Cleavage of Carbon Suboxide to Give Ketenylidene and Carbyne Ligands at a Reactive Tungsten Site: A Theoretical Mechanistic Study

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Electronic Supplementary Information

Figure S1: Reaction paths of C_3O_2 binding to $WCl_2(PMe_3)_4$

Figure S2: Reaction paths from **int3** to **P** with an extrusion of one CO or Cl^- ligand

Table S1: Gibbs free energies of intermediates and TS from **1** to **int3**

Table S2: Gibbs free energies of intermediates and TS from **int3** to **P**

Table S3: Natural charges of the atoms in C_3O_2 molecule and its fragments

Figure S3: Geometries of **P-ph** with full $PMePh_2$ ligands with some labeled atoms

Table S4: Bond lengths and angles for $WCl_2(PMePh_2)_2(\eta^2_{CC}\text{-}C_2OPMePh_2)$

Tables S5-S28: Theoretical Cartesian coordinates for all complexes in the gas phase.

Reference 40: Full reference.

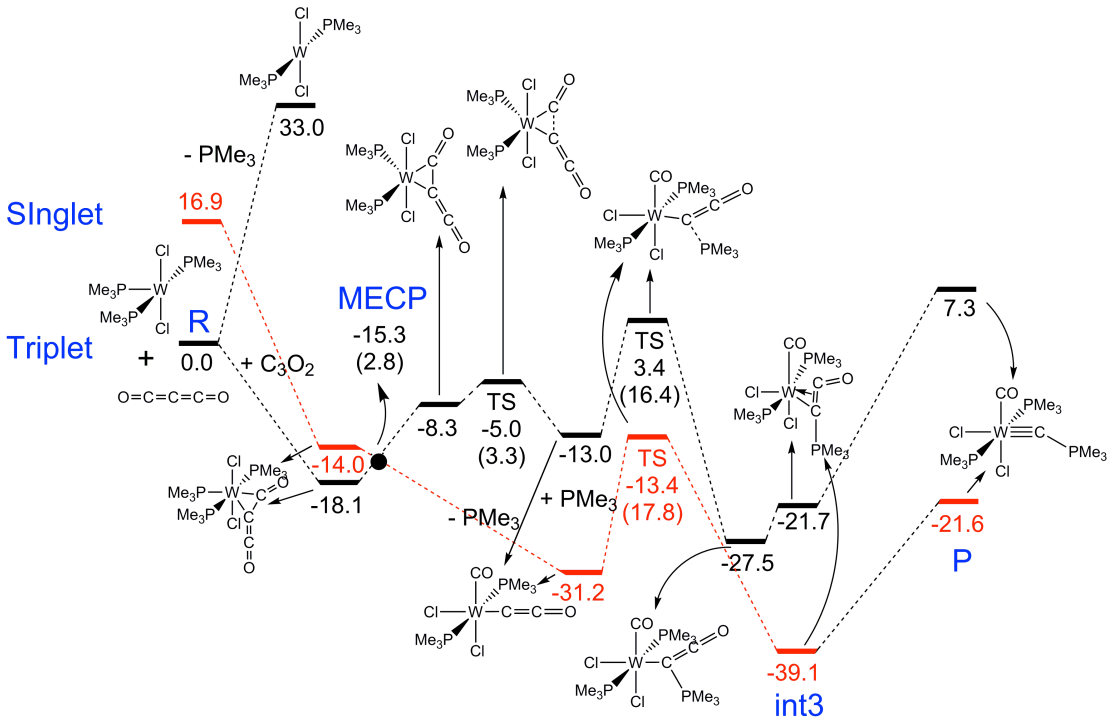

Figure S1 The reaction paths of C_3O_2 binding to $WCl_2(PMe_3)_4$, in singlet and triplet. The energy refers to the Gibbs free energy, in kcal/mol, relative to R plus C_3O_2.

Table S1 The Gibbs free energies and relative energies in reactants, intermediates and transition state of the conversion from reactants to **int3**.

species	Gibbs free energies in gas			Gibbs free energies in toluene			E(solv-gas)[b]	
	Singlet (S)[a]	Triplet (T)[a]	Δ(T-S)[b]	Singlet (S)[a]	Triplet (T)[a]	Δ(T-S)[b]	singlet	triplet
Cl^-	-460.233015			-460.302675				
PMe_3	-460.991291			-460.992651				
C_3O_2	-264.752352			-264.753733				
CO	-113.330599			-113.330937				
1	-2832.275173	-2832.299378	-15.2	-2832.281289	-2832.305872	-15.4	-3.8	-4.1
1-Cl	-2371.835909	-2371.855431	-12.3	-2371.871173	-2371.887326	-10.1	-22.1	-20.0
R	-2371.249672	-2371.276574	-16.9	-2371.256246	-2371.284062	-17.5	-4.1	-4.7
int1	-2636.051344	-2636.057791	-4.0	-2636.060569	-2636.065932	-3.4	-5.8	-5.1
MECP	-2636.053386			-2636.059357			-3.7	
int2	-2175.087373	-2175.05842	18.2	-2175.094529	-2175.065655	18.1	-4.5	-4.5
TS1	-2636.050268			-2636.060691			-6.5	
int3-2		-2636.072742			-2636.083592			-6.8
int3	-2636.091300	-2636.063534	17.4	-2636.109098	-2636.075016	21.4	-11.2	-7.2

[a] in hartree;

[b] in kcal/mol.

Table S2 The Gibbs free energies and relative energies in various intermediates, transition state and product of the conversion from **int3** to **P** including three dissociations of ligands, PMe_3, CO and Cl^-.

Structure	Gibbs free energies in gas			Gibbs free energies in toluene			ΔG(solv-gas)[b]	
	Singlet (S)[a]	Triplet (T)[a]	Δ(T-S)[b]	singlet	Triplet (T)[a]	Δ(T-S)[b]	singlet	triplet
Cl^-	-460.233015			-460.302675				
PMe_3	-460.991291			-460.992651				
C_3O_2	-264.752352			-264.754615				
CO	-113.330599			-113.331117				
Extrusion of PMe_3								
int3	-2636.091300	-2636.063534	17.4	-2636.118150			-16.8	
int4	-2175.071394	-2175.045099	16.5	-2175.098772			-17.2	
TS2	-2175.040326	-2175.012964	17.2	-2175.065088			-15.5	
int5	-2175.045877	-2175.019063	16.8	-2175.069072			-14.6	
int6	-2061.708200	-2061.683760	15.3	-2061.734879			-16.7	
int7	-2061.704386	-2061.668464	22.5	-2061.730838			-16.6	
Prod	-2522.732673	-2522.686681	28.9	-2522.756978			-15.3	
Extrusion of CO								
CO-int1	-2522.695012	-2522.686651	5.2	-2522.715136			-12.6	
CO-TS	-2522.693424	-2522.671888	13.5	-2522.71281			-12.2	
Extrusion of Cl^-								
Cl-int1	-2175.660918			-2175.718002	-2175.686603	19.7	-35.8	
Cl-TS	-2175.650817			-2175.700735			-31.3	
Cl-int2	-2175.657138			-2175.706156	-2175.660310	28.8	-30.8	
Cl-int3	-2062.311006			-2062.365871	-2062.327188	24.3	-34.4	

[a] in hartree;

[b] in kcal/mol.

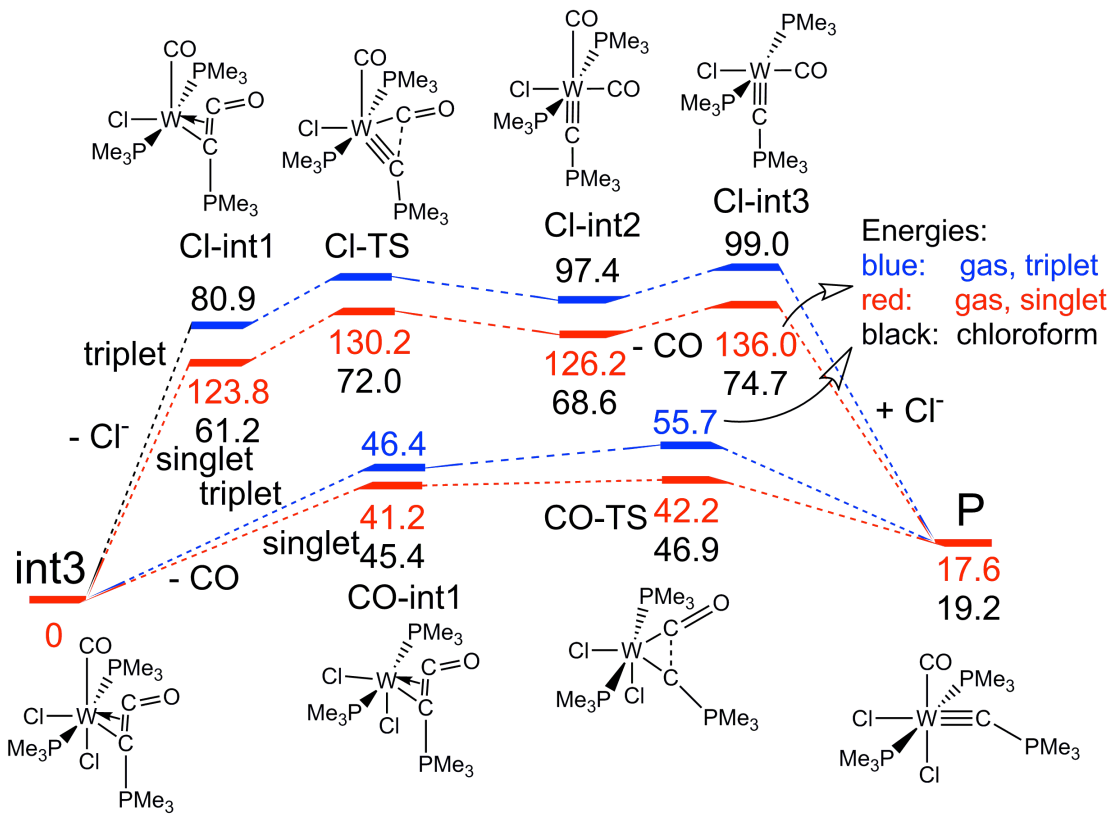

Figure S2 The reaction paths from **int3** to **P** with an extrusion of one CO or Cl^- ligand. The energy refers to the Gibbs free energy in kcal/mol.

Table S3 The natural charges of the atoms in C_3O_2 molecule or fragments.

		O1	C1	C0	C2	O2	Net charge
free	C_3O_2	-0.442	0.714	-0.543	0.714	-0.442	0.001
complex	Int1	-0.583	0.561	-0.516	0.722	-0.493	-0.309
	MECP	-0.573	0.557	-0.491	0.715	-0.489	-0.281
	Int2	-0.473	0.676	-0.373	0.710	-0.436	0.104
	TS1	-0.501	0.629	-0.497	0.712	-0.479	-0.136
	Int3	-0.210	0.005	-0.860	0.201	-0.335	-1.199
	Int4	-0.511	0.616	-0.778	0.569	-0.591	-0.695
	TS2	-0.450	0.714	-0.619	0.602	-0.582	-0.335
	Int5	-0.425	0.744	-0.557	0.534	-0.535	-0.239
	Int6			-0.626	0.602	-0.507	-0.531
	Int7			-0.652	0.625	-0.518	-0.545
	Prod			-0.615	0.672	-0.501	-0.444

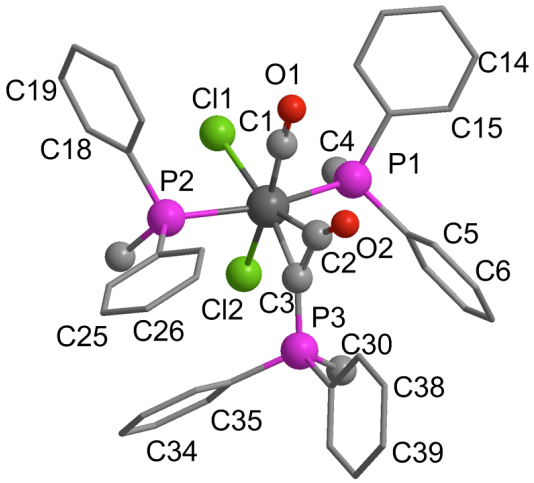

Figure S3 Geometries of **P-ph** with full $PMePh_2$ ligands with some labeled atoms whose data are listed in Table S2.

Table S4 Bond lengths and angle data for **2**, $WCl_2(PMePh_2)_2(C,C':\eta^2\text{-}C_2OPMePh_2)$.

	Exp.	This work		Exp.	This work
W-Cl1	2.474	2.5203	W-C3	1.996	1.9992
W-Cl2	2.575	2.6380	O1-C1	1.175	1.1725
W-P1	2.554	2.5547	O2-C2	1.200	1.2265
W-P2	2.520	2.5376	C2-C3	1.368	1.3807
W-C1	1.921	1.9490	P3-C3	1.753	1.7293
W-C2	2.146	2.1372			
Cl1-W-Cl2	83.2	82.82	P1-W-C3	99.7	100.25
Cl1-W-P1	84.6	82.60	P2-W-C1	90.5	91.32
Cl1-W-P2	81.9	79.91	P2-W-C2	96.7	102.21
Cl1-W-C1	85.8	86.35	P2-W-C3	92.9	95.35
Cl1-W-C2	152.8	155.43	C1-W-C2	67.0	69.19
Cl1-W-C3	168.0	165.58	C1-W-C3	105.1	107.48
Cl2-W-P1	84.4	82.54	C2-W-C3	38.3	38.82
Cl2-W-P2	90.8	89.66	W-C1-O1	176.2	176.91
Cl2-W-C1	168.7	168.78	W-C2-O2	147.8	148.80
Cl2-W-C2	124.0	121.46	W-C2-C3	64.9	65.18
Cl2-W-C3	86.1	83.55	W-C3-P3	149.7	141.81
P1-W-P2	166.2	161.62	W-C3-C2	76.8	76.00
P1-W-C1	91.8	93.20	O2-C2-C3	147.2	146.01
P1-W-C2	96.7	96.05	C2-C3-P3	133.0	142.12

Table S5. The theoretical Cartesian coordinates (in Å) for the structure C_3O_2 in gas phase.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	1.278745
2	8	0	0.000000	0.000000	2.452224
3	6	0	0.000000	0.000000	0.000001
4	6	0	0.000000	0.000000	-1.278746
5	8	0	0.000000	0.000000	-2.452224

Sum of electronic and zero-point Energies=	-264.726215
Sum of electronic and thermal Energies=	-264.721344
Sum of electronic and thermal Enthalpies=	-264.720400
Sum of electronic and thermal Free Energies=	-264.752352

Table S6. The theoretical Cartesian coordinates (in Å) for the structure Cl^- in gas phase.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	17	0	-0.488844	-2.315605	0.008296

Sum of electronic and zero-point Energies=	-460.217992
Sum of electronic and thermal Energies=	-460.216576
Sum of electronic and thermal Enthalpies=	-460.215632
Sum of electronic and thermal Free Energies=	-460.233015

Table S7. The theoretical Cartesian coordinates (in Å) for the structure CO in gas phase.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	-0.654281
2	8	0	0.000000	0.000000	0.490711

Sum of electronic and zero-point Energies=	-113.311449
Sum of electronic and thermal Energies=	-113.309089
Sum of electronic and thermal Enthalpies=	-113.308144
Sum of electronic and thermal Free Energies=	-113.330599

Table S8. The theoretical Cartesian coordinates (in Å) for the structure PMe_3 in gas phase.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	-0.487374	2.673723	-2.998814
2	6	0	-0.838293	2.938904	-4.790038
3	1	0	-0.209207	2.281905	-5.398195
4	1	0	-1.880025	2.688529	-5.011682
5	1	0	-0.658325	3.975567	-5.103086
6	6	0	-1.460322	4.081202	-2.313008
7	1	0	-2.531403	3.888852	-2.427569
8	1	0	-1.262113	4.189508	-1.242303
9	1	0	-1.225430	5.033365	-2.806177
10	6	0	1.189880	3.434478	-2.929667
11	1	0	1.914043	2.797390	-3.446602
12	1	0	1.217218	4.431572	-3.388043
13	1	0	1.519782	3.524061	-1.890207

Sum of electronic and zero-point Energies=	-460.962072
Sum of electronic and thermal Energies=	-460.955428
Sum of electronic and thermal Enthalpies=	-460.954484
Sum of electronic and thermal Free Energies=	-460.991291

Table S9. The theoretical Cartesian coordinates (in Å) for the structure **1** in singlet in gas phase.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	74	0	0.000000	0.000000	0.169450
2	17	0	0.000000	0.000000	2.625364
3	15	0	0.000000	2.394588	0.374433
4	15	0	0.000000	-2.394588	0.374433
5	15	0	-2.371366	0.000000	-0.556600
6	6	0	1.378443	3.115503	1.364580
7	1	0	2.345589	2.963423	0.872981
8	1	0	1.405810	2.602258	2.332401
9	1	0	1.247546	4.190773	1.534551
10	6	0	-1.378443	3.115503	1.364580
11	1	0	-2.345589	2.963423	0.872981
12	1	0	-1.247546	4.190773	1.534551
13	1	0	-1.405810	2.602258	2.332401
14	6	0	0.000000	3.521168	-1.079065
15	1	0	0.877276	3.322226	-1.701680
16	1	0	0.000000	4.577856	-0.785311
17	1	0	-0.877276	3.322226	-1.701680
18	6	0	-3.484179	0.000000	0.900296
19	1	0	-4.536400	0.000000	0.594825
20	1	0	-3.292404	0.881179	1.519057
21	1	0	-3.292404	-0.881179	1.519057
22	6	0	-3.005643	1.396136	-1.549151
23	1	0	-4.059599	1.251796	-1.812074
24	1	0	-2.408601	1.460544	-2.463184
25	1	0	-2.905448	2.337889	-1.001580
26	6	0	-3.005643	-1.396136	-1.549151
27	1	0	-4.059599	-1.251796	-1.812074
28	1	0	-2.905448	-2.337889	-1.001580
29	1	0	-2.408601	-1.460544	-2.463184
30	6	0	1.378443	-3.115503	1.364580
31	1	0	1.247546	-4.190773	1.534551
32	1	0	1.405810	-2.602258	2.332401
33	1	0	2.345589	-2.963423	0.872981
34	6	0	0.000000	-3.521168	-1.079065
35	1	0	-0.877276	-3.322226	-1.701680
36	1	0	0.000000	-4.577856	-0.785311
37	1	0	0.877276	-3.322226	-1.701680
38	6	0	-1.378443	-3.115503	1.364580

39	1	0	-1.405810	-2.602258	2.332401
40	1	0	-1.247546	-4.190773	1.534551
41	1	0	-2.345589	-2.963423	0.872981
42	17	0	0.000000	0.000000	-2.463029
43	15	0	2.371366	0.000000	-0.556600
44	6	0	3.005643	1.396136	-1.549151
45	1	0	4.059599	1.251796	-1.812074
46	1	0	2.905448	2.337889	-1.001580
47	1	0	2.408601	1.460544	-2.463184
48	6	0	3.484179	0.000000	0.900296
49	1	0	4.536400	0.000000	0.594825
50	1	0	3.292404	-0.881179	1.519057
51	1	0	3.292404	0.881179	1.519057
52	6	0	3.005643	-1.396136	-1.549151
53	1	0	2.905448	-2.337889	-1.001580
54	1	0	4.059599	-1.251796	-1.812074
55	1	0	2.408601	-1.460544	-2.463184

Sum of electronic and zero-point Energies= -2832.213269
Sum of electronic and thermal Energies= -2832.178416
Sum of electronic and thermal Enthalpies= -2832.177472
Sum of electronic and thermal Free Energies= -2832.275173

Table S10. The theoretical Cartesian coordinates (in Å) for the structure **1** in triplet in gas phase.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	74	0	0.136926	0.356443	-0.412385
2	17	0	-0.686947	-1.974629	-0.009969
3	15	0	0.249094	0.365618	2.065558
4	15	0	-0.218944	-0.298899	-2.774004
5	15	0	2.556464	-0.147673	-0.583716
6	6	0	-1.319135	-0.041191	2.931138
7	1	0	-2.091994	0.707157	2.735163
8	1	0	-1.671429	-1.002490	2.541981
9	1	0	-1.177998	-0.121767	4.015213
10	6	0	1.270800	-0.943403	2.850005
11	1	0	2.331937	-0.832721	2.610143
12	1	0	1.159315	-0.945443	3.940562
13	1	0	0.928922	-1.905636	2.454232
14	6	0	0.802061	1.878263	2.935533
15	1	0	0.150802	2.715792	2.668901
16	1	0	0.797124	1.747887	4.023632
17	1	0	1.811733	2.142819	2.608486
18	6	0	3.113418	-1.882940	-0.405918
19	1	0	4.201065	-1.976195	-0.503092
20	1	0	2.803706	-2.270916	0.568688
21	1	0	2.628765	-2.504105	-1.164910
22	6	0	3.659654	0.745992	0.581378
23	1	0	4.716916	0.531330	0.387236
24	1	0	3.483446	1.819125	0.451940
25	1	0	3.436749	0.490538	1.621322
26	6	0	3.391696	0.380011	-2.132063
27	1	0	4.473768	0.209194	-2.089932
28	1	0	2.990626	-0.142885	-3.005415
29	1	0	3.204024	1.451075	-2.263196
30	6	0	-1.911911	-0.861668	-3.208902
31	1	0	-1.967552	-1.231307	-4.239341
32	1	0	-2.175266	-1.672820	-2.521348
33	1	0	-2.647667	-0.061727	-3.085567
34	6	0	0.152222	0.912006	-4.095872
35	1	0	1.202833	1.210938	-4.038611
36	1	0	-0.055165	0.507352	-5.093095
37	1	0	-0.443504	1.816079	-3.941853
38	6	0	0.665280	-1.802280	-3.347124

39	1	0	0.404308	-2.616981	-2.663474
40	1	0	0.375719	-2.082173	-4.366560
41	1	0	1.750448	-1.669878	-3.317475
42	17	0	0.955141	2.693027	-0.797736
43	15	0	-2.053948	1.521928	-0.357358
44	6	0	-2.218305	2.880029	0.868682
45	1	0	-3.157137	3.431339	0.740286
46	1	0	-2.175204	2.506351	1.895791
47	1	0	-1.376683	3.565064	0.718014
48	6	0	-3.584475	0.554983	-0.082608
49	1	0	-4.475611	1.192616	-0.079709
50	1	0	-3.686308	-0.203232	-0.864057
51	1	0	-3.518898	0.022740	0.870727
52	6	0	-2.475980	2.517169	-1.842023
53	1	0	-2.596510	1.890328	-2.730098
54	1	0	-3.396993	3.093623	-1.695969
55	1	0	-1.646153	3.208404	-2.023535

Sum of electronic and zero-point Energies= -2832.236256
Sum of electronic and thermal Energies= -2832.201580
Sum of electronic and thermal Enthalpies= -2832.200636
Sum of electronic and thermal Free Energies= -2832.299378

Table S11. The theoretical Cartesian coordinates (in Å) for the structure $[WCl(PMe_3)_4]^-$ in triplet in gas phase.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	74	0	0.309793	0.857802	-0.526819
2	15	0	0.078580	-0.071589	1.687662
3	15	0	-0.334704	-0.650826	-2.305102
4	15	0	2.772390	0.321149	-0.678613
5	6	0	-1.569760	-0.553247	2.318163
6	1	0	-2.210800	0.331018	2.383696
7	1	0	-2.044116	-1.272418	1.643746
8	1	0	-1.500843	-0.998729	3.315572
9	6	0	1.094700	-1.498524	2.216570
10	1	0	2.155625	-1.232895	2.176302
11	1	0	0.857687	-1.792352	3.244153
12	1	0	0.930276	-2.359610	1.561110
13	6	0	0.588106	1.222080	2.877793
14	1	0	-0.040754	2.110176	2.768420
15	1	0	0.505637	0.856103	3.906531
16	1	0	1.623214	1.522711	2.693186
17	6	0	3.439516	-1.379736	-0.567144
18	1	0	4.532459	-1.350452	-0.514859
19	1	0	3.064097	-1.900120	0.316659
20	1	0	3.158455	-1.966410	-1.443766
21	6	0	3.761519	1.184791	0.594047
22	1	0	4.834892	1.084216	0.404449
23	1	0	3.498010	2.245938	0.601710
24	1	0	3.548308	0.769324	1.585266
25	6	0	3.558397	0.915982	-2.218012
26	1	0	4.647211	0.812332	-2.176823
27	1	0	3.191317	0.343577	-3.076598
28	1	0	3.305295	1.968155	-2.374067
29	6	0	-2.070327	-1.201509	-2.476115
30	1	0	-2.182551	-1.911659	-3.301382
31	1	0	-2.417628	-1.675993	-1.553653
32	1	0	-2.711117	-0.338417	-2.679685
33	6	0	-0.048597	0.218511	-3.890230
34	1	0	1.003805	0.499951	-3.986482
35	1	0	-0.320712	-0.417532	-4.738838
36	1	0	-0.643631	1.134677	-3.934762
37	6	0	0.571697	-2.219568	-2.546345
38	1	0	0.572851	-2.806942	-1.623408

39	1	0	0.129722	-2.819385	-3.348109
40	1	0	1.609434	-2.001756	-2.813899
41	17	0	1.101781	3.109994	-0.828814
42	15	0	-1.936124	2.028657	-0.433917
43	6	0	-2.030000	3.283076	0.893500
44	1	0	-2.914932	3.917418	0.780789
45	1	0	-2.083257	2.796380	1.873560
46	1	0	-1.134133	3.909568	0.866727
47	6	0	-3.525717	1.147986	-0.212022
48	1	0	-4.340004	1.871267	-0.102711
49	1	0	-3.746825	0.515708	-1.074319
50	1	0	-3.509654	0.510581	0.674340
51	6	0	-2.290551	3.038968	-1.915511
52	1	0	-2.462612	2.393977	-2.783324
53	1	0	-3.179171	3.661492	-1.769611
54	1	0	-1.434061	3.682993	-2.131348

Sum of electronic and zero-point Energies= -2371.790685
Sum of electronic and thermal Energies= -2371.756829
Sum of electronic and thermal Enthalpies= -2371.755885
Sum of electronic and thermal Free Energies= -2371.855431

Table S12. The theoretical Cartesian coordinates (in Å) for the structure **R** in triplet in gas phase.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	74	0	0.290712	-0.027720	-0.382001
2	17	0	-0.488844	-2.315605	0.008296
3	15	0	0.300941	0.219190	2.080544
4	15	0	-0.181695	-0.408301	-2.782376
5	15	0	2.622045	-0.143096	-0.580733
6	6	0	-1.351330	-0.008351	2.843416
7	1	0	-2.044596	0.746825	2.461498
8	1	0	-1.736321	-0.993507	2.563663
9	1	0	-1.316569	0.067466	3.936444
10	6	0	1.270754	-0.999090	3.045177
11	1	0	2.340625	-0.885919	2.839352
12	1	0	1.109506	-0.894172	4.124115
13	1	0	0.972613	-2.005072	2.733048
14	6	0	0.812823	1.823746	2.786772
15	1	0	0.199719	2.613795	2.345182
16	1	0	0.706777	1.840236	3.877056
17	1	0	1.851764	2.038408	2.522397
18	6	0	3.303979	-1.824154	-0.327119
19	1	0	4.394683	-1.832329	-0.436866
20	1	0	3.039489	-2.186504	0.670357
21	1	0	2.862620	-2.514606	-1.051273
22	6	0	3.638346	0.867561	0.567046
23	1	0	4.713211	0.764336	0.376805
24	1	0	3.353609	1.918585	0.451918
25	1	0	3.435544	0.575169	1.603105
26	6	0	3.415469	0.348832	-2.162091
27	1	0	4.508325	0.273153	-2.118894
28	1	0	3.053471	-0.281891	-2.981903
29	1	0	3.140752	1.385256	-2.383256
30	6	0	-1.963826	-0.640466	-3.150215
31	1	0	-2.144013	-0.831886	-4.214384
32	1	0	-2.341585	-1.485225	-2.566575
33	1	0	-2.522274	0.252966	-2.855549
34	6	0	0.264480	0.906009	-3.971251
35	1	0	1.350794	1.026852	-4.009143
36	1	0	-0.105460	0.683506	-4.978419
37	1	0	-0.156137	1.853674	-3.624474
38	6	0	0.514161	-1.919476	-3.545739
39	1	0	0.217499	-2.784189	-2.944516

40	1	0	0.167865	-2.058702	-4.576230
41	1	0	1.608100	-1.871876	-3.545453
42	17	0	0.329425	2.397488	-0.718177

Sum of electronic and zero-point Energies= -2371.218124
Sum of electronic and thermal Energies= -2371.190373
Sum of electronic and thermal Enthalpies= -2371.189429
Sum of electronic and thermal Free Energies= -2371.276574

Table S13. The theoretical Cartesian coordinates (in Å) for the structure **R** in singlet in gas phase.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	74	0	0.446600	0.701685	0.207116
2	17	0	2.052903	-1.068677	-0.217841
3	15	0	0.843969	0.556887	2.614512
4	15	0	0.672664	1.147283	-2.216672
5	6	0	2.432172	1.359363	3.052822
6	1	0	3.246336	0.878231	2.502490
7	1	0	2.396760	2.412637	2.759758
8	1	0	2.643439	1.293191	4.126152
9	6	0	-0.316501	1.379134	3.767007
10	1	0	-1.284665	0.868427	3.748371
11	1	0	0.059103	1.381495	4.796535
12	1	0	-0.472285	2.411008	3.439016
13	6	0	1.050130	-1.100911	3.361657
14	1	0	1.821561	-1.642070	2.806092
15	1	0	1.337345	-1.041679	4.417667
16	1	0	0.119799	-1.670658	3.279769
17	6	0	0.761666	-0.224333	-3.426586
18	1	0	1.154133	0.118158	-4.390701
19	1	0	1.419221	-1.000133	-3.022599
20	1	0	-0.225174	-0.664923	-3.590183
21	6	0	-0.441269	2.349115	-3.034791
22	1	0	-0.454896	3.263771	-2.434891
23	1	0	-0.109390	2.586937	-4.051860
24	1	0	-1.466855	1.969330	-3.083366
25	6	0	2.291895	1.952721	-2.526290
26	1	0	2.354231	2.873758	-1.938986
27	1	0	3.093929	1.283470	-2.199964
28	1	0	2.439273	2.193244	-3.585683
29	17	0	0.232462	3.118539	0.344966
30	15	0	-1.678700	-0.152326	-0.199518
31	6	0	-3.020748	0.974789	0.366076
32	1	0	-3.999459	0.481577	0.326542
33	1	0	-2.829683	1.309830	1.389769
34	1	0	-3.038628	1.862410	-0.273027
35	6	0	-2.079821	-1.679751	0.751467
36	1	0	-3.060250	-2.089861	0.479784
37	1	0	-1.316527	-2.442989	0.570251
38	1	0	-2.080380	-1.449168	1.821722
39	6	0	-2.345335	-0.664974	-1.835613

40	1	0	-3.407287	-0.927148	-1.764402
41	1	0	-2.234475	0.131578	-2.576822
42	1	0	-1.796366	-1.542649	-2.189951

Sum of electronic and zero-point Energies= -2371.193264
Sum of electronic and thermal Energies= -2371.165947
Sum of electronic and thermal Enthalpies= -2371.165003
Sum of electronic and thermal Free Energies= -2371.249672

Table S14. The theoretical Cartesian coordinates (in Å) for the structure **int1** in triplet in gas phase.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	74	0	0.225701	0.371929	-0.380195
2	17	0	-0.954662	-1.786511	0.041894
3	15	0	0.290052	0.540195	2.194669
4	15	0	-0.213609	-0.255098	-2.783779
5	6	0	-1.221160	-0.025970	3.052239
6	1	0	-2.087491	0.591206	2.797765
7	1	0	-1.435147	-1.049263	2.728916
8	1	0	-1.088213	-0.004914	4.139032
9	6	0	1.537538	-0.517258	2.995585
10	1	0	2.542338	-0.214689	2.692029
11	1	0	1.458307	-0.451051	4.085707
12	1	0	1.386291	-1.555905	2.688026
13	6	0	0.631594	2.179639	2.913324
14	1	0	-0.095895	2.909914	2.549674
15	1	0	0.613918	2.153572	4.008246
16	1	0	1.613341	2.517071	2.571609
17	6	0	-1.887634	-0.828953	-3.236048
18	1	0	-1.901630	-1.213069	-4.261263
19	1	0	-2.166251	-1.631866	-2.545683
20	1	0	-2.633063	-0.032906	-3.158255
21	6	0	0.230167	0.993730	-4.027927
22	1	0	1.275929	1.268871	-3.859224
23	1	0	0.104968	0.613312	-5.047046
24	1	0	-0.377008	1.893489	-3.896960
25	6	0	0.769299	-1.716526	-3.252766
26	1	0	0.559937	-2.520689	-2.541328
27	1	0	0.515715	-2.049360	-4.264819
28	1	0	1.834096	-1.477723	-3.209005
29	17	0	0.726035	2.803169	-0.513265
30	15	0	-2.129989	1.504918	-0.371809
31	6	0	-2.417546	2.774699	0.912582
32	1	0	-3.404221	3.233984	0.790037
33	1	0	-2.357455	2.353861	1.919934
34	1	0	-1.645292	3.542894	0.809891
35	6	0	-3.590811	0.427258	-0.211353
36	1	0	-4.521158	1.005138	-0.225147
37	1	0	-3.604075	-0.306635	-1.021323

38	1	0	-3.524755	-0.139934	0.721391
39	6	0	-2.484566	2.522085	-1.848038
40	1	0	-2.481279	1.923236	-2.762211
41	1	0	-3.457762	3.016733	-1.759524
42	1	0	-1.699185	3.278935	-1.931345
43	6	0	2.111572	0.256003	-1.270450
44	8	0	2.848125	0.607309	-2.169172
45	6	0	2.087504	-0.632387	-0.153441
46	6	0	2.966215	-1.461359	0.327677
47	8	0	3.770476	-2.207631	0.769993

Sum of electronic and zero-point Energies= -2635.995321
Sum of electronic and thermal Energies= -2635.963102
Sum of electronic and thermal Enthalpies= -2635.962158
Sum of electronic and thermal Free Energies= -2636.057791

Table S15. The theoretical Cartesian coordinates (in Å) for the structure **int1** in singlet in gas phase.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	74	0	0.915032	0.246245	0.045340
2	17	0	0.413377	-2.204740	0.006124
3	15	0	0.994192	0.359201	2.552023
4	15	0	0.887520	1.091801	-2.320319
5	6	0	1.917409	1.790475	3.185996
6	1	0	2.848594	1.909891	2.625553
7	1	0	1.325650	2.695818	3.030273
8	1	0	2.132549	1.670070	4.253069
9	6	0	-0.474838	0.348990	3.635259
10	1	0	-0.988834	-0.612739	3.563154
11	1	0	-0.189366	0.518144	4.679240
12	1	0	-1.164023	1.143504	3.330047
13	6	0	1.947953	-1.082319	3.130706
14	1	0	2.942063	-1.062044	2.674936
15	1	0	2.050606	-1.078888	4.221171
16	1	0	1.453199	-2.000988	2.804213
17	6	0	0.945637	-0.268635	-3.533086
18	1	0	0.998968	0.107299	-4.560575
19	1	0	1.826264	-0.882472	-3.323892
20	1	0	0.067584	-0.911041	-3.423975
21	6	0	-0.467739	2.165100	-2.892631
22	1	0	-0.548186	3.013631	-2.206611
23	1	0	-0.267855	2.533338	-3.904016
24	1	0	-1.423403	1.633057	-2.898184
25	6	0	2.352583	2.086955	-2.737417
26	1	0	2.387790	2.963941	-2.085761
27	1	0	3.258985	1.503720	-2.552966
28	1	0	2.332408	2.406096	-3.784731
29	17	0	0.285628	2.647266	0.420532
30	15	0	-1.706930	0.032395	-0.044696
31	6	0	-2.737985	1.539255	-0.017914
32	1	0	-3.800782	1.291269	-0.116191
33	1	0	-2.572829	2.077110	0.919702
34	1	0	-2.444975	2.217900	-0.823093
35	6	0	-2.548464	-0.985761	1.221749
36	1	0	-3.561937	-1.242646	0.894896
37	1	0	-1.980349	-1.905987	1.383189

38	1	0	-2.623045	-0.435341	2.162284
39	6	0	-2.304516	-0.818562	-1.552090
40	1	0	-3.396141	-0.910764	-1.542995
41	1	0	-2.011701	-0.276759	-2.456475
42	1	0	-1.859198	-1.816468	-1.592045
43	6	0	2.782823	-0.468460	-0.364960
44	6	0	3.678117	-1.381523	-0.593233
45	6	0	2.795947	0.968039	0.087671
46	8	0	4.530290	-2.161238	-0.853567
47	8	0	3.663894	1.790593	0.277699

Sum of electronic and zero-point Energies= -2635.989464
Sum of electronic and thermal Energies= -2635.957399
Sum of electronic and thermal Enthalpies= -2635.956455
Sum of electronic and thermal Free Energies= -2636.051344

Table S16. The theoretical Cartesian coordinates (in Å) for the structure **MECP** in gas phase.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	74	0	1.000000	0.321284	0.007419
2	17	0	0.741038	-2.138636	-0.429479
3	15	0	0.869862	0.539461	2.503835
4	15	0	0.918647	1.047184	-2.396694
5	6	0	2.191348	1.585867	3.187750
6	1	0	3.168653	1.169621	2.929324
7	1	0	2.124119	2.575808	2.727313
8	1	0	2.109953	1.676064	4.276033
9	6	0	-0.605868	1.268460	3.284443
10	1	0	-1.499800	0.668255	3.095470
11	1	0	-0.464293	1.351673	4.366926
12	1	0	-0.762664	2.264945	2.862808
13	6	0	1.090855	-1.059687	3.352203
14	1	0	2.011917	-1.528975	2.995778
15	1	0	1.143728	-0.934800	4.439192
16	1	0	0.264950	-1.731225	3.101953
17	6	0	1.057916	-0.358831	-3.548361
18	1	0	1.146281	-0.022574	-4.587169
19	1	0	1.934315	-0.954534	-3.279742
20	1	0	0.185150	-1.009015	-3.442201
21	6	0	-0.490902	2.018580	-3.017445
22	1	0	-0.580072	2.924047	-2.411445
23	1	0	-0.332634	2.295144	-4.064891
24	1	0	-1.428472	1.462068	-2.940006
25	6	0	2.320412	2.116776	-2.848510
26	1	0	2.319885	2.998786	-2.202294
27	1	0	3.261495	1.586846	-2.677768
28	1	0	2.266342	2.426624	-3.897611
29	17	0	0.149351	2.677741	0.259528
30	15	0	-1.582196	-0.173157	-0.066666
31	6	0	-2.779546	1.187541	0.159849
32	1	0	-3.809475	0.815506	0.123220
33	1	0	-2.607133	1.688529	1.116133
34	1	0	-2.635173	1.941911	-0.618116
35	6	0	-2.153381	-1.404814	1.162244
36	1	0	-3.208465	-1.655997	1.007642
37	1	0	-1.545462	-2.307031	1.050953
38	1	0	-2.034877	-1.030736	2.183353
39	6	0	-2.220287	-0.976899	-1.583238

40	1	0	-3.278942	-1.234690	-1.469667
41	1	0	-2.118897	-0.324930	-2.455275
42	1	0	-1.644407	-1.888209	-1.763165
43	6	0	2.955702	-0.246642	0.055159
44	6	0	3.966338	-1.060082	0.000757
45	6	0	2.784826	1.246261	0.150767
46	8	0	4.923386	-1.757077	-0.019956
47	8	0	3.538444	2.187286	0.243052

Sum of electronic and zero-point Energies= -2635.991404
Sum of electronic and thermal Energies= -2635.959134
Sum of electronic and thermal Enthalpies= -2635.958190
Sum of electronic and thermal Free Energies= -2636.053386

Table S17. The theoretical Cartesian coordinates (in Å) for the structure $WCl_2(PMe_3)_2(\eta^2\text{-}C_3O_2)$ in triplet in gas phase.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	74	0	0.344298	0.024157	-0.340922
2	17	0	-0.329820	-2.266206	0.044457
3	15	0	0.333190	0.422557	2.175401
4	15	0	-0.156476	-0.405378	-2.772981
5	6	0	-1.350396	0.502329	2.862542
6	1	0	-1.903404	1.304506	2.366698
7	1	0	-1.866923	-0.440980	2.664747
8	1	0	-1.339903	0.683338	3.942150
9	6	0	1.159951	-0.856682	3.167063
10	1	0	2.229554	-0.866106	2.940955
11	1	0	1.025591	-0.688315	4.240095
12	1	0	0.751248	-1.834214	2.895711
13	6	0	1.100066	1.989181	2.691474
14	1	0	0.596293	2.814760	2.181993
15	1	0	1.038367	2.138116	3.774407
16	1	0	2.150931	1.997791	2.389525
17	6	0	-1.866114	-0.942801	-3.084940
18	1	0	-2.043777	-1.135208	-4.147813
19	1	0	-2.063018	-1.853344	-2.512501
20	1	0	-2.557778	-0.168014	-2.742609
21	6	0	0.097673	1.040515	-3.838339
22	1	0	1.119727	1.403156	-3.690275
23	1	0	-0.065685	0.803132	-4.894238
24	1	0	-0.588528	1.834277	-3.530609
25	6	0	0.872378	-1.722576	-3.485943
26	1	0	0.762970	-2.624214	-2.877252
27	1	0	0.591008	-1.942865	-4.520604
28	1	0	1.921543	-1.416448	-3.458210
29	17	0	-0.916024	2.057931	-0.493342
30	6	0	2.159951	0.490599	-1.146931
31	8	0	2.819889	1.065422	-1.992224
32	6	0	2.354660	-0.492285	-0.101912
33	6	0	3.363253	-1.145177	0.405189
34	8	0	4.292663	-1.704672	0.874996

Sum of electronic and zero-point Energies= -2174.992627
Sum of electronic and thermal Energies= -2174.967052
Sum of electronic and thermal Enthalpies= -2174.966107
Sum of electronic and thermal Free Energies= -2175.050875

Table S18. The theoretical Cartesian coordinates (in Å) for the structure **int2** in singlet in gas phase.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	74	0	0.397717	-0.377877	-0.795168
2	15	0	2.823973	0.029600	-0.255492
3	6	0	3.906737	-1.425590	-0.368258
4	1	0	4.935970	-1.195131	-0.074427
5	1	0	3.506503	-2.199490	0.293432
6	1	0	3.901745	-1.817840	-1.388873
7	6	0	3.127787	0.673208	1.412610
8	1	0	2.726753	-0.036038	2.140706
9	1	0	4.198677	0.819899	1.586531
10	1	0	2.593239	1.618115	1.532779
11	6	0	3.572170	1.275454	-1.351882
12	1	0	4.606944	1.491910	-1.066433
13	1	0	3.550201	0.926024	-2.387159
14	1	0	2.980785	2.192991	-1.290476
15	17	0	0.003118	1.728853	0.467959
16	15	0	-2.018210	-0.846476	-0.251129
17	6	0	-2.506497	-0.419951	1.442563
18	1	0	-3.576458	-0.593575	1.596593
19	1	0	-1.927437	-1.030718	2.139661
20	1	0	-2.262484	0.628754	1.628914
21	6	0	-2.543330	-2.576396	-0.440378
22	1	0	-3.587848	-2.724048	-0.146533
23	1	0	-2.412142	-2.894454	-1.478380
24	1	0	-1.900368	-3.200411	0.187221
25	6	0	-3.155493	0.117396	-1.295801
26	1	0	-4.199953	-0.053673	-1.014934
27	1	0	-2.919041	1.178651	-1.181258
28	1	0	-3.017267	-0.150302	-2.346340
29	6	0	0.299392	0.178160	-2.589328
30	17	0	0.665837	-1.818293	1.294263
31	6	0	0.728513	-2.200257	-1.553779
32	8	0	0.917600	-3.257242	-2.012108
33	6	0	0.268934	0.411757	-3.877884
34	8	0	0.233771	0.667323	-5.025691

Sum of electronic and zero-point Energies= -2175.030847

Sum of electronic and thermal Energies= -2175.005323

Sum of electronic and thermal Enthalpies= -2175.004378
Sum of electronic and thermal Free Energies= -2175.087373

Table S19. The theoretical Cartesian coordinates (in Å) for the structure **TS1** in singlet in gas phase.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	74	0	0.549800	-0.189637	-0.305392
2	17	0	-1.103803	-2.038730	0.329103
3	15	0	0.317551	0.542815	2.085773
4	15	0	-0.264038	-0.419604	-2.681185
5	6	0	-1.343512	0.374438	2.796557
6	1	0	-2.030500	1.007567	2.229524
7	1	0	-1.674534	-0.661288	2.686348
8	1	0	-1.350916	0.668562	3.851421
9	6	0	1.365417	-0.439760	3.209066
10	1	0	2.417286	-0.334129	2.928261
11	1	0	1.239137	-0.133183	4.253018
12	1	0	1.089715	-1.494689	3.106962
13	6	0	0.766639	2.269699	2.431880
14	1	0	0.160353	2.914175	1.789092
15	1	0	0.591508	2.533510	3.480262
16	1	0	1.818422	2.439392	2.185709
17	6	0	-2.008629	-0.892888	-2.851129
18	1	0	-2.291630	-1.003084	-3.903414
19	1	0	-2.178727	-1.828170	-2.311299
20	1	0	-2.623711	-0.121288	-2.380618
21	6	0	-0.108825	1.072644	-3.706893
22	1	0	0.946058	1.338156	-3.817957
23	1	0	-0.553294	0.930746	-4.697552
24	1	0	-0.613164	1.894728	-3.191978
25	6	0	0.625186	-1.701802	-3.625865
26	1	0	0.450600	-2.675613	-3.159883
27	1	0	0.283700	-1.739925	-4.665771
28	1	0	1.700066	-1.502686	-3.608546
29	17	0	-1.292932	1.598792	-0.442385
30	6	0	1.790153	1.255032	-0.778334
31	8	0	2.533043	2.124973	-1.053409
32	6	0	3.228328	-1.128347	0.008016
33	8	0	4.363114	-0.817415	0.085311
34	6	0	1.959581	-1.487273	-0.072069
35	15	0	1.638594	-3.812005	0.612446
36	6	0	1.070164	-4.507814	-0.972079
37	1	0	1.105201	-5.603198	-0.975003

38	1	0	0.044141	-4.172585	-1.150008
39	1	0	1.705376	-4.133518	-1.781087
40	6	0	0.672612	-4.777412	1.835382
41	1	0	0.810326	-5.858227	1.702927
42	1	0	0.971328	-4.509632	2.852737
43	1	0	-0.382567	-4.520977	1.711991
44	6	0	3.309299	-4.549035	0.764628
45	1	0	3.288819	-5.641002	0.667098
46	1	0	3.967841	-4.146922	-0.011593
47	1	0	3.749816	-4.297162	1.733793

Sum of electronic and zero-point Energies= -2635.984503
Sum of electronic and thermal Energies= -2635.951365
Sum of electronic and thermal Enthalpies= -2635.950420
Sum of electronic and thermal Free Energies= -2636.050268

Table S20. The theoretical Cartesian coordinates (in Å) for the structure **int3** in singlet in gas phase.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	74	0	0.395225	-0.367547	-0.944980
2	15	0	2.817995	-0.037409	-0.374183
3	6	0	3.819059	-1.550928	-0.290637
4	1	0	4.852523	-1.340118	0.003844
5	1	0	3.359965	-2.220843	0.442117
6	1	0	3.810652	-2.055827	-1.260448
7	6	0	3.162026	0.807521	1.194381
8	1	0	2.765219	0.197118	2.009132
9	1	0	4.238162	0.961458	1.330371
10	1	0	2.629632	1.761776	1.208792
11	6	0	3.672570	1.005242	-1.606885
12	1	0	4.738682	1.115759	-1.381132
13	1	0	3.560285	0.575086	-2.606834
14	1	0	3.204810	1.996260	-1.596733
15	17	0	-0.026345	1.886076	0.323192
16	15	0	-1.989650	-0.903894	-0.354653
17	6	0	-2.581535	-0.256579	1.233020
18	1	0	-3.653799	-0.442992	1.358564
19	1	0	-2.020493	-0.744301	2.033622
20	1	0	-2.363084	0.813460	1.282171
21	6	0	-2.412415	-2.669917	-0.297813
22	1	0	-3.450340	-2.831525	0.012021
23	1	0	-2.248778	-3.124496	-1.278502
24	1	0	-1.739922	-3.155931	0.415120
25	6	0	-3.158779	-0.190574	-1.563044
26	1	0	-4.197608	-0.445352	-1.327438
27	1	0	-3.047113	0.899270	-1.539047
28	1	0	-2.923089	-0.544765	-2.571527
29	6	0	0.406679	-0.492497	-3.089577
30	8	0	0.505988	-1.127739	-4.129208
31	15	0	-0.062631	2.240524	-3.407701
32	6	0	0.194574	0.778720	-2.564133
33	6	0	-1.500640	2.057827	-4.487542
34	1	0	-1.368458	1.156178	-5.091681
35	1	0	-2.405889	1.944777	-3.886557
36	1	0	-1.613784	2.925510	-5.143576

37	6	0	-0.304349	3.728329	-2.426281
38	1	0	-1.153205	3.585129	-1.754085
39	1	0	0.568653	3.888786	-1.789926
40	1	0	-0.467512	4.591454	-3.080767
41	6	0	1.332197	2.538144	-4.518444
42	1	0	1.499412	1.636990	-5.114610
43	1	0	1.135058	3.385521	-5.181131
44	1	0	2.234239	2.743098	-3.937500
45	17	0	0.607577	-1.469846	1.383431
46	6	0	0.718583	-2.192548	-1.541428
47	8	0	0.907309	-3.280633	-1.938287

Sum of electronic and zero-point Energies= -2636.027872
Sum of electronic and thermal Energies= -2635.995417
Sum of electronic and thermal Enthalpies= -2635.994473
Sum of electronic and thermal Free Energies= -2636.091300

Table S21. The theoretical Cartesian coordinates (in Å) for the structure **int4** in singlet in gas phase.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	74	0	0.040029	-0.536766	-0.338304
2	17	0	-0.847780	-1.221061	1.831720
3	15	0	0.258842	-0.328525	-2.810286
4	6	0	-0.808851	-1.451913	-3.771550
5	1	0	-0.686368	-1.314101	-4.851335
6	1	0	-0.572718	-2.490901	-3.518417
7	1	0	-1.850840	-1.262147	-3.499853
8	6	0	-0.126880	1.305389	-3.506799
9	1	0	0.560319	2.048246	-3.093677
10	1	0	-0.040052	1.301369	-4.598246
11	1	0	-1.143596	1.584102	-3.218839
12	6	0	1.930286	-0.674852	-3.444302
13	1	0	2.238781	-1.680729	-3.141319
14	1	0	1.969695	-0.597360	-4.535532
15	1	0	2.640776	0.030923	-3.004374
16	17	0	-2.148444	0.360795	-0.920909
17	6	0	1.096932	1.054174	-0.360361
18	8	0	1.798223	2.000197	-0.369826
19	6	0	2.198913	-1.044066	-0.356887
20	8	0	3.339049	-0.635556	-0.379670
21	6	0	1.318365	-2.092816	-0.372006
22	15	0	1.338025	-3.687876	0.243513
23	6	0	-0.294554	-4.439409	0.166553
24	1	0	-0.279320	-5.465538	0.543444
25	1	0	-0.975746	-3.832512	0.771954
26	1	0	-0.651599	-4.440211	-0.866739
27	6	0	1.860792	-3.665650	1.965977
28	1	0	1.866337	-4.673687	2.389718
29	1	0	2.862459	-3.234294	2.032074
30	1	0	1.166143	-3.028384	2.522037
31	6	0	2.490644	-4.742776	-0.661622
32	1	0	2.531424	-5.748455	-0.234068
33	1	0	2.184365	-4.810918	-1.708348
34	1	0	3.486656	-4.294652	-0.623550

Sum of electronic and zero-point Energies= -2175.017097

Sum of electronic and thermal Energies= -2174.992650

Sum of electronic and thermal Enthalpies= -2174.991706
Sum of electronic and thermal Free Energies= -2175.071394

Table S22. The theoretical Cartesian coordinates (in Å) for the structure **TS2** in singlet in gas phase.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	74	0	0.051650	-0.514324	-0.405545
2	17	0	-0.773499	-0.445987	1.922377
3	15	0	0.236480	-0.329131	-2.889870
4	6	0	-1.106652	-1.141074	-3.810046
5	1	0	-0.981743	-1.034659	-4.892811
6	1	0	-1.132448	-2.203206	-3.550594
7	1	0	-2.055793	-0.694073	-3.503359
8	6	0	0.255070	1.357990	-3.568078
9	1	0	1.127555	1.900160	-3.192579
10	1	0	0.283732	1.348934	-4.662545
11	1	0	-0.643980	1.878321	-3.228572
12	6	0	1.744898	-1.082680	-3.585658
13	1	0	1.787529	-2.137201	-3.295882
14	1	0	1.770532	-1.009646	-4.677934
15	1	0	2.629093	-0.587576	-3.174387
16	17	0	-2.025655	0.700285	-0.999316
17	6	0	1.122567	1.247440	-0.162609
18	8	0	1.906905	2.090667	-0.024543
19	6	0	1.924674	-1.019272	-0.154673
20	8	0	3.087798	-1.258456	-0.037789
21	6	0	0.526672	-2.333286	-0.417696
22	15	0	1.222197	-3.762453	0.216908
23	6	0	0.004436	-5.091058	0.157834
24	1	0	0.415167	-6.014049	0.577366
25	1	0	-0.877697	-4.791174	0.726512
26	1	0	-0.296462	-5.269235	-0.876763
27	6	0	1.646512	-3.471947	1.943775
28	1	0	1.842230	-4.409423	2.471156
29	1	0	2.531382	-2.832085	1.983799
30	1	0	0.817097	-2.932048	2.413429
31	6	0	2.700253	-4.377572	-0.624654
32	1	0	3.101228	-5.254957	-0.109007
33	1	0	2.455671	-4.651958	-1.653759
34	1	0	3.452907	-3.585227	-0.634310

Sum of electronic and zero-point Energies= -2174.985001

Sum of electronic and thermal Energies= -2174.960309

Sum of electronic and thermal Enthalpies= -2174.959364
Sum of electronic and thermal Free Energies= -2175.040326

Table S23. The theoretical Cartesian coordinates (in Å) for the structure **int5** in singlet in gas phase.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	74	0	-0.351106	-0.565382	-0.565466
2	17	0	-1.200010	-0.289208	1.783414
3	15	0	0.048190	-0.321616	-3.008881
4	6	0	-1.389553	-0.695980	-4.059050
5	1	0	-1.155773	-0.574455	-5.122227
6	1	0	-1.711493	-1.724352	-3.872587
7	1	0	-2.209366	-0.029022	-3.781086
8	6	0	0.548765	1.342322	-3.550827
9	1	0	1.508600	1.609197	-3.098786
10	1	0	0.639496	1.404221	-4.640212
11	1	0	-0.205194	2.054492	-3.204495
12	6	0	1.349343	-1.409228	-3.680077
13	1	0	1.089099	-2.449798	-3.460985
14	1	0	1.468054	-1.290769	-4.762291
15	1	0	2.302302	-1.194995	-3.188301
16	17	0	-2.080210	1.124056	-1.199648
17	6	0	0.863832	1.133945	0.125704
18	8	0	1.574720	1.908280	0.591414
19	6	0	1.456625	-1.276754	-0.254057
20	8	0	2.531928	-1.746577	-0.116910
21	6	0	-0.613523	-2.392409	-0.686131
22	15	0	-0.308216	-3.934099	0.003344
23	6	0	-1.777885	-4.978970	-0.089925
24	1	0	-1.594365	-5.952759	0.372922
25	1	0	-2.600186	-4.482465	0.428935
26	1	0	-2.065377	-5.123417	-1.133416
27	6	0	0.109277	-3.755828	1.747279
28	1	0	0.058803	-4.712090	2.276207
29	1	0	1.116542	-3.339882	1.830560
30	1	0	-0.581111	-3.029015	2.190012
31	6	0	1.035714	-4.845363	-0.793687
32	1	0	1.225577	-5.792484	-0.279972
33	1	0	0.778706	-5.050503	-1.835739
34	1	0	1.943261	-4.235909	-0.768384

Sum of electronic and zero-point Energies= -2174.988269

Sum of electronic and thermal Energies= -2174.962583

Sum of electronic and thermal Enthalpies= -2174.961639
Sum of electronic and thermal Free Energies= -2175.045877

Table S24. The theoretical Cartesian coordinates (in Å) for the structure **int6** in singlet in gas phase.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	74	0	0.050916	-0.756695	-0.516971
2	17	0	-0.124867	-0.278954	1.867772
3	15	0	0.120697	-0.334260	-2.959747
4	6	0	-1.432522	-0.672814	-3.849578
5	1	0	-1.357833	-0.426444	-4.914427
6	1	0	-1.684002	-1.731608	-3.739345
7	1	0	-2.228245	-0.084076	-3.386395
8	6	0	0.489404	1.388711	-3.418808
9	1	0	1.469283	1.682728	-3.032650
10	1	0	0.482181	1.521972	-4.505737
11	1	0	-0.267020	2.035667	-2.966219
12	6	0	1.351920	-1.305267	-3.890546
13	1	0	1.160898	-2.370651	-3.729608
14	1	0	1.315388	-1.092613	-4.964577
15	1	0	2.355537	-1.088101	-3.514983
16	17	0	-1.816888	0.869864	-0.751441
17	6	0	1.972958	-1.139165	-0.451699
18	8	0	3.123968	-1.391185	-0.462633
19	6	0	-0.223573	-2.533731	-0.733988
20	15	0	-0.321675	-4.055417	0.030605
21	6	0	-1.810710	-4.984118	-0.401644
22	1	0	-1.832934	-5.948496	0.114366
23	1	0	-2.691639	-4.406224	-0.115074
24	1	0	-1.843932	-5.151550	-1.480170
25	6	0	-0.304270	-3.908720	1.825673
26	1	0	-0.408037	-4.888148	2.302288
27	1	0	0.630135	-3.433711	2.134942
28	1	0	-1.115270	-3.247252	2.140165
29	6	0	1.088937	-5.083580	-0.434679
30	1	0	1.055487	-6.047944	0.080403
31	1	0	1.084694	-5.250510	-1.514026
32	1	0	2.012447	-4.563729	-0.168280

Sum of electronic and zero-point Energies= -2061.653092
Sum of electronic and thermal Energies= -2061.629871
Sum of electronic and thermal Enthalpies= -2061.628926
Sum of electronic and thermal Free Energies= -2061.708200

Table S25. The theoretical Cartesian coordinates (in Å) for the structure **int7** in singlet in gas phase.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	74	0	0.372207	0.122516	-0.524893
2	15	0	2.809562	0.117186	-0.302164
3	6	0	3.726647	-1.394049	-0.741257
4	1	0	4.793976	-1.296374	-0.514249
5	1	0	3.304200	-2.231048	-0.179938
6	1	0	3.601491	-1.603086	-1.807464
7	6	0	3.357185	0.426513	1.408201
8	1	0	2.949363	-0.362309	2.046157
9	1	0	4.450189	0.431317	1.483985
10	1	0	2.966648	1.384090	1.762317
11	6	0	3.677204	1.399374	-1.266538
12	1	0	4.750151	1.411158	-1.046132
13	1	0	3.538630	1.193519	-2.332540
14	1	0	3.249856	2.381588	-1.047717
15	17	0	-1.354032	0.739664	0.991171
16	15	0	0.065249	2.134293	-3.353233
17	6	0	0.324467	1.391974	-1.840339
18	6	0	-1.231326	1.272248	-4.269924
19	1	0	-0.928763	0.233324	-4.423127
20	1	0	-2.148038	1.274273	-3.676989
21	1	0	-1.417951	1.745405	-5.238666
22	6	0	-0.464510	3.853267	-3.175610
23	1	0	-1.366650	3.888106	-2.562166
24	1	0	0.315503	4.425441	-2.669030
25	1	0	-0.668345	4.305108	-4.150701
26	6	0	1.507084	2.164188	-4.450879
27	1	0	1.855710	1.140117	-4.611979
28	1	0	1.259886	2.612450	-5.418163
29	1	0	2.313734	2.738158	-3.988237
30	17	0	0.748343	-1.959699	0.884658
31	6	0	0.666207	-1.128024	-2.011832
32	8	0	0.762724	-1.832592	-2.948982

Sum of electronic and zero-point Energies= -2061.651224

Sum of electronic and thermal Energies= -2061.628501

Sum of electronic and thermal Enthalpies= -2061.627557
Sum of electronic and thermal Free Energies= -2061.704386

Table S26. The theoretical Cartesian coordinates (in Å) for the structure **P** in singlet in gas phase.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	74	0	0.364531	-0.213907	-0.834126
2	15	0	2.810495	0.090396	-0.348777
3	6	0	3.848398	-1.394541	-0.526533
4	1	0	4.885815	-1.210781	-0.225693
5	1	0	3.418280	-2.177112	0.105735
6	1	0	3.827066	-1.747220	-1.561602
7	6	0	3.196424	0.656534	1.334294
8	1	0	2.800184	-0.079153	2.038868
9	1	0	4.277012	0.768598	1.476656
10	1	0	2.683486	1.603020	1.522069
11	6	0	3.640838	1.331065	-1.401811
12	1	0	4.696260	1.457501	-1.135761
13	1	0	3.570918	1.026428	-2.450893
14	1	0	3.127106	2.291135	-1.281110
15	17	0	0.040715	1.841302	0.676678
16	15	0	-2.021598	-0.736623	-0.238979
17	6	0	-2.491164	-0.338799	1.470096
18	1	0	-3.553138	-0.540294	1.648851
19	1	0	-1.877995	-0.946481	2.140668
20	1	0	-2.257017	0.710533	1.669648
21	6	0	-2.519960	-2.479268	-0.413269
22	1	0	-3.544953	-2.655086	-0.068085
23	1	0	-2.430062	-2.791812	-1.457672
24	1	0	-1.827815	-3.084664	0.179751
25	6	0	-3.251531	0.172581	-1.237135
26	1	0	-4.279480	-0.041252	-0.924105
27	1	0	-3.061357	1.245436	-1.130043
28	1	0	-3.135541	-0.098384	-2.291190
29	15	0	-0.037071	1.944880	-3.534926
30	6	0	0.175449	0.700046	-2.401453
31	6	0	-1.354103	1.664557	-4.747622
32	1	0	-1.134846	0.768553	-5.332176
33	1	0	-2.302457	1.513978	-4.226582
34	1	0	-1.451382	2.519738	-5.423636
35	6	0	-0.457242	3.475394	-2.671007
36	1	0	-1.430046	3.361929	-2.187337
37	1	0	0.273619	3.642701	-1.875050
38	1	0	-0.480652	4.327711	-3.356993

39	6	0	1.437566	2.316121	-4.520714
40	1	0	1.761231	1.419617	-5.054245
41	1	0	1.235017	3.112021	-5.243981
42	1	0	2.245613	2.634534	-3.857644
43	17	0	0.685484	-1.791915	1.237489
44	6	0	0.637318	-1.934914	-1.792335
45	8	0	0.795576	-2.940119	-2.376045

Sum of electronic and zero-point Energies= -2522.670874
Sum of electronic and thermal Energies= -2522.639986
Sum of electronic and thermal Enthalpies= -2522.639042
Sum of electronic and thermal Free Energies= -2522.732673

Table S27. The theoretical Cartesian coordinates (in Å) for the structure **int3-ph** in singlet in gas phase.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	74	0	0.250263	-0.134811	0.199669
2	17	0	-1.080138	-2.192779	-0.777026
3	15	0	0.013764	0.728528	-2.193110
4	15	0	-0.319942	-0.901278	2.550529
5	6	0	-1.602683	0.436509	-2.965312
6	1	0	-2.340787	1.012000	-2.402068
7	1	0	-1.860563	-0.621219	-2.863528
8	1	0	-1.607051	0.756323	-4.012360
9	6	0	-1.487962	-2.290897	2.588614
10	1	0	-2.305187	-2.061682	1.898816
11	1	0	-1.882659	-2.488318	3.590828
12	1	0	-0.984481	-3.180656	2.194830
13	17	0	-2.060536	0.843456	0.434638
14	6	0	0.906598	1.574437	0.867807
15	8	0	1.360197	2.579494	1.266485
16	6	0	2.386892	-0.105086	0.239596
17	8	0	3.424935	0.535484	0.367680
18	6	0	1.829111	-1.342704	-0.012495
19	15	0	2.248493	-2.979317	-0.381602
20	6	0	1.850166	-3.418386	-2.081622
21	1	0	2.137593	-4.456974	-2.272742
22	1	0	2.414084	-2.759493	-2.749903
23	1	0	0.779110	-3.269141	-2.246605
24	6	0	0.287396	2.511994	-2.459560
25	6	0	-0.299867	3.405557	-1.551522
26	6	0	1.006533	3.016061	-3.551848
27	6	0	-0.167671	4.780638	-1.735389
28	1	0	-0.860689	3.018202	-0.700072
29	6	0	1.144512	4.393747	-3.726556
30	1	0	1.464994	2.333523	-4.266414
31	6	0	0.557177	5.278224	-2.820215
32	1	0	-0.623920	5.463105	-1.022869
33	1	0	1.710615	4.774842	-4.573550
34	1	0	0.667439	6.351547	-2.956974
35	6	0	1.224601	-0.080140	-3.286206
36	6	0	2.594834	0.103529	-3.029775
37	6	0	0.837017	-0.908652	-4.346497

38	6	0	3.552521	-0.524021	-3.823796
39	1	0	2.913013	0.746004	-2.208208
40	6	0	1.798868	-1.534985	-5.143997
41	1	0	-0.218244	-1.072986	-4.554441
42	6	0	3.157016	-1.344191	-4.886832
43	1	0	4.608138	-0.371774	-3.610873
44	1	0	1.483449	-2.172057	-5.966922
45	1	0	3.904866	-1.830452	-5.508829
46	6	0	1.094260	-1.437067	3.576981
47	6	0	2.354801	-0.850591	3.392342
48	6	0	0.933241	-2.392533	4.590119
49	6	0	3.437558	-1.232622	4.185439
50	1	0	2.496502	-0.084477	2.632191
51	6	0	2.014168	-2.770855	5.386095
52	1	0	-0.039361	-2.853394	4.755682
53	6	0	3.271924	-2.198340	5.180650
54	1	0	4.408189	-0.770567	4.022541
55	1	0	1.873425	-3.514014	6.168132
56	1	0	4.115062	-2.496518	5.799304
57	6	0	-1.084876	0.374353	3.602149
58	6	0	-0.279599	1.387676	4.138052
59	6	0	-2.464436	0.397057	3.838302
60	6	0	-0.842970	2.397800	4.914377
61	1	0	0.793169	1.390479	3.945546
62	6	0	-3.026654	1.408954	4.616528
63	1	0	-3.107132	-0.362835	3.398607
64	6	0	-2.218235	2.408651	5.158512
65	1	0	-0.207463	3.178836	5.324500
66	1	0	-4.099923	1.419620	4.791031
67	1	0	-2.659070	3.198175	5.762814
68	6	0	4.023066	-3.268820	-0.193961
69	6	0	4.918133	-2.208998	0.002853
70	6	0	4.499839	-4.586274	-0.288147
71	6	0	6.285660	-2.480544	0.102936
72	1	0	4.556318	-1.182405	0.087250
73	6	0	5.864028	-4.844807	-0.191285
74	1	0	3.799777	-5.411945	-0.422055
75	6	0	6.759063	-3.788447	0.004654
76	1	0	6.981113	-1.660086	0.261112
77	1	0	6.228955	-5.866286	-0.262399
78	1	0	7.824908	-3.989397	0.084147
79	6	0	1.466844	-4.183919	0.712815
80	6	0	1.981504	-4.339043	2.008157
81	6	0	0.378816	-4.963196	0.294180

82	6	0	1.418871	-5.276305	2.873201
83	1	0	2.826576	-3.734284	2.340448
84	6	0	-0.177002	-5.899599	1.164167
85	1	0	-0.046319	-4.819072	-0.695558
86	6	0	0.341483	-6.058200	2.452200
87	1	0	1.825409	-5.392151	3.874905
88	1	0	-1.021017	-6.500694	0.836733
89	1	0	-0.094340	-6.791114	3.126851

Sum of electronic and zero-point Energies= -3786.093578
Sum of electronic and thermal Energies= -3786.043085
Sum of electronic and thermal Enthalpies= -3786.042141
Sum of electronic and thermal Free Energies= -3786.179633

Table S28. The theoretical Cartesian coordinates (in Å) for the structure **P-ph** in singlet in gas phase.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	74	0	0.055827	-0.241339	0.196927
2	17	0	-1.422123	-2.189202	-0.767677
3	15	0	0.096859	0.561364	-2.209303
4	15	0	-0.581612	-0.941979	2.526231
5	6	0	-1.434116	0.286445	-3.151518
6	1	0	-2.220991	0.860399	-2.654605
7	1	0	-1.711007	-0.770610	-3.087335
8	1	0	-1.338355	0.616203	-4.191684
9	6	0	-1.909940	-2.181848	2.616406
10	1	0	-2.713004	-1.855588	1.949624
11	1	0	-2.297810	-2.320116	3.631082
12	1	0	-1.540156	-3.129694	2.215334
13	17	0	-2.090717	1.130206	0.300980
14	6	0	1.143352	1.271691	0.880132
15	8	0	1.857393	2.115902	1.277876
16	6	0	1.517627	-1.319752	0.131619
17	15	0	2.431860	-2.747317	-0.112039
18	6	0	1.973044	-3.469963	-1.700799
19	1	0	2.330038	-4.500997	-1.778317
20	1	0	2.378458	-2.866035	-2.517462
21	1	0	0.876183	-3.445458	-1.750011
22	6	0	0.460197	2.325669	-2.529243
23	6	0	0.107728	3.293260	-1.579091
24	6	0	1.041791	2.734173	-3.739548
25	6	0	0.339286	4.645367	-1.835337
26	1	0	-0.363663	2.982999	-0.646672
27	6	0	1.276319	4.085250	-3.990777
28	1	0	1.322676	1.989981	-4.485624
29	6	0	0.925311	5.044367	-3.037689
30	1	0	0.061178	5.387092	-1.090365
31	1	0	1.732936	4.389654	-4.930007
32	1	0	1.110107	6.098499	-3.232338
33	6	0	1.402403	-0.274909	-3.170895
34	6	0	2.737368	-0.111778	-2.760882
35	6	0	1.129747	-1.090261	-4.274758
36	6	0	3.774103	-0.743008	-3.444000
37	1	0	2.956524	0.515259	-1.894786

38	6	0	2.169600	-1.727886	-4.959854
39	1	0	0.102744	-1.238140	-4.603253
40	6	0	3.492101	-1.555196	-4.549699
41	1	0	4.801465	-0.609268	-3.109462
42	1	0	1.941839	-2.359401	-5.815306
43	1	0	4.299360	-2.049557	-5.084662
44	6	0	0.785793	-1.629456	3.529639
45	6	0	2.077416	-1.096196	3.394613
46	6	0	0.575006	-2.644919	4.471973
47	6	0	3.126372	-1.556301	4.190184
48	1	0	2.257079	-0.317563	2.654127
49	6	0	1.626445	-3.112801	5.262081
50	1	0	-0.415640	-3.079259	4.595718
51	6	0	2.903920	-2.566999	5.128070
52	1	0	4.118608	-1.125355	4.072726
53	1	0	1.444955	-3.908116	5.981950
54	1	0	3.721228	-2.929987	5.747528
55	6	0	-1.203999	0.407594	3.587451
56	6	0	-0.306725	1.283572	4.213498
57	6	0	-2.579946	0.635998	3.715738
58	6	0	-0.777150	2.352780	4.973276
59	1	0	0.767326	1.127979	4.111990
60	6	0	-3.049527	1.707456	4.474418
61	1	0	-3.290388	-0.011912	3.207044
62	6	0	-2.150899	2.566642	5.107811
63	1	0	-0.069241	3.021403	5.457557
64	1	0	-4.120387	1.875310	4.561341
65	1	0	-2.517881	3.403011	5.698384
66	6	0	4.209143	-2.438124	-0.090274
67	6	0	4.663397	-1.176209	0.315716
68	6	0	5.127673	-3.413146	-0.504724
69	6	0	6.028937	-0.892858	0.307964
70	1	0	3.937858	-0.420614	0.622681
71	6	0	6.491029	-3.123569	-0.515932
72	1	0	4.779356	-4.395865	-0.821878
73	6	0	6.941413	-1.863951	-0.109468
74	1	0	6.378819	0.087151	0.621608
75	1	0	7.202186	-3.878172	-0.841972
76	1	0	8.005245	-1.640118	-0.120424
77	6	0	2.030094	-4.024888	1.101962
78	6	0	2.968714	-4.559608	1.990377
79	6	0	0.701278	-4.480514	1.112661
80	6	0	2.584433	-5.568274	2.875633
81	1	0	3.993029	-4.187448	1.995532

82	6	0	0.329884	-5.490133	1.997697
83	1	0	-0.037289	-4.027012	0.443434
84	6	0	1.270465	-6.038428	2.874867
85	1	0	3.311633	-5.979854	3.571155
86	1	0	-0.697710	-5.846397	2.003394
87	1	0	0.976672	-6.827454	3.563324

Sum of electronic and zero-point Energies= -3672.735026
Sum of electronic and thermal Energies= -3672.686079
Sum of electronic and thermal Enthalpies= -3672.685135
Sum of electronic and thermal Free Energies= -3672.819528

Reference 40: Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.