Supporting information

Experimental and theoretical aspects of the haptotropic rearrangement of diiron and diruthenium carbonyl complexes bound to 4,6,8-trimethylazulene

Kazuhiro Tsuchiya,[c] Keiko Ideta,[b] Koichi Mogi,[c#]* Yusuke Sunada[c] and Hideo Nagashima[a,c]*

Division of Applied Molecular Chemistry[a] and Analytical Center[b] of Institute for Materials Chemistry and Engineering, Department of Molecular and Materials Science,[c] Graduate School of Engineering Sciences, Kyushu University, Kasuga, Fukuoka, 816-8580, Japan

S-4. Thermodynamic parameters for **3** and **4** by DFT calculation

The spin-saturation transfer (SST) mesurement

The SST studies of **3** and **4** were carried out in the temperature range of 349 to 402 K. The spin-lattice relaxation time of H1 $\{T_{1(H1)}\}$ was determined by the standard inversion recovery method as the average of ten measurements at 381, 385, 390, 394, 398 and 402K for the complex **3**, and 349, 353, 358, 363, 367 and 372 K for the complex **4**. At each temperature, ten raw data of $T_{1(H1)}$ and their average are listed in Tables S-1-1-1 for **3** and S-1-2-1 for **4**. The average data $\{T_{1(H1)}\}_{av}$ are used for the determination of k as described below. The SST measurement led to change of integral value of the peak due to H1: Ten measurements were performed at each temperature for the determination of $I_{f(H1)} / I_{0(H1)}$, where $I_{f(H1)}$ is the final intensity of H1 while $I_{0(H1)}$ is the initial intensity as listed in Tables S-1-1-2 for **3** and S-1-2-2 for **4**. The exchange rate k is defined as $I_{f(H1)} / I_{0(H1)} = \{T_{1(H1)}\}_{av}^{-1} / [k + \{T_{1(H1)}\}_{av}^{-1}$, and the values of ln(k / T) are calculated according to the following equation.

$$\ln(k/T) = \ln(I_{0(H1)}/I_{f(H1)}-1) - \ln\{T_{1(H1)}\}_{av} - \ln(T) \quad \text{(eq. S-1)}$$

The data of ln(k/T) are summarized in Tables S-2-1-1 (for **3**) S-2-2-1 (for **4**). The average of ln(k / T) at each temperature was adopted to an Eyring plot of ln(k/T) vs. 1000/T as shown in Figures S-2-1-1 and S-2-2-1. The best-fit line drawn from a least-squares analysis of the plot provided the enthalpy and entropy of activation from the slope and the intercept, respectively (Table S-2-1-2 and S-2-2-2) . The $\Delta G^{\ddagger}_{373}$, $\Delta H^{\ddagger}_{373}$, and $\Delta S^{\ddagger}_{373}$ calculated by the following equation (eq. S-2, where k_B: Boltzman constant, h: plank constant) for the rearrangement of **3** and **4** are listed in Table S-2-1-3 and S-2-2-3.

$$\ln\left(\frac{k}{T}\right) = \ln\left(\frac{k_B}{h}\right) - \frac{\Delta H}{RT} + \frac{\Delta S}{R} \qquad \text{(eq. S-2)}$$

S-1 Data of SST experiment

S-1-1 The list of data of Fe complex (**3**)

Table S-1-1-1 $\{T_{1(H1)}\}$ measurement of Fe (**3**) complex

Complex	Temperature	The $\{T_{1(H1)}\}$ value observed in each measurement										$\{T_{1(H1)}\}$ of
	K	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	the average
Fe(**3**)	380.8	7.650	7.158	7.117	7.094	7.025	7.124	7.089	7.012	6.962	6.993	7.122±0.186
	385.3	7.440	7.393	7.465	7.061	7.172	7.248	7.278	7.351	7.399	7.180	7.299±0.126
	389.9	7.116	7.152	6.953	7.041	7.009	6.999	6.962	6.940	6.928	6.976	7.008±0.071
	393.6	7.325	7.260	6.866	6.972	6.878	6.794	7.148	6.867	6.816	6.896	6.982±0.182
	398.1	5.526	5.692	5.611	5.660	5.728	5.692	5.714	5.805	5.873	5.771	5.707±0.093
	401.8	6.231	6.155	6.152	6.215	6.223	6.250	6.243	6.335	6.164	6.198	6.217±0.052

Table S-1-1-2 $I_{f(H1)}/I_{0(H1)}$ measurement of Fe (**3**) complex

Complex	Temperature	The $I_{f(H1)}/I_{0(H1)}$ value observed in each measurement									
	K	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th
Fe(**3**)	380.8	0.745	0.751	0.743	0.746	0.742	0.722	0.728	0.735	0.735	0.735
	385.3	0.639	0.672	0.673	0.667	0.627	0.639	0.644	0.612	0.635	0.620
	389.9	0.564	0.569	0.578	0.568	0.560	0.578	0.572	0.572	0.574	0.567
	393.6	0.507	0.500	0.513	0.510	0.524	0.518	0.520	0.510	0.516	0.513
	398.1	0.473	0.493	0.483	0.512	0.503	0.493	0.495	0.494	0.489	0.484
	401.8	0.416	0.397	0.402	0.404	0.409	0.405	0.400	0.403	0.397	0.378

S-1-2 The list of data of Ru complex (**4**)

Table S-1-2-1 $\{T_{1(H1)}\}$ measurement of Ru (**4**) complex

Complex	Temperature	The $\{T_{1(H1)}\}$ value observed in each measurement										$\{T_{1(H1)}\}$ of
	K	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	the average
Ru(**4**)	348.8	6.436	6.255	6.522	7.236	6.412	6.620	6.286	6.428	6.689	6.562	6.545±0.264
	353.4	8.068	7.113	7.644	7.167	8.012	6.984	7.191	6.721	6.712	7.581	7.319±0.462
	357.9	7.568	7.523	7.466	7.503	7.509	7.315	7.426	7.434	7.450	7.287	7.448±0.084
	362.5	7.440	7.393	7.465	7.061	7.172	7.248	7.278	7.351	7.399	7.180	7.299±0.126
	367.1	7.061	7.078	7.063	7.041	7.113	6.977	7.131	7.155	7.257	7.274	7.115±0.089
	371.6	6.903	6.698	6.925	6.425	6.355	6.792	8.087	7.910	6.677	6.841	6.961±0.550

Table S-1-2-2 $I_{f(H1)}/I_{0(H1)}$ measurement of Ru (**4**) complex

Complex	Temperature	The $I_{f(H1)}/I_{0(H1)}$ value observed in each measurement									
	K	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th
Ru(**4**)	348.8	0.844	0.846	0.843	0.841	0.842	0.853	0.835	0.831	0.844	0.834
	353.4	0.704	0.740	0.747	0.747	0.766	0.704	0.750	0.729	0.763	0.768
	357.9	0.627	0.631	0.627	0.608	0.621	0.615	0.622	0.619	0.618	0.617
	362.5	0.531	0.524	0.521	0.522	0.524	0.532	0.526	0.530	0.527	0.531
	367.1	0.403	0.396	0.402	0.399	0.399	0.403	0.402	0.402	0.402	0.402
	371.6	0.354	0.314	0.325	0.330	0.332	0.338	0.344	0.355	0.318	0.322

S-2 Data of the SST measurement

S-2-1 The list of data of Fe complex (**3**)

Table S-2-1-1 The calculated values of ln(k/T)

Exp. No. / K	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	average
380.8	-8.979	-9.009	-8.967	-8.985	-8.964	-8.858	-8.891	-8.926	-8.927	-8.927	-8.943±0.044
385.3	-8.514	-8.659	-8.663	-8.637	-8.459	-8.514	-8.535	-8.399	-8.494	-8.433	-8.531±0.089
389.9	-8.169	-8.191	-8.227	-8.185	-8.153	-8.226	-8.203	-8.202	-8.210	-8.182	-8.195±0.023
393.6	-7.947	-7.919	-7.972	-7.961	-8.015	-7.990	-7.997	-7.957	-7.982	-7.972	-7.971±0.026
398.1	-7.620	-7.700	-7.662	-7.778	-7.740	-7.701	-7.709	-7.706	-7.686	-7.666	-7.697±0.041
401.8	-7.484	-7.404	-7.427	-7.433	-7.455	-7.440	-7.419	-7.431	-7.404	-7.325	-7.422±0.039

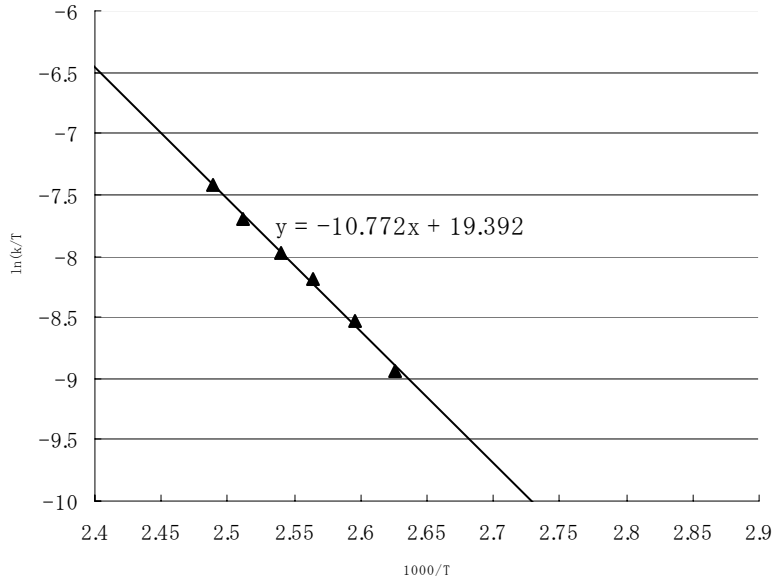

Fig. S-2-1-1. Eyring plot for the haptotropic rearrangement of **3**

Table S-2-1-2 The y-intercept and slope values of Eyring plot

	(**least square method**)
y-intercept	19.392±0.352
slope	-10.722±0.056

Table S-2-1-3 Thermodynamic parameters of complex **3**

$\Delta S^{\neq}$	-33±3 J $K^{-1}mol^{-1}$	-8±1 cal $K^{-1}mol^{-1}$
$\Delta H^{\neq}$	89±1 kJ mol^{-1}	21±1 kcal mol^{-1}
$\Delta G^{\neq}_{373}$	101±2 kJ mol^{-1}	24±1 kcal mol^{-1}

S-2-2 The list of data of Ru complex (**4**)

Table S-2-2-1 The calculated value of ln(k/T)

exp.No. / K	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	average
348.8	-9.420	-9.436	-9.417	-9.399	-9.408	-9.490	-9.352	-9.327	-9.420	-9.348	-9.402±0.046
353.4	-8.724	-8.904	-8.942	-8.942	-9.044	-8.722	-8.954	-8.845	-9.029	-9.055	-8.916±0.114
357.9	-8.408	-8.425	-8.406	-8.326	-8.380	-8.357	-8.388	-8.375	-8.371	-8.364	-8.380±0.027
362.5	-8.006	-7.976	-7.964	-7.969	-7.975	-8.007	-7.985	-8.001	-7.988	-8.004	-7.988±0.015
367.1	-7.475	-7.445	-7.469	-7.460	-7.458	-7.477	-7.472	-7.471	-7.470	-7.472	-7.467±0.009
371.6	-7.255	-7.078	-7.129	-7.152	-7.161	-7.186	-7.212	-7.261	-7.094	-7.112	-7.164±0.061

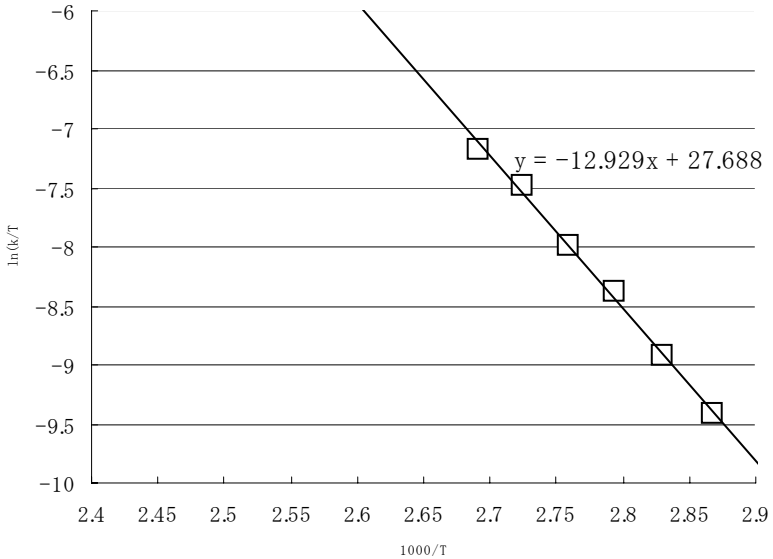

Fig. S-2-2-1. Eyring plot for the haptotropic rearrangement of **4**

Table S-2-2-2 The y-intercept and slope values of Eyring plot

	(**least square method**)
y-intercept	27.688±0.424
slope	-12.929±0.062

Table S-2-2-3 Thermodynamic parameters of complex **4**

$\Delta S^{\neq}$	29±4 J $K^{-1}mol^{-1}$	8±1 cal $K^{-1}mol^{-1}$
$\Delta H^{\neq}$	106±1 kJ mol^{-1}	26±1 kcal mol^{-1}
$\Delta G^{\neq}_{373}$	95±2 kJ mol^{-1}	22±1 kcal mol^{-1}

S-3 x,y,z-coordinates of ground and transition state structures of complex **3** and **4**

Table S-3-1 ground state structures of complex **3**

Fe (**3**)										
B3LYP				B1B95				PBE1PBE		
	x	y	z		x	y	Z		x	y	z
Fe	0.928	−0.085	1.304	Fe	−1.410	−0.582	0.109	Fe	−1.452	−0.528	0.128
Fe	−1.131	−0.562	−0.613	Fe	1.299	−0.269	0.189	Fe	1.306	−0.339	0.147
C	−0.093	1.633	0.578	C	−0.494	0.142	−1.625	C	−0.564	0.235	−1.605
C	−0.101	1.617	2.018	C	−1.277	−1.027	−1.909	C	−1.426	−0.872	−1.920
C	1.242	1.648	2.493	C	−2.628	−0.779	−1.561	C	−2.749	−0.566	−1.499
C	2.098	1.683	1.367	C	−2.705	0.535	−1.055	C	−2.731	0.724	−0.923
C	1.304	1.655	0.167	C	−1.397	1.118	−1.058	C	−1.390	1.237	−0.958
C	1.862	1.559	−1.186	C	−1.081	2.402	−0.440	C	−0.977	2.482	−0.314
C	1.159	1.052	−2.224	C	0.150	2.673	0.030	C	0.285	2.674	0.119
C	−0.250	0.634	−2.322	C	1.397	1.901	−0.063	C	1.490	1.847	−0.044
C	−1.311	1.266	−1.601	C	1.764	1.142	−1.214	C	1.767	1.099	−1.229
C	−1.314	1.579	−0.225	C	0.942	0.197	−1.851	C	0.871	0.214	−1.863
H	1.552	1.641	3.535	H	−3.452	−1.478	−1.658	H	−3.617	−1.214	−1.596
H	3.184	1.698	1.400	H	−3.603	1.021	−0.687	H	−3.588	1.236	−0.493
C	3.311	1.946	−1.360	C	−2.218	3.350	−0.211	C	−2.047	3.499	−0.040
H	1.710	0.939	−3.164	H	0.262	3.618	0.568	H	0.466	3.602	0.673
C	−2.519	−1.173	−1.539	C	3.018	−0.470	0.518	C	3.020	−0.628	0.378
O	−3.419	−1.617	−2.108	O	4.124	−0.644	0.765	O	4.132	−0.862	0.561
C	−0.056	−1.969	−0.900	C	0.802	−0.161	1.895	C	0.902	−0.243	1.872
O	0.523	−2.931	−1.171	O	0.652	−0.098	3.033	O	0.801	−0.199	3.018
C	−1.934	−1.001	0.927	C	1.127	−2.009	−0.140	C	1.053	−2.058	−0.199
O	−2.524	−1.261	1.884	O	1.069	−3.124	−0.409	O	0.960	−3.174	−0.467
C	0.538	−1.253	2.584	C	−1.606	−2.196	0.800	C	−1.713	−2.161	0.722
O	0.321	−1.978	3.454	O	−1.790	−3.246	1.227	O	−1.942	−3.227	1.091
C	2.197	−1.128	0.633	C	−1.890	0.199	1.617	C	−1.828	0.160	1.700
O	3.090	−1.740	0.234	O	−2.291	0.745	2.543	O	−2.166	0.643	2.688
H	3.499	2.974	−1.007	H	−2.768	3.555	−1.140	H	−2.587	3.774	−0.960
H	3.983	1.281	−0.789	H	−2.942	2.938	0.509	H	−2.796	3.117	0.674
H	3.609	1.887	−2.416	H	−1.858	4.302	0.194	H	−1.617	4.413	0.393

H	−2.261	1.407	−2.123	H	2.807	1.169	−1.536	H	2.797	1.089	−1.600
H	−0.987	1.582	2.645	H	−0.891	−1.957	−2.314	H	−1.115	−1.801	−2.388
C	−2.569	2.186	0.371	C	1.512	−0.617	−2.982	C	1.360	−0.575	−3.052
H	−2.806	1.779	1.364	H	1.211	−1.670	−2.931	H	0.990	−1.609	−3.054
H	−2.451	3.278	0.486	H	1.170	−0.225	−3.952	H	1.023	−0.105	−3.991
H	−3.439	2.001	−0.276	H	2.608	−0.587	−2.963	H	2.458	−0.619	−3.063
C	−0.596	0.146	−3.725	C	2.538	2.600	0.647	C	2.692	2.476	0.635
H	−0.369	0.927	−4.474	H	2.675	3.619	0.252	H	2.853	3.503	0.263
H	−0.001	−0.740	−3.992	H	2.334	2.694	1.721	H	2.537	2.545	1.722
H	−1.657	−0.120	−3.830	H	3.487	2.063	0.534	H	3.616	1.908	0.465

Table S-3-2 transition state structures of complex **3**

Fe(TS) (**3**)											
B3LYP				B1B95				PBE1PBE			
	x	y	z		x	y	z		x	y	z
Fe	−0.431	−1.567	0.000	Fe	−0.348	−1.539	0.000	Fe	−0.390	−1.525	0.000
Fe	−0.698	1.189	0.000	Fe	−0.665	1.104	0.000	Fe	−0.634	1.106	0.000
C	0.945	−3.170	0.000	C	1.013	−3.092	0.000	C	0.923	−3.137	0.000
C	1.253	1.990	0.000	C	1.165	2.049	0.000	C	1.203	2.002	0.000
C	1.187	−2.361	1.147	C	1.234	−2.280	1.142	C	1.162	−2.327	1.145
C	1.187	−2.361	−1.147	C	1.234	−2.280	−1.142	C	1.162	−2.327	−1.145
C	1.530	−1.038	0.729	C	1.539	−0.955	0.724	C	1.529	−1.011	0.724
C	1.530	−1.038	−0.729	C	1.539	−0.955	−0.724	C	1.529	−1.011	−0.724
C	1.695	1.387	1.270	C	1.603	1.464	1.268	C	1.667	1.410	1.265
C	1.695	1.387	−1.270	C	1.603	1.464	−1.268	C	1.667	1.410	−1.265
C	1.827	0.075	1.628	C	1.778	0.161	1.623	C	1.797	0.102	1.628
C	1.827	0.075	−1.628	C	1.778	0.161	−1.623	C	1.797	0.102	−1.628
H	0.663	−4.219	0.000	H	0.756	−4.146	0.000	H	0.595	−4.174	0.000
H	1.088	−2.686	−2.179	H	1.140	−2.604	−2.172	H	1.089	−2.653	−2.180
H	1.876	2.114	−2.070	H	1.725	2.190	−2.076	H	1.825	2.138	−2.068
C	2.162	−0.276	−3.056	C	2.062	−0.182	−3.052	C	2.097	−0.247	−3.054
H	2.487	0.610	−3.618	H	2.348	0.707	−3.625	H	2.432	0.635	−3.615
H	2.959	−1.036	−3.111	H	2.864	−0.928	−3.136	H	2.870	−1.026	−3.129
H	1.281	−0.692	−3.578	H	1.168	−0.613	−3.531	H	1.194	−0.632	−3.560
C	2.162	−0.276	3.056	C	2.062	−0.182	3.052	C	2.097	−0.247	3.054

H	2.487	0.610	3.618	H	2.348	0.707	3.625	H	2.432	0.635	3.615
H	1.281	−0.692	3.578	H	1.168	−0.613	3.531	H	1.194	−0.632	3.560
H	2.959	−1.036	3.111	H	2.864	−0.928	3.136	H	2.870	−1.026	3.129
C	1.410	3.511	0.000	C	1.231	3.564	0.000	C	1.300	3.517	0.000
H	0.944	3.962	−0.889	H	0.738	3.981	−0.886	H	0.812	3.944	−0.888
H	0.944	3.962	0.889	H	0.738	3.981	0.886	H	0.812	3.944	0.888
H	2.478	3.799	0.000	H	2.275	3.916	0.000	H	2.352	3.852	0.000
H	1.088	−2.686	2.179	H	1.140	−2.604	2.172	H	1.089	−2.653	2.180
H	1.876	2.114	2.070	H	1.725	2.190	2.076	H	1.825	2.138	2.068
C	−1.005	0.963	−1.794	C	−0.982	0.873	−1.781	C	−0.929	0.918	−1.787
O	−1.304	0.887	−2.905	O	−1.274	0.730	−2.883	O	−1.219	0.870	−2.900
C	−1.651	−1.791	−1.264	C	−1.573	−1.782	−1.242	C	−1.628	−1.718	−1.239
C	−1.651	−1.791	1.264	C	−1.573	−1.782	1.242	C	−1.628	−1.718	1.239
C	−1.005	0.963	1.794	C	−0.982	0.873	1.781	C	−0.929	0.918	1.787
C	−1.519	2.738	0.000	C	−1.574	2.582	0.000	C	−1.575	2.562	0.000
O	−2.428	−2.018	2.088	O	−2.354	−2.017	2.052	O	−2.430	−1.923	2.039
O	−2.428	−2.018	−2.088	O	−2.354	−2.017	−2.052	O	−2.430	−1.923	−2.039
O	−1.304	0.887	2.905	O	−1.274	0.730	2.883	O	−1.219	0.870	2.900
O	−2.101	3.735	0.000	O	−2.193	3.551	0.000	O	−2.229	3.508	0.000

Table S-3-3 ground state structures of complex **4**

Ru (**4**)											
B3LYP				B1B95				PBE1PBE			
	x	y	z		x	y	z		x	y	z
Ru	1.018	−0.143	1.296	Ru	1.521	−0.488	−0.025	Ru	−1.541	−0.466	0.060
Ru	−1.169	−0.505	−0.683	Ru	−1.351	−0.334	−0.132	Ru	1.360	−0.366	0.087
C	0.010	1.809	0.572	C	0.519	0.673	1.645	C	−0.574	0.731	−1.614
C	0.040	1.804	2.014	C	1.385	−0.330	2.204	C	−1.491	−0.226	−2.177
C	1.396	1.825	2.457	C	2.727	−0.054	1.829	C	−2.811	0.069	−1.735
C	2.227	1.821	1.307	C	2.716	1.100	1.012	C	−2.736	1.196	−0.878
C	1.404	1.782	0.125	C	1.362	1.552	0.854	C	−1.364	1.611	−0.762
C	1.928	1.688	−1.239	C	0.959	2.644	−0.025	C	−0.901	2.674	0.127
C	1.180	1.264	−2.286	C	−0.294	2.756	−0.504	C	0.376	2.752	0.558
C	−0.247	0.927	−2.385	C	−1.507	1.982	−0.217	C	1.564	1.963	0.206
C	−1.269	1.551	−1.591	C	−1.802	1.446	1.080	C	1.792	1.434	−1.110

C	−1.228	1.812	−0.203	C	−0.918	0.690	1.874	C	0.858	0.714	−1.886
H	1.730	1.861	3.491	H	3.605	−0.615	2.133	H	−3.716	−0.460	−2.022
H	3.313	1.847	1.315	H	3.589	1.574	0.576	H	−3.581	1.677	−0.390
C	3.399	1.977	−1.427	C	2.038	3.579	−0.485	C	−1.941	3.620	0.653
H	1.716	1.147	−3.234	H	−0.454	3.558	−1.230	H	0.580	3.535	1.297
C	−2.679	−1.003	−1.775	C	−3.235	−0.580	−0.355	C	3.238	−0.651	0.238
O	−3.578	−1.367	−2.396	O	−4.351	−0.787	−0.521	O	4.356	−0.888	0.359
C	−0.095	−2.119	−1.026	C	−0.856	−0.674	−1.990	C	0.932	−0.723	1.951
O	0.418	−3.109	−1.310	O	−0.713	−0.889	−3.106	O	0.830	−0.959	3.070
C	−2.109	−1.082	0.926	C	−1.138	−2.137	0.554	C	1.111	−2.149	−0.614
O	−2.706	−1.394	1.859	O	−1.035	−3.184	1.005	O	0.996	−3.195	−1.070
C	0.530	−1.432	2.618	C	1.780	−2.340	−0.377	C	−1.837	−2.317	0.339
O	0.256	−2.175	3.459	O	1.975	−3.458	−0.561	O	−2.060	−3.438	0.480
C	2.288	−1.377	0.577	C	1.934	−0.104	−1.842	C	−1.893	−0.153	1.895
O	3.124	−2.064	0.173	O	2.255	0.169	−2.911	O	−2.185	0.082	2.984
H	3.666	2.982	−1.058	H	2.572	4.029	0.363	H	−2.494	4.110	−0.164
H	4.027	1.254	−0.876	H	2.788	3.055	−1.098	H	−2.684	3.094	1.278
H	3.679	1.917	−2.487	H	1.619	4.386	−1.095	H	−1.483	4.402	1.273
H	−0.831	1.829	2.662	H	1.069	−1.142	2.851	H	−1.224	−1.026	−2.864
H	−2.223	1.760	−2.083	H	−2.833	1.505	1.434	H	2.810	1.482	−1.508
C	−0.649	0.579	−3.816	C	−2.705	2.524	−0.973	C	2.803	2.474	0.921
H	−0.435	1.424	−4.495	H	−2.868	3.587	−0.733	H	2.974	3.540	0.689
H	−0.078	−0.287	−4.186	H	−2.550	2.455	−2.057	H	2.689	2.391	2.012
H	−1.716	0.336	−3.904	H	−3.625	1.978	−0.734	H	3.707	1.917	0.640
C	−2.453	2.430	0.446	C	−1.426	0.113	3.170	C	1.307	0.159	−3.216
H	−2.678	1.987	1.426	H	−1.063	−0.906	3.343	H	0.916	−0.850	−3.403
H	−2.301	3.512	0.602	H	−1.094	0.728	4.020	H	0.959	0.805	−4.039
H	−3.341	2.294	−0.188	H	−2.521	0.079	3.174	H	2.403	0.100	−3.262

Table S-3-4 transition state structures of complex **4**

Ru(TS) (**4**)									
B3LYP				B1B95			PBE1PBE		
	x	y	z	x	y	z	x	y	z
Ru	−0.350	−1.657	0.000	Ru	−0.415	−1.604	0.000	Ru	−0.446	−1.598	0.000
Ru	−0.724	1.248	0.000	Ru	−0.578	1.242	0.000	Ru	−0.587	1.261	0.000
C	1.423	−3.199	0.000	C	1.170	−3.244	0.000	C	1.121	−3.269	0.000

C	1.428	2.028	0.000	C	1.530	1.955	0.000	C	1.525	1.926	0.000
C	1.558	−2.369	1.148	C	1.367	−2.430	1.139	C	1.333	−2.455	1.146
C	1.558	−2.369	−1.148	C	1.367	−2.430	−1.139	C	1.333	−2.455	−1.146
C	1.776	−1.013	0.732	C	1.672	−1.098	0.726	C	1.666	−1.127	0.729
C	1.776	−1.013	−0.732	C	1.672	−1.098	−0.726	C	1.666	−1.127	−0.729
C	1.807	1.422	1.277	C	1.843	1.323	1.275	C	1.865	1.294	1.274
C	1.807	1.422	−1.277	C	1.843	1.323	−1.275	C	1.865	1.294	−1.274
C	1.970	0.109	1.634	C	1.905	0.006	1.631	C	1.937	−0.024	1.630
C	1.970	0.109	−1.634	C	1.905	0.006	−1.631	C	1.937	−0.024	−1.630
H	1.262	−4.274	0.000	H	0.943	−4.305	0.000	H	0.869	−4.326	0.000
H	1.514	−2.711	−2.179	H	1.295	−2.759	−2.178	H	1.256	−2.790	−2.178
H	1.917	2.146	−2.091	H	1.974	2.040	−2.090	H	2.023	2.008	−2.090
C	2.246	−0.223	−3.081	C	2.069	−0.331	−3.080	C	2.166	−0.374	−3.071
H	2.473	0.682	−3.661	H	2.330	0.554	−3.670	H	2.457	0.510	−3.653
H	3.092	−0.923	−3.181	H	2.842	−1.096	−3.232	H	2.950	−1.139	−3.182
H	1.369	−0.705	−3.549	H	1.126	−0.733	−3.486	H	1.246	−0.781	−3.526
C	2.246	−0.223	3.081	C	2.069	−0.331	3.080	C	2.166	−0.374	3.071
H	2.473	0.682	3.661	H	2.330	0.554	3.670	H	2.457	0.510	3.653
H	1.369	−0.705	3.549	H	1.126	−0.733	3.486	H	1.246	−0.781	3.526
H	3.092	−0.923	3.181	H	2.842	−1.096	3.232	H	2.950	−1.139	3.182
C	1.575	3.548	0.000	C	1.750	3.454	0.000	C	1.782	3.423	0.000
H	1.112	3.998	−0.890	H	1.307	3.920	−0.882	H	1.350	3.903	−0.889
H	1.112	3.998	0.890	H	1.307	3.920	0.882	H	1.350	3.903	0.889
H	2.645	3.827	0.000	H	2.827	3.685	0.000	H	2.867	3.626	0.000
H	1.514	−2.711	2.179	H	1.295	−2.759	2.178	H	1.256	−2.790	2.178
H	1.917	2.146	2.091	H	1.974	2.040	2.090	H	2.023	2.008	2.090
C	−1.050	1.070	−1.954	C	−0.910	1.055	−1.934	C	−0.922	1.106	−1.935
O	−1.297	1.018	−3.077	O	−1.145	0.985	−3.054	O	−1.174	1.070	−3.055
C	−1.696	−1.852	−1.333	C	−1.792	−1.695	−1.306	C	−1.805	−1.679	−1.312
C	−1.696	−1.852	1.333	C	−1.792	−1.695	1.306	C	−1.805	−1.679	1.312
C	−1.050	1.070	1.954	C	−0.910	1.055	1.934	C	−0.922	1.106	1.935
C	−1.489	2.971	0.000	C	−1.300	2.966	0.000	C	−1.273	2.995	0.000
O	−2.486	−2.042	2.155	O	−2.622	−1.741	2.102	O	−2.620	−1.796	2.119
O	−2.486	−2.042	−2.155	O	−2.622	−1.741	−2.102	O	−2.620	−1.796	−2.119
O	−1.297	1.018	3.077	O	−1.145	0.985	3.054	O	−1.174	1.070	3.055
	−2.010	4.003	0.000	O	−1.790	4.007	0.000	O	−1.747	4.046	0.000

S-4 Thermodynamic parameters for **3** and **4** by DFT calculation with three functionals.

The estimation for the thermodynamic parameters of DFT calculation

The calculated thermodynamic parameters for the target complexes were obtained by DFT methodologies using Gaussian 03. Introduction for these calculations was reported by "*Thermochemistry in Gaussian*" on their web site; http://www.gaussian.com/g_whitepap/thermo/thermo.pdf. The Gaussian's output using option (Freq=anal) offers the thermodynamic parameters at 298.15 K temperature under 1 atm pressure. The following in an example of the output files showing the thermodynamic data under these conditions for the ground state of complex **3**, which was obtained by using B3LYP functional.

^^

- Thermochemistry -

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Atom 1 has atomic number 6 and mass 12.00000
Atom 2 has atomic number 6 and mass 12.00000
Atom 3 has atomic number 6 and mass 12.00000
Atom 4 has atomic number 6 and mass 12.00000
Atom 5 has atomic number 6 and mass 12.00000
Atom 6 has atomic number 6 and mass 12.00000
Atom 7 has atomic number 6 and mass 12.00000
Atom 8 has atomic number 6 and mass 12.00000
Atom 9 has atomic number 6 and mass 12.00000
Atom 10 has atomic number 6 and mass 12.00000
Atom 11 has atomic number 1 and mass 1.00783
Atom 12 has atomic number 1 and mass 1.00783
Atom 13 has atomic number 6 and mass 12.00000
Atom 14 has atomic number 1 and mass 1.00783
Atom 15 has atomic number 26 and mass 55.93494
Atom 16 has atomic number 26 and mass 55.93494
Atom 17 has atomic number 6 and mass 12.00000
Atom 18 has atomic number 8 and mass 15.99491
Atom 19 has atomic number 6 and mass 12.00000
Atom 20 has atomic number 8 and mass 15.99491
Atom 21 has atomic number 6 and mass 12.00000
Atom 22 has atomic number 8 and mass 15.99491
Atom 23 has atomic number 6 and mass 12.00000
Atom 24 has atomic number 8 and mass 15.99491
Atom 25 has atomic number 6 and mass 12.00000
Atom 26 has atomic number 8 and mass 15.99491
Atom 27 has atomic number 1 and mass 1.00783
Atom 28 has atomic number 1 and mass 1.00783
Atom 29 has atomic number 1 and mass 1.00783
Atom 30 has atomic number 1 and mass 1.00783
Atom 31 has atomic number 1 and mass 1.00783
Atom 32 has atomic number 6 and mass 12.00000
Atom 33 has atomic number 1 and mass 1.00783
Atom 34 has atomic number 1 and mass 1.00783
Atom 35 has atomic number 1 and mass 1.00783

```
 Atom 36 has atomic number    6 and mass    12.00000
 Atom 37 has atomic number    1 and mass     1.00783
 Atom 38 has atomic number    1 and mass     1.00783
 Atom 39 has atomic number    1 and mass     1.00783
 Molecular mass:     421.95400 amu.
 Principal axes and moments of inertia in atomic units:
                                1             2             3
      EIGENVALUES --    6506.70010    7921.64284    9122.56765
            X                1.00000     0.00104    -0.00277
            Y               -0.00088     0.99834     0.05752
            Z                0.00283    -0.05751     0.99834
 This molecule is an asymmetric top.
 Rotational symmetry number    1.
 Warning -- assumption of classical behavior for rotation
            may cause significant error
 Rotational temperatures (Kelvin)          0.01331       0.01093       0.00949
 Rotational constants (GHZ):               0.27737       0.22782       0.19783
 Zero-point vibrational energy         721238.9 (Joules/Mol)
                                       172.38024 (Kcal/Mol)
 Warning -- explicit consideration of    47 degrees of freedom as
            vibrations may cause significant error
 Vibrational temperatures:      50.11      57.80      99.35     108.98     113.27
           (Kelvin)            120.02     140.10     141.19     151.34     172.19
                               180.88     202.37     234.80     240.57     248.18
                               258.50     275.10     285.79     309.55     349.14
                               403.44     425.87     445.25     457.53     478.82
                               521.59     541.17     557.17     588.79     615.58
                               637.66     647.50     669.63     673.06     707.61
                               709.94     720.37     735.99     751.69     771.49
                               787.31     795.69     814.57     822.35     840.84
                               864.92     876.01     896.43     906.83     928.02
                               940.98     998.72    1029.48    1196.98    1233.83
                              1238.63    1248.36    1300.96    1320.39    1354.64
                              1387.21    1436.75    1453.90    1501.61    1505.09
                              1516.11    1518.96    1541.35    1548.89    1604.40
                              1705.68    1711.12    1765.94    1817.06    1924.07
                              1963.87    1977.70    2011.95    2014.17    2019.47
                              2035.28    2065.96    2084.34    2089.36    2102.06
                              2107.28    2113.32    2117.04    2147.08    2171.49
                              2233.59    2436.14    2905.81    2910.78    2947.58
                              2952.48    3017.81    4337.62    4341.42    4354.82
                              4419.82    4441.99    4460.77    4491.22    4499.86
                              4502.80    4517.64    4529.96    4660.43    4681.26
                              4692.36

 Zero-point correction=                           0.274705 (Hartree/Particle)
 Thermal correction to Energy=                    0.300116
 Thermal correction to Enthalpy=                  0.301061
 Thermal correction to Gibbs Free Energy=         0.220745
 Sum of electronic and zero-point Energies=      -1317.036267
 Sum of electronic and thermal Energies=         -1317.010856
 Sum of electronic and thermal Enthalpies=       -1317.009911
 Sum of electronic and thermal Free Energies=    -1317.090228

                    E (Thermal)             Cv                   S
                     KCal/Mol        Cal/Mol-Kelvin       Cal/Mol-Kelvin
 Total                188.326             95.212              169.039
Electronic              0.000              0.000                0.000
 Translational          0.889              2.981               44.010
 Rotational             0.889              2.981               34.507
 Vibrational          186.548             89.250               90.522
```

Table S-4-A

Table S-4-B

From the above Gaussian's output, we obtained the thermodynamic parameters as shown in Table S-4-A.

Table S-4-A		
entry		the values of energy (Hartree/Particle)
0	The total electronic energy	-1317.310972
1	Zero-point correction	0.274705
2	Thermal correction to Energy	0.300116
3	Thermal correction to Enthalpy	0.301061
4	Thermal correction to Gibbs Free Energy	0.220745
5	Sum of electronic and zero-point Energies	-1317.036267
6	Sum of electronic and thermal Energies	-1317.010856
7	Sum of electronic and thermal Enthalpies	-1317.009911
8	Sum of electronic and thermal Free Energies	-1317.090228

The data summarized in entries 1-8 are those described in the output file shown in page 14. The content of entry 0 is listed in the other part of the same output file, which is not described in this supporting information.

Each entry on this table shows the following value:

1: The zero-point energy is calculated using only the non-imaginary frequencies.

2: Internal thermal correction to energy (E_{tot}) collects the internal thermal energies from translation, rotation, molecular vibration and electronic motion partition functions:

$$E_{tot} = E_t + E_r + E_v + E_e \quad \text{(eq.S-1)}$$

E_t: internal thermal energy due to translation
E_r: internal thermal energy due to rotation (for non linear polyatomic molecule)
E_v: internal thermal energy due to molecular vibration
E_e: internal thermal energy due to electronic motion

We demonstrate the each internal thermal energy on Table S-4-B.

Thermal correction to entropy (S_{tot}) can also be obtained from corresponding four contributions:

$$S_{tot} = S_t + S_r + S_v + S_e \quad \text{(eq.S-2)}$$

S_t : the entropy contribution due to translation
S_r : the entropy contribution due to rotation
(for non linear polyatomic molecule)
S_v : the entropy contribution due to molecular vibration

S_e : the entropy contribution due to electronic motion

3: Internal thermal correction to Enthalpy (H_{corr}) summate thermal correction to energy E_{tot} and Boltzmann's temperature (k_BT) where k_B is Boltzmann's constant.

$$H_{corr} = E_{tot} + k_BT \quad \text{(eq.S-3)}$$

4: Internal thermal correction to Gibbs Free Energy (G_{corr}) can be derived as following standard relation:

$$G_{\text{corr}} = H_{\text{corr}} - TS_{\text{tot}} \quad \text{(eq. S-4)}$$

The total electronic energy (ε_0) added to zero-point Energies (1), internal thermal energies (2), internal enthalpies (3) and internal thermal Gibbs free energies (4) make entries 5-8, respectively.

Table S-4-A2 Total electronic energies, zero-point energies, thermal energies, thermal enthalpies and thermal Gibbs free energies on ground state for complexes **3** using B3LYP functional at 298.15K under 1atm.

	Ground state (B3LYP)
ε_0 (au.)	-1317.31097
ZP (au.)	-1317.03627
E_{thrm} (au.)	-1317.01086
H (au.)	-1317.00991
G (au.)	-1317.09023

Table S-4-B shows the each internal energy in eq. S-1. These energies convert to KCal/Mol or Cal/Mol-Kelvin unit using the relation of physical constant; 1Hartree = 627.50959 kcal.

Table S-4-B

entry	Motion	E(Thermal) KCal/Mol	C_V Cal/Mol-Kelvin	S Cal/Mol-Kelvin
1	Total	188.326	95.212	169.039
2	Electronic	0.000	0.000	0.000
3	Translational	0.889	2.981	44.010
4	Rotational	0.889	2.981	34.507
5	Vibrational	186.548	89.250	90.522

These data show the parameters which are necessary for the estimation of ΔE_{therm}, ΔH, ΔG and ΔS. In similar fashion, the data of **3** and **4** on ground states and transition states calculated by using B3LYP, B1B95 and PBE1PBE functionals are summarized in Table S-4-1 and Table S-4-2, which includes the data of **3** described above for comparison. Estimated ΔE_{therm}, ΔH, ΔG and ΔS by these data are summarized in Table S-4-3.

Table S-4-1. Internal thermal total entropy (S_{tot}) for complexes **3** and **4** using three density functional; B3LYP, B1B95 and PBE1PBE at 298.15K under 1atm.

	Ground state （298.15K）						Transition state（298K）					
Complex	**3** (Fe)			**4** (Ru)			**3** (Fe)			**4** (Ru)		
Function	B3LYP	B1B95	PBE1PBE	B3LYP	B1B95	PBE1PBE	B3LYP	B1B95	PBE1PBE	B3LYP	B1B95	PBE1PBE
S_{tot} (cal/mol·K)	169.039	166.454	166.821	176.134	173.238	173.285	167.747	167.851	165.222	179.970	176.249	178.433
S_t (cal/mol·K)	44.010	44.010	44.010	44.597	44.597	44.597	44.010	44.010	44.010	44.597	44.597	44.597
S_r (cal/mol·K)	34.507	34.386	34.417	34.940	34.826	34.850	34.532	34.415	34.423	34.952	34.826	34.862
S_v (cal/mol·K)	90.522	88.059	88.395	96.597	93.815	93.837	89.205	89.427	86.790	100.421	96.826	98.974
S_e (cal/mol·K)	0	0	0	0	0	0	0	0	0	0	0	0

Table S-4-2. Total electronic energies, zero-point energies, thermal energies, thermal enthalpies and thermal Gibbs free energies on ground states and transition states for complexes **3** and **4** using three density functional; B3LYP, B1B95 and PBE1PBE at 298.15K under 1atm.

	3 (Fe)						**4** (Ru)					
	B3LYP		BIB95		PBE1PBE		B3LYP		BIB95		PBE1PBE	
	Ground state	Transition state	Ground state	Transition state	Ground state	Transition state	Ground state	Transition state	Ground state	Transition state	Ground state	Transition state
ε_0 (au.)	-1317.31097	-1317.26772	-1316.87649	-1316.82412	-1316.00850	-1315.95542	-1258.62056	-1258.59021	-1258.11341	-1258.07308	-1257.38182	-1257.34276
ZP (au.)	-1317.03627	-1316.99459	-1316.59815	-1316.54801	-1315.73043	-1315.67942	-1258.34841	-1258.31896	-1257.83786	-1257.79873	-1257.10646	-1257.06847
E_{thrm} (au.)	-1317.01086	-1316.96953	-1316.57333	-1316.52319	-1315.70553	-1315.65481	-1258.32196	-1258.29206	-1257.81195	-1257.77291	-1257.08056	-1257.04202
H (au.)	-1317.00991	-1316.96859	-1316.57238	-1316.52224	-1315.70459	-1315.65386	-1258.32102	-1258.29111	-1257.81100	-1257.77196	-1257.07962	-1257.04107
G (au.)	-1317.09023	-1317.04829	-1316.65147	-1316.60197	-1315.78385	-1315.73236	-1258.40471	-1258.37662	-1257.89331	-1257.85571	-1257.16195	-1257.12585

Table S-4-3. Thermodynamic parameters for **3** and **4** by DFT calculation with three functionals.(at 298.15K)

Complex	**3** (Fe)			**4** (Ru)		
	B3LYP	BIB95	PBE1PBE	B3LYP	BIB95	PBE1PBE
K	298.15	298.15	298.15	298.15	298.15	298.15
ΔE_{thrm} (kcal/mol.)	25.93	31.46	31.83	18.77	24.50	24.19
ΔH (kcal/mol.)	25.93	31.46	31.83	18.77	24.50	24.19
ΔG (kcal/mol.)	26.32	31.06	32.31	17.62	23.60	22.65
ΔS (cal/mol.)	-1.29	1.35	-1.60	3.84	3.01	5.15

In similar ways, the following procedures gave the thermodynamic parameters at 373K, which is in our experimental condition on the present study, using freqchk utility program.

Then, we used the total electronic energy (ε_0), which is not related to thermal factor, was obtained at the result of condition at 298.15K.

A representative freqchk's output file is shown in p19-20, tables of parameters are summarized in p21-23.

^^

```
-------------------
 - Thermochemistry -
 -------------------
 Temperature     373.000 Kelvin.  Pressure     1.00000 Atm.
 Molecular mass:     421.95400 amu.
 Principal axes and moments of inertia in atomic units:
                                1             2             3
       EIGENVALUES --   6506.70010   7921.64284   9122.56765
                  X        0.76711     -0.47082     -0.43574
                  Y        0.18063     -0.49323      0.85094
                  Z        0.61556      0.73147      0.29333
 This molecule is an asymmetric top.
 Rotational symmetry number    1.
 Warning -- assumption of classical behavior for rotation
            may cause significant error
 Rotational temperatures (Kelvin)          0.01331       0.01093       0.00949
 Rotational constants (GHZ):               0.27737       0.22782       0.19783
 Zero-point vibrational energy          721238.9 (Joules/Mol)
                                        172.38024 (Kcal/Mol)
 Warning -- explicit consideration of   53 degrees of freedom as
            vibrations may cause significant error
 Vibrational temperatures:         50.11        57.80        99.35       108.98       113.27
           (Kelvin)                120.02       140.10       141.19       151.34       172.19
                                   180.88       202.37       234.80       240.57       248.18
                                   258.50       275.10       285.79       309.55       349.14
                                   403.44       425.87       445.25       457.53       478.82
                                   521.59       541.17       557.17       588.79       615.58
                                   637.66       647.50       669.63       673.06       707.61
```

709.94	720.37	735.99	751.69	771.49
787.31	795.69	814.57	822.35	840.84
864.92	876.01	896.43	906.83	928.02
940.98	998.72	1029.48	1196.98	1233.83
1238.63	1248.36	1300.96	1320.39	1354.64
1387.21	1436.75	1453.90	1501.61	1505.09
1516.11	1518.96	1541.35	1548.89	1604.40
1705.68	1711.12	1765.94	1817.06	1924.07
1963.87	1977.70	2011.95	2014.17	2019.47
2035.28	2065.96	2084.34	2089.36	2102.06
2107.28	2113.32	2117.04	2147.08	2171.49
2233.59	2436.14	2905.81	2910.78	2947.58
2952.48	3017.81	4337.62	4341.42	4354.82
4419.82	4441.99	4460.77	4491.22	4499.86
4502.80	4517.64	4529.96	4660.43	4681.26
4692.36				

Zero-point correction= 0.274705 (Hartree/Particle)
Thermal correction to Energy= 0.312442
Thermal correction to Enthalpy= 0.313624
Thermal correction to Gibbs Free Energy= 0.199161

	E (Thermal) KCal/Mol	C_V Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	196.061	111.055	192.563
Electronic	0.000	0.000	0.000
Translational	1.112	2.981	45.122
Rotational	1.112	2.981	35.175
Vibrational	193.837	105.094	112.266

Table S-4-4. Internal thermal total energy (E_{tot}) for complexes **3** and **4** using three density functional; B3LYP, B1B95 and PBE1PBE at 373K under 1atm.

	Ground state						Transition state					
Complex	**3** (Fe)			**4** (Ru)			**3** (Fe)			**4** (Ru)		
Function	B3LYP	B1B95	PBE1PBE	B3LYP	B1B95	PBE1PBE	B3LYP	B1B95	PBE1PBE	B3LYP	B1B95	PBE1PBE
E_{tot} (kcal/mol)	196.061	197.888	197.755	195.250	196.974	196.834	194.779	196.418	196.408	195.003	196.049	196.552
E_t (kcal/mol)	1.112	1.112	1.112	1.112	1.112	1.112	1.112	1.112	1.112	1.112	1.112	1.112
E_r (kcal/mol)	1.112	1.112	1.112	1.112	1.112	1.112	1.112	1.112	1.112	1.112	1.112	1.112
E_v (kcal/mol)	193.837	195.664	195.531	193.026	194.750	194.610	192.555	194.195	194.184	192.779	193.825	194.329
E_v (kcal/mol)	0	0	0	0	0	0	0	0	0	0	0	0

Table S-4-5. Internal thermal total entropy (S_{tot}) for complexes **3** and **4** using three density functional; B3LYP, B1B95 and PBE1PBE at 373K under 1atm.

	Ground state						Transition state					
Complex	**3** (Fe)			**4** (Ru)			**3** (Fe)			**4** (Ru)		
Function	B3LYP	B1B95	PBE1PBE	B3LYP	B1B95	PBE1PBE	B3LYP	B1B95	PBE1PBE	B3LYP	B1B95	PBE1PBE
S_{tot} (cal/mol·K)	192.563	189.735	190.059	200.086	196.960	196.980	190.997	190.933	188.240	204.009	199.636	202.255
S_t (cal/mol·K)	45.122	45.122	45.122	45.710	45.710	45.710	45.122	45.122	45.122	45.710	45.710	45.710
S_r (cal/mol·K)	35.175	35.053	35.084	35.607	35.493	35.518	35.200	35.083	35.090	35.619	35.493	35.529
S_v (cal/mol·K)	112.266	109.559	109.852	118.769	115.756	115.752	110.674	110.728	108.028	122.680	118.433	121.016
S_e (cal/mol·K)	0	0	0	0	0	0	0	0	0	0	0	0

Table S-4-6. Internal thermal total energies, enthalpies and thermal Gibbs free energies on ground states and transition states for complexes **3** and **4** using three density functional; B3LYP, B1B95 and PBE1PBE at 373K under 1atm.

	3 (Fe)						**4** (Ru)					
	B3LYP		BIB95		PBE1PBE		B3LYP		BIB95		PBE1PBE	
	Ground state	Transition state	Ground state	Transition state	Ground state	Transition state	Ground state	Transition state	Ground state	Transition state	Ground state	Transition state
E_{tot} (au.)	0.312442	0.31040	0.315355	0.31301	0.31514	0.31300	0.31115	0.310757	0.31390	0.312424	0.31368	0.313226
H_{corr} (au.)	0.313624	0.31158	0.316536	0.31419	0.31632	0.31418	0.31233	0.311938	0.31508	0.313605	0.31486	0.314407
G_{corr} (au.)	0.199161	0.19805	0.203755	0.20070	0.20335	0.20228	0.19340	0.190673	0.19800	0.194938	0.19777	0.194184

Table S-4-7. Total thermal energies, thermal enthalpies and thermal Gibbs free energies on ground states and transition states for complexes **3** and **4** using three density functional; B3LYP, B1B95 and PBE1PBE at 373K under 1atm.

	3 (Fe)						**4** (Ru)					
	B3LYP		BIB95		PBE1PBE		B3LYP		BIB95		PBE1PBE	
	Ground state	Transition state	Ground state	Transition state	Ground state	Transition state	Ground state	Transition state	Ground state	Transition state	Ground state	Transition state
E_{thrm} (au.)	-1316.99853	-1316.95732	-1316.56113	-1316.51111	-1315.69336	-1315.64242	-1258.30941	-1258.27946	-1257.79952	-1257.76066	-1257.06815	-1257.02953
H (au.)	-1316.99735	-1316.95614	-1316.55995	-1316.50992	-1315.69218	-1315.64124	-1258.30823	-1258.27828	-1257.79834	-1257.75947	-1257.06697	-1257.02835
G (au.)	-1317.11181	-1317.06967	-1316.67273	-1316.62342	-1315.80515	-1315.75313	-1258.42716	-1258.39954	-1257.91541	-1257.87814	-1257.18405	-1257.14857

Table S-4-8. Thermodynamic parameters for **3** and **4** by DFT calculation with three functionals at 373K under 1atm.

Complex	**3** (Fe)			**4** (Ru)		
	B3LYP	BIB95	PBE1PBE	B3LYP	BIB95	PBE1PBE
K	373	373	373	373	373	373
ΔE_{thrm} (kcal/mol.)	25.86	31.39	31.97	18.80	24.39	24.23
ΔH (kcal/mol.)	25.86	31.39	31.97	18.80	24.39	24.23
ΔG (kcal/mol.)	26.44	30.94	32.64	17.33	23.39	22.26
ΔS (cal/mol.)	-1.57	1.20	-1.82	3.92	2.68	5.28

1 (au) = 627.50959 (kcal)

The $\Delta E_{thrm,}$ ΔH, ΔG and ΔS estimated for 3 and 4 by the theoretical study at 373K (Table S-4-8) can be compared with those determined experimentally (Table S-4-9). $\Delta E_{thrm,}$ ΔH and ΔG of the complex 3 and 4 calculated by using the B3LYP functionale are smaller than those estimated using the B1B95 or PBE1PBE functionale. The PBE1PBE method provided ΔH, ΔG and ΔS for 4 close to those determine experimentally; however, these are substantial difference in ΔH and ΔG for 3 between the calculations and experiments. Although ΔH is often used as a standard for estimate the accuracy of the calculation, all of the ΔHs shown in Table S-4-8 are not very consistent with those determined experimentally. This may be attributed to the level of the calculation or solvent effect may be a part of the reasons. From the other standpoint, the ΔH, ΔG and ΔS of 4 calculated by using the PBE1PBE are roughly in accord with those determined experimentally; in contrast, the data of 3 determined experimentally are rather similar to those calculated by using the B3LYP. These seem to be attributed to the method to estimate the thermodynamic parameters of the iron and ruthenium complex.

At present stage, we concluded that the comparison in thermodynamic parameters between theory and experiment requires further investigation giving the calculation method guaranteed more accuracy.

Table S-4-9 Thermodynamic parameters for the rearrangements of **3** and **4** obtained by experimental study.

	3	**4**
$\Delta G^{\ddagger}_{373}$ (kcal mol^{-1})	25±1	23±1
$\Delta H^{\ddagger}$ (kcal mol^{-1})	22±1	25±1
$\Delta S^{\ddagger}$ (cal mol^{-1} K^{-1})	-7±1	7±1

Determined by the SST experiments. Experimental errors were determined by the least squares of the Eyring plot. Note that the T1, which is the basis to calculate k, contains ~10% experimental errors.