Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information

Photochemistry of Phosphenic Chloride ($ClPO_2$): Isomerization with Chlorine Metaphosphite (ClOPO) and Reduction by Carbon Monoxide

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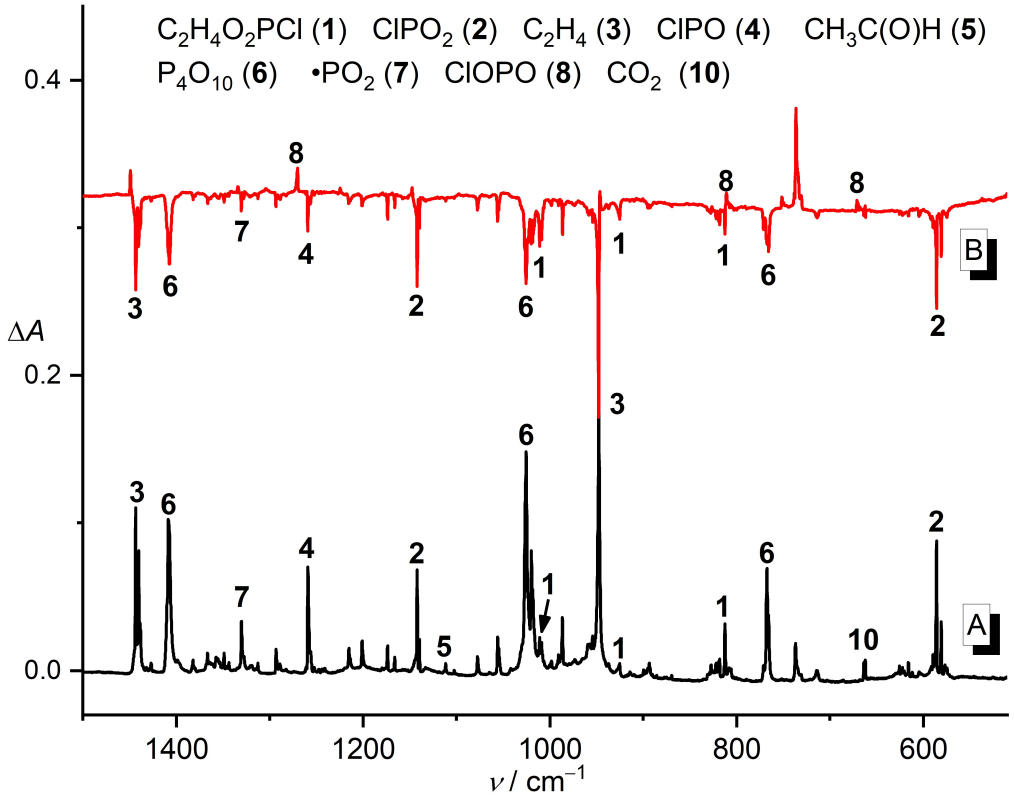

Figure S1. (A) IR spectrum of the high-vacuum flash pyrolysis (HVFP) products of $C_2H_4O_2PCl$ in the solid Ar-matrix at 10 K. (B) IR difference spectrum reflecting the changes of the isolated HVFP products upon 193 nm laser irradiation (53 min).

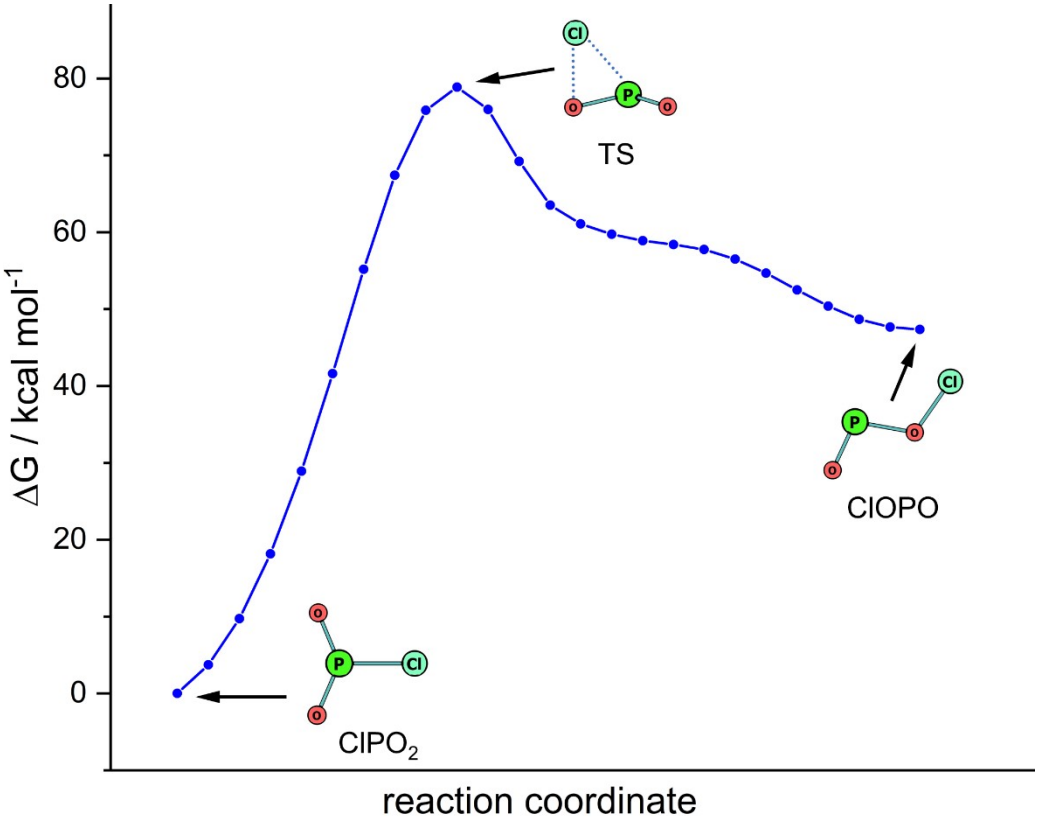

Figure S2. Calculated energy profile along intrinsic reaction coordinate (IRC) for the conversion of $ClPO_2$ to ClOPO via transition state at the B3LYP/6-311+G(3df) level of theory.

Table S1. Calculated vibrational frequencies (cm^{-1}) and intensities (km mol^{-1}, in parentheses) of ClC(O)OPO.

B3LYP/6-311+G(3df)		BP86/6-311+G(3df)		MPW1PW91/6-311+G(3df)	
anti-conformer	*syn*-conformer	*anti*-conformer	*syn*-conformer	*anti*-conformer	*syn*-conformer
44.2 (10)	38.7 (8)	44.4 (8)	37.0 (7)	47.9 (9)	39.9 (7)
95.1 (1)	81.7 (1)	91.0 (1)	76.8 (0)	94.6 (1)	85.8 (1)
139.2 (5)	139.6 (4)	132.7 (5)	138.2 (4)	141.9 (6)	143.7 (3)
280.4 (12)	309.5 (6)	267.8 (13)	295.7 (5)	287.9 (10)	317.1 (7)
390.1 (50)	429.6 (31)	372.1 (47)	406.0 (31)	400.0 (45)	441.0 (32)
478.3 (10)	473.0 (6)	457.0 (14)	449.4 (13)	496.0 (7)	487.1 (4)
678.1 (92)	537.8 (155)	648.2 (91)	508.9 (130)	693.9 (71)	569.7 (135)
726.7 (145)	680.8 (18)	690.2 (102)	650.7 (13)	754.1 (184)	695.1 (18)
817.0 (105)	863.9 (206)	783.4 (114)	814.3 (180)	839.9 (90)	892.6 (211)
1087.8 (972)	1074.0 (678)	1030.5 (876)	1028.4 (543)	1128.9 (971)	1113.9 (662)
1307.8 (67)	1306.7 (87)	1247.4 (57)	1244.8 (82)	1333.0 (66)	1331.4 (90)
1830.4 (353)	1883.4 (520)	1767.2 (308)	1824.4 (464)	1865.4 (350)	1981.6 (528)

Table S2. Calculated vibrational frequencies (cm^{-1}, scaled by a factor of 0.967) and intensities (km mol^{-1}, in parentheses) of ClC(O)OPO.

B3LYP/6-311+G(3df)		BP86/6-311+G(3df)		MPW1PW91/6-311+G(3df)	
anti-conformer	*syn*-conformer	*anti*-conformer	*syn*-conformer	*anti*-conformer	*syn*-conformer
42.7 (10)	37.4 (8)	42.9 (8)	35.7 (7)	46.3 (9)	38.5 (7)
91.9 (1)	79.0.7 (1)	87.9 (1)	74.2 (0)	91.4 (1)	82.9 (1)
134.6 (5)	134.9 (4)	128.3 (5)	133.6 (4)	137.2 (6)	138.9 (3)
271.1 (12)	299.3 (6)	258.9 (13)	285.9 (5)	278.3 (10)	306.6 (7)
377.2 (50)	425.4 (31)	359.8.1 (47)	392.6 (31)	386.8 (45)	426.4 (32)
462.5 (10)	457.3 (6)	441.9 (14)	434.5 (13)	479.6 (7)	471.0 (4)
655.7 (92)	520.0 (155)	626.8 (91)	492.1 (130)	671.0 (71)	550.8 (135)
702.7 (145)	658.3 (18)	667.4 (102)	629.2 (13)	729.2 (184)	672.1 (18)
790.0 (105)	835.3 (206)	757.5 (114)	787.4 (180)	812.1 (90)	863.1 (211)
1051.9 (972)	1038.5 (678)	996.4 (876)	994.4 (543)	1091.6 (971)	1077.1(662)
1264.6 (67)	1263.5 (87)	1206.2 (57)	1203.7 (82)	1289.0 (66)	1287.4 (90)
1769.9 (353)	1821.2 (520)	1708.8 (308)	1764.1 (464)	1803.8 (350)	1916.2 (528)

Table S3. Calculated vibrational frequencies (cm^{-1}) and intensities (km mol^{-1}, in parentheses) of molecular complexes at the B3LYP/6-311+G(3df) level of theory.

complex-1	complex-2	complex-3	complex-4	complex-5	complex-6	complex-7	complex-8
20.7 (5)	13.7 (3)	12.7 (1)	8.7 (1)	50.3 (1)	27.9 (0)	15.1 (0)	11.8 (1)
38.8 (0)	24.7 (9)	31.6 (4)	38.5 (1)	55.9 (0)	28.3 (0)	16.2 (1)	12.1 (0)
50.8 (0)	56.9 (0)	40.5 (2)	68.2 (0)	85.8 (8)	64.5 (0)	53.1 (0)	36.2 (0)
85.1 (0)	57.7 (0)	59.5 (0)	82.2 (16)	185.6 (4)	82.2 (0)	61.2 (0)	38.8 (0)
105.1 (1)	111.1 (1)	105.7 (0)	96.1 (0)	218.1 (1)	84.5 (0)	66.0 (0)	44.9 (0)
308.3 (6)	304.6 (4)	312.3 (3)	299.5 (3)	304.1 (1)	299.6 (2)	301.5 (3)	300.4 (3)
485.9 (156)	485.0 (154)	486.2 (201)	473.3 (151)	374.8 (101)	384.9 (58)	388.7 (36)	388.1 (36)
669.0 (49)	673.2 (39)	669.9 (50)	674.3 (31)	388.3 (12)	389.9 (15)	389.7 (20)	390.1 (19)
678.5 (33)	678.2 (32)	680.2 (27)	676.6 (36)	568.0 (148)	573.5 (146)	574.6 (150)	574.9 (155)
1284.0 (112)	1283.5 (113)	1277.8 (127)	1290.3 (109)	1160.2 (103)	1161.2 (102)	1159.0 (116)	1159.3 (114)
1374.8 (0)	1374.8 (0)	1374.2 (0)	1374.2 (0)	1458.8 (141)	1462.1 (139)	1458.4 (145)	1459.8 (143)
2415.4 (573)	2415.1 (615)	2414.6 (633)	2413.0 (631)	2251.4 (79)	2207.1 (131)	2225.6 (95)	2212.0 (109)

Table S4. Observed and calculated IR spectra of ClPO.

Obs.[a]			Cal.[b]	Mode[c]
N_2-matrix	Ar-matrix	CO-matrix		
1259.3	1259.0	1258.1	1288.7 (114)	ν_a(PO)
489.0	491.1	489.9	481.9 (166)	ν(P-Cl)
n.o.[d]	n.o.	n.o.	299.6 (3)	δ(ClPO)

[a] Observed band position for the most intense matrix site. [b] Calculated frequencies at the B3LYP/6-311+G (3df) level. The IR intensities (km mol^{-1}) are given in parentheses. [c] Tentative assignment of the vibration modes according to the computed vibrational displacement vectors. [d] Not observed.

Calculated atomic coordinates (in Angstroms) and energies (in Hartrees) of all optimized structures.

$ClPO_2$

B3LYP/6-311+G(3df)

P	0.65170754	0.91583146	0.00000000
O	-0.10069244	2.21902650	0.00000000
Cl	-0.36829248	-0.85086035	0.00000000
O	2.15650754	0.91583144	0.00000000

Zero-point correction= 0.009720
Thermal correction to Energy= 0.013818
Thermal correction to Enthalpy= 0.014762
Thermal correction to Gibbs Free Energy= -0.017464
Sum of electronic and zero-point Energies= -952.167251
Sum of electronic and thermal Energies= -952.163153
Sum of electronic and thermal Enthalpies= -952.162209
Sum of electronic and thermal Free Energies= -952.194434

***anti*-ClOPO**

B3LYP/6-311+G(3df)

O	2.21790500	0.35611400	-0.00027100
P	1.00387300	-0.45839700	0.00012000
O	-0.24993000	0.63066300	0.00029400
Cl	-1.81187600	-0.05989700	-0.00011700

Zero-point correction= 0.007817
Thermal correction to Energy= 0.012480
Thermal correction to Enthalpy= 0.013425
Thermal correction to Gibbs Free Energy= -0.020640
Sum of electronic and zero-point Energies= -952.085630
Sum of electronic and thermal Energies= -952.080967
Sum of electronic and thermal Enthalpies= -952.080023
Sum of electronic and thermal Free Energies= -952.114088

***syn*-ClOPO**

B3LYP/6-311+G(3df)

O	1.44046100	1.05588500	0.00000100
P	1.24761300	-0.39373700	-0.00000200
O	-0.31687200	-0.85129200	0.00000300
Cl	-1.62958200	0.25113700	-0.00000100

Zero-point correction= 0.008018

Thermal correction to Energy= 0.012518
Thermal correction to Enthalpy= 0.013462
Thermal correction to Gibbs Free Energy= -0.020415
Sum of electronic and zero-point Energies= -952.090569
Sum of electronic and thermal Energies= -952.086068
Sum of electronic and thermal Enthalpies= -952.085124
Sum of electronic and thermal Free Energies= -952.119001

***cyclic*-$ClPO_2$**

B3LYP/6-311+G(3df)

P	0.34270300	-0.66919600	-0.00203700
Cl	-1.52689300	0.20009900	0.00066700
O	1.30081000	0.41726900	-0.76492200
O	1.30126900	0.41226300	0.76732300

Zero-point correction= 0.007802
Thermal correction to Energy= 0.012069
Thermal correction to Enthalpy= 0.013013
Thermal correction to Gibbs Free Energy= -0.020096
Sum of electronic and zero-point Energies= -952.047598
Sum of electronic and thermal Energies= -952.043332
Sum of electronic and thermal Enthalpies= -952.042387
Sum of electronic and thermal Free Energies= -952.075496

***syn*-OPClO**

B3LYP/6-311+G(3df)

O	-1.69676200	0.91602500	0.00032300
O	1.62343900	0.94360700	-0.00032600
Cl	-1.01711600	-0.47693900	-0.00022900
P	1.19183700	-0.45127200	0.00026100

Zero-point correction= 0.007141
Thermal correction to Energy= 0.012084
Thermal correction to Enthalpy= 0.013028
Thermal correction to Gibbs Free Energy= -0.021895
Sum of electronic and zero-point Energies= -952.005730
Sum of electronic and thermal Energies= -952.000788
Sum of electronic and thermal Enthalpies= -951.999843
Sum of electronic and thermal Free Energies= -952.034766

***anti*-OPClO**

B3LYP/6-311+G(3df)

O	2.06796800	0.53190700	-0.00004200
O	-2.07998800	-0.46202300	-0.00001900
Cl	0.90975100	-0.51880200	0.00005100
P	-1.02464000	0.55070300	-0.00002600

Zero-point correction= 0.006899
Thermal correction to Energy= 0.011975
Thermal correction to Enthalpy= 0.012919
Thermal correction to Gibbs Free Energy= -0.022312
Sum of electronic and zero-point Energies= -952.006131
Sum of electronic and thermal Energies= -952.001055
Sum of electronic and thermal Enthalpies= -952.000111
Sum of electronic and thermal Free Energies= -952.035343

***syn*-ClPOO**

B3LYP/6-311+G(3df)

P	0.00000000	0.98624000	0.00000000
Cl	-1.40548800	-0.46203300	0.00000000
O	1.37105300	0.22529800	0.00000000
O	1.61560900	-1.09267700	0.00000000

Zero-point correction= 0.007491
Thermal correction to Energy= 0.011896
Thermal correction to Enthalpy= 0.012840
Thermal correction to Gibbs Free Energy= -0.020853
Sum of electronic and zero-point Energies= -951.990633
Sum of electronic and thermal Energies= -951.986228
Sum of electronic and thermal Enthalpies= -951.985284
Sum of electronic and thermal Free Energies= -952.018978

***anti*-ClPOO**

B3LYP/6-311+G(3df)

P	0.08773900	-0.69655400	-0.00000100
Cl	-1.70371300	0.26304500	-0.00000800
O	1.06474200	0.54239300	0.00000600
O	2.39113800	0.20467500	0.00001200

Zero-point correction= 0.006816
Thermal correction to Energy= 0.011550
Thermal correction to Enthalpy= 0.012495
Thermal correction to Gibbs Free Energy= -0.021711
Sum of electronic and zero-point Energies= -951.985012

Sum of electronic and thermal Energies=	-951.980278
Sum of electronic and thermal Enthalpies=	-951.979333
Sum of electronic and thermal Free Energies=	-952.013539

triplet *syn*-ClPOO

B3LYP/6-311+G(3df)

P	0.00607500	0.91357600	-0.14990100
Cl	-1.50218200	-0.44934900	0.03009400
O	1.30670200	0.04247400	0.54484500
O	1.87404400	-0.80056200	-0.32772900

Zero-point correction=	0.006422
Thermal correction to Energy=	0.011335
Thermal correction to Enthalpy=	0.012279
Thermal correction to Gibbs Free Energy=	-0.023768
Sum of electronic and zero-point Energies=	-951.975456
Sum of electronic and thermal Energies=	-951.970543
Sum of electronic and thermal Enthalpies=	-951.969599
Sum of electronic and thermal Free Energies=	-952.005646

triplet *anti*-ClPOO

B3LYP/6-311+G(3df)

P	0.08173200	-0.73643000	-0.00000100
Cl	-1.69289700	0.26668500	0.00000600
O	1.11052700	0.67662300	-0.00005200
O	2.33363200	0.13747800	0.00004100

Zero-point correction=	0.006545
Thermal correction to Energy=	0.011560
Thermal correction to Enthalpy=	0.012504
Thermal correction to Gibbs Free Energy=	-0.023912
Sum of electronic and zero-point Energies=	-951.974681
Sum of electronic and thermal Energies=	-951.969666
Sum of electronic and thermal Enthalpies=	-951.968722
Sum of electronic and thermal Free Energies=	-952.005138

ClPO

B3LYP/6-311+G(3df)

P	0.00000000	0.83355800	0.00000000
Cl	-0.68768500	-1.13948600	0.00000000
O	1.46133000	0.85848700	0.00000000

Zero-point correction=	0.004717
Thermal correction to Energy=	0.008219
Thermal correction to Enthalpy=	0.009164
Thermal correction to Gibbs Free Energy=	-0.021776
Sum of electronic and zero-point Energies=	-876.902631
Sum of electronic and thermal Energies=	-876.899128
Sum of electronic and thermal Enthalpies=	-876.898184
Sum of electronic and thermal Free Energies=	-876.929123

complex-1

B3LYP/6-311+G(3df)

P	1.58381200	-0.77031500	0.00061800
Cl	1.20116900	1.28025800	-0.00035900
O	0.32142200	-1.50921700	-0.00286300
C	-2.11800900	0.07851500	0.00087100
O	-2.12978700	0.08820900	-1.15783000
O	-2.12526000	0.08591300	1.15964400

Zero-point correction=	0.017125
Thermal correction to Energy=	0.024947
Thermal correction to Enthalpy=	0.025891
Thermal correction to Gibbs Free Energy=	-0.019497
Sum of electronic and zero-point Energies=	-1065.561699
Sum of electronic and thermal Energies=	-1065.553877
Sum of electronic and thermal Enthalpies=	-1065.552933
Sum of electronic and thermal Free Energies=	-1065.598321

complex-2

B3LYP/6-311+G(3df)

P	-1.28339500	0.85194700	0.31701900
Cl	-1.55383000	-1.14348000	-0.22986500
O	-0.28276300	1.47093100	-0.55232300
C	2.17553000	-0.22863600	0.15880700
O	1.62566500	-0.30681500	1.17873100
O	2.73370500	-0.16014500	-0.85146000

Zero-point correction=	0.017039
Thermal correction to Energy=	0.024942
Thermal correction to Enthalpy=	0.025886
Thermal correction to Gibbs Free Energy=	-0.020560
Sum of electronic and zero-point Energies=	-1065.561684
Sum of electronic and thermal Energies=	-1065.553781

Sum of electronic and thermal Enthalpies= -1065.552837
Sum of electronic and thermal Free Energies= -1065.599283

complex-3

B3LYP/6-311+G(3df)

P	0.86179100	0.41611900	0.00013700
Cl	2.87278500	-0.13300300	-0.00030000
O	0.02464700	-0.78480200	0.00210500
C	-2.80965500	0.09973400	-0.00061400
O	-3.27279900	-0.96008200	-0.00145400
O	-2.36513200	1.17249100	0.00018900

Zero-point correction= 0.017009
Thermal correction to Energy= 0.024930
Thermal correction to Enthalpy= 0.025874
Thermal correction to Gibbs Free Energy= -0.020689
Sum of electronic and zero-point Energies= -1065.561164
Sum of electronic and thermal Energies= -1065.553243
Sum of electronic and thermal Enthalpies= -1065.552298
Sum of electronic and thermal Free Energies= -1065.598862

complex-4

B3LYP/6-311+G(3df)

P	1.45132100	-0.56348700	-0.33105600
Cl	0.87099700	1.43507400	-0.04237200
O	1.40930100	-1.27253100	0.94588000
C	-2.17485300	-0.26044200	-0.08303400
O	-1.52645400	-0.95353400	-0.75323800
O	-2.82380200	0.42840200	0.58040500

Zero-point correction= 0.017076
Thermal correction to Energy= 0.024931
Thermal correction to Enthalpy= 0.025875
Thermal correction to Gibbs Free Energy= -0.020255
Sum of electronic and zero-point Energies= -1065.561415
Sum of electronic and thermal Energies= -1065.553560
Sum of electronic and thermal Enthalpies= -1065.552616
Sum of electronic and thermal Free Energies= -1065.598746

complex-5

B3LYP/6-311+G(3df)

P	-0.55039100	-0.58931800	0.00013800
O	-0.41390900	-1.14032700	1.33686200
Cl	-1.28719500	1.26637300	-0.00004000
O	-0.41524800	-1.14108400	-1.33641100
C	1.99419100	0.29664100	-0.00043900
O	3.10078700	0.47286000	-0.00029500

Zero-point correction= 0.016179
Thermal correction to Energy= 0.023821
Thermal correction to Enthalpy= 0.024765
Thermal correction to Gibbs Free Energy= -0.018103
Sum of electronic and zero-point Energies= -1065.532834
Sum of electronic and thermal Energies= -1065.525192
Sum of electronic and thermal Enthalpies= -1065.524248
Sum of electronic and thermal Free Energies= -1065.567116

complex-6

B3LYP/6-311+G(3df)

P	-0.60692800	0.59628100	-0.00204900
O	-0.43357300	1.13429800	-1.33932200
Cl	-1.23515500	-1.29284400	-0.00073400
O	-0.45060300	1.14196200	1.33417200
C	3.29830300	-0.35833800	-0.00793800
O	2.17314200	-0.37824000	0.01650500

Zero-point correction= 0.015415
Thermal correction to Energy= 0.023614
Thermal correction to Enthalpy= 0.024558
Thermal correction to Gibbs Free Energy= -0.021372
Sum of electronic and zero-point Energies= -1065.529473
Sum of electronic and thermal Energies= -1065.521274
Sum of electronic and thermal Enthalpies= -1065.520330
Sum of electronic and thermal Free Energies= -1065.566260

complex-7

B3LYP/6-311+G(3df)

P	-1.75441400	0.00005400	0.00001900
O	-2.32372900	-1.33643700	0.00001700
Cl	0.23552800	-0.00025900	-0.00003800
O	-2.32320800	1.33677100	0.00001700
C	3.60713800	0.00018300	-0.00012500
O	4.73061300	-0.00002300	0.00010600

Zero-point correction=	0.015285
Thermal correction to Energy=	0.023636
Thermal correction to Enthalpy=	0.024580
Thermal correction to Gibbs Free Energy=	-0.023374
Sum of electronic and zero-point Energies=	-1065.527729
Sum of electronic and thermal Energies=	-1065.519379
Sum of electronic and thermal Enthalpies=	-1065.518434
Sum of electronic and thermal Free Energies=	-1065.566389

complex-8

B3LYP/6-311+G(3df)

P	-1.68767500	-0.00210000	0.00323200
O	-2.24877100	-1.34175300	0.00824100
Cl	0.30215200	0.00728900	-0.01519000
O	-2.26147400	1.33215800	0.00873100
C	4.66092200	-0.01074400	0.03030900
O	3.53687100	0.00610100	-0.01348500

Zero-point correction=	0.015102
Thermal correction to Energy=	0.023597
Thermal correction to Enthalpy=	0.024541
Thermal correction to Gibbs Free Energy=	-0.024985
Sum of electronic and zero-point Energies=	-1065.527265
Sum of electronic and thermal Energies=	-1065.518770
Sum of electronic and thermal Enthalpies=	-1065.517826
Sum of electronic and thermal Free Energies=	-1065.567352

TS (from $ClPO_2$ to ClOPO)

B3LYP/6-311+G(3df)

P	0.78376100	-0.14549600	-0.36981600
O	1.72896300	0.69652300	0.36203800
Cl	-1.44619200	0.37180200	0.01458900
O	-0.12535700	-1.21379700	0.30036500

Zero-point correction=	0.006763
Thermal correction to Energy=	0.011092
Thermal correction to Enthalpy=	0.012036
Thermal correction to Gibbs Free Energy=	-0.021501
Sum of electronic and zero-point Energies=	-952.041628
Sum of electronic and thermal Energies=	-952.037300
Sum of electronic and thermal Enthalpies=	-952.036355
Sum of electronic and thermal Free Energies=	-952.069892

***syn*-ClC(O)OPO**

B3LYP/6-311+G(3df)

C	1.01946900	0.63546100	0.01050300
Cl	1.57640700	-1.05883200	0.08082200
O	1.76988600	1.53479400	-0.10425400
O	-0.30970600	0.75593200	0.13485800
P	-1.51034100	-0.36354200	-0.27224300
O	-2.74275800	0.16433700	0.30022700

Zero-point correction= 0.017813

Thermal correction to Energy= 0.024291

Thermal correction to Enthalpy= 0.025235

Thermal correction to Gibbs Free Energy= -0.014923

Sum of electronic and zero-point Energies= -1065.510905

Sum of electronic and thermal Energies= -1065.504428

Sum of electronic and thermal Enthalpies= -1065.503483

Sum of electronic and thermal Free Energies= -1065.543642

***anti*-ClC(O)OPO**

B3LYP/6-311+G(3df)

C	0.84536500	0.40549800	0.07456000
Cl	2.27614500	-0.60115000	-0.05597600
O	0.87852400	1.58852500	0.12516900
O	-0.25459800	-0.36994400	0.11851000
P	-1.79201400	0.27725900	-0.19821000
O	-2.73473100	-0.76512300	0.19099200

Zero-point correction= 0.017942

Thermal correction to Energy= 0.024369

Thermal correction to Enthalpy= 0.025313

Thermal correction to Gibbs Free Energy= -0.014588

Sum of electronic and zero-point Energies= -1065.513818

Sum of electronic and thermal Energies= -1065.507391

Sum of electronic and thermal Enthalpies= -1065.506447

Sum of electronic and thermal Free Energies= -1065.546348