Supporting Information

The Mechanism of C–P Reductive Elimination from *trans*-[Pd(CH=CHPh)Br($PMePh_2$)$_2$]

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Table S1. Cartesian Coordinates for the Optimized Structure of (*E*)-**1a**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	–4.124182	1.349548	–4.507965
2	1	0	2.781955	–2.802578	–2.040017
3	1	0	–3.311493	–0.610100	–3.267576
4	1	0	–2.731514	–2.598155	–2.303729
5	1	0	2.936704	–3.353115	–0.378429
6	1	0	4.273235	–2.410868	–1.120205
7	6	0	–3.872806	1.449935	–3.455456
8	6	0	3.187782	–2.538603	–1.060268
9	1	0	3.442234	–0.940559	–3.185368
10	6	0	–3.413000	0.337420	–2.747704
11	1	0	4.282851	0.868443	–4.620658
12	35	0	–0.025426	–3.695205	–0.227675
13	1	0	–4.371685	3.546494	–3.365306
14	6	0	–3.163348	–2.459192	–1.309223
15	1	0	–4.248845	–2.339851	–1.382965
16	1	0	–2.914272	–3.344275	–0.720817
17	6	0	–4.012636	2.681441	–2.814255
18	6	0	3.495431	0.067202	–2.785940
19	6	0	3.971673	1.093669	–3.604067
20	6	0	–3.087512	0.439560	–1.385655
21	15	0	2.376336	–1.005237	–0.423329
22	1	0	5.041704	–0.018614	0.525770
23	46	0	–0.007642	–1.102750	–0.353291
24	6	0	3.091307	0.331613	–1.467352
25	15	0	–2.389954	–1.001540	–0.476890
26	6	0	4.050904	2.399284	–3.118153
27	1	0	4.422595	3.197453	–3.755081
28	6	0	–3.687241	2.795799	–1.460934
29	1	0	–0.037982	1.415280	–1.225844
30	6	0	–3.225094	1.686516	–0.752251
31	6	0	4.466202	–0.332281	1.391915
32	6	0	–0.001608	0.917927	–0.254772
33	6	0	3.151562	–0.798206	1.232392
34	1	0	–3.786622	3.750730	–0.952341
35	6	0	3.169433	1.651809	–0.990460

36	6	0	3.648994	2.674346	–1.809303
37	1	0	–5.144953	–0.301713	0.438170
38	1	0	6.054778	0.108179	2.775032
39	1	0	–0.269072	3.581121	–1.078773
40	6	0	5.037718	–0.257877	2.662508
41	1	0	–2.971218	1.793572	0.296639
42	6	0	–3.220064	–0.973405	1.164167
43	1	0	2.855364	1.883138	0.021155
44	6	0	–4.572687	–0.622524	1.304082
45	1	0	3.702629	3.687899	–1.421467
46	6	0	2.424418	–1.192888	2.365300
47	1	0	–0.217792	6.021044	–0.763771
48	6	0	–0.112920	3.986334	–0.083579
49	1	0	–1.454618	–1.658753	2.190176
50	6	0	0.043577	1.637575	0.880066
51	1	0	1.411116	–1.565874	2.244030
52	6	0	–2.497472	–1.374404	2.297103
53	6	0	–0.088047	5.367354	0.095563
54	6	0	4.306384	–0.652385	3.785467
55	6	0	0.051424	3.110157	1.007728
56	1	0	0.095824	1.113992	1.835983
57	6	0	–5.186954	–0.669660	2.555355
58	1	0	–6.233337	–0.392865	2.653006
59	6	0	3.000974	–1.122982	3.634837
60	1	0	4.753836	–0.593220	4.774064
61	6	0	–3.116217	–1.424482	3.548059
62	6	0	–4.459603	–1.070287	3.679151
63	6	0	0.098227	5.916434	1.368227
64	1	0	2.428857	–1.435107	4.504322
65	6	0	0.232557	3.681187	2.281387
66	1	0	0.115692	6.994519	1.504060
67	1	0	–2.546943	–1.740481	4.417944
68	1	0	0.358631	3.024056	3.139312
69	6	0	0.257250	5.063703	2.461790
70	1	0	–4.940176	–1.105763	4.653230
71	1	0	0.400617	5.474523	3.458166

Table S2. Cartesian Coordinates for the Optimized Structure of (*Z*)-**1a**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	1.517730	6.530273	–0.536651
2	1	0	1.358534	6.319367	–3.014695
3	1	0	–2.231982	2.582948	3.986474
4	6	0	1.253269	5.578864	–0.990402
5	1	0	–4.668015	2.357336	4.435602
6	6	0	1.163190	5.459296	–2.379032
7	6	0	–2.874969	2.078047	3.270896
8	1	0	1.063305	4.540017	0.891888
9	6	0	–4.241169	1.947738	3.523888
10	6	0	0.997288	4.461403	–0.190502
11	1	0	–1.254325	1.613022	1.929943
12	6	0	0.822284	4.237295	–2.955731
13	6	0	–2.322422	1.542972	2.105670
14	1	0	0.754907	4.154355	–4.038649
15	6	0	–5.058236	1.280863	2.607761
16	1	0	5.122722	1.746514	3.908725
17	1	0	–6.121345	1.169051	2.803924
18	6	0	0.655904	3.239739	–0.768921
19	1	0	–2.549808	2.502146	–1.359717
20	1	0	4.275766	–0.591198	4.010530
21	1	0	–4.135776	1.698896	–1.475551
22	6	0	0.561368	3.098562	–2.167930
23	6	0	4.594761	1.319431	3.060206
24	6	0	–3.137943	0.881897	1.177604
25	6	0	4.121548	0.007136	3.116736
26	6	0	–4.510702	0.750970	1.439495
27	1	0	0.458593	2.377722	–0.135545
28	6	0	–3.056085	1.560343	–1.587024
29	1	0	4.744294	3.105694	1.857904
30	6	0	4.382795	2.082135	1.910538
31	1	0	–2.812276	1.289977	–2.616379
32	1	0	–5.152155	0.226100	0.736714
33	6	0	0.212726	1.837203	–2.844305
34	1	0	–4.486994	–0.406689	–2.488989
35	6	0	3.441792	–0.544914	2.030607

36	15	0	–2.423181	0.283262	–0.410221
37	1	0	0.161578	1.936753	–3.933560
38	1	0	3.067657	–1.560404	2.090826
39	6	0	3.705708	1.533970	0.820120
40	6	0	3.234942	0.211767	0.866181
41	6	0	–4.301331	–1.283301	–1.876783
42	6	0	–0.032752	0.617278	–2.331811
43	1	0	3.540105	2.148955	–0.058941
44	46	0	–0.063482	–0.112797	–0.446896
45	6	0	–3.378863	–1.235867	–0.820264
46	1	0	–5.707800	–2.484812	–2.978435
47	35	0	–0.116414	–1.293272	1.869602
48	6	0	–4.997114	–2.462738	–2.156429
49	1	0	–0.268116	–0.173619	–3.050984
50	1	0	2.980627	1.279338	–2.114591
51	15	0	2.294353	–0.483098	–0.553012
52	6	0	–3.159726	–2.393605	–0.051982
53	1	0	4.891644	–1.917918	–0.459028
54	1	0	–2.431574	–2.372174	0.754666
55	6	0	3.186096	0.211010	–2.019291
56	6	0	–4.781573	–3.603636	–1.383704
57	1	0	4.264288	0.046217	–1.934539
58	6	0	–3.862000	–3.564816	–0.331855
59	6	0	4.106830	–2.657645	–0.592208
60	1	0	–5.324528	–4.519660	–1.601197
61	1	0	2.810611	–0.283226	–2.918717
62	6	0	2.759721	–2.260458	–0.627804
63	1	0	–3.686183	–4.450533	0.272773
64	1	0	5.492915	–4.301335	–0.675565
65	6	0	4.447971	–4.004554	–0.708798
66	6	0	1.763720	–3.234872	–0.777772
67	1	0	0.720568	–2.935246	–0.777301
68	6	0	3.448707	–4.969198	–0.864646
69	6	0	2.108497	–4.583152	–0.898750
70	1	0	3.716224	–6.018792	–0.953804
71	1	0	1.326771	–5.329477	–1.009772

Table S3. Cartesian Coordinates for the Optimized Structure of (*E*)-**2a**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	35	0	0.127376	–2.401839	–2.561635
2	1	0	–2.419867	–1.634657	–2.491569
3	1	0	–3.468379	–0.292119	–3.016930
4	1	0	–4.187370	–1.670715	–2.141397
5	1	0	2.837824	–2.956014	–1.306998
6	1	0	6.312777	–0.032831	–3.006615
7	6	0	–3.301921	–1.035588	–2.230969
8	1	0	4.652876	–1.496835	–1.932178
9	1	0	–1.624475	–2.746922	–0.383404
10	6	0	5.615273	0.387610	–2.286735
11	1	0	2.389472	–3.353137	0.349964
12	6	0	3.013704	–2.694141	–0.260306
13	6	0	4.673839	–0.443220	–1.673102
14	1	0	4.064474	–2.841569	0.010257
15	1	0	–1.557832	–4.396113	1.448624
16	1	0	6.392531	2.392063	–2.456356
17	46	0	0.277993	–0.451284	–0.769149
18	6	0	5.659579	1.747074	–1.978688
19	6	0	–2.172592	–2.553340	0.535816
20	6	0	3.761707	0.076596	–0.742653
21	15	0	–2.970571	–0.160175	–0.666887
22	15	0	2.445469	–0.955949	0.030340
23	1	0	–1.496052	1.367564	–1.760722
24	6	0	–2.121984	–3.477264	1.579768
25	6	0	–1.482674	0.770057	–0.849257
26	1	0	–5.902385	–0.654499	–0.659998
27	6	0	–2.906563	–1.364299	0.697127
28	1	0	–0.003004	2.923302	–1.803835
29	6	0	–4.429638	0.908865	–0.358316
30	6	0	–5.735953	0.396469	–0.439170
31	6	0	4.751156	2.276213	–1.057547
32	6	0	3.806546	1.451410	–0.449530
33	1	0	–3.233728	2.669975	–0.001706
34	6	0	–4.240097	2.266092	–0.062101
35	6	0	–6.831640	1.231488	–0.227141

36	1	0	–7.838217	0.827969	–0.292574
37	1	0	4.770209	3.335599	–0.815712
38	6	0	–0.645551	1.169927	0.256718
39	6	0	–5.341057	3.099001	0.151057
40	6	0	0.342361	3.249641	–0.827118
41	1	0	3.101403	1.879832	0.257174
42	1	0	0.685963	–1.000470	2.327245
43	6	0	–2.785079	–3.222615	2.783181
44	6	0	–6.634971	2.583987	0.067515
45	1	0	1.221637	5.042204	–1.617039
46	1	0	–5.184286	4.149363	0.379471
47	6	0	2.769723	–0.767654	1.843978
48	1	0	–7.490678	3.233359	0.230560
49	1	0	–2.739452	–3.946653	3.592335
50	6	0	–3.573326	–1.111460	1.905897
51	1	0	–0.925283	0.802072	1.244292
52	6	0	1.686659	–0.865227	2.729964
53	6	0	1.046100	4.447807	–0.723838
54	6	0	0.096392	2.450762	0.306767
55	1	0	4.908425	–0.495849	1.699669
56	6	0	–3.506580	–2.038938	2.947202
57	6	0	4.058102	–0.583490	2.370177
58	1	0	–4.145465	–0.198599	2.036307
59	6	0	1.885391	–0.790155	4.110531
60	6	0	1.530673	4.883757	0.512813
61	6	0	0.589865	2.906526	1.545137
62	1	0	–4.021723	–1.836088	3.881952
63	1	0	1.035922	–0.870955	4.784274
64	1	0	2.078975	5.818709	0.590356
65	6	0	4.256080	–0.499171	3.749012
66	1	0	0.420925	2.304142	2.434984
67	6	0	1.299938	4.102065	1.647426
68	6	0	3.170635	–0.603769	4.622425
69	1	0	5.258956	–0.351986	4.141908
70	1	0	1.669730	4.425275	2.617400
71	1	0	3.326772	–0.537658	5.696116

Table S4. Cartesian Coordinates for the Optimized Structure of (*Z*)-**2a**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	3.635985	–0.781004	–2.884122
2	1	0	3.448747	–2.210504	–1.860853
3	6	0	3.828338	–1.185340	–1.885196
4	1	0	–3.249228	–1.888292	–2.675174
5	35	0	0.589835	–3.160023	–1.325219
6	1	0	4.903828	–1.184192	–1.681259
7	1	0	–1.539579	0.105690	–2.461039
8	1	0	–2.066675	–2.713458	–1.623465
9	6	0	–3.016545	–2.163764	–1.642090
10	1	0	–3.820263	–2.785648	–1.239817
11	1	0	2.277893	–2.618924	0.889911
12	46	0	0.528423	–0.514089	–0.962341
13	1	0	–0.261711	1.923234	–1.750538
14	6	0	–1.435227	0.197752	–1.376826
15	15	0	2.858625	–0.228306	–0.629157
16	1	0	–5.456824	3.502212	–1.243829
17	1	0	–3.364576	2.198035	–1.014508
18	6	0	–0.594583	1.289726	–0.926716
19	6	0	–5.505135	2.425550	–1.107928
20	6	0	–4.324029	1.691990	–0.978720
21	1	0	–7.658482	2.349530	–1.171886
22	15	0	–2.812168	–0.646724	–0.646950
23	6	0	–6.740478	1.778055	–1.066109
24	6	0	3.058938	–2.101591	1.441925
25	6	0	3.547549	1.481174	–0.733350
26	6	0	–4.373442	0.302276	–0.799097
27	1	0	2.067604	2.254584	0.636451
28	1	0	5.143503	1.063975	–2.134254
29	6	0	–6.797366	0.392838	–0.888916
30	6	0	–5.621024	–0.343091	–0.753779
31	1	0	–7.757431	–0.114610	–0.856701
32	6	0	2.926664	2.494841	0.017168
33	6	0	4.641532	1.822905	–1.542923
34	1	0	–5.680419	–1.418237	–0.609976
35	1	0	3.185865	–3.606562	2.972528

36	6	0	3.555467	–0.878649	0.958804
37	6	0	3.394873	3.807263	–0.030303
38	6	0	5.101830	3.141463	–1.601324
39	1	0	–1.124859	–2.625741	0.692618
40	1	0	2.900535	4.574416	0.559942
41	1	0	5.947550	3.387379	–2.238537
42	6	0	3.572781	–2.655455	2.615167
43	1	0	–0.940387	3.932643	–0.724571
44	6	0	4.482951	4.135800	–0.843527
45	6	0	–0.726476	2.067460	0.339095
46	1	0	4.842843	5.160438	–0.888466
47	6	0	–2.679451	–1.160347	1.095598
48	6	0	–1.770872	–2.175328	1.443247
49	6	0	–0.903820	3.462330	0.255974
50	6	0	4.563689	–0.221424	1.679127
51	1	0	–0.455931	0.432921	1.714896
52	6	0	–0.650513	1.495830	1.622131
53	1	0	4.957614	0.725236	1.322546
54	6	0	4.574549	–1.993211	3.328957
55	1	0	–4.188666	0.210907	1.822760
56	6	0	–3.487705	–0.575215	2.081926
57	1	0	–0.973011	–3.372179	3.035916
58	6	0	–1.678081	–2.589227	2.772253
59	6	0	5.067011	–0.774915	2.858829
60	1	0	4.968484	–2.423936	4.246107
61	6	0	–1.026778	4.250283	1.401231
62	1	0	–1.161624	5.324798	1.304106
63	6	0	–0.778053	2.281059	2.768223
64	1	0	5.846005	–0.252103	3.408309
65	6	0	–0.970490	3.661206	2.665718
66	6	0	–3.385219	–0.997410	3.407752
67	6	0	–2.481425	–2.003576	3.753902
68	1	0	–0.710467	1.811320	3.746066
69	1	0	–4.010211	–0.536958	4.167737
70	1	0	–2.403282	–2.331317	4.787114
71	1	0	–1.060765	4.271200	3.560612