Electronic Supplementary Information
(34pages)

$RhCl(PPh_3)_3$-mediated C−H oxyfunctionalization of pyrrolido-functionalized bisazoaromatic pincer: a combined experimental and theoretical scrutiny of redox-active and spectroscopic properties†

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Experimental section

Physical measurements

The elemental analyses (C, H, N) were performed with a Perkin- Elmer model 2400 series II elemental analyzer. FT-IR spectra were recorded on Perkin-Elmer L1600300 spectrometer. ^{1}H and ^{13}C NMR spectral measurement was carried out on Bruker FT 300 MHz spectrometers with TMS as an internal reference. ^{31}P NMR spectra were obtained using a Bruker Avance 500 MHz spectrometer operating at 202.45 MHz. The electrospray ionization mass spectra (ESI-MS positive) were measured in acetonitrile HRMS spectrometers (Model: QTOF Micro YA263). The electronic spectra in dichloromethane solution were obtained using a Perkin-Elmer LAMDA 25 spectrophotometer with a solute concentration of about 10^{-5} M. Electrochemical measurements were carried out at 27°C with VersaStat II Princeton Applied Research potentiostat/galvanostat under argon atmosphere. The cell contained a Pt working electrode and a Pt wire auxiliary electrode. Tetraethylammonium perchlorate (NEt_4ClO_4) was used as a supporting electrolyte and the potentials are referenced to the Ag/AgCl electrode without junction correction.

Crystallographic studies

Crystals of **1** suitable for diffraction analysis was grown by slow evaporation of acetonitrile solution at room temperature. The dark green complex crystallizes in monoclinic $P2_1/c$ space group. X-ray intensity data for compound **1** was measured at 130(2) K on Bruker AXS SMART APEX II equipped with a CCD diffractometer using graphite-monochromator (Mo Kα, λ = 0.71073 Å). Metal atoms were located by direct methods, and the rest of the non-hydrogen atoms emerged from successive Fourier synthesis. The structures were refined by full-matrix least squares procedures on F^2.[1] All the H atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters, Uiso(H) =1.2Ueq(C). Calculations were performed using the SHELXTL v 6.14 program package.[2] Empirical absorption correction was applied using SADABS.[3] The phenyl ring (C69 to C74) connected with P3 shows the rotational disorder (Fig. S5) and refined *via* PART command along with SADI and DFIX instructions. The anisotropic displacement parameter of the carbon atoms in each ring part (either A or B) has been refined *via* EADP command. The asymmetric unit contains two rhodium complexes associated with the three acetonitrile solvent molecules. Out of them two acetonitrile molecules have been removed by using PLATON (2013) SQUEEZE Program[4] because of their large ADP and short intermolecular separation. Thermal ellipsoids are drawn at the 50% probability level. Molecular structure plots were drawn using the Oak Ridge thermal ellipsoid plot ORTEP.[5]

Computational details

The molecular geometry of the singlet ground state (S_0) of **1**, **2a** and **2b** has been calculated in gas phase in their singlet spin state without any ligand simplification by DFT method using the (R)B3LYP[6] hybrid functional approach incorporated in GAUSSIAN 09 program package.[7] The geometries of the complexes were fully optimized in gas phase without imposing any symmetry constraints. The nature of all the stationary points was checked by computing vibration frequencies, and all the species were found to be true potential energy minima, as no imaginary frequency were obtained (NImag = 0). The single crystal X-ray coordinates have been used as the initial input in all calculations. To get an insight into the ground state geometry, electronic structure and nature of FMOs of the one-electron oxidized radical cation species, $\mathbf{1}^{\bullet+}$ and $\mathbf{2a}^{\bullet+}$ were optimized by assuming an S = 1/2 spin state at the (U)B3LYP level. On the basis of the optimized geometries, the absorption and emission spectra properties in dichloromethane (CH_2Cl_2) media were calculated by the time-dependent density functional theory (TD-DFT)[8] approach associated with the conductor-like polarizable continuum model (CPCM).[9] We computed the lowest 100 singlet–singlet transitions in absorption processes. The electronic structure contributions to the differences in observed optoelectronic properties are compared by natural transition orbital (NTO) analysis. This method offers the most compact representation of the transition density between the ground and excited states in terms of an expansion into single-particle transitions (hole and electron states for each given excitation). Here we refer to the unoccupied and occupied NTOs as "electron" and "hole" transition orbitals. The computed vertical transitions were calculated at the equilibrium geometry of the S_0 state and described in terms of one-electron excitations of molecular orbitals of the corresponding S_0 geometry. The calculated transitions with moderate intensities ($f \geq 0.02$) can be envisaged going from the lower to the higher energy region of the spectrum. The rhodium atom was described by a double-ζ basis set with the effective core potential of Hay and Wadt (LANL2DZ)[10] and the 6-311+G(d,p) basis set[11] was used for the other elements present in the complexes except P, Cl and Br to optimize the ground state geometries. The 6-311G (d,p) basis set was used for P, Cl and Br to optimize the compounds. The calculated electronic density plots for frontier molecular orbitals were prepared by using the GaussView 5.0 software. GaussSum program, version 2.2[12] was used to calculate the molecular orbital contributions from groups or atoms.

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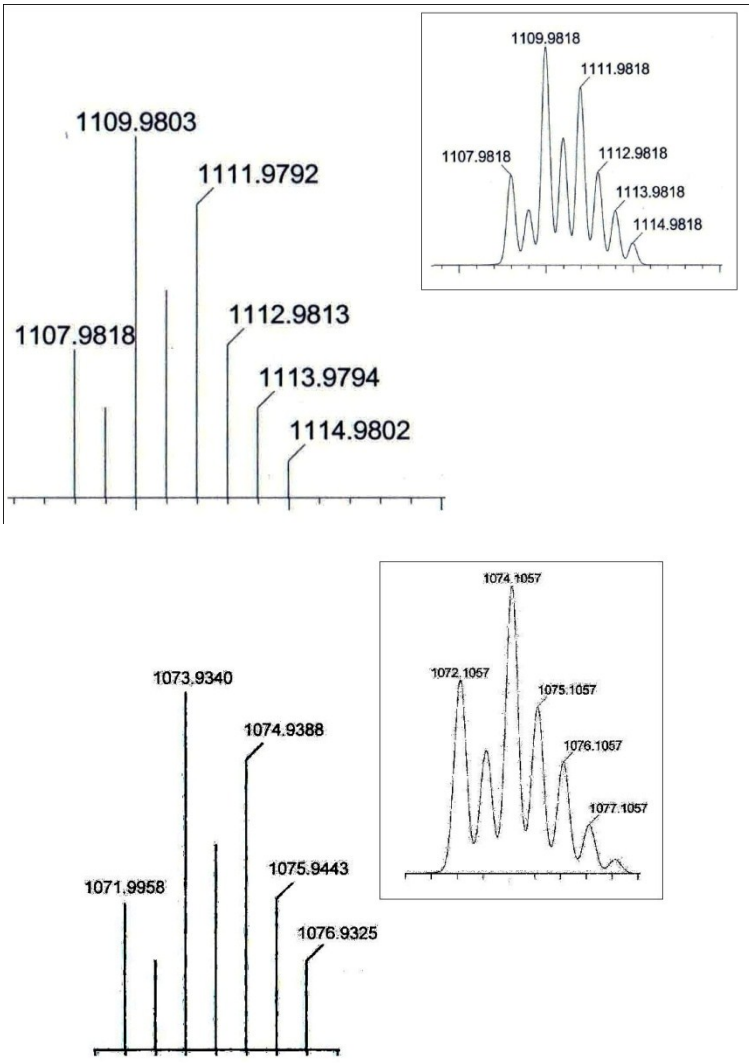


Fig. S1 High-resolution mass spectra of **1** (top) and **2a** (bottom) compounds. Inset: simulated isotropic pattern.

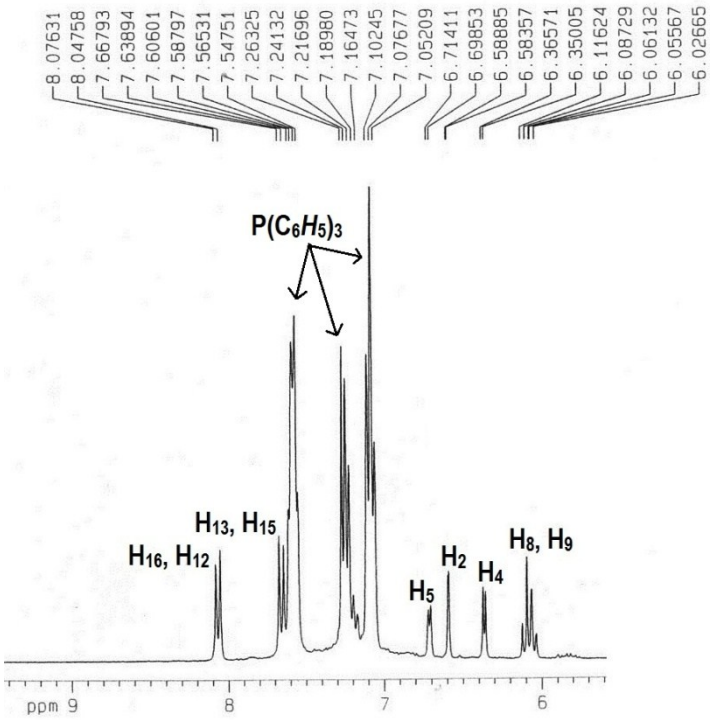


Fig. S2 ^{1}H NMR spectrum of **1** (H labeling is in accordance with the X-ray structure).

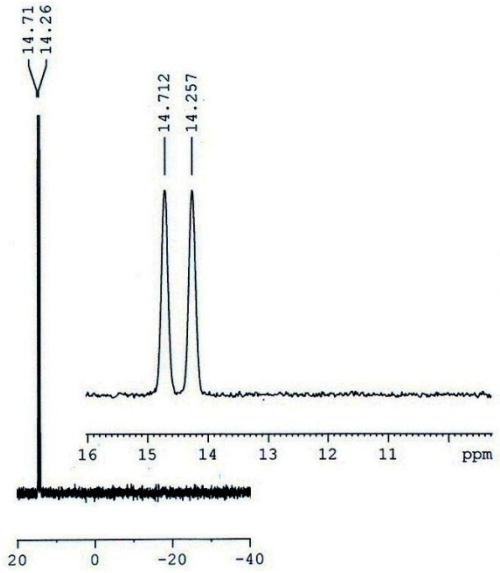


Fig. S3 ^{31}P NMR spectrum of **1**.

Table S1 Crystal data and structure refinement parameters for complex **1**

Empirical formula	$C_{52}H_{39}Br_2ClN_5OP_2Rh \cdot 1/2CH_3CN$
fw	1130.53
T /K	130
Crystal system	Monoclinic
Space group	$P2_1/c$
a / Å	31.4850(11)
b / Å	16.3476(5)
c / Å º	19.3520(6)
α /deg	90
β / deg	99.3320(10)
γ / deg	90
V /Å^3	9828.7(5)
Z	4
D_c /Mgm^{-3}	1.528
μ /mm^{-1}	2.138
F(000)	4536
cryst size/mm^3	0.42×0.33×0.23
θ/deg	2.3-28.4
measured reflns	153092
unique reflns/R_{int}	24442 / 0.0516
GOF on F^2	1.078
$R1$,[a] $wR2$[b] [$I > 2\sigma(I)$]	0.0452, 0.0912
$R1$, $wR2$	0.0690, 0.1048

[a]$R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b]$wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

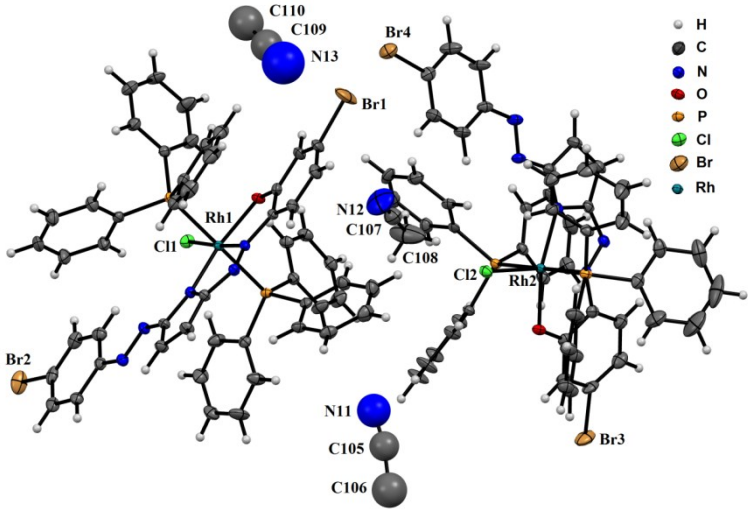


Fig. S4 Asymmetric unit of **1** showing two rhodium complexes and three acetonitrile solvate molecules.

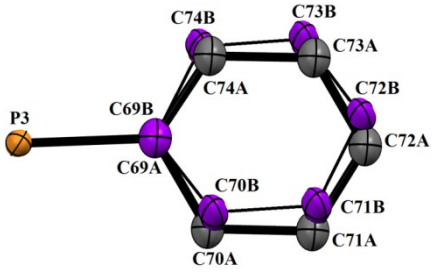


Fig. S5 The rotational disorder of the phenyl ring showing the two different parts (A and B).

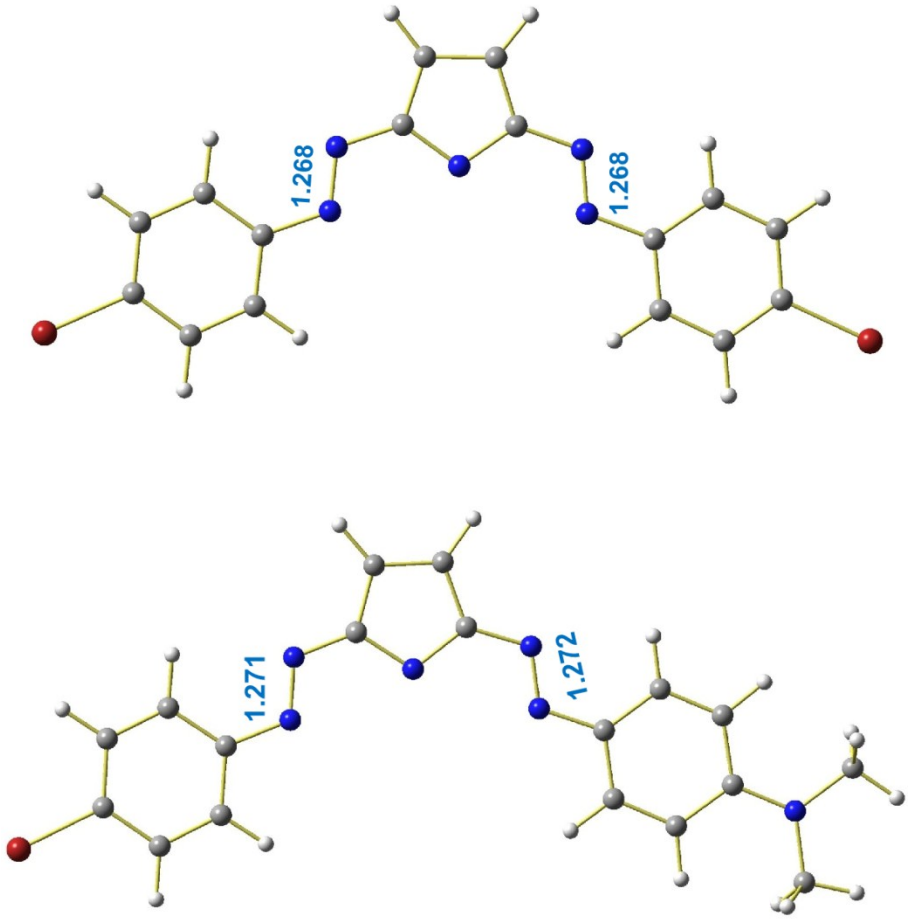


Fig. S6 Optimized Structure of Ligand $\mathbf{HL_1}$(top) and $\mathbf{HL_2}$ (bottom).

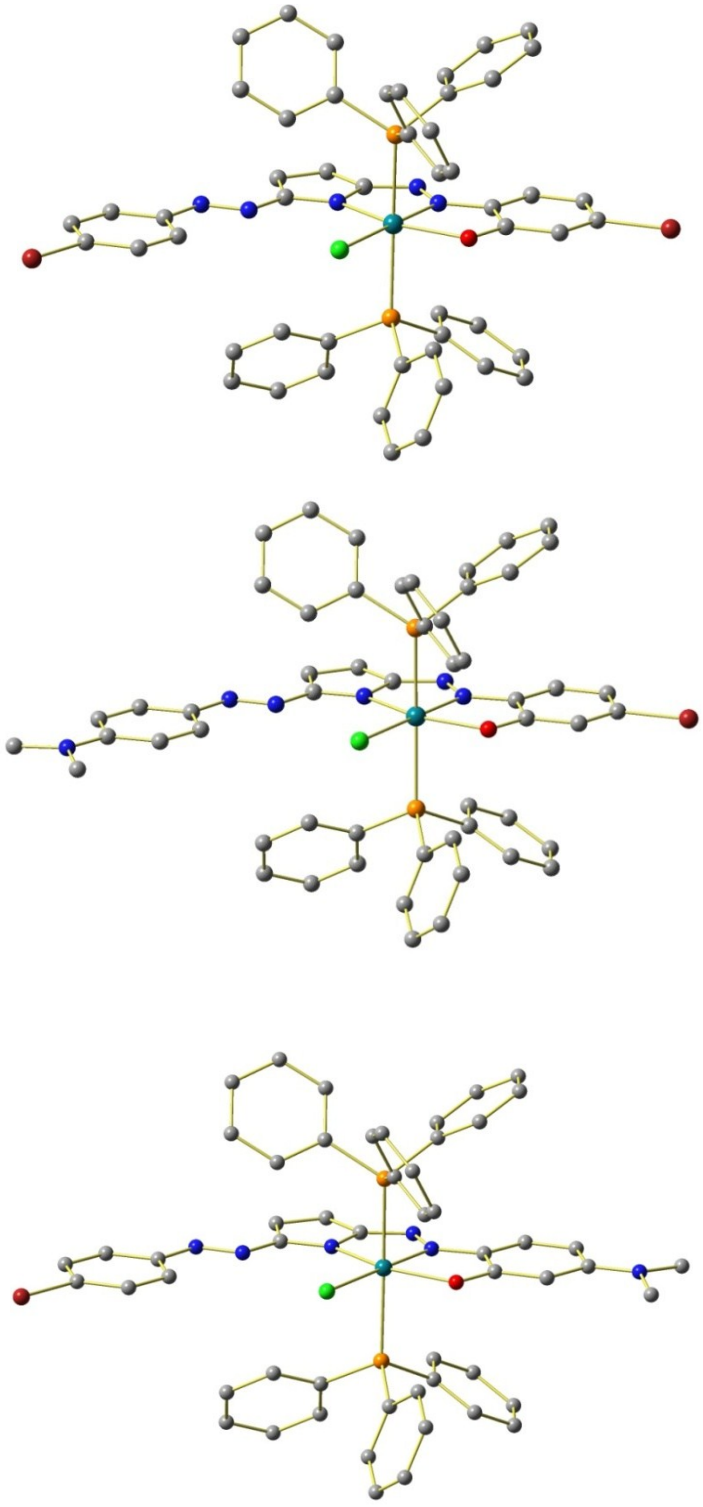


Fig. S7 Optimized molecular structures of **1** (top), **2a** (middle) and **2b** (bottom) (Rh: cyan, N: blue, O: red, C: grey, Br: deep red, Cl: green, P: saffron. Hydrogen atoms are omitted for clarity).

Table S2 Selected optimized geometrical parameters of **1** and **2a** in the ground and lower lying triplet excited states at B3LYP level

Bond lengths (Å)					
1			**2a**		
	S_0	T_1		S_0	T_1
Rh1–Cl3	2.446	2.443	Rh1–Cl3	2.451	2.448
Rh1–P5	2.473	2.478	Rh1– P4	2.471	2.472
Rh1–P6	2.476	2.478	Rh1–P5	2.471	2.476
Rh1–O12	2.120	2.133	Rh1–O11	2.120	2.135
Rh1–N10	2.090	2.081	Rh1–N9	2.092	2.082
Rh1–N7	1.996	1.993	Rh1–N6	1.996	1.992
N7–N8	1.280	1.357	N6–N7	1.283	1.353
N11–N97	1.266	1.325	N10–N96	1.269	1.333
Bond Angles (°)					
	S_0	T_1		S_0	T_1
Cl3–Rh1–P5	86.54	86.48	Cl3–Rh1–P4	86.71	86.51
Cl3–Rh1–P6	86.94	86.49	Cl3–Rh1–P5	86.98	86.56
Cl3–Rh1–O12	98.39	100.10	Cl3–Rh1–O11	98.27	100.10
Cl3–Rh1–N10	103.79	102.99	Cl3–Rh1–N9	103.88	102.84
Cl3–Rh1–N7	178.81	179.47	Cl3–Rh1 –N6	178.67	179.67
P5–Rh1–P6	172.08	171.12	P5–Rh1–P4	172.28	171.17
P5–Rh1–O12	88.49	87.95	P5–Rh1–O11	87.87	87.43
P5–Rh1–N10	93.03	93.43	P5–Rh1–N9	92.96	93.62
P5–Rh1–N7	93.34	93.49	P5–Rh1–N6	93.08	93.56
P6–Rh1–O12	88.01	87.95	P4–Rh1–O11	88.65	88.41
P6–Rh1–N10	92.89	93.43	P4–Rh1–N9	92.87	93.25
P6–Rh1–N7	93.09	93.49	P4–Rh1–N6	93.14	93.34
O12–Rh1–N10	157.82	156.90	O11–Rh1–N9	157.85	157.06
O12–Rh1–N7	80.42	79.37	O11–Rh1–N6	80.41	79.60
N10–Rh1–N7	77.39	77.53	N9–Rh1–N6	77.44	77.46

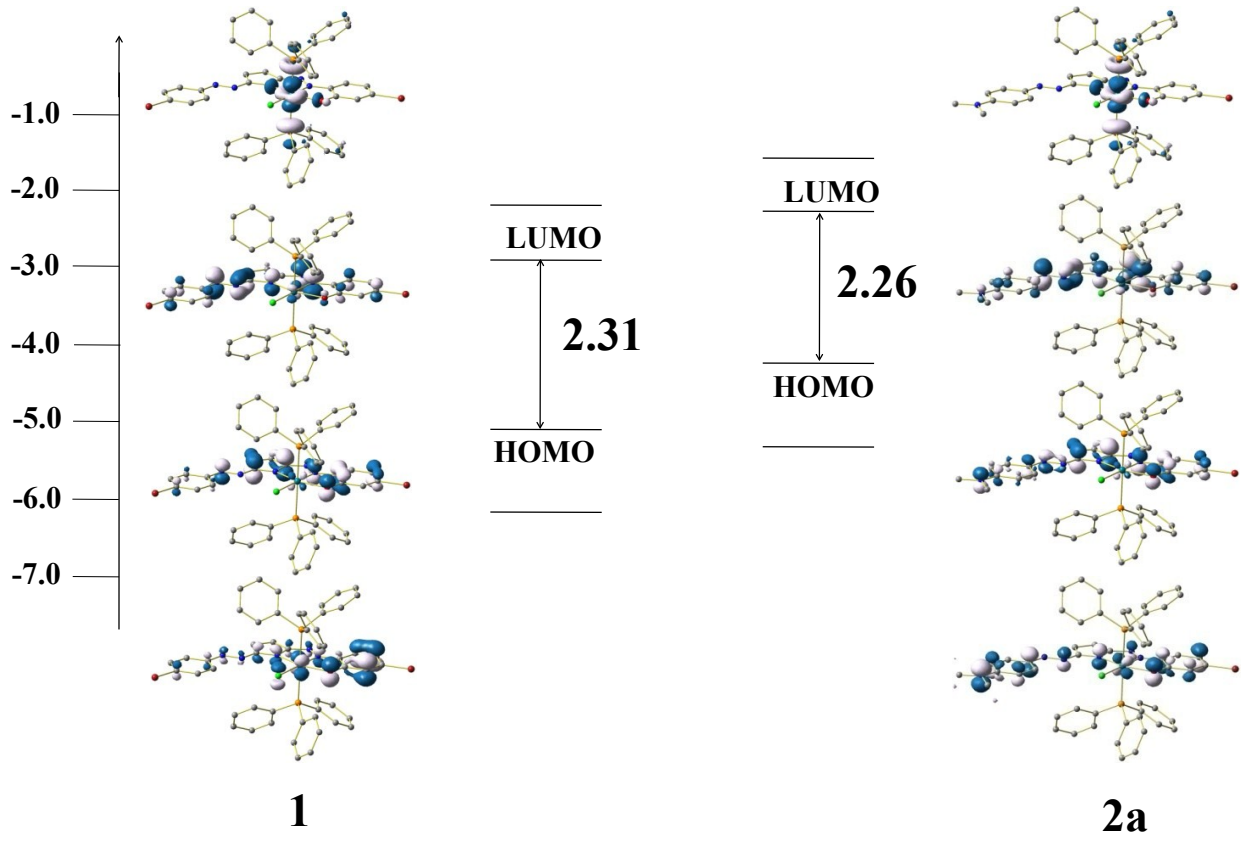


Fig. S8 Isodensity surface plots of some selected FMOs (HOMO − 1 to LUMO + 1) for the complexes **1** and **2a** at their optimized S_0 geometry in gas phase (isodensity value 0.05 e Bohr^{-3}).

Table S3 Frontier Molecular Orbital Composition (%) in the Ground State for **1**

			Contribution(%)								Main Bond Type
Orbital	MO	Energy	Rh	Azo1 (ligated)	Azo2	pyrrolido	phenoxide		PPh_3	Cl	
							Ph	O			
270	L+5	-1.1	1	1	0	0	1	0	96	0	$\pi^*(PPh_3)$
269	L+4	-1.13	0	0	0	2	0	0	98	0	$\pi^*(PPh_3)$
268	L+3	-1.73	54	16	2	7	2	5	4	11	$4d_{x^2-y^2}$(Rh)+π^*(Azo1)+3p(Cl)
267	L+2	-1.85	1	13	23	29	30	0	4	0	π^*(Ph+Pyrrolido+Azo2+Azo1)
266	L+1	-2.39	38	0	0	5	2	2	55	2	$\pi^*(PPh_3)$+$4d_{Z^2}$(Rh)
265	LUMO	-2.95	3	27	22	15	30	1	1	0	π^*(Ph+Azo1+Azo2+Pyrrolido)
264	HOMO	-5.26	2	7	6	32	40	10	2	0	π(Ph+Pyrrolido)+2p(O)
263	H-1	-6.16	9	5	3	11	47	13	6	6	π(Ph+Pyrrolido)+2p(O)
262	H-2	-6.23	6	0	50	7	6	2	3	26	π(Azo2)+3p(Cl)
261	H-3	-6.35	8	0	1	13	7	1	45	26	$\pi(PPh_3$ +Pyrrolido)+3p(Cl)
260	H-4	-6.51	17	0	30	6	3	4	6	35	π(Azo2)+$4d_{zx}$(Rh)+3p(Cl)
259	H-5	-6.63	7	1	0	13	18	1	27	33	$\pi(PPh_3$+Ph+Pyrrolido)+3p(Cl)
HOMO–LUMO gap = 2.31 eV Total Energy = –8755.3421774 Hartree											

Table S4 Frontier Molecular Orbital Composition (%) in the Ground State for **2a**

				Contribution(%)							Main Bond Type
Orbital	MO	Energy (eV)	Rh	Azo1 (ligated)	Azo2 (free)	pyrrolido	phenoxido		PPh_3	Cl	
							Ph	O			
265	L+5	-0.93	2	0	0	0	0	0	98	0	$\pi^*(PPh_3)$
264	L+4	-0.96	0	0	1	1	0	0	98	0	$\pi^*(PPh_3)$
263	L+3	-1.47	5	17	2	7	2	5	4	10	$4d_{x^2-y^2}$(Rh)+π*(Azo1)+3p(Cl)+
262	L+2	-1.49	1	11	27	27	28	0	6	0	π*(Pyrrolido+Azo2+Azo1)
261	L+1	-2.16	3	0	0	5	2	1	55	2	$\pi^*(PPh_3)+4d_{Z^2}$(Rh)+π(Ph)
260	LUMO	-2.58	3	28	19	17	31	1	1	0	π*(Ph+Azo1+Azo2+Pyrrolido)
259	HOMO	-4.84	2	7	6	29	48	7	2	0	π(Ph+Pyrrolido)
258	H-1	-5.62	6	3	5	7	67	11	1	0	π(Ph)+2p(O)
257	H-2	-5.92	3	0	64	6	8	1	2	16	π(Azo2)+3p(Cl)
256	H-3	-6.07	5	3	1	9	24	4	30	24	$\pi(PPh_3$ +Ph)+3p(Cl)
255	H-4	-6.24	2	0	17	3	4	5	4	45	$4d_{zx}$(Rh)+π(Azo2)+3p(Cl)
254	H-5	-6.27	7	2	3	15	40	4	17	12	π(Ph+PPh_3 +Pyrrolido)+3p(Cl)
HOMO–LUMO gap = 2.26 eV Total Energy = –6315.7943522 Hartree											

Table S5 Frontier Molecular Orbital Composition (%) in the Ground State for **2b**

				Contribution(%)							Main Bond Type
Orbital	MO	Energy	Rh	Azo1 (ligate	Azo2 (free)	pyrrolido	phenoxi		PPh_3	Cl	
							Ph	O			
265	L+5	-0.96	1	1	0	2	1	0	95	0	π*(PPh_3)
264	L+4	-0.99	0	0	0	1	0	1	98	0	π*(PPh_3)
263	L+3	-1.48	53	15	2	8	5	5	3	10	$4d_{x^2-y^2}$(Rh)+π*(Azo1+Phenola
262	L+2	-1.53	1	16	20	28	29	0	5	0	π*(Ph+Pyrrolido+Azo2+Azo1)
261	L+1	-2.18	36	0	0	4	2	1	56	2	π*(PPh_3)+$4d_{Z^2}$(Rh)
260	LUM	-2.58	2	25	23	14	33	1	1	0	π*(Ph+Azo1+Azo2+Pyrrolido)
259	HOM	-4.8	1	6	7	32	48	5	1	0	π(Ph+Pyrrolido)
258	H-1	-5.77	6	0	0	2	67	19	6	0	π(Ph)+ 2p(O)
257	H-2	-5.95	3	0	63	9	7	1	2	15	π(Azo2)+3p(Cl)
256	H-3	-6	8	7	6	18	55	1	2	3	π(Pyrrolido +Ph)
255	H-4	-6.16	9	1	0	14	2	0	40	34	π(PPh_3)+π(Pyrrolido)+3p(Cl)
254	H-5	-6.26	21	0	17	5	4	5	4	44	$4d_{zx}$(Rh)+π(Azo2)+3p(Cl)
HOMO–LUMO gap = 2.22 eV Total Energy = –6315.7931338 Hartree											

Table S6 Frontier Molecular Orbital Composition (%) for $\mathbf{1}^{\bullet+}$ (D = ½)

				Contribution(%)							Main Bond Type
Orbital	α–MO	Energy (eV)	Rh	Azo1 (ligated)	Azo2 (free)	pyrrolido	phenoxido		PPh_3	Cl	
							Ph	O			
270	L+5	-3.35	0	0	0	4	0	0	96	0	$\pi^*(PPh_3)$
269	L+4	-3.42	1	1	0	2	30	1	65	0	$\pi^*(PPh_3)+\pi^*(Ph)$
268	L+3	-4.46	51	15	1	5	4	3	9	14	$4d_{x^2-y^2}(Rh)+\pi^*(Azo1)+3p(Cl)$
267	L+2	-4.72	1	13	28	30	27	0	2	0	π*(Pyrrolido+Azo2+Ph+Azo1)
266	L+1	-5.00	43	0	0	7	4	2	48	1	$\pi^*(PPh_3)+4d_{Z^2}(Rh)$
265	LUMO	-5.91	3	26	20	18	31	1	2	0	π*(Ph+Azo1+Azo2+Pyrrolido)
264	SOMO	-8.17	3	8	6	26	51	7	6	0	π(Pyrrolido+Ph)
263	H-1	-8.68	6	1	0	2	2	0	61	27	$\pi(PPh_3)+3p(Cl)$
262	H-2	-8.83	11	1	12	2	4	1	16	55	$4d_{yz}(Rh)+\pi(Azo2)+3p(Cl)+\pi(PPh_3)$
261	H-3	-8.96	3	0	0	2	8	1	60	26	$\pi(PPh_3)+3p(Cl)$
260	H-4	-9.02	7	3	5	7	65	7	12	1	$\pi(Ph+Ligand+PPh_3)$
259	H-5	-9.13	0	0	17	5	2	0	76	0	$\pi(PPh_3)+\pi(Azo2)$
				Contribution(%)							Main Bond Type
Orbital	β–MO	Energy (eV)	Rh	Azo1 (ligated)	Azo2 (free)	pyrrolido	phenoxido		PPh_3	Cl	
							Ph	O			
269	L+5	-3.36	1	0	0	2	14	0	82	0	$\pi^*(PPh_3)+\pi^*(Ph)$
268	L+4	-4.44	52	15	1	0	5	3	8	14	$4d_{x^2-y^2}(Rh)+\pi^*(Azo1)+3p(Cl)$
267	L+3	-4.54	1	11	25	34	28	0	2	0	π*(Pyrrolido+Ph+Azo2+Azo1)
266	L+2	-4.99	43	0	0	7	4	2	48	1	$\pi^*(PPh_3)+4d_{Z^2}(Rh)$
265	L+1	-5.66	3	21	21	14	40	3	2	0	π*(Ph+Azo1+Azo2+Pyrrolido)
264	LUMO	-6.91	2	8	7	31	50	9	2	0	π*(Pyrrolido+Ph)
263	SOMO	-8.66	6	2	0	2	3	1	63	25	$\pi(PPh_3)+3p(Cl)$

262	H-1	-8.82	9	5	6	7	53	7	11	9	π(Ph+PPh_3)
261	H-2	-8.83	11	1	12	3	11	2	15	48	π(PPh_3)+4d_{zx}(Rh)+π(Azo2)+ 3p(Cl)+π(Ph)
260	H-3	-8.96	3	2	1	1	11	1	57	26	π(PPh_3)+3p(Cl)+π(Ph)
259	H-4	-9.13	0	0	19	5	2	0	73	1	π(PPh_3+Azo2)
258	H-5	-9.18	0	0	0	1	2	0	95	1	π(PPh_3)

Table S7 Frontier Molecular Orbital Composition (%) for **2a**$^{\bullet+}$ (D = ½)

				Contribution(%)							Main Bond Type
Orbital	α–MO	Energy (eV)	Rh	Azo1 (ligated)	Azo2 (free)	pyrrolido	phenoxido		PPh_3	Cl	
							Ph	O			
265	L+5	-3.08	0	0	1	2	0	0	97	0	π*(PPh_3)
264	L+4	-3.09	1	1	0	2	16	0	79	0	π*(PPh_3)+π*(Ph)
263	L+3	-4.07	52	15	2	5	3	3	7	13	4$d_{x^2-y^2}$(Rh)+π*(Azo1)+3p(Cl)
262	L+2	-4.27	1	13	26	30	28	0	2	0	π*(Pyrrolido+Azo2+Ph+Azo1)
261	L+1	-4.62	42	0	0	7	2	2	50	1	π*(PPh_3)+4d_{Z^2}(Rh)
260	LUMO	-5.44	3	25	20	17	33	1	1	0	π*(Ph+Azo1+Azo2+Pyrrolido)
259	SOMO	-7.56	2	7	6	22	53	5	4	0	π(Pyrrolido+Ph)
258	H-1	-8.36	6	4	5	7	54	9	11	4	π(Ph)+ π(PPh_3)
257	H-2	-8.4	7	1	1	5	10	1	49	26	π(Ph)+3p(Cl)+π(PPh_3)
256	H-3	-8.49	11	1	19	2	4	2	10	52	4d_{yz}(Rh)+π(Azo2)+π(PPh_3)+ 3p(Cl)
255	H-4	-8.69	3	1	0	1	5	0	62	28	π(PPh_3)+3p(Cl)
254	H-5	-8.82	2	0	40	8	4	0	38	7	π(PPh_3)+π(Azo2)
				Contribution(%)							Main Bond Type

Orbital	β–MO	Energy (eV)	Rh	Azo1 (ligated)	Azo2 (free)	pyrrolido	phenoxido		PPh_3	Cl	
							Ph	O			
264	L+5	-3.08	0	0	1	2	0	0	97	0	$\pi^*(PPh_3)$
263	L+4	-4.05	52	16	2	5	3	3	7	13	$4d_{x^2-y^2}(Rh)+\pi^*(Azo1)+3p(Cl)$
262	L+3	-4.1	1	11	24	35	27	0	2	0	π*(Pyrrolido+Ph+Azo2+Azo1)
261	L+2	-4.61	42	0	0	6	2	2	50	1	$4d_{x^2-y^2}(Rh)+ \pi^*(PPh_3)$
260	L+1	-5.22	3	21	18	13	42	2	1	0	π*(Ph+Azo1+Azo2+Pyrrolido)
259	LUMO	-6.42	2	8	6	28	48	6	2	0	π*(Pyrrolido+Ph)
258	SOMO	-8.1	5	6	10	9	62	7	1	0	π(Ph)+π(Azo2)
257	H-1	-8.37	6	1	0	3	4	1	58	27	$\pi(PPh_3)$+3p(Cl)
256	H-2	-8.48	11	1	19	2	4	2	9	51	$4d_{zx}(Rh)+\pi(Azo2)+3p(Cl)$
255	H-3	-8.67	4	1	0	1	6	0	58	30	$\pi(PPh_3)$+3p(Cl)
254	H-4	-8.79	4	2	5	8	58	8	14	0	$\pi(Ph)+ \pi(PPh_3)$
253	H-5	-8.81	2	0	41	8	6	0	36	8	$\pi(PPh_3)+\pi(Azo2)$

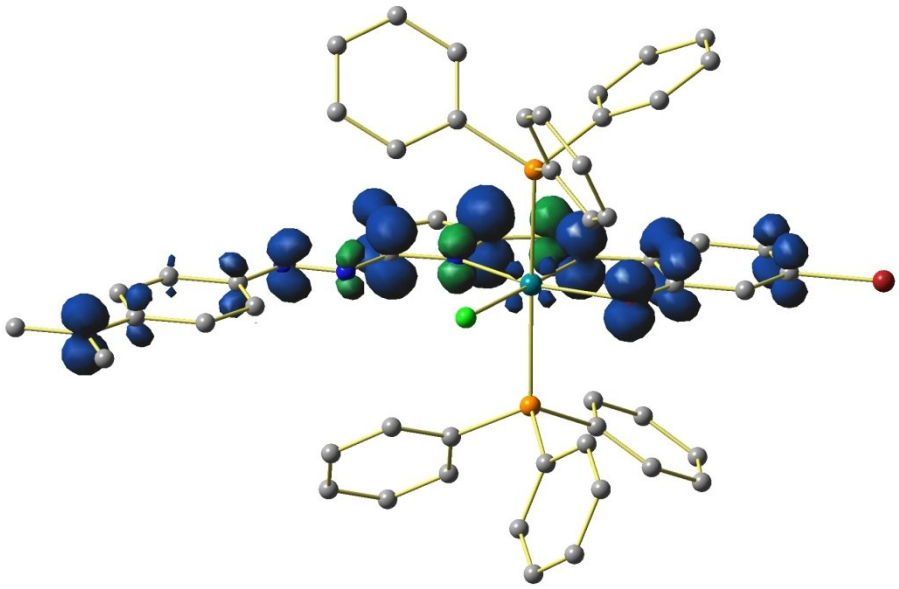


Fig. S9 Net spin density of **2a**$^{\bullet+}$. Isodensity value 0.004 e Bohr^{-3}.

($\rho_L = -0.959$ [$\rho_{Phenoxido} = -0.405$, $\rho_{Pyrrolido} = -0.345$, $\rho_{Phenyl} = -0.194$], $\rho_{Rh} = +0.00004$)

Table S8 Main optical transition at the TD-DFT/B3LYP Level for the complex **1** with composition in terms of molecular orbital contribution of the transition, Computed Vertical excitation energies, and oscillator strength in dichloromethane

Transition	CI	Composition	E (eV)	Oscillator strength (*f*)	λ_{theo} (nm)
$S_0 \rightarrow S_1$	0.69449	H→L (96%)	1.9256	0.6483	643.87
$S_0 \rightarrow S_2$	0.67745	H→ L+1(92%)	2.1020	0.007	589.84
$S_0 \rightarrow S_4$	0.66795	H→ L+3(89%)	2.5523	0.0017	485.78
$S_0 \rightarrow S_5$	0.67111	H – 1→L (90%)	2.7137	0.EV3814	456.88
$S_0 \rightarrow S_6$	0.67788	H – 3→L(96%)	2.7680	0.0249	447.92

$S_0 \rightarrow S_9$	0.47579 0.25433 0.23913	H→L + 2(45%) H – 4→L + 3(13%) H – 4→L + 1(11%)	2.9566	0.0225	419.34
$S_0 \rightarrow S_{10}$	0.48034 0.01364 0.24561 0.23648	H→L+2(46%) H – 4→L+1(14%) H – 4→L+3(13%) H – 2→L+1(11%)	3.0480	0.0587	406.77
$S_0 \rightarrow S_{11}$	0.39601 0.35373 0.31075 0.25048	H – 4→L+3(31%) H – 2→L+1(25%) H – 4 → L+1(19%) H – 2 → L+3(13%)	3.1363	0.0053	395.32
$S_0 \rightarrow S_{12}$	0.46638 0.26094 0.23795	H – 3→L+1(44%) H – 5→L+1(14%) H – 1→L + 1(11%)	3.1730	0.1678	390.75
$S_0 \rightarrow S_{14}$	0.53678 0.41138	H – 6→L(58%) H – 7→L(34%)	3.2860	0.0340	377.31
$S_0 \rightarrow S_{17}$	0.48900 0.24313 0.23328	H – 5→L+1 H – 3→L + 3 H – 1→L+ 1	3.4595	0.0514	358.39
$S_0 \rightarrow S_{18}$	0.45797 0.32370	H – 7→L H – 6→L	3.4606	0.0478	358.27
$S_0 \rightarrow S_{19}$	0.56443 0.27394	H–8→L H–2→L+ 2	3.5175	0.0053	352.48
$S_0 \rightarrow S_{20}$	0.55139 0.25543	H–12→L H–9→L	3.5724	0.0096	347.06
$S_0 \rightarrow S_{27}$	0.37236 0.31547 0.25410 -0.2225	H –14→L H→L+5 H– 6→L+1 H–7→L+1	3.6935	0.1407	335.68

Table S9 Main optical transition at the TD-DFT/B3LYP Level for the complex **2a** with composition in terms of molecular orbital contribution of the transition, Computed Vertical excitation energies, and oscillator strength in dichloromethane

Transition	CI	Composition	E (eV)	Oscillator strength (*f*)	λ_{theo} (nm)
$S_0 \rightarrow S_1$	0.69582	H→L (97%)	1.8857	0.9459	657.49
$S_0 \rightarrow S_2$	0.67490	H→L+1(91%)	1.9478	0.0086	636.53
$S_0 \rightarrow S_3$	0.63307	H→L+2(80%)	2.4130	0.001	513.81
$S_0 \rightarrow S_5$	0.66491	H – 1→L (88%)	2.5122	0.1747	493.52
$S_0 \rightarrow S_6$	0.57119 0.22437	H – 1→L+1(65%) H – 4→L+1(10%)	2.5895	0.0002	478.79
$S_0 \rightarrow S_9$	0.38450 0.32121 0.28109	H – 5→L + 1(30%) H – 2→L + 1(21%) H – 5→L + 2(16%)	3.0296	0.0235	409.24
$S_0 \rightarrow S_{10}$	0.63015	H – 5→L (79%)	3.0323	0.0006	408.88
$S_0 \rightarrow S_{11}$	0.46045 0.33061 0.24185	H – 5→L+2(42%) H – 2→L+1(22%) H – 5→L+1(12%)	3.1237	0.0035	396.91
$S_0 \rightarrow S_{12}$	0.48760 0.25276	H– 1→L+2(48%) H– 5→L (13%)	3.1363	0.024	395.31
$S_0 \rightarrow S_{14}$	0.54062 0.25349 0.25489	H– 4→L (58%) H– 3→L(13%) H→L+3(13%)	3.2422	0.14	382.40
$S_0 \rightarrow S_{17}$	0.65122	H – 6→L(85%)	3.3637	0.033	368.59
$S_0 \rightarrow S_{18}$	0.5449 0.4289	H→L+4 (59%) H→L +5(37%)	3.4357	0.0001	360.87
$S_0 \rightarrow S_{19}$	0.35099 0.27854 0.23035	H – 6→L +1(25%) H – 3→L + 1(16%) H→L+4(11%)	3.4613	0.0446	358.20

$S_0 \rightarrow S_{20}$	0.55139 0.25543	H – 12→L H – 9→L	3.4696	0.0096	347.06
$S_0 \rightarrow S_{27}$	0.37236 0.31547 0.25410 -0.2225	H – 14→L H→L + 5 H – 6→L+1 H – 7→L+1	3.6935	0.1407	335.68

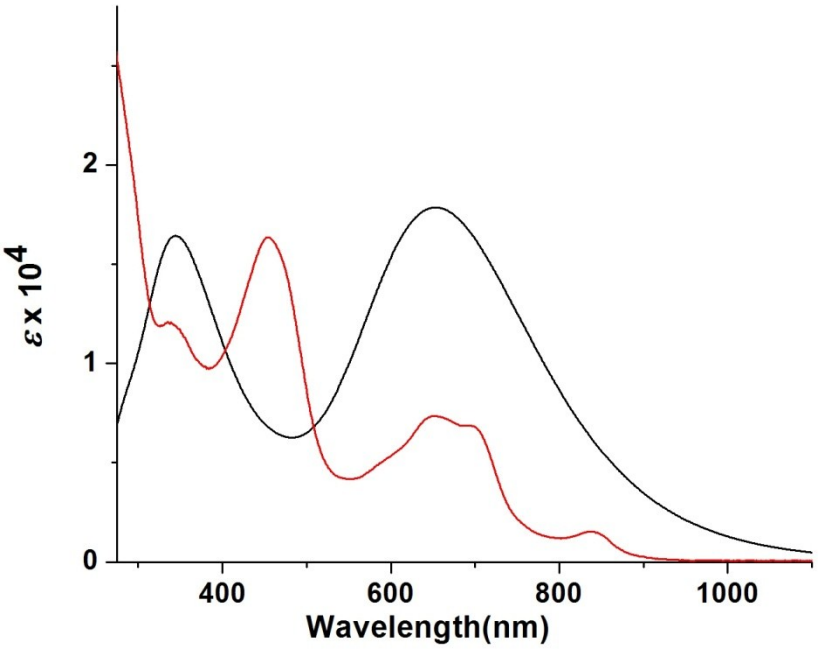


Fig. S10 Experimental (red) and theoretical (black) absorption spectra of **2a** in dichloromethane.

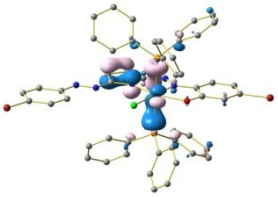
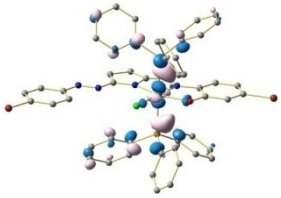
λ_{expt}		Hole	Electron
697, 654 nm	S_1 w = 0.96 1.9256 (0.6483) 643.87 nm ILCT π(phenoxido + pyrrolido) $\rightarrow$ π^*(azo1 + azo2)		
467 nm	S_5 w = 0.90 2.7137 (0.3814) 456.87 nm ILCT/MLCT π(phenoxido) + $4d_{zx}$(Rh) $\rightarrow$ π^*(azo1 + azo2)		
337 nm	S_{15} w = 0.63 3.3706 (0.098) 367.84 nm LLCT/MLCT π(pyrrolido + P) + $4d_{zx}$(Rh) $\rightarrow$ $4d_{yz}$(Rh) + π^*(PPh_3)		
301 nm	S_{50} w = 0.36 4.085 (0.032) 303.48 nm LLCT/MLCT π(PPh_3) + $4d_{z^2}$(Rh) $\rightarrow$ π^*(PPh_3)		

Fig. S11 Natural transition orbitals (NTOs) for complex **1** illustrating the nature of singlet excited states in the absorption bands in the range 300–700 nm. For each state, the respective number of the state, transition energy (eV), and the oscillator strength (in parentheses) are listed. Shown are only occupied (holes) and unoccupied (electrons) NTO pairs that contribute more than 35% to each excited state.

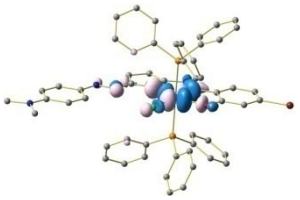
λ_{expt}		Hole	Electron
692, 654 nm	S_1 w = 0.97 1.8857 (0.9459) 657.49 nm ILCT π(phenoxido + pyrrolido + Ph) + 2p(*N*Me$_2$) → π*(azo1 + azo2 + pyrrolido)		
455 nm	S_7 w = 0.73 2.8670 (0.1424) 432.45 nm LMCT/LLCT π(pyrrolido + phenoxido + azo1 + azo2) + 2p(*N*Me$_2$) → 4d$_z^2$(Rh) + 3p(Cl)		
335 nm	S_{25} w = 0.86 3.5776 (0.085) 346.55 nm LMCT π(pyrrolido + azo2 + phenoxido + azo1) + 2p(*N*Me$_2$) → 4d$_{x^2-y^2}$ (Rh)		

Fig. S12 Natural transition orbitals (NTOs) for complex **2a** illustrating the nature of singlet excited states in the absorption bands in the range 300–700 nm. For each state, the respective number of the state, transition energy (eV), and the oscillator strength (in parentheses) are listed. Shown are only occupied (holes) and unoccupied (electrons) NTO pairs that contribute more than 50% to each excited state.

Table S10 Coordinates of optimized geometry **[1]1**

Tag	Symbol	X	Y	Z
1	Rh	25.37605	9.277089	14.6943
2	Br	19.47127	8.994821	18.50335
3	Cl	27.55451	10.03006	15.51376
4	Br	34.56178	10.71456	11.98104
5	P	26.01912	7.028197	15.4966
6	P	24.90559	11.64895	14.16024
7	N	23.58342	8.667394	14.06395
8	N	23.41452	8.279205	12.85571
9	C	22.57152	8.702752	15.01971
10	N	25.73757	8.788581	12.69444
11	N	28.76803	9.047627	11.01415
12	O	24.26639	9.536406	16.48239
13	C	23.01236	9.179551	16.28707
14	C	22.06013	9.258147	17.32616
15	H	22.37345	9.620045	18.30033
16	C	26.974	7.913961	19.41059
17	H	26.68022	8.655942	20.15019
18	C	25.78843	13.62204	10.62027
19	H	25.25603	14.19499	9.863774
20	C	21.00198	12.9329	14.6206
21	H	20.4361	13.50824	15.3503
22	C	27.16827	13.45377	10.53168
23	H	27.72002	13.89187	9.70245
24	C	21.10295	11.6686	12.57226
25	H	20.6161	11.25269	11.69255
26	C	20.36858	12.41191	13.49586
27	H	19.30493	12.57943	13.34032
28	C	32.73685	10.1993	11.70674
29	C	29.23392	4.777836	13.01907
30	H	30.00994	4.258584	12.46046
31	C	25.40101	12.43192	16.83092
32	H	25.15741	11.40736	17.08852
33	C	30.51284	9.90803	12.57874
34	H	29.801	9.96647	13.39818
35	C	26.04117	15.06526	16.16679
36	H	26.29706	16.08875	15.90068
37	C	28.06079	4.113288	13.36925
38	H	27.91643	3.071602	13.08981
39	C	26.03991	14.66608	17.50211
40	H	26.29439	15.37803	18.28471
41	C	27.83904	12.72291	11.51068
42	H	28.91602	12.58447	11.44873
43	C	32.33286	9.750854	10.45226
44	H	33.04319	9.692657	9.63284
45	C	25.7218	14.15306	15.16384
46	H	25.73425	14.47797	14.12736
47	C	20.32181	8.405727	15.83017
48	H	19.28798	8.11401	15.67782
49	C	22.4616	11.44743	12.77361
50	H	23.01408	10.85896	12.04605
51	C	27.90378	6.929909	19.73987
52	H	28.33582	6.89747	20.73804
53	C	23.0124	4.631036	17.0202

54	H	22.66594	4.319634	18.00331
55	C	25.71832	13.35077	17.8294
56	H	25.72455	13.03014	18.86908
57	C	27.235	6.116971	14.45513
58	C	31.00563	9.37883	10.2652
59	H	30.66117	9.024476	9.296585
60	C	27.06626	4.775611	14.08734
61	H	26.16778	4.234722	14.36713
62	C	26.0911	8.251126	10.50362
63	H	26.6267	8.115774	9.573944
64	C	30.08451	9.451375	11.31853
65	C	20.75425	8.876464	17.079
66	C	27.73498	6.03504	17.50307
67	H	28.04619	5.298925	16.76758
68	C	24.55664	8.343754	12.13118
69	C	28.28316	5.990872	18.78305
70	H	29.01251	5.2217	19.02848
71	C	24.76032	8.004812	10.76778
72	H	24.00013	7.629153	10.09346
73	C	27.13693	12.15568	12.57044
74	H	27.66636	11.58459	13.32765
75	C	22.36544	12.72149	14.82148
76	H	22.84594	13.14113	15.70025
77	C	26.79879	7.022352	17.16825
78	C	26.42395	7.966472	18.13156
79	H	25.70595	8.739162	17.87844
80	C	31.83595	10.28046	12.77114
81	H	32.16858	10.63275	13.74355
82	C	23.9044	5.449835	14.51379
83	H	24.23653	5.762193	13.52712
84	C	26.67516	8.73633	11.71374
85	C	28.41705	6.780207	14.09837
86	H	28.55864	7.819514	14.38015
87	C	29.40956	6.110143	13.38847
88	H	30.32113	6.637863	13.11756
89	C	21.24314	8.321814	14.80079
90	H	20.94963	7.962963	13.81847
91	C	24.11824	5.47409	16.91777
92	H	24.62242	5.802209	17.82181
93	C	24.58021	5.88823	15.66301
94	C	25.74858	12.32319	12.66684
95	C	25.39626	12.82944	15.48935
96	C	23.1117	11.98113	13.89692
97	N	27.96342	9.12492	11.98865
98	C	22.35583	4.1912	15.87434
99	H	21.49332	3.533264	15.95647
100	C	25.08008	13.06455	11.68384
101	H	24.00833	13.22467	11.74551
102	C	22.80554	4.603355	14.62015
103	H	22.29657	4.268855	13.71854

Table S11 Coordinates of optimized geometry **[1]2a**

Tag	Symbol	X	Y	Z
1	Rh	25.37793	9.261184	14.657
2	Br	19.61816	8.985557	18.68911
3	Cl	27.59446	9.988047	15.40824
4	P	26.02494	6.996192	15.40271
5	P	24.90747	11.63791	14.17032
6	N	23.55685	8.672913	14.08839
7	N	23.34071	8.299518	12.88041
8	C	22.58055	8.706515	15.08255
9	N	25.66119	8.791473	12.63804
10	N	28.62119	9.042308	10.83646
11	O	24.33819	9.512116	16.48741
12	C	23.07207	9.166859	16.33666
13	C	22.16211	9.2422	17.4116
14	H	22.5156	9.591617	18.37665
15	C	27.117	7.813235	19.29622
16	H	26.85933	8.550958	20.05344
17	C	25.67251	13.66502	10.63347
18	H	25.11871	14.2643	9.913506
19	C	21.03912	12.96859	14.78255
20	H	20.50695	13.54554	15.53585
21	C	27.04233	13.46647	10.47628
22	H	27.56446	13.90681	9.629122
23	C	21.05088	11.7166	12.72427
24	H	20.52754	11.31179	11.86046
25	C	20.35946	12.46309	13.67798
26	H	19.29299	12.64448	13.56191
27	C	32.6778	10.17416	11.31666
28	C	29.13324	4.745375	12.79138
29	H	29.88346	4.226319	12.19817
30	C	25.49762	12.38866	16.83108
31	H	25.24461	11.36527	17.08505
32	C	30.46034	9.875461	12.29886
33	H	29.79969	9.934718	13.16018
34	C	26.16062	15.0179	16.17389
35	H	26.42463	16.04005	15.9101
36	C	27.97708	4.080318	13.19361
37	H	27.82066	3.038483	12.921
38	C	26.1922	14.60557	17.5048
39	H	26.48039	15.30567	18.28653
40	C	27.74042	12.70001	11.40769
41	H	28.80854	12.53249	11.28978
42	C	32.14941	9.729622	10.08082
43	H	32.78142	9.669013	9.201353
44	C	25.7966	14.12098	15.17212
45	H	25.78362	14.45604	14.13887
46	C	20.36066	8.418196	15.97779
47	H	19.31969	8.135274	15.86112
48	C	22.41285	11.47703	12.87559
49	H	22.93221	10.88631	12.12575
50	C	28.03686	6.807448	19.58545
51	H	28.49725	6.753368	20.57004
52	C	23.0392	4.609181	16.98548
53	H	22.71593	4.291788	17.97457

54	C	25.85916	13.29215	17.82854
55	H	25.89058	12.96076	18.86448
56	C	27.19817	6.085267	14.31194
57	C	30.81813	9.366096	9.968591
58	H	30.42269	9.025622	9.013987
59	C	27.01445	4.743272	13.9532
60	H	26.12784	4.20331	14.27049
61	C	25.92279	8.274877	10.43073
62	H	26.4226	8.145937	9.480488
63	C	29.94585	9.427943	11.06534
64	C	20.8434	8.872441	17.21171
65	C	27.78381	5.945358	17.34365
66	H	28.05906	5.21346	16.58971
67	C	24.44968	8.361703	12.11535
68	C	28.36912	5.873957	18.60586
69	H	29.09013	5.087514	18.81967
70	C	24.60122	8.036801	10.74162
71	H	23.81307	7.675447	10.09178
72	C	27.07549	12.12816	12.48895
73	H	27.62553	11.52686	13.20693
74	C	22.40597	12.73821	14.9334
75	H	22.92274	13.14527	15.79735
76	C	26.85663	6.953685	17.04943
77	C	26.52965	7.892523	18.03505
78	H	25.81829	8.681077	17.81294
79	C	31.78648	10.23997	12.42078
80	H	32.13853	10.58293	13.3881
81	C	23.87131	5.445026	14.46409
82	H	24.17926	5.765378	13.47216
83	C	26.55813	8.742535	11.62437
84	C	28.36302	6.748625	13.90328
85	H	28.51618	7.78918	14.17412
86	C	29.32374	6.078312	13.15068
87	H	30.21958	6.608529	12.83559
88	C	21.24299	8.338028	14.91201
89	H	20.90905	7.990782	13.93843
90	C	24.15047	5.442129	16.86125
91	H	24.68214	5.756337	17.75449
92	C	24.58241	5.864653	15.59871
93	C	25.69788	12.32562	12.6541
94	C	25.45882	12.79976	15.49401
95	C	23.10909	11.99455	13.97832
96	N	27.8619	9.118381	11.85069
97	C	22.34693	4.188294	15.85359
98	H	21.47947	3.539155	15.95256
99	C	25.00185	13.1017	11.71806
100	H	23.93756	13.2821	11.83206
101	C	22.76688	4.608821	14.5919
102	H	22.22953	4.289969	13.7011
103	N	34.00406	10.52586	11.44812
104	C	34.86931	10.54606	10.28064
105	H	35.87859	10.82965	10.58584
106	H	34.9294	9.555376	9.809949
107	H	34.52621	11.26626	9.52106
108	C	34.49219	11.08031	12.70117
109	H	34.35557	10.37503	13.5317
110	H	35.56131	11.2829	12.61079
111	H	33.98627	12.02221	12.96405

Table S12 Coordinates of optimized geometry **^{1}2b**

Tag	Symbol	X	Y	Z
1	Rh	25.38295	9.234904	14.71026
2	Cl	27.55235	10.03251	15.52336
3	Br	34.5167	10.85916	11.95978
4	P	26.07855	6.998787	15.49681
5	P	24.86736	11.59211	14.1686
6	N	23.59312	8.589703	14.1008
7	N	23.42051	8.197122	12.89297
8	C	22.6053	8.60674	15.06797
9	N	25.73546	8.748393	12.70878
10	N	28.75722	9.058135	11.00369
11	O	24.29179	9.486345	16.50842
12	C	23.04119	9.09659	16.33437
13	C	22.11265	9.158596	17.38274
14	H	22.46947	9.544332	18.33085
15	C	26.99507	7.878021	19.4213
16	H	26.67892	8.607002	20.16483
17	C	25.70279	13.56175	10.61411
18	H	25.15766	14.11968	9.855346
19	C	20.9592	12.88118	14.60037
20	H	20.39428	13.48201	15.31024
21	C	27.08501	13.41669	10.52148
22	H	27.62613	13.85804	9.686961
23	C	21.06023	11.55726	12.59039
24	H	20.57414	11.11608	11.72269
25	C	20.32609	12.32925	13.4902
26	H	19.26343	12.4964	13.32647
27	C	32.70188	10.30047	11.68962
28	C	29.36183	4.850354	13.01625
29	H	30.15267	4.355909	12.45579
30	C	25.36692	12.39789	16.83178
31	H	25.14496	11.36938	17.09385
32	C	30.48647	9.9579	12.56508
33	H	29.77556	10.00085	13.38625
34	C	25.95263	15.04036	16.15221
35	H	26.18814	16.06714	15.87973
36	C	28.20043	4.156384	13.34778
37	H	28.07976	3.11614	13.05203
38	C	25.97018	14.64662	17.48906
39	H	26.21931	15.36611	18.26661
40	C	27.77168	12.70302	11.50205
41	H	28.85019	12.57978	11.43572
42	C	32.30555	9.841768	10.43659
43	H	33.01524	9.799291	9.615511
44	C	25.64209	14.11794	15.15574
45	H	25.6407	14.43824	14.11766
46	C	20.37686	8.26415	15.92385
47	H	19.35583	7.944938	15.75055
48	C	22.4186	11.34096	12.79923
49	H	22.97122	10.73195	12.0891
50	C	27.95286	6.919849	19.74666
51	H	28.38395	6.893739	20.74554
52	C	23.16871	4.460416	16.98721
53	H	22.84691	4.106833	17.96468
54	C	25.67586	13.32672	17.82385

55	H	25.69907	13.00991	18.86461
56	C	27.32383	6.126784	14.45474
57	C	30.98682	9.439025	10.25237
58	H	30.64925	9.07637	9.284268
59	C	27.18669	4.787566	14.06713
60	H	26.29742	4.2241	14.33126
61	C	26.08512	8.213616	10.51752
62	H	26.61363	8.084468	9.582765
63	C	30.06424	9.490488	11.30634
64	C	20.78144	8.742724	17.2074
65	C	27.81683	6.036738	17.50285
66	H	28.15238	5.316276	16.76248
67	C	24.56159	8.283961	12.15767
68	C	28.36255	5.999393	18.78419
69	H	29.11452	5.251061	19.02601
70	C	24.75863	7.945509	10.79477
71	H	23.99906	7.555504	10.12776
72	C	27.08318	12.13024	12.56773
73	H	27.62459	11.56986	13.32437
74	C	22.32185	12.67232	14.80973
75	H	22.80249	13.11598	15.67652
76	C	26.85263	6.998014	17.17204
77	C	26.44704	7.923439	18.14099
78	H	25.70781	8.676728	17.88889
79	C	31.80133	10.36122	12.755
80	H	32.12696	10.72187	13.72683
81	C	24.00316	5.379889	14.49635
82	H	24.31278	5.730789	13.51558
83	C	26.67232	8.710443	11.71769
84	C	28.49386	6.819883	14.11592
85	H	28.6099	7.858654	14.41074
86	C	29.50596	6.180846	13.40509
87	H	30.40671	6.732716	13.14645
88	C	21.27635	8.200354	14.88397
89	H	20.96697	7.836009	13.90834
90	C	24.24164	5.346427	16.89739
91	H	24.74424	5.666947	17.805
92	C	24.67504	5.811313	15.65033
93	C	25.69278	12.27517	12.66873
94	C	25.34377	12.78986	15.48881
95	C	23.06833	11.90555	13.90735
96	N	27.95138	9.121406	11.98136
97	C	22.51575	4.028535	15.83619
98	H	21.67963	3.335944	15.90804
99	C	25.00803	12.99859	11.68365
100	H	23.93358	13.13883	11.74701
101	C	22.93643	4.491734	14.58992
102	H	22.43022	4.164652	13.68406
103	N	19.8789	8.78831	18.25201
104	C	18.47017	8.511436	18.01891
105	H	17.93133	8.581214	18.96629
106	H	18.01358	9.222535	17.31217
107	H	18.32095	7.496351	17.6292
108	C	20.26938	9.396257	19.51278
109	H	19.44131	9.32132	20.22093
110	H	21.13201	8.878093	19.95161
111	H	20.53172	10.46039	19.3986

Table S13 Coordinates of optimized geometry $^{2}\mathbf{1}^{\bullet+}$

Tag	Symbol	X	Y	Z
1	Rh	25.36357	9.267638	14.68435
2	Br	19.33967	8.880835	18.26668
3	Cl	27.51435	10.01626	15.50486
4	Br	34.58316	10.7295	11.87999
5	P	26.0165	7.005772	15.51803
6	P	24.8987	11.67044	14.16674
7	N	23.59234	8.648344	14.0122
8	N	23.45847	8.255971	12.76733
9	C	22.56405	8.65809	14.89734
10	N	25.77783	8.800532	12.70946
11	N	28.80286	9.081409	11.06666
12	O	24.17692	9.493397	16.4342
13	C	22.95422	9.134955	16.20824
14	C	21.9624	9.195279	17.22118
15	H	22.24146	9.551548	18.20746
16	C	27.02999	7.960476	19.39871
17	H	26.75788	8.718201	20.13001
18	C	25.75046	13.54182	10.56814
19	H	25.20724	14.06163	9.782167
20	C	21.01892	12.98528	14.69609
21	H	20.47761	13.58194	15.42663
22	C	27.13836	13.44162	10.51333
23	H	27.68449	13.88071	9.681442
24	C	21.06139	11.70424	12.65512
25	H	20.55258	11.29797	11.78372
26	C	20.35662	12.4666	13.58687
27	H	19.29525	12.65708	13.44528
28	C	32.76784	10.22032	11.65273
29	C	29.18549	4.738927	13.00723
30	H	29.95534	4.211093	12.44886
31	C	25.41946	12.42013	16.8424
32	H	25.17402	11.39771	17.10388
33	C	30.56695	9.941277	12.58848
34	H	29.87369	10.00449	13.42292
35	C	26.07871	15.05028	16.18645
36	H	26.33947	16.07322	15.92483
37	C	27.99162	4.097222	13.32782
38	H	27.82569	3.065922	13.02472
39	C	26.07544	14.64578	17.51998
40	H	26.33505	15.35281	18.30461
41	C	27.82518	12.78719	11.53522
42	H	28.91005	12.71578	11.50472
43	C	32.33242	9.764681	10.40637
44	H	33.02484	9.701766	9.572593
45	C	25.7523	14.14518	15.17967
46	H	25.76222	14.47636	14.14519
47	C	20.30102	8.333451	15.63104
48	H	19.27306	8.034991	15.45224
49	C	22.41985	11.46303	12.83344
50	H	22.94945	10.86795	12.09435
51	C	27.94591	6.96491	19.73284
52	H	28.38711	6.940213	20.72666
53	C	23.011	4.679495	17.13524
54	H	22.68606	4.385288	18.13065
55	C	25.74405	13.33188	17.84407

56	H	25.74865	13.00892	18.88266
57	C	27.20839	6.093063	14.45751
58	C	31.005	9.395453	10.25236
59	H	30.63506	9.036802	9.295165
60	C	27.00723	4.766272	14.05387
61	H	26.0969	4.23804	14.3183
62	C	26.17827	8.273923	10.50828
63	H	26.75005	8.155884	9.598281
64	C	30.10955	9.477693	11.33445
65	C	20.68109	8.803546	16.92254
66	C	27.73998	6.037467	17.51257
67	H	28.0297	5.282589	16.78746
68	C	24.60709	8.342353	12.10444
69	C	28.29935	6.004345	18.78766
70	H	29.01611	5.22595	19.03898
71	C	24.86246	8.012311	10.7259
72	H	24.12363	7.633064	10.03076
73	C	27.131	12.22516	12.60239
74	H	27.67318	11.72006	13.3968
75	C	22.38254	12.75406	14.8741
76	H	22.88643	13.18046	15.73621
77	C	26.81684	7.036289	17.17299
78	C	26.46817	8.001792	18.12506
79	H	25.76537	8.78749	17.87327
80	C	31.89035	10.30981	12.74349
81	H	32.25224	10.66724	13.70313
82	C	23.86051	5.436313	14.59427
83	H	24.17944	5.715713	13.59346
84	C	26.73181	8.766514	11.76607
85	C	28.41268	6.734517	14.13131
86	H	28.58368	7.758796	14.45047
87	C	29.39398	6.055909	13.41484
88	H	30.32868	6.55895	13.1776
89	C	21.23447	8.262331	14.63094
90	H	20.97288	7.908101	13.63895
91	C	24.11864	5.514834	16.99422
92	H	24.64511	5.853666	17.8814
93	C	24.56072	5.897294	15.72099
94	C	25.73273	12.32461	12.66399
95	C	25.41783	12.82238	15.50187
96	C	23.10064	11.99564	13.94007
97	N	28.00547	9.160931	12.05959
98	C	22.33253	4.215843	16.01158
99	H	21.47459	3.556934	16.12392
100	C	25.04796	12.99222	11.63988
101	H	23.96992	13.11009	11.67756
102	C	22.76077	4.596801	14.73968
103	H	22.2392	4.235545	13.85609

Table S14 Coordinates of optimized geometry ^{2}**2a**$^{\bullet+}$

Tag	Symbol	X	Y	Z
1	Rh	25.37012	9.250341	14.63664
2	Br	19.47943	8.899808	18.43957
3	Cl	27.56649	9.969426	15.38094
4	P	26.01919	6.977435	15.42492
5	P	24.90301	11.65566	14.16966
6	N	23.57002	8.652229	14.0243
7	N	23.38685	8.272855	12.78478
8	C	22.57592	8.666221	14.95363
9	N	25.70534	8.794905	12.63797
10	N	28.67502	9.063759	10.86019
11	O	24.25621	9.478368	16.43339
12	C	23.01832	9.130181	16.24643
13	C	22.06508	9.193053	17.29312
14	H	22.38166	9.541224	18.27095
15	C	27.16883	7.876559	19.28132
16	H	26.92617	8.628181	20.02922
17	C	25.59658	13.61078	10.58147
18	H	25.0231	14.1708	9.846195
19	C	21.06839	13.02233	14.87817
20	H	20.56686	13.61986	15.63606
21	C	26.9738	13.46548	10.43481
22	H	27.48109	13.90917	9.580904
23	C	21.00576	11.75493	12.8295
24	H	20.45428	11.35976	11.97917
25	C	20.35196	12.52005	13.79547
26	H	19.28776	12.72412	13.70192
27	C	32.69123	10.22217	11.30301
28	C	29.06241	4.670078	12.79469
29	H	29.80192	4.133619	12.20422
30	C	25.53098	12.37176	16.83031
31	H	25.26801	11.3526	17.08815
32	C	30.49045	9.91122	12.31611
33	H	29.8324	9.96427	13.17938
34	C	26.22783	14.99313	16.17889
35	H	26.5019	16.01308	15.91874
36	C	27.88887	4.032596	13.18999
37	H	27.70866	2.996071	12.91371
38	C	26.25897	14.5752	17.50784
39	H	26.55858	15.2685	18.29065
40	C	27.69962	12.75675	11.39126
41	H	28.77652	12.64478	11.28672
42	C	32.15895	9.756547	10.06388
43	H	32.79106	9.692093	9.185744
44	C	25.84786	14.10588	15.17468
45	H	25.83115	14.4474	14.14371
46	C	20.33541	8.354926	15.76613
47	H	19.29961	8.065597	15.62175
48	C	22.36715	11.49435	12.94764
49	H	22.85704	10.89714	12.18312
50	C	28.08489	6.868772	19.57597
51	H	28.556	6.828062	20.55554
52	C	23.0343	4.678141	17.12116
53	H	22.7319	4.385989	18.12427
54	C	25.9088	13.26556	17.82953
55	H	25.93898	12.9317	18.86432

56	C	27.16097	6.048683	14.32181
57	C	30.84128	9.385416	9.962862
58	H	30.43966	9.032558	9.016093
59	C	26.94269	4.714122	13.95396
60	H	26.04656	4.191333	14.27237
61	C	26.01767	8.285293	10.41673
62	H	26.54892	8.169019	9.482342
63	C	29.96716	9.45037	11.07558
64	C	20.76791	8.814098	17.03993
65	C	27.79918	5.968513	17.3533
66	H	28.05846	5.219071	16.61118
67	C	24.51541	8.355863	12.07873
68	C	28.39851	5.915625	18.60955
69	H	29.11439	5.126851	18.82966
70	C	24.70974	8.034735	10.68746
71	H	23.93821	7.668813	10.02121
72	C	27.05482	12.18638	12.48486
73	H	27.62644	11.63594	13.22661
74	C	22.43499	12.77125	14.9959
75	H	22.98068	13.18344	15.8392
76	C	26.87531	6.978987	17.05364
77	C	26.56702	7.937324	18.02668
78	H	25.86166	8.730367	17.8058
79	C	31.80424	10.28329	12.4251
80	H	32.16772	10.62937	13.38632
81	C	23.82416	5.432455	14.56047
82	H	24.11936	5.71257	13.55262
83	C	26.63128	8.762794	11.65364
84	C	28.34422	6.685417	13.92049
85	H	28.52742	7.717068	14.20716
86	C	29.28785	5.994916	13.1655
87	H	30.20483	6.497124	12.8654
88	C	21.23517	8.282773	14.73373
89	H	20.93643	7.936333	13.74933
90	C	24.14836	5.499673	16.9524
91	H	24.70258	5.829793	17.82589
92	C	24.55984	5.881134	15.66903
93	C	25.6682	12.33049	12.63851
94	C	25.49365	12.78802	15.4945
95	C	23.10145	12.00905	14.02784
96	N	27.90362	9.140825	11.89512
97	C	22.31903	4.227814	16.01513
98	H	21.45462	3.581471	16.14898
99	C	24.94453	13.05159	11.67965
100	H	23.87503	13.19973	11.78822
101	C	22.71781	4.60698	14.73324
102	H	22.1668	4.257028	13.86299
103	N	33.99147	10.59399	11.41727
104	C	34.88794	10.52604	10.26329
105	H	35.88209	10.85814	10.5628
106	H	34.97065	9.499711	9.884333
107	H	34.54039	11.17642	9.450576
108	C	34.52195	11.07785	12.69242
109	H	34.44063	10.31225	13.47402
110	H	35.57636	11.32534	12.56861
111	H	33.99589	11.98118	13.02542