Chemistry of 2*H*-Azaphosphirene Complexes, 13[◇]

Phosphorus-Bridged Dinuclear Tungsten Amino(aryl)carbene Complexes – New Precursors for (2*H*-Azaphosphirene)tungsten Complexes bearing a σ-P-Bonded Cp* Group☆

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The first syntheses of pentacarbonyl[2-(pentamethyl-2,4-cyclopentadien-1-yl)-2*H*-azaphosphirene]tungsten complexes are reported, using a one-pot reaction of dichloro(pentamethyl-2,4-cyclopentadien-1-yl)phosphane (Cp^*PCl_2) with triethylamine and {[amino(aryl)carbene]pentcarbonyltungsten(0)}. [Pentamethyl-2,4-cyclopentadien-1-yl]phosphanediyl-bridged dinuclear carbene complexes are formed as long-lived intermediates, which, by elimination and rearrangement reactions, led to the final products. If traces of water were present, then by-products were formed; in one case, a dinuclear carbene complex with a P(Cp*)–O–P(Cp*) bridging unit was isolated. Under ordinary reaction conditions 2*H*-azaphosphirene complexes are slowly transformed into {pentacarbonyl[chloro(pentamethyl-2,4-cyclopentadien-1-yl)phosphane]tungsten(0)}. NMR-spectroscopic and single-crystal X-ray structural data of some dinuclear carbene complexes and 2-(pentamethyl-2,4-cyclopentadien-1-yl)-2*H*-azaphosphirene complexes are presented.

The chemistry of (2*H*-azaphosphirene)tungsten complexes has recently been the subject of increased interest, because of their widespread applicability in the synthesis of three-,[2] four-[3] and five-membered[4] heterocycles. Therefore, our interest in further synthetic investigations was enhanced, and one of our most important aims was to develop a new access to 2*H*-azaphosphirene complexes using amino(aryl)carbene complexes, a base and dichloro(organo)phosphanes. Compared to [bis(trimethylsilyl)methylene]chlorophosphane, which was used in our initial synthetic approach,[5] the advantages should be: the ease of accessibility, the option of introducing *P*-functional groups into 2*H*-azaphosphirene complexes and the potential extension of this method to condensation reactions of other dichloro(organo)element compounds of group-15 elements. Furthermore, in order to mimic the bulkyness of the bis(trimethylsilyl)methyl substituent, which is useful for kinetic stabilization, we chose pentamethyl-2,4-cyclopentadien-1-yl (denoted hereafter as Cp*) and the corresponding dichlorophosphane,[6] Cp^*PCl_2.

Our first attempts to treat amino(aryl)carbene complexes **1a**, **b**,[7] **c**,[8] **d**, **e**[7] with Cp^*Cl_2 (**2**) at ambient temperature in ether with an excess of triethylamine failed. Therefore, we switched to the more polar solvent dichloromethane for the reactions reported hereafter. According to ^{31}P-NMR-spectroscopic investigations, the first condensation step and subsequent transformations (paths **a** and **b**) must have occurred very fast, because the mono-condensation products **3** could not be detected. Instead, the first products formed in these reactions were the (Cp*-phosphanediyl)-bridged dinuclear (carbene)metal complexes **4a**−**e**, aside with small amounts of the 2*H*-azaphosphirene complexes **6a**−**e** and complex **7**. **4a**−**e** were most probably formed, according to the two pathways **a**, **b** depicted in Scheme 1. Path **a** describes a further condensation, yielding **4a**−**e**, whereas a base-induced hydrogen chloride elimination, followed by addition of one equivalent of **1** to the short-lived intermediates **5** (cf. ref.[9]), would also explain the generation of the complexes **4a**−**e** (path **b**). Interestingly, upon prolonged reaction, complexes **4a**−**e** eliminated **1** yielding the 2*H*-azaphosphirene complexes **6a**−**e**, probably by unspecified rearrangements of **5**; this elimination reaction has been proven for the case of **4c** by treating a pure sample of **4c** with triethylamine yielding **6c**. We observed that one of the factors that limited the yields of **6a**−**e** was the rate of the reaction of complexes **6a**−**e** with triethylammonium chloride, which led to [{Cp*P(H)Cl}W(CO)$_5$] (**7**) in all cases (Scheme 1). This latter reaction was found to depend strongly on the nature of the *para*-phenyl substituent, the concentration and, most importantly, on the reaction temperature. Therefore, the temperature had to be kept between 0 and 18°C throughout the reactions and subsequent manipulations. Apart from complexes **4a**−**e**, **6a**−**e** and **7**, two other unidentified products (amounts < 5%) were formed transi-

[◇] Part 12: See ref.[1].

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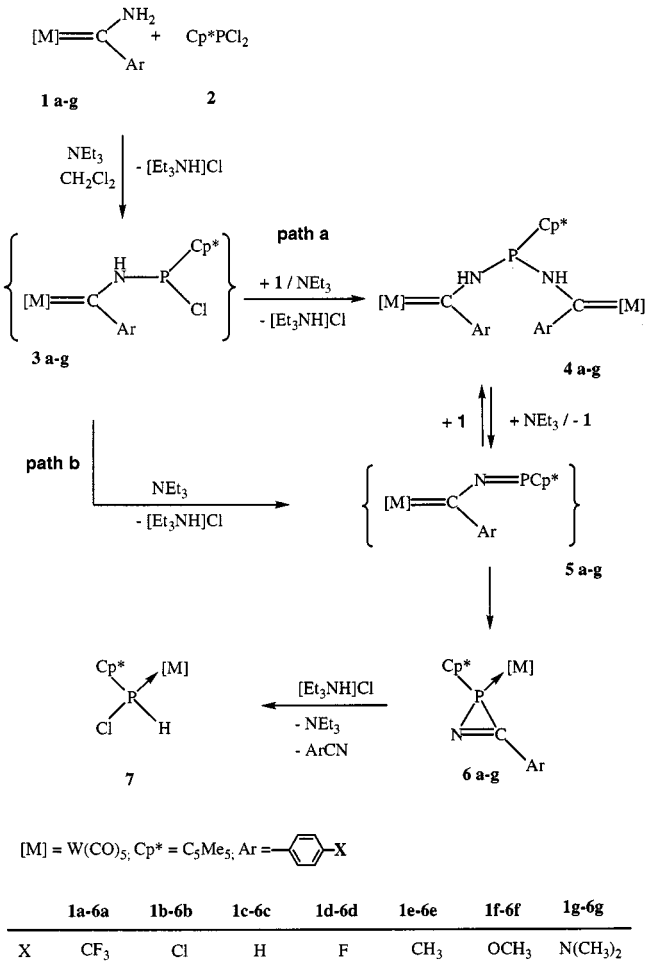
ently; e.g. after generating complex **4c** by treating two equivalents of complex **1c** with one equivalent of **2**, ^{31}P-NMR signals appeared at δ = 42.1 [d, ^{1}J(P,H) = 503.0 Hz] and δ = 28.2 [d, ^{1}J(P,H) = 511.0 Hz]. Based on these ^{31}P-NMR-spectroscopic observations, we tentatively assign these resonances to products with $\sigma^4\lambda^5$-PH-functional structural units, which could arise from hydrogen-shift reactions from the nitrogen to the phosphorus atom in **4c**.

Scheme 1. Proposed reaction course for the formation of metal complexes **4a**–**g**, **6a**–**g** and **7**

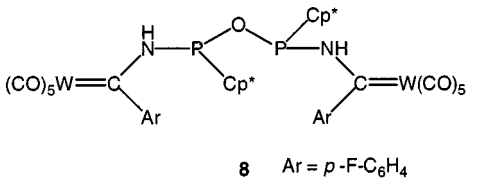


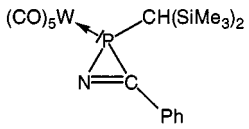
	1a-6a	1b-6b	1c-6c	1d-6d	1e-6e	1f-6f	1g-6g
X	CF_3	Cl	H	F	CH_3	OCH_3	$N(CH_3)_2$

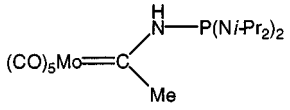
If reactions of **1** with **2** were carried out in the presence of traces of water, other products were formed; in the reaction of **1c** with **2**, we were able to isolate the dinuclear (carbene)metal complex **8** (Scheme 2) having the P(Cp*)-O-P(Cp*) instead of the P(Cp*) bridging unit. This P-O-P bridge most probably resulted from a condensation reaction of two transiently formed (carbene)metal complexes, one having a PCl- and the other a POH-functional group.

Although all complexes described herein have been separated and purified by low-temperature column chromatography and crystallization, we were unable to obtain exact elemental analyses, for reasons that are unclear. Nevertheless, the products were unambigously characterized by several spectroscopic methods. NMR-spectroscopic data of

Scheme 2







complexes **4a**–**e**, **6a**–**e**, **7** and **8** are presented in Tables 1 and 2; information on crystallographic data collection and structure determination of complexes **4a**, **b**, **6b**, **c** and **8** are summarized in Table 3, characteristic structural data of complexes **4a**, **b** and **8** are given in Table 4 and those of **6b**, **c** together with **9**, {2-[bis(trimethylsily)methyl]-3-phenyl-2*H*-azaphosphirene-κP}pentacarbonyltungsten(0)[7], in Table 5.

Table 1. Selected ^{13}C-[a], ^{31}P-NMR-spectroscopic[a] data of dinuclear [(4-X-phenyl)carbene]metal complexes **4a**–**g** and **8**

X	4	δ^{31}P	δ^{13}C-(M=CR_2)	J(P,C)	δ^{13}C-(Ar-C1)	J(P,C)
CF_3	**a**	63.1	285.4	s	155.5	9.7
Cl	**b**	61.9	285.9	s	150.9	9.7
H	**c**	63.0	287.1	s	152.9	10.0
F	**d**	62.1	286.3	s	149.0	9.7
CH_3	**e**	63.0	288.1	s	150.3	9.7
OCH_3	**f**	62.5[b]	[c]	[c]	[c]	[c]
$N(CH_3)_2$	**g**	64.7	282.4	s	151.0	9.7
F	**8**	130.0	283.7	s	149.3	[c]

[a] $CDCl_3$, room temp.; δ/[ppm], J/[Hz]. – [b] Reaction solution. – [c] Not determined.

Significant structural units of complexes **4a**–**g** and **8** such as W=CR_2, Ar–C1 and Cp*P(NR_2)X (X = O, NR_2) are characterized by their typical NMR resonances (Table 1), the latter units displaying chemical shift values in their ^{31}P-NMR spectra at δ = 63±2 and the former at low field at δ = 285±3 (W=CR_2) and 152±4 (Ar-*C*1). It should be noted that the ^{31}P-^{13}C coupling-constant magnitudes are very small for the W=CR_2 carbon atoms (in all cases the signals could not be resolved) and ca. 10 Hz for the Ar-*C*1 carbon atoms. Although no temperature-dependent NMR measurements were undertaken to investigate circumambulatory 1,5-sigmatropic rearrangements of the phosphorus moiety along the Cp* ring in **4a**–**g**, these compounds should show degenerate rearrangements of this type, in contrast to coordinated phosphorus compounds (such as the 2*H*-azaphosphirene complexes **6a**–**g**).[6][10]

2*H*-azaphosphirene complexes **6a**–**g** display trends in chemical shift values and coupling constants (Table 2) that are quite similar, but less pronounced than those of recently

described 2-(*p*-phenyl)-substituted 2*H*-azaphosphirene complexes with the bis(trimethylsilyl)methyl group at phosphorus atom.[7] Compared to the latter complexes, **6a**−**g** have 2*H*-azaphosphirene ring carbon atom resonances that are generally more upfield shifted and have smaller ^{31}P-^{13}C coupling-constant magnitudes. There are remarkable upfield shifts in the ^{1}H- and ^{13}C-NMR resonances of the Cp*−C1 methyl groups, which are even more shielded than in compounds such as Cp*PH_2 (δ = 1.10).[6] Although the origin of this significant effect is not yet understood, two further aspects seem relevant. First, in order to enable better comparison with complex **9**, the ^{15}N-NMR resonance of **6c** was determined [**6c**: δ = −65.2, ^{1}J(P,N) = 39.0 Hz; versus **9**: δ = −53.2, ^{1}J(P,N) = 36.9 Hz]; this presumably points to a higher electron density at the nitrogen atom in **6c**. The second point is discussed below.

Table 2. Selected ^{13}C-[a], ^{31}P-NMR- spectroscopic[a] data of (4-X-phenyl)-substituted complexes **6a**−**g** (exclusively ring atoms of the 2*H*-azaphosphirene ring system)

X	**6**	$\delta^{31}P$	^{1}J(P,W)	$\delta^{13}C$	ΣJ(P,C)
CF_3	**a**	−102.5	289.6	188.3	s
Cl	**b**	−105.3	289.2	186.5	s
H	**c**	−167.3	288.4	189.0	1.7
F	**d**	−105.9	289.0	188.1	s
CH_3	**e**	−110.8	287.2	188.6	s
OCH_3	**f**	−109.8	285.6	187.5	s
$N(CH_3)_2$	**g**	−117.7[b]	285.1[b]	[c]	[c]

[a] $CDCl_3$, room temp.; δ/[ppm], *J*/[Hz]. − [b] Reaction solution. − [c] Not determined.

The molecular structures of the complexes **4a**, **b**, as determined by X-ray crystallography (Figures 1, 2 and Table 3), consist of two Cp*P-bridged amino(aryl)carbene complex moieties, which have an (*E*,*E*) configuration of the pentacarbonyltungsten and the Cp*P fragment with respect to the C−N bond and which differ mainly in their metal−carbon and nitrogen−phosphorus bond lengths of their W−C−P−N skeletons (Table 4). Compared to the structure of [{*N*-[bis(diisopropylamino)phosphanyl]amino}-(methyl)methylene]pentacarbonylmolybdenum(0)[11] (**10**), all P−N bonds of **4a**, **b** are shorter than the related P−N bond of **10** [1.803(2) Å] (Table 4). It is noteworthy that **4a**, **b** always show combinations of short P−N bonds and small N−P−C angles (or the opposite); these differences in bonding *may* serve as picture for an early stage of the elimination process, which was shown to proceed in solution. In contrast to these findings, complex **8** (Figure 3) displays less dissimilar bonds and angles of its structural subunits (Table 4).

2*H*-azaphosphirene complexes **6b**,**c** have molecular structures (Figures 4, 5 and 6) which are somewhat different from the previously reported structure[7] of complex **9** (Table 5). Interesting features are the PCN/arene interplanar angles of 15.4° (**6b**) and 21.3° (**6c**) versus 2° in **9** and the increased bond angles of the C−P−W moieties of **6b**,**c** [C refers in these cases to the directly phosphorus-bonded carbon atoms of the Cp* and $CH(SiMe_3)_2$ groups; Figure 5 shows a better view of the arrangement of the

Figure 1. Molecular structure of **4a** in the crystal (ellipsoids represent 30% probability levels, hydrogen atoms are omitted for clarity)

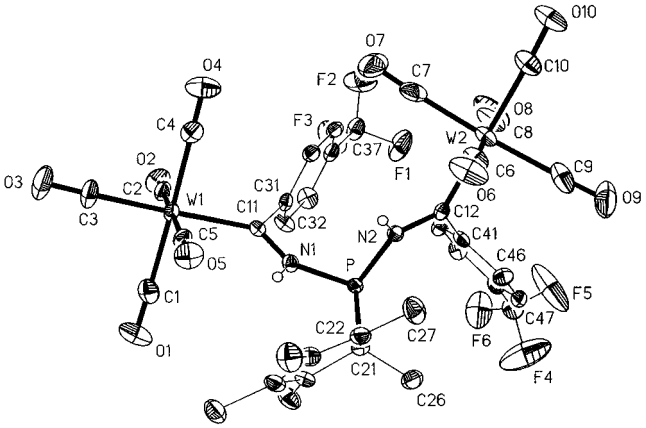


Figure 2. Molecular structure of **4b** in the crystal (ellipsoids represent 50% probability levels, hydrogen atoms are omitted for clarity)

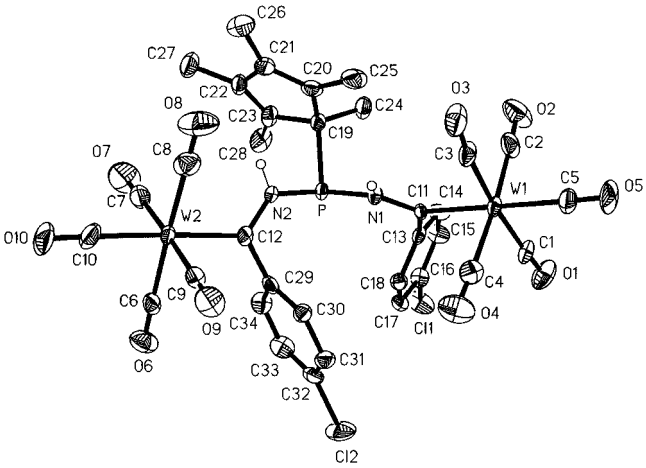


Figure 3. Molecular structure of **6b** in the crystal (ellipsoids represent 50% probability levels, hydrogen atoms are omitted for clarity)

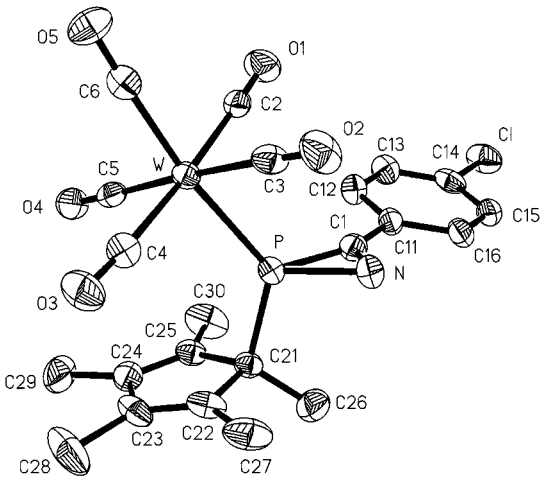


Figure 4. Molecular structure of **6c** in the crystal (ellipsoids represent 50% probability levels, hydrogen atoms are omitted for clarity)

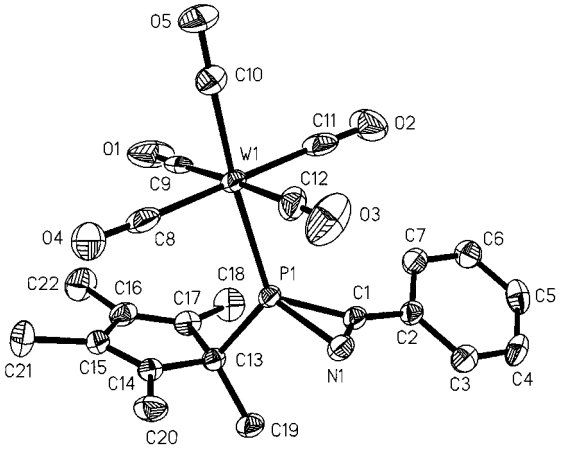


Figure 5. Molecular structure of **6c** in the crystal (view showing the spatial arrangement of the three planar groups of **6c**)

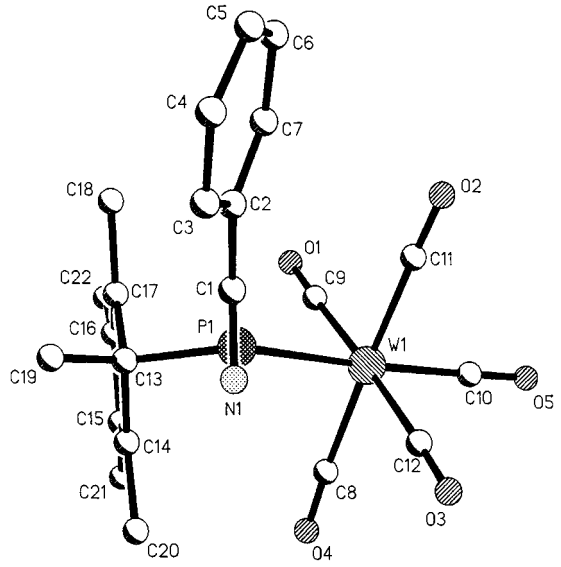
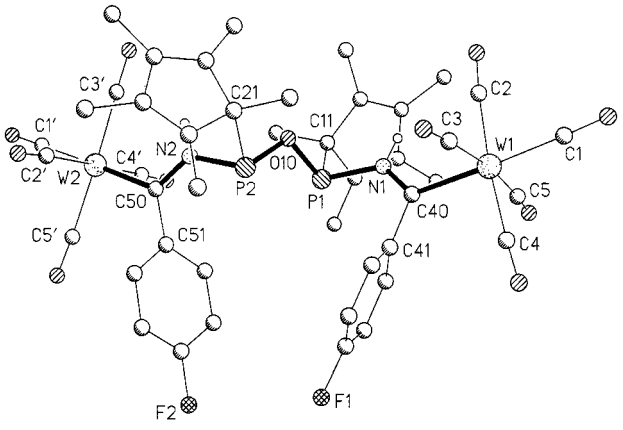


Figure 6. Molecular structure of **8** in the crystal (hydrogen atoms are omitted for clarity)



planar groups of **6c**]. Remarkable are also the arrangements of the Cp* [and $CH(SiMe_3)_2$; cf. ref.[7][9]] group(s); the sterically bulky substituents point away from the pentacarbonyltungsten fragment. Because of this, the Cp*−C1 methyl group points towards the midpoint of the C=N double bond and, therefore, to the π-electron system. If this orientation is retained in solution, a through-space shielding of the atoms of such methyl groups could contribute to the unusual upfield shift of the NMR resonances of the Cp*−C1 methyl group signals.

The chemistry of the compounds reported here is under current investigation with special respect to thermal and photochemical reactions.

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Experimental Section

General: All reactions and manipulations were carried out under deoxygenated dry nitrogen, using standard Schlenk techniques with conventional glassware; solvents were dried according to standard procedures. − NMR spectra were recorded with a Bruker AC-200 or a Bruker AMX-300 spectrometer (AC-200: 200 MHz for ^{1}H; 50.3 MHz for ^{13}C; 81.0 MHz for ^{31}P; AMX-300: 30.4 MHz for ^{15}N, 12.5 MHz for ^{183}W) using [D]chloroform and [D_6]benzene as solvents, the latter as internal standard; shifts are given relative to ext. tetramethylsilane (^{1}H, ^{13}C), H_3CNO_2 (^{15}N), 85% H_3PO_4 (^{31}P) and WO_4^{2-} (^{183}W). ^{15}N-NMR spectra were recorded using ^{31}P- and ^{1}H-based polarisation-transfer techniques (INEPT); ^{183}W spectra were obtained from two-dimensional ^{31}P, ^{183}W{^{1}H} (HMQC) spectra. − Mass spectra were recorded with a Finigan Mat 8430 (70 eV); apart from *m*/*z* values of the molecule ions, only *m*/*z* values with intensities of more than 20% are given. − Infrared spectra were recorded with a Biorad FT-IR 165 (selected data given). − Melting points were obtained with a Büchi 535 capillary apparatus. − Elemental analyses were performed using a Carlo Erba analytical gas chromatograph. − The κ*P* notation serves to differentiate between *P* and *N* coordination of the appropriate heterocycle to the metal center.

General Procedure for the Synthesis of Dinuclear (Carbene)-tungsten Complexes **4a−g** *and 2H-Azaphosphirene Complexes* **6a−g**: To a solution of 2.1 g (5 mmol) of [amino(aryl)carbene]-tungsten complexes **1a−g** in 50 ml of CH_2Cl_2 was added 25 ml of NEt_3 and 1.2 g (5 mmol) of $Me_5C_5PCl_2$ (**2**) at 0°C. The reaction mixtures were stirred at ambient temp. until **2** was consumed (^{31}P NMR). The dark orange reaction mixtures were concentrated to dryness under reduced pressure (0.1 mbar). The crude product mixtures containing approximately 50% of **4**, 40% of **6** and 5% of **7** (according to ^{31}P-NMR signal integration), were separated and purified by low-temperature chromatography [Al_2O_3 (neutral), hexane/diethyl ether 97.5:2.5] and most of them crystallized from pentane at −20°C.

N,N′-[(Pentamethyl-2,4-cyclopentadien-1-yl)phosphanediyl]bis-{[amino(4-trifluoromethylphenyl)methylene]pentacarbonyltungsten(0)} (**4a**): 0.43 g of **4a** (28%) was obtained as a yellow powder, m.p. 148°C (decomp.). − IR (KBr): $\tilde{\nu}$ = 3292 (sw), 3244 (sw) (NH), 2064 (s), 1993 (br), 1980 (br), 1952 (br), 1933 (br), 1916 (br), 1904 (br), 1872 (s) (CO). − ^{1}H NMR ($CDCl_3$): δ = 1.19 [d, ^3J(P,H) = 17.4 Hz, 3 H, Cp*−C1−CH_3], 1.91 (s, 6 H, Cp*−CH_3),

Table 3. Details of crystal structure determination and refinement of complexes **4a**, **b**, **6b**, **c** and **8**

Complex	**4a**	**4b**	**6b**	**6c**	**8**
Formula	$C_{36}H_{25}F_6N_2O_{10}PW_2$	$C_{34}H_{25}Cl_2N_2O_{10}PW_2$	$C_{22}H_{19}ClNO_5PW$	$C_{22}H_{20}NO_5PW$	$C_{44}H_{40}F_2N_2O_{11}P_2W_2$
M_r	1158.25	1091.13	627.65	593.21	1240.42
Crystal habit	yellow prism	orange prism	yellow prism	colourless tablet	yellow needle
Crystal size [mm]	0.55×0.3×0.3	0.6×0.45×0.35	0.55×0.2×0.15	0.6×0.4×0.3	0.6×0.15×0.06
Crystal system	monoclinic	triclinic	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$	$P(-1)$	$P2_1/c$	$P(-1)$	$C2/c$
Cell$_s$constants:					
a [Å]	16.854(4)	9.7548(10)	11.077(4)	8.758(3)	27.504(3)
b [Å]	12.137(6)	10.1874(11)	12.916(5)	10.174(4)	11.1832(12)
c [Å]	19.878(7)	20.137(2)	16.470(6)	14.170(4)	33.104(3)
α [°]	90	87.614(8)	90	74.74(2)	90
β [°]	101.00(3)	78.788(8)	99.38(3)	86.609(14)	108.375(12)
γ [°]	90	77.831(8)	90	66.82(2)	90
V [Å^3]	3992	1918.9	2325	1118.6	9663
Z	4	2	4	2	8
D_x [Mg m^{-3}]	1.927	1.888	1.793	1.762	1.705
μ [mm^{-1}]	5.88	6.23	5.19	5.27	4.89
Transmissions	0.48−0.91	0.48−0.99	0.70−0.84	0.45−0.99	0.62−0.99
F(000)	2208	1040	1216	576	4816
T [°C]	−130	−100	−130	−130	−100
$2\theta_{max}$	50	50	55	50	50
No. of reflections:					
measured	8939	7952	5611	4032	8948
unique	7044	6743	5342	3939	8473
R_{int}	0.029	0.027	0.030	0.008	0.046
Parameters	519	465	285	276	578
Restraints	65	376	42	8	477
wR (F^2, all refl.)	0.074	0.072	0.072	0.068	0.058
R [F, > 4σ(F)]	0.033	0.029	0.034	0.026	0.039
S	1.05	1.04	1.05	1.08	0.78
max. Δρ [e Å^{-3}]	1.41	1.01	0.88	1.46	0.80

Table 4. Selected bond lengths [pm] and angles [°] of complexes **4a**, **b** and **8**

Structural unit	**4a**	**4b**	**8**
W=CR_2	W1−C11 2.165(6) W2−C12 2.193(6)	W1−C11 2.171(4) W2−C12 2.176(4)	W1−C40 2.189(6) W2−C12 2.166(7)
N−C	N1−C11 1.329(7) N2−C12 1.323(7)	N1−C11 1.326(5) N2−C12 1.338(5)	N1−C11 1.16(7) N2−C12 1.332(7)
P−N	P−N1 1.745(5) P−N2 1.768(4)	P−N1 1.760(4) P−N2 1.747(3)	P1−N1 1.755(5) P2−N2 1.753(5)
P−C	P−C21 1.878(6)	P−C21 1.869(4)	P1−C11 1.865(7) P2−C21 1.854(6)
P−O	#	#	P1−O10 1.662(4) P2−O10 1.669(4)
Y−P−X	N1−P−N2 96.1(2) N1−P−C21 96.5(2) N2−P−C21 103.5(2)	N1−P−N2 99.5(2) N1−P−C21 101.0(2) N2−P−C21 95.2(2)	N1−P1−O10 98.5(2) N1−P1−C11 98.1(3) O10−P1−C11 100.9(3)

1.99 (s, 6 H, Cp*−CH_3), 6.45 (m$_c$, 4 H, Ar−*H*), 7.09 (m$_c$, 4 H, Ar−*H*), 8.98 (br, 2 H, N*H*). − ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 11.5/11.7/11.9 (s, Cp*−CH_3), 15.7 [d, ^2J(C,P) = 20.9 Hz, Cp*−C1−CH_3], 60.5 [d, ^1J(C,P) = 26.1 Hz, Cp*−*C*1], 120.6 [q, ^3J(C,F) = 2.2 Hz, Ar−*C*2/2′], 123.6 [q, ^1J(C,F) = 272.4 Hz, CF_3], 125.3 [d, ^4J(C,F) = 3.9 Hz, Ar−*C*3/3′], 130.0 [q, ^2J(C,F) = 33.1 Hz, Ar−*C*4−CF_3], 134.7 [d, J(C,P) = 5.5 Hz, Cp*−C_{Ring}], 142.7 [d, J(C,P) = 3.2 Hz, Cp*−C_{Ring}], 155.5 [d, ^3J(C,P) = 9.7 Hz, Ar−*C*1], 197.3 [s, ^1J(C,W) = 127.6 Hz, *cis*-*C*O], 203.6 (s, *trans*-*C*O), 285.4 (s, W=CR_2). − ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 63.1 (s). − ^{31}P NMR ($CDCl_3$): δ = 63.1 [d, ^2J(P,H) = 18.6 Hz]. − MS (EI, ^{184}W); *m/z* (%): 1158 (4) [$M^{+\bullet}$], 1130 (2) [(M − CO)$^+$]. − $C_{36}H_{25}F_6N_2O_{10}PW_2$ (1158.2): calcd. C 37.33, H 2.18, N 2.42; found C 36.98, H 2.50, N 2.29.

N,N′-[(Pentamethyl-2,4-cyclopentadien-1-yl)phosphanediyl]bis-{[amino(4-chlorophenyl)methylene]pentacarbonyltungsten(0)} (**4b**): 0.51 g of **4b** (33%) was obtained as a yellow powder. − M.p. 123°C (decomp.). − IR (KBr): ṽ = 3312 (sw), 3215 (sw) (NH), 2064 (s), 1990 (s), 1963 (w), 1936 (w), 1910 (w) (CO) cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 1.15 [d, ^3J(P,H) = 17.5 Hz, 3 H, Cp*−C1−CH_3], 1.88 (s, 6 H, Cp*−CH_3), 1.92 (s, 6 H, Cp*−CH_3), 6.37 (m$_c$, 4 H, Ar−*H*), 7.23 (m, 4 H, Ar−*H*), 8.84 (w, 2 H, N*H*). − ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 11.6−12.0 (s, Cp*−CH_3), 15.7 [d, ^2J(C,P) = 21.1 Hz, Cp*−C1−CH_3], 60.3 [d, ^1J(C,P) = 26.1 Hz, Cp*−*C*1], 122.2 [d, ^4J(C,P) = 2.5 Hz, Ar], 128.5 (s, Ar), 134.1 (s, Ar−*C*4), 134.8 [d, J(C,P) = 5.4 Hz, Cp*−C_{Ring}], 142.4 [d, J(C,P) = 3.3 Hz Cp*−C_{Ring}], 150.9 [d, ^3J(C,P) = 9.7 Hz, Ar-*C*1], 197.5 [s, ^1J(C,W) = 128.0 Hz, *cis*-*C*O], 203.8 (s, *trans*-*C*O), 285.9 (s, W=

Table 5. Selected bond lengths [pm] and angles [°] of complexes **6b**, **c** and **9**

Complex	P1−C1	P1−N1	N1−C1	W−P
6b	1.750(5)	1.812(4)	1.270(6)	2.475(2)
6c	1.764(4)	1.811(4)	1.291(5)	2.4720(12)
9	1.759(5)	1.795(4)	1.272(7)	2.470(2)

Complex	C1−P1−N1	C1−N1−P1	N1−C1−P1	C−P−W
6b	41.7(2)	66.5(3)	71.8(3)	128.1(2)
6c	42.3(2)	66.9(2)	70.8(2)	127.01(13)
9	41.9(2)	67.5(3)	70.6(3)	124.3(2)

*C*R$_2$). − ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 61.9 (s). − ^{31}P NMR (CDCl$_3$): δ = 61.9 [d, ^2J(P,H) = 18.9 Hz]. − MS (EI, ^{184}W); *m/z* (%): 1091 (3) [M$^{+\bullet}$], 1063 (4) [(M − CO)$^+$], 810 (12) [(M − 10 CO)$^+$], 323 (30) [(C$_5$O$_5$W)$^+$], 137 (100) [C$_7$H$_4$ClN)$^+$]. − C$_{34}$H$_{25}$Cl$_2$N$_2$O$_{10}$PW$_2$ (1091.1): calcd. C 37.49, H 2.31, N 2.57; found C 36.48, H 2.51, N 2.63.

N,N′-[(Pentamethyl-2,4-cyclopentadien-1-yl)phosphanediyl]bis-{[amino(phenyl)methylene]pentacarbonyltungsten(0)} (**4c**): 0.56 g of **4c** (26%) was obtained as an orange powder. − M.p. 146°C (decomp.). − IR (KBr): ṽ = 2062 (s), 1918 (vs), 1864 (m) (CO) cm^{-1}. − ^{1}H NMR (CDCl$_3$): δ = 1.15 [d, ^3J(P,H) = 17.4 Hz, 3 H, Cp*−C1−C*H*$_3$], 1.92 (s, 6 H, Cp*−C*H*$_3$), 1.99 (s, 3 H, Cp*−C*H*$_3$), 6.45 (m$_c$, 4 H, Ar−*H*), 7.28 (m$_c$, 6 H, Ar−*H*), 8.88 (br, 2 H, N*H*). −^{13}C{^{1}H} NMR (CDCl$_3$): δ = 11.5 (s, Cp*−*C*H$_3$), 11.8 [d, ^3J(P,C) = 7.3 Hz, Cp*−*C*H$_3$], 15.6 [d, ^2J(C,P) = 21.8 Hz, Cp*−C1−*C*H$_3$], 60.6 [d, ^1J(C,P) = 27.6 Hz, Cp*−*C*1], 120.7 [d, ^4J(C,P) = 2.8 Hz, Ar−*C*2/2′], 127.9 (s, Ar−*C*4), 128.2 (s, Ar−*C*3/3′), 135.0 [d, ^3J(C,P) = 5.7 Hz, Cp*−*C*$_{Ring}$], 142.0 [d, ^2J(C,P) = 2.9 Hz, Cp*−*C*$_{Ring}$], 152.9 [d, ^3J(C,P) = 10.0 Hz, Ar−*C*1], 197.7 [s, ^1J(C,W) = 127.7 Hz, *cis*-*C*O], 204.2 (s, *trans*-*C*O), 287.1 (s, W=*C*R$_2$). − ^{15}N NMR (CH$_2$Cl$_2$): δ = −170.5 [dd, ^1J(N,H) = 85, ^1J(P,N) = 67 Hz]. − ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 63.0 (s). − MS [neg. −CI, (isobutane), ^{184}W]; *m/z* (%): 886 (1) [(M − C$_{10}$H$_{16}$)$^-$], 783 (1)[(M − C$_{16}$H$_{20}$N)$^-$], 698 (2) [(M − (C$_5$O$_5$W)$^-$], 324 (100) [C$_5$O$_5$W$^-$]. − C$_{32}$H$_{27}$N$_2$O$_{10}$PW$_2$ (1022.3): calcd. C 39.94, H 2.67, N 2.74; found C 40.09, H 2.76, N 2.72.

N,N′-[(Pentamethyl-2,4-cyclopentadien-1-yl)phosphanediyl]bis-{[amino(4-fluorophenyl)methylene]pentacarbonyltungsten(0)} (**4d**): 0.35 g of **4d** (28%) was obtained as an orange powder. − M.p. 149°C (decomp.). − ^{1}H NMR (CDCl$_3$): δ = 1.19 [d, ^3J(P,H) = 17.4 Hz, 3 H, Cp*−C1−C*H*$_3$], 1.91 (s, 6 H, Cp*−C*H*$_3$), 1.99 (s, 6 H, Cp*−C*H*$_3$), 6.45 (m$_c$, 4 H, Ar−*H*), 7.09 (m$_c$, 4 H, Ar−*H*), 8.98 (w, 2 H, N*H*). − ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 11.5/11.7/11.9 (s, Cp*−*C*H$_3$), 15.6 [d, ^2J(C,P) = 21.1 Hz, Cp*−C1−*C*H$_3$], 60.3 [d, ^1J(C,P) = 26.1 Hz, Cp*−*C*1], 115.3 [d, ^2J(C,F) = 21.9 Hz, Ar−*C*3/3′], 123.1 [dd, ^4J(C,P) = 3.0 Hz, ^3J(C,F) = 8.5 Hz, Ar−*C*2/2′], 134.8 [d, *J*(C,P) = 5.5 Hz, Cp*−C$_{Ring}$], 142.3 [d, *J*(C,P) = 2.9 Hz, Cp*−C$_{Ring}$], 149.0 [dd, ^3J(C,P) = 9.7 Hz, ^4J(C,F) = 3.3 Hz, Ar−*C*1], 162.2 [d, ^1J(C,F) = 249.7 Hz, Ar−*C*4], 197.6 [s, ^1J(C,W) = 127.8 Hz, *cis*-*C*O], 203.9 (s, *trans*-*C*O), 286.3 (s, W=*C*R$_2$). − ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 62.2 (s). − ^{31}P NMR (CDCl$_3$): δ = 62.2 [d, ^2J(P,H) = 16.5 Hz]. − C$_{34}$H$_{25}$F$_2$N$_2$O$_{10}$PW$_2$ (1058.2): calcd. C 38.59, H 2.38, N 2.65; found C 37.69, H 2.51, N 2.57.

N,N′-[(Pentamethyl-2,4-cyclopentadien-1-yl)phosphanediyl]bis-{[amino(4-methylphenyl)methylene]pentacarbonyltungsten(0)} (**4e**): 0.42 g of **4e** (18%) was obtained as an orange powder. − M.p. 117°C (decomp.). − IR (KBr): ṽ = 3297 (s) 3251 (s) (NH), 2067 (br), 1992 (br), 1979 (br), 1949 (br), 1925 (br), 1893 (br), 1860 (br) (CO) cm^{-1}. − ^{1}H NMR (CDCl$_3$): δ = 1.16 [d, ^3J(P,H) = 17.5 Hz, 3 H, Cp*−C1−C*H*$_3$], 1.98 (s, 6 H, Cp*−C*H*$_3$), 1.99 (s, 6 H, Cp*−C*H*$_3$), 2.38 (s, 3 H, Ar−C*H*$_3$), 6.38 (m$_c$, 4 H, Ar−*H*), 7.06 (m$_c$, 4 H, Ar−*H*), 8.82 (br, 2 H, N*H*). − ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 11.5/11.7/11.9 (s, Cp*−*C*H$_3$), 15.6 [d, ^2J(C,P) = 21.6 Hz, Cp*−C1−*C*H$_3$], 21.3 (s, Ar−*C*H$_3$), 60.6 [d, ^1J(C,P) = 27.6 Hz, Cp*−*C*1], 121.3 [d, ^4J(C,P) = 2.5 Hz, Ar], 138.7 (s, Ar), 135.1 [d, *J*(C,P) = 5.7 Hz, Cp*−*C*$_{Ring}$], 138.1 (s, Ar), 141.9 [d, *J*(C,P) = 3.1 Hz, Cp*−*C*$_{Ring}$], 150.3 [d, ^3J(C,P) = 9.7 Hz, Ar−*C*1], 197.8 [s, ^1J(C,W) = 127.6 Hz, *cis*-*C*O], 204.2 (s, *trans*-*C*O), 288.1 (s, W=*C*R$_2$). − ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 63.0 (s). − ^{31}P NMR (CDCl$_3$): δ = 63.0 [d, ^2J(P,H) = 15.8 Hz]. − MS (EI, ^{184}W); *m/z* (%): 1050 (2) [M$^{+\bullet}$], 1022 (2) [(M − CO)$^+$], 992 (48) [(M − 2 CO)$^+$], 966 (46) [(M − 3 CO)$^+$], 267 (100) [C$_{16}$H$_{16}$N$_2$P$^+$], 117 (95) [C$_8$H$_7$N$^+$]. − C$_{36}$H$_{31}$N$_2$O$_{10}$PW$_2$ (1050.3): calcd. C 41.17, H 2.97, N 2.67; found C 40.25, H 3.33, N 2.32.

N,N′-[(Pentamethyl-2,4-cyclopentadien-1-yl)phosphanediyl]bis[{amino[4-(dimethylamino)phenyl]methylene}pentacarbonyltungsten(0)] (**4g**): 0.51 g of **4g** (33%) was obtained as a red powder. − M.p. 105°C (decomp.). − IR (KBr): ṽ = 3239 (w) (NH), 2059 (s), 1909 (br) (CO) cm^{-1}. − ^{1}H NMR (CDCl$_3$): δ = 1.16 (d, ^3J(P,H) = 16.2 Hz, 3 H, Cp*−C1−C*H*$_3$), 1.78 (s, 6 H, Cp*−C*H*$_3$), 1.93 (s, 6 H, Cp*−C*H*$_3$), 2.93 (s, 6 H, N(C*H*$_3$)$_2$), 6.37 (m$_c$, 4 H, Ar−*H*), 6.65 (m$_c$, 4 H, Ar−*H*), 8.82 (br, 2 H, N*H*). − ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 11.4−12.0 (s, Cp*−*C*H$_3$), 15.8 [d, ^2J(C,P) = 20.7 Hz, Cp*−C1−*C*H$_3$], 40.1 [s, N(*C*H$_3$)$_2$], 60.9 [d, ^1J(C,P) = 27.2 Hz, Cp*−*C*1], 110.3 (s, Ar), 111.0 (s, Ar), 126.2 (s, Ar), 135.4 [d, *J*(C,P) = 5.4 Hz, Cp*−*C*$_{Ring}$], 141.5 [d, *J*(C,P) = 3.4 Hz, Cp*−*C*$_{Ring}$], 151.0 (s, Ar−*C*1), 198.5 [s, ^1J(C,W) = 127.6 Hz, *cis*-*C*O], 204.2 (s, *trans*-*C*O), 282.4 (s, W=*C*R$_2$). − ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 64.7 (s). − ^{31}P NMR (CDCl$_3$): δ = 64.7 [d, ^2J(P,H) = 13.5 Hz]. − C$_{38}$H$_{37}$N$_4$O$_{10}$PW$_2$ (1108.1): calcd. C 41.18, H 3.36, N 5.05; found C 42.18, H 3.96, N 4.69.

Pentacarbonyl[2-(pentamethyl-2,4-cyclopentadien-1-yl)-3-(4-trifluoromethyphenyl)-2H-azaphosphirene-κP]tungsten(0) (**6a**): 0.11 g of **6a** (3%) was obtained as a yellow powder. − M.p. 117°C (decomp.). − ^{1}H NMR (CDCl$_3$): δ = 0.57 [d, ^3J(P,H) = 15.1 Hz, 3 H, Cp*−C1−C*H*$_3$], 1.77 [d, ^4J(P,H) = 5.9 Hz, 3 H, Cp*−C*H*$_3$], 1.79 [d, ^4J(P,H) = 6.7 Hz, 3 H, Cp*−C*H*$_3$], 1.91 (s, 3 H, Cp*−C*H*$_3$), 2.04 (s, 3 H, Cp*−C*H*$_3$), 7.84 (m$_c$, 2 H, Ar*H*), 8.13 (m$_c$, 2 H, Ar*H*). − ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 9.98/10.0/10.6/10.8 (s, Cp*−*C*H$_3$), 16.3 [d, ^2J(C,P) = 3.0 Hz, Cp*−C1−*C*H$_3$], 61.4 [d, ^1J(C,P) = 13.7 Hz, Cp*−*C*1], 122.4 [q, ^1J(C,F) = 275.4 Hz, Ar−*C*F$_3$], 124.6 [q, ^3J(C,F) = 3.3 Hz, Ar−*C*3/3′], 128.5 [d, ^2J(C,P) = 15.3 Hz, Ar−*C*1], 128.9 (s, Ar−*C*2/2′), 132.0 [q, ^2J(C,F) = 32.9 Hz, Ar−*C*4−CF$_3$], 132.2 [d, *J*(C,P) = 4.9 Hz, Cp*−*C*$_{Ring}$], 134.8 [d, *J*(C,P) = 1.7 Hz Cp*−*C*$_{Ring}$], 140.8 [d, *J*(C,P) = 6.9 Hz, Cp*−*C*$_{Ring}$], 142.2 [d, *J*(C,P) = 7.6 Hz, Cp*−*C*$_{Ring}$], 188.3 (s, P*C*N), 193.5 [d, ^2J(C,P) = 8.4 Hz, *cis*-*C*O], 195.4 [d, ^2J(C,P) = 38.5 Hz, *trans*-*C*O]. − ^{31}P{^{1}H} NMR (CDCl$_3$): δ = −102.5 [s, ^1J(P,W) = 289.6 Hz]. − C$_{23}$H$_{19}$F$_3$NO$_5$PW (661.3): calcd. C 41.78, H 2.90, N 2.12; found C 40.97, H 2.99, N 2.02.

Pentacarbonyl[3-(4-chlorophenyl)-2-(pentamethyl-2,4-cyclopentadien-1-yl)-2H-azaphosphirene-κP]tungsten(0) (**6b**): 0.4 g of **6b** (17%) was obtained as a yellow powder. − M.p. 91°C (decomp.). − IR (KBr): ṽ = 2072 (s), 1989 (s), 1976 (s), 1932 (s), 1918 (w) (CO) cm^{-1}. − ^{1}H NMR (CDCl$_3$): δ = 0.63 [d, ^3J(P,H) = 14.8 Hz, 3 H, Cp*−C1−C*H*$_3$], 1.84 [d, ^4J(P,H) = 4.7 Hz, 3 H, Cp*−C*H*$_3$], 1.87 [d, ^4J(P,H) = 5.4 Hz, 3 H, Cp*−C*H*$_3$], 1.97 (s, 3 H, Cp*

−CH_3), 2.11 (s, 3 H, Cp*−CH_3), 7.64 (m_c, 2 H, Ar*H*), 8.03 (m_c, 2 H, Ar*H*). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 11.0/11.7/11.9 (s, Cp*−CH_3), 17.3 [d, ^2J(C,P) = 3.3 Hz, Cp*−C1−CH_3], 61.2 [d, ^1J(C,P) = 13.5 Hz, Cp*−*C*1], 124.6 [d, ^2J(C,P) = 15.4 Hz, Ar−*C*1], 130.2 (s, Ar−*C*2/2′), 130.9 (s, Ar−*C*3/3′), 133.4 (d, Cp*−C_{Ring}), 136.1 [d, *J*(C,P) = 1.7 Hz Cp*−C_{Ring}], 140.9 (s, Ar−*C*4), 141.7 [d, *J*(C,P) = 6.7 Hz, Cp*−C_{Ring}], 143.1 [d, *J*(C,P) = 7.7 Hz, Cp*−C_{Ring}], 186.5 (s, P*C*N), 194.7 [d, ^2J(C,P) = 8.7 Hz, ^1J(C,W) = 117.6 Hz, *cis*-*C*O], 196.6 [d, ^2J(C,P) = 38.2 Hz, *trans*-*C*O]. − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −105.3 [s, ^1J(P,W) = 289.2 Hz]. − MS (EI, ^{184}W); *m/z* (%): 627 (18) [$M^{+\bullet}$], 490 (12) [$C_{15}H_{15}PO_5W^+$], 137 (100) [$C_7H_4NCl^+$]. − $C_{22}H_{19}ClNO_5PW$ (627.7): calcd. C 42.10, H 3.05, N 2.23; found C 41.65, H 2.96, N 2.47.

Pentacarbonyl[2-(pentamethyl-2,4-cyclopentadien-1-yl)-3-phenyl-2H-azaphosphirene-κP]tungsten(0) (**6c**): 0.24 g of **6c** (22%) was obtained as a yellow powder. − M.p. 88°C (decomp.). − IR (KBr): $\tilde{\nu}$ = 2072 (s), 1991 (s), 1940 (br) (CO) cm^{-1}. − ^1H NMR (CD_2Cl_2): δ = 0.64 [d, ^3J(P,H) = 14.9 Hz, 3 H, Cp*−C1−CH_3], 1.86 [pt, ^4J(P,H) = 9.7 Hz, 6 H, Cp*−CH_3], 1.99 (s, 3 H, Cp*−CH_3), 2.12 (s, 3 H, Cp*−CH_3), 7.70 (m_c, 3 H, Ar−*H*), 8.12 (m_c, 2 H, Ar−*H*). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 11.2/11.3/11.8/12.0 (s, Cp*−CH_3), 17.5 [d, ^3J(C,P) = 3.5 Hz, Cp*−C1−CH_3], 62.6 [d, ^1J(C,P) = 13.6 Hz, Cp*−*C*1], 126.6 [d, ^2J(C,P) = 15.2 Hz, Ar−*C*1], 130.1 (s, Ar), 130.3 (s, Ar), 134.1 [d, *J*(C,P) = 5.0 Hz, Cp*−C_{Ring}], 134.7 (s, Ar−*C*4), 136.6 [d, *J*(C,P) = 1.7 Hz, Cp*−C_{Ring}], 141.8 [d, *J*(C,P) = 6.7 Hz, Cp*−C_{Ring}], 143.2 [d, *J*(C,P) = 7.7 Hz, Cp*−C_{Ring}], 189.3 [d, *J*(C,P) = 1.3 Hz, P*C*N], 195.3 [d, ^2J(C,P) = 8.4 Hz, *cis*-*C*O], 197.4 [d, ^2J(C,P) = 37.7 Hz, *trans*-*C*O]. − ^{15}N NMR (CH_2Cl_2): δ = −65.2 [d, *J*(P,N) = 39.0 Hz]. − $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = −106.4 [s, ^1J(P,W) = 286.5 Hz]. − ^{183}W NMR (CD_2Cl_2): δ = −3126 (d). − MS [pos. −CI (NH_3), ^{184}W]; *m/z* (%): 594 (6) [(M + H)$^+$], 491 (3) [$C_{15}H_{15}O_5WP^+$], 407 (1) [$C_{12}H_{15}O_5WP^+$], 136 (100) [$C_{10}H_{16}^+$]. − $C_{22}H_{20}NO_5PW$ (593.2): calcd. C 44.54, H 3.40, N 2.36; found C 43.15, H 3.24, N 2.38.

Pentacarbonyl[3-(4-fluorophenyl)-2-(pentamethyl-2,4-cyclopentadien-1-yl)-2H-azaphosphirene-κP]tungsten(0) (**6d**): 0.14 g of **6d** (4%) was obtained as a yellow powder. − M.p. 97°C (decomp.). − IR (KBr): $\tilde{\nu}$ = 2072 (s), 1998 (s), 1976 (s), 1932 (w), 1918 (w) (CO) cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 0.56 [d, ^3J(P,H) = 14.8 Hz, 3 H, Cp*−C1−CH_3], 1.78 [d, ^4J(P,H) = 4.6 Hz, 3 H, Cp*−CH_3], 1.80 [d, ^4J(P,H) = 5.1 Hz, 3 H, Cp*−CH_3], 1.91 [d, ^4J(P,H) = 4.6 Hz, 3 H, Cp*−CH_3], 2.04 (s, 3 H, Cp*−CH_3), 7.28 (m_c, 2 H, Ar*H*), 8.04 [m_c, 2 H, ^3J(C,F) = 8.8 Hz, Ar*H*]. − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 11.1/11.7/11.9 (s, Cp*−CH_3), 17.2 [d, ^2J(C,P) = 3.6 Hz, Cp*−C1−CH_3], 62.3 [d, ^1J(C,P) = 13.6 Hz, Cp*−*C*1], 122.7 [dd, ^2J(C,P) = 15.3 Hz, ^4J(C,F) = 3.1 Hz, Ar−*C*1], 117.8 [d, ^2J(C,F) = 22.5 Hz, Ar−*C*3/3′], 132.2 [d, ^3J(C,F) = 9.6 Hz, Ar−*C*2/2′], 133.4 [d, *J*(C,P) = 4.3 Hz, Cp*−C_{Ring}], 136.2 [d, *J*(C,P) = 2.3 Hz, Cp*−C_{Ring}], 141.5 [d, *J*(C,P) = 6.9 Hz, Cp*−C_{Ring}], 143.0 [d, *J*(C,P) = 6.9 Hz, Cp*−C_{Ring}], 166.4 [d , ^2J(C,F) = 257.4 Hz, Ar−*C*4], 188.1 (s, P*C*N), 194.7 [d, ^2J(C,P) = 8.3 Hz, ^1J(C,W) = 125.6 Hz, *cis*-*C*O], 196.7 [d, ^2J(C,P) = 37.9 Hz, *trans*-*C*O]. − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −105.9 [s, ^1J(P,W) = 289.0 Hz]. − $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ = −102.5 (s). − MS (EI, ^{184}W); *m/z* (%): 611 (2) [$M^{+\bullet}$], 490 (23) [(M − $C_7H_4FN)^+$], 135 (31) [$C_{10}H_{15}^+$], 121 (100) [$C_7H_4FN^+$], 95 (25) [CH_3F^+]. − MS (pos. −CI (NH_3), ^{184}W); *m/z* (%): 612 (100) [(M + H)$^+$], 491 (29) [(M − $C_7H_4FN)^+$], 137 (58) [$C_{10}H_{15}^+$]. − $C_{22}H_{19}FNO_5PW$ (611.2): calcd. C 42.23, H 3.13, N 2.29; found C 42.27, H 3.20 , N 2.32.

Pentacarbonyl[3-(4-methylphenyl)-2-(pentamethyl-2,4-cyclopentadien-1-yl)-2H-azaphosphirene-κP]tungsten(0) (**6e**): 0.3 g of **6e** (8%) was obtained as a yellow powder. − M.p. 78°C (decomp.). − ^1H NMR (C_6D_6): δ = 0.49 [d, ^3J(P,H) = 14.5 Hz, 3 H, Cp*−C1−CH_3], 1.72 [d, ^4J(P,H) = 3.9 Hz, 3 H, Cp*−CH_3], 1.75 [d, ^4J(P,H) = 4.5 Hz, 3 H, Cp*−CH_3], 1.89 (s, 3 H, Cp*−CH_3), 2.10 (s, 3 H, Cp*−CH_3), 6.89 (m_c, 2 H, Ar*H*), 7.95 (m_c, 2 H, Ar*H*). − $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 11.1/11.6/11.8 (s, Cp*−CH_3), 17.1 [d, ^2J(C,P) = 3.8 Hz, Cp*−C1−CH_3], 21.6 (s, Ar−CH_3), 62.5 [d, ^1J(C,P) = 13.5 Hz, Cp*−*C*1], 123.8 [d, ^2J(C,P) = 13.4 Hz, Ar−*C*1], 128.3 (s, Ar), 129.7 (s, Ar), 130.3 [d, ^2J(C,P) = 24.3 Hz, Ar−*C*4], 133.9 (s, Cp*−C_{Ring}), 136.7 (s, Cp*−C_{Ring}), 141.4 [d, *J*(C,P) = 6.3 Hz, Cp*−C_{Ring}], 142.0 [d, *J*(C,P) = 7.9 Hz Cp*−C_{Ring}], 188.6 (s, P*C*N), 195.1 [d, ^2J(C,P) = 8.8 Hz, *cis*-*C*O], 197.5 [d, ^2J(C,P) = 37.5 Hz, *trans*-*C*O]. − $^{31}P\{^1H\}$ NMR (C_6D_6): δ = −110.8 [d, ^2J(P,W) = 287.2 Hz]. − MS (EI, ^{184}W); *m/z* (%): 607 (1) [$M^{+\bullet}$], 490 (16) [$C_{16}H_{15}O_5PW^+$], 406 (19) [($C_{16}H_{15}O_5PW$ − 3 CO)$^+$], 117 (100) [$C_8H_7N^+$]. − MS [pos. −CI (NH_3), ^{184}W]; *m/z* (%): 608 (1) [(M + H)$^+$], 491 (18) [($C_{16}H_{15}O_5PW$ + H)$^+$], 135 (100) [$C_{10}H_{15}^+$]. − MS [neg. −CI (NH_3), ^{184}W]; *m/z* (%): 637 (1) [M^-], 323 (100) [$C_5O_5W^-$]. − $C_{23}H_{22}NO_5PW$ (607.2): calcd. C 45.49, H 3.65, N 2.31; found C 45.76, H 3.64, N 2.17.

Pentacarbonyl[3-(4-methoxyphenyl)-2-(pentamethyl-2,4-cyclopentadien-1-yl)-2H-azaphosphirene-κP]tungsten(0) (**6f**): 0.12 g of **6f** (4%) was obtained as a yellow powder. − M.p. 89°C (decomp.). − IR (KBr): $\tilde{\nu}$ = 2072 (s), 1982 (br), 1958 (br), 1936 (br), 1911 (br) (CO) cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 0.63 [d, ^3J(P,H) = 14.5 Hz, 3 H, Cp*−C1−CH_3], 1.85 (s, 3 H, Cp*−CH_3), 1.88 (s, 3 H, Cp*−CH_3), 1.98 (s, 3 H, Cp*−CH_3), 2.12 (s, 3 H, Cp*−CH_3), 3.92 (s, 3 H, OCH_3), 7.14 (m_c, 2 H, Ar*H*), 8.04 (m_c, 2 H, Ar*H*). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 11.0/11.1/11.6/11.9 (s, Cp*−CH_3), 17.0 [d, ^2J(C,P) = 3.8 Hz, Cp*−C1−CH_3], 55.7 (s, OCH_3), 62.3 [d, ^1J(C,P) = 13.8 Hz, Cp*−*C*1], 115.3 (s, Ar−*C*3/3′), 118.4 [d, ^2J(C,P) = 15.5 Hz, Ar−*C*1], 132.1 (s, Ar−*C*2/2′), 133.7 [d, *J*(C,P) = 4.8 Hz Cp*−C_{Ring}], 136.4 [d, *J*(C,P) = 2.7 Hz Cp*−C_{Ring}], 141.2 [d, *J*(C,P) = 6.9 Hz, Cp*−C_{Ring}], 142.6 [d, *J*(C,P) = 7.6 Hz, Cp*−C_{Ring}], 164.6 (s, Ar−*C*4), 187.5 (s, P*C*N), 194.8 [d, ^2J(C,P) = 8.3 Hz, ^1J(C,W) = 134.1 Hz, *cis*-*C*O], 196.9 [d, ^2J(C,P) = 37.1 Hz, *trans*-*C*O]. − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −109.8 [s, ^1J(P,W) = 285.6 Hz]. − MS [pos. −CI (NH_3), ^{184}W]; *m/z* (%): 624 (2) [(M + H)$^+$], 491 (6) [(M − $C_{10}H_{15}$)$^+$], 405 [(M − 3 CO)$^+$], 151 (100) [(C_7H_7NO + NH_4)$^+$], 136 (11) [($C_{10}H_{15}$ + H)$^+$]. − $C_{23}H_{22}NO_6PW$ (623.0): calcd. C 44.32, H 3.56, N 2.25; found C 45.21, H 3.62, N 2.35.

Pentacarbonyl[chloropentamethyl-2,4-cyclopentadien-1-ylphosphane]tungsten(0) (**7**): 0.19 g of **7** (18%) was obtained as a pale yellow powder. − M.p. 46°C (decomp.). − IR (KBr): $\tilde{\nu}$ = 2072 (s), 1991 (s), 1940 (s, br) (CO) cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 1.57 [d, ^3J(P,H) = 13.9 Hz, 3 H, Cp*−C1−CH_3], 1.79 (s, 3 H, Cp*−CH_3), 1.81 (s, 3 H, Cp*−CH_3), 1.85 (s, 3 H, Cp*−CH_3), 1.97 (s, 3 H, Cp*−CH_3), 7.36 [d, ^1J(P,H) = 337.4 Hz, 1 H, PH]. − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 11.5/11.9/11.95/12.0 (s, Cp*−CH_3), 18.6 [d, ^3J(C,P) = 6.9 Hz, Cp*−C1−CH_3], 60.6 [d, ^1J(C,P) = 10.1 Hz, Cp*−*C*1], 133.9 [d, *J*(C,P) = 4.7 Hz, Cp*−C_{Ring}], 136.6 (s, Cp*−C_{Ring}), 141.5 [d, *J*(C,P) = 6.8 Hz, Cp*−C_{Ring}], 142.9 [d, *J*(C,P) = 8.1 Hz, Cp*−C_{Ring}], 195.2 [d, ^2J(C,P) = 8.5 Hz, *cis*-*C*O], 197.0 [d, ^2J(C,P) = 37.7 Hz, *trans*-*C*O]. − Resonances of the two isotopomers of **7** have been detected: **7** (^{35}Cl): $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 76.75 [s, ^1J(P,W) = 274.2 Hz]; **7** (^{37}Cl) $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 76.73 [s, ^1J(W,P) = 273.9 Hz]. − MS [pos. −CI (NH_3), ^{35}Cl, ^{184}W]; *m/z* (%): 525 (8) [(M − H)$^+$], 491 (95) [$C_{15}H_{15}O_5P^+$], 136 (100) [($C_{10}H_{15}$ + H)$^+$]. − $C_{15}H_{16}ClO_5PW$ (526.6).

P,P′-Oxybis[pentacarbonyl{(4-fluorophenyl)[(pentamethyl-2,4-cyclopentadien-1-yl-phosphanyl)amino]methylene}tungsten(0)] (**8**):

0.09 g of **8** (3%) was obtained as an orange powder. − M.p. 139°C (decomp.). − IR (KBr): $\tilde{\nu}$ = 2062 (s), 1985 (s), 1933 (br), 1893 (br) (CO) cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 1.31 [pt, *J*(P,H) = 7.8 Hz, 3 H, Cp*−C1−CH_3], 1.75/1.85/1.98/2.08 (s, 3 H, Cp*−CH_3), 6.59 (m_c, 4 H, Ar−*H*), 6.89 (m_c, 4 H, Ar−*H*), 9.48 (w, 2 H, N*H*). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 11.4/12.6 (s, Cp*−*C*H_3), 14.0 [pt, *J*(C,P) = 7.0 Hz, Cp*−C1−*C*H_3], 62.7 [pt, *J*(C,P) = 10.5 Hz, Cp*−*C*1], 114.7 [d, ^2J(C,F) = 23.0 Hz, Ar−*C*3/3′], 123.1 (m_c, Ar−*C*2/2′), 133.8 [pt, *J*(C,P) = 7.2 Hz, Cp*−C_{Ring}], 135.3 (s, Cp*−C_{Ring}), 141.3 [pt, *J*(C,P) = 2.3 Hz, Cp*−C_{Ring}], 142.3 (s, Cp*−C_{Ring}), 149.3 (m_c, Ar−*C*1), 161.9 [d, ^1J(C,F) = 249.1 Hz, Ar−*C*4], 197.6 [s, ^1J(C,W) = 127.6 Hz, *cis*-*C*O], 204.1 (s, *trans*-*C*O), 283.8 (s, W=*C*R_2). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 130.1 (s). − ^{31}P NMR ($CDCl_3$): δ = 130.1 [d, ^2J(P,H) = 3.9 Hz]. − $C_{44}H_{40}F_2N_2O_{11}P_2W_2$ (1240.4): calcd. C 42.60, H 3.25, N 2.26; found C 42.16, H 3.40, N 2.17.

Crystal Structure Analyses:[12] Crystal data and refinement details are presented in Table 3. Data were collected with Mo-K_α radiation (λ = 0.71073Å) at low temperature; diffractometer type Stoe Stadi-4 (**4a**, **6b**, **c**) or a Siemens P4 (**4b**, **8**). Absorption corrections were based on ψ scans. Structures were solved by the heavy-atom method and refined anisotropically on F^2 (program SHELXL-93, G. M. Sheldrick, Univ. Göttingen). Hydrogen atoms were included as rigid methyl groups or with a riding model. Weighting schemes were of the form $w^{-1} = \sigma^2 (F^2) + (aP)^2 + bP$, where $3P = (2F_c^2 + F_o^2)$ and *a* and *b* are constants optimized by the program.

☆ Dedicated to Professor *Peter Jutzi* on the occasion of his 60th birthday.

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[12] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-102060 (**4a**), -102061 (**4b**), -102062 (**6b**), -102063 (**6c**) and -102064 (**8**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, UK-Cambridge CB2 1EZ [Fax: int. code + 44(1223)336033; E-mail: deposit@ccdc.cam.ac.uk].

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