Chemistry of 2*H*-Azaphosphirene Complexes, 8[◇]

Synthesis and Spectroscopic Data of *para*-Substituted (3-Phenyl-2*H*-azaphosphirene)tungsten Complexes☆

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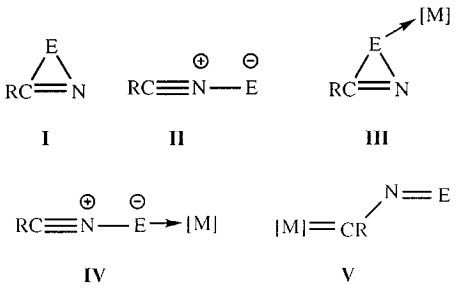
High-yield synthesis of *para*-substituted pentacarbonyl(3-phenyl-2*H*-azaphosphirene)tungsten complexes is reported, using a multi-step rearrangement reaction. Spectroscopic and mass-spectrometric data of these heterocyclic complexes are discussed; the ^{31}P-NMR-chemical shifts clearly reflect the electronic influence of the *para*-phenyl substituents and the correlation with Hammett σ^{p}-constants is almost linear.

2*H*-azirenes and their heterocyclic analogs (**I**), containing a ring system with a C=N moiety and a further heteroatom, are of current theoretical and synthetic interest.[2] The latter heterocycles are expected to suffer from destabilizing effects due to interaction of the lone pair(s) of the E fragment with the π electrons of the C=N double bond. Such is the case with 1*H*-diazirenes (E = NR)[3] and 1*H*-thiazirenes (E = S).[4] The former rearranges, if it is transiently formed, even at low temperatures to give 3*H*-diazirenes[5] or ring-expanded products[6] and the latter yields nitrile sulfides[7] (**II**: E = S, Scheme 1). Recently, a marked increase in stability of a 1-phosphonio-substituted 1*H*-diazirene derivative was observed[8] and a negative hyperconjugation was proposed to explain this phenomenon.[8][9] Interestingly, neither 2*H*-azaphosphirenes nor 1*H*-oxazirenes exist, even in matrices at low temperatures. The latter have been subjected to a theoretical study, in which an asymmetric bonding of the oxygen with respect to the geometric center of the imine bond was predicted, thus minimizing the electronic destabilization.[10] The former has only been mentioned as plausible intermediate.[11] Because of the relationship of the isolobal fragments RP and S, 2*H*-azaphosphirenes should be of particular interest. Moreover, to the best of our knowledge as yet uninvestigated is the influence of coordinating such heteroazirenes and their acyclic zwitterionic isomers, the 1,3-dipoles, to a metal-complex fragment via the "apical"- (**III**) and "terminal"-bonded atom E (**IV**, E = O, S, NR, PR; Scheme 1).

Recently, we reported the first synthesis of coordinated 2*H*-azaphosphirenes (**III**: E = PR), which was also the first access to heteroazirene complexes in general. We explained the product formation by a multi-step rearrangement reaction of transiently formed metal carbene complexes involving metallaheterobutadienes (**V**), which are isomeric to **III**, as key intermediates.[12] Even more recently, we obtained the first evidence for a nitrilium phosphane ylide complex (**IV**: E = PR). The transient formation of such a complex was achieved by thermal ring opening of a 2*H*-azaphosphirene complex.[13]

Scheme 1. Unsaturated three-membered heterocycles containing nitrogen and a second heteroatom and their zwitterionic acyclic isomers, the 1,3-dipoles (propargylic resonance structure). − **I**, **II**: E = CR_2, NR, PR, O, S. − R, R′ = alkyl, aryl. − **III**, **IV**, **V**: E = NR, PR, O, S. − R, R′ = alkyl, aryl. − [M] = metal complex fragment



In order to exploit this synthetic route to 2*H*-azaphosphirene complexes and to study the rearrangement cascade, we have now reacted a variety of *para*-phenyl-substituted (aminocarbene)tungsten complexes **1a**−**c**, **d**,[14] **e**−**h** with [bis(trimethylsilyl)methylene]chlorophosphane (**2**)[15] in the presence of triethylamine (Scheme 2). The reaction proceeded smoothly to the (2*H*-azaphosphirene)tungsten complexes **3a**−**h**, and, as in our first approach, we observed neither long-lived intermediates nor side products. Complexes **3a**−**g** were obtained in good yields, after low-temperature column chromatography, whereas complex **3h** showed some decomposition upon chromatography.

[◇] Part 7: See ref.[1].

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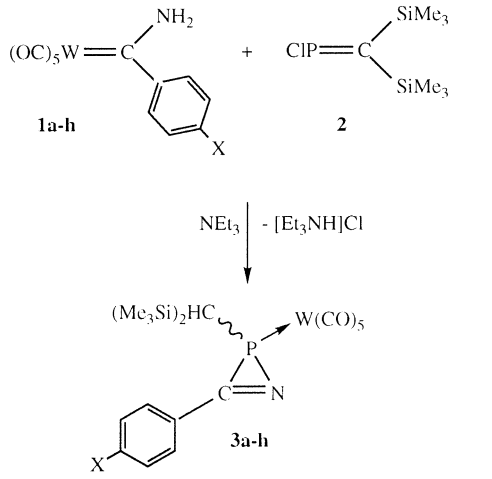
Scheme 2. Synthesis of (2*H*-azaphosphirene)tungsten complexes **3a−h**



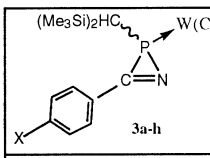
X	1a,3a	1b,3b	1c,3c	1d,3d	1e,3e	1f,3f	1g,3g	1h,3h
	CF_3	Br	Cl	H	F	Me	OMe	NMe_2

With respect to the ring formation reaction, all carbene complexes employed in this study behave approximately equivalently. Nevertheless, longer reaction times were observed for **3e−h**, which bear more electron-releasing *para* substituents. Doubling the reaction time led to the formation of small amounts of [{$(Me_3Si)_2HCP(H)Cl$}$W(CO)_5$]. This product resulted, at least formally, from the ring-cleavage reaction of the (2*H*-azaphosphirene)tungsten complexes **3a−h** with triethylammonium chloride. This has been verified for complex **3d**, which was treated in pure form with triethylammonium chloride under similar reaction conditions.[16]

From the spectroscopic data of these complexes, the phosphorus and carbon nuclear magnetic resonances are the most significant. The phosphorus and carbon resonances as well as the phosphorus-tungsten coupling constants clearly reflect the electronic influence of the *para* substituent of the phenyl group on the three-membered ring. Moreover, the correlation of $\delta^{31}P$ with the Hammett σ^p-constants[17] (Table 1) is almost linear. This should be useful for extrapolations of ^{31}P-NMR chemical-shift values of unknown (2*H*-azaphosphirene)tungsten complexes. EI mass-spectrometric experiments have shown that the (2*H*-azaphosphirene)tungsten complexes **3a−h** undergo predominantly ring cleavage subsequent to the ionization process, yielding aryl nitriles and the terminal (phosphanediyl)-tungsten complex radical cation.

The molecular structure of complex **3d** was confirmed by X-ray crystallography (Figure 1).[18] One very characteristic feature is the three-membered ring with a short C−N distance [1.272(7) Å] and a very acute endocyclic angle at the phosphorus atom [41.9(2)°]. The observation that the endocyclic P−C and P−N bond lengths of **3d** are similar [1.759(5) and 1.795(4) Å], is remarkable. This becomes even more obvious, if the structural data of **3d** are compared to

Table 1. ^{13}C- and ^{31}P-NMR data of the ring atoms of the 2*H*-azaphosphirene ringsystem of **3a−h** (in $CDCl_3$, [*] in C_6D_6) and Hammett σ^p-constants

		$\delta^{31}P$ [ppm]	$^1J_{W,P}$ [Hz]	$\delta^{13}C$ [ppm]	σ^p
X = CF_3	**3a**	- 102.0	297.5	193.1	0.54
Br	**3b**	- 105.2	296.8	192.2	0.23
Cl	**3c**	- 105.4	296.1	192.0	0.23
H	**3d**	- 108.8	294.7	192.3	0.00
F[*]	**3e**	- 109.1	295.6	190.8	0.06
Me	**3f**	- 111.2	293.1	191.4	-0.17
OMe	**3g**	- 115.1	292.5	190.2	-0.27
NMe_2	**3h**	- 117.6	291.5	187.8	-0.83

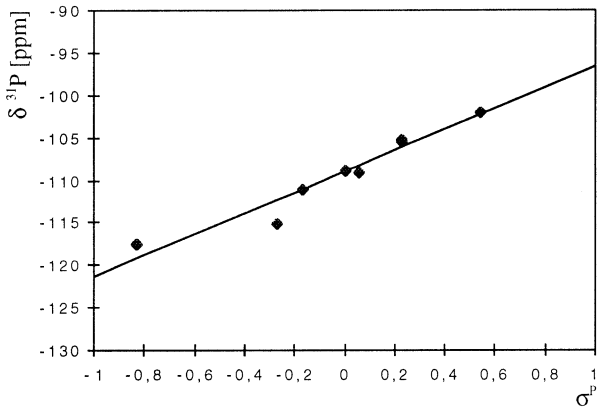
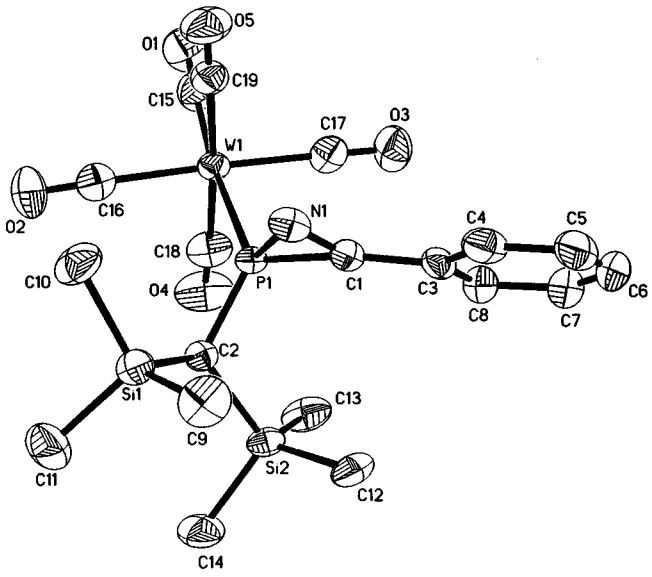


Figure 1. Molecular structure of **3d** in the crystal (ellipsoids represent 50-% probability levels, hydrogen atoms are omitted for clarity)[a]



[a] Selected bond lengths [Å] and angles [°]: P(1)−C(1) 1.759(5), P(1)−C(2) 1.808(5), P(1)−N(1) 1.795(4), W(1)−P(1) 2.470(2), N(1)−C(1) 1.272(7), C(19−C(3) 1.457(7); C(2)−P(1)−W(1) 1.243(2), C(1)−P(1)−N(1) 41.9(2), N(1)−C(1)−P(1) 70.6(3), C(1)−N(1)−P(1) 67.5(3), N(1)−C(1)−C(3) 134.2(5)

those of a related (azaphosphiridine)tungsten complex[19] in which the bond lengths of the saturated three-membered P−C−N ring were determined to P−C 1.835(4), C−N 1.478(5) and P−N 1.728(3) Å. As in the molecular structure of **3g**,[12] **3d** reveals a coplanar arrangement of the two ring moieties (interplanar angle 2°), thus enabling an effective p_π-p_π-electron interaction.

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Experimental Section

General: All operations were carried out under deoxygenated dry nitrogen as inert gas, 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; 188.3 MHz for ^{19}F; 81 MHz for ^{31}P) using [D$_6$]chloroform and [D$_6$]benzene as solvent and internal standard; shifts are given relative to tetramethylsilane (^{1}H,^{13}C), $CFCl_3$ (^{19}F), and 85% H_3PO_4 (^{31}P). − MS: Finnigan Mat 8430 (70 eV). − Elemental analyses: Carlo Erba analytical gaschromatograph. − IR: Biorad FT-IR 165.

General Procedure for the Preparation of {[Amino(aryl)carbene]pentacarbonyltungsten} Complexes: The ethoxy(aryl)carbenetungsten complexes were prepared according to ref.[20] and reacted, without purification, with ammonia. A gentle flow of ammonia was bubbled through a solution of 5 mmol of the ethoxy(aryl)carbenetungsten complexes in 60 ml of diethyl ether until a yellow color persisted and thin-layer liquid chromatography (SiO_2) indicated that all starting material had reacted. All volatile compounds were removed under reduced pressure (0.1 mbar) and the yellow residue was washed twice with a little pentane and subsequently dried in vacuo or, if necessary, purified by column chromatography.

[{Amino(4-trifluoromethylphenyl)carbene}pentacarbonyltungsten(0)] (**1a**): 2.1 g of **1a** (84%) was obtained as a yellow powder after low-temperature chromatography (SiO_2, −10°C; hexane/diethyl ether 10:1). M.p. 106°C (decomp.). − IR (KBr): $\tilde{\nu}$ = 3441 (w) cm^{-1}, 3343 (w), 3288 (w) (NH), 2067 (s), 1963 (m), 1947 (vs), 1893 (vs), 1878 (s) (CO). − ^{1}H NMR ($CDCl_3$): δ = 7.31 (d, $^2J_{HH}$ = 7.38 Hz, 2 H, Ar-*H*), 7.70 (d, $^2J_{HH}$ = 7.38 Hz, 2 H, Ar-*H*), 8.66 (br, 2 H, N*H*$_2$). − ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 122.7 (s, *o*-*C*), 123.7 (q,$^1J_{CF}$ = 272.2 Hz, *C*F$_3$), 127.8 (q,$^3J_{CF}$ = 4.0 Hz, *m*-*C*), 131.3 (q, $^2J_{CF}$ = 32.9 Hz, *p*-*C*), 156.1 (s, *i*-*C*), 197.7 (s, $^1J_{CW}$ = 127.1 Hz, *cis*-*C*O), 203.4 (s, $^1J_{CW}$ = 125.6 Hz, *trans*-*C*O), 266.6 (d, $^1J_{CW}$ = 89.1 Hz, W=*C*R$_2$). − ^{19}F{^{1}H} NMR: δ = −63.2 (s, C*F*$_3$). − MS (70 eV, ^{184}W); *m*/*z* (%): 497 (26) [M$^+$], 469 (22) [M$^+$− CO], 413 (22) [M$^+$− 3 CO], 385 (28) [M$^+$− 4 CO], 357 (100) [M$^+$− 5 CO]. − $C_{13}H_6F_3NO_5W$ (497.0): calcd. C 31.39, H 1.21, N 2.82; found C 31.38, H 1.25, N 2.75.

[{Amino(4-bromophenyl)carbene}pentacarbonyltungsten(0)] (**1b**): 2.4 g of **1b** (93%) was obtained as a yellow orange powder. M.p. 135°C (decomp.). − IR (KBr): $\tilde{\nu}$ = 3425 (w) cm^{-1}, 3342 (w), 3284 (w) (NH), 2064 (s), 1982 (s), 1930 (vs), 1904 (vs), 1882 (s) (CO). − ^{1}H NMR ($CDCl_3$): δ = 7.14 (d, $^2J_{HH}$ = 8.53 Hz, 2 H, Ar-*H*), 7.56 (d, $^2J_{HH}$ = 8.53 Hz, 2 H, Ar-*H*), 8.63 (br, 2 H, N*H*$_2$). − ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 124.5 (s, *p*-*C*), 124.8 (s, *o*-*C*), 131.9 (s, *m*-*C*), 151.6 (s, *i*-*C*), 198.0 (s, $^1J_{CW}$ = 127.6 Hz, *cis*-*C*O), 203.2 (d, $^1J_{CW}$ = 125.3, *trans*-*C*O), 265.2 (s, $^1J_{CW}$ = 89.4 Hz, W=*C*R$_2$). − MS (70 eV, ^{81}Br, ^{184}W); *m*/*z* (%): 509 (20) [M$^+$], 481 (24) [M$^+$− CO], 425 (68) [M$^+$− 3 CO], 296 (34) [W(CO)$_4^+$], 268 (100) [W(CO)$_3^+$]. − $C_{12}H_6BrNO_5W$ (507.8): calcd. 508.8946; found 508.8946 ± 2 ppm.

[{Amino(4-chlorophenyl)carbene}pentacarbonyltungsten(0)] (**1c**): 1.9 g of **1c** (84%) was obtained as a yellow powder after low-temperature chromatography (SiO_2, −10°C; hexane/diethyl ether 10:1). M.p. 116°C (decomp.). − IR (KBr): $\tilde{\nu}$ = 3447 (w) cm^{-1}, 3329 (w), 3271 (w) (NH), 2060 (s), 1983 (s), 1975 (s), 1898 (s) (CO). − ^{1}H NMR ($CDCl_3$): δ = 7.22 (d, $^3J_{HH}$ = 8.50 Hz, 2 H, Ar-*H*), 7.41 (d, $^3J_{HH}$ = 8.50 Hz, 2 H, Ar-*H*), 8.59 (br, 2 H, N*H*$_2$). − ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 124.7 (s, *m*/*o*-*C*), 124.8 (s, m/*o*-*C*), 129.0 (s, *m*-*C*), 131.4 (s, *p*-*C*), 151.0 (s, *i*-*C*), 197.9 (s, *cis*-*C*O), 203.3 (s, *trans*-*C*O), 265.4 (s, W=*C*R$_2$). − MS (70 eV, ^{35}Cl, ^{184}W); *m*/*z* (%): 463 (36) [M$^+$], 435 (32) [M$^+$− CO], 379 (100) [M$^+$− 3 CO], 351 (40) [M$^+$− 4 CO], 323 (80) [M$^+$− 5 CO], 139 (39) [M$^+$− W(CO)$_5^+$]. − $C_{12}H_6ClNO_5W$ (463.0): calcd. C 31.07, H 1.30, N 3.02; found C 31.31, H 1.45, N 3.00.

[{Amino(phenyl)carbene}pentacarbonyltungsten(0)][10] (**1d**): 1.9 g of **1d** (90%) was obtained as a yellow powder. M.p. 83°C (decomp.). − IR (KBr): $\tilde{\nu}$ = 3441 (w) cm^{-1}, 3342 (w), 3288 (w) (NH), 2067 (s), 1963 (m), 1947 (vs), 1893 (vs), 1878 (m) (CO). − ^{1}H NMR ($CDCl_3$): δ = 7.31 (mc, 2 H, m-Ar-*H*), 7.41 (mc, 3 H, *o*-, *p*-Ar-*H*), 8.56 (br, 2 H, N*H*$_2$). − ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 123.3 (s, *m*-*C*), 128.7 (s, *o*-*C*), 130.3 (s, *p*-C), 152.8 (s, *i*-*C*), 198.2 (s, $^1J_{CW}$ = 126.6 Hz, *cis*-*C*O), 202.4 (s, $^1J_{CW}$ = 126.6 Hz, *trans*-*C*O), 266.4 (d, $^1J_{CW}$ = 89.3 Hz, W=*C*R$_2$). − MS (70 eV, ^{184}W); *m*/*z* (%): 429 (32) [M$^+$], 401 (39) [M$^+$− CO], 345 (100) [M$^+$− 3 CO]. − $C_{12}H_7NO_5W$ (429.0): calcd. C 33.59, H 1.64, N 3.26; found C 33.54, H 1.65, N 3.15.

[{Amino(4-fluorophenyl)carbene}pentacarbonyltungsten(0)] (**1e**): 2.0 g of **1e** (90%) was obtained as a yellow powder. M.p. 147°C. - IR (KBr): $\tilde{\nu}$ = 3438 (m) cm^{-1}, 3331 (m), 3271 (m) (NH), 2064 (s), 1968 (s), 1949 (s), 1910 (s), 1881 (s) (CO). − ^{1}H NMR ($CDCl_3$): δ = 7.15 (m$_c$, 2 H, *o*-C), 7.36 (m$_c$, 2 H, *m*-C), 8.66 (s, br, 2 H, NH_2). − ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 115.5 (d, $^2J_{CF}$ = 21.9 Hz, *m*-*C*), 125.8 (d, $^3J_{CF}$ = 8.8 Hz, *o*-*C*), 148.7 (s, *i*-*C*), 163.6 (d, $^1J_{CF}$ = 250.9 Hz, *p*-*C*), 198.0 (s, $^1J_{CW}$ = 127.1 Hz, *cis*-*C*O), 203.2 (s, *trans*-*C*O), 263.6 (s, W=*C*R$_2$). − ^{19}F{^{1}H} NMR ($CDCl_3$): δ = −110.2 (s). − MS (70 eV, ^{184}W); *m*/*z* (%): 447 (43) [M$^+$], 419 (31) [M$^+$− CO], 363 (100) [M$^+$− 3 CO]. − $C_{12}H_6FNO_5W$ (447.0): calcd. C 32.24, H 1.35, N 3.13; found C 32.05, H 1.34, N 3.05.

[{Amino(4-methylphenyl)carbene}pentacarbonyltungsten(0)] (**1f**): 1.7 g of **1f** (75%) was obtained as a yellow powder. M.p. 79°C (decomp.). − IR (KBr): $\tilde{\nu}$ = 3440 (w) cm^{-1}, 3327 (w), 3270 (w) (NH), 2067 (s), 1982 (m), 1934 (vs), 1908 (vs), 1884 (vs) (CO). − ^{1}H NMR ($CDCl_3$): δ = 2.39 (s, 3 H, Me), 7.24 (mc, 5 H, Ar-*H*), 8.55 (br, 2 H, N*H*$_2$). − ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 21.3 (s, Me), 124.1 (s, *m*-*C*), 129.4 (s, *o*-*C*), 141.2 (s, *p*-*C*), 149.8 (s, *i*-*C*), 198.3 (s, $^1J_{CW}$ = 126.6 Hz, *cis*-*C*O), 202.4 (s, *trans*-*C*O), 264.8 (s, W=*C*R$_2$). − MS (70 eV, ^{184}W); *m*/*z* (%): 443 (32) [M$^+$], 415 (38) [M$^+$− CO], 359 (100) [M$^+$− 3 CO]. − $C_{13}H_9NO_5W$ (443.1): calcd. C 35.24, H 2.05, N 3.16; found C 35.43, H 2.00, N 3.19.

[{Amino(4-methoxyphenyl)carbene}pentacarbonyltungsten(0)] (**1g**): 1.6 g of **1g** (68%) was obtained as a yellow powder. M.p. 85°C (decomp.). − IR (KBr): $\tilde{\nu}$ = 3440 (m) cm^{-1}, 3327 (w), 3270 (m) (NH), 2067 (s), 1982 (m), 1934 (vs), 1908 (vs), 1884 (vs) (CO). − ^{1}H NMR ($CDCl_3$): δ = 3.86 (s, 3 H, OMe), 6.95 (m$_c$, 2 H, Ar-*H*), 7.41 (m$_c$, 2 H, Ar-*H*), 8.56 (br, 2 H, N*H*$_2$). − ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 55.7 (s, OMe), 113.0 (s, *m*-*C*), 132.5 (s, *o*-*C*), 142.7 (s, *p*-*C*), 150.6 (s, *i*-*C*), 198.1 (s, *cis*-*C*O), 203.8 (s, *trans*-*C*O), 264.0 (s, W=*C*R$_2$). − MS (70 eV, ^{184}W); *m*/*z* (%): 459 (26) [M$^+$], 431 (36) [M$^+$− CO], 375 (100) [M$^+$− 3 CO]. − $C_{13}H_9NO_6W$ (459.1): calcd. C 33.59, H 1.64, N 3.26; found C 33.54, H 1.65, N 3.15.

[{Amino(4-dimethylaminophenyl)carbene}pentacarbonyltungsten(0)] (**1h**): 1.4 g of **1h** (58%) was obtained as a

yellow powder after low-temperature chromatography (SiO_2, −10°C; hexane/diethyl ether, 2:1). M.p. 135°C (decomp.). − IR (KBr): $\tilde{\nu}$ = 3459 (w) cm^{-1}, 3340 (w), 3261 (w) (NH), 2059 (s), 1966 (m), 1923 (vs), 1893 (vs), 1878 (m) (CO). − ^1H NMR ($CDCl_3$): δ = 3.06 [s, 6 H, N(CH_3)$_2$], 6.68 (d, $^2J_{HH}$ = 9.06 Hz, 2 H, Ar-*H*), 7.51 (d, $^2J_{HH}$ = 9.06 Hz, 2 H, Ar-*H*), 8.01 (s, br, 1 H, N*H*), 8.49 (s, br, 1 H, N*H*). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 40.1 [s, N(CH_3)$_2$], 110.7 (s, Ph), 129.2 (s, Ph), 137.2 (s, Ph), 152.0 (s, *i-C*), 199.0 (s, $^1J_{CW}$ = 127.0 Hz, *cis-C*O), 203.3 (s, $^1J_{CW}$ = 126.9 Hz, *trans-C*O), 254.9 (d, $^1J_{CW}$ = 89.4 Hz, W=*C*R$_2$). − MS (70 eV, ^{184}W); *m/z* (%): 472 (22) [M^+], 444 (36) [M^+ − CO], 388 (66) [M^+ − 3 CO], 360 (44) [M^+ − 4 CO], 332 (40) [M^+ − 5 CO], 240 (100) [$W(CO)_2^+$]. − $C_{14}H_{12}N_2O_5W$ (472.1): calcd. 472.0256; found 472.0256 ± 2 ppm.

General Procedure for the Preparation of Pentacarbonyl(2H-azaphosphirene)tungsten Complexes: To a solution of 1.5 mmol of amino(aryl)carbenetungsten complexes **1a−h** in 15 ml of diethyl ether 0.34 g (1.5 mmol) of **2** and 5 ml of NEt_3 was added at 0°C. The reaction mixture was stirred at ambient temp. until **2** was consumed (^{31}P-NMR control). The yellow-orange reaction mixture was evaporated to dryness under reduced pressure (0.1 mbar). The residue was extracted with 30 ml of pentane and filtered. The filtration residue was washed twice with 5 ml of pentane, the organic phases combined and the solvent removed under reduced pressure. The residue was purified, if necessary, by low-temperature column chromatography on silica gel.

[{2-Bis(trimethylsilyl)methyl-3-(4-trifluoromethylphenyl)-2H-azaphosphirene-κP}pentacarbonyltungsten(0)] (**3a**): After 24 hours stirring, 0.64 g of **3a** (62%) was obtained as a yellow powder, m.p. 112−114°C (decomp.). − IR (KBr): $\tilde{\nu}$ = 2077 (m) cm^{-1}, 1977 (m, br), 1977 (s), 1949 (vs), 1931 (s), 1923 (vs), 1909 (s) (CO), 1616 (w) (CN). − ^1H NMR ($CDCl_3$): δ = 0.11 (s, 9 H, $SiMe_3$), 0.31 (s, 9 H, $SiMe_3$), 0.73 (d, $^2J_{HP}$ = 3.18 Hz, 1 H, PC*H*), 7.90 (d, $^3J_{HH}$ = 8.22 Hz, 2 H, Ar-*H*), 8.14 (d, $^3J_{HH}$ = 8.22 Hz, 2 H, Ar-*H*). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 1.4 (d, $^3J_{CP}$ = 3.4 Hz, $SiMe_3$), 2.1 (d, $^3J_{CP}$ = 3.0 Hz, $SiMe_3$), 27.8 (d, $^1J_{CP}$ = 23.9 Hz, P*C*H), 123.4 (q, $^1J_{CF}$ = 273.1 Hz, *C*F$_3$), 126.8 (q, $^3J_{CF}$ = 11.1 Hz, *m-C*) 129.6 (s, *o-C*), 129.9 (d, $^2J_{CP}$ = 14.3 Hz, *i-C*), 135.4 (q, $^2J_{CF}$ = 33.0 Hz, *p-C*), 193.1 (d, Σ J_{PC} = 1.5 Hz, P*C*N), 195.7 (d, $^1J_{CW}$ = 126.3 Hz, $^2J_{CP}$ = 8.7 Hz, *cis-C*O), 197.4 (d, $^2J_{CP}$ = 37.0 Hz, *trans-C*O). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −102.0 (s, $^1J_{PW}$ = 297.5 Hz). − $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ = −63.7 (s, CF_3). − MS (70 eV, ^{184}W); *m/z* (%): 685 (0.5) [M^+], 514 (28) [$(OC)_5WPCH(SiMe_3)_2^+$], 486 (100) [$(OC)_4WPCH(SiMe_3)_2^+$], 458 (30) [$(OC)_3WPCH(SiMe_3)_2^+$], 430 (41) [$(OC)_2WPCH(SiMe_3)_2^+$], 402 (32) [$(OC)WPCH(SiMe_3)_2^+$], 374 (30) [$WPCH(SiMe_3)_2^+$], 171 (44) [$(CF_3C_6H_4)CN^+$], 73 (77) [$SiMe_3^+$]. − $C_{20}H_{23}F_3NO_5PSi_2W$ (685.4): calcd. C 35.04, H 3.36, N 2.04; found C 34.74, H 3.43, N 1.95.

[{2-Bis(trimethylsilyl)methyl-3-(4-bromophenyl)-2H-azaphosphirene-κP}pentacarbonyltungsten(0)] (**3b**): After 26 hours stirring and purifying by low-temperature chromatography (SiO_2, −10°C; hexane/diethyl ether 50:1) 0.53 g of **3b** (51%) was obtained as a yellow powder, m.p. 117°C. − IR (KBr): $\tilde{\nu}$ = 2075 (m) cm^{-1}, 1946 (m), 1946 (vs), 1930 (s), 1919 (vs), 1907 (m) (CO), 1582 (CN). − ^1H NMR ($CDCl_3$): δ = 0.10 (s, 9 H, $SiMe_3$), 0.29 (s, 9 H, $SiMe_3$), 0.68 (d, $^2J_{HP}$ = 3.10 Hz, 1 H, PC*H*), 7.77 (d, $^3J_{HH}$ = 8.57 Hz, 2 H, Ar-*H*), 7.87 (d, $^3J_{HH}$ = 8.57 Hz, 2 H, Ar-*H*). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 1.4 (d, $^3J_{CP}$ = 3.4 Hz, $SiMe_3$), 2.1 (d, $^3J_{CP}$ = 3.2 Hz, $SiMe_3$), 27.7 (d, $^1J_{CP}$ = 24.0 Hz, P*C*H), 125.5 (d, $^2J_{CP}$ = 15.1 Hz, *i-C*), 129.3 (s, *o-C*), 130.6 (s, *p-C*), 133.2 (s, *m-C*), 192.2 (d, Σ J_{PC} = 1.9 Hz, P*C*N), 195.7 (d, $^1J_{CW}$ = 125.6 Hz, $^2J_{CP}$ = 8.7 Hz, *cis-C*O), 197.5 (d, $^2J_{CP}$ = 36.7 Hz, *trans-C*O). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −105.2 (s, $^1J_{PW}$ = 296.8 Hz). − MS (70 eV, ^{81}Br, ^{184}W); *m/z* (%): 697 (0.5) [M^+], 514 (28) [$(OC)_5WPCH(SiMe_3)_2^+$], 486 (100) [$(OC)_4WPCH(SiMe_3)_2^+$], 458 (40) [$(OC)_3WPCH(SiMe_3)_2^+$], 430 (44) [$(OC)_2WPCH(SiMe_3)_2^+$], 402 (30) [$(OC)WPCH(SiMe_3)_2^+$], 374 (36) [$WPCH(SiMe_3)_2^+$], 181 (46) [$(^{79}BrC_6H_4)CN^+$], 102 (42) [$(C_6H_4)CN^+$], 73 (81) [$SiMe_3^+$]. − $C_{19}H_{23}BrNO_5PSi_2W$ (696.3): calcd. C 32.81, H 3.31, N 2.01; found C 33.29, H 3.54, N 2.04.

[{2-Bis(trimethylsilyl)methyl-3-(4-chlorophenyl)-2H-azaphosphirene-κP}pentacarbonyltungsten(0)] (**3c**): After 21 hours stirring, 0.65 g of **3c** (66%) was obtained as a yellow powder, m.p. 108°C. − IR (KBr): $\tilde{\nu}$ = 2073 (s) cm $^{-1}$, 1985 (s), 1967 (vs), 1938 (vs), 1918 (vs) (CO), 1618 (CN). − ^1H NMR ($CDCl_3$): δ = 0.07 (s, 9 H, $SiMe_3$), 0.26 (s, 9 H, $SiMe_3$), 0.65 (d, $^2J_{HP}$ = 3.1 Hz, 1 H, PC*H*), 7.58 (d, 2 H, $^3J_{HH}$ = 8.53 Hz, *o*-C*H*), 7.74 (d, 2 H, $^3J_{HH}$ = 8.53 Hz, *m*-C*H*). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 1.4 (d, $^3J_{CP}$ = 3.0 Hz, $SiMe_3$), 2.1 (d, $^3J_{CP}$ = 3.3 Hz, $SiMe_3$), 27.7 (d, $^1J_{CP}$ = 24.2 Hz, P*C*H), 125.1 (d, $^2J_{CP}$ = 15.1 Hz, *i-C*), 130.2, 130.6 (s, *m-C*, *o-C*), 140.6 (d, *p-C*), 192.0 (d, Σ J_{CP} = 2.0 Hz, P*C*N), 195.7 (d, $^2J_{CP}$ = 8.9 Hz, *cis-C*O), 197.6 (d, $^2J_{CP}$ = 36.6 Hz, *trans-C*O). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −105.4 (s, $^1J_{PW}$ = 296.1 Hz). − MS (CI, *iso*-C_4H_9, pos., $^{35}Cl^{184}W$); *m/z* (%): 652 (16) [M+H$^+$], 515 (12) [M+H$^+$ − ClC_6H_4CN], 193 (100) [$H_3PCH(SiMe_3)_2^+$]. − $C_{19}H_{23}ClNO_5PSi_2W$ (651.8): calcd. C 35.01, H 3.56, N 2.15; found C 34.92, H 3.46, N 2.25.

[{2-Bis(trimethylsilyl)methyl-3-phenyl-2H-azaphosphirene-κP}pentacarbonyltungsten(0)] (**3d**): After 26 hours stirring 0.68 g of **3d** (73%) was obtained as a yellow powder, m.p. 109−110°C (decomp.). − IR (hexane): $\tilde{\nu}$ = 2076 (s) cm^{-1}, 1989 (s), 1957-1941 (vs, br), 1925 (sh) (CO), 1619 (vw) (CN). − IR (KBr): $\tilde{\nu}$ = 2072 (s) cm^{-1}, 1987 (m), 1967 (s), 1938 (vs), 1922 (vs) (CO), 1619 (vw) (CN). − ^1H NMR ($CDCl_3$): δ = 0.11 (s, 9 H, $SiMe_3$), 0.30 (s, 9 H, $SiMe_3$), 0.68 (d, $^2J_{HP}$ = 2.9 Hz, 1 H, PC*H*), 7.00 (m_c, 3 H, Ar-*H*), 8.03 (m_c, 2 H, Ar-*H*). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 1.3 (d, $^3J_{CP}$ = 3.3 Hz, $SiMe_3$), 2.1 (d, $^3J_{CP}$ = 3.1 Hz, $SiMe_3$), 27.6 (d, $^1J_{CP}$ = 24.0 Hz, P*C*H), 126.6 (d, $^2J_{CP}$ = 14.9 Hz, *i-C*), 129.5 (s, *m-C*), 129.7 (s, *o-C*), 134.1 (s, *p-C*), 192.3 (d, Σ J_{PC} = 1.3 Hz, P*C*N), 195.9 (d, $^1J_{CW}$ = 125.8 Hz, $^2J_{CP}$ = 8.8 Hz, *cis-C*O), 197.7 (d, $^2J_{CP}$ = 36.4 Hz, *trans-C*O). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −108.8 (s, $^1J_{PW}$ = 294.7 Hz). − MS (70 eV, ^{184}W); *m/z* (%): 617 (1) [M^+], 514 (30) [M^+ − PhCN], 486 (100) [M^+ − PhCN − CO], 103 (52) [$PhCN^+$], 73 (80) [$SiMe_3^+$]. − $C_{19}H_{24}NO_5PSi_2W$ (617.4): calcd. C 36.96, H 3.93, N 2.27; found C 36.74, H 3.88, N 2.23.

[{2-Bis(trimethylsilyl)methyl-3-(4-fluorophenyl)-2H-azaphosphirene-κP}pentacarbonyltungsten(0)] (**3e**): After 20 hours stirring 0.68 g of **3e** (71%) was obtained as a yellow powder, m.p. 115°C. − IR (KBr): $\tilde{\nu}$ = 2074 (s) cm $^{-1}$, 1988 (s), 1974 (s), 1938 (s), 1917 (s) (CO), 1598 (CN). − ^1H NMR (C_6D_6): δ = 0.01 (s, 9 H, $SiMe_3$), 0.26 (s, 9 H, $SiMe_3$), 0.68 (d, $^2J_{HP}$ = 3 Hz, 1 H, PC*H*), 6.63 (m_c, 2 H, *o*-C*H*), 7.74 (m_c, 2 H, *m*-C*H*). − $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 1.2 (d, $^3J_{CP}$ = 3.1 Hz, $SiMe_3$), 2.1 (d, $^3J_{CP}$ = 3 Hz, $SiMe_3$), 27.7 (d, $^1J_{CP}$ = 24 Hz, P*C*H), 117.2 (d, $^2J_{CF}$ = 22.5 Hz, *m-C*), 123.1 (dd, $^2J_{CP}$ = 15 Hz, $^4J_{CF}$ = 2.6 Hz, *i-C*), 132 (d, $^3J_{CF}$ = 9.3 Hz, *o-C*), 166.2 (d, $^1J_{CF}$ = 256.5 Hz, *p-C*), 190.8 (d, Σ J_{CP} = 1.7 Hz, P*C*N), 196.3 (d, $^1J_{CW}$ = 135.2 Hz, $^2J_{CP}$ = 8.8 Hz, *cis-C*O), 197.8 (dd, $^1J_{CW}$ = 146.6 Hz, $^2J_{CP}$ = 36 Hz, *trans-C*O). − $^{31}P\{^1H\}$ NMR (C_6D_6): δ = −109.1 (s, $^1J_{PW}$ = 296.1 Hz). − $^{19}F\{^1H\}$ NMR (C_6D_6): δ = −102.6 (s). − MS (CI, NH_3, pos., ^{184}W); *m/z* (%): 636 (100) [M^+], 515 (18) [M^+ − FC_6H_4CN]. − $C_{19}H_{23}FNO_5PSi_2W$ (635.4): calcd. C 35.92, H 3.65, N 2.2; found C 35.93, H 3.59, N 2.12.

[{2-Bis(trimethylsilyl)methyl-3-(4-methylphenyl)-2H-azaphosphirene-κP}pentacarbonyltungsten(0)] (**3f**): Stirring for 48 hours

afforded 0.46 g of **3f** (49%) as a yellow powder, m.p. 104−105°C (decomp.). − For ^{1}H-, ^{13}C- and ^{31}P-NMR data see ref.[8] − MS (CI, isobutane, pos., ^{184}W); *m/z* (%): 632 (6) [(M+H)$^+$·], 604 (5) [(M$^+$ − CO)·], 515 (10) [(M+H)$^+$ − C_8H_7N], 442 (22) [(M+H)$^+$ − C_8H_7N − Me_3Si], 117 (100) [$C_8H_7N^+$]. − $C_{20}H_{26}NO_5PSi_2W$ (631.7): calcd. C 38.02, H 4.20, N 2.22; found C 38.30, H 4.20, N 2.20.

[{2-Bis(trimethylsilyl)methyl-3-(4-methoxyphenyl)-2H-azaphosphirene-κP}pentacarbonyltungsten(0)] (**3g**): Stirring for 48 hours afforded 0.44 g of **3g** (45%) as a yellow powder, m.p. 103−104°C (decomp.). − For ^{1}H-, ^{13}C- and ^{31}P-NMR data see ref.[8]. − MS (70 eV, ^{184}W); *m/z* (%): 647 (1) [M$^+$], 604 (3) [M$^+$ − CO − Me], 486 (6) [M$^+$ − C_8H_7NO − CO], 133 (90) [$C_8H_7NO^+$], 104 (100) [$C_7H_4O^+$]. − $C_{20}H_{26}NO_6PSi_2W$ (647.4): calcd. C 37.08, H 4.05, N 2.16; found C 37.06, H 4.13, N 2.16.

[{2-Bis(trimethylsilyl)methyl-3-(4-dimethylaminophenyl)-2H-azaphosphirene-κP}pentacarbonyltungsten(0)] (**3h**): Stirring for 56 hours and low-temperature column chromatography (two times) of the residue (SiO_2, −10°C; hexane/diethyl ether, 9:1) afforded 0.24 g of **3h** (24%) as a yellow powder, m.p. 110°C (decomp). − IR (KBr): $\tilde{\nu}$ = 2072 (m) cm^{-1}, 2062 (s), 1979 (m), 1945 (vs), 1908 (s), 1885 (s) (CO), 1593 (m) (CN). − ^{1}H NMR ($CDCl_3$): δ = 0.12 (s, 9 H, $SiMe_3$), 0.28 (s, 9 H, $SiMe_3$), 0.61 (d, $^2J_{HP}$ = 2.43 Hz, 1 H, PC*H*), 3.11 (s, 6 H, NCH_3), 6.81 (d, $^3J_{HH}$ = 8.98 Hz, 2 H, Ar-*H*), 7.86 (d, $^3J_{HH}$ = 8.98 Hz, 2 H, Ar-*H*). − ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 1.4 (d, $^3J_{CP}$ = 3.2 Hz, $SiMe_3$), 2.2 (d, $^3J_{CP}$ = 3.2 Hz, $SiMe_3$), 26.5 (d, $^1J_{CP}$ = 24.4 Hz, P*C*H), 40.1 [s, N(CH_3)$_2$], 111.8 (s, *m-C*), 112.6 (d, $^2J_{CP}$ = 15.0 Hz, *i-C*), 131.8 (s, *o-C*), 154.0 (s, *p-C*), 187.8 (d, Σ J_{PC} = 3.1 Hz, P*C*N), 196.2 (d, $^1J_{CW}$ = 127.5 Hz, $^2J_{CP}$ = 8.8 Hz, *cis-C*O), 198.3 (d, $^2J_{CP}$ = 24.0 Hz, *trans-C*O). − ^{31}P{^{1}H} NMR ($CDCl_3$): δ = −117.6 (s, $^1J_{PW}$ = 291.5 Hz). − MS (70 eV): M$^+$ could not be detected by EI MS; using CI MS [($Me_2NC_6H_4$)CN^+] was found to be the basic peak.

Crystal-Structure Determination of **3d**[18]: $C_{19}H_{24}NO_5PSi_2W$, *M* = 617.39, *P*$\bar{1}$, *a* = 9.167(4), *b* = 10.793(4), *c* = 13.775(5) Å, α = 89.27(2)°, β = 85.92(3)°, γ = 64.88(3)°, *V* = 1230.6(8) Å^3, *Z* = 2, d_{calc} = 1.666 Mg/m^3, μ = 4.883 mm^{-1}, *T* = 143 K. A yellow prism (0.7 × 0.7 × 0.4 mm) was mounted in inert oil. 6565 intensities were measured (2Θ 6−50°) using Mo-K_α radiation on a Stoe STADI-4 diffractometer. After absorption correction (ψ scans) 4319 were unique (R_{int} = 0.0251) and 4318 used for all calculations (program SHELXL-93). All hydrogen atoms (except rigid methyl groups) were refined with a riding model. The final *wR(F*^{2}*)* was 0.0883 with conventional *R(F)* 0.0324 for 268 parameters and 129 restraints. Highest peak 1996, hole −1835 e/nm^3.

☆ Dedicated to Professor *Manfred Weidenbruch* on the occasion of his 60th birthday.

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[18] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100687. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, UK-Cambridge CB2 1EZ [fax: int. code +44(1223)336-033; E-mail: deposit@chemcrys.cam.ac.uk].

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