Developing click reactions of a 3-ferrocenyl-2*H*-azaphosphirene complex†

Rainer Streubel,*[a] Janaina Marinas Pérez,[a] Holger Helten,[a] Jörg Daniels[a] and Martin Nieger[b]

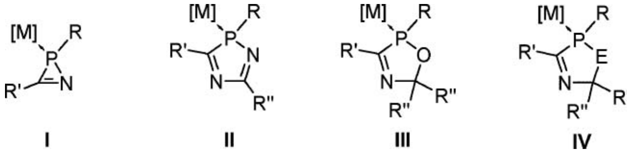
Received 25th June 2010, Accepted 23rd September 2010
DOI: 10.1039/c0dt00730g

Atom efficient reactions of 3-ferrocenyl-2*H*-azaphosphirene complex **1** using a newly developed acid/base ring expansion protocol are presented. Consecutive reaction of **1** in the presence of dimethyl cyanamide with triflic acid and triethylamine yielded the selective formation of 2*H*-1,4,2-diazaphosphole complex **3**. The same protocol using acetone, benzaldehyde and ferrocenyl aldehyde afforded 1,3,5-oxazaphosphol-3-ene complexes **4**, **5a,b** and **6a,b**, the latter as mixtures of diastereomers, which could be separated. Apart from NMR, IR and UV/vis spectroscopic data, the single-crystal X-ray structures of complexes **3**, **4** and **6a** are discussed.

Introduction

The efficient construction of five-membered N-heterocycles such as triazoles using click reactions[1] has received increasing interest during the last years since it usually follows a facile and reliable protocol, *e.g.*, [3+2] cycloaddition of azides and alkynes, and thus can be applied to various fields of research.[2]

Recently, a novel and facile methodology for the ring expansion of various three-membered P-heterocyclic ligands in the coordination sphere of group 6 transition metals such as tungsten was developed. For example, ring expansion of 2*H*-azaphosphirene complexes[3] **I** leading to 2*H*-1,4,2-diazaphosphole complexes **II**[4] (Scheme 1) was achieved *via* formal insertion of a nitrile into the P–N bond of **I** using trifluoromethane sulfonic acid (CF_3SO_3H; hereafter referred to as triflic acid or TfOH) and, subsequently, a nitrogen base such as triethylamine.



Scheme 1 2*H*-Azaphosphirene complexes **I** and ring expansion products **II–IV** ([M] denote a $M(CO)_5$ moiety (M = Cr, Mo, W), R denote common organic substituents, E denote sulfur and/or a NR group).

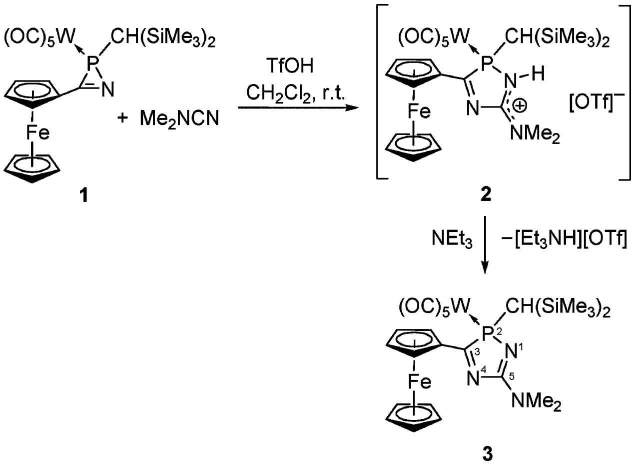
We recently demonstrated that the new concept can also be applied to the atom efficient synthesis of a 2,3-dihydro-1,3-azaphosphete and a 3*H*-1,3-azaphosphole complex *via* insertion of an isonitrile or an alkyne, respectively.[5] Furthermore, we showed that it can easily be extended to oxaphosphirane[6] and azaphosphiridine[7] complex chemistry, thus establishing this efficient and modular method as new version of click chemistry in the field of phosphorus heterocyclic chemistry for the first time. Mechanistic studies revealed that the heteroatom (N or O) of the respective ring system is protonated in the first reaction step,[4–8] which leads to ring opening in the cases of 2*H*-azaphosphirene[4] and oxaphosphirane complexes.[6,8] In the case of azaphosphiridine complexes the protonated ring does not open up spontaneously, but the P–N bond is activated towards the attack of electron-rich nitriles.[7] As we recently entered the attractive field of redox-active complexes possessing one or two ferrocenyl groups[9] in order to investigate redox-switchable phosphorus heterocyclic ligand systems, we decided to examine the applicability of this methodology in this research area.

Here, reactions of a 3-ferrocenyl-2*H*-azaphosphirene complex derivative **I** with a nitrile (to give **II**) and with ketones and aldehydes (to give **III**) are presented. In all cases an acid/base protocol was applied to achieve the ring expansion of **I** thus providing facile access to otherwise hard to access 1,3,5-oxazaphosphol-3-ene complexes **III**.

Results and discussion

Insertion of a nitrile

When triflic acid was added to a solution of 2*H*-azaphosphirene complex **1**[9] in the presence of dimethyl cyanamide the initially red colored reaction mixture turned immediately deep blue (Scheme 2)



Scheme 2 Synthesis of 2*H*-1,4,2-diazaphosphole complex **3**.

---

[a] *Institut für Anorganische Chemie der Rheinischen Friedrich-Wilhelms-Universität Bonn, Gerhard-Domagk-Str., 1, 53121, Bonn, Germany. E-mail: r.streubel@uni-bonn.de; Fax: +49 228 739616; Tel: +49 228 735345*
[b] *Laboratory of Inorganic Chemistry, Department of Chemistry University of Helsinki, P.O. Box 55 (A.I. Virtasen aukio 1), FIN-00014, Finland*

† CCDC reference numbers 777798 (**3**), 777321 (**4**) and 777322 (**6a**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt00730g

and the formation of complex **2** was evidenced by ^{31}P NMR spectroscopy in almost quantitative yield; **2** showed a resonance at 102.6 ppm ($|^{1}J_{\mathrm{WP}}|$ = 253.0 Hz) with a phosphorus–proton coupling constant magnitude of 22.9 Hz, which is characteristic for N^1-protonated 2*H*-1,4,2-diazaphospholium complexes with an amidinium structural unit.[4] Upon subsequent addition of triethylamine the solution turned red again and 2*H*-1,4,2-diazaphosphole complex **3** was selectively and quantitatively formed. Complex **3** was purified by low-temperature column chromatography and unambiguously characterized by multinuclear NMR experiments, mass spectrometry, IR and UV/Vis spectroscopy and a single-crystal X-ray diffraction study (Fig. 1); the purity was examined by elemental analysis.

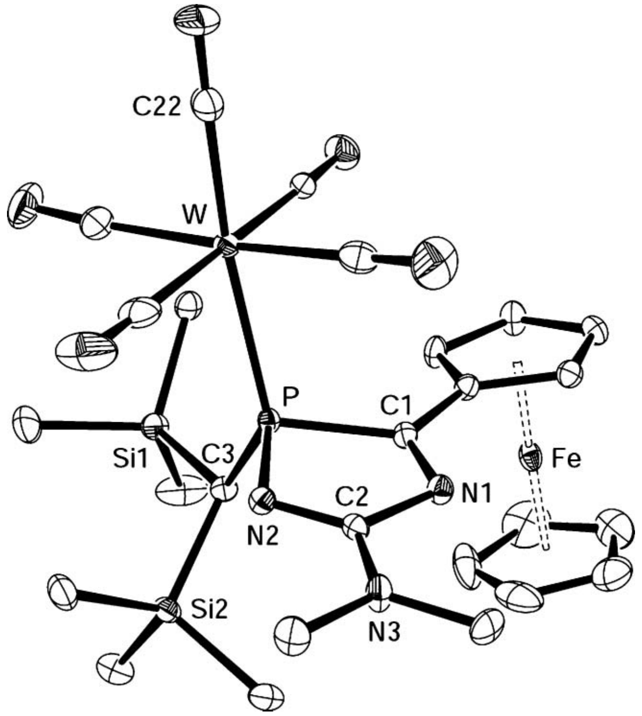


Fig. 1 Molecular structure of complex **3** in the crystal (hydrogen atoms omitted for clarity; displacement parameters drawn at 50% probability level). Selected bond lengths [Å] and angles [°]:W–C22 2.000(4), W–P 2.5359(8), P–N2 1.683(3), P–C1 1.859(3), C1–N1 1.292(4), C2–N2 1.307(4), C2–N3 1.337(4), C1–C12 1.452(4), N2–P–C1 90.74(13), P–C1–N1 110.7(2), C1–N1–C2 108.7(3), N1–C2–N2 120.5(3), C2–N2–P 109.0(2), N2–C2–N3 123.4(3).

Complex **3** displays a ^{31}P resonance at 106.5 ppm, thus being in the same range with the cationic complex **2**. Compared to the latter the tungsten–phosphorus coupling constant of **3** (241.6 Hz) is about 11 Hz smaller. While the ^{13}C resonance of the C^3 center appears at very low field (δ = 206.5) and exhibits a $|^{2+3}J_{\mathrm{PC}}|$ value of 26.8 Hz, the C^5 center resonates at considerably higher field (δ = 165.0) with no resolved coupling to phosphorus (see Scheme 2 for atom numbering). The NMe$_2$ group gives rise to two sets of distinctly different ^{1}H and ^{13}C resonances, thus pointing to a hindered rotation about the C^5–NMe$_2$ bond.

The C–O stretch vibration bands in the IR spectrum reflect the slightly perturbed C_{4v} symmetry of **3**. It shows a single, well separated band at 2071 cm^{-1} and another band with low intensity at 1991 cm^{-1}, which can be assigned to normal modes of local A_1 and B_1 symmetry, respectively. In the range of 1900–1950 cm^{-1} three very intense and partially overlapping bands appear, which are attributable to vibrations of local A_1 and E symmetry. Two bands according to C–N stretch vibrations were observed at 1602 and 1550 cm^{-1}.

The UV/Vis absorption spectrum of **3** shows a low-energy transition at 404 nm that we assign, on the basis of recently published results on related systems,[10] to a metal–diazaphosphole charge transfer (MLCT) process. A more intense π–π* absorption appears at $\lambda_{\max}$ = 296 nm. Another broad visible band appears at $\lambda_{\max}$ = 539 nm, which is assigned either to one or more nearly degenerate *d*–*d* transitions of Fe(II),[11] or to a metal–ligand charge transfer process (d_π–π*) occurring from the iron center to the acceptor-substituted cyclopendadienyl ring.[12,13] This assignment is in accordance with the theoretical treatment (model III) by Marder and coworkers.[12]

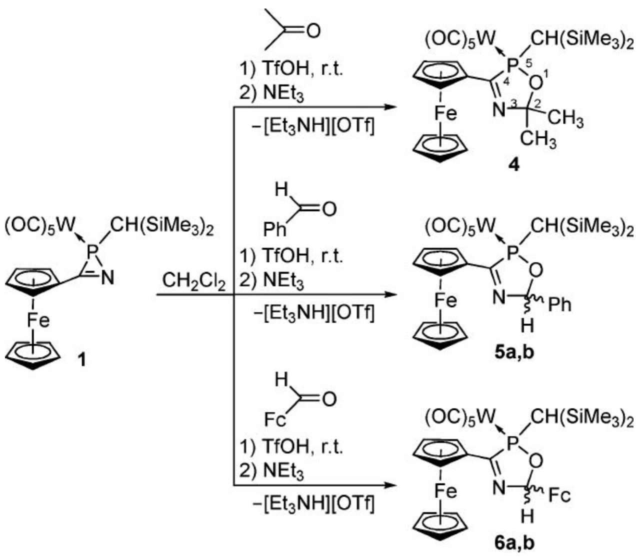
In the solid state the molecular structure of complex **3** shows an essentially planar 2*H*-1,4,2-diazaphosphole ring (mean deviation from least-squares plane: 0.023 Å), which is, to a large extent, coplanar arranged with the adjacent Cp ring of the ferrocenyl substituent. The twist angle with respect to least-squares planes is only 18.1°, and C^1 of the Fc goup (*i.e.* C12) deviates only by 0.007 Å from the regression plane of the heterocyclic system. The dimethylamino nitrogen atom is almost perfectly trigonal planar coordinated (Σ < 360.0°) and the plane of the NMe$_2$ group does not deviate significantly from the regression plane of the diazaphosphole ring (deviations from least-squares plane: 0.015 (N3), 0.058 (C10), and 0.032 Å (C11)).

Insertion of carbonyl compounds

A long-standing challenge in phosphorus chemistry is the insertion of unsaturated C–O π-systems into P–N bonds of free[14,15] and/or ligated phosphane derivatives,[16] *e.g.*, in the case of acyclic P(V) compounds carbon dioxide was successfully inserted to yield cyclic phosphacarbamates.[17] Despite these efforts, aldehyde insertion into P–N bonds of phosphazane derivatives had remained unsatisfactory as insertion was always accompanied by Arbuzov-related rearrangements to yield P^{V}-oxides, instead.[18] A recent report demonstrated that exocyclic P$^{\mathrm{III}}$–N bonds of cyclodiphosphazanes are even more reactive than endocyclic bonds.[19] Therefore, it became even more interesting to examine the versatility of the new acid-induced ring expansion protocol for ring expansion reactions of 3-ferrocenyl-2*H*-azaphosphirene complex **1** with ketones and aldehydes.

When complex **1** in the presence of acetone was treated with stoichiometric amounts of triflic acid in dichloromethane, 1,3,5-oxazaphosphol-3-ene complex **4** was selectively obtained in almost quantitative yield; in the case of benzaldehyde and ferrocenyl aldehyde the formation of two diasteroisomers occurred (ratio **5a,b** 63 : 37, **6a,b** 87 : 13) (Scheme 3), which were separated by low temperature chromatograpy, a standard procedure to prevent/minimize decomposition on the solid phase.

The ^{31}P{^{1}H} NMR resonances of complexes **4–6a,b** were observed in the narrow range of 132–142 ppm with tungsten–phosphorus coupling constant values of 269–281 Hz. In accordance with the observations reported by us beforehand,[20] it was observed that the isomer with the downfield-shifted resonance



Scheme 3 Synthesis of 1,3,5-oxazaphosphol-3-ene complexes **4–6**.

has a smaller coupling constant in each case. The diastereomers with ^{31}P resonances at higher field show larger couplings with the protons, which is increased in the case of the ferrocenyl derivatives **5a,b** and even more in **6a,b**. The ^{13}C{^{1}H} NMR spectra showed that the carbon atoms of the substituted cyclopentadienyl ring of the C^4-bonded ferrocenyl group are not equivalent. Instead of the expected combined signal for Cp–C$^{3/4}$ and Cp–C$^{2/5}$, all carbons have different values as a result of the hindered rotation about the C–C axis. One of the *ortho*-carbon atoms shows a $^3J_{PC}$ coupling and an unusually high chemical shift, while the other *ortho*-carbon atom does not.

The IR spectra of complexes **4–5,6a,b** show one strong band in the carbonyl range (~ 1940–1950 cm^{-1}) which is very broad, most probably being the result of the overlapping of two IR active bands, and another weak band at approximately 2070 cm^{-1} due to the distorted octahedral symmetry of the M(CO)$_5$ fragment.

The UV/vis spectra of the complexes **4–5**, **6a,b** show one λ_{max} at around 240 nm and shoulders that appear at λ_{max} values around 466 nm.

The X-ray single-crystal structures of **4** and **6a** unambiguously confirmed the deduced regiochemistry of the ring enlargement products (Fig. 2 and 3). In **4** the ferrocenyl substituent adopts a *cis* position to the W(CO)$_5$ group, which in **6a** is changed to *trans* and the two ferrocenyl substituents are *cis* oriented instead. The bond lengths are very similar in complexes **4** and **6a** and similar to those reported before.[20] The phosphorus–tungsten distance of complexes **4** and **6a** is shorter than that in **3**, but in the normal range for this kind of complexes. The heterocyclic rings in **4** and **6a** are essentially planar, in both cases the oxygen atom points out of the least-squares plane in an envelope configuration with a small dihedral angle of 6.4° (**4**) and 7.8° (**6a**). The magnitude of the torsion angles between the oxazaphospholene ring and the Cp-ring of the Fc moiety depends on the substituent. If there is only one Fc substituent the torsion angle is smaller (30.6° in complex **4**) than if there are two Fc groups (132.83° in complex **6a**), the torsion angle of the other Cp ring bonded to C2 is 171.7°.

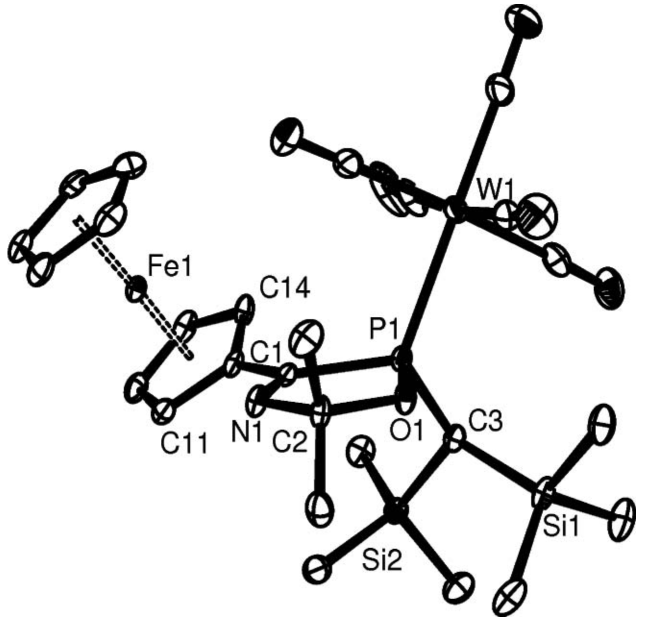


Fig. 2 Molecular structure of complex **4** in the crystal (hydrogen atoms omitted for clarity, displacement parameters drawn at 50% probability level). Selected bond lengths [Å] and angles [°]: W1–P1 2.5121(6), P1–O1 1.6296(14), P1–C1 1.882(2), C1–N1 1.285(2), C2–O1 1.464(2), C2–N1 1.446(3), C1–C10 1.480(3), O1–P1–C1 89.04(8), P1–C1–N1 111.45(16), C1–N1–C2 114.59(18), N1–C2–O1 108.88(15), C2–O1–P1 115.12(12).

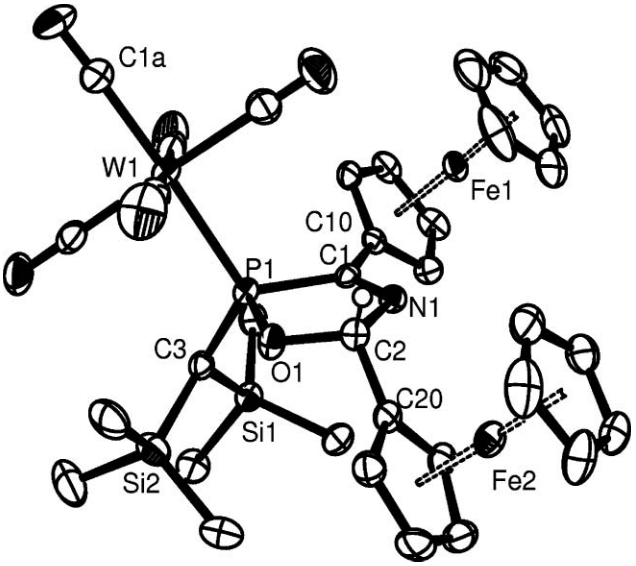


Fig. 3 Molecular structure of complex **6a** in the crystal (hydrogen atoms omitted for clarity, displacement parameters drawn at 50% probability level). Selected bond lengths [Å] and angles [°]: W1–P1 2.4973(7), P1–O1 1.6334(18), P1–C1 1.879(2), C1–N1 1.269(3), C2–O1 1.456(3), C2–N1 1.450(3), C1–C10 1.476(3), C2–C20 1.489(4), O1–P1–C1 88.75(10), P1–C1–N1 112.34(19), C1–N1–C2 113.5(2), N1–C2–O1 109.7(2), C2–O1–P1 114.06(14).

Conclusions

We have demonstrated that the newly developed acid/base protocol can be applied to the regioselective ring expansion of 3-ferrocenyl-2*H*-azaphosphirene complex **1**, thus enabling facile and efficient access to 2*H*-1,4,2-diazaphosphole complex **3** and 1,3,5-oxazaphosphol-3-ene complexes **4**, **5** and **6**. This also illustrates 1) that P-coordination successfully prevented formation of P^V-oxides in the case of **4–6**, which could have occurred otherwise, and 2) that this efficient and modular protocol emerges as a new powerful tool in phosphorus heterocyclic synthesis. Unfortunately, due to the sensitivity of the compounds, a little bit more elaborate purification is necessary than is typical in classic click reactions. Current investigations aim at broadening the application using other three-membered phosphorus heterocycles and various π-substrates.

Experimental

General procedures

All manipulations were carried out in an atmosphere of purified and dried argon using standard Schlenk techniques. Solvents were dried over sodium wire or CaH_2 (CH_2Cl_2) and distilled under argon. 2*H*-Azaphosphirene complex **1**[9] was prepared according to the method described in the literature. Triflic acid, dimethyl cyanamide, benzaldehyde and ferrocenecarbonitrile were purchased from Acros. Melting points were determined using a Büchi apparatus type S; the values are not corrected. Elemental analyses were performed by using an Elementar VarioEL instrument. UV/Vis absorption spectra were recorded on a Shimadzu UV-1650 PC spectrometer (λ = 190–1100 nm) from n-pentane solution at ambient temperature and IR spectra were recorded as KBr pellets using a Thermo Nicolet 380 FT-IR spectrometer. NMR data were recorded on a Bruker Avance 300 spectrometer at 30 °C using C_6D_6 or $CDCl_3$ as solvent and internal standard; coupling constants *J* are reported in Hz, chemical shifts in ppm relative to tetramethylsilane (^1H: 300.13, ^{13}C: 75.5, ^{29}Si: 59.6 MHz) and 85% H_3PO_4 (^{31}P: 121.5 MHz). Mass spectra were recorded on a Kratos Concept 1H (FAB+, *m*NBA) spectrometer or a MAT 95 XL Finnigan (EI, 70 eV, ^{184}W) spectrometer (selected data given).

Preparation of 2*H*-1,4,2-diazaphosphole and 1,3,5-oxazaphos-phol-3-ene complexes

[2-Bis(trimethylsilyl)methyl-5-dimethyl-amino-3-ferrocenyl-2*H*-1,4,2-diazaphosphole-κ*P*]pentacarbonyl-tungsten(0) (3). To a stirred solution of 2*H*-azaphosphirene complex **1** (1.400 g, 1.93 mmol) in CH_2Cl_2 (35 cm^3) were added consecutively dimethyl cyanamide (170 mm^3, 2.09 mmol) and triflic acid (170 mm^3, 1.93 mmol) at ambient temperature. The initially red colored solution turned deep blue. Subsequently, NEt_3 (270 mm^3, 1.92 mmol) was added at ambient temperature while the reaction mixture turned red again. After removement of all volatiles *in vacuo* (~1 Pa) the crude product was dissolved in petroleum ether, filtered through celite, and purified by column chromatography on silica (−35 °C, 3 × 10 cm) using petroleum ether/Et_2O (10 : 1) as eluent. Evaporation of the solvents of the first fraction (~1 Pa) yielded complex **3** (824 mg, 1.04 mmol, 54%) as a red solid; mp 147 °C (Found: C, 39.4; H, 4.3; N, 5.3. Calc. for $C_{26}H_{34}FeN_3O_5PSi_2W$: C, 39.3; H, 4.3; N, 5.3); λ_{max}/nm 520 (ε/dm³ mol⁻¹ cm⁻¹ 1 544), 385sh (4 772), 352 (6 036), 300 (11 978), 252sh (39 209), 231 (65 176), 214sh (51 186); ν_{max}/cm^{-1} 2962w, 2930 w, 2905 w and 2876 w (CH_3/CH), 2071 m, 1991 m, 1950 s, 1928 s and 1906 s (CO), 1602 m and 1550 w (CN); δ_H (C_6D_6) −0.02 (9 H, s_{sat}, J_{SiH} 6.5, J_{CH} 119.8, $SiMe_3$), 0.36 (9 H, s_{sat}, J_{SiH} 6.5, J_{CH} 119.1, $SiMe_3$), 1.30 (1 H, d, J_{PH} 7.9, C*H*($SiMe_3$)$_2$), 2.83 (3 H, s, NMe), 2.95 (3 H, s, NMe), 4.13 (5 H, s, Cp–CH unsubstit.), 4.21 (1 H, m_c, Cp–$C^{3/4}$–H), 4.24 (1 H, m_c, Cp–$C^{3/4}$H), 4.91 (1 H, m_c, Cp–$C^{2/5}$H), 5.10 (1 H, m_c, Cp–$C^{3/4}$H); δ_C (C_6D_6) 3.2 (d_{sat}, J_{PC} 2.3, J_{SiC} 52.5, $SiMe_3$), 3.6 (d_{sat}, J_{PC} 2.6, J_{SiC} 53.1, $SiMe_3$), 25.2 (d, J_{PC} 10.0, *C*H($SiMe_3$)$_2$), 37.6 (s, NMe), 37.6 (s, NMe), 70.5 (s, Cp–$C^{3/4}$), 71.0 (s, Cp–C unsubstit.), 71.1 (s, Cp–$C^{3/4}$), 71.5 (s, Cp–$C^{2/5}$), 75.6 (d, J_{PC} 1.9, Cp–$C^{2/5}$), 79.9 (d, J_{PC} 26.5, Cp–C^1), 165.0 (s, PNC), 198.5 (d_{sat}, J_{WC} 126.6, J_{PC} 6.4, CO_{cis}), 199.8 (d_{sat}, J_{WC} 143.5, J_{PC} 22.0, CO_{trans}), 206.5 (d, J_{PC} 26.8, PCN); δ_{Si} (C_6D_6) −0.1 (d_{sat}, J_{PSi} 7.3, J_{SiC} 52.5), 1.6 (d_{sat}, J_{PSi} 3.5, J_{SiC} 53.1); δ_P (C_6D_6) 106.5 (d_{sat}, J_{WP} 241.6, J_{PH} 7.9); MS (FAB+, *m*NBA): *m*/*z* 779 ($[M + H]^+$, 12%), 722 ($[M - 3CO]^+$, 30), 514 ($(OC)_5W(Me_3Si)PC(H)SiMe_3^+$, 24), 486 ($[M + H - CH(SiMe_3)_2 - C_{10}H_{15}]^+$, 33), 455 ($[M + H - W(CO)_5]^+$, 100), 191 ($Me_3SiP(H)C(H)SiMe_3^+$, 12).

[5-Bis(trimethylsilyl)methyl-2,2-dimethyl-4-ferrocenyl-1,3,5-oxazaphosphol-3-ene-κ*P*]pentacarbonyltungsten(0) (4). To a stirred solution of 0.310 g (0.41 mmol) of 2*H*-azaphosphirene complex **1** in 2 cm^3 CH_2Cl_2 were added consecutively 88 mm^3 (1.2 mmol) acetone and triflic acid (37 mm^3, 0.41 mmol) at ambient temperature. The initially red solution turned into a dark solution. Subsequently, NEt_3 (57 mm^3, 0.41 mmol) was added at ambient temperature while the reaction mixture turned red again. Then the solvent was removed *in vacuo* and the product purified by low temperature column chromatography (SiO_2, *h* = 10 cm, ϕ = 1 cm, *T* = −15 °C) and eluted with a gradient of petroleum ether/diethyl ether 100 to 95 : 5. The last fraction afforded the dark red product after recrystallization from pentane (193 mg, 60%) as a red solid; m.p. 118 °C (Found: C, 39.9; H, 4.6; N, 1.6. Calc. for $C_{26}H_{34}FeNO_6PSi_2W$: C, 39.9; H, 4.4; N, 1.7); λ_{max}/nm 465 (ε/dm³ mol⁻¹ cm⁻¹ 1 202), 239 (189 700); ν_{max}/cm^{-1} 2071 m, 1964 m, 1931 s (CO); δ_H (300 MHz, $CDCl_3$, $SiMe_4$) −0.11 (9 H, s, $SiMe_3$), 0.30 (9 H, s, $SiMe_3$), 1.30 (1 H, d, J_{PH} 2.26, C*H*($SiMe_3$)$_2$), 1.63 (3 H, s, Me), 1.73 (3 H, s, Me), 4.23 (5 H, s, Cp–CH unsubst.), 4.40 (2 H, m, Cp), 4.90 (1H, m, Cp), 4.95 (1 H, m, Cp–CH); δ_C (75 MHz, $CDCl_3$, $SiMe_4$) 1.9 (d_{sat}, J_{PC} 1.9, $SiMe_3$), 2.4 (d_{sat}, J_{PC} 2.6, $SiMe_3$), 27.5 (s, Me), 28.2 (s, Me), 36.7 (d, J_{PC} 13.6, *C*H($SiMe_3$)$_2$), 67.7 (s, Cp–$C^{3/4}$), 68.5 (s, Cp–C^5) 69.5 (s, Cp–C unsubst.), 74.5 (d, J_{PC} 2.9, Cp–C^2), 80.0 (d, J_{PC} 33.6, Cp–C^1), 111.3 (d, J_{PC} 4.2, POC), 171.0 (d, J_{PC} 15.8, PCN), 196.5 (d_{sat}, J_{PC} 7.4, CO_{cis}), 198.3 (d_{sat}, J_{PC} 26.2, CO_{trans}); δ_{Si} (60 MHz, $CDCl_3$, $SiMe_4$) −2.0 (d_{sat}, J_{PSi} 9.8), 0.0 (d_{sat}, J_{PSi} 4.3); δ_P (121.5 MHz, $CDCl_3$, H_3PO_4(85%)) 138.8 (d_{sat}, J_{WP} 275.9, J_{PH} 2.3); MS (EI, 70 eV, ^{184}W, 140 °C): *m*/*z* 783 (M^+, 60%), 727 ($[M - 2CO]^+$, 12), 699 ($[M - 3CO]^+$, 12%), 671 ($[M - 4CO]^+$, 18%) 6433 ($[M - 5CO]^+$, 73%), 459 ($[M - W(CO)_5]^+$, 58), 253($[FcCNCMe_2]^+$, 100).

[5-Bis(trimethylsilyl)methyl-2-phenyl-4-ferrocenyl-1,3,5-oxazaphosphol-3-ene-κ*P*]pentacarbonyltungsten(0) (5a,b). To a stirred solution of 0.310 g (0.41 mmol) of 2*H*-azaphosphirene complex **1** in 2 cm^3 CH_2Cl_2 were added consecutively 100 mm^3 (1.0 mmol) benzaldehyde and triflic acid (37 mm^3, 0.41 mmol) at ambient temperature. The initially red solution turned into a dark solution. Subsequently, NEt_3 (57 mm^3, 0.41 mmol) was added at ambient temperature while the reaction mixture turned red again. Then the solvent was removed *in vacuo* and the product purified by low temperature column chromatography (SiO_2, *h* = 10 cm,

ϕ = 1 cm, T = –15 °C) and eluted with a gradient of petroleum ether/diethyl ether 100 to 90 : 10. The second fraction yielded complex **5b**, and the third fraction yielded complex **5a** (194 mg, 57%) as a red solid; m.p. 120 °C (Found: C, 43.7; H, 4.5; N, 1.5. Calc. for $C_{30}H_{34}FeNO_6PSi_2W$: C,43.4; H, 4.1; N, 1.7); λ_{max}/nm 468 (ε/dm^3 mol^{-1} cm^{-1} 1 715), 246 (169 824); ν_{max}/cm^{-1} 2073 m, 1960 m, 1941 s, (CO); δ_H (300 MHz, CDCl$_3$, SiMe$_4$) 0.10 (9 H, s, SiMe$_3$), 0.30 (9 H, s, SiMe$_3$), 1.50 (1 H, d, J_{PH} 5.70, C*H*(SiMe$_3$)$_2$), 4.18 (5 H, s, Cp–CH unsubst.), 4.47 (2 H, m_c, Cp), 5.03 (1 H, m_c, Cp), 5.09 (1 H, m, Cp), 6.89 (1H, d, J_{PH} 1.8, CHPh), 7.45 (3H, m, Ph), 7.60 (2H, m, Ph); δ_C (75 MHz, CDCl$_3$, SiMe$_4$) 1.8 (d_{sat}, J_{PC} 1.9, SiMe$_3$), 2.0 (d_{sat}, J_{PC} 2.6, SiMe$_3$), 34.3 (d, J_{PC} 18.1, *C*H(SiMe$_3$)$_2$), 68.2 (s, Cp), 68.5 (s, Cp), 69.5 (s, Cp), 69.6 (s, Cp–C unsubstit.), 74.5 (d, J_{PC} 2.9, Cp), 76.8 (d, J_{PC} 36.8, Cp–C^1), 111.3 (d, J_{PC} 4.2, POC), 125.2 (s, Ph), 127.5 (s, Ph), 127.9 (s, Ph) 128.7 (s, Ph), 133.4 (s, Ph), 13 (7.4 (d, J_{PC} 4.2, *i*-Ph), 171.0 (d, J_{PC} 15.8, PCN), 196.5 (d_{sat}, J_{PC} 7.4, CO$_{cis}$), 198.3 (d_{sat}, J_{PC} 26.2, CO$_{trans}$); δ_{Si} (60 MHz, CDCl$_3$, SiMe$_4$) –2.1 (d_{sat}, J_{PSi} 9.8), 0.1 (d_{sat}, J_{PSi} 4.3); δ_P (121.5 MHz, CDCl$_3$, H$_3$PO$_4$(85%)) 134.5 (dd$_{sat}$, J_{WP} 281.0, J_{PH} 1.8, J_{PH} 5.7). MS (EI, 70 eV, ^{184}W, 140 °C): *m*/*z* 831 (M$^+$, 47%), 747 ([M – 3CO]$^+$, 40%), 719 ([M – 4CO]$^+$, 10%), 691 ([M – 5CO]$^+$, 56%), 507 ([M – W(CO)$_5$]$^+$, 73), 253([FcCNCHPh]$^+$, 100).

Complex 5b. (35 mg, 10%) δ_H (300 MHz, CDCl$_3$, SiMe$_4$) –0.11 (9 H, s, SiMe$_3$), 0.08 (9 H, s, SiMe$_3$), 1.34 (1 H, d, J_{PH} 6.40, C*H*(SiMe$_3$)$_2$), 4.31 (5 H, s, Cp–CH unsubstit.), 4.40 (2 H, m, Cp), 5.81 (1 H, m, Cp), 6.00 (1 H, m, Cp), 6.98 (1H, d, J_{PH} 3.21, CHPh), 7.45 (3H, m, Ph), 7.55 (2H, m, Ph); δ_P (121.5 MHz, CDCl$_3$, H$_3$PO$_4$(85%)) 142.1 (dd$_{sat}$, J_{WP} 269.6, J_{PH} 3.3, J_{PH} 6.4).

[5-Bis(trimethylsilyl)methyl-2,4-bisferrocenyl-1,3,5-oxazaphosphol-3-ene-κ*P*]pentacarbonyltungsten(0) (6a,b). To a stirred solution of 0.310 g (0.41 mmol) of 2*H*-azaphosphirene complex **1** in 2 cm^3 CH$_2$Cl$_2$ were added consecutively 0.256 g (1.2 mmol) ferrocenyl aldehyde and triflic acid (37 mm^3, 0.41 mmol) at ambient temperature. The initially red solution turned into a dark solution. Subsequently, NEt$_3$ (57 mm^3, 0.41 mmol) was added at ambient temperature while the reaction mixture turned red again. Then the solvent was removed *in vacuo* and the product purified by low temperature column chromatography (SiO$_2$, h = 10 cm, ϕ = 1 cm, T = –15 °C) and eluted with a gradient of petroleum ether/diethyl ether 100 to 95 : 5. The second fraction yielded complex **6b** thus the third fraction yielded complex **6a**.

Complex 6a. (238 mg, 62%) as a orange solid; mp 125 °C (Found: C, 43.1; H, 4.4; N, 1.5. Calc. for $C_{34}H_{38}Fe_2NO_6PSi_2W$: C, 43.4; H, 4.1; N, 1.5); λ_{max}/nm 466 (ε/dm^3 mol^{-1} cm^{-1} 1 544), 240 (65 176); ν_{max}/cm^{-1} 2073 m, 1960 m, 1943 s (CO); δ_H (300 MHz, CDCl$_3$, SiMe$_4$) 0.05 (9 H, s, SiMe$_3$), 0.30 (9 H, s, SiMe$_3$), 1.40 (1 H, d, J_{PH} 5.09, C*H*(SiMe$_3$)$_2$), 4.17 (5 H, s, Cp–CH unsubst.), 4.25 (2 H, m, Cp), 4.30 (5 H, s, Cp–CH unsubst.), 4.32 (1 H, s, Cp), 4.41 (1 H, m, Cp), 4.44 (2 H, m, Cp), 4.99 (1H, m, Cp), 5.02 (1H, m, Cp), 6.84 (1H, d, J_{PH} 2.36, CHFc); δ_C (75 MHz, CDCl$_3$, SiMe$_4$) 1.8 (d_{sat}, J_{PC} 1.9, SiMe$_3$), 2.0 (d_{sat}, J_{PC} 2.6, SiMe$_3$), 33.1 (d, J_{PC} 9.1, *C*H(SiMe$_3$)$_2$), 65.2 (s, Cp), 65.3 (s, Cp), 65.4 (s, Cp), 67.5 (s, Cp), 67.6 (s, Cp), 68.0 (s, Cp-unsubst.), 68.1 (s, Cp), 68.3 (s, Cp), 69.0 (s, Cp), 69.4 (s, Cp-unsubst), 74.3 (d, J_{PC} 2.6, Cp), 79.0 (d, J_{PC} 34.3, Cp-C^1), 106.1 (d, J_{PC} 5.8, POC), 171.0 (d, J_{PC} 16.6, PCN), 196.2 (d_{sat}, J_{PC} 7.4, CO$_{cis}$), 198.0 (d_{sat}, J_{PC} 26.2, CO$_{trans}$); δ_{Si} (60 MHz, CDCl$_3$, SiMe$_4$) –2.3 (d_{sat}, J_{PSi} 10.0), 0.0 (d_{sat}, J_{PSi} 4.3); δ_P (121.5 MHz, CDCl$_3$, H$_3$PO$_4$(85%)) 134.0 (dd$_{sat}$, J_{WP} 281.0, J_{PH} 2.4, J_{PH} 5.1). MS (EI, 70 eV, ^{184}W, 140 °C): *m*/*z* 939 (M$^+$, 29%), 855 ([M – 3CO]$^+$, 10%), 799 ([M – 5CO]$^+$, 27%), 615 ([M – W(CO)$_5$]$^+$, 60), 409 ([FcCNCHFc]$^+$, 100).

Complex 6b. (35 mg, 9%) δ_H (300 MHz, CDCl$_3$, SiMe$_4$) –0.04 (9 H, s, SiMe$_3$), 0.09 (9 H, s, SiMe$_3$), 1.43 (1 H, d, J_{PH} 8.9, C*H*(SiMe$_3$)$_2$), 4.22 (1 H, m, Cp), 4.25 (2 H, m, Cp), 4.31 (5 H, s, Cp–CH unsubst.), 4.34 (5 H, s, Cp–CH unsubst.), 4.45 (2H, m, Cp), 4.50 (1 H, m, Cp), 4.92 (1 H, m, Cp), 4.95 (1H, m, Cp), 6.93 (1H, d, J_{PH} 5.28, CHFc); δ_P (121.5 MHz, CDCl$_3$, H$_3$PO$_4$(85%)) 140.3 (dd$_{sat}$, J_{WP} 270.8, J_{PH} 5.3, J_{PH} 8.9).

X-ray crystallography

X-ray crystallographic analyses of **3**, **4** and **6a**: Suitable red single crystals were obtained from concentrated diethyl ether (**3**) and pentane (**4,6a**) solutions upon decreasing the temperature from ambient temperature to +4 °C. Data were collected on a Nonius KappaCCD diffractometer equipped with a low-temperature device (Cryostream, Oxford Cryosystems) at 293 (**3**) or 123 K (**4,6a**) using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). The structures were solved by Patterson methods (SHELXS-97)[21] and refined by full-matrix least squares on F^2 (SHELXL-97).[21] All non-hydrogens were refined anisotropically. The hydrogen atoms were localized by difference electron density determination and refined isotropically using the riding model on the bound atoms. Absorption corrections were carried out analytically (**3**) or semi-empirically from equivalents (**4,6a**) (min./max. transmissions = 0.2203/0.5090 (**3**), 0.48199/0.53633 (**4**) and 0.36587/0.53554 (**6a**).

Crystal structure data for complex 3 ($C_{26}H_{34}FeN_3O_5PSi_2W$). Crystal size 0.50 × 0.18 × 0.18 mm, monoclinic, $P2_1/n$, a = 16.0145(5), b = 12.3033(4), c = 16.1955(3) Å, β = 103.387(2), V = 3104.31(15) Å^3, Z = 4, ρ_c = 1.702 Mg m^{-3}, $2\theta_{max}$ = 55°, collected (independent) reflections = 21506 (6845), R_{int} = 0.0336, μ = 4.337 mm^{-1}, 387 refined parameters, 0 restraints, R$_1$ (for $I > 2\sigma(I)$) = 0. 0.257, wR$_2$ (for all data) = 0.0613, S = 1.051, max./min. residual electron density = 3.694/– 1.404 e Å^{-3}.

Crystal structure data for complex 4 ($C_{26}H_{34}FeNO_6PSi_2W$). Crystal size 0.20 × 0.18 × 0.16 mm, monoclinic, $P2_1/c$, a = 11.7925(1), b = 12.2414(1), c = 21.4230(3) Å, β = 98.969(1)°, V = 3054.74(6) Å^3, Z = 4, ρ_c = 1.703 Mg m^{-3}, $2\theta_{max}$ = 55°, collected (independent) reflections = 17330 (6866), R_{int} = 0.0347, μ = 4.407 mm^{-1}, 343 refined parameters, R$_1$ (for $I > 2\sigma(I)$) = 0. 0202, wR$_2$ (for all data) = 0.0449, S = 1.033, max./min. residual electron density = 0.772/– 0.678 e Å^{-3}.

Crystal structure data for complex 6a ($C_{34}H_{38}Fe_2NO_6PSi_2W$). Crystal size 0.35 × 0.25 × 0.15 mm, orthorhombic, Pccn, a = 18.8898(2), b = 28.5021(3), c = 13.8338(1) Å, V = 7448.10(12) Å^3, Z = 8, ρ_c = 1.675 Mg m^{-3}, $2\theta_{max}$ = 55°, collected (independent) reflections = 37905 (8475), R_{int} = 0.0517, μ = 4.00 mm^{-1}, 424 refined parameters, R$_1$ (for $I > 2\sigma(I)$) = 0. 0262, wR$_2$ (for all data) = 0.0532, S = 0.927, max./min. residual electron density = 1.231/– 1.754 e Å^{-3}.

Acknowledgements

Financial support by the DFG (STR 411/25-2), the COST action CM0802 "PhoSciNet" and the Fonds der Chemischen Industrie (Kekulé grant for H. Helten) is gratefully acknowledged.

Notes and references

1 P. Wu, A. K. Feldman, A. K. Nugent, C. J. Hawker, A. Scheel, B. Voit, J. Pyun, J. M. J. Fréchet, K. B. Sharpless and V. V. Fokin, *Angew. Chem.*, 2004, **116**, 4018–4022, (*Angew. Chem., Int. Ed.*, 2004, **43**, 3928–3932); E. J. Yoo, M. Ahlquist, S. H. Kim, I. Bae, V. V. Fokin, K. B. Sharpless and S. Chang, *Angew. Chem.*, 2007, **119**, 1760–1763, (*Angew. Chem., Int. Ed.*, 2007, **46**, 1730–1733); J. E. Hein, J. C. Tripp, L. B. Krasnova, K. B. Sharpless and V. V. Fokin, *Angew. Chem.*, 2009, **121**, 8162–8165, (*Angew. Chem., Int. Ed.*, 2009, **48**, 8018–8021).

2 S. Cronin and P. H. Chandrasekar, *J. Antimicrob. Chemother.*, 2010, **65**, 410–416; J. M. Holub and K. Kirshenbaum, *Chem. Soc. Rev.*, 2010, **39**, 1325–1337.

3 R. Streubel, *Coord. Chem. Rev.*, 2002, **227**, 175–192; R. Streubel, *Top. Curr. Chem.*, 2003, **223**, 92–107.

4 H. Helten, M. Engeser, D. Gudat, R. Schilling, G. Schnakenburg, M. Nieger and R. Streubel, *Chem.–Eur. J.*, 2009, **15**, 2602–2616.

5 H. Helten, G. von Frantzius, G. Schnakenburg, J. Daniels and R. Streubel, *Eur. J. Inorg. Chem.*, 2009, 2062–2065.

6 H. Helten, J. Marinas Pérez, J. Daniels and R. Streubel, *Organometallics*, 2009, **28**, 1221–1226.

7 S. Fankel, H. Helten, G. von Frantzius, G. Schnakenburg, J. Daniels, V. Chu, C. Müller and R. Streubel, *Dalton Trans.*, 2010, **39**, 3472–3481.

8 J. Marinas Pérez, H. Helten, B. Donnadieu, C. A. Reed and R. Streubel, *Angew. Chem.*, 2010, **122**, 2670–2674, (*Angew. Chem., Int. Ed.*, 2010, **49**, 2615–2618).

9 R. Streubel, M. Beckmann, C. Neumann, S. Fankel, H. Helten, O. Feier-Iova, P. G. Jones and M. Nieger, *Eur. J. Inorg. Chem.*, 2009, 2090–2095; H. Helten, S. Fankel, O. Feier-Iova, M. Nieger, A. Espinosa Ferao and R. Streubel, *Eur. J. Inorg. Chem.*, 2009, 3226–3237.

10 H. Helten, J. Daniels, M. Nieger and R. Streubel, *New J. Chem.*, 2010, **34**, 1593–1602.

11 Y. S. Sohn, D. N. Hendrickson and H. B. Gray, *J. Am. Chem. Soc.*, 1971, **93**, 3603–3612; K. Naka, T. Uemura and Y. Chujo, *Macromolecules*, 2000, **33**, 6965–6969.

12 S. Barlow, H. E. Bunting, C. Ringham, J. C. Green, G. U. Bublitz, S. G. Boxer, J. W. Perry and S. R. Marder, *J. Am. Chem. Soc.*, 1999, **121**, 3715–3723.

13 S. J. Higgins, C. L. Jones and S. M. Francis, *Synth. Met.*, 1999, **98**, 211–214; G. E. Southard and M. D. Curtis, *Organometallics*, 2001, **20**, 508–522.

14 G. Örtl, H. Malz and H. Holtschmidt, *Chem. Ber.*, 1964, **97**, 891–902.

15 M. Aresta and E. Quaranta, *J. Org. Chem.*, 1988, **53**, 4153–4154.

16 M. Aresta, M. De, Fazio and P. Bruno, *Inorg. Chem.*, 1982, **21**, 441–444.

17 R. G. Cavell, T. I. Kwat and L Van de Griend, *Inorg. Chem.*, 1981, **20**, 3813–3818.

18 S. Priya, M. S. Balakrishna, J. T. Mague and S. M. Mobin, *Inorg. Chem.*, 2003, **42**, 1272–1281.

19 P. Chandrasekaran, J. T. Mague and M. S. Balakrishna, *Tetrahedron Lett.*, 2007, **48**, 5227–5229.

20 C. Neumann, A. Prehn Junquera, C. Wismach, P. G. Jones and R. Streubel, *Tetrahedron*, 2003, **59**, 6213–6220.

21 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112–122.