# Novel access to azaphosphiridine complexes and first applications using Brønsted acid-induced ring expansion reactions†

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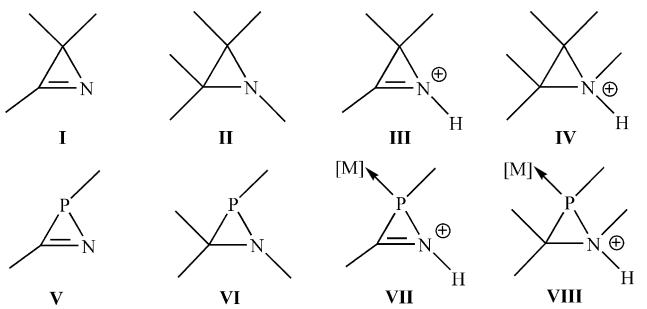
Synthesis of azaphosphiridine complexes **3a-e** was achieved *via* thermal group transfer reaction using 2*H*-azaphosphirene complex **1** and *N*-methyl *C*-aryl imines **2a-e** (i) or *via* reaction of transient Li/Cl phosphinidenoid complex **5** (prepared from dichloro(organo)phosphane complex **4**) using **2a-c** (ii), respectively. Reaction of complexes **3a**,**d** and trifluoromethane sulfonic acid in the presence of dimethyl cyanamide led to a highly bond- and regioselective ring expansion yielding 1,3,4$\sigma^3\lambda^3$-diazaphosphol-2-ene complexes **8a**,**d** after deprotonation with $NEt_3$. $^{31}P$ NMR reaction monitoring revealed that protonation of complex **3a** yields the azaphosphiridinium complex **6a**, unambiguously identified by NMR spectroscopy at low temperature. All isolated products were characterized by multinuclear NMR spectroscopy, IR and UV/Vis (for **3a**,**d**, **6a**, **8a**,**d**), MS and single-crystal X-ray crystallography in the cases of complexes **3b-d**, **8a** and **8d**. DFT studies on the reaction mechanism and compliance constants of the model complex of **6a** are presented.

## Introduction

Brønsted and Lewis acid-induced ring expansion reactions of small, strained N-heterocycles such as 2*H*-azirenes (**I**) and aziridines (**II**) (Scheme 1) enable numerous applications in organic synthesis.[1–3] Surprisingly, evidence for reaction intermediates such as 2*H*-azirenium (**III**) or aziridinium (**IV**) derivatives is scarce.[4–6] Furthermore and by comparison, the chemistry of 2*H*-azaphosphirenes (**V**) and azaphosphiridines[7,8] (**VI**) is largely undeveloped. The synthesis of metal complexes containing ligands **V**[9,10] or **VI**[11] was reported but studies on ring cleavage reactions were focused on complexes of **V**.[12–14] Lammertsma and coworkers reported strong experimental[15] and computational[16] evidence for the intermediacy of azaphosphiridine complexes in thermal reactions of 7-phospha-norbornadiene complexes with imines[17] thus confirming the proposal by Mathey and co-workers made earlier. Recently, we provided strong NMR evidence for a complex of type **VII** at low temperature and demonstrated that ring expansion occurs selectively upon addition of a nitrile derivative.[18] To the best of our knowledge, nothing is known about complexes **VIII** and their chemistry.




**Scheme 1** Three-membered N-heterocycles **I–IV**, related N,P-heterocycles **V**, **VI** and metal complexes thereof **VII**, **VIII** (lines denote organic substituents; [M] = $M(CO)_5$ of Cr, Mo, W).

On the other hand, we recently reported reactions of thermally unstable Li/Cl phosphinidenoid complexes in the synthesis of 2*H*-azaphosphirene[19] and oxaphosphirane[19-21] complexes, both of which can be used to obtain five-membered phosphorus heterocycles.[18,22]

Here, a new, facile access to azaphosphiridine metal complexes is described, and first examples of Brønsted acid-induced ring expansion reactions are presented that selectively yield 1,3,4$\sigma^3\lambda^3$-diazaphosphol-2-ene complexes. In addition, computational studies provide an insight into the mechanistic aspects of the ring expansion.

## Results and discussion

Thermal reaction of 2*H*-azaphosphirene complex **1**[23] with *N*-methyl *C*-aryl imines **2a-e**[24-28] (Scheme 2, **i**) diastereoselectively gave azaphosphiridine complexes **3a-e** in good to moderate yields (according to the method described for the synthesis of **3a**[11]).[29] Yields were significantly improved when Li/Cl phosphinidenoid complex **5**, generated from **4**, was reacted with **2a–c** at low temperature (ii); in the case of **2d**,**e** no reaction to give **3d**,**e** was observed.[30] All complexes were isolated using low temperature column chromatography, except for **3e**, which could be obtained after washing the crude product; selected NMR data for **3a-e** are shown in Table 1.

To test our new ring expansion methodology[18,22] derivatives **3a**,**d** were reacted with trifluoromethane sulfonic acid (triflic acid or

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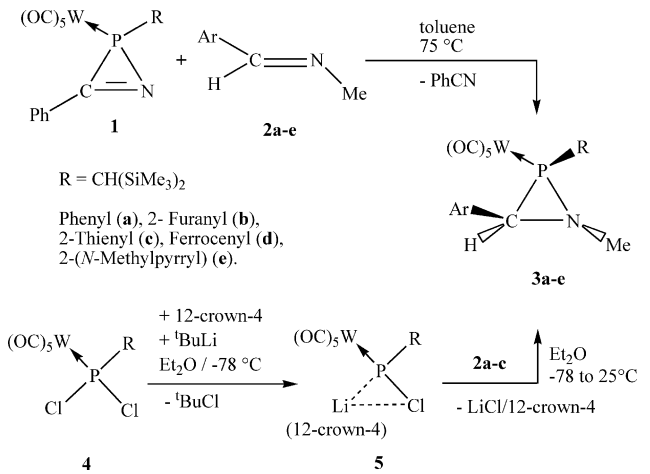
† CCDC reference numbers 743281 (**3b**), 743282 (**3c**), 743281 (**3d**), 695893 (**8a**), and 743283 (**8d**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b922166b

**Table 1** $^{31}$P NMR data of **3a–e**, **6a,d**, **7a,a′** and **8a,a′,d,d′**

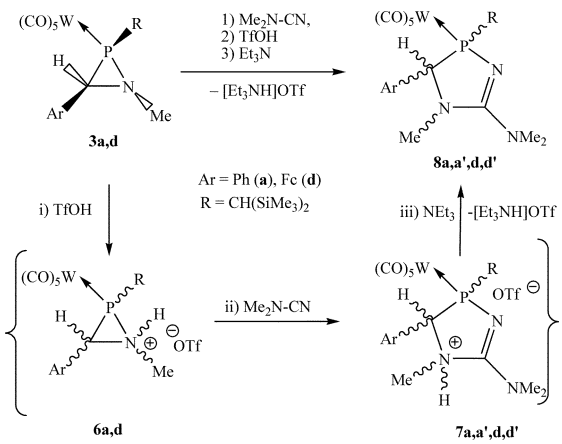
| Ar | No. | $\delta(^{31}P)$ [ppm] | $\lvert^1J(W,P)\rvert$ /Hz | $\lvert^2J(P,H)\rvert$ /Hz P-CHTms$_2$[h] | $\lvert^2J(P,H)\rvert$ /Hz P-CH(Ar)[h]- |
|---|---|---|---|---|---|
| Ph | **3a**[g] | −37.3 | 269.9 | 17.7 | 5.4 |
| Fu[a] | **3b**[g] | −35.9 | 271.8 | 17.5 | 7.0 |
| Th[b] | **3c**[g] | −37.7 | 269.5 | 16.4 | 6.6 |
| Fc[c] | **3d**[g] | −40.7 | 265.8 | 17.8 | 8.3 |
| Py[d] | **3e**[g] | −39.2 | 267.0 | —[i] | —[i] |
| Ph | **6a**[f] | +45.1[k] | 298.2[k] | 17.3[k] | $h_{1/2}$ = ~16[k] |
| Fc[c] | **6d**[f] | +51.0[k] | 301.9[k] | 16.3[k] | $h_{1/2}$ = ~20[k] |
| Ph | **7a**[f,k] | 85.1[k] | 286.5 [k](major) | 19.1/19.7 dd [k] | |
| Ph | **7a′**[f,k] | 90.2[k] | 290.0 [k](minor) | 20.1 d [k] | |
| Ph | **8a**[g] | 103.3 (major) | 279.7 (major) | 9.1 | 6.2 |
| | **8a′**[g] | 90.8 (minor) | 261.9 (minor) | [j] | 5.9 |
| Fc[c] | **8d**[g] | 101.9 (major) | 278.5 (major) | [j] | [j] |
| | **8d′**[g] | 96.9 (minor) | 265.1 (minor) | [j] | [j] |

[a] Fu = 2-furanyl. [b] Th = 2-thienyl. [c] Fc = ferrocenyl. [d] Py = 2-(*N*-methyl pyrryl). [e] In $C_6D_6$. [f] In $CD_2Cl_2$. [g] In $CDCl_3$. [h] From $^1$H NMR spectrum. [i] Not isolated. [j] Not observed. [k] Recorded at 203 K.




**Scheme 2** Synthesis of azaphosphiridine complexes **3a–e** using 2*H*-azaphosphirene complex **1** (i) or *in situ* generated complex **5** (from **4**) (ii) and imines **2a–e**.

TfOH) in $CH_2Cl_2$ in the presence of dimethyl cyanamide and subsequently treated with triethylamine thus forming bond- and regioselectively diastereomeric 1,3,4-diazaphosphol-2-ene complexes **8a**,**a′** (11 : 2) and **8d**,**d′** (22 : 1) (Scheme 3).




**Scheme 3** Ring expansion reaction of complexes **3a**,**d**.

As a more cost-efficient alternative, ring expansion induced by oleum (w($SO_3$) = 0.2) was tested at −25 °C, and complexes **3a**,**d** were used as a good case in point. *C*-Phenyl substituted derivative **3a** showed a selective reaction *via* transient complexes **7a**,**a′** to yield finally complex **8a**, whereas the *C*-ferrocenyl substituted complex **3d** gave complex **8d** together with a complex exhibiting a phosphorus resonance at 91.2 ppm ($^1J_{W,P}$ = 275 Hz, $^1J_{P,H}$ = 352 Hz) in a 1 : 1 ratio, which could not be isolated. For comparison, 1,3,4-diazaphosphol-2-ene-*P*-oxides reported by Zhou *et al.*[31] showed phosphorus resonances in the range of 40–45 ppm.

Monitoring of the reactions of **3a**,**d** with triflic acid at low temperature (−70 °C, $CD_2Cl_2$) by $^{31}$P NMR spectroscopy showed *N*-protonation as a first step, and thus the obtained intermediates **6a**,**d** revealed significantly downfield shifted resonances at 45.1 and 51.0 ppm and increased $^1J_{W,P}$ couplings of about 300 Hz (Table 1). In total, these $^{31}$P NMR data are very similar to those of oxaphosphirane tungsten complexes,[cf. 19-21] which illustrates a similar influence of the cationic N(Me)H unit and the oxygen atom (in oxaphosphiranes) on the P center. In the $^1$H NMR spectrum (−70 °C) of the *C*-phenyl derivative **6a** the resonance of the proton attached to the N atom is at 8.31 ppm. The spectrum further reveals a downfield shifted *N*-methyl resonance from 2.82 (**3a**) to 3.20 ppm (**6a**). Similarly the proton bonded to the azaphosphiridine ring carbon atom is shifted from 3.28 (**3a**) to 4.35 ppm (**6a**). Remarkably the resonance of this proton is more deshielded in complex **6a** (3.28 ppm) than it is in complex **6d** (2.89 ppm), which points to some electron-donation of the ferrocenyl group in this case. Upon warming to ambient temperature complexes **6a**,**d** decomposed.

$^{31}$P NMR spectroscopic monitoring of the reaction of **3a** with TfOH in the presence of dimethyl cyanamide revealed evidence for the formation of *N*-protonated diastereomeric 1,3,4-diazaphosphol-2-ene complexes **7a**,**a′** (Table 1), which, at −70 °C, were observed together with **3a** in a 2 : 12 : 7 ratio (**3a** : **7a** : **7a′**). Upon warming the resonance of **3a** decreased until it vanished at ambient temperature. Further support for the assignment of these data to complex **7a**,**a′** came from the observation that the $^{31}$P NMR resonance was shifted to lower field (by 6–12 ppm) compared with **8a**,**a′**. A similar situation was found recently for *P*-CH(SiMe$_3$)$_2$ substituted 2*H*-1,4,2-diazaphosphole tungsten complexes and their *N*-protonated derivatives.[18] Complex **7a** showed a doublet of doublets ($^2J_{PH}$ = 19.1 and 19.7 Hz), while **7a′** revealed a doublet ($^2J_{PH}$ = 20.0 Hz) in the proton-coupled $^{31}$P NMR spectrum. *N*-Protonation also caused an increase in the magnitude of the tungsten–phosphorus coupling constant by 10–17 Hz. Further support for complex **6a** was also obtained by MS experiments.[32]

In the IR spectra the absorptions due to CO stretch vibrations are of particular interest as the normal mode of local $A_1$ symmetry reveals a hypsochromic shift of 2–4 cm$^{-1}$ for the cationic complexes **6a**,**d** compared to their respective neutral counterparts **3a**,**d**. Complexes **7a**,**d** show a blue shift by 11–13 cm$^{-1}$ compared to **8a**,**d**. This supports the idea that protonation of the heterocyclic ligand leads to weakening of the *trans* C–O bond.[33] All spectra show several overlapping bands in the region around 1900–1960 cm$^{-1}$ which did not allow a clear assignment. In all four cases protonation causes a broadening of the bands in the region of 1840–1980 cm$^{-1}$. In the UV/Vis absorption spectra the bands of the three-membered ring complexes **3a**,**d** and **6a**,**d** did not change significantly upon protonation.

Complexes bearing a ferrocenyl substituent at the imine **2d** or the ring system **3d**, **8d** were investigated by cyclic voltammetric (CV) experiments;[34] Fig. 1 shows the resulting graphs. Whereas imine **2d** shows a reversible CV ($E_{\frac{1}{2}} = 0.647$ V), the 1,3,4-diazaphosphol-2-ene complex **8d** ($E_{\frac{1}{2}} = 0.548$ V) shows a quasi-reversible and the azaphosphiridine complex **3d** an irreversible CV behavior and thus only the value for $E_{pa}$ (0.575 V) could be determined. In total, the three- (**3d**) and five-membered ring (**8d**) substituted ferrocene derivatives allow a more facile oxidation than the imine **2d**.

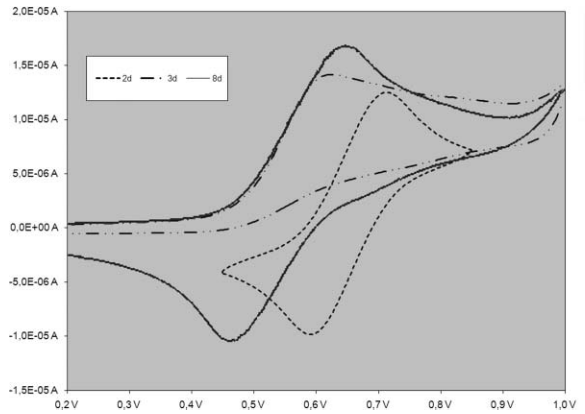



**Fig. 1** Cyclic voltammetric measurements of imine **2d**, complexes **3d** and **8d** (100 mV $s^{-1}$, 3 mmol $L^{-1}$ in $CH_2Cl_2$, 0.1 mol $L^{-1}$ [*n*-$Bu_4N$]$PF_6$, GCE, Pt-wire, Ag/AgCl, 2 mol $L^{-1}$ LiCl in EtOH, direction of scan indicated by the arrow.

The molecular structures of **3b-d** (Fig. 2-4) and **8a**,**d** (Fig. 5 and 6) were determined for the solid state by single-crystal X-ray diffraction studies. Complexes **3b-d** exhibit some common structural features: a) the P–N bond length is ~10 pm shorter than the P–C bond length, b) the P–W bond lengths are around 2.50 Å, c) in all three complexes the endocyclic angles at phosphorus are very narrow (~49°). The situation is markedly different in the *C*-Ph, and *C*-Fc, *P*-CH(SiMe$_3$)$_2$ substituted 2*H*-azaphosphirene tungsten complexes,[9,35,36] in which the P–C and

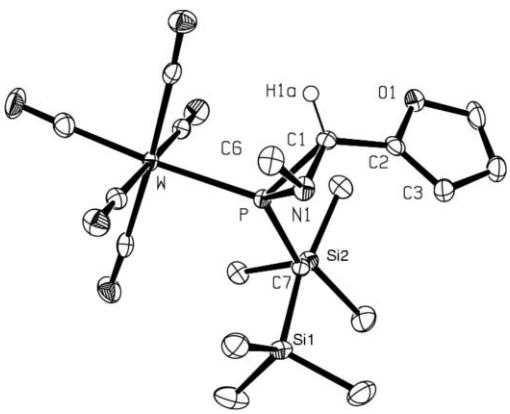



**Fig. 2** Molecular structure of complex **3b** in the crystal (50% probability level, hydrogen atoms except on C(1) are omitted for clarity). Selected bond lengths [Å] and angles [°]: W–P 2.4935(8), P–C(1) 1.838(3), P–N(1) 1.730(3), P–C(7) 1.806(3), C(1)–N(1) 1.470(5), N(1)–C(6) 1.468(5), C(1)–C(2) 1.465(5); N(1)–P–C(1) 48.55(16), C(1)–N(1)–P 69.58(19), N(1)–C(1)–P 61.87(18), C(1)–P–C(7) 108.56(16), N(1)–P–C(7) 103.80(15), P–N(1)–C(6) 123.6(2), C(1)–N(1)–C(6) 117.2(3).

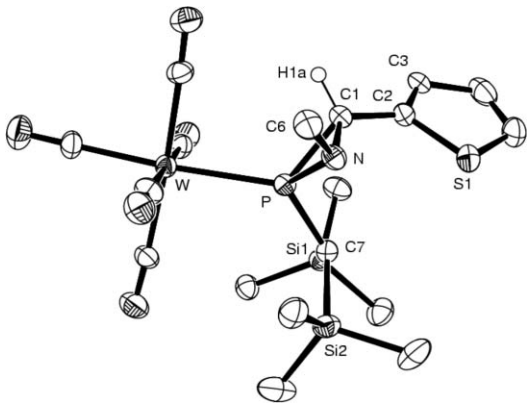



**Fig. 3** Molecular structure of complex **3c** in the crystal (50% probability level, hydrogen atoms except on C(1) are omitted for clarity). Selected bond lengths [Å] and angles [°]: W–P 2.4952(12), P–C(1) 1.846(4), P–N 1.725(4), P–C(7) 1.805(4), C(1)–N 1.483(5), N–C(6) 1.468(6), C(1)–C(2) 1.475(6); N–P–C(1) 48.94(18), C(1)–N–P 69.8(2), N–C(1)–P 61.3(2), C(1)–P–C(7) 109.7(2), N–P–C(7) 104.1(2), P–N–C(6) 124.2(3), C(1)–N–C(6) 117.2(4).

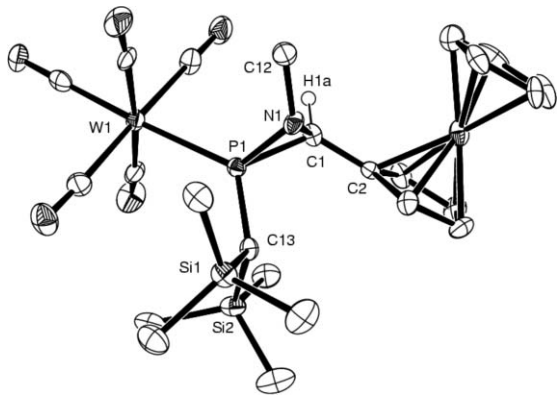



**Fig. 4** Molecular structure of complex **3d** in the crystal (50% probability level, hydrogen atoms except on C(1) are omitted for clarity). Selected bond lengths [Å] and angles [°]: W(1)–P(1) 2.505(9), P(1)–C(1) 1.838(5), P(1)–N(1) 1.735(4), P(1)–C(13) 1.799(6), C(1)–N(1) 1.487(6), N(1)–C(12) 1.472(6), C(1)–C(2) 1.475(6); N(1)–P(1)–C(1) 49.08(19), C(1)–N(1)–P(1) 69.1(3), N(1)–C(1)–P(1) 61.9(2), C(1)–P(1)–C(13) 108.0(2), N(1)–P(1)–C(13) 104.7(2), P(1)–N(1)–C(12) 123.4(3), C(1)–N(1)–C(12) 116.0(5).

P–N bond distances are almost identical (Fc derivative: *d*(PN) = 1.803(3) Å, *d*(PC) = 1.763(4) Å, Ph derivative: *d*(PN) = 1.796 Å, *d*(PC) = 1.759 Å; in both derivatives the *d*(PN) is somewhat longer than *d*(PC)).[9,35,36] The endocyclic angle at phosphorus is significantly more acute (R = Ph:[36] 41.9° and R = Fc:[35] 42.2°) due to the shorter C–N bond in such complexes.

Noteworthy is also the small bond angle sum at phosphorus (not including the W(CO)$_5$ group) of **3b–d**, which is about 261°. A stereochemical feature is the relative orientation of the *N*-Me group in complexes **3b–d**, which was found to be on the same side of the azaphosphiridine ring plane as the W(CO)$_5$ fragment; this was also observed for the structure of **3a**[*cf.* 11]. Some structural features of complexes **8a**,**d**—the first transition metal complexes of this heterocycle—are best revealed through comparison with **3a**,**d**. Whereas the P–W and the P–C3 distances in **8a**,**d** and **3b-d** are virtually identical, the latter is slightly elongated by ~0.05 Å, and the P–C(1) bond is elongated by ~0.07 Å. The bond angle

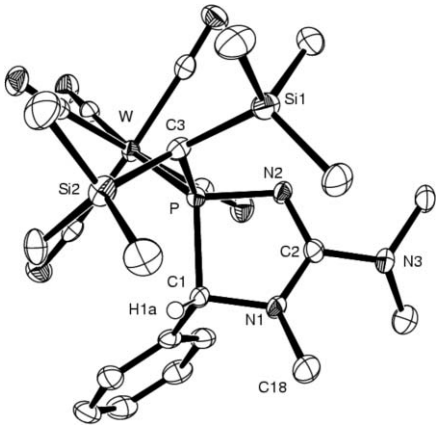



**Fig. 5** Molecular structure of complex **8a** in the crystal (50% probability level, except for H at C(1) all other hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: W–P 2.5286(7), P–C(3) 1.850(3), P–N(2) 1.700(3), P–C(1) 1.917(3), N(2)–C(2) 1.300(4), C(2)–N(1) 1.373(4), N(1)–C(1) 1.458(4), C(1)–C(4) 1.511(4), C(2)–N(3) 1.377(4); C(1)–P–N(2) 93.22(13), P–N(2)–C(2) 110.1(2), N(2)–C(2)–N(1) 119.9(3), C(2)–N(1)–C(1) 114.0(2), N(1)–C(1)–P 100.1(2).

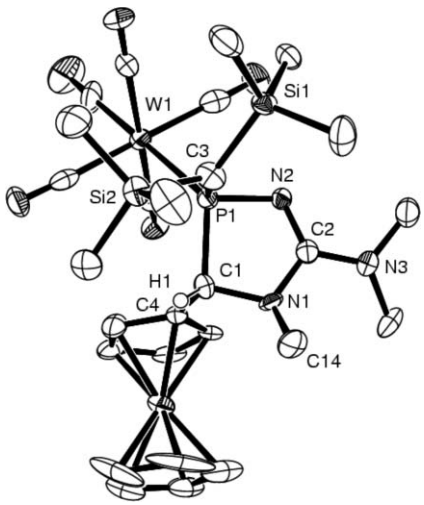



**Fig. 6** Molecular structure of complex **8d** in the crystal (50% probability level, except for H at C(1) all other hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: W–P 2.5276(2), P–C(3) 1.8440(1), P–N(2) 1.6909(1), P–C(1) 1.9010(1), N(2)–C(2) 1.3024(1), C(2)–N(1) 1.4190(1), N(1)–C(1) 1.4711(1), C(1)–C(4) 1.4784(1), C(2)–N(3) 1.3484(1); C(1)–P–N(2) 92.440(3), P–N(2)–C(2) 109.655(4), N(2)–C(2)–N(1) 120.076(5), C(2)–N(1)–C(1) 109.860(4), N(1)–C(1)–P 100.977(4).

sum at phosphorus as well as the endocyclic angle at phosphorus is increased (300–308° and 92–93°, respectively), both are effected by the increasing ring size.

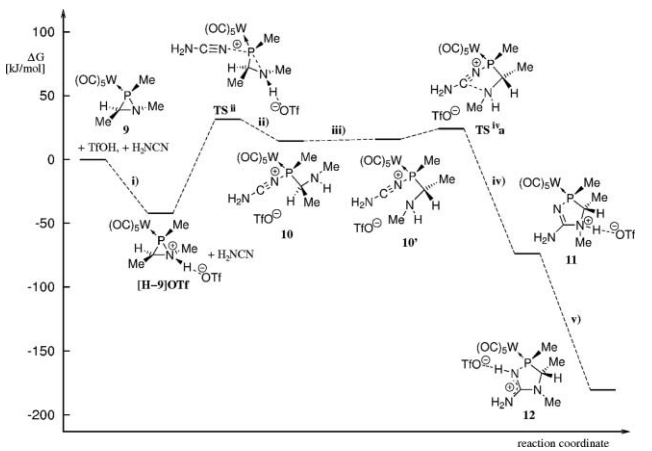
In 1994, Martynov *et al.* published the crystal structure[37] of a 1,3,4-diazaphosphol-2-ene *P*-oxide. In this case the geometry is very much dominated by the P–O bond: the P–C1 bond is shorter by more than 0.05 Å and the P–N2 by ~0.1 Å, compared to the transition metal bound ligands (**8a**,**d**). The C1–N1 bond is shortened by 0.03 Å (**8a**) resp. 0.05 Å (**8d**). The C2–N2 bond is elongated by 0.05 Å. The angle around the P-atom is by 3.5° (**8a**) resp. 4.4° (**8d**) more acute in the *P*-oxide. The distances to the nitrogen atoms around C(2) in **8a** (Fig. 5) are inequivalent: C(2)–N(2) is in the range of a $sp^2$-C–$sp^2$-N double bond.[38] The endocyclic C(2)–(N1) and the exocyclic C(2)–N(3) distances are virtually identical. In **8d** the endocyclic C(2)–(N1) distance is by 0.04 Å longer than in **8a** while the exocyclic C(2)–N(3) distance is by 0.03 Å shorter.

The 1,2,4-diazaphosphol-2-ene rings in **8a** and **8d** show an envelope conformation with only little deviation of the phosphorus atom (**8a**: 0.295, **8d**: 0.505 Å), from the best plane given by C(1)–N(1)–C(2)–N(2); the relative deviation of N(1), N(2), C(1) and C(2) from the best plane is between 0.023 and 0.057 Å. The ring plane bears the *N*-Me group and the bulky $CH(SiMe_3)_2$ group on the same side, which is an important hint for the ring formation and thus for theoretical studies of the mechanism.

Apparently, the ring expansion proceeds *via* an acyclic intermediate with the *N*-methyl group *trans* to the phenyl (or ferrocenyl) group that derives from a P–N bond cleavage. The interplanar angles between the best plane of the five-membered heterocycle and the ring substituents at C(1) are 88.1° (**8a**) and 76.1° (**8d**), respectively.

## Computational studies

A conceivable mechanism of the acid-induced ring expansion was obtained in a theoretical study using DFT calculations on complex **9** (Scheme 4), an all-methyl substituted model system for **3a**,**b**; cyanamide was chosen as the nitrile component (Scheme 4 and Tab. 2).




**Scheme 4** Computed pathway for the reaction of complex **9** with cyanamide in the presence of TfOH. The sum of free energies of the reactants **9** + TfOH + $H_2NCN$ was arbitrarily chosen as zero-point of the $\Delta G$ scale.

**Table 2** Calculated thermochemical data ([kJ $mol^{-1}$]) for reactions shown in Scheme 4 (B3LYP/aug-TZVP/ECP-60-MWB(W), COSMO $CH_2Cl_2$//RI-BLYP/aug-SV(P)/ECP-60-MWB(W), COSMO $CH_2Cl_2$)

| | Reaction | $\Delta G^{\ddagger}_{298}$ | $\Delta_R G_{298}$ |
|---|---|---|---|
| **i)** | **9** + TfOH → [H–**9**][OTf] | [a] | –42.1 |
| **ii)** | [H–**9**][OTf] + $H_2NCN$ → **10** | +73.7 | +56.7 |
| **iii)** | **10** → **10′** | [a] | +1.4 |
| **iv)** | **10′** → **11** | +8.1 | –89.7 |
| **v)** | **11** → **12** | [a] | –106.6 |

[a] The activation barrier was not calculated.

In the first step the azaphosphiridine nitrogen of **9** is protonated by triflic acid with formation of azaphosphiridinium salt [H–**9**][OTf] (i) where the triflate anion remains attached through a hydrogen bond (Fig. 7, left). Different from the situation found for 2*H*-azaphosphirene[18] and oxaphosphirane complexes[22] upon ring-protonation the P,N bond of [H–**9**][OTf] is not spontaneously cleaved, but the phosphorus center becomes prone to a nucleophilic attack of cyanamide (ii) thus leading to ring opening in an $S_N2$-type fashion (**TS$^{ii}$**; Fig. 7, right). Since the attack occurs *trans* to the P,N bond (for stereoelectronic reasons), inversion of the configuration at the phosphorus results. Intermediately *P*-nitrilium substituted phosphane complex **10** is formed.

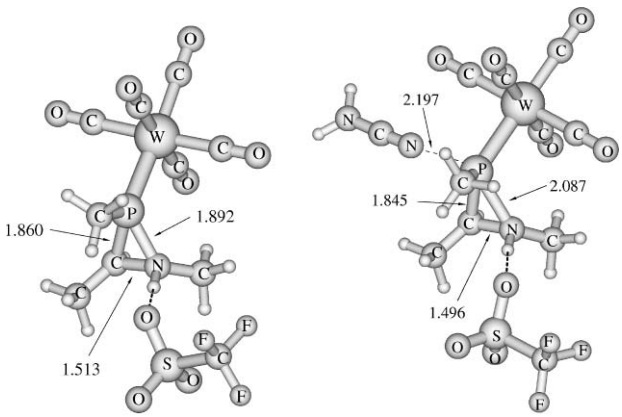



**Fig. 7** Calculated structures of *N*-protonated azaphosphiridine complex [H–**9**][OTf] with the triflate anion attached *via* a hydrogen bond (left) and transition state **TS$^{ii}$** for the nucleophilic ring opening of [H–**9**][OTf] by cyanamide (right) (bond distances in Å).

After a conformational change of **10** (rotation about the P,C bond; iii) to **10′** the latter can undergo facile cyclization to give $N^1$-protonated 1,3,4-diazaphosphol-2-ene complex **11** in a highly exergonic reaction (iv). Owing to the presence of an amidine moiety a subsequent proton transfer to $N^3$ is highly favored (v). Overall, due to inversion of the configuration at phosphorus in step ii, the ring expansion reaction results in the formation of a mixture of diastereomers **12** (4*R*,5*R*/4*S*,5*S*), which is consistent with the experimental observations.

### Calculated compliance constants of chromium model complexes

The influence of *N*-protonation on ring bond strengths of azaphosphiridine complexes was also investigated by calculation of P-/C-/N-methyl substituted chromium model complexes **3$^{Me,Cr}$**, **[H-3$^{Me,Cr}$]$^+$** (Fig. 8).

As a measure of bond strengths DFT compliance constants[40]—diagonal elements of the inverse force field—are calculated: the stronger a bond the *less* compliant it is and *vice versa*. *N*-protonation of azaphosphiridine model complex **3$^{Me,Cr}$** is calculated including dichloromethane as a solvent (simulated by a polarizable continuum model) (Fig. 9, black).

*N*-Protonation weakens P–N by 72% and N–C by 9% while Cr–P is enforced by 15%; P–C remains almost unchanged (Fig. 10).

The positive charge in **[H-3$^{Me,Cr}$]$^+$** concentrates essentially on phosphorus, which leads to enforcement of the P–Cr bond.

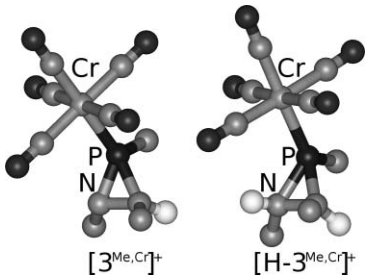



**Fig. 8** ZORA-DFT calculated ((B88+P86)VWN5/tz2p, COSMO $CH_2Cl_2$, ADF 2007.1[39b]) bond lengths [Å] and angles [°] of **[3$^{Me,Cr}$]/[H-3$^{Me,Cr}$]$^+$**: P–N 1.727/1.868, P–C 1.832/1.833, N–C 1.477/1.516, Cr–P 2.351/2.284, N–P–C 48.95/48.34, C–N–P 69.22/64.61, P–C–N 61.83/67.05; Charges (Hirshfeld): Cr +0.20/+0.21, P +0.23/+0.28, C –0.02/+0.02, N –0.14/+0.00, H(N) –/+0.17.

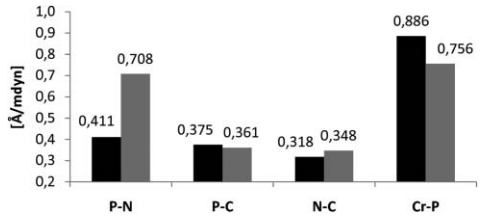



**Fig. 9** DFT (BVP86/tzvp, IEFPCM $CH_2Cl_2$, G03[39a]) compliance constants [Å/mdyn] of **3$^{Me,Cr}$**(black)/**[H-3$^{Me,Cr}$]$^+$**(grey).

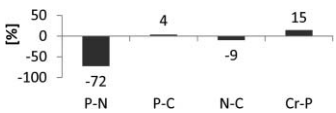



**Fig. 10** Bond strengthening (+)/weakening (–) [%] upon *N*-protonation (BVP86/tzvp, IEFPCM $CH_2Cl_2$, G03[40a]): **3$^{Me,Cr}$/[H-3$^{Me,Cr}$]$^+$**.

## Conclusions

We have demonstrated that the use of a transient Li/Cl phosphinidenoid complex enables a new and facile access to azaphosphiridine complexes, thus facilitating research in this field. Furthermore, we provided the first examples of Brønsted acid-induced ring expansion reactions of azaphosphiridine complexes that selectively yielded 1,3,4-diazaphosphol-2-ene complexes; two of which were characterized by X-ray crystallography. $^{31}$P NMR spectroscopic monitoring at low temperature of the protonation reaction revealed good evidence for azaphosphiridinium complexes formed in the first step; this was further supported by DFT calculations. Compliance constants describe quantitatively the bond strength changes occurring upon *N*-protonation and offer an additional rationale for P–N bond cleavage. Computational studies gave further insight into mechanistic aspects of the ring expansion: the second step is a nucleophilic attack of the nitrile at a partially positively charged phosphorus center, which leads to P–N bond cleavage and transient formation of a *P*-nitrilium substituted phosphane complex. This is followed by facile cyclization to give a $N^1$-protonated 1,3,4-diazaphosphol-2-ene complex in a highly exergonic reaction. A proton transfer from $N^1$ to $N^3$ follows thus forming the (more stable) amidinium moiety, which further supports the structural assignment of intermediates experimentally observed. After deprotonation, the ring expansion reaction results in the formation of a mixture of

diastereomeric 1,3,4-diazaphosphol-2-ene complexes. In total, the reaction sequence represents a new example of click-type reactions in organophosphorus chemistry.

## Experimental section

### General procedures

All operations were performed in an atmosphere of deoxygenated and dried argon using standard Schlenk techniques with conventional glassware. Solvents were distilled from sodium or $CaH_2$ ($CH_2Cl_2$). 2*H*-Azaphosphirene complex **1** was synthesized according to the method described in the literature.[9] Melting points were determined with a Büchi apparatus Type S. The values are not corrected. NMR data were recorded on a Bruker Avance 300 spectrometer ($^1$H: 300.13 MHz; $^{13}$C: 75.5 MHz; $^{29}$Si: 59.6 MHz; $^{31}$P: 121.5 MHz) using $C_6D_6$, $CDCl_3$ or $CD_2Cl_2$ as solvent and internal standard; shifts are referenced to tetramethylsilane ($^1$H; $^{13}$C; $^{29}$Si, $\Xi = 19.867187$ MHz), and 85% $H_3PO_4$ ($^{31}$P, $\Xi = 40.480742$ MHz). Mass spectra were recorded on a Kratos Concept 1H (FAB$^+$, *m*NBA) or a MAT 95 XL Finnigan (EI, 70 eV, $^{184}$W) spectrometer (selected data given). ESI mass spectra and ESI tandem mass spectra were recorded on a Bruker APEX IV Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer equipped with an Apollo ESI source. UV/Vis spectra were recorded on a Shimadzu UV-1650 PC spectrometer. Infrared spectra were recorded on a Thermo Nicolet 380 FT-spectrometer (selected data given). Elemental analyses were performed using an Elementar Vario EL instrument. Cyclic voltammetric measurements were performed using the 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, scan speed: 100 mV s$^{-1}$).

Imines **2b–e** were synthesized from common available aldehydes and methyl imine gas according to the literature.[25-28] *N*-Benzylidenmethyl imine **2a** was used as purchased from Acros.

**Synthesis of the complex 3a *via* the new method.** To a solution of 500 mg (0.85 mmol) of dichlorophosphane complex **1**, 139 µL (0.85 mmol) of 12-crown-4 and 530 µL (4.25 mmol) of *N*-benzylidenmethyl imine **2a** were dissolved in 30 mL of $Et_2O$. At –80 °C 0.68 mL (1.02 mmol) of *tert.*-butyl lithium (1.5 M in hexanes) was slowly added. The yellow solution was stirred for 2 h and warmed up to 0 °C. From the resulting orange solution all volatile components were removed *in vacuo* (*ca.* $10^{-2}$ mbar). The product was subsequently purified by column chromatography on neutral aluminium oxide (–30 °C, petroleum ether/$Et_2O$: 5/1) and obtained as a pale fraction.

**Complex 3a.** Light pale solid, yield: 390 mg (0,62 mmol, 73%) $^{31}$P{$^1$H} NMR ($CDCl_3$): $\delta$ = -37.3 ($d_{sat}$, $^1J$(P,W) = 269.9 Hz), $^{29}$Si{$^1$H} NMR ($CDCl_3$): $\delta = 0.06$ ($d_{sat}$, $^1J$(Si,C) = 6.7, $^2J$(P,Si) = 6.4 Hz), 2.26 ($d_{sat}$, $^1J$(Si,C) = 2.7, $^2J$(P,Si) = 2.4 Hz); IR (Nujol): $\tilde{\nu} = 2072.6$ (w), 2064.8 (vw, CO), 1947.5 (vs, CO), 1941.0 (vs, CO), 1914.8 cm$^{-1}$ (m, CO), UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ (abs.) = 237.0 nm (2.490); other analytical data of **3a** were reported earlier.[11]

**Synthesis of complex 3b.** To a solution of 500 mg (0.85 mmol) of dichlorophosphane complex **4** and 139 µL (0.85 mmol) of 12-crown-4, dissolved in 30 mL $Et_2O$, 0.68 mL (1.02 mmol) of *tert.*-butyl lithium (1.5 M in hexanes) were slowly added at –80 °C. The yellow solution was allowed to stir until the temperature reached –40 °C, then 465 µL (4.25 mmol) of *N*-[(furan-2-yl)methylene]methanamine or *N*-methylfurfurylidenamine **2b** were slowly added. The color of the solution changed to orange. After warming to room temperature all volatile components were removed *in vacuo* ($10^{-2}$ mbar). The product was obtained as a mixture of diastereomers (ratio 5.9 : 1; major isomer: –35.9 ppm ($^1J$(W,P) = 271.8 Hz), minor isomer: –38.5 ppm ($^1J$(W,P) = 277.0 Hz) and subsequently purified by column chromatography on neutral aluminium oxide (–30 °C, petroleum ether/$Et_2O$: 4/1). The product was crystallized from $Et_2O$ at –30 °C.

**Complex 3b.** Light yellow solid, yield: 464 mg (0.74 mmol, 88%); only the analytical data of the mayor isomer are given: $^1$H NMR ($CDCl_3$): $\delta$ = –0.04 (s, 9H; Si(C$H_3$)$_3$), 0.32 (s, 9H; Si(C$H_3$)$_3$), 1.09 (d, $^2J$(P,H) = 17.5 Hz, 1H; C$H$(SiMe$_3$)$_2$), 2.65 (d, $^2J$(P,H) = 17.5 Hz, 3H; N–C$H_3$), 3.09 (d, $^2J$(P,H) = 7.0 Hz, 1H; P–C(*H*)-N), 6.18 ($m_c$, 1H; subst. ring H$^3$), 6.41 ($m_c$, 1H; subst. ring H$^4$), 7.44 ($m_c$, 1H; subst. ring H$^5$); $^{13}$C{$^1$H} NMR ($CDCl_3$): $\delta$ = 196.2 (d, $^2J$(P,C) = 30.3 Hz; $CO_{trans}$), 196.0 ($d_{sat}$, $^2J$(P,C) = 7.6 Hz, $^1J$(W,C) = 125.0 Hz; $CO_{cis}$), 151.5 (d, $^2J$(P,C) = 5.5 Hz; *ipso*-C$_{furanyl}$), 142.7 (d, $^5J$(P,C) = 2.4 Hz; C$^5_{furanyl}$), 110.7 (d, $^4J$(P,C) = 2.5 Hz; C$^4_{furanyl}$), 107.3 (d, $^3J$(P,C) = 4.0 Hz; C$^3_{furanyl}$), 50.1 (d, $^{2+3}J$(P,C) = 2.4 Hz; NCH$_3$), 42.0 (d, $^{1+3}J$(P,C) = 2.2 Hz, PCN), 19.5 (d, $^2J$(P,C) = 26.6 Hz; CH(SiMe$_3$)$_2$), 1.9 (d, $^3J$(P,C) = 3.7 Hz,$^1J$(Si,C) = 52.5 Hz; Si(CH$_3$)$_3$), 0.8 (d, $^3J$(P,C) = 3.9 Hz, $^1J$(Si,C) = 52.6 Hz; Si(CH$_3$)$_3$); $^{29}$Si{$^1$H} NMR ($CDCl_3$): $\delta = 0.06$ ($d_{sat}$, $^1J$(Si,C) = 56.0, $^2J$(P,Si) = 6.4 Hz), 1.61 ($d_{sat}$, $^1J$(Si,C) = 52.3, $^2J$(P,Si) = 2.4 Hz); $^{31}$P{$^1$H} NMR ($CDCl_3$): $\delta$ = -35.1 ($d_{sat}$, $^1J$(W,P) = 270.7 Hz); MS (EI, 70 eV, $^{184}$W): *m*/*z* (%): 623.0 ([M]$^+$, 39), 539.0 ([M–3CO]$^+$, 18), 514.0 ([M–$C_6H_7NO$]$^+$, 13), 486 ([M–$C_6H_7$NO-CO]$^+$, 100), 458 ([M–$C_6H_7$NO-2CO]$^+$, 20), 430 ([M–$C_6H_7$NO-3CO]$^+$, 38), 402 ([M–$C_6H_7$NO-4CO]$^+$, 30), 374 ([M–$C_6H_7$NO-5CO]$^+$, 22), 358.0 ([M–$C_6H_7$NO-5CO-CH$_3$–H]$^+$, 50), 110.1 ([CH(furanyl)NMe+H]$^+$, 15), 73.1 ([Me$_3$Si]$^+$, 40); elemental analysis (%) calculated for $C_{18}H_{26}NO_6PSi_2W$: C 34.68, H 4.20, N 2.25; found: C 34.33, H 4.18, N 2.23.

**Synthesis of complex 3c.** A solution of 617 mg (1.0 mmol) of 2*H*-azaphosphirene complex **1** and 250 µL (2.0 mmol) of *N*-[(thiophen-2-yl)methylene]methanamine or 2-[(methylimino)-methyl]thiophene **2c** in 6.0 mL toluene is stirred for 3 h at 75 °C while the brown solution turned dark red. After removing all volatile components *in vacuo* ($10^{-2}$ mbar) the product was subsequently purified by column chromatography on neutral aluminium oxide (–30 °C, pentane–$Et_2O$: 5/1).

**Complex 3c.** Light brown solid, yield: 165 mg (0.26 mmol, 26%); only the analytical data of the major isomer are given: $^1$H NMR ($CDCl_3$): $\delta$ = -0.10 (s, 9H; Si(C$H_3$)$_3$), 0.32 (s, 9H; Si(C$H_3$)$_3$), 0.89 (d, $^2J$(P,H) = 16.4 Hz, 1H; C$H$(SiMe$_3$)$_2$), 2.66 (d, $^2J$(P,H) = 15.8 Hz, 3H; N–C$H_3$), 3.12 (d, $^2J$(P,H) = 6.6 Hz, 1H; P–C(*H*)-N), 7.12 ($m_c$, 2H; subst. ring H$^{3/4}$), 7.35 ($m_c$, 1H; subst. ring H$^5$). $^{13}$C{$^1$H} NMR ($CDCl_3$): $\delta$ = 196.3 (d, $^2J$(P,C) = 30.1 Hz; $CO_{trans}$), 196.3 ($d_{sat}$, $^2J$(P,C) = 7.7 Hz, $^1J$(W,C) = 125.3 Hz; $CO_{cis}$), 138.4 (d, $^2J$(P,C) = 4.6 Hz; *ipso*-C$_{thienyl}$), 127.8 (d, $^3J$(P,C) = 0.7 Hz; C$^3_{thienyl}$), 126.2 (d, $^4J$(P,C) = 0.8 Hz; C$^4_{thienyl}$), 121.2 (d, $^5J$(P,C) = 3.8 Hz; C$^5_{thienyl}$), 52.8 (d, $^{2+3}J$(P,C) = 2.4 Hz; NCH$_3$), 42.1 (d, $^{1+3}J$(P,C) = 2.4 Hz, PCN), 18.6 (d, $^2J$(P,C) = 26.9 Hz; CH(SiMe$_3$)$_2$), 1.9 (d, $^3J$(P,C) = 3.5 Hz; Si(CH$_3$)$_3$), 1.2 (d, $^3J$(P,C) = 3.9 Hz; Si(CH$_3$)$_3$); $^{29}$Si{$^1$H} NMR ($CDCl_3$): $\delta = 0.06$ ($d_{sat}$, $^2J$(P,Si) = 6.7 Hz), 2.08

($d_{sat}$, $^{2}J$(P,Si) = .5 Hz); $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): $\delta$ = –37.7 ($d_{sat}$, $^{1}J$(W,P) = 269.5 Hz); MS (EI, 70 eV, $^{184}W$): *m/z* (%): 639.0 ([M]$^+$, 13), 543.0 ([M–CH(thienyl)]$^+$, 10), 514.0 ([M–$C_6H_7NO$]$^+$, 13), 486 ([M–$C_6H_7NO$-CO]$^+$, 57), 458 ([M–$C_6H_7NO$-2CO]$^+$, 20), 430 ([M–$C_6H_7NO$-3CO]$^+$, 27), 402 ([M–$C_6H_7NO$-4CO]$^+$, 28), 374 ([M–$C_6H_7NO$-5CO]$^+$, 20), 358.0 ([M–$C_6H_7NO$-5CO-$CH_3$–H]$^+$, 50), 97.0 ([CH(thienyl)+H]$^+$, 15), 73.1 ([$Me_3Si$]$^+$, 40).

**Synthesis of complex 3d.** A solution of 617 mg (1.00 mmol) 2*H*-azaphosphirene complex **1** and 227 mg (1.00 mmol) *N*-[(ferrocenyl)methylene]methanamine or 2-((methylimino)-methyl)ferrocene **2d** in 1.5 mL toluene is stirred for 1.5 h at 75 °C. The brown solution turns dark red. After removing all volatile components *in vacuo* ($10^{-2}$ mbar) the product is subsequently purified by column chromatography on neutral aluminium oxide (–30 °C, n-pentane).

**Complex 3d.** Orange solid, yield: 535 mg (0.72 mmol, 72%); m.p. 99 °C (decomp.), $^{1}$H NMR ($CDCl_3$): $\delta$ = 0.04 (s, 9H; Si(C$H_3$)$_3$), 0.35 (s, 9H; Si(C$H_3$)$_3$), 1.01 (d, $^{2}J$(P,H) = 17.8 Hz, 1H; C$H$(SiMe$_3$)$_2$), 2.68 (d, $^{3}J$(P,H) = 15.7 Hz, 3H; NC$H_3$), 2.89 (d, $^{2}J$(P,H) = 8.3 Hz, 1H; PNC$H$), 4.01 ($m_c$, 2H; subst. ring), 4.05 (s, 5H; unsubst. ring), 4.13 ($m_c$, 1H; subst. ring), 4.24 ($m_c$, 1H; subst. ring); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): $\delta$ = 194.8 (d, $^{2}J$(P,C) = 29.4 Hz; $CO_{trans}$), 194.6 ($d_{sat}$, $^{2}J$(P,C) = 7.4 Hz, $^{1}J$(W,C) = 125.4 Hz; $CO_{cis}$), 83.0 (s, *ipso*-$C_{ferrocenyl}$), 67.5 (s, subst. cp ring), 67.2 (s, unsubst. cp ring), 66.5 (s, subst. cp ring), 65.5 (s, subst. cp ring), 65.0 (s, subst. cp ring), 52.8 (d, $^{2+3}J$(P,C) = 1.9 Hz; $NCH_3$), 40.4 (d, $^{1+3}J$(P,C) = 2.6 Hz, PCN), 17.2 (d, $^{2}J$(P,C) = 27.2 Hz; CH(SiMe$_3$)$_2$), 0.0 (d, $^{3}J$(P,C) = 3.2 Hz; Si($CH_3$)$_3$), -0.5 (d, $^{3}J$(P,C) = 3.9 Hz; Si($CH_3$)$_3$); $^{29}Si\{^{1}H\}$ NMR ($CDCl_3$): $\delta$ = 0.95 ($d_{sat}$, $^{2}J$(P,Si) = 6.5 Hz), 2.34 ($d_{sat}$, $^{2}J$(P,Si) = 3.2 Hz); $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): $\delta$ = -39.2 ($d_{sat}$, $^{1}J$(W,P) = 267.0 Hz); IR (KBr): $\tilde{\nu}$ = 2071.3 (m, sh, CO), 1988.6 (m, CO), 1929.1 (s, CO); UV/Vis (n-pentane): $\lambda_{max}$ (abs.) = 296.0 (0.068), 256.6 (0.300), 233.0 (0.851), 209.5 nm (0.088); MS (FAB pos., mNBA): *m/z* (%): 741.1 ([M+H]$^+$, 20), 657.1 ([M–3CO]$^+$, 22), 599.1 ([M–5CO]$^+$, 10), 358.0 (M–W(CO)$_5$-tms]$^+$, 24), 227 ([Fc-C=NMe]$^+$, 100); elemental analysis (%) calculated for $C_{24}H_{32}FeN_2O_5PSi_2W$: C 38.88, H 4.35, N 1.89; found: C 38.76, H 4.56, N 1.88.

**Synthesis of complex 3e.** A solution of 617 mg (1.0 mmol) 2*H*-azaphosphirene complex **1** and 250 µL (2.0 mmol) *N*-[(1-methyl-2-pyrryl)methylene]methanamine or 2-[(methylimino)methyl](*N*-methyl-1*H*-pyrrole) **2e** in 6.0 mL toluene is stirred for 3 h at 75 °C. The brown solution turns dark red. After removing all volatile components *in vacuo* ($10^{-2}$ mbar) the product is obtained as a mixture of diastereomers (ratio >100 : 1; major isomer: -42.0 ppm ($^{1}J$(W,P) = 265.2 Hz), minor isomer: –45.7 ppm and subsequently extracted with cold pentane. Complex decays at –50 °C on neutral aluminium oxide.

**Complex 3e.** Dark brown oil, yield: 516 mg (0.81 mmol, 81%); only the analytical data of the major isomer are given: $^{1}$H NMR ($CDCl_3$): $\delta$ = –0.10 (s, 9 H; Si(C$H_3$)$_3$), 0.34 (s, 9 H; Si(C$H_3$)$_3$), 1.22 (d, $^{2}J_{H,P}$ = 17.8 Hz, 1 H; PC$H$(SiMe$_3$)$_2$), 2.65 (d, $^{2}J_{P,H}$ = 16.0 Hz, 3 H; $NCH_3$), 2.99 (d, $^{2}J_{P,H}$ = 8.8 Hz, 1 H; PC$H$(1-methylpyrryl)), 3.69 (s, 3 H; 1-C$H_3$-pyrryl), 5.97 (m, 1 H; pyrryl-H$^3$), 6.12 (m, 1 H; pyrryl-H$^4$), 6.68 (m, 1 H; pyrryl-H$^5$); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): $\delta$ = 196.5 (d, $^{2}J$(P,C) = 39.7 Hz; $CO_{trans}$), 196.3 ($d_{sat}$, $^{2}J$(P,C) = 7.7 Hz, $^{1}J$(W,C) = 125.4 Hz; $CO_{cis}$), 127.7 (d, $^{2}J$(P,C) = 4.4 Hz; *ipso*-$C_{pyrryl}$), 123.7 (d, $^{5}J$(P,C) = 2.4 Hz; $C^{5}_{pyrryl}$), 107.4 (d, $^{4}J$(P,C) = 3.5 Hz; $C^{4}_{pyrryl}$), 107.1 (d, $^{3}J$(P,C) = 2.4 Hz; $C^{3}_{pyrryl}$), 50.7 (d, $^{2+3}J$(P,C) = 1.5 Hz; $NCH_3$), 42.3 (d, $^{1+3}J$(P,C) = 2.4 Hz, PCN), 33.9 (s, N-$CH_3$-pryrryl), 17.5 (d, $^{2}J$(P,C) = 25.6 Hz; CH(SiMe$_3$)$_2$), 2.0 (d, $^{3}J$(P,C) = 3.7 Hz,$^{1}J$(Si,C) = 52.6 Hz; Si($CH_3$)$_3$), 0.7 (d, $^{3}J$(P,C) = 3.8 Hz, $^{1}J$(Si,C) = 52.2 Hz; Si($CH_3$)$_3$); $^{29}Si\{^{1}H\}$ NMR ($CDCl_3$): $\delta$ = 0.06 ($d_{sat}$, $^{2}J$(P,Si) = 6.9 Hz, $^{1}J$(Si,C) = 52.3 Hz), 2.20 ($d_{sat}$, $^{2}J$(P,Si) = 3.1 Hz, $^{1}J$(Si,C) = 52.1 Hz); $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): $\delta$ = –40.7 ($d_{sat}$, $^{1}J$(W,P) = 265.8 Hz); MS (EI, 70 eV, $^{184}W$): *m/z* (%): 607.1 ([M-NMe]$^+$, 18), 122.1 ([CH(1-Me-pyrryl)NMe]$^+$, 18), 73.1 ([tms]$^+$, 40); elemental analysis (%) calculated for $C_{19}H_{29}N_2O_5PSi_2W$: C 35.86, H 4.59, N 4.40; found: C 35.26, H 4.64, N 4.20.

**Synthesis of 6a.** To a solution of 95 mg (0.15 mmol) of azaphosphiridine complex **3a** in 0.6 mL of $CD_2Cl_2$ at –70 °C in an NMR tube 13 µL (0.15 mmol) of TfOH were added. The light yellow solution turned greenish. At –70 °C NMR spectra were recorded.

**Complex 6a.** $^{1}$H NMR ($CD_2Cl_2$): $\delta$ = 0.00 (s, 9H; Si(C$H_3$)$_3$), 0.59 (s, 9H; Si(C$H_3$)$_3$), 1.94 (d, $^{2}J$(P,H) = 17.2 Hz, 1H; C$H$(SiMe$_3$)$_2$), 3.20 (s, br, 3H; NC$H_3$), 4.35 (s, br, 1H; PNC$H$), 7.67-7.76 (m, br, 5H; subst. Ph-Ring), 8.31 (s, 1H; N$H$Me); $^{13}C\{^{1}H\}$ NMR ($CD_2Cl_2$): $\delta$ = [$CO_{trans}$ was not observed] 192.7 ($d_{sat}$, br, $^{2}J$(P,C) = 4 Hz, $^{1}J$(W,C) = 128 Hz; $CO_{cis}$), 129.1 (s, br; subst. Ph-Ring), 128.5 (s, br; subst. Ph-Ring), 126.1 (s, br; subst. Ph-Ring), 126.0 (s, br; subst. Ph-Ring), 60.1 (s, br; PN*C*), 39.4 (d, br; N-*C*$H_3$), 17.7 (d, br; *C*H(SiMe$_3$)$_2$), 0.0 (s, br; Si(*C*$H_3$)$_3$), -0.2 (s, br; Si(*C*$H_3$)$_3$); $^{29}Si\{^{1}H\}$ NMR ($CD_2Cl_2$): $\delta$ = 4.95 (d, $^{2}J$(P,Si) = 7.2 Hz), 5.21 (s); $^{31}P\{^{1}H\}$ NMR ($CD_2Cl_2$): $\delta$ = 45.1 ($d_{sat}$, $^{1}J$(W,P) = 298.2 Hz); IR (Nujol): $\tilde{\nu}$ = 2074.4 (m, CO), 1987.9 (w, CO) 1939.9 cm$^{-1}$ (s, broad CO); UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ (abs.) = 296.0 (0.068), 256.5 (0.300), 233.0 (0.851), 209.5 nm (0.088).

**Synthesis of 8a.** To a solution of 279 mg (0.44 mmol) of azaphosphiridine complex **3a** in 6.0 mL of $CH_2Cl_2$ 39 µL (0.48 mmol) of dimethyl cyanamide and 39 µL (0.44 mmol) of TfOH were added. After 2 min, 62 µL (0.44 mmol) of $NEt_3$ was added to the solution at ambient temperature. After filtration and removal of all volatile components *in vacuo* ($10^{-2}$ mbar) a mixture of diastereomers (ratio 11 : 2; major isomer: 103.3 ppm ($^{1}J$(W,P) = 281.0 Hz), minor isomer: 90.8 ppm ($^{1}J$(W,P) = 269.6 Hz) was obtained. The major isomer was purified by column chromatography on neutral aluminium oxide (–30 °C, first petroleum ether/$Et_2O$: 10/1, then pure $CH_2Cl_2$).

**Complex 8a.** Light orange solid, yield: 122 mg (0.17 mmol, 40%); m.p. 154 °C (decomp.); $^{1}$H NMR ($CDCl_3$): $\delta$ = 0.28 (s, 9H; Si(C$H_3$)$_3$), 0.40 (s, 9H; Si(C$H_3$)$_3$), 1.68 (d, $^{2}J$(P,H) = 9.1 Hz, 1H; C$H$(SiMe$_3$)$_2$), 2.90 (s, 6H; N(C$H_3$)$_2$), 2.93 (s, 3H; NC$H_3$), 4.85 (s, 1H, PC(*H*)N), 7.25 ($m_c$, 1H; $H_{phenyl}$), 7.28 ($m_c$, 1H; $H_{phenyl}$), 7.37($m_c$, 2H; $H_{phenyl}$), 7.39 ppm ($m_c$, 1H; $H_{phenyl}$); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): $\delta$ = 199.8 (d, $^{2}J$(P,C) = 25.9 Hz; $CO_{trans}$), 196.8 ($d_{sat}$, $^{2}J$(P,C) = 8.1 Hz, $^{1}J$(W,C) = 126.7 Hz; $CO_{cis}$), 161.6 (d, $^{2+3}J$(P,C) = 5.2 Hz; NCN), 136.7 (d, $^{2}J$(P,C) = 5.2 Hz; *ipso*-$C_{phenyl}$), 127.8 (d, $^{4}J$(P,C) = 1.9 Hz; *meta*-$C_{phenyl}$), 127.4 (d, $^{3}J$(P,C) = 3.3 Hz; *ortho*-$C_{phenyl}$), 127.2 (d, $^{5}J$(P,C) = 1.9 Hz; *para*-$C_{phenyl}$), 78.0 (d, $^{1+4}J$(P,C) = 5.5 Hz; PCN), 64.8 (s, $NCH_3$), 39.8 (s, N($CH_3$)$_2$), 39.4 (s; N($CH_3$)$_2$), 31.7 (d, $^{2}J$(P,C) = 13.9 Hz; CH(SiMe$_3$)$_2$), 2.5 (d, $^{3}J$(P,C) = 1.9 Hz; Si($CH_3$)$_3$), 1.7 (d, $^{3}J$(P,C) = 4.5 Hz; Si($CH_3$)$_3$); $^{31}P\{^{1}H\}$ NMR

($CDCl_3$): $\delta = 103.3$ ($d_{sat}$, $^1J$(W,P) = 281.0 Hz); IR (Nujol): $\tilde{\nu}$ = 2067.8 (w, CO), 1985.1 (w, CO), 1929.9 $cm^{-1}$ (s, CO), 1899.8 (s), 1863.3 (m); UV/Vis (n-pentane): $\lambda_{max}$ (abs.) = 297.5 (0.069), 287.0 (0.062), 258.0 (0.281), 233.0 (0.955), 212.0 nm (0.242); MS (EI, 70 eV, $^{184}$W): *m/z* (%):703.1 (2) $[M]^+$, 675.2 (40) $[M–CO]^+$, 647.2 (25) $[M–2CO]^+$, 619.2 (100) $[M–3CO]^+$, 563.2 (25) $[M–5CO]^+$, 549.1 (45) $[M–5CO\text{-}Me+H]^+$, 491.1 (30) $[M–5CO\text{-}Me_3Si]^+$, 220.1 (5) $M–W(CO)_5\text{-}CHtms_2]^+$, 118.1 (10) $[PhC{=}NMe]^+$, 73.1 (50) $[Me_3Si]^+$; elemental analysis (%) calculated for $C_{23}H_{34}N_3O_5PSi_2W$: C 39.27, H 4.87, N 5.97; found: C 38.89, H 5.10, N 5.61.

**Synthesis of 8d.** To a solution of 300 mg (0.41 mmol) azaphosphiridine complex **3d** and 37 µL (0.45 mmol) dimethyl cyanamide in 3.0 mL $CH_2Cl_2$ 36 µL (0.41 mmol) TfOH and, after 5 min, 57 µL (0.41 mmol) $NEt_3$ were added at room temperature. The light orange solution turned into a red brown one. After removal of all volatile components *in vacuo* ($10^{-2}$ mbar) a mixture of diastereomers (ratio 22 : 1; major isomer: 103.1 ppm ($^1J$(W,P) = 279.8 Hz), minor isomer: 91.0 ppm ($^1J$(W,P) = 263.5 Hz) was obtained as a brown solid and subsequently purified by column chromatography on neutral aluminium oxide (–30 °C, pure petroleum ether).

**Complex 8d.** Light orange solid, yield: 97 mg (0.12 mmol, 29%); m.p. 167 °C (decomp.); $^1$H NMR ($CDCl_3$): $\delta = 0.19$ (s, 9H; $Si(CH_3)_3$), 0.26 (s, 9H; $Si(CH_3)_3$), 1.22 (d, $^2J$(P,H) = 19.3 Hz, 1H; $CH(SiMe_3)_2$), 2.91 (s, 6H; $N(CH_3)_2$), 3.30 (s, 3H; $NCH_3$), 3.84 (s, br, 1H, PC(*H*)NMe), 4.07 ($m_c$, 1H; $H_{Fc\text{-}4/5}$), 4.10 (s, 5H; $H_{Fc\text{-}unsubst}$), 4.21 ($m_c$, 1H; $H_{Fc\text{-}4/5}$), 4.35 ($m_c$, 1H; $H_{Fc\text{-}2/3}$), 4.43 ($m_c$, 1H; $H_{Fc\text{-}2/3}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 199.2$ (d, br, $^1J$(W,C) = 22.7 Hz; $CO_{trans}$), 196.8 ($d_{sat}$, $^1J$(W,C) = 7.8 Hz, $^2J$(P,C) = 127.0 Hz, $CO_{cis}$), 164.6 (s, NCN), 128.8 (s, PCN), 67.8 (s, *ipso*-$C_{ferrocenyl}$), 68.0 (s, subst. Cp ring), 67.6 (s, not subst. Cp ring), 66.4 (s, subst. Cp ring), 66.3 (s, subst. Cp ring), 65.9 (s, subst. Cp ring), 39.9 (s, N-$CH_3$), 39.3 (s, $N(CH_3)_2$), 30.7 (s, $CH(SiMe_3)_2$), 2.22 (s, $Si(CH_3)_3$), 2.18 (s, $Si(CH_3)_3$); $^{29}Si\{^1H\}$ NMR ($CDCl_3$): $\delta$ = –1.8 (d, $^2J$(P,Si) = 2.6 Hz), 1.0 (d, $^2J$(P,Si) = 4.8 Hz); $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 101.9$ ($d_{sat}$, $^1J$(W,P) = 278.5 Hz); IR (Nujol): $\tilde{\nu}$ = 2065.9 (m, CO), 1977.3 (m, CO) 1932.5 $cm^{-1}$ (s, CO). 1916.6 (s), 1899.0 (s); UV/Vis (n-pentane): $\lambda_{max}$ (abs.) = 296.0 (0.068), 256.0 (0.300), 233.0 (0.851), 209.5 nm (0.088); MS (EI, 70 eV, $^{184}$W): *m/z* (%):811.1 (15) $[M]^+$, 783.1 (40) $[M–CO]^+$, 727.1 (30) $[M–3CO]^+$, 699.1 (100) $[M–4CO]^+$, 671.1 (20) $[M–5CO]^+$, 657.1 (100) $[M–5CO\text{-}Me+H]^+$, 629.1 (25) $[M–Cp\text{-}Me_3Si\text{-}NMe_2]^+$, 599.1 (25) $[M–Cp_2Fe\text{-}CO]^+$, 512.0 (10) $[M–5CO\text{-}CH(SiMe_3)_2]^+$, 486.0 (70) $[M–5CO\text{-}Cp_2Fe]^+$, 414.1 (10) $[M–W(CO)_5\text{-}Me_3Si]^+$, 328.1 (25) $[M–W(CO)_5\text{-}CH(SiMe_3)_2]^+$, 227.1 (40) $[Cp_2Fe–C(H){=}NMe]^+$, 143.1 (90) $[M–W(CO)_5\text{-}CH(SiMe_3)_2\text{-}Cp_2Fe]^+$, 73.1 (100) $[Me_3Si]^+$. Elemental analysis (%) calculated for $C_{27}H_{38}FeN_3O_5PSi_2W$ 39.96, H 4.72, N 5.18; found: C 39.98, H 4.76, N 4.97.

## Computational methods

DFT calculations on the mechanism of the acid-induced ring expansion were carried out with the TURBOMOLE V5.8 program package.[41a] For optimizations[41b] the gradient corrected exchange functional by Becke[42] (B88) in combination with the gradient corrected correlation functional by Lee, Yang and Parr[43] (LYP) with the RI approximation[44] and the valence-double-ζ basis set SV(P)[45] was used. For the oxygen atoms belonging to triflate (or triflic acid) the basis was augmented by uncontracted Gaussian functions with an exponent of 0.0845 (one of each type), and the nitrogen and sulfur basis sets were augmented by uncontracted basis functions with exponents of 0.0639 (one of each type) for nitrogen and 0.0405 (one of each type) for sulfur. For tungsten the effective core potential ECP-60-MWB[46] derived from the Stuttgart–Dresden group was used. The influence of the polar solvent was taken into account by employing the COSMO approach[47] with $\varepsilon = 8.93$. For cavity construction the atomic radii of Bondi[48] were used which are obtained from crystallographic data. For tungsten the atomic radius was set to 2.2230 Å. The stationary points were characterized by numerical vibrational frequencies calculations using the SNF 3.3.0 program package.[49] Single point calculations were carried out using the Three Parameter Hybrid Functional Becke3[50] (B3) in combination with the correlation functional LYP[43] using the valence-triple-ζ basis set TZVP,[51] which was augmented as specified above, and the effective core potential ECP-60-MWB[46] for tungsten. The COSMO approach[47] was employed with the same parameters as used for the optimizations. Zero point corrections and thermal corrections to enthalpies and free energies were adopted from the optimizations on the RI-BLYP/aug-SV(P), ECP-60-MWB(W) level. It has been shown that this approach is appropriate for reactions of epoxide, aziridine and thiirane with methanethiolate.[52]

## X-ray crystallographic analyses of 3b,c,d and 8a,d

Suitable single crystals were obtained from concentrated n-pentane or $Et_2O$ solutions upon decreasing the temperature from ambient temperature to +4 °C. Data were collected on Nonius KappaCCD diffractometer equipped with a low-temperature device (Cryostream, Oxford Cryosystems) at 123(2) K using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by Patterson methods (SHELXS-97) and refined by full-matrix least squares on $F^2$ (SHELXL-97).[53] All non-hydrogens were refined anisotropically. The hydrogen atoms were included isotropically using the riding model on the bound atoms. Absorption corrections were carried out by integration (**3c**) or semi-empirically from equivalents (**3b**,**d** and **8a**,**d**) (min./max. transmissions = 0.28704/0.41248 (**3b**), 0.4876/0.6961 (**3c**), 0.48284/0.67580 (**3d**), 0.40853/0.61286 (**8a**), and 0.5996/0.8877 (**8d**)).

**Crystal structure data of complex 3b ($C_{18}H_{26}NO_6PSi_2W$).** Crystal size 0.40 × 0.31 × 0.27 mm, triclinic, *P*-1, $a = 9.2166(3)$, $b = 9.7609(5)$, $c = 15.0733(4)$ Å, $\alpha = 73.292(2)$, $\beta = 74.587(2)$, $\gamma = 78.755(2)°$, $V = 1241.70(8)$ Å$^3$, $Z = 2$, $\rho_c = 1.667$ Mg m$^{-3}$, $2\theta_{max} = 56°$, collected (independent) reflections = 14037 (5794), $R_{int} = 0.0593$, $\mu = 4.843$ mm$^{-1}$, 269 refined parameters, 0 restraints, $R_1$ (for $I > 2\sigma(I)$) = 0.0315, $wR_2$ (for all data) = 0.0661, max./min. residual electron density = 1.305/–3.531 e Å$^{-3}$.

**Crystal structure data of complex 3c ($C_{18}H_{26}NO_5PSSi_2W$).** The thiophene ring is disordered, major layer: 84%: crystal size 0.22 × 0.15 × 0.13 mm, triclinic, *P*-1, $a = 9.3006(4)$, $b = 9.8061(4)$, $c = 15.3241(6)$ Å, $\alpha = 72.925(3)°$, $\beta = 75.155(3)°$, $\gamma = 77.227(3)°$, $V = 1275.21(9)$ Å$^3$, $Z = 2$, $\rho_c = 1.665$ Mg m$^{-3}$, $2\theta_{max}$ = 56°, collected (independent) reflections = 10310 (5790), $R_{int}$ = 0.0282, $\mu = 4.794$ mm$^{-1}$, 289 refined parameters, 6 restraints, $R_1$

(for $I > 2\sigma(I)$) = 0.0322, $wR_2$ (for all data) = 0.0850, max./min. residual electron density = 1.191/−1.253 e Å$^{-3}$.

**Crystal structure data of complex 3d ($C_{24}H_{32}NO_5PFeSi_2W$).** Crystal size 0.20 × 0.20 × 0.08 mm, triclinic, *P*-1, $a$ = 14.5415(2), $b$ = 16.5338(2), $c$ = 19.5865(2) Å, $\alpha$ = 109.0050(7), $\beta$ = 90.3535(6), $\gamma$ = 97.4184 (6)°, $V$ = 4409.30(9) Å$^3$, $Z$ = 6, $\rho_c$ = 1.675 Mg m$^{-3}$, $2\theta_{max}$ = 58°, collected (independent) reflections = 49604 (22997), $R_{int}$ = 0.0853, $\mu$ = 4.572 mm$^{-1}$, 946 refined parameters, 0 restraints, $R_1$ (for $I > 2\sigma(I)$) = 0.0421, $wR_2$ (for all data) = 0.0738, max./min. residual electron density = 1.989/−1.823 e Å$^{-3}$.

**Crystal structure data of complex 8a ($C_{23}H_{34}N_3O_5PSi_2W$).** Crystal size 0.32 × 0.24 × 0.12 mm, triclinic, *P*-1, $a$ = 9.8089(4), $b$ = 10.0809(5), $c$ = 16.4987(9) Å, $\alpha$ = 86.801(2), $\beta$ = 87.041(3), $\gamma$ = 66.682(3)°, $V$ = 1495.07(13) Å$^3$, $Z$ = 2, $\rho_c$ = 1.563 Mg m$^{-3}$, $2\theta_{max}$ = 60°, collected (independent) reflections = 17963 (8457), $R_{int}$ = 0.0587, $\mu$ = 4.032 mm$^{-1}$, 325 refined parameters, 0 restraints, $R_1$ (for $I > 2\sigma(I)$) = 0.0319, $wR_2$ (for all data) = 0.0561, max./min. residual electron density = 1.501/−1.330 e Å$^{-3}$.

**Crystal structure data of complex 8d ($C_{27}H_{38}N_3O_5PSi_2W$).** Crystal size 0.14 × 0.13 × 0.03 mm, monoclinic, $P2_1$ (No. 4), $a$ = 10.642(1), $b$ = 13.2433(8), $c$ = 11.749(1) Å, $\beta$ = 91.68(0), $V$ = 1655.14(27) Å$^3$, $Z$ = 2, $\rho_c$ = 1.628 Mg m$^{-3}$, $2\theta_{max}$ = 51°, collected (independent) reflections = 5726 (4789), $R_{int}$ = 0.0505, $\mu$ = 4.069 mm$^{-1}$, 370 refined parameters, 1 restraints, $R_1$ (for $I > 2\sigma(I)$) = 0.0365, $wR_2$ (for all data) = 0.0724, max./min. residual electron density = 1.159/−1.988 e Å$^{-3}$.

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at $m/z$ = 675.1 [M+H+MeCN]$^+$, which can be assigned to the ring expansion product similar to complexes **7a**,**d** bearing methyl group instead of the dimethylamino group. The single electron transfer-induced ring expansion of *C*-ferrocenyl substituted 2*H*-azaphosphirene complexes was published recently. (H. Helten, S. Fankel, O. Feier-Iova, M. Nieger, A. Espinosa Ferao and R. Streubel, *Eur. J. Inorg. Chem.*, 2009, 3226–3237.) Using nitromethane as solvent and FT-ICR-MS technique complex **6a** $m/z$ = 634.0924 (calc. 634.0826) was found.

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34 Ferrocenyl carboxaldehyde shows a reversible oxidation at $E_{\frac{1}{2}}$ = 0.807 V while the reversible wave for ferrocene (FcH) is at $E_{\frac{1}{2}}$ = 0.530 V. CV data for Ferrocene: $E_{pa}$ = 0.541 V, $E_{pk}$ = 0.482 V, $E_{pa} - E_p/2$ = 0.066 V, $E_{pk} - E_p/2$ = –0.069 V, $I_{pa} = 1.231 \times 10^{-5}$ A, $I_{pk} = -1.231 \times 10^{-5}$ A; Ferrocenyl carboxaldehyde: $E_{pa}$ = 0.811 V, $E_{pk}$ = 0.797 V, $E_{pa} - E_p/2$ = 0.041 V, $E_{pk} - E_p/2$ = –0.042 V, $I_{pa} = 3.379 \times 10^{-5}$ A, $I_{pk} = -3.597 \times 10^{-5}$ A; **2d**: $E_{pa}$ = 0.665 V, $E_{pk}$ = 0.629 V, $E_{pa} - E_p/2$ = 0.042 V, $E_{pk} - E_p/2$ = –0.046 V, $I_{pa} = 1.011 \times 10^{-5}$ A, $I_{pk} = -1.046 \times 10^{-5}$ A; **3d**: $E_{pa}$ = 0.575 V, $E_{pa} - E_p/2$ = 0.052 V, $I_{pa} = 0.926 \times 10^{-5}$ A; **8d**: $E_{pa}$ = 0.597 V, $E_{pk}$ = 0.498 V, $E_{pa} - E_p/2$ = 0.065 V, $E_{pk} - E_p/2$ = –0.069 V, $I_{pa} = 1.231 \times 10^{-5}$ A, $I_{pk} = -1.199 \times 10^{-5}$ A.

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