Syntheses of 2*H*-1,3,2-Diazaphosphole, 2*H*-1,4,2-Diazaphosphole, and Δ^3-1,3,2-Oxazaphospholene Complexes; First Examples of 2*H*-Azaphosphirene Complex Formation by [2+1] Cycloaddition**

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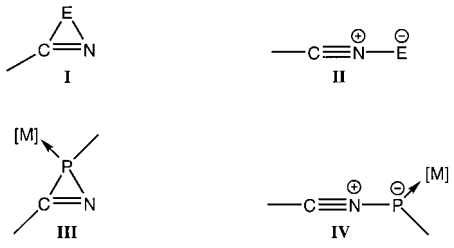
Dedicated to Professor Bernt Krebs on the occasion of his 60th birthday

Abstract: Thermal ring-opening of {[2-bis(trimethylsilyl)methyl-3-phenyl-2*H*-azaphosphirene-κP]pentacarbonyltungsten(0)} (**1**) in the presence of various nitriles is investigated, in which toluene and/or the nitriles are used as solvents. In toluene, for example, the 3-(1-piperidino)-substituted 2*H*-azaphosphirene complex **5b**, 4-(1-piperidino)-5-phenyl- and 4,5-bis(1-piperidino)-substituted 2*H*-1,3,2-diazaphosphole complexes **6b**,**d** are obtained if 1-piperidino nitrile (**2b**) is employed as trapping reagent. Furthermore, a new three-component reaction is presented, using the 2*H*-azaphosphirene complex **1** and a mixture of two different nitriles, thus giving access to 4,5-mixed-substituted 2*H*-1,3,2-diazaphosphole complexes **6a**,**b** and **6e**–**h**. The chemo- and regioselectivity of such reactions is rationalized by [3+2] cycloadditions of transiently formed *C*-dialkylamino-substituted nitrilium phosphane ylide complexes **3b**,**c** to nitriles. Use of two equivalents of dialkyl cyanamides and four equivalents of either ethyl cyanoformate or phenyl glyoxonitrile resulted in dual trapping reactions of complexes **3b**,**c**, forming 2*H*-1,3,2-diazaphosphole complexes **6i**–**k** and Δ^3-1,3,2-oxazaphospholene complexes **8a**–**g**. Reaction of the 2*H*-azaphosphirene complex **1** with ethyl cyanoformate in toluene gave exclusively the 4,5-bis-(ethoxycarbonyl)-2*H*-1,3,2-diazaphosphole complex **6l**; even in benzonitrile, the mixed-substituted 2*H*-1,3,2-diazaphosphole complex **6m** is formed only as a by-product. The first 2*H*-1,4,2-diazaphosphole complex **9** was synthesized along with the regioisomeric 2*H*-1,3,2-diazaphosphole complex **6n** (ratio of **9**:**6n**: 6:1) through thermal ring-opening of 2*H*-azaphosphirene complex **1** in neat benzonitrile. The structures of 2*H*-1,3,2-diazaphosphole complex **6c**, 2*R*,5*S*-Δ^3-1,3,2-oxazaphospholene complex **8a** and 2*H*-1,4,2-diazaphosphole complex **9** were determined by single-crystal X-ray diffraction.

Keywords: cycloadditions · 2*H*-azaphosphirene complexes · phosphorus heterocycles · tungsten

Introduction

The chemistry of three-membered unsaturated nitrogen heterocycles of type **I**, such as 2*H*-azirenes[2] (E = CR_2) or 1*H*-diazirenes[3] (E = NR), and their isomeric nitrilium betaines (**II**), nitrile ylides[4] and nitrile imines,[5] is the subject of current interest, because of their broad versatility as building blocks in heterocycle syntheses (Scheme 1). In contrast to such thoroughly investigated classes of compounds, almost nothing is known about related three-membered heterocycles and nitrilium betaines containing a third-row element, such as silicon and phosphorus (**I**, **II**: E = SiR_2, PR).



Scheme 1. Heteroazirenes (**I**), nitrilium betaines (**II**), 2*H*-azaphosphirene complexes (**III**) and nitrilium phosphane ylide tungsten complexes (**IV**) (**I**–**IV**: R, R′ = alkyl, aryl; [M] = metal complex fragment).

In the synthesis of 2*H*-azirenes and so-called heteroazirenes (ring systems with two heteroatoms and a C–N double bond), it is noteworthy that, apart from recently reported examples of [2+1] cycloadditions of carbenes to benzonitrile to give 2*H*-azirines,[6] no such reactions of either nitrenes or phosphini-

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denes (phosphanediyls)[7] with nitriles have been reported so far. Although only briefly reported, the reaction of a silylene derivative with benzonitrile affording the first stable[8] 2*H*-azasilirene was a real landmark (**I**: E = SiR_2).[9]

With respect to ring opening of three-membered heterocycles of type **I** (E = CR_2, NR), the generation of nitrilium betaines is exclusively established for 2*H*-azirenes. In contrast, transiently formed 1*H*-diazirenes[10] show other rearrangements (instead of ring-opening to yield nitrile imines) giving 3*H*-diazirenes,[10,11] ring-enlarged heterocycles[11] or carbodiimides.[12] Nonetheless, nitrile imines are accessible by other routes, that is, through thermolysis of heterocycles such as oxadiazolinones or sydnones.[5]

Recently, we reported the first syntheses of 2*H*-azaphosphirene complexes **III** using a metal-assisted cyclization,[13] which, at the same time, represented the first access to heteroazirene complexes. Even more recently, we trapped nitrilium phosphane ylide complexes **IV**, generated through thermal ring-opening of {[2-bis(trimethylsilyl)methyl-3-phenyl-2*H*-azaphosphirene-κP]pentacarbonyltungsten(0)} (**1**), with dimethyl acetylenedicarboxylate [14] (DMAD) or dimethyl cyanamide.[15] These investigations became particularly interesting to us in view of our initial investigations on thermolysis of 2*H*-azaphosphirene complexes in which we established that they decompose to aryl nitriles and a short-lived electrophilic terminal phosphanediyl complex.[16] Moreover, reports on the chemistry of 1*H*-thiazirenes and nitrile sulfides (**I**, **II**: E = S) revealed that the latter decompose to nitriles and sulfur in the absence of trapping reagents.[17]

Here we report on thermal ring-opening of {[2-bis(trimethylsilyl)methyl-3-phenyl-2*H*-azaphosphirene-κP]pentacarbonyltungsten(0)} (**1**) in the presence of various nitriles, which yield five-membered heterocycle complexes, among them the first 2*H*-1,4,2-diazaphosphole complex. Nitrile concentration and the electronic influence of the nitrile substituent were examined with respect to reaction courses and product ratios. The quest for the generation of nitrilium phosphane ylide complexes will be discussed and examples of unprecedented [2+1] cycloadditions of a terminal phosphanediyl complex to a nitrile will be given.

Abstract in German: *Die thermische Ringöffnung von {[2-Bis(trimethylsilyl)methyl-3-phenyl-2H-azaphosphirene-κP]-pentacarbonylwolfram(0)} (**1**) in Gegenwart verschiedener Nitrile wird untersucht, wobei Toluol und/oder die Nitrile als Lösungsmittel dienen. So erhält man beispielsweise in Toluol den 3-(1-Piperidino)-substituierten 2H-Azaphosphirenkomplex **5b** sowie die 4-(1-Piperidino)-5-phenyl- und 4,5-Bis(1-piperidino)-substituierten 2H-1,3,2-Diazaphospholkomplexe **6b,d**, wenn 1-Piperidinonitril (**2b**) als Abfangreagenz eingesetzt wird. Weiterhin wird eine neue Dreikomponentenreaktion vorgestellt, bei der der 2H-Azaphosphirenkomplex **1** und eine Mischung aus zwei verschiedenen Nitrilen eingesetzt wird. Man erhält so einen Zugang zu 4,5-gemischt-substituierten 2H-1,3,2-Diazaphospholkomplexen **6a,b** und **6e–h**. Die Chemo- und Regioselektivität solcher Reaktionen wird durch [3+2]-Cycloadditions-Reaktionen von kurzlebigen C-Dialkylamino-substituierten Nitriliumphosphan-Ylid-Komplexen **3b,c** mit Nitrilen erklärt. Verwendet man zwei Äquivalente der Dialkylcyanamide und vier Äquivalente von entweder Ethylcyanoformiat oder Phenylglyoxonitril, so erhält man durch duale Abfangreaktionen der Komplexe **3b,c** die 2H-1,3,2-Diazaphospholkomplexe **6i–k** und Δ³-1,3,2-oxazaphospholenkomplexe **8a–g**. Reaktion von 2H-Azaphosphirenkomplex **1** mit Ethylcyanoformiat in Toluol ergibt exklusiv den 4,5-Bis(ethoxycarbonyl)-2H-1,3,2-diazaphospholkomplex **6l**, und selbst in Benzonitril ist der gemischt-substituierte 2H-1,3,2-Diazaphospholkomplex **6m** nur ein Nebenprodukt. Nimmt man Benzonitril als Lösungsmittel, so entsteht durch thermische Ringöffnung von 2H-Azaphosphirenkomplex **1** der erste 2H-1,4,2-Diazaphospholkomplex **9** zusammen mit dem regioisomeren 2H-1,3,2-Diazaphospholkomplex **6n** (Verhältnis von **9**:**6n** = 6:1). Die Strukturen von 2H-1,3,2-Diazaphospholkomplex **6c**, 2R,5S-Δ³-1,3,2-Oxazaphospholenkomplex **8a** und 2H-1,4,2-Diazaphospholkomplex **9** wurden durch Röntgendiffraktometrie bestimmt.*

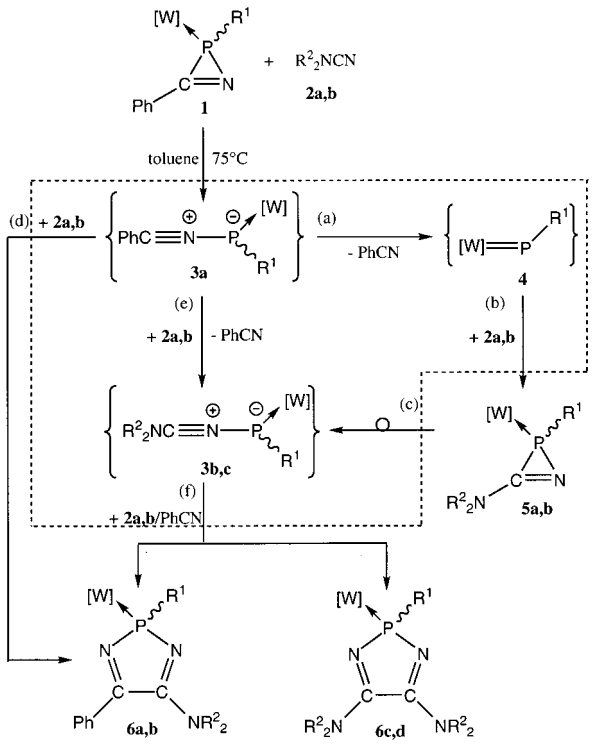
Results

Syntheses of 2*H*-1,3,2-diazaphosphole complexes:

*A: Investigations on thermolysis of 2H-azaphosphirene complex **1** in toluene in the presence of dialkyl cyanamides, R_2NCN ($R_2 = Me_2$, $(CH_2)_5$, iPr_2)*

Dialkylamino-substituted 2*H*-azaphosphirene complexes are not accessible by the metal-assisted cyclization route. Furthermore, we had previously obtained [2+1] cycloaddition products if alkynes[18] or phosphaalkynes[19] were used as trapping reagents. We were interested in investigating the thermolysis of the 2*H*-azaphosphirene complex **1** in the presence of dialkyl cyanamides. Thermolysis of **1** in toluene with two equivalents of the dialkyl cyanamides **2a**,**b** yielded the 2*H*-azaphosphirene complexes **5a**,**b** and the 2*H*-1,3,2-diazaphosphole complexes **6a**,[14] **b**–**d**; selected NMR data are collected in Table 2 (see below) and will be discussed below. In these reactions [$(OC)_5W${P(H)($OSiMe_3$)(CH($SiMe_3$)$_2$)}] (**7**) was formed as a by-product, by an unknown reaction pathway. Depending on the dryness of all the reaction partners, the toluene and the apparatus, the amounts of **7** varied (1–10%) and only traces of **7** were formed if moisture was kept low.[20]

The formation of the 2*H*-azaphosphirene complexes **5a**,**b** in toluene is explained as [2+1] cycloaddition of the transiently formed electrophilic terminal phosphanediyl complex **4** (path a in Scheme 2) to the carbon–nitrogen triple bond of **2a**,**b** (path b). The formation of the five-membered heterocycles can be rationalized by two different [3+2] cycloadditions (**3a** and/or **3b**,**c** + **2a**,**b**/PhCN → **6**) (paths d and f). In order to examine the hypothetical pathways (enclosed with dotted lines in Scheme 2 and thereafter), we thermolysed pure complex **5b** under the same reaction conditions in benzonitrile and obtained **6b**, but in a significantly slower reaction (6 h and 1.5 h, respectively); this indicates preferred formation of complexes **6a**,**b** by paths d and f. Furthermore, the



Scheme 2. Thermal ring-opening of 2*H*-azaphosphirene tungsten complex **1** in toluene in the presence of dialkyl cyanamides **2a**,**b**. [W] = $W(CO)_5$; $R^1 = CH(SiMe_3)_2$; **2a**, **3b**, **6a**, **6c**: $R^2 = Me$; **2b**, **3c**, **5b**, **6b**, **6d**: $R^2_2 = CH_2(CH_2)_3CH_2$.

reaction of **1** with **2b** was studied with respect to different concentrations of **2b**. The product distribution depended strongly on the cyanamide concentration, and an increasing amount of the dialkylamino-substituted 2*H*-azaphosphirene complex **5b** was determined on reducing the cyanamide concentration to two equivalents. Using cyanamide **2b** stoichiometrically, the predominant formation of **6b** was observed (Table 1; amounts of phosphorus-containing products were determined by ^{31}P NMR spectroscopy). Interpreting

Table 1. ^{31}P NMR spectroscopically estimated amounts of **5b** and **6b,d** formed, depending on the 1-piperidino nitrile concentration.

	5b [%]	**6b** [%]	**6d** [%]
1 equiv pipCN	4	58	10
2 equiv pipCN	15	56	17
4 equiv pipCN	9	41	29
neat pipCN	3	8	66

these findings in terms of reaction mechanisms, a transient formation of the terminal phosphanediyl complex **4** seems reasonable in dilute toluene solutions. This assumption is not convincing for the case of neat cyanamide **2b**, in which a substitution-like reaction of the benzonitrile moiety of **3a** by cyanamide **2b** seems to occur (path e). A related observation was reported earlier on reactions of arylnitrile sulfides with arylnitriles, the latter having differently substituted aryl groups.[21]

Because of the similar reaction behavior of the nitrile derivatives **2a**,**b**, we wanted to shed more light on the reaction course; we therefore investigated the more sterically demanding di(isopropyl) cyanamide (**2c**) as trapping reagent. However, we observed only a very low reaction selectivity when **2c** was employed under the same reaction conditions. Unfortunately, no further information could be obtained, because subsequent work-up by column chromatography failed.

B: Syntheses of 2H-1,3,2-diazaphosphole complexes by three-component reactions

From these results, we concluded that a transient generation of nitrilium phosphane ylide complexes should be possible using a three-component methodology. Therefore, we examined the thermolysis of the 2*H*-azaphosphirene complex **1** in the presence of two equivalents of either cyanamide **2a** or **2b** in benzo- or acetonitrile, using the latter as solvents and trapping reagents. The experiments were carried out under the same reaction conditions as those in toluene and yielded 4,5-mixed-substituted 2*H*-1,3,2-diazaphosphole complexes **6a**,**b**,**e**,**f**; in each case the amount of the two main products was more than 65% of the phosphorus-containing reaction products. Besides these products, complexes **6c**,**d** were formed also, but in significantly lower amounts. The complexes **6a**,**b**,**e**,**f** were isolated in moderate to good yields by low-temperature chromatography; selected NMR data of these complexes are shown in Table 2. The reaction of **1** and **2b** in *tert*-butylnitrile furnished complex **6g** along with equal amounts of the phenyl-substituted 2*H*-1,3,2-diazaphosphole complex **6b** (together 80% of the phosphorus-containing products) and **6d** in minor amounts. Furthermore, lowering the *tert*-butylnitrile concentration by using toluene as cosolvent led to a decrease of **6g**, whereas **6b** was increased. Employing **2b** and nine equivalents of 1-adamantylnitrile yielded the 5-(1-adamantyl)-substituted complex **6h** along with equal amounts of **6b** and, in minor amounts, complex **6d**. If the cyanamides **2a**,**b** were employed as solvents *and* trapping reagents, then 4,5-bis(dimethylamino)- and 4,5-bis(1-piperidino)-substituted 2*H*-1,3,2-diazaphosphole complexes **6c**,**d** were formed as main products along with low amounts of **5a**,**b** and **6a**,**b**.

Taking into account that 4,5-diphenyl-, 4,5-dimethyl- and other 4,5-dialkyl-substituted 2*H*-1,3,2-diazaphosphole complexes were not formed (or were unstable under these conditions), then the product formation can be explained by a three-step reaction course (Scheme 3). Thermally induced ring opening of the 2*H*-azaphosphirene complex **1** generates the phenyl-substituted nitrilium phosphane ylide complex **3a**, which reacts predominantly with the cyanamides **2a**,**b** to yield, somehow, the nitrilium phosphane ylide complexes **3b**,**c**. Most probably, the 2*H*-1,3,2-diazaphosphole complexes **6a**–**h** are then formed by regioselective 1,3-dipolar cycloadditions of **3b** and/or **3c** to the different nitriles. Interestingly, only two equivalents of the cyanamides **2a**,**b** are needed to achieve selective formation of 4,5- mixed-substituted 2*H*-1,3,2-diazaphosphole complexes.

To exploit this three-component methodology synthetically, we decided to use toluene as solvent, cyanamides **2a**,**b** (twofold excess) and α-ketonitriles as trapping reagents (fourfold excess). To check this, we performed first a reaction with **1**, **2a** and ethyl cyanoformate (**2d**) at 75 °C and obtained

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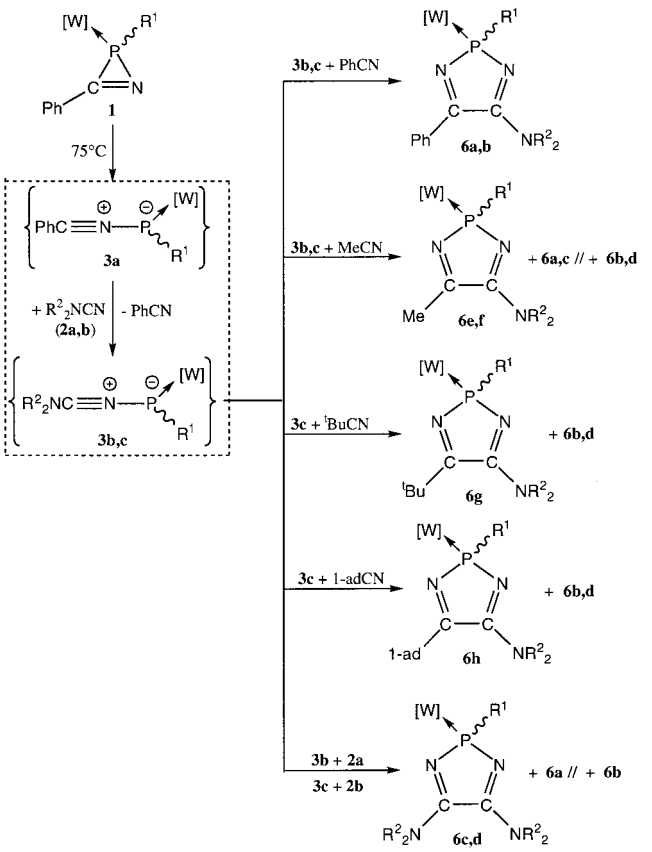
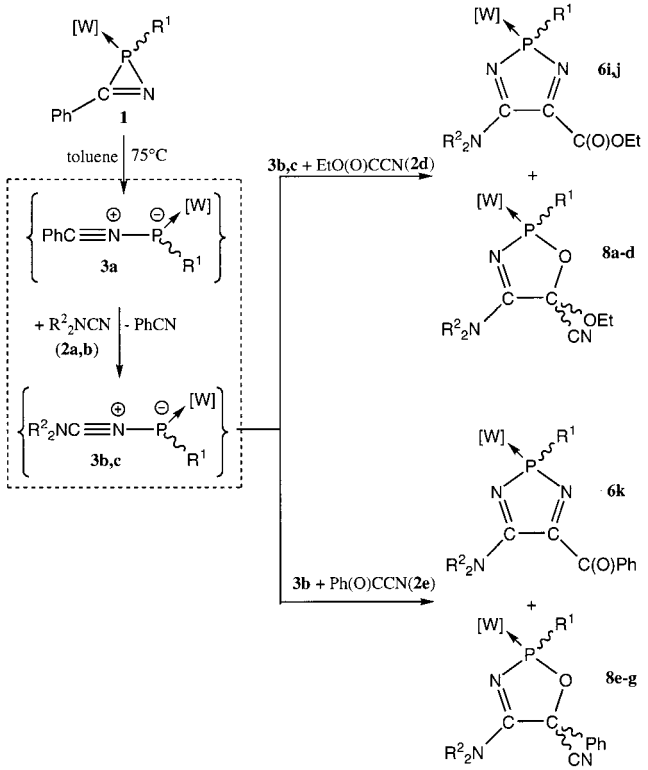


Scheme 3. Syntheses of 2*H*-1,3,2-diazaphosphole complexes **6a–n** by three-component reactions. [W] = $W(CO)_5$; $R^1 = CH(SiMe_3)_2$; 1-ad = 1-adamantyl; **2a**, **3b**, **6a**, **6c, 6e**: R^2 = Me; **2b**, **3c**, **6b**, **6d**, **6f, 6g**: $R^2_2 = CH_2(CH_2)_3CH_2$.

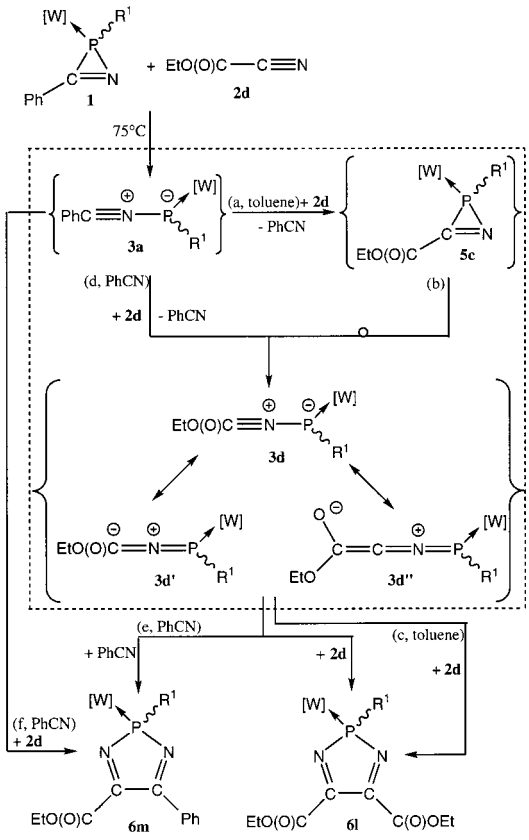


Scheme 4. Dual trapping reactions of transiently formed nitrilium phosphane ylide complexes **3b,c** by ethyl cyanoformate (**2c**) and phenyl glyoxonitrile (**2d**). [W] = $W(CO)_5$; $R^1 = CH(SiMe_3)_2$; **2a**, **3b**, **6i**, **6k, 6e, 8a**, **8b**, **8e–g**: R^2 = Me; **2b**, **3c**, **6j**, **8c**, **8d**: $R^2_2 = CH_2(CH_2)_3CH_2$.

a surprising result, because the C–O and the C–N π system of ethyl cyanoformate had reacted with the transiently formed nitrilium phosphane ylide complex **3b** to give the 2*H*-1,3,2-diazaphosphole complex **6i** and two diastereoisomeric Δ^3-1,3,2-oxazaphospholene complexes **8a,b** (product ratio of 7:1:1). An analogous reaction behavior was observed if cyanamide **2b** and ethyl cyanoformate were employed, giving the complexes **6j** and **8c,d**, although **8d** could not be isolated. Thermolysis of **1** in the presence of cyanamide **2a** and phenyl glyoxonitrile (**2e**) gave the complex **6k** and Δ^3-1,3,2-oxazaphospholene complexes **8e–g** with a product ratio of 2:4:2:1 (Scheme 4); it is probable that another isomeric Δ^3-1,3,2-oxazaphospholene complex was formed in an estimated yield of 3–5%, but could not be isolated ($\delta = 197.9$; $^1J_{(W,P)}$ could not be determined). We suggest that complexes **8e–g** have rigidly folded five-membered rings (two conformeric forms) due to steric repulsions between ring substituents. This would generate a chiral plane aside with the two chiral centers, P and C5, and therefore explain the existence of a third (and/or even a fourth) Δ^3-1,3,2-oxazaphospholene complex isomer. Apart from this, it is noteworthy that in this reaction the formation of Δ^3-1,3,2-oxazaphospholene complexes was preferred.

Whereas the Δ^3-1,3,2-oxazaphospholene complexes **8a** and **8e** were isolated in pure form, **8b** and **8f,g** were characterized only as mixtures, because complex **8b** was slightly contaminated with **8a** and complexes **8f,g** could not be separated from each other. Selected spectroscopic data of **6i–k** and **8a–g** are given in Table 3 and Table 4, respectively. Related ambident [3+2] cycloaddition behavior of α-ketonitriles towards nitrilium betaines, such as nitrile ylides,[22] is well known.

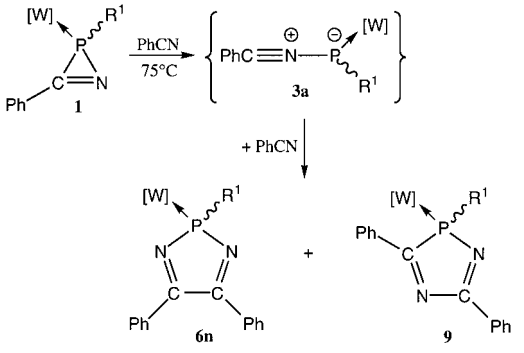
We decided to study more thoroughly the electronic influence on the reaction course of the substituent bonded at the 1,3-dipole carbon atom of the transiently formed nitrilium phosphane ylide complex. Therefore, 2*H*-azaphosphirene complex **1** was thermolysed in the presence of ethyl cyanoformate (**2d**), but *in the absence* of cyanamides **2a,b**. We carried out two different experiments, using toluene or benzonitrile as solvents, and monitored the reactions by ^{31}P NMR spectroscopy. In the first case, the exclusive formation of the symmetrically substituted 2*H*-1,3,2-diazaphosphole complex **6l** was observed, whereas in benzonitrile complex **6l** was merely the major product (67%) along with three other products (together 29%) that could not be identified (Scheme 5). The fact that the reaction course depended on the solvent led us to the following assumptions. In toluene a short-lived 2*H*-azaphosphirene complex **5c** seems plausible (path a), forming nitrilium phosphane ylide complex **3d** through ring-opening (path b) and furnishing 2*H*-1,3,2-diazaphosphole complex **6l** as final product (path c). In contrast, after **3a** is generated in benzonitrile, complex **3a** itself should be the reaction partner for ethyl cyanoformate. Although this takes place too (path f), a substitution of the benzonitrile moiety of **3a** seems more likely, thus forming mesomerically stabilized intermediate **3d** (path d). After this transylidation



Scheme 5. Thermal ring-opening of of 2*H*-azaphosphirene tungsten complex **1** in toluene or benzonitrile in the presence of ethyl cyanoformate (**2d**). [W] = $W(CO)_5$; $R^1 = CH(SiMe_3)_2$.

process, complexes **6l**,**m** are formed (path e); complex **6m** could not be isolated, but the phosphorus NMR data ($\delta =$ 175.6, $^1J_{(W,P)} = 251.8$ Hz; cf. Table 2) provide good evidence. Noteworthy is the fact that no Δ^3-1,3,2-oxazaphospholene complexes were observed under these conditions.

We also studied the thermal ring-opening of complex **1** in benzonitrile, because an intriguing question remained; why had we never observed characteristic by-products resulting from a reaction of nitrilium phosphane ylide complex **3a** with benzonitrile. We carried out the experiment under the same conditions as in the previous reactions and succeeded in synthesising the 2*H*-1,4,2-diazaphosphole tungsten complex **9** (Scheme 6). One of the by-products formed displayed a



Scheme 6. Synthesis of 2*H*-1,4,2-diazaphosphole complex **9**. [W] = $W(CO)_5$; $R^1 = CH(SiMe_3)_2$

phosphorus NMR resonance ($\delta = 165.9$, $^1J_{(W,P)} = 251.1$ Hz; cf. Table 2) that provides good evidence for the 2*H*-1,3,2-diazaphosphole tungsten complex **6n** (ratio of **9**:**6n** approximately 6:1). Complex **9** was obtained by low-temperature chromatography and crystallisation in a yield of 12%, whereas the isolation of complex **6n** failed.

Discussion

Discussion of selected spectroscopic data: Comparison of the NMR spectroscopic data of 2*H*-azaphosphirene complex **5b** to those of aryl-[1] and heteroaryl-substituted[23] 2*H*-azaphosphirene complexes reveals some noteworthy details. Apart from the low-field shifted phosphorus NMR resonances of **5a,b** (**5a** (toluene) $\delta = -70.4$, $^1J_{(W,P)} = 290.7$ Hz; **5b** (toluene) $\delta = -75.0$, $^1J_{(W,P)} = 290.7$ Hz; $\Delta\delta = 30-40$ ppm), the magnitude of the phosphorus–carbon coupling to the ring carbon atom of **5b** is markedly increased ($^{(1+2)}J_{(P,C)} = 12.5$ Hz; cf. 1–3 Hz[1] and 4.0–8.2 Hz[23]). Together with the existence of five NMR resonances for the carbon atoms of the piperidino substituent, the two methylene groups directly bonded to nitrogen have distinctly different chemical shift values ($\delta =$ 46.8 and 50.8), this finding points to a strong π-electron interaction between the lone pair at nitrogen of the piperidino substituent and the π electrons of the C–N double bond of the three-membered ring of **5b** (cf. ref. [23]). This is also manifested in the upfield shifted resonance of the carbon of the three-membered ring ($\delta = 175.4$; cf. $\delta = 180-185$).[1,23]

The 2*H*-1,3,2-diazaphosphole complexes are mainly characterized by the chemical shifts of the atoms of the five-membered ring. ^{31}P NMR resonances are found over a wide range, $\delta = 130-185$, with phosphorus-tungsten coupling constants of about 250–265 Hz. These chemical shifts correlate with the electronic influence of the substituents at C-4 and C-5 (the atom numbering refers to the used nomenclature and to the formulae in Tables 2–4), that is, dialkylamino groups induce a high-field, and ethyl carboxylate a low-field shift. ^{13}C NMR resonances observed in the range of $\delta = 155-180$ were assigned to C-4 and C-5, both having phosphorus–carbon couplings of about 1–11 Hz, which seem to be typical values for such ring systems. Furthermore, we assume that C-4, which in most cases has an amino group directly bonded, has the most constant chemical shift values and the larger magnitude of the phosphorus–carbon coupling. This interpretation is supported by the observed values for C-4 in the Δ^3-1,3,2-oxazaphospholene complexes **8a–g** (see below). Complexes **6i–k** are different, because C-4 and C-5 are more shielded and the phosphorus–carbon coupling is decreased.

The Δ^3-1,3,2-oxazaphospholene complexes **8a–g** have markedly low-field shifted ^{31}P NMR resonances ($\delta = 198-205$) and increased phosphorus–tungsten couplings (304–311 Hz) (Table 3) . This reflects the higher electronegativity of oxygen compared to nitrogen, which is a widely documented phenomenon for triorganophosphane complexes.[24] The ^{13}C NMR resonances at $\delta = 155-158$ can be attributed to C-5 and that at $\delta = 80-85$ to C-4; both types of ring atoms have phosphorus–carbon couplings of about 2–10 Hz. These

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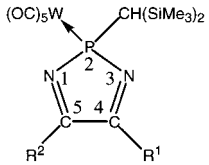
Table 2. Selected NMR data[a,b] of 2*H*-1,3,2-diazaphosphole complexes **6a–n.**

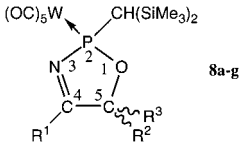


6a-n

Comp.	R^1	R^2	$\delta(^{31}P)$	$^1J(W,P)$	$\delta(^{13}C(C^4)$	$(2+3)J(P,C^4)$	$\delta(^{13}C(C^5))$	$^{(2+3)}J(P,C^5)$
6a	NMe_2	Ph	145.2	256.4	162.1	10.9	164.1	4.3
6b	1-pip	Ph	149.9	259.1	162.3	8.8	165.3	#
6c	NMe_2	NMe_2	133.2	264.7	160.7	6.4	160.7	6.4
6d	1-pip	1-pip	133.2	264.3	160.6	6.6	160.6	6.6
6e	NMe_2	Me	145.2	256.4	162.1	10.9	164.1	4.3
6f	1-pip	Me	145.1	257.4	161.9	10.3	165.1	3.9
6g	1-pip	*t*Bu	139.2	258.2	164.7	10.1	176.7	6.4
6h	1-pip	1-ad	140.7	256.9	166.1	10.7	177.3	6.7
6i	NMe_2	CO_2Et	158.3	262.1	157.8	2.5	154.8	2.1
6j	1-pip	CO_2Et	157.3	261.7	157.0	7.0	155.3	2.1
6k	NMe_2	C(O)Ph	158.2	259.2	158.6	7.0	161.5	4.9
6l	CO_2Et	CO_2Et	184.4	252.9	157.1	1.5	157.1	1.5
6m	CO_2Et	Ph	175.6	251.8	[c]	[c]	[c]	[c]
6n	Ph	Ph	165.9	251.1	[c]	[c]	[c]	[c]

[a] $CDCl_3$, δ [ppm], J [Hz]; #: not resolved. [b] Atom numbering as denoted in the formula. [c] ^{13}C NMR spectrum not recorded; 1-pip = 1-piperidino; 1-ad = 1-adamantyl.

Table 3. Selected NMR data[a,b] of Δ^3-1,3,2-oxazaphospholene complexes **8a–g**.



8a-g

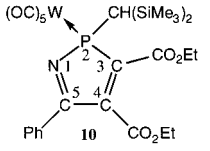
Comp.	R^1	R^2	R^3	$\delta(^{31}P)$	$^1J(W,P)$	$\delta(^{13}C(C^4))$	$^{(2+3)}J(P,C^4)$	$\delta(^{13}C(C^5))$	$^{(2+3)}J(P,C^5)$
8a	NMe_2	CN	OEt	205.4	304.8	155.9	2.0	96.3	7.7
8b	1-pip	CN	OEt	198.2	309.0	155.6	#	96.5	4.8
8c	1-pip	CN	OEt	205.5	304.8	154.6	2.0	96.2	8.0
8d	1-pip	CN	OEt	196.6	305.4	[c]	[c]	[c]	[c]
8e	NMe_2	CN	Ph	203.5	310.6	152.7	2.4	82.0	#
8f,g	NMe_2	CN	Ph	202.4	305.1	156.9	#	80.7	#
				203.0	305.5	157.0	#	82.1	#

[a] $CDCl_3$, δ [ppm], J [Hz]; #: not resolved. [b] Atom numbering as denoted in the formula. [c] ^{13}C NMR spectrum not recorded; 1-pip = 1-piperidino.

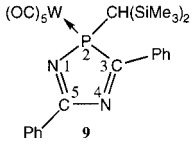
chemical shift values fit with those of related Δ^3-1,3-oxazolenes.[25] Unfortunately, further comparisons with Δ^3-1,3,2-oxaza -phospholenes or their complexes are impossible, because ^{13}C NMR data of such compounds are not available, although a report on the synthesis of Δ^3-1,3,2-oxazaphospholenes has appeared.[26] Furthermore, to the best of our knowledge complexes of such compounds were previously unknown.

Interestingly, the ^{13}C NMR resonances of complex **9** display some common features with compounds **6a** and **10**, which possess the same structural PNC(Ph) unit in the ring (Table 4). The C-3 atom of **9** has a resonance at $\delta = 198.5$,

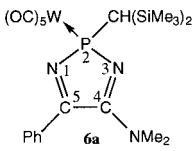
Table 4. Selected NMR data[a,b] of 2*H*-1,2-azaphosphole complex **10**,[14] 2*H*-1,4,2-diazaphosphole complex **9** and 2*H*-1,3,2-diazaphosphole complex **6a**.



10



9



6a

Comp.	$\delta(^{31}P)$	$^1J(W,P)$	$\delta(^{13}C(C^3))$	$^{(1+4)}J(P,C^3)$	$\delta(^{13}C(C^4))$	$^{(2+3)}J(P,C^4)$	$\delta(^{13}C(C^5))$	$^{(2+3)}J(P,C^5)$
10	102.8	237.9	162.7	13.1	162.0	1.4	162.0	1.4
9	110.6	227.8	198.5	22.3	-	-	169.5	5.1
6a	145.2	256.4	-	-	162.1	10.9	164.1	4.3

[a] $CDCl_3$, δ [ppm], J [Hz]. [b] Atom numbering as denoted in the formulae.

which is even more deshielded than those of carbon atoms of the 2*H*-azaphosphirene[1,23] or of the 4*H*-1,2,4-diazaphosphole ring system[27]. Probably even more surprising is the finding that the resonance of C-5 of **9**, **6a** and **10** is rather low, affected by the directly bonded X=Y ring moieties. In all of these cases, the magnitudes of the carbon – phosphorus coupling are small (J(C,P) = 1 – 5 Hz), indicating that at least two scalar couplings contribute to these values.

EI mass spectrometric experiments revealed that 2*H*-1,3,2-diazaphosphole and Δ^3-1,3,2-oxazaphospholene complexes lose carbon monoxide and show preferential fragmention of exocyclic bonds of the heterocycles subsequent to the ionisation process. This is in strong contrast with the fragmentations of 2*H*-1,4,2-diazaphosphole complex **9**, which displays additionally heterocycle fragmentations, after loss of the metal complex fragment. The latter behavior is in accord with observations made for 2*H*-1,3-diazoles[28] and 2*H*-1,4-diazoles.[29] With respect to this problem, further investigations of noncoordinated 2*H*-1,3,2-diazaphospholes and Δ^3-1,3,2-oxazaphospholenes should be undertaken, to test this indication of their higher thermodynamic stability.

Discussion of selected X-ray structural data: The molecular structures of 2*H*-1,3,2-diazaphosphole complex **6c**, 2*R*,5*S*-Δ^3-1,3,2-oxazaphospholene complex **8a** and 2*H*-1,4,2-diazaphosphole complex **9** were confirmed for the solid state by X-ray crystallography (Figures 1, 2 and 3).[30] Comparison of the most interesting structural features of the complexes **6c** and **9** reveals that they both have almost planar five-membered ring systems with mean deviations of 0.028 Å. For **9** the phenyl groups subtend interplanar angles to the five-membered ring of 4.0° (phenyl group at C1) and 7.6° (phenyl group at C7). Furthermore, both five-membered rings have localized endocyclic nitrogen – carbon double bonds of about 1.29 Å, with slightly different values for the nitrogen – carbon bonds of the unequal substituted C–N moieties of **9**. The exocyclic nitrogen – carbon distances (C6–N3 of 1.374(3) and C7–N4) of 1.364(3) Å) are significantly longer and indicate only partial double-bond character, associated with electronic interactions of the lone pairs of the nitrogen of the dimethylamino group with the π electrons of the imino bonds. Furthermore, it should be noted that the endocyclic bond angles at phosphorus of complex **6c** and **9** are significantly different (**6c:** N2-P-N1 97.20(11)°; **9**: C6-P-N1 90.2(3)°).

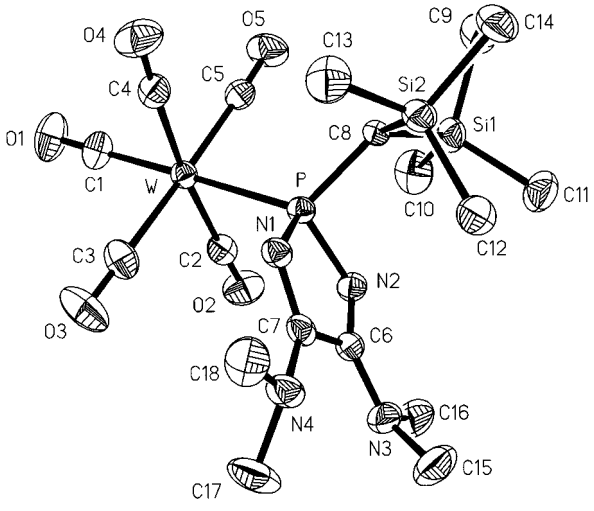


Figure 1. Molecular structure of **6c** in the crystal (ellipsoids represent 50% probability levels, hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: W – C1 2.008(3), W – P 2.4968(8), P – N1 1.707(7), P – N2 1.702(2), N1 – C7 1.296(3), N2 – C6 1.292(3), C6 – C7 1.524(2), N3 – C6 137.4(3), N4 – C7 136.4(3); W-P-C8 117.3(6), N2-P-N1 97.20(11), P-N2-C6 107.8(2), N2-C6-C7 113.6(2), C6-C7-N1 113.3(2), C7-N1-P 107.5(2).

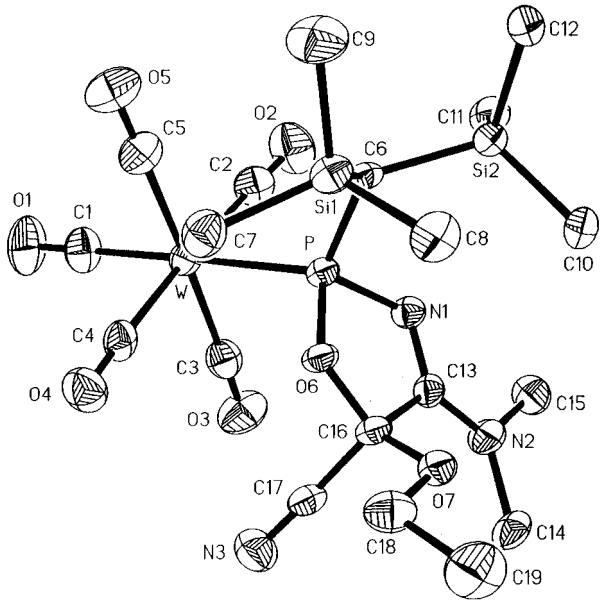


Figure 2. Molecular structure of **8a** in the crystal (ellipsoids represent 50% probability levels, hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: W – C1 2.016(7), W – P 2.463(2), P – N1 1.679(5), N1 – C13 1.293(8), C13 – C16 1.554(9), C16 – O6 1.402(7), O6 – P 1.680(4); W-P-C6 118.9(2), N1-P-O6 94.9(2), C16-O6-P 111.8(4), O6-C16-C13 105.5(5), N1-C13-C16 114.5(5).

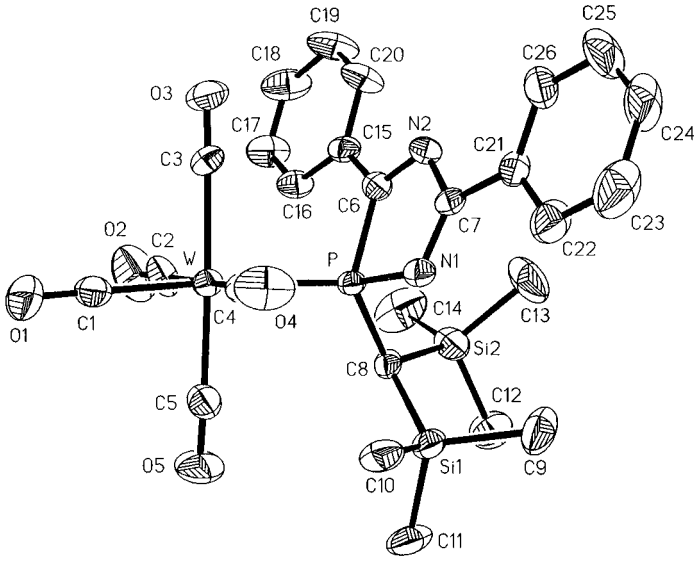


Figure 3. Molecular structure of **9** in the crystal (ellipsoids represent 50% probability levels, hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: W – C1 1.978(8), W – P 2.532(2), P – N1 1.691(6), P – C6 1.867(8), N1 – C7 1.280(7), N2 – C7 1.421(9), N2 – C6 1.302(9); W-P-C8 119.6(3), N1-P-C6 90.2(3), N2-C6-P 109.4(6), C6-N2-C7 109.3(7), N1-C7-N2 121.5(7).

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The molecular structure of the Δ^3-1,3,2-oxazaphospholene complex **8a**[30] is characterized by a slightly folded five-membered ring system; the best plane is given by P-N1-C13-C16 (deviation 0.013 Å) and the oxygen atom lies 0.21 Å out of this plane. Compared to *trans*-5-methoxy-2-methyl-4-phenyl-5-trifluoromethyl-Δ^3-1,3-oxazolene C-N-C-C (deviation 0.036 Å; O is 0.047 Å out of this plane),[5c] **8a** is more flattened. The N2–C13 distance (1.325(7) Å) of complex **8a** is in the typical range of C_{sp^2}–N_{sp^2} double bonds,[31] thus indicating a stronger electronic interaction than in **6c** and **9**. Also noteworthy is that, apart from oxygen, all distances of the atoms bonded to phosphorus are significantly shortened in the structure of **8a**, that is, the tungsten–phosphorus distances are 2.463(2) (**8a**), 2.4968(8) (**6c**) and 2.532(2) Å (**9**); this phenomenon is already documented for triorganophosphane complexes.[32] Moreover, the weakest *trans* effect on the tungsten–carbon distances of the *trans*-carbonyl ligands, among the heterocycle ligands involved in this study, is displayed by **8a** (**8a**: 2.016(7); **6c**: 2.008(3); **9**: 1.978(8) Å).

Conclusion

In all cases the thermolyses of the 2*H*-azaphosphirene tungsten complex **1**, in the presence of nitriles, using toluene and/or various nitriles as solvents, led to the formation of five-membered heterocycle complexes. These heterocycle complexes could be mostly separated by low-temperature chromatography and were fully characterized.

The formation of these heterocycles is rationalized by [3+2] cycloadditions of transiently generated nitrilium phosphane ylide complexes, acyclic isomers of 2*H*-azaphosphirene complexes, to nitriles and or ketones.

The reactions are regioselective, if nitriles with electron donor or acceptor groups, such as NMe_2 or CO_2Et, respectively, are employed. Compared to results and theoretical calculations for nitrile ylides,[33] this result is a strong argument for the assumption of transiently formed nitrilium phosphane ylide complexes as the reactive intermediates. This regioselectivity is as expected for [3+2] cycloadditions of 1,3-dipoles that are directed by a HOMO–dipole LUMO–dipolarophile interaction.[34] The favored cycloaddition product is therefore the one formed by union of the atoms with the largest coefficient of the dipole HOMO and the dipolarophile LUMO, as established for nitrile ylides.[4,33] Interestingly, the regioselectivity of nitrilium phosphane ylide complexes towards nitriles decreases and qualitatively changes if a phenyl group is bonded at the carbon atom of the 1,3-dipole skeleton. This observation is once more in accord with theoretical predictions, as made for *C*-phenyl-substituted nitrile ylides.[4,33] Nevertheless, there is also some evidence for carbene-like behavior of some nitrile ylide derivatives, as expressed through formation of [2+1] cycloaddition products.[35] Moreover, our results here could also be explained in terms of an initial [2+1] cycloaddition giving 2*H*-azirene[6] or oxirane derivatives, respectively, with subsequent ring enlargement.[6] This alternative has to be taken into account, particularly for the case of *C*-dialkylamino-substituted nitrilium phosphane ylide complexes, which are, at least formally, related to bis(dialkylamino)carbenes,[36] and will be the subject of further investigations.

One special feature of transiently formed nitrilium phosphane ylide complexes seems to be the ease of N–P bond making and breaking, thus facilitating transylidation processes. This depends strongly on the electron donor/acceptor ability of the substituent at the carbon atom of the 1,3-dipole skeleton and this finding is best expressed by the selectivity of the three-component reactions.

Another special feature of transiently formed nitrilium phosphane ylide complexes seems to be the lower reactivity towards sterically demanding trapping reagents. This can easily be understood in terms of the sterical demand of the two bulky groups attached to phosphorus and of the trapping reagent, which together should disfavor cycloadditions, because of increased steric repulsions in the transition state.

Experimental Section

General Procedures: All reactions and manipulations were carried out under an atmosphere of deoxygenated dry nitrogen, using standard Schlenk techniques with conventional glassware, and solvents were dried according to standard procedures. NMR spectra were recorded on a Bruker AC-200 spectrometer (200 MHz for ^{1}H; 50.3 MHz for ^{13}C; 81.0 MHz for ^{31}P) using [D]chloroform and [D_6]benzene as solvent and internal standard; shifts are given relative to external tetramethylsilane (^{1}H, ^{13}C) and 85% H_3PO_4 (^{31}P). Mass spectra were recorded on a Finigan Mat 8430 (70 eV); apart from *m/z* values of the molecule ions, only *m/z* values are given that have intensities of more than 20%. Infrared spectra were recorded on a Biorad FT-IR 165 (selected data given). Melting points were obtained on a Büchi 535 capillary apparatus. Elemental analyses were performed using a Carlo Erba analytical gaschromatograph. The κP notation in the used nomenclature shall serve for differentiation between P and N coordination of the appropriate heterocycle to the metal.

{Pentacarbonyl[bis(trimethylsilyl)methyl-3-(1-piperidino)-2*H*-1,2-azaphosphirene-κP]tungsten(0)} (**5b**): 2*H*-azaphosphirene tungsten complex **1** (1.2 g, 2 mmol) was dissolved in toluene (6 mL) and 1-piperidino nitrile ($(CH_2)_5NCN$) (**2b**) (0.4 mL, 4 mmol) and heated at 75 °C for 1.5 h with slow stirring. Afterwards, the solvent was removed in vacuo and the product separated by low-temperature chromatography (–20 °C, 15 × 2 cm, hexane/diethyl ether 95/5). Evaporation of the solvents of the second fraction yielded **5b** as a pale yellow oil (160 mg, 13%). ^{1}H NMR ($CDCl_3$) $\delta = 0.17$ (s, 9H; $SiMe_3$), 0.28 (s, 9H; $SiMe_3$), 0.70 (d, ^2J(P,H) = 2.8 Hz, 1H; C*H*), 1.50–1.87 (m, 6H; $NCH_2CH_2CH_2$), 3.28–3.63 (m, 2H; $NCH_2CH_2CH_2$), 3.65–3.85 (m, 2H; $NCH_2CH_2CH_2$). ^{13}C{^{1}H} NMR (C_6D_6) $\delta = 1.2$ (d, ^3J(P,C) = 2.9 Hz; $SiMe_3$), 2.2 (d, ^3J(P,C) = 3.6 Hz; $SiMe_3$), 24.0 (s, $NCH_2CH_2CH_2$), 25.1 (s, $NCH_2CH_2CH_2$), 25.9 (s, $NCH_2CH_2CH_2$), 30.4 (d, ^1J(P,C) = 26.9 Hz; *C*H), 46.8 (s, $NCH_2CH_2CH_2$), 50.8 (s, $NCH_2CH_2CH_2$), 175.4 (d, $^{(1+2)}J$(P,C) = 12.5 Hz; P*C*N), 197.0 (d, ^2J(P,C) = 9.1 Hz, ^1J(C,W) = 126.1 Hz; *cis*-*C*O), 198.9 (d, ^2J(P,C) = 34.0 Hz; *trans*-*C*O). ^{31}P{^{1}H} NMR ($CDCl_3$) $\delta = -70.3$ (s, ^1J(P,W) = 292.9 Hz); (C_6D_6) $\delta = -74.7$ (d, ^1J(P,W) = 291.8 Hz). IR (neat) $\tilde{\nu} = 2072$ (s), 1984 (s), 1923 (br s) cm^{-1} (CO); 1653 (m), 1650 (w), 1608 (w) cm^{-1} (C=N). MS (70 eV, EI), (^{184}W); *m/z* (%) 624 (20) [$M^{+\cdot}$], 486 (100) [$(OC)_4WPCH(SiMe_3)_2^{+\cdot}$], 458 (40) [$(OC)_3WPCH(SiMe_3)_2^{+\cdot}$], 430 (30) [$(OC)_2WPCH(SiMe_3)_2^{+\cdot}$], 384 (30) [$(OC)_3WPCSiMe_3)^{+\cdot}$], 73 (50) [$(SiMe_3)^+$]. HR EI MS: calcd. for $C_{18}H_{29}NO_5PSi_2W$ 624.0861; found 624.0861 ± 2.

General procedure for the synthesis of 2*H*-1,3,2-diazaphosphole complexes (6a–g): 2*H*-azaphosphirene tungsten complex **1** (0.6 g, 1 mmol) was dissolved in nitrile (3 mL of MeCN, PhCN, *t*BuCN, Me_2NCN or $(CH_2)_5NCN$) and dialkyl cyanamide (0.2 mL, 2 mmol of Me_2NCN or $(CH_2)_5NCN$)). After heating the solution at 75 °C for 1.5 h with slow stirring, the solution was evaporated to dryness. Low-temperature chromatography of the residues (SiO_2, 15 × 2 cm, hexane/diethyl ether 97.5/2.5) afforded the complexes **6a–g**, which were crystallized from pentane at –20 °C.

{Pentacarbonyl[2-bis(trimethylsilyl)methyl-4-phenyl-5-dimethylamino-2-*H*-1,3,2-diazaphosphole-κ*P*]tungsten(0)} (**6a**): Yield: 447 mg, 67%. M.p. 90 °C (decomp). ^{1}H NMR ($CDCl_3$) $\delta = 0.18$ (s, 9H; $SiMe_3$), 0.24 (s, 9H; $SiMe_3$), 1.40 (d, $^2J(P,H) = 7.0$ Hz, 1H; C*H*), 2.90 (s, 6H; NMe_2), 7.46 (m_c, 3H; $CH_{aromatic}$), 7.64 (m_c, 2H; $CH_{aromatic}$). ^{13}C{^{1}H} NMR ($CDCl_3$) $\delta = 2.6$ (d, $^3J(P,C) = 1.9$ Hz; $SiMe_3$), 2.7 (d, $^3J(P,C) = 2.4$ Hz; $SiMe_3$), 24.0 (d, $^1J(P,C) = 1.6$ Hz; *C*H), 41.4 (s, NMe_2), 128.0 (s, *C*$H_{aromatic}$), 128.8 (s, *C*$H_{aromatic}$), 130.4 (s, *C*$H_{aromatic}$), 136.1 (d, $^3J(P,C) = 22.1$ Hz, *C*$_{aromatic}$), 162.4 (d, $^{(2+3)}J(P,C) = 9.4$ Hz; *C*^{4}), 165.0 (d, $^{(2+3)}J(P,C) = 2.5$ Hz; *C*^{5}), 197.3 (d, $^2J(P,C) = 8.5$ Hz, $^1J(C,W) = 126.6$ Hz; *cis*-*C*O), 200.6 (d, $^2J(P,C) = 24.1$ Hz; *trans*-*C*O). ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta = 149.8$ (s, $^1J(P,W) = 257.1$ Hz). IR (KBr): $\tilde{\nu} = 2071$ (s), 1983 (s), 1946 (vs), 1923 (vs), 1912 (vs) cm^{-1} (CO); 1585 (w), 1571 (w), 1562 (w), 1535 (m) cm^{-1} (C=N). MS (70 eV, EI), (^{184}W): *m/z* (%): 687 (16) [$M^{+\bullet}$], 631 (50) [$(M-2CO)^{+\bullet}$], 547 (100) [$(M-5CO)^{+\bullet}$], 73 (25) [$(SiMe_3)^+$]. $C_{22}H_{30}N_3O_5PSi_2W$ (687.5) calcd. C 38.42, H 4.40, N 6.11; found C 38.35, H 4.45, N 5.95.

{Pentacarbonyl[2-bis(trimethylsilyl)methyl-4-phenyl-5-(1-piperidino)-2*H*-1,3,2-diazaphosphole-κ*P*]tungsten(0)} (**6b**): Yield 445 mg, 63%. M.p. 124 °C (decomp). ^{1}H NMR ($CDCl_3$) $\delta = 0.16$ (s, 9H; $SiMe_3$), 0.24 (s, 9H; $SiMe_3$), 1.40 (d, $^2J(P,H) = 6.9$ Hz, 1H; C*H*), 1.58 (br s, 6H; $NCH_2CH_2CH_2$), 3.33 (m_c, 4H; $NCH_2CH_2CH_2$), 7.47 (m_c, 3H; $CH_{aromatic}$), 7.72 (m_c, 2H; $CH_{aromatic}$). ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 2.5$ (d, $^3J(P,C) = 2.6$ Hz; $SiMe_3$), 2.7 (d, $^3J(P,C) = 2.7$ Hz; $SiMe_3$), 24.0 (d, $^1J(P,C) = 5.6$ Hz; *C*H), 24.1 (s, $NCH_2CH_2CH_2$), 25.3 (s, $NCH_2CH_2CH_2$), 50.2 (s, $NCH_2CH_2CH_2$), 127.9 (s, *C*$H_{aromatic}$), 128.7 (s, *C*$H_{aromatic}$), 130.6 (s, *C*$H_{aromatic}$), 135.9 (d, $^3J(P,C) = 22.4$ Hz, *C*$_{aromatic}$), 162.3 (d, $^{(2+3)}J(P,C) = 8.8$ Hz; *C*^{4}), 165.3 (s, *C*^{5}), 197.3 (d, $^2J(P,C) = 7.5$ Hz; *cis*-*C*O), 200.5 (d, $^2J(P,C) = 23.6$ Hz; *trans*-*C*O). ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta = 149.9$ (s, $^1J(P,W) = 259.1$ Hz). IR (KBr): $\tilde{\nu} = 2069$ (s), 1985 (s), 1951 (vs), 1910 (vs) cm^{-1} (CO); 1561 (vw), 1541 (w), 1534 (w), 1530 (w) cm^{-1} (C=N). MS (70 eV, EI), (^{184}W): *m/z* (%): 727 (20) [$M^{+\bullet}$], 671 (45) [$(M-2CO)^{+\bullet}$], 587 (100) [$(M-5CO)^{+\bullet}$], 73 (25) [$(SiMe_3)^+$]. HR EI MS: calcd. for $C_{25}H_{34}N_3O_5PSi_2W$ 727.1285; found 727.1285 ± 2.

{Pentacarbonyl[2-bis(trimethylsilyl)methyl-4,5-bis(dimethylamino)-2*H*-1,3,2-diazaphosphole-κ*P*]tungsten(0)} (**6c**): Yield 197 mg, 31%. M.p. 96 °C (decomp). ^{1}H NMR ($CDCl_3$): $\delta = 0.18$ (s, 18H; $SiMe_3$), 1.27 (d, $^2J(P,H) = 6.2$ Hz, 1H; C*H*), 3.02 (s, 12H; NMe_2). ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 2.6$ (s, $SiMe_3$), 25.6 (d, $^1J(P,C) = 2.2$ Hz; *C*H), 40.5 (s, NMe_2), 160.7 (d, $^{(2+3)}J(P,C) = 6.4$ Hz; *C*^{4,5}), 197.9 (d, $^2J(P,C) = 8.5$ Hz; *cis*-*C*O), 201.5 (d, $^2J(P,C) = 24.1$ Hz; *trans*-*C*O). ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta = 133.2$ (s, $^1J(P,W) = 264.7$ Hz). IR (KBr): $\tilde{\nu} = 2067$ (vs), 1977 (vs), 1928 (vs, sh), 1911 (vs) cm^{-1} (CO); 1581 (s), 1562 (vs) cm^{-1} (C=N). MS (70 eV, EI), (^{184}W): *m/z* (%): 654 (30) [$M^{+\bullet}$], 626 (30) [$(M-CO)^{+\bullet}$], 570 (35) [$(M-3CO)^{+\bullet}$], 542 (50) [$(M-4CO)^{+\bullet}$], 514 (100) [$(M-5CO)^{+\bullet}$], 499 (35) [$(M-5CO-CH_3)^+$]. $C_{18}H_{31}N_4O_5PSi_2W$ (645.1) calcd. C 33.03, H 4.77, N 8.56; found C 33.06, H 4.71, N 8.52.

{Pentacarbonyl[2-bis(trimethylsilyl)methyl-4,5-bis(1-piperidino))-2*H*-1,3,2-diazaphosphole-κ*P*]tungsten(0)} (**6d**): Yield 393 mg, 55%. M.p. 124 °C (decomp). ^{1}H NMR ($CDCl_3$) $\delta = 0.19$ (s, 18H; $SiMe_3$), 1.27 (d, $^2J(P,H) = 6.3$ Hz, 1H; C*H*), 1.65 (br s, 12H; $NCH_2CH_2CH_2$), 3.44 (br s, 8H; $NCH_2CH_2CH_2$). ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 2.6$ (s, $SiMe_3$), 2.7 (s, $SiMe_3$), 24.2 (s, $NCH_2CH_2CH_2$), 25.4 (s, $NCH_2CH_2CH_2$), 25.5 (d, $^1J(P,C) = 3.2$ Hz; *C*H), 49.7 (s, $NCH_2CH_2CH_2$), 160.6 (d, $^{(2+3)}J(P,C) = 6.0$ Hz; *C*^{4,5}), 197.8 (d, $^2J(P,C) = 8.0$ Hz; *cis*-*C*O), 201.4 (d, $^2J(P,C) = 23.4$ Hz; *trans*-*C*O). ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta = 133.2$ (s, $^1J(P,W) = 264.3$ Hz). IR (KBr): $\tilde{\nu} = 2069$ (s), 1982 (s), 1944 (vs), 1909 (vs, sh) cm^{-1} (CO); 1570 (w), 1561 (w), 1542 (s) cm^{-1} (C=N). MS (70 eV, EI), (^{184}W): *m/z* (%): 734 (20) [$M^{+\bullet}$], 706 (20) [$(M-CO)^{+\bullet}$], 650 (20) [$(M-2CO)^{+\bullet}$], 622 (75) [$(M-4CO)^{+\bullet}$], 594 (100) [$(M-5CO)^{+\bullet}$]. $C_{24}H_{39}N_4O_5PSi_2W$ (734.6) calcd. C 39.24, H 5.31, N 7.63; found C 39.75, H 5.33, N 7.33.

{Pentacarbonyl[2-bis(trimethylsilyl)methyl-4-methyl-5-dimethylamino-2*H*-1,3,2-diazaphosphole-κ*P*]tungsten(0)} (**6e**): Yield 200 mg, 33%. M.p. 88 °C (decomp). ^{1}H NMR ($CDCl_3$): $\delta = 0.17$ (s, 9H; $SiMe_3$), 0.19 (s, 9H; $SiMe_3$), 1.26 (d, $^2J(P,H) = 7.2$ Hz, 1H; C*H*), 2.65 (d, $^4J(P,H) = 0.6$ Hz, 3H; C*H*$_3$), 3.23 (s, 6H; NMe_2). ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 2.5$ (d, $^3J(P,C) = 2.1$ Hz; $SiMe_3$), 2.6 (d, $^3J(P,C) = 2.0$ Hz; $SiMe_3$), 23.5 (d, $^3J(P,C) = 22.2$ Hz; *C*H$_3$), 24.1 (d, $^1J(P,C) = 2.7$ Hz; *C*H), 40.9 (s, NMe_2), 162.1 (d, $^{(2+3)}J(P,C) = 10.9$ Hz; *C*^{4}), 164.1 (d, $^{(2+3)}J(P,C) = 4.3$ Hz; *C*^{5}), 197.4 (d, $^2J(P,C) = 7.9$ Hz; *cis*-*C*O), 200.8 (d, $^2J(P,C) = 23.4$ Hz; *trans*-*C*O). ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta = 145.2$ (s, $^1J(P,W) = 256.4$ Hz). IR (KBr): $\tilde{\nu} = 2067$ (s), 1973 (s), 1940 (vs, sh), 1913 (vs) cm^{-1} (CO); 1601 (vw), 1561 (br m) cm^{-1} (C=N). MS (70 eV, EI), (^{184}W): *m/z* (%): 625 (40) [$M^{+\bullet}$], 569 (60) [$(M-2CO)^{+\bullet}$], 513 (40) [$(M-4CO)^{+\bullet}$], 485 (100) [$(M-5CO)^{+\bullet}$]. $C_{17}H_{28}N_3O_5PSi_2W$ (625.1) calcd. C 32.64, H 4.48, N 6.72; found C 32.71, H 4.62, N 6.65. HR EI MS: calcd. for $C_{17}H_{28}N_3O_5PSi_2W$ 625.0814, found 625.0814 ± 3.

{Pentacarbonyl-[2-bis(trimethylsilyl)methyl-4-methyl-5-(1-piperidino)-2*H*-1,3,2-diazaphosphole-κ*P*]tungsten(0)} (**6f**): Yield 517 mg, 80%. M.p. 97 °C (decomp). ^{1}H NMR ($CDCl_3$): $\delta = 0.18$ (s, 9H; $SiMe_3$), 0.19 (s, 9H; $SiMe_3$), 1.27 (d, $^2J(P,H) = 7.2$ Hz, 1H; C*H*), 1.68 (br s, 6H; $NCH_2CH_2CH_2$), 2.60 (d, $^4J(P,H) = 0.8$ Hz, 3H; C*H*$_3$), 2.66 (m_c, 4H; $NCH_2CH_2CH_2$). ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 2.5$ (d, $^3J(P,C) = 3.4$ Hz; $SiMe_3$), 2.6 (d, $^3J(P,C) = 2.9$ Hz; $SiMe_3$), 22.9 (d, $^3J(P,C) = 22.4$ Hz; *C*H$_3$), 23.8 (d, $^1J(P,C) = 2.3$ Hz; *C*H), 24.4 (s, $NCH_2CH_2CH_2$), 25.8 (s, $NCH_2CH_2CH_2$), 49.4 (s, $NCH_2CH_2CH_2$), 161.9 (d, $^{(2+3)}J(P,C) = 10.3$ Hz; *C*^{4}), 165.1 (d, $^{(2+3)}J(P,C) = 3.9$ Hz; *C*^{5}), 198.6 (d, $^2J(P,C) = 7.5$ Hz, $^1J(P,W) = 126.6$ Hz; *cis*-*C*O), 200.7 (d, $^2J(P,C) = 23.5$ Hz; *trans*-*C*O). ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta = 145.1$ (s, $^1J(P,W) = 257.4$ Hz). IR (KBr): $\tilde{\nu} = 2066$ (s), 1987 (s), 1947 (vs), 1937 (vs), 1926 (vs), 1914 (vs) cm^{-1} (CO); 1578 (w), 1545 (m) cm^{-1} (C=N). MS (70 eV, EI), (^{184}W): *m/z* (%): 665 (25) [$M^{+\bullet}$], 609 (60) [$(M-2CO)^{+\bullet}$], 579 (45) [$(M-2CO-C_2H_4)^+$], 553 (35) [$(M-4CO)^{+\bullet}$ or $(M-CO-C_5H_{10}N)^+$], 525 (100) [$(M-2CO-C_5H_{10}N)^+$ or $(M-5CO)^{+\bullet}$], 499 (25) [$(M-2CO-C_6H_{10}N_2)^{+\bullet}$], 73 (35) [$(SiMe_3)^+$]. $C_{20}H_{22}N_3O_5PSi_2W$ (665.4) calcd. C 36.09, H 4.81, N 6.31; found C 36.25, H 4.95, N 6.25.

{Pentacarbonyl[2-bis(trimethylsilyl)methyl-4-*tert*-butyl-5-(1-piperidino)-2*H*-1,3,2-diazaphosphole-κ*P*]tungsten(0)} (**6g**): Yield 247 mg, 36%. M.p. 91 °C (decomp). ^{1}H NMR ($CDCl_3$): $\delta = 0.17$ (s, 9H; $SiMe_3$), 0.23 (s, 9H; $SiMe_3$), 1.30 (d, $^2J(P,H) = 7.8$ Hz, 1H; C*H*), 1.44 (s, 9H; *tert*-Bu), 1.67 (br s, 6H; $NCH_2CH_2CH_2$), 3.44 (br s, 4H; $NCH_2CH_2CH_2$). ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 2.6$ (d, $^3J(P,C) = 2.1$ Hz; $SiMe_3$), 2.7 (d, $^3J(P,C) = 1.8$ Hz; $SiMe_3$), 23.2 (d, $^1J(P,C) = 3.6$ Hz; *C*H), 24.1 (s, $NCH_2CH_2CH_2$), 25.4 (s, $NCH_2CH_2CH_2$), 29.9 (s, *C*$H_{tert\text{-}Bu}$), 38.6 (d, $^3J(P,C) = 19.2$ Hz; *C*Me_3), 51.6 (s, $NCH_2CH_2CH_2$), 164.7 (d, $^{(2+3)}J(P,C) = 10.1$ Hz; *C*^{5}), 176.7 (d, $^{(2+3)}J(P,C) = 6.4$ Hz; *C*^{4}), 197.3 (d, $^2J(P,C) = 7.7$ Hz, $^1J(P,W) = 126.4$ Hz; *cis*-CO), 200.5 (d, $^2J(P,C) = 23.2$ Hz; *trans*-*CO*). ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta = 139.2$ (s, $^1J(P,W) = 258.2$ Hz). IR (KBr): $\tilde{\nu} = 2068$ (s), 1977 (s), 1948 (vs, sh), 1927 (vs), 1912 (vs) cm^{-1} (CO); 1560 (vw), 1542 (vw), 1520 (s) cm^{-1} (C=N). MS (70 eV, EI), (^{184}W): *m/z* (%): 707 (25) [$M^{+\bullet}$], 567 (35) [$(M-5CO)^{+\bullet}$], 541 (100) [$(M-2CO-C_6H_{10}N_2)^{+\bullet}$], 457 (25) [$(M-5CO-C_6H_{10}N_2)^{+\bullet}$], 73 (35) [$(SiMe_3)^+$]. HR EI MS: calcd. for $C_{23}H_{38}N_3O_5PSi_2W$ 707.1597, found 707.1597 ± 3.

{Pentacarbonyl[2-bis(trimethylsilyl)methyl-4-(1-adamantyl)-5-(1-piperidino)-2*H*-1,3,2-diazaphosphole-κ*P*]tungsten(0)} (**6h**): 2*H*-azaphosphirene tungsten complex **1** (0.6 g, 1 mmol) and 1-adamantyl nitrile (1.5 g, 9.3 mmol) were dissolved in toluene (3 mL) and $(CH_2)_5NCN$ (**2b**) (0.2 mL, 2 mmol) and heated at 75 °C for 1.5 h with slow stirring. Afterwards, the product was separated by low temperature chromatography (−50 °C, 10 × 2 cm, hexane). Evaporation of the solvents of the second fraction and crystallisation from pentane at −20 °C yielded **6h** as pale yellow crystals (91 mg, 12%). M.p. 162 °C (decomp). ^{1}H NMR ($CDCl_3$): $\delta = 0.18$ (s, 9H; $SiMe_3$), 0.23 (s, 9H; $SiMe_3$), 1.29 (d, $^2J(P,H) = 7.9$ Hz, 1H; C*H*), 1.67 (m_c, 6H; $NCH_2CH_2CH_2$), 1.76 (br s, 9H; CCH_2CHCH_2), 2.05–2.20 (m, 9H; CCH_2CHCH_2), 3.30–3.50 (m, 4H; $NCH_2CH_2CH_2$). ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 2.6$ (d, $^3J(P,C) = 2.0$ Hz; $SiMe_3$), 2.7 (d, $^3J(P,C) = 2.0$ Hz; $SiMe_3$), 23.0 (d, $^1J(P,C) = 3.3$ Hz; *C*H), 24.1 (s, $NCH_2CH_2CH_2$), 25.3 (s, $NCH_2CH_2CH_2$), 28.5 (s, CCH_2CHCH_2), 36.6 (s, CCH_2CHCH_2), 40.6 (s, CCH_2CHCH_2), 41.6 (d, $^3J(P,C) = 18.7$ Hz; *C*CH_2CHCH_2)), 52.1 (s, $NCH_2CH_2CH_2$), 166.1 (d, $^{(2+3)}J(P,C) = 10.7$ Hz; *C*^{5}), 177.3 (d, $^{(2+3)}J(P,C) = 6.7$ Hz; *C*^{4}), 197.3 (d, $^2J(P,C) = 7.4$ Hz; *cis*-*CO*), 200.4 (d, $^2J(P,C) = 23.6$ Hz; *trans*-*CO*). ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta = 140.7$ (s, $^1J(P,W) = 256.9$ Hz). IR (KBr): $\tilde{\nu} = 2069$ (s), 1980 (s), 1946 (vs), 1917 (vs) cm^{-1} (CO); 1561 (vw), 1536 (vw), 1509 (m, sh) cm^{-1} (C=N). MS (70 eV), (^{184}W): *m/z* (%): 785 (20) [M$^{+\bullet}$], 645 (30) [$(M-5CO)^{+\bullet}$], 619 (100) [$(M-2CO-C_6H_{10}N_2)^+$], 535 (30) [$(M-5CO-C_7H_{10}N_2)^+$], 135 (20) [$(C_{10}H_{15})^+$], 73 (35) [$(SiMe_3)^+$]. $C_{28}H_{44}N_3O_5PSi_2W$ (785.4) calcd. C 44.33, H 5.61, N 5.35; found C 44.00, H 5.65, N 5.46.

General procedure for the synthesis of 2*H*-1,3,2-diazaphosphole complexes 6h–j and Δ^3-1,3,2-oxazaphospholene complexes 8a–g: To a solution of 2*H*-azaphosphirene tungsten complex **1** (0.6 g, 1 mmol) in toluene (3 mL), ethyl cyanoformate (0.4 mL, 4 mmol) or phenyl glyoxonitrile (0.4 mL, 4 mmol) and nitrile **2a** (0.2 mL, 2 mmol) or nitrile **2b** (0.2 mL, 2 mmol) were added, and the solution was heated at 75 °C for 1.5 h with slow stirring. After evaporation to dryness, the products were separated and purified by

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low-temperature chromatography of the residues (hexane/diethyl ether 97.5/2.5) and afterwards crystallised from pentane at −20 °C.

{Pentacarbonyl[2-bis(trimethylsilyl)methyl-4-ethoxycarbonyl-5-dimethylamino-2*H*-1,3,2-diazaphosphole-κ*P*]tungsten(0)} (**6i**): Yield 220 mg, 33 %. M.p. 64 °C (decomp). ^{1}H NMR ($CDCl_3$): $\delta = 0.16$ (s, 9H; $SiMe_3$), 0.23 (s, 9H; $SiMe_3$), 1.34 (d, ^2J(P,H) = 6.6 Hz, 1H; C*H*), 1.37 (t, ^3J(H,H) = 7.1 Hz, 3H; CH_2CH_3), 3.17 (s, 6H; NMe_2), 4.43 (q, ^3J(H,H) = 7.1 Hz, 2H; CH_2CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 2.4$ (d, ^3J(P,C) = 2.6 Hz; $SiMe_3$), 2.5 (d, ^3J(P,C) = 2.6 Hz; $SiMe_3$), 13.8 (s, CH_2CH_3), 24.6 (s, C*H*), 39.7 (s, NMe_2), 62.9 (s, CH_2CH_3), 154.8 (d, $^{(2+3)}J$(P,C) = 2.1 Hz; C^4), 157.8 (d, $^{(2+3)}J$(P,C) = 2.5 Hz; C^5), 165.4 (d, ^3J(P,C) = 28.8 Hz; CO_2R), 196.8 (d, ^2J(P,C) = 7.6 Hz, ^1J(C,W) = 126.6 Hz; *cis*-C*O*), 200.1 (d, ^2J(P,C) = 24.5 Hz; *trans*-C*O*). ^{31}P{^{1}H}NMR ($CDCl_3$): $\delta = 158.3$ (s, ^1J(P,W) = 262.1 Hz). IR (KBr): $\tilde{\nu}$ = 2071 (s), 1982 (s), 1936 (vs, sh), 1899 (vs) cm^{-1} (CO), 1744 (s) cm^{-1} (C(O)OEt); 1608 (m), 1577 (vw), 1571 (w), 1561 (w) cm^{-1} (C=N). MS (70 eV, EI), (^{184}W): *m/z* (%): 683 (20) [$M^{+\bullet}$], 627 (85) [$(M-2CO)^{+\bullet}$], 543 (100) [$(M-5CO)^{+\bullet}$], 515 (80) [$(M-5CO-C_2H_4)^{+\bullet}$], 73 (40) [$(SiMe_3)^+$], 43 (55) [$(SiMe)^+$]. $C_{19}H_{30}N_3O_7PSi_2W$ (683.5) calcd. C 33.39, H 4.42, N 6.15; found C 33.28, H 4.34, N 5.77.

{Pentacarbonyl[2-bis(trimethylsilyl)methyl-5-cyano-5-ethoxy-4-dimethylamino-Δ^3-1,3,2-oxazaphospholene-κ*P*]tungsten(0)} (**8a**,**b**):

8a: Yield 73 mg, 11 %. M.p. 181 °C (decomp). ^{1}H NMR ($CDCl_3$): $\delta = 0.19$ (s, 9H; $SiMe_3$), 0.34 (s, 9H; $SiMe_3$), 1.31 (t, ^3J(H,H) = 7.0 Hz, 3H; CH_2CH_3), 1.50 (br s, 1H; C*H*), 3.19 (br s, 3H; NMe_2), 3.26 (br s, 3H; NMe_2), 4.0 (m_c, 2H; CH_2CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 2.1$ (d, ^3J(P,C) = 3.0 Hz; $SiMe_3$), 2.3 (d, ^3J(P,C) = 1.3 Hz; $SiMe_3$), 14.4 (s, CH_3), 37.0 (s, C*H*), 38.4 (s, NMe_2), 40.1 (s, NMe_2), 63.5 (s, CH_2), 96.3 (d, $^{(2+3)}J$(P,C) = 7.7 Hz; C^5), 113.8 (d, ^3J(P,C) = 3.2 Hz; C*N*), 155.9 (d, $^{(2+3)}J$(P,C) = 2.0 Hz; C^4), 196.8 (d, ^2J(P,C) = 8.6 Hz, ^1J(P,W) = 126.9 Hz; *cis*-C*O*), 200.5 (d, ^2J(P,C) = 29.7 Hz; *trans*-C*O*). ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta = 205.4$ (s, ^1J(P,W) = 304.8 Hz). MS (70 eV, EI), (^{184}W): *m/z* (%): 683 (60) [$M^{+\bullet}$], 599 (35) [$(M-3CO)^{+\bullet}$], 571 (60) [$(M-4CO)^{+\bullet}$], 543 (60) [$(M-5CO)^{+\bullet}$], 514 (100) [$(M-5CO-C_2H_5)^+$], 73 (55) [$(SiMe_3)^+$], 43 (35) [$(SiMe)^+$].

8b: Obtained as a 1:1 mixture with **8a.** M.p. 116 °C (decomp). ^{1}H NMR ($CDCl_3$): $\delta = 0.19$ (s, 9H; $SiMe_3$), 0.29 (s, 9H; $SiMe_3$), 1.31 (t, ^3J(H,H) = 7.0 Hz, 3H; CH_2CH_3), 1.51 (br s, 1H; C*H*), 3.19 (br s, 6H; NMe_2), 4.0 (m_c, 2H; CH_2CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 2.1$ (s, $SiMe_3$), 2.5 (d, ^3J(P,C) = 1.8 Hz; $SiMe_3$), 14.4 (s, CH_2CH_3), 37.9 (s, C*H*), 38.3 (s, NMe_2), 40.3 (s, NMe_2), 63.5 (s, CH_2CH_3), 96.5 (d, $^{(2+3)}J$(P,C) = 4.8 Hz; C^5), 112.9 (d, ^3J(P,C) = 9.3 Hz; C*N*), 155.6 (s, C^4), 196.7 (d, ^2J(P,C) = 8.3 Hz; *cis*-C*O*), 200.5 (d, ^2J(P,C) = 29.7 Hz; *trans*-C*O*). ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta = 198.2$ (s, ^1J(P,W) = 309.0 Hz). IR (KBr): $\tilde{\nu}$ = 2073 (s, sh), 1986 (s, sh), 1950 (vs), 1929 (vs), 1917 (vs) cm^{-1} (CO); 1628 (w) cm^{-1} (C=N). MS (70 eV, EI), (^{184}W): *m/z* (%): 683 (50) [$M^{+\bullet}$], 599 (30) [$(M-3CO)^{+\bullet}$], 571 (45) [$(M-4CO)^{+\bullet}$], 543 (50) [$(M-5CO)^{+\bullet}$], 514 (100) [$(M-5CO-C_2H_5)^+$], 73 (55) [$(SiMe_3)^+$], 43 (45) [$(SiMe)^+$].

{Pentacarbonyl[2-bis(trimethylsilyl)methyl-4-ethoxycarbonyl-5-(1-piperidino)-2*H*-1,3,2-diazaphosphole-κ*P*]tungsten(0)} (**6j**): Yield 379 mg, 54 %. M.p. 124 °C (decomp). ^{1}H NMR ($CDCl_3$): $\delta = 0.18$ (s, 9H; $SiMe_3$), 0.23 (s, 9H; $SiMe_3$), 1.35 (d, ^2J(P,H) = 6.7 Hz, 1H; C*H*), 1.37 (t, ^3J(H,H) = 7.1 Hz, 3H; CH_2CH_3), 1.66 (br s, 6H; $NCH_2CH_2CH_2$), 3.57 (br s, 4H; $NCH_2CH_2CH_2$), 4.41 (dq, ^3J(H,H) = 7.1, ^5J(P,H) = 1.3 Hz, 2H; CH_2CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 2.4$ (d, ^3J(P,C) = 2.3 Hz; $SiMe_3$), 2.5 (d, ^3J(P,C) = 2.4 Hz; $SiMe_3$), 13.9 (s, CH_2CH_3), 24.3 (s, $NCH_2CH_2CH_2$), 24.5 (s, C*H*), 25.8 (s, $NCH_2CH_2CH_2$), 49.0 (s, $NCH_2CH_2CH_2$), 62.8 (s, OCH_2CH_3), 155.3 (d, $^{(2+3)}J$(P,C) = 2.1 Hz; C^4), 157.0 (d, $^{(2+3)}J$(P,C) = 7.0 Hz; C^5), 165.3 (d, ^3J(P,C) = 29.0 Hz; CO_2), 196.8 (d, ^2J(P,C) = 7.7 Hz; *cis*-C*O*), 200.1 (d, ^2J(P,C) = 24.7 Hz; *trans*-CO). ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 157.5 (s, ^1J(P,W) = 261.7 Hz). IR (KBr): $\tilde{\nu}$ = 2071 (s), 1993 (s), 1954 (vs), 1932 (vs), 1903 (vs) cm^{-1} (CO); 1750 (m) cm^{-1} (C(O)OEt); 1603 (w), 1562 (w) cm^{-1} (C=N). MS (70 eV, EI), (^{184}W): *m/z* (%): 723 (20) [$M^{+\bullet}$], 667 (100) [$(M-2CO)^{+\bullet}$], 583 (95) [$(M-5CO)^{+\bullet}$ or $(M-2CO-C_5H_{10}N)^+$], 555 (90) [$M-3CO-C_5H_{10}N)^+$], 73 (30) [$(SiMe_3)^+$]. $C_{22}H_{34}N_3O_7PSi_2W$ (723.5) calcd. C 36.51, H 4.70, N 5.81; found C 36.68, H 4.77, N 5.76.

{Pentacarbonyl[2-bis(trimethylsilyl)methyl-5-cyano-5-ethoxy-4-(1-piperidino)-Δ^3-1,3,2-oxazaphospholene-κ*P*]tungsten(0)} (**8c**): Only one diastereoisomer isolated. Yield 35 mg, 5 %. M.p. 131 °C. ^{1}H NMR ($CDCl_3$): δ = 0.18 (s, 9H; $SiMe_3$), 0.34 (s, 9H; $SiMe_3$), 1.30 (t, ^3J(H,H) = 7.0 Hz, 3H; CH_2CH_3), 1.49 (s, 1H; C*H*), 1.67 (br s, 6H; $NCH_2CH_2CH_3$), 3.53 (br m_c, 2H; $NCH_2CH_2CH_3$), 3.68 (br m_c, 2H; $NCH_2CH_2CH_3$), 3.96 (2 × ddq, ^5J(P,H) and ^2J(H,H) not determined, ^3J(H,H) = 7.0 Hz, 2H; CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 2.1$ (d, ^3J(P,C) = 3.1 Hz; $SiMe_3$), 2.3 (d, ^3J(P,C) = 1.7 Hz; $SiMe_3$), 14.4 (s, CH_2CH_3), 24.2 (s, $NCH_2CH_2CH_3$), 25.1 (s, $NCH_2CH_2CH_3$), 26.0 (s, $NCH_2CH_2CH_3$), 36.9 (br s, C*H*), 48.4 (s, $NCH_2CH_2CH_3$), 48.6 (s, $NCH_2CH_2CH_3$), 63.3 (s, OCH_2CH_3), 96.2 (d, $^{(2+3)}J$(P,C) = 8.0 Hz; C^5), 113.9 (d, ^3J(P,C) = 4.3 Hz; C*N*), 154.6 (d, $^{(2+3)}J$(P,C) = 2.0 Hz; C^5), 196.8 (d, ^2J(P,C) = 8.6 Hz, ^1J(C,W) = 126.5 Hz; *cis*-C*O*), 200.6 (d, ^2J(P,C) = 29.3 Hz; *trans*-C*O*). ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta = 205.0$ (s, ^1J(P,W) = 304.8 Hz). IR (KBr): $\tilde{\nu}$ = 2072 (s), 1982 (s), 1954 (vs), 1937 (vs), 1919 (vs) cm^{-1} (CO); 1606 (s), 1603 (w) cm^{-1} (C=N). MS (70 eV, EI), (^{184}W): *m/z* (%): 723 (20) [$M^{+\bullet}$], 639 (20) [$(M-3CO)^{+\bullet}$ or $(M-C_5H_{10}N)^+$], 611 (55) [$(M-4CO)^{+\bullet}$ or $(M-CO-C_5H_{10}N)^+$], 583 (80) [$(M-5CO)^{+\bullet}$ or $(M-2CO-C_5H_{10}N)^+$], 555 (100) [$(M-C_5H_{10}N-3CO)^+$], 84 (25) [$(C_5H_{10}N)^+$], 73 (60) [$SiMe_3)^+$]. $C_{22}H_{34}N_3O_7PSi_2W$ (723.5) calcd. C 36.51, H 4.70, N 5.81; found C 36.60, H 4.77, N 5.75.

{Pentacarbonyl[2-bis(trimethylsilyl)methyl-4-benzoyl-5-dimethylamino-2*H*-1,3,2-diazaphosphole-κ*P*]tungsten(0)} (**6k**): Yield 125 mg, 18 %. M.p. 123 °C (decomp). ^{1}H NMR ($CDCl_3$): $\delta = 0.21$ (s, 18H; $SiMe_3$), 1.42 (d, ^2J(P,H) = 7.1 Hz, 1H; C*H*), 3.09 (br s, 6H; NMe_2), 7.53 (m_c, 2H; $CH_{aromatic}$), 7.67 (m_c, 1H; $CH_{aromatic}$), 8.04 (m_c, 2H; $CH_{aromatic}$). ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 2.4$ (d, ^3J(P,C) = 2.2 Hz; $SiMe_3$), 2.7 (d, ^3J(P,C) = 2.0 Hz; $SiMe_3$), 24.9 (s, C*H*), 40.5 (s, NMe_2), 129.1 (s, $CH_{aromatic}$), 130.1 (s, $CH_{aromatic}$), 134.1 (s, $C_{aromatic}$), 135.2 (s, $CH_{aromatic}$), 158.6 (d, $^{(2+3)}J$(P,C) = 7.0 Hz; C^4), 161.5 (d, $^{(2+3)}J$(P,C) = 4.9 Hz; C^5), 192.6 (d, ^3J(P,C) = 24.2 Hz; C(O)Ph), 197.1 (d, ^2J(P,C) = 7.1 Hz; *cis*-C*O*), 200.0 (d, ^2J(P,C) = 23.9 Hz; *trans*-C*O*). ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta = 158.2$ (s, ^1J(P,W) = 259.2 Hz). IR (KBr): $\tilde{\nu}$ = 2072 (s), 1988 (s), 1943 (vs), 1922 (vs) cm^{-1} (CO); 1678 (s), 1599 (s) cm^{-1} (C(O)Ph); 1567 (m), 1561 (m) cm^{-1} (C=N). MS (70 eV, EI), (^{184}W): *m/z* (%): 715 (10) [$M^{+\bullet}$], 687 (20) [$(M-CO)^{+\bullet}$], 659 (100) [$(M-2CO)^{+\bullet}$], 603 (25) [$(M-4CO)^{+\bullet}$], 575 (85) [$(M-5CO)^{+\bullet}$], 73 (35) [$(SiMe_3)^+$]. $C_{23}H_{30}N_3O_6PSi_2W$ (715.5) calcd. C 38.60, H 4.19, N 5.87; found C 38.55, H 4.24, N 5.78.

{Pentacarbonyl[2-bis(trimethylsilyl)methyl-5-cyano-5-phenyl-4-dimethylamino-Δ^3-1,3,2-oxazaphospholene-κ*P*]tungsten(0)} (**8e–g**):

8e: Yield 285 mg, 41 %. M.p. 132 °C (decomp). ^{1}H NMR ($CDCl_3$): $\delta = 0.26$ (s, 9H; $SiMe_3$), 0.35 (s, 9H; $SiMe_3$), 1.59 (d, ^2J(P,H) = 0.9 Hz, 1H; C*H*), 2.94 (br s, 3H; NMe_2), 3.32 (br s, 3H; NMe_2), 7.48 (m_c, 5H, $CH_{aromatic}$). ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 2.2$ (d, ^3J(P,C) = 3.1 Hz; $SiMe_3$), 2.3 (d, ^3J(P,C) = 1.2 Hz; $SiMe_3$), 39.8 (m_c; NMe_2), 40.4 (d, ^1J(P,C) = 6.5 Hz; C*H*), 82.0 (s, C^5), 116.4 (s, C*N*), 126.7 (s, $CH_{aromatic}$), 129.7 (s, $CH_{aromatic}$), 130.9 (s, $CH_{aromatic}$), 133.6 (d, ^3J(P,C) = 3.6 Hz; $C_{aromatic}$), 157.7 (d, ^{2+3}J(P,C) = 2.4 Hz; C^4), 197.0 (d, ^2J(P,C) = 8.6 Hz, ^1J(C,W) = 126.5 Hz; *cis*-C*O*), 200.2 (d, ^2J(P,C) = 29.5 Hz; *trans*-C*O*). ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta = 203.5$ (s, ^1J(P,W) = 310.6 Hz). IR (KBr): $\tilde{\nu}$ = 2072 (s), 1986 (s), 1954 (vs), 1912.4 (vs, sh) cm^{-1} (CO); 1618 (s) cm^{-1} (C=N). MS (70 eV, EI), (^{184}W): *m/z* (%): 715 (25) [$M^{+\bullet}$], 603 (100) [$(M-4CO)^{+\bullet}$], 575 (50) [$(M-5CO)^{+\bullet}$], 73 (50) [$(SiMe_3)^+$]. $C_{23}H_{30}N_3O_6PSi_2W$ (715.5) calcd. C 38.60, H 4.19, N 5.87; C 38.92, H 4.27, N 5.69.

8f,g: Obtained as an approximately 1:1 mixture. M.p. 128 °C (decomp). ^{1}H NMR ($CDCl_3$): $\delta = -0.06$ (s, 9H; $SiMe_3$), −0.05 (s, 9H; $SiMe_3$), 0.25 (s, 9H; $SiMe_3$), 0.32 (s, 9H; $SiMe_3$), 1.19 (d, ^2J(P,H) = 3.9 Hz, 1H; C*H*), 1.64 (d, ^2J(P,H) = 1.8 Hz, 1H; C*H*), 2.90 (br s, 6H; NMe_2), 3.30 (br s, 6H; NMe_2), 7.49 (br s, 10H; $CH_{aromatic}$). ^{13}C{^{1}H} NMR ($CDCl_3$) $\delta = 1.9$ (d, ^3J(P,C) = 2.7 Hz; $SiMe_3$), 2.2 (d, ^3J(P,C) = 2.8 Hz; $SiMe_3$), 2.6 (d, ^3J(P,C) = 2.4 Hz; $SiMe_3$), 3.1 (d, ^3J(P,C) = 1.1 Hz; $SiMe_3$), 38.6 (d, ^1J(P,C) = 6.1 Hz; C*H*), 39.8 (m_c; NMe_2), 40.3 (d, ^1J(P,C) = 26.3 Hz; C*H*), 80.7 (s, C^5), 82.1 (s, C^5), 115.7 (s, C*N*), 115.8 (s, C*N*), 126.7 (s, $CH_{aromatic}$), 127.3 (s, CH_{aromat}), 129.5 (s, CH_{aromat}), 129.8 (s, CH_{aromat}), 130.8 (s, CH_{aromat}), 133.9 (s, C_{aromat}), 135.0 (s, CH_{aromat}), 156.9 (s, C^4), 157.0 (s, C^4), 196.7 (d, ^2J(P,C) = 8.4 Hz; *cis*-C*O*), 197.0 (d, ^2J(P,C) = 8.3 Hz; *cis*-C*O*), 199.3 (d, ^2J(P,C) = 28.8 Hz; *trans*-C*O*), 200.6 (d, ^2J(P,C) = 28.7 Hz; *trans*-C*O*). ^{31}P{^{1}H} NMR ($CDCl_3$) $\delta = 202.4$ (s, ^1J(P,W) = 305.1 Hz), 203.0 (s, ^1J(P,W) = 305.3 Hz). MS (70 eV, EI), (^{184}W): *m/z* (%): 715 (20) [$M^{+\cdot}$], 603 (100) [$(M-4CO)^{+\cdot}$], 575 (25) [$(M-5CO)^{+\cdot}$], 73 (25) [$(SiMe_3)^+$]. $C_{23}H_{30}N_3O_6PSi_2W$ (715.5) calcd. C 38.60, H 4.19, N 5.87; C 38.48, H 4.31, N 5.79.

{Pentacarbonyl[2-bis(trimethylsilyl)methyl-4,5-bis(ethoxycarbonyl)-2*H*-1,3,2-diazaphosphole-κ*P*]tungsten(0)} (**6l**): A solution of 2*H*-azaphosphirene tungsten complex **1** (0.6 g, 1 mmol) in toluene (3 mL) and ethylcyano formate (0.4 mL, 4 mmol) was heated at 75 °C for 1.5 h with slow stirring. Afterwards, the solvent and the trapping reagent were removed in vacuo and the product separated by low-temperature chromatography of the residue (Al_2O_3, −50 °C, 10 × 2 cm, pentane/diethyl ether 90:10) of the

residue. Crystallisation from pentane at $-20\,^{\circ}C$ afforded **6l** as dark red crystals (90 mg, 26%). M.p. 84 °C (decomp). ^1H NMR (C_6D_6): $\delta = 0.21$ (s, 18H; $SiMe_3$), 0.88 (t, $^3J(H,H) = 7.1$ Hz, 6H; CH_2CH_3), 1.47 (d, $^2J(P,H) = 8.0$ Hz, 1H; C*H*), 3.96 (q, $^3J(H,H) = 7.1$, 4H; CH_2CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 2.3$ (s, $SiMe_3$), 2.4 (s, $SiMe_3$), 13.6 (s, CH_2CH_3), 21.4 (s, *C*H), 63.0 (s, OCH_2), 157.1 (d, $^{(2+3)}J(P,C) = 1.5$ Hz; $C^{4,5}$), 161.9 (d, $^3J(P,C) = 27.5$ Hz; CO_2), 195.7 (d, $^2J(PC) = 7.7$ Hz, $^1J(C,W) = 121.0$ Hz; *cis*-CO), 197.8 (d, $^2J(P,C) = 25.2$ Hz; *trans*-CO). $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = 184.4$ (s, $^1J(P,W) = 252.9$ Hz). IR (KBr): $\tilde{\nu} = 2076$ (s), 1996 (s), 1960 (vs), 1902 (vs), 1880 (s) cm^{-1} (CO); 1742 (s), 1724 (s) cm^{-1} (C(O)OEt); 1607 (w), 1534 (w) cm^{-1} (C=N). MS, (^{184}W): *m/z* (%): (NH_3, pos.-CI) 713 (100) [$(M+H)^+$], 685 (20) [$(M + H - CO)^+$]; (NH_3, neg.-CI) 711 (20) [$(M-H)^-$], 552 (100) [$(M - CH(SiMe_3)_2)^-$], 324 (30) [$W(CO)_5^-$]. $C_{20}H_{29}N_2O_9PSi_2W$ (712.2) calcd. C 33.71, H 4.16, N 3.93; found C 33.73, H 4.16, N 3.92.

{Pentacarbonyl[2-bis(trimethylsilyl)methyl-3,5-diphenyl-2*H*-1,4,2-diazaphosphole-κP]tungsten(0)} (**9**): 2*H*-azaphosphirene tungsten complex **1** (0.6 g, 1 mmol) was dissolved in benzonitrile (3 mL) and heated at 75 °C for 45 min with slow stirring. The product was separated and purified by low-temperature chromatography of the residue ($-40\,^{\circ}C$, 25×2 cm, hexane/diethyl ether 97.5/2.5). Crystallisation from pentane at $-20\,^{\circ}C$ afforded **9** as orange crystals (84 mg, 12%). M.p. 92 °C (decomp). ^1H NMR ($CDCl_3$): $\delta = -0.11$ (s, 9H; $SiMe_3$), 0.55 (s, 9H; $SiMe_3$), 1.20 (d, $^2J(P,H) = 4.2$ Hz, 1H; C*H*), 7.56 (m_c, 6H; $CH_{aromatic}$), 8.27 (m_c, 2H; $CH_{aromatic}$), 8.53 (m_c, 2H; $CH_{aromatic}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 2.9$ (d, $^3J(P,C) = 2.2$ Hz; $SiMe_3$), 3.7 (d, $^3J(P,C) = 3.1$ Hz; $SiMe_3$), 18.6 (d, $^1J(P,C) = 4.5$ Hz; *C*H), 128.8 (s, $CH_{aromatic}$), 128.9 (s, $CH_{aromatic}$), 130.7 (s, $CH_{aromatic}$), 131.4 (d, $^3J(P,C) = 2.0$ Hz; $CH_{aromatic}$), 132.4 (s, $CH_{aromatic}$), 132.5 (d, $^3J(P,C) = 23.3$ Hz; $C_{aromatic}$), 133.4 (d, $^2J(P,C) = 12.5$ Hz; $C_{aromatic}$), 133.6 (s, $CH_{aromatic}$), 169.5 (d, $^{(2+3)}J(P,C) = 5.1$ Hz; C^5), 197.2 (d, $^2J(P,C) = 6.0$ Hz, $^1J(C,W) = 126.8$ Hz; *cis*-CO), 198.5 (d, $^2J(P,C) = 22.3$ Hz; *trans*-CO), 202.3 (d, $^{(1+4)}J(P,C) = 22.9$ Hz; C^3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 110.6$ (s, $^1J(P,W) = 227.9$ Hz). IR (KBr): $\tilde{\nu} = 2073$ (s), 2065 (s), 2001 (s), 1987 (s), 1937 (vs, sh), 1922 (vs) cm^{-1} (CO); 1552 (vw) cm^{-1} (C=N). MS (70 eV, EI), (^{184}W): *m/z* (%): 720 (10) [$M^{+\bullet}$], 664 (100) [$(M - 2CO)^{+\bullet}$], 580 (25) [$(M - 5CO)^{+\bullet}$], 477 (35) [$(M - 5CO - C_7H_5N)^{+\bullet}$], 461 (35), 293 (25) [$(M - W(CO)_5{-}C_7H_5N)^{+\bullet}$], 190 (20) [$(C_7H_{19}PSi_2)^{+\bullet}$], 176 (55) [$(C_6H_{17}PSi_2)^{+\bullet}$], 73 (95) [$(SiMe_3)^+$]. $C_{26}H_{29}N_2O_5PSi_2W$ (720.3) calcd. C 43.33, H 4.03, N 3.83; found C 41.65, H 4.62, N 3.11.

Solution and refinement of structures 6c, 8a and 9: Crystal data for all structures are presented in Table 5. *Structure determination of* **6c:** A cut yellow block was mounted in inert oil and measured by ω scans using $Mo_{K\alpha}$ radiation (graphite monochromator) on a Siemens P4 diffractometer. After absorption correction (θ scans) all unique data were used for calculations (program SHELXL-93[37]). The structure was solved by heavy-atom method and refined anisotropically by full matrix least squares on F^2. All methyl groups were refined as rigid groups, H8 with a riding model. *Structure determinations of* **8a** and **9**: A cut pale yellow prism (**8a**) or an orange tablet (**9**) was mounted in inert oil and measured by ω/Θ scans by using $Mo_{K\alpha}$ radiation (graphite monochromator) on a Stoe STADI-4 diffractometer. After absorption correction (θ scans) all unique data were used for calculations (program SHELXL-93[37]). The structures were solved by direct methods (**8a**) or heavy atom methods (**9**) and refined anisotropically by full matrix least squares on F^2. All hydrogen atoms (except rigid methyl groups) were refined with a riding model.

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Table 5. Crystal data and structure refinement of **6c**, **8a,** and **9**.

	6c	**8a**	**9**
empirical formula	$C_{18}H_{31}N_4O_5PSi_2W$	$C_{19}H_{30}N_3O_7PSi_2W$	$C_{26}H_{29}N_2O_5PSi_2W$
formula weight [g mol^{-1}]	654.47	683.46	720.51
temperature [K]	173	143	143
wavelength [pm]	0.71073	0.71073	0.71073
crystal system	monoclinic	monoclinic	triclinic
space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a [Å]	11.550(2)	14.029(3)	10.738(4)
b [Å]	14.504(2)	12.113(3)	12.301(5)
c [Å]	16.811(2)	17.062(4)	13.193(5)
α	90	90	96.80(3)
β	103.20(2)	108.68(3)	105.57(3)
γ	90	90	110.90(3)
volume, Z [Å^3]	2741.6(7), 4	2746.5(11), 4	1523.3(10), 2
density (calculated) [Mg m^{-3}]	1.586	1.653	1.571
absorption coefficient [mm^{-1}]	4.391	4.392	3.958
F(000)	1296	1352	712
crystal dimensions [mm^3]	$0.70 \times 0.40 \times 0.30$	$0.30 \times 0.25 \times 0.20$	$0.70 \times 0.40 \times 0.15$
θ range for data collection	3 to 25	3 to 25	3 to 25
limiting indices (*h*/*k*/*l*)	−13/0, −17/7, −19/19	0/16, 0/14, -20/19	−12/12, −14/5, −15/15
reflections collected	10277	5062	7977
independent reflections	6593 [$R_{int} = 0.0214$]	4853 [$R_{int} = 0.0289$]	5378 [$R_{int} = 0.0572$]
max. und min. transmission	0.974 and 0.655	0.785 and 0.667	0.980 and 0.730
data/restraints/parameters	6593/110/290	4853/139/307	5378/181/340
final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0228$, $wR2 = 0.0389$	$R1 = 0.0378$, $wR2 = 0.0697$	$R1 = 0.0481$, $wR2 = 0.0909$
R indices (all data)	$R1 = 0.0391$, $wR2 = 0.0412$	$R1 = 0.0545$, $wR2 = 0.0783$	$R1 = 0.0688$, $wR2 = 0.1014$
largest diff. peak and hole [e Å^{-3}]	0.386 and −0.393	0.808 and −0.536	1.108 and −0.752

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