SUPPORTING INFORMATION
Mechanism of N/O Bond Scission of N_2O by an Unsaturated Rhodium Transient

José G. Andino and Kenneth G. Caulton*
Department of Chemistry, Indiana University, Bloomington, IN 47405

Computational Details

All calculations were carried out using Density Functional Theory as implemented in the Jaguar 7.0 suite[1] of ab initio quantum chemistry programs. Geometry optimizations were performed with the B3LYP[2, 3, 4] functional and the 6-31G** basis set with no symmetry restrictions, which has been shown to work well for many transition metal-containing systems.[5] All transition metals were represented using the Los Alamos basis set (LACVP).[6, 7] Some energies of optimized structures were successfully reevaluated by additional single-point calculations using Dunning's correlation-consistent triple-ζ basis set,[8] cc-pVTZ(-f). Table S1 shows that the double ζ adequately mimic the triple ζ results for several monomeric species. For all transition metals we used a modified version of LACVP, designated LACV3P, in which the exponents were decontracted to match the effective core potential with the triple-ζ quality basis.

We used simplified models by replacing ^{t}-Bu groups with Me groups to make the problem more tractable when computing geometries and energies for dimetallic structures (approx. 90 atoms). All energies and geometries illustrated by drawings use these PMe_2 models. Table S2 compares the full ($PtBu_2$) models and small (PMe_2) models.

References

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

Table S1. Comparison of energies of selected models using a DZ basis set compared with TZ basis set

Model	DZ (ΔE)	TZ (ΔE)
1	0.0	0.0
2	-25.5	-25.0
3	-22.0	-21.6
^{3}8	-49.9	-47.1
6	-64.7	-67.9
9	-32.8	-31.6

Table S2. Comparison of energies of selected models using a truncated and an experimental full model

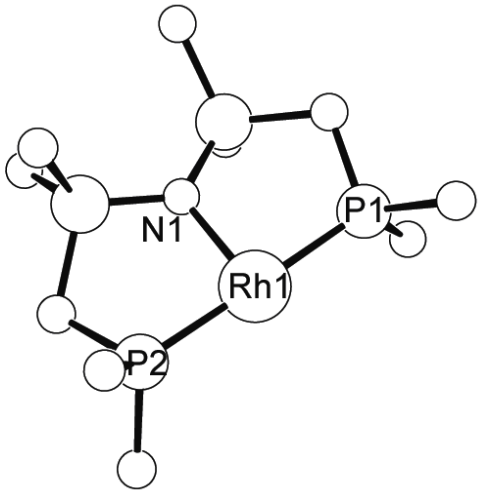
Model	Small (ΔE in kcal/mol)	Full (ΔE in kcal/mol)
1	0.0	0.0
2	-25.5	-19.0

3	-22.0	-16.2
5	-13.9	-8.0
6	-64.7	-59.0
9	-32.8	-26.4

Table S3. Electronic energies of optimized structures (hartrees)

Model	(ΔE in kcal/mol)
N_2O	-184.6562508
1	-1824.0826958
2	-2008.7795366
73	-2008.7507366
3	-2008.7739888
5	-2008.7611404
^{3}7a	-2008.7380988
4	-2008.7688023
$^1TS_{4\text{-}6}$	-2008.7393087
^{3}7$_b$	-2008.7437772
$^1TS_{3\text{-}6}$	-2008.7431564
^{3}7c	-2008.7691029
6$_b$	-1899.3326954
^{1}8	-3832.8897015
$^1TS_{8\text{-}6}$	-3832.8836417
^{3}8	-3832.9011476
$^3TS_{8\text{-}6}$	-3832.9015273
^{1}6	-1899.2684545
^{3}6	-1899.2930778
9	-1933.6556371

Optimized structure of N_2O, PNP-Rh and N_2



N_2O **1**

ΔE(SCF): kcal/mol

ΔE(SCF): 0.0 kcal/mol
ΔG(gas): 0.0 kcal/mol

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

			1
N1-N2	1.134	Rh1-P1	2.336
N2-O1	1.193	Rh1-P2	2.336
N1-N2-O1	179.96	Rh1-N1	2.085
		P1-Rh1-P2	178.80

N_2

N1-N2	1.105

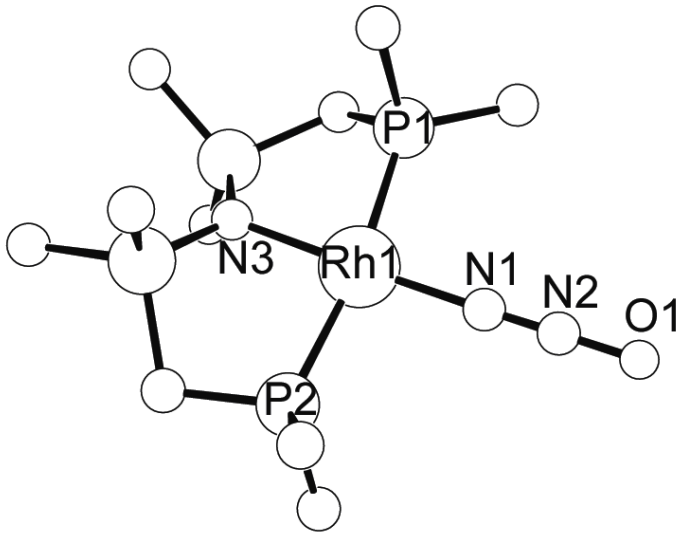
Coordinates of 1

44

Rh	15.867534911	1.870995496	18.341775069
P	16.892303134	0.096091887	19.462994102
P	14.810627440	3.649317583	17.257044550
Si	15.165866540	1.438159392	21.520151754
Si	13.527554357	3.505496510	19.969028843
N	14.776744316	2.303280094	20.065842189
C	16.412772905	2.339071554	22.634788413
H	15.973990279	3.257073557	23.041668274
H	17.307174914	2.633193326	22.074703252
H	16.729549747	1.718891626	23.482400063
C	13.653875052	1.008571330	22.592436325
H	13.150999452	1.889724762	23.003245197
H	13.962772337	0.387773090	23.442635946
H	12.913746005	0.440596997	22.018052650
C	15.920883203	-0.233492796	20.984148276
H	16.507435595	-0.742634523	21.758175249
H	15.085436610	-0.885497719	20.701574063
C	17.071841918	-1.543371917	18.611952569
C	18.621040591	0.348161095	20.084522403
C	13.383698245	4.598391840	21.520127790
H	14.339770868	5.081457901	21.750164904
H	13.067873413	4.045413013	22.410392301
H	12.642777696	5.389953686	21.352400803
C	11.802534827	2.789497975	19.620178826

H	11.813791884	2.132644364	18.743562589	H	16.089163479	-1.885056698	18.276061382
H	11.058148952	3.576543493	19.447187851	H	17.507347899	-2.296302215	19.278505823
H	11.456092867	2.186784232	20.467256369	H	18.661648968	1.251139002	20.697784366
C	14.002041785	4.681978324	18.539824360	H	19.296327724	0.486996349	19.234596103
H	13.172832482	5.278921335	18.141721167	H	18.966487563	-0.506638496	20.677375290
H	14.762873965	5.368645140	18.930533426	H	12.944144945	4.145019139	15.704735056
C	15.809467733	4.821028279	16.220939482	H	12.698894121	2.612363274	16.583339650
H	15.191156467	5.635047777	15.826109848	H	13.839575294	2.677428412	15.233162161
C	13.437177827	3.240931837	16.080496070	H	16.261199831	4.281790719	15.381461646
H	17.715485641	-1.436629721	17.732175782	H	16.614845029	5.243148725	16.828023805

Optimized structure of PNP-Rh-N_2O N-end on linear (singlet)



2

ΔE(SCF): -25.5 kcal/mol
ΔG(gas): -14.8 kcal/mol

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

	2
N1-N2	1.140
N2-O1	1.209
N1-N2-O1	179.75
Rh1-N1	1.985
Rh1-N3	2.117
Rh1-P1	2.336
Rh1-P2	2.359

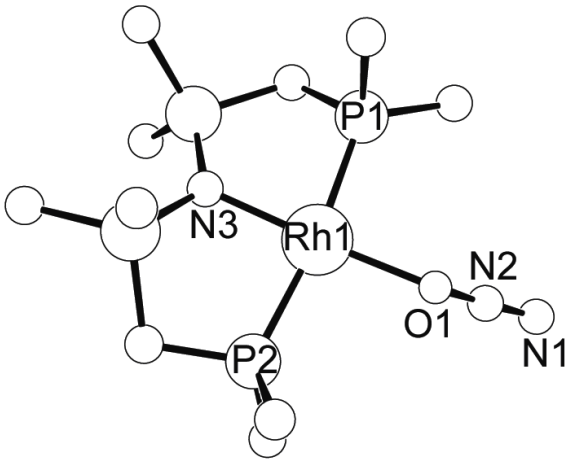
N3-Rh1-O1	178.58
P1-Rh1-P2	170.80
Rh1-N1-N2	178.81

Coordinates of 2

47

N	0.372681437	0.032216428	-0.738343025
Rh	1.456182821	0.042137444	2.192113818
P	1.683101911	2.363317296	2.326663776
N	2.202699439	0.115606130	4.172073935
P	1.415435577	-2.308377033	2.384080613
Si	3.159305819	-1.259648320	4.585309784
C	2.124920358	-2.771997636	4.016814668
Si	1.671925508	1.406482078	5.189709540
C	1.145468318	2.836604195	4.015192276
C	-0.203989147	-3.197607051	2.256036018
C	2.447709401	-3.242966592	1.163655092
H	2.416873771	-4.320786158	1.356884662
H	2.084872966	-3.052636960	0.149502210
H	-0.084555889	-4.273163077	2.425342955
H	-0.894897251	-2.790301090	2.998719762
C	3.427986795	2.959207373	2.217942308
C	0.814143583	3.516386027	1.166770959
H	4.038028440	2.380575179	2.914637625
H	3.505018481	4.025338542	2.458801941
H	1.160343757	3.344418813	0.142714324
H	1.000346019	4.562525352	1.431035038
H	-0.262231882	3.326586014	1.202285443
H	3.809982170	2.790459409	1.207167362
H	-0.636734261	-3.037453734	1.263661557
H	3.482529312	-2.898213087	1.225651026
C	0.166489770	0.986627819	6.267647007
H	-0.664541663	0.632076926	5.647308547
H	0.401101260	0.194263684	6.988223115
H	-0.183154272	1.856810580	6.837386831
C	3.012150569	2.106128708	6.344454085
H	3.315096774	1.386969786	7.112098068
H	3.911573527	2.395424281	5.788961896
H	2.642136212	2.998153840	6.864832436
C	4.832069512	-1.307030648	3.689314796
H	5.371883527	-2.245730346	3.866242612
H	4.704479604	-1.181586386	2.608403620
H	5.473380317	-0.487428606	4.034898375
C	3.515150126	-1.488471890	6.438765034
H	2.605429412	-1.436810240	7.047123800
H	4.215580136	-0.737250744	6.818308797
H	3.971096864	-2.471093255	6.611609189
H	1.533504762	3.817849884	4.315143351
H	0.050587623	2.899094607	3.999680612
H	1.296770730	-2.877822490	4.728340946
H	2.656918624	-3.729045173	3.971457709
N	0.767684488	0.020789191	0.330964338
O	-0.049328615	0.040121203	-1.871113716

Optimized structure of PNP-Rh-ON_2 O-end-on (singlet)



073

ΔE(SCF): -7.4 kcal/mol
ΔG(gas): 5.1 kcal/mol

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

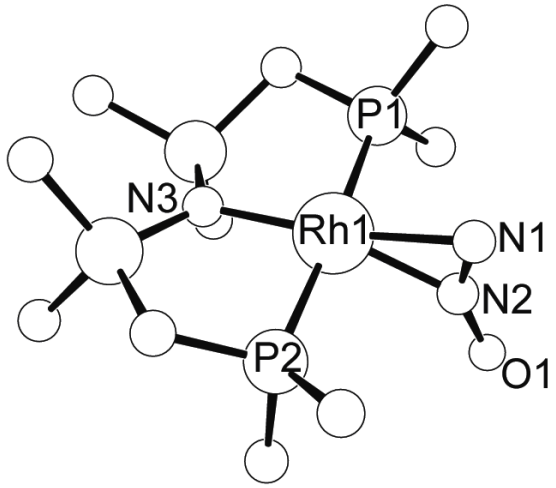
	073
N1-N2	1.139
N2-O1	1.204
N1-N2-O1	173.18
Rh1-O1	2.155
Rh1-N3	2.108
Rh1-P1	2.356
Rh1-P2	2.346
N3-Rh1-O1	175.35
P1-Rh1-P2	172.10
Rh1-O1-N2	135.02

Coordinates of 073

47

N	0.188334854	0.175076056	-0.499475524
Rh	1.582809018	-0.076326752	2.285494127
P	1.681131493	2.255496430	2.395290369
N	2.169755224	0.000399959	4.308262626
P	1.531079680	-2.422301091	2.495831747
Si	3.092456812	-1.369621909	4.817395205
C	2.099507283	-2.882207456	4.185403264
Si	1.769275847	1.373281245	5.281287917
C	1.115936948	2.718230748	4.077515231
C	-0.089738847	-3.294403499	2.261121755
C	2.638103043	-3.411296770	1.384205078
H	2.548618093	-4.486759299	1.575166399
H	2.386394968	-3.214910126	0.337668245
H	-0.001206880	-4.371670094	2.442263923
H	-0.821531335	-2.871475532	2.954184690
C	3.379897964	2.980625053	2.280056661
C	0.737471983	3.351414246	1.230371469
H	4.033605780	2.452829833	2.977917104
H	3.385300429	4.051266916	2.515367982
H	1.090223083	3.202396330	0.204412312
H	0.857500451	4.409348499	1.488189445
H	-0.325714390	3.098046296	1.272387080
H	3.773187836	2.833668857	1.270089432
H	-0.457042126	-3.138038310	1.241633607
H	3.674635136	-3.105254825	1.546517796
C	0.401655475	1.062069171	6.564599173
H	-0.496653287	0.658942703	6.083376521
H	0.719590699	0.341370957	7.326383543
H	0.119327022	1.985702366	7.086345953
C	3.237622124	2.148452327	6.216316812
H	3.662468173	1.466574372	6.959880330
H	4.046769223	2.431548621	5.533172435
H	2.923022415	3.053792542	6.750595603
C	4.840034612	-1.436849939	4.075656264
H	5.360700042	-2.373295002	4.313835768
H	4.809069552	-1.326647825	2.986046496
H	5.449121204	-0.612448868	4.465383967
C	3.288909733	-1.580220318	6.698380121
H	2.326330682	-1.569737291	7.220566688
H	3.920674312	-0.805012245	7.144053137
H	3.767753526	-2.544044892	6.911803320
H	1.417951894	3.736494007	4.353803653
H	0.019875885	2.681224798	4.072789846
H	1.218284330	-2.980704863	4.830568385
H	2.630055346	-3.841265286	4.188381946
O	1.145220008	-0.105531641	0.176081376
N	-0.628653255	0.464019967	-1.238600172

Optimized structure of PNP-Rh-N_2O η^2-N_2O (singlet)



3

ΔE(SCF): -22.0 kcal/mol
ΔG(gas): -7.6 kcal/mol

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

	3
N1-N2	1.200
N2-O1	1.235
N1-N2-O1	145.97
Rh1-N1	2.192
Rh1-N2	2.062
Rh1-N3	2.080
Rh1-P1	2.373
Rh1-P2	2.348
N3-Rh1-N1	168.73
P1-Rh1-P2	175.75
N1-Rh1-N2	32.57

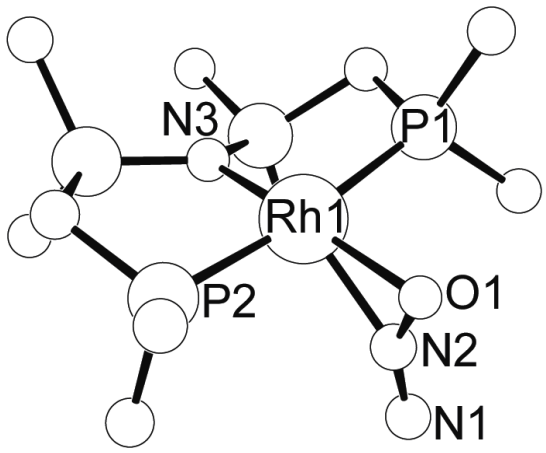
Coordinates of 3

47

N	1.540018354	0.137534853	0.110970336
Rh	1.421284921	0.038418397	2.167466399
P	1.485187795	2.383702343	2.265782927
N	2.056627085	0.048472322	4.147936236
P	1.478931163	-2.333313374	2.194459747
Si	2.887213126	-1.390998867	4.669625708
C	1.927149250	-2.857143438	3.896773767
Si	1.892937662	1.479617095	5.128778668
C	1.173680147	2.860978806	4.006634553
C	-0.071835012	-3.221290260	1.728158220
C	2.736011173	-3.129205870	1.098574466
H	2.702036961	-4.220666212	1.183363680
H	2.549092513	-2.843143712	0.059938211

H	0.053261247	-4.307714436	1.783567929
H	-0.877446107	-2.913277917	2.399639175
C	3.137905771	3.082982744	1.836671266
C	0.339312758	3.373556790	1.209262694
H	3.893636311	2.657174065	2.501219258
H	3.153620161	4.175135605	1.920233284
H	0.545172351	3.166927700	0.155115240
H	0.455542320	4.446419568	1.393865302
H	-0.691810648	3.078168517	1.418885094
H	3.383800492	2.788023540	0.812732300
H	-0.351608073	-2.935875908	0.710044571
H	3.734057677	-2.778797782	1.371353621
C	0.680245498	1.267432815	6.571841403
H	-0.288505199	0.905229151	6.209331899
H	1.044514003	0.550807542	7.315062035
H	0.511484526	2.220588143	7.088262860
C	3.539134296	2.121510338	5.832921135
H	4.014664802	1.392658625	6.498379739
H	4.255310984	2.347096649	5.034439119
H	3.389182299	3.039974199	6.413679327
C	4.688480223	-1.447481477	4.077897958
H	5.171120112	-2.405836788	4.304848018
H	4.759440205	-1.274319822	2.998498734
H	5.273690916	-0.659710676	4.566816381
C	2.894805686	-1.670065396	6.549113163
H	1.879130224	-1.741937885	6.952328912
H	3.414902677	-0.875115854	7.094270867
H	3.410541970	-2.609548129	6.782046818
H	1.556916095	3.860978734	4.242662487
H	0.085445472	2.878978663	4.143035127
H	0.997127153	-2.968871984	4.467540346
H	2.452319449	-3.818898936	3.912891978
N	0.361109853	-0.035085450	0.250249056
O	2.457506328	0.335653312	-0.691273832

Optimized structure of PNP-Rh-ON_2 η^2-ON_2 (singlet)



5

ΔE(SCF): -13.9 kcal/mol
ΔG(gas): -0.4 kcal/mol

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

	5
N1-N2	1.162
N2-O1	1.307
N1-N2-O1	144.13
Rh1-O1	2.188
Rh1-N2	2.103
Rh1-N3	2.080
Rh1-P1	2.371

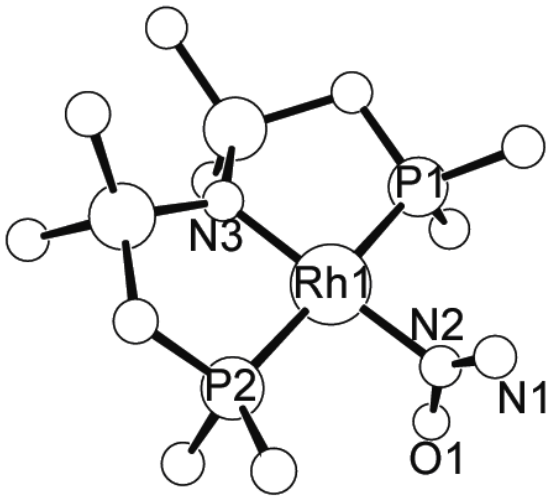
Rh1-P2	2.348
N3-Rh1-O1	175.34
P1-Rh1-P2	172.64
N2-O1-Rh1	68.73

Coordinates of 5

47

N	2.406739372	0.093897385	0.249737955
Rh	1.465817292	0.049923151	2.129552186
P	1.366775793	2.392578782	2.260577151
N	1.943174274	0.038677892	4.154018533
P	1.335199876	-2.316798228	2.196005632
Si	2.798067524	-1.399760190	4.629689430
C	1.783319263	-2.851392245	3.899252205
Si	1.761045332	1.469819586	5.124132362
C	0.941538069	2.790096987	4.000708627
C	-0.327370266	-3.032714783	1.823221975
C	2.437728372	-3.283267565	1.073657184
H	2.300437039	-4.360341615	1.215712679
H	2.209016710	-3.025922062	0.035852102
H	-0.326453472	-4.122909331	1.929823661
H	-1.065256745	-2.604446855	2.506699303
C	2.930766329	3.311145287	1.917492370
C	0.144173410	3.266581640	1.186717427
H	3.724895061	2.931507730	2.564484594
H	2.810526145	4.387016044	2.084294530
H	0.359228464	3.038325119	0.138907943
H	0.175239903	4.350402693	1.339690692
H	-0.859766024	2.898147028	1.413994509
H	3.230147435	3.137470305	0.880302524
H	-0.612368706	-2.767473001	0.801031264
H	3.480849576	-3.023812252	1.268112625
C	0.617711544	1.233683288	6.619935885
H	-0.351121926	0.825481173	6.310591177
H	1.045751126	0.547852963	7.358575921
H	0.434227832	2.188942195	7.127455347
C	3.401742598	2.185186779	5.768705812
H	3.908141083	1.486406628	6.444259243
H	4.097263807	2.404377995	4.950864232
H	3.239659710	3.115104315	6.327654894
C	4.554061779	-1.474513220	3.920193524
H	5.039430419	-2.439257390	4.112173435
H	4.551867566	-1.298613171	2.838918733
H	5.180275431	-0.694417893	4.368620500
C	2.918596235	-1.666309785	6.506155954
H	1.931427659	-1.720071904	6.977050620
H	3.486000216	-0.874260532	7.007006377
H	3.435885995	-2.611191445	6.712070104
H	1.199296485	3.821623862	4.269473200
H	-0.146253431	2.682737812	4.095590886
H	0.861078708	-2.939819599	4.485966198
H	2.283347737	-3.826289286	3.904604271
O	1.132767058	0.017637524	-0.032737904
N	3.470926938	0.158982423	-0.211388811

Optimized structure of PNP-Rh-N_2O η_1-N_2O (triplet)



^{3}7a

ΔE(SCF): 0.0 kcal/mol
ΔG(gas): 12.4 kcal/mol

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

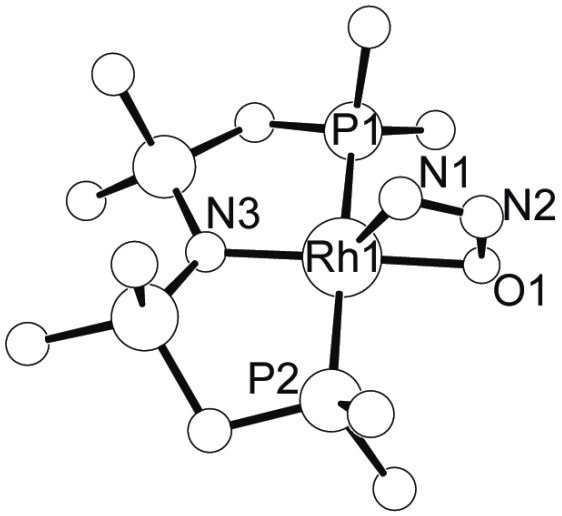
	^{3}**7a**		**Spin Densities**
N1-N2	1.203	Rh1	0.86
N2-O1	1.290	N1	0.73
N1-N2-O1	135.02	O1	0.19
Rh1-O1	2.653	N3	0.19
Rh1-N1	2.922		
Rh1-N3	2.079		
Rh1-P1	2.367		
Rh1-P2	2.358		
Rh1-N2-N1	123.64		
Rh2-N2-O1	101.33		
N3-Rh1-N2	175.89		
P1-Rh1-P2	176.21		

Coordinates of ^{3}7a

47

N	0.771183810	0.070466879	0.232185010
Rh	1.506309434	0.040270317	2.175997522
P	1.559118765	2.396984968	2.237918269
N	2.104797447	0.046258047	4.167338665
P	1.606336901	-2.324141274	2.146984744
Si	2.884281223	-1.417294404	4.724261970
C	1.976924652	-2.866806768	3.863858177
Si	1.990841040	1.511117291	5.117286719
C	1.280338940	2.885618685	3.982933040
C	0.118541455	-3.258678353	1.579802614
C	2.948879364	-3.028575348	1.094612931
H	2.935778486	-4.123630410	1.109902216
H	2.813420487	-2.673110329	0.069532981
H	0.283809970	-4.340614028	1.618065697
H	-0.733612633	-2.998232402	2.212571967
C	3.212145226	3.076290785	1.780169762
C	0.411727715	3.390520369	1.189848461
H	3.980665872	2.637577874	2.421291173
H	3.240675067	4.167435179	1.874529495
H	0.615940094	3.172390694	0.137814809
H	0.535759108	4.463813545	1.367889872
H	-0.620601776	3.102374586	1.403041044
H	3.427494306	2.792106278	0.746588011
H	-0.119819818	-2.959775927	0.555344934
H	3.919955866	-2.675168041	1.449014163
C	0.796579049	1.353960010	6.580933922
H	-0.183902436	0.999563175	6.243483471
H	1.158394599	0.655572456	7.342055154
H	0.652485045	2.326669837	7.067110039
C	3.669309785	2.102073666	5.783992411
H	4.109825475	1.373217082	6.473797913
H	4.392316014	2.265339502	4.977126321
H	3.563644021	3.045373519	6.333477436
C	4.719655253	-1.460119248	4.250273392
H	5.179799351	-2.426607389	4.488310532
H	4.863417299	-1.266714749	3.181727408
H	5.274899407	-0.687189333	4.793958877
C	2.763307223	-1.717619887	6.595080079
H	1.722650402	-1.749803159	6.934700866
H	3.281728770	-0.949488186	7.179379649
H	3.224443712	-2.680280804	6.846782835
H	1.672637450	3.884443420	4.209274450
H	0.193902975	2.913620448	4.132509492
H	1.018119116	-2.999138321	4.380397529
H	2.510591350	-3.823769105	3.894293726
N	-0.395158079	-0.041927494	-0.041069685
O	1.854305570	0.247863243	-0.445735146

Optimized structure of PNP-Rh-N_2O κ^2-N_2O (singlet)



4

ΔE(SCF): -18.8 kcal/mol
ΔG(gas): -5.5 kcal/mol

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

	4
N1-N2	1.231
N2-O1	1.384
N1-N2-O1	108.94
Rh1-O1	2.113
Rh1-N1	1.999
Rh1-N3	2.096
Rh1-P1	2.355
Rh1-P2	2.369
N3-Rh1-O1	179.09
P1-Rh1-P2	176.01
N1-Rh1-O1	62.28

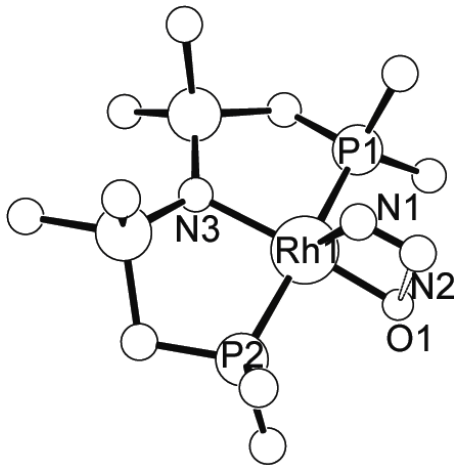
Coordinates of 4

47

N	2.419388228	0.112225738	-0.034521059
Rh	1.473287008	0.026995102	2.292313426
P	1.311722910	2.375357919	2.377736045
N	1.881522662	-0.014862982	4.347695234
P	1.472359742	-2.340948304	2.229192669
Si	2.649737913	-1.493124477	4.858070654
C	1.707492136	-2.905495314	3.961313379
Si	1.963428049	1.493244191	5.213839404
C	1.050990444	2.801471387	4.142258211
C	-0.054896288	-3.128323377	1.559749197

C	2.804369572	-3.140559458	1.240894657
H	2.729937233	-4.231581164	1.294926475
H	2.714183565	-2.819325440	0.200278289
H	0.015069616	-4.220799482	1.582151483
H	-0.920096349	-2.809220823	2.146528791
C	2.808191535	3.302253951	1.837202739
C	-0.033257310	3.150293426	1.383695962
H	3.675383158	2.965074156	2.408555101
H	2.677062313	4.381053569	1.971483525
H	0.097421724	2.852140227	0.339920486
H	-0.018629506	4.241976292	1.465172411
H	-1.000875596	2.773416440	1.724920853
H	2.995970955	3.084402309	0.783034871
H	-0.193407876	-2.787845251	0.529897666
H	3.780791883	-2.821905806	1.610304528
C	1.061640777	1.457035957	6.882066804
H	0.032803113	1.099603039	6.762088033
H	1.556253137	0.804858698	7.608592307
H	1.019208274	2.462547153	7.318329889
C	3.735215942	2.107415115	5.525097360
H	4.265742229	1.440866460	6.215505926
H	4.321046824	2.141706649	4.599984042
H	3.745536917	3.109999917	5.969652832
C	4.476333233	-1.579455522	4.354575091
H	4.904009455	-2.576644529	4.515422762
H	4.608213168	-1.311692042	3.300807017
H	5.070431496	-0.868659893	4.940473126
C	2.540198951	-1.833412723	6.721633187
H	1.507169010	-1.794371261	7.082735745
H	3.127035911	-1.117058965	7.307365265
H	2.935369588	-2.831955935	6.944490536
H	1.332881368	3.835827211	4.371953763
H	-0.022767263	2.695597208	4.342840260
H	0.716652763	-2.985425941	4.425228811
H	2.189449540	-3.888164036	4.018584067
O	1.061523534	0.035578797	0.219350816
N	3.025422091	0.131392158	1.036289411

Optimized structure of TS to liberate N_2 from PNP-Rh-N_2O κ^2-N_2O (singlet)



^{1}TS$_{4\text{-}6}$

ΔE(SCF): -0.2 kcal/mol
ΔG(gas): 10.5 kcal/mol ν_{N-O}=-345 cm^{-1}

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

	^{1}TS$_{4\text{-}6}$
N1-N2	1.143
N2-O1	2.119
N1-N2-O1	91.99
Rh1-O1	1.925

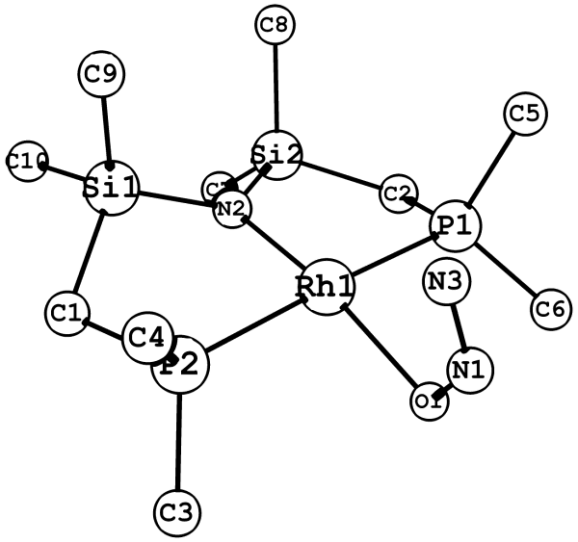
Rh1-N1	2.061
Rh1-N3	2.204
Rh1-P1	2.367
Rh1-P2	2.377
N3-Rh1-O1	172.93
P1-Rh1-P2	173.27
N1-Rh1-O1	75.49

Coordinates of $^{1}TS_{4\text{-}6}$

47

N	0.109250735	-0.013857535	-0.066141484
O	0.015357510	0.002640575	2.050893404
Rh	1.933894156	-0.001140447	1.890304369
P	2.020830630	2.362305282	1.979736444
N	4.136105233	-0.020951165	1.977618501
P	1.939930665	-2.371546747	2.063601848
Si	4.817287079	-1.546963871	1.570744009
C	3.672986224	-2.883863808	2.365063309
Si	4.951060358	1.486033232	2.127944343
C	3.644435600	2.785963102	2.706082799
C	0.858921799	-3.023112703	3.404243128
C	1.365401466	-3.309402380	0.585552741
H	1.393101846	-4.387968680	0.771567907
H	0.340049552	-3.010631010	0.351654138
H	0.850699325	-4.117520834	3.422301073
H	1.207344534	-2.647454114	4.369800955
C	1.935907415	3.239144697	0.361297886
C	0.671904005	3.147824519	2.954691147
H	2.714231950	2.861185823	-0.305203724
H	2.065705548	4.318491740	0.490958443
H	-0.275653024	2.746017432	2.585430572
H	0.686223069	4.238833702	2.870121518
H	0.771304707	2.862750996	4.005144978
H	0.963569452	3.048240673	-0.100449035
H	-0.150008863	-2.638996065	3.230911981
H	1.999558894	-3.077803072	-0.273040415
C	6.313064667	1.540782303	3.451829073
H	5.931130011	1.197303664	4.420025554
H	7.167038547	0.906977944	3.191445947
H	6.691086258	2.562313073	3.583542758
C	5.725739008	2.125238480	0.510705054
H	6.547948987	1.471419762	0.195010345
H	5.001409522	2.142342384	-0.311494004
H	6.137609676	3.136091005	0.619723787
C	4.875350304	-1.884161582	-0.299866718
H	5.156102710	-2.919410561	-0.529999946
H	3.912387563	-1.676868836	-0.779654708
H	5.613415980	-1.229462140	-0.778222448
C	6.564435215	-1.872452517	2.243075276
H	6.614135771	-1.732860535	3.328229185
H	7.306903447	-1.206685235	1.788327083
H	6.875743940	-2.900866709	2.022443059
H	3.935830084	3.823793974	2.504159040
H	3.543619177	2.674012286	3.793308181
H	3.842865151	-2.844689834	3.448257514
H	3.867748620	-3.909022017	2.029150263
N	1.252683090	-0.016120664	-0.055055827

Optimized structure of PNP-Rh-N_2O η_1-N_2O (triplet)



$^{3}7_{b}$

ΔE(SCF): -3.1 kcal/mol
ΔG(gas): 5.1 kcal/mol

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

	$^{3}7_{b}$		**Spin Densities**
N1-N3	1.185	Rh1	0.92
N1-O1	1.373	N1	0.13
N3-N1-O1	125.42	O1	0.11
Rh1-O1	2.115	N3	0.66
Rh1-N1	2.868	N2	0.19
Rh1-N3	2.929		
Rh1-P1	2.348		
Rh1-P2	2.364		
Rh1-O1-N1	108.74		
N3-Rh1-N2	168.00		
P1-Rh1-P2	176.37		

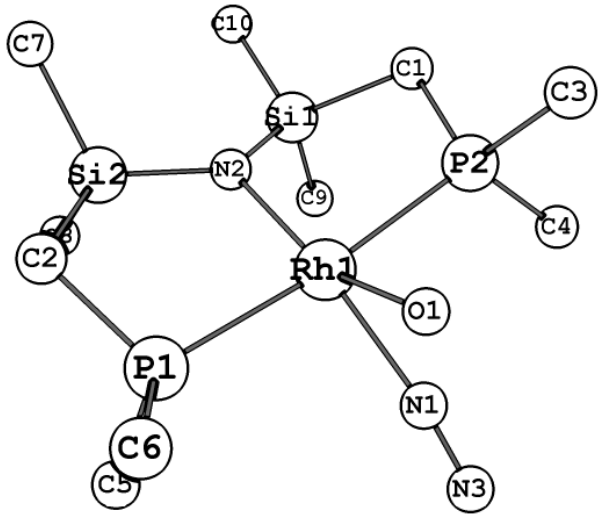
Coordinates of $^{3}7_{b}$

47

N	1.656373200	-0.065013112	-0.524272774
Rh	1.544097930	0.045219397	2.338952238
P	1.417883600	2.388517502	2.421570372
N	1.993770562	0.016818359	4.345821186
P	1.527290033	-2.318065462	2.296953210
Si	2.740600982	-1.470290803	4.898563721
C	1.788231150	-2.883519008	4.029492625
Si	1.929873194	1.496172179	5.282894553
C	1.115706194	2.832364902	4.179122387
C	-0.038701530	-3.066667758	1.673717541
C	2.815395166	-3.185980684	1.299605239
H	2.712129443	-4.273236287	1.384690884
H	2.715834785	-2.887811852	0.253344899
H	0.017602330	-4.158902061	1.627309974
H	-0.863656592	-2.771463183	2.327338909
C	2.933044013	3.322720608	1.931112921
C	0.097717304	3.185738884	1.411722716
H	3.782574993	2.987996323	2.531196772
H	2.798338140	4.401712092	2.064910226
H	0.216440167	2.872309749	0.371395483
H	0.132807021	4.277685315	1.481764364
H	-0.876435804	2.829061704	1.756193412
H	3.156000046	3.113917636	0.881410285
H	-0.234843754	-2.658389860	0.678527090

H	3.809608107	-2.889127577	1.640105889
C	0.852950782	1.353867479	6.836865428
H	-0.143098301	0.971949704	6.586489226
H	1.286931441	0.685439828	7.586767598
H	0.725532438	2.336805958	7.306996172
C	3.651469823	2.103803086	5.806348880
H	4.144104600	1.388662891	6.474974273
H	4.309631375	2.247327173	4.942321796
H	3.587207141	3.058840200	6.341956901
C	4.568844315	-1.548444717	4.404187236
H	5.014272017	-2.524142789	4.633425705
H	4.699968174	-1.353030031	3.334749447
H	5.145068285	-0.787375572	4.942472264
C	2.632882563	-1.762870235	6.770134674
H	1.598090713	-1.759000139	7.127485768
H	3.188050571	-1.010237500	7.341161304
H	3.066867565	-2.739023203	7.018386625
H	1.429961450	3.854789561	4.420834348
H	0.031669749	2.773123270	4.337869453
H	0.805656903	-2.964028026	4.509932487
H	2.273695382	-3.864538410	4.085596719
O	0.663277068	0.052090519	0.416173312
N	2.816496822	-0.133786685	-0.293143650

Optimized structure of TS PNP-Rh-(O)N_2 (singlet)



^{1}TS$_{3\text{-}6}$

ΔE(SCF): -14.2 kcal/mol

ΔG(gas): 12.4 kcal/mol ν_{N-O}=-196 cm^{-1}

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

	^{1}TS$_{3\text{-}6}$
N1-N3	1.132
N1-O1	1.815
N3-N1-Rh1	161.07
Rh1-N1	1.97

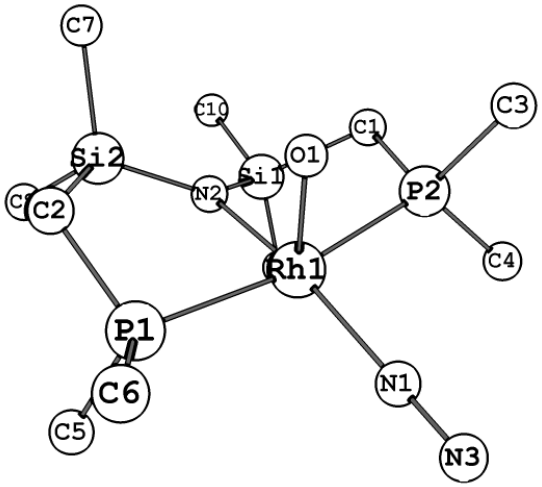
Rh1-N2	2.08
Rh1-P1	2.36
Rh1-P2	2.37
N2-Rh1-O1	146.63
P1-Rh1-P2	171.49
N2-Rh1-N1	159.86

Coordinates of $^{1}TS_{3\text{-}6}$

48

N	-0.127995445	-0.010587733	0.317704836
O	0.434705473	0.053410791	2.041878750
Rh	1.827306124	-0.010251370	0.523227538
P	1.905660440	2.350900847	0.482867308
N	3.843124091	-0.055756604	0.016924271
P	1.909170244	-2.354292825	0.875881324
Si	4.394086321	-1.593045246	-0.607779558
C	3.625754616	-2.922271104	0.533423784
Si	4.745774934	1.434970299	-0.092630161
C	3.669312386	2.788269833	0.732638358
C	1.456990203	-2.813475285	2.596280683
C	0.807710663	-3.409569497	-0.161280353
H	0.921480282	-4.468553466	0.092859507
H	-0.231011741	-3.111075954	0.004027869
H	1.318623333	-3.892754888	2.711864418
H	2.242587868	-2.466929283	3.272452493
C	1.390287410	3.232203898	-1.054614430
C	0.919364163	3.168943568	1.800743396
H	1.979842006	2.875215499	-1.902215077
H	1.522495520	4.314844395	-0.955283115
H	-0.141658400	2.975112118	1.625483401
H	1.103753626	4.247704783	1.827088294
H	1.175493276	2.710568718	2.757548539
H	0.336907475	3.017695433	-1.255139805
H	0.546475236	-2.258473729	2.836452493
H	1.042859287	-3.266767659	-1.218726967
C	6.387228585	1.420853759	0.856546138
H	6.238739406	1.087500327	1.889748835
H	7.132232302	0.763646954	0.398031706
H	6.816226643	2.430039036	0.890174409
C	5.112553887	1.944244428	-1.886053317
H	5.777530240	1.220857146	-2.372628463
H	4.199009039	1.996743002	-2.488641951
H	5.605870535	2.922456971	-1.935174887
C	3.788807305	-1.897967591	-2.378511746
H	4.060529459	-2.897341410	-2.739563307
H	2.700619704	-1.792012046	-2.449436935
H	4.226359839	-1.166719235	-3.067880812
C	6.276409588	-1.835420400	-0.598798640
H	6.701309329	-1.711179703	0.402582248
H	6.788390606	-1.135707069	-1.268908755
H	6.522621736	-2.847552133	-0.942005378
H	3.900546385	3.807708678	0.401606541
H	3.856376946	2.737634927	1.812700036
H	4.177831034	-2.916564026	1.480773747
H	3.654290356	-3.941701221	0.133097768
N	-1.154559822	-0.024565732	-0.159115640

Optimized structure of PNP-Rh-(O)N_2 (triplet)



^{3}7c

ΔE(SCF): -18.9 kcal/mol
ΔG(gas): -8.6 kcal/mol

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

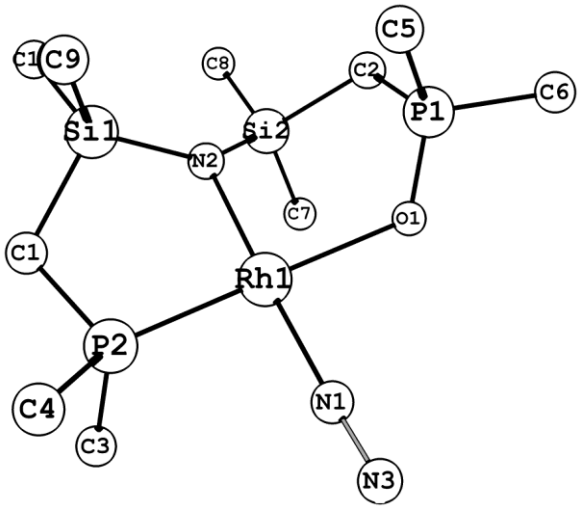
	^{3}**7c**		
N1-N3	1.117	Rh1-O1	2.135
N1-O1	2.981		**Spin Densities**
N3-N1-Rh1	179.50	O1	1.28
Rh1-N1	2.011	Rh1	0.70
Rh1-N2	2.121		
Rh1-P1	2.355		
Rh1-P2	2.376		
N2-Rh1-O1	100.26		
P1-Rh1-P2	170.09		
N2-Rh1-N1	167.78		

Coordinates of ^{3}7$_c$

47

N	0.145151022	-0.039048142	-0.217324036
O	-0.037046301	-0.033240558	2.757689782
Rh	1.496329729	-0.037869626	1.272560404
P	1.418799004	2.291459364	1.611302565
N	3.219350954	0.010899244	2.508150372
P	1.626513566	-2.409328033	1.337226091
Si	4.260992550	-1.346885757	2.266578882
C	3.092053538	-2.865698739	2.345754449
Si	3.401457350	1.282631978	3.670610235
C	1.958638749	2.498644885	3.343185963
C	0.134419610	-3.161867943	2.105778713
C	1.840111251	-3.343062943	-0.243808748
H	1.872770095	-4.422788734	-0.063637834
H	1.008373161	-3.121174013	-0.918430062
H	0.328558360	-4.176035643	2.467051452
H	-0.171375172	-2.495352430	2.916826325
C	2.509836673	3.385951246	0.601966844
C	-0.245278759	3.067252181	1.474274437
H	3.536766803	3.016710270	0.651266874
H	2.481666303	4.421076621	0.958986108
H	-0.574682887	3.080220818	0.430666576
H	-0.244273864	4.090462505	1.862874303
H	-0.929151202	2.445203381	2.057137190
H	2.186913538	3.361445532	-0.442888463
H	-0.676579197	-3.186917761	1.371242401
H	2.769616650	-3.035537068	-0.729430504
C	3.245302071	0.723912670	5.476742896
H	2.316994998	0.160893744	5.623763781
H	4.078604334	0.081927431	5.782548990
H	3.228371514	1.584531882	6.156993738
C	5.037740979	2.239107095	3.511450089
H	5.901432990	1.599016314	3.723120027
H	5.175651446	2.648220831	2.504445810
H	5.074664200	3.075931774	4.220061202
C	5.130547599	-1.338209456	0.579614216
H	5.675795880	-2.271358371	0.390926938
H	4.418880980	-1.185478456	-0.239606940
H	5.854863737	-0.516618424	0.531526334
C	5.607117777	-1.584794060	3.584356905
H	5.185921327	-1.696207718	4.588702906
H	6.315884139	-0.749995212	3.608460242
H	6.184844857	-2.491004999	3.365583529
H	2.176807726	3.543858627	3.591388606

Optimized structure of PNP=O-Rh-N_2 (singlet)



6b

ΔE(SCF): -99.7 kcal/mol
ΔG(gas): -84.9 kcal/mol

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

	6b
N1-N3	1.122
N1-O1	2.841
N3-N1-Rh1	177.53
Rh1-N1	1.936
Rh1-N2	2.124
Rh1-P1	2.221
Rh1-P2	2.251
N2-Rh1-O1	92.10
P1-Rh1-P2	179.03
Rh1-N1-N3	177.54

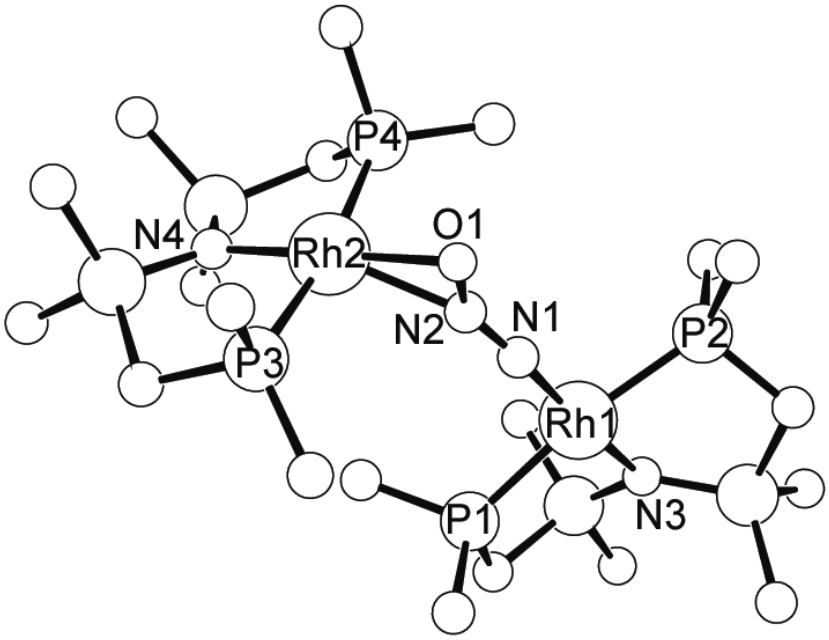
Coordinates of $6b_c$

47

N	-0.514217529	-0.868274126	0.830096293
O	0.513236632	1.629369408	1.713289677
Rh	1.204599712	-0.479743277	1.632975969
P	1.472875881	2.814813737	1.565332419
N	3.088623957	0.023933495	2.474315203
P	1.889183956	-2.621379719	1.517090008
Si	4.356673215	-0.972368530	1.875157634
C	3.655876217	-2.752966030	2.013060232
Si	2.988386697	1.200293879	3.718544858
C	2.609177777	2.956431841	2.964271513
C	0.965151034	-3.854624226	2.539781311
C	1.819370734	-3.395141241	-0.161080251
H	2.171539200	-4.431908362	-0.133464675
H	0.790426820	-3.375396099	-0.531141599
H	1.394019291	-4.857769175	2.440133310
H	1.004404052	-3.546273941	3.587287177
C	2.480992714	2.727969338	0.048326307
C	0.510513357	4.363182423	1.422805177
H	3.112807701	1.839419066	0.106593342
H	3.107317217	3.619077502	-0.060835108
H	-0.138318370	4.314624522	0.543949204
H	1.171214996	5.231373193	1.338094244
H	-0.115623716	4.475175659	2.312023091
H	1.821474242	2.638012708	-0.818997199
H	-0.083384421	-3.878484698	2.228520774
H	2.441476666	-2.821327956	-0.852013894
C	1.593062975	0.866041608	4.953002908
H	0.632093158	0.789342784	4.435646090
H	1.767983052	-0.082881283	5.473506794
H	1.517998219	1.654552041	5.712708044
C	4.578254617	1.486656474	4.716947229
H	4.870253187	0.595715578	5.282539171

H	5.426065654	1.771285218	4.085711399
H	4.418594030	2.295310125	5.440655745
C	4.777245190	-0.646221489	0.050267179
H	5.480980141	-1.387899472	-0.348060763
H	3.876340490	-0.661824226	-0.572921516
H	5.242307410	0.340018615	-0.070763068
C	6.006001348	-0.938914451	2.814818914
H	5.887441427	-1.190861506	3.873445268
H	6.497486964	0.038069373	2.758649199
H	6.691790179	-1.672639136	2.373745720
H	3.537901676	3.441854461	2.642074749

Optimized structure of $(PNP\text{-}Rh)_2\text{-}N_2O$ $\mu_2\text{-}N_2O$ (singlet)

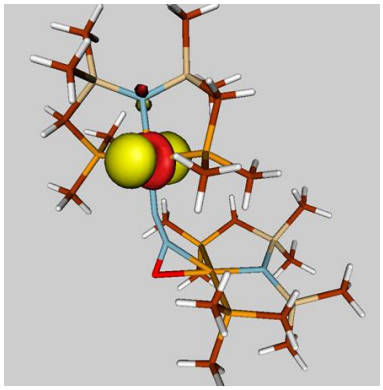


^{1}8

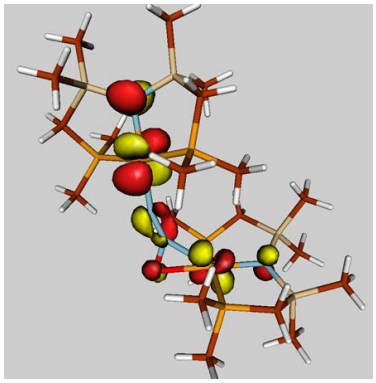
ΔE(SCF): -42.7 kcal/mol
ΔG(gas): -14.6 kcal/mol
Selected bond lengths (in Å) and bond angles (in °):

	^{1}8		**NPA Charges**
N1-N2	1.173	N4	-1.563
N2-O1	1.310	Rh2	0.132
N1-N2-O1	139.18	O1	-0.471
Rh2-O1	2.188	N2	0.227
Rh1-N1	1.967	N1	-0.133
Rh1-N3	2.125	Rh1	-0.069
Rh1-P1	2.347	N3	-1.608
Rh1-P2	2.347		
Rh2-N4	2.098		
P3-Rh2-P4	170.09		
Rh1-N1-N2	161.71		
Rh2-O1-N2	72.52		
N3-Rh1-N1	176.47		
N4-Rh2-O1	178.77		
P1-Rh1-P2	169.71		

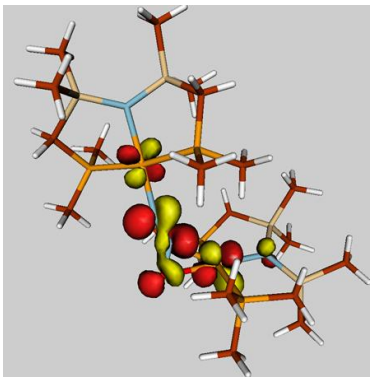
Isodensity MO Plots of ^{1}8



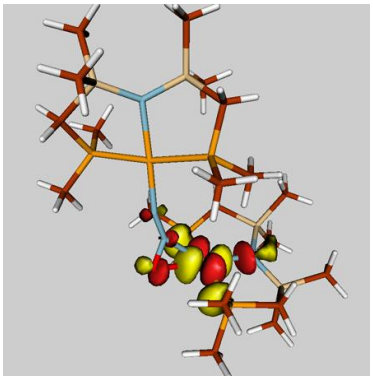
HOMO-1 = -4.427 eV



HOMO = -4.166 eV



LUMO = -1.705 eV



LUMO+1 = -0.570 eV

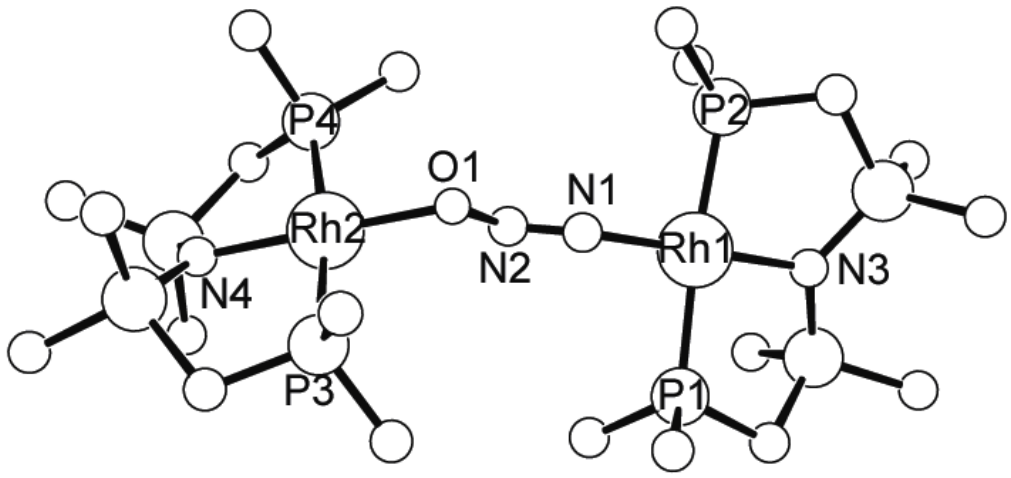
Coordinates of ^{1}**8**

91

Rh	0.057582675	-0.107528363	-2.871783922
P	1.508164791	1.067510776	-4.295062121
N	-1.390209121	0.530529306	-4.290458688
P	-1.673464486	-1.235810608	-1.758903062
Si	-2.896671963	0.858873025	-3.525608599
C	-3.288761105	-0.708329669	-2.485578943
Si	-0.937677037	0.391183726	-5.945699179
C	0.971528647	0.651101832	-6.003758772
C	-1.687875045	-3.087367236	-1.830040677
C	-1.859843054	-0.916867717	0.054360908
H	-2.662228145	-1.522144089	0.491192952
H	-0.917866546	-1.123484715	0.570949955
H	-2.560524166	-3.502818256	-1.313463000
H	-1.705764206	-3.401470869	-2.877176038
C	1.375101005	2.911168443	-4.233604277
C	3.342503521	0.811764448	-4.261082811
H	0.319707510	3.184256315	-4.303711162
H	1.931706438	3.381101159	-5.052343443
H	3.740565115	1.115321273	-3.288094930
H	3.843997368	1.384490365	-5.048672408
H	3.559446862	-0.251363211	-4.395971925
H	1.763736336	3.280702504	-3.280305333
H	-0.774927032	-3.482620226	-1.375713541
H	-2.093183734	0.141086540	0.202601024
C	-1.283384970	-1.315678627	-6.705983643
H	-0.798670472	-2.101195757	-6.114602446
H	-2.358590241	-1.531041266	-6.723679387
H	-0.914071233	-1.391507386	-7.736579671
C	-1.722939904	1.687377221	-7.095339545
H	-2.807240769	1.561022427	-7.178976123
H	-1.535540697	2.707321781	-6.740241556
H	-1.306116803	1.605957763	-8.106815846
C	-2.816900463	2.336774770	-2.335473494
H	-3.748642984	2.467137908	-1.770692170
H	-1.994388051	2.212363745	-1.621963219
H	-2.629677830	3.266641994	-2.886095811
C	-4.361690158	1.163375126	-4.697885699
H	-4.500336441	0.341731049	-5.409579373
H	-4.233900880	2.086015585	-5.274255236
H	-5.291483447	1.263635450	-4.124569769
H	1.293012617	1.408344031	-6.729833743

H	1.453973967	-0.296026654	-6.274244695
H	-3.633055522	-1.490724565	-3.172890162
H	-4.052455511	-0.585528950	-1.709025945
N	2.096526307	-0.660809836	-0.599952212
Rh	2.182247066	-0.441022792	1.573838426
P	2.584894404	1.860895718	1.391633004
N	1.098187236	0.041160042	3.304031170
P	1.976577981	-2.730554434	2.111654512
Si	1.029996978	-1.194198269	4.525171871
C	0.907404455	-2.866671159	3.598491843
Si	0.452984657	1.642723078	3.523567455
C	1.115372354	2.714380309	2.078377174
C	1.357063894	-3.977381308	0.894428579
C	3.590120421	-3.485227741	2.607924823
H	3.465690238	-4.530035320	2.913721029
H	4.278227961	-3.435978632	1.759385527
H	1.392786057	-4.989870195	1.310735625
H	0.325299847	-3.740616187	0.623997411
C	3.999886068	2.451320894	2.422953001
C	2.938211109	2.643208270	-0.243664081
H	3.874267585	2.095099680	3.448057528
H	4.065633344	3.545058499	2.425285787
H	3.854560985	2.213102989	-0.659320164
H	3.058175929	3.727509349	-0.149539727
H	2.112613733	2.425170460	-0.926634214
H	4.931562180	2.036002364	2.028449807
H	1.971573602	-3.938204218	-0.010034302
H	4.025270218	-2.919716165	3.434811653
C	-1.441703591	1.731580187	3.458805123
H	-1.821427728	1.263974609	2.543551550
H	-1.904737383	1.218661832	4.308622990
H	-1.788524832	2.772527227	3.473426901
C	1.006562798	2.470644513	5.146120277
H	0.664156924	1.918966212	6.028671305
H	2.098324743	2.541164940	5.210549129
H	0.602533206	3.487630017	5.224650111
C	2.568588841	-1.224396691	5.639715370
H	2.565675042	-2.079822018	6.326669677
H	3.491746162	-1.263023730	5.050791807
H	2.614987923	-0.313512266	6.248171003
C	-0.480627601	-1.093970703	5.675700325
H	-1.420755893	-1.138080819	5.115395671
H	-0.493993088	-0.177512298	6.275746820
H	-0.472254308	-1.936809738	6.377801579
H	1.325353167	3.752997562	2.362187306
H	0.358285456	2.729406535	1.284743350
H	-0.129079538	-2.964782827	3.252211526
H	1.145537879	-3.746476274	4.207745883
O	3.306306455	-0.989598664	-0.221476291
N	1.460426274	-0.597510067	-1.583657094

Optimized structure of $(PNP\text{-}Rh)_2\text{-}N_2O$ $\mu_2\text{-}N_2O$ TS ($\nu_{O1\text{-}N2}$= -357.7 cm^{-1}) (singlet)



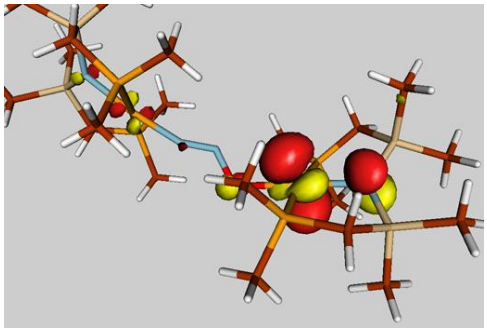
$^{1}TS_{8\text{-}6}$

ΔE(SCF): -38.9 kcal/mol
ΔG(gas): -16.0 kcal/mol

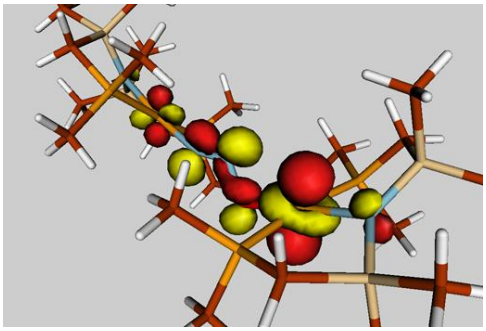
Selected bond lengths (in Å) and bond angles (in ˚):

	$^{1}TS_{8\text{-}6}$		**NPA Charges**
N1-N2	1.189	N4	-1.596
N2-O1	1.352	Rh2	0.186
N1-N2-O1	127.20	O1	-0.524
Rh2-O1	2.188	N2	0.152
Rh1-N1	1.925	N1	-0.174
Rh1-N3	2.096	Rh1	0.060
Rh1-P1	2.358	N3	-1.586
Rh1-P2	2.347		
Rh2-N4	2.129		
P3-Rh2-P4	171.58		
Rh1-N1-N2	158.55		
Rh2-O1-N2	115.11		
N3-Rh1-N1	174.31		
N4-Rh2-O1	178.84		
P1-Rh1-P2	174.97		

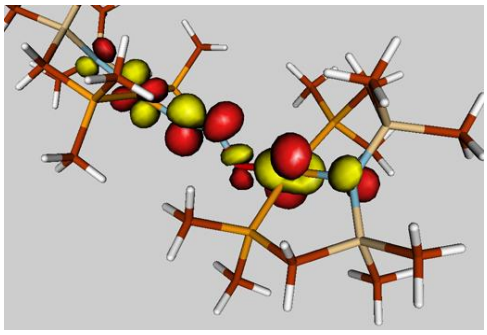
Isodensity MO Plots of $^{1}TS_{8\text{-}6}$



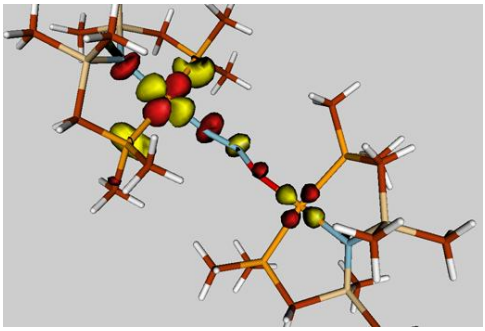
HOMO-1 = -4.564 eV



LUMO = -2.538 eV



HOMO = -3.790 eV



LUMO+1 = -0.153 eV

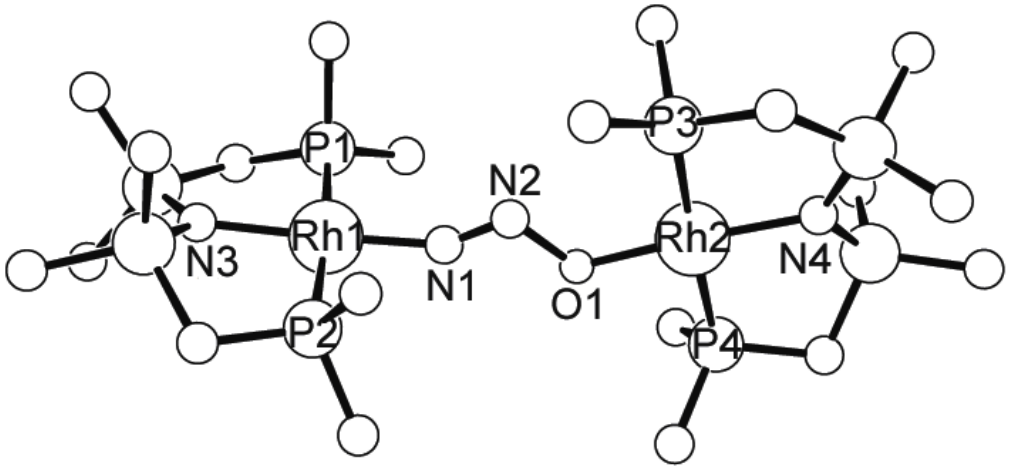
Coordinates of **$^{1}TS_{8\text{-}6}$**

91

N	0.106858452	-0.017374850	0.148261589
O	0.149703386	-0.013803000	1.499275874
Rh	1.979709631	-0.001382540	-2.274634367
P	2.371077197	2.310940030	-2.185169689
N	2.830274702	0.058710563	-4.189249567
P	1.703153513	-2.328907231	-2.535314526
Si	2.244331062	-1.181631644	-5.256521940
C	2.263810763	-2.797193562	-4.226947466
Si	3.855545954	1.379643542	-4.660394176
C	3.875698810	2.614033643	-3.191227180
C	2.608724118	-3.438046750	-1.364438362
C	-0.032797307	-2.955678097	-2.413319831
H	-0.075029489	-4.043655958	-2.537234098
H	-0.450887745	-2.681858372	-1.438496140
H	2.443867001	-4.493770323	-1.608478457
H	3.679607405	-3.218180434	-1.416771202
C	1.068488569	3.378675516	-2.945358699
C	2.647232785	3.139299983	-0.556897797
H	0.843358470	3.017509909	-3.951357254
H	1.388253804	4.425391690	-2.998666303
H	1.752043106	3.034821195	0.063362118
H	2.876084884	4.202874673	-0.684869289
H	3.476544822	2.650868436	-0.039320981
H	0.154847655	3.313036703	-2.347128631
H	2.270240230	-3.243907919	-0.341674008
H	-0.643594205	-2.484466919	-3.189652231
C	5.654921138	0.866386891	-4.978719503
H	6.062953430	0.334857332	-4.111835701
H	5.743310212	0.203284590	-5.846030536
H	6.290662622	1.740905140	-5.166879123
C	3.250519327	2.336247414	-6.190276381
H	3.216860299	1.704276395	-7.083839937
H	2.243036384	2.739537090	-6.039751533
H	3.914839450	3.179300637	-6.416186318
C	0.464586249	-0.874334855	-5.845884010
H	0.069404451	-1.717340925	-6.428464724
H	-0.207126451	-0.698220006	-4.997491844
H	0.418644814	0.017623514	-6.481711463
C	3.310907345	-1.489697575	-6.800886654
H	4.342314095	-1.754895677	-6.539301877
H	3.347694546	-0.621594182	-7.467944030
H	2.892289680	-2.323363179	-7.381071196
H	3.971622134	3.662833982	-3.497963173
H	4.735456608	2.370620903	-2.555199621
H	3.306166118	-3.137178494	-4.159710349
H	1.666299267	-3.619637363	-4.640477392

Rh	-1.648940465	-0.474253251	2.441644957
P	-2.743907692	1.535122310	1.979797985
N	-3.467969395	-0.975552850	3.428460240
P	-0.740784830	-2.507749512	3.191572884
Si	-3.224692437	-1.975872245	4.812997697
C	-1.990885983	-3.340596057	4.261439165
Si	-4.937223692	-0.444302345	2.694239820
C	-4.501528247	1.112362048	1.643114261
C	-0.190902494	-3.791424717	1.975113285
C	0.763188096	-2.337258866	4.254457562
H	1.132454677	-3.311163232	4.593103957
H	1.544001812	-1.829388776	3.681388920
H	0.177715253	-4.690855765	2.479323779
H	-1.029403360	-4.060185382	1.327347443
C	-2.826194706	2.674035562	3.433060034
C	-2.213955259	2.680872316	0.625811304
H	-3.195952952	2.112683492	4.294069431
H	-3.485124622	3.528280110	3.242318206
H	-1.193175509	3.022492563	0.822489647
H	-2.877123552	3.549345475	0.549635168
H	-2.213075793	2.138332905	-0.323140674
H	-1.823346179	3.040166733	3.668205118
H	0.607126373	-3.376427003	1.352375479
H	0.524428002	-1.722689892	5.125847105
C	-5.700477009	-1.717354072	1.505168645
H	-4.973273202	-2.009405030	0.738459777
H	-6.002641243	-2.629499950	2.035504427
H	-6.589157719	-1.323404956	0.998245397
C	-6.303025998	0.071316376	3.919135994
H	-6.684223940	-0.780083972	4.492060248
H	-5.944641096	0.821581491	4.635963139
H	-7.155379413	0.506876501	3.383085972
C	-2.453943197	-1.033954018	6.272974090
H	-2.185609974	-1.700370330	7.101584589
H	-1.551970618	-0.493079627	5.963004139
H	-3.159441752	-0.289923647	6.662643286
C	-4.777211398	-2.855857528	5.474493733
H	-5.310433363	-3.401539804	4.686833069
H	-5.483279056	-2.153006338	5.931038812
H	-4.498243705	-3.582645047	6.247458192
H	-5.173754206	1.960286546	1.821804900
H	-4.572962584	0.851365494	0.580335011
H	-2.552228581	-4.045450131	3.635186100
H	-1.523925783	-3.909569561	5.073437337
N	1.030361332	-0.022512111	-0.599969746

Optimized structure of $(PNP\text{-}Rh)_2\text{-}N_2O$ $\mu_2\text{-}N_2O$ (triplet)



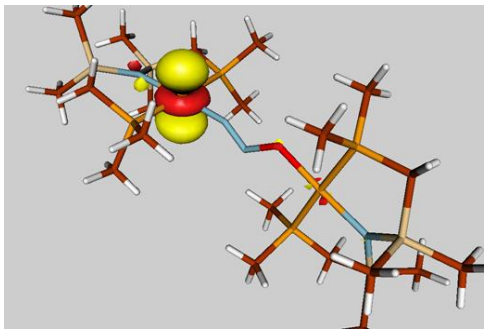
^{3}8

ΔE(SCF): -49.9 kcal/mol
ΔG(gas): -25.7 kcal/mol

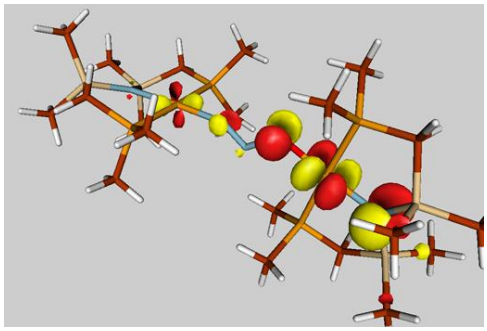
Selected bond lengths (in Å) and bond angles (in ˚):

	^{3}8		**NPA Charges**
N1-N2	1.202	N3	-1.595
N2-O1	1.450	Rh1	0.093
N1-N2-O1	113.22	N1	-0.222
Rh2-O1	1.988	N2	0.056
Rh1-N1	1.940	O1	-0.572
Rh1-N3	2.114	Rh2	0.294
Rh1-P1	2.342	N4	-1.556
Rh1-P2	2.355		**Spin Densities**
Rh2-N4	2.080	Rh1	0.492
P3-Rh2-P4	177.72	Rh2	0.760
Rh1-N1-N2	149.72	N1	0.367
Rh2-O1-N2	120.61	N2	-0.023
N3-Rh1-N1	177.17	O1	0.213
N4-Rh2-O1	171.35	N4	0.130
P1-Rh1-P2	175.38	N3	0.071

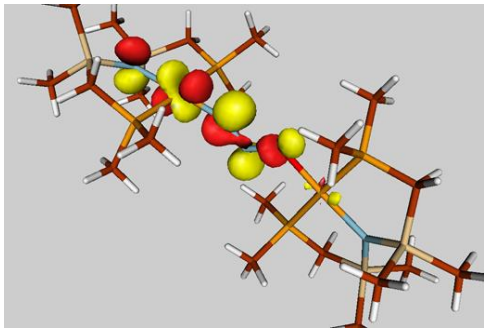
Isodensity MO Plots of ^{3}**8**



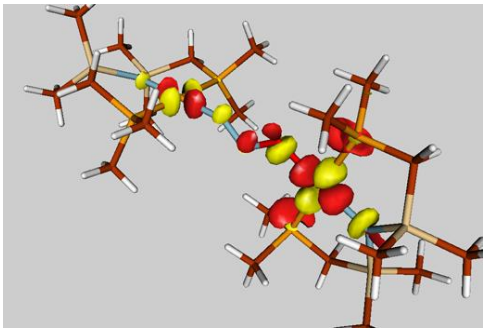
HOMO-2 = -4.997 eV



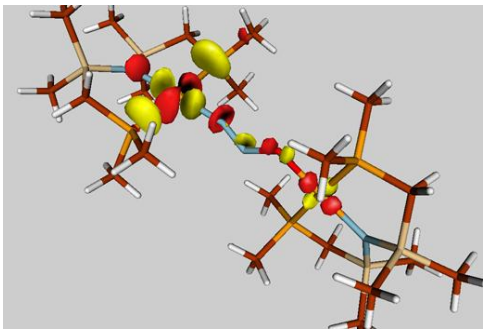
SOMO-1 = -4.940 eV



SOMO = -4.169 eV



LUMO = -0.266 eV



LUMO+1 = 0.109 eV

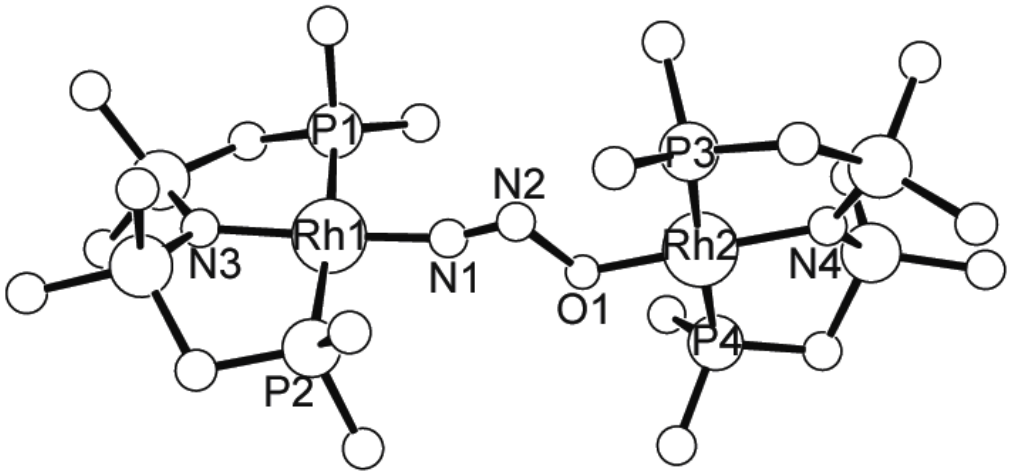
Coordinates of ^{3}**8**

91

Rh	-0.283033240	-0.167134388	-3.391526024
P	1.882686043	0.305894246	-4.147435504
N	-0.911349520	0.170251598	-5.381847131
P	-2.525780564	-0.566740531	-2.792984088
Si	-2.575854009	0.624744988	-5.553117318
C	-3.549705131	-0.470263990	-4.317362483
Si	0.230353452	0.095118585	-6.686148690
C	1.956749555	-0.214359757	-5.905996858
C	-2.920242766	-2.181229713	-1.982097837
C	-3.296895914	0.639562852	-1.622799472
H	-4.337115724	0.374872652	-1.401803034
H	-2.721600279	0.649831620	-0.693024793
H	-3.992813807	-2.279916210	-1.781866390
H	-2.596311224	-2.999004300	-2.631617169
C	2.334351031	2.098247578	-4.171635797
C	3.344789619	-0.448925479	-3.307009283
H	1.566139353	2.657769322	-4.710120943
H	3.305557290	2.261919839	-4.651593593
H	3.354104107	-0.148379289	-2.255054661
H	4.282985313	-0.143545716	-3.782437245
H	3.257283566	-1.538054199	-3.346327260
H	2.373000121	2.473849020	-3.145193700

H	-2.365551085	-2.251525229	-1.041962270
H	-3.266092144	1.642430178	-2.056266172
C	-0.073359396	-1.332919831	-7.902766640
H	-0.141940525	-2.288446740	-7.369588768
H	-1.002165839	-1.201527425	-8.467636783
H	0.745310288	-1.411866969	-8.629530236
C	0.342398285	1.695972458	-7.711140402
H	-0.609167381	1.930317188	-8.201797486
H	0.605598464	2.557478994	-7.086521713
H	1.100837170	1.611825353	-8.499642754
C	-2.892999800	2.448321405	-5.127180242
H	-3.961732551	2.695054109	-5.128182404
H	-2.482927294	2.703012916	-4.143685035
H	-2.401946067	3.101917742	-5.858125353
C	-3.326860115	0.316455429	-7.273476505
H	-3.263821101	-0.738305090	-7.561606469
H	-2.837164060	0.904917282	-8.057256247
H	-4.386669374	0.597307104	-7.275725111
H	2.780163481	0.263222954	-6.451458554
H	2.137331090	-1.296718977	-5.908691409
H	-3.597636636	-1.477186966	-4.750424588
H	-4.574592829	-0.142936673	-4.108984597
N	0.547298862	0.100532898	-0.479567279
Rh	1.369385545	-0.331140923	2.371814346
P	0.826625976	1.967943117	2.224417081
N	2.005342255	0.017137817	4.321418508
P	1.928877459	-2.601985788	2.608530583
Si	3.104265630	-1.178358636	4.963135018
C	2.480884771	-2.879302747	4.339551293
Si	1.634049918	1.514230560	5.138078121
C	0.554474524	2.549217303	3.950457967
C	0.599773612	-3.823689829	2.228665797
C	3.306391039	-3.188159243	1.531797347
H	3.484895487	-4.262241662	1.652025696
H	3.032858786	-2.974163182	0.495562499
H	0.955511293	-4.855033827	2.329007494
H	-0.245746273	-3.663454479	2.902798663
C	2.195787977	3.037342413	1.592846979
C	-0.623332376	2.613513842	1.279474516
H	3.107606813	2.838325565	2.160777092
H	1.945671230	4.101445182	1.671634952
H	-0.493900967	2.374272461	0.222903051
H	-0.725364804	3.696057450	1.413335162
H	-1.532093462	2.121568724	1.636445591
H	2.382077991	2.787737105	0.545121566
H	0.263412385	-3.646999958	1.203262254
H	4.222021816	-2.641548179	1.767941565
C	0.617632164	1.277013934	6.723877046
H	-0.275091223	0.673912100	6.522710653
H	1.184561028	0.776355820	7.514212990
H	0.285880964	2.245311065	7.119735318
C	3.177569437	2.531180726	5.586903816
H	3.828320598	1.992738443	6.284642728
H	3.776023439	2.766220102	4.699596750
H	2.903471214	3.479592792	6.065772324
C	4.880010769	-0.918164443	4.347103439
H	5.546578991	-1.729886571	4.662548519
H	4.915968786	-0.850840009	3.254621916
H	5.290145831	0.019508587	4.740218033
C	3.173108404	-1.268090234	6.859439679
H	2.188910679	-1.474387395	7.293146429
H	3.550217111	-0.343702175	7.311768153
H	3.847170986	-2.076717686	7.167257690
H	0.702713845	3.631738166	4.052461053
H	-0.495850305	2.337992333	4.187001031
H	1.597396012	-3.143182703	4.934042186
H	3.205251668	-3.696864775	4.429545090
O	0.970422787	-0.878999548	0.502712467
N	0.292000642	-0.382155576	-1.550707925

Optimized structure of $(PNP\text{-}Rh)_2\text{-}N_2O$ $\mu_2\text{-}N_2O$ TS ($\nu_{O1\text{-}N2}$= -200.0 cm^{-1}) (triplet)



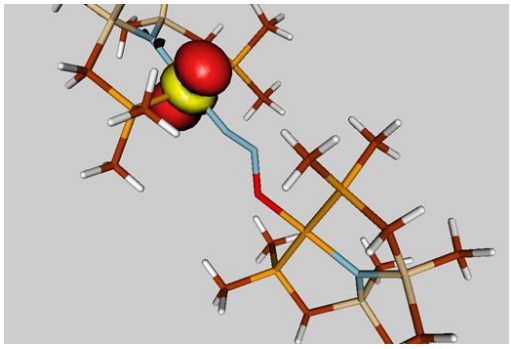
$^3TS_{8\text{-}6}$

ΔE(SCF): -50.2 kcal/mol
ΔG(gas): -25.9 kcal/mol $\nu_{N\text{–}O}$=-200 cm^{-1}

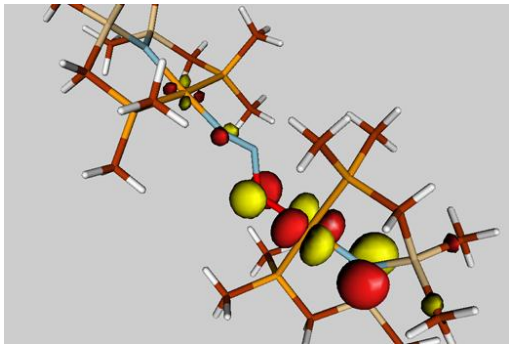
Selected bond lengths (in Å) and bond angles (in °):

	$^3TS_{8\text{-}6}$		**NPA Charges**
N1-N2	1.184	N3	-1.588
N2-O1	1.535	Rh1	0.077
N1-N2-O1	113.19	N1	-0.192
Rh2-O1	1.970	N2	0.049
Rh1-N1	1.941	O1	-0.580
Rh1-N3	2.105	Rh2	0.294
Rh1-P1	2.343	N4	-1.566
Rh1-P2	2.356		**Spin Densities**
Rh2-N4	2.089	Rh1	0.459
P3-Rh2-P4	177.22	Rh2	0.761
Rh1-N1-N2	159.67	N1	0.321
Rh2-O1-N2	119.21	N2	-0.046
N3-Rh1-N1	176.94	O1	0.326
N4-Rh2-O1	170.43	N4	0.122
P1-Rh1-P2	175.55	N3	0.067

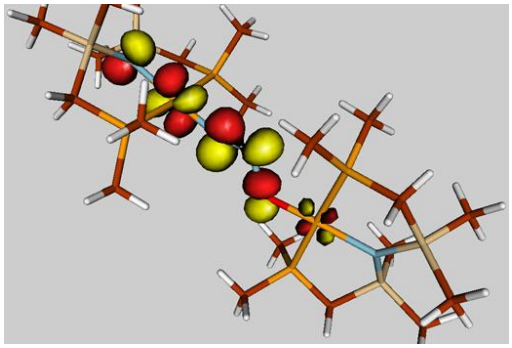
Isodensity MO Plots of ^{3}**TS$_{8\text{-}6}$**



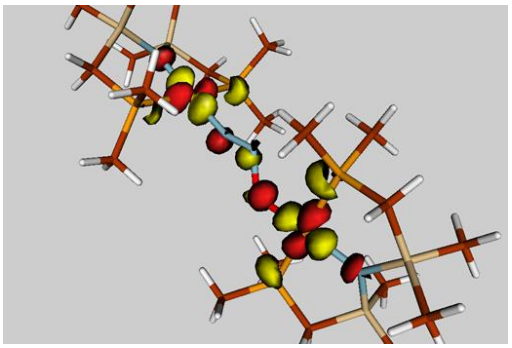
HOMO-2 = -5.053 eV



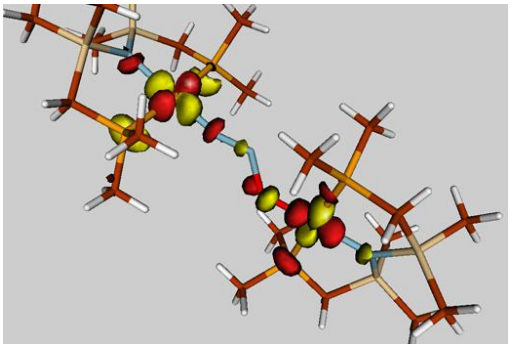
SOMO-1 = -4.860 eV



SOMO = -4.209 eV



LUMO = -0.192 eV



LUMO+1 = 0.024 eV

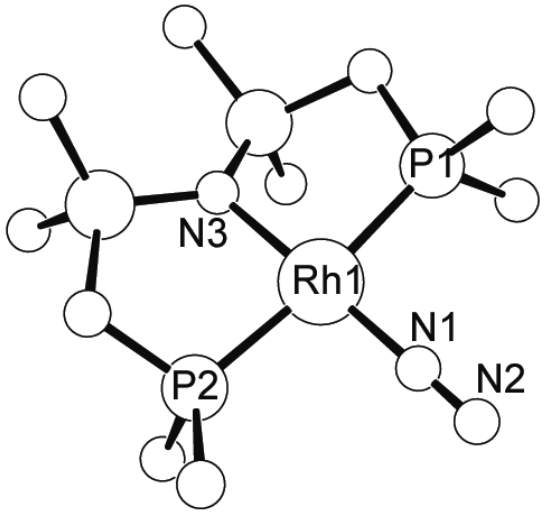
Coordinates of ^{3}**TS$_{8\text{-}6}$**

91

N	-0.217035546	-0.181596584	-0.153791281
O	-0.110140814	-0.215253201	1.377138365
Rh	2.145143049	-0.042677950	-2.123422340
P	2.018972110	2.291245766	-2.280795391
N	3.480915397	0.045992174	-3.748005338
P	2.388442547	-2.385826756	-2.106341228
Si	3.558971247	-1.410684980	-4.688416130
C	3.594243944	-2.844056459	-3.416942515
Si	4.276733279	1.533192702	-4.158802173

C	3.631828455	2.867133296	-2.939330672
C	2.974529164	-3.162650976	-0.534928922
C	0.876223617	-3.381020430	-2.479891835
H	1.088989883	-4.455499313	-2.456117520
H	0.105379566	-3.150023175	-1.739514509
H	3.094197005	-4.246222254	-0.642688624
H	3.932106205	-2.718589168	-0.250487731
C	0.767480396	2.933820561	-3.479636572
C	1.665552477	3.300854284	-0.774426126
H	0.911522663	2.450976035	-4.448951896
H	0.847519082	4.019982282	-3.600064800
H	0.702763996	2.999178453	-0.351810666
H	1.644032143	4.371341262	-1.005169047
H	2.437571852	3.107999184	-0.024843773
H	-0.235371460	2.685317195	-3.121195270
H	2.251258889	-2.951673628	0.258371110
H	0.494861373	-3.113162511	-3.468131980
C	6.164148971	1.477158281	-3.956429743
H	6.435606432	1.132458983	-2.952060784
H	6.633855926	0.799627751	-4.677362508
H	6.606645625	2.470636555	-4.102252257
C	3.914047845	2.147068493	-5.924141339
H	4.271565707	1.440788659	-6.681997244
H	2.839628366	2.284655910	-6.090739619
H	4.406815337	3.107640733	-6.119411646
C	2.053728710	-1.644018116	-5.822321795
H	2.057365372	-2.620842904	-6.321748208
H	1.117164240	-1.547674737	-5.262067220
H	2.040939788	-0.873777162	-6.602662574
C	5.109065262	-1.587381945	-5.775380956
H	6.029291904	-1.545410742	-5.182974028
H	5.172500553	-0.810189533	-6.545070541
H	5.093496765	-2.553319057	-6.294868753
H	3.573247795	3.872563562	-3.374289403
H	4.323905748	2.909833558	-2.089147913
H	4.593845649	-2.851322453	-2.965202083
H	3.400156639	-3.841488963	-3.827788881
Rh	-1.758332488	-0.210366803	2.456353956
P	-3.345285476	-0.435718147	0.714846959
N	-3.342804124	0.033370323	3.795260341
P	-0.243606510	-0.062922650	4.244040062
Si	-2.908821981	0.786404992	5.307754376
C	-1.206555534	0.061635773	5.805732092
Si	-4.988459663	-0.241503280	3.291895793
C	-4.920751992	-0.950725143	1.518896861
C	0.953285002	-1.455845695	4.428778625
C	0.876602680	1.401315621	4.208253831
H	1.599183938	1.380509915	5.031108528
H	1.404661611	1.388884517	3.251220582
H	1.638121308	-1.293859394	5.268055768
H	0.405231418	-2.389271200	4.581610443
C	-3.773585768	1.115659390	-0.195369983
C	-3.127604081	-1.638708837	-0.672690495
H	-4.053453805	1.895133069	0.517841180
H	-4.599438090	0.955448211	-0.897608720
H	-2.258331659	-1.346493664	-1.264785172
H	-4.020669134	-1.668614071	-1.306646901
H	-2.948886948	-2.635368446	-0.258849998
H	-2.891123846	1.452056805	-0.745992263
H	1.522956633	-1.537737320	3.498851769
H	0.288847728	2.320305540	4.267140864
C	-5.903444468	-1.529691456	4.346491274
H	-5.324201745	-2.457898308	4.411437197
H	-6.088102241	-1.181752921	5.367634368
H	-6.876239349	-1.773259534	3.901064215
C	-6.048156031	1.338682783	3.273484242
H	-6.146642792	1.768291977	4.277443874
H	-5.609203421	2.111097018	2.631875030
H	-7.061956817	1.135233331	2.907034388
C	-2.738039946	2.670741324	5.149504837
H	-2.355788772	3.128647145	6.070119739
H	-2.065741708	2.939932459	4.327624833
H	-3.710193578	3.127822898	4.931161133
C	-4.105406363	0.452350118	6.746003093
H	-4.222649922	-0.619488462	6.937696922
H	-5.102355050	0.870535282	6.567138412
H	-3.722254342	0.914379910	7.664144873
H	-5.798763304	-0.703119206	0.909537198
H	-4.880609398	-2.044153828	1.606466014
H	-1.377338217	-0.957110295	6.175499481
H	-0.679360774	0.621171235	6.586948171
N	0.835113184	-0.125758116	-0.693539970

Optimized structure of PNP-Rh-N_2 η^1-N_2 (singlet)



9

ΔE(SCF): -32.8 kcal/mol vs. **1** + N_2
ΔG(gas): -20.2 kcal/mol vs. **1** + N_2

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

	9
N1-N2	1.124
Rh1-N1	1.924
Rh1-N3	2.117
Rh1-P1	2.362
Rh1-P2	2.340
Rh1-N1-N2	179.13
N3-Rh1-N2	179.14
P1-Rh1-P2	173.80

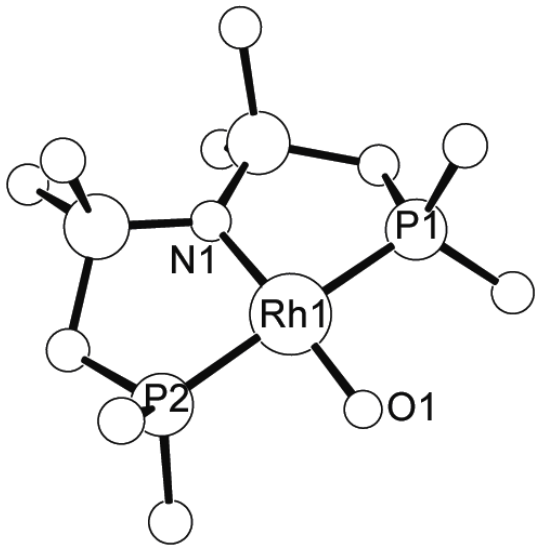
Coordinates of 9

46

Rh	-0.547787477	0.262748093	-3.888141704
P	1.646468676	0.161638306	-4.695669762
N	-1.128724173	0.267204956	-5.923353043
P	-2.837903090	0.325513907	-3.314020644
Si	-2.648572024	1.040101735	-6.213703125
C	-3.824950093	0.354327343	-4.863347429

Si	-0.054857185	-0.314642248	-7.148960639
C	1.579589340	-0.789719176	-6.260069222
C	-3.498293393	-1.068844310	-2.292485643
C	-3.424488621	1.796906765	-2.357396784
H	-4.501211247	1.741931010	-2.163397451
H	-2.891722043	1.849006031	-1.403737665
H	-4.580125798	-0.980229555	-2.147503059
H	-3.276401485	-2.015258648	-2.791483402
C	2.417188690	1.778983650	-5.147745578
C	2.978837720	-0.610797590	-3.670364027
H	1.743076848	2.332016725	-5.805023751
H	3.380854918	1.638608688	-5.649398249
H	3.121597659	-0.034704372	-2.751198561
H	3.927563150	-0.649195210	-4.215521220
H	2.682345447	-1.626392132	-3.395665003
H	2.567778588	2.370983016	-4.240634060
H	-3.006135116	-1.073048188	-1.315218504
H	-3.208599990	2.708778099	-2.919048047
C	-0.658505781	-1.875448231	-8.046570120
H	-0.911247817	-2.661783916	-7.326067998
H	-1.551541166	-1.679986995	-8.649671551
H	0.112783403	-2.270621426	-8.719397241
C	0.383577840	0.968532454	-8.486890118
H	-0.498194101	1.270007996	-9.063514316
H	0.811489386	1.878809630	-8.052380891
H	1.112899207	0.565383799	-9.200348656
C	-2.584399958	2.930213990	-6.042561728
H	-3.578936331	3.389016794	-6.104846670
H	-2.127651498	3.225579147	-5.091479605
H	-1.969669801	3.363911281	-6.840152877
C	-3.446424730	0.654393316	-7.896035526
H	-3.602643338	-0.420693935	-8.034927868
H	-2.845347931	1.014985744	-8.737847007
H	-4.425542447	1.143231983	-7.967502804
H	2.477576349	-0.651875614	-6.874649990
H	1.519500233	-1.848742221	-5.981637389
H	-4.058502254	-0.682300556	-5.133798458
H	-4.769400976	0.894775902	-4.734661197
N	0.333479550	0.294680935	-0.970767810
N	0.004175837	0.273107719	-2.045558711

Optimized structure of PNP-Rh=O (singlet)



^{1}6

ΔE(SCF): -64.3 kcal/mol (2x **1** + **N_2O** → **^{1}6** + **9)**

ΔG(gas): -53.4 kcal/mol (2x **1** + **N_2O** → **^{1}6** + **9)** Calculated $\nu_{Rh\text{-}O}$ 728 cm^{-1}

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

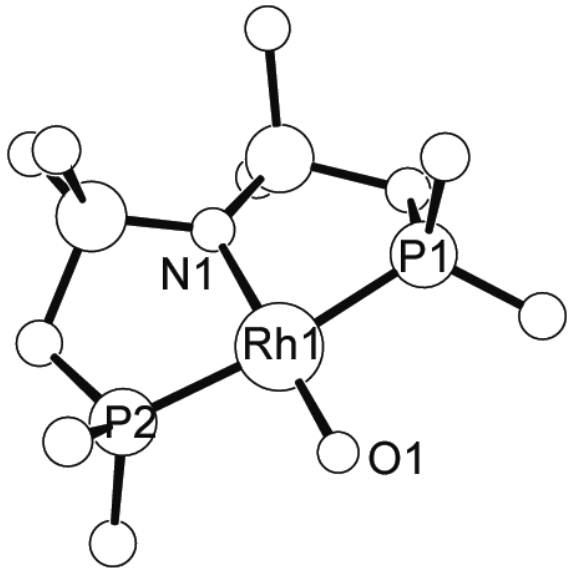
	[1]6
Rh1-O1	1.815
Rh1-N1	2.061
Rh1-P1	2.356
Rh1-P2	2.364
N1-Rh1-O1	170.18
P1-Rh1-P2	178.64

Coordinates of **[1]6**

45

Rh	-0.575204143	0.700468840	-0.218968750
P	-1.108254868	2.974030948	0.095111222
N	-2.563389038	0.211801769	0.020974117
P	-0.021549253	-1.568036293	-0.585593939
Si	-2.902690895	-1.487677537	0.310016417
C	-1.617368854	-2.485136979	-0.700715976
Si	-3.776944358	1.479355023	0.035397935
C	-2.892890172	3.144288029	-0.322558527
C	0.954208176	-1.895512347	-2.112342174
C	0.961662887	-2.441231420	0.710298863
H	1.141580278	-3.487893885	0.442399089
H	0.439835179	-2.400892786	1.669141791
H	0.354997677	-1.628703405	-2.986562542
H	1.272728753	-2.939638898	-2.190434024
C	-0.950517148	3.647061867	1.808301186
C	-0.153770519	4.177048572	-0.918983991
H	-1.528272925	3.030446343	2.501446944
H	-1.300276920	4.683304475	1.871272004
H	0.903873362	3.920754496	-0.813668911
H	-0.332082730	5.215258484	-0.623633259
H	-0.420704267	4.044739458	-1.970699769
H	0.099863703	3.604006406	2.109359534
H	1.823789799	-1.232951910	-2.085959047
H	1.920558165	-1.927165075	0.819785629
C	-5.092426181	1.291310329	-1.319012001
H	-4.623243781	1.161539955	-2.300954194
H	-5.753166426	0.435889459	-1.150022500
H	-5.720811727	2.189304525	-1.367450136
C	-4.662140564	1.593253874	1.711690364
H	-5.220136477	0.675743398	1.931818469
H	-3.952978578	1.748464382	2.532244697
H	-5.380022649	2.422250356	1.726044563
C	-2.711197971	-1.903280148	2.150423879
H	-2.847212581	-2.974548427	2.342191487
H	-1.724639626	-1.610345425	2.525366295
H	-3.455212983	-1.362709405	2.746526591
C	-4.625991288	-2.077410861	-0.226755262
H	-4.811772789	-1.892049213	-1.289832187
H	-5.427850411	-1.593182907	0.342011092
H	-4.717775757	-3.157160661	-0.057188782
H	-3.369572513	4.004252293	0.163125624
H	-2.946560690	3.308024214	-1.406271269
H	-1.936926807	-2.453393401	-1.750060523
H	-1.534095219	-3.538720594	-0.409763834
O	1.108991732	1.140548138	-0.733680632

Optimized structure of PNP-Rh=O (triplet)



^{3}6

ΔE(SCF): -79.7 kcal/mol (2x **1** + N_2O → **^{3}6** + **9)** (-15.0 kcal/mol vs. **^{1}6**)
ΔG(gas): -69.3 kcal/mol (2x **1** + N_2O → **^{1}6** + **9)** Calculated $\nu_{Rh\text{-}O}$ 722 cm^{-1}

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

	^{3}6		**Spin Densities**
Rh1-O1	1.809	Rh1	0.868
Rh1-N1	2.141	O1	1.024
Rh1-P1	2.373	N1	0.074
Rh1-P2	2.378		
N1-Rh1-O1	178.68		
P1-Rh1-P2	173.20		

Coordinates of **^{3}6**

45

Rh	-0.518433313	0.720073106	-0.331645196
P	-1.159070835	2.944284987	0.191986680
N	-2.568715718	0.227414347	0.041299714
P	-0.084929383	-1.591506978	-0.685545474
Si	-2.849796296	-1.413986446	0.525764507
C	-1.676845609	-2.494725431	-0.544854776
Si	-3.794576954	1.447601593	-0.092617438

C	-2.899275025	3.129980969	-0.351443706
C	0.698719190	-2.070085657	-2.286135208
C	1.044297563	-2.369138538	0.549388176
H	1.201324578	-3.432066782	0.335527353
H	0.623881862	-2.263080848	1.551992556
H	0.060134605	-1.750474708	-3.113472782
H	0.863506304	-3.150848922	-2.349880931
C	-1.181861409	3.315410807	1.999966241
C	-0.203541950	4.362899145	-0.497268862
H	-1.770361347	2.555350872	2.518596084
H	-1.607647401	4.304622672	2.201801511
H	0.835535555	4.286899303	-0.164381336
H	-0.620469231	5.323958755	-0.178436741
H	-0.213601081	4.306697962	-1.588701306
H	-0.159818724	3.278050726	2.387139860
H	1.656034366	-1.547823792	-2.373620825
H	2.005102442	-1.847835795	0.524032110
C	-4.945523164	1.222731282	-1.584500443
H	-4.364990844	1.136601337	-2.509934684
H	-5.558769443	0.319866970	-1.493030350
H	-5.628408161	2.074645754	-1.693034101
C	-4.888126277	1.627674732	1.454020835
H	-5.462532961	0.717139036	1.657129735
H	-4.291926539	1.842421980	2.348198375
H	-5.609720069	2.444880992	1.331671980
C	-2.447081222	-1.716238535	2.355999919
H	-2.508041741	-2.777946028	2.624556554
H	-1.443958253	-1.355199932	2.608320274
H	-3.153487592	-1.173186036	2.995151091
C	-4.608522176	-2.066454257	0.221695043
H	-4.894018790	-1.989709905	-0.832912221
H	-5.360246494	-1.529155386	0.810111497
H	-4.672738560	-3.123805608	0.505865011
H	-3.401621077	3.971383734	0.141537833
H	-2.874498764	3.340652289	-1.427601082
H	-2.119535472	-2.545131793	-1.547397592
H	-1.539578524	-3.520889833	-0.185025030
O	1.206708363	1.133695442	-0.687718020

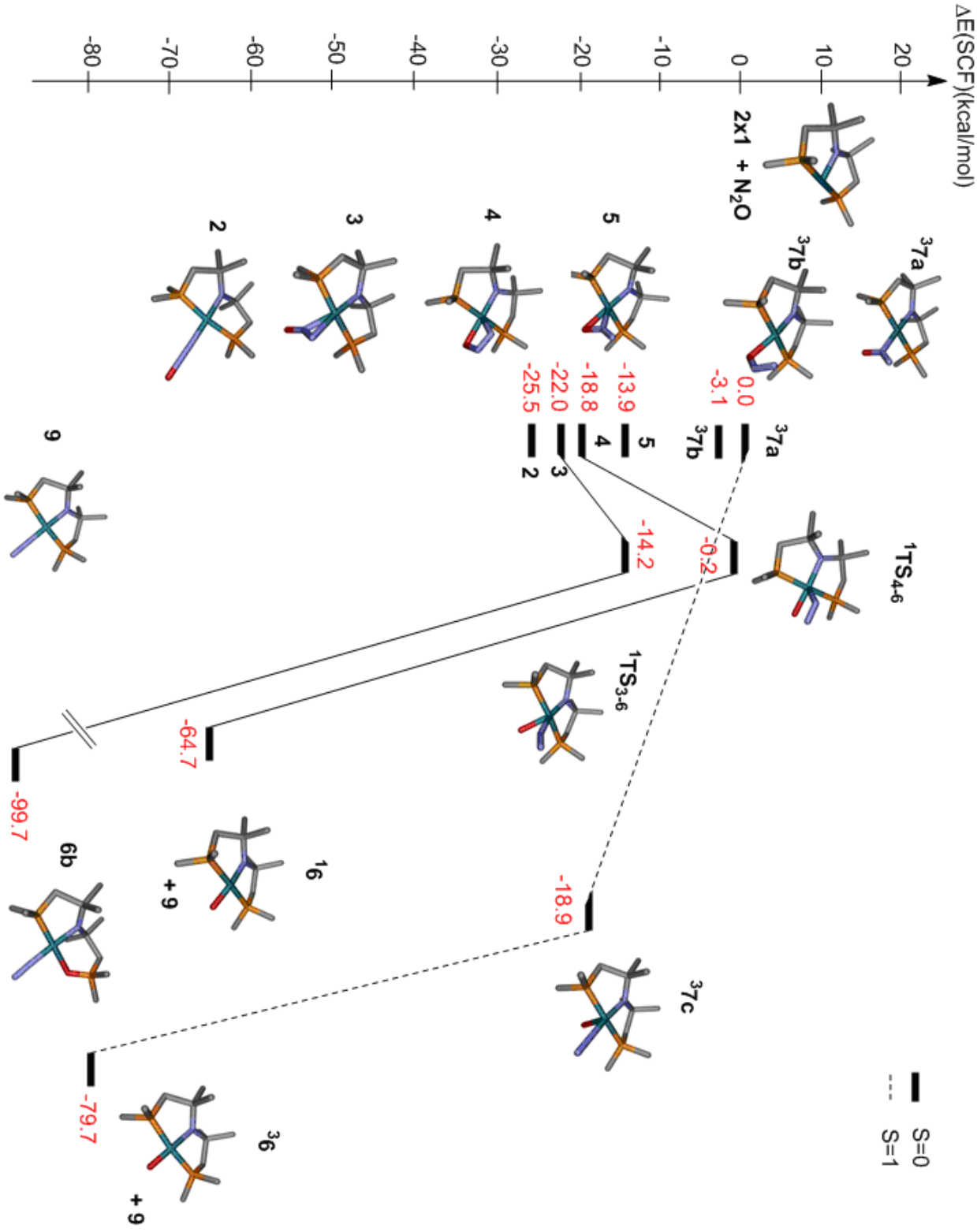


Fig S1. Energy Profile of possible pathways using a single metal complex

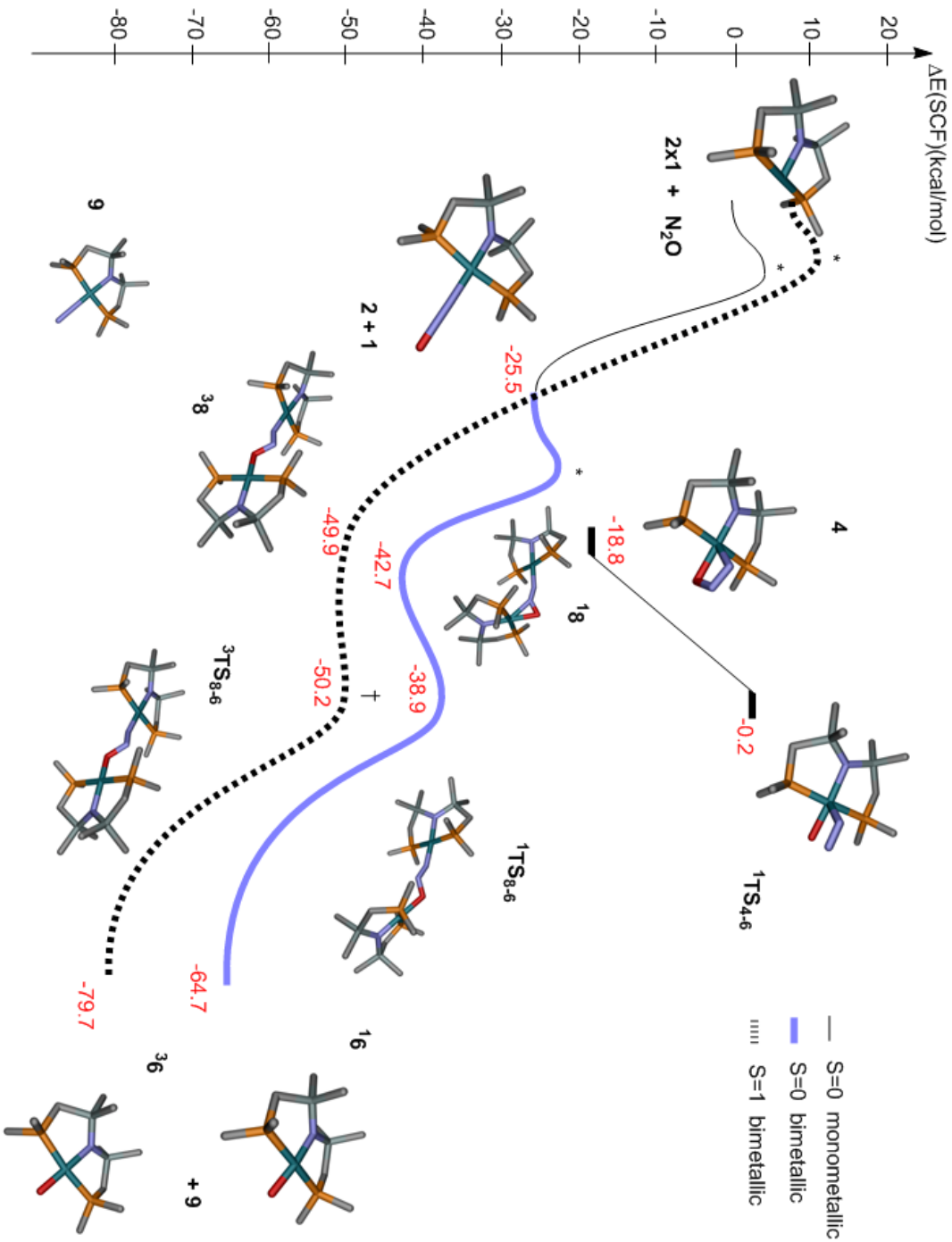


Fig S2. Energy Profile of possible pathways using two metal complexes

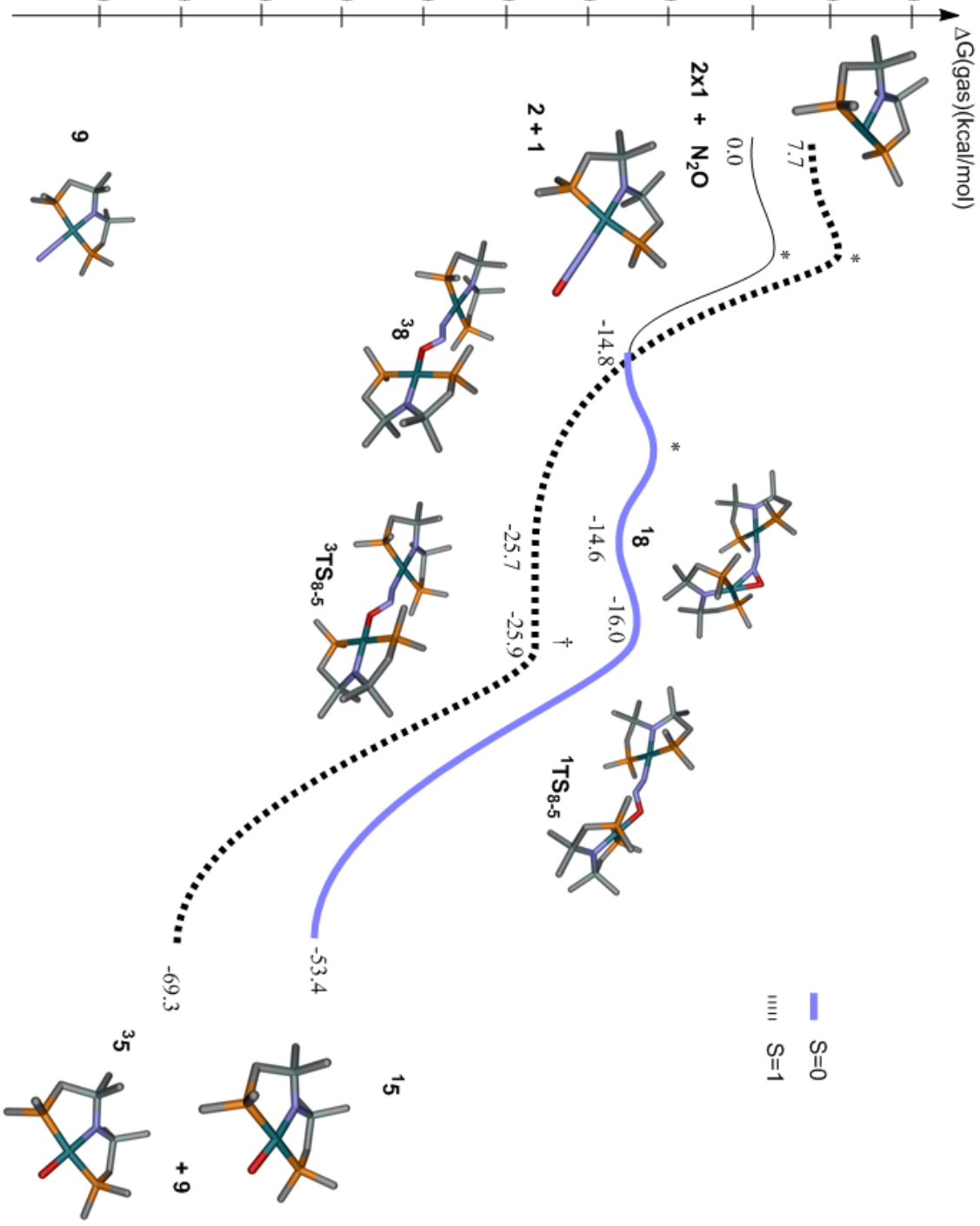


Fig S3. Gas-phase Free Energy Profile of possible pathways using two metal complexes

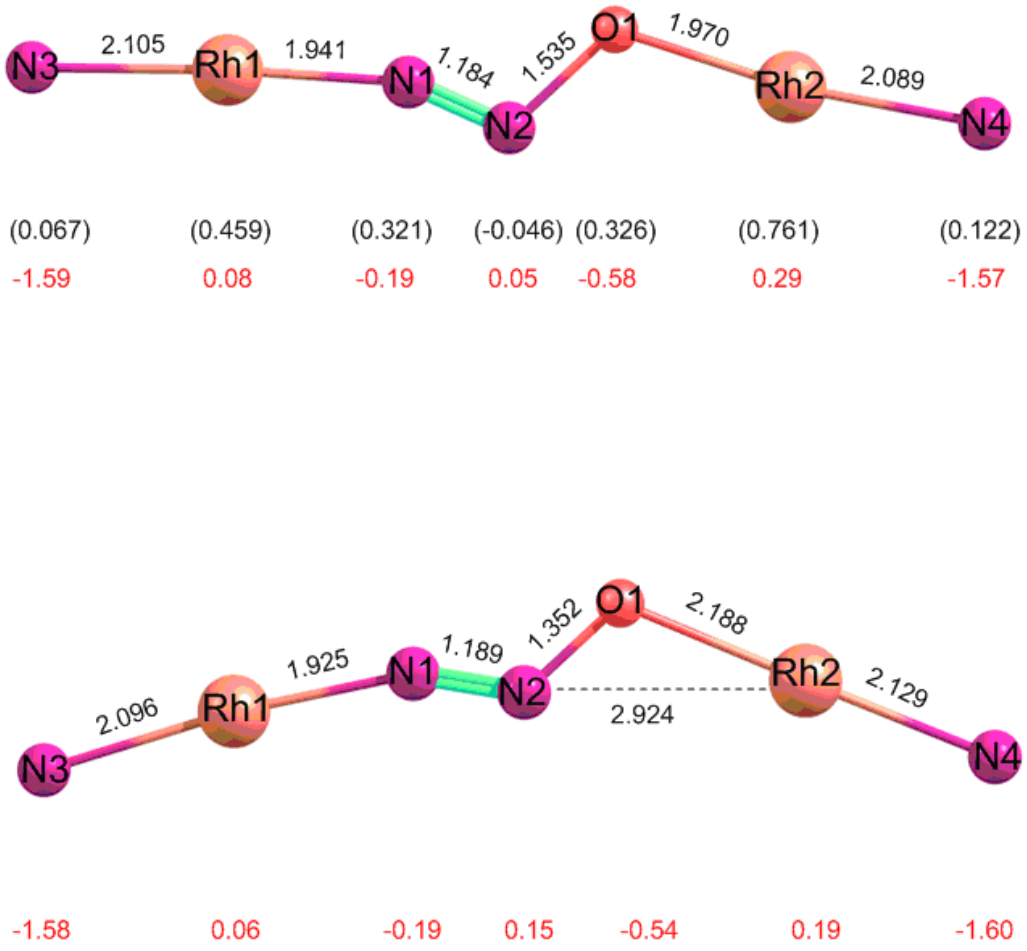


Fig S4. Bond lengths (Å, black), NPA charges (red) and spin densities (in parentheses) in triplet (^{3}**TS$_{8\text{-}6}$**, upper) and singlet (^{1}**TS$_{8\text{-}6}$**, lower) (PNP)RhNNORh(PNP).