Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Structure, Bonding and Adaptive Aromaticity in Rhenium-oxo Complexes: A DFT Study

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Table S1. The π-EDDB comparison of B3LYP and CAM-B3LYP with the def2-TZVP basis set. The α spin and β spin in triplet states are divided by "//", (α spin//β spin)

π-EDDB	**1-S_0**	**2-S_0**	**3-S_0**	**4-S_0**	**1-T_1**	**2-T_1**	**3-T_1**	**4-T_1**
B3LYP	5.36	5.44	5.65	6.58	1.70//1.19	2.21//1.35	2.03//1.76	3.15//3.56
CAM-B3LYP	5.36	5.44	5.64	6.58	1.70//1.18	2.21//1.35	2.02//1.76	3.15//3.56

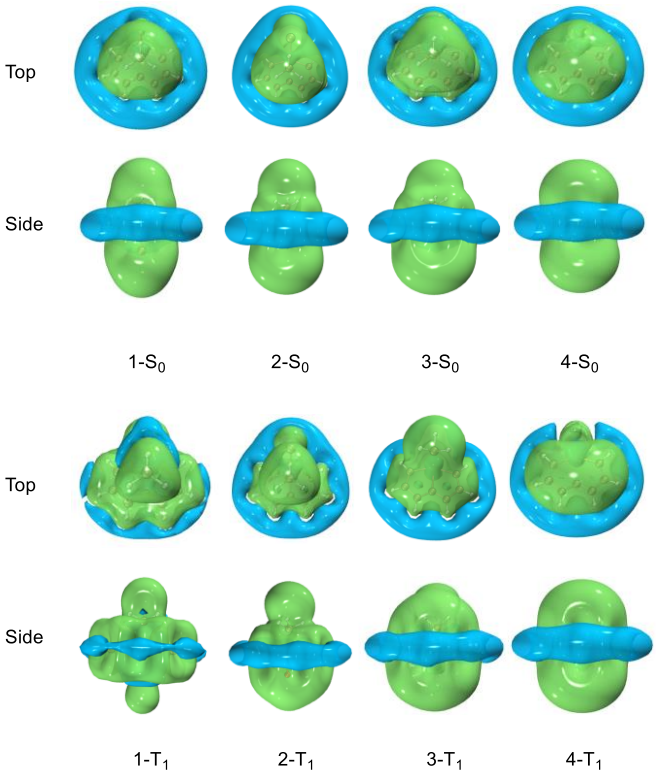

Fig. S1. The $ICSS_{ZZ}$ (iso-chemical shielding surfaces) plots, top and side views, isovalue 2. Spaces in green means magnetic shielding, and blue means magnetic deshielding.

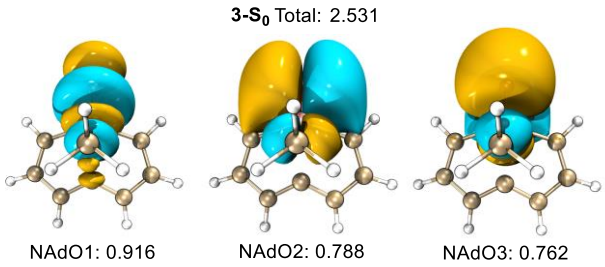

Fig. S2. The BOD analysis of **3-S_0**, isovalue 0.01 a.u.

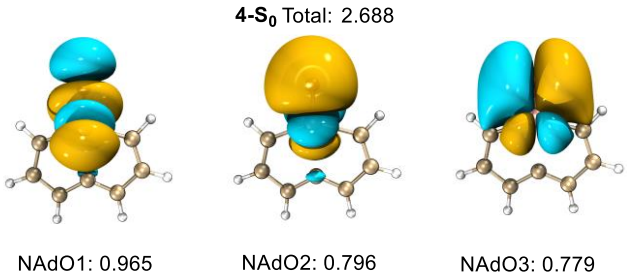

Fig. S3. The BOD analysis of **4-S_0**, isovalue 0.01 a.u.

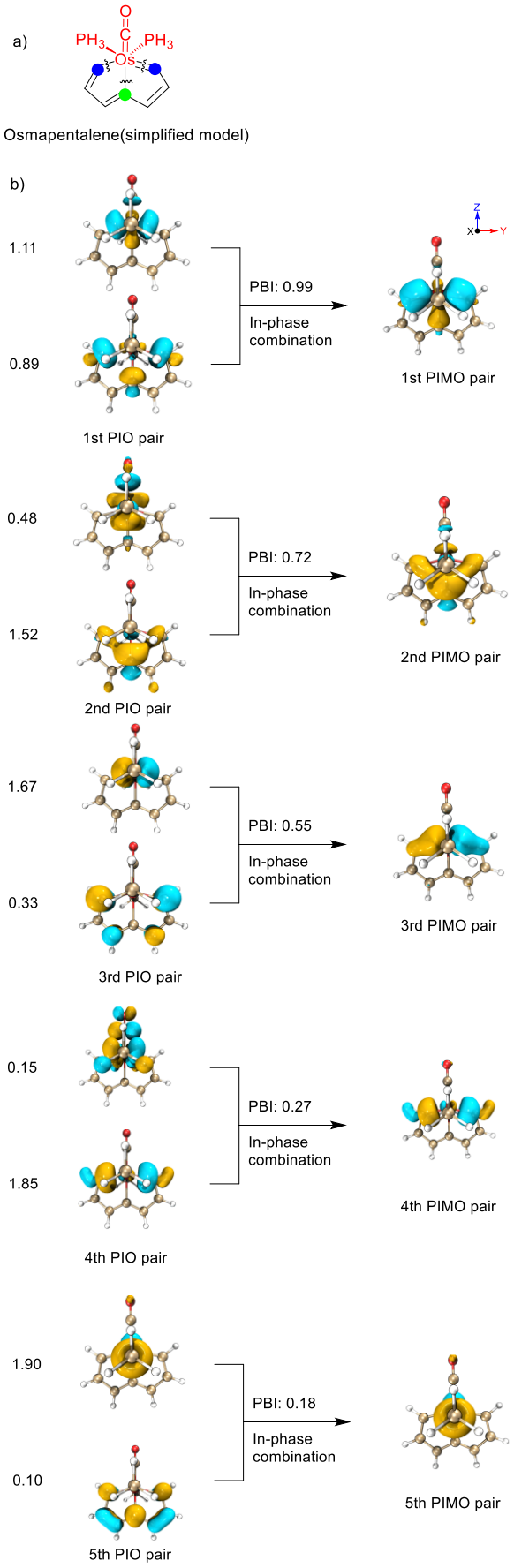

Fig. S4. The PIO analysis of simplified 18e osmapentalene based on reported geometry structure (Zhu C, *et al. Nat. Commun.* 2014, 5 (1), 3265), isovalue 0.05 a.u.

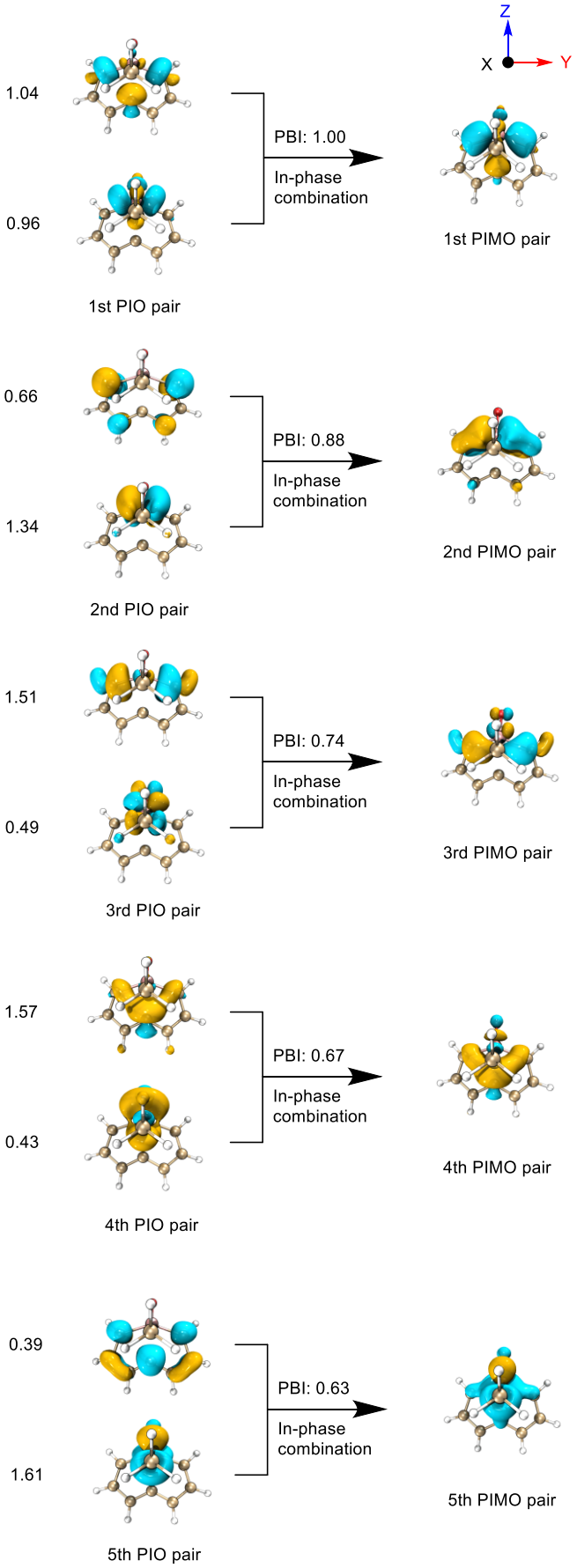

Fig. S5. The PIO analysis of **3-S_0**, isovalue 0.05 a.u.

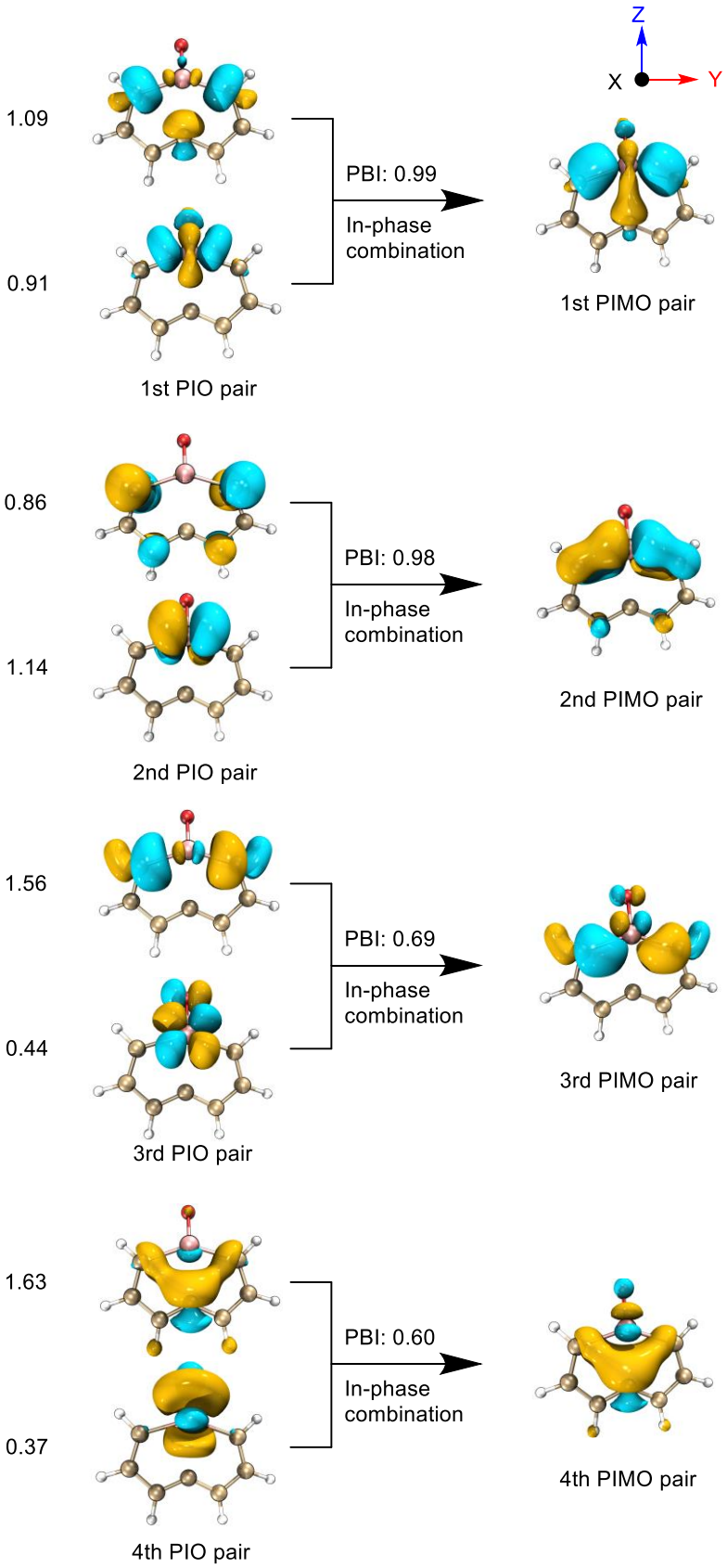

Fig. S6. The PIO analysis of **4-S_0**, isovalue 0.05 a.u.

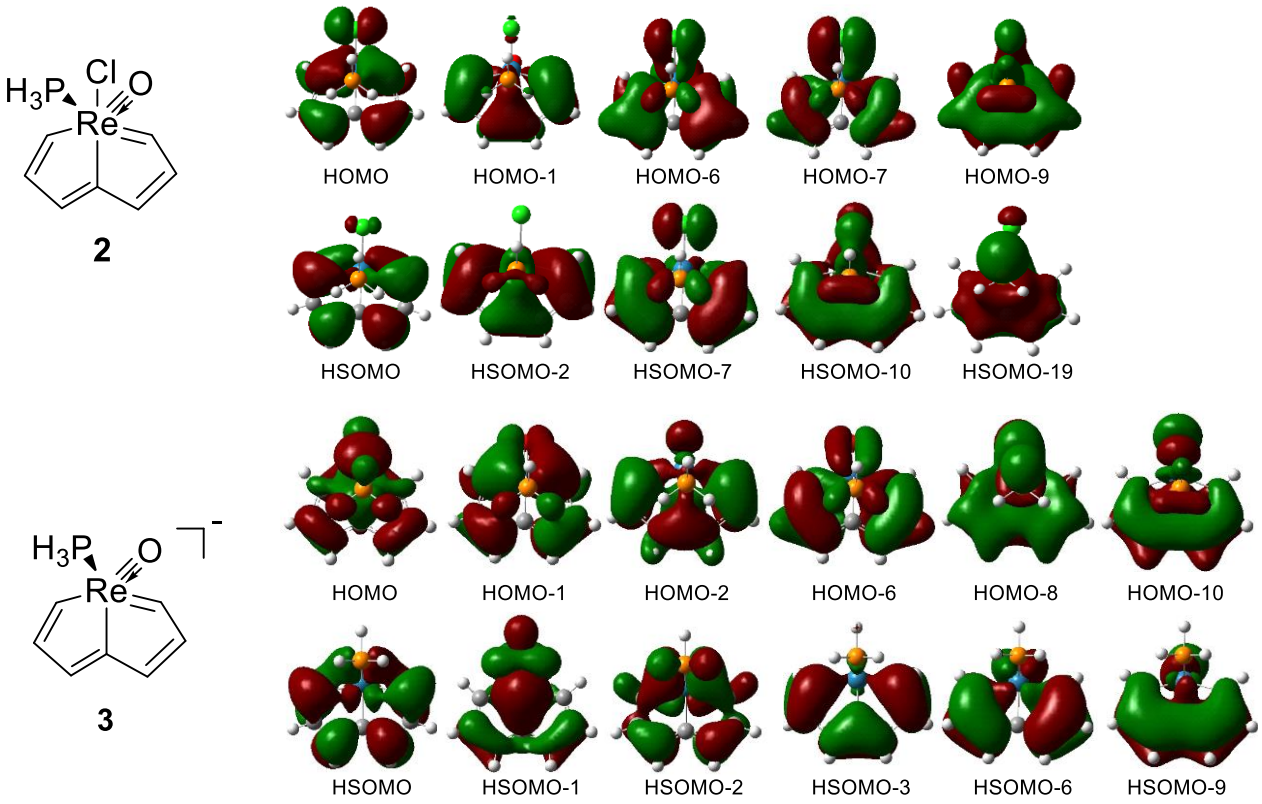

Fig. S7. The occupied π-type molecular orbitals of **2** and **3** in the ground state and triplet states, isovalue 0.02 a.u.

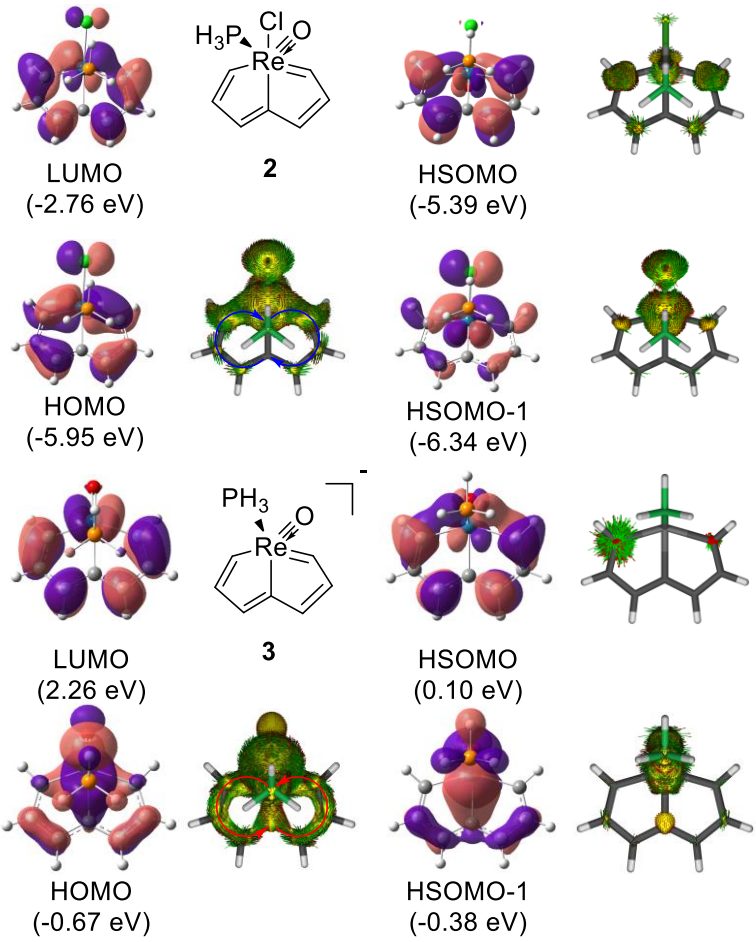

Fig. S8. AICD plots for the HOMO-LUMO of ground states and HSOMO, HSOMO-1 of triplet states of **2** and **3**. The key frontier molecular orbitals in ground states are corresponding to the excitation pattern. The isovalues for MO and AICD are both 0.03 a.u.

Cartesian coordinates together with the electronic energies for all the complexes calculated.

1-S_0

E = -1227.464640 a.u.

C	1.658389	1.641608	1.249754
C	0.974719	1.035684	2.314927
C	0.020798	0.111836	1.939458
C	1.276892	1.178675	-0.0003
C	0.020913	0.110717	-1.939513
C	0.974903	1.03431	-2.315464
C	1.658524	1.640829	-1.250608
H	2.409155	2.413812	1.406184
H	1.187358	1.277051	3.351287
H	-0.510095	-0.46071	2.699132
H	-0.50994	-0.462261	-2.698889
H	1.187609	1.275063	-3.351953
H	2.409334	2.41291	-1.407439
Re	-0.433225	-0.337497	0.000077
Cl	-2.139809	1.292122	-0.000393
P	1.709819	-1.521484	0.000503
H	2.576464	-1.309059	1.086015
H	1.641413	-2.930347	0.000948
H	2.57652	-1.309755	-1.085105
O	-1.157165	-1.907525	0.000453

2-S_0

E = -1227.459063 a.u.

C	-2.442257	-1.246331	-0.217398
C	-1.540736	-2.314299	-0.176855
C	-0.219363	-1.927342	-0.224245
C	-1.833	0.000075	-0.287322
C	-0.219234	1.927359	-0.224079
C	-1.540585	2.314414	-0.176588

C	-2.442175	1.246523	-0.217226
H	-3.52014	-1.37734	-0.194985
H	-1.85704	-3.351119	-0.144982
H	0.567867	-2.652735	-0.428445
H	0.568037	2.652711	-0.428272
H	-1.856804	3.351256	-0.144591
H	-3.52005	1.377598	-0.194786
Re	0.398458	0.00001	-0.380356
P	-0.466057	-0.000162	2.177403
H	-1.260102	-1.071157	2.636206
H	0.508766	-0.000448	3.194368
H	-1.259747	1.070979	2.636489
O	1.070606	0.000039	-1.953183
Cl	2.446762	-0.000044	0.806021

3-S_0

E = -767.254546 a.u.

C	-0.061687	1.914327	-0.339003
C	1.261362	2.309189	-0.574279
C	2.151303	1.246967	-0.673724
C	1.528611	0.000716	-0.489193
C	2.152537	-1.245403	-0.673389
C	1.263554	-2.308106	-0.574373
C	-0.060158	-1.913878	-0.339568
H	1.563971	3.347492	-0.696749
H	3.20544	1.372698	-0.923395
H	3.207055	-1.370112	-0.921907
H	1.56652	-3.346249	-0.696851
H	-0.828787	-2.689703	-0.298344
Re	-0.668985	-0.000317	-0.080042
O	-2.362819	-0.000578	-0.5605
P	0.592868	0.000112	1.913838
H	1.473512	1.079011	2.204982
H	-0.059786	0.00018	3.185455
H	1.473113	-1.079135	2.204409
H	-0.830751	2.689628	-0.29683

4-S_0

E = -424.030870 a.u.

C	-2.28397900	-1.24785900	0.11537400
C	-1.35613100	-2.30056600	0.01344000
C	-0.01969200	-1.92930000	-0.04617100
C	-1.68636100	-0.00002800	0.14411800
C	-0.01975500	1.92928100	-0.04615700
C	-1.35621600	2.30052100	0.01343300
C	-2.28402300	1.24779600	0.11535900
H	-3.36078200	-1.42640200	0.15989100
H	-1.68128900	-3.34210300	0.00426300
H	0.73623200	-2.71508500	-0.00516400
H	0.73614600	2.71508800	-0.00510400
H	-1.68139100	3.34205200	0.00425300
H	-3.36083400	1.42629300	0.15987500
Re	0.60079700	0.00001200	-0.08933000
O	2.19863800	0.00002200	0.56567200

1-T_1

E = -1227.409113 a.u.

C	-1.70012	1.249343	1.584112
C	-0.99581	2.354696	1.014744
C	-0.01102	2.050366	0.138863
C	-1.261653	0.000011	1.165348
C	-0.011015	-2.050365	0.138904
C	-0.995793	-2.354677	1.014802
C	-1.700104	-1.249312	1.58415
H	-2.482393	1.385543	2.326479
H	-1.223423	3.376563	1.30492
H	0.664207	2.804545	-0.257647
H	0.664206	-2.804551	-0.257602
H	-1.223403	-3.376539	1.305003
H	-2.482366	-1.385499	2.326531
Re	0.451808	-0.000003	-0.30375
Cl	2.217893	0.000023	1.146783
P	-1.757627	-0.000019	-1.485498
H	-2.615471	1.08904	-1.270273
H	-1.677707	-0.000035	-2.893571
H	-2.615469	-1.089074	-1.270247
O	0.97744	-0.000028	-1.948836

2-T_1

E = -1227.433944 a.u.

C	-2.356992	-1.262589	-0.229683
C	-1.453387	-2.346759	-0.070545
C	-0.12863	-2.027092	0.014188
C	-1.773077	0.000273	-0.248139
C	-0.128041	2.027129	0.014635
C	-1.452616	2.347199	-0.070293

C	-2.356558	1.263228	-0.229645
H	-3.432693	-1.410191	-0.26905
H	-1.818212	-3.365276	0.026229
H	0.629992	-2.777073	0.220643
H	0.631006	2.776689	0.220995
H	-1.817187	3.365819	0.026419
H	-3.432213	1.41117	-0.269009
Re	0.369031	-0.000063	-0.405551
P	-0.371409	-0.000152	2.236012
H	-1.144364	-1.072886	2.721895
H	0.634455	-0.001033	3.225816
H	-1.14295	1.073382	2.722336
O	0.547808	0.000155	-2.093239
Cl	2.488197	-0.000187	0.583098

3-T_1

E = -767.217611 a.u.

C	0.133219	2.033851	0.021764
C	1.433324	2.348128	0.320306
C	2.323704	1.24752	0.420706
C	1.728541	-0.000799	0.228759
C	2.322645	-1.249559	0.420054
C	1.431291	-2.349508	0.318995
C	0.131559	-2.03393	0.020629
H	1.779168	3.369455	0.484421
H	3.373931	1.368022	0.688683
H	3.372693	-1.371171	0.68826
H	1.776395	-3.371181	0.482504
H	-0.59739	-2.844285	-0.055182
Re	-0.362095	0.000316	-0.367047
O	-1.014166	0.001335	-1.97593
P	-1.630787	-0.000211	1.608302
H	-3.027104	-0.000042	1.333307
H	-1.688025	-1.058491	2.567369
H	-1.688209	1.057256	2.568257
H	-0.594892	2.845004	-0.053466

4-T_1

E = -424.017630 a.u.

C	-2.308982	-1.248463	0.000089
C	-1.390607	-2.304537	0.000234
C	-0.043989	-1.919519	0.000111
C	-1.692442	0.0002	-0.000348
C	-0.043268	1.919509	0.000329
C	-1.3899	2.30495	0.000225
C	-2.308598	1.249082	-0.000299
H	-3.389477	-1.416184	0.000504
H	-1.707711	-3.347674	0.000652
H	0.708795	-2.712745	0.000063
H	0.709616	2.71265	0.000563
H	-1.706574	3.348197	0.000836
H	-3.389061	1.417096	-0.000513
Re	0.598696	-0.000083	-0.000071
O	2.367364	-0.000302	0.000144