Supporting Information for

Phosphine-free Heck reaction: mechanistics insights and catalysis "on water" with a charge-tagged palladium complex

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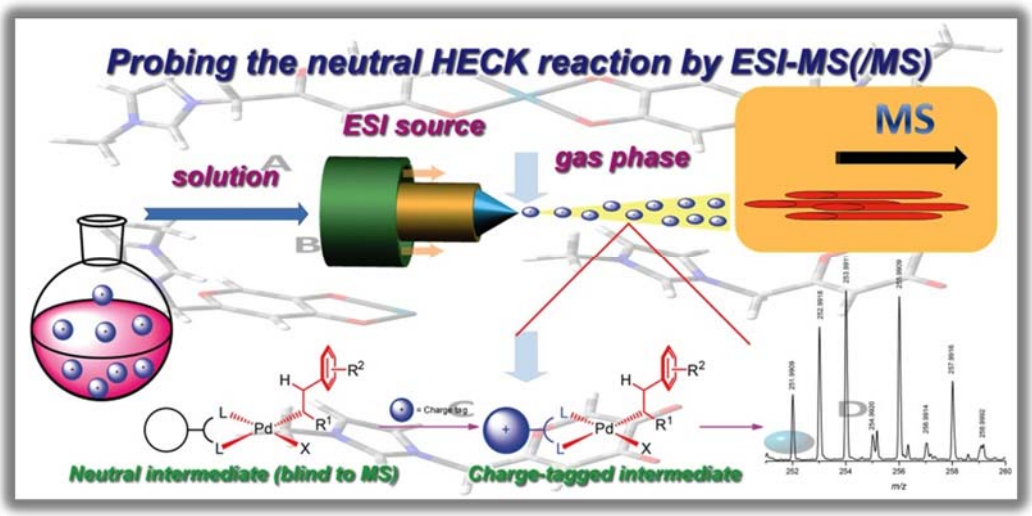


Summary

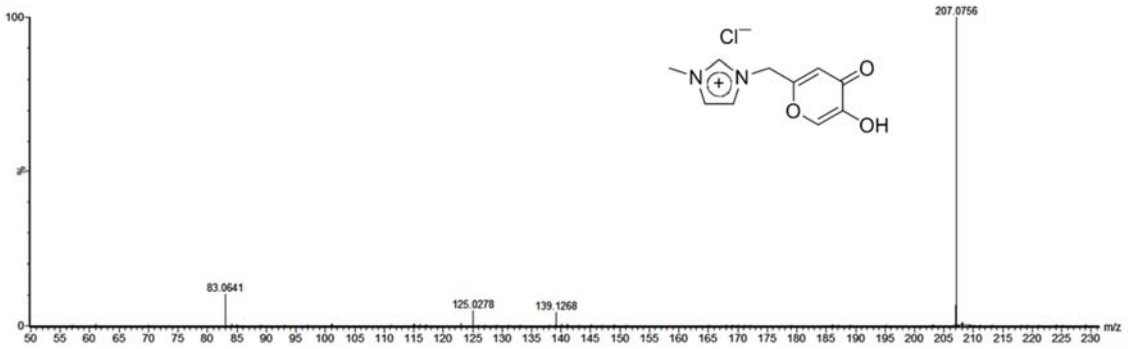


Figure S1. ESI(+)-MS/MS of the ionophilic ligand. The ion of *m/z* 207 refers to the cation without the chlorine anion.

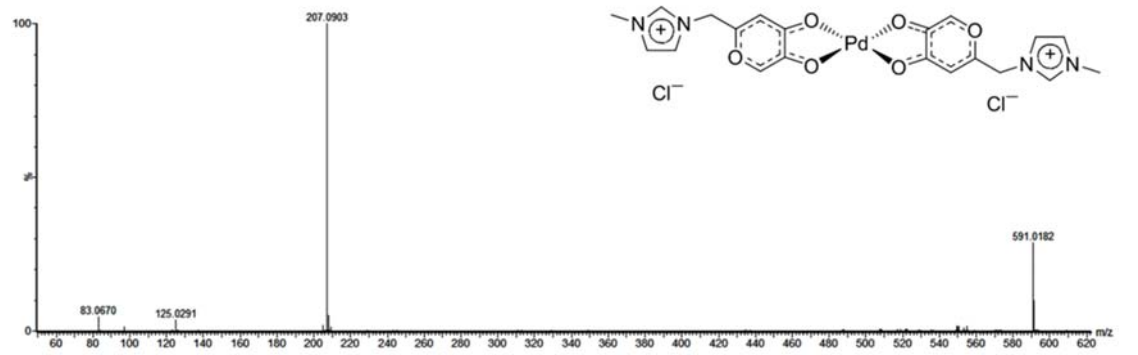


Figure S2. ESI(+)-MS/MS of the protonated **KjPdC**. The extra proton is not shown in the structure.

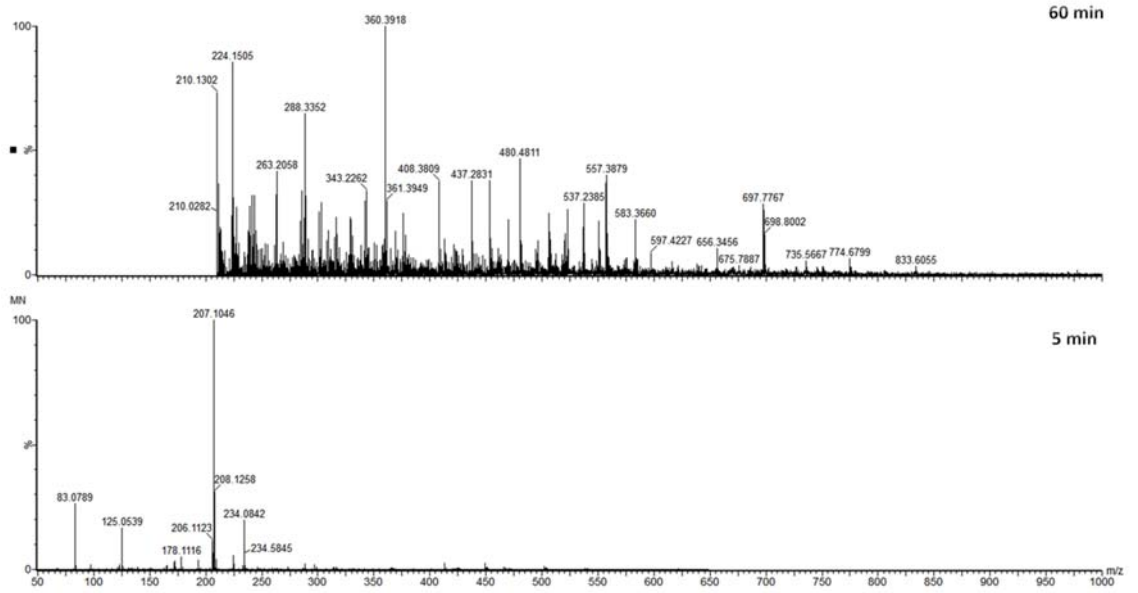


Figure S3. ESI(+)-MS after 5 (bottom) and 60 (top) minutes. Note the MS for 60 minutes was monitored above *m/z* 200 to avoid any signal suppression.

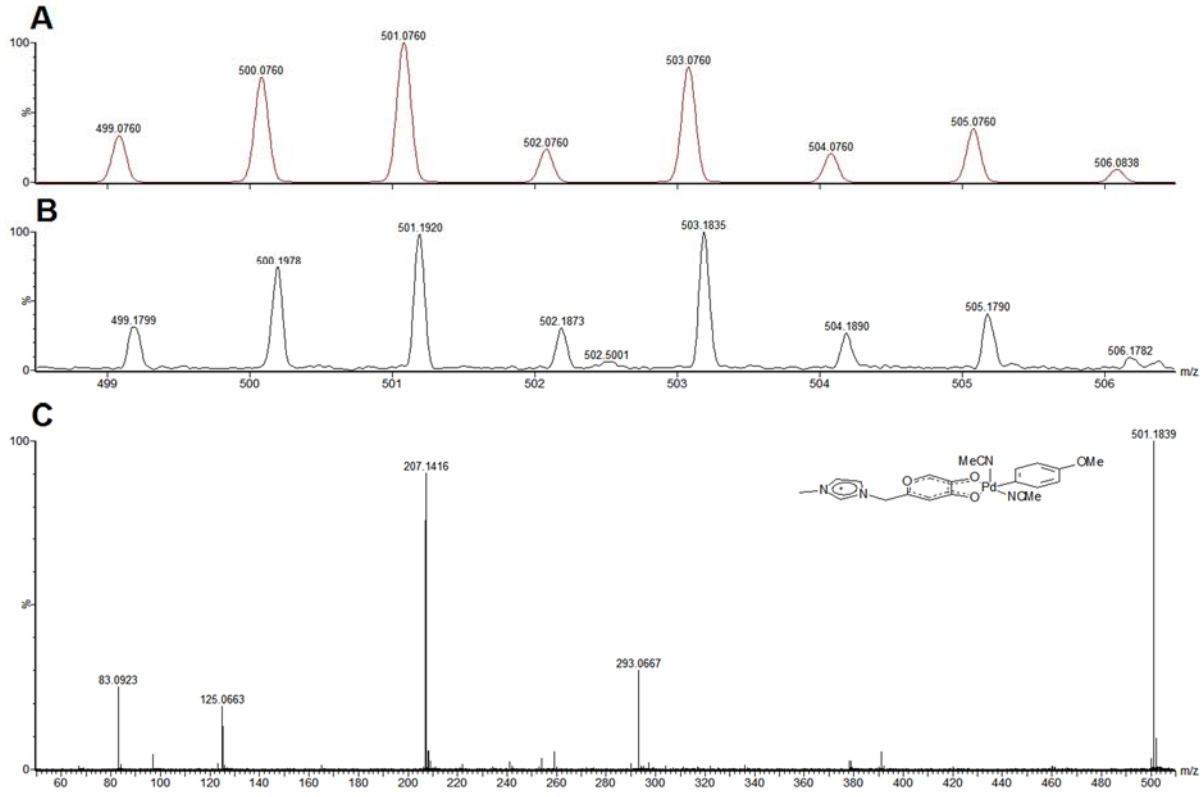


Figure S4. (A) Simulated isotopic pattern for the cation $[C_{21}H_{23}N_4O_4Pd]^+$. (B) Isotopologues from the oxidative addition step. Note the presence of two solvent molecules helping in the intermediate stabilization. Also, note that the charge (+1) is due to the presence of a charge tag (imidazolium ring). (C) ESI-MSMS of the ion of *m/z* 501.

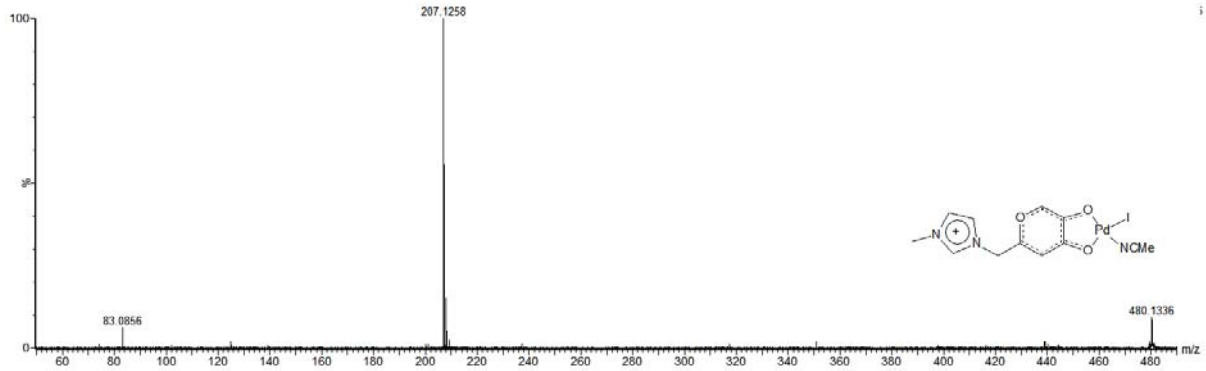


Figure S5. ESI(+)-MS/MS of the ion of *m/z* 480.

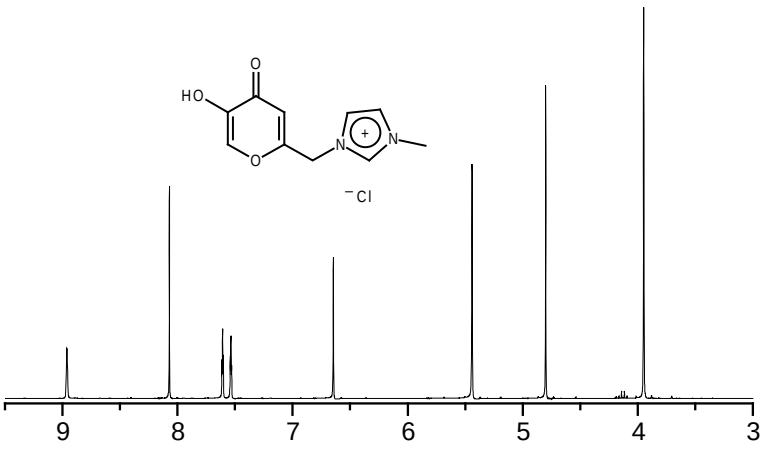


Figure S6. ^{1}H NMR of the charge-tagged ligand (300 MHz, D_2O).

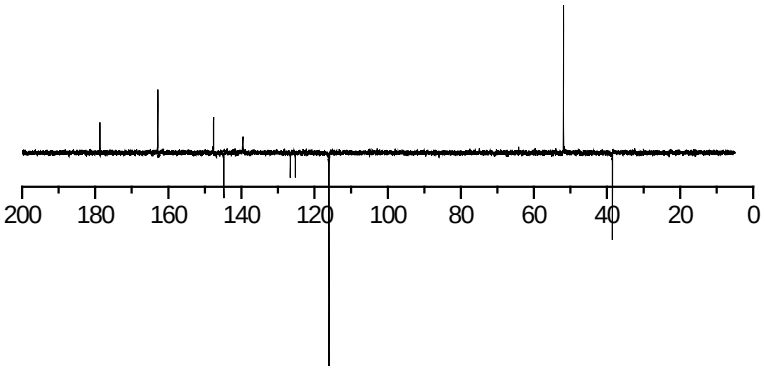


Figure S7. ^{13}C NMR(APT) of the charge-tagged ligand (75 MHz, D_2O).

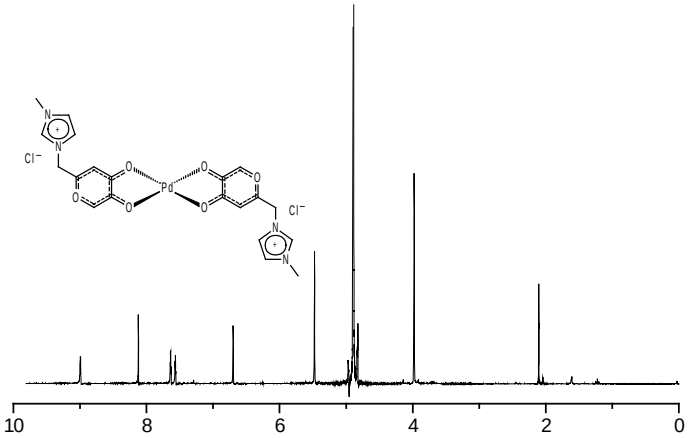


Figure S8. ^{1}H NMR of the **PdKjC** catalyst (300 MHz, D_2O).

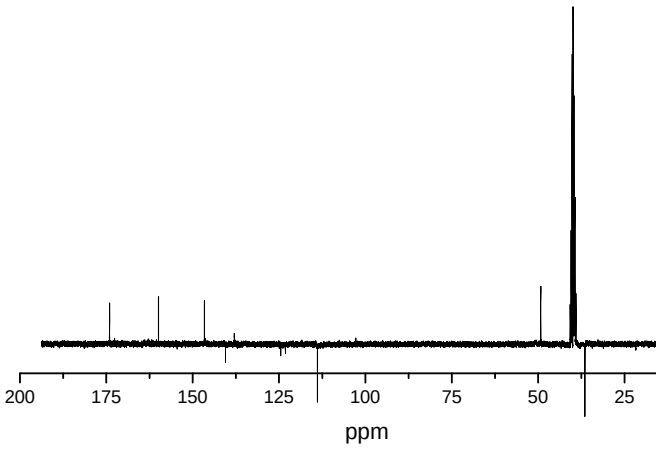
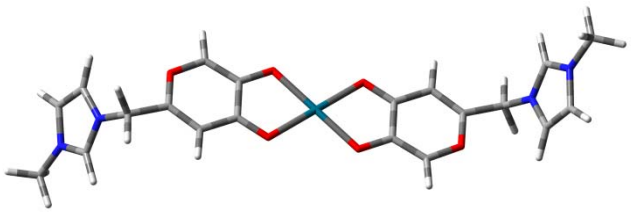


Figure S9. ^{13}C NMR(APT) of the **PdKjC** catalyst (75 MHz, D_2O).

Cartesian coordinates, energy and thermal corrections for all the calculated structures

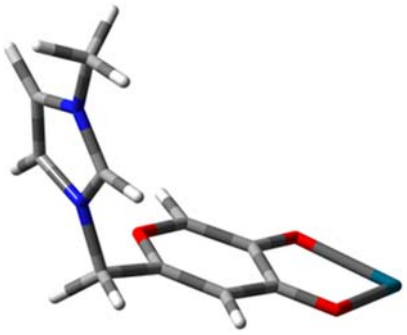


E(M06-2X/6-311++g(2d,2p)//M06-2X/6-311+g(d,p))= -1570.49190771 hartree
Counterpoise: BSSE energy = 0.002527347713 hartree
Zero-point correction = 0.395379 hartree
Thermal correction to Energy at 298.15 K = 0.423517 hartree
Thermal correction to Enthalpy at 298.15 K = 0.424461 hartree
Thermal correction to Gibbs Free Energy at 298.15 K = 0.330179 hartree
Thermal correction to Energy at 353.15 K = 0.433472 hartree
Thermal correction to Enthalpy at 353.15 K = 0.434590 hartree
Thermal correction to Gibbs Free Energy at 353.15 K = 0.311928 hartree
Thermal correction to Energy at 373.15 K = 0.437444 hartree
Thermal correction to Enthalpy at 373.15 K = 0.438626 hartree
Thermal correction to Gibbs Free Energy at 373.15 K = 0.304870 hartree

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	7.356870	-0.287473	-0.567700
2	6	0	7.929147	0.916928	-0.544164
3	1	0	7.762736	1.706623	-1.260095
4	7	0	8.745957	0.980020	0.501760
5	6	0	9.574717	2.132167	0.880077
6	1	0	9.436960	2.918759	0.141690
7	1	0	10.619502	1.827443	0.899494
8	1	0	9.264037	2.488595	1.860538
9	6	0	8.695702	-0.222107	1.174111
10	1	0	9.283300	-0.406084	2.058354
11	6	0	7.823170	-1.018658	0.504733
12	1	0	7.494526	-2.027147	0.691677
13	6	0	4.981546	-0.769265	-0.991815
14	6	0	3.664238	-1.827300	0.619740
15	6	0	3.950590	-0.005626	-1.427477
16	6	0	2.542962	-1.128443	0.267957
17	1	0	3.705152	-2.573569	1.398115
18	6	0	2.669604	-0.156182	-0.808214
19	1	0	4.073673	0.703033	-2.235911
20	8	0	4.858445	-1.650739	-0.007588
21	46	0	0.002667	-0.027741	-0.000800
22	8	0	1.659419	0.510031	-1.149404
23	8	0	1.380832	-1.274358	0.831185
24	7	0	-7.361220	0.320909	0.589997
25	6	0	-7.908634	-0.889338	0.466534
26	1	0	-7.702285	-1.740409	1.096766
27	7	0	-8.753899	-0.871411	-0.558072
28	6	0	-9.580346	-1.996990	-1.013406
29	1	0	-9.330569	-2.875393	-0.422665
30	1	0	-9.368990	-2.189977	-2.063476
31	1	0	-10.631162	-1.747692	-0.876534
32	6	0	-8.748622	0.390381	-1.113173
33	1	0	-9.365021	0.643609	-1.959920
34	6	0	-7.873052	1.139290	-0.394731
35	1	0	-7.568571	2.167617	-0.494447
36	6	0	-4.969993	0.722483	1.010615
37	6	0	-3.657141	1.782937	-0.602478
38	6	0	-3.940490	-0.048446	1.436554

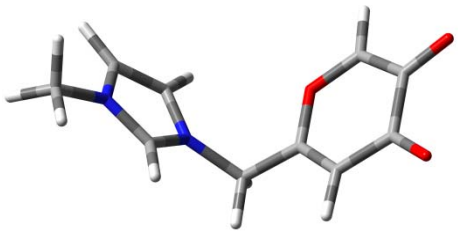
39	6	0	-2.536882	1.077585	-0.260323
40	1	0	-3.699802	2.532102	-1.377945
41	6	0	-2.661537	0.102314	0.813417
42	1	0	-4.062666	-0.761305	2.241440
43	8	0	-4.848634	1.608850	0.031111
44	8	0	-1.651515	-0.566904	1.149076
45	8	0	-1.377272	1.220139	-0.829800
46	6	0	-6.354074	0.709522	1.591369
47	1	0	-6.409464	0.007617	2.421683
48	1	0	-6.626690	1.702025	1.955387
49	6	0	6.370833	-0.750068	-1.559578
50	1	0	6.417880	-0.085556	-2.420538
51	1	0	6.670164	-1.751791	-1.873839



E(M06-2X/6-311++g(2d,2p)//M06-2X/6-311+g(d,p))= -848.56068396 hartree
Counterpoise: BSSE energy = 0.005187426629 hartree
Zero-point correction = 0.196748 hartree
Thermal correction to Energy at 298.15 K = 0.211467 hartree
Thermal correction to Enthalpy at 298.15 K = 0.212411 hartree
Thermal correction to Gibbs Free Energy at 298.15 K = 0.150259 hartree
Thermal correction to Energy at 353.15 K = 0.214980 hartree
Thermal correction to Enthalpy at 353.15 K = 0.216098 hartree
Thermal correction to Gibbs Free Energy at 353.15 K = 0.139658 hartree
Thermal correction to Energy at 373.15 K = 0.216925 hartree
Thermal correction to Enthalpy at 373.15 K = 0.218107 hartree
Thermal correction to Gibbs Free Energy at 373.15 K = 0.135273 hartree

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	3.470918	0.345333	0.639572
2	6	0	4.039218	-0.851769	0.505250
3	1	0	3.857890	-1.707760	1.135876
4	7	0	4.865378	-0.816901	-0.536091
5	6	0	5.697956	-1.926789	-1.012100
6	1	0	5.503243	-2.799978	-0.393762
7	1	0	6.747079	-1.647755	-0.933042
8	1	0	5.440718	-2.146603	-2.046545
9	6	0	4.821024	0.444048	-1.091283
10	1	0	5.412986	0.708637	-1.951363
11	6	0	3.942282	1.172775	-0.355884
12	1	0	3.602722	2.189992	-0.454687
13	6	0	1.070518	0.640514	1.011445
14	6	0	-0.242353	1.600768	-0.656540
15	6	0	0.081081	-0.199556	1.389254
16	6	0	-1.334750	0.817802	-0.382298
17	1	0	-0.221111	2.354541	-1.427743
18	6	0	-1.195207	-0.157896	0.720205
19	1	0	0.222458	-0.901444	2.201186
20	8	0	0.937507	1.520671	0.029172
21	46	0	-3.931708	-0.435964	-0.264536
22	8	0	-2.136181	-0.903087	1.041845
23	8	0	-2.441918	0.901141	-1.030158
24	6	0	2.435263	0.700351	1.628665
25	1	0	2.510552	0.007187	2.464346
26	1	0	2.662484	1.707218	1.982888



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Zero-point correction = 0.194553 hartree
Thermal correction to Energy at 298.15 K = 0.207629 hartree

Thermal correction to Enthalpy at 298.15 K = 0.208573 hartree
Thermal correction to Gibbs Free Energy at 298.15 K = 0.152162 hartree
Thermal correction to Energy at 353.15 K = 0.212250 hartree
Thermal correction to Enthalpy at 353.15 K = 0.213368 hartree
Thermal correction to Gibbs Free Energy at 353.15 K = 0.141350 hartree
Thermal correction to Energy at 373.15 K = 0.214099 hartree
Thermal correction to Enthalpy at 373.15 K = 0.215281 hartree
Thermal correction to Gibbs Free Energy at 373.15 K = 0.137218 hartree

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-1.690705	-0.008870	0.830933
2	6	0	-2.362747	0.886037	0.105206
3	1	0	-2.167910	1.946974	0.077485
4	7	0	-3.311306	0.253815	-0.576976
5	6	0	-4.283768	0.879421	-1.482140
6	1	0	-4.068523	1.943695	-1.544553
7	1	0	-5.287231	0.729240	-1.087823
8	1	0	-4.190624	0.428611	-2.468480
9	6	0	-3.244587	-1.091622	-0.283952
10	1	0	-3.924687	-1.804525	-0.719992
11	6	0	-2.224429	-1.257674	0.596825
12	1	0	-1.831748	-2.142001	1.070174
13	6	0	0.751509	0.146594	0.898119
14	6	0	1.996243	-1.466107	-0.250208
15	6	0	1.625224	1.128050	0.657092
16	6	0	3.026935	-0.547672	-0.601203
17	1	0	2.029400	-2.507256	-0.541801
18	6	0	2.860171	0.888205	-0.123253
19	1	0	1.451786	2.128354	1.035339
20	8	0	0.906860	-1.136813	0.462279
21	8	0	3.655063	1.751478	-0.368077
22	8	0	3.991459	-0.915192	-1.262333
23	6	0	-0.521111	0.283548	1.677678
24	1	0	-0.620350	1.294020	2.070278
25	1	0	-0.543738	-0.420183	2.511718

Palladium atom

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E(M06-2X/LANL2DZ)=                              -126.60395257 hartree
Thermal correction to Energy at 298.15 K =      0.001416 hartree
Thermal correction to Enthalpy at 298.15 K =     0.002360 hartree
Thermal correction to Gibbs Free Energy at 298.15 K =-0.016592 hartree
Thermal correction to Energy at 353.15 K =      0.001678 hartree
Thermal correction to Enthalpy at 353.15 K =     0.002796 hartree
Thermal correction to Gibbs Free Energy at 353.15 K =-0.020126 hartree
Thermal correction to Energy at 373.15 K =      0.001773 hartree
Thermal correction to Enthalpy at 373.15 K =     0.002954 hartree
Thermal correction to Gibbs Free Energy at 373.15 K =-0.021429 hartree
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