# Origin of Inversion versus Retention in the Oxidative Addition of 3-chloro-cyclopentene to $Pd(0)L_n$

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## SUPPORTING INFORMATION

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**Examination along the IRC: Interaction/Distortion.**

In performing an EDA along the reaction coordinate, it is to project the reaction coordinate onto a critical geometrical parameter shared by the reactions being compared. If the behavior along such coordinates is too dissimilar, this type of analysis is of limited value or may even lead to misleading conclusions.

In the present case, the C-Cl distance appears to be a suitable geometrical parameter. We examine the total energy, the interaction energy, and the distortion energy for each fragment as a function of the C-Cl bond distance for L=**$PF_3$**, **$PH_3$**, **$PMe_3$**. Our focus is on the origin of the difference in reaction barriers. Accordingly, we plot the differences between the energies along the reaction coordinate ($\xi$) and the reactant complex, $\Delta E = \Delta E(\xi) - \Delta E^{RC}$.[1] The difference in the energies of the reactant complexes can be compounded to the analysis.

Profiles of the energy components along the C-Cl coordinate under bis-ligation are presented in Figure S1. The energy curves become more compressed along the energy coordinate as the ligand donor strength increases, which is consistent with a decrease in selectivity upon increasing ligand donor strength. The distortion of the Pd fragment along the C-Cl coordinate changes little among the ligands explored (although there is a slight decrease with increasing donor strength[2]). The distortion energy in the allylic fragment changes significantly along the reaction coordinate as might be expected for the fragment comprising the coordinate undergoing the greatest change, the C-Cl distance. It becomes smaller with increasing ligand donation, and the lowering becomes more prominent on the *anti* pathway. Intriguingly, for **$PMe_3$**, the distortion is lower by ~4 kcal/mol for the *anti* pathway until the TS is reached for the *syn* pathway. Further bond cleavage is required until the difference in distortion energy is ~10 kcal/mol favoring *syn*, with a difference in the C-Cl distance of 0.4 Å between the TS's.

The difference in the interaction energy $\Delta E_{int}$ is quite significant for **$PF_3$**, strongly favoring *syn*. Comparison at the TS's between *syn* and *anti* reveals a much smaller difference than implied by an analysis of the entire profile. Once again, the difference diminishes across ligand donor strengths until there is a large difference in interaction favoring *anti* for the **$PMe_3$** case.

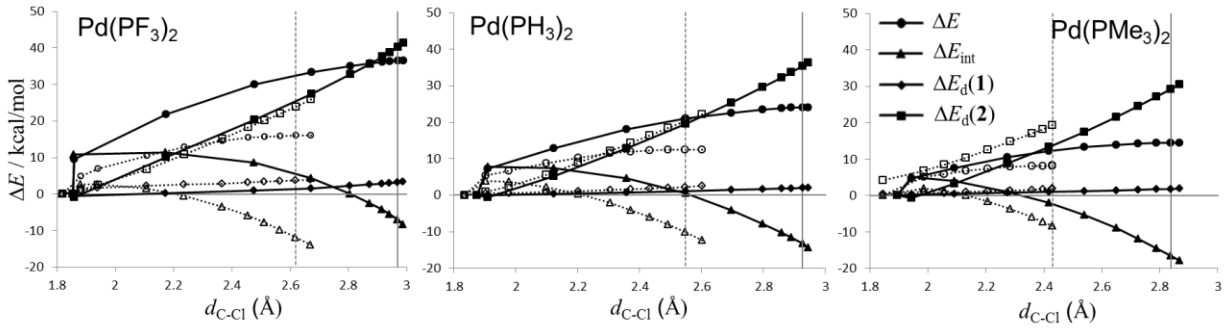



**Figure S1.** Profiles of the total energy $\Delta E$, the interaction energy $\Delta E_{int}$, and the distortion energies $\Delta E_d$(**1**) (for $PdL_2$) and $\Delta E_d$(**2**) (for the allylic fragment) in kcal/mol versus the C-Cl distance in Å. The grey vertical lines mark the transition state locations (dotted=*syn*; solid=*anti*).

The corresponding energy profiles for mono-ligation are presented in Figure S2. Obviously, there is a large difference in C-Cl distance between *syn* and *anti* transition states in each case (cf. Figures S1 and S2). Compared with bis-ligation, C-Cl bond cleavage under mono-ligation is significantly less advanced for the *syn* pathway and only slightly more advanced for the *anti* pathway. The unsaturation at the monoligated Pd center allows for a much lower bond breaking requirement. Consequently, the stabilizing interactions become strong more rapidly for mono-ligation (compared to bis-ligation) resulting in a greatly reduced overall energy barrier.

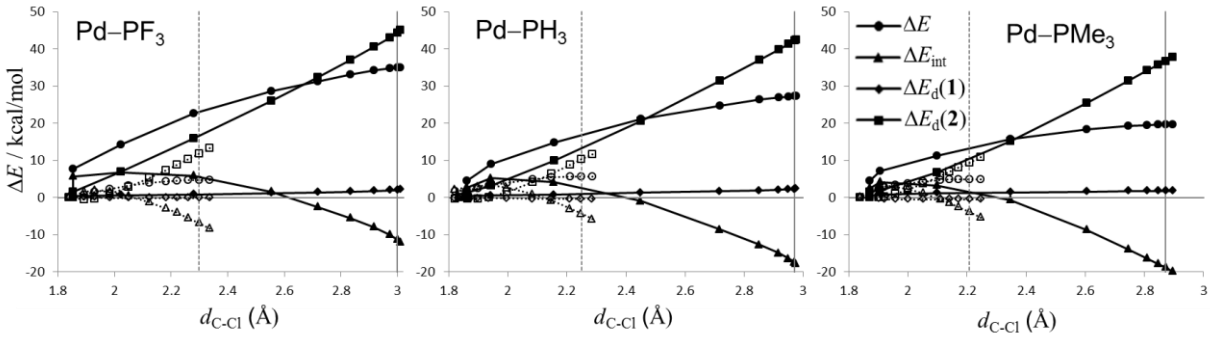



**Figure S2.** Profiles of the total energy $\Delta E$, the interaction energy $\Delta E_{\text{int}}$, and the distortion energies $\Delta E_{\text{d}}$(**1**) (for Pd–L) and $\Delta E_{\text{d}}$(**2**) (for the allylic fragment) in kcal/mol versus the C-Cl distance in Å. The grey vertical lines mark the transition state locations (dotted=*syn*; solid=*anti*).

The above analysis demonstrates how the interplay between the interaction ($\Delta E_{\text{int}}$) and distortion ($\Delta E_{\text{dist}}$) terms dictates the location of the transition state for varying ligation and ligand donor strength. The decrease in selectivity with increasing ligand donor strength can largely be attributed to the sharper increase in interaction along the *anti* than the *syn* pathway. Most of the changes in distortion energy take place within the allylic chloride fragment. Furthermore, qualitative graphical inspection reveals that the higher curvature in the interaction curve and the lower curvature in the corresponding distortion curves for $Pd(PMe_3)_n$ in the *anti* pathway prompts the *anti* TS to be reached with a lower overall energy barrier compared with less donating ligands.

**NOCV Analysis**

According to a natural orbitals of chemical valence (NOCV) analysis, the Pd-Cl interaction corresponds to the second-most dominant orbital interaction ($\Delta\rho_2$) representing to charge transfer from the allylic fragment to the $PdL_2$ fragment for **$PF_3$-TS-$S_{L2}$** and **$PH_3$-TS-$S_{L2}$**. This interaction is strongest in the most electron deficient case (**$PF_3$-TS-$S_{L2}$**) which is in agreement with the overlap analysis performed in Figure 10 of the manuscript.

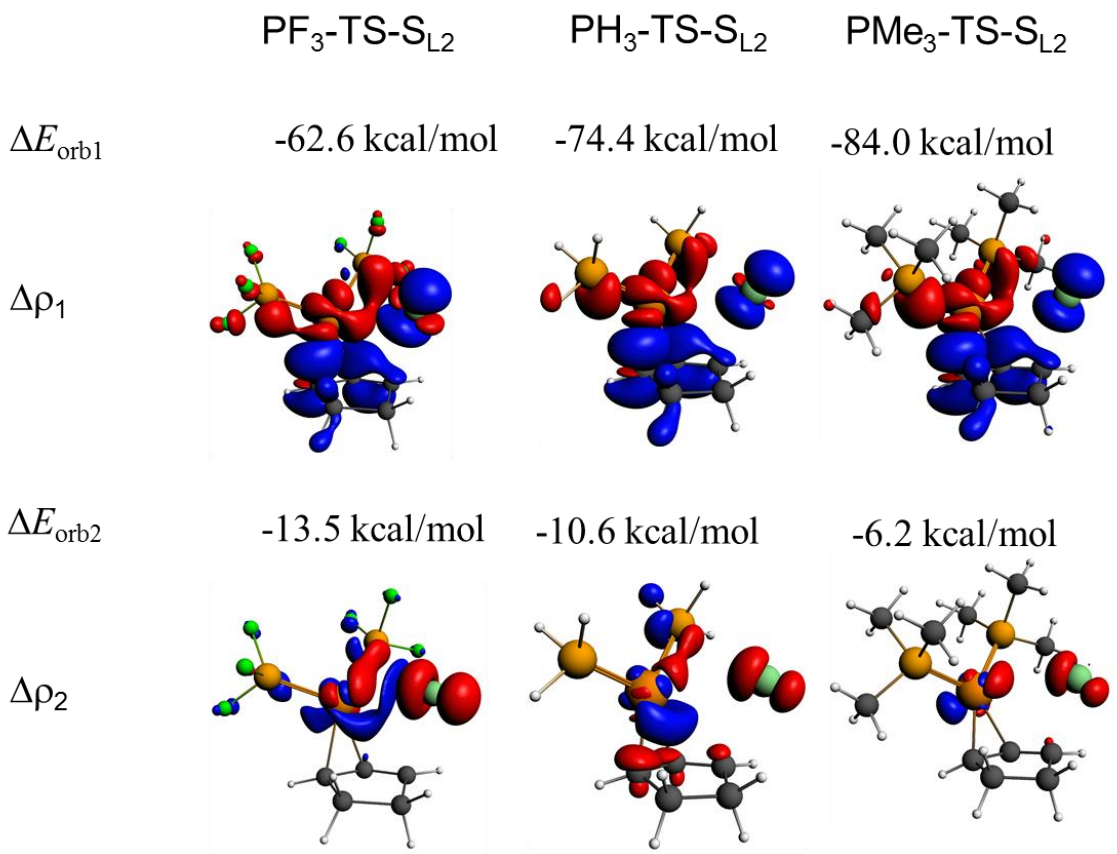



**Figure S3**. The contours of the deformation density contribution. $|\Delta\rho|$ = 0.002 a.u. The negative charge flow occurs from the red contours to the blue contours.

**Table S1** Energy Decomposition Analysis related to Table 2, Table 3, and Figure 4.

| | $E$_SCF(**1**)[a] | $E$_SCF(**2**)[b] | $\Delta E_{Pauli}$ | $\Delta E_{elstat}$ | $\Delta E_{orb}$ | $\Delta E_{disp}$ | $\Delta E_{int}$ | $\Delta E_{d1}$[c] | $\Delta E_{d2}$ |
|---|---|---|---|---|---|---|---|---|---|
| **MA-RC-A$_{L2}$** | -3009.92 | -1700.00 | 99.76 | -77.49 | -49.17 | -10.32 | -37.22 | 2.51 | 4.35 |
| **MA-RC-S$_{L2}$** | -3009.12 | -1698.16 | 104.18 | -80.63 | -52.09 | -10.83 | -39.37 | 3.31 | 6.19 |
| **MA-RC-A$_{L1}$** | -1512.63 | -1699.60 | 119.50 | -97.73 | -56.27 | -6.41 | -40.91 | 0.39 | 4.75 |
| **MA-RC-S$_{L1}$** | -1512.77 | -1699.61 | 132.07 | -101.18 | -68.19 | -7.04 | -44.34 | 0.25 | 4.74 |
| **MA-TS-A$_{L2}$** | -2999.41 | -1653.60 | 158.41 | -98.36 | -101.09 | -11.23 | -52.27 | 13.02 | 50.75 |
| **MA-TS-S$_{L2}$** | -2985.99 | -1686.50 | 165.41 | -118.98 | -92.33 | -10.95 | -56.85 | 26.44 | 17.85 |
| **MA-TS-A$_{L1}$** | -1512.06 | -1656.01 | 142.05 | -94.38 | -89.19 | -6.72 | -48.24 | 0.96 | 48.34 |
| **MA-TS-S$_{L1}$** | -1512.78 | -1686.93 | 168.00 | -118.51 | -94.62 | -7.99 | -53.12 | 0.24 | 17.42 |
| **Et-RC-A$_{L2}$** | -1574.51 | -1697.38 | 137.63 | -107.22 | -62.04 | -7.50 | -39.13 | 8.85 | 6.97 |
| **Et-RC-S$_{L2}$** | -1573.77 | -1694.24 | 142.21 | -109.43 | -65.21 | -8.18 | -40.61 | 9.59 | 10.11 |
| **Et-RC-A$_{L1}$** | -794.81 | -1699.20 | 134.07 | -109.77 | -60.54 | -4.77 | -41.01 | 0.84 | 5.15 |
| **Et-RC-S$_{L1}$** | -794.73 | -1697.26 | 135.95 | -109.25 | -62.47 | -5.32 | -41.09 | 0.92 | 7.09 |
| **Et-TS-A$_{L2}$** | -1570.72 | -1660.61 | 153.62 | -103.33 | -92.20 | -7.85 | -49.76 | 12.64 | 43.74 |
| **Et-TS-S$_{L2}$** | -1560.52 | -1674.81 | 176.14 | -120.81 | -104.15 | -8.38 | -57.20 | 22.84 | 29.54 |
| **Et-TS-A$_{L1}$** | -793.39 | -1655.73 | 173.36 | -116.90 | -105.85 | -5.72 | -55.11 | 2.26 | 48.62 |
| **Et-TS-S$_{L1}$** | -795.59 | -1687.48 | 172.83 | -121.61 | -92.44 | -6.06 | -47.28 | 0.06 | 16.87 |
| **PF$_3$-RC-A$_{L2}$** | -1030.52 | -1698.06 | 124.01 | -98.55 | -57.63 | -7.54 | -39.71 | 6.29 | 6.29 |
| **PF$_3$-RC-S$_{L2}$** | -1030.27 | -1695.96 | 127.04 | -99.39 | -60.40 | -8.40 | -41.15 | 6.54 | 8.39 |
| **PF$_3$-RC-A$_{L1}$** | -527.28 | -1699.81 | 123.61 | -99.04 | -55.45 | -4.95 | -35.83 | 0.69 | 4.54 |
| **PF$_3$-RC-S$_{L1}$** | -527.37 | -1698.40 | 126.02 | -98.57 | -58.73 | -5.61 | -36.89 | 0.60 | 5.95 |
| **PF$_3$-TS-A$_{L2}$** | -1027.24 | -1657.81 | 147.24 | -94.12 | -91.98 | -7.88 | -46.74 | 9.57 | 46.54 |
| **PF$_3$-TS-S$_{L2}$** | -1026.44 | -1672.00 | 174.43 | -112.87 | -105.58 | -8.90 | -52.92 | 10.37 | 32.35 |
| **PF$_3$-TS-A$_{L1}$** | -525.33 | -1655.40 | 161.19 | -103.46 | -98.89 | -6.00 | -47.16 | 2.64 | 48.95 |
| **PF$_3$-TS-S$_{L1}$** | -527.56 | -1686.65 | 158.60 | -110.36 | -85.77 | -6.25 | -43.78 | 0.41 | 17.70 |
| **PH$_3$-RC-A$_{L2}$** | -817.57 | -1695.68 | 152.68 | -120.81 | -70.04 | -6.85 | -45.02 | 12.97 | 8.67 |
| **PH$_3$-RC-S$_{L2}$** | -817.07 | -1692.55 | 164.16 | -127.81 | -76.46 | -7.84 | -47.95 | 13.47 | 11.80 |
| **PH$_3$-RC-A$_{L1}$** | -420.54 | -1699.48 | 130.73 | -105.86 | -57.98 | -4.58 | -37.69 | 1.04 | 4.87 |
| **PH$_3$-RC-S$_{L1}$** | -420.63 | -1697.16 | 138.01 | -108.68 | -62.89 | -5.11 | -38.67 | 0.95 | 7.19 |
| **PH$_3$-TS-A$_{L2}$** | -815.54 | -1660.28 | 175.93 | -119.70 | -107.16 | -7.41 | -58.34 | 15.00 | 44.07 |
| **PH$_3$-TS-S$_{L2}$** | -814.78 | -1672.21 | 180.25 | -120.32 | -109.68 | -8.35 | -58.10 | 15.76 | 32.14 |
| **PH$_3$-TS-A$_{L1}$** | -418.16 | -1657.25 | 185.90 | -125.79 | -109.51 | -5.66 | -55.06 | 3.42 | 47.10 |
| **PH$_3$-TS-S$_{L1}$** | -420.94 | -1686.91 | 173.95 | -120.85 | -90.10 | -5.91 | -42.91 | 0.64 | 17.44 |
| **PMe$_3$-RC-A$_{L2}$** | -3181.81 | -1692.87 | 177.78 | -139.74 | -83.86 | -8.80 | -54.62 | 16.62 | 11.48 |
| **PMe$_3$-RC-S$_{L2}$** | -3181.31 | -1688.76 | 186.60 | -145.04 | -89.50 | -10.50 | -58.44 | 17.12 | 15.59 |
| **PMe$_3$-RC-A$_{L1}$** | -1604.30 | -1698.97 | 134.14 | -108.83 | -59.83 | -4.86 | -39.38 | 1.92 | 5.38 |
| **PMe$_3$-RC-S$_{L1}$** | -1604.96 | -1696.58 | 147.70 | -115.19 | -66.67 | -5.57 | -39.73 | 1.26 | 7.77 |
| **PMe$_3$-TS-A$_{L2}$** | -3180.02 | -1663.65 | 198.12 | -138.07 | -121.15 | -10.09 | -71.19 | 18.41 | 40.70 |
| **PMe$_3$-TS-S$_{L2}$** | -3179.93 | -1673.60 | 184.28 | -128.25 | -111.84 | -10.99 | -66.80 | 18.50 | 30.75 |
| **PMe$_3$-TS-A$_{L1}$** | -1602.50 | -1662.25 | 205.13 | -141.43 | -114.85 | -7.10 | -58.25 | 3.72 | 42.10 |
| **PMe$_3$-TS-S$_{L1}$** | -1605.55 | -1687.16 | 184.44 | -127.88 | -93.47 | -6.71 | -43.62 | 0.67 | 17.19 |
| **Pyr-RC-A$_{L2}$** | -3360.30 | -1689.69 | 205.93 | -166.96 | -104.32 | -6.54 | -71.89 | 32.43 | 14.66 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Pyr-RC-$S_{L2}$** | -3360.07 | -1685.64 | 209.92 | -169.26 | -108.93 | -7.39 | -75.66 | 32.66 | 18.71 |
| **Pyr-RC-$A_{L1}$** | -1692.49 | -1697.44 | 149.20 | -125.05 | -71.43 | -4.35 | -51.63 | 0.17 | 6.91 |
| **Pyr-RC-$S_{L1}$** | -1692.27 | -1694.49 | 163.05 | -132.84 | -78.20 | -5.32 | -53.31 | 0.39 | 9.86 |
| **Pyr-TS-$A_{L2}$** | -3360.29 | -1659.90 | 226.92 | -162.87 | -145.08 | -7.27 | -88.30 | 32.44 | 44.45 |
| **Pyr-TS-$S_{L2}$** | -3359.10 | -1672.22 | 209.04 | -152.42 | -129.39 | -8.22 | -80.99 | 33.63 | 32.13 |
| **Pyr-TS-$A_{L1}$** | -1691.83 | -1659.77 | 206.57 | -146.93 | -123.67 | -5.20 | -69.23 | 0.83 | 44.58 |
| **Pyr-TS-$S_{L1}$** | -1692.18 | -1683.24 | 198.41 | -141.14 | -107.60 | -5.93 | -56.26 | 0.48 | 21.11 |
| **NHC-RC-$A_{L2}$** | -4270.84 | -1688.37 | 205.06 | -159.82 | -104.03 | -8.39 | -67.18 | 31.41 | 15.98 |
| **NHC-RC-$S_{L2}$** | -4270.48 | -1684.25 | 213.59 | -164.44 | -109.48 | -10.31 | -70.64 | 31.77 | 20.10 |
| **NHC-RC-$A_{L1}$** | -2152.96 | -1698.90 | 136.46 | -112.75 | -62.81 | -4.90 | -44.00 | 1.26 | 5.45 |
| **NHC-RC-$S_{L1}$** | -2152.81 | -1696.47 | 141.38 | -114.77 | -66.08 | -5.79 | -45.26 | 1.41 | 7.88 |
| **NHC-TS-$A_{L2}$** | -4268.78 | -1667.66 | 216.37 | -154.78 | -134.01 | -9.35 | -81.77 | 33.47 | 36.69 |
| **NHC-TS-$S_{L2}$** | -4269.63 | -1673.40 | 201.03 | -143.12 | -124.16 | -9.90 | -76.15 | 32.62 | 30.95 |
| **NHC-TS-$A_{L1}$** | -2151.64 | -1661.62 | 196.51 | -137.33 | -116.97 | -6.36 | -64.15 | 2.58 | 42.73 |
| **NHC-TS-$S_{L1}$** | -2153.39 | -1684.50 | 195.02 | -135.76 | -102.63 | -6.75 | -50.12 | 0.83 | 19.85 |

[a] SCF energy of fragment **1** which corresponds to $PdL_n$. [b] SCF energy of fragment **2** which corresponds to the allylic chloride. [c] Distortion enegy of fragment **1**.

**Table S2.** EDA along the reaction coordinate corresponding to Figures 5–8.

| $d_{C\text{-}Cl}$(Å) | $E$_SCF(**1**) | $E$_SCF(**1**) | $\Delta E_{Pauli}$ | $\Delta E_{elstat}$ | $\Delta E_{orb}$ | $\Delta E_{disp}$ | $\Delta E_{int}$ | $\Delta E_{d1}$ | $\Delta E_{d2}$ |
|---|---|---|---|---|---|---|---|---|---|
| **$PH_3$-TS-$A_{L2}$** | | | | | | | | | |
| 2.945 | -815.48 | -1659.38 | 176.94 | -120.26 | -108.54 | -7.45 | -59.31 | 15.06 | 44.97 |
| 2.926 | -815.54 | -1660.28 | 175.93 | -119.70 | -107.16 | -7.41 | -58.34 | 15.00 | 44.07 |
| 2.890 | -815.66 | -1661.92 | 174.30 | -118.87 | -104.75 | -7.35 | -56.67 | 14.88 | 42.43 |
| 2.858 | -815.75 | -1663.39 | 172.81 | -118.09 | -102.67 | -7.31 | -55.26 | 14.79 | 40.96 |
| 2.798 | -815.92 | -1666.10 | 170.05 | -116.67 | -98.92 | -7.26 | -52.80 | 14.62 | 38.25 |
| 2.697 | -816.19 | -1670.41 | 165.89 | -114.69 | -93.03 | -7.22 | -49.05 | 14.35 | 33.94 |
| 2.549 | -816.56 | -1676.20 | 161.62 | -113.36 | -85.49 | -7.23 | -44.46 | 13.98 | 28.15 |
| 2.359 | -816.92 | -1682.84 | 159.50 | -114.42 | -78.14 | -7.33 | -40.39 | 13.62 | 21.51 |
| 2.122 | -817.23 | -1690.55 | 158.98 | -117.51 | -71.71 | -7.37 | -37.61 | 13.31 | 13.80 |
| 1.911 | -817.50 | -1696.34 | 157.14 | -119.35 | -67.63 | -7.28 | -37.12 | 13.04 | 8.01 |
| 1.875 | -817.57 | -1695.68 | 152.68 | -120.81 | -70.04 | -6.85 | -45.02 | 12.97 | 8.67 |
| **$PH_3$-TS-$S_{L2}$** | | | | | | | | | |
| 2.601 | -814.54 | -1670.34 | 181.08 | -119.98 | -112.95 | -8.41 | -60.26 | 16.00 | 34.01 |
| 2.548 | -814.78 | -1672.21 | 180.25 | -120.32 | -109.68 | -8.35 | -58.10 | 15.76 | 32.14 |
| 2.492 | -815.01 | -1674.12 | 179.95 | -121.08 | -106.60 | -8.29 | -56.02 | 15.53 | 30.23 |
| 2.433 | -815.24 | -1676.10 | 179.98 | -122.10 | -103.60 | -8.23 | -53.95 | 15.30 | 28.25 |
| 2.371 | -815.45 | -1678.19 | 180.57 | -123.62 | -100.75 | -8.18 | -51.98 | 15.09 | 26.16 |
| 2.305 | -815.64 | -1680.37 | 181.65 | -125.55 | -98.05 | -8.15 | -50.10 | 14.90 | 23.98 |
| 2.202 | -815.91 | -1683.71 | 183.84 | -128.98 | -94.40 | -8.13 | -47.67 | 14.63 | 20.64 |
| 2.099 | -816.15 | -1686.90 | 185.92 | -132.39 | -91.23 | -8.09 | -45.79 | 14.39 | 17.45 |
| 1.979 | -816.48 | -1690.12 | 186.29 | -134.95 | -87.60 | -8.02 | -44.28 | 14.06 | 14.23 |
| 1.904 | -816.44 | -1691.65 | 179.21 | -131.98 | -83.46 | -7.91 | -44.14 | 14.10 | 12.70 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 1.836 | -817.07 | -1692.55 | 164.16 | -127.81 | -76.46 | -7.84 | -47.95 | 13.47 | 11.80 |
| **$PH_3$-TS-$A_{L1}$** | | | | | | | | | |
| 2.975 | -418.12 | -1657.03 | 186.27 | -125.98 | -109.92 | -5.68 | -55.31 | 3.46 | 47.32 |
| 2.971 | -418.16 | -1657.25 | 185.90 | -125.79 | -109.51 | -5.66 | -55.06 | 3.42 | 47.10 |
| 2.951 | -418.27 | -1658.12 | 184.74 | -125.21 | -108.04 | -5.59 | -54.10 | 3.31 | 46.23 |
| 2.917 | -418.42 | -1659.61 | 183.09 | -124.44 | -105.83 | -5.50 | -52.68 | 3.16 | 44.74 |
| 2.851 | -418.61 | -1662.39 | 180.64 | -123.36 | -102.22 | -5.41 | -50.35 | 2.97 | 41.96 |
| 2.717 | -418.82 | -1668.03 | 175.94 | -121.26 | -95.47 | -5.36 | -46.15 | 2.76 | 36.32 |
| 2.451 | -419.10 | -1678.90 | 166.35 | -117.47 | -82.06 | -5.45 | -38.63 | 2.48 | 25.45 |
| 2.158 | -419.78 | -1689.55 | 161.93 | -118.22 | -71.60 | -5.64 | -33.53 | 1.80 | 14.80 |
| 1.943 | -420.02 | -1696.19 | 160.58 | -120.33 | -67.11 | -5.63 | -32.49 | 1.56 | 8.16 |
| 1.861 | -420.13 | -1698.09 | 159.25 | -122.24 | -66.60 | -5.41 | -35.00 | 1.45 | 6.26 |
| 1.865 | -420.54 | -1699.48 | 130.73 | -105.86 | -57.98 | -4.58 | -37.69 | 1.04 | 4.87 |
| **$PH_3$-TS-$S_{L1}$** | | | | | | | | | |
| 2.286 | -420.95 | -1685.49 | 174.36 | -120.68 | -92.14 | -5.92 | -44.38 | 0.63 | 18.86 |
| 2.249 | -420.94 | -1686.91 | 173.95 | -120.85 | -90.10 | -5.91 | -42.91 | 0.64 | 17.44 |
| 2.212 | -420.93 | -1688.29 | 173.63 | -121.11 | -88.16 | -5.90 | -41.54 | 0.65 | 16.06 |
| 2.147 | -420.90 | -1690.69 | 172.84 | -121.48 | -84.91 | -5.87 | -39.42 | 0.68 | 13.66 |
| 2.084 | -420.88 | -1692.95 | 171.78 | -121.73 | -81.89 | -5.83 | -37.67 | 0.70 | 11.40 |
| 1.998 | -420.84 | -1695.62 | 168.48 | -121.01 | -77.65 | -5.77 | -35.95 | 0.74 | 8.73 |
| 1.937 | -420.84 | -1697.08 | 161.98 | -118.01 | -73.60 | -5.69 | -35.32 | 0.74 | 7.27 |
| 1.899 | -420.84 | -1697.56 | 151.44 | -112.41 | -69.16 | -5.54 | -35.67 | 0.74 | 6.79 |
| 1.822 | -420.81 | -1697.47 | 145.11 | -109.35 | -66.73 | -5.42 | -36.39 | 0.77 | 6.88 |
| 1.864 | -420.76 | -1697.41 | 140.87 | -108.00 | -64.83 | -5.33 | -37.29 | 0.82 | 6.94 |
| 1.835 | -420.63 | -1697.16 | 138.01 | -108.68 | -62.89 | -5.11 | -38.67 | 0.95 | 7.19 |
| **$PF_3$-TS-$A_{L2}$** | | | | | | | | | |
| 2.988 | -1027.07 | -1656.74 | 148.79 | -94.89 | -93.92 | -7.96 | -47.98 | 9.74 | 47.61 |
| 2.969 | -1027.24 | -1657.81 | 147.24 | -94.12 | -91.98 | -7.88 | -46.74 | 9.57 | 46.54 |
| 2.941 | -1027.46 | -1659.25 | 145.52 | -93.27 | -89.63 | -7.80 | -45.18 | 9.35 | 45.10 |
| 2.917 | -1027.64 | -1660.41 | 144.22 | -92.63 | -87.86 | -7.75 | -44.02 | 9.17 | 43.94 |
| 2.874 | -1027.91 | -1662.40 | 142.10 | -91.60 | -84.99 | -7.68 | -42.17 | 8.90 | 41.95 |
| 2.807 | -1028.28 | -1665.30 | 139.03 | -90.13 | -80.94 | -7.62 | -39.66 | 8.53 | 39.05 |
| 2.674 | -1028.91 | -1670.70 | 133.83 | -87.95 | -73.69 | -7.58 | -35.39 | 7.90 | 33.65 |
| 2.478 | -1029.57 | -1677.74 | 130.33 | -88.02 | -65.69 | -7.63 | -31.01 | 7.24 | 26.61 |
| 2.173 | -1030.19 | -1688.02 | 129.56 | -92.04 | -58.00 | -7.76 | -28.24 | 6.62 | 16.33 |
| 1.859 | -1030.94 | -1698.87 | 120.80 | -90.68 | -51.31 | -7.75 | -28.94 | 5.87 | 5.48 |
| 1.855 | -1030.52 | -1698.06 | 124.01 | -98.55 | -57.63 | -7.54 | -39.71 | 6.29 | 6.29 |
| **$PF_3$-TS-$S_{L2}$** | | | | | | | | | |
| 2.671 | -1026.23 | -1670.12 | 176.68 | -113.55 | -109.20 | -8.96 | -55.03 | 10.58 | 34.23 |
| 2.619 | -1026.44 | -1672.00 | 174.43 | -112.87 | -105.58 | -8.90 | -52.92 | 10.37 | 32.35 |
| 2.566 | -1026.65 | -1673.88 | 172.50 | -112.42 | -102.13 | -8.85 | -50.90 | 10.16 | 30.47 |
| 2.512 | -1026.85 | -1675.79 | 170.94 | -112.24 | -98.90 | -8.79 | -48.99 | 9.96 | 28.56 |
| 2.457 | -1027.05 | -1677.74 | 169.71 | -112.33 | -95.79 | -8.73 | -47.14 | 9.76 | 26.61 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 2.367 | -1027.34 | -1680.81 | 168.76 | -113.19 | -91.47 | -8.67 | -44.57 | 9.47 | 23.54 |
| 2.238 | -1027.69 | -1685.11 | 168.99 | -115.55 | -86.45 | -8.64 | -41.65 | 9.12 | 19.24 |
| 2.108 | -1028.01 | -1689.25 | 169.73 | -118.42 | -82.34 | -8.59 | -39.62 | 8.80 | 15.10 |
| 1.941 | -1028.55 | -1693.50 | 166.17 | -119.21 | -76.91 | -8.46 | -38.41 | 8.26 | 10.85 |
| 1.881 | -1029.22 | -1694.77 | 150.15 | -110.09 | -70.30 | -8.23 | -38.47 | 7.59 | 9.58 |
| 1.820 | -1030.27 | -1695.96 | 127.04 | -99.39 | -60.40 | -8.40 | -41.15 | 6.54 | 8.39 |
| **$PF_3$-TS-$A_{L1}$** | | | | | | | | | |
| 3.011 | -525.26 | -1654.79 | 161.43 | -103.37 | -99.88 | -6.04 | -47.86 | 2.71 | 49.56 |
| 2.999 | -525.33 | -1655.40 | 161.19 | -103.46 | -98.89 | -6.00 | -47.16 | 2.64 | 48.95 |
| 2.972 | -525.45 | -1656.73 | 160.42 | -103.47 | -96.88 | -5.92 | -45.85 | 2.52 | 47.62 |
| 2.918 | -525.60 | -1659.18 | 159.48 | -103.64 | -93.89 | -5.82 | -43.87 | 2.37 | 45.17 |
| 2.834 | -525.74 | -1662.70 | 157.99 | -103.62 | -90.06 | -5.76 | -41.45 | 2.23 | 41.65 |
| 2.719 | -525.88 | -1667.35 | 155.02 | -102.81 | -84.90 | -5.75 | -38.44 | 2.09 | 37.00 |
| 2.554 | -526.09 | -1673.87 | 149.91 | -101.27 | -77.20 | -5.80 | -34.36 | 1.88 | 30.48 |
| 2.281 | -526.42 | -1683.82 | 144.95 | -101.88 | -67.10 | -6.04 | -30.07 | 1.55 | 20.53 |
| 2.024 | -526.67 | -1692.84 | 143.73 | -105.15 | -61.58 | -6.09 | -29.09 | 1.30 | 11.51 |
| 1.855 | -526.78 | -1698.35 | 143.82 | -107.94 | -60.00 | -6.02 | -30.14 | 1.19 | 6.00 |
| 1.855 | -527.28 | -1699.81 | 123.61 | -99.04 | -55.45 | -4.95 | -35.83 | 0.69 | 4.54 |
| **$PF_3$-TS-$S_{L1}$** | | | | | | | | | |
| 2.337 | -527.56 | -1685.18 | 158.93 | -110.27 | -87.69 | -6.25 | -45.28 | 0.41 | 19.17 |
| 2.299 | -527.56 | -1686.65 | 158.60 | -110.36 | -85.77 | -6.25 | -43.78 | 0.41 | 17.70 |
| 2.260 | -527.55 | -1688.12 | 158.34 | -110.53 | -83.92 | -6.25 | -42.36 | 0.42 | 16.23 |
| 2.221 | -527.55 | -1689.58 | 158.02 | -110.68 | -82.11 | -6.24 | -41.01 | 0.42 | 14.77 |
| 2.182 | -527.54 | -1691.04 | 157.69 | -110.86 | -80.37 | -6.23 | -39.77 | 0.43 | 13.31 |
| 2.123 | -527.52 | -1693.13 | 157.03 | -111.07 | -77.87 | -6.20 | -38.11 | 0.45 | 11.22 |
| 2.049 | -527.49 | -1695.61 | 155.60 | -111.05 | -74.80 | -6.16 | -36.41 | 0.48 | 8.74 |
| 1.984 | -527.45 | -1697.47 | 152.54 | -109.98 | -71.81 | -6.11 | -35.36 | 0.52 | 6.88 |
| 1.929 | -527.41 | -1698.66 | 145.19 | -106.22 | -67.93 | -6.02 | -34.98 | 0.56 | 5.69 |
| 1.893 | -527.41 | -1698.99 | 131.49 | -98.55 | -62.54 | -5.82 | -35.42 | 0.56 | 5.36 |
| 1.840 | -527.37 | -1698.40 | 126.02 | -98.57 | -58.73 | -5.61 | -36.89 | 0.60 | 5.95 |
| **$PMe_3$-TS-$A_{L2}$** | | | | | | | | | |
| 2.868 | -3179.93 | -1662.36 | 199.20 | -138.67 | -123.02 | -10.11 | -72.60 | 18.50 | 41.99 |
| 2.838 | -3180.02 | -1663.65 | 198.12 | -138.07 | -121.15 | -10.09 | -71.19 | 18.41 | 40.70 |
| 2.788 | -3180.09 | -1665.74 | 195.11 | -136.39 | -117.78 | -10.03 | -69.09 | 18.34 | 38.61 |
| 2.724 | -3180.23 | -1668.35 | 191.69 | -134.55 | -113.64 | -9.99 | -66.49 | 18.20 | 36.00 |
| 2.649 | -3180.38 | -1671.38 | 188.13 | -132.76 | -108.99 | -9.97 | -63.59 | 18.05 | 32.97 |
| 2.539 | -3180.61 | -1675.39 | 183.89 | -131.03 | -102.87 | -9.97 | -59.98 | 17.82 | 28.96 |
| 2.416 | -3180.84 | -1679.56 | 180.80 | -130.43 | -96.98 | -10.01 | -56.62 | 17.59 | 24.79 |
| 2.274 | -3181.08 | -1684.12 | 178.80 | -131.04 | -91.25 | -10.06 | -53.55 | 17.35 | 20.23 |
| 2.092 | -3181.38 | -1689.69 | 177.65 | -132.97 | -85.38 | -10.01 | -50.71 | 17.05 | 14.66 |
| 1.944 | -3181.65 | -1693.53 | 178.28 | -135.71 | -82.14 | -9.89 | -49.46 | 16.78 | 10.82 |
| 1.893 | -3181.81 | -1692.87 | 177.78 | -139.74 | -83.86 | -8.80 | -54.62 | 16.62 | 11.48 |
| **$PMe_3$-TS-$S_{L2}$** | | | | | | | | | |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 2.429 | -3179.93 | -1673.59 | 184.27 | -128.24 | -111.84 | -10.99 | -66.80 | 18.50 | 30.76 |
| 2.429 | -3179.93 | -1673.60 | 184.28 | -128.25 | -111.84 | -10.99 | -66.80 | 18.50 | 30.75 |
| 2.429 | -3179.93 | -1673.60 | 184.29 | -128.26 | -111.85 | -10.99 | -66.81 | 18.50 | 30.75 |
| 2.395 | -3180.08 | -1674.68 | 185.11 | -129.37 | -110.38 | -10.95 | -65.59 | 18.35 | 29.67 |
| 2.359 | -3180.22 | -1675.79 | 186.10 | -130.63 | -108.94 | -10.91 | -64.38 | 18.21 | 28.56 |
| 2.284 | -3180.47 | -1678.04 | 188.43 | -133.50 | -106.20 | -10.86 | -62.13 | 17.96 | 26.31 |
| 2.207 | -3180.70 | -1680.35 | 191.19 | -136.78 | -103.67 | -10.82 | -60.08 | 17.73 | 24.00 |
| 2.130 | -3180.91 | -1682.53 | 193.92 | -140.09 | -101.43 | -10.78 | -58.38 | 17.52 | 21.82 |
| 2.055 | -3181.12 | -1684.47 | 196.25 | -143.09 | -99.46 | -10.73 | -57.03 | 17.31 | 19.88 |
| 1.986 | -3180.92 | -1686.01 | 196.93 | -145.11 | -97.59 | -10.68 | -56.45 | 17.51 | 18.34 |
| 1.846 | -3181.31 | -1688.76 | 186.60 | -145.04 | -89.50 | -10.50 | -58.44 | 17.12 | 15.59 |
| **$PMe_3$-TS-$A_{L1}$** | | | | | | | | | |
| 2.897 | -1602.48 | -1661.27 | 205.73 | -141.76 | -116.13 | -7.13 | -59.29 | 3.74 | 43.08 |
| 2.872 | -1602.50 | -1662.25 | 205.13 | -141.43 | -114.85 | -7.10 | -58.25 | 3.72 | 42.10 |
| 2.847 | -1602.55 | -1663.27 | 204.36 | -140.98 | -113.51 | -7.08 | -57.21 | 3.67 | 41.08 |
| 2.810 | -1602.60 | -1664.75 | 203.22 | -140.32 | -111.63 | -7.05 | -55.78 | 3.62 | 39.60 |
| 2.746 | -1602.66 | -1667.45 | 200.95 | -139.02 | -108.23 | -7.03 | -53.33 | 3.56 | 36.90 |
| 2.606 | -1602.74 | -1673.48 | 194.93 | -135.69 | -100.32 | -7.03 | -48.11 | 3.48 | 30.87 |
| 2.346 | -1602.95 | -1683.84 | 184.81 | -131.36 | -86.34 | -7.23 | -40.12 | 3.27 | 20.51 |
| 2.098 | -1603.21 | -1692.18 | 180.69 | -131.86 | -77.60 | -7.31 | -36.08 | 3.01 | 12.17 |
| 1.906 | -1603.47 | -1696.97 | 180.24 | -134.19 | -73.92 | -7.26 | -35.13 | 2.75 | 7.38 |
| 1.870 | -1603.79 | -1697.41 | 180.82 | -136.18 | -74.44 | -7.07 | -36.87 | 2.43 | 6.94 |
| 1.871 | -1604.30 | -1698.97 | 134.14 | -108.83 | -59.83 | -4.86 | -39.38 | 1.92 | 5.38 |
| **$PMe_3$-TS-$S_{L1}$** | | | | | | | | | |
| 2.245 | -1605.55 | -1685.73 | 184.79 | -127.62 | -95.56 | -6.73 | -45.12 | 0.67 | 18.62 |
| 2.208 | -1605.55 | -1687.16 | 184.44 | -127.88 | -93.47 | -6.71 | -43.62 | 0.67 | 17.19 |
| 2.172 | -1605.55 | -1688.55 | 184.11 | -128.20 | -91.48 | -6.69 | -42.26 | 0.67 | 15.80 |
| 2.141 | -1605.55 | -1689.71 | 183.77 | -128.45 | -89.83 | -6.66 | -41.17 | 0.67 | 14.64 |
| 2.110 | -1605.54 | -1690.83 | 183.35 | -128.67 | -88.24 | -6.64 | -40.20 | 0.68 | 13.52 |
| 2.051 | -1605.53 | -1692.87 | 182.13 | -128.87 | -85.22 | -6.59 | -38.55 | 0.69 | 11.48 |
| 1.999 | -1605.50 | -1694.50 | 179.91 | -128.40 | -82.40 | -6.54 | -37.43 | 0.72 | 9.85 |
| 1.957 | -1605.46 | -1695.60 | 176.41 | -127.01 | -79.74 | -6.47 | -36.81 | 0.76 | 8.75 |
| 1.920 | -1605.39 | -1696.34 | 169.74 | -123.75 | -76.36 | -6.35 | -36.72 | 0.83 | 8.01 |
| 1.901 | -1605.31 | -1696.51 | 164.14 | -120.98 | -74.03 | -6.24 | -37.11 | 0.91 | 7.84 |
| 1.839 | -1604.96 | -1696.58 | 147.70 | -115.19 | -66.67 | -5.57 | -39.73 | 1.26 | 7.77 |

**Table 3.** Orbital overlaps, orbital energies, charge transfer, electron density and the laplacian of the electron density at the Pd-Cl bond critical point along the reaction coordinate.

| $d_{C\text{-}Cl}$(Å) | $\langle \mathbf{1}_{HOMO} \vert \mathbf{2}_{LUMO} \rangle$ | $\langle \mathbf{1}_{HOMO} \vert \mathbf{2}_{LUMO+1} \rangle$ | $\langle \mathbf{1}_{LUMO} \vert \mathbf{2}_{HOMO} \rangle$ | $\langle \mathbf{1}_{LUMO+1} \vert \mathbf{2}_{HOMO} \rangle$ | $\varepsilon(\mathbf{1}_{HOMO})$ | $\varepsilon(\mathbf{1}_{LUMO})$ | $\varepsilon(\mathbf{1}_{LUMO+1})$ | $\varepsilon(\mathbf{2}_{HOMO})$ | $\varepsilon(\mathbf{2}_{LUMO})$ | $\varepsilon(\mathbf{2}_{LUMO+1})$ | $\Delta q$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | **$PF_3$-TS-$A_{L2}$** | | | | | | |
| 2.988 | 0.215 | 0.019 | – | – | -5.51 | -2.79 | -2.36 | -5.24 | -4.70 | -1.44 | 0.363 |
| 2.969 | 0.214 | 0.019 | – | – | -5.52 | -2.79 | -2.37 | -5.27 | -4.66 | -1.41 | 0.354 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 2.941 | 0.213 | 0.019 | – | – | -5.54 | -2.80 | -2.38 | -5.31 | -4.60 | -1.36 | 0.341 |
| 2.917 | 0.212 | 0.019 | – | – | -5.56 | -2.80 | -2.39 | -5.34 | -4.55 | -1.33 | 0.331 |
| 2.874 | 0.210 | 0.021 | – | – | -5.58 | -2.81 | -2.40 | -5.39 | -4.46 | -1.27 | 0.314 |
| 2.807 | 0.205 | 0.025 | – | – | -5.61 | -2.82 | -2.42 | -5.46 | -4.32 | -1.18 | 0.290 |
| 2.674 | 0.195 | 0.039 | – | – | -5.67 | -2.84 | -2.46 | -5.59 | -4.05 | -1.03 | 0.243 |
| 2.478 | 0.178 | 0.063 | – | – | -5.75 | -2.87 | -2.51 | -5.85 | -3.63 | -0.86 | 0.177 |
| 2.173 | 0.164 | 0.085 | – | – | -5.85 | -2.92 | -2.58 | -6.26 | -2.75 | -0.62 | 0.082 |
| 1.859 | 0.192 | 0.017 | – | – | -5.98 | -2.96 | -2.65 | -6.17 | -1.48 | -0.12 | 0.010 |
| 1.855 | 0.241 | 0.050 | – | – | -5.94 | -2.99 | -2.64 | -6.12 | -1.67 | 0.04 | 0.040 |
| | | | | | **$PF_3$-TS-$S_{L2}$** | | | | | | |
| 2.671 | 0.152 | 0.150 | 0.052 | 0.137 | -5.62 | -2.92 | -2.56 | -5.44 | -4.09 | -1.04 | 0.184 |
| 2.619 | 0.152 | 0.155 | 0.053 | 0.139 | -5.64 | -2.93 | -2.57 | -5.50 | -3.99 | -1.00 | 0.171 |
| 2.566 | 0.152 | 0.159 | 0.054 | 0.142 | -5.65 | -2.93 | -2.57 | -5.57 | -3.89 | -0.96 | 0.158 |
| 2.512 | 0.152 | 0.163 | 0.054 | 0.146 | -5.66 | -2.93 | -2.58 | -5.64 | -3.77 | -0.92 | 0.143 |
| 2.457 | 0.153 | 0.167 | 0.053 | 0.150 | -5.68 | -2.94 | -2.58 | -5.72 | -3.65 | -0.88 | 0.128 |
| 2.367 | 0.155 | 0.171 | 0.046 | 0.159 | -5.70 | -2.94 | -2.59 | -5.87 | -3.42 | -0.80 | 0.103 |
| 2.238 | 0.162 | 0.173 | 0.009 | 0.170 | -5.73 | -2.96 | -2.61 | -6.08 | -3.06 | -0.68 | 0.069 |
| 2.108 | 0.175 | 0.167 | 0.104 | 0.149 | -5.76 | -2.97 | -2.62 | -6.22 | -2.63 | -0.51 | 0.038 |
| 1.941 | 0.204 | 0.139 | 0.201 | 0.099 | -5.81 | -2.98 | -2.64 | -6.17 | -2.04 | -0.13 | 0.011 |
| 1.881 | 0.214 | 0.025 | 0.214 | 0.084 | -5.84 | -2.98 | -2.64 | -6.13 | -1.82 | -0.03 | 0.012 |
| 1.820 | 0.250 | 0.034 | 0.280 | 0.004 | -5.90 | -2.97 | -2.62 | -6.18 | -1.50 | -0.22 | 0.043 |
| | | | | | **$PF_3$-TS-$A_{L1}$** | | | | | | |
| 3.011 | 0.145 | 0.052 | – | – | -5.22 | -2.72 | -1.39 | -5.15 | -4.73 | -1.57 | 0.364 |
| 2.999 | 0.146 | 0.051 | – | – | -5.22 | -2.72 | -1.38 | -5.17 | -4.71 | -1.56 | 0.361 |
| 2.972 | 0.147 | 0.048 | – | – | -5.23 | -2.72 | -1.39 | -5.22 | -4.65 | -1.52 | 0.352 |
| 2.918 | 0.147 | 0.044 | – | – | -5.25 | -2.73 | -1.39 | -5.31 | -4.54 | -1.46 | 0.336 |
| 2.834 | 0.146 | 0.037 | – | – | -5.27 | -2.75 | -1.39 | -5.42 | -4.36 | -1.36 | 0.312 |
| 2.719 | 0.142 | 0.027 | – | – | -5.29 | -2.77 | -1.41 | -5.54 | -4.12 | -1.24 | 0.282 |
| 2.554 | 0.132 | 0.011 | – | – | -5.33 | -2.79 | -1.43 | -5.73 | -3.76 | -1.09 | 0.237 |
| 2.281 | 0.119 | 0.009 | – | – | -5.38 | -2.82 | -1.48 | -6.18 | -3.05 | -0.87 | 0.162 |
| 2.024 | 0.123 | 0.011 | – | – | -5.43 | -2.85 | -1.52 | -6.26 | -2.11 | -0.59 | 0.101 |
| 1.855 | 0.138 | 0.110 | – | – | -5.47 | -2.87 | -1.54 | -6.16 | -1.44 | -0.24 | 0.080 |
| 1.855 | 0.121 | 0.131 | – | – | -5.46 | -2.84 | -1.54 | -6.12 | -1.57 | 0.03 | 0.063 |
| | | | | | **$PF_3$-TS-$S_{L1}$** | | | | | | |
| 2.337 | 0.123 | 0.083 | 0.144 | 0.199 | -5.51 | -2.85 | -1.57 | -5.92 | -3.29 | -0.62 | 0.088 |
| 2.299 | 0.122 | 0.082 | 0.132 | 0.202 | -5.51 | -2.85 | -1.58 | -5.98 | -3.18 | -0.59 | 0.076 |
| 2.260 | 0.121 | 0.081 | 0.114 | 0.203 | -5.52 | -2.86 | -1.58 | -6.04 | -3.05 | -0.55 | 0.066 |
| 2.221 | 0.120 | 0.078 | 0.088 | 0.204 | -5.52 | -2.86 | -1.58 | -6.10 | -2.93 | -0.51 | 0.054 |
| 2.182 | 0.119 | 0.075 | 0.052 | 0.201 | -5.52 | -2.86 | -1.58 | -6.15 | -2.79 | -0.46 | 0.043 |
| 2.123 | 0.119 | 0.067 | 0.012 | 0.189 | -5.53 | -2.87 | -1.59 | -6.19 | -2.57 | -0.39 | 0.026 |
| 2.049 | 0.120 | 0.048 | 0.081 | 0.170 | -5.54 | -2.87 | -1.59 | -6.20 | -2.27 | -0.28 | 0.007 |
| 1.984 | 0.122 | 0.009 | 0.121 | 0.155 | -5.54 | -2.88 | -1.59 | -6.18 | -2.00 | -0.19 | -0.008 |
| 1.929 | 0.125 | 0.039 | 0.145 | 0.144 | -5.54 | -2.88 | -1.59 | -6.14 | -1.76 | -0.12 | -0.016 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1.893 | 0.131 | 0.058 | 0.167 | 0.131 | -5.54 | -2.88 | -1.60 | -6.12 | -1.60 | -0.11 | -0.003 |
| 1.840 | 0.153 | 0.074 | 0.251 | 0.072 | -5.49 | -2.85 | -1.56 | -6.16 | -1.45 | -0.21 | 0.052 |
| | | | | | **$PH_3$-TS-$A_{L2}$** | | | | | | |
| 2.945 | 0.216 | 0.032 | – | – | -3.94 | -1.68 | -0.89 | -5.38 | -4.57 | -1.46 | 0.461 |
| 2.926 | 0.216 | 0.032 | – | – | -3.94 | -1.68 | -0.90 | -5.40 | -4.53 | -1.43 | 0.454 |
| 2.890 | 0.214 | 0.034 | – | – | -3.95 | -1.68 | -0.90 | -5.43 | -4.46 | -1.39 | 0.440 |
| 2.858 | 0.213 | 0.036 | – | – | -3.95 | -1.69 | -0.90 | -5.46 | -4.39 | -1.35 | 0.429 |
| 2.798 | 0.209 | 0.040 | – | – | -3.97 | -1.69 | -0.91 | -5.50 | -4.27 | -1.27 | 0.409 |
| 2.697 | 0.203 | 0.051 | – | – | -3.99 | -1.69 | -0.91 | -5.58 | -4.08 | -1.15 | 0.376 |
| 2.549 | 0.193 | 0.070 | – | – | -4.02 | -1.70 | -0.92 | -5.75 | -3.78 | -1.00 | 0.328 |
| 2.359 | 0.183 | 0.092 | – | – | -4.05 | -1.71 | -0.92 | -6.05 | -3.34 | -0.84 | 0.267 |
| 2.122 | 0.184 | 0.101 | – | – | -4.10 | -1.72 | -0.92 | -6.32 | -2.62 | -0.61 | 0.194 |
| 1.911 | 0.210 | 0.061 | – | – | -4.14 | -1.73 | -0.92 | -6.22 | -1.85 | -0.23 | 0.141 |
| 1.875 | 0.244 | 0.068 | – | – | -4.09 | -1.71 | -1.00 | -6.15 | -1.88 | -0.03 | 0.152 |
| | | | | | **$PH_3$-TS-$S_{L2}$** | | | | | | |
| 2.601 | 0.158 | 0.164 | 0.043 | 0.098 | -3.89 | -1.69 | -0.96 | -5.56 | -4.06 | -1.01 | 0.370 |
| 2.548 | 0.159 | 0.169 | 0.047 | 0.105 | -3.90 | -1.69 | -0.96 | -5.62 | -3.95 | -0.97 | 0.354 |
| 2.492 | 0.159 | 0.173 | 0.049 | 0.112 | -3.91 | -1.69 | -0.97 | -5.70 | -3.83 | -0.93 | 0.336 |
| 2.433 | 0.161 | 0.176 | 0.050 | 0.121 | -3.92 | -1.69 | -0.97 | -5.79 | -3.69 | -0.89 | 0.318 |
| 2.371 | 0.163 | 0.179 | 0.049 | 0.132 | -3.94 | -1.69 | -0.98 | -5.89 | -3.53 | -0.85 | 0.297 |
| 2.305 | 0.166 | 0.180 | 0.042 | 0.142 | -3.95 | -1.69 | -0.98 | -6.00 | -3.35 | -0.80 | 0.275 |
| 2.202 | 0.174 | 0.179 | 0.001 | 0.150 | -3.96 | -1.70 | -0.99 | -6.17 | -3.04 | -0.71 | 0.241 |
| 2.099 | 0.186 | 0.172 | 0.111 | 0.129 | -3.98 | -1.70 | -1.00 | -6.27 | -2.70 | -0.57 | 0.210 |
| 1.979 | 0.207 | 0.148 | 0.187 | 0.092 | -4.00 | -1.70 | -1.00 | -6.24 | -2.28 | -0.31 | 0.180 |
| 1.904 | 0.221 | 0.074 | 0.203 | 0.079 | -4.01 | -1.70 | -1.01 | -6.18 | -2.02 | -0.12 | 0.165 |
| 1.836 | 0.257 | 0.050 | 0.258 | 0.010 | -4.04 | -1.69 | -0.97 | -6.18 | -1.73 | -0.29 | 0.160 |
| | | | | | **$PH_3$-TS-$A_{L1}$** | | | | | | |
| 2.975 | 0.152 | 0.027 | – | – | -4.29 | -2.11 | -0.55 | -5.29 | -4.61 | -1.60 | 0.435 |
| 2.971 | 0.152 | 0.027 | – | – | -4.29 | -2.11 | -0.55 | -5.29 | -4.60 | -1.59 | 0.432 |
| 2.951 | 0.152 | 0.027 | – | – | -4.29 | -2.11 | -0.55 | -5.32 | -4.56 | -1.57 | 0.423 |
| 2.917 | 0.151 | 0.027 | – | – | -4.30 | -2.11 | -0.55 | -5.36 | -4.49 | -1.52 | 0.410 |
| 2.851 | 0.150 | 0.025 | – | – | -4.31 | -2.12 | -0.55 | -5.44 | -4.36 | -1.44 | 0.388 |
| 2.717 | 0.146 | 0.018 | – | – | -4.33 | -2.12 | -0.56 | -5.56 | -4.08 | -1.29 | 0.351 |
| 2.451 | 0.132 | 0.002 | – | – | -4.35 | -2.13 | -0.57 | -5.88 | -3.48 | -1.05 | 0.276 |
| 2.158 | 0.125 | 0.001 | – | – | -4.38 | -2.14 | -0.58 | -6.31 | -2.63 | -0.78 | 0.193 |
| 1.943 | 0.137 | 0.045 | – | – | -4.40 | -2.15 | -0.58 | -6.23 | -1.80 | -0.44 | 0.143 |
| 1.861 | 0.147 | 0.100 | – | – | -4.42 | -2.16 | -0.59 | -6.18 | -1.58 | -0.19 | 0.137 |
| 1.865 | 0.096 | 0.141 | – | – | -4.41 | -2.13 | -0.56 | -6.14 | -1.63 | 0.01 | 0.091 |
| | | | | | **$PH_3$-TS-$S_{L1}$** | | | | | | |
| 2.286 | 0.129 | 0.082 | 0.113 | 0.183 | -4.45 | -2.13 | -0.58 | -6.02 | -3.20 | -0.61 | 0.178 |
| 2.249 | 0.128 | 0.080 | 0.096 | 0.184 | -4.45 | -2.13 | -0.58 | -6.08 | -3.08 | -0.58 | 0.165 |
| 2.212 | 0.128 | 0.077 | 0.069 | 0.184 | -4.45 | -2.13 | -0.58 | -6.13 | -2.95 | -0.54 | 0.153 |
| 2.147 | 0.127 | 0.070 | 0.003 | 0.177 | -4.46 | -2.14 | -0.58 | -6.20 | -2.72 | -0.46 | -0.132 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 2.084 | 0.127 | 0.057 | 0.063 | 0.162 | -4.46 | -2.14 | -0.59 | -6.22 | -2.48 | -0.38 | 0.112 |
| 1.998 | 0.130 | 0.020 | 0.122 | 0.143 | -4.46 | -2.15 | -0.59 | -6.20 | -2.12 | -0.25 | 0.087 |
| 1.937 | 0.133 | 0.030 | 0.149 | 0.130 | -4.46 | -2.15 | -0.59 | -6.16 | -1.86 | -0.17 | 0.087 |
| 1.899 | 0.137 | 0.055 | 0.168 | 0.114 | -4.46 | -2.14 | -0.59 | -6.14 | -1.70 | -0.14 | 0.077 |
| 1.822 | 0.141 | 0.061 | 0.186 | 0.096 | -4.45 | -2.14 | -0.58 | -6.14 | -1.64 | -0.16 | 0.086 |
| 1.864 | 0.146 | 0.066 | 0.211 | 0.072 | -4.44 | -2.14 | -0.58 | -6.15 | -1.59 | -0.19 | 0.092 |
| 1.835 | 0.139 | 0.097 | 0.253 | 0.054 | -4.42 | -2.13 | -0.57 | -6.18 | -1.50 | -0.24 | 0.100 |
| | | | | | **$PMe_3$-TS-$A_{L2}$** | | | | | | |
| 2.868 | 0.225 | 0.031 | – | – | -2.82 | -1.07 | -0.31 | -5.46 | -4.47 | -1.45 | 0.578 |
| 2.838 | 0.223 | 0.035 | – | – | -2.83 | -1.08 | -0.32 | -5.48 | -4.42 | -1.41 | 0.568 |
| 2.788 | 0.221 | 0.042 | – | – | -2.84 | -1.08 | -0.32 | -5.51 | -4.33 | -1.34 | 0.551 |
| 2.724 | 0.218 | 0.051 | – | – | -2.85 | -1.09 | -0.33 | -5.56 | -4.22 | -1.26 | 0.530 |
| 2.649 | 0.213 | 0.063 | – | – | -2.86 | -1.09 | -0.34 | -5.63 | -4.08 | -1.17 | 0.505 |
| 2.539 | 0.207 | 0.079 | – | – | -2.88 | -1.10 | -0.35 | -5.77 | -3.87 | -1.05 | 0.468 |
| 2.416 | 0.202 | 0.094 | – | – | -2.90 | -1.11 | -0.36 | -5.95 | -3.61 | -0.93 | 0.427 |
| 2.274 | 0.200 | 0.107 | – | – | -2.92 | -1.12 | -0.38 | -6.20 | -3.25 | -0.79 | 0.378 |
| 2.092 | 0.207 | 0.107 | – | – | -2.95 | -1.13 | -0.40 | -6.37 | -2.69 | -0.56 | 0.315 |
| 1.944 | 0.228 | 0.080 | – | – | -2.98 | -1.15 | -0.41 | -6.27 | -2.17 | -0.27 | 0.270 |
| 1.893 | 0.257 | 0.076 | – | – | -2.97 | -1.14 | -0.43 | -6.16 | -2.07 | 0.00 | 0.266 |
| | | | | | **$PMe_3$-TS-$S_{L2}$** | | | | | | |
| 2.429 | 0.171 | 0.188 | 0.030 | 0.115 | -2.84 | -1.12 | -0.37 | -5.80 | -3.75 | -0.94 | 0.471 |
| 2.429 | 0.171 | 0.188 | 0.030 | 0.115 | -2.84 | -1.12 | -0.37 | -5.80 | -3.75 | -0.94 | 0.471 |
| 2.429 | 0.171 | 0.188 | 0.030 | 0.115 | -2.84 | -1.12 | -0.37 | -5.80 | -3.75 | -0.94 | 0.471 |
| 2.395 | 0.173 | 0.188 | 0.028 | 0.118 | -2.85 | -1.13 | -0.38 | -5.85 | -3.66 | -0.92 | 0.458 |
| 2.359 | 0.175 | 0.189 | 0.026 | 0.122 | -2.85 | -1.13 | -0.38 | -5.91 | -3.57 | -0.90 | 0.444 |
| 2.284 | 0.181 | 0.188 | 0.013 | 0.132 | -2.87 | -1.13 | -0.38 | -6.03 | -3.37 | -0.84 | 0.415 |
| 2.207 | 0.188 | 0.185 | 0.023 | 0.137 | -2.88 | -1.13 | -0.39 | -6.15 | -3.15 | -0.78 | 0.385 |
| 2.130 | 0.199 | 0.178 | 0.092 | 0.119 | -2.89 | -1.14 | -0.40 | -6.23 | -2.90 | -0.69 | 0.356 |
| 2.055 | 0.212 | 0.166 | 0.149 | 0.091 | -2.91 | -1.14 | -0.40 | -6.23 | -2.66 | -0.57 | 0.330 |
| 1.986 | 0.226 | 0.149 | 0.178 | 0.073 | -2.92 | -1.14 | -0.41 | -6.20 | -2.44 | -0.40 | 0.308 |
| 1.846 | 0.275 | 0.041 | 0.243 | 0.003 | -2.98 | -1.16 | -0.41 | -6.19 | -1.94 | -0.33 | 0.272 |
| | | | | | **$PMe_3$-TS-$A_{L1}$** | | | | | | |
| 2.897 | 0.148 | 0.041 | – | – | -3.64 | -1.61 | -0.03 | -5.43 | -4.43 | -1.49 | 0.486 |
| 2.872 | 0.148 | 0.039 | – | – | -3.65 | -1.62 | -0.04 | -5.45 | -4.38 | -1.46 | 0.479 |
| 2.847 | 0.147 | 0.038 | – | – | -3.65 | -1.62 | -0.04 | -5.47 | -4.33 | 1.44 | 0.471 |
| 2.810 | 0.146 | 0.036 | – | – | -3.66 | -1.62 | -0.04 | -5.50 | -4.26 | -1.40 | 0.461 |
| 2.746 | 0.144 | 0.032 | – | – | -3.67 | -1.63 | -0.05 | -5.55 | -4.13 | -1.33 | 0.442 |
| 2.606 | 0.137 | 0.022 | – | – | -3.69 | -1.64 | -0.06 | -5.67 | -3.83 | -1.19 | 0.399 |
| 2.346 | 0.123 | 0.002 | – | – | -3.72 | -1.66 | -0.08 | -6.05 | -3.21 | -0.95 | 0.313 |
| 2.098 | 0.121 | 0.008 | – | – | -3.74 | -1.68 | -0.10 | -6.33 | -2.43 | -0.69 | 0.234 |
| 1.906 | 0.133 | 0.084 | – | – | -3.78 | -1.69 | -0.12 | -6.21 | -1.73 | -0.33 | 0.187 |
| 1.870 | 0.136 | 0.106 | – | – | -3.79 | -1.70 | -0.12 | -6.19 | -1.67 | -0.19 | 0.187 |
| 1.871 | 0.083 | 0.160 | – | – | -3.77 | -1.66 | -0.11 | -6.15 | -1.66 | 0.00 | 0.113 |

| | | | | | **$PMe_3$-TS-$S_{L1}$** | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 2.245 | 0.138 | 0.076 | 0.079 | 0.189 | -3.81 | -1.65 | -0.13 | -6.09 | -3.12 | -0.59 | 0.241 |
| 2.208 | 0.137 | 0.072 | 0.053 | 0.187 | -3.81 | -1.65 | -0.13 | -6.14 | -2.99 | -0.56 | 0.227 |
| 2.172 | 0.136 | 0.067 | 0.019 | 0.182 | -3.82 | -1.65 | -0.13 | -6.18 | -2.86 | -0.52 | 0.212 |
| 2.141 | 0.136 | 0.061 | 0.014 | 0.174 | -3.82 | -1.65 | -0.13 | -6.21 | -2.75 | -0.48 | 0.201 |
| 2.110 | 0.136 | 0.055 | 0.045 | 0.165 | -3.82 | -1.65 | -0.13 | -6.22 | -2.63 | -0.44 | 0.189 |
| 2.051 | 0.136 | 0.036 | 0.094 | 0.149 | -3.82 | -1.66 | -0.14 | -6.22 | -2.40 | -0.36 | 0.168 |
| 1.999 | 0.138 | 0.008 | 0.124 | 0.136 | -3.82 | -1.66 | -0.14 | -6.20 | -2.18 | -0.29 | 0.150 |
| 1.957 | 0.139 | 0.024 | 0.143 | 0.127 | -3.82 | -1.66 | -0.14 | -6.18 | -2.00 | -0.22 | 0.138 |
| 1.920 | 0.142 | 0.055 | 0.159 | 0.116 | -3.82 | -1.66 | -0.14 | -6.15 | -1.84 | -0.19 | 0.129 |
| 1.901 | 0.144 | 0.067 | 0.171 | 0.106 | -3.82 | -1.67 | -0.14 | -6.15 | -1.76 | -0.18 | 0.129 |
| 1.839 | 0.136 | 0.117 | 0.240 | 0.049 | -3.78 | -1.66 | -0.12 | -6.18 | -1.54 | -0.25 | 0.128 |

**Table S4.** Electron density at the Pd-Cl bond critical point along the reaction coordinate.

| **$PF_3$-TS-$S_{L2}$** | | | | | **$PF_3$-TS-$S_{L1}$** | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $d_{C\text{-}Cl}$(Å) | ρ(Pd-Cl) | $\nabla^2$ρ(Pd-Cl) | ρ(C-Cl) | $\nabla^2$ρ(C-Cl) | $d_{C\text{-}Cl}$(Å) | ρ(Pd-Cl) | $\nabla^2$ρ(Pd-Cl) | ρ(C-Cl) | $\nabla^2$ρ(C-Cl) |
| 2.671 | 0.0342 | 0.0989 | 0.0283 | 0.0647 | 2.337 | 0.0460 | 0.1357 | 0.0554 | 0.0780 |
| **2.619** | **0.0334** | **0.0972** | **0.0314** | **0.0674** | **2.299** | **0.0455** | **0.1357** | **0.0600** | **0.0754** |
| 2.566 | 0.0326 | 0.0956 | 0.0350 | 0.0697 | 2.260 | 0.0451 | 0.1359 | 0.0651 | 0.0715 |
| 2.512 | 0.0319 | 0.0942 | 0.0390 | 0.0714 | 2.221 | 0.0447 | 0.1359 | 0.0707 | 0.0661 |
| 2.457 | 0.0312 | 0.0930 | 0.0437 | 0.0723 | 2.182 | 0.0444 | 0.1360 | 0.0769 | 0.0588 |
| 2.367 | 0.0305 | 0.0918 | 0.0526 | 0.0712 | 2.123 | 0.0438 | 0.1360 | 0.0870 | 0.0441 |
| 2.238 | 0.0297 | 0.0909 | 0.0689 | 0.0608 | 2.049 | 0.0430 | 0.1354 | 0.1021 | 0.0167 |
| 2.108 | 0.0292 | 0.0901 | 0.0907 | 0.0324 | 1.984 | 0.0419 | 0.1329 | 0.1173 | -0.0170 |
| 1.941 | 0.0280 | 0.0860 | 0.1291 | -0.0490 | 1.929 | 0.0395 | 0.1253 | 0.1318 | -0.0541 |
| 1.881 | 0.0243 | 0.0732 | 0.1466 | -0.0976 | 1.893 | 0.0323 | 0.1009 | 0.1425 | -0.0849 |
| 1.820 | – | – | 0.1676 | -0.1672 | 1.840 | – | – | 0.1605 | -0.1435 |
| **$PH_3$-TS-$S_{L2}$** | | | | | **$PH_3$-TS-$S_{L1}$** | | | | |
| $d_{C\text{-}Cl}$(Å) | ρ(Pd-Cl) | $\nabla^2$ρ(Pd-Cl) | ρ(C-Cl) | $\nabla^2$ρ(C-Cl) | $d_{C\text{-}Cl}$(Å) | ρ(Pd-Cl) | $\nabla^2$ρ(Pd-Cl) | ρ(C-Cl) | $\nabla^2$ρ(C-Cl) |
| 2.601 | 0.0214 | 0.0610 | 0.0324 | 0.0704 | 2.286 | 0.0403 | 0.1202 | 0.0614 | 0.0762 |
| **2.548** | **0.0209** | **0.0602** | **0.0361** | **0.0726** | **2.249** | **0.0399** | **0.1200** | **0.0665** | **0.0719** |
| 2.492 | 0.0204 | 0.0596 | 0.0405 | 0.0742 | 2.212 | 0.0395 | 0.1198 | 0.0719 | 0.0661 |
| 2.433 | 0.0201 | 0.0592 | 0.0456 | 0.0749 | 2.147 | 0.0388 | 0.1193 | 0.0825 | 0.0520 |
| 2.371 | 0.0198 | 0.0591 | 0.0519 | 0.0741 | 2.084 | 0.0406 | 0.1263 | 0.0946 | 0.0319 |
| 2.305 | 0.0197 | 0.0593 | 0.0596 | 0.0708 | 1.998 | 0.0369 | 0.1155 | 0.1137 | -0.0083 |
| 2.202 | 0.0196 | 0.0598 | 0.0740 | 0.0584 | 1.937 | 0.0347 | 0.1084 | 0.1295 | -0.0482 |
| 2.099 | 0.0196 | 0.0603 | 0.0919 | 0.0332 | 1.899 | 0.0296 | 0.0917 | 0.1405 | -0.0794 |
| 1.979 | 0.0195 | 0.0604 | 0.1185 | -0.0208 | 1.822 | 0.0243 | 0.0751 | 0.1461 | -0.0964 |
| 1.904 | 0.0185 | 0.0578 | 0.1389 | -0.0739 | 1.864 | – | – | 0.1521 | -0.1159 |
| 1.836 | – | – | 0.1610 | -0.1461 | 1.835 | – | – | 0.1620 | -0.1489 |
| **$PMe_3$-TS-$S_{L2}$** | | | | | **$PMe_3$-TS-$S_{L1}$** | | | | |
| $d_{C\text{-}Cl}$(Å) | ρ(Pd-Cl) | $\nabla^2$ρ(Pd-Cl) | ρ(C-Cl) | $\nabla^2$ρ(C-Cl) | $d_{C\text{-}Cl}$(Å) | ρ(Pd-Cl) | $\nabla^2$ρ(Pd-Cl) | ρ(C-Cl) | $\nabla^2$ρ(C-Cl) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 2.429 | 0.0173 | 0.0503 | 0.0458 | 0.0764 | 2.245 | 0.0359 | 0.1071 | 0.0669 | 0.0733 |
| **2.429** | **0.0173** | **0.0503** | **0.0458** | **0.0764** | **2.208** | **0.0356** | **0.1068** | **0.0723** | **0.0675** |
| 2.429 | 0.0173 | 0.0503 | 0.0458 | 0.0764 | 2.172 | 0.0352 | 0.1065 | 0.0782 | 0.0601 |
| 2.395 | 0.0172 | 0.0504 | 0.0492 | 0.0765 | 2.141 | 0.0349 | 0.1062 | 0.0835 | 0.0523 |
| 2.359 | 0.0172 | 0.0506 | 0.0530 | 0.0759 | 2.110 | 0.0346 | 0.1058 | 0.0892 | 0.0431 |
| 2.284 | 0.0172 | 0.0513 | 0.0619 | 0.0721 | 2.051 | 0.0340 | 0.1047 | 0.1012 | 0.0204 |
| 2.207 | 0.0173 | 0.0522 | 0.0728 | 0.0628 | 1.999 | 0.0331 | 0.1025 | 0.1134 | -0.0063 |
| 2.130 | 0.0174 | 0.0532 | 0.0856 | 0.0463 | 1.957 | 0.0319 | 0.0989 | 0.1240 | -0.0327 |
| 2.055 | 0.0175 | 0.0541 | 0.1004 | 0.0209 | 1.920 | 0.0293 | 0.0905 | 0.1343 | -0.0609 |
| 1.986 | 0.0176 | 0.0548 | 0.1163 | -0.0133 | 1.901 | 0.0262 | 0.0808 | 0.1399 | -0.0774 |
| 1.846 | – | – | 0.1569 | -0.1323 | 1.839 | – | – | 0.1603 | -0.1431 |

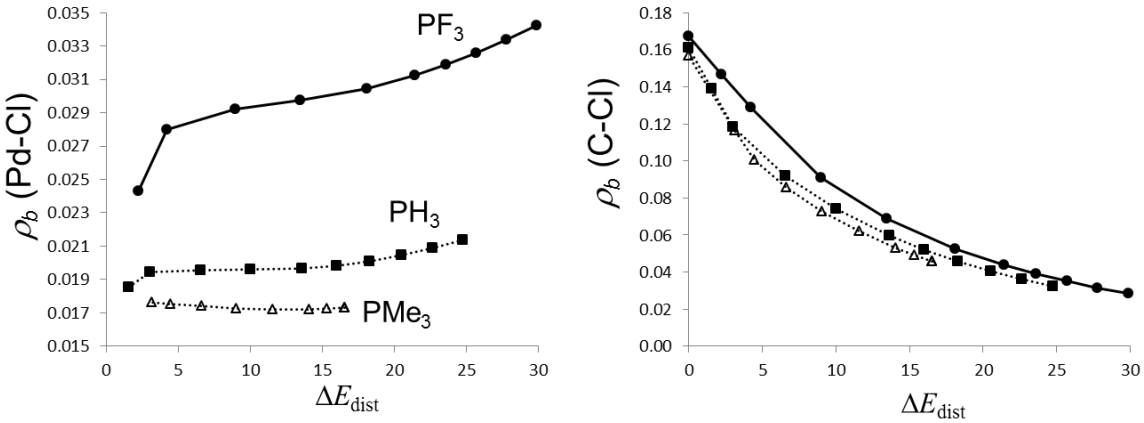



**Figure S4.** Graph of the electron density at the bond critical point (e Å$^{-3}$) of the Pd-Cl bond and C-Cl bond as a function of the energy of distortion $\Delta E_{\text{dist}}$ (kcal/mol).

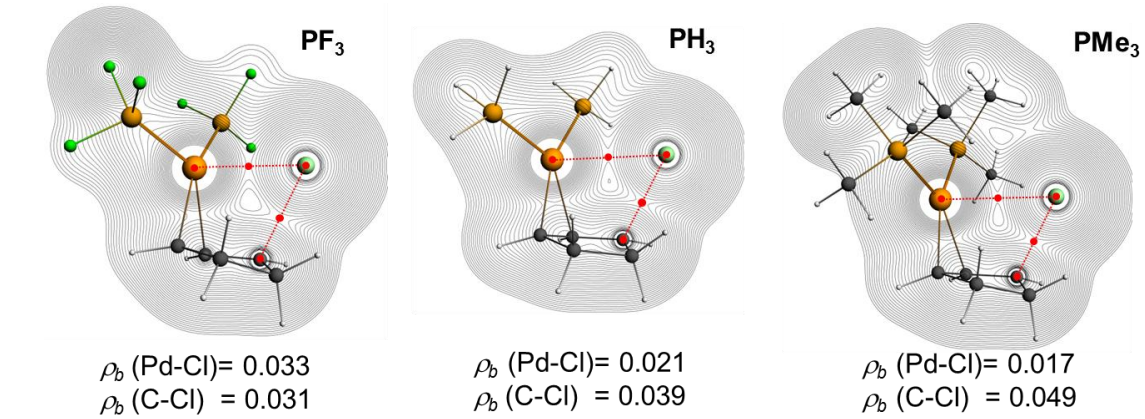



**Figure S5.** Contour plots of the electron density with the value ar the listed bond critical points (e Å$^{-3}$).

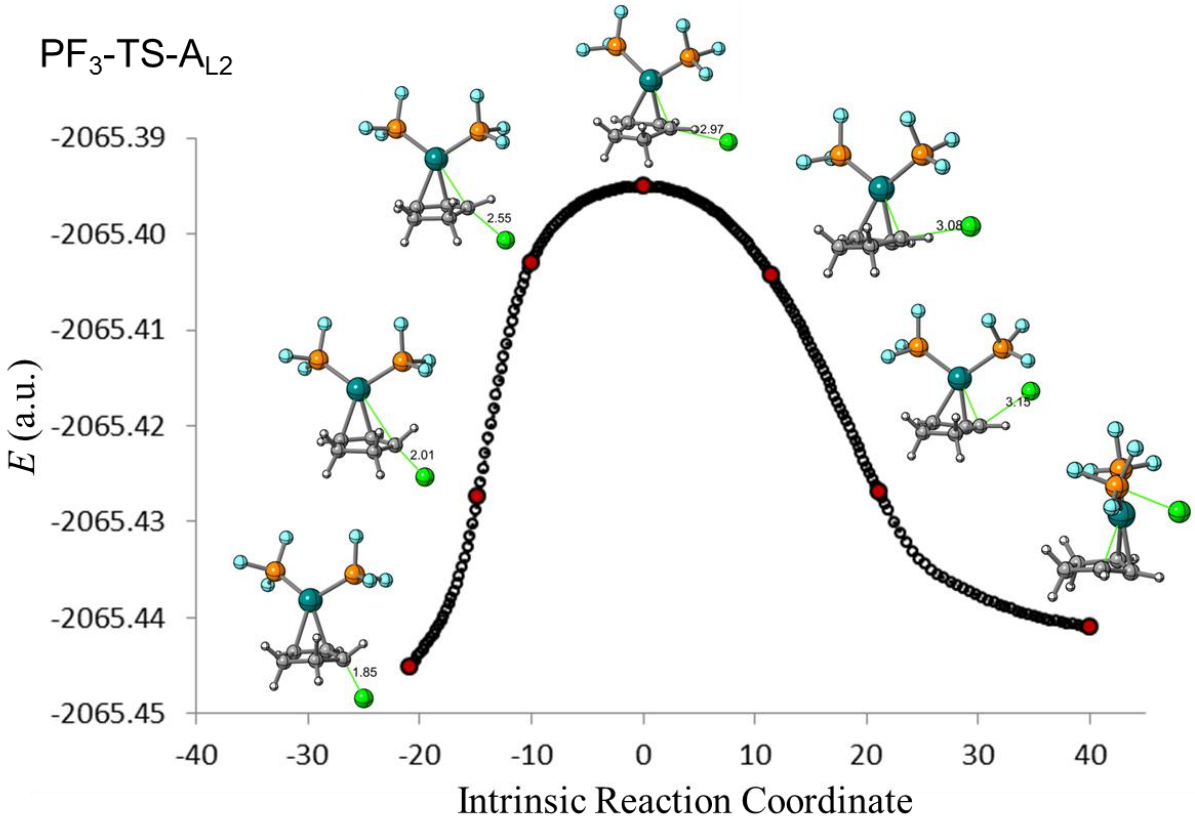
**Table S5.** SCF energies (Hartree) for all stationary points with and without solvation with thermodynamic parameters computed at standard pressure (1 bar) and at room temperature (298.15 K).

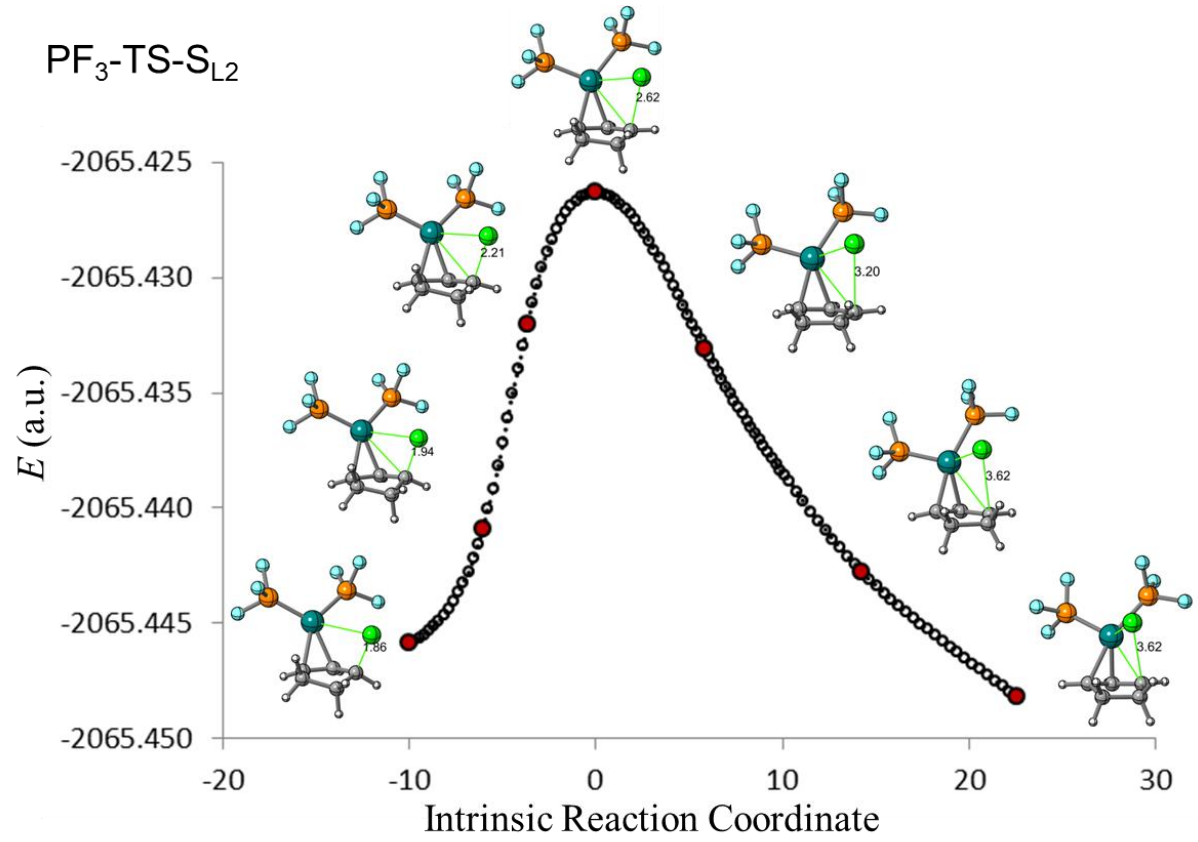
| Name | *E*_TPSS | *E*_TPSS_sol | *E*_B2PLYP | *E*_B2PLYP_sol | ZPVE | *H*_corr | *G*_corr |
|---|---|---|---|---|---|---|---|
| **MA-RC-$A_{L2}$** | -1542.114074 | -1542.126238 | -1540.957145 | -1540.969996 | 0.219327 | 0.240384 | 0.168459 |
| **MA-RC-$S_{L2}$** | -1542.113573 | -1542.125098 | -1540.957296 | -1540.969418 | 0.219427 | 0.240417 | 0.168806 |
| **MA-RC-$A_{L1}$** | -1162.555333 | -1162.566408 | -1161.721911 | -1161.733040 | 0.162239 | 0.177122 | 0.118450 |
| **MA-RC-$S_{L1}$** | -1162.560610 | -1162.569814 | -1161.724454 | -1161.733854 | 0.162317 | 0.177104 | 0.119303 |
| **MA-TS-$A_{L2}$** | -1542.046136 | -1542.070978 | -1540.880557 | -1540.908672 | 0.215188 | 0.236572 | 0.163475 |
| **MA-TS-$S_{L2}$** | -1542.084855 | -1542.097447 | -1540.919356 | -1540.932582 | 0.216697 | 0.238327 | 0.163396 |
| **MA-TS-$A_{L1}$** | -1162.496952 | -1162.520711 | -1161.648608 | -1161.678558 | 0.159767 | 0.174539 | 0.116115 |
| **MA-TS-$S_{L1}$** | -1162.554275 | -1162.564756 | -1161.712732 | -1161.723659 | 0.161432 | 0.175712 | 0.119341 |
| **MA-$PR_{L1}$** | -1162.577828 | -1162.564855 | -1161.738208 | -1161.750752 | 0.162388 | 0.177224 | 0.119949 |
| **MA** | -379.515934 | -379.521150 | -379.190205 | -379.195816 | 0.054366 | 0.060587 | 0.025227 |
| **$Pd(MA)_2$** | -1162.577828 | -1162.564855 | -1161.738208 | -1161.750752 | 0.162388 | 0.177224 | 0.119949 |
| **Pd(MA)** | -886.981115 | -886.998676 | -886.190877 | -886.208872 | 0.110626 | 0.125081 | 0.066855 |
| **Et-RC-$A_{L2}$** | -940.340865 | -940.349952 | -939.645687 | -939.648452 | 0.213335 | 0.228147 | 0.171609 |
| **Et-RC-$S_{L2}$** | -940.337203 | -940.345831 | -939.642659 | -939.644981 | 0.213492 | 0.228160 | 0.172247 |
| **Et-RC-$A_{L1}$** | -861.669658 | -861.676941 | -861.068516 | -861.071141 | 0.159280 | 0.171163 | 0.120301 |
| **Et-RC-$S_{L1}$** | -861.666748 | -861.674163 | -861.066310 | -861.069026 | 0.159279 | 0.171120 | 0.120189 |
| **Et-TS-$A_{L2}$** | -940.292113 | -940.318725 | -939.589533 | -939.612878 | 0.211719 | 0.226678 | 0.169567 |
| **Et-TS-$S_{L2}$** | -940.310216 | -940.322335 | -939.605516 | -939.612040 | 0.210938 | 0.225815 | 0.169861 |
| **Et-TS-$A_{L1}$** | -861.619135 | -861.641282 | -861.008356 | -861.035144 | 0.157504 | 0.169186 | 0.118813 |
| **Et-TS-$S_{L1}$** | -861.661292 | -861.665684 | -861.052123 | -861.056681 | 0.158516 | 0.169695 | 0.121472 |
| **Et-$PR_{L2}$** | -940.334532 | -940.342736 | -939.631307 | -939.640241 | 0.212189 | 0.227462 | 0.170890 |
| **Et-$PR_{L1}$** | -861.694865 | -861.702649 | -861.086868 | -861.095394 | 0.159588 | 0.171383 | 0.121874 |
| **Et** | -78.635517 | -78.636220 | -78.543048 | -78.543770 | 0.050370 | 0.054366 | 0.029493 |
| **$Pd(Et)_2$** | -285.219407 | -285.217945 | -284.894372 | -284.895686 | 0.104614 | 0.113037 | 0.071992 |
| **Pd(Et)** | -206.526354 | -206.533046 | -206.297836 | -206.304001 | 0.051977 | 0.056766 | 0.024800 |
| **PF3-RC-$A_{L2}$** | -2065.453462 | -2065.461372 | -2064.320149 | -2064.324679 | 0.126920 | 0.146270 | 0.072985 |
| **PF3-RC-$S_{L2}$** | -2065.452067 | -2065.459886 | -2064.319447 | -2064.323855 | 0.126805 | 0.146097 | 0.074671 |
| **PF3-RC-$A_{L1}$** | -1424.224128 | -1424.232600 | -1423.404483 | -1423.409422 | 0.116748 | 0.130592 | 0.072662 |
| **PF3-RC-$S_{L1}$** | -1424.223795 | -1424.232196 | -1423.404146 | -1423.409065 | 0.116709 | 0.130556 | 0.072402 |
| **PF3-TS-$A_{L2}$** | -2065.395083 | -2065.421859 | -2064.254142 | -2064.281015 | 0.124572 | 0.144032 | 0.070838 |
| **PF3-TS-$S_{L2}$** | -2065.426321 | -2065.438182 | -2064.284204 | -2064.293086 | 0.125246 | 0.144371 | 0.073924 |
| **PF3-TS-$A_{L1}$** | -1424.167809 | -1424.196122 | -1423.337453 | -1423.367579 | 0.114566 | 0.128266 | 0.071568 |
| **PF3-TS-$S_{L1}$** | -1424.215751 | -1424.225986 | -1423.388125 | -1423.394886 | 0.115663 | 0.129083 | 0.072738 |
| **PF3-$PR_{L2}$** | -2065.450446 | -2065.458240 | -2064.309824 | -2064.318784 | 0.126314 | 0.145794 | 0.075074 |
| **PF3-$PR_{L1}$** | -1424.250406 | -1424.258405 | -1423.423454 | -1423.432422 | 0.116317 | 0.130309 | 0.073322 |
| **$PF_3$** | -641.182506 | -641.183555 | -640.870261 | -640.871628 | 0.008208 | 0.013234 | -0.019004 |
| **$Pd(PF_3)_2$** | -1410.324993 | -1410.330109 | -1409.562700 | -1409.568092 | 0.019440 | 0.031886 | -0.025716 |
| **$Pd(PF_3)$** | -769.088991 | -769.099929 | -768.642530 | -768.653258 | 0.009801 | 0.016440 | -0.021581 |
| **$PH_3$-RC-$A_{L2}$** | -1469.440415 | -1469.448980 | -1468.613576 | -1468.616615 | 0.160063 | 0.175515 | 0.115508 |

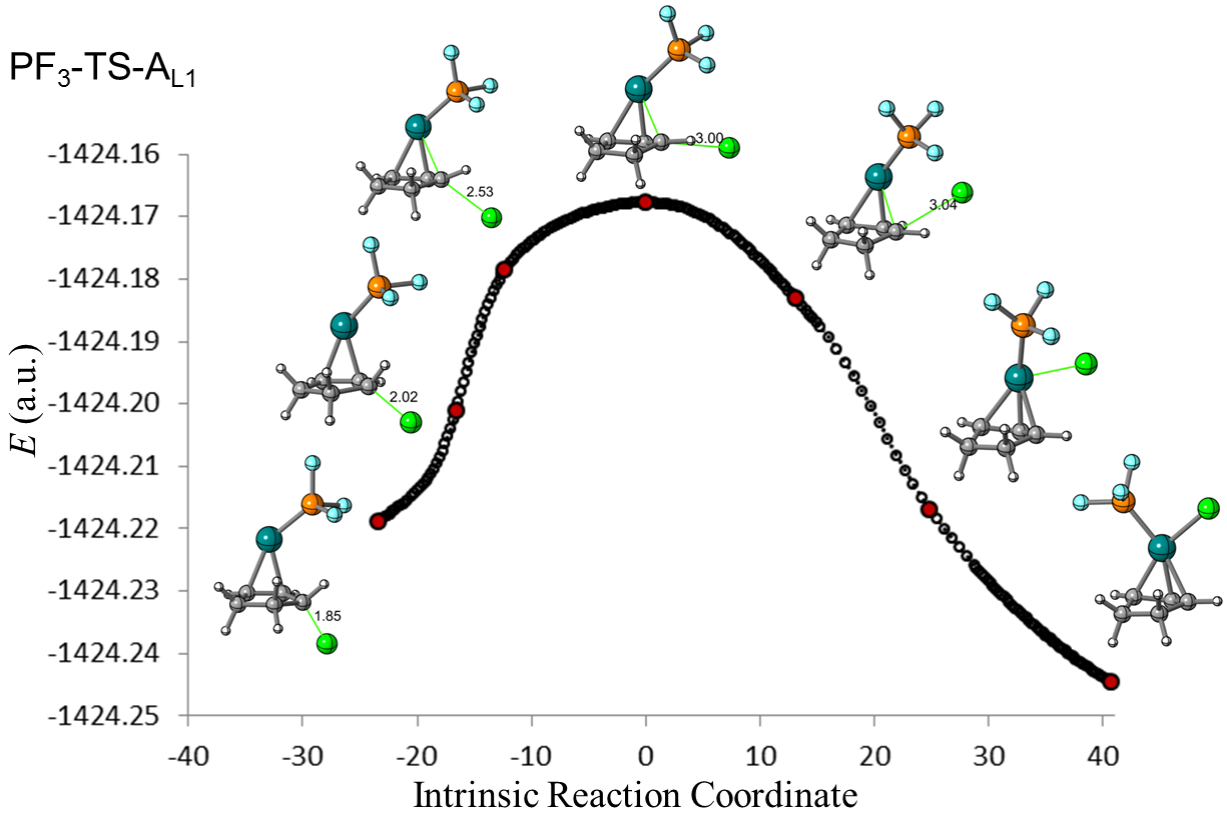
| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **$PH_3$-RC-$S_{L2}$** | -1469.439541 | -1469.447223 | -1468.613402 | -1468.615525 | 0.160592 | 0.175639 | 0.117379 |
| **$PH_3$-RC-$A_{L1}$** | -1126.217356 | -1126.224794 | -1125.551595 | -1125.554575 | 0.133565 | 0.145417 | 0.094231 |
| **$PH_3$-RC-$S_{L1}$** | -1126.215468 | -1126.223261 | -1125.549888 | -1125.553209 | 0.133485 | 0.145308 | 0.093888 |
| **$PH_3$-TS-$A_{L2}$** | -1469.400825 | -1469.429539 | -1468.567700 | -1468.593758 | 0.158792 | 0.174084 | 0.113895 |
| **$PH_3$-TS-$S_{L2}$** | -1469.419165 | -1469.432346 | -1468.584765 | -1468.593046 | 0.159581 | 0.174336 | 0.116660 |
| **$PH_3$-TS-$A_{L1}$** | -1126.172815 | -1126.200589 | -1125.497332 | -1125.524721 | 0.131727 | 0.143363 | 0.092611 |
| **$PH_3$-TS-$S_{L1}$** | -1126.205727 | -1126.215430 | -1125.532151 | -1125.537419 | 0.132445 | 0.143893 | 0.093981 |
| **$PH_3$-$PR_{L2}$** | -1469.450328 | -1469.457944 | -1468.616374 | -1468.624759 | 0.161156 | 0.175930 | 0.120005 |
| **$PH_3$-$PR_{\eta 1}$** | -1469.443333 | -1469.450386 | -1468.611332 | -1468.618924 | 0.160445 | 0.175751 | 0.116993 |
| **$PH_3$-$TS_{\eta 1 \leftrightarrow \eta 3}$** | -1469.438983 | -1469.446296 | -1468.605116 | -1468.613097 | 0.159962 | 0.174416 | 0.118751 |
| **$PH_3$-$TS_{PR}$** | -1469.438637 | -1469.445404 | -1468.605329 | -1468.612754 | 0.158982 | 0.174043 | 0.116653 |
| **$PH_3$-$PR_{L1}$** | -1126.249783 | -1126.257554 | -1125.576396 | -1125.584893 | 0.133475 | 0.145292 | 0.095373 |
| **$PH_3$** | -343.182288 | -343.182849 | -343.023510 | -343.024044 | 0.023830 | 0.027684 | 0.002792 |
| **Pd($PH_3$)$_2$** | -814.318026 | -814.319398 | -813.865914 | -813.864480 | 0.053138 | 0.061699 | 0.018695 |
| **Pd($PH_3$)** | -471.079813 | -471.086407 | -470.786830 | -470.792658 | 0.026735 | 0.031415 | -0.000012 |
| **$PMe_3$-RC-$A_{L2}$** | -1705.525166 | -1705.539560 | -1704.433422 | -1704.438230 | 0.331973 | 0.356728 | 0.276484 |
| **$PMe_3$-RC-$S_{L2}$** | -1705.524292 | -1705.536889 | -1704.433824 | -1704.436893 | 0.332194 | 0.355795 | 0.280300 |
| **$PMe_3$-RC-$A_{L1}$** | -1244.259379 | -1244.269286 | -1243.460997 | -1243.464508 | 0.219205 | 0.235053 | 0.175296 |
| **$PMe_3$-RC-$S_{L1}$** | -1244.257304 | -1244.267614 | -1243.459073 | -1243.462963 | 0.219182 | 0.234921 | 0.175748 |
| **$PMe_3$-TS-$A_{L2}$** | -1705.500614 | -1705.533824 | -1704.403617 | -1704.429325 | 0.330950 | 0.354749 | 0.277627 |
| **$PMe_3$-TS-$S_{L2}$** | -1705.510678 | -1705.527651 | -1704.413829 | -1704.421458 | 0.330707 | 0.355235 | 0.276670 |
| **$PMe_3$-TS-$A_{L1}$** | -1244.226558 | -1244.253737 | -1243.418563 | -1243.442698 | 0.218001 | 0.234367 | 0.173612 |
| **$PMe_3$-TS-$S_{L1}$** | -1244.248702 | -1244.260816 | -1243.443246 | -1243.448931 | 0.218035 | 0.233490 | 0.175463 |
| **$PMe_3$-$PR_{L2}$** | -1705.545271 | -1705.553896 | -1704.449398 | -1704.458452 | 0.332083 | 0.356765 | 0.279003 |
| **$PMe_3$-$PR_{L1}$** | -1244.300400 | -1244.308037 | -1243.495160 | -1243.503342 | 0.219183 | 0.235801 | 0.175449 |
| **$PMe_3$** | -461.212864 | -461.214390 | -460.919512 | -460.920990 | 0.110883 | 0.118640 | 0.081478 |
| **Pd($PMe_3$)$_2$** | -1050.399411 | -1050.402566 | -1049.680458 | -1049.683355 | 0.224850 | 0.242000 | 0.179917 |
| **Pd($PMe_3$)** | -589.121880 | -589.128106 | -588.695717 | -588.701383 | 0.112580 | 0.122002 | 0.078980 |
| **Pyr-RC-$A_{L2}$** | -1279.917292 | -1279.931516 | -1278.890889 | -1278.898650 | 0.284226 | 0.304268 | 0.231128 |
| **Pyr-RC-$S_{L2}$** | -1279.916714 | -1279.929303 | -1278.891373 | -1278.897394 | 0.284398 | 0.304284 | 0.232579 |
| **Pyr-RC-$A_{L1}$** | -1031.459365 | -1031.469342 | -1030.693933 | -1030.699089 | 0.195571 | 0.209846 | 0.150615 |
| **Pyr-RC-$S_{L1}$** | -1031.457159 | -1031.466570 | -1030.692553 | -1030.697001 | 0.195612 | 0.209755 | 0.151592 |
| **Pyr-TS-$A_{L2}$** | -1279.894055 | -1279.928150 | -1278.863072 | -1278.892340 | 0.283244 | 0.303165 | 0.230943 |
| **Pyr-TS-$S_{L2}$** | -1279.901164 | -1279.916481 | -1278.870050 | -1278.878649 | 0.282632 | 0.302570 | 0.229981 |
| **Pyr-TS-$A_{L1}$** | -1031.424444 | -1031.452248 | -1030.650032 | -1030.675986 | 0.194148 | 0.208149 | 0.151091 |
| **Pyr-TS-$S_{L1}$** | -1031.442618 | -1031.454284 | -1030.670237 | -1030.676853 | 0.194356 | 0.208212 | 0.151541 |
| **Pyr-$PR_{L2}$** | -1279.942006 | -1279.952225 | -1278.912739 | -1278.923453 | 0.283887 | 0.303118 | 0.234814 |
| **Pyr-$PR_{L1}$** | -1031.497584 | -1031.512649 | -1030.725485 | -1030.735240 | 0.195509 | 0.209658 | 0.153318 |
| **Pyr** | -248.431822 | -248.434431 | -248.172448 | -248.175205 | 0.087210 | 0.092516 | 0.059760 |
| **Pd(Pyr$)_2$** | -624.793200 | -624.742285 | -624.136701 | -624.142063 | 0.177434 | 0.190465 | 0.134644 |
| **Pd(Pyr)** | -376.300274 | -376.306297 | -375.906775 | -375.912075 | 0.088321 | 0.095560 | 0.055928 |
| **NHC-RC-$A_{L2}$** | -1393.074717 | -1393.092688 | -1391.926184 | -1391.935428 | 0.358683 | 0.384166 | 0.299917 |
| **NHC-RC-$S_{L2}$** | -1393.073714 | -1393.089688 | -1391.926684 | -1391.934138 | 0.358822 | 0.384115 | 0.301756 |

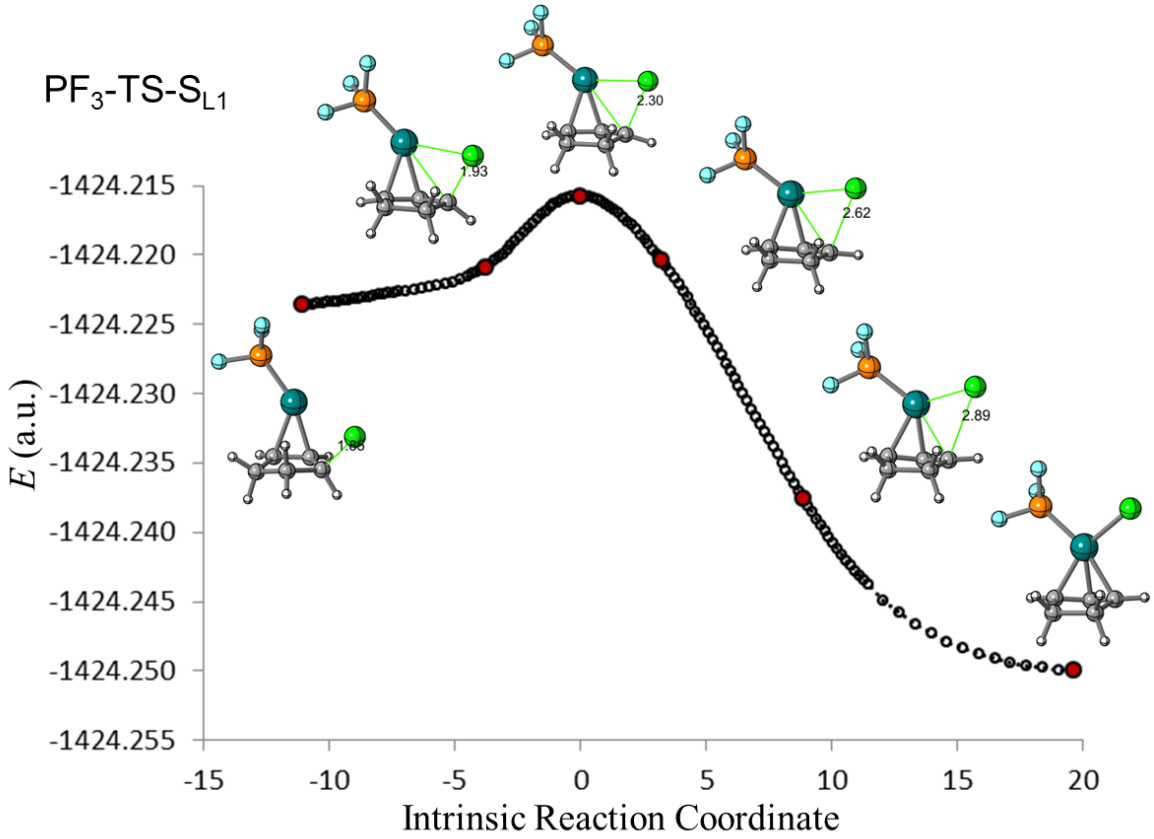
| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **NHC-RC-$A_{L1}$** | -1088.042382 | -1088.054078 | -1087.216366 | -1087.222247 | 0.233066 | 0.250043 | 0.185749 |
| **NHC-RC-$S_{L1}$** | -1088.040484 | -1088.051683 | -1087.215286 | -1087.220593 | 0.233043 | 0.249919 | 0.186038 |
| **NHC-TS-$A_{L2}$** | -1393.060517 | -1393.095600 | -1391.908635 | -1391.936883 | 0.358776 | 0.384066 | 0.301713 |
| **NHC-TS-$S_{L2}$** | -1393.063393 | -1393.073503 | -1391.911051 | -1391.921442 | 0.358416 | 0.383149 | 0.303129 |
| **NHC-TS-$A_{L1}$** | -1088.010721 | -1088.039213 | -1087.176300 | -1087.201944 | 0.231866 | 0.247605 | 0.188305 |
| **NHC-TS-$S_{L1}$** | -1088.028974 | -1088.042155 | -1087.195603 | -1087.202930 | 0.231892 | 0.248402 | 0.186313 |
| **NHC-$PR_{L2}$** | -1393.098853 | -1393.112003 | -1391.948259 | -1391.962057 | 0.360256 | 0.384949 | 0.307066 |
| **NHC-$PR_{L1}$** | -1088.079647 | -1088.089948 | -1087.246881 | -1087.257875 | 0.232925 | 0.249896 | 0.187600 |
| **NHC** | -304.979620 | -304.984708 | -304.660304 | -304.665432 | 0.124405 | 0.132482 | 0.093330 |
| **Pd($NHC_{)2}$** | -737.959968 | -737.968268 | -737.184139 | -737.192367 | 0.251834 | 0.269356 | 0.206168 |
| **Pd(NHC)** | -432.896145 | -432.898056 | -432.441325 | -432.448968 | 0.125810 | 0.135666 | 0.090579 |

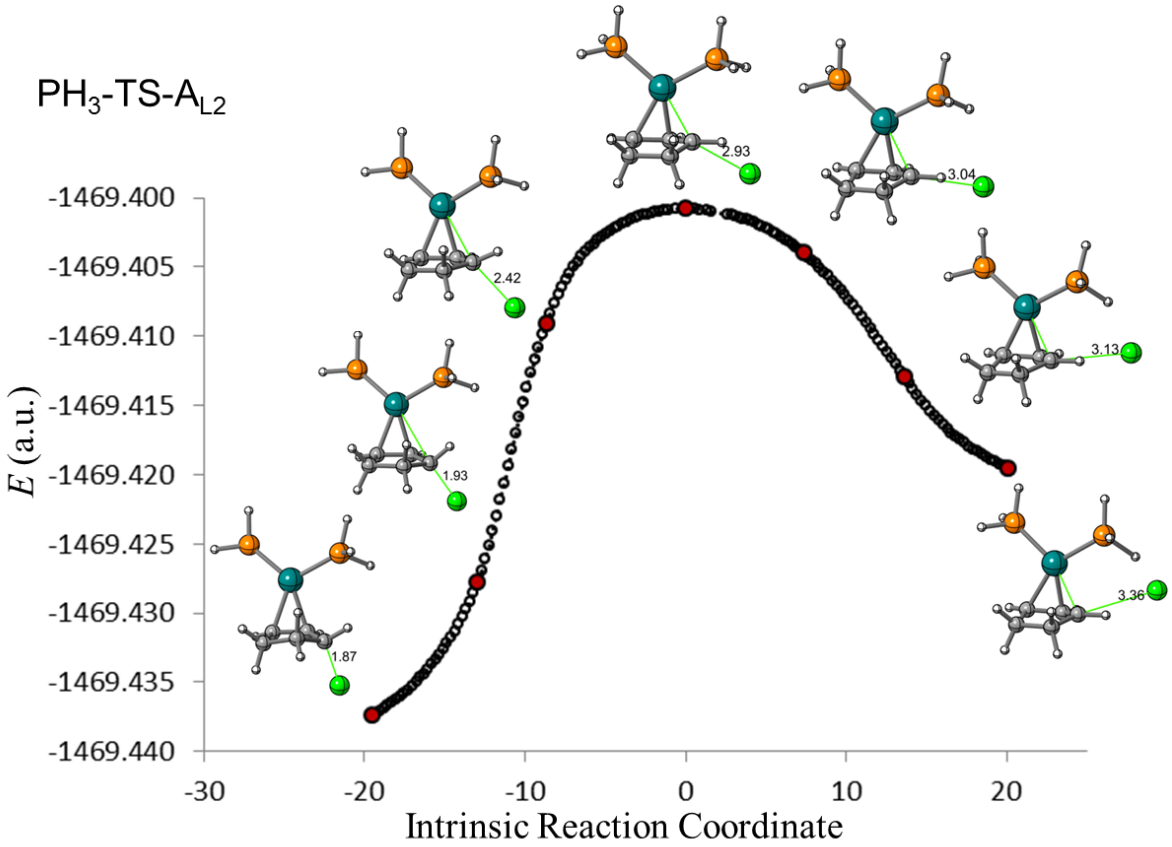
**Intrinsic Reaction Coordinate Diagrams.**

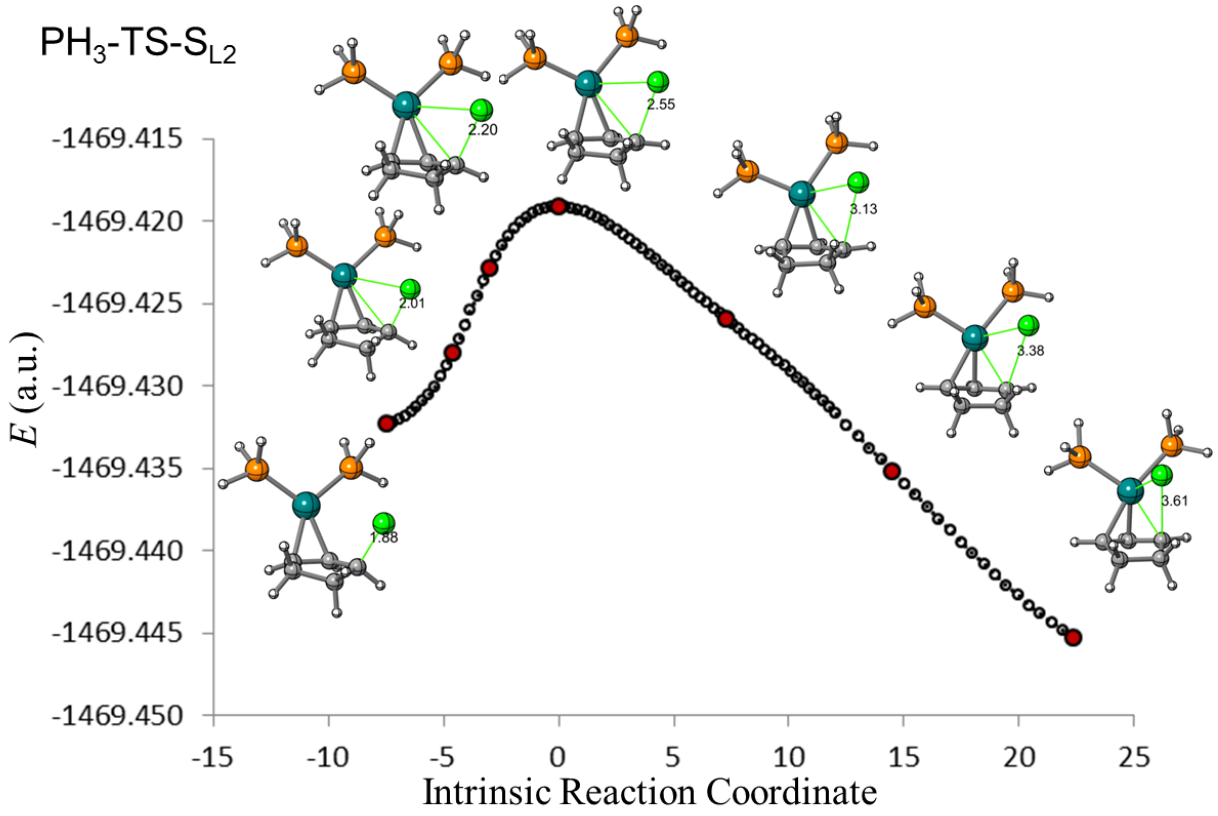


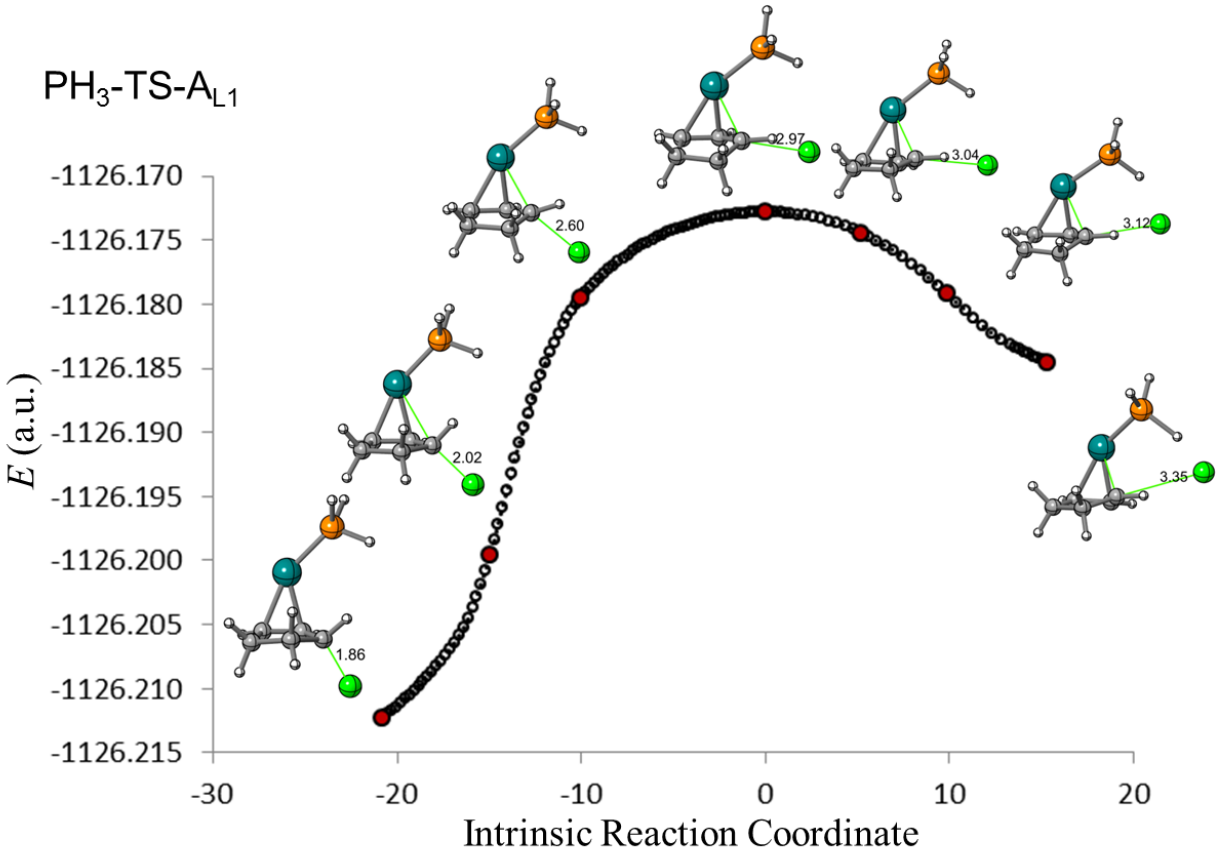

PF3-TS-SL2
-2065.425
-2065.430
-2065.435
-2065.440
-2065.445
-2065.450
E (a.u.)
-20
-10
0
10
20
30
Intrinsic Reaction Coordinate
2.62
2.21
3.20
1.94
3.62
1.86
3.62

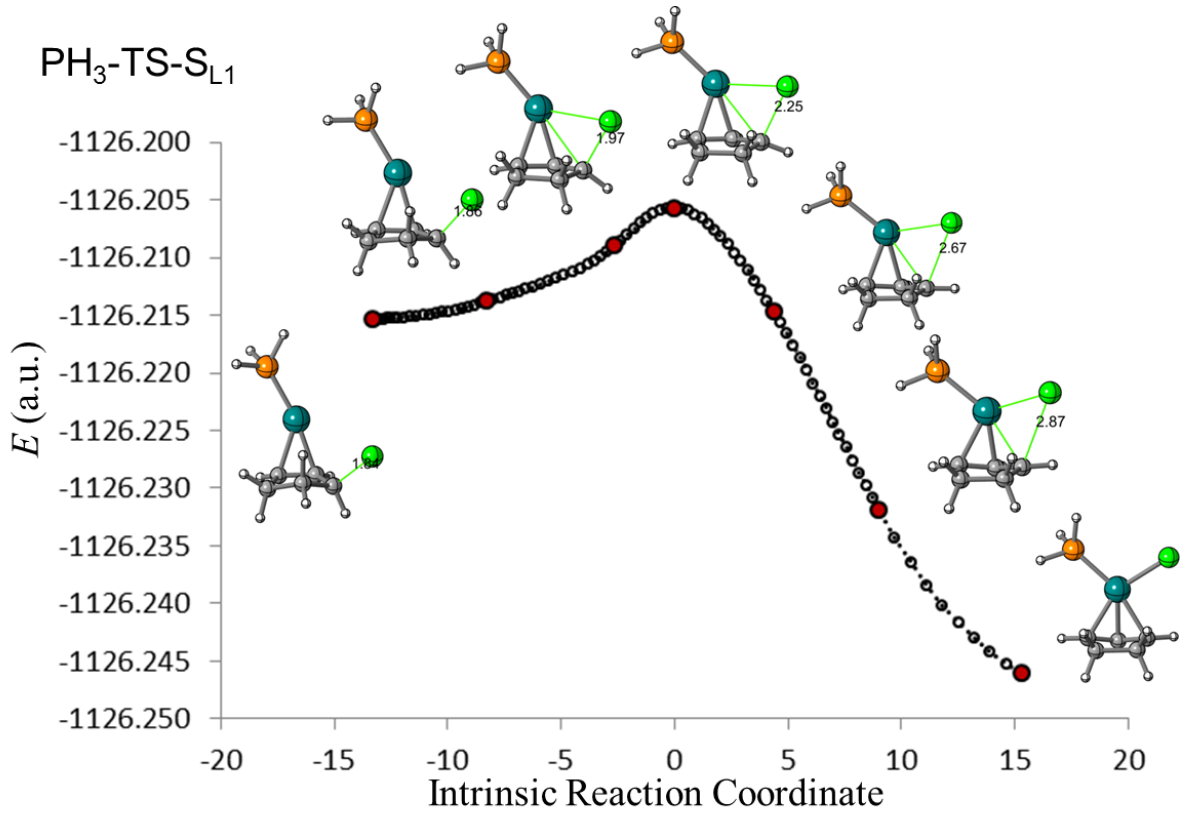

PF3-TS-AL1
-1424.16
-1424.17
-1424.18
-1424.19
-1424.20
-1424.21
-1424.22
-1424.23
-1424.24
-1424.25
E (a.u.)
-40
-30
-20
-10
0
10
20
30
40
Intrinsic Reaction Coordinate
2.53
3.00
3.04
2.02
1.85

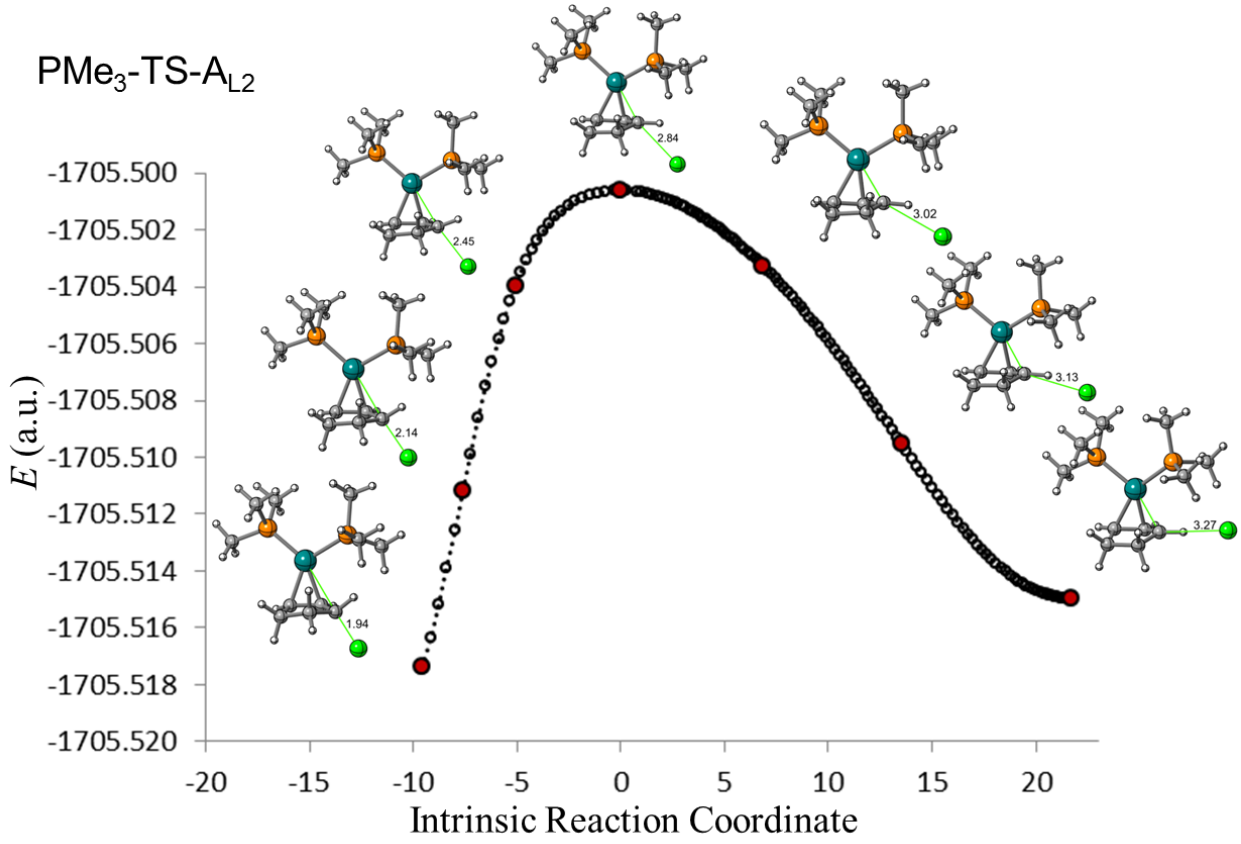

PF3-TS-SL1
-1424.215
-1424.220
-1424.225
-1424.230
-1424.235
-1424.240
-1424.245
-1424.250
-1424.255
E (a.u.)
-15
-10
-5
0
5
10
15
20
Intrinsic Reaction Coordinate
1.93
2.30
2.62
2.89

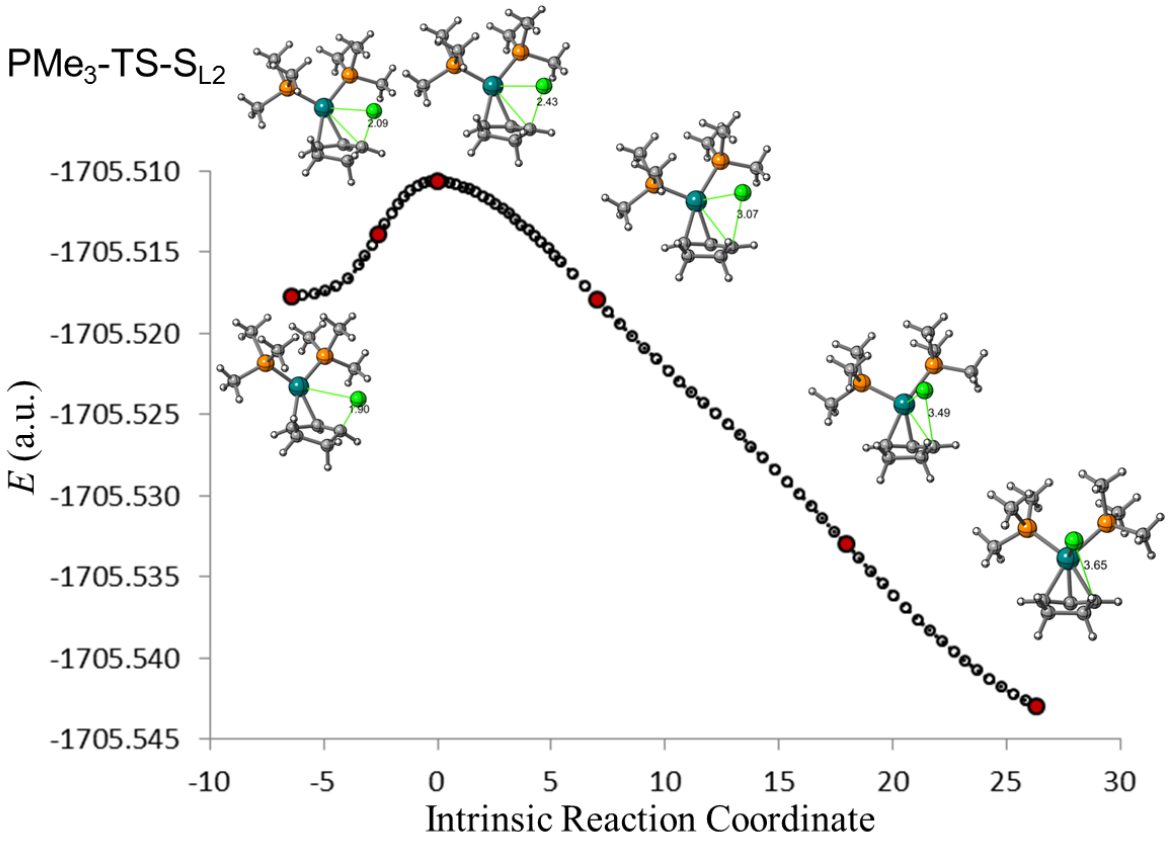

PH3-TS-AL2
-1469.400
-1469.405
-1469.410
-1469.415
-1469.420
-1469.425
-1469.430
-1469.435
-1469.440
E (a.u.)
-30
-20
-10
0
10
20
Intrinsic Reaction Coordinate
1.87
1.93
2.42
2.93
3.04
3.13
3.36

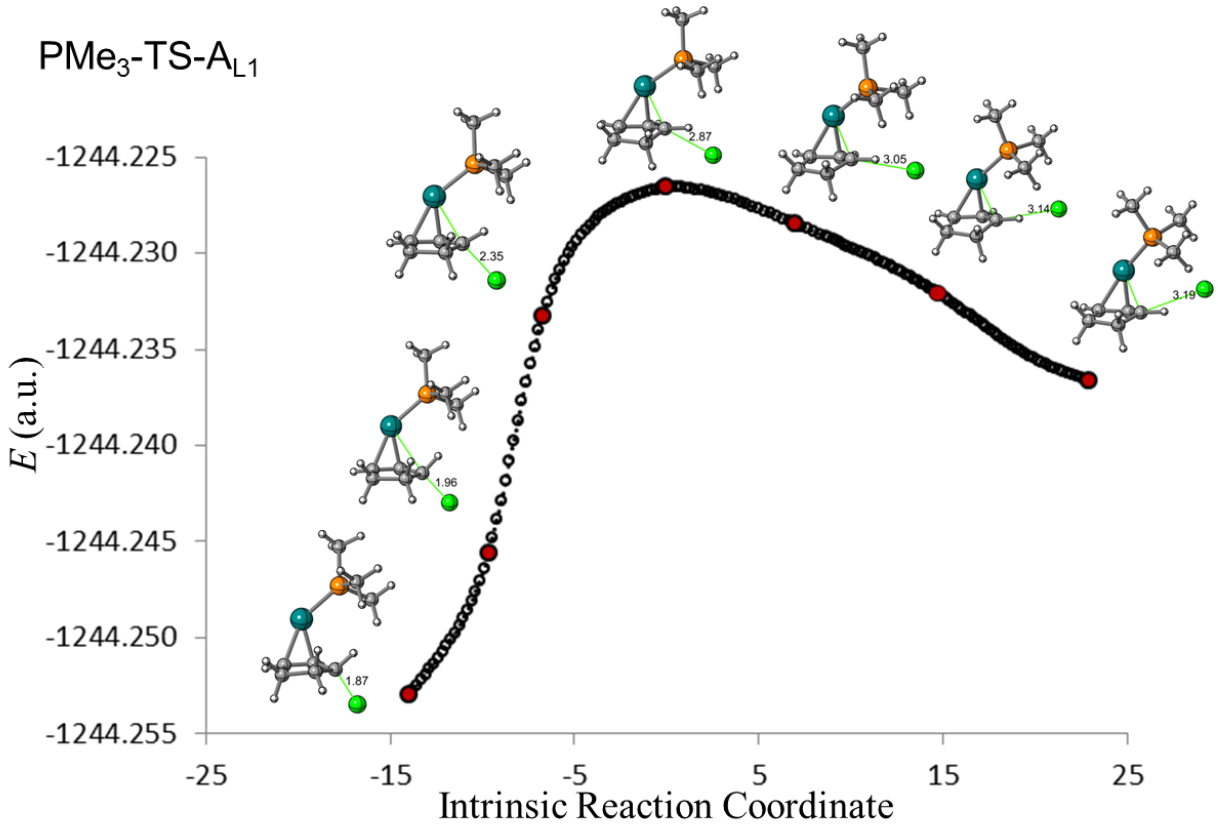

PH3-TS-SL2
-1469.415
-1469.420
-1469.425
-1469.430
-1469.435
-1469.440
-1469.445
-1469.450
E (a.u.)
-15
-10
-5
0
5
10
15
20
25
Intrinsic Reaction Coordinate
2.20
2.55
3.13
2.01
3.38
1.88
3.61

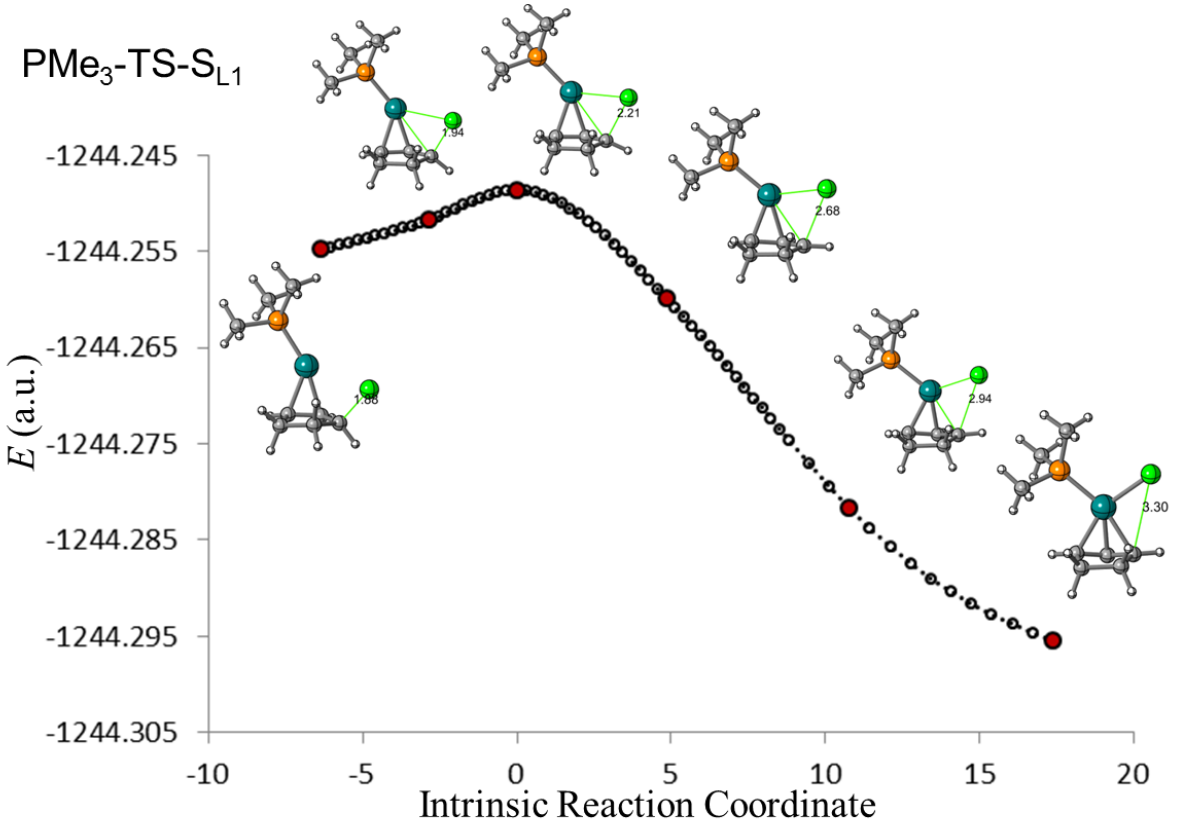

PH3-TS-AL1
-1126.170
-1126.175
-1126.180
-1126.185
-1126.190
-1126.195
-1126.200
-1126.205
-1126.210
-1126.215
E (a.u.)
-30
-20
-10
0
10
20
Intrinsic Reaction Coordinate
2.60
2.97
3.04
3.12
2.02
3.35
1.86

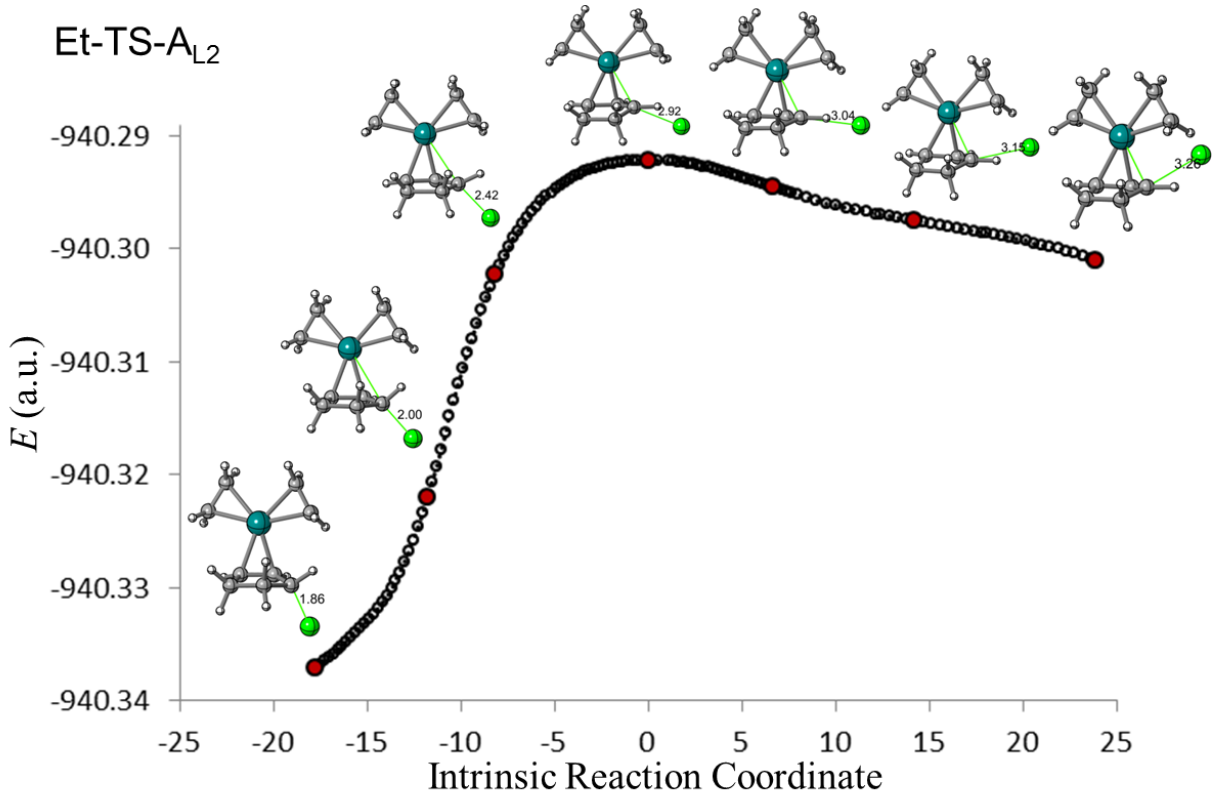

PH3-TS-SL1
-1126.200
-1126.205
-1126.210
-1126.215
-1126.220
-1126.225
-1126.230
-1126.235
-1126.240
-1126.245
-1126.250
E (a.u.)
-20
-15
-10
-5
0
5
10
15
20
Intrinsic Reaction Coordinate
1.66
1.97
2.25
2.67
2.87

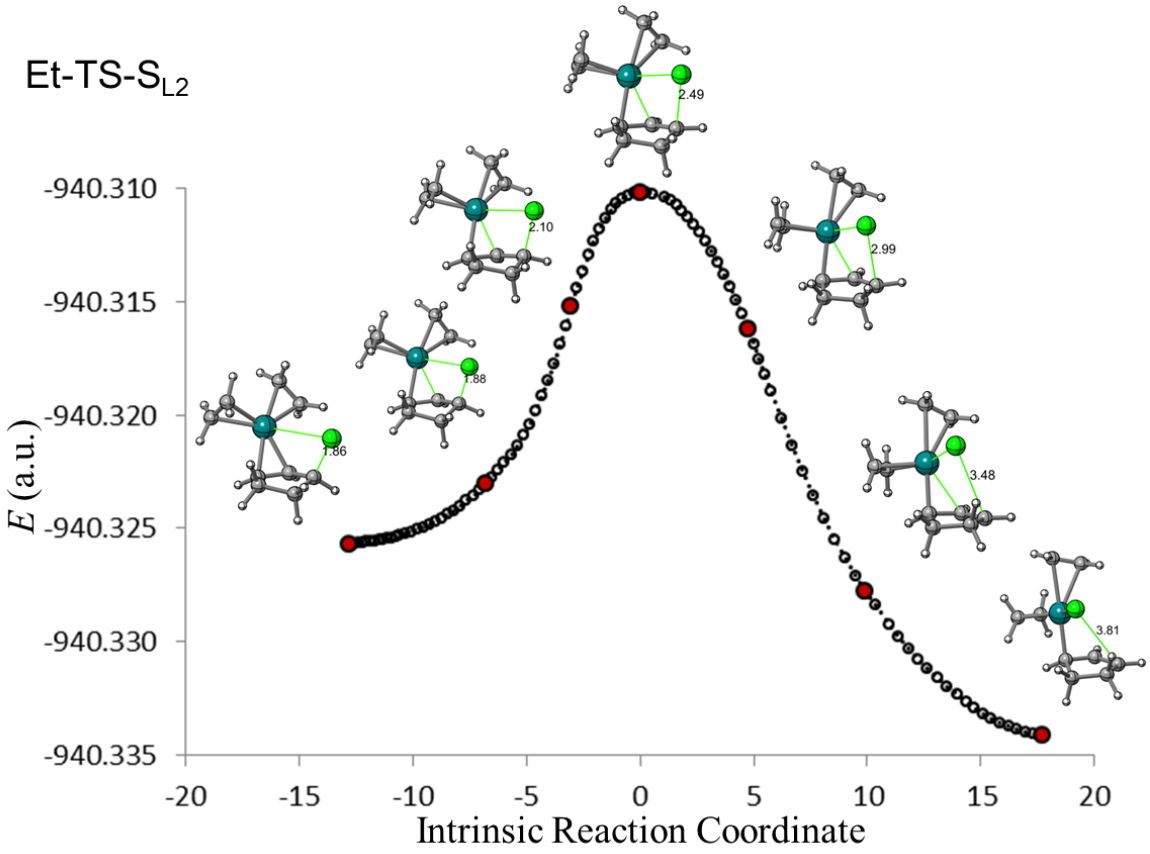

PMe3-TS-AL2
-1705.500
-1705.502
-1705.504
-1705.506
-1705.508
-1705.510
-1705.512
-1705.514
-1705.516
-1705.518
-1705.520
E (a.u.)
-20
-15
-10
-5
0
5
10
15
20
Intrinsic Reaction Coordinate
1.94
2.14
2.45
2.84
3.02
3.13
3.27

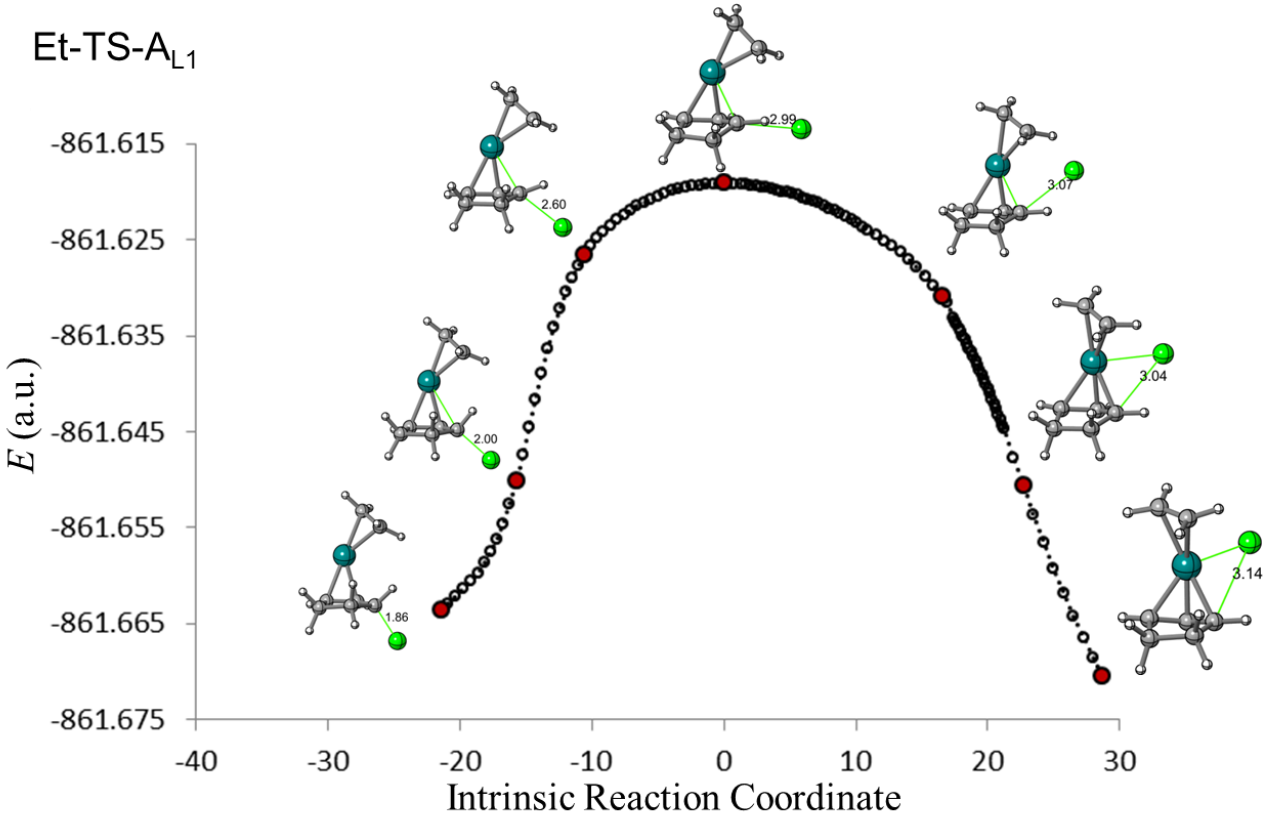

PMe3-TS-SL2
-1705.510
-1705.515
-1705.520
-1705.525
-1705.530
-1705.535
-1705.540
-1705.545
E (a.u.)
-10
-5
0
5
10
15
20
25
30
Intrinsic Reaction Coordinate
2.09
2.43
3.07
1.90
3.49
3.65

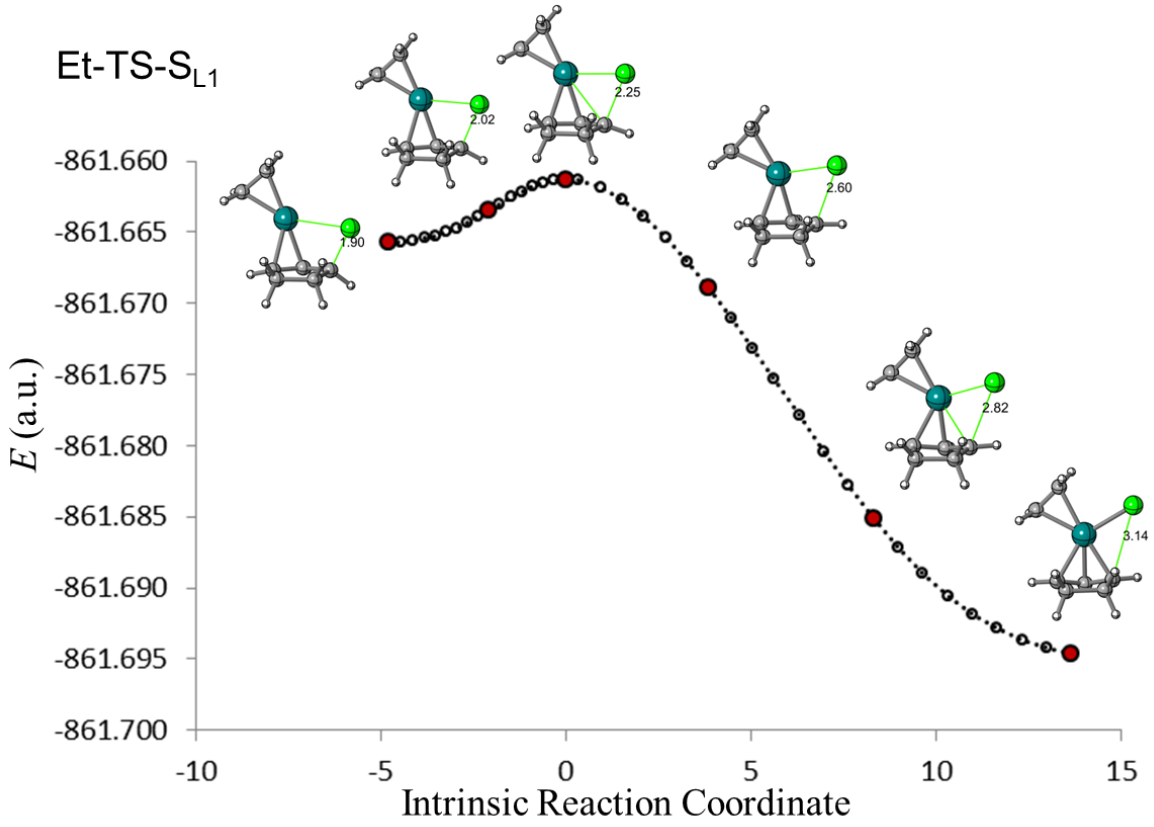

PMe3-TS-AL1
-1244.225
-1244.230
-1244.235
-1244.240
-1244.245
-1244.250
-1244.255
E (a.u.)
-25
-15
-5
5
15
25
Intrinsic Reaction Coordinate
2.87
3.05
2.35
3.14
3.19
1.96
1.87

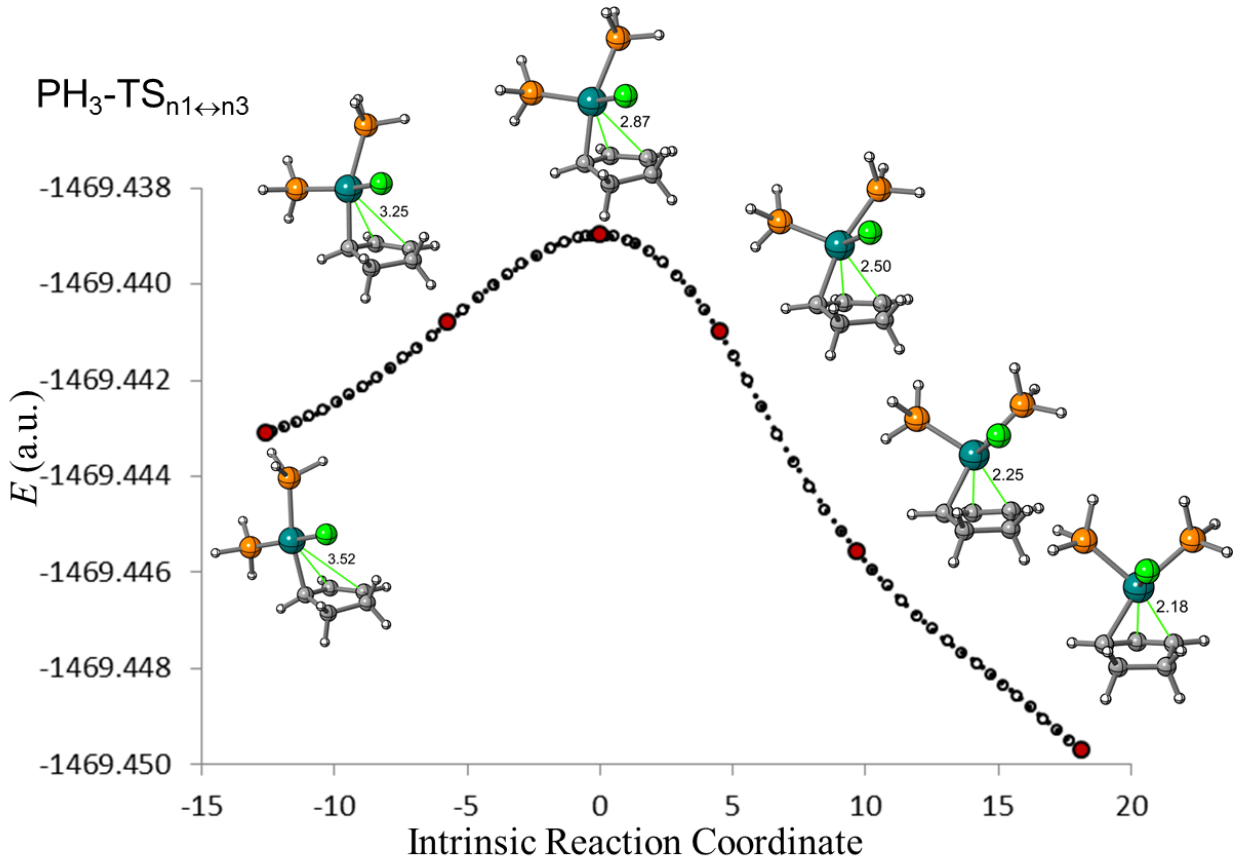

PMe3-TS-SL1
-1244.245
-1244.255
-1244.265
-1244.275
-1244.285
-1244.295
-1244.305
E (a.u.)
-10
-5
0
5
10
15
20
Intrinsic Reaction Coordinate
1.94
2.21
2.68
1.88
2.94
3.30


Et-TS-AL2
-940.29
-940.30
-940.31
-940.32
-940.33
-940.34
E (a.u.)
-25
-20
-15
-10
-5
0
5
10
15
20
25
Intrinsic Reaction Coordinate
2.42
2.92
3.04
2.00
1.86


Et-TS-S$_{L2}$
-940.310
-940.315
-940.320
-940.325
-940.330
-940.335
E (a.u.)
-20
-15
-10
-5
0
5
10
15
20
Intrinsic Reaction Coordinate
2.49
2.10
2.99
1.88
1.86
3.48
3.81


Et-TS-A$_{L1}$
-861.615
-861.625
-861.635
-861.645
-861.655
-861.665
-861.675
E (a.u.)
-40
-30
-20
-10
0
10
20
30
Intrinsic Reaction Coordinate
2.99
2.60
3.07
2.00
3.04
1.86
3.14


Et-TS-S$_{L1}$
-861.660
-861.665
-861.670
-861.675
-861.680
-861.685
-861.690
-861.695
-861.700
E (a.u.)
-10
-5
0
5
10
15
Intrinsic Reaction Coordinate
1.90
2.02
2.25
2.60
2.82
3.14


PH$_3$-TS$_{n1\leftrightarrow n3}$
-1469.438
-1469.440
-1469.442
-1469.444
-1469.446
-1469.448
-1469.450
E (a.u.)
-15
-10
-5
0
5
10
15
20
Intrinsic Reaction Coordinate
3.25
2.87
2.50
2.25
3.52
2.18

## Cartesian Coordinates

**MA-RC-$A_{L2}$**

| | | | |
|---|---|---|---|
| C | 2.02101 | 1.82492 | -0.52885 |
| C | 1.82584 | 1.58979 | 0.97311 |
| C | 0.33437 | 1.68402 | 1.16283 |
| C | -0.22759 | 2.36002 | 0.09576 |
| H | -0.12031 | 1.56420 | 2.14089 |
| H | 2.30593 | 0.70911 | 1.39141 |
| C | 0.82163 | 2.70490 | -0.93595 |
| H | -1.18804 | 2.86028 | 0.12533 |
| Cl | 2.54990 | 2.98373 | 1.93563 |
| Pd | -0.80130 | 0.11248 | -0.07207 |
| H | -3.04692 | -1.27453 | -0.80300 |
| C | -2.49630 | -0.48091 | -1.29344 |
| C | -2.59763 | 0.89916 | -1.09339 |
| H | -3.24336 | 1.42073 | -0.39887 |
| C | 0.61798 | -1.36204 | 0.73175 |
| H | 1.61544 | -1.22311 | 0.33671 |
| C | -0.45334 | -2.01836 | 0.11694 |
| H | -0.48168 | -2.49479 | -0.85553 |
| H | 1.95608 | 0.85534 | -1.03991 |
| H | 2.99030 | 2.26879 | -0.75835 |
| H | 1.05848 | 3.77205 | -0.82652 |
| H | 0.49767 | 2.55566 | -1.96814 |
| C | -1.85459 | -0.69000 | -2.62139 |
| C | -2.08784 | 1.57018 | -2.31293 |
| O | -1.60306 | 0.57592 | -3.18506 |
| O | -1.55940 | -1.70530 | -3.19118 |
| O | -2.05179 | 2.73487 | -2.60597 |
| C | -1.41833 | -2.39106 | 1.18911 |
| C | 0.36721 | -1.36142 | 2.19496 |
| O | -0.89241 | -1.95225 | 2.41782 |
| O | 1.04706 | -0.96534 | 3.10238 |
| O | -2.47594 | -2.95663 | 1.11885 |

**MA-RC-$S_{L2}$**

| | | | |
|---|---|---|---|
| C | 1.76695 | 2.25759 | -0.78043 |
| C | 2.03592 | 1.58542 | 0.57306 |
| C | 0.67113 | 1.43206 | 1.19795 |
| C | -0.22634 | 2.25174 | 0.53736 |
| H | 0.54515 | 1.06003 | 2.20873 |
| Cl | 2.96003 | 0.02779 | 0.40348 |
| C | 0.47323 | 3.06027 | -0.53443 |
| H | -1.18593 | 2.54396 | 0.95592 |
| H | 2.66849 | 2.19583 | 1.22569 |
| Pd | -0.69866 | 0.06216 | -0.03816 |
| H | -2.84924 | -1.04855 | -1.28825 |
| C | -1.97216 | -0.54269 | -1.67408 |
| C | -1.75270 | 0.83497 | -1.81269 |
| H | -2.42875 | 1.63918 | -1.55395 |
| C | -0.06822 | -1.41575 | 1.49685 |
| H | 1.01131 | -1.46962 | 1.53303 |
| C | -0.93310 | -2.03213 | 0.59537 |
| H | -0.69208 | -2.69247 | -0.22897 |
| H | 1.58184 | 1.48120 | -1.52855 |
| H | 2.60578 | 2.86607 | -1.12180 |
| H | 0.70370 | 4.04611 | -0.10377 |
| H | -0.10305 | 3.22738 | -1.44513 |
| C | -1.03350 | -1.23921 | -2.59719 |
| C | -0.74478 | 1.01319 | -2.88595 |
| O | -0.29283 | -0.25774 | -3.28105 |
| O | -0.86310 | -2.41132 | -2.79604 |
| O | -0.33913 | 2.01285 | -3.41838 |
| C | -2.29505 | -2.01464 | 1.19896 |
| C | -0.86915 | -1.00270 | 2.67594 |
| O | -2.20782 | -1.36818 | 2.44617 |
| O | -0.53277 | -0.44494 | 3.68742 |
| O | -3.33742 | -2.44235 | 0.78253 |

**MA-RC-$A_{L1}$**

| | | | |
|---|---|---|---|
| C | -1.84845 | 1.38332 | 0.45293 |
| C | -2.28760 | -0.03125 | 0.85603 |
| C | -1.79773 | -0.90502 | -0.26803 |
| C | -1.49793 | -0.12231 | -1.37911 |
| H | -2.03417 | -1.96686 | -0.30849 |
| H | -1.99141 | -0.33193 | 1.85922 |
| C | -1.73911 | 1.34098 | -1.08562 |
| H | -1.43159 | -0.50592 | -2.39323 |
| Cl | -4.13500 | -0.15992 | 0.88723 |
| Pd | 0.37696 | -0.83808 | -0.40078 |
| C | 1.92161 | 0.46227 | -1.08086 |
| H | 1.80151 | 0.71238 | -2.12764 |
| C | 2.52635 | -0.67347 | -0.51868 |
| H | 2.98059 | -1.51189 | -1.03220 |
| H | -0.85928 | 1.56809 | 0.88701 |
| H | -2.53092 | 2.14960 | 0.82271 |
| H | -2.68758 | 1.63308 | -1.55875 |
| H | -0.96093 | 2.00681 | -1.46795 |
| C | 2.91742 | -0.32610 | 0.86828 |
| C | 1.91482 | 1.52793 | -0.04183 |

| | | | |
|---|---|---|---|
| O | 2.50064 | 1.00489 | 1.12048 |
| O | 1.51422 | 2.66179 | -0.09682 |
| O | 3.48666 | -0.96930 | 1.70804 |

**MA-RC-$S_{L1}$**

| | | | |
|---|---|---|---|
| C | -2.61321 | 0.86207 | 1.42990 |
| C | -2.82296 | 0.11765 | 0.10838 |
| C | -1.97582 | 0.84447 | -0.89465 |
| C | -1.07530 | 1.67173 | -0.23922 |
| H | -2.19086 | 0.83609 | -1.95746 |
| Cl | -2.10690 | -1.63935 | 0.22583 |
| C | -1.31176 | 1.68344 | 1.25889 |
| H | -0.46027 | 2.42020 | -0.72748 |
| H | -3.86028 | -0.07088 | -0.16174 |
| Pd | -0.07933 | -0.26865 | -0.66147 |
| H | 2.00629 | -1.98896 | -1.23625 |
| C | 1.89076 | -1.07821 | -0.66133 |
| C | 1.89169 | 0.25589 | -1.14173 |
| H | 2.02301 | 0.59519 | -2.16220 |
| H | -2.60766 | 0.19338 | 2.29197 |
| H | -3.46371 | 1.54512 | 1.54318 |
| H | -1.43569 | 2.71050 | 1.62110 |
| H | -0.46605 | 1.25859 | 1.81006 |
| C | 2.28604 | -1.03541 | 0.76180 |
| C | 2.27205 | 1.13493 | -0.00654 |
| O | 2.47277 | 0.32820 | 1.12431 |
| O | 2.45884 | -1.91226 | 1.56559 |
| O | 2.40245 | 2.33260 | 0.04437 |

**MA-TS-$A_{L2}$**

$\nu = -22.34\ cm^{-1}$

| | | | |
|---|---|---|---|
| C | 1.24208 | 0.64400 | -2.59277 |
| C | 0.64784 | 1.55609 | -1.56388 |
| C | -0.76393 | 1.41679 | -1.54105 |
| C | -1.06931 | 0.19190 | -2.17760 |
| H | -1.45555 | 2.08505 | -1.03870 |
| H | 1.22096 | 2.36971 | -1.06578 |
| C | 0.06214 | -0.22419 | -3.08435 |
| H | -2.06718 | -0.22765 | -2.25441 |
| Cl | 2.14943 | 3.89059 | -0.07487 |
| Pd | -0.11567 | -0.07424 | -0.08452 |
| H | 0.14923 | -2.18044 | 1.75495 |
| C | 0.01266 | -2.19061 | 0.68123 |
| C | -1.16763 | -2.08046 | -0.04077 |
| H | -2.16589 | -1.89651 | 0.33800 |
| C | 0.42555 | 1.59469 | 1.40806 |
| H | 0.98053 | 2.41046 | 0.89654 |
| C | 0.91547 | 0.42041 | 1.94242 |
| H | 1.93241 | 0.04887 | 1.90602 |
| H | 2.07304 | 0.05409 | -2.18777 |
| H | 1.68551 | 1.26600 | -3.38370 |
| H | -0.22522 | 0.01497 | -4.11841 |
| H | 0.27391 | -1.29523 | -3.07149 |
| C | 1.02917 | -2.80937 | -0.21910 |
| C | -0.95489 | -2.72007 | -1.36541 |
| O | 0.39212 | -3.10086 | -1.44733 |
| O | 2.18325 | -3.06437 | -0.02915 |
| O | -1.72973 | -2.93035 | -2.25799 |
| C | -0.07064 | -0.08601 | 2.93905 |
| C | -0.94381 | 1.79503 | 1.97802 |
| O | -1.18136 | 0.75692 | 2.91637 |
| O | -1.77246 | 2.62735 | 1.74780 |
| O | -0.01358 | -1.04767 | 3.66067 |

**MA-TS-$S_{L2}$**

$\nu = -171.80\ cm^{-1}$

| | | | |
|---|---|---|---|
| C | 2.02285 | -2.99453 | -0.72595 |
| C | 2.56571 | -1.59237 | -0.67975 |
| C | 1.75574 | -0.74065 | -1.50486 |
| C | 0.56676 | -1.42631 | -1.84015 |
| H | 2.05412 | 0.23141 | -1.87995 |
| Cl | 2.25451 | -0.91918 | 1.53626 |
| C | 0.65680 | -2.88395 | -1.44688 |
| H | -0.14219 | -1.07520 | -2.58169 |
| H | 3.61801 | -1.40927 | -0.50926 |
| Pd | 0.23558 | -0.44520 | 0.06490 |
| C | -2.35320 | -1.36698 | -0.69948 |
| C | -1.82579 | -0.05905 | -0.23389 |
| C | -1.59062 | -0.17138 | 1.15704 |
| C | -1.97456 | -1.54047 | 1.56571 |
| C | 1.32330 | 2.22554 | 0.36240 |
| H | 2.29505 | 1.75234 | 0.37279 |
| C | 0.60595 | 2.69497 | 1.39622 |
| H | 0.82406 | 2.65014 | 2.45454 |
| H | 1.97542 | -3.46043 | 0.25938 |
| H | 2.73075 | -3.58581 | -1.32528 |
| H | 0.62675 | -3.50995 | -2.34828 |
| H | -0.18332 | -3.20635 | -0.82345 |
| H | -2.01702 | 0.84187 | -0.80422 |

| | | | |
|---|---|---|---|
| H | -1.55336 | 0.62521 | 1.88862 |
| C | -0.64532 | 3.27600 | 0.86866 |
| C | 0.60048 | 2.55769 | -0.89428 |
| O | -2.38718 | -2.24212 | 0.39676 |
| O | -2.69705 | -1.72312 | -1.79786 |
| O | -1.99049 | -2.07242 | 2.64086 |
| O | -0.60210 | 3.17550 | -0.54141 |
| O | 0.92189 | 2.39520 | -2.04291 |
| O | -1.59312 | 3.74541 | 1.43548 |

**MA-TS-$A_{L1}$**

$\nu$ = –86.36 $cm^{-1}$

| | | | |
|---|---|---|---|
| C | -0.96681 | 1.60946 | 1.55717 |
| C | -1.68178 | 0.50365 | 0.83585 |
| C | -1.93061 | 0.86309 | -0.51619 |
| C | -1.00896 | 1.88996 | -0.82481 |
| H | -2.65223 | 0.35850 | -1.15076 |
| H | -2.15606 | -0.38131 | 1.27287 |
| C | -0.51948 | 2.57135 | 0.42600 |
| H | -0.88208 | 2.31625 | -1.81531 |
| Cl | -3.94590 | -1.36287 | 0.34377 |
| Pd | -0.09736 | -0.20014 | -0.58765 |
| H | 1.64298 | -2.04349 | -1.66167 |
| C | 1.76657 | -1.26942 | -0.91387 |
| C | 1.98263 | 0.09882 | -1.10497 |
| H | 2.07107 | 0.64586 | -2.03523 |
| H | -0.12629 | 1.23648 | 2.15258 |
| H | -1.65895 | 2.08469 | 2.26726 |
| H | -0.99147 | 3.56218 | 0.50141 |
| H | 0.56092 | 2.74386 | 0.42601 |
| C | 2.19549 | -1.59812 | 0.47197 |
| C | 2.52165 | 0.65356 | 0.16781 |
| O | 2.61824 | -0.39329 | 1.08915 |
| O | 2.24000 | -2.64771 | 1.04778 |
| O | 2.84158 | 1.78074 | 0.44269 |

**MA-TS-$S_{L1}$**

$\nu$ = –175.40 $cm^{-1}$

| | | | |
|---|---|---|---|
| C | -2.14147 | 0.93037 | 1.59722 |
| C | -2.64377 | 0.41730 | 0.27140 |
| C | -1.96030 | 1.10462 | -0.79037 |
| C | -0.85285 | 1.79892 | -0.25130 |
| H | -2.30069 | 1.13193 | -1.81843 |
| Cl | -2.01652 | -1.81006 | 0.17710 |
| C | -0.91999 | 1.82248 | 1.26020 |
| H | -0.25894 | 2.51673 | -0.80605 |
| H | -3.65793 | 0.05689 | 0.16707 |
| Pd | -0.24043 | -0.23266 | -0.63294 |
| H | 1.69185 | -2.06711 | -1.28505 |
| C | 1.68079 | -1.14952 | -0.70998 |
| C | 1.74715 | 0.18132 | -1.19477 |
| H | 1.84348 | 0.50828 | -2.22308 |
| H | -1.92352 | 0.12402 | 2.29927 |
| H | -2.95268 | 1.52748 | 2.03787 |
| H | -1.07112 | 2.85298 | 1.60830 |
| H | 0.00771 | 1.47311 | 1.72431 |
| C | 2.16013 | -1.13442 | 0.68922 |
| C | 2.25420 | 1.03152 | -0.08919 |
| O | 2.45439 | 0.21780 | 1.03371 |
| O | 2.32893 | -2.01897 | 1.48233 |
| O | 2.46907 | 2.21785 | -0.05284 |

**MA-$PR_{L1}$**

| | | | |
|---|---|---|---|
| C | -2.14929 | 0.95944 | 1.60820 |
| C | -2.66027 | 0.42453 | 0.29439 |
| C | -1.98824 | 1.09850 | -0.78313 |
| C | -0.87928 | 1.80518 | -0.26363 |
| H | -2.33709 | 1.10902 | -1.80867 |
| Cl | -1.87374 | -1.92158 | 0.16104 |
| C | -0.93422 | 1.85119 | 1.24785 |
| H | -0.29281 | 2.51689 | -0.83394 |
| H | -3.67376 | 0.05861 | 0.20378 |
| Pd | -0.26174 | -0.22948 | -0.61975 |
| H | 1.67260 | -2.06591 | -1.26008 |
| C | 1.66249 | -1.13983 | -0.69877 |
| C | 1.71951 | 0.18383 | -1.20400 |
| H | 1.80615 | 0.49567 | -2.23785 |
| H | -1.92236 | 0.16461 | 2.32045 |
| H | -2.95930 | 1.55991 | 2.04648 |
| H | -1.08670 | 2.88621 | 1.58167 |
| H | -0.00136 | 1.51248 | 1.70952 |
| C | 2.15313 | -1.10181 | 0.69607 |
| C | 2.23208 | 1.05253 | -0.11548 |
| O | 2.44469 | 0.25658 | 1.01781 |
| O | 2.33196 | -1.97367 | 1.50094 |
| O | 2.44242 | 2.24011 | -0.09869 |

**MA**

| | | | |
|---|---|---|---|
| H | -1.35888 | -2.09016 | 0.00038 |
| C | -0.66834 | -1.25706 | 0.00000 |
| C | 0.66841 | -1.25706 | -0.00011 |
| H | 1.35899 | -2.09015 | 0.00022 |
| C | -1.13573 | 0.15433 | 0.00001 |
| C | 1.13585 | 0.15419 | -0.00022 |
| O | -0.00010 | 0.97802 | -0.00005 |
| O | -2.24958 | 0.59928 | 0.00004 |
| O | 2.24952 | 0.59943 | 0.00017 |

**Pd(MA)$_2$**

| | | | |
|---|---|---|---|
| Pd | -0.00007 | -0.52000 | -0.00106 |
| H | 0.84255 | 1.61863 | 1.44742 |
| C | 1.38082 | 0.88275 | 0.86185 |
| C | 1.78326 | -0.40372 | 1.22624 |
| H | 1.63777 | -0.90495 | 2.17590 |
| C | -1.78472 | -0.40330 | -1.22630 |
| H | -1.64068 | -0.90426 | -2.17633 |
| C | -1.38170 | 0.88308 | -0.86208 |
| H | -0.84406 | 1.61899 | -1.44817 |
| C | 2.18086 | 1.28272 | -0.33421 |
| C | 2.86123 | -0.81790 | 0.28739 |
| O | 3.04640 | 0.22195 | -0.64752 |
| O | 2.15943 | 2.29935 | -0.97172 |
| O | 3.51328 | -1.82421 | 0.24975 |
| C | -2.18008 | 1.28284 | 0.33512 |
| C | -2.86149 | -0.81756 | -0.28607 |
| O | -3.04544 | 0.22217 | 0.64920 |
| O | -3.51308 | -1.82414 | -0.24732 |
| O | -2.15826 | 2.29963 | 0.97239 |

**Pd(MA)**

| | | | |
|---|---|---|---|
| Pd | -1.29815 | -0.00012 | -0.18139 |
| H | -0.08349 | 1.37554 | 1.80754 |
| C | 0.24888 | 0.70697 | 1.02167 |
| C | 0.24914 | -0.70715 | 1.02167 |
| H | -0.08287 | -1.37585 | 1.80756 |
| C | 1.28890 | 1.14888 | 0.05077 |
| C | 1.28923 | -1.14859 | 0.05066 |
| O | 1.87417 | 0.00024 | -0.51826 |
| O | 1.65156 | 2.25432 | -0.24957 |
| O | 1.65233 | -2.25392 | -0.24967 |

**Et-RC-A$_{L2}$**

| | | | |
|---|---|---|---|
| C | 1.73017 | -0.75367 | 1.30022 |
| C | 1.95614 | 0.46638 | 0.40000 |
| C | 1.05800 | 0.22878 | -0.77949 |
| C | 0.68484 | -1.11861 | -0.82010 |
| H | 1.09096 | 0.88477 | -1.64184 |
| H | 1.86056 | 1.42939 | 0.89645 |
| C | 1.33977 | -1.87658 | 0.31935 |
| H | 0.38042 | -1.62292 | -1.73133 |
| Cl | 3.71838 | 0.48245 | -0.20743 |
| Pd | -1.04531 | 0.09604 | -0.13981 |
| H | -3.70475 | -0.50592 | -0.43339 |
| C | -2.97371 | -0.90304 | 0.26458 |
| C | -2.05626 | -1.86338 | -0.13929 |
| H | -2.05668 | -2.23507 | -1.15978 |
| C | -0.89162 | 2.28517 | 0.10412 |
| H | -0.17256 | 2.48085 | 0.89415 |
| C | -2.19004 | 1.90461 | 0.41249 |
| H | -2.50384 | 1.79088 | 1.44589 |
| H | 0.87882 | -0.52782 | 1.95558 |
| H | 2.59988 | -0.98433 | 1.91800 |
| H | 2.23832 | -2.38237 | -0.06128 |
| H | 0.70394 | -2.63836 | 0.77877 |
| H | -3.19713 | -0.75742 | 1.31734 |
| H | -1.55100 | -2.48769 | 0.59160 |
| H | -2.98853 | 2.01621 | -0.31500 |
| H | -0.65039 | 2.70244 | -0.86906 |

**Et-RC-S$_{L2}$**

| | | | |
|---|---|---|---|
| C | 1.95684 | 1.35338 | -0.75001 |
| C | 2.25292 | 0.19948 | 0.21701 |
| C | 1.07238 | 0.18191 | 1.16002 |
| C | 0.43967 | 1.43203 | 1.09373 |
| H | 1.08571 | -0.45147 | 2.03946 |
| Cl | 2.58491 | -1.36288 | -0.67161 |
| C | 1.17056 | 2.34687 | 0.12686 |
| H | -0.14268 | 1.84171 | 1.91486 |
| H | 3.17967 | 0.36450 | 0.77667 |
| Pd | -0.87077 | -0.06712 | 0.16272 |
| H | -3.54361 | 0.25463 | -0.38014 |
| C | -2.67203 | 0.52449 | -0.96942 |
| C | -1.93697 | 1.66374 | -0.66750 |
| H | -2.22371 | 2.30989 | 0.15716 |
| C | -0.61032 | -2.21897 | 0.66884 |
| H | 0.36053 | -2.51154 | 0.28571 |
| C | -1.70588 | -2.10884 | -0.16924 |

| | | | |
|---|---|---|---|
| H | -1.61197 | -2.31546 | -1.23161 |
| H | 1.31023 | 0.97572 | -1.54902 |
| H | 2.86330 | 1.77011 | -1.19515 |
| H | 1.86331 | 2.98662 | 0.69444 |
| H | 0.51893 | 3.00801 | -0.45076 |
| H | -2.60395 | 0.06453 | -1.95072 |
| H | -1.28527 | 2.10965 | -1.41386 |
| H | -2.71622 | -2.10778 | 0.22802 |
| H | -0.74573 | -2.28695 | 1.74531 |

**Et-RC-$A_{L1}$**

| | | | |
|---|---|---|---|
| C | -1.52857 | 1.05098 | 1.00600 |
| C | -1.71928 | -0.41177 | 0.57848 |
| C | -0.89529 | -0.54735 | -0.66909 |
| C | -0.57722 | 0.71615 | -1.16646 |
| H | -0.89826 | -1.46683 | -1.24645 |
| H | -1.52770 | -1.14550 | 1.35894 |
| C | -1.18777 | 1.79959 | -0.29999 |
| H | -0.28015 | 0.90687 | -2.19449 |
| Cl | -3.50167 | -0.71868 | 0.12957 |
| Pd | 1.17324 | -0.13153 | -0.19834 |
| H | 3.79461 | 0.09059 | -0.73521 |
| C | 3.29534 | -0.49043 | 0.03639 |
| C | 2.81726 | 0.11310 | 1.18879 |
| H | 2.93061 | 1.18217 | 1.35101 |
| H | -0.66378 | 1.08603 | 1.68096 |
| H | -2.40040 | 1.44759 | 1.52950 |
| H | -2.09925 | 2.17554 | -0.78668 |
| H | -0.52536 | 2.65418 | -0.13422 |
| H | 3.43244 | -1.56800 | -0.01549 |
| H | 2.56975 | -0.47652 | 2.06833 |

**Et-RC-$S_{L1}$**

| | | | |
|---|---|---|---|
| C | 1.92325 | -0.63863 | 1.12062 |
| C | 2.08345 | 0.07973 | -0.23029 |
| C | 0.99044 | -0.49718 | -1.09229 |
| C | 0.54298 | -1.69487 | -0.53196 |
| H | 0.89999 | -0.22001 | -2.13877 |
| Cl | 1.99689 | 1.89537 | -0.06133 |
| C | 1.30218 | -2.00391 | 0.74669 |
| H | 0.03946 | -2.47630 | -1.09631 |
| H | 3.06767 | -0.08890 | -0.67949 |
| Pd | -0.95467 | -0.16521 | -0.22005 |
| H | -3.64604 | -0.19410 | -0.04644 |
| C | -2.95552 | 0.64407 | 0.00614 |
| C | -2.23337 | 0.90423 | 1.15985 |
| H | -2.34012 | 0.27733 | 2.04176 |
| H | 1.21056 | -0.06896 | 1.72563 |
| H | 2.86683 | -0.71683 | 1.66615 |
| H | 2.08707 | -2.74485 | 0.53183 |
| H | 0.67370 | -2.41470 | 1.54211 |
| H | -3.06198 | 1.39941 | -0.76901 |
| H | -1.75001 | 1.86579 | 1.31489 |

**Et-TS-$A_{L2}$**

$\nu = -63.18\ cm^{-1}$

| | | | |
|---|---|---|---|
| C | -0.97848 | 1.59730 | 1.48641 |
| C | -1.37785 | 0.47309 | 0.56997 |
| C | -0.99259 | 0.75579 | -0.75886 |
| C | -0.01979 | 1.77849 | -0.71257 |
| H | -1.39957 | 0.23558 | -1.61757 |
| H | -2.09928 | -0.30832 | 0.79552 |
| C | -0.10088 | 2.52467 | 0.60373 |
| H | 0.42775 | 2.21933 | -1.59637 |
| Cl | -3.82742 | -0.65216 | -0.54847 |
| Pd | 0.81996 | -0.22323 | -0.06910 |
| H | 3.23778 | -1.27603 | -0.89184 |
| C | 3.04184 | -0.41643 | -0.25951 |
| C | 2.67811 | 0.79712 | -0.81045 |
| H | 2.56998 | 0.90846 | -1.88488 |
| C | -0.22293 | -2.09360 | 0.76329 |
| H | -0.58021 | -1.84356 | 1.75734 |
| C | 1.10625 | -2.38506 | 0.56014 |
| H | 1.80424 | -2.40073 | 1.39157 |
| H | -0.45358 | 1.24015 | 2.37943 |
| H | -1.89018 | 2.09703 | 1.83965 |
| H | -0.57740 | 3.50138 | 0.44065 |
| H | 0.87935 | 2.72351 | 1.04785 |
| H | 3.41813 | -0.47338 | 0.75756 |
| H | 2.76344 | 1.71564 | -0.23815 |
| H | 1.43600 | -2.87019 | -0.35388 |
| H | -0.99078 | -2.30175 | 0.02253 |

**Et-TS-$S_{L2}$**

$\nu = -140.23\ cm^{-1}$

| | | | |
|---|---|---|---|
| C | -2.97823 | -0.23999 | -0.17738 |
| C | -2.16707 | 0.54439 | 0.81033 |
| C | -1.22050 | -0.30079 | 1.42097 |

| | | | |
|---|---|---|---|
| C | -1.01296 | -1.44274 | 0.57075 |
| H | -0.78471 | -0.13170 | 2.39939 |
| Cl | -0.98176 | 1.82945 | -0.96776 |
| C | -2.08565 | -1.46130 | -0.51228 |
| H | -0.61214 | -2.37923 | 0.95001 |
| H | -2.51138 | 1.47955 | 1.23348 |
| Pd | 0.60182 | -0.15263 | 0.11921 |
| H | 1.60180 | -2.65055 | 0.47527 |
| C | 1.99971 | -1.78453 | -0.04643 |
| C | 1.57065 | -1.47773 | -1.34026 |
| H | 0.79839 | -2.07112 | -1.82069 |
| C | 1.72535 | 1.65451 | 1.09685 |
| H | 0.89551 | 2.34606 | 1.20462 |
| C | 2.27853 | 1.42383 | -0.13262 |
| H | 1.90338 | 1.93917 | -1.01204 |
| H | -3.29392 | 0.34059 | -1.04272 |
| H | -3.88093 | -0.57887 | 0.35840 |
| H | -2.64718 | -2.40249 | -0.49767 |
| H | -1.65696 | -1.34879 | -1.51246 |
| H | 2.95860 | -1.42762 | 0.31949 |
| H | 2.16784 | -0.85455 | -1.99794 |
| H | 3.21662 | 0.88469 | -0.23273 |
| H | 2.19235 | 1.28144 | 2.00432 |

**Et-TS-$A_{L1}$**

$\nu = -50.68$ cm$^{-1}$

| | | | |
|---|---|---|---|
| C | 0.86652 | 2.49666 | 0.40320 |
| C | -0.13419 | 1.83240 | 1.38755 |
| C | -0.79999 | 0.76260 | 0.56410 |
| C | -0.60642 | 1.03380 | -0.82744 |
| C | 0.56721 | 1.80457 | -0.91165 |
| Pd | 0.93413 | -0.32339 | -0.29352 |
| C | 0.34254 | -2.07726 | 0.94475 |
| H | 0.35656 | -1.74392 | 1.97892 |
| C | 1.51831 | -2.36237 | 0.28195 |
| Cl | -3.38142 | -0.55852 | -0.15795 |
| H | -1.23257 | 0.62419 | -1.61148 |
| H | -1.58552 | 0.07162 | 0.88804 |
| H | 1.03128 | 2.10545 | -1.84723 |
| H | 2.47576 | -2.28456 | 0.79371 |
| H | 0.34777 | 1.43491 | 2.28570 |
| H | -0.90328 | 2.53988 | 1.72992 |
| H | 0.71917 | 3.58156 | 0.30789 |
| H | 1.90484 | 2.35040 | 0.72399 |
| H | 1.50890 | -2.91125 | -0.65751 |
| H | -0.63256 | -2.33968 | 0.54026 |

**Et-TS-$S_{L1}$**

$\nu = -180.55$ cm$^{-1}$

| | | | |
|---|---|---|---|
| C | 2.25990 | -0.63624 | 0.86938 |
| C | 2.00692 | 0.11678 | -0.41952 |
| C | 1.10086 | -0.64933 | -1.23417 |
| C | 0.52382 | -1.68313 | -0.45614 |
| H | 0.97050 | -0.49829 | -2.29914 |
| Cl | 1.01022 | 2.04649 | 0.15872 |
| C | 1.26955 | -1.83097 | 0.85816 |
| H | -0.02253 | -2.51281 | -0.89197 |
| H | 2.80198 | 0.70577 | -0.85792 |
| Pd | -0.65422 | 0.07525 | -0.17788 |
| H | -2.97748 | 1.34833 | 0.13597 |
| C | -2.54876 | 0.50899 | 0.68014 |
| C | -2.57151 | -0.78184 | 0.12420 |
| H | -3.03635 | -0.95722 | -0.84344 |
| H | 2.16147 | 0.00701 | 1.74513 |
| H | 3.29913 | -0.99152 | 0.84495 |
| H | 1.81223 | -2.78652 | 0.88143 |
| H | 0.59694 | -1.82590 | 1.72134 |
| H | -2.43929 | 0.65229 | 1.75223 |
| H | -2.49089 | -1.65823 | 0.76322 |

**Et-$PR_{L2}$**

| | | | |
|---|---|---|---|
| C | -2.52466 | 0.57288 | 0.49639 |
| C | -1.58087 | -0.16721 | 1.41099 |
| C | -1.20998 | -1.41364 | 0.87094 |
| C | -1.39702 | -1.27874 | -0.54997 |
| H | -0.80586 | -2.26440 | 1.40479 |
| Cl | -0.08176 | 2.00305 | -1.09026 |
| C | -2.46052 | -0.23775 | -0.82464 |
| H | -1.19776 | -2.08515 | -1.25041 |
| H | -1.46089 | 0.09106 | 2.45821 |
| Pd | 0.34018 | -0.18586 | 0.06800 |
| H | 2.45556 | -0.19945 | -1.65303 |
| C | 1.66221 | -0.93044 | -1.54796 |
| C | 1.67415 | -1.87453 | -0.52795 |
| H | 2.48855 | -1.92058 | 0.18840 |
| C | 1.32028 | 0.89979 | 1.91995 |
| H | 0.62926 | 1.72434 | 2.06067 |
| C | 2.22695 | 0.92888 | 0.89895 |
| H | 2.25978 | 1.76856 | 0.21334 |

| | | | |
|---|---|---|---|
| H | -2.21020 | 1.60834 | 0.33094 |
| H | -3.53350 | 0.58299 | 0.93343 |
| H | -3.41468 | -0.74105 | -1.04025 |
| H | -2.20547 | 0.40177 | -1.67235 |
| H | 1.01645 | -1.04887 | -2.41154 |
| H | 1.05473 | -2.76463 | -0.58850 |
| H | 3.03198 | 0.20132 | 0.85016 |
| H | 1.37037 | 0.14825 | 2.70261 |

**Et-PR$_{L1}$**

| | | | |
|---|---|---|---|
| C | 2.05418 | -1.08868 | -0.84367 |
| C | 1.34611 | -1.24038 | 0.48932 |
| C | 1.50581 | -0.06862 | 1.26920 |
| C | 1.72041 | 0.98911 | 0.34591 |
| H | 1.34030 | 0.02691 | 2.33572 |
| Cl | -1.76295 | -1.67793 | -0.14229 |
| C | 2.32528 | 0.44298 | -0.93749 |
| H | 1.83822 | 2.02601 | 0.64196 |
| H | 1.05638 | -2.20370 | 0.89182 |
| Pd | -0.29252 | 0.14545 | 0.14797 |
| H | -2.79479 | 1.10306 | 0.20176 |
| C | -2.00174 | 1.37920 | -0.48424 |
| C | -0.99040 | 2.24367 | -0.11107 |
| H | -0.97258 | 2.69325 | 0.87775 |
| H | 1.44076 | -1.45745 | -1.67044 |
| H | 2.98775 | -1.66848 | -0.84810 |
| H | 3.40095 | 0.66640 | -0.97308 |
| H | 1.87695 | 0.88742 | -1.83128 |
| H | -2.16019 | 1.11627 | -1.52536 |
| H | -0.34552 | 2.70059 | -0.85621 |

**Et**

| | | | |
|---|---|---|---|
| H | -1.23743 | 0.92430 | 0.00000 |
| C | -0.66539 | 0.00000 | 0.00000 |
| C | 0.66539 | 0.00000 | 0.00000 |
| H | 1.23743 | 0.92430 | -0.00000 |
| H | -1.23743 | -0.92430 | -0.00000 |
| H | 1.23743 | -0.92430 | 0.00000 |

**Pd(Et)$_2$**

| | | | |
|---|---|---|---|
| Pd | 0.00001 | -0.00008 | -0.00012 |
| H | 2.18413 | -1.54131 | 0.21341 |
| C | 2.04599 | -0.49703 | 0.48337 |
| C | 2.04610 | 0.49719 | -0.48306 |
| H | 2.18440 | 0.25699 | -1.53456 |
| C | -2.04593 | 0.48344 | 0.49720 |
| H | -2.18378 | 0.21372 | 1.54157 |
| C | -2.04621 | -0.48317 | -0.49683 |
| H | -2.18427 | -1.53464 | -0.25634 |
| H | 2.18386 | -0.25677 | 1.53491 |
| H | 2.18399 | 1.54149 | -0.21303 |
| H | -2.18447 | -0.21339 | -1.54114 |
| H | -2.18388 | 1.53493 | 0.25674 |

**Pd(Et)**

| | | | |
|---|---|---|---|
| Pd | 0.51627 | 0.00000 | -0.00000 |
| H | -1.63091 | 1.25608 | -0.91953 |
| C | -1.43542 | 0.70663 | 0.00000 |
| C | -1.43542 | -0.70663 | 0.00000 |
| H | -1.63092 | -1.25608 | -0.91954 |
| H | -1.63077 | 1.25604 | 0.91959 |
| H | -1.63076 | -1.25604 | 0.91960 |

**PF$_3$-RC-A$_{L2}$**

| | | | |
|---|---|---|---|
| C | 2.22572 | -1.10336 | 1.32507 |
| C | 2.68126 | -0.00414 | 0.35634 |
| C | 1.82527 | -0.21696 | -0.86329 |
| C | 1.27145 | -1.50155 | -0.83152 |
| H | 1.97567 | 0.36972 | -1.76316 |
| H | 2.68619 | 1.00140 | 0.77126 |
| C | 1.73935 | -2.24401 | 0.40805 |
| H | 0.92819 | -2.02635 | -1.71781 |
| Cl | 4.44760 | -0.28529 | -0.13388 |
| Pd | -0.32025 | -0.01189 | -0.28844 |
| H | 1.37623 | -0.70774 | 1.89978 |
| H | 3.01069 | -1.39717 | 2.02343 |
| H | 2.57744 | -2.89791 | 0.12978 |
| H | 0.97193 | -2.86625 | 0.87430 |
| P | -2.10401 | -1.30581 | 0.03380 |
| F | -1.97472 | -2.53907 | 1.02192 |
| F | -3.45082 | -0.72242 | 0.62534 |
| F | -2.73548 | -2.06887 | -1.20088 |
| P | -0.60945 | 2.17052 | 0.06822 |
| F | 0.34463 | 2.89457 | 1.10759 |
| F | -1.97633 | 2.73685 | 0.62968 |
| F | -0.44734 | 3.18459 | -1.13602 |

**PF$_3$-RC-S$_{L2}$**

| | | | |
|---|---|---|---|
| C | 1.47083 | -2.47393 | 0.94518 |
| C | 2.35194 | -1.74969 | -0.08474 |
| C | 1.38986 | -1.34482 | -1.17562 |
| C | 0.23515 | -2.13209 | -1.07776 |
| H | 1.74462 | -0.87613 | -2.08772 |
| Cl | 3.28293 | -0.36798 | 0.64815 |
| C | 0.35440 | -3.10500 | 0.08601 |
| H | -0.42238 | -2.33261 | -1.91887 |
| H | 3.13510 | -2.40039 | -0.48744 |
| Pd | -0.24390 | -0.06721 | -0.37191 |
| H | 1.03882 | -1.72281 | 1.61659 |
| H | 2.03137 | -3.19448 | 1.54437 |
| H | 0.67185 | -4.08466 | -0.30046 |
| H | -0.57529 | -3.25605 | 0.64005 |
| P | -2.38406 | -0.20446 | 0.20412 |
| F | -3.46384 | -0.53893 | -0.90641 |
| F | -2.80531 | -1.30795 | 1.26413 |
| F | -3.15361 | 1.00799 | 0.87190 |
| P | 0.62979 | 1.97786 | -0.06101 |
| F | 1.88394 | 2.50872 | -0.86636 |
| F | 1.10219 | 2.37709 | 1.39146 |
| F | -0.30929 | 3.22495 | -0.33499 |

**$PF_3$-RC-$A_{L1}$**

| | | | |
|---|---|---|---|
| C | 2.19983 | -0.18121 | 1.42095 |
| C | 2.06979 | 0.81927 | 0.26402 |
| C | 1.49062 | 0.01326 | -0.86391 |
| C | 1.61885 | -1.34475 | -0.59366 |
| H | 1.33093 | 0.44995 | -1.84399 |
| H | 1.54462 | 1.74015 | 0.50834 |
| C | 2.31638 | -1.56159 | 0.73738 |
| H | 1.57196 | -2.11682 | -1.35861 |
| Cl | 3.74683 | 1.39222 | -0.28364 |
| Pd | -0.47298 | -0.73913 | -0.23143 |
| H | 1.26986 | -0.13548 | 2.00165 |
| H | 3.03541 | 0.05557 | 2.08164 |
| H | 3.36761 | -1.82466 | 0.55385 |
| H | 1.88129 | -2.36458 | 1.34029 |
| P | -2.30515 | 0.37674 | 0.07876 |
| F | -2.19429 | 1.70721 | 0.93491 |
| F | -3.06044 | 1.00271 | -1.16575 |
| F | -3.58261 | -0.22024 | 0.81019 |

**$PF_3$-RC-$S_{L1}$**

| | | | |
|---|---|---|---|
| C | -2.28850 | 0.92947 | 1.25175 |
| C | -2.78949 | 0.10244 | 0.04934 |
| C | -1.87569 | 0.48230 | -1.08253 |
| C | -1.13129 | 1.60711 | -0.73940 |
| H | -2.03673 | 0.11764 | -2.09329 |
| Cl | -2.68913 | -1.70388 | 0.38388 |
| C | -1.54525 | 2.13000 | 0.62104 |
| H | -0.61040 | 2.23212 | -1.45851 |
| H | -3.84639 | 0.26214 | -0.18000 |
| Pd | 0.12721 | -0.19052 | -0.50117 |
| H | -1.57728 | 0.32041 | 1.81778 |
| H | -3.10259 | 1.22044 | 1.91964 |
| H | -2.22445 | 2.98393 | 0.47951 |
| H | -0.70682 | 2.47659 | 1.23074 |
| P | 2.17845 | -0.13326 | 0.17189 |
| F | 2.94056 | -1.36681 | 0.82322 |
| F | 3.32495 | 0.29086 | -0.84001 |
| F | 2.52035 | 0.92126 | 1.30929 |

**$PF_3$-TS-$A_{L2}$**

$\nu = -53.63\ cm^{-1}$

| | | | |
|---|---|---|---|
| C | 1.42332 | -1.75758 | 1.84840 |
| C | 1.84948 | -1.06092 | 0.57804 |
| C | 1.27367 | -1.70551 | -0.54266 |
| C | 0.17113 | -2.45996 | -0.09129 |
| H | 1.62838 | -1.52527 | -1.55381 |
| H | 2.69669 | -0.38456 | 0.44192 |
| C | 0.28921 | -2.72449 | 1.39862 |
| H | -0.46852 | -3.04801 | -0.74121 |
| Cl | 4.02570 | -0.47380 | -1.35493 |
| Pd | -0.22030 | -0.20078 | 0.01647 |
| H | 1.10235 | -1.05915 | 2.62859 |
| H | 2.29004 | -2.29571 | 2.25471 |
| H | 0.55601 | -3.77784 | 1.56004 |
| H | -0.64661 | -2.55520 | 1.94027 |
| P | -2.43054 | -0.22054 | -0.40204 |
| F | -3.33773 | -0.99143 | 0.63001 |
| F | -3.24790 | 1.12085 | -0.47924 |
| F | -2.94755 | -0.88207 | -1.73214 |
| P | 0.49978 | 1.93338 | 0.34090 |
| F | 1.61890 | 2.23209 | 1.39736 |
| F | -0.55489 | 3.00524 | 0.81020 |
| F | 1.07575 | 2.68132 | -0.90216 |

**$PF_3$-TS-$S_{L2}$**

$\nu = -126.71\ cm^{-1}$

| | | | |
|---|---|---|---|
| C | 3.27654 | -1.33726 | 0.30784 |
| C | 2.85432 | -0.21869 | -0.59124 |
| C | 1.84807 | -0.66060 | -1.46819 |
| C | 1.25029 | -1.84663 | -0.91426 |
| H | 1.60841 | -0.19875 | -2.41948 |
| Cl | 1.86210 | 1.13597 | 1.41866 |
| C | 2.11554 | -2.35990 | 0.22840 |
| H | 0.65828 | -2.53099 | -1.51326 |
| H | 3.44972 | 0.67242 | -0.74216 |
| Pd | 0.04995 | -0.19082 | -0.24740 |
| H | 3.53012 | -1.01352 | 1.31548 |
| H | 4.18378 | -1.76733 | -0.14962 |
| H | 2.46889 | -3.37612 | 0.01773 |
| H | 1.57222 | -2.39638 | 1.17658 |
| P | -1.73629 | -1.34238 | 0.21235 |
| F | -2.09694 | -2.55832 | -0.73730 |
| F | -1.89389 | -2.10896 | 1.58737 |
| F | -3.14717 | -0.63450 | 0.19072 |
| P | -0.54463 | 2.06291 | -0.20198 |
| F | 0.44884 | 3.17328 | -0.71297 |
| F | -0.97417 | 2.70028 | 1.16705 |
| F | -1.81218 | 2.51790 | -1.04516 |

**$PF_3$-TS-$A_{L1}$**

$\nu = -60.39\ cm^{-1}$

| | | | |
|---|---|---|---|
| C | 2.06437 | -0.57628 | 1.62455 |
| C | 1.43258 | 0.46127 | 0.73606 |
| C | 1.95486 | 0.33227 | -0.59322 |
| C | 2.40879 | -0.98625 | -0.72385 |
| H | 1.88078 | 1.12598 | -1.32958 |
| H | 0.92459 | 1.38228 | 1.03681 |
| C | 2.63522 | -1.62687 | 0.63178 |
| H | 2.78704 | -1.41612 | -1.64675 |
| Cl | 0.87528 | 3.28443 | -0.10896 |
| Pd | 0.11483 | -0.77612 | -0.52897 |
| H | 1.36242 | -1.00050 | 2.34816 |
| H | 2.86277 | -0.09386 | 2.20751 |
| H | 3.70467 | -1.82693 | 0.78399 |
| H | 2.12615 | -2.59393 | 0.72972 |
| P | -1.91913 | -0.17755 | 0.12988 |
| F | -1.99478 | 0.59153 | 1.49156 |
| F | -2.73411 | 0.80272 | -0.77725 |
| F | -3.04869 | -1.24673 | 0.40291 |

**$PF_3$-TS-$S_{L1}$**

$\nu = -176.25\ cm^{-1}$

| | | | |
|---|---|---|---|
| C | -2.63313 | 0.98915 | 1.03458 |
| C | -2.71425 | 0.13508 | -0.21037 |
| C | -1.84495 | 0.68724 | -1.20925 |
| C | -0.99829 | 1.65793 | -0.62567 |
| H | -1.88115 | 0.42118 | -2.25935 |
| Cl | -1.91715 | -1.94018 | 0.37391 |
| C | -1.49224 | 2.00734 | 0.76691 |
| H | -0.39760 | 2.34910 | -1.20619 |
| H | -3.63505 | -0.37054 | -0.46657 |
| Pd | -0.03600 | -0.25700 | -0.32776 |
| H | -2.48142 | 0.38872 | 1.93292 |
| H | -3.59807 | 1.50121 | 1.14951 |
| H | -1.87756 | 3.03626 | 0.77570 |
| H | -0.69791 | 1.96111 | 1.51729 |
| P | 2.04748 | -0.02600 | 0.12134 |
| F | 2.83621 | -0.84443 | 1.23173 |
| F | 3.09442 | -0.23033 | -1.05195 |
| F | 2.53617 | 1.41341 | 0.58910 |

**$PF_3$-$PR_{L2}$**

| | | | |
|---|---|---|---|
| C | -0.77601 | 2.99361 | 0.58578 |
| C | -1.13091 | 2.23198 | -0.67473 |
| C | 0.00027 | 2.12646 | -1.53708 |
| C | 1.13154 | 2.23163 | -0.67481 |
| H | 0.00020 | 1.93108 | -2.60201 |
| Cl | 0.00013 | 0.03822 | 2.23281 |
| C | 0.77698 | 2.99337 | 0.58572 |
| H | 2.15470 | 2.14077 | -1.02566 |
| H | -2.15412 | 2.14145 | -1.02551 |
| Pd | 0.00004 | 0.37659 | -0.33252 |
| H | -1.17379 | 2.51093 | 1.48279 |
| H | -1.18973 | 4.01035 | 0.53297 |
| H | 1.19101 | 4.00998 | 0.53287 |
| H | 1.17468 | 2.51057 | 1.48270 |
| P | 1.76857 | -1.05324 | -0.18495 |
| F | 2.57309 | -1.51410 | -1.47107 |
| F | 2.98991 | -0.53175 | 0.65128 |
| F | 1.57817 | -2.46083 | 0.47516 |
| P | -1.76891 | -1.05271 | -0.18491 |
| F | -2.99003 | -0.53090 | 0.65146 |
| F | -1.57889 | -2.46040 | 0.47511 |

| | | | |
|---|---|---|---|
| F | -2.57368 | -1.51324 | -1.47098 |

**$PF_3$-$PR_{L1}$**

| | | | |
|---|---|---|---|
| C | 2.88802 | -0.10582 | 0.92570 |
| C | 2.49294 | 0.41614 | -0.44629 |
| C | 1.98605 | -0.63941 | -1.24158 |
| C | 1.49020 | -1.62315 | -0.34383 |
| H | 1.84858 | -0.62544 | -2.31670 |
| Cl | -0.19164 | 2.45444 | 0.22428 |
| C | 2.21978 | -1.51421 | 0.98694 |
| H | 1.00456 | -2.53842 | -0.66493 |
| H | 2.85207 | 1.35904 | -0.84198 |
| Pd | 0.31730 | 0.20678 | -0.20490 |
| H | 2.54609 | 0.55339 | 1.72860 |
| H | 3.98178 | -0.16985 | 1.00590 |
| H | 2.96626 | -2.31611 | 1.07131 |
| H | 1.54537 | -1.61512 | 1.84236 |
| P | -1.78363 | -0.45540 | 0.05284 |
| F | -2.49433 | -0.21032 | 1.43327 |
| F | -2.87001 | 0.16254 | -0.89695 |
| F | -2.16789 | -1.98061 | -0.12412 |

**$PF_3$**

| | | | |
|---|---|---|---|
| P | 0.00000 | -0.00001 | 0.50645 |
| F | -1.20482 | -0.67684 | -0.28136 |
| F | 0.01622 | 1.38181 | -0.28135 |
| F | 1.18859 | -0.70495 | -0.28137 |

**$Pd(PF3)_2$**

| | | | |
|---|---|---|---|
| Pd | 0.00000 | -0.61464 | -0.00000 |
| P | -2.07934 | 0.12553 | 0.00000 |
| F | -3.07253 | -0.16825 | -1.19594 |
| F | -3.07246 | -0.16810 | 1.19603 |
| F | -2.21171 | 1.69790 | -0.00009 |
| P | 2.07934 | 0.12553 | 0.00000 |
| F | 3.07253 | -0.16823 | -1.19595 |
| F | 3.07246 | -0.16812 | 1.19603 |
| F | 2.21171 | 1.69790 | -0.00007 |

**$Pd(PF_3)$**

| | | | |
|---|---|---|---|
| Pd | -1.24174 | -0.00002 | 0.00000 |
| P | 0.84864 | -0.00002 | -0.00001 |
| F | 1.64416 | -0.75684 | -1.14430 |
| F | 1.64396 | 1.36950 | -0.08331 |
| F | 1.64414 | -0.61255 | 1.22762 |

**$PH_3$-RC-$A_{L2}$**

| | | | |
|---|---|---|---|
| C | 1.79381 | -0.74233 | 1.29967 |
| C | 2.05218 | 0.45433 | 0.37503 |
| C | 1.18599 | 0.19655 | -0.82061 |
| C | 0.79517 | -1.15979 | -0.83607 |
| H | 1.26476 | 0.82293 | -1.70293 |
| H | 1.95244 | 1.43034 | 0.84577 |
| C | 1.42247 | -1.89118 | 0.33968 |
| H | 0.53741 | -1.68962 | -1.74877 |
| Cl | 3.84753 | 0.44210 | -0.16584 |
| Pd | -0.89927 | 0.06825 | -0.19535 |
| H | 0.92546 | -0.49448 | 1.92562 |
| H | 2.64450 | -0.96073 | 1.94793 |
| H | 2.32844 | -2.41471 | 0.00229 |
| H | 0.76614 | -2.63142 | 0.80698 |
| P | -2.58440 | -1.44173 | 0.12742 |
| H | -3.34731 | -1.86727 | -0.98706 |
| H | -2.30903 | -2.74533 | 0.61045 |
| H | -3.69736 | -1.22283 | 0.97777 |
| P | -1.61892 | 2.19587 | 0.26266 |
| H | -0.74474 | 3.20283 | 0.74324 |
| H | -2.65950 | 2.48387 | 1.18105 |
| H | -2.15105 | 2.97353 | -0.79426 |

**$PH_3$-RC-$S_{L2}$**

| | | | |
|---|---|---|---|
| C | -1.80483 | -1.47600 | -0.97992 |
| C | -2.27317 | -0.57535 | 0.17208 |
| C | -1.12642 | -0.58343 | 1.14847 |
| C | -0.32556 | -1.72412 | 0.89289 |
| H | -1.24618 | -0.13065 | 2.12826 |
| Cl | -2.75584 | 1.09474 | -0.41836 |
| C | -0.90195 | -2.51251 | -0.27663 |
| H | 0.23870 | -2.23140 | 1.67135 |
| H | -3.19617 | -0.94139 | 0.63376 |
| Pd | 0.73481 | 0.04831 | 0.25651 |
| H | -1.20330 | -0.86937 | -1.66576 |
| H | -2.63754 | -1.91490 | -1.53526 |
| H | -1.50739 | -3.34945 | 0.10394 |
| H | -0.14586 | -2.93444 | -0.94573 |
| P | 2.77250 | -0.59851 | -0.54269 |
| H | 3.15666 | -1.95516 | -0.69851 |
| H | 3.21428 | -0.19581 | -1.82741 |

| | | | |
|---|---|---|---|
| H | 3.95343 | -0.20723 | 0.13516 |
| P | 0.53856 | 2.33135 | 0.00333 |
| H | -0.33624 | 3.09405 | 0.81019 |
| H | 0.05344 | 2.80474 | -1.23632 |
| H | 1.62982 | 3.23417 | 0.08793 |

**$PH_3$-RC-$A_{L1}$**

| | | | |
|---|---|---|---|
| C | -1.63878 | 0.44783 | 1.37344 |
| C | -1.67129 | -0.69207 | 0.34583 |
| C | -0.92297 | -0.15400 | -0.83820 |
| C | -0.79383 | 1.22846 | -0.72947 |
| H | -0.84167 | -0.72476 | -1.75731 |
| H | -1.34062 | -1.65891 | 0.71925 |
| C | -1.47156 | 1.73153 | 0.53120 |
| H | -0.58750 | 1.88257 | -1.57322 |
| Cl | -3.42628 | -1.01423 | -0.19600 |
| Pd | 1.11107 | 0.27647 | -0.21874 |
| H | -0.74787 | 0.30168 | 1.99691 |
| H | -2.52165 | 0.45222 | 2.01551 |
| H | -2.44918 | 2.16289 | 0.27188 |
| H | -0.90297 | 2.50402 | 1.05830 |
| P | 2.98359 | -0.81577 | 0.33434 |
| H | 4.16637 | -0.12654 | 0.70251 |
| H | 3.60799 | -1.69346 | -0.58279 |
| H | 2.99141 | -1.70922 | 1.43107 |

**$PH_3$-RC-$S_{L1}$**

| | | | |
|---|---|---|---|
| C | -1.84193 | 0.90351 | 1.16010 |
| C | -2.21730 | 0.11048 | -0.10530 |
| C | -1.14571 | 0.46081 | -1.10120 |
| C | -0.46500 | 1.60434 | -0.67392 |
| H | -1.19527 | 0.10978 | -2.12819 |
| Cl | -2.30592 | -1.69247 | 0.22299 |
| C | -1.05795 | 2.12193 | 0.62310 |
| H | 0.10261 | 2.25297 | -1.33549 |
| H | -3.22003 | 0.34803 | -0.47386 |
| Pd | 0.79601 | -0.12305 | -0.32598 |
| H | -1.17420 | 0.28301 | 1.76627 |
| H | -2.71608 | 1.16995 | 1.75953 |
| H | -1.73962 | 2.95669 | 0.39792 |
| H | -0.31090 | 2.49112 | 1.33131 |
| P | 2.84429 | -0.34503 | 0.53354 |
| H | 3.46612 | -1.60821 | 0.70745 |
| H | 3.95836 | 0.27435 | -0.08150 |
| H | 3.11637 | 0.12370 | 1.84076 |

**$PH_3$-TS-$A_{L2}$**

$\nu = -57.14\ cm^{-1}$

| | | | |
|---|---|---|---|
| C | 1.09569 | -1.37459 | 1.56745 |
| C | 1.41202 | -0.38854 | 0.46495 |
| C | 1.01490 | -0.92503 | -0.78302 |
| C | 0.05086 | -1.92805 | -0.53903 |
| H | 1.36190 | -0.53868 | -1.73403 |
| H | 2.14291 | 0.42109 | 0.52436 |
| C | 0.19431 | -2.44550 | 0.88421 |
| H | -0.42326 | -2.51180 | -1.32145 |
| Cl | 3.95833 | 0.47649 | -0.68810 |
| Pd | -0.75259 | 0.12093 | -0.07217 |
| H | 0.60853 | -0.90420 | 2.42868 |
| H | 2.04033 | -1.79795 | 1.93175 |
| H | 0.67436 | -3.43369 | 0.87088 |
| H | -0.76631 | -2.56849 | 1.39453 |
| P | -2.98799 | -0.15188 | -0.56055 |
| H | -3.67253 | -1.29298 | -0.08551 |
| H | -3.97540 | 0.79535 | -0.20722 |
| H | -3.35502 | -0.28023 | -1.91768 |
| P | -0.31467 | 2.28938 | 0.62972 |
| H | 0.14438 | 2.46910 | 1.95120 |
| H | -1.25730 | 3.34138 | 0.61505 |
| H | 0.73826 | 2.94565 | -0.03790 |

**$PH_3$-TS-$S_{L2}$**

$\nu = -119.92\ cm^{-1}$

| | | | |
|---|---|---|---|
| C | -2.84231 | -0.45547 | -0.47275 |
| C | -2.24285 | 0.41613 | 0.59374 |
| C | -1.36753 | -0.33684 | 1.39848 |
| C | -1.04164 | -1.57112 | 0.71934 |
| H | -1.08371 | -0.06575 | 2.40952 |
| Cl | -1.09470 | 2.03462 | -1.00432 |
| C | -1.99549 | -1.75479 | -0.45670 |
| H | -0.68256 | -2.44148 | 1.26246 |
| H | -2.70684 | 1.34077 | 0.90695 |
| Pd | 0.51795 | -0.23298 | 0.26018 |
| H | -2.88647 | 0.03977 | -1.44192 |
| H | -3.87676 | -0.67309 | -0.16306 |
| H | -2.62475 | -2.64121 | -0.30513 |
| H | -1.46917 | -1.89538 | -1.40519 |
| P | 1.95679 | -1.62635 | -0.73192 |

| | | | |
|---|---|---|---|
| H | 1.69818 | -3.01518 | -0.82127 |
| H | 2.30370 | -1.44403 | -2.09226 |
| H | 3.27868 | -1.74342 | -0.24365 |
| P | 1.63773 | 1.85523 | 0.40187 |
| H | 1.01841 | 2.91843 | 1.08446 |
| H | 1.90683 | 2.52366 | -0.80611 |
| H | 2.92961 | 2.00497 | 0.97853 |

**$PH_3$-TS-$A_{L1}$**

$\nu$ = –53.91 $cm^{-1}$

| | | | |
|---|---|---|---|
| C | -0.18251 | 1.75413 | 1.46433 |
| C | -0.77616 | 0.71568 | 0.54739 |
| C | -0.58358 | 1.12618 | -0.81539 |
| C | 0.53212 | 1.97543 | -0.82559 |
| H | -1.17484 | 0.75294 | -1.64329 |
| H | -1.54756 | -0.01959 | 0.80360 |
| C | 0.79719 | 2.54783 | 0.55503 |
| H | 0.97499 | 2.39204 | -1.72539 |
| Cl | -3.40786 | -0.46450 | -0.16426 |
| Pd | 0.99901 | -0.21121 | -0.32176 |
| H | 0.30375 | 1.31694 | 2.34134 |
| H | -0.99707 | 2.39106 | 1.83784 |
| H | 0.60858 | 3.63022 | 0.56412 |
| H | 1.83879 | 2.41312 | 0.87196 |
| P | 0.76188 | -2.33980 | 0.46066 |
| H | 1.19090 | -2.71974 | 1.75045 |
| H | 1.22969 | -3.47411 | -0.23745 |
| H | -0.59856 | -2.68919 | 0.56561 |

**$PH_3$-TS-$S_{L1}$**

$\nu$ = –184.10 $cm^{-1}$

| | | | |
|---|---|---|---|
| C | -2.16275 | -0.87143 | -0.98035 |
| C | -2.12555 | -0.03210 | 0.28226 |
| C | -1.22890 | -0.65115 | 1.22042 |
| C | -0.48231 | -1.67192 | 0.57799 |
| H | -1.20695 | -0.41527 | 2.27822 |
| Cl | -1.32121 | 1.98542 | -0.30074 |
| C | -1.09252 | -1.97910 | -0.78011 |
| H | 0.07780 | -2.42330 | 1.12468 |
| H | -3.02320 | 0.47525 | 0.61051 |
| Pd | 0.56904 | 0.16204 | 0.26818 |
| H | -1.99605 | -0.26578 | -1.87251 |
| H | -3.16712 | -1.30624 | -1.06858 |
| H | -1.56370 | -2.97229 | -0.76359 |
| H | -0.34765 | -1.99336 | -1.58120 |
| P | 2.66445 | -0.04371 | -0.40659 |
| H | 3.26334 | 0.70878 | -1.45101 |
| H | 3.69666 | 0.17565 | 0.53684 |
| H | 3.13720 | -1.29963 | -0.85928 |

**$PH_3$-$PR_{L2}$**

| | | | |
|---|---|---|---|
| C | 2.33296 | 0.77785 | 0.96751 |
| C | 1.83393 | 1.13262 | -0.42295 |
| C | 1.91574 | 0.00002 | -1.28603 |
| C | 1.83393 | -1.13261 | -0.42297 |
| H | 1.94454 | 0.00003 | -2.36877 |
| Cl | -0.98045 | -0.00002 | 2.05938 |
| C | 2.33297 | -0.77787 | 0.96749 |
| H | 1.82866 | -2.15522 | -0.78751 |
| H | 1.82866 | 2.15524 | -0.78746 |
| Pd | -0.02384 | 0.00001 | -0.44920 |
| H | 1.67946 | 1.17199 | 1.75071 |
| H | 3.34089 | 1.18774 | 1.12480 |
| H | 3.34089 | -1.18776 | 1.12477 |
| H | 1.67946 | -1.17203 | 1.75068 |
| P | -1.57333 | -1.74228 | -0.42942 |
| H | -1.90492 | -2.58537 | -1.52432 |
| H | -1.29908 | -2.75083 | 0.51028 |
| H | -2.88361 | -1.42354 | -0.03086 |
| P | -1.57334 | 1.74228 | -0.42940 |
| H | -1.29909 | 2.75082 | 0.51032 |
| H | -2.88362 | 1.42353 | -0.03084 |
| H | -1.90492 | 2.58539 | -1.52428 |

**$PH_3$-$PR_{L1}$**

| | | | |
|---|---|---|---|
| C | 2.32766 | 0.74326 | 0.90735 |
| C | 1.72553 | 1.05040 | -0.45505 |
| C | 1.67114 | -0.12748 | -1.23942 |
| C | 1.62177 | -1.21931 | -0.32691 |
| H | 1.53379 | -0.17979 | -2.31346 |
| Cl | -1.67071 | 1.75412 | 0.21092 |
| C | 2.28591 | -0.81488 | 0.98281 |
| H | 1.55234 | -2.25611 | -0.63955 |
| H | 1.68145 | 2.05426 | -0.86183 |
| Pd | -0.16536 | -0.01723 | -0.18900 |
| H | 1.76334 | 1.21249 | 1.71867 |
| H | 3.35634 | 1.12556 | 0.96765 |
| H | 3.29589 | -1.24443 | 1.04559 |

| | | | |
|---|---|---|---|
| H | 1.73220 | -1.16912 | 1.85753 |
| P | -1.94280 | -1.40566 | 0.20780 |
| H | -2.57898 | -1.25266 | 1.45462 |
| H | -3.06029 | -1.20410 | -0.62344 |
| H | -1.91752 | -2.82088 | 0.17292 |

**$PH_3$**

| | | | |
|---|---|---|---|
| P | -0.00001 | 0.00000 | -0.12890 |
| H | 0.79491 | -0.88735 | 0.64447 |
| H | 0.37105 | 1.13203 | 0.64452 |
| H | -1.16587 | -0.24473 | 0.64454 |

**$Pd(PH_3)_2$**

| | | | |
|---|---|---|---|
| Pd | -2.01198 | 0.88088 | 0.39647 |
| P | -3.12630 | -1.06601 | 0.32357 |
| H | -2.76746 | -2.14464 | 1.16124 |
| H | -4.50109 | -1.12558 | 0.59063 |
| H | -3.17626 | -1.81743 | -0.87119 |
| P | -0.87904 | 2.81825 | 0.40221 |
| H | 0.22229 | 3.01744 | 1.26189 |
| H | -1.51499 | 4.02867 | 0.69893 |
| H | -0.23630 | 3.27403 | -0.76793 |

**$Pd(PH_3)$**

| | | | |
|---|---|---|---|
| Pd | 0.63233 | 0.00000 | 0.00000 |
| P | -1.49485 | 0.00000 | 0.00001 |
| H | -2.22165 | 0.95101 | 0.75860 |
| H | -2.22149 | 0.18147 | -1.20298 |
| H | -2.22153 | -1.13256 | 0.44425 |

**$PMe_3$-TS-$A_{L2}$**

| | | | |
|---|---|---|---|
| C | 2.36844 | -0.95970 | 1.30734 |
| C | 2.73357 | 0.19247 | 0.36348 |
| C | 1.90180 | -0.03794 | -0.85541 |
| C | 1.42533 | -1.38083 | -0.85445 |
| H | 2.08260 | 0.54345 | -1.75388 |
| H | 2.69273 | 1.18520 | 0.80654 |
| C | 1.98538 | -2.11286 | 0.35758 |
| H | 1.21740 | -1.92663 | -1.77143 |
| Cl | 4.56638 | 0.04606 | -0.08603 |
| Pd | -0.18319 | -0.05597 | -0.32926 |
| H | 1.48340 | -0.64862 | 1.88028 |
| H | 3.17441 | -1.20277 | 2.00285 |
| H | 2.88405 | -2.67832 | 0.07091 |
| H | 1.28575 | -2.81675 | 0.82065 |
| P | -1.97481 | -1.44363 | 0.02561 |
| C | -1.92679 | -3.11821 | -0.74613 |
| C | -2.24014 | -1.88831 | 1.79643 |
| C | -3.67662 | -0.91097 | -0.45651 |
| H | -1.33331 | -2.36007 | 2.18580 |
| H | -3.08633 | -2.57416 | 1.92183 |
| H | -2.42355 | -0.97829 | 2.37480 |
| H | -3.69880 | -0.70636 | -1.53110 |
| H | -3.93121 | 0.01330 | 0.07058 |
| H | -4.42705 | -1.67505 | -0.22151 |
| H | -1.01226 | -3.62841 | -0.43082 |
| H | -1.89334 | -3.00997 | -1.83429 |
| H | -2.79685 | -3.72592 | -0.47021 |
| P | -0.88924 | 2.09965 | 0.06586 |
| C | 0.38007 | 3.42672 | 0.25025 |
| C | -1.90070 | 2.40702 | 1.58052 |
| C | -1.97162 | 2.84430 | -1.23000 |
| H | -1.43322 | 2.85821 | -2.18196 |
| H | -2.27152 | 3.86642 | -0.97040 |
| H | -2.86494 | 2.22588 | -1.35499 |
| H | -1.32977 | 2.10130 | 2.46237 |
| H | -2.81033 | 1.80065 | 1.53867 |
| H | -2.17789 | 3.46299 | 1.68114 |
| H | 1.01826 | 3.19551 | 1.10841 |
| H | -0.07261 | 4.41478 | 0.39639 |
| H | 1.01109 | 3.44448 | -0.64295 |

**$PMe_3$-TS-$S_{L2}$**

| | | | |
|---|---|---|---|
| C | 1.45873 | -2.51383 | 0.87763 |
| C | 2.37204 | -1.75177 | -0.09122 |
| C | 1.45337 | -1.24296 | -1.17002 |
| C | 0.27003 | -2.04926 | -1.14921 |
| H | 1.88471 | -0.83621 | -2.08061 |
| Cl | 3.34491 | -0.45478 | 0.79110 |
| C | 0.38507 | -3.10646 | -0.05679 |
| H | -0.28298 | -2.28000 | -2.05786 |
| H | 3.16369 | -2.39070 | -0.49652 |
| Pd | -0.20053 | -0.08828 | -0.45400 |
| H | 0.99638 | -1.78703 | 1.55493 |
| H | 1.99911 | -3.25765 | 1.46917 |
| H | 0.74041 | -4.05708 | -0.48479 |
| H | -0.55436 | -3.31930 | 0.46511 |
| P | -2.38501 | -0.26960 | 0.21482 |
| C | -3.46236 | -1.42794 | -0.73586 |

| | | | |
|---|---|---|---|
| C | -2.52862 | -0.97906 | 1.91265 |
| C | -3.52441 | 1.17751 | 0.36791 |
| H | -2.01663 | -1.94497 | 1.94331 |
| H | -3.57523 | -1.11479 | 2.21008 |
| H | -2.03453 | -0.31189 | 2.62487 |
| H | -3.60910 | 1.67940 | -0.60040 |
| H | -3.10670 | 1.88968 | 1.08576 |
| H | -4.52314 | 0.87572 | 0.70553 |
| H | -2.97682 | -2.40694 | -0.77983 |
| H | -3.57195 | -1.05925 | -1.76014 |
| H | -4.45550 | -1.53294 | -0.28289 |
| P | 0.55765 | 2.06292 | -0.07999 |
| C | 2.08323 | 2.59638 | -0.96492 |
| C | 0.99451 | 2.45617 | 1.66608 |
| C | -0.55706 | 3.47954 | -0.48718 |
| H | -0.84384 | 3.42143 | -1.54148 |
| H | -0.06880 | 4.44358 | -0.30151 |
| H | -1.46691 | 3.41731 | 0.11560 |
| H | 1.75771 | 1.75008 | 2.00268 |
| H | 0.10770 | 2.33348 | 2.29521 |
| H | 1.37077 | 3.48086 | 1.76804 |
| H | 2.89301 | 1.90736 | -0.71324 |
| H | 2.37082 | 3.62071 | -0.69911 |
| H | 1.90635 | 2.54142 | -2.04354 |

**$PMe_3$-TS-$A_{L1}$**

| | | | |
|---|---|---|---|
| C | 2.25592 | -0.23145 | 1.42671 |
| C | 2.22153 | 0.77724 | 0.26999 |
| C | 1.61356 | 0.02230 | -0.87357 |
| C | 1.63029 | -1.34438 | -0.60214 |
| H | 1.53280 | 0.46861 | -1.85926 |
| H | 1.76261 | 1.73485 | 0.50702 |
| C | 2.28014 | -1.61551 | 0.74135 |
| H | 1.55096 | -2.11233 | -1.36759 |
| Cl | 3.96525 | 1.24942 | -0.21535 |
| Pd | -0.38464 | -0.55065 | -0.29382 |
| H | 1.31865 | -0.11906 | 1.98587 |
| H | 3.09551 | -0.05776 | 2.10287 |
| H | 3.31288 | -1.96132 | 0.58818 |
| H | 1.76358 | -2.37903 | 1.33200 |
| P | -2.43915 | 0.31758 | 0.09189 |
| C | -3.78328 | -0.84055 | 0.60155 |
| C | -3.24914 | 1.20328 | -1.30644 |
| C | -2.54485 | 1.58579 | 1.42522 |
| H | -2.21120 | 1.14542 | 2.36890 |
| H | -3.56809 | 1.96259 | 1.54152 |
| H | -1.87794 | 2.41789 | 1.18329 |
| H | -3.37697 | 0.51312 | -2.14487 |
| H | -2.60339 | 2.02200 | -1.63547 |
| H | -4.22633 | 1.60583 | -1.01385 |
| H | -3.92954 | -1.59336 | -0.17819 |
| H | -4.72632 | -0.30749 | 0.76982 |
| H | -3.49113 | -1.35430 | 1.52180 |

**$PMe_3$-TS-$S_{L1}$**

| | | | |
|---|---|---|---|
| C | 2.39361 | -0.73144 | 1.30148 |
| C | 2.85490 | -0.00132 | 0.02689 |
| C | 1.92187 | -0.48821 | -1.04613 |
| C | 1.27010 | -1.64782 | -0.60768 |
| H | 2.06888 | -0.21010 | -2.08597 |
| Cl | 2.80237 | 1.82499 | 0.23703 |
| C | 1.75516 | -2.03664 | 0.77680 |
| H | 0.83403 | -2.38427 | -1.27758 |
| H | 3.90579 | -0.18989 | -0.21395 |
| Pd | -0.12609 | -0.01593 | -0.51574 |
| H | 1.62178 | -0.12158 | 1.78195 |
| H | 3.21089 | -0.89175 | 2.00963 |
| H | 2.51184 | -2.83159 | 0.68559 |
| H | 0.96232 | -2.41201 | 1.43058 |
| P | -2.27085 | 0.15927 | 0.16369 |
| C | -3.51973 | -0.88560 | -0.70065 |
| C | -2.58684 | -0.29551 | 1.92238 |
| C | -3.08503 | 1.81496 | 0.08282 |
| H | -2.26906 | -1.32857 | 2.08885 |
| H | -3.64809 | -0.19595 | 2.18022 |
| H | -1.99325 | 0.35250 | 2.57322 |
| H | -3.09675 | 2.16352 | -0.95391 |
| H | -2.50910 | 2.53084 | 0.67628 |
| H | -4.11307 | 1.77614 | 0.46174 |
| H | -3.22763 | -1.93608 | -0.61733 |
| H | -3.53900 | -0.62134 | -1.76158 |
| H | -4.52118 | -0.75149 | -0.27427 |

**$PMe_3$-TS-$A_{L2}$**

$\nu = -61.78\ cm^{-1}$

| | | | |
|---|---|---|---|
| C | 1.78485 | -1.42983 | 1.28023 |
| C | 1.94042 | -0.65661 | -0.01361 |
| C | 1.34533 | -1.37301 | -1.07623 |
| C | 0.43522 | -2.30862 | -0.52296 |
| H | 1.49041 | -1.15836 | -2.12846 |

| | | | |
|---|---|---|---|
| H | 2.65904 | 0.14602 | -0.13075 |
| C | 0.85315 | -2.62132 | 0.90819 |
| H | -0.13958 | -3.00796 | -1.12175 |
| Cl | 4.76771 | -0.50424 | -0.20563 |
| Pd | -0.30133 | -0.23618 | -0.23212 |
| H | 1.35952 | -0.81452 | 2.08303 |
| H | 2.78378 | -1.74298 | 1.60129 |
| H | 1.39912 | -3.57466 | 0.93379 |
| H | 0.00323 | -2.71955 | 1.59161 |
| P | -2.57644 | -0.50755 | -0.02604 |
| C | -3.62990 | 0.47940 | -1.16459 |
| C | -3.25677 | -2.19967 | -0.26195 |
| C | -3.26427 | -0.06223 | 1.62146 |
| H | -3.02857 | -2.53973 | -1.27597 |
| H | -4.34126 | -2.22644 | -0.10644 |
| H | -2.77343 | -2.88266 | 0.44238 |
| H | -3.04564 | 0.98715 | 1.83633 |
| H | -2.78450 | -0.67480 | 2.38993 |
| H | -4.34786 | -0.22058 | 1.65908 |
| H | -3.37339 | 0.23421 | -2.19887 |
| H | -3.43774 | 1.54364 | -1.00655 |
| H | -4.69362 | 0.27611 | -0.99823 |
| P | 0.22312 | 2.01370 | 0.07763 |
| C | 1.16542 | 2.33743 | 1.61983 |
| C | -1.09605 | 3.29596 | 0.15085 |
| C | 1.34095 | 2.69046 | -1.21229 |
| H | 2.26607 | 2.10699 | -1.23182 |
| H | 1.58135 | 3.74010 | -1.01005 |
| H | 0.85974 | 2.61241 | -2.19125 |
| H | -1.78852 | 3.06919 | 0.96678 |
| H | -1.65550 | 3.29726 | -0.78912 |
| H | -0.67114 | 4.29284 | 0.31174 |
| H | 0.57519 | 2.02945 | 2.48758 |
| H | 1.41031 | 3.40133 | 1.70909 |
| H | 2.09254 | 1.75779 | 1.60241 |

**$PMe_3$-TS-$S_{L2}$**

$\nu = -131.84\ cm^{-1}$

| | | | |
|---|---|---|---|
| C | -3.55995 | -0.31771 | 0.30151 |
| C | -2.64919 | -1.32276 | -0.34998 |
| C | -1.91842 | -0.68949 | -1.38164 |
| C | -1.95769 | 0.74882 | -1.18767 |
| H | -1.56775 | -1.20975 | -2.26719 |
| Cl | -1.33092 | -1.83047 | 1.62655 |
| C | -2.96621 | 1.06286 | -0.07970 |
| H | -1.87145 | 1.43106 | -2.03066 |
| H | -2.88733 | -2.37801 | -0.35333 |
| Pd | -0.07110 | 0.12211 | -0.51093 |
| H | -3.68666 | -0.47767 | 1.37155 |
| H | -4.54459 | -0.43640 | -0.17948 |
| H | -3.74401 | 1.75240 | -0.42980 |
| H | -2.49539 | 1.52429 | 0.79414 |
| P | 0.76972 | 2.06530 | 0.24042 |
| C | 0.03466 | 3.63792 | -0.37343 |
| C | 0.54478 | 2.23241 | 2.05839 |
| C | 2.56751 | 2.42072 | 0.05271 |
| H | -0.52099 | 2.16630 | 2.29356 |
| H | 0.94420 | 3.18288 | 2.43127 |
| H | 1.04529 | 1.39956 | 2.55910 |
| H | 2.82875 | 2.42331 | -1.00928 |
| H | 3.14363 | 1.63288 | 0.54609 |
| H | 2.83471 | 3.38818 | 0.49352 |
| H | -1.04399 | 3.62010 | -0.19464 |
| H | 0.20019 | 3.71689 | -1.45177 |
| H | 0.47008 | 4.51208 | 0.12449 |
| P | 1.62200 | -1.47555 | -0.19625 |
| C | 1.14077 | -3.21577 | -0.54004 |
| C | 2.28627 | -1.60517 | 1.51266 |
| C | 3.17010 | -1.32142 | -1.18922 |
| H | 2.91995 | -1.35227 | -2.25387 |
| H | 3.87663 | -2.12853 | -0.96337 |
| H | 3.64812 | -0.35983 | -0.98190 |
| H | 1.44269 | -1.78514 | 2.18405 |
| H | 2.76819 | -0.66339 | 1.79310 |
| H | 3.01472 | -2.41938 | 1.59955 |
| H | 0.27628 | -3.44615 | 0.08874 |
| H | 1.96096 | -3.91086 | -0.32538 |
| H | 0.85234 | -3.31033 | -1.59140 |

**$PMe_3$-TS-$A_{L1}$**

$\nu = -55.53\ cm^{-1}$

| | | | |
|---|---|---|---|
| C | 1.89010 | -0.60758 | 1.54086 |
| C | 1.33940 | 0.25442 | 0.43212 |
| C | 1.75968 | -0.28658 | -0.83329 |
| C | 2.00742 | -1.64775 | -0.63094 |
| H | 1.80343 | 0.27974 | -1.75492 |
| H | 1.03462 | 1.29143 | 0.55175 |
| C | 2.23407 | -1.95206 | 0.83951 |
| H | 2.28095 | -2.34155 | -1.41992 |
| Cl | 2.30742 | 2.88324 | -0.20180 |

| | | | |
|---|---|---|---|
| Pd | -0.20879 | -1.00328 | -0.41705 |
| H | 1.18987 | -0.72635 | 2.37313 |
| H | 2.78724 | -0.11553 | 1.94007 |
| H | 3.27243 | -2.26642 | 1.01271 |
| H | 1.59668 | -2.76893 | 1.20101 |
| P | -1.98843 | 0.32657 | 0.12391 |
| C | -2.07235 | 0.77388 | 1.90173 |
| C | -3.72672 | -0.12897 | -0.26440 |
| C | -1.78023 | 1.95210 | -0.69776 |
| H | -0.78560 | 2.35735 | -0.47810 |
| H | -2.54864 | 2.65744 | -0.36172 |
| H | -1.85937 | 1.81970 | -1.78040 |
| H | -3.99965 | -1.03863 | 0.27803 |
| H | -3.82101 | -0.32385 | -1.33633 |
| H | -4.41329 | 0.67774 | 0.01531 |
| H | -2.27347 | -0.11820 | 2.50113 |
| H | -2.85787 | 1.51619 | 2.07980 |
| H | -1.10985 | 1.19245 | 2.20764 |

**$PMe_3$-TS-$S_{L1}$**

$\nu = -182.86\ cm^{-1}$

| | | | |
|---|---|---|---|
| C | -2.60437 | 0.87320 | 1.15359 |
| C | -2.75440 | 0.03424 | -0.10623 |
| C | -1.96521 | 0.63280 | -1.15046 |
| C | -1.13310 | 1.65334 | -0.61463 |
| H | -2.08406 | 0.39592 | -2.20173 |
| Cl | -1.96122 | -1.97349 | 0.35861 |
| C | -1.58723 | 1.99195 | 0.79687 |
| H | -0.65477 | 2.40271 | -1.23759 |
| H | -3.71374 | -0.41957 | -0.32179 |
| Pd | -0.05339 | -0.16308 | -0.43593 |
| H | -2.28520 | 0.26321 | 2.00028 |
| H | -3.58449 | 1.29496 | 1.40980 |
| H | -2.08100 | 2.97485 | 0.80518 |
| H | -0.75655 | 2.04602 | 1.50661 |
| P | 2.09567 | -0.02972 | 0.13497 |
| C | 2.81335 | -1.31285 | 1.25124 |
| C | 3.30940 | -0.05356 | -1.25247 |
| C | 2.59090 | 1.51099 | 1.01747 |
| H | 3.20962 | -0.99244 | -1.80435 |
| H | 4.33832 | 0.04161 | -0.88565 |
| H | 3.08996 | 0.76971 | -1.93764 |
| H | 2.03296 | 1.58420 | 1.95544 |
| H | 2.33637 | 2.37636 | 0.39927 |
| H | 3.66513 | 1.52309 | 1.23651 |
| H | 2.70413 | -2.29623 | 0.78473 |
| H | 2.25506 | -1.32236 | 2.19171 |
| H | 3.87371 | -1.12574 | 1.45904 |

**$PMe_3$-$PR_{L2}$**

| | | | |
|---|---|---|---|
| C | 2.86006 | -1.45716 | 0.22536 |
| C | 2.29245 | -0.70107 | -0.96361 |
| C | 1.33053 | -1.50241 | -1.64564 |
| C | 0.81050 | -2.38836 | -0.65608 |
| H | 1.01174 | -1.40898 | -2.67688 |
| Cl | 0.56796 | -0.05083 | 2.33968 |
| C | 1.83993 | -2.61250 | 0.43945 |
| H | 0.03817 | -3.12039 | -0.86869 |
| H | 2.84860 | 0.09193 | -1.45461 |
| Pd | 0.23786 | -0.30313 | -0.28581 |
| H | 2.93026 | -0.82937 | 1.11768 |
| H | 3.86451 | -1.83895 | -0.00937 |
| H | 2.31224 | -3.59869 | 0.32086 |
| H | 1.39712 | -2.56140 | 1.43777 |
| P | -2.06136 | -0.56934 | -0.07346 |
| C | -2.67879 | -2.28514 | -0.31528 |
| C | -2.78358 | -0.15274 | 1.55692 |
| C | -3.13907 | 0.36186 | -1.24233 |
| H | -2.20944 | -0.67426 | 2.32649 |
| H | -3.84362 | -0.42781 | 1.59988 |
| H | -2.67268 | 0.91744 | 1.74333 |
| H | -2.87640 | 0.09036 | -2.26877 |
| H | -2.96809 | 1.43510 | -1.12011 |
| H | -4.20038 | 0.14845 | -1.07067 |
| H | -2.20505 | -2.93813 | 0.42281 |
| H | -2.41050 | -2.63814 | -1.31517 |
| H | -3.76691 | -2.33553 | -0.19545 |
| P | 0.40103 | 2.01738 | -0.23330 |
| C | 2.01635 | 2.55914 | 0.43910 |
| C | -0.76751 | 2.90475 | 0.86538 |
| C | 0.27168 | 2.96775 | -1.80643 |
| H | 1.02095 | 2.59777 | -2.51248 |
| H | 0.42704 | 4.04093 | -1.64617 |
| H | -0.71708 | 2.80952 | -2.24715 |
| H | -0.70181 | 2.43127 | 1.84919 |
| H | -1.78909 | 2.81296 | 0.48555 |
| H | -0.50944 | 3.96699 | 0.93819 |
| H | 2.14033 | 2.06121 | 1.40519 |
| H | 2.05158 | 3.64735 | 0.56197 |
| H | 2.82065 | 2.24293 | -0.23032 |

**$PMe_3$-$PR_{L1}$**

| | | | |
|---|---|---|---|
| C | 2.28090 | -1.51867 | 0.92709 |
| C | 2.88444 | -0.08143 | 1.01340 |
| C | 2.56702 | 0.52237 | -0.34660 |
| C | 2.10920 | -0.47463 | -1.23007 |
| C | 1.57564 | -1.52950 | -0.42491 |
| Pd | 0.36524 | 0.22202 | -0.23247 |
| P | -1.77470 | -0.52929 | 0.04744 |
| C | -2.14671 | -2.31842 | -0.14401 |
| Cl | -0.39244 | 2.41602 | 0.23544 |
| C | -2.44832 | -0.13545 | 1.70424 |
| C | -2.96088 | 0.27891 | -1.08831 |
| H | 2.03116 | -0.38865 | -2.30807 |
| H | 1.16246 | -2.44219 | -0.84267 |
| H | 2.93688 | 1.49221 | -0.65865 |
| H | 2.44436 | 0.50068 | 1.82961 |
| H | 3.96970 | -0.10493 | 1.18549 |
| H | 3.06891 | -2.28540 | 0.95282 |
| H | 1.59994 | -1.72882 | 1.75734 |
| H | -2.83688 | 1.35921 | -0.97553 |
| H | -3.99227 | -0.01245 | -0.86072 |
| H | -2.72292 | 0.00545 | -2.11999 |
| H | -1.54858 | -2.89109 | 0.57076 |
| H | -1.87586 | -2.63909 | -1.15408 |
| H | -3.20853 | -2.52771 | 0.02706 |
| H | -2.31174 | 0.93710 | 1.86650 |
| H | -1.88418 | -0.67945 | 2.46723 |
| H | -3.50896 | -0.39988 | 1.77757 |

**$PMe_3$**

| | | | |
|---|---|---|---|
| P | -2.00715 | -1.42375 | 0.01966 |
| C | -1.96310 | -3.09972 | -0.77712 |
| C | -2.31938 | -1.94611 | 1.77322 |
| C | -3.73433 | -0.92820 | -0.44595 |
| H | -1.42124 | -2.42450 | 2.17705 |
| H | -3.16099 | -2.64539 | 1.85240 |
| H | -2.53260 | -1.06336 | 2.38469 |
| H | -3.77959 | -0.72926 | -1.52157 |
| H | -4.00275 | -0.00473 | 0.07725 |
| H | -4.46846 | -1.70441 | -0.19667 |
| H | -1.05103 | -3.62410 | -0.47422 |
| H | -1.93847 | -2.98594 | -1.86572 |
| H | -2.83221 | -3.71051 | -0.50295 |

**$Pd(PMe_3)_2$**

| | | | |
|---|---|---|---|
| Pd | -1.90747 | 0.44682 | 0.20179 |
| P | -2.58158 | -1.70718 | 0.07697 |
| C | -1.32677 | -2.96209 | -0.43143 |
| C | -3.22808 | -2.47947 | 1.62400 |
| C | -3.95076 | -2.09963 | -1.09739 |
| H | -2.45332 | -2.44378 | 2.39496 |
| H | -3.52912 | -3.52131 | 1.45904 |
| H | -4.08813 | -1.90571 | 1.98035 |
| H | -3.64962 | -1.81497 | -2.10941 |
| H | -4.83425 | -1.51382 | -0.82874 |
| H | -4.20317 | -3.16700 | -1.07988 |
| H | -0.49111 | -2.94145 | 0.27365 |
| H | -0.94140 | -2.70498 | -1.42204 |
| H | -1.75452 | -3.97181 | -0.45870 |
| P | -1.24260 | 2.60299 | 0.33784 |
| C | 0.49840 | 2.98753 | -0.14056 |
| C | -1.32554 | 3.40789 | 1.99705 |
| C | -2.15733 | 3.83712 | -0.68585 |
| H | -2.07988 | 3.55814 | -1.74040 |
| H | -1.75926 | 4.84988 | -0.54757 |
| H | -3.21481 | 3.82225 | -0.40764 |
| H | -0.70205 | 2.84816 | 2.69981 |
| H | -2.35664 | 3.37815 | 2.36014 |
| H | -0.98381 | 4.44951 | 1.95775 |
| H | 1.18094 | 2.41566 | 0.49427 |
| H | 0.71734 | 4.05748 | -0.03818 |
| H | 0.66275 | 2.68163 | -1.17753 |

**$Pd(PMe_3)_2$**

| | | | |
|---|---|---|---|
| Pd | 1.29625 | 0.00000 | 0.00001 |
| P | -0.84243 | -0.00000 | 0.00003 |
| C | -1.68690 | -1.42115 | 0.82022 |
| C | -1.68690 | 1.42098 | 0.82053 |
| C | -1.68682 | 0.00018 | -1.64083 |
| H | -1.38218 | 1.46587 | 1.86940 |
| H | -2.77813 | 1.31921 | 0.76178 |
| H | -1.38224 | 2.35182 | 0.33503 |
| H | -1.38221 | -0.88567 | -2.20428 |
| H | -1.38219 | 0.88614 | -2.20410 |
| H | -2.77803 | 0.00018 | -1.52317 |
| H | -1.38217 | -1.46628 | 1.86908 |
| H | -1.38226 | -2.35189 | 0.33451 |
| H | -2.77813 | -1.31937 | 0.76151 |

**$Pyr_3$-RC-$A_{L2}$**

| | | | |
|---|---|---|---|
| C | 2.67765 | -1.00817 | 1.38344 |
| C | 3.01043 | 0.16963 | 0.45811 |
| C | 2.20787 | -0.06888 | -0.78186 |
| C | 1.77002 | -1.43947 | -0.80058 |
| H | 2.43475 | 0.50701 | -1.67544 |
| H | 2.92672 | 1.15422 | 0.91686 |
| C | 2.33407 | -2.16119 | 0.41797 |
| H | 1.65268 | -1.99358 | -1.73173 |
| Cl | 4.85586 | 0.10433 | 0.03985 |
| Pd | 0.16728 | -0.18494 | -0.38202 |
| H | 1.78599 | -0.73403 | 1.96298 |
| H | 3.49165 | -1.23622 | 2.07536 |
| H | 3.25036 | -2.70332 | 0.14127 |
| H | 1.64412 | -2.88420 | 0.86631 |
| C | -2.00067 | 2.03530 | -0.72723 |
| C | -2.60958 | 3.28379 | -0.66669 |
| C | -2.00310 | 4.29640 | 0.07484 |
| C | -0.80363 | 4.01246 | 0.72724 |
| C | -0.25607 | 2.74006 | 0.61016 |
| N | -0.83628 | 1.75369 | -0.10565 |
| H | -2.44013 | 1.21694 | -1.28956 |
| H | -3.54317 | 3.45334 | -1.19402 |
| H | -2.45259 | 5.28254 | 0.14134 |
| H | -0.29104 | 4.76582 | 1.31695 |
| H | 0.68126 | 2.47795 | 1.08965 |
| C | -2.00239 | -2.37797 | -0.75854 |
| C | -3.11942 | -3.16200 | -0.49337 |
| C | -3.96552 | -2.80550 | 0.55623 |
| C | -3.65686 | -1.66614 | 1.29743 |
| C | -2.52536 | -0.93092 | 0.96383 |
| N | -1.69674 | -1.27250 | -0.04581 |
| H | -1.30884 | -2.62398 | -1.55578 |
| H | -3.31502 | -4.03989 | -1.10101 |
| H | -4.84213 | -3.40168 | 0.79075 |
| H | -4.28229 | -1.34523 | 2.12460 |
| H | -2.25028 | -0.03472 | 1.51118 |

**Pyr-RC-$S_{L2}$**

| | | | |
|---|---|---|---|
| C | 2.21911 | -2.30504 | 1.03689 |
| C | 2.99012 | -1.39260 | 0.07522 |
| C | 2.02995 | -1.09892 | -1.04690 |
| C | 1.04213 | -2.15397 | -1.05347 |
| H | 2.42928 | -0.65460 | -1.95680 |
| Cl | 3.65383 | 0.09719 | 0.94811 |
| C | 1.32679 | -3.13018 | 0.08594 |
| H | 0.64040 | -2.55230 | -1.98658 |
| H | 3.90908 | -1.86563 | -0.28752 |
| Pd | 0.15529 | -0.37115 | -0.51309 |
| H | 1.59247 | -1.67682 | 1.67855 |
| H | 2.88062 | -2.90807 | 1.66530 |
| H | 1.88452 | -4.00222 | -0.29097 |
| H | 0.42689 | -3.50958 | 0.58248 |
| C | -1.08662 | 2.47348 | -0.70621 |
| C | -1.20382 | 3.85726 | -0.64323 |
| C | -0.18060 | 4.59410 | -0.04835 |
| C | 0.92170 | 3.90752 | 0.45826 |
| C | 0.96806 | 2.52124 | 0.35084 |
| N | -0.02021 | 1.80252 | -0.22313 |
| H | -1.86018 | 1.85926 | -1.15734 |
| H | -2.08323 | 4.34276 | -1.05489 |
| H | -0.24052 | 5.67654 | 0.01632 |
| H | 1.74584 | 4.43425 | 0.92904 |
| H | 1.81236 | 1.94390 | 0.71374 |
| C | -2.69987 | -1.56481 | -0.65328 |
| C | -3.97863 | -1.92445 | -0.24466 |
| C | -4.51750 | -1.33284 | 0.89774 |
| C | -3.74767 | -0.39363 | 1.58243 |
| C | -2.47946 | -0.08295 | 1.10455 |
| N | -1.94664 | -0.65781 | 0.00523 |
| H | -2.23445 | -2.00868 | -1.52712 |
| H | -4.53740 | -2.66032 | -0.81434 |
| H | -5.51140 | -1.59761 | 1.24553 |
| H | -4.12030 | 0.09694 | 2.47624 |
| H | -1.84661 | 0.64457 | 1.60339 |

**Pyr-RC-$A_{L1}$**

| | | | |
|---|---|---|---|
| C | -2.40558 | 0.57543 | 1.41361 |
| C | -2.58709 | -0.65931 | 0.51951 |
| C | -1.91378 | -0.29840 | -0.77211 |
| C | -1.70196 | 1.08798 | -0.82043 |
| H | -1.99589 | -0.94832 | -1.63805 |
| H | -2.28283 | -1.60149 | 0.97141 |
| C | -2.25536 | 1.75129 | 0.42615 |
| H | -1.57792 | 1.64676 | -1.74473 |
| Cl | -4.40850 | -0.92776 | 0.17716 |
| Pd | 0.12514 | 0.09327 | -0.41693 |
| H | -1.46805 | 0.44458 | 1.96827 |
| H | -3.22575 | 0.69638 | 2.12447 |
| H | -3.23536 | 2.19433 | 0.19487 |
| H | -1.61659 | 2.54853 | 0.81890 |
| C | 2.95339 | 1.01732 | 0.12144 |

| | | | |
|---|---|---|---|
| C | 4.31737 | 0.93954 | 0.37297 |
| C | 4.92314 | -0.31254 | 0.46234 |
| C | 4.12806 | -1.44458 | 0.29220 |
| C | 2.77092 | -1.28901 | 0.04055 |
| N | 2.17487 | -0.07690 | -0.04529 |
| H | 2.44539 | 1.97212 | 0.04620 |
| H | 4.88967 | 1.85315 | 0.49655 |
| H | 5.98690 | -0.40376 | 0.65881 |
| H | 4.54859 | -2.44318 | 0.35073 |
| H | 2.12128 | -2.14564 | -0.10065 |

**Pyr-RC-$S_{L1}$**

| | | | |
|---|---|---|---|
| C | 2.71251 | 0.28030 | 1.30868 |
| C | 2.68358 | 0.82966 | -0.12576 |
| C | 2.07588 | -0.27388 | -0.94956 |
| C | 2.16196 | -1.48356 | -0.23146 |
| H | 2.04558 | -0.19000 | -2.03249 |
| Cl | 1.76867 | 2.41784 | -0.23732 |
| C | 2.83724 | -1.24869 | 1.11283 |
| H | 2.21006 | -2.45835 | -0.71238 |
| H | 3.68133 | 1.09570 | -0.49152 |
| Pd | 0.17400 | -0.79181 | -0.25754 |
| H | 1.75332 | 0.51111 | 1.78262 |
| H | 3.51829 | 0.71677 | 1.90539 |
| H | 3.89595 | -1.54538 | 1.05302 |
| H | 2.38659 | -1.81266 | 1.93541 |
| C | -2.86499 | -1.07762 | 0.00084 |
| C | -4.17320 | -0.66621 | 0.22740 |
| C | -4.44280 | 0.69449 | 0.35805 |
| C | -3.38123 | 1.59369 | 0.26059 |
| C | -2.09777 | 1.10881 | 0.04360 |
| N | -1.83093 | -0.21182 | -0.08767 |
| H | -2.61707 | -2.12661 | -0.12081 |
| H | -4.96354 | -1.40708 | 0.29217 |
| H | -5.45563 | 1.04605 | 0.52966 |
| H | -3.53827 | 2.66336 | 0.35374 |
| H | -1.23881 | 1.76785 | -0.03139 |

**Pyr-TS-$A_{L2}$**

$\nu = -49.67\ cm^{-1}$

| | | | |
|---|---|---|---|
| C | 2.00405 | -1.56596 | 1.26349 |
| C | 2.14579 | -0.85172 | -0.06695 |
| C | 1.56988 | -1.62844 | -1.09956 |
| C | 0.61891 | -2.49324 | -0.48275 |
| H | 1.74311 | -1.49770 | -2.16123 |
| H | 2.86701 | -0.05225 | -0.22125 |
| C | 1.03988 | -2.74998 | 0.95881 |
| H | 0.01241 | -3.20479 | -1.03761 |
| Cl | 5.01488 | -0.60366 | 0.06737 |
| Pd | -0.01434 | -0.45145 | -0.33703 |
| H | 1.60697 | -0.90595 | 2.04561 |
| H | 3.00482 | -1.87941 | 1.57920 |
| H | 1.55801 | -3.71667 | 1.03316 |
| H | 0.18780 | -2.78823 | 1.64578 |
| C | -2.70802 | 0.06566 | 1.00769 |
| C | -4.04479 | -0.10148 | 1.34853 |
| C | -4.85302 | -0.90077 | 0.54222 |
| C | -4.28491 | -1.50494 | -0.57873 |
| C | -2.93764 | -1.29793 | -0.84792 |
| N | -2.15016 | -0.52450 | -0.07103 |
| H | -2.04481 | 0.68646 | 1.60168 |
| H | -4.43910 | 0.39163 | 2.23096 |
| H | -5.90134 | -1.04972 | 0.78143 |
| H | -4.87288 | -2.13380 | -1.23911 |
| H | -2.45095 | -1.75634 | -1.70183 |
| C | -0.86174 | 2.50817 | -0.66727 |
| C | -0.79200 | 3.89460 | -0.61059 |
| C | 0.29235 | 4.48913 | 0.03299 |
| C | 1.26602 | 3.66667 | 0.59510 |
| C | 1.12858 | 2.28706 | 0.49416 |
| N | 0.07933 | 1.70690 | -0.12786 |
| H | -1.68597 | 2.00230 | -1.16000 |
| H | -1.57361 | 4.49146 | -1.06928 |
| H | 0.37877 | 5.56989 | 0.08976 |
| H | 2.13449 | 4.07790 | 1.09835 |
| H | 1.87778 | 1.61649 | 0.89944 |

**Pyr-TS-$S_{L2}$**

$\nu = -136.58\ cm^{-1}$

| | | | |
|---|---|---|---|
| C | -3.64919 | -1.00764 | 0.42196 |
| C | -2.54292 | -1.94114 | 0.01515 |
| C | -1.96091 | -1.47960 | -1.19755 |
| C | -2.31251 | -0.07605 | -1.37851 |
| H | -1.56696 | -2.15539 | -1.95168 |
| Cl | -1.17453 | -1.62536 | 1.99272 |
| C | -3.35371 | 0.31478 | -0.32882 |
| H | -2.38216 | 0.36663 | -2.37149 |
| H | -2.55522 | -2.98348 | 0.30614 |
| Pd | -0.39324 | -0.15010 | -0.67794 |

| | | | |
|---|---|---|---|
| H | -3.76077 | -0.90895 | 1.50120 |
| H | -4.57822 | -1.44856 | 0.02337 |
| H | -4.26076 | 0.72793 | -0.78728 |
| H | -2.96914 | 1.06887 | 0.36619 |
| C | 2.68345 | -0.40556 | -0.87112 |
| C | 3.97078 | -0.91248 | -0.74099 |
| C | 4.17026 | -2.04581 | 0.04706 |
| C | 3.06741 | -2.61985 | 0.67483 |
| C | 1.80857 | -2.05264 | 0.49607 |
| N | 1.61181 | -0.96068 | -0.27081 |
| H | 2.48132 | 0.47637 | -1.47189 |
| H | 4.79730 | -0.42384 | -1.24744 |
| H | 5.16359 | -2.46753 | 0.17052 |
| H | 3.17160 | -3.49767 | 1.30478 |
| H | 0.91707 | -2.43767 | 0.98498 |
| C | 0.38620 | 2.86879 | -0.88013 |
| C | 0.69900 | 4.12507 | -0.37199 |
| C | 0.80822 | 4.28969 | 1.00754 |
| C | 0.59989 | 3.18073 | 1.82788 |
| C | 0.29683 | 1.95485 | 1.24915 |
| N | 0.18966 | 1.79370 | -0.08985 |
| H | 0.27907 | 2.69647 | -1.94588 |
| H | 0.84965 | 4.95683 | -1.05293 |
| H | 1.04658 | 5.25951 | 1.43369 |
| H | 0.66826 | 3.25736 | 2.90827 |
| H | 0.11652 | 1.05918 | 1.84009 |

**Pyr-TS-$A_{L1}$**

$\nu$ = –55.96 $cm^{-1}$

| | | | |
|---|---|---|---|
| C | 2.17124 | -0.41744 | 1.66064 |
| C | 1.57037 | 0.42758 | 0.56636 |
| C | 2.04102 | -0.03177 | -0.70902 |
| C | 2.36214 | -1.39523 | -0.53536 |
| H | 2.07564 | 0.57656 | -1.60418 |
| H | 1.13685 | 1.41609 | 0.70690 |
| C | 2.65799 | -1.69760 | 0.92482 |
| H | 2.70608 | -2.04131 | -1.33784 |
| Cl | 2.17956 | 3.15870 | -0.13379 |
| Pd | 0.19632 | -0.96950 | -0.42578 |
| H | 1.45950 | -0.63118 | 2.46373 |
| H | 3.00401 | 0.14066 | 2.11015 |
| H | 3.73145 | -1.88428 | 1.06818 |
| H | 2.13185 | -2.59132 | 1.27982 |
| C | -2.85604 | -1.00507 | 0.16592 |
| C | -4.11074 | -0.45595 | 0.39773 |
| C | -4.25857 | 0.92921 | 0.36149 |
| C | -3.13897 | 1.71392 | 0.09314 |
| C | -1.91426 | 1.09696 | -0.12855 |
| N | -1.76801 | -0.24907 | -0.09376 |
| H | -2.70020 | -2.07893 | 0.18567 |
| H | -4.95198 | -1.10947 | 0.60304 |
| H | -5.22671 | 1.38702 | 0.53964 |
| H | -3.19994 | 2.79613 | 0.05530 |
| H | -1.01859 | 1.67480 | -0.33687 |

**Pyr-TS-$S_{L1}$**

$\nu$ = –195.85 $cm^{-1}$

| | | | |
|---|---|---|---|
| C | 2.44286 | -1.55558 | 1.17062 |
| C | 2.92919 | -0.38329 | 0.31077 |
| C | 2.04043 | -0.38499 | -0.88319 |
| C | 1.36111 | -1.65285 | -0.97096 |
| H | 2.32890 | 0.20158 | -1.75137 |
| H | 3.05542 | 0.56196 | 0.83462 |
| C | 1.88013 | -2.55714 | 0.14229 |
| H | 1.10370 | -2.09971 | -1.92908 |
| Cl | 4.73296 | -0.75584 | -0.21183 |
| Pd | 0.01280 | -0.15030 | -0.32384 |
| H | 1.63059 | -1.17965 | 1.80987 |
| H | 3.23204 | -1.96304 | 1.80660 |
| H | 2.69566 | -3.19199 | -0.23510 |
| H | 1.12358 | -3.22097 | 0.57489 |
| N | -2.93888 | -0.77865 | -1.02536 |
| C | -4.03983 | -1.55225 | -0.68174 |
| C | -3.66925 | -2.29416 | 0.39317 |
| C | -2.88863 | 0.16710 | -2.13090 |
| H | -4.97211 | -1.51157 | -1.22324 |
| H | -4.21767 | -3.02092 | 0.97198 |
| C | -1.86452 | -1.00942 | -0.20081 |
| N | -2.35056 | -1.95524 | 0.67029 |
| C | -1.55163 | -2.52274 | 1.74608 |
| C | -0.63764 | 3.70999 | 1.51056 |
| C | -0.23590 | 4.12681 | 0.28214 |
| N | -0.00822 | 2.98062 | -0.46803 |
| H | -0.90655 | 4.26982 | 2.39281 |
| H | -0.09429 | 5.12024 | -0.11412 |
| C | 0.45256 | 2.96242 | -1.84942 |
| N | -0.64992 | 2.32198 | 1.46995 |
| C | -0.25683 | 1.83458 | 0.24721 |
| C | -1.00016 | 1.45386 | 2.58431 |
| H | -1.47791 | -3.60859 | 1.63523 |

| | | | |
|---|---|---|---|
| H | -1.99284 | -2.28540 | 2.71988 |
| H | -0.55772 | -2.07746 | 1.66777 |
| H | -2.95125 | -0.35667 | -3.08988 |
| H | -1.92735 | 0.68146 | -2.05478 |
| H | -3.70924 | 0.88697 | -2.05130 |
| H | 0.65175 | 1.91775 | -2.09813 |
| H | 1.37031 | 3.54914 | -1.94877 |
| H | -0.31438 | 3.36804 | -2.51756 |
| H | -1.08979 | 0.44550 | 2.17473 |
| H | -1.95047 | 1.77061 | 3.02443 |
| H | -0.21762 | 1.47094 | 3.34962 |

**Pyr-PR$_{L2}$**

| | | | |
|---|---|---|---|
| C | 3.55448 | 0.00515 | 0.05299 |
| C | 2.55429 | 0.48973 | -0.98286 |
| C | 2.03661 | -0.61797 | -1.73858 |
| C | 2.06949 | -1.69393 | -0.78637 |
| H | 1.67807 | -0.62900 | -2.76164 |
| Cl | 0.89546 | 0.02527 | 2.34807 |
| C | 3.20934 | -1.50270 | 0.19890 |
| H | 1.66524 | -2.68171 | -0.99577 |
| H | 2.59203 | 1.50347 | -1.37452 |
| Pd | 0.69433 | -0.18562 | -0.23111 |
| H | 3.43704 | 0.52986 | 1.00427 |
| H | 4.58450 | 0.15918 | -0.30186 |
| H | 4.06149 | -2.14759 | -0.06228 |
| H | 2.89928 | -1.73825 | 1.22014 |
| C | -1.36390 | 1.92821 | -1.19714 |
| C | -2.11985 | 3.09402 | -1.23282 |
| C | -1.91627 | 4.05555 | -0.24381 |
| C | -0.96737 | 3.80505 | 0.74447 |
| C | -0.25616 | 2.60841 | 0.71926 |
| N | -0.44874 | 1.68400 | -0.24116 |
| H | -1.48342 | 1.15225 | -1.94721 |
| H | -2.85009 | 3.24033 | -2.02233 |
| H | -2.48766 | 4.97928 | -0.24406 |
| H | -0.77800 | 4.52112 | 1.53776 |
| H | 0.46381 | 2.32737 | 1.48400 |
| C | -1.65898 | -2.02975 | -1.08342 |
| C | -2.84311 | -2.75449 | -1.01304 |
| C | -3.52978 | -2.80012 | 0.19990 |
| C | -2.99814 | -2.12011 | 1.29302 |
| C | -1.80540 | -1.41714 | 1.14518 |
| N | -1.14620 | -1.36966 | -0.02839 |
| H | -1.08697 | -1.96564 | -2.00458 |
| H | -3.21336 | -3.27168 | -1.89250 |
| H | -4.45775 | -3.35752 | 0.28932 |
| H | -3.49396 | -2.13144 | 2.25845 |
| H | -1.31911 | -0.88108 | 1.95944 |

**Pyr-PR$_{L1}$**

| | | | |
|---|---|---|---|
| C | 3.01714 | -0.39568 | 1.11463 |
| C | 2.72487 | 0.06600 | -0.30521 |
| C | 2.13704 | -1.00496 | -1.04680 |
| C | 1.46170 | -1.80676 | -0.08963 |
| H | 2.09840 | -1.10689 | -2.12542 |
| Cl | 0.39099 | 2.51613 | -0.09420 |
| C | 2.12909 | -1.66865 | 1.27224 |
| H | 0.87419 | -2.68297 | -0.34987 |
| H | 3.25441 | 0.89512 | -0.76136 |
| Pd | 0.61573 | 0.17939 | -0.25283 |
| H | 2.77029 | 0.37465 | 1.85042 |
| H | 4.08457 | -0.63097 | 1.23398 |
| H | 2.73034 | -2.56048 | 1.50111 |
| H | 1.39806 | -1.55953 | 2.07988 |
| C | -2.08127 | -1.25838 | -0.53026 |
| C | -3.44120 | -1.50739 | -0.39683 |
| C | -4.23691 | -0.56827 | 0.25774 |
| C | -3.63526 | 0.58893 | 0.74509 |
| C | -2.26822 | 0.77390 | 0.56574 |
| N | -1.49634 | -0.13880 | -0.05886 |
| H | -1.42422 | -1.96102 | -1.03077 |
| H | -3.86212 | -2.42177 | -0.80198 |
| H | -5.30287 | -0.73520 | 0.38106 |
| H | -4.21259 | 1.35219 | 1.25655 |
| H | -1.74629 | 1.66998 | 0.88978 |

**Pyr**

| | | | |
|---|---|---|---|
| C | -1.14379 | -0.72068 | -0.00025 |
| C | -1.19771 | 0.67312 | 0.00012 |
| C | 0.00033 | 1.38504 | -0.00007 |
| C | 1.19803 | 0.67268 | -0.00002 |
| C | 1.14341 | -0.72127 | 0.00001 |
| N | -0.00029 | -1.42216 | 0.00007 |
| H | -2.06041 | -1.30845 | 0.00065 |
| H | -2.15600 | 1.18458 | -0.00003 |
| H | 0.00044 | 2.47141 | -0.00004 |
| H | 2.15659 | 1.18363 | 0.00043 |
| H | 2.05979 | -1.30939 | -0.00020 |

**Pd(Pyr)$_2$**

| | | | |
|---|---|---|---|
| Pd | 0.00000 | -0.00020 | -0.00025 |
| C | -2.72164 | 0.81952 | 0.81880 |
| C | -4.10980 | 0.84570 | 0.84521 |
| C | -4.82823 | 0.00027 | 0.00049 |
| C | -4.11028 | -0.84524 | -0.84456 |
| C | -2.72210 | -0.81925 | -0.81876 |

| | | | |
|---|---|---|---|
| N | -2.01465 | 0.00008 | -0.00014 |
| H | -2.12765 | 1.46054 | 1.45921 |
| H | -4.61463 | 1.52534 | 1.52449 |
| H | -5.91390 | 0.00034 | 0.00072 |
| H | -4.61550 | -1.52482 | -1.52362 |
| H | -2.12848 | -1.46036 | -1.45942 |
| C | 2.72184 | -0.81914 | 0.81905 |
| C | 4.11001 | -0.84477 | 0.84566 |
| C | 4.82823 | 0.00048 | 0.00058 |
| C | 4.11007 | 0.84526 | -0.84502 |
| C | 2.72189 | 0.81875 | -0.81938 |
| N | 2.01464 | -0.00036 | -0.00036 |
| H | 2.12799 | -1.46011 | 1.45966 |
| H | 4.61502 | -1.52386 | 1.52535 |
| H | 5.91390 | 0.00082 | 0.00098 |
| H | 4.61511 | 1.52463 | -1.52441 |
| H | 2.12812 | 1.45928 | -1.46049 |

**Pd(Pyr)**

| | | | |
|---|---|---|---|
| Pd | 1.63300 | 0.00000 | 0.00004 |
| C | -1.07137 | 1.16088 | -0.00012 |
| C | -2.45923 | 1.19483 | 0.00003 |
| C | -3.17744 | -0.00042 | 0.00013 |
| C | -2.45847 | -1.19527 | 0.00004 |
| C | -1.07068 | -1.16048 | -0.00013 |
| N | -0.36392 | 0.00047 | -0.00023 |
| H | -0.47981 | 2.06776 | -0.00016 |
| H | -2.96385 | 2.15583 | 0.00009 |
| H | -4.26290 | -0.00077 | 0.00029 |
| H | -2.96254 | -2.15655 | 0.00012 |
| H | -0.47850 | -2.06693 | -0.00019 |

**NHC-RC-$S_{L2}$**

| | | | |
|---|---|---|---|
| C | -1.22135 | 2.97528 | 0.44935 |
| C | -2.17302 | 2.17458 | -0.44928 |
| C | -1.27757 | 1.42904 | -1.39795 |
| C | 0.00224 | 2.10759 | -1.42977 |
| H | -1.73369 | 0.99957 | -2.28856 |
| Cl | -3.30416 | 1.10527 | 0.56281 |
| C | -0.05578 | 3.31903 | -0.50018 |
| H | 0.56581 | 2.20313 | -2.35693 |
| H | -2.88956 | 2.82240 | -0.96521 |
| Pd | 0.19008 | 0.22718 | -0.49485 |
| H | -0.86929 | 2.31077 | 1.24690 |
| H | -1.70290 | 3.84602 | 0.90400 |
| H | -0.30078 | 4.22918 | -1.07151 |
| H | 0.87805 | 3.52097 | 0.03689 |
| N | 3.04394 | -0.98450 | -0.55689 |
| C | 4.30402 | -0.92201 | 0.02360 |
| C | 4.23429 | 0.02285 | 0.99628 |
| C | 2.66325 | -1.86602 | -1.65007 |
| H | 5.12623 | -1.54102 | -0.30027 |
| H | 4.98210 | 0.38226 | 1.68596 |
| C | 2.16373 | -0.09736 | 0.01552 |
| N | 2.93432 | 0.51308 | 0.97678 |
| C | 2.41781 | 1.55432 | 1.85180 |
| C | -2.14835 | -2.75663 | 1.53655 |
| C | -2.41309 | -3.12804 | 0.25746 |
| N | -1.64187 | -2.30918 | -0.55661 |
| H | -2.53585 | -3.12522 | 2.47341 |
| H | -3.06689 | -3.89088 | -0.13536 |
| C | -1.64777 | -2.32707 | -2.01084 |
| N | -1.21537 | -1.73192 | 1.46379 |
| C | -0.89359 | -1.41746 | 0.16905 |
| C | -0.72811 | -0.96168 | 2.59754 |
| H | 3.00710 | 2.47016 | 1.74573 |
| H | 2.43881 | 1.22738 | 2.89684 |
| H | 1.38740 | 1.74008 | 1.54069 |
| H | 3.18648 | -1.58826 | -2.57062 |
| H | 1.58612 | -1.74039 | -1.78626 |
| H | 2.89241 | -2.90581 | -1.39648 |
| H | -1.04667 | -1.47401 | -2.33416 |
| H | -2.67000 | -2.21858 | -2.38472 |
| H | -1.21508 | -3.25885 | -2.39089 |
| H | 0.20332 | -0.48589 | 2.28451 |
| H | -0.55036 | -1.62571 | 3.44823 |
| H | -1.45299 | -0.18801 | 2.86946 |

**NHC-RC-$A_{L1}$**

| | | | |
|---|---|---|---|
| C | 2.48212 | -0.70288 | 1.34526 |
| C | 2.68359 | 0.58276 | 0.53056 |
| C | 2.00726 | 0.31380 | -0.77889 |
| C | 1.76241 | -1.05303 | -0.91355 |
| H | 2.07175 | 1.02318 | -1.59794 |
| H | 2.39130 | 1.49823 | 1.04150 |
| C | 2.29225 | -1.81063 | 0.28716 |
| H | 1.59283 | -1.54711 | -1.86663 |
| Cl | 4.51226 | 0.85302 | 0.21076 |
| Pd | -0.07421 | -0.05000 | -0.40708 |
| H | 1.55303 | -0.58542 | 1.91696 |
| H | 3.30626 | -0.88858 | 2.03732 |
| H | 3.25446 | -2.27699 | 0.02841 |
| H | 1.62229 | -2.60474 | 0.63231 |

| | | | |
|---|---|---|---|
| C | -4.24590 | -0.40918 | 0.44553 |
| C | -4.14558 | 0.94559 | 0.42740 |
| N | -2.81700 | 1.23941 | 0.15618 |
| H | -5.09548 | -1.05166 | 0.61575 |
| H | -4.89015 | 1.71064 | 0.58187 |
| C | -2.25822 | 2.58203 | 0.04633 |
| N | -2.97532 | -0.90295 | 0.18787 |
| C | -2.06563 | 0.10444 | 0.00263 |
| C | -2.62240 | -2.31585 | 0.11149 |
| H | -1.19813 | 2.46466 | -0.19315 |
| H | -2.36759 | 3.11784 | 0.99391 |
| H | -2.76043 | 3.13686 | -0.75155 |
| H | -1.54385 | -2.36064 | -0.06126 |
| H | -3.15171 | -2.79615 | -0.71688 |
| H | -2.87251 | -2.81893 | 1.05017 |

**NHC-RC-$S_{L1}$**

| | | | |
|---|---|---|---|
| C | 2.76367 | -0.25608 | 1.37110 |
| C | 3.00157 | 0.30173 | -0.04073 |
| C | 2.15966 | -0.56591 | -0.93606 |
| C | 1.85779 | -1.75581 | -0.26619 |
| H | 2.19171 | -0.44483 | -2.01505 |
| Cl | 2.59650 | 2.09040 | -0.14979 |
| C | 2.46435 | -1.75228 | 1.12724 |
| H | 1.61534 | -2.68715 | -0.77228 |
| H | 4.05713 | 0.27507 | -0.33125 |
| Pd | 0.10366 | -0.53259 | -0.35788 |
| H | 1.86948 | 0.22628 | 1.77855 |
| H | 3.60859 | -0.07530 | 2.04120 |
| H | 3.39560 | -2.34039 | 1.12615 |
| H | 1.80650 | -2.17841 | 1.89085 |
| N | -2.24625 | 1.36672 | 0.15376 |
| C | -3.61323 | 1.42604 | 0.37441 |
| C | -4.06680 | 0.14474 | 0.34674 |
| C | -1.34841 | 2.51738 | 0.10486 |
| H | -4.13696 | 2.35642 | 0.52850 |
| H | -5.05958 | -0.25575 | 0.47952 |
| C | -1.81520 | 0.07855 | -0.02077 |
| N | -2.96305 | -0.65848 | 0.10154 |
| C | -2.98639 | -2.11227 | -0.00642 |
| H | -3.68304 | -2.42080 | -0.79143 |
| H | -3.28277 | -2.56066 | 0.94675 |
| H | -1.97034 | -2.42322 | -0.26254 |
| H | -1.57768 | 3.14080 | -0.76438 |
| H | -0.32994 | 2.12833 | 0.02234 |
| H | -1.44986 | 3.10783 | 1.01991 |

**NHC-TS-$A_{L2}$**

$\nu = -57.57\ cm^{-1}$

| | | | |
|---|---|---|---|
| C | 1.89587 | -1.66140 | 1.42567 |
| C | 2.17476 | -0.81734 | 0.20151 |
| C | 1.60766 | -1.40663 | -0.94143 |
| C | 0.62764 | -2.35334 | -0.51607 |
| H | 1.85470 | -1.14568 | -1.96282 |
| H | 2.83577 | 0.03152 | 0.21250 |
| C | 1.00760 | -2.81969 | 0.88685 |
| H | 0.11399 | -3.01504 | -1.20691 |
| Cl | 4.83080 | -1.24905 | -0.25220 |
| Pd | -0.08972 | -0.32347 | -0.19354 |
| H | 1.38814 | -1.08593 | 2.21218 |
| H | 2.85221 | -2.01003 | 1.82770 |
| H | 1.58998 | -3.74912 | 0.81926 |
| H | 0.14537 | -3.02553 | 1.52840 |
| N | -2.96643 | -0.05638 | -1.27224 |
| C | -4.29500 | -0.38238 | -1.03394 |
| C | -4.32432 | -1.04395 | 0.15133 |
| C | -2.47209 | 0.65209 | -2.44740 |
| H | -5.08837 | -0.11997 | -1.71598 |
| H | -5.14810 | -1.46585 | 0.70530 |
| C | -2.14578 | -0.50112 | -0.27147 |
| N | -3.01117 | -1.10574 | 0.60115 |
| C | -2.57785 | -1.75132 | 1.83428 |
| C | 0.43036 | 3.73414 | 1.21426 |
| C | 1.31707 | 3.73645 | 0.18547 |
| N | 1.20940 | 2.50182 | -0.43497 |
| H | 0.19232 | 4.49013 | 1.94572 |
| H | 2.00335 | 4.49597 | -0.15430 |
| C | 2.02800 | 2.08031 | -1.57298 |
| N | -0.19531 | 2.49558 | 1.18852 |
| C | 0.27876 | 1.70572 | 0.17577 |
| C | -1.20242 | 2.05731 | 2.14569 |
| H | -2.69935 | -2.83584 | 1.76239 |
| H | -3.15702 | -1.37275 | 2.68132 |
| H | -1.52129 | -1.51243 | 1.96733 |
| H | -2.54772 | 0.01832 | -3.33573 |
| H | -1.42374 | 0.89084 | -2.25483 |
| H | -3.04630 | 1.57020 | -2.59916 |
| H | 1.53860 | 1.22083 | -2.03017 |
| H | 3.03001 | 1.78864 | -1.24582 |
| H | 2.09309 | 2.90012 | -2.29236 |
| H | -1.67113 | 1.16454 | 1.73026 |

| | | | |
|---|---|---|---|
| H | -1.94844 | 2.84422 | 2.28604 |
| H | -0.73928 | 1.81619 | 3.10726 |

**NHC-TS-$S_{L2}$**

$\nu$ = –158.06 $cm^{-1}$

| | | | |
|---|---|---|---|
| C | -2.58605 | -2.87615 | -0.33021 |
| C | -1.09550 | -3.00030 | -0.53622 |
| C | -0.68168 | -2.02063 | -1.48247 |
| C | -1.70416 | -0.98396 | -1.58188 |
| H | 0.09896 | -2.22937 | -2.20810 |
| Cl | -0.40711 | -2.59546 | 1.63942 |
| C | -2.93144 | -1.43515 | -0.78236 |
| H | -1.87642 | -0.46855 | -2.52611 |
| H | -0.61460 | -3.96773 | -0.46474 |
| Pd | -0.11069 | -0.13730 | -0.54699 |
| H | -2.91025 | -3.12787 | 0.67988 |
| H | -3.05103 | -3.59398 | -1.02507 |
| H | -3.84225 | -1.41688 | -1.39355 |
| H | -3.11841 | -0.79796 | 0.08665 |
| N | -0.81395 | 2.87003 | -0.60559 |
| C | -1.48633 | 3.84906 | 0.11604 |
| C | -1.99719 | 3.23539 | 1.21436 |
| C | -0.10798 | 3.07934 | -1.86094 |
| H | -1.54437 | 4.87530 | -0.21125 |
| H | -2.58666 | 3.62460 | 2.02971 |
| C | -0.88123 | 1.64742 | 0.01033 |
| N | -1.62361 | 1.89973 | 1.13604 |
| C | -1.95918 | 0.87640 | 2.12252 |
| C | 3.81428 | 0.06885 | 1.29327 |
| C | 4.18061 | -0.02773 | -0.01142 |
| N | 3.00182 | -0.10130 | -0.74124 |
| H | 4.40881 | 0.13876 | 2.19071 |
| H | 5.15528 | -0.06177 | -0.47226 |
| C | 2.92331 | -0.24427 | -2.18736 |
| N | 2.42790 | 0.05085 | 1.31885 |
| C | 1.89244 | -0.05885 | 0.06558 |
| C | 1.61128 | 0.15040 | 2.52428 |
| H | -3.04522 | 0.77054 | 2.19845 |
| H | -1.55349 | 1.15149 | 3.10093 |
| H | -1.51608 | -0.06959 | 1.79502 |
| H | -0.78927 | 3.47517 | -2.62027 |
| H | 0.26601 | 2.09993 | -2.16953 |
| H | 0.72795 | 3.77211 | -1.72047 |
| H | 1.86074 | -0.25437 | -2.44389 |
| H | 3.39018 | -1.18161 | -2.50568 |
| H | 3.41880 | 0.59698 | -2.68245 |
| H | 1.17834 | 1.15261 | 2.59815 |
| H | 2.24385 | -0.04133 | 3.39346 |
| H | 0.81983 | -0.60182 | 2.46412 |

**NHC-TS-$A_{L1}$**

$\nu$ = –52.70 $cm^{-1}$

| | | | |
|---|---|---|---|
| Pd | -0.10061 | -1.02392 | -0.11321 |
| N | -3.01709 | -0.02102 | -0.20443 |
| C | -3.80728 | 1.10621 | -0.05202 |
| C | -2.97716 | 2.10082 | 0.36070 |
| C | -3.50507 | -1.32729 | -0.63324 |
| H | -4.86877 | 1.10212 | -0.24206 |
| H | -3.17489 | 3.13568 | 0.59071 |
| C | -1.70877 | 0.23444 | 0.10358 |
| N | -1.70946 | 1.55417 | 0.45577 |
| C | -0.51421 | 2.32033 | 0.83058 |
| H | -0.83151 | 3.19261 | 1.40395 |
| H | 0.04019 | 2.64112 | -0.05461 |
| H | 0.12823 | 1.69132 | 1.44379 |
| H | -4.15122 | -1.76512 | 0.13285 |
| H | -2.63538 | -1.96991 | -0.78970 |
| H | -4.05724 | -1.22990 | -1.57133 |
| C | 2.32887 | -0.27387 | 1.24561 |
| C | 1.76171 | 0.09477 | -0.10575 |
| C | 1.85092 | -1.05119 | -0.97354 |
| C | 1.86448 | -2.18127 | -0.14909 |
| H | 1.82020 | -1.02735 | -2.05624 |
| H | 1.68087 | 1.12400 | -0.45003 |
| C | 2.29929 | -1.82757 | 1.26068 |
| H | 1.83567 | -3.20318 | -0.51594 |
| Cl | 3.31590 | 2.45247 | -0.74355 |
| H | 1.76839 | 0.16602 | 2.07621 |
| H | 3.34709 | 0.12990 | 1.29781 |
| H | 3.28159 | -2.26845 | 1.48199 |
| H | 1.60360 | -2.21457 | 2.01591 |

**NHC-TS-$S_{L1}$**

$\nu$ = –183.94 $cm^{-1}$

| | | | |
|---|---|---|---|
| C | 2.81343 | 0.11319 | 1.45808 |
| C | 2.96988 | -0.04805 | -0.04592 |
| C | 2.24916 | -1.21742 | -0.46385 |
| C | 1.45076 | -1.71322 | 0.61570 |

| | | | |
|---|---|---|---|
| H | 2.42710 | -1.72137 | -1.40774 |
| Cl | 2.10387 | 1.79135 | -0.95940 |
| C | 1.87621 | -1.03933 | 1.91198 |
| H | 1.07121 | -2.73098 | 0.63274 |
| H | 3.91127 | 0.22357 | -0.50691 |
| Pd | 0.27780 | -0.34527 | -0.44923 |
| H | 2.43046 | 1.10241 | 1.71368 |
| H | 3.80441 | 0.02313 | 1.92159 |
| H | 2.42809 | -1.75211 | 2.54307 |
| H | 1.02490 | -0.68274 | 2.49869 |
| N | -2.17050 | 1.24456 | 0.43187 |
| C | -3.54241 | 1.16807 | 0.61243 |
| C | -3.91393 | -0.08685 | 0.24452 |
| C | -1.35134 | 2.42245 | 0.70525 |
| H | -4.12706 | 1.99771 | 0.97793 |
| H | -4.88428 | -0.55758 | 0.22435 |
| C | -1.65204 | 0.06334 | -0.03751 |
| N | -2.75735 | -0.74291 | -0.14735 |
| C | -2.68891 | -2.11987 | -0.61950 |
| H | -3.20125 | -2.22111 | -1.58093 |
| H | -3.14547 | -2.79192 | 0.11331 |
| H | -1.62657 | -2.35010 | -0.73832 |
| H | -1.71930 | 3.27495 | 0.12757 |
| H | -0.32691 | 2.18825 | 0.40376 |
| H | -1.38093 | 2.66198 | 1.77259 |

**NHC-PR$_{L2}$**

| | | | |
|---|---|---|---|
| C | -2.25660 | -2.72080 | 0.24673 |
| C | -1.06968 | -2.53902 | -0.68470 |
| C | -1.40546 | -1.62574 | -1.72365 |
| C | -2.38881 | -0.75629 | -1.15562 |
| H | -0.96322 | -1.55271 | -2.71140 |
| Cl | -1.13489 | -0.49412 | 2.39854 |
| C | -3.16387 | -1.49928 | -0.07760 |
| H | -2.83191 | 0.06400 | -1.71338 |
| H | -0.32816 | -3.32322 | -0.79748 |
| Pd | -0.43333 | -0.45517 | -0.26117 |
| H | -1.95931 | -2.71929 | 1.29791 |
| H | -2.76596 | -3.67102 | 0.02675 |
| H | -4.14674 | -1.81249 | -0.46034 |
| H | -3.32083 | -0.89016 | 0.81628 |
| N | 0.58682 | 2.33808 | -1.15506 |
| C | 0.34952 | 3.70174 | -1.04606 |
| C | -0.76403 | 3.83517 | -0.28009 |
| C | 1.68887 | 1.75507 | -1.90992 |
| H | 0.98060 | 4.43924 | -1.51625 |

| | | | |
|---|---|---|---|
| H | -1.29771 | 4.71401 | 0.04552 |
| C | -0.34358 | 1.60494 | -0.46409 |
| N | -1.17078 | 2.55510 | 0.06258 |
| C | -2.37474 | 2.25292 | 0.84034 |
| C | 3.62968 | -0.29069 | 1.22335 |
| C | 3.78867 | -1.26348 | 0.29008 |
| N | 2.54174 | -1.45292 | -0.28879 |
| H | 4.33399 | 0.15699 | 1.90650 |
| H | 4.65576 | -1.83564 | 0.00010 |
| C | 2.27980 | -2.40241 | -1.36117 |
| N | 2.29504 | 0.08172 | 1.19185 |
| C | 1.59048 | -0.63240 | 0.26208 |
| C | 1.73634 | 1.15319 | 2.01917 |
| H | -3.23229 | 2.14850 | 0.16879 |
| H | -2.55305 | 3.07475 | 1.53737 |
| H | -2.19916 | 1.32277 | 1.39420 |
| H | 1.80419 | 2.29093 | -2.85578 |
| H | 1.43743 | 0.70949 | -2.09221 |
| H | 2.62299 | 1.80915 | -1.34151 |
| H | 1.35486 | -2.09841 | -1.85172 |
| H | 2.16640 | -3.41534 | -0.96366 |
| H | 3.10835 | -2.38155 | -2.07420 |
| H | 1.80481 | 2.10894 | 1.48920 |
| H | 2.31219 | 1.20728 | 2.94559 |
| H | 0.69399 | 0.89993 | 2.24114 |

**NHC-PR$_{L1}$**

| | | | |
|---|---|---|---|
| C | 2.96939 | 0.22424 | 1.17825 |
| C | 2.80838 | -0.03805 | -0.31231 |
| C | 2.23990 | -1.30862 | -0.52674 |
| C | 1.50993 | -1.63999 | 0.65973 |
| H | 2.22855 | -1.85393 | -1.46410 |
| Cl | 0.31991 | 2.15558 | -1.33663 |
| C | 2.16319 | -0.93545 | 1.84454 |
| H | 0.97453 | -2.57631 | 0.78546 |
| H | 3.34087 | 0.52862 | -1.06728 |
| Pd | 0.60384 | 0.02446 | -0.32781 |
| H | 2.57768 | 1.20813 | 1.45791 |
| H | 4.02909 | 0.20499 | 1.46945 |
| H | 2.82972 | -1.62600 | 2.38227 |
| H | 1.43038 | -0.56540 | 2.56770 |
| N | -2.13822 | 0.66888 | 0.88216 |
| C | -3.46165 | 0.25658 | 0.91869 |
| C | -3.54887 | -0.84820 | 0.13320 |
| C | -1.60074 | 1.82879 | 1.59397 |
| H | -4.21347 | 0.78320 | 1.48473 |

| | | | |
|---|---|---|---|
| H | -4.39198 | -1.46808 | -0.12710 |
| C | -1.38303 | -0.15132 | 0.09778 |
| N | -2.27060 | -1.08398 | -0.35495 |
| C | -1.91306 | -2.15520 | -1.27709 |
| H | -2.43504 | -2.02422 | -2.22904 |
| H | -2.17089 | -3.12627 | -0.84466 |
| H | -0.83599 | -2.08910 | -1.43968 |
| H | -2.39158 | 2.57440 | 1.69757 |
| H | -0.78398 | 2.23692 | 0.99392 |
| H | -1.24206 | 1.53180 | 2.58432 |

**NHC**

| | | | |
|---|---|---|---|
| N | -1.06309 | 0.11851 | 0.00003 |
| C | -0.67927 | -1.21818 | -0.00006 |
| C | 0.67926 | -1.21818 | 0.00004 |
| C | -2.44600 | 0.57586 | -0.00001 |
| H | -1.38388 | -2.03630 | 0.00046 |
| H | 1.38384 | -2.03633 | -0.00038 |
| C | 0.00000 | 0.98687 | -0.00002 |
| N | 1.06310 | 0.11848 | -0.00002 |
| C | 2.44600 | 0.57587 | 0.00004 |
| H | 2.96995 | 0.21636 | -0.89170 |
| H | 2.96925 | 0.21845 | 0.89302 |
| H | 2.42333 | 1.66535 | -0.00125 |
| H | -2.96971 | 0.21683 | -0.89207 |
| H | -2.42342 | 1.66535 | -0.00068 |
| H | -2.96943 | 0.21793 | 0.89266 |

**Pd(NHC)$_2$**

| | | | |
|---|---|---|---|
| Pd | 0.00000 | 0.00003 | 0.00000 |
| N | -2.87222 | -0.76074 | -0.75844 |
| C | -4.20157 | -0.48139 | -0.47996 |
| C | -4.20160 | 0.48134 | 0.47986 |
| C | -2.39982 | -1.73676 | -1.73103 |
| H | -5.01873 | -0.98030 | -0.97741 |
| H | -5.01878 | 0.98033 | 0.97721 |
| C | -2.01277 | 0.00002 | -0.00003 |
| N | -2.87226 | 0.76072 | 0.75837 |
| C | -2.39995 | 1.73664 | 1.73112 |
| C | 4.20159 | 0.48004 | -0.48121 |
| C | 4.20159 | -0.48011 | 0.48119 |
| N | 2.87222 | -0.75869 | 0.76045 |
| H | 5.01878 | 0.97752 | -0.98005 |
| H | 5.01874 | -0.97776 | 0.97993 |
| C | 2.39986 | -1.73169 | 1.73608 |
| N | 2.87225 | 0.75865 | -0.76049 |
| C | 2.01278 | 0.00002 | 0.00001 |
| C | 2.39988 | 1.73176 | -1.73600 |
| H | -2.75222 | 1.47653 | 2.73456 |
| H | -2.75105 | 2.73945 | 1.46703 |
| H | -1.30661 | 1.69911 | 1.69465 |
| H | -2.75063 | -2.73960 | -1.46667 |
| H | -1.30648 | -1.69898 | -1.69470 |
| H | -2.75230 | -1.47696 | -2.73447 |
| H | 1.30653 | -1.69530 | 1.69842 |
| H | 2.75080 | -1.46778 | 2.73900 |
| H | 2.75227 | -2.73503 | 1.47581 |
| H | 1.30654 | 1.69502 | -1.69865 |
| H | 2.75121 | 1.46826 | -2.73888 |
| H | 2.75185 | 2.73517 | -1.47535 |

**Pd(NHC)**

| | | | |
|---|---|---|---|
| Pd | -1.53498 | 0.00060 | -0.00002 |
| N | 1.24278 | 1.07903 | -0.00040 |
| C | 2.57013 | 0.67768 | -0.00023 |
| C | 2.56891 | -0.68079 | -0.00001 |
| C | 0.78271 | 2.46094 | 0.00024 |
| H | 3.38783 | 1.38124 | -0.00042 |
| H | 3.38555 | -1.38560 | 0.00068 |
| C | 0.38698 | 0.00043 | 0.00012 |
| N | 1.24100 | -1.07994 | 0.00037 |
| C | 0.77887 | -2.46110 | -0.00008 |
| H | 1.13436 | -2.98081 | 0.89514 |
| H | 1.13524 | -2.98049 | -0.89511 |
| H | -0.31429 | -2.41772 | -0.00055 |
| H | 1.14018 | 2.97970 | 0.89519 |
| H | -0.31048 | 2.41920 | 0.00102 |
| H | 1.13872 | 2.98017 | -0.89504 |

**PH$_3$-PR$_{\eta 1}$**

| | | | |
|---|---|---|---|
| C | 3.15222 | -0.75222 | 0.17132 |
| C | 2.85440 | 0.21067 | 1.28859 |
| C | 1.92682 | 1.11819 | 0.92706 |
| C | 1.45937 | 0.90038 | -0.45871 |
| H | 1.53825 | 1.89644 | 1.57830 |
| Cl | 0.09982 | -2.18639 | -0.33578 |
| C | 2.46541 | -0.09993 | -1.05336 |
| H | 1.33831 | 1.80269 | -1.06728 |
| H | 3.30905 | 0.14394 | 2.27266 |

| | | | |
|---|---|---|---|
| Pd | -0.50163 | 0.10850 | -0.09923 |
| H | 2.71379 | -1.73454 | 0.38962 |
| H | 4.22828 | -0.90001 | 0.01603 |
| H | 3.20561 | 0.47362 | -1.62948 |
| H | 2.01206 | -0.83480 | -1.71991 |
| P | -1.13722 | 2.22436 | -0.20769 |
| H | -0.34482 | 3.22216 | 0.40233 |
| H | -1.21354 | 2.81372 | -1.48959 |
| H | -2.39549 | 2.65176 | 0.27107 |
| P | -2.52507 | -0.98985 | 0.48083 |
| H | -2.43500 | -1.90500 | 1.54545 |
| H | -3.04171 | -1.85328 | -0.50196 |
| H | -3.75191 | -0.37911 | 0.85914 |

**$PH_3$-$TS_{\eta1\leftrightarrow\eta3}$**

$\nu = -68.22\ cm^{-1}$

| | | | |
|---|---|---|---|
| C | -2.81397 | 0.54041 | 0.35613 |
| C | -2.09210 | -0.08272 | 1.51406 |
| C | -1.39294 | -1.20244 | 1.13981 |
| C | -1.39672 | -1.31246 | -0.31309 |
| H | -0.89696 | -1.88608 | 1.81997 |
| Cl | -0.29566 | 1.94083 | -1.17136 |
| C | -2.52665 | -0.42766 | -0.82139 |
| H | -1.21826 | -2.26760 | -0.80164 |
| H | -2.16456 | 0.28412 | 2.53347 |
| Pd | 0.35508 | -0.14734 | 0.02020 |
| H | -2.42099 | 1.54256 | 0.13406 |
| H | -3.88663 | 0.64478 | 0.56577 |
| H | -3.40269 | -1.06228 | -1.02235 |
| H | -2.27368 | 0.10787 | -1.73859 |
| P | 1.65125 | -1.90518 | -0.48121 |
| H | 1.18249 | -3.22215 | -0.25435 |
| H | 2.05243 | -2.10955 | -1.82277 |
| H | 2.92984 | -2.08492 | 0.09589 |
| P | 1.89295 | 1.43300 | 0.82602 |
| H | 1.35620 | 2.57083 | 1.45460 |
| H | 2.66456 | 2.07526 | -0.15778 |
| H | 2.94217 | 1.18274 | 1.75243 |

**$PH_3$-$TS_{PR}$**

$\nu = -84.38\ cm^{-1}$

| | | | |
|---|---|---|---|
| C | 2.48359 | 0.86782 | 1.05513 |
| C | 1.60949 | 1.44263 | -0.04547 |
| C | 1.66045 | 0.61160 | -1.20126 |
| C | 1.97975 | -0.68781 | -0.72783 |
| H | 1.38399 | 0.88080 | -2.21304 |
| Cl | -1.22854 | 0.65855 | 1.95366 |
| C | 2.75689 | -0.58854 | 0.57544 |
| H | 2.04158 | -1.55910 | -1.37209 |
| H | 1.32087 | 2.48786 | -0.06685 |
| Pd | 0.01390 | -0.04161 | -0.03720 |
| H | 1.97840 | 0.89556 | 2.02423 |
| H | 3.41607 | 1.44308 | 1.15024 |
| H | 3.82721 | -0.75723 | 0.38336 |
| H | 2.44015 | -1.33220 | 1.31135 |
| P | -1.17870 | -1.99533 | 0.17821 |
| H | -1.11315 | -3.11933 | -0.68268 |
| H | -0.98365 | -2.68000 | 1.39334 |
| H | -2.58108 | -1.87914 | 0.23565 |
| P | -2.04566 | 1.41250 | -1.09932 |
| H | -2.07982 | 2.64244 | -0.40792 |
| H | -3.22600 | 0.89713 | -0.52165 |
| H | -2.68847 | 1.90738 | -2.27569 |

**References**

(1) The overall conclusions do not change if the reference points were the same (eg. using **RC-$A_{L2}$** for both pathways).

(2) Wolters, L. P.; Bickelhaupt, F. M. *ChemistryOpen* **2013**, *2*, 106 – 114.

**Complete citation for reference 8.**

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