Supplementary Information for:

Associative vs. dissociative binding of CO_2 on M_4 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(M4)	q(CO2)	E_{ads}	E_{int}
	Å		°			cm^{-1}			Hartree		e		eV	
M4									-0.16544	-0.08863				
g1	1.185	1.194	179.98	546.4877	546.8877	1255.693	2316.8803		-0.1557	-0.08467	-0.098	0.098	-0.291	-0.292
ts1	1.208	1.233	152.28	355.6669	417.0325	1134.4241	2027.6132	-99.5722	-0.16788	-0.11019	0.162	-0.162	-0.094	-0.786
g2	1.295	1.295	132.66	499.1243	704.3078	1136.6188	1543.1267		-0.18492	-0.1171	0.501	-0.501	-2.425	-0.514
ts2	1.285	1.339	131.47	382.0229	677.4506	1036.6535	1473.7833	-114.8602	-0.17398	-0.11286	0.577	-0.577	-1.552	5.135
g3	1.322	3.285	89.87	502.3113	570.9829	688.0796	1271.3071		-0.17063	-0.1155	1.274	-1.274	-4.601	3.583
ts3	1.891	4.344	64.43	440.0199	630.7768	675.2466	720.5144	-406.8712	-0.18736	-0.12079	1.079	-1.079	-3.670	3.016
g4	3.16	4.641	46.31	666.1841	696.4403	741.497	762.1393		-0.18607	-0.12483	1.274	-1.274	-6.614	13.945

Table S1. Reaction path data for $Nb_4 + CO_2$

	r(CO)	r(CO)	θ(OCO)	ν(bend)	ν (bend)	ν (symm_stretch)	ν (asym_stretch)	ν (imag)	E(HOMO)	E(LUMO)	q(M4)	q(CO2)	E_{ads}	E_{int}
	Å		°			cm^{-1}			Hartree		e		eV	
M4									-0.17587	-0.09788				
g1	1.187	1.192	179.12	471.0937	540.1573	1251.116	2333.3913		-0.14407	-0.08817	-0.097	0.097	-0.237	-0.516
ts1	1.182	1.196	178.22	476.1036	540.6541	1265.635	2325.3246	-61.1649	-0.14492	-0.088	-0.103	0.103	-0.221	-0.495
g2	1.248	1.372	149.73	510.1759	726.322	1004.4648	1606.127		-0.19111	-0.12679	0.564	-0.564	-1.753	-1.787
ts2	1.187	1.993	109.14	408.6731	442.822	764.9284	1877.5052	-387.531	-0.18618	-0.13204	0.488	-0.488	-1.115	4.741
g3	1.231	3.363	132.98	459.3812	527.9676	688.3219	1660.0328		-0.19025	-0.14359	0.753	-0.753	-3.275	3.657
ts4	1.222	3.461	146.59	451.7311	518.7942	687.0679	1712.6282	-97.7903	-0.17781	-0.13288	0.742	-0.743	-2.887	3.917
g4	1.251	3.095	129.58	429.2677	487.4766	690.1752	1554.9686		-0.18808	-0.12375	0.848	-0.848	-3.102	3.575
ts4	1.222	3.461	146.59	451.7311	518.7942	687.0679	1712.6282	-296.9138	-0.17781	-0.13288	0.742	-0.743	-2.887	3.917
g5	1.352	3.9	65.41	515.1921	616.0506	945.0793	1163.9478		-0.19298	-0.1206	0.842	-0.842	-2.952	4.381
ts5	2.078	4.169	49.05	538.6176	733.2674	799.4021	945.8019	-384.9728	-0.20655	-0.14798	0.992	-0.992	-1.772	12.647
g6	3.242	4.326	49.8	651.7818	697.7254	713.7014	810.0801		-0.19849	-0.13732	1.126	-1.125	-4.666	15.451

Table S2. Reaction path data for Mo_4 + 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(M4)	q(CO2)	E_{ads}	E_{int}
	Å		°			cm^{-1}			Hartree		e		eV	
M4									-0.18958	-0.13846				
g1	1.185	1.192	179.78	527.2976	579.3413	1267.8556	2323.6483		-0.18025	-0.12753	-0.125	0.125	-0.483	-0.514
ts1	1.181	1.202	176.67	497.1528	568.6247	1251.2395	2302.5262	81.81	-0.18289	-0.1287	-0.115	-0.354	-0.451	-0.470
g2	1.219	1.326	140.01	536.2632	694.9105	1023.3071	1815.9405		-0.22178	-0.16662	0.363	-0.489	-1.510	-0.106
ts2	1.253	1.288	141.43	542.7931	732.3859	1116.7957	1668.5309	-164.7357	-0.21263	-0.15754	0.383	-0.508	-1.076	0.029
g3	1.219	1.326	140.06	536.3115	694.8437	1023.365	1815.7522		-0.22181	-0.16605	0.363	-0.489	-1.510	-0.112
ts3	1.225	1.345	135.82	535.4311	701.3192	975.5275	1754.1972	-130.1199	-0.21561	-0.15967	0.416	-0.525	-1.021	0.753
g4	1.234	1.396	124.38	564.9912	728.9725	875.8912	1666.8579		-0.2144	-0.15977	0.423	-0.513	-2.005	0.871
ts4	1.199	1.884	110.72	480.8376	519.9342	793.1563	1835.1351	-407.8488	-0.21372	-0.15625	0.397	-0.484	-1.622	4.612
g5	1.183	3.535	100.98	468.8391	567.3361	908.3183	1951.5152		-0.221	-0.16829	0.365	-0.441	-2.557	5.187
ts5	1.185	3.893	121.27	443.6027	577.3271	917.6719	1943.5302	-99.9452	-0.23101	-0.17482	0.361	-0.436	-2.455	4.989
g6	1.189	4.609	136.51	450.393	579.6859	923.5124	1918.6593		-0.22541	-0.16658	0.418	-0.258	-2.949	4.872
ts6	1.183	4.073	112.22	432.658	560.1146	913.0537	1948.4002	-103.4979	-0.22766	-0.17626	0.363	-0.230	-2.497	5.286
g7	1.304	3.626	141.75	424.8866	742.2906	920.4343	1254.7953		-0.22431	-0.16807	0.539	-0.510	-1.452	6.416
ts7	1.426	3.745	118.55	523.2453	667.0824	816.1783	901.9957	-631.9306	-0.2106	-0.16798	0.591	-0.493	-0.648	8.608
g8	3.177	3.206	94.24	516.9382	709.2033	921.2737	940.4631		-0.22984	-0.17203	0.720	-0.563	-1.410	18.896

Table S3. Reaction path data for Ru_4 + CO_2. Greyed cells indicate an alternate transition state / intermediate.

	r(CO)	r(CO)	θ(OCO)	ν(bend)	ν (bend)	ν (symm_stretch)	ν (asym_stretch)	ν (imag)	E(HOMO)	E(LUMO)	q(M4)	q(CO2)	E_{ads}	E_{int}
	Å		°			cm^{-1}			Hartree		e		eV	
M4									-0.20726	-0.11349				
g1	1.186	1.192	179.81	572.0186	587.2106	1275.2634	2322.0276		-0.19903	-0.11026	-0.097	0.097	-0.349	-0.351
ts1	1.224	1.248	151.44	544.6175	602.3646	1140.953	1916.457	-45.4423	-0.23694	-0.1515	0.220	-0.220	-0.351	0.333
g2	1.256	1.269	140.26	539.1355	689.385	1127.9569	1705.3346		-0.23268	-0.15673	0.283	-0.283	-0.936	0.404
ts2	1.247	1.318	132.79	551.2789	754.6347	1084.4035	1643.831	-255.5226	-0.2245	-0.16421	0.299	-0.299	-0.757	1.084
g3	1.256	1.269	140.24	539.0833	689.4325	1127.8871	1705.3214		-0.23268	-0.15676	0.283	-0.283	-0.936	0.406
ts4	1.19	1.928	110.13	451.5038	494.1736	746.9533	1879.3339	-464.217	-0.23648	-0.17341	0.324	-0.324	0.516	7.047
g4	1.178	3.371	112.32	445.4471	490.6471	859.8374	1970.6518		-0.23755	-0.17975	0.293	-0.293	-0.205	7.715
ts4	1.179	3.205	130	434.0692	488.6984	790.2196	1966.7496	-152.1399	-0.23396	-0.17235	0.295	-0.295	-0.072	7.787
g5	1.224	3.101	130.76	454.7694	659.5252	692.5343	1694.4544		-0.22485	-0.15327	0.419	-0.419	-1.123	6.124
ts5	1.986	3.27	89.86	579.6867	620.1827	684.8095	714.133	-371.8791	-0.22599	-0.16662	0.582	-0.582	1.417	15.985
g6	2.822	2.954	80.42	599.2326	661.3501	707.8503	753.524		-0.23424	-0.16914	0.610	-0.610	0.794	19.773

Table S4. Reaction path data for Rh_4 + CO_2. Greyed cells indicate an alternate transition state / intermediate.

	r(CO)	r(CO)	θ(OCO)	ν(bend)	ν (bend)	ν (symm_stretch)	ν (asym_stretch)	ν (imag)	E(HOMO)	E(LUMO)	q(M4)	q(CO2)	E_{ads}	E_{int}
	Å		°			cm^{-1}			Hartree		e		eV	
M4									-0.21001	-0.16422				
g1	1.185	1.193	179.96	581.1339	584.5551	1277.0885	2322.2839		-0.20193	-0.15599	-0.080	0.080	-0.333	-0.341
ts1	1.187	1.188	179.96	575.5198	581.2054	1285.8919	2334.7691	-23.1882	-0.19968	-0.15599	-0.082	0.082	-0.298	-0.306
g2	1.185	1.193	178.88	581.0983	584.4364	1277.0561	2322.2313		-0.20195	-0.15782	-0.080	0.080	-0.333	-0.339
ts2	1.191	1.208	167.37	433.6532	559.1983	1214.0953	2210.8822	-121.205	-0.21335	-0.16387	0.006	-0.006	-0.256	-0.156
g3	1.238	1.295	135.98	564.788	729.9815	1113.7706	1703.9773		-0.24539	-0.18141	0.307	-0.307	-0.948	0.507
ts3	1.219	1.261	148.45	563.0636	622.6524	1134.7254	1890.0255	-23.7813	-0.24219	-0.19739	0.289	-0.289	-0.459	0.341
g4	1.247	1.363	128.61	422.3118	717.0861	931.3191	1579.7274		-0.23855	-0.17888	0.365	-0.365	-0.705	1.638
ts4	1.207	2.07	116.34	458.4047	582.2319	640.7656	1771.0721	-260.9735	-0.23016	-0.15754	0.374	-0.374	0.276	6.749
g5	1.201	3.873	161.75	475.8827	545.9816	634.3945	1821.986		-0.23834	-0.16905	0.479	-0.479	-0.802	6.945
ts5	1.201	4.205	93.55	545.7589	548.4699	640.4151	1788.1856	-89.3603	-0.22942	-0.16886	0.423	-0.423	-0.051	7.743
g6	1.224	4.325	72.43	572.4506	578.2811	619.0809	1630.3577		-0.23806	-0.17133	0.455	-0.455	-0.114	7.730
ts6	2.285	3.058	89.04	574.244	580.9841	632.5912	723.7252	-233.8956	-0.24618	-0.17053	0.650	-0.650	3.415	20.863
g7	2.87	2.878	80.3	578.2509	585.7323	653.1829	739.3317		-0.24546	-0.17087	0.695	-0.695	3.302	22.804

Table S5. Reaction path data for Pd_4 + CO_2. Greyed cells indicate an alternate transition state / intermediate.

	r(CO)	r(CO)	θ(OCO)	ν(bend)	ν (bend)	ν (symm_stretch)	ν (asym_stretch)	ν (imag)	E(HOMO)	E(LUMO)	q(M4)	q(CO2)	E_{ads}	E_{int}
	Å		°			cm^{-1}			Hartree		e		eV	
M4									-0.23447	-0.16185				
g1	1.184	1.193	178.47	566.6683	588.1581	1280.4042	2329.6922		-0.2227	-0.15535	-0.114	0.114	-0.430	-0.433
ts1	1.214	1.29	145.65	561.5802	649.5774	1084.4695	1867.861	-14.5156	-0.23777	-0.18988	0.250	-0.250	-0.647	0.265
g2	1.241	1.309	133.97	584.5668	751.5473	1107.9908	1664.7348		-0.25121	-0.19197	0.313	-0.313	-1.207	0.174
ts2	1.243	1.243	147.19	575.265	642.8901	1156.9194	1820.0461	-66.167	-0.25998	-0.19101	0.293	0.000	-0.409	5.376
g3	1.236	1.328	132.39	550.6815	730.8921	1017.02	1673.01		-0.26067	-0.20395	0.268	-0.268	-0.358	1.254
ts3	1.254	1.254	145.12	435.2889	604.4663	1093.6755	1768.4668	-140.1106	-0.25161	-0.18761	0.199	-0.383	-0.619	5.515
g4	1.21	1.283	147.04	564.8885	627.0495	1093.6116	1900.9477		-0.2536	-0.18818	0.230	-0.230	-0.666	0.317
ts4	1.22	1.296	144.37	543.4867	674.5326	1075.5078	1827.5544	-21.7965	-0.24273	-0.20143	0.290	-0.290	-0.663	5.380
g5	1.258	1.416	120.78	512.8058	734.4564	830.5251	1492.5618		-0.23566	-0.18256	0.367	-0.367	-0.123	2.825
ts5	1.222	5.022	124.42	460.8592	753.1649	865.2408	1691.4672	-34.8791	-0.257	-0.20872	0.375	-0.375	-0.092	7.036
g6	1.213	3.18	101.37	474.061	692.7713	828.4351	1751.8047		-0.24851	-0.19505	0.410	-0.410	-0.525	7.071
ts6	1.187	1.962	110.44	463.8684	499.7779	742.4918	1916.8563	-372.4174	-0.26373	-0.19408	0.300	-0.300	0.009	7.562
g7	1.176	4.847	115.97	442.9883	527.0778	857.429	2015.2241		-0.2604	-0.20062	0.250	-0.250	-1.218	6.558
ts7	2.111	3.195	115.18	501.2854	724.3326	775.3822	813.7764	-300.2548	-0.25739	-0.2122	0.568	-0.568	3.581	10.433
g8	3.158	4.264	90.43	576.0223	824.4964	860.4144	861.3725		-0.27598	-0.21744	0.583	-0.584	2.837	23.356

Table S6. Reaction path data for $Pt_4 + CO_2$.

	r(CO)	r(CO)	θ(OCO)	ν(bend)	ν (bend)	ν (symm_stretch)	ν (asym_stretch)	ν (imag)	E(HOMO)	E(LUMO)	q(M4)	q(CO2)	E_{ads}	E_{int}
	Å		°			cm^{-1}			Hartree		e		eV	
M4									-0.19871	-0.13205				
g1	1.185	1.191	179.76	599.0426	606.0267	1292.0351	2330.8052		-0.19227	-0.11503	-0.087	0.087	-0.269	-0.269
ts1	1.208	1.229	152.91	436.1502	508.512	1154.057	2026.4268	-128.6137	-0.21048	-0.13477	0.151	-0.151	-0.031	0.484
g2	1.23	1.253	141.94	511.5317	603.2698	1156.37	1826.6213		-0.22555	-0.14197	0.292	-0.292	-0.120	0.823

Table S7. Reaction path data for Ag_4 + CO_2.