# Synthesis of the First 2*H*-1,2-Azaphosphole Complexes with P,C and P,N Ylide Functional Groups

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*Dedicated to Professor Wolfgang W. Schoeller on the occasion of his 60th birthday*

**Keywords:** Ylides / Phosphorus heterocycles / Tungsten / Cyclization

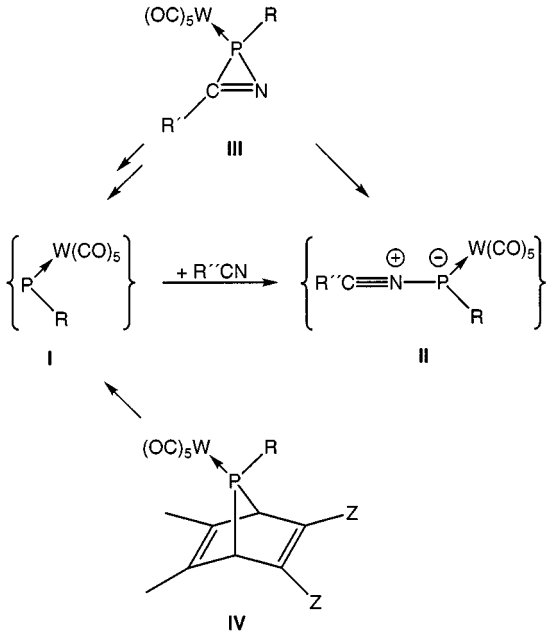
The first $C^5$-functionalized 2*H*-1,2-azaphosphole complexes have been obtained by the reactions of P,C and P,N ylide substituted carbonitriles and terminal phosphanediyl complexes involving transiently formed nitrilium phosphanylide complexes.



## Introduction

The transition metal promoted synthesis of P-heterocycles is of current interest because of the frequently observed outstanding reaction selectivities and product yields.[1] Recently, we presented a new concept in phosphorus heterocycle synthesis, which relies on the use of short-lived 1,3-dipole species that are stabilized through metal coordination, viz. nitrilium phosphanylide complexes **II**.[2] Complexes **II** may be formed by 1,1-addition of thermally generated terminal phosphanediyl complexes **I**[2,3] to carbonitriles, which is a weakly exothermic reaction according to theoretical calculations,[4] or by ring-opening of 2*H*-azaphosphirene complexes **III** (Scheme 1).[2,4] To date, the 1,1-addition of terminal phosphanediyl complexes **I** to carbonitriles has been demonstrated using two different precursor systems for **I**, namely 2*H*-azaphosphirene complexes **III**[2] and 7-phosphanorbornadiene complexes **IV**.[3,5] The former is especially useful for the transient formation of bulky *P*-substituted derivatives of **I** having a bis(trimethylsilyl)methyl (**1a**) or pentamethylcyclopentadienyl group (**1b**) attached to the phosphorus atom, whereas the latter can be employed to generate derivatives of **I** with small and/or functional substituents at the phosphorus atom.

Only two different intramolecular trapping reactions of transient nitrilium phosphanylide complexes **II** have hitherto been observed, which were shown to be very sensitive to the substituent at the phosphorus atom. For example, complex **2a** isomerized to the 2*H*-azaphosphirene complex **4a**[6] while complex **3** led to the C,N,P cage complex **5**[7] through an intramolecular [2+1] cycloaddition of the phosphanediyl phosphorus center of **3** to the Cp* π-system (Scheme 2).




Scheme 1. Generation of terminal phosphanediyltungsten complexes **I** and (nitrilium phosphanylide)tungsten complexes **II** using precursors **III** and **IV**

Furthermore, we showed that *C*-dialkylamino-, *C*-alkyl-, or *C*-aryl-substituted nitrilium phosphanylide complexes **II** reacted with electron-deficient alkynes such as dimethylacetylene dicarboxylate (DMAD) to furnish 2*H*-1,2-azaphosphole complexes through [3+2]-cycloaddition reactions.[2,8,9] It is noteworthy that only complex **2b**, which has

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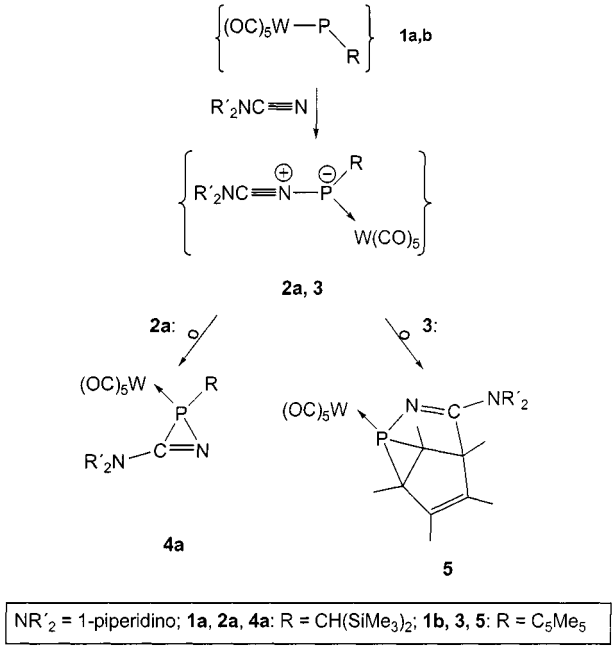
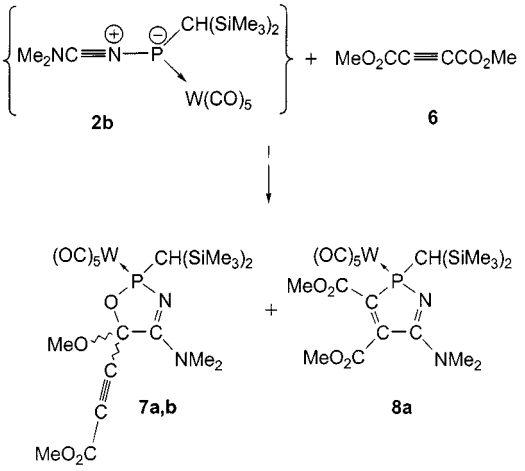



Scheme 2. Generation and intramolecular reactions of (nitrilium phosphanylide)tungsten complexes **2a** and **3**

the dimethylamino group at the carbon atom and a bulky substituent at the phosphorus atom, reacted with DMAD (**6**) to give both the $\Delta^3$-1,3,2-oxazaphospholene complexes **7a**,**b** and the 2*H*-1,2-azaphosphole complex **8a** (Scheme 3).[10]

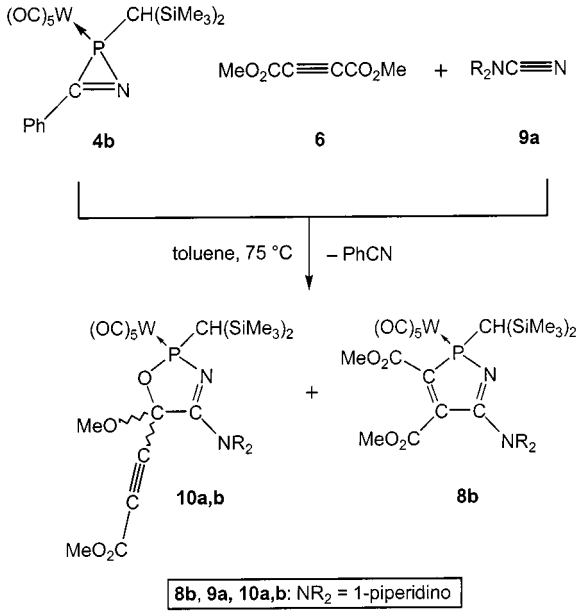



Scheme 3. Reaction modes of transiently formed (nitrilium phosphanylide)tungsten complex **2b** towards DMAD

We report herein on a comparative study of the stereoelectronic effects of various strong π-donor *C*-substituents of transiently formed [nitrilium bis(trimethylsilyl)methylphosphanylide]tungsten complexes **II** on ring-closure reactions of **II** to **III** (e.g. **1a** → **3**) and on the reactivity of **II** towards electronically activated alkynes. In view of the known electronic stabilizing effect of P,C ylide substituents in low-coordinated phosphorus compounds such as thioxophosphanes or selenoxophosphanes of the formula RPX [R = $Ph_3PC(R')$; X = S, Se[11]] we decided to include $Ph_3PC(H)CN$[12] and $Ph_3PNCN$[13] in this study, the latter for comparison purposes. Furthermore, we have also sought an optimized synthesis of 2*H*-1,2-azaphosphole complexes, whereby such systems can be obtained bearing new P,C and P,N ylide functional groups. The first results concerning new three-component reactions are reported herein.

## Results and Discussion

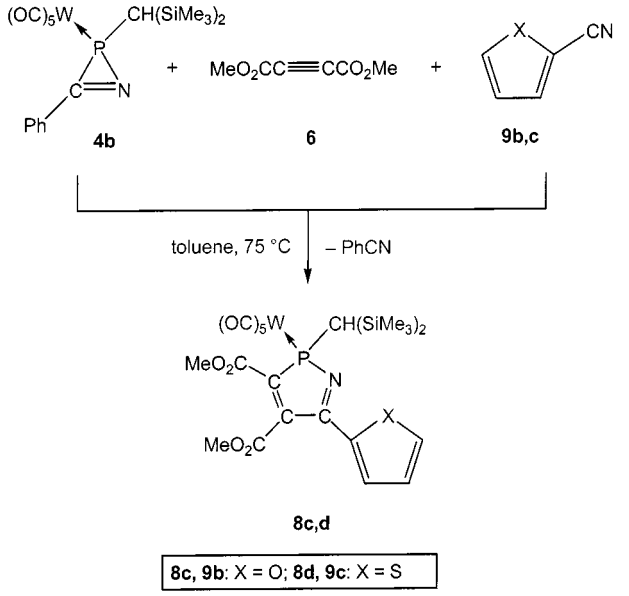
Thermal reaction of the (2*H*-azaphosphirene)tungsten complex **4b**[14] with piperidinocarbonitrile (**9a**) and DMAD (**6**) furnished the $\Delta^3$-1,3,2-oxazaphospholene complexes **10a**,**b** and the 2*H*-1,2-azaphosphole complex **8b** in a 1:1:1 ratio as the phosphorus-containing products. Although only complexes **10a** and **8b** could be isolated by column chromatography, complex **10b** was readily identified by its $^{31}P$ NMR spectroscopic data (δ = 191.8, $^1J_{W,P}$ = 305.7 Hz) (Scheme 4).



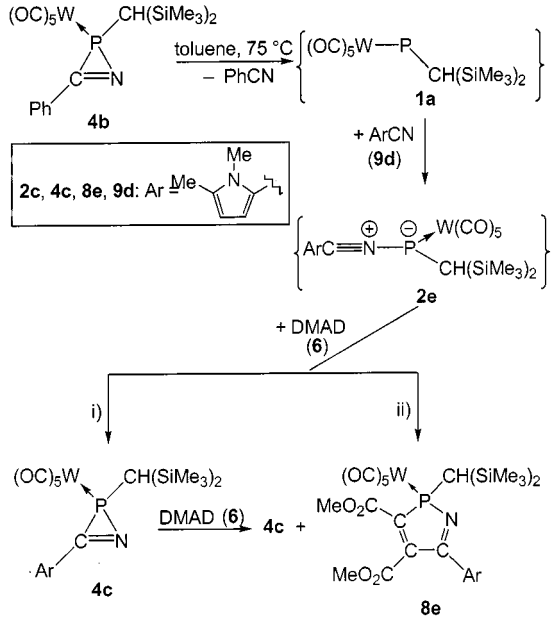

Scheme 4. Three-component reaction of 2*H*-azaphosphirene complex **4b** with DMAD and 1-piperidinocarbonitrile (**9a**)

Very selective reactions were observed with **4b**, 2-furylcarbonitrile (**9b**) or 2-thienylcarbonitrile (**9c**), and **6**. In this case, we obtained exclusively the 2*H*-1,2-azaphosphole complexes **8c**,**d** and no side-reactions leading to $\Delta^3$-1,3,2-oxazaphospholene complexes were observed; complexes **8c**,**d** were isolated and fully characterized (Scheme 5).

To our surprise, reaction of the 2*H*-azaphosphirene complex **4b** (1 equiv.) with the pyrrolyl-substituted carbonitrile **9d** (2 equiv.) and DMAD (2 equiv.) led exclusively to the 2*H*-azaphosphirene complex **4c** (**i**). Even more surprising was that we had to change the ratio of 2*H*-azaphosphirene complex **4b**/pyrrolyl-substituted carbonitrile **9d**/DMAD to 1:4:2 in order to obtain the 2*H*-azaphosphirene complex **4c** and the 2*H*-1,2-azaphosphole complex **8e** in a 1:10 ratio (**ii**) (Scheme 6). This finding was completely counterintuitive. It was also very remarkable that a 2*H*-azaphosphirene complex was formed in a three-component reaction with DMAD; this had not been observed previously. This points



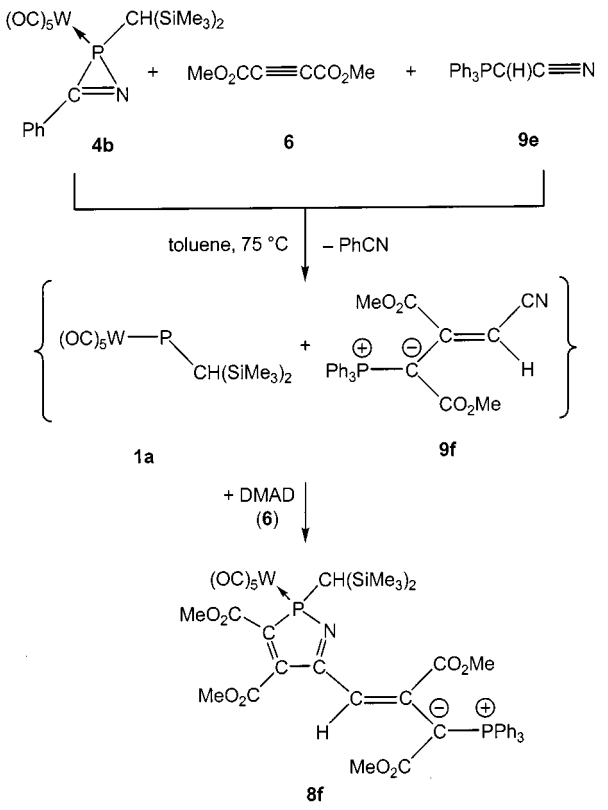

Scheme 5. Three-component reactions of 2*H*-azaphosphirene complex **4b** with DMAD and hetarene-substituted carbonitriles (**9b**,**c**)




Scheme 6. Two- and three-component reactions of 2*H*-azaphosphirene complex **4b** with DMAD and pyrrolecarbonitrile (**9d**) (for explanations of **i** and **ii**, see text)

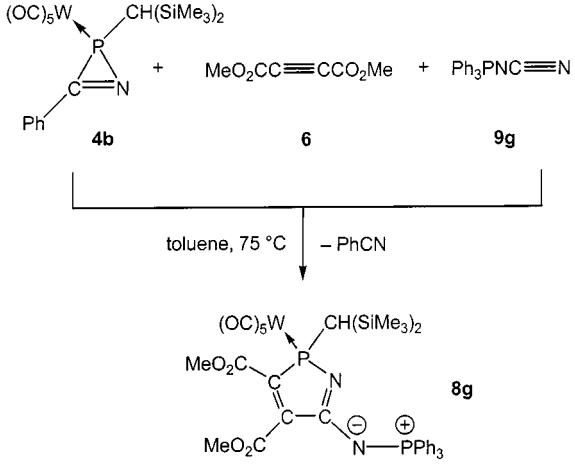
to an increased tendency of nitrilium phosphanylide complex **2e** to isomerize to **4c**, even under such conditions. Furthermore, the pure complex **4c** displayed an enhanced thermal stability in solution and underwent rapid ring-opening to transient **2c** only beyond 78 °C to yield complex **8e** with DMAD (Scheme 6).

The course of the reaction of the 2*H*-azaphosphirene complex **4b** with $Ph_3PC(H)CN$ (**9e**) and DMAD appeared to be more complicated under the same reaction conditions, although the outcome was in some respects not very surprising. Primarily, and at ambient temperature, rapid formation of the carbonitrile derivative **9f** was observed.[15] Nevertheless, this nitrile then selectively led to the 2*H*-1,2-azaphosphole complex **8f** (Scheme 7). Neither formation of $\Delta^3$-1,3,2-oxazaphospholene complexes nor of a 2*H*-azaphosphirene complex was observed.




Scheme 7. Three-component reaction of 2*H*-azaphosphirene complex **4b** with DMAD and $Ph_3PC(H)CN$ (**9e**)

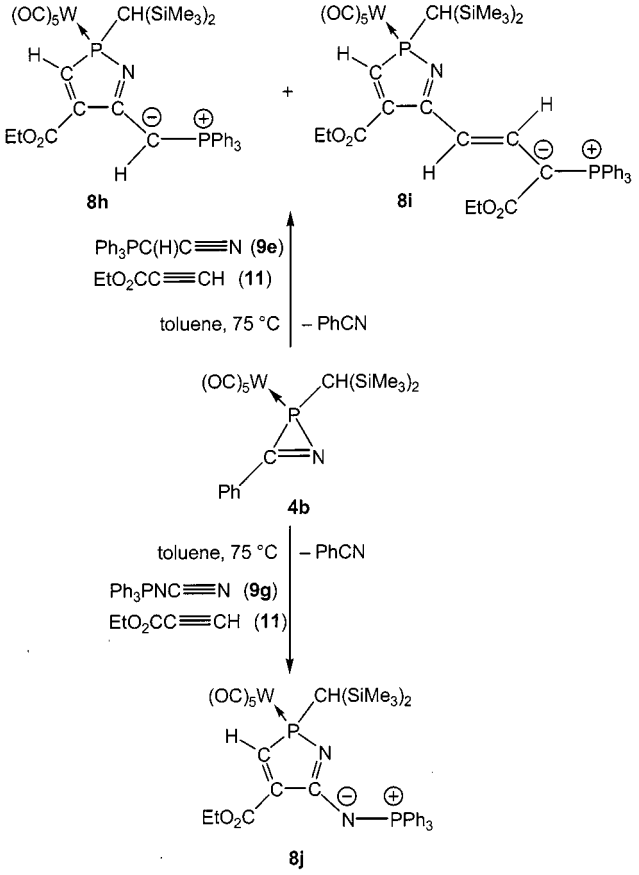
Also very selective was the reaction of the 2*H*-azaphosphirene complex **4b** with $Ph_3PNCN$ (**9g**) and DMAD (1:1:1 ratio). $^{31}P$ NMR spectroscopic monitoring of the reaction showed exclusively the formation of the 2*H*-1,2-azaphosphole complex **8g** as the sole phosphorus-containing product, which was isolated in good yields by column chromatography (Scheme 8).




Scheme 8. Three-component reaction of 2*H*-azaphosphirene complex **4b** with DMAD and $Ph_3PNCN$ (**9g**)

As our former studies on the regioselectivity of reaction of transiently generated nitrilium phosphanylide complexes

**2a**,**b**[8] and **2c**−**e**[9] with ethyl acetylenecarboxylate (**11**) showed, these highly reactive species always yield two regioisomeric 2*H*-1,2-azaphosphole complexes, with formation of the 4-ethoxycarbonyl-substituted 2*H*-1,2-azaphosphole complexes being favored. This was established by X-ray crystal structure analysis of a 5-(1,5-dimethylpyrrol-2-yl)-substituted 2*H*-1,2-azaphosphole complex.[9] Furthermore, we found that the regioisomer ratios showed a marked dependence on the $C^5$ substituent, e.g., 2-furanyl (3:1 ratio), 2-thienyl (5:1 ratio), and 2-(1,5-dimethylpyrrolyl) (8:1 ratio). Therefore, we were interested in examining the regioselectivity of transiently generated nitrilium phosphanylide complexes **2f**,**g** of the general formula RCNP[CH(SiMe$_3$)$_2$]W(CO)$_5$ [**2f**: R = Ph$_3$PC(H); **2g**: R = Ph$_3$PN] towards the terminal alkyne derivative **11**. Applying the aforementioned reaction protocols to the reactions of 2*H*-azaphosphirene complex **4b** with the carbonitriles **9e**,**h** and **11** led to the exclusive formation of only one regioisomer in each case, namely the 4-ethoxycarbonyl-substituted 2*H*-1,2-azaphosphole complexes **8h** and **8j**, which, in the case of **8h**, partially underwent subsequent reaction with the alkyne **11** to additionally yield complex **8i** (Scheme 9). All complexes were isolated in pure form by column chromatography. Related reactions of phosphonium ylides with activated alkynes have been reported previously and were interpreted as [2+2] cycloadditions with subsequent electrocyclic ring-opening, thus leading to new acyclic phosphonium ylides.[15,16]




Scheme 9. Three-component reactions of 2*H*-azaphosphirene complex **4b** with carbonitriles **9e**/**9g** and ethyl acetylenecarboxylate (**11**)

Although spectroscopic data for 1*H*-1,2-azaphosphole derivatives are available in the literature,[17,18] we will not make any comparisons with these because of the significantly different bonding situations. 1*H*-1,2-azaphosphole derivatives can be regarded as 6π-heteroaromatic systems,[19] whereas 2*H*-1,2-azaphosphole derivatives can be expected to have no such aromaticity.[20] The salient NMR spectroscopic data of the 2*H*-1,2-azaphosphole ring atoms of complexes **8b**−**8j** are collected in Table 1. Besides the typical chemical shifts of the $^{31}$P NMR resonances, which are associated with the nature of the element directly bonded to the $C^5$ ring atom, the resonances show tungsten−phosphorus couplings but no phosphorus−phosphorus couplings. The $^{13}C\{^1H\}$ NMR spectra each feature three resonances due to the 2*H*-1,2-azaphosphole ring with different phosphorus−carbon coupling constant magnitudes. The assignments of the resonances and thus the regiochemistry of the rings of **8g**−**8j** were unambiguously established by means of DEPT experiments. Besides the typical small $|J(^{31}P,^{13}C)|$ values for the $C^5$ atoms, we observed that the magnitudes of the phosphorus−carbon coupling constants of the $C^4$ atoms were always greater than those of the $C^3$ atoms, even though the latter are directly bonded to the phosphorus atoms. This means that the $|^{2+3}J(^{31}P,^{13}C)|$ values are considerably larger than the $|^{1+4}J(^{31}P,^{13}C)|$ values! In the case of complexes **8g**,**h** and **8j**, the proposed constitutions were also established through additional phosphorus−carbon couplings of the $C^4$ atom with the ylide phosphorus atom of about 40 to 50 Hz, which were absent in complexes **8f** and **8i** as a consequence of the greater distances of the through-bond coupling pathways.

The $^1$H NMR spectra of **8h**−**8j** show the typical parameters for the protons bonded to the $C^3$ atoms with chemical shifts of $\delta \approx 8.1$ and phosphorus−proton couplings $|^2J(^{31}P,^1H)|$ of ca. 31 Hz. In the case of complexes **8h** and **8j**, long-range couplings $|^5J(^{31}P,^1H)|$ of ca. 3−4 Hz are also seen, but these are absent in the case of complex **8i**. Selected NMR parameters of the ylide functional groups are collected in Table 2; further confirmation of the proposed structures comes from the fact that the $^{13}C\{^1H\}$ NMR spectroscopic data of the side-chain and ylide functionalities are all as expected.[15] The UV/Vis spectra lend further support to the constitutions of **8f**−**8j** by displaying additional absorptions for complexes **8g**, **8h**, and **8j** at $\lambda \approx 420-430$ nm ($\lg \varepsilon \approx 3.8$) and for complexes **8f** and **8i** at $\lambda = 470-510$ nm ($\lg \varepsilon \approx 4.1$), and an additional broad band at $\lambda = 558$ nm ($\lg \varepsilon \approx 3.8$) for complex **8f** (Figure 1). These bands additionally show the existence of more elongated π-systems.[16]

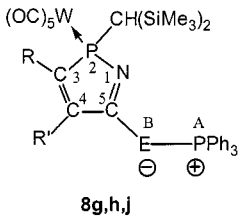
EI mass spectrometric experiments revealed that all of these 2*H*-1,2-azaphosphole complexes lose carbon monoxide following the ionization process as one important fragmentation pathway. Apart from this, other fragmentation pathways can occur, which are highly dependent on the $C^5$ substituent, e.g. cleavage of the tungsten−phosphorus bond in the case of complex **8g**. In this case, the initially formed

Table 1. Selected NMR spectroscopic data of the 2*H*-1,2-azaphosphole complexes **8b**−**8j**

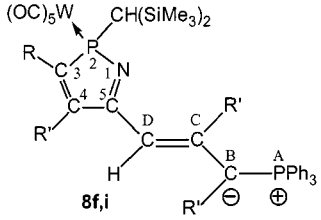
| Compd.[a] | δ($^{31}$P) | $^{1}J_{W,P}$ | δ($^{13}$C$^{3}$) | $^{1+4}J$(P,C$^{3}$) | δ($^{13}$C$^{4}$) | $^{2+3}J$(P,C$^{4}$) | δ($^{13}$C$^{5}$) | $^{2+3}J$(P,C$^{5}$) |
|---|---|---|---|---|---|---|---|---|
| **8b** | 84.5 | 250.1 | 158.0 | 5.9 | 139.2 | 21.4 | 161.5 | 6.8 |
| **8c** | 103.4 | 239.8 | 155.5 | 9.0 | 141.8 | 25.0 | 160.8 | [b] |
| **8d** | 100.6 | 239.9 | 159.4 | 10.0 | 138.8 | 19.3 | 161.6 | [b] |
| **8e** | 100.9 | 244.3 | 157.3 | 8.6 | 145.9 | 27.0 | 157.1 | [b] |
| **8f** | 102.8 | 241.3 | 162.2 | 12.6 | 145.6 | 28.7 | 157.6 | [b] |
| **8g** | 85.8 | 249.6 | 163.1 | 14.0 | 149.0[c] | 25.8 | 153.3 | [b] |
| **8h** | 75.9 | 237.2 | 158.3 | 8.5 | 138.5[c] | 16.5 | 169.3[d] | 4.8 |
| **8i** | 82.8 | 230.2 | 160.5 | [b] | 139.6 | 27.6 | 163.6 | [b] |
| **8j** | 72.2 | 236.1 | 157.0 | 8.1 | 140.3 | 17.4 | 167.0 | [b] |

[a] In $CDCl_3$; δ in ppm and *J* in Hz. [b] Not resolved. [c] **8g**: $^{3}J$(P,C$^{4}$) = 48.1 Hz; **8h**: $^{3}J$(P,C$^{4}$) = 44.3 Hz. [d] **8h**: $^{2}J$(P,C$^{5}$) = 11.3 Hz.

Table 2. Selected NMR spectroscopic data of the P,C and P,N ylide functional groups of 2*H*-1,2-azaphosphole complexes **8f**−**8j** (**8f**: R = R′ = $CO_2Me$; **8g**: R = R′ = $CO_2Me$, E = N; **8h**: R = H, R′ = $CO_2Et$; E = CH; **8i**: R = H, R′ = $CO_2Et$; **8j**: R = H, R′ = $CO_2Et$; E = N)




**8g,h,j**




**8f,i**

| Compd.[a] | δ($^{31}$P) | δ($^{13}$C$^{B}$) | $^{1}J$(P,C$^{B}$) | δ($^{13}$C$^{C}$) | $^{2+4}J$(P,C$^{C}$) | δ($^{13}$C$^{D}$) | $^{3}J$(P,C$^{D}$) | $^{3}J$(P,C$^{D}$) | δ($^{1}$H$^{D/E}$) | $^{4}J$(P,H$^{D}$) |
|---|---|---|---|---|---|---|---|---|---|---|
| **8f** | 18.7 | 61.2 | 116.2 | 149.2 | 9.6 | 108.3 | 7.4 | 17.6 | 5.11 | 1.8 |
| **8g** | 14.7 | – | – | – | – | – | – | – | – | – |
| **8h** | 15.0 | 47.6[b] | 113.3 | – | – | – | – | – | 4.61 | [b] |
| **8i** | 25.3 | 63.9 | 117.2 | 144.4 | 15.5 | 106.2 | 15.7 | 18.5 | 3.80 | 10.2[c] |
| **8j** | 15.0 | – | – | – | – | – | – | – | – | – |

[a] In $CDCl_3$; δ in ppm and *J* in Hz. [b] **8h**: $^{3}J$(P$^{2}$,C) = 22.7, $^{2}J_{P,H}$ = 21.3, $^{3}J_{P,H}$ = 15.7 Hz. [c] $^{3}J_{H,H}$ = 7.1 Hz

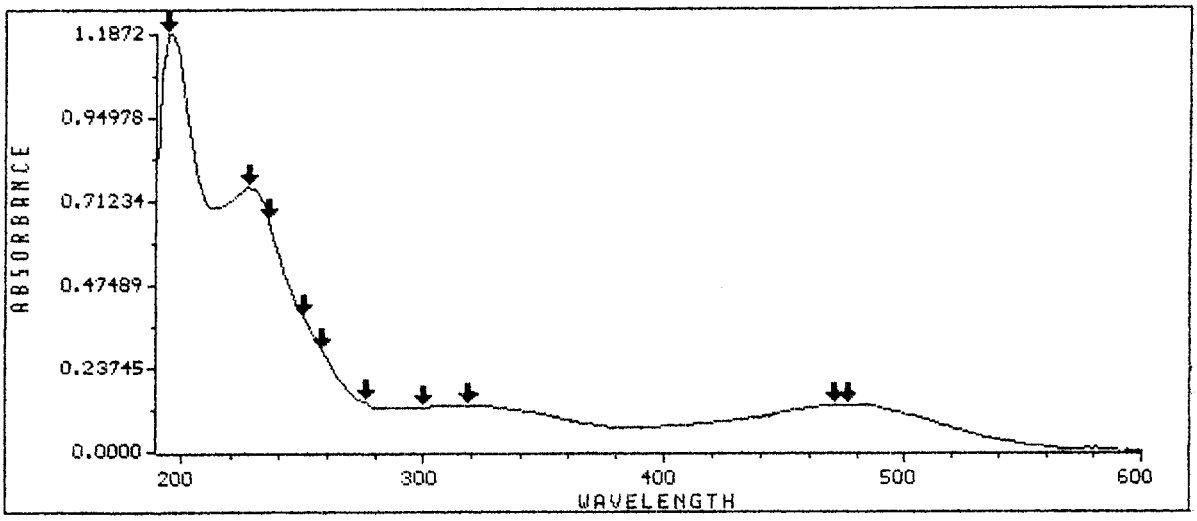
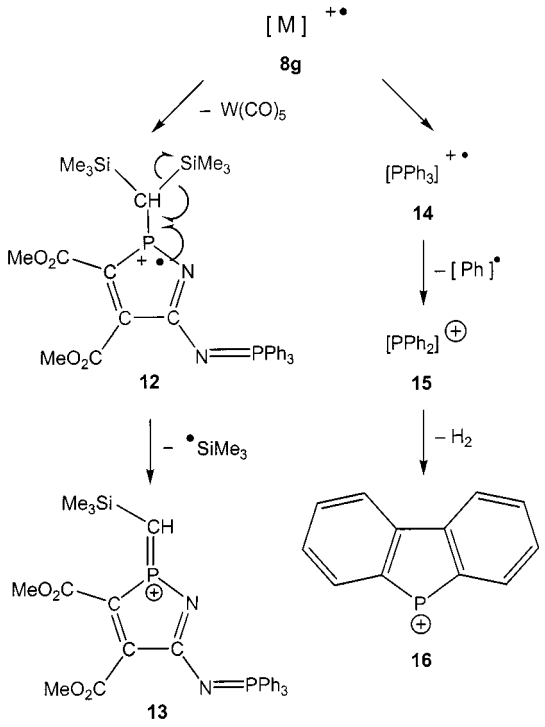



Figure 1. UV/Vis spectrum of 2*H*-1,2-azaphosphole complex **8i** (acetonitrile, $c$ = 9.50 mg dm$^{-3}$)

radical cation **12** undergoes C−Si bond cleavage to yield **13** (Scheme 10). Furthermore, the complexes **8g**−**8j** were seen to undergo cleavage of the P−C or P−N ylide bonds of the C$^{5}$ substituent, e.g. in the case of complex **8g**, thus generating $[Ph_3P]^{+\cdot}$ (**14**) and neutral species such as carbenes and nitrenes. The further degradation of **14** to $[Ph_2P]^{+}$ (**15**) and **16** has been reported previously.[21]

We were able to confirm the constitutions of complexes **4c** (Figure 2, Table 3), **8d**,**8e**, and **8g** by single-crystal X-ray structure analyses (Figure 3, Figure 4, and Figure 5 and




Scheme 10. Fragmentation pathway of complex **8g**

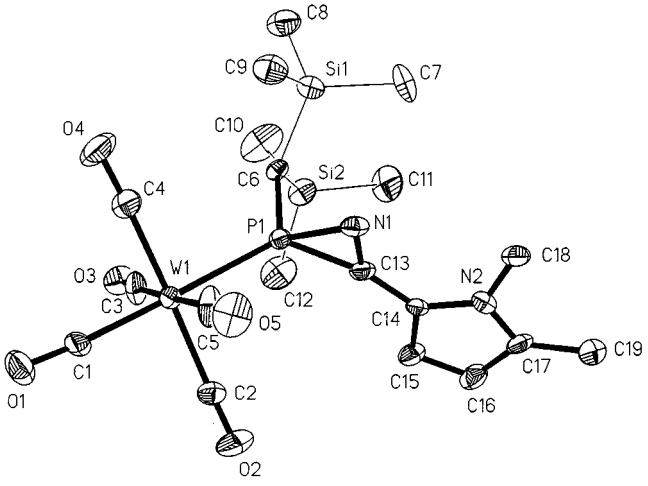



Figure 2. Molecular structure of one of the two independent molecules of **4c** in the crystal (ellipsoids represent 30% probability levels; hydrogen atoms are omitted for clarity); selected bond lengths [Å] and angles [°] (values for both molecules are given): W1−C1 1.980(13), 1.977(14), W1−P1 2.485(3), 2.488(3), P1−N1 1.800(10), 1.785(11), N1−C13 1.313(14), 1.307(14), C13−C14 1.411(16), 1.403(16); W1−P1−C6 120.8(4), 120.7(4), N1−C13−P1 70.7(7), 69.5(7), C13−C14−C15 126.0(12), 126.4(11)

Table 3 and Table 4). The molecular structure of complex **4c** shows an approximately coplanar arrangement of the two ring systems (interplanar angles 12.0° and 6.0° in two independent but closely similar molecules), thus enabling effective electronic interactions between the two rings. This is manifested in a shortened C(13)−C(14) bond of 1.411(16) Å, 1.403(16) Å and an elongated C(13)−N bond of 1.313(14) Å, 1.307(14) Å [compared to analogous C−C and C−N bond lengths of 1.457(7) Å and 1.272(7) Å in the $C^3$-phenyl-substituted (2*H*-azaphosphirene)tungsten complex].[14] It is also noteworthy that the NMe group adopts a position below the C−N double bond, thus pointing away from the phosphorus atom. This is interesting in the light of the observation that two alternative orientations seem to exist in *ortho*-substituted phenyl derivatives, depending on the *ortho* substituent.[22,23] We are currently trying to understand and exploit this aspect of the stereochemistry of 2*H*-azaphosphirene complexes.

The 2*H*-1,2-azaphosphole rings of complexes **8d**, **8e** and **8g** showed no unusual interatomic distances between the ring atoms, nor to the externally bonded atoms (Table 4). In all cases, the 2*H*-1,2-azaphosphole rings are approximately planar (largest mean deviation 0.014 Å in **8e**) and the bis-(trimethylsilyl)methyl group adopts the same preferred relative orientation towards the tungsten center and thus towards the ring as reported previously for other structures of related phosphorus heterocycle complexes. A further common structural motif is that the ester groups bonded to the $C^{13}$ atoms adopt an approximately in-plane orientation, whereas the ester groups bonded to the $C^{14}$ atoms adopt an out-of-plane orientation. The interplanar angles in **8d**, **8e** (22.3° and 24.6°, respectively) and the torsion angle of N(1)−C(15)−N(2)−P(2) of −18.9° in **8g** should, in all cases, enable electronic interactions between the two ring systems or the substituent. It is also noteworthy that in **8g** the $NPPh_3$ group adopts an *s-cis* configuration with respect to the C(15)−N(2) bond and seems to induce a slight elongation of the phosphorus−tungsten bond.

The following short contacts are observed: **8d**: S···O9 3.312 Å (operator $1 + x, y, z$); **8e**: C24−H24···O9 2.39 Å (angle at H 147°, operator $1 + x, y, z$); **8g**: C17−H17···O9 2.34 Å (angle at H 162°, operator $-x, 2 - y, -z$).

## Concluding Remarks

We have shown that the chemistry of transiently generated nitrilium phosphanylide complexes can be further exploited, especially by using reactions of P,C and P,N ylide substituted carbonitriles and terminal phosphanediyl complexes, ultimately leading to the first $C^5$-functionalized 2*H*-1,2-azaphosphole complexes. It is also remarkable that no products were observed that may conceivably have arisen from initial attack of the transiently formed electrophilic terminal phosphanediyl complex at the nucleophilic ylide carbon or nitrogen atoms, which can probably be attributed to steric shielding of these centers. Therefore, the carbonitrile nitrogen atoms are predisposed to act exclusively as efficient donor centers towards the phosphorus atom of the electrophilic terminal phosphanediyl complex. In view of the lack of diazaphosphole complex formation, we conclude that the nitrile/nitrile exchange is a dissociative process (cf. ref.[6]) and, therefore, that the generation of the nitrilium phosphanylide complexes has to be described as 1,1-addition (cf. ref.[3]). With regard to the possible competition of the trapping reagents, nitriles and alkynes, the selectivity of the P,N ylide substituted nitrilium phosphanylide complexes towards alkynes is remarkable. Furthermore, the

Table 3. Crystal data and structure refinement of complexes **4c**, **8d**, **8e**, and **8g**

| Complex | **4c** | **8d** | **8e** | **8g** |
|---|---|---|---|---|
| Empirical formula | $C_{19}H_{27}N_2O_5PSi_2W$ | $C_{23}H_{28}NO_9PSSi_2W$ | $C_{25}H_{33}N_2O_9PSi_2W$ | $C_{37}H_{33}N_2O_9P_2Si_2W$ |
| $M_r$ | 634.43 | 765.52 | 776.53 | 958.68 |
| Crystal size [mm] | 0.40 × 0.24 × 0.20 | 0.26 × 0.23 × 0.07 | 0.25 × 0.24 × 0.09 | 0.38 × 0.28 × 0.13 |
| Crystal system | triclinic | monoclinic | monoclinic | triclinic |
| Space group | $P\bar{1}$ | $P2_1/n$ | $P2_1/n$ | $P\bar{1}$ |
| Unit cell dimensions | | | | |
| $a$ [Å] | 9.374(2) | 10.2984(8) | 10.5410(10) | 12.0023(8) |
| $b$ [Å] | 11.485(2) | 21.6888(14) | 21.9904(10) | 12.8064(8) |
| $c$ [Å] | 24.547(4) | 13.5948(10) | 13.7490(12) | 13.7749(8) |
| α [°] | 99.963(15) | 90 | 90 | 88.298(3) |
| β [°] | 93.937(15) | 101.802(3) | 102.540(2) | 89.684(3) |
| γ [°] | 94.955(15) | 90 | 90 | 74.802(3) |
| $V$ [Å$^3$] | 2583.9(8) | 2972.3(4) | 3111.0(4) | 2042.3(2) |
| $Z$ | 4 | 4 | 4 | 2 |
| $D_x$ [Mg m$^{-3}$] | 1.631 | 1.711 | 1.658 | 1.559 |
| μ [mm$^{-1}$] | 4.655 | 4.139 | 3.892 | 3.018 |
| Transmissions | 0.601−0.980 | 0.482−0.746 | 0.694−0.949 | 0.656−0.928 |
| $F$(000) | 1248 | 1512 | 1544 | 960 |
| $T$ [K] | 173(2) | 143(2) | 143(2) | 133(2) |
| $2\theta_{max}$ [°] | 50 | 60 | 57 | 60 |
| No. of reflections | | | | |
| measured | 9679 | 64172 | 48722 | 44213 |
| unique | 9008 | 8699 | 7914 | 11907 |
| $R_{int}$ | 0.0715 | 0.0559 | 0.0572 | 0.0459 |
| Parameters | 541 | 350 | 371 | 486 |
| Restraints | 220 | 19 | 194 | 73 |
| $wR$ ($F^2$, all reflns.) | 0.1288 | 0.0516 | 0.0445 | 0.0504 |
| $R$ [$F$, $I > 2\sigma(I)$] | 0.0536 | 0.0213 | 0.0203 | 0.0250 |
| $S$ | 0.781 | 1.011 | 0.981 | 1.027 |
| Max. Δρ [e Å$^{-3}$] | 2.161 | 1.153 | 0.759 | 1.272 |

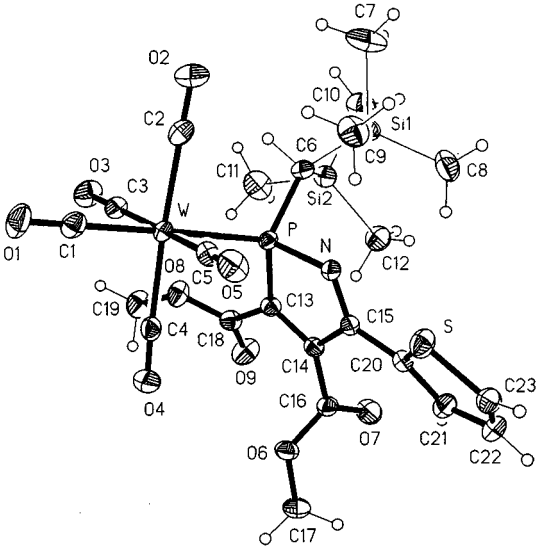



Figure 3. Molecular structure of **8d** in the crystal (ellipsoids represent 50% probability levels); selected angles [°]: W−P−C6 119.08(7), N−P−C13 92.03(9), P−N−C15 112.50(14), N−C15−C14 115.22(17), C13−C14−C15 112.23(17), C14−C13−P 107.87(15)

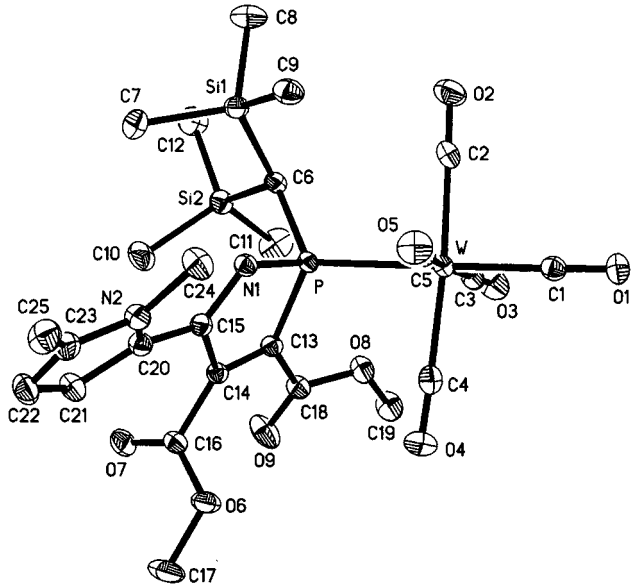



Figure 4. Molecular structure of **8e** in the crystal (ellipsoids represent 50% probability levels; hydrogen atoms are omitted for clarity); selected angles [°]: W−P−C6 117.95(6), N−P−C13 92.14(8), P−N−C15 112.60(13), N−C15−C14 114.69(16), C13−C14−C15 112.06(15), C14−C13−P 108.48(13)

finding that such 1,3-dipoles do not tend to form 2*H*-azaphosphirene complexes is very interesting, and, although no calculations were carried out on such systems, one may assume that the $Ph_3PC(H)$ and $Ph_3PN$ ylide substituents stabilize nitrilium phosphanylide complexes more effectively than 2*H*-azaphosphirene complexes.[4,24] It is also remarkable that no cross-reactions and/or side-reactions of the transiently formed nitrilium phosphanylide complexes were detected, i.e. cycloaddition reactions involving the P−C and/or P−N bond − common organic 1,3-dipoles show

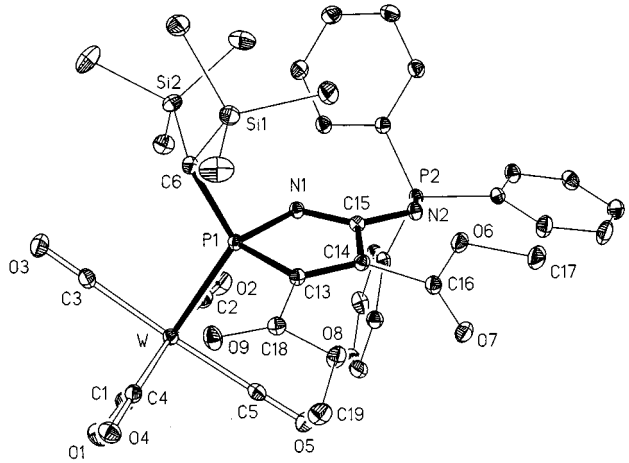



Figure 5. Molecular structure of **8g** in the crystal (ellipsoids represent 30% probability levels; hydrogen atoms are omitted for clarity); selected angles [°]: W−P1−C6 121.36(5), N−P−C13 93.69(7), P−N−C15 110.85(11), N−C15−C14 115.69(13), C13−C14−C15 112.26(14), C14−C13−P 107.41(11)

Table 4. Selected bond lengths [Å] in 2*H*-1,2-azaphosphole complexes **8d**, **8e** and **8g**

| | **8d** | **8e** | **8g** |
|---|---|---|---|
| W−C(1) | 1.997(2) | 2.007(2) | 2.0024(19) |
| W−P | 2.5062(5) | 2.5135(5) | 2.5384(4) |
| P−C(13) | 1.843(2) | 1.8382(18) | 1.8345(16) |
| P−N(1) | 1.7063(17) | 1.7079(16) | 1.7005(14) |
| C(13)−C(14) | 1.348(3) | 1.346(2) | 1.345(2) |
| N(1)−C(15) | 1.297(2) | 1.307(2) | 1.311(2) |
| C(14)−C(15) | 1.492(3) | 1.503(3) | 1.502(2) |
| C(15)−C(20)/C(15)−N(2) | 1.459(3) | 1.446(3) | 1.347(2) |

such cycloaddition reactions with phosphorus ylides such as $Ph_3PC(H)CN$.[16] Overall, very bulky ylide-substituted carbonitriles seem to be very interesting candidates for the generation of stable nitrilium phosphanylide complexes.

We are currently trying to exploit such ylide-substituted carbonitriles in other three-component reactions and to use the ylide functionalities in 2*H*-1,2-azaphosphole complexes to construct more extended N,P-heterocycle ligand structures, e.g. by using Wittig and aza-Wittig reactions.

## Experimental Section

**General Procedures:** All reactions and manipulations were carried out under deoxygenated dry nitrogen in conventional glassware using standard Schlenk techniques. Solvents were dried according to standard procedures. NMR spectra were recorded with a Bruker AC-200 spectrometer (200 MHz for $^1H$; 50.3 MHz for $^{13}C$; 81.0 MHz for $^{31}P$) using [D]chloroform or [$D_6$]benzene as solvent and internal standard; shifts are given relative to external tetramethylsilane ($^1H$, $^{13}C$) or 85% $H_3PO_4$ ($^{31}P$); only coupling constant magnitudes are given. Electron impact (EI) (70 eV), chemical ionization (CI) (ammonia), and fast atom bombardment (FAB) (xenon) mass spectra were recorded with a Finnigan MAT-8430 double-focusing mass spectrometer. Infrared spectra were recorded with a Biorad FT-IR 165 spectrometer (selected data given). UV/Vis spectra were recorded with a Hewlett Packard HP 8452 spectrophotometer. Melting points were obtained with a Büchi 535 capillary apparatus. Elemental analyses were performed using a Carlo Erba analytical gas chromatograph. The *κP* notation in the nomenclature is intended to differentiate between P and N coordination of the relevant heterocycle to the metal ion.

**{2-[Bis(trimethylsilyl)methyl]-3-(1,5-dimethylpyrrol-2-yl)-2*H*-azaphosphirene-*κP*}pentacarbonyltungsten(0) (4c):** A solution of the (2*H*-azaphosphirene)tungsten complex **4b** (0.62 g, 1 mmol) and 1,5-dimethyl-2-pyrrolecarbonitrile **(9d)** (0.617 g, 5 mmol) in toluene (10 mL) was heated at 72 °C for 2 h with slow stirring. Thereafter, the solvent was removed in vacuo (ca. 0.01 mbar) and the product was separated by low-temperature column chromatography ($SiO_2$, −15 °C, 10 × 2 cm, *n*-pentane/diethyl ether, 70:30). Evaporation of the solvents from the second fraction yielded **4c** as a yellow solid. Yield 220 mg (36%); m.p. 131 °C (decomp.). $^1H$ NMR ($CDCl_3$): δ = 0.07 (s, 9 H, $SiMe_3$), 0.15 (s, 9 H, $SiMe_3$), 0.33 [d, $^2J_{P,H}$ = 1.3 Hz, 1 H, C*H*($SiMe_3$)$_2$], 2.23 (s, 3 H, $CH_3$), 3.60 (s, 3 H, $NCH_3$), 5.89 (d, $^3J_{H,H}$ = 3.4 Hz, 1 H, 3-H), 6.66 (d, $^3J_{H,H}$ = 3.9 Hz, 1 H, 4-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 1.2 (d, $^3J_{P,C}$ = 3.2 Hz, $SiMe_3$), 2.0 (d, $^3J_{P,C}$ = 3.1 Hz, $SiMe_3$), 12.4 (s, C*C*$H_3$), 27.0 [d, $^1J_{P,C}$ = 24.3 Hz, *C*H($SiMe_3$)$_2$], 32.1 (s, $NCH_3$), 110.8 (s, $C5_{aryl}$), 119.2 (d, $^2J_{P,C}$ = 19.4 Hz, $C2_{aryl}$), 122.0 (s, $C3_{aryl}$), 135.4 (s, $C4_{aryl}$), 177.4 (d, $^{1+2}J_{P,C}$ = 8.5 Hz, PCN), 196.0 (d, $^2J_{P,C}$ = 9.0 Hz, *cis*-CO), 198.1 (d, $^2J_{P,C}$ = 35.2 Hz, *trans*-CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −131.4 (s, $^1J_{P,W}$ = 294.2 Hz). MS (pos. CI, $^{184}W$): *m/z* = 634 (1) $[M]^{+\cdot}$.

**General Procedure for the Preparation of Complexes 8b−8e:** To a solution of the (2*H*-azaphosphirene)tungsten complex **4b** (0.62 g, 1 mmol) in toluene (10 mL), the respective carbonitrile **9b−9e** (4 mmol) and dimethyl acetylenedicarboxylate (**6**; 0.245 mL, 2 mmol) were added and the resulting mixture was heated at 75 °C for 3.5 h with slow stirring. Thereafter, all volatile components were removed in vacuo (ca. 0.01 mbar) and the products were separated by low-temperature column chromatography ($SiO_2$, −10 °C, 10 × 2 cm, *n*-pentane/diethyl ether, 70:30). Evaporation of the solvents from the respective second fractions yielded **10a** and **8b** as yellow solids and **8c−8e** as red solids.

**{2-[Bis(trimethylsilyl)methyl]-4-methoxy-4-(2-methoxycarbonylethynyl)-5-piperidino-Δ$^3$-1,3,2-oxazaphospholene-*κP*}pentacarbonyltungsten(0) (10a,b):** Yield 84 mg (11%); m.p. 144 °C (decomp.). $^1H$ NMR ($CDCl_3$): δ = 0.01 (s, 9 H, $SiMe_3$), 0.15 (s, 9 H, $SiMe_3$), 1.49 [s, 1 H, C*H*($SiMe_3$)$_2$], 1.54 ($m_c$, 6 H, $NCH_2CH_2CH_2$), 3.44 ($m_c$, 4 H, $NCH_2CH_2CH_2$), 3.63 (s, 3 H, $OCH_3$), 3.80 (s, 3 H, $OCH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 2.0 (d, $^3J_{P,C}$ = 2.4 Hz, $SiMe_3$), 2.3 (s, $SiMe_3$), 24.3 (s, $NCH_2CH_2CH_2$), 24.7 (s, $NCH_2CH_2CH_2$), 36.8 [d, $^1J_{P,C}$ = 5.9 Hz, *C*H($SiMe_3$)$_2$], 48.1 (s, $NCH_2CH_2CH_2$), 52.8 (s, $OCH_3$), 53.2 (s, $OCH_3$), 77.2 (s, C*C*$CO_2Me$), 79.9 (s, *C*C$CO_2Me$), 99.0 (d, $^{2+3}J_{P,C}$ = 7.2 Hz, POC), 152.7 (s, PNC), 156.7 (s, *C*$O_2Me$), 197.2 (d, $^2J_{P,C}$ = 8.6 Hz, *cis*-CO), 201.1 (d, $^2J_{P,C}$ = 28.4 Hz, *trans*-CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 198.3 (s, $^1J_{P,W}$ = 300.9 Hz). IR (KBr): $\tilde{\nu}$ = 2070 (s), 1990 (s), 1951 (vs), 1935 (vs), 1900 $cm^{-1}$ (vs) (CO), 1602 $cm^{-1}$ (s) ($CO_2$). MS (EI, $^{184}W$): *m/z* = 766 (48) $[M]^{+\cdot}$, 626 (100) $[M - 5CO]^{+\cdot}$. $C_{24}H_{35}N_2O_9PSi_2W$ (766.5): calcd. C 37.61, H 4.60, N 3.65; found C 39.22, H 4.94, N 3.58.

**{2-[Bis(trimethylsilyl)methyl]-3,4-bis(methoxycarbonyl)-5-piperidino-2*H*-1,2-azaphosphole-*κP*}pentacarbonyltungsten(0) (8b):** Yield 107 mg (14%); m.p. 112 °C (decomp.). $^1H$ NMR ($CDCl_3$): δ = 0.01 (s, 9 H, $SiMe_3$), 0.26 (s, 9 H, $SiMe_3$), 1.07 [d, $^2J_{P,H}$ = 6.2 Hz, 1 H, C*H*($SiMe_3$)$_2$], 1.57 ($m_c$, 2 H, $NCH_2CH_2CH_2$), 3.45 ($m_c$, 4 H, $NCH_2CH_2CH_2$), 3.77 (s, 3 H, $OCH_3$), 3.81 (s, 3 H, $OCH_3$), 4.05

($m_c$, 4 H, $NCH_2CH_2CH_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 2.7 (d, $^3J_{P,C}$ = 2.0 Hz, $SiMe_3$), 3.3 (d, $^3J_{P,C}$ = 2.5 Hz, $SiMe_3$), 22.1 [s, *C*H($SiMe_3$)$_2$], 24.4 (s, $NCH_2CH_2CH_2$), 25.9 (s, $NCH_2CH_2CH_2$), 48.6 (s, $NCH_2CH_2CH_2$), 52.6 (s, $OCH_3$), 53.2 (s, $OCH_3$), 139.2 (d, $^{2+3}J_{P,C}$ = 21.4 Hz, PC*C*), 158.0 (d, $^{1+4}J_{P,C}$ = 5.9 Hz, P*C*C), 161.5 (d, $^{2+3}J_{P,C}$ = 6.8 Hz, PNC), 163.3 (d, $^3J_{P,C}$ = 10.3 Hz, *C*$O_2$Me), 165.7 (d, $^3J_{P,C}$ = 14.7 Hz, *C*$O_2$Me), 197.5 (d, $^2J_{P,C}$ = 7.2 Hz, *cis*-CO), 199.6 (d, $^2J_{P,C}$ = 23.0 Hz, *trans*-CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 84.5 (s, $^1J_{P,W}$ = 250.1 Hz). MS (EI, $^{184}W$): *m*/*z* = 766 (12) $[M]^{+\cdot}$, 598 (100) $[M - 5CO - CO]^{+\cdot}$. $C_{24}H_{35}N_2O_9PSi_2W$ (766.5): calcd. C 37.61, H 4.60, N 3.65; found C 38.94, H 4.49, N 3.50.

**{2-[Bis(trimethylsilyl)methyl]-3,4-bis(methoxycarbonyl)-5-furyl-2*H*-1,2-azaphosphole-κ*P*}pentacarbonyltungsten(0) (8c):** Yield 240 mg (32%); m.p. 136 °C (decomp.). $^1H$ NMR ($CDCl_3$): δ = 0.21 (s, 9 H, $SiMe_3$), 0.78 (s, 9 H, $SiMe_3$), 1.14 [d, $^2J_{P,H}$ = 6.4 Hz, 1 H, C*H*($SiMe_3$)$_2$], 3.73 (s, 3 H, $OCH_3$), 3.81 (s, 3 H, $OCH_3$), 6.41 ($m_c$, 1 H, $CH_{aryl}$), 7.09 ($m_c$, 1 H, $CH_{aryl}$), 7.41 ($m_c$, 1 H, $CH_{aryl}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 2.7 (d, $^3J_{P,C}$ = 1.7 Hz, $SiMe_3$), 3.2 (d, $^3J_{P,C}$ = 2.2 Hz, $SiMe_3$), 20.0 [s, *C*H($SiMe_3$)$_2$], 52.8 (s, $OCH_3$), 53.2 (s, $OCH_3$), 113.0 (s, $C^3_{aryl}$), 117.0 (s, $C^4_{aryl}$), 141.8 (d, $^{2+3}J_{P,C}$ = 25.0 Hz, PC*C*), 146.7 (s, $C^5_{aryl}$), 149.2 (d, $^3J_{P,C}$ = 21.7 Hz, $C^2_{aryl}$), 155.5 (d, $^1J_{P,C}$ = 9.0 Hz, P*C*C), 160.8 (s, PNC), 162.5 (d, $^2J_{P,C}$ = 12.9 Hz, *C*$O_2$Me), 164.7 (d, $^3J_{P,C}$ = 13.6 Hz, *C*$O_2$Me), 196.7 (d, $^2J_{P,C}$ = 6.7 Hz, *cis*-CO), 198.3 (d, $^2J_{P,C}$ = 23.0 Hz, *trans*-CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 103.4 (s, $^1J_{P,W}$ = 239.8 Hz). UV/Vis ($CH_3CN$): λ (lg ε) = 234 (4.86), 268 (4.30), 278 (4.15), 286 (4.09), 346 (4.04), 400 (3.46). IR (KBr): $\tilde{\nu}$ = 2076 (s, CO), 2001 (s, CO), 1937 (vs, CO), 1909 (vs, CO), 1745 (s, $CO_2$), 1714 $cm^{-1}$ (s, $CO_2$). MS (EI, $^{184}W$): *m*/*z* = 749 (7) $[M]^{+\cdot}$, 581 (100) $[M - 5CO - CO]^{+\cdot}$. $C_{23}H_{28}NO_{10}PSi_2W$: calcd. C 36.86, H 3.77, N 1.87; found C 35.99, H 3.80, N 1.94.

**{2-[Bis(trimethylsilyl)methyl]-3,4-bis(methoxycarbonyl)-5-thienyl-2*H*-1,2-azaphosphole-κ*P*}pentacarbonyltungsten(0) (8d):** Yield 260 mg (33%); m.p. 150 °C (decomp.). $^1H$ NMR ($CDCl_3$): δ = 0.08 (s, 9 H, $SiMe_3$), 0.38 (s, 9 H, $SiMe_3$), 1.31 [d, $^2J_{P,H}$ = 6.3 Hz, 1 H, C*H*($SiMe_3$)$_2$], 3.90 (s, 3 H, $OCH_3$), 3.98 (s, 3 H, $OCH_3$), 7.10 ($m_c$, 1 H, $CH_{aryl}$), 7.54 ($m_c$, 1 H, $CH_{aryl}$), 7.61 ($m_c$, 1 H, $CH_{aryl}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 2.6 (d, $^3J_{P,C}$ = 2.1 Hz, $SiMe_3$), 3.1 (d, $^3J_{P,C}$ = 2.7 Hz, $SiMe_3$), 20.0 [d, $^2J_{P,C}$ = 1.4 Hz, *C*H($SiMe_3$)$_2$], 52.9 (s, $OCH_3$), 53.4 (s, $OCH_3$), 133.3 (s, $C^3_{aryl}$), 134.9 (s, $C^4_{aryl}$), 138.8 (d, $^{2+3}J_{P,C}$ = 19.3 Hz, PC*C*), 139.7 (s, $C^5_{aryl}$), 141.9 (d, $^3J_{P,C}$ = 24.6 Hz, $C^2_{aryl}$), 159.4 (d, $^{1+4}J_{P,C}$ = 10.0 Hz, P*C*C), 161.6 (s, PNC), 162.7 (d, $^2J_{P,C}$ = 12.4 Hz, *C*$O_2$Me), 165.3 (d, $^3J_{P,C}$ = 13.8 Hz, *C*$O_2$Me), 196.7 (d, $^2J_{P,C}$ = 6.4 Hz, *cis*-CO), 198.3 (d, $^2J_{P,C}$ = 22.9 Hz, *trans*-CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 100.6 (s, $^1J_{P,W}$ = 239.9 Hz). UV/Vis ($CH_3CN$): λ (lg ε) = 232 (4.84), 264 (4.34), 284 (4.11), 348 (4.01), 394 (3.53), 404 (3.39), 420 (3.34), 440 (3.33). IR (KBr): $\tilde{\nu}$ = 2075 (s, CO), 1999 (s, CO), 1935 (vs, CO), 1909 (vs, CO), 1744 (s, $CO_2$), 1716 $cm^{-1}$ (s, $CO_2$). MS (EI, $^{184}W$): *m*/*z* = 765 (5) $[M]^{+\cdot}$, 597 (100) $[M - 5CO - CO]^{+\cdot}$. $C_{23}H_{28}NO_9PSSi_2W$: calcd. C 36.09, H 3.69, N 1.83, S 4.19; found C 35.19, H 3.65, N 1.82, S 4.38.

**{2-[Bis(trimethylsilyl)methyl]-3,4-bis(methoxycarbonyl)-5-(1,5-dimethylpyrrol-2-yl)-2*H*-1,2-azaphosphole-κ*P*}pentacarbonyltungsten(0) (8e):** Yield 700 mg (89%); m.p. 143 °C (decomp.). $^1H$ NMR ($CDCl_3$): δ = 0.03 (s, 9 H, $SiMe_3$), 0.31 (s, 9 H, $SiMe_3$), 1.19 [d, $^2J_{P,H}$ = 6.0 Hz, 1 H, C*H*($SiMe_3$)$_2$], 2.25 (s, 3 H, $C_{aryl}$-$CH_3$), 3.82 (s, 3 H, $NCH_3$), 3.88 (s, 3 H, $OCH_3$), 3.89 (s, 3 H, $OCH_3$), 5.93 (d, $^3J_{H,H}$ = 4.1 Hz, 1 H, $CH_{aryl}$), 6.65 (d, $^3J_{H,H}$ = 4.2 Hz, 1 H, $CH_{aryl}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 2.6 (d, $^3J_{P,C}$ = 2.0 Hz, $SiMe_3$), 3.2 (d, $^3J_{P,C}$ = 2.8 Hz, $SiMe_3$), 12.3 (s, C*C*$H_3$), 20.1 [s, *C*H($SiMe_3$)$_2$], 32.1 (s, $NCH_3$), 52.5 (s, $OCH_3$), 53.1 (s, $OCH_3$), 109.4 (s, $C^3_{aryl}$), 118.4 (s, $C^4_{aryl}$), 126.7 (d, $^2J_{P,C}$ = 17.3 Hz, $C^2_{aryl}$), 135.5 (s, $C^5_{aryl}$), 145.9 (d, $^{2+3}J_{P,C}$ = 27.0 Hz, PC*C*), 157.1 (s, PNC), 157.3 (d, $^{1+4}J_{P,C}$ = 8.6 Hz, P*C*C), 162.5 (d, $^2J_{P,C}$ = 13.1 Hz, *C*$O_2$Me), 166.0 (d, $^3J_{P,C}$ = 14.6 Hz, *C*$O_2$Me), 197.1 (d, $^2J_{P,C}$ = 6.8 Hz, *cis*-CO), 198.7 (d, $^2J_{P,C}$ = 23.1 Hz, *trans*-CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 100.9 (s, $^1J_{P,W}$ = 244.3 Hz). UV/Vis ($CH_3CN$): λ (lg ε) = 222 (4.70), 232 (4.78), 248 (4.59), 254 (4.54), 262 (4.45), 276 (4.31), 412 (4.05). IR (KBr): $\tilde{\nu}$ = 2070 (s, CO), 1985 (s, CO), 1951 (vs, CO), 1926 (vs, CO), 1913 (s, CO), 1743 (s, $CO_2$), 1718 $cm^{-1}$ (s, $CO_2$). MS (EI, $^{184}W$): *m*/*z* = 776 (6) $[M]^{+\cdot}$, 608 (100) $[M - 5CO - CO]^{+\cdot}$, (neg. CI, $^{184}W$): *m*/*z* = 776 (2) $[M]^{-\cdot}$, 617 (100) $[M - C_7H_{19}Si_2]^-$; (pos. CI, $^{184}W$): *m*/*z* = 777 (100) $[M + H]^+$. $C_{25}H_{33}N_2O_9PSi_2W$: calcd. C 38.67, H 4.28, N 3.61; found C 38.32, H 4.33, N 3.46.

**General Procedure for the Preparation of Complexes 8f−8j:** To a solution of the 2*H*-azaphosphirene complex **4b** (0.62 g, 1 mmol) in toluene (6 mL), the appropriate carbonitrile **9e** or **9h** (1 mmol) and the appropriate alkyne **6** or **11** (1 mmol) were added and the resulting mixture was heated at 75 °C for 2 h with slow stirring. Thereafter, all volatile components were removed in vacuo (ca. 0.01 mbar) and the products were separated by low-temperature column chromatography ($SiO_2$, −10 °C, 10 × 2 cm, *n*-pentane/diethyl ether, 70:30). Evaporation of the solvents from the respective second fractions yielded **8f** and **8i** as red solids, **8g** and **8h** as yellow solids, and **8j** as a pale-brown solid.

**{2-[Bis(trimethylsilyl)methyl]-3,4-bis(methoxycarbonyl)-5-[2,3-bis(methoxycarbonyl)-3-(triphenylphosphonio)propenylidyl]-2*H*-1,2-azaphosphole-κ*P*}pentacarbonyltungsten(0) (8f):** Yield 452 mg (41%); m.p. 58 °C (decomp.). $^1H$ NMR ($CDCl_3$): δ = 0.01 (s, 9 H, $SiMe_3$), 0.50 (s, 9 H, $SiMe_3$), 1.19 [d, $^2J_{P,H}$ = 5.3 Hz, 1 H, C*H*($SiMe_3$)$_2$], 3.35 (s, $OCH_3$), 3.38 (s, $OCH_3$), 3.86 (s, $OCH_3$), 4.04 (s, $OCH_3$), 5.11 (d, $^4J_{P,H}$ = 1.8 Hz, 1 H, HC=C), 7.64 ($m_c$, 5 H, Ph), 7.70 ($m_c$, 3 H, Ph), 7.89 ($m_c$, 7 H, Ph), $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 2.7 (d, $^3J_{P,C}$ = 1.9 Hz, $SiMe_3$), 3.1 (d, $^3J_{P,C}$ = 2.7 Hz, $SiMe_3$), 21.1 [s, *C*H$Si(Me_3)_2$], 50.3 (s, $OCH_3$), 52.1 (s, $OCH_3$), 52.2 (s, $OCH_3$), 53.0 (s, $OCH_3$), 61.2 (d, $^1J_{P,C}$ = 116.2 Hz, *C*$PPh_3$), 108.3 (dd, $^3J_{P,C}$ = 7.4, $^3J_{P,C}$ = 17.6 Hz, H*C*C*C*$PPh_3$), 123.9 (d, $^1J_{P,C}$ = 91.2 Hz, *ipso*-Ph), 129.0 (d, $^3J_{P,C}$ = 12.5 Hz, *meta*-Ph), 132.6 (d, $^4J_{P,C}$ = 3.0 Hz, *para*-Ph), 133.8 (d, $^2J_{P,C}$ = 9.7 Hz, *ortho*-Ph), 145.6 (d, $^2J_{P,C}$ = 28.7 Hz, PC*C*), 149.2 (d, $^2J_{P,C}$ = 9.6 Hz, HC*C*C$PPh_3$), 157.6 (s, PNC), 162.2 (d, $^1J_{P,C}$ = 12.6 Hz, P*C*C), 163.2 (d, $^3J_{P,C}$ = 13.1 Hz, *C*$O_2$Me), 164.5 (d, $^2J_{P,C}$ = 14.8 Hz, *C*$O_2$Me), 167.1 (d, $^2J_{P,C}$ = 15.1 Hz, *C*$O_2$Me), 168.9 (d, $^3J_{P,C}$ = 14.6 Hz, *C*$O_2$Me), 197.1 (d, $^2J_{P,C}$ = 6.8 Hz, *cis*-CO), 199.4 (d, $^2J_{P,C}$ = 22.4 Hz, *trans*-CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 102.8 (s, $^1J_{P,W}$ = 241.3 Hz), 18.7 (s). UV/Vis ($CH_3CN$): λ (lg ε) = 230 (4.91), 242 (4.75), 260 (4.40), 284 (4.08), 324 (4.08), 428 (3.84), 478 (4.23), 500 (4.28), 558 (3.81). IR (KBr): $\tilde{\nu}$ = 2068 (s, CO), 1983 (vs, CO), 1930 (s, CO), 1731 (vs, $CO_2$), 1721 (vs, $CO_2$), 1675 $cm^{-1}$ (vs, $CO_2$). MS (pos. FAB, *m*-NBA, $^{184}W$): *m*/*z* = 1100 (7) $[M + H]^+$, 776 (100) $[M + H - W(CO)_5]^+$. $C_{44}H_{47}NO_{13}P_2Si_2W$: calcd. C 48.05, H 4.31, N 1.27; found C 47.09, H 4.35, N 1.30.

**{2-[Bis(trimethylsilyl)methyl]-3,4-bis(methoxycarbonyl)-5-[(triphenylphosphonio)imido]-2*H*-1,2-azaphosphole-κ*P*}pentacarbonyltungsten(0) (8g):** Yield 610 mg (64%); m.p. 68 °C (decomp.). $^1H$ NMR ($CDCl_3$): δ = 0.01 (s, 9 H, $SiMe_3$), 0.06 (s, 9 H, $SiMe_3$), 0.94 [d, $^2J_{P,H}$ = 5.7 Hz, 1 H, C*H*($SiMe_3$)$_2$], 3.88 (s, $OCH_3$), 4.02 (s, $OCH_3$), 7.48 ($m_c$, 5 H, Ph), 7.58 ($m_c$, 3 H, Ph), 7.79 ($m_c$, 7 H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 2.8 (d, $^3J_{P,C}$ = 1.8 Hz, $SiMe_3$), 3.0 (d, $^3J_{P,C}$ = 2.9 Hz, $SiMe_3$), 20.8 [s, *C*H($SiMe_3$)$_2$], 52.2 (s, $OCH_3$), 52.5 (s, $OCH_3$), 127.8 (d, $^1J_{P,C}$ = 101.4 Hz, *ipso*-Ph), 128.8 (d, $^3J_{P,C}$ = 12.5 Hz, *meta*-Ph), 132.4 (d, $^4J_{P,C}$ = 2.9 Hz, *para*-Ph), 133.2 (d, $^2J_{P,C}$ = 10.2 Hz, *ortho*-Ph), 149.0 (dd, $^{2+3}J_{P,C}$ = 25.8,

$^3J_{P,C}$ = 48.1 Hz, PC*C*), 153.3 (s, PNC), 163.1 (d, $^1J_{P,C}$ = 14.0 Hz, P*C*C), 164.9 (d, $^2J_{P,C}$ = 9.3 Hz, *C*O$_2$Me), 166.0 (d, $^3J_{P,C}$ = 14.5 Hz, *C*O$_2$Me), 197.9 (d, $^2J_{P,C}$ = 7.3 Hz, *cis*-CO), 200.0 (d, $^2J_{P,C}$ = 22.7 Hz, *trans*-CO). $^{31}$P{$^1$H} NMR (CDCl$_3$): δ = 85.8 (s, $^1J_{P,W}$ = 249.6 Hz), 14.7 (s). UV/Vis (CH$_3$CN): λ (lg ε) = 230 (4.94), 244 (4.75), 248 (4.68), 254 (4.59), 258 (4.51), 264 (4.35), 330 (3.83), 344 (3.85), 356 (3.81). IR (KBr): ṽ = 2068 (vs, CO), 1984 (vs, CO), 1933 (w, CO), 1909 (w, CO), 1744 (vs, CO$_2$), 1718 (vs, CO$_2$) cm$^{-1}$. MS (EI, $^{184}$W): *m*/*z* = 958 (1) [M]$^{+\cdot}$, 634 (100) [M − W(CO)$_5$]$^{+\cdot}$. MS (neg. CI, $^{184}$W): *m*/*z* = 958 (18) [M]$^{-\cdot}$, 475 (100) [M − C$_7$H$_{19}$Si$_2$ − W(CO)$_5$]$^-$. MS (pos. CI, $^{184}$W): *m*/*z* = 959 (36) [M + H]$^+$, 263 (100) [PPh$_3$ + H]$^+$. C$_{37}$H$_{40}$N$_2$O$_9$P$_2$Si$_2$W: calcd. C 46.35, H 4.21, N 2.92; found C 45.96, H 4.31, N 2.88.

**{2-[Bis(trimethylsilyl)methyl]-4-(ethoxycarbonyl)-5-[(triphenylphosphonio)methylidyl]-2*H*-1,2-azaphosphole-κ*P*}pentacarbonyltungsten(0) (8h):** Yield 220 mg (32%); m.p. 52 °C (decomp.). $^1$H NMR (CDCl$_3$): δ = 0.00 (s, 9 H, SiMe$_3$), 0.16 (s, 9 H, SiMe$_3$), 0.88 [d, $^2J_{P,H}$ = 8.1 Hz, 1 H, C*H*(SiMe$_3$)$_2$], 1.28 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH$_2$C*H*$_3$), 4.23 (q, $^3J_{H,H}$ = 7.1 Hz, 2 H, C*H*$_2$CH$_3$), 4.61 (dd, $^3J_{P,H}$ = 21.3, $^2J_{P,H}$ = 15.7 Hz, 1 H, C*H*PPh$_3$), 7.37 (m$_c$, 5 H, Ph), 7.47 (m$_c$, 3 H, Ph), 7.62 (m$_c$, 7 H, Ph), 8.15 (dd, $^2J_{P,H}$ = 30.8, $^5J_{P,H}$ = 3.3 Hz, 1 H, PCH). $^{13}$C{$^1$H} NMR (CDCl$_3$): δ = 2.2 (d, $^3J_{P,C}$ = 2.6 Hz, SiMe$_3$), 2.5 (d, $^3J_{P,C}$ = 2.2 Hz, SiMe$_3$), 14.2 (s, CH$_2$*C*H$_3$), 24.8 [s, *C*H(SiMe$_3$)$_2$], 47.6 (dd, $^1J_{P,C}$ = 113.3, $^3J_{P,C}$ = 22.7 Hz, *C*HPPh$_3$), 60.9 (s, *C*H$_2$CH$_3$), 127.0 (d, $^1J_{P,C}$ = 91.0 Hz, *ipso*-Ph), 128.7 (d, $^3J_{P,C}$ = 12.2 Hz, *meta*-Ph), 132.2 (d, $^4J_{P,C}$ = 2.8 Hz, *para*-Ph), 133.4 (d, $^2J_{P,C}$ = 10.2 Hz, *ortho*-Ph), 138.5 (dd, $^{2+3}J_{P,C}$ = 16.5, $^3J_{P,C}$ = 44.3 Hz, PC*C*), 158.3 (d, $^1J_{P,C}$ = 8.5 Hz, P*C*C), 164.3 (d, $^3J_{P,C}$ = 17.2 Hz, *C*O$_2$Et), 169.3 (dd, $^{2+3}J_{P,C}$ = 4.8, $^2J_{P,C}$ = 11.3 Hz, PNC), 198.1 (d, $^2J_{P,C}$ = 7.4 Hz, *cis*-CO), 201.4 (d, $^2J_{P,C}$ = 18.8 Hz, *trans*-CO). $^{31}$P{$^1$H} NMR (CDCl$_3$): δ = 75.9 (s, $^1J_{P,W}$ = 237.2 Hz), 15.0 (s). UV/Vis (CH$_3$CN): λ (lg ε) = 228 (4.87), 242 (4.75), 256 (4.56), 300 (4.02), 364 (3.83), 380 (3.80), 416 (3.84), 424 (3.84), 432 (3.83). IR (KBr): ṽ = 2063 (vs, CO), 1970 (vs, CO), 1926 (s, CO), 1899 (s, CO), 1718 cm$^{-1}$ (vs, CO$_2$). MS (EI, $^{184}$W): *m*/*z* = 913 (12) [M]$^{+\cdot}$, 698 (100) [M − C$_7$H$_{19}$Si$_2$]$^+$. C$_{37}$H$_{41}$NO$_7$P$_2$Si$_2$W: calcd. C 48.64, H 4.52, N 1.53; found C 47.90, H 4.60, N 1.56.

**{2-[Bis(trimethylsilyl)methyl]-4-(ethoxycarbonyl)-5-[*trans*-2-(ethoxycarbonyl)-3-(triphenylphosphonio)propenylidyl]-2*H*-1,2-azaphosphole-κ*P*}pentacarbonyltungsten(0) (8i):** Yield 600 mg (66%); m.p. 51 °C (decomp.). $^1$H NMR (CDCl$_3$): δ = 0.00 (s, 9 H, SiMe$_3$), 0.07 (s, 9 H, SiMe$_3$), 0.81 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, C*H*$_3$CH$_2$), 0.99 [d, $^2J_{P,H}$ = 8.2 Hz, 1 H, C*H*(SiMe$_3$)$_2$], 1.35 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH$_2$C*H*$_3$), 3.80 (dd, $^4J_{P,H}$ = 10.2, $^3J_{H,H}$ = 7.1 Hz, 1 H, C*H*CHCPPh$_3$), 3.87 (dd, $^3J_{P,H}$ = 26.2, $^3J_{H,H}$ = 7.2 Hz, 1 H, C*H*CPPh$_3$), 3.88 (dq, $^4J_{P,H}$ = 4.9, $^3J_{H,H}$ = 7.1 Hz, 2 H, Ph$_3$PCCO$_2$C*H*$_2$CH$_3$), 4.30 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, PCCCO$_2$C*H*$_2$CH$_3$), 7.41 (m$_c$, 10 H, Ph), 7.49 (m$_c$, 5 H, Ph), 8.15 (d, $^2J_{P,H}$ = 31.8 Hz, 1 H, PCH). $^{13}$C{$^1$H} NMR (CDCl$_3$): δ = 2.3 (d, $^3J_{P,C}$ = 2.4 Hz, SiMe$_3$), 2.5 (d, $^3J_{P,C}$ = 2.2 Hz, SiMe$_3$), 13.8 (s, CH$_2$*C*H$_3$), 14.1 (s, CH$_2$*C*H$_3$), 21.5 [d, $^1J_{P,C}$ = 3.7 Hz, *C*H(SiMe$_3$)$_2$], 58.8 (s, *C*H$_2$CH$_3$), 61.0 (s, *C*H$_2$CH$_3$), 63.9 (d, $^1J_{P,C}$ = 117.2 Hz, *C*PPh$_3$), 106.2 (dd, $^3J_{P,C}$ = 15.7, $^3J_{P,C}$ = 18.5 Hz, *C*CCPPh$_3$), 124.8 (d, $^1J_{P,C}$ = 102.1 Hz, *ipso*-Ph), 128.9 (d, $^3J_{P,C}$ = 12.4 Hz, *meta*-Ph), 132.5 (d, $^4J_{P,C}$ = 2.7 Hz, *para*-Ph), 133.5 (d, $^2J_{P,C}$ = 9.7 Hz, *ortho*-Ph), 139.6 (d, $^2J_{P,C}$ = 27.6 Hz, PC*C*), 144.4 (d, $^2J_{P,C}$ = 15.5 Hz, C*C*CPPh$_3$), 160.5 (s, P*C*C), 163.6 (d, $^3J_{P,C}$ = 18.3 Hz, PCC*C*O$_2$Et), 167.5 (d, $^2J_{P,C}$ = 14.8 Hz, Ph$_3$PC*C*O$_2$Et), 169.3 (d, $^2J_{P,C}$ = 10.9 Hz, PNC), 197.1 (d, $^2J_{P,C}$ = 7.0 Hz, *cis*-CO), 200.4 (d, $^2J_{P,C}$ = 19.3 Hz, *trans*-CO). $^{31}$P{$^1$H} NMR (CDCl$_3$): δ = 82.8 (s, $^1J_{P,W}$ = 230.2 Hz), 25.3 (s). UV/Vis (CH$_3$CN): λ (lg ε) = 228 (4.86), 236 (4.80), 250 (4.57), 258 (4.44), 276 (4.13), 300 (4.09), 318 (4.10), 470 (4.10), 476 (4.10). IR (KBr): ṽ = 2066 (vs, CO), 1979 (vs, CO), 1929 (s, CO), 1722 (vs, CO$_2$), 1671 cm$^{-1}$ (vs, CO$_2$). MS (pos. FAB, *m*-NBA, $^{184}$W): *m*/*z* = 1012 (38) [M + H]$^+$, 688 (100) [M + H − W(CO)$_5$]$^+$. C$_{42}$H$_{47}$NO$_9$P$_2$Si$_2$W: calcd. C 49.86, H 4.68, N 1.38; found C 49.13, H 4.66, N 1.49.

**{2-[Bis(trimethylsilyl)methyl]-4-(ethoxycarbonyl)-5-[(triphenylphosphonio)imido]-2*H*-1,2-azaphosphole-κ*P*}pentacarbonyltungsten(0) (8j):** Yield 200 mg (22%); m.p. 52 °C (decomp.). $^1$H NMR (CDCl$_3$): δ = 0.00 (s, 9 H, SiMe$_3$), 0.15 (s, 9 H, SiMe$_3$), 0.85 [d, $^2J_{P,H}$ = 7.8 Hz, 1 H, C*H*(SiMe$_3$)$_2$], 1.30 (t, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH$_2$C*H*$_3$), 4.31 (q, $^3J_{H,H}$ = 7.0 Hz, 2 H, C*H*$_2$CH$_3$), 7.36 (m$_c$, 5 H, Ph), 7.45 (m$_c$, 3 H, Ph), 7.72 (m$_c$, 7 H, Ph), 8.03 (dd, $^2J_{P,H}$ = 29.8, $^5J_{P,H}$ = 4.0 Hz, 1 H, PCH). $^{13}$C{$^1$H} NMR (CDCl$_3$): δ = 2.2 [d, $^3J_{P,C}$ = 2.5 Hz, Si(CH$_3$)$_3$], 2.5 [d, $^3J_{P,C}$ = 2.2 Hz, Si(CH$_3$)$_3$], 14.3 (s, CH$_2$*C*H$_3$), 22.3 [s, *C*H(SiMe$_3$)$_2$], 61.0 (s, *C*H$_2$CH$_3$), 128.3 (d, $^1J_{P,C}$ = 100.9 Hz, *ipso*-Ph), 128.6 (d, $^3J_{P,C}$ = 12.4 Hz, *meta*-Ph), 132.2 (d, $^4J_{P,C}$ = 2.7 Hz, *para*-Ph), 133.4 (d, $^2J_{P,C}$ = 10.1 Hz, *ortho*-Ph), 140.3 (d, $^{2+3}J_{P,C}$ = 17.4 Hz, PC*C*), 157.0 (d, $^1J_{P,C}$ = 8.1 Hz, P*C*C), 164.6 (d, $^3J_{P,C}$ = 19.8 Hz, *C*O$_2$Et), 167.0 (s, PNC), 197.5 (d, $^2J_{P,C}$ = 7.2 Hz, *cis*-CO), 200.6 (d, $^2J_{P,C}$ = 19.9 Hz, *trans*-CO). $^{31}$P{$^1$H} NMR (CDCl$_3$): δ = 72.2 (s, $^1J_{P,W}$ = 236.1 Hz), 15.0 (s). UV/Vis (CH$_3$CN): λ (lg ε) = 228 (4.82), 238 (4.76), 244 (4.65), 250 (4.57), 256 (4.47), 268 (4.21), 316 (4.00), 340 (3.92), 364 (3.72). IR (KBr): ṽ = 2066 (s, CO), 1973 (s, CO), 1933 (w, CO), 1902 (w, CO), 1716 cm$^{-1}$ (vs, CO$_2$). MS (EI, $^{184}$W): *m*/*z* = 914 (8) [M]$^{+\cdot}$, 858 (100) [M − 2CO]$^{+\cdot}$.

**X-ray Crystallography:** The structure of **4c** was determined with a Siemens P4 diffractometer, while the structures of **8d**, **8e**, and **8g** were determined with a Bruker SMART 1000 CCD diffractometer. The structures were solved by the heavy atom method and refined anisotropically by full-matrix least-squares on $F^2$.[25] CCDC-168172 (**4c**), -168173 (**8d**), -168174 (**8e**), and -168175 (**8g**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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