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Synthesis of functional Δ^3-1,3,5-oxazaphospholene and 2*H*-1,4,2-diazaphosphole complexes via catalytic ring expansion reactions of a 2*H*-azaphosphirene complex

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Abstract—Catalytically-induced ring expansion of 2*H*-azaphosphirene complex **1** using ferrocenium hexafluorophosphate and acetone (**2**), diethylketone (**3**), cyclohexanone (**4**), benzaldehyde (**5**) or *para*-hydroxy-benzaldehyde (**6**) furnished selectively the Δ^3-1,3,5-oxazaphospholene complexes **7**–**11**, whereas with *ortho*- and *para*-hydroxy- or *ortho*- and *para*-amino-substituted benzonitriles the 2*H*-1,4,2-diazaphosphole complexes **16**–**19** were obtained. Two further findings are noteworthy: (1) The significant decreased reaction time in the case of the sterically more demanding carbonyl derivatives **2**–**4** and (2) the formation of diastereomers in the case of **10** and **11** with a ratio of 8:1 and 9:1, respectively. All products were characterized by NMR, MS and elemental analysis and the configuration of complexes **7** and **10a** were determined by X-ray single-crystal diffraction analysis.

Our studies on the synthesis of phosphorus-containing analogues of the 5-membered heterocycle triazole have shown that thermolysis of 2*H*-azaphosphirene complexes **I**[1] in the presence of carbonitriles (i) led in most cases to 2*H*-1,3,2-diazaphosphole complexes **II** (Scheme 1). The product formation was explained by assuming nitrilium phosphane–ylide complexes as reactive intermediates.[2] Only benzonitrile as solvent and trapping reagent led predominantly to the regioisomeric 2*H*-1,4,2-diazaphosphole complexes **III**.[3] If carbonyl derivatives were used in three-component reactions as trapping reagents of nitrilium phosphane–ylide complexes (ii) the result strictly depended on the carbonitrile substituent: In the case of diorgano-amino-substituted derivatives Δ^3-1,3,2-oxazaphospholene complexes **IV** were obtained, whereas with the phenyl-substituted derivative Δ^2-1,3,4-oxazaphospholene complexes **V** were formed. The regioisomeric Δ^3-1,3,5-oxazaphospholene **VI** complexes are not accessible via thermal reactions of 2*H*-azaphosphirene complexes.

Recently, we reported the first selective access to complexes **III** and **VI** using tetracyanoethylene (TCNE)[4] and ferrocenium hexafluorophosphate[5] as catalysts and carbonitriles[4] (iii) or benzaldehyde[5] and cyclohexanone[5] (iv) as π-systems that were inserted into the P,N-bond of the strained ring system of complexes **I** (M=W) under very mild conditions (Scheme 1). Further studies showed that the reaction time of such insertion reactions is reduced in the case of *ortho*-methoxy- and *ortho*-dimethylamino-substituted 2*H*-azaphosphirene complexes.[6]

Our interest in the studies reported here was mainly directed (1) to testing the tolerance of this new synthetic methodology with respect to functional groups such as hydroxy and amino and (2) to obtaining new information about the reaction course using substitutional effects, e.g. on the diastereomeric ratio of Δ^3-1,3,5-oxazaphospholene **VI**.

1. Results and discussion

1.1. Insertion of carbonyl derivatives into the P–N bond of complex 1

If a dichloromethane solution of 2*H*-azaphosphirene complex **1**[7] was treated with acetone (**2**), diethylketone (**3**), cyclohexanone (**4**), benzaldehyde (**5**) or *para*-hydroxy-benzaldehyde (**6**), in the presence of ferrocenium hexafluorophosphate the Δ^3-1,3,5-oxazaphospholene complexes

Keywords: 2*H*-azaphosphirene; 2*H*-1,4,2-diazaphosphole; Δ^3-1,3,5-oxazaphospholene; tungsten; catalytic ring expansion.
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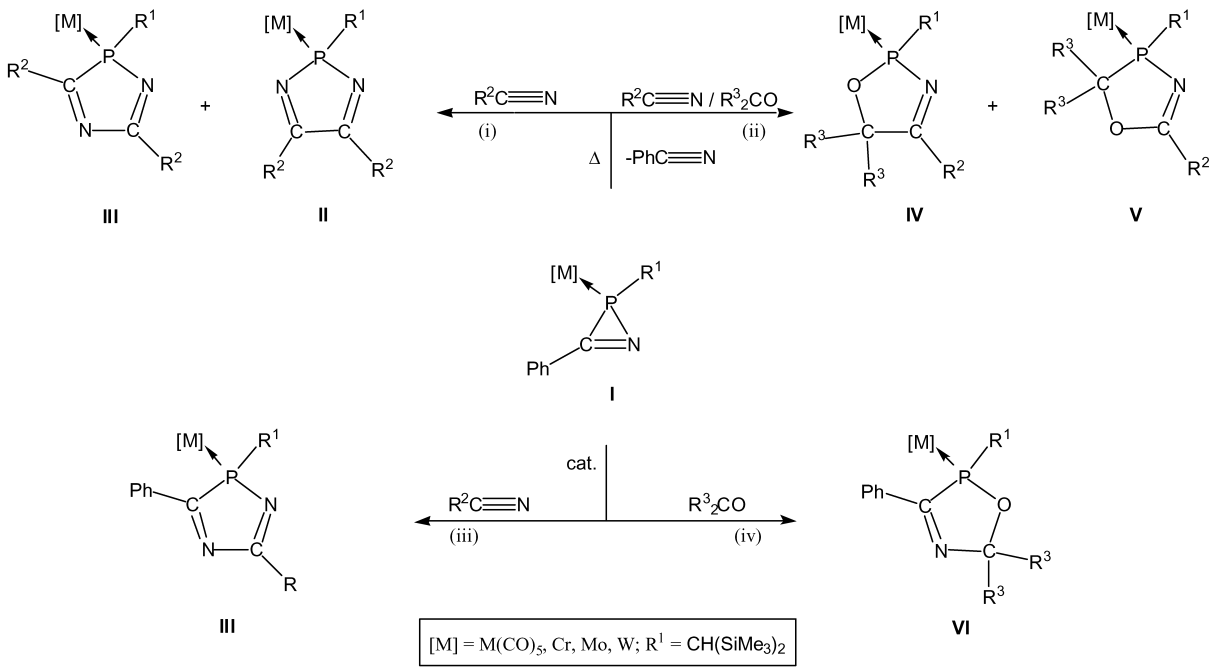
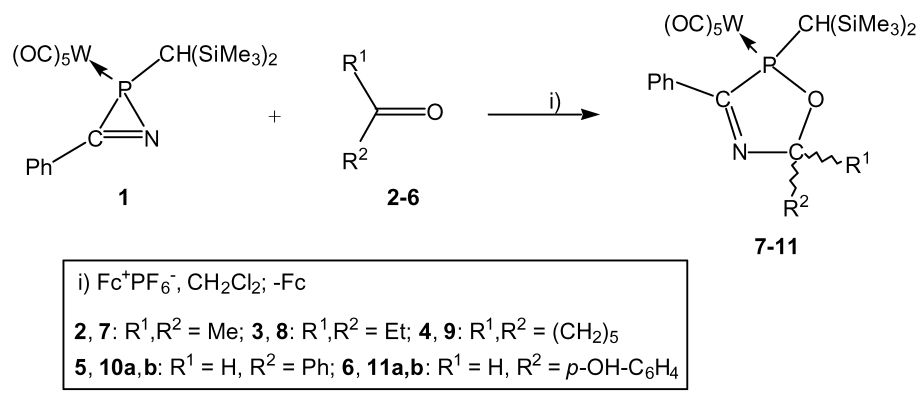


Scheme 1. Ring forming reactions using 2*H*-azaphosphirene complexes and carbonitrile and carbonyl compounds.

7–**11**, respectively were formed selectively at ambient temperature (Scheme 2). No other phosphorus-containing products were observed by $^{31}P\{^{1}H\}$ NMR spectroscopy; in each reaction ferrocene was formed in ca. 5% yield and identified by ^{1}H and ^{13}C NMR spectroscopy.

In the case of *para*-hydroxy-benzaldehyde no side-reactions involving the proton of the hydroxy group were observed. It is remarkable that the reaction time depended significantly on the steric demand of the carbonyl substituents **2**–**4** (**2**: 1 h, **3**: 5 d, **4**: 1.5 h). Further studies of steric influence on the reaction time showed that bulky substituted ketones, e.g. benzophenone, did not react with complex **1**. In the case of **5** and **6** complexes **10a**,**b** and **11a**,**b** were formed in ratios 8:1



Scheme 2. Insertion of carbonyl derivatives into the P–N-bond of complex **1**.

Table 1. Selected NMR data of Δ^3-1,3,5-oxazaphospholene tungsten complexes **7**–**11**

Compound	R^1	R^2	$\delta(^{31}P)$ [ppm] ($^{1}J_{P,W}$) [Hz]	$\delta(^{13}C^3)$ [ppm] ($^{[1+4]}J_{P,C}$) [Hz]	$\delta(^{13}C^5)$ [ppm] ($^{[2+3]}J_{P,C}$) [Hz]
7	Me	Me	135.4 (280.4)	170.2 (15.6)	117.3 (4.3)
8	Et	Et	135.2 (279.5)	170.1 (15.2)	118.6 (5.7)
9	$(CH_2)_5$		136.4 (273.4)	169.7 (15.4)	113.1[a]
10a	H	Ph	135.2 (280.9)	173.6 (13.3)	108.1 (6.2)
10b	H	Ph	141.5 (269.4)	[b]	[b]
11a	H	*p*-OH–C_6H_4	134.3 (279.6)	173.9 (13.3)	115.3 (7.9)
11b	H	*p*-OH–C_6H_4	141.2 (268.4)	[b]	[b]

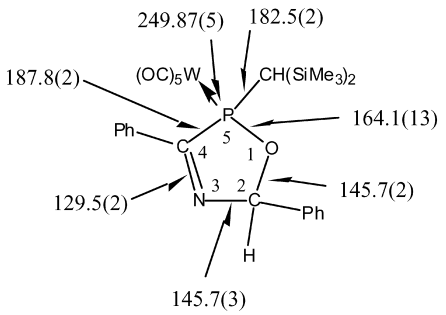
[a] Coupling constant not resolved.
[b] Spectrum not recorded.

and 9:1, respectively. Although we did not succeed in the isolation of **10b** and **11b**, we assume the existence of these isomers on the basis of the similarity of their ^{31}P NMR data with those of **10a** and **11a**. Selected NMR data of **7**–**9**, **10a** and **11a** are given in Table 1.

The ^{31}P NMR resonances of the Δ^3-1,3,5-oxazaphospholene complexes **7**–**11** were observed in the narrow range of 134–142 ppm with tungsten–phosphorus coupling constant magnitudes of 270–280 Hz. In the case of complexes **10a**,**b** and **11a**,**b** the $\Delta\delta$ values are ca. 6–7, whereby the isomer with the downfield-shifted resonance always has a smaller coupling constant. Regarding the five-membered heterocycles, the ^{13}C NMR resonances of **7**–**9**, **10a** and **11a** were determined in the range 169–174 ppm for the C^4 atoms and in the range 108–117 ppm for the C^2 atoms. Proton resonances at 7.09 (s br) and 7.11 ($^3J_{P,H}$=2.2 Hz) were assigned to the C^2–H protons of **10a** and **11a**, respectively. The resonance of the OH-proton in **10a**,**b** is observed at a chemical shift of 12.09 ppm showing a phosphorus–hydrogen coupling constant of 2.9 Hz due to a hydrogen bridge between the proton and the nitrogen atom in the heterocycle. EI mass spectrometric measurements showed that, in contrast to **7**–**9**, radical cations of complexes **11a**,**b** undergo ring cleavage with extrusion of the aldehyde units. It is remarkable that, under the same EI mass spectrometric conditions, radical cations of complexes **12**[8] and **13**[8] (Fig. 1) showed predominantly ring cleavage with extrusion of nitriles, thus expressing nicely one aspect of the reactivity differences of these regioisomeric ring systems.

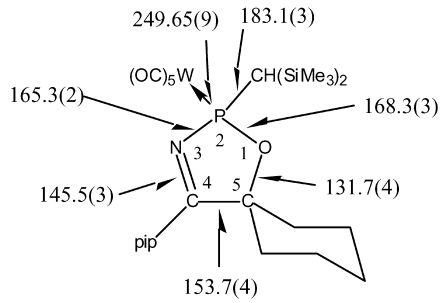
The molecular structures of **7** and **10a** were unambigously established by X-ray single-crystal diffraction analysis (Figs. 2 and 3(a)), thus also establishing the *SS* relative configuration of complex **10a**. Figure 3(b) shows however that **10a** is disordered, with a ratio of 88:12 *SS* to *SR* relative isomers.

The heterocyclic ring systems in complexes **7** and **10a** are



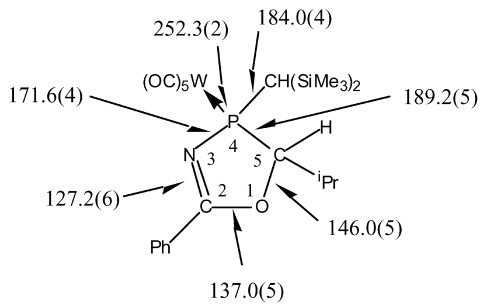
10a

$\delta(^{31}P) = 135.2$ ($^1J_{W,P} = 279.5$ Hz)
$\delta(^{13}C^4) = 173.6$ ($^{[2+3]}J_{P,C} = 13.3$ Hz)
$\delta(^{13}C^2) = 108.1$ ($^{[2+3]}J_{P,C} = 6.2$ Hz)



12[8]

$\delta(^{31}P) = 179.5$ ($^1J_{W,P} = 296.5$ Hz)
$\delta(^{13}C^4) = 165.8$ ($^{[2+3]}J_{P,C} = 2.3$ Hz)
$\delta(^{13}C^5) = 88.8$ ($^{[2+3]}J_{P,C} = 1.5$ Hz)



13[8]

$\delta(^{31}P) = 102.4$ ($^1J_{W,P} = 266.3$ Hz)
$\delta(^{13}C^5) = 86.5$
$\delta(^{13}C^2) = 164.7$ ($^{[2+3]}J_{P,C} = 12.5$ Hz)

Figure 1. Selected bond lengths [pm] and NMR data of **10a**, **12**[8] and **13**.[8]

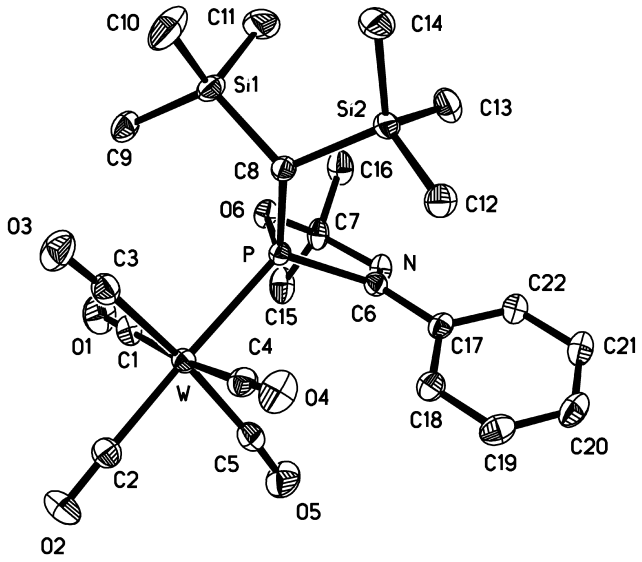


Figure 2. Molecular structure of **7** in the crystal (ellipsoids represent 50% probability levels, hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: P–O(6) 1.629(12), O(6)–C(7) 1.465(2), C(7)–N(1) 1.452(2), N(1)–C(6) 1.271(2), C(6)–P 1.879(18), P–W 2.5122(5), P–C(8) 1.8264(17); C(8)–P–W 114.64(6), O(6)–P–C(6) 88.68(7), N–C(7)–O(6) 108.24(14), C(6)–N–C(7) 114.63(15), N(1)–C(6)–P 111.80 (12).

essentially planar (**7**: mean dev. 0.05 Å; **10a**: mean dev. 0.07 Å). The most significant bond lengths and angles of **7** are shown in Figure 1 in comparison with **12**[8] and **13**.[8] The structural parameters of all three ring systems are surprisingly closely related (the bond lengths and angles of **10a** are very similar) and only the P–W distances seem to depend from the hybridization and the steric demand of the endocyclic carbon atom fragments adjacent to phosphorus, as is seen in complex **13**.

1.2. Insertion of substituted benzonitriles into the P–N bond of complex 1

Reaction of 2*H*-azaphosphirene complex **1** with the nitriles **14a**,**b** and **15a**,**b** in the presence of ferrocenium hexafluorophosphate furnished selectively the 2*H*-1,4,2-diazaphospole complexes **16a**,**b** and **17a**,**b** as the only phosphorus-containing products (Scheme 3); the formation of ferrocene was also observed in these cases. The reactions took 1–3 h at ambient temperature to completion.

Selected NMR data of the complexes **16** and **17** are given in Table 2. The ^{31}P NMR resonances lie in a very small range of 105–110 ppm with tungsten–phosphorus coupling constant magnitudes of ca. 230 Hz, which is low compared to 2*H*-1,3,2-diazaphosphole complexes (250–270 Hz), but similar to other derivatives of such heterocycle complexes.[5,8] The ^{13}C NMR spectra of **16** and **17** showed significantly deshielded resonances of the C^3 atoms at 195–200 ppm with phosphorus–carbon coupling constant magnitudes of 20–22 Hz. The substituent position at the phenyl group has no significant effect on the chemical shifts of the ^{31}P and ^{13}C resonances, but dramatic effects on the chemical shifts of the ^{1}H resonances of the OH and NH_2 groups.

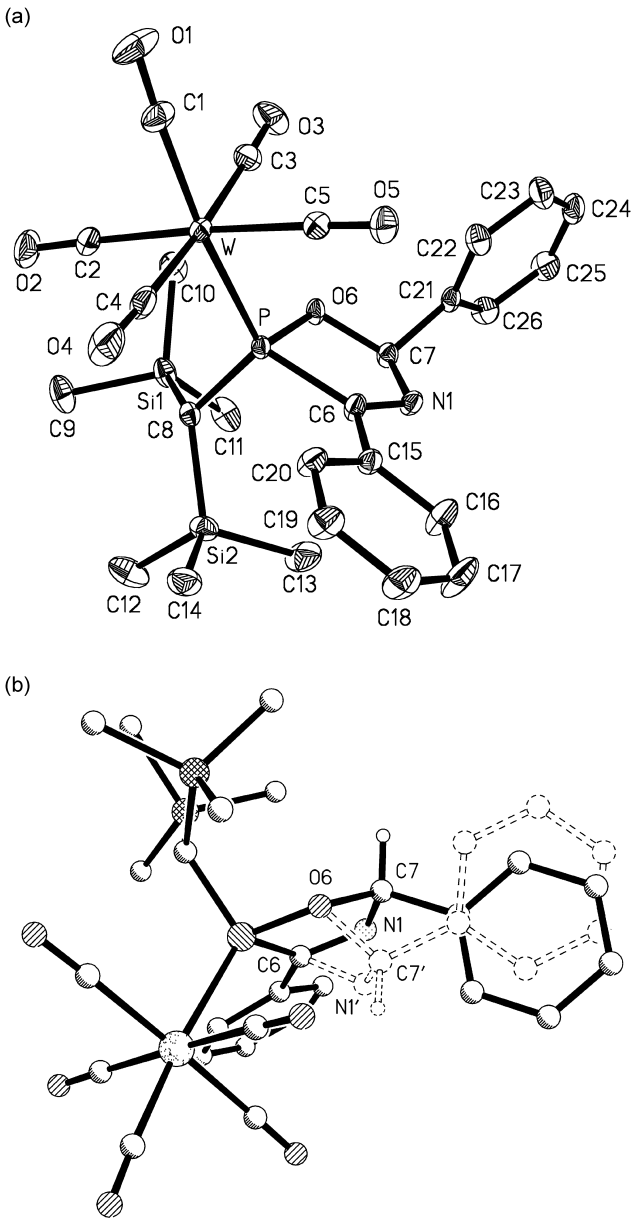


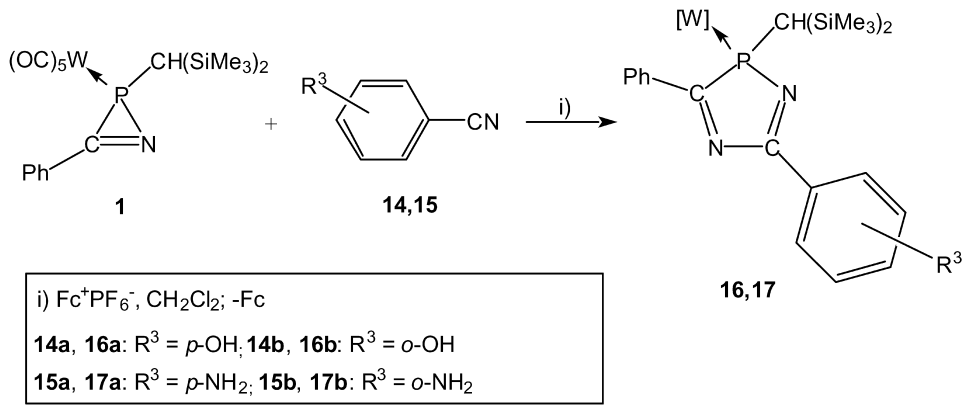
Figure 3. (a) Molecular structure of **10a** in the crystal (ellipsoids represent 50% probability levels, hydrogen atoms are omitted for clarity). Selected bond angles [°]: C(8)–P–W 117.47(6), O(6)–P–C(6) 88.13(8), N–C(7)–O(6) 109.09(15), C(6)–N–C(7) 113.18(17), N(1)–C(6)–P 112.10 (14); (b) Ball-and-stick-model of the disorder in **10a**.

Experiments aiming at the elucidation of the mechanism of these catalytic reactions are currently being performed.

2. Experimental

2.1. General procedures

All reactions and manipulations were carried out under an atmosphere of deoxygenated nitrogen, using standard Schlenk techniques with conventional glassware. 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



Scheme 3. Insertion of carbonitrile derivatives into the P–N-bond of complex **1**.

Table 2. Selected NMR data of 2*H*-1,4,2-diazaphosphole tungsten complexes **16** and **17**

Compound	R^3	$\delta(^{31}P)$ [ppm] ($^1J_{P,W}$) [Hz]	$\delta(^{13}C^3)$ [ppm] ($^{[1+4]}J_{P,C}$) [Hz]	$\delta(^{13}C^5)$ [ppm] ($^{[2+3]}J_{P,C}$) [Hz]
16a	*p*-OH	109.8 (229.2)	198.4 (22.3)	168.9 (5.4)
16b	*o*-OH	109.8 (236.5)	197.6 (22.9)	171.4 (3.8)
17a	*p*-NH_2	108.1 (231.4)	198.1 (16.1)	169.1 (5.8)
17b	*o*-NH_2	107.9 (232.8)	198.1 (22.6)	170.4 (6.1)

[D]chloroform as solvent and internal standard; shifts are given relative to external tetramethylsilane (^1H, ^{13}C) and 85% H_3PO_4 (^{31}P). Mass spectra were recorded on a Finnigan MAT 8430 (70 eV); apart from *m*/*z*-values of the molecule ions, only *m*/*z* values having intensities more than 10% 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 analysis 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 atom to the metal.

2.1.1. {Pentacarbonyl[5-bis(trimethylsilyl)methyl-2,2-dimethyl-4-phenyl-Δ^3-1,3,5-oxazaphospholene-κP]tungsten(0)} (7). 0.63 g (1 mmol) of 2*H*-azaphosphirene complex **1** were dissolved in 2 mL dichloromethane and 2 mL acetone and 60 mg (0.2 mmol) ferrocenium hexafluorophosphate were added. The reaction mixture was stirred at ambient temperature for 1 h. The solvent was then removed in vacuo and the product separated by low temperature column chromatography (SiO_2, −15°C, petrol ether (50/70)/diethylether 95:5). Evaporation of the solvents of the second fraction and recrystallization from *n*-pentane furnished **7**; pale yellow crystals (324 mg, 48%); mp 82°C; ^1H NMR ($CDCl_3$): δ=0.02 (s, 9H, $SiMe_3$), 0.34 (s, 9H, $SiMe_3$), 1.50 (d, 1H, $^2J_{P,H}$=1.3 Hz, C*H*$SiMe_3$), 1.67 (s, 3H, C*Me*), 1.71 (s, 3H, C*Me*), 7.52 (m_c, 3H, *m*-, *p*-Ph), 8.19 (dd, 2H, $^3J_{H,H}$=7.5 Hz, $J_{H,X}$=2.2 Hz, *o*-Ph); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ=3.1 (d, $^3J_{P,C}$=1.8 Hz, $SiMe_3$), 3.5 ($^3J_{P,C}$= 2.7 Hz, $SiMe_3$), 28.5 (s, CH_3), 30.4 (s, CH_3), 36.0 (d, $^1J_{P,C}$=13.4 Hz, *C*H$(SiMe_3)_2$), 117.3 ($^{[2+3]}J_{P,C}$=4.3 Hz, PO*C*), 128.6 (s, *m*-Ph), 130.2 (d, $^3J_{P,C}$=2.4 Hz, *o*-Ph), 132.5 (s, *p*-Ph), 133.4 (d, $^2J_{P,C}$=24.9 Hz, *i*-Ph), 170.2 (d, $^1J_{P,C}$=15.8 Hz, P*C*N), 197.7 (d, $^2J_{P,C}$=7.2 Hz, *cis*-CO), 199.3 (d, $^2J_{P,C}$=26.5 Hz, *trans*-CO); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ=135.4 (s, $^1J_{W,P}$=280.4 Hz); MS (EI, 70 eV, ^{184}W): *m*/*z*=675 (42) [M^+], 647 (20) [M^+-CO], 619 (63) [M^+-2CO], 591 (95) [M^+-3CO], 535 (100) [M^+-5CO], 73 (84) [$SiMe_3^+$]; Anal. calcd for $C_{22}H_{30}NO_6PSi_2W$: C, 39.11; H, 4.44; N, 2.07. Found: C, 39.22; H, 4.56; N 1.96.

2.1.2. {Pentacarbonyl[5-bis(trimethylsilyl)methyl-2,2-diethyl-4-phenyl-Δ^3-1,3,5-oxazaphospholene-κP]tungsten(0)} (8). 0.63 g (1 mmol) of 2*H*-azaphosphirene complex **1** and 0.5 mL (5 mmol) of diethylketone were dissolved in 2 mL dichloromethane and 60 mg (0.2 mmol) ferrocenium hexafluorophosphate were added. The reaction mixture was stirred at room temperature for 5 d. The solvent was then removed in vacuo and the product separated by low temperature column chromatography (SiO_2, −10°C, petrol ether (50/70)/diethylether 95:5). Evaporation of the solvents of the second fraction and recrystallization from *n*-pentane furnished **8**; pale yellow crystals (240 mg, 34%); mp 118°C; ^1H NMR ($CDCl_3$): δ=0.00 (s, 9H, $SiMe_3$), 0.32 (s, 9H, $SiMe_3$), 1.08 (t, 3H, $^3J_{H,H}$=7.4 Hz, CH_3), 1.17 (t, 3H, $^3J_{H,H}$=7.3 Hz, CH_3), 1.53 (d, 1H, $^2J_{P,H}$=2.7 Hz, C*H*$SiMe_3$), 1.88 (q, 2H, $^3J_{H,H}$=7.4 Hz, CH_2), 1.94 (q, 2H, $^3J_{H,H}$= 7.3 Hz, CH_2), 7.54 (m_c, 3H, *m*-, *p*-Ph), 8.12, (dd, 2H, $^4J_{H,H}$= 2.7 Hz, $^3J_{H,H}$=6.6 Hz, *o*-Ph); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ=2.9 (s br, $SiMe_3$), 3.3 (d, $^3J_{P,C}$=2.5 Hz, $SiMe_3$), 8.7 (s, CH_3), 9.4 (s, CH_3), 30.4 (s br, CH_2), 36.7 (d, $^1J_{P,C}$=15.1 Hz, *C*H$(SiMe_3)_2$), 118.6 (d, $^{[2+3]}J_{P,C}$= 5.7 Hz, POC), 128.5 (s, *m*-Ph), 130.6 (d, $^3J_{P,C}$=2.8 Hz, *o*-Ph), 131.7 (s, *p*-Ph), 133.9 (d, $^2J_{P,C}$=22.4 Hz, *i*-Ph), 197.6 (d, $^2J_{P,C}$=7.2 Hz, *cis*-CO), 199.2 (d, $^2J_{P,C}$=25.6 Hz, *trans*-CO); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ=135.2 (s, $^1J_{W,P}$= 279.5 Hz).

2.1.3. {Pentacarbonyl[2-(bistrimethlysilyl-methyl)-3-phenyl-1,4,2-oxazaphopha-spiro[4.5]-dec-3-ene-κP]tungsten(0)} (9). 0.63 g (1 mmol) of 2*H*-azaphosphirene complex **1** and 500 mg (3.5 mmol) of cyclohexanon

were dissolved in 2 mL dichloromethane and 60 mg (0.2 mmol) ferrocenium hexafluorophosphate were added. The reaction mixture was stirred at ambient temperature for 2 h. The solvent was then removed in vacuo and the product separated by low temperature column chromatography (SiO_2, −25°C, petrol ether (50/70)/diethylether 90/10). Evaporation of the solvents of the second fraction and recrystallization from *n*-pentane furnished **9**; pale yellow crystals (314 mg, 44%); mp 140°C; $\tilde{\nu}$=2927 (w, CH), 2071 (m, CO), 1960 (m, CO), 1927 (s, CO), 1916 (s, CO); ^{1}H NMR ($CDCl_3$): δ=0.00 (s, 9H, $SiMe_3$), 0.40 (s, 9H, $SiMe_3$), 0.98 (m_c, 2H, CH_2) 1.32 (m br, 2H, CH_2), 1.51 (s br, 1H, C*H*$SiMe_3$), 1.86 (m_c, 6H, CH_2), 7.49 (m_c, 3H, *m*-, *p*-Ph), 8.12, (dd, 2H, $^3J_{H,H}$=7.7 Hz, $^4J_{H,X}$=2.2 Hz, *o*-Ph); ^{13}C{^{1}H} NMR ($CDCl_3$): δ=3.1 (d, $^3J_{P,C}$=1.7 Hz, $SiMe_3$), 3.4 (d, $^3J_{P,C}$=2.6 Hz, $SiMe_3$), 21.8 (s, *p*-CH_2), 22.0 (s, *m*-CH_2), 23.9 (s, *m*-CH_2), 35.4 (d, $^1J_{P,C}$=13.3 Hz, *C*H($SiMe_3$)$_2$), 36.1 (*o*-CH_2), 36.3 (s, *o*-CH_2), 114.6 (d, $^2J_{P,C}$=4.3 Hz, PO*C*), 128.6 (s, *m*-Ph), 130.6 (d, $^3J_{P,C}$=2.3 Hz, *o*-Ph), 130.8 (s, *p*-Ph), 133.9 (d, $^2J_{P,C}$=25.4 Hz, *i*-Ph), 169.6 (d, $^{[2+3]}J_{P,C}$= 15.4 Hz, P*C*N), 198.1 (d, $^2J_{P,C}$=7.2 Hz, *cis*-CO), 199.6 (d, $^2J_{P,C}$=26.3 Hz, *trans*-CO); ^{31}P{^{1}H} NMR ($CDCl_3$): δ=136.4 (s, $^1J_{W,P}$=273.4 Hz); MS (EI, ^{184}W): *m*/*z*=715 (30) [M^+], 687 (22) [M^+−1CO], 659 (64) [M^+−2CO], 631 (82) [M^+−3CO], 575 (76) [M^+−5CO], 73 (100) [$SiMe_3^+$]; Anal. calcd for $C_{25}H_{34}NO_6PSi_2W$: C, 41.96; H, 4.79; N, 1.96. Found: C, 41.50; H, 4.86; N 1.92.

2.1.4. {Pentacarbonyl[5-bis(trimethylsilyl)methyl-2,4-diphenyl-Δ^3-1,3,5-oxazaphospholene-κP]tungsten(0)} (10a,b). 0.63 g (1 mmol) of 2*H*-azaphosphirene complex **1** and 500 mg (3.5 mmol) of benzaldehyde were dissolved in 2 mL dichloromethane and 60 mg (0.2 mmol) ferrocenium hexafluorophosphate were added. The reaction mixture was stirred at ambient temperature for 1.5 h. The solvent was then removed in vacuo and the product separated by low temperature column chromatography (SiO_2, −15°C, petrol ether (50/70)/diethylether 95/5). Evaporation of the solvents of the second fraction and recrystallization from *n*-pentane furnished **10a**,**b** as two diastereomers (ratio 8:1); pale yellow crystals (327 mg, 45%); mp 92°C.

Compound **10a**. ^{1}H NMR ($CDCl_3$): δ=0.00 (s, 9H, $SiMe_3$), 0.26 (s, 9H, $SiMe_3$), 1.45 (d, $^2J_{P,H}$=2.5 Hz, 1H, C*H*$SiMe_3$), 7.09 (s br, 1H, POC*H*), 7.28 (m_c, 3H, *m*-, *p*-Ph), 7.41 (m_c, 5H, Ar), 8.08 (d, 2H, $^2J_{P,H}$=7.3 Hz, *o*-Ph); ^{13}C{^{1}H} NMR ($CDCl_3$): δ=2.9 (d, $^3J_{P,C}$=1.7 Hz, $SiMe_3$), 3.3 (d, $^3J_{P,C}$= 2.7 Hz, $SiMe_3$), 33.3 (d, $^1J_{P,C}$=16.8 Hz, *C*H($SiMe_3$)$_2$), 108.1 (d, $^2J_{P,C}$=6.2 Hz, PO*C*), 126.5 (s, Ar), 128.5 (s, Ar), 128.6 (s, Ar), 128.9 (s, *p*-Ph), 130.6 (d, $^3J_{P,C}$=2.8 Hz, *o*-Ph), 131.8 (s, *p*-Ph), 132.6 (s, $^3J_{P,C}$=25.3 Hz, *i*-Ph), 137.8 (d, $^3J_{P,C}$=3.5 Hz, *i*-Ar), 173.6 (d, $^{[2+3]}J_{P,C}$=13.3 Hz, PN*C*), 197.1 (d, $^2J_{P,C}$=7.3 Hz, *cis*-CO), 198.7 (d, $^2J_{P,C}$=28.3 Hz, *trans*-CO); ^{31}P{^{1}H} NMR ($CDCl_3$): δ=135.3 (s, $^1J_{W,P}$=280.2 Hz).

Compound **10b**. ^{31}P{^{1}H} NMR ($CDCl_3$): δ=141.5. (s, $^1J_{W,P}$=269.4 Hz).

10a,**b**. MS (EI, 70 eV, ^{184}W): *m*/*z*=723 (28) [M^+], 695 (17) [M^+−1CO], 667 (28), [M^+−2CO], 639 (100) [M^+−3CO] 583 (86) [M^+−5CO], 73 (80) [$SiMe_3^+$]; Anal. calcd for $C_{26}H_{30}NO_6PSi_2W$: C, 43.16; H, 4.18; N, 1.94. Found: C, 42.98; H, 4.17; N 1.80.

2.1.5. {Pentacarbonyl[5-bis(trimethylsilyl)methyl-2-(4-hydroxyphenyl)-4-phenyl-Δ^3-1,3,5-oxazaphospholene-κP]tungsten(0)} (11a,b). 0.63 g (1 mmol) of 2*H*-azaphosphirene complex **1** and 122 mg (0.9 mmol) of *para*-hydroxy benzaldehyde were dissolved in 2 mL dichloromethane and 60 mg (0.2 mmol) ferrocenium hexafluorophosphate were added. The reaction mixture was stirred at ambient temperature for 1.5 h. The solvent was then removed in vacuo and the product separated by low temperature column chromatography (SiO_2, −15°C, petrol ether (50/70)/diethylether 95:5). Evaporation of the solvents of the second fraction and recrystallization from *n*-pentane furnished **11a**,**b** as two diastereomers (ratio 9:1); pale yellow crystals (333 mg, 45%); mp 131°C. $\tilde{\nu}$=3382 (w, OH), 3239 (w, OH), 2075 (m, CO), 1949 (vs sh, CO), 1908 (s, CO).

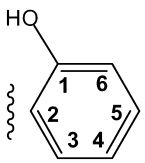
Compound **11a**. ^{1}H NMR ($CDCl_3$): δ=0.08 (s, 9H, $SiMe_3$), 0.33 (s, 9H, $SiMe_3$), 1.52 (d, 1H, $^2J_{P,H}$=3.1 Hz, C*H*$SiMe_3$), 6.83 (m_c, 2H, *m*-Ar), 7.11 (d, 1H, $^3J_{P,H}$=2.2 Hz, POC*H*), 7.33 (m_c, 2H, *o*-Ar), 7.56 (m_c, 3H, *m*-,*p*-Ph), 8.15 (d, 2H, $^3J_{H,H}$=7.8 Hz, *o*-Ph); ^{13}C{^{1}H} NMR ($CDCl_3$): δ=2.9 (d, $^3J_{P,C}$=1.9 Hz, $SiMe_3$), 3.3 (d, $^3J_{P,C}$=2.8 Hz, $SiMe_3$), 33.2 (d, $^1J_{P,C}$=16.9 Hz, *C*H($SiMe_3$)$_2$), 115.3 ($^{[2+3]}J_{P,C}$=7.9 Hz, PO*C*), 115.5 (s, *m*-Ar), 128.1 (s, *m*-Ph), 128.7 (s, *o*-Ar), 130.1 (d, $^3J_{P,C}$=3.6 Hz, *o*-Ar), 130.6 (d, $^3J_{P,C}$=2.8 Hz, *o*-Ph), 132.7 (d, $^2J_{P,C}$=25.1 Hz, *i*-Ph), 156.3 (s, *p*-Ar), 173.9 (d, $^{[2+3]}J_{P,C}$=13.3 Hz, P*C*N), 197.1 (d, $^2J_{P,C}$=7.4 Hz, *cis*-CO), 198.9 (d, $^2J_{P,C}$=28.1 Hz, *trans*-CO); ^{31}P{^{1}H} NMR ($CDCl_3$): δ=134.3 (s, $^1J_{W,P}$=279.6 Hz).

Compoumd **11b**. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 141.2. (s, $^1J_{W,P}$=279.6 Hz); MS (EI, 70 eV, ^{184}W): *m*/*z*=739 (7) [M^+], 683 (20) [M^+−2CO], 655 (44) [M^+−3CO], 599 (51) [M^+−5CO], 478 (20) [M^+−5CO−$C_7H_6O_2^+$], 122 (100) [$C_7H_6O_2^+$], 73 (80) [$SiMe_3^+$]; Anal. calcd for $C_{26}H_{30}NO_7PSi_2W$: C, 42.22; H, 4.06; N, 1.89. Found: C, 41.59; H, 4.37; N 1.82.

2.1.6. {Pentacarbonyl[2-bis(trimethylsilyl)methyl-5-(4-hydroxyphenyl)-3-phenyl-2*H*-1,4,2-diazaphosphole-κP]tungsten(0)} (16a). 0.63 g (1 mmol) of 2*H*-azaphosphirene complex **1** and 113 mg (0.95 mmol) of *para*-hydroxy benzonitrile were dissolved in 3 mL dichloromethane and 60 mg (0.2 mmol) ferrocenium hexafluorophosphate were added. The reaction mixture was stirred at ambient temperature for 1.5 h. The solvent was then removed in vacuo and the product separated by low temperature column chromatography (SiO_2, −15°C, petrol ether (50/70)/diethylether 70:30). Evaporation of the solvents of the second fraction and recrystallization from *n*-pentane furnished **16a**; orange crystals (456 mg, 62%); mp 131°C; ^{1}H NMR ($CDCl_3$): δ=0.00 (s, 9H, $SiMe_3$), 0.66 (s, 9H, $SiMe_3$), 1.37 (d, 1H, $^2J_{P,H}$=3.3 Hz, C*H*$SiMe_3$), 5.70 (s br, 1H, OH), 7.08 (d, 2H, $^2J_{H,H}$=8.8 Hz, *m*-Ar), 7.65 (m_c, 3H, *m*-, *p*-Ph), 8.36 (m_c, 2H, *o*-Ph), 8.56 (d, 2H, $^2J_{H,H}$=8.7 Hz, *o*-Ar); ^{13}C{^{1}H} NMR ($CDCl_3$): δ=2.9 (d, $^3J_{P,C}$=5.3 Hz, $SiMe_3$), 3.7 (d, $^3J_{P,C}$=7.2 Hz, $SiMe_3$), 18.7 (d, $^1J_{P,C}$=12.8 Hz, *C*H($SiMe_3$)$_2$), 115.7 (s, *m*-Ar), 126.4 (d, $^3J_{P,C}$=12.7 Hz, *i*-Ar), 128.9 (s, *m*-Ph), 131.3 (d, $^3J_{P,C}$=2.0 Hz, *o*-Ph), 132.5 (d, $^2J_{P,C}$=23.1 Hz, *i*-Ph), 132.9 (s, *o*-Ar), 133.4 (s, *p*-Ph), 159.5 (s, *p*-Ar), 168.9 (d, $^{[2+3]}J_{P,C}$=5.4 Hz, PN*C*), 197.2 (d, $^2J_{P,C}$=6.1 Hz, *cis*-CO),

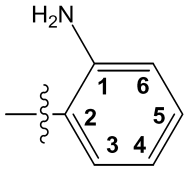
198.4 (d, $^{[1+4]}J_{P,C}$=22.3 Hz, P*C*N), 201.7 (d, $^{2}J_{P,C}$=22.8 Hz, *trans*-CO); $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ=109.8 (s, $^{1}J_{W,P}$=229.2 Hz); MS (EI, 70 eV, ^{184}W): *m/z*=736 (3) [M^+], 680 (10) [M^+-2CO], 10), 652 (5) [M^+-3CO], 73 (100) [$SiMe_3^+$]; Anal. calcd for $C_{26}H_{29}N_2O_6PSi_2W$: C, 42.33; H, 3.93; N, 3.80. Found: C, 41.12; H, 4.18; N 3.61.

2.1.7. {Pentacarbonyl[2-bis(trimethylsilyl)methyl-5-(2-hydroxyphenyl)-3-phenyl-2*H*-1,4,2-diazaphosphole-κP]tungsten(0)} (16b). 0.63 g (1 mmol) of 2*H*-azaphosphirene complex **1** and 112 mg (0.95 mmol) of *ortho*-hydroxy benzonitrile were dissolved in 3 mL dichloromethane and 60 mg (0.2 mmol) ferrocenium hexafluorophosphate were added. The reaction mixture was stirred at ambient temperature for 1.5 h. The solvent was then removed in vacuo and the product separated by low temperature column chromatography (SiO_2, −10°C, petrol ether (50/70)/diethylether 70:30). Evaporation of the solvents of the second fraction and recrystallization from *n*-pentane furnished **16b**; orange crystals (472 mg, 64%); mp 117°C; IR (KBr): $\tilde{\nu}$=2957 (vw, CH), 2074 (m, CO), 2001 (m, CO), 1928 (s, sh, CO); ^{1}H NMR ($CDCl_3$): δ=−0.09 (s, 9H, $SiMe_3$), 0.58 (s, 9H, $SiMe_3$), 1.20 (d, $^{2}J_{P,H}$=3.7 Hz, 1H, C*H*$SiMe_3$), 7.06 (m_c, 2H, Ar-C^{4,5}–*H*), 7.61 (m_c, 4H, *m*-, *p*-Ph; Ar-C^{6}–*H*), 8.27 (dd, 2H, $^{3}J_{H,H}$=8.3 Hz, $^{4}J_{H,X}$=1.7 Hz, *o*-Ph), 8.59 (dd, 1H, $^{3}J_{H,H}$=8.1 Hz, $^{4}J_{H,H}$=1.7 Hz, Ar-C^{3}–*H*), 12.47 (d, 1H, *J*=2.9 Hz, O*H*); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ=2.9 (d, $^{3}J_{P,C}$=2.0 Hz, $SiMe_3$), 3.8 (d, $^{3}J_{P,C}$=3.0 Hz, $SiMe_3$), 19.1 (d, $^{1}J_{P,C}$=5.8 Hz, *C*H($SiMe_3$)$_2$), 116.4 (d, $^{3}J_{P,C}$=7.6 Hz, Ar-*C*^{2}), 117.5 (s, Ar-*C*^{6}), 119.4 (s, Ar-*C*^{2}), 129.1 (s, *m*-Ph), 131.5 (d, $^{3}J_{P,C}$=2.6 Hz, *o*-Ph), 131.9 (d, $^{2}J_{P,C}$=23.1 Hz, *i*-Ph), 132.8 (s, Ar-*C*^{5}), 134.2 (s, Ar-*C*^{4}), 135.2 (s, *p*-Ph), 162.2 (s, 1-Ar), 171.4 (d, $^{[2+3]}J_{P,C}$=3.8 Hz, PN*C*), 196.8 (d, $^{2}J_{P,C}$=6.1 Hz, *cis*-CO), 197.6 (d, $^{[1+4]}J_{P,C}$=22.9 Hz, P*C*N), 200.6 (d, $^{2}J_{P,C}$=19.2 Hz, *trans*-CO); $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ=109.8 (s, $^{1}J_{W,P}$=236.5 Hz); MS (EI, 70 eV, ^{184}W): *m/z*=736 (7) [M^+], 708 (4) [M^+-1CO], 680 (8) [M^+-2CO], 655 (15) [M^+-3CO], 73 (100) [$SiMe_3^+$]; Anal. calcd for $C_{26}H_{29}N_2O_6PSi_2W$: C, 42.40; H, 3.97; N, 3.80. Found: C, 41.72; H, 3.97; N 3.36.



2.1.8. {Pentacarbonyl[2-bis(trimethylsilyl)methyl-5-(4-aminophenyl)-3-phenyl-2*H*-1,4,2-diazaphosphole-κP]tungsten(0)} (17a). 0.63 g (1 mmol) of 2*H*-azaphosphirene complex **1** and 112 mg (0.95 mmol) of *para*-amino benzonitrile were dissolved in 3 mL dichloromethane and 60 mg (0.2 mmol) ferrocenium hexafluorophosphate were added. The reaction mixture was stirred at room temperature for 3 h. The solvent was then removed in vacuo and the product separated by low temperature column chromatography (SiO_2, −10°C, petrol ether (50/70)/diethylether 70:30). Evaporation of the solvents of the second fraction and recrystallization from *n*-pentane furnished **13a**; orange crystals (398 mg, 54%); mp 132°C; IR (KBr): $\tilde{\nu}$=3530 (vw, NH), 3427 (w, NH), 2955 (w, CH), 2899 (w, CH), 2070 (s, CO), 1984 (s, CO), 1923 (s, sh, CO) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ=0.00 (s, 9H, $SiMe_3$), 0.65 (s, 9H, $SiMe_3$), 1.29 (d, 1H, $^{2}J_{P,H}$=4.0 Hz, C*H*$SiMe_3$), 4.20 (s br, 2H, N*H*$_2$), 6.87 (d, $^{3}J_{H,H}$=7.8 Hz, Ar-*C*^{3,5}–H), 7.66 (m_c, 3H, *m*-, *p*-Ph), 8.36 (dd, 2H, $^{3}J_{H,H}$=7.9 Hz, $^{4}J_{H,H}$=1.7 Hz, *o*-Ph), 8.48 (d, 2H, $^{3}J_{H,H}$=8.6 Hz, Ar-*C*^{2,6}–H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ=2.8 (d, $^{3}J_{P,C}$=2.0 Hz, $SiMe_3$), 3.6 (d, $^{3}J_{P,C}$=2.7 Hz, $SiMe_3$), 19.0 (d, $^{1}J_{P,C}$=4.9 Hz, *C*H($SiMe_3$)$_2$), 114.4 (s, Ar-*C*^{3,5}), 123.5 (d, $^{3}J_{P,C}$=12.8 Hz, Ar-*C*^{1}), 128.7 (s, *m*-Ph), 131.2 (d, $^{3}J_{P,C}$=1.8 Hz, *o*-Ph), 132.5 (d, $^{2}J_{P,C}$=23.6 Hz, *i*-Ph), 132.8 (s, Ar-*C*^{2,6}), 133.1 (s, *p*-Ph), 150.5 (s, Ar-*C*^{4}), 169.1 (d, $^{[2+3]}J_{P,C}$=5.8 Hz, PNC), 197.3 (d, $^{2}J_{P,C}$=6.2 Hz, *cis*-CO), 198.1 (d, $^{[1+4]}J_{P,C}$=16.1 Hz, P*C*N), 200.7 (d, $^{2}J_{P,C}$=22.9 Hz, *trans*-CO); $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ=108.1 (s, $^{1}J_{W,P}$=231.4 Hz); MS (EI, 70 eV, ^{184}W): *m/z*=735 (8) [M^+], 707 (20) [M^+-1CO], 679 (34) [M^+-2CO], 651 (10) [M^+-3CO], 73 (100) [$SiMe_3^+$]; Anal. calcd for $C_{26}H_{30}N_3O_5PSi_2W$: C, 42.46; H, 4.11; N, 5.71. Found: C, 42.30; H, 4.22; N 5.58.

2.1.9. {Pentacarbonyl[2-bis(trimethylsilyl)methyl-5-(2-aminophenyl)-3-phenyl-2*H*-1,4,2-diazaphosphole-κP]tungsten(0)} (17b). 0.63 g (1 mmol) of 2*H*-azaphosphirene complex **1** and 112 mg (0.95 mmol) of *ortho*-amino benzonitrile were dissolved in 3 mL dichloromethane and 60 mg (0.2 mmol) ferrocenium hexafluorophosphate were added. The reaction mixture was stirred at ambient temperature for 3.0 h. The solvent was then removed in vacuo and the product separated by low temperature column chromatography (SiO_2, −10°C, petrol ether (50/70)/diethylether 70:30). Evaporation of the solvents of the second fraction and recrystallization from *n*-pentane furnished **17b**; orange crystals (456 mg, 62%); mp 124°C; IR (KBr): $\tilde{\nu}$=3482.7 (w, NH), 3308 (w, NH), 2956 (w, CH), 2899 (w, CH), 2073 (s, CO), 1998.8 (s, CO), 1906 (s, CO) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ=−0.08 (s, 9H, $SiMe_3$), 0.57 (s, 9H, $SiMe_3$), 1.21 (d, $^{2}J_{P,H}$=3.9 Hz, 1H, C*H*$SiMe_3$), 6.52 (s br, 2H, NH_2), 6.80 (m_c, 1H, Ar-*H*), 7.31 (m_c, 2H, Ar-*H*), 7.55 (m_c, 3H, *m*-, *p*-Ph), 8.29 (m_c, 2H, *o*-Ph),. 8.74 (d, 1H, $^{3}J_{H,H}$=7.9 Hz, Ar-C^{3}–*H*); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ=2.9 (d, $^{3}J_{P,C}$=2.0 Hz, $SiMe_3$), 3.8 (d, $^{3}J_{P,C}$=2.7 Hz, $SiMe_3$), 19.0 (d, $^{1}J_{P,C}$=5.4 Hz, *C*H($SiMe_3$)$_2$), 114.4 (d, $^{3}J_{P,C}$=10.0 Hz, Ar-C^{2}), 116.2 (s, Ar-C^{6}), 128.1 (s, *m*-Ph), 131.2 (d, $^{3}J_{P,C}$=2.1 Hz, *o*-Ph), 132.3 (d, $^{2}J_{P,C}$=23.8 Hz, *i*-Ph), 133.4 (s, *p*-Ph), 133.7 (s, Ar), 134.3 (s, Ar), 134.4 (s, Ar), 151.1 (s, Ar-C^{1}), 170.4 (d, $^{[2+3]}J_{P,C}$=6.1 Hz, PN*C*), 197.2 (d, $^{2}J_{P,C}$=6.1 Hz, *cis*-CO), 198.1 (d, $^{[1+4]}J_{P,C}$=22.6 Hz, P*C*N), 198.4 (d, $^{2}J_{P,C}$=20.7 Hz, *trans*-CO); $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ=107.9 (s, $^{1}J_{W,P}$=232.8 Hz); MS (EI, 70 eV, ^{184}W): *m/z*=735 (1) [M^+], 707 (8) [M^+-1CO], 679 (13) [M^+-2CO], 73 (100) [$SiMe_3^+$]; Anal. calcd for $C_{26}H_{30}N_3O_5PSi_2W$: C, 42.46; H, 4.11; N, 5.71. Found: C, 41.29; H, 4.24; N 5.43.



2.2. Crystal structure determination of 7

Crystal data: $C_{22}H_{30}NO_6PSi_2W$, *M*=675.47, $P2_1/n$,

a=1002.70(6), b=1742.21(10), c=1618.36(10) pm, °, β=102.094(3)°, V=2764.4(3) Å^3, Z=4, d_{calc}=1.623 Mg/m^3, μ=4.358 mm^{-1}, T=133(2) K. A pale yellow tablet was mounted in inert oil. 38296 reflections were measured ($2\theta_{max}$ 52.6°) using monochromated Mo Kα radiation on a Bruker Smart 1000 CCD diffractometer, of which 5662 were unique and used for all calculations (program SHELXL-97[9]). An absorption correction was based on multiple scans. The structure was refined anisotropically on F^2. Hydrogen atoms were induced using a riding model or rigid methyl groups. The final $wR(F^2)$ was 0.0340 with conventional $R(F)$ 0.0133, for 306 parameters and 184 restraints; highest peak 0.00540, hole −0.00291 e/pm.[10]

2.3. Crystal structure determination of 10a

Crystal data: $C_{26}H_{30}NO_6PSi_2W$, M=723.51, P(−1), a=10.5808(6), b=10.8598, c=15.2169(11) Å, α=97.158°, β=93.443°, γ=118.408°, V=1511.63(16) Å^3, Z=2, d_{calc}=1.59 Mg/m^3, μ=3.991 mm^{-1}, T=133(2) K. A pale yellow tablet was mounted and measured as above, giving 31664 reflections, 8819 unique. The structure was refined as above. The atoms N1, C7, C21–26 are disordered over two sites with occupation 88%/12%. Appropriate similarity restraints were employed. The final $wR(F^2)$ was 0.0552, with conventional $R(F)$ 0.0216, for 373 parameters and 261 restraints; highest peak 0.01561, hole −0.01159 e/pm.[10]

Acknowledgements

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10. Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 212332 and 21333. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: int. code +44-1223-336-033].