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Synthesis and Characterization of Some 2*H*-1,4,2-Diazaphosphole-, 2*H*-1,3,2-Diazaphosphole- and 2*H*-1,2-Diazaphosphole-*P*-sulfide Derivatives

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Abstract—Partial decomplexation of 2*H*-1,4,2-diazaphosphole and 2*H*-1,2-azaphosphole complexes is observed upon prolonged heating in benzonitrile; the liberated heterocycles were detected spectroscopically, but could not be isolated. The first 2*H*-1,3,2-diazaphosphole derivative, formed by thermal decomplexation using *o*-xylene and 1,2-bis(diphenylphosphino)ethane, was isolated and characterized. In all three cases, the corresponding heterocyclic P(V)-sulfides were obtained by oxidative decomplexation using elemental sulfur. All products were characterized by NMR and MS spectroscopy and two, additionally, by X-ray diffraction. © 1999 Elsevier Science Ltd. All rights reserved.

Very recently, we reported a new and highly efficient synthetic method for five-membered P-heterocycle complexes, based on thermal ring opening of 2*H*-azaphosphirene complexes **I** in solution; this yields nitrilium phosphane-ylid complexes **II** as intermediates, which can be trapped by a wide variety of different π-systems via [3+2] cycloaddition reactions giving **III** (Scheme 1).[1–3]

We have also shown that the nitrile moiety in **II** is only weakly bonded in most cases, thus giving rise to nitrile/nitrile exchange reactions, which can be used to generate new transient derivatives of **II**.[4,5] In view of the current increasing interest in unsaturated P-heterocycles as ligands in homogenous catalysis,[6] especially those with functional groups that enhance their water solubility,[7] we were interested in liberating the five-membered P-heterocycles from their complexes, which themselves can easily be prepared using our new methodology. Furthermore, because unsaturated P(III)-phospholes with one or two *C*-methyl-carboxylate groups attached to the ring system are accessible only with difficulty,[8–10] we were especially interested in gaining access to functional and non-coordinated derivatives of the 2*H*-1,2-azaphosphole system, which should be closely related to the 1*H*-phosphole system. Furthermore, new heterocyclic P(V)-sulfides should possess an interesting coordination chemistry, and their synthesis was therefore also an aim of this study.

As we have already reported, the thermally induced ring opening of the 2*H*-azaphosphirene complex **1**[11] in benzonitrile gave the two regioisomeric diazaphosphole complexes **3**,**4** in a 6:1 ratio, whereby **3** was isolated in moderate yields and also structurally characterized.[2] We have now observed that exclusively **3** showed partial decomplexation upon prolonged heating in benzonitrile (formation of the benzonitrile–tungsten complex seems to be plausible), thus giving another phosphorus-containing product (approximately 85% according to ^{31}P NMR integration) with a phosphorus NMR resonance at δ 103.2 lacking tungsten satellites. Because of the $\Delta\delta$-value of ca. 25,[12] this resonance provides the first evidence for the 2*H*-1,4,2-diazaphosphole **5**.

Furthermore, heating this product mixture with a slight excess of elemental sulfur furnished the 2*H*-1,4,2-azaphosphole-*P*-sulfide **6** in 23% yield after low-temperature chromatography on Al_2O_3; under these conditions **3** and **5** completely disappeared, whereas complex **4** remained unchanged (Scheme 2). The synthesis and the yield of the 2*H*-1,2-azaphosphole complex **7**[1] was significantly improved (43%) if the thermal reaction of complex **1** with dimethyl acetylenedicarboxylate (DMAD) was carried out in a toluene/benzonitrile mixture, instead of using toluene as reported earlier (5%).[1] Under these reaction conditions, complex **7** also showed partial decomplexation leading to two other as yet uncharacterized products **8** and **9** having phosphorus NMR resonances at δ 85.5 and δ 42.1 (Scheme 3). Once more, because of the $\Delta\delta$-value of ca. 25,[12] the former resonance provides some evidence for the 2*H*-1,2-azaphosphole **8**. 2*H*-1,2-azaphosphole-*P*-sulfide **10**

Keywords: P-ligands; 2*H*-azaphosphirene complexes; azaphospholes; diazaphospholes; decomplexation.

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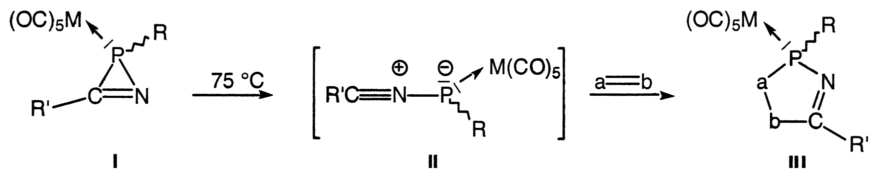
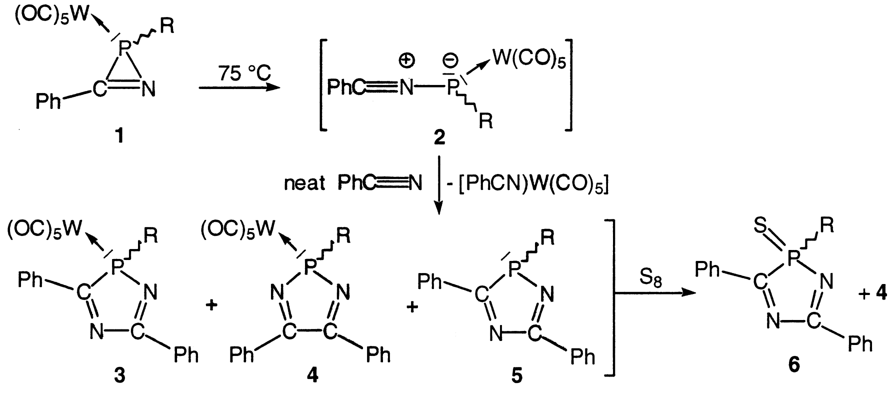
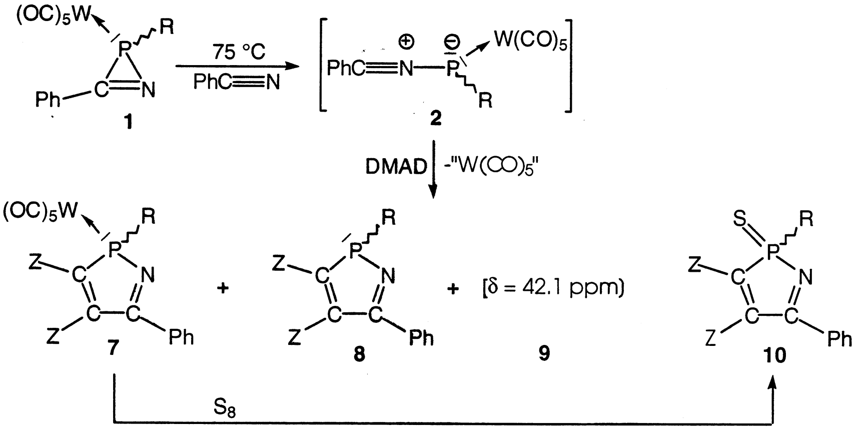


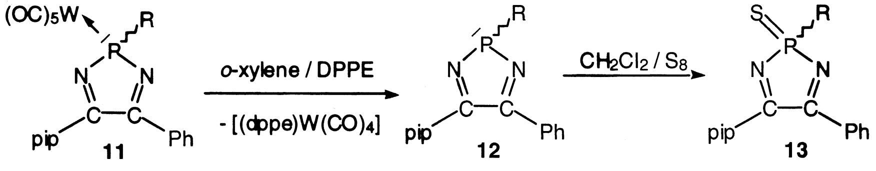
Scheme 1. Trapping of **II** via [3+2] cycloaddition reaction (M=Cr, Mo, W; R,R′=organic substituent).



Scheme 2. Synthesis of 2*H*-1,4,2-diazaphosphole-*P*-sulfide **6** (R=CH(SiMe$_3$)$_2$).



Scheme 3. Improved synthesis of complex **7** and selective formation of **10** by oxidative decomplexation of **7** (R=CH(SiMe$_3$)$_2$, Z=CO$_2$Me).

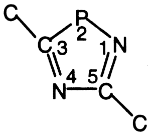


Scheme 4. Decomplexation of **11** and oxidation of 2*H*-1,3,2-diazaphophole **12** with elemental sulfur to **13**.

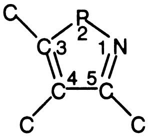
was synthesized using two different routes: (1) heating complex **7** in benzonitrile with elemental sulfur gave compound **10** (65%) and (2) heating complex **7** in benzonitrile resulted in the formation of compound **8**, which was subsequently oxidized with elemental sulfur to give the 2*H*-1,2-azaphosphole-*P*-sulfide **10**.

Using 2*H*-1,3,2-diazaphosphole complex **11**[2] and a slightly modified 1,2-bis(diphenylphosphino)ethane (DPPE)-decomplexation protocol developed by Mathey and co-workers,[9,13] we obtained the 2*H*-1,3,2-diazaphosphole derivative **12** in 75% yield, which was separated from [(dppe)W(CO)$_4$] by low-temperature column chromatography. Derivative **12** showed a clean reaction with elemental sulfur in dichloromethane at ambient temperature to give the corresponding 2*H*-1,3,2-diazaphosphole-*P*-sulfide **13** in 91% yield (Scheme 4). All complexes reported have been characterized by

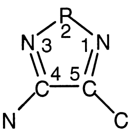
Table 1. Selected NMR data[a],* of 2*H*-1,4,2-diazaphospholes **3**, **5**[2] and **6**, of 2*H*-1,2-azaphospholes **7**,[1] **8** and **10** and of 2*H*-1,3,2-diazaphospholes **11**,[2] **12** and **13**. ([a] CDCl3, δ [ppm], *J* [Hz]; #: not resolved; ×: ^{13}C NMR spectrum not recorded; * atom numbering as denoted in the formulae of the ring systems)



3,5,6



7,8,10



11-13

Comp.	(^{31}P	^{1}J(W,P)	(^{13}C(C^{3})	$^{(2+3)}J$(P,C^{3})	(^{13}C(C^{4})	$^{(2+3)}J$(P,C^{4})	(^{13}C(C^{5})	$^{(2+3)}J$(P,C^{5})
3	110.6	227.8	198.5	22.3	–	–	169.5	5.1
5	103.2	–	×	×	×	×	×	×
6	106.4	–	189.9	26.1	–	–	172.7	#
7	102.8	237.9	142.7	25.9	162.0	1.4	162.7	13.1
8	85.5	–	×	×	×	×	×	×
10	101.0	–	151.0	53.1	161.3	13.8	167.7	#
11	149.9	259.1	#	#	162.3	8.8	165.3	#
12	140.2	–	–	–	163.4	7.1	164.7	7.5
13	123.4	–	–	–	163.6	19.9	167.7	#

heteronuclear NMR experiments, IR and mass spectrometry (see Experimental section); selected NMR data of the complexes are collected in Table 1 and will be discussed hereafter; for X-ray data see the Experimental section.

A comparison of selected NMR data of the various heterocyclic ring systems of **3–8** and **10–13** (Table 1) shows sp^2-carbon atom resonances in the range of 160–170 ppm for **7**, **10–13**; exclusively for **3** and **6** the resonance of the C^3-atoms is significantly deshielded; in the case of compounds **11–13** the assignment of the resonances to ring carbon atoms C^4 and C^5 has been made tentatively.

All carbon atoms directly bonded to phosphorus display carbon–phosphorus coupling constants with magnitudes greater than 20 Hz, which in all cases increases in going from the metal-coordinated to the non-coordinated or the P(V)-sulfide compounds. An analogous trend can be observed for the coupling constants of the C^4- and C^5-carbon atoms.

The EI MS spectra of the heterocyclic P(V)-sulfides **6** and **10** showed that, after the ionization process, they undergo preferential cleavage of one or two exocyclic ring bonds, thus yielding fragment ions in 100% relative intensities. In contrast, in the case of the 2*H*-1,3,2-diazaphosphole-*P*-sulfide **13**, the molecule radical cation, *m*/*z* 437, preferentially loses sulfur to give *m*/*z* 403 (100% relative intensity).

The molecular structures of the complexes **6** and **10** were confirmed in the solid state by X-ray crystallography (Figs. 1 and 2); for further details of crystal data and structure refinement see the Experimental section.[14]

Comparison of 2*H*-1,4,2-diazaphosphole-*P*-sulfide **6** (Fig. 1) and 2*H*-1,2-azaphosphole-*P*-sulfide **10** (Fig. 2) with their tungsten complexes **3**[2] and **7**[1] reveals only slightly

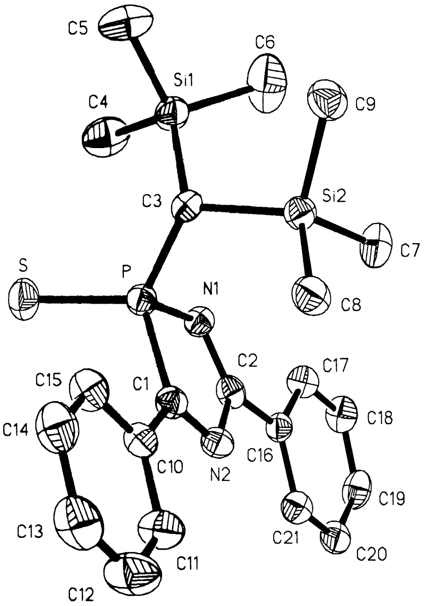


Figure 1. Molecular structure of **6** in the crystal (hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: P–S 1.944(2), P–N(1) 1.695(3), N(1)–C(2) 1.283(3), C(2)–N(2) 1.443(5), N(2)–C(1) 1.280(5), C(1)–P 1.853(4); N(1)–P–C(1) 91.4(2), C(3)–P–S 117.31(14), N(1)–P–S 116.20(13), C(1)–P–S 108.74(14).

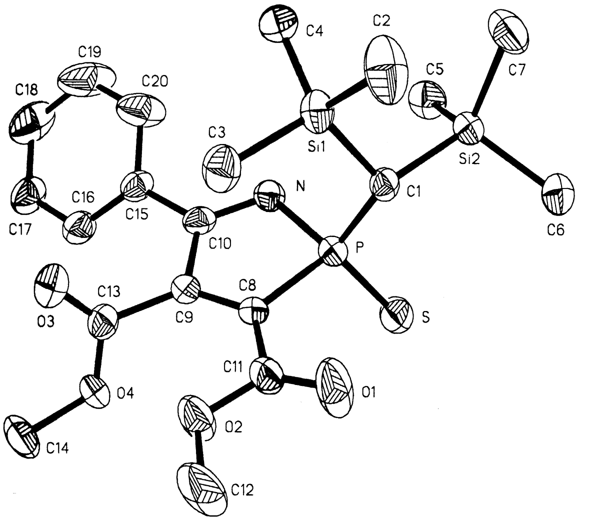
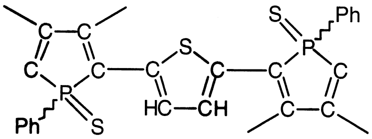


Figure 2. Molecular structure of **10** in the crystal (hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: P–S 1.9417(10), P–N 1.708(2), N–C(10) 1.298(3), C(10)–C(9) 1.509(3), C(9)–C(8) 1.334(3), C(1)–P 1.820(3); N–P–C(8) 93.54(11), C(1)–P–S 117.15(8), N–P–S 112.99(8), C(8)–Ps–S 110.58(9).

shortened endocyclic phosphorus–carbon and phosphorus–nitrogen bonds, but significantly shortened exocyclic phosphorus–carbon bonds: **6**: 1.781(4) Å (vs. 1.844(7) Å (**3**)[2]) and **10**: 1.788(2) Å (vs. 1.845(5) Å (**7**)).[1] In both cases, this is combined with a widening of the N–P–C angle in **6**: 91.4(2)° (vs. 90.2(3)° (**3**)[2]) and in **10**: 93.5(4)(5)° (vs. 91.8(2)° (**7**)).[1] The phosphorus–sulfur bond lengths in **6** and **10** are similar (1.944(2) and 1.9417(19) Å), which seems to be also a common feature for phosphole-*P*-sulfides such as **14** (1.945(1) Å).[15] Both ring systems of **6** and **10** are almost planar; the mean deviation is 0.014 Å for **6** and 0.029 Å for **10**.



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The angle sums at the phosphorus atoms in **6** and **10** are 312° and 314°, respectively, ($\Sigma°$ (P_{PR3}) regards exclusively the C–P–C, C–P–N and N–P–C angles); values, which are almost constant and only slightly different to those of **3** and **7** (**3**: 311° and **7**: 306°).

Experimental

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 ext. tetramethylsilane (^{1}H, ^{13}C) and 85% H_3PO_4 (^{31}P). Mass spectra were recorded on a Finnigan Mat 8430 (70 eV); apart from the *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. The κP-notation in the nomenclature is intended to differentiate between P- and N-coordination of the appropriate heterocycle to the metal.

2-Bis(trimethylsilyl)methyl-3,5-diphenyl-2*H*-1,4,2-diazaphosphole-*P*-sulfide (6). 0.9 g 2*H*-azaphosphirene tungsten complex **1**[11] (1.5 mmol) were dissolved in 5 mL benzonitrile and heated at 75°C for 2.5 h with slow stirring. After adding 0.04 g sulfur to the reaction mixture and heating at 75°C for 1 h, benzonitrile was removed in vacuo and the product separated by low-temperature column chromatography (SiO_2, −20°C, petrolether (40–60°C)/diethylether 97.5:2.5). Evaporation of the solvents of the first fraction and crystallization from pentane at −20°C yielded **6**: orange crystals (165 mg, 23%); mp 145°C (decomp.); IR (KBr) $\tilde{\nu}$ 1598 (s), 1589 (s), 1558 (vs), 1514 (s) cm^{-1} (C=N); ^{1}H NMR ($CDCl_3$) (−0.13 (s, 9H, $SiMe_3$), 0.55 (s, 9H, $SiMe_3$), 1.20 (d, $^{2}J(P,H)=17.9$ Hz, 1H, $CH(SiMe_3)_2$), 7.54 (m_c, 3H, $CH_{aromatic}$), 7.58 (m_c, 3H, $CH_{aromatic}$), 8.51 (m_c, 2H, $CH_{aromatic}$), 8.56 (m_c, 2H, $CH_{aromatic}$); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 1.6 (d, $^{3}J(P,C)=3.4$ Hz, $SiMe_3$), 3.7 (d, $^{3}J(P,C)=2.4$ Hz, $SiMe_3$), 23.2 (d, $^{1}J(P,C)=25.1$ Hz, $CH(SiMe_3)_2$), 128.4 (d, $^{2}J(P,C)=20.6$ Hz, $C_{aromatic}$), 128.7 (s, $CH_{aromatic}$), 129.1 (s, $CH_{aromatic}$), 131.2 (d, $^{3}J(P,C) = 1.5$ Hz, $CH_{aromatic}$), 131.4 (s, $CH_{aromatic}$), 132.8 (d, $^{3}J(P,C)=17.5$ Hz, $C_{aromatic}$), 133.6 (s, $CH_{aromatic}$), 133.8 (s, $CH_{aromatic}$), 172.7 (s, PN*C*), 189.9 (d, $^{1}J(P,C)=26.1$ Hz, P*C*N); $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) δ 106.4 (s); MS (70 eV, EI, ^{32}S) *m/z* 458 (20) [$M^{+\cdot}$], 222 (100) [$(M-Ph–CH(SiMe_3)_2)^{+}$], 207 (85) [$(HCNPCH(SiMe_3)_2)^{+}$], 176 (30) [$(PhCNPS)^{+\cdot}$], 73 (80) [$(SiMe_3)^{+}$]. Anal. Calcd. for $C_{21}H_{29}N_2PSSi_2$: C, 58.88; H, 6.77; N, 6.54; S, 7.48; found: C, 58.82; H, 6.71; N, 6.47; S, 6.71.

{Pentacarbonyl[2-bis(trimethylsilyl)methyl-3,4-bis(methoxycarbonyl)-5-phenyl-2*H*-1,2-azaphosphole-κ*P*]-tungsten(0)} (7). 2*H*-azaphosphirene tungsten complex **1**[11] (1.5 g, 2.4 mmol), dissolved in toluene (7.5 mL) and benzonitrile (2 mL), and dimethyl acetylenedicarboxylate (0.6 mL, 5 mmol) were 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 column chromatography (SiO_2, −20°C, 10 × 4 cm, hexane/diethyl ether 90/10). Evaporation of the second fraction yielded **7**: dark red crystals (680 mg, 43%); 121°C (decomp.); IR (KBr) $\tilde{\nu}$ 2073 (s), 1992 (s), 1953 (vs), 1926 (vs), 1913 (vs) cm^{-1} (CO); 1745 (s), 1719 (s) cm^{-1} (CO_2); 1507 (w), 1491 (w) cm^{-1} (C=N); ^{1}H NMR ($CDCl_3$) δ 0.15 (s, 9H, $SiMe_3$), 0.39 (s, 9H, $SiMe_3$), 1.35 (d, $^{2}J(P,H)=2.4$ Hz, 1H, $CH(SiMe_3)_2$), 3.87 (s, 3H, OCH_3), 3.92 (s, 3H, OCH_3), 7.50 (m_c, 3H; $CH_{aromatic}$), 7.79 (m_c, 2H, $CH_{aromatic}$); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 2.6 (d, $^{3}J(P,C)=1.9$ Hz, $SiMe_3$), 3.2 (d, $^{3}J(P,C)=2.4$ Hz, $SiMe_3$), 18.9 (s, $CH(SiMe_3)_2$), 53.0 (s, OCH_3), 53.2 (s, OCH_3), 128.4 (s, $C_{aromatic}$), 128.8 (s, $C_{aromatic}$), 131.7 (s, $C_{aromatic}$), 134.4 (d, $^{3}J(P,C)=16.6$ Hz, $C_{aromatic}$), 142.7 (d, $^{1}J(P,C)=25.9$ Hz, P*C*C), 162.0 (d, $^{(2+3)}J(P,C)=1.4$ Hz, PC*C*), 162.7 (d, $^{3}J(P,C)=13.1$ Hz, CO_2Me), 165.1 (d, $^{3}J(P,C)=14.2$ Hz, CO_2Me), 167.7 (d, $^{(2+3)}J(P,C)=11.5$ Hz, PN*C*), 196.7 (d, $^{2}J(P,C)=6.5$ Hz, *cis*-CO), 198.0 (d, $^{2}J(P,C)=23.1$ Hz, *trans*-CO); $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) (102.8 (s, $^{1}J(P,W)=237.9$ Hz); MS (70 eV, EI, ^{184}W); *m/z* 759 (4) [$M^{+\cdot}$], 647 (50) [$(M-4CO)^{+\cdot}$], 631 (100) [$(M-3CO)^{+\cdot}$], 603 (40) [$(M-4CO)^{+\cdot}$], 575 (35) [$(M-5CO)^{+\cdot}$], 73 (100) [$(SiMe_3)^{+\cdot}$]. Anal. Calcd. for $C_{25}H_{30}NO_9PSi_2W$: C, 39.54; H, 3.98; N, 1.84; found: C, 39.73; H, 3.85; N, 1.76.

2-Bis(trimethylsilyl)methyl-3,4-bis(methoxycarbonyl)-5-phenyl-2*H*-1,2-azaphosphole-*P*-sulfide (10). 0.2 g 2*H*-1,2-azaphospole tungsten complex **7** (0.25 mmol) and 0.08 g sulfur (2.5 mmol) were dissolved in 3 mL benzonitrile and heated at 75°C for 1.5 h. The benzonitrile was removed in vacuo and the product separated and purified by low-temperature column chromatography (1. SiO_2, −20°C, dichloromethane/*n*-hexane 50/50, 200 mL, dichloromethane, 100 mL; 2. SiO_2, RT, dichloromethane, 100mL). Evaporation of the solvents of the first fraction and crystallization from pentane at −20°C yielded 10: deep red crystals (80 mg, 65%); mp 79°C (decomp.); IR (KBr): $\tilde{\nu}$ 1737 (vs), 1718 (vs) cm^{-1} (CO_2); 1610 (m), 1528 (m) cm^{-1} (C=N);

^{1}H NMR ($CDCl_3$) δ 0.09 (s, 9H, $SiMe_3$), 0.43 (s, 9H, $SiMe_3$), 1.33 (d, ^{2}J(P,H)=21.2 Hz, 1H, CH($(SiMe_3)_2$)), 3.85 (d, ^{6}J(P,H)=0.5 Hz, 3H, OCH_3), 3.89 (d, ^{5}J(P,H)=0.6 Hz, 3H, OCH_3), 7.46 (m_c, 3H, C$H_{aromatic}$), 7.79 (m_c, 2H, C$H_{aromatic}$); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 2.2 (d, ^{3}J(P,C)=3.2 Hz, $SiMe_3$), 3.3 (d, ^{3}J(P,C)=2.9 Hz, $SiMe_3$), 19.9 (d, ^{1}J(P,C)=32.9 Hz, *C*H($(SiMe_3)_2$)), 53.0 (s, O*C*H_3), 53.1 (s, O*C*H_3), 128.6 (s, *C*$H_{aromatic}$), 128.8 (s, *C*$H_{aromatic}$), 133.2 (s, *C*$H_{aromatic}$), 134.0 (d, ^{3}J(P,C) = 23.7 Hz, $C_{aromatic}$), 151.0 (d, ^{1}J(P,C)=53.1 Hz, P*C*C), 161.3 (d, $^{(2+3)}J$(P,C)=13.8 Hz, PC*C*), 164.8 (d, ^{2}J(P,C)=22.4 Hz, *C*O_2Me), 167.7 (s PN*C*), 170.7 (d, ^{3}J(P,C)=7.5 Hz, *C*O_2Me); ^{31}P{^{1}H} NMR ($CDCl_3$) *(*101.0 (s); MS (70 eV, EI, ^{32}S) *m/z* 467 (25) [$M^{+\cdot}$], 452 (50) [$(M\ CH_3)^{+}$], 408 (100) [$(M\ C_2H_3O_2)^{+\cdot}$]. Anal. Calcd. for $C_{20}H_{30}NO_4PSi_2$: C, 51.37; H, 6.47; N, 3.00; S, 6.86; found: C, 51.35, H, 6.60; N, 2.90; S, 6.60.

2-Bis(trimethylsilyl)methyl-4-phenyl-5-(1-piperidino)-2*H*-1,3,2-diazaphosphole (12). 1.15 g 2*H*-1,3,2-diazaphosphole tungsten complex **11**[2] (1.6 mmol) and 0.64 g DPPE (1.5 mmol) were dissolved in 7 mL *ortho*-xylene and heated at 140°C for four days with slow stirring (monitoring by ^{31}PNMR spectroscopy). Afterwards, the solvent was reduced in vacuo and the product was separated by low-temperature column chromatography (Al_2O_3, −50°C, petrol ether (40–60°C)/diethylether 95:5). Evaporation of the solvents of the second fraction yielded **12** as a pale yellow oil (450 mg, 75%); ^{1}H NMR ($CDCl_3$) δ 0.16 (s, 18H, $SiMe_3$), 0.82 (d, ^{2}J(P,H)=2.0 Hz, 1H, CH($(SiMe_3)_2$)), 1.56 (s br, 6H, $NCH_2CH_2CH_2$), 3.18 (s br, 4H, $NCH_2CH_2CH_2$), 7.41 (m_c, 3H, C$H_{aromatic}$), 7.81 (m_c, 2H, C$H_{aromatic}$); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 2.0 (d, ^{3}J(P,C)=3.8 Hz, $SiMe_3$), 17.8 (d, ^{1}J(P,C)=56.9 Hz, *C*H($(SiMe_3)_2$)), 24.2 (s, $NCH_2CH_2CH_2$), 25.4 (s, $NCH_2CH_2CH_2$), 50.0 (s, $NCH_2CH_2CH_2$), 127.6 (d, ^{4}J(P,C)=2.2 Hz, *C*$H_{aromatic}$), 128.3 (s, *C*$H_{aromatic}$), 129.4 (s, *C*$H_{aromatic}$), 137.7 (d, ^{3}J(P,C)=9.9 Hz, $C_{aromatic}$), 163.4 (d, $^{(2+3)}J$(P,C)=7.1 Hz, PN*C*NR_2), 164.7 (d, $^{(2+3)}J$(P,C)=7.5 Hz, PN*C*C); ^{31}P{^{1}H} NMR ($CDCl_3$) δ 140.2 (s); MS (70 eV, EI) *m/z* 403 (100) [$M^{+\cdot}$], 183 (55) [$H_2PCH(SiMe_3)_2)^{+\cdot}$], 73 (55) [$(SiMe_3)^{+}$]. HR EI MS for $C_{20}H_{34}N_3PSi_2$: 403.2020, found 403.2020±2.

2-Bis(trimethylsilyl)methyl-4-phenyl-5-(1-piperidino)-2*H*-1,3,2-diazaphosphole-*P*-sulfide (13). 0.2 g 2*H*-1,3,2-diazaphosphole **12** (0.5 mmol) and 0.04 g sulfur (1.25 mmol) were dissolved in 1.5 mL dichloromethane and slowly stirred at room temperature for 0.5 h. The solvent was removed in vacuo and at room temperature. The product was obtained after purification of the residue, by washing with pentane, as a pale yellow solid (195 mg, 91%), mp 147°C (decomp.); IR (KBr) $\tilde{\nu}$ 1570 (m, sh) cm^{-1} (C=N); ^{1}H NMR ($CDCl_3$) δ 0.30 (s, 9H, $SiMe_3$), 0.31 (s, 9H, $SiMe_3$), 1.00 (d, ^{2}J(P,H)=23.0 Hz, 1H, CH($(SiMe_3)_2$)), 1.58 (s br, 6H, $NCH_2CH_2CH_2$), 3.38 (s br, 4H, $NCH_2CH_2CH_2$), 7.43 (m_c, 3H, C$H_{aromatic}$) 7.66 (m_c, 2H, C$H_{aromatic}$); ^{13}C{^{1}H} NMR ($CDCl_3$) *(*2.3 (d, ^{3}J(P,C)= 1.4 Hz, $SiMe_3$), 2.4 (d, ^{3}J(P,C)=1.3 Hz, $SiMe_3$), 23.9 (s, $NCH_2CH_2CH_2$), 24.0 (d, ^{1}J(P,C)=41.9 Hz, *C*H($(SiMe_3)_2$)), 25.5 (s, $NCH_2CH_2CH_2$), 45.0 (s, $NCH_2CH_2CH_2$), 127.8 (d, ^{4}J(P,C)=1.4 Hz, *C*$H_{aromatic}$), 128.7 (s, *C*$H_{aromatic}$), 131.0 (s, *C*$H_{aromatic}$), 135.8 (d, ^{3}J(P,C)=29.6 Hz, $C_{aromatic}$), 163.6 (d, $^{(2+3)}J$(P,C)=19.9 Hz, PN*C*NR_2), 167.3 (s, PNCC); ^{31}P{^{1}H} NMR ($CDCl_3$) δ 123.4 (s); MS (70 eV, EI, ^{32}S) *m/z* 435 (100) [$M^{+\cdot}$], 420 (70) [$(M-CH_3)^{+}$], 403 (30) [$(M-S)^{+}$], 73 (45) [$(SiMe_3)^{+}$]. HR EI MS for $C_{20}H_{34}N_3PSSi_2$: 435.1750, found 435.1754±2.

Data collection, structure solution and refinement of 6 and 10. Structure determination of **6;** Crystal data: $C_{21}H_{29}N_2PSSi_2$, M=428.67, $P2_1/n$, a=11.004(3), b= 11.168(4), c=18.959(4) Å, β=97.52(2)°, V= 2309.8(1) $Å^3$, Z=4, d_{calc}=1.233 Mg/m^3, μ=0.313 mm^{-1}, T=143 K. A dark orange block (0.80 × 0.40 × 0.30 mm) was mounted in inert oil. 4221 intensities were measured (2Θ 6–50°) using monochromated Mo-Kα radiation on a Stoe STADI-4 diffractometer, of which 4076 were unique (R_{int}=0.0422) and used for all calculations (program SHELXL-93[16]). All hydrogen atoms (except rigid methyl groups) were refined with a riding model. The final $wR(F^2)$ was 0.1281 with conventional $R(F)$ 0.0614 for 250 parameters and 108 restraints; highest peak 336, hole −287 e/nm^3.

Structure determination of **10**; Crystal data: $C_{20}H_{30}NO_4PSSi_2$, M=467.66, $P2_1/c$, a=15.070(2), b= 10.808(1), c=16.846(2) Å, β=113.95(8)°, V= 2507.4(5) $Å^3$, Z=4, d_{calc}=1.239 Mg/m^3, μ=0.313 mm^{-1}, T=173 K. A orange prism (0.60×0.40×0.20 mm) was mounted in inert oil. 4533 intensities were measured (2Θ 6–50°) using monochromated Mo-Kα radiation on a Siemens P4 diffractometer, of which 4370 were unique (R_{int}=0.0181) and used for all calculations (program SHELXL-93[16]). All hydrogen atoms (except rigid methyl groups) were refined with a riding model. The final $wR(F^2)$ was 0.0902 with conventional R(F) 0.0400 for 270 parameters and 149 restraints; highest peak 243, hole −217 e/nm^3.

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