Electronic Supplementary Information (ESI)

The azaphosphiridine to terminal phosphinidene complex rearrangement – looking for non-covalent interactions of a highly reactive species

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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 occurred via silica gel and P_2O_5. Solvents were dried according to standard procedures 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 Thermo Nicolet 380 spectrometer; solid as KBr pellets and liquids as film in a KBr cell.

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. Crystallographic data of complexes **5a** and **9** have been deposited at the Cambridge Crystallographic Data Centre under the number 936605 (**5a**), 949202 (**9**). This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. This material is available free of charge via the Internet at http://pubs.acs.org.

Synthesis of complex **5a**. To a solution of 506 mg (0.9 mmol) of *P*-Cp* dichloro-phosphane complex **1** and 156 mg (1 eq.) of 12-crown-4, dissolved in THF, 1.1 eq. of *tert*-butyl lithium (1.5 M in *n*-hexane) were slowly added at -78 °C. After 15 min. 145 mg (1.5 eq.) of the 2-furyl aldimine **3** was slowly added at -78 °C. The reaction mixture was warmed slowly to ambient temperature. Lithium chloride was filtered, the solvent removed in *vacuo* and the product purified by column chromatography (silica gel, -20 °C, petroleum ether / Et_2O: 5 / 1) and subsequent crystallization from Et_2O at -70°C afforded a light yellow solid. Yield: 380 mg (0.63 mmol, 70 %). ^{1}H NMR(C_6D_6) δ = 0.62 (s, 3H, C1-C*H*$_3$), 1.03 (d, 3H, $^{3}J_{P,H}$ = 17.4 Hz, P-C3-C*H*$_3$), 1.27 (d, 3H, $^{3}J_{P,H}$ = 16.3 Hz, P-C2-C*H*$_3$), 1.32 (dq, 3H, $^{5}J_{H,H}$ = 1.0 Hz, $^{4}J_{P,H}$ = 4.5 Hz, C*H*$_3$-C4=C5), 1.45 (dq, 3H, $^{5}J_{H,H}$ = 1.0 Hz, $^{5}J_{P,H}$ = 1.8 Hz, C*H*$_3$-C5=C4), 2.27 (d, 3H, $^{3}J_{P,H}$ = 11.2 Hz, N-C*H*$_3$), 3.64 (d, 1H, $^{3}J_{P,H}$ = 12.2 Hz, N-C*H*-Fu), 5.92 (dd, 1H, $^{3}J_{H3,H2}$ = 3.2 Hz, $^{4}J_{H3,H1}$ = 0.8 Hz, Fu*H*3), 6.03 (dd, 1H, $^{3}J_{H2,H3}$ = 3.2 Hz, $^{3}J_{H2,H1}$ = 1.9 Hz, Fu*H*2), 7.15 (dd, 1H, $^{3}J_{H1,H2}$ = 1.9 Hz, $^{4}J_{H1,H3}$ = 0.8 Hz, Fu*H*1). ^{13}C{^{1}H} NMR (C_6D_6): δ = 10.6 (d, $^{3}J_{C,P}$ = 1.9 Hz, P-C1-*C*H$_3$), 10.83 (d, $^{1}J_{C,P}$ = 1.8 Hz, P-C2-*C*H$_3$), 12.05 (s, P-C5-*C*H$_3$), 14.12 (d, $^{1}J_{C,P}$ = 9.3 Hz, P-C3-*C*H$_3$), 15.31 (d, $^{3}J_{C,P}$ = 2.8 Hz, P-C4-*C*H$_3$), 35.12 (d, $^{2}J_{C,P}$ = 8.2 Hz, N-*C*H$_3$), 46.37 (s, *C*1), 59.10 (d, $^{1}J_{C,P}$ = 32.0 Hz, *C*3), 65.93 (d, $^{1}J_{C,P}$ = 2.7 Hz, *C*3), 78.00 (d, $^{2}J_{C,P}$ = 1.8, Fu-*C*H-N), 107.70 (s, *C*3Fu), 109.57 (s, *C*2Fu), 131.03 (d, $^{3}J_{C,P}$ = 4.8 Hz, -*C*3=C), 134.93 (d, $^{2}J_{C,P}$ = 9.3 Hz, -C=*C*^{2}), 141.96 (s, -*C*1Fu), 153.40 (s, *C*4Fu), 195.63 (dSat, $^{2}J_{P,C}$ = 8.3 Hz, ^{1}J$_{W,C}$ = 125.7, *cis*-*C*O), 198.00 (d, ^{2}J$_{P,C}$ = 32.1 Hz). ^{31}P{^{1}H} NMR (C_6D_6): -34,1 ppm, $^{1}J_{W,P}$ = 272.8 Hz. MS (EI, 70 eV, ^{184}W): *m*/*z* (%): 599.1, [M]$^{+}$, (40); 543.1, [M-2xCO]$^{+}$, (5); 459.1, [M-5xCO]$^{+}$, (10); 444.1, [M-5xCO-Me]$^{+}$, (10); 406.0, [M-4CO-Me-C_4H_3O]$^{+}$, (100); 378, [M-5xCO-Me-C_4H_3O]$^{+}$, (40). (100). EA: Calc for $C_{21}H_{22}NO_6PW$: C 42.09, H 3.70, N 2.34, Found: C 42.09, H 3.77, N 2.30.

Synthesis of complex **9.** To a solution of 580 mg (1.03 mmol) of *P*-Cp* dichloro-phosphane complex and 179 mg (1 eq.) of 12-crown-4, dissolved in 20 mL THF, 1.1 eq. of *tert.*-butyl lithium (1.5 M in *n*-hexane) were slowly added at -78 °C. After 15 min. 113 mg (1 eq.) of 2-furyl aldimine **3** was slowly added at -78 °C. The reaction mixture was warmed slowly until -30 °C. After having removed about 75 % of the solvent volume in *vacuo* and 10 mL phenyl acetylene was added at -30 °C. The reaction mixture was stirred between -30 and -20 °C for 5 hours. The excess of phenyl acetylene and the remaining solvent was then removed in *vacuo* and the product was purified by column chromatography (SiO_2, d = 3 cm, h = 6 cm, pure petrol ether (40/60)) and then crystallized from a mixture of *n*-pentane and diethyl ether (3/1) at -60 °C to obtain a white solid. Yield: 430 mg (0.62 mmol, 60 %). ^{1}H NMR(C_6D_6): δ = 0.73 (s, 3H, C-C*H*$_3$), 0.85 (quint, 3H, $^{5}J_{H,H}$ = 1.33 Hz + $^{5}J_{P,H}$ = 1.33 Hz, C=C-C*H*$_3$), 1.00 (s, 3H, Fu-CH-C-C*H*$_3$), 1.19 (s, 3H, C-C*H*$_3$), 1.36 (q, 3H, $^{5}J_{H,H}$ = 1.33 Hz, C=C-C*H*$_3$), 1.99 (d, 1H, $^{2}J_{P,H}$ = 13.11 Hz, P-C*H*), 2.51 (d, 3H, $^{3}J_{P,H}$ = 14.70 Hz, N-C*H*$_3$), 3.7 (d, 1H, $^{4}J_{H,H}$ = 0.8 Hz, Fu-C*H*-N), 6.00 (dd, 1H, $^{3}J_{H2,H3}$ = 3.24 Hz, $^{4}J_{H2,H1}$ = 1.85 Hz, Fu*H*^{2}), 6.1 (dt, 1H, $^{3}J_{H3,H2}$ = 3.42 Hz, $^{3}J_{H3,H1}$ = 0.8 Hz, $^{4}J_{H3,CH-N}$ = 0.8 Hz, Fu*H*^{3}), 6.97 (dd, 1H, $^{3}J_{H1,H2}$ = 1.85 Hz, $^{4}J_{H1,H3}$ = 0.8 Hz, Fu*H*^{1}), 7.01 (m, 5H, C-*Ph*). ^{13}C{^{1}H} NMR (C_6D_6): δ = 9.7 (s, C^{10}), 10.7 (s, C^{6}), 12.1 (s, *C*^{9}), 12.8 (s, *C*^{7}), 16.8 (s, *C*^{8}), 40.5 (d, $^{2}J_{C,P}$ = 13.8 Hz, N-*C*H$^{-}_{3}$), 43.5 (d, $^{1}J_{C,P}$ = 6.0 Hz, P-*C*H), 52.5 (d, $^{1}J_{C,P}$ = 21.0 Hz, P-*C*$^{-}$Ph), 55.1 (d, $^{3}J_{C,P}$ = 4.8 Hz, *C*^{1}), 59.1 (d, $^{2}J_{C,P}$ = 2.0 Hz, *C*^{5}), 64.0 (d, $^{2}J_{C,P}$ = 5.1 Hz, N-*C*H), 64.7 (d, $^{2}J_{C,P}$ = 3.1 Hz, *C*^{2}), 109.3 (s, *C*^{3}Fu), 110.5 (s, *C*^{2}Fu), 127.2 (d, $^{3}J_{C,P}$ = 1.5 Hz, ^{ipso}Ph), 127.6 (s, *p*-Ph), 127.9 (s, *o*-Ph), 128.2 (s, *m*-Ph), 138.3 (d, $^{3}J_{C,P}$ = 4.0 Hz, -*C*=C), 139.2 (d, $^{3}J_{C,P}$ = 4.8 Hz, -C=*C*), 140.1 (d, $^{2}J_{C,P}$ = 6.6 Hz), 141.4 (s, *C*^{1}Fu), 154.1 (d, $^{3}J_{C,P}$ = 4.1 Hz, *C*^{4}Fu), 195.9 (dSat, $^{2}J_{P,C}$ = 8.7 Hz, $^{1}J_{W,C}$ = 125.6, *cis*-*C*O), 198.6 (d, $^{2}J_{P,C}$ = 31.6 Hz, *trans*-*C*O). ^{31}P δ = -3.72 ppm, quintSat, $^{1}J_{W,P}$ = 277.6 Hz, $^{x}J_{H,P}$= 14.1 Hz. MS (EI, 70 eV, ^{184}W): *m*/*z* (%):701.1, [M]+, (30); 673.1, [M]+-CO, 10; 617.1, [M]+-3xCO, (30); 561.1, [M]+-4xCO, (30) 534.1, ([M]+-5x CO, (5). IR (KBr): ν̃= 2976 (b, ν-CH), 2073 (s, ν-CO), 1992 (s, ν-CO), 1918 (s, ν-CO),1496 (s, ν-C-C/Ar) cm^{-1}. EA: Calc for $C_{29}H_{28}NO_6PW$: C 49.66, H 4.02, N 2.00, Found: C 49.64, H 4.83, N 2.07.

Low temperature ^{31}P NMR monitoring

Low temperature ^{31}P NMR monitoring showed the formation of four intermediates which rapidly transformed into one final product **5a**. Compared to data of known aza-phosphiridine complex derivatives, intermediates observed at -42.8 ppm ($^{1}J_{WP}$ = 277.8 Hz) and at -38.5 ppm ($^{1}J_{WP}$ = 271.0 Hz) are assigned to transient azaphosphiridine complexes **4a** and **4a'** (Scheme 2). Intermediate showing a ^{31}P NMR resonance at -28.7 ppm ($^{1}J_{WP}$ = 259.0 Hz) is assigned to the cage complex **5a'** which isomerizes to **5a**. The ^{31}P resonance of the phosphinidenoid complex **2** appears at 280.2 ppm ($^{1}J_{WP}$ = 76.5 Hz).

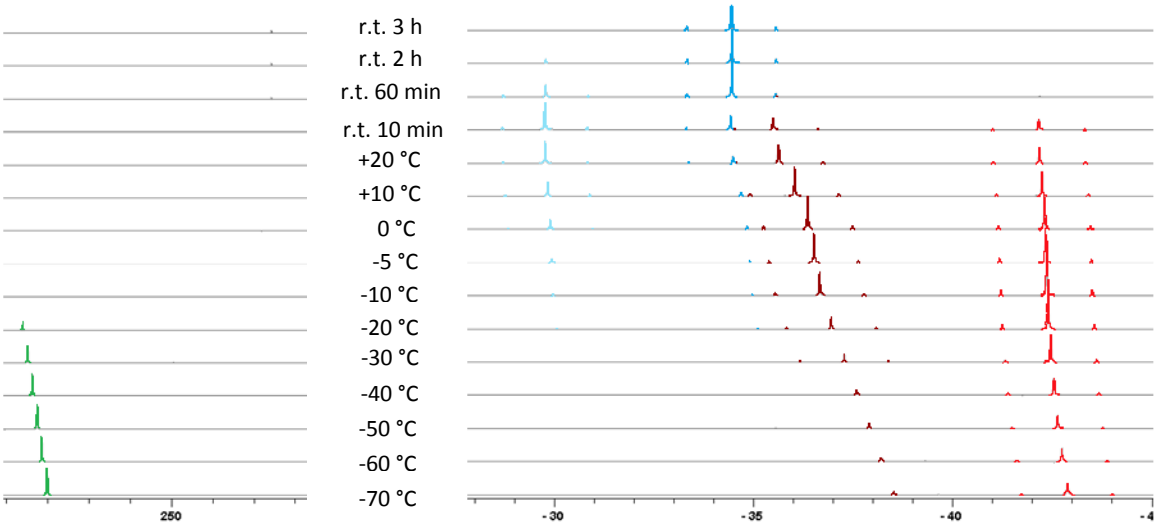

Figure SI 1: Low temperature ^{31}P NMR monitoring of the reaction of *P*-Cp* phosphinidenoid tungsten(0) complex **2** and *C*-furyl-*N*-methyl carbaldimine **3a**.

Computational details

DFT calculations were performed with the ORCA program.[1] All geometry optimizations were run in redundant internal coordinates with tight convergence criteria,[2] in the gas-phase and using the B3LYP functional[3] together with the def2-TZVP basis set,[4] or the def2-SVP basis set[5] for the cases of TS geometries. 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. Wiberg bond indices (WBI)[9] were obtained from the natural bond orbital (NBO) population analysis.[10] Bader's AIM-derived topological analysis of the electron density was conducted with AIM2000[11] and using the so called

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[1] 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 2.9.0. http://www.mpibac.mpg.de/bac/logins/neese/description.php. F. Neese, *WIREs Comput Mol Sci*, 2012, **2**, 73–78.

[2] Energy change $1.0\cdot10^{-6}$ hartree; maximum gradient $1.0\cdot10^{-4}$ hartree/a_0; RMS gradient $3.0\cdot10^{-5}$ hartree/a_0; maximum displacement $1.0\cdot10^{-3}$ a_0; RMS displacement $6.0\cdot10^{-4}$ a_0.

[3] 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.

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

[5] Schaefer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.*, **1992**, *97*, 2571-2577.

[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] Wiberg, K. *Tetrahedron* **1968**, *24*, 1083-1096.

[10] 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).

[11] (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.

wavefunctions (electron densities) generated with Gaussian09,[12] whereas that computed at the B3LYP/def2-SVP(ecp) level for **7b** was used as input for the NCIplot program.

NCIplot analysis

The reduced density gradient, *s* (or RDG), derived from the electron density and its first derivative ($s = 1/(2(3\pi 2)^{1/3})|\nabla\rho|/\rho^{4/3}$), is a fundamental dimensionless property in DFT, used to describe heterogeneous electron distributions.[13] It has large positive values in regions far from the molecule where density decays to zero exponentially but, on the contrary, has very small values (approaching zero) for regions of both covalent and noncovalent interactions. NCIs (non-covalent interactions) can be identified as regions with low ρ and low RDG, originating spikes in RDG *vs* ρ plots,[14] the ρ value of which turns out to be an indicator of the interaction strength. In order to better differentiate among a wide range of weak interactions and especially between stabilizing and destabilizing interactions, the sign of the Laplacian of the density, $\nabla^2\rho$, must be taken into account by decomposing it into a sum of contributions along the three principal axis of maximal variation, $\nabla^2\rho = \lambda_1 + \lambda_2 + \lambda_3$ (being $\lambda_1 \leq \lambda_2 \leq \lambda_3$), a criterion widely applied for the analysis of chemical bonding.[15] Covalent bonding is characterized by dominant negative contributions of the eigenvalues λ_i resulting in an overall negative Laplacian. The Laplacian for weaker interactions (both bonding and nonbonding) is dominated by positive interactions[14a] but here the sign of λ_2 is of diagnostic relevance: the interatomic regions of weak bonding interactions can be identified by a negative value of λ_2 whereas nonbonded contacts (steric clashes) feature $\lambda_2 > 0$. Consequently, in

[12] 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.

[13] Cohen, A. J.; Mori-Sánnchez, P.; Yang, W. *Science.* **2008**, *321*, 792–794.

[14] a) Johnson, E. R.; Keinan, S.; Mori-Sánchez, P.; Contreras García, J.; Cohen, A. J.; Yang, W. *J. Am. Chem. Soc.*, **2010**, *132*, 6498-6506. b) Contreras García, J.; Johnson, E. R.; Keinan, S.; Chaudret, R.; Piquemal, J.-P.; Beratan, D. N.; Yang, W. *J. Chem. Theory Comput.*, **2011**, *7*, 625-632.

[15] a) Bader, R. F. W. *J. Chem. Phys.*, **1984**, *80*, 1943-1960. b) Bader, R. F. W. *J. Phys. Chem. A*, **1998**, *102*, 7314-7323.

the RDG plot, the quantity ρ in the horizontal axis is multiplied by the sign of λ_2 (second highest eigenvalue of the electron density Hessian matrix). Vertical spikes approaching the RDG = 0 regime indicate different types of interactions. Those at the positive side of the sign(λ_2)·ρ axis correspond to nonbonded contacts, whereas at the negative side the bonding interactions are found, with the (absolute) value providing information about their strength.

In 3D NCIplots (Figure 3 in the main text) isosurfaces for a given isovalue of RDG are coloured according to the indicated sign(λ_2)·ρ value: blue denotes strong attraction, green moderate interaction, and red (not present) indicates strong repulsion.

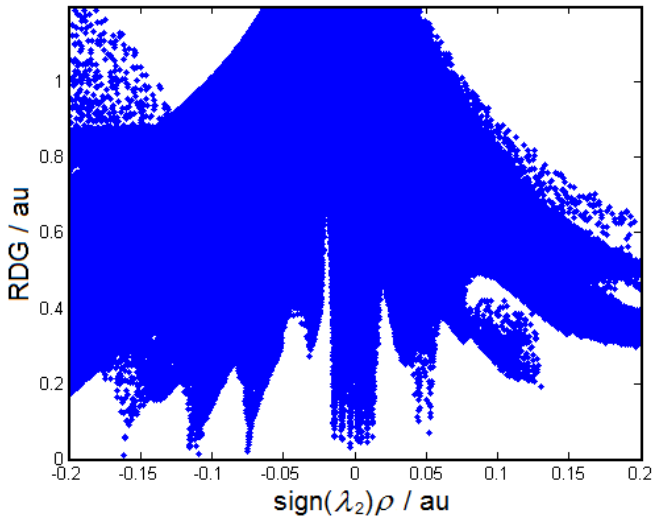


Figure SI 1: NCIplot-derived 2D representation of RDG (au) versus sign(λ_2)·ρ (au) for complex **7b**.

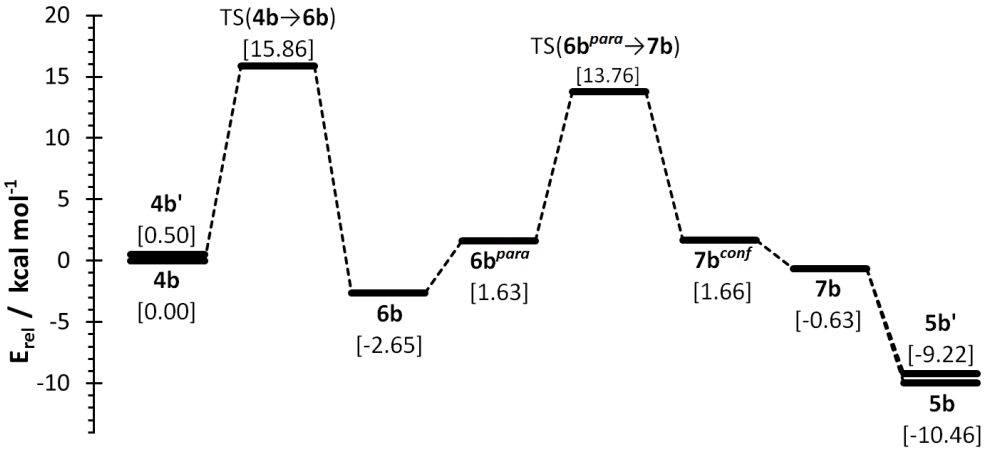
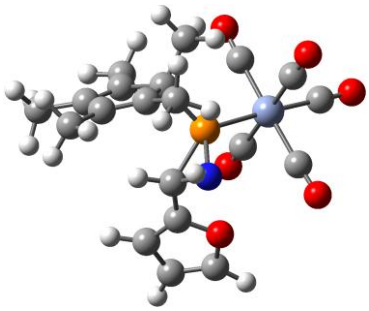


Figure SI 2: Computed (B3LYP-D3/def2-TZVPP) minimum energy profile for the transformation **4b→5b**.

Calculated structures.

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

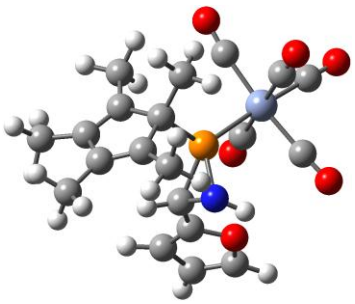


4b: E = -2665.89736192598 au

ZPE = 0.36029218 au

G = -2665.598151385 au

C	-0.042798	0.051403	-0.053658	C	1.266145	1.137938	2.737215
N	1.429876	-0.028980	-0.088896	C	0.224789	0.678977	3.463115
P	0.902028	1.618382	-0.031917	C	-1.004886	1.403502	3.077315
C	-0.806842	-0.457353	-1.190779	C	-0.713772	2.307911	2.119328
O	-0.221392	-0.476381	-2.420862	C	1.524748	3.526551	1.991200
C	-1.148662	-0.945354	-3.301877	H	2.586921	3.420477	1.770552
C	-2.310774	-1.220590	-2.660901	H	1.130019	4.324933	1.368184
C	-2.090332	-0.904062	-1.284094	H	1.421567	3.833151	3.034295
H	-0.828145	-1.021936	-4.325734	C	2.720855	0.815436	2.880305
H	-3.211529	-1.606684	-3.107655	H	2.879377	-0.158593	3.344191
H	-2.789516	-0.996062	-0.469585	H	3.244195	0.819199	1.920923
H	-0.519680	-0.164173	0.898147	H	3.227979	1.558008	3.505536
H	1.822844	-0.430585	0.753999	C	0.241463	-0.355046	4.543452
Cr	1.360730	3.040003	-1.887018	H	-0.036266	0.081018	5.507718
C	1.785742	4.087153	-3.390725	H	-0.482745	-1.148995	4.339959
O	2.051457	4.725786	-4.303908	H	1.222362	-0.814459	4.657919
C	0.523228	4.558145	-1.112137	C	-2.332938	1.106967	3.698000
O	0.008231	5.494844	-0.698516	H	-2.643811	0.078411	3.487919
C	3.036488	3.497365	-1.096011	H	-2.291467	1.204080	4.786504
O	4.045672	3.780483	-0.635627	H	-3.114805	1.770316	3.331910
C	2.186437	1.532438	-2.761550	C	-1.627785	3.254681	1.414098
O	2.699642	0.678781	-3.313601	H	-1.246413	4.278246	1.439935
C	-0.336451	2.593251	-2.662587	H	-1.745140	2.994422	0.356525
O	-1.352688	2.374388	-3.134625	H	-2.622048	3.258509	1.858437
C	0.767236	2.204721	1.792939				

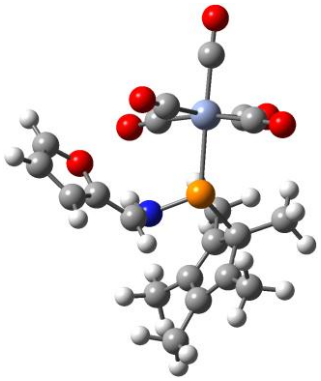


4b': E = -2665.897363173 au

ZPE = 0.36108929 au

G = -2665.593874083 au

C	0.00000000	0.00000000	0.00000000	C	1.19428516	1.01092344	2.75089106
N	1.47890339	0.00000000	0.00000000	C	0.06725740	0.68617051	3.42155648
P	0.84267273	1.61969172	0.00000000	C	-1.02143257	1.60175024	3.03714868
C	-0.73015444	-0.56282488	-1.13125061	C	-0.56046149	2.51522333	2.15985132
O	-0.06182170	-0.70591000	-2.31410203	C	1.87280280	3.33935515	1.98792687
C	-0.92991379	-1.27583375	-3.20093513	H	2.89000103	3.03694806	1.73741582
C	-2.12743629	-1.49611455	-2.60653916	H	1.60759780	4.18413644	1.35413317
C	-1.99747908	-1.04084039	-1.25737310	H	1.86356178	3.67946578	3.02552293
H	-0.54365455	-1.45578807	-4.18818342	C	2.56589681	0.44112917	2.91418735
H	-2.99655446	-1.93563092	-3.06648923	H	2.56769901	-0.40014805	3.60650546
H	-2.74372077	-1.06743808	-0.48031862	H	2.96880660	0.09052413	1.96418474
H	-0.42112084	-0.28290976	0.95916928	H	3.25636494	1.19157750	3.31354601
H	1.85431454	-0.27414615	-0.90407609	C	-0.12584362	-0.38859704	4.44211327
Cr	1.16553341	3.08489118	-1.91153609	H	-0.50950885	0.02852724	5.37778075
C	1.43603261	4.11837649	-3.45348364	H	-0.86119028	-1.12471530	4.10191811
O	1.60020658	4.73633352	-4.40430344	H	0.79797598	-0.91960199	4.66361699
C	0.24240367	4.57831335	-1.15671586	C	-2.41453415	1.48987750	3.56853110
O	-0.24843766	5.53363514	-0.76331902	H	-2.80530682	0.47948787	3.41252796
C	2.76824305	3.80440135	-1.17716219	H	-2.45642837	1.68709164	4.64477905
O	3.73258231	4.28055946	-0.78735574	H	-3.09427253	2.18104484	3.07430600
C	2.19457566	1.71496635	-2.75043011	C	-1.30415930	3.68350642	1.60381740
O	2.84621633	0.93685235	-3.27719398	H	-0.69879847	4.59109125	1.62930177
C	-0.44431381	2.40892933	-2.70905348	H	-1.61071695	3.53706446	0.56413810
O	-1.38787118	2.04263800	-3.23649003	H	-2.20598139	3.88064614	2.18173887
C	0.88830168	2.17570597	1.82969889				



TS(4b→6b): E = -2665.8716116814 au

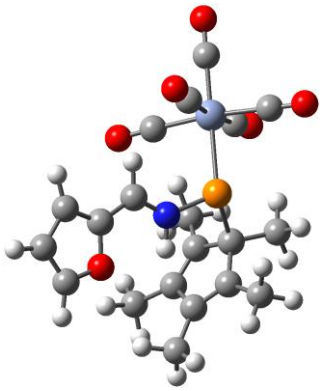
ZPE = 0.35981528 au

G = -2665.57016980056 au

ν = -125.51 cm^{-1}

C	0.00000000	0.00000000	0.00000000	Cr	2.15018950	2.57430438	-2.24682315
N	1.36381358	0.00000000	0.00000000	C	2.54652381	3.27387389	-3.92830387
P	1.57625445	1.72905480	0.00000000	O	2.82324264	3.71636839	-4.95618386
C	-0.76047255	-0.58617993	-1.04415904	C	1.52480268	4.23749943	-1.55434577
O	-0.08360158	-1.00420334	-2.16163318	O	1.14501380	5.22009011	-1.09508647
C	-0.99206893	-1.49995792	-3.02457372	C	3.93421602	3.03092399	-1.80558368
C	-2.25898122	-1.42580247	-2.49449475	O	5.03372545	3.31939129	-1.62105079
C	-2.11446033	-0.83500524	-1.21059168	C	2.72014600	0.81404061	-2.62407107
H	-0.60448546	-1.86406936	-3.97309874	O	3.06836282	-0.27904196	-2.75210548
H	-3.17886171	-1.75208925	-2.97503637	C	0.39781117	2.13482616	-2.87202381
H	-2.89188228	-0.60129408	-0.48544882	O	-0.63892896	1.87381704	-3.29624327
H	-0.51731394	0.31837466	0.90684025	C	2.74279341	1.94195644	1.56543244
H	1.86986156	-0.64770601	-0.60310952	C	3.70619467	0.80065701	1.46104329

C	3.23865224	-0.21683410	2.25002011	H	4.06877674	-1.87670829	3.37435996
C	2.07281318	0.25045762	3.02022073	H	2.96672976	-2.33971543	2.07288805
C	1.80161426	1.54205254	2.67953966	H	4.61032488	-1.79479006	1.67519010
C	3.26982326	3.37451988	1.59941154	C	1.32896885	-0.63463070	3.97333667
H	3.97039800	3.57886548	0.77952002	H	0.85061140	-1.47245564	3.43553070
H	2.45014370	4.10680890	1.52630559	H	2.00197013	-1.09265020	4.71861506
H	3.79893748	3.55494967	2.54945895	H	0.54122677	-0.09305948	4.51621268
C	4.89608025	0.77728826	0.55151535	C	0.77220195	2.47414472	3.23569240
H	5.62648207	0.02213739	0.87474345	H	1.24849804	3.35239371	3.70756528
H	4.62741870	0.54166159	-0.49333878	H	0.10552531	2.86666414	2.44775605
H	5.41100249	1.74921118	0.52761853	H	0.14801600	1.98858493	3.99909608
C	3.75723974	-1.61955702	2.34623586				

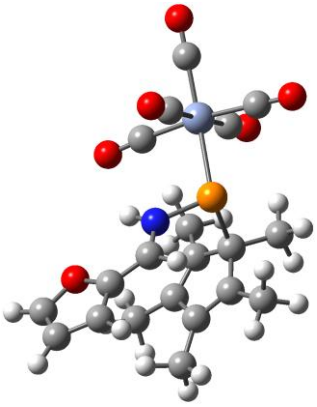


6b: E = -2665.902101352 au

ZPE = 0.36080286 au

G = -2665.599657062 au

C	0.00000000	0.00000000	0.00000000	C	3.78919676	-0.55515897	-1.75367107
N	1.30735399	0.00000000	0.00000000	C	3.59728258	-1.86347035	-1.47906591
P	2.47362358	1.30093964	0.00000000	C	3.75675669	-2.08782784	-0.02908422
C	-0.79480713	-1.12025702	0.34043926	C	4.04509405	-0.91459476	0.58156146
O	-0.18774691	-2.30352970	0.67439140	C	5.21933085	1.11758904	-0.42967077
C	-1.17824590	-3.18014343	0.99262119	H	5.16983448	1.87458351	-1.21123390
C	-2.39826209	-2.59315138	0.86503673	H	5.30898603	1.63014244	0.52997713
C	-2.15806122	-1.25899487	0.44370572	H	6.12556511	0.52979501	-0.58841901
H	-0.86111623	-4.16280677	1.29496922	C	3.84546320	0.09581784	-3.09108261
H	-3.35170850	-3.05422261	1.05922054	H	3.83687930	-0.64305200	-3.89083094
H	-2.88373086	-0.48549199	0.25584654	H	3.00684231	0.77094031	-3.25682801
H	-0.52022618	0.91922040	-0.22316410	H	4.75506698	0.69171814	-3.20162875
H	1.75118893	-0.90358774	0.18896665	C	3.27171396	-2.97222017	-2.42911720
Cr	1.71274346	3.22741829	-1.35989950	H	4.01301680	-3.77535159	-2.37723671
C	1.08942277	4.70437612	-2.32252300	H	2.30267498	-3.42137522	-2.18881407
O	0.71626893	5.60711729	-2.92528536	H	3.22412792	-2.62705701	-3.46039791
C	2.65538922	4.33298665	-0.10985933	C	3.61896417	-3.44596144	0.57961979
O	3.22070880	4.99358629	0.63248975	H	2.62159342	-3.85335726	0.38479125
C	3.24359795	3.29075271	-2.49765103	H	4.33552976	-4.14982184	0.14513061
O	4.13680635	3.41369109	-3.20331345	H	3.77262416	-3.43321817	1.65818254
C	0.84789079	1.97153014	-2.49751398	C	4.36549535	-0.66710578	2.01701713
O	0.32872842	1.18537706	-3.15157871	H	5.40171121	-0.33310195	2.13717341
C	0.14669935	3.36987397	-0.28678806	H	3.73276049	0.12243826	2.43562570
O	-0.82068335	3.50479847	0.31688957	H	4.23866642	-1.56401851	2.62269489
C	3.99766511	0.19280031	-0.45443615				

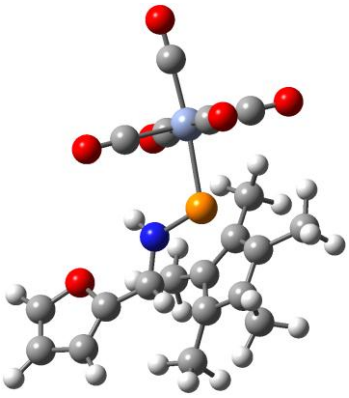


6b^{para}: E = -2665.895791156 au

ZPE = 0.36132676 au

G = -2665.594994636 au

C	0.00000000	0.00000000	0.00000000		C	2.30405008	0.56633046	2.71677857
N	1.29719890	0.00000000	0.00000000		C	1.16780423	-0.01017048	3.17541696
P	2.19698693	1.57590064	0.00000000		C	0.02465546	0.84544976	2.84351666
C	-0.83342839	-1.11934276	0.25338489		C	0.46251673	1.93930551	2.16113277
O	-0.27597068	-2.30695191	0.64444247		C	2.73863835	3.07124452	2.32069407
C	-1.29580738	-3.16781763	0.86140756		H	3.80693704	2.92913852	2.16771625
C	-2.49695155	-2.56792020	0.62320770		H	2.42583656	3.92995121	1.72390558
C	-2.19972738	-1.23943667	0.22910543		H	2.57679730	3.31197639	3.37443412
H	-1.01676667	-4.15925795	1.17420218		C	3.70222527	0.14049149	2.99712747
H	-3.46845443	-3.02178776	0.71917207		H	3.73208480	-0.61895321	3.77778489
H	-2.89337179	-0.45863856	-0.03633742		H	4.20250172	-0.26422651	2.11966042
H	-0.48956848	0.93043947	-0.25925310		H	4.30505997	0.98577921	3.33548514
H	1.76425885	-0.87279783	0.23254501		C	1.02451297	-1.29468433	3.92851516
Cr	4.43796607	1.05551760	-0.94139049		H	0.55143253	-1.14000288	4.90280579
C	6.00255463	0.68546393	-1.90671512		H	0.39514872	-2.00177581	3.37877795
O	6.95531956	0.44500782	-2.50164056		H	1.98468522	-1.78015141	4.09357955
C	4.45242809	2.90087697	-1.45766061		C	-1.36217105	0.52485668	3.29426273
O	4.46086847	4.00564606	-1.75573772		H	-1.67027235	-0.46547822	2.94597138
C	5.49052291	1.52517667	0.57730760		H	-1.41809341	0.50120323	4.38703476
O	6.15771583	1.81747644	1.46332611		H	-2.09339424	1.25021080	2.93813751
C	4.23693127	-0.71214157	-0.32643083		C	-0.33271926	3.10751618	1.68786309
O	4.02268032	-1.77653179	0.06294970		H	-0.05893858	4.01797751	2.23148925
C	3.40680117	0.60741208	-2.47957972		H	-0.13928398	3.30972718	0.62898065
O	2.78662227	0.31915482	-3.39984340		H	-1.40462632	2.95698402	1.82159106
C	1.94325578	1.81701322	1.94707912					



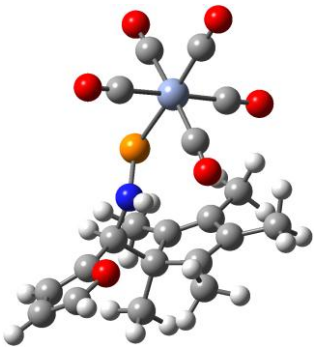
TS(6b^{para}**→7b**^{conf}**)**: E = -2665.875928969 au

ZPE = 0.360780177 au

G = -2665.574700989 au

ν = -286.96 cm^{-1}

C	0.00000000	0.00000000	0.00000000	C	1.32681306	2.02021058	2.24268651
N	1.35935149	0.00000000	0.00000000	C	1.61350781	0.74486522	2.95469536
P	2.27542734	1.46340375	0.00000000	C	0.52740348	-0.07640751	2.82268495
C	-0.71563604	-1.23972224	-0.20744909	C	-0.50599317	0.63964011	2.03911514
O	-0.09737617	-2.41154057	0.11807902	C	-0.72213512	3.07395338	1.09860223
C	-0.94704757	-3.42422551	-0.19468435	H	-0.76814712	3.98676500	1.71681229
C	-2.10977364	-2.92530949	-0.71526665	H	-0.17469308	3.34365770	0.17403022
C	-1.96355870	-1.50262935	-0.72396425	H	-1.75211838	2.80847960	0.82103002
H	-0.58653137	-4.43078488	0.00098402	C	2.05136386	3.31489144	2.51190302
H	-2.96381747	-3.50320639	-1.06208607	H	1.69159143	3.74662957	3.46268927
H	-2.67353881	-0.75891959	-1.08048170	H	3.13516589	3.18100411	2.60933450
H	-0.46975442	0.86358659	-0.47397558	H	1.86736841	4.05678273	1.72023104
H	1.79155037	-0.89338381	0.23916092	C	2.85348405	0.51434849	3.76221523
Cr	4.57188332	0.81932320	-0.18468674	H	3.08360767	-0.55359129	3.87648814
C	6.33212525	0.32274151	-0.60819696	H	3.73169438	0.99550657	3.31171377
O	7.40274820	0.00190304	-0.88541664	H	2.73831381	0.94779441	4.77240395
C	3.94327869	-0.28053547	-1.59820367	C	0.34568880	-1.45830514	3.37174785
O	3.55272556	-0.95936543	-2.44200560	H	0.16202544	-2.19243510	2.56925158
C	4.70874504	2.31546126	-1.35760663	H	1.23225472	-1.79193207	3.92949830
O	4.80605271	3.21974812	-2.05982969	H	-0.51732318	-1.50936570	4.05947216
C	5.15671755	1.92687838	1.24533191	C	-1.96466811	0.28769875	2.14013494
O	5.52761030	2.59536714	2.10778420	H	-2.36817511	0.63292500	3.10796494
C	4.33604829	-0.63135101	1.00664793	H	-2.56472612	0.75303772	1.34321559
O	4.15242705	-1.52966420	1.70600965	H	-2.12488519	-0.79847675	2.08161788
C	-0.01421887	1.96398666	1.80466448				



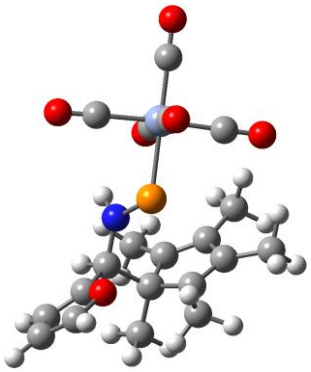
7b^{conf}: E = -2665.896417688 au

ZPE = 0.36199730 au

G = -2665.593391768 au

C	0.00000000	0.00000000	0.00000000	C	6.51119836	0.61906320	-0.58878317
N	1.46495941	0.00000000	0.00000000	O	7.63283045	0.43621584	-0.71730576
P	2.37897725	1.36915416	0.00000000	C	4.73352042	0.17440173	1.39704599
C	-0.52509636	-1.18604474	0.73548918	O	4.78129509	-0.27079675	2.44854690
O	0.06121478	-2.39760705	0.50565062	C	4.96535924	2.67127620	0.28673763
C	-0.58807100	-3.31756126	1.27560849	O	5.16096288	3.73028014	0.66907453
C	-1.57325572	-2.71878020	1.98614520	C	4.53333034	1.58549686	-2.15231259
C	-1.52796976	-1.32998647	1.63948539	O	4.49036240	1.97762562	-3.22747626
H	-0.22610244	-4.32838713	1.20918719	C	4.17653793	-0.80595300	-1.04460845
H	-2.24405440	-3.19879802	2.67862652	O	3.81877387	-1.82216662	-1.43949522
H	-2.15912067	-0.54213035	2.01553119	C	-0.19726444	1.62338460	-1.90997136
H	-0.33298692	0.86829644	0.57043779	C	0.63076095	1.58569506	-2.97730975
H	1.85564733	-0.91065426	-0.20856387	C	0.91563626	0.18092827	-3.32693368
Cr	4.64406980	0.90270765	-0.37337863	C	0.25512437	-0.64151516	-2.48750172

C	-0.52272132	0.20089493	-1.47973800	H	2.82394154	0.19801716	-4.30098190
C	-0.82176997	2.81508875	-1.26554475	H	1.46203991	0.24106575	-5.40351191
H	-0.44044161	3.74476914	-1.68487832	C	0.23623282	-2.13656971	-2.52185028
H	-0.62887584	2.84694182	-0.18892521	H	0.96650903	-2.57841437	-1.83998361
H	-1.90879742	2.81405366	-1.39678380	H	0.46144951	-2.50789192	-3.52171957
C	1.14536648	2.73481165	-3.78360520	H	-0.73868698	-2.53235807	-2.23088205
H	0.69358138	2.73602767	-4.78065034	C	-2.03526095	-0.05509728	-1.55575953
H	2.22428681	2.66724549	-3.92699745	H	-2.40041257	0.18607670	-2.55474337
H	0.92629933	3.69425466	-3.31758876	H	-2.57506419	0.56140357	-0.83391158
C	1.81531155	-0.19048910	-4.46248572	H	-2.27270064	-1.09639387	-1.33945403
H	1.89343084	-1.26887036	-4.58929702				

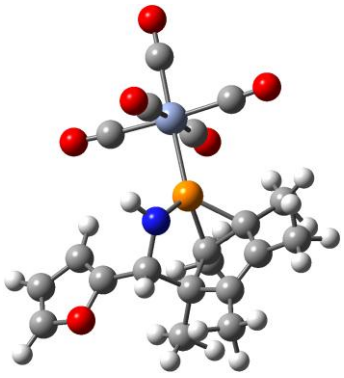


7b: E = -2665.899965446 au

ZPE = 0.36189238 au

G = -2665.598538156 au

C	0.00000000	0.00000000	0.00000000	C	0.85612863	0.61990633	3.26286941
N	1.47461319	0.00000000	0.00000000	C	0.71219096	1.99508298	2.75259332
P	2.46784317	1.32248195	0.00000000	C	-0.07801613	1.99967102	1.65247002
C	-0.60868823	0.54171261	-1.24963150	C	-0.52765099	0.57733000	1.36860673
O	-0.23917116	1.76790362	-1.71312728	C	-0.00300211	-1.69838237	2.61846670
C	-0.95590192	2.01027442	-2.84510587	H	0.47478850	-2.06905260	3.52369731
C	-1.77865240	0.96727774	-3.11233174	H	0.45188969	-2.23934738	1.78038960
C	-1.54887251	0.00830352	-2.07591072	H	-1.05489863	-1.99850527	2.65026626
H	-0.75824250	2.94668293	-3.33648146	C	1.70025866	0.30061911	4.45441244
H	-2.45576041	0.88193221	-3.94548530	H	1.35414000	0.84208521	5.33941838
H	-2.01965165	-0.95408376	-1.96098474	H	2.73656048	0.60624971	4.28690573
H	-0.29865387	-1.05028665	-0.00203542	H	1.70245907	-0.76290223	4.68526950
H	1.85141252	-0.91093055	0.22444337	C	1.31296762	3.17790537	3.44175735
Cr	4.66791912	0.65498769	0.44990562	H	1.17832107	4.09488739	2.87053220
C	6.48812205	0.18886282	0.74272186	H	2.38279485	3.04000320	3.60466829
O	7.57984802	-0.10336066	0.91951561	H	0.86081929	3.32188362	4.42842646
C	4.67785023	1.78454126	1.98708104	C	-0.55998328	3.20563973	0.90793218
O	4.69104362	2.44564465	2.92253273	H	0.14350162	3.49907747	0.12652844
C	5.19702442	2.13555096	-0.64454515	H	-0.69103544	4.05495733	1.58018460
O	5.51348027	3.02389257	-1.29020462	H	-1.51519359	3.01987852	0.41644462
C	4.55957787	-0.49414748	-1.07455952	C	-2.05789405	0.44785899	1.43237925
O	4.45735952	-1.19277113	-1.97474986	H	-2.41744240	0.77064762	2.40986536
C	4.00935949	-0.75657951	1.52910322	H	-2.36785034	-0.58811474	1.27861683
O	3.54449412	-1.59770129	2.15609929	H	-2.54112677	1.05202068	0.66493589
C	0.14324061	-0.21914767	2.48824767				

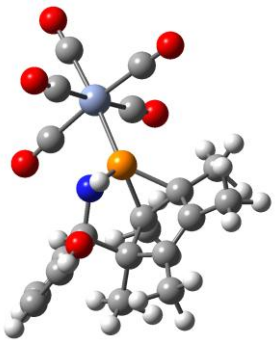


5b: E = -2665.91673436393 au

ZPE = 0.36379251 au

G = -2665.611273825 au

C	-0.068198	-0.027891	0.031134	C	-0.482991	1.223774	-0.833042
N	1.394332	0.040497	0.100269	C	-0.076433	0.913660	-2.275483
P	2.020952	1.611668	0.115247	C	1.067631	1.521188	-2.612286
C	-0.723533	-0.087260	1.373779	C	1.558991	2.402910	-1.518803
O	-1.898583	-0.786393	1.429076	C	-0.103208	3.676639	0.137397
C	-2.381738	-0.667967	2.698618	H	-0.630647	3.487138	1.073392
C	-1.542599	0.084382	3.450531	H	0.674462	4.410450	0.342654
C	-0.462750	0.461779	2.588983	H	-0.809333	4.130392	-0.562585
H	-3.306454	-1.178429	2.903194	C	-1.970188	1.537594	-0.686950
H	-1.663387	0.335486	4.491005	H	-2.569953	0.659704	-0.930276
H	0.388887	1.061883	2.850274	H	-2.222356	1.833022	0.330831
H	-0.369439	-0.929186	-0.508550	H	-2.258643	2.343114	-1.362967
H	1.856320	-0.655837	0.663811	C	-0.884718	-0.037850	-3.097850
Cr	3.920872	2.145010	1.469143	H	-0.392480	-0.289190	-4.035998
C	5.454561	2.541570	2.485414	H	-1.076875	-0.973528	-2.563452
O	6.385720	2.787495	3.105249	H	-1.863551	0.386974	-3.339576
C	4.902541	2.610731	-0.110062	C	1.861449	1.372076	-3.869980
O	5.517751	2.878327	-1.034748	H	2.874479	1.027316	-3.639776
C	3.288715	3.938814	1.655049	H	1.412658	0.661256	-4.561733
O	2.907075	5.011103	1.771025	H	1.965358	2.327111	-4.392198
C	3.024646	1.682882	3.087082	C	2.265525	3.687208	-1.892292
O	2.534841	1.420597	4.087765	H	2.595145	4.251696	-1.021079
C	4.460425	0.324565	1.266290	H	3.147511	3.484715	-2.499634
O	4.762355	-0.773483	1.152971	H	1.595065	4.333121	-2.467411
C	0.473791	2.400464	-0.421276				



5b': E = -2665.914599490 au

ZPE = 0.36283238 au

G = -2665.605808189 au

C	0.00000000	0.00000000	0.00000000	C	-0.48500297	1.19891530	-0.90524589
N	1.47344504	0.00000000	0.00000000	C	-0.12423775	0.91599558	-2.36223507
P	2.06518713	1.59581316	0.00000000	C	1.02392022	1.51602411	-2.70765609
C	-0.53426910	-1.35207055	-0.31444604	C	1.52620028	2.40736602	-1.61991676
O	0.16020985	-2.11522515	-1.21130530	C	-0.07232974	3.62940696	0.11047993
C	-0.53421601	-3.27681077	-1.38127671	H	-0.57117720	3.41601898	1.05712278
C	-1.65155961	-3.26906418	-0.61580919	H	0.71362090	4.35425531	0.31504530
C	-1.64773825	-2.02003359	0.08433492	H	-0.79670995	4.10806671	-0.55353481
H	-0.09862924	-3.99401559	-2.05427500	C	-1.96565189	1.48502411	-0.67812905
H	-2.38244381	-4.05679154	-0.54322197	H	-2.56329715	0.61295937	-0.94714131
H	-2.37579577	-1.66673342	0.79527097	H	-2.16926948	1.71716498	0.36874201
H	-0.33637567	0.23759625	1.01580999	H	-2.30481807	2.32523602	-1.28491574
H	1.86660242	-0.62619868	-0.69030625	C	-0.99937450	0.06291138	-3.22622279
Cr	3.66712801	2.22943633	1.63717155	H	-0.49790275	-0.23923608	-4.14454588
C	4.87892113	2.64157923	3.01632978	H	-1.33652987	-0.83953864	-2.71631151
O	5.60117739	2.89269261	3.86948946	H	-1.90057892	0.61635154	-3.50967523
C	4.99625106	2.40268793	0.27122736	C	1.77767867	1.40142325	-3.99378170
O	5.77145734	2.51188821	-0.56230360	H	2.82028383	1.12915143	-3.80322497
C	3.28178819	4.08225493	1.45882036	H	1.34921338	0.65247824	-4.65763651
O	3.07759445	5.20608930	1.36640764	H	1.79558239	2.35417875	-4.53059190
C	2.22767520	2.04297063	2.88097693	C	2.22505984	3.69025265	-2.01145041
O	1.34386933	1.93236473	3.59903589	H	2.54539165	4.27217518	-1.14945412
C	4.12174338	0.37569513	1.84321017	H	3.11076683	3.48169181	-2.61278467
O	4.42017016	-0.71742972	1.98145943	H	1.55378096	4.32055682	-2.60311503
C	0.48073644	2.37084076	-0.50922678				