Chemistry of 2*H*-Azaphosphirene Complexes, 20[‡]

Study on the Ring Formation of 2*H*-Azaphosphirene Complexes Using Sterically Demanding *C*-2,4,6-Trialkylphenyl-Substituted Aminocarbene Tungsten Complexes − Detection of a Key Intermediate

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Dedicated to Professor Gerd Becker on the occasion of his 60th birthday

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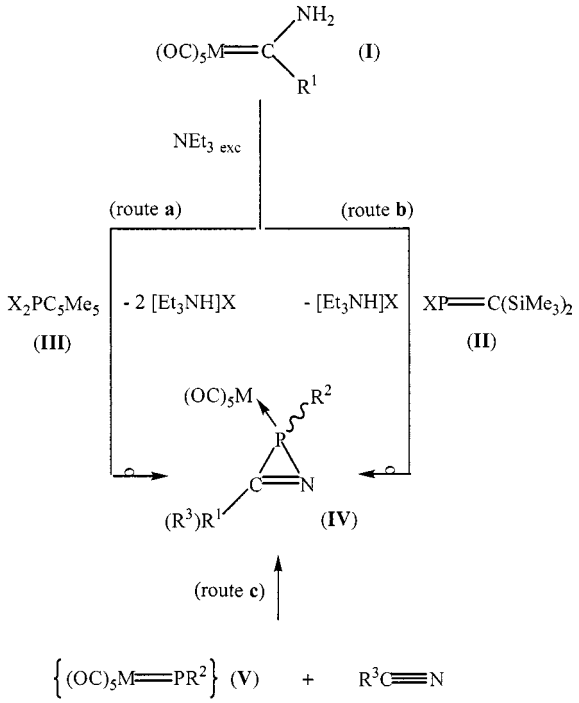
The synthesis of *C*-2,4,6-trialkylphenyl-substituted ethoxy- and aminocarbene tungsten complexes **1a–c** (R = Me, *i*Pr and *t*Bu) and **2a,b** (R = Me, *i*Pr) and the reaction of **2a,b** with [bis(trimethylsilyl)methylene]chlorophosphane (**3**) in the presence of triethylamine is reported. The reaction course, which finally leads to the 2*H*-azaphosphirene complexes **7a,b**, depends strictly on the steric demands of the aryl group bonded to the carbene atom; only in the case of complex **2a** was a dinuclear tungsten carbene complex formed, which was isolated and characterized by single crystal X-ray diffraction. Relative to phenyl-substituted derivatives, the 2*H*-azaphosphirene complexes **7a,b** showed enhanced reactivity towards triethylammonium chloride, furnishing the [bis(trimethylsilyl)methyl]chlorophosphane complex **8**. Condensation of **8** with complex **2a** afforded the novel dinuclear tungsten complex **9a** containing an acyclic C,N,P structural unit with a κ-C and a κ-P coordination mode; an H-bonded adduct of complex **9a** and mesitylnitrile, complex **10**, was investigated by single crystal X-ray diffraction.

Introduction

Two routes are currently known to provide access to 2*H*-azaphosphirene complexes (**IV**) (Scheme 1). The first utilises a rearrangement cascade starting from aminocarbene complexes (**I**) and either [bis(trimethylsilyl)methylene]halophosphanes (**II**) (X = Cl,[2] Br[3]) (route **a**) or alkyldihalophosphanes (**III**) (X = Cl, R = C_5Me_5[4]) (route **b**) in the presence of triethylamine. The second, a [2+1] cycloaddition reaction[5] of an electrophilic terminal phosphanediyl complex (**V**) with dialkylamino nitriles (R = R_2N) (route **c**) was detected quite recently and is especially useful for 3-donor-atom-substituted 2*H*-azaphosphirene complexes that cannot be obtained from routes **a** or **b**. Because of the increasing synthetic usefulness of 2*H*-azaphosphirene complexes as starting material for unsaturated three-,[6] four-[7] and five[5,8]-membered monocyclic and polycyclic[9] P-heterocycle complexes, we were interested in obtaining further insight into the ring forming process of 2*H*-azaphosphirene complexes based on route **a**.



Scheme 1. Routes to 2*H*-azaphosphirene metal complexes **IV** (M = Cr, Mo, W; R, R′ = alkyl, aryl)

Results and Discussion

Our former investigations of the rearrangement cascade leading to 2*H*-azaphosphirene complexes (route **a**) had already shown that, in the case of a chromium complex, a transiently formed 2-aza-1-phospha-4-chroma-1,3-butadiene derivative could be trapped by addition of the NH function of [(aminobenzylidene)pentacarbonylchromium(0)] to

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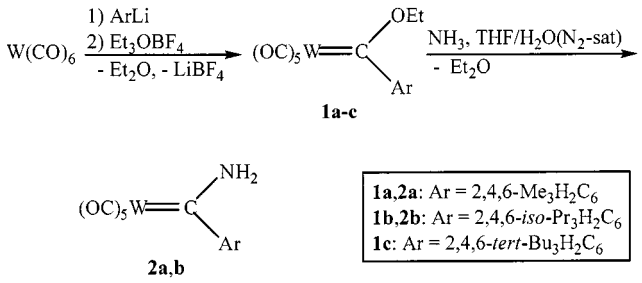


Scheme 2. Synthesis of carbene complexes **1a−c** and **2a,b** with sterically demanding aryl groups

the P−N double bond of the reactive intermediate, giving a dinuclear *N,N′*-PR-bridged carbene chromium complex.[2c] We suggested that this depends mainly on the lifetime of such metallaheterobutadiene intermediates, which should be enhanced by sterically demanding and thus kinetically protecting groups at either the metal or the carbene centre, especially if the rearrangement is truly intramolecular and the ligand does not dissociate prior to the formation of the three-membered ring. Therefore, we decided to investigate the rearrangement route **a** by employing sterically demanding *C*-2,4,6-trialkylphenyl-substituted aminocarbene complexes.

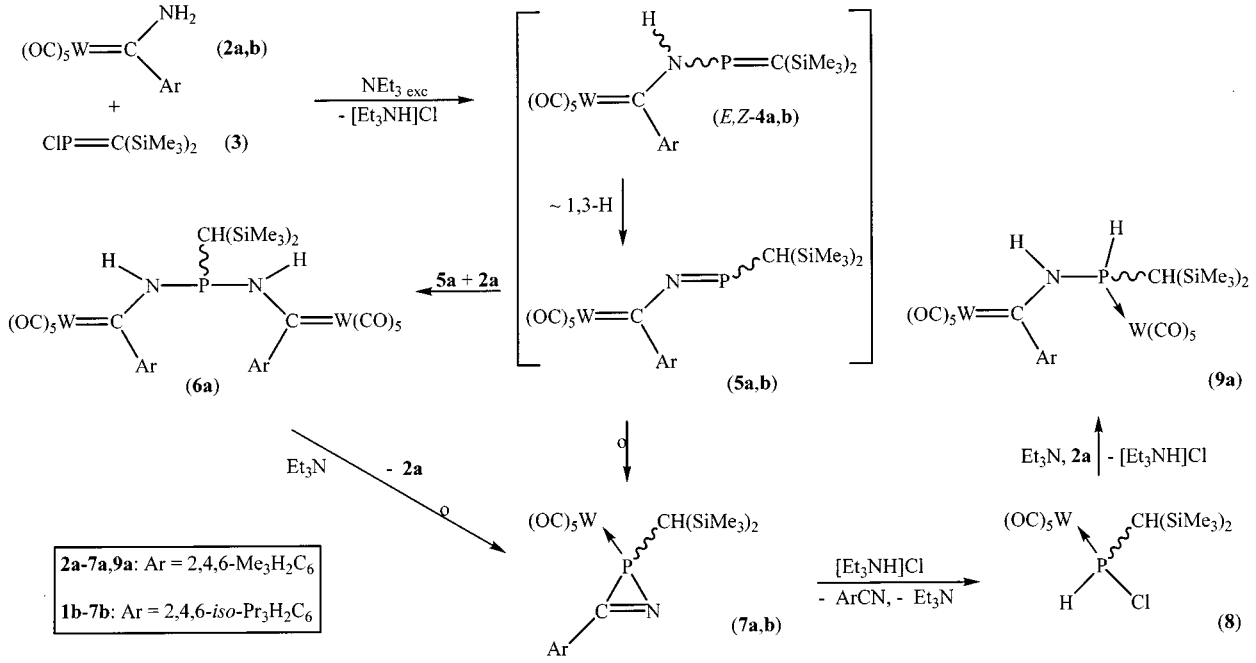
Whereas the ethoxy(aryl)carbene complexes **1a−c** were accessible by reacting aryllithium derivatives, prepared in situ, and hexacarbonyltungsten under standard conditions[10] (Scheme 2), the amino(aryl)carbene complexes **2a**,**b** were obtained only with difficulty by ammonolysis of **1a**,**b** in a 12:1 mixture of THF and a concentrated NH_3/water solution. Even after six weeks under these rather severe conditions (relative to standard procedures[10]) complex **2c** was not formed. The observation that bulky substituted alkoxy(alkyl/aryl)carbene complexes have low reaction rates and/or are remarkably inert in ether towards ammonia had already been reported; this reactivity was explained by their fourth-order reaction rate law.[10]

We therefore reacted, under standard conditions,[2] the *C*-2,4,6-trialkylphenyl-substituted aminocarbene complexes **2a**,**b** and [bis(trimethylsilyl)methylene]chlorophosphane[11] (**3**) in ether in the presence of an excess of triethylamine; the assumed reaction course is shown in Scheme 3. In the case of complex **2a** we obtained a mixture of various phosphorus-containing products, whereby the complexes **6a**, **7a**, **8** and **9a** were final products and the ^{31}P resonances of two transient species at δ = 305 and 330 were assigned to the *E*/*Z*-isomers of complex **4a** (ratio 1:1). Lowering the concentration of this reaction led to the preferred formation of complexes **8** and **9a** (ratio 1:2). It is also noteworthy that complex **6a** was only slowly transformed by base to the 2*H*-azaphosphirene complex **7a**. Whereas complexes **6a**, **8** and **9a** could be isolated in pure form by low temperature column chromatography, complex **7a** decomposed during the chromatographic separation. Nevertheless, a **7a**-enriched solution was obtained by twofold extraction of the reaction mixture with *n*-pentane at low temperature and, therefore, complex **7a** could be unambiguously characterized by ^{13}C and ^{31}P NMR spectroscopy of this solution. The nature of complexes **6a** and **9a** was also confirmed by X-ray analyses, but, to our surprise, complex **9a** crystallised only as the mesitylnitrile adduct **10**.

In the case of complex **2b**, the reaction with **3** in ether was significantly different; ^{31}P NMR spectroscopy revealed completeness of the reaction after ≈20 h, but the only phosphorus-containing product was complex **8**. Repeating the reaction in dichloromethane gave a different picture. Apart from intermediates at δ = 300 and 329 (*E*/*Z* complexes of **4b**), **7b** and **8**, another intermediate compound was formed in relatively large amounts and could be observed throughout the whole reaction, which was complete after ≈2.5 h (Figure 1). This intermediate decreased in favour of the 2*H*-azaphosphirene complex **7b** and the complex **8**, which is formed by a subsequent fast reaction of **7b** with $[Et_3NH]Cl$;[2] the marked tendency of complex **7b** to undergo this reaction is remarkable. Complex **7b** was characterized by its typical ^{31}P NMR parameters [δ = −121.7 (s, $|^1J(W,P)|$ = 303.3 Hz], but could not be isolated either by low temperature column chromatography or by an extraction procedure (see above).

The ^{31}P resonance of this new intermediate at δ = 183.3 is *not* in agreement with either a compound having a free or tungsten-coordinated $P{=}C(SiMe_3)_2$ structural unit,[12] or with analogues of complexes **6a** or **9a**. Assuming that the rearrangement cascade proceeds intramolecularly[13] two conceivable structures for this intermediate remain: complex **5b**, with the 2-aza-1-phospha-4-tungsta-1,3-butadiene moiety (or its zwitterion analogue **5b′**), and the zwitterionic complex **11** with the phosphorus atom incorporated in a three-membered ring with a partially formed P−N double bond.[14] Although the assignment of the NMR spectroscopic data to complex **5b** (**5b′**) seems more plausible, complex **11** cannot be completely excluded (Figure 2). Subsequent intramolecular rearrangements such as a nucleophilic attack of the phosphorus at the "carbene" centre in **5b**/**5b′** (thus forming complex **11**) or a shift of the pentacarbonyltungsten group in **11** from carbon to phosphorus (thus forming complex **7b**) are possible; such rearrangements, however, should be significantly hindered by bulky substituents at the "carbene" centre.

Elemental analyses and IR, MS and NMR spectroscopic data confirm unambiguously the proposed structures of the complexes **1a−c**, **2a,b**, **6a**, **7a**, **8** and **9a**. In particular, for **1a−c**, **2a,b**, **6a** and **9a** the carbene atom resonances, which are observed at low field, are of interest. In the case of the ethoxy-substituted carbene complexes, enhancement of the steric demand of the aryl substituent leads to a deshielding of the carbene atom (**1a**: δ = 334.8; **1b**: δ = 337.2; **1c**: δ = 341.2). This is just the opposite of the expected electronic influence of these aryl groups on the carbene atom. For complexes **2a**, **6a** and **9a** a deshielding of the carbene atoms was also observed [**2a**: δ = 276.2; **6a**: δ = 283.1 and 301.0 ($|^2J(P,C)|$ = 4.2 Hz); **9a**: δ = 288.3 ($|^2J(P,C)|$ = 14.3 Hz)]. Taking into account that the aryl substitution does not effect the aminocarbene resonance (**2b**: δ = 276.1), the formal substitution of an N−H function in **2a** by a PR_2 or a $PR_2W(CO)_5$ moiety influences the chemical shift of the car-



Scheme 3. Formation of 2*H*-azaphosphirene complexes **7a**,**b** and subsequent reactions

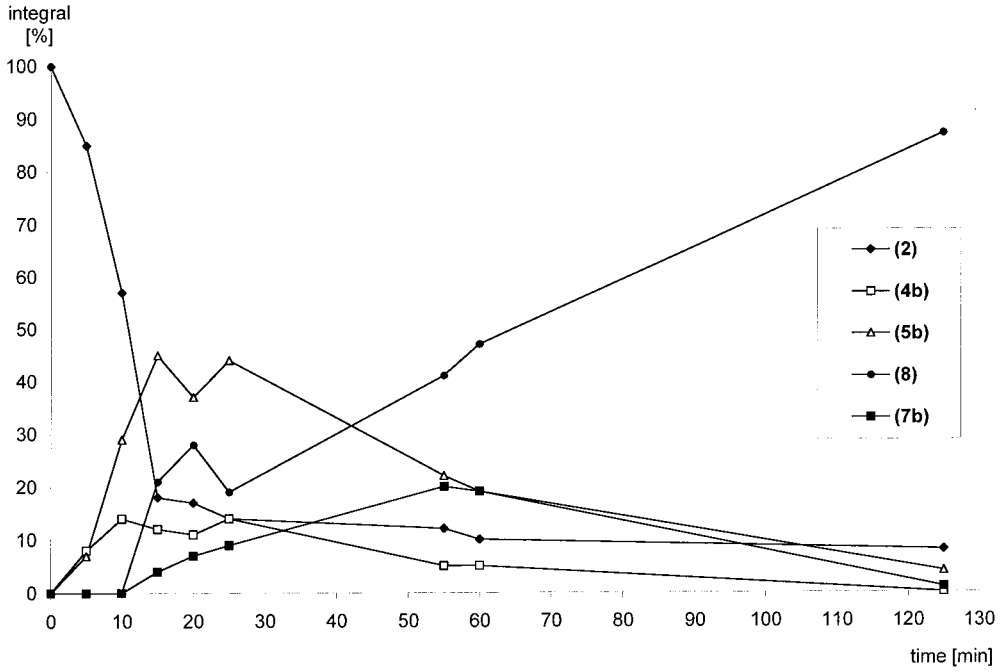


Figure 1. ^{31}P NMR monitoring of the reaction of complex **2b** with **3**

bene atoms mainly electronically. The observation of two magnetically nonequivalent carbene atoms in complex **6a** points to a remarkable intramolecular steric crowding and is so far unique.[2] This special steric situation also explains the relative stability of complex **6a** towards base-induced elimination to form complex **7a**. The P−H functions of complexes **8** and **9a** are well established by their phosphorus−proton coupling constants of $|^1J(P,H)|$ = 349.4 and 378.9 Hz, respectively. It is also remarkable that the two isotopomers of complex **8** could be distinguished by ^{31}P NMR spectroscopy (CH_2Cl_2; at 121.5 instead of 81.0 MHz) [**8**(^{35}Cl): δ = 53.23 ($|^1J(W,P)|$ = 268.38 Hz); **8**(^{37}Cl): δ = 53.3 ($|^1J(W,P)|$ = 268.80 Hz]. EI-MS experiments showed that all complexes analyzed predominantly lost carbon monoxide subsequent to the ionisation process.

The molecular structure of complex **6a**, as determined by X-ray crystallography (Figure 3), consists of two ($Me_3Si)_2$HCP-bridged amino(aryl)carbene complex moieties, which have an *E,E*-configuration of the pentacarbonyltungsten and the ($Me_3Si)_2$HCP fragment with respect to the

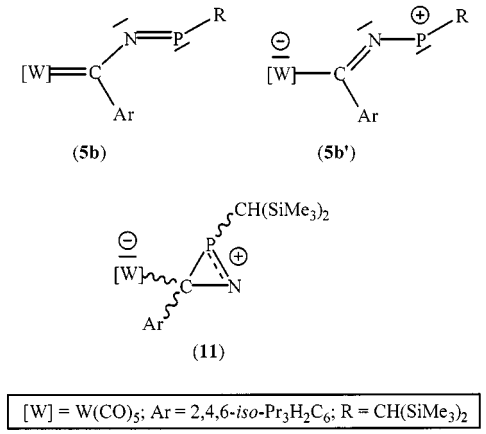


Figure 2. Plausible structures of the new intermediate in the 2*H*-azaphosphirene complex ring forming process

C−N bond, and which differ somewhat in the metal−carbon and nitrogen−phosphorus bond lengths of their nearly planar W−C−P−N skeletons [torsion angles: W(1)−C(28)−N(1)−P = −171°; W(2)−C(18)−N(2)−P = −175°]. The interplanar angle between the W−C−N and the mesityl ring plane [W(1)−C(28)−N(1)/Mes = 89.4° and W(2)−C(18)−N(2)/Mes = 81.9°] excludes any π-electron interactions between the carbene centres and the aryl rings.

The structure of complex **9a** in the mesitylnitrile adduct **10** (Figure 4) is similar with respect to the W−C−N−P subunit [W(2)−C(18)−N(1)−P = 175°] and also to the interplanar angle between the W−C−N and the mesityl ring plane [W(2)−C(18)−N(2)/Mes = 87.9°]. The freely defined hydrogen atoms at nitrogen and phosphorus adopt approximately an *E*-configuration with respect to the N−P bond. Of special interest are the dimensions of the hydrogen bond N(1)−H···N(2) unit: N−H···N = 176(7)°, N(1)···N(2) = 3.049(7) Å, N(1)−H(1) = 0.74(6) Å and N(2)···H(1) = 2.31(7) Å; a similar situation is often found for hydrogen bonds between nitriles and amides.

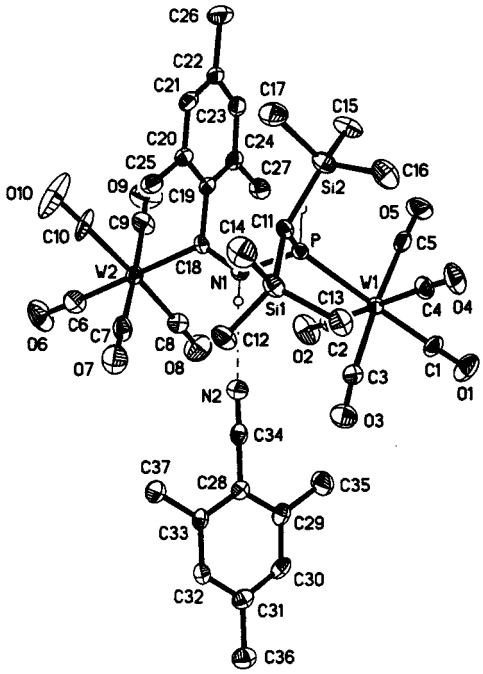


Figure 4. Molecular structure of complex **10** (ellipsoids represent 50% probability level; hydrogen atoms except P–H and N−H are omitted for clarity); selected bond lengths [Å] and angles [°]: W(1)−C(1) 2.015(7), P−W(1) 2.504(2), N(1)−P 1.769(5), P−C(11) 1.820(6), C(18)−N(1) 1.330(7), C(18)−W(2) 2.224(6), W(2)−C(6) 2.017(7); N(1)−C(18)−W(2) 126.7(4), C(18)−N(1)−P 130.1(4)

Experimental Section

General: All operations were carried out under an inert atmosphere of deoxygenated dry nitrogen. Solvents were dried according to standard procedures. − NMR spectra were recorded on a Bruker

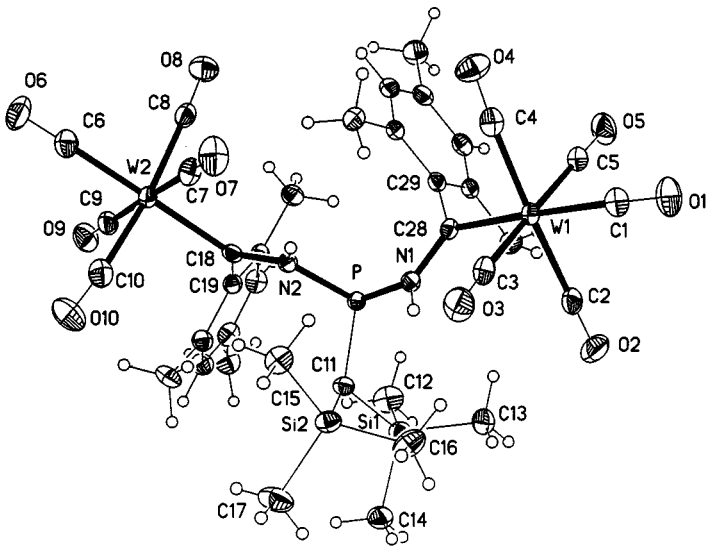


Figure 3. Molecular structure of complex **6a** (ellipsoids represent 50% probability level). Selected bond lengths [Å] and angles [°]: W(1)−C(1) 2.035(3), W(1)−C(28) 2.193(2), C(28)−N(1) 1.333(3), N(1)−P 1.7725(19), P−C(11) 1.832(2), P−N(2) 1.795(2), N(2)−C(18) 1.322(3), C(18)−W(2) 2.222(2), W(2)−C(6) 2.019(3); N(1)−C(28)−W(1) 123.89(16), C(28)−N(1)−P 127.62(16), N(1)−P−N(2) 95.59(9), C(18)−N(2)−P 126.41(17), N(2)−C(18)−W(2) 125.28(17)

AC-200 spectrometer (200 MHz for ^1H; 50.3 MHz for ^{13}C; 81 MHz for ^{31}P) using [D_3]chloroform and [D_6]benzene as solvents, the latter as internal standard, or a Bruker AMX-300 (30.4 MHz for ^{15}N) using dichloromethane as solvent and nitromethane as external standard; shifts are given relative to tetramethylsilane (^1H, ^{13}C), nitromethane (^{15}N) or 85% H_3PO_4 (^{31}P); only coupling constant magnitudes are given. − MS: Finnigan Mat 8430 (70 eV). − Elemental analyses: Carlo Erba analytical gas chromatograph. − IR: Biorad FT-IR-165; only ν(NH) and/or ν(CO) bands are given.

Preparation of {[Ethoxy(2,4,6-trimethylphenyl)carbene]pentacarbonyltungsten(0)} (1a): *n*-Butyllithium (6.25 mL, 1.6 M in *n*-hexane) was added at ambient temperature to a solution of 1-bromo-2,4,6-trimethylbenzene (2.0 g, 10 mmol) in 20 mL diethyl ether. After stirring for 70 min the reaction mixture was added to a suspension of hexacarbonyltungsten (3.5 g, 10 mmol) in 150 mL diethyl ether. The reaction mixture was stirred for 1 hour before the solvent was removed under reduced pressure (0.1 mbar). The residue was dissolved in 80 mL of water and triethyloxonium tetrafluoroborate (2.4 g, 13 mmol) was added in small portions. The mixture was extracted twice with 200 mL of *n*-pentane and the red *n*-pentane phases were filtered through a short column (SiO_2, *n*-pentane). The combined red *n*-pentane phases were concentrated under reduced pressure (0.1 mbar) and the red oily residue was purified by column chromatography (SiO_2, *n*-hexane). Removing the solvent afforded a red oil. The red oil was dissolved in 5 mL of *n*-pentane, the product precipitated at −100 °C and then dried in vacuo to give **1a** (1.95 g, 39%) as an orange powder. M.p. 80 °C (decomp.). − ^1H NMR ($CDCl_3$): δ = 1.65 [t, ^3J(H,H) = 7.10 Hz, 3 H, CH_2-CH_3], 2.17 (s, 6 H, *o*-Ar−CH_3), 2.31 (s, 3 H, *p*-Ar−CH_3), 5.14 [q, ^3J(H,H) = 7.10 Hz, 2 H, O−CH_2], 6.84 (s, 2 H, Ar−*H*3/3′). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 14.1 (s, CH_2-CH_3), 19.3 (s, *o*-Ar−*C*H_3), 20.9 (s, *p*-Ar−*C*H_3), 80.7 (s, O*C*H_2), 126.4 (s, Ar−*C*2/2′), 128.8 (s, Ar−*C*3/3′), 137.5 (s, Ar−*C*4), 153.0 (s, Ar−*C*1), 198.0 (s, *cis*-*C*O), 203.7 (s, *trans*-*C*O), 334.8 (s, W=*C*R_2). − IR (KBr) $\tilde{\nu}$ = 2069 (m), 1984 (m), 1951 (s), 1921 (s), 1913 (s) cm^{-1} (CO). − MS (70 eV; ^{184}W): *m*/*z* (%) = 500 (34) [M^+], 472 (40) [M^+ − CO], 444 (31) [M^+ − 2CO], 416 (46) [M^+ − 3CO], 387 (57) [M^+ − 3CO − C_2H_5], 372 (9) [M^+ − 3CO − C_2H_5 − CH_3], 358 (100) [M^+ − 4CO − $2CH_3$]. − $C_{17}H_{16}O_6W$ (500.2): calcd. C 40.82, H 3.22; found C 41.30, H 3.24.

Preparation of {[Amino(2,4,6-trimethylphenyl)carbene]pentacarbonyltungsten(0)} (2a): Ammonia was slowly bubbled through a solution of 3 mmol of the complex **1a** in 60 mL of THF at 0 °C until it was saturated with ammonia. The reaction mixture was stirred for 20 hours at ambient temperature until a yellow colour persisted and thin 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 purified by column chromatography (SiO_2, 20 °C; *n*-hexane/diethyl ether 10:1) to give **2a** (1.33 g, 94%) as a yellow powder. M.p. 163 °C (decomp.). − ^1H NMR ($CDCl_3$): δ = 2.23 (s, 6 H, *o*-Ar−CH_3), 2.30 (s, 3 H, *p*-Ar−CH_3), 6.86 (s, 2 H, Ar−*H*3/3′), 8.64 (s, br, 1 H, N*H*), 8.97 (s, br, 1 H, N*H*). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 19.6 (s, *o*-Ar−*C*H_3), 20.8 (s, *p*-Ar−*C*H_3), 127.6 (s, Ar−*C*2/2′), 128.8 (s, Ar−*C*3/3′), 137.0 (s, Ar−*C*4), 149.1 (s, Ar−*C*1), 198.1 [s, ^1J(W,C) = 127.4 Hz, *cis*-*C*O], 203.2 (s, *trans*-*C*O), 276.2 (s, W=*C*R_2). − IR (KBr) $\tilde{\nu}$ = 3404 (m), 3275 (m), 3217 (m) (NH); 2065 (s), 1975 (s), 1913 (s), 1883 (s), 1861 (s) cm^{-1} (CO). − MS (70 eV); ^{184}W): *m*/*z* (%) = 471 (42) [M^+], 443 (26) [M^+ − CO], 415 (18) [M^+ − 2CO], 387 (86) [M^+ − 3CO], 359 (76) [M^+ − 4CO], 329 (100) [(M^+ − 4CO − $2CH_3$], 301 (31) [M^+ − 5CO − $2CH_3$]. − $C_{15}H_{13}NO_5W$ (471.1): calcd. C 38.24, H 2.78, N 2.97; found C 38.46, H 2.83, N 2.91.

General Procedure for the Preparation of (2,4,6-Triisopropylphenyl)- and (2,4,6-Tri-*tert*-butylphenyl)-Substituted {[Ethoxy(aryl)carbene]-pentacarbonyltungsten(0)} Complexes 1b and 1c: *n*-Butyllithium (1.6 molar in *n*-hexane, 6.25 mL) was added at −80 °C to a solution of the 1-bromo-2,4,6-trialkylbenzenes (R = *i*Pr, *t*Bu; 10 mmol) in 20 mL THF. After stirring for 90 min at −80 °C hexacarbonyltungsten (3.5 g, 10 mmol) was added in small portions to the reaction mixture, which was stirred for 18 hours and warmed up to ambient temperature before the solvent was removed under reduced pressure (0.1 mbar). The residue was dissolved in 40 mL of dichloromethane and triethyloxonium tetrafluoroborate (2.4 g, 13 mmol) was added in small portions. The solvent was removed under reduced pressure (0.1 mbar) and the residue was purified by low temperature column chromatography (SiO_2, −20 °C, *n*-hexane).

{Ethoxy[(2,4,6-triisopropylphenyl)carbene]pentacarbonyltungsten(0)} (1b): Compound **1b** (0.7 g, 12%) was obtained as a yellow orange powder. M.p. 76 °C (decomp.). − ^1H NMR ($CDCl_3$): δ = 1.04 (s, br, 6 H, *o*-Ar−CH(CH_3)$_2$), 1.21 [d, ^3J(H,H) = 6.8 Hz, 6 H, *o*-Ar−CH(CH_3)$_2$], 1.30 [d, ^3J(H,H) = 6.6 Hz, 6 H, *p*-Ar−CH(CH_3)$_2$], 1.62 (s, br, 3 H, CH_2-CH_3), 2.83 [m_c, br, 3 H, *p*-Ar−C*H*(CH_3)$_2$, *o*-Ar−C*H*(CH_3)$_2$], 5.01 (s, br, 2 H, O−CH_2), 6.94 (s, 2 H, Ar−*H*3/3′). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 13.7 (s, CH_2CH_3), 21.1 [s, *o*-Ar−CH(*C*H_3)$_2$], 23.0 [s, *p*-Ar−CH(*C*H_3)$_2$], 25.2 [s, *o*-Ar−CH(*C*H_3)$_2$], 29.5 [s, *o*-Ar−*C*H(CH_3)$_2$], 33.1 [s, *p*-Ar−*C*H(CH_3)$_2$], 79.4 (s, O*C*H_2), 119.6 (s, br, Ar−*C*3/3′), 138.1 (s, br, Ar−*C*2/2′), 147.7 (s, Ar−*C*4), 149.9 (s, Ar−*C*1), 195.8 (s, *cis*-*C*O), 202.6 (s, *trans*-*C*O), 337.2 (s, W=*C*R_2). − IR (KBr) $\tilde{\nu}$ = 2069 (m), 1989 (m), 1950 (s), 1932 (s), 1905 (s), cm^{-1} (CO). − MS (70 eV; ^{184}W): *m*/*z* (%) = 584 (25) [M^+], 556 (26) [M^+ − CO], 528 (100) [M^+ − 2CO], 500 (64) [M^+ − 3CO], 472 (54) [M^+ − 4CO], 444 (74) [M^+ − 5CO], 231 (74) [($C_6H_2(C_3H_7)_3CO)^+$], 203 (5) [$(C_6H_2(C_3H_7)_3^+$], 43 (20) [$C_3H_7^+$]. − HR-MS ($C_{23}H_{28}O_6W$): calcd. 584.1397; found 584.1395 (±2 ppm).

{Ethoxy[(2,4,6-tri-*tert*-butylphenyl)carbene]pentacarbonyltungsten(0)} (1c): Compound **1c** (3.5 g, 56%) was obtained as a yellow orange powder. M.p. 82 °C (decomp.). − ^1H NMR ($CDCl_3$): δ = 1.29 [s, 9 H, *p*-Ar−C(CH_3)$_3$], 1.31 [s, 18 H, *o*-Ar−C(CH_3)$_3$], 1.77 [t, 3J(H,H) = 7.2 Hz, 3 H, CH_2CH_3], 5.03 [q, ^3J(H,H) = 7.2 Hz, 2 H, OCH_2], 7.29 (s, 2 H, Ar−H3/3′). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 14.2 (s, CH_2CH_3), 31.3 [s, *p*-Ar−C(CH_3)$_3$], 34.5 [s, *o*-Ar−C(CH_3)$_3$], 34.7 [s, *p*-Ar−C(CH_3)$_3$], 38.5 [s, *o*-Ar−C(CH_3)$_3$], 80.9 (s, O*C*H_2), 122.6 (s, Ar−*C*3/3′), 137.8 (s, Ar−*C*2/2′), 149.0 (s, Ar−*C*4), 151.6 (s, Ar−*C*1), 198.3 [s, ^1J(C,W) = 129.0 Hz, *cis*-*C*O], 204.3 (s, *trans*-*C*O), 341.2 (s, W=*C*R_2). − IR (KBr) $\tilde{\nu}$ = 2069 (m), 1981 (m), 1953 (s), 1928 (s), 1910 (s) cm^{-1} (CO). − MS (70 eV; ^{184}W): *m*/*z* (%) = 626 (11) [M^+], 598 (20) [M^+ − CO], 570 (12) [M^+ − 2CO], 542 (86) [M^+ − 3CO], 513 (100) [M^+ − 3CO − C_2H_5], 485 (59) [M^+ − 4CO − C_2H_5], 273 (43) [$C_6H_2(C_4H_9)_3CO^+$], 57 (35) [$C_4H_9^+$]. − $C_{26}H_{34}O_6W$ (626.4): calcd. C 49.85, H 5.47; found C 50.07, H 5.59.

Preparation of {Amino[(2,4,6-triisopropylphenyl)carbene]pentacarbonyltungsten(0)} (2b): A concentrated solution of ammonia in water (4 mL, 50 mmol) was added at ambient temperature to a solution of **1b** (0.7 g, 1.2 mmol) in 60 mL of THF. The reaction mixture was stirred for 21 days at ambient temperature until a yellow colour persisted and thin liquid chromatography (SiO_2) indicated that all starting material was consumed. All volatile compounds were removed under reduced pressure (0.1 mbar) and the yellow residue was purified by low temperature column chromatography (SiO_2, −15 °C; *n*-hexane/diethyl ether 10:1) to give **2b** (0.6 g, 90%) as a yellow powder. M.p. 116 °C (decomp.). − ^1H NMR ($CDCl_3$):

δ = 1.17 [d, ^3J(H,H) = 6.8 Hz, 6 H, *o*-Ar−CH(CH_3)$_2$], 1.25 [d, ^3J(H,H) = 7.0 Hz, 6 H, *p*-Ar−CH(CH_3)$_2$], 1.33 [d, ^3J(H,H) = 6.8 Hz, 6 H, *o*-Ar−CH(CH_3)$_2$], 2.88 [sept, ^3J(H,H) = 7.0 Hz, 1 H, *p*-Ar−C*H*(CH$_3$)$_2$], 2.92 [sept, ^3J(H,H) = 6.8 Hz, 2 H, *o*-Ar−C*H*(CH$_3$)$_2$], 7.0 (s, 2 H, Ar-*H*3/3′), 8.64 (s, br, 1 H, N*H*), 8.97 (s, br, 1 H, N*H*). − ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 23.3 [s, CH(*C*H$_3$)$_2$], 24.0 [s, CH(*C*H$_3$)$_2$], 26.4 [s, CH(*C*H$_3$)$_2$], 30.4 [s, *o*-Ar−*C*H(CH$_3$)$_2$], 34.1 [s, *p*-Ar−*C*H(CH$_3$)$_2$], 121.4 (s, Ar−*C*3/3′), 139.5 (s, Ar−*C*2/2′), 146.5 (s, Ar−*C*1), 148.6 (s, Ar−*C*4), 198.2 [s, ^1J(C,W) = 127.4 Hz, *cis*-*C*O], 202.8 (s, *trans*-*C*O), 276.1 (s, W=*C*R$_2$). − IR (KBr) ṽ = 3413 (m), 3319 (m), (NH); 2063 (s), 1971 (s), 1938 (vs), 1920 (vs), 1903 (vs) cm^{-1} (CO). − MS (70 eV; ^{184}W): *m*/*z* (%) = 555 (20) [M$^+$], 527 (8) [M$^+$ − CO], 499 (19) [M$^+$ − 2CO], 497 (19) [M$^+$ − 2CO − 2CH$_3$], 471 (85) [M$^+$ − 3CO], 469 (100) [M$^+$ − 2CO − 2CH$_3$], 203 (16) [C$_6$H$_2$(C$_3$H$_7$)$_3^+$], 43 (13) [C$_3$H$_7^+$]. − HR-MS (C$_{21}$H$_{25}$NO$_5$W): calcd. 555.1246; found 555.1240 (±2 ppm).

Preparation of *N*,*N*′-Bis{amino[(2,4,6-trimethylphenyl)carbene]pentacarbonyltungsten(0)}bis(trimethylsilyl)methylphosphane (6a), {[2-Bis(trimethylsilyl)methyl-3-(2,4,6-trimethylphenyl)-2*H*-azaphosphirene-κP}pentacarbonyltungsten(0)] (7a) and {Pentacarbonyl-[bis(trimethylsilyl)methylchlorophosphane]tungsten(0)} (8): NEt$_3$ (3.3 mL) was added at ambient temperature to a solution of complex **2a** (0.47 g, 1 mmol) and [bis(trimethylsilyl)methylene]chlorophosphane **3** (0.22 g, 1 mmol) in 10 mL of diethyl ether. The reaction mixture was stirred for 20 hours at ambient temperature until **3** was consumed (^{31}P NMR). To the yellow-orange reaction mixture was added 100 mL of pentane and the mixture then filtered. The solvent was removed under reduced pressure (0.1 mbar) and the residue was separated into two fractions by low temperature column chromatography (SiO$_2$, −20 °C; *n*-hexane/diethyl ether 15:1). Removing the solvent from the first yellow fraction under reduced pressure (0.1 mbar) gave complex **8**; similarly, the second yellow fraction gave a mixture of **6a** and **7a** as a yellow powder. The yellow powder was washed twice with 10 mL of *n*-pentane. The remaining yellow-orange residue was identified as **6a**. The solvent of the combined organic pentane phases was removed under reduced pressure (0.1 mbar) to give a yellow-orange powder, which was **7a**−enriched.

***N*,*N*′-Bis{amino[(2,4,6-trimethylphenyl)carbene]pentacarbonyltungsten(0)}bis(trimethylsilyl)methylphosphane (6a):** Compound **6a** (50 mg, 8.8%) was obtained as a yellow-orange powder. M.p. 166 °C (decomp.). − ^{1}H NMR (CDCl$_3$): δ = −0.08 [s, 9 H, Si(CH_3)$_3$], 0.32 [d, ^2J(P,H) = 4.7 Hz, 1 H, PC*H*], 0.52 [s, 9 H, Si(CH_3)$_3$], 1.07 (s, 3 H, *o*-Ar−CH_3), 2.06 (s, br, 3 H, *o*-Ar−CH_3), 2.19 (s, br, 6 H, *o*-Ar−CH_3), 2.28 (s, 3 H, *p*-Ar−CH_3), 2.50 (s, 3 H, *p*-Ar−CH_3), 6.90 (s, 1 H, Ar−*H*3/3′), 6.97 (s, 1 H, Ar-*H*3/3′), 7.03 (s, 1 H, Ar−*H*3/3′), 7.24 (s, 1 H, Ar−*H*3/3′), 9.29 (s, br, 1 H, N*H*), 9.95 (s, br, 1 H, N*H*). − ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 0.9 [s, Si(*C*H$_3$)$_3$], 3.5 [s, Si(*C*H$_3$)$_3$], 17.9 (s, Ar−*C*H$_3$), 18.1 (s, Ar−*C*H$_3$), 20.5 (s, Ar−*C*H$_3$), 20.7 (s, Ar−*C*H$_3$), 20.8 [d, ^1J(P,C) = 50.5 Hz, P*C*H], 21.0 (s, Ar−*C*H$_3$), 22.5 (s, Ar−*C*H$_3$), 125.5 (s, Ar−*C*2/2′), 126.5 (s, Ar−*C*2/2′), 126.6 [d, ^4J(P,C) = 2.2 Hz, Ar−*C*2/2′], 127.5 (s, Ar−*C*2/2′), 129.0 (s, Ar−*C*3/3′), 129.1 (s, Ar−*C*3/3′), 129.2 (s, Ar−*C*3/3′), 129.9 (s, Ar−*C*3/3′), 138.1 (s, Ar−*C*4), 139.1 (s, Ar−*C*4), 146.3 [d, ^3J(P,C) = 11.9 Hz, Ar−*C*1], 147.7 [d, ^3J(P,C) = 8.8 Hz, Ar−*C*1], 197.6 [s, ^1J(W,P) = 127.4 Hz, *cis*-*C*O], 198.2 [s, ^1J(P,W) = 127.1 Hz, *cis*-*C*O], 202.2 (s, *trans*-*C*O), 202.7 (s, *trans*-*C*O), 283.1 (s, W=*C*R$_2$), 301.0 [d, ^2J(P,C) = 4.2 Hz, W=*C*R$_2$]. − ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 110.3 (s). − IR (KBr) ṽ = 3324 (w), 3310 (w) (NH); 2064 (s), 1992 (m), 1984 (s), 1952 (s), 1941 (s), 1924 (s), 1913 (s), 1899 (s) cm^{-1} (CO). − MS (*pos.*-CI, NH$_3$, ^{184}W): *m*/*z* (%) = 1130 (2) [M$^+$], 661 (86) [(M + H)$^+$ −{(CO)$_5$W=C(C$_9$H$_{11}$)NH}], 469 (100) [{(CO)$_5$W=C(C$_9$H$_{11}$)NH}$^+$]. − C$_{37}$H$_{43}$N$_2$O$_{10}$PSi$_2$W$_2$ (1130.6): calcd. C 39.31, H 3.83, N 2.48; found C 39.62, H 3.95, N 2.39.

{[2-Bis(trimethylsilyl)methyl-3-(2,4,6-trimethylphenyl)-2H-azaphosphirene-κP}pentacarbonyltungsten(0)] (7a): ^{1}H NMR (C$_6$D$_6$): δ = −0.17 [s, 9 H, Si(CH_3)$_3$], 0.32 [s, 9 H, Si(CH_3)$_3$], 0.65 [d, 1 H, ^2J(P,H) = 3.6 Hz, PC*H*], 1.80 (s, 3 H, *p*-Ar−CH_3), 2.11 (s, 6 H, *o*-Ar−CH_3), 6.55 (s, 2 H, Ar-*H*3/3′). − ^{13}C{^{1}H} NMR (*n*C$_5$H$_{12}$/C$_6$D$_6$): δ = 1.8 [d, ^3J(P,C) = 2.2 Hz, Si(*C*H$_3$)$_3$], 2.3 [d, ^3J(P,C) = 3.0 Hz, Si(*C*H$_3$)$_3$], 29.2 [d, ^1J(P,C) = 25.7 Hz, P*C*H], 122.3 [d, ^2J(P,C) = 11.6 Hz, Ar−*C*1], 130.7 (s, Ar−*C*3,5), 141.9 (s, Ar−*C*2,6), 142.1 (s, Ar−*C*2,6), 144.1 (s, Ar−*C*4), 191.1 [(d, $^{(1+2)}J$(P,C) = 3.8 Hz, P*C*N], 196.7 [d, ^2J(P,C) = 8.6 Hz, *cis*-*C*O], 201.9 [d, ^2J(P,C) = 35.4 Hz, *trans*-*C*O]. − ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ = −122.3 [s, ^1J(W,P) = 298.7 Hz].

{Pentacarbonyl{[bis(trimethylsilyl)methyl]chlorophosphane}tungsten(0)} (8): Compound **8** (204 mg, 37%) was obtained as a pale yellow solid. M.p. 52 °C (decomp.). − ^{1}H NMR (CDCl$_3$): δ = 0.26 [s, 9 H, Si(CH_3)$_3$], 0.34 [s, 9 H, Si(CH_3)$_3$], 1.11 [dd, ^2J(P,H) = 6.5, ^3J(H,H) = 1.5 Hz, PCH], 7.88 [dd, ^1J(P,H) = 349.4, ^1J(W,H) = 5.8, ^3J(H,H) = 1.5 Hz, 1 H, PH]. − ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 0.1 [d, ^3J(P,C) = 3.0 Hz, SiMe$_3$], 2.1 [s, ^3J(P,C) = 4.3 Hz, SiMe$_3$], 24.6 [d, ^1J(P,C) = 4.8 Hz, PCH], 195.9 [d, ^1J(W,C) = 126.5, ^2J(P,C) = 6.9 Hz, *cis*-CO], 198.7 [d, ^2J(P,C) = 31.3 Hz, *trans*-CO]. − ^{31}P{^{1}H} NMR (81.0 MHz, CDCl$_3$): δ = 53.3 [d, ^1J(P,H) = 349.4, ^1J(W,P) = 268.8 Hz]. − MS (*pos.*-CI, isobutane, ^{35}Cl, ^{184}W): *m*/*z* = 550 (100) [M$^+$], 515 (56) [M − ^{35}Cl$^+$], 191 (51) [C$_7$H$_{20}$PSi$_2^+$], 73 (96) [Me$_3$Si$^+$]. − ^{31}P NMR (81.0 MHz, CDCl$_3$): δ = 53.7 [dd, ^1J(P,H) = 349.4, ^1J(W,P) = 268.8, ^2J(P,H) = 6.5 Hz]. − C$_{12}$H$_{20}$ClO$_5$PSi$_2$W (550.7): calcd. C 26.17, H 3.66; found C 26.45, H 3.80.

Preparation of *N*-{Amino[(2,4,6-trimethylphenyl)carbene]pentacarbonyltungsten(0)}-[bis(trimethylsilyl)methylphosphane]pentacarbonyltungsten(0) (9a): [Bis(trimethylsilyl)methylene]chlorophosphane **3** (0.49 g, 2.2 mmol) and 11 mL of NEt$_3$ were added at 0 °C to a solution of complex **2a** (1.10 g, 2.2 mmol) in 33 mL of diethyl ether. The reaction mixture was stirred for 70 hours at ambient temperature until **3** was consumed (^{31}P NMR) and a 1:2 mixture of **8**:**9a** was detected. The solvent was evaporated slowly to dryness under reduced pressure (0.1 mbar). The residue was extracted twice with 50 mL of *n*-pentane and filtered. The remaining residue was washed twice with 5 mL of *n*-pentane, the organic phases combined and the solvent removed under reduced pressure. The residue was separated in two fractions by low temperature column chromatography. Removing the solvent of the first yellow fraction (SiO$_2$, −20 °C; *n*-pentane) under reduced pressure (0.1 mbar) gave complex **8**. Removing the solvent of the second yellow fraction (SiO$_2$, −20 °C; *n*-pentane/diethyl ether 7:1) under reduced pressure (0.1 mbar) gave **9a**. Orange crystals of the mesitylnitrile adduct **10** were obtained by crystallisation of **9a** in the presence of mesitylnitrile in *n*-pentane.

9a: 0.44 g (40%) as an orange powder. M.p. 112 °C (decomp.). − ^{1}H NMR (C$_6$D$_6$): δ = −0.3 [d, 9 H, ^4J(P,H) = 1.1 Hz, Si(CH_3)$_3$], 0.21 [s, 9 H, Si(CH_3)$_3$], 1.33 [dd, ^3J(H^C,H^P) = 19.0 Hz, ^2J(P,H) = 3.1 Hz, 1 H, PC*H*], 1.97 (s, 3 H, Ar−CH_3), 2.10 (s, 3 H, Ar−CH_3), 2.18 (s, 3 H, Ar−CH_3), 6.45 (s, 1 H, Ar−*H*), 6.52 (s, 1 H, Ar−*H*), 6.87 [ddd, ^1J(P,H) = 378.9 Hz, ^3J(H^P,H^C) = 19.0 Hz, ^3J(H^P,H^N) = 8.0 Hz, 1 H, P*H*], 9.6 [dd, br, ^3J(H^N,P) = 27.5 Hz, ^3J(H^N,H^P) = 8.0 Hz, 1 H, N*H*]. − ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ = 0.4 [d, ^3J(P,C) = 5.1 Hz, Si(*C*H$_3$)$_3$], 2.0 [d, ^3J(P,C) = 3.3 Hz, Si(*C*H$_3$)$_3$], 18.8 [d, ^1J(P,C) = 17.1 Hz, P*C*H], 19.6 (s, Ar−*C*H$_3$), 20.5 (s, Ar−*C*H$_3$),

21.6 (s, Ar−*C*H$_3$), 126.5, (s, Ar−*C*2,2′), 127.8, (s, Ar−*C*2,2′), 129.5, (s, Ar−*C*3,3′), 129.7, (s, Ar−*C*3,3′), 137.8 (s, Ar−*C*4), 145.6 [d, ^3J(P,C) = 7.4 Hz, Ar−*C*1], 195.7 [d, ^2J(P,C) = 6.6 Hz, *cis*-*C*O], 198.4 (s, *cis*-*C*O), 198.7 [d, ^2J(P,C) = 32.5 Hz, *trans*-*C*O], 202.6 [d, ^4J(P,C) = 1.9 Hz, *trans*-*C*O], 288.3 [d, ^2J(P,C) = 14.3 Hz, W=*C*R$_2$]. − ^{31}P NMR (C$_6$D$_6$): δ = 27.5 [ddd, ^1J(P,H) = 378.9 Hz, ^2J(P,H^N) = 27.5 Hz, ^2J(P,H^C) = 3.1 Hz, ^1J(P,W) = 255.5 Hz]. − IR (KBr) $\tilde{\nu}$ = 3177 (w) (NH); 2079 (m), 2065 (s), 1986(m), 1963(s), 1950 (s), 1930 (vs), 1913 (s), 1902 (s) cm^{-1} (CO). − $C_{27}H_{32}NO_{10}PSi_2W_2$ (985.4): C 32.91, H 3.27, N 1.42; found C 33.38, H 3.41, N 1.35.

Attempted Synthesis of {[2-Bis(trimethylsilyl)methyl-3-(2,4,6-triisopropylphenyl)-2*H*-azaphosphirene-κP]pentacarbonyltungsten(0)} (7b): To a solution of complex **2b** (0.05 g, 0.08 mmol) in 0.8 mL of dichloromethane were added [bis(trimethylsilyl)methylene]chlorophosphane **3** (0.02 g, 0.08 mmol) and 0.3 mL of NEt$_3$ at ambient temperature. The reaction was monitored by ^{31}P NMR spectroscopy; ^{31}P NMR signal integrals were determined ([%], relaxation time = 0) after different reaction times (t [min]).

7b: ^{31}P{^{1}H} NMR (reaction mixture, CH$_2$Cl$_2$/Et$_3$N): δ = −121.5 [s, ^1J(W,P) = 303.0 Hz].

Structure Determination of Complex 6a·CH$_2$Cl$_2$: Crystal data: $C_{38}H_{44}Cl_2N_2O_{10}PSi_2W_2$, M = 1214.50, $P\bar{1}$, a = 11.7890(10), b = 12.2501(10), c = 17.7820(14) Å, α = 83.779(3), β = 80.145(3), γ = 65.843(3)°, V = 2306.5(3) Å^3, Z = 2, $d_{calcd.}$ = 1.749 Mg/m^3, μ = 5.239 mm^{-1}, T = 143 K. The crystal (0.27 × 0.23 × 0.18 mm) was mounted in inert oil. 27513 intensities were measured (4 ≤ 2θ ≤ 60) using Mo-K_α radiation on a Bruker SMART 1000 CCD diffractometer. After absorption correction (multiple-scans) 13311 were unique (R_{int} = 0.0287) and used for all calculations (program SHELXL-97).[15] All hydrogen atoms (except rigid methyl groups) were refined with a riding model. The final $wR(F^2)$ was 0.0556 with conventional R(F) = 0.0231 for 526 parameters and 73 restraints. Highest peak 1.366, hole −1.528 e/Å^3.

Structure Determination of Complex 10: Crystal data: $C_{37}H_{43}N_2O_{10}PSi_2W_2$, M = 1130.58, $P2_1/c$, a = 14.645(2), b = 19.406(2), c = 15.262(2) Å, β = 93.51(1)°, V = 4329.5(9) Å^3, Z = 4, $d_{calcd.}$ = 1.734 Mg/m^3, μ = 5.455 mm^{-1}, T = 173 K. The crystal (0.50 × 0.40 × 0.30 mm) was mounted in inert oil. 8825 intensities were measured (6 ≤ 2θ ≤ 50) using Mo-K_α radiation on a Siemens P4 diffractometer. After absorption correction (psi-scans) 7594 were unique (R_{int} = 0.0332) and used for all calculations (program SHELXL-93).[16] All hydrogen atoms [except rigid methyl groups and freely refined (N1)−H1/(P)−H2] were refined with a riding model. The final $wR(F^2)$ was 0.0804 with conventional R(F) = 0.0336 for 507 parameters and 254 restraints. Highest peak 1.641, hole −1.806 e/Å^3. 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-138591 **(6a)** and CCDC-138592 **(10)**. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge, UK CB2 1EZ [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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