

Supporting Materials for
Simultaneous Functionalization of Methane and Carbon Dioxide Mediated by Single Platinum
Atomic Anions

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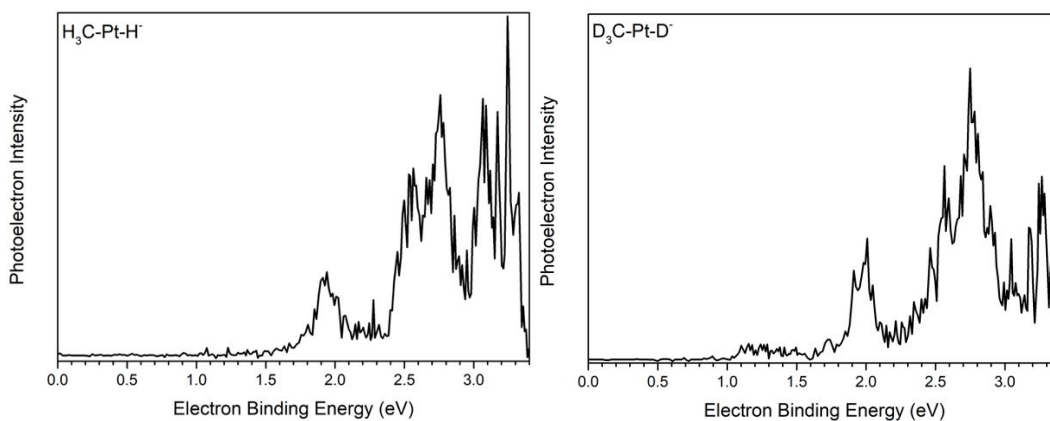


Figure S1 Photoelectron spectrum of $\text{H}_3\text{C-Pt-H}^-$ and $\text{D}_3\text{C-Pt-D}^-$.

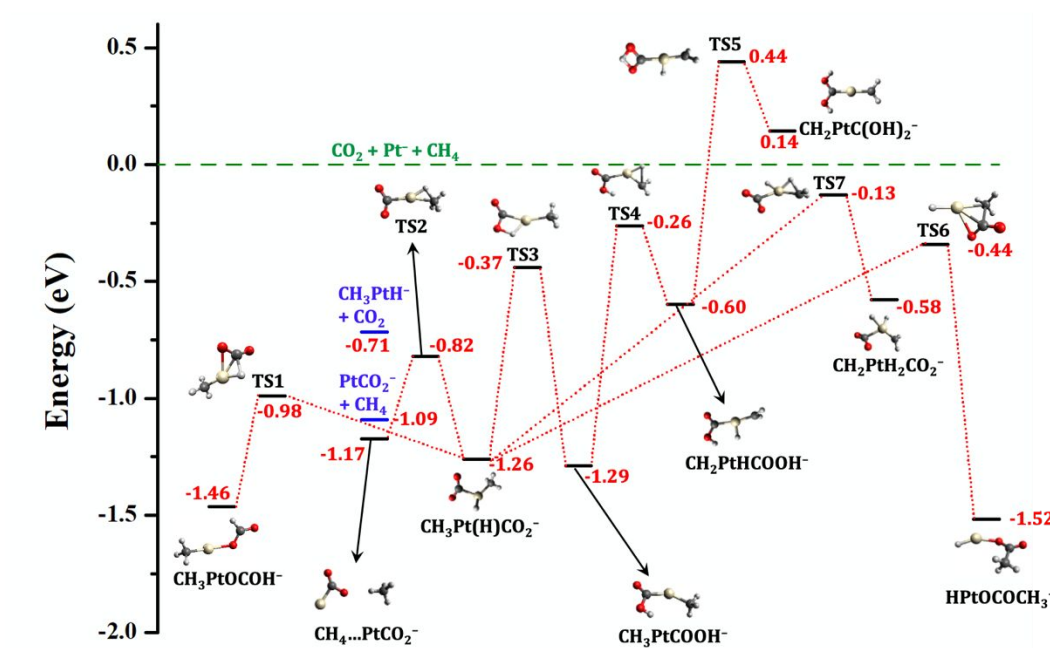


Figure S2 A more complete reaction profile for the reactions among Pt^- , CH_4 , and CO_2 , showing the route where Pt^- reacts first with CO_2 then with CH_4 , and the path that involves breaking multiple C-H bonds in CH_4 .

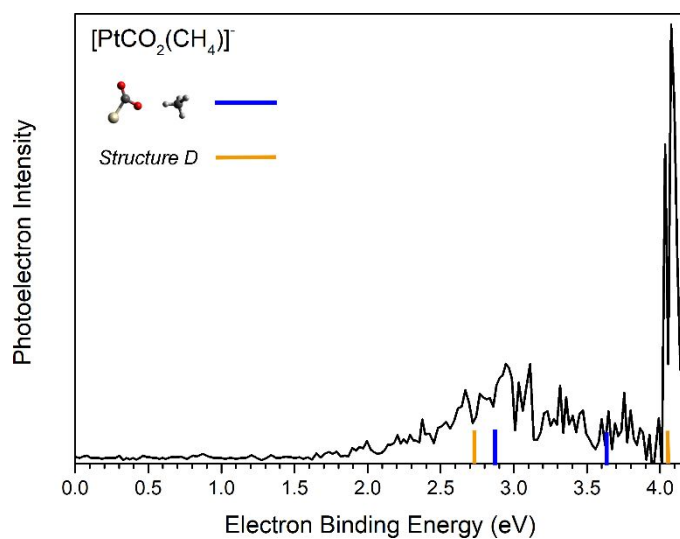


Figure S3 Photoelectron spectrum of $[\text{PtCO}_2(\text{CH}_4)]^-$ made by reacting Pt^- first with CO_2 in the laser vaporization source then with CH_4 in the reaction cell.

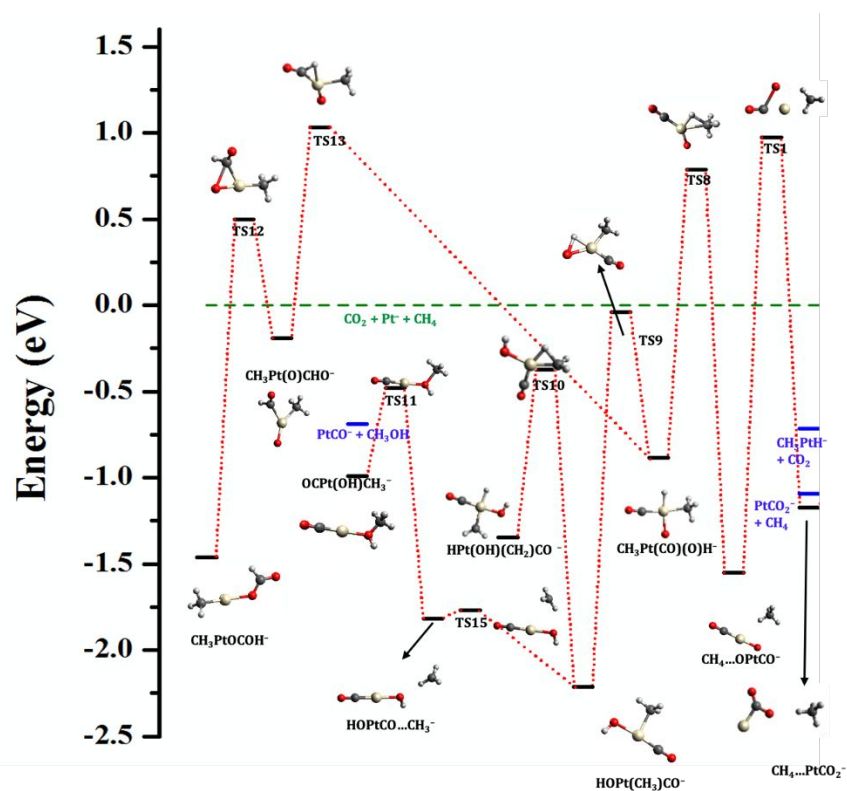


Figure S4 A complete reaction profile for the reactions between Pt, CH₄, and CO₂, showing routes that involves the breakage of C=O bond in CO₂.

Table S1. MRCI+Q excitation energies (eV) for the neutral counterparts of structures A, B, C, and D. The calculated vertical detachment energies to corresponding excited states are listed on the right of the MRCI+Q results

	A	B	C	D
S = 0	0.00/3.86	0.00/3.88	0.00/2.50	0.00/2.71
	0.22/4.08	0.14/4.02	0.88/3.38	1.54/4.25
	0.59/4.45	0.62/4.50	1.56/4.06	2.18/4.89
	0.91/4.77	0.79/4.67	1.78/4.28	2.56/5.27
		0.96/4.84	2.66/5.16	3.59/6.30
S = 1	0.00/5.27	0.00/4.02	0.66/3.46	0.00/4.02
	0.22/5.49	0.28/4.30	1.16/4.62	1.25/5.27

0.62/5.89	0.37/4.39	1.30/4.76	1.73/5.75
	0.72/4.74	2.57/6.03	2.15/6.17

Table S2. Cartesian coordinates (Å) and harmonic vibrational frequencies (cm⁻¹) for the B3LYP/aug-cc-pVTZ(C,H,O), aug-cc-pVTZ-PP(Pt) optimal structures of all intermediates. Note that the nomenclature of these structures is derived from Figure S2.

CH₂PtC(OH)₂⁻

Pt	-0.388622	-0.000033	0.000041
C	-2.381911	0.000110	-0.000187
H	-3.020001	0.893999	0.000603
H	-3.020439	-0.893452	-0.001193
C	1.542325	0.000014	0.000003
O	2.368390	-1.079393	0.000006
O	2.368265	1.079544	-0.000141
H	1.748685	-1.821140	-0.000110
H	1.748539	1.821243	-0.000292

CH₂PtH₂CO₂⁻

Pt	-0.358553	-0.223487	0.067231
C	-1.514023	1.334976	-0.566371
H	-1.437368	2.331530	-0.118394
H	-2.290101	1.308933	-1.333873
C	1.663119	0.237549	-0.074285
O	2.515050	-0.153944	-0.819729
O	1.439817	1.046332	0.833565
H	-1.221435	-1.225012	-0.726885
H	0.382513	-1.557683	0.668344

CH₂PtHCOOH⁻

Pt	-0.379083	-0.026033	-0.000044
H	1.947797	-1.685997	0.000077
C	-2.358863	0.160449	0.000177
H	-2.986697	0.215104	-0.896722

H	-2.986422	0.215538	0.897244
C	1.662977	0.185218	0.000064
O	2.218483	1.268641	0.000053
O	2.534653	-0.921846	0.000047
H	-0.255977	-1.562473	0.000569

CH₃PtCOOH⁻

Pt	0.342368	-0.180624	-0.000001
H	-1.284066	1.921480	0.000028
C	2.227109	0.719082	0.000006
H	2.393647	1.329755	0.891754
H	2.393633	1.329788	-0.891722
H	2.962284	-0.099541	-0.000017
C	-1.641085	0.076497	-0.000025
O	-2.096041	1.396612	0.000000
O	-2.489749	-0.792395	0.000015

CH₃Pt(H)CO₂⁻

Pt	0.342466	-0.254052	0.042185
H	0.017626	-1.208275	1.300527
C	1.748139	1.250024	-0.316098
H	1.663923	2.041278	0.428869
H	1.555698	1.670519	-1.310528
H	2.759757	0.832402	-0.297515
C	-1.668805	0.346364	-0.036259
O	-1.884579	1.482398	0.333650
O	-2.263590	-0.619669	-0.495852

CH₄...PtCO₂⁻

Pt	-0.878927	-0.246202	0.001785
C	4.899077	-0.662683	0.010571
H	5.365811	-0.318025	0.933160
H	4.980696	-1.747774	-0.050036
H	5.412671	-0.215350	-0.840265
H	3.849406	-0.372903	-0.000394
C	0.578913	1.061711	-0.007127
O	0.554204	2.275090	0.010737
O	1.455766	0.157860	-0.036028

HPtOCOCH₃⁻

Pt	-0.849882	-0.015525	-0.019213
C	2.285606	1.360921	0.018237
H	1.907967	1.751272	0.964268
H	1.632391	1.750389	-0.762714
H	3.309595	1.693082	-0.142510
H	-2.065128	0.969088	0.234760
O	1.060049	-0.690684	0.259960
C	2.224662	-0.164409	0.028102
O	3.245497	-0.825811	-0.144112

CH₃PtOCOH⁻

Pt	-0.464294	-0.096563	-0.046932
C	-2.367256	0.565975	0.189529
H	-2.810639	0.276873	1.148100
H	-2.957730	0.084639	-0.606828
H	-2.469154	1.648462	0.062115
O	1.536080	-0.417098	0.287944
C	2.475104	0.425354	-0.006461
O	3.674774	0.183364	-0.010804
H	2.118528	1.443864	-0.258240

PtCO₂⁻

Pt	-0.497553	-0.037089	0.000000
O	1.479956	1.260347	0.000004
O	2.273962	-0.900597	0.000005
C	1.462963	0.002496	-0.000015

HPtCH₃⁻

Pt	0.210398	0.019524	0.000000
H	1.485757	-0.970370	0.000000
C	-1.861084	-0.066488	0.000000
H	-2.221063	0.975366	-0.000000
H	-2.254617	-0.564453	0.892562
H	-2.254617	-0.564453	-0.892562

TS1

H	-2.144965	1.123187	-1.379407
C	-2.207085	0.438343	-0.525851
H	-2.801700	-0.424262	-0.853123
H	-2.774959	0.950824	0.258559
H	0.861265	-0.927862	0.892369
O	1.459684	1.328173	0.215430
C	1.726293	0.142372	-0.096346
O	2.671515	-0.460928	-0.545307
Pt	-0.298775	-0.142874	0.095562

TS2

Pt	0.000000	0.293656	0.000000
H	0.383554	1.835714	0.000000
C	-0.995125	2.254539	0.000000
H	-1.600374	2.141675	0.899397
H	-0.589182	3.272133	0.000000
H	-1.600374	2.141675	-0.899397
C	0.398596	-1.751036	0.000000
O	1.580146	-2.098956	0.000000
O	-0.706952	-2.315719	0.000000

TS3

Pt	-0.309656	0.073689	-0.026651
H	0.710271	1.392694	0.138874
C	-2.351144	-0.427613	0.113311
H	-2.936247	0.155518	-0.605507
H	-2.743463	-0.266464	1.120734
H	-2.450778	-1.488493	-0.140379
C	1.683278	-0.253192	0.021765
O	2.036734	1.034582	0.076931
O	2.410841	-1.216598	0.017397

TS4

Pt	0.426580	-0.220396	-0.000048
H	-1.341017	1.918313	-0.000623
C	1.515687	1.355935	0.000303
H	2.043888	1.633551	0.915119
H	2.045263	1.633308	-0.913759
H	1.928971	-0.830931	0.000000
C	-1.655540	0.050756	-0.000008
O	-2.136859	1.370056	-0.000202
O	-2.502048	-0.820495	0.000353

TS5

Pt	0.402791	0.019254	-0.000018
H	-3.188443	-0.150832	0.000095
C	2.371431	-0.170546	-0.000010
H	2.996014	-0.212514	-0.898787
H	2.996203	-0.212851	0.898627
C	-1.640867	-0.016707	-0.000112
O	-2.351617	-1.118331	0.000180
O	-2.516479	0.949478	-0.000147
H	0.339893	1.548734	0.001944

TS6

H	1.890665	-0.940799	-0.284640
C	-1.051173	1.545047	0.376854
O	-1.229045	-1.073184	0.932240
C	-1.566914	-0.287392	0.009806
O	-2.438307	-0.269573	-0.832800
Pt	0.596732	-0.019491	-0.054840
H	-0.191268	2.003171	0.879925
H	-1.874225	1.567937	1.090374
H	-1.322961	2.086105	-0.523634

TS7

Pt	-0.330620	-0.097126	-0.118469
H	0.565630	-1.019752	-1.105935
C	-2.077688	0.460098	0.716748
H	-2.909041	0.867390	0.136425
H	-2.430357	0.102465	1.686763
H	-1.678581	-0.976538	0.047997
C	1.770151	0.111946	0.134636
O	1.674982	1.319808	-0.129853
O	2.585761	-0.673562	0.550729

Frequencies

$\text{CH}_2\text{PtC(OH)}_2^-$	$\text{CH}_2\text{PtH}_2\text{CO}_2^-$	$\text{CH}_2\text{PtHCOOH}^-$	$\text{CH}_3\text{PtCOOH}^-$	$\text{CH}_3\text{Pt(H)CO}_2^-$
53.4	51.0	67.8	51.0	50.0
109.2	137.3	108.9	72.9	66.0
122.4	186.6	144.8	100.6	119.6
296.5	258.6	263.8	272.3	213.2
322.2	280.4	272.0	291.2	261.0
532.0	492.3	285.0	476.5	321.5
557.7	519.9	506.4	505.4	470.0
587.8	549.0	515.2	576.0	498.8
632.5	578.6	547.6	617.1	638.1
648.8	615.5	578.7	675.6	683.6
662.3	688.8	667.2	676.7	705.3
696.5	716.1	698.6	976.6	714.1
1039.1	725.2	718.5	1122.9	1133.5
1088.8	830.1	959.8	1247.7	1245.2
1320.7	1213.3	1235.1	1425.5	1430.8
1386.4	1389.6	1390.7	1449.0	1446.5
1394.4	1910.7	1685.8	1692.3	1839.5
2964.7	1951.5	2261.2	2945.4	1925.2
3003.2	2346.7	2985.1	3020.6	2971.6
3738.1	3002.6	3035.6	3047.7	3033.6
3746.0	3075.9	3784.5	3729.8	3082.9

$\text{CH}_4\cdots\text{PtCO}_2^-$	HPtOCOCH_3^-	$\text{CH}_3\text{PtOCOH}^-$	PtCO_2^-	HPtCH_3^-
-4.4	66.1	66.6	228.4	195.4
10.0	89.7	86.0	322.5	425.2
14.3	103.6	111.2	596.7	479.3
64.8	258.8	141.8	737.4	669.8
126.7	296.1	172.9	1194.6	678.2
129.3	410.6	316.3	1767.0	1117.0
229.3	463.4	511.3		1421.0
324.0	602.3	641.3		1445.9
596.8	657.8	754.2		1908.7
740.9	916.6	786.2		2923.8
1194.1	1021.0	1055.7		2998.2
1316.0	1057.9	1180.7		3023.4
1355.1	1320.2	1278.4		
1355.5	1377.0	1388.5		
1561.2	1462.5	1416.6		
1561.2	1472.1	1452.3		
1762.8	1669.0	1681.3		
3010.3	2120.5	2876.5		
3106.6	3032.1	2931.8		
3106.9	3093.5	3001.5		
3126.1	3113.3	3027.9		

TS1	TS2	TS3	TS4	TS5	TS6	TS7
-186.7	-788.4	-1367.7	-78.7	-1832.6	-402.6	-945.2
58.6	61.6	32.6	78.1	72.8	140.0	54.0
75.6	71.6	82.6	154.6	110.7	190.9	122.2
135.0	75.8	89.7	204.0	128.4	244.7	240.3
318.6	116.8	292.6	257.5	267.8	345.5	260.5
330.6	258.0	397.3	330.2	279.1	370.0	268.5
527.3	291.8	464.9	599.8	284.9	459.4	460.7
563.6	476.0	486.2	636.4	484.4	553.8	491.1
587.4	545.3	528.6	652.6	490.0	566.9	579.0
689.7	723.3	614.2	668.9	564.7	662.5	612.3
706.5	840.8	645.8	705.0	696.8	788.2	660.2
735.5	899.5	724.2	765.7	730.6	844.5	693.1
1159.9	1221.8	1074.1	788.1	949.4	1178.1	792.3
1217.0	1223.7	1117.7	956.6	1152.7	1195.8	849.3
1426.7	1450.6	1434.8	1261.3	1266.7	1439.1	1206.2
1431.4	1461.7	1442.7	1332.3	1350.7	1454.8	1393.7
1855.0	1665.7	1697.4	1689.6	1390.9	1772.6	1839.0
2085.2	2216.9	1768.4	1992.8	2103.6	2055.0	1962.1
2991.7	2986.1	2975.4	2998.4	2333.2	2979.6	2032.1
3040.0	3045.4	3038.4	3085.8	2994.7	3072.3	3021.7
3053.2	3101.0	3052.4	3736.3	3046.4	3142.3	3081.7

