Electronic Supplementary Information for Dalton Transactions

Electronic supplementary information (ESI)

The Hydrolysis Process of the Anticancer Complex [ImH][*trans*-$RuCl_4(Im)_2$]: A Theoretical Study

Jincan Chen,[a] Lanmei Chen,[a] Siyan Liao,[a] Kangcheng Zheng,[*a] and Liangnian Ji[*a,b]

[a] School of Chemistry and Chemical Engineering / The Key Laboratory of Bioinorganic and Synthetic Chemistry of Ministry of Education / The Key Laboratory of Gene Engineering of Ministry of Education, Sun Yat-Sen University, Guangzhou 510275, China. E-mail: ceszkc@mail.sysu.edu.cn;
Fax: +86-20-8411-2245; Tel: +86-20-8411-0696
[b] Department of Chemistry, Tongji University, Shanghai, 200092, China.
E-mail: cesjln@mail.sysu.edu.cn

Table S1. Optimized geometric of ICR in each spin state at the level of UB3LYP/(LanL2DZ + 6-31G(d))[a] (cf. Fig. 1)

	ICR(*S*=1/2)	ICR(*S*=3/2)	ICR(*S*=5/2)	ICR(exp.)[b]
Cl2–Ru	2.44	2.81	2.53	2.36
Cl3–Ru	2.44	2.40	2.59	2.38
Cl4–Ru	2.44	2.81	2.53	2.35
Cl5–Ru	2.44	2.40	2.59	2.34
N6–Ru	2.10	2.10	2.40	2.08
N7–Ru	2.10	2.10	2.40	2.08
Cl2–Ru–Cl3	91.2	90.0	90.4	89.6
Cl2–Ru–Cl4	180.0	180.0	179.9	180.0
Cl2–Ru–Cl5	88.8	90.0	89.6	90.0
Cl2–Ru–N6	89.6	90.6	90.1	90.0
Cl2–Ru–N7	90.4	89.4	89.9	90.1
Cl3–Ru–N6	89.6	90.0	89.3	90.7
Cl3–Ru–N7	90.4	90.0	90.7	89.3
Cl4–Ru–Cl5	88.8	90.0	90.4	90.1
N6–Ru–N7	180.0	180.0	180.0	180.0

[a] The bond length in Å and bond angle in degree.

[b] The experimental values come from the X-ray structure of [ImH][*trans*-$RuCl_4Im_2$]. [76]

Table S2. The gas-phase ZPE-corrected energies of ICR in each spin state at the level of UB3LYP/(LanL2DZ + 6-31G(d))

	$E_{tot/ZEP}$(g)/a.u.
ICR(*S*=1/2)	-2387.2097
ICR(*S*=3/2)	-2387.1712
ICR(*S*=5/2)	-2387.1430

Table S3. Cartesian coordinates of optimized geometries

R

C	-0.043893	-0.143390	-0.024308
N	-0.135007	0.684879	-1.046303
C	-0.335608	-0.075249	-2.177783
C	-0.366258	-1.397846	-1.828633
N	-0.179180	-1.425016	-0.454645
Ru	0.009105	2.776630	-0.905583
Cl	-1.908119	3.025288	-2.397225
Cl	-1.451558	2.729779	1.050705
Cl	1.926266	2.527921	0.586277
N	0.153240	4.868342	-0.764838
C	0.353921	5.628471	0.366622
C	0.384449	6.951074	0.017477
N	0.197450	6.978234	-1.356520
C	0.062210	5.696606	-1.786857
Cl	1.469641	2.823531	-2.862034
H	0.457776	5.153008	1.328501
H	0.517552	7.850969	0.597601
H	0.165799	7.797189	-1.942663
H	-0.096129	5.394037	-2.809423
H	-0.439479	0.400224	-3.139654
H	-0.499456	-2.297740	-2.408738
H	-0.146963	-2.244007	0.131414
H	0.114469	0.159162	0.998260

I-1

C	2.991375	-1.098164	-0.174721
N	2.241938	-0.024761	-0.336058
C	3.089202	1.046065	-0.522240
C	4.383534	0.606155	-0.471361
N	4.304596	-0.760226	-0.249411
Ru	0.137996	-0.018758	-0.309969
Cl	0.110920	1.573647	-2.124696
Cl	0.175161	-1.895376	-1.853723
Cl	0.151149	-1.604390	1.568378
N	-1.979880	-0.035741	-0.268171

C	-2.817508	-1.067575	-0.641616
C	-4.111661	-0.708700	-0.385271
N	-4.046288	0.570473	0.142318
C	-2.741633	0.931329	0.207561
Cl	0.210475	1.870859	1.288172
O	-2.044203	0.373396	3.214860
H	-1.661264	-0.454348	2.870839
H	-1.385251	1.008545	2.877347
H	2.612523	-2.093121	-0.005169
H	2.689937	2.034575	-0.681371
H	5.327350	1.119448	-0.569407
H	5.077809	-1.400013	-0.158406
H	-2.409820	-1.969026	-1.070531
H	-5.047972	-1.224320	-0.531570
H	-4.811345	1.102582	0.525835
H	-2.375340	1.861801	0.609152

TS1

C	2.854038	-1.113281	-0.048632
N	2.102579	-0.028181	-0.095151
C	2.940424	1.045340	-0.321581
C	4.226262	0.593224	-0.411180
N	4.155291	-0.781927	-0.233240
Ru	-0.016014	-0.019136	-0.061985
Cl	-0.125508	1.977810	-1.431958
Cl	0.036848	-1.381054	-2.000711
Cl	0.111563	-2.135549	1.301760
N	-2.128814	-0.090410	-0.221167
C	-2.915925	-1.219603	-0.166840
C	-4.231813	-0.849479	-0.211224
N	-4.225471	0.533939	-0.294488
C	-2.934164	0.949776	-0.297234
Cl	1.049191	2.182452	2.010337
O	-1.260605	0.390838	2.342393
H	-0.834440	-0.460324	2.554317
H	-0.544718	1.065172	2.483408
H	2.482874	-2.111802	0.117264
H	2.540082	2.043351	-0.376793
H	5.162851	1.105882	-0.564645
H	4.927432	-1.429198	-0.226874
H	-2.465787	-2.196245	-0.086678
H	-5.146276	-1.421569	-0.194903
H	-5.031511	1.137356	-0.336914
H	-2.609897	1.976471	-0.356360

I-2

C	2.772108	-1.186357	-0.515379
N	1.979933	-0.192692	-0.153335
C	2.786115	0.842716	0.285036
C	4.093145	0.454994	0.179091
N	4.068297	-0.832968	-0.332030
Ru	-0.132034	-0.265119	-0.210066
Cl	-0.174495	1.674495	-1.596537
Cl	-0.046361	-1.857806	-2.003613
Cl	-0.099553	-2.000259	1.514864
N	-2.237761	-0.308249	-0.230423
C	-3.077784	-1.381177	-0.435635
C	-4.375153	-0.957283	-0.340788
N	-4.304890	0.400231	-0.071394
C	-2.995039	0.751172	-0.013648
Cl	1.314642	3.219572	2.460509
O	-0.384405	1.039127	1.490950
H	-0.251984	0.430914	2.241672
H	0.241725	1.838557	1.694029
H	2.435165	-2.130156	-0.913132
H	2.376626	1.766084	0.678436
H	5.012946	0.962351	0.423738
H	4.865246	-1.416009	-0.533639
H	-2.674350	-2.360126	-0.638602
H	-5.315487	-1.477388	-0.435513
H	-5.082646	1.028478	0.057395
H	-2.625800	1.745974	0.177233

P1

C	2.877264	-1.145034	-0.714799
N	2.015547	-0.287265	-0.191183
C	2.749808	0.749241	0.352335
C	4.079734	0.505588	0.152210
N	4.141583	-0.699587	-0.523794
Ru	-0.088045	-0.433846	-0.236550
O	0.030258	-2.251899	1.065058
N	-2.220856	-0.533347	-0.287901
C	-3.010394	0.339698	0.320217
N	-4.304065	0.084278	0.014521
C	-4.342444	-1.003377	-0.837681

C	-3.039327	-1.375188	-1.020265
Cl	0.029300	-1.978904	-2.061569
Cl	-0.194171	1.555152	-1.429907
Cl	-0.205667	0.568690	2.001335
H	-0.078329	-1.782969	1.920836
H	-0.794449	-2.745338	0.915786
H	-2.673148	1.134413	0.966506
H	-2.620450	-2.151969	-1.640049
H	-5.266365	-1.396007	-1.232082
H	-5.096397	0.616870	0.342284
H	2.262100	1.575894	0.842382
H	4.963170	1.063417	0.419492
H	4.978404	-1.166638	-0.839678
H	2.611395	-2.049335	-1.238662

I-3

C	2.995960	-1.094244	0.209387
N	2.248871	-0.075031	-0.183445
C	3.106831	0.942257	-0.552519
C	4.396210	0.522800	-0.377124
N	4.306013	-0.769630	0.106036
Ru	0.140802	-0.091327	-0.192300
O	0.158895	0.577174	-2.319984
Cl	0.191113	-2.269969	-1.185436
Cl	0.155254	-0.726180	2.060561
N	-1.991700	-0.139431	-0.189404
C	-2.830545	-0.868542	-1.014936
C	-4.128191	-0.641791	-0.649724
N	-4.063403	0.235402	0.415290
C	-2.763758	0.515090	0.670079
Cl	0.081007	2.317028	0.118123
O	-1.474133	2.117037	3.034780
H	-0.307658	-0.129721	-2.801271
H	-0.419591	1.362588	-2.294498
H	-0.958985	1.298965	3.158148
H	-0.982927	2.559345	2.318236
H	2.622645	-2.044759	0.554676
H	2.729104	1.891346	-0.896164
H	5.342864	1.011464	-0.544720
H	5.077764	-1.373432	0.347485
H	-2.436595	-1.532778	-1.767762
H	-5.061920	-1.022142	-1.032848
H	-4.843105	0.594759	0.946536

H	-2.426005	1.155709	1.481401

TS2

C	2.923130	-1.072401	0.239459
N	2.163399	-0.016512	-0.013741
C	3.013153	1.033433	-0.314960
C	4.305194	0.595620	-0.235466
N	4.227551	-0.740148	0.115767
Ru	0.041191	-0.082478	-0.074604
O	0.022744	0.831772	-2.084196
Cl	0.185070	-2.048673	-1.357812
Cl	0.175531	-1.457296	1.901970
N	-2.071402	-0.154855	-0.184447
C	-2.892340	-1.254420	-0.353963
C	-4.194695	-0.856871	-0.239092
N	-4.150789	0.505160	0.003079
C	-2.855828	0.891686	0.035673
Cl	0.194518	2.847429	-0.069192
O	-0.926773	1.278358	2.173186
H	-0.828575	0.593552	-2.489325
H	-0.027422	1.784241	-1.804004
H	-0.448856	0.605989	2.690862
H	-0.298605	2.001003	1.991525
H	2.559179	-2.051401	0.504395
H	2.623920	2.013314	-0.540740
H	5.246491	1.099427	-0.387715
H	5.004009	-1.368827	0.258909
H	-2.476402	-2.231015	-0.541461
H	-5.123149	-1.401834	-0.302570
H	-4.942362	1.110196	0.165559
H	-2.509476	1.892012	0.243859

I-4

C	2.893329	-1.200509	0.574709
N	2.113313	-0.240870	0.099191
C	2.941487	0.743120	-0.411737
C	4.243187	0.367315	-0.229658
N	4.191307	-0.864687	0.395243
Ru	-0.005059	-0.264038	-0.007492
O	0.110411	1.348443	-1.466356
Cl	0.095616	-1.715024	-1.862029
Cl	-0.084631	-1.947081	1.646989

N	-2.111304	-0.255883	-0.113766
C	-2.915125	-1.371657	-0.256797
C	-4.223794	-0.980974	-0.224762
N	-4.201419	0.391929	-0.058496
C	-2.912913	0.796194	0.007349
Cl	-0.907029	3.670949	0.064302
O	-0.038472	1.242485	1.504396
H	-0.423824	1.080384	-2.234075
H	-0.276400	2.214571	-1.102015
H	0.830016	1.346372	1.927418
H	-0.320654	2.155851	1.152070
H	2.542951	-2.109706	1.037620
H	2.534192	1.621233	-0.887309
H	5.174670	0.847413	-0.484672
H	4.982143	-1.431045	0.666059
H	-2.486240	-2.354052	-0.367894
H	-5.143685	-1.538666	-0.300838
H	-5.002844	1.001893	0.011649
H	-2.594658	1.825568	0.131832

P2-1

C	2.914980	-1.184661	0.744385
N	2.122813	-0.295457	0.148951
C	2.944213	0.650874	-0.437508
C	4.246857	0.318828	-0.191332
N	4.207054	-0.841968	0.554675
Ru	0.004064	-0.243471	0.191986
O	0.156119	-1.312248	2.120000
N	-2.106144	-0.212427	0.245264
C	-2.854396	0.882267	0.171460
N	-4.159924	0.542133	0.195824
C	-4.259885	-0.830759	0.286557
C	-2.973086	-1.292534	0.316313
O	-0.182007	-2.152520	-0.882513
Cl	-0.070406	0.743438	-1.918201
Cl	0.101584	1.684015	1.505190
H	-0.604304	-1.896173	-1.726940
H	0.697073	-2.491363	-1.131339
H	0.424984	-0.588511	2.722774
H	-0.716817	-1.603789	2.440072
H	-2.480433	1.891963	0.107287
H	-2.615170	-2.310253	0.360601
H	-5.209203	-1.342118	0.317620

H	-4.932433	1.193739	0.149662
H	2.534117	1.484109	-0.984679
H	5.174196	0.793212	-0.471531
H	5.006973	-1.348777	0.909787
H	2.591034	-2.040138	1.317587

I-3´

Ru	0.085516	-0.119438	-0.207758
Cl	-0.017187	2.297581	0.248593
Cl	0.275556	-0.847312	2.008429
N	2.225638	-0.034270	-0.292659
Cl	0.173666	-2.256790	-1.259792
N	-2.014328	-0.216990	-0.118397
C	3.049477	1.077356	-0.259441
C	4.352840	0.668549	-0.201142
N	4.309399	-0.712904	-0.193304
C	3.013548	-1.098836	-0.245399
C	-2.851791	-0.813168	-1.043474
C	-4.146134	-0.661038	-0.632569
N	-4.078012	0.036644	0.559153
C	-2.778853	0.288620	0.841430
O	-0.103141	0.680267	-2.268115
O	-1.434983	1.779387	3.249890
H	-0.874060	0.983448	3.283889
H	-0.990912	2.307952	2.562908
H	0.734267	0.483937	-2.722638
H	-0.102491	1.639586	-2.067002
H	2.636188	2.073354	-0.247710
H	5.279968	1.217986	-0.157948
H	5.101216	-1.336858	-0.139666
H	2.673705	-2.122223	-0.250624
H	-2.456271	-1.314352	-1.911751
H	-5.081322	-0.981314	-1.063794
H	-4.856296	0.313301	1.139163
H	-2.435770	0.824297	1.722784

TS2´

Ru	-0.056636	0.162353	-0.032389
Cl	-0.018329	2.578315	0.508912
Cl	0.457949	-2.129256	1.584618
N	2.090413	0.219627	-0.048721
Cl	-0.031913	-1.780262	-1.630526

N	-2.144324	0.058396	-0.083023
C	2.961683	1.293301	0.044309
C	4.247467	0.834686	-0.030219
N	4.144677	-0.537111	-0.171160
C	2.834652	-0.871200	-0.176427
C	-2.899134	-1.089158	0.057782
C	-4.222440	-0.746419	0.058699
N	-4.255469	0.629488	-0.084907
C	-2.981183	1.079728	-0.163396
O	-0.077347	1.008993	-2.010364
O	-0.624569	0.367741	2.262361
H	-0.209594	-0.485390	2.549155
H	-0.041499	1.096204	2.538392
H	0.018158	0.158680	-2.513318
H	0.748553	1.515676	-2.112607
H	2.591535	2.297503	0.176557
H	5.197979	1.342896	0.009708
H	4.909536	-1.193088	-0.234043
H	2.450008	-1.875525	-0.249425
H	-2.424140	-2.052965	0.150822
H	-5.119657	-1.338415	0.145332
H	-5.081842	1.207743	-0.116464
H	-2.691839	2.115530	-0.248642

I-4´

Ru	-0.130195	0.240258	-0.176269
Cl	-0.185934	2.465497	0.735123
Cl	2.054550	-1.860067	2.798967
N	1.978528	0.225332	-0.195870
Cl	-0.170462	-1.813278	-1.457760
N	-2.244093	0.222953	-0.123153
C	2.844147	1.307308	-0.107282
C	4.120225	0.841107	0.022638
N	4.019499	-0.538324	0.005192
C	2.720138	-0.873655	-0.104468
C	-3.032197	-0.894853	0.080105
C	-4.345256	-0.517006	0.075109
N	-4.341495	0.850330	-0.138110
C	-3.058211	1.261124	-0.250027
O	-0.081386	1.108012	-2.204673
O	-0.195029	-0.615981	1.659715
H	0.705267	-1.107385	2.081691
H	-0.493512	0.039701	2.316150

H	0.053399	0.277114	-2.709979
H	0.752012	1.606743	-2.272369
H	2.472944	2.319984	-0.097189
H	5.064885	1.350007	0.129611
H	4.758055	-1.195577	0.211897
H	2.346255	-1.883180	-0.100177
H	-2.589754	-1.870407	0.201375
H	-5.257380	-1.079017	0.198347
H	-5.152539	1.449348	-0.189966
H	-2.746639	2.283927	-0.390079

P2-2

C	-0.335619	0.260558	-0.093977
N	-0.186454	1.506890	0.351900
C	0.721722	1.454427	1.400991
C	1.113023	0.157931	1.582279
N	0.436709	-0.575723	0.628275
Ru	-1.158922	3.218443	-0.458143
O	-2.431834	3.329143	1.229585
Cl	-2.828351	1.825851	-1.449019
N	-2.131074	4.929701	-1.268497
C	-3.035963	4.982344	-2.320397
C	-3.428208	6.278608	-2.501352
N	-2.755814	7.011885	-1.544294
C	-1.984785	6.175632	-0.820614
Cl	0.509342	4.611423	0.534062
O	0.114008	3.108235	-2.145707
H	-3.298279	2.971874	0.948415
H	-2.112849	2.762291	1.956157
H	0.981953	3.460641	-1.863101
H	-0.202110	3.679183	-2.870337
H	-3.349852	4.089988	-2.837595
H	-4.112033	6.730682	-3.202565
H	-2.825018	8.010824	-1.400419
H	-1.337627	6.478195	-0.012564
H	1.038027	2.347003	1.916322
H	1.798494	-0.294102	2.281908
H	0.504254	-1.574921	0.485410
H	-0.985558	-0.042178	-0.899731

Table S4. Vibrational frequencies of TS species

TS1

-153.0278	26.4855	28.0497
42.7915	51.0733	68.1132
84.3983	101.7120	118.8565
120.3138	129.1050	140.6819
162.3589	185.1535	204.3968
212.0311	218.0728	221.3884
243.1198	258.6191	264.4421
283.6682	305.2508	326.2970
416.2424	448.4476	466.3816
637.3272	639.0518	640.6485
662.3168	669.9965	681.6413
684.5118	798.3802	820.5134
826.9945	853.2332	858.3959
932.0378	934.5047	952.7491
955.3984	1077.9167	1081.5544
1114.7974	1117.3695	1163.3874
1167.4550	1194.5020	1198.8674
1291.4716	1295.1230	1384.7070
1392.4858	1471.5193	1472.4263
1531.9913	1534.9528	1599.5351
1602.2007	1689.9166	3295.7397
3298.4435	3299.7211	3320.2838
3323.1778	3323.5232	3341.4735
3675.0273	3676.8004	3677.5453

TS2

-141.2592	31.8238	47.7799
52.0485	56.8355	78.1386
87.6880	112.0506	116.9309
120.4286	145.6210	162.1987
184.5696	192.0278	206.2083
218.0805	233.7214	254.7615
259.2724	272.8894	275.3726
300.9413	310.9426	321.3333
343.3353	358.1722	526.4202
540.3382	551.2801	569.3662
646.2340	648.4104	669.3665

675.7364	697.0347	718.9964
724.6250	823.3691	840.9440
857.9766	871.7056	884.4964
935.1629	935.8756	956.2150
958.2968	1085.7359	1087.8551
1121.4278	1124.7021	1165.2843
1167.0750	1199.8584	1202.5495
1294.8141	1298.7642	1377.3697
1382.6351	1474.5146	1476.3792
1539.4519	1542.5990	1597.0253
1598.6540	1621.9125	1652.4002
3304.2996	3307.0593	3314.8859
3319.9072	3322.4116	3328.2171
3334.3772	3634.3353	3663.1265
3664.9516	3746.7311	3756.6790

TS2´

-167.1558	33.7412	35.6748
40.9346	66.7958	78.0428
90.0467	103.5001	130.2470
143.9868	160.5719	164.5306
168.9227	195.7958	206.6777
214.7798	222.5498	253.7608
267.1124	272.7547	280.2007
300.9223	319.9361	322.0277
349.1125	387.1913	530.4585
555.4484	646.2433	649.6240
663.9396	672.6298	678.0087
720.8660	722.5889	750.9421
808.4710	827.8889	833.2331
857.5557	871.5219	877.8457
934.9462	935.7860	952.7044
964.2618	1085.8996	1088.4839
1120.1457	1125.8550	1165.9015
1167.6856	1196.9670	1204.2970
1294.2496	1300.4860	1374.2018
1389.2524	1472.4209	1476.4719
1535.9824	1543.0240	1594.0510
1602.0404	1610.9987	1613.9608
3302.8386	3306.1943	3316.7842
3320.5120	3325.4227	3332.9604
3347.0138	3362.2428	3661.7302
3667.2931	3732.8703	3742.2433

Table S5. Gas-phase energies, total solvation energies, thermal contributions to enthalpies, standard entropies, enthalpies, and gibbs free energies at 298.15 K for all intermediate species and transition states of the first and the second aquation processes[a]

species	E_{tot}(g)	$E_{tot/ZPE}$(g)	G_{solv}[b]	E_{tot}(aq)	G_{therm}[c]	H_{therm}[c]	$H°$(aq)	$S°$(aq)	$G°$(g)	$G°$(aq)
	a.u.	a.u.	kcal/mol	a.u.	kcal/mol	kcal/mol	a.u.	cal/K·mol	a.u.	a.u.
I-1	-2464.184	-2464.008	-72.87	-2464.306	76.781	124.285	-2463.926	159.330	-2463.885	-2464.001
TS1	-2464.139	-2463.963	-77.96	-2464.266	77.775	123.539	-2463.890	153.494	-2463.839	-2463.963
I-2	-2464.180	-2464.004	-79.16	-2464.310	77.734	123.870	-2463.932	154.740	-2463.880	-2464.006
					Path 1					
I-3	-2080.307	-2080.105	-26.38	-2080.360	94.340	140.572	-2079.923	155.062	-2079.955	-2079.997
TS2	-2080.275	-2080.073	-26.73	-2080.327	94.702	139.648	-2079.893	150.752	-2079.922	-2079.965
I-4	-2080.308	-2080.106	-32.74	-2080.368	95.071	139.919	-2079.935	150.421	-2079.955	-2080.007
					Path 2					
I-3´	-2080.307	-2080.105	-26.51	-2080.360	94.283	140.611	-2079.923	155.386	-2079.955	-2079.997
TS2´	-2080.258	-2080.056	-32.68	-2080.317	94.967	139.706	-2079.885	150.053	-2079.905	-2079.957
I-4´	-2080.285	-2080.086	-40.27	-2080.357	91.925	138.675	-2079.929	156.798	-2079.939	-2080.004

[a] E_{tot}, the single-point energy calculated at the level of UB3LYP/(LanL2DZ(f) + 6-311++G(3df, 2pd)) on structures optimized at the UB3LYP/(LanL2DZ + 6-31G(d)) level; total enthalpies, and Gibbs free energies (including solvation and zero-point energy) were obtained as follows: $H°(aq) = E_{tot/ZPE}(g) + G_{solv} + H_{therm}$; $G°(aq) = E_{tot/ZPE}(g) + G_{solv} + G_{therm}$; $G°(aq) = H°(aq) - 298.15\ S°(aq)$.

[b] The solvation energy corrections to the single-point energies calculated using the CPCM solvation model at the level of UB3LYP/(LanL2DZ(f) + 6-311++G(3df, 2pd)).

[c] Thermal correction obtained through frequency calculation at the level of UB3LYP/(LanL2DZ + 6-31G(d)) at 298.15 K and 1 atm on the optimized stationary point geometries.