1,2-Azaphosphol-5-ene Complexes through Metal-Assisted Synthesis

Rainer Streubel,*,† Hendrik Wilkens,‡ Frank Ruthe,‡ and Peter G. Jones‡

Institut für Anorganische Chemie, Rheinische Friedrich-Wilhelms-Universität Bonn, Gerhard-Domagk-Strasse 1, 53121 Bonn, Germany, and Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Hagenring 30, 38106 Braunschweig, Germany

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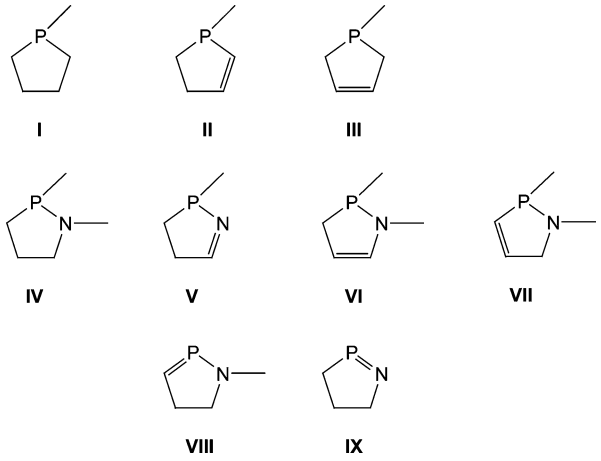
Thermal ring opening of {[2-bis(trimethylsilyl)methyl-3-phenyl-2*H*-azaphosphirene-κP]pentacarbonyltungsten(0)} (**1**) in toluene in the presence of 1-piperidino carbonitrile (**2**) and various mono- and disubstituted alkenes, i.e., ethyl acrylate (**4**), *E*-stilbene (**6**), fumaronitrile (**7**), and maleic anhydride (**10**), was investigated. Special emphasis was placed on the dependence of the regio- and stereoselectivity of the transiently formed nitrilium phosphane-ylide complex **3** on the electronic properties of the alkenes. Three-component reaction of **1**, **2**, and **4** yielded regioselectively a 1:1 mixture of the diastereomeric 4-ethoxycarbonyl-substituted 1,2-azaphosphol-5-ene complexes **5a**,**b**; the constitution of **5a** was unambiguously established by single-crystal X-ray diffraction. Whereas *E*-stilbene (**6**) gave no reaction with complex **3**, fumaronitrile (**7**) reacted with transient **3** to furnish the diastereomeric 1,2-azaphosphol-5-ene complexes **8a**,**b** together with the 2*H*-1,3,2-diazaphosphole complex **9**; the product ratio of 2:1:1 was determined by $^{31}P\{^1H\}$ NMR spectroscopy. Reaction of **1**, **2**, and maleic anhydride (**10**) resulted in a complicated product mixture, whereby the constitution of the spirocyclic complexes **11a,b** (bearing a 1,3,2-oxazaphosphol-3-ene moiety) is based on their NMR data. Further examination showed that the C−O double bond system of **10** did not participate in a [3+2] cycloaddition reaction if the thermal decomposition of complex **1** was carried out in neat benzonitrile, thus showing the preference of the transiently formed *C*-phenyl-substituted nitrilium phosphane-ylide complex **12** for the C−C double bond of **6**: In this case, the bicyclic complexes **13a**,**b** were formed exclusively.

Introduction

Metal-assisted synthesis is an important and well-established concept in organometallic and coordination chemistry, in general. This methodology was introduced to organophosphorus chemistry through the fundamental work of Marinetti and Mathey by demonstrating the selective use of phosphinidenes—if stabilized as terminal phosphinidene complexes—in phosphorus heterocyclic chemistry.[1] Historically the background to the chemistry of P-heterocycles[2] such as phospholanes **I**, phosphol-2-enes **II**, and phosphol-3-enes **III** (Scheme 1) was spurred by the seminal discovery of the McCormack reaction in 1953.[3] Meanwhile, the matured chemistry has led to several applications, e.g., phospholane-based ligands such as DuPHOS in various catalytic industrial processes.[2]

The chemistry of 1,2λ^3-azaphospholanes **IV** started around 1970 by the work of Pudovik[4] and Oehme,[5] who first reported the use of cyclocondensation reactions, which were then used for years as the method of choice. Recently, Malisch achieved the synthesis of functionalized 1,2λ^3-azaphospholanes in the coordination sphere of a transition metal center using hydrophosphination reactions of a primary phosphine iron complex.[6] In contrast to this, 1,2λ^3-azaphospholenes **V**−**IX** (Scheme 1) are still elusive species,[7] because of a significant lack of synthetic strategies for these ring systems. For example, there are only two short communications on complexes having a

Scheme 1. λ^3-Phospholanes (I−III), 1,2λ^3-Azaphospholanes (IV), and 1,2λ^3-Azaphospholenes (V−IX) (lines denote ubiquitous organic substituents)



* Corresponding author. E-mail: r.streubel@uni-bonn.de. Fax: (49)228-739616. Tel: (49)228-735345.
† Rheinische Friedrich-Wilhelms-Universität Bonn.
‡ Technische Universität Braunschweig.

(1) (a) Reviews: Mathey, F.; Tran Huy, N. H.; Marinetti, A. *Helv. Chim. Acta* **2001**, *84*, 2938. (b) Lammertsma, K. *Top. Curr. Chem.* **2003**, *229*, 95.

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(6) Malisch, W.; Klüpfel, B.; Schumacher, D.; Nieger, M. *J. Organomet. Chem.* **2002**, *661*, 95−110.

(7) To the best of our knowledge, ring systems **VIII** and **IX** with a λ^3-phosphorus are experimentally unknown; for derivatives of type **IX** with a λ^5-phosphorus see for example: Schmidpeter, A.; Zeiss, W. *Angew. Chem.* **1971**, *83*, 397−398; *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 396−397. Comment: the λ^3 notation is used exclusively in the Introduction.

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1,2λ^3-azaphosphol-4-ene (**V**),[8,9] some on 1,2λ^3-azaphosphol-3-enes (**VI**)—either free[10] or in a P-ligated fashion[11]—and on 1,2λ^3-azaphosphol-3-enes (**VII**).[12,13] Very recently, the latter, chiral so-called Wilke's-azaphospholene, has received increased attention in catalysis.[14,15]

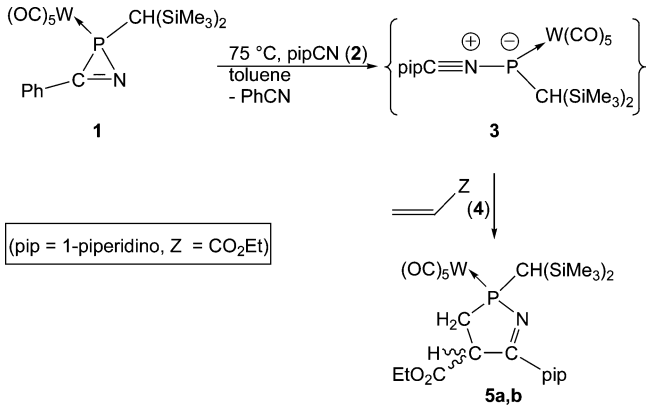
Recently, we had shown that transient nitrilium phosphane-ylides can be used efficiently as new 1,3-dipoles in the chemistry of unsaturated five-membered phosphorus heterocycles, if the phosphorus is coordinated to a transition metal.[16,17] As we are trying to exploit this continuously, we decided to investigate their potential for the synthesis of complexes bearing 1,2λ^3-azaphosphol-5-ene ligands using our three-component reaction protocol for the generation of such complexes and the results obtained earlier by trapping reactions with alkynes.[18] Here, we report on metal-assisted synthesis, X-ray structure, and NMR data of various mono- and bicyclic 1,2λ^3-azaphosphol-5-ene complexes with functional groups. Furthermore, we provide the first strong spectroscopic evidence for C^5-spirocyclic 1,3,2-oxazaphosphol-3-ene complexes.

Experimental Results

First we studied the thermal reaction of 2*H*-azaphosphirene complex **1**[19] in toluene in the presence of 1-piperidino carbonitrile (**2**) and ethyl acrylate (**3**), the latter as an example of an electronically activated and sterically nondemanding monosubstituted alkene. In this case, we obtained a clean [3+2] cycloaddition reaction of the transiently formed nitrilium phosphane-ylide complex **4** to the alkene, thus yielding regioselectively a 1:1 mixture of the diastereomeric 4-ethoxycarbonyl-substituted 1,2λ^3-azaphospholene complexes **5a**,**b** (Scheme 2); no phosphirane complex formation was observed in this case.[18] Although complexes **5a**,**b** could not be separated by column chromatography, their NMR data were recorded (Table 1) and unambiguously assigned on the basis of DEPT experiments; furthermore, the structure of isomer **5a** was established by single-crystal X-ray crystallography.

To our surprise, no reaction occurred between 2*H*-azaphosphirene complexes **1**, **2**, and *E*-stilbene (**6**), thus demonstrating an electronic and/or steric mismatch of **6** with complex **3**. In marked contrast, complexes **1**, **2**, and fumaronitrile (**7**) reacted with transient complex **3** to furnish the diastereomeric 1,2-azaphosphol-5-ene complexes **8a**,**b** together with the 2*H*-1,3,2-diazaphosphole complex **9** in a ratio of 2:1:1 (determined by $^{31}P\{^1H\}$ NMR spectroscopy) (Scheme 3). Complexes **8a** and **9** were isolated in pure form and fully characterized by NMR

Scheme 2. Trapping of Transient 1,3-Dipole Complex 3 with Ethyl Acrylate (4)



spectroscopy; complex **8b** was tentatively assigned on the basis of its $^{31}P\{^1H\}$ NMR spectroscopic data; selected NMR data of **8a** are collected in Table 1 and will be discussed below together with those of other products mentioned hereafter.

Reacting **1**, **2**, and maleic anhydride (**10**) resulted in the formation of spirocyclic 1,3,2-oxazaphosphol-3-ene complexes **11a**,**b** together with two not yet firmly identified complexes[20] in a 1:1:2:4 ratio (Scheme 4). In this case, product separation using column chromatography failed. Nevertheless, the assignment of these NMR data to the C^5-spirocyclic 1,3,2-oxazaphosphol-3-ene complexes **11a**,**b** can be achieved by comparison. as the resonances at 196.5 ppm ($|J(W,P)| = 300.9$ Hz) and at 188.1 ($|J(W,P)| = 309.0$ Hz) are typical for this ring system, as we know from our earlier studies. The only example of a structurally confirmed 1,3,2-oxazaphosphol-3-ene complex, obtained by reaction of complex **3′** (**3′**: NMe_2 instead of 1-piperidino) with DMAD,[19] shows data (191.6 ppm and $|J(W,P)| = 305.9$ Hz) that are in very good accordance with those of **11a**,**b**.

Further studies showed that this reaction can be tuned into a selective one, meaning the C−O double bond system of alkene **10** was discarded if the thermal decomposition of complex **1** was carried out in *neat* benzonitrile, thus promoting the formation of the transient *C*-phenyl-substituted nitrilium phosphane-ylide complex **12**. In this case, exclusively the bicyclic complexes **13a**,**b** were formed, from which **13a** was isolated and fully characterized (Scheme 5; for selected NMR data see Table 1). This result clearly underlines the preference of transient complex **12** for the C−C double bond of **10**.

Studies devoted to obtain nonligated 1,2-azaphosphol-5-enes are currently underway.

Discussion of Selected NMR Spectroscopic Data

The analytical data including elemental analyses, MS spectrometric data, and IR and NMR spectroscopic data readily confirm the molecular structures of all compounds reported herein, which had been separated (unless otherwise stated) and purified by column chromatography at low temperature and

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(16) Review: Streubel, R. *Top. Curr. Chem.* **2002**, *223*, 91−109.
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(20) $^{31}P\{^1H\}$ NMR data: a resonance at 105.4 ppm with a $|J(W,P)|$ of 279.3 Hz and at 114.5 ppm with a $|J(W,P)|$ of 276.8 Hz was recorded; the data could be in accordance with two isomeric 1,2-azaphosphol-5-ene complexes.
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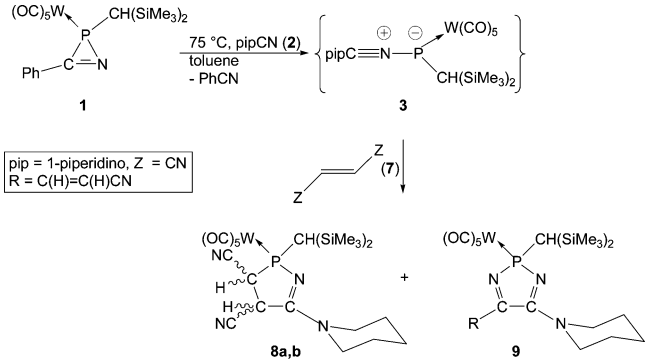
Table 1. Comparison of Selected ^{31}P and ^{13}C NMR Data[a] of 1,2-Azaphosphol-5-ene Complexes 5a,b, 8a, 13a, and 14[8]

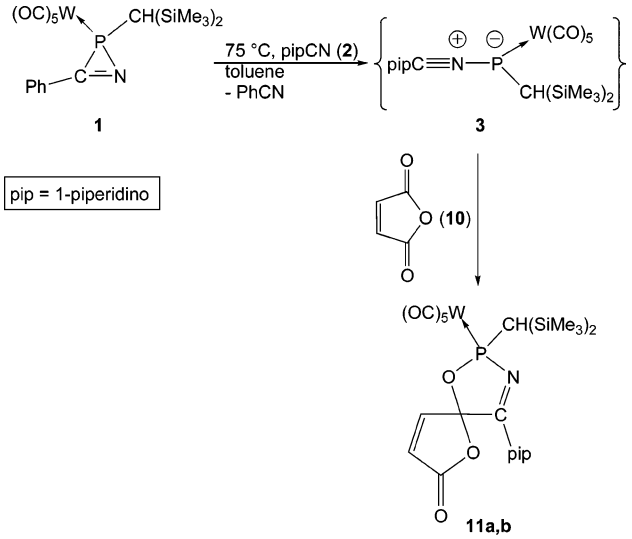
	$\delta(^{31}P)$ ($^1J(P,W)$)	$\delta(^{13}C^3)$ ($^1J(P,C)$)	$\delta(^{13}C^4)$ ($^{(2+3)}J(P,C)$)	$\delta(^{13}C^5)$ ($^{(2+3)}J(P,C)$)
5a	96.4 (260.2)	35.0 (9.0)	50.7 (6.5)	160.2 (nr)
5b	92.7 (256.9)	39.6 (nr)	50.8 (6.2)	161.2 (nr)
8a	119.5 (284.4)	40.5 (nr)	40.9 (nr)	152.8 (8.7)
13a	134.7 (272.3)	59.1 (13.0)	51.1 (mc, br)	164.9 (3.9)
14[8]	158.5 (306.7)	54.1 (27.6)	49.6 (20.6)	144.9 (10.7)

[a] $CDCl_3$, δ [ppm], J [Hz]; only coupling magnitudes; nr = not resolved.

Scheme 3. π-Substrate Competition of Alkene 7 in [3+2] Cycloaddition Reactions with Transient Complex 3

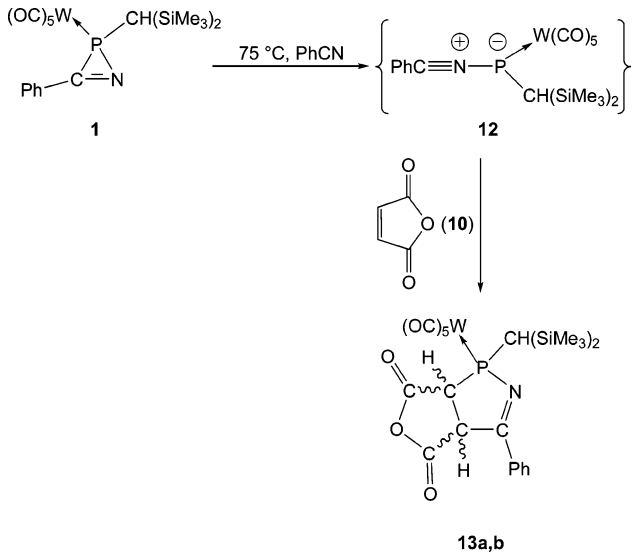


Scheme 4. Formation of C^5-Spirocyclic 1,3,2-Oxazaphosphol-3-ene Complexes 11a,b



subsequent crystallization in most cases. NMR data will be discussed hereafter; for further analytical data see the Experimental Section. The assignment of the resonances to the carbon atoms of the heterocyclic system in 2*H*-1,2-azaphosphol-5-ene complexes is obvious, if the carbon atoms are bonded either to phosphorus or to hydrogen, leading in the first case to significantly greater magnitudes of $|J(P,C)|$ (in general) and/or to characteristic spectra, if DEPT experiments were performed. Furthermore, because of the unambiguously established structure of complex **5a** (for X-ray structure analysis see next chapter), we assign the resonances in the range 160−165 ppm having small $|J(P,C)|$ values to the C^5 atom (Table 1). A comparison of the NMR spectroscopic data of the 2*H*-1,2-azaphosphol-5-ene complexes **5a,b**, **8a**, and **13a** reveals for all derivatives ^{31}P NMR resonances in the range 92−135 ppm, which clearly indicate the presence of electron-withdrawing groups at the neighboring endocyclic carbon centers. That such groups may have a surprisingly strong effect on the phosphorus shielding—and thus the chemical shift—was already observed in the case of the related 3,3′,4,4′-tetracyano-substituted 2*H*-1,2-azaphosphol-5-ene complex **14**, which displayed a resonance at 158.5 ppm.[8] It also became apparent through this study that the substitution pattern also significantly effects the phosphorus−tungsten—and phosphorus−carbon—coupling constants but to an extent hardly foreseeable: the difference between complex **5b** and **14** is about 50 Hz! Another somewhat surprising result was that the resonances of the C^5 atoms would become more shielded if the number of electron-withdrawing groups at C^3 and C^4 increases.

Scheme 5. π-Selective Reaction of Transient Nitrilium Phosphane-ylide Complex 12 with Alkene 10 under Formation of Bicyclic 1,2-Azaphosphol-5-ene Complexes 13a,b



Discussion of Selected X-ray Structural Data of Complex 5a

The molecular structure of the 1,2-azaphosphol-5-ene complex **5a** was confirmed for the solid state by X-ray crystallography (Figure 1). Comparison of the most interesting structural features of the complexes **5a** and **15**[19] (Figure 2) reveals that complex **5a** has a nonplanar five-membered ring system (in contrast to **15**), whereby the phosphorus atom lies 36 pm out of the plane of N(1)−C(6)−C(7)−C(8) (rms deviation 3.6 pm: cf. **15**: $\Delta = 0.362$ Å). The planar environment at N(2) (angle sum 357.3°) (**15**: 359.9°) together with a shortened C(6)−N(2) distance of 134.8(6) pm (**15**: 133.7(4) pm) indicate a $p_\pi-p_\pi$ electron interaction between the lone pair of the nitrogen center of the diorganoamino group and the C−C double bond of the 1,2-azaphosphol-5-ene ring in complex **5a**, very similar to that in **15**.

Interestingly, the endocyclic nitrogen−carbon double-bond distance is shorter in **5a** (128.0(6) pm) than in **15** (130.1(4) pm); there is also a slight difference in the W−P distance, which is 251.06(14) pm in complex **5a** and 247.48(9) pm in complex **15**.

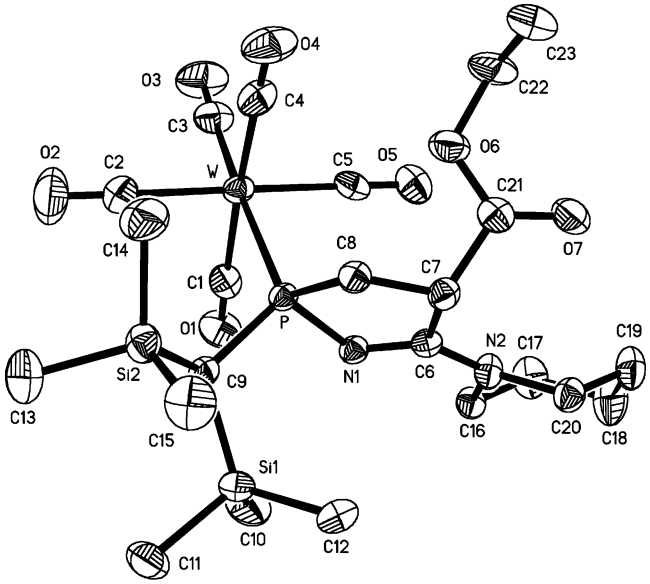
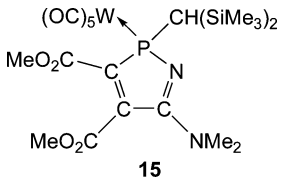


Figure 1. Molecular structure of **5a** (ellipsoids represent 50% probability level; hydrogen atoms are omitted for clarity). Selected bond lengths (pm) and angles (deg): P−N(1) 169.8(4), N(1)−C(6) 128.0(6), C(6)−C(7) 155.5(6), C(7)−C(8) 153.9(2), P−C(8) 181.5(5), P−C(9) 182.6(5), P−W 251.06(14); W−P−C(9) 117.42(16), N(1)−P−C(8) 94.1(2), C(6)−N(1)−P 113.7(3), N(1)−C(6)−C(7) 117.8(4), C(6)−C(7)−C(8) 105.6(4), C(7)−C(8)−P 105.1(3).



15

Figure 2. Complex **15**.[19]

Conclusions

Our investigations of the thermolysis of the 2*H*-azaphosphirene complex **1** in toluene in the presence of piperidino nitrile and various, electronically different alkenes (1) led to new mono- and bicyclic 1,2-azaphosphol-5-ene derivatives with functional groups, (2) revaled a significant effect of the *C*-substituent of transiently generated nitrilium phosphane-ylide complexes **3** and **12** and the alkene substitution pattern on the reaction course, whereby (3) complex **3** tended to avoid sterically congested ring systems and/or is significantly less π-selective than complex **12**. In total, it provides further insight into the chemistry of these phosphorus-containing 1,3-dipoles.

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 having intensities of more than 20% are given. 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 gas chromatograph. All products were separated by column chromatography at low temperature. The κP notation in the nomenclature is intended to differentiate between P- and N-coordination of the appropriate heterocycle to the metal.

{**Pentacarbonyl[2-bis(trimethylsilyl)methyl-4-ethoxycarbonyl-5-(1-piperidino)-1,2-azaphosphol-5-ene-κP]tungsten(0)**} **(5a,b).** 2*H*-Azaphosphirene tungsten complex **1** (0.62 g, 1 mmol) was dissolved in 3.0 mL of toluene together with 0.2 mL of 1-piperidino nitrile (2 mmol), and 2 mmol of the alkene **4** was added. 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 afforded the products (SiO_2, 10 × 2 cm, −20 °C; petrol ether (40/60)/diethyl ether 95:5); complex **5a** was crystallized from *n*-pentane at −20 °C.

Yield: 430 mg (62%) of a pale red solid. Mp: 112 °C (dec). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 2.5 (d, ^3J(P,C) = 1.2 Hz, $SiMe_3$), 2.6 (s, $SiMe_3$), 2.7 (s, $SiMe_3$), 2.9 (d, ^3J(P,C) = 1.7 Hz, $SiMe_3$), 14.1 (s, CH_2CH_3), 14.2 (s, CH_2CH_3), 22.3 (s, $NCH_2CH_2CH_2$), 22.4 (s, $NCH_2CH_2CH_2$), 25.6 (s br, $NCH_2CH_2CH_2$), 28.1 (d, ^1J(P,C) = 3.5 Hz, $CH(SiMe_3)_2$), 29.8 (s, $CH(SiMe_3)_2$), 35.0 (d, ^1J(P,C) = 9.0 Hz, PCH_2), 39.6 (m_c, PCH_2), 48.0 (s br, $NCH_2CH_2CH_2$), 50.7 (d, $^{(2+3)}J$(P,C) = 6.5 Hz, PCH_2CH), 50.8 (d, $^{(2+3)}J$(P,C) = 8.2 Hz, PCH_2CH), 61.9 (s, CH_2CH_3), 62.2 (s, CH_2CH_3), 160.2 (s, PN*C*), 161.2 (s, PN*C*), 170.2 (d, ^3J(P,C) = 4.3 Hz, CO_2Et), 171.4 (d, ^3J(P,C) = 8.1 Hz, CO_2Et), 198.2 (d, ^2J(P,C) = 7.9 Hz, *cis*-CO), 198.5 (d, ^2J(P,C) = 7.8 Hz, *cis*-CO), 201.3 (d, ^2J(P,C) = 22.1 Hz, *trans*-CO), 202.0 (d, ^2J(P,C) = 22.8 Hz, *trans*-CO). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 92.7 (s, ^1J(P,W) = 256.9 Hz), 96.4 (s, ^1J(P,W) = 260.2 Hz). IR (KBr): $\tilde{\nu}$ 2067 (s), 1978 (s), 1903 (vs, br) cm^{-1} (CO); 1729 (s) cm^{-1} (CO_2); 1567 (vs, sh), cm^{-1} (C═N). MS (70 eV, EI), (^{184}W); *m*/*z* (%): 724 (10) [M$^{+\bullet}$], 668 (100) [(M − 2 CO)$^{+\bullet}$], 584 (65) [(M − 5 CO)$^{+\bullet}$], 73 (20) [$(SiMe_3)^{+\bullet}$]. Anal. Calcd for $C_{22}H_{35}N_2O_7PSi_2W$ (724.5): C 38.13, H 5.15, N 3.87. Found: C 38.19, H 5.21, N 3.82.

{**Pentacarbonyl[2-bis(trimethylsilyl)methyl-3,4-cyano-5-(1-piperidino)-1,2-azaphosphol-5-ene-κP]tungsten(0)**} **(8a).** 2*H*-Azaphosphirene tungsten complex **1** (0.62 g, 1 mmol) was dissolved in 3.0 mL of toluene together with 0.2 mL of 1-piperidino nitrile (2 mmol), and 2 mmol of the alkene **6** was added. 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 afforded the products (SiO_2, 10 × 2 cm, −20 °C; petrol ether (40/60)/diethyl ether 90:10).

Yield: 150 mg (22%) of a pale brown, amorphous solid. Mp: 188 °C (dec). ^{1}H NMR ($CDCl_3$): δ 0.26 (s, 9 H, $SiMe_3$), 0.37 (d, ^4J(P,H) = 0.2 Hz, 9 H, $SiMe_3$), 1.69 (s br, 6 H, $NCH_2CH_2CH_2$), 3.54 (m_c, 4 H, $NCH_2CH_2CH_2$), 3.78 (dd, ^3J(P,H) = 6.2 Hz, ^3J(H,H) = 7.4 Hz, 1 H, PCHC*H*), 4.22 (dd, ^2J(P,H) = 2.0 Hz, ^3J(H,H) = 7.4 Hz, 1 H, PC*H*CH). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 2.8 (s, $SiMe_3$), 2.8 (d, ^3J(P,C) = 2.2 Hz, $SiMe_3$), 24.0 (s, $NCH_2CH_2CH_2$), 25.6 (s br, $NCH_2CH_2CH_2$), 31.1 (d, ^1J(P,C) = 9.1 Hz, P*C*HCH), 40.5 (s, $CH(SiMe_3)_2$), 40.8 (s, PCH*C*H), 48.9 (s br, $NCH_2CH_2CH_2$), 115.4 (d, ^2J(P,C) = 4.1 Hz, CN), 117.6 (d, ^3J(P,C) = 6.9 Hz, *C*N), 152.8 (d, $^{(2+3)}J$(P,C) = 8.7 Hz, PN*C*), 197.0 (d, ^2J(P,C) = 7.8 Hz, ^1J(C,W) = 126.3 Hz, *cis*-CO), 199.4 (d, ^2J(P,C) = 17.4 Hz, t*rans*-CO). ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 119.5 (s, ^1J(P,W) = 284.4 Hz). IR (KBr): $\tilde{\nu}$ 2071 (s), 1987 (s), 1944 (vs), 1930 (vs) cm^{-1} (CO); 1598 (s br), cm^{-1} (C═N). MS (70 eV, EI), (^{184}W); *m*/*z* (%): 704 (20) [M$^{+\bullet}$], 646 (25) [(M − 2 CO)$^{+\bullet}$], 590 (30) [(M − 4 CO)$^{+\bullet}$], 562 (100) [(M − 5 CO)$^{+\bullet}$], 73 (50) [$(SiMe_3)^{+\bullet}$]. Anal. Calcd for $C_{22}H_{35}N_4O_7PSi_2W$ (702.5): C 37.61, H 4.45, N 7.98. Found: C 36.55, H 4.87, N 6.95. HR-EI-MS (^{182}W): ber. 700.1080; gef. 700.1046 ± 2.

8b: ^{31}P{^{1}H} NMR ($CDCl_3$): δ 118.1 ppm, ^1J(P,W) = 283.2 Hz.

{**Pentacarbonyl[2-bis(trimethylsilyl)methyl-4-(2-cyanoethenyl)-5-(1-piperidino)-2*H*-1,3,2-diazaphosphole-κP]}tungsten(0)**} **(9).** Yield: 105 mg (15%) of a red oil. ^{1}H NMR ($CDCl_3$): δ 0.16 (s, 9 H, $SiMe_3$), 0.21 (s, 9 H, $SiMe_3$), 1.38 (d, ^2J(P,H) = 6.8 Hz, 1 H, $CH(SiMe_3)_2$), 1.70 (s br, 6 H, $NCH_2CH_2CH_2$), 3.42 (m_c, 4 H, NCH_2-

CH_2CH_2), 6.50 (d, ^3J(H,H) = 16.0 Hz, 1 H, C*H*), 7.30 (d, ^3J(H,H) = 16.0 Hz, 1 H, C*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 2.4 (d, ^3J(P,C) = 2.3 Hz, $SiMe_3$), 2.6 (d, ^3J(P,C) = 2.1 Hz, $SiMe_3$), 24.1 (s, *C*H-($SiMe_3$)$_2$, $NCH_2CH_2CH_2$), 25.5 (s, $NCH_2CH_2CH_2$), 50.2 (s, NCH_2-CH_2CH_2), 108.3 (d, ^4J(P,C) = 1.8 Hz, NCH*C*H), 116.3 (s, *C*N), 140.9 (d, ^3J(P,C) = 23.0 Hz, N*C*HCH), 158.8 s, PN*C*N), 160.7 (d, $^{(2+3)}J$(P,C) = 6.1 Hz, PN*C*C), 196.9 (d, ^2J(P,C) = 7.2 Hz, *cis*-*C*O), 199.8 (d, ^2J(P,C) = 24.0 Hz, *trans*-*C*O). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 155.0 (s, ^1J(P,W) = 257.5 Hz). Anal. Calcd for $C_{19}H_{29}N_3O_5PSi_2W$ (650.4): C 35.08, H 4.49, N 6.46. Found: C 35.49, H 4.62, N 6.35.

{**Pentacarbonyl[2-bis(trimethylsilyl)methyl-5-(1-piperidino)-1,6-dioxa-3-aza-2-phosphaspiro[4.4]-3,3-diene-7-on-κP]tungsten-(0)**} **(11a,b).** 2*H*-Azaphosphirene tungsten complex **1** (0.62 g, 1 mmol) was dissolved in 3.0 mL of toluene together with 0.2 mL of 1-piperidino nitrile (2 mmol), and 2 mmol of the alkene **7** was added. After heating the solution at 75 °C for 1.5 h with slow stirring, the solution was evaporated to dryness. Neither low-temperature chromatography nor extraction of the residue afforded the products.

$^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 188.1 (^1J(P,W) = 309 Hz) and 196.5 (^1J(P,W) = 300.9 Hz).

{**Pentacarbonyl[*P*-bis(trimethylsilyl)methyl-8-phenyl-1,5,4-oxazaphosphabicyclo[3.3]oct-5-en-2,8-dione-κP]tungsten(0)**} **(13a,b).** 2*H*-Azaphosphirene tungsten complex **1** (0.62 g, 1 mmol) was dissolved in 3.0 mL of benzonitrile, and 2 mmol of the alkene **10** was added. After heating the solution at 75 °C for 1.5 h with slow stirring, the solution was evaporated to dryness. In this case, low-temperature column chromatography failed and only extraction of the residue with small amounts of *n*-pentane at 0 °C yielded **13a**.

13a: Yield: 275 mg (40%) of a pale brown, amorphous solid. Mp: 191 °C. ^1H NMR ($CDCl_3$): δ 0.12 (s, 9 H, $SiMe_3$), 0.46 (s, 9 H, $SiMe_3$), 1.71 (d, ^2J(P,H) = 10.0 Hz, 1 H, C*H*($SiMe_3$)$_2$), 4.27 (dd, ^3J(H,H) = 5.2 Hz, ^3J(P,H) = 10.0 Hz, 1 H, PCC*H*),), 5.45 (dd, ^3J(H,H) = 5.2 Hz, ^3J(P,H) = 10.0 Hz, 1 H, PC*H*), 7.59 (m_c, 3 H, C$H_{aromat.}$), 8.08 (m_c, 2 H, C$H_{aromat.}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 2.4 (d, ^3J(P,C) = 2.3 Hz, $SiMe_3$), 2.5 (s, $SiMe_3$), 28.5 (s, *C*H-($SiMe_3$)$_2$), 51.1 (m_c, PCH*C*H), 59.1 (d, ^1J(P,C) = 13.0 Hz, P*C*HCH), 129.1 (s, *C*H$_{aromat.}$), 130.9 (s, *C*H$_{aromat.}$), 131.5 (d, ^3J(P,C) = 18.3 Hz, *C*$_{aromat.}$), 133.6 (s, *C*H$_{aromat.}$), 164.6 (d, $^{(2+3)}J$(P,C) = 14.3 Hz, PN*C*), 164.9 (d, ^2J(P,C) = 14.3 Hz, *C*O_2), 167.9 (d, ^3J(P,C) = 3.9 Hz, *C*O_2), 195.9 (d, ^2J(P,C) = 7.1 Hz, ^1J(P,W) = 126.2 Hz, *cis*-*C*O), 198.6 (d, ^2J(P,C) = 27.8 Hz, *trans*-*C*O). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 134.7 (s, ^1J(P,W) = 272.3 Hz). IR (KBr): $\tilde{\nu}$ 2075 (vs), 1985 (vs), 1931 (vs, sh) cm^{-1} (CO); 1795 (m), 1778 (s) cm^{-1} (CO_2); 1596 (m, sh), 1571 (m) cm^{-1} (C═N). ***MS*** (70 eV, EI), (^{184}W); *m*/*z* (%): 715 (25) [$M^{+\bullet}$], 687 (70) [$(M - CO)^{+\bullet}$], 659 (30) [$(M - 2\ CO)^{+\bullet}$], 587 (55) [$(M - CO - SiMe_3)^{+\bullet}$], 531 (65) [$(M - 3\ CO - SiMe_3)^{+\bullet}$], 503 (65) [$(M - 4\ CO - SiMe_3)^{+\bullet}$], 73 (100) [$(SiMe_3)^{+\bullet}$]. Anal. Calcd for $C_{23}H_{26}NO_8PSi_2W$ (715.5): C 38.61, H 3.66, N 1,-96. Found: C 38.55, H 3.67, N 1.93.

13b: $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 122.0 (s, ^1J(P,W) = 271.6 Hz).

X-ray Crystallographic Analysis. Structure determination of **5a**: Crystal data: $C_{23}H_{37}N_2O_7PSi_2W$, M = 724.55, $P2_1/n$, a = 1004.9(3) pm, b = 1710.5(4) pm, c = 1762.3(10) pm, β = 95.50-(4)°, V = 3.015 nm^3, Z = 4, d_{calc} = 1.596 M/m^3, μ = 4.0 mm^{-1}, T = 143 K. A yellow prism (0.60 × 0.45 × 0.30 mm) was used to record 7116 intensities ($2\theta_{max}$ 6−50°) using monchromated Mo Kα radiation on a Stoe STADI-4 diffractometer. After absorption correction (psi-scans) 5306 were unique (R_{int} = 0039) and were used for all calculations (program SHELXL-97).[21] Hydrogen atoms were refined as rigid methyl groups or with a riding model. The final $wR(F^2)$ was 0.082, with conventional $R(F)$ 0.033, for 332 parameters and 47 restraints; highest peak 1089, hole −1803 e/nm^3.

Crystallographic data for **5a** (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre under the number CCDC 297491. Copies may be requested free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, England (E-mail: deposit@ccdc.cam.ac.uk).

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Supporting Information Available: Crystallographic data for **5a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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