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Synthesis, Structure, and Ring-Expansion Reactions of a 3-Ferrocenyl-Substituted 2*H*-Azaphosphirene Tungsten Complex

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Reaction of *C*-ferrocenyl-substituted aminocarbene tungsten complex **1** with [bis(trimethylsilyl)methylene]chlorophosphane (**2**) and triethylamine yielded 2*H*-azaphosphirene complex **3** in good yield. Reaction of complex **3** with aryl nitriles **4a**–**c**, *N*-piperidinonitrile (**4d**), and acetonitrile (**4e**) in the presence of ferrocenium hexafluorophosphate yielded regioselectively 2*H*-1,4,2-diazaphosphole complexes **5a**–**e** through single-electron-transfer-induced ring expansion together with complex **6** in varying amounts; isolation of the latter failed. Apart from the NMR spectroscopic parameters of complexes **1**, **3**, and **5a**–**e**, cyclic voltammetric (**1**, **3**, **5a**–**d**), and single-crystal X-ray diffraction data (**1**, **3**, and **5d**) are presented and discussed.

Introduction

Generation of radical cationic intermediates has emerged as a useful synthetic tool in organic[1–4] and organometallic chemistry.[5] Oxidation of closed-shell organic molecules by single-electron transfer (SET) results in strongly destabilized odd-electron species that very often tend to fragment. Although the spin density of most organometallic radicals is localized mainly at the metal center, organometallic radicals can show both metal-centered and/or ligand-centered reactivity, whereas 17e cationic complexes often show the latter behavior.[6] Ferrocenium salts are often used as mild single-electron oxidants in organic[7] and organometallic synthesis,[6] as they have the advantage of being chemically soft (avoiding the otherwise common side reactions) and easy to recycle. These advantages attracted our attention, and therefore, we became interested in exploring reactions of 3-aryl-substituted 2*H*-azaphosphirene complexes[8] with ferrocenium hexafluorophosphate ([FcH]PF_6) and various π substrates.[9] Interestingly, ligand-centered reactivity[6] was observed under such oxidative SET conditions, that is, P–N bond-selective ring expansion occurred to give five-membered heterocyclic complexes. Our studies showed that these reactions require polar solvents such as dichloromethane or carbonitriles, reactants with a π system having a lone pair at one terminus, and substituents that are not (too) bulky. In all [FcH]PF_6-induced ring expansions, the formation of small amounts of ferrocene was observed,[9b,9c] indicating the transient formation of radical cationic species, which was recently supported by DFT calculations.[10] Nevertheless, fundamental questions regarding the synthetic and conceptual range of these findings are still open: (1) Can the method be used for ring expansions of other P-heterocycles and/or (only) complexes thereof? (2) How do other redox-sensitive groups interfere with or even prevent the ring expansion? To address the latter question, the synthesis and reactions of the first 3-ferrocenyl-substituted 2*H*-azaphosphirene complex with nitriles of varying donor abilities under oxidative SET conditions were investigated and are reported herein.

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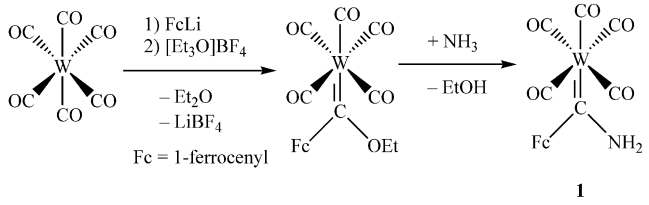
Results and Discussion

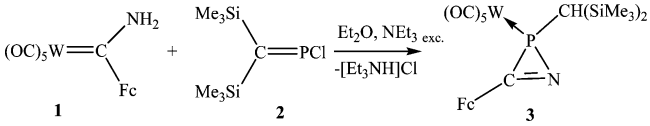
The strategy to gain access to the ferrocenyl-substituted 2*H*-azaphosphirene tungsten complex **3** follows the carbene complex rearrangement route first described by us in 1994[11] and later exploited for *C*-aryl derivatives;[12] during these studies, we recognized that sterically hindered and/or electronically stabilized carbene derivatives may not undergo the rearrangement, yielding other products instead.[12c] According to the chosen strategy, the first step was the synthesis of amino(ferrocenyl)carbene complex **1** via the ethoxy(ferrocenyl)carbene derivative[13] by using the well-established ammonolysis route depicted in Scheme 1.

Complex **1** was easily purified by column chromatography at low temperature and fully characterized by NMR spectroscopy. Interestingly, it showed a $^{13}C\{^1H\}$ NMR resonance at δ = 254.8 ppm, indicating a more shielded carbene center than the phenyl derivative (δ =266.4 ppm).[14]



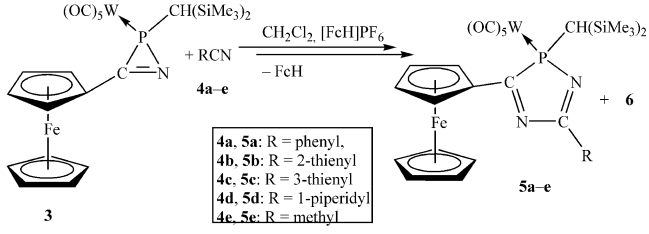
Scheme 1. Synthesis of amino(ferrocenyl)carbene complex **1**.

Despite the NMR indication of a potentially complicated situation, complex **1** reacted smoothly with methylene(chloro)phosphane[15] **2** and triethylamine to yield 2*H*-azaphosphirene complex **3**, which after some workup optimization, was obtained in good yields (Scheme 2).



Scheme 2. Synthesis of 2*H*-azaphosphirene complex **3**.

Subsequent reactions of complex **3** with various nitrile derivatives **4a**–**e** in the presence of substoichiometric amounts of $[FcH]PF_6$ (0.2 equiv.) regioselectively yielded 2*H*-1,4,2-diazaphosphole complexes **5a**–**e** by SET-induced ring expansion (Scheme 3). Although careful reaction monitoring was undertaken in each case, no further information regarding reactive intermediates was obtained. In contrast to previously reported reactions,[10] byproduct **6** with a $^{31}P\{^1H\}$ NMR resonance at 114.4 [^1J(W,P) = 234.0 Hz] was always observed in varying ratios (**5a/6** 4:1, **5b/6** 8:1, **5c/6** 10:1, and **5e/6** 1:1). Apparently, the amount of **6** correlates with and, perhaps, depends on the donor ability of the nitrile and follows the series Me > Ph > 2-thienyl > 3-thienyl > *N*-piperidyl.



Scheme 3. Ferrocenium hexafluorophosphate initiated ring expansion reaction of 2*H*-azaphosphirene complex **3** with nitrile derivatives **4a**–**e**.

After column chromatography at low temperature, complexes **5a**–**e** were obtained in moderate to good yields, but isolation of unknown complex **6** unfortunately failed. Complexes **5a**–**e** were unambiguously identified by multinuclear NMR, IR, and UV/Vis spectroscopy, mass spectrometry, and cyclic voltammetry. The $^{31}P\{^1H\}$ NMR spectroscopic data of complexes **3** and **5a**–**e**, which are given in Table 1, display data for **3** that are similar to those of *C*-aryl-substituted 2*H*-azaphosphirene complexes.[8,12] The NMR spectroscopic data for complexes **5a**–**e** involve a resonance in the range of 105 to 115 ppm and also display a trend in their tungsten–phosphorus coupling constant magnitudes; ^1J(W,P) values increase with increasing donor ability[16] of the C5-substituent[17] in the order: phenyl < 2-thienyl ≈ 3-thienyl < 2-furyl < 1-piperidyl. On the basis of the $^{31}P\{^1H\}$ NMR spectroscopic data [114.4 ppm; ^1J(W,P) = 234.0 Hz], product **6** seems to belong to the class of 2*H*-1,4,2-diazaphosphole complexes, but with an unknown substitution pattern. We could rule out the possibility that **6** is merely an atropisomer of respective complexes **5a**–**e**, because the ratios did not change during temperature-dependent $^{31}P\{^1H\}$ NMR experiments.

Table 1. $^{31}P\{^1H\}$ NMR spectroscopic data of **3** and **5a**–**e**.

	3[a]	**5a**[a]	**5b**[a]	**5c**[a]	**5d**[a]	**5e**[b]
δ_P	–115.3	114.7	114.7	113.4	105.0	111.9
^1J(W,P) [Hz]	299.4	228.7	230.5	230.4	240.5	230.2

[a] In $CDCl_3$. [b] In C_6D_6.

The $^{13}C\{^1H\}$ NMR resonance of complex **3** and those for the C3 centers of **5a**–**e** (Table 2) are very much deshielded for **5a**–**e**, especially in comparison to the values for the C5 carbon centers. Furthermore, the sum of the scalar phosphorus–carbon couplings reveal some cancelling effects in the case of ^{1+2}J(P,C) and ^{2+3}J(P,C) couplings, whereas the magnitudes for ^{1+4}J(P,C) couplings of **5a**–**e** are significantly larger.

Table 2. $^{13}C\{^1H\}$ NMR spectroscopic data for C3 of **3** and **5a**–**e** and C5 centers, respectively.

	3[a]	**5a**[a]	**5b**[a]	**5c**[a]	**5d**[a]	**5e**[b]
δ_{C3}	192.5	208.5	208.6	208.0	205.6	207.2
^{1+4}J(P,C) [Hz]	3.4[c]	24.3	24.0	24.0	26.4	23.9
δ_{C5}	–	168.5	163.4	164.0	163.4	171.5
^{2+3}J(P,C) [Hz]	–	5.3	4.5	5.2	–[d]	7.1

[a] In $CDCl_3$. [b] In C_6D_6. [c] ^{1+2}J(P,C). [d] Not observed.

The molecular structures of complexes **1**, **3**, and **5d** were determined and confirmed by X-ray single-crystal diffraction analysis. The data of complex **1** (Figure 1) structurally support the assumption of a strong electronic interaction between the amino group and the carbene center; a short C6–N1 bond length [1.306(5) Å] is observed together with a comparatively long W–C6 bond length of 2.249(4) Å.

The structure of complex **3** (Figure 2) displays a coplanar arrangement of the Cp^{Fc}- and the PCN-ring system. The ferrocenyl and the organic substituent at phosphorus display a mutual *trans* configuration at the three-membered ring, thus minimizing steric repulsion. The P–N bond length is 1.803(3) Å; such long bonds are typical for 2*H*-azaphosphirene complexes.[8]

Complex **5d** (Figure 3) features an almost planar P-heterocycle (mean deviation 0.026 Å). The interplanar angle between the best plane of the P-heterocycle and the Cp^{Fc} plane is 21.6°. Interestingly, the piperidyl substituent is not

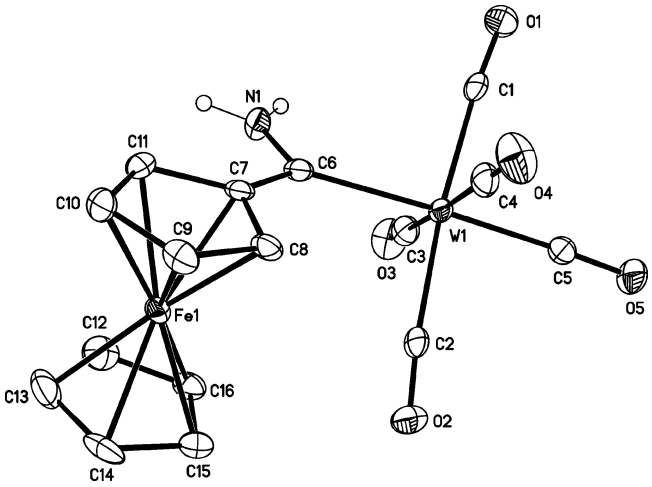


Figure 1. Molecular structure of complex **1** in the crystal (50% probability level, Cp hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: C6–N1 1.306(5), C6–C7 1.489(5), W1–C6 2.249(4), W1–C5 1.986(4); W1–C6–N1 120.6(3), W1–C6–C7 126.7(3), N1–C6–C7 112.7(4).

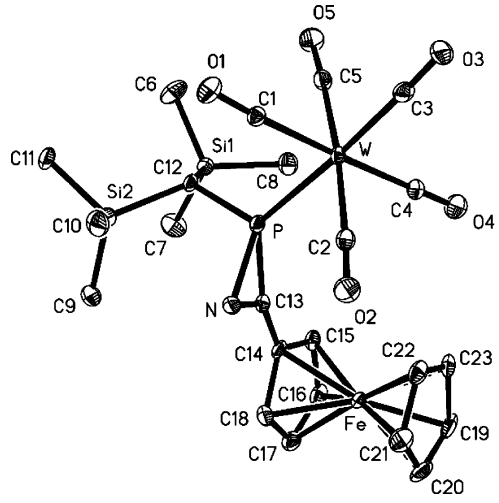


Figure 2. Molecular structure of complex **3** in the crystal (50% probability level, hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: W–P 2.487(10), W–C3 2.015(4), P–C13 1.7634, P–N 1.803(3), P–C12 1.823(4), C13–N 1.285(5), C13–C14 1.44(5); N–P–C13 42.23(18), P–N–C13 67.2(2), P–C13–N 70.5(2).

fully involved in π conjugation with the C=N bond, as indicated by the distances C7–N3 1.349(2) Å versus C7–N1 1.304(2) Å.

By cyclic voltammetry, reversible one-electron redox processes were observed for all complexes **1**, **3**, and **5a**–**d**, with decreasing half-wave potentials in the order **1** >> **3** > **5a** > **5b** > **5c** >> 5**d** (Table 3). Under the assumption that oxidation takes place at the ferrocenyl moiety, it can be concluded that the carbene complex unit in complex **1** has by far the strongest electron-withdrawing effect within this series, followed by the 2*H*-azaphosphirene complex unit (complex **3**). Whereas the $E_{1/2}$ values of 2*H*-1,4,2-diazaphosphole complexes **5a**–**c** are in the same range, complex **5d** is the easiest to oxidize due to its substitution pattern.

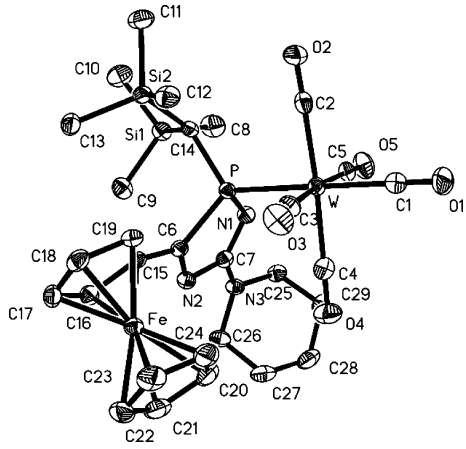


Figure 3. Molecular structure of complex **5d** in the crystal (50% probability level, hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: W–P 2.5326(5), W–C1 2.005(2), P–C6 1.8745(19), P–N1 1.6889(16), P–C14 1.8474(19), C6–N2 1.292(2), N2–C7 1.432(2), C7–N1 1.304(2), C7–N3 1.349(2), C13–C15 1.460(3); N1–P–C6 90.41(8), P–C6–N2 109.92(13), C6–N2–C7 109.58(16), N2–C7–N1 120.68(17), C7–N1–P 109.02(14), P–C6–C15 129.03(14), N1–C7–N3 123.03(18).

Table 3. $E_{1/2}$ values (vs. FcH/FcH^+, CH_2Cl_2, 100 mV/s) of complexes **1**, **3**, and **5a**–**d**.

	1	**3**	**5a**	**5b**	**5c**	**5d**
$E_{1/2}$ [mV]	406	265	244	239	236	195

Conclusions

The first synthesis of a *C*-ferrocenyl-substituted 2*H*-azaphosphirene complex **3** is described; it was obtained by the base-induced cascade reaction of carbene complex **1** with chlorophosphaalkene **2**, which first undergoes condensation followed by multiple rearrangement reactions. Furthermore, the ring expansion of complex **3** was investigated by using a variety of electronically different nitriles in the presence of substoichiometric amounts of ferrocenium hexafluorophosphate, which yielded regioselectively 2*H*-1,4,2-diazaphosphole complexes **5a**–**e**. As evidenced by the formation of unknown product **6**, the ferrocenyl substituent significantly effects the reaction pathway. Theoretical studies are currently underway to address this problem.

Experimental Section

General Procedures: All reactions and manipulations were carried out under an atmosphere of deoxygenated nitrogen or argon by using standard Schlenk techniques with conventional glassware. Solvents were dried according to standard procedures. Bis(trimethylsilyl)methylene(chloro)phosphane (**2**) was synthesized according to the method described in the literature.[15] NMR spectra were recorded with a Bruker AC-200 spectrometer (200 MHz for ^1H; 50.3 MHz for ^{13}C; 81.0 MHz for ^{31}P) or a Bruker Avance 300 spectrometer (300.13 MHz for ^1H; 75.5 MHz for ^{13}C; 121.5 MHz for ^{31}P) by using [D_6]benzene or [D]chloroform as solvent and internal secondary standard; shifts are given relative to external tetramethylsilane (^1H, ^{13}C) and 85% H_3PO_4 (^{31}P). Mass spectra were

recorded on a Finnigan MAT 8430 (70 eV) or a Kratos Concept 1H spectrometer (FAB+, *m*NBA); apart from *m*/*z* values of the molecule ions, only *m*/*z* values having intensities more than 10% are given. Infrared spectra were recorded with a Biorad FTIR 165 (selected data given) or a Bruker FTIR IFS113V spectrometer. UV/Vis spectra were recorded with a Shimadzu UV-1650 PC spectrometer. Cyclovoltammetric measurements were performed with a EG&G-Potentiostat/Galvanostat M273 with an Ag/AgCl reference electrode and 0.1 mol [*n*-Bu_4N]PF_6 [$E_{1/2}$ values are given in mV vs. $E_{1/2}$ (FcH/FcH^+), scanspeed: 100 mV/s]. Melting points were obtained with a Büchi 535 capillary apparatus or a Büchi apparatus Type S. The values are not corrected. Elemental analyses were performed with a Carlo Erba analytical gas chromatograph or an Elementar VarioEL instrument.

[Amino(ferrocenyl)carbene]pentacarbonyltungsten(0) (1): To a suspension of $W(CO)_6$ (5.3 g, 15.0 mmol) in Et_2O (100 mL) was added freshly prepared lithioferrocene (FcLi, 20 mmol)[18] in THF (20 mL) slowly at ambient temperature. Stirring of the reaction mixture for 2 h resulted in a red solution. After removing the solvent in vacuo (ca. 10^{-2} mbar), the brown residue was dissolved in CH_2Cl_2 (50 mL) and Et_3OBF_4[19] (3.8 g, 20.0 mmol) in CH_2Cl_2 (10 mL) was added at 0 °C, forming a red to violet colored solution of the ethoxycarbene complex. Upon treatment with ammonia gas at 0 °C, orange-red aminocarbene complex **1** was formed; the conversion was monitored by TLC (petroleum ether/Et_2O, 10:1). The product was separated and purified by column chromatography (SiO_2; 25 °C; petroleum ether/Et_2O, 1:1). Yield: 3.6 g (0.67 mmol, 45%). Orange solid. M.p. 141 °C. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 4.25 (s, 5 H, unsubst. Cp), 4.71 (t, 2 H, Cp-H^3,H^4), 4.74 (t, 2 H, Cp-H^2,H^5), 7.95 (br. s, 1 H, N*H*), 8.5 (br. s, 1 H, N*H*) ppm. ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 70.6 (s, Cp unsubst.), 70.9 (s, Cp-C^2,C^5), 73.6 (s, Cp-C^3,C^4), 88.6 (s, Cp-C^1), 198.9 [s, ^1J(W,C) = 124.9 Hz, *cis*-*C*O], 202.7 (s, *trans*-*C*O), 254.8 (s, W=*C*) ppm. IR (KBr): $\tilde{\nu}$ = 3438 (w), 3337 (w), 3268 (w), 2060 (m), 1973 (s), 1916 (s), 1900 (s) cm^{-1}. UV/Vis (MeCN): λ (log ε) = (4.6), 234 (4.85), 280 (3.9), 352 (3.87) nm. CV: $E_{1/2}$ = +265 mV. MS (EI, 70 eV, ^{184}W): *m*/*z* (%) = 537 (30) $[M]^+$, 481 (18) $[M - 2CO]^+$, 453 (23) $[M - 3CO]^+$, 425 (15) $[M - 4CO]^+$, 397(100) $[M - 5CO]^+$, 211 (20) $[FcCN]^+$, 121 (32) $[FeCp]^+$, 186 (28) $[FcH]^+$. Suitable orange single crystals of **1** were obtained from concentrated Et_2O solution upon decreasing the temperature from ambient temperature to +4 °C. Data were collected with a Nonius KappaCCD diffractometer at 123(2) K by using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). The structure was solved by Patterson methods (SHELXS-97)[20] and refined by full-matrix least-squares on F^2 (SHELXL-97).[20] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were localized by electron density determination and refined by using a riding model [H(N) were refined free]. A semiempirical absorption correction was carried out from equivalents (min./max. transmissions = 0.54925/0.33758). $C_{16}H_{11}FeNO_5W$; crystal size 0.20 × 0.10 × 0.05 mm, monoclinic, $P2_1/n$, a = 11.4002(2) Å, b = 10.9032(2) Å, c = 13.7675 (2) Å, β = 107.111(1)°, V = 1635.53(5) Å^3, Z = 4, $\rho_{calcd.}$ = 2.181 Mg m^{-3}, $2\theta_{max}$ = 55°, collected (independent) reflections = 18827 (3687), R_{int} = 0. 0710, μ = 7.939 mm^{-1}, 223 refined parameters, 2 restraints, R_1 [for $I > 2\sigma(I)$] = 0. 0295, wR_2 (for all data) = 0.0680, max./min. residual electron density = 1.810/–3.353 e Å^{-3}.

{2-[Bis(trimethylsilyl)methyl]-3-ferrocenyl-2*H*-azaphosphirene-κ*P*}-pentacarbonyltungsten(0) (3): Complex **1** (2.0 g, 3.70 mmol) and chlorophosphaalkene **2** (0.84 g, 3.75 mmol) were dissolved in Et_2O (45 mL). After adding NEt_3 (16 mL, excess) the red solution was stirred at ambient temperature for 42 h; the end of the reaction was established by ^{31}P{^{1}H} NMR spectroscopy. Triethylammonium chloride was filtered off, and the solvent was removed in vacuo (ca. 10^{-2} mbar). The product was separated and purified by column chromatography (SiO_2; –20 °C; petroleum ether/Et_2O, 95:5). Yield: 1.3 g (1.81 mmol, 49%). Orange solid. M.p. 101 °C. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 0.08 [s, 9 H, Si(CH_3)$_3$], 0.17 [s, 9 H, Si(CH_3)$_3$], 0.57 (d, 1 H, C*H*), 4.31 (s, 5 H, unsubst. Cp), 4.63 (m, 2 H, Cp-H^3,H^4), 4.76 (m, 2 H, Cp-H^2,H^5) ppm. ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 1.2 [d, ^3J(P,C) = 2.8 Hz, Si(*C*H_3)$_3$], 2.1 [d, ^3J(P,C) = 3.8 Hz, Si(*C*H_3)$_3$], 28.6 [d, ^1J(P,C) = 23.5 Hz, *C*H], 68.7 [d, ^2J(P,C) = 17.7 Hz Cp-*C*1], 70.31 (s, Cp unsubst.) 70.56 [d, ^3J(P,C) = 6.8 Hz, Cp-C^2,C^5], 71.8 [d, ^3J(P,C) = 39.8 Hz Cp-C^3,C^4], 192.5 [d, ^2J(P,C) = 3.4 Hz, P-*C*=N], 196.2 [d, ^2J(P,C) = 9.0 Hz, *cis*-*C*O], 197.7 [d, ^2J(P,C) = 35.8 Hz, *trans*-*C*O] ppm. ^{31}P{^{1}H} NMR (81.0 MHz, 25 °C, $CDCl_3$): δ = –115.3 [s_{sat}, ^1J(W,P) = 299.4 Hz] ppm. IR (KBr): $\tilde{\nu}$ = 3439 (w), 3446 (w), 2958 (w), 2925 (w), 2900 (w), 1989 (m), 2072 (m), 1939 (vs), 1927 (s) cm^{-1}. UV/Vis (MeCN): λ (log ε) = (4.74), 232 (4.83), 352 (4.6), 280 (4.14), 470 (2.97) nm. CV: $E_{1/2}$ = +406 mV. MS (EI, 70 eV, ^{184}W): *m*/*z* (%) = 725.0 (0.5) $[M]^+$, 514.0 (5) $[M - FcCN]^+$, 486.0 (25) $[M - FcCN - CO]^+$, 430.0 (5) $[M - FcCN - 3CO]^+$, 402.0 (5) $[M - FcCN - 4CO]^+$, 357.0 (15) $[M - FcCN - 3CO - SiMe_3]^+$, 211.0 (100) $[FcCN]^+$, 121.0 (35) $[FeCp]^+$, 73.1 (20) $[Si(Me_3)_3]^+$. Suitable orange single crystals of **3** were obtained from a concentrated Et_2O solution upon decreasing the temperature from ambient temperature to +4 °C. Data were collected with a Bruker SMART 1000 CCD diffractometer at 133(2) K by using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). The structure was solved by Patterson methods and refined by full-matrix least-squares on F^2 (SHELXL-97).[20] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included isotropically by using a riding model or rigid methyl groups. Semiempirical absorption correction was carried out from equivalents (min./max. transmissions = 0.928/0.580). $C_{23}H_{28}FeNO_5PSi_2W$; orange-red tablet 0.3 × 0.3 × 0.2 mm, triclinic, $P\bar{1}$, a = 9.2863(6) Å, b = 11.2144(7) Å, c = 13.9400(9) Å, α = 82.903(3)°, β = 87.191(3)°, γ = 74.933(3)°, V = 1390.85(15) Å^3, Z = 2, $\rho_{calcd.}$ = 1.732 Mg m^{-3}, $2\theta_{max}$ = 56.6°, collected (independent) reflections = 19360 (6875), R_{int} = 0. 0353, μ = 4.83 mm^{-1}, 313 refined parameters, R_1 [for $I > 2\sigma(I)$] = 0. 0361, wR_2 (for all data) = 0.0985, max./min. residual electron density = 3.66/–3.27 e Å^{-3}.

General Procedure for the Synthesis of Complexes 5a–e: To a solution of 2*H*-azaphosphirene complex **3** (362 mg, 0.5 mmol) in CH_2Cl_2 (3 mL) was added the appropriate nitrile (**4a**: 54.5 mg, 0.5 mmol; **4b**: 54.6 mg, 0.5 mmol; **4c**: 54.6 mg, 0.5 mmol; **4d**: 55.1 mg, 0.5 mmol; **4e**: 36 μL, 1.1 mmol) and ferrocenium hexafluorophosphate (30.0 mg, 0.1 mmol) sequentially. The dark red reaction mixture was stirred for the appropriate time (**4a**: 16 h, **4b**: 2 h, **4c**: 18 h, **4d**: 5 d, **4e**: 4 h) at ambient temperature, and the solution then turned violet [reaction monitoring by ^{31}P(^{1}H) NMR spectroscopy]. After the solvent was removed in vacuo (ca. 10^{-2} mbar), the products were separated and purified by column chromatography [SiO_2; –30 °C; *n*-pentane (**5a**,**c**) or *n*-pentane/Et_2O, 95:5 (**5b**,**d**,**e**)]; despite several attempts, trace amounts of unknown product **6** remained in most complexes **5a**–**e**.

{2-[Bis(trimethylsilyl)methyl]-3-ferrocenyl-5-phenyl-2*H*-1,4,2-diazaphosphole-κ*P*}pentacarbonyltungsten(0) (5a): Yield: 211 mg (0.25 mmol, 51%). Violet solid. M.p. 94 °C. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 0.05 [s, 9 H, Si(CH_3)$_3$], 0.28 [s, 9 H, Si(CH_3)$_3$], 1.26 [d, ^2J(P,H) = 10.2 Hz, 1 H, C*H*], 4.28 (s, 5 H, unsubst. Cp), 4.6 (d, 2 H, Cp-H^3,H^4), 5.06 (d, 2 H, Cp-H^2,H^5), 7.5 (mc, 3 H, aryl-*H*), 8.4 (mc, 2 H, aryl-*H*) ppm. ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 3.1 [d, ^3J(P,C) = 2.7 Hz, Si(*C*H_3)$_3$], 3.2 [d, ^3J(P,C) = 2.9 Hz, Si(*C*H_3)$_3$], 19.8 [d, ^1J(P,C) = 9.2 Hz, *C*H-

($SiMe_3$)$_2$], 70.4 (s, Cp-*C*5), 70.8 (s, Cp unsubst.), 71.6 (s,Cp-C^4), 71.7 (s, Cp-C^3), 75.2 [d, ^4J(P,C) = 1.9 Hz, Cp-C^2], 79.0 [d, ^2J(P,C) = 29.5 Hz, Cp-C^1], 128.7 (s, phenyl-C^3,C^5), 129.1 [d, ^3J(P,C) = 33.6 Hz, phenyl-C^1], 130.7 (s, phenyl-C^2,C^6), 132.1 (s, phenyl-C^4), 168.1 [d, ^2J(P,C) = 5.3 Hz, PN*C*], 197.1 [d, ^2J(P,C) = 6.1 Hz, *cis*-*C*O], 198.5 [d, ^2J(P,C) = 22.3 Hz, *trans*-*C*O], 208.5 [d, ^1J(P,C) = 24.3 Hz, P*C*N] ppm. ^{31}P{^{1}H} NMR (81.0 MHz, $CDCl_3$, 25 °C): δ = 114.7 [s_{sat}, ^1J(W,P) = 228.7 Hz] ppm. IR (KBr): $\tilde{\nu}$ = 2070 (m), 1989 (m), 1980 (m), 1922 (m) cm^{-1}. UV/Vis (MeCN): λ (log ε) = 198 (4.85), 232 (4.81), 290 (4.18), 324 (4.02), 392 (3.51), 560 (3.37) nm. CV: $E_{1/2}$ = +244 mV. MS (EI, 70 eV, ^{184}W): *m*/*z* (%) = 828 (30) $[M]^+$, 772 (98) $[M - 2CO]^+$, 744 (18) $[M - 3CO]^+$, 688 (28) $[M - 5CO]^+$, 504 (38) $[M - W(CO)_5]^+$, 401 (7) [M – 5CO – PhCN]$^+$, 73 (100) $[SiMe_3]^+$.

{2-[Bis(trimethylsilyl)methyl]-3-ferrocenyl-5-(thien-2-yl)-2*H*-1,4,2-diazaphosphole-κ*P*}pentacarbonyltungsten(0) (5b): Yield: 240 mg (0.29 mmol, 57%). Violet solid. M.p. 90 °C. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 0.05 [s, 9 H, Si(CH_3)$_3$], 0.28 [s, 9 H, Si(CH_3)$_3$], 1.16 (d, 1 H, CH,) 4.28 (s, 5 H, unsubst. Cp), 4.6 (d, 2 H, Cp-H^3,H^4), 5.06 (d, 2 H, Cp-H^2,H^5 subst. Cp), 7.2 (mc, 1 H thienyl-CH^4), 7.6 [d, ^3J(H,H) = 3.0 Hz, 1 H, thienyl-CH^5], 8.0 [mc, ^3J(H,H) = 3 Hz, 1 H, thienyl-CH^3] ppm. ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 3.1 [d, ^3J(P,C) = 2.7 Hz, Si(*C*H$_3$)$_3$], 3.2 [d, ^3J(P,C) = 2.8 Hz, Si(*C*H$_3$)$_3$], 20.5 [d, ^1J(P,C) = 9.7 Hz, *C*H-($SiMe_3$)$_2$], 70.3 (s, Cp-C^4), 70.8 (s, Cp unsubst.), 71.7 (s, Cp-C^5), 71.8 (s, Cp-C^3), 75.4 [d, ^4J(P,C) = 1.9 Hz, Cp-C^2], 78.7 [d, ^2J(P,C) = 28.8 Hz, Cp-C^1], 128.4 (s, thienyl-C^3), 132.9 (s, thienyl-C^5), 133.3 (s, thienyl-C^4), 138.4 [d, ^3J(P,C) = 14.3 Hz, thienyl-C^2], 163.4 [d, ^2J(P,C) = 4.5 Hz, PN*C*], 197.0 [d, ^2J(P,C) = 6.0 Hz, *cis*-*C*O], 198.0 [d, ^2J(P,C) = 22 Hz, *trans*-*C*O], 208.6 [d, ^1J(P,C) = 24 Hz, P*C*N] ppm. ^{31}P{^{1}H} NMR (81.0 MHz, $CDCl_3$, 25 °C): δ = 114.7 [s_{sat}, ^1J(W,P) = 230.5 Hz] ppm. IR (KBr): $\tilde{\nu}$ = 2071 (m), 1983 (m), 1947 (s), 1936 (s), 1921 (vs), 1910 (vs) cm^{-1}. UV/Vis (MeCN): λ (log ε) = 202 (4.7), 232 (4.7), 320 (4.1), 360 (3.8), 390 (3.5), 452 (3.1), 560 (3.26) nm. CV: $E_{1/2}$ = +239 mV. MS (EI, 70 eV, ^{184}W): *m*/*z* (%) = 834 (17) $[M]^+$, 806 (10) $[M - CO]^+$, 778 (26) $[M - 2CO]^+$, 750 (17) $[M - 3CO]^+$, 722 (20) $[M - 4CO]^+$, 694 (18) $[M - 5CO]^+$, 510 (32) $[M - W(CO)_5]^+$, 73 (100) $[SiMe_3]^+$.

{2-[Bis(trimethylsilyl)methyl]-3-ferrocenyl-5-(thien-3-yl)-2*H*-1,4,2-diazaphosphole-κ*P*}pentacarbonyltungsten(0) (5c): Yield: 190 mg (0.23 mmol, 46%). Black violet solid. M.p. 112 °C. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 0.04 [s, 9 H, Si(CH_3)$_3$], 0.27 [s, 9 H, Si(CH_3)$_3$], 1.16 (d, 1 H, C*H*), 4.27 (s, 5 H, unsubst. Cp), 4.63 [d, ^3J(H,H) = 2.1 Hz, 2 H, Cp-H^3,H^4], 5.06 (s, 2 H,Cp-H^2,H^5), 7.4 (mc, 1 H, thienyl-H^4), 7.8 [d, ^3J(H,H) = 3.0 Hz, 1 H, thienyl-H^5], 8.4 [mc, ^3J(H,H) = 4.5 Hz, 1 H, thienyl-H^2] ppm. ^{13}C{^{1}H} NMR (50.3 MHz, 25 °C, C_6D_6): δ = 3.1 [d, ^3J(P,C) = 2.6 Hz, Si-(*C*H$_3$)$_3$], 3.2 [d, ^3J(P,C) = 2.6 Hz, Si(*C*H$_3$)$_3$], 20.0 [d, ^1J(P,C) = 9.4 Hz, *C*H(SiMe$_3$)$_2$], 70.3 (s, Cp-C^4), 70.8 (s, Cp unsubst.), 71.7 (s, Cp-C^5), 71.8 (s, Cp-C^3), 75.2 [d, ^3J(P,C) = 1.9 Hz, Cp-C^2], 78.8 [d, ^2J(P,C) = 29.5 Hz, Cp-C^1], 126.5 (s, thienyl-C^3), 128.3 (s, thienyl-C^5), 133.3 (s, thienyl-C^4), 137.3 [d, ^3J(P,C) = 13.1 Hz, thienyl-C^2], 164.0 [d, ^2J(P,C) = 5.2 Hz, PN*C*], 197.0 [d, ^2J(P,C) = 6.5 Hz, ^2J(W,C) = 125.8 Hz, *cis*-*C*O], 198.6 [d, ^2J(P,C) = 22.3 Hz, *trans*-*C*O], 208.0 [d, ^1J(P,C) = 24.0 Hz, P*C*N] ppm ^{31}P{^{1}H} NMR (81.0 MHz, C_6D_6, 25 °C): δ = 113.4 [s_{sat}, ^1J(P, W) = 230.4 Hz] ppm. IR (KBr): $\tilde{\nu}$ = 2071 (m), 1989 (m), 1936 (s), 1922 (vs), 1908 (s) nm. UV/Vis (MeCN): λ (log ε) = 202 (4.81), 230 (4.82), 278 (4.22), 302 (4.19), 324 (4.13), 370 (3.68), 398 (3.60), 568 (3.42) nm. CV: $E_{1/2}$ = +236 mV. MS (EI, 70 eV, ^{184}W): *m*/*z* (%) = 834 (32) $[M]^+$, 806 (17) $[M - CO]^+$, 778 (89) $[M - 2CO]^+$, 750 (23) $[M - 3CO]^+$, 722 (18) $[M - 4CO]^+$, 694 (38) $[M - 5CO]^+$, 510 (32) $[M - W(CO)_5]^+$, 73 (100) $[SiMe_3]^+$.

{2-[Bis(trimethylsilyl)methyl]-3-ferrocenyl-5-(1-piperidinyl)-2*H*-1,4,2-diazaphosphole-κ*P*}pentacarbonyltungsten(0) (5d): Yield: 225 mg (0.27 mmol, 54%). Red violet solid. M.p. 105 °C. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = –0.03 [s, 9 H, Si(CH_3)$_3$], 0.24 [s, 9 H, Si(CH_3)$_3$], 1.16 (d, 1 H, C*H*), 1.67 [br. s, 6 H, N(CH_2CH_2CH_2)], 3.8 (br. s, 2 H, NCH_2CH$_2$CH$_2$), 4.05 (br. s, 2 H, NCH_2CH$_2$CH$_2$) 4.21 (s, 5 H, unsubst. Cp), 4.5 (d, 2 H, Cp-H^3,H^4), 4.9 (d, 2 H, Cp-H^2,H^5) ppm. ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 3.1 [d, ^3J(P,C) = 2.5 Hz, Si(*C*H$_3$)$_3$], 3.3 [d, ^3J(P,C) = 2.5 Hz, Si(*C*H$_3$)$_3$], 24.0 [d, ^1J(P,C) = 10.7 Hz, C*H*-($SiMe_3$)$_2$], 24.7 (br. s, N*C*H$_2$*C*H$_2$*C*H$_2$), 25.7 (br. s, N*C*H$_2$CH$_2$CH$_2$), 26.7 (br. s, N*C*H$_2$CH$_2$CH$_2$), 46.8 (br. s, N*C*H$_2$CH$_2$CH$_2$), 47.3 (br. s, N*C*H$_2$CH$_2$CH$_2$), 70.0 (s, Cp-C^5), 70.5 (s, Cp unsubst.), 70.8 (s, Cp-C^3), 71.1 (s, Cp-C^4), 75.1 (s, Cp-C^2), 79.2 [d, ^2J(P,C) = 26.6 Hz, Cp-C^1], 163.4 (s, PN*C*), 198.0 [d, ^2J(P,C) = 76.7 Hz, *cis*-*C*O], 199.8 [d, ^2J(P,C) = 21.9 Hz, *trans*-*C*O], 205.6 [d, ^1J(P,C) = 26.4 Hz, P*C*N] ppm. ^{31}P{^{1}H} NMR (81.0 MHz, $CDCl_3$, 25 °C): δ = 105.0 [s_{sat}, ^1J(W,P) = 240.5 Hz] ppm. IR (KBr): $\tilde{\nu}$ = (m), 1967 (m), 1926 (vs), 1901 (vs), 1581 (m) cm^{-1}. UV/Vis (MeCN): λ (log ε) = 200 (4.79), 230 (4.79), 302 (4.09), 356 (3.77), 430 (3.22), 526 (3.22) nm. CV: $E_{1/2}$ = +195 mV. MS (EI, 70 eV, ^{184}W): *m*/*z* (%):835 (10) $[M]^+$, 807 (42) $[M - CO]^+$, 779 (28) $[M - 2CO]^+$, 751 (30) $[M - 3CO]^+$, 723 (98) $[M - 4CO]^+$, 695 (32) $[M - 5CO]^+$, 511 (32) $[M - W(CO)_5]^+$, 73 (100) [$SiMe_3^+$]. Suitable red-purple single crystals of **5d** were obtained from a concentrated Et_2O solution upon decreasing the temperature from ambient temperature to +4 °C. Experimental details as for **3**. Min./max. transmissions = 0.928/0.678. $C_{29}H_{38}FeN_3O_5PSi_2W$; red tablet 0.3 × 0.2 × 0.07 mm, monoclinic, $P2_1/c$, a = 12.5714(8) Å, b = 12.2780(8) Å, c = 22.2434(14) Å, β = 104.515(3)°, V = 3323.7(4) Å^3, Z = 4, $\rho_{calcd.}$ = 1.670 Mg m^{-3}, $2\theta_{max}$ = 56.6°, collected (independent) reflections = 60881 (8250), R_{int} = 0. 0327, μ = 4.06 mm^{-1}, 385 refined parameters, R_1 [for $I > 2\sigma(I)$] = 0. 0177, wR_2 (for all data) = 0.0433, max./min. residual electron density = 1.01/–0.33 e Å^{-3}.

{2-[Bis(trimethylsilyl)methyl]-3-ferrocenyl-5-methyl-2*H*-1,4,2-diazaphosphole-κ*P*}pentacarbonyltungsten(0) (5e): Yield: 198 mg (0.26 mmol, 52%). Violet oil. ^{1}H NMR (300.1 MHz, C_6D_6, 25 °C): δ = 0.00 [s, 9 H, Si(CH_3)$_3$], 0.26 [s, 9 H, Si(CH_3)$_3$], 1.14 [d, ^2J(P,H) = 9.9 Hz, 1 H, C*H*], 2.4 (s, NCH_3), 4.01 (s, 5 H, unsubst. Cp), 4.23 (m, 2 H, Cp-H^3,H^4), 5.01 (m, 2 H, Cp-H^2,H^5) ppm. ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6, 25 °C): δ = 1.8 [d, ^3J(P,C) = 2.6 Hz, Si(*C*H$_3$)$_3$], 2.1 [d, ^3J(P,C) = 3.2 Hz, Si(*C*H$_3$)$_3$], 17.7 [d, ^1J(P,C) = 9.1 Hz, C*H*-($SiMe_3$)$_2$], 20.6 [d, ^3J(P,C) = 11 Hz, N*C*H$_3$], 69.7 (s, unsubst. Cp), 69.8 (s, Cp-C^5), 70.7 [d, ^4J(P,C) = 1.9 Hz, Cp-C^3/C^4], 73.8 [d, ^3J(P,C) = 1.9 Hz, Cp-C^2], 77.2 [d, ^2J(P,C) = 29.1 Hz, subst. Cp-C^1], 171.5 [d, ^2J(P,C) = 7.1 Hz, PN*C*], 196.3 [d, ^2J(P,C) = 6.4 Hz, ^1J(W,C) = 126.8 Hz, *cis*-*C*O], 197.2 [d, ^2J(P,C) = 22.0 Hz, *trans*-*C*O], 207.2 [d, ^1J(P,C) = 23.9 Hz, P*C*N] ppm. ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6, 25 °C): δ = 111.9 [s_{sat}, ^1J(W,P) = 230.2 Hz] ppm. MS (EI, 70 eV, ^{184}W): *m*/*z* (%) = 766 (10) $[M]^+$, 710 (14) $[M - 2CO]^+$, 626 (5) $[M - 5CO]^+$, 442 (100) [M – 5CO – W]$^+$, 190 (50) [M – 5CO – W – $FeC_3H_3N_2$]$^+$, 73 (67) $[C_3H_9Si]^+$.

CCDC-697107 (for **1**), -697334 (for **3**), and -697333 (for **5d**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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