Supporting Information

O-H and C-H Bond Activation of Water and Methane by RuO^{2+} and $(NH_3)RuO^{2+}$: Ground and Excited States

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Table S1. MRCI optimal geometries (Cartesian coordinates in Å) of the reactants, transition state, and products of the $RuO^{2+} + H_2O \rightarrow Ru(OH)_2^{2+}$ reaction for the first singlet (1^1A), the first two triplet (1^3A, 2^3A), and the first quintet (1^5A) states. Red data indicate DFT/MN15 optimized structures.

	Reactants				Transition State				Products			
1^1A	Ru	0.2631322560	0.2350629353	-0.1954543789	Ru	0.2908139024	-0.2903874669	0.0890582951	Ru	-0.0000000001	-0.0000000240	-0.0006935511
	O	-1.1258466849	0.1965294727	0.3940700775	O	-0.2358431511	1.3587715693	-0.1073080751	O	0.0000010634	1.6724379080	0.0007711461
	O	2.2469979545	0.0133377690	0.2240406858	O	-1.5849175140	-0.2536446911	0.0608316829	O	-0.0000010633	-1.6724379085	0.0007711452
	H	2.8413633629	0.7067895765	0.5516789783	H	-1.3577608088	1.0795805737	-0.0053110040	H	0.0000143784	2.6608826592	0.0058212826
	H	2.7173653231	-0.8307248577	0.3119092366	H	-2.1566210714	-0.7753710903	0.6551284292	H	-0.0000143784	-2.6608826347	0.0058212832
1^3A	Ru	0.2989627441	0.2432285452	-0.4257258192	Ru	0.4311953167	-0.0924648067	-0.0633171477	Ru	0.0003683269	-0.0000884409	-0.4958533768
	O	-0.9444565883	0.1834231868	0.5336261355	O	-0.2787677915	1.4885876104	-0.3396764220	O	-0.0224758501	1.6295839362	0.0450247521
	O	2.1899064845	0.0130648538	0.2307362100	O	-1.3403754699	-0.1753258157	0.4886988931	O	0.0212291467	-1.6309275299	0.0419874879
	H	2.7505270591	0.7135667678	0.5967794524	H	-1.3214243642	1.0604947914	0.0509681350	H	0.5228366894	2.2329237992	0.5997374798
	H	2.6480725122	-0.8322884576	0.3508286206	H	-1.7239684808	-0.5370436730	1.3086396254	H	-0.5219583129	-2.2314917647	0.6016716754
2^3A	Ru	0.2651660863	0.2181803383	-0.2254992356	Ru	0.3950124067	-0.0807519457	-0.0397564109	Ru	0.0002502948	-0.0002264688	-0.4376704726
	O	-1.1758684170	0.2164354448	0.4035946034	O	-0.2780995659	1.5228620765	-0.3245889208	O	0.0216718979	1.6539268250	0.0214664216
	O	2.2606056818	0.0076996805	0.2362511230	O	-1.3937356925	-0.2668842781	0.4168238423	O	-0.0228184437	-1.6553452559	0.0182532357
	H	2.8488643910	0.7069862473	0.5583009439	H	-1.2814962592	1.0340594005	0.0752483550	H	0.5046074227	2.2921119415	0.5942998086
	H	2.7442444692	-0.8283068152	0.3135971646	H	-1.6750213736	-0.4650372729	1.3175861142	H	-0.5037111717	-2.2904670418	0.5962190251
1^5A	Ru	0.2847756346	0.2708249065	-0.6532995659	Ru	0.401469	-0.167403	-0.000000	Ru	-0.0041449432	0.0010311607	-1.0742546763
	O	-0.6608394905	0.1515497928	0.6798842964	O	-0.305014	1.398252	-0.000004	O	0.1881774574	1.3780803689	-0.0164497276
	O	2.1504852598	0.0233042569	0.1750098590	O	-1.467028	-0.435088	0.000017	O	-0.1833580155	-1.3792215430	-0.0176385782
	H	2.6266448563	0.7059659727	0.6713809256	H	-1.428180	0.891179	-0.000009	H	0.2060102898	1.5309590902	0.9510308040
	H	2.5419459513	-0.8306500329	0.4132690843	H	-2.060130	-1.230743	-0.000087	H	-0.2066847883	-1.5308490770	0.9498801965

Table S2. MRCI optimal geometries (Cartesian coordinates in Å) of the reactants, transition state, and products of the $RuO^{2+} + CH_4 \rightarrow CH_3RuOH^{2+}$ reaction for the first singlet (1^1A), the first two triplet (1^3A, 2^3A), and the first quintet (1^5A) states. Red data indicate DFT/MN15 optimized structures.

	Reactants				Transition State				Products			
1^1A	Ru	-0.1833143594	0.0749440162	0.0004251052	Ru	0.285346	-0.292888	-0.000001	Ru	-0.0975062205	-0.3790906129	0.0044716496
	O	-1.7225158502	0.0006877977	-0.0004658063	O	0.694253	1.276643	0.000005	O	-1.3301246754	0.8729154101	-0.1253356990
	C	2.0634372921	0.1863724123	0.0000287976	C	-1.838480	0.123255	0.000013	C	1.6449557109	0.6993603455	0.0170360422
	H	3.1498878864	0.2416433485	-0.0004323611	H	-2.169201	-0.312415	-0.943739	H	1.7614338896	1.2604557724	0.9360237565
	H	1.7533075051	0.7073963679	-0.9320706174	H	-2.169161	-0.312058	0.943940	H	2.0995399767	-0.3198297321	0.0395593214
	H	1.7539466131	0.7107181064	0.9303415826	H	-2.096318	1.212357	-0.000237	H	1.7790848188	1.2309573364	-0.9171447075
	H	1.8349629129	-0.9016780490	0.0019362993	H	-0.643678	1.346515	-0.000046	H	-1.8030595001	1.3108814807	0.6184126368
1^3A	Ru	-0.2478085913	0.4222768111	-0.4833218392	Ru	0.380687	-0.238699	0.000000	Ru	-0.0912932982	-0.0464384533	0.1548517757
	O	-1.3066755138	0.0833323748	0.6320397248	O	0.144209	1.433486	-0.000001	O	-1.3717799172	1.1062428468	0.2202274711
	C	1.9783482401	0.0619853266	-0.0792299786	C	-1.749549	-0.219370	-0.000005	C	1.7899826480	0.6410045054	-0.0091094820
	H	2.9034736289	0.4163450215	0.3896081075	H	-1.993362	-0.748767	-0.930552	H	2.0269198652	1.1872175641	0.9002495175
	H	1.9279818027	0.7422528284	-0.9526308220	H	-1.993331	-0.748887	0.930484	H	2.1689657695	-0.4019722696	-0.0404562537
	H	1.3283631021	0.2830216470	0.8170268789	H	-2.330154	0.748914	0.000094	H	1.8750314237	1.1827589126	-0.9475114600
	H	2.0660293314	-0.9891300095	-0.3237290713	H	-1.089745	1.099851	0.000001	H	-2.3435064911	1.0068468937	0.2947684311
2^3A	Ru	-0.2468855407	0.2525101181	0.0042116064					Ru	-0.0951411468	-0.0115910866	0.1410895104
	O	-1.8167753498	0.0921488540	-0.0054686887					O	-1.3661703011	1.1715316170	0.2341321549
	C	2.0954385882	0.1002014758	0.0007335133					C	1.7965065010	0.6011051885	-0.0099749722
	H	3.1139309848	0.4840141113	-0.0043972023					H	1.9652681108	1.1746460361	0.9054267046
	H	1.6831379578	0.5378829815	-0.9429372527					H	2.2646534694	-0.3948755119	-0.0418580768
	H	1.6886954733	0.5399021312	0.9450755102					H	1.8126777808	1.1560192342	-0.9499983433
	H	2.1321698866	-0.9865756720	0.0025455139					H	-2.3234744142	0.9788245225	0.2942030218

1^5A	Ru	-0.3033622771	0.0687688533	0.0072493484	Ru	-0.384719	0.239997	-0.000036	Ru	-0.0811886723	-0.5193964802	-0.0522850657
	O	-1.9430339506	-0.0099670717	-0.0060277800	O	-0.126406	-1.464589	0.000223	O	-1.3118146201	0.7454925134	-0.0014201109
	C	2.0996916571	0.1882265818	-0.0001515579	C	1.744702	0.237084	0.000316	C	1.5623048528	0.6417480767	0.0276923275
	H	3.1897390198	0.2436422239	-0.0028587793	H	1.993862	0.756379	-0.932394	H	1.5610535488	1.1818365242	0.9704612798
	H	1.8398265147	0.7112134652	-0.9310039210	H	1.993903	0.751519	0.935708	H	2.2757406100	-0.1927855906	0.0087856126
	H	1.8437201610	0.7144453457	0.9300332941	H	2.336543	-0.734135	-0.003465	H	1.5763528253	1.2580014297	-0.8679438655
	H	1.9231308752	-0.8962453983	0.0025223956	H	1.146352	-1.039433	-0.001955	H	-1.5281245444	1.5607535268	0.4877328221

Table S3. MRCI optimal geometries (Cartesian coordinates in Å) of the reactants, transition state, and products of the $(NH_3)RuO^{2+}$ + $H_2O \rightarrow (NH_3)Ru(OH)_2^{2+}$ reaction for the first singlet (1^1A), the first two triplet (1^3A, 2^3A), and the first quintet (1^5A) states. Red data indicate DFT/MN15 optimized structures.

	Reactants				**Transition State**				**Products**			
1^1A	Ru	0.0777015596	-0.0529350430	-0.1472120102	Ru	0.5516311217	0.1855018219	0.7532652324	Ru	0.2024345656	0.0416959235	-0.3670535237
	O	-1.1017312636	0.1618317372	0.8815475757	O	-0.0843537515	1.2972085796	-0.5030857627	O	-0.2751258972	1.5785780334	0.4250924225
	O	2.1311447063	0.0057939985	0.0601512421	O	-1.3194154130	-0.1003929303	0.6543779774	O	-0.0246852176	-1.4551822456	0.5346150859
	H	2.6543776461	0.8093119468	0.1799975327	H	-1.1469865543	0.8791408810	-0.2279304203	H	0.3009033548	2.0811958067	1.0405304456
	H	2.6629586881	-0.7372045038	0.3791671288	H	-1.8921921613	-0.7421433823	0.9699689047	H	-0.8452791327	-1.9789490577	0.5897622035
	N	0.0490510547	0.8629118238	-2.0424835422	N	1.7044245230	-0.8532262960	-0.6045561927	N	1.0414472421	0.1099877015	-2.2859275674
	H	0.9622565881	0.9729034886	-2.4906463052	H	2.6241117947	-0.4178306265	-0.7471625039	H	1.9825629717	0.5137196603	-2.3098626714
	H	-0.5327651660	0.3562430779	-2.7154324678	H	1.8882579829	-1.8211941560	-0.3118474651	H	1.1387547197	-0.8349249704	-2.6774113818
	H	-0.3433037705	1.8062132062	-1.9814658270	H	1.2714977452	-0.9193316300	-1.5297757415	H	0.4797011540	0.6314028695	-2.9657386274
1^3A	Ru	0.4291542878	0.3075025877	-0.2980298390	Ru	0.7812217243	0.4401845632	0.8689982494	Ru	0.2013593704	0.0503623784	-0.2514561386
	O	-0.8396970435	0.0855987613	0.6281915708	O	0.0266830318	1.3780478722	-0.5759940591	O	-0.1515194457	1.6933962686	0.2359986790
	O	2.3229190790	-0.0341188581	0.4167363716	O	-1.0053574638	-0.1969451350	0.6521910521	O	0.0820184903	-1.5626449199	0.4152513644
	H	2.8524485819	0.5922298624	0.9294848089	H	-0.9411458542	0.6777297572	-0.2639755744	H	0.3199192148	2.2640971585	0.8758466819
	H	2.7561249369	-0.8976597653	0.4652145654	H	-1.6042291917	-0.1817371847	1.3840384072	H	-0.7101826574	-2.1094284502	0.5904465394

	N	-0.1550160904	0.9458339017	-2.2317422597	N	1.5888994019	-0.8038934718	-0.5668542942	N	0.9703162253	0.0184207415	-2.1892564621
	H	0.6203645960	1.0174920132	-2.8978322417	H	2.5114963675	-0.4549244838	-0.7857530076	H	1.9142777701	0.4095476316	-2.2538321446
	H	-0.8245013971	0.3023871801	-2.6615558409	H	1.7033917255	-1.7787124471	-0.2688591447	H	1.0324170865	-0.9415774687	-2.5487613209
	H	-0.6021069083	1.8658040485	-2.2268438085	H	1.0724655217	-0.8159140116	-1.4496740974	H	0.3831587827	0.5331046084	-2.8528316273
2^3A	Ru	0.4068924005	0.3036775742	-0.2801435437	Ru	0.6759485783	0.2545600207	0.8220420263	Ru	0.2442819647	0.0597018665	-0.3645882483
	O	-0.8413066415	0.0728987189	0.6703465443	O	-0.0234459167	1.2179381690	-0.6692149602	O	-0.2698242907	1.5565560004	0.3996923853
	O	2.3447044057	-0.0436307760	0.4397477690	O	-1.2049231854	-0.0247875680	0.7628272844	O	0.0730135757	-1.4052257524	0.5938212989
	H	2.8769287858	0.5809571613	0.9490675797	H	-1.0727710689	0.7975351262	-0.1755063868	H	0.2443625621	2.0572402315	1.0634160695
	H	2.7836936003	-0.9025849908	0.4879942049	H	-1.7740882416	-0.0506533606	1.5722564275	H	-0.7658018754	-1.8865239906	0.7355179975
	N	-0.1682978376	0.9567379483	-2.2653798622	N	1.7374775488	-0.8345412346	-0.6185317889	N	1.0201189960	0.0040178229	-2.3263239016
	H	0.6030799002	1.0284133675	-2.9265341457	H	2.6818293691	-0.4645744837	-0.7925068261	H	1.9635855455	0.4031264321	-2.3914416388
	H	-0.8347903791	0.3112606877	-2.6937997722	H	1.8541413889	-1.8232667318	-0.3802281098	H	1.0913752412	-0.9540633993	-2.6903154391
	H	-0.6112141920	1.8773400404	-2.2576754472	H	1.2592567904	-0.8083744784	-1.5270201350	H	0.4406531178	0.5204487371	-2.9983729524
1^5A	Ru	-0.033548	-0.265691	-0.000040	Ru	0.024732	-0.225495	-0.000359	Ru	0.087421	-0.174500	-0.000021
	O	-1.643586	-0.852959	0.000086	O	-0.493554	1.428065	-0.000181	O	-0.106570	1.602065	0.000012
	O	2.081126	0.052809	0.000057	O	-1.893454	-0.272810	0.000828	O	1.857767	-0.414245	0.000053
	H	2.660158	0.065947	0.784729	H	-1.635101	1.028132	0.000809	H	0.636236	2.252548	0.000014
	H	2.660224	0.066829	-0.784548	H	-2.653001	-0.894702	0.001565	H	2.842064	-0.378788	0.000038
	N	-0.691783	1.690190	0.000046	N	2.110753	0.034891	0.000744	N	-2.013868	-0.364828	0.000048
	H	0.071524	2.377711	0.000274	H	2.658694	-0.836086	-0.043145	H	-2.435833	0.092308	-0.819505
	H	-1.286624	1.874974	-0.821085	H	2.425390	0.606695	-0.796081	H	-2.365376	-1.331434	0.001346
	H	-1.287002	1.874799	0.820935	H	2.436617	0.531446	0.842244	H	-2.436125	0.094611	0.818157

Table S4. MRCI optimal geometries (Cartesian coordinates in Å) of the reactants, transition state, and products of the $(NH_3)RuO^{2+}$ + $CH_4 \rightarrow CH_3Ru(NH_3)OH^{2+}$ reaction for the first singlet (1^1A), the first two triplet (1^3A, 2^3A), and the first quintet (1^5A) states. Red data indicate DFT/MN15 optimized structures.

	Reactants			Transition State			Products		
1^1A	Ru	-0.040324	-0.200994	0.000043	Ru	0.050451	0.184467	-0.333863	Ru	-0.149179	-0.026381	0.248097
	O	-0.552532	-1.663906	-0.000116	O	-0.577353	1.155161	0.872497	O	-1.619396	-0.481825	-0.521789
	C	2.008317	0.646889	-0.000013	C	-1.519643	-1.119488	0.169185	C	0.474163	1.763699	-0.340487
	H	2.821283	1.386375	-0.000524	H	-1.134740	-2.084047	0.489821	H	-0.424869	2.358483	-0.112727
	H	1.487758	0.910933	-0.962530	H	-2.238701	-0.863843	1.016010	H	1.257203	1.952379	0.416314
	H	1.488188	0.911315	0.962550	H	-2.150467	-1.121272	-0.720164	H	0.828910	1.831655	-1.364726
	H	2.470160	-0.349874	0.000053	H	-1.472633	0.048216	0.904730	H	-2.030864	-1.375598	-0.636893
	N	-1.330144	1.456260	-0.000070	N	1.753382	-0.617558	0.456708	N	1.605049	-0.976315	-0.271482
	H	-1.256415	2.062945	0.826300	H	2.543274	0.036250	0.361090	H	1.665329	-1.902471	0.173659
	H	-1.258682	2.061001	-0.828048	H	2.032171	-1.493723	-0.009534	H	2.460609	-0.479272	0.011081
	H	-2.296663	1.097118	0.001788	H	1.664271	-0.839592	1.455992	H	1.682406	-1.117809	-1.285352
1^3A	Ru	-0.006891	-0.053439	-0.027547	Ru	-0.044520	-0.278374	-0.328047	Ru	-0.058321	0.044480	0.012115
	O	-0.162735	-1.654383	0.052419	O	0.639746	-0.977343	1.055398	O	-1.159304	1.390544	0.021887
	C	2.131642	0.690398	0.067797	C	1.376316	1.272644	0.036432	C	-0.907555	-1.711322	-0.025818
	H	3.047735	0.888166	-0.509106	H	0.852336	2.195334	0.262872	H	-1.364923	-1.993582	-0.974467
	H	1.987230	-0.376003	-0.283458	H	2.144368	1.156787	0.854461	H	0.198637	-1.997100	0.015537
	H	1.474268	1.484777	-0.365159	H	1.960005	1.264336	-0.884698	H	-1.430545	-1.998740	0.887118
	H	2.320562	0.787457	1.133565	H	1.323146	0.181081	0.912170	H	-1.477176	2.268537	-0.288759
	N	-1.891599	0.824879	0.036036	N	-1.676392	0.710604	0.417030	N	2.018779	0.079074	-0.018034
	H	-2.601366	0.089166	0.171132	H	-1.825777	1.641419	0.006352	H	2.461697	-0.383202	0.786936
	H	-2.019134	1.482243	0.816936	H	-1.594624	0.846170	1.432747	H	2.331706	1.059787	0.014713
	H	-2.152862	1.314022	-0.830228	H	-2.541694	0.171995	0.269180	H	2.435031	-0.322763	-0.868084

1^5A	Ru 0.000666 -0.130956 -0.001465 O -0.164435 1.562484 0.000890 C 2.297195 -0.302710 0.002764 H 3.291787 0.161096 0.004629 H 1.890619 0.121081 0.957184 H 2.400969 -1.387386 0.000885 H 1.893530 0.124769 -0.951381 N -2.079716 -0.386371 0.002653 H -2.514137 0.068998 -0.812100 H -2.392091 -1.365650 -0.001724 H -2.509640 0.060131 0.824690	Ru 0.065536 -0.083867 0.000027 O -0.699214 1.481772 -0.000021 C -2.006242 -0.716800 -0.000031 H -2.025687 -1.302694 0.923443 H -2.899230 -0.053036 -0.000435 H -2.025185 -1.303044 -0.923300 H -1.697583 0.674807 -0.000034 N 2.219759 -0.187289 -0.000041 H 2.608848 -1.138879 0.001521 H 2.624149 0.286686 0.818485 H 2.623972 0.283936 -0.820241	Ru -0.058358 -0.217575 -0.000038 O -1.836730 -0.479462 -0.000070 C -0.185809 1.813225 -0.000038 H -0.755147 2.025586 0.911512 H 0.833216 2.196881 -0.003445 H -0.761731 2.026718 -0.907032 H -2.780024 -0.752178 0.000789 N 2.062488 -0.289242 0.000062 H 2.416908 -1.255188 0.000542 H 2.492851 0.156726 0.819531 H 2.492944 0.155815 -0.819862

Table S5. Harmonic vibrational frequencies (cm^{-1}) of the reactants, transition state, and products of the $RuO^{2+} + H_2O \rightarrow Ru(OH)_2^{2+}$ reaction for the first singlet (1^1A), the first two triplet (1^3A, 2^3A), and the first quintet (1^5A) states.

1^1A			1^3A			2^3A			1^5A		
Reactants	TS	Products	Reactants	TS	Products	Reactants	TS	Products	Reactants	TS	Products
72	1860 i	109	148	1972 i	136	140	2013 i	146		2198 i	72
140	497	502	310	481	440	223	415	502		409	140
509	643	506	518	583	518	491	537	571		488	509
543	700	694	520	685	693	530	554	722		701	543
728	837	694	775	817	772	729	766	733		884	728
1364	919	1024	1232	874	924	1269	949	926		890	1364
1730	1194	1039	1740	1202	942	1735	1158	960		926	1730
3723	1940	3482	3737	1911	3547	3742	1879	3549		1735	3723
3777	3686	3539	3798	3693	3589	3798	3833	3591		3513	3777

Table S6. Relative energies (kcal/mol) for the infinitely separated reactants (ISR) of the reactants (R), transition state (TS), and products (P) of the $RuO^{2+} + H_2O \rightarrow Ru(OH)_2^{2+}$ reaction at the MRCI+Q level of theory.

	1^1A	1^3A	2^3A	3^3A	4^3A	1^5A
ISR	0.0	5.4	5.4	5.6	5.6	14.4
R	-82.0	-77.3	-72.2	-64.2	-61.9	-62.3
TS	15.0	-1.5	5.4	12.9	14.7	-10.9
P	-46.7	-41.6	-39.9	-23.1	-23.0	-43.2

Table S7. Relative energies (kcal/mol) for the infinitely separated reactants (ISR) of the reactants (R), transition state (TS), and products (P) of the $RuO^{2+} + CH_4 \rightarrow CH_3RuOH^{2+}$ reaction at the MRCI+Q level of theory.

	1^1A	1^3A	2^3A	3^3A	4^3A	1^5A
ISR	0.0	5.3	5.3	5.6	5.6	17.3
R	-54.0	-45.1	-39.5	-35.5	-35.3	-38.0
TS	8.5	-10.5	-1.8	1.1	2.9	-17.1
P	-47.1	-55.5	-54.2	-41.1	-39.1	-63.3

Table S8. Relative energies (kcal/mol) for the infinitely separated reactants (ISR) of the reactants (R), transition state (TS), and products (P) of the $(NH_3)RuO^{2+} + H_2O \rightarrow (NH_3)Ru(OH)_2^{2+}$ reaction at the MRCI+Q level of theory.

	1^1A	1^3A	2^3A	3^3A	4^3A	1^5A
ISR	0.0	2.4	6.8	12.7	14.7	11.4
R	-68.7	-69.2	-54.2	-51.4	-44.2	-46.5
TS	11.9	12.8	28.1	33.3	34.4	-0.5
P	-22.4	-36.7	-22.2	-13.6	24.2	-16.8

Table S9. Relative energies (kcal/mol) for the infinitely separated reactants (ISR) of the reactants (R), transition state (TS), and products (P) of the $(NH_3)RuO^{2+} + CH_4 \rightarrow CH_3Ru(NH_3)OH^{2+}$ reaction at the MRCI+Q level of theory.

	1^1A	1^3A	2^3A	3^3A	4^3A	1^5A
ISR	0.0	2.3	6.7	12.7	14.6	11.3
R	-38.0	-37.7	-22.8	-20.0	-10.2	-26.6
TS	13.2	0.1	25.1	34.3	37.3	9.9
P	-32.9	-35.6	-21.3	-13.1	5.4	-38.5

Table S10. Exact energies (a.u.) for the infinitely separated reactants (ISR) of the reactants (R), transition state (TS), and products (P) of the $RuO^{2+} + H_2O \rightarrow Ru(OH)_2^{2+}$ reaction at the MRCI and MRCI+Q level of theory.

	1^1A	1^3A	2^3A	3^3A	4^3A	1^5A
			MRCI			
ISR	-244.502443	-244.493964	-244.493964	-244.493292	-244.493292	-244.477352
R	-244.630369	-244.621782	-244.614656	-244.601977	-244.598529	-244.596052
TS	-244.461259	-244.488373	-244.478872	-244.465929	-244.462206	-244.501065
P	-244.553702	-244.546184	-244.543935	-244.517322	-244.517263	-244.550714
			MRCI+Q			
ISR	-244.564284	-244.555690	-244.555690	-244.555322	-244.555322	-244.541330
R	-244.694912	-244.687418	-244.679383	-244.666579	-244.662869	-244.663619
TS	-244.540349	-244.566618	-244.555645	-244.543723	-244.540922	-244.581692
P	-244.638714	-244.630594	-244.627879	-244.601053	-244.600983	-244.633119

Table S11. Exact energies (a.u.) for the infinitely separated reactants (ISR) of the reactants (R), transition state (TS), and products (P) of the $RuO^{2+} + CH_4 \rightarrow CH_3RuOH^{2+}$ reaction at the MRCI and MRCI+Q level of theory.

	1^1A	1^3A	2^3A	3^3A	4^3A	1^5A
			MRCI			
ISR	-208.604547	-208.596120	-208.596120	-208.595460	-208.595460	-208.574370
R	-208.684690	-208.669183	-208.662141	-208.655782	-208.655501	-208.654128
TS	-208.574683	-208.602751	-208.587625	-208.584526	-208.578674	-208.610596
P	-208.668188	-208.679952	-208.677997	-208.657380	-208.654561	-208.690273
			MRCI+Q			
ISR	-208.663369	-208.654852	-208.654852	-208.654495	-208.654495	-208.635858
R	-208.749482	-208.735183	-208.726377	-208.719888	-208.719594	-208.723960
TS	-208.649883	-208.680089	-208.666244	-208.661698	-208.658686	-208.690691
P	-208.738349	-208.751783	-208.749703	-208.728871	-208.725639	-208.764162

Table S12. Exact energies (a.u.) for the infinitely separated reactants (ISR) of the reactants (R), transition state (TS), and products (P) of the $(NH_3)RuO^{2+} + H_2O \rightarrow (NH_3)Ru(OH)_2^{2+}$ reaction at the MRCI and MRCI+Q level of theory.

	1^1A	1^3A	2^3A	3^3A	4^3A	1^5A
			MRCI			
ISR	-301.070002	-301.066127	-301.059329	-301.049913	-301.047193	-301.048856
R	-301.176904	-301.177752	-301.154587	-301.150227	-301.139561	-301.139179
TS	-301.037931	-301.033231	-301.011621	-301.002849	-301.000724	-301.057191
P	-301.088622	-301.108703	-301.086789	-301.071191	-301.015724	-301.082875
			MRCI+Q			
ISR	-301.187481	-301.183689	-301.176703	-301.167229	-301.164098	-301.169309
R	-301.296893	-301.297743	-301.273835	-301.269427	-301.257926	-301.261646
TS	-301.168541	-301.167049	-301.142696	-301.134464	-301.132612	-301.188273
P	-301.223098	-301.245920	-301.222875	-301.209066	-301.148912	-301.214181

Table S13. Exact energies (a.u.) for the infinitely separated reactants (ISR) of the reactants (R), transition state (TS), and products (P) of the $(NH_3)RuO^{2+} + CH_4 \rightarrow CH_3Ru(NH_3)OH^{2+}$ reaction at the MRCI and MRCI+Q level of theory.

	1^1A	1^3A	2^3A	3^3A	4^3A	1^5A
			MRCI			
ISR	-265.174349	-265.170514	-265.163713	-265.154292	-265.151561	-265.153389
R	-265.227561	-265.227278	-265.204282	-265.199566	-265.184784	-265.208548
TS	-265.135088	-265.154127	-265.115606	-265.100147	-265.096119	-265.141236
P	-265.212967	-265.210997	-265.188307	-265.175521	-265.145640	-265.216733
			MRCI+Q			
ISR	-265.287512	-265.283791	-265.276813	-265.267315	-265.264189	-265.269591
R	-265.348068	-265.347533	-265.323789	-265.319449	-265.303692	-265.329893
TS	-265.266514	-265.287437	-265.247554	-265.232781	-265.228058	-265.271815
P	-265.339898	-265.344204	-265.321455	-265.308362	-265.278920	-265.348874

Table S14. Exact energies (a.u.) for the infinitely separated reactants (ISR) of the reactants (R), transition state (TS), and products (P) of the $XRuO^{2+} + YH \rightarrow YRu(X)OH^{2+}$ reaction at the CCSD(T) level of theory.

	1^1A	1^3A	1^5A	1^1A	1^3A	1^5A
	X = −; Y = OH			**X = −; Y = CH_3**		
ISR	-244.5749255			-208.6701422		
R	-244.7106730	-244.7001351	-244.6842588	-208.7637864	-208.7444145	-208.7163370
TS	-244.5724776	-244.5818615	-244.6136832	-208.6728155	-208.6867639	-208.7207656
P	-244.6722024	-244.6613484	-244.6693221	-208.7581151	-208.7523077	-208.7887866
	X = NH_3; Y = OH			**X = NH_3; Y = CH_3**		
ISR	-301.2238853			-265.3144507		
R	-301.3362557	-301.3367084	-301.3080580	-265.3886576	-265.3614680	-265.3739840
TS	-301.2188972	-301.2227299	-301.2465957	-265.3159530	-265.3414687	-265.3272720
P	-301.2796162	-301.3022620	-301.2913600	-265.3874629	-265.3724662	-265.4068038

Table S15. Exact energies (a.u.) for the infinitely separated reactants (ISR) of the reactants (R), transition state (TS), and products (P) of the $XRuO^{2+} + CH_4 \rightarrow CH_3Ru(X)OH^{2+}$ reaction at the CCSD(T)-augC level of theory.

	1^1A	1^3A	1^5A
		X = −	
ISR	-208.6720467		
R	-208.7663032	-208.7467935	-208.7190143
TS	-208.6754932	-208.6894369	-208.7233003
P	-208.7608192	-208.7548517	-208.7915169
		X = NH_3	
ISR	-265.3163526		
R	-265.3911946	-265.3638160	-265.3764693
TS	-265.3187278	-265.3442258	-265.3299934
P	-265.3905507	-265.3749225	-265.4097347

Table S16. MN15 optimal geometries (Cartesian coordinates in Å) of the reactants, transition state, and products of the $RuO^{2+} + H_2O \rightarrow Ru(OH)_2^{2+}$ reaction for the first singlet (1^1A) state.

	Reactants				Transition State				Products			
1^1A	Ru	0.158460	-0.152944	-0.000573	Ru	0.409937	-0.146218	0.000531	Ru	0.000000	-0.000000	0.000765
	O	1.543211	0.512506	0.002046	O	-0.376386	1.330051	0.026746	O	0.000000	1.687263	-0.001315
	O	-1.823637	0.221037	0.000659	O	-1.446946	-0.497882	-0.084729	O	-0.000000	-1.687263	-0.001315
	H	-2.366403	0.421207	0.798922	H	-1.470583	0.855858	-0.073937	H	-0.000035	2.689552	-0.006313
	H	-2.362441	0.439968	-0.795336	H	-1.979994	-1.079601	0.514426	H	0.000035	-2.689552	-0.006313

Table S17. CCSD(T)//MN15 and CCSD(T)//MRCI energetics for the lowest singlet state along the $RuO^{2+} + H_2O \rightarrow Ru(OH)_2^{2+}$ reaction coordinate. ISR = infinitely separated reactants; R = reactants (interacting complex); TS = transition state; P = products.

	Exact energy		Relative energy		Difference
	CCSD(T)//MRCI	CCSD(T)//MN15	CCSD(T)//MRCI	CCSD(T)//MN15	
ISR	-244.5749248	-244.5752983	0.00	0.00	0.00
R	-244.7106696	-244.7132450	-85.18	-86.56	-1.38
TS	-244.5719219	-244.5701173	1.88	3.25	1.37
P	-244.6722055	-244.6741879	-61.04	-62.05	-1.01