 

# The Influence of N-Substitution on the Reductive Elimination Behaviour of Hydrocarbyl Palladium Carbene Complexes – A DFT Study

*David C. Graham, Kingsley J. Cavell*[†] *and Brian F. Yates**

School of Chemistry, University of Tasmania, Private Bag 75, Hobart, Tasmania 7001, Australia. [†]Chemistry Department, Cardiff University, Park Place, Cardiff, Wales, CF10 3TB, U.K.

Brian.Yates@utas.edu.au

## Supporting Information

# 1. Free Carbenes

**CB(Cl)**

B3lyp/6-31G(d) optimized geometry
Energy = -1145.261963 a.u.
Enthalpy Correction (inc. ZPVE) = 0.056936
NIMAG = 0

B3lyp/6-311+G(2d,p) single point
Energy = -1145.392273

| Atom | x-coord | y-coord | z-coord |
|---|---|---|---|
| N | -0.000006 | 0.028730 | 1.031572 |
| C | 0.000073 | -0.860083 | 0.000000 |
| N | -0.000006 | 0.028730 | -1.031572 |
| C | -0.000006 | 1.378298 | 0.678052 |
| C | -0.000006 | 1.378298 | -0.678052 |
| H | -0.000058 | 2.180724 | 1.398508 |
| H | -0.000058 | 2.180724 | -1.398508 |
| Cl | -0.000005 | -0.474787 | -2.677120 |
| Cl | -0.000005 | -0.474787 | 2.677120 |

**CB(H)**

B3lyp/6-31G(d) optimized geometry
Energy = -226.166693 a.u.
Enthalpy Correction (inc. ZPVE) = 0.076113
NIMAG = 0

B3lyp/6-311+G(2d,p) single point
Energy = -226.245505

| Atom | x-coord | y-coord | z-coord |
|---|---|---|---|
| N | 1.049811 | -0.402516 | 0.000031 |
| C | 0.000003 | -1.285707 | -0.000045 |
| N | -1.049809 | -0.402520 | 0.000032 |
| C | 0.678012 | 0.940198 | -0.000018 |
| C | -0.678017 | 0.940196 | -0.000019 |
| H | 1.385867 | 1.755236 | 0.000015 |
| H | -1.385873 | 1.755230 | 0.000014 |
| H | -2.006591 | -0.721674 | 0.000012 |
| H | 2.006595 | -0.721666 | 0.000011 |

**CB(Ph)**

B3lyp/6-31G(d) optimized geometry
Energy = -688.097549 a.u.
Enthalpy Correction (inc. ZPVE) = 0.248401
NIMAG = 0

B3lyp/6-311+G(2d,p) single point
Energy = -688.462370

| Atom | x-coord | y-coord | z-coord |
|---|---|---|---|

| | | | |
|---|---|---|---|
| N | 1.078128 | 0.532259 | -0.002824 |
| C | 0.000000 | -0.344774 | -0.000142 |
| N | -1.078141 | 0.532282 | 0.002471 |
| C | 0.677765 | 1.884890 | -0.003352 |
| C | -0.677749 | 1.884901 | 0.002238 |
| H | 1.366401 | 2.710573 | -0.028395 |
| H | -1.366326 | 2.710644 | 0.026788 |
| C | 2.434012 | 0.076594 | -0.011952 |
| C | 2.708820 | -1.241349 | -0.407516 |
| C | 4.027679 | -1.697602 | -0.423995 |
| C | 5.080855 | -0.850416 | -0.054567 |
| C | 4.800017 | 0.459990 | 0.344201 |
| C | 3.480932 | 0.925807 | 0.372531 |
| H | 1.879752 | -1.880075 | -0.683600 |
| H | 4.233336 | -2.717917 | -0.731651 |
| H | 6.104894 | -1.208541 | -0.073791 |
| H | 5.605000 | 1.123533 | 0.643708 |
| H | 3.277465 | 1.934425 | 0.713510 |
| C | -2.434023 | 0.076598 | 0.011923 |
| C | -3.481135 | 0.925972 | -0.371672 |
| C | -4.800195 | 0.460088 | -0.343067 |
| C | -5.080840 | -0.850531 | 0.055121 |
| C | -4.027481 | -1.697864 | 0.423693 |
| C | -2.708647 | -1.241566 | 0.406911 |
| H | -3.277904 | 1.934805 | -0.712148 |
| H | -5.605312 | 1.123777 | -0.641890 |
| H | -6.104859 | -1.208700 | 0.074565 |
| H | -4.232973 | -2.718348 | 0.730906 |
| H | -1.879444 | -1.880394 | 0.682348 |

**CB(Me)**

B3lyp/6-31G(d) optimized geometry
Energy = -304.792467 a.u.
Enthalpy Correction (inc. ZPVE) = 0.134959
NIMAG = 0

B3lyp/6-311+G(2d,p) single point
Energy = -304.886266

| Atom | x-coord | y-coord | z-coord |
|---|---|---|---|
| C | 0.000000 | -2.441852 | 0.573994 |
| N | 0.000000 | -1.062650 | 0.119338 |
| C | 0.000000 | 0.000000 | 0.988179 |
| N | 0.000000 | 1.062650 | 0.119338 |
| C | 0.000000 | 2.441852 | 0.573994 |
| C | 0.000000 | -0.678259 | -1.218255 |
| C | 0.000000 | 0.678259 | -1.218255 |
| H | 0.000000 | 2.423891 | 1.664095 |
| H | -0.891011 | 2.972882 | 0.219251 |
| H | 0.891011 | 2.972882 | 0.219251 |
| H | 0.891011 | -2.972882 | 0.219251 |
| H | -0.891011 | -2.972882 | 0.219251 |
| H | 0.000000 | -2.423891 | 1.664095 |
| H | 0.000000 | -1.383412 | -2.036935 |

H 0.000000 1.383412 -2.036935

**CB(iPr)**
B3lyp/6-31G(d) optimized geometry
Energy = -462.056976 a.u.
Enthalpy Correction (inc. ZPVE) = 0.253733
NIMAG = 0

B3lyp/6-311+G(2d,p) single point
Energy = -462.196000

| Atom | x-coord | y-coord | z-coord |
|---|---|---|---|
| N | 1.065312 | -0.000042 | -0.070802 |
| C | 0.000012 | 0.001029 | -0.935923 |
| N | -1.065303 | -0.000167 | -0.070807 |
| C | 0.678407 | -0.001764 | 1.266950 |
| C | -0.678396 | -0.001846 | 1.266951 |
| H | 1.375490 | -0.002855 | 2.091931 |
| H | -1.375468 | -0.003105 | 2.091938 |
| C | 2.453601 | 0.000669 | -0.548328 |
| H | 2.350286 | 0.001815 | -1.637001 |
| C | -2.453575 | 0.000529 | -0.548317 |
| H | -2.350263 | 0.001213 | -1.636994 |
| C | 3.189875 | -1.274045 | -0.118316 |
| H | 3.299468 | -1.326773 | 0.971689 |
| H | 2.646567 | -2.164138 | -0.451045 |
| H | 4.194313 | -1.297739 | -0.555535 |
| C | 3.189522 | 1.274671 | -0.115621 |
| H | 2.646018 | 2.165312 | -0.446554 |
| H | 3.299013 | 1.325164 | 0.974499 |
| H | 4.193987 | 1.299515 | -0.552716 |
| C | -3.190000 | -1.273915 | -0.117786 |
| H | -3.299600 | -1.326186 | 0.972238 |
| H | -4.194447 | -1.297660 | -0.554989 |
| H | -2.646829 | -2.164231 | -0.450144 |
| C | -3.189426 | 1.274781 | -0.116156 |
| H | -4.193718 | 1.299698 | -0.553650 |
| H | -3.299342 | 1.325517 | 0.973910 |
| H | -2.645650 | 2.165261 | -0.447041 |

**CB(Cy)**
B3lyp/6-31G(d) optimized geometry
Energy = -695.530582 a.u.
Enthalpy Correction (inc. ZPVE) = 0.390222
NIMAG = 0

B3lyp/6-311+G(2d,p) single point
Energy = -695.729436

| Atom | x-coord | y-coord | z-coord |
|---|---|---|---|
| N | -1.065930 | -0.034628 | 0.116897 |
| C | 0.000048 | 0.000463 | -0.747528 |
| N | 1.065854 | -0.029679 | 0.117272 |

| | | | |
|---|---|---|---|
| C | -0.678478 | -0.081634 | 1.453973 |
| C | 0.678149 | -0.079393 | 1.454172 |
| H | -1.375517 | -0.114501 | 2.278191 |
| H | 1.375065 | -0.110387 | 2.278567 |
| C | -4.668414 | -1.232507 | -0.489832 |
| C | -3.227485 | -1.270664 | 0.045150 |
| C | -2.451103 | -0.005495 | -0.358890 |
| C | -3.184999 | 1.268225 | 0.095537 |
| C | -4.626023 | 1.301599 | -0.438464 |
| C | -5.404992 | 0.038681 | -0.041014 |
| H | -3.250254 | -1.350567 | 1.141882 |
| H | -2.696722 | -2.155313 | -0.326279 |
| H | -4.645759 | -1.267738 | -1.588880 |
| H | -5.212261 | -2.126985 | -0.161397 |
| H | -3.203584 | 1.304483 | 1.194675 |
| H | -2.623393 | 2.147625 | -0.241333 |
| H | -5.139047 | 2.199647 | -0.072352 |
| H | -4.602238 | 1.381627 | -1.535134 |
| H | -5.530621 | 0.018608 | 1.051937 |
| H | -6.414364 | 0.063990 | -0.470692 |
| H | -2.353067 | 0.015013 | -1.449470 |
| C | 4.629552 | 1.300612 | -0.431449 |
| C | 3.188874 | 1.268345 | 0.103573 |
| C | 2.451110 | -0.000510 | -0.358249 |
| C | 3.223870 | -1.270418 | 0.037757 |
| C | 4.664813 | -1.233361 | -0.497111 |
| C | 5.405078 | 0.033260 | -0.041386 |
| H | 3.209005 | 1.297698 | 1.202861 |
| H | 2.629579 | 2.151636 | -0.227002 |
| H | 4.605175 | 1.386716 | -1.527664 |
| H | 5.145527 | 2.195175 | -0.060908 |
| H | 3.245804 | -1.357049 | 1.134011 |
| H | 2.690354 | -2.151041 | -0.339263 |
| H | 5.206214 | -2.131208 | -0.173788 |
| H | 4.641938 | -1.262388 | -1.596338 |
| H | 5.530709 | 0.006795 | 1.051431 |
| H | 6.414483 | 0.058076 | -0.470962 |
| H | 2.353508 | 0.027006 | -1.448718 |

**CB(neoPe)**

B3lyp/6-31G(d) optimized geometry
Energy = -619.307608 a.u.
Enthalpy Correction (inc. ZPVE) = 0.372277
NIMAG = 0

B3lyp/6-311+G(2d,p) single point
Energy = -619.489863

| Atom | x-coord | y-coord | z-coord |
|---|---|---|---|
| N | -0.974321 | 0.341707 | 0.431645 |
| C | -0.000009 | -0.522990 | 0.000016 |
| N | 0.974312 | 0.341689 | -0.431628 |
| C | -0.619845 | 1.680553 | 0.274682 |
| C | 0.619851 | 1.680542 | -0.274692 |
| H | 1.264651 | 2.498792 | -0.558761 |

| | | | |
|---|---|---|---|
| C | -2.247229 | -0.119680 | 0.978398 |
| H | -2.042510 | -1.074820 | 1.469345 |
| C | 2.247209 | -0.119730 | -0.978383 |
| H | -2.560099 | 0.595257 | 1.749822 |
| H | 2.560064 | 0.595158 | -1.749860 |
| H | 2.042468 | -1.074896 | -1.469270 |
| C | 3.711083 | 1.012741 | 0.771613 |
| C | 3.401288 | -0.307434 | 0.042492 |
| H | 3.966590 | 1.811710 | 0.062887 |
| H | 2.860209 | 1.350822 | 1.372470 |
| H | 4.565963 | 0.885411 | 1.446418 |
| C | 3.041602 | -1.398365 | 1.067013 |
| C | 4.640441 | -0.746332 | -0.762249 |
| H | 2.880076 | -2.364339 | 0.574416 |
| H | 3.852183 | -1.520583 | 1.796148 |
| H | 2.121703 | -1.154083 | 1.606196 |
| H | 5.493512 | -0.916781 | -0.095239 |
| H | 4.452199 | -1.679643 | -1.307085 |
| H | 4.936412 | 0.016942 | -1.493295 |
| C | -4.640504 | -0.746130 | 0.762258 |
| C | -3.401287 | -0.307436 | -0.042495 |
| H | -4.452336 | -1.679348 | 1.307277 |
| H | -4.936481 | 0.017293 | 1.493146 |
| H | -5.493546 | -0.916664 | 0.095231 |
| C | -3.710953 | 1.012661 | -0.771811 |
| C | -3.041643 | -1.398535 | -1.066850 |
| H | -2.860035 | 1.350584 | -1.372695 |
| H | -4.565829 | 0.885308 | -1.446616 |
| H | -3.966407 | 1.811753 | -0.063204 |
| H | -3.852179 | -1.520759 | -1.796036 |
| H | -2.121669 | -1.154434 | -1.605985 |
| H | -2.880270 | -2.364465 | -0.574115 |
| H | -1.264637 | 2.498816 | 0.558735 |

**CB(tBu)**

B3lyp/6-31G(d) optimized geometry
Energy = -540.682558 a.u.
Enthalpy Correction (inc. ZPVE) = 0.311986
NIMAG = 0

B3lyp/6-311+G(2d,p) single point
Energy = -540.841687

| Atom | x-coord | y-coord | z-coord |
|---|---|---|---|
| N | -1.060063 | -0.242355 | -0.000032 |
| C | 0.021603 | 0.593911 | -0.000182 |
| N | 1.077119 | -0.281484 | -0.000232 |
| C | -0.691560 | -1.588114 | -0.000049 |
| C | 0.663924 | -1.611522 | -0.000020 |
| H | -1.396641 | -2.405338 | 0.000045 |
| H | 1.336336 | -2.454095 | -0.000326 |
| C | -2.472481 | 0.220705 | 0.000017 |
| C | 2.482601 | 0.216215 | 0.000004 |
| C | -3.170177 | -0.312956 | 1.265943 |
| H | -3.177726 | -1.408028 | 1.295716 |

| | | | |
|---|---|---|---|
| H | -2.660828 | 0.049070 | 2.165158 |
| H | -4.210538 | 0.029185 | 1.296962 |
| C | -3.170466 | -0.313602 | -1.265486 |
| H | -2.661059 | 0.047648 | -2.164977 |
| H | -3.178408 | -1.408692 | -1.294502 |
| H | -4.210709 | 0.028878 | -1.296659 |
| C | 2.689132 | 1.070867 | 1.263230 |
| H | 2.564956 | 0.462684 | 2.166678 |
| H | 3.696942 | 1.502002 | 1.272912 |
| H | 1.952459 | 1.877502 | 1.289106 |
| C | 3.466285 | -0.961317 | -0.000357 |
| H | 4.489260 | -0.571843 | -0.000227 |
| H | 3.350442 | -1.589202 | 0.890157 |
| H | 3.350483 | -1.588637 | -0.891283 |
| C | 2.689169 | 1.071786 | -1.262602 |
| H | 3.696886 | 1.503152 | -1.271884 |
| H | 2.565220 | 0.464234 | -2.166504 |
| H | 1.952334 | 1.878301 | -1.287977 |
| C | -2.509577 | 1.754527 | -0.000358 |
| H | -3.555760 | 2.082138 | -0.000161 |
| H | -2.006622 | 2.162671 | 0.879209 |
| H | -2.007144 | 2.162245 | -0.880435 |

## 2. C2 Protonated Free Carbenes (Imidazolium Salts)

**$CBH^+$(Cl)**
B3lyp/6-31G(d) optimized geometry
Energy = -1145.664113 a.u.
Enthalpy Correction (inc. ZPVE) = 0.071078
NIMAG = 0

B3lyp/6-311+G(2d,p) single point
Energy = -1145.786688

| Atom | x-coord | y-coord | z-coord |
|---|---|---|---|
| N | -1.072047 | 0.076649 | 0.000000 |
| C | 0.000094 | -0.728940 | 0.000004 |
| N | 1.072199 | 0.077123 | 0.000000 |
| C | -0.682154 | 1.405564 | 0.000001 |
| C | 0.681833 | 1.405762 | 0.000000 |
| H | -1.397330 | 2.214083 | 0.000000 |
| H | 1.396541 | 2.214708 | 0.000000 |
| Cl | 2.683828 | -0.476192 | -0.000001 |
| Cl | -2.683804 | -0.476214 | 0.000000 |
| H | 0.000698 | -1.808608 | 0.000005 |

**$CBH^+$(H)**
B3lyp/6-31G(d) optimized geometry
Energy = -226.592174 a.u.
Enthalpy Correction (inc. ZPVE) = 0.09015
NIMAG = 0

B3lyp/6-311+G(2d,p) single point
Energy = -226.65926

| Atom | x-coord | y-coord | z-coord |
|---|---|---|---|
| N | -1.074276 | -0.348597 | -0.000051 |
| C | -0.000021 | -1.142904 | 0.000052 |
| N | 1.074264 | -0.348635 | -0.000048 |
| C | -0.681609 | 0.978297 | 0.000019 |
| C | 0.681644 | 0.978274 | 0.000017 |
| H | -1.391670 | 1.790627 | -0.000171 |
| H | 1.391735 | 1.790579 | -0.000171 |
| H | 2.033422 | -0.680031 | 0.000535 |
| H | -2.033447 | -0.679959 | 0.000542 |
| H | -0.000039 | -2.222597 | -0.000561 |

**$CBH^+$(Ph)**
B3lyp/6-31G(d) optimized geometry
Energy = -688.541309 a.u.
Enthalpy Correction (inc. ZPVE) = 0.26256
NIMAG = 0

B3lyp/6-311+G(2d,p) single point
Energy = -688.894972

| Atom | x-coord | y-coord | z-coord |
|---|---|---|---|
| N | 1.095727 | 0.530137 | -0.007826 |
| C | 0.000000 | -0.260985 | 0.000000 |
| N | -1.095727 | 0.530136 | 0.007826 |
| C | 0.683364 | 1.866464 | -0.005971 |
| C | -0.683364 | 1.866464 | 0.005971 |
| H | 1.389633 | 2.677351 | -0.029168 |
| H | -1.389634 | 2.677351 | 0.029167 |
| C | 2.466910 | 0.066651 | -0.031203 |
| C | 2.846420 | -0.903004 | -0.966245 |
| C | 4.171199 | -1.349836 | -0.975313 |
| C | 5.099388 | -0.820894 | -0.070117 |
| C | 4.704917 | 0.155550 | 0.853235 |
| C | 3.380981 | 0.603268 | 0.882316 |
| H | 2.132881 | -1.281413 | -1.690700 |
| H | 4.478191 | -2.098064 | -1.696907 |
| H | 6.126763 | -1.166317 | -0.085727 |
| H | 5.422026 | 0.561787 | 1.557147 |
| H | 3.063265 | 1.337660 | 1.614651 |
| C | -2.466910 | 0.066650 | 0.031203 |
| C | -3.380981 | 0.603267 | -0.882317 |
| C | -4.704916 | 0.155550 | -0.853236 |
| C | -5.099388 | -0.820893 | 0.070117 |
| C | -4.171199 | -1.349834 | 0.975314 |
| C | -2.846420 | -0.903004 | 0.966246 |
| H | -3.063265 | 1.337658 | -1.614653 |
| H | -5.422026 | 0.561786 | -1.557149 |
| H | -6.126763 | -1.166316 | 0.085727 |

| | | | |
|---|---|---|---|
| H | -4.478193 | -2.098062 | 1.696909 |
| H | -2.132881 | -1.281412 | 1.690702 |
| H | 0.000000 | -1.336399 | 0.000002 |

**$CBH^+$(Me)**

B3lyp/6-31G(d) optimized geometry
Energy = -305.230760 a.u.
Enthalpy Correction (inc. ZPVE) = 0.149350
NIMAG = 0

B3lyp/6-311+G(2d,p) single point
Energy = -305.314266

| Atom | x-coord | y-coord | z-coord |
|---|---|---|---|
| C | -2.483131 | -0.552989 | 0.000017 |
| N | -1.089141 | -0.084295 | -0.000004 |
| C | 0.000009 | -0.862025 | 0.000010 |
| N | 1.089141 | -0.084254 | -0.000041 |
| C | 2.483162 | -0.552989 | 0.000027 |
| C | -0.681612 | 1.237394 | 0.000005 |
| C | 0.681582 | 1.237400 | -0.000021 |
| H | 2.490356 | -1.643220 | -0.000165 |
| H | 2.989169 | -0.185193 | 0.894897 |
| H | 2.989339 | -0.184909 | -0.894632 |
| H | -2.490364 | -1.643224 | 0.000173 |
| H | -2.989240 | -0.185207 | -0.894812 |
| H | -2.989255 | -0.184933 | 0.894715 |
| H | -1.387715 | 2.053703 | -0.000036 |
| H | 1.387642 | 2.053750 | 0.000082 |
| H | 0.000006 | -1.941676 | -0.000128 |

**$CBH^+$(iPr)**

B3lyp/6-31G(d) optimized geometry
Energy = -462.504223 a.u.
Enthalpy Correction (inc. ZPVE) = 0.268029
NIMAG = 0

B3lyp/6-311+G(2d,p) single point
Energy = -462.632901

| Atom | x-coord | y-coord | z-coord |
|---|---|---|---|
| C | -2.504551 | 0.000034 | -0.541415 |
| N | -1.092490 | -0.000004 | -0.046645 |
| C | -0.000033 | 0.000035 | -0.819522 |
| N | 1.092619 | -0.000014 | -0.046400 |
| C | 2.504484 | 0.000024 | -0.541421 |
| C | -0.682193 | -0.000094 | 1.273852 |
| C | 0.681973 | -0.000081 | 1.273841 |
| H | 2.409314 | 0.000052 | -1.632046 |
| H | -2.409691 | 0.000092 | -1.632114 |
| H | -1.380684 | -0.000148 | 2.095360 |
| H | 1.380164 | -0.000127 | 2.095634 |

| | | | |
|---|---|---|---|
| C | -3.216501 | 1.280246 | -0.097879 |
| H | -3.331026 | 1.320345 | 0.990559 |
| H | -2.678517 | 2.174150 | -0.427309 |
| H | -4.217970 | 1.302982 | -0.537342 |
| C | -3.216519 | -1.280216 | -0.098017 |
| H | -3.331045 | -1.320431 | 0.990417 |
| H | -4.217988 | -1.302894 | -0.537483 |
| H | -2.678545 | -2.174092 | -0.427540 |
| C | 3.216640 | -1.280162 | -0.098004 |
| H | 4.218036 | -1.302825 | -0.537605 |
| H | 3.331311 | -1.320180 | 0.990433 |
| H | 2.678670 | -2.174137 | -0.427273 |
| C | 3.216596 | 1.280209 | -0.097931 |
| H | 2.678596 | 2.174184 | -0.427154 |
| H | 3.331257 | 1.320170 | 0.990509 |
| H | 4.217993 | 1.302931 | -0.537525 |
| H | -0.000159 | 0.000088 | -1.899235 |

**$CBH^+$(Cy)**

B3lyp/6-31G(d) optimized geometry
Energy = -695.982942 a.u.
Enthalpy Correction (inc. ZPVE) = 0.404616
NIMAG = 0

B3lyp/6-311+G(2d,p) single point
Energy = -696.171393

| Atom | x-coord | y-coord | z-coord |
|---|---|---|---|
| N | -1.093329 | -0.027845 | 0.133560 |
| C | 0.000007 | 0.004399 | -0.638609 |
| N | 1.093350 | -0.029355 | 0.133462 |
| C | -0.682075 | -0.083861 | 1.452272 |
| C | 0.682127 | -0.084676 | 1.452230 |
| H | -1.380389 | -0.119030 | 2.272898 |
| H | 1.380472 | -0.120742 | 2.272794 |
| C | -4.695479 | -1.235993 | -0.485340 |
| C | -3.252187 | -1.275542 | 0.048239 |
| C | -2.500743 | 0.000972 | -0.359791 |
| C | -3.219399 | 1.274634 | 0.112193 |
| C | -4.662960 | 1.300103 | -0.420948 |
| C | -5.434089 | 0.031026 | -0.029612 |
| H | -3.271439 | -1.350060 | 1.144230 |
| H | -2.720965 | -2.158235 | -0.326621 |
| H | -4.676236 | -1.277181 | -1.583519 |
| H | -5.225222 | -2.134201 | -0.150705 |
| H | -3.235910 | 1.294125 | 1.210598 |
| H | -2.665070 | 2.160897 | -0.218369 |
| H | -5.169155 | 2.193352 | -0.039770 |
| H | -4.642736 | 1.397357 | -1.515574 |
| H | -5.566718 | 0.005072 | 1.061343 |
| H | -6.439052 | 0.054833 | -0.464565 |
| H | -2.410630 | 0.026933 | -1.452041 |
| C | 4.661908 | 1.300386 | -0.423144 |
| C | 3.218353 | 1.274655 | 0.109966 |

| | | | |
|---|---|---|---|
| C | 2.500775 | -0.000419 | -0.359845 |
| C | 3.253218 | -1.275590 | 0.050497 |
| C | 4.696485 | -1.235785 | -0.483161 |
| C | 5.434051 | 0.032601 | -0.029595 |
| H | 3.234715 | 1.296047 | 1.208338 |
| H | 2.663308 | 2.159879 | -0.222184 |
| H | 4.641648 | 1.395719 | -1.517937 |
| H | 5.167360 | 2.194697 | -0.043477 |
| H | 3.272614 | -1.348154 | 1.146614 |
| H | 2.722715 | -2.159376 | -0.322793 |
| H | 5.226935 | -2.132990 | -0.146964 |
| H | 4.677275 | -1.278895 | -1.581265 |
| H | 5.566650 | 0.008634 | 1.061409 |
| H | 6.439019 | 0.056473 | -0.464534 |
| H | 2.410738 | 0.023442 | -1.452155 |
| H | -0.000030 | 0.050346 | -1.717015 |

**$CBH^+$(neoPe)**

B3lyp/6-31G(d) optimized geometry
Energy = -619.755330 a.u.
Enthalpy Correction (inc. ZPVE) = 0.386570
NIMAG = 0

B3lyp/6-311+G(2d,p) single point
Energy = -619.928980

| Atom | x-coord | y-coord | z-coord |
|---|---|---|---|
| N | 0.999102 | 0.344522 | -0.441680 |
| C | -0.000001 | -0.430263 | 0.000001 |
| N | -0.999103 | 0.344525 | 0.441681 |
| C | 0.623514 | 1.665375 | -0.275907 |
| C | -0.623512 | 1.665377 | 0.275905 |
| H | 1.267921 | 2.481303 | -0.562402 |
| H | -1.267917 | 2.481307 | 0.562399 |
| C | 2.289454 | -0.138476 | -0.986890 |
| H | 2.082271 | -1.098271 | -1.468513 |
| C | -2.289456 | -0.138468 | 0.986891 |
| H | -0.000003 | -1.508973 | 0.000003 |
| H | 2.572948 | 0.569974 | -1.770038 |
| H | -2.572952 | 0.569987 | 1.770034 |
| H | -2.082275 | -1.098261 | 1.468522 |
| C | -3.776372 | 1.061409 | -0.697626 |
| C | -3.432945 | -0.291790 | -0.048659 |
| H | -4.044648 | 1.813552 | 0.054635 |
| H | -2.949450 | 1.453474 | -1.301289 |
| H | -4.636174 | 0.948414 | -1.365665 |
| C | -3.053927 | -1.318270 | -1.131287 |
| C | -4.649757 | -0.806666 | 0.748819 |
| H | -2.805664 | -2.294073 | -0.694931 |
| H | -3.896082 | -1.472655 | -1.813262 |
| H | -2.206535 | -0.983350 | -1.742011 |
| H | -5.505987 | -0.939709 | 0.080206 |
| H | -4.444245 | -1.774347 | 1.221337 |
| H | -4.947579 | -0.100264 | 1.532399 |

| | | | |
|---|---|---|---|
| C | 4.649751 | -0.806684 | -0.748817 |
| C | 3.432945 | -0.291790 | 0.048658 |
| H | 4.444231 | -1.774369 | -1.221322 |
| H | 4.947576 | -0.100294 | -1.532405 |
| H | 5.505982 | -0.939726 | -0.080204 |
| C | 3.776382 | 1.061416 | 0.697606 |
| C | 3.053925 | -1.318253 | 1.131303 |
| H | 2.949468 | 1.453490 | 1.301274 |
| H | 4.636192 | 0.948428 | 1.365636 |
| H | 4.044651 | 1.813550 | -0.054667 |
| H | 3.896080 | -1.472629 | 1.813279 |
| H | 2.206534 | -0.983321 | 1.742022 |
| H | 2.805660 | -2.294062 | 0.694961 |

**$CBH^+$(tBu)**

B3lyp/6-31G(d) optimized geometry
Energy = -541.132071 a.u.
Enthalpy Correction (inc. ZPVE) = 0.326306
NIMAG = 0

B3lyp/6-311+G(2d,p) single point
Energy = -541.282777

| Atom | x-coord | y-coord | z-coord |
|---|---|---|---|
| C | 2.521617 | -0.220987 | 0.000017 |
| N | 1.097063 | 0.308271 | -0.000084 |
| C | 0.000000 | -0.462235 | -0.000161 |
| N | -1.097063 | 0.308271 | -0.000073 |
| C | -2.521617 | -0.220987 | 0.000016 |
| C | 0.682217 | 1.626331 | -0.000028 |
| C | -0.682217 | 1.626331 | -0.000030 |
| H | 1.370765 | 2.453677 | 0.000022 |
| H | -1.370765 | 2.453677 | 0.000020 |
| C | 2.711437 | -1.063716 | 1.271874 |
| H | 2.536544 | -0.466855 | 2.172520 |
| H | 2.045954 | -1.933186 | 1.294218 |
| H | 3.738701 | -1.438108 | 1.305786 |
| C | 3.490129 | 0.966788 | -0.000075 |
| H | 3.378013 | 1.589239 | 0.893522 |
| H | 4.511317 | 0.576694 | -0.000047 |
| H | 3.377989 | 1.589086 | -0.893772 |
| C | -2.711525 | -1.063973 | -1.271652 |
| H | -3.738776 | -1.438416 | -1.305370 |
| H | -2.536759 | -0.467287 | -2.172437 |
| H | -2.046014 | -1.933422 | -1.293896 |
| C | -3.490129 | 0.966788 | -0.000116 |
| H | -3.377975 | 1.589298 | 0.893435 |
| H | -3.378028 | 1.589027 | -0.893859 |
| H | -4.511317 | 0.576694 | -0.000024 |
| C | -2.711462 | -1.063688 | 1.271888 |
| H | -2.536570 | -0.466811 | 2.172524 |
| H | -3.738730 | -1.438065 | 1.305795 |
| H | -2.045993 | -1.933168 | 1.294257 |
| C | 2.711549 | -1.063944 | -1.271665 |

| | | | |
|---|---|---|---|
| H | 2.046054 | -1.933406 | -1.293936 |
| H | 2.536784 | -0.467244 | -2.172441 |
| H | 3.738806 | -1.438373 | -1.305380 |
| H | 0.000000 | -1.539084 | -0.000256 |

## 3. Hammett Parameters for N-Substituents*

| | |
|---|---|
| **Cl** | 0.23 |
| **H** | 0.00 |
| **Ph** | -0.01 |
| **Me** | -0.17 |
| **IPr** | -0.15 |
| **Cy** | -0.21 |
| **NeoPe** | -0.23 |
| **TBu** | -0.20 |

*Taken from Reference 62

## 4. N-Substituted Complexes

**CX(Cl)**
B3lyp/lanl2dz optimized geometry
Energy = -673.708197 a.u.
Enthalpy Correction (inc. ZPVE) = 0.349797
NIMAG = 0
Pd-P Relaxed B3lyp/lanl2dz Energy = -673.7086589
Mulliken Charge on Pd (@B3LYP/lanl2dz:6-31G(d)) = -0.33

B3lyp/lanl2dzaug:6-311+G(2d,p) single point
Energy = -2234.312118

| Atom | x-coord | y-coord | z-coord |
|---|---|---|---|
| C | 3.960120 | -0.426863 | -0.690214 |
| N | 2.609756 | -0.315406 | -1.073733 |
| C | 1.719227 | -0.386123 | -0.026074 |
| N | 2.582124 | -0.534064 | 1.036379 |
| C | 3.942036 | -0.567804 | 0.673434 |
| Pd | -0.309866 | -0.406244 | -0.053308 |
| C | -0.081162 | -2.493702 | -0.218143 |
| P | -0.471012 | 2.059755 | 0.154732 |
| C | -0.911053 | 2.991299 | -1.429538 |
| P | -2.754485 | -0.823054 | -0.075829 |
| C | -3.347712 | -2.462726 | -0.787616 |
| C | -1.672944 | 2.794630 | 1.416159 |
| C | 1.139930 | 2.907744 | 0.659508 |
| C | -3.849253 | 0.398001 | -1.010440 |
| C | -3.494434 | -0.829551 | 1.658122 |
| H | -0.604037 | -2.950820 | 0.630955 |
| H | -0.536374 | -2.795969 | -1.167617 |
| H | 0.967481 | -2.802080 | -0.202247 |
| H | 4.740740 | -0.684545 | 1.386367 |
| H | 4.777295 | -0.398353 | -1.391088 |
| H | 1.007916 | 3.994947 | 0.688930 |

| | | | |
|---|---|---|---|
| H | 1.445446 | 2.559700 | 1.651245 |
| H | 1.928774 | 2.665917 | -0.059591 |
| H | -1.891129 | 2.673559 | -1.796400 |
| H | -0.929879 | 4.071785 | -1.246949 |
| H | -0.165510 | 2.772113 | -2.200334 |
| H | -3.279190 | 0.117706 | 2.160707 |
| H | -4.579274 | -0.977235 | 1.614538 |
| H | -3.046418 | -1.640249 | 2.240888 |
| H | -2.860834 | -3.298274 | -0.279389 |
| H | -4.432634 | -2.548508 | -0.660831 |
| H | -3.106753 | -2.513772 | -1.853842 |
| H | -3.772838 | 1.398437 | -0.575627 |
| H | -3.538368 | 0.441991 | -2.058871 |
| H | -4.895205 | 0.075193 | -0.963933 |
| H | -1.582487 | 3.886532 | 1.434676 |
| H | -1.445802 | 2.402679 | 2.412706 |
| H | -2.704871 | 2.534290 | 1.162917 |
| Cl | 2.105094 | -0.144556 | -2.768381 |
| Cl | 2.034232 | -0.705532 | 2.717304 |

**CX(H)**

B3lyp/lanl2dz optimized geometry
Energy = -645.151517 a.u.
Enthalpy Correction (inc. ZPVE) = 0.369460
NIMAG = 0
Pd-P Relaxed B3lyp/lanl2dz Energy = -645.1518935
Mulliken Charge on Pd (@B3LYP/lanl2dz:6-31G(d)) = -0.36

B3lyp/lanl2dzaug:6-311+G(2d,p) single point
Energy = -1315.178945

| Atom | x-coord | y-coord | z-coord |
|---|---|---|---|
| C | 4.218804 | -1.012053 | -0.668740 |
| N | 2.884164 | -0.813397 | -1.071858 |
| C | 2.033220 | -0.683695 | -0.001777 |
| N | 2.868230 | -0.800448 | 1.082520 |
| C | 4.208705 | -1.003666 | 0.701614 |
| Pd | 0.009468 | -0.470842 | -0.018775 |
| C | -0.000518 | -2.577250 | -0.032061 |
| P | 0.149239 | 2.005197 | -0.009201 |
| C | -0.550262 | 2.913504 | -1.511553 |
| P | -2.463677 | -0.654201 | -0.000521 |
| C | -3.154153 | -1.959257 | -1.171789 |
| C | -0.676421 | 2.900963 | 1.436781 |
| C | 1.896524 | 2.720425 | 0.070850 |
| C | -3.574695 | 0.819108 | -0.402670 |
| C | -3.111864 | -1.197921 | 1.684443 |
| H | -0.763626 | -2.946992 | 0.663342 |
| H | -0.240741 | -2.877788 | -1.060161 |
| H | 0.968555 | -2.994543 | 0.253681 |
| H | 5.010875 | -1.123417 | 1.410531 |
| H | 5.031203 | -1.140733 | -1.364294 |
| H | 1.861574 | 3.815553 | 0.075147 |
| H | 2.399168 | 2.377290 | 0.980416 |
| H | 2.475947 | 2.386689 | -0.795555 |

| | | | |
|---|---|---|---|
| H | -1.622451 | 2.722001 | -1.602710 |
| H | -0.388127 | 3.993026 | -1.415764 |
| H | -0.054174 | 2.557813 | -2.420243 |
| H | -2.880478 | -0.434909 | 2.434221 |
| H | -4.196399 | -1.350628 | 1.649784 |
| H | -2.628475 | -2.133312 | 1.981055 |
| H | -2.682933 | -2.925376 | -0.976666 |
| H | -4.237260 | -2.053652 | -1.036165 |
| H | -2.946373 | -1.671135 | -2.207087 |
| H | -3.383870 | 1.648547 | 0.284236 |
| H | -3.393715 | 1.154205 | -1.428646 |
| H | -4.625932 | 0.524500 | -0.311138 |
| H | -0.517866 | 3.982503 | 1.359027 |
| H | -0.250769 | 2.545657 | 2.380637 |
| H | -1.751742 | 2.701627 | 1.445010 |
| H | 2.563121 | -0.805702 | -2.030789 |
| H | 2.532698 | -0.781459 | 2.036364 |

**CX(Ph)**

B3lyp/lanl2dz optimized geometry
Energy = -1107.170813 a.u.
Enthalpy Correction (inc. ZPVE) = 0.539985
NIMAG = 0
Pd-P Relaxed B3lyp/lanl2dz Energy = -1107.171057
Mulliken Charge on Pd (@B3LYP/lanl2dz:6-31G(d)) = -0.41

B3lyp/lanl2dzaug:6-311+G(2d,p) single point
Energy = -1777.393902

| Atom | x-coord | y-coord | z-coord |
|---|---|---|---|
| C | 0.537451 | -3.593311 | -0.624779 |
| N | 0.992858 | -2.259553 | -0.556754 |
| C | -0.067927 | -1.372836 | -0.508555 |
| N | -1.189085 | -2.182650 | -0.548142 |
| C | -0.826995 | -3.545139 | -0.619506 |
| Pd | 0.030510 | 0.670279 | -0.365114 |
| C | 0.005739 | 0.703636 | -2.470074 |
| P | 0.062287 | 0.534506 | 2.110963 |
| C | 1.746776 | 0.842006 | 2.909491 |
| P | 0.125606 | 3.145831 | -0.479128 |
| C | 0.808927 | 3.899611 | -2.066279 |
| C | -1.091405 | 1.661279 | 3.098617 |
| C | -0.394109 | -1.150420 | 2.830579 |
| C | 1.129673 | 4.085508 | 0.816019 |
| C | -1.578565 | 3.944622 | -0.349431 |
| H | -0.840401 | 1.322452 | -2.798561 |
| H | 0.944947 | 1.157513 | -2.807662 |
| H | -0.091687 | -0.298035 | -2.899678 |
| H | -1.558910 | -4.331315 | -0.699110 |
| H | 1.213187 | -4.428136 | -0.706951 |
| H | -0.341683 | -1.124001 | 3.924695 |
| H | -1.410446 | -1.416239 | 2.525479 |
| H | 0.298594 | -1.910847 | 2.457764 |
| H | 2.087019 | 1.858909 | 2.694854 |
| H | 1.692410 | 0.704065 | 3.995582 |

| | | | |
|---|---|---|---|
| H | 2.473791 | 0.138329 | 2.491667 |
| H | -2.048254 | 3.673417 | 0.600812 |
| H | -1.500919 | 5.035797 | -0.415186 |
| H | -2.212174 | 3.581364 | -1.164357 |
| H | 0.248993 | 3.537043 | -2.931604 |
| H | 0.733625 | 4.991674 | -2.021953 |
| H | 1.859540 | 3.617689 | -2.187062 |
| H | 0.749775 | 3.886402 | 1.821884 |
| H | 2.177631 | 3.773640 | 0.764474 |
| H | 1.071370 | 5.163108 | 0.626099 |
| H | -0.990724 | 1.464895 | 4.172140 |
| H | -2.126724 | 1.472214 | 2.797446 |
| H | -0.859041 | 2.713628 | 2.910785 |
| C | -2.566900 | -1.750214 | -0.452769 |
| C | -3.064729 | -0.744209 | -1.299626 |
| C | -4.416545 | -0.368803 | -1.201721 |
| C | -5.268131 | -0.999210 | -0.274018 |
| C | -4.762358 | -2.012568 | 0.563004 |
| C | -3.410223 | -2.388848 | 0.478403 |
| H | -2.414091 | -0.280170 | -2.030174 |
| H | -4.807715 | 0.400724 | -1.861781 |
| H | -6.313929 | -0.711903 | -0.210460 |
| H | -5.414573 | -2.506668 | 1.277754 |
| H | -3.016617 | -3.164865 | 1.130326 |
| C | 2.397429 | -1.918055 | -0.477245 |
| C | 2.975154 | -1.042003 | -1.412840 |
| C | 4.349279 | -0.753975 | -1.328271 |
| C | 5.141839 | -1.343559 | -0.324293 |
| C | 4.555681 | -2.228429 | 0.601574 |
| C | 3.180891 | -2.516982 | 0.528834 |
| H | 2.367829 | -0.611653 | -2.200000 |
| H | 4.802386 | -0.085597 | -2.055413 |
| H | 6.204681 | -1.124966 | -0.270235 |
| H | 5.163401 | -2.692346 | 1.373552 |
| H | 2.724751 | -3.197173 | 1.244195 |

**CX(Me)**

B3lyp/lanl2dz optimized geometry
Energy = -723.759039 a.u.
Enthalpy Correction (inc. ZPVE) = 0.428106
NIMAG = 0
Pd-P Relaxed B3lyp/lanl2dz Energy = -723.7594587
Mulliken Charge on Pd (@B3LYP/lanl2dz:6-31G(d)) = -0.43

B3lyp/lanl2dzaug:6-311+G(2d,p) single point
Energy = -1393.822057

| Atom | x-coord | y-coord | z-coord |
|---|---|---|---|
| C | 4.074150 | -0.651267 | -0.674171 |
| N | 2.733405 | -0.555515 | -1.088107 |
| C | 1.886399 | -0.505990 | -0.003455 |
| N | 2.717759 | -0.573839 | 1.091744 |
| C | 4.064154 | -0.662511 | 0.695775 |
| Pd | -0.158407 | -0.445685 | -0.020095 |
| C | -0.023296 | -2.544461 | -0.013570 |

| | | | |
|---|---|---|---|
| C | 2.265029 | -0.593970 | 2.490726 |
| C | 2.300104 | -0.560088 | -2.493722 |
| P | -0.188988 | 2.034045 | -0.000038 |
| C | -0.672582 | 2.892919 | -1.613926 |
| P | -2.620444 | -0.743508 | -0.011605 |
| C | -3.278486 | -2.362046 | -0.718502 |
| C | -1.297927 | 2.896657 | 1.267446 |
| C | 1.471752 | 2.856431 | 0.370650 |
| C | -3.702640 | 0.507797 | -0.923715 |
| C | -3.346333 | -0.731863 | 1.729773 |
| H | -0.608355 | -2.921570 | 0.835550 |
| H | -0.449990 | -2.900596 | -0.959001 |
| H | 1.007738 | -2.895753 | 0.076704 |
| H | 1.173328 | -0.572543 | 2.501089 |
| H | 2.606606 | -1.509075 | 2.985436 |
| H | 2.654667 | 0.274029 | 3.034028 |
| H | 1.208873 | -0.528345 | -2.518798 |
| H | 2.705386 | 0.308552 | -3.024174 |
| H | 2.639772 | -1.474591 | -2.990856 |
| H | 4.876446 | -0.728717 | 1.401235 |
| H | 4.896468 | -0.707079 | -1.368821 |
| H | 1.380459 | 3.946575 | 0.306851 |
| H | 1.802888 | 2.587003 | 1.378499 |
| H | 2.224973 | 2.517375 | -0.346674 |
| H | -1.680001 | 2.594145 | -1.916724 |
| H | -0.643649 | 3.981696 | -1.491896 |
| H | 0.027278 | 2.606300 | -2.405477 |
| H | -3.126063 | 0.220575 | 2.221293 |
| H | -4.431949 | -0.876936 | 1.696849 |
| H | -2.896270 | -1.538090 | 2.317293 |
| H | -2.823727 | -3.213202 | -0.206453 |
| H | -4.366039 | -2.407325 | -0.593585 |
| H | -3.037122 | -2.426248 | -1.784073 |
| H | -3.584365 | 1.508178 | -0.497659 |
| H | -3.420805 | 0.535830 | -1.980986 |
| H | -4.756458 | 0.217804 | -0.847103 |
| H | -1.169931 | 3.983518 | 1.210338 |
| H | -1.032271 | 2.560948 | 2.275037 |
| H | -2.349792 | 2.656848 | 1.085767 |

**CX(iPr)**

B3lyp/lanl2dz optimized geometry
Energy = -880.999887 a.u.
Enthalpy Correction (inc. ZPVE) = 0.546892
NIMAG = 0
Pd-P Relaxed B3lyp/lanl2dz Energy = -881.0002132
Mulliken Charge on Pd (@B3LYP/lanl2dz:6-31G(d)) = -0.44

B3lyp/lanl2dzaug:6-311+G(2d,p) single point
Energy = -1551.132413

| Atom | x-coord | y-coord | z-coord |
|---|---|---|---|
| C | -3.700817 | -0.646802 | -0.371125 |
| N | -2.354183 | -1.045151 | -0.421380 |
| C | -1.521994 | 0.041200 | -0.267224 |

| | | | |
|---|---|---|---|
| N | -2.364945 | 1.119953 | -0.116807 |
| C | -3.707397 | 0.709676 | -0.180182 |
| Pd | 0.526066 | 0.050532 | -0.357625 |
| C | 0.241572 | 0.375396 | -2.416078 |
| C | -1.915275 | 2.537833 | 0.008163 |
| C | -1.887962 | -2.437103 | -0.689452 |
| P | 0.751783 | -0.335187 | 2.081775 |
| C | 1.468287 | -2.000766 | 2.619523 |
| P | 2.953966 | 0.132761 | -0.856562 |
| C | 3.473838 | -0.543742 | -2.538008 |
| C | 1.797792 | 0.894944 | 3.067935 |
| C | -0.858106 | -0.302440 | 3.070828 |
| C | 4.202686 | -0.725203 | 0.272304 |
| C | 3.602706 | 1.903488 | -0.905917 |
| H | 0.827980 | 1.253562 | -2.718254 |
| H | 0.603287 | -0.520274 | -2.936183 |
| H | -0.808631 | 0.541879 | -2.668085 |
| H | -0.826855 | 2.475801 | 0.121923 |
| H | -0.798417 | -2.391597 | -0.576789 |
| H | -4.536571 | 1.390495 | -0.085106 |
| H | -4.523194 | -1.335130 | -0.470613 |
| H | -0.664555 | -0.541359 | 4.122624 |
| H | -1.312000 | 0.690807 | 3.008294 |
| H | -1.563507 | -1.030157 | 2.659128 |
| H | 2.480007 | -2.124726 | 2.224810 |
| H | 1.500449 | -2.067267 | 3.713019 |
| H | 0.842072 | -2.811238 | 2.232753 |
| H | 3.468492 | 2.376725 | 0.071737 |
| H | 4.665950 | 1.918699 | -1.170245 |
| H | 3.040869 | 2.477011 | -1.649387 |
| H | 2.922525 | -0.038334 | -3.334324 |
| H | 4.547639 | -0.386576 | -2.689139 |
| H | 3.257596 | -1.615534 | -2.588547 |
| H | 4.143812 | -0.326657 | 1.289214 |
| H | 4.000927 | -1.800747 | 0.298178 |
| H | 5.218357 | -0.566905 | -0.106862 |
| H | 1.789581 | 0.637701 | 4.133239 |
| H | 1.390803 | 1.903540 | 2.942917 |
| H | 2.832272 | 0.891648 | 2.711900 |
| C | -2.237096 | 3.319966 | -1.282573 |
| H | -1.771838 | 2.849171 | -2.155086 |
| H | -3.319032 | 3.377834 | -1.455480 |
| H | -1.856358 | 4.344750 | -1.200054 |
| C | -2.524594 | 3.203398 | 1.257954 |
| H | -3.613701 | 3.304032 | 1.173985 |
| H | -2.303573 | 2.633476 | 2.168041 |
| H | -2.110654 | 4.211397 | 1.375569 |
| C | -2.220583 | -2.844728 | -2.139688 |
| H | -1.809916 | -3.839439 | -2.348983 |
| H | -3.304334 | -2.888528 | -2.304966 |
| H | -1.789710 | -2.135811 | -2.855044 |
| C | -2.468614 | -3.422549 | 0.343990 |
| H | -2.228555 | -3.118837 | 1.370152 |
| H | -3.559096 | -3.505168 | 0.258013 |
| H | -2.050159 | -4.421353 | 0.174801 |

**CX(Cy)**

B3lyp/lanl2dz optimized geometry
Energy = -1114.432765 a.u.
Enthalpy Correction (inc. ZPVE) = 0.683757
NIMAG = 0
Pd-P Relaxed B3lyp/lanl2dz Energy = -1114.433084
Mulliken Charge on Pd (@B3LYP/lanl2dz:6-31G(d)) = -0.45

B3lyp/lanl2dzaug:6-311+G(2d,p) single point
Energy = -1784.66776

| Atom | x-coord | y-coord | z-coord |
|---|---|---|---|
| C | 0.770314 | -3.364818 | -0.035954 |
| N | 1.150636 | -2.013846 | -0.086884 |
| C | 0.040084 | -1.200808 | -0.124415 |
| N | -1.036006 | -2.059820 | -0.094408 |
| C | -0.599213 | -3.393706 | -0.040401 |
| Pd | 0.003036 | 0.841063 | -0.301619 |
| C | 0.017206 | 0.464145 | -2.372285 |
| P | -0.022656 | 1.167930 | 2.156612 |
| C | 1.398557 | 2.141753 | 2.937177 |
| P | -0.091220 | 3.236238 | -0.937742 |
| C | 1.042233 | 3.720500 | -2.364664 |
| C | -1.546678 | 2.037328 | 2.863325 |
| C | 0.009152 | -0.402792 | 3.206660 |
| C | 0.276187 | 4.617075 | 0.298397 |
| C | -1.797288 | 3.727789 | -1.576187 |
| H | -0.761826 | 1.066651 | -2.857313 |
| H | 1.008888 | 0.756507 | -2.741083 |
| H | -0.157042 | -0.590649 | -2.598030 |
| H | -1.273554 | -4.232830 | -0.010142 |
| H | 1.479463 | -4.174618 | -0.001664 |
| H | -0.019328 | -0.148030 | 4.272178 |
| H | -0.852240 | -1.031970 | 2.965218 |
| H | 0.920141 | -0.971352 | 2.998385 |
| H | 1.417119 | 3.163741 | 2.550480 |
| H | 1.285142 | 2.175444 | 4.026797 |
| H | 2.350521 | 1.659257 | 2.693567 |
| H | -2.542539 | 3.592062 | -0.786101 |
| H | -1.801170 | 4.775245 | -1.898127 |
| H | -2.069258 | 3.092495 | -2.424313 |
| H | 0.846284 | 3.082319 | -3.229663 |
| H | 0.873467 | 4.766515 | -2.643600 |
| H | 2.087189 | 3.592881 | -2.064845 |
| H | -0.394861 | 4.552082 | 1.159995 |
| H | 1.311845 | 4.541465 | 0.644007 |
| H | 0.137159 | 5.592479 | -0.181003 |
| H | -1.480904 | 2.103450 | 3.955302 |
| H | -2.445176 | 1.472574 | 2.594664 |
| H | -1.636336 | 3.047117 | 2.451915 |
| C | 4.853718 | -1.499901 | 0.920813 |
| C | 3.406517 | -2.038214 | 1.016849 |
| C | 2.557171 | -1.532102 | -0.171734 |
| C | 3.196560 | -1.921830 | -1.526345 |
| C | 4.644517 | -1.387291 | -1.620514 |
| C | 5.506309 | -1.868944 | -0.431281 |

| | | | |
|---|---|---|---|
| H | 3.434175 | -3.138074 | 1.011501 |
| H | 2.944978 | -1.733499 | 1.966566 |
| H | 4.846402 | -0.404040 | 1.034309 |
| H | 5.448636 | -1.899223 | 1.752371 |
| H | 3.206976 | -3.017995 | -1.623688 |
| H | 2.585514 | -1.528638 | -2.348799 |
| H | 5.092008 | -1.709175 | -2.569589 |
| H | 4.627775 | -0.285947 | -1.636981 |
| H | 5.631600 | -2.961087 | -0.489615 |
| H | 6.511409 | -1.432181 | -0.493573 |
| H | 2.488872 | -0.437340 | -0.122254 |
| C | -4.560522 | -1.602288 | -1.620784 |
| C | -3.090640 | -2.073673 | -1.527244 |
| C | -2.461808 | -1.638657 | -0.181476 |
| C | -3.284748 | -2.163741 | 1.017689 |
| C | -4.754045 | -1.689346 | 0.922499 |
| C | -5.396392 | -2.103659 | -0.421257 |
| H | -3.055232 | -3.170492 | -1.610372 |
| H | -2.502059 | -1.665581 | -2.358823 |
| H | -4.590622 | -0.501599 | -1.652277 |
| H | -4.998033 | -1.955638 | -2.563314 |
| H | -3.264831 | -3.263747 | 1.027071 |
| H | -2.832648 | -1.827160 | 1.961163 |
| H | -5.327259 | -2.102871 | 1.762320 |
| H | -4.793619 | -0.592681 | 1.021701 |
| H | -5.475957 | -3.200755 | -0.464252 |
| H | -6.419187 | -1.710304 | -0.484813 |
| H | -2.438949 | -0.541505 | -0.148023 |

**CX(neoPe)**

B3lyp/lanl2dz optimized geometry
Energy = -1038.219285 a.u.
Enthalpy Correction (inc. ZPVE) = 0.665951
NIMAG = 0
Pd-P Relaxed B3lyp/lanl2dz Energy = -1038.219710
Mulliken Charge on Pd (@B3LYP/lanl2dz:6-31G(d)) = -0.47

B3lyp/lanl2dzaug:6-311+G(2d,p) single point
Energy = -1708.421634

| Atom | x-coord | y-coord | z-coord |
|---|---|---|---|
| N | -1.975380 | 1.309021 | -0.513037 |
| C | -3.354879 | 1.126363 | -0.312688 |
| C | -3.527473 | -0.147396 | 0.154976 |
| N | -2.252634 | -0.736795 | 0.219072 |
| C | -1.282448 | 0.159152 | -0.185098 |
| C | -1.993433 | -2.127683 | 0.655086 |
| C | -2.438064 | -3.266269 | -0.317769 |
| C | -3.978320 | -3.314122 | -0.490146 |
| Pd | 0.745640 | -0.156438 | -0.333198 |
| P | 1.088017 | -0.141748 | 2.123011 |
| C | 2.258994 | 1.181422 | 2.797616 |
| C | -1.373584 | 2.520588 | -1.122420 |
| C | -1.361444 | 3.826515 | -0.269780 |
| C | -2.790051 | 4.340195 | 0.042934 |

| | | | |
|---|---|---|---|
| C | -1.764152 | -3.104369 | -1.699928 |
| C | -1.965832 | -4.590457 | 0.342285 |
| P | 3.133023 | -0.451988 | -0.936066 |
| C | 4.398864 | -1.139405 | 0.287418 |
| C | 0.411967 | -0.172576 | -2.412962 |
| C | 3.918708 | 1.189075 | -1.435906 |
| C | 3.476407 | -1.545380 | -2.433559 |
| C | -0.586912 | 3.613138 | 1.050959 |
| C | -0.625479 | 4.884734 | -1.136412 |
| C | -0.431128 | 0.141173 | 3.211604 |
| C | 1.779251 | -1.723012 | 2.900932 |
| H | 1.088417 | 0.545075 | -2.897096 |
| H | 0.625651 | -1.190219 | -2.758890 |
| H | -0.620628 | 0.080561 | -2.663654 |
| H | -0.343609 | 2.251110 | -1.371552 |
| H | -1.909647 | 2.716492 | -2.060706 |
| H | -0.910922 | -2.201699 | 0.804673 |
| H | -2.491539 | -2.277006 | 1.623138 |
| H | -4.081298 | 1.891594 | -0.523684 |
| H | -4.425438 | -0.666178 | 0.442180 |
| H | -0.145944 | 0.121298 | 4.269419 |
| H | -0.878953 | 1.110938 | 2.980063 |
| H | -1.173764 | -0.639843 | 3.028622 |
| H | 2.753636 | -1.966098 | 2.470761 |
| H | 1.888775 | -1.597865 | 3.984225 |
| H | 1.096283 | -2.556800 | 2.708475 |
| H | 3.907025 | 1.881507 | -0.588444 |
| H | 4.953734 | 1.037795 | -1.762354 |
| H | 3.346393 | 1.633045 | -2.256013 |
| H | 2.926837 | -1.178907 | -3.303363 |
| H | 4.548624 | -1.543038 | -2.659292 |
| H | 3.156369 | -2.570822 | -2.223480 |
| H | 4.423344 | -0.540881 | 1.202401 |
| H | 4.145762 | -2.173378 | 0.541623 |
| H | 5.395838 | -1.125429 | -0.166762 |
| H | 2.347787 | 1.095151 | 3.886512 |
| H | 1.867975 | 2.172699 | 2.549653 |
| H | 3.252627 | 1.077115 | 2.351881 |
| H | -0.874025 | -4.611037 | 0.466537 |
| H | -2.426689 | -4.738884 | 1.328742 |
| H | -2.244110 | -5.446169 | -0.284196 |
| H | -4.355360 | -2.457799 | -1.061475 |
| H | -4.262003 | -4.218560 | -1.041969 |
| H | -4.495010 | -3.345672 | 0.479714 |
| H | -2.051364 | -3.933857 | -2.357999 |
| H | -2.064424 | -2.169485 | -2.188383 |
| H | -0.670002 | -3.103629 | -1.611684 |
| H | 0.401507 | 4.570905 | -1.369157 |
| H | -1.149593 | 5.063353 | -2.084904 |
| H | -0.569870 | 5.841287 | -0.603048 |
| H | -3.320063 | 3.683773 | 0.743567 |
| H | -2.736444 | 5.332225 | 0.508168 |
| H | -3.392988 | 4.439150 | -0.870626 |
| H | -0.516910 | 4.555421 | 1.608678 |
| H | -1.094666 | 2.882344 | 1.692458 |
| H | 0.433791 | 3.256919 | 0.855090 |

**CX(tBu)**
B3lyp/lanl2dz optimized geometry
Energy = -959.5981766 a.u.
Enthalpy Correction (inc. ZPVE) = 0.605890
NIMAG = 0
Pd-P Relaxed B3lyp/lanl2dz Energy = -959.5988133
Mulliken Charge on Pd (@B3LYP/lanl2dz:6-31G(d)) = -0.53

B3lyp/lanl2dzaug:6-311+G(2d,p) single point
Energy = -1629.761884

| Atom | x-coord | y-coord | z-coord |
|---|---|---|---|
| C | -3.693508 | -0.568832 | -0.098625 |
| N | -2.370972 | -1.041002 | -0.179404 |
| C | -1.483424 | 0.029339 | -0.209207 |
| N | -2.285723 | 1.163687 | -0.132222 |
| C | -3.640854 | 0.791316 | -0.068254 |
| Pd | 0.593397 | -0.040284 | -0.348869 |
| C | 0.326072 | 0.010217 | -2.438186 |
| C | -1.882087 | 2.630494 | -0.276659 |
| C | -2.077968 | -2.525546 | -0.388632 |
| P | 0.882480 | -0.098323 | 2.113541 |
| C | 1.707433 | -1.625988 | 2.866224 |
| P | 3.013033 | -0.029902 | -0.892608 |
| C | 3.513829 | -1.000324 | -2.430019 |
| C | 1.898434 | 1.297172 | 2.890790 |
| C | -0.698705 | -0.006641 | 3.146374 |
| C | 4.308309 | -0.643333 | 0.339164 |
| C | 3.631651 | 1.709122 | -1.283962 |
| H | 0.896964 | 0.852705 | -2.851797 |
| H | 0.711713 | -0.934110 | -2.839562 |
| H | -0.725336 | 0.119007 | -2.711307 |
| H | -4.448133 | 1.496226 | 0.001164 |
| H | -4.552523 | -1.212316 | -0.059122 |
| H | -0.456248 | -0.025872 | 4.214896 |
| H | -1.241234 | 0.914628 | 2.917024 |
| H | -1.346595 | -0.855523 | 2.910361 |
| H | 2.726319 | -1.732493 | 2.486013 |
| H | 1.742573 | -1.538335 | 3.958057 |
| H | 1.140631 | -2.522299 | 2.599543 |
| H | 3.535677 | 2.346900 | -0.399565 |
| H | 4.682099 | 1.684457 | -1.595387 |
| H | 3.030031 | 2.139006 | -2.090414 |
| H | 2.971571 | -0.630897 | -3.303311 |
| H | 4.590026 | -0.892962 | -2.604649 |
| H | 3.276694 | -2.059887 | -2.292244 |
| H | 4.248814 | -0.086457 | 1.278488 |
| H | 4.152054 | -1.707196 | 0.542958 |
| H | 5.310706 | -0.510821 | -0.082833 |
| H | 1.917124 | 1.193539 | 3.981628 |
| H | 1.459624 | 2.265281 | 2.633269 |
| H | 2.926741 | 1.272259 | 2.518204 |
| C | -1.695143 | 2.938931 | -1.782978 |
| H | -0.849655 | 2.386480 | -2.198458 |
| H | -2.596677 | 2.678120 | -2.350321 |

| | | | |
|---|---|---|---|
| H | -1.508160 | 4.011093 | -1.918258 |
| C | -3.008818 | 3.528275 | 0.295615 |
| H | -2.647000 | 4.561510 | 0.318284 |
| H | -3.910202 | 3.521758 | -0.326973 |
| H | -3.278113 | 3.244840 | 1.320225 |
| C | -1.915576 | -2.778124 | -1.907971 |
| H | -1.792955 | -3.852156 | -2.092414 |
| H | -2.802649 | -2.438628 | -2.456193 |
| H | -1.041691 | -2.257794 | -2.304757 |
| C | -3.268554 | -3.361613 | 0.146053 |
| H | -4.167162 | -3.257706 | -0.471937 |
| H | -2.985965 | -4.419205 | 0.118822 |
| H | -3.514844 | -3.106984 | 1.183930 |
| C | -0.588362 | 2.933075 | 0.504393 |
| H | -0.322722 | 3.985238 | 0.349712 |
| H | -0.731450 | 2.774181 | 1.579891 |
| H | 0.246054 | 2.315313 | 0.156518 |
| C | -0.811874 | -2.953542 | 0.378524 |
| H | -0.952477 | -2.837732 | 1.460093 |
| H | -0.616132 | -4.012396 | 0.173468 |
| H | 0.065268 | -2.377094 | 0.066462 |

## 5. N-Substituted Transition Structures

**TS(Cl)**
B3lyp/lanl2dz optimized geometry
Energy = -673.678002 a.u.
Enthalpy Correction (inc. ZPVE) = 0.347779
Pd-P Relaxed B3lyp/lanl2dz Energy = -673.6784152
NIMAG = 1

B3lyp/lanl2dzaug:6-311+G(2d,p) single point
Energy = -2234.277878

| Atom | x-coord | y-coord | z-coord |
|---|---|---|---|
| Pd | 0.347925 | -0.328311 | -0.028211 |
| P | 0.423829 | 2.146654 | 0.110302 |
| P | 2.766760 | -0.875148 | -0.052832 |
| C | -0.714664 | -2.378557 | -0.165482 |
| H | -0.170282 | -2.615499 | -1.084566 |
| H | -0.206502 | -2.750211 | 0.729241 |
| H | -1.698489 | -2.851522 | -0.221811 |
| C | -1.612412 | -0.696577 | -0.035166 |
| N | -2.515592 | -0.462032 | -1.085277 |
| N | -2.490614 | -0.623664 | 1.058527 |
| C | -3.849345 | -0.274590 | -0.663238 |
| H | -4.662782 | -0.114634 | -1.350805 |
| C | -3.833035 | -0.376125 | 0.700508 |
| H | -4.629625 | -0.319650 | 1.423159 |
| C | 3.598601 | -0.901105 | 1.643085 |
| C | 0.904113 | 3.009559 | -1.497084 |
| C | -1.214900 | 2.972372 | 0.549579 |
| H | -1.111815 | 4.063357 | 0.537169 |
| H | -1.982198 | 2.677558 | -0.172946 |

| | | | |
|---|---|---|---|
| H | -1.530340 | 2.655002 | 1.548278 |
| C | 1.606462 | 2.903012 | 1.371002 |
| H | 2.635821 | 2.608769 | 1.144214 |
| H | 1.538644 | 3.996698 | 1.350956 |
| H | 1.352136 | 2.547309 | 2.374133 |
| C | 3.945749 | 0.199835 | -1.064807 |
| H | 3.950204 | 1.223051 | -0.674972 |
| H | 4.965543 | -0.198180 | -1.018032 |
| H | 3.620538 | 0.222554 | -2.109868 |
| C | 3.159418 | -2.601014 | -0.714100 |
| H | 2.861401 | -2.671533 | -1.765330 |
| H | 4.231859 | -2.810849 | -0.634158 |
| H | 2.608193 | -3.354635 | -0.142457 |
| H | 0.927161 | 4.096417 | -1.357641 |
| H | 1.891257 | 2.668206 | -1.822089 |
| H | 0.176769 | 2.762490 | -2.276329 |
| H | 4.657323 | -1.169096 | 1.552427 |
| H | 3.517471 | 0.083752 | 2.113583 |
| H | 3.099394 | -1.633196 | 2.285922 |
| Cl | -1.998317 | -0.289734 | -2.777024 |
| Cl | -1.931186 | -0.688349 | 2.744615 |

**TS(H)**

B3lyp/lanl2dz optimized geometry
Energy = -645.117722 a.u.
Enthalpy Correction (inc. ZPVE) = 0.367168
Pd-P Relaxed B3lyp/lanl2dz Energy = -645.1181193
NIMAG = 1

B3lyp/lanl2dzaug:6-311+G(2d,p) single point
Energy = -1315.142335

| Atom | x-coord | y-coord | z-coord |
|---|---|---|---|
| Pd | -0.054249 | -0.424503 | -0.004804 |
| P | 0.218527 | 2.040449 | -0.006880 |
| P | -2.521701 | -0.673597 | 0.001088 |
| C | 0.777087 | -2.582633 | 0.003473 |
| H | 0.193391 | -2.820927 | 0.899455 |
| H | 0.233613 | -2.829565 | -0.915256 |
| H | 1.691573 | -3.180984 | 0.027453 |
| C | 1.861719 | -1.029664 | -0.001133 |
| N | 2.727915 | -0.946666 | 1.092356 |
| N | 2.731683 | -0.961844 | -1.091752 |
| C | 4.076606 | -0.868019 | 0.685711 |
| H | 4.894120 | -0.809282 | 1.384892 |
| C | 4.078631 | -0.876914 | -0.681952 |
| H | 4.898310 | -0.825876 | -1.379173 |
| C | -3.402280 | -0.325313 | -1.635618 |
| C | 0.121241 | 2.844846 | 1.699129 |
| C | 1.886922 | 2.652357 | -0.646377 |
| H | 1.968235 | 3.739886 | -0.537608 |
| H | 2.694866 | 2.172245 | -0.085707 |
| H | 1.993449 | 2.391453 | -1.704170 |
| C | -0.995298 | 3.080327 | -1.013259 |
| H | -2.009286 | 2.954153 | -0.620719 |

| | | | |
|---|---|---|---|
| H | -0.726218 | 4.141578 | -0.961631 |
| H | -0.980332 | 2.758686 | -2.059268 |
| C | -3.529075 | 0.362564 | 1.220240 |
| H | -3.414456 | 1.427296 | 0.991654 |
| H | -4.592134 | 0.102697 | 1.163660 |
| H | -3.172283 | 0.183267 | 2.239533 |
| C | -3.129852 | -2.418886 | 0.400936 |
| H | -2.819525 | -2.696537 | 1.413787 |
| H | -4.222336 | -2.473042 | 0.337574 |
| H | -2.698239 | -3.135713 | -0.305411 |
| H | 0.249900 | 3.930539 | 1.621677 |
| H | -0.849460 | 2.630549 | 2.156442 |
| H | 0.906823 | 2.438518 | 2.343836 |
| H | -4.482035 | -0.486365 | -1.538447 |
| H | -3.221393 | 0.709209 | -1.943874 |
| H | -3.011475 | -0.991346 | -2.411773 |
| H | 2.410094 | -0.980476 | 2.050686 |
| H | 2.416487 | -0.998007 | -2.050877 |

**TS(Ph)**

B3lyp/lanl2dz optimized geometry
Energy = -1107.138448 a.u.
Enthalpy Correction (inc. ZPVE) = 0.538061
Pd-P Relaxed B3lyp/lanl2dz Energy = -1107.138645
NIMAG = 1

B3lyp/lanl2dzaug:6-311+G(2d,p) single point
Energy = -1777.356466

| Atom | x-coord | y-coord | z-coord |
|---|---|---|---|
| Pd | -0.006906 | 0.650584 | -0.203661 |
| P | 0.082933 | 1.146031 | 2.224685 |
| P | 0.022368 | 2.925514 | -1.190697 |
| C | -0.036547 | -0.726991 | -2.054765 |
| H | -0.787974 | -0.063885 | -2.493574 |
| H | 0.971287 | -0.507577 | -2.413651 |
| H | -0.305330 | -1.751988 | -2.323844 |
| C | -0.038676 | -1.363804 | -0.193081 |
| N | -1.157361 | -2.158957 | 0.120748 |
| N | 1.061919 | -2.197465 | 0.074334 |
| C | -0.740193 | -3.432739 | 0.570643 |
| H | -1.436006 | -4.175178 | 0.922237 |
| C | 0.619220 | -3.456708 | 0.542613 |
| H | 1.303238 | -4.221769 | 0.867725 |
| C | 1.700805 | 3.795226 | -1.242423 |
| C | -1.544261 | 1.652175 | 3.041467 |
| C | 0.628238 | -0.310405 | 3.297243 |
| H | 0.627667 | -0.032707 | 4.357428 |
| H | -0.054772 | -1.152216 | 3.146098 |
| H | 1.636655 | -0.623677 | 3.009204 |
| C | 1.254497 | 2.514724 | 2.796046 |
| H | 0.967329 | 3.466948 | 2.338457 |
| H | 1.220392 | 2.620984 | 3.886363 |
| H | 2.279351 | 2.274949 | 2.495015 |
| C | -1.085783 | 4.259153 | -0.436661 |

| | | | |
|---|---|---|---|
| H | -0.797107 | 4.442258 | 0.603646 |
| H | -1.000572 | 5.197090 | -0.996977 |
| H | -2.128686 | 3.926549 | -0.457421 |
| C | -0.496761 | 2.990162 | -3.007200 |
| H | -1.532694 | 2.650318 | -3.109209 |
| H | -0.417545 | 4.011531 | -3.395876 |
| H | 0.146636 | 2.333713 | -3.601916 |
| H | -1.398371 | 1.815194 | 4.115377 |
| H | -1.917417 | 2.575813 | 2.587971 |
| H | -2.290526 | 0.864699 | 2.898302 |
| H | 1.614664 | 4.775387 | -1.725301 |
| H | 2.083796 | 3.930448 | -0.225848 |
| H | 2.412705 | 3.182456 | -1.804823 |
| C | -2.536814 | -1.835945 | -0.138313 |
| C | -3.025800 | -0.521786 | 0.001375 |
| C | -4.378868 | -0.245575 | -0.260680 |
| C | -5.257620 | -1.273757 | -0.648283 |
| C | -4.766599 | -2.586247 | -0.786047 |
| C | -3.412602 | -2.868816 | -0.541267 |
| H | -2.355292 | 0.275114 | 0.311604 |
| H | -4.748305 | 0.770669 | -0.149465 |
| H | -6.304316 | -1.057631 | -0.841758 |
| H | -5.431617 | -3.387162 | -1.096929 |
| H | -3.042016 | -3.878690 | -0.690498 |
| C | 2.448146 | -1.914260 | -0.196644 |
| C | 2.985173 | -0.622283 | -0.028795 |
| C | 4.345183 | -0.388180 | -0.297321 |
| C | 5.182415 | -1.437314 | -0.719102 |
| C | 4.643013 | -2.727570 | -0.884835 |
| C | 3.282173 | -2.967446 | -0.633504 |
| H | 2.345132 | 0.189565 | 0.306549 |
| H | 4.752239 | 0.611068 | -0.165472 |
| H | 6.234439 | -1.254173 | -0.917621 |
| H | 5.275891 | -3.543667 | -1.222163 |
| H | 2.873326 | -3.959208 | -0.803424 |

**TS(Me)**

B3lyp/lanl2dz optimized geometry
Energy = -723.722773 a.u.
Enthalpy Correction (inc. ZPVE) = 0.426119
Pd-P Relaxed B3lyp/lanl2dz Energy = -723.7232434
NIMAG = 1

B3lyp/lanl2dzaug:6-311+G(2d,p) single point
Energy = -1393.782624

| Atom | x-coord | y-coord | z-coord |
|---|---|---|---|
| Pd | 0.209677 | -0.351191 | -0.008330 |
| P | 0.161175 | 2.128261 | 0.010795 |
| P | 2.644672 | -0.821508 | -0.007348 |
| C | -0.825663 | -2.429122 | -0.024811 |
| H | -0.258022 | -2.707786 | -0.918269 |
| H | -0.303191 | -2.728648 | 0.888979 |
| H | -1.783033 | -2.958941 | -0.056236 |
| C | -1.769840 | -0.802102 | -0.002951 |
| N | -2.623314 | -0.638881 | -1.100358 |

| | | | |
|---|---|---|---|
| C | -2.211897 | -0.747172 | -2.504835 |
| H | -1.136870 | -0.565911 | -2.579937 |
| H | -2.438586 | -1.741831 | -2.909006 |
| H | -2.735808 | 0.003659 | -3.105326 |
| N | -2.611398 | -0.667237 | 1.106693 |
| C | -2.182333 | -0.796339 | 2.504048 |
| H | -1.113972 | -0.577095 | 2.575043 |
| H | -2.727965 | -0.080472 | 3.127242 |
| H | -2.368912 | -1.808151 | 2.885395 |
| C | -3.951324 | -0.458096 | -0.671242 |
| H | -4.767243 | -0.316015 | -1.361188 |
| C | -3.943607 | -0.475200 | 0.696919 |
| H | -4.751588 | -0.349063 | 1.399161 |
| C | 3.489344 | -0.728026 | 1.682219 |
| C | 0.599000 | 2.959256 | -1.629267 |
| C | -1.513668 | 2.906510 | 0.407907 |
| H | -1.467253 | 3.997605 | 0.315038 |
| H | -2.270222 | 2.516920 | -0.280140 |
| H | -1.807406 | 2.647730 | 1.430091 |
| C | 1.305192 | 3.016987 | 1.224810 |
| H | 2.347868 | 2.763703 | 1.007569 |
| H | 1.180753 | 4.103237 | 1.147902 |
| H | 1.075351 | 2.703325 | 2.248009 |
| C | 3.785051 | 0.253694 | -1.066741 |
| H | 3.743102 | 1.293177 | -0.724572 |
| H | 4.821022 | -0.097310 | -0.999766 |
| H | 3.463366 | 0.215225 | -2.112580 |
| C | 3.137569 | -2.556612 | -0.581163 |
| H | 2.858985 | -2.692672 | -1.631515 |
| H | 4.218110 | -2.708430 | -0.478382 |
| H | 2.616038 | -3.309808 | 0.018794 |
| H | 0.569242 | 4.050403 | -1.528583 |
| H | 1.601705 | 2.655640 | -1.944554 |
| H | -0.115632 | 2.653289 | -2.399900 |
| H | 4.562154 | -0.933244 | 1.593040 |
| H | 3.349589 | 0.268574 | 2.112824 |
| H | 3.041623 | -1.463471 | 2.358649 |

**TS(iPr)**

B3lyp/lanl2dz optimized geometry
Energy = -880.961544 a.u.
Enthalpy Correction (inc. ZPVE) = 0.545043
Pd-P Relaxed B3lyp/lanl2dz Energy = -880.9620817
NIMAG = 1

B3lyp/lanl2dzaug:6-311+G(2d,p) single point
Energy = -1551.090657

| Atom | x-coord | y-coord | z-coord |
|---|---|---|---|
| Pd | -0.550523 | 0.118294 | -0.262676 |
| P | -0.856963 | -1.060266 | 1.897762 |
| P | -2.899537 | 0.502612 | -0.958976 |
| C | 0.712836 | 0.992380 | -2.006162 |
| H | 0.202973 | 0.325861 | -2.709038 |

| | | | |
|---|---|---|---|
| H | 0.193774 | 1.952587 | -1.924295 |
| H | 1.716982 | 1.184962 | -2.394068 |
| C | 1.476192 | 0.259328 | -0.460232 |
| N | 2.324837 | -0.824249 | -0.713114 |
| C | 1.937949 | -2.050992 | -1.462390 |
| H | 0.858947 | -1.956300 | -1.632557 |
| N | 2.271179 | 1.171163 | 0.244097 |
| C | 1.820836 | 2.512830 | 0.707112 |
| H | 0.747737 | 2.548246 | 0.485093 |
| C | 3.608997 | -0.565229 | -0.202761 |
| H | 4.421971 | -1.267298 | -0.283447 |
| C | 3.575387 | 0.667776 | 0.389158 |
| H | 4.354728 | 1.204654 | 0.903619 |
| C | -3.762149 | 1.977946 | -0.145568 |
| C | -1.518335 | -2.824623 | 1.739640 |
| C | 0.660173 | -1.317809 | 2.997007 |
| H | 0.400767 | -1.908928 | 3.882901 |
| H | 1.441668 | -1.837087 | 2.434138 |
| H | 1.053608 | -0.348404 | 3.317562 |
| C | -2.084115 | -0.296122 | 3.116563 |
| H | -3.075616 | -0.237062 | 2.656208 |
| H | -2.151981 | -0.901218 | 4.028055 |
| H | -1.762208 | 0.715655 | 3.382288 |
| C | -4.194013 | -0.859899 | -0.735901 |
| H | -4.319111 | -1.088734 | 0.327685 |
| H | -5.161139 | -0.543793 | -1.143222 |
| H | -3.869281 | -1.767479 | -1.255203 |
| C | -3.118829 | 0.908665 | -2.794866 |
| H | -2.823363 | 0.046289 | -3.401895 |
| H | -4.162801 | 1.157097 | -3.016880 |
| H | -2.486696 | 1.760314 | -3.067434 |
| H | -1.690454 | -3.263491 | 2.729226 |
| H | -2.458823 | -2.817807 | 1.181024 |
| H | -0.797189 | -3.443104 | 1.196006 |
| H | -4.784754 | 2.087890 | -0.524439 |
| H | -3.796145 | 1.838454 | 0.939758 |
| H | -3.203119 | 2.894898 | -0.359289 |
| C | 2.185994 | -3.314412 | -0.612353 |
| H | 1.665946 | -3.252439 | 0.350627 |
| H | 1.819239 | -4.198672 | -1.146347 |
| H | 3.254697 | -3.466303 | -0.416912 |
| C | 2.663698 | -2.119995 | -2.823423 |
| H | 3.749417 | -2.208045 | -2.692663 |
| H | 2.322925 | -2.998573 | -3.383738 |
| H | 2.464298 | -1.229528 | -3.430272 |
| C | 2.540626 | 3.635318 | -0.071765 |
| H | 2.156513 | 4.612515 | 0.243678 |
| H | 3.620700 | 3.623889 | 0.120309 |
| H | 2.385424 | 3.539640 | -1.152425 |
| C | 2.005214 | 2.662690 | 2.231278 |
| H | 1.603933 | 3.628627 | 2.559175 |
| H | 1.478780 | 1.869485 | 2.773605 |
| H | 3.064310 | 2.630966 | 2.515537 |

**TS(Cy)**
B3lyp/lanl2dz optimized geometry

Energy = -1114.394495 a.u.
Enthalpy Correction (inc. ZPVE) = 0.681750
Pd-P Relaxed B3lyp/lanl2dz Energy = -1114.394992
NIMAG = 1

B3lyp/lanl2dzaug:6-311+G(2d,p) single point
Energy = -1784.626306

| Atom | x-coord | y-coord | z-coord |
|---|---|---|---|
| Pd | 0.039431 | 0.860805 | -0.273043 |
| P | -0.105154 | 1.330967 | 2.157686 |
| P | 0.289346 | 3.139095 | -1.220323 |
| C | 0.023370 | -0.539860 | -2.128142 |
| H | -0.812409 | 0.039821 | -2.533492 |
| H | 0.982990 | -0.155174 | -2.486251 |
| H | -0.081799 | -1.569719 | -2.479936 |
| C | -0.052552 | -1.173072 | -0.359214 |
| N | -1.198317 | -1.923940 | -0.078095 |
| N | 1.013005 | -2.017992 | -0.033629 |
| C | -0.838817 | -3.201073 | 0.384911 |
| H | -1.565026 | -3.945960 | 0.664110 |
| C | 0.527917 | -3.258794 | 0.413652 |
| H | 1.176262 | -4.061530 | 0.722266 |
| C | 2.076807 | 3.750687 | -1.329835 |
| C | -1.680470 | 2.218570 | 2.711528 |
| C | -0.064288 | -0.144320 | 3.340912 |
| H | -0.148380 | 0.191266 | 4.381111 |
| H | -0.892581 | -0.822653 | 3.114513 |
| H | 0.873933 | -0.693290 | 3.216038 |
| C | 1.242155 | 2.438946 | 2.888341 |
| H | 1.233843 | 3.412292 | 2.387592 |
| H | 1.079523 | 2.590083 | 3.961782 |
| H | 2.223250 | 1.977541 | 2.737024 |
| C | -0.565703 | 4.621953 | -0.412756 |
| H | -0.184330 | 4.766558 | 0.603616 |
| H | -0.382294 | 5.535323 | -0.990054 |
| H | -1.644992 | 4.444322 | -0.362471 |
| C | -0.284558 | 3.326246 | -3.014056 |
| H | -1.365680 | 3.161374 | -3.073861 |
| H | -0.056685 | 4.328094 | -3.395510 |
| H | 0.216943 | 2.584822 | -3.644893 |
| H | -1.658269 | 2.410314 | 3.790598 |
| H | -1.775558 | 3.170132 | 2.180033 |
| H | -2.552896 | 1.600637 | 2.476259 |
| H | 2.121239 | 4.758023 | -1.759519 |
| H | 2.523688 | 3.766900 | -0.330507 |
| H | 2.659716 | 3.069525 | -1.958594 |
| C | -4.728076 | -1.754433 | -1.659553 |
| C | -3.289396 | -2.270131 | -1.419721 |
| C | -2.592294 | -1.459303 | -0.299554 |
| C | -3.417623 | -1.494752 | 1.009028 |
| C | -4.855888 | -0.978938 | 0.767300 |
| C | -5.560335 | -1.771227 | -0.357499 |
| H | -3.328780 | -3.331141 | -1.130785 |
| H | -2.702840 | -2.211559 | -2.346320 |
| H | -4.688447 | -0.726814 | -2.054429 |

| | | | |
|---|---|---|---|
| H | -5.212978 | -2.368367 | -2.429342 |
| H | -3.464015 | -2.527248 | 1.386748 |
| H | -2.916393 | -0.891658 | 1.778398 |
| H | -5.431744 | -1.048068 | 1.699396 |
| H | -4.821569 | 0.087838 | 0.494043 |
| H | -5.709593 | -2.812364 | -0.032636 |
| H | -6.557628 | -1.352180 | -0.543359 |
| H | -2.506233 | -0.412244 | -0.619695 |
| C | 4.695785 | -1.338612 | 0.952884 |
| C | 3.211455 | -1.729491 | 1.145978 |
| C | 2.449859 | -1.676867 | -0.199939 |
| C | 3.126407 | -2.580333 | -1.259797 |
| C | 4.610083 | -2.188019 | -1.451758 |
| C | 5.382996 | -2.221637 | -0.113742 |
| H | 3.156368 | -2.746923 | 1.561654 |
| H | 2.728431 | -1.056865 | 1.867557 |
| H | 4.759202 | -0.282205 | 0.646763 |
| H | 5.223854 | -1.420961 | 1.911875 |
| H | 3.068843 | -3.630081 | -0.935405 |
| H | 2.585489 | -2.509726 | -2.213038 |
| H | 5.076706 | -2.865879 | -2.178010 |
| H | 4.669153 | -1.175776 | -1.882499 |
| H | 5.436926 | -3.259003 | 0.250541 |
| H | 6.416944 | -1.887010 | -0.267939 |
| H | 2.467293 | -0.638140 | -0.555587 |

**TS(neoPe)**

B3lyp/lanl2dz optimized geometry
Energy = -1038.179941 a.u.
Enthalpy Correction (inc. ZPVE) = 0.664039
Pd-P Relaxed B3lyp/lanl2dz Energy = -1038.180409
NIMAG = 1

B3lyp/lanl2dzaug:6-311+G(2d,p) single point
Energy = -1708.379218

| Atom | x-coord | y-coord | z-coord |
|---|---|---|---|
| C | -2.846102 | 1.833936 | 0.246370 |
| N | -2.232346 | 0.588612 | 0.017672 |
| C | -0.942797 | 0.776670 | -0.504213 |
| N | -0.792818 | 2.171301 | -0.583698 |
| C | -1.967536 | 2.806256 | -0.137239 |
| Pd | 0.578852 | -0.560078 | -0.243701 |
| C | -0.615952 | -0.052159 | -2.160629 |
| C | 0.335207 | 2.879378 | -1.229938 |
| C | -2.783686 | -0.719228 | 0.438185 |
| P | 0.892911 | -0.690544 | 2.212871 |
| C | 0.557191 | -2.402926 | 2.944023 |
| P | 2.338885 | -2.098365 | -1.072168 |
| C | 1.897571 | -2.956332 | -2.701035 |
| C | 2.622881 | -0.322423 | 2.882195 |
| C | -0.182317 | 0.397198 | 3.327708 |
| C | 2.941931 | -3.568630 | -0.044852 |
| C | 3.975196 | -1.258878 | -1.519640 |
| H | 0.278541 | 0.235506 | -2.719807 |

| | | | |
|---|---|---|---|
| H | -0.823671 | -1.121140 | -2.266935 |
| H | -1.466917 | 0.492808 | -2.576883 |
| H | 0.962207 | 2.115725 | -1.699466 |
| H | -0.080415 | 3.513194 | -2.026413 |
| H | -1.981295 | -1.449789 | 0.282493 |
| H | -2.977699 | -0.670424 | 1.520338 |
| H | -2.078927 | 3.876396 | -0.129735 |
| H | -3.828279 | 1.926200 | 0.675036 |
| H | 0.036163 | 0.198487 | 4.383379 |
| H | 0.008664 | 1.453371 | 3.116731 |
| H | -1.239585 | 0.189554 | 3.136979 |
| H | 1.187351 | -3.147984 | 2.450238 |
| H | 0.767795 | -2.411568 | 4.019908 |
| H | -0.491434 | -2.673117 | 2.784394 |
| H | 4.404250 | -0.784528 | -0.631218 |
| H | 4.691129 | -1.986942 | -1.918112 |
| H | 3.797194 | -0.485927 | -2.274525 |
| H | 1.611761 | -2.210627 | -3.450471 |
| H | 2.748087 | -3.533493 | -3.081128 |
| H | 1.051399 | -3.633566 | -2.543188 |
| H | 3.399534 | -3.213474 | 0.884467 |
| H | 2.096369 | -4.218727 | 0.202871 |
| H | 3.684439 | -4.150011 | -0.603152 |
| H | 2.639704 | -0.413801 | 3.974383 |
| H | 2.918461 | 0.692761 | 2.602312 |
| H | 3.344646 | -1.027474 | 2.457069 |
| C | -4.355621 | -2.636758 | 0.330357 |
| C | -4.082330 | -1.228280 | -0.265394 |
| H | -3.521189 | -3.325453 | 0.137488 |
| H | -4.518408 | -2.591252 | 1.416064 |
| H | -5.255689 | -3.071539 | -0.120277 |
| C | -5.303633 | -0.318125 | 0.029631 |
| C | -3.889094 | -1.344129 | -1.795849 |
| H | -5.239232 | 0.641754 | -0.496214 |
| H | -6.222804 | -0.809228 | -0.312428 |
| H | -5.415798 | -0.124708 | 1.105885 |
| H | -4.804194 | -1.728411 | -2.262844 |
| H | -3.671701 | -0.368683 | -2.248572 |
| H | -3.073777 | -2.035620 | -2.048015 |
| C | 2.335928 | 4.351722 | -1.265623 |
| C | 1.253165 | 3.759633 | -0.323256 |
| H | 2.917038 | 3.560978 | -1.760243 |
| H | 1.888872 | 4.983640 | -2.044894 |
| H | 3.037243 | 4.973717 | -0.696750 |
| C | 0.476315 | 4.923322 | 0.342796 |
| C | 1.927782 | 2.895012 | 0.765074 |
| H | -0.233577 | 4.564944 | 1.097811 |
| H | 1.177549 | 5.596206 | 0.851770 |
| H | -0.071571 | 5.521296 | -0.398879 |
| H | 2.606799 | 3.507098 | 1.372441 |
| H | 1.177746 | 2.451967 | 1.430790 |
| H | 2.510636 | 2.078145 | 0.317173 |

**TS(tBu)**
B3lyp/lanl2dz optimized geometry

Energy = -959.556957 a.u.
Enthalpy Correction (inc. ZPVE) = 0.603369
Pd-P Relaxed B3lyp/lanl2dz Energy = -959.5572842
NIMAG = 1

B3lyp/lanl2dzaug:6-311+G(2d,p) single point
Energy = -1629.718186

| Atom | x-coord | y-coord | z-coord |
|---|---|---|---|
| Pd | 0.648521 | 0.008200 | -0.240693 |
| P | 0.948862 | -0.148073 | 2.216089 |
| P | 2.989895 | 0.060955 | -1.056527 |
| C | -0.654142 | 0.108111 | -2.177742 |
| H | -0.141208 | 1.017289 | -2.500679 |
| H | -0.160948 | -0.779654 | -2.581587 |
| H | -1.673510 | 0.136338 | -2.572483 |
| C | -1.386616 | 0.031678 | -0.426913 |
| N | -2.195231 | 1.146002 | -0.103988 |
| C | -1.926452 | 2.634364 | -0.280160 |
| N | -2.218163 | -1.090784 | -0.208675 |
| C | -1.972782 | -2.561624 | -0.515083 |
| C | -3.487811 | 0.702308 | 0.240136 |
| H | -4.280511 | 1.370335 | 0.524270 |
| C | -3.501699 | -0.655001 | 0.176418 |
| H | -4.308110 | -1.330000 | 0.398508 |
| C | 3.776273 | -1.617725 | -1.436005 |
| C | 1.754393 | 1.332208 | 3.076345 |
| C | -0.630932 | -0.361887 | 3.233420 |
| H | -0.405074 | -0.388227 | 4.305597 |
| H | -1.313994 | 0.468274 | 3.027862 |
| H | -1.129156 | -1.293723 | 2.948561 |
| C | 2.014241 | -1.575492 | 2.853984 |
| H | 3.032020 | -1.480602 | 2.461940 |
| H | 2.053643 | -1.570616 | 3.949352 |
| H | 1.600296 | -2.531042 | 2.516704 |
| C | 4.336356 | 0.876049 | -0.006638 |
| H | 4.458045 | 0.327539 | 0.933589 |
| H | 5.294544 | 0.878938 | -0.538549 |
| H | 4.052643 | 1.908557 | 0.221790 |
| C | 3.218821 | 0.962192 | -2.705900 |
| H | 2.957123 | 2.019209 | -2.588214 |
| H | 4.256832 | 0.889562 | -3.050054 |
| H | 2.562721 | 0.522183 | -3.464655 |
| H | 1.858158 | 1.144457 | 4.151311 |
| H | 2.743895 | 1.516741 | 2.647756 |
| H | 1.140431 | 2.226705 | 2.930549 |
| H | 4.793105 | -1.492423 | -1.825164 |
| H | 3.813589 | -2.224363 | -0.525507 |
| H | 3.172825 | -2.147369 | -2.180665 |
| C | -2.689413 | 3.405984 | 0.831916 |
| H | -2.471088 | 2.993988 | 1.824269 |
| H | -2.367524 | 4.452920 | 0.819303 |
| H | -3.774057 | 3.406382 | 0.681283 |
| C | -2.461359 | 3.077385 | -1.669193 |
| H | -3.513315 | 2.794461 | -1.793791 |
| H | -2.391963 | 4.167947 | -1.760554 |

| | | | |
|---|---|---|---|
| H | -1.886769 | 2.634601 | -2.488972 |
| C | -2.479410 | -2.866482 | -1.951188 |
| H | -2.431834 | -3.945942 | -2.138021 |
| H | -3.521516 | -2.548626 | -2.074856 |
| H | -1.874702 | -2.366891 | -2.714268 |
| C | -2.779510 | -3.417628 | 0.500127 |
| H | -2.472305 | -4.464274 | 0.400505 |
| H | -2.585203 | -3.102575 | 1.532220 |
| H | -3.859098 | -3.385894 | 0.318897 |
| C | -0.486962 | -2.952002 | -0.370449 |
| H | -0.382728 | -4.010609 | -0.637294 |
| H | 0.174803 | -2.375745 | -1.022376 |
| H | -0.142707 | -2.825131 | 0.661510 |
| C | -0.430292 | 2.985346 | -0.142353 |
| H | 0.200427 | 2.467302 | -0.868983 |
| H | -0.315683 | 4.063512 | -0.307060 |
| H | -0.057884 | 2.752826 | 0.860717 |

## 6. N-Substituted Products

**PR(H)**
B3lyp/lanl2dz optimized geometry
Energy = -645.147702 a.u.
Enthalpy Correction (inc. ZPVE) = 0.369981
NIMAG = 0

B3lyp/lanl2dzaug:6-311+G(2d,p) single point
Energy = -1315.170628

| Atom | x-coord | y-coord | z-coord |
|---|---|---|---|
| Pd | -0.049441 | -0.313785 | 0.052669 |
| P | 2.290171 | -1.132430 | -0.027571 |
| P | -2.480020 | -0.774196 | -0.122556 |
| C | -0.634910 | 1.836090 | 1.998909 |
| H | -1.669241 | 1.489695 | 1.944873 |
| H | -0.082779 | 1.136928 | 2.633769 |
| H | -0.622256 | 2.829897 | 2.470198 |
| C | -0.014360 | 1.914880 | 0.611284 |
| N | -0.668278 | 2.553511 | -0.453071 |
| N | 1.313239 | 2.339502 | 0.461017 |
| C | 0.246694 | 3.184820 | -1.303909 |
| H | -0.045016 | 3.661950 | -2.224557 |
| C | 1.486593 | 3.055875 | -0.730231 |
| H | 2.446337 | 3.410975 | -1.066575 |
| C | -3.332697 | -1.377351 | 1.453911 |
| C | 3.274551 | -0.732028 | -1.591844 |
| C | 3.532191 | -0.681965 | 1.330544 |
| H | 4.466997 | -1.238382 | 1.196753 |
| H | 3.765758 | 0.388948 | 1.297767 |
| H | 3.113192 | -0.924206 | 2.312388 |
| C | 2.375518 | -3.020073 | 0.008839 |
| H | 1.784048 | -3.426526 | -0.817476 |
| H | 3.411409 | -3.366472 | -0.085770 |

| | | | |
|---|---|---|---|
| H | 1.956334 | -3.388302 | 0.950427 |
| C | -2.830324 | -2.193358 | -1.320301 |
| H | -2.282785 | -3.084423 | -0.997968 |
| H | -3.902203 | -2.421269 | -1.349649 |
| H | -2.490494 | -1.921139 | -2.324313 |
| C | -3.710030 | 0.533570 | -0.737306 |
| H | -3.408427 | 0.891131 | -1.728328 |
| H | -4.716474 | 0.107100 | -0.816070 |
| H | -3.756472 | 1.377960 | -0.038420 |
| H | 4.273720 | -1.181136 | -1.550895 |
| H | 2.741474 | -1.123521 | -2.463941 |
| H | 3.370873 | 0.352393 | -1.706640 |
| H | -4.372199 | -1.660043 | 1.251342 |
| H | -2.794385 | -2.246240 | 1.844945 |
| H | -3.318791 | -0.592231 | 2.217184 |
| H | -1.661929 | 2.473817 | -0.619352 |
| H | 2.041230 | 2.112756 | 1.124447 |

**PR(Ph)**

B3lyp/lanl2dz optimized geometry
Energy = -1107.181159 a.u.
Enthalpy Correction (inc. ZPVE) = 0.540573
NIMAG = 0

B3lyp/lanl2dzaug:6-311+G(2d,p) single point
Energy = -1777.400980

| Atom | x-coord | y-coord | z-coord |
|---|---|---|---|
| Pd | 1.694169 | -0.297676 | 0.486752 |
| P | 0.732099 | -0.154937 | 2.768078 |
| P | 3.216824 | -0.530736 | -1.456854 |
| C | -0.835259 | 0.152946 | -1.871741 |
| H | -0.743484 | 1.043325 | -2.500266 |
| H | 0.136591 | -0.008590 | -1.352339 |
| H | -1.036885 | -0.720377 | -2.498748 |
| C | -1.909398 | 0.333402 | -0.864418 |
| N | -2.309438 | 1.515745 | -0.305272 |
| N | -2.686691 | -0.650072 | -0.317512 |
| C | -3.369753 | 1.275005 | 0.586578 |
| H | -3.828819 | 2.067385 | 1.153137 |
| C | -3.604940 | -0.074801 | 0.578894 |
| H | -4.305706 | -0.671640 | 1.137814 |
| C | 2.859107 | -1.863972 | -2.752239 |
| C | -0.082403 | 1.451970 | 3.352626 |
| C | -0.549201 | -1.434818 | 3.323515 |
| H | -0.794140 | -1.307041 | 4.384799 |
| H | -1.463350 | -1.330349 | 2.729150 |
| H | -0.148168 | -2.441262 | 3.167326 |
| C | 2.071295 | -0.384338 | 4.082899 |
| H | 2.830384 | 0.395370 | 3.966718 |
| H | 1.645820 | -0.330218 | 5.092221 |
| H | 2.553651 | -1.356719 | 3.943809 |
| C | 4.983314 | -0.968833 | -0.946982 |
| H | 4.978640 | -1.918423 | -0.402798 |
| H | 5.636114 | -1.055613 | -1.823862 |

| | | | |
|---|---|---|---|
| H | 5.371796 | -0.192125 | -0.280992 |
| C | 3.505939 | 0.985311 | -2.551829 |
| H | 3.871111 | 1.812687 | -1.934998 |
| H | 4.242554 | 0.769321 | -3.334850 |
| H | 2.564085 | 1.289843 | -3.020614 |
| H | -0.347253 | 1.390777 | 4.415044 |
| H | 0.610202 | 2.286514 | 3.204182 |
| H | -0.988733 | 1.645011 | 2.768614 |
| H | 3.645152 | -1.888321 | -3.516313 |
| H | 2.806054 | -2.841245 | -2.261844 |
| H | 1.897001 | -1.664243 | -3.236216 |
| C | -1.726775 | 2.822491 | -0.554793 |
| C | -0.344621 | 3.013526 | -0.368046 |
| C | 0.195366 | 4.293030 | -0.588807 |
| C | -0.636101 | 5.362124 | -0.976536 |
| C | -2.018416 | 5.153644 | -1.152343 |
| C | -2.571793 | 3.877792 | -0.945186 |
| H | 0.294434 | 2.189260 | -0.047924 |
| H | 1.260230 | 4.454113 | -0.447100 |
| H | -0.212059 | 6.348913 | -1.139309 |
| H | -2.660173 | 5.975632 | -1.455747 |
| H | -3.633883 | 3.705775 | -1.099854 |
| C | -2.579507 | -2.074141 | -0.581654 |
| C | -1.345514 | -2.724645 | -0.391547 |
| C | -1.269725 | -4.109020 | -0.627060 |
| C | -2.411206 | -4.828237 | -1.032490 |
| C | -3.639459 | -4.161365 | -1.211005 |
| C | -3.729064 | -2.775760 | -0.989269 |
| H | -0.467494 | -2.169768 | -0.057046 |
| H | -0.324058 | -4.623538 | -0.482411 |
| H | -2.345659 | -5.898480 | -1.206688 |
| H | -4.519454 | -4.713490 | -1.527815 |
| H | -4.668520 | -2.251891 | -1.145969 |

**PR(Me)**

B3lyp/lanl2dz optimized geometry
Energy = -723.764941 a.u.
Enthalpy Correction (inc. ZPVE) = 0.429433
NIMAG = 0

B3lyp/lanl2dzaug:6-311+G(2d,p) single point
Energy = -1393.824778

| Atom | x-coord | y-coord | z-coord |
|---|---|---|---|
| Pd | -1.138413 | 0.455693 | -0.025647 |
| P | 0.186525 | 2.552092 | -0.018634 |
| P | -2.968452 | -1.217264 | -0.076381 |
| C | 1.326480 | -1.728907 | -1.153307 |
| H | 0.509123 | -0.998270 | -0.948076 |
| H | 1.614988 | -1.640131 | -2.203367 |
| H | 0.911062 | -2.732436 | -0.993199 |
| C | 2.481117 | -1.478543 | -0.249338 |
| N | 2.417793 | -1.362922 | 1.108503 |
| C | 1.181449 | -1.481182 | 1.915085 |
| H | 0.378016 | -0.880464 | 1.454186 |

| | | | |
|---|---|---|---|
| H | 0.873815 | -2.530149 | 1.981133 |
| H | 1.381632 | -1.100791 | 2.919199 |
| N | 3.789518 | -1.307869 | -0.606446 |
| C | 4.318117 | -1.348470 | -1.985888 |
| H | 3.911623 | -0.522608 | -2.577040 |
| H | 5.404790 | -1.251820 | -1.946677 |
| H | 4.068187 | -2.300478 | -2.462276 |
| C | 3.700252 | -1.120361 | 1.615157 |
| H | 3.892207 | -1.000226 | 2.668259 |
| C | 4.558905 | -1.082641 | 0.543505 |
| H | 5.623179 | -0.920854 | 0.505711 |
| C | -3.405423 | -1.964784 | -1.758697 |
| C | 0.219754 | 3.503236 | 1.616761 |
| C | 2.022968 | 2.587585 | -0.495598 |
| H | 2.415310 | 3.610800 | -0.457142 |
| H | 2.598937 | 1.961555 | 0.195506 |
| H | 2.141247 | 2.201146 | -1.513957 |
| C | -0.513058 | 3.855769 | -1.195946 |
| H | -1.560512 | 4.044260 | -0.941252 |
| H | 0.050905 | 4.793771 | -1.126490 |
| H | -0.472621 | 3.481692 | -2.223763 |
| C | -4.627999 | -0.480564 | 0.449408 |
| H | -4.871664 | 0.363733 | -0.202841 |
| H | -5.427050 | -1.229125 | 0.387913 |
| H | -4.554554 | -0.111674 | 1.477156 |
| C | -2.896735 | -2.767811 | 1.010176 |
| H | -2.776570 | -2.473750 | 2.058047 |
| H | -3.815588 | -3.357554 | 0.908781 |
| H | -2.043611 | -3.390113 | 0.718090 |
| H | 0.728682 | 4.467687 | 1.500477 |
| H | -0.807503 | 3.676093 | 1.952126 |
| H | 0.734805 | 2.912249 | 2.381270 |
| H | -4.290633 | -2.607758 | -1.684032 |
| H | -3.605201 | -1.157923 | -2.470727 |
| H | -2.563232 | -2.555617 | -2.134325 |

**PR(iPr)**

B3lyp/lanl2dz optimized geometry
Energy = -881.005378 a.u.
Enthalpy Correction (inc. ZPVE) = 0.548453
NIMAG = 0

B3lyp/lanl2dzaug:6-311+G(2d,p) single point
Energy = -1551.134858

| Atom | x-coord | y-coord | z-coord |
|---|---|---|---|
| Pd | -1.610928 | 0.475724 | 0.029407 |
| P | -0.656173 | 2.594693 | -0.835933 |
| P | -3.202637 | -1.263060 | 0.799791 |
| C | 1.018733 | -1.324965 | 1.302990 |
| H | 1.190722 | -0.990855 | 2.328054 |
| H | 0.149080 | -0.740878 | 0.899770 |
| H | 0.721250 | -2.379385 | 1.333941 |
| C | 2.223387 | -1.128433 | 0.454344 |
| N | 3.337177 | -0.394621 | 0.765696 |

| | | | |
|---|---|---|---|
| C | 3.564097 | 0.335647 | 2.062145 |
| H | 3.122415 | -0.296088 | 2.841204 |
| N | 2.387300 | -1.598966 | -0.818724 |
| C | 1.386886 | -2.416707 | -1.589307 |
| H | 0.729047 | -2.864175 | -0.837126 |
| C | 4.205276 | -0.396601 | -0.334886 |
| H | 5.155454 | 0.107364 | -0.330571 |
| C | 3.613676 | -1.146120 | -1.319423 |
| H | 3.968696 | -1.392424 | -2.305075 |
| C | -3.193266 | -2.980879 | 0.000755 |
| C | -0.509062 | 4.015017 | 0.406390 |
| C | 1.033302 | 2.680108 | -1.692905 |
| H | 1.243017 | 3.698452 | -2.041517 |
| H | 1.819753 | 2.371192 | -0.995937 |
| H | 1.038611 | 2.001045 | -2.551915 |
| C | -1.761691 | 3.374155 | -2.158177 |
| H | -2.767548 | 3.513679 | -1.750390 |
| H | -1.364187 | 4.343284 | -2.483224 |
| H | -1.831009 | 2.701906 | -3.019155 |
| C | -4.999763 | -0.743620 | 0.525314 |
| H | -5.170318 | -0.575079 | -0.542578 |
| H | -5.691853 | -1.513700 | 0.886959 |
| H | -5.190047 | 0.193755 | 1.057040 |
| C | -3.223564 | -1.713307 | 2.638514 |
| H | -3.376231 | -0.805138 | 3.230226 |
| H | -4.027083 | -2.426274 | 2.859031 |
| H | -2.263487 | -2.155787 | 2.925290 |
| H | -0.196737 | 4.941832 | -0.090013 |
| H | -1.480056 | 4.172701 | 0.886007 |
| H | 0.218715 | 3.757868 | 1.183082 |
| H | -4.018382 | -3.593892 | 0.382694 |
| H | -3.296559 | -2.877100 | -1.084218 |
| H | -2.245987 | -3.487228 | 0.216838 |
| C | 2.836898 | 1.696346 | 2.035728 |
| H | 1.764851 | 1.579270 | 1.838199 |
| H | 2.952601 | 2.191937 | 3.006386 |
| H | 3.266268 | 2.351695 | 1.267946 |
| C | 5.067062 | 0.477918 | 2.358112 |
| H | 5.557117 | 1.179576 | 1.672360 |
| H | 5.188808 | 0.878273 | 3.370102 |
| H | 5.585270 | -0.486848 | 2.314052 |
| C | 2.094041 | -3.548338 | -2.358061 |
| H | 1.335910 | -4.214592 | -2.783575 |
| H | 2.692407 | -3.166318 | -3.193855 |
| H | 2.740897 | -4.143476 | -1.703072 |
| C | 0.545038 | -1.500920 | -2.501883 |
| H | -0.163482 | -2.112185 | -3.073146 |
| H | -0.033530 | -0.774585 | -1.913543 |
| H | 1.182806 | -0.966324 | -3.217547 |

**PR(Cy)**

B3lyp/lanl2dz optimized geometry
Energy = -1114.438821 a.u.
Enthalpy Correction (inc. ZPVE) = 0.685533
NIMAG = 0

B3lyp/lanl2dzaug:6-311+G(2d,p) single point
Energy = -1784.670897

| Atom | x-coord | y-coord | z-coord |
|---|---|---|---|
| Pd | -1.500614 | -1.383484 | 0.270417 |
| P | -0.685283 | -1.304812 | 2.611239 |
| P | -2.790752 | -1.925597 | -1.777033 |
| C | 0.548363 | 0.517341 | -1.700702 |
| H | -0.129020 | 1.111524 | -2.321113 |
| H | 1.109986 | -0.156397 | -2.352776 |
| H | -0.088373 | -0.118047 | -1.028387 |
| C | 1.453709 | 1.386091 | -0.906811 |
| N | 2.737327 | 1.094324 | -0.532010 |
| N | 1.127249 | 2.593930 | -0.352881 |
| C | 3.219277 | 2.130868 | 0.277808 |
| H | 4.211911 | 2.135683 | 0.691402 |
| C | 2.218490 | 3.062516 | 0.388807 |
| H | 2.207677 | 4.000811 | 0.914224 |
| C | -3.736067 | -0.544830 | -2.663418 |
| C | 0.095850 | -2.912982 | 3.230963 |
| C | 0.567668 | -0.030649 | 3.246383 |
| H | 0.748137 | -0.165962 | 4.319652 |
| H | 1.514875 | -0.144095 | 2.708815 |
| H | 0.182617 | 0.979736 | 3.074317 |
| C | -2.087527 | -1.073201 | 3.860206 |
| H | -2.838445 | -1.854053 | 3.705348 |
| H | -1.712070 | -1.130138 | 4.889213 |
| H | -2.565762 | -0.101519 | 3.700906 |
| C | -4.178772 | -3.165036 | -1.443660 |
| H | -4.868694 | -2.746627 | -0.704122 |
| H | -4.728552 | -3.397014 | -2.363780 |
| H | -3.751579 | -4.085667 | -1.034232 |
| C | -1.899514 | -2.752650 | -3.228694 |
| H | -1.401300 | -3.661134 | -2.875341 |
| H | -2.606028 | -3.016295 | -4.025008 |
| H | -1.140176 | -2.075718 | -3.635254 |
| H | 0.323492 | -2.853124 | 4.302169 |
| H | -0.599184 | -3.739814 | 3.055052 |
| H | 1.016989 | -3.115655 | 2.675009 |
| H | -4.327679 | -0.945046 | -3.495500 |
| H | -4.405293 | -0.050989 | -1.951651 |
| H | -3.031024 | 0.198048 | -3.052304 |
| C | 5.712158 | -1.240229 | -1.372560 |
| C | 5.001847 | 0.065864 | -0.941667 |
| C | 3.477081 | -0.163987 | -0.883555 |
| C | 3.111279 | -1.308433 | 0.093239 |
| C | 3.835044 | -2.613625 | -0.316364 |
| C | 5.363400 | -2.411159 | -0.425455 |
| H | 5.378732 | 0.352764 | 0.051160 |
| H | 5.239233 | 0.881226 | -1.638052 |
| H | 5.419315 | -1.497159 | -2.401972 |
| H | 6.796280 | -1.072757 | -1.386918 |
| H | 3.420270 | -1.017440 | 1.108929 |
| H | 2.023859 | -1.463962 | 0.109679 |
| H | 3.606041 | -3.399702 | 0.414358 |
| H | 3.440967 | -2.961601 | -1.283824 |

| | | | |
|---|---|---|---|
| H | 5.778500 | -2.207763 | 0.573545 |
| H | 5.837856 | -3.333752 | -0.782793 |
| H | 3.141960 | -0.442144 | -1.891537 |
| C | -2.585579 | 3.386500 | 0.413833 |
| C | -1.197571 | 2.725871 | 0.591965 |
| C | -0.210655 | 3.265542 | -0.472380 |
| C | -0.086349 | 4.802610 | -0.406255 |
| C | -1.478512 | 5.447849 | -0.611008 |
| C | -2.498054 | 4.929481 | 0.429175 |
| H | -0.801312 | 2.958398 | 1.592236 |
| H | -1.290308 | 1.632925 | 0.512845 |
| H | -3.025900 | 3.053247 | -0.538926 |
| H | -3.257012 | 3.034248 | 1.207069 |
| H | 0.295194 | 5.108896 | 0.578949 |
| H | 0.621117 | 5.162356 | -1.165526 |
| H | -1.384318 | 6.538706 | -0.541385 |
| H | -1.840557 | 5.226385 | -1.626648 |
| H | -2.199620 | 5.270092 | 1.432475 |
| H | -3.486563 | 5.362455 | 0.230015 |
| H | -0.592914 | 3.002166 | -1.467469 |

**PR(neoPe)**

B3lyp/lanl2dz optimized geometry
Energy = -1038.230299 a.u.
Enthalpy Correction (inc. ZPVE) = 0.667236
NIMAG = 0

B3lyp/lanl2dzaug:6-311+G(2d,p) single point
Energy = -1708.430288

| Atom | x-coord | y-coord | z-coord |
|---|---|---|---|
| C | -2.885955 | 1.763222 | -1.544668 |
| N | -1.705344 | 1.482877 | -0.844172 |
| C | -2.020450 | 0.874609 | 0.339065 |
| N | -3.385758 | 0.772843 | 0.391622 |
| C | -3.931876 | 1.323738 | -0.775878 |
| Pd | 1.975228 | -0.778208 | 0.009076 |
| C | -1.054441 | 0.422367 | 1.381607 |
| C | -4.199772 | 0.217796 | 1.508902 |
| C | -0.337693 | 1.803222 | -1.347732 |
| P | 1.185705 | -2.200257 | -1.863043 |
| C | 1.914578 | -1.784391 | -3.559569 |
| P | 3.387975 | 0.151435 | 1.822997 |
| C | 3.570812 | 2.017167 | 2.101210 |
| C | 1.707098 | -4.007748 | -1.668341 |
| C | -0.648500 | -2.407511 | -2.302142 |
| C | 5.196944 | -0.358142 | 1.610438 |
| C | 3.039759 | -0.447289 | 3.584709 |
| H | -0.142423 | -0.018536 | 0.927885 |
| H | -0.731890 | 1.263808 | 2.006971 |
| H | -1.501005 | -0.337118 | 2.025255 |
| H | -3.594189 | 0.272325 | 2.418671 |
| H | -5.052198 | 0.894501 | 1.641323 |
| H | 0.373529 | 1.118991 | -0.859840 |
| H | -0.338692 | 1.565364 | -2.418575 |

| | | | |
|---|---|---|---|
| H | -4.992779 | 1.361915 | -0.952889 |
| H | -2.881575 | 2.236289 | -2.511448 |
| H | -0.770632 | -3.087928 | -3.153561 |
| H | -1.185848 | -2.817686 | -1.440225 |
| H | -1.081827 | -1.434858 | -2.560543 |
| H | 3.006388 | -1.768275 | -3.486303 |
| H | 1.613693 | -2.524625 | -4.310838 |
| H | 1.578583 | -0.791162 | -3.875418 |
| H | 3.050331 | -1.541674 | 3.602014 |
| H | 3.794398 | -0.068012 | 4.284193 |
| H | 2.049560 | -0.105669 | 3.904715 |
| H | 2.611881 | 2.444673 | 2.413650 |
| H | 4.319998 | 2.223388 | 2.874944 |
| H | 3.879622 | 2.497146 | 1.166782 |
| H | 5.262195 | -1.449702 | 1.567209 |
| H | 5.581414 | 0.047484 | 0.669402 |
| H | 5.809277 | 0.010563 | 2.442298 |
| H | 1.411818 | -4.599830 | -2.543073 |
| H | 1.242595 | -4.427822 | -0.770670 |
| H | 2.793688 | -4.056796 | -1.547684 |
| C | 1.578561 | 3.334018 | -1.684505 |
| C | 0.121678 | 3.281138 | -1.150553 |
| H | 2.221949 | 2.620586 | -1.153084 |
| H | 1.622527 | 3.097312 | -2.756275 |
| H | 1.994640 | 4.339576 | -1.550029 |
| C | -0.759425 | 4.267475 | -1.958131 |
| C | 0.101926 | 3.673091 | 0.346894 |
| H | -1.787151 | 4.314205 | -1.575858 |
| H | -0.344059 | 5.280127 | -1.889637 |
| H | -0.792992 | 3.999115 | -3.023526 |
| H | 0.478131 | 4.695645 | 0.471676 |
| H | -0.914718 | 3.648967 | 0.763294 |
| H | 0.742495 | 3.007871 | 0.939120 |
| C | -5.532521 | -1.573697 | 2.595525 |
| C | -4.724449 | -1.239911 | 1.312431 |
| H | -4.909221 | -1.505103 | 3.497267 |
| H | -6.389849 | -0.898773 | 2.719758 |
| H | -5.922405 | -2.596660 | 2.539491 |
| C | -5.658436 | -1.338941 | 0.079972 |
| C | -3.551879 | -2.239771 | 1.160781 |
| H | -5.118604 | -1.180793 | -0.861976 |
| H | -6.105699 | -2.338819 | 0.032642 |
| H | -6.482917 | -0.614611 | 0.138822 |
| H | -3.942783 | -3.254726 | 1.021512 |
| H | -2.925507 | -2.007321 | 0.288994 |
| H | -2.913464 | -2.256141 | 2.054534 |

**PR(tBu)**
B3lyp/lanl2dz optimized geometry
Energy = -959.604965 a.u.
Enthalpy Correction (inc. ZPVE) = 0.608262
NIMAG = 0

B3lyp/lanl2dzaug:6-311+G(2d,p) single point
Energy = -1629.766915

| Atom | x-coord | y-coord | z-coord |
|---|---|---|---|
| Pd | 1.612724 | 0.291396 | -0.013929 |
| P | 1.242272 | 2.728709 | -0.283508 |
| P | 2.798445 | -1.876774 | 0.194645 |
| C | -1.800120 | -2.314961 | 0.309518 |
| H | -1.181686 | -2.652902 | -0.518720 |
| H | -1.208355 | -2.409905 | 1.217077 |
| H | -2.664888 | -2.985636 | 0.391906 |
| C | -2.240624 | -0.899052 | 0.107069 |
| N | -2.504168 | -0.300698 | -1.099043 |
| C | -2.324546 | -0.894899 | -2.506878 |
| N | -2.514178 | 0.008593 | 1.098563 |
| C | -2.336813 | -0.169489 | 2.616587 |
| C | -2.947303 | 1.003438 | -0.854802 |
| H | -3.221191 | 1.688339 | -1.634459 |
| C | -2.953864 | 1.194154 | 0.499668 |
| H | -3.237480 | 2.066477 | 1.056849 |
| C | 3.375153 | -2.363888 | 1.931216 |
| C | 0.467515 | 3.378267 | -1.886686 |
| C | 0.265564 | 3.710904 | 1.011003 |
| H | 0.292018 | 4.785339 | 0.792506 |
| H | -0.775821 | 3.371923 | 1.020609 |
| H | 0.702187 | 3.535510 | 1.999682 |
| C | 2.881915 | 3.672058 | -0.275333 |
| H | 3.519909 | 3.295086 | -1.080597 |
| H | 2.718322 | 4.747773 | -0.413297 |
| H | 3.393638 | 3.500928 | 0.676848 |
| C | 4.442673 | -1.848149 | -0.740191 |
| H | 5.045723 | -1.009172 | -0.379682 |
| H | 4.997096 | -2.783325 | -0.594548 |
| H | 4.253024 | -1.700648 | -1.808076 |
| C | 2.080193 | -3.524343 | -0.415404 |
| H | 1.781274 | -3.426747 | -1.464668 |
| H | 2.822558 | -4.326987 | -0.330323 |
| H | 1.202375 | -3.793260 | 0.182560 |
| H | 0.478066 | 4.474710 | -1.914216 |
| H | 1.033949 | 2.992582 | -2.740461 |
| H | -0.566889 | 3.026506 | -1.965825 |
| H | 3.996060 | -3.267426 | 1.900694 |
| H | 3.956906 | -1.541436 | 2.359231 |
| H | 2.508513 | -2.544218 | 2.576110 |
| C | -2.714935 | 0.182345 | -3.545912 |
| H | -2.046728 | 1.050841 | -3.511327 |
| H | -2.620910 | -0.261742 | -4.541494 |
| H | -3.754300 | 0.513684 | -3.437048 |
| C | -3.277254 | -2.104793 | -2.664455 |
| H | -4.323305 | -1.803644 | -2.533253 |
| H | -3.166346 | -2.513694 | -3.675044 |
| H | -3.055732 | -2.912147 | -1.961212 |
| C | -3.281346 | -1.294964 | 3.104362 |
| H | -3.164162 | -1.409709 | 4.187844 |
| H | -4.329839 | -1.046760 | 2.901132 |
| H | -3.058314 | -2.263610 | 2.649115 |
| C | -2.741568 | 1.150905 | 3.314034 |
| H | -2.650587 | 1.001293 | 4.394226 |
| H | -2.079383 | 1.981412 | 3.043125 |

| | | | |
|---|---|---|---|
| H | -3.782625 | 1.429535 | 3.112897 |
| C | -0.844030 | -0.464772 | 2.933805 |
| H | -0.628132 | -0.144782 | 3.958943 |
| H | -0.604695 | -1.531294 | 2.878969 |
| H | -0.168644 | 0.071534 | 2.252214 |
| C | -0.834422 | -1.280786 | -2.720708 |
| H | -0.607882 | -2.290576 | -2.365679 |
| H | -0.611039 | -1.264539 | -3.793033 |
| H | -0.157443 | -0.579660 | -2.213879 |

## 7. N-Substituted Separated Products

**Pdbis(TMP)**
B3lyp/lanl2dz optimized geometry
Energy = -379.246117 a.u.
Enthalpy Correction (inc. ZPVE) = 0.249051
NIMAG = 0

B3lyp/lanl2dzaug:6-311+G(2d,p) single point
Energy = -1049.160267

| Atom | x-coord | y-coord | z-coord |
|---|---|---|---|
| C | -3.348744 | 1.630737 | -0.420653 |
| H | -4.440506 | 1.518720 | -0.401051 |
| H | -3.048051 | 2.394509 | 0.304007 |
| P | -2.480045 | -0.000544 | -0.001396 |
| C | -3.326971 | -1.177017 | -1.222128 |
| H | -3.017379 | -2.204297 | -1.003478 |
| H | -4.420171 | -1.103125 | -1.155617 |
| H | -3.006028 | -0.931418 | -2.239726 |
| C | -3.364813 | -0.468119 | 1.608023 |
| H | -4.455430 | -0.442636 | 1.485677 |
| H | -3.055370 | -1.474443 | 1.908845 |
| H | -3.070102 | 0.231642 | 2.396964 |
| H | -3.034049 | 1.960029 | -1.416373 |
| Pd | -0.000114 | 0.006385 | 0.015679 |
| P | 2.479824 | -0.000704 | -0.000385 |
| C | 3.343947 | 1.529223 | -0.710297 |
| H | 3.047181 | 2.410491 | -0.132186 |
| H | 4.435905 | 1.422099 | -0.678381 |
| H | 3.022094 | 1.674520 | -1.746710 |
| C | 3.327064 | -1.376047 | -0.991977 |
| H | 3.020947 | -2.348073 | -0.591529 |
| H | 3.003082 | -1.317951 | -2.036257 |
| H | 4.420247 | -1.288759 | -0.943004 |
| C | 3.370344 | -0.167688 | 1.663985 |
| H | 3.076198 | 0.662797 | 2.314170 |
| H | 3.064587 | -1.103466 | 2.143280 |
| H | 4.460424 | -0.162179 | 1.535120 |

**Pdbis(TMP)-Relaxed Pd-P Bonds**
B3lyp/lanl2dz optimized geometry

Energy = -379.248794 a.u.

| Atom | x-coord | y-coord | z-coord |
|---|---|---|---|
| Pd | 0.000039 | 0.000367 | 0.002350 |
| P | 2.381198 | -0.000132 | -0.000159 |
| P | -2.381117 | -0.000116 | -0.000323 |
| C | 3.248842 | 1.614397 | -0.484148 |
| H | 2.938061 | 1.899821 | -1.494525 |
| H | 2.942075 | 2.407278 | 0.205899 |
| H | 4.340727 | 1.505999 | -0.454372 |
| C | 3.254174 | -0.389686 | 1.636941 |
| H | 2.950446 | -1.385006 | 1.977593 |
| H | 4.345655 | -0.359244 | 1.524701 |
| H | 2.944355 | 0.340561 | 2.391700 |
| C | 3.249352 | -1.224434 | -1.158222 |
| H | 2.940561 | -2.242794 | -0.900329 |
| H | 2.941111 | -1.023257 | -2.189441 |
| H | 4.341246 | -1.142643 | -1.080401 |
| C | -3.253356 | -0.598776 | 1.572734 |
| H | -2.948792 | -1.629483 | 1.782047 |
| H | -2.943750 | 0.028210 | 2.415319 |
| H | -4.344940 | -0.554591 | 1.465644 |
| C | -3.251614 | 1.662209 | -0.270471 |
| H | -4.343251 | 1.547916 | -0.258851 |
| H | -2.949421 | 2.358016 | 0.519127 |
| H | -2.938536 | 2.079197 | -1.233269 |
| C | -3.247679 | -1.065129 | -1.307481 |
| H | -2.940603 | -0.730453 | -2.303786 |
| H | -2.936677 | -2.107794 | -1.185050 |
| H | -4.339603 | -0.996361 | -1.219018 |

**CB2Me$^+$(Cl)**

B3lyp/6-31G(d) optimized geometry
Energy = -1184.997622 a.u.
Enthalpy Correction (inc. ZPVE) = 0.100614
NIMAG = 0

B3lyp/6-311+G(2d,p) single point
Energy = -1185.130964

| Atom | x-coord | y-coord | z-coord |
|---|---|---|---|
| N | 1.072189 | -0.307479 | -0.000017 |
| C | -0.003314 | 0.511115 | -0.000009 |
| N | -1.063670 | -0.326607 | 0.000000 |
| C | 0.693519 | -1.642977 | -0.000014 |
| C | -0.665075 | -1.655113 | -0.000005 |
| H | 1.417021 | -2.443405 | -0.000017 |
| H | -1.374827 | -2.467842 | 0.000004 |
| C | -0.040409 | 1.993482 | -0.000017 |
| H | 0.971726 | 2.399935 | -0.000356 |
| H | -0.567888 | 2.361680 | -0.887093 |
| H | -0.567303 | 2.361716 | 0.887395 |
| Cl | -2.685931 | 0.194710 | 0.000011 |
| Cl | 2.694950 | 0.216318 | 0.000015 |

**CB2Me$^+$(H)**

B3lyp/6-31G(d) optimized geometry
Energy = -265.923661 a.u.
Enthalpy Correction (inc. ZPVE) = 0.119607
NIMAG = 0

B3lyp/6-311+G(2d,p) single point
Energy = -266.001650

| Atom | x-coord | y-coord | z-coord |
|---|---|---|---|
| N | -0.158225 | 1.070713 | -0.006572 |
| C | 0.652145 | 0.000000 | -0.013585 |
| N | -0.158235 | -1.070717 | -0.006599 |
| C | -1.488168 | 0.679803 | 0.006596 |
| C | -1.488169 | -0.679797 | 0.006612 |
| H | -2.298967 | 1.391247 | 0.008972 |
| H | -2.298981 | -1.391227 | 0.008971 |
| C | 2.140174 | -0.000004 | 0.008610 |
| H | 2.533231 | 0.885933 | -0.497234 |
| H | 2.512366 | -0.000849 | 1.040241 |
| H | 2.533266 | -0.885082 | -0.498717 |
| H | 0.169187 | -2.030315 | -0.009677 |
| H | 0.169222 | 2.030300 | -0.009750 |

**CB2Me$^+$(Ph)**

B3lyp/6-31G(d) optimized geometry
Energy = -728.040183 a.u.
Enthalpy Correction (inc. ZPVE) = 0.289713
NIMAG = 0

B3lyp/6-311+G(2d,p) single point
Energy = -728.234021

| Atom | x-coord | y-coord | z-coord |
|---|---|---|---|
| N | 1.087410 | -0.494310 | -0.342633 |
| C | -0.000003 | 0.174097 | 0.099406 |
| N | -1.087407 | -0.494321 | -0.342636 |
| C | 0.678806 | -1.610166 | -1.062032 |
| C | -0.678792 | -1.610137 | -1.062089 |
| H | 1.393157 | -2.276580 | -1.518689 |
| H | -1.393133 | -2.276530 | -1.518791 |
| C | 2.466558 | -0.136280 | -0.096794 |
| C | 3.256804 | -0.993531 | 0.670930 |
| C | 4.594621 | -0.662503 | 0.886627 |
| C | 5.124096 | 0.510490 | 0.343767 |
| C | 4.320090 | 1.357358 | -0.422528 |
| C | 2.982494 | 1.035406 | -0.652899 |
| H | 2.830565 | -1.896165 | 1.098473 |
| H | 5.219466 | -1.319906 | 1.482831 |
| H | 6.165587 | 0.763696 | 0.515852 |
| H | 4.734185 | 2.264413 | -0.851353 |
| H | 2.356441 | 1.672834 | -1.269996 |

| | | | |
|---|---|---|---|
| C | -2.466558 | -0.136294 | -0.096795 |
| C | -3.256772 | -0.993486 | 0.671030 |
| C | -4.594589 | -0.662456 | 0.886728 |
| C | -5.124093 | 0.510479 | 0.343770 |
| C | -4.320117 | 1.357287 | -0.422624 |
| C | -2.982521 | 1.035333 | -0.652996 |
| H | -2.830510 | -1.896077 | 1.098642 |
| H | -5.219412 | -1.319811 | 1.483008 |
| H | -6.165583 | 0.763687 | 0.515856 |
| H | -4.734236 | 2.264296 | -0.851523 |
| H | -2.356489 | 1.672714 | -1.270164 |
| C | -0.000021 | 1.390037 | 0.957557 |
| H | -0.000135 | 2.307362 | 0.357949 |
| H | -0.891258 | 1.401273 | 1.589291 |
| H | 0.891309 | 1.401398 | 1.589153 |

**CB2Me$^+$(Me)**

B3lyp/6-31G(d) optimized geometry
Energy = -344.557658 a.u.
Enthalpy Correction (inc. ZPVE) = 0.178892
NIMAG = 0

B3lyp/6-311+G(2d,p) single point
Energy = -344.651859

| Atom | x-coord | y-coord | z-coord |
|---|---|---|---|
| C | -2.485444 | 0.226158 | -0.002168 |
| N | -1.090672 | -0.238929 | -0.003349 |
| C | 0.003738 | 0.548029 | -0.006064 |
| N | 1.082227 | -0.260787 | 0.000706 |
| C | 2.480548 | 0.189372 | -0.004310 |
| C | -0.696167 | -1.565730 | 0.002454 |
| C | 0.663357 | -1.579333 | 0.004563 |
| H | 2.659915 | 0.862838 | 0.836387 |
| H | 2.709944 | 0.696241 | -0.944836 |
| H | 3.122127 | -0.685666 | 0.096638 |
| H | -2.681283 | 0.828113 | 0.887580 |
| H | -3.134641 | -0.648968 | 0.009493 |
| H | -2.688981 | 0.808316 | -0.903604 |
| H | -1.410728 | -2.373836 | 0.004131 |
| H | 1.362146 | -2.401204 | 0.007566 |
| C | 0.032929 | 2.036412 | 0.005365 |
| H | -0.938700 | 2.448061 | -0.273572 |
| H | 0.289170 | 2.418187 | 1.001665 |
| H | 0.776381 | 2.416487 | -0.701987 |

**CB2Me$^+$(iPr)**

B3lyp/6-31G(d) optimized geometry
Energy = -501.827696 a.u.
Enthalpy Correction (inc. ZPVE) = 0.297779
NIMAG = 0

B3lyp/6-311+G(2d,p) single point
Energy = -501.966932

| Atom | x-coord | y-coord | z-coord |
|---|---|---|---|
| C | -2.529198 | 0.315620 | 0.000071 |
| N | -1.095579 | -0.111234 | -0.000065 |
| C | 0.004382 | 0.673585 | 0.000038 |
| N | 1.085680 | -0.135429 | -0.000085 |
| C | 2.516502 | 0.295681 | 0.000065 |
| C | -0.695407 | -1.437260 | -0.000216 |
| C | 0.662094 | -1.452045 | -0.000234 |
| H | 2.486027 | 1.387407 | 0.000208 |
| H | -2.509889 | 1.406430 | 0.000277 |
| H | -1.402722 | -2.250579 | -0.000320 |
| H | 1.352259 | -2.280160 | -0.000377 |
| C | 0.057715 | 2.166018 | 0.000126 |
| H | -0.941052 | 2.601365 | -0.000167 |
| H | 0.581189 | 2.538742 | 0.887037 |
| H | 0.581762 | 2.538795 | -0.886422 |
| C | -3.219474 | -0.163575 | 1.280568 |
| H | -3.281148 | -1.256017 | 1.322772 |
| H | -2.697656 | 0.191269 | 2.174460 |
| H | -4.241230 | 0.226525 | 1.303945 |
| C | -3.219651 | -0.163137 | -1.280468 |
| H | -3.281167 | -1.255573 | -1.323111 |
| H | -4.241479 | 0.226808 | -1.303448 |
| H | -2.698105 | 0.192155 | -2.174336 |
| C | 3.209797 | -0.180685 | -1.279908 |
| H | 4.230567 | 0.211961 | -1.302891 |
| H | 3.273721 | -1.273118 | -1.321366 |
| H | 2.687941 | 0.171644 | -2.174911 |
| C | 3.209658 | -0.180952 | 1.280003 |
| H | 2.687813 | 0.171298 | 2.175040 |
| H | 3.273491 | -1.273391 | 1.321312 |
| H | 4.230473 | 0.211586 | 1.303080 |

**CB2Me$^+$(Cy)**

B3lyp/6-31G(d) optimized geometry
Energy = -735.305969 a.u.
Enthalpy Correction (inc. ZPVE) = 0.434452
NIMAG = 0

B3lyp/6-311+G(2d,p) single point
Energy = -735.505396

| Atom | x-coord | y-coord | z-coord |
|---|---|---|---|
| N | 1.088926 | -0.135703 | -0.169100 |
| C | 0.005771 | 0.115550 | 0.597603 |
| N | -1.094140 | -0.121782 | -0.150925 |
| C | 0.666195 | -0.531399 | -1.425096 |
| C | -0.691678 | -0.523059 | -1.414036 |
| H | 1.357588 | -0.782963 | -2.212630 |
| H | -1.398103 | -0.766193 | -2.190586 |
| C | 0.055647 | 0.568861 | 2.019470 |
| H | 0.659058 | 1.476731 | 2.118778 |
| H | -0.940152 | 0.793220 | 2.400198 |

| | | | |
|---|---|---|---|
| H | 0.493522 | -0.202881 | 2.662351 |
| C | 4.750404 | -1.110723 | 0.519310 |
| C | 3.290403 | -1.295526 | 0.068362 |
| C | 2.513448 | 0.020081 | 0.239086 |
| C | 3.173267 | 1.183450 | -0.520165 |
| C | 4.634910 | 1.354461 | -0.071732 |
| C | 5.430893 | 0.049591 | -0.221899 |
| H | 3.273834 | -1.597517 | -0.987599 |
| H | 2.803682 | -2.094889 | 0.639547 |
| H | 4.774138 | -0.921726 | 1.601909 |
| H | 5.296614 | -2.045987 | 0.356450 |
| H | 3.141174 | 0.975003 | -1.598349 |
| H | 2.605119 | 2.107173 | -0.356054 |
| H | 5.097623 | 2.158560 | -0.653946 |
| H | 4.655519 | 1.679664 | 0.978186 |
| H | 5.522895 | -0.201684 | -1.288072 |
| H | 6.450400 | 0.187391 | 0.154210 |
| H | 2.485571 | 0.266531 | 1.304218 |
| C | -4.649281 | 1.350165 | -0.095873 |
| C | -3.185994 | 1.177397 | -0.538683 |
| C | -2.522163 | 0.035894 | 0.249249 |
| C | -3.289935 | -1.288557 | 0.107337 |
| C | -4.751756 | -1.101701 | 0.551602 |
| C | -5.437728 | 0.037658 | -0.216697 |
| H | -3.152898 | 0.945285 | -1.611857 |
| H | -2.623086 | 2.107301 | -0.394127 |
| H | -4.673183 | 1.700013 | 0.946032 |
| H | -5.115618 | 2.137797 | -0.697346 |
| H | -3.269673 | -1.615533 | -0.941001 |
| H | -2.799125 | -2.070609 | 0.698522 |
| H | -5.292311 | -2.043543 | 0.409087 |
| H | -4.778565 | -0.888584 | 1.629655 |
| H | -5.527129 | -0.238521 | -1.276931 |
| H | -6.458441 | 0.178318 | 0.155038 |
| H | -2.506365 | 0.307184 | 1.307467 |

**CB2Me$^+$(neoPe)**

B3lyp/6-31G(d) optimized geometry
Energy = -659.078443 a.u.
Enthalpy Correction (inc. ZPVE) = 0.416366
NIMAG = 0

B3lyp/6-311+G(2d,p) single point
Energy = -659.262394

| Atom | x-coord | y-coord | z-coord |
|---|---|---|---|
| N | 1.002980 | 0.327333 | -0.385425 |
| C | -0.015397 | -0.455165 | 0.034158 |
| N | -1.018823 | 0.357070 | 0.433452 |
| C | 0.633067 | 1.654994 | -0.253703 |
| C | -0.622341 | 1.673639 | 0.262353 |
| H | -1.264788 | 2.498351 | 0.525182 |
| C | 2.300513 | -0.131216 | -0.934915 |
| H | 2.148840 | -1.149347 | -1.300490 |
| C | -2.341758 | -0.035564 | 0.972926 |

| | | | |
|---|---|---|---|
| H | 2.498230 | 0.500359 | -1.806104 |
| H | -2.567665 | 0.688789 | 1.760763 |
| H | -2.220493 | -1.006862 | 1.457015 |
| C | -3.758986 | 1.300437 | -0.673847 |
| C | -3.505503 | -0.085836 | -0.052805 |
| H | -3.958481 | 2.057919 | 0.094358 |
| H | -2.917164 | 1.640516 | -1.287682 |
| H | -4.636775 | 1.260891 | -1.326876 |
| C | -3.221884 | -1.112060 | -1.164097 |
| C | -4.748974 | -0.522930 | 0.749900 |
| H | -3.069610 | -2.118988 | -0.757455 |
| H | -4.072943 | -1.164053 | -1.850583 |
| H | -2.344078 | -0.839711 | -1.762916 |
| H | -5.619562 | -0.583672 | 0.089400 |
| H | -4.609901 | -1.509882 | 1.206765 |
| H | -4.986630 | 0.191285 | 1.546820 |
| C | 4.716202 | -0.598111 | -0.781266 |
| C | 3.511229 | -0.085389 | 0.035801 |
| H | 4.555055 | -1.620366 | -1.143452 |
| H | 4.918674 | 0.042404 | -1.647550 |
| H | 5.615746 | -0.605624 | -0.157786 |
| C | 3.793984 | 1.351721 | 0.512228 |
| C | 3.285716 | -1.002245 | 1.251440 |
| H | 2.997103 | 1.740487 | 1.156105 |
| H | 4.718278 | 1.373957 | 1.098314 |
| H | 3.928126 | 2.039152 | -0.332416 |
| H | 4.155071 | -0.966392 | 1.915951 |
| H | 2.416008 | -0.695245 | 1.845442 |
| H | 3.154388 | -2.048742 | 0.949826 |
| H | 1.289981 | 2.460484 | -0.538642 |
| C | -0.018267 | -1.946572 | 0.021856 |
| H | -0.082223 | -2.328928 | -1.003510 |
| H | 0.891546 | -2.340897 | 0.479711 |
| H | -0.871433 | -2.340915 | 0.573436 |

**CB2Me$^+$(tBu)**

B3lyp/6-31G(d) optimized geometry
Energy = -580.444389 a.u.
Enthalpy Correction (inc. ZPVE) = 0.356713
NIMAG = 0

B3lyp/6-311+G(2d,p) single point
Energy = -580.605746

| Atom | x-coord | y-coord | z-coord |
|---|---|---|---|
| C | -2.573443 | -0.046571 | 0.004660 |
| N | -1.100315 | 0.366078 | -0.008809 |
| C | 0.000001 | -0.431070 | 0.004643 |
| N | 1.100308 | 0.366084 | -0.008915 |
| C | 2.573440 | -0.046552 | 0.004668 |
| C | -0.677360 | 1.682877 | -0.019256 |
| C | 0.677342 | 1.682882 | -0.019310 |
| H | -1.356931 | 2.515290 | -0.030211 |
| H | 1.356908 | 2.515299 | -0.030331 |
| C | 0.000027 | -1.926631 | 0.002681 |

| | | | |
|---|---|---|---|
| H | -0.876528 | -2.318473 | 0.513916 |
| H | 0.000498 | -2.320403 | -1.019625 |
| H | 0.876132 | -2.318442 | 0.514737 |
| C | -2.851229 | -1.008854 | -1.163368 |
| H | -2.560576 | -0.558609 | -2.118020 |
| H | -2.350130 | -1.972463 | -1.063716 |
| H | -3.925951 | -1.209008 | -1.201710 |
| C | -3.436608 | 1.211056 | -0.196648 |
| H | -3.218531 | 1.716753 | -1.142622 |
| H | -4.482880 | 0.896637 | -0.227863 |
| H | -3.341140 | 1.923125 | 0.628834 |
| C | 2.910570 | -0.655714 | 1.377203 |
| H | 3.981503 | -0.876758 | 1.412664 |
| H | 2.684646 | 0.050778 | 2.182016 |
| H | 2.381339 | -1.589303 | 1.582096 |
| C | 3.436594 | 1.211018 | -0.197050 |
| H | 3.218420 | 1.716466 | -1.143135 |
| H | 3.341221 | 1.923300 | 0.628258 |
| H | 4.482861 | 0.896583 | -0.228283 |
| C | 2.851243 | -1.009219 | -1.163031 |
| H | 2.560235 | -0.559465 | -2.117805 |
| H | 3.926020 | -1.209050 | -1.201533 |
| H | 2.350488 | -1.972951 | -1.062844 |
| C | -2.910582 | -0.656149 | 1.377006 |
| H | -2.381405 | -1.589830 | 1.581619 |
| H | -2.684599 | 0.050079 | 2.182035 |
| H | -3.981528 | -0.877131 | 1.412409 |

## 8. Fluorine Substituted Complexes and Transition Structures

**CX(CH2F)**

B3lyp/lanl2dz optimized geometry
Energy = -922.241756709 a.u.
Enthalpy Correction (inc. ZPVE) = 0.414950
NIMAG = 0

B3lyp/lanl2dzaug:6-311+G(2d,p) single point
Energy = -1592.35379781

| Atom | x-coord | y-coord | z-coord |
|---|---|---|---|
| C | 3.818190 | -1.078559 | 0.605089 |
| C | 3.852066 | -0.872740 | -0.741561 |
| N | 2.509950 | -0.683771 | -1.156279 |
| C | 1.638812 | -0.751857 | -0.088983 |
| N | 2.456065 | -1.011955 | 0.991102 |
| C | 2.092096 | -0.374939 | -2.500530 |
| F | 2.050762 | 1.068474 | -2.673834 |
| Pd | -0.373677 | -0.498521 | -0.094895 |
| P | -2.852944 | -0.557533 | -0.082417 |
| C | -3.511715 | -1.117596 | 1.592861 |
| C | 1.969440 | -1.116696 | 2.344086 |
| F | 1.912625 | 0.206693 | 2.941563 |
| C | -0.481221 | -2.595467 | -0.324165 |
| P | -0.130163 | 1.951740 | 0.200604 |
| C | 1.632581 | 2.590031 | 0.409687 |

| | | | |
|---|---|---|---|
| H | 2.651895 | -1.707774 | 2.958130 |
| H | 2.810302 | -0.755907 | -3.229258 |
| C | -0.748851 | 3.028686 | -1.220314 |
| C | -0.962143 | 2.680210 | 1.732031 |
| C | -3.631594 | -1.780695 | -1.285686 |
| C | -3.870365 | 0.992816 | -0.432995 |
| H | -1.215254 | -2.998582 | 0.384923 |
| H | -0.806298 | -2.789645 | -1.354165 |
| H | 0.482155 | -3.085118 | -0.152739 |
| H | 4.614767 | -1.260954 | 1.308160 |
| H | 4.683278 | -0.843836 | -1.427381 |
| H | 1.618913 | 3.675705 | 0.557300 |
| H | 2.093141 | 2.116927 | 1.281077 |
| H | 2.211628 | 2.361033 | -0.488859 |
| H | -1.815940 | 2.867890 | -1.392694 |
| H | -0.578360 | 4.087887 | -0.996399 |
| H | -0.197024 | 2.762716 | -2.127291 |
| H | -3.206274 | -0.407496 | 2.367497 |
| H | -4.605433 | -1.182091 | 1.575500 |
| H | -3.100471 | -2.100909 | 1.840483 |
| H | -3.213836 | -2.778663 | -1.134619 |
| H | -4.715721 | -1.818855 | -1.132761 |
| H | -3.426759 | -1.465700 | -2.313756 |
| H | -3.609123 | 1.796302 | 0.260850 |
| H | -3.687425 | 1.332090 | -1.457147 |
| H | -4.936858 | 0.767093 | -0.323499 |
| H | -0.797428 | 3.762820 | 1.774911 |
| H | -0.526025 | 2.219803 | 2.624245 |
| H | -2.038424 | 2.485992 | 1.725552 |
| H | 0.950786 | -1.506295 | 2.345206 |
| H | 1.079176 | -0.741165 | -2.671343 |

**TS(CH2F)**

B3lyp/lanl2dz optimized geometry
Energy = -922.205265881 a.u.
Enthalpy Correction (inc. ZPVE) = 0.412408
NIMAG = 1

B3lyp/lanl2dzaug:6-311+G(2d,p) single point
Energy = -1592.31512405

| Atom | x-coord | y-coord | z-coord |
|---|---|---|---|
| C | -3.863898 | 0.324380 | -0.638950 |
| C | -3.849426 | 0.285294 | 0.718611 |
| N | -2.520899 | -0.016335 | 1.121472 |
| C | -1.697737 | -0.249699 | 0.001032 |
| N | -2.544360 | 0.047178 | -1.086777 |
| C | -2.109754 | -0.235462 | 2.473060 |
| H | -1.049929 | -0.004719 | 2.597609 |
| Pd | 0.307682 | -0.194326 | -0.016109 |
| P | 2.573332 | -1.202809 | -0.030015 |
| C | 3.987704 | -0.394397 | -0.988197 |
| C | -2.163575 | -0.095898 | -2.457390 |
| H | -1.104827 | 0.134607 | -2.591225 |
| C | -1.042974 | -2.045346 | -0.056668 |

| | | | |
|---|---|---|---|
| P | 0.875791 | 2.219226 | 0.033042 |
| C | -0.567797 | 3.399796 | 0.320992 |
| F | -2.334790 | -1.479347 | -2.893557 |
| F | -2.261904 | -1.643378 | 2.831996 |
| C | 2.110480 | 2.760843 | 1.353874 |
| C | 1.640264 | 2.894369 | -1.555323 |
| C | 2.595683 | -2.959075 | -0.727637 |
| C | 3.340914 | -1.449709 | 1.679564 |
| H | -0.584984 | -2.401732 | -0.983859 |
| H | -0.584496 | -2.455371 | 0.848140 |
| H | -2.090003 | -2.359676 | -0.064966 |
| H | -4.671203 | 0.530027 | -1.323317 |
| H | -4.641813 | 0.451150 | 1.430662 |
| H | -0.223742 | 4.439931 | 0.300315 |
| H | -1.323554 | 3.257567 | -0.457549 |
| H | -1.026516 | 3.196464 | 1.293677 |
| H | 3.063009 | 2.241349 | 1.210757 |
| H | 2.283459 | 3.841516 | 1.295974 |
| H | 1.724357 | 2.514364 | 2.347750 |
| H | 4.210305 | 0.593818 | -0.572407 |
| H | 4.891465 | -1.010989 | -0.928137 |
| H | 3.706166 | -0.281567 | -2.040031 |
| H | 2.335182 | -2.941081 | -1.790967 |
| H | 3.589404 | -3.405941 | -0.612233 |
| H | 1.864539 | -3.579949 | -0.199968 |
| H | 1.897447 | 3.953067 | -1.436067 |
| H | 2.544652 | 2.331414 | -1.802680 |
| H | 0.930026 | 2.792824 | -2.381941 |
| H | 4.312979 | -1.948619 | 1.596387 |
| H | 3.476625 | -0.482787 | 2.174423 |
| H | 2.677626 | -2.065231 | 2.295701 |
| H | -2.742390 | 0.323571 | 3.166137 |
| H | -2.806206 | 0.506799 | -3.103168 |

**CX(CHF2)**

B3lyp/lanl2dz optimized geometry
Energy = -1120.72030152 a.u.
Enthalpy Correction (inc. ZPVE) = 0.398959
NIMAG = 0

B3lyp/lanl2dzaug:6-311+G(2d,p) single point
Energy = -1790.89552097

| Atom | x-coord | y-coord | z-coord |
|---|---|---|---|
| C | -3.704973 | -0.520510 | -0.653360 |
| N | -2.342355 | -0.912491 | -0.746232 |
| C | -1.483968 | 0.130813 | -0.478653 |
| N | -2.335942 | 1.184044 | -0.232970 |
| C | -3.700852 | 0.802047 | -0.329764 |
| Pd | 0.544358 | 0.114094 | -0.427964 |
| C | 0.428077 | 0.740553 | -2.445530 |
| C | -1.854821 | 2.490630 | 0.130011 |
| C | -1.872775 | -2.241047 | -1.032341 |
| P | 0.563719 | -0.570124 | 1.955704 |
| C | 1.264227 | -2.279408 | 2.343753 |

| | | | |
|---|---|---|---|
| P | 3.002086 | 0.193294 | -0.749988 |
| C | 3.601443 | -0.456552 | -2.413688 |
| C | 1.488844 | 0.579929 | 3.133410 |
| C | -1.127996 | -0.661945 | 2.789565 |
| C | 4.163552 | -0.707104 | 0.432673 |
| C | 3.658112 | 1.960001 | -0.713365 |
| H | 1.119932 | 1.577925 | -2.598731 |
| H | 0.725222 | -0.113602 | -3.065755 |
| H | -0.579657 | 1.056674 | -2.730887 |
| H | -4.509108 | 1.498594 | -0.181712 |
| H | -4.517844 | -1.201098 | -0.844255 |
| H | -1.010514 | -0.974949 | 3.833066 |
| H | -1.608734 | 0.320361 | 2.766984 |
| H | -1.757732 | -1.392541 | 2.273958 |
| H | 2.308867 | -2.348581 | 2.031136 |
| H | 1.200275 | -2.477193 | 3.419548 |
| H | 0.681917 | -3.036953 | 1.809810 |
| H | 3.466442 | 2.410669 | 0.265261 |
| H | 4.736300 | 1.970555 | -0.907691 |
| H | 3.153251 | 2.557779 | -1.477907 |
| H | 3.093863 | 0.062287 | -3.229889 |
| H | 4.681385 | -0.297543 | -2.507345 |
| H | 3.390729 | -1.527708 | -2.491033 |
| H | 4.036131 | -0.345815 | 1.456460 |
| H | 3.965123 | -1.782609 | 0.403382 |
| H | 5.201592 | -0.534585 | 0.128043 |
| H | 1.413097 | 0.208185 | 4.161428 |
| H | 1.044572 | 1.579063 | 3.084746 |
| H | 2.545291 | 0.650685 | 2.860416 |
| H | -0.899234 | 2.726398 | -0.338463 |
| F | -2.834333 | -2.903753 | -1.805819 |
| H | -0.904476 | -2.239940 | -1.534052 |
| F | -2.827094 | 3.438462 | -0.213740 |
| F | -1.748367 | -2.982123 | 0.177118 |
| F | -1.691247 | 2.573274 | 1.541577 |

**TS(CHF2)**

B3lyp/lanl2dz optimized geometry
Energy = -1120.69157165 a.u.
Enthalpy Correction (inc. ZPVE) = 0.397048
NIMAG = 1

B3lyp/lanl2dzaug:6-311+G(2d,p) single point
Energy = -1790.86137227

| Atom | x-coord | y-coord | z-coord |
|---|---|---|---|
| C | 3.627353 | 0.731590 | -0.086988 |
| N | 2.286437 | 1.213165 | -0.133920 |
| C | 1.404793 | 0.247685 | -0.660131 |
| N | 2.262181 | -0.846040 | -0.896793 |
| C | 3.612922 | -0.540194 | -0.555402 |
| Pd | -0.557322 | 0.144936 | -0.353058 |
| C | 0.526533 | 0.873131 | -2.273043 |
| C | 1.787126 | -2.129211 | -1.274257 |
| F | 1.531388 | -2.938418 | -0.113101 |

| | | | |
|---|---|---|---|
| C | 1.855721 | 2.454578 | 0.402396 |
| F | 1.799553 | 2.398026 | 1.833231 |
| P | -0.645482 | -0.791391 | 1.941702 |
| C | -1.761915 | 0.110605 | 3.163886 |
| P | -2.978651 | 0.368959 | -0.840270 |
| C | -3.377647 | 0.438569 | -2.685319 |
| C | -1.233150 | -2.579836 | 2.016278 |
| C | 1.007205 | -0.850922 | 2.842230 |
| C | -3.774803 | 1.953214 | -0.191415 |
| C | -4.165469 | -0.967867 | -0.233444 |
| F | 2.788702 | -2.806002 | -1.989288 |
| F | 2.805616 | 3.451881 | 0.108160 |
| H | -0.060658 | 0.182945 | -2.888135 |
| H | 0.072539 | 1.868984 | -2.243431 |
| H | 1.521569 | 0.962648 | -2.716952 |
| H | 4.411369 | -1.249808 | -0.695297 |
| H | 4.441482 | 1.345528 | 0.261290 |
| H | 0.872491 | -1.272189 | 3.844849 |
| H | 1.702331 | -1.483242 | 2.282373 |
| H | 1.420814 | 0.157554 | 2.926761 |
| H | -2.797355 | 0.105260 | 2.809993 |
| H | -1.720669 | -0.378650 | 4.143634 |
| H | -1.428646 | 1.147295 | 3.271295 |
| H | -4.185474 | -0.985911 | 0.860896 |
| H | -5.179584 | -0.772673 | -0.599001 |
| H | -3.839090 | -1.947260 | -0.596979 |
| H | -3.117584 | -0.514509 | -3.157679 |
| H | -4.444938 | 0.630254 | -2.842147 |
| H | -2.801718 | 1.236907 | -3.164491 |
| H | -1.233197 | -2.932746 | 3.053827 |
| H | -2.244167 | -2.665945 | 1.608313 |
| H | -0.555815 | -3.203343 | 1.425747 |
| H | -4.838741 | 1.984261 | -0.451168 |
| H | -3.670811 | 2.006317 | 0.896751 |
| H | -3.277331 | 2.823803 | -0.630734 |
| H | 0.869711 | 2.753958 | 0.046312 |
| H | 0.862599 | -2.097305 | -1.851638 |

**CX(CF3)**

B3lyp/lanl2dz optimized geometry
Energy = -1319.18895517 a.u.
Enthalpy Correction (inc. ZPVE) = 0.381856
NIMAG = 0

B3lyp/lanl2dzaug:6-311+G(2d,p) single point
Energy = -1989.43583377

| Atom | x-coord | y-coord | z-coord |
|---|---|---|---|
| C | -3.715467 | -0.559640 | -0.448456 |
| N | -2.356798 | -0.992036 | -0.440446 |
| C | -1.461467 | 0.056421 | -0.290298 |
| N | -2.311010 | 1.147792 | -0.186067 |
| C | -3.686568 | 0.786728 | -0.288443 |
| Pd | 0.562217 | 0.018669 | -0.352970 |
| C | 0.286521 | 0.330948 | -2.429561 |

| | | | |
|---|---|---|---|
| C | -1.850811 | 2.499297 | -0.010490 |
| C | -1.953390 | -2.366842 | -0.562204 |
| P | 0.831684 | -0.345230 | 2.085342 |
| C | 1.570964 | -1.998490 | 2.617869 |
| P | 2.982910 | 0.105696 | -0.885014 |
| C | 3.484424 | -0.576615 | -2.567058 |
| C | 1.865943 | 0.931384 | 3.016492 |
| C | -0.769053 | -0.317208 | 3.087508 |
| C | 4.226308 | -0.754590 | 0.243014 |
| C | 3.602017 | 1.884437 | -0.928904 |
| H | 0.885470 | 1.198852 | -2.727532 |
| H | 0.628982 | -0.584515 | -2.922359 |
| H | -0.757507 | 0.519217 | -2.692894 |
| H | -4.483692 | 1.508629 | -0.234587 |
| H | -4.542475 | -1.239786 | -0.561912 |
| H | -0.553386 | -0.507480 | 4.144731 |
| H | -1.248724 | 0.661601 | 2.996001 |
| H | -1.448197 | -1.093581 | 2.722999 |
| H | 2.591473 | -2.102190 | 2.240975 |
| H | 1.585336 | -2.072409 | 3.711133 |
| H | 0.963028 | -2.812533 | 2.211724 |
| H | 3.464554 | 2.351538 | 0.050967 |
| H | 4.663854 | 1.914738 | -1.197240 |
| H | 3.029241 | 2.453932 | -1.666755 |
| H | 2.932685 | -0.072293 | -3.363067 |
| H | 4.557778 | -0.422416 | -2.722924 |
| H | 3.265405 | -1.647853 | -2.611987 |
| H | 4.176931 | -0.350212 | 1.257562 |
| H | 4.017713 | -1.828345 | 0.273547 |
| H | 5.239973 | -0.603889 | -0.144365 |
| H | 1.871895 | 0.708118 | 4.089233 |
| H | 1.437354 | 1.926380 | 2.861534 |
| H | 2.897088 | 0.934543 | 2.652215 |
| F | -1.040524 | 2.622651 | 1.118170 |
| F | -1.171964 | -2.598838 | -1.682423 |
| F | -2.945408 | 3.333295 | 0.156844 |
| F | -3.081865 | -3.166451 | -0.646946 |
| F | -1.216673 | -2.783209 | 0.549874 |
| F | -1.118845 | 2.960209 | -1.094032 |

**TS(CF3)**

B3lyp/lanl2dz optimized geometry
Energy = -1319.16884878 a.u.
Enthalpy Correction (inc. ZPVE) = 0.380192
NIMAG = 1

B3lyp/lanl2dzaug:6-311+G(2d,p) single point
Energy = -1989.40762203

| Atom | x-coord | y-coord | z-coord |
|---|---|---|---|
| Pd | -0.572083 | 0.032582 | -0.296483 |
| P | -0.901378 | -0.415343 | 2.120401 |
| P | -2.949125 | 0.166738 | -0.990801 |
| C | 0.494513 | 0.348392 | -2.296147 |
| H | 0.000455 | -0.513517 | -2.751631 |

```
H    -0.002039    1.302055   -2.492084
H     1.514849    0.406415   -2.685280
C     1.392240    0.100764   -0.522114
N     2.304563   -0.987376   -0.554920
C     1.911346   -2.346841   -0.592324
N     2.264050    1.185709   -0.237975
C     1.823580    2.494880    0.077875
C     3.660286   -0.559464   -0.386422
H     4.488326   -1.246609   -0.430508
C     3.635226    0.777024   -0.192296
H     4.437379    1.477789   -0.033815
C    -3.714435    1.876076   -0.764165
C    -1.588002   -2.127804    2.492356
C     0.668053   -0.347539    3.157886
H     0.437542   -0.573604    4.205123
H     1.384701   -1.084509    2.784729
H     1.107317    0.651585    3.095172
C    -2.057298    0.763276    3.027099
H    -3.066739    0.701816    2.609582
H    -2.099277    0.507266    4.091808
H    -1.691216    1.788726    2.920228
C    -4.233134   -0.981068   -0.220647
H    -4.344092   -0.766537    0.847000
H    -5.204772   -0.842914   -0.707522
H    -3.919269   -2.022182   -0.343969
C    -3.189893   -0.156267   -2.834490
H    -2.925819   -1.192832   -3.067628
H    -4.233630    0.017582   -3.118492
H    -2.548816    0.509774   -3.420377
H    -1.684714   -2.271195    3.574424
H    -2.568684   -2.250697    2.025193
H    -0.908118   -2.882915    2.087843
H    -4.747842    1.886020   -1.128137
H    -3.703687    2.155238    0.293761
H    -3.132100    2.616092   -1.321868
F     3.015726   -3.155119   -0.808906
F     2.909523    3.352778    0.154477
F     0.927321    3.009136   -0.860619
F     0.969374   -2.613160   -1.584708
F     1.155705    2.563049    1.317896
F     1.321066   -2.776621    0.618665
```

## 9. LANL2DZAUG:6-311+G(2d,p) Basis Set Implementation

Gaussian98 Basis Set and Pseudopotential genecp cards:

```
! basis set for high-level single points
-C -H -N -P 0
6-311+G(2d,p)
****
-Pd 0
S 3 1.00
```

```
           0.278700D+01 -.161024D+01
           0.196500D+01 0.184898D+01
           0.624300D+00 0.603749D+00
S 3 1.00
           0.278700D+01 0.135408D+01
           0.196500D+01 -.167809D+01
           0.624300D+00 -.855938D+00
S 1 1.00
           0.208100D+00 0.100000D+01
S 1 1.00
           0.832000D-01 0.100000D+01
S 1 1.00
           0.333000D-01 0.100000D+01
P 3 1.00
           0.599900D+01 -.103491D+00
           0.144300D+01 0.745695D+00
           0.526400D+00 0.365649D+00
P 1 1.00
           0.175500D+00 0.100000D+01
P 1 1.00
           0.585000D-01 0.100000D+01
P 1 1.00
           0.195000D-01 0.100000D+01
D 2 1.00
           0.609100D+01 0.376146D-01
           0.171900D+01 0.520048D+00
D 1 1.00
           0.605600D+00 0.100000D+01
D 1 1.00
           0.188300D+00 0.100000D+01
D 1 1.00
           0.628000D-01 0.100000D+01
F 2 1.00
           0.361217D+01 0.173786D+00
           0.129541D+01 0.597338D+00
F 1 1.00
           0.554710D+00 0.100000D+01
F 1 1.00
           0.237530D+00 0.100000D+01
****
```

## 10. BDE and Eact Correlation

Relaxed Bond Dissociation Energies (BDEs) are calculated at the optimization level of theory:

i.e. B3LYP/LANL2DZ (in kCal/mol)

The difficulty in forming the transition structure (ie the activation barrier) will be related to the energy required to break the palladium carbene bond minus the energy that should be regained (or at least partially regained) in the ts by forming the methyl-carbene bond.

i.e. 'Difficulty of Activation' = BDE(Pd-Carb) – BDE(Carbene-CH3)

| | Pd-Carb BDE | Carb-CH3 BDE | Difficulty of Activation (kCal/mol) |
|---|---|---|---|
| Cl | 215.71 | 154.72 | 61.0 |
| H | 224.24 | 165.67 | 58.6 |
| Ph | 223.04 | 175.40 | 47.6 |
| Me | 225.71 | 171.60 | 54.1 |
| iPr | 226.10 | 174.95 | 51.2 |
| Cy | 227.30 | 178.11 | 49.2 |
| neoPe | 223.19 | 175.95 | 47.2 |
| tBu | 215.93 | 170.64 | 45.3 |