Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supplementary Information

Ruthenium-hydride mediated stabilisation of azo anion radical of azobis(benzothiazole) and its reversible electron reservoir feature

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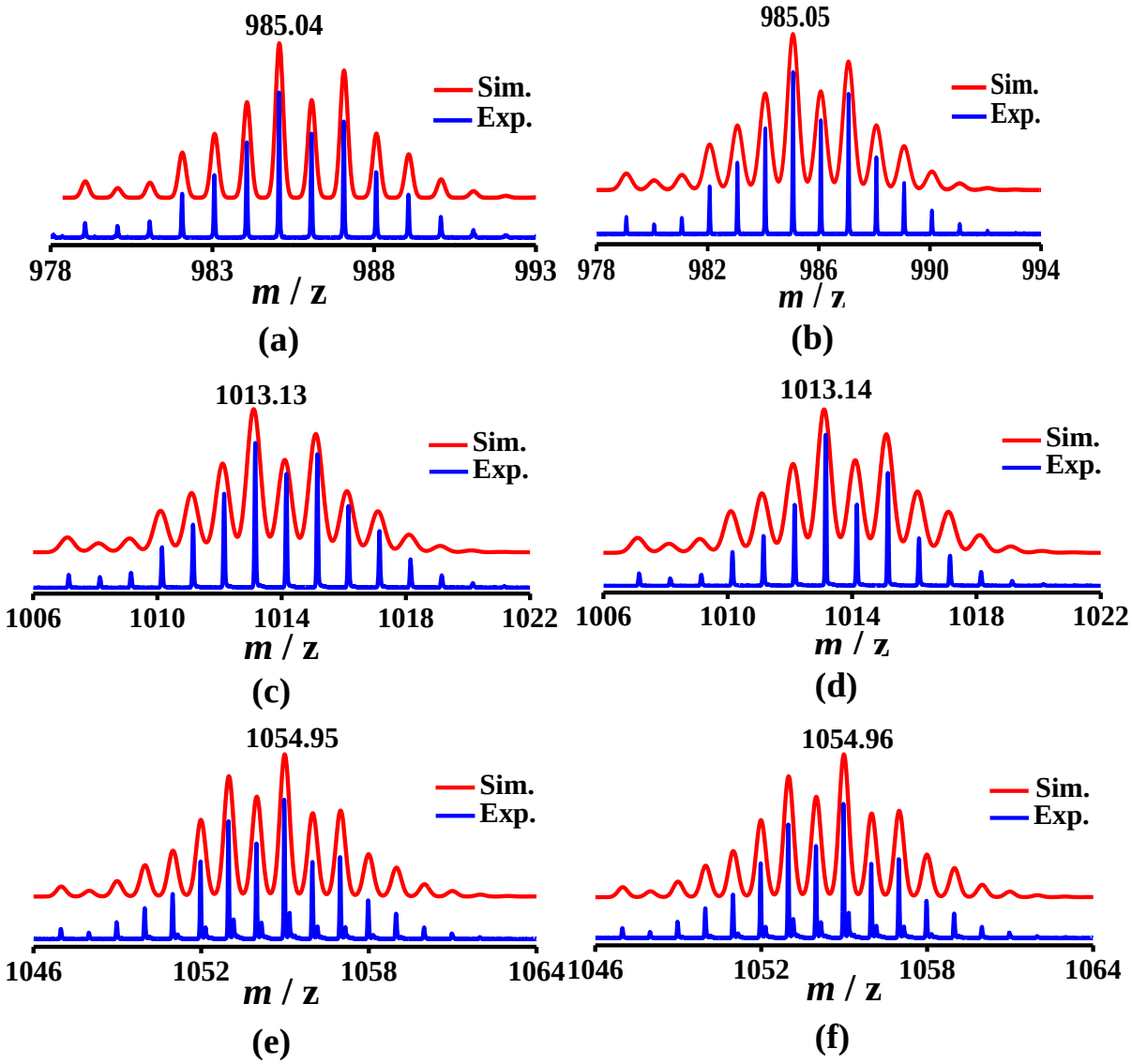


Fig. S1 Experimental and simulated ESI(+) mass spectra of (a) $\{\mathbf{1}\}^+$, (b) $\{([\mathbf{1}](ClO_4)\text{-}ClO_4\}^+$, (c) $\{\mathbf{2}\}^+$, (d) $\{([\mathbf{2}]ClO_4)\text{-}ClO_4\}^+$, (e) $\{\mathbf{3}\}^+$ and (f) $\{([\mathbf{3}](ClO_4)\text{-}ClO_4\}^+$ in CH_3CN (red line, simulated and blue line, experimental).

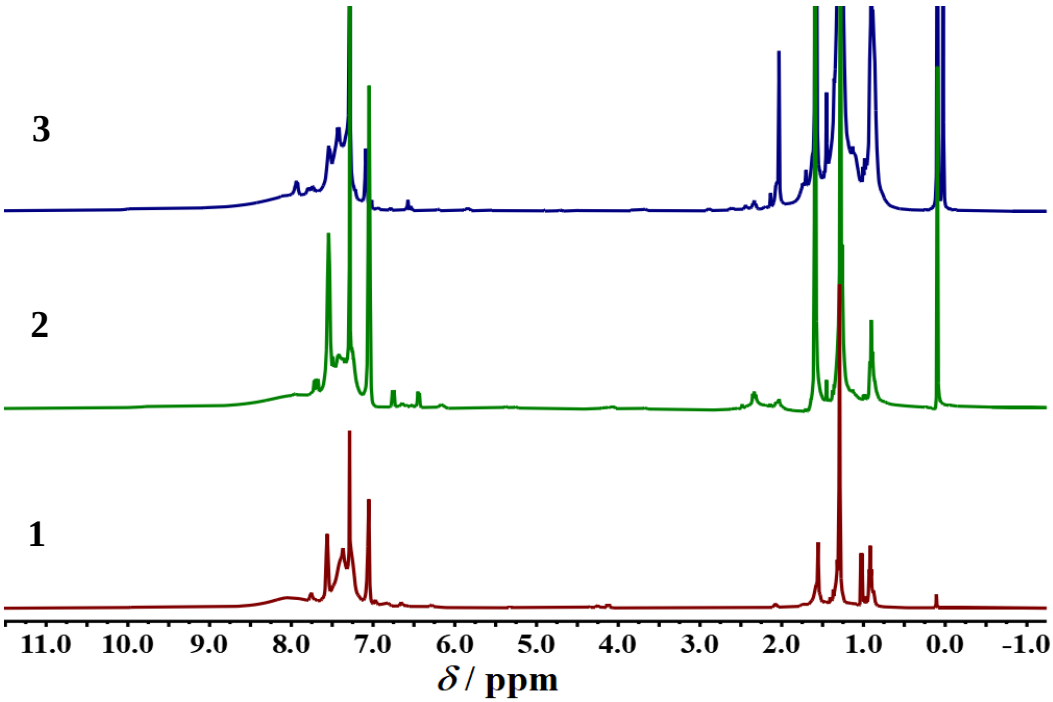


Fig. S2 ^{1}H NMR of complexes **1**, **2** and **3** in $CDCl_3$ with TMS (δ = 0 ppm) as internal standard.

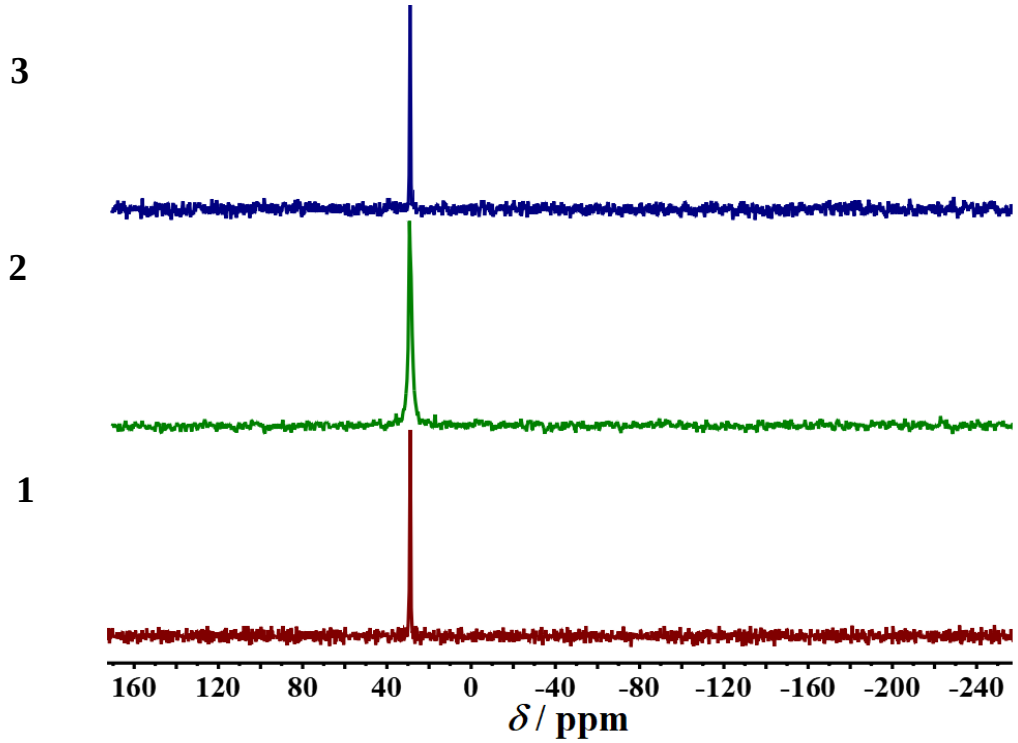


Fig. S3 ^{31}P NMR of complexes **1**, **2** and **3** in $CDCl_3$ with TMS (δ = 0 ppm) as internal standard.

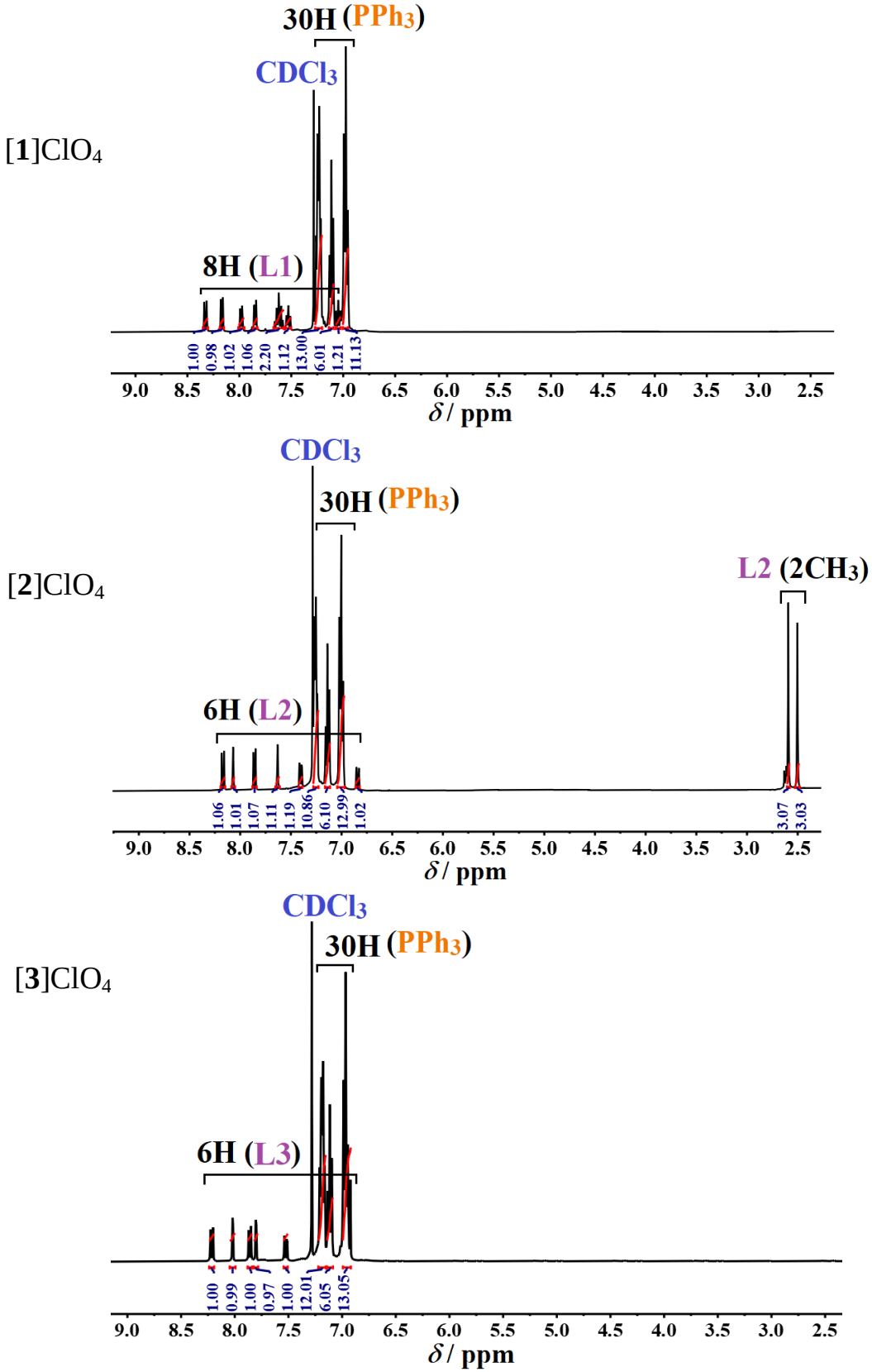


Fig. S4 ^{1}H NMR of complexes [**1**]ClO_4, [**2**]ClO_4 and [**3**]ClO_4 in $CDCl_3$ with TMS (δ = 0 ppm) as internal standard.

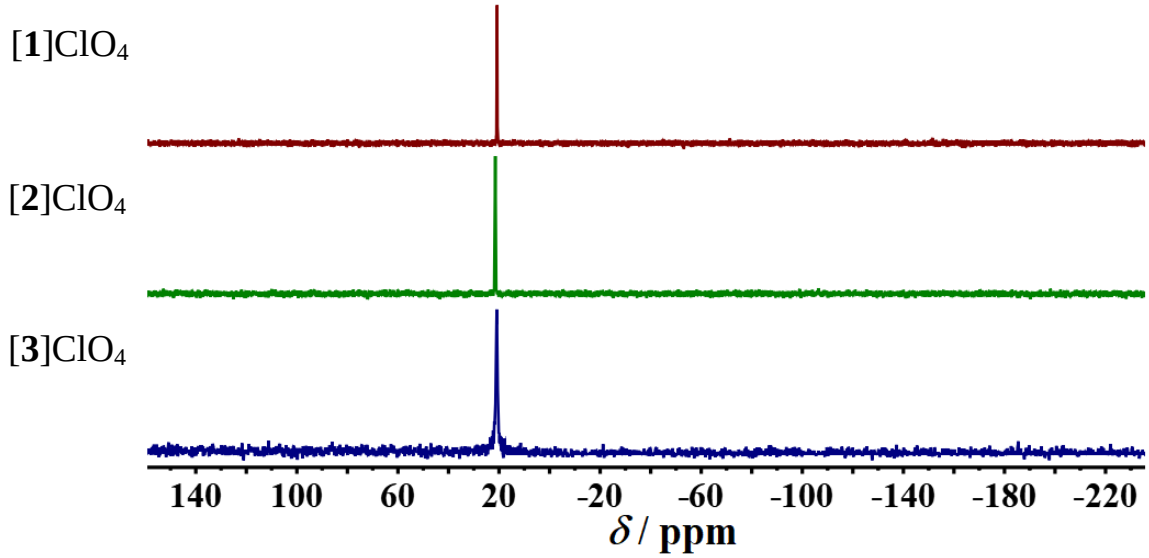


Fig. S5 ^{31}P NMR of complexes [**1**]ClO_4, [**2**]ClO_4 and [**3**]ClO_4 in $CDCl_3$ with TMS (δ = 0 ppm) as internal standard.

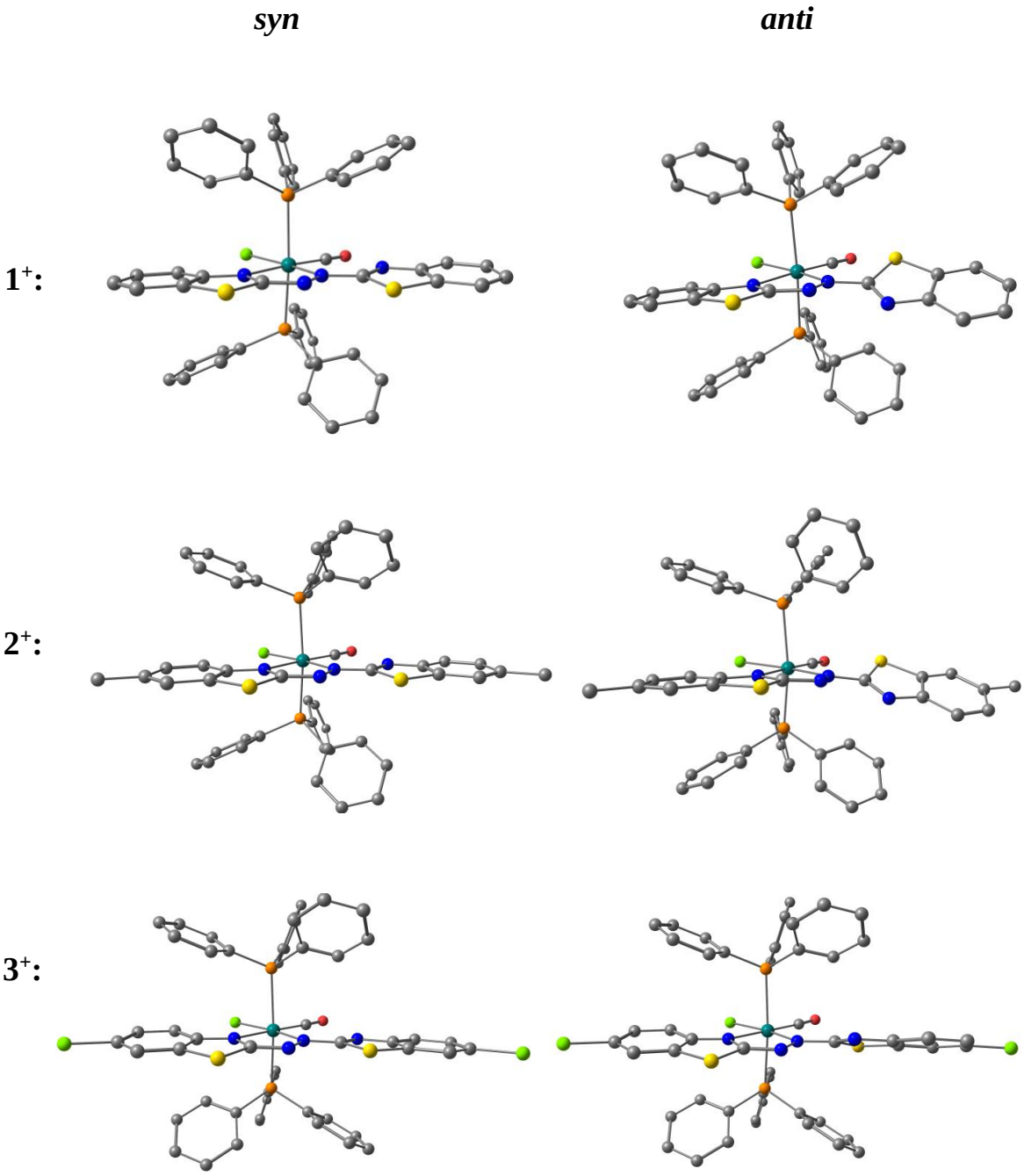


Fig. S6 *Syn* and *anti* forms of L in **1**$^{+}$-**3**$^{+}$.

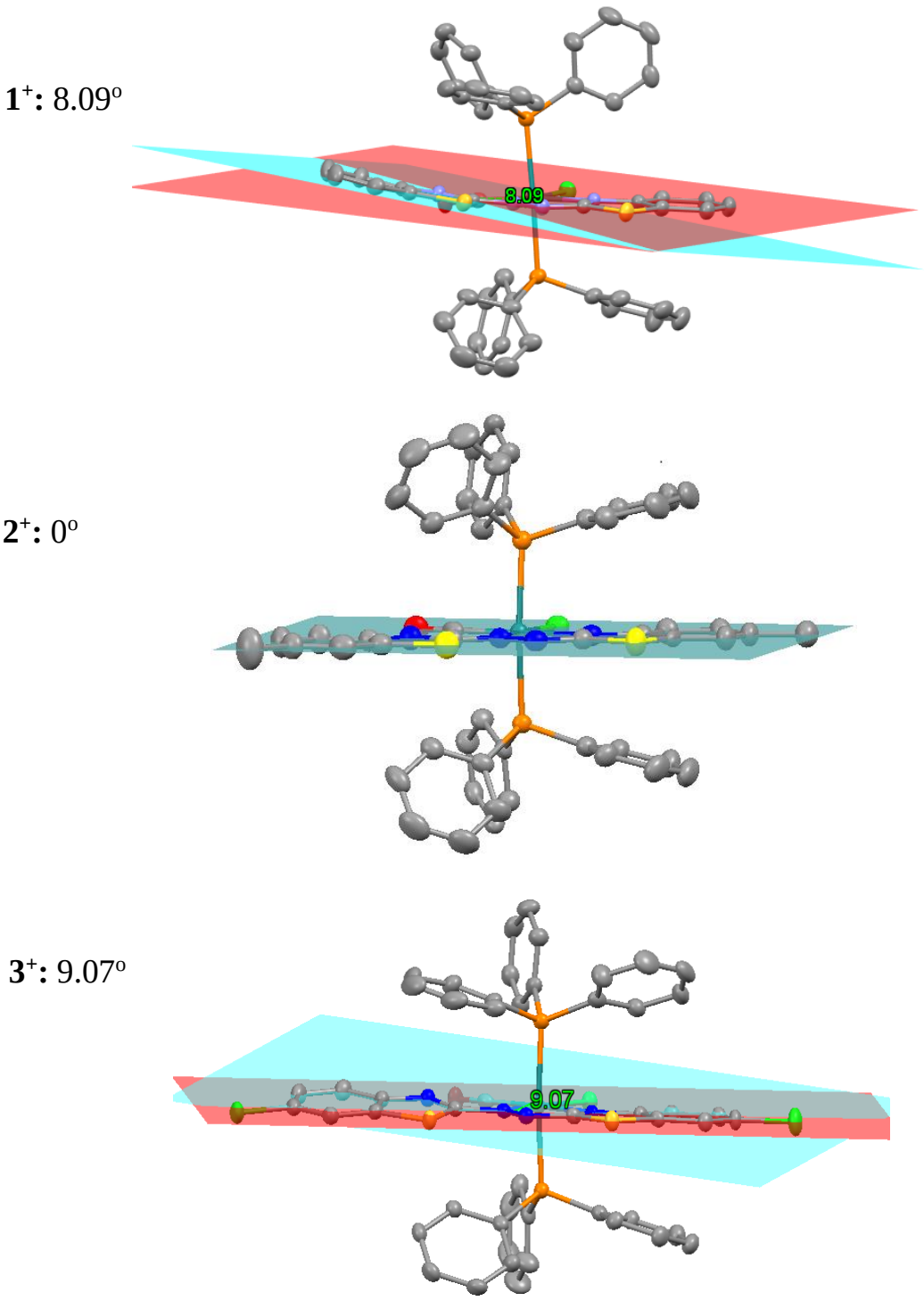


Fig. S7 Planarity and non-planarity of the coordinated L2 and L1/L3 in $\mathbf{2}^{+}$ and $\mathbf{1}^{+}/\mathbf{3}^{+}$.

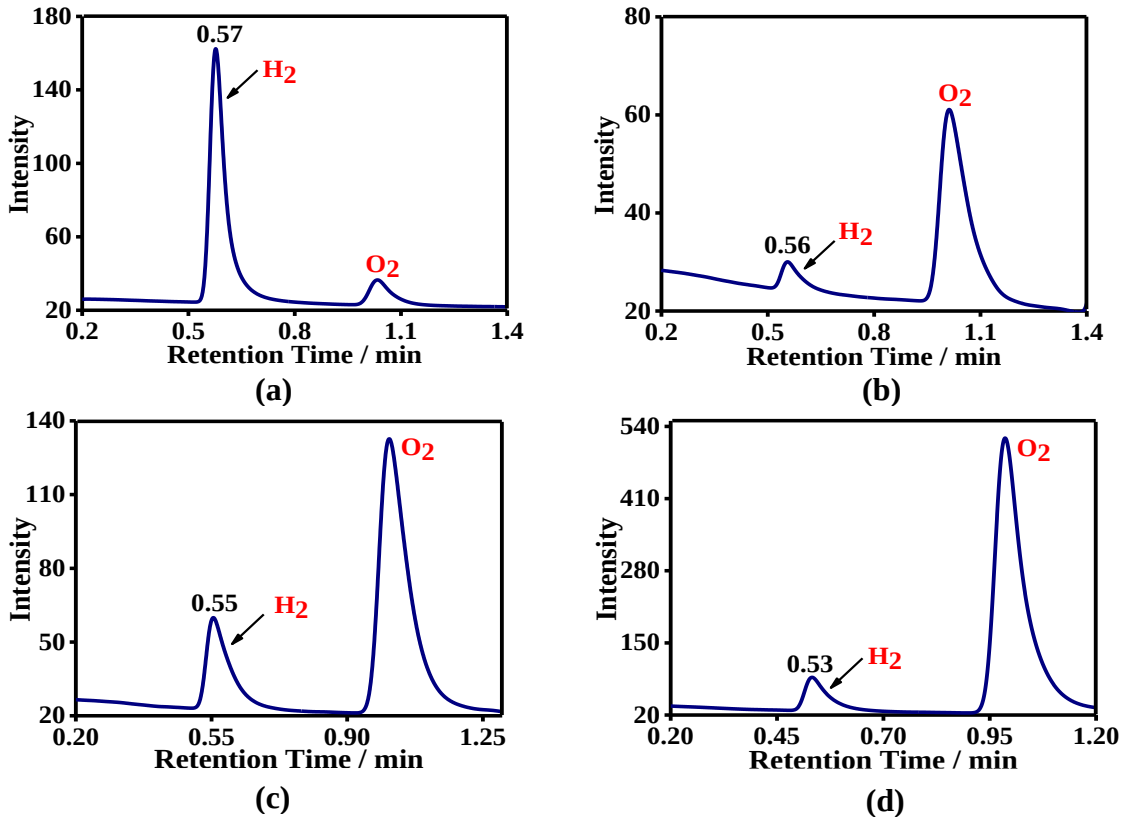


Fig. S8 Gas chromatograms of (a) pure hydrogen. Headspace gas analysis of the reaction mixture in dry THF involving $[Ru^{II}(H)(Cl)(CO)(PPh_3)_3]$ and (b) L1, (c) L2 and (d) L3.

Table S1 Selected crystallographic parameters

Complex	[**1**]ClO_4	[**2**]$ClO_4.3C_6H_6$	[**3**]$ClO_4.2CH_3CN$
empirical formula	$C_{51}H_{38}Cl_{1.8}N_4O_{4.2}P_2S_2Ru$	$C_{71}H_{60}Cl_2N_4O_5P_2S_2Ru$	$C_{55}H_{42}Cl_4N_6O_5P_2S_2Ru$
formula weight	1064.99	1347.26	1235.87
crystal system	Orthorhombic	Orthorhombic	Triclinic
space group	*Pbca*	$Pmn2_1$	$P\bar{1}$
a (Å)	19.4970(3)	16.9228(4)	12.2190(5)
b (Å)	14.2023(2)	10.5794(2)	12.8734(5)
c (Å)	32.8171(5)	18.1360(4)	17.3515(6)
α (deg)			98.711(3)
β (deg)			91.236(3)
γ (deg)			94.357(3)
V (Å^3)	9087.1(2)	3246.94(12)	2688.60(18)
Z	8	2	2
μ (mm^{-1})	0.666	0.491	0.682
T (K)	150.00(10)	150.00(10)	150.00(10)
ρ_{calcd} (g cm^{-3})	1.557	1.378	1.527
F(000)	4338	1388	1256
θ range(deg)	1.622 to 24.996	1.646 to 24.997	1.605 to 25.000
data/restraints /parameters	8003/0/604	5920/8/438	9466/0/678
R1, wR2 [I>2σ(I)]	0.0410, 0, 0.0966	0.0398, 0, 0.0828	0.0464, 0, 0.1106
R1, wR2 (all data)	0.0524, 0, 0.1026	0.0477, 0, 0.0877	0.0587, 0, 0.1177
GOF	1.065	1.046	1.098
largest diff. peak/hole [e Å^{-3}]	1.505/-0.701	0.579/-0.484	0.791/-0.792

$R1 = |\Sigma |F_o|-|F_c|| / |\Sigma |F_o||$.

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

$GOF = \{\Sigma [w(F_o^2 - F_c^2)^2] / (n-p)\}^{1/2}$

Table S2 Selected experimental and DFT calculated bond lengths (Å)

Bond lengths	[**1**]ClO_4		[**2**]$ClO_4.3C_6H_6$		[**3**]$ClO_4.2CH_3CN$	
	X-ray	DFT	X-ray	DFT	X-ray	DFT
Ru1-N1	2.014(3)	2.058	2.026(5)	2.064	2.009(3)	2.058
Ru1-N2	2.174(3)	2.204	2.166(7)	2.204	2.128(3)	2.200
Ru1-Cl1	2.4210(9)	2.460	2.408(2)	2.462	2.4049(10)	2.460
Ru1-P1	2.4257(9)	2.529	2.4229(13)	2.527	2.4245(11)	2.528
Ru1-P2	2.4461(9)	2.535	-	-	2.4191(11)	2.535
Ru1-C1	1.865(4)	1.887	1.883(11)		1.876(4)	1.888
C1-O1	1.140(4)		1.091(11)	-	1.143(5)	
N1-N4	1.309(4)	1.302	1.307(11)	1.302	1.304(5)	1.303
N1-C2	1.399(4)	1.397	1.398(12)	1.394	1.409(5)	1.395
N4-C9	1.357(4)	1.350	1.345(11)	1.348	1.365(5)	1.348
N2-C9	1.331(4)	1.384	1.304(10)		1.334(5)	1.331
N3-C2	1.287(4)	1.298	1.293(12)	1.299	1.292(5)	1.367

Table S3 Selected experimental and DFT calculated bond angles (deg)

Bond angles	[**1**]ClO_4		[**2**]$ClO_4.3C_6H_6$		[**3**]$ClO_4.2CH_3CN$	
	X-ray	DFT	X-ray	DFT	X-ray	DFT
N1-Ru1-N2	76.00(10)	75.26	75.9(3)	75.28	75.50(12)	75.30
N1-Ru1-C1	96.94(12)	97.76	98.6(4)	97.74	97.46(15)	97.83
N1-Ru1-P1	93.24(8)	92.93	94.06(3)	95.57	94.06(9)	93.45
N1-Ru1-P2	90.27(8)	95.78	-	-	91.68(9)	93.04
N2-Ru1-Cl1	95.49(7)	94.59	93.44(19)	94.51	96.44(9)	94.54
N2-Ru1-P1	88.74(7)	91.07	90.00(5)	91.00	88.89(9)	91.08
N2-Ru1-P2	94.92(7)	92.36	-	-	90.95(9)	92.06
N1-Ru1-Cl1	171.44(8)	169.76	169.4(3)	169.71	171.93(10)	169.79
Cl1-Ru1-C1	91.61(10)	92.39	92.0(3)	97.74	90.61(12)	92.32
N2-Ru1-C1	172.13(12)	172.95	174.5(4)	172.95	172.94(14)	173.08
P1-Ru1-P2	175.45(3)	171.19	-	-	174.03(4)	171.44
P1-Ru1-P1	-	-	171.63(6)	171.50	-	-
Ru1-N1-C2	128.9(2)	128.51	129.7(6)	128.53	126.7(3)	128.59
Ru1-N1-N4	120.5(2)	119.63	119.2(6)	119.41	121.5(2)	119.56
Ru1-N2-C9	108.1(2)	108.02	108.2(6)	107.99	110.3(2)	108.12
Ru1-P1-C16	118.75(12)	117.75	-	-	118.62(15)	116.48
Ru1-P1-C18	-	-	118.43(19)	116.25	-	-
Ru1-P1-C22	113.00(12)	113.92	-	-	111.47(13)	113.35
Ru1-P1-C24	-	-	110.1(2)	113.71		
Ru1-P1-C28	113.39(11)	112.16	-	-	114.30(13)	113.26
Ru1-P1-C30	-	-	117.5(2)	113.51	-	-
Ru1-P2-C34	116.55(11)	116.24	-	-	119.66(14)	117.83
Ru1-P2-C40	118.91(12)	113.67	-	-	113.14(14)	113.79
Ru1-P2-C46	109.59(11)	113.34	-	-	109.59(13)	112.03

Table S4 Determination of solution magnetic moment (Evans method) of **1**, **2** and **3**

Solution magnetic moments of **1**, **2** and **3** were determined by Evans method. The $CDCl_3$ (~0.56 cm^3) solution of **1** (2.8 mg) or **2** (3.1 mg) or **3** (2.9 mg) was taken in a NMR tube (5 mm). In another coaxial NMR tube with reference $CDCl_3$ solvent was taken. Proton NMR of the sample together with the Evans tube was recorded (400 MHz NMR spectrometer, 298 K) and the shift in $CDCl_3$ peak due to the paramagnetic $L^{\bullet-}$ centre in **1** or **2** or **3** with respect to the reference $CDCl_3$ was calculated to be 0.03 ppm in each case, respectively.

$$\chi_g = \frac{-3\Delta f}{4\pi \nu_0 m} + \chi_0 + \frac{\chi_0(d_0 - d_s)}{m} \qquad \text{..... eq. 1}$$

The mass susceptibility (χ_g) was calculated by using eq. 1, where Δf, ν_0, m, d_0/d_s, χ_0 corresponded to the shift in frequency in Hz, operating frequency of NMR spectrometer in Hz, concentration of the substance (g/mL), densities of $CDCl_3$ solvent/solution, mass susceptibility of the solvent, respectively. The molar susceptibility (χ_m) was obtained by multiplying χ_g by the molar mass and the effective magnetic moment μ_{eff} was calculated based on eq. 2.

For **1**:

$$\chi_M = 141.1 \times 10^{-5} \text{ cm}^3/\text{mol}$$

$$\mu_{eff} = 2.83 \times (\chi_M T)^{1/2} \text{ BM} \qquad \text{..... eq. 2}$$

$$= 2.83 \times (141.1 \times 10^{-5} \times 298.15)^{1/2} \text{ BM}$$

$$= 1.83 \text{ BM}$$

For **2**:

$$\chi_M = 132.5 \times 10^{-5} \text{ cm}^3/\text{mol}$$

$$\mu_{eff} = 2.83 \times (\chi_M T)^{1/2} \text{ BM} \qquad \text{..... eq. 2}$$

$$= 2.83 \times (132.5 \times 10^{-5} \times 298.15)^{1/2} \text{ BM}$$

$$= 1.78 \text{ BM}$$

For **3**:

$$\chi_M = 146.0 \times 10^{-5} \text{ cm}^3/\text{mol}$$

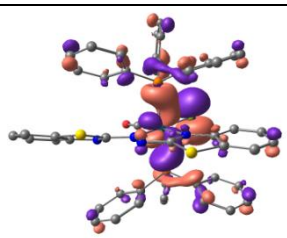
$$\mu_{eff} = 2.83 \times (\chi_M T)^{1/2} \text{ BM} \qquad \text{..... eq. 2}$$

$$= 2.83 \times (146.0 \times 10^{-5} \times 298.15)^{1/2} \text{ BM}$$

$$= 1.86 \text{ BM}$$

Table S5 Composition and energies of selected molecular orbitals of $\mathbf{1}^{+}$ (*S*=0)

MO	energy (eV)	% composition				
		Ru	L1	PPh_3	Cl	CO
HOMO-5	-8.914	0.03	0.17	0.77	0.03	0.00
HOMO-4	-8.901	0.05	0.36	0.50	0.08	0.01
HOMO-3	-8.812	0.03	0.36	0.57	0.04	0.00
HOMO-2	-8.701	0.22	0.21	0.48	0.08	0.01
HOMO-1	-8.657	0.28	0.11	0.11	0.46	0.03
HOMO	-8.351	0.18	0.05	0.41	0.35	0.00
LUMO	-6.033	0.14	0.77	0.08	0.01	0.00
LUMO+1	-3.728	0.33	0.08	0.54	0.03	0.01
LUMO+2	-3.314	0.05	0.83	0.10	0.00	0.02
LUMO+3	-3.064	0.29	0.33	0.27	0.08	0.03
LUMO+4	-2.901	0.07	0.13	0.74	0.02	0.03
LUMO+5	-2.859	0.10	0.11	0.69	0.00	0.10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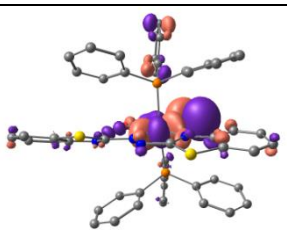
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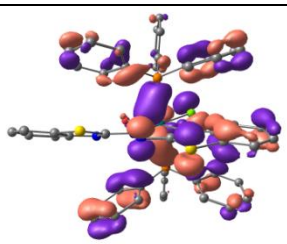
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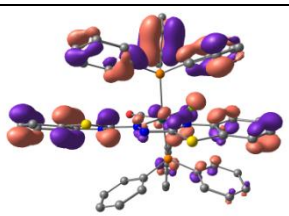
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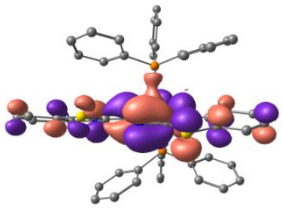
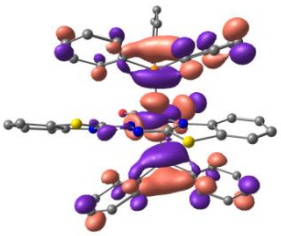

LUMO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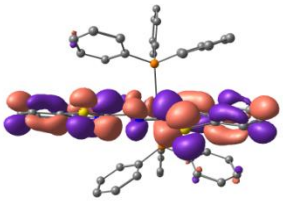

LUMO+2

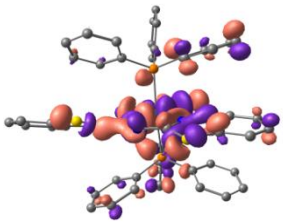

LUMO+3

Table S6 Composition and energies of selected molecular orbitals of **1** (*S*=1/2)

MO	energy (eV)	% composition				
		Ru	L1	PPh_3	Cl	CO
			α-spin			
HOMO-5	-6.105	0.02	0.93	0.05	0.00	0.00
HOMO-4	-5.968	0.19	0.53	0.19	0.08	0.00
HOMO-3	-5.880	0.07	0.48	0.42	0.04	0.00
HOMO-2	-5.615	0.42	0.08	0.03	0.43	0.05
HOMO-1	-5.463	0.33	0.15	0.17	0.34	0.00
HOMO	-5.873	0.13	0.78	0.08	0.01	0.00
LUMO	-0.908	0.30	0.06	0.61	0.01	0.01
LUMO+1	-0.513	0.03	0.02	0.93	0.00	0.01
LUMO+2	-0.469	0.04	0.06	0.89	0.01	0.01
LUMO+3	-0.307	0.03	0.07	0.89	0.00	0.01
LUMO+4	-0.273	0.03	0.39	0.57	0.00	0.00
LUMO+5	-0.170	0.13	0.06	0.78	0.00	0.02
			β-spin			
HOMO-5	-6.114	0.14	0.49	0.34	0.00	0.02
HOMO-4	-6.010	0.01	0.95	0.04	0.01	0.00
HOMO-3	-5.793	0.24	0.35	0.40	0.01	0.00
HOMO-2	-5.765	0.07	0.53	0.21	0.18	0.01
HOMO-1	-5.581	0.41	0.11	0.03	0.41	0.04
HOMO	-5.281	0.40	0.24	0.09	0.27	0.00
LUMO	-2.174	0.11	0.79	0.09	0.00	0.00
LUMO+1	-0.889	0.30	0.06	0.62	0.01	0.01
LUMO+2	-0.511	0.03	0.02	0.94	0.00	0.01
LUMO+3	-0.464	0.04	0.04	0.91	0.01	0.01
LUMO+4	-0.304	0.03	0.05	0.91	0.00	0.01
LUMO+5	-0.233	0.04	0.17	0.78	0.00	0.01

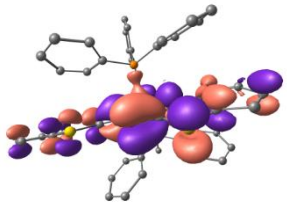
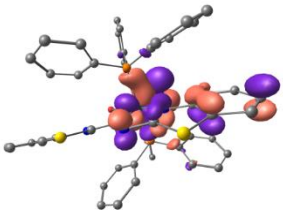
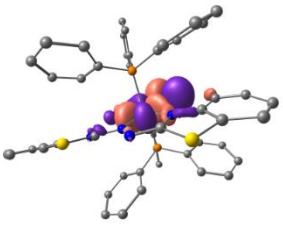
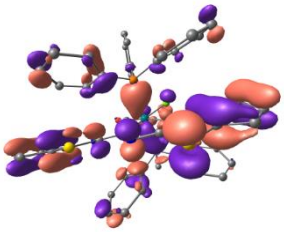
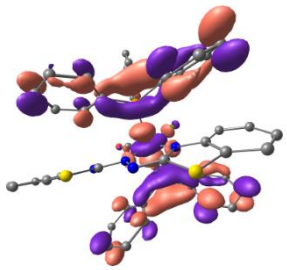
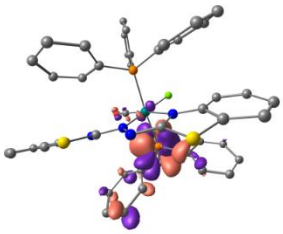
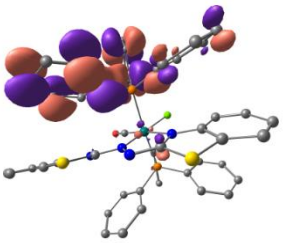
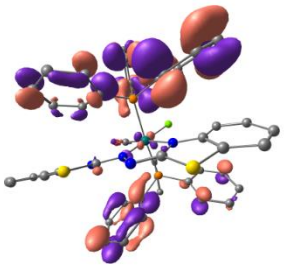
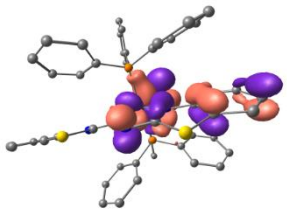
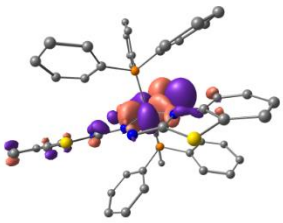
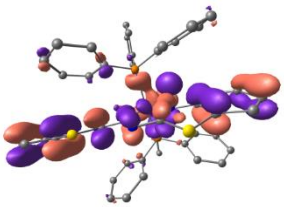
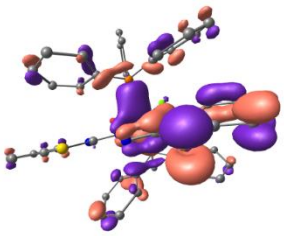
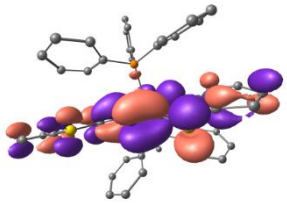
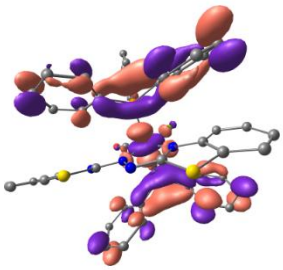
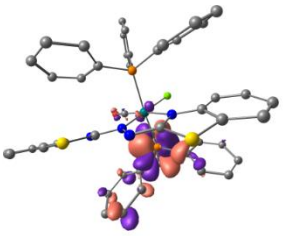
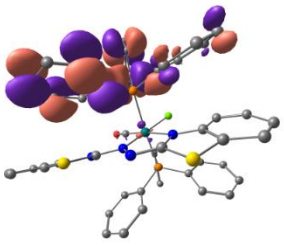
α-spin			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S7 Composition and energies of selected molecular orbitals of $\mathbf{1}^{-}$ (*S*=0)

MO	energy (eV)	% composition				
		Ru	L1	PPh_3	Cl	CO
HOMO-5	-3.002	0.02	0.94	0.02	0.02	0.00
HOMO-4	-2.908	0.17	0.59	0.22	0.01	0.01
HOMO-3	-2.792	0.29	0.45	0.04	0.21	0.01
HOMO-2	-2.614	0.50	0.09	0.02	0.33	0.05
HOMO-1	-2.303	0.36	0.43	0.05	0.15	0.01
HOMO	0.006	0.11	0.79	0.10	0.00	0.00
LUMO	1.692	0.19	0.04	0.76	0.00	0.01
LUMO+1	1.713	0.07	0.02	0.91	0.00	0.00
LUMO+2	1.836	0.08	0.03	0.87	0.00	0.00
LUMO+3	2.047	0.01	0.02	0.96	0.00	0.00
LUMO+4	2.131	0.03	0.01	0.95	0.00	0.01
LUMO+5	2.323	0.08	0.03	0.88	0.00	0.00

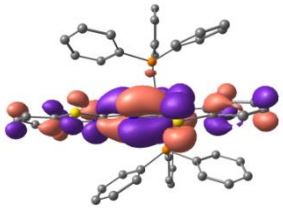
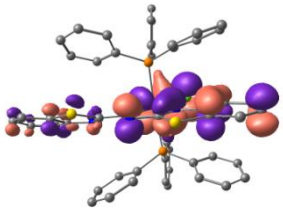
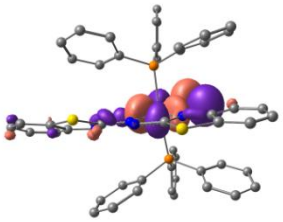
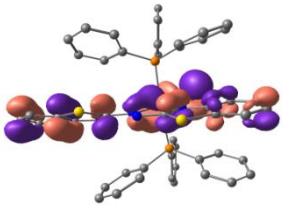
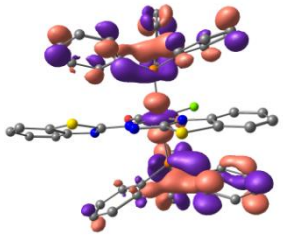
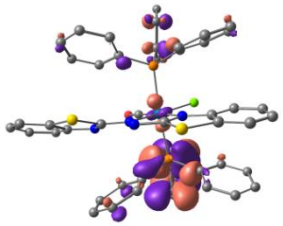
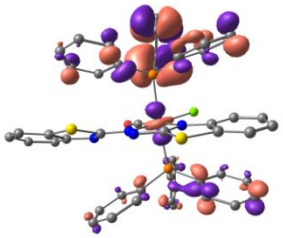
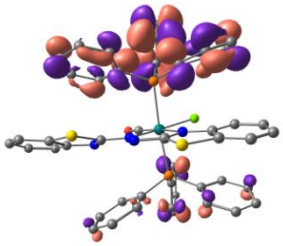
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S8 Composition and energies of selected molecular orbitals of $\mathbf{2}^{+}$ (*S*=0)

MO	energy (eV)	% composition				
		Ru	L2	PPh_3	Cl	CO
HOMO-5	-8.739	0.01	0.01	0.98	0.01	0.00
HOMO-4	-8.726	0.03	0.11	0.85	0.01	0.00
HOMO-3	-8.615	0.12	0.28	0.54	0.06	0.00
HOMO-2	-8.563	0.25	0.05	0.19	0.47	0.03
HOMO-1	-8.520	0.06	0.55	0.38	0.00	0.00
HOMO	-8.268	0.21	0.11	0.32	0.36	0.00
LUMO	-6.036	0.12	0.70	0.17	0.01	0.00
LUMO+1	-3.570	0.31	0.08	0.55	0.05	0.00
LUMO+2	-3.176	0.01	0.78	0.21	0.00	0.01
LUMO+3	-3.120	0.32	0.28	0.26	0.09	0.05
LUMO+4	-2.927	0.04	0.68	0.26	0.00	0.02
LUMO+5	-2.882	0.07	0.14	0.77	0.00	0.01

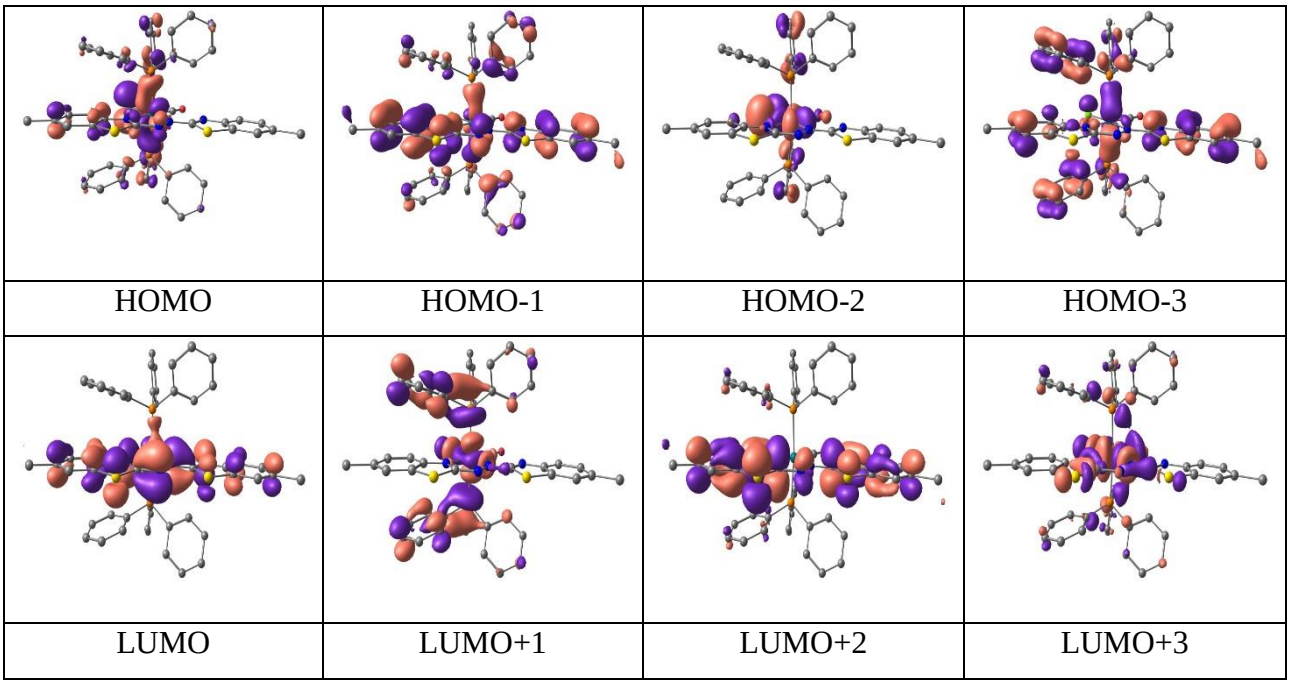


Table S9 Composition and energies of selected molecular orbitals of **2** (*S*=1/2)

MO	energy (eV)	% composition				
		Ru	L2	PPh_3	Cl	CO
			α-spin			
HOMO-5	-6.032	0.01	0.75	0.23	0.01	0.00
HOMO-4	-5.867	0.18	0.54	0.24	0.04	0.00
HOMO-3	-5.756	0.06	0.48	0.31	0.15	0.00
HOMO-2	-5.662	0.41	0.06	0.04	0.45	0.04
HOMO-1	-5.440	0.32	0.32	0.09	0.27	0.00
HOMO	-3.943	0.12	0.71	0.16	0.01	0.00
LUMO	-0.846	0.24	0.06	0.67	0.02	0.01
LUMO+1	-0.577	0.06	0.05	0.88	0.02	0.00
LUMO+2	-0.576	0.02	0.01	0.95	0.00	0.01
LUMO+3	-0.307	0.07	0.20	0.73	0.00	0.00
LUMO+4	-0.296	0.05	0.07	0.86	0.01	0.01
LUMO+5	-0.109	0.10	0.06	0.83	0.00	0.00
			β-spin			
HOMO-5	-6.035	0.12	0.37	0.65	0.03	0.01
HOMO-4	-5.942	0.01	0.21	0.03	0.03	0.00
HOMO-3	-5.735	0.16	0.27	0.25	0.01	0.01
HOMO-2	-5.642	0.42	0.04	0.03	0.41	0.05
HOMO-1	-5.634	0.18	0.22	0.06	0.28	0.00
HOMO	-5.230	0.31	0.62	0.04	0.11	0.01
LUMO	-2.296	0.09	0.82	0.09	0.00	0.00
LUMO+1	-0.833	0.23	0.04	0.66	0.01	0.01
LUMO+2	-0.576	0.06	0.02	0.93	0.01	0.00
LUMO+3	-0.572	0.02	0.01	0.96	0.00	0.01
LUMO+4	-0.280	0.08	0.03	0.91	0.00	0.01
LUMO+5	-0.263	0.04	0.05	0.92	0.00	0.01

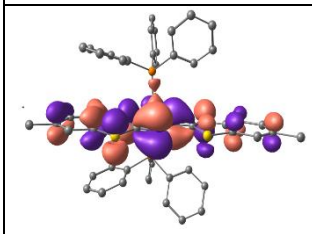
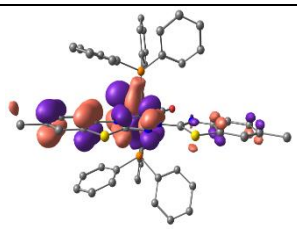
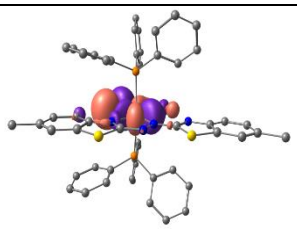
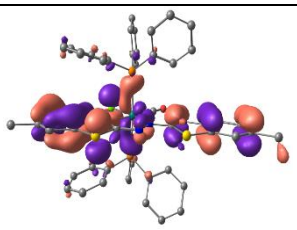
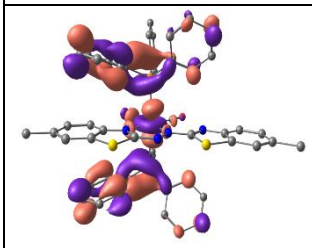
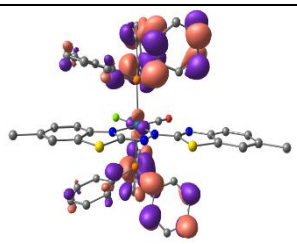
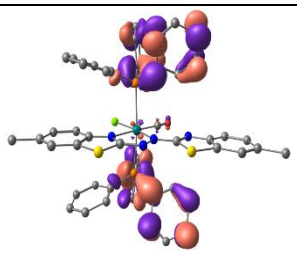
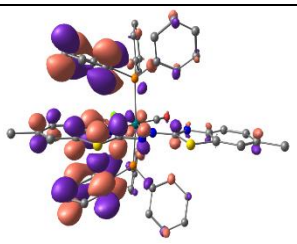
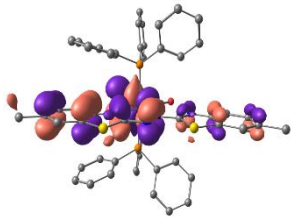
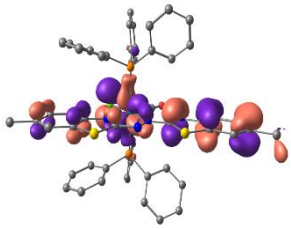
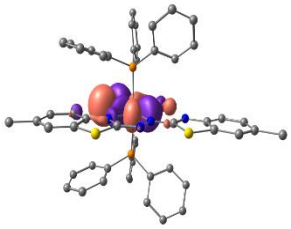
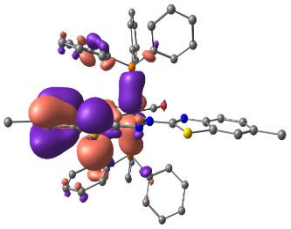
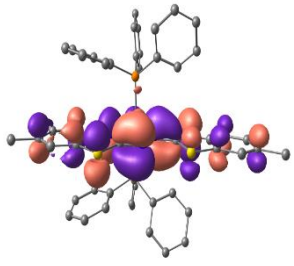
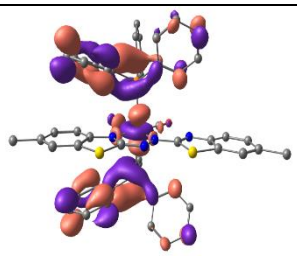
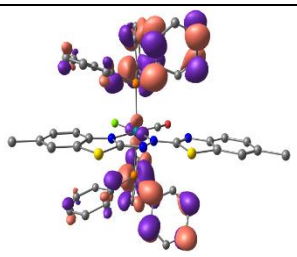
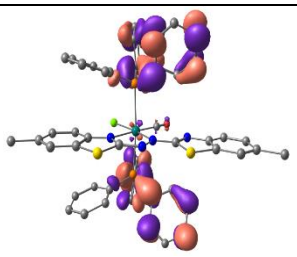
α-spin			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S10 Composition and energies of selected molecular orbitals of $\mathbf{2}^{-}$ (*S*=0)

MO	energy (eV)	% composition				
		Ru	L2	PPh_3	Cl	CO
HOMO-5	-3.048	0.02	0.85	0.11	0.03	0.00
HOMO-4	-2.848	0.12	0.74	0.12	0.01	0.01
HOMO-3	-2.802	0.36	0.25	0.16	0.23	0.00
HOMO-2	-2.767	0.50	0.05	0.03	0.35	0.06
HOMO-1	-2.287	0.24	0.59	0.08	0.09	0.00
HOMO	-0.170	0.09	0.72	0.19	0.00	0.00
LUMO	1.611	0.07	0.03	0.88	0.00	0.01
LUMO+1	1.659	0.01	0.00	0.98	0.00	0.00
LUMO+2	1.769	0.18	0.05	0.75	0.01	0.00
LUMO+3	2.003	0.01	0.03	0.94	0.00	0.01
LUMO+4	2.106	0.01	0.01	0.97	0.01	0.00
LUMO+5	2.191	0.15	0.02	0.84	0.00	0.00

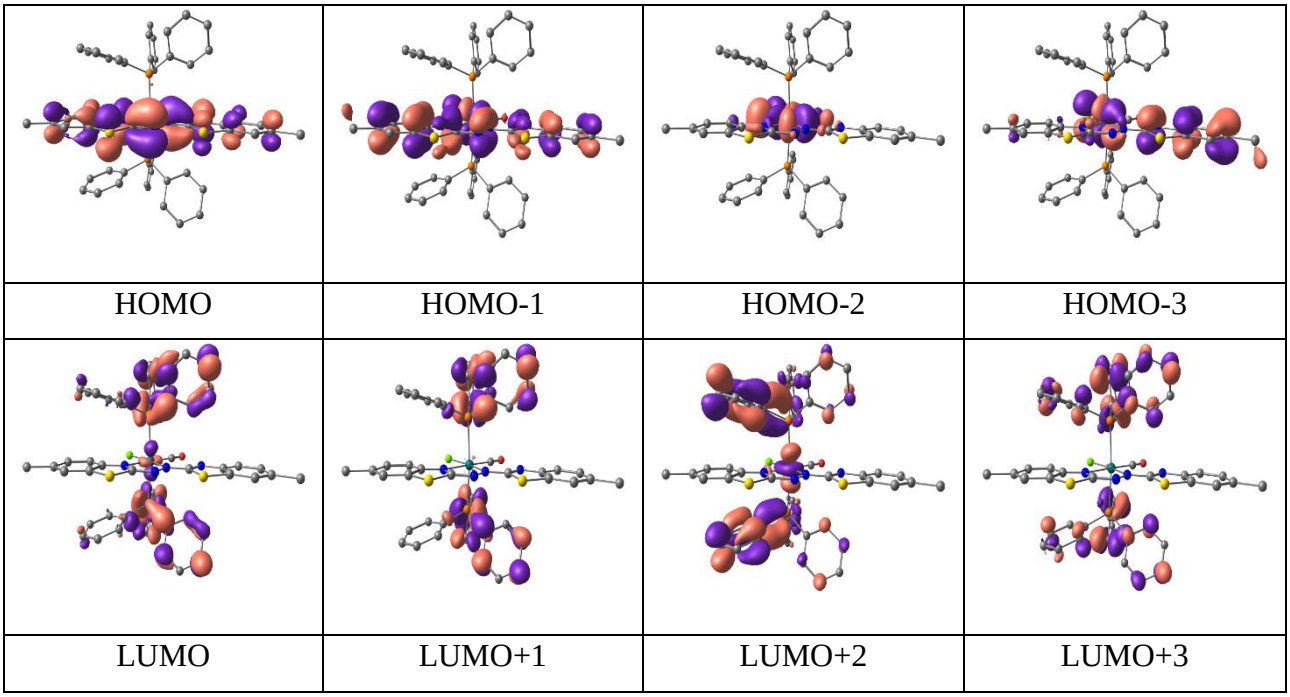


Table S11 Composition and energies of selected molecular orbitals of $\mathbf{3}^{+}$ (*S*=0)

MO	energy (eV)	% composition				
		Ru	L3	PPh_3	Cl	CO
HOMO-5	-9.037	0.27	0.09	0.22	0.39	0.03
HOMO-4	-8.910	0.02	0.05	0.90	0.03	0.00
HOMO-3	-8.857	0.06	0.03	0.76	0.14	0.01
HOMO-2	-8.810	0.13	0.21	0.42	0.24	0.00
HOMO-1	-8.756	0.07	0.62	0.29	0.01	0.01
HOMO	-8.540	0.17	0.11	0.47	0.25	0.00
LUMO	-6.652	0.11	0.82	0.06	0.01	0.00
LUMO+1	-4.213	0.39	0.11	0.42	0.08	0.00
LUMO+2	-3.672	0.33	0.36	0.19	0.04	0.08
LUMO+3	-3.632	0.11	0.77	0.09	0.02	0.02
LUMO+4	-3.228	0.05	0.78	0.16	0.00	0.01
LUMO+5	-3.131	0.02	0.82	0.14	0.01	0.01

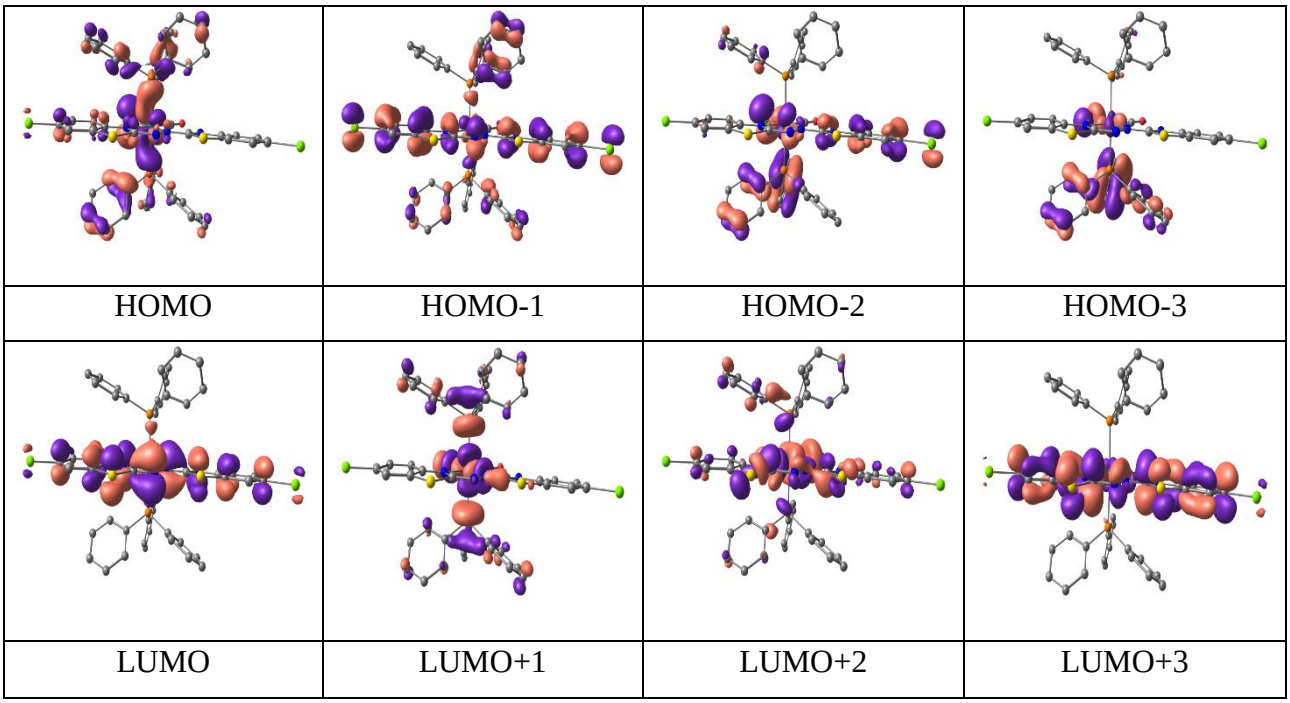


Table S12 Composition and energies of selected molecular orbitals of **3** (*S*=1/2)

MO	energy (eV)	% composition				
		Ru	L3	PPh_3	Cl	CO
			α-spin			
HOMO-5	-6.478	0.03	0.89	0.06	0.03	0.00
HOMO-4	-6.321	0.24	0.25	0.45	0.05	0.01
HOMO-3	-6.166	0.37	0.07	0.07	0.45	0.04
HOMO-2	-6.122	0.10	0.54	0.15	0.20	0.00
HOMO-1	-5.887	0.26	0.38	0.13	0.23	0.00
HOMO	-4.659	0.11	0.83	0.05	0.01	0.00
LUMO	-1.455	0.35	0.06	0.53	0.04	0.01
LUMO+1	-0.871	0.22	0.15	0.56	0.04	0.03
LUMO+2	-0.751	0.03	0.05	0.91	0.00	0.01
LUMO+3	-0.724	0.03	0.56	0.40	0.00	0.01
LUMO+4	-0.676	0.14	0.18	0.61	0.04	0.03
LUMO+5	-0.633	0.05	0.28	0.66	0.00	0.01
			β-spin			
HOMO-5	-6.504	0.08	0.66	0.25	0.00	0.01
HOMO-4	-6.377	0.02	0.91	0.03	0.03	0.00
HOMO-3	-6.231	0.25	0.23	0.38	0.12	0.02
HOMO-2	-6.137	0.33	0.10	0.16	0.37	0.04
HOMO-1	-5.980	0.28	0.33	0.10	0.30	0.00
HOMO	-5.665	0.20	0.64	0.05	0.10	0.00
LUMO	-3.069	0.08	0.85	0.06	0.00	0.00
LUMO+1	-1.431	0.35	0.06	0.54	0.03	0.01
LUMO+2	-0.849	0.18	0.13	0.63	0.03	0.02
LUMO+3	-0.749	0.02	0.03	0.93	0.00	0.01
LUMO+4	-0.687	0.07	0.18	0.73	0.01	0.01
LUMO+5	-0.653	0.12	0.12	0.70	0.03	0.04

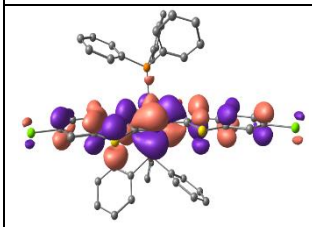
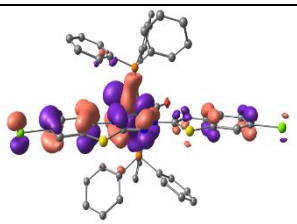
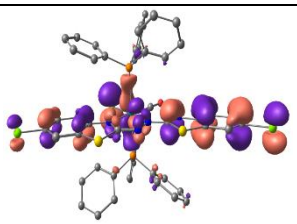
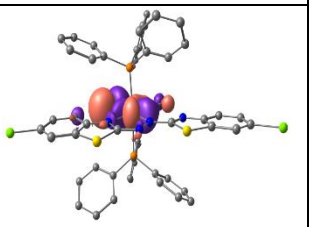
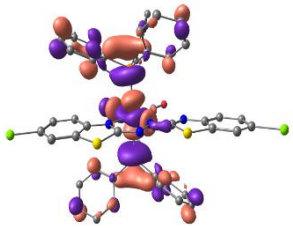
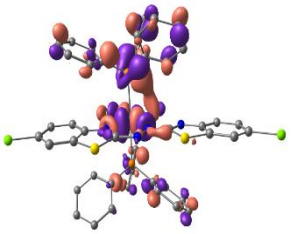
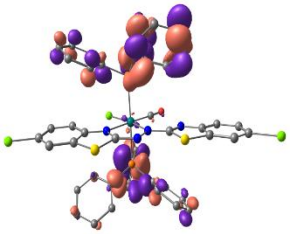
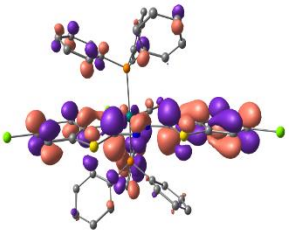
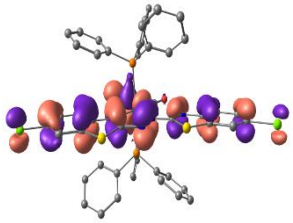
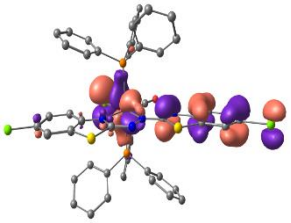
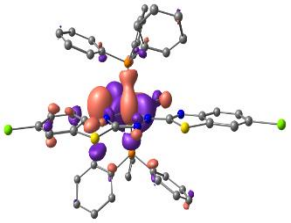
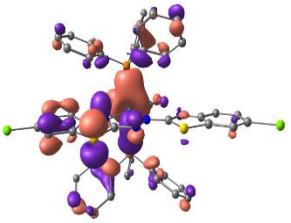
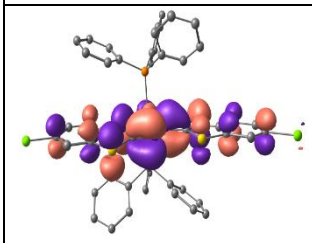
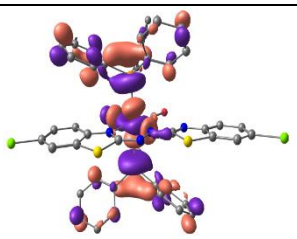
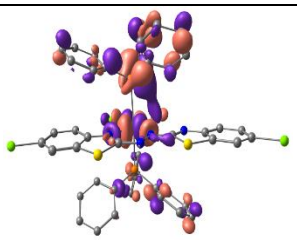
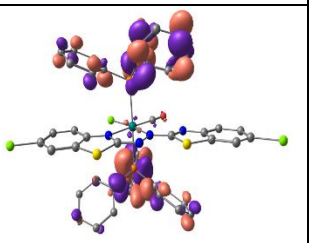
α-spin			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-spin			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S13 Composition and energies of selected molecular orbitals of $\mathbf{3}^{-}$ (*S*=0)

MO	energy (eV)	% composition				
		Ru	L3	PPh_3	Cl	CO
HOMO-5	-3.518	0.15	0.76	0.05	0.03	0.01
HOMO-4	-3.493	0.07	0.77	0.11	0.04	0.01
HOMO-3	-3.397	0.47	0.09	0.04	0.34	0.06
HOMO-2	-3.269	0.43	0.29	0.04	0.24	0.00
HOMO-1	-2.811	0.14	0.78	0.03	0.04	0.01
HOMO	-1.010	0.08	0.86	0.06	0.00	0.00
LUMO	1.110	0.31	0.05	0.62	0.02	0.01
LUMO+1	1.363	0.02	0.01	0.96	0.00	0.00
LUMO+2	1.384	0.01	0.01	0.97	0.00	0.01
LUMO+3	1.583	0.07	0.04	0.89	0.00	0.01
LUMO+4	1.633	0.02	0.01	0.96	0.00	0.01
LUMO+5	1.799	0.13	0.03	0.84	0.00	0.00