Supplementary Information for:

Associative vs. dissociative binding of CO_2 on M_5 transition metal clusters

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	r(CO)	r(CO)	θ(OCO)	ν(bend)	ν (bend)	ν (symm_stretch)	ν (asym_stretch)	ν (imag)	E(HOMO)	E(LUMO)	q(M5)	q(CO2)	E_{ads}	E_{int}
	Å		°			cm^{-1}			Hartree		e		eV	
M5									-0.16666	-0.10465				
g1	1.182	1.193	179.96	553.5658	576.876	1276.5886	2340.6443		-0.15919	-0.10033	-0.142	0.142	-0.483	-0.484
ts1	1.222	1.327	132.17	371.7307	709.0994	1109.5649	1726.4537	-56.8589	-0.18717	-0.13278	0.418	-0.418	-0.573	1.212
g2	1.282	1.312	132.67	482.3571	707.4356	1132.4489	1541.25		-0.18243	-0.11599	0.497	-0.497	-2.463	-0.444
ts2	1.266	1.372	127.19	466.8703	697.0335	994.0995	1516.0432	-66.7277	-0.19401	-0.1161	0.590	-0.590	-2.199	0.207
g3	1.39	1.404	116.34	567.5587	626.4673	988.4696	1056.6941		-0.18108	-0.11851	0.641	-0.641	-3.003	1.152
ts3	1.7	4.173	72.92	485.3839	607.3202	631.4852	716.5344	-366.073	-0.17221	-0.11299	1.050	-1.050	-2.215	10.438
g4	1.284	3.396	92.93	490.2889	611.4769	887.3325	1398.5032		-0.19439	-0.12701	0.785	-0.785	-2.654	5.156
ts4	1.7	4.173	72.92	485.3839	607.3202	631.4852	716.5344	-330.7486	-0.17221	-0.11299	1.050	-1.050	-4.069	8.584
g5	2.77	3.657	68.78	600.4482	671.546	672.5742	700.7793		-0.16848	-0.11514	1.273	-1.273	-6.778	12.486
ts3b	1.296	1.692	121.26	462.646	558.8128	609.9728	1359.8563	-335.632	-0.17902	-0.12054	0.649	-0.649	-2.087	2.925
g4b	1.34	3.595	122.14	500.2116	623.6668	673.7944	1215.8452		-0.17605	-0.11575	0.926	-0.926	-4.436	4.131
ts4b	1.89	3.468	77.67	566.1126	653.6813	696.8263	747.1924	-475.5851	-0.18228	-0.1154	1.008	-1.008	-3.928	10.280
g5b	3.39	3.925	81.83	602.9637	682.8957	764.5902	901.6891		-0.18045	-0.12197	1.259	-1.259	-6.052	14.262
ts5b	3.08	3.576	83.78	639.53	681.5477	720.697	866.314	-140.1948	-0.17016	-0.11666	1.243	-1.243	-6.013	13.851
g6b	2.937	3.352	108.55	613.392	678.0525	679.9405	692.9518		-0.16939	-0.11563	1.251	-1.251	-6.680	13.270
ts6b	2.93	2.882	89.5	595.9234	647.5031	682.4822	690.1	-64.74	-0.16584	-0.10944	1.265	-1.265	-5.600	13.704

Table S1. Reaction path data for $Nb_5 + CO_2$.

	r(CO)	r(CO)	θ(OCO)	ν(bend)	ν (bend)	ν (symm_stretch)	ν (asym_stretch)	ν (imag)	E(HOMO)	E(LUMO)	q(M5)	q(CO2)	E_{ads}	E_{int}
	Å		°			cm^{-1}			Hartree		e		eV	

	r(CO)	r(CO)	θ(OCO)	ν(bend)	ν (bend)	ν (symm_stretch)	ν (asym_stretch)	ν (imag)	E(HOMO)	E(LUMO)	q(M5)	q(CO2)	E_{ads}	E_{int}
	Å		°			cm^{-1}			Hartree		e		eV	
M5									-0.16899	-0.09599				
g1	1.184	1.19	179.98	560.1485	560.2182	1279.386	2339.9683		-0.16124	-0.08841	-0.119	0.118	-0.438	-0.439
ts1	1.191	1.8	122.03	441.9316	508.0624	767.2144	1888.4601	-355.913	-0.1877	-0.12791	0.494	-0.494	-1.455	3.812
g2	1.249	3.509	140.78	484.5937	520.983	929.3701	1574.5969		-0.19446	-0.13621	0.795	-0.795	-3.257	4.097
ts2	1.329	3.655	93.45	465.1742	566.3971	907.9497	1237.0518	-239.7418	-0.19025	-0.13335	0.837	-0.837	-2.092	5.621
g3	1.359	4.025	79.73	453.6968	640.9102	917.7948	1083.5819		-0.19477	-0.13197	0.845	-0.845	-2.547	5.840
ts3	3.183	4.215	50.86	634.6632	687.7368	730.0102	954.6667	-165.1958	-0.20475	-0.13264	1.114	-1.114	-4.041	15.342
g4	1.382	4.04	63.77	560.8301	636.0416	944.5952	1038.636		-0.19035	-0.12821	0.869	-0.869	-2.767	4.523
ts4	3.183	4.215	50.86	634.6632	687.7368	730.0102	954.6667	-157.6774	-0.20475	-0.13264	1.114	-1.114	-4.041	15.342
g5	3.714	4.84	44.41	632.1592	704.5578	734.3566	936.9198		-0.1973	-0.13465	1.183	-1.183	-4.905	15.176
ts4b	1.59	4.027	62.77	556.9525	633.9984	665.4613	937.0388	-120.0284	-0.19469	-0.14018	0.945	-0.945	-2.194	8.028
g5b	3.34	3.446	59.2	640.8732	659.7428	722.1593	939.5447		-0.2076	-0.13544	1.157	-1.157	-4.635	14.831

Table S2. Reaction path data for $Mo_5 + CO_2$.

	r(CO)	r(CO)	θ(OCO)	ν(bend)	ν (bend)	ν (symm_stretch)	ν (asym_stretch)	ν (imag)	E(HOMO)	E(LUMO)	q(M5)	q(CO2)	E_{ads}	E_{int}
	Å		°			cm^{-1}			Hartree		e		eV	
M5									-0.17617	-0.10727				
g1	1.266	1.292	178.72	547.639	738.2504	1145.269	1623.5782		-0.20783	-0.10351	0.381	-0.381	-0.361	-0.370
ts1	1.236	1.309	138.05	510.3612	690.1417	1063.9547	1730.6117	-35.4775	-0.20566	-0.14974	0.374	-0.374	-1.320	0.361
g2	1.226	1.284	144.55	534.6916	669.9669	1105.3679	1835.1278		-0.20738	-0.13833	0.322	-0.322	-0.846	0.271
ts2	1.225	1.292	143.48	475.786	655.1531	1062.3144	1819.6708	-76.3738	-0.2056	-0.15005	0.345	-0.345	-0.635	0.552
g3	1.266	1.291	137.07	547.5182	738.2949	1146.006	1623.3891		-0.20784	-0.13915	0.381	-0.381	-1.921	-0.347
ts3	1.181	4.357	103.84	444.7586	475.3573	921.6729	1935.136	-163.4808	-0.22609	-0.16693	0.395	-0.395	-2.033	5.893
g4	1.189	5.334	132.82	459.0183	517.1028	921.7447	1906.0104		-0.22545	-0.1685	0.456	-0.456	-2.411	5.469
ts4	1.187	5.975	153.95	456.1409	500.8111	919.9805	1906.4355	-133.7811	-0.22619	-0.17042	0.437	-0.437	-2.196	5.563
g5	1.217	5.986	158.22	440.829	499.9407	926.185	1747.7452		-0.22501	-0.16152	0.550	-0.550	-2.640	5.341
ts5	1.19	4.223	169.82	466.5868	525.9877	811.1419	1904.8806	-131.2566	-0.22114	-0.15059	0.490	-0.491	-2.145	5.871
g6	1.217	5.985	179.6	441.1896	500.0899	926.2779	1746.486		-0.22498	-0.1577	0.550	-0.550	-2.640	5.188
ts6	1.848	5.895	59.01	420.9047	622.0412	751.5739	936.0783	-389.5251	-0.23073	-0.16672	0.707	-0.707	0.267	14.653
g7	3.106	5.927	51.07	419.4157	734.351	825.2914	937.8582		-0.23441	-0.17585	0.795	-0.795	-0.757	19.878
ts7	3.534	4.825	64.99	598.9046	682.5529	714.7734	944.7602	-165.1038	-0.22265	-0.1677	0.861	-0.861	-1.569	18.911
g8	3.196	4.607	67.67	641.1821	658.3857	762.3973	937.8894		-0.22157	-0.16408	0.838	-0.838	-2.174	17.503
g1b	1.188	1.191	179.73	461.5704	584.6698	1254.2387	2325.9287		-0.17041	-0.10319	-0.098	0.098	-0.462	-0.466
ts1b	1.255	1.337	130.62	529.6011	725.6545	1058.9124	1574.3293	-89.225	-0.20001	-0.14662	0.434	-0.434	-0.638	1.403
ts99	1.193	3.05	144.07	498.9136	558.4882	653.502	1898.9078	-333.2065	-0.20148	-0.15754	0.444	-0.444	-1.687	5.683

Table S3. Reaction path data for Ru_5 + CO_2.

	r(CO)	r(CO)	θ(OCO)	ν(bend)	ν (bend)	ν (symm_stretch)	ν (asym_stretch)	ν (imag)	E(HOMO)	E(LUMO)	q(M5)	q(CO2)	E_{ads}	E_{int}
	Å		°			cm^{-1}			Hartree		e		eV	
g1	1.188	1.19	179.47	546.1177	571.3651	1268.2408	2325.2175		-0.18263	-0.12757	-0.094	0.094	-0.282	-0.452
g1ax	1.256	1.293	179.9	562.6196	743.4627	1132.0574	1636.6723		-0.22544	-0.11995	0.336	-0.336	-0.183	-0.436
ts1ax	1.186	1.197	179.18	514.1069	574.934	1256.7544	2295.3962	-31.5252	-0.1895	-0.12333	-0.075	0.075	-0.278	-0.477
ts1eq	1.185	1.201	176.89	496.4561	568.8613	1243.5843	2283.9416	-63.4888	-0.1848	-0.12162	-0.076	0.076	-0.048	-0.086
g2	1.256	1.293	135.91	562.6351	743.5519	1132.3786	1636.5068		-0.22545	-0.1549	0.336	-0.336	-1.613	-0.084
ts2a	1.183	4.591	107.71	446.635	523.6121	902.5708	1949.7494	-32.7873	-0.23213	-0.17017	0.310	-0.310	-1.058	5.709
ts2b	1.183	5.015	116.12	444.4973	517.0508	863.1753	1946.4301	-364.5112	-0.23255	-0.16683	0.321	-0.321	-0.262	7.541
g3a	3.733	5.097	48.66	527.2626	672.0883	832.3422	1041.2939		-0.24023	-0.1549	0.544	-0.544	-1.068	16.860
g3b	1.186	2.052	108.99	444.7933	467.5419	782.8741	1893.9572		-0.22616	-0.16425	0.312	-0.312	-1.171	5.572
ts3b	1.181	4.288	101.27	455.0308	526.3408	881.1852	1960.1749	-207.0244	-0.24034	-0.16122	0.305	-0.305	-1.197	6.511
ts3a	1.184	6.414	125.93	458.6649	523.0389	868.9254	1940.2411	-214.2944	-0.23618	-0.16978	0.331	-0.331	1.923	9.740
g4b	1.225	4.288	129.9	450.123	665.8959	862.6002	1679.5299		-0.23512	-0.16392	0.428	-0.428	-1.598	6.260
ts4b	1.949	4.231	116.39	572.3451	606.7123	746.9317	869.3629	-362.7478	-0.23457	-0.17434	0.545	-0.545	1.195	16.343
g5b	2.817	3.344	144.32	594.969	638.9352	851.5335	904.8458		-0.22958	-0.16325	0.657	-0.657	-0.083	18.838

Table S4. Reaction path data for square pyramidal Rh_5 + CO_2.

	r(CO)	r(CO)	θ(OCO)	ν(bend)	ν (bend)	ν (symm_stretch)	ν (asym_stretch)	ν (imag)	E(HOMO)	E(LUMO)	q(M5)	q(CO2)	E_{ads}	E_{int}
	Å		°			cm^{-1}			Hartree		e		eV	
M5									-0.19457	-0.12282				
g1	1.188	1.191	179.65	527.5153	571.1292	1266.3294	2328.3061		-0.18479	-0.11857	-0.106	0.106	-0.188	-0.499
ts1	1.186	1.193	179.9	567.418	577.841	1268.8333	2321.1436	-42.7174	-0.19145	-0.12607	-0.111	0.111	-0.303	-0.463
g2	1.257	1.284	136.7	547.2457	739.7803	1138.4115	1661.5834		-0.23356	-0.15136	0.313	-0.313	-1.549	0.006
ts2	1.192	1.916	108.72	433.6217	501.5822	756.8841	1862.7199	-570.1385	-0.23127	-0.1726	0.314	-0.314	-0.221	6.441
g3	1.181	4.164	108.55	434.2143	523.3141	862.8204	1961.8717		-0.23573	-0.16147	0.290	-0.290	-1.379	6.488
ts3	1.184	5.252	141.13	431.7459	516.4684	858.0235	1938.136	-43.6664	-0.23357	-0.17278	0.306	-0.306	-0.751	7.091
g4	1.184	4.912	176.72	420.3342	535.0678	829.0629	1949.543		-0.23842	-0.17289	0.343	-0.343	-1.439	6.291
ts4	1.184	4.811	175.99	422.1787	535.2095	812.2169	1948.6554	-40.2501	-0.23745	-0.16409	0.341	-0.341	-1.408	6.324
g5	1.184	3.817	178.87	534.1351	538.3754	654.2765	1951.1195		-0.22691	-0.15832	0.376	-0.376	-1.976	5.748
ts5	1.203	3.889	155.41	458.5073	478.8507	666.3458	1797.1666	-182.3379	-0.23272	-0.17053	0.434	-0.434	-1.488	6.432
g6	1.206	3.206	130.61	481.4524	519.0718	592.9379	1776.7693		-0.23312	-0.16898	0.373	-0.373	-1.345	6.466
ts6	1.893	3.41	108.57	573.6224	606.6085	669.5842	769.6552	-385.9373	-0.2279	-0.15977	0.568	-0.567	1.099	15.938
g7	2.848	3.132	87.98	541.5395	548.8976	574.4191	940.003		-0.22501	-0.16135	0.571	-0.571	0.094	19.275

Table S5. Reaction path data for trigonal bipyramidal Rh_5 + CO_2.

	r(CO)	r(CO)	θ(OCO)	ν(bend)	ν (bend)	ν (symm_stretch)	ν (asym_stretch)	ν (imag)	E(HOMO)	E(LUMO)	q(M5)	q(CO2)	E_{ads}	E_{int}
	Å		°			cm^{-1}			Hartree		e		eV	
M5									-0.20411	-0.16420				
g1a	1.185	1.192	179.56	583.2764	586.5111	1280.8311	2325.8134		-0.1949	-0.15578	-0.086	0.086	-0.301	-0.346
ts1a	1.188	1.196	176.68	502.5495	576.4459	1253.8723	2288.3903	-21.2747	-0.20632	-0.16325	-0.037	0.037	-0.245	-0.278
g2	1.244	1.28	137.77	551.3403	752.1013	1157.0142	1709.4021		-0.22953	-0.1761	0.286	-0.286	-1.340	-0.041
ts2a	1.175	2.213	106.72	374.559	448.3637	743.4134	1973.4826	-256.7614	-0.24211	-0.19743	0.312	-0.312	1.079	8.122
g3a	1.168	3.228	97.85	331.7614	458.4936	797.7595	2027.9319		-0.24313	-0.19722	0.297	-0.297	0.938	8.810
ts3a	1.202	3.262	115.17	426.0474	589.6891	766.72	1799.3546	-61.5642	-0.24833	-0.20069	0.430	-0.430	0.886	8.892
g4a	1.219	3.622	122.04	456.4636	528.0847	773.1791	1700.4791		-0.24231	-0.19023	0.523	-0.523	0.504	8.479
ts4a	2.288	4.438	120.46	609.8147	619.1497	735.1472	789.0033	-276.8171	-0.25253	-0.19443	0.665	-0.665	4.453	22.307
g5a	3.128	3.672	83.33	555.0175	574.5098	587.3889	814.4079		-0.24347	-0.17528	0.808	-0.808	1.993	22.556
g1b	1.185	1.192	179.76	581.2325	586.6236	1277.9195	2325.2682		-0.19744	-0.15626	-0.088	0.088	-0.368	-0.369
ts1b	1.188	1.209	170.5	459.9236	566.3176	1220.8677	2231.8165	-103.9079	-0.20638	-0.1649	-0.008	0.008	-0.282	-0.208

Table S6. Reaction path data for Pd_5 + CO_2.

	r(CO)	r(CO)	θ(OCO)	ν(bend)	ν (bend)	ν (symm_stretch)	ν (asym_stretch)	ν (imag)	E(HOMO)	E(LUMO)	q(M5)	q(CO2)	E_{ads}	E_{int}
	Å		°			cm^{-1}			Hartree		e		eV	
M5									-0.21464	-0.16831				
g1	1.185	1.192	178.33	552.1728	564.1784	1276.7019	2336.0679		-0.20602	-0.1623	-0.121	0.121	-0.516	-0.547
ts1	1.215	1.294	145.41	546.2618	647.6853	1066.4911	1862.371	-34.2677	-0.23724	-0.19405	0.247	-0.247	-0.827	0.242
g2	1.251	1.298	133.21	573.3993	767.5551	1152.5905	1634.2055		-0.23291	-0.18442	0.295	-0.295	-1.673	-0.098
ts2	1.255	1.278	140.36	448.9557	623.1653	1079.2427	1675.0853	-169.5442	-0.24172	-0.19034	0.264	-0.263	-0.571	0.771
g3	1.209	3.264	103.51	462.9402	630.6249	838.0781	1764.8714		-0.25787	-0.2017	0.420	-0.420	-0.769	7.107
ts3	1.189	3.252	92.49	435.996	510.321	835.265	1894.3152	-227.5451	-0.24824	-0.19969	0.328	-0.328	-0.587	7.431
g4	1.176	4.609	116.23	404.1526	524.1259	873.8564	2005.8629		-0.25566	-0.20346	0.257	-0.257	-1.504	6.456
ts4	2.073	5.061	109.82	348.9429	573.7709	864.1135	918.9867	-313.2943	-0.26258	-0.20524	0.472	-0.472	3.850	20.434
g5	3.265	4.147	106.22	469.582	640.5195	864.4903	1006.0145		-0.26689	-0.20686	0.556	-0.556	2.666	24.241

Table S7. Reaction path data for trigonal bipyramidal Pt_5 + CO_2.

	r(CO)	r(CO)	θ(OCO)	ν(bend)	ν (bend)	ν (symm_stretch)	ν (asym_stretch)	ν (imag)	E(HOMO)	E(LUMO)	q(M5)	q(CO2)	E_{ads}	E_{int}
	Å		°			cm^{-1}			Hartree		e		eV	
M5									-0.20293	-0.16110				
p_ax	1.186	1.195	178.480	550.943	570.3298	1260.5167	2309.7549		-0.20088	-0.15698	-0.095	0.095	-0.360	-0.377
p_eq	1.185	1.192	178.97	558.9764	576.1973	1275.9527	2330.1125		-0.19635	-0.15503	-0.114	0.114	-0.367	-0.389
g1	1.186	1.195	178.48	550.943	570.3298	1260.5167	2309.7549		-0.20088	-0.15698	-0.095	0.095	-0.360	-0.377
ts1	1.247	1.247	145.54	570.0216	652.2718	1148.0578	1770.136	-147.5884	-0.23722	-0.18784	0.332	-0.332	-0.511	0.448
g2	1.219	1.302	143.12	545.792	669.8298	1060.546	1824.6552		-0.23721	-0.19014	0.306	-0.306	-0.843	0.349
ts2	1.217	1.98	106.89	468.3475	595.7926	688.3904	1711.4745	-275.5387	-0.23516	-0.1864	0.393	-0.393	0.247	7.134
g3	1.206	4.755	133.12	450.5655	550.314	851.4642	1791.8624		-0.24728	-0.20701	0.384	-0.384	-0.876	7.202

Table S8. Reaction path data for square pyramidal Pt_5 + CO_2.

	r(CO)	r(CO)	θ(OCO)	ν(bend)	ν (bend)	ν (symm_stretch)	ν (asym_stretch)	ν (imag)	E(HOMO)	E(LUMO)	q(M5)	q(CO2)	E_{ads}	E_{int}
	Å		°			cm^{-1}			Hartree		e		eV	
M5									-0.19323	-0.10833				
g1	1.187	1.192	179.53	593.1877	605.0678	1280.5118	2314.224		-0.18647	-0.10337	-0.043	0.043	-0.133	-0.133
ts1	1.199	1.217	160.9	298.097	474.8337	1152.3698	2120.7417	-266.5709	-0.19386	-0.11235	0.112	-0.112	0.038	0.298
g2	1.235	1.283	136.77	429.3525	681.0263	1146.1249	1696.3928		-0.22775	-0.1213	0.357	-0.357	-0.289	1.129
ts2	1.164	2.327	104.89	272.9111	304.4031	428.0552	2037.3838	-56.497	-0.2379	-0.11756	0.244	-0.245	1.767	9.174

Table S9. Reaction path data for Ag_5 + CO_2.

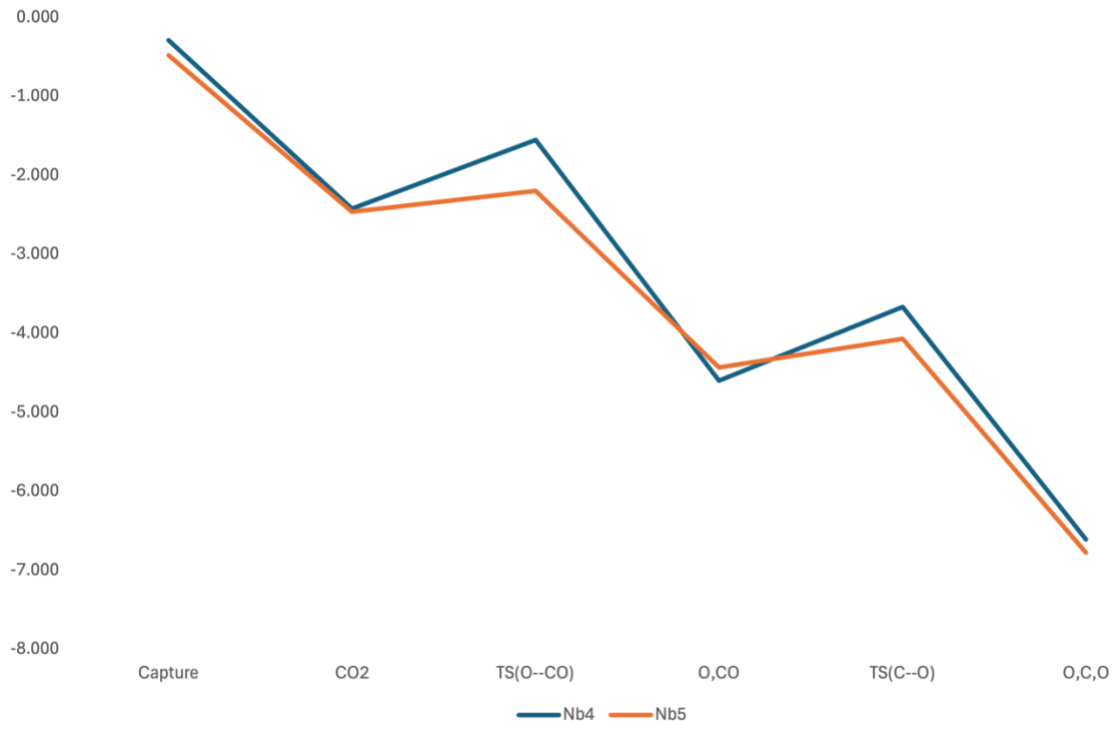

Figure S1: Reaction profile comparing key species in the addition of CO_2 to Nb_4 vs Nb_5. Energies (E_ads) in eV.

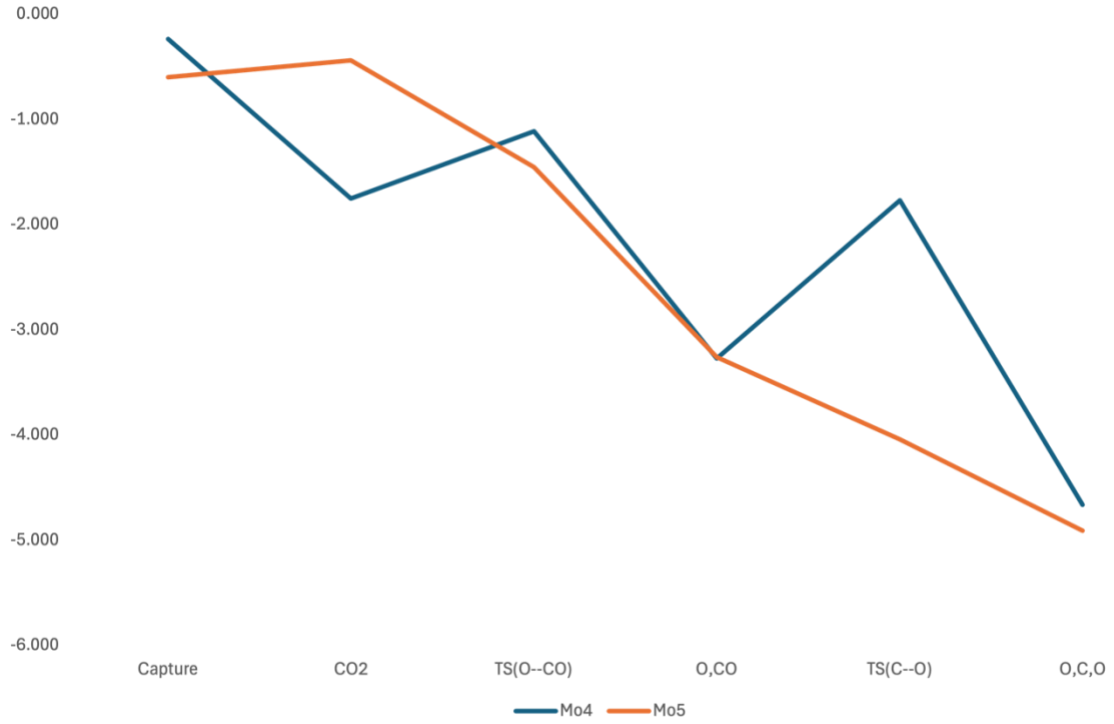

Figure S2: Reaction profile comparing key species in the addition of CO_2 to Mo_4 vs Mo_5. Energies (E_ads) in eV.

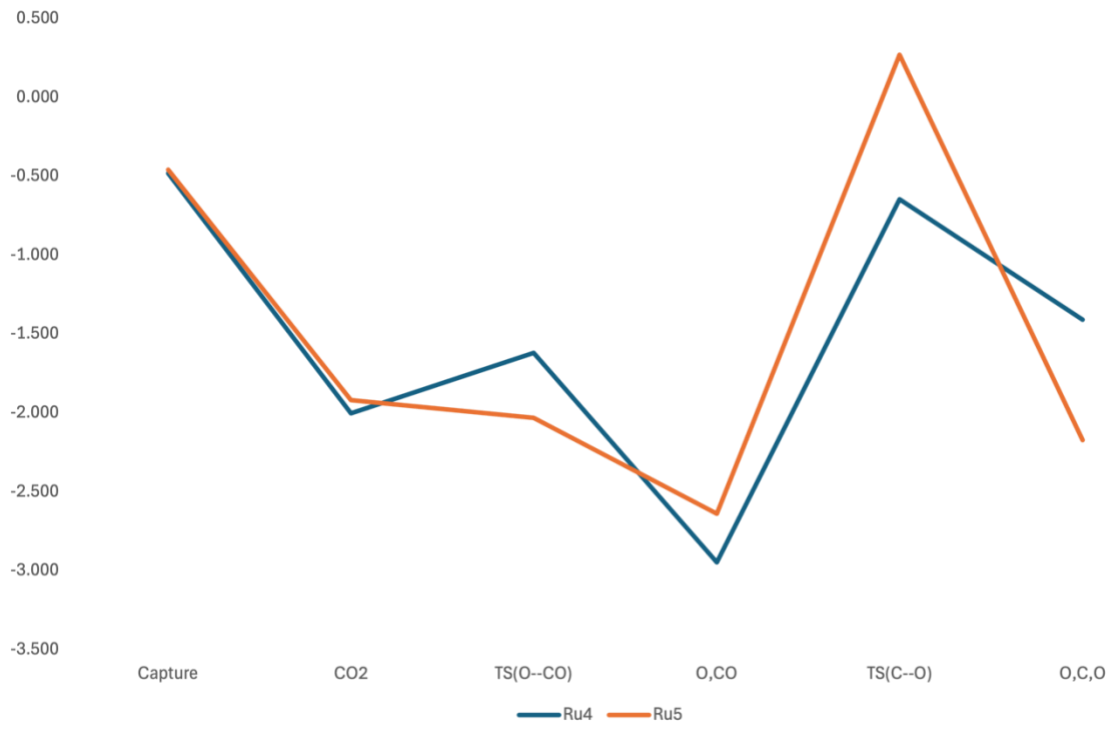

Figure S3: Reaction profile comparing key species in the addition of CO_2 to Ru_4 vs Ru_5. Energies (E_ads) in eV.

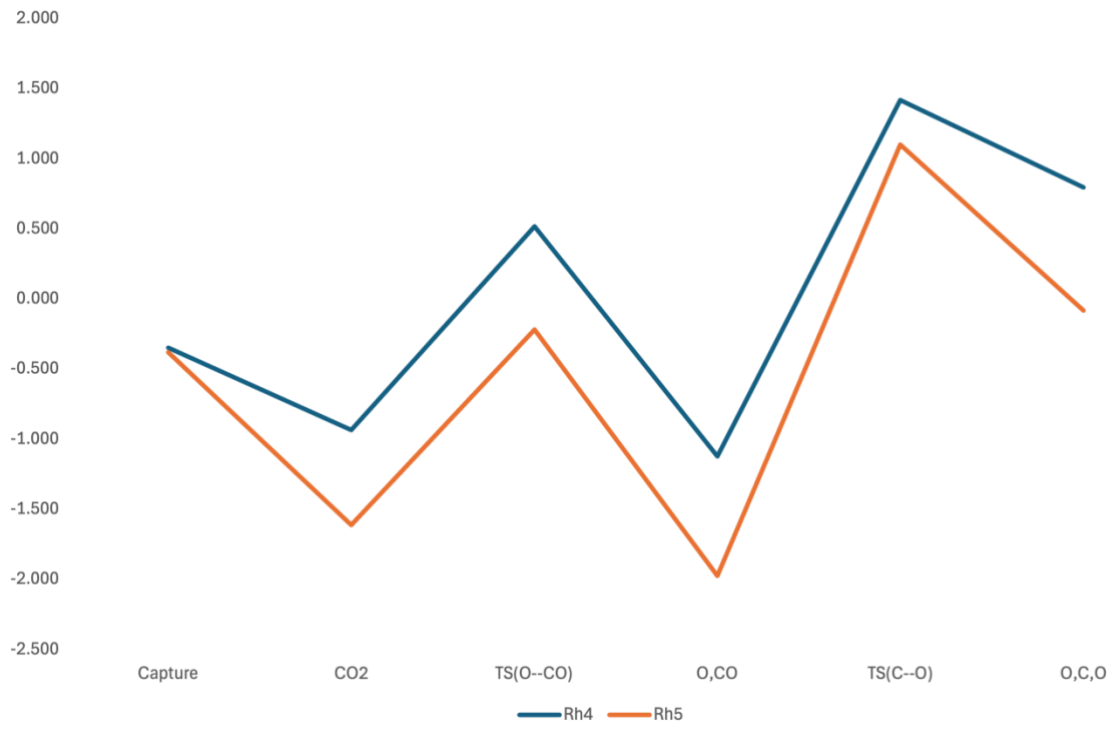

Figure S4: Reaction profile comparing key species in the addition of CO_2 to Rh_4 vs Rh_5. Energies (E_ads) in eV.

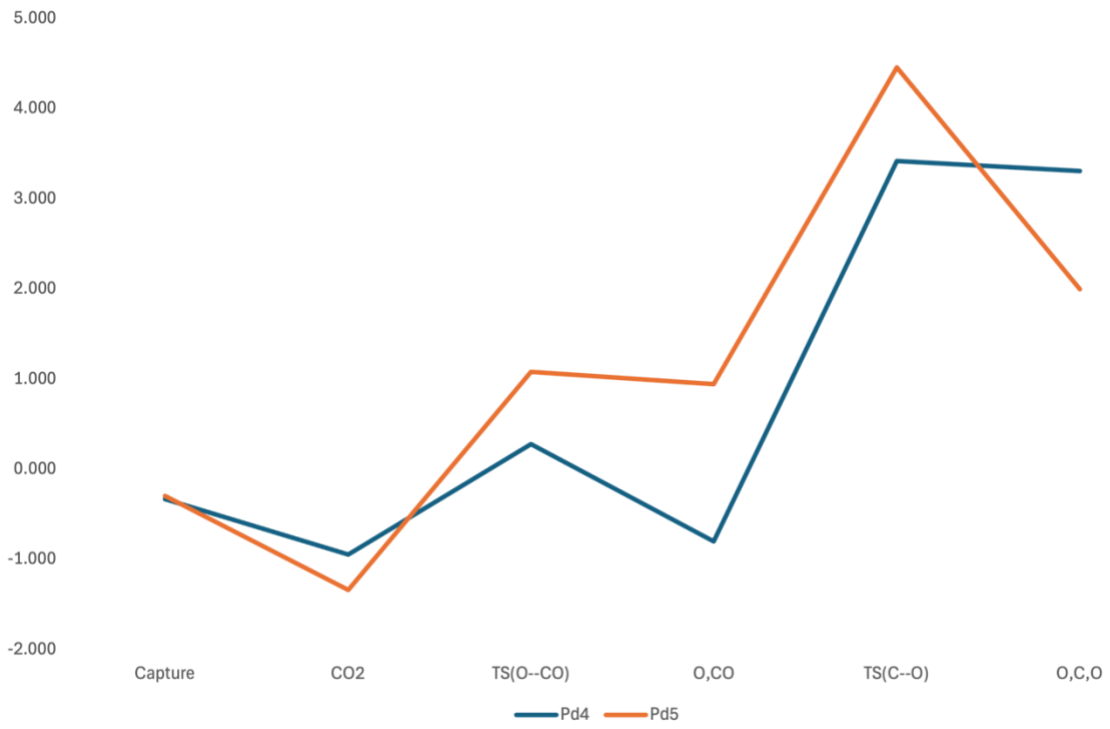

Figure S5: Reaction profile comparing key species in the addition of CO_2 to Pd_4 vs Pd_5. Energies (E_ads) in eV.

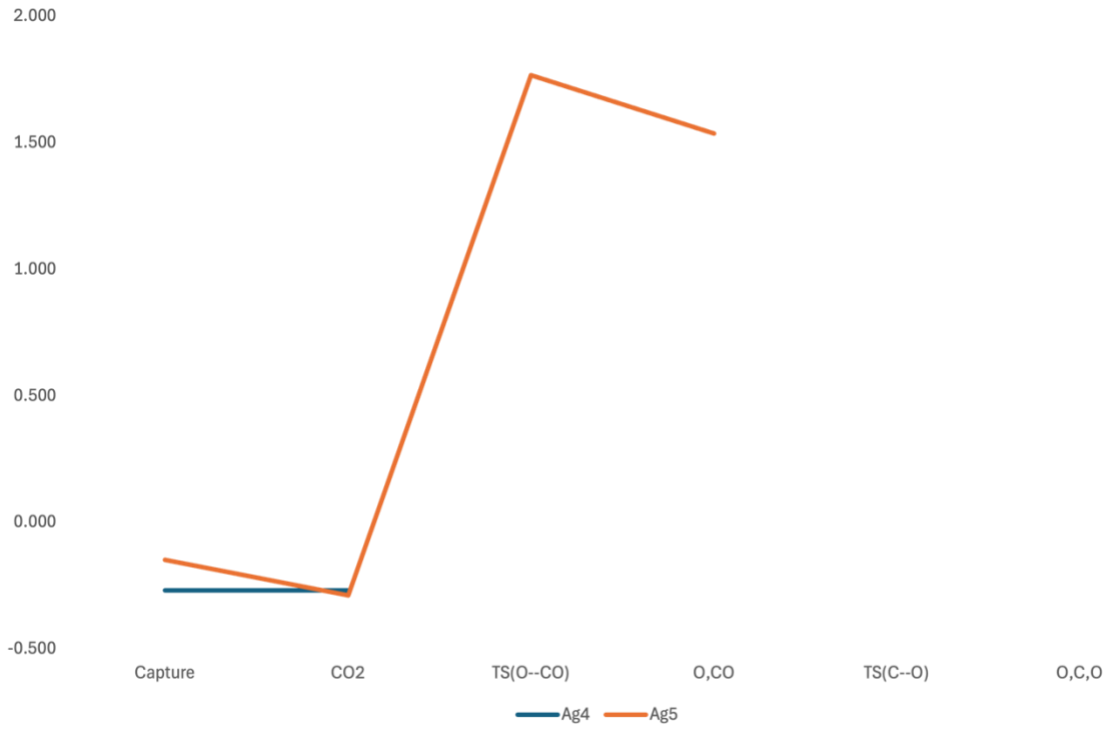

Figure S5: Reaction profile comparing key species in the addition of CO_2 to Ag_4 vs Ag_5. Energies (E_ads) in eV.

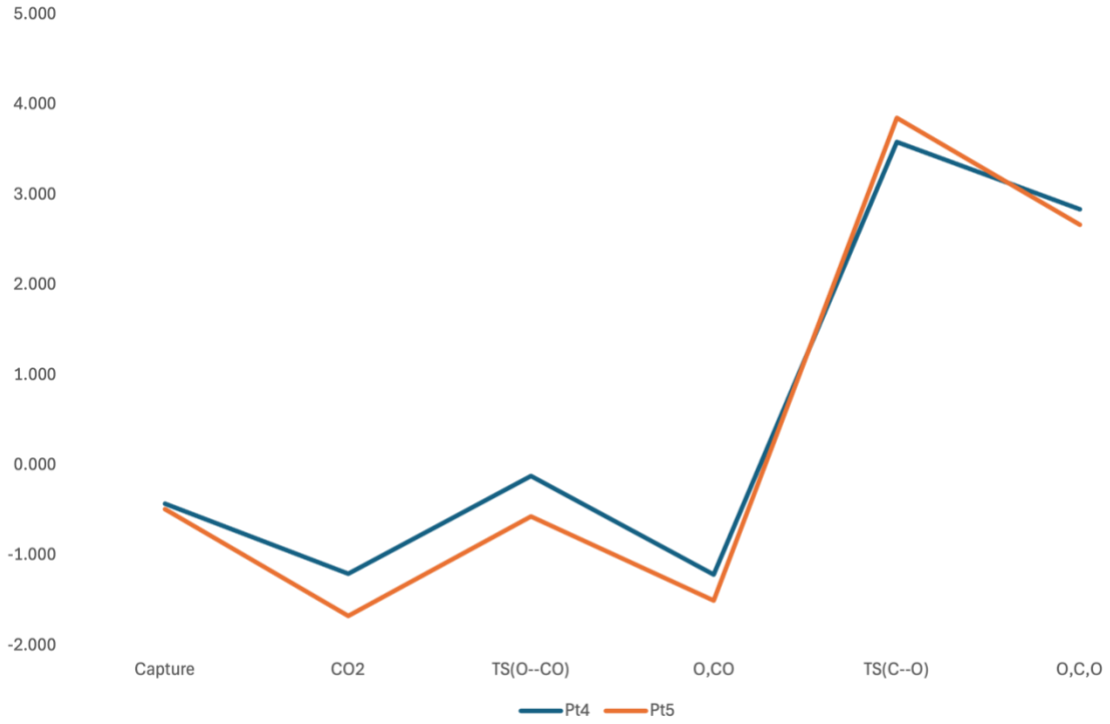

Figure S5: Reaction profile comparing key species in the addition of CO_2 to Pt_4 vs Pt_5. Energies (E_ads) in eV.