Electronic Supplementary Information (ESI)

Origin of ligand effects on reactivities of pincer-Pd catalyzed hydrocarboxylation of allenes and alkenes with formate salts: a computational study

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Comparison of hydrocarboxylation barriers using different functionals

The barriers of the CO_2 insertion with allylpalladium and benzylpalladium intermediates were calculated using M06L, M06 and B3LYP-D3 (Table S1). Although the absolute activation energies differ by a few kcal/mol among the methods tested, the trend of the CO_2 insertion reactivity, i.e. **11-TS** with allylpalladium is lower than **14-TS** and **15-TS** with benzylpalladium, is only slightly affected by the choice of the density functional in single point calculations. Further, All these methods suggest that the Pd catalyst with Et-substituted *PGeP*-pincer ligand (**15-TS**) is more reactive than that with Ph-substituted ligand (**14-TS**).

Table S1. Comparison of activation free energies ($\Delta G^{\ddagger}_{sol}$ kcal/mol) of hydrocarboxylation transition states 11-TS, 14-TS and 15-TS

Method for single point energy calculation[a]	11-TS ($\Delta G^{\ddagger}_{sol}$)	14-TS ($\Delta G^{\ddagger}_{sol}$)	15-TS ($\Delta G^{\ddagger}_{sol}$)	$\Delta\Delta G^{\ddagger}_{sol}$ (14-TS-15-TS)
M06L/SDD−6-311+G(d,p)/SMD	21.6	34.8	28.4	6.4
B3LYP-D3/SDD−6-311+G(d,p)/SMD	16.9	32.6	26.6	6.0
M06/SDD−6-311+G(d,p)/SMD	20.8	36.4	31.2	5.2

[a] Geometries were optimized at B3LYP/LANL2DZ–6-31G(d) level. The calculated $\Delta G^{\ddagger}_{sol}$ are with respect to the corresponding allylpalladium and benzylpalladium intermediates.

Energy profile of Pd-catalyzed styrene hydrocarboxylation

The energy profile for Ph-substituted *PGeP*-pincer Pd catalyzed (**cat1** shown in Scheme 1) styrene hydrocarboxylation with formate was shown in Fig. S1. Similar to the energy profile for allene hydrocarboxylation shown in Fig. 1 in the manuscript, the rate-determining step is CO_2 insertion into benzylpalladium intermediate (**S8**). The transition state (**14-TS**) has a quite high barrier, 34.8 kcal/mol with respect to **S8**. This is consistent with the experimental observation that **cat1** is ineffective to promote the styrene hydrocarboxylation.

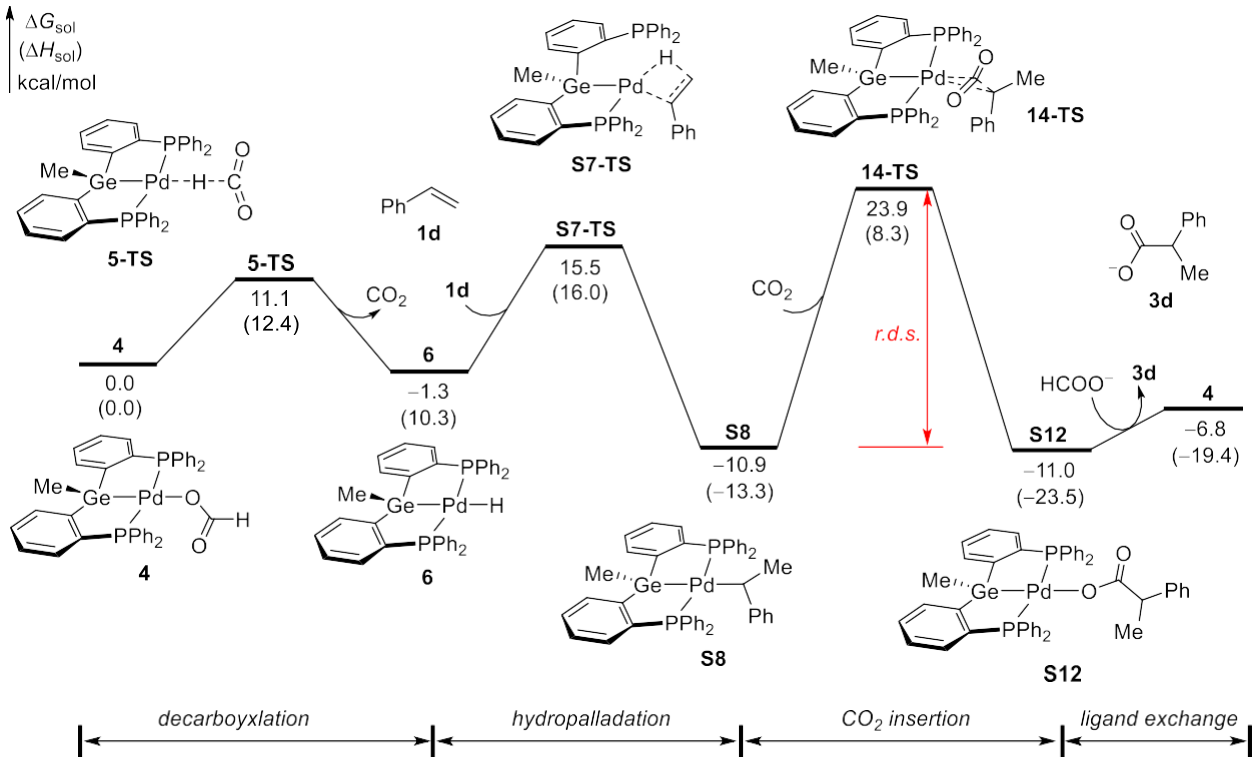


Fig. S1 Energy profile of Ph-substituted *PGeP*-pincer Pd catalyzed hydrocarboxylation of styrene. Energies are with respect to the Pd formate **4**.

Distortion/interaction analysis for 11-TS, 14-TS and 15-TS

As shown in Fig. S2, the trend of the total interaction energies of **11-TS**, **14-TS** and **15-TS** is not consistent with the trend of their activation energies. This indicates that the contribution of interaction energies is negative to the CO_2 insertion reactivity. For example, although the total interaction energy in **14-TS** is 6.4 kcal/mol larger than that in **15-TS**, the total distortion energy in **14-TS** is 10.3 kcal/mol higher than that in **15-TS**. Thus, the neat result suggests that the higher barrier of **14-TS** is attributed to the larger distortion energies.

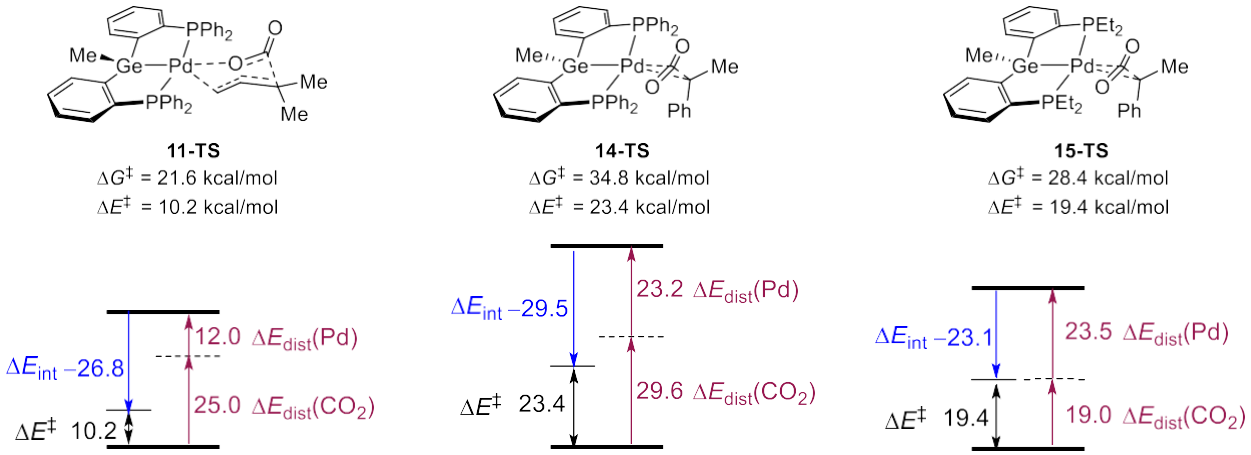
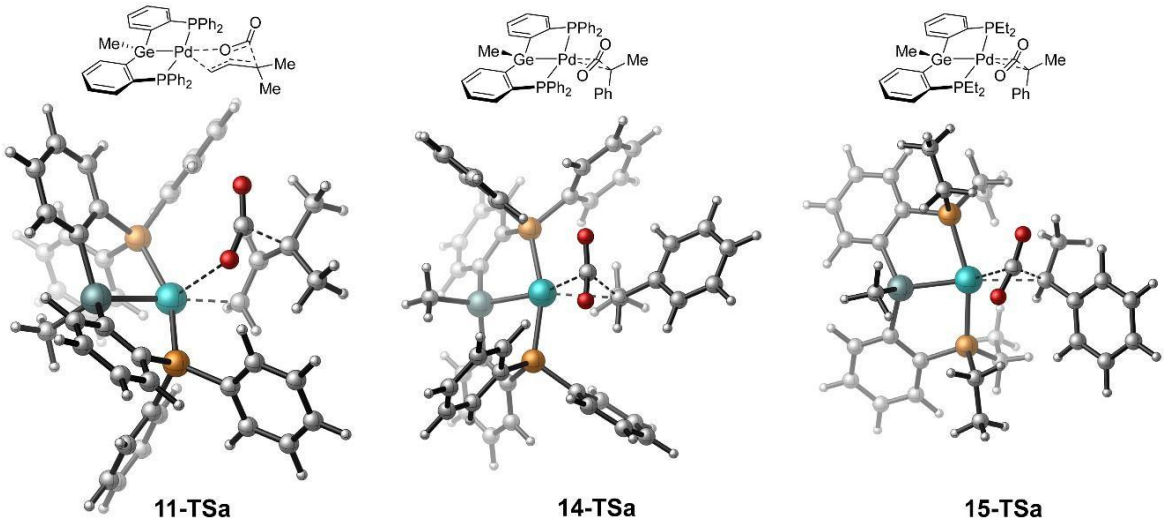


Fig. S2 Distortion/interaction analysis for **11-TS**, **14-TS** and **15-TS**. Energies are given in kcal/mol.

Disfavored conformers of CO_2 insertion transition states

For CO_2 insertion into the Pd–C(allyl) and Pd–C(benzyl) intermediates with the *PGeP*-pincer ligands, CO_2 can approach these Pd–C bonds from both sides of the pincer structure. We calculated both of these possibilities for CO_2 insertion. The transition states **11-TS**, **14-TS** and **15-TS** shown in Fig. 2 in the manuscript are favored over **11-TSa**, **14-TSa** and **15-TSa** shown in Fig. S3, respectively. The higher barriers of transition states **11-TSa**, **14-TSa** and **15-TSa** are due to the larger distortion energies (ΔE_{dist}, Fig. S3) than those of **11-TS** (ΔE_{dist} = 37.1 kcal/mol), **14-TS** (ΔE_{dist} = 52.8 kcal/mol) and **15-TS** (ΔE_{dist} = 42.5 kcal/mol), respectively.



11-TSa
$\Delta G^{\ddagger}$ = 23.9 kcal/mol
$\Delta E^{\ddagger}$ = 12.5 kcal/mol
ΔE_{dist} = 41.0 kcal/mol

14-TSa
$\Delta G^{\ddagger}$ = 36.6 kcal/mol
$\Delta E^{\ddagger}$ = 29.1 kcal/mol
ΔE_{dist} = 54.6 kcal/mol

15-TSa
$\Delta G^{\ddagger}$ = 29.8 kcal/mol
$\Delta E^{\ddagger}$ = 24.5 kcal/mol
ΔE_{dist} = 49.3 kcal/mol

Fig. S3 Disfavored CO_2 insertion transition states.

Ligand electronic effects on CO_2 insertion reactivity

In the transition states of CO_2 insertion, the γ-C in allylpalladium **III** and the α-C in benzylpalladium **IV** nucleophilically attack the central carbon of CO_2. This nucleophilicity would be affected by the electron-donating ability of the different pincer ligands. Thus, we computed the NBO charges on the γ-C in allylpalladium **III** and the α-C in benzylpalladium **IV** supported by pincer ligands with different *P*-bound R substituents (R = Ph, Me, Et, ^{i}Pr, Cy, ^{t}Bu). Poor and moderate correlations between the NBO charges and the activation energy were observed for allylpalladium **III** (R^2 = 0.42, Fig. S3) and benzylpalladium **IV** (R^2 = 0.81), respectively. In contrast, as shown in Fig. 3 in the manuscript, the activation energy and the total distortion energy of CO_2 and Pd-allyl/Pd-benzyl complexes have excellent linear correlations (R^2 = 0.95 for allylpalladium **III**; R^2 = 0.97 for benzylpalladium **IV**). These results indicate that the reactivity of CO_2 insertion is dominated by the total distortion energy of CO_2 and Pd-allyl/Pd-benzyl intermediates.

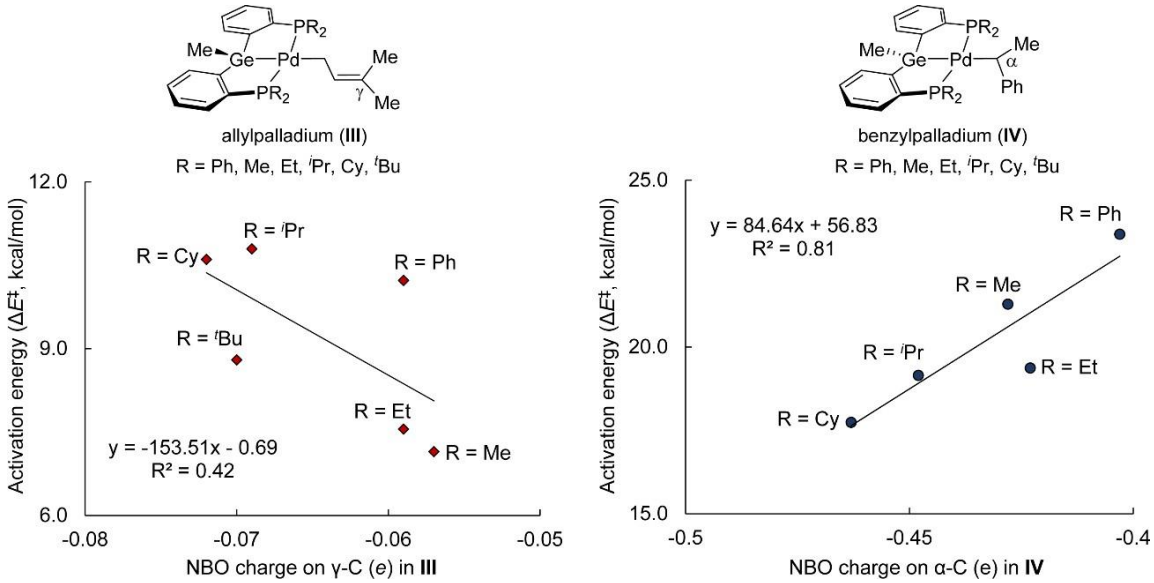


Fig. S4 Relationships between NBO charges and activation energies of CO_2 insertion.

Previously, the Wu group did computational study on CO_2 insertion with ***PSiP***-pincer Pd allyl complex (ref. 47 in the manuscript). They suggested that the *P*-bond Ph substituents lead to a lower activation energy than *P*-bond ^{i}Pr substituents due to electronic effects. To compare with Wu's results, we calculated the reaction of CO_2 with ***PSiP***-pincer Pd allyl complex using our method. As shown in Fig. S4, the activation free energy of **TS1** is 20.2 kcal/mol, which is comparable with the number of the same transition state reported by Wu ($\Delta G^{‡}$ = 21.2 kcal/mol). Also, the trend of reactivity between **TS1** and **TS2** is consistent with Wu's result, ***i.e.*** the ***PSiP*** pincer ligand with *P*-bound Ph substituents is more reactive than that with ^{i}Pr groups ($\Delta G^{‡}$ = 20.2 kcal/mol for **TS1** vs $\Delta G^{‡}$ = 21.7 kcal/mol for **TS2**). Based on the distortion/interaction

analysis, the disfavored **TS2** is mainly attributed to the larger total distortion energy of CO_2 and Pd-allyl fragments (ΔE_{dist} = 35.7 kcal/mol) compared to that of **TS1** (ΔE_{dist} = 34.2 kcal/mol). To study the ligand's electronic effect on CO_2 insertion reactivity, we calculated the NBO charges in **TS1**, **TS2** and Pd-allyl intermediates with Ph and ^{i}Pr substituents. The results show that the charge populations on the γ-carbon in **TS1** and **TS2** are opposite to the nature of nucleophilic addition to CO_2. The α-carbon has the same trend. Although the *PSiP*-pincer ligand with ^{i}Pr groups has stronger electron-donating ability, **TS2** obtains a higher barrier than **TS1** with the Ph substituted *PSiP*-pincer ligand. This indicates that the electron donicity of ligands exerts insignificant effects on the CO_2 insertion reactivity. The Pd-allyl intermediates with Ph and ^{i}Pr substituents give the same trend of charge populations with these transition states (not shown).

In addition, we compared the NBO charges in the CO_2 insertion transition states Ph- and ^{i}Pr-substituted *PGeP*-pincer ligands (**TSa-Ph** and **TSa-^{i}Pr**, shown below). Although the charges on γ- and α-carbon atoms in **TSa-^{i}Pr** are more negative than those in **TSa-Ph**, these two transition states have comparable activation free energies of nucleophilic addition to CO_2. In contrast, the total distortion energies in **TSa-Ph** and **TSa-^{i}Pr** are comparable.

Taken together, the electronic effects of Ph and ^{i}Pr substituents are insignificant to the reactivity of CO_2 insertion. Instead, the distortions of CO_2 and Pd-allyl in the transition states show good consistence with the CO_2 insertion reactivity.

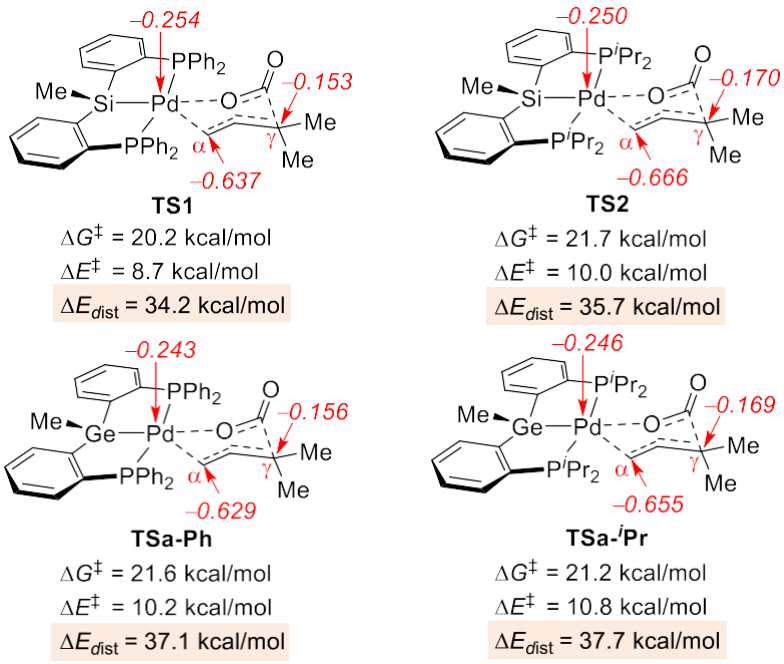


Fig. S5 Charge populations in the CO_2 insertion transition states.

Cartesian coordinates (Å) and energies of key optimized structures

1c

B3LYP SCF energy: -195.29021278 a.u.
B3LYP enthalpy: -195.169994 a.u.
B3LYP free energy: -195.206460 a.u.
M06 SCF energy in solution: -195.31534984 a.u.
M06 enthalpy in solution: -195.195131 a.u.
M06 free energy in solution: -195.231597 a.u.
Three lowest frequencies (cm-1): 170.8162 183.7385 187.0846

Cartesian coordinates

ATOM	X	Y	Z
C	0.934524	-0.004028	0.067840
C	2.240433	-0.007061	0.148449
H	2.870667	-0.069243	-0.738040
H	2.757090	0.052590	1.105756
C	-0.374821	-0.000758	-0.013097
C	-1.177762	-1.285158	0.021946
H	-0.533646	-2.162669	0.121521
H	-1.884819	-1.277183	0.862855
H	-1.773217	-1.394914	-0.894853
C	-1.160825	1.287691	-0.146249
H	-1.758288	1.283616	-1.068281
H	-1.864751	1.400251	0.689793
H	-0.504929	2.161936	-0.164436

3c

B3LYP SCF energy: -384.52269439 a.u.
B3LYP enthalpy: -384.374416 a.u.
B3LYP free energy: -384.417679 a.u.
M06 SCF energy in solution: -384.69167233 a.u.
M06 enthalpy in solution: -384.543394 a.u.
M06 free energy in solution: -384.586657 a.u.
Three lowest frequencies (cm-1): 45.9316 114.4858 227.8476

Cartesian coordinates

ATOM	X	Y	Z
C	2.687623	5.443121	0.611322
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O 0.558639 2.719987 -1.585190

4

B3LYP SCF energy: -4502.04876041 a.u.
B3LYP enthalpy: -4501.413908 a.u.
B3LYP free energy: -4501.535166 a.u.
M06 SCF energy in solution: -4505.71554801 a.u.
M06 enthalpy in solution: -4505.080696 a.u.
M06 free energy in solution: -4505.201954 a.u.
Three lowest frequencies (cm-1): 12.9148 20.1952 35.9416

Cartesian coordinates

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H	-2.760990	1.018070	4.827165
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H	-4.259828	-0.918245	5.269163
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C	-5.069952	3.573713	-1.642043
C	-4.748156	1.687255	-0.162248

C	-2.922342	2.454648	-1.563820
C	-3.748850	3.456574	-2.076577
C	-5.567660	2.690487	-0.680708
H	-5.138481	1.014390	0.595685
H	-1.879612	2.410138	-1.862081
H	-3.347262	4.155873	-2.804567
H	-6.591303	2.785764	-0.327883
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C	3.068232	0.368306	4.011511
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H	-0.000542	4.535245	0.497898

5-TS

B3LYP SCF energy: -4502.01504026 a.u.
B3LYP enthalpy: -4501.385795 a.u.
B3LYP free energy: -4501.509151 a.u.
M06 SCF energy in solution: -4505.69012816 a.u.
M06 enthalpy in solution: -4505.060883 a.u.
M06 free energy in solution: -4505.184239 a.u.
Three lowest frequencies (cm-1): -244.5253 9.2269 17.3338
Imaginary frequency: -244.5253 cm-1

Cartesian coordinates

ATOM	X	Y	Z
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C	-1.715910	-2.265788	-1.165983
C	-1.975547	-3.394153	-1.954147

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C	4.083146	-2.935285	-2.239755
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H	3.253614	-4.857591	-2.758621
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C	-0.228522	-3.174931	1.534996
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H	-0.240259	-4.228152	1.231643
H	-1.146201	-2.960038	2.089969
C	-3.152993	-0.169112	1.563292
C	-4.330933	-0.651749	4.064545
C	-4.089631	-1.201008	1.718485
C	-2.804135	0.613257	2.677542
C	-3.394928	0.375817	3.917732
C	-4.674424	-1.439493	2.965411
H	-4.360471	-1.822587	0.870384
H	-2.066676	1.405090	2.571947
H	-3.118046	0.988664	4.771188
H	-5.397365	-2.243680	3.074585
H	-4.785673	-0.840087	5.033390
C	-3.313618	1.620173	-0.713408
C	-4.750191	3.771949	-1.794397
C	-4.699421	1.726024	-0.503706
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C	-3.371319	3.683016	-1.989154
C	-5.412817	2.794594	-1.046950
H	-5.219479	0.984907	0.096822
H	-1.574816	2.577113	-1.564241
H	-2.843807	4.454096	-2.543159
H	-6.483728	2.869366	-0.877161
H	-5.306622	4.608436	-2.209011
C	3.114571	-0.069830	1.596752
C	4.261405	-0.236555	4.149998
C	3.912405	-1.169192	1.943452
C	2.887251	0.946251	2.543087
C	3.465375	0.860834	3.809166
C	4.482114	-1.250145	3.217222
H	4.090226	-1.962991	1.224693
H	2.261535	1.799623	2.291412
H	3.287005	1.651966	4.532368
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C	4.749924	3.304079	-2.343545
C	2.664612	2.159311	-1.904620
C	4.649530	1.588867	-0.639713

C	5.375307	2.544704	-1.352252
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H	1.601788	2.039319	-2.090745
H	5.138537	1.015037	0.142194
H	6.426636	2.701450	-1.125845
H	2.896802	3.716486	-3.369408
H	5.314846	4.053181	-2.891922
H	0.071867	2.164572	0.143091
C	0.433021	3.649982	0.445509
O	0.855570	3.660594	1.568626
O	0.149602	4.225628	-0.567217

6

B3LYP SCF energy: -4313.44181517 a.u.
B3LYP enthalpy: -4312.827934 a.u.
B3LYP free energy: -4312.943329 a.u.
M06 SCF energy in solution: -4317.06042199 a.u.
M06 enthalpy in solution: -4316.446541 a.u.
M06 free energy in solution: -4316.561936 a.u.
Three lowest frequencies (cm-1): 9.7308 17.3538 21.2248

Cartesian coordinates

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C	-3.755051	-0.596024	-2.145317
C	-1.620688	-1.680248	-1.634780
C	-1.849743	-2.545920	-2.712329
C	-3.948293	-1.462300	-3.222909
H	-4.496432	0.169092	-1.935012
H	-1.115699	-3.311808	-2.951976
H	-4.837883	-1.367536	-3.840243
H	-3.138755	-3.115670	-4.346277
C	2.673461	-0.893064	-1.177098
C	3.200493	-2.898730	-3.051680
C	1.681911	-1.863419	-1.440992
C	3.900001	-0.918965	-1.859909
C	4.161151	-1.918192	-2.798023
C	1.980256	-2.867163	-2.373872
H	4.648433	-0.155112	-1.669889
H	5.109777	-1.928454	-3.328501
H	1.244594	-3.639700	-2.586817
H	3.398699	-3.680586	-3.780950
Ge	-0.029808	-1.719163	-0.422052
C	-0.189109	-3.394929	0.641117
H	0.651954	-3.480597	1.336102
H	-0.194917	-4.277878	-0.008699
H	-1.118414	-3.382827	1.218995
C	-3.136638	-0.406162	1.528554
C	-4.332244	-1.583443	3.780609
C	-4.008169	-1.494714	1.382285
C	-2.863794	0.081639	2.818041

C	-3.462455	-0.500085	3.934509
C	-4.601366	-2.079606	2.504849
H	-4.220268	-1.891024	0.394064
H	-2.175506	0.913634	2.942936
H	-3.243665	-0.112777	4.926088
H	-5.272428	-2.925249	2.378417
H	-4.792854	-2.040908	4.652199
C	-3.328238	1.905376	-0.206842
C	-4.838353	4.203732	-0.769081
C	-4.702345	1.941664	0.080207
C	-2.717557	3.038339	-0.762993
C	-3.470474	4.177884	-1.049045
C	-5.451920	3.085764	-0.200010
H	-5.186660	1.081557	0.533777
H	-1.646012	3.026912	-0.940726
H	-2.984990	5.050419	-1.478232
H	-6.513597	3.104538	0.032220
H	-5.422307	5.095085	-0.983190
C	3.142393	-0.184114	1.648044
C	4.332607	-0.979131	4.063732
C	4.042741	-1.258396	1.675780
C	2.835427	0.482018	2.847428
C	3.432016	0.089694	4.044740
C	4.633400	-1.652676	2.879657
H	4.279453	-1.792843	0.761139
H	2.121939	1.301979	2.836713
H	3.187661	0.613586	4.965032
H	5.327249	-2.489279	2.888668
H	4.791983	-1.288398	4.998880
C	3.283795	1.862324	-0.409363
C	4.715785	4.098287	-1.319189
C	2.656354	2.833690	-1.203130
C	4.633054	2.031420	-0.062530
C	5.343789	3.145265	-0.515377
C	3.370692	3.940421	-1.661684
H	1.600769	2.726713	-1.436378
H	5.128135	1.299964	0.569707
H	6.386694	3.268936	-0.235226
H	2.873152	4.686326	-2.275890
H	5.269402	4.965696	-1.669026
H	0.043053	2.237381	0.733470

7-TS

B3LYP SCF energy: -4508.71538958 a.u.
B3LYP enthalpy: -4507.981456 a.u.
B3LYP free energy: -4508.111353 a.u.
M06 SCF energy in solution: -4512.37524883 a.u.
M06 enthalpy in solution: -4511.641315 a.u.
M06 free energy in solution: -4511.771212 a.u.
Three lowest frequencies (cm-1): -808.7685 11.4705 21.7615
Imaginary frequency: -808.7685 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Pd	0.098606	1.042141	0.256037

P	1.949362	-0.530045	0.242707
P	-2.194280	-0.021442	0.278860
C	1.888972	-1.586844	-1.276855
C	1.782322	-3.086335	-3.632915
C	2.613494	-2.784494	-1.386267
C	1.089385	-1.130703	-2.343694
C	1.060960	-1.897078	-3.518710
C	2.558446	-3.533649	-2.561103
H	3.215021	-3.137107	-0.553370
H	0.448896	-1.572363	-4.357645
H	3.116925	-4.463101	-2.638039
H	1.732965	-3.667816	-4.550567
C	-2.768966	-0.212926	-1.481024
C	-3.640191	-0.430532	-4.132716
C	-1.857888	0.042140	-2.525791
C	-4.094997	-0.576224	-1.768984
C	-4.530451	-0.688227	-3.087920
C	-2.323920	-0.069069	-3.846494
H	-4.795976	-0.763079	-0.960546
H	-5.560309	-0.965332	-3.298241
H	-1.647054	0.138755	-4.672267
H	-3.973187	-0.504982	-5.165275
Ge	0.028324	0.553536	-2.127826
C	0.606254	1.767285	-3.591747
H	0.559924	1.278186	-4.571787
H	1.639460	2.084399	-3.419341
H	-0.030607	2.657122	-3.616132
C	3.561658	0.367377	0.101578
C	5.928988	1.883281	-0.058829
C	4.371706	0.308864	-1.041566
C	3.954236	1.202323	1.162829
C	5.129730	1.947107	1.086684
C	5.545222	1.064605	-1.120595
H	4.089786	-0.328075	-1.873702
H	3.336237	1.270270	2.053870
H	5.420556	2.581110	1.920489
H	6.160445	1.006637	-2.014945
H	6.842928	2.468144	-0.120813
C	2.281444	-1.713795	1.625402
C	2.646302	-3.548515	3.724517
C	3.571061	-2.137398	1.987937
C	1.180580	-2.213840	2.337358
C	1.361022	-3.130538	3.374055
C	3.750485	-3.047895	3.031135
H	4.437941	-1.749597	1.461426
H	0.179750	-1.879674	2.081991
H	0.494374	-3.510916	3.907809
H	4.754477	-3.364489	3.302350
H	2.788442	-4.256099	4.537326
C	-3.543325	1.001400	1.039205
C	-5.531011	2.692680	2.098608
C	-4.737942	0.470477	1.553887
C	-3.360506	2.393722	1.071010
C	-4.347987	3.232370	1.591104
C	-5.721631	1.309505	2.080388
H	-4.899828	-0.602989	1.555531
H	-2.436463	2.816447	0.686481

H	-4.187592	4.307302	1.604949
H	-6.638788	0.880021	2.475669
H	-6.297839	3.344211	2.509389
C	-2.482185	-1.695431	1.009997
C	-2.670708	-4.248125	2.195643
C	-2.461177	-2.857775	0.222369
C	-2.582083	-1.837471	2.406933
C	-2.686229	-3.099591	2.992155
C	-2.552491	-4.121102	0.811224
H	-2.376817	-2.777593	-0.856731
H	-2.589677	-0.954883	3.041173
H	-2.780893	-3.184788	4.071928
H	-2.535703	-5.007038	0.181751
H	-2.749170	-5.231535	2.651349
C	0.186213	1.994736	2.299969
H	0.907655	1.466930	2.919913
H	-0.831589	2.033442	2.681974
C	0.627100	2.909487	1.347177
C	1.318565	4.025837	1.119198
C	1.736630	4.894209	2.289184
H	1.327731	5.909493	2.187823
H	2.830575	4.997660	2.321177
H	1.399764	4.479770	3.242919
C	1.735328	4.517181	-0.241380
H	1.311281	3.899196	-1.036157
H	2.829570	4.493241	-0.339504
H	1.424860	5.560484	-0.393441
H	-0.241026	2.607148	-0.127305

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B3LYP SCF energy: -4508.78177436 a.u.
B3LYP enthalpy: -4508.040902 a.u.
B3LYP free energy: -4508.172632 a.u.
M06 SCF energy in solution: -4512.43633202 a.u.
M06 enthalpy in solution: -4511.695460 a.u.
M06 free energy in solution: -4511.827190 a.u.
Three lowest frequencies (cm-1): 11.1669 13.3926 19.2533

Cartesian coordinates

ATOM	X	Y	Z
Pd	0.008808	0.362628	0.171744
P	2.331296	0.027270	0.212415
P	-2.285033	-0.079363	0.205687
C	2.682703	-1.761099	0.550808
C	3.179445	-4.481077	0.930865
C	3.870262	-2.180546	1.170013
C	1.717529	-2.697628	0.122200
C	1.999824	-4.057229	0.314229
C	4.115584	-3.540606	1.363787
H	4.597558	-1.448641	1.510334
H	1.283976	-4.807967	-0.011966
H	5.032158	-3.862254	1.851552
H	3.365030	-5.542265	1.078943
C	-2.574523	-1.886925	0.500254
C	-2.974385	-4.631611	0.810773

C	-1.566899	-2.776483	0.070441
C	-3.754974	-2.364287	1.090277
C	-3.951698	-3.736764	1.249384
C	-1.801342	-4.149933	0.224854
H	-4.515461	-1.668412	1.433503
H	-4.863143	-4.103516	1.714406
H	-1.053088	-4.865654	-0.107599
H	-3.122764	-5.702133	0.931002
Ge	0.068787	-1.955686	-0.735101
C	0.112411	-2.547438	-2.636066
H	0.138438	-3.640344	-2.714999
H	0.999578	-2.142244	-3.132959
H	-0.776694	-2.182637	-3.160168
C	3.165158	0.370369	-1.399586
C	4.359459	0.963123	-3.871879
C	4.319176	-0.312611	-1.814975
C	2.611096	1.346624	-2.243204
C	3.208872	1.643892	-3.469172
C	4.911550	-0.016686	-3.043921
H	4.750317	-1.085085	-1.185362
H	1.709005	1.869269	-1.937779
H	2.769734	2.402396	-4.111663
H	5.801925	-0.556363	-3.355877
H	4.820434	1.189803	-4.829662
C	3.354085	0.924222	1.459738
C	4.778674	2.304922	3.451623
C	4.452262	1.727694	1.122271
C	2.971055	0.831376	2.809539
C	3.682809	1.508998	3.797670
C	5.158276	2.414466	2.114059
H	4.761538	1.817390	0.085995
H	2.110965	0.225614	3.084206
H	3.377069	1.423245	4.837011
H	6.007153	3.033964	1.836608
H	5.328896	2.839700	4.221176
C	-3.097392	0.268738	-1.414240
C	-4.242267	0.880005	-3.903946
C	-4.189585	-0.469774	-1.895152
C	-2.577066	1.309152	-2.201203
C	-3.150669	1.615042	-3.436159
C	-4.758382	-0.163641	-3.133264
H	-4.589402	-1.292592	-1.310162
H	-1.717369	1.870384	-1.844921
H	-2.738897	2.422388	-4.035869
H	-5.601280	-0.745483	-3.497010
H	-4.684003	1.114177	-4.868976
C	-3.360260	0.744752	1.459505
C	-4.891660	1.965427	3.475753
C	-2.896466	0.785230	2.785662
C	-4.593933	1.338089	1.155310
C	-5.353651	1.944838	2.159639
C	-3.659907	1.382794	3.786995
H	-1.928279	0.354497	3.028518
H	-4.965716	1.329030	0.135615
H	-6.307332	2.401933	1.908795
H	-3.288550	1.403680	4.808103
H	-5.483291	2.439153	4.254576

C	-0.037682	2.314135	1.160451
H	0.669326	2.207455	1.988736
H	-1.037661	2.488824	1.559499
C	0.409340	3.329830	0.192543
C	-0.307961	4.247868	-0.501412
C	-1.795443	4.451083	-0.350651
H	-2.319532	4.339391	-1.311826
H	-2.015551	5.472046	-0.001838
H	-2.250497	3.753887	0.357353
C	0.365541	5.197717	-1.462794
H	1.445186	5.019672	-1.522871
H	0.215572	6.247367	-1.165104
H	-0.046336	5.111488	-2.480966
H	1.486865	3.335016	0.007041

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B3LYP SCF energy: -4508.70230095 a.u.
B3LYP enthalpy: -4507.968244 a.u.
B3LYP free energy: -4508.096957 a.u.
M06 SCF energy in solution: -4512.36495838 a.u.
M06 enthalpy in solution: -4511.630901 a.u.
M06 free energy in solution: -4511.759614 a.u.
Three lowest frequencies (cm-1): -820.1305 7.0119 14.9013
Imaginary frequency: -820.1305 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Pd	0.039350	-0.093290	1.325529
P	-2.076816	0.242458	-0.043564
P	2.042584	0.220472	-0.126474
C	-2.050263	-0.981529	-1.440925
C	-2.061230	-2.947132	-3.434901
C	-2.877497	-0.848142	-2.568847
C	-1.210545	-2.104665	-1.302799
C	-1.240868	-3.077789	-2.314684
C	-2.880792	-1.823604	-3.563984
H	-3.513276	0.025482	-2.680001
H	-0.596042	-3.950897	-2.237421
H	-3.520888	-1.707157	-4.435001
H	-2.058137	-3.713401	-4.206555
C	2.620174	-1.423883	-0.777841
C	3.511970	-3.930839	-1.638206
C	1.799684	-2.549016	-0.578028
C	3.865954	-1.554118	-1.412816
C	4.309978	-2.802990	-1.844622
C	2.272226	-3.797729	-1.012104
H	4.499654	-0.683450	-1.556637
H	5.279398	-2.896796	-2.327318
H	1.664684	-4.686061	-0.853726
H	3.858422	-4.910312	-1.959511
Ge	0.017494	-2.299295	0.269400
C	-0.469700	-4.014338	1.144578
H	-0.495889	-4.843464	0.427894
H	-1.462052	-3.925312	1.597145
H	0.250587	-4.255335	1.932702

C	-3.654439	-0.244299	0.819133
C	-5.988144	-1.112904	2.135980
C	-4.918366	-0.079346	0.226436
C	-3.582762	-0.854534	2.079416
C	-4.740278	-1.287074	2.733146
C	-6.073768	-0.506583	0.879475
H	-5.004327	0.391160	-0.748046
H	-2.611963	-0.994714	2.545067
H	-4.661795	-1.757729	3.709807
H	-7.042283	-0.368899	0.405371
H	-6.889588	-1.446696	2.643263
C	-2.525153	1.851900	-0.833407
C	-2.985214	4.417288	-1.915016
C	-3.381837	2.764112	-0.191113
C	-1.888397	2.258974	-2.019088
C	-2.123731	3.524727	-2.556514
C	-3.609483	4.032862	-0.727564
H	-3.886881	2.479104	0.726291
H	-1.207396	1.585734	-2.530985
H	-1.624926	3.811832	-3.478048
H	-4.281386	4.717776	-0.216424
H	-3.166471	5.402985	-2.335445
C	3.595596	0.840607	0.679037
C	5.963439	1.592586	2.002944
C	4.539548	1.663305	0.044559
C	3.855408	0.403359	1.989126
C	5.031378	0.772700	2.642839
C	5.712754	2.037660	0.704225
H	4.362442	2.018083	-0.965692
H	3.124383	-0.214911	2.501101
H	5.214538	0.425018	3.656199
H	6.432004	2.676537	0.197950
H	6.877022	1.884935	2.513911
C	1.901693	1.272756	-1.641293
C	1.541669	2.927267	-3.892671
C	1.780566	0.718705	-2.924944
C	1.815139	2.669555	-1.501639
C	1.649452	3.489109	-2.617178
C	1.597655	1.540813	-4.040567
H	1.832830	-0.356915	-3.057260
H	1.886830	3.119976	-0.515348
H	1.597990	4.567107	-2.489132
H	1.508735	1.092739	-5.026874
H	1.413043	3.566063	-4.762607
C	-0.023376	1.671865	2.854233
C	0.386457	0.473591	3.440395
C	0.976266	-0.062961	4.504472
H	-0.367986	-0.860040	2.713893
H	1.233927	-1.115871	4.563553
H	1.209457	0.556684	5.370780
C	-1.441382	2.169465	3.069881
H	-2.150809	1.351132	3.211833
H	-1.778799	2.779642	2.225196
H	-1.477797	2.806840	3.969304
C	0.993185	2.769379	2.599120
H	1.040265	3.443254	3.471264
H	0.703173	3.382937	1.737767

H	1.995085	2.373145	2.427694

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B3LYP SCF energy: -4508.75539924 a.u.
B3LYP enthalpy: -4508.014793 a.u.
B3LYP free energy: -4508.142652 a.u.
M06 SCF energy in solution: -4512.42084694 a.u.
M06 enthalpy in solution: -4511.680241 a.u.
M06 free energy in solution: -4511.808100 a.u.
Three lowest frequencies (cm-1): 10.0344 13.0293 26.6662

Cartesian coordinates

ATOM	X	Y	Z
Pd	-0.031090	0.497327	0.295227
P	-2.360581	0.198932	-0.025559
P	2.290840	0.079151	-0.061231
C	-2.695198	-1.253196	-1.138404
C	-3.190758	-3.543160	-2.658418
C	-3.877766	-1.360717	-1.887828
C	-1.736791	-2.284583	-1.152807
C	-2.015965	-3.429438	-1.913027
C	-4.122050	-2.503086	-2.649941
H	-4.601429	-0.550909	-1.891248
H	-1.302340	-4.249289	-1.936349
H	-5.034711	-2.578434	-3.235525
H	-3.376631	-4.436702	-3.249545
C	2.530469	-1.411641	-1.151639
C	2.895475	-3.763005	-2.619173
C	1.517317	-2.389190	-1.143547
C	3.702899	-1.603914	-1.900802
C	3.881795	-2.775073	-2.636552
C	1.730832	-3.566272	-1.875747
H	4.470557	-0.836442	-1.923906
H	4.787866	-2.914161	-3.220751
H	0.973678	-4.346611	-1.876681
H	3.031117	-4.679805	-3.187949
Ge	-0.100314	-1.984246	-0.058631
C	-0.147640	-3.337662	1.403537
H	-0.174014	-4.356009	0.998656
H	-1.035438	-3.189199	2.026414
H	0.741789	-3.238431	2.033635
C	-3.270047	-0.240536	1.523620
C	-4.542335	-0.938112	3.930414
C	-4.579783	-0.748179	1.517680
C	-2.604556	-0.102192	2.750354
C	-3.236723	-0.446476	3.947129
C	-5.211733	-1.090395	2.713171
H	-5.105092	-0.887899	0.577845
H	-1.583362	0.268013	2.757126
H	-2.706907	-0.333392	4.889139
H	-6.225065	-1.482755	2.693632
H	-5.035568	-1.208861	4.860190
C	-3.372775	1.524407	-0.824646
C	-4.775285	3.575152	-2.143318
C	-4.451401	2.165990	-0.200084

C	-3.000818	1.931423	-2.118006
C	-3.699349	2.943820	-2.773653
C	-5.147067	3.184841	-0.857110
H	-4.750798	1.876310	0.801722
H	-2.162572	1.450363	-2.615433
H	-3.400192	3.243408	-3.774476
H	-5.979909	3.672967	-0.357779
H	-5.316796	4.368296	-2.651751
C	3.207403	-0.395493	1.473842
C	4.493075	-1.176419	3.848638
C	4.518387	-0.899107	1.444620
C	2.549177	-0.300024	2.708018
C	3.187076	-0.687610	3.888497
C	5.157174	-1.282332	2.623704
H	5.041426	-1.000808	0.498800
H	1.530881	0.075174	2.735776
H	2.661817	-0.607894	4.836535
H	6.171811	-1.669932	2.585111
H	4.991131	-1.479224	4.765924
C	3.357052	1.327771	-0.902241
C	4.863539	3.256733	-2.288926
C	3.036537	1.673066	-2.227486
C	4.433527	1.973825	-0.279610
C	5.184098	2.928446	-0.972583
C	3.785001	2.625732	-2.916176
H	2.201034	1.188433	-2.726227
H	4.692193	1.732416	0.744672
H	6.016696	3.418698	-0.474915
H	3.525989	2.876173	-3.941449
H	5.447340	4.000476	-2.824727
C	0.031022	2.722386	0.726792
C	1.174738	2.896930	1.655323
C	2.299021	3.616748	1.482202
H	1.035950	2.428620	2.634186
H	3.049594	3.682706	2.266321
H	2.512716	4.153510	0.563362
C	-1.236408	3.162550	1.481315
H	-1.379591	2.608809	2.417662
H	-2.141880	3.052451	0.879796
H	-1.163435	4.230869	1.753410
C	0.162738	3.513402	-0.571471
H	0.233167	4.598551	-0.370323
H	-0.711504	3.362652	-1.214741
H	1.053334	3.232968	-1.142531

11-TS

B3LYP SCF energy: -4697.34077400 a.u.
B3LYP enthalpy: -4696.584218 a.u.
B3LYP free energy: -4696.720478 a.u.
M06 SCF energy in solution: -4701.05509090 a.u.
M06 enthalpy in solution: -4700.298535 a.u.
M06 free energy in solution: -4700.434795 a.u.
Three lowest frequencies (cm-1): -311.8515 9.2273 12.1296
Imaginary frequency: -311.8515 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Pd	-0.064399	0.195128	0.177671
P	2.226199	-0.413615	0.258599
P	-2.415306	0.003805	0.169793
C	2.317869	-2.188514	0.783199
C	2.412668	-4.917815	1.366098
C	3.409793	-2.721657	1.483421
C	1.252894	-3.015312	0.370483
C	1.329847	-4.383271	0.663901
C	3.452604	-4.084691	1.780355
H	4.218664	-2.075089	1.810805
H	0.529077	-5.050134	0.354685
H	4.295147	-4.492166	2.332944
H	2.441328	-5.980401	1.594276
C	-2.909100	-1.748432	0.494084
C	-3.624417	-4.431442	0.772801
C	-1.995156	-2.744254	0.097658
C	-4.152045	-2.091218	1.048078
C	-4.505157	-3.433248	1.193464
C	-2.386461	-4.084158	0.227557
H	-4.838416	-1.314867	1.374459
H	-5.464626	-3.697047	1.630499
H	-1.715298	-4.878541	-0.089589
H	-3.897542	-5.478500	0.877731
Ge	-0.238386	-2.133412	-0.616166
C	-0.143580	-2.694568	-2.517059
H	-0.947383	-2.216428	-3.085060
H	-0.252403	-3.781586	-2.604685
H	0.816222	-2.402157	-2.952085
C	3.137757	-0.399006	-1.343669
C	4.466449	-0.395971	-3.813589
C	4.398108	-1.007983	-1.474577
C	2.551473	0.208422	-2.462071
C	3.217257	0.210291	-3.690968
C	5.057171	-1.005483	-2.702111
H	4.863509	-1.491749	-0.620910
H	1.582692	0.689632	-2.376848
H	2.755260	0.694948	-4.546224
H	6.029969	-1.481611	-2.792713
H	4.982178	-0.394865	-4.770311
C	3.321072	0.488353	1.433533
C	4.839436	1.975030	3.271290
C	4.261640	1.427434	0.982850
C	3.136603	0.317762	2.816582
C	3.896007	1.050963	3.728005
C	5.015743	2.163554	1.899693
H	4.390689	1.601634	-0.080133
H	2.404085	-0.396922	3.182844
H	3.748036	0.902768	4.794421
H	5.739370	2.888088	1.536295
H	5.428543	2.548874	3.981567
C	-3.206589	0.420039	-1.441436
C	-4.344235	1.122795	-3.907332
C	-4.451801	-0.105784	-1.825092
C	-2.531703	1.292968	-2.309117
C	-3.104881	1.643848	-3.534195

C	-5.015845	0.245294	-3.051581
H	-4.977478	-0.797909	-1.174431
H	-1.559744	1.696368	-2.041929
H	-2.570603	2.321002	-4.194679
H	-5.977436	-0.170929	-3.340453
H	-4.784771	1.392562	-4.863680
C	-3.356674	0.967740	1.428746
C	-4.678968	2.431602	3.429000
C	-3.053854	0.759771	2.785852
C	-4.319125	1.927923	1.087480
C	-4.975379	2.655065	2.084766
C	-3.715367	1.480648	3.777896
H	-2.295536	0.032426	3.064969
H	-4.560626	2.109634	0.045315
H	-5.719390	3.396344	1.805627
H	-3.473936	1.305917	4.822926
H	-5.190508	2.998110	4.202435
C	-0.025546	2.131680	1.399754
H	0.321566	1.613565	2.296442
H	-1.069654	2.428328	1.453581
C	0.880659	3.104005	0.907919
C	0.620441	4.203165	0.071433
C	-0.817798	4.571878	-0.235465
H	-0.870543	5.292235	-1.059567
H	-1.302161	5.033552	0.638485
H	-1.406494	3.697618	-0.523484
C	1.584214	5.379338	0.139619
H	2.613550	5.042957	0.287674
H	1.317185	6.048530	0.971363
H	1.558686	5.975346	-0.779774
H	1.927060	2.971326	1.183597
C	1.318850	3.231262	-1.618860
O	0.358735	2.736118	-2.169132
O	2.509990	3.402812	-1.683141

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B3LYP SCF energy: -4697.38523739 a.u.
B3LYP enthalpy: -4696.626024 a.u.
B3LYP free energy: -4696.762621 a.u.
M06 SCF energy in solution: -4701.08109079 a.u.
M06 enthalpy in solution: -4700.321877 a.u.
M06 free energy in solution: -4700.458474 a.u.
Three lowest frequencies (cm-1): 11.5274 13.1742 17.0737

Cartesian coordinates

ATOM	X	Y	Z
Pd	-0.039597	0.027369	0.045112
P	-2.393027	-0.109715	-0.054134
P	2.259632	-0.513053	-0.067312
C	-2.922468	-1.677306	-0.887380
C	-3.612611	-4.083388	-2.129938
C	-4.191743	-1.834732	-1.462463
C	-1.977909	-2.724351	-0.937887
C	-2.349272	-3.925378	-1.555120
C	-4.534085	-3.036206	-2.085202

H	-4.905429	-1.016245	-1.445017
H	-1.644907	-4.752312	-1.602719
H	-5.514601	-3.149414	-2.539894
H	-3.873482	-5.018329	-2.619429
C	2.499991	-2.155370	-0.892841
C	2.764867	-4.658949	-2.107338
C	1.389866	-3.024917	-0.932914
C	3.722993	-2.536346	-1.464014
C	3.852996	-3.785740	-2.072720
C	1.548076	-4.278982	-1.536213
H	4.567736	-1.853808	-1.451122
H	4.799496	-4.071652	-2.523683
H	0.712108	-4.973188	-1.574594
H	2.860622	-5.630678	-2.585214
Ge	-0.249469	-2.368520	-0.035057
C	-0.345393	-3.267997	1.732466
H	0.577246	-3.100473	2.295823
H	-0.487714	-4.347324	1.604406
H	-1.187025	-2.869436	2.306867
C	-3.099660	-0.145924	1.644120
C	-4.059967	-0.071254	4.276169
C	-4.074258	-1.060317	2.066212
C	-2.598799	0.802444	2.554356
C	-3.084817	0.840384	3.860612
C	-4.550492	-1.021573	3.379927
H	-4.459198	-1.804568	1.375357
H	-1.826063	1.498640	2.234448
H	-2.695256	1.577583	4.557521
H	-5.304015	-1.736403	3.700134
H	-4.431291	-0.043684	5.297182
C	-3.329740	1.222447	-0.907903
C	-4.745795	3.185881	-2.318907
C	-4.645407	1.550628	-0.539000
C	-2.721334	1.899482	-1.975063
C	-3.432946	2.875263	-2.676717
C	-5.349705	2.526167	-1.245546
H	-5.116484	1.054098	0.304439
H	-1.680938	1.709906	-2.219514
H	-2.948294	3.403062	-3.493178
H	-6.366311	2.775102	-0.952478
H	-5.293715	3.949678	-2.864663
C	2.951351	-0.680533	1.630154
C	3.913699	-0.795813	4.260514
C	3.738597	-1.762493	2.047672
C	2.638958	0.341281	2.544728
C	3.126075	0.283752	3.849863
C	4.215703	-1.818304	3.360407
H	3.976999	-2.562804	1.353418
H	2.009483	1.170749	2.230001
H	2.883060	1.078842	4.549577
H	4.822590	-2.662670	3.676725
H	4.285436	-0.841519	5.280737
C	3.432470	0.611840	-0.927971
C	5.205078	2.232925	-2.370230
C	2.976295	1.344517	-2.033603
C	4.777785	0.714403	-0.536223
C	5.659021	1.520831	-1.257509

C	3.865162	2.147001	-2.751711
H	1.923122	1.336226	-2.293916
H	5.136599	0.173105	0.334257
H	6.697484	1.596656	-0.945765
H	3.500185	2.717652	-3.601194
H	5.892013	2.863499	-2.928808
C	2.677892	5.374476	0.645731
H	3.701041	5.598303	0.354005
H	2.413131	5.591539	1.676972
C	1.810718	4.861062	-0.229653
C	0.355115	4.502999	0.016184
C	-0.081978	4.745215	1.465761
H	-1.131294	4.461336	1.597709
H	0.016708	5.806481	1.725424
H	0.512103	4.155903	2.168449
C	-0.518973	5.346411	-0.942889
H	-0.237190	5.160347	-1.981867
H	-0.401539	6.414724	-0.725598
H	-1.578086	5.084677	-0.829611
H	2.144018	4.660110	-1.247694
C	0.215696	2.998706	-0.396065
O	0.087255	2.159880	0.568767
O	0.261588	2.712375	-1.606299

13-TS

B3LYP SCF energy: -4697.28455017 a.u.
B3LYP enthalpy: -4696.528487 a.u.
B3LYP free energy: -4696.662705 a.u.
M06 SCF energy in solution: -4701.01499410 a.u.
M06 enthalpy in solution: -4700.258931 a.u.
M06 free energy in solution: -4700.393149 a.u.
Three lowest frequencies (cm-1): -165.3664 15.8229 16.7079
Imaginary frequency: -165.3664 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Pd	-0.014267	0.437800	-0.016961
P	-2.406002	0.029672	-0.030442
P	2.338764	-0.086648	0.025057
C	-2.774889	-1.246890	-1.323701
C	-3.207187	-3.274921	-3.200916
C	-4.017365	-1.363924	-1.964947
C	-1.737800	-2.158980	-1.607252
C	-1.978422	-3.171557	-2.544616
C	-4.228877	-2.371416	-2.908110
H	-4.817484	-0.665813	-1.740169
H	-1.200113	-3.892776	-2.779110
H	-5.189295	-2.447476	-3.410940
H	-3.365371	-4.058262	-3.937854
C	2.675823	-1.431232	-1.211375
C	3.071972	-3.558105	-2.987757
C	1.599135	-2.286670	-1.518760
C	3.940978	-1.657351	-1.775632
C	4.134607	-2.712028	-2.669286
C	1.820850	-3.350235	-2.403435

H	4.774146	-1.008366	-1.527126
H	5.114189	-2.871018	-3.112202
H	1.010817	-4.031799	-2.649323
H	3.216757	-4.379077	-3.685465
Ge	-0.084519	-1.952181	-0.533474
C	-0.167844	-3.299224	0.920429
H	-0.194239	-4.306411	0.488144
H	-1.066084	-3.152782	1.525940
H	0.713437	-3.215447	1.562029
C	-2.998386	-0.758371	1.537053
C	-3.858402	-1.943928	3.935310
C	-3.996135	-1.746608	1.527163
C	-2.433030	-0.372835	2.763823
C	-2.867826	-0.960810	3.953760
C	-4.421333	-2.335260	2.718976
H	-4.435923	-2.069496	0.589226
H	-1.673673	0.401132	2.787252
H	-2.425195	-0.648742	4.895857
H	-5.190992	-3.102263	2.694206
H	-4.188948	-2.404687	4.862492
C	-3.634181	1.369586	-0.337705
C	-5.401438	3.506318	-0.797854
C	-4.291439	1.993942	0.733059
C	-3.865884	1.838838	-1.642449
C	-4.747633	2.895195	-1.869649
C	-5.169175	3.053824	0.501754
H	-4.112405	1.660530	1.749040
H	-3.365737	1.375189	-2.487186
H	-4.918344	3.242886	-2.884907
H	-5.668639	3.527403	1.342483
H	-6.084346	4.332758	-0.974883
C	2.817214	-0.864547	1.639285
C	3.491861	-2.031900	4.107652
C	3.620341	-2.015165	1.690237
C	2.353951	-0.305596	2.842889
C	2.697352	-0.884814	4.066062
C	3.952494	-2.594590	2.916536
H	3.982892	-2.469668	0.774497
H	1.746968	0.593274	2.823830
H	2.336908	-0.436098	4.987913
H	4.571155	-3.488027	2.936916
H	3.750078	-2.484731	5.061323
C	3.674649	1.145154	-0.283577
C	5.744469	2.979573	-0.779215
C	4.008118	1.508394	-1.598385
C	4.361826	1.747120	0.780064
C	5.388356	2.658699	0.531428
C	5.047959	2.405312	-1.843683
H	3.471207	1.076092	-2.437432
H	4.103729	1.502051	1.803846
H	5.914693	3.111507	1.367304
H	5.304259	2.662639	-2.867939
H	6.553319	3.679810	-0.970331
C	-0.012500	3.235816	-0.646087
C	1.240452	4.010695	-0.549659
C	2.160538	4.200168	-1.510079
H	1.392078	4.531575	0.394188

H	3.032158	4.823696	-1.333229
H	2.090921	3.745045	-2.493501
C	-1.212000	4.116921	-0.294903
H	-1.012429	4.751964	0.574415
H	-2.106333	3.534105	-0.073067
H	-1.440058	4.784331	-1.144210
C	-0.209535	2.586573	-2.015756
H	-0.237406	3.366215	-2.800131
H	-1.156900	2.046376	-2.083764
H	0.598171	1.896420	-2.286576
C	0.050169	2.453206	1.593278
O	-1.097569	2.403067	1.981337
O	1.198886	2.549846	1.962005

14-TS

B3LYP SCF energy: -4811.63975893 a.u.
B3LYP enthalpy: -4810.862200 a.u.
B3LYP free energy: -4810.997684 a.u.
M06 SCF energy in solution: -4815.38823978 a.u.
M06 enthalpy in solution: -4814.610681 a.u.
M06 free energy in solution: -4814.746165 a.u.
Three lowest frequencies (cm-1): -205.7241 22.0561 22.9591
Imaginary frequency: -205.7241 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Pd	-0.039360	-0.325454	-0.289888
P	2.299556	0.226198	-0.039209
P	-2.412525	-0.043428	-0.043187
C	2.566740	1.901773	-0.762846
C	2.843549	4.496506	-1.753211
C	3.791208	2.321322	-1.297299
C	1.462619	2.775416	-0.721274
C	1.626788	4.077240	-1.207827
C	3.924969	3.617320	-1.800375
H	4.633813	1.638033	-1.335511
H	0.798442	4.780199	-1.178306
H	4.871626	3.935647	-2.228664
H	2.942398	5.505134	-2.146229
C	-2.853821	1.535340	-0.883817
C	-3.382532	4.012773	-2.046369
C	-1.868145	2.541913	-0.831423
C	-4.083505	1.763452	-1.511023
C	-4.342969	3.003372	-2.100002
C	-2.159648	3.782447	-1.408554
H	-4.828732	0.975168	-1.557212
H	-5.291239	3.175613	-2.601944
H	-1.425321	4.582958	-1.382801
H	-3.578827	4.977028	-2.508108
Ge	-0.190371	2.084121	0.125634
C	-0.271430	2.876441	1.940629
H	-1.176630	2.562449	2.464762
H	-0.276000	3.969306	1.852095
H	0.604210	2.577671	2.523070
C	2.673493	0.444796	1.758000

C	3.183521	0.688523	4.508842
C	3.501277	1.470164	2.239477
C	2.103115	-0.457787	2.670277
C	2.364776	-0.339715	4.036082
C	3.749583	1.593315	3.608446
H	3.946289	2.178819	1.547618
H	1.460999	-1.257712	2.312308
H	1.923422	-1.050387	4.729773
H	4.385678	2.397224	3.969487
H	3.378327	0.785550	5.573637
C	3.728521	-0.785495	-0.636212
C	5.893446	-2.315487	-1.573714
C	4.667945	-1.318936	0.260795
C	3.883531	-1.031841	-2.012347
C	4.962893	-1.787799	-2.471865
C	5.741603	-2.079577	-0.207099
H	4.568070	-1.145228	1.326068
H	3.148612	-0.653156	-2.711809
H	5.069596	-1.969329	-3.538036
H	6.459393	-2.484576	0.501505
H	6.729453	-2.907702	-1.936566
C	-2.883503	0.254343	1.720931
C	-3.554031	0.655450	4.418425
C	-3.931957	1.118648	2.072635
C	-2.173268	-0.404126	2.736434
C	-2.512191	-0.209158	4.076670
C	-4.261811	1.319796	3.414089
H	-4.484554	1.643691	1.299475
H	-1.351615	-1.064355	2.475065
H	-1.953827	-0.725137	4.853170
H	-5.070467	1.997939	3.673468
H	-3.810669	0.814944	5.462317
C	-3.657379	-1.295812	-0.588266
C	-5.519791	-3.220338	-1.441390
C	-3.739102	-1.653847	-1.946601
C	-4.510527	-1.923313	0.335414
C	-5.433686	-2.879981	-0.091047
C	-4.671057	-2.605171	-2.363973
H	-3.058206	-1.207213	-2.662610
H	-4.461879	-1.668006	1.387999
H	-6.086769	-3.355097	0.636217
H	-4.724144	-2.870787	-3.416338
H	-6.240068	-3.964125	-1.771853
C	-0.092553	-2.575727	-1.719251
H	-1.168586	-2.687172	-1.846371
C	0.668266	-3.291680	-2.839814
H	1.697410	-2.931790	-2.937094
H	0.179943	-3.128276	-3.806314
H	0.710051	-4.377599	-2.658378
C	0.304671	-3.042500	-0.359677
C	0.992919	-4.109831	2.202255
C	1.630313	-3.433122	-0.042139
C	-0.664751	-3.238142	0.659357
C	-0.327692	-3.755216	1.910439
C	1.963835	-3.948912	1.208651
H	2.404672	-3.340395	-0.795150
H	-1.707835	-3.034302	0.433987

H	-1.110105	-3.908810	2.651020
H	2.994248	-4.237157	1.404176
H	1.254693	-4.525991	3.171505
C	-0.034863	-0.721613	-2.853991
O	-1.172102	-0.568876	-3.245688
O	1.102715	-0.358240	-3.069008

15-TS

B3LYP SCF energy: -4201.98082594 a.u.
B3LYP enthalpy: -4201.309432 a.u.
B3LYP free energy: -4201.428719 a.u.
M06 SCF energy in solution: -4205.63310236 a.u.
M06 enthalpy in solution: -4204.961708 a.u.
M06 free energy in solution: -4205.080995 a.u.
Three lowest frequencies (cm-1): -206.9033 19.0672 21.9917
Imaginary frequency: -206.9033 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Pd	-0.194368	-0.527889	0.173885
P	-1.464299	1.430125	0.722154
P	1.812003	-1.820673	0.083529
C	-0.530178	2.988573	0.325874
C	0.938464	5.302902	-0.279489
C	-0.979240	4.252267	0.747590
C	0.675927	2.882488	-0.393160
C	1.391024	4.050668	-0.695147
C	-0.249004	5.402084	0.448111
H	-1.894263	4.347729	1.323561
H	2.316716	3.989592	-1.262698
H	-0.605649	6.371970	0.784651
H	1.510525	6.196293	-0.516619
C	3.304509	-0.752062	-0.151931
C	5.499192	0.950483	-0.500130
C	3.093018	0.572084	-0.585720
C	4.606975	-1.210263	0.106261
C	5.700308	-0.360566	-0.064204
C	4.205804	1.406161	-0.761013
H	4.774515	-2.224588	0.457541
H	6.703761	-0.719490	0.148412
H	4.069277	2.431150	-1.096685
H	6.347548	1.617607	-0.630159
Ge	1.210436	1.069625	-0.963583
C	0.990602	1.001624	-2.939751
H	1.650886	1.737077	-3.414438
H	-0.042654	1.233048	-3.214240
H	1.244109	0.010297	-3.327682
C	-1.742446	-2.546238	-0.184502
H	-0.877749	-2.607285	-0.853630
C	-1.970145	-3.948299	0.394179
H	-2.807961	-3.993893	1.097982
H	-1.084909	-4.302510	0.932947
H	-2.189231	-4.673113	-0.407178
C	-2.872521	-1.964542	-0.938021
C	-5.003546	-0.861160	-2.474038

C	-4.215723	-2.050642	-0.507988
C	-2.643302	-1.310524	-2.172429
C	-3.683420	-0.770233	-2.925974
C	-5.256760	-1.506589	-1.260522
H	-4.443114	-2.539697	0.432752
H	-1.623786	-1.246761	-2.548555
H	-3.464972	-0.289769	-3.877612
H	-6.278320	-1.593625	-0.896601
H	-5.819216	-0.448394	-3.061939
C	1.877772	-3.102612	-1.276614
H	1.630224	-2.567828	-2.201476
H	1.031172	-3.771631	-1.077677
C	2.157321	-2.791511	1.631846
H	1.265583	-3.403609	1.796484
H	3.001804	-3.467225	1.448471
C	-3.137126	1.557048	-0.080562
H	-3.631330	0.621191	0.203845
H	-2.966456	1.480713	-1.159106
C	-1.811407	1.634631	2.541334
H	-2.550880	0.872365	2.799493
H	-2.278136	2.615460	2.690045
C	2.417233	-1.921692	2.866809
H	1.551403	-1.290509	3.079298
H	3.296914	-1.282972	2.736733
H	2.587335	-2.559751	3.741201
C	3.164503	-3.914070	-1.466274
H	3.419933	-4.495782	-0.574090
H	4.015084	-3.270115	-1.709551
H	3.037346	-4.623868	-2.292013
C	-4.033784	2.758731	0.237978
H	-4.228697	2.858326	1.311498
H	-5.002572	2.626596	-0.257498
H	-3.604862	3.698724	-0.123098
C	-0.564873	1.497879	3.423370
H	-0.128679	0.498932	3.329655
H	-0.828628	1.652528	4.475894
H	0.201916	2.234072	3.157434
C	-1.783112	-1.792926	2.086200
O	-0.812555	-2.236793	2.638833
O	-2.886066	-1.329493	2.160275

CO2

B3LYP SCF energy: -188.57757052 a.u.
B3LYP enthalpy: -188.562367 a.u.
B3LYP free energy: -188.586668 a.u.
M06 SCF energy in solution: -188.63297388 a.u.
M06 enthalpy in solution: -188.617770 a.u.
M06 free energy in solution: -188.642071 a.u.
Three lowest frequencies (cm-1): 646.8590 646.8590 1370.4469

Cartesian coordinates

ATOM	X	Y	Z
C	0.000000	0.000000	0.000000
O	0.000000	0.000000	1.169583
O	0.000000	0.000000	-1.169583

HCOO

B3LYP SCF energy:	-189.17318093 a.u.
B3LYP enthalpy:	-189.149023 a.u.
B3LYP free energy:	-189.176737 a.u.
M06 SCF energy in solution:	-189.33137975 a.u.
M06 enthalpy in solution:	-189.307222 a.u.
M06 free energy in solution:	-189.334936 a.u.
Three lowest frequencies (cm-1):	764.6702 1069.3226 1370.1625

Cartesian coordinates

ATOM	X	Y	Z
C	-3.911251	-0.481833	0.000000
H	-5.063939	-0.481833	0.000000
O	-3.392668	0.660068	0.000000
O	-3.392668	-1.623733	0.000000