Electronic supplementary information (ESI)

Di-ruthenium complexes of 1,4-diazabutadiene ligands: Synthesis, characterization and utilization as catalyst-precursor for oxidative coupling of amine to imine in air

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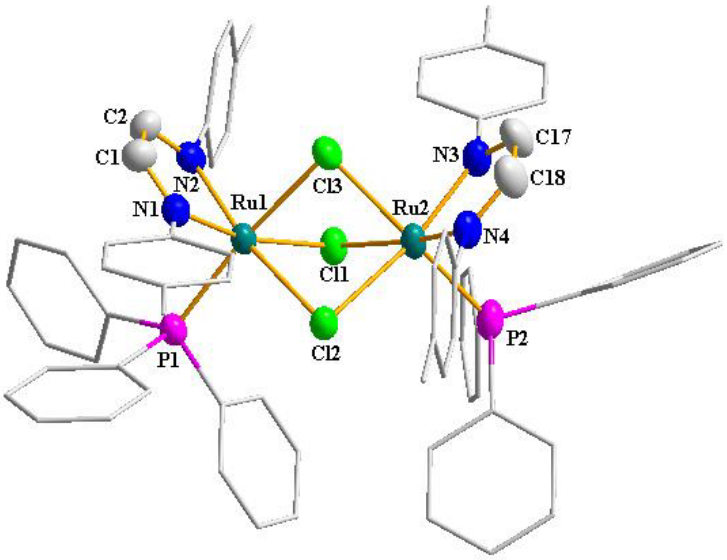


Fig. S1 Crystal structure of the complex cation in **2**.

Table S1 Selected bond distances and bond angles for complex **2**

Bond distances (Å)			
Ru1-N1	2.056(2)	Ru2-N3	2.029(3)
Ru1-N2	2.021(2)	Ru2-N4	2.012(3)
Ru1- P1	2.3011(9)	Ru2-P2	2.3140(9)
Ru1- Cl1	2.4151(7)	Ru2-Cl1	2.4221(8)
Ru1- Cl2	2.4773(8)	Ru2-Cl2	2.4756(8)
Ru1- Cl3	2.4456(7)	Ru2-Cl3	2.4585(8)
N1-C1	1.290(4)	N3-C17	1.303(5)
N1-C3	1.435(4)	N3-C19	1.439(4)
C1-C2	1.408(4)	C17-C18	1.409(5)
N2-C2	1.300(4)	N4-C18	1.300(4)
N2-C10	1.438(4)	N4-C26	1.437(4)
Bond angles (°)			
N1-Ru1-N2	78.11(10)	Ru1- Cl1- Ru2	84.12(2)
N3-Ru2-N4	77.82(11)	Ru1- Cl2- Ru2	81.73(3)
Ru1- Cl3- Ru2	82.72(2)		

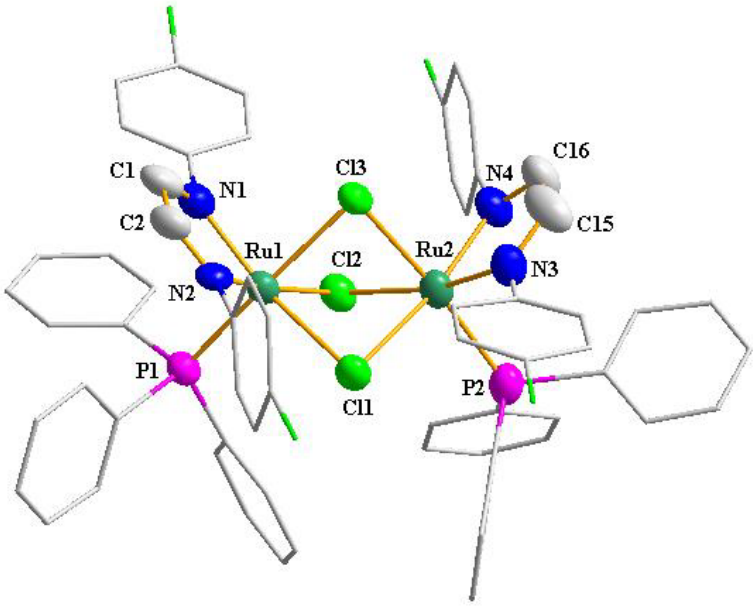


Fig. S2 Crystal structure of the complex cation in **4**.

Table S2 Selected bond distances and bond angles for complex **4**

Bond distances (Å)			
Ru1-N1	2.041(9)	Ru2-N3	2.021(9)
Ru1-N2	2.034(9)	Ru2-N4	2.045(9)
Ru1- P1	2.312(3)	Ru2-P2	2.325(4)
Ru1- Cl1	2.413(3)	Ru2-Cl1	2.429(3)
Ru1- Cl2	2.448(3)	Ru2-Cl2	2.461(3)
Ru1- Cl3	2.481(2)	Ru2-Cl3	2.492(3)
N1-C1	1.302(15)	N3-C15	1.312(15)
N1-C3	1.445(13)	N3-C17	1.449(13)
C1-C2	1.402(14)	C15-C16	1.398(17)
N2-C2	1.296(14)	N4-C16	1.288(14)
N2-C9	1.444(12)	N4-C23	1.437(13)
Bond angles (°)			
N1-Ru1-N2	77.7(4)	Ru1- Cl1- Ru2	84.18(8)
N3-Ru2-N4	77.7(4)	Ru1- Cl2- Ru2	82.78(8)
Ru1- Cl3- Ru2	81.49(8)		

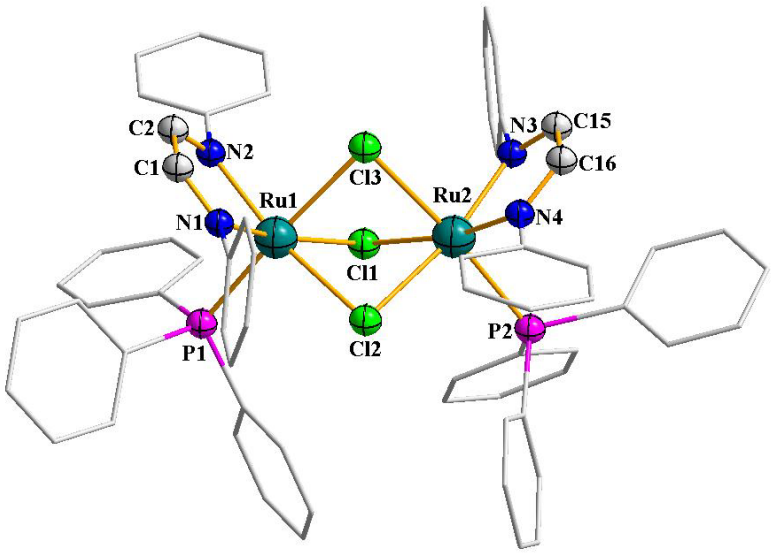


Fig. S3 DFT-optimized structure of complex cation in **3**.

Table S3 Some computed bond distances and bond angles for the complex cation in **3**

Bond distances (Å)			
Ru1-N1	2.0578	Ru2-N3	2.0639
Ru1-N2	2.0875	Ru2-N4	2.0747
Ru1- P1	2.4079	Ru2-P2	2.4034
Ru1- Cl1	2.5211	Ru2-Cl1	2.5285
Ru1- Cl2	2.5137	Ru2-Cl2	2.5145
Ru1- Cl3	2.5576	Ru2-Cl3	2.5526
N1-C1	1.3106	N3-C15	1.3109
N1-C3	1.4280	N3-C17	1.4269
C1-C2	1.4269	C15-C16	1.4273
N2-C2	1.3116	N4-C16	1.3091
N2-C9	1.4286	N4-C23	1.4292
Bond angles (°)			
N1-Ru1-N2	78.25	Ru1- Cl1- Ru2	83.97
N3-Ru2-N4	78.22	Ru1- Cl2- Ru2	84.41
Ru1- Cl3- Ru2	82.75		

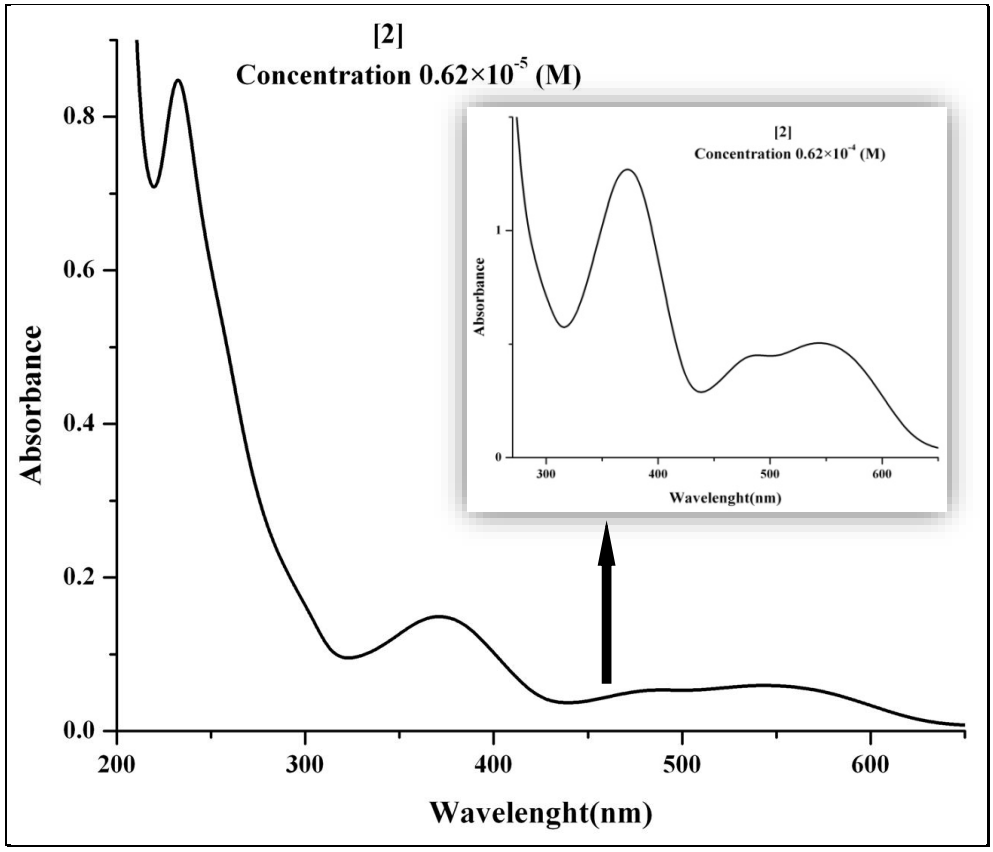


Fig. S4 Electronic absorption spectrum of complex **2** in dichloromethane solution.

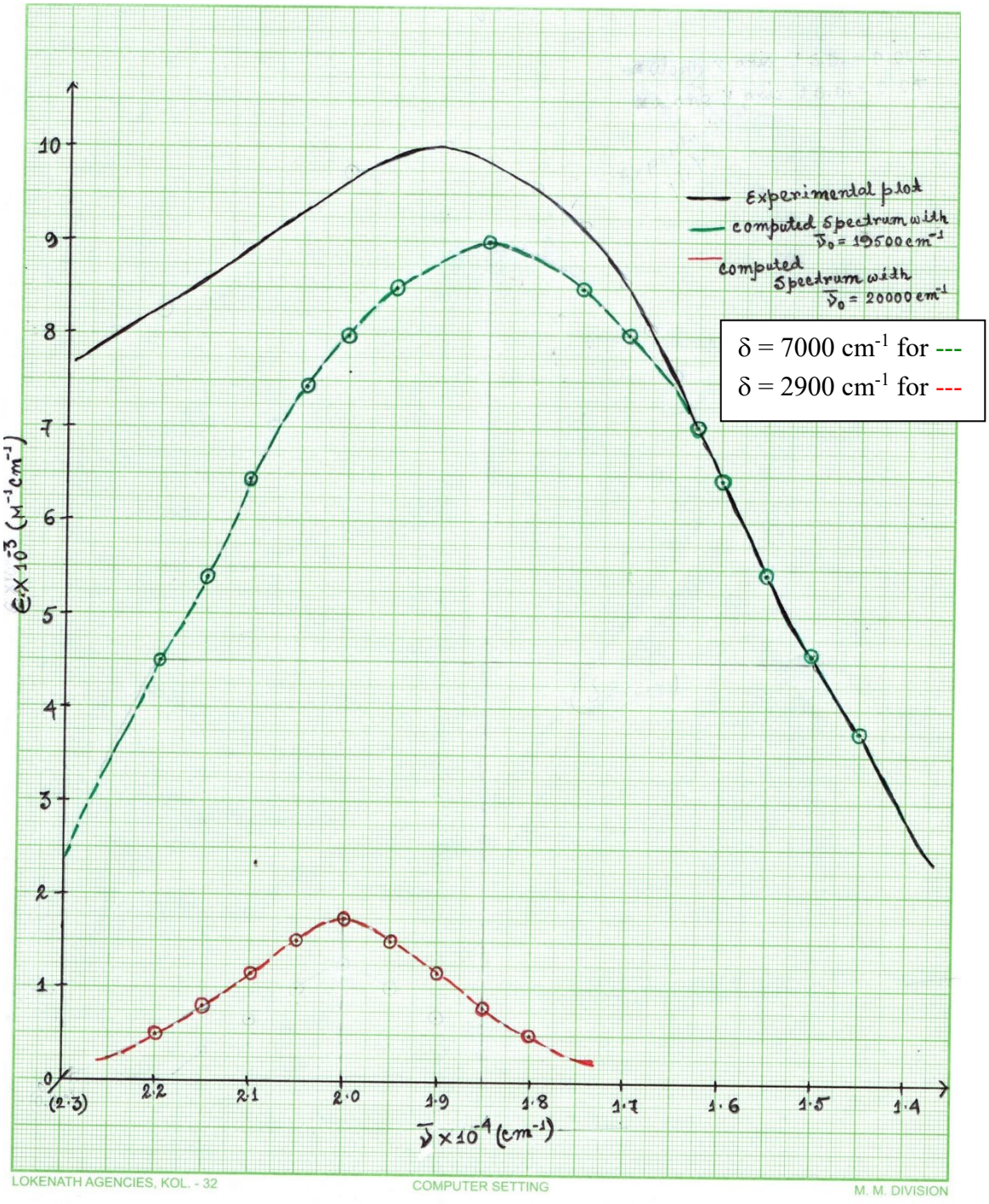


Fig. S5 Electronic absorption spectrum of complex **3** (——) and its Gaussian components (--- and ---).

Table S4 Computed parameters from TDDFT calculations on complex **1** for electronic spectral properties in dichloromethane solution

Excited State	Composition	CI value	*E* (eV)	Oscillator strength (*f*)	λ_{theo} (nm)	Assignment	λ_{exp} (nm)
1	H-5 → L+1	0.11000	2.3242	0.0564	533.44	MLCT/ILCT	548
	H-3 → L	0.39293				MLCT/ILCT	
	H-3 → L+1	0.12345				MLCT/ILCT	
	H-2 → L+1	0.49334				MLCT/ILCT	
	H → L	0.19366				MLCT/ILCT	
2	H-6 → L+1	0.13693	2.5768	0.4669	481.15	ILCT/MLCT	493
	H-4 → L	0.61592				ILCT/MLCT	
	H-4 → L+1	0.11538				MLCT/ILCT	
	H-2 → L+1	0.14221				MLCT/ILCT	
	H → L	0.13757				MLCT/ILCT	
3	H-9 → L	0.47180	3.1265	0.0127	396.55	MLCT/ILCT	406
	H-9→ L+1	0.23324				MLCT/ILCT	
	H-2 → L+2	0.17700				LLCT	
	H-1 → L+4	0.15092				LLCT	
	H → L+5	0.26872				LMCT	
4	H-31 → L	0.14232	5.377	0.0750	230.58	ILCT/LLCT/MLCT	232
	H-26 → L+1	0.17726				ILCT/LMCT	
	H-25 → L	0.10217				ILCT/LLCT	
	H-25 → L+1	0.41700				ILCT/LLCT	
	H-24 → L	0.27590				ILCT/LLCT/LMCT	
	H-14 → L+2	0.12650				LMCT/ILCT/LLCT	
	H-4 → L+11	0.10550				ILCT/MLCT	
	H-1 → L+12	0.10760				ILCT/MLCT/LLCT	
	H → L+12	0.12803				MLCT/ILCT/LLCT	
	H→L+13	0.16245				MLCT/ILCT/LLCT	

Table S5 Compositions of the molecular orbitals of complex **1** associated with the electronic spectral transitions

% Contribution of fragments to	Fragments			
	Ru	PMe_3	L-OCH_3	Cl
HOMO (H)	53	3	33	11
H-1	52	1	37	10
H-2	54	2	33	11
H-3	67	1	24	8
H-4	35	2	58	5
H-5	46	3	47	4
H-6	36	2	58	4
H-9	36	3	53	8
H-14	5	6	33	56
H-24	5	1	84	10
H-25	16	11	42	31
H-26	2	1	92	5
H-31	20	21	43	16
LUMO (L)	14	1	83	2
L+1	14	1	83	2
L+2	58	7	24	11
L+4	52	22	16	10
L+5	62	2	26	10
L+11	4	2	93	1
L+12	6	32	62	0
L+13	13	2	85	0

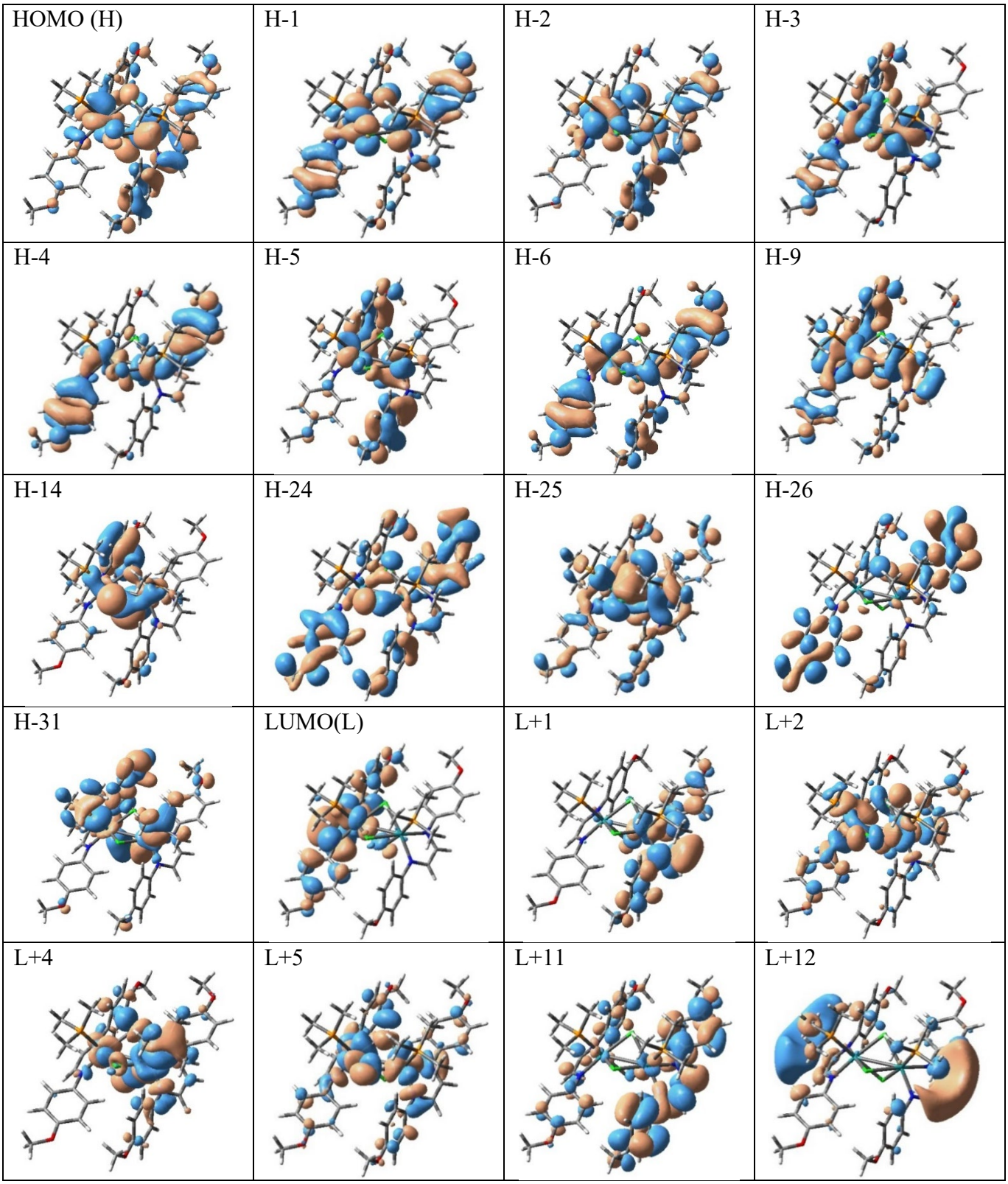


Fig. S6 Contour plots of the molecular orbitals of complex **1**, which are associated with the electronic spectral transitions (See **Table S4**).

Table S6 Computed parameters from TDDFT calculations on complex **2** for electronic spectral properties in dichloromethane solution

Excited State	Composition	CI value	*E* (eV)	Oscillator strength (*f*)	λ_{theo} (nm)	Assignment	λ_{exp} (nm)
1	H-3 → L+1	0.18735	2.2621	0.0612	548.09	MLCT/ILCT	544
	H-2 → L	0.47769				MLCT/ILCT	
	H-1 → L+1	0.42587				MLCT/LLCT	
	H → L	0.20560				MLCT/ILCT/LLCT	
2	H-4 → L	0.66239	2.6934	0.0536	460.33	MLCT/ILCT	486
	H-1 → L+1	0.15025				MLCT/LLCT	
3	H-9 → L	0.50844	3.2731	0.0185	378.78	ILCT/LMCT	373
	H-8 → L+1	0.39464				ILCT/LLCT/LMCT	
	H-2 → L+4	0.11230				MLCT/ILCT	
	H-1 → L+3	0.15904				MLCT/LLCT	
4	H-15 → L+2	0.13853	5.1850	0.1283	239.12	LMCT/LLCT/ILCT	232
	H-12 → L+2	0.12656				LMCT/LLCT	
	H-10 → L+2	0.41806				LMCT/LLCT	
	H-9 → L+4	0.22004				LMCT/LLCT	
	H-8 → L+3	0.29231				LMCT/LLCT	
	H-8 → L+5	0.13579				LMCT/LLCT	
	H-3 → L+9	0.25740				MLCT/ILCT	

Table S7 Compositions of the molecular orbitals of complex **2** associated with the electronic spectral transitions

% Contribution of fragments to	Fragments			
	Ru	PMe_3	L-CH_3	Cl
HOMO (H)	66	4	15	15
H-1	72	0	8	20
H-2	78	0	13	9
H-3	66	3	29	2
H-4	56	3	38	3
H-8	2	0	76	22
H-9	4	1	91	4
H-10	0	0	86	14
H-12	1	0	89	10
H-15	6	24	4	66
LUMO (L)	14	1	82	3
L+1	16	0	84	0
L+2	56	6	26	12
L+3	47	27	13	13
L+4	53	18	19	10
L+5	59	2	29	10
L+9	4	2	93	1

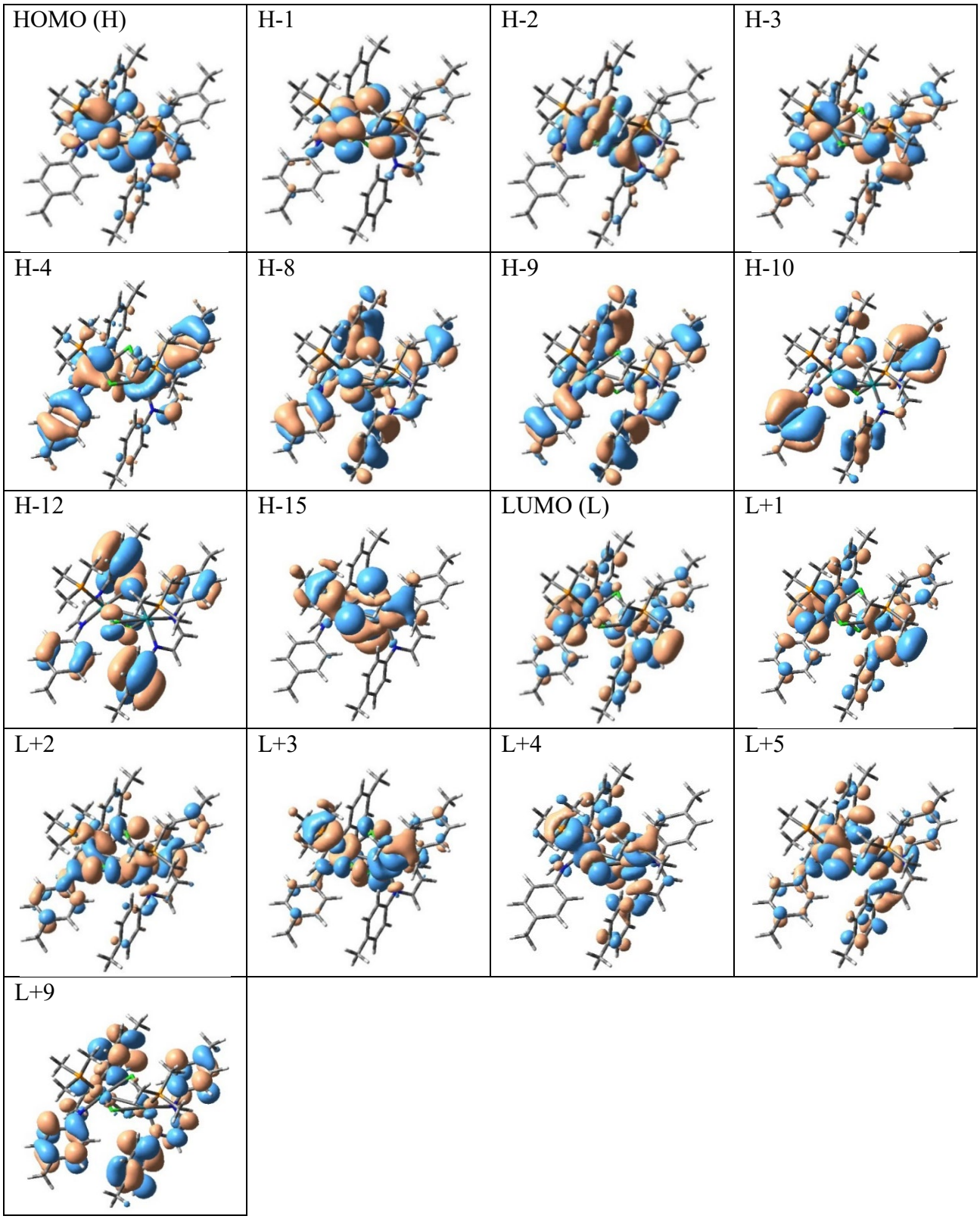


Fig. S7 Contour plots of the molecular orbitals of complex **2**, which are associated with the electronic spectral transitions (See **Table S6**).

Table S8 Computed parameters from TDDFT calculations on complex **3** for electronic spectral properties in dichloromethane solution

Excited State	Composition	CI value	*E* (eV)	Oscillator strength (*f*)	λ_{theo} (nm)	Assignment	λ_{exp} (nm)
1	H-3 → L+1	0.56856	2.3302	0.0153	532.07	MLCT/ILCT	523
	H-2 → L	0.25391				MLCT/ILCT	
	H-1 → L+1	0.10614				MLCT/LLCT	
	H → L	0.30764				MLCT/ILCT/LLCT	
2	H-7 → L	0.33846	3.3654	0.0202	368.41	ILCT/MLCT	358
	H-6 → L+1	0.25469				ILCT	
	H-4 → L+3	0.11357				MLCT/LLCT	
	H-2 → L+2	0.13737				MLCT/ILCT	
	H-2 → L+3	0.25381				MLCT	
	H-1 → L+4	0.39272				MLCT/LLCT	
	H → L+2	0.10146				MLCT	
3	H-17 → L+3	0.12378	5.5602	0.0706	222.98	LMCT	223
	H-14 → L+4	0.13964				LMCT/LLCT	
	H-6 → L+4	0.15586				LMCT/LLCT	
	H-5 → L+7	0.11469				MLCT/LLCT/ILCT	
	H-5 → L+8	0.50238				MLCT/LLCT/ILCT	
	H-5 → L+9	0.16654				MLCT/LLCT/ILCT	
	H-4 → L+6	0.10066				MLCT/ILCT	
	H-4 → L+11	0.21133				MLCT/ILCT	

Table S9 Compositions of the molecular orbitals of complex **3** associated with the electronic spectral transitions

% Contribution of fragments to	Fragments			
	Ru	PMe_3	L-H	Cl
HOMO (H)	68	4	12	16
H-1	73	0	7	20
H-2	79	1	12	8
H-3	73	4	22	1
H-4	70	4	23	3
H-5	63	4	20	13
H-6	15	3	80	2
H-7	18	0	78	4
H-14	10	20	5	65
H-17	11	32	12	45
LUMO (L)	14	1	82	3
L+1	17	0	82	1
L+2	56	4	28	12
L+3	48	27	12	13
L+4	53	19	18	10
L+6	2	0	98	0
L+7	2	0	98	0
L+8	4	2	93	1
L+9	6	3	90	1
L+11	3	0	97	0

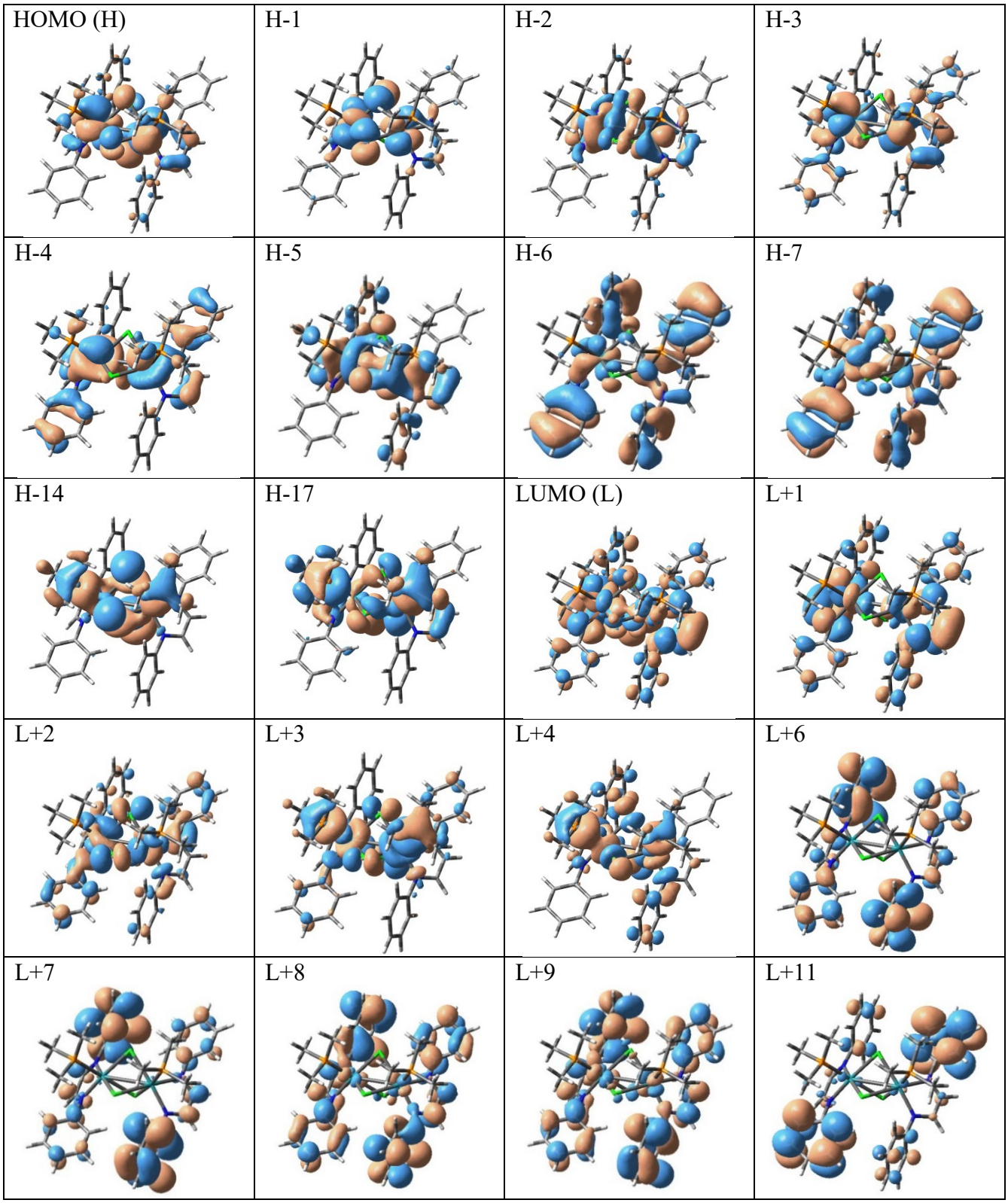


Fig. S8 Contour plots of the molecular orbitals of complex **3**, which are associated with the electronic spectral transitions (See **Table S8**).

Table S10 Computed parameters from TDDFT calculations on complex **4** for electronic spectral properties in dichloromethane solution

Excited State	Composition	CI value	*E* (eV)	Oscillator strength (*f*)	λ_{theo} (nm)	Assignment	λ_{exp} (nm)
1	H-3 → L+1	0.20748	2.2288	0.0591	556.29	MLCT/ILCT	548
	H-2 → L	0.47636				MLCT/ILCT	
	H-1 → L+1	0.42279				MLCT/LLCT	
	H → L	0.20132				MLCT/LLCT/ILCT	
2	H-5 → L+1	0.11180	2.6662	0.0361	465.02	MLCT/ILCT	488
	H-4 → L	0.65662				MLCT/ILCT	
	H-1 → L+1	0.15371				MLCT/LLCT	
3	H-10 → L	0.10027	3.2731	0.0179	378.80	ILCT/LLCT/LMCT	362
	H-9 → L	0.52022				ILCT	
	H-8 → L+1	0.39456				ILCT/LMCT	
	H-2 → L+3	0.10472				MLCT	
	H-1 → L+4	0.13492				MLCT/LLCT	
4	H-15 → L+3	0.10955	5.2387	0.1013	236.67	LMCT/LLCT	233
	H-10 → L+3	0.38167				LMCT/LLCT	
	H-9 → L+2	0.10371				LMCT/LLCT/ILCT	
	H-8 → L+4	0.32627				LMCT/LLCT	
	H-5 → L+7	0.16350				MLCT/ILCT	
	H-4 → L+10	0.15908				MLCT/ILCT	
	H-4 → L+11	0.17974				MLCT/ILCT	

Table S11 Compositions of the molecular orbitals of complex **4** associated with the electronic spectral transitions

% Contribution of fragments to	Fragments			
	Ru	PMe_3	L-Cl	Cl
HOMO (H)	66	4	14	16
H-1	71	0	9	20
H-2	77	1	14	8
H-3	65	3	30	2
H-4	46	3	48	3
H-5	48	3	40	9
H-8	2	0	89	9
H-9	9	1	86	4
H-10	0	0	56	44
H-15	4	1	42	53
LUMO (L)	15	0	82	3
L+1	17	0	82	1
L+2	55	3	31	11
L+3	51	20	20	9
L+4	47	26	14	13
L+7	3	0	96	1
L+10	3	1	96	0
L+11	4	2	93	1

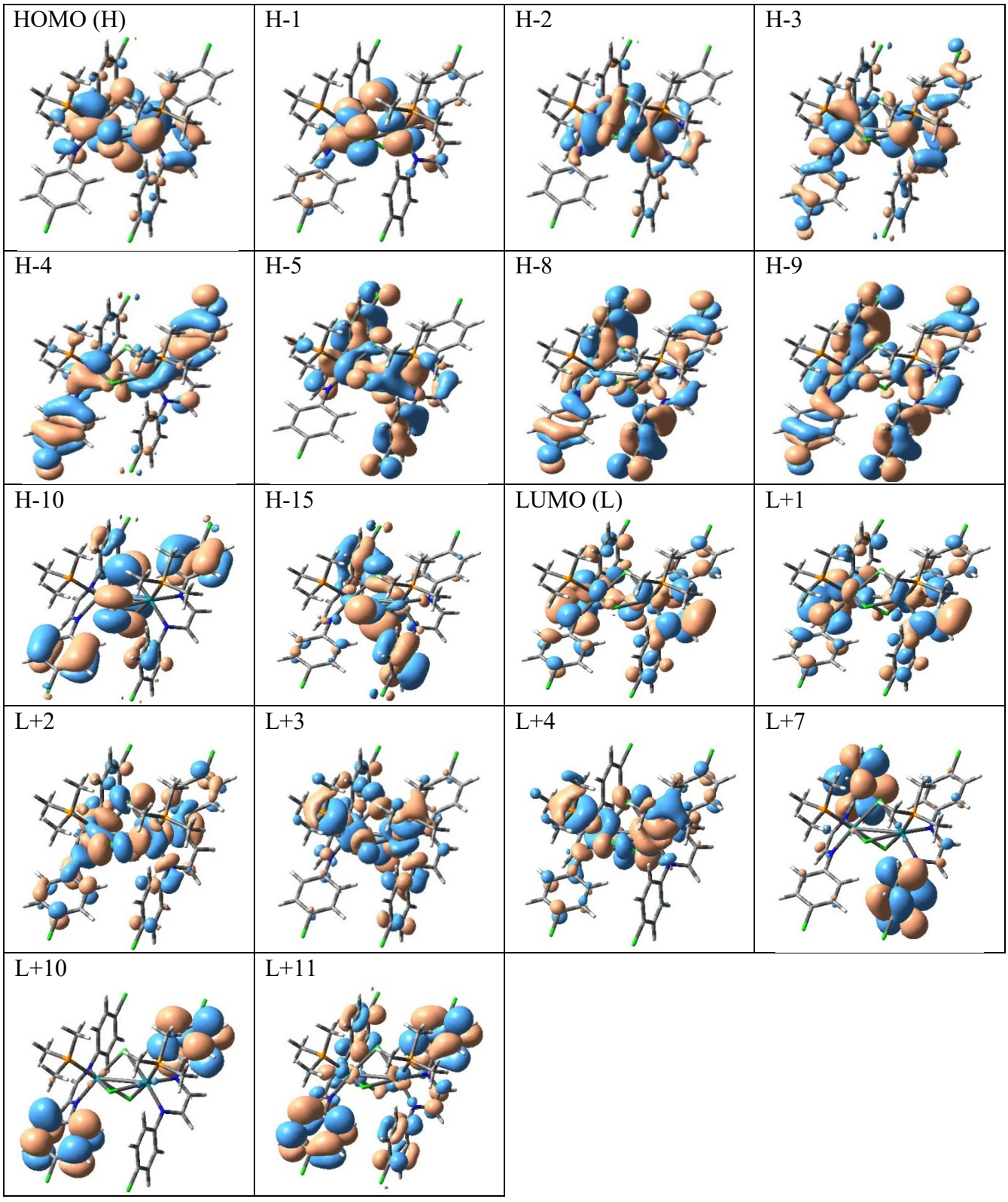
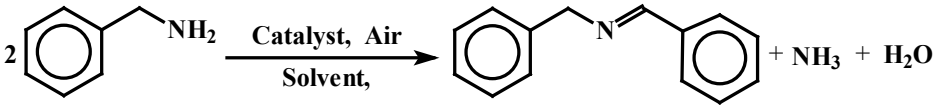


Fig. S9 Contour plots of the molecular orbitals of complex **4**, which are associated with the electronic spectral transitions (See **Table S10**).

Table S12 Optimization of the reaction conditions for the oxidative coupling of benzylamine to imines[a]



Entry	Catalyst	Mole % of catalyst	Solvent	Temp, ºC	Time, h	Yeild[b], %
1	**1**	1	Toluene	110	4	>99
2	**1**	0.5	Toluene	110	4	>99
3	**1**	0.1	Toluene	110	4	>99
4	**1**	0.01	Toluene	110	4	>99
5	**1**	0.01	Toluene	110	1	>99
6	**1**	0.001	Toluene	110	1	>99
7	**1**	0.001	Toluene	110	30 min	99
8	**1**	0.001	Toluene	110	10 min	78
9	**1**	0.001	Toluene-EtOH (8:2)	110	30 min	67
10	**1**	0.001	EtOH	80	30 min	65
11	**1**	0.0001	Toluene	110	30 min	35
12	**1**	0.001	Toluene	rt	30 min	N.O.
13	**1**	0.5	Toluene	rt[c]	2	71
14	**1**	0.5	Toluene	rt[c]	4	99
15	**1**	0.001	Acetonitrile	85	30 min	78
16	**1**	0.001	Toluene	110	30 min	11[d]
17	**1**	0.00	Toluene	110	30 min	N.O.
18	**2**	0.001	Toluene	110	30 min	98
19	**3**	0.001	Toluene	110	30 min	95
20	**4**	0.001	Toluene	110	30 min	96

[a] Reaction conditions: Catalyst, $[Ru_2(PPh_3)_2(L\text{-}OCH_3)_2Cl_3]Cl$; substrate, benzylamine(0.5mmol); solvent (5.0 mL).
[b] Yield was determined by GCMS and the selectivity of imine was 100%.
[c] Room temperature stirring. [d] Reaction was performed under nitrogen atmosphere.

Table S13 Crystallographic data for complexes **1**, **2** and **4**

complex	**1**	**2**	**4**
empirical formula	$C_{68}H_{62}Cl_3N_4O_4P_2Ru_2$, C_7H_8, Cl^-, $2H_2O$	$C_{68}H_{62}Cl_3N_4P_2Ru_2$, C_7H_8, Cl^-, H_2O	$C_{64}H_{50}Cl_7N_4P_2Ru_2$, C_7H_8, Cl^-, 0.7 H_2O
formula weight	1532.00	1450.19	1526.60
crystal system	Monoclinic	Monoclinic	Monoclinic
space group	C2/c	C2/c	C2/c
a (Å)	33.324(3)	32.5574(15)	32.926(5)
b (Å)	17.1944(14)	17.2458(6)	17.173(2)
c (Å)	26.901(3)	26.4277(10)	26.459(3)
α (◦)	90	90	90
β (◦)	115.272(3)	112.892(3)	113.647(4)
γ (◦)	90	90	90
V (Å^3)	13939(2)	13669.9(10)	13705(3)
Z	8	8	8
D_{calcd} /mg m^{-3}	1.428	1.409	1.480
F (000)	6140	5548	5584
crystal size (mm)	0.20 × 0.18 × 0.12	0.12 × 0.11 × 0.08	0.15 × 0.12 × 0.10
T (K)	273	296	273
μ (mm^{-1})	0.688	0.687	0.845
R1[a]	0.0657	0.0397	0.1066
wR2[b]	0.1637	0.1103	0.3686
GOF[c]	1.089	1.109	1.110

[a] $R1 = \Sigma \left| |F_o| - |F_c| \right| / \Sigma |F_o|$.

[b] $wR2 = [\Sigma\{w(F_o^2-F_c^2)^2\}/\Sigma\{w(F_o^2)\}]^{1/2}$.

[c] $GOF = [\Sigma(w(F_o^2-F_c^2)^2)/(M-N)]^{1/2}$, where M is the number of reflections and N is the number of parameters refined.