

Supporting Information for

Dirhodium(II) Complexes Catalyzed Dehydrosilylation of Styrenes: Theoretical Investigations on Mechanism, Selectivity, and Ligands Effects

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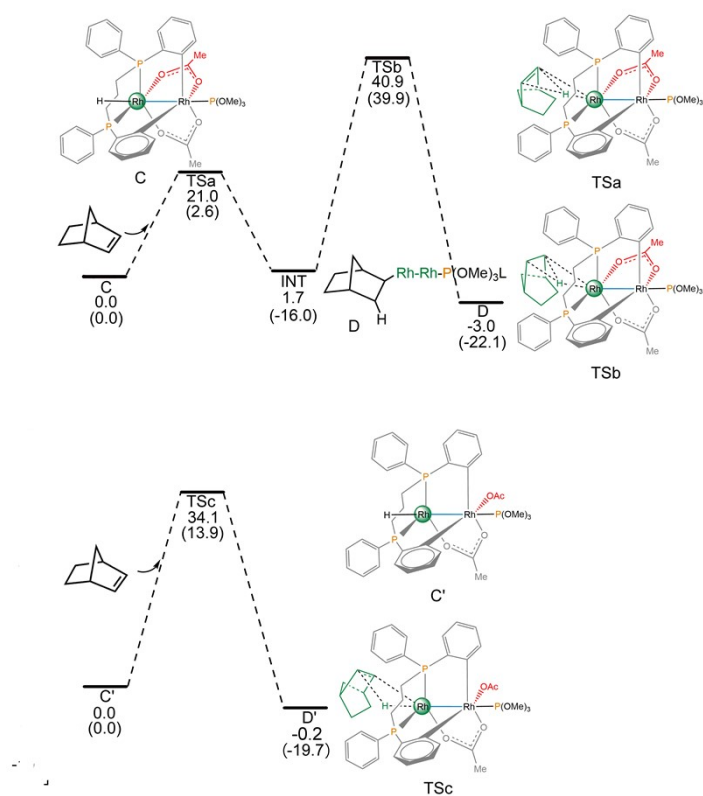
Contents

Figure S1 Free energy profiles without translational entropy correction in the solution	S2
Scheme S1 Frontier molecular orbitals of C'(a) HOMO (b) LUMO.	S4
Scheme S2 Other three isomers of the catalyst C.	S5
Scheme S3 The NPA parameters of C'/C". (The red numbers are the Wiberg bond indices, and the blue numbers are the NPA charges.).....	S6
Table S1 Gibbs free energies of alkylene insertion reaction ($E' \rightarrow TS3 \rightarrow F'$, in kcal/ mol) calculated using different DFT methods.	S7
Table S2 The absolute electronic energy without corrections, correction to free energy, sum of E_{elec} and G_{corr} , the output G from THERMO of each species and relative Gibbs free energies.....	S9
Table S3 ADF results for TSa, INT, TSb and TSc.	S13
Table S4 ADF results for the simplified of the TSa, INT, TSb and TSc.....	S13
Table S5 ADF results for TS4a, TS4b and TS5.	S14

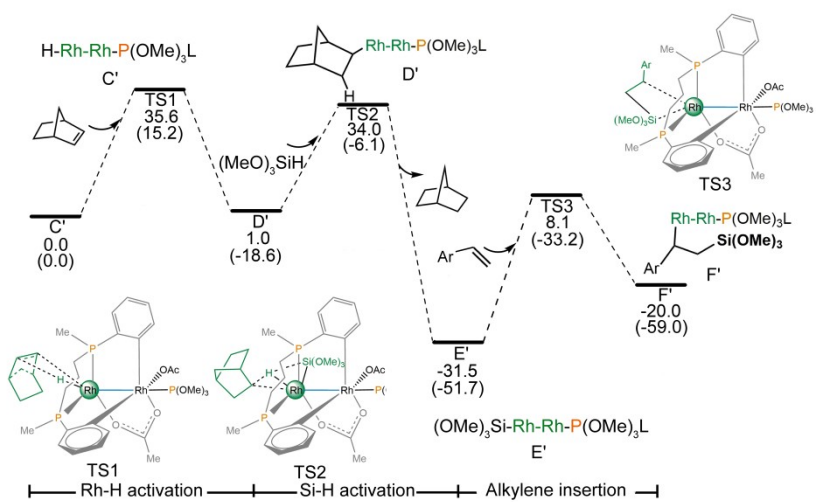
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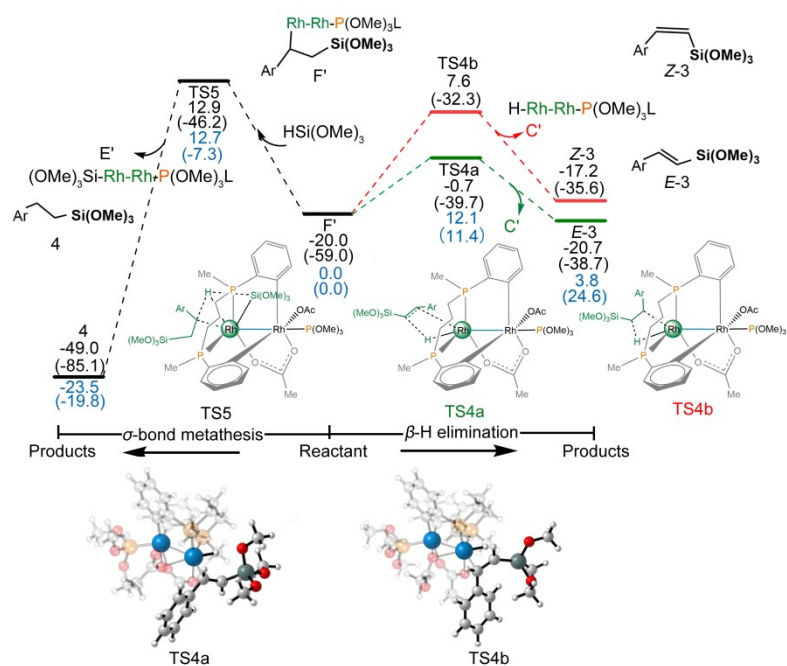
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(a)



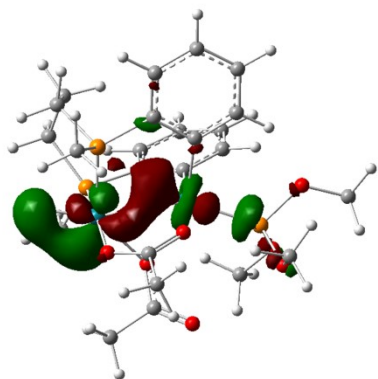
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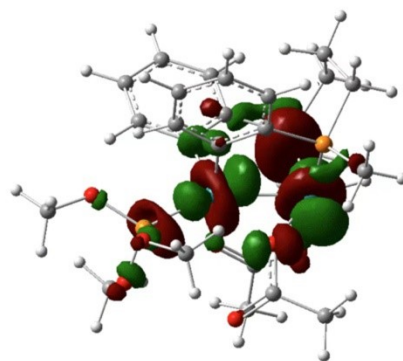
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Figure S1 Free energy profiles without translational entropy correction in the solution

Scheme S1 Frontier molecular orbitals of C'(a) HOMO (b) LUMO.

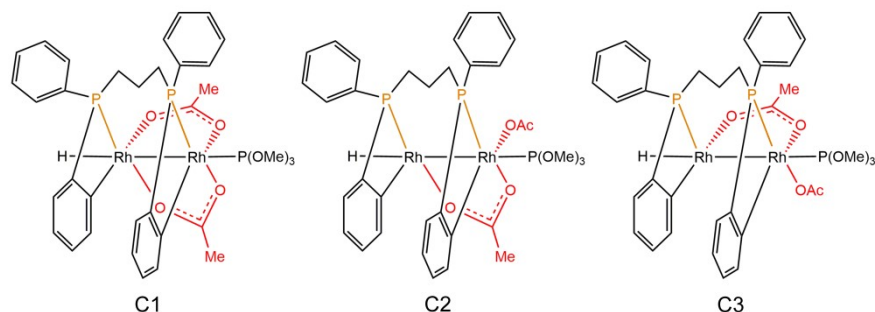


(a) HOMO(-2.31eV)



(b) LUMO(-1.31eV)

Scheme S2 Other three isomers of the catalyst C.



C1, C2, and C3 are the other three isomers of C (two Rh-P bonds on the same Rh atom). In all of these three isomers, one Rh-P bond on each Rh, rather than both to the same Rh. In C1, the two OAc ligands are bidentate two Rh atoms. In both C2 and C3, one OAc ligand is bidentate and the other OAc groups in monodentate. The difference between C2 and C3 are the positions of bidentate OAc and dppp ligand. In C2, the bidentate OAc locates at the opposite of dppp ligand. In C3, the bidentate OAc is neighbor to the dppp ligand. The free energy of C1, C2, and C3 is 28.1kcal/mol, 33.5kcal/mol, and 33.8 kcal/mol higher than that of C.

Scheme S3 The NPA parameters of C'/C". (The red numbers are the Wiberg bond indices, and the blue numbers are the NPA charges.)

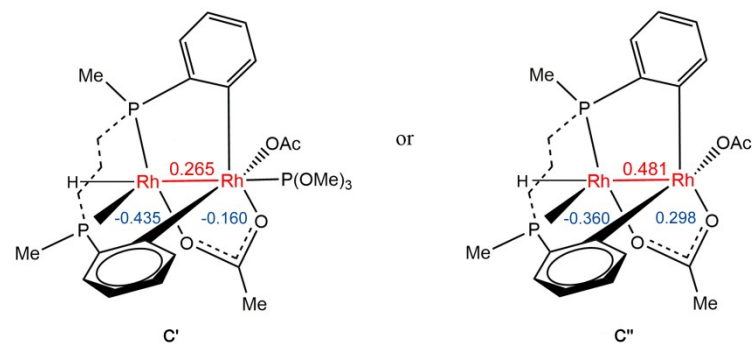


Table S1 Gibbs free energies of alkylene insertion reaction ($E' \rightarrow \text{TS3} \rightarrow F'$, in kcal/ mol) calculated using different DFT methods.

	GGA		mGGA		hybrid GGA			hybrid mGGA		
	BP86	M06L	B97D	PBE	B3LYP	B3PW91	PBE0	M06	M06-D3	M062X
$\Delta G_{\text{Thermo}}^{\ddagger}$	27.7	26.0	38.1	32.6	35.0	29.0	30.5	48.9	22.3	29.0
ΔG_{Thermo}	2.5	2.7	8.3	4.7	6.2	2.3	2.4	24.7	-0.2	2.0

In order to ensure the accuracy of the calculation results, different DFT methods (M06, M062X, M06L, BP86, B97D, PBE, B3LYP, B3PW91, PBE0) were used to calculate the single point energies of above process. $\Delta G_{\text{Thermo}}^{\ddagger}$ is the Gibbs free energy barrier and ΔG_{Thermo} is the free energy changes. As it is shown, the results of mGGA and GGA functionals are poor, those using M062X density functionals of hybrid mGGA, B3PW91 and PBE0 of hybrid GGA give better results comparing to other density functionals. The benchmarking indicates that the hybrid GGA performs better than hybrid mGGA for free energy barriers, which is the same as the conclusions of Schoenebeck's group (Chem. Rev. 2015, 115, 9532). Therefore, the results gotten from PBE0 method are used for the free energy discussion.

Refs:

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Table S2 The absolute electronic energy without corrections (E_{ele} , in Hartee), correction to free energy(G_{corr} , in Hartee), sum of E_{ele} and G_{corr} (G , in Hartee), the output G from THERMO (G_{Thermo} , in Hartee) of each species and relative Gibbs free energies(ΔG , in kcal/mol).

	E_{ele}	G_{corr}	$G_{(E_{\text{ele}}+G_{\text{corr}})}$	ΔG	G_{Thermo}	ΔG_{Thermo}
H-Rh-Rh(dppp)(POMe ₃)(OAc) ₂ (C)	-3090.0125	0.5573	-3089.4552		-3089.4419	
NBE	-272.4993	0.1111	-272.3882		-272.3734	
C+NBE	-3362.5118	0.6684	-3361.8434	0.0	-3361.8153	0.0
TSa	-3362.5070	0.6972	-3361.8098	21.0	-3361.7967	11.7
INT	-3362.5415	0.7009	-3361.8406	1.7	-3361.8274	-7.6
TSb	-3362.4744	0.6989	-3361.7755	40.9	-3361.7623	40.9
H-NBE-Rh-Rh(dppp)(POMe ₃)(OAc) ₂ (D)	-3362.5542	0.7063	-3361.8479	-3.0	-3361.8348	-12.2
H-Rh-Rh(dppp)(POMe ₃)(OAc) ₂ -monodentated (C')	-3089.9936	0.5557	-3089.4379		-3089.4246	
C'+NBE	-3362.4929	0.6668	-3361.8261	0.0	-3361.798	0.0
TSc	-3362.4712	0.6996	-3361.7716	34.1	-3361.7584	24.8
H-NBE-Rh-Rh(dppp)(POMe ₃)(OAc) ₂ - monodentated (D')	-3362.5313	0.7050	-3361.8263	-0.2	-3361.8130	-9.5
H-Rh-Rh(dppp)(POMe ₃)(OAc) ₂ -monodentated	-2706.8382	0.4617	-2706.3765		-2706.3631	

(C'-model)						
C'-model+NBE	-2979.3375	0.5728	-2978.7647	0.0	-2978.7365	0.0
TS1	-2979.3139	0.6058	-2978.7081	35.6	-2978.6946	26.3
H-NBE-Rh-Rh(dppp)(POMe ₃)(OAc) ₂ - monodentated (D'-model)	-2977.9308	0.6114	-2977.3194	1.0	-2978.7498	-8.3
(MeO) ₃ SiH (2)	-635.2546	0.0881	-635.1665		-635.1523	
TS2	-3614.6095	0.7325	-3613.877	34.0	-3613.8637	15.7
H-NBE	-273.7374	0.1343	-273.6031		-273.5884	
(MeO) ₃ Si-Rh-Rh(dppp)(POMe ₃)(OAc) ₂ - monodentated (E'-model)	-3340.9474	0.5690	-3340.3784		-3340.3650	
H-NBE+E'-model	-3614.6848	0.7033	-3613.9815	-31.5	-3613.9534	-40.6
Ph-CH=CH ₂ (1)	-309.3796	0.0894	-309.2902		-309.2756	
TS3	-3650.2998	0.6943	-3649.6055	8.1	-3649.5921	-10.2
[(MeO) ₃ Si]H ₈ C ₈ -Rh-Rh(dppp)(POMe ₃)(OAc) ₂ - monodentated (F'-model)	-3650.3418	0.6918	-3649.6500	-20.0	-3649.6369	-38.3
TS4a	-3650.3074	0.6880	-3649.6194	-0.7	-3649.6061	-18.9
<i>Tran</i> -(MeO) ₃ Si-C=C-Ph (<i>E</i> -3)	-943.4646	0.1898	-943.2748		-943.2609	

<i>E</i> -3+C'-model	-3650.3028	0.6515	-3649.6513	-20.7	-3649.624	-30.2
TS4b	-3650.2940	0.6878	-3649.6062	7.6	-3649.5930	-10.7
<i>Cis</i> -(MeO) ₃ Si-C=C-Ph (Z-3)	-942.9566	0.1906	-942.7660		-943.2552	
Z-3+C'-mode)	-3649.7948	0.6523	-3649.1425	-17.2	-3649.6183	-26.6
TS5	-4285.5755	0.8112	-4284.7643	12.9	-4284.7512	-14.5
(MeO) ₃ Si-C-C-Ph (4)	-944.6949	0.2102	-944.4847		-944.4706	
4+E'-model	-4285.6423	0.7792	-4284.8631	-49.0	-4284.8356	-67.4
[(MeO) ₃ Si]H ₈ C ₈ -Rh-Rh(dppp)(OAc) ₂ - monodentated (F''-model)	-2963.8401	0.5734	-2963.2667	0.0	-2963.2535	0.0
TS4a''	-2963.8177	0.5702	-2963.2475	12.1	-2963.2342	12.1
H-Rh-Rh(dppp)(OAc) ₂ -monodentated (C''-model)	-2020.3310	0.3451	-2019.9859		-2019.9723	
C''-model+E-3	-2963.7956	0.5349	-2963.2607	3.8	-2963.2332	12.7
TS5''	-3599.1075	0.6944	-3598.4131	12.7	-3598.3999	3.7
(MeO) ₃ Si-Rh-Rh(dppp)(POMe ₃)(OAc) ₂ - monodentated (E''-model)	-2654.4364	0.4503	-2653.9861		-2653.9727	
E''-model+4	-3599.1313	0.6605	-3598.4708	-23.5	-3598.4433	-23.6
H-Rh-Rh(dppp)(POMe ₃)(OAc) ₂ (C-model)	-2706.8594	0.4635	-2706.3959		-2706.3825	

TSa-model	-2979.3541	0.6024	-2978.7517	-2978.7384
INT-model	-2979.3861	0.6060	-2978.7801	-2978.7668
TSb-model	-2979.3194	0.6043	-2978.7151	-2978.7017
H-NBE-Rh-Rh(dppp)(POMe ₃)(OAc) ₂ (D-model)	-2979.3978	0.6127	-2978.7851	-2978.7718
(MeO) ₃ Si-Rh-Rh(dppp)(POMe ₃)(OAc) ₂ (E-model)	-3340.9669	0.5696	-3340.3973	-3340.3840

1 Hartree = 627.5094kcal/mol

Table S3 ADF results for TSa, INT, TSb and TSc.

kcal/mol	TSa	INT	TSb	TSc
E_{Pauli}	52.5	24.7	154.7	172.8
E_{electr}	-25.7	-13.8	-76.3	111.9
E_{orb}	-168.2	-197.6	-227.6	-213.1
E_{disp}	-10.6	-9.3	-11.9	-12.4
E_{int}	-152.1	-196.7	-161.1	-164.6
E_{steric}	26.7	10.9	78.4	60.9
$E_{\text{electr}}\%$	12.6	6.3	24.2	33.2
$E_{\text{orb}}\%$	82.2	89.3	72.3	63.2
$E_{\text{disp}}\%$	5.2	4.5	3.8	4.4
$E_{\text{steric}}\%$	51.0	44.0	50.7	35.2

Table S4 ADF results for the simplified of the TSa, INT, TSb and TSc.

kcal/mol	TSa	INT	TSb	TSc
E_{Pauli}	50.2	21.2	138.3	180.8
E_{electr}	-24.1	-11.3	-68.0	-115.8
E_{orb}	-167.0	-186.7	-219.9	-220.6
E_{disp}	-9.0	-8.1	-9.9	-10.2
E_{int}	-149.8	-184.8	-159.4	-165.8
E_{steric}	26.2	10.0	70.4	65.0
$E_{\text{electr}}\%$	12.0	5.5	22.8	33.4
$E_{\text{orb}}\%$	83.5	90.6	73.8	63.6
$E_{\text{disp}}\%$	4.5	3.9	3.3	2.9
$E_{\text{steric}}\%$	52.1	47.0	50.9	35.9

Table S5 ADF results for TS4a, TS4b and TS5.

kcal/mol	TS4a	TS5	TS4b
E_{Pauli}	183.5	146.0	189.7
E_{electr}	-108.5	-81.8	-102.9
E_{orb}	-98.3	-94.9	-102.9
E_{disp}	-17.6	-16.3	-15.1
E_{int}	-40.9	-47.0	-27.9
E_{steric}	75.0	64.3	86.8
$E_{\text{electr}}\%$	48.4	42.4	46.6
$E_{\text{orb}}\%$	43.8	46.6	48.4
$E_{\text{disp}}\%$	7.8	8.4	6.8
$E_{\text{steric}}\%$	40.9	44.0	45.8

$$E_{\text{electr}}\% = E_{\text{electr}}/(E_{\text{orb}} + E_{\text{disp}} + E_{\text{electr}}); E_{\text{orb}}\% = E_{\text{orb}}/(E_{\text{orb}} + E_{\text{disp}} + E_{\text{electr}}); E_{\text{disp}}\% = E_{\text{disp}}/(E_{\text{orb}} + E_{\text{disp}} +$$

$$E_{\text{electr}}); E_{\text{steric}}\% = E_{\text{steric}}/E_{\text{Pauli}}$$