Electronic Supplementary Information (ESI)

Coordination chemistry of a low-coordinate non-metal element: the case of electrophilic terminal phosphinidene complexes

José Manuel Villalba Franco,[a] Gregor Schnakenburg,[a] Arturo Espinosa Ferao,*[b] and Rainer Streubel*[a]

[a] Institut für Anorganische Chemie der Rheinischen Friedrich-Wilhelms-Universität Bonn, Gerhard-Domagk-Str.1, 53121 Bonn, Germany. Fax: +49 228 739616; Tel: +49 228 735345; E-mail: r.streubel@uni-bonn.de
[b] Departamento de Química Orgánica, Universidad de Murcia,Campus de Espinardo, 30100 – Murcia, Spain. Fax: +34 868 884149; Tel: +34 868 887489; E-mail: artuesp@um.es

Table of contents

Experimental methods

Analytical methods

Melting point measurements were determined with a Büchi (530) capillary apparatus.

Elemental analysis were performed using an ElementarVarioEL 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).

IR spectra were recorded with a SMART iTR Nicolet 380 FT IR spectrometer.

Single-crystal structure analysis: Reflection data for the X-ray crystallographic analysiswere recorded on a STOE IPDS-2T diffractometer (STOE&Cie GmbH, Darmstadt, Germany), using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). The diffractometer was equipped with a low-temperature device (Cryostream 700er series, Oxford Cryosystems, 123K). Intensities were measured by fine-slicing ω-scans at different φ-angels and corrected for background, polarization and Lorentz effects. The structures were solved by Patterson methods or Direct Methods (SHELXS-97) and refined by full-matrix least squares on F^2 (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.

Synthesis of **2**: A 180 mg (0.25 mmol) 5 mL Et_2O solution of 3-imino-azaphosphiridine complex **1**[1] was stirred under a CO (20 bar) atmosphere for 20 hours at room temperature. The solvent was removed in *vacuo* (~10^{-2} mbar) and a yellow oil was obtained. The product was then crystallized from Et_2O at -20 °C and obtained as white solid; yield: 130 mg (0.175 mmol, 70%), m.p. = 162-163 °C; ^{1}H NMR (C_6D_6): δ = 0.63 (d, 3H, C=N-CH-CH_3, $^{3}J_{H,H}$ = 6.0 Hz), 1.11 (d, 3H, C=N-CH-CH_3, $^{3}J_{H,H}$ = 6.0 Hz), 1.13 (d, 3H, C-N-CH-CH_3, $^{3}J_{H,H}$ = 7.0 Hz), 1.29 (d, 3H, C-N-CH-CH_3, $^{3}J_{H,H}$ = 7.0 Hz), 3.20 (sept, 1H, C=N-CH(CH_3)$_2$, $^{3}J_{H,H}$ = 6.0 Hz), 4.00 (sept, 1H, C -N-CH(CH_3)$_2$, $^{3}J_{H,H}$ = 7.0 Hz), 7.1-7.7 (m, 15H, 3 x C_6H_5); ^{13}C NMR (C_6D_6): δ= 19.6 (s, N-CH-CH$_3$), 19.9 (s, N=CH-CH$_3$), 23.0 (s, C=N-CH-CH$_3$), 24.5 (s, N-CH-CH$_3$), 47.5 (d, C-N-CH, $^{1}J_{P,C}$ = 4.2 Hz), 57.7 (d, $^{1}J_{P,C}$ = 9.4 Hz, C=N-CH), 64.8 (d, CPh$_3$, $^{1}J_{P,C}$ = 2.0 Hz), 128.2 (d, $J_{P,C}$ = 2.2 Hz, C-C^{Ph}), 128.4 (d, $J_{P,C}$ = 2.0, Hz, C-C^{Ph}), 128.5 (d, $J_{P,C}$ = 2.4, Hz, C-C^{Ph}), 128.6 (d, $J_{P,C}$ = 2.4, Hz, C-C^{Ph}), 128.9 (s, C-C^{Ph}), 129.2 (d, $J_{P,C}$ = 0.5 Hz, C-C^{Ph})130.1 (d, $J_{P,C}$ = 2.5, HzC-C^{Ph}), 130.5 (d, $J_{P,C}$ = 8.7 Hz, C-C^{Ph}), 132.1 (d, $J_{P,C}$ = 8.0 Hz, C-C^{Ph}),140.1 (d, $^{2}J_{P,C}$ = 5.3 Hz, C-$C^{ipso\text{-}Ph}$), 141.0 (d, $^{2}J_{P,C}$ = 1.5 Hz, C-$C^{ipso\text{-}Ph}$), 141.5 (d, $^{2}J_{P,C}$ = 8.5 Hz, C-$C^{ipso\text{-}Ph}$), 148.9 (d, P-C=N, $^{1+3}J_{P,C}$

1

= 13.2 Hz), 169.6 (d, P-*C*=O, $^{1+3}J_{P,C}$ = 52.1 Hz),195.2 (dSat, $^{2}J_{P,C}$ = 5.4 Hz, $^{1}J_{W,C}$ = 126.7, *cis*-*C*O), 197.7 (d, $^{2}J_{P,C}$ = 29.1 Hz, *trans*-*C*O); ^{31}P NMR (C_6D_6): δ= 94.9 (s, $^{1}J_{W,P}$ = 226.5 Hz); MS (EI, ^{184}W) : m/z (%): 752.0, $[M]^+$ (2); 243, $[CPh_3]^+$ (100); IR (ATR): ῦ = 2972 (b,ν–CH_2), 2076 (s, ν-CO), 1997 (s, ν-CO), 1919 (s, ν-CO), 1767 (s,ν-C=O), 1661 (b, ν-C=N) cm^{-1}; Elemental analysis for $C_{38}H_{30}F_5N_2O_6PW$ Calcd (%): C 51.08, H 3.88, N 3.72, found (%): C 50.77, H 4.34, N 3.46.

General procedure for the formation of complexes **4a,b**: To a Et_2O solution of 3-imino-azaphosphiridine complex **1**, 1 eq. of isocyanide (**3a,b**) was added at room temperature. The reaction mixture was stirred for 15 hours. When the reaction was completed the solvent was removed in *vacuo* (~10^{-2} mbar) and a yellow oil was obtained. The product was then crystallized from Et_2O at -40 °C and obtained as yellow solid. **4a**: yield: 309 mg (0.45 mmol, 60%); m.p. = 116-117 °C; ^{1}H NMR (C_6D_6): δ= 0.67 (s, 9H, C-C*H*$_3$), 6.9-7.1 (m, 9H, C_6H_5), 7.4-7.5 (m, 6H, C-C_6H_5); ^{13}C NMR (C_6D_6): δ= 28.7 (s, C-N-CH-*C*H_3), 58.6 (d, *C*Ph_3, $^{1}J_{P,C}$ = 25.0 Hz), 60.9 (s, N-*C*$(CH_3)_3$), 126.8 (d, $J_{P,C}$ = 1.8 Hz, C-*C*^{Ph}), 128.1 (s, C-*C*^{Ph}), 130.4 (d, $J_{P,C}$ = 8.2, Hz, C-*C*^{Ph}), 146.9 (d, N≡*C*-P, $^{1}J_{P,C}$ = 6.8 Hz), 197.9 (dSat, $^{2}J_{P,C}$ = 3.6 Hz, $^{1}J_{W,C}$ = 126.6, *cis*-*C*O), 201.0 (d, $^{2}J_{P,C}$ = 16.7 Hz, *trans*-*C*O); ^{31}P NMR (C_6D_6): δ= -50.0 ppm (s, $^{1}J_{W,P}$ = 117.7 Hz). MS (EI, ^{184}W): m/z (%): 681.0 $[M]^+$ (2.5); 598.0 $[M\text{-}^{t}BuN{\equiv}C]^+$ (2); 514.0 $[M\ \text{-}^{t}BuNC\ \text{-}\ 2xCO]^+$ (4); 243 $[CPh_3]^+$ (100); IR (ATR): ῦ = 2988 (b, ν-CH_2), 2142 (b, ν-N≡C), 2060 (s, ν-CO), 1923 (s, ν-CO), 1889 (s, ν-CO), 1847 (s, ν-CO), cm^{-1}; UV-vis (CH_2Cl_2): λ_{max} (abs., ε / $Lmol^{-1}cm^{-1}$) = 232.0 (1.51, 100733); 212.5 (0.82, 54666); Elemental analysis for $C_{29}H_{24}NO_5PW$ Calcd (%): C 51.12, H 3.55, N 2.06, found (%): C 50.90, H 3.93, N 2.61. **4b**: ^{1}H NMR ($CDCl_3$): δ= 0.80 (t, 3H, $^{3}J_{H,H}$ = 7.4 Hz, CH_2-C*H*$_3$), 1.18 (m, 2H, -C*H*$_2$-CH_3), 1.40 (m, 2H, -CH_2-C*H*$_2$-CH_2), 3.56 (dt, 2H, $^{3}J_{H,H}$ = 6.7 Hz, $^{4}J_{P,H}$ = 4.4 Hz, N-C*H*$_2$-CH_2), 7.1-7.3 (m, 15H, C_6H_5); ^{13}C NMR ($CDCl_3$): δ= 13.3 (s, CH_2-*C*H_3), 19.8 (s, -*C*H_2-CH_3), 30.8 (d, $^{4}J_{P,C}$ = 2.1 Hz CH_2-*C*H_2-CH_2), 46.7 (s, N-*C*H_2-CH_2), 58.8 (d, *C*Ph_3, $^{1}J_{P,C}$ = 24.7 Hz), 126.9 (d, $J_{P,C}$ = 1.8 Hz, C-*C*^{Ph}), 128.2 (s, C-*C*^{Ph}), 130.4 (d, $J_{P,C}$ = 8.2, Hz, C-*C*^{Ph}), 146.6 (d, N≡C-P, $^{1}J_{P,C}$ = 6.6 Hz), 197.7 (dSat, $^{2}J_{P,C}$ = 3.5 Hz, $^{1}J_{W,C}$ = 126.4, *cis*-*C*O), 201.3 (d, $^{2}J_{P,C}$ = 17.2 Hz, *trans*-*C*O); ^{31}P NMR ($CDCl_3$): δ= -51.8 ppm (s, $^{1}J_{W,P}$ = 118.2 Hz).

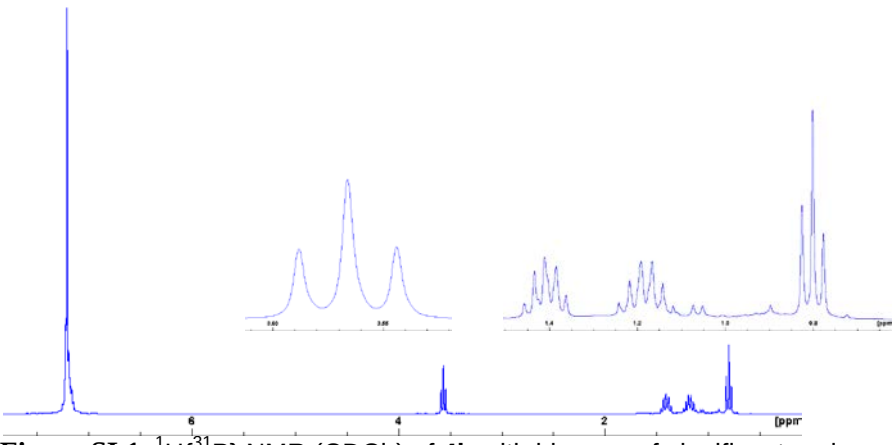


Figure SI 1. ^{1}H{^{31}P} NMR ($CDCl_3$) of **4b** with blow-up of significant regions.

Synthesis of **5**: To a 15 mL toluene solution of 350 mg (0.48 mmol) of 3-imino-azaphosphiridine complex **1**, 15.5 mg (1/8 eq.) of elemental sulfur (S_8) was added at room temperature. The reaction mixture was stirred for 24 hours. When the reaction was completed the solvent was removed in *vacuo* (~10^{-2} mbar) and a yellow oil was obtained. The product was then crystallized from Et_2O at -50 °C and washed with pentane at -50 °C. **5**was obtained as a white solid. Yield: 237 mg (0.31 mmol, 65%); m.p. = 142-143 °C; ^{1}H NMR ($CDCl_3$): δ= 0.91 (d, 3H, P-N-CH-C*H*$_3$, $^3J_{H,H}$ = 6.6 Hz), 1.01 (d, 3H, C-N-CH-C*H*$_3$, $^3J_{H,H}$ = 6.2 Hz), 1.06 (d, 3H, C=N-CH-C*H*$_3$, $^3J_{H,H}$ = 6.2 Hz), 1.49 (d, 3H, C=N-CH-C*H*$_3$, $^3J_{H,H}$ = 6.6 Hz), 2.86 (dsept, 1H, C=N-C*H*$(CH_3)_2$, $^3J_{H,H}$ = 6.2 Hz, $^3J_{P,H}$ = 2.9 Hz), 2.98 (dsept, 1H, P-N-C*H*$(CH_3)_2$, $^3J_{H,H}$ = 6.6 Hz,$^3J_{P,H}$ = 11.7 Hz), 6.92-6.98 (m, 2H, C-Ph), 7.26-7.45 (m, 13H, C-Ph), 7.70-7.77 (m, 2H, C-Ph); ^{13}C NMR ($CDCl_3$): δ= 19.7 (d, P-N-CH-*C*H$_3$, $^2J_{P,C}$ = 1.5 Hz), 20.6 (d, P-N-C-*C*H$_3$, $^2J_{P,C}$ = 2.0 Hz), 24.0 (s, C=N-C-*C*H$_3$), 24.3 (s, C=N-C-*C*H$_3$), 53.7 (d, $^2J_{P,C}$ = 1.2 Hz, P-N-*C*H-CH$_3$), 54.0 (d, C=N-*C*H-CH3, $^2J_{P,C}$ = 1.1 Hz), 71.1 (d, P-*C*Ph$_3$, $^1J_{P,C}$ = 13.7 Hz), 127.9 (d, $J_{C,P}$ = 2.0 Hz, *C*-Ph),128.0 (d, $J_{C,P}$ = 1.8 Hz, *C*-Ph), 128.3 (d, $J_{C,P}$ = 3.0 Hz, *C*-Ph), 128.5 (d, $J_{C,P}$ = 2.9 Hz, *C*-Ph) 128.8 (s, *C*-Ph), 129.0 (d, $J_{C,P}$ = 1.2 Hz, *C*-Ph),129.4 (s, *C*-Ph), 129.7 (d, $J_{C,P}$ = 2.8 Hz, *C*-Ph), 131.3 (d, $J_{C,P}$ = 3.5 Hz, *C*-Ph), 131.4 (d, $J_{C,P}$ = 2.3 Hz, *C*-Ph), 139.1 (d, $^{2+2}J_{C,P}$ = 6.8 Hz, *C*=N-^{i}Pr), 140.4 (d, $^2J_{C,P}$ = 4.5 Hz, *C*^{ipso}-Ph), 141.2 (d, $^2J_{C,P}$ = 4.9 Hz, *C*^{ipso}-Ph), 142.5 (d, $^2J_{C,P}$ = 11.9 Hz, *C*^{ipso}-Ph), 196.5 (dSat, $^2J_{P,C}$ = 6.7 Hz, $^1J_{W,C}$ = 128.0, *cis*-*C*O), 198.6 (d, $^2J_{P,C}$ = 37.1 Hz, *trans*-*C*O); ^{31}P NMR ($CDCl_3$): 122.6 (dSat, $J_{P,H}$ = 10.7 Hz, $^1J_{W,P}$ = 280.5 Hz); MS (EI, ^{184}W) : m/z (%): calcd:$[M+H]^+$ = 757.1120, found: $[M+H]^+$ = 757.1123; IR (ATR): ῦ = 2975 (b, ν-CH_2), 2932 (b, ν-CH_2), 2073 (s, ν–CO), 1988 (s, ν-CO), 1928 (s, ν-CO), 1677 (s, ν-CO), 1599 (b, ν-C=N) cm^{-1}; Elemental analysis for $C_{31}H_{29}N_2O_5PSW$ Calcd (%): C 49.32, H 3.86, N 3.70, S 4.24 found (%): C 49.36, H 3.98, N 3.66, S 4.28.

X-ray crystallographic analysis

Single crystals of **2**, **4a**, and **5** were obtained from recrystallization in 1/1 pentane/Et_2O mixtures at -40 °C. Crystal data are summarized in Tables SI1, 2, 3. 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-1440416 (**2**), 1440417 (**4a**), 1440415 (**5**), and can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request.cif.

Table SI 1. Crystal data and structure refinement for **2**.

Identification code	GSTR414, JMV-460 // GXray4051g
Device Type	Bruker X8-KappaApexII
Empirical formula	$C_{32}H_{29}N_2O_6PW$
Moiety formula	C32 H29 N2 O6 P W
Formula weight	752.38
Temperature/K	100
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	9.5330(5)
b/Å	10.1180(5)
c/Å	17.1899(8)
α/°	96.245(3)
β/°	104.796(3)
γ/°	103.755(3)
Volume/$Å^3$	1531.52(14)
Z	2
$\rho_{calc}g/cm^3$	1.632
μ/mm^{-1}	3.869
F(000)	744.0
Crystal size/mm^3	0.12 × 0.11 × 0.04
Absorption correction	empirical
Tmin; Tmax	0.625; 0.7460
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.272 to 50.05°
Completeness to theta	0.890
Index ranges	-11 ≤ h ≤ 11, -10 ≤ k ≤ 12, -20 ≤ l ≤ 20
Reflections collected	11086
Independent reflections	4823 [R_{int} = 0.1137, R_{sigma} = 0.2368]
Data/restraints/parameters	4823/66/383
Goodness-of-fit on F^2	0.963
Final R indexes [I>=2σ (I)]	R_1 = 0.0532, wR_2 = 0.0930
Final R indexes [all data]	R_1 = 0.1433, wR_2 = 0.1130
Largest diff. peak/hole / e $Å^{-3}$	3.00/-3.53

Table SI 2. Crystal data and structure refinement for **4a.**

Identification code	GSTR421, JMV474 // GXray4100f
Device Type	Bruker X8-KappaApexII
Empirical formula	$C_{29}H_{24}NO_5PW$
Moiety formula	C29 H24 N O5 P W
Formula weight	681.31

Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	13.1709(10)
b/Å	13.0975(9)
c/Å	15.6670(12)
α/°	90
β/°	91.408(2)
γ/°	90
Volume/$Å^3$	2701.8(3)
Z	4
$\rho_{calc}g/cm^3$	1.675
μ/mm^{-1}	4.373
F(000)	1336.0
Crystal size/mm^3	0.24 × 0.22 × 0.2
Absorption correction	empirical
Tmin; Tmax	0.4719; 0.7460
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.06 to 55.996°
Completeness to theta	0.995
Index ranges	-17 ≤ h ≤ 16, -17 ≤ k ≤ 14, -20 ≤ l ≤ 20
Reflections collected	26300
Independent reflections	6503 [R_{int} = 0.0405, R_{sigma} = 0.0355]
Data/restraints/parameters	6503/0/337
Goodness-of-fit on F^2	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.0217, wR_2 = 0.0460
Final R indexes [all data]	R_1 = 0.0265, wR_2 = 0.0473
Largest diff. peak/hole / e $Å^{-3}$	0.78/-0.63

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

Identification code	GSTR386, JMV416 // GXray3815
Device Type	STOE IPDS 2T
Empirical formula	$C_{31}H_{29}N_2O_5PSW$
Formula weight	756.44
Temperature/K	123(2)
Crystal system	triclinic
Space group	$P\bar{1}$
a/Å	9.6390(6)
b/Å	9.9715(5)
c/Å	16.9758(11)
α/°	78.438(5)
β/°	89.320(5)

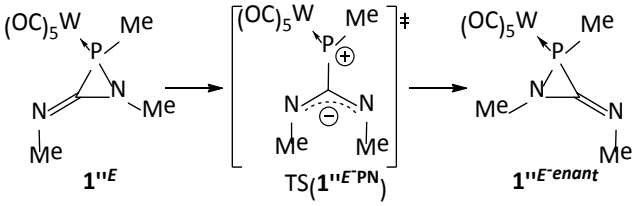
γ/°	73.325(4)
Volume/Å^3	1529.49(16)
Z	2
ρ_{calc}g/cm^3	1.643
μ/mm^{-1}	3.938
F(000)	748.0
Crystal size/mm^3	0.12 × 0.09 × 0.03
Absorption correction	integration
Tmin; Tmax	0.4692; 0.6566
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.22 to 50.5°
Completeness to theta	0.976
Index ranges	-11 ≤ h ≤ 11, -11 ≤ k ≤ 11, -20 ≤ l ≤ 19
Reflections collected	10474
Independent reflections	5403 [R_{int} = 0.0652, R_{sigma} = 0.1334]
Data/restraints/parameters	5403/0/374
Goodness-of-fit on F^2	0.899
Final R indexes [I>=2σ (I)]	R_1 = 0.0429, wR_2 = 0.0726
Final R indexes [all data]	R_1 = 0.0694, wR_2 = 0.0762
Largest diff. peak/hole / e Å^{-3}	1.27/-1.04

Computational details

DFT calculations were performed with the ORCA program.[2] All geometry optimizations were run in redundant internal coordinates with tight convergence criteria and using the B3LYP functional[3] together with the def2-TZVP basis set.[4] For W atoms the [SD(60,MWB)] effective core potential[5] (ECP) was used. The latest Grimme's semiempirical atom-pair-wise London dispersion correction (DFT-D3) was included in all calculations.[6] Solvent effects (toluene by default) were taken into account via the COSMO solvation model.[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 and obtained by means of the recently developed near linear scaling domain-based local pair natural orbital (DLPNO) method[9] to achieve coupled cluster theory with single-double and perturbative triple excitations (CCSD(T)). For the sake of comparison, in case of all model systems, energy values were also computed with other high level single reference method, such as CEPA (Coupled Electron-Pair Approximation),[10] here the slightly modified NCEPA/1 version implemented in ORCA was used,[11] with the aid of local pair natural orbital (LPNO) schemes;[12] the spin component-scaled Møller-Plesset 2 (SCS-MP2) method[13] and the double-hybrid-meta-GGA functional PWPB95[14] together with the D3 correction were also used. For a set of twenty-six values with model systems (see Table SI 4), the LPNO-NCEPA1 method performed very accurately according to the small RMSD (root mean square deviation) displayed (0.22 kcal/mol) in relation to DLPNO-CCSD(T); among the less computationally demanding methods, therefore accessible for bigger molecular systems, SCS-MP2 clearly outperformed (RMSD = 0.23 kcal/mol) PWPB95-D3 (RMSD = 0.88 kcal/mol). Basis set superposition errors (BSSE) were computed for every series at the **6''**·CO and the **6''**·CNMe stages. Wiberg bond indices (WBI) were obtained from the natural bond orbital (NBO) population analysis.[15] Bader's AIM-derived topological analysis of the electron density was conducted with AIM2000.[16] Bond dissociation energies (BDE) for complexes displayed in Table 1 were computed according to the scission reaction [W]P(R)-L → [W]PR + :L.

Theoretical study of the P-N bond cleavage process in E-configured imino-azaphosphiridine complexes.

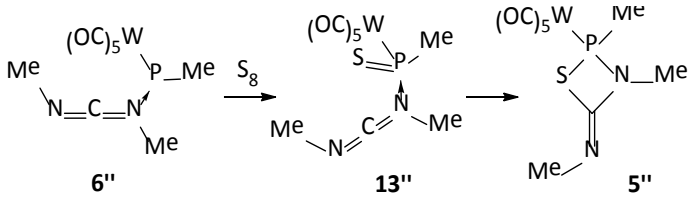
Ring opening via increase of the endocyclic PCN bond angle of the 3.07 kcal/mol less stable *E*-isomer **1''**^{E} allowed racemisation at P through a high energy transition state ($\Delta E^{\neq}_{ZPE}$ = 40.76 kcal/mol):



Scheme SI 2. P-N ring cleavage for model complex **1''**^{E}.

Theoretical study of the thionation reaction of 1''.

Preliminary studies of the reaction of imino-azaphosphiridine complexes **1** with heavier chalcogens was computationally addressed for the case of the thionation process leading to model 4-imino-1,3,2-thiazaphosphetidine complex **5''**, assuming the intermediacy of a carbodiimide *end-on* adduct with a phosphinidene-thione complex **13''**. This intermediate results from direct *P*-thionation of the open-chain derivative **6''** and quickly cyclizes to **5''** in an exergonic (ΔE_{ZPE} = -18.80 kcal/mol) almost barrierless process ($\Delta E^{\neq}_{ZPE}$ = 1.70 kcal/mol).



Scheme SI 3. Proposed mechanism for the formation of complexes **5''**.

Table SI 4: Relative zero-point corrected energies (kcal/mol) computed at the optimization level[a] and as single-points at other selected levels.[b]

Level	1''	TS(1''→6'')	6''	TS(1''→7'')	7''	1''^{E}	TS(1''$^{E\text{-}PN}$)
Optimization	0.00	13.27	10.82	34.57	-6.73	3.50	35.67
B3LYP-D3	0.00	17.03	14.53	38.13	-2.89	7.25	39.41
PWPB95-D3	0.00	15.70	13.45	38.43	-3.74	3.25	39.28
SCS-MP2	0.00	16.61	13.42	41.08	-5.60	3.12	40.40
LPNO-NCEPA/1	0.00	18.51	14.21	41.23	-7.70	2.97	40.44

DLPNO-CCSD(T)	0.00	17.92	13.88	40.33	-6.80	3.07	40.76

Table SI 4 (continued)

1'' + CO	**6''**·CO	**TS**$^{(6''\cdot CO \rightarrow 8''\cdot 9)}$	**8''·9**	**TS**$^{(8''\cdot 9 \rightarrow 10'')}$	**10''**	**TS**$^{(10'' \rightarrow 2'')}$	**2''**	**TS**$^{(2'' \rightarrow 4''\cdot 11)}$	**4''·11**
0.00	8.06	11.85	1.94	3.38	1.72	2.18	-34.13	15.63	-10.35
0.00	11.79	15.58	-16.07	6.30	5.44	5.89	-30.40	19.36	-6.59
0.00	12.13	16.67	6.79	9.22	6.11	6.78	-32.12	20.55	-5.83
0.00	13.44	20.82	10.68	14.40	11.92	12.28	-27.00	26.03	-2.35
0.00	14.07	22.66	12.94	16.99	13.80	14.98	-27.29	28.54	0.76
0.00	13.75	21.26	11.84	15.12	12.68	13.59	-27.68	26.86	0.38

Table SI 4 (continued)

1''+NCMe	**6''**·NCMe	**TS**$^{(3''\cdot CNMe \rightarrow 4''\cdot 9)}$	**4''·9**	**TS**$^{(4''\cdot 9 \rightarrow 12'')}$	**12''**	**13''**	**TS**$^{(13'' \rightarrow 5'')}$	**5''**	**TS**$^{(4''\cdot 9 \rightarrow 12'')}$
0.00	6.32	7.23	-10.56	1.50	-37.66	0.00	1.38	-15.22	1.50
0.00	10.02	10.95	-6.83	-9.22	-33.90	0.00	1.39	-15.21	-9.22
0.00	9.93	11.23	-6.53	5.96	-36.74	0.00	1.13	-17.82	5.96
0.00	11.52	13.99	-3.27	10.29	-33.54	0.00	1.34	-16.97	10.29
0.00	12.22	15.80	-0.78	12.97	-34.12	0.00	1.85	-19.13	12.97
0.00	11.85	14.53	-1.74	11.06	-34.82	0.00	1.70	-18.80	11.06

Table SI 4 (continued)

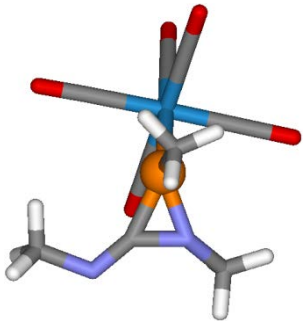
BDE(**4''**)	BDE(**6''**)	BDE(**8''**)	*RMSE* [c]
38.92	23.10	26.10	*1.51*
37.73	23.15	26.12	*1.69*
38.32	22.67	24.40	*0.88*
33.73	18.93	18.14	*0.23*
29.11	17.23	15.13	*0.22*
31.22	18.65	16.72	*0.00*

[a] $COSMO_{toluene}$/B3LYP-D3/def2-TZVPecp. [b] $COSMO_{toluene}$/level/def2-TZVPPecp.

[c] Root mean square deviation for 26 energy values, taking all non-zero columns, relative to the DLPNO-CCSD(T) level.

Calculated structures

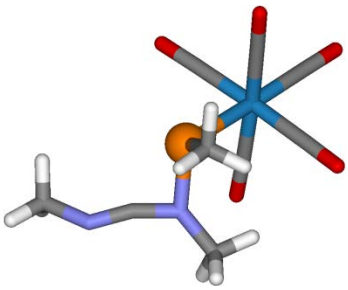
Cartesian coordinates (in Å) and energies for all computed species



1‘‘: E = -1240.35612103398 au (COSMO$_{tol}$/DLPNO-CCSD(T)/def2-TZVPPecp)

ZPE = 0.17158604 au (COSMO$_{tol}$/B3LYP-D3/def2-TZVPecp)

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				



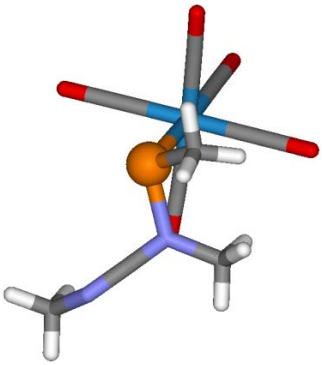
TS(1‘‘→6‘‘): E = -1240.32595984979 au (COSMO$_{tol}$/DLPNO-CCSD(T)/def2-TZVPPecp)

ZPE = 0.16998294 au (COSMO$_{tol}$/B3LYP-D3/def2-TZVPecp)

ν = -224.80 cm^{-1}

N	0.578918	-0.420263	0.460548	O	-3.432787	-1.806179	1.432134
P	0.159670	-0.066919	2.182149	C	0.045796	-3.347163	1.869126
C	1.785074	-0.010547	0.530279	O	0.568042	-3.972934	1.060225
N	2.884436	0.378602	0.280490	C	0.863303	-2.309444	4.439819
W	-0.849581	-2.164349	3.292768	O	1.821472	-2.384653	5.063125
C	-1.683808	-3.760797	4.212287	C	-1.087559	1.267537	1.916153
O	-2.179511	-4.662951	4.728097	H	-1.967072	0.899936	1.384497
C	-1.670154	-0.890180	4.692982	H	-1.405418	1.616391	2.900807
O	-2.115493	-0.170031	5.465602	H	-0.654942	2.108990	1.373631
C	-2.512857	-1.944996	2.105040	C	-0.073700	-1.091607	-0.671365

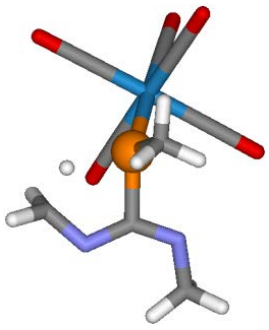
H	-0.919800	-1.647673	-0.277765	H	4.061159	0.636843	1.971124
H	-0.424421	-0.351556	-1.390346	H	4.683460	-0.543078	0.791221
H	0.619704	-1.779713	-1.151615	H	4.783353	1.194007	0.440830
C	4.181723	0.418048	0.907724				



6‘‘: E = -1240.33424534319 au (COSMO$_{tol}$/DLPNO-CCSD(T)/def2-TZVPPecp)

ZPE = 0.17183463 au (COSMO$_{tol}$/B3LYP-D3/def2-TZVPecp)

N	0.617075	0.014547	0.679948	O	1.584468	-1.757380	5.489984
P	-0.002287	0.292158	2.444853	C	-1.501533	1.268459	1.969954
C	1.867197	0.086375	0.567736	H	-2.237112	0.713345	1.387187
N	3.031417	0.261716	0.457588	H	-1.971740	1.547649	2.916194
W	-0.717780	-2.068023	3.271953	H	-1.228875	2.187498	1.448359
C	-1.238191	-3.883582	4.003513	C	-0.206613	-0.473688	-0.445820
O	-1.545637	-4.918840	4.404428	H	-0.610905	-1.448824	-0.188962
C	-2.033090	-1.070503	4.513193	H	-1.019635	0.229490	-0.605690
O	-2.747039	-0.477468	5.186377	H	0.399462	-0.546494	-1.346301
C	-2.189264	-2.194930	1.845494	C	4.244441	-0.490474	0.718957
O	-3.013760	-2.253024	1.046655	H	4.809546	0.040976	1.482831
C	0.673717	-2.823558	1.977146	H	4.017342	-1.502372	1.050894
O	1.483357	-3.150921	1.224494	H	4.835206	-0.514688	-0.194463
C	0.759235	-1.872126	4.703067				



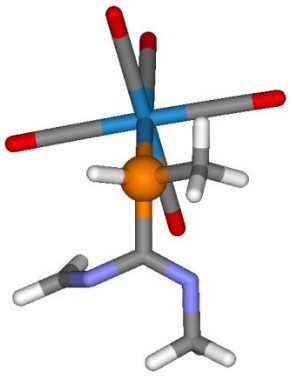
TS(1‘‘→7‘‘): E = -1240.28576903883 au (COSMO$_{tol}$/DLPNO-CCSD(T)/def2-TZVPPecp)

ZPE = 0.16550496 au (COSMO$_{tol}$/B3LYP-D3/def2-TZVPecp)

ν = -783.96 cm^{-1}

N	-0.239736	-0.309059	-0.330187	C	-1.115776	-3.804462	4.304959
P	0.333370	-0.115453	2.192964	O	-1.506860	-4.749173	4.816141
C	0.816808	-0.170504	0.380398	C	-1.639344	-0.917812	4.562266
N	2.115552	-0.023353	0.157504	O	-2.299868	-0.244763	5.209057
W	-0.428538	-2.099024	3.378585	C	-1.943996	-2.279927	1.960656

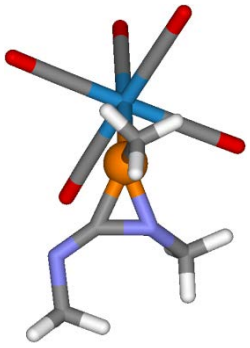
O	-2.764195	-2.382365	1.177398	C	-0.100236	-0.771715	-1.699830
C	0.812654	-3.196021	2.143217	H	-0.886191	-0.333419	-2.315604
O	1.504199	-3.782450	1.447250	H	0.882157	-0.516652	-2.114220
C	1.098016	-1.937004	4.773128	H	-0.211699	-1.860219	-1.745091
O	1.943313	-1.844018	5.535433	C	2.895099	-0.126088	1.274649
C	-0.418707	1.525734	2.409025	H	2.086265	0.189619	2.238152
H	-0.771410	1.670598	3.428035	H	3.118845	-1.125738	1.667375
H	0.282797	2.310741	2.127036	H	3.764662	0.531148	1.311155
H	-1.268176	1.556701	1.720118				



7‘‘: E = -1240.36489581074 au (COSMO$_{tol}$/DLPNO-CCSD(T)/def2-TZVPPecp)

ZPE = 0.16951685 au (COSMO$_{tol}$/B3LYP-D3/def2-TZVPecp)

N	0.194463	-0.026224	-0.519154	O	2.507118	-1.886931	4.815340
P	0.130867	-0.029106	2.183581	C	-1.154141	1.215764	1.853701
C	0.832481	-0.386181	0.511553	H	-1.521647	1.586694	2.810904
N	1.976642	-1.197340	0.524155	H	-0.766195	2.035582	1.253096
W	-0.472008	-2.009193	3.636589	H	-1.973796	0.737385	1.320201
C	-0.980592	-3.533951	4.874876	C	0.707260	-0.383997	-1.835255
O	-1.270097	-4.386210	5.588070	H	-0.126544	-0.431365	-2.534487
C	-1.128289	-0.655083	5.042910	H	1.391535	0.393590	-2.186903
O	-1.500225	0.101096	5.819670	H	1.247413	-1.335251	-1.836483
C	-2.349303	-2.023653	2.777395	C	3.110288	-0.750545	0.857756
O	-3.387886	-2.023897	2.295397	H	1.187669	0.762094	2.683644
C	0.179835	-3.367642	2.214366	H	3.292690	0.292016	1.133401
O	0.534477	-4.132240	1.442679	H	3.960579	-1.428142	0.870961
C	1.436413	-1.941950	4.411605				

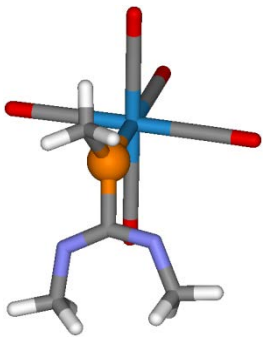


1‘‘*E*: E = -1240.35114773954 au (COSMO$_{tol}$/DLPNO-CCSD(T)/def2-TZVPPecp)

ZPE = 0.17150406 au (COSMO$_{tol}$/B3LYP-D3/def2-TZVPecp)

N	-0.072660	0.020037	0.276399	P	1.678396	0.020628	0.215762

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



TS(1‘‘$^{E\text{-PN}}$): E = -1240.28876936083 au (COSMO$_{tol}$/DLPNO-CCSD(T)/def2-TZVPPecp)

ZPE = 0.16919317 au (COSMO$_{tol}$/B3LYP-D3/def2-TZVPecp)

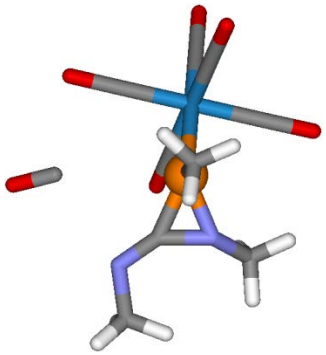
ν = -165.33 cm^{-1}

N	-0.390732	-0.243965	0.114833	O	4.696862	2.715579	-1.919322
P	2.054198	0.382273	0.064177	C	2.596293	0.504780	1.787477
C	0.317797	0.841819	-0.011015	H	3.646098	0.246639	1.906124
N	0.243095	2.113704	-0.275855	H	2.416816	1.529404	2.123590
W	3.380960	-0.224837	-1.839613	H	1.970006	-0.160133	2.387704
C	4.516876	-0.725335	-3.493769	C	-1.760730	-0.353634	-0.357547
O	5.149874	-0.998729	-4.403576	H	-2.057692	-1.402993	-0.346082
C	4.856902	-0.882690	-0.560751	H	-2.450935	0.187562	0.302251
O	5.650450	-1.243931	0.178570	H	-1.893983	0.028987	-1.374144
C	2.524254	-2.125652	-1.883384	C	-0.912432	2.750678	-0.886362
O	2.047159	-3.158529	-1.915354	H	-1.861347	2.383430	-0.480752
C	1.800959	0.451030	-3.001283	H	-0.861410	3.825410	-0.708333
O	0.911820	0.818282	-3.613196	H	-0.930549	2.593645	-1.970464
C	4.233850	1.675412	-1.884979				

CO: E = -113.158011405906 au (COSMO$_{tol}$/DLPNO-CCSD(T)/def2-TZVPPecp)

ZPE = 0.0050358 au (COSMO$_{tol}$/B3LYP-D3/def2-TZVPecp)

C	0.000000	0.000000	0.000000	O	1.124879	0.000000	0.000000



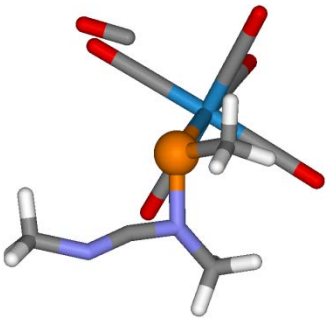
1''^{E}·CO: E = -1353.512786649725 au (COSMO$_{tol}$/DLPNO-CCSD(T)/def2-TZVPecp)

ZPE = 0.17724514 au (COSMO$_{tol}$/B3LYP-D3/def2-TZVPecp)

$d_{P\cdots CO}$ = 3.451 Å; WBI = 0.009; ρ(r) = 0.70·10^{-2} e/a_0^3;

$d_{N\cdots CO}$ = 3.161 Å; WBI = 0.008; ρ(r) = 0.68·10^{-2} e/a_0^3)

N	-0.153729	-0.373446	0.335724	C	2.444394	-0.953226	1.290395
P	1.528620	-0.182859	-0.081576	H	2.547386	-2.020212	1.084808
C	0.215593	0.922133	0.503594	H	3.438826	-0.509270	1.336376
N	-0.318497	2.035584	0.705653	H	1.925135	-0.803626	2.234922
W	2.413519	-0.308285	-2.409812	C	-1.350208	-0.917933	-0.289025
C	3.183969	-0.443886	-4.292226	H	-1.121811	-1.905618	-0.685526
O	3.624984	-0.525949	-5.347134	H	-2.138832	-1.011944	0.457677
C	4.310918	-0.522738	-1.630738	H	-1.701684	-0.271677	-1.095768
O	5.362830	-0.637531	-1.193835	C	0.522120	3.220875	0.733175
C	2.131259	-2.353186	-2.341784	H	0.375363	3.750425	1.676630
O	1.959998	-3.483751	-2.292297	H	1.586513	2.988160	0.617020
C	0.514358	-0.075514	-3.192187	H	0.224412	3.896435	-0.071383
O	-0.530458	0.059372	-3.637492	C	4.341000	2.161428	0.517280
C	2.616457	1.748548	-2.418344	O	4.974744	3.050108	0.248452
O	2.708910	2.888322	-2.404420				



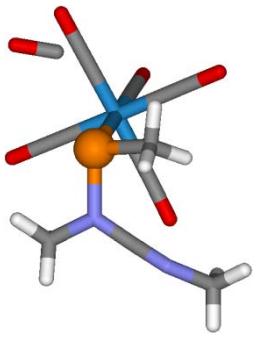
TS(1''^{E}·CO→**6''**·CO**)**: E = -1353.48688685051 au (COSMO$_{tol}$/DLPNO-CCSD(T)/def2-TZVPecp)

ZPE = 0.17581876 au (COSMO$_{tol}$/B3LYP-D3/def2-TZVPecp)

ν = -224.91 cm^{-1}

N	0.198089	0.567102	-0.040703	O	5.405540	-1.231471	-1.193125
P	1.978151	0.706954	-0.332264	C	1.750942	-2.206338	-1.708907
C	0.005862	1.817523	0.122344	O	1.286488	-3.142356	-1.233351
N	-0.453822	2.878241	0.420435	C	0.757981	0.050037	-3.302677
W	2.576414	-0.510610	-2.526826	O	-0.260696	0.389713	-3.710426
C	3.061581	-1.526463	-4.205897	C	3.384839	1.227113	-3.296598
O	3.331429	-2.125011	-5.151572	O	3.825735	2.190522	-3.732802
C	4.397479	-0.979158	-1.675344	C	2.582463	-0.185443	1.165306

H	2.295783	-1.238166	1.151530	C	-0.301978	4.258411	0.033723
H	3.671480	-0.125965	1.160337	H	-0.896326	4.465454	-0.856828
H	2.213007	0.284342	2.077469	H	-0.640901	4.898283	0.844901
C	-0.811420	-0.489669	-0.178805	H	0.750152	4.461545	-0.178442
H	-0.919733	-0.767637	-1.225372	C	4.821971	2.277809	-0.316552
H	-0.482858	-1.354426	0.393324	O	4.982828	3.288127	-0.785527
H	-1.763272	-0.133163	0.209787				

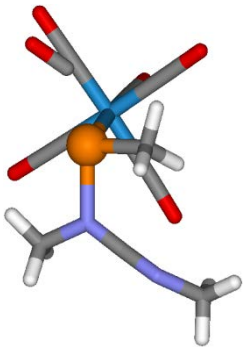


6‘‘·CO: E = -1353.49389432525 au (COSMO$_{tol}$/DLPNO-CCSD(T)/def2-TZVPPecp)

ZPE = 0.17769235 au (COSMO$_{tol}$/B3LYP-D3/def2-TZVPecp)

BSSE = 0.00060698 au (DLPNO-CCSD(T)/def2-TZVPPecp)

N	0.179129	1.275388	-0.546548	C	2.738660	1.800714	0.402702
P	1.931199	1.475280	-1.229541	H	2.704955	0.965995	1.104437
C	-0.042401	1.050084	0.667130	H	3.786598	1.992787	0.166861
N	-0.185964	0.997615	1.844377	H	2.330220	2.695986	0.874774
W	2.587136	-0.910914	-2.059322	C	-0.923208	1.274610	-1.528935
C	3.090320	-2.755304	-2.718959	H	-0.662396	1.986770	-2.308310
O	3.372394	-3.812211	-3.079849	H	-1.027203	0.281190	-1.960436
C	4.058193	-0.994483	-0.617466	H	-1.852382	1.570716	-1.047376
O	4.868187	-1.033304	0.193214	C	-0.294937	-0.050530	2.841761
C	1.234864	-1.635292	-0.711271	H	-0.180180	-1.036370	2.395431
O	0.458038	-1.969460	0.072727	H	0.475044	0.118374	3.592572
C	1.128234	-0.753681	-3.501308	H	-1.267312	0.039014	3.323286
O	0.316886	-0.662810	-4.309587	C	4.201467	3.260828	-2.554025
C	3.934814	-0.050536	-3.373290	O	3.994177	3.888817	-3.465388
O	4.681558	0.411466	-4.109502				

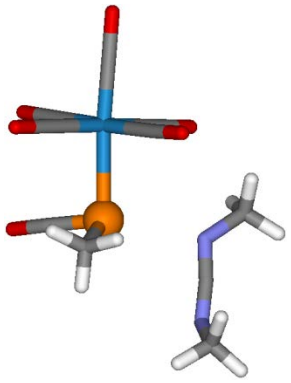


TS(6‘‘·CO→**8‘‘**·**9)**: E = -1353.48254840981 au (COSMO$_{tol}$/DLPNO-CCSD(T)/def2-TZVPPecp)

ZPE = 0.17830783 au (COSMO$_{tol}$/B3LYP-D3/def2-TZVPecp)

ν = -217.27 cm^{-1}

N	0.168843	1.302549	-0.540176	C	2.726951	1.763794	0.501002
P	2.059226	1.599775	-1.223696	H	2.551591	0.861534	1.085745
C	-0.110128	1.091828	0.655555	H	3.801771	1.912707	0.445211
N	-0.313185	1.039195	1.828446	H	2.279629	2.618704	1.009269
W	2.686912	-0.788510	-2.140395	C	-0.874677	1.331585	-1.579597
C	3.146592	-2.668781	-2.705277	H	-0.453500	1.835833	-2.446217
O	3.408601	-3.749926	-3.003984	H	-1.159375	0.318097	-1.855132
C	4.343056	-0.713928	-0.911230	H	-1.746722	1.880025	-1.227502
O	5.261444	-0.651237	-0.228946	C	-0.440206	-0.024876	2.806700
C	1.518264	-1.500457	-0.623123	H	-0.270966	-1.002299	2.359164
O	0.836024	-1.869865	0.228328	H	0.284158	0.154845	3.599694
C	1.060580	-0.767526	-3.396708	H	-1.438088	0.025248	3.240028
O	0.160967	-0.767569	-4.111110	C	3.805094	2.592666	-2.132187
C	3.817941	-0.037425	-3.702795	O	4.087554	3.283984	-2.988113
O	4.437741	0.350771	-4.584795				

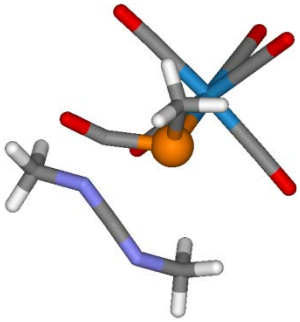


8''·9: E = -1353.49802199452 au ($COSMO_{tol}$/DLPNO-CCSD(T)/def2-TZVPPecp)

ZPE = 0.17877305 au ($COSMO_{tol}$/B3LYP-D3/def2-TZVPecp)

P-CH_3 (in **8''**): d = 1.868 Å; WBI = 0.921; ρ(r) = $15.30 \cdot 10^{-2}$ e/a_0^3.

N	-0.272129	0.541138	-0.113615	C	2.891929	1.150001	0.656439
P	2.390746	1.416405	-1.123789	H	2.207961	0.382544	1.014883
C	-0.518206	1.183118	0.892562	H	3.912134	0.788605	0.753086
N	-0.619878	1.918032	1.853467	H	2.748107	2.058336	1.237681
W	2.987675	-0.645988	-2.657662	C	-1.231191	0.086499	-1.112552
C	3.302506	-2.304691	-3.744437	H	-0.988738	0.546641	-2.070131
O	3.485747	-3.259286	-4.360526	H	-1.142632	-0.993383	-1.224257
C	4.636898	-1.049816	-1.486649	H	-2.259300	0.337283	-0.846981
O	5.555284	-1.265821	-0.837293	C	-0.840446	1.535688	3.241508
C	1.808772	-1.774496	-1.389320	H	-0.844449	0.453041	3.382307
O	1.168283	-2.434446	-0.707898	H	-0.054392	1.974788	3.856235
C	1.338607	-0.169805	-3.802374	H	-1.794008	1.944115	3.577526
O	0.423259	0.091072	-4.439240	C	3.742818	2.374395	-1.589611
C	4.192467	0.429710	-3.943046	O	4.535704	3.087114	-2.008365
O	4.872563	1.019942	-4.649786				

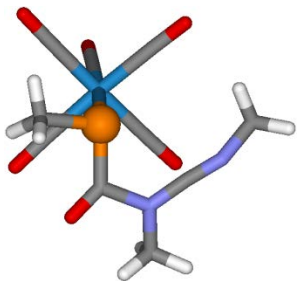


TS(8''·9→10''): E = -1353.49324293658 au (COSMO$_{tol}$/DLPNO-CCSD(T)/def2-TZVPPecp)

ZPE = 0.17921511 au (COSMO$_{tol}$/B3LYP-D3/def2-TZVPecp)

ν = -134.85 cm^{-1}

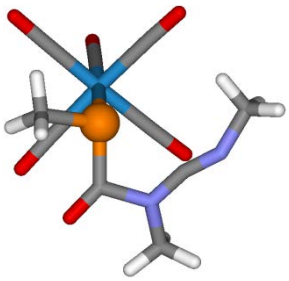
N	-0.293675	0.580554	-0.255230	C	4.377279	-0.961093	2.148646
P	3.007464	-0.547681	0.953769	H	4.416028	-2.049497	2.204647
C	0.685730	1.256788	-0.185745	H	5.348225	-0.594254	1.819370
N	1.691965	1.941065	0.040646	H	4.152424	-0.572191	3.141223
W	3.828350	-1.082007	-1.518056	C	-0.780461	-0.433103	-1.169484
C	4.548957	-1.627481	-3.308175	H	-0.303270	-0.356700	-2.145209
O	4.974302	-1.940395	-4.332362	H	-0.572612	-1.411241	-0.736392
C	5.301526	0.337357	-1.235567	H	-1.857486	-0.322163	-1.271808
O	6.094514	1.141280	-1.045386	C	1.909611	3.309373	-0.419407
C	5.023374	-2.542238	-0.668936	H	0.979907	3.876371	-0.405142
O	5.692198	-3.361113	-0.230915	H	2.624541	3.773703	0.257769
C	2.280451	-2.430092	-1.646499	H	2.322816	3.303617	-1.428060
O	1.404307	-3.168105	-1.707536	C	3.196457	1.200703	1.095089
C	2.662631	0.306423	-2.469418	O	3.749842	2.106604	1.565558
O	2.005587	1.057689	-3.041671				



10'': E = -1353.49862367648 au (COSMO$_{tol}$/DLPNO-CCSD(T)/def2-TZVPPecp)

ZPE = 0.18071884 au (COSMO$_{tol}$/B3LYP-D3/def2-TZVPecp)

N	-0.129801	0.542512	-0.408005	C	4.396207	-0.801698	2.113030
P	3.006233	-0.528592	0.919867	H	4.547843	-1.877095	2.205656
C	0.845773	1.145326	-0.185190	H	5.324099	-0.343324	1.772077
N	1.831870	1.873650	0.149611	H	4.139424	-0.400454	3.093395
W	3.813733	-1.125178	-1.538116	C	-0.789608	-0.445788	-1.214552
C	4.545515	-1.672856	-3.326770	H	-0.451549	-0.370673	-2.246640
O	4.976778	-1.982191	-4.350396	H	-0.534796	-1.425877	-0.811435
C	5.310686	0.265878	-1.216709	H	-1.864233	-0.298109	-1.150385
O	6.110420	1.057366	-1.007006	C	1.944945	3.270492	-0.311381
C	4.950686	-2.617309	-0.651150	H	0.951791	3.692247	-0.439887
O	5.576606	-3.451635	-0.181513	H	2.487719	3.809493	0.460015
C	2.235155	-2.425758	-1.682514	H	2.495293	3.303840	-1.250143
O	1.328602	-3.129449	-1.747760	C	3.011761	1.268450	0.956658
C	2.684688	0.295818	-2.462808	O	3.699337	2.079663	1.508646
O	2.025806	1.083426	-2.990880				

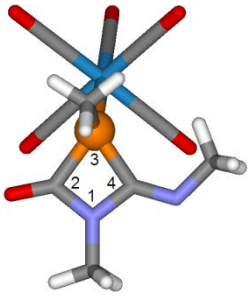


TS(10''→2''): E = -1353.49663012064 au (COSMO$_{tol}$/DLPNO-CCSD(T)/def2-TZVPPecp)

ZPE = 0.18016822 au (COSMO$_{tol}$/B3LYP-D3/def2-TZVPecp)

ν = -169.41 cm^{-1}

N	-0.139565	0.667296	-0.325878	C	4.072311	-0.956937	2.124686
P	2.946759	-0.456089	0.748227	H	4.091706	-2.045531	2.169456
C	0.919724	1.127890	-0.104817	H	5.086258	-0.595904	1.950989
N	1.903391	1.923130	0.121244	H	3.711765	-0.571039	3.078022
W	3.908495	-1.076353	-1.615958	C	-0.796804	-0.467262	-0.913086
C	4.708162	-1.617205	-3.381536	H	-0.686933	-0.435096	-1.996453
O	5.175496	-1.922332	-4.389779	H	-0.318934	-1.369088	-0.523146
C	5.402596	0.308307	-1.249538	H	-1.848964	-0.457718	-0.643681
O	6.205774	1.091331	-1.023525	C	1.974437	3.284181	-0.439369
C	5.005784	-2.561402	-0.675187	H	0.995003	3.752263	-0.383863
O	5.605785	-3.389549	-0.162011	H	2.683976	3.826619	0.180660
C	2.334887	-2.374864	-1.833302	H	2.321947	3.248923	-1.470014
O	1.426814	-3.071144	-1.935869	C	3.063775	1.339533	0.879635
C	2.788610	0.351524	-2.552468	O	3.799268	2.098677	1.447032
O	2.129461	1.140011	-3.074755				



2'': E = -1353.56483581642 au (COSMO$_{tol}$/DLPNO-CCSD(T)/def2-TZVPPecp)

ZPE = 0.18260352 au (COSMO$_{tol}$/B3LYP-D3/def2-TZVPecp)

N1-C2: d = 1.381 Å; WBI = 1.116; $\rho(r) = 31.71 \cdot 10^{-2}\ e/a_0^3$.

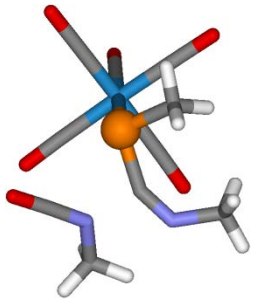
N1-C4: d = 1.403 Å; WBI = 1.051; $\rho(r) = 30.28 \cdot 10^{-2}\ e/a_0^3$.

P3-C2: d = 1.898 Å; WBI = 0.800; $\rho(r) = 15.43 \cdot 10^{-2}\ e/a_0^3$.

P3-C4: d = 1.878 Å; WBI = 0.814; $\rho(r) = 15.50 \cdot 10^{-2}\ e/a_0^3$.

N	-0.322186	0.294457	0.202430	O	0.691852	-5.804857	4.818846
P	0.130391	-0.081196	4.070233	C	1.583551	-2.327292	6.102363
C	0.749004	-0.046452	0.655408	O	2.176145	-2.109484	7.058576
N	1.782536	-0.300470	1.251569	C	-1.251910	-2.677031	5.389043
W	0.538958	-2.685212	4.362895	O	-2.247096	-2.691743	5.956132
C	0.639176	-4.667659	4.646459	C	-0.481980	-2.947418	2.591248

O	-1.051153	-3.095289	1.608748	H	-2.216709	-0.544293	0.001757
C	2.332006	-2.741874	3.339087	H	-1.466718	-0.022423	-1.507124
O	3.335913	-2.800959	2.792685	C	3.135484	-0.203027	0.719115
C	-0.204318	0.700119	5.740735	H	3.170026	0.329966	-0.232766
H	-1.226647	0.404519	5.979867	H	3.760127	0.319756	1.443532
H	0.455797	0.334963	6.523509	H	3.545506	-1.204321	0.588059
H	-0.159874	1.785642	5.676503	C	1.797328	0.327308	4.010112
C	-1.276906	-0.507226	-0.549447	O	2.900322	0.624470	3.956087
H	-0.925290	-1.525127	-0.720485				

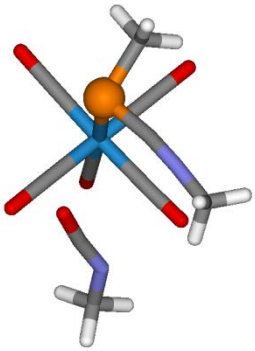


TS(2''→4''·11): E = -1353.47456026139 au (COSMO$_{tol}$/DLPNO-CCSD(T)/def2-TZVPPecp)

ZPE = 0.17925252 au (COSMO$_{tol}$/B3LYP-D3/def2-TZVPecp)

ν = -294.25 cm^{-1}

N	0.423300	0.261903	0.531162	C	2.985996	-1.468984	1.844792
P	3.296410	-0.103054	0.623157	H	2.338918	-2.259549	1.469532
C	1.613172	0.457796	0.391069	H	3.960546	-1.909077	2.062315
N	1.825968	2.042061	-0.379624	H	2.580273	-1.069455	2.774371
W	3.870118	-1.058921	-1.784011	C	-0.264025	-0.957078	0.913930
C	4.395703	-1.814311	-3.570672	H	-1.329122	-0.839973	0.730002
O	4.690036	-2.253945	-4.595073	H	0.108732	-1.803530	0.335691
C	5.852236	-0.911128	-1.207632	H	-0.109903	-1.158661	1.975170
O	6.946767	-0.822015	-0.883970	C	0.804364	2.447822	-1.356780
C	3.760307	-2.961416	-0.988353	H	-0.102138	1.919063	-1.066715
O	3.683870	-4.012922	-0.539907	H	0.642307	3.521723	-1.315630
C	1.879511	-1.146371	-2.265079	H	1.117426	2.144432	-2.353551
O	0.756943	-1.167079	-2.511275	C	2.793851	2.731070	-0.037553
C	3.930226	0.853857	-2.514033	O	3.668713	3.405810	0.285473
O	3.931920	1.935977	-2.906401				

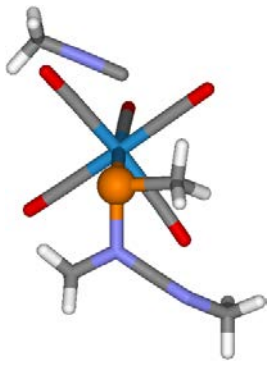


4''·11: E = -1353.51617448694 au (COSMO$_{tol}$/DLPNO-CCSD(T)/def2-TZVPPecp)

ZPE = 0.17865724 au (COSMO$_{tol}$/B3LYP-D3/def2-TZVPecp)

N	0.732711	-0.434861	1.149575	P	3.626161	-0.575644	1.115887

C	1.883823	-0.570210	1.162879	H	3.409273	-3.013519	1.649738
N	0.749572	2.147666	-1.194631	H	4.988396	-2.322491	2.046728
W	3.994751	-0.960546	-1.480885	H	3.615236	-2.023370	3.121071
C	4.408711	-1.216857	-3.428800	C	-0.661295	-0.189391	1.107087
O	4.642325	-1.366921	-4.547909	H	-0.884045	0.356603	0.190583
C	6.013438	-0.992689	-1.025209	H	-1.195127	-1.139032	1.103343
O	7.130255	-1.021448	-0.774792	H	-0.958528	0.402009	1.972995
C	3.901333	-2.999188	-1.187430	C	0.732282	2.361802	-2.620675
O	3.838624	-4.130654	-1.016253	H	0.324836	1.476275	-3.102594
C	1.981514	-0.978416	-1.870971	H	0.098269	3.215620	-2.861597
O	0.849851	-1.014250	-2.067527	H	1.738395	2.542815	-2.996573
C	4.060004	1.084528	-1.697980	C	1.290610	2.517758	-0.197971
O	4.086121	2.224879	-1.824448	O	1.743069	2.773943	0.856093
C	3.911863	-2.150365	2.080669	O	2.900322	0.624470	3.956087

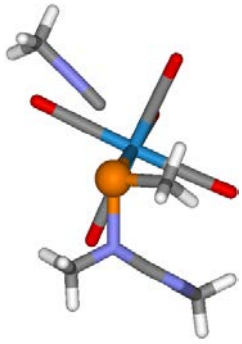


6‘‘·CNMe: E = -1372.83430861822 au ($COSMO_{tol}$/DLPNO-CCSD(T)/def2-TZVPPecp)

ZPE = 0.21782485 au ($COSMO_{tol}$/B3LYP-D3/def2-TZVPecp)

BSSE = 0.00105564 au (DLPNO-CCSD(T)/def2-TZVPPecp)

N	-0.256272	-0.047915	0.062075	H	2.877592	1.749253	-0.891311
P	1.620190	-0.134671	-0.181239	H	1.257165	1.862578	-1.579337
C	-0.882843	1.038429	0.064263	C	-0.965069	-1.318045	0.319144
N	-1.438656	2.074605	-0.108505	H	-0.371508	-2.112302	-0.127316
W	2.570633	-0.404726	2.240572	H	-1.053709	-1.484529	1.389959
C	3.340463	-0.510960	4.106135	H	-1.951353	-1.292238	-0.139469
O	3.766692	-0.546016	5.176487	C	-1.858709	3.178874	0.734265
C	3.817725	1.195804	1.837295	H	-1.530368	3.040874	1.762427
O	4.499162	2.092229	1.631061	H	-1.438077	4.094425	0.321935
C	1.050748	0.858991	2.751039	H	-2.944319	3.250191	0.686618
O	0.144555	1.545955	2.943292	C	4.816436	-0.035926	-1.508182
C	1.375532	-2.019316	2.657324	N	5.205759	-1.110280	-1.717406
O	0.724024	-2.931940	2.915514	C	5.657533	-2.436747	-1.947433
C	3.960254	-1.735007	1.497135	H	6.123897	-2.497883	-2.929902
O	4.705342	-2.504807	1.085503	H	6.379518	-2.711498	-1.180520
C	1.816066	1.639076	-0.669066	H	4.810313	-3.119573	-1.901777
H	1.552615	2.355546	0.111309				



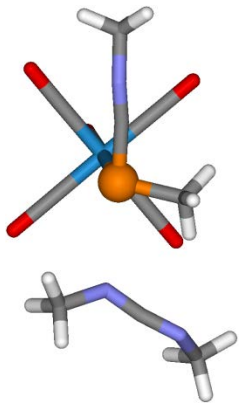
TS(6‘‘·CNMe →**4’’**·**9)**:

E = -1372.82971742416 au (COSMO$_{tol}$/DLPNO-CCSD(T)/def2-TZVPPecp)

ZPE = 0.21750337 au (COSMO$_{tol}$/B3LYP-D3/def2-TZVPecp)

ν = -215.77 cm^{-1}

N	-0.279057	-0.086919	-0.289508	H	2.793615	1.954039	-1.273235
P	1.772771	-0.126056	-0.513374	H	1.351849	1.588515	-2.240221
C	-0.865640	0.803299	0.346552	C	-0.964191	-1.270700	-0.817994
N	-1.364026	1.758567	0.858203	H	-0.580022	-2.152975	-0.306973
W	2.573605	0.040987	2.010817	H	-2.040178	-1.197774	-0.666388
C	3.160098	0.100716	3.936550	H	-0.738320	-1.354098	-1.879626
O	3.489034	0.141680	5.042007	C	-1.723910	2.117020	2.217725
C	4.348748	0.903682	1.404956	H	-1.445455	1.339618	2.927625
O	5.333081	1.392592	1.078425	H	-1.218299	3.046560	2.469842
C	1.803106	1.937740	2.132468	H	-2.799044	2.286333	2.253854
O	1.403100	3.014764	2.178840	C	4.014458	-0.529487	-1.258136
C	0.780513	-0.790351	2.545722	N	4.811878	-1.367556	-1.355564
O	-0.244617	-1.232424	2.830376	C	5.757883	-2.424789	-1.398937
C	3.404612	-1.820146	1.722259	H	5.908510	-2.738814	-2.430936
O	3.885333	-2.844505	1.522847	H	6.703694	-2.083838	-0.979532
C	1.769165	1.593432	-1.231998	H	5.381252	-3.261346	-0.811034
H	1.197789	2.284688	-0.613720				



4’’·**9**: E = -1372.85618942236 au (COSMO$_{tol}$/DLPNO-CCSD(T)/def2-TZVPPecp)

ZPE = 0.21804488 au (COSMO$_{tol}$/B3LYP-D3/def2-TZVPecp)

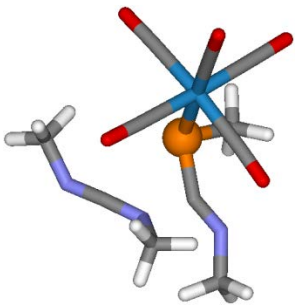
P-C (in **4’’**): d = 1.742 Å; WBI = 1.237; ρ(r) = 15.11·10^{-2} e/a_0^3.

N-C (in **4’’**): d = 1.162 Å; WBI = 2.282; ρ(r) = 45.86·10^{-2} e/a_0^3.

P-CH$_3$ (in **4’’**): d = 1.869 Å; WBI = 0.929; ρ(r) = 15.24·10^{-2} e/a_0^3.

N	0.322975	-0.038268	0.058024	P	3.387193	-0.012952	-0.120882

C	-0.305051	1.003400	0.062691	H	3.326170	1.850247	-1.740802
N	-0.776353	2.122380	0.007294	C	-0.112685	-1.346615	-0.403480
W	3.620342	-0.098426	2.538012	H	0.704341	-1.805462	-0.959668
C	3.651587	-0.120266	4.542564	H	-0.329734	-1.981686	0.455581
O	3.667682	-0.123047	5.695691	H	-0.996566	-1.288763	-1.041698
C	5.070856	1.352996	2.464744	C	-1.544035	2.801706	1.042328
O	5.892407	2.153112	2.392910	H	-1.696391	2.180007	1.926203
C	2.151795	1.353079	2.583872	H	-1.014553	3.708388	1.335442
O	1.338932	2.158727	2.620726	H	-2.512685	3.092240	0.634606
C	2.159247	-1.560044	2.504528	C	5.107933	-0.113011	-0.313671
O	1.351762	-2.371509	2.494179	N	6.249863	-0.320781	-0.476831
C	5.073143	-1.550955	2.459015	C	7.592062	-0.354454	0.016586
O	5.896658	-2.349702	2.402650	H	7.934636	-1.388230	0.025635
C	3.184081	1.763564	-0.664240	H	8.230684	0.222446	-0.650142
H	2.157366	2.037413	-0.427344	H	7.632361	0.059182	1.024372
H	3.857061	2.440246	-0.141999				

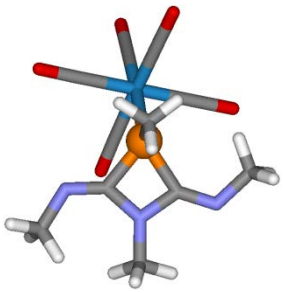


TS(4‘‘·9 →12’’): E = -1372.83672239526 au ($COSMO_{tol}$/DLPNO-CCSD(T)/def2-TZVPPecp)

ZPE = 0.21898044 au ($COSMO_{tol}$/B3LYP-D3/def2-TZVPecp)

ν = -320.57 cm^{-1}

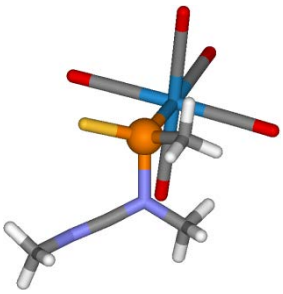
N	0.931008	0.208570	-0.209052	H	-0.111374	0.087838	5.661404
P	0.094250	-0.323818	3.218260	H	-1.023248	1.281491	4.710381
C	1.660003	0.296531	0.725682	C	0.002831	-0.798509	-0.686100
N	2.384116	0.527788	1.712850	H	0.545289	-1.703429	-0.957304
W	1.042367	-2.780482	3.496641	H	-0.705160	-1.024364	0.113430
C	1.698767	-4.659676	3.774493	H	-0.526197	-0.412465	-1.552332
O	2.085618	-5.732954	3.944421	C	3.825626	0.253717	1.763495
C	2.653947	-1.931098	4.448255	H	4.060524	-0.677353	1.252545
O	3.536547	-1.397074	4.952957	H	4.376818	1.075199	1.306092
C	0.017046	-2.909937	5.291899	H	4.113157	0.168710	2.807725
O	-0.547758	-3.001920	6.283237	C	1.487296	0.794696	3.312195
C	-0.638548	-3.393096	2.476818	N	1.966117	1.661923	4.007623
O	-1.571222	-3.695279	1.880831	C	2.947950	2.692030	3.824294
C	2.025507	-2.724933	1.710767	H	3.834975	2.461576	4.416683
O	2.567518	-2.712835	0.692383	H	3.227620	2.796135	2.773020
C	-0.739188	0.231490	4.782607	H	2.544310	3.639379	4.182030
H	-1.643114	-0.368226	4.896237				



12'': E = -1372.91302604377 au ($COSMO_{tol}$/DLPNO-CCSD(T)/def2-TZVPPecp)

ZPE = 0.22216631 au ($COSMO_{tol}$/B3LYP-D3/def2-TZVPecp)

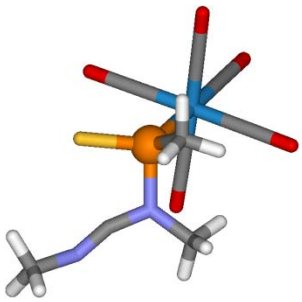
N	0.382352	0.520994	0.407973	H	-0.430940	0.551090	5.151000
P	0.697186	-0.322401	3.221134	H	-0.563824	1.691117	3.787612
C	0.929389	0.462259	1.534159	C	-0.873606	-0.172191	0.194639
N	2.136699	1.053659	1.919576	H	-0.752437	-0.911544	-0.598848
W	0.969508	-2.776778	3.614257	H	-1.246277	-0.684789	1.090028
C	1.270064	-4.752949	3.990937	H	-1.629801	0.543060	-0.135181
O	1.442504	-5.866132	4.208749	C	3.034482	1.773990	1.032050
C	1.696138	-2.317908	5.499179	H	2.754144	1.524318	0.010500
O	2.093998	-2.081903	6.544226	H	2.946098	2.852844	1.168208
C	-0.946097	-2.877202	4.369988	H	4.062688	1.466796	1.210813
O	-2.013378	-2.912198	4.783818	C	2.232311	0.717508	3.282389
C	0.257967	-3.244471	1.734952	N	3.024139	0.950121	4.225936
O	-0.132151	-3.515658	0.693618	C	4.211854	1.781035	4.088942
C	2.867455	-2.567885	2.826163	H	5.068393	1.158398	3.815936
O	3.909490	-2.419243	2.377134	H	4.114850	2.580914	3.350871
C	-0.596358	0.641812	4.076914	H	4.433623	2.230846	5.056388
H	-1.573908	0.221822	3.840527				



13'': E = -1638.12283036197 au ($COSMO_{tol}$/DLPNO-CCSD(T)/def2-TZVPPecp)

ZPE = 0.17367835 au ($COSMO_{tol}$/B3LYP-D3/def2-TZVPecp)

N	-0.025136	0.013049	-0.156062	O	5.550367	0.505364	-1.586054
P	1.847255	0.522981	-0.298495	C	2.417849	-0.800674	0.832272
C	-0.823559	0.913968	0.208741	H	2.201653	-1.792658	0.434800
N	-1.536329	1.827114	0.422105	H	3.500260	-0.689803	0.911135
W	2.551925	0.249359	-2.713255	H	1.975326	-0.674021	1.819552
C	3.231028	0.078547	-4.622570	C	-0.489092	-1.348035	-0.484661
O	3.616776	-0.026549	-5.699390	H	0.158242	-1.739867	-1.264193
C	2.633377	-1.785500	-2.489957	H	-0.424537	-1.984423	0.396054
O	2.663808	-2.926031	-2.354523	H	-1.511211	-1.320286	-0.854989
C	0.598131	0.116470	-3.337314	C	-2.101215	2.569730	1.522941
O	-0.504460	0.041158	-3.646379	H	-1.982022	2.032597	2.462627
C	2.439559	2.316090	-2.894996	H	-1.581559	3.525577	1.573737
O	2.371378	3.449418	-3.006721	H	-3.153333	2.753150	1.317253
C	4.486954	0.415774	-1.997561	S	1.915408	2.252198	0.640720



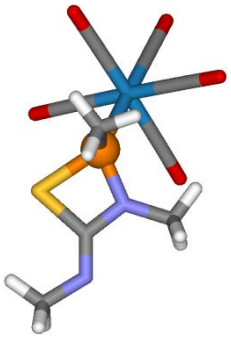
TS(13''→5''):

E = -1638.11951013939 au (COSMO$_{tol}$/DLPNO-CCSD(T)/def2-TZVPPecp)

ZPE = 0.17305988 au (COSMO$_{tol}$/B3LYP-D3/def2-TZVPecp)

ν = -231.47 cm^{-1}

N	0.049383	0.005486	-0.171694	O	5.564936	0.292834	-1.582546
P	1.774801	0.521458	-0.380552	C	2.518950	-0.640743	0.818256
C	-0.684441	0.946259	0.318543	H	2.424657	-1.670482	0.469426
N	-1.648589	1.572969	0.584305	H	3.579635	-0.395754	0.887549
W	2.575831	0.237310	-2.753251	H	2.059151	-0.522319	1.798990
C	3.259729	0.023156	-4.658633	C	-0.500824	-1.334168	-0.444658
O	3.645528	-0.108073	-5.732098	H	0.039581	-1.745757	-1.293450
C	2.535882	-1.799057	-2.525563	H	-0.369551	-1.983171	0.420343
O	2.506232	-2.938839	-2.384236	H	-1.555105	-1.257926	-0.699840
C	0.616784	0.228325	-3.383921	C	-2.192747	2.455803	1.574290
O	-0.487840	0.222736	-3.691250	H	-2.501505	1.890126	2.453554
C	2.603003	2.306889	-2.940400	H	-1.411986	3.167516	1.853532
O	2.614820	3.442199	-3.051763	H	-3.045954	2.986744	1.160509
C	4.504331	0.276061	-2.012729	S	1.552153	2.315113	0.502104



5'': E = -1638.15369579607 au (COSMO$_{tol}$/DLPNO-CCSD(T)/def2-TZVPPecp)

ZPE = 0.17457843 au (COSMO$_{tol}$/B3LYP-D3/def2-TZVPecp)

N	0.050332	-0.040849	-0.109377	C	2.495759	2.286219	-2.875883
P	1.695748	0.320672	-0.426196	O	2.447011	3.425096	-2.934083
C	-0.426533	1.081249	0.531960	C	4.483260	0.329101	-1.986341
N	-1.587017	1.289755	0.947457	O	5.538983	0.390218	-1.548451
W	2.568416	0.217107	-2.744859	C	2.641919	-0.589569	0.838272
C	3.299246	0.071661	-4.650036	H	2.705268	-1.636854	0.535534
O	3.711386	-0.019036	-5.714811	H	3.653822	-0.184765	0.883667
C	2.607667	-1.833153	-2.563841	H	2.164819	-0.508599	1.813574
O	2.621651	-2.972704	-2.445163	C	-0.755449	-1.190479	-0.473562
C	0.626706	0.128255	-3.445987	H	-0.161363	-1.842450	-1.112502
O	-0.453652	0.079895	-3.816528	H	-1.064895	-1.749235	0.411316

H	-1.643637	-0.873058	-1.020480	H	-1.093113	3.222360	1.700539
C	-1.943463	2.538217	1.586267	H	-2.716040	3.042678	1.001865
H	-2.358777	2.337608	2.575980	S	1.087444	2.134273	0.546363

References

[1] J. M. Villalba Franco, T. Sasamori, G. Schnakenburg, A. Espinosa Ferao, R. Streubel, *Chem. Eur. J.*, 2015, **21**, 9650.

[2] 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.

[3] a) A. D. Becke, *J. Chem. Phys.*, 1993, ***98***, 5648. b) C. T. Lee, W. T. Yang, R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.

[4] F. Weigend, R. Ahlrichs, Phys. *Chem. Chem. Phys.*, 2005, **7**, 3297.

[5] D. Andrae, U. Haeussermann, M. Dolg, H. Stoll, H. Preuss, *Theor. Chim. Acta*, 1990, **77**, 123. 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/.

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

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

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

[9] C. Riplinger, B. Sandhoefer, A. Hansen, F. Neese, *J. Chem. Phys.*, 2013, **139**, 134101.

[10] a) H. P. Kelly, *Phys. Rev.*, 1964, **134**, A1450-A1453; b) W. Meyer, *J. Chem. Phys.*, 1973, **58**, 1017; c) R. Ahlrichs, H. Lischka, V. Staemmler, W. Kutzelnigg, *J. Chem. Phys.*, 1975, **62**, 1225; d) C. Kollmar, F. Nesse, *Mol. Phys.*, 2010, **108**, 2449.

[11] F. Wennmohs, F. Neese, *Chem. Phys.*, 2008, **343**, 217.

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

[13] 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.

[14] a) L. Goerigk and S. Grimme *J. Chem. Theory Comput.*, 2011, **7**, 291; b) ibid. *Phys. Chem. Chem. Phys.*, 2011, **13**, 6670.

[15] 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).

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