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Click reactions of 2*H*-azaphosphirene chromium and molybdenum complexes and a surprisingly facile access to a 2*H*-1,4,2-diazaphosphole derivative

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Dedicated to Prof. F. Mathey on the occasion of his 70th birthday

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ABSTRACT

Ring expansion reactions of 2*H*-azaphosphirene chromium and molybdenum complexes **1a,b** with dimethyl cyanamide, triflic acid, and, subsequently at ambient temperature, with triethylamine gave a mixture of the respective 2*H*-1,4,2-diazaphosphole complex **2a,b** and the non-ligated heterocycle **3**. If the deprotonation with NEt₃ was carried out at low temperature, the selective formation of complexes **2a,b** was observed, which were isolated in excellent yields and fully characterized (including single-crystal X-ray crystallography). Experimental and computational results revealed that the P, Cr and P, Mo bonds of 2*H*-1,4,2-diazaphosphole complexes are significantly weakened upon *N*-protonation of the heterocyclic ligand. When mixtures of **1a,b**, TfOH, and Me₂NCN were warmed to ambient temperature, the primarily formed *N*-protonated of 2*H*-1,4,2-diazaphosphole complexes **4a,b** could be observed by ³¹P NMR spectroscopy. The latter underwent decomplexation to give the *N*-protonated free ligand **5**, which could be isolated from a one-pot reaction of **1b** with TfOH and Me₂NCN by adding NEt₃ to a solution of intermediately formed **5**.

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achieved *via* formal insertion of a nitrile into the P–N bond of **I** using trifluoromethane sulfonic acid (CF₃SO₃H; hereafter referred

1. Introduction

The construction of N-heterocycles such as triazoles using click reactions [1–5] based on facile and reliable synthetic protocols, has received considerable interest during the last decade, as it can be applied to various fields of research [6–8]. Nonetheless, this chemistry has yet to be extended to heavier main group element heterocycles. A promising approach to gain access to new and novel phosphorus heterocycles [9,10] is the ring expansion of small, strained heterocycles [11–16] by selective activation of an endocyclic bond. In particular, the insertion of easily available diatomic π -systems such as nitriles, alkynes, alkenes, or carbonyl derivatives into endocyclic P,N bonds is a current challenge of special interest. A recent report demonstrated that exocyclic P^{III}–N bonds of cyclodiphosphazanes are even more reactive than endocyclic bonds [17].

Recently, we developed a novel and facile methodology for the ring expansion of three-membered P-heterocyclic ligands in the coordination sphere of tungsten. For example, ring expansion of 2*H*-azaphosphirene complexes (**I**) [15,16] leading to 2*H*-1,4,2-diazaphosphole complexes (**II**: a = b = RCN; Scheme 1) was

to as triflic acid or TfOH) and, subsequently, a nitrogen base such as triethylamine was used for deprotonation [18–20].
We recently demonstrated that the new concept can also be applied to the atom efficient synthesis of 2,3-dihydro-1,3-aza-phosphete, 3*H*-1,3-azaphosphole, and 1,3,5-oxazaphosphol-3-ene

physica to the atom enterint synthesis of 2,3-adhydro1,3-azaphosphete, 3*H*-1,3-azaphosphole, and 1,3,5-oxazaphosphol-3-ene complexes *via* insertion of an isonitrile, an alkyne [21], or carbonyl derivatives [22], respectively. Furthermore, we showed that it can easily be extended to oxaphosphirane [23,24] and azaphosphiridine [25] complex chemistry, thus establishing the click chemistry concept to the field of strained phosphorus heterocycles; separation *via* column chromatography is necessary, sometimes. Mechanistic studies revealed that the heteroatom (N or O) of the respective three-membered ring system is protonated in the first reaction step [18,21,23–27], which leads to ring opening in the cases of 2*H*-azaphosphirene [18,21] and oxaphosphirane complexes [23,24,26,27]. 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 [25].

Herein, we report the extension of the new concept to reactions of 2H-azaphosphirene chromium and molybdenum complexes, which gives access – not only to 2H-1,4,2-diaza-phosphole chromium and molybdenum complexes – but also to the free (*N*-protonated or neutral) ligands in a one-pot reaction.



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Scheme 1. 2*H*-Azaphosphirene complexes (**I**), five-membered phosphorus heterocyclic complexes **II** derived from **I**, oxaphosphirane and/or azaphosphiridine complexes **III**, and five-membered phosphorus heterocycles **IV** derived from **III** $(a = b: \pi$ -system; [W] = W(CO)₅; **III**, **IV**: E = O, NMe).

2. Experimental

2.1. 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. 2H-Azaphosphirene complexes **1a**,**b** [28] were prepared according to the method described in the literature. Dimethyl cyanamide was purchased from Acros and distilled from CaH₂. 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 ($\lambda = 190-1100 \text{ nm}$) 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 C₆D₆ or CD₂Cl₂ as solvent and internal standard; coupling constants *I* are reported in Hz, chemical shifts in ppm relative to tetramethylsilane (¹H: 300.13, ¹³C: 75.5, ²⁹Si: 59.6 MHz), nitromethane (¹⁵N: 30.4 MHz), and 85% H₃PO₄ (³¹P: 121.5 MHz). Mass spectra were recorded on a Kratos Concept 1H (FAB+, mNBA) spectrometer or a MAT 95 XL Finnigan spectrometer (EI, 70 eV); selected data are given.

2.2. Synthesis of [2-bis(trimethylsilyl)methyl-5-dimethylamino-3-phenyl-2H-1,4,2-diazaphosphole- κ P]pentacarbonylchromium(0) (**2a**)

To a stirred solution of 250 mg (0.51 mmol) of 2*H*-azaphosphirene complex **1a** in 7 mL of CH₂Cl₂ were added consecutively 45 μ L (0.55 mmol) of dimethyl cyanamide and 46 μ L (0.52 mmol) of TfOH at -30 °C while the initially yellow colored solution turned deep red. After 1 min 74 μ L (0.53 mmol) of NEt₃ was added while the reaction mixture turned light red. Then, all volatiles were removed *in vacuo* ($\sim 10^{-2}$ mbar), and the product was purified by column chromatography on silica (-30 °C, 2×6 cm, petroleum ether/Et₂O: 100/1). Evaporation of the solvents of the first fraction ($\sim 10^{-2}$ mbar) yielded **2a**.

2a: Orange solid; yield: 242 mg (0.44 mmol, 85%); m.p.: 110 °C; ¹H NMR (300.13 MHz, C₆D₆): $\delta = -0.19$ (s_{sat}, |²J_{SiH}| = 6.5 Hz, |¹J_{CH}| = 119.6 Hz, 9H; Si(CH₃)₃), 0.50 (s_{sat}, |²J_{SiH}| = 6.5 Hz, |¹J_{CH}| = 119.7 Hz, 9H; Si(CH₃)₃), 1.02 (d, |²J_{PH}| = 2.7 Hz, 1H; CH(SiMe₃)₂), 2.80 (s, 3H; NCH₃), 2.95 (s, 3H; NCH₃), 7.16 (m_c, 3H; *meta* + *para*-H_{phenyl}), 8.15 (m_c, 2H; *ortho*-H_{phenyl}); ¹³C{¹H} NMR (75.5 MHz, C₆D₆): $\delta = 3.2$ (d_{sat}, |³J_{PC}| = 1.9 Hz, |¹J_{SiC}| = 52.0 Hz; Si(CH₃)₃), 4.1 (d_{sat}, |³J_{PC}| = 2.3 Hz, |¹J_{SiC}| = 53.0 Hz; Si(CH₃)₃), 22.5 (d, |¹J_{PC}| = 9.7 Hz; CH(SiMe₃)₂), 37.6 (s; NCH₃), 37.7 (s; NCH₃), 128.7 (s; *meta*-C_{phenyl}), 131.6 (d, |³J_{PC}| = 1.6 Hz; *ortho*-C_{phenyl}), 133.1 (s; *para*-C_{phenyl}), 133.2 (d, |²J_{PC}| = 20.7 Hz; *ipso*-C_{phenyl}), 163.7 (s; PNC), 200.5 (d, |¹⁺⁴J_{PC}| = 31.7 Hz; PCN), 217.4 (d, |²J_{PC}| = 12.6 Hz; CO_{cis}), 222.0 (d, |²J_{PC}| = 6.8 Hz; CO_{trans}); ²⁹Si{¹H} NMR (59.6 MHz, C₆D₆): $\delta = 1.4$ (d_{sat}, |²J_{PSi}| = 11.0 Hz, |¹J_{SiC}| = 52.2 Hz), 2.3 (d_{sat}, |²J_{PSi}| = 3.3 Hz, |¹J_{SiC}| = 53.0 Hz); ³¹P NMR (121.5 MHz, C₆D₆): δ = 146.3 (s); IR (KBr): nu(tilde) = 2959 (w, CH₃/CH), 2931 (w, CH₃/CH), 2901 (w, CH₃/CH), 2855 (w, CH₃/CH), 2059 (m, sh, CO), 1981 (m, sh, CO), 1927 (s, CO), 1917 (s, CO), 1606 (m, CN), 1538 cm⁻¹ (w, CN); UV–Vis (*n*-pentane): λ_{max} (abs.) = 202 (sh, 0.901), 209 (sh, 1.012), 225 (1.217), 234 (sh, 1.156), 253 (sh, 0.951), 286 (0.458), 351 (0.102), 390 (0.082), 439 nm (sh, 0.049); MS (FAB+, ⁵²Cr): *m*/*z* (%): 443.1 ([M–4CO]⁺, 76), 415.1 ([M–5CO]⁺, 100), 400.1 ([M–5CO–CH₃]⁺, 46), 364.2 ([M+H–W(CO)₅]⁺, 63); MS (EI, ⁵²Cr): *m*/*z* (%): 555.1 ([M]⁺, 48), 540.1 ([M–CCI]⁺, 100), 400.1 ([M–5CO–CH₃]⁺, 67), 363.1 ([M–Cr(CO)₅]⁺, 36), 290.1 ([M–Cr(CO)₅–SiMe₃]⁺, 31), 73.0 ([SiMe₃]⁺, 48); elemental analysis (%) *Anal.* Calc. for C₂₂H₃₀CrN₃O₅PSi₂: C, 47.56; H, 5.44; N, 7.56. Found: C, 47.09; H, 5.66; N, 7.36%.

2.3. Synthesis of [2-bis(trimethylsilyl)methyl-5-dimethylamino-3-phenyl-2H-1,4,2-diazaphosphole-κP]pentacarbonylmolybdenum(0) (**2b**)

To a stirred solution of 273 mg (0.52 mmol) of 2*H*-azaphosphirene complex **1b** in 7 mL of CH₂Cl₂ were added consecutively 45 μ L (0.55 mmol) of dimethyl cyanamide and 46 μ L (0.52 mmol) of TfOH at -30 °C while the initially yellow colored solution turned deep red. After 2 min 74 μ L (0.53 mmol) of NEt₃ was added while the reaction mixture turned light orange. Then, all volatiles were removed *in vacuo* (~10⁻² mbar), and the product was purified by column chromatography on silica (-30 °C, 2×6 cm, petroleum ether/Et₂O: 100/1). Evaporation of the solvents of the first fraction (~10⁻² mbar) yielded **2b**.

2b: Yellow solid; yield: 274 mg (0.46 mmol, 89%); m.p.: 104 °C (decomp.); ¹H NMR (300.13 MHz, C_6D_6): $\delta = -0.18$ (s_{sat}, $|^{2}J_{SiH}| = 6.2 \text{ Hz}, |^{1}J_{CH}| = 119.5 \text{ Hz}, 9\text{H}; Si(CH_{3})_{3}), 0.51$ (s_{sat}, $|^{2}J_{\text{SiH}}| = 6.4 \text{ Hz}, |^{1}J_{\text{CH}}| = 119.8 \text{ Hz}, 9\text{H}; \text{Si}(\text{CH}_{3})_{3}), 0.91$ (d. $|^{2}J_{PH}| = 2.4 \text{ Hz}, 1\text{H}; CH(SiMe_{3})_{2}), 2.82 \text{ (s, 3H; NCH}_{3}), 2.98 \text{ (s, 3H; }$ NCH₃), 7.16 (m_c, 3H; meta + para-H_{phenyl}), 8.17 (m_c, 2H; ortho-H_{phe-} _{nyl}); ¹³C{¹H} NMR (75.5 MHz, C_6D_6): $\delta = 3.1$ (d_{sat} , $|^3J_{PC}| = 1.6$ Hz, $|^{1}J_{SiC}| = 52.0 \text{ Hz}; \text{ Si}(CH_{3})_{3}), 3.9 (d_{sat}, |^{3}J_{PC}| = 2.6 \text{ Hz}, |^{1}J_{SiC}| = 52.9 \text{ Hz};$ Si(CH₃)₃), 21.4 (d, $|{}^{1}J_{PC}|$ = 11.6 Hz; CH(SiMe₃)₂), 37.7 (s; NCH₃), 37.7 (s; NCH₃), 128.9 (s; *meta*-C_{phenvl}), 131.3 (d, $|{}^{3}J_{PC}|$ = 2.6 Hz; ortho-C_{phenyl}), 133.1 (d, $|^{2}J_{PC}| = 20.4 \text{ Hz}$; *ipso*-C_{phenyl}), 133.2 (s; *para*-C_{phenyl}), 164.7 (d, $|^{2+3}J_{PC}| = 0.7$ Hz; PNC), 201.3 (d, $|^{1+4}J_{PC}| = 29.7 \text{ Hz}; \text{ PCN}$, 206.5 (d, $|^{2}J_{PC}| = 8.4 \text{ Hz}; \text{ CO}_{cis}$), 211.1 (d, $|^{2}J_{PC}| = 23.0 \text{ Hz}; \text{ CO}_{trans}); ^{29}\text{Si}\{^{1}\text{H}\} \text{ NMR} (59.6 \text{ MHz}, \text{ C}_{6}\text{D}_{6}): \delta = 2.2$ $(d_{sat}, |^2 J_{PSi}| = 11.8 \text{ Hz}, |^1 J_{SiC}| = 52.0 \text{ Hz}), 2.3 (d_{sat}, |^2 J_{PSi}| = 1.3 \text{ Hz},$ ${}^{1}J_{\text{SiC}}$ = 53.0 Hz); ³¹P NMR (121.5 MHz, C₆D₆): δ = 122.7 (s); IR (KBr): nu(tilde) = 2957 (w, CH₃/CH), 2930 (w, CH₃/CH), 2901 (w, CH₃/CH), 2855 (w, CH₃/CH), 2070 (m, sh, CO), 1988 (m, sh, CO), 1952 (s, CO), 1929 (s, CO), 1919 (s, CO), 1604 (m, CN), 1538 cm⁻¹ (w, CN); UV–Vis (*n*-pentane): λ_{max} (abs.) = 208 (sh, 0.758), 228 (1.013), 234 (1.016), 250 (sh, 0.828), 286 (0.306), 348 (0.080), 396 nm (0.058); MS (FAB+, ⁹⁸Mo): m/z (%): 602.0 ([M+H]⁺, 3), 545.1 ([M-2CO]⁺, 21), 447.0 ([M+H-5CO-CH₃]⁺, 16), 364.2 ([M+H–W(CO)₅]⁺, 100); MS (EI, ⁹⁸Mo): *m*/*z* (%): 601.1 ([M]⁺, 4), 573.1 ($[M-CO]^+$, 11), 545.1 ($[M-2CO]^+$, 21), 447.0 ($[M-3CO-Me_2NCN]^+$, 37), 363.2 ($[M-Mo(CO)_5]^+$, 94), 290.1 ($[M-Mo(CO)_5]^+$, 94), 290.1 ([M-Mo(CO)₅-SiMe₃]⁺, 84), 190.0 ([Me₃SiPC(H)SiMe₃]⁺, 22), 73.0 $([SiMe_3]^+, 100)$; elemental analysis (%) Anal. Calc. for C₂₂H₃₀Mo-N₃O₅PSi₂: C, 44.07; H, 5.04; N, 7.01. Found: C, 44.20; H, 5.06; N, 6.85%

2.4. Synthesis of 2-bis(trimethylsilyl)methyl-5-dimethylamino-3-phenyl-2H-1,4,2-diazaphosphole (**3**)

To a stirred solution of 100 mg (0.19 mmol) of 2*H*-azaphosphirene complex **1b** in 4 mL of CH_2Cl_2 were added consecutively 16 μ L

(0.20 mmol) of dimethyl cyanamide and 17 μ L (0.19 mmol) of TfOH at -60 °C while the initially yellow colored solution turned deep red. After 6 min the cooling bath was removed, and the reaction mixture turned brownish while warming to room temperature. After 7 h the reaction mixture was cooled to -30 °C and 32 μ L (0.40 mmol, 2 equiv.) of pyridine was added. Subsequently, *n*-pentane was added while rigorous stirring and the formation of a brownish precipitate was observed. After filtering off the precipitate, all volatiles were removed *in vacuo* ($\sim 10^{-2}$ mbar). Then the crude product was dissolved in 17 mL of *n*-pentane and filtered over a small amount of silanized silica gel at -50 °C. Evaporation of the solvent ($\sim 10^{-2}$ mbar) gave **3**.

3: Yellow oil; yield: 14.7 mg (0.04 mmol, 21%); ¹H NMR (300.13 MHz, C₆D₆): $\delta = 0.26$ (s, 18H; Si(CH₃)₃), 0.75 (d_{sat}, $|^{2}J_{PH}| = 0.8$ Hz, $|^{2}J_{SiH}| = 8.8$ Hz, 1H; *CH*(SiMe₃)₂), 3.11 (s, 6H; N(CH₃)₂), 7.16 (m_c, 3H; *meta* + *para*-H_{phenyl}), 8.01 (m_c, 2H; *ortho*-H_{phenyl}); ¹³C{¹H} NMR (75.5 MHz, C₆D₆): $\delta = 2.0$ (br_{sat}, $|^{1}J_{SiC}| = 51$ Hz; Si(CH₃)₃), 18.6 (d_{sat}, $|^{1}J_{PC}| = 56.9$ Hz, $|^{1}J_{SiC}| = 39.0$ Hz; *CH*(SiMe₃)₂), 38.2 (s; N(CH₃)₂), 128.5 (d, $|^{3}J_{PC}| = 8.1$ Hz; *ortho*-C_{phenyl}), 129.1 (s; *meta*-C_{phenyl}), 131.4 (d, $|^{5}J_{PC}| = 2.3$ Hz; *para*-C_{phenyl}), 135.8 (d, $|^{2}J_{PC}| = 15.8$ Hz; *ipso*-C_{phenyl}), 167.4 (d, $|^{2+3}J_{PC}| = 1.1$ Hz; PNC), 210.6 (d, $|^{1+4}J_{PC}| = 52.4$ Hz; PCN); ³¹P NMR (121.5 MHz, C₆D₆): $\delta = 95.4$ (s).

2.5. Synthesis of 2-bis(trimethylsilyl)-methyl-5-dimethylamino-3-phenyl-2H-1,4,2-diazaphosphol-1-ium trifluoromethanesulfonate (**5**)

To a stirred solution of 100 mg (0.19 mmol) of 2*H*-azaphosphirene complex **1b** in 4 mL of CH₂Cl₂ were added consecutively 16 μ L (0.20 mmol) of dimethyl cyanamide and 17 μ L (0.19 mmol) of TfOH at $-60 \,^{\circ}$ C while the initially yellow colored solution turned deep red. After 6 min the cooling bath was removed, and the reaction mixture turned brownish while warming to room temperature. The protonated intermediate **4b** was identified by ³¹P NMR spectroscopy (121.5 MHz, CH₂Cl₂): $\delta = 130.6 \, (d, |^{2+5}J_{PH}| = 22.9 \text{ Hz}, |^2J_{PH}| = 6.4 \text{ Hz}$). After 7 h *n*-pentane was added under rigorous stirring and the formation of a light green precipitate was observed, which was filtered, washed with *n*-pentane, and dried *in vacuo* ($\sim 10^{-2}$ mbar) to give **5**.

5: Light green solid; yield: 85 mg (0.17 mmol, 88%); ¹H NMR CD_2Cl_2): $\delta = 0.01$ $|^{2}I_{\text{SiH}}| = 6.5 \text{ Hz},$ (300.13 MHz, (s_{sat}, $|^{1}J_{CH}| = 120.7 \text{ Hz}, 9\text{H}; \text{Si}(CH_{3})_{3}), 0.27 \text{ (d}_{sat}, |^{4}J_{PH}| = 0.7 \text{ Hz},$ $|{}^{1}J_{CH}| = 118.3 \text{ Hz}, 9\text{H}; \text{Si}(CH_{3})_{3}), 0.93 \text{ (d, } |{}^{2}J_{PH}| = 4.0 \text{ Hz}, 1\text{H};$ $CH(SiMe_3)_2)$, 3.49 (d, $|^{5+6}J_{PH}| = 2.6$ Hz, 3H; NCH₃), 3.67 (d, $|^{5+6}J_{PH}| = 1.7$ Hz, 3H; NCH₃), 7.62 (m_c, 2H; meta-H_{phenvl}), 7.75 (m_c, 1H; para-H_{phenyl}), 7.95 (m_c, 2H; ortho-H_{phenyl}), 9.78 (d, $|^{2+5}J_{PH}| = 28.3 \text{ Hz}, h_{1/2} = 9.1 \text{ Hz}, 1\text{H}; \text{ NH}); {}^{13}\text{C}{}^{1}\text{H} \text{NMR} (75.5 \text{ MHz}, 13); {}^{13}\text{C}{}^{1}\text{C} \text{NM} (75.5 \text{ MHz}, 13); {}^{13}\text{C} \text{NM} (75.5 \text{ MHz},$ CD₂Cl₂): $\delta = 1.3 \text{ (d}_{sat}, |^{3}J_{PC}| = 7.8 \text{ Hz}, |^{1}J_{SiC}| = 52.4 \text{ Hz}; \text{ Si}(CH_{3})_{3}), 1.9$ $(d_{sat}, |{}^{3}J_{PC}| = 3.2 \text{ Hz}, |{}^{1}J_{SiC}| = 52.5 \text{ Hz}; Si(CH_{3})_{3}), 21.1 (d,$ $|^{1}J_{PC}| = 63.7 \text{ Hz}; CH(SiMe_{3})_{2}), 39.6 (d, |^{4+5}J_{PC}| = 1.3 \text{ Hz}; NCH_{3}), 41.1$ (d, $|^{4+5}J_{PC}| = 1.9 \text{ Hz}$; NCH₃), 120.7 (q, $|^{1}J_{FC}| = 319.7 \text{ Hz}$; CF₃), 129.8 $(d, |^{3}J_{PC}| = 10.3 \text{ Hz}; ortho-C_{phenyl}), 129.9 (s; meta-C_{phenyl}), 132.6 (d,)$ $|^{2}J_{PC}| = 17.8 \text{ Hz}; ipso-C_{phenyl}), 135.7 (d, |^{5}J_{PC}| = 1.6 \text{ Hz}; para-C_{phenyl}),$ 165.9 (d, $|^{2+3}J_{PC}| = 0.4$ Hz; PNC), 211.8 (d, $|^{1+4}J_{PC}| = 40.4$ Hz; PCN); ¹⁵N NMR (30.418 MHz, CD_2Cl_2): $\delta = -277$ (NMe₂), -276 $(|^{1+4}J_{PN}| = 28 \text{ Hz}, |^{1}J_{NH}| = 91 \text{ Hz}; \text{ N}^{1}\text{H}); {}^{29}\text{Si}{}^{1}\text{H} \text{ NMR} (59.6 \text{ MHz},$ CD₂Cl₂): $\delta = 5.3$ (d, $|^{2}J_{PSi}| = 3.5$ Hz), 5.8 (d, $|^{2}J_{PSi}| = 17.4$ Hz); ³¹P NMR (121.5 MHz, CD_2Cl_2): $\delta = 100.7$ (d, $|^2J_{PH}| = 28.0$ Hz).

2.6. Reaction of [2-bis(trimethylsilyl)methyl-3-phenyl-2Hazaphosphirene- κ P]pentacarbon-ylchromium(0) (**1a**) with dimethyl cyanamide and trifluoromethanesulfonic acid

To a stirred solution of 97 mg (0.20 mmol) of 2*H*-azaphosphirene complex **1a** in 4 mL of CH_2Cl_2 were added consecutively 16 μ L (0.20 mmol) of dimethyl cyanamide and 17 μ L (0.19 mmol) of TfOH at $-60 \,^{\circ}\text{C}$ while the initially yellow colored solution turned deep red. The protonated intermediate **4a** was identified by ^{31}P NMR spectroscopy (121.5 MHz, CH₂Cl₂): δ = 157.7 (d, $|^{2+5}J_{\text{PH}}|$ = 22.9 Hz, $|^{2}J_{\text{PH}}|$ = 8.9 Hz).

2.7. X-ray crystallography

Suitable single crystals of **2a,b** were obtained from concentrated *n*-pentane 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 123 K using graphite monochromated Mo K α radiation (λ = 0.71073 Å). The structures were solved by Patterson methods (SHELXS-97) [29] and refined by full-matrix least squares on F^2 (SHELXL-97) [29]. 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 semi-empirically from equivalents (minimum/maximum transmissions = 0.86208/0.89804 (**2a**) and 0.87878/0.89913 (**2b**).

2.7.1. Crystal structure data for complex **2a** (C₂₂H₃₀CrN₃O₅PSi₂)

Crystal size $0.52 \times 0.18 \times 0.18$ mm, monoclinic, P_{21} , a = 9.2995(3), b = 12.7072(8), c = 11.6982(6) Å, $\beta = 92.008(3)$, V = 1381.53(12) Å³, Z = 2, $\rho_{calc} = 1.336$ mg m⁻³, $2\theta_{max} = 58^{\circ}$, collected (independent) reflections = 11154 (6490), $R_{int} = 0.0402$, $\mu = 0.594$ mm⁻¹, 316 refined parameters, 8 restraint, R_1 (for $I > 2\sigma(I)$) = 0.0346, wR_2 (for all data) = 0.0621, S = 0.961, maximum/minimum residual electron density = 0.447/-0.379 e Å⁻³.

2.7.2. Crystal structure data for complex **2b** (C₂₂H₃₀MoN₃O₅PSi₂)

Crystal size $0.60 \times 0.08 \times 0.08$ mm, monoclinic, $P2_1$, a = 9.3471(5), b = 12.7344(11), c = 11.8746(9)Å, $\beta = 93.523(4)$, V = 1410.76(18)Å³, Z = 2, $\rho_{calc} = 1.411$ mg m⁻³, $2\theta_{max} = 58^{\circ}$, collected (independent) reflections = 10766 (6251), $R_{int} = 0.0465$, $\mu = 0.641$ mm⁻¹, 317 refined parameters, 1 restraint, R_1 (for $I > 2\sigma(I)$) = 0.0380, wR_2 (for all data) = 0.0676, S = 0.713, maximum/minimum residual electron density = 0.434/-0.438 e Å⁻³.

2.8. Computational methods

DFT calculations were carried out with the TURBOMOLE V5.9.1 program package [30]. Optimizations [31] were done with the local Slater-Dirac exchange [32,33] and the correlation energy density functional (No.V) by Vosko, Wilk, and Nusair (VWN (V)) [34] together with Becke's gradient corrected exchange functional B88 [35] in combination with the gradient corrected correlation functional by Perdew (P86) [36] within the RI (Resolution of the Identity) approximation [37-39] (hereafter referred to as RI-BP86). The split valence shell basis set SV(P) [40] was used for all atoms, and the inner shell electrons of molybdenum and tungsten were substituted by the scalar-relativistic effective core potential ECP-28-MWB or ECP-60-MWB [41], respectively. The influence of the polar solvent was taken into account by employing the COSMO approach [42] with ε = 8.93. For cavity construction the atomic radii of Bond [43], obtained from crystallographic data, were used; the atomic radius of tungsten was set to 2.2230 Å. The stationary points were characterized by numerical vibrational frequencies calculations [44–46]. Single point calculations were carried out with the same density functional combination but with the valence-triple- ζ basis set TZVP [47], ECP-28-MWB for molybdenum, and ECP-60-MWB for tungsten. The COSMO approach was employed with the same parameters as used for optimizations. Zero point corrections and thermal corrections to free energies were adopted from frequencies calculations on the optimization level.



Scheme 2. Synthesis of 2H-1,4,2-diazaphosphole complexes 2a,b.

3. Results and discussion

With the aim of preparing the 2*H*-1,4,2-diazaphosphole complexes **2a,b**, a CH₂Cl₂ solution of 2*H*-azaphosphirene complex **1a** or **1b** [28], respectively, and dimethyl cyanamide was treated with triflic acid and, subsequently, with triethylamine (Scheme 2). When the acid was added either at ambient temperature or at -30 °C and the reaction mixture was then warmed to room temperature (i), after the addition of NEt₃ ³¹P{¹H} NMR spectroscopic monitoring revealed the resonance of the free 2*H*-1,4,2-diazaphosphole ligand **3** (δ = 95.4) besides that of the desired product **2a,b**. During the addition of TfOH initially intensely red colored solutions were formed, but upon warming up, the solutions turned greenish brown, which also served as a visual indication for the onset of decomplexation.

By careful control of the reaction conditions the decomplexation could completely be prevented. When the addition of TfOH was carried out at about -30 °C and deprotonation with NEt₃ was performed within few minutes, 2*H*-1,4,2-diazaphosphole complexes **2a,b** were the only reaction products observed by ³¹P{¹H} NMR spectroscopy (ii, Scheme 2). Complexes **2a,b** were purified by low-temperature column chromatography and obtained in excellent yields (85% and 89%, respectively). They were characterized by multinuclear NMR experiments, mass spectrometry, IR and UV–Vis spectroscopy, and single-crystal X-ray diffraction studies (Fig. 1).

The NMR spectroscopic data of **2a**,**b** are best compared to those of their pentacarbonyl tungsten analogue **2c**, which we reported recently [18,48]. The ³¹P{¹H} resonance of **2b** appears about 21 ppm downfield from that of **2c**, and complex **2a** resonates further 24 ppm at lower field (Table 1), which is a common trend for tungsten, molybdenum, and chromium complexes of a given class of ligands [49,50]. The ¹³C{¹H} NMR data for the heterocyclic ligand of **2a–c** are almost unaffected by variation of the metal. As anticipated, the carbonyl carbon resonances show a stronger dependance on variation of the transition metal: the δ values continuously increase within the series M = W < Mo < Cr for both the *cis*- and the *trans*-CO carbon coupling constant magnitude than the *cis*-CO groups, which is also a common feature of pentacarbonyl phosphane chromium complexes [49,50].

The IR spectra of **2a,b** showed the characteristic C=O stretch vibration bands for $M(CO)_5$ complexes with slightly perturbed C_{4v} symmetry. They both show a single, well-separated band at 2059 (**2a**) or 2070 cm⁻¹ (**2b**), respectively, assigned to an A_1 vibration. Another band with low intensity appears at 1980–1990 cm⁻¹, assigned to a normal mode of local B_1 symmetry. In the range of 1900–1950 cm⁻¹ two or three very intense and partially overlapping bands appear, which are attributable to vibrations of local



Fig. 1. Molecular structure of complex **2a** (M = Cr) in the crystal (50% probability level, hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles in [°]: Cr-C18 1.870(2), Cr-P 2.4208(6), P-C3 1.828(2), P-N2 1.682(2), P-C1 1.887(2), C1-N1 1.292(3), C2-N2 1.311(2), C2-N3 1.337(3), N2-P-C1 90.35(10), P-C1-N1 109.18(18), C1-N1-C2 110.16(18), N1-C2-N2 120.8(2), C2-N2-P 108.93(18), N2-C2-N3 122.1(2). For isotypic complex **2b** (M = Mo): Mo-C18 2.003(4), Mo-P 2.5487(10), P-C3 1.830(4), P-N2 1.673(3), P-C1 1.877(4), C1-N1 1.293(5), C2-N2 1.315(5), C2-N3 1.341(6), N2-P-C1 90.91(17), P-C1-N1 109.2(3), C1-N1-C2 110.0(3), N1-C2-N2 120.8(4), C2-N2-P 108.7(3), N2-C2-N3 123.0(4).

Table 1

Comparison of selected NMR spectroscopic data for chromium, molybdenum, and tungsten complexes **2a-c**, ligand **3**, and *N*-protonated ligand **5**.

	2a ^a	2b ^a	2c ^{a,b}	3 ^a	5 ^c
$\delta_{\rm P}$	146.3	122.7	101.8	95.4	100.7
$\delta_{\rm C}({\rm C}_{\rm exo})$	22.5	21.4	22.0	18.6	21.1
$ ^{1}J_{PC} /Hz$	9.7	11.6	5.8	56.9	63.7
$\delta_{C}(C^{3})$	200.5	201.3	200.3	210.6	211.8
$ ^{1+4}J_{PC} /Hz$	31.7	29.7	25.5	52.4	40.4
$\delta_{C}(C^{5})$	163.7	164.7	165.0	167.4	165.9
²⁺³ J _{PC} /Hz	0.8	0.7	-	1.1	0.4
$\delta_{\rm C}({\rm CO}_{\rm cis})$	217.4	206.5	198.6	-	-
$ ^2 J_{PC} /Hz$	12.6	8.4	6.5	-	-
$\delta_{C}(CO_{trans})$	222.0	211.1	199.6	-	-
$ ^{2}J_{PC} /Hz$	6.8	23.0	22.3	-	-

^a In C₆D₆.

^b From Ref. [18].

^c In CD₂Cl₂.

 A_1 and *E* symmetry. Two bands assigned to C–N stretch vibrations were observed at around 1605 and 1540 cm⁻¹.

In the UV–Vis spectra both complexes **2a,b** show two π – π * absorption bands at similar wavelengths (286 and *ca*. 350 nm for both complexes). Furthermore, they show a low-energy absorption, which is, on the basis of recently published results on related systems [19], assigned to a metal-diazaphosphole-ligand charge transfer (MLCT) process. It is noteworthy that this band is in the case of the chromium complex **2a** at significantly longer wavelength. As a result also its optical end absorption appears at longer wavelength ($\lambda_{max} = 439 \text{ nm}$; $\lambda_{onset} = 554 \text{ nm}$; cf. **2b**: $\lambda_{max} = 396 \text{ nm}$; $\lambda_{onset} = 505 \text{ nm}$).

Complexes **2a,b** (and also **2c**) crystallize in the monoclinic space group $P2_1$ and are isotypic; apart from their pentacarbonyl metal fragments they exhibit almost identical bond lengths and angles. The 2*H*-1,4,2-diazaphosphole rings are essentially planar (mean deviations from least-squares planes: 0.033 Å (**2a**) and 0.027 (**2b**)) and, to a large extent, coplanar arranged with the adjacent phenyl ring (twist angles: 7.6 (**2a**) and 8.6 (**2b**)). The dimethylamino nitrogen atoms are almost perfectly trigonal planar coordinated ($\Sigma_{<}$ 360.0° (**2a**) and 359.9° (**2b**)) and the planes of the NMe₂ groups do not deviate significantly from the regression plane of the respective diazaphosphole ring (twist angles: 6.4° (**2a**) and 5.1° (**2b**)).

Insight into metal-phosphorus bond strengths of 2*H*-1,4,2diazaphosphole complexes was obtained from FAB-(positive mode) and El-mass spectra. While in the case of the chromium complex **2a** m/z 415 assigned to [**2a**-5CO]⁺ represented the base peak of the FAB spectrum, the signal of protonated heterocycle [**3** + H]⁺ (m/z 364) was the base peak of the spectrum of molybdenum complex **2b**. Similar results were obtained also for 2*H*-1,4,2diazaphosphole tungsten complexes (e.g. **2c**), but for complex **2b** this signal clearly dominated the spectrum while the abundance of the molecular ion ([**2b** + H]⁺: m/z 602) was only 3%; for **2a** the molecular cation was not even detected by FAB-MS. Under El conditions, also loss of SiMe₃ and methyl groups as well as ring fragmentations were observed for **2a,b**. Furthermore, the radical cationic heterocycle [**3**]⁺ was detected (m/z 363), in the spectrum of complex **2a** as the base peak.

From these results it can be concluded that the Cr,P and Mo,P bonds of **2a**,**b** are more labile than the W,P bond of **2c**, and, more important, the metal–phosphorus bonds become significantly weakened through protonation of the heterocyclic ligand. This may serve as an explanation why fast decomplexation was observed in reactions of **1a**,**b** with Me₂NCN and TfOH (Scheme 2, i);

obviously, it occurred from protonated, intermediately formed 2*H*-1,4,2-diazaphosphole complexes.

To investigate the influence of the triflate anion on the decomplexation reaction in the absence of any Brønsted acid, complex **2b** was reacted in methylene chloride with $[{}^{n}Bu_{4}N][OTf]$. Also here, the resonance of the liberated ligand **3** was detected, but the decomplexation was significantly slower than in the presence of the acid; after 24 h the reaction mixture still contained 81% of unreacted **2b** and approximately 19% of **3**.

In order to get more insight into the effects of protonation of 2*H*-1,4,2-diazaphosphole complexes, the isodesmic reactions (**A**) and (**B**) were calculated using DFT methods (Table 2). These model reactions provide information on the change in the metal–phosphorus bond strengths induced by *N*-protonation of 2*H*-1,4,2-diazaphosphole complexes as they describe the transfer of a penta-carbonyl metal fragment from a cationic to a neutral ligand system [51]. Here, the cationic complexes in reactions (**A**) were used as models for N¹-protonated complexes; reactions (**B**) were calculated to estimate the effect of (hypothetical) N⁴-protonation. The main result is that all reactions are thermodynamically favored, which points to a weakening of the metal–phosphorus bonds upon protonation.

By taking advantage of this effect, 2H-1,4,2-diazaphosphole **3** was synthesized in a one-pot reaction from complex **1b** and Me₂NCN *via* treatment with triflic acid in methylene chloride. When pyridine was added after several hours, heterocycle **3** was obtained as the only phosphorus-containing product (Scheme 3).

By ³¹P NMR spectroscopic monitoring of reactions of **1a,b** with TfOH and dimethyl cyanamide evidence was obtained for the formation of N¹-protonated 2*H*-1,4,2-diazaphosphole complexes **4a** ($\delta = 157.7$, $|^{2+5}J_{PH}| = 22.9$ Hz) and **4b** ($\delta = 130.6$, $|^{2+5}J_{PH}| = 22.9$ Hz) in the primary reaction step (Scheme 3 and Fig. 2). Their resonances are slightly downfield from those of the respective neutral complexes **2a,b** (**4a**: $\delta = 157.7$; **4b**: $\delta = 130.6$) and show large phosphorus–proton couplings about 23 Hz in magnitude as observed also for N¹-protonated complexes cf. [18,19,22]. During the reactions of both complexes these signals decreased in favor of a resonance at $\delta = 100.7$ ($|^{2}J_{PH}| = 28.0$ Hz). Adding of cold *n*-pentane yielded a light green precipitate, which, after workup, was identified as the 2*H*-1,4,2-diazaphospholium **5** by multinuclear NMR and diverse shift-correlated 2D NMR experiments (Table 1).

The ³¹P resonance of the neutral ligand **3** appears 27.3 ppm upfield from complex **2b** (Table 1), but only slightly upfield from that of its tungsten complex (**2c**: δ = 101.8 [18]). The ¹³C NMR chemical shifts of the 2*H*-1,4,2-diazaphosphole ring carbons are almost

Table 2

Calculated thermochemical data for isodesmic W(CO)₅ exchange reactions (RI-BP86/TZVP/ECP-28-MWB(Mo)/ECP-60-MWB(W), COSMO (ε = 8.93)//RIBP86/SV(P)/ ECP-28-MWB(Mo)/ECP-60-MWB(W), COSMO (ε = 8.93); all values in kJ mol⁻¹).

(OC) ₅ M A) Me	Me N-H Me Me Me	e N <u>Me</u> N Me	Me (OC)₅M N P⊕→ H Me P N + N Me	Ле I Me		
(OC)₅M B) Me ⊕N H	$Me \qquad Me \qquad Me \qquad Me \qquad Me \qquad Me \qquad Me \qquad A$	e N <u>→ Me ∬</u> ⊕N Me H	$Me (OC)_5M N$ $Me Ne Ne$	Ле J Me B		
М	$\Delta_{\rm R} E_0$	$\Delta_{\rm R} H_{298}$	$\Delta_{\rm R}G_{298}$	$\Delta_{\rm R} E_0$	$\Delta_{\rm R} H_{298}$	$\Delta_{\rm R}G_{298}$
Cr	-37.4	-36.4	-37.9	-34.0	-33.0	-35.6
W0 W	-35.0 -36.3	-34.4 -35.7	-35.3 -37.3	-32.0 -33.4	-31.2 -32.7	-32.2 -34.4
	5515	550	3.13	33.1	320	5



Scheme 3. Consecutive reaction of 2H-azaphosphirene complexes 1a,b with dimethyl cyanamide, TfOH, and pyridine.



Fig. 2. ³¹P{¹H} NMR spectra recorded during the reaction of **1b** with Me₂NCN and TfOH (Scheme 3). Expansions of the resonances from proton-coupled ³¹P NMR spectra show signal splitting due to ³¹P, ¹H coupling.

unaffected by decomplexation. On the other hand, all phosphorus– carbon coupling constant magnitudes are significantly increased, except for $|^{2+3}J_{PC}|$ of C⁵ where the effect is negligible. Noteworthy is that the NMe₂ moiety shows only one ¹H and ¹³C resonance for both methyl groups, thus pointing to a fast rotation about the exocyclic C⁵,N bond in solution. This is in marked contrast to complexes **2a–c**. Interestingly, **3** also shows only one resonance corresponding to the trimethylsilyl groups in ¹H and ¹³C{¹H} NMR spectra. According to calculations on DFT niveau [52,53] this is due to a fast inversion of the pyramidal phosphorus center in **3** ($\Sigma_{<}(PR_3)$ 306.2°) [54]; the activation barrier was predicted to be only ΔG^{\neq} = 54.9 kJ mol⁻¹.

Comparison of the NMR data for **5** and its neutral congener **3** reveals that the ³¹P NMR chemical shift is slightly increased (by 5.3 ppm), while the ¹³C{¹H} NMR data are almost unaffected by protonation. The constitution of **5** was further supported by ¹H, ¹⁵N HMQC NMR experiments; the assignment of the ¹⁵N NMR data is shown in Fig. 3. The data for **5** are comparable to those that were found for its tungsten complex (also protonated at N¹; $\delta(N^1) = -264$, $|^{1+4}J_{PN}| = 15$ Hz; $\delta(NMe_2) = -269$) cf. [18]. Also here, the protonated nitrogen atom showed a long-range correlation with the CH proton of the bis(trimethylsilyl)methyl group.



Fig. 3. Assignment of the 15 N NMR spectroscopic data for N¹-protonated 2*H*-1,4,2-diazaphosphole 5 (CD₂Cl₂).

Unlike **3**, the protonated heterocycle **5** shows two sets of resonances corresponding to the SiMe₃ groups in ¹H, ¹³C{¹H}, and ²⁹Si{¹H} MMR spectra; the barrier of inversion about phosphorus is in **5** significantly higher (ΔG^{\neq} = 75.5 kJ mol⁻¹; $\Sigma_{<}(PR_3)$ 305.2°) [52]. Presumably, the perturbation of the cyclic 6π -electron system in the planar transition structure by the dimethylamino-nitrogen lone pair is more pronounced for the cationic system **5** than for **3** (see Supporting Information). Furthermore, in the spectra of **5** two sets of ¹H and ¹³C resonances were detected for the NMe₂ substituent. This observation is easily understood, since rotation about

the exocyclic C^5 ,N bond should be restricted through formation of a more pronounced π interaction between the dimethylamino-nitrogen and C^5 due to protonation at N¹.

4. Conclusions

It was shown that the newly established protocol for the ring expansion of three-membered P-heterocycle complexes using triflic acid and NEt₃ can successfully be applied to the synthesis of 2*H*-1,4,2-diazaphosphole chromium and molybdenum complexes *via* highly selective reactions; complexes **2a,b** were isolated in excellent yields. Additionally, depending on the specific reaction conditions, this provides facile access to non-ligated 2*H*-1,4,2-diazaphosphole ligands (*N*-protonated or neutral) in a one-pot reaction from the same precursors. This opens up options to apply these newly accessible heterocycles to further modification/functionalization and/or to use them in coordination chemistry. Current investigations aim at broadening the application of this click protocol by using other three-membered phosphorus heterocycles and π -substrates.

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Appendix A. Supplementary data

CCDC 804573 and 804574 contains the supplementary crystallographic data for **2a,b**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/ j.poly.2011.04.014.

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