SUPPORTING INFORMATION

Mechanism and Origin of Enantioselectivity in the $Rh_2(OAc)(DPTI)_3$-Catalyzed Cyclopropenation of Alkynes

Daniel T. Nowlan III and Daniel A. Singleton*

Department of Chemistry, Texas A&M University, PO Box 30012,

College Station, Texas 77842

singleton@mail.chem.tamu.edu

Table of Contents

Theoretical Results

All structures and energies were obtained using Gaussian98[1] or Gaussian03.[2] All structures were obtained using the Becke3LYP method. Structures **3** thru **6** used an SDD basis set on Rh while structures **7** and **8** used a LANL2dz basis set on Rh. Structures **3**, **5**, **6**, **7**, and **8** used a 6-31+G(d) basis set on the remaining atoms, while **4** used 6-31G(d) on the remaining atoms.

Vibrational frequency analyses were carried out on all stationary points, with the exception of structures **7** and **8**.

1. Gaussian 98, Revision A.11.3, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M.

Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, N. Rega, P. Salvador, J. J. Dannenberg, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 2002.

2. Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

3. Singleton, D. A.; Hang, C.; Szymanski, M. J.; Greenwald, E. E. *J. Am. Chem. Soc.* **2003**, *125*, 1176-1177.

Pentyne, B3LYP/6-31+G 5D*

File /home/singletn/rh2/pentyne631PS5D
E(RB+HF-LYP) = -195.287088896

Zero-point correction=	0.113318 (Hartree/Particle)
Thermal correction to Energy=	0.119621
Thermal correction to Enthalpy=	0.120565
Thermal correction to Gibbs Free Energy=	0.084174
Sum of electronic and zero-point Energies=	-195.173771
Sum of electronic and thermal Energies=	-195.167468
Sum of electronic and thermal Enthalpies=	-195.166524
Sum of electronic and thermal Free Energies=	-195.202915

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	75.063	21.866	76.592

C,0,1.7113210798,1.5763167393,0.3529785534

```
C,0,0.9899403749,0.3236578349,-0.1547538875
C,0,-0.476056686,0.2604402839,0.3283326202
C,0,-1.1921596477,-0.9273646551,-0.1416997136
C,0,-1.7704493806,-1.9142774234,-0.5381719937
H,0,1.731447893,1.6079733963,1.4500112474
H,0,2.7489234681,1.6035572937,0.0003780274
H,0,1.0038678426,0.2986307202,-1.2515985447
H,0,1.5150084556,-0.5779404942,0.1848230729
H,0,-0.4983018712,0.2853628961,1.4272637556
H,0,-1.0090584383,1.1612743831,-0.0080788479
H,0,-2.2838471393,-2.7827651157,-0.8854812615
H,0,1.2163853476,2.491270243,0.0025690777
```

Pentyne, B3LYP/6-31G 5D*

```
File /home/singletn/rh2/pentyne631S5D
E(RB+HF-LYP) = -195.277081393

 Zero-point correction=                           0.113557 (Hartree/Particle)
 Thermal correction to Energy=                    0.119879
 Thermal correction to Enthalpy=                  0.120823
 Thermal correction to Gibbs Free Energy=         0.084402
 Sum of electronic and zero-point Energies=           -195.163525
 Sum of electronic and thermal Energies=              -195.157203
 Sum of electronic and thermal Enthalpies=            -195.156258
 Sum of electronic and thermal Free Energies=         -195.192679

                    E (Thermal)             CV                S
                     KCAL/MOL        CAL/MOL-KELVIN    CAL/MOL-KELVIN
 TOTAL                  75.225             21.904             76.654

 C,0,1.7111548118,1.5736411687,0.3514284643
 C,0,0.9870073764,0.3230788829,-0.154062094
 C,0,-0.4782228867,0.2614479556,0.3297081319
 C,0,-1.1919921897,-0.926281521,-0.1411033094
 C,0,-1.7654811098,-1.9122337224,-0.5387180796
 H,0,1.7315887745,1.6059914183,1.4478403703
 H,0,2.747871557,1.5993876996,-0.001802712
 H,0,0.9996352744,0.2962007402,-1.2504603839
 H,0,1.5102359102,-0.5794776436,0.1844632741
 H,0,-0.4987217875,0.2890081769,1.428652318
 H,0,-1.0090078281,1.1641243555,-0.0054063068
 H,0,-2.273354708,-2.7816935157,-0.8884869152
 H,0,1.2169567948,2.4885421861,0.0016816766
```

Structure 3, Conventional Transition Structure

```
/home/singletn/rh2/RhForm4PentyneSDD631PS
E(RB+HF-LYP) = -1440.39203475

 Zero-point correction=                           0.283197 (Hartree/Particle)
 Thermal correction to Energy=                    0.311328
 Thermal correction to Enthalpy=                  0.312272
 Thermal correction to Gibbs Free Energy=         0.220942
 Sum of electronic and zero-point Energies=          -1440.108838
 Sum of electronic and thermal Energies=             -1440.080707
 Sum of electronic and thermal Enthalpies=           -1440.079763
 Sum of electronic and thermal Free Energies=        -1440.171093
```

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	195.361	97.983	192.220

```
C,0,-1.3516498646,0.7654719373,-0.7644702791
C,0,-1.846854866,2.1399716046,-0.5543504656
O,0,-1.8708856892,2.8748675871,-1.5307273366
Rh,0,0.4354908101,0.1366644382,-0.2651925617
O,0,-0.0096752041,-1.7650391679,-0.9462253948
C,0,0.8992709603,-2.655945602,-0.8722805101
O,0,2.0716188912,-2.5439904654,-0.4232829821
Rh,0,2.7070444268,-0.6962232245,0.286288595
O,0,3.2962660109,-0.1792062162,-1.6247512686
C,0,2.4335553485,0.3365494432,-2.3838574579
O,0,1.2120656822,0.5925804899,-2.1303181886
O,0,-0.0749603499,-0.4187172992,1.6761874279
C,0,0.8076564807,-0.9354593367,2.4399243108
O,0,2.0125086422,-1.1758198878,2.1765969866
O,0,1.044095358,1.9880784829,0.4446199982
C,0,2.238685085,2.1058810462,0.8732540423
O,0,3.1388896141,1.2259515693,0.9400033121
O,0,-2.1371496879,2.4894955861,0.6941320628
C,0,-2.5176454468,3.8686109964,0.8958712732
C,0,-3.0940824956,-0.637638834,0.965825842
C,0,-4.1377362091,-0.7117917581,0.3500272715
C,0,-5.4087572134,-0.822159331,-0.3672341883
C,0,-6.4489527857,-1.6831980788,0.3867566154
C,0,-7.7734219066,-1.7884016984,-0.3757758665
H,0,-1.9442343279,0.1842219134,-1.4744112988
H,0,-1.6868010702,4.5262716885,0.6295506766
H,0,-2.7494976491,3.9454492429,1.9576605125
H,0,-3.3927005139,4.114082103,0.2884277272
H,0,0.4554357165,-1.1961431647,3.447640265
H,0,2.7605246121,0.6063363936,-3.3975500549
H,0,0.6092292254,-3.646082949,-1.2511055915
H,0,2.5067442144,3.1106681243,1.22936904
H,0,-5.8227466053,0.1818950765,-0.5379185722
H,0,-5.2303104843,-1.2564666506,-1.3613689631
H,0,-2.1844936232,-0.6072939186,1.5327161312
H,0,-6.0280263522,-2.6826163524,0.55228938
H,0,-6.6181012706,-1.2467076277,1.3789680645
H,0,-8.4942549869,-2.4031585094,0.1755316238
H,0,-8.2264142903,-0.8004776447,-0.5284617806
H,0,-7.6310269143,-2.2467801062,-1.3626791211
```

Structure 3, Approximate Canonical Variational Transition Structure

```
E(RB+HF-LYP) = -1440.39281569

 Zero-point correction=                           0.283480 (Hartree/Particle)
 Thermal correction to Energy=                    0.311470
 Thermal correction to Enthalpy=                  0.312414
 Thermal correction to Gibbs Free Energy=         0.222001
 Sum of electronic and zero-point Energies=          -1440.109336
 Sum of electronic and thermal Energies=             -1440.081345
 Sum of electronic and thermal Enthalpies=           -1440.080401
 Sum of electronic and thermal Free Energies=        -1440.170814
```

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	195.451	97.772	190.291

C,0,1.5143943814,0.5634204341,0.6159065487
C,0,2.0280388249,1.9514631917,0.5404802311
O,0,2.103424917,2.5861158395,1.5818701681
Rh,0,-0.3508280348,0.0654464647,0.1789816285
O,0,0.0220356244,-1.9335165845,0.5564456229
C,0,-0.9536205058,-2.7509693019,0.4887604129
O,0,-2.1595014575,-2.5120265804,0.2089642702
Rh,0,-2.7266415061,-0.5519344765,-0.1821118157
O,0,-3.0522901777,-0.2564065083,1.8339464546
C,0,-2.0694880516,0.0957368741,2.5395597071
O,0,-0.8688800265,0.3057623926,2.1721499252
O,0,-0.0949938502,-0.2529515165,-1.8598140584
C,0,-1.0967424639,-0.6081427408,-2.5668929537
O,0,-2.2780829306,-0.8122951319,-2.188776024
O,0,-0.9005832542,2.0257920316,-0.2196283951
C,0,-2.124815987,2.2676969698,-0.4768906509
O,0,-3.0893184334,1.4576787584,-0.5353236685
O,0,2.2679085066,2.4351624244,-0.6768670643
C,0,2.6321423896,3.8305079927,-0.7394725876
C,0,2.8859204085,-0.5739165673,-1.2776037522
C,0,3.8508086009,-0.7312207375,-0.5536677724
C,0,5.0111811944,-0.9365141997,0.3123943113
C,0,6.1768394366,-1.6561646226,-0.4070820015
C,0,7.3779505004,-1.8676779997,0.5199518737
H,0,2.047508598,-0.0517478218,1.3424158984
H,0,1.8100090444,4.446534218,-0.3673150212
H,0,2.8192757173,4.0282533318,-1.7946221645
H,0,3.5300620901,4.0172629199,-0.1442840057
H,0,-0.8855799887,-0.7495105736,-3.6362625138
H,0,-2.2577621969,0.2445603861,3.6119164019
H,0,-0.6969937127,-3.7982829256,0.7025979877
H,0,-2.3589124085,3.3237101918,-0.6731368633
H,0,5.362075973,0.0334435385,0.6923899344
H,0,4.7083152592,-1.5251281355,1.1901731437
H,0,2.0535720291,-0.4735427997,-1.9455176244
H,0,5.8178821662,-2.6205019816,-0.78685451
H,0,6.473665404,-1.0644798043,-1.2818000862
H,0,8.1931896447,-2.3756237411,-0.0077683994
H,0,7.7672642388,-0.9123798636,0.8942923296
H,0,7.1091537698,-2.4824431652,1.3882358767

Structure 4, Conventional Transition Structure

File /home/singletn/rh2/RhAm3OAcPentyne631SrotAnti
E(RB+HF-LYP) = -1498.66889892

Zero-point correction=	0.406173 (Hartree/Particle)
Thermal correction to Energy=	0.438996
Thermal correction to Enthalpy=	0.439940
Thermal correction to Gibbs Free Energy=	0.340495
Sum of electronic and zero-point Energies=	-1498.262726
Sum of electronic and thermal Energies=	-1498.229903
Sum of electronic and thermal Enthalpies=	-1498.228959

Sum of electronic and thermal Free Energies= -1498.328404

		E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin		S Cal/Mol-Kelvin
Total		275.474	116.307		209.300
1	6	0	1.819457	0.639374	0.331182
2	45	0	-0.053513	0.072991	0.206374
3	8	0	-0.700803	2.004502	-0.109948
4	6	0	-1.970211	2.204261	-0.195004
5	7	0	-2.912122	1.303755	-0.168937
6	6	0	-4.301759	1.735080	-0.223672
7	6	0	2.243716	2.041762	0.111309
8	8	0	2.244286	2.473403	-1.148675
9	6	0	2.506736	3.877757	-1.322507
10	8	0	2.475711	2.736383	1.089970
11	8	0	0.463654	-1.917083	0.518720
12	6	0	-0.464443	-2.790381	0.537084
13	8	0	-1.702648	-2.629717	0.388219
14	45	0	-2.440958	-0.674158	0.074027
15	7	0	-2.184827	-0.927621	-1.943139
16	6	0	-3.257270	-1.455877	-2.773481
17	7	0	-0.415037	0.257851	2.248446
18	6	0	0.640399	0.664679	3.171491
19	8	0	0.009528	-0.221130	-1.872323
20	6	0	-1.032999	-0.661716	-2.485027
21	8	0	-2.628926	-0.420143	2.119783
22	6	0	-1.595831	-0.028682	2.749413
23	6	0	2.963226	-0.463878	-1.697876
24	6	0	4.093932	-0.540809	-1.259532
25	6	0	5.442293	-0.637875	-0.703404
26	6	0	5.700592	-1.950997	0.066821
27	6	0	7.123108	-2.020878	0.628297
28	1	0	2.531977	0.056860	0.915906
29	1	0	1.714571	4.466986	-0.854495
30	1	0	2.518593	4.035896	-2.400571
31	1	0	3.470218	4.147475	-0.882049
32	1	0	-0.906708	-0.819770	-3.565799
33	1	0	-1.709742	0.081543	3.838293
34	1	0	-0.116891	-3.820965	0.707215
35	1	0	-2.258881	3.259813	-0.301654
36	1	0	0.252527	0.744526	4.195322
37	1	0	1.450789	-0.074802	3.173115
38	1	0	1.056491	1.631869	2.877620
39	1	0	-2.945572	-1.553811	-3.822987
40	1	0	-3.562458	-2.443369	-2.408523
41	1	0	-4.131064	-0.794655	-2.733695
42	1	0	-4.826015	1.420393	0.685793
43	1	0	-4.383596	2.827592	-0.313506
44	1	0	-4.808631	1.279980	-1.082811
45	1	0	5.622991	0.219920	-0.038300
46	1	0	6.173622	-0.540288	-1.519044
47	1	0	1.981021	-0.438302	-2.135259
48	1	0	4.968634	-2.036108	0.879432
49	1	0	5.516421	-2.797686	-0.605229
50	1	0	7.284315	-2.956984	1.173702
51	1	0	7.870779	-1.968855	-0.172737
52	1	0	7.319655	-1.193328	1.321094

Alternative Conventional Transition Structure to Structure 4 with propyl group twisted toward ester, Slightly higher in energy, very similar isotope effects (1.007, 1.007, 1.007 at C1, C2, and C3 of pentyne, respectively)

/home/singletn/rh2/RhAm3OAcPentyne631Sbetter
SDD on Rh, 6-31+G* on remaining atoms
E(RB+HF-LYP) = -1498.66892818

Zero-point correction=	0.406214 (Hartree/Particle)
Thermal correction to Energy=	0.439055
Thermal correction to Enthalpy=	0.439999
Thermal correction to Gibbs Free Energy=	0.340539
Sum of electronic and zero-point Energies=	-1498.262714
Sum of electronic and thermal Energies=	-1498.229873
Sum of electronic and thermal Enthalpies=	-1498.228929
Sum of electronic and thermal Free Energies=	-1498.328389

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	275.511	116.303	209.332

C,0,1.8284769803,0.2467722098,0.3827986308
Rh,0,-0.1100901069,0.0130481313,0.2659285019
O,0,-0.0171400796,-1.0963769773,-1.5180015884
C,0,-1.0999360309,-1.5659845705,-2.0307793981
N,0,-2.3039244937,-1.3927329642,-1.5710328813
C,0,-3.4233754052,-2.0238580308,-2.2550609811
C,0,2.555086171,1.3474086668,-0.2925687737
O,0,2.6337584635,1.2771336687,-1.6197047281
C,0,3.2106639809,2.4237871794,-2.2697419877
O,0,2.9552752522,2.2841803977,0.384299095
O,0,-0.3428856674,1.744051266,-0.8276920278
C,0,-1.539416941,2.0961595669,-1.1481461921
N,0,-2.6434413768,1.4493805428,-0.9007281918
Rh,0,-2.5921017934,-0.3102788338,0.1443150586
O,0,-2.8093079478,0.7690921046,1.9011260623
C,0,-1.7456490162,1.1959746026,2.4511025943
N,0,-0.5115776154,1.0513726416,2.0226912458
C,0,0.5683722632,1.6030688448,2.8353393038
O,0,-0.0189585971,-1.7464444508,1.3737949298
C,0,-1.1057156292,-2.3659107806,1.6174613041
O,0,-2.2777781429,-2.0681638152,1.273640945
C,0,-3.9114905749,2.0379115838,-1.3079459709
C,0,2.8356904975,-1.7538969415,-0.9536446642
C,0,3.9348529576,-1.7898451432,-0.4377123537
C,0,5.2589999875,-1.7877270377,0.1824570487
C,0,6.0622628427,-0.4955651713,-0.0858356024
C,0,7.4485903084,-0.53262333,0.5626467924
H,0,2.3865006923,-0.1962070391,1.208469203
H,0,2.5836936916,3.3031627621,-2.1040503719
H,0,3.2419475191,2.1675870909,-3.3283771084
H,0,4.2171352625,2.6173731159,-1.8893158333
H,0,-0.9622845279,-2.1670384825,-2.9411471591
H,0,-1.8788173038,1.7493657273,3.3928366715

H,0,-0.9829396875,-3.2849679711,2.2107673041
H,0,-1.6029282853,3.0510967402,-1.6893875747
H,0,0.1662511555,2.1501792759,3.6978795834
H,0,1.2098724998,0.7974983086,3.2131824253
H,0,1.1845793487,2.2851809653,2.2434898472
H,0,-3.0914169877,-2.5873850023,-3.1383924146
H,0,-3.9373442727,-2.7139070791,-1.5760014114
H,0,-4.1464033824,-1.2667067802,-2.5808741883
H,0,-4.5446235638,2.2061212292,-0.4293995793
H,0,-3.7653324036,2.9983847329,-1.822106187
H,0,-4.4441455812,1.3614015208,-1.9868121911
H,0,5.1571033933,-1.9392332477,1.2669406714
H,0,5.8263647553,-2.6537353842,-0.1886082925
H,0,1.8729923014,-1.7637085634,-1.4329966644
H,0,6.1553645542,-0.3564725839,-1.1698418115
H,0,5.4944428755,0.3633621858,0.2927348201
H,0,8.0004157898,0.3922781339,0.3628173439
H,0,7.3761871723,-0.6482095079,1.6509675308
H,0,8.0464443007,-1.3679875167,0.17783395

Structure 4, Approximate Canonical Variational Transition Structure

/home/singletn/rh2/RhAm3OAcPentyne631S2.5rotAnti
E(RB+HF-LYP) = -1498.66837663

Zero-point correction=	0.406212 (Hartree/Particle)
Thermal correction to Energy=	0.438170
Thermal correction to Enthalpy=	0.439115
Thermal correction to Gibbs Free Energy=	0.342400
Sum of electronic and zero-point Energies=	-1498.262164
Sum of electronic and thermal Energies=	-1498.230206
Sum of electronic and thermal Enthalpies=	-1498.229262
Sum of electronic and thermal Free Energies=	-1498.325976

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	274.956	114.255	203.553

C,0,1.7837915626,0.5727415578,0.4346316609
Rh,0,-0.1031845277,0.0172664832,0.2918160924
O,0,-0.6892845566,1.9217387395,-0.2359684577
C,0,-1.9476730382,2.1388455786,-0.4007384703
N,0,-2.9137570596,1.2671120166,-0.3226473131
C,0,-4.2868858424,1.7177271292,-0.4979999736
C,0,2.2166786831,1.9578567456,0.1248075548
O,0,2.2944349222,2.2826644789,-1.1655901745
C,0,2.5394548698,3.6737842559,-1.4391579215
O,0,2.3842170629,2.737697157,1.0507555838
O,0,0.3504771653,-1.9439982768,0.8171358855
C,0,-0.6040764836,-2.7831285237,0.9117478502
O,0,-1.8341736897,-2.6051708292,0.7200437123
Rh,0,-2.5068727746,-0.6793395903,0.1599918042
N,0,-2.1887156799,-1.1659250325,-1.8062205921
C,0,-3.2428229796,-1.7733236553,-2.6052403227
N,0,-0.5148353657,0.4022518067,2.2962221304
C,0,0.5327315455,0.8277133681,3.2201812426
O,0,0.0130971498,-0.4835874672,-1.7446429606
C,0,-1.017311573,-0.9762997927,-2.3378174899

```
O,0,-2.7530513897,-0.1900346438,2.1565581293
C,0,-1.7214189995,0.2130977734,2.7813586111
C,0,2.9277118662,-0.6830392684,-1.3996148741
C,0,4.0410210461,-0.6608907283,-0.9105426268
C,0,5.3784247163,-0.6187451109,-0.3230770502
C,0,6.4580204351,-1.2332813184,-1.2451098538
C,0,7.8531952579,-1.162234115,-0.618803769
H,0,2.4479073014,0.0617561294,1.131972966
H,0,1.7125817626,4.2803593238,-1.0622907869
H,0,2.605954482,3.7453744821,-2.5245380325
H,0,3.4727361744,4.0009693754,-0.9730412674
H,0,-0.8619770144,-1.2542799332,-3.3903095371
H,0,-1.8621422448,0.4273891231,3.851469759
H,0,-0.2913803185,-3.7982522844,1.2014655183
H,0,-2.2035331383,3.1824992686,-0.6338133151
H,0,0.118411222,1.0125410821,4.219778981
H,0,1.2989227321,0.0475351707,3.3111594624
H,0,1.0114823312,1.7433553318,2.863489247
H,0,-2.9035286364,-1.986022457,-3.6289503967
H,0,-3.5678484161,-2.7134873045,-2.1448115739
H,0,-4.1106815664,-1.1056808406,-2.6612949676
H,0,-4.8655137932,1.51432533,0.410237822
H,0,-4.3359343991,2.795503559,-0.7087305178
H,0,-4.7596478541,1.1822629887,-1.3300593927
H,0,5.3771443584,-1.1528680593,0.6375522948
H,0,5.6471381265,0.4239279887,-0.1011152637
H,0,1.9704635899,-0.7454608095,-1.8871772551
H,0,6.1911755205,-2.2750969196,-1.4588431047
H,0,6.4470974172,-0.7038818801,-2.2053541942
H,0,8.6035252998,-1.6019003302,-1.2847850283
H,0,8.1489927613,-0.1246038707,-0.4215491284
H,0,7.8916099332,-1.7064628221,0.33262164
```

Structure 5

/home/dan/RhCalcs/SDD/RhNMeacet3OAcOpenCarbIs1SDD.out
E(RB+HF-LYP) = -1303.37563884

Zero-point correction=	0.289150 (Hartree/Particle)
Thermal correction to Energy=	0.315143
Thermal correction to Enthalpy=	0.316088
Thermal correction to Gibbs Free Energy=	0.234320
Sum of electronic and zero-point Energies=	-1303.086489
Sum of electronic and thermal Energies=	-1303.060495
Sum of electronic and thermal Enthalpies=	-1303.059551
Sum of electronic and thermal Free Energies=	-1303.141319

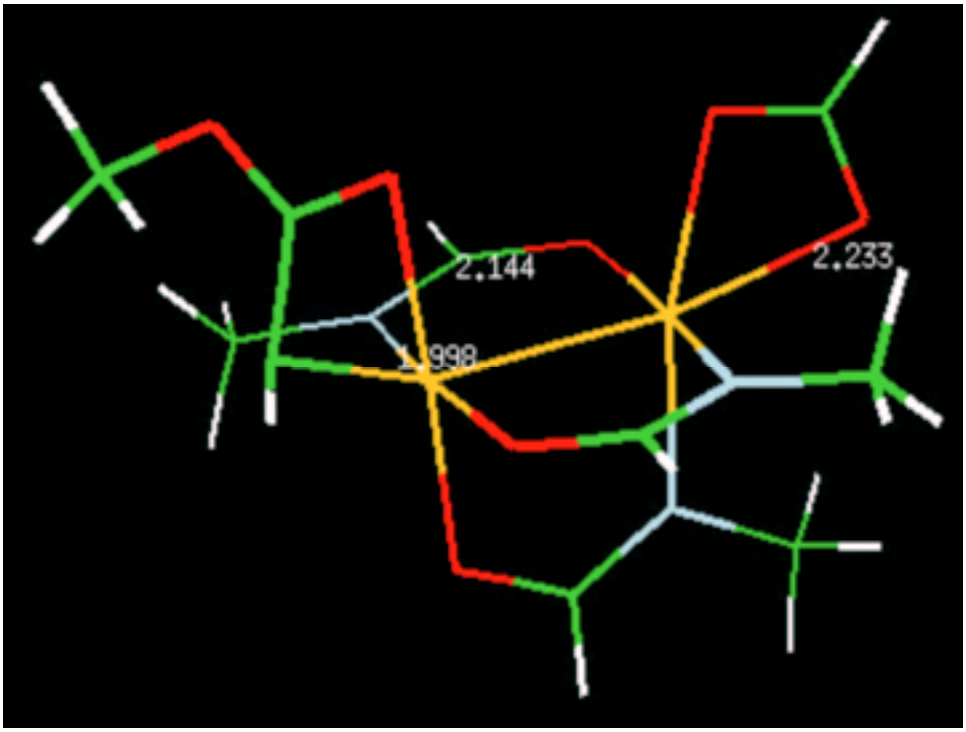
	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	197.755	92.750	172.094

```
C,0,-2.802193738,0.0016835447,-1.3116062516
C,0,-3.1812393121,-1.1706089589,-0.5540622686
O,0,-4.2232414681,-1.7507860137,-0.3614939266
Rh,0,-1.0966743809,0.4394862149,-0.4458528635
O,0,-0.497915218,2.2368805575,-1.1022419705
C,0,0.7530186913,2.5192553683,-0.9384739866
N,0,1.6418052917,1.7453390515,-0.3952175263
```

```
Rh,0,1.2516766067,-0.140260069,0.3139426956
O,0,1.1783372867,-2.0738894051,1.200300697
C,0,2.3794214151,-2.0194770185,1.6379066646
O,0,3.1284893658,-1.0442724946,1.3804395677
O,0,-0.4603044446,-0.358241603,-2.2935099428
C,0,0.7050143295,-0.8838043416,-2.4230062652
N,0,1.643187764,-0.9445971276,-1.519655508
N,0,-1.4359705746,1.2411373646,1.4039513789
C,0,-0.4737127206,1.2014643861,2.3047401707
O,0,0.6684500522,0.6622288557,2.1732648573
O,0,-1.9782922885,-1.4720365369,0.1486450177
C,0,-2.0481898061,-2.2151606621,1.394012828
H,0,-2.9489157635,0.0227759375,-2.3914919695
H,0,-2.5676093066,-1.6189951018,2.149111057
H,0,-1.0139107461,-2.4064777224,1.6735341449
H,0,-2.5904434884,-3.1428640244,1.2043031741
H,0,0.906004837,-1.315383803,-3.4135646804
H,0,-0.6772231921,1.6824548203,3.273486843
H,0,1.0438102886,3.5142196973,-1.2968158888
H,0,2.7462930358,-2.8602358424,2.2470547457
C,0,-2.6359840291,2.0353167191,1.6514068752
C,0,3.0166091838,2.2147609885,-0.2438535839
C,0,2.9006124641,-1.613894669,-1.8332275965
H,0,-2.6218626528,2.450401553,2.6677653345
H,0,-2.6950433153,2.8611217678,0.9338967726
H,0,-3.5323290043,1.4176322294,1.5330194166
H,0,2.9289402637,-1.9187781524,-2.8877908035
H,0,3.7449517653,-0.9455378801,-1.6359757881
H,0,3.0243045862,-2.5042928525,-1.2082030856
H,0,3.6984619976,1.5685209866,-0.8068898514
H,0,3.1261729914,3.2452763182,-0.6065146133
H,0,3.3058150259,2.175551464,0.8112304213
```

Alternative to Structure 5, Higher in Energy

/home/dan/RhCalcs/SDD/RhNMeacet3OAcOpenCarbIs2SDD.out



SDD on Rh, 6-31+G* on remaining atoms
E(RB+HF-LYP) = -1303.37508964

Zero-point correction=	0.289404 (Hartree/Particle)
Thermal correction to Energy=	0.315265
Thermal correction to Enthalpy=	0.316209
Thermal correction to Gibbs Free Energy=	0.234418
Sum of electronic and zero-point Energies=	-1303.085685
Sum of electronic and thermal Energies=	-1303.059825
Sum of electronic and thermal Enthalpies=	-1303.058881
Sum of electronic and thermal Free Energies=	-1303.140672

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	197.832	92.224	172.144

C,0,-2.8433160375,-0.202483259,-0.8447092847
Rh,0,-0.9836786087,0.4277456843,-0.4769196256
O,0,-1.838022818,-0.8254639615,1.0382366512
C,0,-2.9293680712,-0.8995183712,0.3834453816
O,0,-3.9719173525,-1.5090418747,0.9427094424
O,0,-0.2160853396,1.69472128,-1.8589985685
C,0,1.0619185784,1.8521918694,-1.8275049208
N,0,1.8819760439,1.2403423649,-1.0234671753
C,0,3.3091015975,1.5455701336,-1.0686036903
Rh,0,1.3265443248,-0.1715919009,0.3598825994
O,0,1.0012850213,1.332281433,1.7914274782
C,0,-0.0467634161,2.0516524962,1.7383609896
N,0,-1.0421916357,1.935836989,0.8852865181
C,0,-2.12552305,2.9100845467,0.8796307374
O,0,-0.6449089607,-1.1391342432,-1.8596242545
C,0,0.4436367036,-1.8158881576,-1.8442988848
N,0,1.4614453179,-1.6497811552,-1.0430690138
C,0,2.608495951,-2.5437140022,-1.1411946066

```
O,0,1.2239222698,-1.6132255757,1.9331699331
C,0,2.4616643647,-1.479504767,2.1815861735
O,0,3.186728178,-0.7259051877,1.4638325953
H,0,-3.0468443845,-0.6836440992,-1.8006044872
H,0,0.5050989332,-2.6144881987,-2.5975978622
H,0,-0.1135351486,2.8623238016,2.4790834404
H,0,1.4611738591,2.5768565506,-2.5484452632
H,0,2.9053495012,-2.02815796,3.0252785618
H,0,-1.9604830581,3.6794560463,1.6456382549
H,0,-2.187085416,3.3970159095,-0.1001714577
H,0,-3.0826101663,2.4147024757,1.0756762922
H,0,2.5068779494,-3.2162816083,-2.0033109345
H,0,3.5314662341,-1.9656347802,-1.2516893568
H,0,2.6979350874,-3.1518926844,-0.2345347253
H,0,3.8792808173,0.6549611351,-1.3543638456
H,0,3.5172191544,2.345300584,-1.7914583445
H,0,3.650491337,1.8612574991,-0.0778947471
C,0,-5.1629263044,-1.6077246904,0.1411349002
H,0,-5.9203594886,-2.0420492157,0.7935246814
H,0,-5.480361216,-0.6159952834,-0.1979861214
H,0,-4.9907091842,-2.2632875676,-0.7188371964
```

Structure 6

/home/dan/RhCalcs/SDD/RhNMeacet3OAcPentTSopenSDD.out
E(RB+HF-LYP) = -1498.63414779

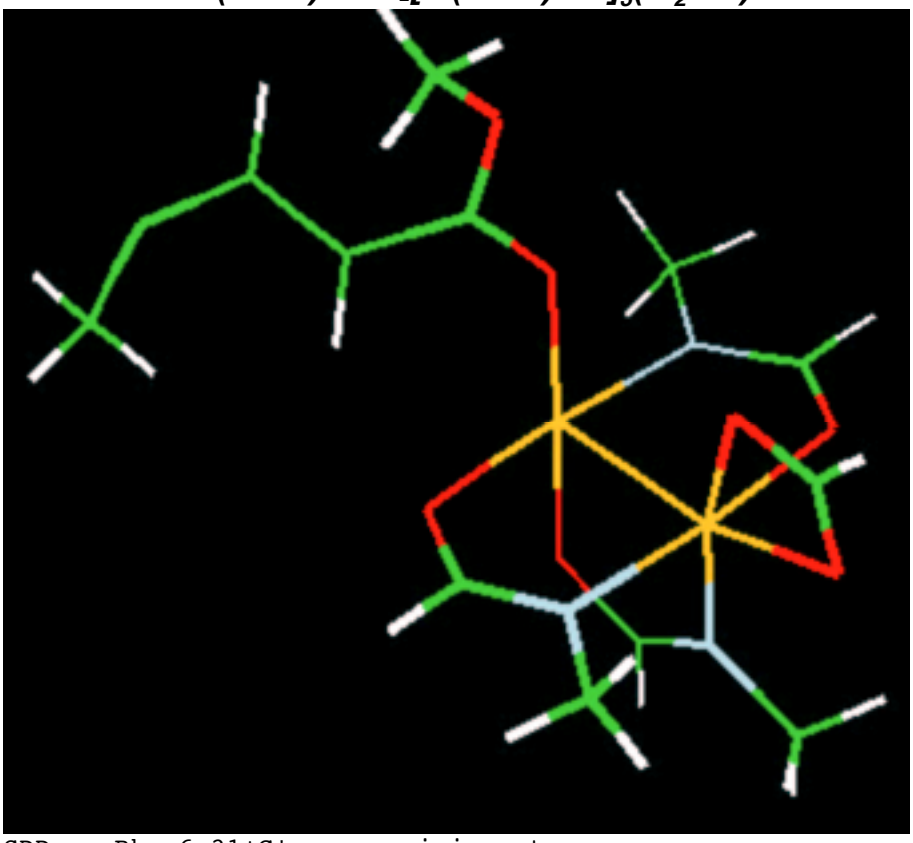
Zero-point correction=	0.403078 (Hartree/Particle)
Thermal correction to Energy=	0.436294
Thermal correction to Enthalpy=	0.437239
Thermal correction to Gibbs Free Energy=	0.338533
Sum of electronic and zero-point Energies=	-1498.231069
Sum of electronic and thermal Energies=	-1498.197853
Sum of electronic and thermal Enthalpies=	-1498.196909
Sum of electronic and thermal Free Energies=	-1498.295615

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	273.779	117.484	207.744

```
C,0,3.0485600576,0.1685459537,0.610185999
C,0,4.1067224951,0.4081872079,-0.4001918915
O,0,4.1009781054,1.1984783021,-1.3297347532
Rh,0,1.0941549944,-0.2999809517,0.3359858714
O,0,1.3019521534,-0.3682555585,-1.7447458652
C,0,0.2978754673,-0.1173979944,-2.4993322342
N,0,-0.9500485615,0.0536181932,-2.1341567687
Rh,0,-1.4516639399,-0.1766488465,-0.1537678915
O,0,-3.4997013826,0.376127492,-0.5581334947
C,0,-4.5859678555,-0.0782450927,-0.01159768
O,0,-4.7494404063,-1.1218594713,0.6177595765
C,0,1.6799875213,1.830954599,0.1694558802
C,0,0.4375124893,1.7626006088,0.3798477459
C,0,-0.878322846,2.3903424309,0.610176018
C,0,-0.9087780914,3.8636967055,0.1367626098
C,0,-2.2696920451,4.5161132269,0.4012708001
O,0,0.7566095732,-2.3218534659,0.3927402629
C,0,-0.3310550401,-2.8258061764,-0.0585050018
```

N,0,-1.4002566056,-2.1577402861,-0.3815854098
N,0,0.6036081087,-0.3534039813,2.3572788745
C,0,-0.6693760681,-0.4310774376,2.6883111426
O,0,-1.6830528936,-0.3439726793,1.9225990587
O,0,5.1279104138,-0.4400663548,-0.1374104355
C,0,6.2315540622,-0.4074516674,-1.0652783979
H,0,3.3627242459,0.5085639679,1.6015394339
H,0,5.8840443802,-0.6449153482,-2.0738377592
H,0,6.9269625806,-1.1666270382,-0.7067787039
H,0,6.7004771748,0.5803243128,-1.0635588159
H,0,0.533487808,-0.0400052513,-3.570817068
H,0,-0.8978428677,-0.5732029067,3.7554119839
H,0,-0.3471765122,-3.9183090284,-0.1588260908
H,0,-5.4501599799,0.6002320858,-0.1855660333
C,0,1.6042144398,-0.5439058115,3.4003130052
C,0,-2.5773966822,-2.8497086617,-0.9064480791
C,0,-1.9527382167,0.3439233388,-3.1573873802
H,0,2.5207418732,2.314424144,-0.3027151134
H,0,-1.7114799819,1.8777858634,0.0767977964
H,0,-1.1345847114,2.3198345093,1.6738455106
H,0,-0.1135368556,4.4107314345,0.6589083472
H,0,-0.6710282157,3.8994319697,-0.9329508506
H,0,-2.2698752218,5.5565516339,0.0570898568
H,0,-3.073649544,3.9860712327,-0.1225489687
H,0,-2.5108375221,4.5165874794,1.4712502616
H,0,-1.4830117712,0.4399575267,-4.1452578384
H,0,-2.7028998348,-0.4518476324,-3.1944352976
H,0,-2.4795159062,1.2722027363,-2.9183695118
H,0,1.1264301209,-0.7295847423,4.3707968087
H,0,2.2447155914,-1.3992476361,3.1591797504
H,0,2.2364881881,0.3465645364,3.5035760862
H,0,-3.448203519,-2.6058804355,-0.2930121118
H,0,-2.7677090648,-2.5290077174,-1.936391636
H,0,-2.4004211315,-3.9330257517,-0.9039860191

MeCCHCHC(OMe)ORh$_2$[O(NMe)CH]$_3$(O$_2$CH)



SDD on Rh, 6-31+G* on remaining atoms
E(RB+HF-LYP) = -1420.05899857

Zero-point correction=	0.348540 (Hartree/Particle)
Thermal correction to Energy=	0.378339
Thermal correction to Enthalpy=	0.379283
Thermal correction to Gibbs Free Energy=	0.288019
Sum of electronic and zero-point Energies=	-1419.710459
Sum of electronic and thermal Energies=	-1419.680660
Sum of electronic and thermal Enthalpies=	-1419.679716
Sum of electronic and thermal Free Energies=	-1419.770979

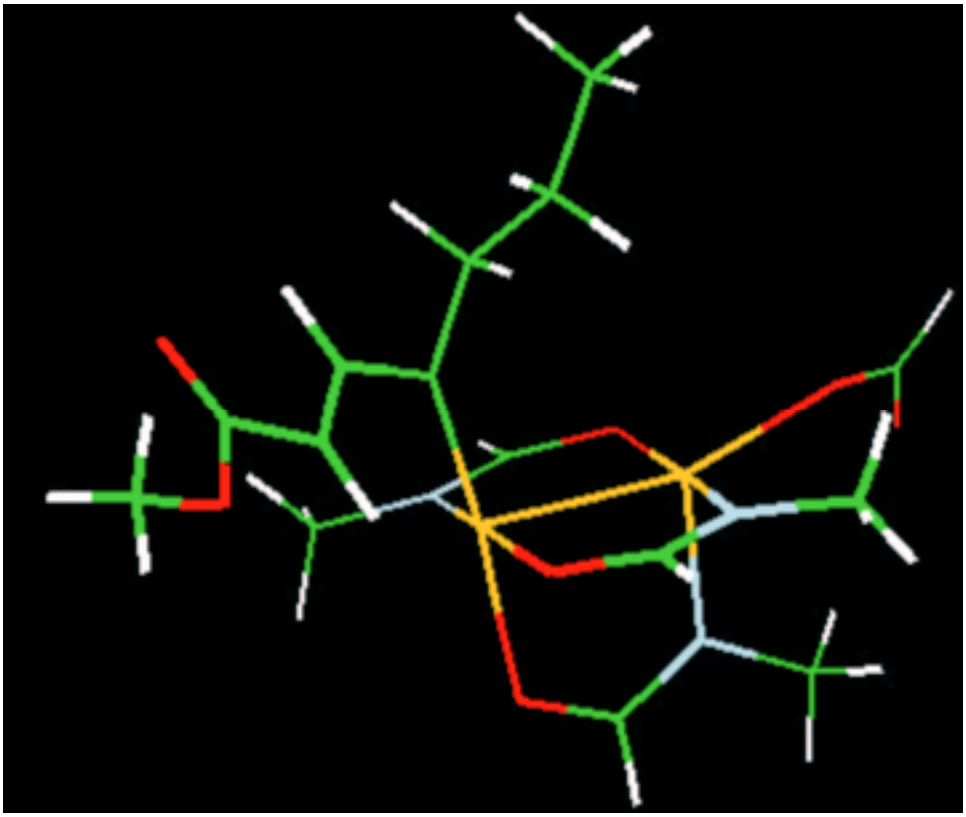
	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	237.411	105.157	192.080

C,0,-3.4685909147,0.2015097021,0.1331190212
Rh,0,-0.2844447942,-1.0538401191,0.1356877618
O,0,-0.8936636172,0.0701302172,1.8088196857
C,0,-0.1352163645,1.0324262433,2.1935595391
N,0,0.9660439738,1.4417397796,1.620025045
C,0,1.6899511537,2.5626298662,2.2088627096
C,0,-2.6831694365,0.4260953792,-1.0751216718
O,0,-1.5184639857,0.0108665685,-1.183320451
O,0,-3.1971280501,0.9957478603,-2.1790236402
C,0,-4.1668311527,2.0585545393,-2.1100974977
O,0,0.8599571788,-2.2060298886,1.3470838554
C,0,2.102043003,-1.9071806559,1.4738059682
N,0,2.6756463598,-0.8502349714,0.9751078919

```
Rh,0,1.6367567336,0.5310139746,-0.1032662269
O,0,3.0381964043,2.2019163789,-0.6683734514
C,0,2.07572018,2.7010644388,-1.3217126861
O,0,0.9210490198,2.1716992694,-1.2993370703
N,0,0.4577247647,-2.0157496783,-1.5097837192
C,0,1.488476317,-1.5261452757,-2.1563713981
O,0,2.1671381105,-0.4889999928,-1.8456000596
C,0,4.1084962243,-0.6395065449,1.1305691691
C,0,-0.1835866919,-3.227216806,-1.9985919913
C,0,-4.8465008085,0.0648011172,0.1728426919
C,0,-5.4907555231,0.287033107,1.3882148065
C,0,-5.1568963242,-0.4356475018,2.6205768962
H,0,-2.8794187224,0.1585676789,1.0450177626
H,0,-0.4631722546,1.5597388133,3.1022621514
H,0,1.819137408,-2.0548929507,-3.0635218315
H,0,2.7060189518,-2.6152032599,2.0572807115
H,0,2.2342480418,3.6146336147,-1.9159660704
H,0,0.3229304147,-3.6150519489,-2.8939922
H,0,-0.1628966993,-4.006084172,-1.2261041775
H,0,-1.2315851034,-3.0291595505,-2.2589553904
H,0,1.2218386128,2.8861776696,3.1488337219
H,0,2.7271009539,2.2773012578,2.4145108669
H,0,1.711115138,3.4111359212,1.5171203711
H,0,4.3009438745,0.3036304081,1.6545664545
H,0,4.5673670465,-1.4594892088,1.6995757406
H,0,4.5838760539,-0.5803038276,0.1456555771
H,0,-3.8874410731,2.7605653469,-2.8980887282
H,0,-5.1701009092,1.6709961135,-2.3063732282
H,0,-4.1419677332,2.5595364217,-1.1395719861
H,0,-5.4323807676,0.0420385695,-0.7449414612
H,0,-5.3116662806,0.1576308039,3.5272742659
H,0,-5.9098590527,-1.2474907497,2.6558181082
H,0,-4.1695493133,-0.9305353153,2.6232614586
```

$MeO_2CCHCHC(Pr)=Rh_2[O(NMe)CH]_3(O_2CH)$

/home/dan/RhCalcs/SDD/RhNMeacet3OAcIRCcarbene2.out



E(RB+HF-LYP) = -1498.75665754

Zero-point correction=	0.408272 (Hartree/Particle)
Thermal correction to Energy=	0.441634
Thermal correction to Enthalpy=	0.442578
Thermal correction to Gibbs Free Energy=	0.340599
Sum of electronic and zero-point Energies=	-1498.348386
Sum of electronic and thermal Energies=	-1498.315024
Sum of electronic and thermal Enthalpies=	-1498.314080
Sum of electronic and thermal Free Energies=	-1498.416058

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	277.129	115.945	214.632

C,0,3.6211582045,0.0685754082,-0.1930974572
C,0,5.1002475205,0.2087298104,-0.239450753
O,0,5.7632698251,0.9542567835,0.4600857247
Rh,0,0.534566674,-0.8141305342,0.4265603157
O,0,1.0150678046,-0.8723687878,-1.5978869835
C,0,0.1977163787,-0.3759189902,-2.4521095386
N,0,-0.9745220208,0.1536446548,-2.2011535118
Rh,0,-1.6912288022,0.1636893392,-0.2742238828
O,0,-3.170637587,1.5061236146,-0.8236854491
C,0,-4.373203119,1.6713984779,-0.3380903008
O,0,-5.0739350406,0.8535166793,0.2438288297
C,0,2.8945086068,0.8319376231,0.6587204817
C,0,1.4408863704,0.8032014261,0.7879977078
C,0,0.8403710781,2.0737472339,1.3188624329
C,0,0.7538987073,3.166299827,0.2152563325
C,0,0.143402629,4.4673453692,0.7479732809

```
O,0,-0.377664597,-2.7314603567,0.1065009542
C,0,-1.6036948974,-2.7488885451,-0.2143170427
N,0,-2.3680058188,-1.7008917453,-0.4327279313
N,0,-0.2598951634,-0.8903379622,2.328331275
C,0,-1.4456790278,-0.3855750601,2.5739833232
O,0,-2.2054544245,0.2160300327,1.7402218291
O,0,5.6288828441,-0.6154464405,-1.1686209186
C,0,7.0620511618,-0.5774629394,-1.3029496774
H,0,3.157991511,-0.6250647325,-0.8870803159
H,0,7.389273218,0.4275463076,-1.5829760831
H,0,7.2968004587,-1.2950980291,-2.0890619887
H,0,7.5378531794,-0.8630819749,-0.3609026826
H,0,0.5359326142,-0.4060559162,-3.4973846363
H,0,-1.8351958901,-0.4667525888,3.5994291525
H,0,-2.087839505,-3.7298922216,-0.3268346135
H,0,-4.7489053351,2.6965454708,-0.5376946901
C,0,0.4503309116,-1.5991412877,3.3865444728
C,0,-3.7706100235,-1.8598081661,-0.816279348
C,0,-1.7774947776,0.6507457731,-3.3179859985
H,0,3.4466272169,1.5456776996,1.2763074325
H,0,-0.1611906069,1.899356416,1.721655496
H,0,1.4679863897,2.466833898,2.1355295028
H,0,1.7560966619,3.3585829584,-0.1890267572
H,0,0.1487688873,2.7868969478,-0.6182277581
H,0,0.0856377678,5.2213150576,-0.0456471093
H,0,-0.8718923617,4.3019660758,1.127245441
H,0,0.7462735293,4.8842394342,1.5643740299
H,0,-1.2099965288,0.6026103686,-4.2563928165
H,0,-2.6885709955,0.0525175205,-3.4258449275
H,0,-2.080835488,1.6829690965,-3.1288694111
H,0,-0.1222861181,-1.590085447,4.3239563402
H,0,0.6202542567,-2.6418622049,3.093919056
H,0,1.4255713198,-1.1312715737,3.5705968968
H,0,-4.4051307686,-1.2415878371,-0.1776058975
H,0,-3.9188620458,-1.5445269355,-1.8557649754
H,0,-4.0571735179,-2.9151566097,-0.7238863711
```

Structure 7

/home/dan/RhCalcs/lanl/CorCatMajorEng6-31+G.out **(7)**
E(RB+HF-LYP) = -2444.72125815

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.111253	2.637967	0.426792
2	6	0	0.836746	3.680428	-0.575879
3	8	0	-0.321972	4.034886	-0.737575
4	45	0	1.430392	0.777503	0.063072
5	8	0	3.474346	1.202753	-0.245463
6	6	0	4.246906	0.269775	-0.666601
7	7	0	3.936949	-0.988831	-0.810897
8	6	0	4.913205	-1.915453	-1.366018
9	8	0	1.072277	0.976240	-1.982245
10	6	0	1.166396	-0.065368	-2.713242
11	8	0	1.488545	-1.233298	-2.378555

12	45	0	2.051815	-1.614080	-0.355707
13	8	0	0.056976	-2.181008	0.100240
14	6	0	-0.760400	-1.224460	0.232442
15	7	0	-0.492933	0.071984	0.288805
16	6	0	-1.712442	0.868283	0.472089
17	8	0	1.847089	0.475269	2.061910
18	6	0	2.314966	-0.673199	2.408347
19	7	0	2.512626	-1.709181	1.640191
20	6	0	3.054494	-2.929217	2.222367
21	8	0	1.892919	4.127259	-1.248162
22	6	0	1.624137	5.088114	-2.295516
23	1	0	1.158199	2.981762	1.466211
24	1	0	0.964949	4.645051	-3.045532
25	1	0	2.599625	5.318457	-2.722571
26	1	0	1.160755	5.985153	-1.877033
27	1	0	5.267134	0.592522	-0.921236
28	7	0	-2.138229	-1.450208	0.375934
29	1	0	2.560584	-0.758715	3.476974
30	1	0	0.927450	0.100661	-3.775299
31	6	0	-2.886521	-0.179625	0.269543
32	6	0	-1.786836	1.574129	1.816396
33	1	0	5.867759	-1.412165	-1.574514
34	1	0	5.102354	-2.737129	-0.664681
35	1	0	4.534754	-2.345208	-2.301062
36	1	0	3.207314	-2.826399	3.306163
37	1	0	2.370081	-3.767292	2.045661
38	1	0	4.018634	-3.174530	1.760586
39	1	0	-1.776824	1.619985	-0.319442
40	6	0	-3.625561	0.013207	-1.042908
41	1	0	-3.598050	-0.112384	1.094588
42	16	0	-2.902317	-2.978837	0.307454
43	8	0	-4.285841	-2.699881	0.707303
44	8	0	-2.616396	-3.657593	-0.955816
45	6	0	-2.074926	-3.879445	1.629883
46	1	0	-2.510545	-4.882099	1.624622
47	1	0	-1.008756	-3.911755	1.402813
48	1	0	-2.277895	-3.373646	2.575490
49	6	0	-4.853786	0.687365	-1.035152
50	6	0	-5.535843	0.939501	-2.228169
51	6	0	-4.997473	0.511436	-3.444718
52	6	0	-3.776711	-0.170306	-3.458764
53	6	0	-3.092618	-0.415407	-2.266204
54	1	0	-5.286100	1.004536	-0.088341
55	1	0	-6.491315	1.457475	-2.204939
56	1	0	-5.530308	0.696975	-4.373856
57	1	0	-3.358729	-0.521345	-4.398839
58	1	0	-2.156401	-0.965907	-2.290333
59	6	0	-2.273834	2.887170	1.881875
60	6	0	-2.421592	3.532635	3.114307
61	6	0	-2.078777	2.871430	4.296155
62	6	0	-1.581752	1.564030	4.238132
63	6	0	-1.435574	0.922284	3.007626
64	1	0	-2.523608	3.410842	0.962664
65	1	0	-2.796764	4.552496	3.147120
66	1	0	-2.189836	3.371089	5.255234
67	1	0	-1.302151	1.047449	5.153151
68	1	0	-1.027722	-0.083526	2.967701

Structure 8

/home/dan/RhCalcs/lanl/CorCatMinorEng6-31+G.out
E(RB+HF-LYP) = -2444.71819554

C,0,-0.9940886552,2.0544985194,2.3685388819
C,0,-1.3629497099,2.3527973451,1.0488443218
C,0,-1.6135181208,3.6864212106,0.7041722357
C,0,-1.5096373332,4.7034936989,1.6583555762
C,0,-1.151683518,4.3958114997,2.9727482181
C,0,-0.8906893807,3.0663816847,3.3240263238
C,0,-1.5711118765,1.2580506282,0.0125611615
N,0,-0.5380208418,0.2153420735,0.0214189022
C,0,-1.000191159,-0.9081304314,0.5529109818
N,0,-2.3655378055,-0.7862696118,0.8571436983
C,0,-2.9131233619,0.4545718684,0.262897558
O,0,-0.3548428894,-1.9632514658,0.8189085047
Rh,0,1.6885915381,-1.9857600451,0.2328305567
N,0,2.2250826904,-1.0138203171,1.962085526
C,0,2.5170433674,-1.7687584915,3.1733316496
Rh,0,1.3765491997,0.3065595366,-0.7326113638
O,0,2.0647487482,1.1091986227,1.032683298
C,0,2.307842523,0.2894639858,1.993813899
S,0,-3.3740128087,-2.0709042218,1.3734766655
C,0,-2.5846868085,-2.5799771829,2.9097565292
C,0,-3.732922127,0.2572805961,-0.9998106111
C,0,-4.8766063362,1.0430936861,-1.1933845933
C,0,-5.6225012881,0.9394959463,-2.3704475104
C,0,-5.2331660964,0.0404752299,-3.3668637893
C,0,-4.0977090962,-0.7533449314,-3.1767793543
C,0,-3.3499246123,-0.6439523221,-2.0028616165
C,0,1.3695721787,1.9521772059,-1.7239896084
H,0,1.0277246938,1.888574959,-2.7630692704
O,0,3.3805876072,0.1243109305,-1.3904440934
C,0,4.0421358425,-0.9367751013,-1.1062128857
N,0,3.6129706513,-1.9650269092,-0.4294994275
C,0,4.4828768402,-3.1149386867,-0.2304095341
O,0,0.729344534,-0.6390028579,-2.4838787003
C,0,0.7517953709,-1.9132489348,-2.5485128827
O,0,1.0839749558,-2.7381280995,-1.6601589784
O,0,-4.6500206668,-1.4159303207,1.6806070016
O,0,-3.3216535576,-3.1928180537,0.4366348702
H,0,5.0734767552,-0.9529759417,-1.4876727611
H,0,2.6149565497,0.771182064,2.9335033227
H,0,0.4299600741,-2.3273523346,-3.5164588576
H,0,5.4679798976,-2.9541216337,-0.690208032
H,0,4.6292116401,-3.3031767017,0.8402297701
H,0,4.0331403767,-4.009446783,-0.6774171778
H,0,2.7727600634,-1.1045799989,4.0112239511
H,0,1.6464901372,-2.3703836186,3.4607618402
H,0,3.359404772,-2.450625286,3.0050337918
H,0,-1.6160864193,1.7160330245,-0.9794323427
H,0,-3.5218779664,0.967042605,1.0094326814
H,0,-3.1771986927,-3.4190487742,3.284035931
H,0,-1.564574851,-2.8893029183,2.6797583221
H,0,-2.6123891336,-1.7427679633,3.6093778077
H,0,-5.1941789082,1.7295841416,-0.4112735934

H,0,-6.5118066553,1.5506608653,-2.5019375994
H,0,-5.8156495824,-0.0496402661,-4.2802082768
H,0,-3.7957282546,-1.4647794023,-3.9411413813
H,0,-2.4785900794,-1.276520864,-1.8631006967
H,0,-1.874787732,3.9359448585,-0.3214444368
H,0,-1.6995592697,5.7341152004,1.3696080812
H,0,-1.0696809186,5.1839114539,3.7171090684
H,0,-0.6044175326,2.8192573223,4.3437468782
H,0,-0.7749682251,1.0274121461,2.6471371063
C,0,1.8794137917,3.2755184678,-1.3455321259
O,0,3.144914258,3.3652457305,-0.9591132262
O,0,1.0653821914,4.1911817709,-1.3694715373
C,0,3.5778807619,4.666186539,-0.5030467703
H,0,4.6376262081,4.5480281378,-0.2792931717
H,0,3.426224204,5.4144213578,-1.2854396083
H,0,3.0201590967,4.9494658991,0.3928339906

Experimental Procedures

All reactions were performed in flame dried glassware under positive pressure of nitrogen. Chlorobenzene, 1-hexyne, and 1-pentyne were purchased from Aldrich and used without purification. Ethyl diazoacetate was prepared according to the method of Searle (Searle, N. E. *Org. Syn.* **1963**, *4*, 424-426) and distilled under reduced pressure (1 mm) to remove traces of dichloromethane. $Rh_2(OAc)(DPTI)_3$ was prepared according to the protocol recently described. (Lou, Y.; Horikawa, N.; Kloster, R. A.; Hawryluk, N. A.; Corey, E. J. *J. Am. Chem. Soc.* **2004**, *126*, 8916-8918). In the large scale preparation of $Rh_2(OAc)(DPTI)_3$, the catalyst was purified using Bakerbond Cyano 40-μm prep LC Packing silica gel purchased from J. T. Baker.

Cyclopropenation of 1-pentyne using ethyl diazoacetate and $Rh_2(OAc)_4$. Example Procedure. A 100 mL 3-neck flask was fitted with a Dewar condenser and an addition funnel and charged with 40 mg (0.09 mmol) of $Rh_2(OAc)_4$, 35 mL of chlorobenzene, and 4.6 g (68 mmol) of 1-pentyne. To the resulting mixture was added dropwise at 25 °C 11.0 g (96 mmol) of ethyl diazoacetate. After N_2 evolution ceased, an aliquot of the reaction was analyzed directly by ^1H NMR after diluting with $CDCl_3$, and the conversion, based on integration of the alkynyl hydrogen versus the vinylic cyclopropene hydrogen (δ 1.95 and δ 6.34), was 71%. The unreacted pentyne was then recovered by a vacuum transfer followed by a fractional distillation to give 700 mg of 1-pentyne contaminated with 5% chlorobenzene.

Enantioselective cyclopropenation of 1-pentyne using ethyl diazoacetate and $Rh_2(OAc)(DPTI)_3$. Example Procedure. A 100 mL 3-neck flask was fitted

with a Dewar condenser and an addition funnel and charged with 160 mg (0.10 mmol) of $Rh_2(OAc)(DPTI)_3$, 35 mL of chlorobenzene and 4.5 g (66 mmol) of 1-pentyne. To the resulting mixture was added dropwise at 25 °C 8.5 g (74 mmol) of ethyl diazoacetate. After N_2 evolution ceased, an aliquot of the reaction was analyzed directly by ^1H NMR after diluting with $CDCl_3$, and the conversion, based on integration of the alkynyl hydrogen versus the vinylic cyclopropene hydrogen (δ 1.95 and δ 6.34), was 76%. The unreacted pentyne was then recovered by a vacuum transfer followed by a fractional distillation to afford 366 mg of 1-pentyne contaminated with 3% chlorobenzene. In addition, approximately 3 g of the starting reaction mixture was chromatographed on silica gel using ethyl acetate/hexanes (5:95) as eluent to give 700 mg of the cyclopropene product. After removal of solvent under reduced pressure, the enantiomeric excess was determined to be 93% by measuring the relative peak heights/areas of diastereomeric signals present in the ^1H NMR in C_6D_6 using the chiral shift reagent $Eu(hfc)_3$.

NMR Measurements. For the racemic reaction, NMR samples were prepared by adding 360 mg of 1-pentyne to a 5 mm NMR tube and diluting to the 5.0 cm mark with $CDCl_3$. In the case of the enantioselective reactions, 260 mg of 1-pentyne was diluted to the 5.0 cm mark with $CDCl_3$. For 1-hexyne, 200 mg was diluted to 5.0 cm with $CDCl_3$. The ^{13}C spectra for the racemic cylcopropenation of 1-pentyne were recorded at 125.69 MHz using inverse gated decoupling, 180 s delays between calibrated π/2 pulses, and 5.999 s acquisition time to collect 155,712 points. The ^{13}C spectra for the enatioselective cylcopropenation of 1-pentyne were recorded at 125.69 MHz using inverse gated decoupling, 154 or 174 s delays between calibrated π/2 pulses, and 5.999 s acquisition time to collect 155,712 points. The ^{13}C spectra for the enantioselective cylcopropenation of 1-hexyne were collected 2 FIDs at a time and recorded at 125.69 MHz using inverse gated decoupling, 111 s delays between calibrated π/2 pulses, and 3.999 s acquisition time to collect 103,808 points. Integrations were determined numerically using a constant integration region for each peak. A zero-order baseline correction was generally applied, but in no case was a first-order (tilt) correction applied. Six spectra were obtained for each sample of recovered alkyne along with corresponding samples of the alkyne that were not subjected to the reaction conditions. The resulting ^{13}C integrations for these spectra are given below. From the ^{13}C integrations the KIEs and uncertainties were calculated as previously described (Singleton, D. A.; Thomas, A. A. *J. Am. Chem. Soc.* **1995**, *117*, 9357-9358)

For the ^{13}C spectra of 1-pentyne and 1-hexyne the integrations of carbon 4 were set at 1000. The average integrations for the other carbons are shown in Table 1 along with the number of spectra recorded for each sample (n).

Table 1: Average ^{13}C integrations for 1-pentyne and 1-hexyne.

% Conversion	C_1	C_2	C_3	C_4	C_5	C_6	n
Reaction of 1-pentyne/$Rh_2(OAc)_4$							
Standard	1021.91	937.04	988.90	1000	944.13		6
71 $\pm$ 1 %	1037.23	937.99	987.74	1000	944.40		6
78 $\pm$ 1 %	1040.67	941.69	989.15	1000	946.00		6
Reaction of 1-pentyne/$Rh_2(OAc)(DPTI)_3$							
Standard	1023.78	929.89	988.02	1000	949.78		6
78 $\pm$ 1 %	1036.86	934.08	987.56	1000	948.49		6
Standard	1024.18	935.95	989.36	1000	948.84		6
76 $\pm$ 1 %	1034.47	935.08	987.38	1000	948.84		6
Reaction of 1-hexyne/$Rh_2(OAc)(DPTI)_3$							
Standard	1050.74	935.07	1020.77	1000	979.84	951.99	6
83 $\pm$ 1 %	1069.28	940.72	1020.99	1000	985.15	954.17	6

The values for R/Ro, calculated as the ratio of average integrations in Table 1 relative to standard, are shown in Table 2. The standard deviations were calculated from the formula:

$$\Delta R / R_0 = R / R_0 \_((\Delta IntSample / IntSample)^2 + (\Delta IntStandard / IntStandard)^2)^{1/2}$$

Table 2: R/R_0 for ^{13}C

R/R_0 and stand dev	C_1	C_2	C_3	C_5	C_6
Reaction of 1-pentyne/$Rh_2(OAc)_4$					
71 $\pm$ 1 %	1.015	1.001	0.999	1.000	
stand dev	0.004	0.004	0.005	0.004	
78 $\pm$ 1 %	1.018	1.005	1.000	1.002	
stand dev	0.004	0.005	0.003	0.003	
Reaction of 1-pentyne/$Rh_2(OAc)(DPTI)_3$					
78 $\pm$ 1 %	1.013	1.005	1.000	0.999	
stand dev	0.005	0.002	0.003	0.005	
76 $\pm$ 1 %	1.010	0.999	0.998	0.999	

stand dev	0.005	0.003	0.004	0.004	
Reaction of 1-hexyne/$Rh_2(OAc)(DPTI)_3$					
83 ± 1 %	1.018	1.006	1.000	1.005	1.002
stand dev	0.007	0.008	0.007	0.011	0.005

The ^{13}C KIEs for 1-pentyne and 1-hexyne were then calculated from eq. 2, with the standard deviations calculated from eq. 3, 4, and 5. All of these equations are taken from: Singleton, D. A.; Thomas, A. A. *J. Am. Chem. Soc.* **1995**, *117*, 9357, its Supporting Information, and references therein.

$$KIE_{calcd} = \frac{\ln(1 - F)}{\ln[(1 - F)R/R_0]} \quad (2)$$

$$\Delta KIE_F = \frac{\partial KIE}{\partial F}\Delta F = \frac{-\ln(R/R_0)}{(1 - F)\ln^2[(1 - F)R/R_0]}\Delta F \quad (3)$$

$$\Delta KIE_R = \frac{\partial KIE}{\partial (R/R_0)}\Delta(R/R_0) = \frac{-\ln(1 - F)}{(R/R_0)\ln^2[(1 - F)R/R_0]}\Delta(R/R_0) \quad (4)$$

$$\Delta KIE = KIE*((\Delta KIE_R/KIE)^2 + (\Delta KIE_F/KIE)^2)^{1/2} \quad (5)$$

Table 3: ^{13}C KIEs.

Sample	C_1	C_2	C_3	C_5	C_6
Reaction of 1-pentyne/$Rh_2(OAc)_4$					
71 ± 1 %	1.012(3)	1.001(3)	0.999(4)	1.000(4)	
78 ± 1 %	1.012(3)	1.003(3)	1.000(2)	1.001(2)	
Reaction of 1-pentyne/$Rh_2(OAc)(DPTI)_3$					
78 ± 1 %	1.008(3)	1.003(1)	1.000(2)	0.999(3)	
76 ± 1 %	1.007(4)	0.999(2)	0.999(3)	0.999(3)	
Reaction of 1-hexyne/$Rh_2(OAc)(DPTI)_3$					
83 ± 1 %	1.010(4)	1.003(4)	1.000(4)	1.003(6)	1.001(3)