*-azaphosphirene complexes **1a** and **4a** furnished the corresponding λ^3-1*H*-diphosphirene complexes **30a** and **30b** in good yields (Scheme 23); meanwhile, ring opening reactions of complex **30a** have been also investigated [95].



1a, **30a**: R = CH(SiMe$_3$)$_2$; **1b**, **30b**: R = C$_5$Me$_5$

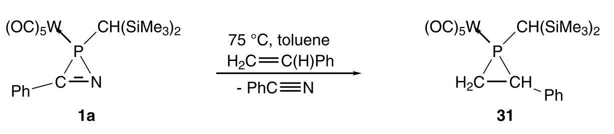
Scheme 23. Thermal ring cleavage of λ^3-2*H*-azaphosphirene metal complex **1a** in the presence of a *C*-amino-substituted phosphaalkyne.

5.1.3. λ^3-Phosphirane metal complexes

λ^3-2*H*-azaphosphirene complex **1a** and a variety of alkene derivatives were reacted to give λ^3-phosphirane complexes in, most often, only moderate yields. At first, this finding was surprising, but the instability of the rings was explained later on by assuming steric repulsion between the ring substituents, which also facilitated subsequently occurring epimerization. An example of a clean reaction was that of complex **1a**, which reacted with stilbene to the λ^3-phosphirane complex **31** (Scheme 24) [96].

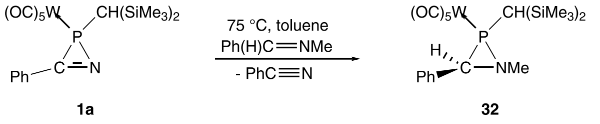
5.1.4. λ^3-Azaphosphiridine metal complexes

So far, only one reaction of λ^3-2*H*-azaphosphirene complex **1a** and an imine derivative was described, leading to the λ^3-azaphosphiridine complex **32**, which



Scheme 24. Thermal ring cleavage of λ^3-2*H*-azaphosphirene metal complex **1a** in the presence of alkenes.

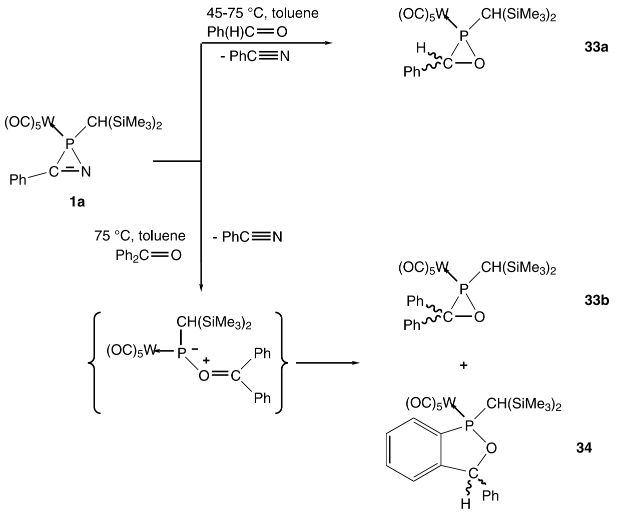
represents the only known complex of this ring system (Scheme 25) [5]. Reactions of a 7-phosphanorbornadiene complex with this imine derivative exclusively led to the 1,2,3-azadiphosphetidine complex **16** and the 1,3,4-diazaphospholane complex **17** as it was already shown in Scheme 11 [65].



Scheme 25. Thermal ring cleavage of λ^3-2*H*-azaphosphirene metal complex **1a** in the presence of an imine derivative.

5.1.5. *λ^3-Oxaphosphirane metal complexes*

As already mentioned in the general introduction, the first λ^3-oxaphosphirane complex was obtained by oxidation of a phosphaalkene complex with *m*-CPBA as reported by Mathey et al. in 1990 [4]. Shortly afterwards, λ^3-2*H*-azaphosphirene complex **1a** was reacted in toluene with benzaldeyde to yield λ^3-oxaphosphirane complex **33a** (Scheme 26) [33]. Later on, it was recognized that P,O-ylide complexes are reactive intermediates in such reactions, e.g. in the reaction of complex **1a** with benzophenone, thus leading to λ^3-oxaphosphirane complex **33b** and the bicyclic oxaphospholane complex **34** (Scheme 26) [5].



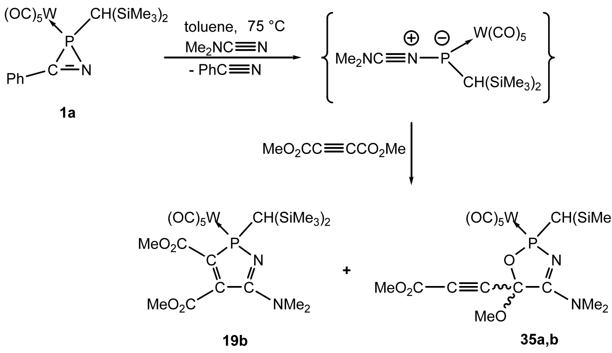
Scheme 26. Thermal ring cleavage of λ^3-2*H*-azaphosphirene metal complex **1a** in the presence of carbonyl derivatives.

Further investigations have shown that the reactions of λ^3-2*H*-azaphosphirene complex **1a** with other carbonyl derivatives, having alkyl groups attached to the carbonyl carbon atom, did not yield λ^3-oxaphosphirane complexes, instead acyclic products were obtained [5] Related results were reported also by the group of Mathey [97,98].

5.2. *Synthesis of five-membered phosphorus heterocycles*

5.2.1. *λ^3-2H-1,2-Azaphosphole metal complexes*

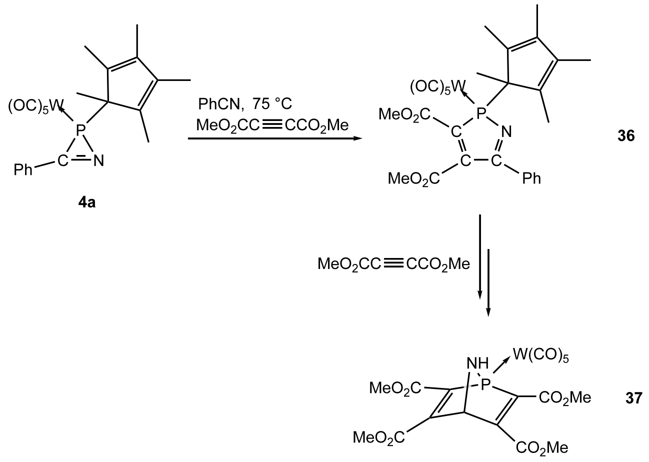
As described in Section 4.3.1, the synthesis of λ^3-2*H*-1,2-azaphosphole metal complexes relies entirely on three-component reactions and their main idea of *transylidation*, which was first described in 1998 [67]. A good illustration of this reaction principle is given by the reaction of λ^3-2*H*-azaphosphirene complex **1a** with dimethylcyanamide and DMAD in toluene, which led to the λ^3-2*H*-1,2-azaphosphole complex **19b** and the diastereomeric λ^3-Δ^3-1,3,2-oxazaphospholene complexes **35a** and **35b** (1:1:1 ratio) (Scheme 27); formation of either the λ^3-1*H*-phosphirene complex **18** or the λ^3-2*H*-1,2-azaphosphole complex **19a** was not observed [67].



Scheme 27. Thermal three-component reaction of λ^3-2*H*-azaphosphirene metal complex **1a** with dimethylcyanamide and DMAD.

Detailed studies were carried out on reactions of λ^3-2*H*-azaphosphirene complex **1a**, **6** and **7** with respect to influences of the metal atom, the nitrile substituent, the alkyne substituents on the product formation and the regiochemistry [83]. Recent studies showed that 7-phosphanorbornadiene complexes can be employed in the synthesis of λ^3-2*H*-1,2-azaphosphole complexes [99]. Even more recently, this methodology was exploited by using λ^3-2*H*-azaphosphirene complex **1a**, DMAD and hetarene-substituted carbonitriles [49] or carbonitriles with P,C- and P,N-ylide substituents [100]. Investigations on the reaction of λ^3-2*H*-azaphosphirene complex **4a** with DMAD in benzonitrile showed the formation of the 7-aza-1-phosphanorbornadiene complex **37** as main product [92], which was totally unexpected. The intermediately formed λ^3-2*H*-1,2-azaphosphole complex **36**

[91] showed a surprising instability under these reaction conditions and led to the final product via an unknown pathway (Scheme 28).

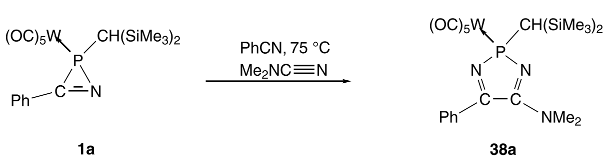


Scheme 28. Thermal three-component reaction of λ^3-2*H*-azaphosphirene metal complex **4a** with benzonitrile and DMAD.

Preliminary studies on photochemical reactions of λ^3-2*H*-azaphosphirene complex **1a** showed that λ^3-2*H*-1,2-azaphosphole complexes are also accessible in *n*-pentane at low temperatures [101].

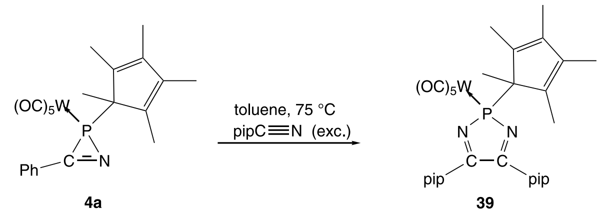
5.2.2. *λ^3-2H-1,3,2-Diazaphosphole metal complexes*

First access to λ^3-2*H*-1,3,2-diazaphosphole metal complexes was reported in 1997 by Streubel et al. They reacted λ^3-2*H*-azaphosphirene complex **1a** and dimethylcyanamide in benzonitrile at 75 °C, which selectively led to the λ^3-2*H*-1,3,2-diazaphosphole complex **38a** (Scheme 29) [102].



Scheme 29. Thermal three-component reaction of λ^3-2*H*-azaphosphirene metal complex **1a** with dimethylcyanamide and benzonitrile.

Subsequent investigations showed that the three-component reaction conditions can be employed in a wide variety of reactions of complexes **1a**, **6** and **7** if the second carbonitrile component, the trapping reagent, was used in excess or, even better, as solvent [48]. This method also provided access to ester-functionalized λ^3-2*H*-1,3,2-diazaphosphole complexes. As already described in Section 2.2, a polycyclic C,P,N-carbon cage compound was obtained as main product if λ^3-2*H*-azaphosphirene complex **4a** and 1-piperidinocarbonitrile were employed in 1:1 ratio [14]. If an excess of 1-piperidinocarbonitrile was used instead, then the 4,5-bis(1-piperidino)-substituted λ^3-2*H*-1,3,2-diazaphosphole complex **39** was obtained (Scheme 30).

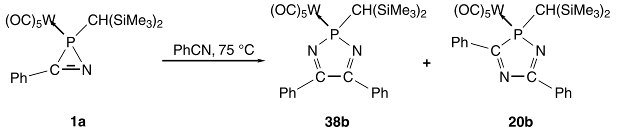


Scheme 30. Thermal reaction of λ^3-2*H*-azaphosphirene metal complex **4a** with 1-piperidinocarbonitrile.

Meanwhile, 7-phosphanorbornadiene complexes can also be employed in the synthesis of λ^3-2*H*-1,3,2-diazaphosphole complexes [51].

5.2.3. *λ^3-2H-1,4,2-Diazaphosphole metal complexes*

λ^3-2*H*-1,4,2-Diazaphosphole complexes were first discovered in thermolytic reactions of λ^3-2*H*-azaphosphirene complex **1a** in benzonitrile, whereby both regioisomers, complexes **38b** and **20b**, were formed, the latter being the main product (Scheme 31) [48].



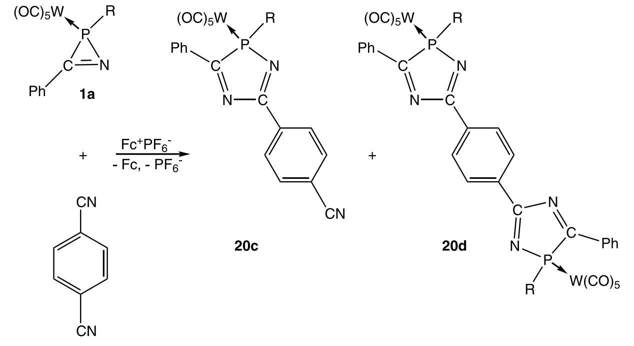
Scheme 31. Thermal reaction of λ^3-2*H*-azaphosphirene metal complex **1a** with benzonitrile.

Apart from photochemical reactions of λ^3-2*H*-azaphosphirene complex **1a** [101] with ethyl cyanoformate in *n*-pentane/benzonitrile mixtures at low temperatures, the TCNE- [70] or ferrocenium salt-catalyzed [71] reactions are the most convenient and versatile routes to λ^3-2*H*-1,4,2-diazaphosphole complexes and can be carried out with functional 2*H*-azaphosphirene complexes and/or functional carbonitriles. For example, λ^3-2*H*-azaphosphirene complex **1a** was reacted with *para*-benzodinitrile to furnish the λ^3-2*H*-1,4,2-diazaphosphole complexes **20c** and **d** (Scheme 32) [103].

5.2.4. *λ^3-2H-1,2,3-Azadiphosphole metal complexes*

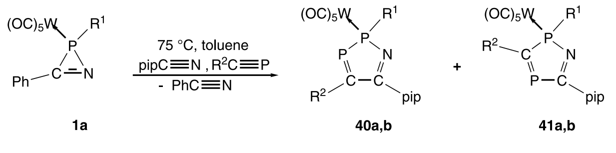
Recently, thermal reactions of λ^3-2*H*-azaphosphirene complex **1a** with 1-piperidinocarbonitrile and *tert*-butyl or 1-adamantyl methylidynephosphane in toluene yielded λ^3-2*H*-1,2,3-azadiphosphole complexes **40a** and **40b** (Scheme 33) [104], thus providing the first access to this five-membered unsaturated heterocyclic ring system.

Although the regioisomeric λ^3-2*H*-1,2,4-azadiphosphole complexes **41a** and **40b** were formed also (accord-



R = CH(SiMe$_3$)$_2$; Fc$^+$ = (C$_5$H$_5$)$_2$Fe(III); Fc = (C$_5$H$_5$)$_2$Fe(II)

Scheme 32. P–N bond-selective ring expansion reaction of λ^3-2*H*-azaphosphirene metal complex **1a**.



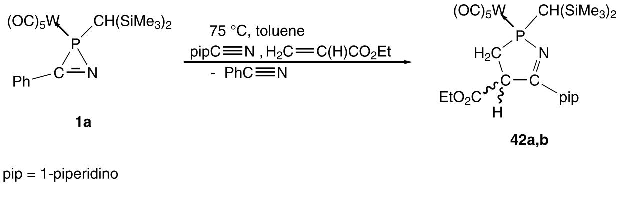
pip = 1-piperidino; CH(SiMe$_3$)$_2$; **40a, 41a**: R = ^{t}Bu; **40b, 41b**: R = 1-ad

Scheme 33. Thermal three-component reaction of λ^3-2*H*-azaphosphirene metal complex **1a** with 1-piperidinocarbonitrile and phosphaalkynes.

ing to ^{31}P-NMR spectroscopy), they could not be isolated by column chromatography.

5.2.5. λ^3-Δ^4-1,2-Azaphospholene metal complexes

Apart from the thermal reaction of λ^3-2*H*-azaphosphirene complex **1a** with 1-piperidinocarbonitrile and TCNE [70], other electronically activated alkene derivatives reacted also readily to λ^3-Δ^4-1,2-azaphospholene complexes, e.g. the acryl ester furnished regioselectively the diastereomeric complexes **42a** and **42b** (Scheme 34) [85].

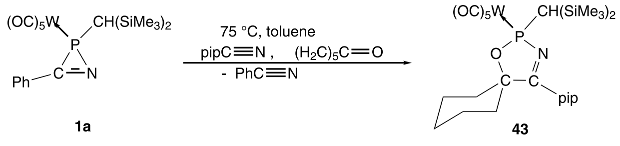


pip = 1-piperidino

Scheme 34. Thermal three-component reaction of λ^3-2*H*-azaphosphirene metal complex **1a** with 1-piperidinocarbonitrile and an acryl ester.

5.2.6. λ^3-Δ^3-1,3,2-Oxazaphospholene metal complexes

The thermal reaction of λ^3-2*H*-azaphosphirene complex **1a** with 1-piperidinocarbonitrile and carbonyl derivatives led regioselectively to λ^3-Δ^3-1,3,2-oxazaphospholene complexes, e.g. cyclohexanone furnished regioselectively complex **43** (Scheme 35) [85].

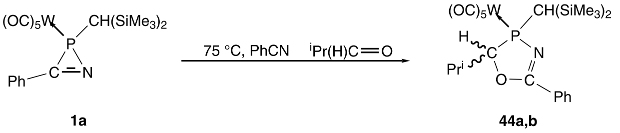


pip = 1-piperidino

Scheme 35. Thermal three-component reaction of λ^3-2*H*-azaphosphirene metal complex **1a** with 1-piperidinocarbonitrile and cyclohexanone.

5.2.7. λ^3-Δ^2-1,3,4-Oxazaphospholene metal complexes

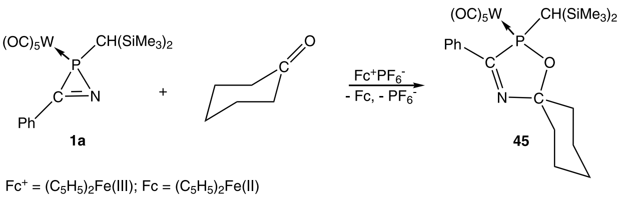
More surprising was the observation that the regiochemistry of such reactions seemed to be largely determined by the *C*-substituent of the transiently formed nitrilium phosphanylide complexes. For example, thermal reaction of λ^3-2*H*-azaphosphirene complex **1a** with carbonyl derivatives led preferably to λ^3-Δ^2-1,3,4-oxazaphospholene complexes, e.g. with isopropyl aldehyde the diastereomeric complexes **44a** and **44b** were obtained regioselectively, whereby and surprisingly the isomer with the isopropyl group and the pentacarbonyltungsten group on the same side of the five-membered ring was largely preferred (Scheme 36) [85].



Scheme 36. Thermal three-component reaction of λ^3-2*H*-azaphosphirene metal complex **1a** with 1-piperidinocarbonitrile and isopropyl aldehyde.

5.2.8. λ^3-Δ^3-1,3,5-Oxazaphospholene metal complexes

Although recently discovered, λ^3-Δ^3-1,3,5-oxazaphospholene complexes represent just another scientific spin-off of the chemistry of λ^3-2*H*-azaphosphirene metal complexes. Such heterophospholene complexes are readily obtained under very mild conditions using the ferrocenium salt-catalyzed reaction protocol [71]. For example, λ^3-2*H*-azaphosphirene complex **1a** reacted under such conditions with cyclohexanone in dichloromethane bond- and regioselectively to the λ^3-Δ^3-1,3,5-oxazaphospholene complex **45** (Scheme 37) [103].



Fc$^+$ = (C$_5$H$_5$)$_2$Fe(III); Fc = (C$_5$H$_5$)$_2$Fe(II)

Scheme 37. P–N bond-selective ring expansion reaction of λ^3-2*H*-azaphosphirene metal complex **1a** using cyclohexanone.

Acknowledgements

I am very grateful to all of my coworkers who helped me in exploring and developing the chemistry of λ^3-2*H*-azaphosphirene metal complexes. I am also very grateful to Professor Dr. W.-W. du Mont, the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie* for financial support.

References

[1] (a) R.I. Wagner, US Patents 3086053 and 3086056 (1963).;
(b) R.I. Wagner, Chem. Abstr. 59 (1963) 10124;
(c) R.I. Wagner, Chem. Abstr. 60 (1964) 559.

[2] For reactive intermediates and acyclic valence isomers methylene(oxo)phosphoranes see: H. Heydt, in: M. Regitz, O.J. Scherer (Eds.), Multiple Bonds and Low Coordination Chemistry in Phosphorus Chemistry, Georg Thieme Verlag, Stuttgart, 1990, pp. 375.

[3] W.W. Schoeller, in: M. Regitz, O.J. Scherer (Eds.), Multiple Bonds and Low Coordination Chemistry in Phosphorus Chemistry, Georg Thieme Verlag, Stuttgart, 1990, p. 5.

[4] (a) S. Bauer, A. Marinetti, L. Ricard, F. Mathey, Angew. Chem. Angew. Chem. 102 (1990) 1098;
(b) S. Bauer, A. Marinetti, L. Ricard, F. Mathey, Int. Ed. Engl. 29 (1990) 1166.

[5] (a) R. Streubel, A. Ostrowski, H. Wilkens, F. Ruthe, J. Jeske, P.G. Jones, Angew. Chem. 109 (1997) 409;
(b) R. Streubel, A. Ostrowski, H. Wilkens, F. Ruthe, J. Jeske, P.G. Jones, Angew. Chem. Int. Ed. Engl. 36 (1997) 378.

[6] H. Quast, Nachr. Chem. Tech. Lab. 27 (1979) 120.

[7] M. Baudler, Pure Appl. Chem. 52 (1980) 755.

[8] (a) M. Baudler, Angew. Chem. 94 (1982) 520;
(b) M. Baudler, Angew. Chem. Int. Ed. Engl. 21 (1982) 492.

[9] L.D. Quin, The Heterocyclic Chemistry of Phosphorus, Wiley, New York, 1981, p. 176.

[10] Y.G. Gololobov, N.I. Gusa'r, A.S. Tarasevich, Russ. Chem. Rev. (Engl. Transl.) 52 (1983) 446.

[11] (a) K. Blatter, W. Rösch, U.-J. Vogelbacher, J. Fink, M. Regitz, Angew. Chem. 98 (1987) 67 (German version);
(b) K. Blatter, W. Rösch, U.-J. Vogelbacher, J. Fink, M. Regitz, Angew. Chem. Int. Ed. Engl. 26 (1987) 85.

[12] (a) E.P.O. Fuchs, W. Rösch, M. Regitz, Angew. Chem. 98 (1987) 1058 (German version);
(b) E.P.O. Fuchs, W. Rösch, M. Regitz, Angew. Chem. Int. Ed. Engl. 26 (1987) 1011.

[13] (a) U. Rohde, F. Ruthe, P.G. Jones, R. Streubel, Angew. Chem. 111 (1999) 158;
(b) U. Rohde, F. Ruthe, P.G. Jones, R. Streubel, Angew. Chem. Int. Ed. 38 (1999) 215.

[14] R. Streubel, U. Schiemann, N. Hoffmann, Y. Schiemann, P.G. Jones, D. Gudat, Organometallics 19 (2000) 475.

[15] (a) J. Liedtke, S. Loss, G. Alcaraz, V. Gramlich, H.-J. Grützmacher, Angew. Chem. 111 (1999) 1724;
(b) J. Liedtke, S. Loss, G. Alcaraz, V. Gramlich, H.-J. Grützmacher, Angew. Chem. Int. Ed. 38 (1999) 1623.

[16] (a) J. Liedtke, H. Ruegger, S. Loss, H.-J. Grützmacher, Angew. Chem. 112 (2000) 2596;
(b) J. Liedtke, H. Ruegger, S. Loss, H.-J. Grützmacher, Angew. Chem. Int. Ed. (2000) 39.

[17] A. Marinetti, F. Mathey, J. Fischler, A. Mitschler, J. Am. Chem. Soc. 104 (1982) 4484.

[18] F. Mathey, A. Marinetti, Bull. Soc. Chim. Belg. 93 (1984) 533.

[19] F. Mathey, Pure Appl. Chem. 59 (1987) 993.

[20] F. Mathey, Chem. Rev. 90 (1990) 997.

[21] F. Mathey, Acc. Chem. Res. 25 (1992) 90.

[22] F. Mathey, M. Regitz, in: A.R. Katritzky, C.W. Rees, E.F.V. Scriven (Eds.), Comprehensive Heterocyclic Chemistry, vol. 1A, Pergamon, Oxford, 1996, p. 277.

[23] H. Heydt, Science of Synthesis, vol. 9, Thieme Verlag, Stuttgarh, 2001, p. 1.

[24] K.B. Dillon, F. Mathey, J.F. Nixon, Phosphorus: The Carbon Copy, Wiley, Chichester, 1998, p. 181.

[25] A. Padwa, Acc. Chem. Res. 9 (1976) 371.

[26] V. Nair, K.H. Kim, Heterocycles 7 (1977) 353.

[27] H.-J. Hansen, H. Heimgartner, in: A. Padwa (Ed.), 1,3-Dipolar Cycloaddition Chemistry (Ch. 2), Wiley, New York, 1984, p. 177.

[28] E.F. Scriven, K. Turnbull, Chem. Rev. 88 (1988) 297.

[29] A. Padwa, A.D. Woolhouse, in: A.R. Katritzky, C.W. Rees, E.F.V. Scriven (Eds.), Comprehensive Heterocyclic Chemistry, vol. 7, Pergamon, Oxford, 1989, p. 47.

[30] M. Rahmoune, Y.Y.C. Yeung Lam Ko, F. Tonnard, R. Carrie, PSI-BLOCS Conference, Palaiseau, France, 1988, poster abstract.

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

[32] H. Heydt, Science of Synthesis, vol. 9, Thieme Verlag, Stuttgart, 2001, p. 125.

[33] (a) R. Streubel, J. Jeske, P.G. Jones, R. Herbst-Irmer, Angew. Chem. 106 (1994) 115;
(b) R. Streubel, J. Jeske, P.G. Jones, R. Herbst-Irmer, Angew. Chem. Int. Ed. Engl. 33 (1994) 80.

[34] R. Streubel, A. Kusenberg, Phosphorus Sulfur Relat. Elem. 93–94 (1994) 281.

[35] R. Streubel, A. Ostrowski, H. Wilkens, S. Priemer, U. Rohde, Phosphorus Sulfur Relat. Elem. 124–125 (1998) 93.

[36] R. Streubel, U. Rohde, unpublished results.

[37] R. Streubel, A. Ostrowski, S. Priemer, U. Rohde, J. Jeske, P.G. Jones, Eur. J. Inorg. Chem. (1998) 257.

[38] C. Neumann, E. Ionescu, U. Schiemann, M. Schlenker, M. Bode, F. Ruthe, P.G. Jones, R. Streubel, J. Organomet. Chem., in press.

[39] R. Streubel, S. Priemer, P.G. Jones, unpublished results.

[40] R. Streubel, S. Priemer, F. Ruthe, P.G. Jones, Eur. J. Inorg. Chem. (2000) 1253.

[41] R. Streubel, S. Priemer, F. Ruthe, P.G. Jones, D. Gudat, Eur. J. Inorg. Chem. (1998) 575.

[42] R. Streubel, Habilitationsschrift, University of Braunschweig, 1997.

[43] R. Streubel, F. Ruthe, P.G. Jones, Eur. J. Inorg. Chem. (1998) 571.

[44] R. Streubel, S. Priemer, J. Jeske, P.G. Jones, J. Organomet. Chem. 617–618 (2001) 423.

[45] R. Streubel, M. Hobbold, S. Priemer, J. Organomet. Chem. 613 (2000) 56.

[46] R. Streubel, U. Rohde, J. Jeske, F. Ruthe, P.G. Jones, Eur. J. Inorg. Chem. (1998) 2005.

[47] N. Burford, J.A.C. Clyburne, S. Mason, Inorg. Chem. 32 (1993) 4988.

[48] H. Wilkens, F. Ruthe, P.G. Jones, R. Streubel, Chem. Eur. J. 4 (1998) 1542.

[49] R. Streubel, N. Hoffmann, F. Ruthe, P.G. Jones, Polyhedron 21 (2002) 119.

[50] (a) F. Mathey, Angew. Chem. 99 (1987) 285;
(b) F. Mathey, Angew. Chem. Int. Ed. Engl. 26 (1987) 275.

[51] R. Streubel, U. Schiemann, N. Hoffmann, N.H. Tran Huy, F. Mathey, Eur. J. Inorg. Chem. (2001) 3175.

[52] J. Mason, Multinuclear NMR, Plenum Press, New York, 1987.

[53] S.W. Kirtley, in: G. Wilkinson (Ed.), Comprehensive Organometallic Chemistry, vol. 3, Pergamon Press, Oxford, 1982.

[54] A. Holm, N. Harrit, I. Trabjerg, J. Chem. Soc., Perkin Trans. I, (1978) 746.

[55] S. Priemer, PhD Thesis, University of Braunschweig, 1999.

[56] R. Appel, in: M. Regitz, O.J. Scherer (Eds.), Multiple Bonds and Low Coordination Chemistry in Phosphorus Chemistry, Georg Thieme Verlag, Stuttgart, 1990, p. 157.

[57] M.T. Nguyen, A.f. Hegarthy, J. Chem. Soc. Perkin Trans II (1985) 1999.

[58] M.T. Nguyen, A.f. Hegarthy, J. Chem. Soc. Perkin Trans II (1985) 2005.

[59] L. Ermolaeva, A. Ionkin, Heterat. Chem. 3 (1992) 435.

[60] W.W. Schoeller, R. Streubel, to be published.

[61] R. Streubel, C. Neumann, P.G. Jones, to be published.

[62] W.J. Richter, Angew. Chem. Int. Ed. Engl. 21 (1982) 292.

[63] A. Marinetti, F. Mathey, Organometallics 3 (1984) 456.

[64] A. Marinetti, F. Mathey, Tetrahedron Lett. 28 (1987) 5021.

[65] N.H. Tran Huy, L. Ricard, F. Mathey, Heteroat. Chem. 9 (1998) 597.

[66] A. Ostrowski, J. Jeske. P.G. Jones, R. Streubel, J. Chem. Soc. Chem. Commun. (1995) 2507.

[67] H. Wilkens, F. Ruthe, P.G. Jones, R. Streubel, J. Chem. Soc. Chem. Commun. (1998) 1529.

[68] R.K. Howe, J.E. Franz, J. Org. Chem. 39 (1974) 962.

[69] M. Paton, Chem. Soc. Rev. 18 (1989) 33.

[70] R. Streubel, H. Wilkens, P.G. Jones, Chem. Eur. J. 7 (2000) 3997.

[71] R. Streubel, C. Neumann, P.G. Jones, J. Chem. Soc. Dalton Trans. (2000) 2495.

[72] N.G. Connelly, W.E. Geiger, Chem. Rev. 96 (1996) 877.

[73] R. Streubel, C. Neumann, unpublished results.

[74] A.H. Cowley, Acc. Chem. Res. 30 (1997) 445; and references herein.

[75] B.T. Sterenberg, K.A. Udachin, A.J. Carthy, Organometallics 20 (2001) 2657.

[76] (a) F. Mathey, Angew. Chem. 99 (1987) 285;
(b) F. Mathey, Angew. Chem. Int. Ed. Engl. 26 (1987) 275.

[77] K.B. Dillon, F. Mathey, J.F. Nixon, Phosphorus: The Carbon Copy, Wiley, Chichester, 1998, p. 19.

[78] A.W. Ehlers, K. Lammertsma, E.J. Baerends, Organometallics 17 (1998) 2738.

[79] S. Creve, K. Pierloot, M.T. Nguyen, Chem. Phys. Lett. 285 (1998) 429.

[80] G. Frison, F. Mathey, A. Sevin, J. Organomet. Chem. 570 (1998) 225.

[81] S. Creve, K. Pierloot, M.T. Nguyen, L.G. Vanquickenborne, Eur. J. Inorg. Chem. (1999) 107.

[82] S,. Grigoleit, A. Alijah, A. Rozhenko, R. Streubel, W.W. Schoeller, J. Organomet. Chem., in press.

[83] H. Wilkens, A. Ostrowski, J. Jeske, F. Ruthe, P.G. Jones, R. Streubel, Organometallics 18 (1999) 5627.

[84] A. Marinetti, C. Charrier, F. Mathey, J. Fischer, Organometallics 4 (1985) 2134.

[85] H. Wilkens, Ph.D. Thesis, University of Braunschweig, (2000).

[86] B. Deschamps, F. Mathey, J. Organomet. Chem. 354 (1988) 83.

[87] A. Ostrowski, J. Jeske, F. Ruthe, P.G. Jones, R. Streubel, Z. Anorg. Allg. Chem. 623 (1997) 1897.

[88] R. Streubel, H. Wilkens, F. Ruthe, P.G. Jones, Z. Anorg. Allg. Chem. 625 (1999) 102.

[89] R. Streubel, H. Wilkens, F. Ruthe, P.G. Jones, J. Chem. Soc. Chem. Commun. (1998) 1761.

[90] H. Wilkens, R. Streubel, Phosphorus Sulfur Relat. Elem. 147 (1999) 429.

[91] R. Streubel, H. Wilkens, U. Rohde, A. Ostrowski, J. Jeske, F. Ruthe, P.G. Jones, Eur. J. Inorg. Chem. (1999) 1567.

[92] U. Schiemann, PhD Thesis, University of Braunschweig, 2001.

[93] R. Streubel, L. Ernst, J. Jeske, P.G. Jones, J. Chem. Soc., Chem. Commun. (1995) 2113.

[94] U. Rohde, H. Wilkens, R. Streubel, Phosphorus Sulfur Relat. Elem. 124–125 (1998) 545.

[95] (a) R. Streubel, U. Schiemann, P.G. Jones, J. Grunenberg, H.-M. Schiebel, D. Gudat, Angew. Chem. 113 (2001) 2531;
(b) R. Streubel, U. Schiemann, P.G. Jones, J. Grunenberg, H.-M. Schiebel, D. Gudat, Angew. Chem. Int. Ed. 40 (2001) 2471.

[96] A. Ostrowski, J. Jeske, P.G. Jones, R. Streubel, Z. Anorg. Allg. Chem. 627 (2001) 1135.

[97] Y. Inubushi, N.H. Tran Huy, F. Mathey, J. Chem. Soc., Chem. Commun. (1996) 1903.

[98] Y. Inubushi, N.H. Tran Huy, L. Ricard, F. Mathey, J. Organomet. Chem. 533 (1997) 83.

[99] (a) R. Streubel, U. Schiemann, P.G. Jones, N.H. Tran Huy, F. Mathey, Angew. Chem. 112 (2000) 3845;
(b) R. Streubel, U. Schiemann, P.G. Jones, N.H. Tran Huy, F. Mathey, Angew. Chem. Int. Ed. 39 (2000) 3686.

[100] R. Streubel, N. Hoffmann, H.-M. Schiebel, F. Ruthe, P.G. Jones, Eur. J. Inorg. Chem., accepted for publication.

[101] R. Streubel, H. Wilkens, F. Ruthe, P.G. Jones, J. Chem. Soc. Chem. Commun. (1999) 2127.

[102] H. Wilkens, J. Jeske, P.G. Jones, R. Streubel, J. Chem. Soc. Chem. Commun. (1997) 2317.

[103] R. Streubel, H. Wilkens, C. Neumann, Phosphorus Sulfur Relat. Elem., in press.

[104] G.N. Cloke, P.B. Hitchcock, U. Schiemann, R. Streubel, J.F. Nixon, D.J. Wilson, J. Chem. Soc. Chem. Commun. (2000) 1659.