

Supporting Information

Computational Part

Half-Sandwich Ruthenium Carbene Complexes Link *trans*-Hydrogenation and *gem*-Hydrogenation of Internal Alkynes

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1. Computational methods

Density functional theory (DFT) was used to elucidate the mechanism of the Ru(II) catalyzed hydrogenation of alkynes. All geometry optimizations were performed using the M06¹ functional. The triple- ζ quality def2-TZVP² basis set was used for all atoms. The 28 inner-shell core electrons of the ruthenium atom were described by the corresponding def2 effective core potential³ accounting for scalar relativistic effects (def2-ecp).

Stationary points were characterized by evaluating the harmonic vibrational frequencies at the optimized geometries. Zero-point vibrational energies (ZPVE) were computed from the corresponding harmonic vibrational frequencies without scaling. Relative free energies (ΔG) were determined at standard pressure (1 bar) and at room temperature (298 K). The thermal and entropic contributions were evaluated within the rigid-rotor harmonic-oscillator approximation. Solvation contributions were included for dichloromethane on the optimized gas-phase geometries employing the SMD solvation model⁴ using the same functional and basis set. All calculations were performed using Gaussian09 with the ultrafine grid.⁵

Energies derived from coupled cluster theory were obtained using the domain-based pair natural orbital coupled cluster method with single and double excitations, DLPNO-CCSD, and with a perturbational estimate of the triples contributions, DLPNO-CCSD(T). The def2-TZVP² basis set was used for all atoms in conjunction with the resolution of identity approximation⁶ applying the RIJCOX method.⁷ The 28 inner-shell core electrons of the ruthenium atom were described by the corresponding def2 effective core potential³ accounting for scalar relativistic effects (def2-ecp). All coupled cluster calculations were performed using Orca 4.0.⁸

2. DFT results

The Supporting Information of our previous communication⁹ documents the Cartesian coordinates of all relevant optimized geometries as well as all relevant DFT-based energies and energy corrections required to evaluate free energies. These data are not presented again here.

3. CCSD and CCSD(T) results

Single-point CCSD and CCSD(T) calculations were performed at the DFT-optimized geometries of all stationary points in the hydrogenation reactions of 2-butyne with the neutral Ru(II) catalyst. Table S1 lists the calculated total and relative energies (DFT, CCSD, and CCSD(T)). Figure S1 shows an overlay of the computed energy profiles for the reactions yielding the *E*-alkene (**E2**) and carbene (**C2**) complexes. Figures S2 and S3 show analogous overlays for the H₂ associative pathways leading from the carbene (**C2**) complex to the side products, for the approach of H₂ from the side of the methyl group and the ethyl group, respectively. The notation is the same as in our previous communication.⁹

Table S1. Total energies (atomic units), Gibbs energy corrections (G_{corr} , atomic units), and relative Gibbs energies (kcal/mol) for the stationary points of the investigated reactions evaluated at the DFT-optimized geometries. All energies listed are obtained in the gas phase.

	G_{corr}	Total energy			Relative free energy		
	M06	M06	CCSD	CCSD(T)	M06	CCSD	CCSD(T)
H ₂	-0.001642	-1.170676	-1.168424	-1.168424	-	-	-
COD	0.148036	-311.885137	-311.354971	-311.412209	-	-	-
2-butyne	0.054557	-155.909153	-155.638631	-155.666657	-	-	-
A0	0.357267	-1257.045711	-1254.821193	-1254.993435	0.00	0.00	0.00
A1	0.275921	-1102.221195	-1100.253115	-1100.389989	20.70	21.30	25.16
TS _{A1-A2}	0.276381	-1102.210663	-1100.244256	-1100.383789	27.60	27.14	29.34
A2	0.278153	-1102.212742	-1100.245678	-1100.386875	27.40	27.36	28.51
TS _{A2-A3}	0.275004	-1102.205382	-1100.241586	-1100.382558	30.00	27.95	29.25
A3	0.278601	-1102.215509	-1100.249976	-1100.389332	25.95	24.95	27.25
TS _{A3-E1}	0.279117	-1102.215400	-1100.249493	-1100.388942	26.34	25.57	27.82
E1	0.279811	-1102.231583	-1100.262956	-1100.407695	16.62	17.56	16.49
TS _{E1-E2}	0.279170	-1102.223233	-1100.250745	-1100.394614	21.46	24.82	24.30
E2	0.284219	-1102.287611	-1100.319354	-1100.455562	-15.77	-15.06	-10.78
TS _{E1-C1}	0.279224	-1102.220078	-1100.251883	-1100.395422	23.47	24.14	23.82
C1	0.278611	-1102.223333	-1100.255458	-1100.399928	21.04	21.51	20.61
TS _{C1-C2}	0.277775	-1102.221485	-1100.254972	-1100.399108	21.68	21.29	20.60
C2	0.280593	-1102.252791	-1100.284475	-1100.422472	3.80	4.55	7.71
TS _{C2-Z1}	0.279344	-1102.225181	-1100.257358	-1100.400584	20.34	20.78	20.66
Z1	0.279260	-1102.228292	-1100.260529	-1100.404349	18.34	18.74	18.24
TS _{Z1-Z2}	0.280024	-1102.217448	-1100.247871	-1100.391740	25.62	27.16	26.63
Z2	0.279233	-1102.226201	-1100.256055	-1100.401370	19.64	21.53	20.10
TS _{Z2-Z3}	0.278856	-1102.224513	-1100.252564	-1100.396856	20.46	23.48	22.69

Z3	0.285069	-1102.284838	-1100.316589	-1100.453238	-13.50	-12.79	-8.79
TS _{A3-Z1}	0.279276	-1102.210127	-1100.244579	-1100.384125	29.75	28.76	30.94
TS _{C2-R1}	0.294651	-1103.420214	-1101.447838	-1101.585596	15.70	17.58	20.89
R1	0.299383	-1103.428659	-1101.458015	-1101.596652	13.37	14.16	16.92
TS _{R1-R2}	0.299586	-1103.419613	-1101.451250	-1101.592179	19.17	18.53	19.85
R2	0.298507	-1103.419820	-1101.451387	-1101.591769	18.36	17.77	19.43
TS _{R2-R3}	0.297909	-1103.417505	-1101.449984	-1101.588791	19.44	18.27	20.92
R3	0.302813	-1103.430921	-1101.461142	-1101.599168	14.10	14.35	17.49
TS _{R3-D1}	0.303033	-1103.425875	-1101.455193	-1101.592502	17.40	18.22	21.81
D1	0.304014	-1103.451315	-1101.484335	-1101.622567	2.06	0.55	3.56
TS _{D1-D2}	0.301143	-1103.444955	-1101.479661	-1101.619333	4.24	1.68	3.79
D2	0.303441	-1103.452982	-1101.486025	-1101.626438	0.65	-0.87	0.77
TS _{D2-D3}	0.298833	-1103.447956	-1101.482303	-1101.620574	0.91	-1.43	1.56
D3	0.301559	-1103.454030	-1101.486046	-1101.622372	-1.19	-2.06	2.14
D4	0.284134	-1102.285234	-1100.318637	-1100.454906	-14.33	-14.67	-10.42
TS _{R3-B1}	0.301364	-1103.424607	-1101.454014	-1101.591025	17.15	17.91	21.69
B1	0.304278	-1103.457568	-1101.491208	-1101.627895	-1.70	-3.60	0.38
TS _{B1-B2}	0.303507	-1103.456506	-1101.490109	-1101.626595	-1.52	-3.39	0.72
B2	0.300968	-1103.484055	-1101.517291	-1101.646955	-20.40	-22.04	-13.65
TS _{C2'-R1'}	0.292892	-1103.420451	-1101.447048	-1101.584239	14.44	16.97	20.63
R1'	0.298501	-1103.429110	-1101.458530	-1101.596677	12.53	13.28	16.35
TS _{R1'-R2'}	0.297657	-1103.418818	-1101.450800	-1101.590146	18.46	17.60	19.92
R2'	0.298564	-1103.419326	-1101.451191	-1101.591131	18.71	17.93	19.87
TS _{R2'-R3'}	0.296647	-1103.418023	-1101.450719	-1101.589324	18.32	17.02	19.80
R3'	0.302535	-1103.429657	-1101.460435	-1101.598380	14.72	14.62	17.81
TS _{R3'-D1'}	0.303243	-1103.425761	-1101.454991	-1101.592206	17.61	18.48	22.13
D1'	0.303036	-1103.452310	-1101.486229	-1101.624768	0.82	-1.25	1.57
TS _{D1'-D2'}	0.301516	-1103.447590	-1101.481549	-1101.621102	2.83	0.73	2.91
D2'	0.302996	-1103.450916	-1101.482293	-1101.622934	1.67	1.19	2.69
TS _{D2'-D3'}	0.299987	-1103.448324	-1101.482067	-1101.620550	1.41	-0.55	2.30
D3'	0.302087	-1103.462960	-1101.492102	-1101.629358	-6.46	-5.53	-1.91
TS _{R3'-B1'}	0.302406	-1103.424333	-1101.453478	-1101.590571	17.98	18.90	22.63
B1'	0.302908	-1103.457099	-1101.490766	-1101.627643	-2.27	-4.18	-0.32
TS _{B1'-B2'}	0.303495	-1103.456013	-1101.488209	-1101.624214	-1.22	-2.21	2.20
B2'	0.300507	-1103.483869	-1101.516424	-1101.645921	-20.57	-21.79	-13.29

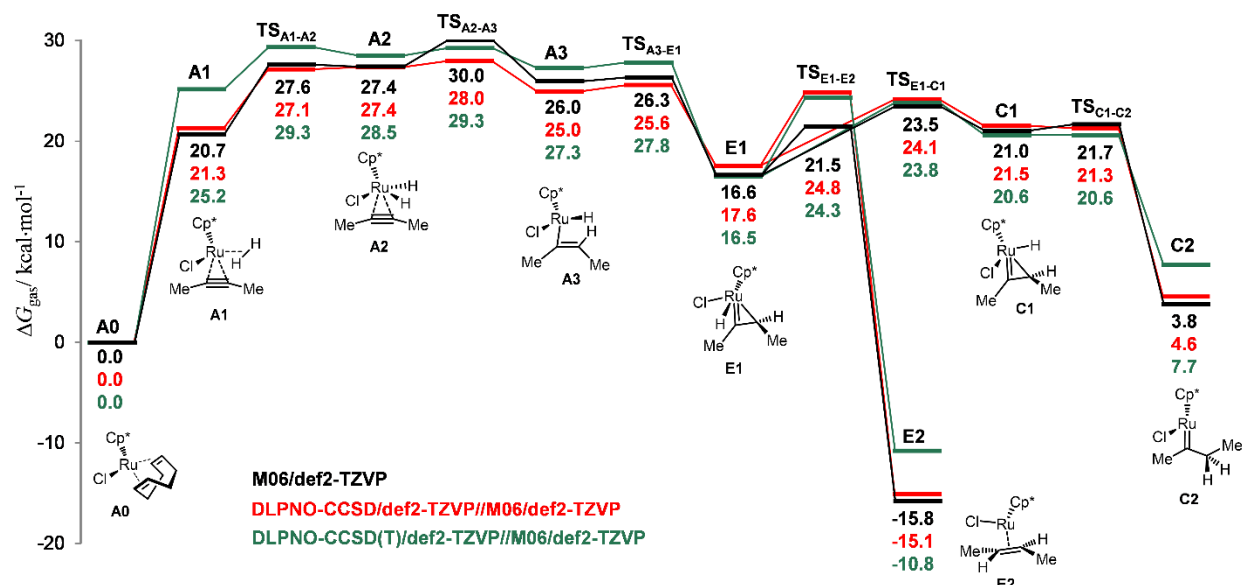


Figure S1. Overlay of the computed energy profiles for the reactions yielding the *E*-alkene (E2) and carbene (C2) complexes.

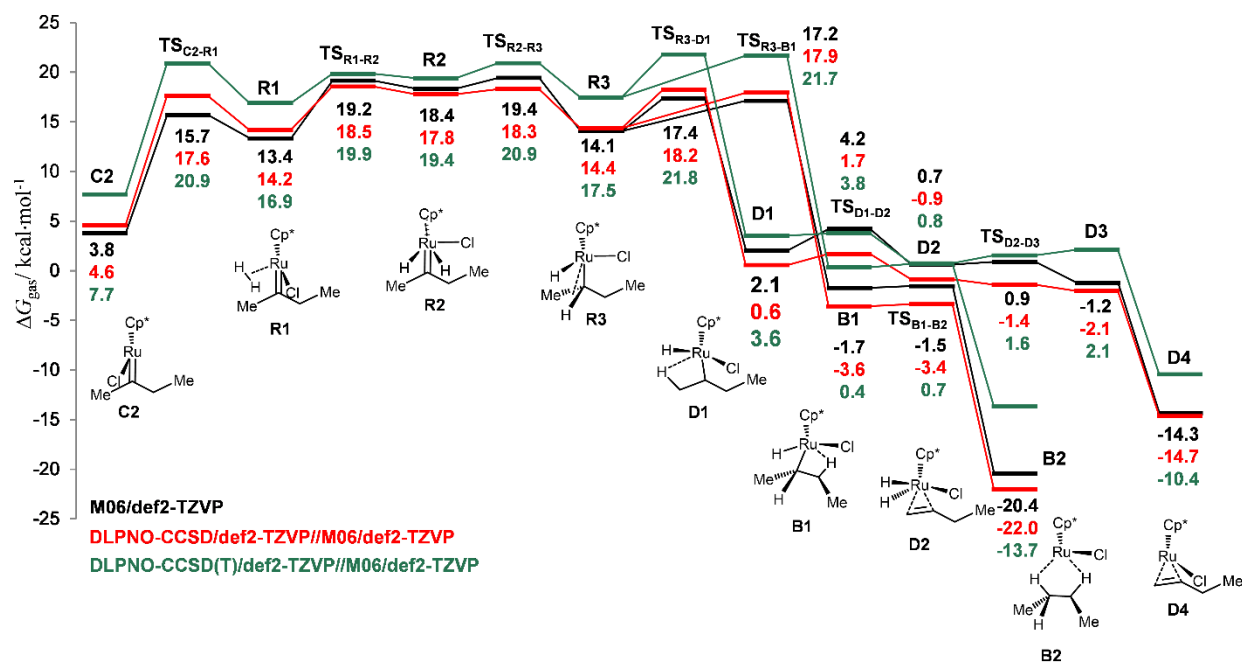


Figure S2. Overlay of the computed energy profiles for the H₂ associative pathways, through approach from the side of the methyl group, leading from the carbene (C2) complex to the side products B2 and D4.

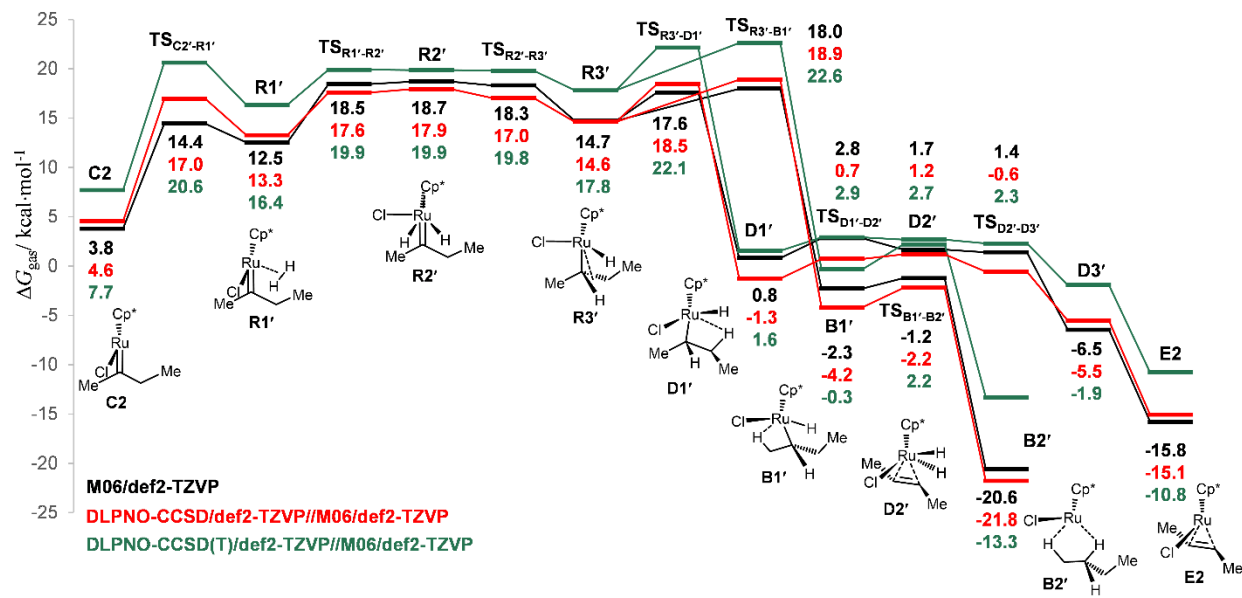


Figure S3. Overlay of the computed energy profiles for the H₂ associative pathways, through approach from the side of the ethyl group, leading from the carbene (**C2**) complex to the side products **B2'** and **E2**.

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