Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supplementary Information

Insights into elusive and cooperative multi-oxidant mechanisms in enabling catalytic methane-to-methanol conversion over atomically dispersed metals

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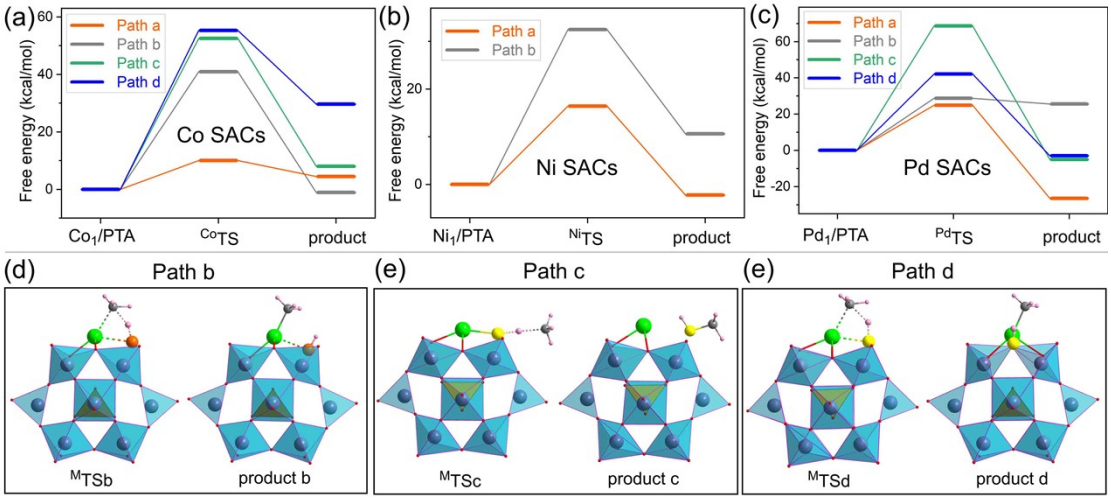


Fig. S1. The four possible reaction paths of removing O_b or O_c for Ni (only O_b), Co and Pd SACs shown in (a), (b) and (c), respectively. The corresponding of geometry structures of path b, c and d were shown in (d), (e) and (f).

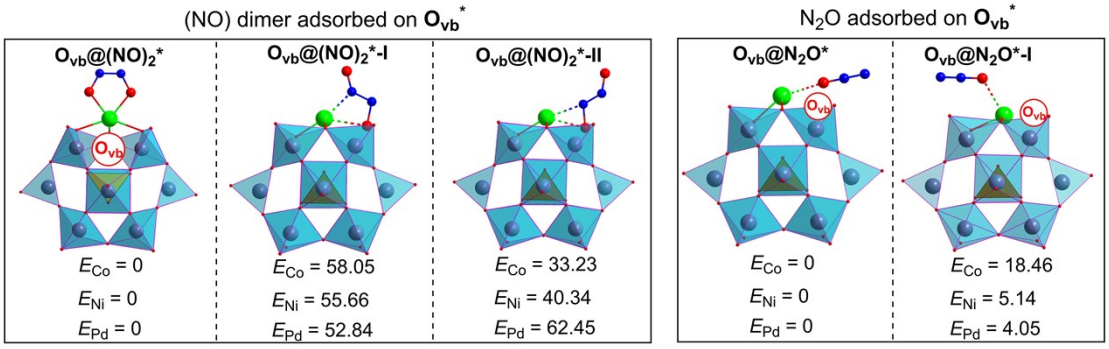


Fig. S2. The adsorption model of NO dimer and N_2O molecules on O_{vb}-based Co, Ni and Pd SACs with corresponding relative energies (kcal/mol).

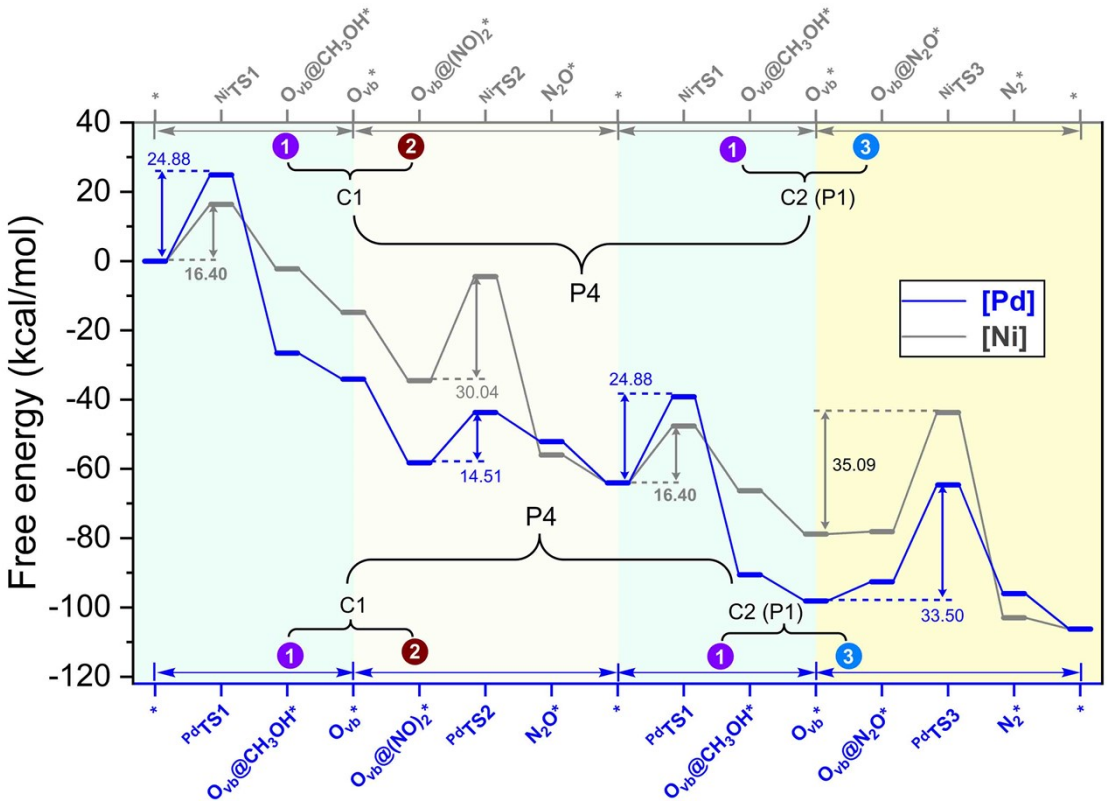


Fig. S3. Calculated free energy profiles of P1 and P4 over Ni and Pd system (kcal/mol).

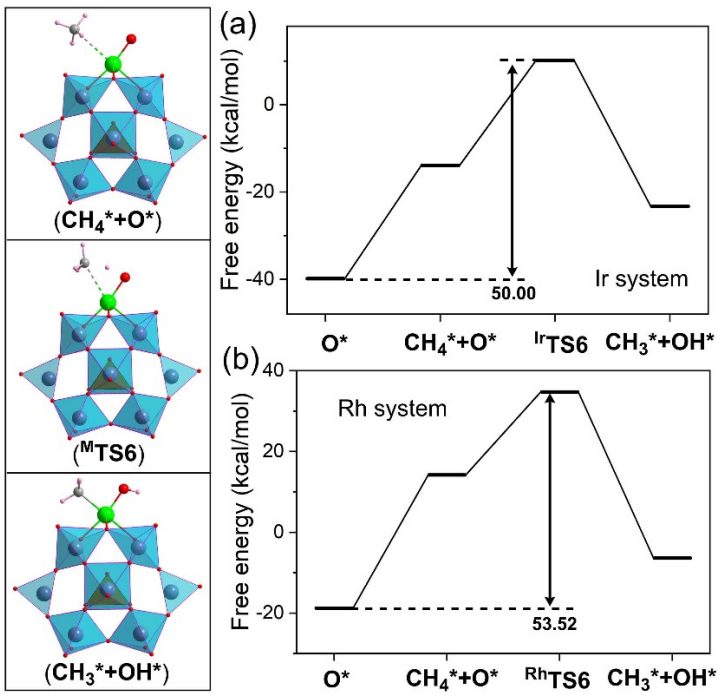


Fig. S4. Calculated free energy profiles of precursor-mediated mechanism in reaction 5 over Rh and Ir system (kcal/mol).

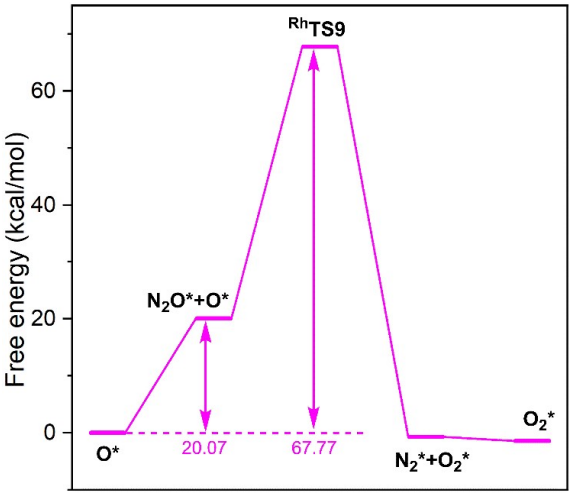


Fig. S5. Reaction 6 for Rh_1/PTA SACs.

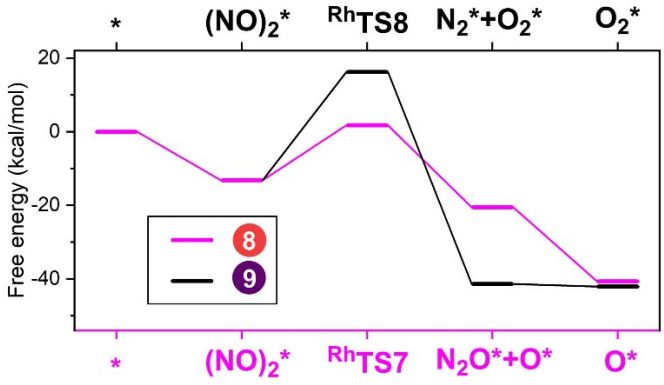


Fig. S6. Calculated free energy profiles of reaction 8 and 9 over Rh_1/PTA.

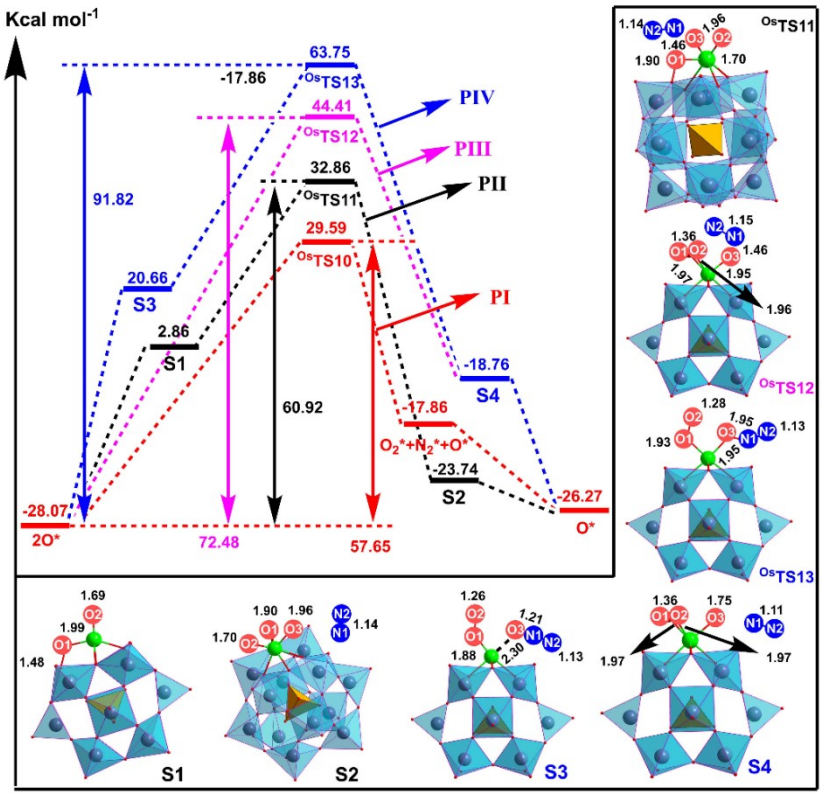


Fig. S7. The direct N_2O dissociation on $2O@Os_1$/PTA SACs (kcal/mol).

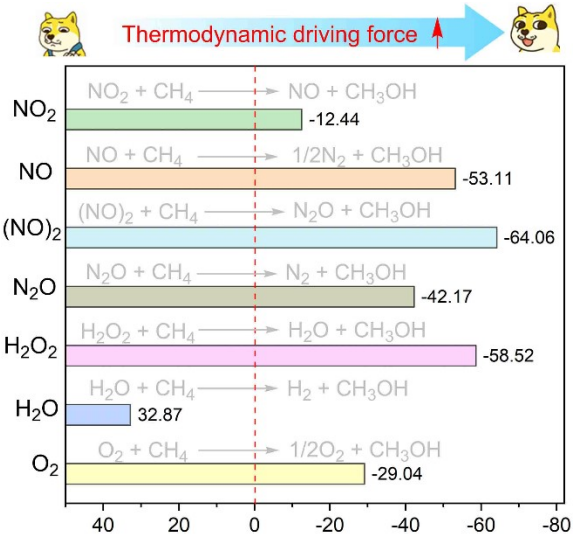


Figure S8. Reaction energies of DSCMM by various oxidants (kcal/mol).

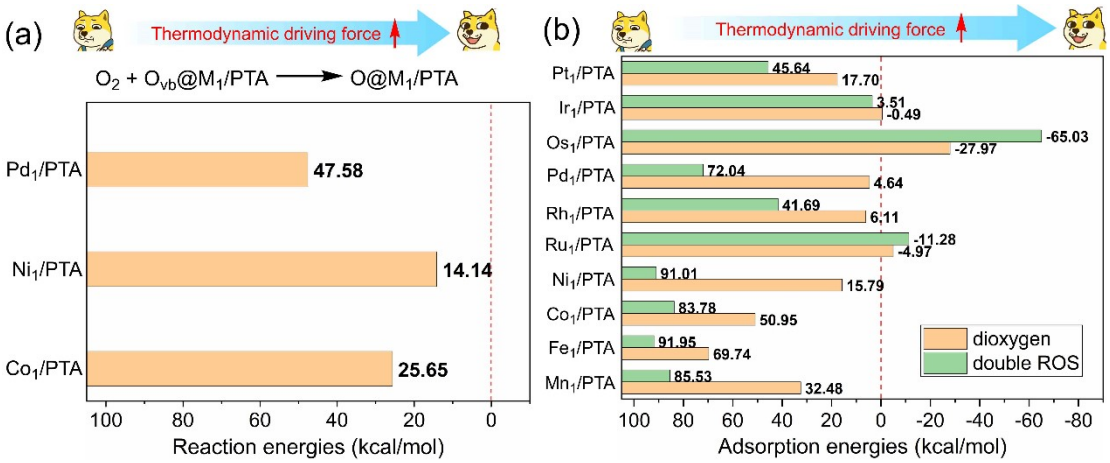


Fig. S9. (a) Adsorption energies of dioxygen or double ROS over M_1/PTA SACs. (b) E_r of replenishing oxygen vacancy with O_2 for Co, Ni and Pd systems.

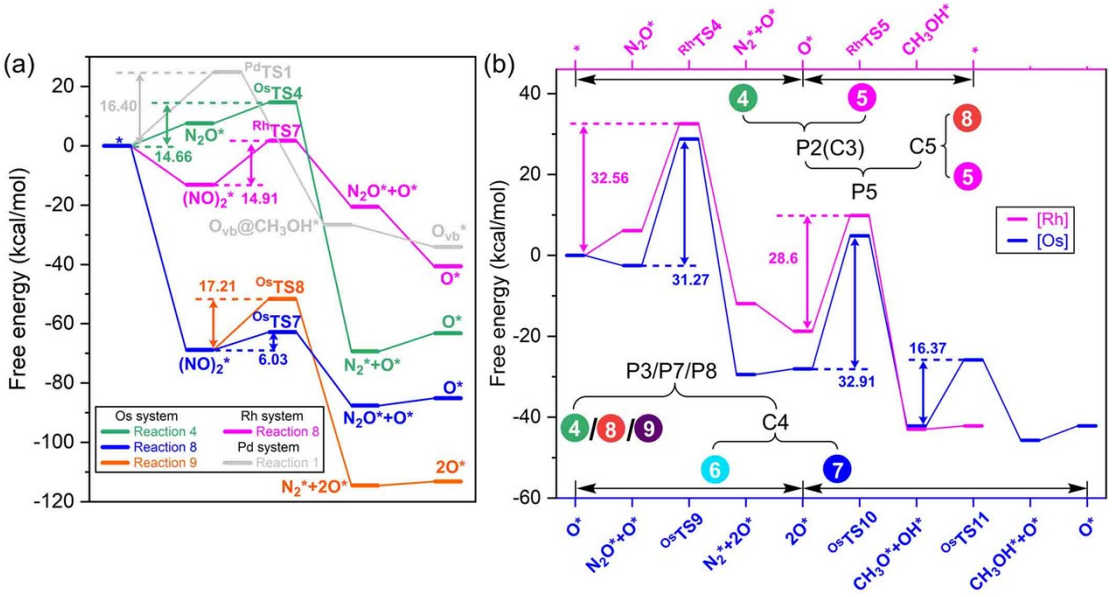


Fig. S10. (a) Calculated free energy profiles of reaction 8 of Rh_1/PTA, reaction 1 of Pd_1/PTA and reactions 1, 3 and 4 of Os_1/PTA SACs, respectively. (b) Calculated free energy profiles of C3 over Rh system, and C4 over Os system, respectively.

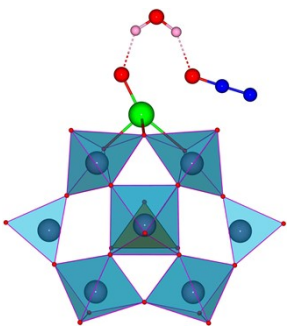


Fig. S11. Hydrogen bonding cooperativity of $N_2O\cdots HOH\cdots O@M_1$/PTA.

Table S1. DFT–derived single point energy (kcal/mol) for the clean M_1/PTA and adsorption complexes with one CH_4, one CH_3OH, one O_2, one a dissociative adsorption state of O_2 ($^dO_2$), one N_2, one N-end N_2O, one O-end N_2O and two complexed NO ($(NO)_2$) with different spin states

M_1/POM	Spin multiplicity	Total energy (a.u.)	Total energy (kcal/mol)	Relative energy (kcal/mol)
Clean M_1/POM				
Mn-PTA	1	-4270.5197	-2679793.8220	56.5126
	3	-4270.5658	-2679822.7150	27.6196
	5	-4270.6098	-2679850.3350	0.0000
Fe-PTA	2	-4290.0626	-2692057.1800	16.5990
	4	-4290.0890	-2692073.7500	0.0292
	6	-4290.0890	-2692073.7790	0.0000
Co-PTA	1	-4311.6939	-2705631.0430	8.9823
	3	-4311.7082	-2705640.0250	0.0000
	5	-4311.6818	-2705623.4190	16.6061
Ni-PTA	2	-4335.9193	-2720832.7008	0.0000
	4	-4335.8915	-2720815.2941	17.4068
Ru-PTA	2	-4260.4496	-2673474.7420	0.0000
	4	-4260.4460	-2673472.4580	2.2840
	6	-4260.4246	-2673459.0440	15.6981
Rh-PTA	1	-4276.0667	-2683274.5860	0.0000
	3	-4276.0660	-2683274.1740	0.4128
	5	-4276.0370	-2683255.9940	18.5918
Pd-PTA	2	-4293.2793	-2694075.7160	0.0000
	4	-4293.2793	-2694075.7150	0.0005
Os-PTA	2	-4257.5725	-2671669.2940	0.0000
	4	-4257.5715	-2671668.6640	0.6307
	6	-4257.5390	-2671648.3000	20.9946
Ir-PTA	1	-4271.2155	-2680230.4690	0.0000
	3	-4271.2179	-2680231.9620	-1.4930
	5	-4271.1670	-2680199.9980	30.4708
Pt-PTA	2	-4285.6571	-2689292.7050	0.0000
	4	-4285.6257	-2689272.9750	19.7300
One CH_4				
Mn-PTA	1	-4311.0386	-2705219.8354	58.4473
	3	-4311.0786	-2705244.9238	33.3588
	5	-4311.1317	-2705278.2826	0.0000
Fe-PTA	2	-4330.5811	-2717482.9155	23.1297
	4	-4330.6069	-2717499.1277	6.9176
	6	-4330.6179	-2717506.0452	0.0000
Co-PTA	1	-4352.2065	-2731053.0883	8.5810

	3	-4352.2202	-2731061.6693	0.0000
	5	-4352.2105	-2731055.5974	6.0719
Ni-PTA	2	-4376.4340	-2746256.1021	0.0000
	4	-4376.4127	-2746242.7095	13.3927
Ru-PTA	2	-4300.9724	-2698903.1794	0.0000
	4	-4300.9665	-2698899.5047	3.6747
	6	-4300.9471	-2698887.3417	15.8377
Rh-PTA	1	-4316.5899	-2708703.2978	0.0000
	3	-4316.5833	-2708699.1956	4.1023
	5	-4316.5592	-2708684.0577	19.2401
Pd-PTA	2	-4333.7960	-2719500.3342	0.0000
	4	-4333.7855	-2719493.7412	6.5931
Os-PTA	2	-4298.0942	-2697097.0659	0.0000
	4	-4298.0825	-2697089.7198	7.3461
	6	-4298.0506	-2697069.7007	27.3652
Ir-PTA	1	-4311.7395	-2705659.6409	0.0000
	3	-4311.7311	-2705654.3650	5.2760
	5	-4311.6888	-2705627.8242	31.8167
Pt-PTA	2	-4326.1690	-2714714.3308	0.0000
	4	-4326.1460	-2714699.9019	14.4290
		One CH_3OH		
Mn-PTA	1	-4386.2722	-2752429.6888	54.1157
	3	-4386.3186	-2752458.8050	24.9994
	5	-4386.3585	-2752483.8044	0.0000
Fe-PTA	2	-4405.8165	-2764693.9073	22.2814
	4	-4405.8379	-2764707.3573	8.8313
	6	-4405.8520	-2764716.1886	0.0000
Co-PTA	1	-4427.4464	-2778266.8592	4.3867
	3	-4427.4533	-2778271.2459	0.0000
	5	-4427.4452	-2778266.1316	5.1144
Ni-PTA	2	-4451.6627	-2793462.8404	0.0000
	4	-4451.6474	-2793453.2325	9.6079
Ru-PTA	2	-4376.2047	-2746112.1989	0.0000
	4	-4376.1983	-2746108.2014	3.9975
	6	-4376.1785	-2746095.7975	16.4014
Rh-PTA	1	-4391.8232	-2755912.9755	0.0000
	3	-4391.8143	-2755907.4193	5.5562
	5	-4391.7875	-2755890.5780	22.3975
Pd-PTA	2	-4409.0289	-2766709.7060	0.0000
	4	-4409.0125	-2766699.4125	10.2935
Os-PTA	2	-4373.3288	-2744307.5345	0.0000
	4	-4373.3202	-2744302.1506	5.3840
	6	-4373.2867	-2744281.1120	26.4226
Ir-PTA	1	-4386.9724	-2752869.0543	0.0000

	3	-4386.9668	-2752865.5407	3.5136
	5	-4386.9229	-2752837.9668	31.0875
Pt-PTA	2	-4401.4041	-2761925.1064	0.0000
	4	-4401.3761	-2761907.5475	17.5590
		One N_2		
Mn-PTA	1	-4380.0636	-2748533.7063	49.9424
	3	-4380.0985	-2748555.6081	28.0407
	5	-4380.1432	-2748583.6488	0.0000
Fe-PTA	2	-4399.5949	-2760789.7788	21.1710
	4	-4399.6184	-2760804.5522	6.3976
	6	-4399.6286	-2760810.9498	0.0000
Co-PTA	1	-4421.2282	-2774364.8859	4.0361
	3	-4421.2346	-2774368.9220	0.0000
	5	-4421.2213	-2774360.5770	8.3450
Ni-PTA	2	-4445.4461	-2789561.9059	0.0000
	4	-4445.4270	-2789549.9140	11.9919
Ru-PTA	2	-4369.9976	-2742217.1706	0.0000
	4	-4369.9826	-2742207.7624	9.4082
	6	-4369.9590	-2742192.9927	24.1779
Rh-PTA	1	-4385.6141	-2752016.7319	0.0000
	3	-4385.6020	-2752009.0868	7.6452
	5	-4385.5710	-2751989.6575	27.0744
Pd-PTA	2	-4402.8130	-2762809.1605	0.0000
	4	-4402.7984	-2762800.0530	9.1075
Os-PTA	2	-4367.1342	-2740420.3953	0.0000
	4	-4367.1122	-2740406.5841	13.8112
	6	-4367.0668	-2740378.0932	42.3021
Ir-PTA	1	-4380.7768	-2748981.2716	0.0000
	3	-4380.7618	-2748971.8670	9.4046
	5	-4380.7074	-2748937.6719	43.5997
Pt-PTA	2	-4395.1938	-2758028.0595	0.0000
	4	-4395.1620	-2758008.1316	19.9279
		O_2		
Mn-PTA	1	-4420.8847	-2774149.3833	36.8423
	3	-4420.9435	-2774186.2256	0.0000
	5	-4420.9366	-2774181.9485	4.2771
	7	-4420.9285	-2774176.8615	9.3641
Fe-PTA	2	-4440.4138	-2786404.0920	2.1023
	4	-4440.4172	-2786406.1943	0.0000
	6	-4440.4073	-2786399.9535	6.2408
	8	-4440.4108	-2786402.1646	4.0298
Co-PTA	1	-4461.9977	-2799948.1889	16.1989
	3	-4462.0234	-2799964.3206	0.0672
	5	-4462.0235	-2799964.3878	0.0000

	7	-4462.0027	-2799951.3203	13.0675
Ni-PTA	2	-4486.2364	-2815158.1850	0.0000
	4	-4486.2349	-2815157.2646	0.9204
	6	-4486.2039	-2815137.7959	20.3891
Ru-PTA	2	-4410.7971	-2767819.3192	3.1378
	4	-4410.8021	-2767822.4570	0.0000
	6	-4410.7607	-2767796.4531	26.0039
	8	-4410.7424	-2767784.9920	37.4650
Rh-PTA	1	-4426.3888	-2777603.2325	2.8060
	3	-4426.3933	-2777606.0384	0.0000
	5	-4426.3833	-2777599.7644	6.2740
	7	-4426.3548	-2777581.8780	24.1605
Pd-PTA	2	-4443.6014	-2788404.3418	0.0000
	4	-4443.5959	-2788400.8323	3.5095
	6	-4443.5829	-2788392.7357	11.6061
Os-PTA	2	-4407.9381	-2766025.2405	9.3208
	4	-4407.9530	-2766034.5613	0.0000
	6	-4407.8934	-2765997.1740	37.3873
	8	-4407.8132	-2765946.8318	50.3422
Ir-PTA	1	-4421.5542	-2774569.4674	2.2772
	3	-4421.5578	-2774571.7445	0.0000
	5	-4421.5321	-2774555.6349	16.1097
		-4421.4821	-2774524.2555	47.4890
Pt-PTA	2	-4435.9813	-2783622.6095	0.0000
	4	-4435.9539	-2783605.4219	17.1876
	6	-4435.9431	-2783598.6380	23.9715
		One $^{d}O_2$		
Mn-PTA	5	-4420.8458	-2774124.9618	0.0000
Fe-PTA	6	-4440.3450	-2786360.9192	0.0000
Co-PTA	3	-4461.9173	-2799897.6946	16.2994
	5	-4461.9432	-2799913.9940	0.0000
Ni-PTA	4	-4486.1176	-2815083.6789	0.0000
Ru-PTA	2	-4410.8041	-2767823.6923	0.0000
	4	-4410.7906	-2767815.1978	8.4945
	6	-4410.7428	-2767785.2169	38.4753
Rh-PTA	1	-4426.3270	-2777564.4697	15.3208
	3	-4426.3220	-2777561.2972	18.4933
	5	-4426.3514	-2777579.7905	0.0000
Pd-PTA	2	-4443.4957	-2788337.9639	5.0241
	4	-4443.5037	-2788342.9880	0.0000
	6	-4443.4988	-2788339.9405	3.0475
Os-PTA	2	-4408.0300	-2766082.9352	0.0000
	4	-4407.9888	-2766057.0818	25.8534
	6	-4407.9082	-2766006.4547	50.6270

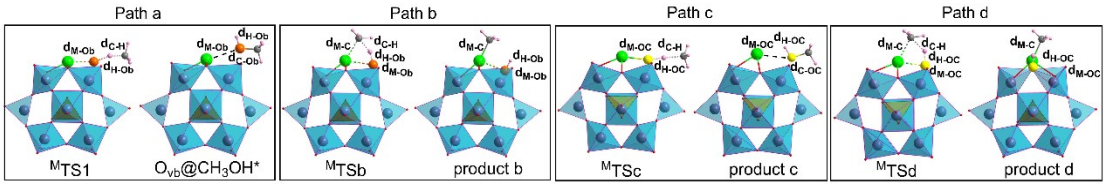
Ir-PTA	1	-4421.5749	-2774582.4848	1.0737
	3	-4421.5766	-2774583.5584	0.0000
	5	-4421.5609	-2774573.6985	9.8599
Pt-PTA	2	-4435.9242	-2783586.8115	0.0000
	4	-4435.9186	-2783583.2977	3.5138
One N-end N_2O				
Mn-PTA	1	-4455.2093	-2795688.3821	52.6121
	3	-4455.2479	-2795712.5910	28.4033
	5	-4455.2931	-2795740.9942	0.0000
Fe-PTA	2	-4474.7457	-2807947.6920	22.1571
	4	-4474.7689	-2807962.2055	7.6436
	6	-4474.7810	-2807969.8491	0.0000
Co-PTA	1	-4496.3756	-2821520.6568	4.8708
	3	-4496.3834	-2821525.5277	0.0000
	5	-4496.3738	-2821519.5131	6.0146
Ni-PTA	2	-4520.5949	-2836718.5316	0.0000
	4	-4520.5778	-2836707.7592	10.7724
Ru-PTA	2	-4445.1420	-2789371.0533	0.0000
	4	-4445.1321	-2789364.8186	6.2347
	6	-4445.1103	-2789351.1787	19.8747
Rh-PTA	1	-4460.7587	-2799170.7027	0.0000
	3	-4460.7499	-2799165.1874	5.5153
	5	-4460.7227	-2799148.1258	22.5768
Pd-PTA	2	-4477.9615	-2809965.6380	0.0000
	4	-4477.9494	-2809958.0531	7.5849
Os-PTA	2	-4442.2722	-2787570.2489	0.0000
	4	-4442.2570	-2787560.6843	9.5646
	6	-4442.2181	-2787536.3038	33.9451
Ir-PTA	1	-4455.9145	-2796130.9187	0.0000
	3	-4455.9042	-2796124.4498	6.4690
	5	-4455.8565	-2796094.4829	36.4359
Pt-PTA	2	-4470.3383	-2805182.0150	0.0000
	4	-4470.3124	-2805165.7237	16.2913
One O-end N_2O				
Mn-PTA	1	-4455.2037	-2795684.8693	54.4736
	3	-4455.2417	-2795708.7451	30.5977
	5	-4455.2905	-2795739.3429	0.0000
Fe-PTA	2	-4474.7425	-2807945.6709	21.5598
	4	-4474.7662	-2807960.5221	6.7085
	6	-4474.7769	-2807967.2307	0.0000
Co-PTA	1	-4496.3716	-2821518.1142	4.9244
	3	-4496.3794	-2821523.0386	0.0000
	5	-4496.3693	-2821516.6767	6.3619
Ni-PTA	2	-4520.5940	-2836717.9409	0.0000

	4	-4520.5750	-2836706.0472	11.8937
Ru-PTA	2	-4445.1361	-2789367.3385	0.0000
	4	-4445.1266	-2789361.3834	5.9551
	6	-4445.1065	-2789348.7920	18.5465
Rh-PTA	1	-4460.7527	-2799166.9005	0.0000
	3	-4460.7456	-2799162.4768	4.4237
	5	-4460.7183	-2799145.3293	21.5712
Pd-PTA	2	-4477.9574	-2809963.0435	0.0000
	4	-4477.9456	-2809955.6490	7.3945
Os-PTA	2	-4442.2576	-2787561.0973	0.0000
	4	-4442.2437	-2787552.3441	8.7532
	6	-4442.2112	-2787531.9332	29.1641
Ir-PTA	1	-4455.9012	-2796122.5334	0.0000
	3	-4455.8938	-2796117.9133	4.6201
	5	-4455.8473	-2796088.7366	33.7967
Pt-PTA	2	-4470.3307	-2805177.2209	0.0000
	4	-4470.3065	-2805162.0255	15.1954
		$(NO)_2$		
Mn-PTA	1	-4530.3860	-2842862.5468	17.5437
	3	-4530.4140	-2842880.0905	0.0000
	5	-4530.3995	-2842870.9695	9.1210
Fe-PTA	2	-4549.8864	-2855099.1859	7.9874
	4	-4549.8961	-2855105.3036	1.8697
	6	-4549.8991	-2855107.1733	0.0000
Co-PTA	1	-4571.4909	-2868656.2461	3.1853
	3	-4571.4960	-2868659.4314	0.0000
Ni-PTA	2	-4595.6873	-2883839.7233	0.0000
	4	-4595.6710	-2883829.5118	10.2115
Ru-PTA	2	-4520.3073	-2836538.0327	0.0000
	4	-4520.2833	-2836522.9531	15.0797
	6	-4520.2283	-2836488.4499	49.5829
Rh-PTA	1	-4535.8877	-2846314.8939	0.6028
	3	-4535.8887	-2846315.4968	0.0000
	5	-4535.8388	-2846284.2336	31.2632
Pd-PTA	2	-4553.0702	-2857097.1118	0.0000
	4	-4553.0532	-2857086.3880	10.7239
Os-PTA	2	-4517.4784	-2834762.8869	0.0000
	4	-4517.4511	-2834745.7215	17.1655
	6	-4517.3699	-2834694.8151	68.0718
Ir-PTA	1	-4531.0810	-2843298.6104	0.0000
	3	-4531.0722	-2843293.1144	5.4960
	5	-4531.0152	-2843257.3581	41.2523
Pt-PTA	2	-4545.4736	-2852330.1078	0.0000
	4	-4545.4481	-2852314.1625	15.9452

One N-end NO				
Mn-PTA	2	-4400.521	-2761370.979	0.000
	4	-4400.521	-2761370.839	0.139
	6	-4400.502	-2761358.913	12.066
Fe-PTA	1	-4420.013	-2773602.314	3.103
	3	-4420.018	-2773605.417	0.000
	5	-4420.006	-2773597.997	7.420
Co-PTA	2	-4441.635	-2787170.600	0.000
	4	-4441.613	-2787156.883	13.717
	6	-4441.581	-2787136.603	33.997
Ni-PTA	1	-4465.845	-2802362.460	0.000
	3	-4465.818	-2802345.641	16.819
Ru-PTA	1	-4390.432	-2755040.059	0.000
	3	-4390.409	-2755025.722	14.337
	5	-4390.368	-2754999.528	40.530
Rh-PTA	2	-4406.014	-2764817.885	0.000
	4	-4405.991	-2764803.116	14.769
	6	-4405.933	-2764767.022	50.864
Pd-PTA	1	-4423.216	-2775611.968	0.000
	3	-4423.204	-2775604.819	7.149
Os-PTA	1	-4387.589	-2753256.201	0.000
	3	-4387.566	-2753241.387	14.814
	5	-4387.501	-2753200.988	55.213
Ir-PTA	2	-4401.193	-2761792.412	0.000
	4	-4401.148	-2761764.603	27.810
	6	-4401.064	-2761711.441	80.971
Pt-PTA	1	-4415.594	-2770829.634	0.000
	3	-4415.583	-2770822.566	7.068
One O-end NO				
Mn-PTA	2	-4400.477	-2761343.354	17.679
	4	-4400.505	-2761361.032	0.000
	6	-4400.499	-2761357.250	3.783
Fe-PTA	1	-4419.961	-2773569.904	18.949
	3	-4419.987	-2773586.098	2.755
	5	-4419.991	-2773588.853	0.000
Co-PTA	2	-4441.605	-2787151.823	0.000
	4	-4441.585	-2787138.693	13.130
	6	-4441.574	-2787131.898	19.926
Ni-PTA	1	-4465.826	-2802350.332	0
	3	-4465.797	-2802332.402	17.930
Ru-PTA	1	-4390.369	-2755000.461	0.000
	3	-4390.358	-2754993.248	7.213
	5	-4390.342	-2754983.209	17.252
Rh-PTA	2	-4405.976	-2764793.985	0.000

	4	-4405.963	-2764785.670	8.315
	6	-4405.927	-2764763.034	30.951
Pd-PTA	1	-4423.205	-2775605.102	0.000
	3	-4423.192	-2775597.320	7.782
Os-PTA	1	-4387.504	-2753202.513	0.000
	3	-4387.490	-2753193.643	8.870
	5	-4387.464	-2753177.504	25.009
Ir-PTA	2	-4401.119	-2761746.086	0.000
	4	-4401.110	-2761740.233	5.854
	6	-4401.058	-2761707.819	38.268
Pt-PTA	1	-4415.563	-2770810.218	0.000
	3	-4415.548	-2770800.648	9.570

Table S2. The relative energies (kcal/mol) and key geometry parameters of each state.

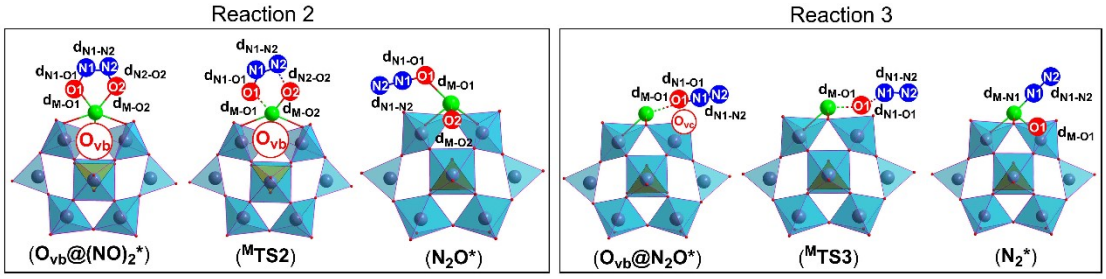


	Co	Ni	Pd
	Relative energies		
	Path a		
*	0.00	0.00	0.00
^{M}TS1	10.100	16.40	24.88
O_{vb}@CH_3OH*	4.46	-2.25	-26.55
	Path b		
^{M}TSb	40.92	32.47	28.73
Product b	-1.15	10.61	25.58
	Path c		
^{M}TSc	52.53		68.58
Product c	7.98		-5.07
	Path d		
^{M}TSd	55.30		42.14
Product d	29.63		-3.06

		Co	Ni	Pd
		Key geometry parameters		
		Path a		
^{M}TS1	d_{M-Ob}	1.884	1.832	2.028
	d_{C-H}	1.387	1.390	1.352
	d_{H-Ob}	2.772	3.359	1.190
O_{vb}@CH_3OH*	d_{M-Ob}	2.067	2.099	2.282
	d_{C-Ob}	1.59	1.459	1.451
	d_{H-Ob}	0.974	0.974	0.973
			Path b	
^{M}TSb	d_{M-C}	2.085	2.071	2.216
	d_{M-Ob}	1.884	2.010	2.189
	d_{H-Ob}	2.772	1.267	1.307
	d_{C-H}	1.387	1.377	1.363
Product b	d_{M-C}	2.004	1.939	2.034
	d_{M-Ob}	2.072	1.970	2.149
	d_{H-Ob}	0.975	0.975	0.978
			Path c	
^{M}TSc	d_{M-Oc}	1.927		2.211
	d_{C-H}	1.435		1.308

	d_{H-Oc}	1.143		1.234
Product c	d_{M-Oc}	2.151		2.853
	d_{C-Oc}	1.461		1.475
	d_{H-Oc}	0.975		0.993
			Path d	
^{M}TSd	d_{M-C}	2.085		2.189
	d_{M-Ob}	1.884		2.179
	d_{H-Ob}	2.772		2.802
	d_{C-H}	1.387		1.397
Product d	d_{M-C}	1.917		2.026
	d_{M-Oc}	2.017		2.158
	d_{H-Oc}	0.974		0.975

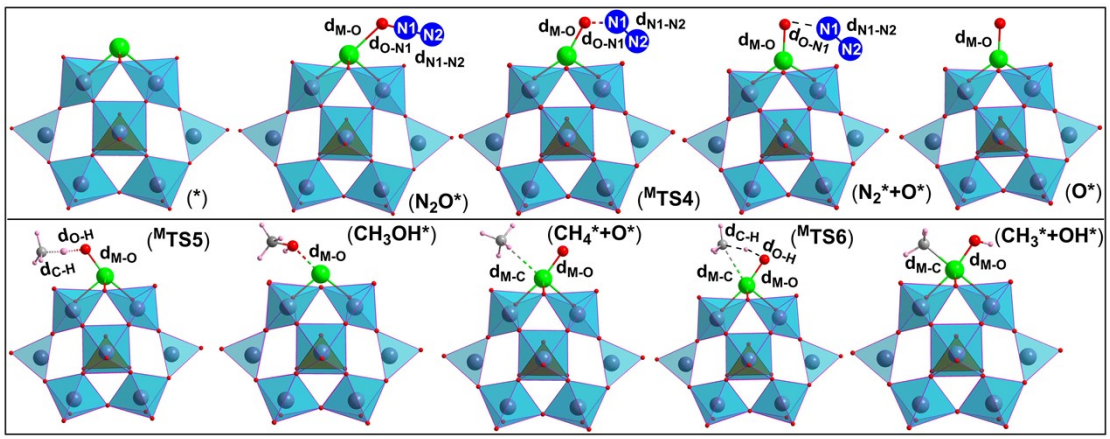
Table S3. The relative energies (kcal/mol) and key geometry parameters of each state of reactions 2 and 3.



		Co	Ni	Pd
		Relative energies		
		Reaction 2		
O_{vb}*		-15.34	-14.78	-34.07
O_{vb}@$(NO)_2$*		-35.38	-34.49	-58.26
^{M}TS2		-13.20	-4.45	-43.75
N_2O*		-46.86	-56.00	-52.16
*		-64.06	-64.06	-64.06
		Reaction 3		
O_{vb}@N_2O*		-8.21	-14.10	-28.52
^{M}TS3		39.44	20.32	-0.57
N_2*		2.05	-38.93	-31.96
*		-42.17	-42.17	-42.17
		Co	Ni	Pd
		Key geometry parameters		
		Reaction 2		
O_{vb}@$(NO)_2$*	d_{M-O1}	1.792	1.953	1.988
	d_{M-O2}	1.792	1.933	1.998
	d_{N1-O1}	1.339	1.288	1.311
	d_{N2-O2}	1.339	1.291	1.307
	d_{N1-N2}	1.254	1.291	1.267
^{M}TS2	d_{M-O1}	1.955	1.928	2.075
	d_{M-O2}	1.687	1.684	1.864
	d_{N1-O1}	1.266	1.262	1.275
	d_{N2-O2}	2.100	2.122	1.827
	d_{N1-N2}	1.160	1.158	1.184
N_2O*	d_{M-O1}	2.188	2.262	4.250
	d_{M-O2}	1.921	1.890	2.135
	d_{N1-O1}	1.204	1.201	1.169
	d_{N1-N2}	1.132	1.133	1.143
			Reaction 3	
O_{vb}@N_2O*	d_{M-O1}	2.315	2.258	2.389
	d_{N1-O1}	1.204	1.203	1.202

	d_{N1-N2}	1.132	1.132	1.134
^{M}TS3	d_{M-O1}	2.099	1.995	2.074
	d_{N1-O1}	1.337	1.405	1.457
	d_{N1-N2}	1.142	1.136	1.143
N_2*	d_{M-O1}	1.928	1.894	2.138
	d_{M-N1}	2.111	2.239	2.161
	d_{N1-N2}	1.108	1.108	1.109

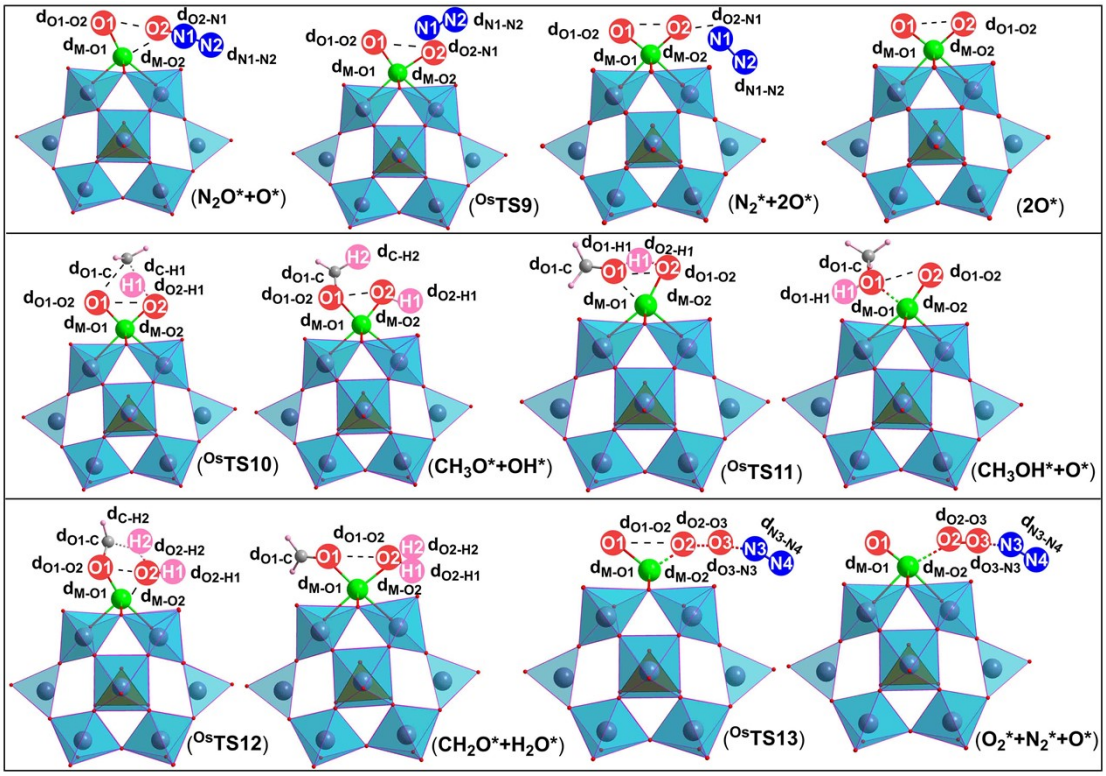
Table S4. The relative energies (kcal/mol) and key geometry parameters.



		Rh	Os	Ir
		Relative energies		
*		0.00	0.00	0.00
N_2O*		6.10	7.57	10.09
^{M}TS4		32.56	14.66	28.81
N_2*+O*		-11.94	-69.36	-23.35
O*		-18.75	-63.23	-39.85
^{M}TS5		9.85		12.11
CH_3OH*		-42.97		-42.59
*		-42.17		-42.17
CH_4*+O*		14.22		-13.90
^{M}TS6		34.77		10.15
CH_3*+OH*		-6.35		-23.26
		Rh	Os	Ir
		Key geometry parameters		
N_2O*	d_{M-O}	2.27	2.29	2.28
	d_{O-N1}	1.21	1.21	1.21
	d_{N1-N2}	1.13	1.13	1.13
^{M}TS4	d_{M-O}	1.90	1.96	1.95
	d_{O-N1}	1.62	1.38	1.52
	d_{N1-N2}	1.13	1.14	1.14
N_2*+O*	d_{M-O}	1.78	1.68	1.70
	d_{O-N1}	4.11	5.20	2.74
	d_{N1-N2}	1.11	1.20	1.11
O*	d_{M-O}	1.78	1.68	1.69
^{M}TS5	d_{M-O}	1.87		1.91
	d_{O-H}	1.17		1.07
	d_{C-H}	1.40		1.43
CH_3OH*	d_{M-O}	2.15		2.17
CH_4*+O*	d_{M-O}	1.77		1.79

	d_{M-C}	2.74	2.74
^{M}TS6	d_{M-O}	1.84	1.91
	d_{O-H}	1.27	1.07
	d_{C-H}	1.40	1.43
	d_{M-C}	2.28	3.70
CH_3*+OH*	d_{M-O}	1.90	1.89
	d_{M-C}	2.05	2.04

Table S5. The relative energies (kcal/mol) and key geometry parameters of each state.

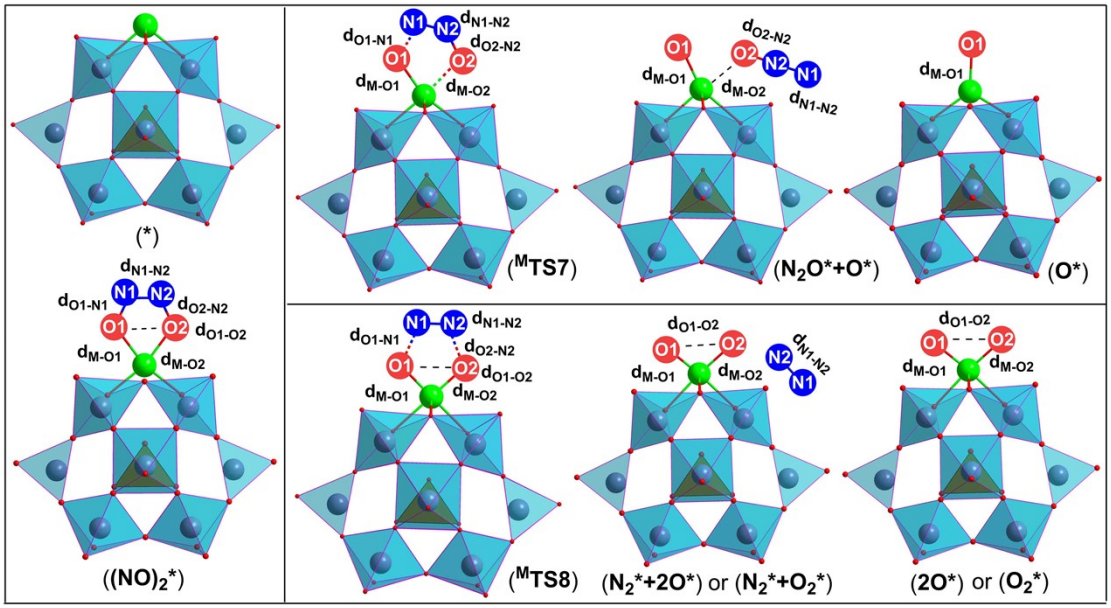


		Os
		Relative energies
O*		0.00
N_2O*+O*		-2.51
^{Os}TS9		28.76
N_2*+2O*		-29.44
2O*		-28.07
^{Os}TS10		4.84
CH_3O*+OH*		-42.19
		Methanol-forming pathway
^{Os}TS11		-25.82
CH_3O*+OH*		-45.70
		Water-forming pathway
^{Os}TS12		-13.69
CH_2O*+H_2O*		-34.23
		N_2O dissociation over 2O@Os_1/PTA
^{Os}TS13		29.59
O_2*+N_2*+O*		-17.86
O*		-26.27
		Key geometry parameters
N_2O*+O*	d_{M-O1}	1.72
	d_{M-O2}	2.46
	d_{O1-O2}	2.73

	d_{O2-N1}	1.20
	d_{N1-N2}	2.13
^{Os}TS9	d_{M-O1}	1.71
	d_{M-O2}	1.97
	d_{O1-O2}	2.61
	d_{O2-N1}	1.49
	d_{N1-N2}	1.14
N_2*+2O*	d_{M-O1}	1.73
	d_{M-O2}	1.73
	d_{O1-O2}	2.65
	d_{O2-N1}	3.27
	d_{N1-N2}	1.10
2O*	d_{M-O1}	1.73
	d_{M-O2}	1.73
	d_{O1-O2}	2.64
	d_{M-O2}	1.86
	d_{O1-O2}	2.55
	d_{O1-C}	2.65
	d_{C-H1}	1.09
	d_{O2-H1}	2.62
CH_3O*+OH*	d_{M-O1}	1.90
	d_{M-O2}	1.90
	d_{O1-O2}	2.67
	d_{O1-C}	1.41
	d_{C-H2}	1.10
	d_{O2-H1}	2.53
	Methanol-forming pathway	
^{Os}TS11	d_{M-O1}	1.81
	d_{M-O2}	2.09
	d_{O1-O2}	2.24
	d_{O1-C}	1.42
	d_{O1-H1}	2.09
	d_{O2-H1}	3.47
CH_3O*+OH*	d_{M-O1}	1.73
	d_{M-O2}	2.20
	d_{O1-O2}	2.71
	d_{O1-C}	3.05
	d_{O1-H1}	2.57
	d_{O2-H1}	2.04
	Water-forming pathway	
^{Os}TS12	d_{M-O1}	1.91
	d_{M-O2}	2.05
	d_{O1-O2}	2.48
	d_{O1-C}	1.33

	d_{C-H2}	1.10
	d_{O2-H1}	1.23
	d_{O2-H2}	2.91
$CH_2O^*+H_2O^*$	d_{M-O1}	2.04
	d_{M-O2}	2.20
	d_{O1-O2}	3.20
	d_{O1-C}	1.24
	d_{O2-H1}	0.98
	d_{O2-H2}	0.98
N_2O dissociation over $2O@Os_1$/PTA		
^{Os}TS13	d_{M-O1}	1.72
	d_{M-O2}	1.79
	d_{O1-O2}	2.65
	d_{O2-O3}	1.70
	d_{O3-N3}	1.67
	d_{N3-N4}	1.12
$O_2^*+N_2^*+O^*$	d_{M-O1}	1.69
	d_{M-O2}	2.25
	d_{O2-O3}	1.24
	d_{O3-N3}	2.87
	d_{N3-N4}	1.10

Table S6. The relative energies (kcal/mol) and key geometry parameters of each state.



	Rh	Os
	Relative energies	
*	0.00	0.00

$(NO)_2$*		-13.17	-68.85
Relative energies (single ROS pathway)			
^{M}TS7		1.74	-62.82
N_2O*+O*		-20.56	-87.63
O*		-40.63	-85.11
Relative energies (double ROS pathway)			
^{M}TS8		16.21	-51.64
N_2*+2O*			-114.56
or (N_2*+O_2*)		-41.33	
(**2O***)			-113.18
O_2*		-42.04	-76.12
		Rh	Os
Key geometry parameters			
$(NO)_2$*	d_{M-O1}	2.02	1.93
	d_{M-O2}	2.02	1.93
	d_{O1-O2}	2.42	2.36
	d_{O1-N1}	1.29	1.36
	d_{O2-N2}	1.29	1.36
	d_{N1-N2}	1.29	1.25
Key geometry parameters (single ROS pathway)			
^{M}TS7	d_{M-O1}	1.86	1.81
	d_{M-O2}	2.14	1.20
	d_{O1-N1}	1.71	1.71
	d_{O2-N2}	1.26	1.33
	d_{N1-N2}	1.19	1.20
N_2O*+O*	d_{M-O1}	1.78	1.72
	d_{M-O2}	2.34	2.46
	d_{O2-N2}	1.21	1.20
	d_{N1-N2}	1.13	1.13
O*	d_{M-O1}	1.78	1.68
Key geometry parameters (double ROS pathway)			
^{M}TS8	d_{M-O1}	1.81	1.73
	d_{M-O2}	1.81	1.96
	d_{O1-O2}	2.65	2.59
	d_{O1-N1}	1.90	2.37
	d_{O2-N2}	1.90	1.47
	d_{N1-N2}	1.14	1.15
N_2*+2O*	d_{M-O1}		1.73
	d_{M-O2}		1.73
	d_{O1-O2}		2.65
	d_{N1-N2}		1.11
or (N_2*+O_2*)	d_{M-O1}	2.10	

	d_{M-O2}	2.12	
	d_{O1-O2}	2.18	
	d_{N1-N2}	2.11	
(**2O***)	d_{M-O1}		1.73
	d_{M-O2}		1.73
	d_{O1-O2}		2.64
O_2*	d_{M-O1}	2.10	1.96
	d_{M-O2}	2.10	1.97
	d_{O1-O2}	1.28	1.40