[5 + 1 + 2 + 1] vs. [5 + 1 + 1 + 2] Rhodium-Catalyzed Cycloaddition Reactions of Vinylcyclopropanes with Terminal Alkynes and Carbon Monoxide: Density Functional Theory Investigations of Convergent Mechanistic Pathways and Reaction Regioselectivity.

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Supporting Information

Stationary point geometries were first obtained at the PM3 semi-empirical level of theory[1] as implemented in the Spartan'16 computational software package.[2] These geometries were used as initial points for density functional theory (DFT) geometry optimization at the B3LYP[3]/6-31G* level. Improved geometries and energies were then obtained from these coordinates first by optimization at the ωB97XD[4]/def2TZVPP[5], and then a full geometry optimization at the ωB97XD/SDD[6]–6-31G* level (Stuttgart/Dresden ECP on rhodium, with 6-31G* on all other atoms), with solvent corrections (toluene, ε = 2.3741) applied via the polarizable continuum model.[7] The final DFT level optimizations were performed with the Gaussian09 (Revision C.01) software suite.[8] Vibrational analyses were conducted to confirm the nature of all stationary points and to produce thermal corrections (enthalpy and entropy) for 298 K, 1 bar, gas phase. To account for entropy overestimation in gas phase calculations, the solution Gibbs energy was corrected by applying free volume theory, such that $\Delta G°_{sol} = \Delta G°_{gas} - X$ where X = 2.6, 5.0, and 7.3 kcal/mol for bi-, tri-, and tetramolecular processes respectively.[9] AIM analyses were performed with the AIMAll software suite[10] using .wfx files generated from the Gaussian optimized structures.

Thermodynamic parameters for all stationary points reported in the manuscript are tabulated below.

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Table S1: Thermodynamic parameters for Figure 1 and Figure 4 in the main text.

	Enthalpy (hartree)	ZPE (hartree)	Entropy (cal/mol•K)	Gibbs Energy (hartree)
INT 1	-993.679384	0.160680	113.789	-993.733449
TS 1-2	-993.678406	0.160474	110.143	-993.730738
INT 2	-993.677820	0.161346	116.154	-993.733009
INT 3	-993.691586	0.162386	112.568	-993.745070
INT 4	-1106.982789	0.170671	125.128	-1107.042242
TS 4-5	-1106.955690	0.170612	121.142	-1107.013249
INT 5	-1106.996646	0.173134	120.455	-1107.053877
INT 6a	-1184.268623	0.202276	134.534	-1184.332544
TS 6a-7a	-1184.228156	0.201877	129.068	-1184.289480
INT 7a	-1184.282881	0.206061	129.715	-1184.344513
INT 8a	-1297.578794	0.214937	142.709	-1297.646600
TS 8a-11	-1297.524794	0.213213	142.259	-1297.592386
INT 6b	-1220.283545	0.180920	133.120	-1220.346795
TS 6b-7b	-1220.242830	0.181204	129.957	-1220.304577
INT 7b	-1220.273903	0.182691	130.950	-1220.336121
INT 8b	-1220.246213	0.181938	128.921	-1220.307467
INT 9b	-1297.528379	0.211775	143.007	-1297.596326
TS 9b-10b	-1297.500779	0.210729	142.346	-1297.568412
INT 11	-1297.560272	0.215988	140.724	-1297.627135
TS 11-12	-1297.548867	0.215088	135.960	-1297.613466
INT 12	-1297.617443	0.218205	136.169	-1297.682141
INT 13	-613.489310	0.207709	108.286	-613.540761
INT 14	-613.464411	0.206196	109.755	-613.516559
TS 14-15	-613.432276	0.204780	106.056	-613.482666
INT 15	-613.504643	0.207674	105.278	-613.554664
TS 15-17	-613.435465	0.200556	106.612	-613.486120
INT 16	-613.865143	0.220145	107.283	-613.916117
INT 17	-498.282656	0.165005	91.689	-498.326221
MeOH	-115.623248	0.052151	56.670	-115.650174
C2H2	-77.263401	0.027037	47.908	-77.286164
CO	-113.263344	0.005109	47.226	-113.285783
VCP	-309.552896	0.148945	85.674	-309.593602
H3O+	-76.702700	0.035255	48.315	-76.725655
H2O	-76.365327	0.021635	45.104	-76.386757

Table S2: Thermodynamic parameters for Figure 6 in the main text.

	Enthalpy (hartree)	ZPE (hartree)	Entropy (cal/mol•K)	Gibbs Energy (hartree)
INT 6c	-1223.553705	0.231324	142.218	-1223.621277
TS 6c-7c	-1223.507055	0.231089	136.471	-1223.571896
INT 7c	-1223.554223	0.233439	142.461	-1223.621910
INT 6c'	-1223.554538	0.231300	142.253	-1223.622128
TS 6c'-7c'	-1223.515093	0.230394	137.263	-1223.580311
INT 7c'	-1223.532477	0.232919	140.189	-1223.599085
INT 9c	-1336.813118	0.240024	153.309	-1336.885960
TS 9c-10c	-1336.781228	0.239855	148.830	-1336.851942
INT 10c	-1336.822049	0.243416	148.970	-1336.892829
INT 9c'	-1336.815614	0.240868	149.449	-1336.886622
TS 9c'-10c'	-1336.787937	0.239387	150.821	-1336.859597
INT 10c'	-1336.820653	0.242969	149.804	-1336.891830
INT 9c Ph	-1528.425280	0.294383	168.498	-1528.505339
TS 9c-10c Ph	-1528.395506	0.293804	164.320	-1528.473580
INT 10c Ph	-1528.436607	0.297225	166.014	-1528.515485
INT 9c' Ph	-1528.430605	0.294348	166.782	-1528.509849
TS 9c'-10c' Ph	-1528.403007	0.293981	164.991	-1528.481400
INT 10c' Ph	-1528.431527	0.296461	166.948	-1528.510850
INT 6c Ph	-1415.169032	0.285246	159.283	-1415.244712
TS 6c-7c Ph	-1415.123320	0.284699	153.346	-1415.196179
INT 7c Ph	-1415.166451	0.288207	153.904	-1415.239576
INT 6c' Ph	-1415.169056	0.285192	159.611	-1415.244892
TS 6c'-7c' Ph	-1415.130975	0.284957	154.622	-1415.204440
INT 7c' Ph	-1415.157199	0.287714	154.655	-1415.230681

Table S3: Thermodynamic parameters for Figure 11 in the main text.

	Enthalpy (hartree)	ZPE (hartree)	Entropy (cal/mol•K)	Gibbs Energy (hartree)
INT 12	-1297.617443	0.218205	136.169	-1297.682141
TS 12-18	-1297.564838	0.217391	132.198	-1297.627649
INT 18	-1297.622827	0.219843	129.971	-1297.684581
TS 18-19	-1297.551376	0.216208	131.272	-1297.613748
INT 19	-1297.553107	0.217109	134.916	-1297.617210
TS 19-20	-1297.551082	0.212720	133.832	-1297.614670
INT 20	-1297.650943	0.217751	140.508	-1297.717703
INT 21	-1181.997812	0.162249	123.031	-1182.056268
INT 22	-1182.011672	0.162757	123.644	-1182.070420

Table S4: Thermodynamic parameters for Figure 13 in the main text.

	Enthalpy (hartree)	ZPE (hartree)	Entropy (cal/mol•K)	Gibbs Energy (hartree)
INT 5	-1106.996646	0.173134	120.455	-1107.053877
TS 5-23	-1106.958102	0.171623	118.392	-1107.014354
INT 23	-1106.980249	0.173044	121.520	-1107.037988
INT 6b	-1220.283545	0.180920	133.120	-1220.346795
TS 6b-24	-1220.236272	0.179952	131.010	-1220.298519
INT 24	-1220.310406	0.182539	134.875	-1220.374489

Table S5: Thermodynamic parameters for Table 1 in the main text.

	Enthalpy (hartree)	ZPE (hartree)	Entropy (cal/mol•K)	Gibbs Energy (hartree)
INT 1a	-1032.955247	0.189353	120.098	-1033.012309
TS 1a-2a	-1032.954144	0.188978	117.196	-1033.009827
INT 2a	-1032.955964	0.190444	120.266	-1033.013107
INT 1b	-1032.955423	0.189760	118.775	-1033.011857
TS 1b-2b	-1032.951904	0.188909	117.850	-1033.007899
INT 2b	-1032.949367	0.189610	123.523	-1033.008056
INT 1c	-1032.951807	0.189627	121.013	-1033.009304
TS 1c-2c	-1032.950031	0.189244	117.151	-1033.005693
INT 2c	-1032.952000	0.189817	122.707	-1033.010302
INT 1d	-1032.946536	0.189741	121.580	-1033.004303
TS 1d-2d	-1032.945310	0.189903	115.261	-1033.000075
INT 2d	-1032.951662	0.189759	122.062	-1033.009658
INT 1e	-1106.947053	0.170649	123.710	-1107.005831
TS 1e-2e	-1106.944095	0.169794	121.836	-1107.001983
INT 2e	-1106.947141	0.170784	126.235	-1107.007119
INT 2f	-1106.963660	0.171754	124.329	-1107.022733
INT 1g	-1106.941514	0.170583	126.367	-1107.001555
TS 1g-2g	-1106.939164	0.170683	119.868	-1106.996117
INT 2g	-1106.957636	0.171755	122.900	-1107.016030
INT 1h	-1106.946541	0.170417	123.493	-1107.005217
TS 1h-2h	-1106.943205	0.169762	122.039	-1107.001189
INT 2h	-1106.948921	0.170459	126.276	-1107.008919

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