Journal of the Serbian Chemical Society
JSCS@tmf.bg.ac.rs • www.shd.org.rs/JSCS
J. Serb. Chem. Soc. 81 (5) S159–S182 (2016) *Supplementary material*

SUPPLEMENTARY MATERIAL TO

Effect of principal and secondary ligands on electronic structures and spectra of a series of ruthenium(II) complexes

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J. Serb. Chem. Soc. 81 (5) (2016) 521–539

TABLE S-I. Calculated frequencies (cm^{-1}) of complexes $RuCO(AsPh_3)L^1$ (**A**), $RuCO(PPh_3)L^1$ (**B**), $RuCO(Py)L^1$ (**C**), $RuCO(AsPh_3)L^2$ (**D**), $RuCO(PPh_3)L^2$ (**E**), $RuCO(Py)L^2$ (**F**), $RuCO(AsPh_3)L^3$ (**G**), $RuCO(PPh_3)L^3$ (**H**), $RuCO(Py)L^3$ (**I**), $RuCO(AsPh_3)L^4$ (**J**), $RuCO(PPh_3)L^4$ (**K**) and $RuCO(Py)L^4$ (**L**), together with the experimental values in parentheses[1]

Complex	$\nu_{C=N-}$	ν_{Ph-C-O}	ν_{C-S}	ν_{Py}
A	1599 (1602)	1338 (1306)	737 (737)	–
B	1599 (1603)	1339 (1290)	738 (746)	–
C	1598 (1602)	1339 (1302)	748 (746)	1040 (1030)
D	1599 (1619)	1292 (1282)	729 (741)	–
E	1600 (1609)	1374 (1329)	782 (745)	–
F	1599 (1600)	1381 (1305)	730 (738)	1040 (1027)
G	1599 (1601)	1346 (1310)	743 (737)	–
H	1600 (1602)	1346 (1320)	738 (743)	–
I	1599 (1600)	1346 (1315)	739 (744)	1040 (1025)
J	1599 (1615)	1377 (1357)	760 (737)	–
K	1600 (1614)	1313 (1310)	761 (744)	–
L	1598 (1614)	1313 (1298)	759 (744)	1041 (1032)

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TABLE S-II. Calculated bond lengths and angles for $RuCO(AsPh_3)L^1$ (**A**), $RuCO(PPh_3)L^1$ (**B**) and $RuCO(Py)L^1$ (**C**) at the B3LYP, PBE1PBE and M06 levels with the 6-31G(d)-LANL2DZ basis set

$RuCO(AsPh_3)L^1$		$RuCO(PPh_3)L^1$		$RuCO(Py)L^1$	
		Bond lengths, Å			
Ru–As	2.49 (2.44)[a] [2.45][b]	Ru–P	2.39 (2.34)[a] [2.34][b] {2.41}[c]	Ru–N	2.17 (2.13)[a] [2.15][b]
Ru–C	1.90 (1.89)[a] [1.89][b]	Ru–C	1.90 (1.89)[a] [1.89][b] {1.87}[c]	Ru–C	1.91 (1.89)[a] [1.90][b]
$Ru–N_2$	2.05 (2.03)[a] [2.06][b]	$Ru–N_2$	2.06 (2.03)[a] [2.06][b] {2.11}[c]	$Ru–N_2$	2.05 (2.03)[a] [2.05][b]
$Ru–O_1$	2.11 (2.09)[a] [2.11][b]	$Ru–O_1$	2.11 (2.09)[a] [2.12][b] {2.10}[c]	$Ru–O_1$	2.10 (2.07)[a] [2.09][b]
Ru–S	2.51 (2.46)[a] [2.48][b]	Ru–S	2.51 (2.46)[a][2.49][b] {2.36}[c]	Ru–S	2.53 (2.48)[a] [2.50][b]
		Bond angles, °			
As–Ru–C	91.65 (91.86)[a] [91.16][b]	P–Ru–C	92.41 (92.32)[a] [91.77][b] {87.50}[c]	N–Ru–C	93.06 (93.33)[a] [94.45][b]
$As–Ru–N_2$	98.36 (97.27)[a] [96.13][b]	$P–Ru–N_2$	98.52 (97.77)[a] [96.90][b] {94.70}[c]	$N–Ru–N_2$	95.56 (95.11)[a] [93.41][b]
$C–Ru–N_2$	169.16 (169.70)[a] [171.49][b]	$C–Ru–N_2$	168.31 (168.90)[a] [170.29][b] {173.31}[c]	$C–Ru–N_2$	170.63 (170.54)[a] [171.37][b]
$O_1–Ru–S$	154.42 (154.43)[a] [153.28][b]	$O_1–Ru–S$	153.91 (154.01)[a] [152.92][b] {168.27}[c]	$O_1–Ru–S$	155.56 (155.93)[a] [154.63][b]

[a]Calculated at the PBE1PBE level; [b]calculated at the M06 level; [c]from ref. 2

TABLE S-III. Molecular orbital compositions in the ground state for $RuCO(AsPh_3)L^1$ (**A**) at the B3LYP/6-31G(d)-LanL2DZ level in dichloromethane

MO	Energy eV	Contribution										Assign
		Ru	Ph_1	$Ph_{(2+3+4)}$	Fu	CO	C_1	O_1	C_2	As	a(C+S+N)	
L+2	–1.36	41	0	0	0	1	1	4	0	3	C(2)+S(19)+N(7)	$p(S_a)+d(Ru)$
L+1	–1.58	2	36	0	0	2	27	4	0	0	C(2)+S(5)+N(18)	$\pi^*(Ph_1)+p(C_1+N_a)$
L	–2.10	2	0	0	33	0	0	0	26	0	C(8)+S(7)+N(17)	$\pi^*(Fu)+p(C_2+N_a)$
H	–5.14	17	12	0	0	0	0	6	0	0	C(25)+S(15)+N(8)	$\pi(Ph_1)+p(C_a+S_a)+d(Ru)$
H-1	–5.42	9	33	0	0	0	0	17	0	2	C(6)+S(5)+N(11)	$\pi(Ph_1)+p(N_a+O_1)$
H-2	–6.15	22	12	0	15	3	2	8	1	0	C(3)+S(19)+N(12)	$\pi(Ph_1+Fu)+p(S_a+N_a)+d(Ru)$
H-3	–6.34	36	11	0	12	6	0	12	0	0	C(1)+S(6)+N(3)	$\pi(Ph_1+Fu)+p(O_1)+d(Ru)$

TABLE S-IV. Molecular orbital compositions in the ground state for $RuCO(PPh_3)L^1$ (**B**) at the B3LYP/6-31G(d)-LanL2DZ level in dichloromethane

MO	Energy eV	Contribution										Assign
		Ru	Ph_1	$Ph_{(2+3+4)}$	Fu	CO	C_1	O_1	C_2	P	a(C+S+N)	
L+2	–1.39	37	0	9	0	2	1	4	0	5	C(1)+S(17)+N(8)	$p(S_a)+d(Ru)$
L+1	–1.55	2	35	0	0	2	27	3	0	0	C(2)+S(5)+N(18)	$\pi^*(Ph_1)+p(C_1+N_a)$
L	–2.07	2	0	0	33	0	0	0	26	0	C(8)+S(7)+N(17)	$\pi^*(Fu)+p(C_2+N_a)$
H	–5.14	15	8	0	0	0	0	5	0	1	C(27)+S(16)+N(8)	$p(C_a+S_a)+d(Ru)$
H-1	–5.39	10	37	0	0	0	0	18	0	2	C(5)+S(4)+N(11)	$\pi(Ph_1)+p(O_1+N_a)+d(Ru)$
H-2	–6.12	22	12	0	13	2	2	8	1	0	C(3)+S(19)+N(11)	$\pi(Ph_1+Fu)+p(S_a+N_a)+d(Ru)$
H-3	–6.34	34	11	0	14	6	0	11	0	0	C(1)+S(5)+N(4)	$\pi(Ph_1+Fu)+p(O_1)+d(Ru)$

TABLE S-V. Molecular orbital compositions in the ground state for $RuCO(Py)L^1$ (**C**) at the B3LYP/6-31G(d)-LanL2DZ level in dichloromethane

MO	Energy eV	Contribution								Assign
		Ru	Ph	Fu	CO	C_1	O_1	C_2	Py	a(C+S+N)	
L+2	–1.31	3	0	0	1	0	0	0	84	C(0)+S(3)+N(0)	$\pi^*(Py)$
L+1	–1.58	2	34	0	1	27	4	0	2	C(2)+S(5)+N(18)	$\pi^*(Ph)+p(C_1+N_a)$
L	–2.07	1	0	37	0	0	0	27	0	C(7)+S(7)+N(18)	$\pi^*(Fu)+p(C_2+N_a)$
H	–5.09	22	16	0	0	0	9	0	0	C(20)+S(12)+N(6)	$\pi(Ph)+p(C_a+S_a)+d(Ru)$
H-1	–5.50	12	28	0	0	0	12	0	0	C(11)+S(8)+N(11)	$\pi(Ph)+p(O_1+C_a+N_a)+d(Ru)$
H-2	–6.10	27	13	16	3	3	5	1	0	C(2)+S(14)+N(11)	$\pi(Ph+Fu)+p(S_a+N_a)+d(Ru)$
H-3	–6.26	42	16	5	6	0	12	0	0	C(0)+S(9)+N(2)	$\pi(Ph)+p(O_1)+d(Ru)$

TABLE S-VI. Molecular orbital compositions in the ground state for $RuCO(AsPh_3)L^2$ (**D**) at the B3LYP/6-31G(d)-LanL2DZ level in dichloromethane

MO	Energy eV	Contribution											Assign
		Ru	Ph_1	$Ph_{(2+3+4)}$	Fu	CO	C_1	O_1	C_2	CH_3	As	a(C+S+N)	
L+2	–1.25	34	6	0	0	3	5	4	0	0	3	C(2)+S(14)+N(9)	$p(S_a)+d(Ru)$
L+1	–1.47	6	28	0	0	1	22	3	0	0	1	C(1)+S(10)+N(16)	$\pi^*(Ph_1)+p(C_1+S_a+N_a)$
L	–2.07	2	0	0	33	0	0	0	26	0	0	C(8)+S(7)+N(17)	$\pi^*(Fu)+p(C_2+N_a)$
H	–5.09	17	11	0	0	0	0	7	0	0	0	C(24)+S(15)+N(7)	$\pi(Ph_1)+p(C_a+S_a)+d(Ru)$
H-1	–5.33	10	34	0	0	0	0	18	0	0	2	C(6)+S(5)+N(10)	$\pi(Ph_1)+p(N_a+O_1)+d(Ru)$
H-2	–6.09	21	9	0	11	3	2	10	1	0	0	C(3)+S(20)+N(11)	$\pi(Fu)+p(S_a+N_a+O_1)+d(Ru)$
H-3	–6.28	34	14	0	13	6	1	10	0	0	0	C(2)+S(5)+N(5)	$\pi(Ph_1+Fu)+p(O_1)+d(Ru)$

TABLE S-VII. Molecular orbital compositions in the ground state for $RuCO(PPh_3)L^2$ (**E**) at the B3LYP/6-31G(d)-LanL2DZ level in dichloromethane

MO	Energy, eV	Contribution											Assign
		Ru	Ph_1	$Ph_{(2+3+4)}$	Fu	CO	C_1	O_1	C_2	CH_3	P	a(C+S+N)	
L+2	–1.28	30	7	5	0	4	6	4	0	0	4	C(2)+S(12)+N(10)	$p(S_a+N_a)+d(Ru)$
L+1	–1.44	7	28	0	0	0	21	3	0	0	2	C(1)+S(10)+N(16)	$\pi^*(Ph_1)+p(C_1+S_a+N_a)$
L	–2.04	2	0	0	34	0	0	0	26	0	0	C(8)+S(7)+N(17)	$\pi^*(Fu)+p(C_2+N_a)$
H	–5.09	15	8	0	0	0	0	5	0	0	1	C(26)+S(17)+N(8)	$p(C_a+S_a)+d(Ru)$
H-1	–5.33	11	37	0	0	0	0	19	0	0	2	C(4)+S(4)+N(11)	$\pi(Ph_1)+p(O_1+N_a)+d(Ru)$
H-2	–6.07	22	9	0	10	3	2	11	1	0	0	C(3)+S(20)+N(11)	$\pi(Fu)+p(S_a+N_a+O_1)+d(Ru)$
H-3	–6.28	32	14	0	16	6	1	9	0	0	0	C(2)+S(5)+N(5)	$\pi(Ph_1+Fu)+d(Ru)$

TABLE S-VIII. Molecular orbital compositions in the ground state for $RuCO(Py)L^2$ (**F**) at the B3LYP/6-31G(d)-LanL2DZ level in dichloromethane

MO	Energy, eV	Contribution										Assign
		Ru	Ph	Fu	CO	C_1	O_1	C_2	CH_3	Py	a(C+S+N)	
L+2	–1.28	3	0	0	1	2	0	0	0	81	C(0)+S(4)+N(0)	π*(Py)
L+1	–1.47	3	31	0	1	23	3	0	0	7	C(2)+S(8)+N(17)	π*(Ph)+p(C_1+N_a)
L	–2.04	1	0	37	0	0	0	27	0	0	C(7)+S(7)+N(18)	π*(Fu)+p(C_2+N_a)
H	–5.03	23	16	0	0	0	10	0	0	0	C(19)+S(12)+N(6)	π(Ph)+p(C_a+S_a+O_1)+d(Ru)
H-1	–5.44	12	27	0	0	0	13	0	0	0	C(12)+S(8)+N(10)	π(Ph)+p(O_1+C_a+N_a)+d(Ru)
H-2	–6.04	26	9	16	3	3	7	1	0	0	C(2)+S(16)+N(12)	π(Fu)+p(S_a+N_a)+d(Ru)
H-3	–6.18	40	17	6	6	0	11	0	0	0	C(0)+S(7)+N(2)	π(Ph)+p(O_1)+d(Ru)

TABLE S-IX. Molecular orbital compositions in the ground state for $RuCO(AsPh_3)L^3$ (**G**) at the B3LYP/6-31G(d)-LanL2DZ level in dichloromethane

MO	Energy eV	Contribution											Assign
		Ru	Ph_1	$Ph_{(2+3+4)}$	Fu	CO	C_1	O_1	C_2	OCH_3	As	a(C+S+N)	
L+2	–1.36	40	0	0	0	2	2	4	0	0	3	C(2)+S(17)+N(8)	p(S_a)+d(Ru)
L+1	–1.50	3	30	0	0	2	27	4	0	0	0	C(2)+S(6)+N(18)	π*(Ph_1)+p(C_1+N_a)
L	–2.07	2	0	0	33	0	0	0	26	0	0	C(8)+S(7)+N(17)	π*(Fu)+p(C_2+N_a)
H	–5.03	15	35	0	0	0	0	15	0	5	0	C(11)+S(6)+N(3)	π(Ph_1)+p(C_a+O_1)+d(Ru)
H-1	–5.25	5	15	0	0	0	0	6	0	3	3	C(20)+S(13)+N(12)	π(Ph_1)+p(C_a+N_a+S_a)
H-2	–6.07	12	33	0	11	1	2	1	1	5	0	C(2)+S(9)+N(15)	π(Ph_1+Fu)+p(N_a)+d(Ru)
H-3	–6.20	42	10	0	0	5	0	15	0	3	0	C(0)+S(14)+N(0)	π(Ph_1)+p(O_1+S_a)+d(Ru)

TABLE S-X. Molecular orbital compositions in the ground state for $RuCO(PPh_3)L^3$ (**H**) at the B3LYP/6-31G(d)-LanL2DZ level in dichloromethane

MO	Energy eV	Contribution										Assign
		Ru	Ph_1	$Ph_{(2+3+4)}$	Fu	CO	C_1	O_1	C_2	OCH_3	P	a(C+S+N)	
L+2	–1.36	36	0	5	0	2	3	4	0	0	4	C(1)+S(16)+N(8)	$p(S_a)+d(Ru)$
L+1	–1.50	4	30	0	0	1	26	4	0	0	1	C(2)+S(6)+N(18)	$\pi^*(Ph_1)+p(C_1+N_a)$
L	–2.04	2	0	0	33	0	0	0	26	0	0	C(8)+S(7)+N(17)	$\pi^*(Fu)+p(C_2+N_a)$
H	–5.03	14	33	0	0	0	0	14	0	5	0	C(12)+S(7)+N(3)	$\pi(Ph_1)+p(O_1+C_a)+d(Ru)$
H-1	–5.22	5	16	0	0	0	0	6	0	3	2	C(19)+S(13)+N(12)	$\pi(Ph_1)+p(C_a+S_a+N_a)$
H-2	–6.04	12	32	0	11	1	2	2	1	5	0	C(2)+S(10)+N(15)	$\pi(Ph_1+Fu)+p(S_a+N_a)+d(Ru)$
H-3	–6.18	42	12	0	0	5	0	14	0	4	0	C(0)+S(13)+N(0)	$\pi(Ph_1)+p(O_1+S_a)+d(Ru)$

TABLE S-XI. Molecular orbital compositions in the ground state for $RuCO(Py)L^3$ (**I**) at the B3LYP/6-31G(d)-LanL2DZ level in dichloromethane

MO	Energy eV	Contribution									Assign
		Ru	Ph	Fu	CO	C_1	O_1	C_2	OCH_3	Py	a(C+S+N)	
L+2	–1.28	3	0	0	1	1	0	0	0	83	C(0)+S(3)+N(0)	$\pi^*(Py)$
L+1	–1.52	3	30	0	1	27	5	0	0	4	C(2)+S(6)+N(18)	$\pi^*(Ph)+p(C_1+N_a)$
L	–2.04	1	0	37	0	0	0	27	0	0	C(7)+S(7)+N(18)	$\pi^*(Fu)+p(C_2+N_a)$
H	–4.98	19	29	0	0	0	13	0	4	0	C(13)+S(7)+N(3)	$\pi(Ph)+p(C_a+O_1)+d(Ru)$
H-1	–5.36	7	21	0	0	0	6	0	4	0	C(19)+S(12)+N(10)	$\pi(Ph)+p(C_a+S_a+N_a)$
H-2	–5.99	25	27	13	4	2	0	1	5	0	C(0)+S(5)+N(11)	$\pi(Ph+Fu)+p(N_a)+d(Ru)$
H-3	–6.15	45	6	0	5	0	15	0	1	0	C(0)+S(17)+N(1)	$p(O_1+S_a)+d(Ru)$

TABLE S-XII. Molecular orbital compositions in the ground state for $RuCO(AsPh_3)L^4$ (**J**) at the B3LYP/6-31G(d)-LanL2DZ level in dichloromethane

MO	Energy eV	Contribution										Assign
		Ru	Naph	$Ph_{(2+3+4)}$	Fu	CO	C_1	O_1	C_2	As	a(C+S+N)	
L+2	–1.39	40	0	3	0	1	0	4	0	3	C(1)+S(20)+N(7)	$p(S_a)$+d(Ru)
L+1	–1.88	0	50	0	0	1	21	0	0	0	C(2)+S(3)+N(16)	π*(Naph)+$p(C_1+N_a)$
L	–2.10	2	0	0	33	0	0	0	26	0	C(7)+S(7)+N(17)	π*(Fu)+$p(C_2+N_a)$
H	–5.06	15	50	0	0	0	0	18	0	0	C(6)+S(4)+N(0)	π(Naph)+$p(O_1)$+d(Ru)
H-1	–5.28	5	12	0	0	0	0	4	0	3	C(25)+S(15)+N(10)	π(Naph)+$p(C_a+S_a+N_a)$+d(Ru)
H-2	–6.01	15	48	0	6	1	0	2	0	0	C(1)+S(5)+N(14)	π(Naph)+$p(N_a)$+d(Ru)
H-3	–6.18	36	6	0	2	5	0	17	0	0	C(0)+S(17)+N(2)	$p(O_1+S_a)$+d(Ru)

TABLE S-XIII. Molecular orbital compositions in the ground state for $RuCO(PPh_3)L^4$ (**K**) at the B3LYP/6-31G(d)-LanL2DZ level in dichloromethane

MO	Energy, eV	Contribution										Assign
		Ru	Naph	$Ph_{(2+3+4)}$	Fu	CO	C_1	O_1	C_2	P	a(C+S+N)	
L+2	–1.42	36	0	10	0	1	0	3	1	5	C(1)+S(20)+N(7)	$p(S_a)$+d(Ru)
L+1	–1.88	0	50	0	0	1	21	0	0	0	C(2)+S(2)+N(16)	π*(Naph)+$p(C_1+N_a)$
L	–2.07	2	0	0	33	0	0	0	26	0	C(8)+S(7)+N(17)	π*(Fu)+$p(C_2+N_a)$
H	–5.06	15	49	0	0	0	0	17	0	0	C(7)+S(4)+N(0)	π(Naph)+$p(O_1)$+d(Ru)
H-1	–5.25	5	13	0	0	0	0	4	0	2	C(25)+S(15)+N(10)	π(Naph)+$p(C_a+S_a+N_a)$
H-2	–6.01	14	48	0	5	1	0	1	0	0	C(1)+S(5)+N(14)	π(Naph)+$p(N_a)$+d(Ru)
H-3	–6.18	36	6	0	2	4	0	17	0	0	C(0)+S(17)+N(2)	$p(O_1+S_a)$+d(Ru)

TABLE S-XIV. Molecular orbital compositions in the ground state for $RuCO(Py)L^4$ (**L**) at the B3LYP/6-31G(d)-LanL2DZ level in dichloromethane

MO	Energy eV	Contribution									Assign
		Ru	Naph	Fu	CO	C_1	O_1	C_2	Py	a(C+S+N)	
L+2	–1.31	3	0	0	1	0	0	0	88	C(0)+S(2)+N(0)	π*(Py)
L+1	–1.90	1	49	0	1	21	0	0	0	C(2)+S(3)+N(16)	π*(Naph)+p(C_1+N_a)
L	–2.07	1	0	36	0	0	0	27	0	C(7)+S(7)+N(18)	π*(Fu)+p(C_2+N_a)
H	–5.01	20	43	0	0	0	16	0	0	C(8)+S(5)+N(0)	π(Naph)+p(O_1)+d(Ru)
H-1	–5.36	6	21	0	0	0	4	0	0	C(24)+S(14)+N(8)	π(Naph)+p(C_a+S_a)
H-2	–5.96	28	33	9	5	1	0	1	0	C(0)+S(4)+N(12)	π(Naph)+p(N_a)+d(Ru)
H-3	–6.15	38	8	1	5	0	16	0	0	C(0)+S(18)+N(2)	p(O_1+S_a)+d(Ru)

TABLE S-XV. Presentation of the H-L energy gaps (ΔE / eV) for complexes $RuCO(AsPh_3)L^1$ (**A**), $RuCO(PPh_3)L^1$ (**B**) and $RuCO(Py)L^1$ (**C**) at various levels: a – calculated at the B3LYP/6-31G(d)-LANL2DZ level, b – calculated at the PBE1PBE/6-31G(d)-LANL2DZ level, c – calculated at the M06/6-31G(d)-LANL2DZ level and d – calculated at the B3LYP/def2-SVP level

Level	$RuCO(AsPh_3)L^1$	$RuCO(PPh_3)L^1$	$RuCO(Py)L^1$
a	3.04	3.07	3.02
b	3.23	3.24	3.21
c	3.23	3.24	3.20
d	2.66	2.67	2.65

TABLE S-XVI. Presentation of the lowest-lying absorption wavelengths (λ_{max} / nm) for complexes $RuCO(AsPh_3)L^1$ (**A**), $RuCO(PPh_3)L^1$ (**B**), and $RuCO(Py)L^1$ (**C**) at various levels: a – calculated at the TD-CAM-B3LYP/def2-SVP//B3LYP/6-31G(d)-LANL2DZ level, b – calculated at the TD-CAM-B3LYP/def2-SVP//PBE1PBE/6-31G(d)-LANL2DZ level, c – calculated at the TD-CAM-B3LYP/def2-SVP//M06/6-31G(d)-LANL2DZ level and d – calculated at the TD-CAM-B3LYP/def2-SVP//B3LYP/def2-SVP level

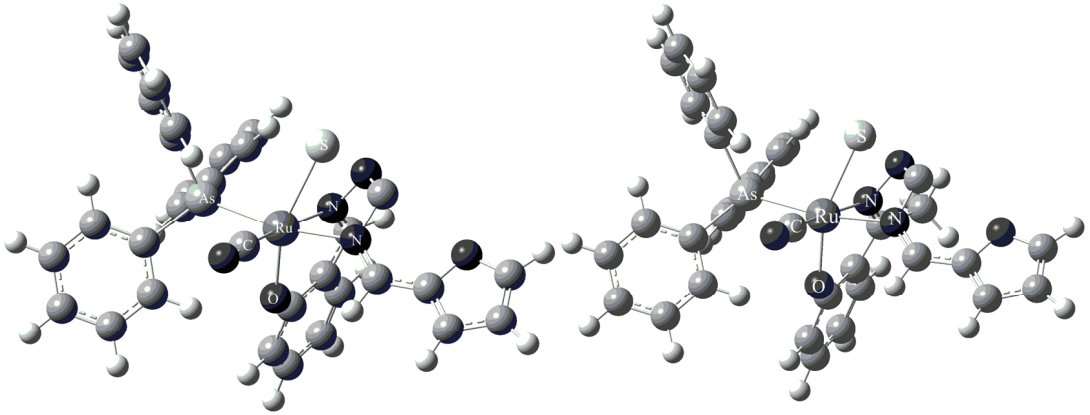
Level	$RuCO(AsPh_3)L^1$	$RuCO(PPh_3)L^1$	$RuCO(Py)L^1$
a	485	483	477
b	469	468	466
c	472	467	464
d	486	487	480

TABLE S-XVII. Calculated absorptions of complexes $RuCO(AsPh_3)L^1$ (**A**), $RuCO(PPh_3)L^1$ (**B**) and $RuCO(Py)L^1$ (**C**) in dichloromethane medium at the TD-CAM-B3LYP level

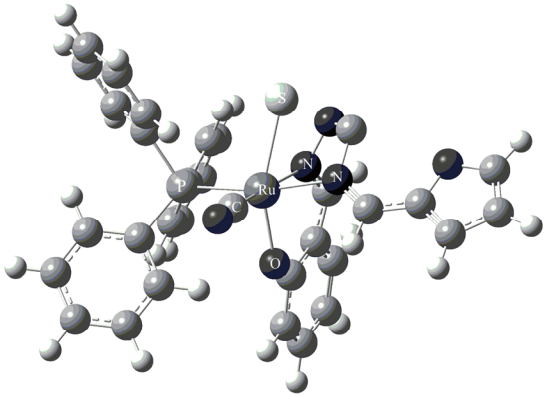
Complex	States	λ / nm	Oscillator strength	Main configuration	Assignments
A	S_1	485	0.0015	H→L (56 %)	$Ph_1/C_a/S_a/N_2/Ru→Fu/C_2/S_a$ IL/MLCT
	S_4	364	0.0328	H→L+1 (45 %)	$Ph_1/C_a/S_a/N_2/Ru→Ph_1/C_1/N_2$ IL/MLCT
	S_{15}	280	0.6838	H-4→L (37 %)	$Ph_1/Fu/C_a/N_1/Ru→Fu/C_2/S_a$ IL/MLCT
	S_{41}	222	0.1503	H→L+6 (17 %)	$Ph_1/C_a/S_a/N_2/Ru→Ph_2/Ph_4$ IL/LLCT

TABLE S-XVII. Continued

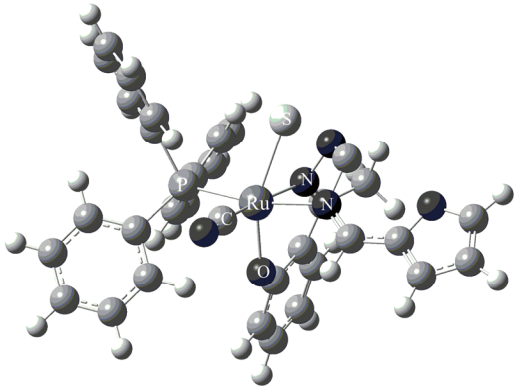
Complex	States	λ / nm	Oscillator strength	Main configuration	Assignments
B	S_1	483	0.0029	H→L (77 %)	$Ph_1/S_a/C_a/Ru \rightarrow Fu/C_2/N_1/S_a$ IL/MLCT
	S_4	363	0.0328	H→L+1 (45 %)	$Ph_1/S_a/C_a/Ru \rightarrow Ph_1/C_1/N_2$ IL/MLCT
	S_9	314	0.2307	H-2→L (32 %)	$Ph_1/Fu/O_1/S_a/C_a/N_1/Ru \rightarrow Fu/C_2/N_1/S_a$ LL/MLCT
	S_{15}	280	0.7178	H-4→L (39 %)	$Ph_1/Fu/C_a/N_1/N_2/Ru \rightarrow Fu/C_2/N_1/S_a$ LL/MLCT
	S_{42}	222	0.1945	H-5→L+1 (10 %)	$Ph_1/Ph_2/Ph_4/Fu/S_a/Ru \rightarrow Ph_1/C_1/N_2$ LL/MLCT
C	S_1	477	0.0031	H→L (50 %)	$Ph/C_a/S_a/Ru \rightarrow Fu/C_2/S_a/N_a$ IL/MLCT
	S_3	382	0.0319	H→L+1 (73 %)	$Ph/C_a/S_a/Ru \rightarrow Ph/C_1/N_2$ IL/MLCT
	S_9	315	0.2612	H-2→L (28 %)	$Ph/Fu/C_a/S_a/Ru \rightarrow Fu/C_2/S_a/N_a$ MLCT
	S_{16}	280	0.2852	H-4→L (41 %)	$Ph/Fu/C_a/S_a/Ru \rightarrow Fu/C_2/S_a/N_a$ IL/MLCT
	S_{33}	235	0.0674	H-3→L+6 (10 %)	$S_a/O_1/Ru \rightarrow CO/C_a/Ru$ IL/MLCT/MC
	S_{41}	221	0.3749	H-6→L+1 (15 %)	$Ph/S_a/N_a/Ru \rightarrow Ph/C_1/N_2$ IL/MLCT



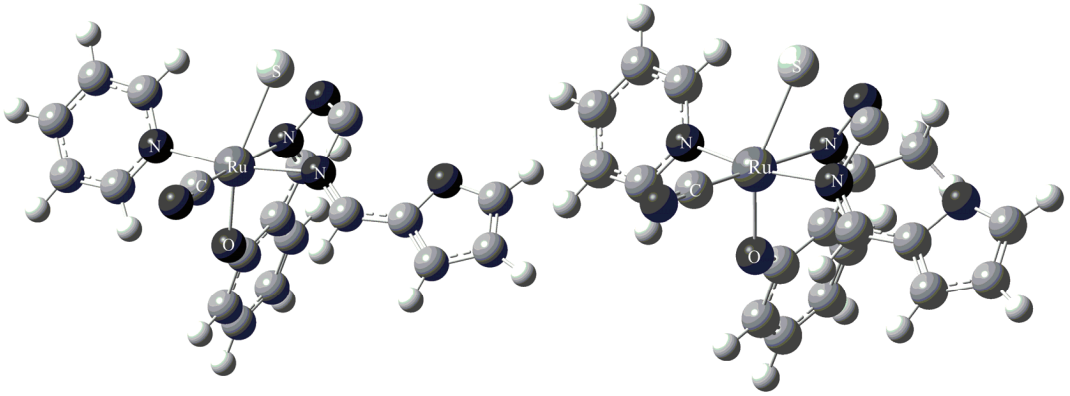
(A) **(D)**



(**B**)

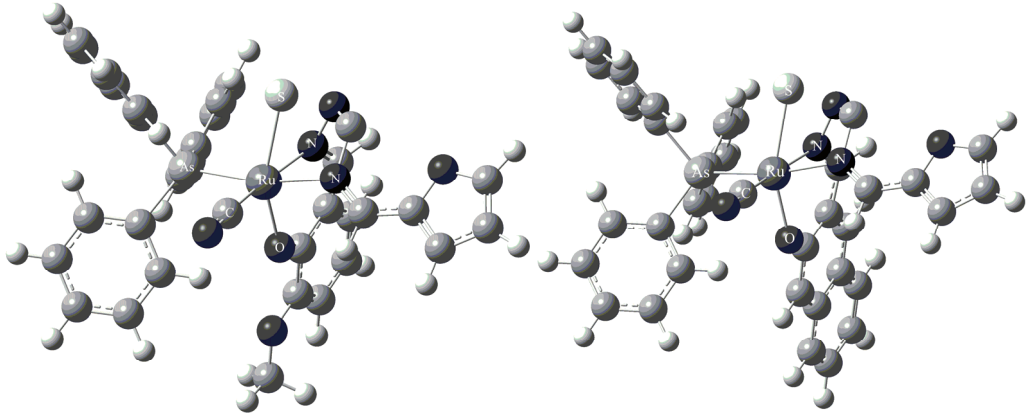


(**E**)

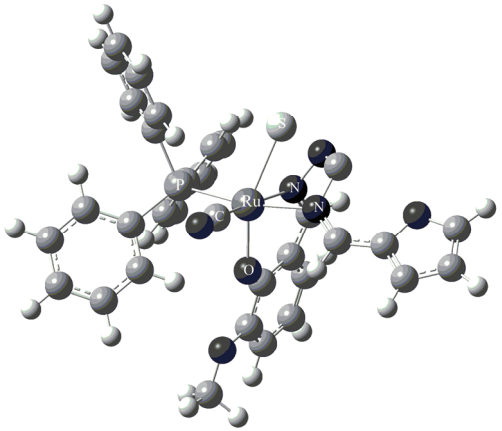


(**C**) (**F**)

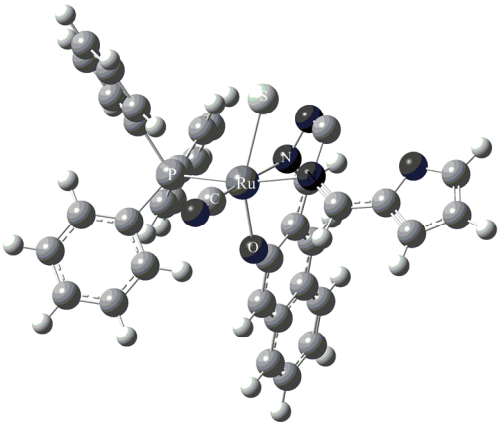
Fig. S-1. The optimized geometric structures of complexes $RuCO(AsPh_3)L^1$ (**A**), $RuCO(PPh_3)L^1$ (**B**), $RuCO(Py)L^1$ (**C**), $RuCO(AsPh_3)L^2$ (**D**), $RuCO(PPh_3)L^2$ (**E**) and $RuCO(Py)L^2$ (**F**).



(**G**) (**J**)



(**H**)



(**K**)

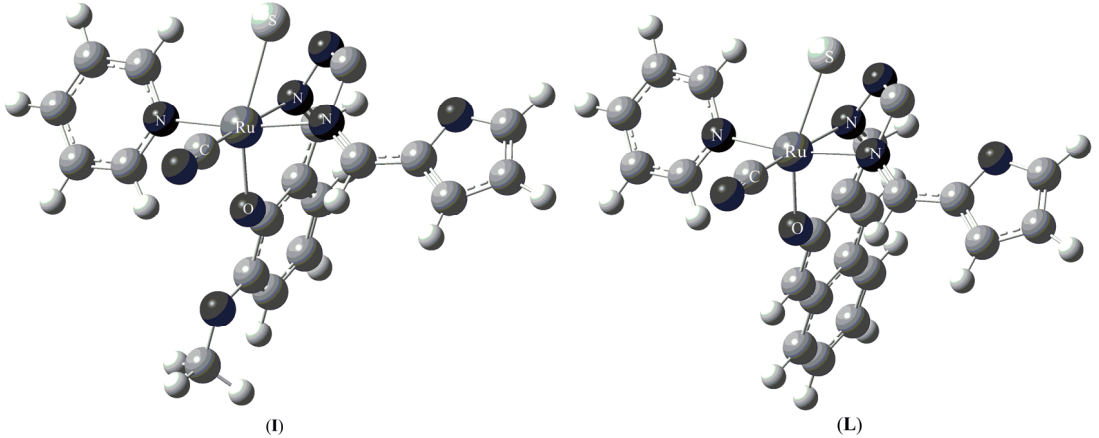
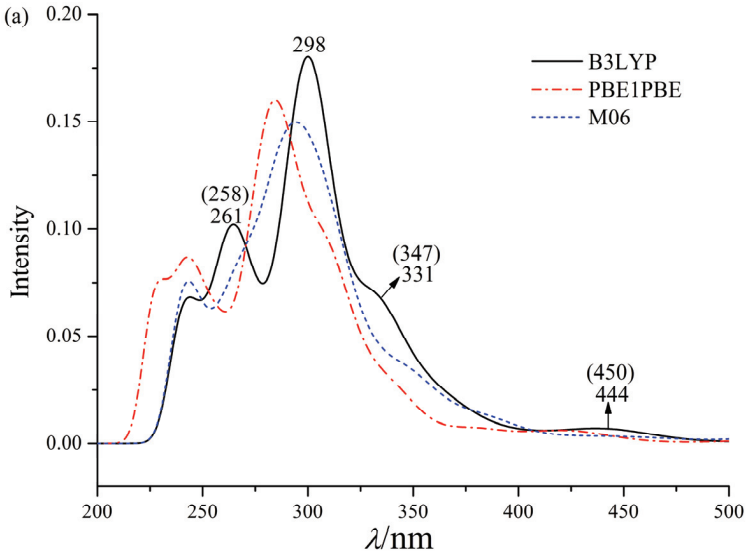
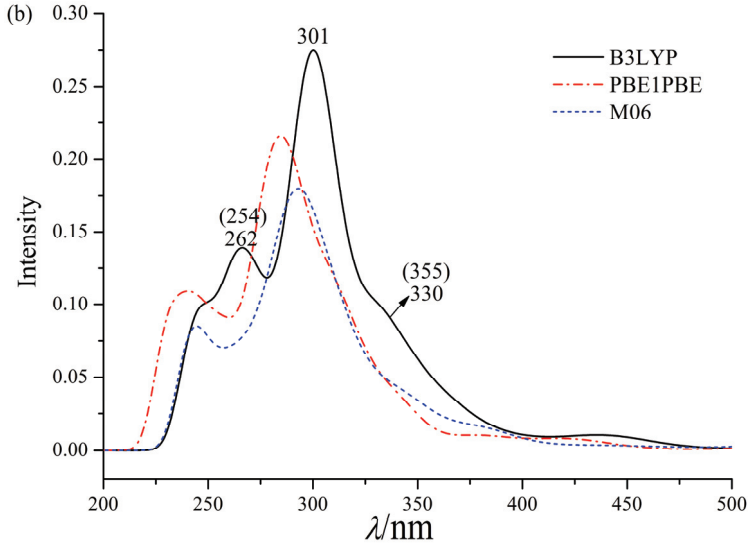


Fig. S-2**.** The optimized geometric structures of complexes $RuCO(AsPh_3)L^3$ (**G**), $RuCO(PPh_3)L^3$ (**H**), $RuCO(Py)L^3$ (**I**), $RuCO(AsPh_3)L^4$ (**J**), $RuCO(PPh_3)L^4$ (**K**) and $RuCO(Py)L^4$ (**L**).


(a)
0.20
0.15
0.10
0.05
0.00
Intensity
298
(258)
261
(347)
331
(450)
444
B3LYP
PBE1PBE
M06
200
250
300
350
400
450
500
λ/nm


(b)
0.30
0.25
0.20
0.15
0.10
0.05
0.00
Intensity
301
(254)
262
(355)
330
B3LYP
PBE1PBE
M06
200
250
300
350
400
450
500
λ/nm

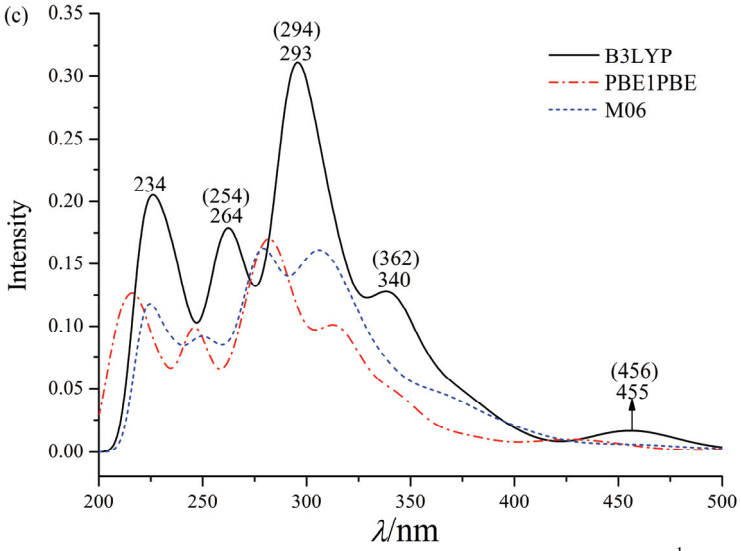


Fig. S-3. Simulated absorption spectra in dichloromethane for complexes (a) $RuCO(AsPh_3)L^1$ (**A**), (b) $RuCO(PPh_3)L^1$ (**B**), and (c) $RuCO(Py)L^1$ (**C**) at three TD-DFT-PCM/LANL2DZ levels together with the experimental values in parentheses.

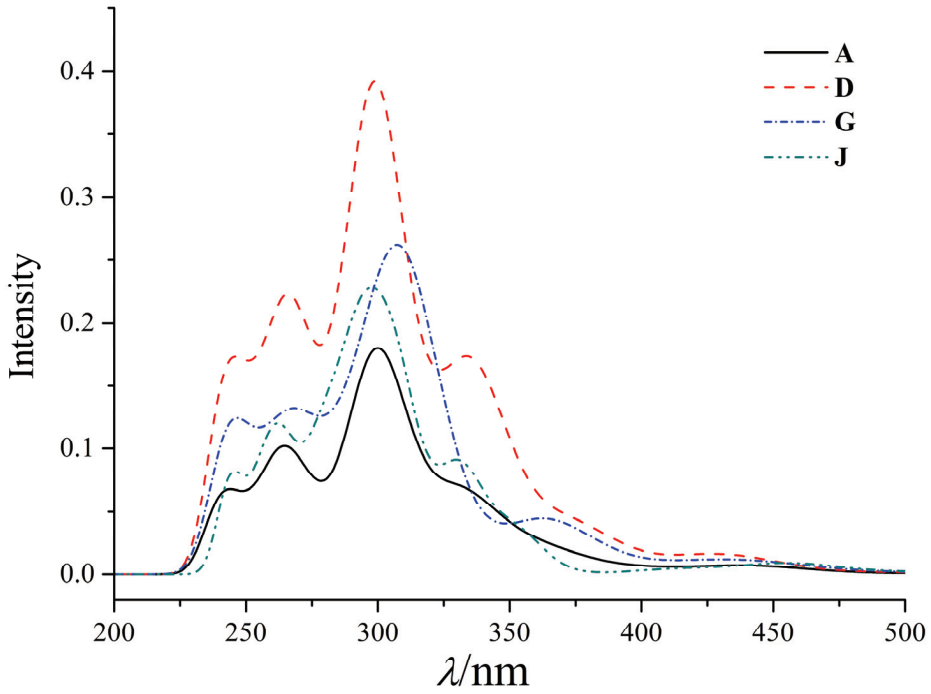


Fig. S-4. Simulated absorption spectra in dichloromethane of complexes $RuCO(AsPh_3)L^1$ (**A**), $RuCO(AsPh_3)L^2$ (**D**), $RuCO(AsPh_3)L^3$ (**G**) and $RuCO(AsPh_3)L^4$ (**J**) from TD-B3LYP(PCM) calculations.

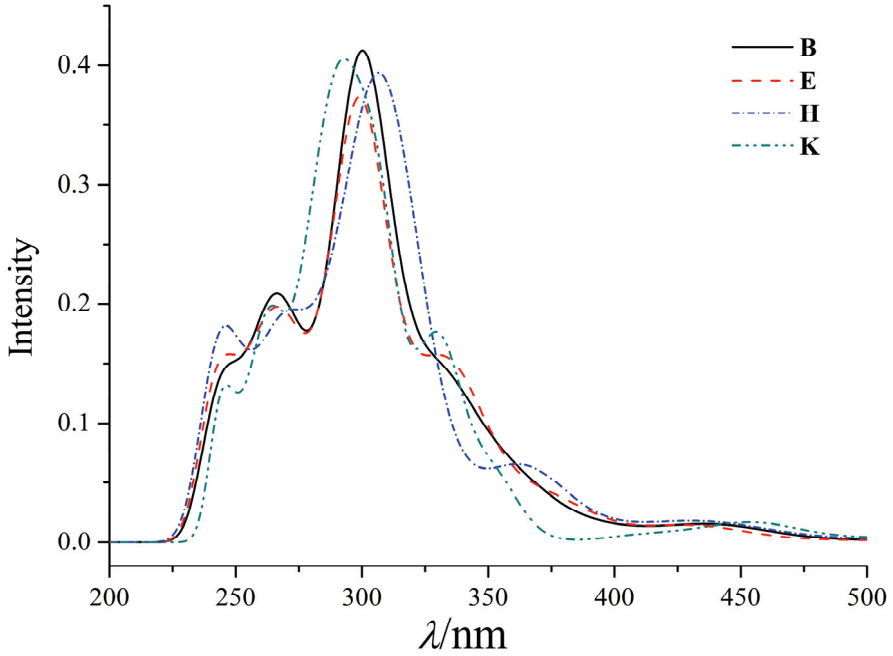


Fig. S-5. Simulated absorption spectra in dichloromethane of complexes $RuCO(PPh_3)L^1$ (**B**), $RuCO(PPh_3)L^2$ (**E**), $RuCO(PPh_3)L^3$ (**H**) and $RuCO(PPh_3)L^4$ (**K**) from TD-B3LYP(PCM) calculations.

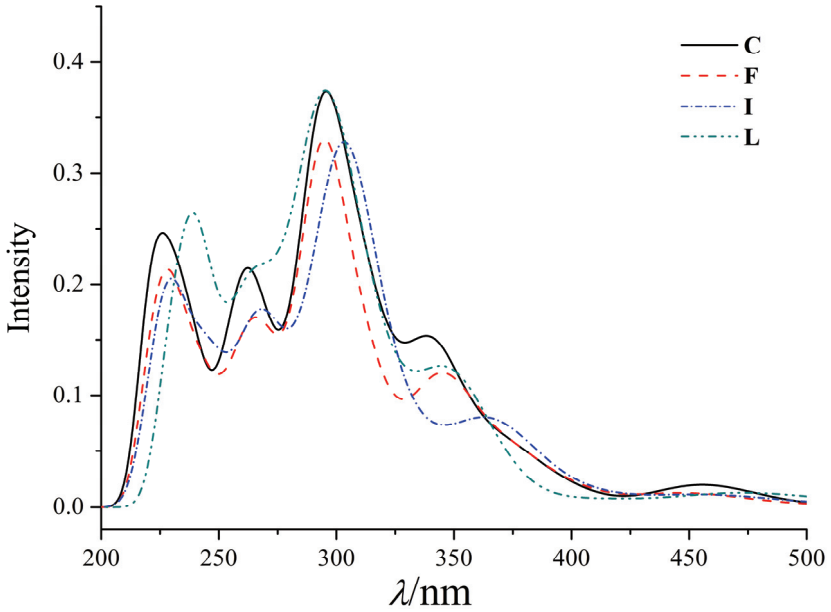
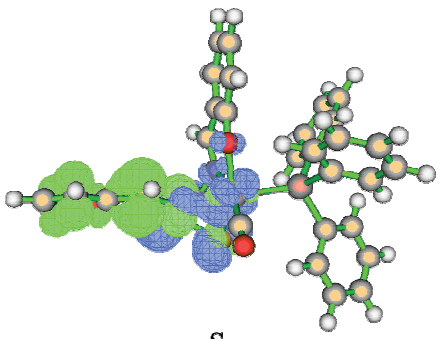
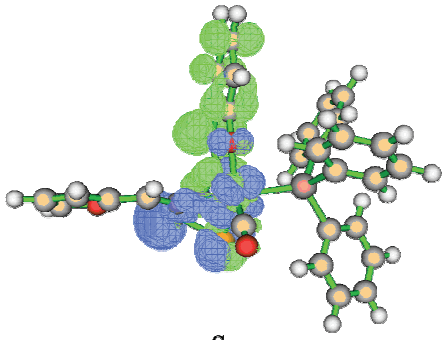


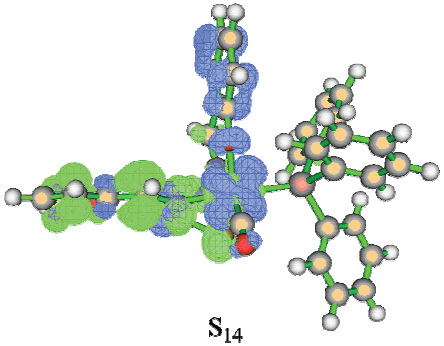
Fig. S-6. Simulated absorption spectra in dichloromethane of complexes RuCO(Py)L^1 (**C**), RuCO(Py)L^2 (**F**), RuCO(Py)L^3 (**I**), and RuCO(Py)L^4 (**L**) from TD-B3LYP(PCM) calculations.



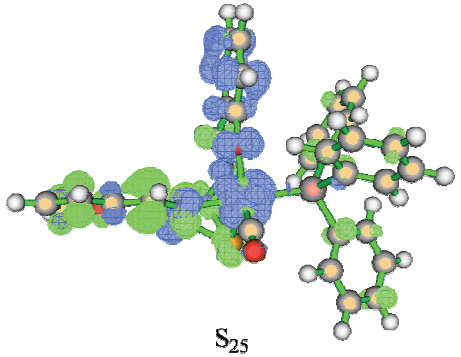
S_1



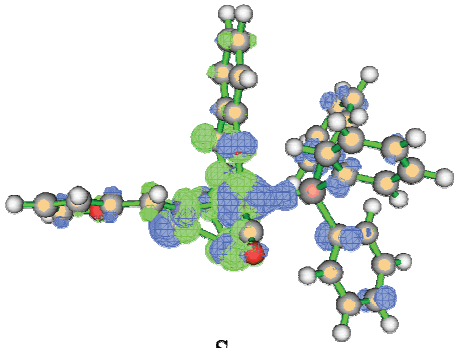
S_4



S_{14}



S_{25}



S_{51}

Fig. S-7. The distributions of electrons–holes for the excited states of complex **A**.

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1. G. Raja, N. Sathya, C. Jayabalakrishnan, *J. Coord. Chem.* **64** (2011) 817
2. S. Kannan, M. Sivagamasundari, R. Ramesh, Y. Liu, *J. Organomet. Chem.* **693** (2008) 2251.