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How To Tune Acid-Induced Ring Enlargement Reactions – The Strange Case of 2*H*-Azaphosphirene Complexes and Its Surprising Dichotomy

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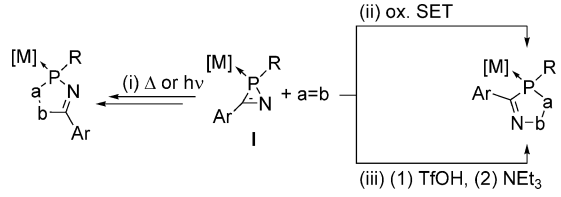
2*H*-Azaphosphirene complex **1a** reacted with TfOH, cyclohexyl isocyanide, and subsequently with NEt_3 – P–N-bond-selectively – to give the first 2,3-dihydro-1,3-azaphosphete complex **2**. Under the same conditions, 2*H*-azaphosphirene complex **1b** underwent a P–C-bond-selective ring enlargement with phenylacetylene with formation of 2*H*-1,2-azaphosphole complex **3**. Apart from X-ray crystallographic data (**2**, **3**), DFT calculations are discussed, which provide first insight into this surprising dichotomy.

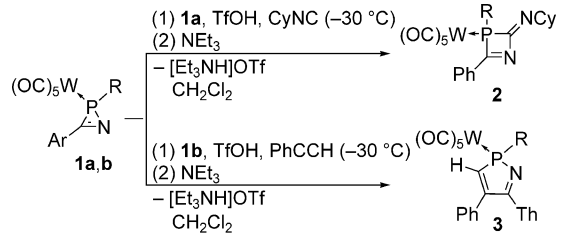
Ring enlargement of small, strained heterocycles with easily available π-systems like nitriles, alkynes, alkenes, or carbonyl derivatives enables numerous applications in organic synthesis.[1] Such transformations have become of current interest also in phosphorus heterocyclic chemistry[2,3] in the last decades. 2*H*-Azaphosphirene complexes **I**[4] react thermally or photochemically by P–C bond cleavage, and thus intermediately formed nitrilium phosphane ylide complexes[5] can undergo [3+2] cycloaddition reactions with various π-systems [Scheme 1 (i)].[6–8] On the other hand, we demonstrated that the P–N bond of **I** can be addressed selectively by using two different highly efficient yet soft methods: oxidative single electron transfer (ox. SET)[9,10] (ii) or protonation with trifluoromethanesulfonic acid (TfOH) (followed by reaction with triethylamine) (iii), thus yielding neutral, closed-shell five-membered heterocycles by ring-enlargement reactions. In the case of (iii), *N*-protonation of the heterocyclic ligand in **I** represents the first step in the bond activation.[11]

As the latter methodology offers interesting perspectives to design larger ligand architectures for coordination chemistry, we became interested in exploring the boundaries of applicability and improving the understanding of the effect of *N*-protonation on all bonds within the ligand system. Here, preliminary results on an ambiguous behavior of 2*H*-azaphosphirene complexes towards the system TfOH/NEt_3 and isocyanide or alkyne are presented, and a first explanation to rationalize the bond activation is provided.



Scheme 1. Bond-selective insertion reactions of a=b into the 2*H*-azaphosphirene ring system (a=b denotes a π-system. [M] = $W(CO)_5$; R, Ar denote organic substitutents).

The reaction of 2*H*-azaphosphirene complex **1a**[12] with TfOH and cyclohexyl isocyanide, and subsequently with NEt_3, selectively yielded complex **2**, which contains the novel 2,3-dihydro-1,3-azaphosphete ligand system (Scheme 2).[13] It is remarkable that complex **2** could not be obtained by treating **1a** with the isocyanide *in the absence* of TfOH.[14]



Scheme 2. TfOH-induced ring enlargement reactions of complexes **1a**,**b**.

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Whereas complex **1a** and phenylacetylene did not selectively react under these conditions, the *C*-thienyl-substituted 2*H*-azaphosphirene complex **1b**[15] unexpectedly formed 2*H*-1,2-azaphosphole complex **3** (Scheme 2) instead of a 3*H*-1,3-azaphosphole complex. Hence, instead of P–N-bond-selective ring enlargement, which was observed in reactions with nitriles,[11] isonitriles (here) and carbonyl compounds,[16] the P–C bond was selectively addressed in this case.

Complexes **2** and **3** were purified by low-temperature column chromatography and the constitutions unambiguously identified by NMR spectroscopy and mass spectrometry. Single-crystal X-ray diffraction of **2** and **3** (Figures 1 and 2) confirmed the proposed bond selectivity for both complexes, and the regiochemistry in the case of **3**. The structural motif of localized C–N or C–C double bonds is common to both P-heterocycle complexes.

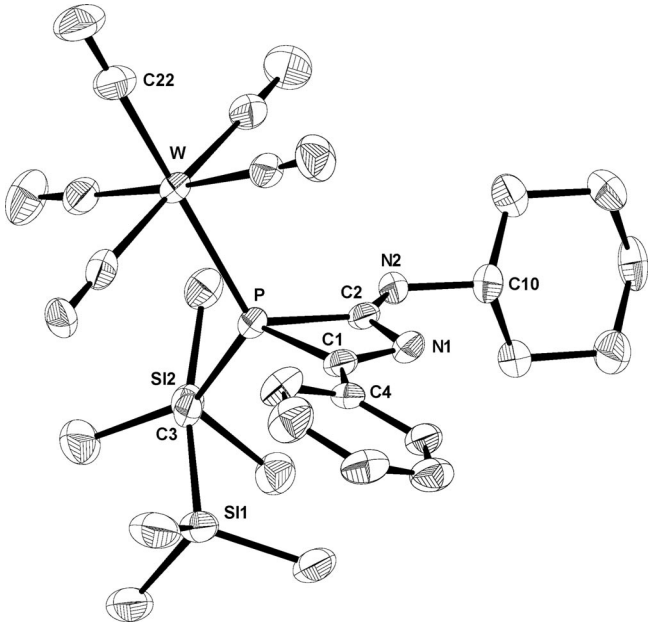


Figure 1. Molecular structure of complex **2** in the crystal (50% probability level, hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: W–P 2.4982(13), P–C(3) 1.834(5), P–C(1) 1.878(6), P–C(2) 1.874(6), C(1)–N(1) 1.312(7), C(2)–N(1) 1.436(7), C(1)–C(4) 1.443(8), C(2)–N(2) 1.239(7), N(2)–C(10) 1.460(7); C(1)–P–C(2) 68.0(3), P–C(1)–N(1) 98.4(4), C(1)–N(1)–C(2) 99.4(5), N(1)–C(2)–P 94.2(4).

The central phosphorus heterocycles of **2** and **3** are almost planar [mean deviations from least-square planes 0.037 (**2**) and 0.073 Å (**3**)]. The phenyl substituent of **2** adopts an almost coplanar arrangement with the central heterocycle (twist angle with respect to least-square planes 19.0°). Likewise, complex **3** features a coplanar arrangement of the 2*H*-1,2-azaphosphole and the 2-thienyl ring (interplanar angle 8.31°), but the phenyl moiety is orientated in an almost perpendicular fashion relative to the central heterocycle (interplanar angle 74.01°). Whereas the sum of angles at the phosphorus atom ($\Sigma\angle PR_3$) in complex **3** is 312.4°, which is typical for this class of compounds, it is only 293.3° in complex **2**.

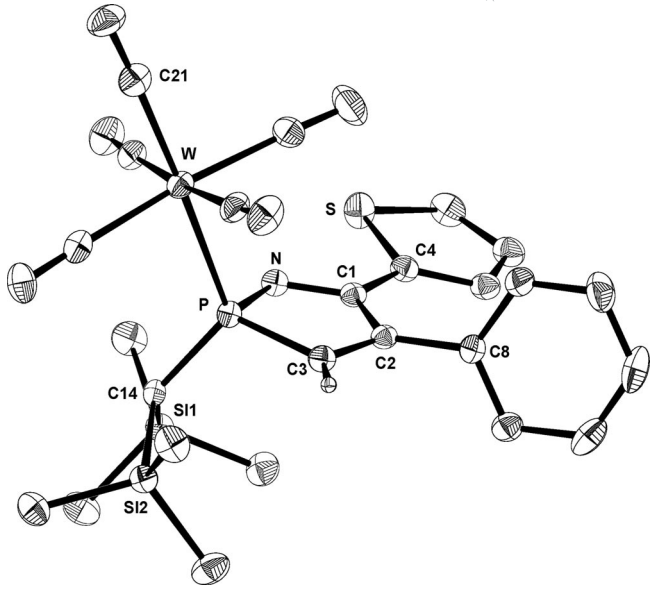
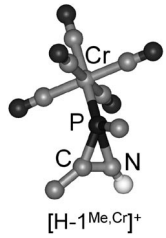


Figure 2. Molecular structure of complex **3** in the crystal [50% probability level; except for H at C(3), all other hydrogen atoms are omitted for clarity]. Selected bond lengths [Å] and angles [°]: W–C(21) 2.000(3), W–P 2.5113(6), P–C(14) 1.819(2), P–N 1.712(2), P–C(3) 1.800(2), N–C(1) 1.298(3), C(1)–C(2) 1.494(3), C(2)–C(3) 1.341(3), C(1)–C(4) 1.457(3), C(2)–C(8) 1.493(3); C(3)–P–N 93.05(11), P–N–C(1) 109.99(16), N–C(1)–C(2) 116.5(2), C(1)–C(2)–C(3) 110.7(2), C(2)–C(3)–P 108.79(17), N–C(1)–C(4) 119.0(2), C(3)–C(2)–C(8) 124.3(2).

The influence of *N*-protonation on ring bond strengths of 2*H*-azaphosphirene complexes was investigated by DFT[17a,17b] calculation of *P*,*C*-dimethyl-substituted chromium model complexes $\mathbf{1}^{\mathbf{Me,Cr}}$ and $[\mathbf{H\text{-}1}^{\mathbf{Me,Cr}}]^+$ (Figure 3). As a measure of bond strengths, DFT compliance constants[18] – diagonal elements of the inverse force field – are calculated: the stronger a bond the *less* compliant it is and vice versa.



$[H\text{-}1^{Me,Cr}]^+$

Figure 3. ZORA-DFT-calculated [(B88+P86)VWN5/tz2p, (COSMO CH_2Cl_2), ADF 2007.1[17b]] bond lengths [Å] and angles [°] of $[\mathbf{H\text{-}1}^{\mathbf{Me,Cr}}]^+$: P–N 1.811, P–C 1.831, N–C 1.279, Cr–P 2.271, N–P–C 41.12; C–N–P 70.29, P–C–N 68.59; charges (Hirshfeld): Cr +0.21, P +0.29, C +0.15, N –0.01, H(N) +0.22; $\Sigma Cr(CO)_5$ 0.00, ΣNPC +0.42.

Upon *N*-protonation, the compliances of $\mathbf{1}^{\mathbf{Me,Cr}}$ in dichloromethane (simulated by a polarizable continuum model) (Figure 4) change as follows: P–N becomes more compliant by 9%, P–C weakens by 24%, whereas N–C and

Cr–P strengthen by 10 and 14%, respectively (Figure 5). Note that the activation of P–N cannot be concluded from bond-length considerations: P–N is by 0.3% shorter in [**H-1^{Me,Cr}**]$^+$ than it is in **1^{Me,Cr}** (1.811 vs 1.819 Å).

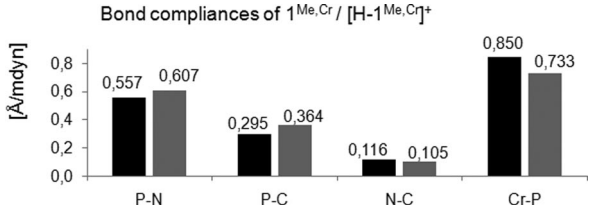


Figure 4. DFT (BVP86/tzvp, IEFPCM CH_2Cl_2, G03[17a]) compliance constants [Å/mdyn] of **1^{Me,Cr}**(black)/[**H-1^{Me,Cr}**]$^+$ (grey).

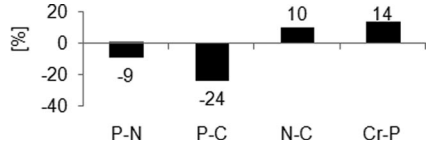


Figure 5. Bond strengthening (+)/weakening (–) [%] upon *N*-protonation of **1^{Me,Cr}**/[**H-1^{Me,Cr}**]$^+$ (BVP86/tzvp, IEFPCM CH_2Cl_2, G03[17a]).

Conclusions

An unprecedented case of acid-induced ring-enlargement dichotomy of 2*H*-azaphosphirene complexes is described, which shows P–N-bond-selective reaction with an isontrile derivative, whereas phenylacetylene was selectively inserted into the P–C bond. As inferred from the calculations, the position of the largest compliance of the protonated three-membered ring is its activated P–N bond, but also the P–C bond is weakened through *N*-protonation. However, further investigations are underway to exploit the synthetic methodology and to further the understanding of how bond activation can be used in small-ring heterocyclic chemistry.

Experimental Section

General: All reactions were carried out under purified and dried argon by using standard Schlenk techniques. Solvents were dried with sodium wire or CaH_2 (CH_2Cl_2) and distilled under argon. NMR spectroscopic data were recorded with a Bruker Avance 300 spectrometer at 30 °C by using C_6D_6 or $CDCl_3$ as solvent and internal standard; chemical shifts are given relative to tetramethylsilane (^{13}C: 75.5 MHz) and 85% H_3PO_4 (^{31}P: 121.5 MHz). Mass spectra were recorded with a Kratos Concept 1H spectrometer (FAB+, *m*NBA) or a MAT 95 XL Finnigan spectrometer (EI, 70 eV, ^{184}W). Melting points were determined with a Büchi apparatus, with samples sealed in capillaries under argon. Selected NMR and MS data are given hereafter.

Synthesis of 2: To a solution of 2*H*-azaphosphirene complex **1a** (300 mg, 0.49 mmol) and cyclohexyl isocyanide (60 μL, 0.50 mmol) in CH_2Cl_2 (5.4 mL) TfOH (43 μL, 0.49 mmol) was added at −30 °C. The initially yellow solution turned deep red. After 1 min, the cooling bath was removed, and, after 5 min, NEt_3 (69 μL, 0.49 mmol) was added; the reaction mixture turned brownish yellow. After filtration and removal of all volatile components in vacuo (10^{-2} mbar), the product was purified by column chromatography on neutral silica (−30 °C; petroleum ether/Et_2O, 10:1). Yield 286 mg (0.39 mmol, 81%). M.p. 122 °C (decomp.). ^{13}C{^{1}H} NMR (C_6D_6): δ = 199.2 [d_{sat}, ^2J(P,C) = 23.6 Hz, ^1J(W,C) = 143.5 Hz; CO_{trans}], 198.5 [d, ^{1+3}J(P,C) = 8.4 Hz, PCPh], 197.3 [d_{sat}, ^2J(P,C) = 5.8 Hz, ^1J(W,C) = 125.8 Hz, CO_{cis}], 156.6 [d, ^{1+3}J(P,C) = 67.2 Hz, PCNCy], 133.9 (s, *para*-C_{phenyl}), 132.9 [d, ^2J(P,C) = 20.7 Hz, *ipso*-C_{phenyl}], 129.9 [d, ^3J(P,C) = 1.9 Hz, *ortho*-C_{phenyl}], 129.0 (s, *meta*-C_{phenyl}), 58.9 [d, ^3J(P,C) = 11.5 Hz, CH(1)], 34.6 [d, ^4J(P,C) = 1.3 Hz, Cy-$C^{2/6}H_2$], 34.2 [d, ^4J(P,C) = 0.6 Hz, Cy-$C^{2/6}H_2$], 26.0 (s, Cy-C^4H_2), 25.7 [d, ^1J(P,C) = 24.6 Hz, $CH(SiMe_3)_2$], 24.6 (s, Cy-$C^{3/5}H_2$), 24.5 (s, Cy-$C^{3/5}H_2$), 3.0 [d, ^3J(P,C) = 2.3 Hz, $Si(CH_3)_3$], 2.5 [d, ^3J(P,C) = 3.2 Hz, $Si(CH_3)_3$] ppm. ^{31}P NMR (C_6D_6): δ = 104.0 [d_{sat}, ^1J(P,W) = 220.0 Hz, ^2J(P,H) = 9.4 Hz] ppm. MS (EI, 70 eV, ^{184}W): *m*/*z* (%) = 726.1 (85) [$M^{\cdot+}$].

Synthesis of 3: To a solution of 2*H*-azaphosphirene complex **1b** (400 mg, 0.64 mmol) and phenylacetylene (3.1 mL, 28 mmol) in CH_2Cl_2 (6.5 mL) TfOH (89 μL, 1.01 mmol) was added at −30 °C, while the initially yellow solution turned deep brown. After the cooling bath was removed, the reaction mixture was stirred for further 5 min; then NEt_3 (146 μL, 1.03 mmol) was added. After filtration and removal of all volatile components in vacuo (10^{-2} mbar), the product was purified by column chromatography on neutral silica (−30 °C; petroleum ether/Et_2O, 100:1). Yield: 60 mg (0.08 mmol, 13%). ^{13}C{^{1}H} NMR (C_6D_6): δ = 199.4 [d, ^2J(P,C) = 20.0 Hz, CO_{trans}], 197.4 [d_{sat}, ^2J(P,C) = 6.8 Hz, ^1J(W,C) = 126.2 Hz, CO_{cis}], 165.5 [d, ^{2+3}J(P,C) = 6.5 Hz, PNC], 155.5 [d, ^{1+4}J(P,C) = 13.6 Hz, C^5H], 148.0 [d, ^{2+3}J(P,C) = 20.0 Hz, PC*C*], 140.5 [d, ^3J(P,C) = 22.3 Hz, $C_{thienyl\text{-}2}$], 135.8 [d, ^3J(P,C) = 13.6 Hz, *ipso*-C_{phenyl}], 132.4 (s, $C_{thienyl\text{-}3}$), 132.1 (s, $C_{thienyl\text{-}5}$), 129.1 (s, *ortho*-C_{phenyl}), 129.0 (s, *para*-C_{phenyl}), 128.8 (s, *meta*-C_{phenyl}), 128.3 (s, $C_{thienyl\text{-}4}$), 20.1 [d, ^1J(P,C) = 4.2 Hz, $CH(SiMe_3)_2$], 2.7 [d, ^3J(P,C) = 2.3 Hz, $SiMe_3$], 2.3 [d, ^3J(P,C) = 3.2 Hz, $SiMe_3$] ppm. ^{31}P NMR (C_6D_6): δ = 88.9 [^1J(P,W) = 228.9 Hz, ^2J(P,H) = 34.3, 9.1 Hz] ppm. MS (FAB+, *m*NBA): *m*/*z* (%) = 726.0 (22) [M^+ + H].

X-ray Crystallographic Analyses of 2 and 3: Suitable yellow single crystals of **2** and **3** were obtained from concentrated *n*-pentane solutions upon decreasing the temperature from ambient temperature to +4 °C. Data were collected with a Nonius KappaCCD diffractometer equipped with a low-temperature device (Cryostream, Oxford Cryosystems) at 123 (**2**) and 100 K (**3**) by using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). The structures were solved by Patterson methods (SHELXS-97)[19a] and refined by full-matrix least squares on F^2 (SHELXL-97).[19b] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included isotropically by using a riding model on the bound atoms. Absorption corrections were carried out analytically (**3**) and semi-empirically (**2**) from equivalents [min./max. transmissions = 0.50118/0.74247 (**2**), 0.3345/0.5666 (**3**)]. CCDC-695892 (**2**) and -695894 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal-Structure Data of Complex 2: $C_{26}H_{35}N_2O_5PSi_2W$, crystal size 0.20 × 0.20 × 0.08 mm, triclinic, $P\bar{1}$, a = 12.6471(4), b = 15.3265(4), c = 17.0715(5) Å, α = 80.0252(17), β = 78.5027(14), γ = 76.7204(16)°, V = 3127.67(16) Å^3, Z = 4, $\rho_{calcd.}$ = 1.543 Mg m^{-3}, $2\theta_{max}$ = 58°, collected (independent) reflections = 42891 (16145), R_{int} = 0.0885, μ = 3.856 mm^{-1}, 679 refined parameters, 0 restraints, R_1 [for $I > 2\sigma(I)$] = 0.0493, wR_2 (for all data) = 0.1041, max./min. residual electron density = 3.783/–1.906 e Å^{-3}.

Crystal Structure Data of Complex 3: $C_{25}H_{28}NO_5PSSi_2W$, crystal size 0.35 × 0.32 × 0.16 mm, monoclinic, $P2_1/n$, a = 11.4717(2), b = 16.4816(3), c = 16.2627(3) Å, β = 95.6310(10)°, V = 3059.98(10) Å^3, Z = 4, $\rho_{calcd.}$ = 1.575 Mg m^{-3}, $2\theta_{max}$ = 55°, collected (independent) reflections = 36599 (6903), R_{int} = 0.0536, μ = 4.006 mm^{-1}, 437 refined parameters, 0 restraints, R_1 [for $I > 2\sigma(I)$] = 0.0224, wR_2 (for all data) = 0.0509, max./min. residual electron density = 0.938/–0.976 e Å^{-3}.

Acknowledgments

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