Electronic Supplementary Material (ESI) for Dalton Transactions

SUPPORTING INFORMATION

Reactivity of the Terminal Oxo Species $(({}^{t}Bu_2PCH_2SiMe_2)_2N)RhO$

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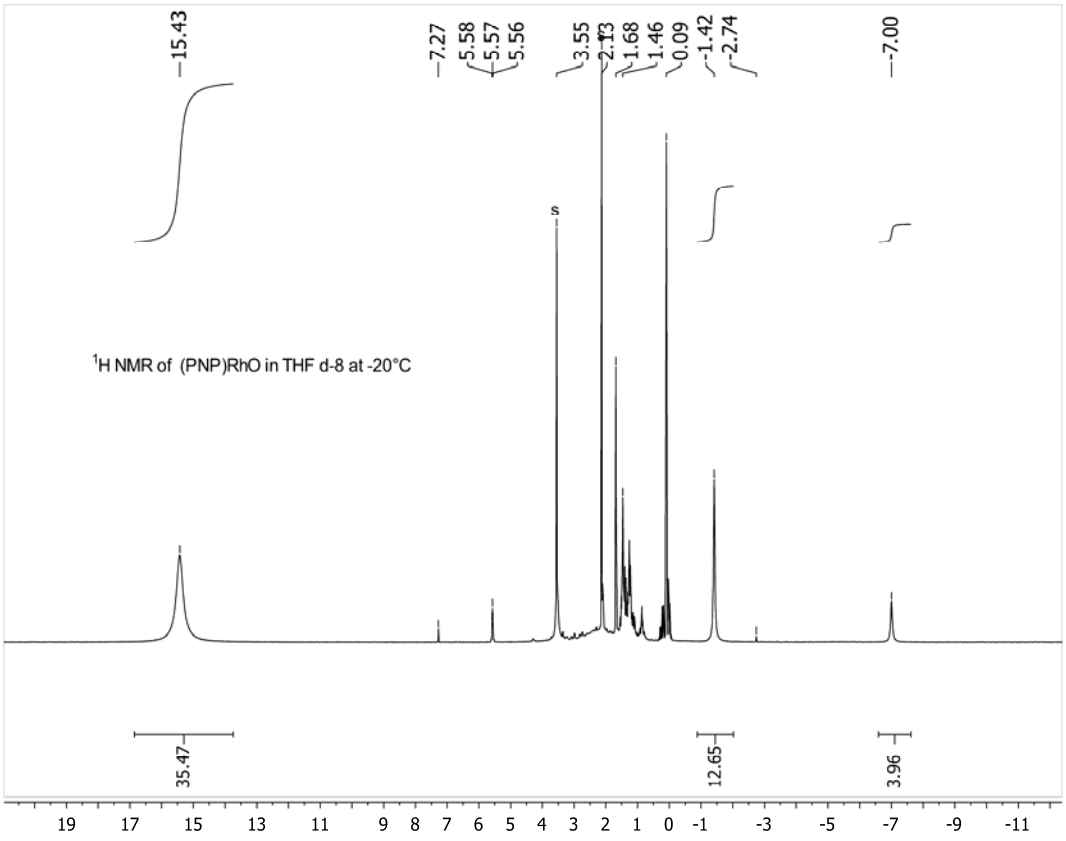
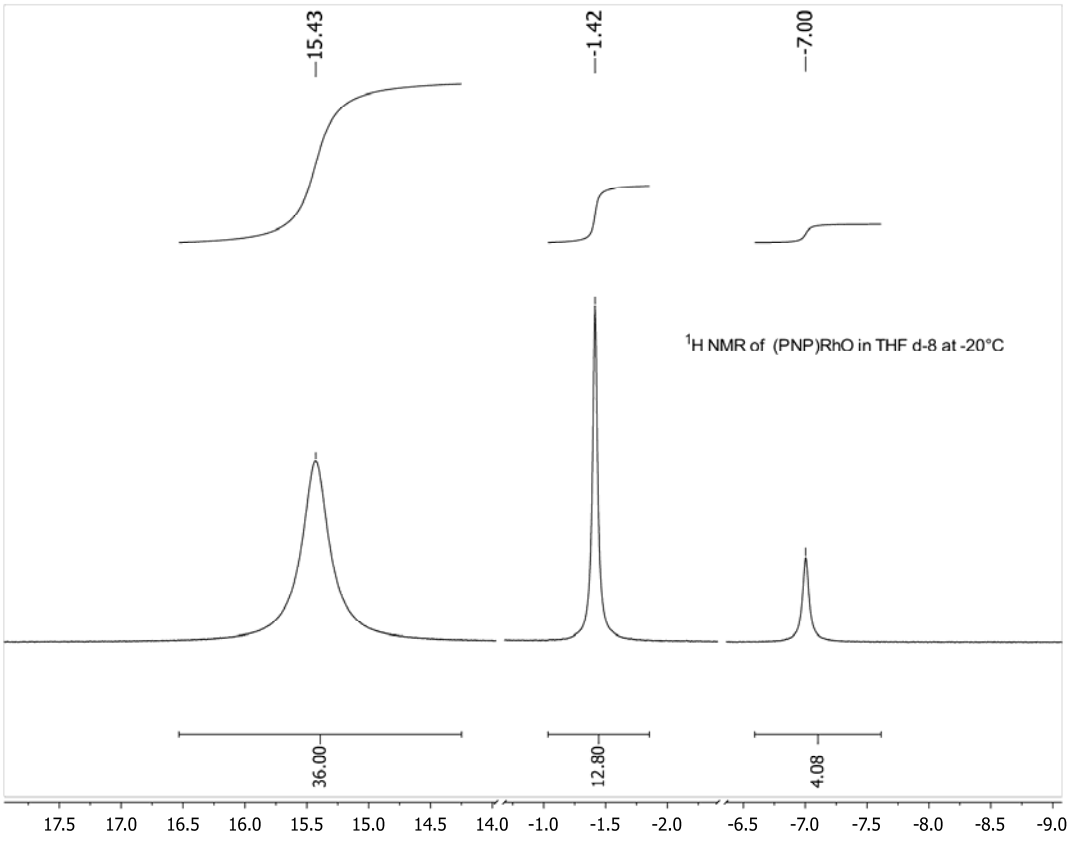
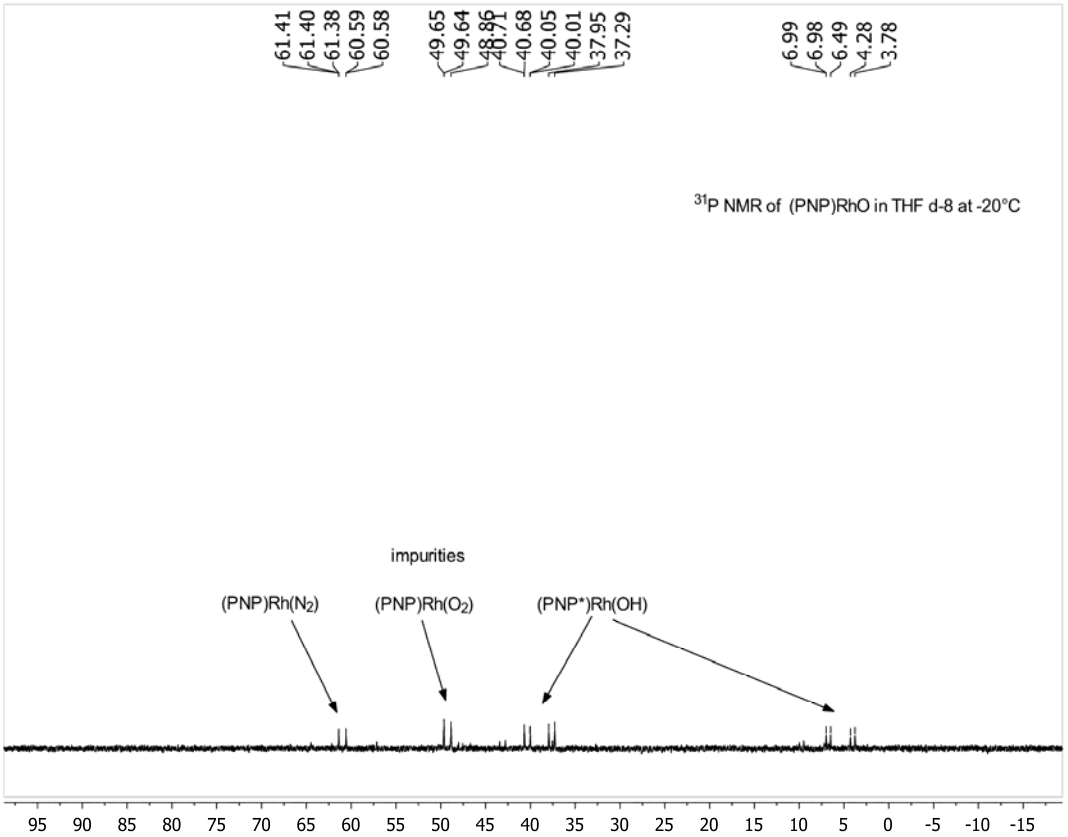
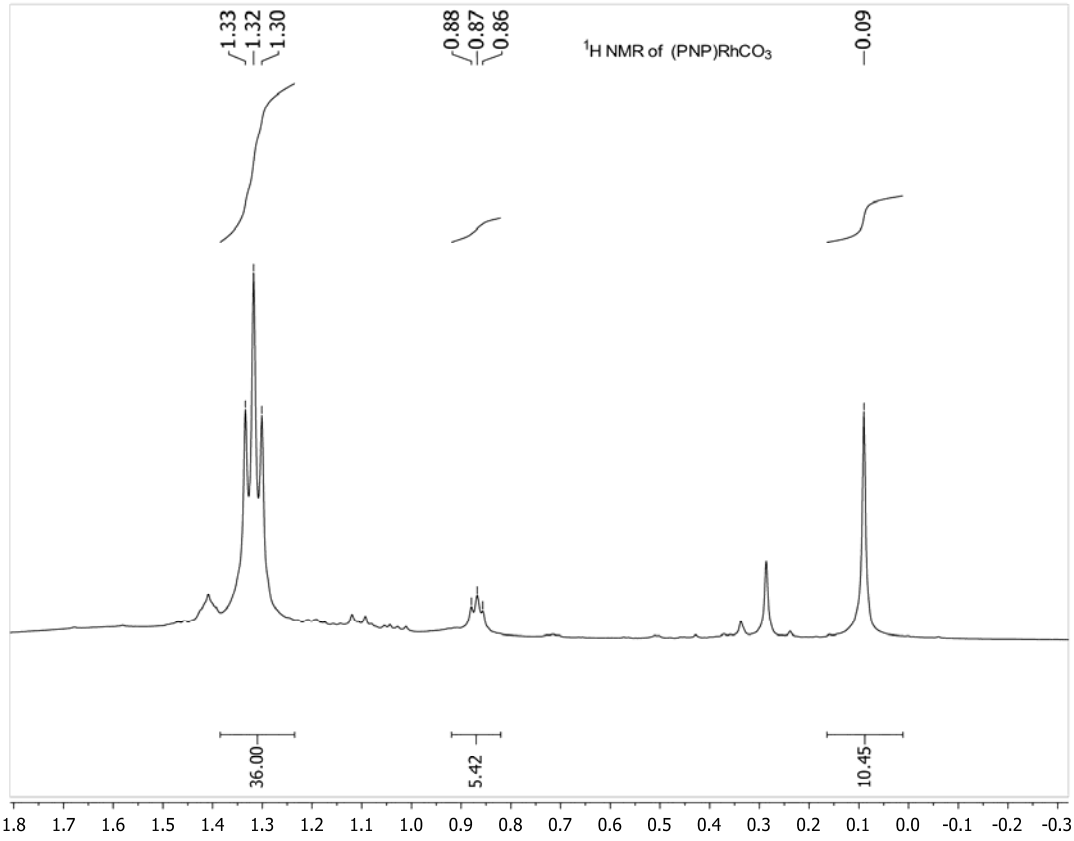
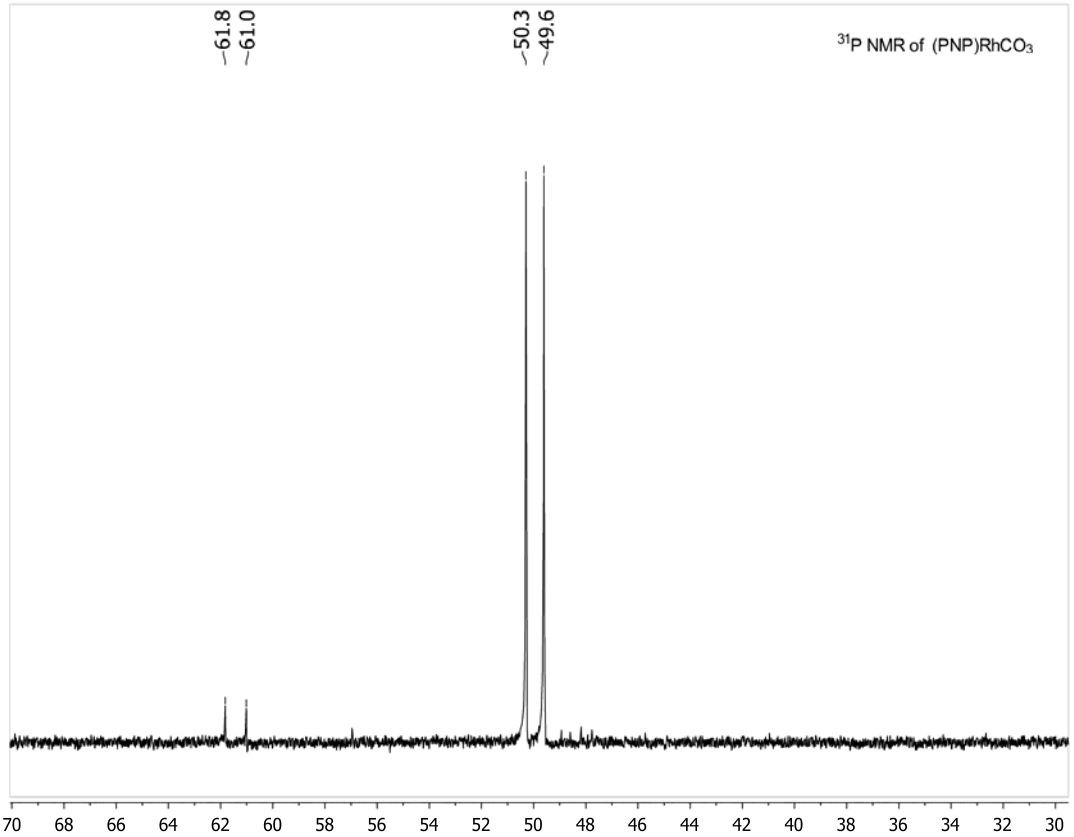
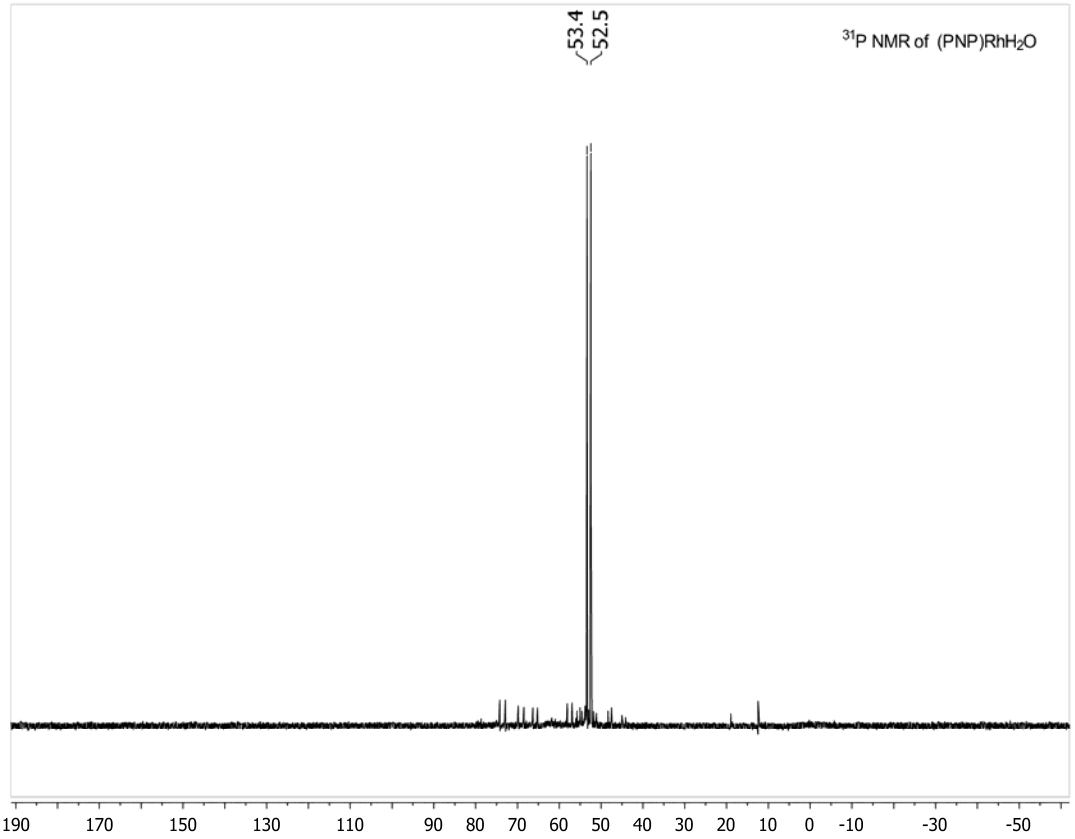


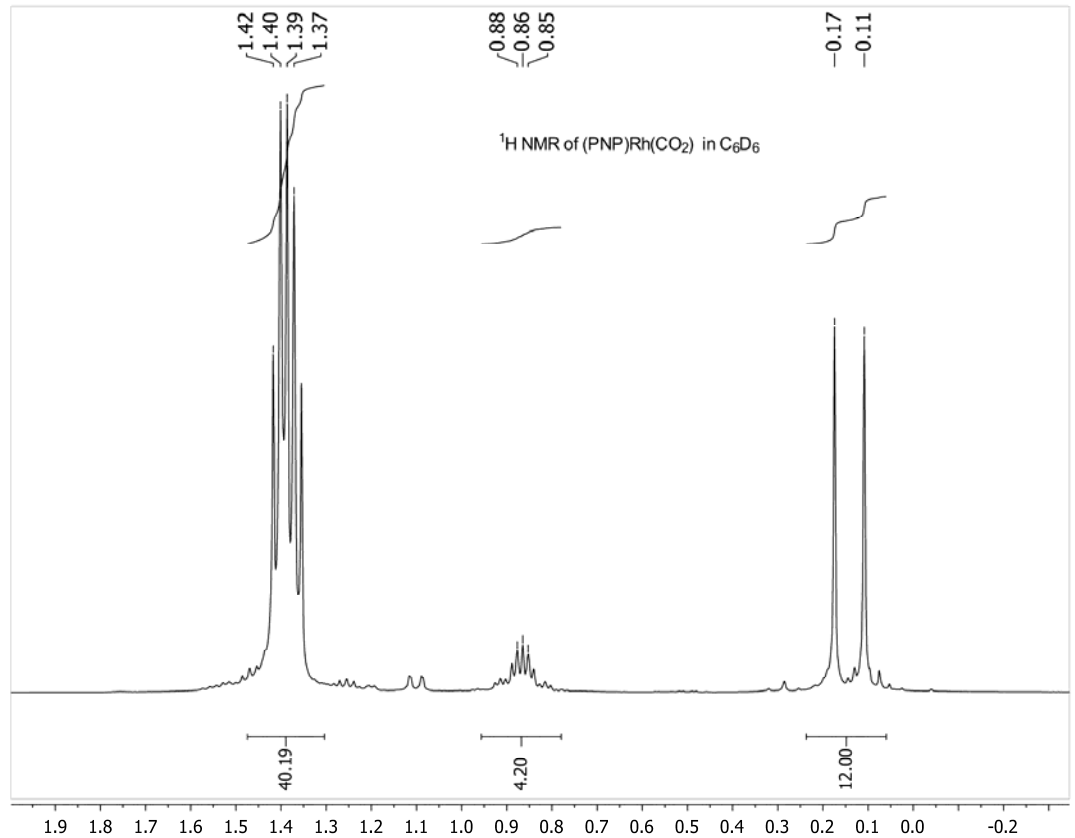


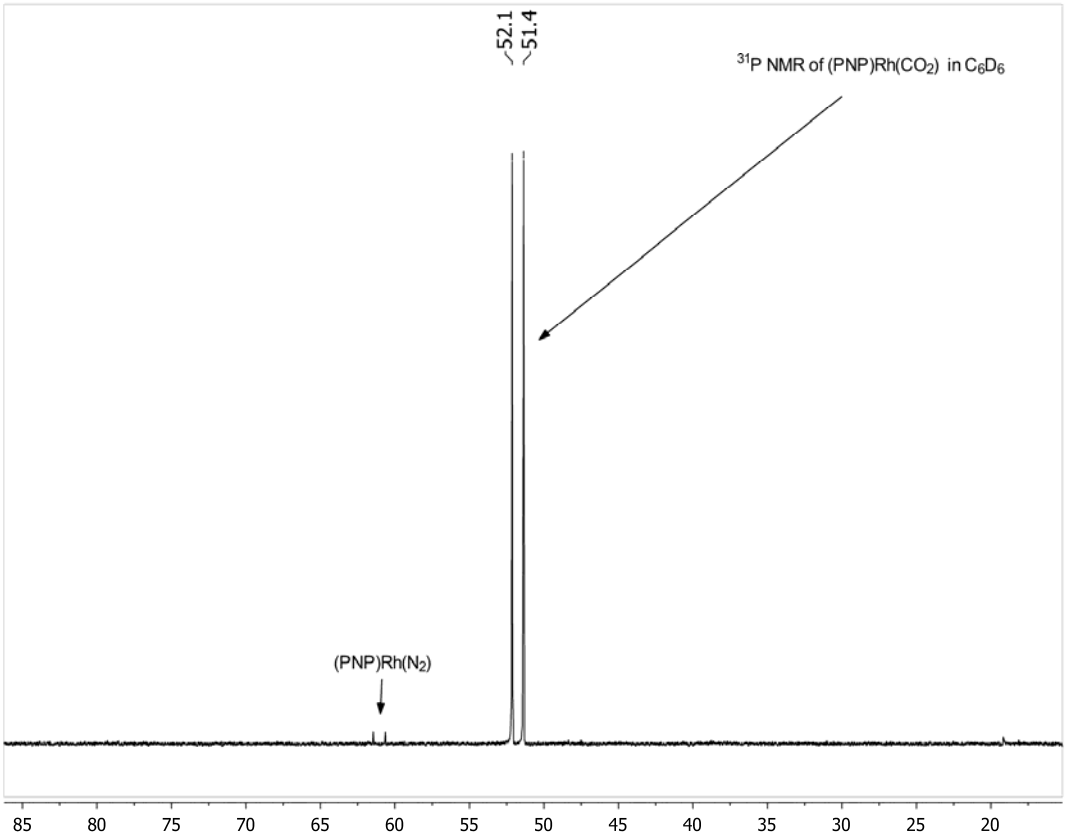


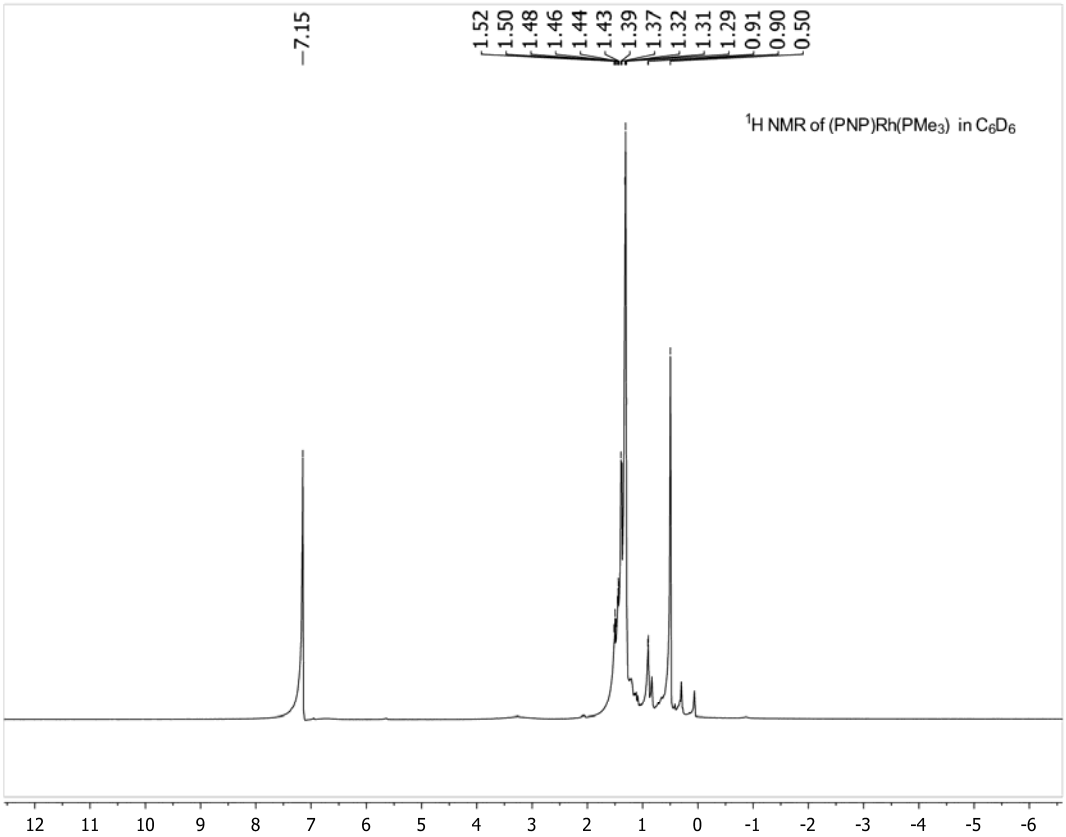


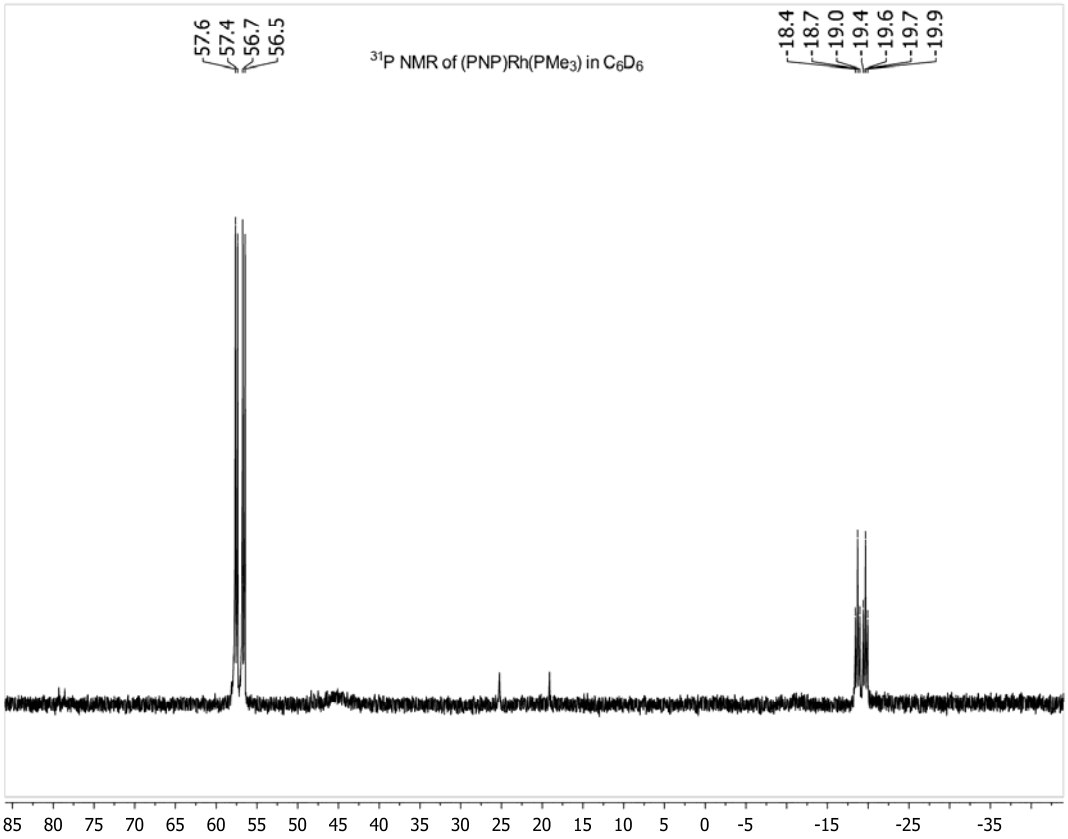


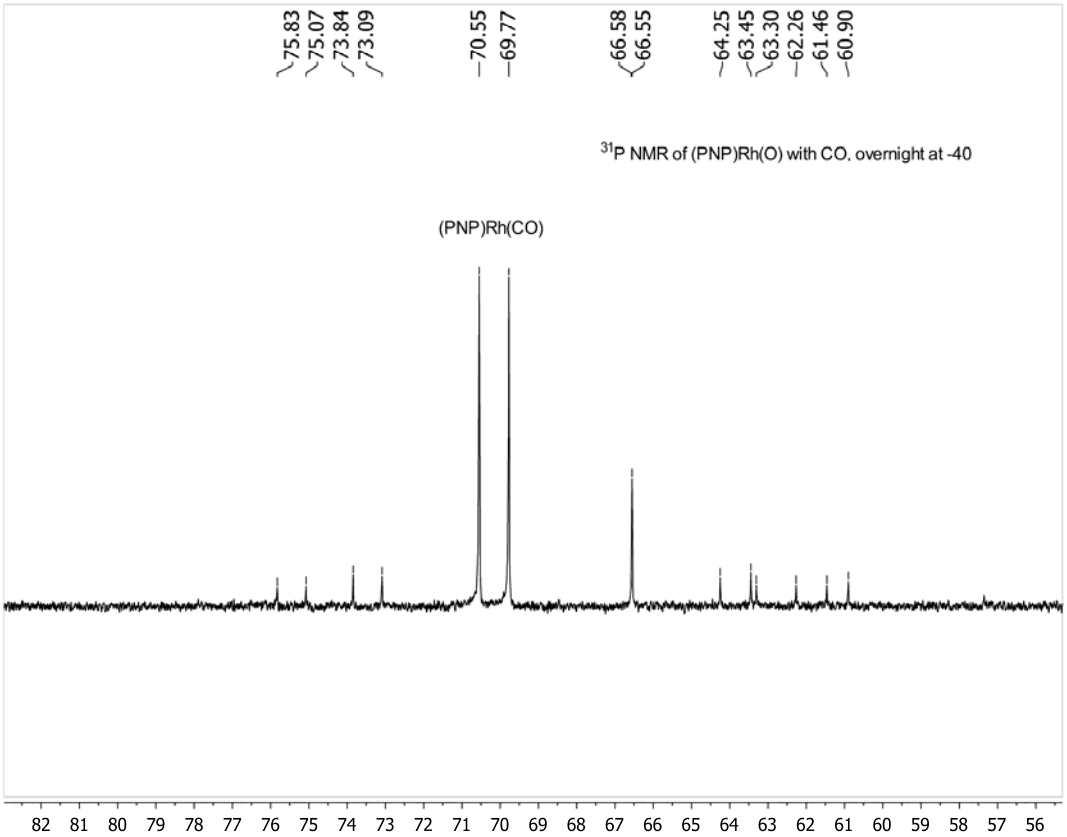


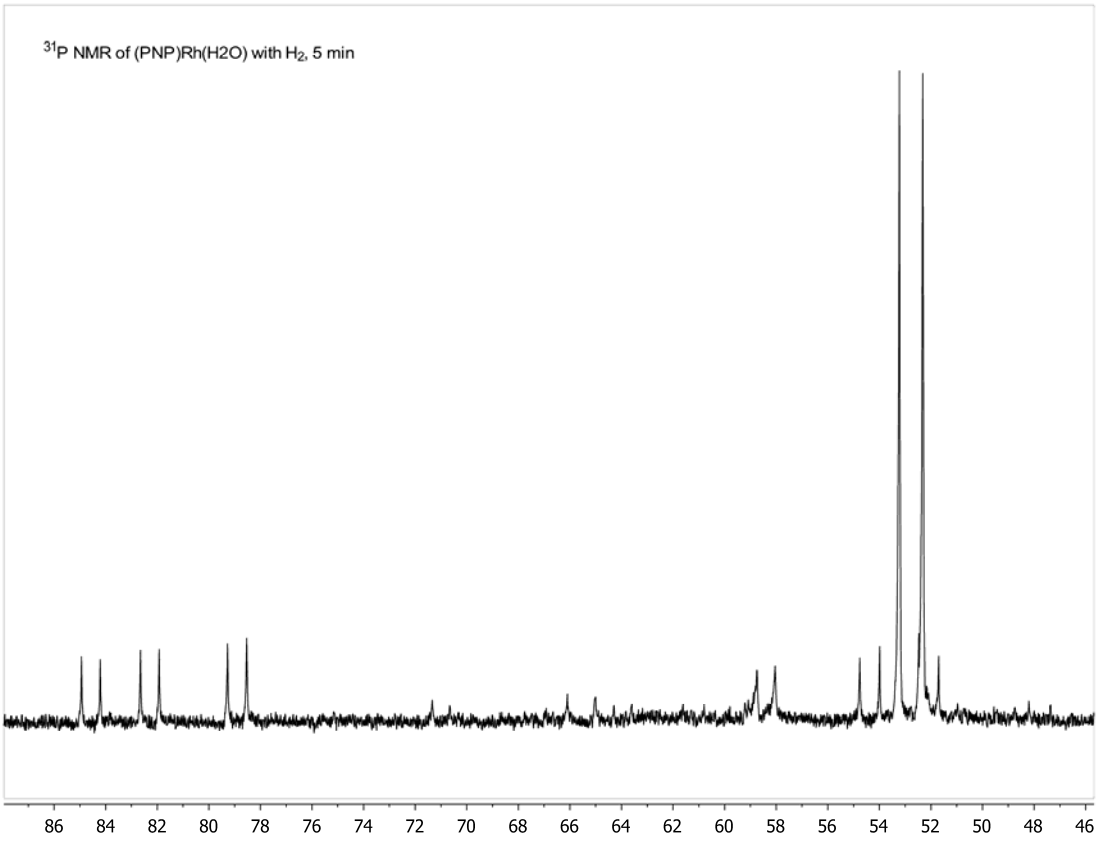


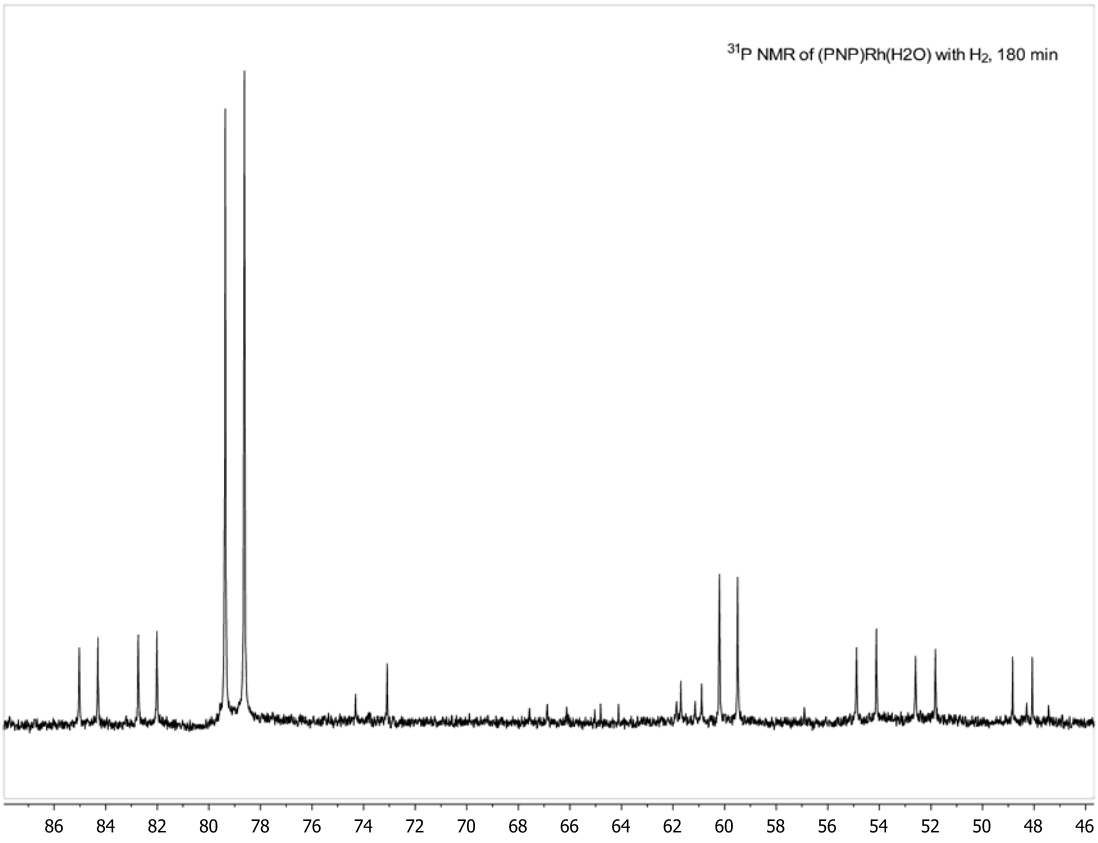





57.6
57.4
56.7
56.5
^{31}P NMR of (PNP)Rh(PMe$_3$) in C$_6$D$_6$
-18.4
-18.7
-19.0
-19.4
-19.6
-19.7
-19.9
85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -15 -25 -35


75.83
75.07
73.84
73.09
70.55
69.77
66.58
66.55
64.25
63.45
63.30
62.26
61.46
60.90
^{31}P NMR of (PNP)Rh(O) with CO, overnight at -40
(PNP)Rh(CO)
82 81 80 79 78 77 76 75 74 73 72 71 70 69 68 67 66 65 64 63 62 61 60 59 58 57 56





Computational Details

All calculations were carried out using Density Functional Theory as implemented in the Jaguar 7.0 suite[1] of ab initio quantum chemistry programs. Geometry optimizations were performed with the B3LYP[2-4] functional and the 6-31G** basis set with no symmetry restrictions, which has been shown to work well for many transition metal-containing systems.[5] We are aware of the tendency of B3LYP to overstabilize HS states, but we have qualitatively captured the energetic ordering of states when compared to our experimental results and focused on the singlet PES. All transition metals were represented using the Los Alamos basis set (LACVP).[6, 7] Energies of the optimized structures were reevaluated by additional single-point calculations on each optimized geometry using Dunning's correlation-consistent triple-ζ basis set,[8] cc-pVTZ(-f). For all transition metals we used a modified version of LACVP, designated LACV3P, in which the exponents were decontracted to match the effective core potential with the triple-ζ quality basis.

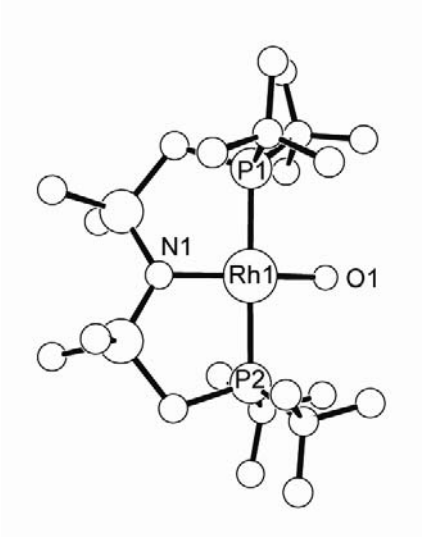
The models used in this study consist of ~80 atoms, which represent the non-truncated substrates that were used in the experimental work. All intermediates are confirmed minima with no imaginary frequencies associated with them and all transition states possess a single imaginary frequency. All models in this document are singlets.

References

1. Jaguar, version 7.0, *Schrödinger, L.L.C, New York, NY,* **2007**.
2. Becke, A. D., *Phys. Rev. A* **1988**, *38*, 3098.
3. Lee, C.; Yang, W.; Parr, R. G., *Phys. Rev. B* **1988**, *37*, 785.
4. Becke, A. D., *J. Chem. Phys.***1993**, *98*, 5648.
5. Siegbahn, E. M., Blomberg, R. A. *Chem. Rev.* **2000**, *100*, 421.
6. Hay, P. J.; Wadt, W. R., *J. Chem. Phys.* **1985,** *82*, 270.
7. Wadt, W. R.; Hay, P. J., *J. Chem. Phys.* **1985,** *82*, 284.
8. Dunning, T. H., *J. Chem. Phys.* **1989,** *90*, 1007.

H1-H2 in free H_2 is 0.74 Å

Optimized structure of (PNP)Rh=O **(1)**



1

ΔE(SCF)(**1**): 0.00 kcal/mol

Selected bond lengths (in Å) and bond angles (in ˚):

	1
Rh1-P1	2.413
Rh1-P2	2.411
Rh1-N1	2.045
Rh1-O1	1.819
P1-Rh1-P2	178.36
N1-Rh1-O1	166.17

Coordinates of 1

Rh	-0.557863364	0.704971986	-0.230435974
P	-1.063666048	3.019113074	0.231074323
N	-2.503959771	0.205352703	0.151013389
P	-0.014734022	-1.608703953	-0.633562456
Si	-2.904291348	-1.467379530	0.509678424
C	-1.495576923	-2.605416365	-0.109066728
Si	-3.730032368	1.451490973	-0.019742948
C	-2.909011586	3.178477551	0.099093503
C	0.192870678	-2.004175053	-2.499646418
C	1.433199524	-2.256320994	0.441916033
C	1.052117537	-1.899722331	1.897759997
H	1.875039596	-2.188287157	2.563633716
H	0.882713254	-0.824397400	2.011129333
H	0.154746593	-2.425492228	2.240448155
C	2.728107577	-1.494526277	0.084296089
H	3.469664085	-1.651333947	0.878470947
H	3.168725938	-1.859173631	-0.846852235
H	2.543362514	-0.422355643	-0.028393936
C	-1.053338819	-1.391801152	-3.181216505
H	-0.981451582	-1.550105955	-4.264721392
H	-1.987702722	-1.853358334	-2.844416940
H	-1.121054395	-0.316218185	-2.996639613
C	0.253975381	-3.506231595	-2.836779653
H	1.168224714	-3.975517725	-2.466872775
H	0.244020958	-3.628663008	-3.927663207
H	-0.599103608	-4.067106029	-2.441254606
C	-0.650067792	3.485514392	2.043015859
C	-0.372550488	4.294907899	-1.017307722
C	-1.563173983	2.622680374	2.943119985
H	-2.614818192	2.917910892	2.879473130
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H	-1.252354809	2.747594740	3.987816214
C	-0.873969757	4.969488004	2.384514491
H	-1.880006776	5.311351909	2.118042388
H	-0.148085425	5.619321991	1.888951417
H	-0.755967906	5.115472147	3.466331448
C	1.146347292	4.462870787	-0.816046061
H	1.553513491	5.046024697	-1.652255842
H	1.385076659	5.008836211	0.102047033
H	1.638329770	3.486541275	-0.804811896
C	-0.603457459	3.663368881	-2.411152931
H	-0.047720160	2.727395301	-2.500085358
H	-1.663447154	3.467905260	-2.611793383
H	-0.249684103	4.361060753	-3.181279452
C	-1.069818458	5.668631053	-0.970446214
H	-0.659549165	6.298707710	-1.770077573
H	-2.148776329	5.597770197	-1.138923656
H	-0.910430956	6.194388248	-0.027015571

C	0.811571518	3.091541334	2.344553451
H	1.020098580	3.266012973	3.407905308
H	0.985897823	2.033456719	2.129480094
H	1.532779719	3.671394859	1.765253666
C	1.444760785	-1.288711709	-3.052730584
H	2.363635809	-1.812164852	-2.774343420
H	1.397853085	-1.278415948	-4.149619707
H	1.510142709	-0.259727365	-2.685971805
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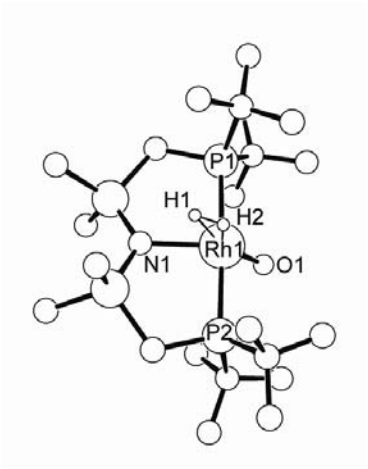
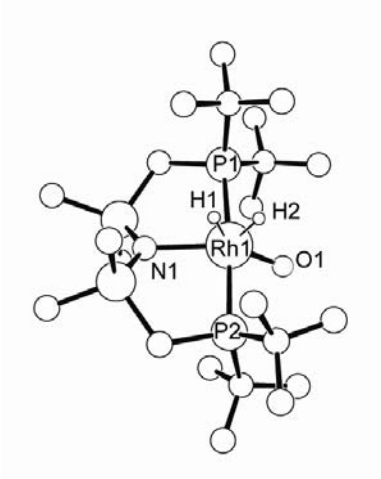
H	0.763713345	-4.358040109	0.538114533
H	2.064532837	-4.068736904	-0.628719983
H	2.413766572	-4.071694905	1.099187006
C	-4.557603209	1.369248337	-1.724418139
H	-3.808234723	1.463161344	-2.519002473
H	-5.083177835	0.421276572	-1.878118975
H	-5.286469323	2.179174736	-1.853462031
C	-5.083268872	1.362095783	1.311981978
H	-5.654035434	0.428224910	1.273684279
H	-4.661048151	1.449481589	2.319204094
H	-5.797528349	2.184081994	1.179526320
C	-3.087472068	-1.713700265	2.382357899
H	-3.302346705	-2.761494633	2.627220103
H	-2.170716035	-1.425090476	2.908186578
H	-3.903474079	-1.105519880	2.788153467
C	-4.498599975	-2.094290373	-0.317433799
H	-4.434005846	-2.034524076	-1.410076814
H	-5.389864572	-1.537687477	-0.008728623
H	-4.667956545	-3.146201530	-0.055249237
H	-3.327224168	3.785849725	0.908697713
H	-3.134507673	3.709158848	-0.831825054
H	-1.859209739	-3.207470888	-0.947846513
H	-1.215917181	-3.314247140	0.677190994
O	1.033194761	1.161762254	-0.984435713

Optimized structure of (PNP)Rh(H_2)(O) **(2)** and H_2 splitting (PNP)Rh^{III}(H_2)(O) to (PNP)Rh^{V}($H)_2$(O) **(TS_{2-3})**



2



TS_{2-3}

ΔE(SCF)**(2)**: 6.94 kcal/mol

ΔE(SCF) **(TS_{2-3})**: 12.52 kcal/mol

Selected bond lengths (in Å) and bond angles (in ˚):

2		**TS_{2-3}**	
Rh1-P1	2.479	Rh1-P1	2.456
Rh1-P2	2.433	Rh1-P2	2.427
Rh1-N1	2.165	Rh1-N1	2.193
Rh1-O1	1.814	Rh1-O1	1.867
Rh1-H1	1.977	Rh1-H1	1.634
Rh1-H2	1.940	Rh1-H2	1.556
H1-H2	0.782	H1-H2	1.149
P1-Rh1-P2	173.52	P1-Rh1-P2	174.98

N1-Rh1-O1	133.69	N1-Rh1-O1	138.81

Coordinates of 2

Rh	-0.483060036	0.662278746	-0.058587288
P	-1.080349522	3.046481143	0.261165073
N	-2.573338200	0.139684660	0.157554428
P	0.007310135	-1.651150878	-0.628739541
Si	-2.916004024	-1.520575600	0.506372339
C	-1.525668588	-2.622946480	-0.228683509
Si	-3.753866707	1.391529408	-0.044715721
C	-2.931956853	3.122120020	0.120194529
C	0.260035064	-1.954754695	-2.510014500
C	1.433820407	-2.430688406	0.400922473
C	0.979122549	-2.498510079	1.875903074
H	1.807465702	-2.882584310	2.484235583
H	0.717181880	-1.513255153	2.269581158
H	0.127599703	-3.166789400	2.030586852
C	2.665833506	-1.502318340	0.335706191
H	3.444808624	-1.888163106	1.006081609
H	3.091212427	-1.439450728	-0.667308603
H	2.413045914	-0.485869927	0.650890762
C	-0.834424470	-1.125338238	-3.221045102
H	-0.768027575	-1.305841323	-4.301804349
H	-1.844427363	-1.405333517	-2.902340291
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H	-5.144675301	0.430299625	-1.909239794
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H	-5.698960628	0.399037760	1.244615263
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H	-5.844442766	2.152685425	1.124861396
C	-3.013615136	-1.888750269	2.371891886
H	-3.205103028	-2.952545615	2.560386195
H	-2.088344465	-1.625804754	2.897133171
H	-3.826395581	-1.320400037	2.838372418
C	-4.538332735	-2.151940393	-0.261351393
H	-4.532972250	-2.039310541	-1.351302360
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H	-3.366592547	3.678100600	0.957157312
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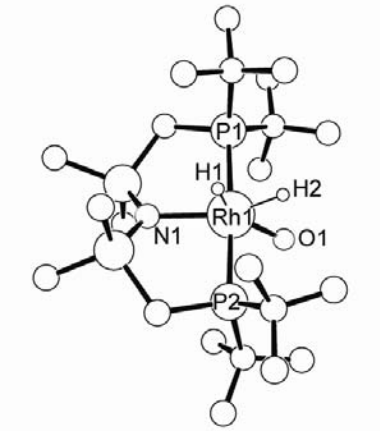
H	-1.913687755	-3.057947250	-1.154210350
H	-1.297803944	-3.467193032	0.429994843
O	0.554885779	1.118388440	-1.475192224
H	-0.321754906	0.248505841	1.830166452
H	-1.093458299	0.371758695	1.798877091

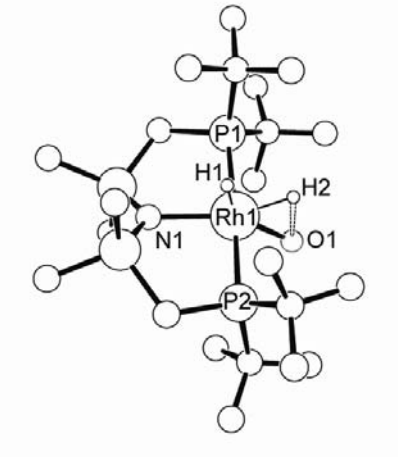
Coordinates of $TS_{2\text{-}3}$

O	0.200441619	0.033455544	-0.214810376
H	-0.312523257	-0.055563444	2.403777329
Rh	0.949374035	0.010686700	1.495144867
P	1.116275984	-2.439294548	1.462718994
N	2.932687341	0.064942819	2.428629627
P	0.986140819	2.437052138	1.459847536
Si	3.160607573	1.416225745	3.466570596
C	2.363311319	2.939019176	2.598748163
Si	3.971981575	-1.224062604	1.954838186
C	2.914492457	-2.816530132	1.729950581
C	1.473831278	3.172202816	-0.246222427
C	-0.608868414	3.246415963	2.153346650
C	-0.704521174	2.895162044	3.654706728
H	-1.650126765	3.288044182	4.048209673
H	-0.699839359	1.815869229	3.826481322
H	0.102781603	3.336676828	4.245426771
C	-1.844252501	2.651814660	1.444270961
H	-2.752140333	3.051258322	1.914141990
H	-1.880008020	2.904127125	0.383475225
H	-1.867553970	1.562081070	1.522421637
C	2.630541855	2.290317525	-0.769146133
H	2.985337754	2.703224373	-1.721971695
H	3.483517092	2.262847701	-0.083310794
H	2.287838315	1.268528368	-0.939429269
C	1.968795884	4.631648197	-0.176308111
H	1.195892993	5.331302348	0.145034234
H	2.285547920	4.934758195	-1.182195484
H	2.833611021	4.756284873	0.482066198
C	0.238671561	-3.286135968	2.955019547
C	0.693496982	-3.263826330	-0.217732595
C	0.882003599	-2.726370133	4.246224865
H	1.914958073	-3.061094363	4.376415522

H	0.879905131	-1.634709444	4.278074152
H	0.311115700	-3.092489593	5.108547539
C	0.394395552	-4.820562420	2.976661459
H	1.429983543	-5.139929183	2.823635230
H	-0.229060985	-5.309247212	2.225737940
H	0.077171561	-5.198319737	3.957047473
C	-0.780425421	-2.985033732	-0.573871685
H	-0.973057182	-3.347060210	-1.592215428
H	-1.476478824	-3.508584309	0.088365266
H	-0.969420621	-1.908240651	-0.545827044
C	1.578986693	-2.557840471	-1.272157129
H	1.370655128	-1.486108153	-1.283102743
H	2.647841966	-2.726391203	-1.106591361
H	1.335468063	-2.973026019	-2.258296801
C	0.984530494	-4.776554804	-0.275025540
H	0.920982406	-5.102282166	-1.320916844
H	1.988194092	-5.030749819	0.081343323
H	0.262249129	-5.368041346	0.290093351
C	-1.261873122	-2.930845094	2.967664275
H	-1.723756495	-3.349062208	3.870866883
H	-1.427150828	-1.849726884	2.980174477
H	-1.795238338	-3.340512357	2.106852959
C	0.296440268	3.060411728	-1.235412338
H	-0.501101650	3.775222336	-1.009368334
H	0.660221857	3.294938814	-2.244232501
H	-0.102333462	2.041880782	-1.230764273
C	-0.621691829	4.781705268	2.017441500
H	0.273331612	5.245851793	2.444467196
H	-0.713445178	5.100627313	0.976700716
H	-1.488578524	5.183305870	2.557777617
C	4.857945275	-0.901047180	0.306479158
H	4.146872384	-0.695582556	-0.500629304
H	5.517531712	-0.028814137	0.389270251
H	5.477864104	-1.753681488	0.000979751
C	5.317805906	-1.665401383	3.223977268
H	6.066974667	-0.873155202	3.321645217
H	4.894625550	-1.849447273	4.218131917
H	5.847466564	-2.575138970	2.914651289
C	2.391859477	1.216649784	5.193450848
H	2.511992534	2.129327437	5.790914078
H	1.322974766	0.982085292	5.159885836
H	2.888963360	0.403014005	5.734761385
C	4.980649010	1.890372533	3.753141169
H	5.533901263	1.981833406	2.811513935
H	5.502224013	1.157176474	4.377021697
H	5.044292396	2.857337662	4.267862637
H	3.030927155	-3.450052155	2.614710254
H	3.294365093	-3.397433749	0.883923583
H	3.153939582	3.389672040	1.990043856
H	2.038847644	3.713671756	3.301699713
H	0.604189754	0.022782701	3.092043404

Optimized structure of (PNP)Rh$(H)_2(O)$ **(3)** and (PNP)$Rh^{V}(H)_2(O)$ to (PNP)$Rh^{III}(H)(OH)$ **(TS_{3-4})**





3 **TS_{3-4}**

ΔE(SCF)(**3**) : 10.88 kcal/mol ΔE(SCF) **(TS_{3-4})**: 11.55 kcal/mol

Selected bond lengths (in Å) and bond angles (in ˚):

	3		**TS_{3-4}**
Rh1-P1	2.433	Rh1-P1	2.428
Rh1-P2	2.428	Rh1-P2	2.421
Rh1-N1	2.130	Rh1-N1	2.137
Rh1-O1	1.890	Rh1-O1	1.917
Rh1-H1	1.575	Rh1-H1	1.555
Rh1-H2	1.547	Rh1-H2	1.554

H1-H2	1.785	H1-H2	1.904
H2-O1	2.123	H2-O1	1.844
H1-N1	2.427	H1-N1	2.399
H1-Rh1-N1	80.33	H1-Rh1-N1	79.31
H2-Rh1-O1	75.57	H2-Rh1-O1	63.16
P1-Rh1-P2	177.13	P1-Rh1-P2	177.40
N1-Rh1-O1	134.91	N1-Rh1-O1	142.49
H1-Rh1-H2	69.77	H1-Rh1-H2	75.52

Coordinates of 3

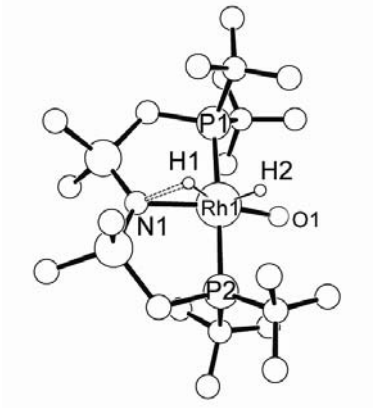
O	-0.104971251	0.018366560	0.092225401
H	-0.099880124	-0.035562087	2.214492475
Rh	1.231613563	-0.006704111	1.427967520
P	1.199994167	-2.427826919	1.662658249
N	3.360404380	-0.080528635	1.423917295
P	1.364259699	2.411532338	1.261119391
Si	4.144585987	1.287999350	2.140002191
C	3.126265564	2.841631561	1.658532194
Si	4.050052982	-1.526268957	0.757917973
C	2.894144175	-3.003626717	1.176619126
C	1.100573487	3.088730620	-0.516602755
C	0.296401928	3.348500785	2.550190763
C	0.838497428	2.992532411	3.951825374
H	0.196792608	3.462525472	4.707278139
H	0.826985691	1.913696230	4.126934518
H	1.856520347	3.356176283	4.117498946
C	-1.169549293	2.873799910	2.475927659
H	-1.742340811	3.364785566	3.272815139
H	-1.645242639	3.119953481	1.525473236
H	-1.248203348	1.793017535	2.616496714
C	1.857147322	2.116947504	-1.451551674
H	1.786464612	2.492688230	-2.480225150
H	2.920702774	2.036082061	-1.203376075
H	1.407330666	1.123631801	-1.407222999
C	1.659133873	4.510218381	-0.731152459
H	1.145723859	5.267581236	-0.136859973
H	1.521987850	4.775657867	-1.786958768
H	2.730206944	4.583419364	-0.520485715
C	1.027942101	-3.016691087	3.488631059
C	0.004186598	-3.320955368	0.459442316
C	2.212175776	-2.412427982	4.278972005
H	3.174456751	-2.841611126	3.985209772
H	2.276371808	-1.328919367	4.161148506
H	2.070234388	-2.633555149	5.344083016
C	1.083810312	-4.549779077	3.649214362
H	1.921827817	-5.000275851	3.108166282
H	0.163915755	-5.034926807	3.319019897
H	1.214920722	-4.791106356	4.711507929
C	-1.435945611	-2.831384948	0.712373370
H	-2.095356203	-3.265150175	-0.050640296
H	-1.821074373	-3.148175171	1.686117692
H	-1.474172892	-1.741235102	0.627544136
C	0.413910529	-2.870762677	-0.963440598
H	0.371622892	-1.781943312	-1.042702551
H	1.408580891	-3.227223750	-1.249497212
H	-0.299940985	-3.301376657	-1.676882039
C	0.072036603	-4.859219891	0.523865785
H	-0.464530289	-5.267020327	-0.342065936
H	1.097162141	-5.242229569	0.479186492
H	-0.406010751	-5.264681962	1.417566225
C	-0.281261275	-2.487415997	4.105849584
H	-0.316038351	-2.764998103	5.166757583
H	-0.344988647	-1.397867044	4.042150013
H	-1.168879361	-2.909887021	3.628591324
C	-0.394802975	3.052259956	-0.889299103
H	-0.968029079	3.826914915	-0.370402138
H	-0.494129885	3.247484627	-1.964957860
H	-0.811501326	2.065125293	-0.670975215
C	0.350819170	4.879855014	2.379634074
H	1.376328346	5.262160017	2.349179874
H	-0.167626073	5.209918877	1.476309866
H	-0.150009921	5.354425814	3.233127518
C	4.195833692	-1.433351350	-1.130166911
H	3.222451900	-1.239298690	-1.593454535
H	4.867775020	-0.619895300	-1.428474642
H	4.594641957	-2.363223229	-1.555173056
C	5.763392890	-1.992270003	1.438466501
H	6.543047625	-1.295601749	1.115015992
H	5.774211133	-2.021869177	2.534209417
H	6.051155447	-2.987880991	1.078218747
C	4.281846644	1.197996463	4.030765216
H	4.752665222	2.100845364	4.439874461
H	3.304411779	1.084092780	4.510105820
H	4.897758070	0.342300834	4.331141771
C	5.900880812	1.607782245	1.482316249
H	5.936362894	1.597002934	0.386945544
H	6.624041343	0.871987574	1.848157810
H	6.249993638	2.594334076	1.812622829
H	3.336385748	-3.589758207	1.987798047
H	2.819426357	-3.673741009	0.315021446
H	3.587781457	3.251529684	0.754648277
H	3.183039384	3.630497770	2.415958652
H	1.505362309	0.169165478	2.968802849

Coordinates $TS_{3\text{-}4}$

O	-0.149931490	0.024520687	0.152856187
H	-0.063946078	-0.013770255	1.994500781
Rh	1.349348791	-0.004781194	1.347367405
P	1.314032434	-2.419217507	1.605632062
N	3.484485998	-0.086938427	1.386300077
P	1.489990512	2.401244189	1.120910212
Si	4.258164674	1.306194129	2.059885946
C	3.258167447	2.837832658	1.480085818
Si	4.186053993	-1.538207992	0.752635686
C	3.004729602	-3.008647466	1.126196814

C	1.197732334	3.017072931	-0.674837767
C	0.442027580	3.382136232	2.392434446
C	0.991889439	3.053206221	3.797494753
H	0.363829229	3.549787765	4.547438638
H	0.966263303	1.978922506	3.998965461
H	2.016568532	3.405223417	3.944987234
C	-1.030430057	2.924580743	2.343248339
H	-1.588158117	3.440693243	3.135029757
H	-1.512632048	3.155093453	1.392454820
H	-1.122333291	1.848606787	2.508438705
C	1.913236503	1.994644358	-1.587416146
H	1.835345673	2.334573195	-2.627987976
H	2.978049973	1.891908296	-1.352659245
H	1.439323796	1.014973242	-1.502493603
C	1.780019519	4.417598826	-0.954794582
H	1.308024597	5.203739268	-0.363266577
H	1.607503062	4.655990004	-2.011844410
H	2.859922713	4.470570109	-0.787621472
C	1.121325206	-2.960242556	3.440484866
C	0.123708740	-3.340864149	0.420271910
C	2.356327513	-2.430409159	4.206341964
H	3.272589499	-2.965763391	3.941133251
H	2.524919766	-1.364926797	4.033565393
H	2.193001770	-2.580488895	5.280705303
C	1.055747785	-4.488706959	3.631375767
H	1.852393119	-5.014716083	3.095657676
H	0.096140559	-4.902162516	3.313509134
H	1.170891849	-4.720056592	4.697989376
C	-1.330114138	-2.935248382	0.733252414
H	-1.991072393	-3.367102030	-0.029368973
H	-1.669593661	-3.313886638	1.702440546
H	-1.425950373	-1.845750562	0.696330014
C	0.465639987	-2.832109899	-1.000426094
H	0.339937637	-1.748186931	-1.053429731
H	1.480558580	-3.102513978	-1.310824052
H	-0.225140282	-3.303661110	-1.710672999
C	0.275075879	-4.874984668	0.437207546
H	-0.296081518	-5.288610663	-0.403307208
H	1.313546645	-5.198705416	0.311364869
H	-0.115235771	-5.331242049	1.348055804
C	-0.136902806	-2.317045376	4.057753931
H	-0.206927959	-2.609181848	5.113070166
H	-0.091530921	-1.226132837	4.012962730
H	-1.058221598	-2.638724887	3.566443094
C	-0.305899833	2.995640316	-1.014103452
H	-0.850870423	3.806830946	-0.521094430
H	-0.425328041	3.140736740	-2.095655341
H	-0.739934762	2.030496589	-0.737472857
C	0.513607401	4.907840831	2.183924245
H	1.543462518	5.276964486	2.139795768
H	-0.004896492	5.221783923	1.274960150
H	0.022361493	5.409262227	3.027636970
C	4.400805855	-1.463380896	-1.131268416
H	3.445261835	-1.271995981	-1.632044425
H	5.083950433	-0.653248681	-1.412988297
H	4.813104560	-2.397246603	-1.533898214
C	5.872162187	-2.009977766	1.494155848
H	6.665444040	-1.317005139	1.196839987
H	5.843235778	-2.035457117	2.589545232
H	6.169096427	-3.007750240	1.147538952
C	4.355495435	1.293534437	3.955875354
H	4.793732957	2.222673823	4.341746466
H	3.373753805	1.168098323	4.423029363
H	4.989550500	0.466519511	4.296763080
C	6.032776339	1.593962104	1.436819370
H	6.099388579	1.538654105	0.344254898
H	6.741928850	0.871178150	1.852709868
H	6.376987694	2.591886932	1.736586017
H	3.426099136	-3.639156622	1.915114154
H	2.922931651	-3.639665362	0.236164225
H	3.719382010	3.165971942	0.542980278
H	3.332122976	3.684151246	2.171280366
H	1.617318221	0.173911357	2.869089825

Optimized structure of $(PNP)Rh^{V}(H_2)(O)$ to $(PNHP)Rh^{III}(H)(O)$ **($TS_{3\text{-}6}$)**



$TS_{3\text{-}6}$

ΔE(SCF) **($TS_{3\text{-}6}$)**: 16.63 kcal/mol

Selected bond lengths (in Å) and bond angles (in °):

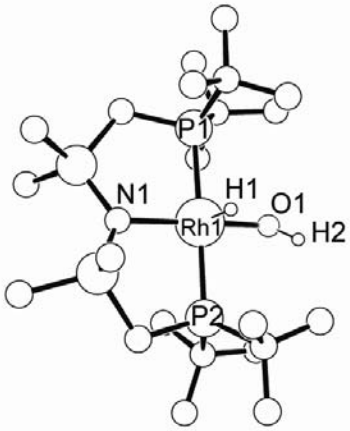
	$TS_{3\text{-}6}$
Rh1-P1	2.419

Rh1-P2	2.391
Rh1-N1	2.236
Rh1-O1	1.910
Rh1-H1	1.586
Rh1-H2	1.520
H1-H2	1.896
H2-O1	2.123
H1-N1	1.669
H1-Rh1-N1	48.20
H2-Rh1-O1	75.51
P1-Rh1-P2	175.60
N1-Rh1-O1	161.41
H1-Rh1-H2	75.20

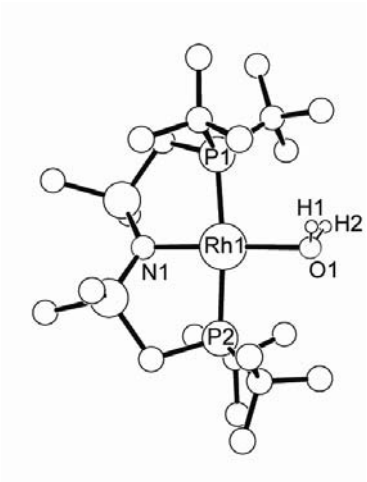
Coordinates $TS_{3\text{-}6}$

H	-0.052448788	-0.083646551	0.156818390
N	-0.005286924	0.011336297	1.822891367
O	3.216366726	0.042402648	-0.699831715
H	1.174390931	0.109150575	-1.276154513
Rh	1.530719076	0.008068309	0.198156341
P	1.486432340	-2.409863745	0.153503512
P	1.672631326	2.386912637	0.397247802
Si	-0.871350515	1.508160461	2.029907193
C	0.253390442	2.954198251	1.463577397
Si	-0.205524671	-1.484515775	2.691510878
C	0.667272540	-2.913344926	1.747610570
C	3.234640417	2.877424814	1.401487581
C	1.526637818	3.346034457	-1.248909503
C	0.162835322	2.952722932	-1.861385947
H	0.050543628	3.462363892	-2.825814145
H	0.096384911	1.876587510	-2.040399469
H	-0.685081665	3.248600609	-1.235367183
C	2.651102381	2.890851748	-2.208267431
H	2.369380731	3.143750186	-3.238434049
H	3.590713893	3.406846411	-1.993610186
H	2.842544357	1.814885983	-2.128912010
C	3.243197595	1.937174576	2.630123080
H	4.103380973	2.189231952	3.262996028
H	2.342252616	2.031677178	3.244996072
H	3.344348598	0.890805334	2.330329253
C	3.235190881	4.336093911	1.899302873
H	3.291300977	5.057775361	1.081943278
H	4.122084482	4.488361951	2.527362142
H	2.362655007	4.583576172	2.511833559
C	0.387363903	-3.174526795	-1.222260878
C	3.221429816	-3.220992512	0.234458861
C	-1.064630217	-2.721611393	-0.949107982
H	-1.466545253	-3.132718399	-0.018814583
H	-1.149458907	-1.632018819	-0.907135714
H	-1.706039806	-3.074619240	-1.766051411
C	0.421674382	-4.715067079	-1.253386344
H	0.219342655	-5.161006125	-0.274105634
H	1.382317689	-5.093988267	-1.610497394
H	-0.348631107	-5.079543946	-1.944941554
C	3.923446458	-3.071176651	-1.129754474
H	4.977041145	-3.359705385	-1.020231423
H	3.489717995	-3.726836411	-1.891434565
H	3.877885151	-2.026000993	-1.453870784
C	4.019444812	-2.396478979	1.271772777
H	4.131684951	-1.368304117	0.919601398
H	3.548119265	-2.393986327	2.262301413
H	5.013825870	-2.846168260	1.388682219
C	3.210517237	-4.696876891	0.678242405
H	4.249226259	-5.032549651	0.789338282
H	2.720949516	-4.844680678	1.646001986
H	2.731855045	-5.357255574	-0.046536223
C	0.801778181	-2.624322011	-2.602725581
H	0.101210380	-2.997256101	-3.360561272
H	0.771170654	-1.532044566	-2.625195180
H	1.806431264	-2.933774141	-2.895404206
C	4.506097967	2.603651153	0.572674956
H	4.669039447	3.376467672	-0.184486792
H	5.376123326	2.616648435	1.242055146
H	4.437823887	1.627814325	0.078550148
C	1.560382853	4.876838431	-1.075012512
H	0.822206716	5.237732878	-0.350563123
H	2.546157416	5.230450814	-0.764070183
H	1.334862913	5.352944007	-2.037843808
C	0.608503260	-1.396422181	4.402639400
H	1.672010216	-1.145870328	4.317185835
H	0.140084586	-0.631737585	5.031484634
H	0.530261654	-2.353504045	4.933721112
C	-2.023255478	-1.982142432	2.937199543
H	-2.574069945	-1.237850320	3.523322697
H	-2.541884597	-2.090666004	1.978050142
H	-2.103632606	-2.937685572	3.470180553
C	-2.465508293	1.566947392	1.003090803
H	-2.979247198	2.530870910	1.105762266
H	-2.263841468	1.410470194	-0.062674623
H	-3.163730245	0.785105483	1.323163245
C	-1.331411962	1.835011251	3.842343827
H	-0.445578193	1.852499384	4.486734793
H	-2.016127876	1.078133169	4.240635609
H	-1.831446787	2.806550211	3.938906122
H	-0.022089443	-3.749954547	1.588245950
H	1.451715615	-3.293685301	2.410020174
H	0.654810483	3.441200268	2.357798304
H	-0.334026373	3.716785221	0.941186590

Optimized structure of (PNP)RhH(OH) **(4)** and (PNP)Rh(H_2O) **(5)**



4



5

ΔE(SCF)(**4**): -52.23 kcal/mol

ΔE(SCF)(**5**): -55.51 kcal/mol

Selected bond lengths (in Å) and bond angles (in ˚):

	4		**5**
Rh1-P1	2.394	Rh1-P1	2.388
Rh1-P2	2.385	Rh1-P2	2.382
Rh1-N1	2.144	Rh1-N1	2.114
Rh1-O1	2.064	Rh1-O1	2.271
Rh1-H1	1.508	Rh1-H1	2.622
H1-H2	2.638	H1-H2	1.549
H2-O1	0.964	H1-O1	0.968
H1-O1	2.629	H2-O1	0.966
P1-Rh1-P2	178.33	P1-Rh1-P2	173.06
N1-Rh1-O1	168.97	N1-Rh1-O1	177.45
N1-Rh1-H1	97.48	H1-O1-H2	106.45
H1-Rh1-O1	93.46		
Rh1-O1-H2	109.77		

Coordinates of 4

Rh	-0.532201302	0.705557783	-0.245444358
P	-1.086104783	2.994809946	0.183988037
N	-2.576329586	0.172409273	0.122069891
P	-0.031717024	-1.593925311	-0.630432872
Si	-2.879055299	-1.461101320	0.594252081
C	-1.585279133	-2.551792475	-0.312331037
Si	-3.787159444	1.406202157	0.078812799
C	-2.927344456	3.124099791	0.014777184
C	0.336256177	-1.868478514	-2.496158202
C	1.297552951	-2.408947629	0.485425392
C	0.719829800	-2.472718611	1.915722319
H	1.496620993	-2.844011837	2.595786820
H	0.410420099	-1.485197374	2.269716753
H	-0.135957536	-3.147331698	1.996475082
C	2.568988496	-1.537142627	0.538800353
H	3.305252863	-2.015797683	1.197060956

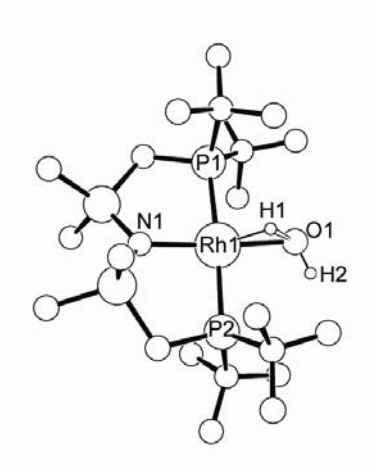
H	3.037652617	-1.408068231	-0.438959666
H	2.350483945	-0.549303029	0.954624158
C	-0.691230870	-0.975351005	-3.232930776
H	-0.571766164	-1.107974181	-4.315931536
H	-1.727167926	-1.223800248	-2.981058535
H	-0.529589978	0.084382471	-3.011146565
C	0.156763008	-3.322184174	-2.974915016
H	0.889035469	-4.003999321	-2.538443877
H	0.290258085	-3.353262499	-4.063785276
H	-0.841192143	-3.716210988	-2.761245499
C	-0.702112244	3.569555523	1.970969382
C	-0.399419300	4.226678266	-1.119630960
C	-1.596580884	2.733122584	2.912082017
H	-2.653935061	2.993724250	2.815403766
H	-1.492150344	1.660674299	2.726754832
H	-1.303929205	2.930710965	3.950883097
C	-0.994889298	5.063053216	2.211809055
H	-2.009820576	5.343487575	1.911717957
H	-0.289087563	5.711251163	1.686396720
H	-0.900677540	5.280664072	3.283646156
C	1.097719767	4.505109713	-0.881086645
H	1.497561333	5.053121780	-1.744530951
H	1.266221120	5.131571367	0.000207307
H	1.646113977	3.564475328	-0.784193653
C	-0.537921503	3.493464730	-2.474574554
H	0.105730469	2.610861853	-2.498230895
H	-1.571813225	3.194665308	-2.685516091
H	-0.226547768	4.169056834	-3.281871285
C	-1.173875148	5.558182460	-1.192885195
H	-0.749619323	6.164689332	-2.003346759
H	-2.235226415	5.418429337	-1.417534038
H	-1.098485822	6.144072958	-0.274736081
C	0.770656650	3.272486689	2.321755223
H	0.949170579	3.542203197	3.370602467
H	1.001379554	2.211357321	2.199298507
H	1.473339309	3.839385525	1.708707201
C	1.747866501	-1.363038623	-2.852080300
H	2.531147260	-2.022251707	-2.464349760
H	1.856317029	-1.345674623	-3.944231884
H	1.900563460	-0.347734521	-2.472061306
C	1.669606082	-3.835877852	0.037798382
H	0.790931999	-4.478189896	-0.079141266
H	2.225105185	-3.839115515	-0.903554395
H	2.313683153	-4.297486025	0.797318489
C	-4.866854866	1.322079510	-1.485224370
H	-4.247942589	1.378664577	-2.388881973
H	-5.429755730	0.383430354	-1.533941226
H	-5.592609485	2.144402395	-1.524028344
C	-4.987437128	1.413011662	1.559134116
H	-5.595123214	0.501621364	1.591701611
H	-4.459400904	1.486230768	2.515789053
H	-5.682810684	2.259566325	1.494762296
C	-2.797614316	-1.756159441	2.471025403
H	-2.849690370	-2.821863474	2.728032768
H	-1.885836083	-1.345321758	2.914974938
H	-3.646956579	-1.261968670	2.957665652
C	-4.568063804	-2.144970883	0.035170501
H	-4.698387021	-2.062212746	-1.049857744
H	-5.408635326	-1.625628153	0.508677964
H	-4.657267052	-3.206321671	0.299401158
H	-3.354345645	3.827420292	0.738274725
H	-3.132582053	3.544270452	-0.975394020
H	-2.033837674	-2.788684492	-1.283146643
H	-1.387689583	-3.510814946	0.177973065
O	1.307408774	1.305735657	-0.964636573
H	2.009310773	0.878162282	-0.461733692
H	-0.038544667	0.581100904	1.174347120

Coordinates of 5

Rh	-0.444076346	0.699091534	-0.170687541
P	-1.076604705	2.971129344	0.206992489
N	-2.487131548	0.216864221	0.077819585
P	-0.085654747	-1.610736253	-0.631539140
Si	-2.744329331	-1.301883019	0.845686276
C	-1.500815019	-2.560221934	0.108213654
Si	-3.635517591	1.372385886	-0.468798152
C	-2.851799162	3.120870956	-0.301806482
C	-0.180523965	-1.980997297	-2.518572982
C	1.469338084	-2.461104679	0.139185747
C	1.527390486	-1.954166068	1.598223026
H	2.417530305	-2.363165009	2.094310513
H	1.572839137	-0.862669809	1.642873069
H	0.653469843	-2.269950249	2.177188572
C	2.757437099	-2.023767360	-0.585865237
H	3.629235786	-2.374578245	-0.017596864
H	2.831767454	-2.460196041	-1.586301109
H	2.826466866	-0.937384943	-0.673194773
C	-1.621688968	-1.642488310	-2.958581312
H	-1.673239909	-1.652310287	-4.055183453
H	-2.351157531	-2.370963717	-2.592483814
H	-1.923570575	-0.654649331	-2.603558226
C	0.131604222	-3.434282309	-2.915043389
H	1.188577832	-3.682662899	-2.784958783
H	-0.106334440	-3.581567919	-3.977117246
H	-0.463989065	-4.155291216	-2.345446017
C	-1.058415148	3.472243205	2.067570537
C	-0.222164911	4.366346545	-0.838523511
C	-2.134664783	2.608043860	2.759496208
H	-3.147182183	2.919341711	2.485798581
H	-2.023723113	1.551930587	2.505123125
H	-2.039604023	2.718581052	3.847757616
C	-1.355624708	4.952726965	2.363938803
H	-2.285471253	5.289127717	1.893565665
H	-0.548696408	5.617091460	2.041774886
H	-1.471487155	5.090098652	3.447405424
C	1.194135354	4.687854555	-0.320859427
H	1.702328893	5.357670167	-1.026427954
H	1.177796914	5.190825172	0.649631900
H	1.823482067	3.796785002	-0.217836173
C	-0.107789793	3.802243074	-2.273146991
H	0.441508783	2.855357156	-2.308530385
H	-1.090137702	3.605114695	-2.714034455
H	0.406201109	4.527122479	-2.917776273
C	-1.015315463	5.688631378	-0.918606576
H	-0.511557057	6.369679998	-1.617703270
H	-2.032417605	5.538441175	-1.290174630
H	-1.081242347	6.199695958	0.043063185
C	0.308573519	3.082565661	2.668945042
H	0.308617929	3.279662649	3.748823259
H	0.497034201	2.013591928	2.521032901
H	1.139018654	3.651096836	2.237952437
C	0.768049457	-1.018796540	-3.263012566
H	1.819713300	-1.185537688	-3.017156733
H	0.654829362	-1.158136508	-4.346151352
H	0.519410437	0.019757061	-3.022172333
C	1.419416966	-4.002558874	0.172972686
H	0.537122913	-4.383491681	0.694467203
H	1.438047126	-4.446834785	-0.823287098
H	2.299414306	-4.375188027	0.713825778
C	-4.128604913	1.217174165	-2.301729487
H	-3.261909517	1.328528624	-2.963572978

H	-4.576438852	0.238750315	-2.511750381
H	-4.864083997	1.982686155	-2.582180854
C	-5.279474401	1.405544184	0.495612029
H	-5.897192824	0.527096214	0.283262022
H	-5.124114283	1.448295083	1.579446545
H	-5.865208288	2.288049795	0.208949228
C	-2.430608953	-1.297003168	2.723249614
H	-2.539495350	-2.301640304	3.152208411
H	-1.422147318	-0.937713924	2.955120969
H	-3.139127186	-0.640675946	3.242062025
C	-4.484582134	-2.041335452	0.613560866
H	-4.791392481	-2.059622652	-0.437933965
H	-5.245882836	-1.489703735	1.173741108
H	-4.500628408	-3.075776425	0.979592347
H	-3.416931983	3.780279495	0.367196060
H	-2.877469754	3.587131875	-1.292534780
H	-1.974500820	-3.209770774	-0.634494207
H	-1.129724325	-3.213920452	0.902495640
O	1.772154503	1.157080269	-0.359200957
H	1.930285850	1.595697882	0.489348820
H	1.828805112	1.843333280	-1.036544868

Optimized structure of (PNP)Rh(H)(OH) to (PNP)Rh(H_2O) **(TS_{4-5})**



TS_{4-5}

ΔE(SCF) (**TS_{4-5}**) : -38.67 kcal/mol

Selected bond lengths (in Å) and bond angles (in ˚):

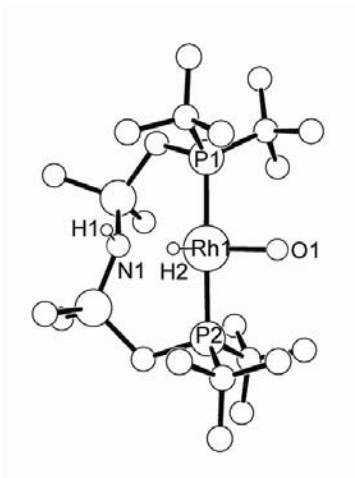
	TS_{4-5}
Rh1-P1	2.386
Rh1-P2	2.404
Rh1-N1	2.112
Rh1-O1	2.160
Rh1-H1	1.580
H1-H2	1.906
H1-O1	1.440
H2-O1	0.964
P1-Rh1-P2	176.63
N1-Rh1-O1	176.14
H1-O1-H2	103.16

Coordinates of TS_{4-5}

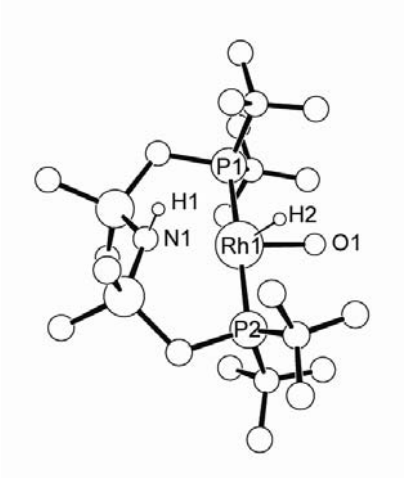
H	-0.098820748	-0.013442482	0.151962807
O	-0.216428651	0.032329837	1.586003608
Rh	1.478040163	0.005360100	0.246478527
P	1.375804301	2.389048076	0.199122816

N	3.130919499	0.121259229	-1.063803713
P	1.695522214	-2.388215012	0.211358745
Si	3.438647062	-1.248118316	-2.072176278
C	3.002093972	-2.799516961	-1.038101007
Si	4.100704753	1.557389667	-1.045871569
C	3.085741345	2.959187779	-0.221308575
C	2.414617743	-3.057355245	1.870852612
C	0.177194782	-3.417690821	-0.380991117
C	-0.097538633	-2.971404651	-1.834504517
H	-1.020561753	-3.448403915	-2.187381774
H	-0.229498721	-1.887046097	-1.900648243
H	0.702595691	-3.259592965	-2.520753655
C	-1.087614946	-3.089583982	0.439197918
H	-1.931414027	-3.669043649	0.043460896
H	-0.989817483	-3.348387731	1.496306623
H	-1.357889067	-2.033516854	0.358876149
C	3.521369169	-2.049269934	2.259722922
H	3.977340387	-2.361780035	3.208094972
H	4.318252829	-1.993279779	1.511797577
H	3.115085929	-1.041492980	2.387443375
C	3.041207547	-4.463187441	1.787929274
H	2.301188443	-5.246830266	1.617006482
H	3.541089293	-4.687813327	2.738857358
H	3.797897679	-4.537276312	1.001588399
C	0.267070656	3.100831840	-1.195411953
C	0.998796296	3.237465022	1.884404304
C	0.923003569	2.695801494	-2.533131321
H	1.854463479	3.239363776	-2.713761682
H	1.139013857	1.624679596	-2.570198857
H	0.237482474	2.939307851	-3.354708650
C	0.128824252	4.634509572	-1.159291443
H	1.099896522	5.139701448	-1.129661473
H	-0.463739846	4.978085276	-0.307541526
H	-0.384364965	4.971515211	-2.069425727
C	-0.508413462	3.197107379	2.206187173
H	-0.657685411	3.522786866	3.244061410
H	-1.084516483	3.878394553	1.572750533
H	-0.906387353	2.184660650	2.107254602
C	1.739687704	2.388323830	2.943925610
H	1.350216532	1.368054781	2.962322668
H	2.819952578	2.347069524	2.762709304
H	1.592200534	2.840494572	3.933447775
C	1.505732584	4.691622648	1.976400811
H	1.316488933	5.066262617	2.990594671
H	2.581747908	4.773352470	1.798538524
H	0.997462781	5.362975430	1.281660433
C	-1.132106039	2.452554659	-1.141156193
H	-1.740635130	2.844965743	-1.966246393
H	-1.064614662	1.367449337	-1.259705545
H	-1.662767777	2.657913543	-0.209579686
C	1.347061614	-3.038565261	2.981618543
H	0.584490586	-3.809465524	2.838589451
H	1.825627271	-3.234098653	3.949874066
H	0.854447506	-2.063217696	3.053528791
C	0.407652786	-4.940847891	-0.359577799
H	1.342247185	-5.232042053	-0.848592313
H	0.415782507	-5.339931886	0.658164710
H	-0.411102143	-5.439015009	-0.894965212
C	5.677996706	1.374908783	0.001885693
H	5.432514837	1.073208126	1.026985408
H	6.347880727	0.612956705	-0.412309039
H	6.242622766	2.314804841	0.053967628
C	4.675781226	2.179782572	-2.754127784
H	5.411062376	1.508225446	-3.209730939
H	3.846348893	2.285100181	-3.461244883
H	5.157170594	3.161324792	-2.657456071
C	2.460454982	-1.236670169	-3.700356608
H	2.572138841	-2.174851539	-4.258641460
H	1.392303056	-1.063878341	-3.537258826
H	2.826782612	-0.428429066	-4.344827982
C	5.263368237	-1.498574350	-2.564734085
H	5.917842827	-1.557457740	-1.687742287
H	5.646218156	-0.704869670	-3.214206773
H	5.370234003	-2.441573135	-3.116206056
H	3.081118993	3.883199074	-0.810302113
H	3.583625265	3.198196220	0.724604173
H	3.917182247	-3.072481506	-0.502200930
H	2.727212463	-3.670240373	-1.641785221
H	-0.428802481	-0.879284046	1.818131295

Optimized structure of (PNHP)RhH(O) **(6)** and (PNHP)RhH(O) to (PNHP)Rh(OH) **($TS_{6\text{-}7}$)**



6



TS_{6-7}

ΔE(SCF) (**6**): -15.84 kcal/mol ΔE(SCF) (**TS_{6-7}**): -6.83 kcal/mol

Selected bond lengths (in Å) and bond angles (in ˚):

6		**TS_{6-7}**	
Rh1-P1	2.400	Rh1-P1	2.380
Rh1-P2	2.371	Rh1-P2	2.354
Rh1-N1	2.482	Rh1-N1	2.438
Rh1-O1	1.858	Rh1-O1	1.955
Rh1-H1	2.651	Rh1-H1	2.532
Rh1-H2	1.563	Rh1-H2	1.546
H2-O1	2.879	H2-O1	1.769
H1-H2	2.186	H1-H2	3.003
H1-N1	1.020	H1-N1	1.021
P1-Rh1-P2	171.87	P1-Rh1-P2	177.68
N1-Rh1-O1	169.73	N1-Rh1-O1	173.53
H2-Rh1-O1	114.34	H2-Rh1-O1	59.33

Coordinates of 6

Rh	-0.439920126	0.708207311	-0.068238132
P	-1.029573961	3.013440632	0.245326542
N	-2.761654311	0.170258644	0.623505317
P	-0.033654178	-1.550550102	-0.663462972
Si	-2.952645991	-1.610068072	0.671986882
C	-1.555792225	-2.553169595	-0.224992277
Si	-3.795172123	1.448450558	-0.070408342
C	-2.896606955	3.124268884	0.087492582
C	0.126259304	-1.805232750	-2.568072347
C	1.408950334	-2.386011198	0.287314399
C	1.073912226	-2.254974464	1.790380246
H	1.895928840	-2.688741817	2.373270432
H	0.963450551	-1.207812816	2.081139451
H	0.160021682	-2.791046220	2.069883342
C	2.704985753	-1.587528873	0.014535264
H	3.433517341	-1.799552374	0.807901648
H	3.163977411	-1.881065740	-0.932980585
H	2.509807130	-0.509601557	-0.028334706
C	-1.061594749	-1.035065668	-3.187594300
H	-1.018690830	-1.127915381	-4.280417178
H	-2.033329409	-1.426871175	-2.865453426
H	-1.015781710	0.026763812	-2.932201177
C	0.055327245	-3.268397259	-3.045308784
H	0.913581196	-3.857380212	-2.718417637
H	0.052869609	-3.281505082	-4.142983052
H	-0.853486585	-3.784033425	-2.717382863
C	-0.673166347	3.699870566	2.008008463
C	-0.392916678	4.206577332	-1.120405482
C	-1.551747754	2.902096157	2.997450924
H	-2.622842572	3.082598172	2.858588358
H	-1.356230312	1.827937811	2.921627140
H	-1.304743935	3.207946022	4.021722162
C	-0.973488906	5.198835719	2.188779118
H	-1.987436473	5.466142702	1.871539313

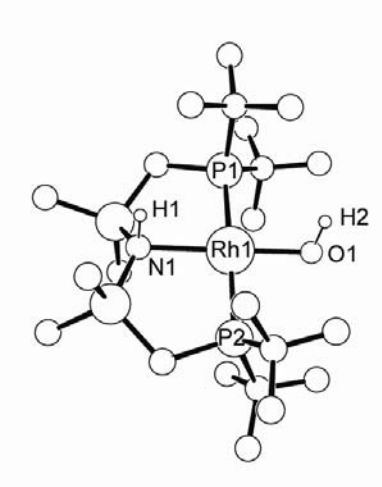
H	-0.266249559	5.824634826	1.639693582
H	-0.883309464	5.463813125	3.250560881
C	1.128168319	4.392680626	-0.947802808
H	1.529415145	4.893059366	-1.839185485
H	1.371378056	5.025639502	-0.088546911
H	1.607293831	3.412427373	-0.845929373
C	-0.626101691	3.469875651	-2.460016757
H	-0.050683984	2.541723995	-2.480284393
H	-1.684302952	3.241579371	-2.637353610
H	-0.292201280	4.117284715	-3.281527724
C	-1.102279208	5.572832245	-1.183006828
H	-0.709832394	6.129193233	-2.043788372
H	-2.184059138	5.483253028	-1.328463017
H	-0.931922176	6.185348624	-0.296613524
C	0.801348908	3.411453470	2.363153153
H	0.978224187	3.675151445	3.414217699
H	1.039247006	2.353643504	2.224228930
H	1.497876429	3.990696742	1.754541539
C	1.431442370	-1.148371421	-3.063806928
H	2.302198883	-1.776149173	-2.854079464
H	1.378766938	-1.021149321	-4.153356273
H	1.574154503	-0.171334104	-2.586859364
C	1.619581533	-3.877103003	-0.035671674
H	0.703951718	-4.469764500	0.070919478
H	2.007411231	-4.027595727	-1.045360363
H	2.359815573	-4.295174558	0.658967600
C	-4.139842445	1.088695014	-1.886823954
H	-3.211047160	0.965230774	-2.450612006
H	-4.746187153	0.188550194	-2.027255126
H	-4.692996919	1.925253583	-2.330115047
C	-5.429984933	1.580273015	0.879459831
H	-6.029812340	0.667864899	0.791894483
H	-5.260667570	1.764074517	1.947107185
H	-6.036613402	2.410378670	0.497782601
C	-2.939231436	-2.076170405	2.503748850
H	-3.012181957	-3.161944909	2.635089651
H	-2.013390510	-1.749050321	2.990670227
H	-3.779758872	-1.621089758	3.039689811
C	-4.580754646	-2.163131183	-0.115725649
H	-4.613045022	-1.957311259	-1.190676757
H	-5.453038066	-1.689220216	0.346004803
H	-4.692252951	-3.247348458	0.006915525
H	-3.328146008	3.723372035	0.897084854
H	-3.118729202	3.672584116	-0.834764826
H	-1.971411239	-2.986761462	-1.140357366
H	-1.270988047	-3.405733810	0.402781991
O	1.163591249	1.174664070	-0.883559920
H	-2.507939248	0.451211791	1.570231402
H	-0.324430328	0.422977018	1.463918663

Coordinates of $TS_{6\text{-}7}$

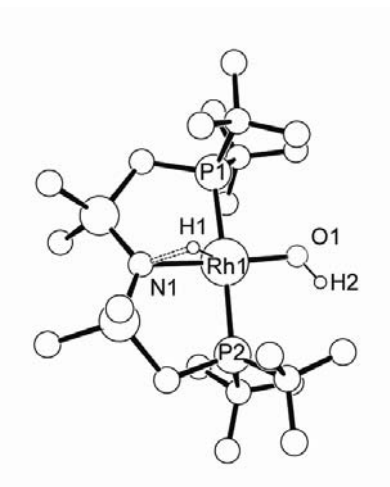
H	-0.126265823	0.008485695	-0.022583392
O	-0.056712135	0.004347511	1.742752548
Rh	1.361252097	-0.000258435	0.395261744
P	1.432620345	2.378233531	0.414647886
N	2.927486818	0.045593472	-1.467866040
P	1.375097171	-2.353720139	0.422830918
Si	3.307855673	-1.616885058	-2.020387542
C	2.661551511	-2.942628204	-0.810835738
Si	4.006524588	1.440798459	-1.184154689
C	2.904194877	2.893750742	-0.633933419
C	2.022908939	-3.011675608	2.107000981
C	-0.246025322	-3.227389190	-0.111828601
C	-0.539625173	-2.729816526	-1.544772386
H	-1.502522595	-3.139844814	-1.873052666
H	-0.605073520	-1.638853276	-1.582129322
H	0.216131942	-3.059863636	-2.265331466
C	-1.396660800	-2.765206912	0.813307907
H	-2.355546352	-2.931999579	0.305101185
H	-1.417770403	-3.344896944	1.740119737
H	-1.295198015	-1.705844822	1.083999458
C	3.274745371	-2.161277974	2.423047578
H	3.682115758	-2.468544341	3.394580545
H	4.072762383	-2.284703168	1.681662413
H	3.020776492	-1.099262405	2.483581885
C	2.425981304	-4.497556874	2.123208074
H	1.571045010	-5.163472449	1.993930843
H	2.877331345	-4.734035014	3.095382151
H	3.166826250	-4.745078096	1.355094965
C	-0.065374585	3.219637387	-0.443092010
C	1.788944897	3.133168864	2.145261800
C	-0.198954647	2.548942178	-1.830205097
H	0.670659098	2.730697386	-2.473667972
H	-0.342956182	1.469628334	-1.734463122
H	-1.071959913	2.966783947	-2.346757305
C	0.072191499	4.738708280	-0.655165868
H	0.990066167	5.008884355	-1.189111993
H	0.052546693	5.292099316	0.285158291
H	-0.771773523	5.096345250	-1.259247266
C	0.628457879	2.771302165	3.097056646
H	0.961126730	2.909544624	4.134558835
H	-0.234678094	3.425224636	2.945546082
H	0.311153516	1.729971158	2.941417703
C	3.058945724	2.414371106	2.651670756
H	2.912100499	1.331259240	2.682453489
H	3.941281184	2.632558241	2.041795849
H	3.276172078	2.753052407	3.672432847
C	2.048658740	4.650868954	2.162111737
H	2.395975617	4.941429361	3.162209417
H	2.819896130	4.964358004	1.449566555
H	1.143841105	5.226646742	1.957979838
C	-1.337058375	2.898810979	0.374614815
H	-2.222998738	3.037246527	-0.258606921
H	-1.322197314	1.870863648	0.756232963
H	-1.441446270	3.573763106	1.228131065
C	0.964010194	-2.720487308	3.191334307
H	0.154750642	-3.456113020	3.168286829
H	1.433683841	-2.786330176	4.181726507
H	0.534477364	-1.718302863	3.053951976
C	-0.172114848	-4.765499791	-0.140573128
H	0.669600079	-5.144138837	-0.731558831
H	-0.103648567	-5.191314422	0.862756242
H	-1.090287665	-5.159370841	-0.595550103
C	5.299103331	0.976188007	0.106752337
H	4.850304010	0.492706328	0.978661701
H	6.051262765	0.298586468	-0.309732707
H	5.828552489	1.870407682	0.455451878
C	4.883811117	1.986897574	-2.773391140
H	5.577749787	1.225669602	-3.145589067
H	4.166949988	2.203419600	-3.574120172
H	5.464010930	2.901516682	-2.599773080
C	2.513075464	-1.809117447	-3.724961260
H	2.630504718	-2.830345015	-4.105851241
H	1.440267355	-1.588865546	-3.706079220
H	2.980164337	-1.131221531	-4.448585294
C	5.173994086	-1.882585599	-2.171714421
H	5.684036988	-1.806548426	-1.205923287
H	5.646655649	-1.176457588	-2.862029017
H	5.362717246	-2.892432155	-2.555942356

H	2.543492659	3.403745148	-1.534745029
H	3.519992872	3.631262074	-0.105822769
H	3.525658775	-3.305230728	-0.243080773
H	2.296190342	-3.806865610	-1.378558216
H	2.112472726	0.361027200	-1.996355433

Optimized structure of (PNHP)Rh(OH) **(7)** and [from (PNHP)Rh(OH) to (PNP)RhH(OH)] **(TS_{7-4})**



7



TS_{7-4}

ΔE(SCF) (**7**): -55.78 kcal/mol

ΔE(SCF) (**TS_{7-4}**): -44.51 kcal/mol

Selected bond lengths (in Å) and bond angles (in ˚):

7		**TS_{7-4}**	
Rh1-P1	2.351	Rh1-P1	2.375
Rh1-P2	2.358	Rh1-P2	2.385
Rh1-N1	2.317	Rh1-N1	2.221
Rh1-O1	2.057	Rh1-O1	2.028
Rh1-H1	2.560	Rh1-H1	1.579
Rh1-H2	2.483	Rh1-H2	2.528
H2-O1	0.967	H2-O1	0.962
H1-H2	4.627	H1-H2	3.758
H1-N1	1.023	H1-N1	1.489
P1-Rh1-P2	174.50	P1-Rh1-P2	177.45
N1-Rh1-O1	178.53	N1-Rh1-O1	176.11

Coordinates of 7

Rh	-0.501047805	0.729521929	-0.111677736
P	-1.039199333	2.988708431	0.256848871
N	-2.629083709	0.180186583	0.622809281
P	-0.063169944	-1.516054294	-0.682554780
Si	-2.911970075	-1.600725220	0.678638299
C	-1.616234139	-2.520294503	-0.357186837
Si	-3.730773881	1.428166415	-0.051186478
C	-2.913595371	3.116992188	0.241583828
C	0.231200881	-1.785834020	-2.568217376
C	1.283940868	-2.407020875	0.369816908

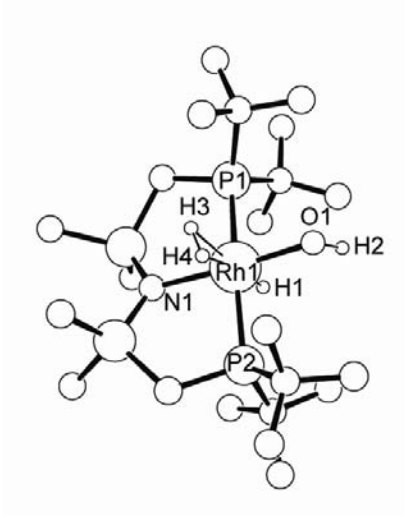
C	0.845342100	-2.207199848	1.837119544
H	1.631952458	-2.581251560	2.505126122
H	0.678705193	-1.146760201	2.055451616
H	-0.069812952	-2.758990512	2.073785676
C	2.641251452	-1.695970425	0.176103074
H	3.303045368	-1.942714382	1.017205854
H	3.143340840	-2.027889248	-0.735864809
H	2.516030395	-0.611186339	0.109045396
C	-0.887033745	-0.985447387	-3.272413531
H	-0.746466509	-1.047760157	-4.359554789
H	-1.887697124	-1.374492051	-3.051049949
H	-0.857080529	0.066048288	-2.973114056
C	0.160995491	-3.247739367	-3.047368164
H	0.986541387	-3.852085593	-2.666525687
H	0.221448516	-3.271028429	-4.143671065
H	-0.775741694	-3.740933362	-2.766167589
C	-0.559440010	3.684118917	1.994151497
C	-0.525675866	4.209740463	-1.146819380
C	-1.283093633	2.798706600	3.033307183
H	-2.372036578	2.911284388	3.007429808
H	-1.029723033	1.743071692	2.884299239
H	-0.955665805	3.080703680	4.042105578
C	-0.933530552	5.154703216	2.247335096
H	-1.982562259	5.366149255	2.013511451
H	-0.310005472	5.839206944	1.666890665
H	-0.779543289	5.398504574	3.307308499
C	1.001495311	4.415318568	-1.133308334
H	1.297748926	4.952510790	-2.044180174
H	1.329613207	5.022723130	-0.283760839
H	1.511468064	3.447019036	-1.122299194
C	-0.884369460	3.478352736	-2.460457797
H	-0.369546935	2.516111381	-2.517279002
H	-1.961482850	3.305113406	-2.561335478
H	-0.572068719	4.096914745	-3.312400094
C	-1.233146385	5.578321437	-1.137282398
H	-0.939283175	6.131992868	-2.038458992
H	-2.324682142	5.496756285	-1.156618025
H	-0.958240002	6.191675827	-0.277767165
C	0.954734210	3.485203838	2.215180641
H	1.214225858	3.763828597	3.245221619
H	1.232998932	2.436648155	2.068636655
H	1.562599791	4.098628340	1.546711094
C	1.583407766	-1.158661502	-2.970406423
H	2.423460644	-1.802673669	-2.695879536
H	1.613580258	-1.037828586	-4.061733505
H	1.728334587	-0.181391975	-2.498314158
C	1.451448837	-3.915108959	0.111121290
H	0.508920974	-4.469438033	0.180144740
H	1.894221195	-4.118363039	-0.866488613
H	2.129020714	-4.337465981	0.865378939
C	-4.019207407	1.118223170	-1.886130745
H	-3.069930135	1.052705261	-2.423821868
H	-4.578967578	0.195035759	-2.068169297
H	-4.601920002	1.940926011	-2.318150818
C	-5.394446213	1.444714676	0.861984325
H	-5.989341559	0.545563779	0.673315528
H	-5.257233428	1.533028773	1.946470487
H	-5.992949162	2.305959017	0.540449602
C	-2.860028558	-2.072091719	2.509442398
H	-2.894250892	-3.160126387	2.638004638
H	-1.955964049	-1.709483759	3.008305900
H	-3.725436129	-1.653658808	3.037144174
C	-4.608463877	-2.102232237	0.002134719
H	-4.747713442	-1.825047288	-1.047780875
H	-5.437189767	-1.679651240	0.578681271
H	-4.695671659	-3.194624392	0.058098263
H	-3.294650187	3.578174925	1.159233935
H	-3.226591509	3.776927867	-0.574361002
H	-2.080757195	-2.747978386	-1.323420603
H	-1.388245455	-3.490639841	0.099970045
O	1.407103232	1.203187994	-0.716406293
H	-2.400615110	0.452332802	1.581906515
H	1.815107608	1.606017158	0.062237019

Coordinates of $TS_{7\text{-}4}$

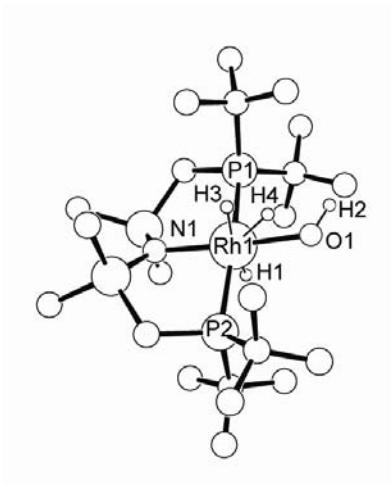
H	-0.068844419	-0.053167029	0.219996731
N	-0.093989267	0.005449228	1.707348978
Rh	1.509093464	-0.006245793	0.169861519
P	1.376606604	-2.376462987	0.084647947
P	1.628617714	2.368004317	0.360392793
Si	-0.864896359	1.530431582	2.064463330
C	0.377238400	2.916906330	1.626322948
Si	-0.296862841	-1.484905553	2.597974909
C	0.572206447	-2.917324327	1.669158413
C	3.307842919	2.918683527	1.125457507
C	1.191837687	3.395976096	-1.205075542
C	-0.302096830	3.133455926	-1.495063627
H	-0.567717977	3.597490965	-2.453280323
H	-0.509457628	2.061425181	-1.571638103
H	-0.960028034	3.559468323	-0.733154571
C	1.989865420	2.882241270	-2.421214582
H	1.688992736	3.445493061	-3.313964605
H	3.069072190	3.012457225	-2.306748861
H	1.780997972	1.825363561	-2.611304239
C	3.558172048	1.939159951	2.297040798
H	4.520805084	2.180882116	2.765904839
H	2.788929937	2.007816124	3.073205442
H	3.592524614	0.901912692	1.952891692
C	3.331879368	4.356069935	1.680528373
H	3.265666012	5.112988350	0.897415945
H	4.279852350	4.516882595	2.209760011
H	2.527181484	4.542249949	2.398456209
C	0.232201265	-3.046894135	-1.301132200
C	3.073904737	-3.275470391	0.083044122
C	-1.205585139	-2.590566282	-0.970095475
H	-1.597776951	-3.063089668	-0.064912399
H	-1.267534833	-1.505358479	-0.847957422
H	-1.868188597	-2.871614891	-1.798392154
C	0.235897107	-4.581490755	-1.430950730
H	0.001981888	-5.080477832	-0.484263364
H	1.193753602	-4.962864237	-1.792787665
H	-0.530062204	-4.885656033	-2.156318252
C	3.705260555	-3.236990377	-1.323394300
H	4.747394293	-3.575739472	-1.252508197
H	3.197563444	-3.909813630	-2.021370237
H	3.695526790	-2.218539933	-1.720110616
C	3.972367954	-2.448775487	1.032177796
H	4.119628775	-1.441188573	0.636824071
H	3.555979179	-2.374340694	2.043639547
H	4.951182024	-2.938992638	1.116850615
C	3.017074284	-4.729522582	0.592107194
H	4.035548603	-5.138509352	0.599112969
H	2.634330415	-4.804058035	1.614398643
H	2.409997487	-5.377792051	-0.042793437
C	0.636530625	-2.400953347	-2.643020462

H	-0.093828684	-2.681955065	-3.413174619
H	0.659593574	-1.311495162	-2.560241873
H	1.621193413	-2.726238197	-2.983057823
C	4.444058673	2.732259140	0.100850688
H	4.403175870	3.476833183	-0.700432259
H	5.410380535	2.857635146	0.605891950
H	4.418575155	1.729786253	-0.338080069
C	1.412051399	4.912217569	-1.051013171
H	0.940091317	5.315919377	-0.149444764
H	2.473752948	5.171329657	-1.026745398
H	0.971808749	5.433002203	-1.911448993
C	0.519700032	-1.404908958	4.309529997
H	1.576529990	-1.128397688	4.221586627
H	0.038431316	-0.670917856	4.963618606
H	0.468003493	-2.378395448	4.813406217
C	-2.121286772	-1.952774976	2.856169653
H	-2.653451415	-1.203630123	3.453359936
H	-2.653162502	-2.049626791	1.903484986
H	-2.208900756	-2.909193645	3.386565125
C	-2.491269372	1.753031807	1.113466143
H	-2.912418759	2.756492850	1.252973959
H	-2.370087481	1.586931807	0.038760384
H	-3.235244441	1.032384104	1.473068355
C	-1.276697611	1.754957020	3.904403051
H	-0.381370955	1.698490874	4.532365129
H	-1.989594339	1.008729661	4.271259147
H	-1.731583670	2.740590836	4.063626716
H	-0.091450770	-3.777131964	1.523551941
H	1.373432739	-3.260642041	2.332085741
H	0.921801581	3.130914027	2.552336073
H	-0.111651755	3.853414901	1.336998548
O	3.013411124	-0.138550595	-1.184121843
H	3.087810243	0.681642083	-1.681277853

Optimized structure of (PNP)RhH(H_2)(OH) **(8)** and [(PNP)RhH(H_2)(OH) to (PNP)RhH_2(HOH)] **(TS_{8-9})**



8



TS_{8-9}

ΔE(SCF) (**8**): -59.63 kcal/mol

ΔE(SCF) (**TS_{8-9}**) : -49.40 kcal/mol

Selected bond lengths (in Å) and bond angles (in ˚):

8		**TS_{8-9}**	
Rh1-P1	2.406	Rh1-P1	2.413
Rh1-P2	2.402	Rh1-P2	2.424
Rh1-N1	2.180	Rh1-N1	2.129
Rh1-O1	2.075	Rh1-O1	2.227
Rh1-H1	1.525	Rh1-H1	1.559
Rh1-H3	1.987	Rh1-H3	1.929
Rh1-H4	1.986	Rh1-H4	1.903
H3-H4	0.767	H3-H4	1.023
H4-O1	2.701	H4-O1	1.274
H2-O1	0.964	H2-O1	0.965

P1-Rh1-P2	169.05	P1-Rh1-P2	171.08
N1-Rh1-O1	172.91	N1-Rh1-O1	167.32
H3-Rh1-H4	22.26	H3-Rh1-H4	30.96

Coordinates of 8

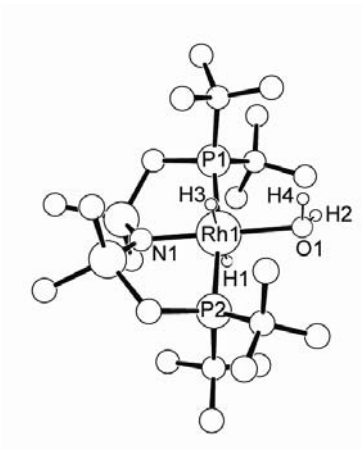
Rh	-0.605605557	0.749099122	-0.473170559
P	-1.062815243	3.006716444	0.206529516
N	-2.585391104	0.208730211	0.262109151
P	-0.058318802	-1.582379810	-0.709002326
Si	-2.890848150	-1.438834864	0.651525030
C	-1.592920749	-2.521601021	-0.276257278
Si	-3.780440462	1.445968689	0.185725030
C	-2.905581067	3.166263697	0.165631063
C	0.415026346	-2.193686710	-2.478335329
C	1.265884134	-2.167608824	0.564827541
C	0.633788691	-2.091697255	1.970423930
H	1.406083178	-2.313629908	2.717927141
H	0.236960357	-1.096432383	2.186151165
H	-0.170952228	-2.818493643	2.105061851
C	2.489805495	-1.227615020	0.550780234
H	3.218379086	-1.581586373	1.291715343
H	2.991243094	-1.193376620	-0.417910161
H	2.204597726	-0.209101658	0.825755759
C	-0.555783209	-1.517270584	-3.471529075
H	-0.410860312	-1.958780932	-4.465300890
H	-1.609488464	-1.659696666	-3.204896769
H	-0.353617802	-0.448235143	-3.553453045
C	0.274047490	-3.719406827	-2.664052622
H	0.960130549	-4.295463108	-2.043783262
H	0.495351457	-3.966258509	-3.710264467
H	-0.742638841	-4.068430916	-2.458285918
C	-0.580533888	3.359465877	2.031534787
C	-0.415970332	4.399091962	-0.955709937
C	-1.449916306	2.436109268	2.914165071
H	-2.498601971	2.745904077	2.919802976
H	-1.407845711	1.395085343	2.583976437
H	-1.087238665	2.488939588	3.948653898
C	-0.833759942	4.819393977	2.456830438
H	-1.852342727	5.150636663	2.230179010
H	-0.132405886	5.515093485	1.989014098
H	-0.699063045	4.903550088	3.542939170
C	1.096365962	4.616586340	-0.754323162
H	1.466802646	5.287197719	-1.540836099
H	1.328888875	5.088589324	0.204658057
H	1.629057320	3.665639127	-0.842165020
C	-0.617444403	3.886996952	-2.399670707
H	0.003485900	3.005931233	-2.579349543
H	-1.666298354	3.652712284	-2.618315630
H	-0.313660389	4.674694361	-3.101039702
C	-1.172477852	5.734163023	-0.801765462
H	-0.796696610	6.438352105	-1.555223686
H	-2.248158673	5.624829589	-0.970161531
H	-1.029653104	6.197236111	0.175825107
C	0.900933124	3.010908325	2.285549921
H	1.129509087	3.178982943	3.345819732
H	1.105700400	1.961399358	2.060339323
H	1.588329544	3.623644712	1.698998525
C	1.839877295	-1.726465446	-2.837909134
H	2.609740985	-2.291496237	-2.304386881
H	2.010247442	-1.886400302	-3.910688969
H	1.956708425	-0.659137702	-2.620874521
C	1.740132686	-3.618199536	0.345865500
H	0.906700362	-4.325732219	0.290374682
H	2.348839377	-3.726851173	-0.554542617
H	2.365017094	-3.919040621	1.196633653
C	-4.823571847	1.412322152	-1.408255214
H	-4.190442404	1.462007490	-2.302495992
H	-5.412086845	0.490534553	-1.477088031
H	-5.525517662	2.255257695	-1.451940316
C	-5.022899508	1.447486386	1.629111780
H	-5.632843465	0.536798302	1.636682356
H	-4.522315058	1.512363108	2.601203519
H	-5.714083488	2.296191997	1.549554820
C	-2.876933241	-1.824434954	2.515528559
H	-2.913284952	-2.902921717	2.716857838
H	-2.001248917	-1.414043980	3.026428974
H	-3.762805998	-1.377821802	2.983577599
C	-4.568247550	-2.101822485	0.026991866
H	-4.669769446	-1.983541465	-1.058263534
H	-5.419378698	-1.592791490	0.493801740
H	-4.670161677	-3.170786524	0.254960169
H	-3.275562440	3.832949793	0.952924426
H	-3.163861904	3.643512801	-0.786682670
H	-2.075406041	-2.782653199	-1.226118497
H	-1.371266366	-3.470734180	0.225227654
O	1.168909572	1.289689175	-1.403458017
H	1.881970668	1.200468962	-0.760325513
H	0.034178645	0.583972699	0.900840401
H	-1.419458361	1.385761752	-2.168907922
H	-1.482173939	0.625953409	-2.252487937

Coordinates of $TS_{8\text{-}9}$

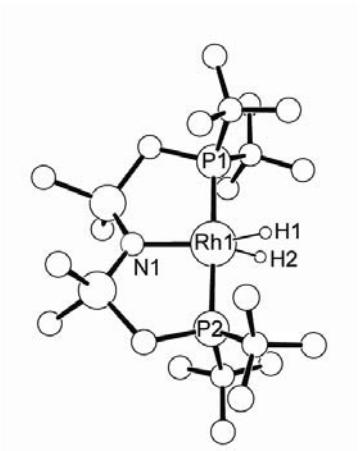
H	-0.021211316	-0.041557875	0.443640025
O	-0.040162411	-0.006202816	1.716789593
Rh	1.898985896	0.004760145	0.622021702
P	2.056210026	-2.403267145	0.853327294
N	3.492827865	-0.146352258	-0.781361245
P	2.115559578	2.400554545	0.433387418
Si	4.670587561	1.108334135	-0.745272109
C	3.717432162	2.743693760	-0.431221343
Si	3.337644482	-1.508954981	-1.828707875
C	2.684590094	-2.988542320	-0.787707850
C	0.817938177	3.294226421	-0.686026085
C	2.285960069	3.296864388	2.131577402
C	3.624107547	2.855183192	2.763861177
H	3.679047179	3.256031113	3.782829295
H	3.700612070	1.767359359	2.824094371
H	4.493031221	3.232157821	2.218523542
C	1.158117440	2.845526713	3.080979306
H	1.297023367	3.324212787	4.058226400
H	0.165942845	3.136333574	2.723077148
H	1.176972782	1.763161256	3.233020918

C	0.800199129	2.520624352	-2.026330860
H	0.017140301	2.947040467	-2.666486225
H	1.747812795	2.608195090	-2.566942466
H	0.587091124	1.460196002	-1.882947486
C	1.158558715	4.768436892	-0.993456095
H	1.003959620	5.428017712	-0.138380500
H	0.498765723	5.120344966	-1.795948740
H	2.186135157	4.898105855	-1.343205749
C	3.406210970	-2.924182033	2.126054808
C	0.433536333	-3.415341764	1.127401142
C	4.758303168	-2.414293529	1.582248474
H	5.079794116	-2.967696502	0.694672801
H	4.715693021	-1.356221833	1.324005563
H	5.526932132	-2.555257287	2.352859911
C	3.529853789	-4.444124474	2.345546783
H	3.636028776	-4.996357320	1.406668042
H	2.683267727	-4.857364238	2.898734471
H	4.430744108	-4.641063786	2.940851273
C	-0.062804459	-3.254031016	2.577812309
H	-1.065615721	-3.692264504	2.663788125
H	0.576707935	-3.777925633	3.293965085
H	-0.130256641	-2.198792340	2.856807870
C	-0.643661175	-2.834215054	0.184267965
H	-0.927427141	-1.825216207	0.479103429
H	-0.322637625	-2.811820667	-0.862153292
H	-1.535444780	-3.471297396	0.240901547
C	0.580357919	-4.914307994	0.784770591
H	-0.406646313	-5.386085706	0.870204226
H	0.924665594	-5.074786732	-0.241213393
H	1.252563818	-5.448297842	1.454256119
C	3.142398576	-2.238411088	3.482490135
H	3.970125060	-2.467633869	4.165255784
H	3.084292231	-1.153270674	3.369635045
H	2.219351647	-2.579648800	3.956047641
C	-0.586483424	3.219148778	-0.056628365
H	-0.668082384	3.831616143	0.847023616
H	-1.326707001	3.601298551	-0.771405472
H	-0.871118552	2.191387543	0.185621782
C	2.283900788	4.834270137	2.024775050
H	3.006006371	5.204632334	1.290523136
H	1.297582080	5.228206338	1.764700287
H	2.556441147	5.261993188	2.998176091
C	2.089392851	-1.260828417	-3.236378938
H	1.098135358	-1.013743381	-2.841860883
H	2.399627301	-0.439606639	-3.892994302
H	1.992596192	-2.161054398	-3.856253531
C	4.965187039	-2.075942103	-2.635679436
H	5.285289051	-1.404608016	-3.438988205
H	5.784665612	-2.153282227	-1.912392064
H	4.826063032	-3.067769835	-3.084298578
C	6.030070375	0.946093463	0.575100618
H	6.677756566	1.832661554	0.574702933
H	5.630755741	0.827286679	1.586756965
H	6.666748948	0.077405520	0.368841324
C	5.596501074	1.360604246	-2.388203137
H	4.912628189	1.451038466	-3.239001774
H	6.292898480	0.544632620	-2.602442321
H	6.186946360	2.284372419	-2.341133746
H	3.439552256	-3.772374230	-0.665982577
H	1.848046698	-3.443041962	-1.327943721
H	3.495459611	3.175087826	-1.412499053
H	4.306518577	3.490659699	0.110295831
H	-0.283335226	0.898914437	1.948185725
H	3.017478363	0.119910614	1.701237435
H	0.366487154	-0.122257583	-0.499624545

Optimized structure of *trans* $(PNP)Rh(H)_2(OH_2)$ **(9)** and $(PNP)Rh(H)_2$ **(10)**



9



10

ΔE(SCF)(**9**): -56.71 kcal/mol

ΔE(SCF)(**10**): -84.77 kcal/mol

Selected bond lengthss (in Å) and bond angles (in ˚):

9		**10**	
Rh1-P1	2.424	Rh1-P1	2.370

Rh1-P2	2.386	Rh1-P2	2.372
Rh1-N1	2.122	Rh1-N1	2.155
Rh1-O1	2.262	Rh1-H1	1.557
Rh1-H1	1.666	Rh1-H2	1.539
Rh1-H3	1.666	H1-H2	1.638
Rh1-H4	2.596	P1-Rh1-P2	178.57
H3-H4	2.456	P1-Rh1-H1	152.99
H4-O1	0.965	P1-Rh1-H2	143.11
H2-O1	0.967		
P1-Rh1-P2	173.34		
N1-Rh1-O1	175.89		
H3-Rh1-H4	66.26		
H1-Rh1-H3	178.75		

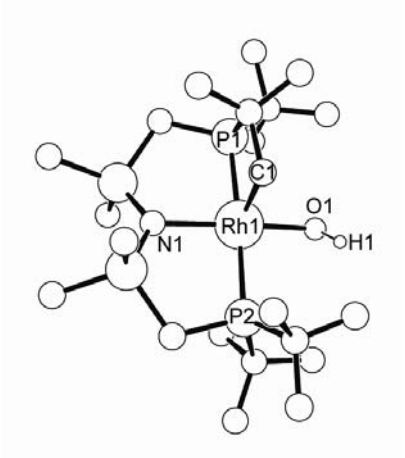
Coordinates of 9

H	-0.441794589	0.287969995	0.885787163
O	0.249733764	0.008016620	1.498647345
Rh	2.002277338	-0.024999865	0.069073759
P	2.080518558	-2.409581885	0.123729094
N	3.564882633	-0.148314908	-1.361409937
P	2.156312839	2.385069245	-0.143386973
Si	4.726960702	1.115299526	-1.285769278
C	3.707514781	2.730806477	-1.092366750
Si	3.338612839	-1.408179425	-2.513835750
C	2.599665698	-2.914656081	-1.578852765
C	0.786299000	3.263928335	-1.197718369
C	2.403545130	3.340220875	1.528651589
C	3.817719476	3.026784971	2.060788768
H	3.914377130	3.443531119	3.071628362
H	3.988512586	1.949663238	2.113864837
H	4.603249606	3.476432849	1.448405641
C	1.405121315	2.821992852	2.585867411
H	1.490667883	3.420289015	3.501741989
H	0.361076501	2.891491061	2.260393264
H	1.657599191	1.791662654	2.863192528
C	0.635563402	2.435292525	-2.491978628
H	-0.190115085	2.849708977	-3.084618719
H	1.535854743	2.477169017	-3.113396584
H	0.431898574	1.385395943	-2.273725545
C	1.113885497	4.713351020	-1.617006941
H	1.052265714	5.427232358	-0.796770959
H	0.390456828	5.031137800	-2.378465064
H	2.108065392	4.796218391	-2.065514233
C	3.432715809	-3.130885430	1.294857919
C	0.414786587	-3.363811151	0.382103670
C	4.787924707	-2.629741435	0.749590723
H	5.055162108	-3.112060664	-0.195900772
H	4.778112808	-1.550071590	0.594311300
H	5.573825421	-2.873811817	1.476086755
C	3.474060776	-4.669728109	1.361452467
H	3.516274147	-5.134449206	0.370976532
H	2.621928481	-5.087023071	1.904627350
H	4.379346117	-4.975920923	1.901857093
C	-0.025860362	-3.319631499	1.858907938
H	-1.045363869	-3.718382243	1.943772835
H	0.613036433	-3.936267277	2.496986262
H	-0.029830541	-2.299428502	2.249977708
C	-0.665467445	-2.665484923	-0.472607052
H	-0.835976032	-1.635805353	-0.159955568
H	-0.405595674	-2.639216316	-1.534818626
H	-1.607629149	-3.219779876	-0.371843244
C	0.473419037	-4.835942644	-0.084185847
H	-0.528970682	-5.273035895	0.011654657
H	0.766577905	-4.929083514	-1.133212679
H	1.150843993	-5.447084929	0.510976147
C	3.254998152	-2.561484615	2.717214943
H	4.094040999	-2.893354751	3.342278648
H	3.252559875	-1.468486860	2.693686382
H	2.334429410	-2.902423779	3.197567734
C	-0.557925473	3.234221387	-0.446792825
H	-0.550340152	3.850730691	0.457257778
H	-1.355336454	3.617770343	-1.095214760
H	-0.838540726	2.211607868	-0.169234806
C	2.264097350	4.870699879	1.420966068
H	2.900902170	5.290094124	0.636837298
H	1.234280609	5.187634130	1.237046700
H	2.575774061	5.324065528	2.371313256
C	2.147070012	-1.010942751	-3.939194167
H	1.166959379	-0.712328692	-3.555958516
H	2.530652613	-0.188683934	-4.555051134
H	2.008765222	-1.878009435	-4.598250342
C	4.951271495	-2.011656892	-3.329948580
H	5.360140665	-1.283011363	-4.036732167
H	5.730114908	-2.236365582	-2.592635736
H	4.754219928	-2.932383276	-3.893906667
C	6.029349435	0.972274687	0.088301337
H	6.604641119	1.901223135	0.192139626
H	5.589048863	0.732439419	1.058974824
H	6.740996762	0.175563982	-0.159634083
C	5.729338905	1.353256349	-2.888999987
H	5.089840895	1.420364504	-3.776316809
H	6.446803848	0.543089921	-3.052964299
H	6.305181784	2.285735593	-2.826926527
H	3.283715582	-3.769993089	-1.554182460
H	1.704481424	-3.241439332	-2.117482082
H	3.416811065	3.008207344	-2.110972319
H	4.257145867	3.582183619	-0.678791013
H	0.392542884	0.748802660	2.103718242
H	3.118254504	0.142472085	1.295275613
H	0.864368739	-0.209563653	-1.133740757

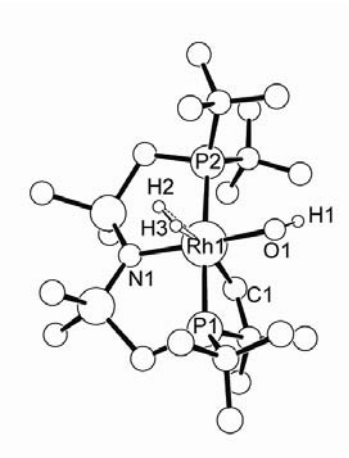
Coordinates of 10

Rh	-0.526369302	0.704294785	-0.202771184
P	-1.076781433	2.976145140	0.198474099
N	-2.592888579	0.174902138	0.100038243
P	-0.023408886	-1.570414507	-0.639255821
Si	-2.910405557	-1.467055526	0.535682171
C	-1.555144970	-2.558616044	-0.274843062
Si	-3.793192733	1.417101859	0.048138210
C	-2.918191252	3.131695415	0.023104437
C	0.310007089	-1.916764182	-2.503196596
C	1.337398383	-2.335364623	0.476499014
C	0.816004553	-2.213362406	1.925949829
H	1.600831218	-2.543978315	2.617770051
H	0.562245567	-1.177391021	2.170603481
H	-0.065096079	-2.834166191	2.109038468
C	2.643768597	-1.521728762	0.378059342
H	3.360449317	-1.907827563	1.113955420
H	3.113865527	-1.594529580	-0.604795976
H	2.471229166	-0.464325630	0.593044808
C	-0.772961669	-1.114408636	-3.260730620
H	-0.644262478	-1.263544717	-4.340555077
H	-1.787310214	-1.433045607	-3.000672051
H	-0.696651105	-0.045086779	-3.045222195
C	0.194669046	-3.399097175	-2.911013847
H	0.979833614	-4.019450669	-2.475249106
H	0.285940418	-3.475014162	-4.002151243
H	-0.770329938	-3.835463942	-2.638239226
C	-0.713387373	3.542103315	1.998048845
C	-0.387445653	4.233844096	-1.084063012
C	-1.605799696	2.669094113	2.908802197
H	-2.666024794	2.916113122	2.808465115
H	-1.482441012	1.603900938	2.693701052
H	-1.325694439	2.843041299	3.955329998
C	-1.025548126	5.025698482	2.269977854
H	-2.028665160	5.312541072	1.938762080
H	-0.301912293	5.692172678	1.792790801
H	-0.972896719	5.213053212	3.350374572
C	1.128187963	4.428684702	-0.890820175
H	1.535306376	4.985237271	-1.744568669
H	1.357377595	5.006583273	0.009251608
H	1.655464320	3.471672482	-0.832569116
C	-0.623438421	3.596016095	-2.472865773
H	-0.112690690	2.634064386	-2.562125712
H	-1.686059611	3.434370360	-2.682238229
H	-0.235882358	4.269205087	-3.248318419
C	-1.088452993	5.608026075	-1.060233074
H	-0.712018649	6.214986595	-1.893614418
H	-2.171892011	5.524493991	-1.184973946
H	-0.897279305	6.164206202	-0.141265482
C	0.756500286	3.256659599	2.366333301
H	0.921000739	3.527606521	3.417055529
H	0.993581997	2.196705333	2.246592954
H	1.463926090	3.831942434	1.764560180
C	1.691807481	-1.382024628	-2.925226679
H	2.507544813	-2.008476025	-2.553312133
H	1.759697951	-1.380929148	-4.020550462
H	1.854333364	-0.357255681	-2.578507774
C	1.636147308	-3.816340715	0.173644702
H	0.731375174	-4.431456832	0.144889895
H	2.165786717	-3.941379094	-0.774611744
H	2.283732456	-4.223706470	0.960756226
C	-4.847556199	1.361904175	-1.535156152
H	-4.214937574	1.425050661	-2.428633430
H	-5.417038539	0.428323632	-1.604152747
H	-5.566539451	2.190314196	-1.573525089
C	-5.021651115	1.415238397	1.506018163
H	-5.637208075	0.508221455	1.506640579
H	-4.514179755	1.464580762	2.475358142
H	-5.708330546	2.268892867	1.444296106
C	-2.913198009	-1.767989548	2.412747670
H	-3.025299854	-2.832078724	2.657268959
H	-1.992311497	-1.408330935	2.882908881
H	-3.748526582	-1.235184352	2.882002913
C	-4.563295045	-2.163732429	-0.114156784
H	-4.637558175	-2.068719606	-1.203838508
H	-5.430001453	-1.651851800	0.319542320
H	-4.662431764	-3.228406010	0.132818807
H	-3.337415734	3.819413876	0.766162251
H	-3.119783012	3.580753847	-0.955093842
H	-1.968384297	-2.915734422	-1.223792123
H	-1.325175097	-3.452641953	0.314426681
H	0.686221791	1.108347372	-1.092114008
H	0.809662083	0.916714200	0.530263915

Optimized structure of (PNP*) Rh (OH) **(11)** and (PNP*) Rh (OH)(H_2) **(12)**



11



12

ΔE(SCF)(**11**): -14.67 kcal/mol

ΔE(SCF)(**12**): 20.30 kcal/mol

Selected bond lengthss (in Å) and bond angles (in °):

	11		**12**
Rh1-P1	2.319	Rh1-P1	2.326
Rh1-P2	2.439	Rh1-P2	2.490
Rh1-N1	2.169	Rh1-N1	2.182
Rh1-O1	2.059	Rh1-O1	2.076
Rh1-C1	2.060	Rh1-C1	2.082
C1-H1	3.014	C1-H1	2.976
O1-H1	0.965	Rh1-H2	2.093
P1-Rh1-P2	173.99	Rh1-H3	2.036
N1-Rh1-O1	170.90	O1-H1	0.965
C1-Rh1-O1	93.08	H2-H3	0.761
		H2-Rh1-H3	21.19
		P1-Rh1-P2	170.45
		N1-Rh1-O1	174.64
		C1-Rh1-O1	94.20

Coordinates of 11

Rh	-0.575191366	0.841509192	-0.333580796
P	-1.269247233	3.033242140	-0.027862716
N	-2.587902199	0.241750512	0.210450979
P	0.044761601	-1.515475251	-0.430292208
Si	-2.779079264	-1.335054782	0.875727826
C	-1.472429943	-2.474433309	0.044723142
Si	-3.809997002	1.363319393	-0.256173443
C	-3.111137456	3.143598621	-0.025587853
C	0.306690846	-1.921130717	-2.293203550
C	1.464031412	-2.231677153	0.645536689
C	0.990742256	-2.203277296	2.115462565
H	1.815065618	-2.533026663	2.760571934
H	0.707007302	-1.196636764	2.431823812
H	0.145068605	-2.870422632	2.299681654
C	2.711263693	-1.329177135	0.540446863
H	3.500020158	-1.724778843	1.193142537
H	3.116414955	-1.281120081	-0.472141932
H	2.493219705	-0.310037262	0.872897845
C	-0.772383092	-1.085675416	-3.023653250
H	-0.713584652	-1.282118370	-4.102037833
H	-1.788707152	-1.326167813	-2.697016313
H	-0.608571272	-0.011563990	-2.879126923
C	0.119103604	-3.403807795	-2.667774583
H	0.885920044	-4.048677279	-2.234724679
H	0.186577378	-3.503449338	-3.758679313
H	-0.858082495	-3.794430200	-2.369034959
C	-0.651014565	2.842885373	1.779024319
C	-0.626717678	4.531410089	-1.014397207

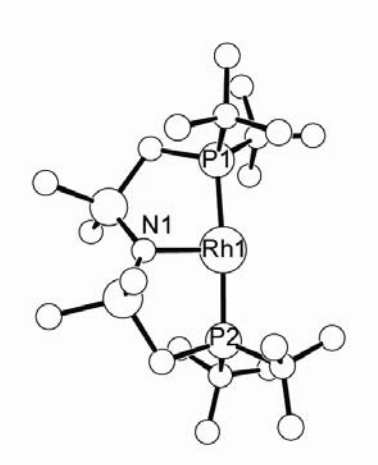
C	-1.814707862	2.797908043	2.781647884
H	-2.313406958	3.769082416	2.873633905
H	-2.555472825	2.042842473	2.510709222
H	-1.420403417	2.535932990	3.771546743
C	0.395962267	3.854673799	2.269377702
H	-0.002423672	4.874007092	2.313615485
H	1.289953653	3.857518839	1.644658313
H	0.705228649	3.578798653	3.285733590
C	0.912984174	4.618478984	-0.972021186
H	1.247932093	5.295508358	-1.768562602
H	1.270914880	5.035485567	-0.028116910
H	1.360830144	3.631713345	-1.130722180
C	-1.043975559	4.259601198	-2.478240741
H	-0.552426915	3.360414137	-2.860423211
H	-2.125887804	4.144273333	-2.600907503
H	-0.733864741	5.107802611	-3.100961423
C	-1.259765409	5.844963830	-0.518170970
H	-0.896312530	6.677893857	-1.134010959
H	-2.352010336	5.835376919	-0.587784529
H	-0.987449796	6.062397224	0.519561937
C	-0.035590742	1.437580656	1.563465535
H	-0.411380697	0.704167173	2.277810552
H	1.931333594	1.002184505	-0.678404812
H	1.057058685	1.466977837	1.570475384
C	1.687143856	-1.428232637	-2.768690331
H	2.501701637	-2.056389315	-2.394513981
H	1.725395502	-1.475824385	-3.864857575
H	1.851906273	-0.389466196	-2.464595386
C	1.843074935	-3.679023830	0.279935578
H	0.974362854	-4.345113580	0.270313407
H	2.335128184	-3.741956509	-0.693850347
H	2.547390980	-4.069569442	1.026259547
C	-4.281703153	1.237656097	-2.093839685
H	-3.405636497	1.385062269	-2.736662793
H	-4.689525076	0.246424964	-2.324533485
H	-5.036631526	1.980961739	-2.379673540
C	-5.428294149	1.291831484	0.742499886
H	-6.001021891	0.380416743	0.544011397
H	-5.245478169	1.342387755	1.822075461
H	-6.070804760	2.140832489	0.477140535
C	-2.586377495	-1.422055987	2.766882714
H	-2.655392464	-2.454837038	3.131838521
H	-1.639515745	-1.006671184	3.124110890
H	-3.391356600	-0.852741322	3.247363147
C	-4.451767890	-2.172469888	0.511263006
H	-4.709177304	-2.131512005	-0.553453359
H	-5.275609846	-1.717663477	1.070818222
H	-4.413488692	-3.230755499	0.799445892
H	-3.486758040	3.634279186	0.877024364
H	-3.421271471	3.758683076	-0.876613672
H	-1.941070058	-2.833452415	-0.877966789
H	-1.230013720	-3.367028263	0.631240671
O	1.215447270	1.443112448	-1.152157135

Coordinates of 12

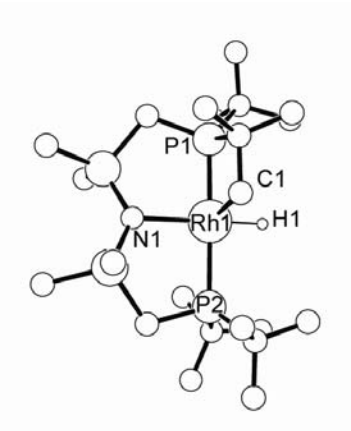
Rh	-0.640317864	0.876961614	-0.412904383
P	-1.268022702	3.064906161	0.063449746
N	-2.637202631	0.213967427	0.166142509
P	0.091391291	-1.500601174	-0.514107748
Si	-2.923373691	-1.460178518	0.446458119
C	-1.479735035	-2.467880437	-0.332638935
Si	-3.863542004	1.420771480	0.153639262
C	-3.048868271	3.116751150	0.550576895
C	0.810102277	-2.085951748	-2.216533669
C	1.242667366	-2.149325251	0.889795115
C	0.441023656	-2.078593092	2.207372436
H	1.107046334	-2.331451759	3.042012101
H	0.032515083	-1.085645000	2.397116613
H	-0.383968764	-2.794590208	2.220346595
C	2.490618074	-1.249206677	1.022942614
H	3.073176998	-1.569978765	1.896089722
H	3.147206406	-1.310159819	0.153243629
H	2.225360885	-0.200808377	1.171782225
C	0.009473593	-1.380154533	-3.331377304
H	0.314060782	-1.794463005	-4.300370977
H	-1.072269729	-1.533869379	-3.242381236
H	0.215554803	-0.309939954	-3.342856389
C	0.686047853	-3.606646620	-2.449836043
H	1.264519705	-4.203642800	-1.745741925
H	1.059429331	-3.836268891	-3.455923336
H	-0.352796407	-3.947054877	-2.407013954
C	-0.219838433	2.905154356	1.635217800
C	-0.964034648	4.587445053	-1.042849375
C	-0.823996222	3.446657174	2.937894881
H	-0.939729768	4.537019822	2.913620590
H	-1.796902807	3.003262103	3.168009243
H	-0.154782198	3.203772421	3.773282501
C	1.195587530	3.472415089	1.445392916
H	1.203574071	4.567223346	1.430587413
H	1.645611326	3.094286805	0.525443871
H	1.815120857	3.151955088	2.293113690
C	0.493439559	4.630949996	-1.551587356
H	0.548793098	5.317084722	-2.406475758
H	1.175593487	5.009387499	-0.787655423
H	0.849722039	3.641951833	-1.854377143
C	-1.895059430	4.436670800	-2.267129680
H	-1.635337872	3.554556268	-2.861088093
H	-2.953504020	4.368910902	-1.999363256
H	-1.776258310	5.314792787	-2.913770720
C	-1.308391378	5.882541512	-0.281111361
H	-1.151760695	6.745762344	-0.940933391
H	-2.350935603	5.907246918	0.052021322
H	-0.667372682	6.018704138	0.595848086
C	-0.184701437	1.352711483	1.562322415
H	-0.979796508	0.902861898	2.162242748
H	1.877179460	1.128366914	-0.572522548
H	0.788213672	0.964666631	1.870888925
C	2.276724551	-1.634490286	-2.365079582
H	2.958012164	-2.197502174	-1.721612132
H	2.600773299	-1.804371286	-3.400057943
H	2.372610619	-0.564823264	-2.153546528
C	1.704484921	-3.609536339	0.713709755
H	0.867468515	-4.294740834	0.546727797
H	2.418302220	-3.727804984	-0.104313243
H	2.209987905	-3.933386904	1.632815275
C	-4.718626271	1.625416331	-1.534233455
H	-3.995437845	1.842477274	-2.328584654
H	-5.239530549	0.702874325	-1.815182674
H	-5.460587368	2.433920527	-1.526575521
C	-5.241970935	1.187632000	1.447109994
H	-5.825400462	0.275681251	1.278209819
H	-4.830627311	1.131934518	2.461630466
H	-5.945212875	2.029425162	1.419025800
C	-3.144297109	-1.924703379	2.279675792
H	-3.175587301	-3.011414655	2.430597343
H	-2.352255860	-1.517527242	2.914906692
H	-4.094490900	-1.519715057	2.647872986
C	-4.475180916	-2.143522628	-0.430356416
H	-4.433435924	-1.963827966	-1.511275886

H	-5.399895178	-1.687758351	-0.058581021
H	-4.566873993	-3.226497464	-0.277186709
H	-3.143513990	3.358272749	1.612934178
H	-3.559444663	3.914539723	0.002527749
H	-1.818435341	-2.690383250	-1.351876494
H	-1.320427600	-3.437885025	0.152474185
O	1.198215507	1.501432153	-1.147860785
H	-1.479992247	0.549158675	-2.302011732
H	-1.201331433	1.256805591	-2.332796413

Optimized structure of (PNP)Rh **(13)** and (PNP*)Rh(H) (**14**)



13



14

ΔE(SCF)(**13**): 0.00 kcal/mol

ΔE(SCF)(**14**): 2.81 kcal/mol

Selected bond lengths (in Å) and bond angles (in ˚):

13		**14**	
Rh1-P1	2.365	Rh1-P1	2.303
Rh1-P2	2.356	Rh1-P2	2.402
Rh1-N1	2.075	Rh1-N1	2.231
P1-Rh1-P2	176.34	Rh1-C1	2.070
		Rh1-H1	1.586
		N1-Rh1-H1	176.39
		N1-Rh1-C1	96.43
		P1-Rh1-P2	175.01

Coordinates of 13

Rh	-0.519068508	0.699834396	-0.202313709
P	-1.076383371	2.952065388	0.257996014
N	-2.503659297	0.212957356	0.157129039
P	-0.109639693	-1.569354274	-0.687972533
Si	-2.726799002	-1.343037520	0.878545643
C	-1.531032928	-2.555440824	-0.009848511
Si	-3.663664674	1.393092225	-0.348541290
C	-2.868696394	3.137446905	-0.183427372
C	-0.068628698	-2.040142123	-2.554225143
C	1.469043615	-2.197326409	0.206384669
C	1.173143041	-2.155845417	1.720695012
H	2.097974366	-2.364384105	2.273532832
H	0.809288269	-1.169147278	2.024064982
H	0.434701065	-2.902741725	2.025344556
C	2.601960240	-1.183654291	-0.066651861
H	3.494694014	-1.463315910	0.507522804
H	2.887959472	-1.137693690	-1.119640510
H	2.306997056	-0.176476555	0.254032101
C	-1.305772695	-1.347083979	-3.168940370
H	-1.327972617	-1.535441900	-4.250354919
H	-2.243942055	-1.723033481	-2.748865634
H	-1.278487332	-0.267702252	-2.996820852

C	-0.156594149	-3.550645416	-2.847286566
H	0.731516212	-4.097209807	-2.525386424
H	-0.258984415	-3.700969342	-3.929866718
H	-1.027234955	-4.015071483	-2.375002004
C	-0.964507337	3.449456203	2.110293193
C	-0.174453117	4.236966716	-0.858500312
C	-2.045346865	2.626814886	2.846060190
H	-3.057153680	2.971103434	2.612377954
H	-1.980031403	1.564997491	2.595423347
H	-1.903644506	2.737370843	3.928796028
C	-1.192127287	4.942940135	2.401944718
H	-2.120478150	5.315707221	1.956330494
H	-0.366452345	5.565670949	2.046371402
H	-1.267071024	5.095482105	3.486880026
C	1.303720122	4.364357782	-0.441349165
H	1.852223610	4.939236621	-1.198745745
H	1.422551023	4.887637191	0.511558936
H	1.790480614	3.385925454	-0.355570219
C	-0.220995209	3.642163222	-2.285736541
H	0.235305219	2.647464571	-2.323737993
H	-1.245486665	3.544836475	-2.659543916
H	0.320004712	4.303744454	-2.975082700
C	-0.823703014	5.634125222	-0.900380756
H	-0.322323848	6.243756374	-1.663587936
H	-1.883156362	5.586389041	-1.169278602
H	-0.741515838	6.167235295	0.048000353
C	0.409670146	3.008803320	2.657032957
H	0.444879382	3.178288549	3.740949303
H	0.573184185	1.942532331	2.470132483

Coordinates of 14

Rh	-0.588727499	0.816588790	-0.310141583
P	-1.253350823	3.002991890	-0.022582795
N	-2.673191903	0.190037286	0.180755974
P	0.055126093	-1.494885608	-0.409237398
Si	-2.850618638	-1.407432991	0.775252537
C	-1.462361381	-2.491716823	-0.007567691
Si	-3.858077819	1.366518279	-0.200241626
C	-3.098835353	3.123378295	0.076427845
C	0.393334377	-1.882659105	-2.262320412
C	1.444670224	-2.194935581	0.705443384
C	0.916809450	-2.160969352	2.157439125
H	1.713915711	-2.495835599	2.833223351
H	0.626175377	-1.153031326	2.462128604
H	0.059875763	-2.822580282	2.308621210
C	2.685237315	-1.280630804	0.624556859
H	3.417767433	-1.597818893	1.377743550
H	3.175668805	-1.327738169	-0.350141851
H	2.425950183	-0.236458591	0.817019209
C	-0.658083404	-1.037818570	-3.022441558
H	-0.551567538	-1.202293201	-4.102655744
H	-1.685482871	-1.292680093	-2.745773330
H	-0.513763144	0.035210927	-2.837319646
C	0.224077451	-3.361237500	-2.660862198
H	0.967550644	-4.010227328	-2.193397222
H	0.344996719	-3.453946648	-3.747883652
H	-0.766813573	-3.751930110	-2.412441333
C	-0.535459111	2.870907469	1.754727707
C	-0.686212380	4.505125451	-1.055917696
C	-1.606669255	3.017386000	2.846633223
H	-2.006050774	4.037212937	2.895839267
H	-2.437708792	2.322984342	2.699917716
H	-1.157412008	2.792246400	3.822146330
C	0.645535931	3.799715258	2.073874175
H	0.361844523	4.857609759	2.067253962
H	1.477486228	3.655907293	1.381074898
H	1.014842386	3.565933160	3.080651784
C	0.847963891	4.561747193	-1.183481424
H	1.114731496	5.270132303	-1.977936357
H	1.328195102	4.908578015	-0.266836004
H	1.263013642	3.583738623	-1.444833872
C	-1.268681794	4.282626630	-2.470979838
H	-0.875876371	3.364463357	-2.918746979
H	-2.361142432	4.224613640	-2.479156015
H	-0.981108073	5.123268142	-3.114550686
C	-1.222980932	5.825671279	-0.470767134
H	-0.929859757	6.662089384	-1.118438963
H	-2.314847319	5.830624391	-0.400519109
H	-0.818675723	6.025056043	0.526603301
C	-0.064845613	1.400186354	1.605255484
H	-0.615451325	0.728187774	2.266756764
H	1.011246324	1.291778621	1.751835577
C	1.795521230	-1.398878888	-2.677619788
H	2.586993090	-2.047546099	-2.290412235
H	1.873211186	-1.415052750	-3.772376164
H	1.984358465	-0.375566035	-2.340352876
C	1.840627591	-3.642645282	0.358082780
H	0.977871775	-4.316503580	0.340044757
H	2.348647792	-3.710155933	-0.607632304
H	2.536379058	-4.021729153	1.118086119
C	-4.392445398	1.335344369	-2.027033344
H	-3.530912103	1.474618585	-2.691321441
H	-4.843893543	0.369202824	-2.282027438
H	-5.127324329	2.116138126	-2.261250518
C	-5.450890712	1.316756329	0.843204905
H	-6.032919083	0.407512127	0.657038992
H	-5.232064787	1.354230981	1.916852809
H	-6.099246414	2.169852518	0.607714376
C	-2.748333446	-1.554696268	2.671411776
H	-2.795624960	-2.599809090	3.003842621
H	-1.832592216	-1.116295619	3.080976727
H	-3.593390876	-1.028221570	3.131775331
C	-4.471435881	-2.288828768	0.291642206
H	-4.647582831	-2.251663292	-0.789881118
H	-5.342265130	-1.840979481	0.783047969
H	-4.443738094	-3.345673503	0.585753092
H	-3.415486890	3.564600179	1.026034426
H	-3.453791405	3.792833174	-0.713903834
H	-1.877980355	-2.859316637	-0.952298506
H	-1.222414856	-3.381947701	0.584555372
H	0.866879045	1.260296744	-0.755372736

Figure S1. Electronic Energy Profile of Reaction of **1** + H_2

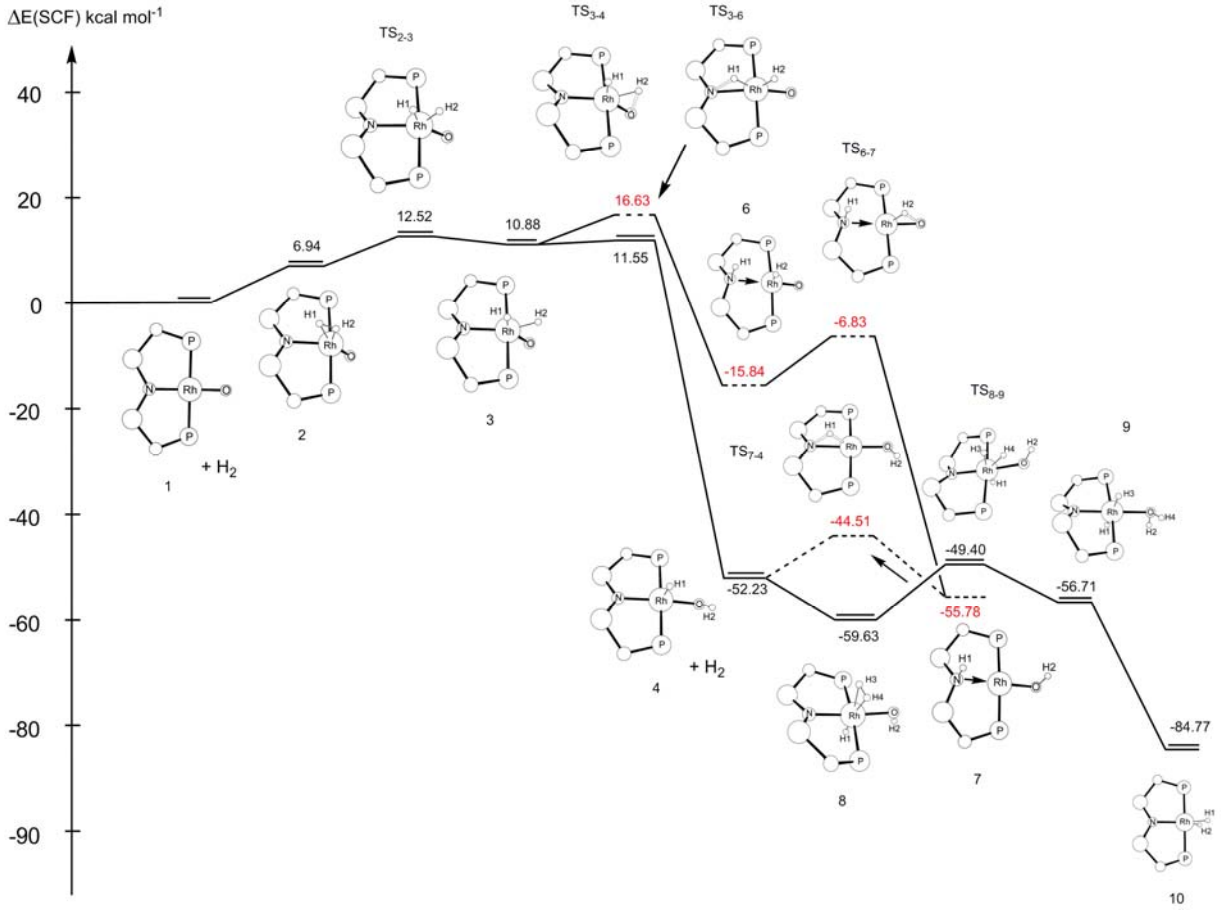
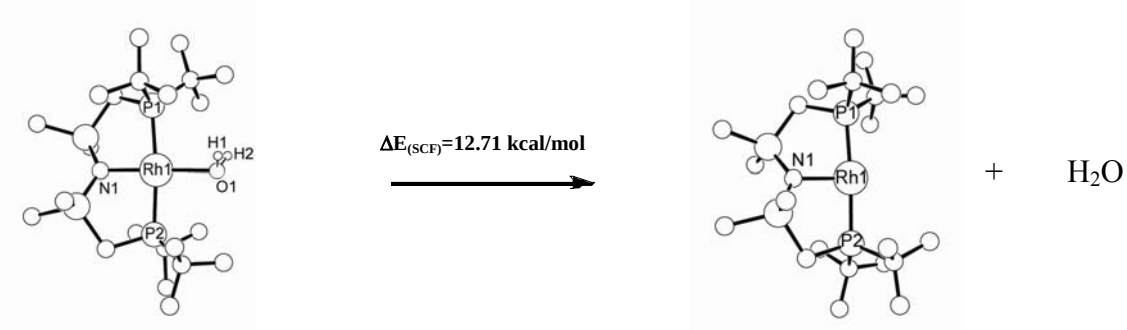
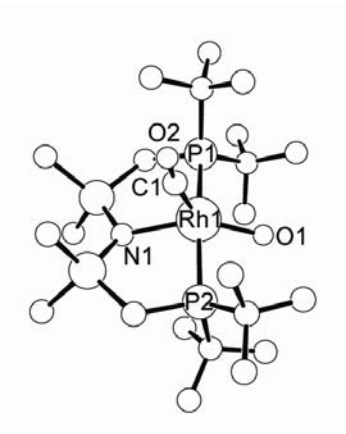


Figure S2. Dissociation Energy of (PNP)Rh(H_2O) (**5**)

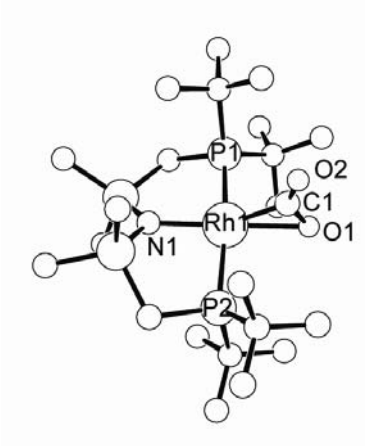


C–O distance in CO_2 is 1.181 Å
C–O distance in CO is 1.149 Å

Optimized structure of (PNP)Rh=O(CO) (**A**) and of (PNP)Rh(η^2-CO_2) (**B**)



A



B

ΔE(SCF)(**A**): 0.48 kcal/mol

ΔE(SCF)(**B**): -66.44 kcal/mol

Selected bond lengths (in Å) and bond angles (in ˚):

	A		**B**
Rh1-P1	2.501	Rh1-P1	2.423
Rh1-P2	2.418	Rh1-P2	2.455
Rh1-N1	2.226	Rh1-N1	2.075
Rh1-O1	1.847	Rh1-O1	2.207
Rh1-O2	3.019	Rh1-O2	2.999
Rh1-C1	1.872	Rh1-C1	2.006
C1-O1	3.382	C1-O1	1.257
C1-O2	1.158	C1-O2	1.206
P1-Rh1-P2	163.26	P1-Rh1-P2	171.70
N1-Rh1-O1	143.03	N1-Rh1-O1	176.07
C1-Rh1-O1	130.90	C1-Rh1-O1	34.30
O2-C1-Rh1	169.80	O2-C1-Rh1	136.65

Coordinates of A

Rh	-0.406128327	0.636489942	0.180256806
P	-1.007312886	3.063003239	0.238098668
N	-2.560204910	0.104711969	0.002277834
P	0.084202218	-1.610237219	-0.566414287
Si	-2.927739987	-1.558563711	0.307101801
C	-1.346064202	-2.626768280	0.003505058
Si	-3.714524596	1.392769178	-0.001699327
C	-2.815243647	3.086101576	-0.165595418
C	0.047037970	-1.722091303	-2.484579676
C	1.675000193	-2.405816302	0.161890820
C	1.511184100	-2.447395942	1.697459207
H	2.407135814	-2.910556435	2.127541339
H	1.425847225	-1.446179447	2.123159095
H	0.654047018	-3.041242647	2.028131122
C	2.907411569	-1.523090951	-0.141742249
H	3.730093126	-1.825750584	0.518505885
H	3.255565850	-1.640055376	-1.168819005
H	2.688413742	-0.463568745	0.013865756
C	-1.070130621	-0.782048283	-2.986505909
H	-1.145519903	-0.884673263	-4.076615025
H	-2.045640395	-1.017062113	-2.556126804
H	-0.846131700	0.260329936	-2.755551416
C	-0.265730870	-3.145482721	-2.992417871
H	0.429119033	-3.901096234	-2.621084462
H	-0.192996197	-3.143941040	-4.087142757

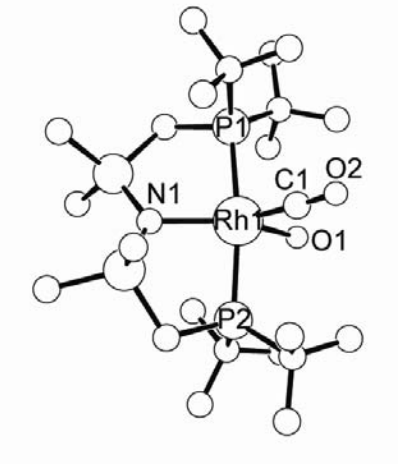
H	-1.282343485	-3.461653872	-2.741585740
C	-0.828983578	3.938307036	1.941214273
C	-0.210800817	4.112353705	-1.164417161
C	-1.907653615	3.363061819	2.885235597
H	-2.915303492	3.672298265	2.595515427
H	-1.890274593	2.273683557	2.940239245
H	-1.727754631	3.742622508	3.898796715
C	-1.022763166	5.466589721	1.895001273
H	-1.961851254	5.754607121	1.412248190
H	-0.200028020	5.973839959	1.386289587
H	-1.053701138	5.850059207	2.923064617
C	1.284037397	4.332621981	-0.859520331
H	1.760739730	4.801622698	-1.729932511
H	1.441506560	5.002882110	-0.008962608
H	1.771965740	3.372220077	-0.673086947
C	-0.317100123	3.281006155	-2.464030268
H	0.249388383	2.354298403	-2.366553547
H	-1.353817737	3.045998927	-2.730717549
H	0.101642781	3.871074443	-3.289136993
C	-0.918938814	5.461476648	-1.407530657
H	-0.486317041	5.920084218	-2.305571444
H	-1.991290352	5.343894085	-1.592158812
H	-0.791391300	6.170465776	-0.589766755
C	0.564647404	3.624052878	2.527673822
H	0.652020094	4.092694576	3.516075976
H	0.723693962	2.550910065	2.652048126
H	1.375578817	4.009052875	1.905616487
C	1.384964993	-1.234976350	-3.076531489
H	2.183180851	-1.971710334	-2.949798388
H	1.255631942	-1.081116149	-4.155265868
H	1.690093568	-0.290705864	-2.617856565
C	1.904813744	-3.843391190	-0.343188396
H	1.037684113	-4.489612553	-0.169012212
H	2.150130970	-3.872233746	-1.407581190
H	2.754648823	-4.281879119	0.195714595
C	-4.875811952	1.327834739	-1.507168059
H	-4.304549327	1.317358850	-2.442562154
H	-5.511753361	0.436531609	-1.501568906
H	-5.538277980	2.202631845	-1.528738579
C	-4.841383898	1.465559533	1.531507620
H	-5.523172721	0.607337481	1.555565720
H	-4.274355881	1.455891952	2.467748668
H	-5.463610573	2.369547917	1.524242929
C	-3.447989509	-1.965539357	2.093293833
H	-3.604238222	-3.045269790	2.215387540
H	-2.692612678	-1.656819658	2.824021627
H	-4.384932073	-1.466802218	2.364097954
C	-4.303639408	-2.251533237	-0.809047818
H	-4.100116018	-2.090219782	-1.873034046
H	-5.274278463	-1.794008385	-0.587420299
H	-4.413267048	-3.331401097	-0.648203659
H	-3.341802875	3.870740584	0.389325852
H	-2.891918060	3.361125873	-1.222963763
H	-1.546577895	-3.468045630	-0.666116541
H	-1.076604741	-3.061140998	0.971727763
O	1.087191397	1.092338082	-0.805627589
O	-0.524620304	0.071355310	3.143417116
C	-0.605729496	0.273451104	2.005609905

Coordinates of B

Rh	-0.452621207	0.697511023	-0.131127271
P	-1.090492399	2.980927554	0.149857916
N	-2.421124064	0.200409841	0.195813358
P	-0.066814407	-1.623167952	-0.702759779
Si	-2.670382209	-1.398880323	0.860283477
C	-1.587214526	-2.565984533	-0.200046603
Si	-3.688069164	1.331588369	-0.230654740
C	-2.853653096	3.045048743	-0.420819893
C	-0.025962320	-1.724056379	-2.627307730
C	1.364633952	-2.644693958	0.104784727
C	1.144770272	-2.534668076	1.632119090
H	1.964936439	-3.071902002	2.142819973
H	1.157220500	-1.491526371	1.981142584
H	0.200762297	-3.003444442	1.952342732
C	2.746193665	-2.055829770	-0.250606532
H	3.507127157	-2.517687896	0.404024049
H	3.031393025	-2.281552876	-1.289737936
H	2.798371449	-0.967258430	-0.112547945
C	-1.272889606	-0.942757676	-3.102427850
H	-1.286148943	-0.930299710	-4.207990594
H	-2.219175855	-1.392911157	-2.760338569
H	-1.248768908	0.098842135	-2.739550151
C	-0.086462536	-3.155223772	-3.191493830
H	0.855980001	-3.702705979	-3.042150576
H	-0.266947377	-3.107318240	-4.281124237
H	-0.903557843	-3.749684608	-2.749523593
C	-1.171306566	3.679400818	1.943517504
C	-0.180120644	4.197508265	-1.039890562
C	-2.218080911	2.819985300	2.684156980
H	-3.242580826	3.022305426	2.334318654
H	-2.015395238	1.742877032	2.566673853
H	-2.181745540	3.064904040	3.761135060
C	-1.600784097	5.158247402	2.001818151
H	-2.520687691	5.362434832	1.428604129
H	-0.808669078	5.834073525	1.642762236
H	-1.805946457	5.427310050	3.054475723
C	1.221840948	4.547479054	-0.503101392
H	1.774581948	5.104888885	-1.281698213
H	1.176538844	5.194333093	0.387540470
H	1.803467034	3.643693245	-0.263951037
C	-0.016829630	3.423571767	-2.368871107
H	0.595393173	2.519585028	-2.230496544
H	-0.987277715	3.121879097	-2.799820417
H	0.482598615	4.078016291	-3.107174869
C	-0.968739696	5.493232838	-1.319860517
H	-0.419792223	6.083256978	-2.076508484
H	-1.972767083	5.295626709	-1.728089863
H	-1.081697601	6.126203366	-0.428328974
C	0.179780755	3.506913375	2.665313078
H	0.079628267	3.903735229	3.692293767
H	0.474481268	2.450711605	2.737137462
H	0.999544334	4.057502639	2.180619944
C	1.225981727	-0.990259100	-3.150000947
H	2.148716160	-1.564759042	-2.977666644
H	1.130579038	-0.838965773	-4.240601590
H	1.343622398	-0.003714697	-2.672945718
C	1.352214538	-4.138650040	-0.280319717
H	0.375508493	-4.620697704	-0.113056095
H	1.642069040	-4.307244043	-1.327502897
H	2.087954831	-4.668555177	0.352044722
C	-4.477679188	0.938855240	-1.919992625
H	-3.723925947	0.947209456	-2.725094654
H	-4.954262668	-0.056156576	-1.920821849
H	-5.258021062	1.678576628	-2.173870101
C	-5.145876171	1.438708032	1.000350759
H	-5.868583812	0.626199513	0.819947804
H	-4.826737698	1.377757124	2.053181095
H	-5.692003130	2.389199842	0.867402834
C	-2.186521016	-1.498887503	2.692614285
H	-2.198614485	-2.533696251	3.077445227
H	-1.183900127	-1.075174843	2.862382202
H	-2.902355789	-0.912905702	3.295421335
C	-4.462092442	-2.038581271	0.717900814
H	-4.865827229	-1.942433297	-0.303937100
H	-5.146732759	-1.518546126	1.406684116
H	-4.487008996	-3.110595371	0.982656263
H	-3.415337159	3.860448251	0.066831182

H	-2.833610248	3.272565176	-1.500859148	O	1.695144495	1.199526374	-0.411183958
H	-2.163008917	-2.848489602	-1.098175620	O	1.783079602	0.770329460	1.894215000
H	-1.319733277	-3.499536585	0.320226410	C	1.324107402	0.912578863	0.773850478

Optimized structure of TS from **A** to **B**



TS_{A-B}

ΔE(SCF): 7.33 kcal/mol

Selected bond lengths (in Å) and bond angles (in ˚):

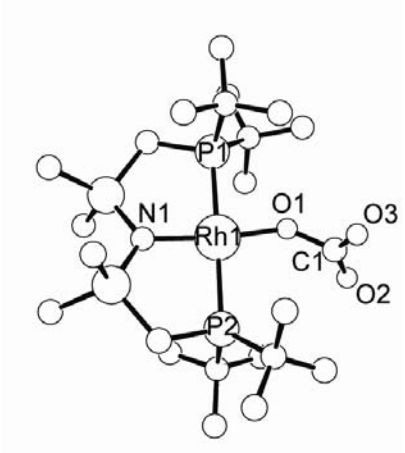
	TS_{A-B}
Rh1-P1	2.447
Rh1-P2	2.430
Rh1-N1	2.167
Rh1-O1	1.987
Rh1-O2	2.966
Rh1-C1	1.809
C1-O1	2.477
C1-O2	1.157
P1-Rh1-P2	167.85
N1-Rh1-O1	144.28
C1-Rh1-O1	81.31
O2-C1-Rh1	178.33

Coordinates of TS_{A-B}

C	0.247695989	-0.053840064	0.362110341	N	-3.223955290	0.062408237	0.105987549
O	-0.139516632	0.111175170	2.760104289	P	-1.571031373	2.372964636	1.435724274
O	1.290837528	-0.069585131	-0.174915755	Si	-3.376829144	1.491557861	-0.886177407
Rh	-1.365806928	-0.008823935	1.146735822	C	-2.848471888	2.962837766	0.226748158
P	-1.608160671	-2.441793867	1.325525072	Si	-4.300375814	-1.306322076	0.109439714

C	-3.416627423	-2.741127264	1.038671446
C	-2.350677626	2.710314824	3.166816468
C	-0.008238078	3.443038616	1.142242547
C	0.359766312	3.296190332	-0.353008331
H	1.269945319	3.892326618	-0.544600897
H	0.584746867	2.258333545	-0.633027827
H	-0.427267415	3.673263222	-1.026278449
C	1.150883707	2.911150115	2.022525904
H	2.115801257	3.126937646	1.530682090
H	1.160002546	3.410909278	3.003838486
H	1.059149446	1.824402202	2.217654475
C	-3.454553292	1.641569171	3.339023445
H	-3.978147223	1.824470466	4.295453739
H	-4.202742258	1.663241208	2.529664335
H	-3.025832034	0.627450133	3.380067907
C	-2.997725279	4.105527501	3.277563409
H	-2.267311843	4.923431497	3.202445789
H	-3.475489749	4.181858528	4.271048236
H	-3.786344433	4.279230744	2.527232477
C	-0.743843009	-3.522847184	-0.017272130
C	-1.276379296	-3.070251510	3.110854854
C	-1.175067974	-2.912080868	-1.370225267
H	-2.248969690	-3.061136700	-1.562044127
H	-0.966475097	-1.831654949	-1.425990984
H	-0.619370266	-3.414202826	-2.182657353
C	-1.177210162	-5.004086635	0.012172947
H	-2.270300415	-5.141257599	0.029589655
H	-0.751089530	-5.541845137	0.872049235
H	-0.801332802	-5.498722076	-0.901963200
C	0.229305221	-2.952328724	3.425518263
H	0.375874831	-3.117555036	4.509082244
H	0.832131834	-3.707642989	2.897793013
H	0.570849315	-1.927914947	3.181333927
C	-2.018550717	-2.091165622	4.049534660
H	-1.560911819	-1.090437140	3.954806542
H	-3.886389037	-2.823465254	2.034388961
H	-3.742924032	3.292249652	0.781924741
H	-2.485443399	3.834754578	-0.342622218
H	-3.103346767	-2.033233868	3.850164899
H	-1.898765482	-2.446478407	5.089265520
C	-1.791407680	-4.501864711	3.349097810
H	-1.676685958	-4.740065298	4.422381996
H	-2.859506468	-4.617666559	3.098858125
H	-1.222154128	-5.256587730	2.786418024
C	0.793143803	-3.468055657	0.098369648
H	1.225964221	-3.971508459	-0.785278810
H	1.188155415	-2.444277876	0.120781492
H	1.162416902	-3.996413330	0.989134842
C	-1.292656557	2.515851454	4.267999055
H	-0.591273432	3.364865990	4.314922246
H	-1.802589845	2.452621411	5.246867654
H	-0.726022057	1.583324865	4.075068648
C	-0.263580826	4.937110842	1.425689593
H	-1.136299220	5.335386471	0.880266787
H	-0.400118845	5.133735652	2.499781311
H	0.621452637	5.513460739	1.099345449
C	-5.891703382	-0.957519209	1.096508543
H	-5.653247685	-0.636939977	2.124907214
H	-6.487027920	-0.156739846	0.626540968
H	-6.533274009	-1.854370200	1.159183743
C	-4.860294830	-1.921504131	-1.608924137
H	-5.570211741	-1.209953170	-2.063276562
H	-4.019801320	-2.039274583	-2.311992717
H	-5.379533685	-2.893160510	-1.533104272
C	-2.273843329	1.420796917	-2.432047179
H	-2.307089568	2.361451327	-3.009337291
H	-1.224071825	1.219626967	-2.162754950
H	-2.606624865	0.606659564	-3.099019580
C	-5.151620754	1.877171503	-1.467097938
H	-5.853379877	1.951160589	-0.619377570
H	-5.539097745	1.112436409	-2.160469020
H	-5.173963224	2.842599546	-2.002386810
H	-3.584600328	-3.709218892	0.536752977

Optimized structure of (PNP)Rh(κ^1- OCO2) (**C**)



C

ΔE(SCF)(**C**): 6.13 kcal/mol

Selected bond lengths (in Å) and bond angles (in ˚):

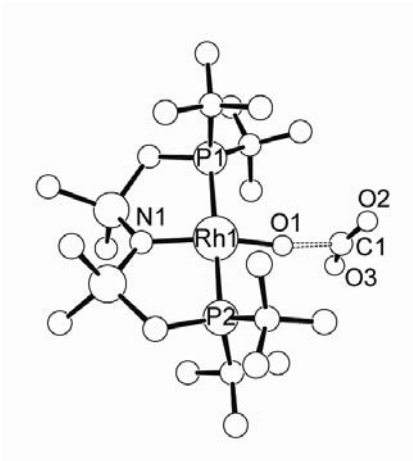
	C
Rh1-P1	2.418
Rh1-P2	2.487
Rh1-N1	1.994
Rh1-O1	1.900
Rh1-O2	3.799
Rh1-C1	3.125
C1-O1	1.396
C1-O2	1.240
C1-O3	1.241
P1-Rh1-P2	179.06
N1-Rh1-O1	173.28
N1-Rh1-O2	160.86
O2-C1-O3	133.23

Coordinates of C

Rh	-0.472203277	0.642385247	-0.076449564
P	-0.990627941	2.984420484	0.271422671
N	-2.409984063	0.211934576	0.092992580
P	-0.041661548	-1.669048951	-0.504567212
Si	-2.888964768	-1.427660580	0.607604988
C	-1.471922933	-2.629934752	0.183241242
Si	-3.659435378	1.450359091	-0.182712914
C	-2.796279624	3.140840111	-0.148684528
C	-0.074391725	-2.002167398	-2.392097018
C	1.501513170	-2.455024485	0.333013330
C	1.570981256	-1.816513771	1.740214697
H	2.393321882	-2.288282080	2.308767087
H	1.766020507	-0.735747859	1.674077674
H	0.641413304	-1.970999642	2.316560608
C	2.795312669	-2.118347019	-0.436278394
H	3.660269029	-2.410559981	0.186341510
H	2.872845252	-2.680327607	-1.381134349
H	2.878777043	-1.044376752	-0.652546197
C	-1.496687516	-1.637192896	-2.871546411
H	-1.526172518	-1.695877255	-3.974444111
H	-2.262126166	-2.330549474	-2.484883343
H	-1.771601489	-0.612455332	-2.573037603
C	0.220624749	-3.467660375	-2.762035032
H	1.263569564	-3.749201500	-2.549149905
H	0.059190473	-3.605937109	-3.846949002
H	-0.445108495	-4.176982932	-2.240572040
C	-0.886281274	3.453841503	2.128674175
C	-0.197025057	4.349126441	-0.845032317
C	-1.869647076	2.520916811	2.866803410
H	-2.920519881	2.748571702	2.624545869
H	-1.676841903	1.461676012	2.629516972
H	-1.744507497	2.658787264	3.956017300
C	-1.270736254	4.915496998	2.422761678
H	-2.273654855	5.173886422	2.041226800
H	-0.545464175	5.630927961	2.006486886
H	-1.290874498	5.068575010	3.517508857
C	1.164523265	4.836531046	-0.309091008
H	1.647275208	5.445174138	-1.094819053
H	1.045559350	5.486095373	0.573559717
H	1.857695811	4.025665387	-0.047359529
C	-0.003095121	3.680625933	-2.225001066
H	0.761832698	2.888853157	-2.191109321
H	-0.943533617	3.250815562	-2.614022210
H	0.333006875	4.445675532	-2.948842337
C	-1.115573300	5.581103934	-1.008499147
H	-0.579189064	6.328184172	-1.621059740
H	-2.056229856	5.353476798	-1.534091852
H	-1.365678173	6.059970152	-0.049592407
C	0.537610187	3.156145056	2.641898337
H	0.558874582	3.302123358	3.737755691
H	0.839512192	2.119832484	2.423881443
H	1.301034293	3.809457408	2.198439793
C	0.927057664	-1.056769861	-3.091417879
H	1.973898984	-1.290062153	-2.851321703
H	0.804354644	-1.155278956	-4.185554102
H	0.755466696	-0.004376923	-2.815758256
C	1.383997045	-3.986823127	0.478444568
H	0.531376809	-4.293373690	1.105374332
H	1.298550705	-4.502558275	-0.489611067
H	2.298843825	-4.359993071	0.973396176
C	-4.418385702	1.223851293	-1.910352604
H	-3.638113321	1.278393240	-2.687835085
H	-4.929845656	0.253357739	-2.013334193
H	-5.158413601	2.017477567	-2.114055775
C	-5.081661018	1.427117552	1.084936517
H	-5.675352774	0.499883472	1.040324441
H	-4.723062203	1.546682625	2.119663039
H	-5.768851438	2.264025098	0.869576742
C	-3.125264827	-1.456522090	2.491495950
H	-3.390938871	-2.471102477	2.836527691
H	-2.193584690	-1.154866268	2.998910494
H	-3.923154641	-0.769572288	2.816846642
C	-4.479353608	-2.063741844	-0.223605694
H	-4.373605560	-2.110353209	-1.319937591
H	-5.364937810	-1.449133292	0.003567835
H	-4.690883622	-3.086340238	0.135209128
H	-3.306508887	3.876205372	0.497309241
H	-2.846394829	3.536075032	-1.177261969
H	-1.784343624	-3.450625668	-0.484996730
H	-1.139381541	-3.093581840	1.127179779

O	2.813592110	1.874512143	-1.583324153
C	2.485827643	1.711440472	-0.380708682
O	1.463298004	0.823146725	-0.191269203
O	2.992327680	2.186876458	0.666290071

Optimized structure of (PNP)Rh =O + CO2 ➔ (PNP)Rh((κ^1- OCO2) (**$TS_{1\text{-}C}$**)



$TS_{1\text{-}C}$

ΔE(SCF)(**$TS_{1\text{-}C}$**) : 8.26 kcal/mol

Selected bond lengths (in Å) and bond angles (in °):

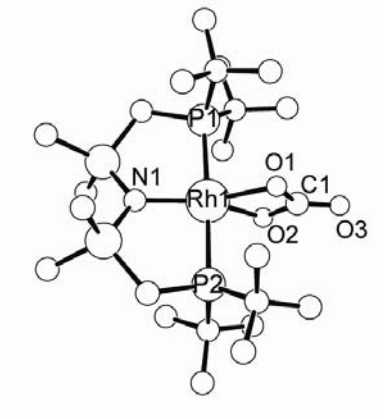
	$TS_{1\text{-}C}$
Rh1-P1	2.461
Rh1-P2	2.411
Rh1-N1	2.013
Rh1-O1	1.842
Rh1-O2	4.154
Rh1-C1	3.619
C1-O1	1.823
C1-O2	1.197
C1-O3	1.197
P1-Rh1-P2	174.80
N1-Rh1-O1	167.86
N1-Rh1-O2	172.23
O2-C1-O3	150.86

Coordinates of $TS_{1\text{-}C}$

C	-0.088297118	0.708523668	0.110945552
O	0.232354930	0.243548587	1.823077400
Rh	1.209105377	0.000207002	3.386739337
P	3.205207185	-0.889359925	2.341603147
N	2.208184283	-0.028388767	5.152878656
P	-0.761817398	0.701701561	4.552455106
Si	1.332646547	-0.078848985	6.694716438
C	-0.504919354	0.313778696	6.349467953
Si	3.974230658	0.135045527	5.153327080
C	4.621930741	-0.485881696	3.471203302
C	-1.006166865	2.601105887	4.486466916
C	-2.358021372	-0.265892042	4.094825636
C	-1.909654629	-1.739788447	3.961482711
H	-2.790877484	-2.365562703	3.729438302
H	-1.176213305	-1.854858209	3.147993403
H	-1.460369955	-2.132171800	4.890658545
C	-2.913887908	0.199714654	2.735655824
H	-3.721357536	-0.489141363	2.427337325

H	-3.350404525	1.209955861	2.790138443
H	-2.133386095	0.183464459	1.960304936
C	0.232962665	3.203137096	5.186277042
H	0.217926174	4.300191786	5.056420615
H	0.245826644	2.999612796	6.269526035
H	1.168482038	2.818362430	4.746608483
C	-2.282033506	3.081676290	5.202402677
H	-3.193634222	2.792665388	4.656095286
H	-2.270810905	4.185832429	5.257288760
H	-2.359973963	2.703630179	6.236238416
C	3.116574340	-2.806906734	2.337024125
C	3.786750256	-0.197612490	0.645217325
C	3.033748288	-3.244836883	3.816269856
H	3.973462055	-3.058321399	4.362214130
H	2.217987942	-2.725788714	4.345527585
H	2.838932536	-4.331978582	3.856006916
C	4.331777848	-3.485932805	1.679662653
H	5.288150840	-3.153324391	2.118333501
H	4.369031755	-3.313381960	0.592875615
H	4.264109790	-4.578445435	1.835728712
C	2.965217071	-0.804096252	-0.508674437
H	3.159932681	-0.224053362	-1.428745924
H	3.260327088	-1.846148697	-0.715442824
H	1.881519733	-0.781798596	-0.326188433
C	3.528247937	1.324612444	0.726122726
H	2.458521619	1.557348444	0.836368761
H	4.075534708	1.793045946	1.563429496
H	3.888062259	1.798250439	-0.205455397
C	5.286724986	-0.435508294	0.370088181
H	5.533415727	0.009931571	-0.610782430
H	5.940772073	0.045054735	1.114913314
H	5.549481146	-1.502441075	0.322694581
C	1.812647154	-3.240977525	1.634557318
H	1.700309363	-4.336542254	1.727719877
H	0.935628292	-2.762212274	2.099675735
H	1.800030371	-2.991522712	0.563731062
C	-1.007266369	3.078021526	3.020102302
H	-1.891650740	2.735280748	2.464156204
H	-1.016126307	4.183426050	3.008412090
H	-0.120893057	2.731565515	2.468716546
C	-3.459638885	-0.167655278	5.169891825
H	-3.128664975	-0.529712092	6.156728136
H	-3.841705212	0.856186256	5.293761590
H	-4.309547996	-0.802424724	4.859868323
C	4.473364357	1.960304859	5.319032278
H	4.024544685	2.554682899	4.505370606
H	4.135982868	2.392041079	6.275275441
H	5.569880067	2.077543652	5.264254257
C	4.849794817	-0.857882295	6.524126651
H	4.569127916	-0.533962845	7.539357614
H	4.636372388	-1.936584013	6.444467024
H	5.941817981	-0.725108862	6.429545425
C	1.400973168	-1.827429497	7.440177041
H	0.803421836	-1.879566842	8.367287909
H	0.994715357	-2.568910737	6.731441068
H	2.431244566	-2.130289924	7.687486387
C	1.982364380	1.145539802	8.002943540
H	1.958078091	2.186104410	7.640319517
H	3.016759903	0.924236381	8.312825352
H	1.352249656	1.090257727	8.907991842
H	5.320667727	-1.334564307	3.569478605
H	5.187789640	0.340179470	3.009019914
H	-0.894748566	1.114766463	7.000877048
H	-1.084698953	-0.595378378	6.582617451
O	0.151263019	1.893834829	0.047088845
O	-0.469549401	-0.309908137	-0.419602301

Optimized structure of (PNP)Rh(κ^2- OCO2)



D

ΔE(SCF)(**D**): -34.34 kcal/mol

Selected bond lengths (in Å) and bond angles (in °):

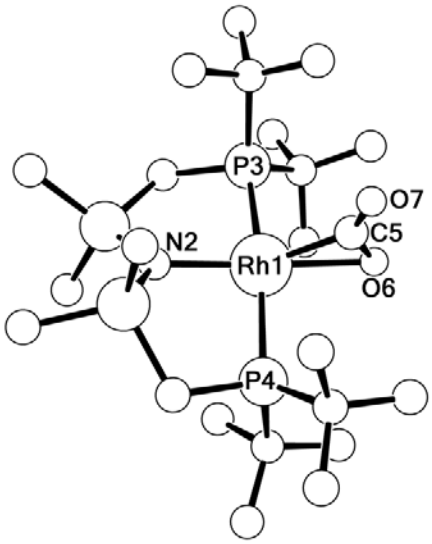
	D
Rh1-P1	2.466

Rh1-P2	2.469
Rh1-N1	2.032
Rh1-O1	2.062
Rh1-O2	2.051
Rh1-C1	2.539
C1-O3	1.218
C1-O1	1.330
C1-O2	1.333
P1-Rh1-P2	177.32
N1-Rh1-O1	150.89
N1-Rh1-O2	146.09
O2-C1-O3	126.31

Coordinates of D

Rh	-0.472846167	0.725109500	-0.146992747
P	-1.066785392	3.047943067	0.249338170
N	-2.409498062	0.239039962	0.109745416
P	-0.000295310	-1.609171289	-0.589705257
Si	-2.851740831	-1.409788413	0.591444089
C	-1.469982145	-2.577687301	0.011068786
Si	-3.692440175	1.440714096	-0.126621607
C	-2.896983714	3.166866008	-0.050029702
C	0.029161655	-1.981272878	-2.483404461
C	1.461971142	-2.428896509	0.369031375
C	1.244027880	-2.019939052	1.845219197
H	2.054184841	-2.458153400	2.456154669
H	1.278444917	-0.925529814	1.956336533
H	0.289998303	-2.394375676	2.254331940
C	2.840446674	-1.908925249	-0.086952152
H	3.608789088	-2.350515720	0.574277126
H	3.084802027	-2.217804178	-1.114436634
H	2.940974655	-0.817997296	-0.014622091
C	-1.229574599	-1.277136623	-3.041925676
H	-1.265394148	-1.424931475	-4.136994680
H	-2.165772138	-1.681396562	-2.620693892
H	-1.205253819	-0.194289315	-2.837073699
C	-0.033259842	-3.482304165	-2.826479467
H	0.893982822	-4.008972190	-2.555791067
H	-0.161874993	-3.587225841	-3.919388330
H	-0.877521394	-4.007865502	-2.350467385
C	-0.876562158	3.570943844	2.095916674
C	-0.364576865	4.375087205	-0.965077982
C	-1.711910778	2.544910905	2.894541709
H	-2.792566295	2.641741668	2.699284262
H	-1.410331878	1.509998251	2.664366746
H	-1.553895975	2.720439267	3.974093601
C	-1.399854236	4.990540152	2.390894779
H	-2.417789035	5.171842663	2.006834924
H	-0.732477669	5.766104138	1.984013980
H	-1.434447403	5.134450092	3.486623448
C	1.118473957	4.688689470	-0.681444056
H	1.498512479	5.338271812	-1.491407471
H	1.247194885	5.243635916	0.261454122
H	1.759857633	3.795954661	-0.654566141
C	-0.492152958	3.751783418	-2.375449354
H	0.120213835	2.842367525	-2.461722955
H	-1.537039153	3.505491962	-2.634156253
H	-0.138366052	4.488683375	-3.119599178
C	-1.165279874	5.694348038	-0.933167132
H	-0.772971763	6.354232007	-1.728342824
H	-2.239495445	5.551422107	-1.132730671
H	-1.063866927	6.233461970	0.019710966
C	0.591779461	3.465442062	2.558714197
H	0.627385903	3.646956715	3.648826921
H	1.018450831	2.474655073	2.346927864
H	1.236306566	4.218402175	2.080793632
C	1.273407071	-1.360207488	-3.151364394
H	2.190995112	-1.920580880	-2.914628893
H	1.140995381	-1.401892581	-4.248130712
H	1.417162025	-0.310723246	-2.854121904
C	1.459433490	-3.968547817	0.258702604
H	0.487359747	-4.425122949	0.505852231
H	1.755446713	-4.315941467	-0.742734994
H	2.199419182	-4.369991636	0.975053639
C	-4.459410580	1.238613446	-1.853181169
H	-3.677220821	1.299516672	-2.628899699
H	-4.970743314	0.269232762	-1.968189180
H	-5.199616868	2.034072384	-2.050272358
C	-5.092265799	1.374429764	1.166735230
H	-5.655689284	0.427905185	1.143804762
H	-4.710735195	1.509846810	2.192275815
H	-5.812913987	2.187299077	0.968396123
C	-2.998638473	-1.513174275	2.481532882
H	-3.230132359	-2.541895194	2.808836838
H	-2.053880599	-1.204460525	2.959967500
H	-3.796288985	-0.852998789	2.860768899
C	-4.467497622	-2.060782957	-0.186260781
H	-4.402795579	-2.084591541	-1.287460127
H	-5.360285466	-1.475552057	0.085367946
H	-4.640344502	-3.096464146	0.157067920
H	-3.386364571	3.818206345	0.694074644
H	-3.042845901	3.644409775	-1.033417885
H	-1.844205760	-3.243852857	-0.783900298
H	-1.160720217	-3.226786746	0.846200538
O	1.146888814	1.249749511	-1.370580423
C	2.005937126	1.355399166	-0.356284543
O	1.369479018	1.046039114	0.776816134
O	3.189760884	1.683369081	-0.444763563

Optimized structure of (PNP)Rh(CO_2).



(PNP)Rh + CO_2 → (PNP)Rh(CO_2) ΔE(SCF) = -14.0 kcal/mol

Unscaled calculated stretching frequencies:
Terminal C=O: 1908 cm^{-1}
Bidentate binding C-O: 1193 cm^{-1}

Select bond lengths (Å) and bond angles (°).

Rh1-N2	2.074
Rh1-P3	2.424
Rh1-P4	2.452
Rh1-C5	2.006
Rh1-O6	2.211
Rh1-O7	3.000
C5-O6	1.258
C5-O7	1.207
P3-Rh1-P4	170.5
N2-Rh1-O6	175.4
O6-Rh1-C5	34.3
Rh1-C5-O7	136.6

Optimized coordinates of (PNP)Rh(CO_2).

Rh	15.433443075	2.160764103	18.558868341
P	16.481978712	0.062203220	19.273447659
P	14.050895566	4.044451777	17.914802517
Si	15.677170243	1.711175097	21.726126276
Si	13.068534882	3.014350554	20.694491854
N	14.640979870	2.313939129	20.469649973
C	17.140193962	2.858454628	22.084441890
H	16.775856109	3.782725105	22.549343581
H	17.669304552	3.139146966	21.169235648
H	17.863691881	2.408497721	22.775655593
C	14.809910677	1.397711126	23.390412303
H	14.514143632	2.325165083	23.890868281
H	15.499834685	0.875185083	24.065233802
H	13.917449694	0.770649813	23.287298755
C	16.280993696	0.002376488	21.116675433
H	17.199318596	-0.335051143	21.605733149
H	15.502952933	-0.725854575	21.369848318
C	15.402630911	-1.383556793	18.602485188
C	18.365858973	-0.268491705	19.010104751
C	12.905362168	4.209740918	22.168953722
H	13.756577108	4.890506381	22.265643249
H	12.813330853	3.659465634	23.111306599
H	11.998915706	4.819804162	22.067559168
C	11.709087821	1.708327448	20.946178351
H	11.673775266	1.006961964	20.104588209
H	10.719254560	2.174201984	21.036756769
H	11.877193065	1.121578587	21.856473382
C	12.610699859	3.925709277	19.072810984
H	11.855684415	3.308109510	18.574083425
H	12.144716613	4.901070509	19.249764400
C	14.723856427	5.826750534	18.169201856
C	13.727162739	6.920248558	17.739844401
H	14.103193083	7.894785900	18.077004575
H	12.733561237	6.787585575	18.178692511
H	13.620012818	6.975370355	16.653837935
C	13.269705185	3.841330687	16.165007230
C	15.644109140	-2.737761517	19.296410410
C	15.607148557	-1.530678755	17.080975324
C	13.935002340	-0.966419821	18.851206248
C	18.840565993	-1.612478640	19.600330153
C	19.110768925	0.872222760	19.742032252
C	18.758955879	-0.224811556	17.518106663
C	11.936594246	4.598275418	15.989760757
C	12.994396793	2.328623028	15.998578787
C	14.254600711	4.273176083	15.059926104
C	15.005667496	5.977584878	19.678370682
C	16.055420538	6.034446848	17.421108600
H	20.188786776	0.738261085	19.587080007
H	18.936285608	0.859270982	20.821241725
H	18.841224959	1.856150091	19.354290951
H	19.937673230	-1.630367474	19.593499498
H	18.503608506	-2.466265005	19.008962727
H	18.520124909	-1.764245868	20.635234048
H	19.853344856	-0.247847950	17.445765486

H	18.412757882	0.676415116	17.012588521
H	18.381934350	-1.088124965	16.965915630
H	14.886426057	-3.453851952	18.953950806
H	15.558312448	-2.671620385	20.385552892
H	16.620657186	-3.162917431	19.059694125
H	14.813169369	-2.166276447	16.669447520
H	16.559611936	-2.007902081	16.837986473
H	15.567960253	-0.565072177	16.568087060
H	13.273296680	-1.761557536	18.484228034
H	13.686539794	-0.042455695	18.321058986
H	13.713601547	-0.811365021	19.911157176
H	15.531283923	6.925664432	19.846740126
H	15.636081511	5.168501670	20.056325528
H	14.086656063	6.005420584	20.267873954
H	16.399052948	7.061065762	17.602333624
H	15.961672769	5.911395570	16.340930268
H	16.832053264	5.356861210	17.775482292
H	11.522634691	4.356966696	15.002356534
H	12.054395430	5.682296084	16.036879074
H	11.188902551	4.306314095	16.732984780
H	13.844610968	3.980936174	14.084566836
H	15.227281475	3.786091966	15.169385875
H	14.398982739	5.357308506	15.034688849
H	12.514383951	2.157486461	15.026434378
H	12.317412069	1.940487706	16.768156318
H	13.920468924	1.750361157	16.030786808
O	16.416608240	2.095167617	16.579948591
C	17.016958431	2.744013837	17.475167561