Electronic Supplementary Information (ESI)

Going for strain: synthesis of the first 3-imino-azaphosphiridine complexes and their surprising conversion into oxaphosphirane complex valence isomers

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Table of contents

Experimental data. S2
Figure SI 1: Low temperature ^{1}H NMR monitoring of **5a**. S5
X-Ray crystallographic analysis S6
Figure SI 2: X-ray crystallography analysis of **4a** S7
Figure SI 3: X-ray crystallography analysis of **5a** S8
Figure SI 4: Computed chemical shifts of **5a** S10
Figure SI 5: X-ray crystallography analysis of **5b** S10
Figure SI 6: Homodesmotic reactions used for obtaining RSE S12
Computational details. S13
Figure SI 7: NCIplot-derived RDG versus sign(λ_2)·ρ graph for $\mathbf{4}^{E}\mathbf{d}\cdot H_2O$. S15
Calculated structures: Cartesian coordinates and energies for all computed species S16

Experimental data

Preparative methods

All reactions and manipulations were carried out under an atmosphere of dry argon, using Schlenk and vacuum line techniques. Argon was cleaned over a BTS catalyst; the drying of the Ar gas occured via silica gel and P_2O_5. Solvents were dried according to standard procedures using sodium or sodium/benzophenone and stored in brown glasses over sodium wire, and under inert gas atmosphere.

Analytical methods

Melting point measurements were determined with a Büchi (530) capillary apparatus.
Elemental analysis were performed using an Elementar VarioEL analytical gas chromatograph.
Mass spectrometry: Electron ionization (70eV) mass spectra were recorded on a Kratos MS 50 or on a MAT 95XL Finnigan spectrometer.
NMR spectra were recorded on a Bruker AX 300 spectrometer (^{1}H: 300.1 MHz, ^{13}C: 75.0 MHz and ^{31}P: 121.5 MHz,) using $CDCl_3$ as solvent; shifts are given relative to external tetramethylsilane (^{1}H, ^{13}C,) and 85% H_3PO_4 (^{31}P).
UV/vis spectra were recorded on a Shimadzu UV-1650 PC spectrometer using dichloromethane as solvent and quartz glass cells.
IR spectra were recorded with a SMART iTR Nicolet 380 FT IR spectrometer.
Single-crystal structure analysis: Crystal structures were recorded on a Nonius Kappa CCD diffractometer and a Nonius MACH3 diffractometer. The structures were solved by Patterson methods or Direct Methods (SHELXS-97) and refined by full-matrix least squares on F2 (SHELXL-97). All non-hydrogens were refined anisotropically. Hydrogen atoms were included isotropically using the riding model on the bound atoms; in some (denoted) cases hydrogen atoms were located in the Fourier difference electron density. Absorption corrections were carried out analytically or semi-empirically from equivalents. Additionally, some calculation of bond lengths and angles were obtained using the Ortep32 program.

General procedure for the synthesis of imino azaphosphiridine complexes ***4a,b***. To a THF solution of dichloro(pentamethylcyclopentadienyl)phosphane tungsten complex **1** and 1 eq. of 12-crown-4, 1.1 eq. of *tert*-butyl lithium (1.7 M in *n*-hexane) were slowly added at -78 °C. After 15 min. 1 eq. of *N,N'*-dialkylcarbodiimide **3a,b** was slowly added at -78 °C. The reaction mixture was stirred and warmed up slowly (4 h) to room temperature. The solvent was then removed in *vacuo* (~10^{-2} mbar) and LiCl filtered from a pentane solution; the products were crystallized from *n*-pentane at -50 °C.

4a: Yield 412 mg (75 %), m.p. 153-154 °C, ^{1}H NMR ($CDCl_3$): δ = 1.14 (d, 3H, P-C-C*H*$_3$, $^{3}J_{P,H}$ = 14.1 Hz), 1.24 (d, 3H, C-N-CH-C*H*$_3$, $^{3}J_{H,H}$ = 6.5 Hz), 1.27 (d, 3H, C-N-CH-C*H*$_3$, $^{3}J_{H,H}$ = 6.5 Hz), 1.44 (d, 3H, C=N-CH-C*H*$_3$, $^{3}J_{H,H}$ = 6.6 Hz), 1.47 (d, 3H, C=N-CH-C*H*$_3$, $^{3}J_{H,H}$ = 6.5 Hz), 1.84 (d, 6H, Cp*-C*H*$_3$, $^{4}J_{P,H}$ = 4.9 Hz), 1.89 (s, 3H, Cp*-C*H*$_3$), 1.97 (s, 3H, Cp*-C*H*$_3$), 3.65 (sept, 1H, N-C*H*$(CH_3)_2$, $^{3}J_{H,H}$ = 6.5 Hz), 3.65 (dsept, 1H, N-C*H*$(CH_3)_2$, $^{3}J_{H,H}$ = 6.5 Hz, $^{4}J_{P,H}$ = 2.3 Hz), ^{13}C NMR : δ = 11.0 (d, Cp*-*C*H$_3$, $^{4}J_{P,C}$ = 3.3 Hz), 11.5 (d, Cp*-*C*H$_3$, $^{4}J_{P,C}$ = 1.6 Hz), 12.00 (d, Cp*-*C*H$_3$, $^{3}J_{P,C}$ = 5.7 Hz), 12.00 (d, Cp*-*C*H$_3$, $^{3}J_{P,C}$ = 5.7 Hz), 16.56 (d, P-*C*-C*H*$_3$, $^{2}J_{P,C}$ = 4.3 Hz), 21.78 (d, C-N-C-*C*H$_3$, $^{2}J_{P,C}$ = 1.9 Hz), 22.41 (d, C-N-C-*C*H$_3$, $^{2}J_{P,C}$ = 1.6 Hz), 25.14 (s, C=N-C-*C*H$_3$), 25.30 (s, C=N-C-*C*H$_3$), 51.62 (s, C=N-*C*H-CH$_3$), 57.71 (d, N-*C*H-CH3, $^{2}J_{P,C}$ = 13.5 Hz), 64.64 (d, P-*C*(Cp*), $^{1}J_{P,C}$ = 15.5 Hz), 133.33 (d, C=*C*, $J_{P,C}$ = 7.1 Hz), 135.55 (s, C=*C*,), 139.7 (d, N=*C*, $^{1}J_{P,C}$ = 5.5 Hz), 142.71 (d, C=*C*, $J_{P,C}$ = 6.0 Hz), 144.12 (d, C=*C*, $J_{P,C}$ = 7.8 Hz), 195.02 (dsat, $^{2}J_{P,C}$ = 7.6 Hz, $^{1}J_{W,C}$ = 125.1, *cis*-*C*O), 196.45 (d, $^{2}J_{P,C}$ = 33.3 Hz, *trans*-*C*O), ^{31}P NMR ($CDCl_3$): δ = 4.03 (ssat, $^{1}J_{W,P}$ = 265.8 Hz), MS (EI, ^{184}W) : m/z (%): 618.1, [M+] (4); 588.1, [M]+-CO (5); 560.1, [M]+-2xCO, (2); 532.1, [M]+-3xCO, (2); 504.1, [M]+-4xCO (2); 476.1, [M]+-5xCO,(2), IR (ATR): ῡ = 2969 (b, ν-CH_2), 2924 (b, ν-CH_2), 2071 (s, ν-CO), 2074 (s, ν-CO), 1995 (s, ν-CO), 1895 (b, ν-CO), 1609 (b, ν-C=N) cm^{-1}; elemental analysis for $C_{22}H_{29}N_2O_5PW$ Calc (%): C 42.88, H 4.74, N 2.55, found (%): C 42.72 , H 5,06 , N 4.28.

4b: Yield 250 mg (63 %), ^{1}H NMR ($CDCl_3$): δ =1.06 (d, 3H, $^{3}J_{P,H}$ = 14.2 Hz, Cp*-C^{1}*H*$_3$), 1.10-1.33 (br m, 10H, Cy-C*H*$_2$), 1.42-1.90 (br m, 10H, Cy-C*H*$_2$), 1.77 (s, 3H, Cp*-C*H*$_3$), 1.78 (s, 3H, Cp*-C*H*$_3$), 1.83 (s, 3H, Cp*-C*H*$_3$), 1.90 (s, 3H, Cp*-C*H*$_3$), 3.15 (br m, 2H, 2 x NC*H*), ^{13}C NMR : δ = 10.5 (d, Cp*-*C*H$_3$, $^{3}J_{P,C}$ = 2.7 Hz), 11.3 (s, Cp*-*C*H$_3$), 11.7 (s, Cp*-*C*H$_3$), 11,9 (s, Cp*-*C*H$_3$), 16.3 (d, Cp*-*C*H$_3$, $^{2}J_{P,C}$ = 3.7 Hz), 24.7 (s,

Cy*C*H$_2$), 24.9 (s, Cy*C*H$_2$), 25.1 (d, Cy*C*H$_2$, $^3J_{P,C}$ = 18.2 Hz), 25.1 (d, Cy*C*H$_2$, $^3J_{P,C}$ = 17.6 Hz), 25.4 (s, Cy*C*H$_2$), 25.5 (s, Cy*C*H$_2$), 34.9 (s, Cy*C*H$_2$), 34.9 (s, Cy*C*H$_2$), 35.2 (s, Cy*C*H$_2$), 35.5 (s, Cy*C*H$_2$), 55.7 (s, N-*C*H), 58.8 (s, N-*C*H), 64.64 (d, P-*C*(Cp*), $^1J_{P,C}$ = 13.5 Hz), 133.15 (d, C=*C*, $J_{P,C}$ = 6.9 Hz), 135.45 (d, C=*C*, $J_{P,C}$ = 1.5 Hz), 139.95 (d, N=*C*, $^1J_{P,C}$ = 5.2 Hz), 142.33 (d, C=*C*, $J_{P,C}$ = 6.0 Hz), 143.87 (d, C=*C*, $J_{P,C}$ = 78.6 Hz), 194.85 (dSat, $^2J_{P,C}$ = 7.5 Hz, $^1J_{W,C}$ = 125.5, *cis*-*C*O), 196.28 (d, $^2J_{P,C}$ = 33.1 Hz, *trans*-*C*O), ^{31}P NMR ($CDCl_3$): δ = 1.47 (s, $^1J_{W,P}$ = 265.8 Hz), IR (ATR): ῡ = 2971 (b, ν-CH_2), 2922 (b, ν-CH_2), 2070 (s, ν-CO), 2069 (s, ν-CO), 1993 (s, ν-CO), 1890 (b, ν-CO), 1613 (b, ν-C=N) cm^{-1}.

General procedure for the synthesis of complex **5a,b**. To a THF solution of **4a,b**, 1 eq. of water was added at room temperature and the reaction mixture was stirred during 10 minutes. The solvent was then removed in *vacuo* (~10^{-2} mbar) and a yellow oil was obtained. The compound was then crystallized from pure Et_2O at -20 °C.

5a: Yield 250 mg (80 %), m.p. 164-165 °C, ^{1}H NMR ($CDCl_3$): δ = 1.24-1.30 (m, 12H, $^{i\text{-}Pr}$C*H*$_3$), 1.43 (d, 3H, Cp*-C*H*$_3$, $^3J_{P,H}$ = 16.7 Hz), 1.73 (bs, 3H, Cp*-C*H*$_3$), 1.82 (dd, 3H, Cp*-C*H*$_3$, $J_{P,H}$ = 3.3 Hz, $J_{H,H}$ = 1.1 Hz), 1.86 (bs, 3H, Cp*-C*H*$_3$), 2.05 (bs, 3H, Cp*-C*H*$_3$), 3.89 (m, 2H, , $^{i\text{-}Pr}$C*H*), 6.79 (bs, 2H, N-*H*); ^{13}C NMR : δ = 10.9 (s, Cp*-*C*H$_3$), 11.7 (d, Cp*-*C*H$_3$, $J_{C,P}$ = 1.0 Hz), 12.9 (s, Cp*-*C*H$_3$), 13.0 (s, Cp*-*C*H$_3$), 16.0 (d, P-C-*C*H$_3$, $^2J_{C,P}$ = 5.8 Hz), 23.6 (s, 2 x ^{i}Pr-*C*H3), 23.7 (s, 2 x ^{i}Pr-*C*H3), 47.1 (s, 2 x $^{i\text{-}Pr}$*C*H), 66.2 (d, $^1J_{C,P}$ = 2.7 Hz, P-Cp*-*C1*), 135.0 (d, $J_{C,P}$ = 2.7 Hz, C=C), 135.2 (d, $J_{C,P}$ = 4.7 Hz, C=C), 139.9 (d, $J_{C,P}$ = 6.7 Hz, C=C), 143.4 (d, $J_{C,P}$ = 3.7 Hz, C=C), 65.3 (d, Cp**C*^{1}, $^1J_{C,P}$ = 2.7 Hz), 134.2 (d, C=*C*, $^3J_{C,P}$ = 2.7 Hz), 134.3 (d, *C*=C, $^2J_{C,P}$ = 4.5 Hz), 171.9 (d, N-*C*-N, $^1J_{P,C}$ = 14.4 Hz), 198.6 (dsat, $^2J_{P,C}$ = 8.4 Hz, $^1J_{W,C}$ = 126.4, *cis*-*C*O), 200.7 (d, $^2J_{P,C}$ = 23.6 Hz, *trans*-*C*O, $^1J_{W,C}$ = 143.4, *trans*-*C*O), ^{31}P NMR ($CDCl_3$): δ = 84.3 (qsat, $^1J_{W,P}$ = 269.0 Hz, $J_{P,H}$ = 16.0 Hz); MS (EI, 184W) : m/z (%): 634.1, [M+], (10); 579.0, 606.1, [M]+-CO, (1); 523.0, 578.1, [M]+-2xCO, (1); 550.1, [M]+-3xCO, (5); 499.0, [M]+-Cp*, (100); 471.0, [M]+-Cp*-CO, (60); 443.0, [M]+-Cp*-2xCO,(80); 415.0, [M]+-Cp*-3xCO,(85); 387.0, [M]+-Cp*-4xCO,(40); 359.0, [M]+-Cp*-5xCO,(20); 175.1, [M]+-Cp*-W(CO)5,(15); 58.0, $CHMe_2NH$, (20); IR (ATR): ῡ = 3387 (b, NH) 2977 (b, ν-CH_2), 2918 (b, ν-CH_2), 2065 (s, ν-CO), 1978 (s, ν-CO), 1910 (s, ν-CO), 1888 (s, ν-

CO), 1609 (b, ν-C=N) cm^{-1}; elemental analysis for $C_{22}H_{31}N_2O_6PW$ Calc (%): C 41.66, H 4.93, N 4.42, found (%): C 41.52 , H 5.104 , N 4.29.

5b: Yield 215 mg (70 %), m.p. 174-175 °C, ^{1}H NMR ($CDCl_3$): δ = 1.19-1.37 (br m, 10H, Cy-C*H*$_2$), 1.43 (d, 3H, $^3J_{P,H}$ = 16.8 Hz, Cp*-C^1*H*$_3$), 1.65-1.69 (br m, 2H, Cy), 1.73 (s, 3H, Cp*-C*H*$_3$), 1.82 (d, 3H, $J_{P,H}$ = 3.4 Hz, Cp*-C*H*$_3$), 1.83-1.90 (broad m, 8H, CyC*H*$_2$), 1.86 (s, 3H, Cp*-C*H*$_3$), 3.42 (br m, 2H, 2 x NC*H*), 6.8 (br s, 2 x N*H*); ^{13}C NMR : δ = 9.9 (s, Cy*C*), 10.7 (d, Cy*C*, $J_{C,P}$ = 0.6 Hz), 11.97 (d, Cy*C,* $J_{C,P}$ = 2.8 Hz), 12.01 (s, Cy*C*), 14.91 (s, Cy*C*), 23.49 (s, Cp*-*C*H$_3$), 23.64 (s, Cp*-*C*H$_3$), 23.8 (s, Cp*-*C*H$_3$), 32.95 (s, Cp*-*C*H$_3$), 32.99 (s, Cp*-*C*H$_3$), 53.4 (s, Cy*C*), 65.3 (d, Cp**C*^{1,} $^1J_{C,P}$ = 2.7 Hz), 134.2 (d, C=*C*, $^3J_{C,P}$ = 2.7 Hz), 134.3 (d, *C*=C, $^2J_{C,P}$ = 4.5 Hz), 138.8 (d, *C*=C, $^2J_{C,P}$ = 6.7 Hz), 142.2 (d, *C*=C, $^3J_{C,P}$ = 4.0 Hz), 170.8 (d, N-*C*-N, $^1J_{C,P}$ = 14.5 Hz), 197.6 (dsat, $^2J_{P,C}$ = 8.6 Hz, $^1J_{W,C}$ = 126.0, *cis*-*C*O), 199.7 (d, $^2J_{P,C}$ = 23.5 Hz, *trans*-*C*O), ^{31}P NMR ($CDCl_3$): δ = 85.0 (qsat, $^1J_{W,P}$ = 269.8 Hz, $J_{P,H}$ = 16.8 Hz), MS (EI, 184W) : m/z (%): 714.1, [M+], (5); 579.0, [M]+-Cp*(80); 551.0, [M]+-Cp*-CO, (60); 523.0, [M]+-Cp*-2xCO, (90); 495.2, [M]+-Cp*-3xCO, (90); 467.2, [M]+-Cp*-4xCO,(50), IR (ATR): ῡ = 3390 (b, NH), 2932 (b, ν-CH_2), 2857 (b, ν-CH_2), 2062 (s, ν-CO), 1971 (s, ν-CO), 1912 (s, ν-CO), 1892 (s, ν-CO), 1618 (b, ν-C=N) cm^{-1}; elemental analysis for $C_{28}H_{39}N_2O_6PW$ Calc (%): C 47.07, H 5.50, N 3.92, found (%): C 47.27 , H 5.83 , N 3.74.

Low temperature ^{1}H NMR monitoring

The ^{1}H NMR spectra ($CDCl_3$) of **5a** showed a broad singlet at 6.7 ppm for the N-*H* hydrogen atoms at ambient temperature. For **4a**, the ^{1}H NMR shows a multiplet consisting in a septet ($^3J_{H,H}$ = 6.5 Hz) and a doublet of septets ($^3J_{H,H}$ = 6.5 Hz, $^3J_{P,H}$ = 2.3 Hz) at 3.6 ppm , corresponding to the isopropyl C*H* protons. Upon cooling from room temperature to -70 °C the N-*H* signal splits into two doublets at 5.1 and 8.0 ppm ($^4J_{P,C}$ = 8.0 Hz) revealing the rotation around the P-C^N bond is hampered due to an O-H-N hydrogen bonding. According to the Gutowsky–Holms equation (Kc = $\pi\nabla/\sqrt{2}$),[14a,b] and the Eyring equation {$\Delta G^{\neq}c$ = 4.58Tc[10.32 + log (Tc/Kc)]}[14b,15] the free energy activation at coalescence temperature was calculated to be between 11.1-11.3 kcal mol^{-1}.

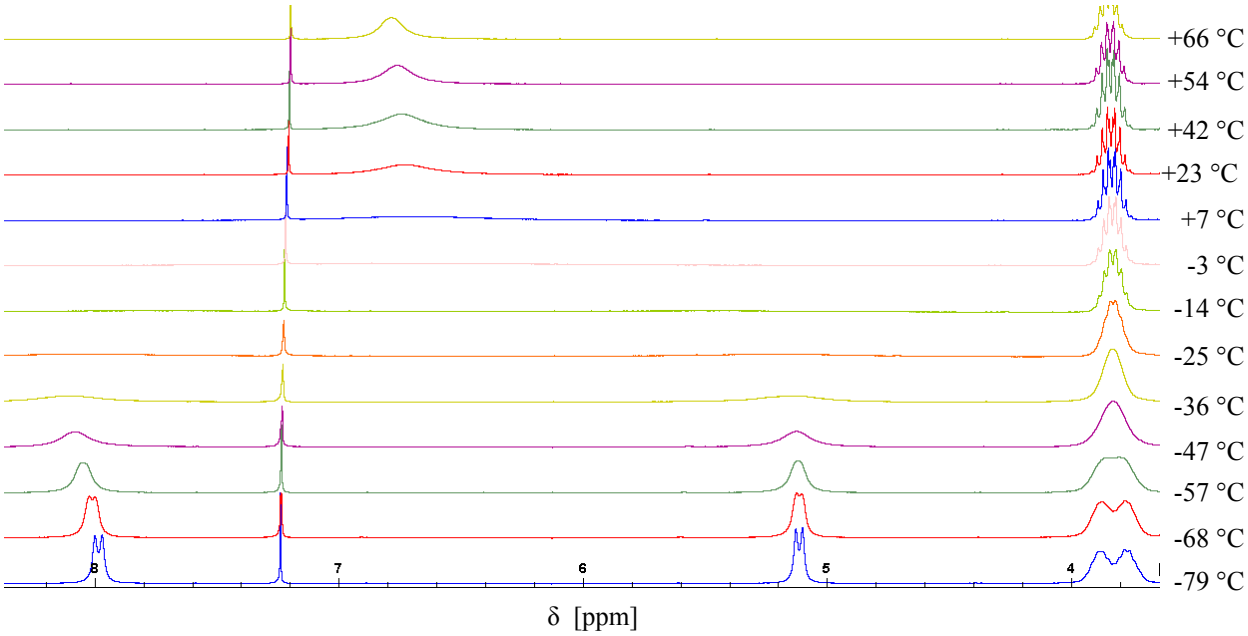

Figure SI 1: Low temperature ^{31}P NMR monitoring of **5a**.

According to the Gutowsky–Holms equation ($K_c = \pi\nabla/\sqrt{2}$),[14a,b] and the Eyring equation $\{\Delta G^{\neq}_c = 4.58T_c[10.32 + \log (T_c/K_c)]\}$[14b,15] the free energy activation at coalescence temperature for this process was calculated to be between 10.9 and 11.4 kcal mol^{-1}.

$K_c = \pi\nabla/\sqrt{2} = \pi\ 861/\sqrt{2} = 1912.7$

$\{\Delta G^{\neq}_c = 4.58 \times 264\ [10.32 + \log (264/1912.7)] = 11.4$ kcal mol^{-1}

$K_c = \pi\nabla/\sqrt{2} = \pi\ 33/\sqrt{2} = 73.3$

$\{\Delta G^{\neq}_c = 4.58 \times 221\ [10.32 + \log (221/73.3)] = 10.9$ kcal mol^{-1}

X-ray crystallographic analysis

Single crystals of **4a**, **5a**, and **5b** were obtained from recrystallizations in Et_2O at -30 °C. Crystal data are summarized in Tables 1, 2, 3. In the analysis for compound **4a**, disorder was found (in the ratio of 67:33), which has been appropriately solved. The disordered parts were restricted with using the instructions of SADI, EADP, and EXYZ). In the analysis of **5b**, DELU instructions were adopted for the W–C bonds. The residual peaks are located close to W and P atoms. All hydrogen atoms were placed using AFIX instructions, while all other atoms were refined anisotropically. Supplementary crystallographic data were deposited at the Cambridge Crystallographic Data Centre (CCDC) under the numbers CCDC-1039383 (**5b**), 1039384 (**4a**), and

1039385 (**5a**), respectively, and can be obtained free of charge from *via* www.ccdc.cam.ac.uk/data_request.cif.

X-ray crystallography analysis of 4a.

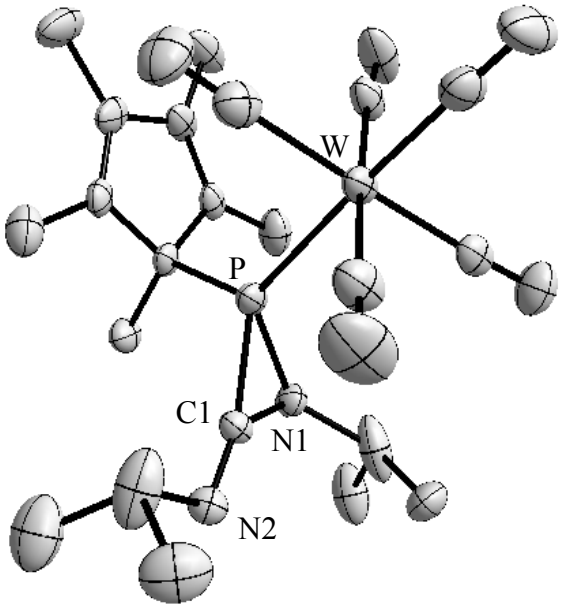

Figure SI 2. Figure 1. Molecular structure of 3-imino-azaphosphiridine complex **4a**. (50 % probability level, hydrogen atoms are omitted for clarity). Selected X-ray crystal structure data (distances [Å] and angles [°]): P-W 2.4779(9), P-C(1) 1.840(6), C(1)-N(1) 1.366(8), C(1)-N(2) 1.249(6), P-N(1) 1.795(5), C(1)-P-N(1) 44.1(3), N(1)-C(1)-P 66.2(3), P-N(1)-C(1) 69.7(4).

Table 1. Crystal data and structure refinement for **4a.**

Device Type	Bruker X8-KappaApex-II
Empirical formula	$C_{22}H_{29}N_2O_5PW$
Formula weight	616.29
Temperature/K	100.15
Crystal system	triclinic
Space group	P-1
a/Å	10.9909(5)
b/Å	11.0605(6)
c/Å	12.8740(10)
α/°	108.084(4)
β/°	95.194(4)
γ/°	118.186(2)

Volume/Å^3	1257.68(14)
Z	2
ρ_{calc}g/cm^3	1.627
μ/mm^{-1}	4.688
F(000)	608.0
Crystal size/mm^3	0.26 × 0.06 × 0.02
Absorption correction	empirical
Tmin; Tmax	0.5393; 0.7460
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.316 to 55.994°
Completeness to theta	0.996
Index ranges	-14 ≤ h ≤ 14, -14 ≤ k ≤ 14, -16 ≤ l ≤ 16
Reflections collected	12812
Independent reflections	6035 [R_{int} = 0.0322, R_{sigma} = 0.0489]
Data/restraints/parameters	6035/2/339
Goodness-of-fit on F^2	1.026
Final R indexes [I>=2σ (I)]	R_1 = 0.0290, wR_2 = 0.0569
Final R indexes [all data]	R_1 = 0.0409, wR_2 = 0.0610
Largest diff. peak/hole / e Å^{-3}	0.97/-1.27

X-ray crystallography analysis of 5a.

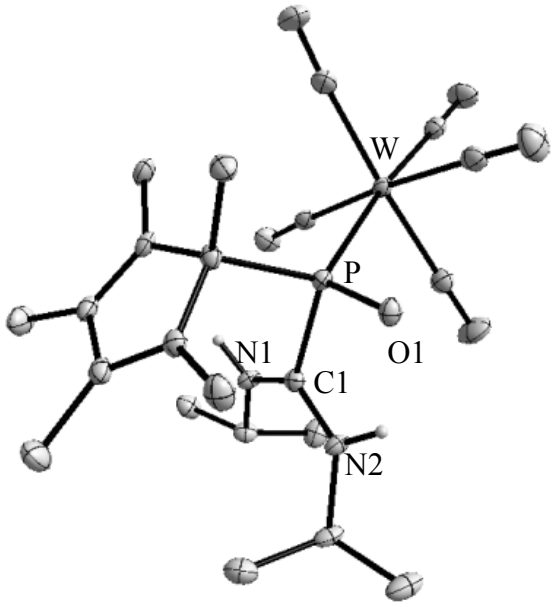

Figure SI 3. Molecular structure of complex **5a** (50% probability levels, hydrogen atoms, except at N, are omitted for clarity). Selected X-ray crystal structure data (distances [Å] and angles [°]): P-W 2.5384(6), P-C(1) 1.897(2), C(1)-N(1) 1.319(3),

C(1)-N(2) 1.311(3), P-O 1.5201(16), C(1)-P-O 100.61(10), N(1)-C(C1)-N(2) 127.1(2), N(1)-C(1)-P 122.71(17), N(2)-C(1)-P 110.03(16).

Table 2. Crystal data and structure refinement for **5a**.

Empirical formula	$C_{22}H_{31}N_2O_6PW$
Formula weight	634.31
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/c$ (#14)
a/Å	9.5748(5)
b/Å	27.7242(13)
c/Å	10.5851(5)
β/°	115.3400(10)
Volume/Å^3	2539.5(2)
Z	4
ρ_{calc} g/cm^3	1.659
μ/mm^{-1}	4.649
F(000)	1256.0
Crystal size/mm^3	0.13 × 0.10 × 0.04
Absorption correction	empirical
Tmin; Tmax	0.5227; 0.7460
Radiation	MoKα (λ = 0.71073 Å)
2*θ* range for data collection/°	5.54 to 56°
Completeness to theta	0.995
Index ranges	$-12 \le h \le 11$, $-36 \le k \le 36$, $-13 \le l \le 13$
Reflections collected	19281
Independent reflections	6102 [R_{int} = 0.0297, R_{sigma} = 0.0302]
Data/restraints/parameters	6102/0/298
Goodness-of-fit on F^2	1.021
Final R indexes [$I>2\sigma(I)$]	R_1 = 0.0205, wR_2 = 0.0462
Final R indexes [all data]	R_1 = 0.0248, wR_2 = 0.0476
Largest diff. peak/hole / e Å^{-3}	0.98/-0.63

In order to determine the position of protons, the structure of **5a** was computationally determined (see Computational Details). Computed structural parameters and calculated ^{1}H and ^{31}P NMR chemical shifts of "Structure A" are in good agreement with those experimentally observed. Accordingly, compound **5a** should exhibit "Structure A" structure with two protons at the two nitrogen atoms, whereas structures B and C correspond to intermediates (not isolated nor detected) **6a^{conf}** and **6a**, respectively.

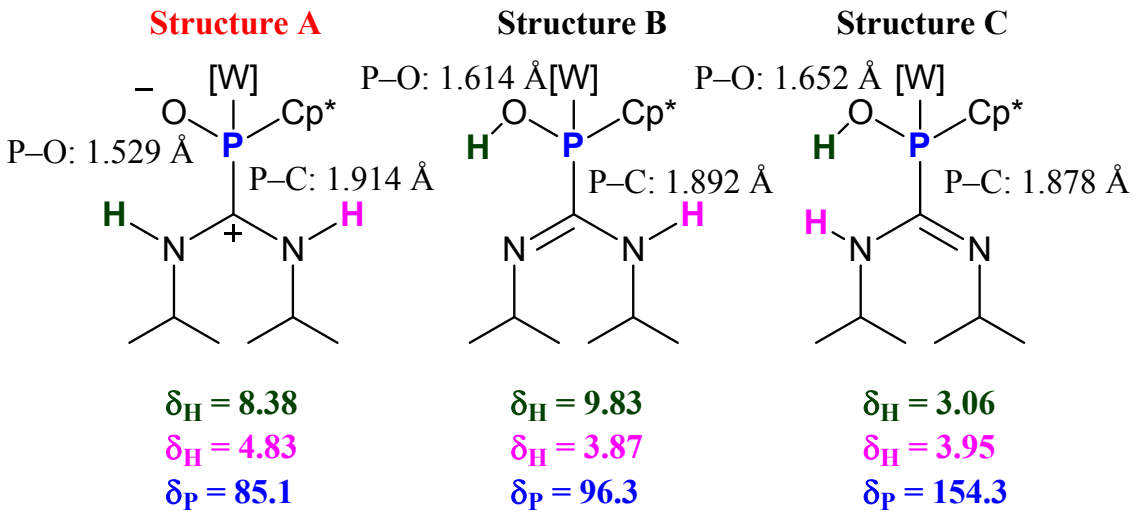

Figure SI 4. Computed ^{1}H and ^{31}P NMR chemical shifts (ppm) for **5a** and related structures.

X-ray crystallography analysis of 5b.

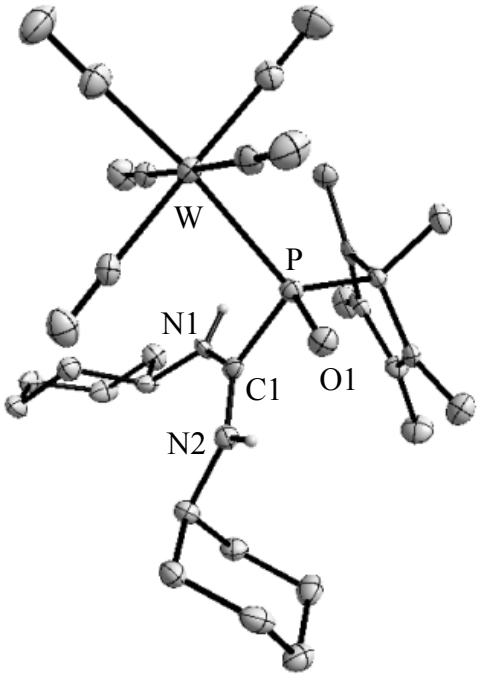

Figure SI 5. Molecular structure of complex **5b**. (50% probability levels, hydrogen atoms, except at N, are omitted for clarity). Selected X-ray crystal structure data (distances [Å] and angles [°]): P-W 2.5440(11), P-C(1) 1.902(4), C(1)-N(1) 1.317(5),

C(1)-N(2) 1.305(5), P-O1 1.521(3), C(1)-P-O 101.76(19), N(1)-C(C1)-N(2) 128.0(4), N(1)-C(1)-P 121.3(3), N(2)-C(1)-P 110.5(3).

Table 3. Crystal data and structure refinement for **5b.**

Device Type	Nonius KappaCCD
Empirical formula	C28 H39 N2 O6 P W
Moiety formula	C28 H39 N2 O6 P W
Formula weight	714.43
Temperature	123(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 21/c
Unit cell dimensions	a = 10.9216(4) A alpha = 90 deg. b = 23.5529(11) A beta = 126.717(2) deg. c = 14.5767(4) A gamma = 90 deg.
Volume	3005.7(2) A^3
Z, Calculated density	4, 1.579 Mg/m^
Absorption coefficient	3.938 mm^-1
F(000)	1432
Crystal size	0.24 x 0.07 x 0.04 mm
Theta range for data collection	2.57 to 28.00 deg.
Limiting indices	-11<=h<=14, -28<=k<=31, -19<=l<=19
Reflections collected / unique	24433 / 7162 [R(int) = 0.0803]
Completeness to theta = 28.00	98.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8584 and 0.4516
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7162 / 5 / 348
Goodness-of-fit on F^2	0.843
Final R indices [I>2sigma(I)]	R1 = 0.0360, wR2 = 0.0545
R indices (all data)	R1 = 0.0782, wR2 = 0.0631
Largest diff. peak and hole	2.838 and -2.320 e.A^-3

Homodesmotic reactions used for obtaining ring strain energies

Ring strain can be quantitatively evaluated using homodesmotic reactions in which the number and type of bonds and valencies of all atoms are conserved and by changing the sign of the obtained reaction energy. The three obtained values are then averaged.

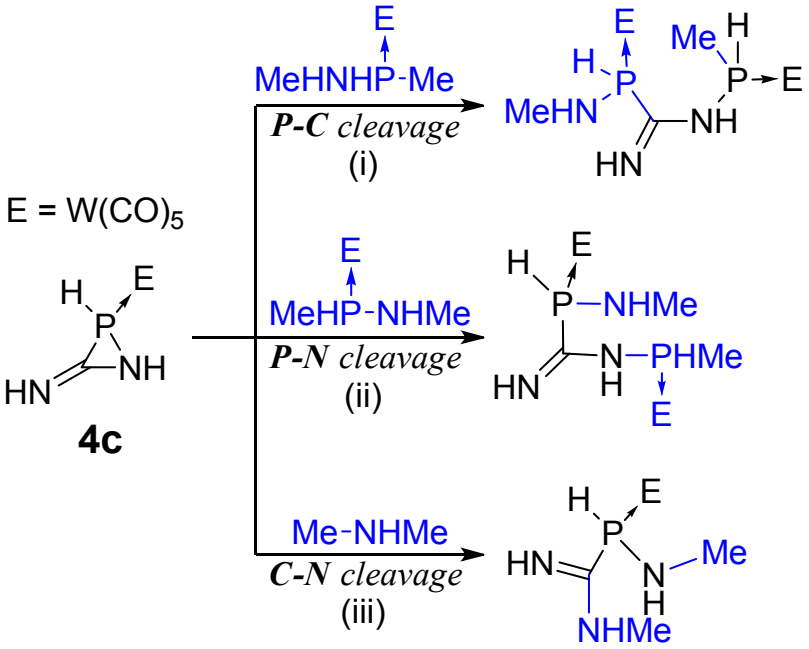

Figure SI 6: Homodesmic reactions for ring-opening of azaphosphiridine **4c**.

A RSE of 49.90 and 51.52 kcal/mol was obtained at the SCS-MP2/def2-TZVPP level for diastereomers $\mathbf{4}^{Z}\mathbf{c}$ and $\mathbf{4}^{E}\mathbf{c}$ respectively (in good agreement with corresponding values of 50.58 and 52.26 kcal mol^{-1} al LPNO-NCEPA1/def2-TZVPP). As a reference, the RSE computed (same SCS-MP2/def2-TZVPP level) for the parent azaphosphiridine, aziridine and oxirane ring systems are 23.9,[1] 27.4[1] and 25.0[2] kcal/mol, respectively.

[1] A. Espinosa and R. Streubel, *Chem. Eur. J.*, 2011, **17**, 3166-3178.
[2] O. Krahe, F. Neese and R. Streubel, *Chem. Eur. J.*, 2009, **15**, 2594-2601.

Computational details

DFT calculations were performed with the ORCA program.[3] All geometry optimizations were run in redundant internal coordinates with tight convergence criteria, in the gas-phase (see below) and using the B3LYP functional[4] together with the def2-TZVP basis set.[5] For W atoms the [SD(60,MWB)] effective core potential[6] (ECP) was used. The latest Grimme's semiempirical atom-pair-wise London dispersion correction (DFT-D3) was included in all calculations.[7] Harmonic frequency calculations verified the nature of ground states or transition states (TS) having all positive frequencies or only one imaginary frequency, respectively. From these optimized geometries all reported data were obtained by means of single-point (SP) calculations using the more polarized def2-TZVPP[8] basis set. Reported energies were corrected for the zero-point vibrational term at the optimization level. Unless otherwise stated, final energies were obtained by means of local correlation schemes of type LPNO (Local Pair Natural Orbital) for high level single reference methods, such as CEPA (Coupled Electron-Pair Approximation)[9], here the slightly modified NCEPA/1 version implemented in ORCA was used.[10] RSE energies were additionally obtained at the spin component scaled (SCS) Moeller-Plesset MP2 level.[11] Calculations related to the parent complex **4c** (E/Z-isomerism, adduct formation with water and homodesmotic reactions) were entirely run

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[3] ORCA - An *ab initio*, DFT and semiempirical SCF-MO package. Written by F. Neese, Max Planck Institute for Bioinorganic Chemistry, D-45470 Mülheim/Ruhr, 2012. Version 3.0.2. Web page: http://www.cec.mpg.de/forum/portal.php. F. Neese, "The ORCA program system", *WIREs Comput Mol Sci* **2012**, *2*, 73–78.

[4] Becke, A. D. *J. Chem. Phys.,* **1993**, *98*, 5648-5652. Lee, C. T.; Yang, W. T.; Parr, R. G. *Phys. Rev. B,* **1988**, *37*, 785-789.

[5] Weigend, F.; Ahlrichs, R. Phys. *Chem. Chem. Phys.*, **2005**, *7*, 3297-3305.

[6] Andrae, D.; Haeussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta*, **1990**, *77*, 123-141. ECP basis sets for W [SD(60,MWB)] have been obtained from Turbomole basis set library at ftp://ftp.chemie.uni-karlsruhe.de/pub/basen/.

[7] Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.*, **2010**, *132*, 154104.

[8] Bergner, A.; Dolg, M.; Kuchle, W.; Stoll, H.; Preuss, H. *Mol. Phys.* **1993**, *80*, 1431−1441. Obtained from the EMSL Basis Set Library at https://bse.pnl.gov/bse/portal. D. Feller, *J. Comp. Chem.*, **1996**, *17*, 1571-1586.

[9] a) F. Neese, F. Wennmohs and A. Hansen, *J. Chem. Phys.,* 2009, **130**, 114108; b) F. Neese, A. Hansen, F. Wennmohs and S. Grimme, *Acc. Chem. Res.,* 2009, **42**, 641–648.

[10] F. Wennmohs and F. Neese, *Chem. Phys.,* 2008, **343**, 217–230.

[11] a) S. Grimme, *J. Chem. Phys.*, 2003, **118**, 9095–9102; b) S. Grimme, L. Goerigk, F. F. Reinhold, *WIREs Comput. Mol. Sci.*, 2012, **2**, 886-906.

in the gas-phase. For all other computed systems, solvent effects (toluene by default; also THF and chloroform) were taken into account via the COSMO solvation model.[12] SP calculations related with the energy profile depicted in Figure 3 were done in THF as solvent, whereas chloroform was used as solvent for both the optimization and subsequent SP calculations for the study of the P-C bond rotation in **5d**. Wiberg bond indices (WBI) were obtained from the natural bond orbital (NBO) population analysis.[13] Bader's AIM-derived topological analysis of the electron density was conducted with AIM2000.[14] Figure 4 in the main text was drawn with VMD.[15]

Magnetic shielding tensors for determination of chemical shifts for **5a** were obtained with Gaussian09[16] at the GIAO-CPCM($CHCl_3$)/B3PW91/6-311G(2d,p) [6-311+G(3d) for P and DZP[17] for W] level.

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[12] a) A. Klamt, G. Schüürmann, *J. Chem. Soc. Perkin Trans. 2,* **1993**, *220*, 799-805; b) A. Klamt, *J. Phys. Chem.* **1995**, *99*, 2224-2235.

[13] Using the NBO 5.9 code interfaced to Gaussian09. Glendening, E. D.; Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Bohmann, J. A.; Morales, C. M.; Weinhold, F. Theoretical Chemistry Institute, University of Wisconsin, Madison (2001).

[14] (a) AIM2000 v. 2.0, designed by Biegler-König, F. and Schönbohm, J. 2002. Home page http://www.aim2000.de/. Biegler-König, F.; Schönbohm, J.; Bayles, D. J. *Comp. Chem.* **2001**, *22*, 545-559. (b) Biegler-König, F.; Schönbohm, J. *J. Comp. Chem.* **2002**, *23*, 1489-1494.

[15] VMD — Visual Molecular Dynamics. W. Humphrey, A. Dalke, K. Schulten, *J. Molec. Graphics*, **1996**, *14*, 33-38. Home page http://www.ks.uiuc.edu/Research/vmd/.

[16] Gaussian 09, Revision A.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

[17] A. Canal Neto, F. E. Jorge, *Chem. Phys. Lett.* **2013**, *582*, 158-162

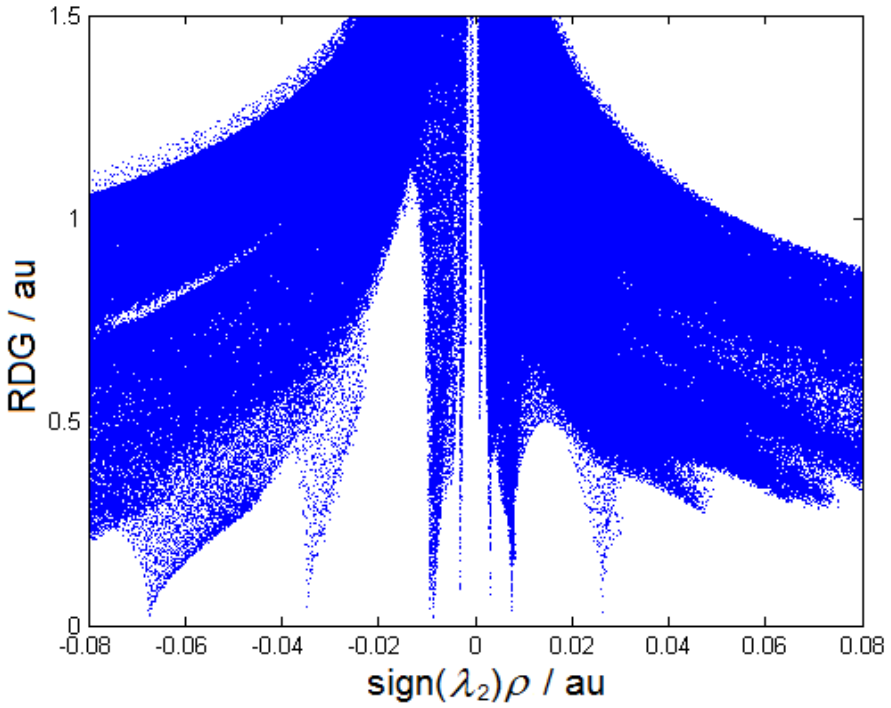
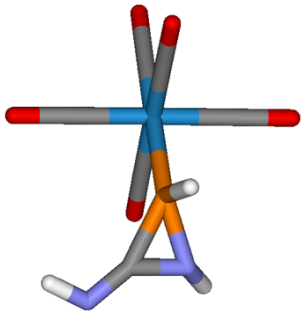


Figure SI 7: NCIplot-derived representation of RDG (au) versus sign(λ_2)·ρ (au) for complex $\mathbf{4}^{E}\mathbf{d}\cdot H_2O$.

Calculated structures.

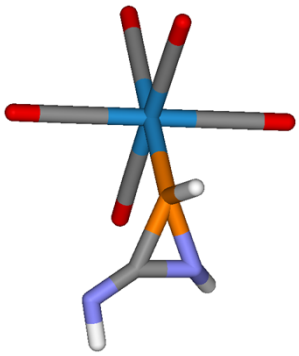
Cartesian coordinates (in Å) and energies for all computed species.-



4c: E = -1122.51045249284 au (gas-phase)

ZPE = 0.0874409 au

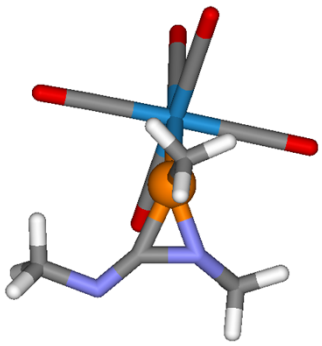
N	-0.066521	0.293599	-0.199800	C	1.879444	-2.429286	-2.435344
P	1.616966	-0.196684	-0.145638	O	1.226976	-3.343222	-2.645935
C	0.706380	1.350670	0.179792	C	1.839776	0.377128	-3.270519
N	0.569485	2.581761	0.357141	O	1.148094	1.013437	-3.920544
W	3.061230	-0.771765	-2.060058	C	4.233196	0.897168	-1.689900
C	4.249788	-1.269361	-3.648693	O	4.872322	1.820769	-1.484142
O	4.912175	-1.553102	-4.536546	H	-0.723894	0.300817	-0.972205
C	4.246502	-1.905239	-0.799156	H	1.434081	3.036697	0.636938
O	4.891741	-2.529559	-0.092567	H	1.625034	-0.921845	1.065918



4^{E}c: E = -1122.507747427 au (gas-phase)

ZPE = 0.08723091 au

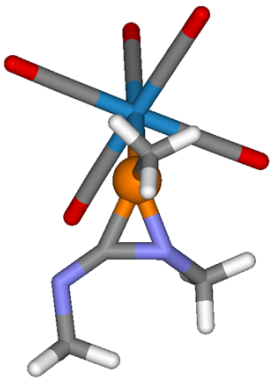
N	-0.111132	0.212398	-0.171717	C	1.855636	-2.385414	-2.433354
P	1.614959	-0.167775	-0.122179	O	1.194186	-3.290293	-2.657465
C	0.647979	1.320975	0.145952	C	1.834994	0.430587	-3.225447
N	0.620822	2.558371	0.323673	O	1.141858	1.082878	-3.858984
W	3.050312	-0.745315	-2.038048	C	4.250989	0.908951	-1.662400
C	4.231629	-1.239510	-3.633405	O	4.913328	1.815979	-1.466037
O	4.889839	-1.522258	-4.524623	H	-0.722789	0.163807	-0.980427
C	4.223246	-1.903433	-0.786990	H	-0.315364	2.951292	0.200813
O	4.858001	-2.542555	-0.084407	H	1.679738	-0.824399	1.125455



4d: E = -1240.22494671172 au (toluene)

ZPE = 0.17158604 au (toluene)

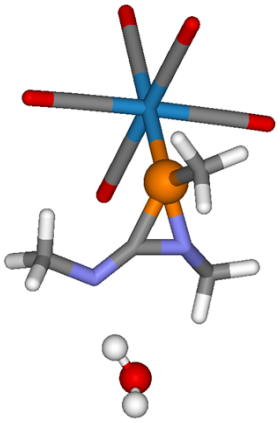
N	0.094696	-0.102987	0.035571	O	1.939200	-1.486325	4.952313
P	-0.034856	-0.083193	1.777785	C	-0.617560	1.588329	2.200616
C	1.334896	-0.048005	0.595423	H	-1.708625	1.600039	2.182847
N	2.532152	-0.171895	0.255220	H	-0.287124	1.820384	3.214602
W	-0.643736	-2.078125	3.137676	H	-0.223311	2.324810	1.503283
C	-1.123243	-3.709762	4.262519	C	-0.386558	-0.989739	-1.014316
O	-1.395097	-4.626578	4.894700	H	-1.456646	-0.840297	-1.141842
C	-1.807836	-0.882106	4.352031	H	0.122435	-0.740477	-1.944731
O	-2.455160	-0.212110	5.016980	H	-0.190465	-2.038463	-0.776184
C	-2.281041	-2.417301	1.922425	C	3.558945	-0.085252	1.281128
O	-3.188739	-2.598758	1.249799	H	3.151352	0.143038	2.273241
C	0.536178	-3.240668	1.900084	H	4.097610	-1.033766	1.334756
O	1.196559	-3.877757	1.217255	H	4.282165	0.685859	1.008625
C	1.012813	-1.703575	4.317761				



4^{E}d: E = -1240.22013315231 au (toluene)

ZPE = 0.17150406 au (toluene)

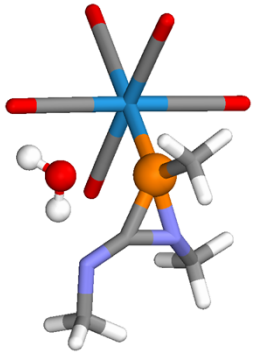
N	-0.072660	0.020037	0.276399	O	5.119070	1.350991	-1.388381
P	1.678396	0.020628	0.215762	C	2.234680	-0.000474	1.946542
C	0.428984	1.263355	-0.061755	H	2.339276	-1.035449	2.275262
N	0.108071	2.400461	-0.475060	H	3.213917	0.479165	1.995378
W	2.974590	-1.030346	-1.633283	H	1.530263	0.528787	2.585469
C	4.023334	-1.843494	-3.179963	C	-1.055566	-0.796030	-0.429734
O	4.608227	-2.305972	-4.050783	H	-1.004293	-1.813637	-0.047633
C	4.079627	-2.128940	-0.282547	H	-2.054392	-0.403009	-0.245368
O	4.690677	-2.740763	0.467789	H	-0.874049	-0.809110	-1.507593
C	1.620800	-2.582609	-1.759557	C	-1.301685	2.691114	-0.726468
O	0.879243	-3.451820	-1.830098	H	-1.990069	1.987447	-0.249140
C	1.821340	0.085296	-2.939196	H	-1.522737	3.696267	-0.366424
O	1.164184	0.698015	-3.646010	H	-1.483080	2.683258	-1.804362
C	4.350736	0.509934	-1.482672				



4d·H_2O: E = -1316.57436852286 au (THF)

ZPE = 0.19633466 au

N	0.320975	-0.115068	0.256420	C	2.751996	-0.489887	1.653465
P	2.045142	-0.060703	0.027460	H	2.847487	-1.575006	1.721823
C	0.731021	1.171925	0.195432	H	3.750400	-0.056233	1.727582
N	0.239132	2.324417	0.114511	H	2.122672	-0.120389	2.460731
W	3.188252	-0.669022	-2.085913	C	-0.820288	-0.791855	-0.347276
C	4.139601	-1.180852	-3.822430	H	-0.873527	-1.807427	0.040155
O	4.673550	-1.469564	-4.792513	H	-1.722581	-0.240512	-0.084648
C	4.805000	-1.323107	-0.984901	H	-0.723012	-0.824853	-1.435304
O	5.691972	-1.677338	-0.354560	C	1.128966	3.468521	0.016763
C	2.328781	-2.546845	-1.972439	H	2.186713	3.183282	0.038218
O	1.841770	-3.578750	-1.897553	H	0.931665	4.002753	-0.914551
C	1.550112	0.012647	-3.150947	H	0.930527	4.158961	0.839277
O	0.645207	0.394349	-3.735046	O	-2.583765	1.860989	0.351536
C	3.998925	1.232984	-2.156465	H	-1.669265	2.196428	0.247917
O	4.431827	2.290760	-2.176270	H	-2.918661	2.265337	1.157402



4^{E}d·H_2O: E = -1316.570365205 au (THF)

ZPE = 0.19693522 au

N	-0.044409	0.050843	-0.177655	C	4.518553	-1.478105	-0.803775
P	1.710616	-0.077679	-0.150556	O	5.302517	-1.856205	-0.062034
C	0.564584	1.277588	-0.137323	C	2.161245	-2.660652	-2.077271
N	0.396669	2.521853	-0.188719	O	1.657192	-3.688234	-2.055326
W	3.067509	-0.797193	-2.118837	C	1.579962	-0.092116	-3.369166
C	4.206898	-1.373881	-3.718361	O	0.744110	0.308203	-4.042061
O	4.847520	-1.692654	-4.612566	C	3.950938	1.080939	-2.159784

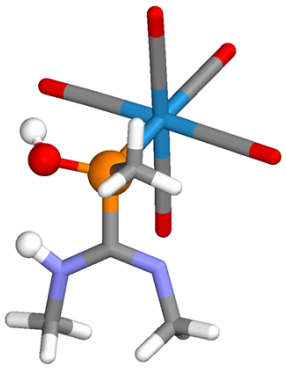
O	4.430903	2.118466	-2.190741	H	-1.082035	-0.083775	-2.020954
C	2.171846	-0.532532	1.549169	C	-0.941647	3.078434	-0.348474
H	2.388133	-1.599800	1.605428	H	-1.740597	2.329951	-0.324919
H	3.075704	0.033305	1.783864	H	-1.119478	3.802276	0.449211
H	1.381620	-0.263213	2.247717	H	-0.996802	3.618317	-1.296538
C	-1.127848	-0.471299	-1.000473	O	3.176350	2.634445	0.699246
H	-1.051664	-1.557433	-1.029889	H	2.292273	2.921221	0.401621
H	-2.088778	-0.202907	-0.559279	H	3.797266	3.033519	0.081428

TS(4^{E}d·H_2O→6d): E = -1316.54017637404 au (THF)

ZPE = 0.19513515 au

ν = -294.96 cm^{-1}

N	0.032015	-0.028839	0.007566	C	2.446592	-0.498249	1.762590
P	2.152591	-0.015967	0.032442	H	2.012270	-1.484319	1.923131
C	0.756517	1.063513	-0.011764	H	3.523182	-0.550916	1.925091
N	0.818459	2.355385	-0.026986	H	2.001105	0.224257	2.444264
W	3.116220	-1.276936	-1.887322	C	-1.407110	-0.198214	-0.060074
C	3.839819	-2.332629	-3.487821	H	-1.708114	-1.032049	0.576292
O	4.238163	-2.921677	-4.385332	H	-1.937267	0.698761	0.272965
C	4.962345	-1.350816	-0.957989	H	-1.720707	-0.426712	-1.083474
O	5.982785	-1.381915	-0.439458	C	-0.382204	3.175977	-0.045824
C	2.579619	-3.039534	-0.926953	H	-0.897550	3.165759	0.921759
O	2.284995	-3.998471	-0.378981	H	-0.107720	4.207912	-0.264374
C	1.233457	-1.167626	-2.766989	H	-1.095741	2.847944	-0.809810
O	0.192285	-1.096272	-3.229275	O	3.284662	1.752837	0.293525
C	3.643401	0.515857	-2.763659	H	2.419159	2.341796	0.167964
O	3.945087	1.534424	-3.195421	H	3.873921	1.923042	-0.452524

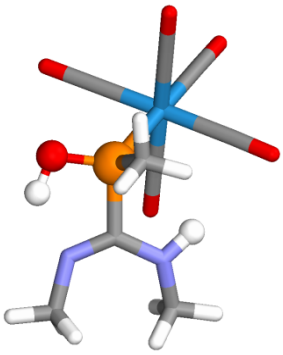


6d: E = -1316.62802572005 au (THF)

ZPE = 0.19935974 au

P	0.198234	-0.005345	-0.116969	O	0.569986	3.986520	-0.603460
O	0.551430	0.047340	1.498796	C	-2.219138	1.893576	1.010728
C	1.856616	0.087337	-0.851887	O	-2.557054	2.026793	2.100683
H	2.219655	1.112809	-0.784239	C	-2.851732	-0.008468	-1.104416
H	1.776676	-0.206819	-1.897298	O	-3.530844	-0.924830	-1.193421
H	2.539863	-0.584060	-0.330725	C	-0.238056	-1.788677	-0.364888
W	-1.565884	1.607529	-0.920336	N	-0.536317	-2.478698	0.772808
C	-2.977747	2.911788	-1.623663	H	-0.287930	-2.009596	1.628705
O	-3.761243	3.648060	-2.021130	C	-1.249852	-3.741343	0.890690
C	-0.883611	1.253153	-2.855924	H	-2.049095	-3.799124	0.154530
O	-0.501154	1.056179	-3.913761	H	-0.594153	-4.607589	0.771794
C	-0.201260	3.147053	-0.719905	H	-1.703191	-3.790174	1.880532

N	-0.277788	-2.070112	-1.604217	H	-0.299666	-4.216645	-1.571803
H	0.035005	0.728599	1.944024	H	-0.189171	-3.439636	-3.154206
C	-0.637515	-3.360339	-2.163224	H	-1.721627	-3.437794	-2.294449



6b^{conf}: E = -1316.63255483309 au (THF)

ZPE = 0.19992879 au

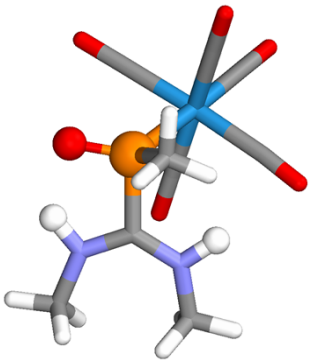
P	-0.026734	-0.003570	-0.131471	C	-3.090556	0.372093	-1.070225
O	0.198196	-0.210228	1.448257	O	-3.888308	-0.445112	-1.176824
C	1.656077	0.017651	-0.843730	C	-0.579734	-1.753274	-0.539340
H	2.147678	0.945689	-0.549800	N	-0.913818	-1.973843	-1.841737
H	1.592085	-0.011257	-1.932636	H	-0.938336	-1.132130	-2.396791
H	2.232726	-0.833583	-0.480638	C	-1.793856	-3.027264	-2.345390
W	-1.612209	1.802349	-0.903024	H	-1.381684	-4.014247	-2.152812
C	-2.924110	3.241552	-1.533736	H	-2.794052	-2.959586	-1.910415
O	-3.665148	4.035705	-1.899448	H	-1.879209	-2.903123	-3.423527
C	-1.037785	1.453614	-2.841701	N	-0.559657	-2.508615	0.486840
O	-0.700040	1.225014	-3.917067	H	0.029845	-1.184521	1.597020
C	-0.076600	3.185460	-0.716251	C	-0.889683	-3.924088	0.506495
O	0.783085	3.933081	-0.613105	H	-1.923939	-4.118200	0.211753
C	-2.137899	2.130638	1.092939	H	-0.758533	-4.294526	1.522213
O	-2.420570	2.307949	2.183253	H	-0.229413	-4.500968	-0.148777

TS(6b^{conf}→5d): E = -1316.62714592042 au (THF)

ZPE = 0.19646833 au

ν = -1217.69 cm^{-1}

P	0.020932	-0.112250	0.001292	C	-1.091765	-3.125990	0.019272
O	1.585195	-0.179226	-0.020398	O	-0.947883	-3.895268	-0.819137
C	-0.461934	1.655623	0.029731	C	-0.155487	-0.458984	-1.862275
H	-0.296561	2.042348	1.035928	N	-1.359824	-0.535220	-2.437043
H	-1.523208	1.755890	-0.205689	H	-2.141054	-0.507816	-1.800872
H	0.137343	2.226476	-0.680328	C	-1.681461	-0.901246	-3.812443
W	-1.362488	-1.662607	1.450221	H	-1.067236	-0.343547	-4.515689
C	-2.444007	-2.915325	2.655962	H	-1.551729	-1.971453	-3.987020
O	-3.059263	-3.609529	3.330036	H	-2.723323	-0.645106	-3.995808
C	-3.058024	-1.096203	0.462224	N	1.039423	-0.583466	-2.326320
O	-3.978502	-0.772212	-0.153627	H	1.696227	-0.387101	-1.223968
C	-1.608091	-0.094667	2.782528	C	1.496576	-0.879352	-3.672259
O	-1.745305	0.797343	3.486866	H	0.960177	-1.718334	-4.117196
C	0.432397	-2.227914	2.369458	H	2.552318	-1.140723	-3.621839
O	1.416318	-2.541519	2.851793	H	1.397522	-0.009334	-4.326644



5d: E = -1316.64207773216 au (THF)

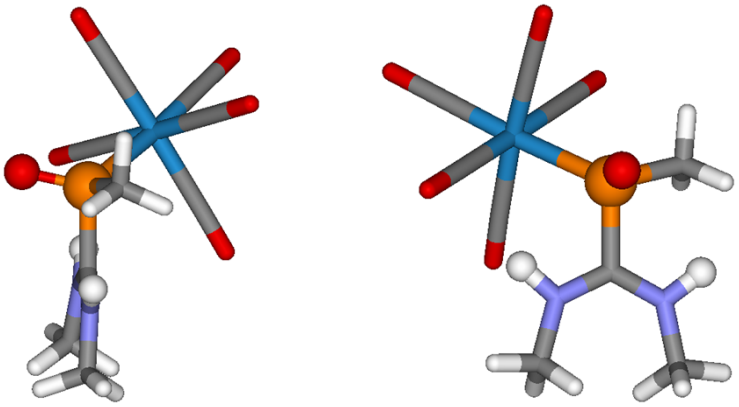
ZPE = 0.20173013 au

P	0.020909	0.017679	-0.021650	C	-3.126057	0.035263	-0.609479
O	0.339825	-0.014897	1.462041	O	-3.813187	-0.866516	-0.419411
C	1.571623	-0.016571	-1.000776	C	-0.527769	-1.783640	-0.321109
H	2.040475	0.964005	-0.909734	N	-0.826652	-2.224351	-1.529411
H	1.372007	-0.201431	-2.057667	H	-0.731892	-1.538797	-2.262319
H	2.251602	-0.774178	-0.609093	C	-1.464251	-3.476229	-1.938182
W	-1.785664	1.550211	-0.954906	H	-0.934131	-4.336780	-1.539502
C	-3.212426	2.825996	-1.651652	H	-2.507907	-3.504373	-1.624435
O	-4.012313	3.546390	-2.054306	H	-1.427898	-3.523003	-3.023481
C	-1.471603	0.790506	-2.816906	N	-0.614565	-2.429052	0.813587
O	-1.275542	0.296171	-3.841509	H	-0.287262	-1.829494	1.581135
C	-0.283314	2.935912	-1.259451	C	-1.042197	-3.788677	1.126109
O	0.578779	3.670473	-1.428851	H	-2.015977	-4.005934	0.694586
C	-2.048380	2.226141	0.999174	H	-1.120018	-3.865803	2.207420
O	-2.191632	2.580859	2.073965	H	-0.313700	-4.520818	0.777377

5d: E = -1316.64085515112 au ($CHCl_3$)

ZPE = 0.20150105 au ($CHCl_3$)

P	0.007538	0.012738	-0.030777	C	-3.150799	0.061013	-0.632041
O	0.339324	0.014245	1.452585	O	-3.856438	-0.826143	-0.445504
C	1.551993	-0.037420	-1.016550	C	-0.543369	-1.786669	-0.304495
H	2.026598	0.941579	-0.938274	N	-0.850150	-2.225008	-1.510332
H	1.345815	-0.233339	-2.069994	H	-0.765067	-1.538291	-2.243223
H	2.229551	-0.795708	-0.621704	C	-1.432790	-3.501398	-1.927072
W	-1.789709	1.563646	-0.962701	H	-0.875402	-4.338503	-1.516758
C	-3.198605	2.860932	-1.644963	H	-2.479335	-3.569330	-1.630307
O	-3.989719	3.598381	-2.038160	H	-1.375444	-3.547291	-3.011237
C	-1.487303	0.834635	-2.844503	N	-0.614212	-2.437003	0.828647
O	-1.306869	0.378766	-3.887964	H	-0.284033	-1.849482	1.599567
C	-0.273846	2.935344	-1.247262	C	-1.030035	-3.802677	1.137611
O	0.595148	3.665603	-1.403846	H	-1.991673	-4.032570	0.686869
C	-2.052244	2.222986	0.991963	H	-1.127634	-3.875912	2.217363
O	-2.195706	2.570359	2.070390	H	-0.284703	-4.524424	0.804238



TS(5d$^{PC\text{-}rot}$): E = -1316.62870144929 au ($CHCl_3$)

ZPE = 0.20148691 au ($CHCl_3$)

ν = -34.73 cm^{-1}

P	0.054278	-0.091761	-0.095265	C	-2.953981	0.665516	1.118906
O	0.659674	-0.319781	1.272954	O	-3.575245	0.175477	1.952765
C	1.393441	0.171615	-1.319223	C	-0.491811	-1.860518	-0.607609
H	1.774304	1.179196	-1.148855	N	0.353323	-2.636698	-1.251221
H	1.024805	0.113194	-2.344594	H	1.210876	-2.184901	-1.525718
H	2.226460	-0.519887	-1.167237	C	0.265908	-4.055689	-1.608880
W	-1.877969	1.567827	-0.381697	H	-0.033667	-4.655705	-0.754692
C	-3.340014	2.965195	-0.557557	H	-0.425627	-4.211792	-2.435653
O	-4.168638	3.757190	-0.660788	H	1.257923	-4.371226	-1.920604
C	-2.751051	0.368504	-1.798087	N	-1.679264	-2.210212	-0.161770
O	-3.213140	-0.326040	-2.588682	H	-2.160243	-1.460672	0.315230
C	-0.819880	2.528160	-1.870266	C	-2.395180	-3.485910	-0.193758
O	-0.244091	3.071867	-2.698540	H	-2.395061	-3.910576	-1.193264
C	-0.866947	2.678008	1.046298	H	-3.423972	-3.284905	0.092619
O	-0.294920	3.279258	1.832578	H	-1.969407	-4.195673	0.514175