

## Supplementary information

**Table S1** The B3LYP optimised coordinates for [1]<sup>+</sup> and [2]<sup>+</sup>

[1] <sup>+</sup>			
C	0.325392	-3.073295	-0.840570
N	-0.493616	-2.070318	-0.492040
C	-1.774473	-2.355603	-0.107960
C	-2.226243	-3.675280	-0.052897
C	-1.366449	-4.713499	-0.405095
C	-0.068478	-4.408587	-0.810133
Ru	-0.110457	0.002999	-0.538723
N	-1.997936	0.000155	0.052228
C	-2.625268	1.185146	0.211774
C	-3.967989	1.207738	0.597050
C	-4.633785	-0.002955	0.790580
C	-3.968288	-1.211943	0.585739
C	-2.625541	-1.186069	0.200692
C	-1.773992	2.357329	-0.086017
N	-0.493392	2.075211	-0.473267
C	0.325842	3.080936	-0.813205
C	-0.067402	4.416045	-0.770067
C	-1.364972	4.717707	-0.361275
C	-2.225109	3.676642	-0.018395
Cl	-0.979869	0.012760	-2.807438
N	2.014323	0.007285	-0.981515
N	2.764801	-0.002684	0.182658
C	4.121114	-0.000302	-0.089658
C	4.214368	0.011547	-1.461648
C	2.895999	0.016015	-1.985871
C	2.072125	-0.009614	1.391429
N	0.710485	-0.006851	1.298254
N	0.014824	-0.012490	2.426419
C	0.722886	-0.020849	3.577630
N	2.077246	-0.024441	3.669141
N	2.744006	-0.018396	2.532847
C	2.497624	0.027479	-3.426265
C	5.207316	-0.009196	0.935912
N	0.032708	-0.026311	4.733777
H	1.412756	0.047021	-3.540533
H	-0.975291	-0.024300	4.727792
H	2.927498	0.901699	-3.929302
H	2.893281	-0.860087	-3.934333
H	5.130732	0.016481	-2.034376
H	6.171608	-0.005952	0.421812
H	5.154358	0.863571	1.593697
H	5.152864	-0.892115	1.579872
H	0.536277	-0.032899	5.608221
H	1.319298	2.789843	-1.134822
H	0.631783	5.193728	-1.057409
H	-1.708059	5.746447	-0.316662
H	-3.242502	3.890394	0.288416
H	-4.493224	2.145980	0.731893
H	-5.677932	-0.004198	1.085937
H	-4.493778	-2.151259	0.711794
H	-3.243888	-3.891360	0.251423
H	-1.710062	-5.742445	-0.370406
H	0.630585	-5.183853	-1.104219

H 1.319390 -2.780039 -1.158536

[2]<sup>+</sup>

N	-4.014189	-0.000032	0.357669
C	-2.690065	-0.000018	0.393727
N	-1.881053	0.000045	-0.706917
N	-2.463945	0.000122	-1.889120
C	-3.817962	0.000127	-1.907381
N	-4.620859	0.000036	-0.811150
N	-2.034734	-0.000077	1.626603
N	-0.655906	-0.000053	1.603448
C	-0.265615	-0.000098	2.880085
C	-1.399272	-0.000154	3.725060
C	-2.518617	-0.000138	2.920312
Ru	0.146666	0.000015	-0.368976
Cl	0.745527	0.000080	-2.705204
C	1.175252	-0.000089	3.283625
C	-3.962642	-0.000177	3.302316
N	-4.410100	0.000233	-3.113097
N	0.554667	-2.067183	-0.335474
C	-0.302283	-3.077139	-0.551026
C	0.091264	-4.412352	-0.557419
C	1.432828	-4.716358	-0.335247
C	2.331785	-3.674013	-0.123481
C	1.876629	-2.354075	-0.134131
C	2.761602	-1.184551	0.041104
N	2.112275	-0.000008	-0.000079
C	2.761615	1.184526	0.041171
C	4.148752	1.208962	0.208052
C	4.838183	-0.000032	0.301810
C	4.148738	-1.209013	0.207983
C	1.876657	2.354071	-0.133995
N	0.554690	2.067205	-0.335351
C	-0.302248	3.077183	-0.550842
C	0.091314	4.412393	-0.557157
C	1.432882	4.716370	-0.334970
C	2.331828	3.674002	-0.123268
H	-4.487302	0.877953	2.914009
H	-3.845780	0.000232	-3.950345
H	-4.034353	-0.000237	4.392776
H	-4.487280	-0.878276	2.913913
H	-1.396299	-0.000200	4.805527
H	1.696981	-0.884811	2.904109
H	1.257212	-0.000131	4.373227
H	1.696949	0.884682	2.904180
H	-5.417324	0.000173	-3.174808
H	-1.332246	2.795098	-0.734371
H	-0.643700	5.188872	-0.739092
H	1.777641	5.745421	-0.333431
H	3.382184	3.886085	0.039933
H	4.688404	2.147853	0.247233
H	5.915900	-0.000042	0.427753
H	4.688379	-2.147912	0.247111
H	3.382139	-3.886117	0.039709
H	1.777576	-5.745412	-0.333768
H	-0.643758	-5.188812	-0.739401
H	-1.332277	-2.795031	-0.734540

**Table S2** Singlet excited states of  $[1]^+$  computed at the TD-DFT /B3LYP// B3LYP/ LanL2DZ level\* (geometry optimised)

State	Energy ( $\times 10^3 \text{ cm}^{-1}$ )	Oscillator strength	$\Psi_O - \Psi_V^a$	Type of transitions
1	13.74	0.0001	HOMO-1 ----> LUMO (0.68)	$\text{Ru}_{\text{dxz}}, \text{Cl} \text{ ----> } \pi^* (\text{N}_t)$
2	14.88	0.0066	HOMO-2 ----> LUMO (0.56)	$\text{Ru}_{\text{dxy}} \text{ ----> } \pi^* (\text{N}_t)$
			HOMO ----> LUMO (0.38)	$\text{Ru}_{\text{dxz}}, \text{Cl} \text{ ----> } \pi^* (\text{N}_t)$
3	18.52	0.0058	HOMO-2 ----> LUMO+1 (0.13)	$\text{Ru}_{\text{dxy}} \text{ ----> } \pi^* (\text{trpy})$
			HOMO ----> LUMO+1 (0.68)	$\text{Ru}_{\text{dxz}}, \text{Cl} \text{ ----> } \pi (\text{trpy})$
4	<b>19.00</b>	<b>0.1282</b>	<b>HOMO ----&gt; LUMO (0.39)</b>	<b><math>\text{Ru}_{\text{dxz}}, \text{Cl} \text{ ----&gt; } \pi^* (\text{N}_t)</math></b>
5	19.92	0.0319	HOMO-1 ----> LUMO+1 (0.45)	$\text{Ru}_{\text{dxz}}, \text{Cl} \text{ ----> } \pi^* (\text{trpy})$
			HOMO ----> LUMO (0.26)	$\text{Ru}_{\text{dxz}}, \text{Cl} \text{ ----> } \pi^* (\text{N}_t)$
			HOMO ----> LUMO+2 (0.38)	$\text{Ru}_{\text{dxz}}, \text{Cl} \text{ ----> } \pi^* (\text{trpy})$
6	20.68	0.000	HOMO-2 ----> LUMO+1 (0.66)	$\text{Ru}_{\text{dxy}} \text{ ----> } \pi^* (\text{trpy})$
7	<b>20.85</b>	<b>0.0169</b>	<b>HOMO-2 ----&gt; LUMO+1 (0.16)</b>	<b><math>\text{Ru}_{\text{dxy}} \text{ ----&gt; } \pi^* (\text{trpy})</math></b>
			HOMO-1 ----> LUMO+2 (0.67)	$\text{Ru}_{\text{dxz}}, \text{Cl} \text{ ----> } \pi^* (\text{trpy})$
8	21.20	0.0016	HOMO-6 ----> LUMO+1 (0.59)	$n_n(\text{N}_t) \text{ ----> } \pi^* (\text{trpy})$
9	21.52	0.0163	HOMO-2 ----> LUMO (0.10)	$\text{Ru}_{\text{dxy}} \text{ ----> } \pi^* (\text{N}_t)$
			HOMO-2 ----> LUMO+2 (0.15)	$\text{Ru}_{\text{dxy}} \text{ ----> } \pi^* (\text{trpy})$
			HOMO ----> LUMO+2 (0.56)	$\text{Ru}_{\text{dxz}}, \text{Cl} \text{ ----> } \pi^* (\text{trpy})$
10	23.15	0.0036	HOMO-2 ----> LUMO+2 (0.67)	$\text{Ru}_{\text{dxy}} \text{ ----> } \pi^* (\text{trpy})$

\*Los Alamos effective core potential for the Ru core electrons with DZ functions for the valence orbitals and a 6-31G\* basis set for all other elements.

<sup>a</sup> $\Psi_O$  and  $\Psi_V$  are the occupied and virtual orbitals respectively, that define the transition. trpy – terpyridine,  $\text{N}_t$  – tetrazine,  $\text{N}_p$  – pyrazol,  $n_n$  –  $\sigma$ –type lone pair orbital.

**Table S3** Singlet excited states of [2]<sup>+</sup> computed at the TD-DFT/B3LYP// B3LYP/LanL2DZ level\* (geometry optimised)

State	Energy ( $\times 10^3 \text{ cm}^{-1}$ )	Oscillator strength	$\Psi_{\text{O}}-\Psi_{\text{V}}$ <sup>a</sup>	Type of transitions
1	11.55	0.0001	HOMO -----> LUMO (0.69)	Ru <sub>dyz</sub> , Cl -----> $\pi^*$ (N <sub>t</sub> )
2	12.92	0	HOMO-1 -----> LUMO (0.69)	Ru <sub>dxz</sub> , Cl -----> $\pi^*$ (N <sub>t</sub> )
3	<b>15.97</b>	<b>0.0087</b>	<b>HOMO -----&gt; LUMO+1 (0.69)</b>	<b>Ru<sub>dyz</sub>, Cl -----&gt; <math>\pi^*</math> (trpy)</b>
4	17.99	0.0014	HOMO -----> LUMO+2(0.51)	Ru <sub>dyz</sub> , Cl -----> $\pi^*$ (trpy)
5	<b>19.24</b>	<b>0.0661</b>	<b>HOMO-2 -----&gt; LUMO (0.15)</b>	<b>Ru<sub>dxz</sub> -----&gt; <math>\pi^*</math> (N<sub>t</sub>)</b>
			HOMO-1 -----> LUMO+1(0.46)	Ru <sub>dxz</sub> , Cl -----> $\pi^*$ (trpy)
			HOMO -----> LUMO+2 (0.47)	Ru <sub>dyz</sub> , Cl -----> $\pi^*$ (trpy)
6	19.68	0.0143	HOMO-1 -----> LUMO+2(0.70)	Ru <sub>dxz</sub> , Cl -----> $\pi^*$ (trpy)
7	20.84	0.0022	HOMO-6 -----> LUMO(0.63)	n <sub>n</sub> (N <sub>t</sub> ) -----> $\pi^*$ (N <sub>t</sub> )
8	21.74	0.0003	HOMO-2 -----> LUMO (0.68)	Ru <sub>dxz</sub> -----> $\pi^*$ (N <sub>t</sub> )
9	21.75	0.0936	HOMO-3 -----> LUMO (0.20)	Ru <sub>dyz</sub> , Cl -----> $\pi^*$ (N <sub>t</sub> )
			HOMO-2 -----> LUMO+1 (0.55)	Ru <sub>dxz</sub> -----> $\pi^*$ (trpy)
10	22.74	0.0101	HOMO-3 -----> LUMO(0.64)	Ru <sub>dyz</sub> , Cl -----> , $\pi^*$ (N <sub>t</sub> )
			HOMO -----> LUMO+3 (0.20)	Ru <sub>dyz</sub> , Cl -----> $\pi^*$ (trpy), $\pi^*$ ( N <sub>t</sub> )

\*Los Alamos effective core potential for the Ru core electrons with DZ functions for the valence orbitals and a 6-31G\* basis set for all other elements.

<sup>a</sup> $\Psi_{\text{O}}$  and  $\Psi_{\text{V}}$  are the occupied and virtual orbitals respectively, that define the transition. trpy – terpyridine, N<sub>t</sub> – tetrazine, N<sub>p</sub> – pyrazol, n<sub>n</sub> – $\sigma$ -type lone pair orbital.

**Table S4** Singlet excited states of  $[1]^+$  computed at the TD-DFT/B3LYP level for X-ray structure\*

State	Energy ( $\times 10^3 \text{ cm}^{-1}$ )	Oscillator strength	$\Psi_O - \Psi_V^a$	Type of transitions
1	13.21	0.0001	HOMO ----> LUMO (0.65)	Ru <sub>dyz</sub> , Cl ----> $\pi^*$ (N <sub>t</sub> )
2	14.81	0.0068	HOMO-2 ----> LUMO+1 (0.55)	Ru <sub>dxz</sub> ----> $\pi^*$ (trpy)
			HOMO-1 ----> LUMO+1 (0.37)	Ru <sub>dxz</sub> , Cl ----> $\pi^*$ (trpy)
3	18.48	0.0049	HOMO-2 ----> LUMO+1 (0.13)	Ru <sub>dxz</sub> ----> $\pi^*$ (trpy)
			HOMO-1 ----> LUMO+1 (0.64)	Ru <sub>dxz</sub> , Cl ----> $\pi^*$ (trpy)
			HOMO ----> LUMO+1 (0.22)	Ru <sub>dyz</sub> , Cl ----> $\pi^*$ (trpy)
4	18.92	0.0621	HOMO-2 ----> LUMO (0.22)	Ru <sub>dxz</sub> ----> $\pi^*$ (N <sub>t</sub> )
			HOMO ----> LUMO+1 (0.57)	Ru <sub>dyz</sub> , Cl ----> $\pi^*$ (trpy)
<b>5</b>	<b>20.03</b>	<b>0.0836</b>	<b>HOMO-1 ----&gt; LUMO (0.38)</b>	<b>Ru<sub>dxz</sub>, Cl ----&gt; <math>\pi^*</math> (N<sub>t</sub>)</b>
			<b>HOMO ----&gt; LUMO (0.10)</b>	<b>Ru<sub>dyz</sub>, Cl ----&gt; <math>\pi^*</math> (N<sub>t</sub>)</b>
			<b>HOMO --&gt; LUMO+1 (0.28)</b>	<b>Ru<sub>dyz</sub>, Cl ----&gt; <math>\pi^*</math> (trpy)</b>
6	20.43	0.0126	HOMO ----> LUMO+2 (0.68)	Ru <sub>dyz</sub> , Cl ----> $\pi^*$ (trpy)
7	20.98	0.0021	HOMO-2 ----> LUMO+1 (0.67)	Ru <sub>dxz</sub> ----> $\pi^*$ (trpy)
<b>8</b>	<b>21.14</b>	<b>0.0128</b>	<b>HOMO-2 ----&gt; LUMO+2 (0.12)</b>	<b>Ru<sub>dxz</sub> ----&gt; <math>\pi^*</math> (trpy)</b>
			<b>HOMO-1 ----&gt; LUMO+2 (0.62)</b>	<b>Ru<sub>dxz</sub>, Cl ----&gt; <math>\pi^*</math> (trpy)</b>
			HOMO ----> LUMO+1 (0.20)	Ru <sub>dyz</sub> , Cl ----> $\pi^*$ (trpy)
9	21.58	0.0012	HOMO-5 ----> LUMO (0.12)	Ru <sub>dxz</sub> , Cl ----> $\pi^*$ (N <sub>t</sub> )
			HOMO-4 ----> LUMO (0.59)	n <sub>n</sub> (N <sub>t</sub> ) ----> $\pi^*$ (N <sub>t</sub> )
10	23.48	0.0063	HOMO-2 ----> LUMO+2 (0.68)	Ru <sub>dxz</sub> ----> $\pi^*$ (trpy)

\*Los Alamos effective core potential for the Ru core electrons with DZ functions for the valence orbitals and a 6-31G\* basis set for all other elements.

<sup>a</sup> $\Psi_O$  and  $\Psi_V$  are the occupied and virtual orbitals respectively, that define the transition. trpy – terpyridine, N<sub>t</sub> – tetrazine, N<sub>p</sub> – pyrazol, n<sub>n</sub> – $\sigma$ -type lone pair orbital.

**Table S5** Singlet excited states of [2]<sup>+</sup> computed at the TD-DFT/B3LYP level for X-ray structure\*

State	Energy ( $\times 10^3 \text{ cm}^{-1}$ )	Oscillator strength	$\Psi_O - \Psi_V^a$	Type of transitions
1	10.53	0.0006	HOMO ----> LUMO (0.69)	Ru <sub>dyz</sub> , Cl ----> $\pi^*$ (N <sub>t</sub> )
2	12.58	0.0022	HOMO-1 ----> LUMO (0.68)	Ru <sub>dxz</sub> , Cl ----> $\pi^*$ (N <sub>t</sub> )
<b>3</b>	<b>15.35</b>	<b>0.0114</b>	<b>HOMO ----&gt; LUMO+1 (0.69)</b>	<b>Ru<sub>dyz</sub>, Cl ----&gt; <math>\pi^*</math> (trpy)</b>
4	17.60	0.0008	HOMO-1 ----> LUMO+1 (0.45)	Ru <sub>dxz</sub> , Cl ----> $\pi^*$ (trpy)
			HOMO ----> LUMO+2 (0.53)	Ru <sub>dyz</sub> , Cl ----> $\pi^*$ (trpy)
<b>5</b>	<b>19.03</b>	<b>0.0545</b>	<b>HOMO-2 ----&gt; LUMO (0.12)</b>	<b>Ru<sub>dxz</sub>, Cl ----&gt; <math>\pi^*</math> (N<sub>t</sub>)</b>
			<b>HOMO-1 ----&gt; LUMO+1(0.49)</b>	<b>Ru<sub>dxz</sub>, Cl ----&gt; <math>\pi^*</math> (trpy)</b>
6	19.72	0.0126	HOMO-1 ----> LUMO+2 (0.69)	Ru <sub>dxz</sub> , Cl ----> $\pi^*$ (trpy)
7	21.33	0.013	HOMO-6 ----> LUMO (0.53)	n <sub>n</sub> (N <sub>t</sub> ) ----> $\pi^*$ (N <sub>t</sub> )
8	22.09	0.0576	HOMO-6 ----> LUMO+1 (0.27)	n <sub>n</sub> (N <sub>t</sub> ) ----> $\pi^*$ (trpy)
			HOMO-3 ----> LUMO (0.22)	Ru <sub>dyz</sub> , Cl ----> $\pi^*$ (N <sub>t</sub> )
			HOMO-2 ----> LUMO (0.42)	Ru <sub>dxz</sub> ----> $\pi^*$ (N <sub>t</sub> )
			HOMO-2 ----> LUMO+1 (0.12)	Ru <sub>dxz</sub> ----> $\pi^*$ (trpy)
9	22.21	0.0012	HOMO-4 ----> LUMO (0.12)	Ru <sub>dyz</sub> , Cl ----> $\pi^*$ (N <sub>t</sub> )
			HOMO-2 ----> LUMO+1 (0.53)	Ru <sub>dxz</sub> ----> $\pi^*$ (trpy)
10	22.33	0.0223	HOMO-3 ----> LUMO (0.54)	Ru <sub>dyz</sub> , Cl ----> $\pi^*$ (N <sub>t</sub> )
			HOMO-2 ----> LUMO (0.17)	Ru <sub>dxz</sub> ----> $\pi^*$ (N <sub>t</sub> )
			HOMO ----> LUMO+3 (0.25)	Ru <sub>dyz</sub> , Cl ----> $\pi^*$ (N <sub>t</sub> ), $\pi^*$ (N <sub>p</sub> )

\*Los Alamos effective core potential for the Ru core electrons with DZ functions for the valence orbitals and a 6-31G\* basis set for all other elements.

<sup>a</sup> $\Psi_O$  and  $\Psi_V$  are the occupied and virtual orbitals respectively, that define the transition. trpy – terpyridine, N<sub>t</sub> – tetrazine, N<sub>p</sub> – pyrazol, n<sub>n</sub> – $\sigma$ -type lone pair orbital.

**Table S6** Calculated energies of frontier molecular orbitals computed at the B3LYP level

MO No.	$[1]^+$		$[2]^+$	
	eV	$\text{cm}^{-1}$	eV	$\text{cm}^{-1}$
HOMO-4	-9.3909	-75743	-9.2682	-74754
HOMO-3	-9.1360	-73687	-9.1104	-73481
HOMO-2	-8.485	-68437	-8.5950	-69324
HOMO-1	-8.1808	-65983	-8.0165	-64658
<b>HOMO</b>	-8.1550	-65775	-7.8489	-63306
<b>LUMO</b>	-5.5870	-45063	-5.5313	-44613
LUMO+1	-4.9914	-40259	-4.9829	-40191
LUMO+2	-4.8523	-39137	-4.8393	-39032
LUMO+3	-4.0733	-32853	-4.1579	-33536
LUMO+4	-3.8656	-31178	-3.8463	-31023

$$[1]^+ \text{ HOMO} - \text{LUMO} = 20712 \text{ cm}^{-1}$$

$$[2]^+ \text{ HOMO} - \text{LUMO} = 18693 \text{ cm}^{-1}$$

**Table S7** Delocalisation energy of back-bonding ( $d\pi$  to  $\pi^*$ ) in  $[1]^+$  computed at the NBO/B3LYP//B3LYP/LanL2DZ<sup>a</sup>

Donor $d\pi$	Acceptor <sup>b</sup> $\pi^*$	Occupancy of $\pi^*$	Delocalisation energy kcal/mole
Ru	N3–N4	0.6449	22.59
Ru	N8–C8	0.4236	5.50
Ru	N9–C17	0.5159	9.31
Ru	N1–C2	0.4257	0.67
Ru	N10–C22	0.5220	5.17

<sup>a</sup>Los Alamos effective core potential for the Ru core electrons with DZ functions for the valence orbitals with f-polarization and a 6-31G\* basis set for all other elements.

<sup>b</sup>Refer to X-ray structure[Fig. 1a] for atom numbers.



**Table S8** Delocalisation energy of back-bonding ( $d\pi$  to  $\pi^*$ ) in  $[2]^+$  computed at the NBO/B3LYP//B3LYP/LanL2DZ\*<sup>a</sup>

Donor $d\pi$	Acceptor <sup>b</sup> $\pi^*$	Occupancy of $\pi^*$	Delocalisation energy kcal/mole
Ru	N3–C6	0.5593	10.69
Ru	N8–C8	0.4287	4.91
Ru	N9–C17	0.5219	9.08
Ru	N1–C2	0.4465	3.68
Ru	N10–C22	0.4287	4.91

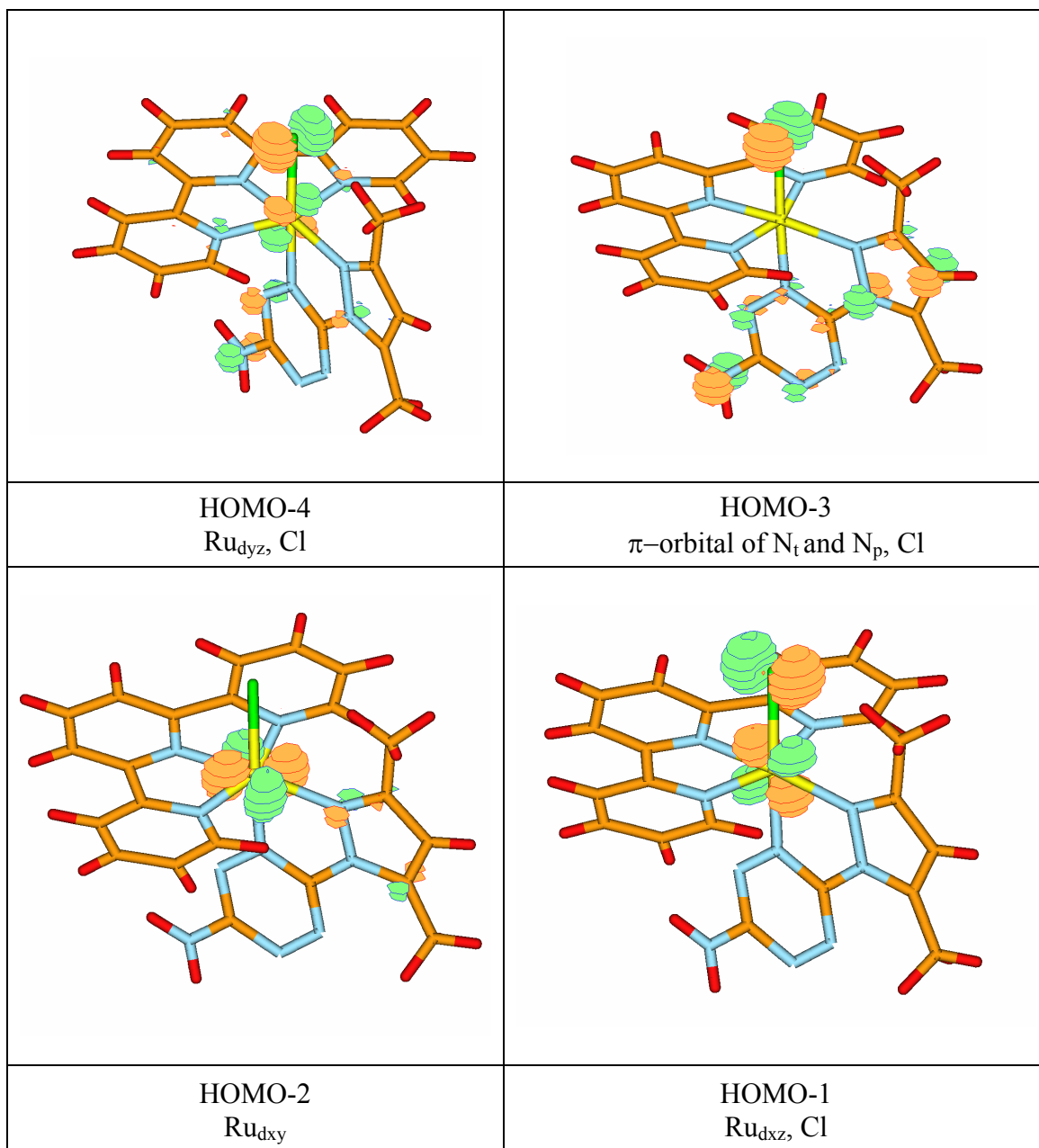
<sup>a</sup>Los Alamos effective core potential for the Ru core electrons with DZ functions for the valence orbitals with f-polarization and a 6–31G\* basis set for all other elements.

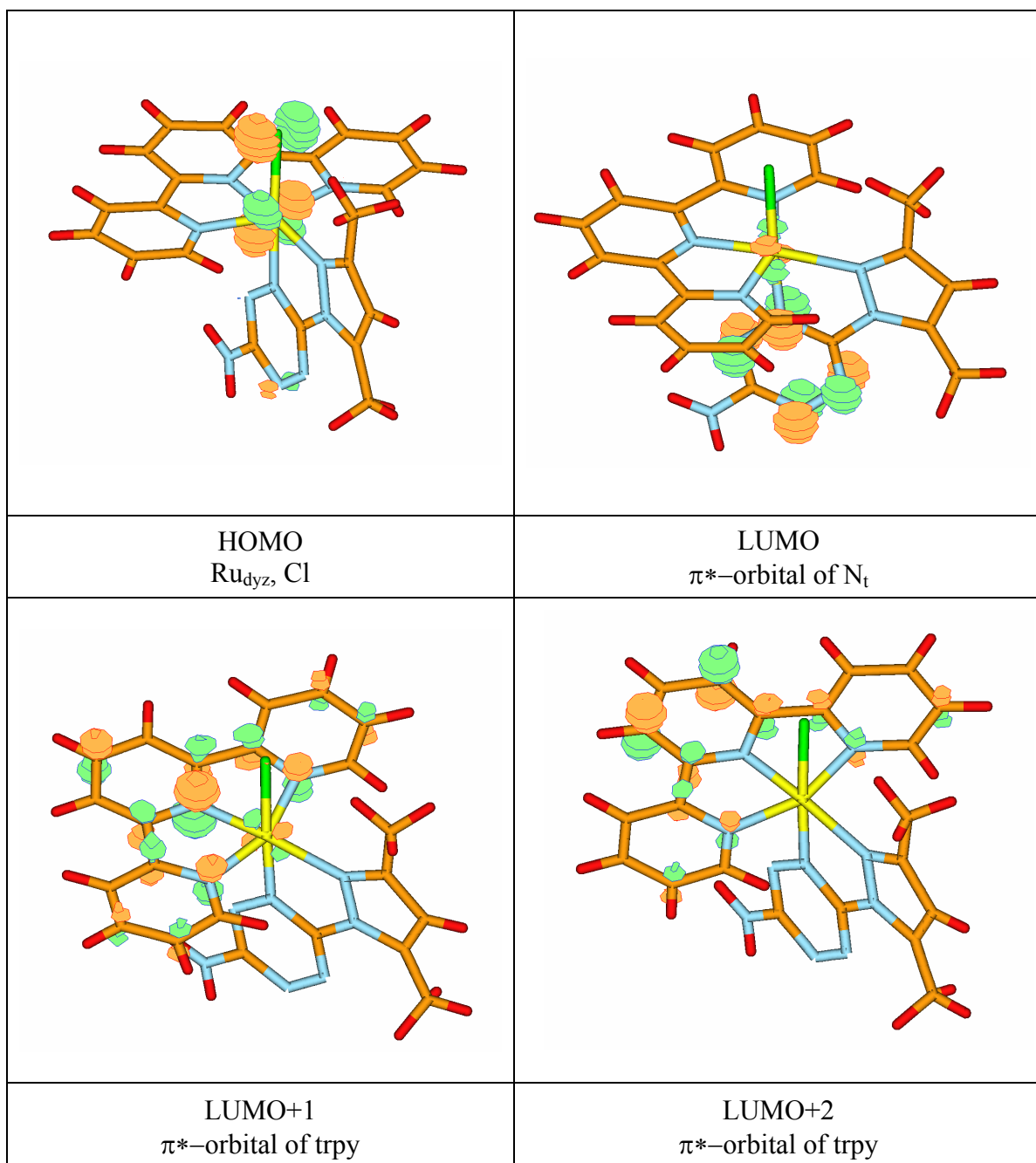
<sup>b</sup>Refer to X-ray structure [Fig. 1b] for atom numbers.

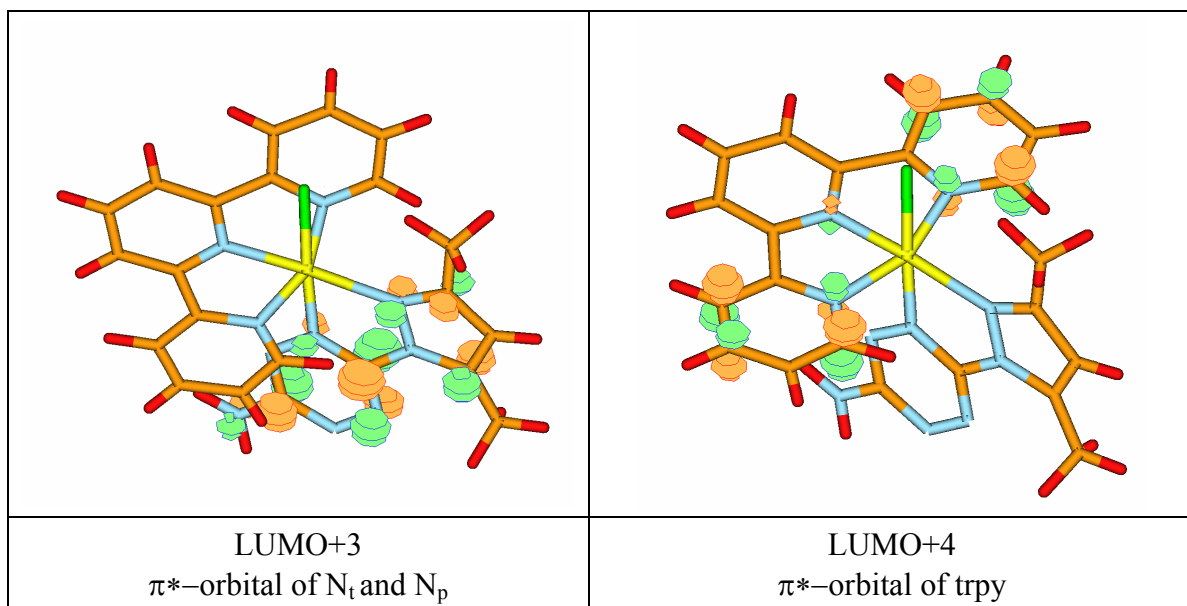
**Table S9** Total energies of complex [1]<sup>+</sup> and [2]<sup>+</sup>

Complex	Energy/a.u.	Difference, kcal/mol (cm <sup>-1</sup> )
[1] <sup>+</sup>	-1951.8711444	0.00
[2] <sup>+</sup>	-1951.8621541	5.64 (1973)

**Fig. S1** Orbital contours diagrams of the frontier Kohn–Sham orbitals of  $[1]^+$







**Fig. S2** Orbital contours diagrams of the frontier Kohn–Sham orbitals of  $[2]^+$

