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Computational and experimental study on the electrocatalytic reduction of CO_2 to CO by a new mononuclear ruthenium(II) complex

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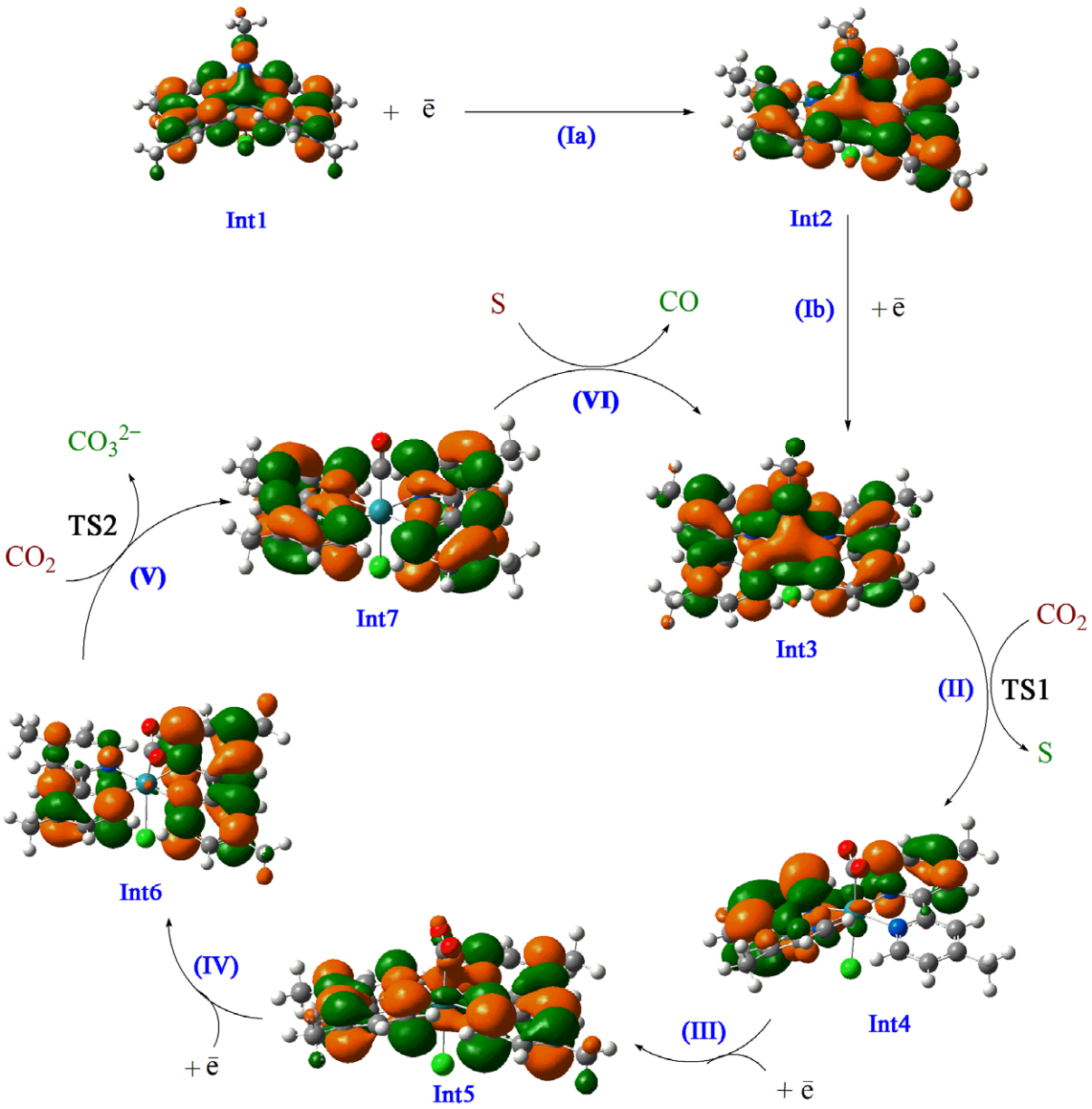
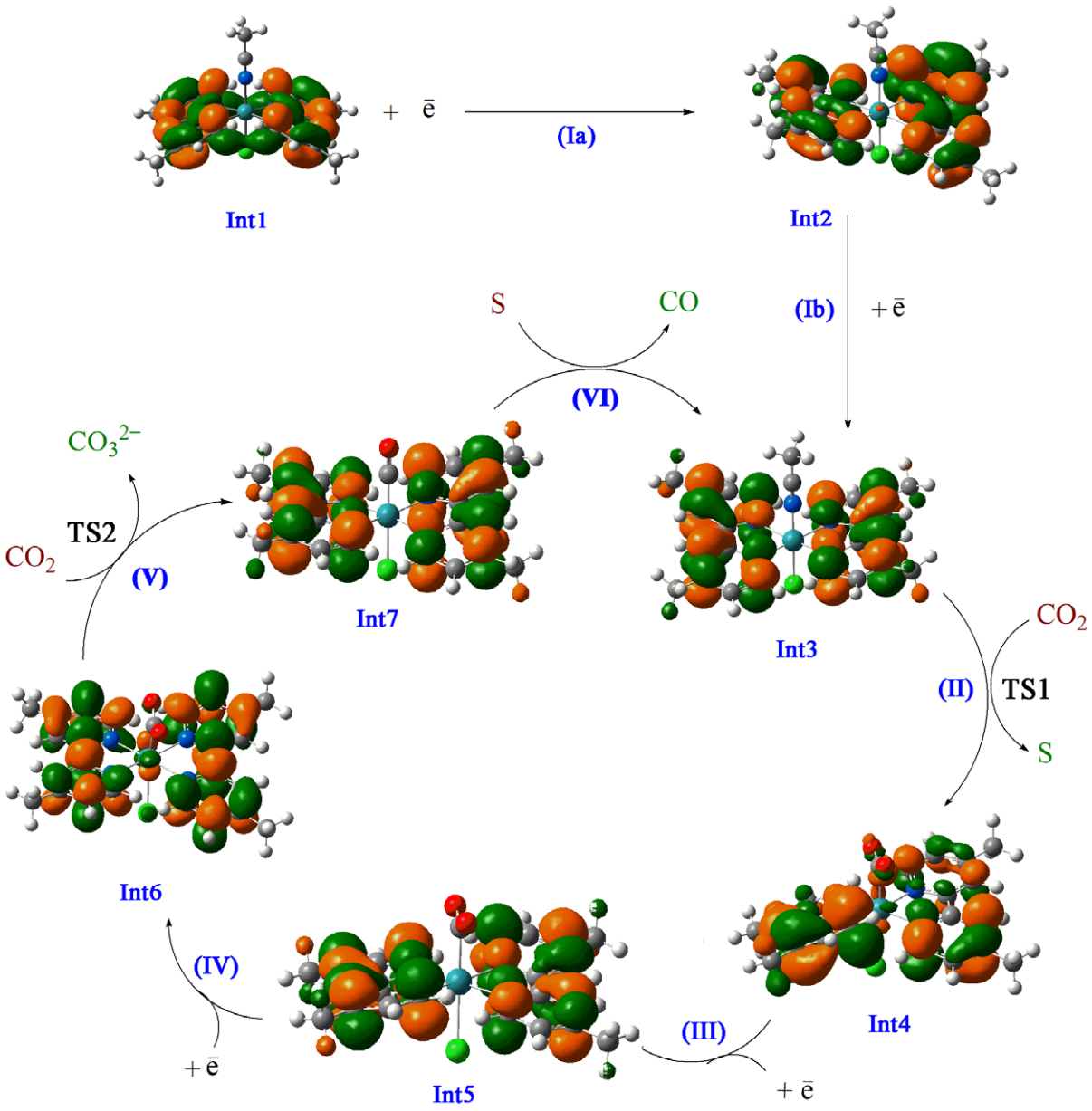
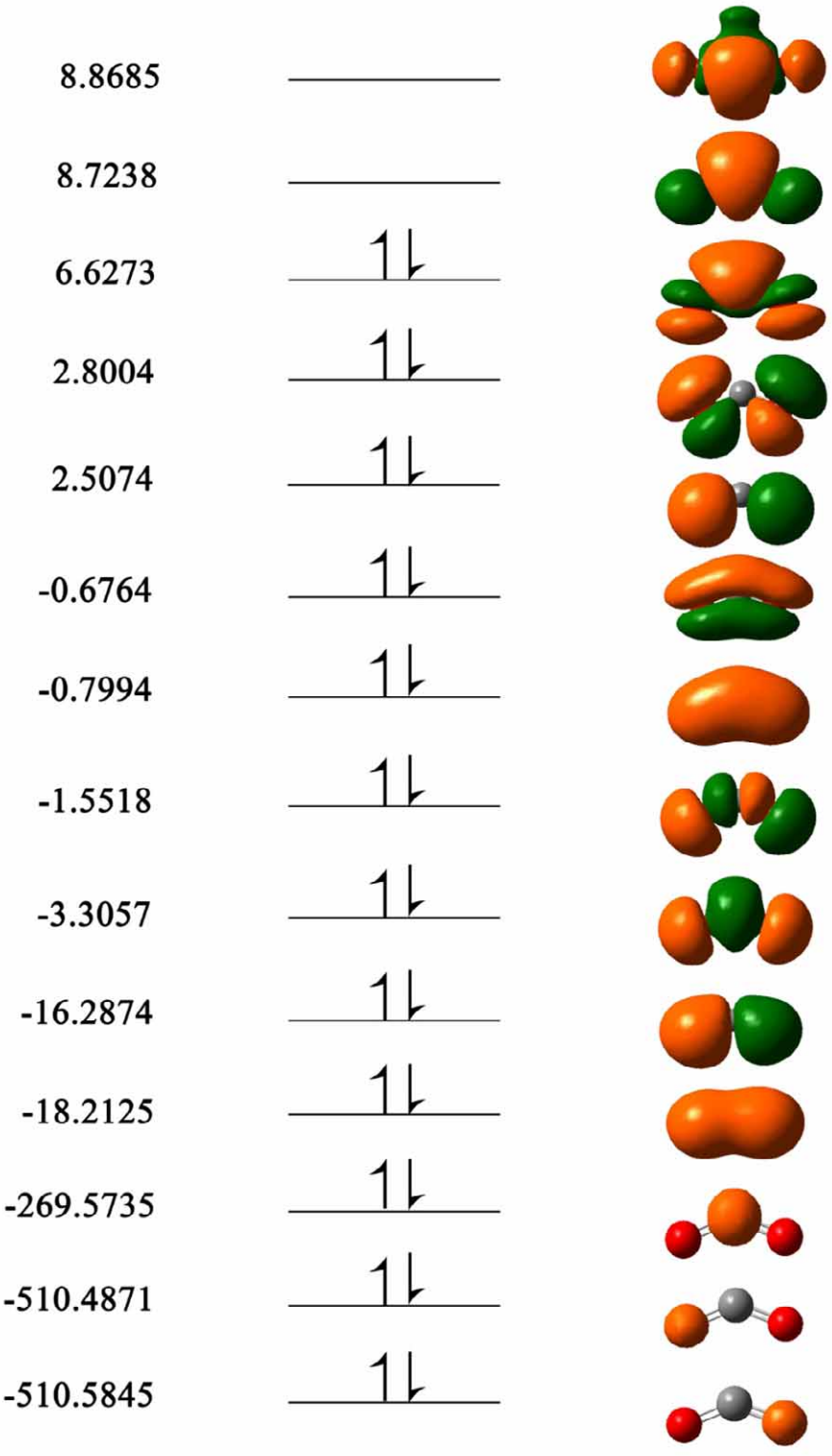


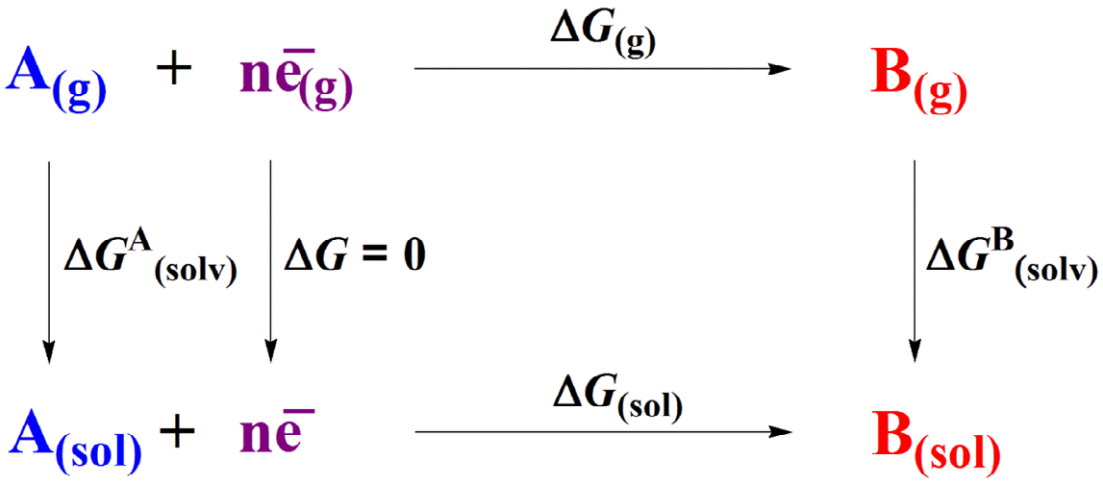
Scheme S1 The schematic representation of HOMOs of the species in the proposed mechanism for the electrocatalytic reduction of CO_2 by the Ru(II) complex.



Scheme S2 The schematic representation of LUMOs of the species in the proposed mechanism for electrocatalytic reduction of CO_2 by the Ru(II) complex.



Scheme S3 Schematic representation of the calculated molecular-orbitals in CO_2^{2-} (bent geometry) with their energy levels (eV).



Scheme S4 Thermodynamic cycle for a typical reaction. In the proposed catalytic cycle, **n** can be 0 (steps **II**, **V** and **VI**) or 1 (steps **I**, **III** and **IV**). It should be mentioned that in steps **II**, **V** and **VI**, there are more than one reactant (and also one product) but the overall pattern of eqns does not change.

Table S1

Mulliken atomic charges and their changes (Q(Int)) of the species presented in step **I** of the proposed mechanism

N	Atom	Q(Int(1))(N)	Q(Int(2))(N)	Q(Int(3))(N)	Q(Int(2))(N) – Q(Int(1))(N)	Q(Int(3))(N) – Q(Int(2))(N)
1	1Ru	–1.381091	–1.622468	–1.734969	–0.241377	–0.112501
2	2Cl	0.079096	0.075345	0.006317	–0.003751	–0.069028
3	3C	0.309381	0.150969	0.026933	–0.158412	–0.124036
4	4C	–0.448016	–0.583746	–0.708073	–0.13573	–0.124327
5	5C	0.292613	–0.011982	0.296101	–0.304595	0.308083
6	6C	–0.869607	–0.480664	–0.364215	0.388943	0.116449
7	7C	0.272685	0.307132	0.256172	0.034447	–0.05096
8	8C	0.314656	0.006295	0.021153	–0.308361	0.014858
9	9C	–0.443749	–0.617344	–0.759593	–0.173595	–0.142249
10	10C	0.295911	0.059086	0.226947	–0.236825	0.167861
11	11C	–0.872056	–0.233748	–0.488852	0.638308	–0.255104
12	12C	0.278399	0.184021	0.293679	–0.094378	0.109658
13	13H	0.193828	0.166699	0.147601	–0.027129	–0.019098
14	14H	0.204498	0.176369	0.151383	–0.028129	–0.024986
15	15H	0.145458	0.195986	0.100871	0.050528	–0.095115
16	16H	0.193802	0.167368	0.147738	–0.026434	–0.01963
17	17H	0.204495	0.174314	0.152509	–0.030181	–0.021805
18	18H	0.145143	0.133247	0.165481	–0.011896	0.032234
19	19N	0.362029	0.333449	0.482872	–0.02858	0.149423
20	20N	0.359443	0.478732	0.415665	0.119289	–0.063067
21	21C	–0.664175	–0.543967	–0.780325	0.120208	–0.236358
22	22H	0.223568	0.216503	0.202214	–0.007065	–0.014289
23	23H	0.227915	0.202624	0.191337	–0.025291	–0.011287
24	24H	0.251836	0.224852	0.211091	–0.026984	–0.013761
25	25C	–0.66409	–0.718711	–0.701356	–0.054621	0.017355
26	26H	0.227997	0.201987	0.191476	–0.02601	–0.010511
27	27H	0.223536	0.21542	0.201989	–0.008116	–0.013431
28	28H	0.251825	0.226305	0.210812	–0.02552	–0.015493
29	29C	0.309829	0.208054	0.032935	–0.101775	–0.175119
30	30C	0.272916	0.366036	0.289623	0.09312	–0.076413
31	31C	–0.877847	–0.78129	–0.488775	0.096557	0.292515
32	32C	0.294726	0.151926	0.22816	–0.1428	0.076234
33	33C	–0.446764	–0.88426	–0.749717	–0.437496	0.134543
34	34C	0.317363	0.419594	0.017362	0.102231	–0.402232
35	35C	0.275548	0.338868	0.262175	0.06332	–0.076693
36	36C	–0.882026	–0.795202	–0.372944	0.086824	0.422258
37	37C	0.297088	0.242805	0.294709	–0.054283	0.051904
38	38C	–0.441419	–0.470133	–0.703748	–0.028714	–0.233615
39	39H	0.144845	0.194428	0.165464	0.049583	–0.028964
40	40H	0.204509	0.184112	0.152515	–0.020397	–0.031597
41	41H	0.193811	0.176735	0.147707	–0.017076	–0.029028
42	42H	0.144921	0.138991	0.100938	–0.00593	–0.038053
43	43H	0.204498	0.18389	0.151435	–0.020608	–0.032455
44	44H	0.193826	0.175367	0.147635	–0.018459	–0.027732
45	45N	0.360183	0.326756	0.480453	–0.033427	0.153697
46	46N	0.362171	0.417124	0.414187	0.054953	–0.002937
47	47C	–0.664014	–0.621479	–0.704266	0.042535	–0.082787
48	48H	0.251814	0.235997	0.210873	–0.015817	–0.025124
49	49H	0.228067	0.208308	0.191514	–0.019759	–0.016794
50	50H	0.223516	0.21272	0.201833	–0.010796	–0.010887
51	51C	–0.663649	–0.65161	–0.780116	0.012039	–0.128506
52	52H	0.227989	0.208227	0.191374	–0.019762	–0.016853
53	53H	0.251833	0.233225	0.211133	–0.018608	–0.022092
54	54H	0.223539	0.213844	0.202116	–0.009695	–0.011728
55	55C	0.491291	0.380052	0.359897	–0.111239	–0.020155
56	56C	–1.258641	–1.175032	–1.218215	0.083609	–0.043183
57	57H	0.263418	0.253508	0.236137	–0.00991	–0.017371
58	58H	0.261563	0.249598	0.236044	–0.011965	–0.013554
59	59H	0.263107	0.248146	0.234453	–0.014961	–0.013693
60	60N	0.25666	0.326621	0.294153	0.069961	–0.032468

Table S2

Contribution of different parts of the intermediates involved in step **I** from the added negative charge (1ē). (Based on the data reported in Table S1)

$\sum_{N} Q(Int(i+1))(N) - Q(Int(i))(N)$ or $Q(Int(i+1))(N) - Q(Int(i))(N)$ (for step **Ia**, i = 1 and for step **Ib**, i = 2)	The change of Mulliken charge (or total Mulliken charge) values for different parts of intermediates involved in step **I**	Specification of the Ru and ligands using atomic numbering (N values in the first column) in the optimized structures of intermediates involved in step **I**
Q(Int(2))(1) – Q(Int(1))(1)	–0.241377	Ru
Q(Int(2))(2) – Q(Int(1))(2)	–0.003751	Cl
$\sum_{N=3}^{54} Q(Int(2))(N) - Q(Int(1))(N)$	–0.760369	dmb ligands
$\sum_{N=55}^{60} Q(Int(2))(N) - Q(Int(1))(N)$	0.005495	CH_3CN
Q(Int(3))(1) – Q(Int(2))(1)	–0.112501	Ru
Q(Int(3))(2) – Q(Int(2))(2)	–0.069028	Cl
$\sum_{N=3}^{54} Q(Int(3))(N) - Q(Int(2))(N)$	–0.678044	dmb ligands
$\sum_{N=55}^{60} Q(Int(3))(N) - Q(Int(2))(N)$	–0.140424	CH_3CN

Table S3

Calculated molecular orbital energies (eV) of the species

Orbital	*trans*-[Ru(dmb)$_2$(Cl)(EtOH)]$^+$	**Int1**	**Int2**	**Int3**	**Int4**	**Int5**	**Int6**	**Int7**
LUMO+5	–3.694	–3.644	–0.300	2.289	2.091	4.611	6.257	2.174
LUMO+4	–3.760	–3.646	–0.358	2.279	2.041	4.456	6.074	2.141
LUMO+3	–3.934	–3.675	–0.537	2.172	1.877	4.091	5.982	2.083
LUMO+2	–4.120	–4.026	–0.858	2.154	1.727	4.079	5.221	2.055
LUMO+1	–4.586	–4.480	–1.068	1.994	1.531	3.966	5.182	2.026
LUMO	–4.928	–4.717	–1.931	1.788	0.706	3.959	5.116	1.737
HOMO	–7.504	–7.605	–2.745	0.031	–0.128	2.615	4.924	–0.292
HOMO–1	–7.734	–7.836	–4.545	–0.161	–1.138	2.428	4.478	–0.446
HOMO–2	–8.336	–8.367	–4.778	–1.561	–2.029	1.761	4.127	–2.511
HOMO–3	–9.007	–8.934	–5.263	–1.849	–2.052	0.950	3.404	–2.681
HOMO–4	–9.345	–9.041	–5.927	–2.198	–2.525	0.830	2.536	–2.974
HOMO–5	–9.566	–9.394	–6.086	–3.078	–3.130	0.491	2.442	–3.473

Table S4

Mulliken atomic charges (Q(**Int**)) of the species presented in steps **III** and **IV** of the proposed mechanism

N	Atom	Q(Int4)(N)	Q(Int5)(N)	Q(Int6)(N)	Q(Int5)(N) – Q(Int4)(N)	Q(Int6)(N) – Q(Int5)(N)
1	1Ru	–1.154373	–1.261666	–0.968879	–0.107293	0.292787
2	2Cl	–0.262416	–0.393286	–0.465222	–0.13087	–0.07194
3	3C	0.227388	0.334556	–0.370854	0.107168	–0.70541
4	4C	–0.758904	–0.793417	–1.249718	–0.034513	–0.4563
5	5C	0.078835	–0.069085	–2.241609	–0.14792	–2.17252
6	6C	–0.608771	–0.396261	0.772515	0.21251	1.168776
7	7C	0.467151	0.165123	–0.488538	–0.302028	–0.65366
8	8C	0.069962	0.293732	–0.581884	0.22377	–0.87562
9	9C	–0.434208	–0.682517	–0.782823	–0.248309	–0.10031
10	10C	0.226001	0.23088	–2.667903	0.004879	–2.89878
11	11C	–0.359738	–0.6531	0.926483	–0.293362	1.579583
12	12C	0.134007	0.258934	–0.505031	0.124927	–0.76397
13	13H	0.151781	0.135817	0.141153	–0.015964	0.005336
14	14H	0.157971	0.136305	0.132818	–0.021666	–0.00349
15	15H	0.198301	0.113477	0.131591	–0.084824	0.018114
16	16H	0.153009	0.137243	0.14306	–0.015766	0.005817
17	17H	0.15662	0.137401	0.136827	–0.019219	–0.00057
18	18H	0.160012	0.15493	0.130106	–0.005082	–0.02482
19	19N	0.257278	0.348884	0.363246	0.091606	0.014362
20	20N	0.277501	0.364341	0.334512	0.08684	–0.02983
21	21C	–0.735555	–0.84926	2.322425	–0.113705	3.171685
22	22H	0.211907	0.196494	0.19581	–0.015413	–0.00068
23	23H	0.193463	0.182983	0.191892	–0.01048	0.008909
24	24H	0.207415	0.196336	0.193144	–0.011079	–0.00319
25	25C	–0.748225	–0.701863	1.468094	0.046362	2.169957
26	26H	0.192294	0.182203	0.189715	–0.010091	0.007512
27	27H	0.208875	0.194201	0.191657	–0.014674	–0.00254
28	28H	0.211333	0.200606	0.196467	–0.010727	–0.00414
29	29C	0.58472	0.388057	–0.516781	–0.196663	–0.90484
30	30C	0.397251	0.16987	–0.432001	–0.227381	–0.60187
31	31C	–0.924913	–0.551736	0.866313	0.373177	1.418049
32	32C	–0.224516	0.106439	–1.274202	0.330955	–1.38064
33	33C	–0.895261	–0.824991	–1.191946	0.07027	–0.36696
34	34C	–0.021917	0.241617	–0.518316	0.263534	–0.75993
35	35C	0.239293	0.462255	–0.695331	0.222962	–1.15759
36	36C	–0.545769	–0.487555	1.624713	0.058214	2.112268
37	37C	0.157485	0.205774	–2.962149	0.048289	–3.16792
38	38C	–0.140134	–0.853039	–1.622994	–0.712905	–0.76996
39	39H	0.262403	0.159951	0.136864	–0.102452	–0.02309
40	40H	0.168908	0.137798	0.132886	–0.03111	–0.00491
41	41H	0.160884	0.135429	0.138324	–0.025455	0.002895
42	42H	0.125622	0.111051	0.131551	–0.014571	0.0205
43	43H	0.165208	0.136646	0.138988	–0.028562	0.002342
44	44H	0.162294	0.137636	0.150945	–0.024658	0.013309
45	45N	0.332472	0.333127	0.191447	0.000655	–0.14168
46	46N	0.357596	0.35505	0.250589	–0.002546	–0.10446
47	47C	–0.66982	–0.756714	2.747387	–0.086894	3.504101
48	48H	0.223349	0.199105	0.201062	–0.024244	0.001957
49	49H	0.198659	0.183245	0.202043	–0.015414	0.018798
50	50H	0.20195	0.194113	0.19039	–0.007837	–0.00372
51	51C	–0.722952	–0.761114	0.947324	–0.038162	1.708438
52	52H	0.195576	0.182508	0.189559	–0.013068	0.007051
53	53H	0.217203	0.198494	0.19243	–0.018709	–0.00606
54	54H	0.213424	0.195585	0.191807	–0.017839	–0.00378
55	55O	–0.434526	–0.477325	–0.490742	–0.042799	–0.01342
56	56C	0.542085	0.579494	0.516037	0.037409	–0.06346
57	57O	–0.205484	–0.26476	–0.275251	–0.059276	–0.01049

Table S5

Contribution of different parts of the intermediates involved in steps **III** and **IV** from the added negative charge (1ē). (Based on the data reported in Table S4)

$\sum_{N} Q(Int(i+1))(N) - Q(Int(i))(N)$ or $Q(Int(i+1))(N) - Q(Int(i))(N)$ (for step **III**, i = 4 and for step **IV**, i = 5)	The change of Mulliken charge (or total Mulliken charge) values for different parts of intermediates involved in steps **III** and **IV**	Specification of the Ru and ligands using atomic numbering (N values in the first column) in the optimized structures of intermediates involved in steps **III** and **IV**
Q(Int(5))(1) – Q(Int(4))(1)	–0.107293	Ru
Q(Int(5))(2) – Q(Int(4))(2)	–0.13087	Cl
$\sum_{N=3}^{54} Q(Int(5))(N) - Q(Int(4))(N)$	–0.697174	dmb ligands
$\sum_{N=55}^{57} Q(Int(5))(N) - Q(Int(4))(N)$	–0.064666	CO_2
Q(Int(6))(1) – Q(Int(5))(1)	0.292787	Ru
Q(Int(6))(2) – Q(Int(5))(2)	–0.07194	Cl
$\sum_{N=3}^{54} Q(Int(6))(N) - Q(Int(5))(N)$	–1.13349	dmb ligands
$\sum_{N=55}^{57} Q(Int(6))(N) - Q(Int(5))(N)$	–0.08737	CO_2

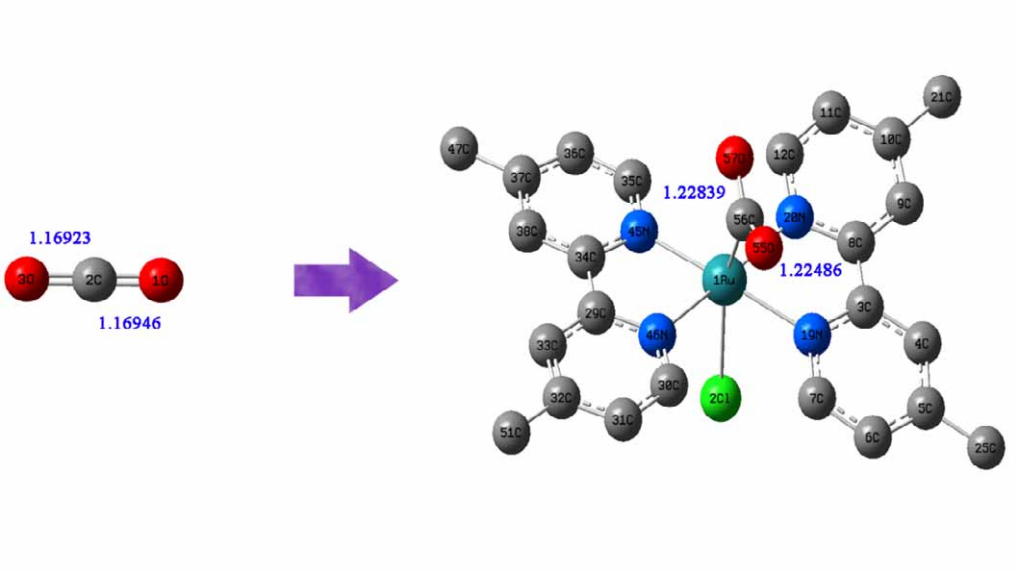


Fig. S1 The optimized structures of free CO_2 and **Int6** in the gas phase. The bond lengths are in angstroms.