Supporting Information

Catalytic Efficiency is a Function of How Rhodium(I) (5+2)-Catalysts Accommodate a Conserved Substrate Transition State Geometry: Induced Fit Model for Explaining Transition Metal Catalysis

Thomas J. L. Mustard,[†] Paul A. Wender,*[‡] Paul Ha-Yeon Cheong*[†]

paulc@science.oregonstate.edu, wenderp@stanford.edu

†Department of Chemistry, Oregon State University, 153 Gilbert Hall, Corvallis, OR 97331-4003

‡Departments of Chemistry and Chemical and Systems Biology, Stanford University, Stanford, CA 94305-5080

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1. RhCOCl

1.a. Additional Figures

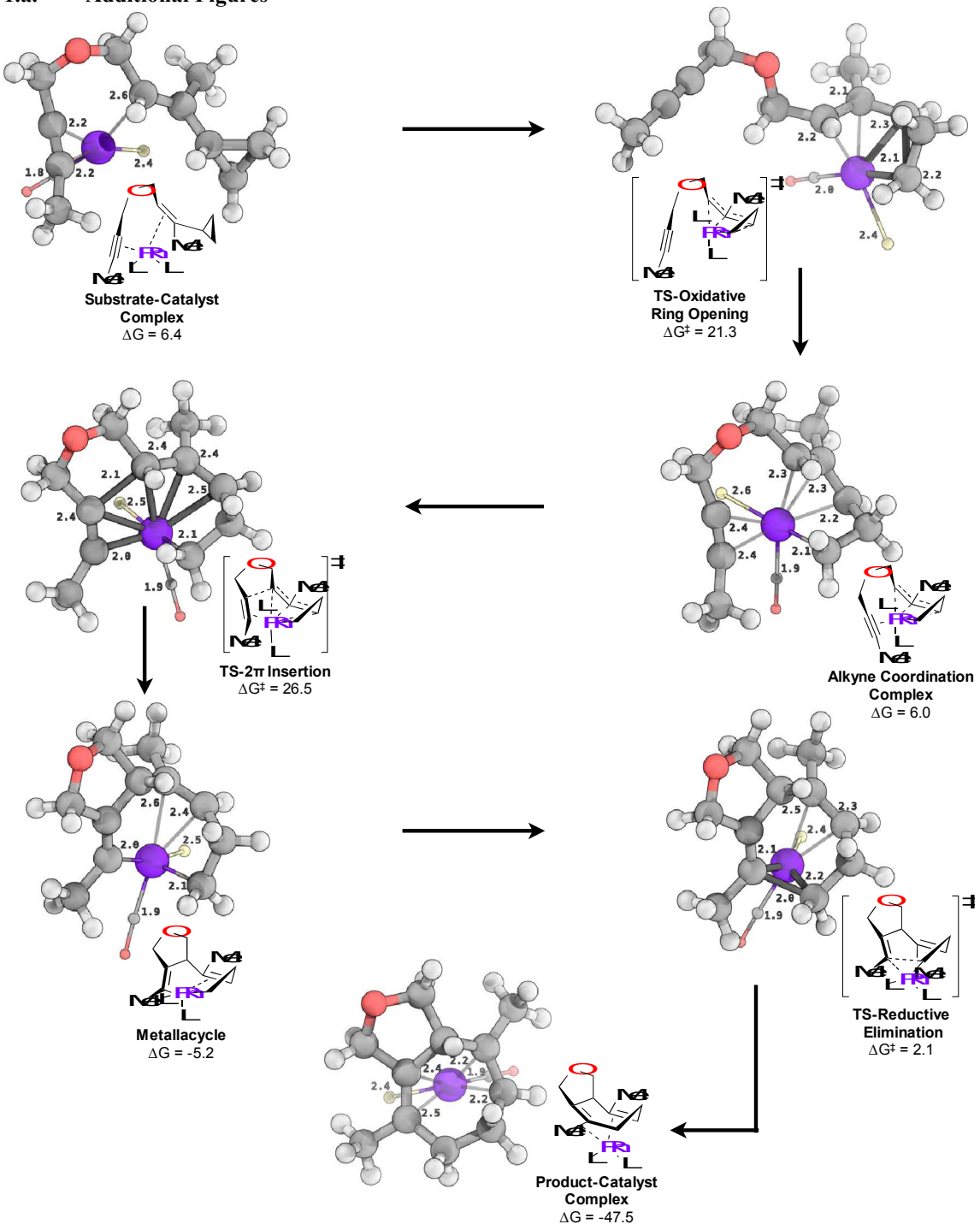

Figure S1. Computed geometries for RhCOCl.

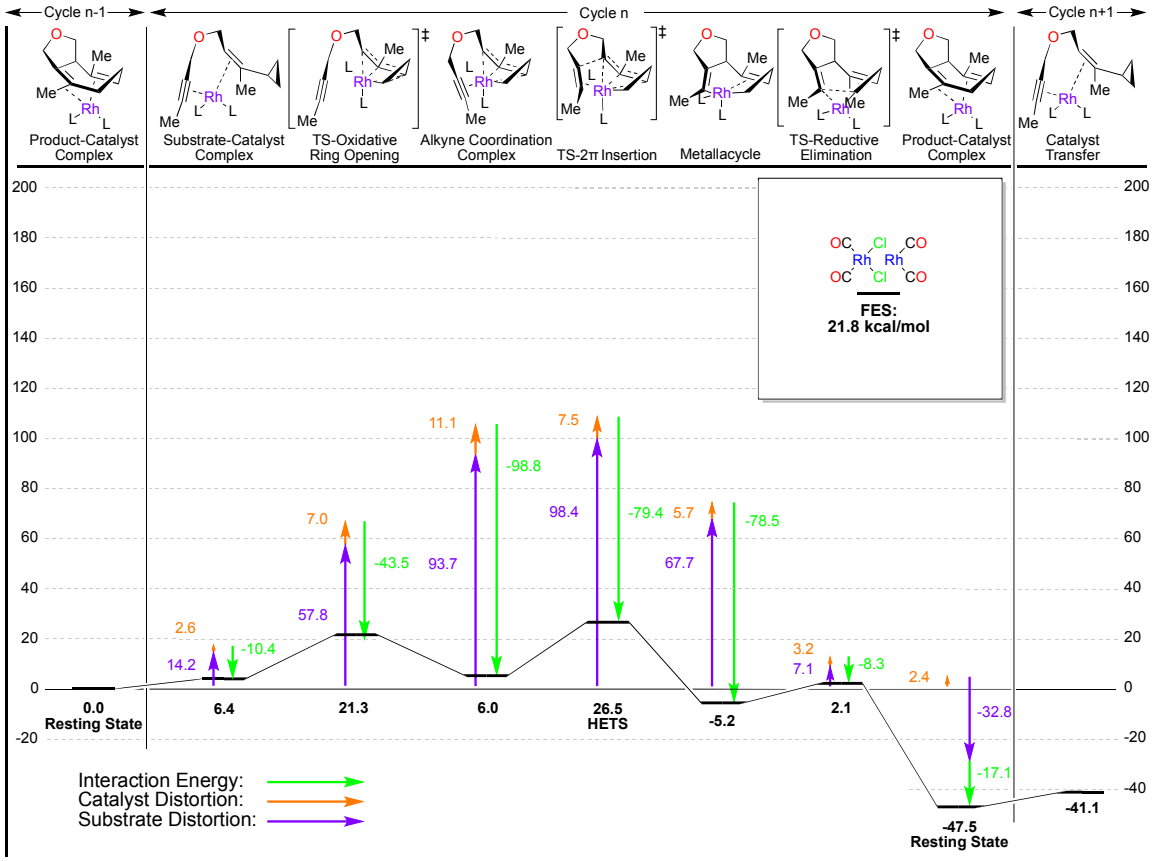

Figure S2. Reaction coordinate diagram for RhCOCl. Interaction, catalyst and substrate distortion shown with colored arrows.

Substrate-Catalyst Complex RhCOCl

Using Gaussian 03: AM64L-G03RevC.02 12-Jun-2004

opt=(maxcycle=250,nofreeze) freq=noraman b3lyp geom=connectivity gen pseudo=read scf=(direct,tight,maxcycle=300,xqc) gfinput gfprint iop(1/8=20)
#N Geom=AllCheck Guess=Read SCRF=Check Test GenChk RB3LYP/ChkBas Freq

Pointgroup= C1 Stoichiometry= C12H16ClO2Rh C1[X(C12H16ClO2Rh)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -1187.01306971 Predicted Change= -1.499199D-07

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00003	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00355	0.00180	[NO]	0.00355	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.807424	1.590133	-0.019938
Rh	-0.641912	-0.511335	-0.080754
C	1.926540	0.811925	-0.107824
C	2.574178	0.337044	1.143586
C	-1.973663	1.138630	0.335331
C	-1.903756	0.497542	1.405736
H	0.491233	1.903844	0.972564
C	0.193617	2.424220	-1.134267
H	0.872366	3.241973	-1.408448
H	0.003342	1.834005	-2.043132
C	-2.144250	2.254746	-0.626654
H	-2.405251	1.856706	-1.618913
H	-2.956633	2.911618	-0.295872
C	-1.981324	-1.739513	-0.339891
O	-2.834282	-2.492123	-0.518761
Cl	0.754029	-2.098108	-1.221851
H	2.094887	0.709601	2.046246
C	3.203501	-1.041605	1.271865
C	4.088274	0.163059	1.243034
H	4.682578	0.341344	0.352026
H	3.047459	-1.555356	2.216364
H	3.161272	-1.689523	0.403216
H	4.557785	0.497498	2.164082
O	-0.994908	3.083445	-0.707499
C	-2.173032	0.074193	2.789982
H	-2.831278	0.795950	3.288982
H	-2.656312	-0.909150	2.813607
H	-1.244206	-0.003946	3.365561
C	2.623260	0.567870	-1.421012
H	1.957037	0.709794	-2.273482
H	3.456461	1.278479	-1.517445
H	3.025714	-0.444965	-1.489573

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -1187.01306971 Predicted Change= -1.499199D-07
Zero-point correction (ZPE)= -1186.7584 0.25464
Internal Energy (U)= -1186.7388 0.27421
Enthalpy (H)= -1186.7379 0.27515
Gibbs Free Energy (G)= -1186.8075 0.20548

Frequencies -- 33.9518 52.0300 62.6374
SCF Energy (M06) = -1186.544315
SCF Energy (M06/def2-tzvp) = -1187.909664

Oxidative-Addition TS RhCOCl

Using Gaussian 03: AM64L-G03RevC.02 12-Jun-2004

#B3LYP/ChkBas GenChk gfprint gfinput scf=(direct,xqc,tight,maxcycle=250) opt=(maxcycle=250,calcfc,ts,noeigentest,nofreeze) Freq=Noraman
Geom=AllCheck Guess=Read SCRF=Check
#N Geom=AllCheck Guess=Read SCRF=Check GenChk RB3LYP/ChkBas Freq

Pointgroup= C1 Stoichiometry= C12H16ClO2Rh C1[X(C12H16ClO2Rh)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -1186.98663596 Predicted Change= -3.808433D-09

Optimization completed on the basis of negligible forces. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00380	0.00180	[NO]	0.00380	0.00180	[YES]

Atomic Coordinates (Angstroms)

Type	X	Y	Z
C	-5.365884	-0.454310	-0.638512
Rh	1.560462	-0.344896	-0.222272
C	-4.682297	0.023094	0.238351
C	-3.838942	0.599142	1.295028
C	-1.697900	0.067013	0.395792
C	-0.465472	0.735365	-0.146970
C	0.495236	1.348216	0.657813
C	1.644114	1.990607	0.002505
C	1.600384	2.787171	-1.258806
C	2.172925	1.448000	-1.618160
H	3.250341	1.397217	-1.723007
H	1.606955	0.859331	-2.338073
H	2.271361	3.642005	-1.304235
H	0.608332	3.002865	-1.649928
H	-0.519953	1.012425	-1.199147
H	-3.677623	-0.149753	2.088925
H	-4.342117	1.458496	1.752695
H	-1.455381	-0.609057	1.226706
H	-2.167067	-0.538274	-0.389538
H	2.495966	2.192896	0.644507
O	-2.589756	1.099222	0.831643
C	-6.201028	-1.030318	-1.689350
H	-6.059822	-0.504803	-2.641664
H	-5.965865	-2.088772	-1.853739
H	-7.264375	-0.961866	-1.429016
C	0.417385	1.410325	2.162174
H	1.415342	1.436845	2.610476
H	-0.122083	2.318477	2.461854
H	-0.121445	0.553091	2.569795
C	3.299043	-1.102607	-0.148267
O	4.355915	-1.541076	-0.032810
Cl	0.672469	-2.405656	0.545610

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -1186.98663596 Predicted Change= -3.808433D-09
Zero-point correction (ZPE)= -1186.7338 0.25279
Internal Energy (U)= -1186.7140 0.27255
Enthalpy (H)= -1186.7131 0.27349
Gibbs Free Energy (G)= -1186.7860 0.20061

Frequencies -- -193.8067 18.8719 21.2927
SCF Energy (M06) = -1186.514763
SCF Energy (M06/def2-tzvp) = -1187.884564

Alkyne Coordination Complex RhCOCl

Using Gaussian 03: AM64L-G03RevC.02 12-Jun-2004

# opt=(loose,modredundant,maxcycle=250) b3lyp geom=connectivity gen
pseudo=read gfprint gfinput scf=(direct,xqc,tight,maxcycle=250)
Modredundant Input: B 3 6 3.0000 F
#B3LYP/ChkBas GenChk gfprint gfinput scf=(direct,xqc,tight,maxcycle=250)
opt=(maxcycle=250,nofreeze) Freq=Noraman Geom=AllCheck Guess=Read
SCRF=Check
#N Geom=AllCheck Guess=Read SCRF=Check GenChk RB3LYP/ChkBas Freq

Pointgroup= C1 Stoichiometry= C12H16ClO2Rh C1[X(C12H16ClO2Rh)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -1187.01835077 Predicted Change= -4.027491D-07

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00011	0.00045	[YES]	0.00001	0.00030	[YES]
Displ	0.00637	0.00180	[NO]	0.00637	0.00180	[NO]

Atomic Type	X	Y	Z
C	-1.115996	2.034345	-0.475157
Rh	-0.439552	-0.213036	-0.001073
C	0.102614	2.094985	-0.310097
C	1.491218	2.526663	-0.043280
C	2.759085	0.553832	-0.419083
C	1.670560	-0.389535	-0.859012
C	1.372599	-1.610795	-0.205718
C	0.172338	-2.272052	-0.583599
C	-0.467034	-2.130483	-1.966860
C	-1.045274	-0.713909	-1.954356
H	-2.132144	-0.688529	-2.050271
H	-0.593818	-0.015610	-2.663262
H	-1.247930	-2.888744	-2.082707
H	0.269561	-2.300042	-2.763564
H	1.407041	-0.277728	-1.907711
H	1.686399	2.386664	1.029259
H	1.565398	3.593599	-0.281491
H	3.707423	0.298513	-0.909738
H	2.908337	0.513129	0.667180
H	-0.128396	-3.117966	0.030142
O	2.486528	1.891847	-0.828406
C	-2.526175	2.340942	-0.745839
H	-2.911743	1.736606	-1.573837
H	-3.148909	2.148541	0.134585
H	-2.631742	3.397575	-1.018170
C	2.162194	-2.101954	0.983628
H	3.151836	-2.432805	0.641691
H	2.290151	-1.322918	1.738636
H	1.665059	-2.949161	1.463077
C	-2.156543	-0.594432	0.762692
O	-3.157394	-0.838711	1.268068
Cl	0.280747	0.273810	2.410426

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -1187.01835077 Predicted Change= -4.027491D-07
Zero-point correction (ZPE)= -1186.7635 0.25477
Internal Energy (U)= -1186.7446 0.27370
Enthalpy (H)= -1186.7436 0.27465
Gibbs Free Energy (G)= -1186.8100 0.20834

Frequencies -- 59.3022 70.5780 76.6907
SCF Energy (M06) = -1186.54779
SCF Energy (M06/def2-tzvp) = -1187.912115

2π-Insertion TS RhCOCl

Using Gaussian 03: AM64L-G03RevC.02 12-Jun-2004

#b3lyp gen pseudo=read scf=(direct,tight,maxcycle=300,xqc) gfinput gfprint
opt=(maxcycle=250,modredundant) iop(1/8=20) geom=connectivity
Modredundant Input: B 4 7 F
#b3lyp GenChk ChkBas scf=(direct,tight,maxcycle=300,xqc)
opt=(calcfc,ts,noeigentest,maxcycle=250,nofreeze) freq=noraman iop(1/8=20)
gfinput gfprint Geom=AllCheck Guess=Read SCRF=Check
#N Geom=AllCheck Guess=Read SCRF=Check Test GenChk RB3LYP/ChkBas Freq

Pointgroup= C1 Stoichiometry= C12H16ClO2Rh C1[X(C12H16ClO2Rh)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -1186.99268497 Predicted Change= -8.573902D-10

Optimization completed. {Found 3 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00033	0.00180	[YES]	0.00033	0.00180	[YES]

Atomic Type	X	Y	Z
C	-0.139240	1.793994	-0.599653
Rh	-0.710721	-0.091092	-0.035516
Cl	-0.556260	0.491741	2.427793
C	1.081572	1.410759	-0.509539
C	2.458516	1.947115	-0.261832
C	2.991866	-0.221253	0.121860
C	1.624526	-0.595041	-0.434958
C	0.940780	-1.746376	0.204926
C	-0.048450	-2.432966	-0.474414
C	-0.456337	-2.183544	-1.921012
C	-0.866649	-0.709214	-2.045634
C	-2.549024	0.106466	0.123117
O	-3.685344	0.245366	0.233867
H	-1.878896	-0.588156	-2.434787
H	-0.182781	-0.097888	-2.641228
H	-1.295939	-2.843416	-2.160315
H	0.361107	-2.461906	-2.603541
H	1.654808	-0.662214	-1.521354
H	2.517879	2.296262	0.782087
H	2.657187	2.791453	-0.929880
H	3.717065	-1.003831	-0.126885
H	2.956488	-0.102551	1.213718
H	-0.495062	-3.282404	0.038555
O	3.439980	0.962288	-0.504263
C	-0.971276	3.000059	-0.834746
H	-1.532483	3.246155	0.073650
H	-0.350281	3.861274	-1.109587
H	-1.695696	2.827307	-1.638574
C	1.361673	-2.194781	1.587057
H	0.736468	-3.026703	1.922394
H	2.404032	-2.539586	1.576387
H	1.260130	-1.386799	2.317262

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -1186.99268497 Predicted Change= -8.573902D-10
Zero-point correction (ZPE)= -1186.7374 0.25527
Internal Energy (U)= -1186.7197 0.27289
Enthalpy (H)= -1186.7188 0.27384
Gibbs Free Energy (G)= -1186.7823 0.21037

Frequencies -- -225.6127 63.9476 71.6126
SCF Energy (M06) = -1186.517152
SCF Energy (M06/def2-tzvp) = -1187.879585

Metallacycle RhCOCl

Using Gaussian 03: AM64L-G03RevC.02 12-Jun-2004

# opt=(maxcycle=250,nofreeze) freq=noraman b3lyp geom=connectivity gen
pseudo=read scf=(direct,tight,maxcycle=300,xqc) gfinput gfprint
iop(1/8=20)
#N Geom=AllCheck Guess=Read SCRF=Check Test GenChk RB3LYP/ChkBas Freq

Pointgroup= C1 Stoichiometry= C12H16ClO2Rh C1[X(C12H16ClO2Rh)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -1187.04655064 Predicted Change= -1.442490D-07

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00003	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00746	0.00180	[NO]	0.00746	0.00180	[NO]

Atomic Type	X	Y	Z
C	-0.657333	1.359567	-0.057338
Rh	0.961932	0.108749	-0.070975
Cl	2.714392	-1.452492	-0.862153
C	-1.874508	0.800343	0.025831
C	-3.231928	1.432816	-0.272726
C	-3.446601	-0.856486	-0.510084
C	-2.161412	-0.661272	0.317241
C	-0.972352	-1.573196	0.073560
C	-0.007740	-1.737507	1.031737
C	0.094880	-0.957926	2.338163
C	1.000035	0.229398	2.011519

C	2.221385	1.472013	-0.311077
O	3.028414	2.278191	-0.422946
H	2.051561	0.065819	2.254527
H	0.649223	1.193434	2.377925
H	0.527396	-1.592489	3.121309
H	-0.885689	-0.616907	2.681155
H	-2.468932	-0.753869	1.369724
H	-3.230074	1.953829	-1.242626
H	-3.563912	2.145444	0.493237
H	-4.075962	-1.684386	-0.171181
H	-3.224923	-0.992510	-1.579672
H	0.771903	-2.472268	0.847289
O	-4.168026	0.350664	-0.287858
C	-0.484558	2.842037	-0.295834
H	0.085949	3.308368	0.518619
H	0.062808	3.048735	-1.224308
H	-1.445971	3.367212	-0.356591
C	-0.938191	-2.406408	-1.186297
H	0.015236	-2.929943	-1.286879
H	-1.751613	-3.144965	-1.174028
H	-1.081771	-1.787944	-2.079743

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -1187.04655064 Predicted Change= -1.442490D-07
Zero-point correction (ZPE)= -1186.7889 0.25762
Internal Energy (U)= -1186.7711 0.27544
Enthalpy (H)= -1186.7701 0.27638
Gibbs Free Energy (G)= -1186.8353 0.21118

Frequencies -- 31.9510 42.0925 78.2664
SCF Energy (M06) = -1186.568483
SCF Energy (M06/def2-tzvp) = -1187.927433

Reductive Elimination TS RhCOCl

Using Gaussian 03: AM64L-G03RevC.02 12-Jun-2004

#b3lyp gen pseudo=read scf=(direct,tight,maxcycle=300,xqc) gfinput gfprint
opt=(maxcycle=250,modredundant) iop(1/8=20) geom=connectivity
Modredundant Input: B 1 11 F
#b3lyp GenChk ChkBas scf=(direct,tight,maxcycle=300,xqc)
opt=(calcfc,ts,noeigentest,maxcycle=250,nofreeze) freq=noraman iop(1/8=20)
gfinput gfprint Geom=AllCheck Guess=Read SCRF=Check
#N Geom=AllCheck Guess=Read SCRF=Check Test GenChk RB3LYP/ChkBas Freq

Pointgroup= C1 Stoichiometry= C12H16ClO2Rh C1[X(C12H16ClO2Rh)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -1187.02343046 Predicted Change= -1.153524D-10

Optimization completed. {Found 3 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00015	0.00180	[YES]	0.00015	0.00180	[YES]

Atomic Type	X	Y	Z
C	-0.565840	1.403128	0.142482
Rh	1.020141	0.034897	0.055340
Cl	2.375158	-1.661800	-0.947907
C	-1.760516	0.806500	-0.047101
C	-2.949312	1.393776	-0.791352
C	-3.103015	-0.903060	-0.903097
C	-2.126616	-0.634724	0.260120
C	-0.930954	-1.557329	0.453091
C	-0.111137	-1.378824	1.537218
C	-0.291169	-0.245955	2.539989
C	0.273300	1.038129	1.920784
C	2.306685	1.232157	-0.583891
O	3.126444	1.940743	-0.966219
H	1.327073	1.208819	2.166244
H	-0.268456	1.937265	2.213609
H	0.245836	-0.480448	3.465687
H	-1.348582	-0.120135	2.800579
H	-2.738330	-0.664313	1.178567
H	-2.645454	1.834760	-1.754215
H	-3.482558	2.169401	-0.223516
H	-3.810275	-1.715493	-0.716281
H	-2.562721	-1.105286	-1.840483
H	0.648679	-2.130095	1.739335
O	-3.851275	0.305462	-0.996235
C	-0.351488	2.854481	-0.233174
H	-0.174727	2.949932	-1.312217
H	-1.222452	3.474325	0.016579
H	0.515165	3.286028	0.275935
C	-0.818254	-2.781291	-0.419942
H	0.082306	-3.352825	-0.190605
H	-1.698709	-3.421133	-0.264039
H	-0.782282	-2.522166	-1.482188

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -1187.02343046 Predicted Change= -1.153524D-10
Zero-point correction (ZPE)= -1186.7668 0.25653
Internal Energy (U)= -1186.7497 0.27372
Enthalpy (H)= -1186.7487 0.27466
Gibbs Free Energy (G)= -1186.8118 0.21156

Frequencies -- -379.7070 45.8650 51.2967
SCF Energy (M06) = -1186.55735
SCF Energy (M06/def2-tzvp) = -1187.916615

Product-Catalyst Complex RhCOCl

Using Gaussian 03: AM64L-G03RevC.02 12-Jun-2004

# opt=(maxcycle=250,nofreeze) freq=noraman b3lyp geom=connectivity gen
pseudo=read scf=(direct,tight,maxcycle=300,xqc) gfinput gfprint
iop(1/8=20)
#N Geom=AllCheck Guess=Read SCRF=Check Test GenChk RB3LYP/ChkBas Freq

Pointgroup= C1 Stoichiometry= C12H16ClO2Rh C1[X(C12H16ClO2Rh)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -1187.10407546 Predicted Change= -3.807245D-08

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00002	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00194	0.00180	[NO]	0.00194	0.00180	[YES]

Atomic Type	X	Y	Z
C	1.249600	-1.064014	1.047561
Rh	-0.828481	-0.160302	-0.012927
C	1.592817	-0.241396	0.007880
C	2.281454	-0.722522	-1.268901
C	2.046706	1.522657	-1.526007
C	1.557778	1.298325	-0.074846
C	0.137046	1.768142	0.233270
C	-0.397198	1.399413	1.483923
C	0.464041	0.852563	2.613198
C	0.857029	-0.621202	2.446133
H	0.020124	-1.252066	2.768887
H	1.691523	-0.868772	3.122189
H	-0.072415	0.961919	3.561040
H	1.367909	1.472660	2.700669
H	2.286384	1.750279	0.617302
H	1.559334	-1.147577	-1.982447
H	3.060159	-1.465660	-1.074148
H	2.610185	2.449567	-1.658044
H	1.200014	1.515394	-2.228636
H	-1.306903	1.909371	1.795590
C	-2.583948	0.370629	-0.323700
O	-3.671563	0.695181	-0.509875
Cl	-1.259514	-2.215739	-1.134395
O	2.916963	0.436820	-1.796488
C	-0.446395	2.927525	-0.544607
H	0.158202	3.831343	-0.376254
H	-0.474768	2.747370	-1.622791
H	-1.466093	3.145493	-0.212021
C	1.483416	-2.556238	0.931748
H	1.401301	-2.916591	-0.094166
H	2.485416	-2.799268	1.315875
H	0.755700	-3.111603	1.530382

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -1187.10407546 Predicted Change= -3.807245D-08
Zero-point correction (ZPE)= -1186.8441 0.25988
Internal Energy (U)= -1186.8270 0.27707
Enthalpy (H)= -1186.8260 0.27801
Gibbs Free Energy (G)= -1186.8891 0.21492

Frequencies -- 48.6950 59.0418 78.6943
SCF Energy (M06) = -1186.639709
SCF Energy (M06/def2-tzvp) = -1187.997234

2. RhCOD

2.a. Additional Figures

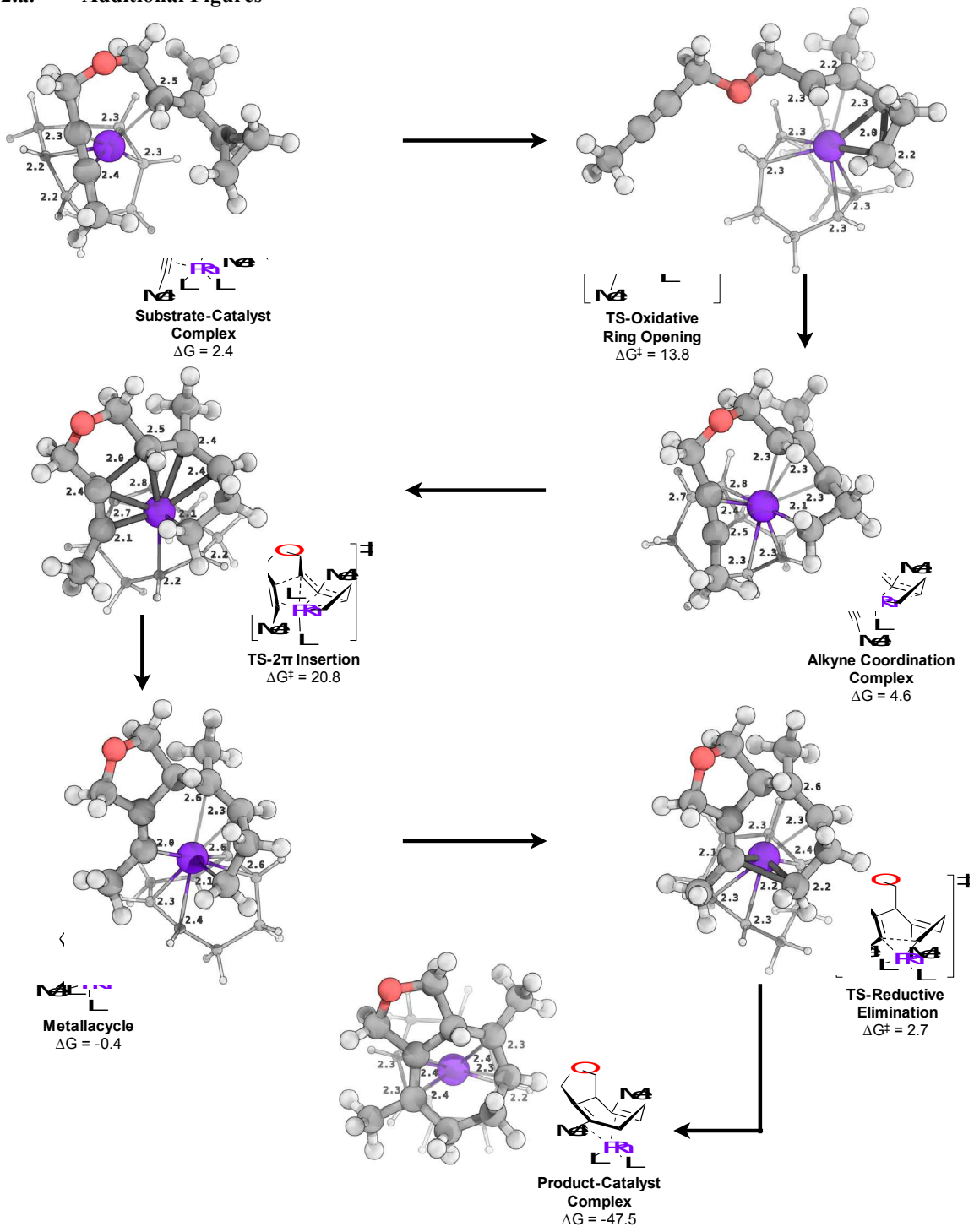

Figure S3. Computed geometries for RhCOD.

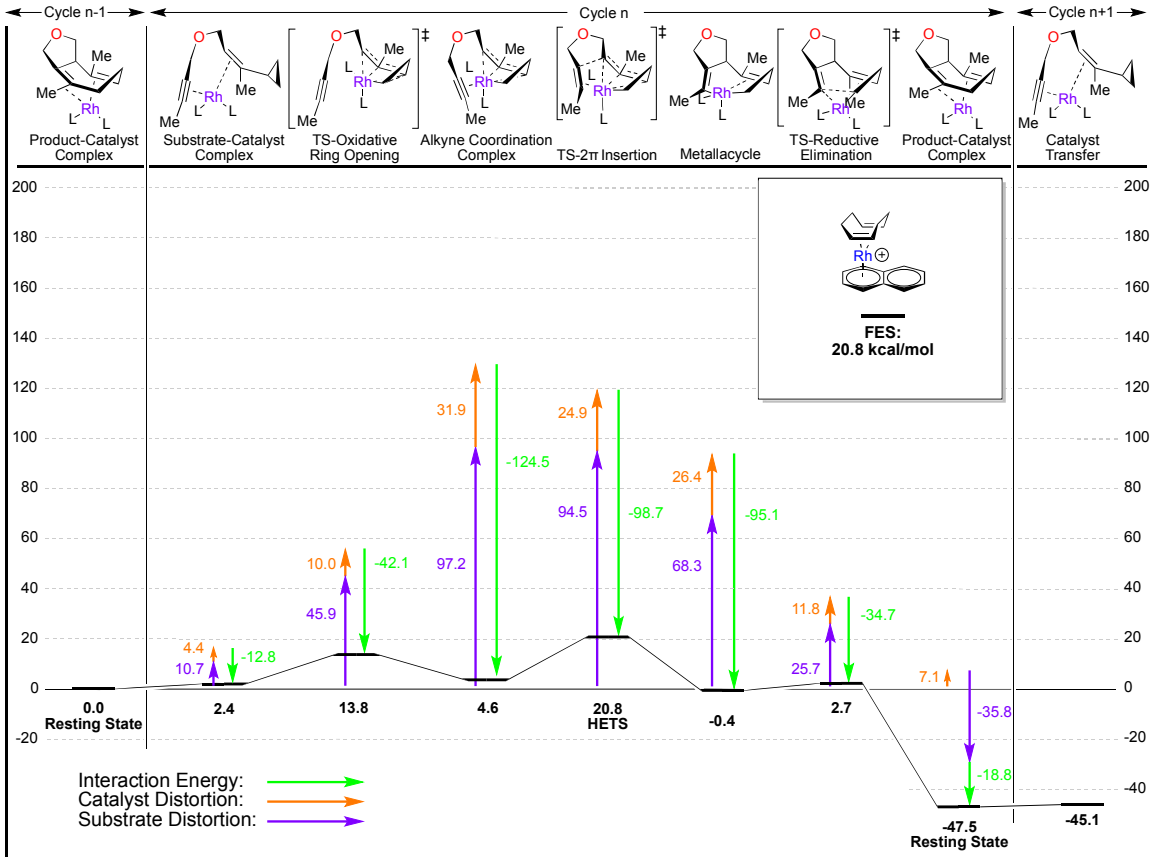

Figure S4. Reaction coordinate diagram for RhCOD. Interaction, catalyst and substrate distortion shown with colored arrows.

Substrate-Catalyst Complex RhCOD

Using Gaussian 03: IA64L-G03RevD.01 13-Oct-2005

# freq=noraman b3lyp gen pseudo gfprint gfinput
scf=(direct,xqc,maxcycle=300) geom=check guess=read

Pointgroup= C1 Stoichiometry= C19H28ORh(1+) C1[X(C19H28ORh)] #Atoms= 49
Charge = 1 Multiplicity = 1

SCF Energy= -925.282766214 Predicted Change= -3.221468D-07

Optimization incomplete.

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00006 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.00538 ||	0.00180	[NO]	0.00538 ||	0.00180	[NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z
Rh	-0.440257	0.169179	0.083972
C	2.131303	-0.951294	-0.731676
C	2.594473	-1.850916	0.361082
C	4.024100	-1.697701	0.894077
C	2.854589	-1.416272	1.785846
C	0.150309	2.347689	0.483751
C	0.055185	1.958283	1.648072
H	4.600929	-2.605010	1.045968
H	4.597167	-0.850809	0.527503
H	2.615057	-2.132934	2.566163
H	2.664889	-0.383255	2.062324
H	2.284861	-2.886773	0.236029
C	-2.408881	0.131772	1.060541
H	-2.301024	0.713163	1.971875
C	-2.947864	-1.280089	1.263593
C	-2.482239	0.872563	-0.133195
H	-2.434816	1.955607	-0.027329
C	-3.046869	0.404800	-1.455628
C	-0.939489	-2.020414	-0.140514
H	0.029906	-2.507818	-0.076335
C	-1.268177	-1.405935	-1.341072
C	-2.674314	-1.052642	-1.797447
H	-0.516175	-1.419991	-2.125141
H	-3.287507	-1.379763	2.299226
C	-1.894260	-2.371936	0.979922
H	-3.836400	-1.425192	0.642067
H	-4.139593	0.535096	-1.458669
H	-2.663742	1.069735	-2.238189
H	-3.392915	-1.750411	-1.359441
H	-2.736241	-1.193592	-2.881350
H	-1.297520	-2.539988	1.882941
H	-2.384955	-3.332068	0.759514
C	1.985770	0.399846	-0.571901
H	2.289198	0.830462	0.378459
C	1.945388	1.424768	-1.700069
H	2.902850	1.424254	-2.234180
C	0.528493	3.094841	-0.746875
H	-0.225775	2.946542	-1.534195
O	1.817049	2.749542	-1.205977
H	1.156573	1.212026	-2.437738
H	0.566339	4.162960	-0.508689
C	0.056518	1.741346	3.098103
H	0.435586	2.643883	3.592698
H	-0.945254	1.539775	3.489912
H	0.705630	0.903534	3.373887
C	2.062874	-1.615620	-2.085038
H	3.083557	-1.887135	-2.387549
H	1.496607	-2.553973	-2.053590
H	1.646461	-0.976263	-2.866541

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -925.282766214 Predicted Change= -3.221468D-07
Zero-point correction (ZPE)= -924.8534 0.42932
Internal Energy (U)= -924.8299 0.45285
Enthalpy (H)= -924.8289 0.45380
Gibbs Free Energy (G)= -924.9057 0.37701

Frequencies -- 34.9833 44.7152 51.7861
SCF Energy (M06) = -924.6561001
SCF Energy (M06/def2-tzvp) = -926.0497593

Oxidative-Addition TS RhCOD

Using Gaussian 03: AM64L-G03RevC.02 12-Jun-2004

# opt=(gdiis,modredundant,maxcycle=250) b3lyp geom=connectivity gen
pseudo=read gfprint gfinput scf=(direct,xqc,tight,maxcycle=250)
Modredundant Input: B 3 5 F
#B3LYP/ChkBas GenChk gfprint gfinput scf=(direct,xqc,tight,maxcycle=250)
opt=(maxcycle=250,calcfc,ts,noeigentest,nofreeze) Freq=Noraman
Geom=AllCheck Guess=Read SCRF=Check
#N Geom=AllCheck Guess=Read SCRF=Check GenChk RB3LYP/ChkBas Freq

Pointgroup= C1 Stoichiometry= C19H28ORh(1+) C1[X(C19H28ORh)] #Atoms= 49
Charge = 1 Multiplicity = 1

SCF Energy= -925.270265099 Predicted Change= -5.640279D-10

Optimization completed on the basis of negligible forces. {Found 3 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00218	0.00180	[NO]	0.00218	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
Rh	1.010903	-0.035936	-0.343069
C	1.143881	-2.130767	0.463043
C	2.240183	-2.012147	-0.472950
C	2.209792	-2.398884	-1.917632
C	1.948436	-0.933963	-2.133248
C	-4.609321	-0.433721	0.118337
C	-5.399660	0.353400	-0.348558
H	3.155842	-2.778597	-2.303115
H	1.388312	-3.061666	-2.190265
H	2.822456	-0.348716	-2.403310
H	1.033809	-0.678605	-2.679890
H	3.224168	-1.828603	-0.048839
C	-0.469933	1.440538	0.688812
H	-1.410273	0.925746	0.498609
C	-0.317294	2.830754	0.090631
C	0.347454	0.907992	1.666513
H	-0.041945	0.052500	2.212579
C	1.583991	1.529687	2.276816
C	1.745020	1.936642	-1.174987
H	2.124056	1.691404	-2.165052
C	2.575841	1.652000	-0.100587
C	2.486624	2.290592	1.277631
H	3.514210	1.150207	-0.329505
H	-1.314160	3.211827	-0.152904
C	0.543470	2.860483	-1.191575
H	0.090816	3.511762	0.842889
H	1.294560	2.201127	3.099290
H	2.166038	0.725259	2.740296
H	2.146939	3.324692	1.169262
H	3.495855	2.348155	1.698066
H	-0.080543	2.575355	-2.046700
H	0.877978	3.888166	-1.399417
C	-0.156768	-1.971837	-0.032458
H	-0.335469	-2.095246	-1.100520
C	-1.425439	-2.077869	0.767640
H	-1.778625	-3.124761	0.722940
C	-3.698878	-1.404199	0.707592
H	-3.676800	-1.295672	1.804420
O	-2.374905	-1.212035	0.180392
H	-1.278832	-1.840037	1.832732
H	-4.029926	-2.432022	0.489129
C	-6.361274	1.294838	-0.915257
H	-6.061796	1.604693	-1.923309
H	-7.354691	0.837525	-0.991021
H	-6.453324	2.195666	-0.297555
C	1.487182	-2.397317	1.909165
H	1.610070	-3.478603	2.054022
H	2.431065	-1.919857	2.189400
H	0.708986	-2.065640	2.599166

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy=	-925.270265099	Predicted Change= -5.640279D-10	
Zero-point correction (ZPE)=	-924.8426	0.42760	
Internal Energy (U)=	-924.8193	0.45091	
Enthalpy (H)=	-924.8184	0.45185	
Gibbs Free Energy (G)=	-924.8958	0.37439	

Frequencies -- -213.5920 21.2559 36.5263
SCF Energy (M06) = -924.6352954
SCF Energy (M06/def2-tzvp) = -926.0314525

Alkyne Coordination Complex RhCOD

Using Gaussian 03: AM64L-G03RevC.02 12-Jun-2004

opt=maxcycle=250 freq=noraman b3lyp geom=connectivity gen pseudo=read
gfprint gfinput scf=(direct,xqc,tight,maxcycle=250)
#N Geom=AllCheck Guess=Read SCRF=Check GenChk RB3LYP/ChkBas Freq

Pointgroup= C1 Stoichiometry= C19H28ORh(1+) C1[X(C19H28ORh)] #Atoms= 49
Charge = 1 Multiplicity = 1

SCF Energy= -925.284643782 Predicted Change= -9.616118D-08

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00316	0.00180	[NO]	0.00316	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	1.326215	-1.959885	0.003125
C	0.490086	-2.138868	1.130751
C	0.822112	-1.582104	2.514865
C	0.614627	-0.078251	2.359107
C	1.278113	1.905915	-0.279424
C	0.517359	2.349845	0.582703
H	0.141764	-2.013914	3.254328
H	1.841373	-1.854186	2.815789
H	-0.208614	0.317948	2.957478
H	1.506191	0.537810	2.489208
H	-0.245168	-2.937096	1.070816
C	2.171371	-0.823303	0.006223
H	2.593927	-0.494353	0.951563
C	3.011406	-0.392495	-1.169659
H	3.953586	-0.954344	-1.177039
C	2.336575	1.866748	-1.320760
H	1.889020	1.661729	-2.306520
O	3.391810	0.969058	-1.060295
H	2.507334	-0.571173	-2.131173
H	2.793303	2.860963	-1.362043
C	-0.126258	3.227865	1.567851
H	0.459439	4.149974	1.658613
H	-1.143055	3.501891	1.269427
H	-0.170020	2.761691	2.557789
C	1.214065	-2.893124	-1.178641
H	2.010328	-3.644773	-1.096763
H	0.260377	-3.427355	-1.188119
H	1.349417	-2.392851	-2.140607
Rh	0.031527	-0.062679	0.364812
C	-1.406982	-0.777820	-1.934689
C	-1.093263	0.536200	-2.008176
C	-2.137216	-0.648795	0.989391
C	-2.107424	0.730362	0.841868
C	-2.726950	-1.336590	-1.452128
H	-0.708415	-1.487724	-2.367680
H	-0.177642	0.801927	-2.532727
C	-1.961373	1.701192	-1.590287
H	-1.980746	-1.026447	1.998091
C	-2.773254	-1.659043	0.058287
H	-1.924065	1.292313	1.752877
C	-2.776394	1.512330	-0.285573
H	-3.531151	-0.643688	-1.712960
H	-2.940528	-2.259822	-2.001803
H	-1.314444	2.575993	-1.481012
H	-2.654705	1.946152	-2.408064
H	-3.822764	-1.783907	0.366730
H	-2.306022	-2.633524	0.234235
H	-3.032251	2.507005	0.094954
H	-3.736545	1.036783	-0.508566

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy=	-925.284643782	Predicted Change= -9.616118D-08	
Zero-point correction (ZPE)=	-924.8539	0.43066	
Internal Energy (U)=	-924.8314	0.45321	
Enthalpy (H)=	-924.8304	0.45416	
Gibbs Free Energy (G)=	-924.9025	0.38208	

Frequencies -- 61.0702 75.5528 86.6094
SCF Energy (M06) = -924.6576917
SCF Energy (M06/def2-tzvp) = -926.0514691

2π-Insertion TS RhCOD

Using Gaussian 03: AM64L-G03RevC.02 12-Jun-2004

#b3lyp/gen pseudo=read gfprint gfinput scf=(direct,xqc,tight,maxcycle=250)
opt=(maxcycle=250,modredundant) geom=connectivity
Modredundant Input: B 5 12 F
#B3LYP/ChkBas GenChk gfprint gfinput scf=(direct,xqc,tight,maxcycle=250)
opt=(maxcycle=250,calcfc,ts,noeigentest,nofreeze) Freq=Noraman
Geom=AllCheck Guess=Read SCRF=Check
#N Geom=AllCheck Guess=Read SCRF=Check GenChk RB3LYP/ChkBas Freq

Pointgroup= C1 Stoichiometry= C19H28ORh(1+) C1[X(C19H28ORh)] #Atoms= 49
Charge = 1 Multiplicity = 1

SCF Energy= -925.262229380 Predicted Change= -9.095485D-10

Optimization completed. {Found 3 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00046	0.00180	[YES]	0.00046	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	1.316985	-1.791183	-0.291983
C	0.612451	-2.367463	0.751860
C	0.739400	-1.975789	2.220321
C	0.426027	-0.480115	2.320574
C	1.682740	1.363075	0.009106
C	0.641350	1.813756	0.608597
H	0.022644	-2.565452	2.798825
H	1.736364	-2.233443	2.605646
H	-0.383649	-0.244869	3.014067
H	1.287140	0.150835	2.551581
H	0.023665	-3.252244	0.517894
C	2.182172	-0.619359	-0.043250
H	2.560678	-0.571398	0.975651
C	3.309948	-0.353772	-1.039076
H	4.079671	-1.124387	-0.925652
C	2.888307	1.848781	-0.746926
H	2.596614	2.081428	-1.785338
O	3.907778	0.879995	-0.725194
H	2.949224	-0.366697	-2.077873
H	3.273608	2.760297	-0.279555
C	0.177254	3.041967	1.304886
H	0.950065	3.818301	1.263574
H	-0.742142	3.446143	0.873060
H	-0.022489	2.825552	2.361439
C	1.291717	-2.428524	-1.665506
H	2.230965	-2.969293	-1.840286
H	0.477929	-3.153783	-1.746853
H	1.188050	-1.700088	-2.474260
Rh	-0.184488	-0.099506	0.366610
C	-1.608909	-0.503616	-1.959543
C	-1.214055	0.790434	-1.917986
C	-2.230289	-0.621562	0.978229
C	-2.122582	0.781288	0.959023
C	-2.947058	-1.029001	-1.492488
H	-0.960840	-1.215998	-2.462676
H	-0.280290	1.048604	-2.414999
C	-2.012415	1.958396	-1.382869
H	-2.124629	-1.093774	1.953388
C	-2.952274	-1.503048	-0.021725
H	-1.926501	1.243092	1.923874
C	-2.787847	1.702396	-0.066055
H	-3.716860	-0.268807	-1.647553
H	-3.233157	-1.877278	-2.123732
H	-1.320541	2.792899	-1.235786

```
 H      -2.719960    2.298869   -2.152770
 H      -3.993434   -1.615573    0.319204
 H      -2.518220   -2.507721    0.036689
 H      -2.969266    2.670246    0.412822
 H      -3.782423    1.302390   -0.287404
---------------------------------------------------------------------
 Statistical Thermodynamic Analysis
 Temperature= 298.150 Kelvin       Pressure= 1.00000 Atm
=====================================================================
 SCF Energy=    -925.262229380     Predicted Change= -9.095485D-10
 Zero-point correction (ZPE)=           -924.8320       0.43019
 Internal Energy (U)=                                  -924.8106       0.45162
 Enthalpy (H)=                                                        -924.8096       0.45257
 Gibbs Free Energy (G)=                                -924.8795       0.38272
---------------------------------------------------------------------
 Frequencies --  -237.9369              63.3908              68.4420
 SCF Energy (M06) =  -924.6324734
 SCF Energy (M06/def2-tzvp) =  -926.0245505
```

Metallacycle RhCOD

```
---------------------------------------------------------------------
 Using  Gaussian 03:  IA64L-G03RevD.01 13-Oct-2005
=====================================================================
 # opt=maxcycle=250 freq=noraman b3lyp gen pseudo gfprint gfinput
 scf=(direct,xqc,maxcycle=300) geom=check guess=read
 #N Geom=AllCheck Guess=Read SCRF=Check GenChk RB3LYP/ChkBas Freq
---------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C19H28ORh(1+)   C1[X(C19H28ORh)]  #Atoms= 49
 Charge = 1       Multiplicity = 1
---------------------------------------------------------------------
 SCF Energy= -925.303843887        Predicted Change= -4.934228D-06
=====================================================================
 Optimization completed. {Found  1 times}
 Item      Max Val.   Criteria   Pass?     RMS Val.   Criteria   Pass?
 Force     0.00002 ||  0.00045   [ YES ]     0.00000 ||  0.00030   [ YES ]
 Displ     0.04333 ||  0.00180   [ NO ]      0.04333 ||  0.00180   [ NO ]
---------------------------------------------------------------------
    Atomic              Coordinates (Angstroms)
    Type              X                 Y                 Z
---------------------------------------------------------------------
    Rh      0.412375     0.010127    -0.109396
    C      -1.560846    -1.599026     0.162488
    C      -0.669824    -1.901777    -0.842857
    C      -0.679945    -1.333900    -2.261504
    C       0.277916    -0.149929    -2.196415
    C      -2.390803     0.765528    -0.137896
    C      -1.161208     1.288602    -0.282515
    H      -0.343851    -2.096697    -2.973572
    H      -1.682777    -1.015958    -2.557286
    H       1.289975    -0.366769    -2.536535
    H      -0.092722     0.777351    -2.630058
    H       0.046381    -2.695584    -0.644977
    C       2.318542    -1.254638     1.194816
    H       1.678893    -1.966300     1.715630
    C       2.976492    -0.194317     2.053956
    C       2.587616    -1.492900    -0.113584
    H       2.177712    -2.399673    -0.552800
    C       3.528269    -0.723016    -1.008919
    C       1.690990     1.676537     0.784619
    H       0.966546     2.475598     0.897993
    C       2.208510     1.480354    -0.483454
    C       3.539302     0.812643    -0.813153
    H       1.800742     2.112062    -1.268031
    H       3.057409    -0.576156     3.077148
    C       2.198913     1.138113     2.103141
    H       4.001731    -0.025511     1.715717
    H       4.551092    -1.104896    -0.878329
    H       3.270802    -0.951760    -2.048143
    H       4.256751     1.084134    -0.033502
    H       3.919622     1.266055    -1.734054
    H       1.334110     1.029851     2.771922
    H       2.822649     1.915171     2.572040
    C      -2.748715    -0.702965    -0.105132
    H      -3.175830    -0.969357    -1.083725
    C      -3.945277    -0.667893     0.870114
    H      -4.624279    -1.518821     0.776368
    C      -3.694485     1.508524     0.141277
    H      -4.069873     2.071945    -0.722452
    O      -4.648680     0.494584     0.454477
    H      -3.580601     2.210837     0.981152
    H      -3.616771    -0.582911     1.917901
    C      -1.001592     2.784224    -0.467389
    H      -1.880965     3.210574    -0.963898
    H      -0.888947     3.315129     0.488306
    H      -0.138571     3.043826    -1.088685
    C      -1.477505    -2.299701     1.495208
    H      -1.483989    -1.588883     2.329738
    H      -2.355405    -2.945643     1.628822
    H      -0.585357    -2.926757     1.573490
---------------------------------------------------------------------
 Statistical Thermodynamic Analysis
 Temperature= 298.150 Kelvin       Pressure= 1.00000 Atm
=====================================================================
 SCF Energy=    -925.303843887     Predicted Change= -4.934228D-06
 Zero-point correction (ZPE)=           -924.8713       0.43252
 Internal Energy (U)=                                  -924.8496       0.45416
 Enthalpy (H)=                                                        -924.8487       0.45510
 Gibbs Free Energy (G)=                                -924.9199       0.38393
---------------------------------------------------------------------
 Frequencies --   31.1516              61.4716              82.9671
 SCF Energy (M06) =  -924.667433
 SCF Energy (M06/def2-tzvp) =  -926.0553635
```

Reductive Elimination TS RhCOD

```
---------------------------------------------------------------------
 Using  Gaussian 03:  AM64L-G03RevC.02 12-Jun-2004
=====================================================================
 #b3lyp/gen pseudo=read gfprint gfinput scf=(direct,xqc,tight,maxcycle=250)
 opt=(maxcycle=250,modredundant) geom=connectivity
 Modredundant Input:  B   4        6 F
 Modredundant Input:  B   4   29 2.2000 F
 #B3LYP/ChkBas GenChk gfprint gfinput scf=(direct,xqc,tight,maxcycle=250)
 opt=(maxcycle=250,calcfc,ts,noeigentest,nofreeze) Freq=Noraman
 Geom=AllCheck Guess=Read SCRF=Check
 #N Geom=AllCheck Guess=Read SCRF=Check GenChk RB3LYP/ChkBas Freq
---------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C19H28ORh(1+)   C1[X(C19H28ORh)]  #Atoms= 49
 Charge = 1       Multiplicity = 1
---------------------------------------------------------------------
 SCF Energy= -925.291041139        Predicted Change= -2.287980D-08
=====================================================================
 Optimization completed. {Found  2 times}
 Item      Max Val.   Criteria   Pass?     RMS Val.   Criteria   Pass?
 Force     0.00001 ||  0.00045   [ YES ]     0.00000 ||  0.00030   [ YES ]
 Displ     0.00192 ||  0.00180   [ NO ]      0.00192 ||  0.00180   [ YES ]
---------------------------------------------------------------------
    Atomic              Coordinates (Angstroms)
    Type              X                 Y                 Z
---------------------------------------------------------------------
    C       1.506327    -1.563004     0.475778
    C       0.705253    -1.405530     1.585638
    C       0.907979    -0.307722     2.624447
    C       0.239235     0.953283     2.096241
    C       2.248079     0.794854    -0.115313
    C       1.059924     1.392559     0.110276
    H       0.448964    -0.607917     3.573174
    H       1.973195    -0.142331     2.816394
    H      -0.797765     1.078071     2.412553
    H       0.781121     1.877461     2.279475
    H       0.021607    -2.214407     1.834608
    C       2.668287    -0.616949     0.241028
    H       3.277898    -0.574045     1.158479
    C       3.666178    -0.895545    -0.906340
    H       4.399752    -1.672322    -0.679644
    C       3.413041     1.388284    -0.898479
    H       3.896475     2.226452    -0.379820
    O       4.362360     0.336009    -1.027663
    H       3.085499     1.749184    -1.886763
    H       3.146658    -1.152073    -1.843187
    C       0.893708     2.868232    -0.181085
    H       1.698636     3.453725     0.280354
    H       0.940475     3.059600    -1.261655
    H      -0.048784     3.281393     0.182895
    C       1.442190    -2.815606    -0.361164
    H       1.344756    -2.601757    -1.430889
    H       2.379133    -3.375341    -0.237994
    H       0.625241    -3.473873    -0.054486
    Rh     -0.491509     0.013029     0.194137
    C      -1.812572     1.304953    -1.162338
    C      -2.199862     1.508143     0.156188
    C      -1.782590    -1.610977    -0.855962
    C      -2.460950    -1.400851     0.324926
    C      -2.550184     0.456968    -2.188314
    H      -1.100237     2.014057    -1.572746
    H      -1.787878     2.382412     0.654539
    C      -3.391793     0.910399     0.871661
    H      -1.099085    -2.455234    -0.883226
    C      -2.106915    -1.022828    -2.214631
    H      -2.211175    -2.048504     1.162745
    C      -3.705306    -0.552269     0.495282
    H      -3.627015     0.532963    -2.012017
    H      -2.377062     0.888518    -3.179071
    H      -3.200588     0.968861     1.949645
    H      -4.272476     1.545993     0.692885
    H      -2.877948    -1.634195    -2.706542
    H      -1.211373    -1.114622    -2.839087
    H      -4.323762    -0.990854     1.285052
    H      -4.305437    -0.593953    -0.417578
---------------------------------------------------------------------
 Statistical Thermodynamic Analysis
 Temperature= 298.150 Kelvin       Pressure= 1.00000 Atm
=====================================================================
 SCF Energy=    -925.291041139     Predicted Change= -2.287980D-08
 Zero-point correction (ZPE)=           -924.8595       0.43150
 Internal Energy (U)=                                  -924.8385       0.45252
 Enthalpy (H)=                                                        -924.8375       0.45346
 Gibbs Free Energy (G)=                                -924.9071       0.38386
---------------------------------------------------------------------
 Frequencies --  -326.1231              42.6173              54.6085
 SCF Energy (M06) =  -924.6623814
 SCF Energy (M06/def2-tzvp) =  -926.0507014
```

Product-Catalyst Complex RhCOD

```
---------------------------------------------------------------------
 Using  Gaussian 03:  IA64L-G03RevD.01 13-Oct-2005
=====================================================================
 # freq=noraman b3lyp gen pseudo gfprint gfinput
 scf=(direct,xqc,maxcycle=300) geom=check guess=read
---------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C19H28ORh(1+)   C1[X(C19H28ORh)]  #Atoms= 49
 Charge = 1       Multiplicity = 1
---------------------------------------------------------------------
 SCF Energy= -925.368591573        Predicted Change= -1.347109D-05
=====================================================================
 Optimization incomplete.
 Item      Max Val.   Criteria   Pass?     RMS Val.   Criteria   Pass?
 Force     0.00013 ||  0.00045   [ YES ]     0.00002 ||  0.00030   [ YES ]
 Displ     0.05113 ||  0.00180   [ NO ]      0.05113 ||  0.00180   [ NO ]
---------------------------------------------------------------------
    Atomic              Coordinates (Angstroms)
    Type              X                 Y                 Z
---------------------------------------------------------------------
    Rh     -0.380093     0.043756     0.202338
    C       1.349080    -1.152390     1.260289
    C       0.868716    -0.229795     2.170243
    C       1.540387     1.108915     2.427373
    C       1.330824     2.174520     1.339441
    C       1.869197     0.499752    -0.548486
    C       1.370126     1.704418    -0.106307
    H       1.179656     1.511956     3.377833
    H       2.615745     0.927960     2.562594
    H       0.371380     2.679525     1.506125
    H       2.092603     2.962118     1.449190
```

H	0.216427	-0.601689	2.957880
C	-1.932852	1.227234	-1.023766
H	-1.465336	2.206257	-1.091922
C	-3.290414	1.198069	-0.339760
C	-1.400328	0.227273	-1.820194
H	-0.583353	0.511723	-2.480435
C	-2.007277	-1.125845	-2.116129
C	-2.255117	-0.484109	1.299845
H	-1.940181	-0.630316	2.331464
C	-1.998560	-1.526485	0.413496
C	-2.715830	-1.774371	-0.906441
H	-1.461093	-2.381510	0.814464
H	-3.685810	2.218621	-0.314204
C	-3.230659	0.655944	1.105560
H	-3.749555	-1.425664	-0.833904
H	-2.704937	-1.041106	-2.962923
H	-1.200663	-1.783932	-2.457557
H	-3.994568	0.617870	-0.941473
H	-2.773385	-2.854825	-1.072757
H	-2.937278	1.465723	1.782965
H	-4.233132	0.340905	1.432445
C	2.412190	-0.678561	0.278639
H	3.319057	-0.372727	0.824024
C	2.833223	-1.659933	-0.839328
H	3.672953	-2.302170	-0.567761
C	2.293170	0.221408	-1.995114
H	2.781900	1.081127	-2.462442
O	3.248119	-0.820233	-1.902370
H	1.446447	-0.081204	-2.632110
H	1.987937	-2.290611	-1.156201
C	1.140913	2.827049	-1.099929
H	0.396836	3.540865	-0.733029
H	2.077007	3.387832	-1.232041
H	0.827792	2.478931	-2.087678
C	1.102411	-2.631135	1.435625
H	2.027644	-3.100287	1.799884
H	0.327834	-2.822666	2.183615
H	0.832087	-3.141630	0.507364

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -925.368591573 Predicted Change= -1.347109D-05
Zero-point correction (ZPE)= -924.9345 0.43409
Internal Energy (U)= -924.9132 0.45538
Enthalpy (H)= -924.9122 0.45633
Gibbs Free Energy (G)= -924.9829 0.38564

Frequencies -- 30.6187 47.1145 64.0949
SCF Energy (M06) = -924.7442374
SCF Energy (M06/def2-tzvp) = -926.1306984

3. RhNHC-IPr

3.a. Additional Figures

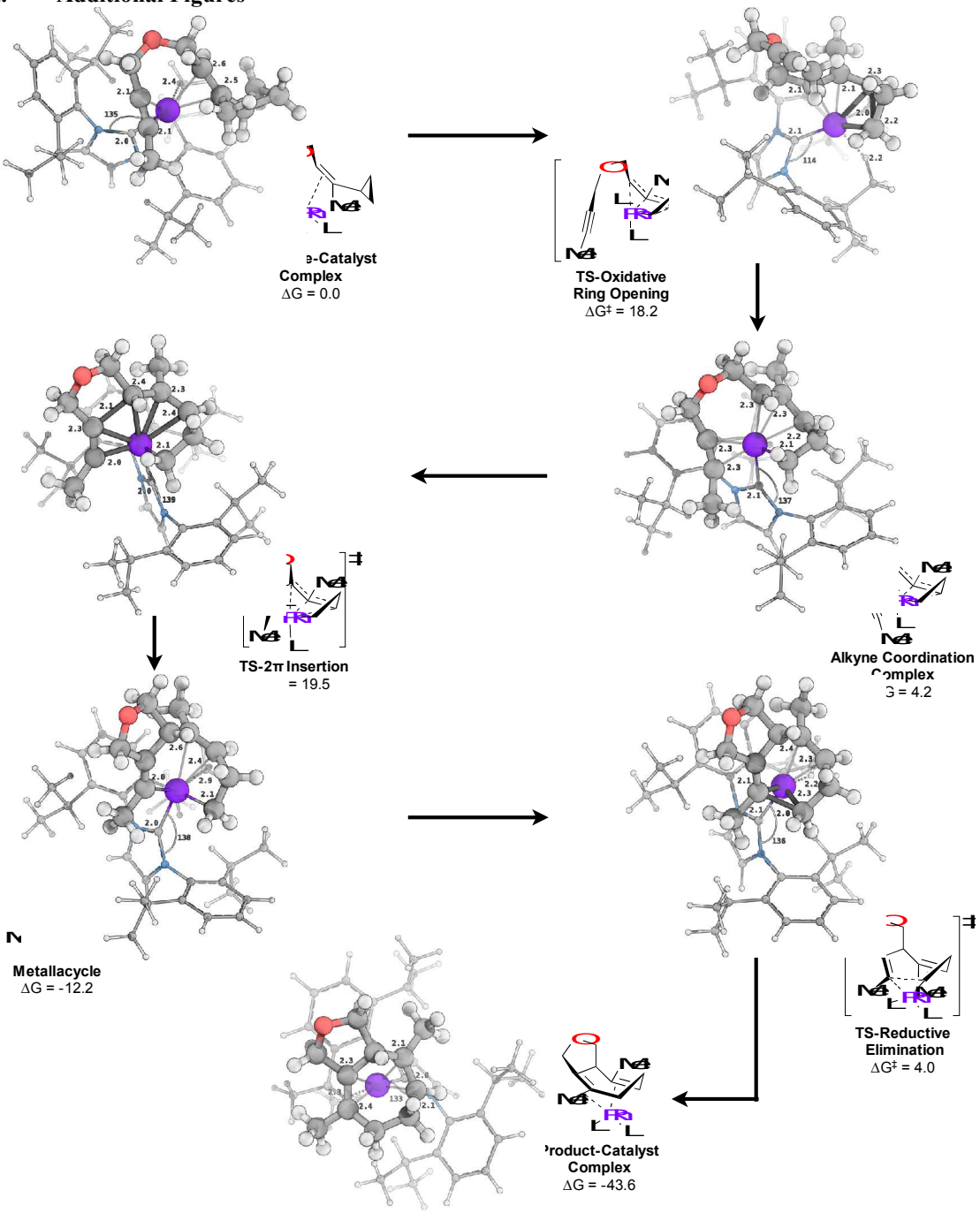

Figure S5. Computed geometries for RhNHC-IPr.

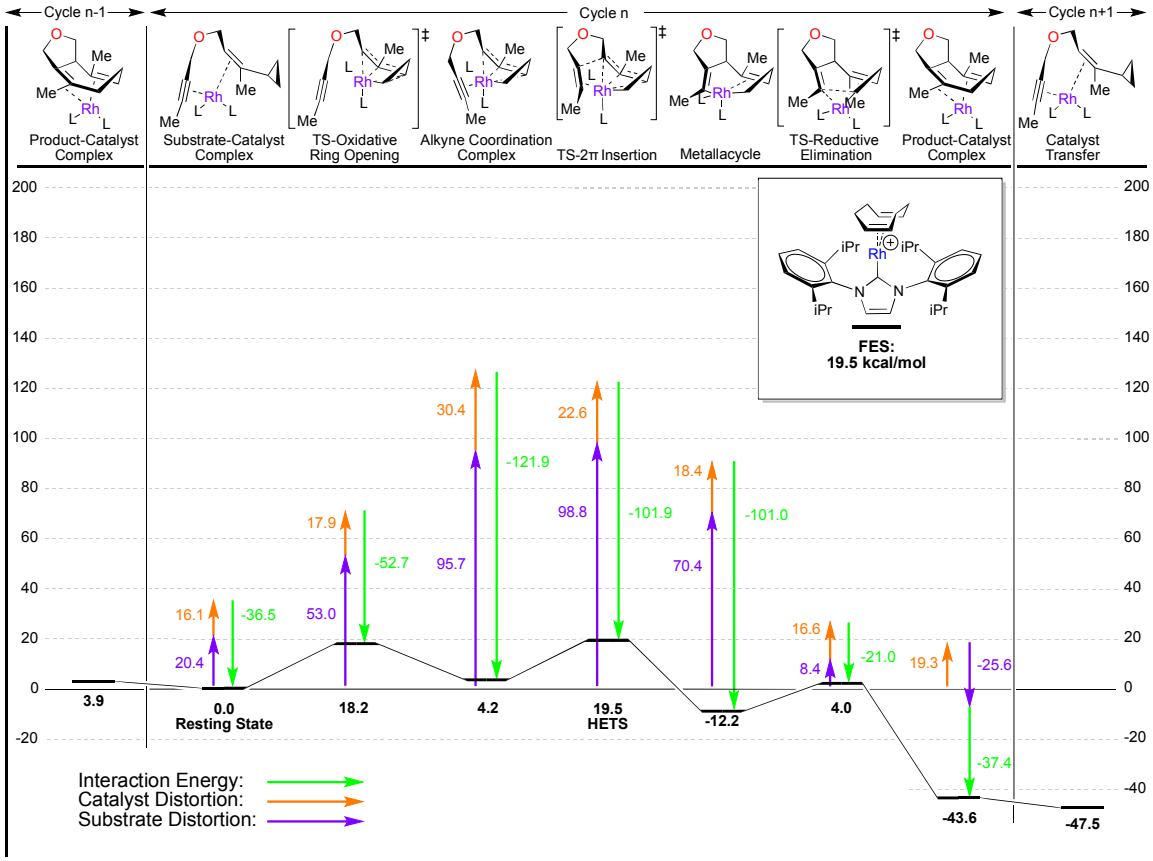

Figure S6. Reaction coordinate diagram for NHC-IPr. Interaction, catalyst and substrate distortion shown with colored arrows.

Substrate-Catalyst Complex RhNHC-IPr

Using Gaussian 03: AM64L-G03RevE.01 11-Sep-2007

opt=(gdiis,maxcycle=250) freq b3lyp geom=connectivity gen pseudo=read
gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
#N Geom=AllCheck Guess=Read SCRF=Check GenChk RB3LYP/ChkBas Freq

Pointgroup= C1 Stoichiometry= C38H52N2ORh(1+) C1[X(C38H52N2ORh)] #Atoms= 94
Charge = 1 Multiplicity = 1

SCF Energy= -1773.31167298 Predicted Change= -1.087739D-07

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00002 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.01779 ||	0.00180	[NO]	0.01779 ||	0.00180	[NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z
Rh	-0.428446	-0.899424	-0.417532
C	-1.919469	-2.620840	-1.378708
C	-3.231069	-2.168201	-0.813212
C	-4.382882	-3.168478	-0.735737
C	-3.788685	-2.605768	0.522526
C	1.240774	-1.469534	-1.512336
C	0.629449	-0.635489	-2.237270
H	-5.365514	-2.834648	-1.055292
H	-4.159200	-4.204881	-0.973796
H	-4.361825	-1.871174	1.079303
H	-3.206694	-3.278404	1.145308
H	-3.535129	-1.177467	-1.151658
C	-0.938825	-3.186920	-0.594319
H	-1.136245	-3.286681	0.474035
C	0.228530	-4.033648	-1.063097
H	0.062674	-5.062632	-0.723979
C	2.134436	-2.611561	-1.194905
H	2.542939	-3.007736	-2.140079
O	1.468670	-3.641059	-0.478275
H	0.311353	-4.058551	-2.156755
H	2.968982	-2.294348	-0.565106
C	0.381221	0.232485	-3.401436
H	1.132504	0.045019	-4.178047
H	-0.608451	0.049240	-3.831126
H	0.433016	1.291469	-3.126348
C	-1.901043	-2.641707	-2.891620
H	-2.504906	-3.485479	-3.250714
H	-2.362397	-1.732982	-3.293145
H	-0.899798	-2.736957	-3.313513
C	0.313950	0.840190	0.297804
N	1.565055	1.287877	0.622677
N	-0.522786	1.855926	0.671619
C	1.493571	2.554391	1.200057
C	2.830035	0.577296	0.540848
C	0.187643	2.912317	1.228833
C	-1.968746	1.771344	0.638163
H	2.378407	3.065923	1.542649
C	3.156203	-0.338050	1.564246
C	3.729164	0.914526	-0.494159
H	-0.302344	3.799565	1.597644
C	-2.666735	2.307866	-0.465428
C	-2.621841	1.199126	1.753051
C	2.233531	-0.653507	2.737960
C	4.420126	-0.942274	1.508231
C	4.978482	0.281506	-0.493398
C	3.411803	1.953506	-1.566720
C	-1.959812	3.035506	-1.604716
C	-4.063838	2.210818	-0.447341
C	-4.020080	1.124368	1.710484
C	-1.859946	0.682021	2.971589
C	1.997874	-2.167770	2.902314
H	1.260057	-0.194953	2.541828
C	2.779816	-0.034096	4.041554
H	4.704536	-1.649942	2.280604
C	5.322465	-0.639010	0.493350
H	5.696380	0.518804	-1.271877
C	4.116669	3.293986	-1.266389
H	2.331324	2.134972	-1.553210
C	3.781092	1.471034	-2.982677
H	-0.903945	2.743884	-1.584927
C	-2.024296	4.563750	-1.390703
C	-2.515193	2.666360	-2.992251
H	-4.637744	2.616074	-1.274366
C	-4.733507	1.618740	0.621533
H	-4.557704	0.692088	2.548551
H	-0.842832	1.084251	2.931380
C	-1.745115	-0.853650	2.947727
C	-2.473538	1.161606	4.301116
H	2.915609	-2.691390	3.192328
H	1.630953	-2.622814	1.976077
H	1.261775	-2.347640	3.694475
H	2.900165	1.051455	3.952995
H	3.756078	-0.457570	4.302523
H	2.096314	-0.233535	4.874851
H	6.299458	-1.113573	0.475688
H	5.205408	3.169759	-1.264494
H	3.828137	3.701134	-0.291699
H	3.864316	4.038420	-2.029997
H	3.356120	0.485078	-3.195003

H	4.865594	1.404658	-3.120555
H	3.405208	2.178733	-3.730009
H	-1.575844	4.859996	-0.436326
H	-3.062087	4.915450	-1.394265
H	-1.488414	5.085019	-2.191812
H	-3.534217	3.040251	-3.139167
H	-2.529907	1.582245	-3.147580
H	-1.894079	3.115984	-3.774752
H	-5.818361	1.561096	0.614036
H	-1.242151	-1.204169	2.031663
H	-2.730306	-1.329395	2.988940
H	-1.156582	-1.213030	3.799012
H	-3.463450	0.728201	4.480025
H	-2.573981	2.251661	4.324380
H	-1.831669	0.861993	5.136569

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -1773.31167298 Predicted Change= -1.087739D-07
Zero-point correction (ZPE)= -1772.4906 0.82103
Internal Energy (U)= -1772.4443 0.86731
Enthalpy (H)= -1772.4434 0.86825
Gibbs Free Energy (G)= -1772.5704 0.74124

Frequencies -- 12.8667 24.6478 30.3515
SCF Energy (M06) = -1772.045947
SCF Energy (M06/def2-tzvp) = -1773.748655

Oxidative-Addition TS RhNHC-IPr

Using Gaussian 03: AM64L-G03RevE.01 11-Sep-2007

# b3lyp/gen pseudo=read gfprint gfinput
scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,readfc,ts,noeigentest,gdiis) freq geom=check guess=read
#N Geom=AllCheck Guess=Read SCRF=Check GenChk RB3LYP/ChkBas Freq

Pointgroup= C1 Stoichiometry= C38H52N2ORh(1+) C1[X(C38H52N2ORh)] #Atoms= 94
Charge = 1 Multiplicity = 1

SCF Energy= -1773.28176816 Predicted Change= -3.953775D-09

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00786	0.00180	[NO]	0.00786	0.00180	[YES]

Atomic Type	X	Y	Z
C	4.129874	-3.876549	-0.782163
Rh	0.530586	0.447678	-1.202848
C	3.033821	-4.155026	-0.348294
C	1.738184	-4.556961	0.214836
C	0.524763	-2.475112	0.046235
C	1.045884	-1.607554	-1.072845
C	0.269351	-1.360403	-2.255859
C	0.904146	-0.520952	-3.248200
C	2.367053	-0.427062	-3.554601
C	2.263967	0.716673	-2.585485
H	2.138935	1.697786	-3.037693
H	2.930374	0.690961	-1.720350
H	2.601151	-0.179443	-4.589720
H	2.959522	-1.274962	-3.211528
H	2.130131	-1.636931	-1.168585
H	1.765880	-4.458472	1.311822
H	1.544609	-5.610117	-0.014155
H	-0.527184	-2.261334	0.234235
H	1.082496	-2.275054	0.970296
H	0.241787	-0.048344	-3.970846
O	0.603406	-3.858163	-0.299565
C	5.460413	-3.578992	-1.309022
H	5.460299	-3.552969	-2.405217
H	5.835465	-2.614483	-0.946507
H	6.177084	-4.348845	-0.999387
C	-1.075813	-1.969238	-2.551511
H	-1.655756	-1.340934	-3.234174
H	-0.925570	-2.944535	-3.033369
H	-1.666231	-2.135316	-1.648723
C	-0.601261	0.673746	0.559775
N	-1.842977	0.413156	1.072560
N	-0.030351	1.509059	1.479197
C	-2.034481	1.098958	2.272233
C	-2.885863	-0.396091	0.468160
C	-0.894866	1.784927	2.531341
C	1.284079	2.081267	1.283142
H	-2.962602	1.037969	2.816581
C	-3.629018	0.147723	-0.601529
C	-3.167363	-1.669420	1.018377
H	-0.622438	2.436133	3.347015
C	2.399141	1.468485	1.896090
C	1.392237	3.241524	0.482950
C	-3.447726	1.576574	-1.108421
C	-4.633648	-0.651344	-1.162854
C	-4.185201	-2.418542	0.413513
C	-2.479216	-2.216907	2.270286
C	2.263182	0.272184	2.832836
C	3.655280	2.036091	1.650957
C	2.677270	3.753937	0.260753
C	0.171626	3.931386	-0.123978
C	-3.242816	1.643088	-2.632928
H	-2.549965	1.995252	-0.645389
C	-4.640396	2.455875	-0.675666
H	-5.223949	-0.262106	-1.986464
C	-4.903369	-1.924461	-0.671691
H	-4.425512	-3.401096	0.805671
C	-3.372778	-2.001298	3.512974
H	-1.551810	-1.653718	2.425531
C	-2.104247	-3.709413	2.166820
H	1.270393	-0.164131	2.678424
C	2.347575	0.728501	4.305510
C	3.298378	-0.832791	2.552087
H	4.536746	1.598349	2.108452
C	3.796618	3.156612	0.834318
H	2.801920	4.640733	-0.352479
H	-0.718449	3.569597	0.400846
C	0.007027	3.567566	-1.611529
C	0.204852	5.461775	0.054300
H	-4.116809	1.276024	-3.181490
H	-2.375795	1.048342	-2.941281
H	-3.075197	2.679707	-2.946870
H	-4.766294	2.452520	0.412582
H	-5.577533	2.102519	-1.120163
H	-4.487806	3.492654	-0.996957
H	-5.687786	-2.526058	-1.121892
H	-4.309275	-2.562410	3.418459
H	-3.634709	-0.948818	3.661402
H	-2.860259	-2.351523	4.415975
H	-1.504371	-3.936319	1.280516
H	-2.992971	-4.349267	2.143651
H	-1.526592	-4.001527	3.051145
H	1.581858	1.474742	4.543936
H	3.324861	1.174230	4.523157
H	2.209155	-0.125017	4.978433
H	4.319527	-0.504596	2.774740
H	3.271637	-1.164227	1.508348
H	3.095784	-1.700845	3.189227
H	4.783024	3.576551	0.658933
H	-0.169354	2.481909	-1.758659
H	0.891802	3.844347	-2.195048
H	-0.862992	4.071880	-2.046633
H	1.005204	5.929071	-0.529363
H	0.348940	5.736568	1.104069
H	-0.741654	5.897160	-0.283630

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -1773.28176816 Predicted Change= -3.953775D-09
Zero-point correction (ZPE)= -1772.4629 0.81882
Internal Energy (U)= -1772.4164 0.86532
Enthalpy (H)= -1772.4154 0.86627
Gibbs Free Energy (G)= -1772.5456 0.73607

Frequencies -- -219.7296 11.4576 16.0260
SCF Energy (M06) = -1772.011779
SCF Energy (M06/def2-tzvp) = -1773.717276

Alkyne Coordination Complex RhNHC-IPr

Using Gaussian 03: AM64L-G03RevE.01 11-Sep-2007

opt=(gdiis,maxcycle=250) freq b3lyp geom=connectivity gen pseudo=read
gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
#N Geom=AllCheck Guess=Read SCRF=Check GenChk RB3LYP/ChkBas Freq

Pointgroup= C1 Stoichiometry= C38H52N2ORh(1+) C1[X(C38H52N2ORh)] #Atoms= 94
Charge = 1 Multiplicity = 1

SCF Energy= -1773.31389410 Predicted Change= -2.601199D-07

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00002	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00829	0.00180	[NO]	0.00829	0.00180	[NO]

Atomic Type	X	Y	Z
C	1.129204	1.140698	-2.264655
Rh	0.524481	-0.733964	-1.079874
C	2.044628	0.317162	-2.419364
C	3.328433	-0.286270	-2.858812
C	2.792523	-2.592849	-2.791417
C	1.349000	-2.479655	-2.372063
C	0.823592	-3.013730	-1.173326
C	-0.511375	-2.676841	-0.826981
C	-1.547920	-2.284686	-1.886807
C	-1.119075	-0.889160	-2.319155
H	-1.818508	-0.100738	-2.055316
H	-0.772032	-0.781628	-3.349054
H	-2.544207	-2.269343	-1.438693
H	-1.561710	-3.004965	-2.715556
H	0.680593	-2.340388	-3.217122
H	3.989721	-0.429613	-1.988566
H	3.815004	0.422571	-3.537303
H	2.933506	-3.468845	-3.435269
H	3.468438	-2.698465	-1.930004
H	-0.875594	-3.025883	0.133420
O	3.197068	-1.485793	-3.589882
C	0.330221	2.351465	-2.508553
H	0.056857	2.860412	-1.581260
H	0.897266	3.050712	-3.133297
H	-0.593926	2.099382	-3.037150
C	1.692666	-3.757435	-0.186083
H	1.167502	-3.917921	0.757255
H	1.952504	-4.740709	-0.597877
H	2.633484	-3.239387	0.025915
C	-0.376096	0.438699	0.437573
N	0.432451	1.075571	1.352871
N	-1.645611	0.824065	0.800212
C	-0.314101	1.856944	2.229155
C	1.869301	0.900661	1.508722
C	-1.609948	1.702076	1.883836
C	-2.933652	0.349879	0.312533
H	0.149775	2.438904	3.008394
C	2.339719	-0.226659	2.231232
C	2.741262	1.909546	1.040232
H	-2.512472	2.117859	2.301064
C	-3.656705	1.145478	-0.602905
C	-3.477877	-0.826447	0.882312
C	1.406013	-1.182814	2.978712
C	3.727539	-0.379278	2.349455

C	4.118313	1.701731	1.198683
C	2.252476	3.244086	0.482499
C	-3.157175	2.496127	-1.109036
C	-4.919588	0.689178	-1.004870
C	-4.743532	-1.231707	0.438420
C	-2.794313	-1.598334	2.010504
C	2.023340	-2.563858	3.264626
H	0.509998	-1.335856	2.366397
C	0.963681	-0.564941	4.326641
H	4.126831	-1.233173	2.884583
C	4.609554	0.560803	1.822582
H	4.813858	2.454210	0.842136
C	2.304934	4.331329	1.580314
H	1.205578	3.126195	0.187125
C	3.042002	3.721861	-0.750657
H	-2.086160	2.561690	-0.895211
C	-3.852699	3.650265	-0.354078
C	-3.344148	2.676885	-2.627978
H	-5.497184	1.275137	-1.712336
C	-5.453742	-0.492247	-0.503198
H	-5.189138	-2.131917	0.847851
H	-1.715820	-1.426101	1.934346
C	-3.028770	-3.119967	1.949174
C	-3.259040	-1.067778	3.386112
H	2.781833	-2.509477	4.053399
H	2.489971	-3.008768	2.382597
H	1.245170	-3.247681	3.620683
H	0.416161	0.371893	4.201044
H	1.836257	-0.367550	4.959620
H	0.310477	-1.262435	4.863461
H	5.681120	0.419553	1.932172
H	3.335277	4.497459	1.913965
H	1.713513	4.061113	2.461143
H	1.918747	5.281133	1.193598
H	3.095470	2.949616	-1.523077
H	4.065729	4.010963	-0.490088
H	2.561897	4.608048	-1.180326
H	-3.682338	3.594122	0.726159
H	-4.935370	3.629849	-0.521468
H	-3.475907	4.617804	-0.704686
H	-4.400981	2.766897	-2.900176
H	-2.928268	1.838440	-3.197626
H	-2.849814	3.596718	-2.959634
H	-6.434504	-0.826994	-0.828617
H	-2.831692	-3.534267	0.955012
H	-4.056684	-3.384917	2.218940
H	-2.373039	-3.625021	2.666984
H	-4.339505	-1.205238	3.507336
H	-3.038247	-0.004022	3.513042
H	-2.757350	-1.613377	4.193590

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -1773.31389410 Predicted Change= -2.601199D-07
Zero-point correction (ZPE)= -1772.4918 0.82204
Internal Energy (U)= -1772.4464 0.86747
Enthalpy (H)= -1772.4454 0.86841
Gibbs Free Energy (G)= -1772.5679 0.74598

Frequencies -- 20.3922 25.8838 33.9922
SCF Energy (M06) = -1772.043934
SCF Energy (M06/def2-tzvp) = -1773.750339

2π-Insertion TS RhNHC-IPr

Using Gaussian 03: AM64L-G03RevE.01 11-Sep-2007

# b3lyp geom=check gen pseudo=read gfprint gfinput guess=read
scf=(direct,tight,maxcycle=300,xqc) guess=read
opt=(gdiis,maxcycle=250,readfc,ts,noeigentest,nofreeze) freq
#N Geom=AllCheck Guess=Read SCRF=Check GenChk RB3LYP/ChkBas Freq

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Pointgroup= C1 Stoichiometry= C38H52N2ORh(1+) C1[X(C38H52N2ORh)] #Atoms= 94
Charge = 1 Multiplicity = 1

SCF Energy= -1773.29653225 Predicted Change= -2.049915D-08

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00265	0.00180	[NO]	0.00265	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-1.007771	-2.408540	0.530665
Rh	-0.625866	-0.815213	-0.684332
C	-1.922029	-2.697831	-0.338142
C	-3.142501	-3.569510	-0.470273
C	-3.441628	-2.466203	-2.430458
C	-2.022899	-1.934367	-2.274323
C	-1.761513	-0.533106	-2.669238
C	-0.480258	-0.137289	-3.019299
C	0.694733	-1.103317	-3.126968
C	0.891640	-1.733304	-1.746453
H	1.848013	-1.501587	-1.289334
H	0.696133	-2.807549	-1.692351
H	1.588009	-0.549260	-3.424577
H	0.512927	-1.852993	-3.910686
H	-1.313601	-2.648833	-2.687778
H	-3.969011	-3.117997	0.105551
H	-2.934796	-4.561537	-0.057297
H	-3.663344	-2.614639	-3.492319
H	-4.187109	-1.776016	-2.008618
H	-0.338001	0.884766	-3.360590
O	-3.519220	-3.732466	-1.816327
C	-2.919352	0.441244	-2.726904
H	-3.631417	0.144959	-3.507297
H	-3.469247	0.492805	-1.780727
H	-2.569725	1.447723	-2.963017
C	-0.477175	-3.017148	1.782645
H	0.478788	-3.509051	1.578388
H	-0.299454	-2.270763	2.560812
H	-1.165309	-3.773751	2.178409
C	0.515868	0.384444	0.512028
N	-0.150355	1.294343	1.299773
N	1.831259	0.523689	0.881720
C	0.724207	1.959836	2.151847
C	-1.542067	1.677152	1.139542
C	1.959667	1.479507	1.890943
C	3.024021	-0.034638	0.262944
H	0.382396	2.710083	2.846451
C	-1.837936	2.749516	0.263112
C	-2.533193	1.045826	1.923756
H	2.921542	1.723932	2.311094
C	3.623157	-1.180043	0.828300
C	3.601558	0.666982	-0.821942
C	-0.753209	3.594393	-0.404370
C	-3.183826	3.105219	0.113163
C	-3.862690	1.443499	1.726322
C	-2.187440	0.062562	3.037230
C	3.085026	-1.861998	2.082613
C	4.796840	-1.656645	0.228916
C	4.772240	0.138406	-1.379947
C	3.056967	2.000218	-1.332836
C	-1.025863	3.913571	-1.884538
H	0.188149	3.039239	-0.363108
C	-0.553444	4.906668	0.387207
H	-3.448581	3.923125	-0.549364
C	-4.188406	2.448291	0.819771
H	-4.650688	0.977758	2.308731
C	-2.095918	0.805595	4.389018
H	-1.197178	-0.349563	2.821823
C	-3.172989	-1.113578	3.147393
H	2.032156	-1.583368	2.192967
C	3.833974	-1.361744	3.337676
C	3.158192	-3.398807	2.008878
H	5.282190	-2.538339	0.633643
C	5.359574	-1.015757	-0.869803
H	5.240674	0.646246	-2.216591
H	2.007850	2.077097	-1.031023
C	3.098920	2.144157	-2.865152
C	3.821739	3.174576	-0.681605
H	-1.926995	4.521480	-2.018664
H	-1.139559	3.004005	-2.481798
H	-0.188444	4.485039	-2.299927
H	-0.304598	4.716148	1.436307
H	-1.462911	5.517650	0.367680
H	0.259171	5.496504	-0.051486
H	-5.225454	2.744241	0.688555
H	-3.060059	1.253452	4.654795
H	-1.351218	1.608148	4.363674
H	-1.814880	0.109977	5.187818
H	-3.295684	-1.627201	2.188630
H	-4.161682	-0.788921	3.488843
H	-2.805683	-1.839439	3.880967
H	3.740006	-0.278506	3.466327
H	4.901964	-1.598872	3.274228
H	3.434663	-1.842840	4.237827
H	4.190763	-3.760568	2.056066
H	2.713124	-3.786492	1.085725
H	2.628925	-3.840110	2.860569
H	6.268687	-1.405667	-1.318561
H	2.603947	1.309056	-3.370699
H	4.123929	2.204915	-3.245686
H	2.592213	3.068747	-3.163168
H	4.883258	3.142715	-0.951704
H	3.753994	3.152326	0.410427
H	3.415271	4.132764	-1.025180

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -1773.29653225 Predicted Change= -2.049915D-08
Zero-point correction (ZPE)= -1772.4746 0.82184
Internal Energy (U)= -1772.4300 0.86647
Enthalpy (H)= -1772.4291 0.86741
Gibbs Free Energy (G)= -1772.5501 0.74638

Frequencies -- -205.4828 29.4456 33.7696
SCF Energy (M06) = -1772.020053
SCF Energy (M06/def2-tzvp) = -1773.724226

Metallacycle RhNHC-IPr

Using Gaussian 03: AM64L-G03RevE.01 11-Sep-2007

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opt=(gdiis,maxcycle=250) freq b3lyp geom=connectivity gen pseudo=read
gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
#N Geom=AllCheck Guess=Read SCRF=Check GenChk RB3LYP/ChkBas Freq

---

Pointgroup= C1 Stoichiometry= C38H52N2ORh(1+) C1[X(C38H52N2ORh)] #Atoms= 94
Charge = 1 Multiplicity = 1

SCF Energy= -1773.34912438 Predicted Change= -2.109130D-07

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00923	0.00180	[NO]	0.00923	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-1.207346	-1.861837	0.368127
Rh	-0.498249	-0.466687	-0.886023
C	-2.231213	-2.595852	-0.089255
C	-3.130989	-3.543258	0.706073
C	-4.270006	-2.907947	-1.204147
C	-2.787116	-2.606232	-1.499595
C	-2.407892	-1.390012	-2.319416
C	-1.200079	-1.327046	-2.961931
C	-0.055188	-2.332058	-2.859366

C	0.846085	-1.742596	-1.775389
H	1.643141	-1.103692	-2.163386
H	1.256307	-2.455781	-1.059165
H	0.456565	-2.429628	-3.825036
H	-0.418323	-3.322938	-2.574978
H	-2.397528	-3.505810	-1.998014
H	-3.519540	-3.055033	1.613198
H	-2.630771	-4.471991	1.006737
H	-4.812626	-3.347456	-2.044859
H	-4.807232	-2.011088	-0.858985
H	-1.031150	-0.480948	-3.630443
O	-4.196995	-3.889055	-0.176953
C	-0.589856	-2.092061	1.719028
H	0.382980	-2.581273	1.607333
H	-0.427551	-1.172370	2.283650
H	-1.215792	-2.755863	2.328479
C	-3.446779	-0.312200	-2.522991
H	-4.321178	-0.720752	-3.046074
H	-3.804146	0.093142	-1.569083
H	-3.054364	0.515581	-3.119629
C	0.666024	0.532740	0.455867
N	1.984487	0.568935	0.821285
N	0.094722	1.586182	1.123121
C	2.216228	1.624860	1.699764
C	3.085292	-0.224168	0.291516
C	1.035312	2.261728	1.888887
C	-1.270025	2.038126	0.911948
H	3.199936	1.821592	2.094288
C	3.568966	-1.317883	1.039810
C	3.692795	0.201208	-0.912319
H	0.777333	3.125582	2.480783
C	-1.543373	2.812678	-0.240781
C	-2.257114	1.750111	1.880948
C	3.034626	-1.683503	2.421962
C	4.645605	-2.037827	0.503718
C	4.765314	-0.558014	-1.395475
C	3.291954	1.484361	-1.638319
C	-0.456762	3.323178	-1.185313
C	-2.871715	3.203456	-0.455912
C	-3.563737	2.178135	1.614366
C	-1.943441	1.082866	3.216139
C	2.869401	-3.201931	2.624371
H	2.048892	-1.222840	2.538485
C	3.950368	-1.105501	3.523827
H	5.039492	-2.888657	1.049505
C	5.229609	-1.673963	-0.705041
H	5.253700	-0.262388	-2.318208
C	4.257150	2.631395	-1.265122
H	2.293779	1.774160	-1.295549
C	3.218024	1.331677	-3.169129
H	0.502360	2.904694	-0.867253
C	-0.331783	4.858464	-1.084350
C	-0.683639	2.890402	-2.645109
H	-3.116167	3.795350	-1.332773
C	-3.875380	2.877847	0.451396
H	-4.347377	1.970689	2.335747
H	-0.942124	0.645507	3.152259
C	-2.927080	-0.049420	3.565685
C	-1.910083	2.134777	4.346785
H	3.836843	-3.711533	2.686921
H	2.303361	-3.667460	1.810262
H	2.341983	-3.398587	3.564066
H	4.040498	-0.016294	3.453036
H	4.959447	-1.526714	3.453439
H	3.552213	-1.346548	4.515870
H	6.063352	-2.247671	-1.099437
H	5.278947	2.401976	-1.587336
H	4.280070	2.806844	-0.184366
H	3.951081	3.563865	-1.753068
H	2.557150	0.511341	-3.470017
H	4.202125	1.146138	-3.612225
H	2.834936	2.255961	-3.615705
H	-0.139213	5.177142	-0.054426
H	-1.245979	5.358347	-1.422646
H	0.494521	5.213228	-1.710333
H	-1.621590	3.288333	-3.047993
H	-0.721127	1.797275	-2.738585
H	0.129992	3.254674	-3.281940
H	-4.897326	3.197497	0.268501
H	-3.013798	-0.772916	2.748871
H	-3.929178	0.335913	3.782159
H	-2.584788	-0.579188	4.461227
H	-2.887846	2.614457	4.467015
H	-1.176746	2.924525	4.148778
H	-1.647776	1.660954	5.299196

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -1773.34912438 Predicted Change= -2.109130D-07
Zero-point correction (ZPE)= -1772.5256 0.82349
Internal Energy (U)= -1772.4806 0.86843
Enthalpy (H)= -1772.4797 0.86937
Gibbs Free Energy (G)= -1772.6033 0.74581

Frequencies -- 14.6753 25.0346 29.1482
SCF Energy (M06) = -1772.069882
SCF Energy (M06/def2-tzvp) = -1773.768725

Reductive Elimination TS RhNHC-IPr

Using Gaussian 03: AM64L-G03RevE.01 11-Sep-2007

# b3lyp/gen pseudo=read gfprint gfinput
scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,readfc,ts,noeigentest) freq
#N Geom=AllCheck Guess=Read SCRF=Check GenChk RB3LYP/ChkBas Freq

---

Pointgroup= C1 Stoichiometry= C38H52N2ORh(1+) C1[X(C38H52N2ORh)] #Atoms= 94
Charge = 1 Multiplicity = 1

SCF Energy= -1773.31019756 Predicted Change= -4.276102D-09

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000 ‖	0.00045	[YES]	0.00000 ‖	0.00030	[YES]
Displ	0.00151 ‖	0.00180	[YES]	0.00151 ‖	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-0.571588	-2.180603	0.286174
Rh	-0.488849	-0.510819	-0.920629
C	-1.741831	-2.838680	0.107162
C	-2.534517	-3.601957	1.152707
C	-3.991088	-2.895961	-0.497400
C	-2.590731	-2.836367	-1.142216
C	-2.237068	-1.705644	-2.096425
C	-1.028552	-1.743669	-2.759660
C	0.035049	-2.802498	-2.495609
C	0.743957	-2.402669	-1.203085
H	1.587353	-1.723691	-1.350337
H	1.109658	-3.239078	-0.609159
H	0.751868	-2.835192	-3.323743
H	-0.409223	-3.800714	-2.414063
H	-2.464673	-3.799414	-1.665291
H	-2.621969	-3.036818	2.093305
H	-2.095251	-4.580162	1.395027
H	-4.769448	-3.291422	-1.154327
H	-4.304267	-1.910158	-0.119664
H	-0.876232	-1.069838	-3.601914
O	-3.818517	-3.822631	0.570844
C	0.174345	-2.272952	1.594063
H	-0.323084	-1.683198	2.373271
H	0.231935	-3.310629	1.949273
H	1.191835	-1.899028	1.494879
C	-3.334776	-0.757352	-2.517701
H	-2.985218	-0.053185	-3.277386
H	-4.172445	-1.323338	-2.947573
H	-3.733157	-0.183451	-1.673196
C	0.568690	0.710859	0.350286
N	-0.071379	1.768603	0.937120
N	1.894306	0.917106	0.639941
C	0.828220	2.622853	1.562578
C	-1.490636	2.035912	0.818876
C	2.058694	2.091716	1.371679
C	3.031641	0.125854	0.201515
H	0.507763	3.519199	2.069529
C	-1.941434	2.720207	-0.331614
C	-2.351353	1.657523	1.869431
H	3.033612	2.436307	1.674684
C	3.712872	-0.677950	1.146085
C	3.470193	0.257149	-1.135905
C	-0.980623	3.206827	-1.414773
C	-3.317472	2.954580	-0.444239
C	-3.715182	1.934215	1.709185
C	-1.842392	1.029590	3.163259
C	3.379945	-0.694284	2.639319
C	4.803260	-1.427193	0.683634
C	4.564797	-0.520452	-1.536058
C	2.883402	1.275560	-2.111593
C	-0.921899	2.221390	-2.594633
H	0.023293	3.254856	-0.980105
C	-1.313356	4.624386	-1.919020
H	-3.704552	3.471278	-1.316537
C	-4.196525	2.559897	0.561721
H	-4.410579	1.661789	2.496571
C	-1.757457	2.088032	4.284134
H	-0.827871	0.658066	2.982125
C	-2.695943	-0.167540	3.618597
H	2.365423	-0.302327	2.771232
C	4.346193	0.229287	3.416100
C	3.420969	-2.103284	3.264240
H	5.345188	-2.060692	1.377914
C	5.215962	-1.366199	-0.643466
H	4.926134	-0.445994	-2.556696
H	1.924622	1.620497	-1.714747
C	2.612402	0.692288	-3.510432
C	3.810394	2.507270	-2.208192
H	-1.907517	2.079193	-3.049059
H	-0.549847	1.224770	-2.279715
H	-0.229970	2.570171	-3.369333
H	-1.390310	5.332968	-1.088313
H	-2.254800	4.655850	-2.477699
H	-0.523919	4.975108	-2.592361
H	-5.259211	2.761408	0.461050
H	-2.746700	2.504080	4.505902
H	-1.101004	2.920931	4.009421
H	-1.366577	1.639263	5.204126
H	-2.814297	-0.901809	2.815236
H	-3.696531	0.140270	3.940708
H	-2.221779	-0.663036	4.473076
H	4.327112	1.259817	3.047852
H	5.377464	-0.130791	3.330322
H	4.082585	0.246550	4.479496
H	4.444094	-2.488680	3.327451
H	2.826089	-2.827919	2.700869
H	3.030446	-2.064685	4.286845
H	6.063380	-1.958671	-0.976228
H	1.960021	-0.186556	-3.461454
H	3.535889	0.398355	-4.020370
H	2.124247	1.443754	-4.141200
H	4.793552	2.230317	-2.604851
H	3.965383	2.972115	-1.228419
H	3.377983	3.260640	-2.876666

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -1773.31019756 Predicted Change= -4.276102D-09
Zero-point correction (ZPE)= -1772.4878 0.82233
Internal Energy (U)= -1772.4435 0.86661
Enthalpy (H)= -1772.4426 0.86755
Gibbs Free Energy (G)= -1772.5634 0.74672

Frequencies -- -424.7894 26.3770 27.5935
SCF Energy (M06) = -1772.045125
SCF Energy (M06/def2-tzvp) = -1773.743704

Product-Catalyst Complex RhNHC-IPr

Using Gaussian 03: AM64L-G03RevE.01 11-Sep-2007

---

opt=(gdiis,maxcycle=250) freq b3lyp geom=connectivity gen pseudo=read
gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
#N Geom=AllCheck Guess=Read SCRF=Check GenChk RB3LYP/ChkBas Freq

---

Pointgroup= C1 Stoichiometry= C38H52N2ORh(1+) C1[X(C38H52N2ORh)] #Atoms= 94
Charge = 1 Multiplicity = 1

SCF Energy= -1773.38853685 Predicted Change= -8.281237D-09

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00102	0.00180	[YES]	0.00102	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-0.543716	-3.440435	-0.389300
Rh	-0.318953	-1.069375	-0.146760
C	-1.501292	-2.797085	-1.141053
C	-3.009558	-2.827568	-0.881404
C	-2.772465	-1.698832	-2.836649
C	-1.319928	-2.125190	-2.514660
C	-0.312735	-1.003269	-2.284334
C	0.974151	-1.397431	-1.805369
C	1.470201	-2.832397	-1.909020
C	0.857207	-3.785578	-0.868703
H	1.509654	-3.811914	0.011371
H	0.842723	-4.816178	-1.255679
H	2.558204	-2.843843	-1.798170
H	1.262662	-3.195553	-2.925704
H	-0.971171	-2.834962	-3.280557
H	-3.328209	-2.030707	-0.186598
H	-3.359487	-3.787967	-0.493791
H	-3.016821	-1.740937	-3.899838
H	-2.978755	-0.685139	-2.461776
H	1.753738	-0.642298	-1.846530
O	-3.592254	-2.639427	-2.159889
C	-0.490959	0.318463	-2.988191
H	-0.375800	0.170420	-4.072843
H	-1.477002	0.758329	-2.825851
H	0.265187	1.039641	-2.668854
C	-0.932579	-4.171793	0.880196
H	-1.904625	-3.869252	1.274522
H	-0.970575	-5.253528	0.687068
H	-0.184784	-4.019661	1.666645
C	0.327169	0.795048	0.384455
N	1.569014	1.329900	0.592971
N	-0.537267	1.734357	0.881086
C	1.474321	2.569019	1.219929
C	2.847116	0.701095	0.317988
C	0.156745	2.822512	1.401713
C	-1.983101	1.622369	0.909812
H	2.351201	3.138804	1.482256
C	3.362137	-0.212953	1.259585
C	3.555470	1.080876	-0.843498
H	-0.350305	3.661385	1.850083
C	-2.743360	2.520598	0.131238
C	-2.581518	0.651153	1.751877
C	2.675900	-0.519175	2.588225
C	4.598615	-0.806062	0.971523
C	4.790156	0.460564	-1.072749
C	3.060423	2.164606	-1.800362
C	-2.128257	3.594534	-0.765645
C	-4.140572	2.428363	0.217385
C	-3.979554	0.603255	1.783559
C	-1.763249	-0.283891	2.651637
C	2.395642	-2.022080	2.768775
H	1.709673	-0.006221	2.603557
C	3.501847	0.033034	3.768923
H	5.024345	-1.517174	1.673082
C	5.301785	-0.482692	-0.184873
H	5.364299	0.724701	-1.955016
C	3.792651	3.498182	-1.534378
H	1.994757	2.330471	-1.604857
C	3.201874	1.774578	-3.284408
H	-1.054593	3.398804	-0.853362
C	-2.305242	4.999007	-0.148907
C	-2.711122	3.575887	-2.192846
H	-4.754202	3.110088	-0.362730
C	-4.753546	1.482877	1.028186
H	-4.478371	-0.121424	2.415827
H	-0.911049	-0.686897	2.061782
C	-2.546185	-1.500653	3.170159
C	-1.151346	0.477194	3.847894
H	3.319748	-2.609850	2.792082
H	1.774848	-2.405074	1.950614
H	1.869858	-2.200232	3.714013
H	3.669543	1.111086	3.670536
H	4.482285	-0.451684	3.833144
H	2.978911	-0.144068	4.715530
H	6.261264	-0.950737	-0.385613
H	4.868593	3.394648	-1.714190
H	3.660704	3.838683	-0.501834
H	3.413338	4.281904	-2.199680
H	2.725333	0.813374	-3.504749
H	4.251268	1.703804	-3.589230
H	2.734164	2.537803	-3.915958
H	-1.870068	5.070658	0.853750
H	-3.366670	5.257365	-0.063587
H	-1.826054	5.755531	-0.780028
H	-3.765340	3.871771	-2.207925
H	-2.637213	2.584481	-2.650387
H	-2.166113	4.284211	-2.826335
H	-5.837061	1.428509	1.078323
H	-3.054050	-2.043992	2.367004
H	-3.300063	-1.205679	3.907941
H	-1.861062	-2.192780	3.670156
H	-1.952372	0.894657	4.468652
H	-0.503362	1.300007	3.536015
H	-0.561194	-0.202658	4.472370

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -1773.38853685 Predicted Change= -8.281237D-09
Zero-point correction (ZPE)= -1772.5631 0.82538
Internal Energy (U)= -1772.5187 0.86975
Enthalpy (H)= -1772.5178 0.87070
Gibbs Free Energy (G)= -1772.6398 0.74869

Frequencies -- 15.7615 23.4679 33.7136
SCF Energy (M06) = -1772.122855
SCF Energy (M06/def2-tzvp) = -1773.819378

4. $RhTPPh_3$

4.a. Additional Figures

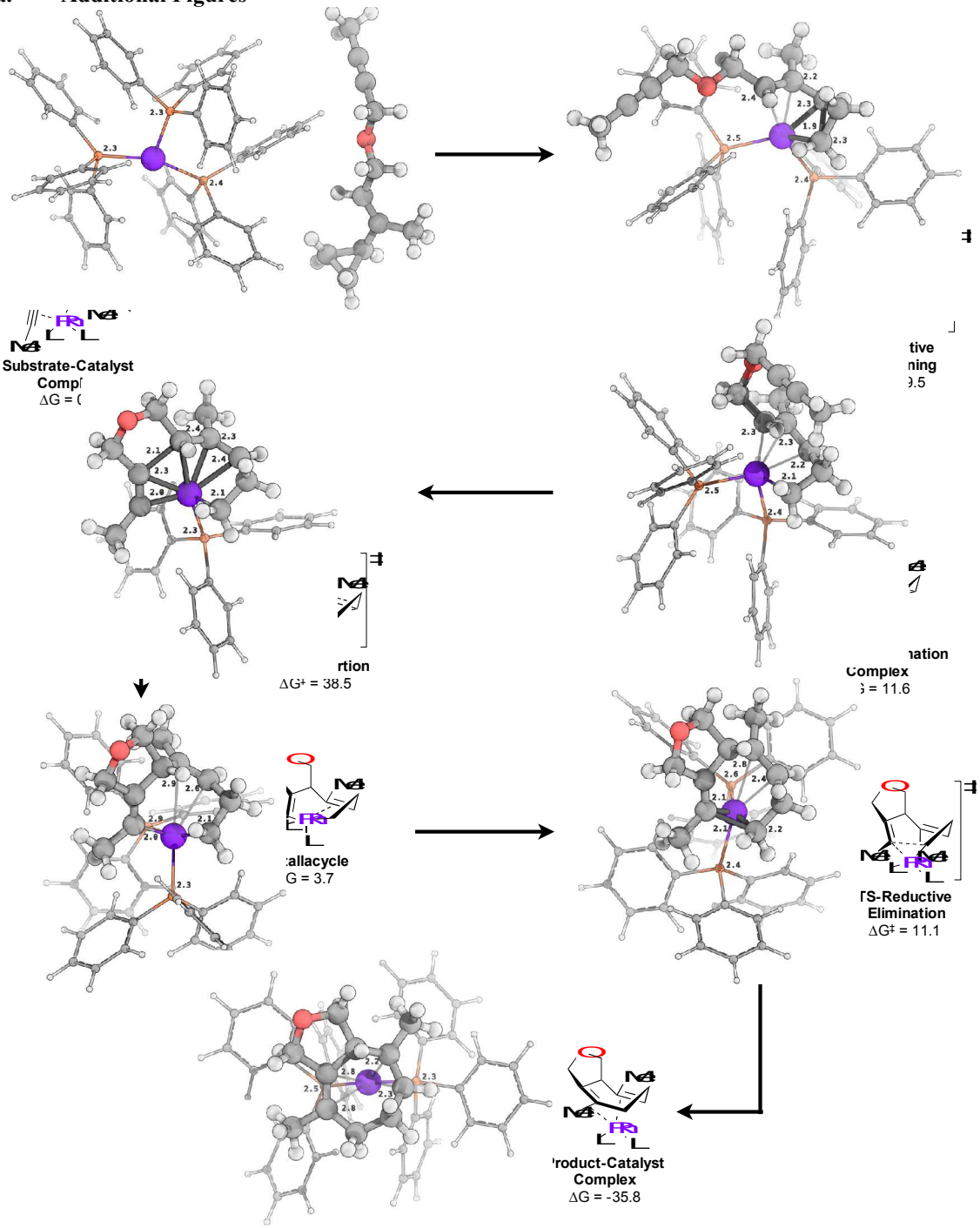

Figure S7. Computed geometries for Wilkinson's catalyst.

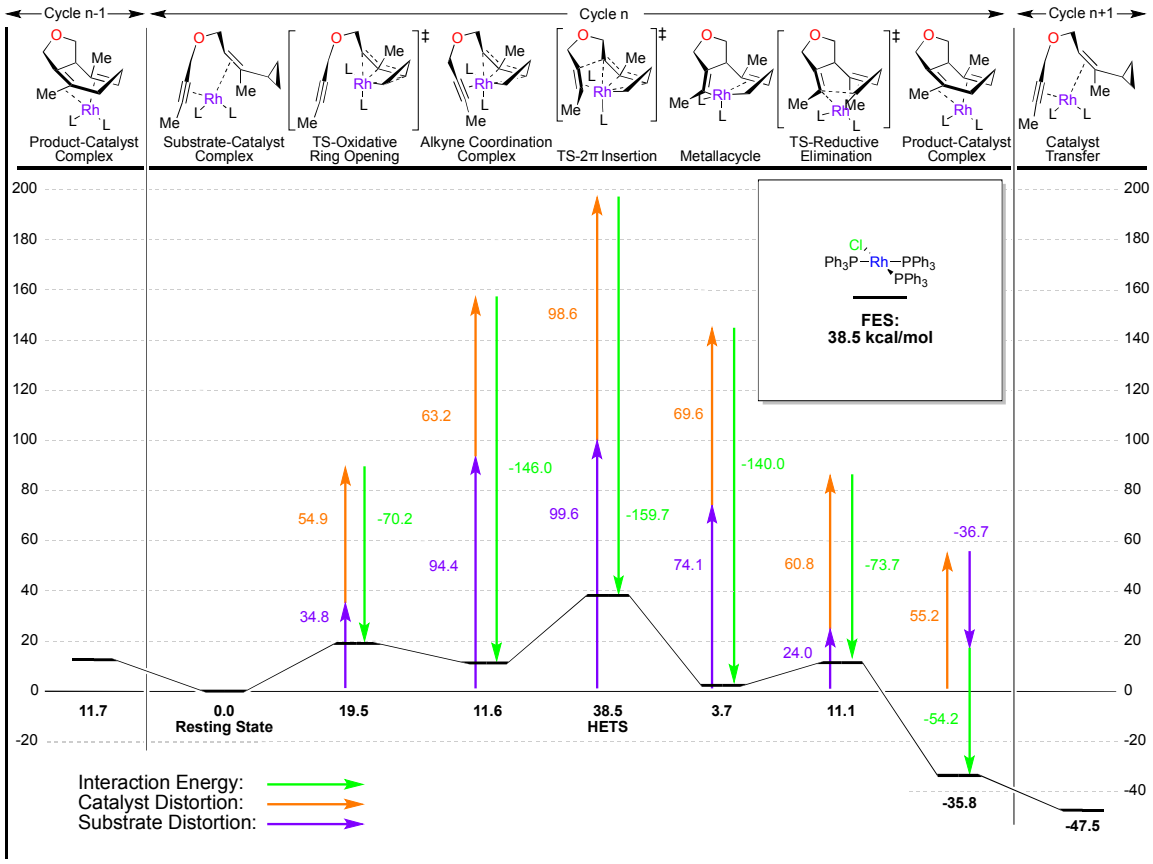

Figure S8. Reaction coordinate diagram for Wilkinson's catalyst. Interaction, catalyst and substrate distortion shown with colored arrows.

Rh(PPh3)3 (Tris)

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

# b3lyp/gen pseudo=read gfprint gfinput
scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/ChkBas Freq

Pointgroup= C1 Stoichiometry= C54H45P3Rh(1+) C1[X(C54H45P3Rh)] #Atoms= 103
Charge = 1 Multiplicity = 1

SCF Energy= -3218.26561799 Predicted Change= -1.415008D-08

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00238	0.00180	[NO]	0.00238	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
Rh	0.066340	0.440675	0.052843
P	2.286551	1.076997	0.043226
P	0.257368	-1.807448	0.045907
C	3.209126	1.211288	1.626065
C	2.734779	0.534845	2.759299
C	4.334897	2.045110	1.746655
C	3.386781	0.669254	3.987385
C	4.985132	2.175022	2.973106
C	4.514158	1.484558	4.093851
C	1.816095	2.819231	-0.332824
C	2.210150	3.533107	-1.476602
C	0.913212	3.419681	0.569120
C	1.712981	4.815024	-1.707170
C	0.407867	4.698980	0.324299
C	0.806263	5.396924	-0.815154
C	3.477478	0.557281	-1.250824
C	3.022969	0.502165	-2.581476
C	4.793137	0.166109	-0.966534
C	3.877906	0.102471	-3.607004
C	5.643154	-0.245955	-1.995623
C	5.192712	-0.270951	-3.315392
C	-0.349876	-2.668169	1.561265
C	-0.987320	-1.942176	2.577011
C	-0.145456	-4.049068	1.739610
C	-1.434456	-2.581291	3.736529
C	-0.598628	-4.686354	2.894430
C	-1.246084	-3.954635	3.894117
C	-0.668233	-2.512455	-1.387414
C	-1.507156	-3.630912	-1.290742
C	-0.493855	-1.901935	-2.642373
C	-2.142352	-4.136598	-2.427651
C	-1.120077	-2.415772	-3.777195
C	-1.946426	-3.537339	-3.671622
C	1.947568	-2.548465	-0.128288
C	2.425851	-3.043833	-1.350268
C	3.703294	-3.602062	-1.436510
C	4.054285	-3.179040	0.913067
C	4.519539	-3.673150	-0.308004
P	-2.344835	0.675463	0.020421
C	-2.998125	1.288721	1.635166
C	-2.089902	1.698880	2.624127
C	-4.375073	1.386021	1.900458
C	-2.541728	2.205253	3.844325
C	-4.825955	1.893818	3.119792
C	-3.911690	2.305956	4.092481
C	-2.586756	2.080977	-1.155604
C	-1.842043	2.072867	-2.348499
C	-3.472472	3.143003	-0.916283
C	-1.993513	3.094013	-3.288092
C	-3.616681	4.165762	-1.855002
C	-2.881901	4.142462	-3.042427
C	-3.614899	-0.564602	-0.488492
C	-4.207866	-0.533494	-1.758752
C	-3.992568	-1.574623	0.413945
C	-5.164449	-1.486756	-2.115242
C	-4.953134	-2.519682	0.056010
C	-5.542619	-2.478250	-1.209870
H	1.845550	-0.083749	2.678938
H	4.698839	2.598404	0.885432
H	3.011558	0.140016	4.858836
H	5.854826	2.820476	3.056341
H	5.021338	1.590216	5.048617
H	2.913573	3.096375	-2.177486
H	-0.284528	5.149131	1.029627
H	0.642331	2.905012	1.487957
H	0.422207	6.394955	-1.004732
H	2.039036	5.365817	-2.585100
H	1.998132	0.780523	-2.813801
H	5.157876	0.175150	0.054444
H	3.517960	0.078230	-4.631826
H	6.660633	-0.545366	-1.761045
H	5.859323	-0.584746	-4.113583
H	-1.924088	-2.002489	4.514738
H	-1.123818	-0.872321	2.462032
H	0.378773	-4.625661	0.983499
H	-1.591784	-4.453286	4.795167
H	-0.437736	-5.753602	3.017491
H	0.140508	-1.023356	-2.726012

H	-1.678737	-4.107669	-0.332562
H	-0.966707	-1.939317	-4.741644
H	-2.793532	-5.001073	-2.335654
H	-2.438819	-3.936903	-4.553584
H	1.801635	-3.014744	-2.235938
H	4.053837	-3.988252	-2.389359
H	4.678329	-3.237514	1.800511
H	5.509160	-4.116017	-0.376152
H	-5.096469	1.058023	1.158479
H	-1.022274	1.600033	2.440503
H	-5.893047	1.963686	3.310998
H	-1.825280	2.514522	4.600386
H	-4.266560	2.697530	5.041548
H	-1.147037	1.259197	-2.538975
H	-4.050348	3.176528	0.001127
H	-1.416985	3.071133	-4.208713
H	-4.307295	4.981006	-1.658054
H	-2.999987	4.939095	-3.771534
H	-3.551331	-1.618437	1.405063
H	-3.938093	0.240269	-2.469655
H	-5.244291	-3.285445	0.769764
H	-5.621143	-1.443696	-3.100072
H	-6.295284	-3.211450	-1.485751
C	2.780304	-2.620334	1.002319
H	2.428097	-2.261083	1.963505

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -3218.26561799 Predicted Change= -1.415008D-08
Zero-point correction (ZPE)= -3217.4360 0.82953
Internal Energy (U)= -3217.3834 0.88217
Enthalpy (H)= -3217.3824 0.88311
Gibbs Free Energy (G)= -3217.5302 0.73539

Frequencies -- 13.6178 15.4121 17.8334
SCF Energy (M06) = -3720.038519
SCF Energy (M06/def2-tzvp) = -3218.471068

Rh(PPh3)3 (Tris)-Substrate-Complex

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

# b3lyp/gen pseudo=read gfprint gfinput
scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/ChkBas Freq

---

Pointgroup= C1 Stoichiometry= C65H61OP3Rh(1+) C1[X(C65H61OP3Rh)] #Atoms= 131
Charge = 1 Multiplicity = 1

SCF Energy= -3722.14632596 Predicted Change= -4.302477D-08

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00511	0.00180	[NO]	0.00511	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
Rh	-0.441799	0.341149	-0.684550
C	6.704454	0.537945	-2.115834
C	7.754126	-0.395439	-1.593037
C	8.982330	0.153431	-0.883852
C	7.977868	-0.680983	-0.130350
C	0.904485	1.380754	-1.851179
C	-0.191441	1.208213	-2.520294
C	5.638788	0.884631	-1.374897
C	4.559406	1.858565	-1.730860
C	2.218881	2.066747	-1.950722
O	3.288680	1.197785	-1.646535
C	-0.883413	1.478408	-3.805121
C	6.996071	1.037454	-3.512277
H	9.951912	-0.275405	-1.121609
H	9.001300	1.220041	-0.675427
H	8.252599	-1.694501	0.148405
H	7.354125	-0.176582	0.601423
H	7.967773	-1.223918	-2.269626
H	5.521928	0.441667	-0.388802
H	4.560691	2.701986	-1.018638
H	2.334973	2.464319	-2.976419
H	4.687915	2.279859	-2.737566
H	2.222787	2.933252	-1.267157
H	-0.143751	1.692460	-4.588180
H	-1.501273	0.635325	-4.128861
H	-1.542731	2.350100	-3.718843
H	7.167678	0.189915	-4.188988
H	6.196089	1.647259	-3.938344
H	7.918837	1.631857	-3.522765
P	-1.597533	2.084704	0.234693
P	-2.212183	-1.522525	-0.837881
C	-2.944164	2.866430	-0.756244
C	-3.532052	2.209425	-1.841011
C	-3.410375	4.146791	-0.398475
C	-4.566020	2.814092	-2.562057
C	-4.442796	4.745523	-1.117125
C	-5.021300	4.081767	-2.203529
C	-0.552689	3.580925	0.574311
C	-0.019921	4.281284	-0.523172
C	-0.361265	4.102935	1.862613
C	0.690897	5.464975	-0.335606
C	0.358773	5.287271	2.047805
C	0.886978	5.970417	0.953024
C	-2.385882	1.697556	1.850417
C	-1.589315	1.252055	2.919674
C	-3.768316	1.844114	2.046162
C	-2.158559	0.987010	4.164721
C	-4.335104	1.572321	3.292962
C	-3.533493	1.151382	4.354816
C	-1.150576	-2.971872	-1.295076
C	-0.102931	-2.772742	-2.212337
C	-1.343293	-4.258919	-0.768225
C	0.704571	-3.835731	-2.617404
C	-0.525334	-5.318116	-1.165956
C	0.494668	-5.112468	-2.095434
C	-3.379217	-2.201728	0.427057
C	-4.349875	-3.163294	0.080188
C	-3.298720	-1.778260	1.758660
C	-5.208309	-3.685061	1.045422
C	-4.163039	-2.301558	2.725715
C	-5.117557	-3.253290	2.372664
C	-3.358112	-1.399299	-2.305372
C	-2.967327	-1.787059	-3.596681
C	-3.844784	-1.662325	-4.677193
C	-5.532308	-0.767153	-3.206849
C	-5.129844	-1.153235	-4.487373
P	1.291650	-0.776738	1.187523
C	2.631387	0.371346	1.751947
C	3.833570	-0.117027	2.293982
C	2.444697	1.755382	1.668573
C	4.815069	0.764181	2.747953
C	3.426123	2.639751	2.126171
C	4.613333	2.145730	2.666321
C	0.698985	-1.498015	2.793387
C	1.112481	-1.008314	4.043281
C	-0.218174	-2.562909	2.765162
C	0.629851	-1.573777	5.227018
C	-0.689288	-3.135026	3.947466
C	-0.268274	-2.641023	5.184005
C	2.318349	-2.154455	0.471234
C	3.068445	-1.867841	-0.682702
C	2.441022	-3.422420	1.058361
C	3.930815	-2.822724	-1.221314
C	3.294242	-4.380879	0.504055
C	4.044642	-4.084414	-0.633404
H	-3.183077	1.226853	-2.127302
H	-2.969344	4.677423	0.439057
H	-5.009050	2.286156	-3.401160
H	-4.792712	5.733246	-0.831053
H	-5.821702	4.554256	-2.765807
H	-0.173514	3.907852	-1.530565
H	0.492544	5.677642	3.052642
H	-0.781575	3.604194	2.727618
H	1.438666	6.894657	1.098698
H	1.086724	5.996364	-1.196473
H	-0.522789	1.110364	2.784764
H	-4.404869	2.175381	1.233893
H	-1.526883	0.641498	4.977121
H	-5.405594	1.693456	3.431239
H	-3.976978	0.948999	5.325692
H	1.506615	-3.660270	-3.327572
H	0.085154	-1.783005	-2.621779
H	-2.135686	-4.444268	-0.052164
H	1.126657	-5.939341	-2.405640
H	-0.692133	-6.307579	-0.749200
H	-2.559837	-1.042738	2.049971
H	-4.437118	-3.502999	-0.946906
H	-4.083543	-1.957345	3.752301
H	-5.949426	-4.427020	0.761626
H	-5.791117	-3.657445	3.123319
H	-1.986889	-2.217701	-3.765912
H	-3.524144	-1.980945	-5.665209
H	-6.534956	-0.382142	-3.041643
H	-5.815065	-1.068500	-5.325957
H	1.532882	2.147056	1.233574
H	4.004411	-1.187090	2.360693
H	3.258062	3.710763	2.055652
H	5.737029	0.371940	3.168802
H	5.379660	2.829671	3.020543
H	1.824230	-0.192213	4.100721
H	-0.554327	-2.965933	1.814389
H	0.971664	-1.185944	6.183076
H	-1.388936	-3.964618	3.899520
H	-0.633310	-3.087430	6.104747
H	1.890765	-3.669750	1.958596
H	3.015584	-0.886939	-1.142947
H	3.379398	-5.355735	0.976802
H	4.522347	-2.569241	-2.096948
H	4.718311	-4.826876	-1.052833
C	-4.654393	-0.883559	-2.128233
H	-4.991556	-0.585300	-1.140158

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -3722.14632596 Predicted Change= -4.302477D-08
Zero-point correction (ZPE)= -3721.0707 1.07562
Internal Energy (U)= -3721.0031 1.14318
Enthalpy (H)= -3721.0021 1.14413
Gibbs Free Energy (G)= -3721.1819 0.96434

Frequencies -- 9.6914 13.3363 19.0278=
SCF Energy (M06) = -3720.052968

Triphenylphosphine

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

#b3lyp/gen opt freq
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/ChkBas Freq

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Pointgroup= C1 Stoichiometry= C18H15P C1[X(C18H15P)] #Atoms= 34
Charge = 0 Multiplicity = 1

SCF Energy= -1036.28170050 Predicted Change= -2.351745D-06

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00014	0.00045	[YES]	0.00003	0.00030	[YES]
Displ	0.05710	0.00180	[NO]	0.05710	0.00180	[NO]

Atomic Coordinates (Angstroms)

Type	X	Y	Z
P	-0.000749	-0.000526	-1.207752
C	1.153888	-1.206357	-0.402573
C	1.314475	-2.451047	-1.035482
C	1.891507	-0.947631	0.763277
C	2.170248	-3.418014	-0.507559
H	0.767305	-2.660599	-1.951868
C	2.757054	-1.911527	1.286047
H	1.792918	0.011307	1.263065
C	2.896176	-3.149124	0.655153
H	2.278367	-4.376177	-1.009294
H	3.322703	-1.693771	2.188575
H	3.571048	-3.897165	1.062886
C	0.467226	1.602931	-0.404574
C	-0.136575	2.122412	0.751089
C	1.479165	2.353445	-1.027890
C	0.268016	3.353497	1.273009
H	-0.927694	1.565362	1.243850
C	1.891363	3.577320	-0.500496
H	1.943639	1.976206	-1.936211
C	1.284063	4.081981	0.651776
H	-0.211929	3.742353	2.167649
H	2.678368	4.141300	-0.994496
H	1.596683	5.039921	1.059070
C	-1.623528	-0.396481	-0.404167
C	-2.780740	0.094199	-1.033285
C	-1.769722	-1.170927	0.757129
C	-4.046412	-0.162662	-0.505789
H	-2.687542	0.678356	-1.946064
C	-3.037620	-1.438288	1.279105
H	-0.890601	-1.569583	1.254208
C	-4.177925	-0.932655	0.652217
H	-4.929435	0.228630	-1.004452
H	-3.132998	-2.042136	2.178100
H	-5.163547	-1.142560	1.059343

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy=	-1036.28170050	Predicted Change= -2.351745D-06	
Zero-point correction (ZPE)=	-1036.0072	0.27440	
Internal Energy (U)=	-1035.9913	0.29030	
Enthalpy (H)=	-1035.9904	0.29125	
Gibbs Free Energy (G)=	-1036.0536	0.22806	

Frequencies -- 22.4218 26.1225 39.9091
SCF Energy (M06) = -1035.690649
SCF Energy (M06/def2-tzvp) = -1035.978894

Substrate

Using Gaussian 03: AM64L-G03RevC.02 12-Jun-2004

# b3lyp/6-31+G* 5D gfprint gfinput scf=(direct,xqc,tight,maxcycle=250)
opt=(gdiis,maxcycle=250) freq=noraman geom=connectivity
#N Geom=AllCheck Guess=Read SCRF=Check GenChk RB3LYP/6-31+G(d) Freq

Pointgroup= C1 Stoichiometry= C11H16O C1[X(C11H16O)] #Atoms= 28
Charge = 0 Multiplicity = 1

SCF Energy= -503.909332222 Predicted Change= -1.355676D-06

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.01064	0.00180	[NO]	0.01064	0.00180	[NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	2.205750	-0.371089	0.345458
C	3.329212	0.591144	0.595869
C	4.545544	0.619446	-0.317538
C	3.607306	1.802672	-0.256352
C	-3.617219	-0.183469	-0.185615
C	-4.612708	0.391851	0.194214
H	5.531549	0.705667	0.132984
H	4.511839	0.002916	-1.213072
H	3.945911	2.706616	0.243659
H	2.977024	1.986828	-1.121502
H	3.567307	0.703367	1.655169
C	1.112175	-0.010671	-0.348427
H	1.036033	1.015205	-0.704366
C	-0.066184	-0.860752	-0.716155
H	-0.122558	-0.971169	-1.815038
C	-2.432242	-0.895732	-0.659086
H	-2.424433	-1.923209	-0.255436
O	-1.252051	-0.208331	-0.257370
H	-0.006624	-1.872589	-0.290010
H	-2.459220	-0.982025	-1.759429
C	-5.806613	1.101328	0.651252
H	-6.402305	0.483353	1.334218
H	-5.531865	2.018870	1.186003
H	-6.448262	1.386134	-0.191577
C	2.444689	-1.737551	0.947860
H	3.310199	-2.222416	0.475888
H	2.684723	-1.643087	2.015832
H	1.588829	-2.410874	0.856757

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy=	-503.909332222	Predicted Change= -1.355676D-06	
Zero-point correction (ZPE)=	-503.6673	0.24202	
Internal Energy (U)=	-503.6527	0.25663	
Enthalpy (H)=	-503.6517	0.25757	
Gibbs Free Energy (G)=	-503.7119	0.19739	

Frequencies -- 17.8485 32.7582 42.0991
SCF Energy (M06) = -503.505363
SCF Energy (M06/def2-tzvp) = -503.7101042

Substrate-Catalyst Complex RhPPh3 (Mono)

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

opt=maxcycle=250 freq=noraman b3lyp/gen geom=connectivity gfinput
gfprint pseudo=read scf=(direct,tight,maxcycle=300,xqc)
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/ChkBas Freq

Pointgroup= C1 Stoichiometry= C29H31OPRh(1+) C1[X(C29H31OPRh)] #Atoms= 63
Charge = 1 Multiplicity = 1

SCF Energy= -1649.53216441 Predicted Change= -1.029713D-08

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00613	0.00180	[NO]	0.00613	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	4.003731	-0.459715	-0.105567
Rh	-0.562771	-1.414376	0.342250
C	5.349772	-0.412762	-0.151213
C	6.040337	0.750820	0.475951
C	0.173065	-2.169032	-1.385860
C	-0.972864	-2.703327	-1.195995
H	3.479034	0.368262	0.371853
C	3.106149	-1.531266	-0.632726
H	3.657023	-2.401746	-1.010410
H	2.434560	-1.890864	0.167293
C	1.377067	-1.904598	-2.236157
H	1.858395	-2.870909	-2.461679
H	1.039560	-1.474667	-3.186381
H	5.357118	1.431785	0.979267
C	7.416376	0.647067	1.116414
C	7.250735	1.429430	-0.151432
H	7.662023	1.015863	-1.067544
H	7.573215	1.184235	2.047430
H	7.938358	-0.303561	1.062823
H	7.285317	2.514203	-0.105176
O	2.299242	-0.988619	-1.696831
C	-2.143167	-3.528586	-1.559326
H	-1.873662	-4.223473	-2.364034
H	-2.512927	-4.111730	-0.710448
H	-2.961689	-2.893098	-1.918292
C	6.210979	-1.483115	-0.778191
H	5.635423	-2.197453	-1.369585
H	6.964116	-1.044115	-1.442198
H	6.755064	-2.048781	-0.011376
P	-1.630630	0.505993	0.062796
C	-3.192685	0.589958	-0.853189
C	-3.454581	1.639085	-1.749327
C	-4.139720	-0.439433	-0.689348
C	-4.657728	1.665468	-2.455945
H	-2.727633	2.430493	-1.896392
C	-5.341369	-0.399887	-1.393235
H	-3.935455	-1.265220	-0.014005
C	-5.601074	0.652328	-2.277066
H	-4.855728	2.479799	-3.146263
H	-6.073123	-1.190511	-1.256128
H	-6.536388	0.678269	-2.828222
C	-0.629262	1.987197	-0.256038
C	0.603485	1.876330	-0.919518
C	-1.081177	3.242979	0.192739
C	1.369641	3.023181	-1.141959
H	0.980741	0.909811	-1.242603
C	-0.307370	4.378396	-0.036869
H	-2.026962	3.334415	0.720069
C	0.916310	4.268825	-0.705973
H	2.323707	2.934240	-1.652705
H	-0.656019	5.346665	0.309725
H	1.516904	5.156758	-0.880708
C	-1.906758	0.324365	1.855037
C	-3.149081	0.235000	2.507402
C	-0.721556	-0.026076	2.554043
C	-3.198380	-0.161245	3.840805
H	-4.062462	0.486206	1.977802
C	-0.791621	-0.448106	3.889829
H	0.258895	0.155113	2.102392
C	-2.026961	-0.512570	4.528415
H	-4.155317	-0.200198	4.352999
H	0.119327	-0.700103	4.424073
H	-2.084986	-0.827979	5.565686

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy=	-1649.53216441	Predicted Change= -1.029713D-08	
Zero-point correction (ZPE)=	-1649.0110	0.52113	
Internal Energy (U)=	-1648.9778	0.55428	
Enthalpy (H)=	-1648.9769	0.55522	
Gibbs Free Energy (G)=	-1649.0822	0.44991	

Frequencies -- 9.0904 13.7030 18.5281
SCF Energy (M06) = -1648.568622
SCF Energy (M06/def2-tzvp) = -1650.134581

Ox.-Add. TS RhPPh3 (Mono)

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

# b3lyp/gen pseudo=read gfprint gfinput
scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,calcfc,ts,noeigentest) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/ChkBas Freq

Pointgroup= C1 Stoichiometry= C29H31OPRh(1+) C1[X(C29H31OPRh)] #Atoms= 63
Charge = 1 Multiplicity = 1

SCF Energy= -1649.52183423 Predicted Change= -6.233666D-10

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00144	0.00180	[YES]	0.00144	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
Rh	0.829118	-1.387199	-0.291643
P	0.525510	0.942336	-0.061881
C	1.921371	0.820341	-1.249317
C	3.240318	1.259306	-1.025525
C	1.647121	0.015280	-2.383986
C	4.247249	0.925402	-1.926017
H	3.467736	1.873471	-0.160147
C	2.676410	-0.325457	-3.276945
H	0.615818	-0.232627	-2.641344
C	3.971244	0.127429	-3.046851
H	5.256557	1.291505	-1.760810
H	2.449531	-0.918925	-4.157958
H	4.767337	-0.123497	-3.741420
C	-0.818406	1.833708	-0.914500
C	-0.579152	3.038467	-1.600942
C	-2.112693	1.292094	-0.882767
C	-1.630405	3.694564	-2.238566
H	0.421911	3.459565	-1.638551
C	-3.161195	1.960534	-1.519276
H	-2.300559	0.350688	-0.373187
C	-2.921716	3.157711	-2.194812
H	-1.443316	4.622681	-2.770834
H	-4.159708	1.535621	-1.481104
H	-3.737596	3.674101	-2.692598
C	1.044791	1.946888	1.374347
C	0.373763	3.129159	1.724069
C	2.107187	1.496643	2.180014
C	0.770303	3.853803	2.849676
H	-0.454572	3.485745	1.121621
C	2.505848	2.230905	3.295944
H	2.624715	0.574837	1.930118
C	1.836404	3.410524	3.633453
H	0.244518	4.767496	3.110753
H	3.334325	1.880401	3.904748
H	2.143399	3.978548	4.506680
C	0.794157	-2.540110	1.493361
C	1.712370	-3.290224	0.664033
C	1.388591	-4.425485	-0.253907
C	1.317977	-3.321054	-1.272718
C	-4.988558	-0.886532	0.651704
C	-5.924156	-0.738249	-0.100410
H	2.190388	-5.153370	-0.376675
H	0.440908	-4.923441	-0.048451
H	2.216680	-3.160765	-1.862332
H	0.376016	-3.233320	-1.822844
H	2.770969	-3.119327	0.846782
C	-0.542718	-2.411439	1.017179
H	-0.943753	-3.179389	0.355506
C	-1.636731	-1.736472	1.801212
H	-1.294128	-0.807056	2.280679
C	-3.903483	-1.076468	1.606162
H	-3.707868	-0.143567	2.160341
O	-2.715126	-1.490333	0.919589
H	-1.961724	-2.419021	2.609367
H	-4.180259	-1.841760	2.349599
C	-7.062184	-0.580936	-1.002805
H	-7.464214	0.438317	-0.966734
H	-6.773277	-0.792090	-2.039178
H	-7.872286	-1.270077	-0.737395
C	1.276138	-1.994027	2.814527
H	1.031711	-2.704821	3.615653
H	2.361794	-1.858283	2.816237
H	0.807951	-1.037905	3.060880

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -1649.52183423 Predicted Change= -6.233666D-10
Zero-point correction (ZPE)= -1649.0024 0.51943
Internal Energy (U)= -1648.9696 0.55215
Enthalpy (H)= -1648.9687 0.55309
Gibbs Free Energy (G)= -1649.0704 0.45140

Frequencies -- -214.8780 13.6117 24.5064
SCF Energy (M06) = -1648.557021
SCF Energy (M06/def2-tzvp) = -1650.121832

Alkyne Coord. Complex RhPPh3 (Mono)

Using Gaussian 03: AM64L-G03RevE.01 11-Sep-2007

opt=(gdiis,maxcycle=250) freq b3lyp geom=connectivity gen pseudo=read
gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
#N Geom=AllCheck Guess=Read SCRF=Check GenChk RB3LYP/ChkBas Freq

Pointgroup= C1 Stoichiometry= C29H31OPRh(1+) C1[X(C29H31OPRh)] #Atoms= 63
Charge = 1 Multiplicity = 1

SCF Energy= -1649.54758210 Predicted Change= -8.612871D-08

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.01659	0.00180	[NO]	0.01659	0.00180	[NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	4.532579	2.039793	-0.231417
Rh	0.216199	-1.320426	-0.943594
C	4.470409	1.232055	0.669390
C	4.441108	0.282951	1.790294
C	2.382612	-0.855578	1.258363
C	2.151546	-0.978892	-0.237483
C	2.293137	-2.277184	-0.906664
C	1.953332	-2.317228	-2.247975
C	1.841071	-1.075371	-3.142672
C	0.661349	-0.255221	-2.631508
H	-0.237428	-0.333931	-3.254928
H	0.871172	0.792039	-2.405517
H	1.690836	-1.393787	-4.178664
H	2.780245	-0.508780	-3.109135
H	2.550503	-0.119917	-0.776916
H	3.983245	0.760706	2.670601
H	5.461723	-0.001811	2.065444
H	1.889761	-1.658375	1.815365
H	1.976982	0.095286	1.625268
H	1.878809	-3.292308	-2.725334
O	3.779543	-0.955737	1.520504
C	4.652795	3.017724	-1.311527
H	3.671781	3.320799	-1.697033
H	5.163446	3.921299	-0.958025
H	5.234906	2.616617	-2.149378
C	2.575529	-3.540424	-0.129524
H	2.496056	-4.425719	-0.765770
H	3.589157	-3.490983	0.284112
H	1.894617	-3.665806	0.720082
P	-1.272111	0.182136	0.073261
C	-1.264971	-0.207378	1.865352
C	-1.093695	0.771588	2.854171
C	-1.384604	-1.557803	2.244452
C	-1.044418	0.403451	4.201258
H	-1.001375	1.816969	2.577875
C	-1.337159	-1.919136	3.590137
H	-1.540991	-2.326507	1.488992
C	-1.163340	-0.937378	4.570377
H	-0.916502	1.168312	4.961660
H	-1.438804	-2.962586	3.873880
H	-1.124954	-1.218438	5.618640
C	-0.984464	1.982212	-0.094647
C	0.325289	2.483181	0.009082
C	-2.047260	2.875481	-0.303022
C	0.562515	3.854649	-0.079407
H	1.162544	1.809643	0.166230
C	-1.801596	4.246334	-0.401656
H	-3.063797	2.505609	-0.388248
C	-0.500024	4.737725	-0.288425
H	1.576846	4.231248	0.015629
H	-2.630231	4.929073	-0.564820
H	-0.313528	5.805047	-0.363053
C	-2.984765	-0.135624	-0.506032
C	-4.063678	-0.263881	0.383562
C	-3.216037	-0.256325	-1.888240
C	-5.348407	-0.508248	-0.104832
H	-3.904378	-0.173287	1.453146
C	-4.501841	-0.498568	-2.370601
H	-2.395577	-0.144863	-2.592167
C	-5.569053	-0.627865	-1.478534
H	-6.177048	-0.604545	0.590559
H	-4.669526	-0.587523	-3.439906
H	-6.569863	-0.820674	-1.853426

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -1649.54758210 Predicted Change= -8.612871D-08
Zero-point correction (ZPE)= -1649.0264 0.52108
Internal Energy (U)= -1648.9932 0.55432
Enthalpy (H)= -1648.9923 0.55526
Gibbs Free Energy (G)= -1649.0967 0.45083

Frequencies -- 10.9344 19.6510 25.7879
SCF Energy (M06) = -1648.571688
SCF Energy (M06/def2-tzvp) = -1650.135281

2π-Insertion TS RhPPh3 (Mono)

Using Gaussian 03: AM64L-G03RevE.01 11-Sep-2007

# b3lyp/gen pseudo=read gfprint gfinput
scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,calcfc,ts,noeigentest,gdiis) freq
#N Geom=AllCheck Guess=Read SCRF=Check GenChk RB3LYP/ChkBas Freq

Pointgroup= C1 Stoichiometry= C29H31OPRh(1+) C1[X(C29H31OPRh)] #Atoms= 63
Charge = 1 Multiplicity = 1

SCF Energy= -1649.54358952 Predicted Change= -1.344592D-08

Optimization completed on the basis of negligible forces. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.01233	0.00180	[NO]	0.01233	0.00180	[NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-1.742227	-1.791741	-0.495476
Rh	-1.146339	0.134138	-0.282880
C	-2.933590	-1.297717	-0.335382
C	-4.332978	-1.809022	-0.088907
C	-4.820924	0.389357	0.204734
C	-3.462309	0.705147	-0.411464
C	-2.654469	1.786482	0.205602
C	-1.724026	2.489472	-0.540536
C	-1.501558	2.298908	-2.037156
C	-0.976766	0.873651	-2.218602
H	0.054328	0.825509	-2.564213
H	-1.604610	0.214797	-2.824867
H	-0.771792	3.034366	-2.387055
H	-2.427078	2.479820	-2.599910
H	-3.554084	0.783599	-1.493446
H	-4.402376	-2.153019	0.957131
H	-4.542732	-2.656020	-0.748870

H	-5.536480	1.170969	-0.070254
H	-4.766872	0.330524	1.301328
H	-1.178414	3.286713	-0.042511
O	-5.295678	-0.815780	-0.346305
C	-1.137002	-3.147084	-0.640574
H	-0.769047	-3.300964	-1.661101
H	-0.286581	-3.273342	0.036799
H	-1.871588	-3.933075	-0.428229
C	-2.866449	2.131866	1.665945
H	-2.087509	2.813485	2.017025
H	-3.835029	2.626360	1.812075
H	-2.856356	1.243379	2.307627
P	1.123807	-0.045535	0.062257
C	1.336216	-1.181676	1.489269
C	0.526658	-0.987911	2.624441
C	2.236104	-2.257948	1.467976
C	0.624863	-1.846817	3.718478
H	-0.171237	-0.153840	2.661109
C	2.326114	-3.119224	2.564426
H	2.868577	-2.425895	0.602607
C	1.524088	-2.916320	3.688431
H	0.001759	-1.681691	4.592688
H	3.027529	-3.948016	2.537881
H	1.599192	-3.587235	4.539068
C	1.897944	1.550166	0.555662
C	2.384973	1.785667	1.849242
C	1.986534	2.573829	-0.405405
C	2.940387	3.025897	2.177019
H	2.342318	1.006125	2.602073
C	2.545393	3.806529	-0.075494
H	1.636380	2.403227	-1.419996
C	3.019391	4.037069	1.219994
H	3.317117	3.194542	3.181680
H	2.617209	4.585438	-0.829265
H	3.454398	4.998443	1.476829
C	2.200418	-0.670754	-1.283745
C	1.653896	-1.418813	-2.337622
C	3.586171	-0.432154	-1.258038
C	2.476341	-1.927319	-3.344166
H	0.584088	-1.593798	-2.373096
C	4.404853	-0.945255	-2.263889
H	4.024885	0.154564	-0.456792
C	3.851898	-1.692410	-3.307270
H	2.042290	-2.500939	-4.157962
H	5.474019	-0.756860	-2.235049
H	4.491611	-2.085333	-4.092070

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -1649.54358952 Predicted Change= -1.344592D-08
Zero-point correction (ZPE)= -1649.0212 0.52237
Internal Energy (U)= -1648.9902 0.55338
Enthalpy (H)= -1648.9892 0.55433
Gibbs Free Energy (G)= -1649.0855 0.45803

Frequencies -- -220.6489 12.1668 16.7544
SCF Energy (M06) = -1648.576519
SCF Energy (M06/def2-tzvp) = -1650.1385

Metallacycle RhPPh3 (Mono)

Using Gaussian 03: AM64L-G03RevE.01 11-Sep-2007

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opt=(gdiis,maxcycle=250) freq b3lyp geom=connectivity gen pseudo=read
gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
#N Geom=AllCheck Guess=Read SCRF=Check GenChk RB3LYP/ChkBas Freq

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Pointgroup= C1 Stoichiometry= C29H31OPRh(1+) C1[X(C29H31OPRh)] #Atoms= 63
Charge = 1 Multiplicity = 1

SCF Energy= -1649.58752318 Predicted Change= -4.112610D-09

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00128	0.00180	[YES]	0.00128	0.00180	[YES]

Atomic Type	X	Y	Z
C	1.889462	-1.196564	0.219269
Rh	0.910546	0.533114	-0.125955
C	3.215608	-1.065578	0.350039
C	4.268773	-2.168660	0.469871
C	5.401019	-0.237042	-0.009512
C	3.980590	0.252322	0.360432
C	3.312393	1.291837	-0.512716
C	2.494011	2.253964	0.020275
C	2.129170	2.407587	1.498811
C	1.113764	1.295239	1.783930
H	0.141671	1.635168	2.143824
H	1.493253	0.492495	2.418147
H	1.688118	3.396620	1.651921
H	3.010060	2.340701	2.146985
H	4.028479	0.612854	1.395413
H	4.294494	-2.786868	-0.442808
H	4.115054	-2.830369	1.328747
H	6.199426	0.409030	0.362135
H	5.517310	-0.361131	-1.096737
H	2.093199	3.006066	-0.661334
O	5.502432	-1.486682	0.656899
C	1.181035	-2.525809	0.240619
H	0.451939	-2.595227	1.055011
H	0.641500	-2.722595	-0.690878
H	1.902246	-3.340586	0.381134
C	3.623795	1.290288	-1.991911
H	4.660566	1.606401	-2.164408
H	3.518833	0.289315	-2.425666
H	2.973275	1.977820	-2.540112
P	-1.309866	-0.126698	-0.010307
C	-1.800146	-1.442251	-1.186287
C	-1.125170	-1.525779	-2.418278
C	-2.808332	-2.372491	-0.893602
C	-1.468272	-2.507165	-3.347075
H	-0.329546	-0.822014	-2.656572
C	-3.143474	-3.358117	-1.824467
H	-3.330773	-2.334688	0.056296
C	-2.479228	-3.425559	-3.049920
H	-0.944237	-2.559036	-4.296873
H	-3.925103	-4.073971	-1.588073
H	-2.743170	-4.193901	-3.770480
C	-2.050309	1.441932	-0.630472
C	-2.099796	2.556680	0.230249
C	-2.490221	1.585485	-1.957661
C	-2.581210	3.782276	-0.228433
H	-1.793051	2.462067	1.267715
C	-2.970172	2.815310	-2.409909
H	-2.477572	0.737423	-2.633851
C	-3.013478	3.914949	-1.550383
H	-2.626240	4.630101	0.448916
H	-3.318193	2.910164	-3.434284
H	-3.390481	4.869281	-1.905978
C	-2.131659	-0.465385	1.587539
C	-1.404727	-1.013688	2.655835
C	-3.503288	-0.198951	1.751617
C	-2.040425	-1.302772	3.864353
H	-0.342863	-1.207413	2.548984
C	-4.132894	-0.490209	2.961392
H	-4.076610	0.239035	0.939987
C	-3.403415	-1.043311	4.017350
H	-1.469563	-1.725902	4.685558
H	-5.192063	-0.281815	3.080022
H	-3.896440	-1.266450	4.958904

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -1649.58752318 Predicted Change= -4.112610D-09
Zero-point correction (ZPE)= -1649.0626 0.52489
Internal Energy (U)= -1649.0317 0.55580
Enthalpy (H)= -1649.0307 0.55675
Gibbs Free Energy (G)= -1649.1270 0.46052

Frequencies -- 14.7697 15.7728 22.9073
SCF Energy (M06) = -1648.615978
SCF Energy (M06/def2-tzvp) = -1650.172595

Reductive Elimination TS RhPPh3 (Mono)

Using Gaussian 03: AM64L-G03RevE.01 11-Sep-2007

# b3lyp/gen pseudo=read gfprint gfinput
scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,calcfc,ts,noeigentest,gdiis) freq
#N Geom=AllCheck Guess=Read SCRF=Check GenChk RB3LYP/ChkBas Freq

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Pointgroup= C1 Stoichiometry= C29H31OPRh(1+) C1[X(C29H31OPRh)] #Atoms= 63
Charge = 1 Multiplicity = 1

SCF Energy= -1649.55171239 Predicted Change= -7.244992D-09

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00116	0.00180	[YES]	0.00116	0.00180	[YES]

Atomic Type	X	Y	Z
C	1.659265	0.779538	-1.494126
Rh	0.759819	-0.612932	-0.276454
C	2.936645	0.975058	-1.093621
C	3.713781	2.281515	-1.119378
C	4.665301	0.925728	0.479669
C	3.829241	-0.032918	-0.395371
C	3.051177	-1.167934	0.255593
C	2.441652	-2.114493	-0.544973
C	2.405154	-2.021788	-2.065308
C	1.324678	-0.999515	-2.418090
H	0.321774	-1.429226	-2.518303
H	1.525521	-0.421743	-3.318402
H	2.156492	-2.996772	-2.499065
H	3.378759	-1.726119	-2.471620
H	4.534036	-0.453944	-1.130962
H	3.137140	3.101287	-0.661090
H	3.993517	2.598368	-2.133059
H	5.633562	0.521770	0.783809
H	4.110553	1.244177	1.376356
H	2.078028	-3.028605	-0.078744
O	4.909052	2.027533	-0.386465
C	0.887428	1.858160	-2.221838
H	0.035420	1.451054	-2.772843
H	0.494033	2.603459	-1.520450
H	1.523473	2.384558	-2.945044
C	3.196700	-1.390735	1.741806
H	2.569759	-2.218088	2.085259
H	4.241129	-1.633074	1.983543
H	2.933095	-0.498308	2.318766
P	-1.385170	0.155539	0.036502
C	-1.779045	1.836229	0.625818
C	-0.732644	2.642954	1.109135
C	-3.088470	2.342752	0.601903
C	-0.998923	3.927114	1.582924
H	0.286218	2.263121	1.109879
C	-3.345929	3.631626	1.070291
H	-3.903363	1.737648	0.218229
C	-2.305595	4.422269	1.562839
H	-0.187465	4.543495	1.958663
H	-4.360709	4.017661	1.048860
H	-2.510974	5.425468	1.924564
C	-1.107946	-0.942675	1.478417
C	-0.867298	-0.460250	2.784659
C	-0.954222	-2.326891	1.216565

C	-0.504823	-1.339805	3.798228
H	-0.985790	0.597153	2.998778
C	-0.577792	-3.199679	2.246441
H	-1.203684	-2.727904	0.238455
C	-0.356217	-2.708944	3.531057
H	-0.344288	-0.963863	4.804418
H	-0.484883	-4.262294	2.041876
H	-0.080329	-3.388723	4.331920
C	-2.821460	-0.472795	-0.894461
C	-2.825893	-0.355461	-2.294291
C	-3.921026	-1.060987	-0.245676
C	-3.917255	-0.811884	-3.033451
H	-1.979165	0.092028	-2.807592
C	-5.007279	-1.520307	-0.991456
H	-3.929948	-1.162265	0.835712
C	-5.006899	-1.395278	-2.382904
H	-3.914963	-0.715690	-4.115128
H	-5.853268	-1.975467	-0.484955
H	-5.854214	-1.754209	-2.959591

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -1649.55171239 Predicted Change= -7.244992D-09
Zero-point correction (ZPE)= -1649.0280 0.52362
Internal Energy (U)= -1648.9977 0.55398
Enthalpy (H)= -1648.9967 0.55493
Gibbs Free Energy (G)= -1649.0906 0.46105

Frequencies -- -402.2206 24.5631 29.2993
SCF Energy (M06) = -1648.595291
SCF Energy (M06/def2-tzvp) = -1650.152517

Product-Catalyst Complex RhPPh3 (Mono)

Using Gaussian 03: AM64L-G03RevE.01 11-Sep-2007

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opt=(gdiis,maxcycle=250) freq b3lyp geom=connectivity gen pseudo=read
gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
#N Geom=AllCheck Guess=Read SCRF=Check GenChk RB3LYP/ChkBas Freq

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Pointgroup= C1 Stoichiometry= C29H31OPRh(1+) C1[X(C29H31OPRh)] #Atoms= 63
Charge = 1 Multiplicity = 1

SCF Energy= -1649.62738467 Predicted Change= -1.754522D-09

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00063	0.00180	[YES]	0.00063	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-3.028510	-1.152285	0.207174
Rh	-0.951667	-0.061549	-0.094766
C	-3.249487	0.177432	-0.093942
C	-3.851770	1.211949	0.860653
C	-3.613359	2.300100	-1.120362
C	-3.189795	0.854416	-1.475117
C	-1.755709	0.661577	-1.962285
C	-1.319797	-0.678122	-2.130454
C	-2.293626	-1.846439	-2.186760
C	-2.854322	-2.264057	-0.815699
H	-2.187823	-3.013603	-0.372793
H	-3.824637	-2.769156	-0.940711
H	-1.798260	-2.709792	-2.640765
H	-3.114971	-1.578788	-2.866105
H	-3.919929	0.426523	-2.178735
H	-3.086292	1.685324	1.500243
H	-4.630098	0.796125	1.506032
H	-4.180751	2.797225	-1.909357
H	-2.738976	2.918900	-0.866899
H	-0.387622	-0.817137	-2.675244
O	-4.460070	2.167681	0.010722
C	-1.034260	1.793228	-2.654784
H	-1.601238	2.095995	-3.547562
H	-0.919999	2.681342	-2.027207
H	-0.042958	1.472907	-2.989419
C	-3.279688	-1.666020	1.609620
H	-3.285398	-0.875808	2.362773
H	-4.252347	-2.177344	1.646659
H	-2.521633	-2.401827	1.899256
P	1.364948	0.063529	0.020108
C	0.952644	-0.524445	1.705368
C	0.050378	0.293882	2.429807
C	1.294624	-1.790757	2.216647
C	-0.473494	-0.146515	3.653674
H	-0.159714	1.308907	2.091827
C	0.773209	-2.211513	3.436843
H	1.976252	-2.430682	1.665181
C	-0.112390	-1.394637	4.154727
H	-1.142701	0.498271	4.215909
H	1.061394	-3.178670	3.838591
H	-0.508176	-1.733015	5.107673
C	2.295288	1.624905	0.202348
C	2.252453	2.574476	-0.831765
C	3.070740	1.881900	1.345923
C	2.978570	3.760533	-0.725061
H	1.654367	2.390161	-1.718651
C	3.789584	3.073427	1.448916
H	3.114801	1.156446	2.152638
C	3.744696	4.012035	0.415521
H	2.942258	4.489184	-1.529485
H	4.385815	3.266315	2.335893
H	4.305307	4.938350	0.499296
C	2.465457	-1.147863	-0.785601
C	1.922156	-2.369616	-1.222280
C	3.831151	-0.889016	-0.984245
C	2.737525	-3.323227	-1.829798
H	0.863572	-2.571484	-1.080931
C	4.639628	-1.844637	-1.601382
H	4.263048	0.052238	-0.660413
C	4.096621	-3.060185	-2.022024
H	2.312410	-4.266682	-2.159688
H	5.694941	-1.637786	-1.752295
H	4.729637	-3.800278	-2.502640

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -1649.62738467 Predicted Change= -1.754522D-09
Zero-point correction (ZPE)= -1649.1003 0.52700
Internal Energy (U)= -1649.0700 0.55733
Enthalpy (H)= -1649.0691 0.55827
Gibbs Free Energy (G)= -1649.1630 0.46429

Frequencies -- 19.7262 26.4524 32.4598
SCF Energy (M06) = -1648.672528
SCF Energy (M06/def2-tzvp) = -1650.227608

Substrate-Catalyst Complex RhPPh3 (Bis)

Using Gaussian 03: AM64L-G03RevE.01 11-Sep-2007

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opt=maxcycle=250 freq=noraman b3lyp gen pseudo=read geom=connectivity
gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
#N Geom=AllCheck Guess=Read SCRF=Check GenChk RB3LYP/ChkBas Freq

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Pointgroup= C1 Stoichiometry= C47H46OP2Rh(1+) C1[X(C47H46OP2Rh)] #Atoms= 97
Charge = 1 Multiplicity = 1

SCF Energy= -2685.86570695 Predicted Change= -3.316737D-07

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.05085	0.00180	[NO]	0.05085	0.00180	[NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-4.246541	0.533959	-0.919595
Rh	0.384846	0.130371	-1.167587
C	-5.228361	0.768580	-0.028570
C	-6.335280	-0.226712	0.091511
C	-0.346752	1.334894	-2.748582
C	0.861305	1.071467	-3.000988
H	-4.299888	-0.369267	-1.527263
C	-3.033647	1.366777	-1.202117
H	-3.141658	2.409195	-0.867461
H	-2.140747	0.957321	-0.684995
C	-1.640762	2.034123	-3.005563
H	-1.594772	3.027923	-2.530190
H	-1.732569	2.181940	-4.087649
H	-6.202742	-1.089569	-0.557773
C	-7.042923	-0.524092	1.408032
C	-7.785997	0.172878	0.306069
H	-8.022026	1.224888	0.434898
H	-7.285463	-1.560733	1.625957
H	-6.771835	0.060140	2.282895
H	-8.537113	-0.381214	-0.249248
O	-2.794473	1.334420	-2.608231
C	2.144273	1.070906	-3.731664
H	2.093062	1.753029	-4.589314
H	2.969752	1.383000	-3.083400
H	2.380007	0.069905	-4.109698
C	-5.267484	1.978457	0.875156
H	-4.515540	2.724275	0.608185
H	-6.245935	2.471264	0.840095
H	-5.092882	1.696526	1.921793
P	1.197225	1.607332	0.335857
P	0.553243	-1.991247	-0.070239
C	0.253547	-2.975715	-1.598055
C	-0.815019	-3.877209	-1.728767
C	1.107909	-2.765059	-2.698766
C	-1.022978	-4.549954	-2.933914
H	-1.481608	-4.058638	-0.892576
C	0.898379	-3.444121	-3.898813
H	1.948519	-2.081899	-2.606792
C	-0.171332	-4.334184	-4.019508
H	-1.850780	-5.247593	-3.022107
H	1.569190	-3.280028	-4.737326
H	-0.338020	-4.860587	-4.954750
C	-0.773899	-2.489816	1.099544
C	-2.067823	-1.975280	0.905921
C	-0.539681	-3.366983	2.168495
C	-3.107680	-2.331064	1.764203
H	-2.269925	-1.296899	0.081534
C	-1.582391	-3.717891	3.029166
H	0.451553	-3.775628	2.333419
C	-2.864055	-3.201620	2.830825
H	-4.101022	-1.923574	1.598963
H	-1.389953	-4.397779	3.854224
H	-3.671409	-3.478136	3.503063
C	2.110322	-2.658856	0.647833
C	2.707937	-3.829629	0.154101
C	2.706023	-1.992245	1.732999
C	3.882232	-4.318036	0.730902
H	2.258722	-4.365142	-0.675132
C	3.874339	-2.489571	2.309824
H	2.255365	-1.091815	2.137841
C	4.467562	-3.650555	1.807609
H	4.334186	-5.224943	0.339541
H	4.321678	-1.967278	3.150682
H	5.379658	-4.034063	2.255783
C	3.006683	1.877965	0.148672
C	3.821784	0.824872	-0.297411
C	3.599699	3.110549	0.475748
C	5.202220	0.998788	-0.410360
H	3.373394	-0.129131	-0.554807
C	4.980258	3.279230	0.360028
H	2.987629	3.940438	0.814439
C	5.782975	2.225545	-0.083047

H	5.821635	0.175732	-0.755008
H	5.426992	4.236210	0.613818
H	6.856624	2.361845	-0.175168
C	0.445464	3.273584	0.077777
C	0.812095	4.035444	-1.046095
C	-0.515962	3.787312	0.961050
C	0.234963	5.283764	-1.273781
H	1.556849	3.659361	-1.740265
C	-1.098541	5.035301	0.724415
H	-0.806156	3.225548	1.842193
C	-0.725701	5.785840	-0.390441
H	0.537516	5.866265	-2.139408
H	-1.836985	5.421826	1.420997
H	-1.175099	6.758195	-0.569752
C	0.921153	1.265374	2.123644
C	-0.300604	0.702270	2.526367
C	1.882593	1.581243	3.097747
C	-0.560317	0.465022	3.876549
H	-1.047724	0.438208	1.785169
C	1.620417	1.337020	4.447145
H	2.835443	2.011554	2.808831
C	0.400902	0.780676	4.839121
H	-1.507424	0.022424	4.170422
H	2.371960	1.583194	5.191832
H	0.202422	0.590898	5.889997

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -2685.86570695 Predicted Change= -3.316737D-07
Zero-point correction (ZPE)= -2685.0681 0.79752
Internal Energy (U)= -2685.0172 0.84846
Enthalpy (H)= -2685.0162 0.84940
Gibbs Free Energy (G)= -2685.1626 0.70309

Frequencies -- 7.0325 14.3236 15.7476
SCF Energy (M06) = -2684.330841
SCF Energy (M06/def2-tzvp) = -2686.18237

Ox.-Add. TS RhPPh3 (Bis)

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

# b3lyp/gen pseudo=read gfprint gfinput
scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,calcfc,ts,noeigentest) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/ChkBas Freq

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Pointgroup= C1 Stoichiometry= C47H46OP2Rh(1+) C1[X(C47H46OP2Rh)] #Atoms= 97
Charge = 1 Multiplicity = 1

SCF Energy= -2685.84024310 Predicted Change= -4.611699D-10

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00023	0.00180	[YES]	0.00023	0.00180	[YES]

Atomic Type	X	Y	Z
Rh	0.270682	-1.232355	0.032277
P	2.379469	-0.130638	-0.215704
P	-1.141245	0.755129	0.322435
C	3.773214	-1.316362	-0.542917
C	4.247652	-2.114357	0.514612
C	4.342840	-1.477093	-1.814755
C	5.259373	-3.050072	0.302445
H	3.846418	-1.983814	1.516452
C	5.356571	-2.417714	-2.024927
H	4.009157	-0.862676	-2.644550
C	5.814893	-3.207302	-0.970942
H	5.621527	-3.649194	1.133331
H	5.790902	-2.523305	-3.015054
H	6.605432	-3.933629	-1.135482
C	3.036438	0.741842	1.268995
C	2.206647	0.978067	2.372194
C	4.389394	1.123892	1.345692
C	2.703181	1.604253	3.517443
H	1.171004	0.662186	2.332916
C	4.882333	1.755284	2.486490
H	5.065825	0.907765	0.524659
C	4.039379	1.999040	3.574352
H	2.045404	1.780860	4.363674
H	5.927958	2.046209	2.530373
H	4.427450	2.485273	4.464777
C	2.495910	1.023892	-1.652168
C	3.317088	2.160847	-1.673766
C	1.739516	0.711811	-2.794718
C	3.383047	2.961632	-2.815551
H	3.892906	2.438574	-0.798271
C	1.811247	1.510276	-3.937447
H	1.081089	-0.152470	-2.787153
C	2.634175	2.638574	-3.949283
H	4.020829	3.841168	-2.816686
H	1.219419	1.255260	-4.811849
H	2.688620	3.264464	-4.835348
C	-0.461577	2.459861	0.625448
C	-0.584980	3.110349	1.863137
C	0.191653	3.131471	-0.422265
C	-0.059512	4.390553	2.050701
H	-1.106532	2.634244	2.685137
C	0.711673	4.411860	-0.232739
H	0.277859	2.668278	-1.398520
C	0.591760	5.045096	1.005612
H	-0.172400	4.878169	3.015000
H	1.207018	4.913286	-1.059048
H	0.993967	6.043622	1.151219
C	-2.124266	1.016092	-1.220215
C	-2.729810	2.254805	-1.497673
C	-2.287710	-0.034578	-2.134500
C	-3.468012	2.434983	-2.667358
H	-2.619365	3.083632	-0.806389
C	-3.022425	0.148725	-3.306870
H	-1.854885	-1.004916	-1.919553
C	-3.609960	1.385024	-3.578103
H	-3.926463	3.399085	-2.868796
H	-3.139391	-0.676655	-4.003303
H	-4.174703	1.531646	-4.494777
C	-2.387473	0.596580	1.680227
C	-3.756765	0.808931	1.470055
C	-1.944276	0.280001	2.976567
C	-4.656821	0.723516	2.536359
H	-4.130850	1.025782	0.476150
C	-2.843001	0.203929	4.042108
H	-0.888810	0.096310	3.159626
C	-4.204661	0.427006	3.823242
H	-5.714634	0.892410	2.355123
H	-2.480408	-0.030068	5.039310
H	-4.906929	0.367270	4.649703
C	-0.335139	-3.033735	1.162686
C	0.899039	-3.377253	0.464628
C	0.958039	-4.264295	-0.745979
C	0.998799	-2.907708	-1.368598
C	-5.883615	-1.504160	-0.694800
C	-6.576852	-0.896337	-1.477069
H	1.867459	-4.856504	-0.829313
H	0.064703	-4.859212	-0.929755
H	1.975997	-2.585366	-1.700216
H	0.163431	-2.634201	-2.011571
H	1.828271	-3.281961	1.016673
C	-1.485310	-2.845143	0.397345
H	-1.502703	-3.205507	-0.628523
C	-2.870453	-2.692229	0.957737
H	-2.894665	-2.082493	1.870159
C	-5.084067	-2.242357	0.275777
H	-5.262822	-1.846414	1.288096
O	-3.695157	-2.131702	-0.045972
H	-3.242919	-3.699192	1.228599
H	-5.375061	-3.306161	0.287667
C	-7.405752	-0.163052	-2.429796
H	-6.807727	0.577009	-2.974844
H	-7.860341	-0.836320	-3.166023
H	-8.216314	0.372509	-1.921455
C	-0.304931	-2.995563	2.671054
H	-0.488211	-4.003631	3.068450
H	0.672467	-2.668907	3.039062
H	-1.070732	-2.333486	3.079850

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -2685.84024310 Predicted Change= -4.611699D-10
Zero-point correction (ZPE)= -2685.0426 0.79761
Internal Energy (U)= -2684.9929 0.84734
Enthalpy (H)= -2684.9919 0.84828
Gibbs Free Energy (G)= -2685.1302 0.70995

Frequencies -- -262.2775 15.2013 19.1212
SCF Energy (M06) = -2684.321356
SCF Energy (M06/def2-tzvp) = -2686.172375

Alkyne Coord. Complex RhPPh3 (Bis)

Using Gaussian 03: AM64L-G03RevE.01 11-Sep-2007

#b3lyp gen pseudo=read geom=check guess=read gfprint gfinput
scf=(direct,tight,maxcycle=300,xqc) opt=(nofreeze,maxcycle=250)
freq=noraman
#N Geom=AllCheck Guess=Read SCRF=Check GenChk RB3LYP/ChkBas Freq

---

Pointgroup= C1 Stoichiometry= C47H46OP2Rh(1+) C1[X(C47H46OP2Rh)] #Atoms= 97
Charge = 1 Multiplicity = 1

SCF Energy= -2685.86472214 Predicted Change= -7.010565D-06

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00002	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.07604	0.00180	[NO]	0.07604	0.00180	[NO]

Atomic Type	X	Y	Z
C	5.098381	-3.220798	-1.611925
Rh	0.181756	-0.841132	0.046100
C	5.185627	-2.872161	-0.454992
C	5.369516	-2.459885	0.945474
C	3.272263	-1.349918	1.384102
C	2.172372	-1.868755	0.484231
C	1.119142	-2.686903	0.988032
C	0.112190	-3.081334	0.083626
C	0.333123	-3.115705	-1.433982
C	0.362824	-1.651517	-1.855263
H	-0.485533	-1.335602	-2.461331
H	1.294760	-1.295153	-2.296232
H	-0.492512	-3.655630	-1.904003
H	1.262350	-3.644972	-1.680862
H	2.518654	-2.099291	-0.519664
H	5.887308	-1.487535	0.976459
H	6.009686	-3.185639	1.458517
H	2.872573	-0.965405	2.325955
H	3.808902	-0.527234	0.895888
H	-0.750757	-3.611683	0.475843
O	4.182626	-2.398450	1.731059
C	5.014312	-3.681338	-2.997267
H	4.292546	-3.095397	-3.579432
H	5.987113	-3.593976	-3.495759
H	4.710844	-4.733620	-3.048774
C	0.945077	-2.933003	2.469711
H	-0.010718	-3.419307	2.684335
H	1.753640	-3.583652	2.822404
H	1.006331	-2.007756	3.053177
P	-2.247668	-0.590477	-0.105159

P	1.071895	1.449825	-0.123384
C	1.656615	1.756943	1.604505
C	2.898229	2.336845	1.903542
C	0.830088	1.343089	2.664198
C	3.300440	2.497987	3.231433
H	3.557444	2.660709	1.105562
C	1.232002	1.511494	3.990363
H	-0.142671	0.902809	2.460726
C	2.471906	2.086425	4.276979
H	4.265661	2.947354	3.447035
H	0.574425	1.195495	4.795365
H	2.789906	2.213696	5.307637
C	2.550182	1.777814	-1.180713
C	3.309341	0.711206	-1.684020
C	2.979359	3.092351	-1.445100
C	4.467141	0.944626	-2.429365
H	3.005794	-0.307731	-1.484386
C	4.133720	3.324011	-2.193002
H	2.412801	3.937301	-1.068179
C	4.880019	2.251414	-2.688035
H	5.043564	0.101797	-2.799471
H	4.450690	4.344785	-2.386720
H	5.778488	2.435669	-3.269943
C	-0.009289	2.908910	-0.488512
C	-0.682439	3.596289	0.532785
C	-0.191587	3.328369	-1.817659
C	-1.512825	4.678222	0.231098
H	-0.549185	3.307273	1.569364
C	-1.015755	4.413383	-2.114570
H	0.331914	2.825224	-2.625707
C	-1.681413	5.090875	-1.090746
H	-2.015561	5.206627	1.036326
H	-1.133012	4.732505	-3.146302
H	-2.319710	5.938705	-1.322054
C	-3.085112	0.334908	-1.457632
C	-2.342111	0.873498	-2.514536
C	-4.489757	0.424107	-1.495114
C	-2.984284	1.496271	-3.588511
H	-1.260423	0.805960	-2.499361
C	-5.126849	1.059637	-2.558137
H	-5.084877	-0.012118	-0.698026
C	-4.374439	1.593597	-3.609624
H	-2.395951	1.903523	-4.405791
H	-6.210807	1.127576	-2.573692
H	-4.874439	2.077355	-4.443828
C	-2.761951	0.195570	1.479483
C	-3.448539	1.418234	1.531098
C	-2.383729	-0.419981	2.688993
C	-3.770166	1.995855	2.761874
H	-3.734001	1.922378	0.614656
C	-2.716294	0.155197	3.916183
H	-1.834106	-1.357924	2.674173
C	-3.412400	1.366134	3.954745
H	-4.307764	2.939526	2.784947
H	-2.434423	-0.343462	4.839427
H	-3.672809	1.815063	4.908799
C	-3.192909	-2.187217	-0.185223
C	-3.218931	-2.863734	-1.418935
C	-3.867599	-2.754141	0.904958
C	-3.886615	-4.080027	-1.551887
H	-2.738761	-2.428139	-2.291054
C	-4.535957	-3.974957	0.768487
H	-3.896921	-2.244882	1.861422
C	-4.543851	-4.643574	-0.454834
H	-3.902032	-4.582386	-2.515050
H	-5.059521	-4.394598	1.622922
H	-5.066761	-5.589803	-0.558065

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -2685.86472214 Predicted Change= -7.010565D-06
Zero-point correction (ZPE)= -2685.0658 0.79888
Internal Energy (U)= -2685.0156 0.84904
Enthalpy (H)= -2685.0147 0.84998
Gibbs Free Energy (G)= -2685.1562 0.70843

Frequencies -- 10.5158 14.6076 17.7091
SCF Energy (M06) = -2684.33231
SCF Energy (M06/def2-tzvp) = -2686.182407

2π-Insertion TS RhPPh3 (Bis)

Using Gaussian 03: AM64L-G03RevE.01 11-Sep-2007

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opt=(gdiis,modredundant,maxcycle=250) freq b3lyp geom=check guess=read
gen pseudo=read gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
Modredundant Input: B 3 6 F

#N Geom=AllCheck Guess=Read SCRF=Check GenChk RB3LYP/ChkBas Freq

---

Pointgroup= C1 Stoichiometry= C47H46OP2Rh(1+) C1[X(C47H46OP2Rh)] #Atoms= 97
Charge = 1 Multiplicity = 1

SCF Energy= -2685.82853253 Predicted Change= -1.834560D-08

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000 ‖	0.00045	[YES]	0.00000 ‖	0.00030	[YES]
Displ	0.00137 ‖	0.00180	[YES]	0.00137 ‖	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.038256	-2.057225	-1.343349
Rh	-0.143954	-0.981227	0.368704
C	0.673070	-3.207984	-1.262152
C	1.241262	-4.242212	-2.191117
C	2.330863	-4.970125	-0.262246
C	1.425580	-4.038174	0.513942
C	1.917932	-2.929934	1.358807
C	1.100998	-2.321251	2.268112
C	-0.336827	-2.726628	2.574371
C	-1.214535	-2.503318	1.341134
H	-2.236094	-2.233970	1.608688
H	-1.236439	-3.363235	0.672083
H	-0.696873	-2.112596	3.406331
H	-0.387137	-3.772992	2.916191
H	0.539563	-4.543583	0.891143
H	2.100496	-3.822799	-2.746798
H	0.508093	-4.600821	-2.921758
H	2.541432	-5.894119	0.287238
H	3.289164	-4.490959	-0.511349
H	1.542820	-1.550100	2.894002
O	1.654299	-5.380496	-1.446957
C	-0.411764	-1.475005	-2.665297
H	-1.502669	-1.487036	-2.759527
H	-0.067051	-0.443309	-2.786953
H	-0.006251	-2.059019	-3.500767
C	3.371676	-2.535224	1.248769
H	4.015843	-3.376486	1.535830
H	3.649849	-2.258524	0.225372
H	3.605849	-1.695001	1.904100
P	-2.174700	0.053646	0.016412
P	1.732936	0.962177	-0.150575
C	2.913042	0.755025	-1.558987
C	3.086329	-0.512707	-2.135339
C	3.678257	1.830126	-2.047271
C	4.003089	-0.703482	-3.172446
H	2.495058	-1.349891	-1.781484
C	4.591685	1.636400	-3.083435
H	3.560500	2.821116	-1.621195
C	4.756328	0.369423	-3.649105
H	4.123880	-1.690664	-3.610200
H	5.174844	2.476931	-3.448950
H	5.466197	0.221864	-4.457931
C	2.830422	1.041288	1.341407
C	2.235737	1.034167	2.615869
C	4.229243	1.106155	1.256725
C	3.015270	1.105235	3.771743
H	1.154500	0.979320	2.713054
C	5.009559	1.163836	2.414319
H	4.717265	1.108063	0.288470
C	4.407334	1.165789	3.673297
H	2.536094	1.106964	4.746968
H	6.091493	1.209992	2.328100
H	5.016698	1.213077	4.571104
C	1.214748	2.732492	-0.355658
C	0.705224	3.146284	-1.598831
C	1.327963	3.679403	0.673801
C	0.342733	4.475080	-1.811096
H	0.614977	2.436345	-2.415588
C	0.946456	5.007738	0.462821
H	1.741929	3.395695	1.635332
C	0.460387	5.410960	-0.780031
H	-0.032017	4.778977	-2.783757
H	1.051822	5.728843	1.268724
H	0.181067	6.447186	-0.948023
C	-2.430173	1.578022	-1.000874
C	-2.415293	1.470070	-2.403259
C	-2.798557	2.803746	-0.423711
C	-2.755533	2.558631	-3.203877
H	-2.170930	0.528418	-2.878373
C	-3.141307	3.891006	-1.230314
H	-2.843327	2.916608	0.652379
C	-3.122703	3.773189	-2.619429
H	-2.749490	2.451322	-4.284843
H	-3.432287	4.828027	-0.764597
H	-3.401762	4.617248	-3.243643
C	-3.616027	-0.956967	-0.525344
C	-4.891333	-0.360631	-0.541681
C	-3.477337	-2.281217	-0.963554
C	-6.002892	-1.087112	-0.963884
H	-5.017810	0.671941	-0.230006
C	-4.592989	-3.000537	-1.399023
H	-2.501872	-2.751638	-0.968644
C	-5.855751	-2.408731	-1.394634
H	-6.982429	-0.617975	-0.964466
H	-4.470508	-4.024520	-1.739853
H	-6.722457	-2.970674	-1.730303
C	-2.489914	0.572706	1.753897
C	-1.612299	1.500941	2.348090
C	-3.506624	0.000920	2.535528
C	-1.758095	1.852103	3.691518
H	-0.837232	1.978305	1.754743
C	-3.644042	0.353539	3.879197
H	-4.196180	-0.713356	2.098517
C	-2.771211	1.275884	4.460667
H	-1.084707	2.581669	4.132480
H	-4.438629	-0.092085	4.470538
H	-2.884710	1.549125	5.505611

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -2685.82853253 Predicted Change= -1.834560D-08
Zero-point correction (ZPE)= -2685.0286 0.79990
Internal Energy (U)= -2684.9807 0.84778
Enthalpy (H)= -2684.9798 0.84873
Gibbs Free Energy (G)= -2685.1109 0.71755

Frequencies -- -231.7512 19.6821 25.1923
SCF Energy (M06) = -2684.296381
SCF Energy (M06/def2-tzvp) = -2686.137843

Metallacycle RhPPh3 (Bis)

Using Gaussian 03: AM64L-G03RevE.01 11-Sep-2007

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opt=maxcycle=250 freq=noraman b3lyp gen pseudo=read geom=connectivity
gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
#N Geom=AllCheck Guess=Read SCRF=Check GenChk RB3LYP/ChkBas Freq

---

Pointgroup= C1 Stoichiometry= C47H46OP2Rh(1+) C1[X(C47H46OP2Rh)] #Atoms= 97

Charge = 1 Multiplicity = 1

SCF Energy= -2685.88261381 Predicted Change= -2.166814D-06

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00003	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.08690	0.00180	[NO]	0.08690	0.00180	[NO]

Atomic Type	X	Y	Z
C	-0.483066	2.272581	0.922497
Rh	-0.319126	0.917659	-0.579723
C	-0.099217	3.534831	0.697879
C	-0.060556	4.671702	1.726072
C	1.062581	5.442778	-0.100994
C	0.419299	4.129095	-0.608062
C	1.298919	3.157990	-1.368189
C	0.794400	2.382367	-2.366058
C	-0.630335	2.459800	-2.904730
C	-1.598910	2.009788	-1.808481
H	-2.406997	1.382526	-2.187713
H	-2.037940	2.832545	-1.243018
H	-0.704135	1.799558	-3.775695
H	-0.860491	3.472557	-3.267152
H	-0.435420	4.412456	-1.234414
H	0.720676	4.493749	2.486106
H	-1.011688	4.831351	2.243308
H	1.063195	6.244576	-0.843084
H	2.092499	5.281707	0.249779
H	1.498298	1.751908	-2.904585
O	0.226161	5.841763	0.974595
C	-0.926518	1.809571	2.286596
H	-2.005483	1.627718	2.346679
H	-0.441874	0.876229	2.587930
H	-0.680267	2.563599	3.044625
C	2.772960	3.142558	-1.060527
H	3.272654	2.296948	-1.538107
H	3.237771	4.062747	-1.440360
H	2.973326	3.100714	0.013792
P	-2.140724	-0.435652	0.022808
P	1.945939	-0.696329	0.073011
C	3.249768	0.337003	0.880301
C	2.866995	1.087991	2.005806
C	4.578786	0.418992	0.438131
C	3.794070	1.878205	2.687543
H	1.837941	1.058841	2.350690
C	5.501227	1.223159	1.111514
H	4.900865	-0.134227	-0.437014
C	5.115044	1.949551	2.239202
H	3.482775	2.441988	3.562622
H	6.525358	1.277693	0.753200
H	5.836688	2.569488	2.763241
C	1.956015	-2.243381	1.104326
C	2.469587	-2.284517	2.409171
C	1.386115	-3.411145	0.564721
C	2.417578	-3.466376	3.154794
H	2.927608	-1.403477	2.845975
C	1.338235	-4.587725	1.310855
H	0.990475	-3.409529	-0.446685
C	1.853006	-4.619946	2.609707
H	2.834041	-3.483782	4.158264
H	0.903661	-5.482674	0.874203
H	1.820110	-5.538823	3.188012
C	2.708427	-1.348491	-1.480941
C	3.822469	-2.208116	-1.449051
C	2.150491	-1.026056	-2.726185
C	4.377581	-2.696939	-2.630856
H	4.249309	-2.506880	-0.496562
C	2.702649	-1.519246	-3.911388
H	1.266926	-0.397925	-2.775351
C	3.822118	-2.349446	-3.865563
H	5.240377	-3.355498	-2.587570
H	2.255192	-1.258415	-4.866500
H	4.254545	-2.733707	-4.784868
C	-2.363025	-1.117879	1.718451
C	-1.263164	-1.660072	2.401514
C	-3.624191	-1.132278	2.338248
C	-1.419133	-2.210837	3.673072
H	-0.283910	-1.661986	1.940844
C	-3.773871	-1.678579	3.614485
H	-4.491380	-0.724194	1.832905
C	-2.675006	-2.218180	4.284311
H	-0.556071	-2.631267	4.180221
H	-4.754395	-1.682255	4.081660
H	-2.796526	-2.642388	5.276850
C	-1.979302	-1.901849	-1.079385
C	-2.143384	-3.213743	-0.608215
C	-1.687673	-1.697740	-2.441064
C	-2.018353	-4.295801	-1.482520
H	-2.373210	-3.393340	0.436207
C	-1.560774	-2.781733	-3.309445
H	-1.582232	-0.689762	-2.833201
C	-1.723867	-4.083950	-2.830590
H	-2.157107	-5.305742	-1.107325
H	-1.341095	-2.609561	-4.359092
H	-1.628277	-4.928258	-3.506985
C	-3.799859	0.266746	-0.361726
C	-4.146060	1.537234	0.130676
C	-4.751790	-0.466152	-1.086971
C	-5.419783	2.058013	-0.092270
H	-3.418216	2.128045	0.677388
C	-6.024927	0.062981	-1.313197
H	-4.508494	-1.450537	-1.472240
C	-6.361765	1.322345	-0.816348
H	-5.674219	3.040688	0.294236
H	-6.752125	-0.514140	-1.876937
H	-7.352297	1.731045	-0.993459

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -2685.88261381 Predicted Change= -2.166814D-06
Zero-point correction (ZPE)= -2685.0806 0.80193
Internal Energy (U)= -2685.0323 0.85026
Enthalpy (H)= -2685.0314 0.85120
Gibbs Free Energy (G)= -2685.1667 0.71583

Frequencies -- 9.3911 17.5414 19.5034
SCF Energy (M06) = -2684.352451
SCF Energy (M06/def2-tzvp) = -2686.193405

Reductive Elimination TS RhPPh3 (Bis)

Using Gaussian 03: AM64L-G03RevE.01 11-Sep-2007

opt=(gdiis,modredundant,maxcycle=250) freq b3lyp geom=check guess=read
gen pseudo=read gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
Modredundant Input: B 1 10 F

#N Geom=AllCheck Guess=Read SCRF=Check GenChk RB3LYP/ChkBas Freq

Pointgroup= C1 Stoichiometry= C47H46OP2Rh(1+) C1[X(C47H46OP2Rh)] #Atoms= 97
Charge = 1 Multiplicity = 1

SCF Energy= -2685.86019668 Predicted Change= -5.232804D-08

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00240	0.00180	[NO]	0.00240	0.00180	[YES]

Atomic Type	X	Y	Z
C	0.102889	-2.941977	0.125242
Rh	-0.117271	-1.018814	-0.590821
C	-1.003799	-3.712142	0.149241
C	-1.280246	-4.837673	1.148719
C	-3.310334	-4.096527	0.338945
C	-2.266039	-3.603168	-0.681587
C	-2.469588	-2.275588	-1.377926
C	-1.576976	-1.881141	-2.337282
C	-0.419729	-2.754194	-2.801651
C	0.748884	-2.561208	-1.836316
H	1.509431	-1.884498	-2.237243
H	1.267983	-3.484675	-1.589437
H	-0.126806	-2.459649	-3.815622
H	-0.727468	-3.804782	-2.851411
H	-2.232831	-4.386163	-1.459837
H	-1.091318	-4.516788	2.184488
H	-0.684505	-5.741495	0.963524
H	-4.228544	-4.483194	-0.110580
H	-3.573593	-3.308436	1.062390
H	-1.821672	-1.000834	-2.926932
O	-2.653753	-5.182403	0.977652
C	1.280307	-3.308484	0.997114
H	1.436059	-2.585098	1.803225
H	1.146801	-4.293403	1.457465
H	2.205832	-3.354036	0.417781
C	-3.796484	-1.586526	-1.197238
H	-4.594220	-2.287216	-1.480733
H	-3.987018	-1.298532	-0.158660
H	-3.887923	-0.702729	-1.828154
P	1.999590	-0.091824	-0.015952
P	-1.393297	1.115075	0.087673
C	-2.412371	0.753707	1.587002
C	-2.476192	-0.556102	2.086903
C	-3.117791	1.768959	2.259112
C	-3.240832	-0.850668	3.219234
H	-1.916119	-1.346062	1.594012
C	-3.884988	1.471465	3.385553
H	-3.057812	2.795866	1.912716
C	-3.950251	0.161266	3.867033
H	-3.276585	-1.869429	3.595187
H	-4.426254	2.265914	3.891358
H	-4.544884	-0.066323	4.747052
C	-2.587114	1.597663	-1.242885
C	-2.114396	1.658650	-2.565368
C	-3.926426	1.929875	-0.991324
C	-2.957523	2.046277	-3.608476
H	-1.078114	1.414379	-2.780464
C	-4.771123	2.308834	-2.037162
H	-4.322847	1.879813	0.016392
C	-4.291083	2.368019	-3.346590
H	-2.573766	2.094009	-4.623808
H	-5.807270	2.556698	-1.825081
H	-4.950686	2.662883	-4.157470
C	-0.653632	2.760735	0.534139
C	-0.098549	2.951558	1.811226
C	-0.654342	3.837330	-0.365565
C	0.438522	4.185577	2.177228
H	-0.100644	2.145881	2.535892
C	-0.117236	5.071933	0.004900
H	-1.086254	3.728225	-1.353412
C	0.429940	5.251509	1.275257
H	0.853005	4.314132	3.173248
H	-0.138227	5.896123	-0.702485
H	0.838115	6.215920	1.564174
C	2.340323	0.236909	1.763435
C	1.351994	-0.044140	2.718749
C	3.589559	0.713930	2.203272
C	1.593803	0.165284	4.078756
H	0.389297	-0.430023	2.398326
C	3.825413	0.932442	3.560495
H	4.387868	0.896618	1.490944
C	2.828048	0.660411	4.500837
H	0.817752	-0.062102	4.804011
H	4.793233	1.304589	3.883904
H	3.018393	0.822756	5.557813
C	3.518529	-1.021927	-0.554672
C	4.233189	-1.830457	0.346830
C	3.969129	-0.947086	-1.884026

C	5.359170	-2.542207	-0.070203
H	3.926309	-1.897170	1.384343
C	5.092402	-1.663581	-2.299315
H	3.465506	-0.307724	-2.600565
C	5.790543	-2.465001	-1.395025
H	5.900382	-3.153399	0.646389
H	5.426327	-1.583570	-3.329829
H	6.668189	-3.017402	-1.717667
C	2.198814	1.494509	-0.946638
C	2.846497	2.622474	-0.424788
C	1.742595	1.532639	-2.276444
C	3.054447	3.749236	-1.222800
H	3.176273	2.639766	0.606819
C	1.959632	2.656546	-3.074583
H	1.217663	0.675034	-2.690572
C	2.622706	3.767222	-2.549403
H	3.555252	4.615796	-0.801125
H	1.611870	2.663339	-4.103966
H	2.794882	4.643086	-3.168221

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -2685.86019668 Predicted Change= -5.232804D-08
Zero-point correction (ZPE)= -2685.0575 0.80267
Internal Energy (U)= -2685.0104 0.84973
Enthalpy (H)= -2685.0095 0.85068
Gibbs Free Energy (G)= -2685.1380 0.72216

Frequencies -- -288.1092 21.3697 27.1699
SCF Energy (M06) = -2684.346903
SCF Energy (M06/def2-tzvp) = -2686.187807

Product-Catalyst Complex RhPPh3 (Bis)

Using Gaussian 03: AM64L-G03RevE.01 11-Sep-2007

opt=maxcycle=250 freq=noraman b3lyp gen pseudo=read geom=connectivity
gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
#N Geom=AllCheck Guess=Read SCRF=Check GenChk RB3LYP/ChkBas Freq

Pointgroup= C1 Stoichiometry= C47H46OP2Rh(1+) C1[X(C47H46OP2Rh)] #Atoms= 97
Charge = 1 Multiplicity = 1

SCF Energy= -2685.93408968 Predicted Change= -1.738538D-06

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00002 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.03032 ||	0.00180	[NO]	0.03032 ||	0.00180	[NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	1.966202	-2.597454	-1.705566
Rh	0.053839	-1.068167	-0.269949
C	1.999556	-3.049870	-0.422775
C	3.289931	-3.112512	0.388366
C	1.611144	-3.798394	1.793417
C	0.946703	-3.794674	0.399949
C	-0.437807	-3.177291	0.328581
C	-0.994930	-2.961618	-0.933618
C	-0.404244	-3.527020	-2.213247
C	0.868963	-2.843473	-2.720741
H	0.604048	-1.891794	-3.199658
H	1.308233	-3.453135	-3.526623
H	-1.158968	-3.474202	-3.004587
H	-0.202871	-4.597744	-2.059204
H	0.889602	-4.843074	0.057836
H	3.658988	-2.120424	0.668442
H	4.086509	-3.623334	-0.166575
H	1.320380	-4.648942	2.414725
H	1.377940	-2.868573	2.334766
H	-2.064909	-2.790955	-0.965583
O	3.000374	-3.896678	1.540398
C	-1.304710	-3.319812	1.558498
H	-1.415304	-4.388738	1.795790
H	-0.878867	-2.835536	2.441931
H	-2.304795	-2.920577	1.390803
C	3.241601	-2.048851	-2.317014
H	3.844296	-1.479600	-1.604576
H	3.859848	-2.881619	-2.683354
H	3.034177	-1.403118	-3.173986
P	1.456435	0.968022	0.054230
P	-1.988937	0.015691	0.037308
C	2.936427	0.422376	1.023434
C	2.731723	-0.236806	2.249691
C	4.254504	0.635232	0.590820
C	3.810585	-0.642826	3.035364
H	1.721861	-0.444226	2.591407
C	5.334514	0.215452	1.373117
H	4.447466	1.129799	-0.354434
C	5.117563	-0.416460	2.597963
H	3.630612	-1.149096	3.979099
H	6.347617	0.388129	1.021066
H	5.959059	-0.739585	3.203483
C	0.931484	2.506184	0.957395
C	1.194468	2.700168	2.322665
C	0.261580	3.520189	0.251974
C	0.793763	3.872769	2.965115
H	1.736896	1.953749	2.890710
C	-0.134922	4.691844	0.897236
H	0.064551	3.411746	-0.808447
C	0.126837	4.872029	2.256060
H	1.017181	4.007089	4.019727
H	-0.644176	5.465930	0.330361
H	-0.176989	5.787539	2.755532
C	2.132867	1.681936	-1.507293
C	1.849357	1.071322	-2.735694
C	2.922084	2.846895	-1.498449
C	2.349070	1.597535	-3.929483
H	1.228418	0.181796	-2.754279
C	3.425359	3.369700	-2.689141
H	3.136855	3.351503	-0.561665
C	3.140644	2.745977	-3.907180
H	2.117695	1.112538	-4.873956
H	4.035717	4.267895	-2.666065
H	3.530090	3.158139	-4.833630
C	-2.138520	1.513340	-1.037992
C	-1.606435	1.442201	-2.335782
C	-2.816532	2.678916	-0.651270
C	-1.758067	2.502467	-3.230827
H	-1.066706	0.551992	-2.644770
C	-2.970082	3.737684	-1.548084
H	-3.209859	2.780201	0.352606
C	-2.444291	3.653441	-2.838717
H	-1.336171	2.429963	-4.229055
H	-3.498780	4.632692	-1.232379
H	-2.565271	4.480044	-3.532877
C	-2.366044	0.523989	1.766955
C	-1.401353	0.320059	2.762420
C	-3.613809	1.062336	2.137029
C	-1.659672	0.661485	4.091221
H	-0.450113	-0.122031	2.485712
C	-3.868431	1.410392	3.463062
H	-4.398944	1.186626	1.398112
C	-2.891469	1.212886	4.442664
H	-0.900532	0.493788	4.849979
H	-4.835180	1.825648	3.732771
H	-3.095831	1.478730	5.475785
C	-3.529608	-0.909963	-0.453027
C	-4.315511	-1.583949	0.496969
C	-3.909209	-0.979870	-1.804636
C	-5.446234	-2.305238	0.106474
H	-4.063777	-1.535253	1.550700
C	-5.038069	-1.701811	-2.192145
H	-3.335895	-0.457769	-2.562986
C	-5.810200	-2.368857	-1.238455
H	-6.043512	-2.811553	0.859395
H	-5.318384	-1.734496	-3.241167
H	-6.691109	-2.927238	-1.541272

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -2685.93408968 Predicted Change= -1.738538D-06
Zero-point correction (ZPE)= -2685.1291 0.80491
Internal Energy (U)= -2685.0817 0.85238
Enthalpy (H)= -2685.0807 0.85333
Gibbs Free Energy (G)= -2685.2111 0.72296

Frequencies -- 18.6188 23.3449 26.8201
SCF Energy (M06) = -2684.422435
SCF Energy (M06/def2-tzvp) = -2686.261487

5. RhCOF

5.a. Additional Figures

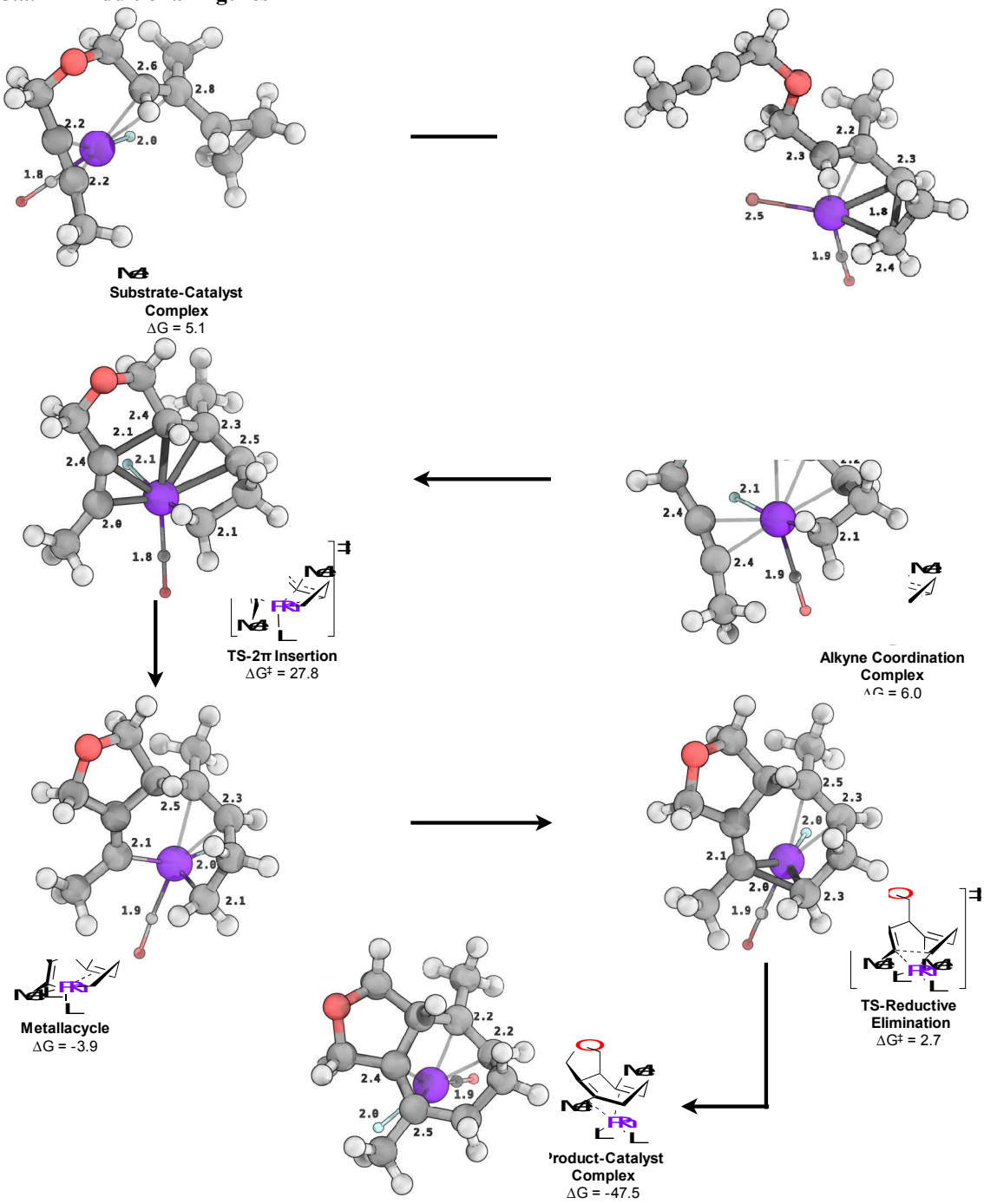

Figure S10. Computed geometries for RhCOF.

Substrate-Catalyst Complex RhCOF

Using Gaussian 03: AM64L-G03RevC.02 12-Jun-2004

#b3lyp/gen pseudo=read gfprint gfinput scf=(direct,xqc,tight,maxcycle=250) opt=(maxcycle=250,gdiis) freq=noraman
#N Geom=AllCheck Guess=Read SCRF=Check GenChk RB3LYP/ChkBas Freq

Pointgroup= C1 Stoichiometry= C12H16FO2Rh C1[X(C12H16FO2Rh)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -826.628689018 Predicted Change= -4.741596D-09

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00056	0.00180	[YES]	0.00056	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.855446	1.567329	0.251048
Rh	-0.528677	-0.569261	-0.254884
C	1.931136	0.784472	-0.052319
C	2.598797	0.027586	1.047084
C	-1.918952	0.919924	0.453391
C	-1.850894	0.062390	1.360708
H	0.581471	1.668719	1.299911

C	0.201756	2.616387	-0.633654
H	0.841908	3.506331	-0.688091
H	0.041133	2.259417	-1.661041
C	-2.126416	2.220513	-0.228327
H	-2.345709	2.054840	-1.294363
H	-2.977574	2.745400	0.219730
C	-1.802679	-1.764608	-0.812450
O	-2.607290	-2.499511	-1.188537
F	0.825738	-1.540784	-1.331638
H	2.301658	0.359945	2.039615
C	2.890205	-1.465189	0.926114
C	4.025368	-0.491706	0.934247
H	4.565574	-0.324419	0.007516
H	2.713129	-2.063915	1.815881
H	2.583045	-1.930554	-0.003733
H	4.643299	-0.414571	1.824940
O	-1.019608	3.097254	-0.079428
C	-2.142576	-0.649539	2.616826
H	-2.819771	-0.057809	3.244854
H	-2.613227	-1.619522	2.418939
H	-1.224077	-0.841434	3.182358
C	2.518482	0.718193	-1.436268
H	1.980127	1.352522	-2.143723
H	3.564948	1.043557	-1.419091
H	2.460057	-0.311183	-1.803876

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -826.628689018 Predicted Change= -4.741596D-09
Zero-point correction (ZPE)= -826.3727 0.25589
Internal Energy (U)= -826.3538 0.27483
Enthalpy (H)= -826.3529 0.27578
Gibbs Free Energy (G)= -826.4203 0.20831

Frequencies -- 46.8868 56.0439 65.4770
SCF Energy (M06) = -826.1566785

Oxidative-Addition TS RhCOF

Using Gaussian 03: AM64L-G03RevC.02 12-Jun-2004

#b3lyp/gen pseudo=read gfprint gfinput scf=(direct,xqc,tight,maxcycle=250)
opt=(maxcycle=250,modredundant,gdiis)
Modredundant Input: B 8 10 F
#B3LYP/ChkBas GenChk gfprint gfinput scf=(direct,xqc,tight,maxcycle=250)
opt=(maxcycle=250,calcfc,ts,noeigentest,nofreeze,gdiis) Freq=Noraman
Geom=AllCheck Guess=Read SCRF=Check
#N Geom=AllCheck Guess=Read SCRF=Check GenChk RB3LYP/ChkBas Freq

---

Pointgroup= C1 Stoichiometry= C12H16FO2Rh C1[X(C12H16FO2Rh)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -826.594193996 Predicted Change= -7.056730D-09

Optimization completed on the basis of negligible forces. {Found 3 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00255	0.00180	[NO]	0.00255	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-5.378606	-0.414138	-0.532811
Rh	1.542212	-0.517158	-0.209265
C	-4.605479	-0.094731	0.341466
C	-3.655844	0.295302	1.394122
C	-1.615711	-0.042194	0.220023
C	-0.383928	0.674975	-0.260077
C	0.568936	1.228868	0.602973
C	1.783109	1.804332	0.003948
C	1.873546	2.580529	-1.263907
C	2.382804	1.200241	-1.582728
H	3.460504	1.086544	-1.616286
H	1.836415	0.659893	-2.353364
H	2.596591	3.393306	-1.276121
H	0.926218	2.853699	-1.724436
H	-0.392484	0.989903	-1.302604
H	-3.415314	-0.582640	2.017605
H	-4.109252	1.048747	2.048397
H	-1.332480	-0.873900	0.881089
H	-2.145701	-0.472817	-0.639469
H	2.610145	1.954650	0.691574
O	-2.461055	0.889784	0.904100
C	-6.321199	-0.799749	-1.579966
H	-6.336471	-0.063097	-2.392515
H	-6.062068	-1.772379	-2.015523
H	-7.341168	-0.874699	-1.183342
C	0.424976	1.273872	2.103324
H	1.402231	1.238561	2.595302
H	-0.079975	2.203241	2.397545
H	-0.179992	0.441682	2.467575
C	3.230271	-1.358369	0.077115
O	4.260879	-1.808094	0.324637
F	0.549715	-2.078414	0.427857

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -826.594193996 Predicted Change= -7.056730D-09
Zero-point correction (ZPE)= -826.3407 0.25347
Internal Energy (U)= -826.3213 0.27279
Enthalpy (H)= -826.3204 0.27374
Gibbs Free Energy (G)= -826.3920 0.20212

Frequencies -- -214.6704 17.4949 24.5594
SCF Energy (M06) = -826.1191431

Alkyne Coordination Complex RhCOF

Using Gaussian 03: AM64L-G03RevC.02 12-Jun-2004

#B3LYP/genecp gfprint gfinput scf=(direct,xqc,tight,maxcycle=250)
Opt=(Maxcycle=250,Nofreeze,gdiis) Freq=Noraman
#N Geom=AllCheck Guess=Read SCRF=Check GenChk RB3LYP/GenECP Freq

---

Pointgroup= C1 Stoichiometry= C12H16FO2Rh C1[X(C12H16FO2Rh)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -826.629986251 Predicted Change= -3.802705D-07

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00510	0.00180	[NO]	0.00510	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	1.113149	2.082189	0.301236
Rh	0.413863	-0.198746	-0.129239
F	-0.532698	0.226803	-1.964463
C	-0.093921	2.141079	0.080008
C	-1.485607	2.456519	-0.291998
C	-2.755589	0.542942	0.315448
C	-1.664685	-0.385258	0.788624
C	-1.365908	-1.603757	0.128529
C	-0.153720	-2.257281	0.481749
C	0.521331	-2.107461	1.846530
C	1.129331	-0.701148	1.788544
C	2.091029	-0.552739	-0.964999
O	3.072612	-0.789239	-1.514469
H	2.219823	-0.706911	1.848709
H	0.725110	0.006328	2.518247
H	1.284436	-2.883935	1.962060
H	-0.201442	-2.242492	2.662076
H	-1.398069	-0.268432	1.836547
H	-1.621265	2.093987	-1.319545
H	-1.622025	3.543080	-0.256582
H	-3.687992	0.344907	0.859997
H	-2.940537	0.405952	-0.755602
H	0.142266	-3.097905	-0.142153
O	-2.464752	1.913501	0.581376
C	2.514245	2.357292	0.638852
H	3.181043	2.109006	-0.194183
H	2.640284	3.420020	0.876156
H	2.830348	1.774110	1.510322
C	-2.091663	-2.015678	-1.130327
H	-1.748251	-2.994796	-1.476698
H	-3.172640	-2.069444	-0.960138
H	-1.871502	-1.265428	-1.901707

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -826.629986251 Predicted Change= -3.802705D-07
Zero-point correction (ZPE)= -826.3742 0.25577
Internal Energy (U)= -826.3559 0.27404
Enthalpy (H)= -826.3550 0.27498
Gibbs Free Energy (G)= -826.4191 0.21085

Frequencies -- 56.7557 68.5071 76.1503
SCF Energy (M06) = -826.1577661

2π-Insertion TS RhCOF

Using Gaussian 03: AM64L-G03RevC.02 12-Jun-2004

#b3lyp/gen pseudo=read gfprint gfinput scf=(direct,xqc,tight,maxcycle=250)
opt=(maxcycle=250,modredundant,gdiis)
Modredundant Input: B 4 7 F
#B3LYP/ChkBas GenChk gfprint gfinput scf=(direct,xqc,tight,maxcycle=250)
opt=(maxcycle=250,calcfc,ts,noeigentest,nofreeze,gdiis) Freq=Noraman
Geom=AllCheck Guess=Read SCRF=Check
#N Geom=AllCheck Guess=Read SCRF=Check GenChk RB3LYP/ChkBas Freq

---

Pointgroup= C1 Stoichiometry= C12H16FO2Rh C1[X(C12H16FO2Rh)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -826.602346179 Predicted Change= -2.510173D-09

Optimization completed. {Found 3 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00044	0.00180	[YES]	0.00044	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.110311	1.865460	0.250760
Rh	0.732368	-0.037953	-0.144062
F	0.222411	0.127514	-2.143157
C	-1.093744	1.425958	0.284019
C	-2.511774	1.872770	0.097709
C	-2.942283	-0.346669	-0.095087
C	-1.539051	-0.613414	0.429229
C	-0.819615	-1.775199	-0.146483
C	0.233097	-2.346657	0.545654
C	0.681732	-1.945238	1.946651
C	1.060465	-0.453720	1.904721
C	2.537713	0.223910	-0.430906
O	3.659329	0.401679	-0.625180
H	2.091668	-0.283243	2.220680
H	0.403139	0.188730	2.498806
H	1.541952	-2.562978	2.223314
H	-0.106955	-2.169159	2.680687
H	-1.519116	-0.585517	1.517400
H	-2.657907	2.152526	-0.958805
H	-2.715255	2.747306	0.724581
H	-3.619496	-1.139839	0.240305
H	-2.954515	-0.308078	-1.193030
H	0.714827	-3.205856	0.082738
O	-3.423477	0.859287	0.462163

C	0.897974	3.121084	0.330908
H	1.427065	3.297360	-0.612289
H	0.250903	3.982404	0.536744
H	1.649919	3.058553	1.125813
C	-1.199248	-2.278311	-1.520007
H	-0.611288	-3.164637	-1.776163
H	-2.260389	-2.549274	-1.572784
H	-0.973081	-1.485624	-2.245644

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -826.602346179 Predicted Change= -2.510173D-09
Zero-point correction (ZPE)= -826.3463 0.25600
Internal Energy (U)= -826.3292 0.27307
Enthalpy (H)= -826.3283 0.27402
Gibbs Free Energy (G)= -826.3900 0.21230

Frequencies -- -222.1335 63.8127 74.5511
SCF Energy (M06) = -826.1243671

Metallacycle RhCOF

Using Gaussian 03: AM64L-G03RevC.02 12-Jun-2004

#B3LYP/genecp gfprint gfinput scf=(direct,xqc,tight,maxcycle=250)
Opt=(Maxcycle=250,Nofreeze,gdiis) Freq=Noraman
#N Geom=AllCheck Guess=Read SCRF=Check GenChk RB3LYP/GenECP Freq

Pointgroup= C1 Stoichiometry= C12H16FO2Rh C1[X(C12H16FO2Rh)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -826.653997823 Predicted Change= -6.152748D-09

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00080	0.00180	[YES]	0.00080	0.00180	[YES]

Atomic Type	X	Y	Z
C	-0.309599	1.339273	0.034829
Rh	1.105123	-0.130345	-0.172438
F	2.034837	-1.656474	-1.111313
C	-1.586063	0.935687	0.132341
C	-2.860319	1.752580	-0.063828
C	-3.363309	-0.467801	-0.485066
C	-2.050914	-0.500167	0.319638
C	-0.983095	-1.525679	-0.020084
C	-0.023804	-1.857370	0.901444
C	0.200239	-1.164053	2.239941
C	1.194911	-0.045791	1.917625
C	2.524072	1.058593	-0.432873
O	3.424082	1.760996	-0.552527
H	2.234474	-0.305289	2.132099
H	0.939016	0.927041	2.335730
H	0.605488	-1.873225	2.971666
H	-0.729219	-0.755213	2.645266
H	-2.350218	-0.637770	1.370021
H	-2.814279	2.362075	-0.979443
H	-3.088159	2.422180	0.775983
H	-4.086110	-1.235548	-0.193913
H	-3.179604	-0.544965	-1.567475
H	0.682901	-2.639241	0.632090
O	-3.924356	0.798333	-0.151527
C	0.050150	2.800374	-0.095673
H	0.709485	3.116960	0.724091
H	0.586651	3.009065	-1.030279
H	-0.831681	3.452663	-0.068837
C	-1.045898	-2.266430	-1.336532
H	-0.081693	-2.732822	-1.551365
H	-1.832504	-3.033303	-1.308950
H	-1.284645	-1.588748	-2.163276

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -826.653997823 Predicted Change= -6.152748D-09
Zero-point correction (ZPE)= -826.3954 0.25850
Internal Energy (U)= -826.3781 0.27582
Enthalpy (H)= -826.3772 0.27677
Gibbs Free Energy (G)= -826.4405 0.21341

Frequencies -- 42.1506 47.8021 80.7261
SCF Energy (M06) = -826.1760336

Reductive Elimination TS RhCOF

Using Gaussian 03: AM64L-G03RevC.02 12-Jun-2004

#b3lyp/gen pseudo=read gfprint gfinput scf=(direct,xqc,tight,maxcycle=250)
opt=(maxcycle=250,modredundant,gdiis)
Modredundant Input: B 1 11 F
Modredundant Input: B 2 11 F
#B3LYP/ChkBas GenChk gfprint gfinput scf=(direct,xqc,tight,maxcycle=250)
opt=(maxcycle=250,modredundant) Geom=AllCheck Guess=Read SCRF=Check
Modredundant Input: B 1 11 F
Modredundant Input: B 2 11 A
#B3LYP/ChkBas GenChk gfprint gfinput scf=(direct,xqc,tight,maxcycle=250)
opt=(maxcycle=250,calcfc,ts,noeigentest,nofreeze,gdiis) Freq=Noraman
Geom=AllCheck Guess=Read SCRF=Check
#N Geom=AllCheck Guess=Read SCRF=Check GenChk RB3LYP/ChkBas Freq

Pointgroup= C1 Stoichiometry= C12H16FO2Rh C1[X(C12H16FO2Rh)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -826.632891090 Predicted Change= -1.443962D-08

Optimization completed on the basis of negligible forces. {Found 4 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00383	0.00180	[NO]	0.00383	0.00180	[YES]

Atomic Type	X	Y	Z
C	-0.224156	1.347255	0.278873
Rh	1.112999	-0.230056	-0.094132
F	1.772941	-1.725431	-1.176233
C	-1.504310	0.951054	0.113494
C	-2.636673	1.777246	-0.473354
C	-3.105310	-0.447520	-0.853891
C	-2.045955	-0.461054	0.265769
C	-0.968117	-1.538605	0.260194
C	-0.093303	-1.612339	1.315406
C	-0.067364	-0.590778	2.444218
C	0.638499	0.667725	1.916884
C	2.566919	0.800985	-0.690216
O	3.486585	1.384710	-1.058091
H	1.717943	0.662061	2.103485
H	0.254455	1.588879	2.357205
H	0.478036	-0.993250	3.304767
H	-1.082493	-0.353856	2.783425
H	-2.609813	-0.537699	1.211542
H	-2.326277	2.295974	-1.394912
H	-3.033621	2.535624	0.216670
H	-3.905925	-1.180853	-0.723212
H	-2.645286	-0.590890	-1.843400
H	0.572817	-2.470163	1.378110
O	-3.687810	0.848515	-0.748235
C	0.182752	2.787714	0.046989
H	0.281959	2.989651	-1.027301
H	-0.555953	3.492990	0.449768
H	1.146012	3.019391	0.510721
C	-1.014569	-2.632981	-0.777453
H	-0.083419	-3.200697	-0.779240
H	-1.860441	-3.304566	-0.571863
H	-1.150083	-2.229201	-1.784618

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -826.632891090 Predicted Change= -1.443962D-08
Zero-point correction (ZPE)= -826.3757 0.25714
Internal Energy (U)= -826.3587 0.27409
Enthalpy (H)= -826.3578 0.27503
Gibbs Free Energy (G)= -826.4202 0.21262

Frequencies -- -370.3819 47.4754 56.6043
SCF Energy (M06) = -826.1646759

Product-Catalyst Complex RhCOF

Using Gaussian 03: AM64L-G03RevC.02 12-Jun-2004

#B3LYP/genecp gfprint gfinput scf=(direct,xqc,tight,maxcycle=250)
Opt=(Maxcycle=250,Nofreeze,gdiis) Freq=Noraman
#N Geom=AllCheck Guess=Read SCRF=Check GenChk RB3LYP/GenECP Freq

Pointgroup= C1 Stoichiometry= C12H16FO2Rh C1[X(C12H16FO2Rh)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -826.715575239 Predicted Change= -2.872117D-08

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00293	0.00180	[NO]	0.00293	0.00180	[YES]

Atomic Type	X	Y	Z
C	1.331957	-1.264476	0.614230
Rh	-0.777161	-0.378415	-0.314326
C	1.543198	-0.040256	0.033534
C	2.338627	0.154375	-1.252867
C	1.687646	2.242695	-0.629755
C	1.191903	1.370299	0.551115
C	-0.316556	1.413002	0.811788
C	-0.833778	0.468135	1.720406
C	0.056422	-0.327214	2.668165
C	0.786328	-1.506009	2.009068
H	0.101851	-2.360781	1.948416
H	1.621948	-1.841472	2.644820
H	-0.550408	-0.714325	3.493038
H	0.787359	0.356318	3.123625
H	1.766520	1.627310	1.455190
H	1.725290	-0.072831	-2.138679
H	3.241610	-0.463366	-1.291936
H	2.075910	3.215857	-0.318938
H	0.881809	2.397814	-1.362311
H	-1.852653	0.631349	2.066935
C	-2.588730	-0.105713	-0.670443
O	-3.709764	0.071623	-0.864882
F	-0.491245	-1.598594	-1.828699
O	2.750669	1.516062	-1.223992
C	-1.093388	2.670202	0.485368
H	-0.718472	3.508735	1.091270
H	-1.015897	2.964292	-0.565180
H	-2.154601	2.541962	0.721493
C	1.799518	-2.509269	-0.114454
H	1.265903	-2.585810	-1.069236
H	2.878605	-2.475430	-0.312572
H	1.592529	-3.409695	0.471093

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -826.715575239 Predicted Change= -2.872117D-08
Zero-point correction (ZPE)= -826.4548 0.26072
Internal Energy (U)= -826.4382 0.27736
Enthalpy (H)= -826.4372 0.27830

Gibbs Free Energy (G)=	-826.4984	0.21710	Frequencies --	52.4112	65.7164	77.3922

SCF Energy (M06) = -826.249231

6. RhCOBr

6.a. Additional Figures

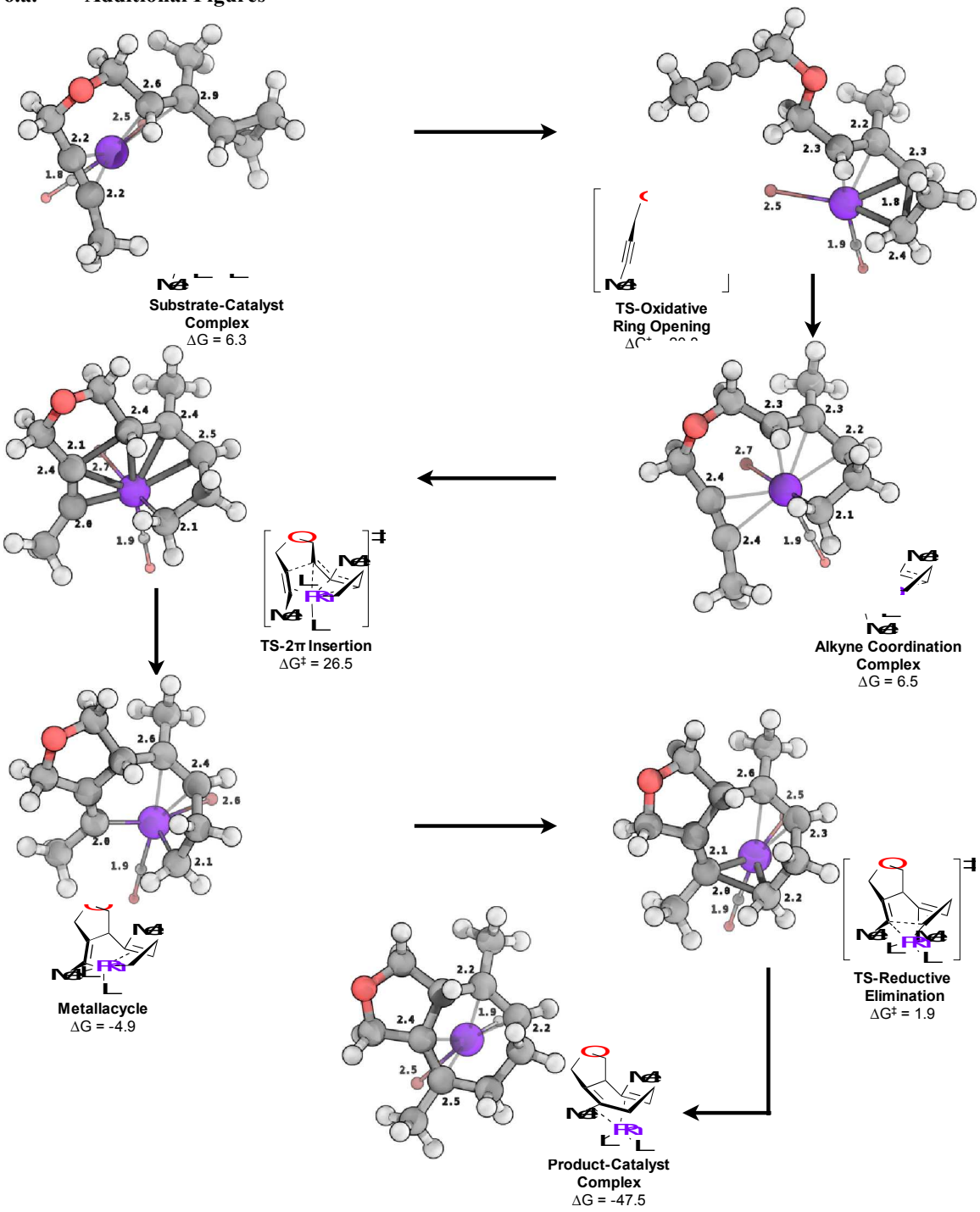

Figure S11. Computed geometries for RhCOBr.

Substrate-Catalyst Complex RhCOBr

Using Gaussian 03: AM64L-G03RevC.02 12-Jun-2004

#b3lyp/gen pseudo=read gfprint gfinput scf=(direct,xqc,tight,maxcycle=250) opt=(maxcycle=250,gdiis) freq=noraman
#N Geom=AllCheck Guess=Read SCRF=Check GenChk RB3LYP/ChkBas Freq

Pointgroup= C1 Stoichiometry= C12H16BrO2Rh C1[X(C12H16BrO2Rh)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -3298.23120857 Predicted Change= -2.219370D-08

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00002	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00157	0.00180	[YES]	0.00157	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z

C	-0.407162	-1.898071	-0.254468
Rh	0.664778	0.398999	0.085965
C	-1.647767	-1.336762	-0.149225
C	-2.284008	-1.245471	1.192000
C	2.275898	-1.052172	0.124065
C	2.164564	-0.662039	1.305343
H	0.021397	-2.337366	0.643633
C	0.268909	-2.371596	-1.532424
H	-0.280365	-3.223070	-1.954170
H	0.304634	-1.587330	-2.303453
C	2.572246	-1.903397	-1.053986
H	2.705489	-1.273896	-1.946761
H	3.500002	-2.462106	-0.886590
C	1.767627	1.863282	0.062778
O	2.489576	2.760772	0.036292
Br	-1.082742	2.044032	-0.696315
H	-1.675786	-1.672362	1.986432
C	-3.164099	-0.080162	1.613746
C	-3.791036	-1.416323	1.373986
H	-4.401774	-1.543640	0.485260
H	-3.044245	0.267146	2.636177
H	-3.319334	0.715317	0.893040
H	-4.115995	-2.009604	2.224261
O	1.573165	-2.885754	-1.280212
C	2.430032	-0.480448	2.741833
H	3.229635	-1.155214	3.071520
H	2.734742	0.549730	2.958124
H	1.533688	-0.688299	3.336445
C	-2.463286	-0.979932	-1.364819
H	-1.841551	-0.846235	-2.251728
H	-3.173400	-1.794192	-1.567160
H	-3.029598	-0.056521	-1.224066

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -3298.23120857 Predicted Change= -2.219370D-08
Zero-point correction (ZPE)= -3297.9768 0.25434
Internal Energy (U)= -3297.9571 0.27410
Enthalpy (H)= -3297.9561 0.27504
Gibbs Free Energy (G)= -3298.0269 0.20425

Frequencies -- 28.5472 51.7631 61.1623
SCF Energy (M06) = -3297.63319

Oxidative-Addition TS RhCOBr

Using Gaussian 03: AM64L-G03RevC.02 12-Jun-2004

#b3lyp/gen pseudo=read gfprint gfinput scf=(direct,xqc,tight,maxcycle=250)
opt=(maxcycle=250,modredundant,gdiis)
Modredundant Input: B 8 10 F
#B3LYP/ChkBas GenChk gfprint gfinput scf=(direct,xqc,tight,maxcycle=250)
opt=(maxcycle=250,calcfc,ts,noeigentest,nofreeze,gdiis) Freq=Noraman
Geom=AllCheck Guess=Read SCRF=Check
#N Geom=AllCheck Guess=Read SCRF=Check GenChk RB3LYP/ChkBas Freq

Pointgroup= C1 Stoichiometry= C12H16BrO2Rh C1[X(C12H16BrO2Rh)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -3298.20582794 Predicted Change= -1.619851D-09

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00565	0.00180	[NO]	0.00565	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-5.419151	-0.320525	-0.700044
Rh	1.503474	-0.012903	-0.283898
C	-4.756909	0.119407	0.212104
C	-3.937399	0.649992	1.310564
C	-1.778491	0.250684	0.388826
C	-0.566932	0.992270	-0.102965
C	0.381519	1.566212	0.742511
C	1.506247	2.294311	0.140726
C	1.436124	3.183794	-1.056390
C	2.053907	1.902725	-1.530556
H	3.132686	1.897535	-1.633383
H	1.510673	1.358617	-2.301346
H	2.075469	4.063584	-1.030376
H	0.436324	3.397588	-1.428979
H	-0.633797	1.345519	-1.131100
H	-3.753028	-0.145944	2.051970
H	-4.470858	1.458460	1.823271
H	-1.517146	-0.471768	1.173827
H	-2.226291	-0.315364	-0.437160
H	2.353015	2.472679	0.796438
O	-2.704077	1.221904	0.889448
C	-6.228325	-0.852013	-1.793805
H	-6.104001	-0.255636	-2.705876
H	-5.952446	-1.886582	-2.030942
H	-7.294375	-0.842342	-1.535729
C	0.314761	1.498505	2.247694
H	1.314745	1.530172	2.690974
H	-0.260184	2.354096	2.625811
H	-0.182643	0.587454	2.584977
C	3.258393	-0.721681	-0.290918
O	4.330879	-1.133659	-0.228113
Br	0.666247	-2.287300	0.301882

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -3298.20582794 Predicted Change= -1.619851D-09
Zero-point correction (ZPE)= -3297.9533 0.25248
Internal Energy (U)= -3297.9333 0.27246
Enthalpy (H)= -3297.9324 0.27340
Gibbs Free Energy (G)= -3298.0069 0.19887

Frequencies -- -208.3443 15.1042 19.7752
SCF Energy (M06) = -3297.604664

Alkyne Coordination Complex RhCOBr

Using Gaussian 03: AM64L-G03RevC.02 12-Jun-2004

#B3LYP/genecp gfprint gfinput scf=(direct,xqc,tight,maxcycle=250)
Opt=(Maxcycle=250,Nofreeze,gdiis) Freq=Noraman
#N Geom=AllCheck Guess=Read SCRF=Check GenChk RB3LYP/GenECP Freq

Pointgroup= C1 Stoichiometry= C12H16BrO2Rh C1[X(C12H16BrO2Rh)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -3298.23573790 Predicted Change= -2.020953D-07

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00002	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00360	0.00180	[NO]	0.00360	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-1.148014	-1.299815	1.686451
Rh	-0.501681	0.296120	0.023723
Br	0.546382	-1.529433	-1.662146
C	0.083531	-1.302820	1.699226
C	1.508321	-1.657677	1.876303
C	2.640942	0.273688	1.081970
C	1.470719	1.173555	0.783017
C	1.209863	1.741483	-0.488505
C	-0.055968	2.362631	-0.672151
C	-0.860590	2.984078	0.471396
C	-1.379469	1.771619	1.247002
C	-2.116096	-0.033021	-0.955455
O	-3.061920	-0.231275	-1.575167
H	-2.467383	1.687196	1.243327
H	-0.999911	1.664826	2.265821
H	-1.677312	3.582591	0.055592
H	-0.238338	3.659691	1.073339
H	1.077550	1.669841	1.666923
H	1.841586	-2.173806	0.964453
H	1.581777	-2.350005	2.722369
H	3.512829	0.866109	1.388591
H	2.917892	-0.325226	0.205067
H	-0.308244	2.655780	-1.688704
O	2.370753	-0.578326	2.192957
C	-2.570005	-1.546982	1.955501
H	-3.067675	-1.980388	1.081120
H	-2.674711	-2.245911	2.793539
H	-3.091253	-0.620256	2.218606
C	2.128838	1.544894	-1.669911
H	1.636005	1.832044	-2.602168
H	3.013914	2.181781	-1.537119
H	2.452470	0.507488	-1.774573

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -3298.23573790 Predicted Change= -2.020953D-07
Zero-point correction (ZPE)= -3297.9812 0.25444
Internal Energy (U)= -3297.9621 0.27356
Enthalpy (H)= -3297.9612 0.27451
Gibbs Free Energy (G)= -3298.0286 0.20709

Frequencies -- 55.8645 62.8419 72.0193
SCF Energy (M06) = -3297.635783

2π-Insertion TS RhCOBr

Using Gaussian 03: AM64L-G03RevC.02 12-Jun-2004

#b3lyp/gen pseudo=read gfprint gfinput scf=(direct,xqc,tight,maxcycle=250)
opt=(maxcycle=250,modredundant,gdiis)
#b3lyp/gen pseudo=read gfprint gfinput scf=(direct,xqc,tight,maxcycle=250)
opt=(maxcycle=250,modredundant) geom=connectivity

CARD - FULL OPTIMIZATION - Following PARTIAL OPT
#B3LYP/ChkBas GenChk gfprint gfinput scf=(direct,xqc,tight,maxcycle=250)
Opt=(Maxcycle=250,Nofreeze) Freq=Noraman Geom=AllCheck Guess=Read
SCRF=Check

CARD - FULL OPTIMIZATION - Continued from Checkpoint File
#B3LYP/ChkBas GenChk gfprint gfinput scf=(direct,xqc,tight,maxcycle=250)
opt=(maxcycle=250,readfc,nofreeze) Freq=Noraman Geom=AllCheck Guess=Read
SCRF=Check

CARD - TRANSITION STRUCTURE OPTIMIZATION - Following PARTIAL OPT
%chk=025-COBr-TS-2Pi-Insertion-Yne-Boat.chk %mem=1800MB
#B3LYP/ChkBas GenChk gfprint gfinput scf=(direct,xqc,tight,maxcycle=250)
opt=(maxcycle=250,calcfc,ts,noeigentest,nofreeze) Freq=Noraman
Geom=AllCheck Guess=Read SCRF=Check

CARD - TRANSITION STRUCTURE OPTIMIZATION - Continued from Checkpoint File
#B3LYP/ChkBas GenChk gfprint gfinput scf=(direct,xqc,tight,maxcycle=250)
opt=(maxcycle=250,readfc,ts,noeigentest,nofreeze) Freq=Noraman
Geom=AllCheck Guess=Read SCRF=Check
Modredundant Input: B 4 7 F
#B3LYP/ChkBas GenChk gfprint gfinput scf=(direct,xqc,tight,maxcycle=250)
opt=(maxcycle=250,calcfc,ts,noeigentest,nofreeze,gdiis) Freq=Noraman
Geom=AllCheck Guess=Read SCRF=Check
#N Geom=AllCheck Guess=Read SCRF=Check GenChk RB3LYP/ChkBas Freq

Pointgroup= C1 Stoichiometry= C12H16BrO2Rh C1[X(C12H16BrO2Rh)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -3298.21036002 Predicted Change= -6.887141D-09

Optimization completed. {Found 3 times}

Item Max Val. Criteria Pass? RMS Val. Criteria Pass?
Force 0.00000 || 0.00045 [YES] 0.00000 || 0.00030 [YES]
Displ 0.00104 || 0.00180 [YES] 0.00104 || 0.00180 [YES]

Atomic Coordinates (Angstroms)
Type X Y Z

C	-0.033336	-0.578089	1.857157
Rh	-0.561297	0.431832	0.153226
Br	-1.034554	-1.814980	-1.207122
C	1.168122	-0.630067	1.410562
C	2.412575	-1.458129	1.495375
C	3.035633	-0.319303	-0.362105
C	1.841920	0.597282	-0.128045
C	1.137718	1.089926	-1.337382
C	0.360308	2.231479	-1.274644
C	0.233967	3.141821	-0.060140
C	-0.258687	2.288423	1.116462
C	-2.403662	0.542791	0.348409
O	-3.544715	0.601289	0.482921
H	-1.181437	2.671093	1.555233
H	0.478650	2.141099	1.910595
H	-0.484310	3.933211	-0.295551
H	1.192282	3.643453	0.143995
H	2.094927	1.388657	0.575709
H	2.224403	-2.428404	1.006780
H	2.674628	-1.633936	2.543726
H	3.857798	0.252820	-0.805845
H	2.774499	-1.147003	-1.036044
H	-0.111319	2.553779	-2.200802
O	3.501389	-0.803802	0.879831
C	-0.886806	-1.059607	2.971563
H	-1.651177	-1.743802	2.586536
H	-0.290537	-1.585293	3.727140
H	-1.401775	-0.224440	3.459675
C	1.317400	0.371042	-2.657034
H	0.689424	0.828597	-3.426174
H	2.361800	0.439833	-2.989237
H	1.035631	-0.683124	-2.584723

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -3298.21036002 Predicted Change= -6.887141D-09
Zero-point correction (ZPE)= -3297.9555 0.25479
Internal Energy (U)= -3297.9376 0.27268
Enthalpy (H)= -3297.9367 0.27363
Gibbs Free Energy (G)= -3298.0016 0.20872

Frequencies -- -223.7547 51.5862 61.8346
SCF Energy (M06) = -3297.605466

Metallacycle RhCOBr

Using Gaussian 03: AM64L-G03RevC.02 12-Jun-2004

#B3LYP/genecp gfprint gfinput scf=(direct,xqc,tight,maxcycle=250)
Opt=(Maxcycle=250,Nofreeze,gdiis) Freq=Noraman
#N Geom=AllCheck Guess=Read SCRF=Check GenChk RB3LYP/GenECP Freq

Pointgroup= C1 Stoichiometry= C12H16BrO2Rh C1[X(C12H16BrO2Rh)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -3298.26486842 Predicted Change= -3.611484D-08

Optimization completed. {Found 1 times}
Item Max Val. Criteria Pass? RMS Val. Criteria Pass?
Force 0.00002 || 0.00045 [YES] 0.00000 || 0.00030 [YES]
Displ 0.00311 || 0.00180 [NO] 0.00311 || 0.00180 [YES]

Atomic Coordinates (Angstroms)
Type X Y Z

C	-1.134686	1.336854	-0.206633
Rh	0.640676	0.362322	0.084833
Br	2.736577	-1.008159	-0.603276
C	-2.259096	0.609833	-0.144217
C	-3.657668	0.985981	-0.629978
C	-3.536352	-1.317505	-0.547696
C	-2.359443	-0.831535	0.321200
C	-1.038801	-1.578351	0.265264
C	-0.145801	-1.503783	1.301470
C	-0.280510	-0.601617	2.524629
C	0.359862	0.729891	2.122865
C	1.711130	1.869937	-0.197054
O	2.390414	2.785099	-0.324652
H	1.374368	0.865992	2.502601
H	-0.253683	1.608921	2.316431
H	0.239206	-1.055480	3.376337
H	-1.328541	-0.463220	2.807054
H	-2.729551	-0.838837	1.357222
H	-3.638751	1.354418	-1.667633
H	-4.149063	1.746306	-0.009781
H	-4.068859	-2.179980	-0.137024
H	-3.213852	-1.553061	-1.573313
H	0.740278	-2.131647	1.254094
O	-4.433091	-0.212063	-0.537333
C	-1.142671	2.786638	-0.629118
H	-0.748881	3.431923	0.167614
H	-0.520443	2.959880	-1.515994
H	-2.154438	3.142041	-0.861463
C	-0.786564	-2.519575	-0.889485
H	0.237052	-2.900235	-0.873071
H	-1.483468	-3.367877	-0.844446
H	-0.946953	-2.022925	-1.853061

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -3298.26486842 Predicted Change= -3.611484D-08
Zero-point correction (ZPE)= -3298.0072 0.25761
Internal Energy (U)= -3297.9893 0.27547
Enthalpy (H)= -3297.9884 0.27641
Gibbs Free Energy (G)= -3298.0543 0.21051

Frequencies -- 25.7565 41.4384 78.4475
SCF Energy (M06) = -3297.657258

Reductive Elimination TS RhCOBr

Using Gaussian 03: AM64L-G03RevC.02 12-Jun-2004

#b3lyp/gen pseudo=read gfprint gfinput scf=(direct,xqc,tight,maxcycle=250)
opt=(maxcycle=250,modredundant,gdiis)
#b3lyp/gen pseudo=read gfprint gfinput scf=(direct,xqc,tight,maxcycle=250)
opt=(maxcycle=250,modredundant) geom=connectivity

CARD - FULL OPTIMIZATION - Following PARTIAL OPT
#B3LYP/ChkBas GenChk gfprint gfinput scf=(direct,xqc,tight,maxcycle=250)
Opt=(Maxcycle=250,Nofreeze) Freq=Noraman Geom=AllCheck Guess=Read
SCRF=Check

CARD - FULL OPTIMIZATION - Continued from Checkpoint File
#B3LYP/ChkBas GenChk gfprint gfinput scf=(direct,xqc,tight,maxcycle=250)
opt=(maxcycle=250,readfc,nofreeze) Freq=Noraman Geom=AllCheck Guess=Read
SCRF=Check

CARD - TRANSITION STRUCTURE OPTIMIZATION - Following PARTIAL OPT
%chk=035-COBr-TS-ReductiveElim-Yne-Boat.chk %mem=1800MB
#B3LYP/ChkBas GenChk gfprint gfinput scf=(direct,xqc,tight,maxcycle=250)
opt=(maxcycle=250,calcfc,ts,noeigentest,nofreeze) Freq=Noraman
Geom=AllCheck Guess=Read SCRF=Check

CARD - TRANSITION STRUCTURE OPTIMIZATION - Continued from Checkpoint File
#B3LYP/ChkBas GenChk gfprint gfinput scf=(direct,xqc,tight,maxcycle=250)
opt=(maxcycle=250,readfc,ts,noeigentest,nofreeze) Freq=Noraman
Geom=AllCheck Guess=Read SCRF=Check
Modredundant Input: B 1 11 F
Modredundant Input: B 2 11 F
#B3LYP/ChkBas GenChk gfprint gfinput scf=(direct,xqc,tight,maxcycle=250)
opt=(maxcycle=250,modredundant) Geom=AllCheck Guess=Read SCRF=Check
Modredundant Input: B 1 11 F
Modredundant Input: B 2 11 A
#B3LYP/ChkBas GenChk gfprint gfinput scf=(direct,xqc,tight,maxcycle=250)
opt=(maxcycle=250,calcfc,ts,noeigentest,nofreeze,gdiis) Freq=Noraman
Geom=AllCheck Guess=Read SCRF=Check
#N Geom=AllCheck Guess=Read SCRF=Check GenChk RB3LYP/ChkBas Freq

Pointgroup= C1 Stoichiometry= C12H16BrO2Rh C1[X(C12H16BrO2Rh)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -3298.24205820 Predicted Change= -1.792834D-09

Optimization completed. {Found 4 times}
Item Max Val. Criteria Pass? RMS Val. Criteria Pass?
Force 0.00000 || 0.00045 [YES] 0.00000 || 0.00030 [YES]
Displ 0.00087 || 0.00180 [YES] 0.00087 || 0.00180 [YES]

Atomic Coordinates (Angstroms)
Type X Y Z

C	-1.151005	1.370179	-0.006373
Rh	0.693475	0.388016	0.186787
Br	2.585591	-1.088530	-0.570557
C	-2.168554	0.508368	-0.205893
C	-3.380819	0.738736	-1.095218
C	-3.054839	-1.534651	-0.917038
C	-2.255823	-0.935311	0.257488
C	-0.918093	-1.554734	0.638826
C	-0.253849	-1.092993	1.744608
C	-0.753970	0.069510	2.593077
C	-0.424981	1.378886	1.865190
C	1.747635	1.769289	-0.492801
O	2.415207	2.615699	-0.892661
H	0.538212	1.807454	2.162358
H	-1.174571	2.156703	2.008753
H	-0.260185	0.053756	3.570926
H	-1.832359	-0.015632	2.772105
H	-2.924599	-0.990830	1.133976
H	-3.088190	1.115893	-2.088299
H	-4.107114	1.446502	-0.671234
H	-3.594194	-2.453055	-0.670236
H	-2.408215	-1.720833	-1.788042
H	0.622314	-1.639428	2.085570
O	-4.023707	-0.531661	-1.207053
C	-1.210455	2.786266	-0.538446
H	-0.934691	2.809835	-1.600507
H	-2.216626	3.215555	-0.446572
H	-0.520343	3.450504	-0.010204
C	-0.477392	-2.811706	-0.067783
H	0.513488	-3.127597	0.262734
H	-1.198014	-3.616135	0.139309
H	-0.436100	-2.678202	-1.152645

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -3298.24205820 Predicted Change= -1.792834D-09
Zero-point correction (ZPE)= -3297.9858 0.25622
Internal Energy (U)= -3297.9684 0.27364
Enthalpy (H)= -3297.9674 0.27458
Gibbs Free Energy (G)= -3298.0318 0.21022

Frequencies -- -382.3534 38.0302 52.3138
SCF Energy (M06) = -3297.646242

Product-Catalyst Complex RhCOBr

Using Gaussian 03: AM64L-G03RevC.02 12-Jun-2004

#B3LYP/genecp gfprint gfinput scf=(direct,xqc,tight,maxcycle=250)
Opt=(Maxcycle=250,Nofreeze,gdiis) Freq=Noraman
#N Geom=AllCheck Guess=Read SCRF=Check GenChk RB3LYP/GenECP Freq

Pointgroup= C1 Stoichiometry= C12H16BrO2Rh C1[X(C12H16BrO2Rh)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -3298.32265463 Predicted Change= -3.125961D-08

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00004	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00206	0.00180	[NO]	0.00206	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.849482	-1.325046	1.243914
Rh	-0.482575	0.504504	0.137728
C	1.383916	-1.060335	0.012178
C	1.387583	-2.061494	-1.142734
C	2.432155	-0.209749	-1.947331
C	2.232383	0.139647	-0.452943
C	1.464350	1.428436	-0.168073
C	1.090631	1.666720	1.168851
C	1.672931	0.882526	2.336132
C	1.077477	-0.520933	2.511277
H	0.113448	-0.437202	3.027354
H	1.717619	-1.122134	3.177321
H	1.512328	1.443297	3.262371
H	2.762791	0.812194	2.207288
H	3.216703	0.144009	0.042722
H	0.419414	-2.080120	-1.665859
H	1.627758	-3.078225	-0.817288
H	3.380249	0.147833	-2.356549
H	1.606419	0.190568	-2.554431
H	0.742654	2.670086	1.407367
C	-1.602341	1.951222	-0.170732
O	-2.291401	2.854675	-0.353332
Br	-2.375916	-1.020230	-0.451220
O	2.437468	-1.626315	-1.999579
C	1.528241	2.565264	-1.165033
H	2.566757	2.915107	-1.265036
H	1.180297	2.280409	-2.161845
H	0.924959	3.413521	-0.826599
C	0.150654	-2.647788	1.484576
H	-0.368269	-3.014856	0.597827
H	0.888913	-3.399739	1.801031
H	-0.592424	-2.557045	2.282055

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -3298.32265463 Predicted Change= -3.125961D-08
Zero-point correction (ZPE)= -3298.0630 0.25964
Internal Energy (U)= -3298.0456 0.27696
Enthalpy (H)= -3298.0447 0.27791
Gibbs Free Energy (G)= -3298.1086 0.21397

Frequencies -- 41.6867 60.3645 80.3334
SCF Energy (M06) = -3297.728667

7. RhCSCl

7.a. Additional Figures

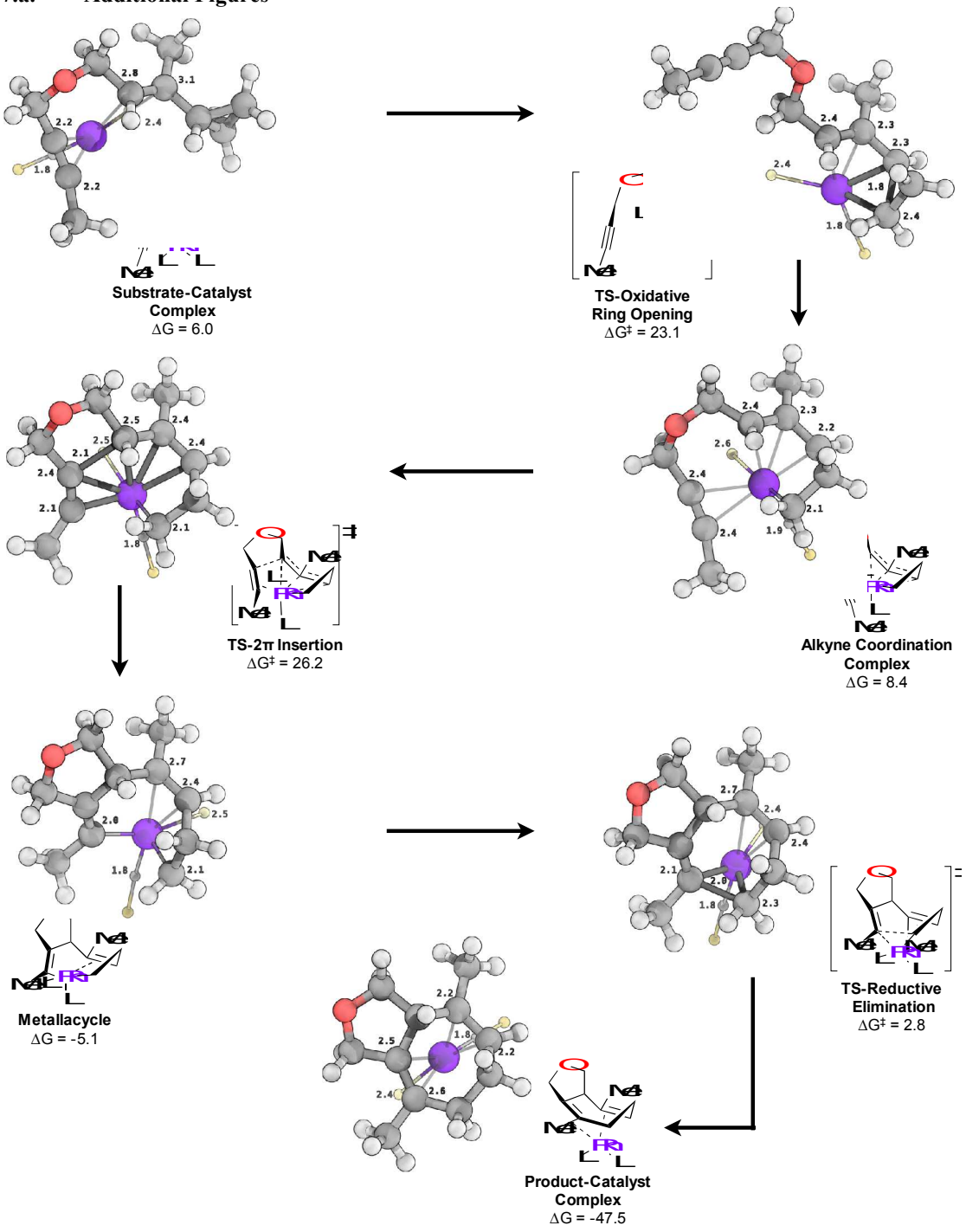

Figure S12. Computed geometries for RhCSCl.

Substrate-Catalyst Complex RhCSCl

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

# b3lyp/gen pseudo=read gfprint gfinput
scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/ChkBas Freq

Pointgroup= C1 Stoichiometry= C12H16ClORhS C1[X(C12H16ClORhS)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -1509.94221211 Predicted Change= -1.035736D-08

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00208	0.00180	[NO]	0.00208	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z

C	1.518911	1.431894	-0.132251
Rh	-0.660125	-0.286708	0.016777
C	2.366412	0.373095	-0.225771
C	2.952721	-0.194164	1.019519
C	-1.337761	1.732240	0.354940
C	-1.454216	1.151192	1.455731
H	1.344661	1.862152	0.852058
C	1.040260	2.319359	-1.268420
H	1.875895	2.914540	-1.658273
H	0.628316	1.742488	-2.110342
C	-1.227097	2.808742	-0.662070
H	-1.629000	2.452482	-1.622735
H	-1.818123	3.674918	-0.343596
C	-2.274743	-0.997438	-0.213731
Cl	0.293094	-2.247642	-0.947189
H	2.667653	0.351838	1.916534
C	3.182321	-1.683507	1.221226
C	4.361699	-0.779356	1.046044
H	4.910435	-0.829859	0.110400
H	2.967380	-2.076109	2.211277
H	2.898877	-2.347552	0.412093
H	4.977248	-0.539268	1.908711
O	0.096119	3.289568	-0.821252
C	-1.806643	0.895952	2.862362
H	-2.173415	1.814593	3.336296
H	-2.587802	0.131127	2.934054
H	-0.940427	0.535372	3.427458
C	2.846006	-0.151267	-1.555186
H	2.184681	0.138972	-2.374015
H	3.845779	0.252076	-1.768130
H	2.908608	-1.242035	-1.562879
S	-3.694620	-1.592560	-0.447877

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -1509.94221211 Predicted Change= -1.035736D-08
Zero-point correction (ZPE)= -1509.6897 0.25241
Internal Energy (U)= -1509.6699 0.27230
Enthalpy (H)= -1509.6689 0.27325
Gibbs Free Energy (G)= -1509.7401 0.20208

Frequencies -- 28.8555 46.5056 56.7809
SCF Energy (M06) = -1509.470701

Oxidative-Addition TS RhCSCl

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

# b3lyp/gen pseudo=read gfprint gfinput
scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,calcfc,ts,noeigentest) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/ChkBas Freq

Pointgroup= C1 Stoichiometry= C12H16ClORhS C1[X(C12H16ClORhS)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -1509.91173116 Predicted Change= -1.011479D-08

Optimization completed on the basis of negligible forces. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.01490	0.00180	[NO]	0.01490	0.00180	[NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-5.647480	-0.673757	-0.618868
Rh	1.399450	-0.224133	-0.207466
C	-4.977380	-0.166429	0.251585
C	-4.147577	0.442068	1.300562
C	-2.008310	0.061995	0.329609
C	-0.804403	0.800217	-0.185622
C	0.114568	1.437109	0.623881
C	1.278447	2.103485	0.008176
C	1.247563	2.905070	-1.251270
C	1.895956	1.600761	-1.604841
H	2.977065	1.601429	-1.676648
H	1.382599	0.989296	-2.344728
H	1.877480	3.791898	-1.265591
H	0.260893	3.078356	-1.676299
H	-0.790122	0.995191	-1.257050
H	-3.919645	-0.310684	2.074227
H	-4.691816	1.259250	1.787241
H	-1.728362	-0.641057	1.127474
H	-2.456569	-0.527203	-0.479774
H	2.090004	2.346545	0.686604
O	-2.942668	1.028746	0.819955
C	-6.465974	-1.286876	-1.661781
H	-6.363012	-0.751317	-2.613377
H	-6.180044	-2.331561	-1.833657
H	-7.528063	-1.272769	-1.388151
C	0.004502	1.487597	2.127795
H	0.992064	1.536182	2.596115
H	-0.564018	2.379010	2.422513
H	-0.520399	0.614438	2.519667
C	3.134967	-0.773064	-0.119741
Cl	0.580682	-2.326378	0.499848
S	4.631699	-1.186352	0.025214

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -1509.91173116 Predicted Change= -1.011479D-08
Zero-point correction (ZPE)= -1509.6612 0.25050
Internal Energy (U)= -1509.6411 0.27062
Enthalpy (H)= -1509.6401 0.27157
Gibbs Free Energy (G)= -1509.7149 0.19678

Frequencies -- -204.7763 17.0950 20.5724
SCF Energy (M06) = -1509.438094

Alkyne Coordination Complex RhCSCl

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

# b3lyp/gen pseudo=read gfprint gfinput
scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/ChkBas Freq

Pointgroup= C1 Stoichiometry= C12H16ClORhS C1[X(C12H16ClORhS)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -1509.94049865 Predicted Change= -1.796601D-08

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00142	0.00180	[YES]	0.00142	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-0.382486	2.290575	-0.508599
Rh	-0.323915	-0.106254	-0.108973
Cl	0.155930	0.097184	2.393548
C	0.774500	2.077841	-0.150536
C	2.159150	2.159595	0.359430
C	3.093818	0.009319	-0.060952
C	1.916194	-0.673988	-0.701057
C	1.265036	-1.805071	-0.186828
C	0.006641	-2.170994	-0.768331
C	-0.364658	-1.855967	-2.218405
C	-0.693680	-0.361478	-2.167378
C	-2.120990	-0.199364	0.327729
H	-1.729574	-0.133684	-2.420154
H	-0.017053	0.291040	-2.724427
H	-1.232735	-2.454685	-2.511174
H	0.452360	-2.106852	-2.907681
H	1.777997	-0.410563	-1.746131
H	2.145641	1.875568	1.421031
H	2.486658	3.201998	0.275063
H	4.034262	-0.380049	-0.472225
H	3.104310	-0.143651	1.025692
H	-0.541203	-2.965021	-0.266922
O	3.119042	1.403483	-0.361749
C	-1.642342	2.883099	-0.971941
H	-2.428208	2.775213	-0.217278
H	-1.499308	3.950805	-1.175352
H	-1.989456	2.403066	-1.892845
C	1.736535	-2.513505	1.061084
H	0.968996	-3.193143	1.439142
H	2.630590	-3.103708	0.819351
H	1.978435	-1.814556	1.864203
S	-3.603436	-0.308169	0.781991

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -1509.94049865 Predicted Change= -1.796601D-08
Zero-point correction (ZPE)= -1509.6882 0.25226
Internal Energy (U)= -1509.6689 0.27159
Enthalpy (H)= -1509.6679 0.27254
Gibbs Free Energy (G)= -1509.7361 0.20436

Frequencies -- 45.8672 53.5271 55.5839
SCF Energy (M06) = -1509.469082

2π-Insertion TS RhCSCl

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

# b3lyp/gen pseudo=read gfprint gfinput
scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,calcfc,ts,noeigentest) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/ChkBas Freq

Pointgroup= C1 Stoichiometry= C12H16ClORhS C1[X(C12H16ClORhS)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -1509.91958447 Predicted Change= -8.355967D-10

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00035	0.00180	[YES]	0.00035	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.014660	1.795371	-0.615929
Rh	-0.517636	-0.120427	-0.058276
Cl	-0.358978	0.465051	2.403558
C	1.245480	1.469753	-0.494022
C	2.602241	2.019424	-0.195572
C	3.219252	-0.141092	0.152851
C	1.883579	-0.579334	-0.420612
C	1.207588	-1.723687	0.207019
C	0.216321	-2.411177	-0.479830
C	-0.155665	-2.190397	-1.940612
C	-0.609890	-0.730868	-2.077383
C	-2.324998	0.001372	0.054707
H	-1.618182	-0.638070	-2.481475
H	0.070085	-0.096122	-2.651786
H	-0.966295	-2.878724	-2.198066
H	0.690650	-2.443492	-2.596772
H	1.910203	-0.616910	-1.507919
H	2.629400	2.332087	0.861153
H	2.795638	2.892317	-0.827889
H	3.989290	-0.879932	-0.097178
H	3.168525	-0.039859	1.245990
H	-0.245275	-3.248683	0.039218

O	3.618380	1.072732	-0.451079
C	-0.880996	2.949525	-0.876293
H	-1.479437	3.161758	0.016367
H	-0.303301	3.844385	-1.137182
H	-1.573148	2.731565	-1.696911
C	1.609581	-2.168452	1.595902
H	0.980859	-2.999403	1.926811
H	2.652258	-2.512648	1.596338
H	1.499377	-1.358517	2.322462
S	-3.869649	0.121195	0.193504

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -1509.91958447 Predicted Change= -8.355967D-10
Zero-point correction (ZPE)= -1509.6668 0.25276
Internal Energy (U)= -1509.6488 0.27073
Enthalpy (H)= -1509.6479 0.27168
Gibbs Free Energy (G)= -1509.7126 0.20692

Frequencies -- -221.3057 53.1375 55.5049
SCF Energy (M06) = -1509.44328

Metallacycle RhCSCl

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

# b3lyp/gen pseudo=read gfprint gfinput
scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/ChkBas Freq

Pointgroup= C1 Stoichiometry= C12H16ClORhS C1[X(C12H16ClORhS)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -1509.97310803 Predicted Change= -1.175539D-08

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00169	0.00180	[YES]	0.00169	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-0.569420	1.370747	-0.012667
Rh	0.811473	-0.142884	-0.056871
C	-1.869158	1.035826	0.031840
C	-3.070233	1.930735	-0.275694
C	-3.738722	-0.261367	-0.550875
C	-2.452037	-0.343215	0.291477
C	-1.483459	-1.486832	0.053475
C	-0.577857	-1.843124	1.008984
C	-0.316683	-1.099400	2.312997
C	0.843573	-0.144160	2.027588
H	1.825963	-0.559074	2.259649
H	0.726793	0.857729	2.438793
H	-0.056931	-1.811727	3.106459
H	-1.199187	-0.540371	2.635701
H	-2.788227	-0.378746	1.339014
H	-2.948842	2.447671	-1.240294
H	-3.260597	2.690815	0.492939
H	-4.525296	-0.951796	-0.233254
H	-3.534268	-0.422436	-1.620500
H	0.051199	-2.708552	0.817277
O	-4.205343	1.062230	-0.313454
C	-0.139476	2.806563	-0.201362
H	0.491402	3.138211	0.633545
H	0.452091	2.941896	-1.115147
H	-0.993655	3.493050	-0.253065
C	-1.607095	-2.293794	-1.218339
H	-2.559985	-2.840403	-1.234572
H	-1.594447	-1.648644	-2.104745
H	-0.787055	-3.009304	-1.312084
C	2.269449	0.933160	-0.191234
Cl	2.170927	-2.035656	-0.872185
S	3.574277	1.763058	-0.273305

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -1509.97310803 Predicted Change= -1.175539D-08
Zero-point correction (ZPE)= -1509.7177 0.25535
Internal Energy (U)= -1509.6996 0.27346
Enthalpy (H)= -1509.6987 0.27440
Gibbs Free Energy (G)= -1509.7650 0.20805

Frequencies -- 33.6445 38.1898 65.6135
SCF Energy (M06) = -1509.494316

Reductive Elimination TS RhCSCl

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

# b3lyp/gen pseudo=read gfprint gfinput
scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,calcfc,ts,noeigentest) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/ChkBas Freq

Pointgroup= C1 Stoichiometry= C12H16ClORhS C1[X(C12H16ClORhS)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -1509.94972487 Predicted Change= -2.778480D-10

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00035	0.00180	[YES]	0.00035	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.445557	-1.402887	0.220434
Rh	-0.844851	0.250395	0.114251
Cl	-1.768665	2.150847	-0.991411
C	1.725960	-1.081638	-0.056933
C	2.707742	-1.956468	-0.823825
C	3.406710	0.228616	-1.027564
C	2.442097	0.240096	0.174235
C	1.525385	1.435837	0.379694
C	0.738791	1.484950	1.492788
C	0.689477	0.373021	2.531997
C	-0.200508	-0.764871	2.016707
C	-2.367712	-0.643759	-0.277885
H	-1.246116	-0.665789	2.326522
H	0.128820	-1.754010	2.334255
H	0.281260	0.763343	3.471082
H	1.698257	0.002453	2.747593
H	3.081052	0.138195	1.068443
H	2.264723	-2.331826	-1.760191
H	3.059516	-2.825583	-0.250252
H	4.295493	0.850778	-0.892467
H	2.896434	0.528827	-1.955446
H	0.161382	2.387175	1.681721
O	3.837070	-1.127198	-1.096811
C	-0.083664	-2.791213	-0.066264
H	-0.347299	-2.889609	-1.126815
H	0.658132	-3.565759	0.168308
H	-0.986547	-3.010865	0.509548
C	1.630980	2.607278	-0.562737
H	0.911925	3.387011	-0.306281
H	2.645743	3.027540	-0.518880
H	1.439439	2.313296	-1.599423
S	-3.719879	-1.346471	-0.588401

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -1509.94972487 Predicted Change= -2.778480D-10
Zero-point correction (ZPE)= -1509.6952 0.25446
Internal Energy (U)= -1509.6778 0.27190
Enthalpy (H)= -1509.6768 0.27285
Gibbs Free Energy (G)= -1509.7410 0.20864

Frequencies -- -383.5338 39.4106 48.8380
SCF Energy (M06) = -1509.482293

Product-Catalyst Complex RhCSCl

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

# b3lyp/gen pseudo=read gfprint gfinput
scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/ChkBas Freq

Pointgroup= C1 Stoichiometry= C12H16ClORhS C1[X(C12H16ClORhS)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -1510.03125987 Predicted Change= -5.186987D-08

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00002	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00155	0.00180	[YES]	0.00155	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	1.743611	-0.902404	0.962116
Rh	-0.639311	-0.306246	0.019740
C	1.882534	0.005263	-0.043918
C	2.578446	-0.306746	-1.366364
C	1.875081	1.842288	-1.557809
C	1.535268	1.506419	-0.084627
C	0.079725	1.732830	0.318870
C	-0.326010	1.234659	1.572122
C	0.662238	0.769224	2.631846
C	1.276714	-0.612910	2.376073
H	0.544876	-1.383792	2.648357
H	2.133682	-0.770629	3.050627
H	0.159066	0.745894	3.603770
H	1.461295	1.520049	2.719884
H	2.211453	2.079996	0.570326
H	1.913624	-0.863870	-2.045451
H	3.502001	-0.878437	-1.235466
H	2.225525	2.867130	-1.702569
H	1.002611	1.667003	-2.205704
H	-1.282656	1.588978	1.950695
C	-2.404316	-0.002846	-0.148207
Cl	-0.741999	-2.372310	-1.141609
O	2.929172	0.962255	-1.906781
C	-0.698770	2.839736	-0.358614
H	-0.218913	3.808219	-0.151991
H	-0.750110	2.722644	-1.444451
H	-1.722093	2.887098	0.024554
C	2.237869	-2.320701	0.760169
H	2.078971	-2.671698	-0.261231
H	3.311593	-2.380298	0.991469
H	1.716540	-3.013806	1.426671
S	-3.937014	0.236185	-0.283510

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -1510.03125987 Predicted Change= -5.186987D-08
Zero-point correction (ZPE)= -1509.7735 0.25769
Internal Energy (U)= -1509.7560 0.27518
Enthalpy (H)= -1509.7551 0.27612
Gibbs Free Energy (G)= -1509.8195 0.21168

Frequencies -- 40.8001 57.0536 63.4771
SCF Energy (M06) = -1509.565524

8. RhDiEt

8.a. Additional Figures

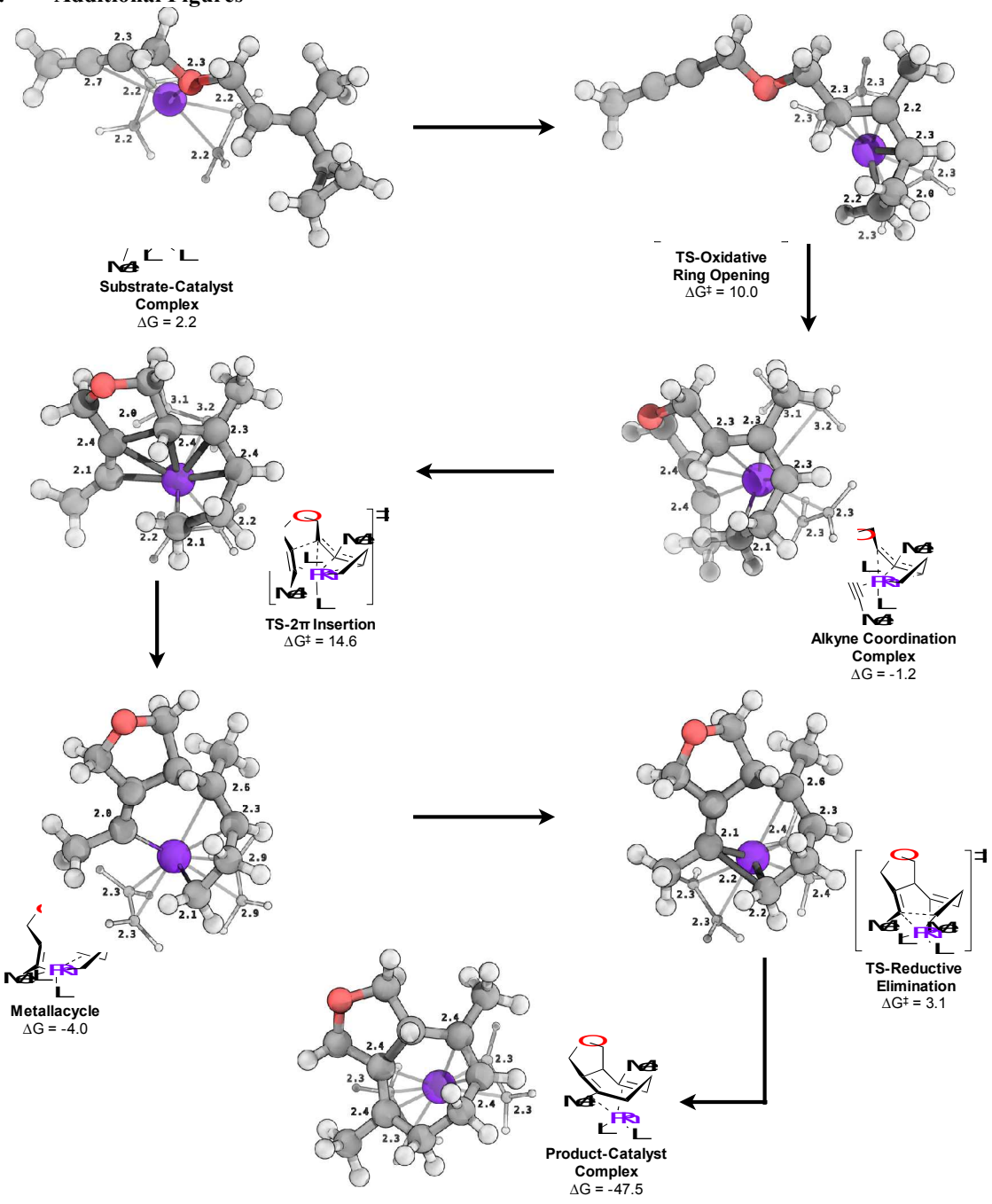

Figure S13. Computed geometries for RhDiEth.

Substrate-Catalyst Complex RhDiEt

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

# b3lyp/gen pseudo=read gfprint gfinput
scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/ChkBas Freq

Pointgroup= C1 Stoichiometry= C15H24ORh(1+) C1[X(C15H24ORh)] #Atoms= 41
Charge = 1 Multiplicity = 1

SCF Energy= -770.430457367 Predicted Change= -4.890011D-07

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00002 ‖	0.00045	[YES]	0.00000 ‖	0.00030	[YES]
Displ	0.01216 ‖	0.00180	[NO]	0.01216 ‖	0.00180	[NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z
Rh	1.387873	-0.402414	0.012597
C	-3.320370	0.150692	0.471869
C	-4.379523	-0.568215	-0.298948
C	-5.657171	0.161968	-0.699127
C	-4.701451	-0.324221	-1.753428

C	2.261311	1.777522	-0.065885
C	3.380573	1.396420	-0.373527
H	-6.602876	-0.353806	-0.561952
H	-5.695236	1.232190	-0.515283
H	-4.983840	-1.187375	-2.349146
H	-4.142051	0.424401	-2.306425
H	-4.546558	-1.585370	0.054529
C	2.873402	-1.853604	-0.570986
H	3.544183	-1.369171	-1.275473
C	2.969204	-1.624601	0.808001
H	3.702106	-0.933767	1.218398
C	-0.133259	-1.834884	-0.556431
H	-0.891151	-1.232528	-1.050655
C	-0.024099	-1.821880	0.836130
H	-0.704856	-1.224541	1.437271
C	-2.377693	0.893229	-0.142531
H	-2.381360	0.948645	-1.228953
C	-1.352893	1.754812	0.506915
H	-1.474520	2.801919	0.197124
C	0.966995	2.415276	0.217420
H	0.939524	2.804723	1.243637
O	-0.006733	1.372257	0.048224
H	-1.362797	1.713997	1.599626
H	0.766699	3.239321	-0.479985
C	4.756467	1.071860	-0.735367
H	5.392867	1.942990	-0.540178
H	5.150613	0.237268	-0.145078
H	4.840074	0.822034	-1.798591
C	-3.455224	-0.015798	1.967305
H	-4.408235	0.407704	2.307430
H	-3.483059	-1.081598	2.227882
H	-2.655874	0.453104	2.546498
H	0.278705	-2.648375	-1.145160
H	0.468651	-2.633216	1.363325
H	2.418157	-2.767569	-0.940353
H	2.592795	-2.351881	1.520394

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -770.430457367 Predicted Change= -4.890011D-07
Zero-point correction (ZPE)= -770.0755 0.35489
Internal Energy (U)= -770.0535 0.37694
Enthalpy (H)= -770.0525 0.37788
Gibbs Free Energy (G)= -770.1290 0.30142

Frequencies -- 16.1854 25.7061 37.1956
SCF Energy (M06) = -769.902515

Oxidative-Addition TS RhDiEt

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

# b3lyp/gen pseudo=read gfprint gfinput
scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,calcfc,ts,noeigentest) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/ChkBas Freq

Pointgroup= C1 Stoichiometry= C15H24ORh(1+) C1[X(C15H24ORh)] #Atoms= 41
Charge = 1 Multiplicity = 1

SCF Energy= -770.412236073 Predicted Change= -1.535604D-09

Optimization completed on the basis of negligible forces. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00281	0.00180	[NO]	0.00281	0.00180	[YES]

Atomic Type	X	Y	Z
Rh	1.239980	-0.536294	0.041697
C	1.312771	1.692183	-0.252051
C	2.413427	1.392194	0.641333
C	2.379916	1.463361	2.135651
C	2.165794	-0.014768	1.986458
C	-4.553067	0.298162	0.034175
C	-5.395508	-0.459303	0.456526
H	3.319451	1.767601	2.594810
H	1.539518	2.020093	2.548919
H	3.045242	-0.634302	2.135446
H	1.237012	-0.415251	2.409683
H	3.402041	1.333849	0.193622
C	-0.479987	-1.564095	-1.092401
H	-1.338151	-0.967148	-0.793908
C	0.394109	-1.141981	-2.062910
H	0.250020	-0.201411	-2.584657
C	2.247483	-2.556489	0.211851
H	2.368212	-2.750760	1.274358
C	3.118949	-1.726509	-0.464731
H	3.942790	-1.240980	0.050201
C	0.018065	1.419368	0.201214
H	-0.160700	1.307899	1.270525
C	-1.250354	1.716741	-0.551106
H	-1.504689	2.782285	-0.399741
C	-3.575420	1.234594	-0.497123
H	-3.581077	1.218088	-1.599134
O	-2.261532	0.887233	-0.020739
H	-1.144385	1.569505	-1.638071
H	-3.808933	2.264810	-0.184868
C	-6.415576	-1.368553	0.970593
H	-6.083588	-1.844814	1.900519
H	-7.345169	-0.829525	1.187253
H	-6.646297	-2.160662	0.249036
C	1.642115	2.270037	-1.606451
H	1.744072	3.359774	-1.518457
H	2.590018	1.879553	-1.988539
H	0.861665	2.076647	-2.345441
H	1.109112	-1.822590	-2.516053
H	-0.465740	-2.594656	-0.747903
H	1.633391	-3.271698	-0.326852
H	3.193042	-1.740622	-1.547353

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -770.412236073 Predicted Change= -1.535604D-09
Zero-point correction (ZPE)= -770.0596 0.35261
Internal Energy (U)= -770.0379 0.37432
Enthalpy (H)= -770.0369 0.37526
Gibbs Free Energy (G)= -770.1110 0.30121

Frequencies -- -221.3047 23.4057 34.9129
SCF Energy (M06) = -769.8898058

Alkyne Coordination Complex RhDiEt

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

# b3lyp/gen pseudo=read gfprint gfinput
scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/ChkBas Freq

Pointgroup= C1 Stoichiometry= C15H24ORh(1+) C1[X(C15H24ORh)] #Atoms= 41
Charge = 1 Multiplicity = 1

SCF Energy= -770.431727035 Predicted Change= -7.447566D-08

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00464	0.00180	[NO]	0.00464	0.00180	[YES]

Atomic Type	X	Y	Z
C	-1.326025	-1.616700	-0.341814
C	-0.140112	-2.211165	-0.835189
C	0.467340	-1.857286	-2.196518
C	1.017786	-0.445972	-2.003581
C	-0.240407	2.049015	-0.132839
C	0.983955	2.151262	-0.272441
H	1.257672	-2.572262	-2.440797
H	-0.286209	-1.921861	-2.991013
H	2.105813	-0.377543	-2.059167
H	0.556651	0.338416	-2.605756
H	0.184900	-3.133052	-0.359355
C	-1.669215	-0.349910	-0.876573
H	-1.424042	-0.149347	-1.915791
C	-2.815266	0.505963	-0.404268
H	-3.731708	0.210402	-0.929447
C	-1.644681	2.508238	0.049764
H	-1.916442	2.435279	1.114051
O	-2.606536	1.864150	-0.753573
H	-3.002682	0.407131	0.674545
H	-1.679740	3.565102	-0.233635
C	2.301565	2.743656	-0.545781
H	2.165992	3.805537	-0.781415
H	2.974583	2.670726	0.313717
H	2.785970	2.270667	-1.406824
C	-2.075649	-2.255824	0.803352
H	-2.964759	-2.761757	0.405580
H	-1.466715	-3.009575	1.309178
H	-2.423190	-1.531065	1.544002
Rh	0.458319	-0.195187	-0.029976
C	0.178879	-0.629794	3.111078
C	-0.434978	0.525326	2.828190
C	2.288875	-1.459210	0.616676
C	2.644623	-0.130525	0.688073
H	-0.360356	-1.571934	3.153528
H	-1.505138	0.568712	2.646581
H	2.596069	-2.061727	-0.232339
H	3.246846	0.312387	-0.096922
H	2.609739	0.412782	1.627633
H	1.959769	-2.009757	1.491547
H	0.092145	1.474970	2.846070
H	1.232633	-0.664439	3.374741

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -770.431727035 Predicted Change= -7.447566D-08
Zero-point correction (ZPE)= -770.0772 0.35450
Internal Energy (U)= -770.0554 0.37629
Enthalpy (H)= -770.0544 0.37724
Gibbs Free Energy (G)= -770.1263 0.30534

Frequencies -- 41.5354 53.8898 70.6854
SCF Energy (M06) = -769.9118042

2π-Insertion TS RhDiEt

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

# b3lyp/gen pseudo=read gfprint gfinput
scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,calcfc,ts,noeigentest) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/ChkBas Freq

Pointgroup= C1 Stoichiometry= C15H24ORh(1+) C1[X(C15H24ORh)] #Atoms= 41
Charge = 1 Multiplicity = 1

SCF Energy= -770.409597250 Predicted Change= -1.408120D-09

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00105	0.00180	[YES]	0.00105	0.00180	[YES]

Atomic Type	X	Y	Z
Rh	0.722362	-0.006941	-0.099948

C	-0.697560	-1.809491	0.249932
C	0.344336	-2.365700	-0.474154
C	0.629509	-2.086872	-1.946796
C	0.841553	-0.577154	-2.085249
C	-1.286023	1.219314	-0.416590
C	-0.156084	1.808644	-0.593566
H	1.528175	-2.636384	-2.239301
H	-0.187916	-2.461881	-2.578409
H	1.817692	-0.300883	-2.486816
H	0.059075	-0.042485	-2.627885
H	0.925752	-3.146213	0.012073
C	0.278489	1.156941	2.706828
H	-0.779178	0.917768	2.782033
C	1.229448	0.261810	3.000600
H	0.992155	-0.748432	3.322907
C	2.637314	1.024413	-0.180469
H	2.787365	1.445031	-1.170150
C	2.877473	-0.332652	0.052304
H	3.212404	-0.978801	-0.753624
C	-1.565056	-0.780238	-0.373947
H	-1.615913	-0.860560	-1.458333
C	-2.975731	-0.619747	0.196843
H	-3.573336	-1.497826	-0.068374
C	-2.731126	1.593629	-0.179529
H	-2.840550	1.948814	0.858837
O	-3.571942	0.493915	-0.417693
H	-2.965481	-0.516270	1.291532
H	-3.020055	2.400156	-0.859867
C	0.389368	3.140661	-0.960053
H	-0.423644	3.852616	-1.143412
H	1.032099	3.544384	-0.170664
H	0.991816	3.075797	-1.873285
C	-1.005469	-2.306886	1.646354
H	-1.923459	-2.908248	1.638351
H	-0.199494	-2.943746	2.019667
H	-1.158671	-1.492316	2.359233
H	2.283072	0.528881	2.991065
H	0.519599	2.184026	2.446651
H	2.664294	1.737242	0.638321
H	3.080813	-0.699703	1.053620

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -770.409597250 Predicted Change= -1.408120D-09
Zero-point correction (ZPE)= -770.0550 0.35458
Internal Energy (U)= -770.0344 0.37511
Enthalpy (H)= -770.0335 0.37605
Gibbs Free Energy (G)= -770.1027 0.30682

Frequencies -- -222.1580 38.7417 66.4517
SCF Energy (M06) = -769.8881467

Metallacycle RhDiEt

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

==========

# b3lyp/gen pseudo=read gfprint gfinput
scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/ChkBas Freq

---

Pointgroup= C1 Stoichiometry= C15H24ORh(1+) C1[X(C15H24ORh)] #Atoms= 41
Charge = 1 Multiplicity = 1

SCF Energy= -770.445989720 Predicted Change= -1.961152D-08

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00125	0.00180	[YES]	0.00125	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
Rh	-0.923285	0.184950	-0.089836
C	0.907120	-1.614454	0.002783
C	-0.116695	-1.744636	0.913900
C	-0.213934	-1.061795	2.277232
C	-1.076823	0.160310	2.003100
C	1.923610	0.686630	0.029109
C	0.744987	1.330623	-0.051836
H	-0.672325	-1.739303	3.007093
H	0.769640	-0.774391	2.655208
H	-2.139348	0.026834	2.211459
H	-0.703843	1.101101	2.404597
H	-0.891526	-2.474653	0.691819
C	-2.816499	-1.616952	-1.286252
H	-2.217927	-2.521121	-1.339258
C	-3.434209	-1.247416	-0.152685
H	-3.355618	-1.833895	0.758906
C	-2.178406	1.717614	-1.191699
H	-1.470059	2.232759	-1.833363
C	-2.297509	2.014901	0.145458
H	-1.701813	2.788111	0.613324
C	2.128248	-0.782466	0.319901
H	2.371683	-0.886087	1.386592
C	3.453588	-1.033707	-0.435796
H	4.018186	-1.893491	-0.067978
C	3.322363	1.253803	-0.220066
H	3.637821	1.982725	0.535171
O	4.201925	0.136194	-0.143431
H	3.381958	1.734339	-1.209159
H	3.293153	-1.143376	-1.519157
C	0.713415	2.838647	-0.158093
H	1.705752	3.220644	-0.422687
H	0.020481	3.227414	-0.908890
H	0.450512	3.299188	0.803341
C	0.911549	-2.425616	-1.268934
H	1.067878	-1.798818	-2.154527
H	1.741170	-3.144196	-1.243372
H	-0.013121	-2.991890	-1.398911
H	-3.155959	1.669887	0.713253
H	-2.946494	1.146409	-1.703245
H	-2.966273	-1.091248	-2.225729
H	-4.116339	-0.402160	-0.121162

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -770.445989720 Predicted Change= -1.961152D-08
Zero-point correction (ZPE)= -770.0888 0.35714
Internal Energy (U)= -770.0682 0.37769
Enthalpy (H)= -770.0673 0.37863
Gibbs Free Energy (G)= -770.1366 0.30930

Frequencies -- 37.1740 58.0310 72.5422
SCF Energy (M06) = -769.920197

Reductive Elimination TS RhDiEt

Using Gaussian 03: AM64L-G03RevE.01 11-Sep-2007

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# b3lyp/gen pseudo=read gfprint gfinput
scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,calcfc,ts,noeigentest) freq=noraman
#N Geom=AllCheck Guess=Read SCRF=Check GenChk RB3LYP/ChkBas Freq

---

Pointgroup= C1 Stoichiometry= C15H24ORh(1+) C1[X(C15H24ORh)] #Atoms= 41
Charge = 1 Multiplicity = 1

SCF Energy= -770.428476711 Predicted Change= -1.410029D-08

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00118	0.00180	[YES]	0.00118	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.892895	-1.647738	0.266367
C	-0.036487	-1.574217	1.279744
C	0.046287	-0.604183	2.454254
C	-0.585230	0.701094	2.004383
C	1.755591	0.732657	0.069328
C	0.564792	1.353516	0.223467
H	-0.500330	-1.015270	3.310998
H	1.084018	-0.455996	2.768993
H	-1.663352	0.764494	2.167670
H	-0.109791	1.607498	2.368786
H	-0.760587	-2.381325	1.351894
C	2.095453	-0.727742	0.281791
H	2.593845	-0.820010	1.260890
C	3.216603	-0.898233	-0.767995
H	3.893446	-1.730676	-0.564191
C	3.030605	1.373026	-0.468210
H	3.465142	2.105774	0.224183
O	3.956683	0.306056	-0.632057
H	2.842701	1.885240	-1.425438
H	2.808801	-1.003492	-1.785634
C	0.510348	2.865714	0.160424
H	1.150047	3.309521	0.933477
H	0.887426	3.227934	-0.805537
H	-0.488842	3.281580	0.297746
C	0.894615	-2.795477	-0.709347
H	0.937260	-2.458338	-1.750767
H	1.792212	-3.405536	-0.540219
H	0.026762	-3.446514	-0.579196
Rh	-1.018268	0.047501	-0.100122
C	-1.885344	1.630003	-1.487807
C	-2.572028	1.702010	-0.293725
C	-2.280078	-1.504690	-1.336948
C	-2.940841	-1.427001	-0.140273
H	-1.069207	2.303995	-1.716427
H	-2.320999	2.440482	0.459750
H	-1.567784	-2.297494	-1.536959
H	-2.760486	-2.137597	0.659244
H	-3.821559	-0.806110	-0.017574
H	-2.643452	-0.970997	-2.208946
H	-3.550856	1.247915	-0.186641
H	-2.298898	1.096477	-2.336882

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

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SCF Energy= -770.428476711 Predicted Change= -1.410029D-08
Zero-point correction (ZPE)= -770.0714 0.35704
Internal Energy (U)= -770.0521 0.37632
Enthalpy (H)= -770.0512 0.37726
Gibbs Free Energy (G)= -770.1172 0.31119

Frequencies -- -316.9295 45.8613 49.6956
SCF Energy (M06) = -769.9108324

Reductive Elimination TS Rh-Mono-Et

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

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# b3lyp/gen pseudo=read gfprint gfinput
scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,calcall,ts,noeigentest)

Pointgroup= C1 Stoichiometry= C13H20ORh(1+) C1[X(C13H20ORh)] #Atoms= 35
Charge = 1 Multiplicity = 1

SCF Energy= -691.817574094 Predicted Change= -9.180737D-10

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00050	0.00180	[YES]	0.00050	0.00180	[YES]

Atomic	Coordinates (Angstroms)

Type	X	Y	Z
Rh	-0.760655	0.083520	-0.218485
C	0.541092	-1.796164	-0.288800
C	-0.584911	-2.242285	0.384564
C	-0.979088	-1.822947	1.799198
C	-1.212169	-0.311756	1.759735
C	1.263445	1.224491	0.061986
C	0.167600	1.904853	0.005177
H	-1.892611	-2.351243	2.084278
H	-0.205771	-2.110709	2.523639
H	-2.242327	-0.011729	1.953027
H	-0.523297	0.294139	2.352226
H	-1.176974	-3.018906	-0.094237
C	-2.595639	1.200991	-0.584186
H	-2.424465	1.855104	-1.434944
C	-2.848674	-0.158985	-0.784519
H	-2.858735	-0.576609	-1.789137
C	1.417493	-0.770501	0.330797
H	1.357721	-0.742218	1.417865
C	2.885883	-0.752458	-0.103157
H	3.394040	-1.626213	0.316939
C	2.753473	1.501816	0.007802
H	3.018192	1.755227	-1.031574
O	3.484240	0.389320	0.453467
H	2.988918	-0.771029	-1.197218
H	2.996978	2.351577	0.652261
C	-0.292215	3.317924	0.051991
H	0.553494	3.992647	0.227182
H	-0.776942	3.610986	-0.885139
H	-1.017839	3.465040	0.859454
C	0.895922	-2.361205	-1.648223
H	1.794799	-2.986834	-1.582957
H	0.085132	-2.984157	-2.033880
H	1.100436	-1.574603	-2.383289
H	-3.372934	-0.742171	-0.033072
H	-2.915538	1.696120	0.328473

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -691.817574094 Predicted Change= -9.180737D-10
Zero-point correction (ZPE)= -691.5165 0.30100
Internal Energy (U)= -691.5001 0.31742
Enthalpy (H)= -691.4992 0.31836
Gibbs Free Energy (G)= -691.5589 0.25859

Frequencies -- -213.0195 72.5718 86.4542
SCF Energy (M06) = -691.3586927

Ethylene

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

b3lyp/gen gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/ChkBas Freq

Pointgroup= CS Stoichiometry= C2H4 CS[SG(C2H4)] #Atoms= 6
Charge = 0 Multiplicity = 1

SCF Energy= -78.5858248474 Predicted Change= -2.375630D-08

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00009	0.00045	[YES]	0.00003	0.00030	[YES]
Displ	0.00015	0.00180	[YES]	0.00015	0.00180	[YES]

Atomic Coordinates (Angstroms)

Type	X	Y	Z
C	0.000000	0.665618	0.000000
H	-0.923772	1.239626	0.000000
H	0.923772	1.239626	0.000000
C	0.000000	-0.665618	0.000000
H	0.923772	-1.239626	0.000000
H	-0.923772	-1.239627	0.000000

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -78.5858248474 Predicted Change= -2.375630D-08
Zero-point correction (ZPE)= -78.5345 0.05123
Internal Energy (U)= -78.5315 0.05427
Enthalpy (H)= -78.5306 0.05522
Gibbs Free Energy (G)= -78.5567 0.02905

Frequencies -- 835.2126 956.4483 975.8595
SCF Energy (M06) = -78.5098784606

Product-Catalyst Complex RhDiEt

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

b3lyp/gen pseudo=read gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/ChkBas Freq

Pointgroup= C1 Stoichiometry= C15H24ORh(1+) C1[X(C15H24ORh)] #Atoms= 41
Charge = 1 Multiplicity = 1

SCF Energy= -770.505795816 Predicted Change= -5.237088D-08

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00343	0.00180	[NO]	0.00343	0.00180	[YES]

Atomic Coordinates (Angstroms)

Type	X	Y	Z
Rh	0.893516	-0.098964	-0.122378
C	-0.474002	1.760910	0.443459
C	0.208188	1.403611	1.589156
C	-0.389076	0.530543	2.677698
C	-0.460907	-0.966597	2.343795
C	-1.508677	-0.489100	0.032375
C	-0.920180	-1.339913	0.942744
H	0.196024	0.651927	3.593344
H	-1.396008	0.906379	2.905396
H	0.520882	-1.425744	2.517769
H	-1.139977	-1.466841	3.051405
H	1.055043	2.021148	1.878005
C	1.971388	-1.996625	-0.783885
H	1.677179	-2.749725	-0.059197
C	1.133651	-1.626690	-1.810123
H	0.154966	-2.079673	-1.916563
C	2.942468	0.806877	0.121019
H	2.868087	1.575464	0.882295
C	2.524050	1.049821	-1.173271
H	2.098734	2.006789	-1.457833
C	-1.771159	1.023192	0.148891
H	-2.500588	1.214980	0.951565
C	-2.465331	1.311526	-1.201270
H	-3.169596	2.144515	-1.164115
C	-2.339822	-0.957433	-1.168863
H	-2.967175	-1.821386	-0.930566
O	-3.196745	0.128805	-1.469079
H	-1.717756	-1.213914	-2.040414
H	-1.729165	1.499198	-1.998232
C	-1.009919	-2.839386	0.735946
H	-0.190174	-3.363047	1.237644
H	-1.941127	-3.206520	1.189905
H	-1.021658	-3.141210	-0.314034
C	-0.143710	3.026376	-0.307642
H	-0.911022	3.779542	-0.077865
H	0.818699	3.440964	0.005383
H	-0.141141	2.899599	-1.393691
H	1.495481	-1.087856	-2.679978
H	3.032174	-1.768498	-0.818940
H	2.873991	0.434864	-1.996359
H	3.618122	-0.010689	0.354552

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -770.505795816 Predicted Change= -5.237088D-08
Zero-point correction (ZPE)= -770.1460 0.35973
Internal Energy (U)= -770.1264 0.37931
Enthalpy (H)= -770.1255 0.38025
Gibbs Free Energy (G)= -770.1923 0.31341

Frequencies -- 33.2757 63.1107 92.2130
SCF Energy (M06) = -769.9936668

9. RhCOT

9.a. Additional Figures

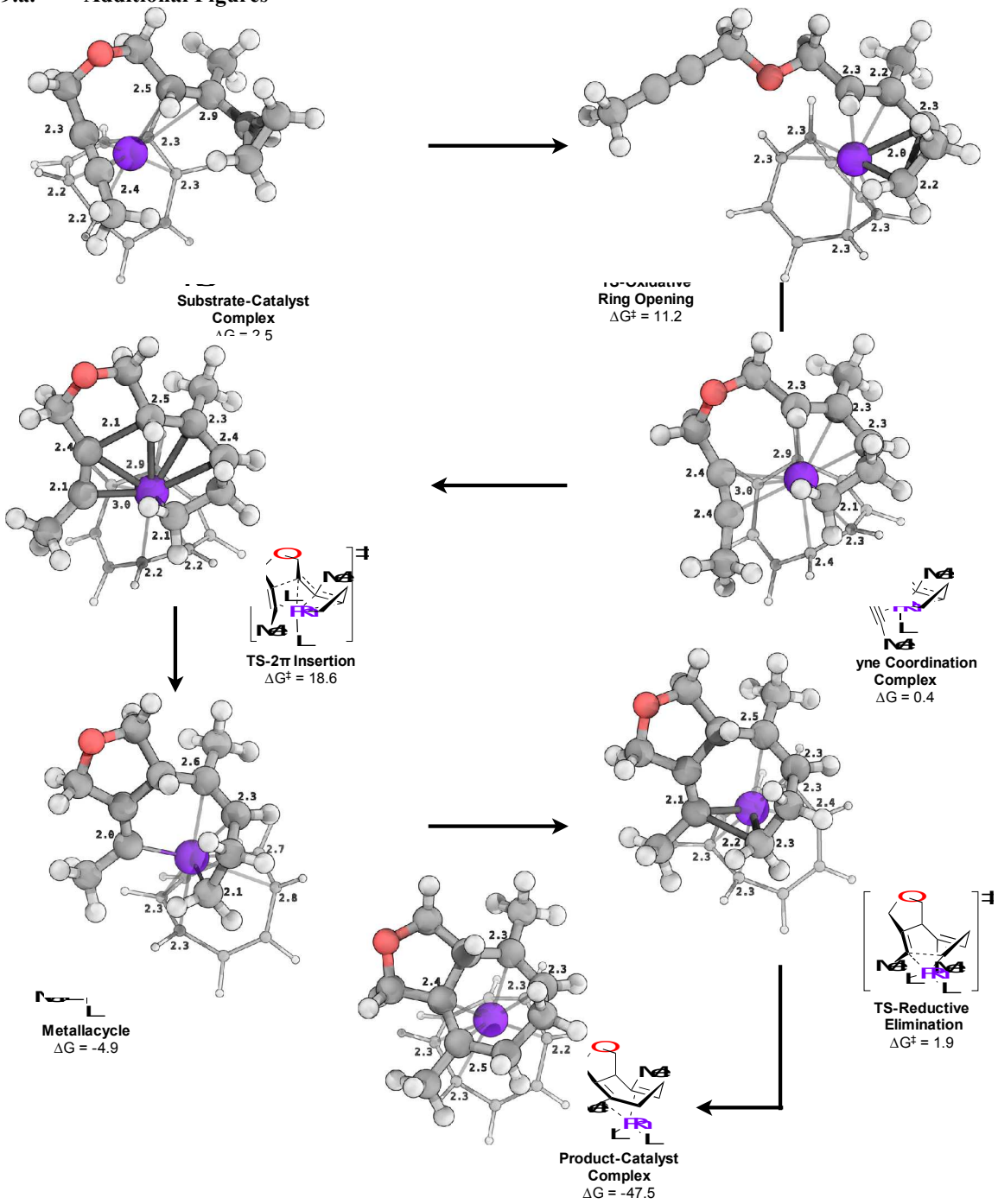

Figure S14. Computed geometries for RhCOT.

Substrate-Catalyst Complex RhCOT

Supporting Information: 000-COT-VCP-Complex-BisCoord2.log

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

# b3lyp/gen pseudo=read gfprint gfinput
scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/ChkBas Freq

Pointgroup= C1 Stoichiometry= C19H24ORh(1+) C1[X(C19H24ORh)] #Atoms= 45
Charge = 1 Multiplicity = 1

SCF Energy= -922.824614402 Predicted Change= -3.565694D-08

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00152	0.00180	[YES]	0.00152	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	2.116199	-0.941262	-0.647197
C	2.568830	-1.754615	0.512437
C	3.966153	-1.500943	1.096125

C	2.746342	-1.227793	1.918559
C	-0.012938	2.344124	0.324553
C	-0.064871	2.028358	1.514255
H	4.576209	-2.370131	1.322531
H	4.515019	-0.650103	0.702704
H	2.503477	-1.909861	2.728129
H	2.493626	-0.191822	2.122950
H	2.312632	-2.809274	0.433995
C	1.908066	0.411513	-0.576839
H	2.176402	0.912702	0.348967
C	1.858660	1.358266	-1.771501
H	2.833657	1.371694	-2.272782
C	0.335094	3.010799	-0.960670
H	-0.397901	2.754877	-1.739475
O	1.649489	2.704658	-1.372395
H	1.107696	1.057627	-2.517807
H	0.308233	4.095004	-0.808492
C	-0.040220	1.909675	2.975366
H	0.371055	2.833814	3.399251
H	-1.040044	1.763857	3.396211
H	0.589707	1.074609	3.298571
C	2.124915	-1.685829	-1.958672
H	3.168014	-1.927725	-2.205243
H	1.600912	-2.646573	-1.891392
H	1.715158	-1.112677	-2.793081
Rh	-0.496249	0.124743	0.075836
C	-0.994685	-2.088054	-0.135332
C	-1.191918	-1.483872	-1.374451
C	-2.420111	0.069524	1.120742
C	-2.597249	0.685468	-0.139189
C	-2.093229	-2.351117	0.829427
H	-0.062593	-2.623983	0.032680
H	-0.402311	-1.578258	-2.115501
C	-2.511501	-1.035535	-1.887070
H	-2.386059	0.728700	1.984940
C	-2.757307	-1.347647	1.409759
H	-2.658393	1.772981	-0.147221
C	-3.158521	-0.013180	-1.320952
H	-2.319677	-3.390952	1.059265
H	-2.906155	-1.544011	-2.765122
H	-3.548071	-1.537644	2.133737
H	-4.105542	0.349202	-1.717396

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -922.824614402 Predicted Change= -3.565694D-08
Zero-point correction (ZPE)= -922.4443 0.38027
Internal Energy (U)= -922.4213 0.40326
Enthalpy (H)= -922.4204 0.40420
Gibbs Free Energy (G)= -922.4963 0.32829

Frequencies -- 26.6787 41.2744 61.2722
SCF Energy (M06) = -922.2023053

Oxidative-Addition TS RhCOT

Supporting Information: 015-COT-VCP-Opening-TS-Linear.log

Using Gaussian 03: AM64L-G03RevE.01 11-Sep-2007

# b3lyp/gen pseudo=read gfprint gfinput
scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,calcfc,ts,noeigentest) freq=noraman
#N Geom=AllCheck Guess=Read SCRF=Check GenChk RB3LYP/ChkBas Freq

Pointgroup= C1 Stoichiometry= C19H24ORh(1+) C1[X(C19H24ORh)] #Atoms= 45
Charge = 1 Multiplicity = 1

SCF Energy= -922.815406945 Predicted Change= -1.365868D-10

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00042	0.00180	[YES]	0.00042	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
Rh	1.042665	0.014611	-0.310882
C	1.128956	-2.065383	0.481834
C	2.209156	-2.009512	-0.479119
C	2.140383	-2.408953	-1.917348
C	1.930263	-0.932970	-2.106583
C	-4.641163	-0.370779	0.124845
C	-5.441055	0.382292	-0.380229
H	3.067469	-2.817109	-2.318095
H	1.289451	-3.037568	-2.178140
H	2.817278	-0.369834	-2.381085
H	1.011072	-0.636334	-2.622663
H	3.206539	-1.852590	-0.076372
C	-0.461084	1.475384	0.632613
H	-1.418438	0.963245	0.544914
C	-0.294684	2.726699	-0.151607
C	0.391808	1.090516	1.657077
H	0.041146	0.312202	2.332328
C	1.575615	1.858126	2.113741
C	1.883886	1.994410	-1.083906
H	2.215656	1.822207	-2.107352
C	2.731655	1.581752	-0.060541
C	2.644711	2.066706	1.337435
H	3.665631	1.098353	-0.345046
H	-1.113320	3.443172	-0.104098
C	0.770897	2.965249	-0.925262
H	1.564062	2.213519	3.143259
H	3.516337	2.593114	1.724262
H	0.831377	3.877343	-1.516956
C	-0.176598	-1.868864	0.005024
H	-0.384660	-2.024841	-1.053231
C	-1.428168	-1.929250	0.837397
H	-1.771546	-2.979846	0.871848
C	-3.714882	-1.297631	0.757274
H	-3.688013	-1.134215	1.847130
O	-2.396367	-1.113392	0.211969
H	-1.261376	-1.617828	1.880695
H	-4.031016	-2.339958	0.592240
C	-6.411187	1.284844	-0.993566
H	-6.017590	1.709079	-1.924732
H	-7.339388	0.754921	-1.236892
H	-6.663616	2.115731	-0.324713
C	1.488104	-2.316153	1.926448
H	1.544724	-3.398925	2.099686
H	2.463752	-1.888171	2.174333
H	0.745822	-1.914928	2.619464

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -922.815406945 Predicted Change= -1.365868D-10
Zero-point correction (ZPE)= -922.4371 0.37820
Internal Energy (U)= -922.4142 0.40111
Enthalpy (H)= -922.4133 0.40205
Gibbs Free Energy (G)= -922.4905 0.32488

Frequencies -- -227.6317 17.9266 32.7448
SCF Energy (M06) = -922.1849636

Alkyne Coordination Complex RhCOT

Supporting Information: 020-COT-Open-VCP-Complex-Ene.log

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

# b3lyp/gen pseudo=read gfprint gfinput
scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/ChkBas Freq

Pointgroup= C1 Stoichiometry= C19H24ORh(1+) C1[X(C19H24ORh)] #Atoms= 45
Charge = 1 Multiplicity = 1

SCF Energy= -922.834487984 Predicted Change= -1.232560D-07

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00201	0.00180	[NO]	0.00201	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
Rh	0.029356	-0.030859	0.387148
C	1.465215	-1.818513	0.067568
C	0.650939	-2.044007	1.200185
C	0.930846	-1.417322	2.568046
C	0.594983	0.057253	2.373785
C	0.980206	1.996159	-0.372741
C	0.162269	2.405945	0.454466
H	0.292108	-1.885457	3.322175
H	1.971246	-1.587243	2.871427
H	-0.274219	0.395646	2.942294
H	1.423153	0.758238	2.491179
H	-0.020529	-2.898171	1.160345
C	-1.449529	0.447873	-2.123087
H	-0.759409	1.007004	-2.755354
C	-2.556676	1.224881	-1.531231
C	-1.318120	-0.896624	-2.075566
H	-0.534617	-1.351288	-2.680267
C	-2.253598	-1.832995	-1.417310
C	-2.213432	0.500492	0.857868
H	-2.158306	1.025308	1.809315
C	-2.087616	-0.883052	0.913901
C	-2.573845	-1.831722	-0.115916
H	-1.950326	-1.314798	1.903414
H	-3.114007	1.854587	-2.224029
C	-2.880760	1.249856	-0.232308
H	-2.668520	-2.612562	-2.055702
H	-3.243218	-2.605009	0.260004
H	-3.700275	1.891593	0.090929
C	2.209586	-0.609174	0.044707
H	2.615656	-0.235177	0.980686
C	2.996424	-0.125740	-1.148208
H	4.003813	-0.558959	-1.125046
C	2.031442	2.013253	-1.422174
H	1.607997	1.676296	-2.382274
O	3.192793	1.277920	-1.107730
H	2.529900	-0.415884	-2.101088
H	2.357234	3.051265	-1.544868
C	-0.602497	3.264075	1.366893
H	-0.159991	4.266934	1.364895
H	-1.646585	3.352068	1.052413
H	-0.575406	2.890168	2.395893
C	1.401442	-2.772280	-1.101385
H	2.234946	-3.481503	-1.012666
H	0.474085	-3.350193	-1.099097
H	1.508245	-2.277707	-2.069356

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -922.834487984 Predicted Change= -1.232560D-07
Zero-point correction (ZPE)= -922.4531 0.38137
Internal Energy (U)= -922.4307 0.40369
Enthalpy (H)= -922.4298 0.40463
Gibbs Free Energy (G)= -922.5021 0.33237

Frequencies -- 57.3766 66.0326 76.1570
SCF Energy (M06) = -922.2096651

2π-Insertion TS RhCOT

Supporting Information: 025-COT-TS-2Pi-Insertion-Ene2.log

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

# b3lyp/gen pseudo=read gfprint gfinput
scf=(direct,tight,maxcycle=300,xqc)

opt=(maxcycle=250,calcfc,ts,noeigentest) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/ChkBas Freq

---

Pointgroup= C1 Stoichiometry= C19H24ORh(1+) C1[X(C19H24ORh)] #Atoms= 45
Charge = 1 Multiplicity = 1

SCF Energy= -922.811300380 Predicted Change= -2.206133D-08

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00002	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00161	0.00180	[YES]	0.00161	0.00180	[YES]

Atomic Type	X	Y	Z
C	1.302417	-1.752168	-0.294494
C	0.613689	-2.340497	0.753095
C	0.761246	-1.950389	2.220399
C	0.399295	-0.466610	2.332219
C	1.623004	1.407142	-0.025738
C	0.550636	1.866587	0.510184
H	0.080826	-2.565010	2.816052
H	1.776816	-2.167293	2.580139
H	-0.431633	-0.263397	3.010225
H	1.232113	0.199547	2.567496
H	0.012362	-3.217104	0.521908
C	2.164307	-0.580316	-0.041530
H	2.545354	-0.529586	0.976284
C	3.288963	-0.300655	-1.036330
H	4.065259	-1.064661	-0.922228
C	2.848106	1.898513	-0.753584
H	2.574867	2.133316	-1.795902
O	3.872881	0.937105	-0.715753
H	2.930041	-0.315005	-2.075459
H	3.217616	2.809685	-0.273361
C	0.004163	3.143084	1.040196
H	0.742640	3.946289	0.934872
H	-0.909632	3.432263	0.515192
H	-0.236827	3.045719	2.105251
C	1.238133	-2.356705	-1.681199
H	2.165205	-2.905259	-1.892535
H	0.410096	-3.065650	-1.762161
H	1.124730	-1.602810	-2.464765
Rh	-0.195683	-0.078488	0.391946
C	-1.691368	-0.458742	-2.114126
C	-1.650541	0.888129	-2.011265
C	-2.228589	-0.704508	0.924401
C	-2.158776	0.705635	1.014280
C	-2.685305	-1.346810	-1.476742
H	-1.011397	-0.935807	-2.818650
H	-0.928315	1.427649	-2.624752
C	-2.613952	1.712071	-1.253982
H	-2.157779	-1.249027	1.864328
C	-2.904969	-1.458146	-0.157719
H	-2.024992	1.111765	2.015664
C	-2.826007	1.632851	0.065339
H	-3.236029	-2.001118	-2.151820
H	-3.154508	2.461953	-1.830891
H	-3.628594	-2.195558	0.188253
H	-3.542238	2.313425	0.524901

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy=	-922.811300380	Predicted Change= -2.206133D-08	
Zero-point correction (ZPE)=	-922.4297	0.38150	
Internal Energy (U)=	-922.4087	0.40252	
Enthalpy (H)=	-922.4078	0.40346	
Gibbs Free Energy (G)=	-922.4773	0.33392	

Frequencies -- -228.5597 54.8829 62.2199
SCF Energy (M06) = -922.1822673

Metallacycle RhCOT

Supporting Information: 030-COT-Metallacycle-Ene.log

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

# b3lyp/gen pseudo=read gfprint gfinput
scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/ChkBas Freq

---

Pointgroup= C1 Stoichiometry= C19H24ORh(1+) C1[X(C19H24ORh)] #Atoms= 45
Charge = 1 Multiplicity = 1

SCF Energy= -922.854101296 Predicted Change= -8.951722D-08

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00010	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00316	0.00180	[NO]	0.00316	0.00180	[YES]

Atomic Type	X	Y	Z
Rh	-0.466152	0.042607	0.077661
C	1.490353	-1.583899	-0.102151
C	0.553371	-1.866459	0.867506
C	0.518786	-1.299919	2.286327
C	-0.365916	-0.064346	2.164955
C	2.341445	0.773470	0.081772
C	1.113415	1.314450	0.116464
H	0.098170	-2.041578	2.974332
H	1.519441	-1.041593	2.641213
H	-1.395149	-0.197354	2.497739
H	0.066862	0.856330	2.553665
H	-0.186868	-2.629928	0.636357
C	-2.411571	-1.413116	-1.091022
H	-1.892396	-2.299901	-1.455272
C	-2.724822	-0.397638	-2.118259
C	-2.851576	-1.424206	0.191435
H	-2.647491	-2.314090	0.788008
C	-3.731347	-0.418664	0.819962
C	-1.829732	1.611531	-0.891938
H	-1.164247	2.420643	-1.175201
C	-2.216353	1.552761	0.439931
C	-3.436694	0.880526	0.944220
H	-1.800627	2.308496	1.102338
H	-3.128920	-0.784342	-3.052982
C	-2.467667	0.918973	-2.029376
H	-4.650554	-0.799602	1.262950
H	-4.123787	1.534180	1.480574
H	-2.666904	1.548424	-2.895320
C	2.675084	-0.695596	0.203467
H	3.011001	-0.886706	1.232732
C	3.948799	-0.760546	-0.669219
H	4.604447	-1.603403	-0.438544
C	3.668091	1.477302	-0.197273
H	3.987388	2.146493	0.611078
O	4.631388	0.432034	-0.309301
H	3.616555	2.064612	-1.126999
H	3.708770	-0.773478	-1.743589
C	0.935958	2.817148	0.107554
H	1.845586	3.311241	0.467957
H	0.735653	3.213826	-0.896605
H	0.125369	3.152052	0.762939
C	1.443092	-2.280666	-1.438729
H	1.513183	-1.570319	-2.270306
H	2.300786	-2.959939	-1.532195
H	0.533181	-2.874320	-1.558971

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy=	-922.854101296	Predicted Change= -8.951722D-08	
Zero-point correction (ZPE)=	-922.4703	0.38375	
Internal Energy (U)=	-922.4491	0.40498	
Enthalpy (H)=	-922.4481	0.40592	
Gibbs Free Energy (G)=	-922.5186	0.33541	

Frequencies -- 37.7177 63.8244 83.9586
SCF Energy (M06) = -922.2211138

Reductive Elimination TS RhCOT

Supporting Information: 035-COT-TS-ReductiveElim-Ene.log

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

# b3lyp/gen pseudo=read gfprint gfinput
scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,calcfc,ts,noeigentest) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/ChkBas Freq

---

Pointgroup= C1 Stoichiometry= C19H24ORh(1+) C1[X(C19H24ORh)] #Atoms= 45
Charge = 1 Multiplicity = 1

SCF Energy= -922.834789935 Predicted Change= -6.503556D-09

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00002	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00137	0.00180	[YES]	0.00137	0.00180	[YES]

Atomic Type	X	Y	Z
Rh	-0.549676	-0.006106	0.162134
C	1.399192	-1.604145	0.320110
C	0.605902	-1.532894	1.447054
C	0.823389	-0.535394	2.580150
C	0.152021	0.762488	2.161821
C	2.201519	0.774428	-0.022197
C	1.016032	1.358260	0.254581
H	0.370182	-0.916334	3.502472
H	1.890106	-0.387896	2.776843
H	-0.897859	0.841974	2.449566
H	0.672846	1.673391	2.444705
H	-0.091544	-2.348199	1.624168
C	-1.979475	-1.520485	-0.922507
H	-1.378502	-2.407678	-1.110021
C	-2.430523	-0.780896	-2.129228
C	-2.518251	-1.370757	0.342521
H	-2.295076	-2.136894	1.083151
C	-3.619979	-0.439059	0.677564
C	-1.728474	1.407907	-1.203325
H	-1.024493	2.163558	-1.542121
C	-2.251187	1.536519	0.080511
C	-3.499885	0.884580	0.549983
H	-1.917337	2.386237	0.672507
H	-2.826981	-1.378652	-2.948617
C	-2.309684	0.545512	-2.259332
H	-4.539715	-0.881391	1.057715
H	-4.319832	1.548674	0.819948
H	-2.602356	1.040449	-3.183977
C	2.588624	-0.674812	0.178568
H	3.201924	-0.748168	1.091636
C	3.574719	-0.851248	-0.998659
H	4.288260	-1.667007	-0.863356
C	3.383186	1.424424	-0.729777
H	3.887875	2.181551	-0.115565
O	4.302859	0.368306	-0.983879
H	3.066779	1.908593	-1.667637
H	3.046010	-0.987738	-1.955104
C	0.869109	2.858233	0.117527
H	1.025507	3.172996	-0.922943
H	-0.107070	3.232830	0.430960
H	1.620267	3.381421	0.722628
C	1.289349	-2.763273	-0.636347
H	1.187893	-2.435511	-1.676440
H	2.208579	-3.362031	-0.581737
H	0.453572	-3.422192	-0.387872

Statistical Thermodynamic Analysis

Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -922.834789935 Predicted Change= -6.503556D-09
Zero-point correction (ZPE)= -922.4521 0.38260
Internal Energy (U)= -922.4317 0.40306
Enthalpy (H)= -922.4307 0.40400
Gibbs Free Energy (G)= -922.4992 0.33558

Frequencies -- -348.0643 44.4661 59.1036
SCF Energy (M06) = -922.2104806

Product-Catalyst Complex RhCOT

Supporting Information: 040-COT-Product-Complex-Ene-Boat2.log

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

# b3lyp/gen pseudo=read gfprint gfinput
scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/ChkBas Freq

Pointgroup= C1 Stoichiometry= C19H24ORh(1+) C1[X(C19H24ORh)] #Atoms= 45
Charge = 1 Multiplicity = 1

SCF Energy= -922.911959486 Predicted Change= -1.809687D-07

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00004	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00233	0.00180	[NO]	0.00233	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	1.238907	-1.394492	0.981526
C	0.739000	-0.657721	2.047246
C	1.440812	0.571122	2.603523
C	1.291824	1.845503	1.759474
C	1.828618	0.582780	-0.429274
C	1.360129	1.684208	0.251076
H	1.058922	0.775833	3.607451
H	2.505469	0.329218	2.725987
H	0.339239	2.331138	2.003479
H	2.068137	2.571926	2.046470
H	0.063931	-1.174073	2.727766
C	2.330633	-0.758352	0.135290
H	3.240542	-0.605474	0.737134
C	2.725789	-1.497495	-1.164310
H	3.541125	-2.211400	-1.034541
C	2.263127	0.604673	-1.899372
H	2.791439	1.524223	-2.167329
O	3.175827	-0.469475	-2.028808
H	1.413068	0.484428	-2.590527
H	1.859447	-2.016448	-1.602502
C	1.167685	2.991966	-0.489024
H	0.380320	3.599284	-0.031585
H	2.095914	3.577178	-0.422144
H	0.939346	2.865538	-1.550031
C	0.985799	-2.877040	0.858349
H	1.919103	-3.406785	1.097987
H	0.231927	-3.218577	1.572255
H	0.691092	-3.188487	-0.147433
Rh	-0.434279	-0.004167	0.181746
C	-1.527916	0.375400	-1.841815
C	-1.852145	1.416285	-0.987262
C	-2.073420	-1.542793	0.293471
C	-2.390737	-0.497262	1.166503
C	-2.367902	-0.826518	-2.054528
H	-0.741607	0.554265	-2.573986
H	-1.313261	2.352658	-1.111851
C	-3.078995	1.477430	-0.155690
H	-1.653303	-2.443015	0.736012
C	-2.624621	-1.699417	-1.074705
H	-2.195575	-0.654067	2.226435
C	-3.318070	0.611828	0.835844
H	-2.746560	-0.990230	-3.062244
H	-3.764647	2.300380	-0.351220
H	-3.218675	-2.591660	-1.266758
H	-4.200544	0.716862	1.465142

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -922.911959486 Predicted Change= -1.809687D-07
Zero-point correction (ZPE)= -922.5265 0.38544
Internal Energy (U)= -922.5058 0.40610
Enthalpy (H)= -922.5049 0.40705
Gibbs Free Energy (G)= -922.5743 0.33762

Frequencies -- 23.0851 57.0532 75.2880
SCF Energy (M06) = -922.2913007

10. RhdnCOT

10.a. Additional Figures

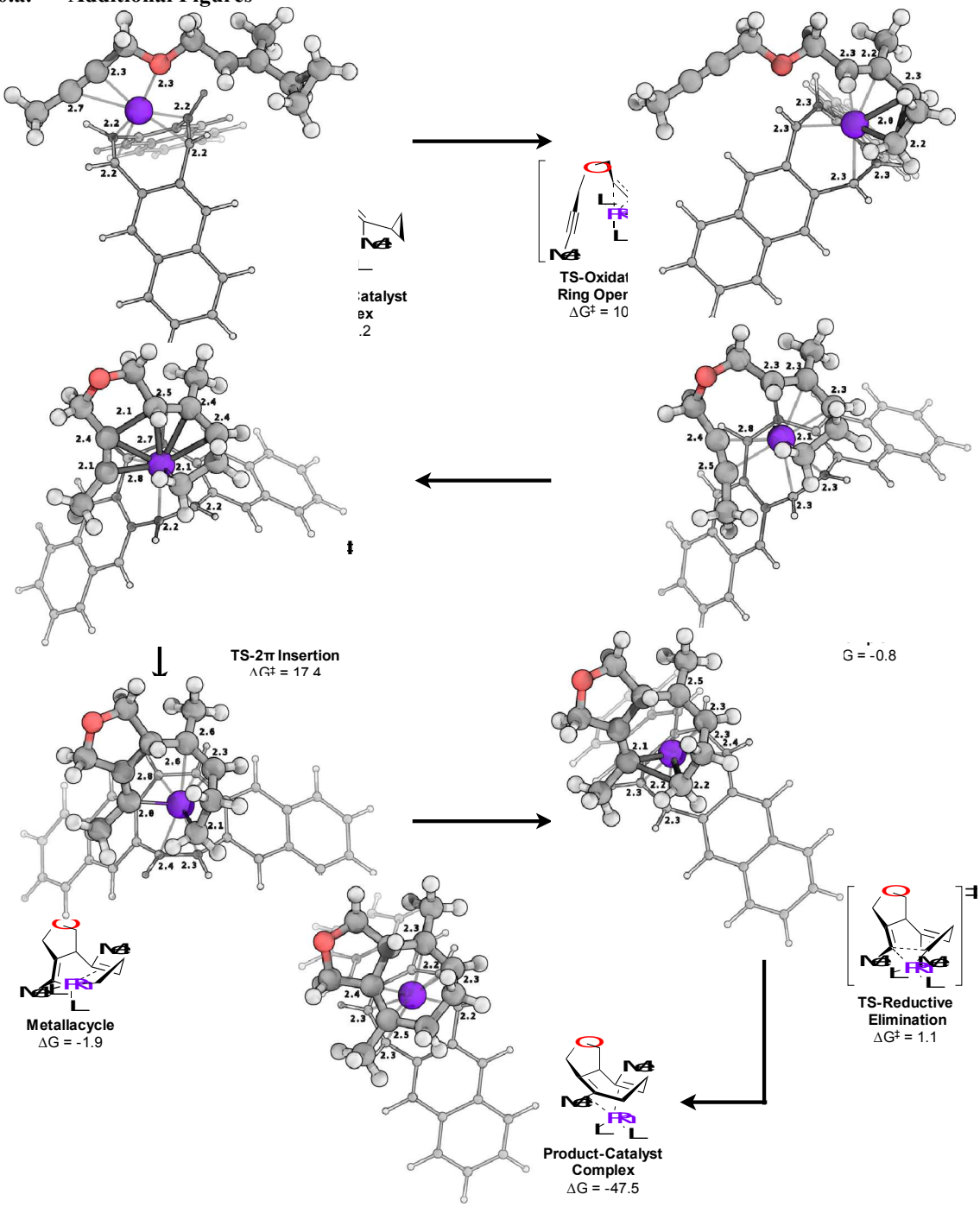

Figure S15. Computed geometries for RhdnCOT.

Substrate-Catalyst Complex RhdnCOT

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

# b3lyp/gen pseudo=read gfprint gfinput
scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/ChkBas Freq

Pointgroup= C1 Stoichiometry= C35H32ORh(1+) C1[X(C35H32ORh)] #Atoms= 69
Charge = 1 Multiplicity = 1

SCF Energy= -1537.43332309 Predicted Change= -1.436827D-08

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00374	0.00180	[NO]	0.00374	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-3.973396	-0.176332	-2.179885
C	-3.910920	0.823315	-3.290017
C	-5.196365	1.341138	-3.923901
C	-4.298756	2.276344	-3.160366

C	-2.381884	-0.727229	3.396131
C	-1.439552	-0.594462	4.161405
C	-4.103110	0.202085	-0.893269
C	-4.295112	-0.685933	0.287251
C	-3.614548	-0.875077	2.609068
O	-3.281056	-0.385855	1.301059
C	-0.412135	-0.464285	5.190340
C	-3.917921	-1.607452	-2.661556
H	-5.238661	1.413705	-5.006640
H	-6.133066	1.053793	-3.454048
H	-3.711155	2.999182	-3.718978
H	-4.658001	2.648940	-2.205789
H	-3.119970	0.610805	-4.009258
H	-4.141230	1.263880	-0.659958
H	-5.262321	-0.485191	0.769738
H	-3.920576	-1.928753	2.559639
H	-4.241393	-1.753175	0.052819
H	-4.438171	-0.287580	3.036206
H	-0.789970	-0.882908	6.130476
H	0.500628	-1.010159	4.928197
H	-0.156185	0.586061	5.366749
H	-4.796581	-1.830840	-3.279360
H	-3.043164	-1.755638	-3.307591
H	-3.873990	-2.349015	-1.860312
Rh	-1.032660	-0.277166	1.525647
C	0.987939	-0.967540	1.848165
C	0.941300	0.435413	2.045731
C	-0.481725	-0.671734	-0.535182
C	-0.538119	0.726617	-0.340748
C	1.500444	-1.640149	0.624920
C	1.390848	1.456608	1.061648
C	0.762817	-1.484979	-0.581348
C	0.642116	1.606843	-0.138731
C	1.168872	-2.135371	-1.727078
C	2.341910	-2.936700	-1.738343
C	3.083684	-3.094703	-0.521149
C	2.620857	-2.443287	0.652988
C	2.792350	-3.601434	-2.909659
C	3.926245	-4.382746	-2.880612
C	4.658856	-4.538980	-1.677923
C	4.245731	-3.911120	-0.523859
C	0.980706	2.588394	-1.046000
C	2.098320	3.436634	-0.824651
C	2.853000	3.285325	0.385378
C	2.456549	2.292411	1.320498
C	2.480502	4.441178	-1.752929
C	3.561765	5.255666	-1.499101
C	4.307150	5.106255	-0.303406
C	3.959213	4.144584	0.619110
H	0.990161	-1.585027	2.746797
H	0.923070	0.776991	3.080323
H	-1.359034	-1.119594	-1.001582
H	-1.451132	1.217353	-0.676706
H	0.590327	-2.041509	-2.643597
H	3.168512	-2.587391	1.581902
H	2.229218	-3.481732	-3.831741
H	4.264397	-4.883915	-3.782809
H	5.550891	-5.158379	-1.670538
H	4.806392	-4.030975	0.399675
H	0.390344	2.724377	-1.949473
H	3.011160	2.200324	2.251966
H	1.906907	4.555837	-2.669182
H	3.848149	6.018587	-2.217028
H	5.157154	5.756075	-0.117225
H	4.529645	4.029389	1.537236

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -1537.43332309 Predicted Change= -1.436827D-08
Zero-point correction (ZPE)= -1536.8646 0.56868
Internal Energy (U)= -1536.8306 0.60270
Enthalpy (H)= -1536.8296 0.60365
Gibbs Free Energy (G)= -1536.9333 0.50001

Frequencies -- 13.3944 21.1444 22.3200
SCF Energy (M06) = -1536.322608

Oxidative-Addition TS RhdnCOT

Using Gaussian 03: AM64L-G03RevE.01 11-Sep-2007

# b3lyp/gen pseudo=read gfprint gfinput
scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,calcfc,ts,noeigentest) freq=noraman
#N Geom=AllCheck Guess=Read SCRF=Check GenChk RB3LYP/ChkBas Freq

---

Pointgroup= C1 Stoichiometry= C35H32ORh(1+) C1[X(C35H32ORh)] #Atoms= 69
Charge = 1 Multiplicity = 1

SCF Energy= -1537.41546254 Predicted Change= -2.111574D-09

Optimization completed on the basis of negligible forces. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00700	0.00180	[NO]	0.00700	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
Rh	-0.291566	-1.481555	-1.035460
C	-0.257460	-3.640527	-0.448571
C	0.144720	-3.628441	-1.839071
C	-0.749420	-3.808694	-3.023663
C	-0.691564	-2.307054	-3.050429
C	-4.817332	-0.991488	2.460525
C	-5.592122	-0.063952	2.495116
C	-1.539256	-3.169159	-0.136038
C	-2.149332	-3.146348	1.238284
C	-3.908451	-2.128349	2.457260
O	-3.092405	-2.095202	1.275632
C	-6.534279	1.050932	2.532878
C	0.745040	-4.141872	0.563287
H	-0.288029	-4.323907	-3.865634
H	-1.727881	-4.231465	-2.795815
H	0.021165	-1.881920	-3.750866
H	-1.651470	-1.782405	-2.989110
H	1.211062	-3.706653	-2.034319
H	-2.294709	-3.124927	-0.920284
H	-2.649463	-4.117002	1.414107
H	-3.263514	-2.109701	3.351490
H	-1.397148	-3.030890	2.034081
H	-4.470859	-3.075644	2.483325
H	-6.501564	1.622163	1.597639
H	-7.561720	0.693630	2.668153
H	-6.306602	1.738883	3.355440
H	0.678949	-5.236144	0.624580
H	1.767674	-3.885567	0.271691
H	0.563427	-3.748295	1.565169
C	-0.707313	0.075827	0.602205
C	-0.729957	1.397031	-0.077433
C	0.430513	-0.611387	1.002035
C	1.845402	-0.194282	0.829649
C	0.456214	0.392938	-2.072488
C	1.586001	-0.326452	-1.682593
C	2.412036	-0.085740	-0.476063
C	-0.151941	1.555810	-1.371875
C	-0.240837	2.774346	-2.016287
C	-0.853615	3.896390	-1.400676
C	-1.436725	3.735186	-0.101206
C	-1.376425	2.460829	0.519824
C	-0.926691	5.164244	-2.036810
C	-1.544245	6.225431	-1.413061
C	-2.120617	6.066107	-0.127986
C	-2.070365	4.848123	0.512711
C	2.647102	-0.007974	1.938490
C	4.019505	0.333097	1.816845
C	4.589819	0.432701	0.505714
C	3.757975	0.193419	-0.618233
C	4.849007	0.554293	2.947964
C	6.181501	0.864352	2.788240
C	6.745565	0.962269	1.491740
C	5.968256	0.749047	0.375040
H	-1.649921	-0.249065	1.040508
H	0.273896	-1.399137	1.736522
H	0.183266	0.309123	-3.123862
H	2.070160	-0.912632	-2.463326
H	0.167665	2.888454	-3.018111
H	-1.850486	2.328522	1.489703
H	-0.485155	5.284787	-3.022743
H	-1.592144	7.192319	-1.905275
H	-2.603653	6.912896	0.350709
H	-2.512016	4.724246	1.498186
H	2.225688	-0.122097	2.935004
H	4.198242	0.243121	-1.611869
H	4.415581	0.478488	3.941887
H	6.807659	1.036233	3.658736
H	7.797770	1.207935	1.382819
H	6.399576	0.824343	-0.619852

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -1537.41546254 Predicted Change= -2.111574D-09
Zero-point correction (ZPE)= -1536.8484 0.56698
Internal Energy (U)= -1536.8149 0.60051
Enthalpy (H)= -1536.8140 0.60146
Gibbs Free Energy (G)= -1536.9163 0.49913

Frequencies -- -226.1564 12.9518 18.3679
SCF Energy (M06) = -1536.309758

Alkyne Coordination Complex RhdnCOT

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

# b3lyp/gen pseudo=read gfprint gfinput
scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/ChkBas Freq

---

Pointgroup= C1 Stoichiometry= C35H32ORh(1+) C1[X(C35H32ORh)] #Atoms= 69
Charge = 1 Multiplicity = 1

SCF Energy= -1537.43419288 Predicted Change= -1.865573D-07

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00002	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00489	0.00180	[NO]	0.00489	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	2.088079	-2.781175	0.299609
C	2.254448	-2.239352	-0.997948
C	1.781005	-2.951944	-2.265700
C	0.262899	-2.816537	-2.208353
C	-1.782771	-2.864385	0.474326
C	-2.247360	-2.378303	-0.559017
C	1.005423	-3.676547	0.486516
C	0.565994	-4.206244	1.828861
C	-1.717776	-3.600372	1.761586
O	-0.779508	-4.653663	1.795734
C	-3.123406	-2.051612	-1.689339
C	2.971783	-2.301491	1.426533
Rh	0.127659	-1.760627	-0.428291
H	2.203905	-2.455422	-3.143633
H	2.125184	-3.993394	-2.284162
H	-0.156570	-2.192068	-3.000009
H	-0.295619	-3.750979	-2.127934
H	2.988468	-1.444397	-1.105999
H	0.739143	-4.347537	-0.325638
H	1.157514	-5.091703	2.092231
H	-1.534291	-2.894752	2.587980

H	0.696574	-3.464432	2.630679
H	-2.694978	-4.065292	1.927447
H	-4.048225	-2.633390	-1.600238
H	-3.386480	-0.989996	-1.699185
H	-2.657472	-2.309908	-2.646547
H	3.841345	-2.969877	1.481412
H	3.343883	-1.289031	1.249995
H	2.484920	-2.335185	2.403581
C	0.676157	0.113791	1.528066
C	-0.678409	0.034421	1.537691
C	0.670307	0.227263	-1.502939
C	-0.719811	0.136038	-1.481253
C	1.535773	1.048780	0.762057
C	-1.642053	0.870517	0.787238
C	1.537680	1.093413	-0.668112
C	-1.655362	0.923058	-0.639588
C	-2.588339	1.580969	1.502604
C	-3.547184	2.410334	0.866846
C	-3.556033	2.471861	-0.563752
C	-2.610000	1.694615	-1.280132
C	-4.501056	3.168192	1.596577
C	-5.418862	3.955929	0.937647
C	-5.427117	4.017345	-0.478362
C	-4.518088	3.289564	-1.213959
C	2.424233	1.932435	-1.319949
C	3.306095	2.791806	-0.616626
C	3.306429	2.746476	0.814362
C	2.423282	1.845143	1.463354
C	4.198529	3.674121	-1.280906
C	5.050121	4.479909	-0.557791
C	5.050454	4.435475	0.858700
C	4.199350	3.586126	1.531129
H	1.190189	-0.454592	2.300359
H	-1.118665	-0.598972	2.306989
H	1.134411	-0.085668	-2.436439
H	-1.163704	-0.239675	-2.400666
H	-2.597322	1.517452	2.588636
H	-2.636555	1.720997	-2.367847
H	-4.492989	3.120855	2.682450
H	-6.142243	4.536243	1.502705
H	-6.156396	4.644497	-0.982553
H	-4.523334	3.336489	-2.299958
H	2.448183	1.945758	-2.407774
H	2.445641	1.791507	2.549791
H	4.196842	3.707085	-2.367374
H	5.726941	5.155614	-1.072258
H	5.727734	5.077718	1.413823
H	4.198898	3.551825	2.617518

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -1537.43419288 Predicted Change= -1.865573D-07
Zero-point correction (ZPE)= -1536.8638 0.57036
Internal Energy (U)= -1536.8312 0.60293
Enthalpy (H)= -1536.8303 0.60387
Gibbs Free Energy (G)= -1536.9257 0.50848

Frequencies -- 21.6814 33.0368 47.6321
SCF Energy (M06) = -1536.337561

2π-Insertion TS RhdnCOT

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

# b3lyp/gen pseudo=read gfprint gfinput
scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,calcfc,ts,noeigentest) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/ChkBas Freq

---

Pointgroup= C1 Stoichiometry= C35H32ORh(1+) C1[X(C35H32ORh)] #Atoms= 69
Charge = 1 Multiplicity = 1

SCF Energy= -1537.41075495 Predicted Change= -3.933960D-09

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00069	0.00180	[YES]	0.00069	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	3.069367	-1.642731	-0.324795
C	2.611016	-2.162652	0.875807
C	3.004579	-1.644938	2.254820
C	2.591433	-0.171805	2.311583
C	3.227564	1.542432	-0.342416
C	2.255171	1.986070	0.368340
C	3.880366	-0.409122	-0.331352
C	4.780735	-0.154834	-1.538030
C	4.244423	2.032647	-1.337329
O	5.325607	1.137219	-1.429272
C	1.747371	3.265955	0.924978
C	2.823709	-2.396121	-1.615295
Rh	1.599698	0.003219	0.496610
C	-0.118299	-0.638226	-1.542718
C	-0.152864	0.717695	-1.538892
C	-0.235668	-0.692512	1.481154
C	-0.250791	0.721425	1.463854
C	-0.994461	-1.576937	-0.797859
C	-1.091667	1.584562	-0.789186
C	-1.035335	-1.609642	0.632898
C	-1.139998	1.579329	0.637761
C	-1.900423	2.455369	-1.495236
C	-2.822655	3.316709	-0.846748
C	-2.877223	3.307205	0.584307
C	-2.002892	2.441581	1.290303
C	-3.677754	4.194484	-1.564394
C	-4.550745	5.022277	-0.893626
C	-4.604450	5.013111	0.522631
C	-3.784269	4.176368	1.246682
C	-1.722809	-2.505989	-1.516658
C	-2.553452	-3.467624	-0.885079
C	-2.594000	-3.501125	0.545990
C	-1.801814	-2.572510	1.266859
C	-3.325856	-4.405499	-1.619417
C	-4.106842	-5.332350	-0.964402
C	-4.146746	-5.365874	0.451898
C	-3.404962	-4.471921	1.191910
H	2.476100	-2.231305	3.011570
H	4.078263	-1.797191	2.434984
H	1.905206	0.059115	3.128516
H	3.419703	0.539829	2.326456
H	2.031255	-3.081934	0.826654
H	4.435632	-0.248411	0.590172
H	5.617367	-0.861334	-1.518982
H	3.759759	2.154726	-2.320810
H	4.238336	-0.277204	-2.486780
H	4.632760	3.003748	-1.015248
H	2.404176	4.094490	0.635150
H	0.732896	3.479814	0.579949
H	1.722392	3.223565	2.020335
H	3.728101	-2.953115	-1.893295
H	2.013030	-3.119659	-1.498148
H	2.582117	-1.739360	-2.454701
H	0.514616	-1.100268	-2.297025
H	0.473712	1.223886	-2.273029
H	0.058246	-1.135169	2.431599
H	0.048328	1.188268	2.401130
H	-1.842700	2.480058	-2.581294
H	-2.020900	2.462886	2.378065
H	-3.635774	4.200533	-2.650516
H	-5.204633	5.687664	-1.449578
H	-5.298988	5.671421	1.036087
H	-3.824451	4.168346	2.332896
H	-1.669044	-2.502650	-2.603294
H	-1.809550	-2.620798	2.353901
H	-3.294925	-4.379124	-2.705604
H	-4.697972	-6.043898	-1.533299
H	-4.768142	-6.102416	0.952599
H	-3.434748	-4.495969	2.278222

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -1537.41075495 Predicted Change= -3.933960D-09
Zero-point correction (ZPE)= -1536.8400 0.57065
Internal Energy (U)= -1536.8087 0.60199
Enthalpy (H)= -1536.8078 0.60294
Gibbs Free Energy (G)= -1536.9008 0.50988

Frequencies -- -233.9919 20.8584 28.7426
SCF Energy (M06) = -1536.309851

Metallacycle RhdnCOT

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

# b3lyp/gen pseudo=read gfprint gfinput
scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/ChkBas Freq

---

Pointgroup= C1 Stoichiometry= C35H32ORh(1+) C1[X(C35H32ORh)] #Atoms= 69
Charge = 1 Multiplicity = 1

SCF Energy= -1537.44782399 Predicted Change= -3.002060D-08

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00185	0.00180	[NO]	0.00185	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-2.045896	-2.820318	0.926355
C	-1.194210	-3.353062	-0.013818
C	-1.529022	-3.630481	-1.474333
C	-1.086335	-2.350219	-2.179273
C	-3.624971	-1.170355	-0.178145
C	-2.670301	-0.463325	-0.790323
C	-3.476583	-2.484760	0.558141
C	-4.539363	-2.298220	1.662140
C	-5.080476	-0.743484	0.044067
O	-5.616966	-1.694743	0.961237
C	-2.965147	0.764237	-1.606076
C	-1.657407	-2.772426	2.382424
Rh	-0.756727	-1.132799	-0.525614
C	0.715934	-0.337895	1.482588
C	-0.143833	0.714020	1.485444
C	1.007680	-0.164653	-1.604158
C	0.093282	0.875323	-1.555940
C	1.987239	-0.550565	0.747633
C	-0.059731	1.991700	0.752369
C	2.100312	-0.522812	-0.687179
C	0.046745	2.059332	-0.669728
C	0.040224	3.297884	-1.291203
C	-0.003954	4.509981	-0.558183
C	-0.110696	4.441292	0.868178
C	-0.164427	3.163570	1.480505
C	0.026934	5.781597	-1.189406
C	-0.038412	6.934219	-0.438060
C	-0.143587	6.866434	0.973699
C	-0.181917	5.647180	1.613999
C	3.085258	-0.948341	1.492358
C	4.331890	-1.273429	0.904543
C	4.437626	-1.264681	-0.525687
C	3.295290	-0.921237	-1.280074
C	5.467430	-1.634034	1.676926
C	6.652566	-1.966083	1.059085
C	6.757165	-1.958607	-0.356129
C	5.674101	-1.617709	-1.133089
H	-0.985049	-4.515053	-1.823227

H	-2.596300	-3.822445	-1.611650
H	-0.123446	-2.449573	-2.687590
H	-1.828075	-1.917473	-2.852729
H	-0.214056	-3.686741	0.331666
H	-3.867029	-3.281201	-0.092741
H	-4.905501	-3.233310	2.093281
H	-5.688482	-0.777749	-0.867797
H	-5.136406	0.273253	0.460017
H	-4.175670	-1.646767	2.472127
H	-4.043522	0.964243	-1.603329
H	-2.460074	1.660089	-1.235536
H	-2.677262	0.623576	-2.655384
H	-1.828913	-1.785516	2.824942
H	-2.278914	-3.481094	2.946003
H	-0.612783	-3.056320	2.535575
H	0.537763	-1.082471	2.255800
H	-0.930532	0.673334	2.238383
H	1.079159	-0.656159	-2.571901
H	-0.446621	1.014856	-2.488327
H	0.076758	3.352582	-2.377155
H	-0.284329	3.111534	2.560415
H	0.106057	5.831998	-2.272254
H	-0.009733	7.903628	-0.926588
H	-0.194324	7.784881	1.550876
H	-0.263943	5.594426	2.696446
H	2.994500	-1.008727	2.574561
H	3.366507	-0.942106	-2.365270
H	5.388760	-1.641084	2.760715
H	7.518061	-2.237185	1.656293
H	7.700508	-2.223931	-0.823714
H	5.750872	-1.610042	-2.217096

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -1537.44782399 Predicted Change= -3.002060D-08
Zero-point correction (ZPE)= -1536.8753 0.57246
Internal Energy (U)= -1536.8435 0.60426
Enthalpy (H)= -1536.8426 0.60520
Gibbs Free Energy (G)= -1536.9379 0.50984

Frequencies -- 18.8989 23.8572 26.8118
SCF Energy (M06) = -1536.340605

Reductive Elimination TS RhdnCOT

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

# b3lyp/gen pseudo=read gfprint gfinput
scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,calcfc,ts,noeigentest) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/ChkBas Freq

Pointgroup= C1 Stoichiometry= C35H32ORh(1+) C1[X(C35H32ORh)] #Atoms= 69
Charge = 1 Multiplicity = 1

SCF Energy= -1537.43660713 Predicted Change= -4.854606D-09

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00094	0.00180	[YES]	0.00094	0.00180	[YES]

Atomic Type	X	Y	Z
C	3.186012	-0.878048	-1.599188
C	2.351998	-1.973169	-1.660367
C	2.470994	-3.190654	-0.750439
C	1.752253	-2.852901	0.548300
C	3.883851	-0.760668	0.838204
C	2.665465	-1.038664	1.347649
C	4.331607	-0.858449	-0.605288
C	5.364029	0.289878	-0.640870
C	5.059195	-0.156405	1.594857
O	6.034655	0.151964	0.604395
C	2.462443	-1.024949	2.847737
C	3.164535	0.178562	-2.674479
Rh	1.170107	-0.771018	-0.066016
C	-0.034336	0.489535	1.414479
C	-0.602142	-0.783648	1.377330
C	-0.131473	0.510577	-1.521728
C	-0.727873	-0.738019	-1.551626
C	-0.497997	1.691366	0.686917
C	-1.836938	-1.197626	0.661581
C	-0.575373	1.695193	-0.737178
C	-1.896316	-1.184251	-0.761831
C	-2.909813	-1.677666	1.386473
C	-4.100885	-2.114773	0.749250
C	-4.159573	-2.102347	-0.682724
C	-3.024843	-1.652682	-1.406460
C	-5.222934	-2.584248	1.481298
C	-6.354701	-3.016281	0.825194
C	-6.413039	-3.003478	-0.590473
C	-5.338578	-2.559020	-1.329018
C	-0.964176	2.845210	-1.394016
C	-1.334055	4.019017	-0.685693
C	-1.246974	4.016451	0.745214
C	-0.798936	2.839373	1.396297
C	-1.763553	5.199533	-1.346968
C	-2.096027	6.324358	-0.624400
C	-2.009295	6.321961	0.790202
C	-1.591962	5.193965	1.460842
H	2.001354	-4.057836	-1.228670
H	3.520509	-3.445830	-0.570413
H	0.691559	-3.111383	0.557777
H	2.221488	-3.231918	1.452423
H	1.684277	-2.051292	-2.514741
H	4.916061	-1.785646	-0.723863
H	6.110732	0.194411	-1.432475
H	5.508643	-0.850904	2.316848
H	4.754608	0.748704	2.144272
H	4.874571	1.273064	-0.722279
H	3.171830	-1.697837	3.346091
H	2.638645	-0.020266	3.255106
H	1.461490	-1.333269	3.154918
H	3.068730	1.188872	-2.262435
H	4.112418	0.150148	-3.228537
H	2.357668	0.012360	-3.392786
H	0.621818	0.695111	2.256082
H	-0.324867	-1.444591	2.196068
H	0.524792	0.742431	-2.357656
H	-0.468920	-1.377100	-2.394268
H	-2.853601	-1.724400	2.471977
H	-3.057155	-1.675039	-2.493651
H	-5.177211	-2.594627	2.567213
H	-7.210267	-3.369646	1.393037
H	-7.312678	-3.347016	-1.092373
H	-5.381621	-2.549442	-2.415030
H	-0.991522	2.863560	-2.481372
H	-0.703802	2.846395	2.480023
H	-1.828675	5.201938	-2.431924
H	-2.427077	7.221854	-1.138473
H	-2.274801	7.217230	1.344519
H	-1.524571	5.189878	2.545674

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -1537.43660713 Predicted Change= -4.854606D-09
Zero-point correction (ZPE)= -1536.8650 0.57159
Internal Energy (U)= -1536.8340 0.60255
Enthalpy (H)= -1536.8331 0.60349
Gibbs Free Energy (G)= -1536.9257 0.51088

Frequencies -- -333.1046 20.5632 28.7384
SCF Energy (M06) = -1536.336923

Product-Catalyst Complex RhdnCOT

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

# b3lyp/gen pseudo=read gfprint gfinput
scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/ChkBas Freq

Pointgroup= C1 Stoichiometry= C35H32ORh(1+) C1[X(C35H32ORh)] #Atoms= 69
Charge = 1 Multiplicity = 1

SCF Energy= -1537.51325222 Predicted Change= -9.269183D-08

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00239	0.00180	[NO]	0.00239	0.00180	[YES]

Atomic Type	X	Y	Z
C	3.203879	-0.068157	-1.507528
C	2.680256	-1.268230	-1.965315
C	3.232743	-2.622881	-1.548549
C	2.838910	-3.081670	-0.136792
C	3.430873	-0.784562	0.884903
C	2.853410	-2.030530	0.959539
C	4.139108	-0.116883	-0.308802
C	4.547587	1.239204	0.310943
C	3.775537	0.074213	2.106926
O	4.808440	0.939699	1.671194
C	2.431496	-2.580766	2.306701
C	3.138019	1.192205	-2.335566
H	2.895226	-3.379829	-2.262114
H	4.327521	-2.589693	-1.635740
H	1.835192	-3.523594	-0.166844
H	3.504696	-3.898410	0.183811
H	2.129621	-1.239598	-2.903952
H	5.057316	-0.669061	-0.564850
H	5.455368	1.664765	-0.120876
H	4.168124	-0.518105	2.938597
H	2.909760	0.648719	2.474297
H	3.732011	1.973722	0.228204
H	1.578374	-3.259782	2.210035
H	3.258996	-3.168808	2.728592
H	2.176953	-1.805967	3.033726
H	4.149999	1.428125	-2.694949
H	2.506044	1.059020	-3.217216
H	2.784227	2.062998	-1.776588
Rh	1.302942	-0.547287	-0.261647
C	0.080314	0.575986	1.360340
C	-0.332860	-0.748869	1.347228
C	-0.105346	0.642261	-1.545259
C	-0.514100	-0.695916	-1.567987
C	-0.575387	1.720203	0.685421
C	-1.524926	-1.309392	0.660060
C	-0.681792	1.744731	-0.735589
C	-1.599799	-1.304716	-0.764425
C	-2.516769	-1.928595	1.394310
C	-3.641457	-2.526229	0.767636
C	-3.711864	-2.528475	-0.664375
C	-2.657201	-1.928387	-1.398821
C	-4.684560	-3.140505	1.509793
C	-5.750827	-3.726478	0.864163
C	-5.820078	-3.729428	-0.551460
C	-4.822169	-3.145749	-1.299712
C	-1.238066	2.843480	-1.360486
C	-1.754777	3.936871	-0.617630
C	-1.643115	3.912974	0.811562
C	-1.023549	2.795241	1.428084
C	-2.355912	5.060931	-1.243347
C	-2.829620	6.111204	-0.488654
C	-2.719049	6.087704	0.924081
C	-2.136871	5.014047	1.560499
H	0.796818	0.843254	2.136223
H	0.082064	-1.380620	2.129160

H	0.447424	0.973495	-2.421470
H	-0.229059	-1.263306	-2.453049
H	-2.446007	-1.962847	2.479359
H	-2.696086	-1.956811	-2.485657
H	-4.630349	-3.138735	2.595367
H	-6.546104	-4.190673	1.439845
H	-6.667548	-4.195787	-1.045025
H	-4.873929	-3.147256	-2.385404
H	-1.288782	2.881257	-2.446606
H	-0.910700	2.792110	2.510058
H	-2.439350	5.078630	-2.326940
H	-3.291547	6.965103	-0.975293
H	-3.097390	6.923829	1.504641
H	-2.051054	4.995156	2.643857

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -1537.51325222 Predicted Change= -9.269183D-08
Zero-point correction (ZPE)= -1536.9385 0.57469
Internal Energy (U)= -1536.9075 0.60571
Enthalpy (H)= -1536.9065 0.60666
Gibbs Free Energy (G)= -1536.9993 0.51386

Frequencies -- 20.1360 24.3004 32.8143
SCF Energy (M06) = -1536.417344

11. RhNHC-H_2

11.a. Additional Figures

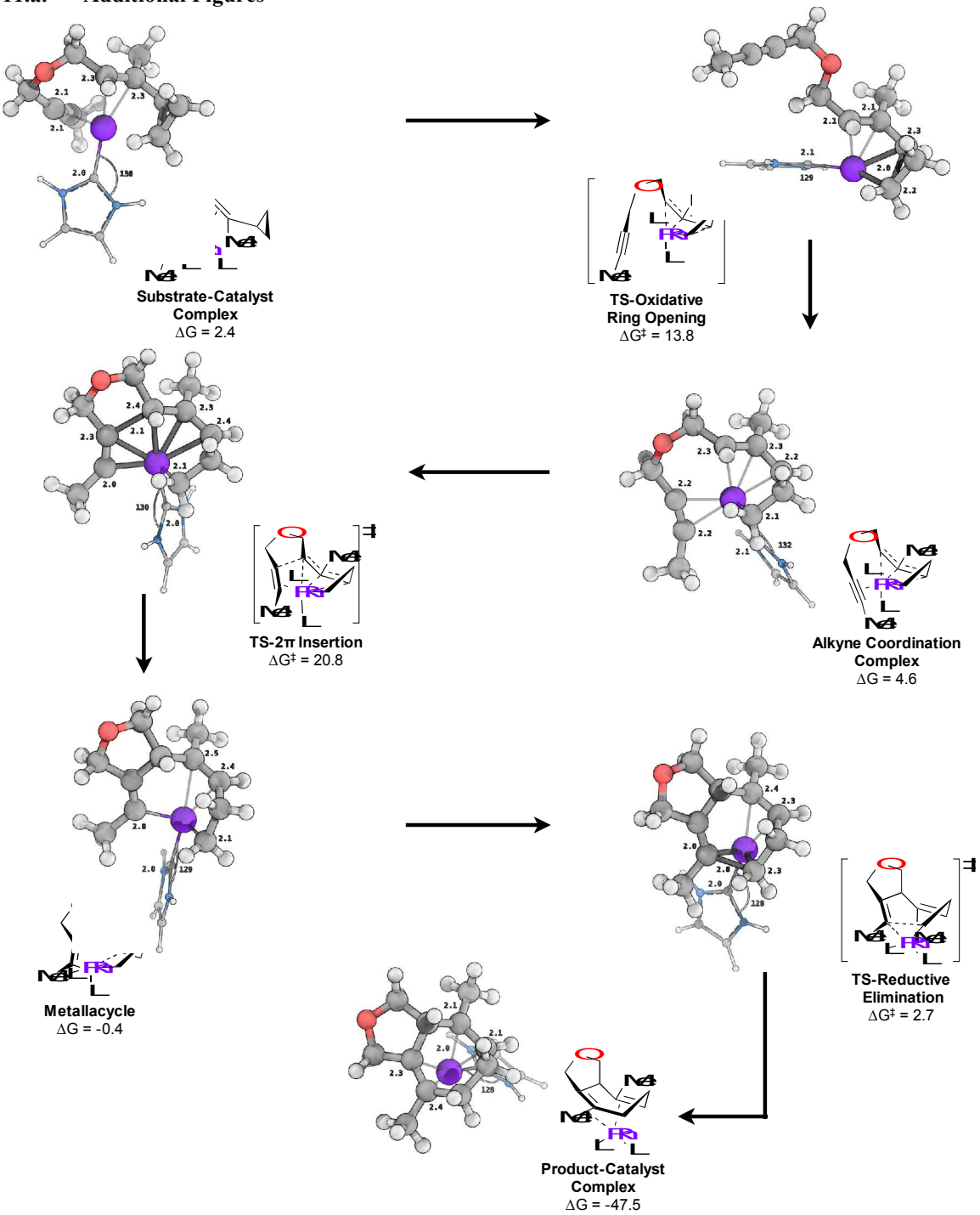

Figure S16. Computed geometries for RhNHC-H_2.

Substrate-Catalyst Complex RhNHC-H2

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

opt=maxcycle=250 freq=noraman b3lyp/gen geom=connectivity gfinput
gfprint pseudo=read scf=(direct,tight,maxcycle=300,xqc)
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/ChkBas Freq

Pointgroup= C1 Stoichiometry= C14H20N2ORh(1+) C1[X(C14H20N2ORh)] #Atoms= 38

Charge = 1 Multiplicity = 1

SCF Energy= -839.463890959 Predicted Change= -2.970332D-08

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00201	0.00180	[NO]	0.00201	0.00180	[YES]

Atomic Coordinates (Angstroms)

Type	X	Y	Z
Rh	-0.015556	0.169472	-0.034533
C	2.091257	0.787603	0.555541
C	1.611412	2.205027	0.473807
C	1.970036	3.156037	-0.625021
C	0.555027	2.637164	-0.627759
C	0.122647	-1.937616	-0.071452
C	-0.285338	-1.634135	1.080854
H	2.114946	4.197116	-0.353439
H	2.633335	2.796306	-1.406165
H	-0.232883	3.316109	-0.318935
H	0.292873	1.992581	-1.473562
H	1.421367	2.660791	1.441179
C	2.202047	0.030783	-0.598502
H	2.086859	0.522759	-1.565392
C	2.761928	-1.363762	-0.752149
H	3.754761	-1.310124	-1.212977
C	0.849071	-2.766841	-1.074276
H	1.175751	-3.689405	-0.566301
O	1.959540	-2.109383	-1.663991
H	2.866754	-1.889334	0.205112
H	0.198472	-3.051393	-1.906402
C	-0.802989	-1.825836	2.447239
H	-0.788370	-2.890826	2.709395
H	-0.197632	-1.282317	3.179966
H	-1.833282	-1.462970	2.536178
C	2.572252	0.344511	1.916233
H	3.559093	0.782428	2.119568
H	1.895218	0.690388	2.704837
H	2.667923	-0.739885	1.994975
C	-2.047927	0.257910	-0.146086
N	-2.898488	-0.746313	-0.474500
N	-2.878447	1.321364	0.022222
C	-4.220444	-0.329238	-0.517249
C	-4.209353	0.990288	-0.196938
H	-5.034424	-0.989795	-0.771240
H	-5.011050	1.706510	-0.109389
H	-2.570551	-1.685162	-0.655639
H	-2.554652	2.238304	0.294636

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -839.463890959 Predicted Change= -2.970332D-08
Zero-point correction (ZPE)= -839.1440 0.31983
Internal Energy (U)= -839.1243 0.33954
Enthalpy (H)= -839.1234 0.34049
Gibbs Free Energy (G)= -839.1925 0.27138

Frequencies -- 30.8383 47.0309 65.9560
SCF Energy (M06) = -838.9275505

Oxidative-Addition TS RhNHC-H2

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

# b3lyp/gen pseudo=read gfprint gfinput
scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,calcfc,ts,noeigentest) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/ChkBas Freq

Pointgroup= C1 Stoichiometry= C14H20N2ORh(1+) C1[X(C14H20N2ORh)] #Atoms= 38
Charge = 1 Multiplicity = 1

SCF Energy= -839.426481449 Predicted Change= -2.496024D-09

Optimization completed on the basis of negligible forces. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00210	0.00180	[NO]	0.00210	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	4.968385	-0.325610	-0.575050
Rh	-1.677110	-0.016580	-0.477266
C	4.261056	-0.669217	0.345340
C	3.425222	-1.091817	1.472277
C	1.319032	-0.457058	0.544866
C	0.060201	-1.112330	0.030669
C	-1.028503	-1.470289	0.902591
C	-2.151995	-2.120507	0.272171
C	-2.135948	-3.023194	-0.927175
C	-2.410833	-1.739422	-1.656229
H	-3.461534	-1.530086	-1.857585
H	-1.723971	-1.477602	-2.465650
H	-2.924055	-3.775877	-0.934022
H	-1.168269	-3.476393	-1.142653
H	0.256174	-1.757111	-0.826776
H	3.364654	-0.287688	2.223770
H	3.856995	-1.969711	1.962827
H	1.105381	0.315040	1.299178
H	1.852100	0.026189	-0.287560
H	-3.091184	-2.088265	0.821181
O	2.103110	-1.499321	1.095219
C	5.851011	0.065805	-1.671309
H	5.562349	-0.426341	-2.607556
H	5.834567	1.149203	-1.838879
H	6.886532	-0.221315	-1.454252
C	-1.040537	-1.235861	2.389797
H	-2.062125	-1.168989	2.775741
H	-0.543443	-2.078536	2.887649
H	-0.499057	-0.327947	2.665601
C	-0.953215	1.895719	-0.058142
N	-1.480124	2.819763	0.790029
N	0.063802	2.578407	-0.648945
C	-0.817570	4.036101	0.731906
C	0.168783	3.882293	-0.190305
H	-1.097254	4.884827	1.336035
H	0.915439	4.572003	-0.551186
H	0.668171	2.163446	-1.344470
H	-2.262654	2.620964	1.397785

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -839.426481449 Predicted Change= -2.496024D-09
Zero-point correction (ZPE)= -839.1088 0.31766
Internal Energy (U)= -839.0885 0.33794
Enthalpy (H)= -839.0875 0.33888
Gibbs Free Energy (G)= -839.1619 0.26457

Frequencies -- -205.3511 17.1268 27.2039
SCF Energy (M06) = -838.8789072

Alkyne Coordination Complex RhNHC-H2

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

opt=maxcycle=250 freq=noraman b3lyp/gen geom=connectivity gfinput
gfprint pseudo=read scf=(direct,tight,maxcycle=300,xqc)
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/ChkBas Freq

Pointgroup= C1 Stoichiometry= C14H20N2ORh(1+) C1[X(C14H20N2ORh)] #Atoms= 38
Charge = 1 Multiplicity = 1

SCF Energy= -839.478084463 Predicted Change= -2.907883D-09

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00053	0.00180	[YES]	0.00053	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.015777	2.188053	0.216430
Rh	-0.070606	-0.031067	0.028501
C	-1.172597	1.881145	-0.025640
C	-2.602666	2.121383	-0.381395
C	-3.380160	-0.123984	-0.464086
C	-2.223118	-0.835592	0.185105
C	-1.397017	-1.819645	-0.411732
C	-0.243393	-2.221662	0.313485
C	-0.121324	-2.062341	1.835100
C	0.059940	-0.558026	2.022291
H	1.027068	-0.242500	2.417664
H	-0.738449	-0.030240	2.546152
H	0.742912	-2.628509	2.195301
H	-1.003625	-2.453354	2.357024
H	-2.312639	-0.836306	1.268608
H	-2.676467	2.215263	-1.477644
H	-2.902682	3.078113	0.058019
H	-4.319467	-0.640578	-0.235144
H	-3.285569	-0.066681	-1.558119
H	0.439841	-2.909065	-0.178485
O	-3.534261	1.176743	0.094063
C	1.151069	3.070970	0.548495
H	1.561432	2.824502	1.533944
H	1.962745	2.983545	-0.180354
H	0.818455	4.114773	0.570261
C	-1.571366	-2.259970	-1.847959
H	-0.668086	-2.743196	-2.229905
H	-2.392481	-2.984745	-1.912602
H	-1.826230	-1.427909	-2.512879
C	1.992182	-0.047081	-0.216598
N	3.006706	-0.452866	0.586752
N	2.637604	0.329630	-1.352475
C	4.250525	-0.338479	-0.024707
C	4.014942	0.159588	-1.263310
H	5.169422	-0.616782	0.466747
H	4.686444	0.403171	-2.071455
H	2.157774	0.687671	-2.166614
H	2.864034	-0.806610	1.521639

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -839.478084463 Predicted Change= -2.907883D-09
Zero-point correction (ZPE)= -839.1580 0.32002
Internal Energy (U)= -839.1386 0.33945
Enthalpy (H)= -839.1376 0.34039
Gibbs Free Energy (G)= -839.2061 0.27194

Frequencies -- 19.9637 47.0288 57.7685
SCF Energy (M06) = -838.9320662

2π-Insertion TS RhNHC-H2

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

# b3lyp/gen pseudo=read gfprint gfinput
scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,calcfc,ts,noeigentest) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/ChkBas Freq

Pointgroup= C1 Stoichiometry= C14H20N2ORh(1+) C1[X(C14H20N2ORh)] #Atoms= 38
Charge = 1 Multiplicity = 1

SCF Energy= -839.455116675 Predicted Change= -7.850273D-08

Optimization completed on the basis of negligible forces. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.02652	0.00180	[NO]	0.02652	0.00180	[NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-0.306655	1.866815	0.036805
Rh	0.187346	-0.086777	-0.035659
C	-1.530665	1.444368	-0.065905

C	-2.906090	2.002607	-0.337715
C	-3.505057	-0.187562	-0.399007
C	-2.145611	-0.503230	0.219001
C	-1.422946	-1.700068	-0.287581
C	-0.510491	-2.371256	0.508847
C	-0.214397	-2.014131	1.962093
C	0.344107	-0.588755	1.967350
H	1.384174	-0.538634	2.290096
H	-0.255211	0.149160	2.507201
H	0.520042	-2.719899	2.359752
H	-1.116194	-2.112863	2.581814
H	-2.216167	-0.461971	1.304948
H	-2.983237	2.245114	-1.410929
H	-3.057143	2.920633	0.238450
H	-4.249552	-0.900427	-0.030621
H	-3.476078	-0.242890	-1.496695
H	-0.057881	-3.273699	0.104700
O	-3.908470	1.089087	0.036342
C	-1.717850	-2.201086	-1.687612
H	-2.732727	-2.613401	-1.747605
H	-1.647965	-1.403846	-2.436663
H	-1.021635	-2.995222	-1.969755
C	0.415099	3.168700	0.115951
H	0.890369	3.286044	1.097982
H	1.202448	3.233179	-0.642317
H	-0.267518	4.015240	-0.021853
C	2.176500	0.017441	-0.217638
N	2.943789	-0.602876	-1.153197
N	3.082321	0.729938	0.500705
C	4.290728	-0.285560	-1.024705
C	4.379345	0.561895	0.030700
H	5.048085	-0.683945	-1.681126
H	5.229951	1.050273	0.479273
H	2.821458	1.321276	1.276712
H	2.563115	-1.232369	-1.845515

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -839.455116675 Predicted Change= -7.850273D-08
Zero-point correction (ZPE)= -839.1350 0.32006
Internal Energy (U)= -839.1165 0.33857
Enthalpy (H)= -839.1156 0.33951
Gibbs Free Energy (G)= -839.1825 0.27260

Frequencies -- -213.7773 14.2458 53.9326
SCF Energy (M06) = -838.9050431

Metallacycle RhNHC-H2

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

==========

opt=maxcycle=250 freq=noraman b3lyp/gen geom=connectivity gfinput
gfprint pseudo=read scf=(direct,tight,maxcycle=300,xqc)
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/ChkBas Freq

---

Pointgroup= C1 Stoichiometry= C14H20N2ORh(1+) C1[X(C14H20N2ORh)] #Atoms= 38
Charge = 1 Multiplicity = 1

SCF Energy= -839.502136388 Predicted Change= -5.605600D-08

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00002	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00284	0.00180	[NO]	0.00284	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.332751	1.185309	-0.185780
Rh	-0.496107	-0.587480	0.241678
C	1.670092	1.169681	-0.267139
C	2.617152	2.369688	-0.352040
C	3.886697	0.557279	0.256740
C	2.563481	-0.062388	-0.249100
C	1.954284	-1.228264	0.503528
C	1.198823	-2.176255	-0.134838
C	0.783658	-2.182740	-1.604661
C	-0.576331	-1.483342	-1.602446
H	-1.425531	-2.175929	-1.548531
H	-0.719475	-0.751396	-2.401747
H	0.721321	-3.211497	-1.978103
H	1.502003	-1.647315	-2.229988
H	2.744401	-0.351570	-1.292250
H	2.499148	3.021200	0.528721
H	2.472006	2.977329	-1.251899
H	4.776687	-0.003741	-0.036799
H	3.885526	0.684969	1.349561
H	0.860705	-3.028956	0.457571
O	3.924715	1.813727	-0.403888
C	-0.501541	2.433771	-0.323985
H	-1.153831	2.385402	-1.203724
H	-1.141503	2.613011	0.546568
H	0.141491	3.313517	-0.446338
C	2.286317	-1.380060	1.971273
H	1.714918	-2.190676	2.432027
H	3.352138	-1.609576	2.098548
H	2.092827	-0.456652	2.529398
C	-2.383032	0.105530	0.189353
N	-3.153836	0.476435	1.245780
N	-3.221212	0.235435	-0.868155
C	-4.439527	0.829595	0.858132
C	-4.481703	0.675205	-0.490217
H	-5.193199	1.148482	1.560774
H	-5.280783	0.832458	-1.197480
H	-2.942216	0.028911	-1.817382
H	-2.820944	0.487673	2.200345

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -839.502136388 Predicted Change= -5.605600D-08
Zero-point correction (ZPE)= -839.1795 0.32254
Internal Energy (U)= -839.1612 0.34090
Enthalpy (H)= -839.1602 0.34184
Gibbs Free Energy (G)= -839.2264 0.27571

Frequencies -- 30.2498 46.7792 60.2230
SCF Energy (M06) = -838.9495075

Reductive Elimination TS RhNHC-H2

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

==========

# b3lyp/gen pseudo=read gfprint gfinput
scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,calcall,ts,noeigentest)

Pointgroup= C1 Stoichiometry= C14H20N2ORh(1+) C1[X(C14H20N2ORh)] #Atoms= 38
Charge = 1 Multiplicity = 1

SCF Energy= -839.456784412 Predicted Change= -8.136552D-11

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00025	0.00180	[YES]	0.00025	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-0.321852	0.857870	0.862110
Rh	0.458458	-0.720653	-0.185072
C	-1.602206	1.059318	0.459890
C	-2.320681	2.390400	0.326009
C	-3.361030	0.875695	-1.066272
C	-2.555849	0.010359	-0.072387
C	-1.844658	-1.248821	-0.549812
C	-1.263265	-2.083799	0.382086
C	-1.182603	-1.751877	1.868166
C	-0.039186	-0.750542	2.031992
H	0.940487	-1.225891	2.159783
H	-0.158781	-0.046964	2.854340
H	-0.976794	-2.656581	2.450583
H	-2.127015	-1.338792	2.238186
H	-3.265796	-0.256302	0.727864
H	-1.711631	3.117454	-0.235714
H	-2.571275	2.845894	1.293667
H	-4.353718	0.482581	-1.295843
H	-2.810224	1.035018	-2.006367
H	-0.945312	-3.077132	0.064284
O	-3.533850	2.099725	-0.360097
C	0.512738	1.995206	1.410900
H	1.457726	1.648597	1.834799
H	0.750241	2.725231	0.626888
H	-0.027300	2.531394	2.202216
C	-2.028109	-1.690688	-1.982815
H	-1.471839	-2.608947	-2.195096
H	-3.089755	-1.891394	-2.182462
H	-1.711187	-0.921954	-2.696725
C	2.323508	0.067274	-0.304871
N	2.768913	1.049436	-1.131724
N	3.459000	-0.353095	0.312739
C	4.141696	1.233683	-1.041482
C	4.582406	0.338456	-0.120626
H	4.672406	1.966715	-1.628384
H	5.573215	0.134967	0.253933
H	3.471651	-1.098491	0.995033
H	2.154256	1.576575	-1.736406

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -839.456784412 Predicted Change= -8.136552D-11
Zero-point correction (ZPE)= -839.1356 0.32116
Internal Energy (U)= -839.1176 0.33909
Enthalpy (H)= -839.1167 0.34003
Gibbs Free Energy (G)= -839.1818 0.27497

Frequencies -- -436.1592 33.5564 42.5757
SCF Energy (M06) = -838.9168352

Product-Catalyst Complex RhNHC-H2

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

==========

opt=maxcycle=250 freq=noraman b3lyp/gen geom=connectivity gfinput
gfprint pseudo=read scf=(direct,tight,maxcycle=300,xqc)
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/ChkBas Freq

---

Pointgroup= C1 Stoichiometry= C14H20N2ORh(1+) C1[X(C14H20N2ORh)] #Atoms= 38
Charge = 1 Multiplicity = 1

SCF Energy= -839.535885725 Predicted Change= -3.717090D-08

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00002	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00408	0.00180	[NO]	0.00408	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	1.871524	-1.350816	-0.296652
Rh	-0.259064	-0.347474	-0.388251
C	2.008853	0.020731	-0.322426
C	2.586019	0.833779	-1.483667
C	2.192049	2.353396	0.158860
C	1.818771	1.013880	0.841375
C	0.361380	0.850580	1.266570
C	-0.021815	-0.454102	1.719858
C	1.005178	-1.495992	2.142444
C	1.708788	-2.189463	0.961666

H	1.138701	-3.085442	0.688805
H	2.701418	-2.552743	1.267387
H	0.518784	-2.256707	2.759608
H	1.743297	-1.006054	2.792793
H	2.510894	0.822092	1.674987
H	1.819625	1.085007	-2.240924
H	3.413386	0.330616	-1.990878
H	2.693176	3.059583	0.823362
H	1.302201	2.839984	-0.269916
H	-0.980674	-0.512267	2.234113
O	3.097237	2.004854	-0.874819
C	-0.453898	2.057605	1.664453
H	-0.006602	2.514071	2.559935
H	-0.483054	2.833400	0.894124
H	-1.480602	1.776729	1.915510
C	2.182139	-2.168256	-1.534649
H	2.184099	-1.576372	-2.453487
H	3.171381	-2.637672	-1.437117
H	1.460244	-2.984582	-1.656562
C	-2.269924	-0.042901	-0.348689
N	-3.242806	-0.892083	0.075851
N	-2.975426	1.021166	-0.815848
C	-4.516986	-0.380670	-0.127210
C	-4.346244	0.841165	-0.694773
H	-5.412171	-0.918690	0.142254
H	-5.062940	1.580379	-1.016277
H	-2.535474	1.845902	-1.199794
H	-3.043058	-1.796933	0.478946

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -839.535885725 Predicted Change= -3.717090D-08
Zero-point correction (ZPE)= -839.2113 0.32458
Internal Energy (U)= -839.1934 0.34248
Enthalpy (H)= -839.1924 0.34342
Gibbs Free Energy (G)= -839.2575 0.27831

Frequencies -- 34.4555 45.3352 52.7331
SCF Energy (M06) = -838.9971722

12. Substrate and Product

12.a. Additional Figures

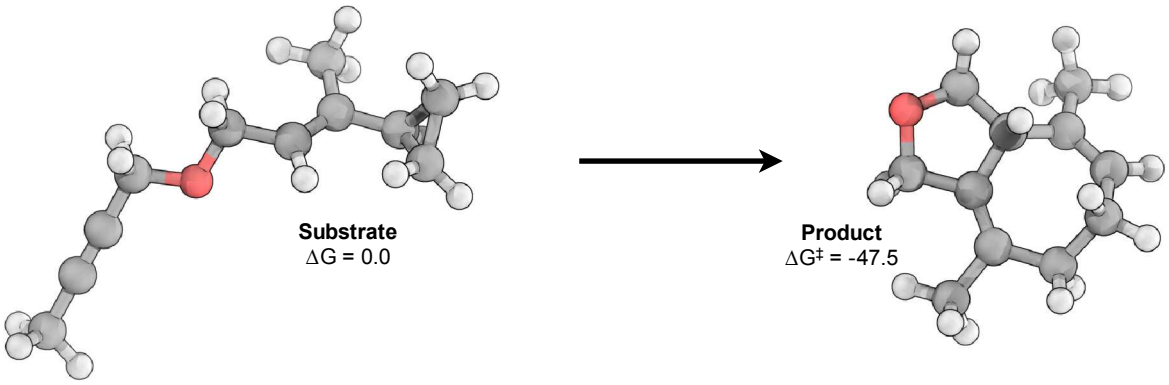

Figure S17. Computed geometries for the substrate and product.

Substrate

Supporting Information: SM-VCP-Linear.output

Using Gaussian 03: AM64L-G03RevC.02 12-Jun-2004

# b3lyp/6-31+G* 5D gfprint gfinput scf=(direct,xqc,tight,maxcycle=250)
opt=(gdiis,maxcycle=250) freq=noraman geom=connectivity
#N Geom=AllCheck Guess=Read SCRF=Check GenChk RB3LYP/6-31+G(d) Freq

Pointgroup= C1 Stoichiometry= C11H16O C1[X(C11H16O)] #Atoms= 28
Charge = 0 Multiplicity = 1

SCF Energy= -503.909332222 Predicted Change= -1.355676D-06

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.01064	0.00180	[NO]	0.01064	0.00180	[NO]

Atomic Type	X	Y	Z
C	2.205750	-0.371089	0.345458
C	3.329212	0.591144	0.595869
C	4.545544	0.619446	-0.317538
C	3.607306	1.802672	-0.256352
C	-3.617219	-0.183469	-0.185615
C	-4.612708	0.391851	0.194214
H	5.531549	0.705667	0.132984
H	4.511839	0.002916	-1.213072
H	3.945911	2.706616	0.243659
H	2.977024	1.986828	-1.121502
H	3.567307	0.703367	1.655169
C	1.112175	-0.010671	-0.348427
H	1.036033	1.015205	-0.704366
C	-0.066184	-0.860752	-0.716155
H	-0.122558	-0.971169	-1.815038
C	-2.432242	-0.895732	-0.659086
H	-2.424433	-1.923209	-0.255436
O	-1.252051	-0.208331	-0.257370
H	-0.006624	-1.872589	-0.290010
H	-2.459220	-0.982025	-1.759429
C	-5.806613	1.101328	0.651252
H	-6.402305	0.483353	1.334218
H	-5.531865	2.018870	1.186003
H	-6.448262	1.386134	-0.191577
C	2.444689	-1.737551	0.947860
H	3.310199	-2.222416	0.475888
H	2.684723	-1.643087	2.015832
H	1.588829	-2.410874	0.856757

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -503.909332222 Predicted Change= -1.355676D-06
Zero-point correction (ZPE)= -503.6673 0.24202
Internal Energy (U)= -503.6527 0.25663
Enthalpy (H)= -503.6517 0.25757
Gibbs Free Energy (G)= -503.7119 0.19739

Frequencies -- 17.8485 32.7582 42.0991
SCF Energy (M06) = -503.505363

Product

Supporting Information: Product.output

Using Gaussian 03: AM64L-G03RevC.02 12-Jun-2004

# b3lyp/6-31+G* 5D gfprint gfinput scf=(direct,xqc,tight,maxcycle=250)
opt=(gdiis,maxcycle=250) freq=noraman geom=connectivity
#N Geom=AllCheck Guess=Read SCRF=Check GenChk RB3LYP/6-31+G(d) Freq

Pointgroup= C1 Stoichiometry= C11H16O C1[X(C11H16O)] #Atoms= 28
Charge = 0 Multiplicity = 1

SCF Energy= -503.991118055 Predicted Change= -2.890105D-09

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00031	0.00180	[YES]	0.00031	0.00180	[YES]

Atomic Type	X	Y	Z
C	-1.374295	-1.056837	0.115239
C	-0.673694	-2.186788	-0.064168
C	0.647588	-2.239054	-0.789584
C	1.781127	-1.522977	-0.033491
C	0.537412	0.702681	-0.061109
C	1.646245	-0.023054	0.158852
H	0.942243	-3.283136	-0.948600
H	0.553419	-1.790480	-1.790440
H	1.912479	-1.996744	0.952951
H	2.726517	-1.704308	-0.569279
H	-1.055444	-3.117778	0.355530
C	-0.860850	0.244179	-0.496375
H	-0.849539	0.118581	-1.592314
C	-1.692729	1.513595	-0.211548
H	-2.560254	1.632988	-0.865796
C	0.457544	2.220698	0.078243
H	1.226069	2.759491	-0.484777
O	-0.807812	2.598281	-0.464855
H	0.519739	2.535568	1.134955
H	-2.031262	1.543281	0.836118
C	2.932017	0.625638	0.629685
H	3.336593	0.089346	1.499812
H	3.705054	0.579014	-0.151607
H	2.809850	1.673604	0.917043
C	-2.681258	-1.054750	0.873798
H	-3.500597	-0.630449	0.277012
H	-2.965477	-2.074314	1.155092
H	-2.621535	-0.460895	1.795885

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -503.991118055 Predicted Change= -2.890105D-09
Zero-point correction (ZPE)= -503.7431 0.24798
Internal Energy (U)= -503.7316 0.25950
Enthalpy (H)= -503.7306 0.26044
Gibbs Free Energy (G)= -503.7799 0.21119

Frequencies -- 65.3949 111.9348 118.3282
SCF Energy (M06) = -503.594655

13. Dispersion Corrections

13.a B3LYP/6-31G*/LANL2DZ Geometries w/ M06 SP Corrections

Table S1. Comparison of both M06/6-31G*/LANL2DZ and M06/def2-tzvp single point corrections using the B3LYP/6-31G*/LANL2DZ geometries.

	Pdt-Cat-Comp	Sub-Cat-Comp	Ox-Ring-TS	Alkyne-Comp	2π-Insert	Metalla-cycle	Red-Elim	Pdt-Cat-Comp	Sub-Cat-Comp	FES
RhCOCl	n-1	Cycle n							n+1	$\Delta G_{Exp.}$ = 27.7
M06/6-31Gd/LANL2DZ// B3LYP/6-31Gd/LANL2DZ	**0.0**	6.4	21.3	6.0	**26.5**	-5.2	2.1	-47.5	-41.1	26.5
M06/def2-tzvp//B3LYP/ 6-31Gd/LANL2DZ	**0.0**	8.6	21.6	8.8	**30.5**	1.0	8.0	-40.5	-31.9	30.5
RhCOD	n-1	Cycle n							n+1	$\Delta G_{Exp.}$ = 21.4
M06/6-31Gd/LANL2DZ// B3LYP/6-31Gd/LANL2DZ	**0.0**	2.4	13.8	4.6	**20.8**	-0.4	2.7	-47.5	-45.1	20.8
M06/def2-tzvp//B3LYP/ 6-31Gd/LANL2DZ	**0.0**	4.9	14.8	7.0	**24.3**	5.7	8.6	-40.5	-35.5	24.3
RhNHC-IPr	n-1	Cycle n							n+1	$\Delta G_{Exp.}$ = 20.3
M06/6-31Gd/LANL2DZ// B3LYP/6-31Gd/LANL2DZ	3.9	**0.0**	18.2	4.2	**19.5**	-12.2	4.0	-43.6	-47.5	19.5
M06/def2-tzvp//B3LYP/ 6-31Gd/LANL2DZ	0.7	**0.0**	16.4	1.9	**18.6**	-9.7	6.5	-39.7	-40.5	18.6
Rh(PPh3)3	n-1	Cycle n							n+1	$\Delta G_{Exp.}$ = 30.7
M06/6-31Gd/LANL2DZ// B3LYP/6-31Gd/LANL2DZ	11.7	**0.0**	19.5	11.6	**38.5**	3.7	11.1	-35.8	-47.5	38.5
M06/def2-tzvp//B3LYP/ 6-31Gd/LANL2DZ	14.3	**0.0**	21.6	14.4	**41.1**	12.1	19.6	-26.2	-40.5	41.1

13.b B3LYP-D3/6-31G*/LANL2DZ Geometries w/ M06 SP Corrections

Table S2. Comparison of the M06/6-31G*/LANL2DZ//B3LYP/6-31G*/LANL2DZ energies and B3LYP-D3/6-31G*/LANL2DZ, M06/6-31G*/LANL2DZ, and M06/def2-tzvp single point corrections using the B3LYP-D2/6-31G*/LANL2DZ geometries.

	Pdt-Cat-Comp	Sub-Cat-Comp	Ox-Ring-TS	Alkyne-Comp	2π-Insert	Metalla-cycle	Red-Elim	Pdt-Cat-Comp	Sub-Cat-Comp	FES
RhCOCl	n-1	Cycle n							n+1	$\Delta G_{Exp.}$ = 27.7
M06/6-31Gd/LANL2DZ// B3LYP/6-31Gd/LANL2DZ	**0.0**	6.4	21.3	6.0	**26.5**	-5.2	2.1	-47.5	-41.1	26.5
B3LYP-D3/6-31Gd/LANL2DZ	0.0	3.5	17.9	**-1.1**	**17.2**	-15.1	-1.0	-49.7	-46.1	18.4
M06/6-31Gd/LANL2DZ// B3LYP-D3/6-31Gd/LANL2DZ	**0.0**	6.5	21.3	5.8	**26.1**	-5.1	2.0	-47.2	-40.7	26.1
M06/def2-tzvp//B3LYP-D3/6-31Gd/LANL2DZ	**0.0**	8.6	21.7	8.5	**30.0**	1.0	8.0	-40.2	-31.5	30.0
RhNHC-IPr	n-1	Cycle n							n+1	$\Delta G_{Exp.}$ = 20.3
M06/6-31Gd/LANL2DZ// B3LYP/6-31Gd/LANL2DZ	3.9	**0.0**	18.2	4.2	**19.5**	-12.2	4.0	-43.6	-47.5	19.5
B3LYP-D3/6-31Gd/LANL2DZ	6.0	0.0	19.7	-1.5	11.5	**-19.6**	**3.2**	-43.6	-49.7	22.8
M06/6-31Gd/LANL2DZ// B3LYP-D3/6-31Gd/LANL2DZ	0.5	**0.0**	17.8	1.2	**16.2**	-14.1	1.8	-46.7	-47.2	16.2
M06/def2-tzvp//B3LYP-D3/6-31Gd/LANL2DZ	**0.0**	2.1	**18.6**	1.3	17.8	-8.9	7.7	-40.2	-38.0	18.6

Substrate-Catalyst Complex RhCOCl

Using: Gaussian 09, Revision D.01

b3lyp/gen pseudo=read gfprint gfinput scf=(direct,tight,maxcycle=300 ,xqc) opt=(maxcyc=250) EmpiricalDispersion=GD3 freq=noraman

Pointgroup=C1 Stoichiometry=C12H16ClO2Rh C1[X(C12H16ClO2Rh)]
Charge = 0 Multiplicity = 1 Basis = Nuclear

SCF Energy = -1187.05274116 Predicted Change = -1.055911D-07

Optimization completed. ---------- Optimization step: 1

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.000058	0.000450	YES	0.000011	0.000300	YES
Disp	0.006558	0.001800	NO!	0.000950	0.001200	YES

Atomic Type:	Coordinates (Angstroms) X	Y	Z
C	0.759926	1.642741	0.008078

Rh -0.607832 -0.519439 -0.094752
C 1.87733 0.864978 -0.08037
C 2.507169 0.363159 1.169137
C -1.989097 1.083163 0.349238
C -1.870898 0.443368 1.415404
H 0.428806 1.943997 0.999579
C 0.133304 2.467158 -1.103279
H 0.784447 3.313449 -1.356455
H -0.018089 1.879694 -2.021616
C -2.200753 2.193105 -0.612118
H -2.436558 1.78273 -1.605871
H -3.043528 2.812652 -0.285724
C -1.917635 -1.785653 -0.330649
O -2.755445 -2.560232 -0.485609
Cl 0.815922 -2.018202 -1.311958
H 2.032778 0.735326 2.074876
C 3.085038 -1.040313 1.271982
C 4.012275 0.133555 1.266449
H 4.612515 0.308937 0.37851
H 2.908997 -1.565682 2.20664
H 3.013303 -1.666768 0.389723
H 4.492989 0.432967 2.193853
O -1.08728 3.071788 -0.683082
C -2.07657 0.003374 2.804223
H -2.744279 0.695058 3.332053
H -2.517394 -0.999577 2.834181
H -1.12293 -0.041711 3.341835
C 2.592521 0.653213 -1.389267
H 1.917591 0.730688 -2.243009
H 3.368846 1.425051 -1.488987
H 3.070411 -0.326152 -1.445902
Statistical Thermodynamic Analysis for 000-COCl-Complex-Alkyne-Bent-Yne-original.log
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
==========

SCF Energy= -1187.05274116
Zero-point correction (ZPE)= 0.255251 -1186.797490
Internal Energy (U)= 0.274522 -1186.778219
Enthalpy (H)= 0.275467 -1186.777275
Gibbs Free Energy (G)= 0.206755 -1186.845986
Entropy (S) [Cal/Mol-Kelvin]= 144.615
Entropy (S): electronic= 0.000
Entropy (S): translational= 43.277
Entropy (S): rotational= 33.184
Entropy (S): vibrational= 68.154
Frequencies: 33.4174 52.4257 72.4635 75.9198 80.6365

SCF Energy (M06) = -1186.544998
SCF Energy (M06/def2-tzvp) = -1187.910435

Oxidative-Addition TS RhCOCl

Using: Gaussian 09, Revision D.01

==========

b3lyp/gen pseudo=read gfprint gfinput scf=(direct,tight,maxcycle=300
,xqc) opt=(maxcycle=250,calcfc,ts,noeigentest) EmpiricalDispersion=GD3
freq=noraman

Pointgroup=C1 Stoichiometry=C12H16ClO2Rh C1[X(C12H16ClO2Rh)]
Charge = 0 Multiplicity = 1 Basis = Nuclear

SCF Energy = -1187.02488391 Predicted Change = -2.220996D-09

Optimization completed. ---------- Optimization step: 1
Item Max Val. Criteria Pass? RMS Val. Criteria Pass?
Force 0.000004 || 0.000450 YES 0.000001 || 0.000300 YES
Disp 0.001126 || 0.001800 YES 0.000220 || 0.001200 YES

Atomic Coordinates (Angstroms)
Type: X Y Z

C -5.227507 -0.706951 -0.717077
Rh 1.447062 -0.302686 -0.110736
C -4.64231 0.019653 0.052833
C -3.895547 0.88204 0.976843
C -1.708758 0.214037 0.306362
C -0.433649 0.796073 -0.240395
C 0.498554 1.48939 0.58042
C 1.684707 1.988176 -0.064194
C 1.814552 2.372745 -1.504205
C 2.187686 0.931052 -1.766812
H 3.248534 0.712059 -1.831065
H 1.566981 0.393147 -2.488786
H 2.598143 3.107562 -1.696345
H 0.877858 2.697104 -1.961091
H -0.507677 1.069333 -1.291298
H -3.776315 0.368848 1.947057
H -4.445584 1.811115 1.162504
H -1.544933 -0.303591 1.264224
H -2.111819 -0.524839 -0.399527
H 2.532042 2.212586 0.580456
O -2.622318 1.293919 0.484394
C -5.95211 -1.575911 -1.6407
H -5.717341 -2.632732 -1.465054
H -7.036075 -1.451086 -1.528433
H -5.698099 -1.344817 -2.682325
C 0.325423 1.706279 2.064726
H 1.294073 1.749291 2.572378
H -0.198184 2.655406 2.232151
H -0.268544 0.915453 2.52766
C 0.887754 -1.570281 1.263107
O 0.619776 -2.29156 2.11358
Cl 3.344513 -1.712392 -0.506388
Statistical Thermodynamic Analysis for 015-COCl-VCP-Opening-TS-LI-original.log
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
==========

SCF Energy= -1187.02488391
Zero-point correction (ZPE)= 0.253053 -1186.771831
Internal Energy (U)= 0.272487 -1186.752397
Enthalpy (H)= 0.273431 -1186.751453
Gibbs Free Energy (G)= 0.201761 -1186.823123
Entropy (S) [Cal/Mol-Kelvin]= 150.842
Entropy (S): electronic= 0.000
Entropy (S): translational= 43.277
Entropy (S): rotational= 34.035
Entropy (S): vibrational= 73.530
Frequencies: -204.5505 17.8831 21.7399 50.0962 52.3506

SCF Energy (M06) = -1186.516373
SCF Energy (M06/def2-tzvp) = -1187.884649

Alkyne Coordination Complex RhCOCl

Using: Gaussian 09, Revision D.01

==========

b3lyp/gen pseudo=read gfprint gfinput scf=(direct,tight,maxcycle=300
,xqc) opt=(maxcycle=250) EmpiricalDispersion=GD3 freq=noraman

---

Pointgroup=C1 Stoichiometry=C12H16ClO2Rh C1[X(C12H16ClO2Rh)]
Charge = 0 Multiplicity = 1 Basis = Nuclear

SCF Energy = -1187.06221427 Predicted Change = -1.946806D-08

Optimization completed. ---------- Optimization step: 1
Optimization completed on the basis of negligible forces.
Item Max Val. Criteria Pass? RMS Val. Criteria Pass?
Force 0.000004 || 0.000450 YES 0.000001 || 0.000300 YES
Disp 0.003258 || 0.001800 NO! 0.000451 || 0.001200 YES

Atomic Coordinates (Angstroms)
Type: X Y Z

C -1.110763 2.026067 -0.473383
Rh -0.440149 -0.208173 0.018882
C 0.109997 2.093073 -0.335165
C 1.505649 2.513363 -0.092524
C 2.742215 0.516191 -0.451063
C 1.641684 -0.415391 -0.885342
C 1.336935 -1.632896 -0.22801
C 0.119495 -2.274941 -0.580331
C -0.545056 -2.118284 -1.949975
C -1.113821 -0.698231 -1.912914
H -2.203097 -0.665193 -1.973857
H -0.679145 0.003868 -2.628582
H -1.330759 -2.871969 -2.060477
H 0.179265 -2.280286 -2.758814
H 1.372361 -0.293659 -1.931645
H 1.706109 2.385179 0.980611
H 1.589349 3.575464 -0.347951
H 3.689189 0.241878 -0.933492
H 2.881792 0.485288 0.636806
H -0.184032 -3.116276 0.03872
O 2.483775 1.851979 -0.878837
C -2.529406 2.302768 -0.727284
H -2.90912 1.677967 -1.54279
H -3.133861 2.101641 0.163807
H -2.662466 3.353546 -1.008905
C 2.143418 -2.13685 0.94337
H 3.093051 -2.539459 0.566885
H 2.355359 -1.345086 1.66403
H 1.615546 -2.933449 1.473593
C -2.144882 -0.555859 0.821733
O -3.145919 -0.773831 1.339064
Cl 0.399501 0.30877 2.373875
Statistical Thermodynamic Analysis for 020-COCl-OpenVCP-Complex-Yne-SqrPyr-LI-original.log
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
==========

SCF Energy= -1187.06221427
Zero-point correction (ZPE)= 0.255088 -1186.807126
Internal Energy (U)= 0.273871 -1186.788343
Enthalpy (H)= 0.274816 -1186.787399
Gibbs Free Energy (G)= 0.208830 -1186.853385
Entropy (S) [Cal/Mol-Kelvin]= 138.879
Entropy (S): electronic= 0.000
Entropy (S): translational= 43.277
Entropy (S): rotational= 32.667
Entropy (S): vibrational= 62.935
Frequencies: 52.7203 66.0891 71.9870 80.5668 95.9677

SCF Energy (M06) = -1186.548207
SCF Energy (M06/def2-tzvp) = -1187.912694

2π-Insertion TS RhCOCl

Using: Gaussian 09, Revision D.01

==========

b3lyp/gen pseudo=read gfprint gfinput scf=(direct,tight,maxcycle=300
,xqc) opt=(maxcycle=250,calcfc,ts,noeigentest) EmpiricalDispersion=GD3
freq=noraman

Pointgroup=C1 Stoichiometry=C12H16ClO2Rh C1[X(C12H16ClO2Rh)]
Charge = 0 Multiplicity = 1 Basis = Nuclear

SCF Energy = -1187.03506338 Predicted Change = -5.281016D-10

Optimization completed. ---------- Optimization step: 1
Item Max Val. Criteria Pass? RMS Val. Criteria Pass?
Force 0.000002 || 0.000450 YES 0.000001 || 0.000300 YES
Disp 0.000221 || 0.001800 YES 0.000045 || 0.001200 YES

Atomic Coordinates (Angstroms)
Type: X Y Z

C -0.174475 1.766689 -0.63198
Rh -0.717504 -0.10144 -0.013559
Cl -0.418997 0.557302 2.407813
C 1.050502 1.392221 -0.573135
C 2.421815 1.955363 -0.358184
C 2.970687 -0.192648 0.096168
C 1.610247 -0.59096 -0.457825
C 0.946224 -1.741972 0.207371
C -0.04742 -2.446864 -0.443786
C -0.48667 -2.213836 -1.883743
C -0.930469 -0.74899 -2.009371

C -2.550072 0.102731 0.181359
O -3.683662 0.253338 0.306813
H -1.956071 -0.65024 -2.369008
H -0.275724 -0.129856 -2.629382
H -1.313708 -2.894214 -2.107636
H 0.328582 -2.4735 -2.575588
H 1.647876 -0.680715 -1.542998
H 2.478735 2.343187 0.672323
H 2.603694 2.77675 -1.05873
H 3.701243 -0.980133 -0.117931
H 2.92131 -0.035943 1.182814
H -0.476593 -3.294366 0.086756
O 3.413293 0.972311 -0.568637
C -1.030466 2.956291 -0.851414
H -1.557857 3.201864 0.077251
H -0.433996 3.822321 -1.16239
H -1.783804 2.756929 -1.621793
C 1.406761 -2.172582 1.58219
H 0.786142 -2.99275 1.952588
H 2.445719 -2.524688 1.539005
H 1.338063 -1.351834 2.300716
Statistical Thermodynamic Analysis for 025-COCl-TS-2Pi-Insertion-Yne-Boat-original.log
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
==========

SCF Energy= -1187.03506338
Zero-point correction (ZPE)= 0.255664 -1186.779399
Internal Energy (U)= 0.273147 -1186.761917
Enthalpy (H)= 0.274091 -1186.760972
Gibbs Free Energy (G)= 0.210924 -1186.824139
Entropy (S) [Cal/Mol-Kelvin]= 132.945
Entropy (S): electronic= 0.000
Entropy (S): translational= 43.277
Entropy (S): rotational= 32.763
Entropy (S): vibrational= 56.906
Frequencies: -215.7116 61.6608 72.2993 78.8215 84.3116

SCF Energy (M06) = -1186.517855
SCF Energy (M06/def2-tzvp) = -1187.880505

Metallacycle RhCOCl

Using: Gaussian 09, Revision D.01
==========

b3lyp/gen pseudo=read gfprint gfinput scf=(direct,tight,maxcycle=300
,xqc) opt=(maxcycle=250) EmpiricalDispersion=GD3 freq=noraman

---

Pointgroup=C1 Stoichiometry=C12H16ClO2Rh C1[X(C12H16ClO2Rh)]
Charge = 0 Multiplicity = 1 Basis = Nuclear

SCF Energy = -1187.08820016 Predicted Change = -6.869148D-09

Optimization completed. ---------- Optimization step: 1
Item Max Val. Criteria Pass? RMS Val. Criteria Pass?
Force 0.000007 || 0.000450 YES 0.000002 || 0.000300 YES
Disp 0.000626 || 0.001800 YES 0.000142 || 0.001200 YES

Atomic Coordinates (Angstroms)
Type: X Y Z

C -0.648283 1.355973 -0.059061
Rh 0.966156 0.103605 -0.07296
Cl 2.634463 -1.530872 -0.862995
C -1.863634 0.796416 0.028076
C -3.216062 1.424043 -0.294941
C -3.395132 -0.865847 -0.574294
C -2.157112 -0.662464 0.317668
C -0.956855 -1.57653 0.150838
C -0.013324 -1.671901 1.138482
C 0.057648 -0.79648 2.384794
C 1.013524 0.330513 1.999104
C 2.215977 1.461556 -0.377938
O 3.009985 2.275987 -0.521118
H 2.058476 0.13097 2.24538
H 0.709419 1.326815 2.319552
H 0.430489 -1.375501 3.238616
H -0.923839 -0.39237 2.645054
H -2.521744 -0.744604 1.353017
H -3.185082 1.976065 -1.246549
H -3.577568 2.108823 0.483432
H -4.029557 -1.705211 -0.27531
H -3.115353 -0.989714 -1.631906
H 0.773889 -2.413121 1.024015
O -4.140007 0.332558 -0.376875
C -0.4691 2.837377 -0.291138
H 0.130543 3.285055 0.512514
H 0.058361 3.043299 -1.231286
H -1.42452 3.375761 -0.320311
C -0.892433 -2.472557 -1.061934
H 0.060529 -3.003394 -1.11242
H -1.716263 -3.198798 -1.03952
H -1.001752 -1.890434 -1.984148
Statistical Thermodynamic Analysis for 030-COCl-Metallacycle-Yne-TrigPyr-original.log
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
==========

SCF Energy= -1187.08820016
Zero-point correction (ZPE)= 0.258165 -1186.830035
Internal Energy (U)= 0.275731 -1186.812469
Enthalpy (H)= 0.276676 -1186.811525
Gibbs Free Energy (G)= 0.212452 -1186.875749
Entropy (S) [Cal/Mol-Kelvin]= 135.171
Entropy (S): electronic= 0.000
Entropy (S): translational= 43.277
Entropy (S): rotational= 33.012
Entropy (S): vibrational= 58.882
Frequencies: 36.2613 51.1408 82.3776 89.6075 99.4554

SCF Energy (M06) = -1186.569141
SCF Energy (M06/def2-tzvp) = -1187.928284

Reductive Elimination TS RhCOCl

Using: Gaussian 09, Revision D.01
==========

b3lyp/gen pseudo=read gfprint gfinput scf=(direct,tight,maxcycle=300
,xqc) opt=(maxcycle=250,calcfc,ts,noeigentest) EmpiricalDispersion=GD3
freq=noraman

Pointgroup=C1 Stoichiometry=C12H16ClO2Rh C1[X(C12H16ClO2Rh)]
Charge = 0 Multiplicity = 1 Basis = Nuclear

SCF Energy = -1187.06557212 Predicted Change = -5.745308D-10

Optimization completed. ---------- Optimization step: 1
Item Max Val. Criteria Pass? RMS Val. Criteria Pass?
Force 0.000003 || 0.000450 YES 0.000001 || 0.000300 YES
Disp 0.000251 || 0.001800 YES 0.000064 || 0.001200 YES

Atomic Coordinates (Angstroms)
Type: X Y Z

C -0.560833 1.405362 0.153342
Rh 1.023537 0.034327 0.051761
Cl 2.327315 -1.694247 -0.9473
C -1.755206 0.808179 -0.028555
C -2.938158 1.395286 -0.778951
C -3.0736 -0.899435 -0.912548
C -2.119146 -0.634656 0.268744
C -0.925011 -1.556605 0.467284
C -0.101412 -1.37375 1.547312
C -0.280141 -0.235509 2.544831
C 0.289983 1.044259 1.922561
C 2.291643 1.241963 -0.600624
O 3.091124 1.970846 -0.98859
H 1.3479 1.207211 2.15448
H -0.242646 1.947326 2.220279
H 0.250977 -0.467475 3.474121
H -1.338485 -0.102574 2.796418
H -2.743979 -0.671635 1.177542
H -2.622128 1.847456 -1.732878
H -3.478788 2.163555 -0.208192
H -3.773126 -1.722985 -0.74684
H -2.5122 -1.085547 -1.841204
H 0.660578 -2.12287 1.749807
O -3.831793 0.303434 -1.004677
C -0.348161 2.853161 -0.233637
H -0.18557 2.934989 -1.315746
H -1.214125 3.476538 0.0236
H 0.528328 3.282554 0.260033
C -0.812709 -2.775203 -0.411328
H 0.070061 -3.366059 -0.163908
H -1.712509 -3.39435 -0.289622
H -0.735946 -2.501213 -1.46749
Statistical Thermodynamic Analysis for 035-COCl-TS-ReductiveElim-Yne-Boat-original.log
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
==========

SCF Energy= -1187.06557212
Zero-point correction (ZPE)= 0.257003 -1186.808569
Internal Energy (U)= 0.274018 -1186.791554
Enthalpy (H)= 0.274962 -1186.790610
Gibbs Free Energy (G)= 0.212333 -1186.853239
Entropy (S) [Cal/Mol-Kelvin]= 131.814
Entropy (S): electronic= 0.000
Entropy (S): translational= 43.277
Entropy (S): rotational= 32.952
Entropy (S): vibrational= 55.585
Frequencies: -384.6088 45.7534 52.0262 85.6661 90.6302

SCF Energy (M06) = -1186.557697
SCF Energy (M06/def2-tzvp) = -1187.917041

Product-Catalyst Complex RhCOCl

Using: Gaussian 09, Revision D.01
==========

b3lyp/gen pseudo=read gfprint gfinput scf=(direct,tight,maxcycle=300
,xqc) opt=(maxcycle=250) EmpiricalDispersion=GD3 freq=noraman

---

Pointgroup=C1 Stoichiometry=C12H16ClO2Rh C1[X(C12H16ClO2Rh)]
Charge = 0 Multiplicity = 1 Basis = Nuclear

SCF Energy = -1187.14716493 Predicted Change = -6.629254D-08

Optimization completed. ---------- Optimization step: 1
Item Max Val. Criteria Pass? RMS Val. Criteria Pass?
Force 0.000030 || 0.000450 YES 0.000006 || 0.000300 YES
Disp 0.002449 || 0.001800 NO! 0.000464 || 0.001200 YES

Atomic Coordinates (Angstroms)
Type: X Y Z

C 1.351578 -0.927149 1.075556
Rh -0.811816 -0.238874 -0.001878
C 1.602207 -0.096323 0.017386
C 2.320121 -0.546012 -1.253735
C 1.82163 1.640487 -1.58708
C 1.40995 1.42772 -0.110807
C -0.040392 1.770989 0.218142
C -0.524621 1.374551 1.480299
C 0.400272 0.935031 2.606666
C 0.918672 -0.50158 2.465886
H 0.137064 -1.196555 2.796246
H 1.770053 -0.667512 3.145314
H -0.126788 1.021619 3.56181
H 1.248189 1.632685 2.658888
H 2.111676 1.974159 0.538883
H 1.633951 -1.080968 -1.928172
H 3.181034 -1.188597 -1.045992
H 2.257486 2.623204 -1.782605
H 0.956634 1.490704 -2.251383
H -1.476212 1.799772 1.794718
C -2.601391 0.148411 -0.319947
O -3.70647 0.407976 -0.507958
Cl -0.977408 -2.323887 -1.12686

O 2.808142 0.655573 -1.841608
C -0.734889 2.860003 -0.568423
H -0.218901 3.817787 -0.406878
H -0.744275 2.666778 -1.644386
H -1.771455 2.977632 -0.237706
C 1.72642 -2.390309 0.971179
H 1.581478 -2.781323 -0.03681
H 2.779933 -2.519315 1.259024
H 1.117052 -2.997953 1.645995
Statistical Thermodynamic Analysis
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

SCF Energy= -1187.14716493
Zero-point correction (ZPE)= 0.260594 -1186.886571
Internal Energy (U)= 0.277471 -1186.869694
Enthalpy (H)= 0.278415 -1186.868750
Gibbs Free Energy (G)= 0.216399 -1186.930765
Entropy (S) [Cal/Mol-Kelvin]= 130.522
Entropy (S): electronic= 0.000
Entropy (S): translational= 43.277
Entropy (S): rotational= 32.754
Entropy (S): vibrational= 54.491
Frequencies: 51.9793 67.3197 82.9041 98.0489 110.4367

SCF Energy (M06) = -1186.640203
SCF Energy (M06/def2-tzvp) = -1187.997835

Substrate-Catalyst Complex RhNHC-IPr

Using: Gaussian 09, Revision D.01

b3lyp/gen pseudo=read gfprint gfinput scf=(direct,tight,maxcycle=300
,xqc) opt=(maxcycle=250) EmpiricalDispersion=GD3 freq=noraman

Pointgroup=C1 Stoichiometry=C38H52N2ORh(1+) C1[X(C38H52N2ORh)]
Charge = 1 Multiplicity = 1 Basis = Nuclear

SCF Energy = -1773.46469581 Predicted Change = -5.939265D-08

Optimization completed. ---------- Optimization step: 1
Item Max Val. Criteria Pass? RMS Val. Criteria Pass?
Force 0.000020 || 0.000450 YES 0.000003 || 0.000300 YES
Disp 0.002126 || 0.001800 NO! 0.000316 || 0.001200 YES

Atomic Coordinates (Angstroms)
Type: X Y Z

Rh -0.384113 -0.810838 -0.461072
C -1.843559 -2.382758 -1.510485
C -3.115804 -1.948174 -0.850672
C -4.286942 -2.925207 -0.78703
C -3.612501 -2.477843 0.476691
C 1.325531 -1.274056 -1.542599
C 0.724531 -0.397271 -2.221967
H -5.276177 -2.544526 -1.023611
H -4.099796 -3.941742 -1.122515
H -4.132879 -1.771811 1.114235
H -3.013153 -3.205239 1.015533
H -3.406116 -0.923814 -1.088092
C -0.859429 -3.059652 -0.822032
H -1.025372 -3.276813 0.233729
C 0.299899 -3.841806 -1.403814
H 0.124878 -4.908625 -1.225165
C 2.221791 -2.428052 -1.292334
H 2.701029 -2.706929 -2.245815
O 1.529553 -3.542812 -0.742821
H 0.396394 -3.70054 -2.487404
H 3.002431 -2.167196 -0.574338
C 0.507126 0.549916 -3.327475
H 1.240062 0.36863 -4.122141
H -0.49594 0.444482 -3.748832
H 0.622018 1.58597 -2.991429
C -1.863205 -2.227265 -3.01468
H -2.507701 -2.99947 -3.453963
H -2.29317 -1.257932 -3.289924
H -0.873667 -2.30516 -3.467545
C 0.306169 0.878135 0.356915
N 1.537814 1.319021 0.729577
N -0.552847 1.857681 0.754355
C 1.440482 2.557366 1.363767
C 2.776826 0.576119 0.652801
C 0.127083 2.899191 1.37546
C -1.986404 1.68406 0.695725
H 2.312209 3.059105 1.751081
C 3.022929 -0.416727 1.619443
C 3.703902 0.917239 -0.349809
H -0.386726 3.760873 1.771207
C -2.679872 2.099925 -0.457919
C -2.620076 1.082701 1.802076
C 2.0107 -0.811189 2.686593
C 4.270208 -1.055144 1.578529
C 4.932538 0.24699 -0.344808
C 3.406209 1.979149 -1.399699
C -1.958748 2.781062 -1.611515
C -4.064616 1.898606 -0.479084
C -4.007586 0.907439 1.72776
C -1.839122 0.596069 3.017278
C 1.702339 -2.319531 2.631832
H 1.074987 -0.283575 2.485939
C 2.485186 -0.382035 4.087439
H 4.498883 -1.820323 2.31363
C 5.217975 -0.723554 0.614101
H 5.676678 0.48902 -1.096486
C 4.088631 3.315235 -1.043983
H 2.323351 2.146552 -1.406554
C 3.813564 1.528283 -2.813869
H -0.916088 2.449109 -1.586396
C -1.965909 4.311501 -1.419957
C -2.531352 2.39804 -2.985226
H -4.639141 2.210289 -1.344669
C -4.721447 1.309771 0.601546
H -4.533901 0.450831 2.559951
H -0.837419 1.035299 2.982994
C -1.670835 -0.933839 2.971249
C -2.474353 1.037822 4.347504
H 2.580969 -2.918795 2.894247
H 1.379024 -2.627027 1.631569
H 0.912486 -2.569485 3.348562
H 2.660838 0.698566 4.134151
H 3.418356 -0.88621 4.36209
H 1.731384 -0.63935 4.84054
H 6.18049 -1.226788 0.60497
H 5.176925 3.193315 -1.003215
H 3.759413 3.693915 -0.070714
H 3.860408 4.076699 -1.798208
H 3.418125 0.533671 -3.041714
H 4.901877 1.492598 -2.930084
H 3.43184 2.235012 -3.55881
H -1.490004 4.598285 -0.475953
H -2.99185 4.69629 -1.410457
H -1.424999 4.803478 -2.236051
H -3.525405 2.827557 -3.149654
H -2.611877 1.310485 -3.094603
H -1.881827 2.777705 -3.781015
H -5.797952 1.168435 0.565734
H -1.171335 -1.256072 2.044948
H -2.639811 -1.4401 3.020367
H -1.05961 -1.280066 3.811031
H -3.45056 0.568956 4.511987
H -2.611684 2.123591 4.380332
H -1.828139 0.74904 5.183301
Statistical Thermodynamic Analysis
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

SCF Energy= -1773.46469581
Zero-point correction (ZPE)= 0.824376 -1772.640320
Internal Energy (U)= 0.869496 -1772.595200
Enthalpy (H)= 0.870440 -1772.594256
Gibbs Free Energy (G)= 0.748652 -1772.716044
Entropy (S) [Cal/Mol-Kelvin]= 256.324
Entropy (S): electronic= 0.000
Entropy (S): translational= 45.322
Entropy (S): rotational= 37.500
Entropy (S): vibrational= 173.502
Frequencies: 20.9548 35.2894 38.1276 42.2949 50.4673

SCF Energy (M06) = -1772.050888
SCF Energy (M06/def2-tzvp) = -1773.754571

Oxidative-Addition TS RhNHC-IPr

Using: Gaussian 09, Revision D.01

b3lyp/gen pseudo=read gfprint gfinput scf=(direct,tight,maxcycle=300
,xqc) opt=(maxcycle=250,calcfc,ts,noeigentest) EmpiricalDispersion=GD3
freq=noraman

Pointgroup=C1 Stoichiometry=C38H52N2ORh(1+) C1[X(C38H52N2ORh)]
Charge = 1 Multiplicity = 1 Basis = Nuclear

SCF Energy = -1773.42702389 Predicted Change = -6.868792D-09

Optimization completed. ---------- Optimization step: 1
Item Max Val. Criteria Pass? RMS Val. Criteria Pass?
Force 0.000011 || 0.000450 YES 0.000001 || 0.000300 YES
Disp 0.001717 || 0.001800 YES 0.000252 || 0.001200 YES

Atomic Coordinates (Angstroms)
Type: X Y Z

C -3.612771 3.802827 -0.969239
Rh -0.512066 -0.575215 -1.123696
C -2.506734 4.17289 -0.645534
C -1.168978 4.602353 -0.218382
C -0.163361 2.413628 -0.186191
C -0.765592 1.514149 -1.233153
C 0.00897 1.050011 -2.350017
C -0.699865 0.197406 -3.28168
C -2.155762 0.243956 -3.628978
C -2.205548 -0.813832 -2.560607
H -2.178311 -1.841181 -2.917521
H -2.884418 -0.637049 -1.722256
H -2.395681 -0.0635 -4.646404
H -2.651775 1.180381 -3.373682
H -1.832642 1.675388 -1.370935
H -1.14552 4.684194 0.880801
H -0.937478 5.591364 -0.626649
H 0.858584 2.110474 0.031602
H -0.740566 2.34987 0.744135
H -0.082416 -0.423743 -3.928255
O -0.102368 3.760205 -0.659889
C -4.953668 3.367753 -1.353087
H -5.006165 3.123093 -2.420841
H -5.262401 2.48123 -0.785165
H -5.68888 4.157796 -1.159832
C 1.432996 1.448595 -2.632659
H 1.94474 0.697401 -3.240461
H 1.434389 2.397381 -3.184437
H 2.008789 1.594145 -1.717753
C 0.51341 -0.655104 0.677471
N 1.750523 -0.453672 1.209952
N -0.184381 -1.272823 1.67155
C 1.820239 -0.966737 2.506119
C 2.862834 0.147892 0.511753
C 0.597926 -1.478865 2.800568
C -1.547221 -1.682174 1.430276
H 2.729221 -0.922059 3.082504
C 3.501174 -0.598575 -0.497539
C 3.268306 1.451706 0.873844
H 0.219282 -1.965533 3.685338
C -2.590975 -0.807884 1.798732
C -1.764459 -2.903671 0.758493

C	3.143408	-2.04623	-0.816426
C	4.555124	0.017753	-1.183708
C	4.325407	2.016531	0.149977
C	2.653281	2.215988	2.044654
C	-2.316562	0.477	2.567531
C	-3.892154	-1.189852	1.456462
C	-3.086527	-3.226863	0.425424
C	-0.614836	-3.826285	0.367002
C	2.841244	-2.256456	-2.310445
H	2.239251	-2.313077	-0.262494
C	4.26535	-2.990327	-0.340362
H	5.074901	-0.529491	-1.963993
C	4.956902	1.313445	-0.873615
H	4.66318	3.017819	0.394402
C	3.537446	2.057018	3.300719
H	1.673433	1.776028	2.264529
C	2.43594	3.714789	1.756893
H	-1.273545	0.757569	2.383859
C	-2.472295	0.230917	4.082614
C	-3.19468	1.653765	2.112355
H	-4.726091	-0.550431	1.725946
C	-4.136807	-2.379006	0.768252
H	-3.295897	-4.152839	-0.100307
H	0.276104	-3.520431	0.925131
C	-0.292589	-3.678075	-1.130563
C	-0.890956	-5.298692	0.720256
H	3.715868	-2.047925	-2.935722
H	2.024465	-1.605743	-2.640684
H	2.547597	-3.295587	-2.495346
H	4.45352	-2.872127	0.732364
H	5.20362	-2.788462	-0.868953
H	3.991398	-4.035033	-0.527298
H	5.774191	1.773448	-1.42145
H	4.525971	2.497606	3.128905
H	3.689172	1.007749	3.572762
H	3.082196	2.567814	4.156471
H	1.875646	3.891979	0.834739
H	3.388069	4.251061	1.6832
H	1.880164	4.166898	2.586065
H	-1.801143	-0.560962	4.433051
H	-3.498552	-0.069876	4.322135
H	-2.244633	1.143314	4.644731
H	-4.248116	1.501858	2.372346
H	-3.128801	1.820511	1.032739
H	-2.871843	2.573219	2.612841
H	-5.155861	-2.650987	0.508337
H	0.052084	-2.653506	-1.381585
H	-1.165721	-3.90028	-1.752772
H	0.525813	-4.342418	-1.427931
H	-1.711437	-5.715725	0.126531
H	-1.149724	-5.408918	1.778117
H	-0.000792	-5.904673	0.52079

Statistical Thermodynamic Analysis
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

SCF Energy= -1773.42702389
Zero-point correction (ZPE)= 0.821359 -1772.605665
Internal Energy (U)= 0.866974 -1772.560050
Enthalpy (H)= 0.867918 -1772.559106
Gibbs Free Energy (G)= 0.742437 -1772.684587
Entropy (S) [Cal/Mol-Kelvin]= 264.097
Entropy (S): electronic= 0.000
Entropy (S): translational= 45.322
Entropy (S): rotational= 37.664
Entropy (S): vibrational= 181.111
Frequencies: -215.5961 20.1889 24.8402 27.6334 30.7810

SCF Energy (M06) = -1772.016297
SCF Energy (M06/def2-tzvp) = -1773.722056

Alkyne Coordination Complex RhNHC-IPr

Using: Gaussian 09, Revision D.01

b3lyp/gen pseudo=read gfprint gfinput scf=(direct,tight,maxcycle=300
,xqc) opt=(maxcycle=250) EmpiricalDispersion=GD3 freq=noraman

Pointgroup=C1 Stoichiometry=C38H52N2ORh(1+) C1[X(C38H52N2ORh)]
Charge = 1 Multiplicity = 1 Basis = Nuclear

SCF Energy = -1773.46843464 Predicted Change = -4.917293D-07

Optimization completed. ---------- Optimization step: 1

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.000039	0.000450	YES	0.000007	0.000300	YES
Disp	0.048627	0.001800	NO!	0.006813	0.001200	NO!

Atomic Type:	Coordinates (Angstroms) X	Y	Z
C	1.144342	1.605477	-1.819112
Rh	0.495256	-0.482726	-1.142271
C	2.073675	0.838975	-2.106727
C	3.373918	0.295615	-2.567068
C	2.806073	-1.955389	-3.085052
C	1.335992	-1.919	-2.748681
C	0.744218	-2.670915	-1.708332
C	-0.59632	-2.378858	-1.335248
C	-1.59783	-1.736044	-2.302299
C	-1.109681	-0.298175	-2.42138
H	-1.787553	0.446123	-2.014912
H	-0.719259	0.010411	-3.39359
H	-2.599132	-1.77648	-1.868187
H	-1.618153	-2.262719	-3.265118
H	0.721657	-1.592545	-3.584144
H	3.942238	-0.071808	-1.696128
H	3.9417	1.116232	-3.018406
H	2.992655	-2.655235	-3.907418
H	3.416897	-2.274663	-2.227722
H	-0.993347	-2.907635	-0.476355
O	3.272301	-0.696833	-3.566589
C	0.312346	2.814738	-1.774866
H	-0.042251	3.02472	-0.763472
H	0.884845	3.678109	-2.130073
H	-0.564706	2.69539	-2.417556
C	1.575841	-3.576726	-0.829273
H	0.989325	-3.957149	0.008973
H	1.940275	-4.43214	-1.409726
H	2.45106	-3.058171	-0.425008
C	-0.393883	0.379989	0.528346
N	0.429126	0.840126	1.523736
N	-1.649012	0.726512	0.945163
C	-0.295611	1.50379	2.510771
C	1.850796	0.560653	1.589913
C	-1.596495	1.432996	2.148579
C	-2.91316	0.296988	0.380127
H	0.180963	1.934537	3.375657
C	2.272731	-0.747568	1.947276
C	2.761184	1.605148	1.329354
H	-2.491531	1.795172	2.627275
C	-3.653459	1.201731	-0.403668
C	-3.391533	-0.989596	0.714057
C	1.299944	-1.833755	2.424466
C	3.651791	-0.995576	1.925026
C	4.127291	1.294973	1.335255
C	2.323733	3.05203	1.14159
C	-3.185536	2.627654	-0.66212
C	-4.885565	0.766275	-0.9084
C	-4.62801	-1.372395	0.180259
C	-2.655102	-1.907533	1.684873
C	1.948247	-3.216512	2.612066
H	0.510808	-1.932377	1.668857
C	0.636732	-1.448899	3.766581
H	4.025609	-1.977861	2.185744
C	4.568241	0.005094	1.606058
H	4.852542	2.076472	1.1354
C	2.479857	3.821555	2.471552
H	1.262448	3.055846	0.879903
C	3.089864	3.78495	0.025563
H	-2.124519	2.683623	-0.405185
C	-3.937351	3.612069	0.257227
C	-3.334767	3.051536	-2.134631
H	-5.479654	1.439183	-1.517966
C	-5.363901	-0.510062	-0.630398
H	-5.028505	-2.353602	0.409562
H	-1.583516	-1.712515	1.586377
C	-2.881877	-3.40572	1.414974
C	-3.062416	-1.584505	3.139059
H	2.624969	-3.21987	3.474086
H	2.513445	-3.554643	1.741394
H	1.167017	-3.9578	2.811294
H	0.011661	-0.559127	3.693594
H	1.402484	-1.271121	4.53011
H	-9.2e-05	-2.269339	4.114974
H	5.631339	-0.218142	1.601897
H	3.531951	3.852551	2.776023
H	1.916936	3.354991	3.286437
H	2.127676	4.853089	2.360576
H	3.09761	3.209202	-0.903523
H	4.128888	3.981249	0.310523
H	2.623241	4.756409	-0.169895
H	-3.795186	3.365494	1.314798
H	-5.013406	3.589108	0.052019
H	-3.582277	4.636069	0.095834
H	-4.386443	3.15474	-2.421926
H	-2.876314	2.328031	-2.817661
H	-2.859824	4.025753	-2.29478
H	-6.32123	-0.829838	-1.031545
H	-2.757959	-3.664103	0.358306
H	-3.886004	-3.724183	1.715389
H	-2.170132	-3.998273	2.000177
H	-4.138614	-1.737925	3.276416
H	-2.829837	-0.551034	3.409457
H	-2.532438	-2.241372	3.837549

Statistical Thermodynamic Analysis
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

SCF Energy= -1773.46843464
Zero-point correction (ZPE)= 0.824947 -1772.643488
Internal Energy (U)= 0.869460 -1772.598975
Enthalpy (H)= 0.870404 -1772.598031
Gibbs Free Energy (G)= 0.749981 -1772.718453
Entropy (S) [Cal/Mol-Kelvin]= 253.451
Entropy (S): electronic= 0.000
Entropy (S): translational= 45.322
Entropy (S): rotational= 37.510
Entropy (S): vibrational= 170.619
Frequencies: 7.7469 25.9229 34.8329 42.3040 47.7786

SCF Energy (M06) = -1772.050255
SCF Energy (M06/def2-tzvp) = -1773.757274

2π-Insertion TS RhNHC-IPr

Using: Gaussian 09, Revision D.01

b3lyp/gen pseudo=read gfprint gfinput scf=(direct,tight,maxcycle=300
,xqc) opt=(maxcycle=250,calcfc,ts,noeigentest) EmpiricalDispersion=GD3
freq=noraman

Pointgroup=C1 Stoichiometry=C38H52N2ORh(1+) C1[X(C38H52N2ORh)]
Charge = 1 Multiplicity = 1 Basis = Nuclear

SCF Energy = -1773.44857974 Predicted Change = -7.298505D-10

Optimization completed. ---------- Optimization step: 1

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.000013	0.000450	YES	0.000001	0.000300	YES
Disp	0.000403	0.001800	YES	0.000087	0.001200	YES

Atomic Type:	Coordinates (Angstroms) X	Y	Z
C	-1.015259	-2.345414	0.370204

Rh	-0.556759	-0.690703	-0.699632
C	-1.912008	-2.564396	-0.539606
C	-3.150773	-3.395764	-0.740957
C	-3.38379	-2.111412	-2.597644
C	-1.938176	-1.683322	-2.376926
C	-1.588302	-0.273122	-2.693856
C	-0.282379	0.078017	-2.994245
C	0.86811	-0.919298	-3.082969
C	0.9628	-1.634952	-1.73386
H	1.90944	-1.496322	-1.223466
H	0.698687	-2.695631	-1.752683
H	1.793794	-0.375648	-3.282745
H	0.718517	-1.61552	-3.92084
H	-1.270473	-2.410947	-2.836848
H	-3.963737	-2.977093	-0.122054
H	-2.96689	-4.425661	-0.420348
H	-3.600828	-2.149615	-3.669611
H	-4.091514	-1.418901	-2.117672
H	-0.086585	1.104876	-3.290781
O	-3.533503	-3.421205	-2.096541
C	-2.696745	0.759263	-2.723364
H	-3.407459	0.535927	-3.528517
H	-3.258652	0.788431	-1.783051
H	-2.29514	1.75897	-2.89742
C	-0.488286	-3.031554	1.581458
H	-0.171274	-2.321537	2.348311
H	-1.233829	-3.707735	2.015324
H	0.389874	-3.625176	1.307299
C	0.5322	0.325282	0.645542
N	-0.166558	1.097043	1.538251
N	1.831989	0.443087	1.038167
C	0.681015	1.661063	2.486528
C	-1.535629	1.495818	1.289195
C	1.932222	1.247428	2.177356
C	3.001581	-0.003941	0.313849
H	0.31301	2.308257	3.266333
C	-1.744178	2.624691	0.466435
C	-2.593068	0.770119	1.873731
H	2.886585	1.447799	2.63664
C	3.670119	-1.156805	0.75825
C	3.440215	0.767148	-0.787093
C	-0.599068	3.522799	0.010483
C	-3.068573	2.966103	0.169658
C	-3.897847	1.148851	1.532764
C	-2.331488	-0.294166	2.927432
C	3.171529	-1.978175	1.93955
C	4.832792	-1.533174	0.071766
C	4.598219	0.336029	-1.442007
C	2.708507	2.030812	-1.234342
C	-0.607896	3.8146	-1.497752
H	0.34472	3.020592	0.230612
C	-0.613972	4.832067	0.825901
H	-3.269379	3.831416	-0.454307
C	-4.133235	2.224582	0.678164
H	-4.739454	0.612825	1.958318
C	-2.357033	0.352636	4.329013
H	-1.32146	-0.67719	2.763724
C	-3.305909	-1.479724	2.864272
H	2.14029	-1.674934	2.148964
C	4.011143	-1.691518	3.199967
C	3.154083	-3.486009	1.629498
H	5.38063	-2.413541	0.391545
C	5.290939	-0.797281	-1.015811
H	4.96998	0.89337	-2.294339
H	1.637704	1.86242	-1.080491
C	2.895667	2.36829	-2.722779
C	3.133406	3.245067	-0.380787
H	-1.523199	4.324826	-1.816477
H	-0.510393	2.890797	-2.073826
H	0.235534	4.46383	-1.757203
H	-0.568295	4.63033	1.901752
H	-1.526278	5.407219	0.632447
H	0.245516	5.457003	0.558849
H	-5.153472	2.505305	0.432229
H	-3.344634	0.777122	4.541709
H	-1.621105	1.159676	4.413066
H	-2.132713	-0.393465	5.099469
H	-3.354199	-1.899084	1.855394
H	-4.31872	-1.191472	3.165259
H	-2.979253	-2.268484	3.55013
H	3.978306	-0.631286	3.473603
H	5.060553	-1.961444	3.036374
H	3.639582	-2.273506	4.050777
H	4.166081	-3.894978	1.539682
H	2.627182	-3.696042	0.691939
H	2.656119	-4.031052	2.439029
H	6.192057	-1.106383	-1.537529
H	2.684187	1.513309	-3.372548
H	3.913403	2.710144	-2.940056
H	2.217266	3.182027	-3.000462
H	4.203845	3.442764	-0.506343
H	2.940026	3.089108	0.683546
H	2.584624	4.140812	-0.693988

Statistical Thermodynamic Analysis
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

SCF Energy=	-1773.44857974	
Zero-point correction (ZPE)=	0.824517	-1772.624063
Internal Energy (U)=	0.868337	-1772.580243
Enthalpy (H)=	0.869281	-1772.579299
Gibbs Free Energy (G)=	0.750918	-1772.697662
Entropy (S) [Cal/Mol-Kelvin]=	249.117	
Entropy (S): electronic=	0.000	
Entropy (S): translational=	45.322	
Entropy (S): rotational=	37.539	
Entropy (S): vibrational=	166.256	

Frequencies: -200.7708 29.5658 35.6020 37.3312 41.1009

SCF Energy (M06) = -1772.027394
SCF Energy (M06/def2-tzvp) = -1773.731815

Metallacycle RhNHC-IPr

Using: Gaussian 09, Revision D.01

b3lyp/gen pseudo=read gfprint gfinput scf=(direct,tight,maxcycle=300 ,xqc) opt=(maxcycle=250) EmpiricalDispersion=GD3 freq=noraman

Pointgroup=C1 Stoichiometry=C38H52N2ORh(1+) C1[X(C38H52N2ORh)]
Charge = 1 Multiplicity = 1 Basis = Nuclear

SCF Energy = -1773.50000197 Predicted Change = -2.101462D-08

Optimization completed. ---------- Optimization step: 1

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.000023	0.000450	YES	0.000003	0.000300	YES
Disp	0.001693	0.001800	YES	0.000295	0.001200	YES

Atomic Type:	Coordinates (Angstroms) X	Y	Z
C	-0.995519	-1.90583	-0.091242
Rh	-0.521069	-0.151198	-0.928549
C	-2.029196	-2.557629	-0.636735
C	-2.782492	-3.761111	-0.078599
C	-4.208324	-2.571871	-1.470755
C	-2.783046	-2.16359	-1.888872
C	-2.505009	-0.749795	-2.360565
C	-1.375256	-0.465705	-3.082211
C	-0.20679	-1.413868	-3.344143
C	0.781051	-1.066072	-2.230597
H	1.501729	-0.295653	-2.510143
H	1.295697	-1.908388	-1.766143
H	0.20904	-1.250362	-4.345942
H	-0.520434	-2.458473	-3.27673
H	-2.494783	-2.865824	-2.68471
H	-2.983697	-3.648846	0.996424
H	-2.249593	-4.708812	-0.228657
H	-4.888931	-2.739882	-2.30938
H	-4.655441	-1.831837	-0.788306
H	-1.286643	0.531629	-3.515831
O	-4.005499	-3.82063	-0.817805
C	-0.189934	-2.440112	1.056326
H	0.84454	-2.588067	0.737048
H	-0.168779	-1.760862	1.912537
H	-0.57259	-3.408684	1.400352
C	-3.565669	0.299454	-2.127408
H	-4.502608	0.014235	-2.622599
H	-3.785614	0.410495	-1.058833
H	-3.25765	1.276259	-2.510091
C	0.680887	0.452689	0.579691
N	1.988356	0.392541	0.954549
N	0.089706	1.261406	1.506385
C	2.198763	1.153702	2.105095
C	3.065277	-0.236782	0.216058
C	1.0063	1.699196	2.452789
C	-1.271554	1.724746	1.345204
H	3.176052	1.23815	2.550671
C	3.637142	-1.419975	0.721008
C	3.536736	0.407138	-0.950719
H	0.724448	2.352225	3.26352
C	-1.502017	2.77998	0.433308
C	-2.302275	1.114252	2.085295
C	3.231594	-2.036106	2.056066
C	4.681539	-1.993551	-0.018157
C	4.577775	-0.214295	-1.646823
C	2.98978	1.758579	-1.407018
C	-0.371536	3.506815	-0.28824
C	-2.829951	3.172344	0.228173
C	-3.609997	1.556799	1.848532
C	-2.027937	0.060389	3.146964
C	3.10336	-3.570609	2.000697
H	2.256186	-1.629535	2.34119
C	4.244763	-1.64155	3.152196
H	5.147477	-2.905913	0.338772
C	5.138555	-1.407273	-1.192762
H	4.963727	0.239802	-2.552241
C	3.653001	2.906143	-0.615712
H	1.919561	1.780361	-1.182415
C	3.13519	2.016914	-2.915464
H	0.582568	3.1163	0.077534
C	-0.385016	5.015241	0.0243
C	-0.420199	3.261156	-1.806549
H	-3.047329	3.973913	-0.471037
C	-3.873744	2.563506	0.922045
H	-4.429925	1.112591	2.403592
H	-0.985569	-0.257004	3.04636
C	-2.914727	-1.184242	2.972141
C	-2.188593	0.667256	4.555241
H	4.081847	-4.053353	1.907439
H	2.487659	-3.904748	1.159983
H	2.648318	-3.939066	2.926251
H	4.332966	-0.555769	3.261471
H	5.241094	-2.029391	2.912501
H	3.942377	-2.05688	4.119937
H	5.946906	-1.87068	-1.750894
H	4.731904	2.928197	-0.805389
H	3.501221	2.800301	0.46235
H	3.23487	3.87232	-0.921889
H	2.736197	1.193872	-3.518305
H	4.180979	2.167504	-3.20392
H	2.593077	2.929168	-3.185982
H	-0.34471	5.195001	1.103565
H	-1.28604	5.501858	-0.364174
H	0.481492	5.502169	-0.436349
H	-1.363173	3.61234	-2.239809
H	-0.326912	2.191788	-2.046419
H	0.401316	3.78165	-2.310113
H	-4.89655	2.887728	0.752923
H	-2.848637	-1.568348	1.950495
H	-3.966239	-0.964098	3.185828
H	-2.599218	-1.9727	3.66385
H	-3.215932	1.011675	4.718545
H	-1.522162	1.525111	4.700829

H -1.955995 -0.080161 5.321597
Statistical Thermodynamic Analysis
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

SCF Energy= -1773.50000197
Zero-point correction (ZPE)= 0.826708 -1772.673294
Internal Energy (U)= 0.870596 -1772.629406
Enthalpy (H)= 0.871541 -1772.628461
Gibbs Free Energy (G)= 0.752786 -1772.747216
Entropy (S) [Cal/Mol-Kelvin]= 249.940
Entropy (S): electronic= 0.000
Entropy (S): translational= 45.322
Entropy (S): rotational= 37.622
Entropy (S): vibrational= 166.996
Frequencies: 21.2904 33.6974 35.6208 44.6674 47.0461

SCF Energy (M06) = -1772.077571
SCF Energy (M06/def2-tzvp) = -1773.776229

Reductive Elimination TS RhNHC-IPr

Using: Gaussian 09, Revision D.01
---
b3lyp/gen pseudo=read gfprint gfinput scf=(direct,tight,maxcycle=300
,xqc) opt=(maxcycle=250,calcfc,ts,noeigentest) EmpiricalDispersion=GD3
freq=noraman

Pointgroup=C1 Stoichiometry=C38H52N2ORh(1+) C1[X(C38H52N2ORh)]
Charge = 1 Multiplicity = 1 Basis = Nuclear

SCF Energy = -1773.46270865 Predicted Change = -2.295727D-08

Optimization completed. ---------- Optimization step: 1
Item Max Val. Criteria Pass? RMS Val. Criteria Pass?
Force 0.000027 || 0.000450 YES 0.000003 || 0.000300 YES
Disp 0.002752 || 0.001800 NO! 0.000473 || 0.001200 YES

Atomic Coordinates (Angstroms)
Type: X Y Z

C -0.417935 -1.896238 -1.031906
Rh -0.445187 0.162663 -1.014847
C -1.618735 -2.34765 -1.459077
C -2.339834 -3.586717 -0.988367
C -3.890373 -1.896733 -1.467225
C -2.62422 -1.584113 -2.291077
C -2.260489 -0.121911 -2.511035
C -1.112699 0.214196 -3.197287
C -0.071113 -0.795582 -3.662491
C 0.771584 -1.133942 -2.439132
H 1.577751 -0.424764 -2.234432
H 1.220816 -2.126086 -2.452348
H 0.553583 -0.363803 -4.452283
H -0.545514 -1.693621 -4.072834
H -2.746629 -2.078329 -3.269674
H -2.06493 -3.873315 0.033572
H -2.150416 -4.450805 -1.644242
H -4.819414 -1.824647 -2.039321
H -3.955817 -1.235494 -0.590919
H -0.992684 1.2464 -3.524429
O -3.733981 -3.257704 -1.055326
C 0.454567 -2.718342 -0.117033
H 0.032246 -2.764376 0.893327
H 0.559497 -3.74769 -0.482192
H 1.451192 -2.28861 -0.04336
C -3.32587 0.913918 -2.237882
H -2.989345 1.91584 -2.517517
H -4.22761 0.68374 -2.82117
H -3.617955 0.935433 -1.182482
C 0.585582 0.36039 0.717257
N -0.106866 0.819632 1.797671
N 1.890186 0.3695 1.113961
C 0.747486 1.141727 2.845732
C -1.525758 1.096451 1.733578
C 2.002435 0.862668 2.413964
C 3.02021 0.018358 0.283124
H 0.384275 1.545041 3.777396
C -1.925063 2.353502 1.23594
C -2.43994 0.105113 2.145184
H 2.959821 0.969849 2.895295
C 3.73012 -1.169277 0.564928
C 3.383033 0.896247 -0.759597
C -0.914537 3.387671 0.753763
C -3.299901 2.603588 1.144807
C -3.801246 0.410226 2.035879
C -1.968239 -1.224533 2.717108
C 3.432933 -2.046757 1.779607
C 4.796721 -1.493967 -0.282841
C 4.453627 0.51367 -1.577495
C 2.741275 2.267569 -0.950481
C -0.812596 3.349975 -0.780723
H 0.070011 3.126184 1.154335
C -1.232788 4.812778 1.239769
H -3.647837 3.556416 0.759471
C -4.227184 1.643335 1.541085
H -4.539893 -0.322544 2.340953
C -1.726867 -1.101852 4.236802
H -1.007681 -1.459541 2.245773
C -2.930817 -2.388908 2.429312
H 2.413986 -1.830629 2.120272
C 4.405491 -1.703901 2.929382
C 3.512424 -3.556618 1.482155
H 5.366464 -2.398784 -0.100029
C 5.145451 -0.673376 -1.35195
H 4.765395 1.165065 -2.387542
H 1.819215 2.30533 -0.366138
C 2.362234 2.562074 -2.411986
C 3.6788 3.358868 -0.394145
H -1.777641 3.5695 -1.247979
H -0.485423 2.355984 -1.148841
H -0.072875 4.068315 -1.148682
H -1.344977 4.842002 2.328156
H -2.154057 5.203309 0.794633
H -0.421054 5.492945 0.960699
H -5.289867 1.855982 1.467415
H -2.655734 -0.83326 4.752358
H -0.978377 -0.33877 4.471921
H -1.375544 -2.056034 4.644874
H -3.224359 -2.441283 1.3773
H -3.845438 -2.312969 3.028033
H -2.453507 -3.336966 2.700312
H 4.364334 -0.646913 3.209771
H 5.437495 -1.923039 2.633512
H 4.172797 -2.300334 3.818392
H 4.543898 -3.879339 1.305814
H 2.919638 -3.839878 0.608128
H 3.142238 -4.121839 2.34399
H 5.974286 -0.94832 -1.997811
H 1.664904 1.813322 -2.802662
H 3.239007 2.585719 -3.067211
H 1.879672 3.542698 -2.483542
H 4.623878 3.383827 -0.948032
H 3.913285 3.179185 0.660829
H 3.210301 4.346306 -0.477458
Statistical Thermodynamic Analysis
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

SCF Energy= -1773.46270865
Zero-point correction (ZPE)= 0.825142 -1772.637567
Internal Energy (U)= 0.868615 -1772.594093
Enthalpy (H)= 0.869559 -1772.593149
Gibbs Free Energy (G)= 0.751755 -1772.710954
Entropy (S) [Cal/Mol-Kelvin]= 247.941
Entropy (S): electronic= 0.000
Entropy (S): translational= 45.322
Entropy (S): rotational= 37.524
Entropy (S): vibrational= 165.095
Frequencies: -445.0464 28.1326 33.8346 36.3392 43.6721

SCF Energy (M06) = -1772.051172
SCF Energy (M06/def2-tzvp) = -1773.748738

Product-Catalyst Complex RhNHC-IPr

Using: Gaussian 09, Revision D.01
---
b3lyp/gen pseudo=read gfprint gfinput scf=(direct,tight,maxcycle=300
,xqc) opt=(maxcycle=250) EmpiricalDispersion=GD3 freq=noraman
---
Pointgroup=C1 Stoichiometry=C38H52N2ORh(1+) C1[X(C38H52N2ORh)]
Charge = 1 Multiplicity = 1 Basis = Nuclear

SCF Energy = -1773.53954754 Predicted Change = -3.568075D-08

Optimization completed. ---------- Optimization step: 1
Item Max Val. Criteria Pass? RMS Val. Criteria Pass?
Force 0.000014 || 0.000450 YES 0.000002 || 0.000300 YES
Disp 0.003217 || 0.001800 NO! 0.000619 || 0.001200 YES

Atomic Coordinates (Angstroms)
Type: X Y Z

C -0.358007 -3.327546 -0.846456
Rh -0.175274 -1.03519 -0.192988
C -1.389661 -2.596766 -1.39133
C -2.86622 -2.746275 -1.015486
C -2.833767 -1.191348 -2.664096
C -1.356457 -1.647287 -2.605199
C -0.344847 -0.563111 -2.257095
C 0.985669 -0.994991 -1.980984
C 1.493244 -2.370341 -2.387654
C 1.021077 -3.503742 -1.461797
H 1.737735 -3.603009 -0.638399
H 1.041189 -4.466731 -1.994063
H 2.586857 -2.359031 -2.399911
H 1.174046 -2.566603 -3.420543
H -1.097949 -2.174113 -3.536134
H -3.127393 -2.145978 -0.127222
H -3.155754 -3.784891 -0.834004
H -3.187772 -0.980625 -3.675145
H -2.995199 -0.302895 -2.033984
H 1.745697 -0.221405 -1.930923
O -3.576628 -2.287381 -2.153186
C -0.621508 0.869271 -2.640163
H -0.717349 0.950236 -3.732647
H -1.545892 1.242517 -2.197793
H 0.194863 1.523683 -2.324072
C -0.637514 -4.303172 0.281268
H -1.542338 -4.063948 0.844131
H -0.752472 -5.317502 -0.125945
H 0.197812 -4.334369 0.988114
C 0.341463 0.781353 0.510933
N 1.548401 1.348307 0.780439
N -0.574821 1.635023 1.05608
C 1.393021 2.530307 1.499845
C 2.820557 0.757292 0.438111
C 0.060725 2.71045 1.674092
C -2.004018 1.409971 1.031645
H 2.240343 3.115237 1.819209
C 3.295211 -0.304468 1.229094
C 3.516717 1.257023 -0.679399
H -0.492031 3.485041 2.17805
C -2.818439 2.307191 0.312852
C -2.52842 0.284608 1.715834
C 2.553332 -0.800651 2.464719
C 4.498852 -0.905309 0.840817
C 4.724223 0.631328 -1.01192
C 3.015469 2.455486 -1.478569
C -2.273264 3.539093 -0.405687
C -4.199447 2.05971 0.30214
C -3.911472 0.087699 1.661347
C -1.640882 -0.67991 2.511786
C 1.957174 -2.197844 2.222317
H 1.718071 -0.121682 2.659248

C 3.447125 -0.787618 3.718028
H 4.892158 -1.734955 1.420325
C 5.204309 -0.446146 -0.269075
H 5.295639 0.99041 -1.861662
C 3.784803 3.727949 -1.068039
H 1.96002 2.612611 -1.2285
C 3.099611 2.245911 -3.001217
H -1.194111 3.408066 -0.542197
C -2.505086 4.80622 0.445863
C -2.890201 3.748657 -1.802591
H -4.855922 2.735957 -0.234837
C -4.740873 0.965351 0.963347
H -4.35764 -0.756863 2.172019
H -0.781817 -0.982825 1.870189
C -2.329107 -1.987583 2.924536
C -1.026495 -0.004447 3.754034
H 2.741288 -2.943365 2.046948
H 1.312065 -2.18891 1.330265
H 1.360142 -2.524693 3.081573
H 3.864492 0.208893 3.896185
H 4.281956 -1.49075 3.627951
H 2.864372 -1.077483 4.599574
H 6.139837 -0.921286 -0.549878
H 4.850845 3.625728 -1.300382
H 3.697047 3.924379 0.006014
H 3.401339 4.601149 -1.607303
H 2.582416 1.333782 -3.316984
H 4.136924 2.17942 -3.34568
H 2.639103 3.093945 -3.519482
H -2.067747 4.725874 1.446017
H -3.578227 4.986779 0.574929
H -2.070941 5.683397 -0.046173
H -3.94078 4.051327 -1.740979
H -2.839573 2.846204 -2.418159
H -2.354605 4.548034 -2.325492
H -5.812192 0.790028 0.938338
H -2.797155 -2.495814 2.076754
H -3.098744 -1.810856 3.683509
H -1.589436 -2.66673 3.360273
H -1.825266 0.285851 4.445948
H -0.452864 0.890768 3.505879
H -0.361162 -0.700586 4.276249
Statistical Thermodynamic Analysis
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
==========
SCF Energy= -1773.53954754
Zero-point correction (ZPE)= 0.827913 -1772.711635
Internal Energy (U)= 0.871339 -1772.668209
Enthalpy (H)= 0.872283 -1772.667265
Gibbs Free Energy (G)= 0.753971 -1772.785577
Entropy (S) [Cal/Mol-Kelvin]= 249.008
Entropy (S): electronic= 0.000
Entropy (S): translational= 45.322
Entropy (S): rotational= 37.488
Entropy (S): vibrational= 166.199
Frequencies: 22.3874 27.4320 32.0410 39.0786 42.4319

SCF Energy (M06) = -1772.130582
SCF Energy (M06/def2-tzvp) = -1773.827285

Product

Using: Gaussian 09, Revision D.01
==========
# b3lyp/gen gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(m
axcycle=250) EmpiricalDispersion=GD3 freq=noraman

Pointgroup=C1 Stoichiometry=C11H16O C1[X(C11H16O)]
Charge = 0 Multiplicity = 1 Basis = Nuclear

SCF Energy = -503.999209550 Predicted Change = -1.536180D-08

Optimization completed. ---------- Optimization step: 1
Item Max Val. Criteria Pass? RMS Val. Criteria Pass?
Force 0.000020 || 0.000450 YES 0.000004 || 0.000300 YES
Disp 0.001748 || 0.001800 YES 0.000402 || 0.001200 YES

Atomic Coordinates (Angstroms)
Type: X Y Z

C -1.386434 -1.042255 0.106706
C -0.701912 -2.178174 -0.073282
C 0.62255 -2.240497 -0.791082
C 1.756135 -1.546445 -0.015066
C 0.546263 0.692525 -0.066112
C 1.641943 -0.04417 0.16347
H 0.904833 -3.285196 -0.964296
H 0.54298 -1.772969 -1.78375
H 1.858243 -2.016321 0.975934
H 2.708676 -1.747774 -0.529748
H -1.093189 -3.105565 0.343855
C -0.858589 0.255419 -0.492885
H -0.858531 0.150085 -1.59049
C -1.66638 1.533399 -0.179357
H -2.55703 1.656578 -0.801477
C 0.488795 2.212792 0.053413
H 1.257612 2.728403 -0.532096
O -0.779629 2.60394 -0.462636
H 0.592031 2.533226 1.106051
H -1.972273 1.557046 0.879547
C 2.93586 0.590899 0.626831
H 3.343535 0.043508 1.487948
H 3.700583 0.542983 -0.16186
H 2.827171 1.637345 0.924117
C -2.693645 -1.019922 0.860779
H -3.49906 -0.567356 0.266453
H -3.005938 -2.032981 1.13381
H -2.620131 -0.433959 1.786603
Statistical Thermodynamic Analysis
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
==========
SCF Energy= -503.999209550
Zero-point correction (ZPE)= 0.248925 -503.750285
Internal Energy (U)= 0.260334 -503.738875
Enthalpy (H)= 0.261279 -503.737931
Gibbs Free Energy (G)= 0.212266 -503.786944
Entropy (S) [Cal/Mol-Kelvin]= 103.156
Entropy (S): electronic= 0.000
Entropy (S): translational= 41.195
Entropy (S): rotational= 30.615
Entropy (S): vibrational= 31.345
Frequencies: 63.4359 115.3932 124.3408 164.1437 197.7355

SCF Energy (M06) = -503.5947979
SCF Energy (M06/def2-tzvp) = -503.7883521

Substrate

Using: Gaussian 09, Revision D.01
==========
# b3lyp/gen gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(m
axcycle=250) EmpiricalDispersion=GD3 freq=noraman

Pointgroup=C1 Stoichiometry=C11H16O C1[X(C11H16O)]
Charge = 0 Multiplicity = 1 Basis = Nuclear

SCF Energy = -503.905916409 Predicted Change = -2.587229D-08

Optimization completed. ---------- Optimization step: 1
Optimization completed on the basis of negligible forces.
Item Max Val. Criteria Pass? RMS Val. Criteria Pass?
Force 0.000004 || 0.000450 YES 0.000001 || 0.000300 YES
Disp 0.019337 || 0.001800 NO! 0.003483 || 0.001200 NO!

Atomic Coordinates (Angstroms)
Type: X Y Z

C 2.234134 -0.380519 0.345283
C 3.338375 0.602667 0.588924
C 4.503939 0.692172 -0.381073
C 3.54332 1.847824 -0.233865
C -3.621938 -0.194368 -0.178686
C -4.620858 0.392844 0.163798
H 5.509544 0.788089 0.020417
H 4.437884 0.103428 -1.2929
H 3.884308 2.743857 0.277687
H 2.863565 2.041674 -1.058258
H 3.623218 0.680492 1.63958
C 1.091746 -0.019975 -0.256375
H 0.954257 1.020372 -0.543657
C -0.073488 -0.890559 -0.618122
H -0.095734 -1.056542 -1.712924
C -2.430453 -0.925354 -0.603142
H -2.432552 -1.936717 -0.15689
O -1.261967 -0.217734 -0.217019
H -0.01952 -1.885595 -0.149048
H -2.447735 -1.068394 -1.699439
C -5.819494 1.113701 0.584098
H -6.417521 0.521314 1.287623
H -5.554255 2.053602 1.083684
H -6.458761 1.362032 -0.272162
C 2.561361 -1.774577 0.827289
H 3.406395 -2.186604 0.259727
H 2.877058 -1.748484 1.879024
H 1.725715 -2.473786 0.744914
Statistical Thermodynamic Analysis
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
==========
SCF Energy= -503.905916409
Zero-point correction (ZPE)= 0.242739 -503.663177
Internal Energy (U)= 0.257281 -503.648635
Enthalpy (H)= 0.258225 -503.647691
Gibbs Free Energy (G)= 0.198125 -503.707792
Entropy (S) [Cal/Mol-Kelvin]= 126.492
Entropy (S): electronic= 0.000
Entropy (S): translational= 41.195
Entropy (S): rotational= 32.018
Entropy (S): vibrational= 53.279
Frequencies: 20.2278 26.5908 43.1312 58.1385 71.4467

SCF Energy (M06) = -503.5054512
SCF Energy (M06/def2-tzvp) = -503.7102041