Electronic Supplementary Material for Dalton Transactions



Supporting Information for:

# Oxygen Insertion in a Carbon-Phosphorus Bond of the Phenylethynyl-di-(tert-butyl)-phosphine Bridged Dicobalt Complex: Exploring the Nature of Oxygen Migration using DFT

By

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**Supporting Information:**

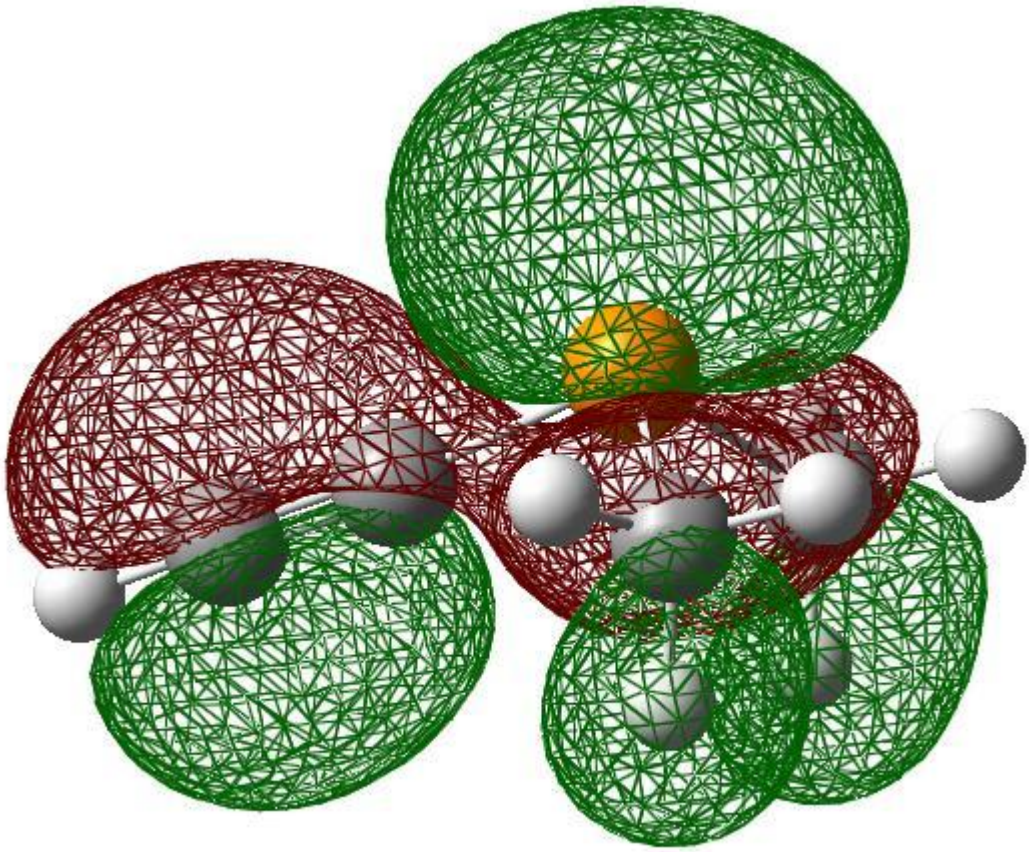

**Fig. S1** Geometry of $HC{\equiv}CPMe_2$ **RP**. Highest occupied molecular orbital (HOMO) plotted at an isovalue of 0.020.

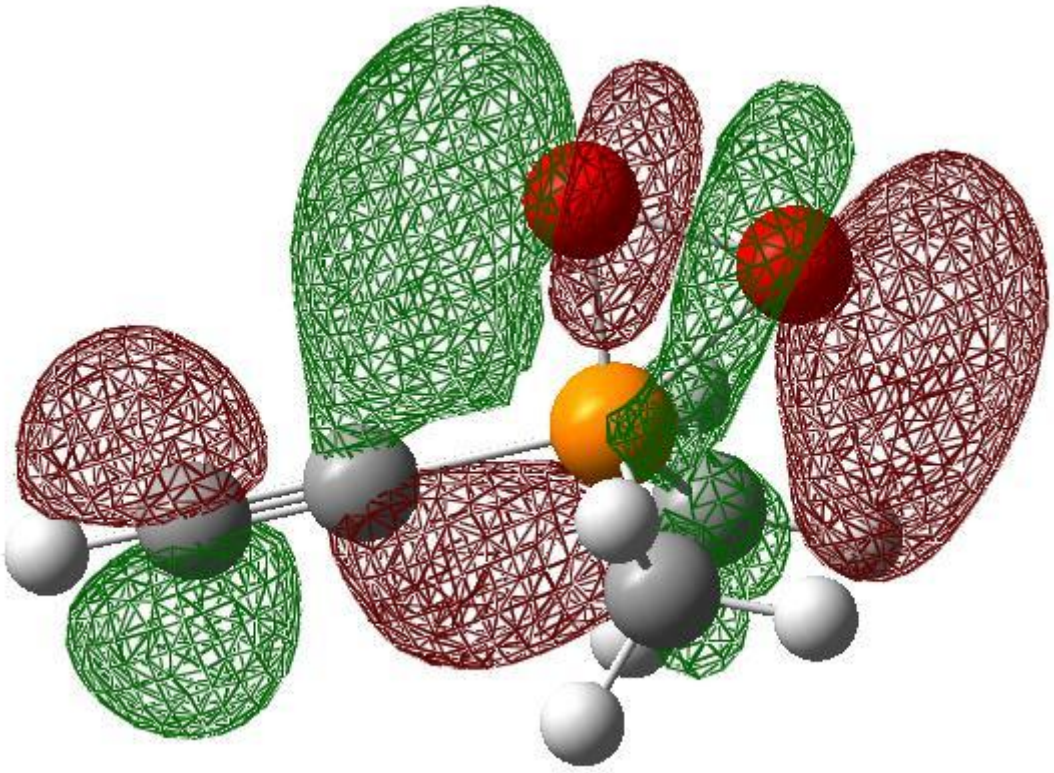

**Fig. S2** Geometry of $HC{\equiv}CPMe_2(\eta^2\text{-}O_2)$ **CP1O**. Lowest unoccupied molecular orbital (LUMO) plotted at an isovalue of 0.020.

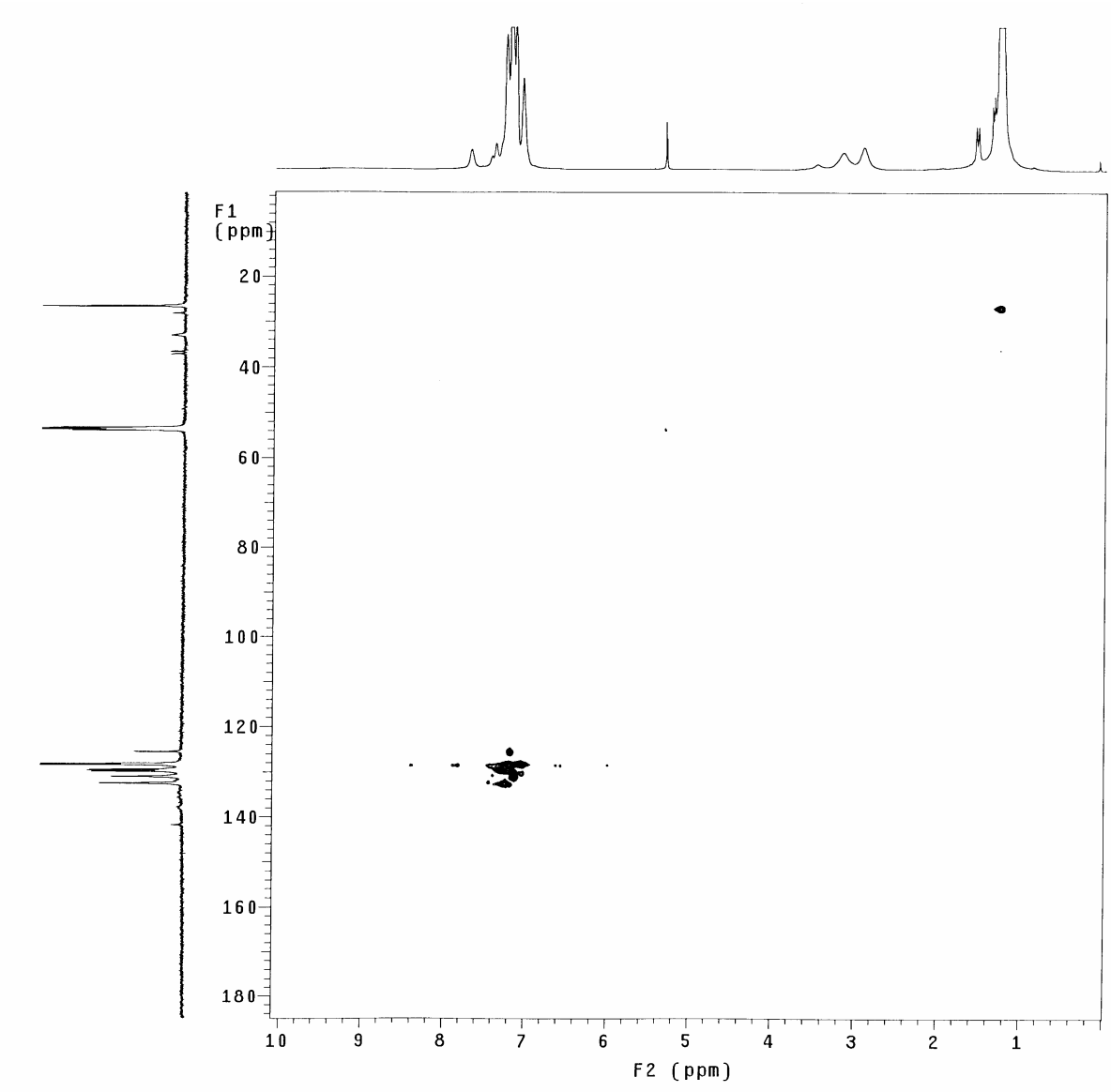


**Fig. S3** $^{1}H$-$^{13}C$ heteronuclear shift correlation NMR experiment of **5**

Redoing calculation with higher level of basis set 6-31+G(d,p) instead of original 6-31G(d,p). The energy differentia of using new basis set is not much and is not the important effect on the activation energy. See below:

**Table S1.** Relative energies of using different basis set

| Geometry | 6-31G(d,p) | 6-31G+(d,p) |
|---|---|---|
| **CP1** | 0.000000 | 0.000000 |
| **TS1** | 22.231279 | 21.492077 |
| **CP2** | -80.606897 | -81.249464 |
| **CP3** | -85.714168 | -86.204251 |

| | | |
|---|---|---|
| **CP1O** | 0.000000 | 0.000000 |
| **TS1O** | 25.159222 | 24.979755 |
| **CP2O** | -78.787758 | -78.587584 |
| **CP3O** | -79.309216 | -79.324903 |
| | | |
| **CP1O+RP** | 0.000000 | 0.000000 |
| **TSPO** | 2.393308 | 1.831690 |
| **PO+PO** | -99.836189 | -99.841209 |

Cartesian coordinate for optimized geometries and energies of the work at B3LYP/631LAN level of theory (LANL2DZ for Co and 6-31G(d,p) basis set for the other atoms)

XYZ Structures and energies for **Route M**

**CP1**, SCF Done: E(RB+HF-LYP) = -1618.51438084 A.U.

| | | | |
|---|---|---|---|
| O | -0.50373600 | 3.79074400 | -1.16671200 |
| C | -0.71002300 | 2.74957300 | -0.72668400 |
| O | -0.91367700 | 1.67999900 | 2.85257200 |
| C | -0.96673300 | 1.45969100 | 1.72635900 |
| Co | -1.03144600 | 1.12759400 | -0.06082200 |
| C | 0.69693400 | 0.20455100 | -0.42923400 |
| C | -0.16502400 | 0.02783400 | -1.43821900 |
| Co | -0.56719000 | -1.29143100 | -0.05485300 |
| C | -0.44327800 | -1.56423000 | 1.74181900 |
| O | -0.36260200 | -1.73873800 | 2.87361700 |
| C | 0.41565800 | -2.67249100 | -0.63957900 |
| O | 1.01375300 | -3.57055300 | -1.02272500 |
| H | -0.23769700 | 0.00810000 | -2.51504200 |
| C | -2.79300500 | 1.01359800 | -0.48762400 |
| C | -2.19974700 | -1.92039700 | -0.56712800 |
| O | -3.90357600 | 0.95477000 | -0.77055600 |
| O | -3.21608500 | -2.32645800 | -0.91096000 |
| P | 2.52443300 | 0.36739500 | -0.12642500 |
| C | 2.83329300 | 2.02277300 | -0.83680700 |
| H | 3.77415900 | 2.41469500 | -0.44620100 |
| H | 2.93404400 | 1.89851200 | -1.91870100 |
| H | 2.01751700 | 2.71579200 | -0.62953700 |
| C | 2.59204500 | 0.36710400 | 1.69375900 |
| H | 2.62797300 | -0.67447800 | 2.02384600 |
| H | 3.51136800 | 0.85758600 | 2.01895600 |
| H | 1.72248800 | 0.85390800 | 2.13589800 |
| O | 4.14197800 | -0.23474100 | -0.36526400 |
| O | 2.91721300 | -0.96620600 | -0.97366900 |

**TS1**, SCF Done: E(RB+HF-LYP) = -1618.47676884 A.U.

| | | | |
|---|---|---|---|
| O | -0.04836000 | 3.75329900 | -1.35648300 |
| C | -0.35156400 | 2.77931600 | -0.83039700 |
| O | -0.39848700 | 1.80937400 | 2.84185800 |
| C | -0.57031700 | 1.58564900 | 1.72876400 |
| Co | -0.83341900 | 1.24387500 | -0.04975800 |
| C | 0.71545500 | 0.01064200 | -0.50317600 |

| | | | |
|---|---|---|---|
| C | -0.23185300 | 0.00998900 | -1.45119600 |
| Co | -0.79165400 | -1.23772000 | -0.06530500 |
| C | -0.78306800 | -1.50703000 | 1.73613100 |
| O | -0.79832100 | -1.67442400 | 2.87216100 |
| C | 0.02760300 | -2.72679300 | -0.61689100 |
| O | 0.56585800 | -3.67240100 | -0.97683600 |
| H | -0.35213500 | 0.01540500 | -2.52360900 |
| C | -2.61559300 | 1.35549600 | -0.32403500 |
| C | -2.49202100 | -1.61903000 | -0.62160100 |
| O | -3.74619100 | 1.44451300 | -0.50216800 |
| O | -3.54072700 | -1.88134100 | -1.00419900 |
| P | 2.76905200 | 0.03414900 | -0.12858900 |
| C | 2.91011300 | 1.84126700 | 0.09337600 |
| H | 3.87108600 | 2.06169100 | 0.56383500 |
| H | 2.89598800 | 2.30033800 | -0.89873800 |
| H | 2.09293400 | 2.24271000 | 0.69211300 |
| C | 2.64824200 | -0.80764600 | 1.48575000 |
| H | 2.50592300 | -1.87529700 | 1.30105900 |
| H | 3.59067700 | -0.67385700 | 2.02171400 |
| H | 1.81691600 | -0.42811300 | 2.07937400 |
| O | 4.23807400 | -0.39225100 | -0.63920000 |
| O | 2.52537900 | -0.61832800 | -1.53270200 |

**CP2**, SCF Done: E(RB+HF-LYP) = -1618.64402936 A.U.

| | | | |
|---|---|---|---|
| O | 0.46724400 | 3.60628000 | -1.42995300 |
| C | 0.01754800 | 2.70183200 | -0.88505900 |
| O | 0.23136400 | 1.68530900 | 2.72989700 |
| C | -0.13724700 | 1.53785700 | 1.65121800 |
| Co | -0.69232500 | 1.28658800 | -0.05947100 |
| C | 0.46794200 | -0.09102400 | -0.81901500 |
| C | -0.64994600 | 0.04667300 | -1.57103400 |
| Co | -1.02926500 | -1.15525900 | -0.10071600 |
| C | -0.76393200 | -1.51621200 | 1.65919100 |
| O | -0.61035500 | -1.72855500 | 2.77728800 |
| C | -0.51191600 | -2.70188100 | -0.83278700 |
| O | -0.18236300 | -3.69120000 | -1.30946600 |
| H | -0.93792800 | 0.11065100 | -2.60984300 |
| C | -2.45772700 | 1.77539500 | -0.03451300 |

| | | | |
|---|---|---|---|
| C | -2.85485800 | -1.27325000 | -0.29586600 |
| O | -3.56733500 | 2.06288100 | -0.05895000 |
| O | -3.98360700 | -1.33905400 | -0.48337800 |
| P | 3.13677800 | -0.31613200 | -0.17870800 |
| C | 3.45385400 | 1.44873600 | 0.12283700 |
| H | 4.33063300 | 1.54639100 | 0.76879100 |
| H | 3.67049000 | 1.92900500 | -0.83455000 |
| H | 2.60120200 | 1.94353600 | 0.59355000 |
| C | 2.65929500 | -1.06442700 | 1.40714800 |
| H | 2.30026100 | -2.08093200 | 1.23206700 |
| H | 3.56028400 | -1.12043100 | 2.02457000 |
| H | 1.89921000 | -0.48967400 | 1.93736100 |
| O | 4.21633800 | -1.03221300 | -0.90471900 |
| O | 1.76234000 | -0.29152800 | -1.13559400 |

**CP3**, SCF Done: E(RB+HF-LYP) = -1618.65233965 A.U.

| | | | |
|---|---|---|---|
| O | -0.15491200 | 3.68930300 | -1.40748700 |
| C | -0.48308500 | 2.71694100 | -0.89031100 |
| O | -0.24777500 | 1.74979100 | 2.71065800 |
| C | -0.54079000 | 1.53237100 | 1.62081800 |
| C | 3.13306700 | 1.71060700 | 0.70517000 |
| Co | -0.98182400 | 1.19665900 | -0.10486500 |
| P | 2.95442100 | 0.02559300 | 0.04039000 |
| C | 0.43674000 | 0.05704300 | -0.84310700 |
| C | -0.68172800 | -0.02770400 | -1.59941800 |
| O | 1.76011400 | 0.17460900 | -1.12254600 |
| Co | -0.75930000 | -1.25658600 | -0.08962900 |
| C | -0.22293800 | -1.53879300 | 1.64642000 |
| C | 4.35097800 | -0.25510300 | -1.08543000 |
| O | 0.07160000 | -1.71484100 | 2.73755900 |
| C | -0.00704200 | -2.68567200 | -0.84860400 |
| O | 0.48564500 | -3.59093700 | -1.35210700 |
| O | 2.71654700 | -1.03206300 | 1.06281400 |
| H | 2.27633200 | 1.94366800 | 1.33977000 |
| H | 4.03656700 | 1.75184500 | 1.31994600 |
| H | 3.20415800 | 2.44847000 | -0.09820700 |
| H | 4.40594900 | 0.52271300 | -1.85104700 |
| H | 5.27878600 | -0.26776800 | -0.50763600 |

| | | | |
|---|---|---|---|
| H | 4.22201900 | -1.22763400 | -1.56625500 |
| H | -0.98193100 | -0.05192100 | -2.63635400 |
| C | -2.80701800 | 1.34752300 | -0.15806300 |
| C | -2.52881500 | -1.74278400 | -0.09180800 |
| O | -3.94833000 | 1.43016000 | -0.24096100 |
| O | -3.63839600 | -2.02749900 | -0.14902100 |

XYZ Structures and energies for **Route O**

**CP1O**, SCF Done: E(RB+HF-LYP) = -648.280545084 A.U.

| | | | |
|---|---|---|---|
| C | 1.58587700 | -0.00013600 | -0.15882300 |
| C | 2.79140000 | -0.00021300 | -0.29199500 |
| H | 3.85058100 | -0.00031300 | -0.42012000 |
| P | -0.22776200 | 0.00000000 | 0.04177400 |
| C | -0.39903600 | -1.51613800 | 1.04021700 |
| H | -1.34556000 | -1.49841200 | 1.58338500 |
| H | -0.41091100 | -2.36263700 | 0.34808900 |
| H | 0.44246800 | -1.63060500 | 1.72634400 |
| C | -0.39946900 | 1.52034200 | 1.03385800 |
| H | -0.41167700 | 2.36421400 | 0.33846600 |
| H | -1.34631400 | 1.50422600 | 1.57649100 |
| H | 0.44174100 | 1.63808600 | 1.71973900 |
| O | -1.83162100 | -0.00075900 | -0.61613500 |
| O | -0.57794500 | -0.00395300 | -1.53868500 |

**TS1O**, SCF Done: E(RB+HF-LYP) = -648.238180642 A.U.

| | | | |
|---|---|---|---|
| C | 1.55079700 | -0.00004700 | -0.18550200 |
| C | 2.77232100 | -0.00005000 | -0.05413700 |
| H | 3.83965400 | -0.00009300 | -0.02061300 |
| P | -0.43022100 | 0.00001000 | 0.01893000 |
| C | -0.69862500 | 1.50996300 | -0.97430700 |
| H | -1.75590000 | 1.59088000 | -1.23635100 |
| H | -0.42920100 | 2.36488400 | -0.34846600 |
| H | -0.07841700 | 1.51412000 | -1.87183800 |
| C | -0.69885400 | -1.50942500 | -0.97502900 |
| H | -0.42985100 | -2.36467100 | -0.34945000 |
| H | -1.75609700 | -1.58992500 | -1.23733600 |
| H | -0.07845900 | -1.51347200 | -1.87243500 |
| O | -1.63383600 | -0.00020900 | 1.07170400 |

| | | | |
|---|---|---|---|
| O | 0.33230500 | -0.00035700 | 1.40159500 |

**CP2O**, SCF Done: E(RB+HF-LYP) = -648.407284877 A.U.

| | | | |
|---|---|---|---|
| C | -1.82398500 | -0.00042700 | -0.41856500 |
| C | -2.91118600 | 0.00001200 | 0.10667200 |
| H | -3.88529300 | 0.00025500 | 0.53350700 |
| P | 0.78181300 | 0.00005600 | -0.08279600 |
| C | 0.57400300 | 1.47300200 | 0.96077000 |
| H | 1.36833000 | 1.49707800 | 1.71122700 |
| H | 0.66315600 | 2.35766400 | 0.32590300 |
| H | -0.40063400 | 1.47606100 | 1.45493000 |
| C | 0.57477300 | -1.47269800 | 0.96114900 |
| H | 0.66493400 | -2.35745600 | 0.32655700 |
| H | 1.36883400 | -1.49588000 | 1.71191600 |
| H | -0.40006300 | -1.47646800 | 1.45490100 |
| O | 1.95415900 | 0.00021800 | -0.99028900 |
| O | -0.65266900 | -0.00039700 | -1.00185600 |

**CP3O**, SCF Done: E(RB+HF-LYP) = -648.408092868 A.U.

| | | | |
|---|---|---|---|
| C | 0.50060200 | 1.64924600 | -0.66112500 |
| P | 0.66544100 | 0.05646000 | 0.20000500 |
| C | -1.88090800 | -0.39843100 | -0.16733500 |
| C | -3.01873000 | -0.04107400 | 0.01047500 |
| O | -0.65863800 | -0.81312200 | -0.41085500 |
| C | 1.95802300 | -0.92245100 | -0.61393700 |
| O | 0.73752300 | 0.14007900 | 1.68118600 |
| H | -0.43915300 | 2.11333500 | -0.35160000 |
| H | 1.32741600 | 2.30183100 | -0.37084000 |
| H | 0.49572800 | 1.51716300 | -1.74592700 |
| H | 1.79072000 | -0.98754000 | -1.69140000 |
| H | 2.92848900 | -0.46020700 | -0.41749400 |
| H | 1.95398300 | -1.92682900 | -0.18428600 |
| H | -4.02380600 | 0.25595800 | 0.19035600 |

XYZ Structures and energies for **CP1OR**, **TS1OR** and **CP2OR**

**CP1OR**, SCF Done: E(RB+HF-LYP) = -648.290261263 A.U.

| | | | |
|---|---|---|---|
| P | -0.24936200 | 0.05651900 | -0.01068600 |
| C | -0.89776600 | 0.29627900 | 1.68005300 |

| | | | |
|---|---|---|---|
| H | -1.98670500 | 0.20004500 | 1.62241300 |
| H | -0.51588800 | -0.48168400 | 2.34249500 |
| H | -0.64103600 | 1.28676700 | 2.06320300 |
| O | -0.58415700 | -1.65491800 | -0.09563800 |
| O | -1.15743000 | -0.66463300 | -1.14870400 |
| C | -0.33103300 | 1.78621900 | -0.68582300 |
| H | 0.27637200 | 2.46219600 | -0.07632700 |
| H | 0.04450800 | 1.80492500 | -1.71251100 |
| H | -1.36866000 | 2.13588400 | -0.68532600 |
| C | 1.51567500 | -0.12240900 | 0.03102700 |
| C | 2.72565400 | -0.19573900 | 0.05578900 |
| H | 3.78935400 | -0.28560900 | 0.07479600 |

**TS1OR**, SCF Done: E(RB+HF-LYP) = -648.246060170 A.U.

| | | | |
|---|---|---|---|
| P | -0.26316500 | -0.16387400 | -0.02379400 |
| C | -0.92048200 | -0.13113100 | 1.69290000 |
| H | -2.01128900 | -0.12878800 | 1.60537100 |
| H | -0.61405900 | -1.03804600 | 2.21628600 |
| H | -0.59294500 | 0.75370300 | 2.23993900 |
| O | -0.58374200 | -1.67879700 | -0.46076400 |
| O | -1.08387700 | 0.02378400 | -1.33086700 |
| C | 1.50729100 | -0.13930800 | 0.00914800 |
| C | 2.71878200 | -0.09323400 | 0.03492700 |
| H | 3.78618600 | -0.07595000 | 0.04941200 |
| C | -0.34988500 | 1.93499900 | -0.20822500 |
| H | 0.34018900 | 2.20900900 | 0.59398600 |
| H | 0.01321400 | 2.27883600 | -1.17380600 |
| H | -1.36711400 | 2.27149700 | -0.01373600 |

**CP2OR**, SCF Done: E(RB+HF-LYP) = -648.425927071 A.U.

| | | | |
|---|---|---|---|
| P | -0.03291400 | -0.55640000 | -0.16262300 |
| C | -0.47247900 | -1.05469600 | 1.52911200 |
| H | -1.41829600 | -1.60260500 | 1.48541300 |
| H | 0.30512800 | -1.72010100 | 1.91272900 |
| H | -0.57283000 | -0.19646900 | 2.19931400 |
| O | 0.12757800 | -1.67864500 | -1.12233300 |
| O | -1.17590600 | 0.49670600 | -0.63531400 |
| C | 1.42372400 | 0.45115800 | 0.02265400 |

| | | | |
|---|---|---|---|
| C | 2.44616500 | 1.09443200 | 0.13530800 |
| H | 3.35108200 | 1.65525000 | 0.22007300 |
| C | -1.43632400 | 1.75048900 | 0.01257700 |
| H | -2.18481800 | 2.25725500 | -0.59780600 |
| H | -1.83699000 | 1.59786200 | 1.02089000 |
| H | -0.52946400 | 2.36201600 | 0.06199600 |

XYZ Structures and energies for **CP1O-Fn**, **TS1O-Fn**, **CP2O-Fn** and **CP3O-Fn** (n= 1, 6, 7)

**CP1O-F1**, SCF Done: E(RB+HF-LYP) = -747.490495028 A.U.

| | | | |
|---|---|---|---|
| C | -1.12292700 | 0.00014300 | 0.00783500 |
| C | -2.33093300 | 0.00003300 | 0.07455700 |
| P | 0.69707200 | 0.00003700 | -0.04595100 |
| C | 0.95199900 | -1.51846200 | -1.02220300 |
| H | 1.94023400 | -1.50096800 | -1.48515000 |
| H | 0.90845900 | -2.36266300 | -0.32850400 |
| H | 0.17042300 | -1.63675800 | -1.77524500 |
| C | 0.95223300 | 1.51953700 | -1.02057600 |
| H | 0.90854500 | 2.36303000 | -0.32602400 |
| H | 1.94056100 | 1.50251400 | -1.48334100 |
| H | 0.17080700 | 1.63861400 | -1.77365300 |
| O | 2.24506600 | -0.00052100 | 0.73948100 |
| O | 0.92087900 | -0.00084300 | 1.55637600 |
| F | -3.61387900 | -0.00010200 | 0.13962800 |

**TS1O-F1**, SCF Done: E(RB+HF-LYP) = -747.449623160 A.U.

| | | | |
|---|---|---|---|
| C | -1.08428800 | 0.00024400 | -0.30184700 |
| C | -2.29544500 | 0.00005900 | -0.08498400 |
| F | -3.57200800 | -0.00003500 | 0.01528600 |
| P | 0.89320500 | -0.00000600 | 0.02249300 |
| C | 1.21387100 | -1.50757300 | -0.95498600 |
| H | 2.28503200 | -1.58980300 | -1.15303800 |
| H | 0.90630000 | -2.36309900 | -0.34792200 |
| H | 0.64819500 | -1.50830900 | -1.88774900 |
| C | 1.21366800 | 1.50929500 | -0.95236400 |
| H | 0.90595800 | 2.36373600 | -0.34384200 |
| H | 2.28481700 | 1.59202000 | -1.15026700 |
| H | 0.64796200 | 1.51150700 | -1.88510200 |
| O | 2.03546700 | -0.00091500 | 1.14206000 |

| | | | |
|---|---|---|---|
| O | 0.06264300 | -0.00130800 | 1.36519600 |

**CP2O-F1**, SCF Done: E(RB+HF-LYP) = -747.606563609 A.U.

| | | | |
|---|---|---|---|
| C | -1.31377900 | -0.00001500 | -0.58317500 |
| C | -2.44454100 | -0.00024700 | -0.18423800 |
| P | 1.25972200 | 0.00001100 | -0.05393800 |
| C | 0.98100500 | 1.47210600 | 0.97564800 |
| H | 1.72995600 | 1.50024900 | 1.77125800 |
| H | 1.10299800 | 2.35771000 | 0.34756200 |
| H | -0.01982000 | 1.47253600 | 1.41427500 |
| C | 0.98113600 | -1.47193500 | 0.97589600 |
| H | 1.10336400 | -2.35763300 | 0.34798900 |
| H | 1.72997700 | -1.49980600 | 1.77161900 |
| H | -0.01975200 | -1.47245100 | 1.41438100 |
| O | 2.49969200 | 0.00000500 | -0.86689700 |
| O | -0.09296500 | -0.00016400 | -1.07872600 |
| F | -3.66658900 | 0.00011700 | 0.24468800 |

**CP3O-F1**, SCF Done: E(RB+HF-LYP) = -747.608229879 A.U.

| | | | |
|---|---|---|---|
| C | 1.00425200 | 1.64706600 | -0.68200700 |
| P | 1.13894900 | 0.06556300 | 0.20651300 |
| C | -1.37166900 | -0.46984800 | -0.24001800 |
| C | -2.52662200 | -0.18700800 | -0.09710900 |
| O | -0.12283700 | -0.83476500 | -0.47360600 |
| C | 2.50103900 | -0.89283100 | -0.51312200 |
| O | 1.11549300 | 0.17122100 | 1.68834600 |
| H | 0.05191600 | 2.11335200 | -0.41766400 |
| H | 1.81532500 | 2.30771700 | -0.36625700 |
| H | 1.04582200 | 1.50142300 | -1.76428000 |
| H | 2.39615100 | -0.98393600 | -1.59659500 |
| H | 3.44643200 | -0.39988900 | -0.27367400 |
| H | 2.50003600 | -1.88824200 | -0.06315600 |
| F | -3.76924000 | 0.12113500 | 0.09550500 |

**CP1O-F6**, SCF Done: E(RB+HF-LYP) = -1243.66283920 A.U.

| | | | |
|---|---|---|---|
| C | -0.00047800 | 1.92522400 | -0.04460600 |
| C | -0.00084400 | 3.09149700 | -0.37108100 |
| H | -0.00115300 | 4.11597200 | -0.67169800 |

| | | | |
|---|---|---|---|
| P | 0.00001000 | 0.23852000 | 0.54479000 |
| C | -1.53324400 | -0.39565400 | -0.36398700 |
| C | 1.53336000 | -0.39515800 | -0.36416100 |
| O | 0.00034900 | -0.97687500 | 1.73442700 |
| O | 0.00025600 | 0.54483000 | 2.12234400 |
| F | 1.48341300 | -1.72616100 | -0.49501100 |
| F | 2.62831600 | -0.06426400 | 0.33456900 |
| F | 1.62309400 | 0.14709100 | -1.58929100 |
| F | -1.62170200 | 0.14489000 | -1.58999600 |
| F | -1.48434800 | -1.72685200 | -0.49284200 |
| F | -2.62839300 | -0.06280200 | 0.33353500 |

**TS1O-F6**, SCF Done: E(RB+HF-LYP) = -1243.62370186 A.U.

| | | | |
|---|---|---|---|
| C | 0.00296600 | 1.82186200 | -0.46223400 |
| C | 0.00485700 | 2.99503400 | -0.82630000 |
| H | 0.00642900 | 3.98791400 | -1.22142700 |
| P | 0.00005000 | 0.23222600 | 0.57982900 |
| C | -1.52075100 | -0.52263700 | -0.25915800 |
| F | -1.57953500 | -1.83951200 | -0.01868400 |
| F | -2.62332600 | 0.05924000 | 0.23715200 |
| F | -1.49773500 | -0.33968100 | -1.58901300 |
| C | 1.51957800 | -0.52582500 | -0.25841300 |
| F | 2.62249900 | 0.06609000 | 0.22522900 |
| F | 1.58630400 | -1.83973500 | -0.00533300 |
| F | 1.48712300 | -0.35596800 | -1.58996700 |
| O | -0.00170700 | -0.47890000 | 1.99082500 |
| O | 0.00107500 | 1.49942400 | 1.51244400 |

**CP2O-F6**, SCF Done: E(RB+HF-LYP) = -1243.77868334 A.U.

| | | | |
|---|---|---|---|
| C | -1.12751100 | 2.04691700 | 0.30826000 |
| C | -1.74531600 | 2.79948700 | -0.39798400 |
| H | -2.28805100 | 3.45857900 | -1.03322400 |
| P | 0.16217300 | -0.21466900 | 0.81323700 |
| C | -1.13618800 | -1.02891200 | -0.30224200 |
| C | 1.60680300 | 0.16681000 | -0.34510000 |
| O | 0.52187900 | -0.97040100 | 2.02514300 |
| O | -0.46548500 | 1.27502700 | 1.15146100 |
| F | -2.35240000 | -0.85251200 | 0.22963000 |

| | | | |
|---|---|---|---|
| F | -1.11706900 | -0.49601400 | -1.53537500 |
| F | -0.88501800 | -2.33861600 | -0.39590600 |
| F | 1.94000000 | -0.95954200 | -0.99805600 |
| F | 1.29551300 | 1.11059900 | -1.24553600 |
| F | 2.65426200 | 0.58259900 | 0.37238000 |

**CP3O-F6**, SCF Done: E(RB+HF-LYP) = -1243.78147909 A.U.

| | | | |
|---|---|---|---|
| C | -0.39586900 | 1.51716100 | -0.08694100 |
| P | -0.08199800 | -0.24257100 | 0.52519900 |
| C | -2.25255000 | -1.37902200 | -0.35054600 |
| C | -3.42088900 | -1.64096800 | -0.24053100 |
| O | -0.96470200 | -1.14239300 | -0.54395800 |
| C | 1.62438500 | -0.68664400 | -0.14628000 |
| O | -0.28855500 | -0.44183600 | 1.97203700 |
| H | -4.45625800 | -1.86030900 | -0.12968300 |
| F | 2.47854200 | 0.28334400 | 0.22563200 |
| F | 2.02360900 | -1.84652000 | 0.38443100 |
| F | 1.64202900 | -0.78815700 | -1.48003400 |
| F | 0.22629100 | 2.40156300 | 0.69972000 |
| F | 0.05233600 | 1.66714100 | -1.34486400 |
| F | -1.71371500 | 1.76146900 | -0.06567800 |

**CP1O-F7**, SCF Done: E(RB+HF-LYP) = -1342.87355842 A.U.

| | | | |
|---|---|---|---|
| C | 1.61065300 | -0.04362600 | 0.21271500 |
| C | 2.80675500 | -0.06719500 | 0.04157600 |
| P | -0.12972000 | -0.00168300 | 0.58229300 |
| C | -0.59354700 | 1.55026800 | -0.39508800 |
| C | -0.68963700 | -1.51503100 | -0.40431600 |
| O | -1.49080600 | 0.03433600 | 1.60433600 |
| O | -0.03383600 | -0.02278400 | 2.18576500 |
| F | 4.06680600 | -0.09321300 | -0.15322900 |
| F | 0.03193300 | -1.65955500 | -1.52720000 |
| F | -0.53782600 | -2.61382300 | 0.34801400 |
| F | -1.97882900 | -1.39200200 | -0.74521100 |
| F | -1.90962500 | 1.59484000 | -0.62538700 |
| F | -0.23424900 | 2.63602600 | 0.30543800 |
| F | 0.04374500 | 1.57065300 | -1.57848200 |

**TS1O-F7**, SCF Done: E(RB+HF-LYP) = -1342.83530735 A.U.

| | | | |
|---|---|---|---|
| C | 1.57846600 | -0.03028000 | -0.11419100 |
| C | 2.80435700 | -0.05713900 | -0.18538200 |
| F | 4.05969400 | -0.08520700 | -0.37794300 |
| P | -0.17089700 | -0.00089800 | 0.63807500 |
| C | -0.71870000 | 1.53711700 | -0.31891300 |
| F | -2.02941800 | 1.75557400 | -0.16887700 |
| F | -0.04742400 | 2.60531000 | 0.14113400 |
| F | -0.46077000 | 1.39661200 | -1.63102900 |
| C | -0.80929200 | -1.49664300 | -0.33235400 |
| F | -0.52580200 | -2.61227000 | 0.35672300 |
| F | -2.14068000 | -1.39895200 | -0.47495600 |
| F | -0.26527900 | -1.59783300 | -1.55344500 |
| O | -1.12928700 | 0.01205000 | 1.89613500 |
| O | 0.89448500 | -0.04629500 | 1.79254800 |

**CP2O-F7**, SCF Done: E(RB+HF-LYP) = -1342.97932517 A.U.

| | | | |
|---|---|---|---|
| C | 1.89778400 | -0.44693600 | 0.68624800 |
| C | 2.97837900 | -0.54743600 | 0.18423700 |
| P | -0.68667500 | 0.11056600 | 0.79411200 |
| C | -0.26692600 | 1.56306200 | -0.34881000 |
| C | -1.18400800 | -1.28195700 | -0.38381100 |
| O | -1.66630100 | 0.40204000 | 1.85469200 |
| O | 0.77152800 | -0.37775600 | 1.38750500 |
| F | -1.38452300 | 2.22747100 | -0.65766600 |
| F | 0.57770100 | 2.39265200 | 0.27797500 |
| F | 0.30872500 | 1.13385100 | -1.48580800 |
| F | -0.14647800 | -1.72337400 | -1.11169500 |
| F | -1.68162700 | -2.30284200 | 0.31966700 |
| F | -2.13001300 | -0.82066600 | -1.21929800 |
| F | 4.11254200 | -0.63744300 | -0.42055500 |

**CP3O-F7**, SCF Done: E(RB+HF-LYP) = -1342.98239790 A.U.

| | | | |
|---|---|---|---|
| C | 0.37868000 | 1.60646200 | -0.08786100 |
| P | 0.19779000 | -0.17045600 | 0.52689700 |
| C | -2.20738200 | -0.66136100 | -0.30785800 |
| C | -3.39734700 | -0.62765700 | -0.20173000 |
| O | -0.90264500 | -0.79523400 | -0.53239700 |

| | | | |
|---|---|---|---|
| C | 1.71472700 | -1.06328800 | -0.15096200 |
| O | -0.04975000 | -0.30158900 | 1.97551400 |
| F | 1.20071000 | 2.29669300 | 0.70903700 |
| F | -0.82643000 | 2.19569700 | -0.09022500 |
| F | 0.87158600 | 1.62510800 | -1.33801100 |
| F | 1.69977000 | -1.16336000 | -1.48503800 |
| F | 2.80287000 | -0.36452000 | 0.21879200 |
| F | 1.78358100 | -2.28934600 | 0.37698000 |
| F | -4.67428300 | -0.54399700 | -0.05352600 |

XYZ Structures and energies for **Route PO**

(**CP1O+RP**) , SCF Done: E(RB+HF-LYP) = -1146.22194152 A.U.

| | | | |
|---|---|---|---|
| C | -3.83497800 | -0.30566900 | 0.00794600 |
| C | -5.03551200 | -0.47788700 | 0.01236100 |
| H | -6.09297800 | -0.61983800 | 0.01599800 |
| P | -2.03066100 | -0.05151600 | 0.00165300 |
| C | -1.60121500 | -0.92610700 | 1.54029900 |
| H | -0.55082800 | -1.22294700 | 1.50386700 |
| H | -1.74469600 | -0.22816700 | 2.36963500 |
| H | -2.24928800 | -1.79217200 | 1.68895800 |
| C | -1.60053100 | -1.00994100 | -1.48573500 |
| H | -1.74270400 | -0.35892000 | -2.35258900 |
| H | -0.55033800 | -1.30493500 | -1.43195400 |
| H | -2.24905000 | -1.88250400 | -1.58690000 |
| O | -0.63289400 | 0.99571400 | -0.02647600 |
| O | -2.07996300 | 1.56876200 | -0.04265500 |
| H | 6.07294700 | -1.75909700 | 0.04853900 |
| C | 5.10875000 | -1.30434100 | 0.03594700 |
| C | 4.01813800 | -0.77014400 | 0.02108600 |
| P | 2.35368200 | -0.13819800 | 0.00406800 |
| C | 2.42830300 | 1.09110400 | 1.40254100 |
| C | 2.42450700 | 1.00866500 | -1.46262000 |
| H | 1.46835800 | 1.61489500 | 1.41853100 |
| H | 2.55297500 | 0.55725000 | 2.34816900 |
| H | 3.24540200 | 1.80847500 | 1.28764300 |
| H | 2.54731300 | 0.42152500 | -2.37638400 |
| H | 1.46423800 | 1.53034400 | -1.50606400 |
| H | 3.24140700 | 1.73190800 | -1.39115800 |

**TSPO**, SCF Done: E(RB+HF-LYP) = -1146.21744688 A.U.

| | | | |
|---|---|---|---|
| C | -3.62135500 | 0.16233000 | -0.00033300 |
| C | -4.83248900 | 0.23391000 | -0.00057900 |
| H | -5.89801800 | 0.28311000 | -0.00080600 |
| P | -1.79389000 | 0.06528400 | 0.00003600 |
| C | -1.48784900 | 1.04452000 | -1.51113700 |
| H | -0.48155800 | 1.46488000 | -1.48213600 |
| H | -1.56193600 | 0.36370900 | -2.36376700 |
| H | -2.23737700 | 1.83059700 | -1.62204800 |
| C | -1.48867100 | 1.04104100 | 1.51363500 |
| H | -1.56252100 | 0.35809000 | 2.36457300 |
| H | -0.48265100 | 1.46212400 | 1.48593900 |
| H | -2.23867800 | 1.82640500 | 1.62631900 |
| O | -0.21102600 | -0.75028500 | -0.00064200 |
| O | -1.72216100 | -1.52696600 | -0.00160700 |
| H | 5.01691500 | 2.60919100 | 0.00028200 |
| C | 4.25502300 | 1.86312800 | 0.00020100 |
| C | 3.40781400 | 0.99193500 | 0.00012100 |
| P | 2.01896900 | -0.12744000 | -0.00010500 |
| C | 2.43203800 | -1.21072900 | -1.44531700 |
| C | 2.43151600 | -1.21077000 | 1.44522700 |
| H | 1.66243400 | -1.98345500 | -1.50071700 |
| H | 2.39757900 | -0.61819000 | -2.36283600 |
| H | 3.42041800 | -1.66824400 | -1.35266100 |
| H | 2.39641400 | -0.61833400 | 2.36278800 |
| H | 1.66207100 | -1.98369000 | 1.50013300 |
| H | 3.42005600 | -1.66804000 | 1.35306700 |

(**PO+PO**) , SCF Done: E(RB+HF-LYP) = -1146.38359843 A.U.

| | | | |
|---|---|---|---|
| C | 3.77910300 | -0.00185300 | 0.29068100 |
| C | 4.95968500 | -0.00342300 | 0.56383500 |
| H | 5.99768000 | -0.00479600 | 0.81041700 |
| P | 2.02788100 | 0.00047900 | -0.04904900 |
| C | 1.79186900 | 1.45340700 | -1.12184600 |
| H | 0.75567900 | 1.42387900 | -1.47089600 |
| H | 1.96621200 | 2.36386700 | -0.54359600 |
| H | 2.47664800 | 1.42948500 | -1.97398200 |

| | | | |
|---|---|---|---|
| C | 1.78868500 | -1.44830900 | -1.12689500 |
| H | 1.96257600 | -2.36116600 | -0.55230300 |
| H | 0.75196600 | -1.41610700 | -1.47455200 |
| H | 2.47229100 | -1.42205900 | -1.97991500 |
| O | -1.19680100 | 0.00230800 | -1.20817900 |
| O | 1.19694700 | -0.00060600 | 1.20829900 |
| H | -5.99745300 | -0.00056400 | -0.81106600 |
| C | -4.95951200 | -0.00028600 | -0.56428900 |
| C | -3.77897000 | -0.00036100 | -0.29093300 |
| P | -2.02778300 | -0.00000300 | 0.04911200 |
| C | -1.79108800 | 1.44935400 | 1.12671000 |
| C | -1.78989800 | -1.45231300 | 1.12237800 |
| H | -0.75473800 | 1.41852100 | 1.47534800 |
| H | -1.96543000 | 2.36176100 | 0.55153400 |
| H | -2.47568500 | 1.42267600 | 1.97891200 |
| H | -1.96322100 | -2.36321500 | 0.54449100 |
| H | -0.75367300 | -1.42149200 | 1.47136300 |
| H | -2.47473200 | -1.42884900 | 1.97448500 |