Supporting Information

Rhodium-Catalyzed Hetero-(5 + 2) Cycloaddition of Vinyl Aziridines and Alkynes: A Theoretical View of Mechanism and Chirality Transfer

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1. Complete Reference for Gaussian 09

Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N.

J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2013**.

2. Comparison of Different DFT Results

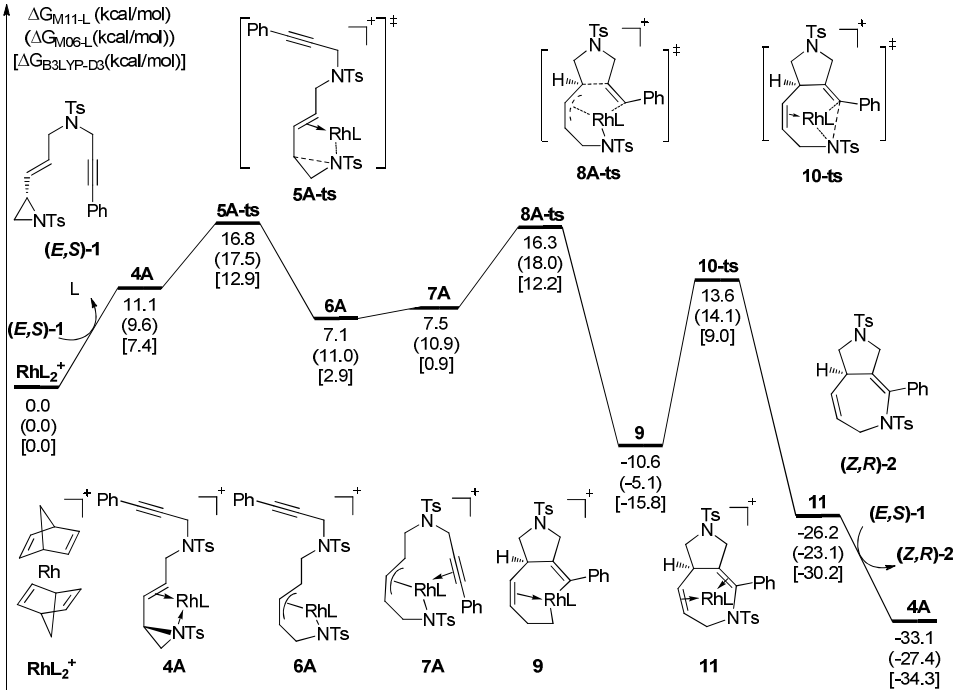

Figure S1. Free energy profiles of different DFT results for the intramolecular formal hetero-(5+2) cycloaddition of reactant (*E, S*)-**1**.

To investigate whether this discrepancy is due to the employed functional, we recalculated the free energy profile using the M06L and B3LYP-D3 methods by performing single-point calculations on the B3LYP-optimized geometries. Indeed, the calculations show that the energy profile changes depending on the functional employed, which is shown in figure S1. The computation results indicate that when different functionals are taken into consideration, the fluctuation tendency of free energy in this pathway is almost the same among these functionals. Therefore, taken

together, all the B3LYP-D3 , M06L and M11-L functionals give a quite similar overall picture of the reaction mechanism. we can draw the conclusion as that the M11-L functional could provide great accuracy in energetic information for this work and the use of other functionals will not affect the over conclusions on which are the preferred pathways.

3. Absolute Calculation Energies, Enthalpies, and Free Energies

Table S1. The absolute calculation energies, enthalpies, and free energies.

Geometry	$E_{(elec\text{-}B3LYP)}$[1]	$G_{(corr\text{-}B3LYP)}$[2]	$H_{(corr\text{-}B3LYP)}$[3]	$E_{(solv,M11\text{-}L)}$[4]	IF[5]
NBD	-271.4723186	0.100906	0.134829	-271.504391	-
RhL_2^+	-653.4040931	0.221926	0.27489	-653.6789874	-
(E,S)-1	-2290.33219	0.432264	0.54319	-2290.457389	-
(Z,R)-2	-2290.401807	0.442099	0.545223	-2290.537785	-
(Z,S)-2	-2290.410145	0.438538	0.545198	-2290.546955	-
(Z,S)-3	-2290.333285	0.433536	0.543419	-2290.461308	-
4A	-2672.275743	0.555957	0.683591	-2672.61691	-
4B	-2672.279563	0.557908	0.683752	-2672.630774	
5A-ts	-2672.262732	0.556393	0.682069	-2672.608381	-102.21
5B-ts	-2672.23502	0.559935	0.681251	-2672.5846	-376.43
5C-ts	-2672.230443	0.551656	0.680309	-2672.585487	-190.78
6A	-2672.268996	0.557706	0.682471	-2672.625171	-
6B	-2672.264929	0.559078	0.683154	-2672.614185	-
6C	-2672.252514	0.554874	0.68276	-2672.607064	-
7A	-2672.268461	0.562768	0.683768	-2672.629462	-
7B	-2672.284466	0.564665	0.684571	-2672.639716	-
8A-ts	-2672.247848	0.563359	0.681924	-2672.616037	-195.21
8B-ts	-2672.281079	0.564967	0.683606	-2672.62853	-200.26
9	-2672.300634	0.565872	0.683417	-2672.661413	-
10-ts	-2672.269849	0.565014	0.682675	-2672.622034	-104.19

11	-2672.339213	0.567356	0.685614	-2672.687879	-
12-ts	-2672.266078	0.558419	0.682751	-2672.6044	-200.20
13	-2672.274334	0.554252	0.683276	-2672.618392	-
14-ts	-2672.250895	0.55838	0.682369	-2672.60254	-55.51
15	-2672.250965	0.556938	0.682426	-2672.604831	-
16	-2672.216119	0.562771	0.682856	-2672.592428	-
17-ts	-2672.213113	0.561913	0.681131	-2672.597661	-198.90
18	-2672.262677	0.562933	0.683845	-2672.635144	-
19-ts	-2672.238532	0.563815	0.682038	-2672.588093	-235.39
20	-2672.265684	0.565824	0.68403	-2672.615708	-
(E,S)-21	-2290.344343	0.441763	0.544691	-2290.485196	-
(E,R)-21	-2290.349859	0.440657	0.544733	-2290.488151	-
22	-2672.266452	0.554971	0.683565	-2672.610515	-
23-ts	-2672.251705	0.560133	0.682434	-2672.598401	-163.33
24	-2672.272422	0.562635	0.683993	-2672.625534	-
25	-2672.26659	0.562784	0.68368	-2672.614749	-
26-ts	-2672.249155	0.563243	0.682281	-2672.608564	-164.82
27	-2672.29566	0.565823	0.684186	-2672.643308	-
28-ts	-2672.281515	0.564566	0.682399	-2672.628986	-152.62
29	-2672.337472	0.566493	0.685453	-2672.691891	-
30-ts	-2672.251384	0.556984	0.682208	-2672.598196	-14.89
31	-2672.271971	0.554646	0.683098	-2672.615981	-
32-ts	-2672.24811	0.558827	0.68214	-2672.601138	-79.49
33	-2672.24723	0.556749	0.683112	-2672.600253	-
34	-2672.228295	0.561788	0.682969	-2672.590923	-
35-ts	-2672.218112	0.562465	0.681545	-2672.593777	-246.33
36	-2672.263453	0.562156	0.684077	-2672.624595	-
37-ts	-2672.236237	0.561223	0.682148	-2672.592097	-162.82
38	-2672.268547	0.567912	0.683435	-2672.621832	-

[1]The electronic energy calculated by B3LYP in gas phase. [2]The thermal correction to

Gibbs free energy calculated by B3LYP in gas phase. [3]The thermal correction to enthalpy calculated by B3LYP in gas phase. [4]The electronic energy calculated by M11-L in Dichloroethane (DCE) [5]The B3LYP calculated imaginary frequencies for the transition states.

Table S2. The electronic single point energy calculated by B3LYP-D3 and M06-L in Dichloroethane (DCE).

Geometry	$E_{(solv,B3LYP-D3)}$ [1]	$E_{(solv,M06-L)}$ [2]
NBD	-271.5617564	-271.5079249
RhL_2^+	-653.6392403	-653.5816048
(E,S)-1	-2290.838188	-2290.620791
(Z,R)-2	-2290.90488	-2290.689571
4A	-2672.882632	-2672.681899
5A-ts	-2672.873015	-2672.669633
6A	-2672.887107	-2672.681417
7A	-2672.883417	-2672.686544
8A-ts	-2672.866593	-2672.675841
9	-2672.910993	-2672.715137
10-ts	-2672.869565	-2672.869565
11	-2672.930415	-2672.930415

[1]The electronic energy calculated by B3LYP-D3 in Dichloroethane (DCE) solvent. [2]The electronic energy calculated by M06-L in Dichloroethane (DCE) solvent.