Supporting information

Metal-bipyridine complexes as electrocatalysts for the reduction of CO_2: A density functional theory study

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Table S1. Adsorption energies (E_{ad}) of CO on $[Mn(bpy)(CO)_3]^0$ with different supercell size. All results are in unit of eV.

E_{ad}/eV	25×25×20	30×30×25	40×40×30
CO	0.73	0.73	0.73

Table S2. Calculated total energies (*E*), zero-point energies (*ZPE*), and *TS* values. *T* is temperature and equals 298.15 K. *S* is the entropy. All results are in the unit of eV. The corresponding structures are shown in Fig. 2.

		A	B	C	D	E	F	G	H	I
V	*E*	-51858.944	-51862.8244	-48768.776	-48772.431	-53915.200	-53927.074	-53930.511	-53943.691	-48768.776
	ZPE	5.095	5.085	4.882	4.822	5.230	5.552	5.445	5.833	4.882
	TS	1.178	1.147	0.750	0.771	1.103	1.101	1.128	1.075	0.750
Cr	*E*	-54540.323	-54543.350	-51450.018	-51453.506	-56595.472	-56607.644	-56611.856	-56624.887	-51450.018
	ZPE	5.180	5.082	4.953	4.882	5.187	5.539	5.519	5.904	4.953
	TS	1.179	1.052	1.033	0.785	1.112	1.170	1.193	1.053	1.033
Mn	*E*	-57388.872	-57391.482	-54299.468	-54302.937	-59445.076	-59457.946	-59461.005	-59473.811	-54299.468
	ZPE	5.119	4.986	4.948	4.900	5.227	5.593	5.488	5.852	4.948
	TS	1.165	1.022	0.951	0.863	0.996	1.135	0.998	1.200	0.951
Nb	*E*	-129309.734	-129313.692	-126219.612	-126223.360	-131365.033	-131377.796	-131381.487	-131394.546	-126219.612
	ZPE	5.061	5.049	4.850	4.835	5.166	5.524	5.424	5.787	4.850
	TS	1.139	1.260	0.947	1.073	1.033	1.242	1.216	1.279	0.947
Mo	*E*	-136621.541	-136624.655	-133531.287	-133534.736	-138676.802	-138688.840	-138693.130	-138706.191	-133531.287
	ZPE	5.130	5.033	4.923	4.850	5.156	5.495	5.484	5.862	4.923
	TS	0.962	0.997	0.806	0.905	1.025	1.252	1.044	1.195	0.806
Ta	*E*	-419179.405	-419183.426	-416088.822	-416092.649	-421235.580	-421247.680	-421251.468	-421263.971	-416088.822
	ZPE	5.095	5.074	4.880	4.821	5.198	5.540	5.455	5.803	4.880
	TS	1.093	1.164	0.994	1.095	1.075	1.167	1.082	1.163	0.994
W	*E*	-459151.466	-459154.677	-456060.808	-456064.501	-461206.807	-461218.746	-461223.116	-461235.889	-456060.808
	ZPE	5.157	5.064	4.946	4.859	5.204	5.526	5.520	5.894	4.946
	TS	1.084	1.202	0.758	0.971	1.092	1.120	1.341	1.193	0.758
Re	*E*	-404812.425	-404815.215	-401722.610	-401726.125	-406868.448	-406881.398	-406884.648	-406897.245	-401722.610
	ZPE	5.104	5.021	4.939	4.871	5.215	5.564	5.470	5.873	4.939
	TS	0.946	1.160	0.805	0.865	1.096	1.012	1.070	1.081	0.805

Table S3. The reaction free energies of elemental steps at the electrode potential $U = 0$ V. All results are in the unit of eV. The reaction free energies of single electron reduction steps are shown in red colour.

Step	1	2	3	4	5	6	7	8	9	10	11
V	0.42	1.90	1.78	0.54	-0.95	-0.18	0.71	-1.58	-1.37	0.83	0.54
Cr	1.28	1.30	1.62	0.97	-0.24	-0.51	0.03	-1.54	-1.13	0.48	0.97
Mn	1.68	0.01	0.84	0.85	-0.20	-1.27	1.25	-1.15	-1.27	0.22	0.85
Nb	0.19	1.70	1.50	0.39	-0.56	-0.24	0.51	-1.28	-1.39	0.87	0.39
Mo	1.03	1.22	1.60	0.66	-0.14	-0.55	0.19	-1.43	-1.46	0.90	0.66
Ta	0.17	1.99	1.86	0.29	-0.79	-0.48	0.49	-1.05	-0.86	0.94	0.29
W	0.86	1.60	2.17	0.29	-0.34	-0.27	-0.22	-1.20	-0.88	1.11	0.29
Re	1.19	0.63	1.19	0.64	-0.47	-1.14	0.88	-0.76	-0.83	0.52	0.64

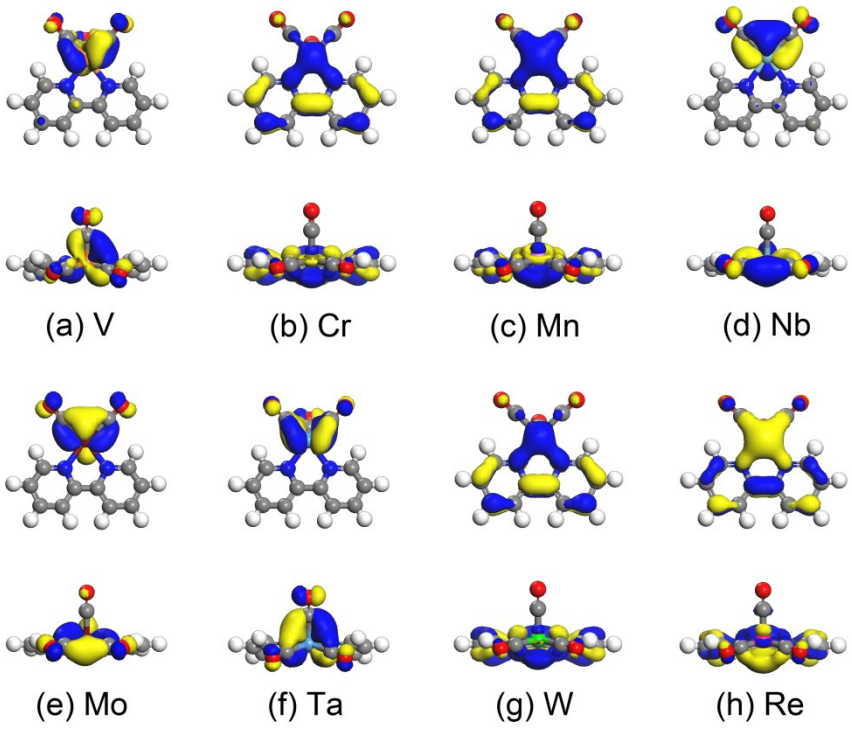

Fig. S1. Highest occupied molecule orbitals (HOMO) of $[M(bpy)(CO)_3]^{-1}$.

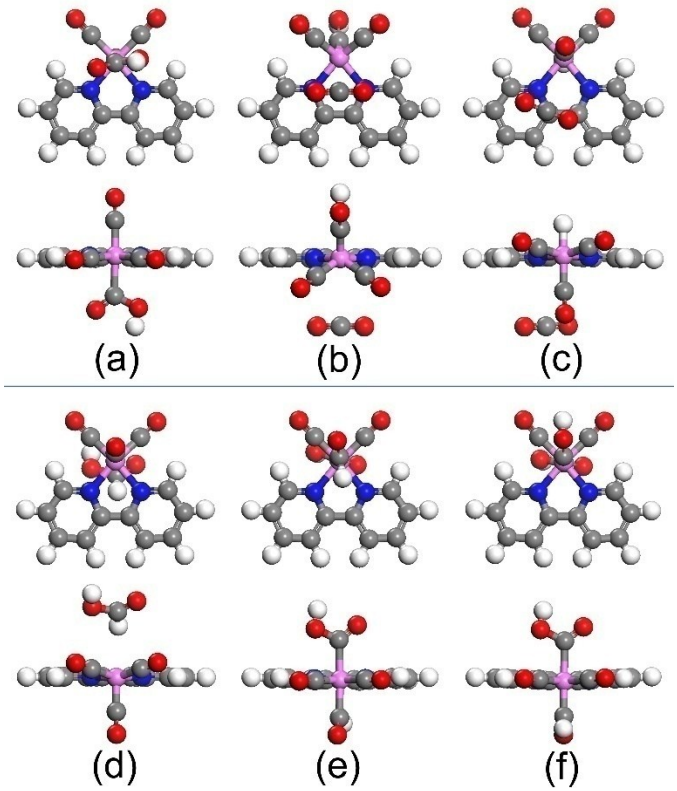

Figure S2. Different products of hydrogenation steps of $[Mn(bpy)(CO)_3CO_2]^{-1}$ and $[Mn(bpy)(CO)_3COOH]^{-1}$. (a) the structure F and (d) the structure H in Figure 2.

Table S4. Electronic and spin states of transition metals in $M(bpy)(CO)_4$ based on Mulliken charge population with GGA-PW91 functional by the DMol^3 code.

$V(bpy)(CO)_4$			$Cr(bpy)(CO)_4$			$Mn(bpy)(CO)_4$		
3*d*	4*s*	spin	3*d*	4*s*	spin	3*d*	4*s*	spin
4.179	0.23	0.3515	5.36	0.299	0	6.139	0.254	0
$Nb(bpy)(CO)_4$			$Mo(bpy)(CO)_4$					
4*d*	5*s*	spin	4*d*	5*s*	spin			
3.975	0.295	0.245	5.161	0.318	0			
$Ta(bpy)(CO)_4$			$W(bpy)(CO)_4$			$Re(bpy)(CO)_4$		
5*d*	6*s*	spin	5*d*	6*s*	spin	5*d*	6*s*	spin
3.669	0.525	0.118	4.806	0.642	0	5.086	0.745	0

Table S5. Electronic and spin states of transition metals in $M(bpy)(CO)_4$ based on Mulliken charge population with B3LYP functional by the DMol^3 code.

$V(bpy)(CO)_4$			$Cr(bpy)(CO)_4$			$Mn(bpy)(CO)_4$		
3*d*	4*s*	spin	3*d*	4*s*	spin	3*d*	4*s*	spin
4.197	0.18	0.419	5.387	0.234	0	6.169	0.213	0
$Nb(bpy)(CO)_4$			$Mo(bpy)(CO)_4$					
4*d*	5*s*	spin	4*d*	5*s*	spin			
3.87	0.232	0	5.099	0.261	0			
$Ta(bpy)(CO)_4$			$W(bpy)(CO)_4$			$Re(bpy)(CO)_4$		
5*d*	6*s*	spin	5*d*	6*s*	spin	5*d*	6*s*	spin
3.518	0.495	0	4.657	0.615	0	5.637	0.707	0

Table S6. Relative energy of different products of hydrogenation steps of $[Mn(bpy)(CO)_3CO_2]^{-1}$ and $[Mn(bpy)(CO)_3COOH]^{-1}$ in Fig. S2. All results are in the unit eV. The energies of structures (a) and (d) in Fig. S2 are defined as 0 eV. The positive energy value indicates that the corresponding structure are unstable compared with the reference structure.

Structure	a	b	c
Energy	0	5.04	3.14
Structure	d	e	f
Energy	0	1.11	2.51

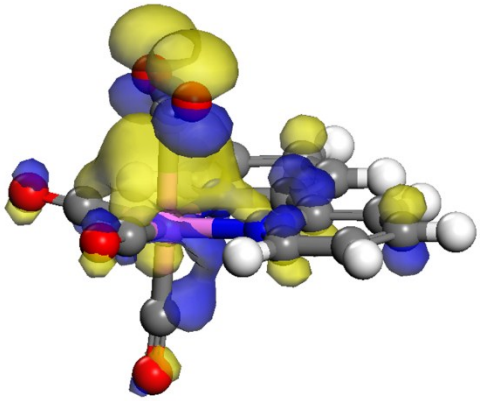

Fig. S3. Highest occupied molecule orbital (HOMO) of $[Mn(bpy)(CO)_3CO_2]^{-1}$.