

Supporting Information for

ARYLATION REACTIONS OF MONOCARBA-*CLOSO*-DODECABORATE AT THE BORON VERTICES

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1. The acidity measurement of C1-carborane carboxylic acid derivatives

Instrumentation

UV-visible absorption measurements were performed with a JASCO V-670 spectrophotometer.

Method

1. Phosphate buffer (pH 1.5, 2.0, 2.5, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0) was prepared by mixing disodium hydrogenphosphate (pK_a 12.7), sodium dihydrogenphosphate (pK_a 7.21), phosphoric acid (pK_a 2.1).
2. 2.0 mg/mL solution of each carboxylate derivative in MeCN was prepared (about 5 mM).
3. 1.5 mL of phosphate buffer and 1.5 mL of MeCN were added to a cell and mixed with inversion.
4. After baseline correction, absorbance was measured as baseline.
5. 30 μ L of MeCN solution of sample was added to the cell and mixed with inversion.
6. Absorbance was measured.
7. Measurements using phosphate buffer of different pH were conducted similarly.
8. By choosing the wavelength at which absorbance change drastically with different pH, the change of absorbance was recorded.

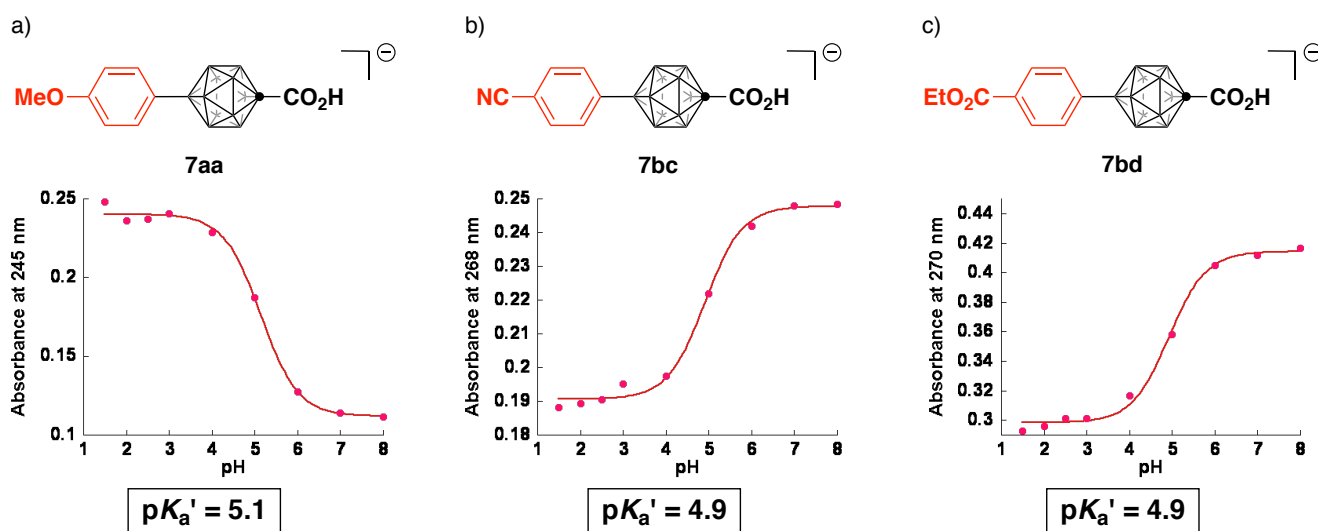


Figure S1. pK_a' of the C1-carborane carboxylic acid derivatives (in H₂O/MeCN)

The pK_a' of the C1-carborane carboxylic acid derivatives depended on the substituents on the aromatic ring at the 12-B vertex. While the change was not drastic, these data clearly showed that there should be the electronic interaction between π -aromatic ring and σ -aromatic carborane cage, in the direction from the 12-B vertex to the 1-C vertex.

2. DFT Calculations

2.1 Computational details

All calculations were carried with the Gaussian 09 program package.¹ The molecular structures and harmonic vibrational frequencies were obtained using the hybrid density functionals based on Becke's three-parameter exchange function and the Lee-Yang-Parr nonlocal correlation functional (B3LYP) in gas phase.² We used SDD³ for Pd, Zn, and I, and the 6-31+G*⁴ basis set for other atoms. We used an additional Integral keyword to specify an ultrafine grid. All stationary points were optimized without any symmetry assumptions, and characterized by normal coordinate analysis at the B3LYP/6-31+G* of theory (number of imaginary frequencies, NIMAG, 0 for minima and 1 for TSs). The intrinsic reaction coordinate (IRC) method was used to track minimum energy paths from transition structures to the corresponding local minima.⁵

¹ Gaussian 09, Revision D.01 or E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

² (a) A. D. Beche, *Phys. Rev.* 1988, **A38**, 3098; (b) A. D. Beche, *J. Chem. Phys.* 1993, **98**, 1372; (c) A. D. Beche, *J. Chem. Phys.* 1993, **98**, 5648-5652; (d) C. Lee, W. Yang, R. G. Parr, *Phys. Rev.* 1988, **B37**, 785.

³ (a) P. Fuentealba, H. Preuss, H. Stoll, L. V. Szentpaly, *Chem. Phys. Lett.* 1982, **89**, 418; (b) L. V. Szentpaly, P. Fuentealba, H. Preuss, H. Stoll, *Chem. Phys. Lett.* 1982, **93**, 555.

⁴ M. J. Frisch, J. A. Pople, J. S. Binkley, *J. Chem. Phys.*, 1984, **80**, 3265.

⁵ (a) K. Fukui, *Acc. Chem. Res.* 1981, **14**, 363; (b) K. Ishida, K. Morokuma, A. Komornicki, *J. Chem. Phys.* 1977, **66**, 2153; (c) C. Gonzalez and H. B. Schlegel, *J. Chem. Phys.* 1989, **90**, 2154-2161; (d) H. B. Schlegel and C. Gonzalez, *J. Phys. Chem.* 1990, **94**, 5523.

2.2 Oxidative addition of 4a: Comparison between 4a and iodobenzene

All calculations were performed at the B3LYP/SDD&6-31+G* levels of theory. The activation barrier of oxidative addition of **4a** ($\Delta G^\ddagger = +31.8$ kcal/mol) was much larger than that of iodobenzene ($\Delta G^\ddagger = +17.8$ kcal/mol), and the former process was endothermic, while the latter one was exothermic to stabilize the product **INT**_{OA2}' (Figure S2).

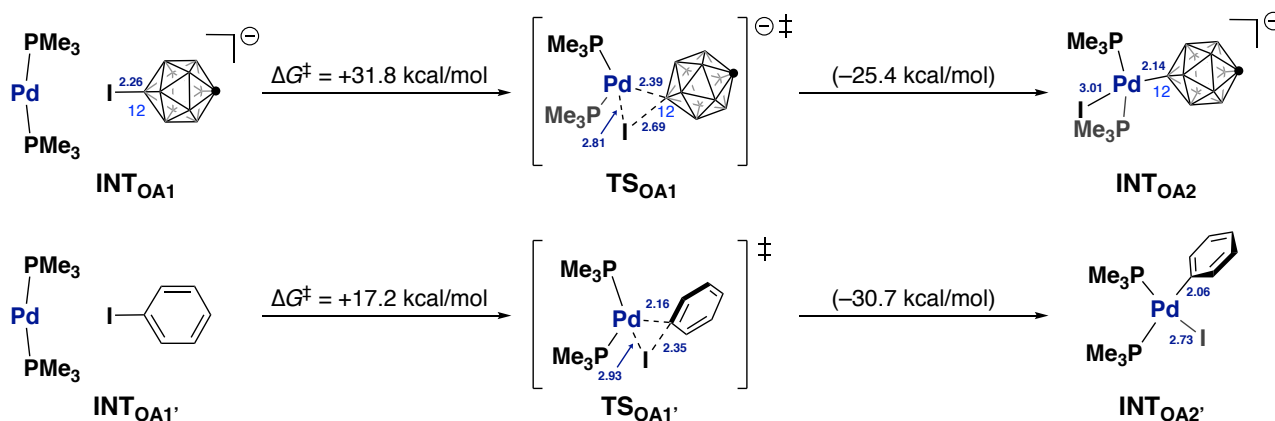


Figure S2. The oxidative addition of **4a** and iodobenzene to $\text{Pd}(\text{PMe}_3)_2$

Energy changes and bond lengths at the B3LYP/SDD (for Pd, I) and 6-31+G* (for the other atoms) levels of theory are shown in kcal/mol and Å, respectively.

2.3 Consideration of the transmetalation step with a phenylzinc reagent

The modeled transmetalation step with $\text{Pd}(\text{12-carborane})\text{I}(\text{PCy}_3)$ and phenylzinc chloride was found to be rather endothermic ($\Delta\Delta G = +18.8$ kcal/mol) (Figure S3, same as Eq.1 in the manuscript). While the subsequent reductive elimination step should be irreversible, the energy-uphill reaction should be unfavourable and need excess amount of organozinc reagent to displace the equilibrium to the right side.

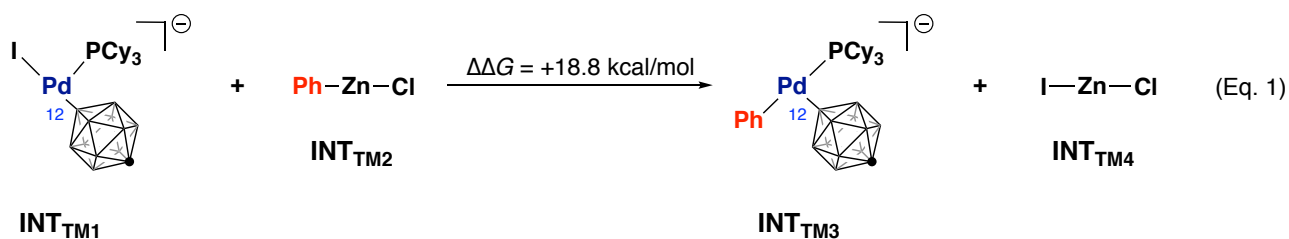


Figure S3. The transmetalation step with $\text{Pd}(\text{II})(\text{12-carborane})$ complex and PhZnCl

Energy changes at the B3LYP/SDD (for Pd, Zn) and 6-31+G* (for the other atoms) levels of theory are shown in kcal/mol.

2.4 Intramolecular arylation cyclization pathway

The modeled intramolecular arylation cyclization pathway at the B3LYP/SDD&6-31+G* levels of theory is summarized in **Figure S4** (same as Figure 2 in the manuscript). The methoxy group occupied one of the vacant site of palladium center in **INT₁**. Instead, the structure of **INT₁'**, revealed the rather strong agnostic interaction between the palladium center and the *ortho* B–H bond on the C1-carborane cage. This should be important for the selective B–H bond disconnection at the 2-B vertex.

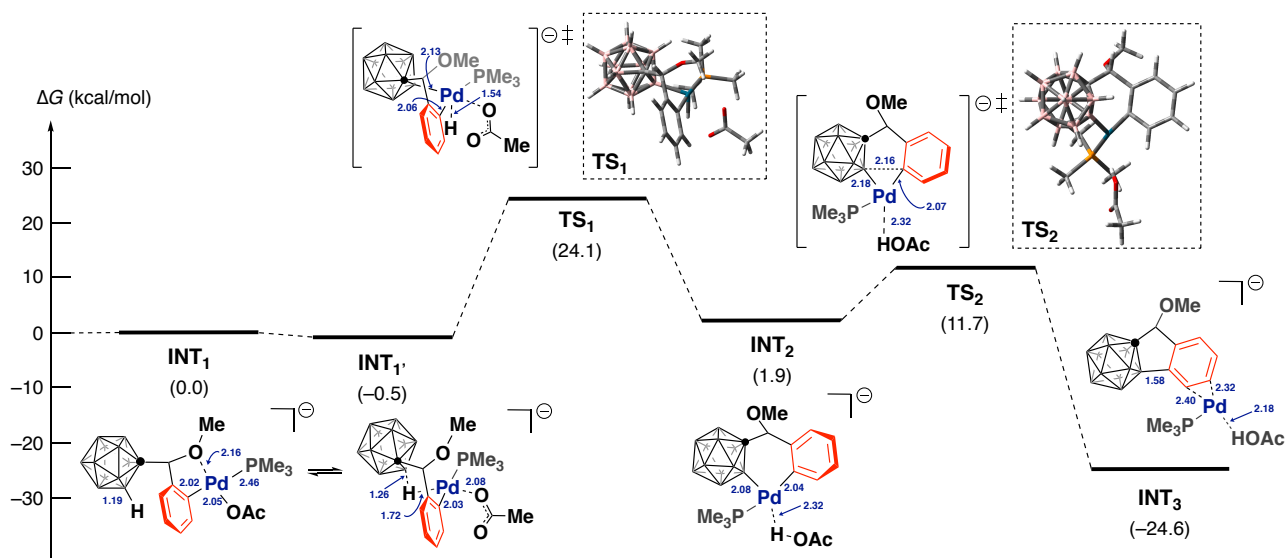
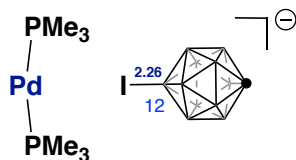


Figure S4 Modeled reaction pathway of the intramolecular arylation cyclization step
Energy changes and bond lengths at the B3LYP/SDD (for Pd) and 6-31+G* (for the other atoms) levels of theory are shown in kcal/mol and Å, respectively.

2.5 Cartesian coordinates and energies

Oxidative addition



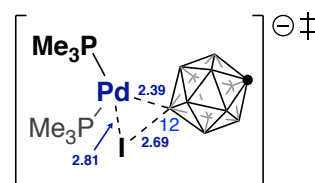
INT_{OA1}

Energy (RB3LYP): -1380.06790303 A.U.

Gibbs Free Energy: -1379.730032 A.U.

| | | | |
|----|-----------|-----------|-----------|
| B | 2.259806 | -0.984753 | 1.350592 |
| B | 2.823916 | -1.354360 | -0.304754 |
| B | 3.077580 | 0.187600 | -1.168147 |
| B | 2.709316 | 1.511059 | -0.027836 |
| B | 2.184337 | 0.793840 | 1.519577 |
| B | 3.561266 | -0.112948 | 2.179963 |
| B | 3.954193 | -1.432000 | 1.055553 |
| H | 1.541385 | -1.711673 | 1.963709 |
| B | 4.458879 | -0.713456 | -0.493002 |
| H | 2.534426 | -2.361689 | -0.869394 |
| B | 4.388021 | 1.051281 | -0.323138 |
| H | 2.944830 | 0.295060 | -2.351088 |
| B | 3.838072 | 1.421174 | 1.328954 |
| H | 2.337788 | 2.583016 | -0.384493 |
| H | 1.410939 | 1.337275 | 2.246696 |
| H | 3.867654 | -0.211140 | 3.326622 |
| H | 4.510525 | -2.406789 | 1.455899 |
| H | 5.350566 | -1.211792 | -1.106548 |
| H | 5.231998 | 1.726574 | -0.824790 |
| H | 4.317550 | 2.343994 | 1.910420 |
| Pd | -0.439453 | -0.017322 | -0.231050 |
| P | -0.570375 | -2.301038 | -0.835711 |
| P | -0.622619 | 2.235224 | -0.889154 |
| C | -0.388206 | 3.606435 | 0.331358 |
| H | -0.591650 | 4.583716 | -0.125710 |
| H | -1.082057 | 3.441967 | 1.162377 |
| H | 0.631455 | 3.591132 | 0.722834 |
| C | 0.161153 | -2.716769 | -2.491383 |
| H | 1.228368 | -2.489592 | -2.508685 |
| H | 0.008518 | -3.776760 | -2.734992 |
| H | -0.335167 | -2.103846 | -3.251900 |
| C | -2.322202 | -2.822264 | -1.150712 |

| | | | |
|---|-----------|-----------|-----------|
| H | -2.787800 | -2.140038 | -1.868751 |
| H | -2.350846 | -3.845896 | -1.548391 |
| H | -2.898169 | -2.758816 | -0.224216 |
| C | 0.317449 | 2.801165 | -2.387211 |
| H | 1.390938 | 2.664112 | -2.254533 |
| H | -0.004290 | 2.195651 | -3.241844 |
| H | 0.106426 | 3.857161 | -2.602323 |
| C | -2.340635 | 2.599935 | -1.488001 |
| H | -3.054311 | 2.445196 | -0.675306 |
| H | -2.403709 | 3.631576 | -1.860108 |
| H | -2.602428 | 1.909887 | -2.296983 |
| B | 1.700278 | 0.020221 | -0.033817 |
| C | 4.788526 | 0.049110 | 0.997388 |
| H | 5.817799 | 0.058004 | 1.340218 |
| C | -0.001846 | -3.699784 | 0.236838 |
| H | -0.229999 | -4.665557 | -0.232793 |
| H | 1.071893 | -3.625988 | 0.419155 |
| H | -0.519746 | -3.634875 | 1.199330 |
| I | -3.082960 | 0.022998 | 1.169952 |

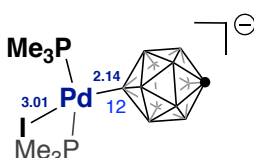


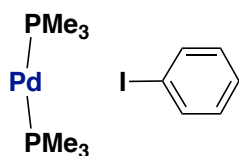
TS_{OA1}

Energy (RB3LYP): -1380.02234305 A.U.

Gibbs Free Energy: -1379.689548 A.U.

| | | | |
|---|----------|-----------|-----------|
| B | 2.907072 | -0.899828 | 0.837833 |
| B | 2.057091 | -1.456208 | -0.631392 |
| B | 1.518331 | 0.000000 | -1.551107 |
| B | 2.057091 | 1.456208 | -0.631391 |
| B | 2.907072 | 0.899827 | 0.837834 |
| B | 4.347344 | 0.000000 | 0.320927 |
| B | 3.828994 | -1.438279 | -0.581926 |
| H | 2.910556 | -1.532458 | 1.845182 |
| B | 2.969425 | -0.892586 | -2.042231 |
| H | 1.462393 | -2.487616 | -0.665792 |
| B | 2.969426 | 0.892586 | -2.042231 |
| H | 0.562427 | 0.000001 | -2.274911 |
| B | 3.828994 | 1.438279 | -0.581925 |

| | | | | | | | |
|---|-----------|-----------|-----------|-------|-----------|-----------|-----------|
| H | 1.462394 | 2.487616 | -0.665791 | B | 4.235904 | -1.453485 | 0.473439 |
| H | 2.910557 | 1.532457 | 1.845182 | B | 4.248497 | -0.897868 | -1.234912 |
| H | 5.410386 | -0.000001 | 0.857934 | B | 5.753937 | 0.000068 | -1.502302 |
| H | 4.548569 | -2.385616 | -0.645177 | B | 5.746249 | 1.440733 | -0.455187 |
| H | 3.123864 | -1.475103 | -3.070089 | H | 3.731390 | 1.528159 | -2.104224 |
| H | 3.123865 | 1.475104 | -3.070089 | B | 5.734316 | 0.889693 | 1.238567 |
| H | 4.548569 | 2.385615 | -0.645176 | H | 3.710470 | 2.471468 | 0.801778 |
| Pd | -0.852688 | 0.000000 | -0.303792 | B | 5.733995 | -0.891372 | 1.237977 |
| P | -1.785242 | -2.158552 | -0.714902 | H | 3.697826 | -0.000933 | 2.597079 |
| P | -1.785242 | 2.158553 | -0.714901 | B | 5.745734 | -1.441294 | -0.456147 |
| C | -1.420060 | 3.504414 | 0.517932 | H | 3.709543 | -2.472105 | 0.800134 |
| H | -1.938934 | 4.442786 | 0.274799 | H | 3.730836 | -1.526892 | -2.105236 |
| H | -1.720428 | 3.167436 | 1.515675 | H | 6.415842 | 0.000280 | -2.492862 |
| H | -0.340310 | 3.682700 | 0.544388 | H | 6.403253 | 2.387391 | -0.757747 |
| C | -1.381603 | -3.060032 | -2.296312 | H | 6.383307 | 1.474447 | 2.048630 |
| H | -0.296377 | -3.182092 | -2.373269 | H | 6.382778 | -1.476900 | 2.047648 |
| H | -1.860094 | -4.049012 | -2.343381 | H | 6.402395 | -2.387987 | -0.759339 |
| H | -1.713264 | -2.461040 | -3.151915 | Pd | -3.468352 | 0.000059 | 0.003318 |
| C | -3.647952 | -2.300218 | -0.759330 | P | -3.209929 | 2.289301 | 0.003811 |
| H | -4.042733 | -1.673997 | -1.567292 | P | -3.210661 | -2.289249 | 0.003804 |
| H | -3.984517 | -3.336419 | -0.912122 | C | -2.251048 | -2.978534 | -1.427164 |
| H | -4.060359 | -1.928446 | 0.185257 | H | -2.115431 | -4.064927 | -1.337679 |
| C | -1.381602 | 3.060034 | -2.296310 | H | -2.774127 | -2.756528 | -2.363441 |
| H | -0.296376 | 3.182093 | -2.373267 | H | -1.268797 | -2.496359 | -1.464014 |
| H | -1.713263 | 2.461042 | -3.151914 | C | -2.241301 | 2.975609 | 1.430092 |
| H | -1.860093 | 4.049013 | -2.343379 | H | -1.259149 | 2.492744 | 1.460153 |
| C | -3.647951 | 2.300220 | -0.759329 | H | -2.105587 | 4.062075 | 1.341642 |
| H | -4.060359 | 1.928447 | 0.185258 | H | -2.758832 | 2.752303 | 2.369137 |
| H | -3.984516 | 3.336421 | -0.912120 | C | -4.688190 | 3.421971 | 0.009485 |
| H | -4.042733 | 1.673999 | -1.567291 | H | -5.299154 | 3.223241 | 0.896795 |
| B | 1.487007 | 0.000000 | 0.228904 | H | -4.390214 | 4.479480 | 0.009554 |
| C | 4.265741 | 0.000000 | -1.382716 | H | -5.304710 | 3.224912 | -0.874346 |
| H | 5.199112 | 0.000000 | -1.935644 | C | -2.242569 | -2.975977 | 1.430254 |
| C | -1.420061 | -3.504414 | 0.517931 | H | -1.260187 | -2.493590 | 1.460451 |
| H | -1.938935 | -4.442785 | 0.274797 | H | -2.760128 | -2.752401 | 2.369219 |
| H | -0.340311 | -3.682700 | 0.544387 | H | -2.107362 | -4.062510 | 1.341850 |
| H | -1.720430 | -3.167436 | 1.515674 | C | -4.689310 | -3.421416 | 0.009119 |
| I | -0.097284 | -0.000001 | 2.404413 | H | -5.305583 | -3.224093 | -0.874825 |
| ----- | | | | H | -4.391702 | -4.479029 | 0.009190 |
|  | | | | H | -5.300385 | -3.222521 | 0.896315 |
| INT_{OA2} | | | | B | 3.335326 | 0.000004 | -0.004704 |
| Energy (RB3LYP): -1380.06521493 A.U. | | | | C | 6.529160 | -0.000580 | 0.018212 |
| Gibbs Free Energy: -1379.737332 A.U. | | | | H | 7.613888 | -0.000774 | 0.025939 |
| ----- | | | | C | -2.250400 | 2.978309 | -1.427345 |
| B | 4.248817 | 0.898370 | -1.234314 | H | -2.114377 | 4.064649 | -1.337836 |
| B | 4.236423 | 1.452852 | 0.474408 | H | -1.268325 | 2.495794 | -1.464448 |
| B | 4.228949 | -0.000665 | 1.529907 | H | -2.773780 | 2.756536 | -2.363510 |
| ----- | | | | I | 1.075294 | 0.000361 | -0.019480 |
| ----- | | | | ----- | | | |

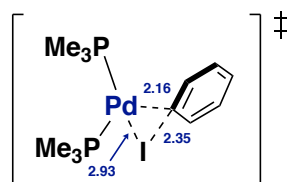


INT_{OA1'}

Energy (RB3LYP): -1293.26995263 A.U.

Gibbs Free Energy: -1293.016405 A.U.

| | | | |
|----|-----------|-----------|-----------|
| Pd | 2.656959 | 0.001939 | -0.152904 |
| P | 2.706032 | -2.307830 | -0.185168 |
| P | 2.705490 | 2.311929 | -0.168169 |
| C | 1.412697 | 3.194097 | -1.167432 |
| H | 1.540840 | 4.283507 | -1.123261 |
| H | 1.471556 | 2.869687 | -2.211542 |
| H | 0.417300 | 2.937363 | -0.790392 |
| C | 1.586561 | -3.172642 | -1.388124 |
| H | 1.809500 | -2.833716 | -2.405099 |
| H | 1.705480 | -4.262928 | -1.339442 |
| H | 0.544305 | -2.918426 | -1.169216 |
| C | 2.285681 | -3.203936 | 1.386286 |
| H | 1.266505 | -2.948023 | 1.694126 |
| H | 2.358423 | -4.292425 | 1.263242 |
| H | 2.968163 | -2.888122 | 2.182202 |
| C | 2.543024 | 3.188255 | 1.461149 |
| H | 1.583257 | 2.932372 | 1.921884 |
| H | 3.339765 | 2.858495 | 2.135949 |
| H | 2.602162 | 4.278012 | 1.342176 |
| C | 4.253809 | 3.093520 | -0.831615 |
| H | 4.414637 | 2.768344 | -1.864663 |
| H | 4.197471 | 4.189654 | -0.805214 |
| H | 5.113560 | 2.765012 | -0.238536 |
| C | 4.338417 | -3.087097 | -0.604874 |
| H | 4.276441 | -4.183220 | -0.601385 |
| H | 4.661484 | -2.750214 | -1.595303 |
| H | 5.093966 | -2.769023 | 0.120938 |
| I | -4.865209 | 0.009499 | -0.849462 |
| C | -3.317991 | -0.007338 | 0.646510 |
| C | -1.980834 | -0.002162 | 0.247579 |
| C | -3.674436 | -0.023256 | 1.995816 |
| C | -0.978355 | -0.013089 | 1.224817 |
| H | -1.712703 | 0.010233 | -0.804093 |
| C | -2.662408 | -0.034086 | 2.962835 |
| H | -4.717462 | -0.027185 | 2.295040 |
| C | -1.317834 | -0.029026 | 2.580846 |
| H | 0.067986 | -0.008983 | 0.913511 |
| H | -2.933719 | -0.046514 | 4.015708 |
| H | -0.535784 | -0.037502 | 3.335718 |

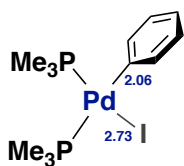


TS_{OA1'}

Energy (RB3LYP): -1293.24940134 A.U.

Gibbs Free Energy: -1292.988990 A.U.

| | | | |
|----|-----------|-----------|-----------|
| Pd | 0.433724 | 0.195857 | 0.129304 |
| P | 2.585997 | -0.742874 | 0.625691 |
| P | 0.254536 | 2.448511 | -0.631603 |
| C | -0.722080 | 2.794658 | -2.176421 |
| H | -0.713833 | 3.862068 | -2.433039 |
| H | -0.301216 | 2.223321 | -3.010533 |
| H | -1.759859 | 2.472904 | -2.042653 |
| C | 2.770886 | -1.694867 | 2.213434 |
| H | 2.072702 | -2.538721 | 2.218229 |
| H | 3.791176 | -2.079362 | 2.342513 |
| H | 2.524518 | -1.048168 | 3.062326 |
| C | 4.061026 | 0.383127 | 0.752767 |
| H | 3.898681 | 1.112534 | 1.553760 |
| H | 4.983690 | -0.173948 | 0.961914 |
| H | 4.185266 | 0.934307 | -0.185295 |
| C | -0.492395 | 3.688390 | 0.533780 |
| H | -1.498380 | 3.363757 | 0.818280 |
| H | 0.111960 | 3.740216 | 1.445868 |
| H | -0.549022 | 4.689242 | 0.086058 |
| C | 1.841245 | 3.319509 | -1.062839 |
| H | 2.352683 | 2.775473 | -1.864407 |
| H | 1.666011 | 4.352260 | -1.392161 |
| H | 2.501421 | 3.334045 | -0.189175 |
| C | 3.217080 | -1.988520 | -0.597887 |
| H | 4.187329 | -2.403574 | -0.295921 |
| H | 2.491010 | -2.802042 | -0.696436 |
| H | 3.320982 | -1.516093 | -1.580456 |
| I | -1.153715 | -1.781971 | -1.340914 |
| C | -1.620806 | -0.389805 | 0.502518 |
| C | -1.354228 | -0.963076 | 1.762780 |
| C | -2.699701 | 0.507548 | 0.350735 |
| C | -2.067808 | -0.511345 | 2.887760 |
| H | -0.644342 | -1.776325 | 1.860758 |
| C | -3.407341 | 0.924029 | 1.473497 |
| H | -2.960519 | 0.880285 | -0.634481 |
| C | -3.085811 | 0.428882 | 2.750737 |
| H | -1.842824 | -0.937384 | 3.863004 |
| H | -4.217889 | 1.640345 | 1.356664 |
| H | -3.652366 | 0.754167 | 3.619191 |



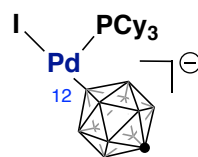
INT2_{OA2'}

Energy (RB3LYP): -1293.30433185 A.U.

Gibbs Free Energy: -1293.037996 A.U.

| | | | |
|----|-----------|-----------|-----------|
| Pd | 0.154712 | 0.249212 | -0.006279 |
| P | 2.600071 | 0.457017 | 0.017203 |
| P | -0.606622 | 2.451628 | -0.025640 |
| C | -1.796809 | 2.873881 | -1.373496 |
| H | -2.105136 | 3.923010 | -1.292518 |
| H | -1.322374 | 2.716144 | -2.347827 |
| H | -2.674937 | 2.227557 | -1.312275 |
| C | 3.386376 | -0.384278 | 1.464659 |
| H | 3.049265 | -1.422790 | 1.506337 |
| H | 4.479930 | -0.351561 | 1.387835 |
| H | 3.078377 | 0.115475 | 2.389657 |
| C | 3.516651 | 2.075528 | 0.059160 |
| H | 3.260241 | 2.640369 | 0.960999 |
| H | 4.598081 | 1.893664 | 0.063338 |
| H | 3.272543 | 2.686292 | -0.814867 |
| C | -1.517526 | 2.959034 | 1.499222 |
| H | -2.373122 | 2.296970 | 1.653157 |
| H | -0.857200 | 2.879694 | 2.369228 |
| H | -1.869162 | 3.993913 | 1.410749 |
| C | 0.592739 | 3.854299 | -0.196153 |
| H | 1.152835 | 3.764576 | -1.131677 |
| H | 0.053108 | 4.808911 | -0.201841 |
| H | 1.302458 | 3.859364 | 0.634945 |
| C | 3.418182 | -0.340627 | -1.437028 |
| H | 4.509690 | -0.319662 | -1.332348 |
| H | 3.074822 | -1.374855 | -1.519937 |
| H | 3.137035 | 0.190673 | -2.352929 |
| I | 0.530396 | -2.463020 | -0.013516 |
| C | -1.853799 | -0.218430 | 0.007118 |
| C | -2.546094 | -0.371945 | 1.218158 |
| C | -2.549819 | -0.457854 | -1.188177 |
| C | -3.897337 | -0.743970 | 1.235626 |
| H | -2.028796 | -0.230141 | 2.164810 |
| C | -3.900222 | -0.829688 | -1.174589 |
| H | -2.036012 | -0.378732 | -2.143721 |
| C | -4.582229 | -0.969404 | 0.038269 |
| H | -4.408363 | -0.867677 | 2.188614 |
| H | -4.414349 | -1.020610 | -2.114701 |
| H | -5.629083 | -1.263219 | 0.050082 |

Transmetalation



INT_{TM1}

Energy (RB3LYP): -1505.01783536 A.U.

Gibbs Free Energy: -1504.432015 A.U.

| | | | |
|----|-----------|-----------|-----------|
| B | -3.538740 | 1.073751 | -0.642139 |
| B | -3.155237 | -0.273337 | -1.755919 |
| B | -2.887107 | -1.737265 | -0.743129 |
| B | -3.130113 | -1.301132 | 0.986401 |
| B | -3.521001 | 0.443850 | 1.041698 |
| B | -5.056472 | 0.674360 | 0.183488 |
| B | -4.832380 | 0.229554 | -1.527522 |
| H | -3.273855 | 2.207329 | -0.899169 |
| B | -4.420143 | -1.505616 | -1.598856 |
| H | -2.583494 | -0.109177 | -2.789139 |
| B | -4.403866 | -2.134888 | 0.081125 |
| H | -2.082871 | -2.576548 | -1.058878 |
| B | -4.806414 | -0.782419 | 1.175379 |
| H | -2.541408 | -1.852909 | 1.863673 |
| H | -3.233645 | 1.126576 | 1.977711 |
| H | -5.927271 | 1.433225 | 0.473276 |
| H | -5.555845 | 0.700358 | -2.347919 |
| H | -4.872585 | -2.182840 | -2.466466 |
| H | -4.846234 | -3.218153 | 0.297091 |
| H | -5.511261 | -0.973759 | 2.115736 |
| Pd | -0.450655 | -0.938557 | -0.303896 |
| P | 0.856106 | 0.849020 | 0.195252 |
| B | -2.360722 | -0.163886 | -0.161569 |
| C | -5.460253 | -0.881343 | -0.396536 |
| H | -6.513515 | -1.127156 | -0.478345 |
| I | 1.454850 | -3.056864 | -0.519237 |
| C | 1.513803 | 0.722379 | 1.976386 |
| C | 0.407733 | 0.176579 | 2.911197 |
| C | 2.790411 | -0.132029 | 2.138647 |
| H | 1.755648 | 1.753305 | 2.282559 |
| C | 0.864453 | 0.138508 | 4.379072 |
| H | 0.149642 | -0.837963 | 2.581351 |
| H | -0.512106 | 0.762588 | 2.820442 |
| C | 3.249559 | -0.183228 | 3.608510 |
| H | 2.596112 | -1.149088 | 1.774063 |
| H | 3.610362 | 0.269395 | 1.532846 |
| C | 2.144455 | -0.692733 | 4.544382 |
| H | 0.057762 | -0.272126 | 5.001451 |
| H | 1.046090 | 1.164947 | 4.737811 |
| H | 4.140667 | -0.821609 | 3.687286 |

| | | | |
|---|-----------|-----------|-----------|
| H | 3.557255 | 0.825754 | 3.929153 |
| H | 2.487934 | -0.670419 | 5.588695 |
| H | 1.924501 | -1.743037 | 4.303831 |
| C | 0.357589 | 2.675021 | 0.119222 |
| C | -0.167932 | 3.083033 | -1.273309 |
| C | -0.639761 | 3.097866 | 1.218396 |
| H | 1.296250 | 3.221106 | 0.304427 |
| C | -0.505873 | 4.584146 | -1.342964 |
| H | -1.061381 | 2.493194 | -1.507076 |
| H | 0.572632 | 2.850730 | -2.044983 |
| C | -0.963830 | 4.601615 | 1.140648 |
| H | -1.564944 | 2.521299 | 1.119466 |
| H | -0.232844 | 2.877817 | 2.211594 |
| C | -1.492037 | 5.002445 | -0.243567 |
| H | -0.916825 | 4.819174 | -2.334578 |
| H | 0.421479 | 5.171213 | -1.240304 |
| H | -1.697988 | 4.855332 | 1.917743 |
| H | -0.054504 | 5.183094 | 1.364918 |
| H | -1.673088 | 6.086186 | -0.284875 |
| H | -2.458351 | 4.509680 | -0.417550 |
| C | 2.403528 | 0.762241 | -0.892802 |
| C | 2.111852 | 0.461555 | -2.380441 |
| C | 3.385878 | 1.945891 | -0.767530 |
| H | 2.893404 | -0.140365 | -0.504613 |
| C | 3.419421 | 0.165908 | -3.135833 |
| H | 1.606996 | 1.312668 | -2.856364 |
| H | 1.438181 | -0.397683 | -2.454000 |
| C | 4.697174 | 1.651589 | -1.521643 |
| H | 2.933045 | 2.852886 | -1.193005 |
| H | 3.607136 | 2.171007 | 0.284138 |
| C | 4.434761 | 1.311630 | -2.997447 |
| H | 3.199078 | -0.019162 | -4.196237 |
| H | 3.852735 | -0.763340 | -2.739176 |
| H | 5.374649 | 2.514240 | -1.441954 |
| H | 5.206787 | 0.804092 | -1.039052 |
| H | 5.377885 | 1.051963 | -3.499114 |
| H | 4.044676 | 2.207036 | -3.507553 |

Ph-Zn-Cl

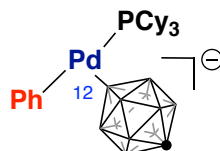
INT_{TM2}

Energy (RB3LYP): -919.048433475 A.U.

Gibbs Free Energy: -918.991583 A.U.

| | | | |
|----|-----------|-----------|-----------|
| Zn | -1.174742 | 0.000006 | -0.000000 |
| Cl | -3.299414 | -0.000006 | 0.000000 |
| C | 0.746411 | 0.000001 | -0.000000 |
| C | 1.469622 | 1.208260 | -0.000000 |
| C | 1.469617 | -1.208261 | -0.000000 |
| C | 2.868742 | 1.209120 | 0.000000 |
| C | 2.868737 | -1.209125 | 0.000000 |

| | | | |
|---|----------|-----------|-----------|
| C | 3.570063 | -0.000004 | 0.000000 |
| H | 3.409179 | 2.152912 | 0.000000 |
| H | 3.409171 | -2.152920 | 0.000000 |
| H | 4.657350 | -0.000006 | 0.000001 |
| H | 0.948723 | -2.163410 | -0.000000 |
| H | 0.948731 | 2.163412 | -0.000001 |



INT_{TM3}

Energy (RB3LYP): -1725.16675049 A.U.

Gibbs Free Energy: -1724.497356 A.U.

| | | | |
|----|-----------|-----------|-----------|
| B | 2.626746 | -1.314960 | -1.589266 |
| B | 3.858759 | -0.146377 | -1.023381 |
| B | 3.902346 | -0.211455 | 0.764800 |
| B | 2.699127 | -1.421441 | 1.304209 |
| B | 1.919231 | -2.109922 | -0.151285 |
| B | 3.157100 | -2.941940 | -1.102901 |
| B | 4.349969 | -1.736391 | -1.638164 |
| H | 2.015783 | -1.160273 | -2.604149 |
| B | 5.132592 | -1.061039 | -0.192675 |
| H | 4.124359 | 0.838745 | -1.636406 |
| B | 4.421510 | -1.841898 | 1.236705 |
| H | 4.198101 | 0.727461 | 1.434945 |
| B | 3.201485 | -3.007829 | 0.674568 |
| H | 2.143314 | -1.341354 | 2.358757 |
| H | 0.799733 | -2.521960 | -0.139175 |
| H | 3.017139 | -3.950638 | -1.724031 |
| H | 5.001322 | -1.954377 | -2.612698 |
| H | 6.302237 | -0.832753 | -0.213146 |
| H | 5.119836 | -2.128842 | 2.159510 |
| H | 3.090948 | -4.059521 | 1.226286 |
| Pd | 0.630829 | 0.884544 | -0.008367 |
| P | -1.559388 | -0.221138 | 0.107643 |
| B | 2.336969 | -0.365004 | -0.097279 |
| C | 4.603178 | -2.682273 | -0.238753 |
| H | 5.361427 | -3.456975 | -0.285996 |
| C | -2.093085 | -0.894504 | 1.798901 |
| C | -1.143040 | -2.015835 | 2.279739 |
| C | -2.107355 | 0.236461 | 2.855592 |
| H | -3.112403 | -1.303494 | 1.712871 |
| C | -1.535012 | -2.547211 | 3.669287 |
| H | -0.120814 | -1.621854 | 2.316121 |
| H | -1.119566 | -2.844755 | 1.568721 |
| C | -2.485116 | -0.282756 | 4.255365 |
| H | -1.108865 | 0.695598 | 2.891350 |
| H | -2.807596 | 1.031597 | 2.576997 |

| | | | |
|---|-----------|-----------|-----------|
| C | -1.566897 | -1.423662 | 4.714084 |
| H | -0.825124 | -3.328780 | 3.971685 |
| H | -2.527252 | -3.025074 | 3.617660 |
| H | -2.452394 | 0.548664 | 4.973778 |
| H | -3.527296 | -0.640800 | 4.238562 |
| H | -1.895612 | -1.809814 | 5.689628 |
| H | -0.547672 | -1.034704 | 4.853604 |
| C | -2.211622 | -1.434881 | -1.211172 |
| C | -1.335870 | -1.338242 | -2.481704 |
| C | -2.350275 | -2.911877 | -0.787914 |
| H | -3.222138 | -1.082588 | -1.467878 |
| C | -1.906103 | -2.191190 | -3.628326 |
| H | -0.320033 | -1.670991 | -2.241449 |
| H | -1.238453 | -0.296650 | -2.807373 |
| C | -2.935375 | -3.763297 | -1.930627 |
| H | -1.363545 | -3.309846 | -0.521233 |
| H | -2.989212 | -3.006040 | 0.098917 |
| C | -2.087950 | -3.657302 | -3.207510 |
| H | -1.240312 | -2.126071 | -4.499497 |
| H | -2.879681 | -1.781408 | -3.944295 |
| H | -3.009527 | -4.811497 | -1.607711 |
| H | -3.962802 | -3.427521 | -2.145804 |
| H | -2.548589 | -4.237008 | -4.020270 |
| H | -1.099683 | -4.102242 | -3.021327 |
| C | -2.755904 | 1.241680 | -0.125789 |
| C | -2.548548 | 1.942317 | -1.487536 |
| C | -4.256959 | 0.961427 | 0.100643 |
| H | -2.430135 | 1.956401 | 0.644174 |
| C | -3.376980 | 3.235278 | -1.586480 |
| H | -2.850067 | 1.266696 | -2.301150 |
| H | -1.484645 | 2.163013 | -1.638398 |
| C | -5.092890 | 2.252344 | 0.000312 |
| H | -4.620255 | 0.248287 | -0.653388 |
| H | -4.427073 | 0.493154 | 1.077250 |
| C | -4.870424 | 2.972743 | -1.338435 |
| H | -3.229753 | 3.696351 | -2.572792 |
| H | -3.004783 | 3.958476 | -0.845355 |
| H | -6.158567 | 2.017970 | 0.135861 |
| H | -4.813239 | 2.926534 | 0.824527 |
| H | -5.435434 | 3.915248 | -1.362248 |
| H | -5.267852 | 2.348006 | -2.153971 |
| C | 1.911704 | 2.436831 | -0.059606 |
| C | 2.174247 | 3.113984 | -1.270802 |
| C | 2.312158 | 3.088381 | 1.127268 |
| C | 2.769445 | 4.381654 | -1.296370 |
| C | 2.908252 | 4.355812 | 1.110774 |
| C | 3.138017 | 5.013067 | -0.103138 |
| H | 2.957157 | 4.871324 | -2.251970 |
| H | 3.204939 | 4.825587 | 2.048576 |
| H | 3.608980 | 5.994768 | -0.119767 |

| | | | |
|---|----------|----------|-----------|
| H | 2.169748 | 2.592040 | 2.085048 |
| H | 1.923271 | 2.637538 | -2.216572 |

I—Zn—Cl

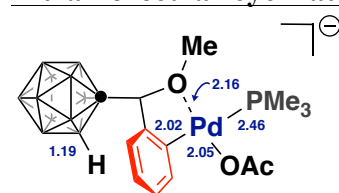
INT_{TM4}

Energy (RB3LYP): -698.871491653 A.U.

Gibbs Free Energy: -698.896345 A.U.

| | | | |
|----|-----------|-----------|-----------|
| I | -0.006215 | -1.504159 | 0.000000 |
| Zn | 0.000000 | 0.932386 | 0.000000 |
| Cl | 0.019377 | 3.044050 | -0.000000 |

Intramolecular cyclization



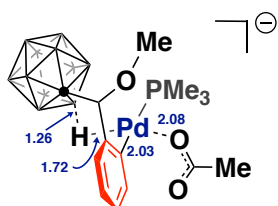
INT₁

Energy (RB3LYP): -1520.84108544 A.U.

Gibbs Free Energy: -1520.431207 A.U.

| | | | |
|---|-----------|-----------|-----------|
| B | 1.799772 | -0.860470 | -1.132204 |
| B | 2.779260 | 0.605678 | -1.352142 |
| B | 3.981319 | 0.645387 | -0.037289 |
| B | 3.760424 | -0.802159 | 0.969676 |
| B | 2.414450 | -1.738308 | 0.296336 |
| B | 2.864926 | -2.270179 | -1.327452 |
| B | 3.097159 | -0.821975 | -2.345923 |
| B | 4.453850 | 0.121355 | -1.662532 |
| B | 5.063355 | -0.750274 | -0.225205 |
| B | 4.086074 | -2.229288 | -0.020551 |
| B | 4.513104 | -1.662844 | -1.657525 |
| H | 3.863334 | -0.698777 | 2.155081 |
| H | 0.629975 | -0.821358 | -1.346938 |
| H | 4.255061 | 1.678790 | 0.489579 |
| H | 2.439512 | -3.296819 | -1.768048 |
| H | 5.277134 | -2.268731 | -2.348721 |
| H | 4.524116 | -3.225642 | 0.473249 |
| H | 6.204805 | -0.683327 | 0.121952 |
| H | 5.164319 | 0.802783 | -2.339073 |
| H | 2.257763 | 1.611476 | -1.703574 |
| H | 2.839226 | -0.818471 | -3.511659 |
| H | 1.659228 | -2.291674 | 1.027808 |
| C | 2.413985 | -0.009190 | 0.220222 |
| C | 1.501008 | 0.783074 | 1.184599 |
| H | 2.101814 | 0.974147 | 2.079210 |
| C | 0.872539 | 2.076696 | 0.706823 |
| C | -0.473465 | 2.057128 | 0.284405 |

| | | | | | | | |
|----|-----------|-----------|-----------|---|-----------|-----------|-----------|
| C | 1.581201 | 3.286428 | 0.738229 | B | 2.811134 | -1.123071 | -1.804041 |
| C | -1.078960 | 3.251679 | -0.118268 | B | 4.293557 | -0.203302 | -1.421187 |
| C | 0.967286 | 4.473421 | 0.332113 | B | 4.826949 | -0.680295 | 0.215488 |
| H | 2.618592 | 3.295819 | 1.064020 | B | 3.680787 | -1.892580 | 0.844214 |
| C | -0.363847 | 4.454923 | -0.097950 | B | 4.129891 | -1.897771 | -0.884444 |
| H | -2.112628 | 3.229783 | -0.452139 | H | 3.717925 | 0.220077 | 2.466016 |
| H | 1.527094 | 5.406029 | 0.350714 | H | 0.440867 | -0.555501 | -1.153919 |
| H | -0.846805 | 5.377853 | -0.415818 | H | 4.348902 | 1.938285 | 0.163585 |
| O | 0.387641 | -0.083101 | 1.624364 | H | 1.874739 | -3.211871 | -0.537022 |
| C | 0.115576 | 0.059530 | 3.026169 | H | 4.783431 | -2.777635 | -1.359613 |
| H | -0.116485 | 1.102346 | 3.273289 | H | 4.007537 | -2.748359 | 1.610455 |
| H | -0.744323 | -0.571112 | 3.252213 | H | 5.976398 | -0.668840 | 0.538799 |
| H | 0.987926 | -0.284026 | 3.595305 | H | 5.054608 | 0.147860 | -2.271187 |
| Pd | -1.349482 | 0.243267 | 0.376048 | H | 2.294820 | 1.473181 | -1.919258 |
| P | -2.135185 | -2.089588 | 0.475277 | H | 2.503745 | -1.426276 | -2.916585 |
| C | -1.630792 | -3.130962 | -0.960826 | H | 1.297244 | -1.345261 | 1.848213 |
| C | -3.937850 | -2.466038 | 0.666427 | C | 2.308668 | 0.498449 | 0.409457 |
| C | -1.434816 | -3.069985 | 1.891361 | C | 1.511401 | 1.664833 | 1.044528 |
| H | -1.964618 | -4.168065 | -0.827213 | H | 2.257326 | 2.387585 | 1.408102 |
| H | -2.075688 | -2.706527 | -1.863420 | C | 0.581388 | 2.394817 | 0.084315 |
| H | -0.540975 | -3.111738 | -1.058443 | C | -0.518023 | 1.751749 | -0.511809 |
| H | -4.102052 | -3.546439 | 0.771151 | C | 0.822017 | 3.750821 | -0.186537 |
| H | -4.331033 | -1.959725 | 1.555408 | C | -1.349312 | 2.481330 | -1.373219 |
| H | -4.466105 | -2.097359 | -0.215583 | C | -0.003480 | 4.471646 | -1.052989 |
| H | -1.721317 | -4.126626 | 1.813755 | H | 1.674644 | 4.242303 | 0.281102 |
| H | -0.342853 | -2.999559 | 1.885592 | C | -1.092450 | 3.830875 | -1.649234 |
| H | -1.806624 | -2.681681 | 2.846863 | H | -2.203887 | 1.993993 | -1.835759 |
| O | -2.941896 | 1.038387 | -0.645228 | H | 0.203364 | 5.519900 | -1.259018 |
| C | -3.612243 | 0.436410 | -1.579386 | H | -1.745794 | 4.376557 | -2.328413 |
| O | -3.500074 | -0.745149 | -1.930228 | O | 0.813167 | 1.144254 | 2.176620 |
| C | -4.614541 | 1.360283 | -2.275124 | C | 0.216100 | 2.130468 | 2.995472 |
| H | -4.072554 | 2.010012 | -2.973621 | H | -0.593346 | 2.660541 | 2.476104 |
| H | -5.343561 | 0.770987 | -2.837662 | H | -0.196426 | 1.602660 | 3.860188 |
| H | -5.122639 | 2.005097 | -1.550592 | H | 0.962633 | 2.865059 | 3.343421 |



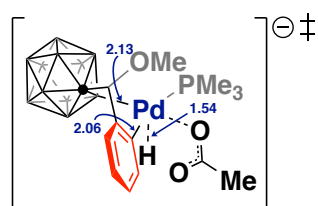
INT₁

Energy (RB3LYP): -1520.84088540 A.U.

Gibbs Free Energy: -1520.432029 A.U.

| | | | | | | | |
|---|----------|-----------|-----------|----|-----------|-----------|-----------|
| B | 1.578764 | -0.634394 | -0.622256 | Pd | -0.938412 | -0.208459 | -0.191695 |
| B | 2.709062 | 0.570612 | -1.272673 | P | -1.587494 | -2.554971 | -0.006401 |
| B | 3.943347 | 0.835069 | -0.029080 | C | -1.292384 | -3.543753 | -1.541850 |
| B | 3.558640 | -0.199450 | 1.364271 | C | -3.388045 | -2.842525 | 0.294401 |
| B | 2.088924 | -1.130281 | 0.996201 | C | -0.818605 | -3.607080 | 1.307181 |
| B | 2.434261 | -2.164865 | -0.402916 | H | -1.641578 | -4.577957 | -1.427042 |
| | | | | H | -1.825277 | -3.075492 | -2.376154 |
| | | | | H | -0.223008 | -3.549242 | -1.773637 |
| | | | | H | -3.616744 | -3.915894 | 0.309858 |
| | | | | H | -3.670162 | -2.400171 | 1.255349 |
| | | | | H | -3.968524 | -2.346174 | -0.488237 |
| | | | | H | -1.219930 | -4.628439 | 1.277900 |
| | | | | H | 0.265314 | -3.637902 | 1.171148 |
| | | | | H | -1.025092 | -3.167933 | 2.288954 |
| | | | | O | -2.701647 | 0.405744 | 0.735153 |
| | | | | C | -3.793866 | 0.497891 | 0.043677 |

| | | | |
|---|-----------|----------|-----------|
| O | -3.948931 | 0.154860 | -1.138039 |
| C | -4.954869 | 1.120579 | 0.824629 |
| H | -4.898654 | 2.211918 | 0.721493 |
| H | -5.911053 | 0.785658 | 0.411951 |
| H | -4.893201 | 0.883210 | 1.891297 |



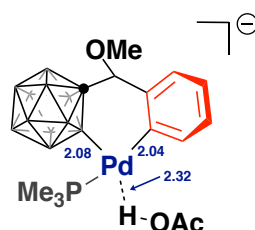
TS₁

Energy (RB3LYP): -1520.80161197 A.U.

Gibbs Free Energy: -1520.392748 A.U.

| | | | |
|---|-----------|-----------|-----------|
| B | 1.203410 | -0.602368 | -0.528230 |
| B | 2.312423 | 0.557243 | -1.323385 |
| B | 3.801449 | 0.624034 | -0.355150 |
| B | 3.653679 | -0.529988 | 0.989613 |
| B | 2.068854 | -1.317464 | 0.869589 |
| B | 1.990733 | -2.210404 | -0.647124 |
| B | 2.124479 | -1.059075 | -1.995530 |
| B | 3.747229 | -0.290911 | -1.878677 |
| B | 4.587417 | -0.964171 | -0.456145 |
| B | 3.509476 | -2.161508 | 0.300778 |
| B | 3.554273 | -2.010976 | -1.474047 |
| H | 4.081228 | -0.237625 | 2.063587 |
| H | -1.479558 | -0.096514 | -1.341546 |
| H | 4.331138 | 1.675545 | -0.167844 |
| H | 1.360416 | -3.219934 | -0.737935 |
| H | 4.007380 | -2.877091 | -2.162301 |
| H | 3.912445 | -3.117864 | 0.894073 |
| H | 5.777142 | -1.064439 | -0.409936 |
| H | 4.331765 | 0.098722 | -2.844648 |
| H | 1.904552 | 1.558271 | -1.800772 |
| H | 1.580267 | -1.233373 | -3.044014 |
| H | 1.480715 | -1.578213 | 1.864718 |
| C | 2.285442 | 0.332104 | 0.399461 |
| C | 1.628777 | 1.427542 | 1.267342 |
| H | 2.407818 | 1.954861 | 1.835324 |
| C | 0.811616 | 2.393580 | 0.436258 |
| C | -0.273402 | 1.866741 | -0.293357 |
| C | 1.124843 | 3.754728 | 0.383176 |
| C | -1.011523 | 2.743616 | -1.097630 |
| C | 0.377448 | 4.619795 | -0.423800 |
| H | 1.968001 | 4.136018 | 0.958678 |
| C | -0.687655 | 4.106748 | -1.167327 |
| H | -1.838453 | 2.367569 | -1.693223 |
| H | 0.629949 | 5.676975 | -0.475067 |
| H | -1.270526 | 4.765246 | -1.809897 |

| | | | |
|----|-----------|-----------|-----------|
| O | 0.754083 | 0.755725 | 2.203528 |
| C | 0.224956 | 1.602041 | 3.211352 |
| H | -0.422130 | 2.383539 | 2.791942 |
| H | -0.362167 | 0.961688 | 3.875731 |
| H | 1.035890 | 2.074468 | 3.788500 |
| Pd | -0.786971 | -0.096414 | 0.037985 |
| P | -1.569103 | -2.415017 | 0.279822 |
| C | -1.639333 | -3.354870 | -1.308529 |
| C | -3.327575 | -2.545336 | 0.849642 |
| C | -0.749240 | -3.591537 | 1.449417 |
| H | -2.067659 | -4.354308 | -1.159872 |
| H | -2.259757 | -2.793385 | -2.014618 |
| H | -0.633708 | -3.447344 | -1.725976 |
| H | -3.613612 | -3.598075 | 0.971064 |
| H | -3.454747 | -2.019039 | 1.800267 |
| H | -3.986579 | -2.076581 | 0.114680 |
| H | -1.253985 | -4.565986 | 1.428492 |
| H | 0.301165 | -3.718057 | 1.181717 |
| H | -0.797077 | -3.185196 | 2.465411 |
| O | -2.963167 | 0.562073 | 0.501023 |
| C | -3.620722 | 0.565698 | -0.584596 |
| O | -3.187266 | 0.162559 | -1.706156 |
| C | -5.040991 | 1.130038 | -0.537250 |
| H | -4.994103 | 2.205621 | -0.751418 |
| H | -5.672481 | 0.661368 | -1.297925 |
| H | -5.478297 | 1.003187 | 0.457612 |



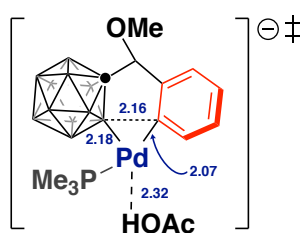
INT₂

Energy (RB3LYP): -1520.83446027 A.U.

Gibbs Free Energy: -1520.428066 A.U.

| | | | |
|---|-----------|-----------|-----------|
| B | 0.649849 | -0.917890 | -0.359360 |
| B | 1.437142 | -0.341935 | -1.856729 |
| B | 3.114485 | -0.926413 | -1.844735 |
| B | 3.365025 | -1.858184 | -0.354062 |
| B | 1.835661 | -1.872905 | 0.562898 |
| B | 0.622150 | -2.698235 | -0.423601 |
| B | 0.357653 | -1.748122 | -1.909833 |
| B | 1.894934 | -1.748874 | -2.828483 |
| B | 3.094833 | -2.692297 | -1.899571 |
| B | 2.307740 | -3.279603 | -0.412653 |
| B | 1.390363 | -3.211667 | -1.943906 |
| H | 4.397457 | -1.761824 | 0.231054 |
| H | -1.736147 | 0.788000 | -1.229224 |

| | | | |
|----|-----------|-----------|-----------|
| H | 3.980521 | -0.203533 | -2.230621 |
| H | -0.251199 | -3.331233 | 0.088318 |
| H | 1.037534 | -4.203913 | -2.510927 |
| H | 2.617635 | -4.303205 | 0.121466 |
| H | 3.978496 | -3.297620 | -2.429994 |
| H | 1.915436 | -1.674501 | -4.020879 |
| H | 1.201927 | 0.739650 | -2.281605 |
| H | -0.704286 | -1.693815 | -2.454136 |
| H | 1.860040 | -1.821431 | 1.746962 |
| C | 2.308563 | -0.499256 | -0.377260 |
| C | 2.787361 | 0.784279 | 0.323840 |
| H | 3.760463 | 1.047578 | -0.117261 |
| C | 1.857366 | 1.982961 | 0.179771 |
| C | 0.458645 | 1.864985 | 0.334526 |
| C | 2.445131 | 3.235539 | -0.051143 |
| C | -0.293478 | 3.057311 | 0.276272 |
| C | 1.676672 | 4.402897 | -0.111798 |
| H | 3.524270 | 3.298887 | -0.192094 |
| C | 0.295488 | 4.311590 | 0.064437 |
| H | -1.378680 | 3.017304 | 0.380951 |
| H | 2.151958 | 5.363934 | -0.298981 |
| H | -0.326500 | 5.204782 | 0.017902 |
| O | 3.011410 | 0.476137 | 1.709695 |
| C | 3.829781 | 1.398324 | 2.392272 |
| H | 3.363705 | 2.391582 | 2.475380 |
| H | 3.985234 | 0.990777 | 3.396444 |
| H | 4.810278 | 1.509925 | 1.896831 |
| Pd | -0.678968 | 0.223965 | 0.752892 |
| P | -2.292297 | -1.405327 | 1.445216 |
| C | -3.204844 | -2.414582 | 0.193892 |
| C | -3.701388 | -0.598729 | 2.347734 |
| C | -1.747186 | -2.672633 | 2.681418 |
| H | -3.906558 | -3.104937 | 0.679976 |
| H | -3.760836 | -1.736747 | -0.460818 |
| H | -2.491877 | -2.982313 | -0.409670 |
| H | -4.429685 | -1.342543 | 2.696993 |
| H | -3.322767 | -0.043870 | 3.213782 |
| H | -4.197725 | 0.103412 | 1.670849 |
| H | -2.582393 | -3.315209 | 2.989622 |
| H | -0.955070 | -3.287507 | 2.245935 |
| H | -1.339410 | -2.166470 | 3.563185 |
| O | -4.085146 | 0.964713 | -0.773097 |
| C | -3.526274 | 1.235077 | -1.826892 |
| O | -2.217174 | 1.120828 | -2.042593 |
| C | -4.247351 | 1.742429 | -3.058678 |
| H | -3.831490 | 2.709436 | -3.362426 |
| H | -4.092172 | 1.046703 | -3.890863 |
| H | -5.314000 | 1.842290 | -2.849600 |



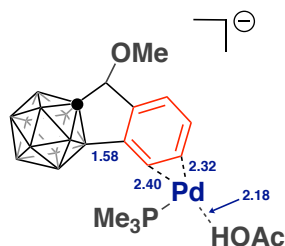
TS₂

Energy (RB3LYP): -1520.81826078 A.U.

Gibbs Free Energy: -1520.412540 A.U.

| | | | |
|---|-----------|-----------|-----------|
| B | -0.891974 | -0.546253 | 0.696274 |
| B | -2.234801 | -0.280017 | 1.852798 |
| B | -3.630227 | -1.231017 | 1.301598 |
| B | -3.165100 | -2.115389 | -0.163805 |
| B | -1.466486 | -1.729545 | -0.531625 |
| B | -0.453142 | -2.289078 | 0.817018 |
| B | -0.917474 | -1.378144 | 2.278869 |
| B | -2.626667 | -1.798854 | 2.650563 |
| B | -3.207245 | -2.943019 | 1.411168 |
| B | -1.866019 | -3.248921 | 0.276510 |
| B | -1.529167 | -3.046203 | 2.016734 |
| H | -3.944455 | -2.237710 | -1.054912 |
| H | 2.161758 | 0.378124 | 1.185603 |
| H | -4.715692 | -0.741984 | 1.369660 |
| H | 0.661213 | -2.675184 | 0.636927 |
| H | -1.155524 | -3.958021 | 2.694061 |
| H | -1.733113 | -4.286368 | -0.302579 |
| H | -4.038336 | -3.769532 | 1.644892 |
| H | -3.046227 | -1.791957 | 3.769456 |
| H | -2.437207 | 0.795638 | 2.309596 |
| H | -0.135744 | -1.100528 | 3.136759 |
| H | -1.152206 | -1.631564 | -1.670969 |
| C | -2.515857 | -0.562236 | 0.166481 |
| C | -2.890339 | 0.687759 | -0.642158 |
| H | -3.946965 | 0.934341 | -0.453438 |
| C | -2.016340 | 1.843443 | -0.166309 |
| C | -0.708249 | 1.568233 | 0.307554 |
| C | -2.561679 | 3.125326 | -0.054001 |
| C | -0.025773 | 2.616368 | 0.962611 |
| C | -1.837756 | 4.169558 | 0.533640 |
| H | -3.582758 | 3.302389 | -0.390960 |
| C | -0.571375 | 3.904260 | 1.055706 |
| H | 0.939183 | 2.432037 | 1.424274 |
| H | -2.276589 | 5.161768 | 0.617893 |
| H | -0.009345 | 4.691468 | 1.556191 |
| O | -2.749784 | 0.402644 | -2.039267 |
| C | -3.302611 | 1.382161 | -2.889334 |
| H | -2.773328 | 2.344075 | -2.815988 |
| H | -3.207465 | 0.998500 | -3.910022 |
| H | -4.371682 | 1.550347 | -2.669404 |

| | | | | | | | |
|----|----------|-----------|-----------|---|-----------|-----------|-----------|
| Pd | 0.693353 | 0.307168 | -0.535867 | H | -5.670964 | 0.329895 | -3.114006 |
| P | 2.354189 | -0.753573 | -1.830923 | H | -3.829804 | -1.834906 | -1.867259 |
| C | 3.236144 | -2.239313 | -1.169254 | H | -2.660271 | 0.383914 | -3.684676 |
| C | 3.777123 | 0.266600 | -2.445906 | H | -1.844970 | 1.325324 | 1.076298 |
| C | 1.666406 | -1.417396 | -3.422070 | C | -3.513939 | -0.218029 | 0.013324 |
| H | 3.877853 | -2.691814 | -1.937163 | C | -3.038300 | -1.420202 | 0.865719 |
| H | 3.850372 | -1.933749 | -0.317386 | H | -3.699363 | -2.275307 | 0.648046 |
| H | 2.501161 | -2.973537 | -0.826005 | C | -1.624213 | -1.743647 | 0.382639 |
| H | 4.419195 | -0.309496 | -3.125842 | C | -1.177635 | -0.986588 | -0.716100 |
| H | 3.400227 | 1.149469 | -2.973927 | C | -0.825407 | -2.741622 | 0.958251 |
| H | 4.367248 | 0.596846 | -1.585745 | C | 0.092601 | -1.272304 | -1.264815 |
| H | 2.441904 | -1.913954 | -4.020797 | C | 0.433837 | -3.013540 | 0.423771 |
| H | 0.866546 | -2.130427 | -3.198712 | H | -1.184539 | -3.292278 | 1.824722 |
| H | 1.230013 | -0.599303 | -4.005175 | C | 0.898278 | -2.295884 | -0.705436 |
| O | 4.555409 | 0.135573 | 0.968467 | H | 0.403774 | -0.780200 | -2.182998 |
| C | 3.946237 | 0.452349 | 1.979388 | H | 1.055402 | -3.795431 | 0.853512 |
| O | 2.622284 | 0.588241 | 2.058047 | H | 1.804986 | -2.618697 | -1.213186 |
| C | 4.610289 | 0.735333 | 3.311352 | O | -3.021330 | -1.223843 | 2.275910 |
| H | 4.327746 | 1.731262 | 3.669626 | C | -4.266160 | -1.463277 | 2.911723 |
| H | 4.261351 | 0.011429 | 4.056387 | H | -4.601589 | -2.500888 | 2.744575 |
| H | 5.694707 | 0.667195 | 3.206726 | H | -4.102439 | -1.308406 | 3.982670 |



INT₃

Energy (RB3LYP): -1520.87379302 A.U.

Gibbs Free Energy: -1520.470484 A.U.

| | | | | | | | |
|---|-----------|-----------|-----------|----|----------|-----------|-----------|
| B | -2.275431 | 0.075558 | -1.128455 | Pd | 1.688103 | -0.355745 | 0.280376 |
| B | -3.822018 | -0.669739 | -1.615686 | P | 2.561662 | 1.436676 | 1.358196 |
| B | -5.101072 | 0.004464 | -0.590781 | C | 3.049340 | 2.903216 | 0.334466 |
| B | -4.358685 | 1.185457 | 0.514206 | C | 4.072258 | 1.234490 | 2.417679 |
| B | -2.616168 | 1.240885 | 0.176053 | C | 1.377391 | 2.211185 | 2.559139 |
| B | -2.356892 | 1.807810 | -1.487644 | H | 3.362624 | 3.744540 | 0.967581 |
| B | -3.103234 | 0.616294 | -2.599491 | H | 3.877397 | 2.618929 | -0.321856 |
| B | -4.871128 | 0.581745 | -2.262940 | H | 2.200373 | 3.214266 | -0.282643 |
| B | -5.208323 | 1.738465 | -0.945262 | H | 4.332457 | 2.173393 | 2.925460 |
| B | -3.663090 | 2.499315 | -0.466329 | H | 3.892453 | 0.458874 | 3.169887 |
| B | -3.971094 | 2.121757 | -2.184547 | H | 4.908503 | 0.923337 | 1.784270 |
| H | -4.743419 | 1.282744 | 1.635805 | H | 1.811367 | 3.101804 | 3.033925 |
| H | 3.510992 | -0.602171 | -0.883136 | H | 0.456785 | 2.490061 | 2.036895 |
| H | -5.970684 | -0.711068 | -0.196763 | H | 1.111664 | 1.483821 | 3.333412 |
| H | -1.380510 | 2.431462 | -1.779038 | O | 5.598344 | 0.589795 | -0.723840 |
| H | -4.148245 | 2.987463 | -2.989386 | C | 5.347369 | -0.317860 | -1.500458 |
| H | -3.607340 | 3.614251 | -0.040430 | O | 4.179390 | -0.964492 | -1.559453 |
| H | -6.249335 | 2.319240 | -0.865461 | C | 6.329841 | -0.848981 | -2.525003 |
| | | | | H | 6.476799 | -1.925334 | -2.382927 |
| | | | | H | 5.927073 | -0.705538 | -3.534037 |
| | | | | H | 7.283002 | -0.325729 | -2.429315 |

