Supporting information for: On the Acid-Base Mechanism for Ruthenium Water Oxidation Catalysts

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Full citations for Gaussian 03 and Q-Chem in the original paper are provided in the Bibliography. (Refs. 4 and 5)

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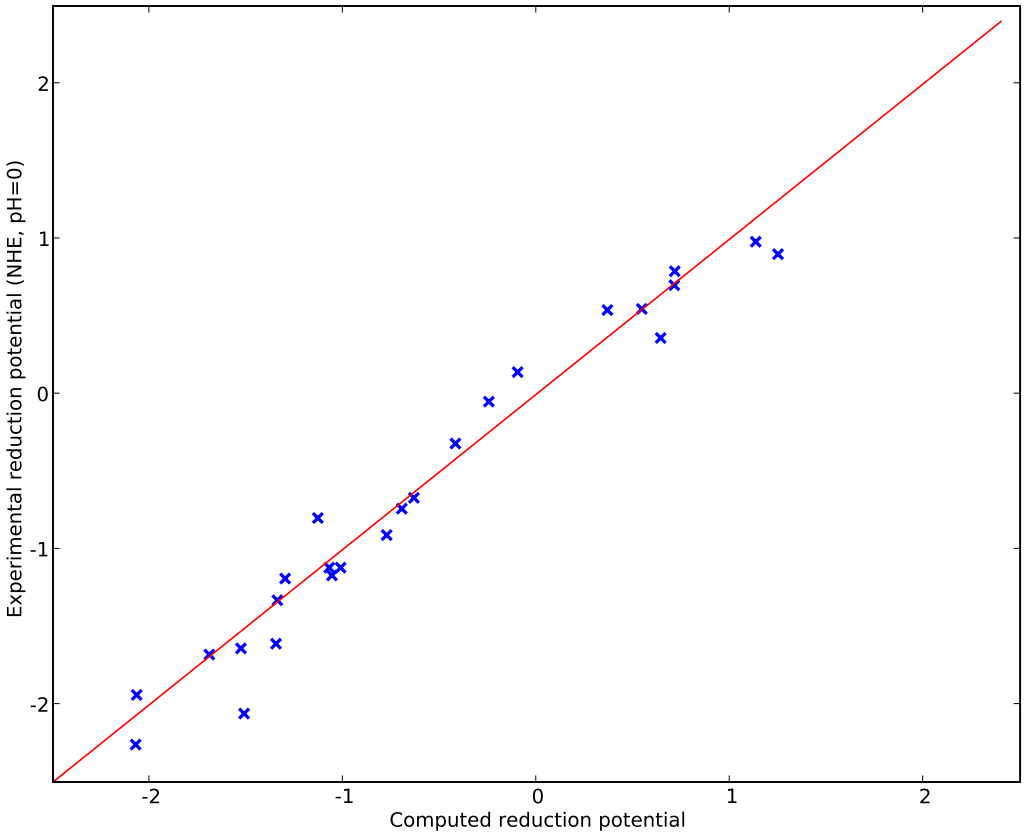

Figure S1: Correlation diagram of calculated and experimental redox potentials for various organic molecules and metallocenes as reported in Baik and Friesner.[1] No linear fit was performed. R^2 = 0.98, MAE = 0.150V

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Table S1: Redox potentials of relevant half-reactions vs. NHE. All potentials are standardized to pH 0 by applying a -0.059V/pH correction. For compounds 1 through 19, see Baik and Friesner.[1]

No.	Complex	Couple	E°_{calc}	E°_{expt}
1	Anthracene	-1/0	-1.692	-1.679
2	Azobenzene	-1/0	-1.072	-1.119
3	Benzophenone	-1/0	-1.528	-1.639
4	Nitrobenzene	-1/0	-0.775	-0.909
5	TCNQ	-2/-1	-0.247	-0.049
6	TCNQ	-1/0	0.641	0.361
7	TTF	0/+1	0.366	0.541
8	TTF	+1/+2	1.248	0.901
9	$FeCp(H_3COC)_2$	0/+1	1.133	0.981
10	$FeCp_2$	0/+1	0.544	0.548
11	$FeCp^*_2$	0/+1	-0.098	0.141
12	$CoCp_2$	0/+1	-0.634	-0.669
13	$Cr(Me_3Ph)_2$	0/+1	-0.697	-0.739
14	FeCpPh	0/+1	-1.013	-1.119
15	$CoCp^*_2$	0/+1	-1.300	-1.189
16	FeCpPh*	0/+1	-1.340	-1.329
17	FeCp*Ph*	0/+1	-1.347	-1.609
18	$RhCp_2$	-1/0	-2.067	-1.939
19	$RhCp_2$	0/+1	-1.058	-1.169
20	$CrCp^*_2$	-1/0	-1.512	-2.059
21	$CrCp^*_2$	0/+1	-1.131	-0.799
22	$MnCp^*_2$	-1/0	-2.073	-2.259
23	$MnCp^*_2$	0/+1	-0.420	-0.319
24	$RuCp^*_2$	0/+1	0.714	0.791
25	$OsCp^*_2$	0/+1	0.712	0.701

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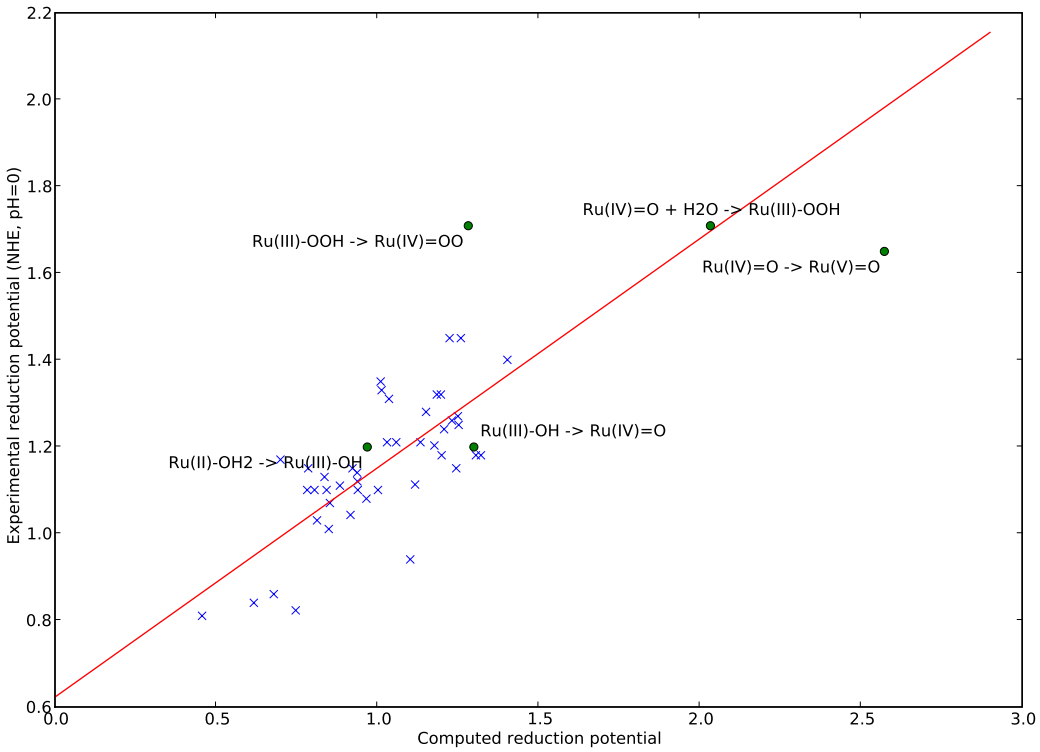

Figure S2: Correlation diagram and linear fit of calculated and experimental redox potentials for various Ru-OH2 coordination complexes. $R^2 = 0.55$, MAE = 0.110V

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Table S2: Redox potentials of relevant half-reactions vs. NHE. All potentials are standardized to pH 0 by applying a -0.059V/pH correction. For compounds 1 through 19, see Dovletoglou and Meyer.[2] For compounds 20 through 22, see Masllorens and coworkers.[3]

No.	Complex	$E^{\circ,II/III}_{calc}$	$E^{\circ,II/III}_{expt}$	$E^{\circ,III/IV}_{calc}$	$E^{\circ,III/IV}_{expt}$
1	$[Ru(tpy)(acac)(H_2O)]^{2+}$	0.617	0.840	1.030	1.210
2	$[Ru(tpy)(C_2O_4)(H_2O)]^{2+}$	0.456	0.810	0.939	1.100
3	$[Ru(tpy)(H_2O)_3]^{2+}$	0.747	0.823	1.117	1.113
4	*trans*-$[Ru(tpy)(pic)(H_2O)]^{2+}$	0.679	0.860	1.002	1.100
5	*cis*-$[Ru(tpy)(pic)(H_2O)]^{2+}$	0.813	1.030	1.134	1.210
6	*cis*-$[Ru(6,6'Me_2(bpy)_2(H_2O)_2]^{2+}$	0.917	1.043	1.177	1.203
7	$[Ru(tpy)(tmen)(H_2O)]^{2+}$	0.849	1.010	1.207	1.240
8	$[Ru(tpy)(phen)(H_2O)]^{2+}$	0.923	1.150	1.252	1.250
9	*cis*-$[Ru(bpy)_2(py)(H_2O)]^{2+}$	0.853	1.070	1.321	1.180
10	$[Ru(tpy)(bpy)(H_2O)]^{2+}$	0.937	1.140	1.250	1.270
11	$[Ru(tpy)(4,4'-CO_2Et)_2(bpy)(H_2O)]^{2+}$	1.036	1.310	1.259	1.450
12	$[Ru(tpy)(4,4'$-Me2-bpy$)(H_2O)]^{2+}$	0.938	1.120	1.231	1.260
13	*cis*-$[Ru(bpy)_2(AsPh_3)(H_2O)]^{2+}$	0.785	1.150	1.184	1.320
14	*cis*-$[Ru(bpy)(biq)(PEt_3)(H_2O)]^{2+}$	0.842	1.100	1.151	1.280
15	$[Ru(tpm)(4,4'-(NO_2)_2(bpy)(H_2O)]^{2+}$	1.059	1.210	1.403	1.400
16	*cis*-$[Ru(bpy)_2(PEt_3)(H_2O)]^{2+}$	0.884	1.110	1.197	1.320
17	*cis*-$[Ru(bpy)(biq)(PPh_3)(H_2O)]^{2+}$	0.836	1.130	1.010	1.350
18	*cis*-$[Ru(bpy)_2(P(i\text{-}Pr)_3)(H_2O)]^{2+}$	0.782	1.100	1.013	1.330
19	*cis*-$[Ru(bpy)_2(SbPh_3)(H_2O)]^{2+}$	0.699	1.170	1.224	1.450
20	$[Ru(CNC)(bpy)(H_2O)]^{2+}$	0.805	1.100	1.245	1.150
21	*cis*-$[Ru(CNC)(nBu\text{-}CN)(H_2O)]^{2+}$	0.966	1.080	1.102	0.940
22	*trans*-$[Ru(CNC)(nBu\text{-}CN)(H_2O)]^{2+}$	1.199	1.180	1.306	1.180