Supplementary Material (ESI) for Chemical Communications

Supporting Information for:

A Computational Study of the Methanolysis of Palladium-Acyl Bonds

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Contents

Computed structures (Cartesian coordinates, Å) and SCF energies (hartrees) for all stationary points, including corrections for zero-point energies (Enthalpy 0K), temperature effects (Enthalpy 298K) and entropy (Free Energy 298K). Values for the unique imaginary eigenvalues (cm^{-1}) associated with each transition state structure are also supplied. Complex numbers are those defined in the main text.

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Computational Details

Gaussian 03, Revision C.02[1] and employed the BP86 functional. Pd and P were described using the Stuttgart RECPs and the associated basis sets[2] and a polarisation function was added for P (ζ = 0.387).[3] 6-31G** basis sets were used for C, O and H atoms.[4] All stationary points were characterised via analytical frequency calculations which furnished the zero-point energy corrections that are included in the figures quoted in the text. Energies were then corrected to temperature and entropic effects to 298.15 K and 1 atm pressure.

1. Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.
2. Andrae, D.; Häusserman, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1990**, *77*, 123.
3. Höllwarth, A.; Böhme, M.; Dapprich, S.; Ehlers, A. W.; Gobbi, A.; Jonas, V.; Köhler, K. F.; Stegmann, R.; Veldkamp, A.; Frenking, G. *Chem. Phys. Lett*. **1993**, *208*, 237.
4. (a) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys*. **1972**, *56*, 2257. (b) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

$[Pd(dhpp)\{C(O)Et\}(MeOH)]^+$, **1** SCF Energy= -569.624085096 Enthalpy 0K= -569.377670 Enthalpy 298K= -569.358974 Free Energy 298K= -569.426379	**TS_{1A}** SCF Energy= -569.561810260 Enthalpy 0K= -569.319662 Enthalpy 298K= -569.301304 Free Energy 298K= -569.368765 Nimag=1 (-118.95 cm^{-1})
Pd -0.177385 0.269393 0.009668	Pd -0.295421 -0.108607 -0.545002
P 0.742954 -1.787194 0.328645	P -0.928029 1.960571 0.186487
H 0.928059 -2.124596 1.709421	H -0.621266 2.361553 1.531666
H 0.047766 -2.964866 -0.094334	H -0.782102 3.260624 -0.416403
C 2.450497 -2.089220 -0.386080	C -2.816079 1.824419 0.271704
P 2.034618 1.307832 0.166609	P -1.882508 -1.744740 -0.135074
H 2.205958 2.564601 -0.499014	H -2.350863 -2.830088 -0.955599
H 2.525244 1.688365 1.460134	H -1.875343 -2.462418 1.108856
C 3.479842 0.310828 -0.499388	C -3.477691 -0.734826 0.051902
C -2.114012 -0.391975 -0.284297	C 2.628728 -0.160484 -0.354045
O -2.804388 0.405603 -0.913122	O 2.730064 -1.025182 -1.163388
C -2.686865 -1.693596 0.253195	C 3.153477 1.229488 -0.204472
C -4.213939 -1.809541 0.148937	C 4.603142 1.190872 0.354324
H -2.190271 -2.504869 -0.315982	H 3.133900 1.682486 -1.209628
H -2.328758 -1.804428 1.295005	H 2.495039 1.803865 0.462858
H -4.540849 -2.783132 0.546632	H 4.974954 2.224750 0.421235
H -4.713775 -1.016424 0.726460	H 4.632812 0.749647 1.362364
H -4.547464 -1.730749 -0.896738	H 5.271443 0.623044 -0.310466
O -1.032839 2.243864 -0.418180	O 1.974644 -0.608456 1.101941
H -1.889330 1.912264 -0.812008	H 0.911150 -0.437142 0.812199
C -1.322549 3.226385 0.616823	C 2.166332 -2.038265 1.417680
H -0.364493 3.505835 1.076459	H 3.181544 -2.137256 1.823511
H -1.772048 4.115901 0.147968	H 1.417964 -2.289327 2.180588
H -1.998873 2.817142 1.385662	H 2.035843 -2.647499 0.511840
C 3.555425 -1.117624 0.080232	C -3.372097 0.536969 0.931529
H 2.714591 -3.123589 -0.107313	H -3.180150 2.711846 0.816265
H 2.339524 -2.062352 -1.484675	H -3.175967 1.913144 -0.768706
H 3.359119 0.279462 -1.596773	H -3.795751 -0.471519 -0.972543
H 4.410150 0.861233 -0.286285	H -4.245919 -1.410451 0.463428
H 4.519802 -1.551878 -0.239585	H -4.403969 0.777276 1.247690
H 3.599203 -1.086813 1.185324	H -2.828397 0.316002 1.869592

P_{1A} SCF Energy= -569.572414202 Enthalpy 0K= -569.331324 Enthalpy 298K= -569.312352 Free Energy 298K= -569.382222	**TS_{1B}** SCF Energy= -685.307339473 Enthalpy 0K= -685.013899 Enthalpy 298K= -684.991239 Free Energy 298K= -685.068405 Nimag=1 (-649.93 cm^{-1})
Pd 0.374419 -0.482479 -0.675949 P 1.439912 -1.696359 0.979335 H 1.053771 -1.499539 2.345444 H 1.754781 -3.096312 1.064493 C 3.169164 -0.917896 0.946774 P 1.335774 1.563465 -1.171647 H 1.588631 2.199450 -2.435781 H 0.929558 2.733023 -0.448856 C 3.098198 1.304317 -0.516786 C -3.037838 0.374930 0.489574 O -3.887197 1.224171 0.591095 C -3.082007 -0.945069 -0.240019 C -4.329057 -1.092163 -1.119713 H -2.142697 -1.046525 -0.830467 H -3.027812 -1.743019 0.525170 H -4.334433 -2.081859 -1.601114 H -5.244866 -0.994392 -0.516986 H -4.357424 -0.321989 -1.905865 O -1.775370 0.551992 1.164988 H -0.617163 0.160671 0.406663 C -1.644242 1.812418 1.906282 H -2.391049 1.821819 2.711431 H -0.627702 1.802259 2.319814 H -1.804189 2.668935 1.236176 C 3.218852 0.631336 0.876281 H 3.696703 -1.266748 1.850546 H 3.691052 -1.363258 0.081060 H 3.625983 0.708342 -1.282647 H 3.582172 2.295335 -0.495625 H 4.212554 0.920041 1.265259 H 2.495701 1.074692 1.586582	Pd -0.172689 0.307491 -0.025934 P -0.919503 -1.806094 0.071569 C -2.690569 -2.054999 0.656042 P -2.420471 1.321588 -0.441895 C -3.818905 0.282867 0.288031 C 2.668086 -0.464675 -0.053438 O 3.211943 0.584339 -0.297446 C 2.788965 -1.808012 -0.708146 C 2.871511 -1.713540 -2.239032 C -3.754389 -1.214497 -0.083662 O 2.177865 -0.703714 1.496182 C 2.680432 0.291449 2.457673 O 1.049427 2.166319 0.023400 C 0.670597 3.421379 -0.599256 H -0.959419 -2.471659 -1.201641 H -0.270315 -2.866022 0.799741 H -2.911589 -3.129681 0.542527 H -2.699890 -1.829773 1.737358 H -2.860380 2.627072 -0.021270 H -2.896239 1.438654 -1.795238 H -3.764263 0.409494 1.384075 H -4.778258 0.711517 -0.042598 H 3.726646 -2.232470 -0.288196 H 1.978594 -2.468172 -0.365029 H 3.041192 -2.716514 -2.659307 H 1.935117 -1.314789 -2.660882 H 3.701258 -1.062030 -2.552045 H -4.736917 -1.655359 0.165686 H -3.649346 -1.337659 -1.178597 H 1.121304 -0.468096 1.170517 H 3.773045 0.193903 2.496882 H 2.381834 1.305332 2.155368 H 2.234698 0.021126 3.424112 H 1.972468 1.932459 -0.231887 H -0.295672 3.711295 -0.165108 H 1.419379 4.193935 -0.360124 H 0.571783 3.315085 -1.692878

P_{1B} SCF Energy= -685.375341886 Enthalpy 0K= -685.077930 Enthalpy 298K= -685.056381 Free Energy 298K= -685.132203	$[Pd(dhpp)\{C(O)Et\}(C_2H_4)]^+$, **2** SCF Energy = -532.483879 Enthalpy 0K= -532.237364 Enthalpy 298K= -532.218178 Free Energy 298K= -532.285542
Pd 0.790259 0.144649 -0.260560	Pd 0.195892 0.482166 0.011499
P 2.194258 1.874328 -0.050340	P -0.595958 -1.727482 -0.126438
C 3.846095 1.580853 0.784053	H -0.695348 -2.274762 -1.447954
P 2.531980 -1.520906 -0.193188	H 0.177482 -2.763156 0.488914
C 4.112774 -1.018035 0.688381	C -2.310417 -2.063786 0.556494
C -4.120173 0.129114 0.455916	P -2.072425 1.228647 -0.489697
O -3.124648 -0.055591 -0.261287	H -2.477958 2.566591 -0.173028
C -5.364903 0.861529 0.001309	H -2.397144 1.252220 -1.887004
C -5.320007 1.308121 -1.462900	C -3.505378 0.235164 0.210716
C 4.647381 0.368346 0.262186	C 2.041469 -0.506493 0.353094
O -4.222775 -0.292564 1.727349	O 2.341441 -0.847495 1.471049
C -3.087519 -1.000591 2.287300	C 2.845424 -0.802429 -0.912267
O -0.833656 -1.248060 -0.420890	C 4.320154 -1.139853 -0.637829
C -0.971534 -1.992418 -1.661131	H 2.327007 -1.656592 -1.395178
H 2.562742 2.455659 -1.305893	H 2.726170 0.039527 -1.616816
H 1.717220 3.041121 0.621363	H 4.823286 -1.398181 -1.582734
H 4.427434 2.509481 0.651348	H 4.849314 -0.283425 -0.190914
H 3.638129 1.476603 1.863750	H 4.409189 -1.992028 0.052332
H 2.261022 -2.797434 0.400433	C 1.790468 2.094918 0.539594
H 3.050797 -1.989955 -1.445867	C 0.600978 2.706971 0.171749
H 3.889613 -1.030475 1.770007	H 2.617340 2.016369 -0.173188
H 4.872918 -1.793420 0.502172	H 2.033489 1.928941 1.593434
H -6.226404 0.198297 0.202103	H 0.470429 3.117151 -0.836337
H -5.502474 1.720414 0.684791	H -0.089147 3.070681 0.940389
H -6.252418 1.831865 -1.724445	C -3.447454 -1.270184 -0.121209
H -4.477505 1.993100 -1.646608	H -2.482980 -3.146987 0.442471
H -5.209255 0.447108 -2.140615	H -2.265561 -1.848528 1.638783
H 5.672439 0.463009 0.663492	H -3.491022 0.393618 1.303776
H 4.757674 0.422080 -0.837575	H -4.440062 0.674456 -0.173981
H -0.254746 1.317270 -0.279288	H -4.400053 -1.716814 0.216358
H -2.864483 -1.904882 1.699603	H -3.422702 -1.422081 -1.216699
H -2.201816 -0.345507 2.316610	
H -3.392597 -1.273604 3.305216	
H -1.714120 -0.765125 -0.259369	
H -0.073637 -2.617104 -1.776860	
H -1.856811 -2.644522 -1.588070	
H -1.073249 -1.320943 -2.529693	

TS_{2B} SCF Energy= -648.189324 Enthalpy 0K= -647.892977 Enthalpy 298K= -647.870491 Free Energy 298K= -647.944540 Nimag = 1 (-113.53 cm^{-1})	**P_{2B}** SCF Energy= -648.224810759 Enthalpy 0K= -647.928427 Enthalpy 298K= -647.906869 Free Energy 298K= -647.983860
Pd 0.15856 0.93079 -0.32284	Pd -0.923278 0.794903 -0.046583
P 1.56775 0.77168 1.59678	P -3.278350 0.444056 -0.109464
H 2.53744 1.82390 1.71749	C -3.894826 -1.296183 -0.440769
H 1.05849 0.86296 2.93815	P -0.415948 -1.429624 0.266126
C 2.67846 -0.74211 1.75260	C -1.713904 -2.703943 -0.178830
P 1.43891 -0.62658 -1.57360	C -3.137546 -2.396413 0.335951
H 0.99873 -1.52740 -2.60785	H -3.941740 0.772436 1.116901
H 2.37125 0.09557 -2.39319	H -4.083778 1.222187 -1.001137
C 2.62448 -1.77198 -0.65647	H -4.968276 -1.319681 -0.192425
C -1.66930 -1.06659 0.63364	H -3.807185 -1.461237 -1.529325
O -1.03034 -2.06297 0.72620	H 0.754657 -1.920829 -0.381926
C -2.50893 -0.24328 1.55740	H -0.095952 -1.746567 1.622514
C -3.82583 -1.00120 1.87673	H -1.707339 -2.788995 -1.280045
H -2.71828 0.73427 1.10366	H -1.359403 -3.667652 0.224111
H -1.91102 -0.08821 2.47094	H -3.726263 -3.326216 0.241926
H -4.41113 -0.39094 2.58187	H -3.119854 -2.169103 1.418718
H -4.43084 -1.15014 0.96932	C 3.928320 -0.298559 0.190521
H -3.62425 -1.97749 2.34268	O 4.996505 0.078023 0.636859
C -0.96901 2.75337 -0.06386	C 3.672016 -0.815498 -1.216563
C -1.27059 2.25295 -1.35651	C 4.867907 -0.597715 -2.150553
H -0.22406 3.54880 0.05814	H 2.755770 -0.333842 -1.607248
H -1.71081 2.70462 0.74189	H 3.434324 -1.894114 -1.130332
H -0.75312 2.65234 -2.23599	H 4.662089 -1.021816 -3.145945
H -2.27409 1.86217 -1.56774	H 5.088275 0.474853 -2.269046
O -2.24757 -0.72127 -0.95452	H 5.771425 -1.077791 -1.745352
H -1.50964 -0.00679 -1.18814	O 2.770691 -0.317316 0.951089
C -2.17517 -1.85720 -1.88177	C 2.974590 0.106452 2.327921
H -1.34110 -2.51916 -1.60395	H 0.651024 0.808868 0.080203
H -3.13368 -2.38680 -1.80626	H 3.619207 -0.611616 2.858539
H -2.03738 -1.44786 -2.89157	H 3.449452 1.098651 2.362062
C 3.44877 -1.08667 0.45728	H 1.973949 0.135064 2.781338
H 3.38310 -0.56818 2.58191	C 0.074942 2.813578 -0.223373
H 2.02647 -1.58391 2.04698	C -1.309548 2.975564 -0.334743
H 2.01607 -2.59149 -0.23383	H 0.706945 2.796566 -1.117003
H 3.30058 -2.21836 -1.40395	H 0.585974 3.024104 0.721373
H 4.26115 -1.78282 0.73440	H -1.773134 3.092380 -1.320369
H 3.95843 -0.18772 0.06010	H -1.894185 3.322964 0.524414

[Pd(dhpp){C(O)Et}(CO)]$^{+}$, **3** SCF Energy= -567.219505588 Enthalpy 0K= -567.018776 Enthalpy 298K= -567.001006 Free Energy 298K= -567.067109	**TS_{3B}** SCF Energy= -682.920395884 Enthalpy 0K= -682.668766 Enthalpy 298K= -682.647526 Free Energy 298K= -682.721143 Nimag=1 (-102.6266cm-1)
Pd 0.212814 0.452069 -0.039783 P -0.666369 -1.730834 -0.428031 H -0.866266 -2.036393 -1.812316 H 0.106966 -2.872126 -0.044774 C -2.344774 -2.111753 0.317909 P -2.070404 1.351407 -0.178432 H -2.346066 2.607443 0.451048 H -2.554805 1.663941 -1.490653 C -3.444363 0.262054 0.495819 C 2.038661 -0.505916 0.427794 O 2.110441 -0.864803 1.576213 C 3.095659 -0.649643 -0.650354 C 4.326723 -1.460491 -0.219335 H 2.596719 -1.073941 -1.543137 H 3.364046 0.384020 -0.947331 H 5.050059 -1.496955 -1.048802 H 4.819528 -1.001549 0.651083 H 4.055120 -2.493716 0.046861 C -3.481375 -1.157364 -0.110971 H -2.590227 -3.146953 0.028510 H -2.209812 -2.099637 1.414102 H -3.300842 0.216797 1.589981 H -4.400641 0.778053 0.311472 H -4.428408 -1.623981 0.214749 H -3.545178 -1.104983 -1.214098 C 1.139272 2.166151 0.006954 O 1.581205 3.232055 0.012960	Pd 0.136836 0.687430 -0.532772 P 1.737613 1.317210 1.191587 C 2.986167 0.014012 1.738528 P 1.505875 -1.119101 -1.311905 C 2.831061 -1.800320 -0.156102 C 3.674445 -0.724216 0.567500 H 2.620258 2.377638 0.797067 H 1.359228 1.876283 2.459884 H 3.741599 0.505390 2.372828 H 2.439046 -0.701837 2.377634 H 1.068146 -2.338851 -1.936266 H 2.319624 -0.661132 -2.401048 H 2.312076 -2.441486 0.578646 H 3.488033 -2.454019 -0.752746 H 4.559903 -1.238317 0.983524 H 4.078542 0.003530 -0.162164 C -1.767644 -0.821393 0.896713 O -1.136115 -1.768069 1.225781 C -2.568143 0.243329 1.575036 C -3.878620 -0.374076 2.134231 H -2.783327 1.060330 0.874453 H -1.933900 0.633044 2.389233 H -4.429302 0.420368 2.661328 H -4.518252 -0.753933 1.323241 H -3.669546 -1.187149 2.845535 O -2.426668 -0.927146 -0.742195 C -2.420005 -2.285825 -1.297906 H -1.678701 -0.363793 -1.181997 H -1.561461 -2.852468 -0.905918 H -3.365859 -2.753432 -0.996284 H -2.367026 -2.193014 -2.391261 C -1.164298 1.953576 -1.140710 O -1.785171 2.850081 -1.549478

P_{3B} SCF Energy= -682.953215319 Enthalpy 0K= -682.702066 Enthalpy 298K= -682.680284 Free Energy 298K= -682.761924	$[Pd(dhpp)\{C(O)Et\}(MeCN)]^+$, **4** SCF Energy= -586.664058573 Enthalpy 0K= -586.425153 Enthalpy 298K= -586.405029 Free Energy 298K= -586.477600
Pd 0.757503 0.649551 -0.082273 P 3.144321 0.951999 0.239712 C 4.123103 -0.563147 0.757127 P 0.976167 -1.631641 -0.498890 C 2.470702 -2.516935 0.199824 C 3.826034 -1.828518 -0.079472 H 3.847537 1.388614 -0.928880 H 3.605328 1.946856 1.158364 H 5.192733 -0.306331 0.690931 H 3.894471 -0.737751 1.823539 H -0.116989 -2.466113 -0.120926 H 1.037339 -1.918887 -1.898063 H 2.297513 -2.617110 1.286018 H 2.461820 -3.533557 -0.227826 H 4.613375 -2.566208 0.157331 H 3.939767 -1.617398 -1.159494 C -3.938084 -0.391934 -0.099686 O -5.052175 -0.347217 -0.587025 C -3.601380 -0.589845 1.368978 C -4.830274 -0.956044 2.208903 H -3.140207 0.349406 1.731467 H -2.810704 -1.359222 1.446251 H -4.554462 -1.057795 3.270377 H -5.608031 -0.182206 2.122276 H -5.270907 -1.907288 1.871932 O -2.792643 -0.245924 -0.868564 C -3.063604 -0.006645 -2.278364 H -0.758869 0.273455 -0.333808 H -3.586690 -0.868770 -2.719848 H -3.688013 0.890849 -2.405281 H -2.080263 0.134542 -2.748528 C 0.049471 2.429947 0.188260 O -0.423061 3.469260 0.338462	Pd 0.100041 0.089788 -0.091465 P -1.386683 -1.666457 -0.142170 H -1.729844 -2.147633 -1.448341 H -1.015848 -2.910615 0.463328 C -3.076990 -1.357652 0.611417 P -1.737373 1.689795 -0.443132 H -1.595513 3.053708 -0.019972 H -2.150261 1.956029 -1.792181 C -3.380302 1.232222 0.349880 C 1.590732 -1.267935 0.364325 O 1.798352 -1.499938 1.532953 C 2.391954 -1.821498 -0.808962 C 3.617732 -2.647973 -0.392245 H 1.683543 -2.415295 -1.420326 H 2.663207 -0.961643 -1.450566 H 4.135950 -3.025131 -1.287974 H 4.328668 -2.039940 0.188537 H 3.325110 -3.508480 0.228649 C -3.871781 -0.187346 -0.008552 H -3.643536 -2.297773 0.503294 H -2.912238 -1.194847 1.691307 H -3.236319 1.326424 1.441013 H -4.132795 1.979594 0.051497 H -4.910133 -0.276410 0.359074 H -3.938985 -0.307599 -1.106509 N 1.601505 1.549387 -0.002770 C 2.415872 2.378785 0.131538 C 3.430746 3.408456 0.302401 H 2.981372 4.408366 0.186530 H 3.876035 3.329104 1.308016 H 4.225389 3.283266 -0.451530

TS_{4B} SCF Energy= -702.348865979 Enthalpy 0K= -702.061353 Enthalpy 298K= -702.037628 Free Energy 298K= -702.118298 Nimag=1 (-261.61 cm^{-1})	**P_{4B}** SCF Energy= -702.408062928 Enthalpy 0K= -702.117668 Enthalpy 298K= -702.093863 Free Energy 298K= -702.178693
Pd -0.007047 -0.589463 -0.362500	Pd 1.786214 -0.143718 -0.436751
P -1.538059 -1.601335 1.287676	P 1.026611 -0.555663 1.810329
C -3.145783 -0.636771 1.525375	C -0.456180 -1.679943 2.012501
P -1.650849 0.511468 -1.531302	P 0.744314 -1.945058 -1.310240
C -3.223188 0.933368 -0.582321	C -0.658876 -2.726604 -0.357076
C -3.846507 -0.242221 0.204777	C -0.381294 -2.957642 1.145080
H -2.087800 -2.893427 0.971137	H 1.992290 -1.154553 2.685484
H -1.245442 -1.911255 2.664380	H 0.675159 0.563909 2.632496
H -3.827734 -1.238764 2.147083	H -0.551553 -1.938384 3.079246
H -2.888077 0.267507 2.105675	H -1.329715 -1.074259 1.711351
H -1.516534 1.719484 -2.304541	H 0.196404 -1.796646 -2.620097
H -2.195172 -0.298842 -2.584775	H 1.646246 -3.030153 -1.549211
H -2.967160 1.764015 0.099617	H -1.520265 -2.048343 -0.486285
H -3.951033 1.323035 -1.313434	H -0.881707 -3.680939 -0.864161
H -4.878719 0.058087 0.462656	H -1.158996 -3.650609 1.513181
H -3.957749 -1.127063 -0.451441	H 0.578537 -3.488411 1.294935
C 0.901784 1.787649 0.696771	C -3.398816 0.760615 -0.046880
O 0.021318 2.591340 0.710320	O -2.378346 0.063245 -0.072839
C 1.786104 1.197221 1.755342	C -4.070533 1.237106 1.231988
C 2.795746 2.269350 2.243190	C -5.356660 2.058449 1.076614
H 2.305054 0.313187 1.361471	H -3.300507 1.807570 1.784795
H 1.122904 0.881010 2.577463	H -4.248355 0.329726 1.838607
H 3.412739 1.830160 3.042558	H -5.742034 2.343753 2.068470
H 3.464693 2.586415 1.428225	H -5.178624 2.979446 0.500415
H 2.277954 3.152335 2.647562	H -6.140272 1.484288 0.558437
O 1.769325 1.671696 -0.769075	O -4.034177 1.184647 -1.158614
C 1.516947 2.772435 -1.704754	C -3.454143 0.777582 -2.422790
H 1.215764 0.778782 -1.079962	H 2.216816 -0.007785 -1.944186
H 0.555492 3.253724 -1.467811	H -3.447323 -0.320671 -2.506477
H 2.345276 3.484721 -1.593691	H -4.100425 1.217326 -3.193016
H 1.504195 2.348541 -2.718329	H -2.425185 1.159713 -2.514661
N 1.833850 -1.579886 -0.324276	N 2.896209 1.539185 -0.042441
C 2.724446 -2.338351 -0.426098	C 3.565876 2.487783 0.091961
C 3.821748 -3.287030 -0.564112	C 4.402998 3.667961 0.249618
H 3.924923 -3.893814 0.350732	H 4.302782 4.074634 1.269157
H 3.625602 -3.960190 -1.415448	H 5.458236 3.402945 0.070704
H 4.768741 -2.753331 -0.748765	H 4.101251 4.440026 -0.477347

trans-[Pd(PH_3)$_2${C(O)Et}(MeOH)]$^+$, ***trans*-5**	**TS$_{trans\text{-}5B}$**
SCF Energy= -452.869870026 Enthalpy 0K= -452.692292 Enthalpy 298K= -452.674057 Free Energy 298K= -452.743141	SCF Energy= -568.562037288 Enthalpy 0K= -568.334688 Enthalpy 298K= -568.312850 Free Energy 298K= -568.390277 Nimag=1 (-213.39 cm^{-1})
Pd -0.315512 0.015903 -0.052155 P -0.235960 -2.348829 -0.100389 H 0.869505 -3.028132 -0.701183 H -0.235961 -3.013467 1.165655 H -1.297812 -3.067296 -0.735509 P -0.395077 2.384620 -0.003830 H 0.770875 3.191311 0.178958 H -0.962245 3.052434 -1.133438 H -1.214350 2.943011 1.025887 C 1.644228 0.018628 0.432944 O 1.931874 -0.106780 1.597809 C 2.617572 0.187147 -0.731375 C 4.083454 -0.065967 -0.344338 H 2.279608 -0.468425 -1.554720 H 2.469585 1.218020 -1.109258 H 4.726805 0.098721 -1.222851 H 4.406557 0.614000 0.458129 H 4.233186 -1.099789 0.003544 O -2.622946 0.189683 -0.503883 H -2.853342 -0.039820 -1.424518 C -3.665349 -0.314916 0.379093 H -3.704231 -1.417849 0.374431 H -3.417044 0.040391 1.388325 H -4.642866 0.095915 0.079634	Pd 0.671156 0.129822 -0.240046 P 0.551027 2.401127 0.201890 H 1.695354 3.198124 -0.126218 H -0.441615 3.242804 -0.395268 H 0.380608 2.849217 1.552097 P 0.920087 -2.044152 -1.026503 H 1.451382 -3.031189 -0.134768 H -0.129505 -2.841844 -1.591205 H 1.868335 -2.200257 -2.086250 C -2.037949 0.096445 0.674829 O -2.348145 1.172871 1.071598 C -2.077234 -1.284938 1.253639 C -3.539718 -1.667392 1.601357 H -1.634844 -1.999828 0.547858 H -1.451627 -1.255675 2.162831 H -3.536741 -2.668907 2.058987 H -3.977316 -0.955862 2.317366 H -4.169272 -1.703910 0.699116 O 3.276495 -0.295911 0.163536 H 3.822956 0.201037 -0.473645 C 3.986803 -0.339759 1.422481 H 4.144985 0.669018 1.844958 H 3.359864 -0.921032 2.114034 H 4.960965 -0.848202 1.314007 O -2.163494 -0.093380 -1.078828 H -1.109195 0.030982 -1.157869 C -2.863624 1.006470 -1.745658 H -3.899798 0.678711 -1.901231 H -2.835240 1.908985 -1.114408 H -2.367712 1.187767 -2.709421

$P_{trans\text{-}5B}$ SCF Energy= -568.612438951 Enthalpy 0K= -568.382957 Enthalpy 298K= -568.361386 Free Energy 298K= -568.440135	*cis*-$[Pd(PH_3)_2\{C(O)Et\}(MeOH)]^+$, ***cis*-5** SCF Energy= -452.865378243 Enthalpy 0K= -452.686810 Enthalpy 298K= -452.669488 Free Energy 298K= -452.734214
Pd -1.403759 0.044609 -0.132266 P -0.753875 -2.176437 -0.022474 H -1.728190 -3.227069 -0.013422 H 0.090072 -2.642905 -1.071633 H 0.023429 -2.563737 1.108136 P -1.374274 2.363937 -0.280664 H -0.812144 3.104362 0.804633 H -0.644977 2.957755 -1.355872 H -2.612887 3.065974 -0.423819 C 3.120061 -0.037084 0.051396 O 2.039940 -0.627375 -0.088451 C 3.251342 1.460269 0.280027 C 4.670534 2.010207 0.471218 H 2.754813 1.941590 -0.583935 H 2.613903 1.690357 1.154254 H 4.632792 3.100276 0.626021 H 5.162216 1.558184 1.346347 H 5.300417 1.811630 -0.409340 O -3.681613 -0.051887 -0.164530 H -4.029589 -0.481423 -0.968988 C -4.427921 -0.543858 0.985905 H -4.238644 -1.616085 1.163849 H -4.084013 0.040300 1.850010 H -5.504632 -0.368818 0.832673 O 4.306295 -0.667217 0.010608 H 0.132511 0.152992 -0.116806 C 4.268932 -2.101534 -0.215753 H 5.319460 -2.417207 -0.233996 H 3.727534 -2.603023 0.601317 H 3.778422 -2.323861 -1.175896	Pd -0.383536 -0.138454 -0.044420 P 0.012203 -2.380374 0.118133 H 0.786803 -3.017922 -0.901050 H 0.680029 -2.892511 1.274368 H -1.126955 -3.243230 0.110478 P -2.866974 -0.265879 -0.050242 H -3.499978 0.073117 -1.288303 H -3.587317 -1.474770 0.217219 H -3.624439 0.599284 0.803792 C 1.608863 0.308540 -0.279521 O 1.777485 1.295737 -0.979556 C 2.747789 -0.442757 0.391079 C 4.124974 0.212825 0.217317 H 2.471688 -0.559471 1.457105 H 2.738459 -1.469793 -0.027824 H 4.890455 -0.397884 0.720982 H 4.392933 0.300951 -0.846354 H 4.143071 1.220849 0.659418 O -0.675943 2.033488 -0.302814 H 0.167925 2.227177 -0.787571 C -0.833125 2.987583 0.790490 H 0.043166 2.983204 1.459364 H -0.985197 3.991926 0.365367 H -1.729741 2.690808 1.350741

$TS_{cis\text{-}5B}$ SCF Energy= -568.556548165 Enthalpy 0K= -568.329055 Enthalpy 298K= -568.307719 Free Energy 298K= -568.383035 Nimag=1 (-191.52 cm^{-1})	**$P_{cis\text{-}5}$** SCF Energy= -568.626860163 Enthalpy 0K= -568.396405 Enthalpy 298K= -568.375570 Free Energy 298K= -568.451599
Pd -0.826079 0.340790 -0.179039	Pd 1.816613 0.352329 -0.149753
P -0.145927 2.476827 -0.568859	P 0.738401 2.355368 0.304090
H 0.195046 3.340143 0.526439	H 0.013479 2.944266 -0.775567
H 0.896273 2.931871 -1.453389	H -0.258617 2.411562 1.326082
H -1.189581 3.292965 -1.117106	H 1.547872 3.468257 0.682357
P -2.747673 0.127823 1.247544	P 3.258860 -1.295063 -0.919189
H -2.678334 0.638147 2.586600	H 3.396543 -1.431327 -2.333884
H -3.916735 0.866607 0.865283	H 4.637233 -1.200465 -0.559123
H -3.438186 -1.088635 1.584942	H 3.004581 -2.658251 -0.567303
C 2.011708 -0.467960 -0.194855	C -3.036109 -0.078582 -0.070672
O 1.973823 -1.522529 -0.759940	O -1.866898 0.122892 0.309586
C 2.907579 0.726465 -0.299302	C -4.021318 1.048982 -0.305905
C 4.354674 0.343782 0.112246	C -5.450641 0.647699 -0.690389
H 2.877964 1.049625 -1.353883	H -4.007928 1.660683 0.615103
H 2.525520 1.540625 0.333013	H -3.565796 1.691131 -1.083717
H 4.996347 1.229818 -0.012808	H -6.063556 1.551803 -0.829982
H 4.402076 0.032547 1.167048	H -5.470639 0.073442 -1.629210
H 4.747319 -0.465093 -0.521889	H -5.922246 0.034547 0.093012
O -0.754771 -1.850687 -0.950174	O 0.426452 -1.019214 0.870434
H 0.149367 -2.039141 -1.281923	H -0.508238 -0.692694 0.669977
C -1.728600 -2.337109 -1.911949	C 0.571737 -1.164617 2.306203
H -1.646223 -1.805348 -2.875068	H 0.485462 -0.195695 2.828385
H -1.600028 -3.421222 -2.065875	H -0.196176 -1.858672 2.686195
H -2.720571 -2.152938 -1.476240	H 1.565837 -1.593240 2.497456
O 1.425853 -0.481235 1.414368	O -3.543470 -1.291207 -0.314200
H 0.477593 -0.039541 1.191656	H 2.794189 1.279591 -0.888754
C 1.223627 -1.833630 1.962641	C -2.674621 -2.438850 -0.122800
H 2.220416 -2.243198 2.169413	H -2.394423 -2.530758 0.938399
H 0.658669 -1.706770 2.896226	H -3.271648 -3.305151 -0.432923
H 0.673507 -2.460230 1.246347	H -1.771996 -2.348293 -0.746556

$[Pd(PH_3)\{C(O)Et\}(MeOH)]^+$, **6** SCF Energy= -444.475286161 Enthalpy 0K= -444.323260 Enthalpy 298K= -444.308975 Free Energy 298K= -444.367506	**TS_{6B}** SCF Energy= -560.180697404 Enthalpy 0K= -559.978693 Enthalpy 298K= -559.961417 Free Energy 298K= -560.025999 Nimag=1 (-244.7191cm-1)
Pd -0.533225 0.493574 0.087810 P 0.723968 2.382175 -0.154152 H 1.756947 2.671923 0.790162 H 1.440641 2.606451 -1.370468 H -0.018078 3.602020 -0.082118 C 0.936682 -0.806879 0.416044 O 0.687319 -1.525450 1.346781 C 2.121923 -0.839229 -0.534095 C 2.936591 -2.139644 -0.427549 H 1.743428 -0.656055 -1.555595 H 2.738649 0.044918 -0.276325 H 3.788236 -2.083163 -1.123498 H 3.325386 -2.284743 0.591332 H 2.328479 -3.016266 -0.698028 O -2.225794 -0.867192 0.232043 H -2.242129 -1.367801 1.071660 C -2.719407 -1.724784 -0.847294 H -2.031299 -2.566236 -1.026806 H -3.721397 -2.093906 -0.580670 H -2.786983 -1.089803 -1.739866	Pd 1.042248 0.299408 -0.062119 P 1.024532 2.512888 0.218357 H 0.053026 3.171190 1.041342 H 2.199892 3.089911 0.797679 H 0.915658 3.356662 -0.934494 C -1.640485 -0.505323 -0.344930 O -1.536952 -1.636645 -0.721203 C -2.333401 0.700872 -0.896984 C -3.872674 0.500969 -0.824512 H -2.029127 1.597741 -0.339655 H -2.002888 0.802965 -1.944418 H -4.357304 1.384564 -1.267544 H -4.183589 -0.389541 -1.391033 H -4.216658 0.406286 0.216861 O -1.415507 -0.254486 1.282211 H -0.400162 0.146439 1.155551 C -1.365951 -1.492224 2.085623 H -0.621598 -2.187165 1.672403 H -1.096511 -1.177097 3.102305 H -2.373064 -1.926984 2.067067 O 1.228289 -1.854590 -0.276869 H 0.494445 -2.229900 -0.805804 C 2.492273 -2.479977 -0.661230 H 2.402068 -3.572731 -0.558727 H 2.770537 -2.210679 -1.692757 H 3.248679 -2.107892 0.042400

P_{6B}	**MeOH**
SCF Energy= -560.195501892 Enthalpy 0K= -559.993925 Enthalpy 298K= -559.975853 Free Energy 298K= -560.045063	SCF Energy= -115.717913963 Enthalpy 0K= -115.668009 Enthalpy 298K= -115.664693 Free Energy 298K= -115.690760
Pd -1.343297 -0.019564 -0.235887 P -1.772750 -2.197824 0.021751 H -0.934954 -3.143418 -0.645554 H -1.756391 -2.751546 1.339086 H -3.056080 -2.650656 -0.419439 C 2.542945 -0.052798 0.337544 O 3.350850 0.696969 0.831693 C 2.551233 -0.682042 -1.036042 C 3.651962 -0.110775 -1.938236 H 2.679338 -1.772026 -0.890054 H 1.544065 -0.564320 -1.482992 H 3.642633 -0.620259 -2.913879 H 3.511491 0.968257 -2.108338 H 4.643878 -0.250795 -1.482850 O 1.410924 -0.488439 1.096612 H 0.052717 -0.370294 0.416264 C 1.369204 0.021127 2.473475 H 1.440182 1.117703 2.478542 H 0.410730 -0.323615 2.882275 H 2.210632 -0.410369 3.032654 O -0.932207 2.081363 -0.487599 H -0.672350 2.334476 -1.393906 C -1.785370 3.131457 0.078385 H -1.255831 4.094174 0.014066 H -2.750987 3.182824 -0.449344 H -1.942537 2.866228 1.131608	O 0.754556 0.122638 0.000015 H 1.130487 -0.776020 -0.000105 C -0.663527 -0.019221 0.000013 H -1.050650 -0.544376 0.898982 H -1.084505 0.999286 -0.000265 H -1.050621 -0.544670 -0.898809
	PH_3 SCF Energy= -8.36081752650 Enthalpy 0K= -8.337767 Enthalpy 298K= -8.334848 Free Energy 298K= -8.358855
	P -0.000025 -0.000033 -0.133641 H -1.159948 -0.314485 0.668424 H 0.852685 -0.847053 0.668246 H 0.307635 1.162035 0.667951