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

Supporting Information for:

Dative versus Electron-Sharing Bonding in N-Oxides and Phosphane Oxides R_3EO and Relative Energies of the R_2EOR Isomers (E = N, P; R = H, F, Cl, Me, Ph). A Theoretical Study

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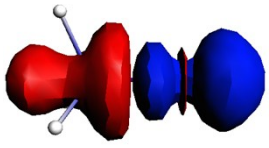
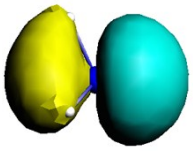
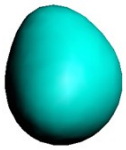
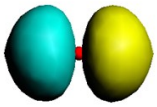
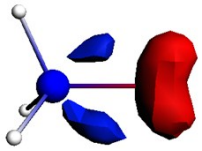
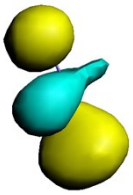
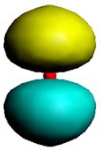
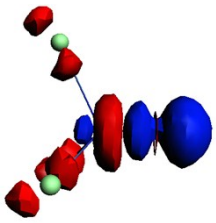
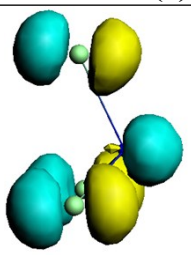
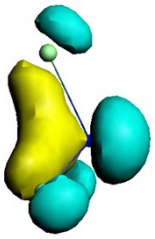
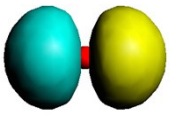
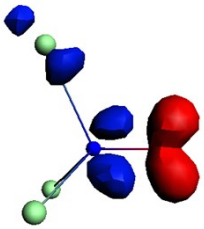
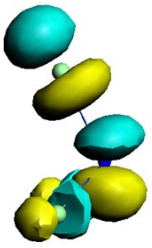
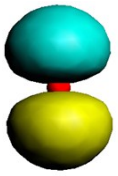
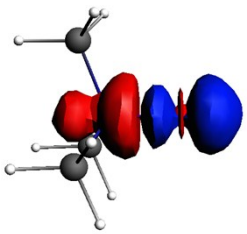
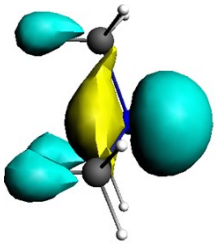
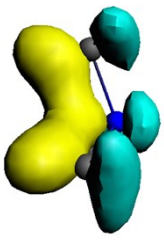
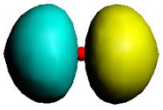
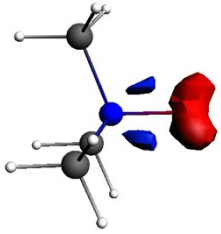
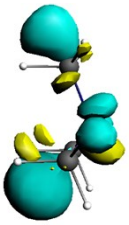
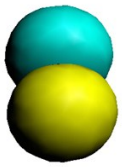
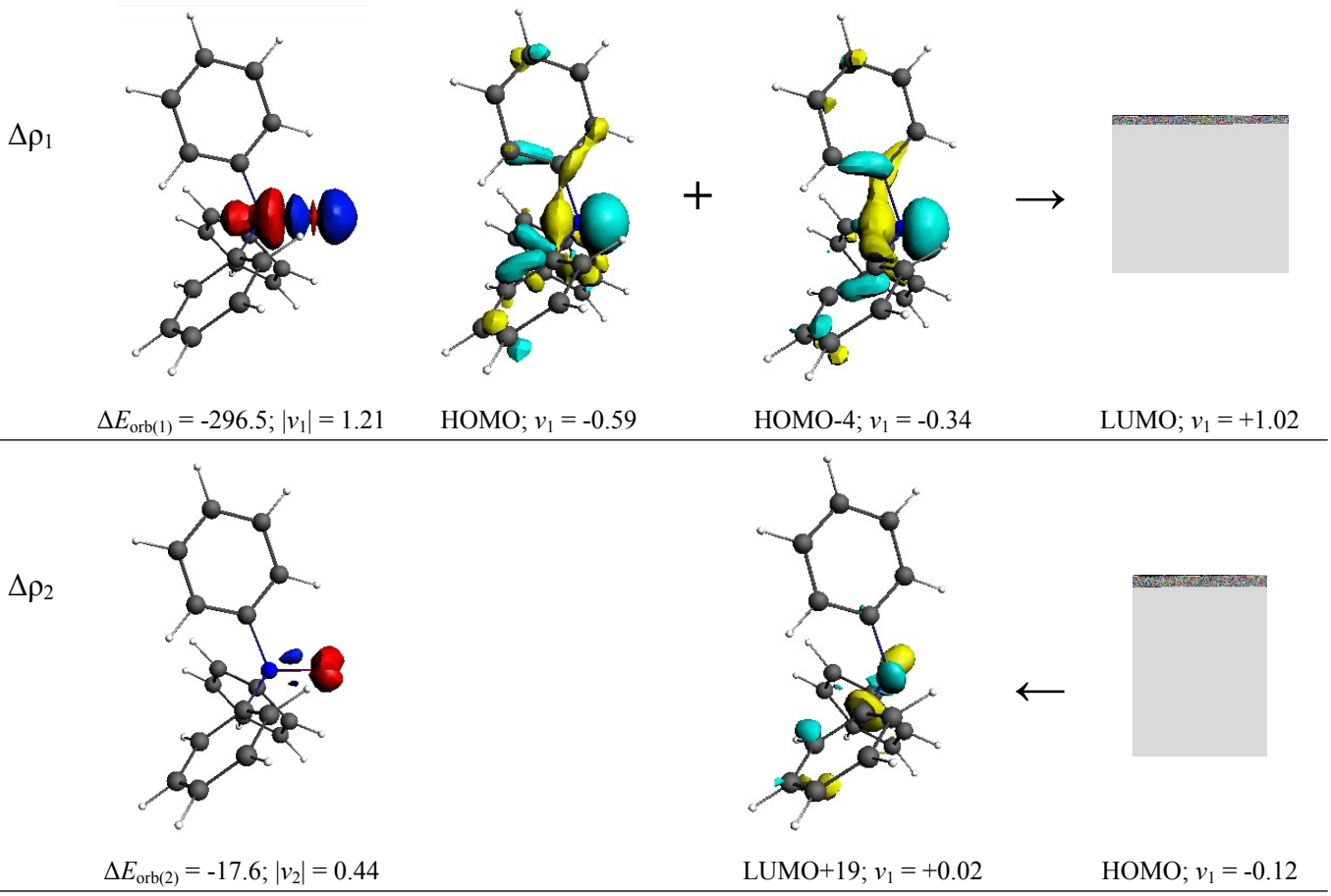
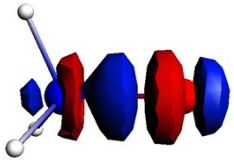
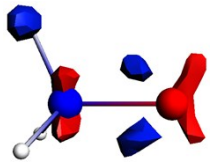
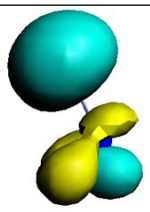
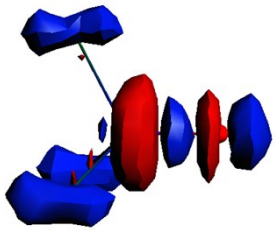
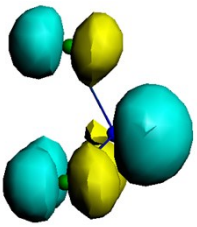
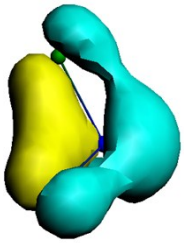
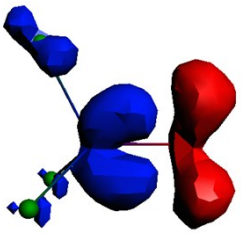
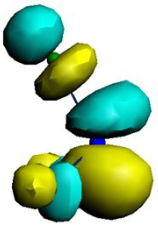
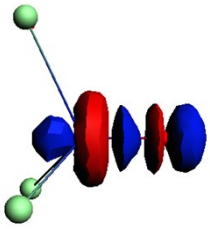
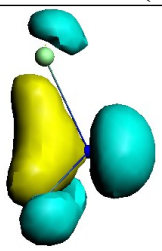
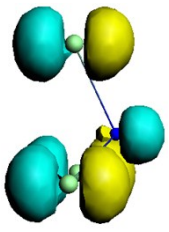
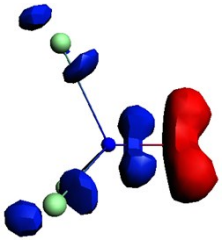
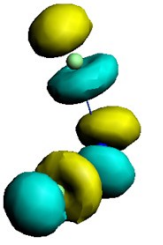
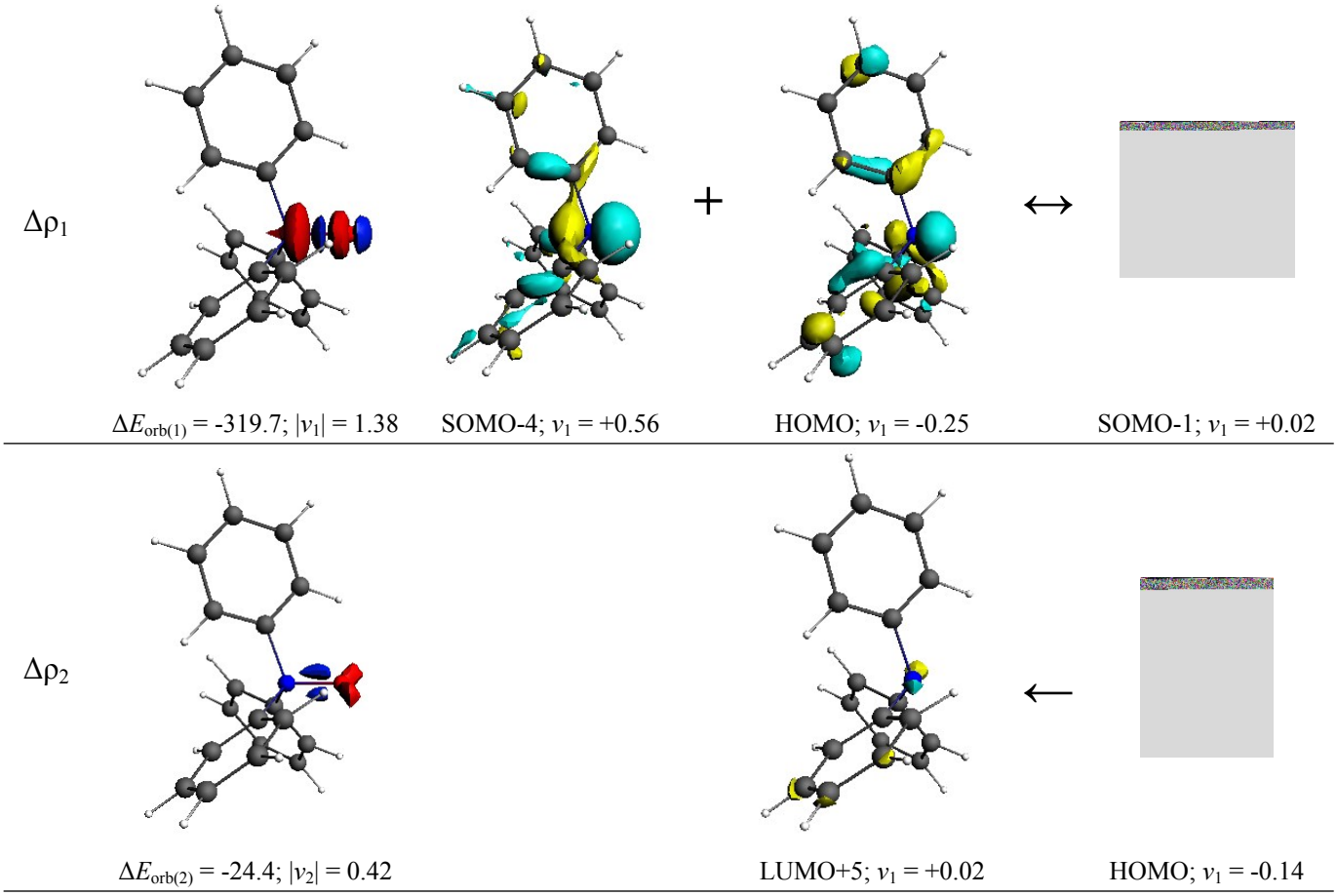
$\Delta\rho_1$			+		→	
	$\Delta E_{orb(1)}$ = -300.0; $\|v_1\|$ = 1.16	HOMO; v_1 = -1.01		HOMO-2; v_1 = -0.05		LUMO ; v_1 = +1.00
$\Delta\rho_2$					←	
	$\Delta E_{orb(2)}$ = -15.4; $\|v_2\|$ = 0.41			LUMO+2; v_1 = +0.08		HOMO ; v_1 = -0.13
(a) H_3NO							
$\Delta\rho_1$			+		→	
	$\Delta E_{orb(1)}$ = -417.3; $\|v_1\|$ = 1.35	HOMO-1; v_1 = -0.63		HOMO-4; v_1 = -0.54		LUMO ; v_1 = +1.15
$\Delta\rho_2$					←	
	$\Delta E_{orb(2)}$ = -62.8; $\|v_2\|$ = 0.84			LUMO+1; v_1 = +0.45		HOMO ; v_1 = -0.46
(b) Cl_3NO							
$\Delta\rho_1$			+		→	
	$\Delta E_{orb(1)}$ = -311.9; $\|v_1\|$ = 1.20	HOMO; v_1 = -0.96		HOMO-5; v_1 = -0.06		LUMO-1; v_1 = +1.03
$\Delta\rho_2$					←	
	$\Delta E_{orb(2)}$ = -15.5; $\|v_2\|$ = 0.41			LUMO+7; v_1 = +0.05		HOMO; v_1 = -0.14
(c) Me_3NO							



(d) Ph_3NO

Fig. S1 Plot of deformation densities Δρ (isovalue 0.01) and shape of the most important occupied and vacant orbitals (isovalue = 0.06) of the pairwise orbital interaction for the N-oxides with dative bonds $R_3N \rightarrow O$ in R_3NO (R = H, Cl, Me, Ph). The color code of the deformation densities is red→blue.

$\Delta\rho_1$				+		↔	
	$\Delta E_{orb(1)}$ = -240.3; $\lvert v_{1\alpha}\rvert$ = 1.14		SOMO; v_1 = -0.07		HOMO-2; v_1 = -0.07		SOMO-1; v_1 = -0.02
$\Delta\rho_2$						←	
	$\Delta E_{orb(2)}$ = -23.2; $\lvert v_{2\alpha}\rvert$ = 0.45				LUMO+1; v_1 = +0.10		HOMO; v_1 = -0.14
(a) H_3NO							
$\Delta\rho_1$				+		↔	
	$\Delta E_{orb(1)}$ = -418.6; $\lvert v_{1\alpha}\rvert$ = 1.31		SOMO; v_1 = +0.34		HOMO-4; v_1 = -0.37		SOMO-1; v_1 = +0.12
$\Delta\rho_2$						←	
	$\Delta E_{orb(2)}$ = -102.2; $\lvert v_{2\alpha}\rvert$ = 0.71				LUMO+1; v_1 = +0.41		HOMO; v_1 = -0.45
(b) F_3NO							
$\Delta\rho_1$				+		↔	
	$\Delta E_{orb(1)}$ = -369.9; $\lvert v_{1\alpha}\rvert$ = 1.29		SOMO-4; v_1 = +0.33		HOMO-2; v_1 = -0.34		SOMO-1; v_1 = +0.16
$\Delta\rho_2$						←	
	$\Delta E_{orb(2)}$ = -99.4; $\lvert v_{2\alpha}\rvert$ = 0.91				LUMO+1; v_1 = +0.48		HOMO; v_1 = -0.49
(c) Cl_3NO							

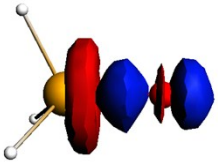
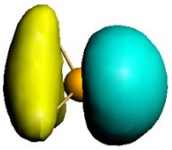
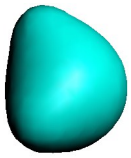
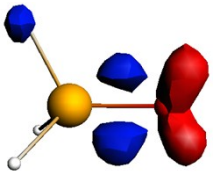
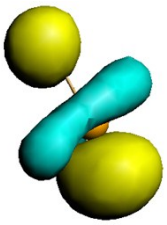
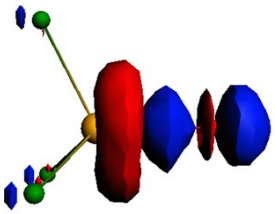
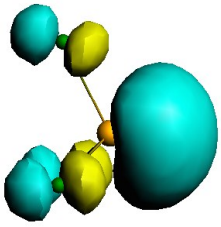
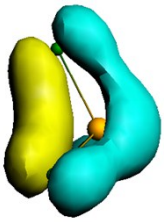
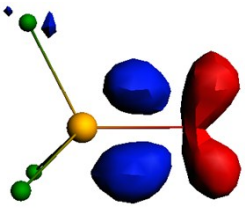
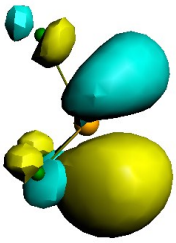
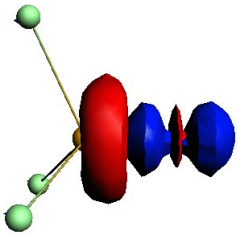
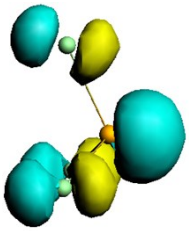
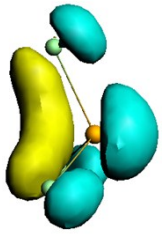
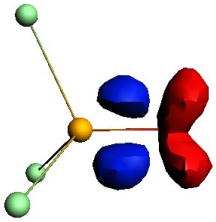
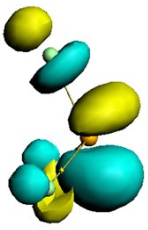


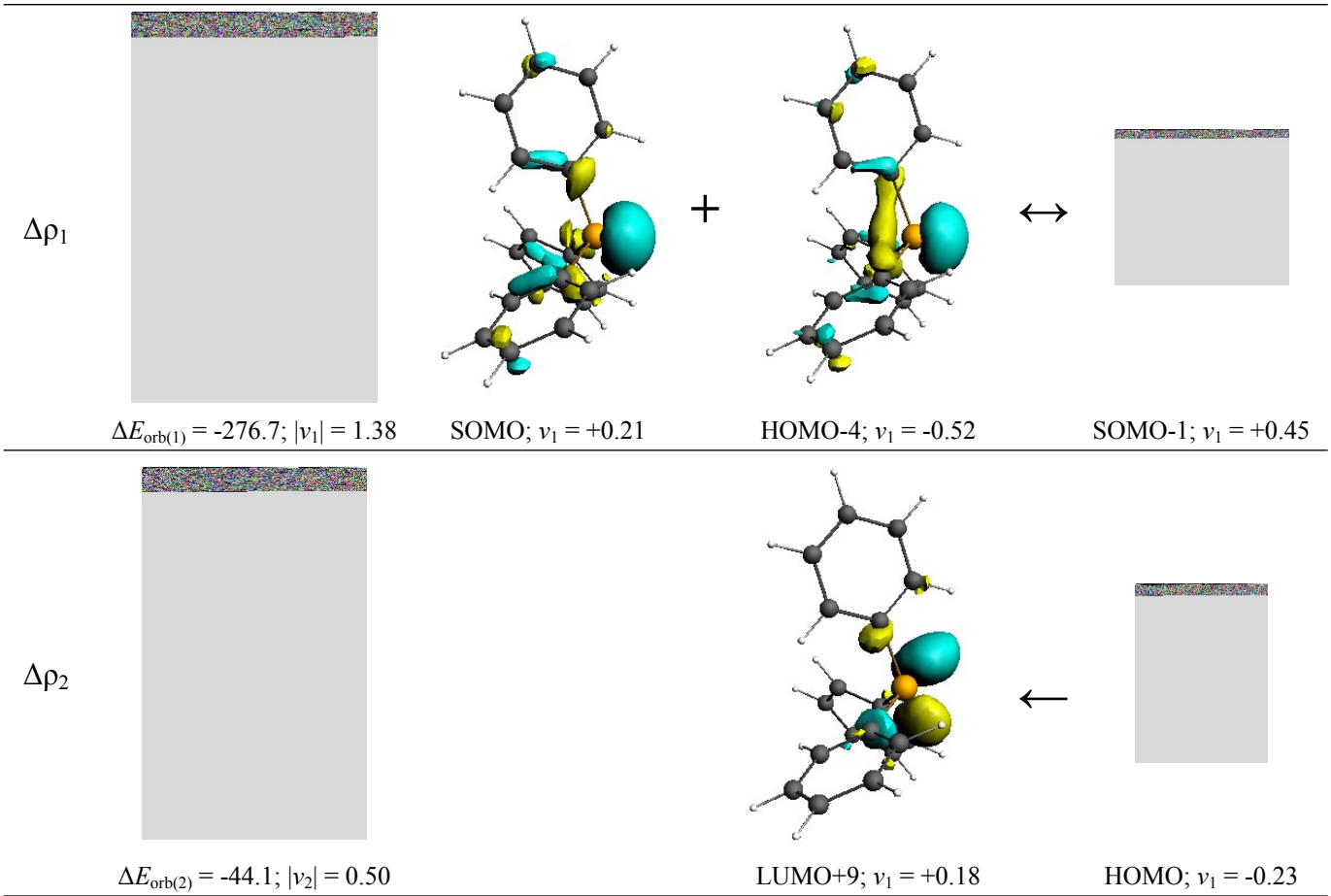
$\Delta E_{orb(1)}$ = -319.7; $|v_1|$ = 1.38 SOMO-4; v_1 = +0.56 HOMO; v_1 = -0.25 SOMO-1; v_1 = +0.02

$\Delta E_{orb(2)}$ = -24.4; $|v_2|$ = 0.42 LUMO+5; v_1 = +0.02 HOMO; v_1 = -0.14

(d) Ph_3NO

Fig. S2 Plot of deformation densities Δρ (isovalue 0.01) and shape of the most important occupied and vacant orbitals (isovalue = 0.06) of the pairwise orbital interaction for the N-oxides with electron-sharing bonds R_3N^+-O^- (R = H, F, Cl, Ph). The color code of the deformation densities is red→blue.

$\Delta\rho_1$			+		↔		
	$\Delta E_{orb(1)}$ = -209.0; $\|v_{1\alpha}\|$ = 1.10	SOMO; v_1 = -0.31		HOMO-2; v_1 = -0.12		SOMO-1; v_1 = +0.36	
$\Delta\rho_2$					←		
	$\Delta E_{orb(2)}$ = -49.7; $\|v_{2\alpha}\|$ = 0.54			LUMO; v_1 = +0.26		HOMO; v_1 = -0.32	
(a) H_3PO							
$\Delta\rho_1$			+		↔		
	$\Delta E_{orb(1)}$ = -234.7; $\|v_{1\alpha}\|$ = 1.11	SOMO; v_1 = -0.21		HOMO-4; v_1 = -0.13		SOMO-1; v_1 = +0.39	
$\Delta\rho_2$					←		
	$\Delta E_{orb(2)}$ = -59.2; $\|v_{2\alpha}\|$ = 0.54			LUMO; v_1 = +0.32		HOMO; v_1 = -0.36	
(b) F_3PO							
$\Delta\rho_1$			+		↔		
	$\Delta E_{orb(1)}$ = -240.7; $\|v_{1\alpha}\|$ = 1.26	HOMO; v_1 = -0.04		HOMO-4; v_1 = -0.06		SOMO-1; v_1 = +0.39	
$\Delta\rho_2$					←		
	$\Delta E_{orb(2)}$ = -59.5; $\|v_{2\alpha}\|$ = 0.60			LUMO+1; v_1 = +0.31		HOMO; v_1 = -0.38	
(c) Cl_3PO							



(d) Ph_3PO

Fig. S3 Plot of deformation densities Δρ (isovalue 0.01) and shape of the most important occupied and vacant orbitals (isovalue = 0.06) of the pairwise orbital interaction for the phosphane oxides with electron-sharing bonds R_3P^+-O^- (R = H, F, Cl, Ph). The color code of the deformation densities is red→blue.

Energies and Cartesian coordinates of R_3EO, R_2EOR, and ER_3 (E = N, P; R = H, F, Cl, Me, Ph).

(I) BP86/def2-TZVPP Optimized Geometries.

O(^{3}P)

```
O     0.000000    0.000000    0.000000
Energy: -75.0930319532 a.u.
CCSD(T)/def2-TZVPP: -74.97662162 a.u.
```

NH_3

```
N     0.000000    0.000000    0.117937
H     0.000000    0.943357   -0.275185
H    -0.816971   -0.471679   -0.275185
H     0.816971   -0.471679   -0.275185
Energy: -56.5901217438 a.u.
CCSD(T)/def2-TZVPP: -56.47580781 a.u.
```

NF_3

```
N     0.000000    0.000000    0.493688
F     0.000000    1.256833   -0.127993
F    -1.088449   -0.628417   -0.127993
F     1.088449   -0.628417   -0.127993
Energy: -354.282920572 a.u.
CCSD(T)/def2-TZVPP: -353.69440128 a.u.
```

NCl_3

```
N     0.000000    0.000000    0.575528
Cl    0.000000    1.673462   -0.078994
Cl   -1.449260   -0.836731   -0.078994
Cl    1.449260   -0.836731   -0.078994
Energy: -1435.465860141 a.u.
CCSD(T)/def2-TZVPP: -1433.72183965 a.u.
```

NMe_3

```
N     0.000005   -0.000016    0.376426
C    -0.072235    1.387056   -0.060912
H    -0.987733    1.853178    0.328542
H     0.789798    1.945859    0.328662
H    -0.077684    1.493466   -1.169987
C    -1.165140   -0.756073   -0.060921
H    -2.080083   -0.288922    0.328672
H    -1.254515   -0.813910   -1.169972
H    -1.111193   -1.782058    0.328434
C     1.237374   -0.630973   -0.060921
H     1.332145   -0.679505   -1.169950
H     2.098867   -0.071156    0.328392
H     1.290363   -1.656900    0.328742
Energy: -174.5457198733 a.u.
CCSD(T)/def2-TZVPP: -174.16461111 a.u.
```

NPh_3

```
N     0.000126    0.000121   -0.001287
C    -1.110520    0.885883   -0.000598
C    -1.094181    2.054150   -0.783514
C    -2.245309    0.609616    0.782959
C    -2.183852    2.924330   -0.773616
C    -3.335958    1.478619    0.774638
C    -3.313267    2.642902    0.000958
H    -0.222310    2.273498   -1.398894
H    -2.264970   -0.289695    1.397656
H    -2.153622    3.823972   -1.389251
H    -4.205799    1.248696    1.390895
H    -4.165071    3.322477    0.001653
C     1.322536    0.518861   -0.000638
C     2.326332   -0.080520   -0.782466
C     1.650724    1.640529    0.781823
```

C 3.624868 0.427815 -0.772689
C 2.948735 2.150294 0.773342
C 3.945859 1.547452 0.000682
H 2.080494 -0.945956 -1.396885
H 0.881647 2.108081 1.395762
H 4.388944 -0.049100 -1.387520
H 3.184456 3.019234 1.388678
H 4.960347 1.945192 0.001185
C -0.211896 -1.404548 -0.000640
C 0.593975 -2.249315 0.783518
C -1.231405 -1.974282 -0.784212
C 0.386467 -3.628294 0.775053
C -1.440467 -3.353004 -0.774451
C -0.632730 -4.190563 0.000632
H 1.382252 -1.816812 1.398806
H -1.856748 -1.328761 -1.400016
H 1.019923 -4.266755 1.391789
H -2.234359 -3.776460 -1.390656
H -0.795526 -5.268010 0.001117
Energy: -749.9974928101 a.u.

H_3NO
N 0.000000 0.000000 -0.526097
H 0.000000 0.958096 -0.954118
H -0.829735 -0.479048 -0.954118
H 0.829735 -0.479048 -0.954118
O 0.000000 0.000000 0.818129
Energy: -131.7557198331 a.u.
CCSD(T)/def2-TZVPP: -131.49909986 a.u.

H_2NOH
N -0.696809 0.000242 0.157147
H -1.046000 -0.814653 -0.359472
H -1.046133 0.813549 -0.361999
O 0.731627 -0.000257 -0.141039
H 1.116779 0.001470 0.749753
Energy: -131.7928993157 a.u.
CCSD(T)/def2-TZVPP: -131.54360957 a.u.

F_3NO
N 0.000000 0.000000 0.213725
F 0.000000 1.301036 -0.462038
F -1.126731 -0.650518 -0.462038
F 1.126731 -0.650518 -0.462038
O 0.000000 0.000000 1.372369
Energy: -429.5147727009 a.u.
CCSD(T)/def2-TZVPP: -428.77412735 a.u.

F_2NOF
N -0.505649 0.000131 0.468711
F -0.948443 -1.100779 -0.292328
F -0.948621 1.100505 -0.292709
O 0.656588 0.000327 0.800149
F 1.706712 -0.000119 -0.490759
Energy: -429.4609955352 a.u.
CCSD(T)/def2-TZVPP: -428.71631769 a.u.

Cl_3NO
N 0.000000 0.000000 0.506122
Cl 0.000000 1.763709 -0.332641
Cl -1.527416 -0.881854 -0.332641
Cl 1.527416 -0.881854 -0.332641
O 0.000000 0.000000 1.677728
Energy: -1510.694019772 a.u.
CCSD(T)/def2-TZVPP: -1508.79337179 a.u.

Cl_2NOCl
N -0.532364 -0.000045 -0.651618
Cl -1.110548 1.470399 0.226969

Cl	-1.108450	-1.471406	0.226892
O	0.622986	0.000338	-1.059290
Cl	2.145037	0.000867	0.312941

Energy: -1510.683223353 a.u.
CCSD(T)/def2-TZVPP: -1508.78207401 a.u.

Me_3NO

N	-0.000024	-0.000025	0.095946
O	-0.000133	-0.000090	1.449029
C	1.360527	-0.404204	-0.423066
H	1.566822	-1.396858	-0.013616
H	1.392091	-0.413242	-1.522028
H	2.075309	0.314547	-0.013089
C	-1.030300	-0.975985	-0.423255
H	-0.765428	-1.954484	-0.013408
H	-1.993124	-0.658282	-0.013893
H	-1.053720	-0.998783	-1.522256
C	-0.330103	1.380285	-0.423112
H	-0.336619	1.412387	-1.522071
H	-1.310547	1.639675	-0.014415
H	0.425711	2.055351	-0.012483

Energy: -249.7383941797 a.u.
CCSD(T)/def2-TZVPP: -249.22431391 a.u.

Me_2NOMe

N	0.391410	-0.000061	-0.334382
O	-0.758626	-0.006958	0.573569
C	1.141199	1.211097	-0.011299
H	0.518121	2.089098	-0.218208
H	1.468415	1.240849	1.045866
H	2.026236	1.250934	-0.661249
C	1.152721	-1.204515	-0.013623
H	2.038857	-1.233761	-0.662626
H	1.479190	-1.233671	1.043810
H	0.538524	-2.088061	-0.223300
C	-1.948539	-0.001432	-0.207996
H	-2.018826	0.900300	-0.837949
H	-2.018145	-0.893622	-0.851363
H	-2.775524	-0.006873	0.514653

Energy: -249.7563724566 a.u.
CCSD(T)/def2-TZVPP: -249.24069385 a.u.

Ph_3NO

N	0.000942	-0.000398	0.728785
C	1.442076	0.065989	0.219846
C	2.389312	-0.590044	1.001279
C	1.803205	0.756995	-0.933927
C	3.727132	-0.565440	0.607760
C	3.152157	0.786735	-1.311243
C	4.113069	0.124654	-0.547091
H	2.053272	-1.073004	1.916811
H	1.058413	1.279807	-1.530665
H	4.474292	-1.077652	1.214322
H	3.444531	1.337745	-2.205327
H	5.161807	0.154019	-0.843056
C	-0.663296	-1.280573	0.219881
C	-0.235287	-1.949065	-0.924039
C	-1.717652	-1.761451	0.991671
C	-0.886239	-3.131130	-1.301133
C	-2.367400	-2.930877	0.598147
C	-1.952430	-3.620589	-0.546910
H	0.599228	-1.574184	-1.513248
H	-1.976412	-1.221937	1.900691
H	-0.547302	-3.667995	-2.187354
H	-3.194582	-3.312626	1.196956
H	-2.453356	-4.542461	-0.842777
C	-0.776497	1.214392	0.218577
C	-0.685195	2.362479	1.000556
C	-1.552212	1.180992	-0.937420

C	-1.375576	3.508137	0.605414
C	-2.252559	2.333686	-1.316420
C	-2.162975	3.496749	-0.551587
H	-0.101425	2.313230	1.917725
H	-1.629933	0.274430	-1.534409
H	-1.308268	4.411217	1.212414
H	-2.873466	2.311047	-2.212215
H	-2.713036	4.389750	-0.848720
O	0.000231	-0.001054	2.087149

Energy: -825.1560164583 a.u.

Ph_2NOPh

N	0.382653	0.042867	0.027532
C	1.416901	1.015611	0.037940
C	1.069906	2.374302	-0.075865
C	2.771758	0.658977	0.134977
C	2.063772	3.349316	-0.101414
C	3.758036	1.646211	0.089721
C	3.414994	2.994326	-0.027908
H	0.020532	2.657464	-0.136724
H	3.052784	-0.386130	0.249368
H	1.777969	4.398050	-0.187290
H	4.805486	1.352644	0.165856
H	4.189152	3.760557	-0.056205
C	0.636388	-1.355408	0.049278
C	1.334662	-1.922745	-1.032210
C	0.156487	-2.185646	1.072355
C	1.572753	-3.294945	-1.066762
C	0.386125	-3.562274	1.015060
C	1.098979	-4.124972	-0.044960
H	1.681346	-1.281696	-1.842278
H	-0.398381	-1.751612	1.900678
H	2.117460	-3.720508	-1.909987
H	0.005081	-4.197653	1.815106
H	1.275722	-5.199510	-0.082285
O	-0.668768	0.426191	0.926366
C	-1.918082	0.520785	0.321164
C	-2.964552	0.830846	1.198846
C	-2.154351	0.342056	-1.042862
C	-4.258112	0.966392	0.697668
C	-3.459604	0.480355	-1.526079
C	-4.514442	0.791295	-0.666540
H	-2.749717	0.965021	2.258695
H	-1.329991	0.100535	-1.709561
H	-5.071730	1.209947	1.381376
H	-3.646333	0.340729	-2.591262
H	-5.527513	0.895673	-1.053584

Energy: -825.2036170434 a.u.

PH_3

P	0.000000	0.000000	0.131339
H	0.000000	1.192080	-0.656695
H	-1.032372	-0.596040	-0.656695
H	1.032372	-0.596040	-0.656695

Energy: -343.1982325409 a.u.
CCSD(T)/def2-TZVPP: -342.68916700 a.u.

PF_3

P	0.000000	0.000000	0.505891
F	0.000000	1.390041	-0.281051
F	-1.203811	-0.695021	-0.281051
F	1.203811	-0.695021	-0.281051

Energy: -641.1964161087 a.u.
CCSD(T)/def2-TZVPP: -640.23999606 a.u.

PCl_3

P	0.000000	0.000000	0.729357
Cl	0.000000	1.851667	-0.214517
Cl	-1.603590	-0.925833	-0.214517

```
Cl     1.603590    -0.925833    -0.214517
Energy: -1722.284910249 a.u.
CCSD(T)/def2-TZVPP: -1720.15159743 a.u.
```

PMe_3

```
P      0.000003     0.000029    -0.602137
C      1.470545     0.715875     0.279185
H      2.376355     0.171367    -0.019339
H      1.600717     1.764659    -0.019344
H      1.371192     0.667552     1.374165
C     -0.115275    -1.631439     0.279161
H      0.727907    -2.268634    -0.019306
H     -0.107417    -1.521154     1.374159
H     -1.039725    -2.143696    -0.019198
C     -1.355275     0.915527     0.279210
H     -1.263792     0.853543     1.374175
H     -1.336581     1.972243    -0.019177
H     -2.328663     0.503904    -0.019416
Energy: -461.2029093069 a.u.
CCSD(T)/def2-TZVPP: -460.42747376 a.u.
```

PPh_3

```
P     -0.000271    -0.000227    -1.198736
C      1.313110    -1.022629    -0.398057
C      1.599262    -2.265023    -0.992840
C      2.060869    -0.625297     0.721656
C      2.588412    -3.097893    -0.468017
C      3.062132    -1.453263     1.237866
C      3.325718    -2.692012     0.648596
H      1.042226    -2.576931    -1.878606
H      1.862153     0.338349     1.191084
H      2.793062    -4.059799    -0.939389
H      3.636307    -1.128021     2.106379
H      4.107298    -3.336050     1.052586
C     -1.542762    -0.626204    -0.398790
C     -2.761810    -0.247294    -0.990188
C     -1.573001    -1.477695     0.716953
C     -3.977962    -0.687034    -0.465591
C     -2.791026    -1.930470     1.232765
C     -3.995545    -1.533667     0.647195
H     -2.753270     0.395201    -1.872964
H     -0.639202    -1.791706     1.183638
H     -4.913282    -0.378754    -0.934073
H     -2.796707    -2.594425     2.098154
H     -4.944360    -1.887981     1.051015
C      0.228882     1.648437    -0.398862
C     -0.495650     2.102152     0.714675
C      1.169549     2.512904    -0.988092
C     -0.278048     3.383282     1.230397
C      1.397446     3.785838    -0.463576
C      0.670758     4.226167     0.646981
H     -1.237043     1.452090     1.179643
H      1.723600     2.182917    -1.869170
H     -0.852055     3.721556     2.094034
H      2.134465     4.440215    -0.930412
H      0.838873     5.224961     1.050708
Energy: -1036.628030944 a.u.
```

H_3PO

```
P      0.000000     0.000000     0.383381
H      0.000000     1.268725     1.036250
H      1.098748    -0.634363     1.036250
H     -1.098748    -0.634363     1.036250
O      0.000000     0.000000    -1.107433
Energy: -418.4764304583 a.u.
CCSD(T)/def2-TZVPP: -417.83587021 a.u.
```

H_2POH

```
P      0.561460     0.141584     0.003368
```

H 0.936232 -0.762286 -1.045673
H 0.935599 -0.811556 1.007905
O -1.092703 -0.155904 -0.003313
H -1.552107 0.697306 0.013744
Energy: -418.4764179631 a.u.
CCSD(T)/def2-TZVPP: -417.83691804 a.u.

F_3PO
P 0.000000 0.000000 0.150319
F 0.000000 1.382940 -0.558693
F -1.197661 -0.691470 -0.558693
F 1.197661 -0.691470 -0.558693
O 0.000000 0.000000 1.603741
Energy: -716.5019375512 a.u.
CCSD(T)/def2-TZVPP: -715.42373944 a.u.

F_2POF
P 0.590737 0.000013 0.521374
F 0.880791 1.192489 -0.488431
F 0.880801 -1.192508 -0.488400
O -1.003586 0.000013 0.723644
F -1.854078 -0.000015 -0.535365
Energy: -716.3243287228 a.u.
CCSD(T)/def2-TZVPP: -715.22046539 a.u.

Cl_3PO
P 0.000000 0.000000 0.428773
Cl 0.000000 1.839242 -0.423647
Cl -1.592831 -0.919621 -0.423647
Cl 1.592831 -0.919621 -0.423647
O 0.000000 0.000000 1.896797
Energy: -1797.578954904 a.u.
CCSD(T)/def2-TZVPP: -1795.32063618 a.u.

Cl_2POCl
P -0.596491 -0.000113 0.845154
Cl -1.041714 -1.591292 -0.401530
Cl -1.043263 1.590523 -0.401645
O 1.014615 0.000474 0.977953
Cl 2.133827 0.000646 -0.402761
Energy: -1797.488662948 a.u.
CCSD(T)/def2-TZVPP: -1795.21907274 a.u.

Me_3PO
P -0.000032 -0.000008 0.183304
O -0.000000 -0.000218 1.679308
C 1.173926 1.188814 -0.554577
H 2.186628 0.948315 -0.206934
H 1.152560 1.167529 -1.652168
H 0.920854 2.198340 -0.206610
C 0.442567 -1.610912 -0.554943
H 1.443417 -1.896492 -0.207039
H -0.272017 -2.367822 -0.207505
H 0.434863 -1.581562 -1.652574
C -1.616479 0.422311 -0.554665
H -1.586852 0.415417 -1.652199
H -2.363975 -0.302273 -0.207617
H -1.915093 1.419144 -0.206260
Energy: -536.5148574021 a.u.
CCSD(T)/def2-TZVPP: -535.61013400 a.u.

Me_2POMe
P 0.340305 -0.011396 -0.541872
O -0.952581 -0.338502 0.481387
C 1.017030 1.531744 0.233318
H 0.344188 2.374888 0.028796
H 1.141160 1.422510 1.320075
H 1.990666 1.765181 -0.221814
C 1.512125 -1.226814 0.199934

H	2.519837	-1.041857	-0.197706
H	1.534951	-1.145305	1.295826
H	1.213453	-2.244332	-0.081036
C	-2.260954	-0.033218	-0.012964
H	-2.481021	1.044025	0.066592
H	-2.378677	-0.341770	-1.064068
H	-2.977686	-0.584656	0.608592

Energy: -536.4676384116 a.u.
CCSD(T)/def2-TZVPP: -535.56125460 a.u.

Ph_3PO

P	0.000257	0.000104	0.920247
C	-1.577850	0.600835	0.216777
C	-2.298099	1.530218	0.984777
C	-2.096103	0.175432	-1.015647
C	-3.511457	2.036983	0.516730
C	-3.310981	0.685464	-1.481317
C	-4.017336	1.618311	-0.717670
H	-1.905438	1.832565	1.956138
H	-1.561508	-0.569865	-1.605897
H	-4.067146	2.755489	1.119947
H	-3.710429	0.346027	-2.437467
H	-4.967429	2.011962	-1.080135
C	1.309515	1.066328	0.216679
C	1.199021	1.729291	-1.014865
C	2.475899	1.223299	0.982984
C	2.248259	2.525849	-1.481320
C	3.521416	2.020431	0.514309
C	3.410559	2.669321	-0.719241
H	0.285287	1.640489	-1.603800
H	2.542556	0.730963	1.953704
H	2.153074	3.042464	-2.436855
H	4.422463	2.141023	1.116387
H	4.226546	3.294977	-1.082171
C	0.269098	-1.666858	0.216562
C	-0.172694	-2.755668	0.985755
C	0.892981	-1.902382	-1.017855
C	-0.005919	-4.059688	0.516791
C	1.057561	-3.209331	-1.484495
C	0.605583	-4.287868	-0.719716
H	-0.627926	-2.567077	1.958550
H	1.269052	-1.066448	-1.609028
H	-0.348097	-4.900480	1.120847
H	1.548016	-3.385109	-2.442386
H	0.738696	-5.307335	-1.083005
O	0.000214	-0.000125	2.419506

Energy: -1111.934038949 a.u.

Ph_2POPh

P	0.188156	-0.156259	0.854201
C	1.601071	-1.190986	0.285999
C	1.912428	-2.317972	1.064052
C	2.355532	-0.928535	-0.869254
C	2.952731	-3.173343	0.691664
C	3.392359	-1.784406	-1.242449
C	3.692440	-2.906875	-0.462701
H	1.333406	-2.521944	1.966695
H	2.131932	-0.049321	-1.474085
H	3.186543	-4.044926	1.303671
H	3.972215	-1.574366	-2.141928
H	4.506870	-3.570799	-0.754363
C	0.709686	1.513984	0.279455
C	1.627297	2.221818	1.075575
C	0.181038	2.132833	-0.862877
C	2.027515	3.510354	0.721466
C	0.575464	3.428844	-1.209966
C	1.500530	4.118292	-0.423094
H	2.031571	1.760809	1.979737
H	-0.538853	1.596117	-1.480635

```
H     2.745332    4.045538    1.343994
H     0.156992    3.899790   -2.100297
H     1.806023    5.128877   -0.695246
O    -0.893618   -0.581023   -0.381648
C    -2.260036   -0.584036   -0.174713
C    -3.017002   -1.393734   -1.031670
C    -2.894320    0.194626    0.800764
C    -4.405643   -1.423016   -0.907489
C    -4.286423    0.148648    0.919570
C    -5.048329   -0.655512    0.069628
H    -2.501089   -1.990907   -1.782958
H    -2.304765    0.830024    1.461843
H    -4.988883   -2.055563   -1.577421
H    -4.775305    0.755741    1.682132
H    -6.133414   -0.682907    0.165282
Energy: -1111.904112174 a.u.
```

(II) M06-2X/def2-TZVPP Optimized Geometries.

H_3NO

```
N     3.913316   -0.730741   -3.786606
H     3.913306    0.218367   -3.391459
H     4.735272   -1.205041   -3.391265
H     3.091379   -1.205019   -3.391271
O     3.913326   -0.730434   -5.141495
Energy: -131.6779111410 a.u.
CCSD(T)/def2-TZVPP: -131.50017279 a.u.
```

H_2NOH

```
N     0.677794   -0.000860    0.151908
H     1.042345    0.812703   -0.332578
H     1.042289   -0.809186   -0.341268
O    -0.713606    0.000975   -0.139761
H    -1.120342   -0.005295    0.728573
Energy: -131.7188661260 a.u.
CCSD(T)/def2-TZVPP: -131.54358218 a.u.
```

F_3NO

```
N     0.000000    0.000000    0.190239
F     0.000000    1.246661   -0.448049
F    -1.079640   -0.623330   -0.448049
F     1.079640   -0.623330   -0.448049
O     0.000000    0.000000    1.345706
Energy: -429.2906459075 a.u.
CCSD(T)/def2-TZVPP: -428.77522880 a.u.
```

F_2NOF

```
N     0.542819   -0.000031    0.526326
F     0.844011    1.058480   -0.274816
F     0.843806   -1.058632   -0.274570
O    -0.756855    0.000291    0.731926
F    -1.437250   -0.000083   -0.510580
Energy: -429.2361063263 a.u.
CCSD(T)/def2-TZVPP: -428.71942612 a.u.
```

Cl_3NO

```
N     0.000000    0.000000    0.469014
Cl    0.000000    1.694517   -0.322022
Cl   -1.467495   -0.847258   -0.322022
Cl    1.467495   -0.847258   -0.322022
O     0.000000    0.000000    1.642501
Energy: -1510.3861432530 a.u.
CCSD(T)/def2-TZVPP: -1508.79300005 a.u.
```

Cl_2NOCl

```
N    -0.553184    0.000158    0.694987
Cl   -0.988055   -1.414755   -0.212661
```

Cl	-0.986433	1.415600	-0.212559
O	0.748595	-0.000499	1.000823
Cl	1.849990	-0.000675	-0.331926

Energy: -1510.3848722180 a.u.
CCSD(T)/def2-TZVPP: -1508.78542839 a.u.

Me_3NO

N	0.000073	0.000027	0.079729
O	0.000549	0.000515	1.436160
C	-0.309944	1.366167	-0.415850
H	0.450519	2.026993	-0.012089
H	-0.320519	1.395127	-1.505571
H	-1.277950	1.635811	-0.005625
C	1.338053	-0.415041	-0.415859
H	2.055960	0.288735	-0.006829
H	1.530060	-1.403595	-0.010922
H	1.367902	-0.421607	-1.505587
C	-1.028570	-0.951557	-0.415022
H	-1.049337	-0.975008	-1.504718
H	-0.778054	-1.924878	-0.005278
H	-1.980718	-0.623302	-0.010380

Energy: -249.6058861227 a.u.
CCSD(T)/def2-TZVPP: -249.22526030 a.u.

Me_2NOMe

N	0.390557	-0.124231	-0.300698
O	-0.709234	-0.183291	0.598707
C	1.042084	1.148296	-0.052473
H	0.349667	1.954430	-0.284106
H	1.367838	1.242695	0.990744
H	1.907623	1.226306	-0.708862
C	1.253317	-1.241544	0.038156
H	2.118761	-1.223860	-0.622846
H	1.589475	-1.193910	1.081057
H	0.711547	-2.172238	-0.119778
C	-1.886215	-0.439643	-0.131465
H	-2.079167	0.354140	-0.856094
H	-1.823363	-1.394893	-0.658745
H	-2.694997	-0.478532	0.596320

Energy: -249.6226579350 a.u.
CCSD(T)/def2-TZVPP: -249.24098055 a.u.

Ph_3NO

N	0.021113	-0.008802	0.737245
C	-1.400651	0.080500	0.261356
C	-2.240558	0.889023	1.008383
C	-1.849220	-0.582748	-0.866453
C	-3.556899	1.043202	0.606143
C	-3.176334	-0.425362	-1.255806
C	-4.028555	0.387299	-0.526185
H	-1.844858	1.355853	1.897877
H	-1.189281	-1.218852	-1.438342
H	-4.220147	1.672248	1.184301
H	-3.536957	-0.947286	-2.131526
H	-5.059121	0.505190	-0.832158
C	0.790710	1.183393	0.243354
C	0.450002	1.852071	-0.919271
C	1.880416	1.566928	1.005601
C	1.226916	2.931211	-1.327641
C	2.649777	2.640273	0.584800
C	2.326134	3.324875	-0.581052
H	-0.407818	1.551988	-1.502946
H	2.080288	1.028455	1.919674
H	0.961636	3.463836	-2.230640
H	3.501357	2.948600	1.175832
H	2.924483	4.167228	-0.900230
C	0.647673	-1.274948	0.229953
C	0.320049	-2.428092	0.925153
C	1.480693	-1.309375	-0.872774

C	0.829226	-3.641234	0.495018
C	1.993845	-2.535457	-1.289875
C	1.667646	-3.698995	-0.614160
H	-0.307868	-2.338673	1.798932
H	1.740899	-0.406792	-1.405374
H	0.576942	-4.545642	1.031872
H	2.652344	-2.569050	-2.147022
H	2.069410	-4.647966	-0.942379
O	0.035719	-0.024575	2.100400

Energy: -824.7820819366 a.u.

Ph_2NOPh

N	0.393478	-0.029590	-0.076553
C	1.497054	-0.913757	-0.044561
C	1.240866	-2.274816	0.126790
C	2.810433	-0.470785	-0.169984
C	2.289872	-3.175342	0.179838
C	3.854657	-1.383512	-0.100282
C	3.604585	-2.735753	0.074577
H	0.217689	-2.614066	0.213309
H	3.017809	0.576994	-0.331448
H	2.078360	-4.228015	0.311533
H	4.871595	-1.028428	-0.200259
H	4.422283	-3.441293	0.123068
C	0.514738	1.375375	-0.098597
C	1.250156	1.998775	0.912258
C	-0.146697	2.149740	-1.046498
C	1.348858	3.378304	0.945951
C	-0.050028	3.534368	-0.992005
C	0.699960	4.156501	-0.006662
H	1.733607	1.393214	1.667118
H	-0.734644	1.669734	-1.813881
H	1.924006	3.849348	1.731812
H	-0.568225	4.127255	-1.733718
H	0.771489	5.234513	0.028408
O	-0.603391	-0.510911	-0.923537
C	-1.830666	-0.659387	-0.314613
C	-2.843136	-1.119608	-1.148896
C	-2.074155	-0.381176	1.021052
C	-4.113881	-1.307366	-0.632839
C	-3.357323	-0.575528	1.520540
C	-4.378828	-1.036332	0.705125
H	-2.615341	-1.325588	-2.185745
H	-1.278109	-0.019878	1.653974
H	-4.902020	-1.668226	-1.280032
H	-3.552663	-0.359145	2.562294
H	-5.372493	-1.182589	1.104546

Energy: -824.8268607047 a.u.

H_3PO

P	0.000000	0.000000	0.380047
H	0.000000	1.256045	1.011410
H	1.087767	-0.628023	1.011410
H	-1.087767	-0.628023	1.011410
O	0.000000	0.000000	-1.091867

Energy: -418.3672820631 a.u.
CCSD(T)/def2-TZVPP: -417.83637557 a.u.

H_2POH

P	-0.562516	-0.116680	0.000021
H	-0.850105	0.824659	-1.022104
H	-0.849645	0.824921	1.022037
O	1.083018	-0.086203	-0.000003
H	1.473346	0.790240	-0.000224

Energy: -418.3714632740 a.u.
CCSD(T)/def2-TZVPP: -417.83731187 a.u.

F_3PO

P	0.000000	0.000000	0.145373

F 0.000000 1.358931 -0.548296
F -1.176869 -0.679465 -0.548296
F 1.176869 -0.679465 -0.548296
O 0.000000 0.000000 1.577923
Energy: -716.3037449873 a.u.
CCSD(T)/def2-TZVPP: -715.42524001 a.u.

F_2POF
P -0.612753 -0.000020 0.529538
F -0.778948 -1.168934 -0.498574
F -0.777941 1.169621 -0.497872
O 1.009156 -0.000730 0.713767
F 1.681116 -0.000005 -0.520579
Energy: -716.1025968857 a.u.
CCSD(T)/def2-TZVPP: -715.22308169 a.u.

Cl_3PO
P 0.000000 0.000000 0.421831
Cl 0.000000 1.813252 -0.417245
Cl -1.570322 -0.906626 -0.417245
Cl 1.570322 -0.906626 -0.417245
O 0.000000 0.000000 1.869001
Energy: -1797.2792560230 a.u.
CCSD(T)/def2-TZVPP: -1795.32139145 a.u.

Cl_2POCl
P 0.613274 0.000060 0.864817
Cl 0.967552 1.563041 -0.411967
Cl 0.968005 -1.562817 -0.412010
O -1.004210 -0.000202 0.959554
Cl -2.004111 -0.000182 -0.390652
Energy: -1797.1852747100 a.u.
CCSD(T)/def2-TZVPP: -1795.22072308 a.u.

Me_3PO
P 0.000148 -0.000068 0.180480
O 0.001469 -0.000463 1.658595
C 1.374873 -0.919873 -0.548799
H 1.326392 -1.951461 -0.202940
H 1.343683 -0.898882 -1.637519
H 2.310163 -0.482122 -0.202678
C -1.484930 -0.730887 -0.546833
H -1.573144 -1.760029 -0.201407
H -2.353806 -0.173583 -0.199394
H -1.452170 -0.713561 -1.635585
C 0.108608 1.651253 -0.547405
H 0.101940 1.614558 -1.636162
H -0.736279 2.242755 -0.197487
H 1.027946 2.124083 -0.204565
Energy: -536.3456842656 a.u.
CCSD(T)/def2-TZVPP: -535.61066527 a.u.

Me_2POMe
P 0.341873 -0.019692 -0.545795
O -0.922059 -0.416986 0.446327
C 0.894160 1.549136 0.235590
H 0.160965 2.332564 0.046235
H 1.024275 1.427458 1.311326
H 1.838522 1.860713 -0.213197
C 1.567702 -1.141947 0.213073
H 2.560171 -0.888530 -0.160837
H 1.553987 -1.049024 1.299210
H 1.345791 -2.170560 -0.064926
C -2.218181 -0.065150 0.002664
H -2.367834 1.017695 0.029800
H -2.396818 -0.418447 -1.015633
H -2.932773 -0.532838 0.676372
Energy: -536.3019675237 a.u.
CCSD(T)/def2-TZVPP: -535.56182502 a.u.

Ph_3PO

P	-0.005148	-0.004161	0.929651
C	1.510276	0.703806	0.237620
C	2.663485	0.602133	1.013590
C	1.567357	1.324203	-1.008236
C	3.866308	1.104544	0.538633
C	2.772955	1.823724	-1.481749
C	3.921840	1.711313	-0.709657
H	2.600062	0.144076	1.992549
H	0.668646	1.432378	-1.603571
H	4.758830	1.028624	1.144935
H	2.813341	2.308837	-2.447653
H	4.859798	2.105824	-1.077401
C	-0.146985	-1.665255	0.223842
C	0.380619	-2.022019	-1.014955
C	-0.828961	-2.613844	0.983930
C	0.213172	-3.313049	-1.496969
C	-0.992867	-3.903842	0.500440
C	-0.475572	-4.252320	-0.740740
H	0.936349	-1.297989	-1.598130
H	-1.209402	-2.333236	1.957995
H	0.628484	-3.587832	-2.457174
H	-1.518509	-4.639250	1.094464
H	-0.601354	-5.259510	-1.115009
C	-1.368163	0.955176	0.222568
C	-1.822940	2.041444	0.968366
C	-1.963081	0.659851	-1.001473
C	-2.856039	2.831345	0.485984
C	-2.996236	1.453210	-1.482225
C	-3.440757	2.538855	-0.739743
H	-1.372534	2.245063	1.931645
H	-1.633383	-0.198837	-1.573332
H	-3.209775	3.670866	1.068961
H	-3.460202	1.217631	-2.430483
H	-4.250235	3.152265	-1.112338
O	-0.012104	-0.007482	2.409837

Energy: -1111.5264587910 a.u.

Ph_2POPh

P	-0.324705	-0.617943	-0.959957
C	-1.909585	-1.234603	-0.297399
C	-2.687941	-2.048118	-1.115117
C	-2.357284	-0.925584	0.987749
C	-3.903923	-2.546741	-0.660135
C	-3.562375	-1.431013	1.445681
C	-4.338348	-2.239425	0.619632
H	-2.339442	-2.293762	-2.111016
H	-1.757508	-0.286056	1.623909
H	-4.505646	-3.175125	-1.302999
H	-3.904495	-1.191448	2.443713
H	-5.282913	-2.627192	0.977813
C	-0.445729	1.139197	-0.460524
C	-1.273813	1.978259	-1.207146
C	0.288653	1.672227	0.594725
C	-1.381470	3.323069	-0.890924
C	0.186333	3.023518	0.905944
C	-0.648669	3.848928	0.167478
H	-1.841364	1.574681	-2.038734
H	0.939142	1.030605	1.175680
H	-2.032351	3.963269	-1.471518
H	0.761305	3.429192	1.727761
H	-0.727367	4.899822	0.411382
O	0.650690	-1.200701	0.257051
C	2.004414	-1.317798	0.092934
C	2.644503	-2.310865	0.826757
C	2.736177	-0.473799	-0.734641
C	4.017558	-2.460129	0.726051
C	4.112516	-0.639835	-0.831824

C	4.758849	-1.628277	-0.105823
H	2.048747	-2.950981	1.462650
H	2.239714	0.310096	-1.292007
H	4.511319	-3.234703	1.297579
H	4.678982	0.016938	-1.478405
H	5.830139	-1.749788	-0.184328

Energy: -1111.4972945550 a.u.