Supporting Information

Mix and (Mis)Match: Further studies of the electronic structure and mixed-valence characteristics of 1,4-diethynylbenzene-bridged bimetallic complexes

Parvin Safari, Stephen A. Moggach, Paul J. Low*

School of Molecular Sciences, University of Western Australia, 35 Stirling Highway, Crawley, WA, 6009, Australia

paul.low@uwa.edu.au

Single crystal X-ray diffraction: {Cp*(CO)$_3$W}(μ-C≡CC$_6$H$_4$C≡C){Ru(dppe)Cp*} (5a)

Crystals of **5a** were small and weakly diffracting. This problem was exasperated as increased collection times and exposure to the high-intensity X-rays from our PhotonJet (Cu) X-ray source caused decomposition over the duration of the diffraction experiment. In order to maximise the resolution of the data set, whilst collecting data as fast as possible, a single colourless block with dimensions 0.09 × 0.07 × 0.04 mm^3 was selected and mounted on a XtaLAB Synergy diffractometer. The crystal was kept at a steady T = 120.0(2) K during data collection and collected for 17 hours. A resolution of 1.2 Å was obtained using this strategy. The structure was solved with the **ShelXT** 2014/5 solution program using dual methods,[1, 2] and by using **Olex2** as the graphical interface.[3, 4] The model was refined with **ShelXL** 2018/3 using full matrix least squares minimisation on F^2.[5] All phenyl groups and the disordered Cp* ligand were refined as rigid bodies. The carbonyl C-O bond lengths were restrained to be equal. Thermal similarity constraints were applied to the rigid bodies, due to the low resolution of the data set. The supplementary crystallographic data have been deposited into the Cambridge Structural Database (CCDC 1995547).

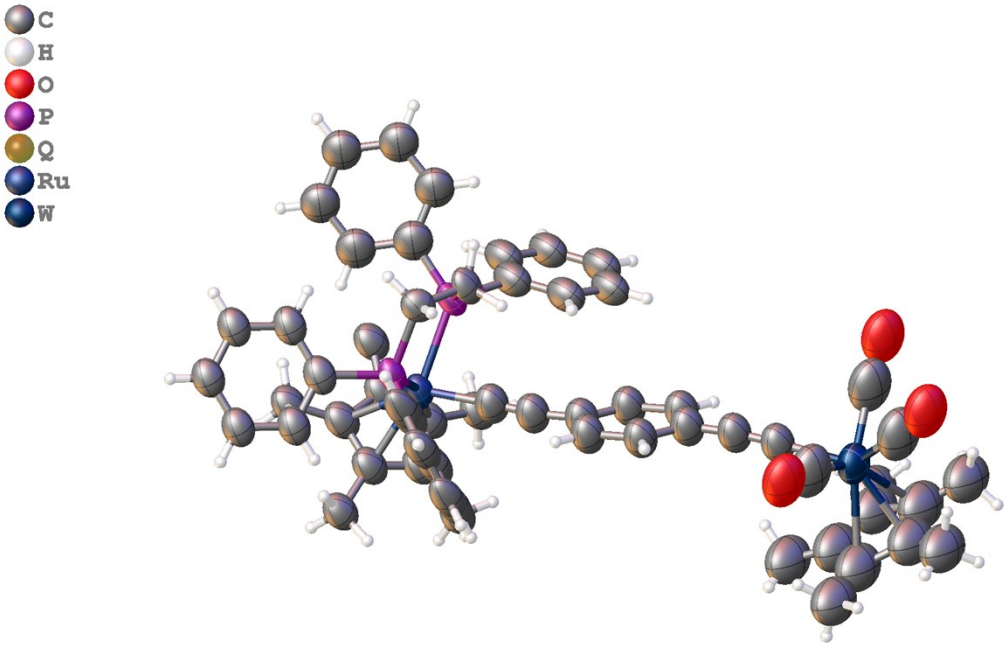


Figure S1: Molecular structure of **5a** with anisotropic displacement parameters drawn at 50% probability. The disorder on the Cp* ligand has been removed for clarity.

Crystal Data. $C_{59}H_{55}O_3P_2RuW$, M_r = 1158.89, monoclinic, $P2_1/c$ (No. 14), a = 14.6530(18) Å, b = 22.4069(19) Å, c = 16.827(3) Å, β = 110.409(17)°, α = γ = 90°, V = 5177.9(13) Å^3, T = 120.0(2) K, Z = 4, Z' = 1, μ(Cu K$_\alpha$) = 7.324, 26569 reflections measured, 5209 unique (R_{int} = 0.1865) which were used in all calculations. The final wR_2 was 0.2979 (all data) and R_1 was 0.1053 (I > 2(I)).

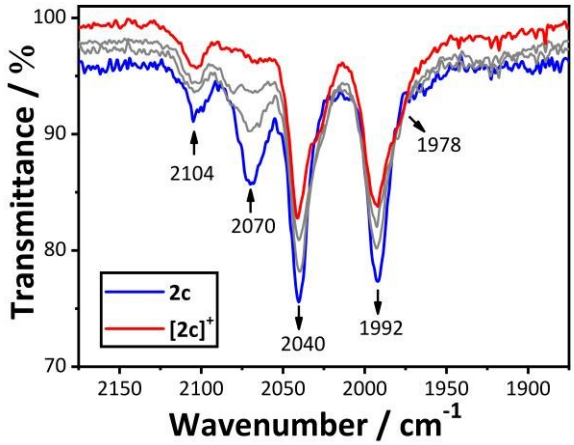


Figure S2 The IR spectroelectrochemical data for [**2c**]$^{n+}$ (n = 0, 1)

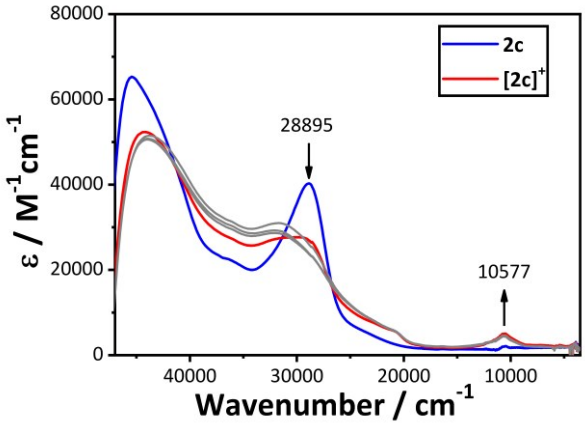


Figure S3 The UV-vis-NIR spectroelectrochemical data for [**2c**]$^{n+}$ (n = 0, 1)

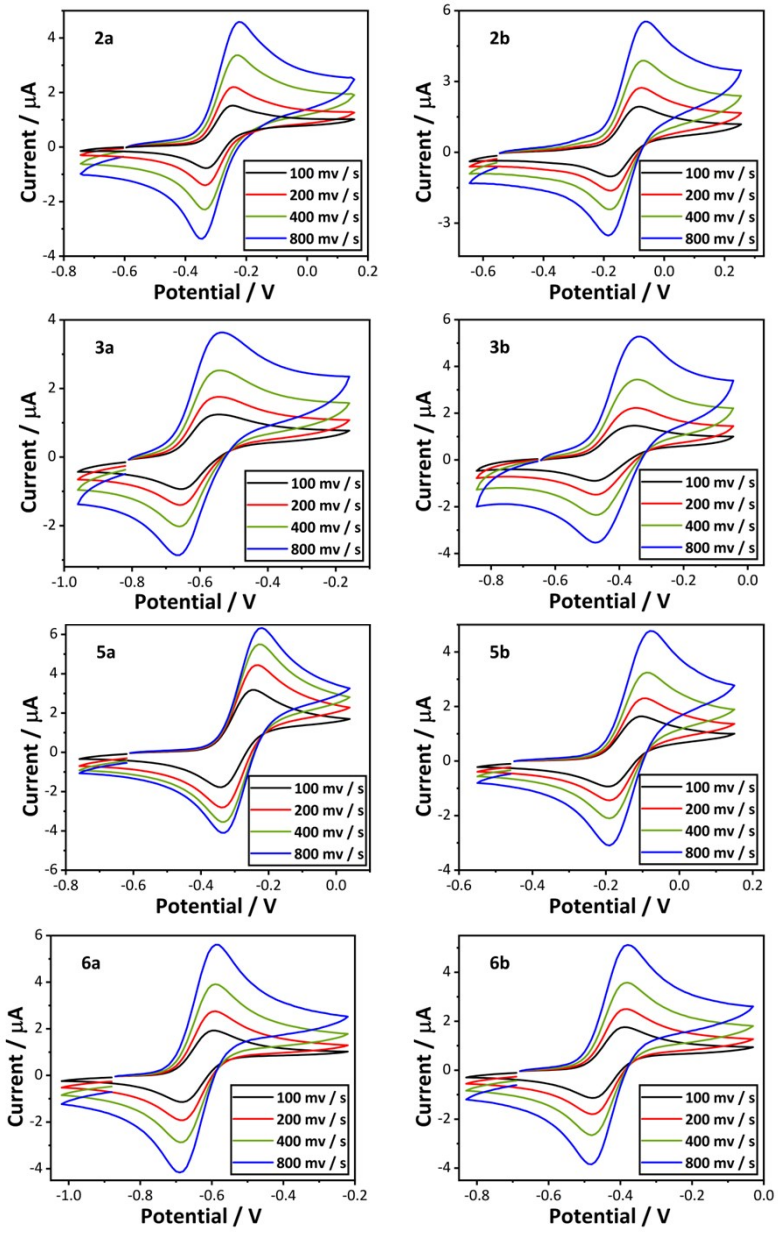


Figure S4 Plots of the reversible first wave observed by cyclic voltammetry (CV) from complexes **2**, **3**, **5** and **6** (CH_2Cl_2, 0.1 M NBu_4PF_6, R.T.) vs ferrocene.

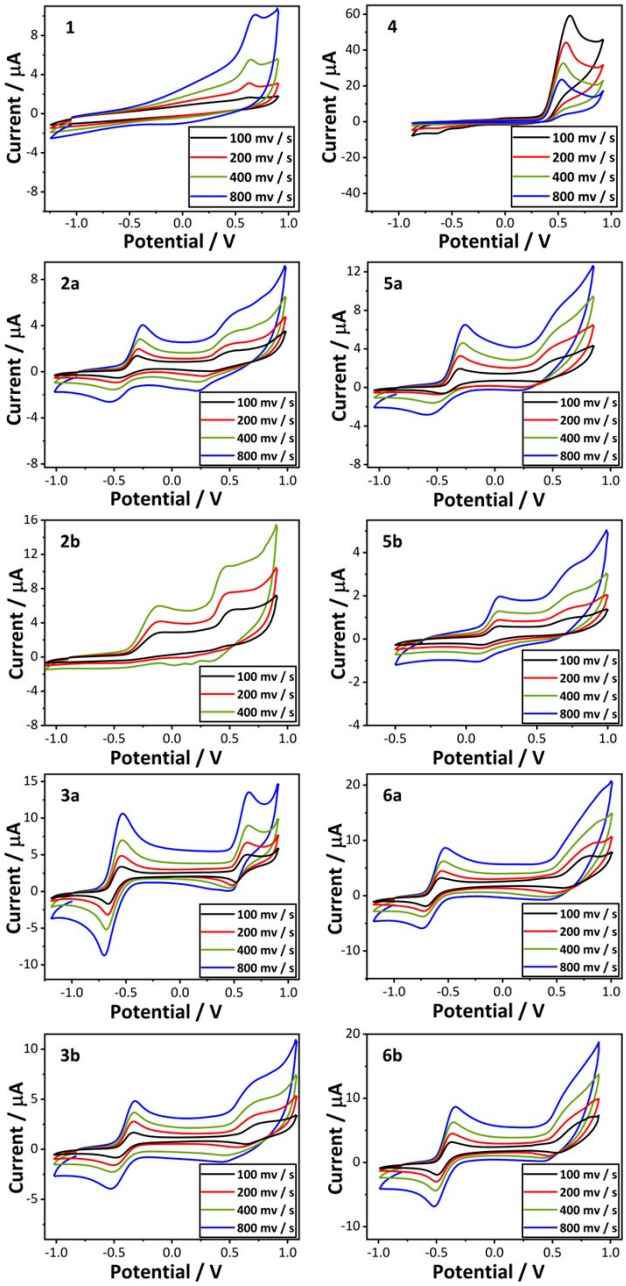


Figure S5 Plots of the cyclic voltammograms of complexes **1**, **2**, **3**, **4**, **5** and **6** (CH_2Cl_2, 0.1 M NBu_4PF_6, R.T.) vs ferrocene.

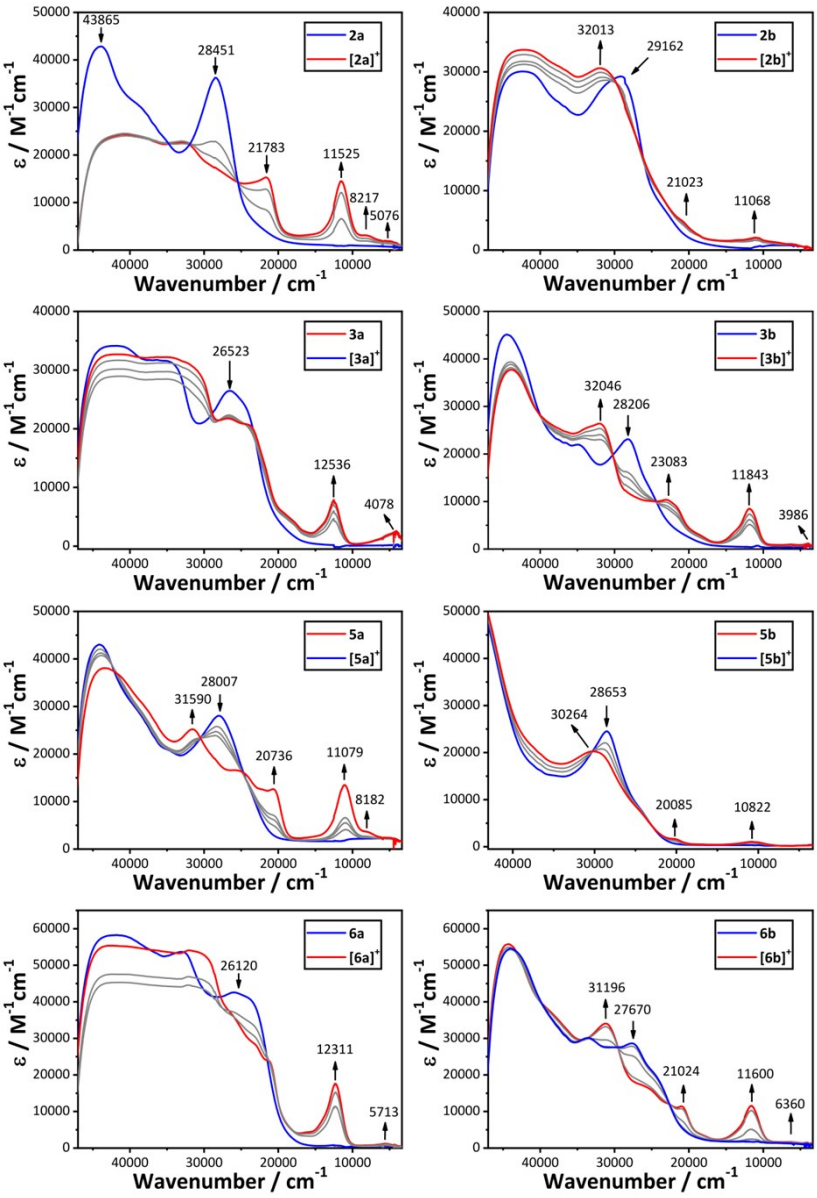
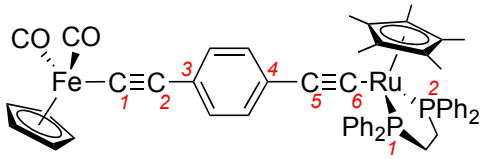


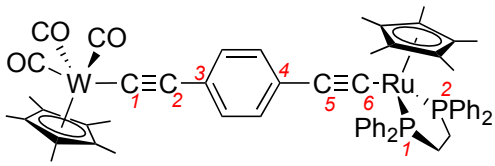
Figure S6 Plots of the UV-vis-NIR spectroelectrochemical data for complexes **2**, **3**, **5** and **6**.

Quantum chemical calculations

Table S1: Selected bond lengths (Å) and angles (°) from DFT optimised geometries of **2a**, [**2a**]$^+$, **5a**, [**5a**]$^+$.



	2a	[**2a**]$^+$
Fe-C1	1.9297	1.9424
C1-C2	1.2208	1.2222
C2-C3	1.4291	1.4207
C4-C5	1.4249	1.4109
C5-C6	1.2279	1.2386
C6-Ru	2.0297	1.9578
Ru-P1	2.3483	2.4098
Ru-P2	2.3390	2.3881
Fe-C1-C2	179.20	179.35
C1-C2-C3	179.40	179.51
C4-C5-C6	178.52	179.02
C5-C6-Ru	176.36	175.79
P1-Ru-P2	83.53	82.10



	5a	[**5a**]$^+$
W-C1	2.1545	2.1468
C1-C2	1.2214	1.2231
C2-C3	1.4278	1.4189
C4-C5	1.4245	1.4105
C5-C6	1.2281	1.2387
C6-Ru	2.0291	1.9575
Ru-P1	2.3478	2.4075
Ru-P2	2.3384	2.3876
W-C1-C2	179.47	179.75
C1-C2-C3	179.76	179.84
C4-C5-C6	179.10	179.24
C5-C6-Ru	176.51	175.71
P1-Ru-P2	83.53	82.12

Table S2. Summary of energy and composition of selected frontier molecular orbitals of **2a**

MO		eV	Cp	$(CO)_2$	Fe	C≡C	C_6H_4	C≡C	Ru	dppe	Cp*
228	L+5	0.06	3	17	10	6	25	5	3	29	2
227	L+4	0	1	73	23	2	1	0	0	1	0
226	L+3	0	0	0	0	0	0	0	2	96	1
225	L+2	-0.11	1	1	1	0	0	0	15	72	10
224	L+1	-0.23	16	36	45	3	0	0	0	0	0
223	LUMO	-0.25	18	17	42	4	13	2	1	2	0
222	HOMO	-4.83	0	0	1	8	22	28	27	5	8
221	H-1	-5.34	0	0	0	0	1	14	50	10	25
220	H-2	-5.83	1	0	2	8	9	23	27	8	21
219	H-3	-6.04	1	0	3	15	13	14	26	8	18
218	H-4	-6.57	2	0	4	11	4	8	16	21	33
217	H-5	-6.75	0	0	0	2	0	6	48	18	24

Table S3. Summary of energy and composition of selected α- and β-spin orbitals of [**2a**]$^+$

Alpha MO		eV	Cp	$(CO)_2$	Fe	C≡C	C_6H_4	C≡C	Ru	dppe	Cp*
227	L+4	-0.48	17	35	44	3	0	0	0	2	0
226	L+3	-0.48	1	1	3	0	0	1	4	87	3
225	L+2	-0.66	0	0	1	0	2	5	20	62	10
224	L+1	-0.81	3	4	8	10	51	13	3	6	2
223	LUMO	-1.16	0	0	0	0	1	0	29	47	23
222	HOMO	-5.94	2	1	5	24	33	17	8	5	5
221	H-1	-6.79	1	0	2	6	3	7	23	20	38
220	H-2	-6.8	1	0	3	7	4	6	23	16	38
219	H-3	-7.11	0	0	1	5	3	43	28	8	12
218	H-4	-7.25	6	1	13	69	5	3	2	1	1

Beta MO		eV	Cp	$(CO)_2$	Fe	C≡C	C_6H_4	C≡C	Ru	dppe	Cp*
227	L+5	-0.45	0	0	1	0	0	1	7	87	4
226	L+4	-0.48	17	36	44	3	0	0	0	0	0
225	L+3	-0.6	1	1	2	1	3	2	13	71	6
224	L+2	-0.63	8	7	18	9	34	7	6	8	2
223	L+1	-1	0	0	0	0	1	0	27	50	21
222	LUMO	-3.32	0	0	1	4	15	23	43	6	8
221	HOMO	-6.29	3	1	8	33	30	7	10	3	4
220	H-1	-6.71	0	0	0	0	1	16	41	11	31
219	H-2	-6.92	0	0	0	1	2	34	31	9	23
218	H-3	-7.2	2	0	4	11	3	6	8	33	31

Table S4. Summary of energy and composition of selected frontier molecular orbitals of **2b**.

MO		eV	Cp	$(CO)_2$	Fe	C≡C	C_6H_4	C≡C	Ru	dppe	Cp
208	L+5	0.04	2	9	6	3	13	3	3	61	1
207	L+4	0.01	1	73	23	2	1	0	0	1	0
206	L+3	-0.08	1	1	2	0	1	0	1	94	0
205	L+2	-0.15	0	0	1	0	0	0	18	72	9
204	L+1	-0.23	16	36	45	3	0	0	0	0	0
203	LUMO	-0.26	18	17	42	4	14	2	0	3	0
202	HOMO	-4.91	1	0	2	10	25	29	24	4	6
201	H-1	-5.73	0	0	0	0	2	29	54	7	8
200	H-2	-6.06	1	0	3	15	12	10	29	11	18
199	H-3	-6.18	1	0	3	13	9	16	34	7	16
198	H-4	-6.81	5	1	12	77	5	0	0	0	0
197	H-5	-6.93	3	1	4	8	4	13	4	46	17

Table S5. Summary of energy and composition of selected α- and β-spin orbitals of [**2b**]$^+$

Alpha MO		eV	Cp	$(CO)_2$	Fe	C≡C	C_6H_4	C≡C	Ru	dppe	Cp
207	L+4	-0.51	17	36	44	3	0	0	0	0	0
206	L+3	-0.52	1	1	1	0	1	1	3	90	2
205	L+2	-0.6	0	0	1	0	1	5	22	60	9
204	L+1	-0.92	3	3	7	11	54	14	3	4	1
203	LUMO	-1.21	0	0	0	0	0	0	32	49	19
202	HOMO	-6.03	2	1	5	25	34	17	8	3	4
201	H-1	-7.02	4	1	6	14	6	7	18	24	21
200	H-2	-7.17	1	0	1	5	3	37	41	5	6
199	H-3	-7.3	5	0	10	54	3	2	9	6	10
198	H-4	-7.34	2	0	4	18	3	16	19	16	23

Beta MO		eV	Cp	$(CO)_2$	Fe	C≡C	C_6H_4	C≡C	Ru	dppe	Cp
207	L+5	-0.49	1	1	3	0	0	2	8	82	3
206	L+4	-0.51	17	36	44	3	0	0	0	0	0
205	L+3	-0.55	0	0	0	0	0	1	7	89	3
204	L+2	-0.68	7	7	17	11	40	8	5	4	2
203	L+1	-1.06	0	0	0	0	0	0	30	52	17
202	LUMO	-3.51	0	0	1	5	19	27	37	5	7
201	HOMO	-6.39	3	1	9	34	28	6	12	3	4
200	H-1	-6.96	0	0	0	1	3	41	46	5	4
199	H-2	-7.2	0	0	0	1	1	9	31	25	32
198	H-3	-7.29	6	1	13	73	5	1	1	0	0

Table S6. Summary of energy and composition of selected frontier molecular orbitals of **5a**

MO		eV	Cp*	$(CO)_3$	W	C≡C	C_6H_4	C≡C	Ru	dppe	Cp*
254	L+5	0.13	0	2	0	1	5	1	1	89	0
253	L+4	0	0	0	0	0	1	0	2	95	1
252	L+3	-0.04	1	8	3	10	40	8	5	21	3
251	L+2	-0.13	0	1	0	2	7	1	13	66	8
250	L+1	-0.51	9	72	19	0	0	0	0	0	0
249	LUMO	-0.72	13	53	20	12	1	0	0	0	0
248	HOMO	-4.81	1	1	3	9	22	26	26	5	7
247	H-1	-5.35	0	0	0	0	1	13	50	11	26
246	H-2	-5.82	2	8	18	20	13	4	16	7	13
245	H-3	-5.92	0	1	3	2	2	32	35	6	18
244	H-4	-6.01	6	23	45	20	1	1	2	0	1
243	H-5	-6.45	1	6	12	3	5	12	7	20	35

Table S7. Summary of energy and composition of selected α- and β-spin orbitals of [**5a**]$^+$

Alpha MO		eV	Cp*	$(CO)_3$	W	C≡C	C_6H_4	C≡C	Ru	dppe	Cp*
253	L+4	-0.65	0	0	0	1	3	5	20	61	10
252	L+3	-0.74	9	72	18	0	1	0	0	0	0
251	L+2	-0.79	2	10	5	10	48	13	3	7	2
250	L+1	-0.99	12	48	18	12	7	2	1	0	0
249	LUMO	-1.16	0	0	0	0	1	0	29	47	23
248	HOMO	-5.8	2	7	16	23	27	12	5	3	3
247	H-1	-6.29	7	25	49	17	1	0	0	0	0
246	H-2	-6.62	1	8	17	6	5	9	14	18	23
245	H-3	-6.79	0	0	0	0	0	10	33	12	45
244	H-4	-7.12	0	0	0	0	4	45	31	8	12

Beta MO		eV	Cp*	$(CO)_3$	W	C≡C	C_6H_4	C≡C	Ru	dppe	Cp*
253	L+5	-0.58	1	7	3	11	42	8	7	18	3
252	L+4	-0.6	0	2	1	2	9	4	13	64	6
251	L+3	-0.74	9	72	19	0	0	0	0	0	0
250	L+2	-0.97	11	47	17	10	1	0	4	6	3
249	L+1	-1	2	6	2	2	2	0	24	44	17
248	LUMO	-3.33	0	0	1	4	15	23	43	6	8
247	HOMO	-6.06	3	11	25	26	20	4	7	2	3
246	H-1	-6.29	7	25	49	17	1	0	0	0	0
245	H-2	-6.7	0	0	0	0	1	16	42	10	31
244	H-3	-6.93	0	0	0	0	3	34	32	9	23

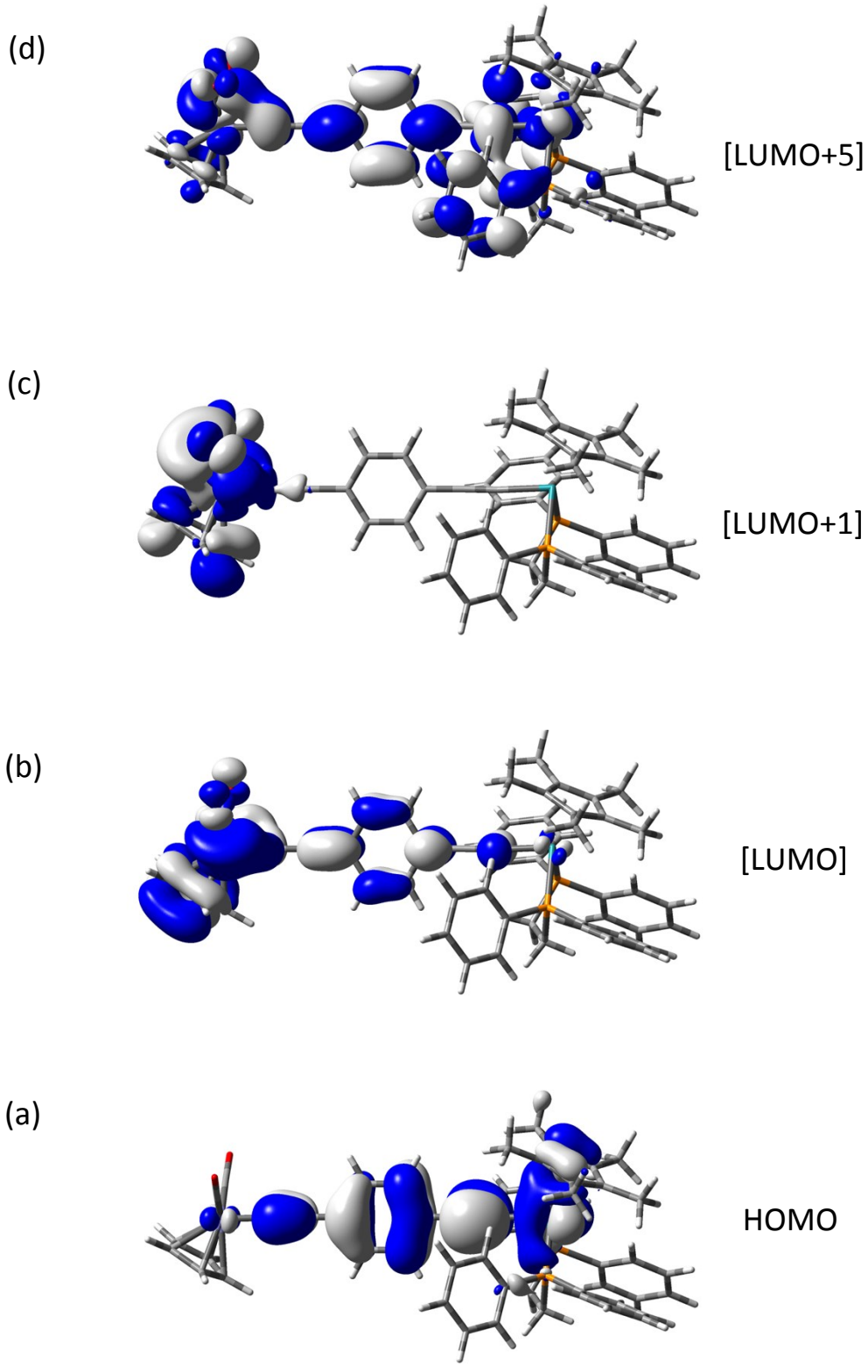


Figure S7. Plots of the (a) HOMO, (b) LUMO, (c) [LUMO+1] and (d) [LUMO+5] of **2a** (contours plotted at 0.02 $(e/bohr^3)^{1/2}$).

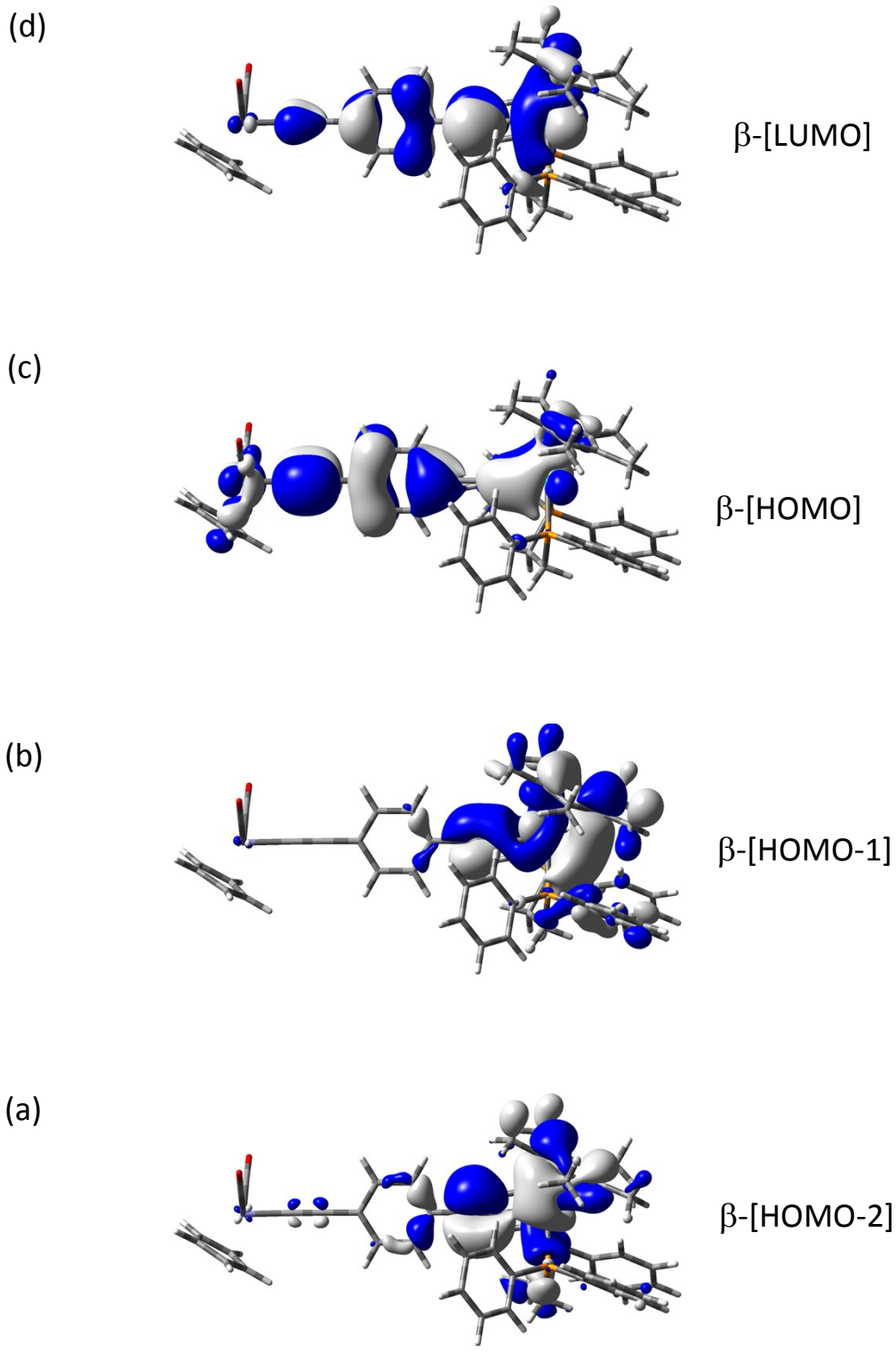


Figure S8. Plots of the (a) β[], (b) β[1], (c) β and (d) βLUMO of [**2a**]$^{+}$ (contours plotted at 0.02 (e/bohr^{3})$^{1/2}$).

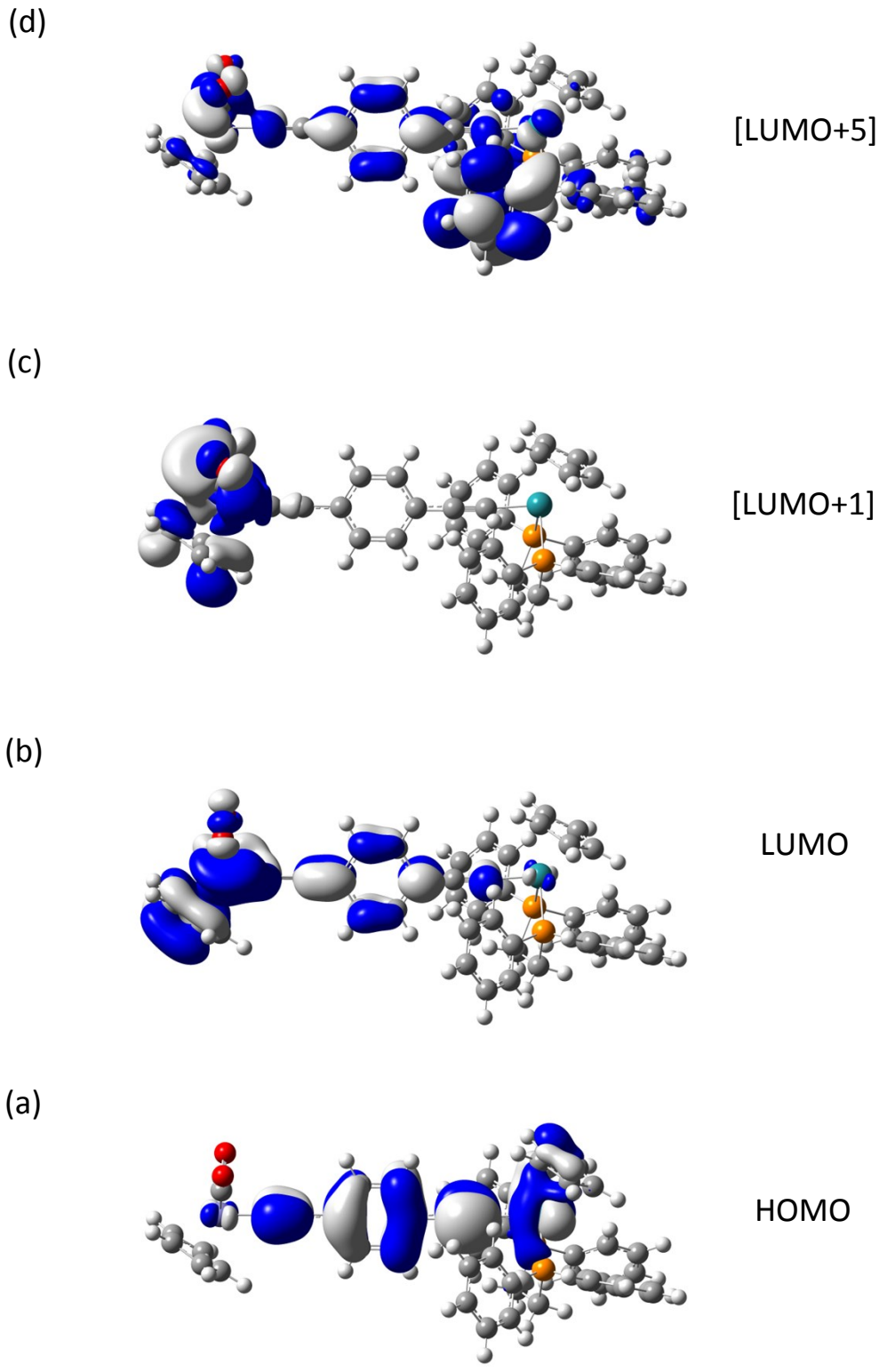


Figure S9. Plots of the (a) HOMO, (b) LUMO, (c) [LUMO+1] and (d) [LUMO+5] of **2b** (contours plotted at 0.02 $(e/bohr^3)^{1/2}$).

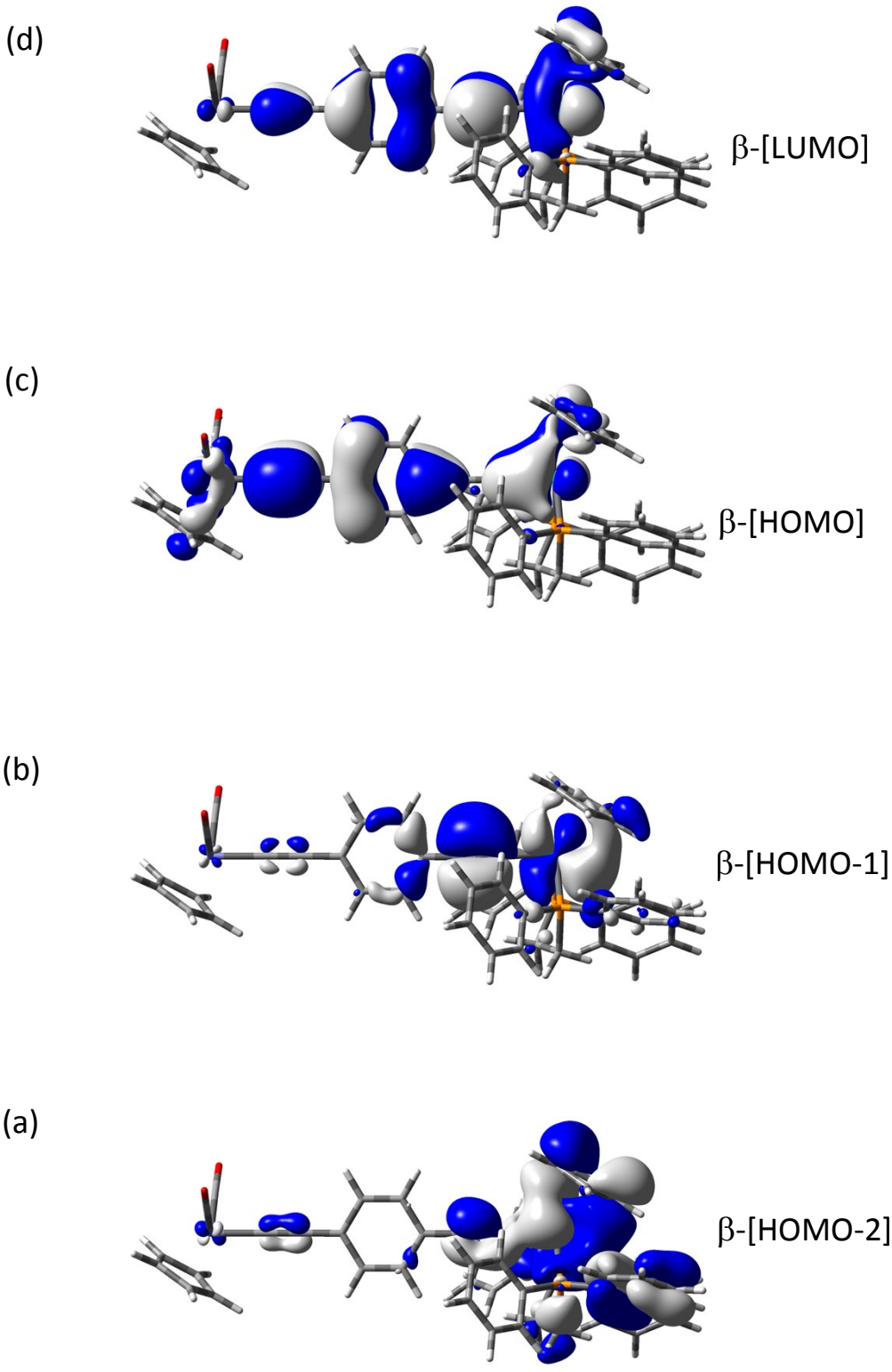


Figure S10. Plots of the (a) β□□□□□□□□□], (b) β□□□□□□□□1], (c) β□□□□□□ and (d) β□LUMO of [**2b**]$^{+}$ (contours plotted at 0.02 (e/bohr^{3})$^{1/2}$).

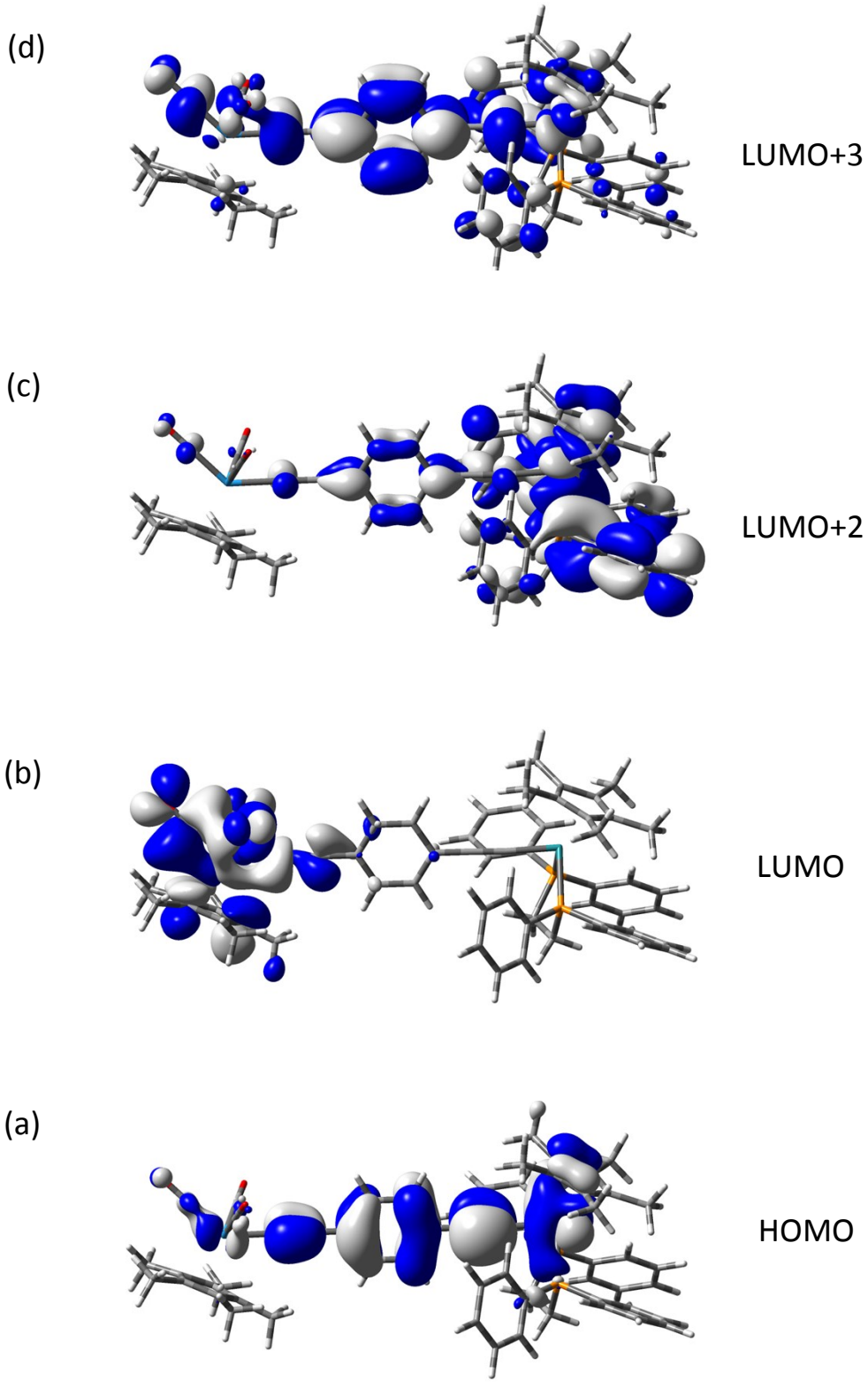


Figure S11. Plots of the (a) HOMO, (b) LUMO, (c) [LUMO+2] and (d) [LUMO+3] of **5a** (contours plotted at 0.02 $(e/bohr^3)^{1/2}$).

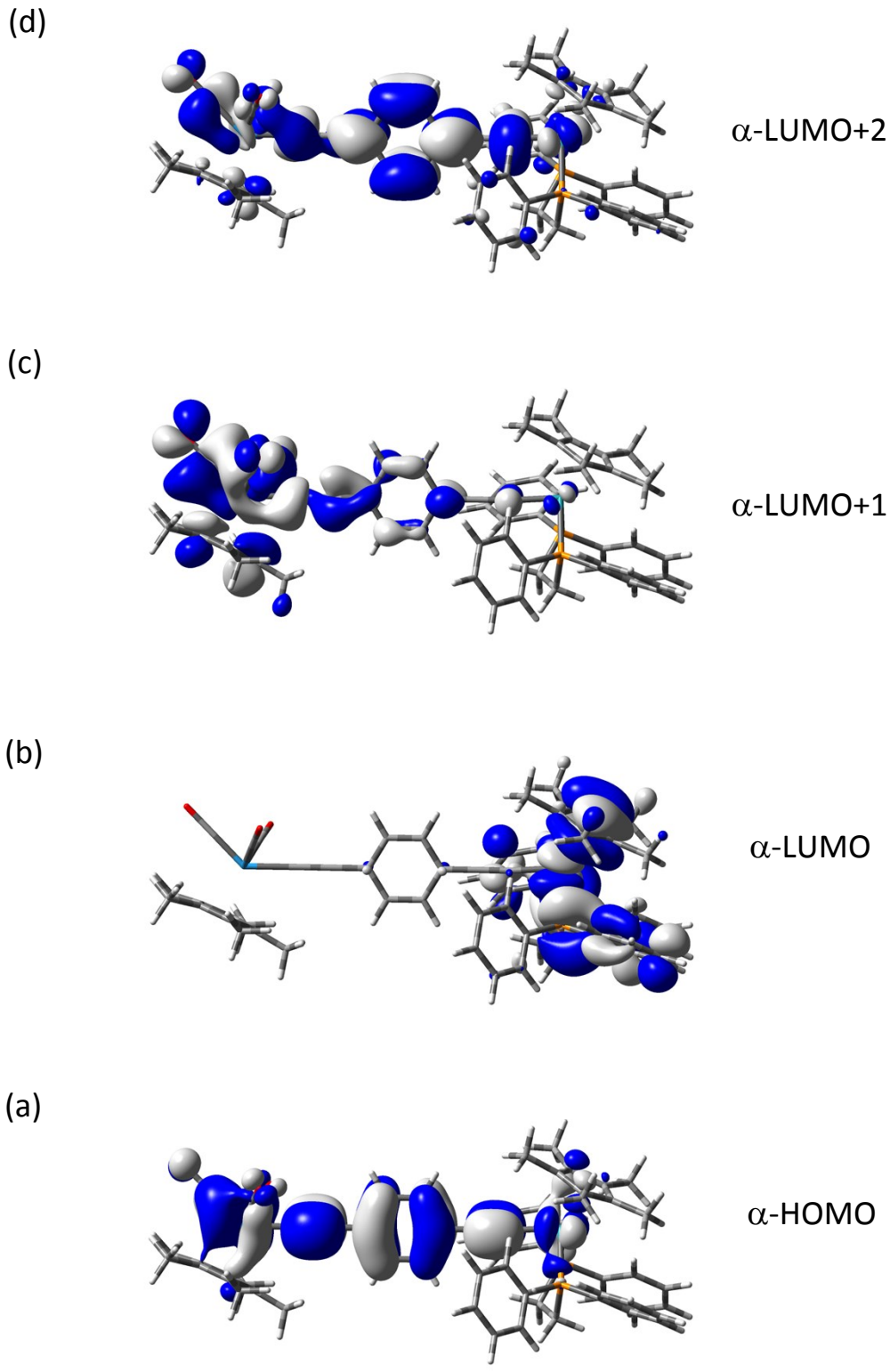


Figure S12. Plots of the (a) α-HOMO, (b) α-LUMO, (c) α-[LUMO+1] and (d) α-[LUMO+2] of [**5a**]$^{+}$ (contours plotted at 0.02 (e/bohr^{3})$^{1/2}$).

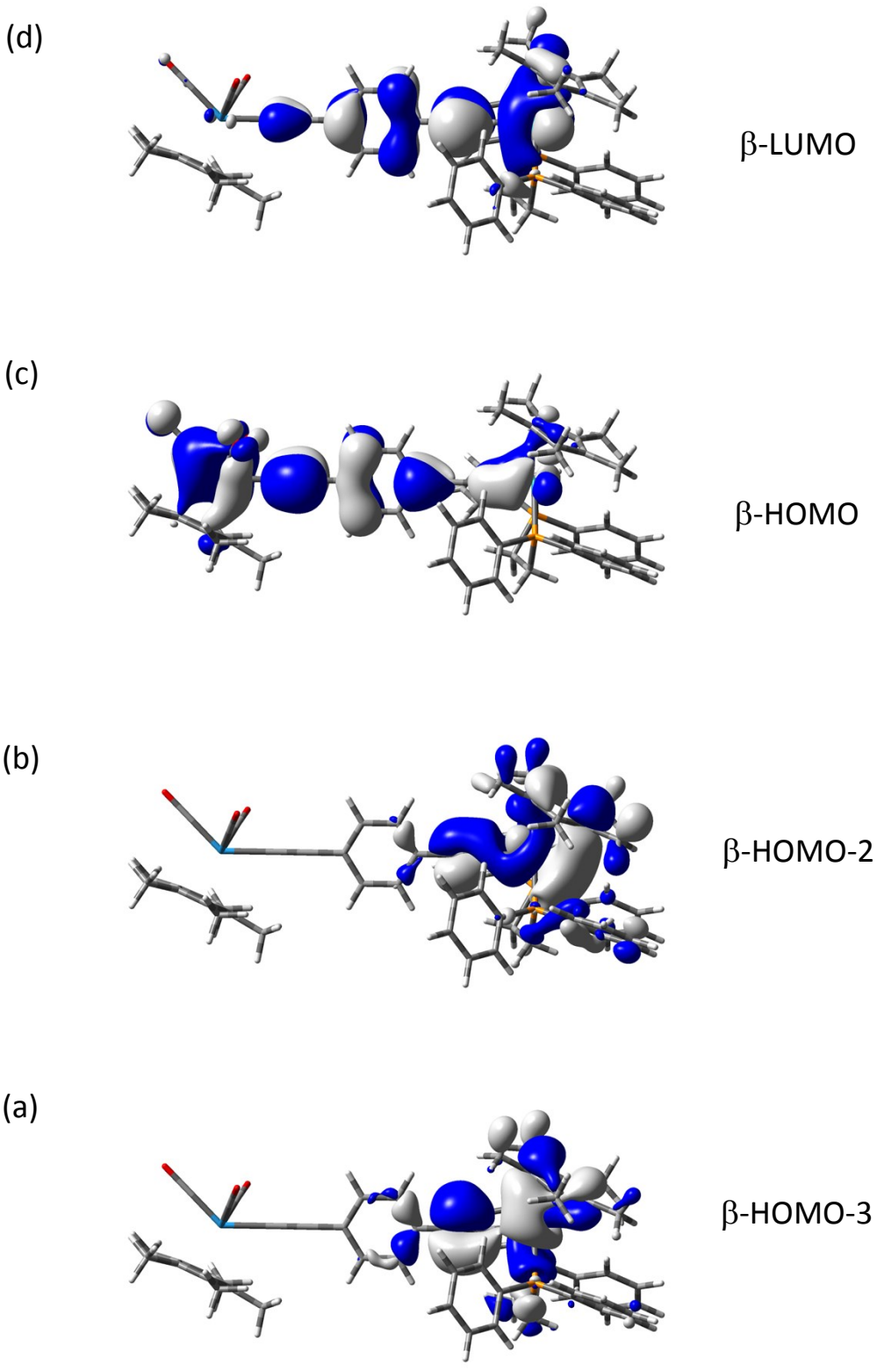


Figure S13. Plots of the (a) β-[HOMO-3], (b) β-[HOMO-2], (c) β-[HOMO] and (d) β-LUMO of [**5a**]$^{+}$ (contours plotted at 0.02 (e/bohr^{3})$^{1/2}$).

Table S8 Summary of TD-DFT results from **2a** and change in distribution of electron density (%)

Energy (cm-1)	Osc. Strength	Major contributions	Cp	$(CO)_2$	Fe	C≡C	C_6H_4	C≡C	Ru	dppe	Cp*
20746	0.0002	(a)	11-->13 (2)	3-->28 (25)	20-->47 (27)	13-->4 (-9)	10-->3 (-7)	10-->1 (-9)	11-->1 (-10)	16-->2 (-14)	7-->0 (-7)
21769	0.0343	HOMO->LUMO (11%)	7-->14 (7)	2-->21 (19)	18-->41 (23)	15-->4 (-11)	11-->9 (-2)	10-->2 (-8)	12-->1 (-11)	16-->7 (-9)	8-->1 (-7)
23776	0.0141	HOMO->L+2 (52%), HOMO->L+17 (12%)	1-->1 (0)	0-->3 (3)	2-->4 (2)	8-->0 (-8)	19-->2 (-17)	25-->1 (-24)	26-->17 (-9)	9-->63 (54)	10-->9 (-1)
24556	0.0007	H-1->L+2 (50%), H-1->L+17 (13%)	0-->1 (1)	0-->2 (2)	0-->4 (4)	2-->0 (-2)	4-->2 (-2)	16-->1 (-15)	46-->23 (-23)	11-->59 (48)	22-->9 (-13)
24728	0.0162	H-16->L+1 (19%), H-6->L+1 (18%)	17-->13 (-4)	5-->29 (24)	31-->48 (17)	26-->4 (-22)	6-->3 (-3)	4-->0 (-4)	4-->0 (-4)	4-->1 (-3)	3-->0 (-3)
26118	0.0001	H-21->LUMO (26%), H-16->LUMO (26%)	33-->14 (-19)	9-->19 (10)	47-->38 (-9)	5-->4 (-1)	2-->11 (9)	1-->2 (1)	1-->2 (1)	1-->9 (8)	1-->1 (0)
27214	0.0057	H-2->L+2 (16%)	1-->1 (0)	0-->2 (2)	2-->4 (2)	8-->0 (-8)	12-->2 (-10)	20-->1 (-19)	30-->27 (-3)	11-->55 (44)	16-->7 (-9)
28252	0.0018	H-25->LUMO (13%), H-6->LUMO (24%), HOMO->L+1 (10%)	7-->14 (7)	3-->24 (21)	26-->40 (14)	33-->4 (-29)	9-->9 (0)	7-->2 (-5)	7-->1 (-6)	5-->6 (1)	4-->1 (-3)
28594	0.069	(b)	0-->1 (1)	0-->4 (4)	1-->6 (5)	5-->1 (-4)	8-->4 (-4)	19-->2 (-17)	38-->24 (-14)	10-->54 (44)	19-->6 (-13)
28970	0.035	H-1->L+20 (15%)	0-->1 (1)	0-->1 (1)	1-->3 (2)	4-->0 (-4)	7-->2 (-5)	17-->2 (-15)	41-->36 (-5)	10-->50 (40)	20-->5 (-15)
29658	1.1336	HOMO->LUMO (35%), HOMO->L+5 (35%)	1-->8 (7)	0-->16 (16)	2-->21 (19)	8-->4 (-4)	20-->15 (-5)	26-->3 (-23)	27-->5 (-22)	6-->26 (20)	9-->1 (-8)
31025	0.0015	HOMO->L+1 (16%), HOMO->L+4 (51%)	1-->4 (3)	0-->63 (63)	3-->28 (25)	9-->2 (-7)	18-->1 (-17)	23-->0 (-23)	25-->0 (-25)	9-->2 (-7)	10-->0 (-10)
31338	0.0149	HOMO->L+3 (15%), HOMO->L+6 (64%)	0-->1 (1)	0-->6 (6)	1-->2 (1)	8-->2 (-6)	22-->8 (-14)	27-->2 (-25)	27-->3 (-24)	6-->77 (71)	8-->1 (-7)
31726	0.0225	HOMO->L+3 (60%), HOMO->L+6 (16%)	0-->0 (0)	0-->2 (2)	1-->1 (0)	8-->1 (-7)	22-->2 (-20)	27-->0 (-27)	27-->4 (-23)	6-->86 (80)	8-->2 (-6)
32755	0.0002	HOMO->L+1 (52%), HOMO->L+4 (16%)	3-->11 (8)	1-->39 (38)	5-->44 (39)	10-->4 (-6)	19-->1 (-18)	23-->0 (-23)	23-->0 (-23)	9-->1 (-8)	8-->0 (-8)

32835	0.03	H-21->L+1 (10%), H-16->L+1 (13%), HOMO->LUMO (24%), HOMO->L+5 (15%)	14-->12 (-2)	4-->24 (20)	23-->37 (14)	10-->4 (-6)	12-->8 (-4)	14-->2 (-12)	14-->1 (-13)	4-->11 (7)	4-->0 (-4)
33019	0.0282	H-1->LUMO (28%), H-1->L+5 (33%)	0-->8 (8)	0-->18 (18)	1-->20 (19)	2-->4 (2)	3-->17 (14)	16-->4 (-12)	44-->3 (-41)	10-->25 (15)	23-->1 (-22)
33346	0.0307	HOMO->L+7 (50%), HOMO->L+17 (10%)	1-->1 (0)	0-->4 (4)	2-->4 (2)	8-->1 (-7)	20-->4 (-16)	26-->1 (-25)	28-->13 (-15)	6-->69 (63)	9-->3 (-6)
33870	0.0113	H-1->L+3 (80%)	0-->0 (0)	0-->1 (1)	0-->1 (1)	1-->0 (-1)	2-->1 (-1)	14-->0 (-14)	49-->5 (-44)	10-->89 (79)	24-->2 (-22)
34182	0.0012	HOMO->L+2 (10%), HOMO->L+8 (28%)	1-->1 (0)	0-->2 (2)	2-->4 (2)	8-->0 (-8)	16-->2 (-14)	23-->1 (-22)	29-->19 (-10)	8-->66 (58)	13-->4 (-9)

(a) H-25->LUMO (3%), H-25->L+1 (2%), H-24->L+1 (4%), H-23->L+1 (3%), H-20->L+1 (4%), H-19->L+1 (4%), H-16->LUMO (6%), H-12->L+1 (3%), H-7->L+1 (3%), H-6->LUMO (4%), H-4->L+1 (5%), H-3->L+1 (7%), H-2->L+1 (4%), HOMO->L+1 (9%)

(b) H-5->L+2 (3%), H-3->L+2 (5%), H-2->L+2 (7%), H-2->L+7 (2%), H-2->L+17 (4%), H-1->L+2 (4%), H-1->L+3 (2%), H-1->L+5 (3%), H-1->L+7 (7%), H-1->L+8 (2%), H-1->L+10 (3%), H-1->L+17 (6%), H-1->L+20 (6%), H-1->L+21 (4%), HOMO->LUMO (2%), HOMO->L+3 (4%), HOMO->L+5 (5%), HOMO->L+7 (3%), HOMO->L+20 (3%)

Table S9 Summary of TD-DFT results from [**2a**]$^+$ and change in distribution of electron density (%)

Energy (cm-1)	Osc. Strength	Major contributions	Cp	$(CO)_2$	Fe	C≡C	C_6H_4	C≡C	Ru	dppe	Cp*
5611	0.0018	H-2(B)->LUMO(B) (16%), H-1(B)->LUMO(B) (72%)	0-->0 (0)	0-->0 (0)	0-->1 (1)	1-->4 (3)	2-->16 (14)	19-->23 (4)	39-->43 (4)	10-->6 (-4)	28-->8 (-20)
8615	0.0014	H-2(B)->LUMO(B) (63%)	0-->0 (0)	0-->0 (0)	1-->1 (0)	1-->4 (3)	2-->15 (13)	25-->23 (-2)	28-->43 (15)	24-->6 (-18)	19-->8 (-11)
12972	0.4786	HOMO(B)->LUMO(B) (83%)	4-->0 (-4)	1-->0 (-1)	8-->1 (-7)	30-->4 (-26)	28-->16 (-12)	8-->23 (15)	10-->43 (33)	8-->6 (-2)	5-->8 (3)
14545	0.0129	(a)	9-->13 (4)	3-->20 (17)	25-->33 (8)	14-->4 (-10)	14-->16 (2)	8-->4 (-4)	9-->2 (-7)	12-->8 (-4)	6-->1 (-5)
15020	0	(b)	14-->14 (0)	4-->32 (28)	30-->42 (12)	15-->4 (-11)	10-->4 (-6)	6-->1 (-5)	7-->0 (-7)	9-->3 (-6)	5-->0 (-5)
17686	0.0011	H-22(A)->L+4(A) (10%), H-10(A)->L+4(A) (10%), H-21(B)->L+4(B) (10%), H-10(B)->L+4(B) (10%)	21-->14 (-7)	7-->35 (28)	45-->45 (0)	23-->5 (-18)	2-->0 (-2)	1-->0 (-1)	1-->0 (-1)	1-->1 (0)	1-->0 (-1)
17907	0.0017	H-3(B)->LUMO(B) (44%)	2-->0 (-2)	0-->0 (0)	3-->1 (-2)	9-->4 (-5)	2-->15 (13)	7-->23 (16)	12-->43 (31)	43-->6 (-37)	21-->8 (-13)
18372	0	H-10(A)->L+6(A) (11%), H-10(B)->L+7(B) (10%),	32-->13 (-19)	8-->23 (15)	41-->36 (-5)	9-->3 (-6)	4-->12 (8)	2-->3 (1)	2-->1 (-1)	2-->7 (5)	1-->1 (0)
18721	0.0006	H-16(B)->LUMO(B) (15%), H-14(B)->LUMO(B) (14%), H-13(B)->LUMO(B) (12%), H-3(B)->LUMO(B) (22%), H-2(B)->LUMO(B) (12%)	2-->0 (-2)	0-->0 (0)	2-->1 (-1)	5-->4 (-1)	2-->15 (13)	8-->23 (15)	17-->43 (26)	49-->6 (-43)	16-->8 (-8)
20646	0.0001	H-22(A)->L+6(A) (12%), H-21(B)->L+7(B) (12%)	12-->12 (0)	6-->20 (14)	56-->33 (-23)	21-->4 (-17)	2-->16 (14)	1-->4 (3)	1-->2 (1)	1-->8 (7)	0-->1 (1)
21403	0.0001	(c)	13-->15 (2)	4-->32 (28)	27-->42 (15)	16-->4 (-12)	12-->3 (-9)	7-->1 (-6)	7-->0 (-7)	10-->3 (-7)	5-->0 (-5)
22030	0.0377	HOMO(A)->L+1(A) (18%), H-5(B)->LUMO(B) (28%)	6-->2 (-4)	1-->3 (2)	6-->6 (0)	14-->5 (-9)	15-->24 (9)	11-->18 (7)	10-->29 (19)	32-->6 (-26)	5-->6 (1)
22470	0.0386	(d)	9-->13 (4)	3-->25 (22)	31-->36 (5)	21-->4 (-17)	12-->12 (0)	6-->3 (-3)	6-->1 (-5)	7-->5 (-2)	4-->1 (-3)
23294	0.0002	H-2(A)->LUMO(A) (16%),	1-->0	0-->0	3-->0	10-->1	3-->3	10-->3	29-->30	14-->43	30-->19

		H-1(A)->LUMO(A) (17%), H-1(B)->L+1(B) (28%)	(-1)	(0)	(-3)	(-9)	(0)	(-7)	(1)	(29)	(-11)
23398	0.0047	H-4(B)->LUMO(B) (71%)	5-->1 (-4)	1-->1 (0)	11-->2 (-9)	58-->4 (-54)	4-->15 (11)	2-->20 (18)	5-->41 (36)	7-->9 (2)	8-->9 (1)
24062	0.2907	HOMO(A)->L+1(A) (23%), H-5(B)->LUMO(B) (17%)	3-->3 (0)	1-->3 (2)	5-->6 (1)	19-->5 (-14)	25-->29 (4)	11-->15 (4)	9-->23 (14)	22-->10 (-12)	4-->6 (2)
24817	0.0479	HOMO(A)->LUMO(A) (32%)	2-->0 (-2)	0-->0 (0)	4-->1 (-3)	13-->1 (-12)	17-->7 (-10)	12-->6 (-6)	14-->31 (17)	23-->35 (12)	14-->18 (4)
25027	0.0015	H-22(A)->L+4(A) (10%), H-19(A)->L+4(A) (12%), H-19(B)->L+4(B) (11%), H-10(B)->L+4(B) (12%)	25-->15 (-10)	8-->36 (28)	53-->44 (-9)	11-->5 (-6)	2-->0 (-2)	1-->0 (-1)	0-->0 (0)	1-->1 (0)	0-->0 (0)
25070	0.0024	H-3(A)->LUMO(A) (16%), H-2(B)->L+1(B) (30%)	1-->0 (-1)	0-->0 (0)	1-->0 (-1)	4-->0 (-4)	4-->1 (-3)	28-->1 (-27)	29-->28 (-1)	17-->49 (32)	17-->20 (3)
25156	0.0013	H-18(B)->LUMO(B) (18%), H-8(B)->LUMO(B) (13%)	1-->0 (-1)	0-->0 (0)	2-->0 (-2)	4-->3 (-1)	11-->14 (3)	11-->20 (9)	15-->42 (27)	47-->11 (-36)	9-->10 (1)

(a) H-21(A)->L+6(A) (8%), H-18(A)->L+6(A) (2%), H-5(A)->L+6(A) (5%), H-2(A)->L+6(A) (2%), H-1(A)->L+6(A) (2%), HOMO(A)->L+1(A) (2%), HOMO(A)->L+6(A) (6%), H-20(B)->L+2(B) (2%), H-20(B)->L+7(B) (4%), H-19(B)->L+7(B) (2%), H-11(B)->L+7(B) (2%), H-5(B)->L+7(B) (2%), H-3(B)->L+7(B) (2%), HOMO(B)->L+2(B) (3%), HOMO(B)->L+7(B) (5%)

(b) H-22(A)->L+6(A) (3%), H-21(A)->L+4(A) (6%), H-21(A)->L+16(A) (3%), H-18(A)->L+4(A) (2%), H-10(A)->L+6(A) (4%), H-5(A)->L+4(A) (4%), H-4(A)->L+6(A) (2%), H-2(A)->L+4(A) (2%), HOMO(A)->L+4(A) (5%), H-21(B)->L+7(B) (2%), H-20(B)->L+4(B) (4%), H-20(B)->L+17(B) (2%), H-19(B)->L+4(B) (2%), H-11(B)->L+4(B) (2%), H-10(B)->L+2(B) (2%), H-10(B)->L+7(B) (3%), H-5(B)->L+4(B) (2%), H-4(B)->L+7(B) (2%), HOMO(B)->L+4(B) (5%), HOMO(B)->L+17(B) (2%)

(c) H-22(A)->L+6(A) (3%), H-21(A)->L+4(A) (4%), H-10(A)->L+6(A) (3%), H-5(A)->L+4(A) (3%), H-4(A)->L+6(A) (3%), HOMO(A)->L+4(A) (6%), H-20(B)->L+4(B) (5%), H-20(B)->L+17(B) (2%), H-19(B)->L+4(B) (2%), H-11(B)->L+4(B) (2%), H-10(B)->L+7(B) (3%), H-5(B)->L+4(B) (2%), H-3(B)->L+4(B) (2%), HOMO(B)->L+4(B) (9%), HOMO(B)->L+17(B) (2%)

(d) H-22(A)->L+4(A) (4%), H-22(A)->L+16(A) (2%), H-21(A)->L+6(A) (4%), H-5(A)->L+6(A) (3%), H-4(A)->L+4(A) (3%), HOMO(A)->L+1(A) (5%), HOMO(A)->L+6(A) (4%), H-21(B)->L+4(B) (5%), H-21(B)->L+17(B) (2%), H-20(B)->L+2(B) (2%), H-20(B)->L+7(B) (4%), H-4(B)->L+4(B) (3%), HOMO(B)->L+2(B) (2%), HOMO(B)->L+7(B) (7%)

Table S10 Summary of TD-DFT results from **2b** and change in distribution of electron density (%)

Energy (cm^{-1})	Osc. Strength	Major contributions	Cp	$(CO)_2$	Fe	C≡C	C_6H_4	C≡C	Ru	dppe	Cp
20746	0.0001	HOMO->L+1 (10%)	10-->13 (3)	3-->28 (25)	19-->47 (28)	14-->4 (-10)	11-->3 (-8)	10-->1 (-9)	12-->1 (-11)	16-->4 (-12)	6-->0 (-6)
21767	0.0326	HOMO->LUMO (12%)	7-->14 (7)	2-->20 (18)	19-->41 (22)	15-->4 (-11)	12-->9 (-3)	11-->2 (-9)	13-->1 (-12)	16-->10 (-6)	6-->0 (-6)
23843	0.0153	HOMO->L+2 (51%), HOMO->L+13 (10%)	1-->0 (-1)	0-->1 (1)	2-->1 (-1)	10-->0 (-10)	21-->1 (-20)	25-->1 (-24)	25-->20 (-5)	9-->66 (57)	8-->8 (0)
24725	0.015	H-24->L+1 (13%), H-15->L+1 (19%), H-4->L+1 (19%)	17-->13 (-4)	5-->29 (24)	33-->48 (15)	26-->4 (-22)	5-->2 (-3)	3-->0 (-3)	4-->1 (-3)	4-->2 (-2)	2-->0 (-2)
25544	0.0009	H-1->L+2 (32%)	1-->0 (-1)	0-->2 (2)	1-->3 (2)	5-->0 (-5)	10-->1 (-9)	26-->2 (-24)	40-->27 (-13)	8-->58 (50)	9-->7 (-2)
26097	0	H-21->LUMO (25%), H-15->LUMO (25%)	33-->14 (-19)	9-->19 (10)	48-->38 (-10)	5-->3 (-2)	2-->10 (8)	1-->2 (1)	1-->1 (0)	1-->13 (12)	0-->0 (0)
27606	0.0032	H-3->L+2 (18%), H-3->L+13 (10%), H-2->L+2 (17%)	1-->0 (-1)	0-->2 (2)	2-->2 (0)	11-->0 (-11)	10-->1 (-9)	14-->1 (-13)	29-->22 (-7)	18-->63 (45)	13-->7 (-6)
28268	0.0003	H-24->LUMO (19%), H-4->LUMO (24%)	7-->14 (7)	4-->24 (20)	30-->39 (9)	33-->3 (-30)	8-->8 (0)	6-->2 (-4)	6-->1 (-5)	4-->9 (5)	2-->0 (-2)
29016	0.0529	H-1->L+2 (28%)	1-->1 (0)	0-->2 (2)	1-->3 (2)	6-->1 (-5)	11-->2 (-9)	25-->2 (-23)	37-->24 (-13)	10-->59 (49)	9-->7 (-2)
29828	0.241	H-1->L+13 (11%), H-1->L+20 (20%)	0-->2 (2)	0-->6 (6)	0-->8 (8)	2-->1 (-1)	7-->4 (-3)	28-->3 (-25)	46-->28 (-18)	7-->44 (37)	9-->4 (-5)
30210	0.9492	HOMO->LUMO (29%), HOMO->L+5 (13%)	1-->6 (5)	0-->11 (11)	2-->16 (14)	8-->3 (-5)	19-->9 (-10)	28-->2 (-26)	30-->9 (-21)	6-->41 (35)	7-->2 (-5)
31243	0.001	HOMO->L+1 (15%), HOMO->L+4 (53%)	2-->3 (1)	0-->64 (64)	3-->27 (24)	11-->2 (-9)	21-->1 (-20)	24-->0 (-24)	24-->0 (-24)	9-->2 (-7)	8-->0 (-8)
31445	0.0056	HOMO->L+3 (45%), HOMO->L+5 (33%), HOMO->L+6 (12%)	1-->1 (0)	0-->6 (6)	2-->4 (2)	10-->2 (-8)	25-->7 (-18)	29-->2 (-27)	25-->2 (-23)	4-->76 (72)	6-->1 (-5)
31898	0.0889	HOMO->L+3 (35%), HOMO->L+5 (11%), HOMO->L+6 (42%)	1-->1 (0)	0-->7 (7)	2-->4 (2)	10-->2 (-8)	25-->10 (-15)	29-->2 (-27)	24-->2 (-22)	4-->72 (68)	6-->1 (-5)

33027	0.0262	H-21->L+1 (13%), H-15->L+1 (16%), HOMO->LUMO (16%)	18-->12 (-6)	5-->25 (20)	30-->39 (9)	12-->4 (-8)	10-->5 (-5)	11-->1 (-10)	9-->1 (-8)	2-->12 (10)	2-->0 (-2)
33140	0.0002	HOMO->L+1 (51%), HOMO->L+4 (15%)	3-->11 (8)	1-->38 (37)	5-->44 (39)	11-->4 (-7)	21-->1 (-20)	24-->0 (-24)	21-->1 (-20)	9-->1 (-8)	6-->0 (-6)
33658	0.0134	HOMO->L+7 (65%)	1-->1 (0)	0-->6 (6)	2-->3 (1)	10-->2 (-8)	24-->7 (-17)	28-->2 (-26)	25-->7 (-18)	4-->70 (66)	6-->2 (-4)
34490	0.0041	H-1->LUMO (30%), H-1->L+5 (19%), H-1->L+6 (11%)	0-->8 (8)	0-->15 (15)	1-->18 (17)	2-->4 (2)	3-->12 (9)	26-->3 (-23)	50-->2 (-48)	8-->38 (30)	10-->1 (-9)
34666	0.0145	HOMO->LUMO (11%), HOMO->L+2 (11%), HOMO->L+8 (12%)	6-->6 (0)	2-->11 (9)	10-->17 (7)	11-->2 (-9)	16-->4 (-12)	19-->1 (-18)	21-->12 (-9)	9-->44 (35)	7-->3 (-4)
34888	0.0351	HOMO->LUMO (11%), HOMO->L+8 (19%)	6-->6 (0)	2-->12 (10)	10-->17 (7)	11-->2 (-9)	18-->5 (-13)	21-->1 (-20)	20-->8 (-12)	7-->47 (40)	6-->2 (-4)

Table S11 Summary of TD-DFT results from [**2b**]$^{+}$ and change in distribution of electron density (%)

Energy (cm^{-1})	Osc. Strength	Major contributions	Cp	$(CO)_2$	Fe	C≡C	C_6H_4	C≡C	Ru	dppe	Cp
6601	0.0005	H-1(B)->LUMO(B) (95%)	0-->0 (0)	0-->0 (0)	0-->1 (1)	1-->5 (4)	3-->19 (16)	40-->26 (-14)	45-->36 (-9)	5-->5 (0)	4-->7 (3)
10493	0.0011	H-2(B)->LUMO(B) (69%)	0-->0 (0)	0-->0 (0)	1-->1 (0)	2-->5 (3)	1-->19 (18)	8-->26 (18)	27-->36 (9)	34-->5 (-29)	27-->6 (-21)
12157	0.5685	HOMO(B)->LUMO(B) (87%)	4-->0 (-4)	1-->0 (-1)	8-->1 (-7)	31-->5 (-26)	26-->19 (-7)	6-->26 (20)	12-->36 (24)	8-->5 (-3)	4-->6 (2)
14669	0.0077	(a)	8-->14 (6)	3-->21 (18)	19-->37 (18)	12-->3 (-9)	12-->12 (0)	8-->3 (-5)	10-->2 (-8)	22-->6 (-16)	5-->1 (-4)
15110	0	(b)	14-->13 (-1)	4-->29 (25)	26-->42 (16)	13-->5 (-8)	9-->4 (-5)	6-->1 (-5)	8-->3 (-5)	15-->2 (-13)	4-->0 (-4)
17733	0.0013	H-22(A)->L+4(A) (10%), H-10(A)->L+4(A) (11%), H-21(B)->L+4(B) (10%), H-10(B)->L+4(B) (11%)	20-->13 (-7)	6-->31 (25)	41-->44 (3)	21-->5 (-16)	3-->2 (-1)	2-->0 (-2)	3-->3 (0)	3-->1 (-2)	2-->0 (-2)
18427	0	H-10(A)->L+6(A) (13%), H-10(B)->L+7(B) (11%)	26-->13 (-13)	7-->24 (17)	37-->39 (2)	10-->4 (-6)	5-->9 (4)	3-->2 (-1)	4-->2 (-2)	7-->5 (-2)	2-->1 (-1)
20619	0	H-22(A)->L+6(A) (12%), H-21(B)->L+7(B) (12%)	13-->12 (-1)	6-->21 (15)	48-->34 (-14)	22-->3 (-19)	3-->13 (10)	1-->5 (4)	2-->4 (2)	2-->6 (4)	2-->1 (-1)
21037	0.0034	H-4(B)->LUMO(B) (61%)	5-->1 (-4)	1-->1 (0)	7-->3 (-4)	10-->6 (-4)	9-->22 (13)	10-->24 (14)	7-->32 (25)	42-->5 (-37)	9-->6 (-3)
21245	0.0009	H-17(B)->LUMO(B) (13%), H-16(B)->LUMO(B) (28%), H-2(B)->LUMO(B) (20%)	1-->1 (0)	0-->1 (1)	2-->2 (0)	4-->5 (1)	2-->19 (17)	7-->26 (19)	25-->35 (10)	37-->6 (-31)	22-->6 (-16)
21481	0	H-3(B)->LUMO(B) (10%)	11-->11 (0)	3-->25 (22)	24-->36 (12)	21-->5 (-16)	9-->6 (-3)	5-->5 (0)	7-->7 (0)	15-->3 (-12)	4-->1 (-3)
21751	0.0002	H-3(B)->LUMO(B) (71%)	7-->3 (-4)	1-->6 (5)	16-->9 (-7)	59-->5 (-54)	6-->17 (11)	2-->21 (19)	3-->29 (26)	5-->5 (0)	2-->5 (3)
22478	0.0065	H-16(B)->LUMO(B) (16%), H-6(B)->LUMO(B) (28%), H-4(B)->LUMO(B) (15%)	5-->1 (-4)	1-->1 (0)	5-->2 (-3)	5-->5 (0)	6-->20 (14)	7-->25 (18)	14-->34 (20)	46-->6 (-40)	10-->6 (-4)
22573	0.0469	(c)	9-->12	3-->23	26-->36	18-->5	12-->12	6-->3	8-->3	14-->5	4-->1

			(3)	(20)	(10)	(-13)	(0)	(-3)	(-5)	(-9)	(-3)
23656	0.002	H-11(B)->LUMO(B) (64%), H-8(B)->LUMO(B) (18%)	0-->0 (0)	0-->0 (0)	0-->1 (1)	0-->5 (5)	53-->20 (-33)	0-->26 (26)	1-->35 (34)	44-->6 (-38)	1-->6 (5)
24087	0.3862	HOMO(A)->L+1(A) (40%)	4-->4 (0)	1-->6 (5)	8-->10 (2)	19-->7 (-12)	26-->37 (11)	10-->13 (3)	8-->11 (3)	18-->9 (-9)	4-->2 (-2)
24211	0.0008	H-2(A)->LUMO(A) (19%), H-2(B)->L+1(B) (14%), H-1(B)->L+1(B) (19%)	1-->0 (-1)	0-->0 (0)	2-->0 (-2)	7-->0 (-7)	3-->2 (-1)	22-->1 (-21)	31-->29 (-2)	20-->52 (32)	13-->16 (3)
24700	0.0172	H-1(A)->LUMO(A) (19%), HOMO(A)->LUMO(A) (46%)	3-->0 (-3)	1-->0 (-1)	6-->0 (-6)	17-->0 (-17)	20-->2 (-18)	15-->1 (-14)	16-->30 (14)	13-->49 (36)	8-->18 (10)
24954	0.0016	H-4(A)->LUMO(A) (10%), H-2(B)->L+1(B) (13%), H-1(B)->L+1(B) (15%)	1-->0 (-1)	0-->0 (0)	2-->1 (-1)	6-->1 (-5)	3-->3 (0)	18-->3 (-15)	30-->28 (-2)	24-->49 (25)	16-->15 (-1)
25009	0.0016	H-22(A)->L+4(A) (10%), H-18(A)->L+4(A) (13%), H-18(B)->L+4(B) (15%), H-10(B)->L+4(B) (11%)	24-->13 (-11)	8-->32 (24)	50-->44 (-6)	10-->5 (-5)	2-->1 (-1)	1-->0 (-1)	2-->3 (1)	2-->1 (-1)	2-->0 (-2)

(a) H-21(A)->L+6(A) (2%), H-20(A)->L+6(A) (5%), H-19(A)->L+6(A) (5%), H-15(A)->L+6(A) (3%), H-5(A)->L+6(A) (3%), H-1(A)->L+6(A) (5%), HOMO(A)->L+1(A) (2%), HOMO(A)->L+6(A) (8%), H-19(B)->L+2(B) (3%), H-19(B)->L+7(B) (7%), H-19(B)->L+21(B) (2%), H-12(B)->L+7(B) (2%), H-6(B)->L+7(B) (2%), H-4(B)->L+7(B) (2%), HOMO(B)->L+2(B) (3%), HOMO(B)->L+7(B) (6%)

(b) H-22(A)->L+6(A) (3%), H-20(A)->L+4(A) (3%), H-19(A)->L+4(A) (3%), H-19(A)->L+16(A) (2%), H-15(A)->L+4(A) (2%), H-10(A)->L+6(A) (5%), H-5(A)->L+4(A) (2%), H-3(A)->L+6(A) (2%), H-1(A)->L+4(A) (3%), HOMO(A)->L+4(A) (6%), HOMO(A)->L+16(A) (2%), H-21(B)->L+7(B) (2%), H-19(B)->L+4(B) (6%), H-19(B)->L+17(B) (3%), H-10(B)->L+7(B) (3%), H-6(B)->L+4(B) (2%), H-4(B)->L+4(B) (2%), H-3(B)->L+7(B) (2%), HOMO(B)->L+4(B) (6%), HOMO(B)->L+17(B) (2%)

(c) H-22(A)->L+4(A) (5%), H-22(A)->L+16(A) (2%), H-20(A)->L+6(A) (2%), H-19(A)->L+6(A) (3%), H-3(A)->L+4(A) (3%), H-1(A)->L+6(A) (3%), HOMO(A)->L+1(A) (7%), HOMO(A)->L+6(A) (4%), H-21(B)->L+4(B) (5%), H-21(B)->L+17(B) (2%), H-19(B)->L+2(B) (3%), H-19(B)->L+7(B) (5%), H-4(B)->L+7(B) (2%), H-3(B)->L+4(B) (4%), HOMO(B)->L+7(B) (8%)

Table S12 Summary of TD-DFT results from **5a** and change in distribution of electron density (%)

Energy (cm-1)	Osc. Strength	Major contributions	Cp*	$(CO)_3$	W	C≡C	C_6H_4	C≡C	Ru	dppe	Cp*
23764	0.0139	HOMO->L+2 (44%), HOMO->L+3 (10%), HOMO->L+15 (12%)	1-->1 (0)	3-->3 (0)	5-->1 (-4)	9-->2 (-7)	19-->10 (-9)	22-->2 (-20)	25-->16 (-9)	7-->58 (51)	8-->8 (0)
24054	0.0334	H-2->LUMO (30%), HOMO->LUMO (56%)	1-->13 (12)	4-->53 (49)	9-->20 (11)	12-->12 (0)	17-->1 (-16)	18--> 0 (-18)	21-->0 (-21)	7-->0 (-7)	11-->0 (-11)
24514	0.0004	H-1->L+2 (43%), H-1->L+15 (15%)	0-->1 (1)	1-->3 (2)	1-->2 (1)	2-->2 (0)	4-->8 (4)	15-->2 (-13)	45-->20 (-25)	11-->54 (43)	22-->7 (-15)
26639	0.0033	H-2->L+1 (26%), HOMO->L+1 (63%)	1-->9 (8)	4-->72 (68)	8-->19 (11)	11-->0 (-11)	18-->0 (-18)	19-->0 (-19)	22-->0 (-22)	7-->0 (-7)	10-->0 (-10)
27195	0.0083	H-3->L+2 (16%)	1-->2 (1)	2-->4 (2)	4-->3 (-1)	5-->2 (-3)	10-->7 (-3)	22-->2 (-20)	32-->23 (-9)	9-->52 (43)	15-->6 (-9)
27717	0.0275	H-4->LUMO (84%)	6-->13 (7)	21-->52 (31)	40-->20 (-20)	18-->11 (-7)	3-->2 (-1)	4-->0 (-4)	4-->0 (-4)	2-->1 (-1)	2-->0 (-2)
28530	0.1702	HOMO->L+3 (12%)	0-->2 (2)	1-->5 (4)	3-->3 (0)	4-->3 (-1)	8-->10 (2)	20-->3 (-17)	37-->20 (-17)	9-->49 (40)	17-->5 (-12)
29032	0.1454	H-1->L+16 (10%)	0-->2 (2)	1-->6 (5)	2-->5 (3)	3-->1 (-2)	7-->6 (-1)	19-->2 (-17)	39-->26 (-13)	9-->48 (39)	19-->4 (-15)
29301	1.1305	HOMO->L+2 (15%), HOMO->L+3 (46%)	1-->3 (2)	2-->11 (9)	4-->5 (1)	7-->6 (-1)	17-->21 (4)	23-->4 (-19)	29-->12 (-17)	7-->33 (26)	11-->4 (-7)
30617	0.0822	H-4->L+1 (35%), H-2->LUMO (13%), HOMO->LUMO (24%)	3-->11 (8)	11-->56 (45)	22-->18 (-4)	14-->7 (-7)	11-->3 (-8)	12-->1 (-11)	14-->1 (-13)	6-->4 (-2)	7-->0 (-7)
31312	0.0428	HOMO->L+4 (14%), HOMO->L+5 (64%), HOMO->L+6 (10%)	1-->1 (0)	2-->4 (2)	4-->1 (-3)	9-->1 (-8)	21-->4 (-17)	25-->1 (-24)	25-->3 (-22)	5-->84 (79)	7-->1 (-6)
31636	0.029	H-4->L+1 (29%), H-2->LUMO (14%), HOMO->L+4 (14%)	3-->10 (7)	10-->50 (40)	20-->15 (-5)	14-->4 (-10)	12-->1 (-11)	12-->0 (-12)	16-->1 (-15)	6-->17 (11)	8-->0 (-8)
31776	0.0573	HOMO->L+4 (45%), HOMO->L+5 (23%)	1-->2 (1)	3-->10 (7)	6-->3 (-3)	10-->2 (-8)	20-->4 (-16)	23-->1 (-22)	24-->3 (-21)	5-->74 (69)	8-->1 (-7)
32735	0.0031	H-3->L+3 (11%),	0-->4	0-->17	1-->7	1-->9	1-->24	16-->5	46-->6	10-->25	24-->3

		H-1->LUMO (20%), H-1->L+2 (11%), H-1->L+3 (41%)	(4)	(17)	(6)	(8)	(23)	(-11)	(-40)	(15)	(-21)
32894	0.0009	H-5->L+1 (11%), H-2->L+1 (38%), HOMO->L+1 (33%)	2-->9 (7)	5-->71 (66)	11-->19 (8)	12-->0 (-12)	15-->0 (-15)	13-->0 (-13)	20-->0 (-20)	10-->0 (-10)	13-->0 (-13)
33323	0.0326	HOMO->L+6 (52%), HOMO->L+15 (11%)	1-->1 (0)	2-->3 (1)	4-->2 (-2)	9-->1 (-8)	21-->3 (-18)	25-->1 (-24)	26-->12 (-14)	6-->74 (68)	8-->3 (-5)
33881	0.0102	H-1->L+4 (80%)	0-->0 (0)	0-->1 (1)	0-->1 (1)	0-->1 (1)	1-->3 (2)	14-->1 (-13)	49-->4 (-45)	11-->87 (76)	25-->2 (-23)
34180	0.0018	HOMO->L+7 (32%)	1-->2 (1)	2-->5 (3)	4-->3 (-1)	7-->1 (-6)	15-->4 (-11)	24-->1 (-23)	30-->15 (-15)	7-->65 (58)	12-->3 (-9)
34378	0.0004	H-1->LUMO (73%), H-1->L+3 (10%)	0-->10 (10)	0-->41 (41)	0-->15 (15)	1-->11 (10)	2-->7 (5)	14-->1 (-13)	48-->2 (-46)	10-->12 (2)	24-->1 (-23)
34529	0.0143	HOMO->L+7 (32%)	1-->3 (2)	2-->7 (5)	4-->4 (0)	6-->1 (-5)	12-->3 (-9)	24-->1 (-23)	31-->15 (-16)	7-->64 (57)	14-->3 (-11)

Table S13 Summary of TD-DFT results from [**5a**]$^+$ and change in distribution of electron density (%)

Energy (cm-1)	Osc. Strength	Major contributions	Cp*	$(CO)_3$	W	C≡C	C_6H_4	C≡C	Ru	dppe	Cp*
5623	0.0019	H-3(B)->LUMO(B) (17%), H-2(B)->LUMO(B) (73%)	0-->0 (0)	0-->1 (1)	1-->1 (0)	0-->4 (4)	1-->16 (15)	19-->22 (3)	38-->42 (4)	12-->7 (-5)	28-->8 (-20)
8643	0.0014	H-3(B)->LUMO(B) (63%)	1-->0 (-1)	0-->1 (1)	0-->1 (1)	0-->4 (4)	2-->16 (14)	24-->22 (-2)	28-->42 (14)	25-->7 (-18)	19-->8 (-11)
12416	0.5681	HOMO(B)->LUMO(B) (79%)	3-->0 (-3)	10-->1 (-9)	22-->1 (-21)	22-->4 (-18)	18-->16 (-2)	5-->22 (17)	8-->42 (34)	6-->6 (0)	5-->8 (3)
17845	0.0012	H-5(B)->LUMO(B) (24%), H-4(B)->LUMO(B) (31%)	3-->0 (-3)	5-->1 (-4)	10-->1 (-9)	3-->4 (1)	7-->16 (9)	8-->22 (14)	13-->42 (29)	36-->7 (-29)	16-->8 (-8)
18051	0.0001	H-1(B)->LUMO(B) (93%)	7-->0 (-7)	24-->1 (-23)	48-->1 (-47)	17-->4 (-13)	2-->16 (14)	0-->23 (23)	1-->42 (41)	1-->6 (5)	1-->8 (7)
18683	0.0006	H-17(B)->LUMO(B) (13%), H-15(B)->LUMO(B) (13%), H-14(B)->LUMO(B) (15%), H-5(B)->LUMO(B) (10%), H-4(B)->LUMO(B) (14%), H-3(B)->LUMO(B) (12%)	1-->0 (-1)	2-->1 (-1)	4-->1 (-3)	1-->4 (3)	3-->16 (13)	8-->22 (14)	18-->42 (24)	47-->7 (-40)	14-->8 (-6)
20832	0.0006	H-19(B)->LUMO(B) (13%), H-5(B)->LUMO(B) (24%), H-4(B)->LUMO(B) (28%), HOMO(B)->LUMO(B) (14%)	6-->0 (-6)	7-->1 (-6)	14-->1 (-13)	10-->4 (-6)	11-->16 (5)	9-->22 (13)	10-->41 (31)	21-->7 (-14)	12-->8 (-4)
22598	0.3007	HOMO(A)->L+1(A) (17%), HOMO(A)->L+2(A) (29%)	2-->4 (2)	8-->16 (8)	17-->7 (-10)	18-->8 (-10)	26-->30 (4)	9-->8 (-1)	6-->9 (3)	8-->14 (6)	5-->3 (-2)
23297	0.0003	H-3(A)->LUMO(A) (37%), H-2(B)->L+1(B) (27%)	0-->1 (1)	0-->5 (5)	1-->2 (1)	1-->1 (0)	1-->2 (1)	13-->1 (-12)	34-->24 (-10)	18-->45 (27)	32-->17 (-15)
23879	0.0173	H-1(A)->L+1(A) (42%), H-1(B)->L+2(B) (38%)	7-->10 (3)	24-->41 (17)	46-->15 (-31)	17-->11 (-6)	3-->8 (5)	1-->2 (1)	1-->4 (3)	1-->6 (5)	0-->3 (3)
24176	0.009	H-2(A)->L+1(A) (13%), HOMO(A)->L+1(A) (38%), HOMO(A)->L+2(A) (14%), HOMO(B)->L+2(B) (13%)	2-->10 (8)	9-->39 (30)	19-->15 (-4)	19-->11 (-8)	20-->13 (-7)	10-->3 (-7)	7-->3 (-4)	8-->5 (-3)	7-->2 (-5)
24721	0.0276	H-2(A)->LUMO(A) (24%),	2-->0	5-->1	11-->1	11-->1	13-->5	9-->6	12-->30	26-->38	11-->18

		HOMO(A)->LUMO(A) (30%)	(-2)	(-4)	(-10)	(-10)	(-8)	(-3)	(18)	(12)	(7)
24849	0	H-1(A)->L+3(A) (46%), H-1(B)->L+3(B) (45%)	8-->9 (1)	24-->71 (47)	47-->19 (-28)	18-->0 (-18)	2-->1 (-1)	1-->0 (-1)	0-->0 (0)	0-->0 (0)	0-->0 (0)
25070	0.0011	H-4(A)->LUMO(A) (17%), H-3(B)->L+1(B) (26%)	1-->1 (0)	1-->6 (5)	1-->2 (1)	2-->2 (0)	3-->3 (0)	27-->2 (-25)	27-->23 (-4)	23-->45 (22)	16-->16 (0)
25130	0.0007	H-20(B)->LUMO(B) (19%)	1-->0 (-1)	2-->1 (-1)	3-->1 (-2)	3-->3 (0)	7-->13 (6)	11-->17 (6)	15-->37 (22)	48-->19 (-29)	10-->10 (0)
25319	0.002	H-12(B)->LUMO(B) (80%)	0-->0 (0)	0-->1 (1)	0-->1 (1)	0-->4 (4)	81-->17 (-64)	2-->22 (20)	2-->41 (39)	12-->7 (-5)	1-->8 (7)
25367	0.0081	H-20(B)->LUMO(B) (36%), H-8(B)->LUMO(B) (14%)	2-->0 (-2)	1-->1 (0)	2-->1 (-1)	2-->3 (1)	12-->13 (1)	18-->19 (1)	21-->38 (17)	34-->15 (-19)	10-->9 (-1)
26225	0.0014	HOMO(A)->L+1(A) (14%), HOMO(B)->L+2(B) (52%)	3-->10 (7)	11-->43 (32)	23-->16 (-7)	21-->9 (-12)	18-->3 (-15)	6-->1 (-5)	7-->5 (-2)	5-->9 (4)	5-->4 (-1)
26495	0.0102	H-8(B)->LUMO(B) (18%)	4-->0 (-4)	1-->1 (0)	2-->1 (-1)	1-->2 (1)	2-->10 (8)	8-->13 (5)	17-->29 (12)	51-->36 (-15)	13-->8 (-5)
2658304	0.0037	H-8(B)->LUMO(B) (15%), H-2(B)->L+4(B) (10%)	3-->0 (-3)	1-->1 (0)	1-->1 (0)	1-->2 (1)	2-->9 (7)	12-->11 (-1)	26-->25 (-1)	33-->44 (11)	21-->7 (-14)

REFERENCES

1. G. M. Sheldrick, *Acta Crystallogr A*, 2015, **71**, 3-8.
2. G. M. Sheldrick, *Acta Crystallogr C*, 2015, **71**, 3-8.
3. H. Puschmann and O. Dolomanov, *Acta Crystallogr A*, 2006, **62**, S246-S246.
4. O. V. Dolomanov, A. J. Blake, N. R. Champness and M. Schroder, *J Appl Crystallogr*, 2003, **36**, 1283-1284.
5. I. Uson and G. M. Sheldrick, *Acta Crystallogr D*, 2018, **74**, 106-116.